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ULTRAFAST SOLUTION DYNAMICS:
PART I--DYNAMICS IN IONIC LIQUIDS;
PART II--NON-RADIATIVE DEACTIVATION OF MALONONITRILES

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ABSTRACT

This thesis work is aimed at understanding two related topics of ultrafast solution dynamics: dynamics in ionic liquids, and the non-radiative deactivation of malononitriles. Following a brief introduction in chapter 1, chapter 2 explains the general experimental techniques and data analysis used. Chapters 3 to 5 focus on the properties and dynamics of ionic liquids. Chapter 6 examines the fundamental details of the non-radiative deactivation of malononitriles.

Chapter 3 reports physical properties of 4 room-temperature ionic liquids consisting of the 1-butyl-3-methyl-imidazolium cation with various perfluorinated anions and the bis(trifluoromethylsulfonyl)imide (Tf₂N⁻) anion with 12 pyrrolidinium, ammonium, and hydroxyl-containing cations. Electronic structure methods are used to calculate properties related to the size, shape, and dipole moment of individual ions. Experimental measurements of phase transition temperatures, densities, refractive indices, surface tensions, solvatochromic polarities based on absorption of Nile Red, ¹⁹F chemical shifts of the Tf₂N⁻ anion, temperature dependent viscosities, conductivities, and cation diffusion coefficients are reported. Correlations among the measured quantities as well as the use of surface tension and molar volume for estimating Hildebrand solubility parameters of ionic liquids are also discussed.

In chapter 4, steady-state emission spectroscopy and time-resolved emission spectroscopy with 25 ps resolution are used to measure equilibrium and dynamic aspects of the solvation of coumarin 153 (C153) in a diverse collection of 21 room temperature ionic liquids. Steady-state absorption and emission spectra are used to extract solvation free energies and reorganization energies associated with the S₀→S₁ transition of C153. These quantities, especially the solvation free energy, vary relatively little in ionic liquids compared to conventional solvents. Some
correlation is found between these quantities and the mean separation between ions (or molar volume). Time-resolved anisotropies are used to observe solute rotation. Rotation times measured in ionic liquids correlate with solvent viscosity in similar way that they do in conventional polar solvents. No special frictional coupling between the C153 and ionic liquid solvents is indicated by these times. But, in contrast to what is observed in most low-viscosity conventional solvents, rotational correlation functions in ionic liquids are non-exponential. Time-resolved Stokes shift measurements are used to characterize solvation dynamics. The solvation response functions in ionic liquids are also non-exponential and can be reasonably represented by stretched exponential functions of time. The solvation times observed are correlated to the solvent viscosity, and the much slower solvation in ionic liquids compared to dipolar solvents can be attributed to their much larger viscosities. Solvation times of the majority of ionic liquids studied appear to follow a single correlation with solvent viscosity. Only liquids incorporating the largest phosphonium cation appear to follow a distinctly different correlation.

In chapter 5, the excitation wavelength dependence of emission kinetics of several solutes is measured by steady-state and time-resolved emission spectroscopy and used to demonstrate the presence of dynamic heterogeneity in several room temperature ionic liquids. The solute kinetics examined here include rotational and solvation dynamics of Coumarin 153, isomerization of two malononitriles, trans-2-[4-(dimethylamino)styryl]benzothiazole isomerization, and intramolecular electron transfer in crystal violet lactone. The rates of most of these processes vary significantly with excitation wavelength, especially when excited on the red edges of the solute absorption bands, indicating that energetically selected subpopulations relax at distinct rates. The results presented here suggest more generally that dynamic process taking place on the sub-nanosecond time scale in typical ionic liquids near room temperature are likely to be heterogeneous in character. Similar heterogeneous dynamics are also observed in low temperature 1-propanol, which indicates dynamic heterogeneity is not unique to ionic liquids.
4-N,N-dimethylamino-benzylidenemalononitrile (DMN) and joulolidine-malononitrile (JDMN) have long been examined for their non-linear optical properties and as microviscosity probes in conventional solvents, polymers, biological systems and recently ionic liquids. In Chapter 6, we focus on the details of non-radiative deactivation in these two malononitriles. Malononitriles are studied in a collection of conventional room-temperature solvents with different viscosities and polarities by both steady-state and time-resolved emission spectroscopy. Both the absorption and emission spectra of DMN and JDMN show large shifts with solvent polarity and these shifts are reasonably correlated to dielectric properties. The quantum yields of malononitriles are sensitive to solvent viscosity but the relationship is not simple. The quantum yields of malononitriles do not seem to be sensitive to solvent polarity. Our quantum yields do not agree with previous reported values, but the decay times deduced from them are consistent with time-resolved measurements from TCSPC and the Kerr-gated emission technique. Temperature dependent data on malononitriles in 2-methyltetrahydrofuran and 1-propanol over a wide temperature range are also presented. The temperature dependence of the emission of malononitriles in MTHF and PrOH provides further information about non-radiative deactivation. We observe an unusual behavior of spectral shifts with temperature, which result from different temperature dependence of the solvation time and lifetime. Non-radiative deactivation times correlate with \((\eta/T)^p\) with \(p\) values of 1.0, 0.60 and 0.44 for MTHF, PrOH and \([N_{\text{ip}311}^+]\)\([Tf_2N^-]\) respectively. The smaller values of \(p\), thus the weaker correlation between reactive motion and viscosity, appear to be related to the complexity of the solvation dynamics over the temperature range observed. The detailed spectral dynamics of DMN at low temperature are complex due to the interplay between solvation and reaction dynamics.
TABLE OF CONTENTS

LIST OF FIGURES ................................................................. viii
LIST OF TABLES ................................................................. xi
ACKNOWLEDGEMENTS ........................................................ xiii
Chapter 1 Introduction ....................................................... 1
  References and Notes ....................................................... 5
Chapter 2 Main Experimental Technique and Data Analysis Methods ........................................ 6
  2.1 TCSPC Technique Introduction .................................. 6
  2.2 TCSPC Components .................................................. 1
    2.2.1 Light Source ....................................................... 10
    2.2.2 Optics .............................................................. 12
    2.2.3 Detectors and Electronics .................................... 14
  2.3 Data Analysis .......................................................... 17
    2.3.1 Instrumental Function and Convolution .................. 17
    2.3.2 Formulation of the Decays and Least-Square Fitting .... 17
    2.3.3 Anisotropy Analysis ........................................... 18
    2.3.4 Reconstruction of Time-Resolved Spectra ................ 20
    2.3.5 Estimation of Time-Zero Spectrum .......................... 21
  References and Notes .................................................... 24
Chapter 3 Physical Properties of Ionic Liquids ................................................ 25
  3.1 Introduction .......................................................... 26
  3.2 Materials and Methods .............................................. 29
  3.3 Results ............................................................... 34
    3.3.1 Calculated Ion Properties ................................... 34
    3.3.2 Thermal Properties ............................................. 39
    3.3.3 Static Properties ............................................... 42
    3.3.4 Dynamical Properties ......................................... 54
  3.4 Summary & Conclusions ............................................. 61
  References and Notes .................................................... 62
Chapter 4 Solvational and Rotational Dynamics of Ionic Liquids ........................................ 69
  4.1 Introduction .......................................................... 70
  4.2 Materials and Experimental Methods ............................ 72
  4.3 Results and Discussion ............................................. 77
    4.3.1 Solvation Energies ............................................. 77
    4.3.2 Rotational Dynamics ........................................... 85
    4.3.3 Solvation Dynamics ............................................. 95
  4.4 Summary and Conclusions ......................................... 106
Chapter 5 Heterogeneous Solute Dynamics in Ionic Liquids

5.1 Introduction
5.2 Material and Methods
5.3 Results and Discussion
  5.3.1 C153 Rotational and Solvational Dynamics
  5.3.2 Malononitrile Isomerization
  5.3.3 CVL Intramolecular Charge Transfer Reaction
5.4 Summaries and Conclusions

Chapter 6 Non-Radiative Deactivation of Malononitriles

6.1 Introduction
6.2 Material and Methods
  6.2.1 Materials and Experimental Methods
  6.2.2 Quantum Yield Measurement of Malononitriles
6.3 Results and Discussion
  6.3.1 Solvatochromism of Malononitriles
  6.3.2 Transition Moments and Radiative Rates
  6.3.3 Quantum Yield and Lifetime
  6.3.4 Temperature Dependence
  6.3.5 Modeling the Observed Spectral Shift
  6.3.6 Spectral Dynamics at Low Temperature
6.4 Summary and Conclusions

Appendix
LIST OF FIGURES

Figure 1.1 Schematic of the dynamic Strokes shift ............................................................... 2

Figure 2.1 Schematic for time-correlated single photon counting ............................................. 7

Figure 2.2 Schematic of TCSPC instrument in Maroncelli’s group ........................................... 8

Figure 3.1 Structures of the ions for ILs studied in this work and their designations .............. 27

Figure 3.2 Representative DSC thermogram of [Nip311⁺][Tf₂N⁻] ........................................ 41

Figure 3.3 Surface tensions γ of ionic liquids and alkali halides plotted versus molar volume \(V_m\) .......................................................... 45

Figure 3.4 Hildebrand solubility parameters \(\delta_h\) versus the correlating factor \(\gamma/V_m^{1/3}\) ....... 46

Figure 3.5 Trends in the refractive index \(n_D\), the Hildebrand solubility parameter \(\delta_h\), and the \(^{19}\)F chemical shift of the Tf₂N⁻ anion \(\delta_F\) plotted against cation mass for the Tf₂N⁻ ionic liquids. .......................................................... 51

Figure 3.6 \(^{19}\)F chemical shifts plotted versus “mean ion separation” \(V_m^{-1/3}\) ...................... 53

Figure 3.7 Example viscosity data and fits to eq 3.8 ............................................................. 56

Figure 3.8 Cation diffusion coefficients (25 °C) and molar conductivity (22 °C) plotted as functions of viscosity .......................................................... 58

Figure 4.1 Structures of the ionic liquids .......................................................... 73

Figure 4.2 Absorption and emission spectra of C153 in representative conventional solvents and in the ionic liquid [Pr₃¹⁺][Tf₂N⁻] .................................................. 79

Figure 4.3 Solvation free energy differences \((S_1-S_0)\) of C153 in conventional dipolar liquids and in ionic liquids .................................................. 81

Figure 4.4 Solvent reorganization energies of C153 in conventional dipolar liquids and in ionic liquids .................................................. 82

Figure 4.5 Representative anisotropy decay data in [Pr₃¹⁺][Tf₂N⁻] at 313 K ....................... 86

Figure 4.6 Rotational correlation times of C153 in 27 dipolar solvents at room temperature and in ionic liquids plotted versus \(\eta/T\) .................................................. 92

Figure 4.7 Rotational coupling factors of C153 measured in ionic liquids ......................... 94

Figure 4.8 Time resolved spectra of C153 in [Nip311⁺][Tf₂N⁻] at 298 K ...................... 96
Figure 4.9 Representative peak frequency data $\nu_{pk}(t)$ obtained from log-normal fits of time-resolved spectra in the [Pr$_{nl}$$^+$][Tf$_2$N$^-$/] and [N$_{ip11}$$^+$][Tf$_2$N$^-$/] series at 298 K.
.......................................................................................................................... 97

Figure 4.10 Integral solvation times $<\tau_{solv}>$ in conventional dipolar solvents and in ionic liquids plotted versus solvent viscosity .......................................................... 100

Figure 4.11 Correlation of the observed solvation times in ionic liquids $<\tau_{solv}>$ with $\eta/T$ and the cation radius $R_+$. ................................................................................................. 104

Figure 5.1 Schematic representations of two different sources of non-exponential correlation decays .................................................................................................................. 117

Figure 5.2 Illustration of distribution selection by different excitation along the red edge of absorption spectrum ............................................................................................................. 119

Figure 5.3 Excitation frequency dependence of the emission frequencies, rotation times, and solvation times of C153 in [N$_{ip311}$$^+$][Tf$_2$N$^-$/] at 25 °C .......................................................... 123

Figure 5.4 Representative anisotropy decay data of C153 in [N$_{ip311}$$^+$][Tf$_2$N$^-$/] at 25 °C ............... 126

Figure 5.5 (a) Time-resolved emission spectra of C153 in [N$_{ip311}$$^+$][Tf$_2$N$^-$/] at 25 °C excited at 380 nm (b) Peak frequencies versus time derived from log-normal fits to such spectra ........................................................................................................ 129

Figure 5.6 Excitation wavelength dependence of the emission frequencies and lifetimes of DMN and JDMN in [N$_{ip311}$$^+$][Tf$_2$N$^-$/] at 25 °C .................................................................................................................. 133

Figure 5.7 Results comparison of DMN in [N$_{ip311}$$^+$][Tf$_2$N$^-$/], DMSO and CHEX.................. 137

Figure 5.8 Results comparison of JDMN in [N$_{ip311}$$^+$][Tf$_2$N$^-$/] and DMSO ................................. 138

Figure 5.9 Excitation wavelength dependence of the emission frequencies and lifetimes of DMN in [N$_{101}$$^+$][Bet$_i$] at 25 °C and 45 °C ............................................................... 140

Figure 5.10 Excitation wavelength dependence of the emission frequencies and lifetimes of DMN in 1-PrOH at 135 K ........................................................................................................ 142

Figure 5.11 Excitation wavelength dependence of the emission frequencies and lifetimes of DMASBT in [N$_{ip311}$$^+$][Tf$_2$N$^-$/] at 25 °C .................................................................................................................. 143

Figure 5.12 Top panel: Steady-state emission spectra of CVL in [Pr$_{31}$$^+$][Tf$_2$N$^-$/] at 25 °C at excitation frequencies of 25.0, 25.6, 26.3, 27.0, 27.8 and 28.6×10$^3$ cm$^{-1}$/.
Bottom panel: Normalized values of the peak LE emission and the ratio of the LE to the CT band areas determined from these spectra ........................................................................ 145

Figure 6.1 Comparison of unpolarized and polarized correction files .......................................................................................................................... 162
Figure 6.2 Comparison of malononitrile spectra measured with the unpolarized and polarized setups................................................................. 164

Figure 6.3 Representative absorption and steady-state emission spectra of malononitriles in DMSO................................................................. 166

Figure 6.4 Comparison between observed and calculated spectral shifts of DMN .......... 169

Figure 6.5 Comparison between observed and calculated spectral shifts of JDMN .......... 170

Figure 6.6 Correlations between malononitrile lifetime and solvent viscosity ................. 181

Figure 6.7 Viscosities of MTHF and 1-PROH at different temperatures and their correlations ................................................................. 185

Figure 6.8 Densities of MTHF and 1-PROH at different temperatures and their correlations ................................................................. 186

Figure 6.9 Representative absorption spectra of DMN in MTHF at different temperatures... 187

Figure 6.10 Comparison of spectra shift and bandwidth change between C153 and DMN in MTHF at different temperatures ................................ 189

Figure 6.11 Representative emission spectra of DMN in MTHF at different temperatures .... 191

Figure 6.12 Spectral shifts of malononitriles and C153 at different temperatures .......... 192

Figure 6.13 Comparison between lifetimes measured using TCSPC and estimated from emission quantum yields ................................................. 196

Figure 6.14 Correlations between \( \tau_{os} \) and \( \eta/T \) ................................................................. 198

Figure 6.15 Modeling observed spectral shifts................................................................. 202

Figure 6.16 Time-resolved spectra............................................................................. 203

Figure 6.17 Peak frequency and integrated intensity change with time........................ 204
LIST OF TABLES

Table 3.1 Calculated ion properties ................................................................. 35
Table 3.2 Calorimetric data ............................................................................. 40
Table 3.3 Static properties .............................................................................. 43
Table 3.4 Dynamic properties ........................................................................ 55
Table 4.1 Ionic liquids studied and some of their characteristics ..................... 74
Table 4.2 C153 spectral frequencies and energy estimates ............................... 78
Table 4.3 Summary of dynamical quantities .................................................... 89
Table 4.4 Dynamic characteristics averaged over cation classes ..................... 90
Table 5.1 Emission frequencies of C153 in [N\textsubscript{ip311}\textsuperscript{+}][Tf\textsubscript{2}N\textsuperscript{-}] at 25 °C ........................................ 124
Table 5.2 Rotation Times of C153 in [N\textsubscript{ip311}\textsuperscript{+}][Tf\textsubscript{2}N\textsuperscript{-}] at 25 °C ................................................. 127
Table 5.3 Integral solvation times of C153 in [N\textsubscript{ip311}\textsuperscript{+}][Tf\textsubscript{2}N\textsuperscript{-}] at 25 °C ........................................ 130
Table 5.4 Emission frequencies, quantum yields, and estimated isomerization times of DMN in [N\textsubscript{ip311}\textsuperscript{+}][Tf\textsubscript{2}N\textsuperscript{-}] at 25 °C ......................................................... 134
Table 5.5 Emission frequencies, quantum yields, and estimated isomerization times of JDMN in [N\textsubscript{ip311}\textsuperscript{+}][Tf\textsubscript{2}N\textsuperscript{-}] at 25 °C ......................................................... 135
Table 5.6 Characteristics of the emission of CVL in [Pr\textsubscript{31}+][Tf\textsubscript{2}N\textsuperscript{-}] at 25 °C ......................................................... 146
Table 5.7 Summary of dynamic heterogeneity observed by experiments ............ 150
Table 6.1 Comparisons of quantum yields measured with unpolarized and polarized setups ................................................................. 163
Table 6.2 Spectral data summary of malononitriles ........................................... 167
Table 6.3 Summary of first excited state dipole moments $\mu_{\text{e}}$ of malononitriles ......... 173
Table 6.4 DMN absorption transition moment and radiative rate summary .......... 175
Table 6.5 JDMN transition moment and radiative rate summary ....................... 176
Table 6.6 Radiative rates of malononitriles ..................................................... 178
Table 6.7 Quantum yield and lifetime summary of malononitriles ........................................ 180

Table 6.8 Table 6.8 Comparison between steady-state measurements and Kerr-gated measurements of DMN ...................................................................................................................................... 182

Table 6.9 Spectral data summary of C153 and DMN in MTHF at different temperatures .... 188

Table 6.10 Summary of emission spectra at different temperatures ........................................ 194

Table 6.11 Summary of fits to TCSPC data on DMN and JDMN in MTHF ................. 195

Table 6.12 Fitting parameters of fits to the relation \( \tau_{or} = A(\eta/T)^\theta \) ................................................................. 199

Table 6.13 Fitting parameters for correlations of peak frequency and integrated intensity with time using eq 6.25 and eq 6.26 ................................................................. 205
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Chapter 1

Introduction

The importance of solvents to chemical reaction and modern civilization cannot be overstated. While the most common solvent in everyday life is water, organic molecular solvents are primarily used in chemical synthesis and other industrial processes. Most chemical reaction dynamics and chemical rate processes in solution are strongly influenced by both general and specific interactions between the solvent and the reactants. Understanding the effect of solvent on reaction rates, yields and products is a fundamental important issue in chemistry for helping to select ideal solvent in any particular application.

The study of solvation dynamics can provide a full characterization of the static as well as dynamic properties of solute-solvent interactions. Solvation dynamics is the time-dependent response of a solvent to an electrical perturbation of a solute\(^1\). The most common experimental method used to study solvation dynamics is measurement of the time-dependent emission spectrum of a probe solute after electronic excitation\(^1\). This process is depicted in Figure 1.1\(^2\). It is assumed that there is a large increase in the probe’s dipole moment upon electronic excitation. Before excitation, the solution is in an equilibrium state. After introducing a pulse of light with sufficient energy, the probe will be at its first excited state (S\(_1\)). The electronic transition is instantaneous relative to nuclear motions of the solvents. Thus the system is no longer in equilibrium and the solvent responds accordingly. The S\(_1\) state stabilizes and the fluorescence energy decreases as the solvent relaxes around the dipole. Using time-resolved spectroscopy, this energy relaxation can be recorded and used to monitor solvation dynamics.
Figure 1.1 Schematic of the dynamic Stokes shift. $S_0$ and $S_1$ are the first two electronic energy levels of the probe. The purple circle is the probe molecule and the yellow arrow the excited dipole. The ovals are the polar solvent molecules with partial charges shown as different colors on two sides. When the probe is electronically excited, its dipole moment increases, and the solvent dipoles respond to the new electrostatic field, lowering the energy of the system.
There has been recent explosion of interest in ionic liquids (ILs) as a result of the discovery of a vast number of new ILs and a wide range of interesting applications. Unlike conventional molten salts, ionic liquids are salts with melting points less than 100 °C and often even below room temperature. ILs are usually made from a bulky and asymmetric organic cation and an anion with considerable charge delocalization. These features preclude good crystal packing and decrease inter-ionic interactions, thereby resulting in low melting points. The synthesis of ILs is usually achieved by ion exchange reactions.

ILs exhibit many advantageous physical and chemical properties compared to conventional organic solvents. The most appealing property is the negligible vapor pressures of ILs, which makes them less polluting than volatile organic solvents. In addition, ILs also possess low toxicity, high chemical stability, high thermal stability, high conductivity, wide electrochemical windows and the ability to dissolve a wide range of organic and inorganic compounds. These characteristics make them appealing as replacements for conventional organic solvents, catalytic media, electrolytes for batteries, and even as advanced heat transfer fluids and lubricants.

The research described in this thesis involves ultrafast solution dynamics. The outline can be divided into two main parts: dynamics in ionic liquids and non-radiative deactivation of malononitriles. Following the present brief introduction, Chapter 2 describes the general experimental techniques and data analysis used in the following chapters. Chapter 3 focuses on measuring the physical properties of sixteen different ionic liquids, some of which are required in the studies described in the following chapters. Experimental measurements of phase-transition temperatures, densities, refractive indices, surface tensions, solvatochromic polarities, NMR shifts, temperature-dependent viscosities, conductivities and cation diffusion coefficients are reported in this chapter. Chapter 4 begins with the measurement of solvation and rotational dynamics in a diverse collection of ionic liquids probed by Coumarin 153 (C153). Chapter 5 is
an extension of the work from Chapter 4 where we explore the origins of non-exponential dynamics in ILs. The excitation wavelength dependence of the kinetics of several solutes is used to demonstrate the presence of dynamic heterogeneity in ILs. Chapter 6 concerns an investigation of the non-radiative deactivation of two malononitriles used in Chapter 5. Malononitriles in different conventional solvents and at different temperatures are studied to elucidate the details of their non-radiative deactivation. Some of the chapters in this thesis are revised version of my first-author publications. Most papers from our research group are done as a team, so my co-authors deserve recognition and gratitude. Publication information and a description of the contributions of my co-authors is provided at the beginning of each chapter.
References and Notes

2 http://research.chem.psu.edu/maroncelli/
Chapter 2

Main Experimental Technique and Data Analysis Methods

The main experimental approach used throughout this thesis is time-resolved fluorescence spectroscopy measured by time-correlated single photon counting (TCSPC) technique. In this chapter, TCSPC technique, experimental setup and data analysis methods will be described in details.

2.1 TCSPC Technique Introduction

TCSPC is a time-resolved fluorescence technique\(^1\) widely used for many applications including studies of solvation and rotational dynamics\(^2,3\). TCSPC is based on recording arrival times of single photons after pulsed excitation using a high-repetition rate source. The principles of TCSPC can be illustrated using the instrument schematic\(^4\) shown in Figure 2.1. The experiment starts with an excitation pulse, which excites the sample and produces a start signal to trigger the voltage ramp of the time-to-amplitude (TAC) converter. The voltage ramp is stopped when detecting the first fluorescence photon from the sample. An output pulse from the TAC is proportional to the time between the start and stop signals. A multichannel analyzer (MCA) converts this voltage to a time channel using an analog-to-digital (ATD) converter. The MCA builds up a probability histogram of photon counts versus time channel, which represents the sample intensity decay after summing over many pulses\(^4\).

A schematic of the TCSPC instrument used in our lab is shown in Figure 2.2\(^5\). A continuous argon ion laser is used to pump the mode-locked Ti:Sapphire oscillator. A pulse picker reduces the repetition rate of the oscillator output pulses and feeds the resulting pulses to a
Figure 2.1 Schematic for time-correlated single photon counting\(^4\).
Figure 2.2 Schematic of the TCSPC instrument in Maroncelli’s group. Solid lines show electrical signal paths, while dashed lines show the laser beam path. Abbreviations: CW (continuous wavelength), PD (photodiode), $2\omega$, $3\omega$ (frequency doubling/tripling optics), MCP (micro-channel plate photomultiplier), AMP (amplifier), CFD (constant fraction discriminator), TAC (time-to-amplitude converter) and MCA (multi-channel analyzer).
photodiode (PD) and the frequency conversion (2\omega, 3\omega) part of the instrument. Frequency conversion generates excitation light with the desired wavelength which is directed into the sample holder. The resulting fluorescence is detected by a micro-channel plate photomultiplier tube (MCP-PMT).
2.2 TCSPC Components

Although principles of TCSPC are simple and straightforward, there are many subtleties which are not obvious at first examination. The different components that constitute a TCSPC instrument can be separated to four main categories: light sources, optics, detectors, and electronics. Each component plays a distinct and important role in the TCSPC system, and effective use of this method requires understanding these various components.

2.2.1 Light Source

The light source for TCSPC varies from cheap flash lamps to picosecond dye lasers, solid-state lasers, and more expensive femtosecond Titanium:Sapphire (Ti:Sapphire) lasers. In all cases the requirements are the same: stable pulsed radiation with known temporal character. Flash lamps operate by generating spark discharges in a gaseous (usually H$_2$ or N$_2$) environment. Although simple in principle and inexpensive, flash lamps have a number of drawbacks such as low stability, low repetition rate, and weak pulse intensity. The dye laser is a passive device which requires an optical pump source, usually an argon ion laser, and can provide pulses about 5 ps wide with repetition rates up to 80 MHz. Mode-locked Ti:Sapphire lasers provide remarkable pulse widths near 100 fs. An important advantage of the Ti:Sapphire laser is that it is a solid-state device. There are no flowing dyes to be replaced and the Ti:Sapphire crystal has a long operating life. The disadvantage of dye lasers and Ti:Sapphire lasers is their expenses. Less expensive solid-state lasers such as diode-pumped Nd:YAG lasers seem more promising in the future. Pulsed diode lasers are also currently quite popular. With each light source having both pros and cons, Ti:Sapphire lasers have been mostly commonly used for TCSPC instruments and it is used for our own TCSPC setup.
Ti:Sapphire lasers have excellent stability and flexibility, which is ideal for TCSPC instrument. The spectral output can range from 720 nm to 1000 nm with repetition rates around 80 Hz\(^4\). The most important feature of Ti:Sapphire lasers as mentioned previously is their use of a solid-state gain medium. The single gain medium is advantageous over dye lasers, which need multiple dye solutions to cover a suitable range of excitation wavelength and require replacing dye solutions regularly. Another advantage of Ti:Sapphire lasers are the use of simple continuous wavelength lasers as pump sources, whereas dye lasers need more complex mode-locked pump sources. Mode-locking of Ti:Sapphire lasers is easy using an approach called Kerr-lense mode locking.

The excitation requirements for high time-resolution fluorescence spectroscopy are mostly satisfied by Ti:Sapphire lasers with some additional equipment. Resolution of a dynamic process needs an instantaneous excitation compared with the lifetime of the dynamic process to avoid complications. This means the excitation pulse duration needs to be much shorter than the dynamic process itself. The temporal width, defined as Full-Width at Half-Maximum (FWHM) time spread, of the Ti:Sapphire laser pulses are usually 100-150 fs, which is ideal for the excitation.

Another important requirement of the excitation source is the range of frequencies over which it can be effectively operated (tunability). A typical Ti:Sapphire laser usually operates over the range 720 nm to 1000 nm, depending on the quality of the cavity optics. Such frequencies are not suitable for common fluorescence spectroscopy. Non-linear conversion methods are used to generate ultraviolet (UV) and visible wavelengths useful for excitation of common fluorophores. The most widely used conversion schemes are frequency doubling (2\(\omega\)) and tripling (3\(\omega\)). Higher-order processes and mixing schemes are also applicable. While frequency conversion is not very efficient and tripling and high-order non-linear processes have
strict phase-matching requirements, these methods are still commonly used in experimental practice.

The repetition rate of the excitation is also crucial for TCSPC experiments. If the spacing between two excitation pulses is not large enough, the population of excited states will not have enough time to relax and reach equilibrium before the next excitation. This will not satisfy random decay collection and will distort experimental results. It will take more than five lifetimes of the fluorophore to get a reasonable relaxation, which equals to more than 99% of the molecules already relax to ground state. Typical fluorophores have averaged lifetimes from 1 ns to 10 ns in conventional liquid solvents, which means the spacing of pulses have to be more than 50 ns or a repetition rate of 20 MHz. Typical Ti:Sapphire system have a repetition rate around 80 MHz, which is too fast for most of the fluorophores. For this reason, an external pulse picker must be added to Ti:Sapphire system for controlling repetition rate. Pulse picker diffracts individual pulses at selected repetition rate and undiffracted pulses will be thrown away. The Ti:Sapphire beam after the pulse picker can operate at much lower repetition rate, making it ideal for TCSPC measurements.

2.2.2 Optics

The optical components in a TCSPC system serve multiple purposes: beam steering, frequency conversion, polarization and detection. Choosing the proper optics is important for proper functioning of a TCSPC system.

Steering optics are used for beam alignment throughout the whole TCSPC system. Many varieties of mirrors are available and the choice depends on the excitation source employed. Systems using Ti:Sapphire lasers usually use gold or dielectric-coated mirrors whereas visible dye lasers use aluminum-coated optics. Detailed specifications such as wavelength range,
incident angle and group velocity dispersion (GVD) need to be taken into consideration when choosing steering optics. Using wrong mirrors will induce polarization, decrease total beam power and broaden pulses thereby degrading the quality of the data available, which bring difficulties to TCSPC experiments.

Although frequency conversion processes are complex, the optical components are relatively simple. A frequency-conversion arrangement usually includes one or more non-linear optical crystals. Optics used in frequency conversion should be chosen carefully according to specification requirements mentioned in previous paragraph. Additionally, crystals used for frequency conversion need to be carefully chosen. These crystals can combine two incident photons \((\omega_1 \& \omega_2)\) into a third photon at the sum of the incident photon frequencies \((\omega_{out} = \omega_1 + \omega_2)\) due to their special symmetry properties. Crystal selection will depend mostly on the range of frequencies combined. The most common doubling \((2\omega)\) crystal for Ti:Sapphire laser is \(\beta\)-barium borate (BBO).

Another type of optical component that plays an important role in TCSPC system is polarizer. In order to extract useful information from fluorescence decays, both the excitation and emission polarization should be strictly controlled. A polarizer is a device that converts an unpolarized or mixed-polarization beam into a beam with a linear polarization. Polarizers can be divided into two types: absorptive polarizers, in which unwanted polarizations are absorbed, and beam-splitting polarizers where an unpolarized beam is split into two beams with opposite polarization states. The excitation light source is usually passed through a polarizer to ensure vertically polarized sample excitation. A second adjustable polarizer is used before detection to filter the emission, which is especially important for anisotropy measurements.

Wave plates, unlike polarizers, rotate the polarization of an incident beam. A half-wave plate rotates the polarization of an incoming linearly polarized beam by \(90^\circ\) and is commonly used for TCSPC to yield the proper polarization for experiment. The lens system used for
collecting the fluorescence is also important and is often given insufficient attention. The difference between using lenses with high versus low solid angles throughout can often cause an order of magnitude change in sensitivity. The lenses should be adjustable in position for optimizing the signal, which is particularly important for samples with high optical density.

Monochromators are used to disperse polychromatic light into different wavelengths, usually using diffraction gratings. Monochromators vary according to their dispersions, efficiencies and stray light levels. A monochromator should have low stray levels to avoid scattering or stray light, which is light transmitted by the monochromators at wavelengths outside the chosen range. Monochromators also need to be highly efficient in order to detect low light levels. Optical filters are also often used in addition to monochromator in TCSPC. Optical filters can filter unwanted wavelengths from non-ideal behavior of monochromators. Most filters are colored-glass filters, which can transmit a range of wavelengths.

2.2.3 Detectors and Electronics

There are many requirements on the detector used for TCSPC. Low timing jitter, insensitivity of the timing to wavelength and point of illumination, high amplification, low noise, and wide spectral range are all important considerations. At present, the most common choice of detector for TCSPC is multichannel plate photomultiplier tube (MCP-PMT). Other choices include dynode-chain PMTs and photodiodes (PDs). A PMT takes an incident photon and converts it to a current at the photocathode which then produces many electrons. The design of a MCP-PMT is quite different from that of a dynode-chain PMT. The main factor that limits the temporal response of a PMT is the distribution of transit times though the detector, called the transit time spread (TTS). In a dynode chain PMT, TTS is minimized by designing the dynodes so that all electrons tend to travel along the same path. In MCPs, instead of using a discrete set of
dynodes, electrons are amplified along narrow channels lined with dynode material. Small channels result in small TTS. The time response with MCP-PMT is impressive and can be as short as 25 ps. Also MCP-PMTs usually do not produce after-pulses, which are always present in dynode PMTs. But dynodes PMTs cost much less than MCP-PMTs and are sometimes adequate, especially for flash lamp excitation experiments.

Photodiodes (PDs) are also commonly used as detectors for TCSPC. PDs are less expensive and have faster response times than MCP-PMTs. But PDs do not have the gain characteristics of MCP-PMTs and are inefficient for single photon detection. For the above reasons, PDs are usually not used to detect fluorescence but instead are used to monitor the laser pulse timing where low light intensity is not an issue.

The TCSPC technique utilizes electronics to control timing, and therefore electronics play a crucial role in determining the time resolution of the experiment. Most of the electronics used in TCSPC instrument will be introduced and explained in detail in the following paragraphs.

The constant fraction discriminator (CFD) measures the arrival time of the photoelectron pulse with high time resolution. The variable amplitudes and widths of signal pulses make it difficult to use more common leading-edge discriminators due to the temporal spread that results from the pulse height variation. In a CFD the signal pulse is split into two parts. One part is delayed by about half of the pulse width, and another part is inverted. These two parts are then recombined, which results in a zero-crossing point that is independent of the pulse height. The use of CFD instead of leading-edge discrimination improves jitter time and the precision of TCSPC experiments remarkably. Two CFDs, one for a start and one for a stop signal, send pulses to a time-to-amplitude converter (TAC).

The TAC measures the time between the excitation pulse and the first arriving emitted photon by charging a capacitor during this time interval. The TAC is a rate-limiting component because it usually takes several microseconds to discharge the capacitor and reset voltages to zero
after a measurement. This is not a problem for flash lamp experiments with low repetition rates, but TACs can be overloaded by lasers with repetition rate in the MHz range. A simple solution is to operate the TAC in reverse mode, where the TAC is only activated when an emitted photon is detected. The resulting voltage (time) of each detected photon from the TAC is fed to a Multichannel Analyzer (MCA) to create TCSPC fluorescence decays.

The MCA sorts photons according to their voltage (time) and then builds the intensity decay after many individual photons. MCA usually has 2048-8192 channels, which makes it easy to collect data with high time resolution and different time windows.
2.3 Data Analysis

2.3.1 Instrumental Function and Convolution

It is important to understand that an intensity decay measured using TCSPC is a convolution of an ideal sample signal and the instrumental response function. The ideal fluorescence decay $I(t)$ is what would be observed with $\delta$-function excitation and instrumental response. Unfortunately most instrumental response functions are not ideal $\delta$-functions, so the measured emission decay $N(t)$ is the ideal fluorescence decay $I(t)$ broadened by the temporal response function of the instrument $R(t)$. In order to interpret recorded data correctly, the effects of instrumental broadening have to be removed from measured emission decays. The $R(t)$ is defined as the response detected from a sample possessing $\delta$-function dynamics (a zero-lifetime sample), which can be approximately experimentally measured with a scattering solution such as non-dairy creamer in water. The instantaneous scattering from such a sample gives a temporal profile from all the factors that serve to broaden detected emission.

2.3.2 Formulation of the Decays and Least-Square Fitting

As mentioned above, measured emission decays are the actual sample response $I(t)$ convoluted with instrumental response function $R(t)$. To extract $I(t)$ from the observed $N(t)$ and $R(t)$ data, the iterative reconvolution method using non-linear least square analysis (NLLSA) is typically used. The assumptions of NLLSA include having large numbers of independent data points, a Gaussian distribution for the dependent variable errors, and being able to mathematically describe the system by a fitting function. TCSPC generally meets all of these requirements, and NLLSA seems to be the perfect choice for TCSPC data analysis.
Fitting functions for TCSPC emission decays are usually multi-exponential decay functions (eq 2.1), but can also be more complex forms.

\[
I(t) = \sum_{i=1}^{n} \alpha_i \exp\left(-\frac{t}{\tau_i}\right) \tag{2.1}
\]

When fitting TCSPC data by NLLSA, an estimated sample response \( I_c(t) \) is produced first by an initial guess of the fitting parameters. \( I_c(t) \) is convoluted with the \( R(t) \) to produce an estimated sample decay \( N_c(t) \) and then \( N_c(t) \) is compared with the observed fluorescence decay \( N(t) \). The goodness of fit is measured by the \( \chi^2 \) parameter,

\[
\chi^2 = \sum_{t=1}^{n} \frac{1}{\sigma(t)^2} [N(t) - N_c(t)]^2 = \sum_{t=1}^{n} \frac{[N(t) - N_c(t)]^2}{N_c(t)} \tag{2.2}
\]

where \( \sigma(t) \) is the standard deviation at time \( t \) and \( n \) is the number of data points in the decay. The Poissonian nature of photon statistics makes the standard deviation proportional to the square root of the number of counts at time \( t \). For comparing different data sets the reduced goodness of fit statistic \( \chi^2_p \) is used,

\[
\chi^2_p = \frac{\chi^2}{n-p} \tag{2.3}
\]

where \( n \) is the number of data points and \( p \) is the number of independent parameters fit by \( I_c(t) \). The value of \( \chi^2_p \) for a good fit is expected to be in the range of 0.8 to 1.2. Larger values indicate either an improper mathematical function or systematic errors in the data.

2.3.3 Anisotropy Analysis\textsuperscript{46}

In addition to fluorescence lifetime measurement, TCSPC is also commonly used to study reorientational dynamics. With the use of polarized excitation, fluorescence intensity decays at parallel and perpendicular emission polarizations depend on the rotation of excited fluorophores. If the time scale of fluorophores rotation is comparable to its lifetime, then the
depolarization of emission anisotropy as a function of time can be used to observe molecular rotation. Time-resolved anisotropy can be represented using eq 2.4.

\[
r(t) = \frac{I_{H}(t) - I_{L}(t)}{I_{H}(t) + 2I_{L}(t)} = \frac{I_{d}(t)}{I_{s}(t)}
\]  

(2.4)

Our experimental measurements of time-resolved anisotropy utilize an L-format method. The L-method uses vertical light to excite the sample and emission decays at vertical (parallel) and horizontal (perpendicular) polarizations are recorded separately. The polarization characteristics of different optics used in TCSPC systems have important consequences in the measurement of fluorescence anisotropy. Such measurements must be corrected for the varying efficiencies of each optical component. This correction is expressed as the \( G \) factor. The \( G \) factor is easily measured using horizontally polarized excitation. With horizontally polarized excitation the excited-state distribution is rotated to lie along the observation axis. Both the horizontally and vertically polarized components are equal and proportional to \( I \); because the electric field is equally distributed around the observation axis. Any measured difference in \( I_{HV} \) and \( I_{HH} \) must be due to the detection system and \( G \) factor can be calculated by eq 2.5.

\[
G = \frac{S_{V}}{S_{H}} = \frac{S_{V}I_{L}}{S_{H}I_{HH}} = \frac{I_{HV}}{I_{HH}}
\]  

(2.5)

where \( S_{V} \) and \( S_{H} \) are sensitivities of vertically and horizontally polarized emission.

Mathematical functions used to fit time-resolved anisotropy data are usually multi-exponential functions (eq 2.6a), but stretched exponential decay (eq 2.6b) is often used for ILs\(^7\).

\[
r(t) = r_0 \sum_{j} g_j \exp \left( -\frac{t}{\tau_j} \right)
\]  

(2.6a)

\[
r(t) = r_0 \exp \left( -\frac{t}{\tau} \right)^{\beta}
\]  

(2.6b)

Measured anisotropy decays are also distorted by a finite instrumental response and a similar NLLSA method is typically used to extract information from observed data. Rewriting eq 2.4 we can obtain \( r(t)I_{s}(t) = I_{d}(t) \). The first step in anisotropy analysis is determining the
excited state decay law $I_s(t)$. $I_s(t)$ represents the fluorescence decay measured at magic emission polarization, and can be easily obtained by deconvolution analysis with $R(t)$ using fluorescence decay parameters to a good fit. $I_d(t)$ can be obtained directly from experimental measurements, hence $r(t)$ can be obtained by convoluting $R(t)$ with $r(t)I_s(t)$ using a trial $r(t)$ and fit to $I_d(t)$ using NLLSA method.

The above commonly used method of fitting $I_d(t)$ can give accurate results but has a tendency to mask systematic errors due to the manipulation of the data in constructing the different functions. When the anisotropy decay law is nonexponential, simultaneous fitting to both $I_\parallel(t)$ and $I_\perp(t)$ is preferred. In this method, $I_\parallel(t)$ and $I_\perp(t)$ are calculated as follows using a trial $r(t)$ and fit to experimental $I_\parallel(t)$ and $I_\perp(t)$ simultaneously using NLLSA method:

$$I_\parallel(t) = \frac{1}{3} I_s(t) [1 + 2r(t)]$$  \hspace{1cm} (2.7a)

$$I_\perp(t) = \frac{1}{3} I_s(t) [1 - 2r(t)]$$  \hspace{1cm} (2.7b)

Simultaneous fitting method acts on raw data rather than constructs of it, so it is more sensitive to systematic error and essentially has been the method used this thesis work.

### 2.3.4 Reconstruction of Time-Resolved Spectra

In order to reconstruct time-resolved fluorescence spectra using the TCSPC technique, fluorescence decays are collected at different wavelengths across the emission spectrum. At any particular delay time the spectrum is assembled as follows. First each emission decay $I(\lambda_j, t)$ measured at a fixed wavelength $\lambda_j$ is analyzed as usual by NLLSA using the multi-exponential model

$$I(\lambda_j, t) = \sum_{i=1}^{n} \alpha_i(\lambda_j) \exp \left[ -\frac{t}{\tau_i(\lambda_j)} \right]$$  \hspace{1cm} (2.8)
In this analysis the decay times can be fit as wavelength-dependent or wavelength-independent parameters. In order to reconstruct time-resolved spectra, a new set of normalized intensity decays are computed so that the time-integrated intensity at each wavelength is proportional to the steady-state intensity at the same wavelength \( F(\lambda_j) \). The normalization factor is

\[
H(\lambda_j) = \frac{\int_0^\infty I(\lambda_j, t) \, dt}{\int_0^\infty I(\lambda_j, t) \, dt} = \frac{\int_0^\infty I(\lambda_j, t) \, dt}{\sum_i \alpha_i(\lambda_j) \tau_i(\lambda_j)}
\] (2.9)

Appropriately normalized intensity decay function are obtained by eq 2.10

\[
I(\lambda_j, t) = H(\lambda_j) I(\lambda_j, t) = \sum_{i=1}^\infty \alpha'_i(\lambda_j) \exp \left[ -\frac{t}{\tau_i(\lambda_j)} \right]
\] (2.10)

where \( \alpha'_i(\lambda_j) = H(\lambda_j) \alpha_i(\lambda_j) \). The intensity at any measured wavelength and time can be calculated by eq 2.10, which provides the time-resolved spectra. Because only a moderate number (10-20) of decays are collected, the spectra \( I(\lambda_j, t) \) are usually fit to a log-normal line shape function to provide continuous representations of the time-resolved spectra. Time-dependent peak or average frequency information is extracted from fitted spectra and transformed to solvation (spectral) response functions.

### 2.3.5 Estimation of Time-Zero Spectrum

Due to the limited time-resolution (25 ps) of our TCSPC setup, the time-zero spectra extrapolated from time-resolved data usually do not reflect the real time-zero spectra. Fee and Maroncelli\(^9\) developed a method to estimate time-zero spectra for time-resolved emission studies. This method uses only steady-state spectral data and is not dependent on instrumental time-resolution.
The main assumption of this method is that the spectra of individual molecules in different environment differ only by an overall spectra shift. In a polar solvent, the inhomogenously broadened absorption spectrum can be described by

\[ A_p(\nu) \propto \nu \int g(\nu - \delta) p(\delta) d\delta \] (2.11)

where \( A_p(\nu) \) is the absorption spectrum, \( g(\nu) \) the absorption lineshape function, and \( p(\delta) \) the distribution of solutes among sites. If \( f(\nu) \) represents the corresponding emission lineshape, the fluorescence spectrum \( F_p(\nu, t = 0, \nu_{ex}) \) observed immediately after monochromatic excitation with frequency \( \nu_{ex} \) can be calculated using eq 2.12.

\[ F_p(\nu, t = 0, \nu_{ex}) \propto v^3 \nu_{ex} \times \int g(\nu_{ex} - \delta) p(\delta) f(\nu - \delta) k_{rad}(\delta) d\delta \] (2.12)

where \( k_{rad} \) is the radiative rate constant. Eq 2.11 states that the emission spectrum observed before any solvent relaxation is the convolution of the solvent distribution initially transferred to the exited state \( g(\nu_{ex} - \delta) p(\delta) \) and the intensity function \( f(\nu - \delta) k_{rad}(\delta) \). In order to use eq 2.11 to estimate time-zero spectra, steady-state spectral data need to be used. The lineshape functions \( g(\nu) \) and \( f(\nu) \) can be easily obtained from steady-state absorption and emission spectra measured in a non-polar reference solvent such as hexane:

\[ g(\nu) \propto \nu^{-1} A_{np}(\nu) \] (2.13a)

and

\[ f(\nu) \propto \nu^{-3} F_{np}(\nu) \] (2.13b)

The radiative rate function \( k_{rad}(\delta) \) can be calculated by

\[ k_{rad}(\delta) \propto \frac{\int f(\nu - \delta) \nu^3 d\nu}{\int f(\nu - \delta) d\nu} \] (2.14)

Finally, the site distribution is assumed to be a Gaussian function

\[ p(\delta) = (2\pi\sigma^2)^{-1/2} \exp \left[ -\left( \delta - \delta_0 \right)^2 / 2\sigma^2 \right] \] (2.15)
where $\delta_0$ is the average shift induced by the polar solvent and $\sigma$ is the width of the distribution. The distribution parameter $\delta_0$ and $\sigma$ can be obtained by fitting the polar absorption spectrum using eq 2.11 and a $g(\nu)$ obtained from a nonpolar reference solvent (2.13a) with $\delta_0$ and $\sigma$ as adjustable parameters.
References and Notes


Chapter 3

Physical Properties of Ionic Liquids

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Co-author’s contributions:

This chapter has been reproduced from above publication with only minor modification.
I acknowledge my co-author’s contributions to this work, which include electronic structure
calculations by Mark Maroncelli; density, refractive index, and viscosity measurement by Jing
Dong; surface tension measurement by Sergei Arzhantsev; and NMR measurement by Bernie
O’Hare.
3.1 Introduction

Since the introduction of room temperature ionic liquids (ILs) that is air and water stable in 1992\textsuperscript{1} research into potential applications of these materials has grown at an ever accelerating rate. Room temperature ionic liquids are now being explored in virtually all areas of chemistry - as solvents for organic and inorganic synthesis\textsuperscript{2}, as electrolytes in batteries\textsuperscript{3} and solar cells\textsuperscript{4}, as new types of energetic materials\textsuperscript{5}, as stationary phases in chromatography\textsuperscript{6} and in a variety of other analytical applications\textsuperscript{7-9}, as well as being the subject of fundamental study in physical chemistry\textsuperscript{10}. To support all of these endeavors it is important to know various physical properties of the ILs involved. For this reason, a number of groups, most notably those of MacFarlane & Forsyth\textsuperscript{11-14}, Rogers\textsuperscript{15}, Seddon\textsuperscript{16,17}, Brennecke\textsuperscript{18,19} and Watanabe\textsuperscript{20-24} have been actively gathering physical property data on ILs. A number of compilations\textsuperscript{25-27} as well as an on-line database\textsuperscript{28} providing easy access to such data are beginning to appear. But the number of ionic liquids for which a range of physical properties have been accurately characterized is still limited, especially in comparison to the huge number of ILs currently available. Over the past several years our group has reported spectroscopic studies of solvation in a number of related ionic liquids\textsuperscript{29-35}, few of which have been thoroughly characterized. The purpose of the present paper is to provide basic physical property data on these ILs that we hope will be of value to other workers.

The 16 ionic liquids studied in the present work (Figure 3.1) comprise three groups. The first group is a series of liquids based on the 1-butyl-3-methyl-imidazolium cation (Im\textsubscript{41}\textsuperscript{+}) with the anions BF\textsubscript{4}-, PF\textsubscript{6}-, bis(trifluoromethylsulfonyl)imide (Tf\textsubscript{2}N-) and tris(trifluoromethylsulfonyl)methide (Tf\textsubscript{3}C). Except for [Im\textsubscript{41}+][Tf\textsubscript{3}C], various properties of these liquids have been reported by several groups and they therefore provide useful comparisons for the present measurements. The remaining liquids all contain the Tf\textsubscript{2}N\textsuperscript{-} anion. The second group involves two homologous series of cations, an N-alkyl-N-methylpyrrolidinium (Pr\textsubscript{n1}+)
Figure 3.1 Structures of the ions for ILs studied in this work and their designations.
series and a dimethyl(isopropyl)alkylammonium (N_{ipn1}^+) series having normal alkyl groups of \(n = 3, 4, 6, \text{and } 10\) carbon atoms in length. The cations of the final group are related to the previous imidazolium, pyrrolidinium, and ammonium series via substitution (or addition) of a hydroxyl functionality. With the exception of [Pr_{41}^+][\text{TF}_2\text{N}^-] and some fragmentary data on [Pr_{31}^+][\text{TF}_2\text{N}^-], none of the ILs in the latter two groups have been previously characterized.

The experimental properties reported here include phase transition temperatures, densities, refractive indices, surface tensions, several solvatochromic measures of polarity, viscosities, conductivities and cation diffusion coefficients. The “static” properties, which are relatively insensitive to temperature, were measured at a single temperature (20 or 25 °C), whereas viscosities are reported as functions of temperature to enable estimations of dynamical quantities at other temperatures. In addition, we report a number of characteristics of the individual ions derived from electronic structure calculations and also consider estimation of Hildebrand solubility parameters from measured values of surface tension and molar volumes.
3.2 Materials and Methods

**Computations:** Density functional (DFT) calculations were performed using the Gaussian 03 program at the B3LYP/6-31G(d,p) level of theory. Molecular volumes were estimated from the 0.001\(e/a_0^3\) contours and electrostatic properties calculated using atomic charges derived from fitting the electrostatic potential generated by these wavefunctions. To sample conformations of cations having flexible aliphatic chains, molecular mechanics calculations were performed using the MacroModel program with the MMFF94s force field. The conformational search algorithm employed was based on a multiple minimum Monte Carlo algorithm. The resulting structures were then used as input to the DFT calculations.

**Materials:** 1-butyl-3-methylimidazolium tetrafluoroborate \([\text{Im}^+][\text{BF}_4^-]\) was obtained from Sigma-Aldrich (97%; <100 ppm Cl). It was dissolved in acetonitrile and treated with activated carbon after which the solvent was removed and the sample dried under vacuum for 36 hours at 60 °C. 1-Butyl-3-methylimidazolium hexafluorophosphate \([\text{Im}^+][\text{PF}_6^-]\), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide \([\text{Im}^+][\text{Tf}_2\text{N}]\), and 1-butyl-3-methylimidazolium tris(trifluoromethylsulfonyl)methide \([\text{Im}^+][\text{Tf}_3\text{C}]\) were obtained from Covalent Associates (electrochemical grade, >99.5%, <50 ppm H\(_2\)O) and, except for drying, were used as received. Two series of spectrochemical-grade ILs based on the \(N\)-alkyl-\(N\)-methylpyrrolidinium (Pr\(_n^+\); Figure 3.1) and dimethyl(isopropyl)alkylammonium (N\(_{ippn}^+\)) parent cations with \(n = 3, 4, 6, \) and 10 were also prepared following recently reported procedures, substituting the appropriate 1-bromoalkane and aliphatic amine starting materials. These methods, which evolved from those described earlier by Baker et al. and Nockemann et al., entailed several key modifications essential to obtaining high optical quality materials acceptable for spectroscopic studies, as detailed in Refs. The target ILs were obtained in 85–94% overall yield. The final products were washed exhaustively with water to remove \(\text{Br}^-\) impurities,
which we expect to be below 25 ppm based on AgNO₃ tests, and were dried under vacuum at
room temperature overnight followed by drying at 70 °C for more than 48 h prior to
characterization and spectroscopic studies. ¹H NMR spectra of these compounds were recorded
on a Bruker Avance 400 MHz spectrometer with the observed chemical shifts reported relative to
the residual solvent peak from acetone as an internal reference. ¹H NMR (400 MHz, acetone-δ₆, 
δ/ppm): [Pr₃][Tf₂N⁻]: 3.71 (m, 4H), 3.50 (m, 2H), 3.25 (s, 3H), 2.32 (m, 4H), 1.95 (m, 2H),
1.01 (t, 3H); [Pr₄][Tf₂N⁻]: 3.72 (m, 4H), 3.55 (m, 2H), 2.32 (m, 3H), 1.91 (m, 2H),
1.93 (m, 2H), 1.37 (br m, 6H), 0.89 (t, 3H). [Pr₆][Tf₂N⁻]: 3.72 (m, 4H), 3.55 (m, 2H), 3.26 (s, 3H), 2.32 (m, 4H),
1.93 (m, 2H), 1.37 (br m, 6H), 0.89 (t, 3H). [Pr₁₀][Tf₂N⁻]: 3.72 (m, 4H), 3.54 (m, 2H), 3.26 (s, 3H), 2.32 (m, 4H),
1.93 (m, 2H), 1.37 (br m, 6H), 0.89 (t, 3H). [N₃][Tf₂N⁻]: 3.92 (m, 1H), 3.46 (m, 2H), 1.94 (m, 2H), 0.87 (t, 3H). [N₄][Tf₂N⁻]:
3.94 (m, 1H), 3.51 (m, 2H), 3.22 (s, 6H), 1.89 (m, 2H), 1.51 (m, 6H), 1.00 (t, 3H). [N₆][Tf₂N⁻]: 3.94 (m, 1H), 3.50 (m, 2H), 3.22 (s, 6H), 1.91 (m, 2H), 1.50 (m, 6H), 1.37 (br m, 6H), 0.89 (t, 3H). [N₆][Tf₂N⁻]: 3.94 (m, 1H), 3.51 (m, 2H), 3.22 (s, 6H), 1.92 (m, 2H),
1.51 (m, 6H), 1.40 (br m, 4H), 0.87 (t, 3H). Four related alcoholic ILs (Figure 3.1) were also synthesized for the current work. The full preparation of these functionalized ILs
will be disclosed elsewhere⁴⁵.

Water Content: The water content of each IL was determined using a Mettler-Toledo DL39
Karl-Fisher Coulometer at room temperature. Measurements were performed in triplicate and
average values reported. Because the measurements of the various properties reported here were
made at different times, and the various techniques involve more or less exposure to atmospheric
humidity, the water contents reported later in Tables 3.2 and 3.4 are only representative. The
largest values are representative of samples stored for some time in a dry-nitrogen purged glove
box and the smallest values are representative of samples dried over night immediately prior to
measurement. With the exception of [Pr₃(OH)₃][Tf₂N⁻], based on the reported effects of small
concentrations of water we believe that the samples used for a given measurement contain sufficiently low levels of water that the reported values reliably represent the properties of the neat IL.

**Thermal Analysis:** Differential scanning calorimetry (DSC) was carried out under a helium atmosphere using a TA Instruments DSC Q100 fitted with a liquid nitrogen cooling system. Samples weighing 5-12 mg were hermetically sealed in aluminum pans and heated to 80 °C followed by cooling to −150 °C at a rate of 10 °C min⁻¹, and finally heated back to 80 °C again at a rate of 10 °C min⁻¹. The glass transition temperatures, crystallization temperatures, and melting points, were determined from the DSC thermograms based on analysis of the programmed reheating cycle. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA Q500 under a helium atmosphere with open platinum pans, from 60 to 600 °C at a heating rate of 10 °C min⁻¹.

**Density and Refractive Index:** Densities were measured at room temperature (20 ± 1 °C) using a 1 mL volumetric flask. Samples were evacuated for 1 h prior to measurement to remove any trapped bubbles. Refractive indices at the sodium D line were measured with an Abbé refractometer (Reichert, Mark II). Most samples were measured at 20, 25, and 40 °C. Densities were corrected to 25 °C using the temperature dependence of the refractive index assuming a proportionality between the density and \((n_D^2 - 1)/(n_D^2 + 2)\).

**Surface Tension:** Surface tensions were measured with the maximum bubble pressure method using a home-built apparatus consisting of two glass tubes of internal diameters of 1.5 mm and ~0.06 mm, an open end liquid manometer, and supply of argon or nitrogen gas. The approximate equation developed by Sugden was used to determine the surface tension (\(\gamma\))

\[
\gamma = A\Delta P(1 + 0.69 rgd / \Delta P)
\]  

(3.1)
where $A$ is an empirical constant obtained from calibration of the apparatus, $\Delta P$ is the difference in pressures required to create bubbles in the two glass tubes, $r$ is the radius of the larger tube, $d$ is the mass density of sample, and $g$ the acceleration of gravity. As discussed in Ref.\textsuperscript{50}, the accuracy of such measurements is mainly determined by the accuracy of the pressure readings and it can be as high as 0.1\%. The flow of argon gas was adjusted to have a bubble rate less than 1 bubble per second. Calibration was performed by measuring the surface tension of benzene and the performance of the apparatus was checked by measuring surface tensions of several organic solvents, which deviated by less than 1\% from literature values.

**Electronic Spectroscopy:** Absorption spectra were measured using a Hitachi U-3000 UV/Vis spectrometer at 1 nm resolution. Solutions of Nile Red having optical densities near 1.0 were prepared in 1 cm quartz cuvettes using IL solvents that had been dried in vacuum at 50 °C for 12 h.

**Viscosity:** Viscosities were measured using a Brookfield Model HBDV-III+CP cone/plate viscometer at 5 °C intervals over the temperature range 5-65 °C. The viscometer was calibrated against the NIST-certified viscosity standards N75 and N100 (Cannon Instruments Company). Ionic liquid samples were dried under vacuum at 50 °C overnight prior to all viscosity measurements.

**$^{19}$F Chemical Shifts and NMR Self-Diffusion Coefficients:** $^{19}$F chemical shifts were measured on a Bruker AMX-2-500 spectrometer equipped with a 5mm dual $^{19}$F/$^1$H probe at 25 °C relative to an external reference of neat CF$_3$COOH. All diffusion measurements were made on a Bruker DRX-400 spectrometer using a 5 mm inverse broadband probe (BBI) with triple axis gradients. The gradient strengths were determined using the known self-diffusion coefficient of neat DMSO at 25 °C. Measurements were made using the longitudinal eddy current delay (LED) stimulated echo pulse sequence with bipolar gradient pulses as developed by Wu \textit{et al.}\textsuperscript{52}. A 16 step linearly
ramped gradient experiment in which the gradient strength was increased between 2-95% of the maximum value of 80.7 G/cm was used. Cation diffusion constants were measured from the most upfield $^1$H (usually CH$_3$) resonance for the highest S/N, but different cation protons gave indistinguishable results.

**Conductivity:** Bulk conductivities were measured at room temperature, 22 ± 1 °C, by complex impedance measurements using a computer-controlled Hewlett-Packard 4129A Impedance Analyzer in the frequency range between 5 Hz and 10 MHz. Samples were placed into a homemade cell with electrodes inserted through the cap of a scintillation vial. The cell constant was determined using a standard aqueous 0.053% KCl solution (YSI 3167, NIST-traceable conductivity calibrator solution: 1,000±10 µS cm$^{-1}$ at 25 °C, Yellow Springs Instruments).
3.3 Results

3.3.1 Calculated Ion Properties

The ions examined in this work are illustrated in Figure 3.1, and some calculated properties of the isolated ions are listed in Table 3.1. Because most of the ions examined here possess conformational flexibility, some account of the presence of multiple conformers is necessary when attempting to compute properties. The properties listed in Table 3.1 are therefore conformationally averaged values derived from a sampling of low-energy conformations. To effect an approximate “thermal averaging” we performed a random sampling of conformers having energies within 10 kJ/mol of the lowest energy form. Exploration of the conformational energy surfaces of anions was performed manually, whereas for the cations we employed molecular mechanics calculations and an automated sampling scheme. For cations having butyl or smaller chains, the numbers of low-energy conformations (2nd column of Table 3.1) are reasonably small and in these systems we selected representative conformers and computed their properties using DFT calculations including geometry optimization. For cations containing longer alkyl chains, the number of low-energy conformers is quite large and a randomly chosen set of 10 conformers was selected for DFT calculation without geometry optimization. Although this method of approximating the liquid-state conformer distribution is admittedly crude, the properties so calculated are expected to be reasonable first approximations to the average characteristics of the species present in these ionic liquids. The properties summarized in Table 3.1 are the molecular volume $V$ and effective radius $R$, the inertial asymmetry parameter $\kappa$, and two measures of dipole moment $\mu_{res}$ and $\mu_{CA}$. The molecular volumes are those computed from the spatial extent of the DFT wavefunction (.001  $\text{a}_0$ contour) scaled by a factor of 1.25 in order
Table 3.1 Calculated ion properties. # indicates the number of conformers found having energies within 10 kJ/mol of the lowest energy form using either manual conformational searches in the case of the anions or an automated search using the MMFF94s force field for the cations. Values in parentheses indicate the numbers of conformers selected for electronic structure calculations. The remaining properties (except $M$, the molecular mass) were derived from B3LYP/6-31G (d,p) calculations averaged over the low-energy conformers. $V$ is the molecular volume (averaged over conformers) calculated from the 0.001 $e/a_0^3$ contour and scaled by a factor of 1.25. $R$ is the equivalent spherical radius, $R = (3V / 4\pi)^{1/3}$. $\kappa$, $\mu_{\text{com}}$, and $\mu_{\text{res}}$ are the asymmetry parameter, center of mass dipole (or charge arm) and residual dipole defined by eqs. 2.2-2.4. Values in parentheses in the last three columns are standard deviations over the set of conformers indicated as the last digit each value.

<table>
<thead>
<tr>
<th>Ion</th>
<th>#</th>
<th>$M$ [g mol$^{-1}$]</th>
<th>$V$ [Å$^3$]</th>
<th>$R$ [Å]</th>
<th>$\kappa$</th>
<th>$\mu_{\text{com}}$ [D]</th>
<th>$\mu_{\text{res}}$ [D]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_4^-$</td>
<td>1</td>
<td>86.8</td>
<td>50.5</td>
<td>2.29</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>1</td>
<td>145.0</td>
<td>84.3</td>
<td>2.72</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tf$_2$N$^-$</td>
<td>2</td>
<td>280.1</td>
<td>163</td>
<td>3.39</td>
<td>-.84(8)</td>
<td>4(3)</td>
<td>4(3)</td>
</tr>
<tr>
<td>Tf$_2$C$^+$</td>
<td></td>
<td>411.2</td>
<td>240</td>
<td>3.86</td>
<td>.20</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Im$_{41}^+$</td>
<td>9 (5)</td>
<td>139.2</td>
<td>163</td>
<td>3.39</td>
<td>-.95(5)</td>
<td>4.9(7)</td>
<td>6.6(9)</td>
</tr>
<tr>
<td>Pr$_{31}^+$</td>
<td>4</td>
<td>128.2</td>
<td>166</td>
<td>3.41</td>
<td>-.93(10)</td>
<td>1.7(3)</td>
<td>2.1(3)</td>
</tr>
<tr>
<td>Pr$_{41}^+$</td>
<td>12 (8)</td>
<td>142.3</td>
<td>175</td>
<td>3.47</td>
<td>-.97(3)</td>
<td>3.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Pr$_{61}^+$</td>
<td>48 (10)</td>
<td>170.3</td>
<td>214</td>
<td>3.71</td>
<td>-.99</td>
<td>7.5(3)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>Pr$_{10,1}^+$</td>
<td>216 (10)</td>
<td>226.4</td>
<td>288</td>
<td>4.10</td>
<td>-.99</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>N$_{ip,311}^+$</td>
<td>3</td>
<td>130.3</td>
<td>166</td>
<td>3.41</td>
<td>-.88(6)</td>
<td>1.8(3)</td>
<td>2.0(3)</td>
</tr>
<tr>
<td>N$_{ip,411}^+$</td>
<td>7</td>
<td>144.3</td>
<td>193</td>
<td>3.58</td>
<td>-.94(3)</td>
<td>3.3(3)</td>
<td>3.5(3)</td>
</tr>
<tr>
<td>N$_{ip,611}^+$</td>
<td>28 (10)</td>
<td>158.3</td>
<td>224</td>
<td>3.76</td>
<td>-.96(3)</td>
<td>7.1(5)</td>
<td>7.3(5)</td>
</tr>
<tr>
<td>N$_{ip,10,11}^+$</td>
<td>193 (10)</td>
<td>228.4</td>
<td>301</td>
<td>4.16</td>
<td>-.97</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Im$_{32}(OH)^+$</td>
<td>1</td>
<td>127.2</td>
<td>135</td>
<td>3.18</td>
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<td>4.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Pr$_{22}(OH)^+$</td>
<td>5</td>
<td>130.2</td>
<td>151</td>
<td>3.30</td>
<td>-.93(5)</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>N$_{ip,211}(OH)^+$</td>
<td>5</td>
<td>132.2</td>
<td>162</td>
<td>3.38</td>
<td>-.8</td>
<td>1.3(7)</td>
<td>1.6(5)</td>
</tr>
<tr>
<td>Pr$<em>{11}(OH)</em>{2}^+$</td>
<td>15 (7)</td>
<td>160.2</td>
<td>170</td>
<td>3.44</td>
<td>-.9</td>
<td>1.4(9)</td>
<td>2.3(9)</td>
</tr>
</tbody>
</table>
to achieve average agreement with empirical molecular volumes computed using the van der Waals increments of Bondi\textsuperscript{55}. The effective radii are those of spheres having these molecular volumes. Among the ions studied here there is a much larger variation in the anion volumes (or masses) than there is in the cation volumes (or masses).

The properties summarized in Table 3.1 are the molecular volume $V$ and effective radius $R$, the inertial asymmetry parameter $\kappa$, and two measures of dipole moment $\mu_{es}$ and $\mu_{CA}$. The molecular volumes are those computed from the spatial extent of the DFT wavefunction (.001 $e/a_0$ contour) scaled by a factor of 1.25 in order to achieve average agreement with empirical molecular volumes computed using the van der Waals increments of Bondi\textsuperscript{55}. The effective radii are those of spheres having these molecular volumes. Among the ions studied here there is a much larger variation in the anion volumes (or masses) than there is in the cation volumes (or masses).

The inertial asymmetry parameter is defined by\textsuperscript{56}

$$\kappa = \frac{(2I_{B}^{-1} - I_{A}^{-1} - I_{C}^{-1})}{(I_{A}^{-1} - I_{C}^{-1})}$$

(3.2)

where $I_A \leq I_B \leq I_C$ are the principal moments of inertia of the ion. $\kappa$ measures the inertial shape of a molecule in the sense that $\kappa = -1$ denotes a prolate, $\kappa = 0$ a spherical, and $\kappa = +1$ and oblate inertial ellipsoid. With the exception of the Tf$_2$N$^-$ anion, all of the anions examined here are spherical or nearly spherical rotors, whereas all of the cations are close to the prolate limit. We note that although one might imagine the longer $n$-alkyl chains of cations such as N$_{hp10,11}$ could create globular shapes, with the 1-3 gauche bonds per chain found at low energy, the majority of the geometries adopted are extended forms.

The dipole moment of a charged species depends on the choice of coordinates and is therefore not uniquely defined. Kobrak\textsuperscript{57} suggested that the extent to which reorientation of an ion will alter its electrostatic interactions is closely associated with what he termed the “charge
of the ion, the distance between its center of mass and center of charge. This quantity is
equivalent to the magnitude of the dipole moment calculated using the center of mass as the
coordinate origin,

$$\bar{\mu}_{\text{com}} = \sum_{i=1}^{N} q_{i} r_{i} - \frac{Q}{M} \sum_{i=1}^{N} m_{i} r_{i}$$  \hspace{1cm} (3.3)$$

In this expression $q_{i}$, $r_{i}$, and $m_{i}$ are the charge, position, and mass of atom $i$ and $Q$ and $M$
are the total ion charge and mass. Alternatively, one could take a slightly different perspective
and consider the “residual dipole moment”. The dipole remaining after the net charge on the ion
has been subtracted in equal fractions from the atomic charges:

$$\bar{\mu}_{\text{res}} = \sum_{i=1}^{N} q_{i} r_{i} - \frac{Q}{N} \sum_{i=1}^{N} r_{i}$$  \hspace{1cm} (3.4)$$

For a uniform distribution of mass ($m_{i} = M / N$) these two measures of dipole moment
are identical, and in the present systems we find $\bar{\mu}_{\text{com}} \approx \bar{\mu}_{\text{res}}$ in nearly all cases. The results in
Table 3.1 show that although these dipole moments depend on conformation, with the exception
of the Tf$_2$N$^{-}$ anion, the variations in $\mu$ are relatively modest ($\pm 15\%$). In the case of Tf$_2$N$^{-}$, we find
two conformers whose dipole moments vary substantially, 0.6 D for the $\text{trans}$ form ($\angle C$-$S$-$N$-
$S=91^\circ$) and 5.7 D for the $\text{cis}$ form ($\angle C$-$S$-$N$-$S = 240^\circ$, +3.3 kJ/mol) at the level of theory used
here$^{58}$. In the case of the cations, we find that there is an approximately linear increase in the
magnitudes of these dipole moments with alkyl chain length or molecular weight.

It is not clear that either definition of dipole moment provides a useful measure of
“polarity” of an ion. As shown by the cases of Pr$_{10,1}^{+}$ and N$_{p10,11}^{+}$, increasing the asymmetry of
an ion having a localized charge group and nonpolar appendages leads to large values ($\sim 15$ D) of
these dipole moments. Contrary to what such large dipole moments might suggest, one expects
the electrostatic interactions between these largest ions and other species to be weaker than the interactions among ions with shorter alkyl chains and smaller dipole moments.

Finally, it is interesting to consider how the dipole moments calculated here might relate to the dielectric constants (relative permittivities $\varepsilon$) of the ionic liquids they constitute. In the absence of charges, the Kirkwood-Fröhlich theory\textsuperscript{59} provides the relationship:

$$\gamma g_k = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \quad y \equiv \frac{4\pi}{9k_B T} \sum_k \rho_k \mu_k^2$$  \hspace{1cm} (3.5)

Where $\varepsilon_\infty$ is the relative permittivity at frequencies higher than those where reorientations contribute to the polarization, and $\rho_k$ is the number density and $\mu_k$ the dipole moment of species $k$. $g_k$ is the Kirkwood correlation factor, which measures orientational correlations among molecules. It has a value close to unity in most conventional dipolar liquids\textsuperscript{59}. Although it is not clear that use of eq 3.5, which neglects ionic screening, is appropriate in the case of ionic liquids, it is interesting to examine the dielectric constants it predicts. Using the center of mass dipole moments from Table 3.1, measured molar volumes (Table 3.1), and the approximation $\varepsilon_\infty \equiv 2$, together with the assumption $g_k = 1$, eq 3.4 predicts dielectric constants of nearly all of the liquids studied should fall in the range 11-35. Such values are comparable to values measured to date\textsuperscript{60,61}. Direct comparisons are available for the systems $[\text{Im}_{41}^+]\text{[BF}_4^-]$, $[\text{Im}_{41}^+]\text{[PF}_6^-]$, $[\text{Im}_{41}^+]\text{[Tf}_2\text{N}^-]$, and $[\text{Pr}_{10,11}^+]\text{[Tf}_2\text{N}^-]$ where eq 3.4 predicts values of 22, 20, 23, and 14 compared to experimental values which all fall in the range $11.5 \pm 0.3$\textsuperscript{60}. These comparisons imply Kirkwood correlation factors of 0.5-0.8, which seem reasonable in light of available simulation results\textsuperscript{62}. However, for the liquids $[\text{Pr}_{10,11}^+]\text{[Tf}_2\text{N}^-]$ and $[\text{Na}_{10,11}^+]\text{[Tf}_2\text{N}^-]$ the large dipole moments calculated from either eq 3.3 or 3.4 yield what would seem to be unrealistically large dielectric constants, $\varepsilon \sim 100$ (for $g_k = 1$).
3.3.2 Thermal Properties

Phase transition temperatures and approximate enthalpies measured using differential scanning calorimetry are summarized in Table 3.2. Figure 3.2 shows a representative thermogram which indicates how these various temperatures are measured. With a scanning speed of 10 °C min\(^{-1}\) all of the ILs studied exhibit a heat capacity change at low temperatures corresponding to a glass transition (\(T_g\)) except \([\text{Pr}_{31}\,^+][\text{Tf}_2\text{N}^-]\) and \([\text{Pr}_{21}(\text{OH})\,^+][\text{Tf}_2\text{N}^-]\), which repeatedly froze during cooling. In all but two of the cases, the glass transition temperatures fall in the narrow range 186-193 K. A similar clustering of \(T_g\) in this same range is found in the collection of imidazolium and related ILs studied by Watanabe and coworkers\(^{21}\). In the much larger and more diverse collection of ILs compiled by Zhang et al.\(^{26}\) over 50% of the nearly 200 values of \(T_g\) reported fall between 180-200 K. This commonality of \(T_g\) is curious and worthy of further study. Endothermic and exothermic peaks, corresponding to the melting (at \(T_{\text{fus}}\)) and crystallization (at \(T_{\text{cr}}\)) were also observed for most of the ILs studied. In cases where both transitions are observed \(T_{\text{cr}}\) is typically found 30-60 K lower than \(T_{\text{fus}}\), indicating a slow crystallization rate and a fairly stable supercooled state, features also noted by Tokuda et al.\(^{21}\). As indicated in Table 3.2, additional solid-solid transition peaks appeared in the heating curves of several of the ILs between \(T_c\) and \(T_{\text{fus}}\). Thermograms were especially complex in the case of the alcohols \([\text{Pr}_{21}(\text{OH})\,^+][\text{Tf}_2\text{N}^-]\) and \([\text{N}_{\text{iPr}_{21}}(\text{OH})\,^+][\text{Tf}_2\text{N}^-]\) where two additional peaks were observed. The origin of these extra peaks is unknown.

Thermogravimetric measurements were only made on a few of the ILs. As shown in Table 3.2, these ILs all exhibited excellent short-term thermal stability up to 650 K at the scanning rate of 10 K min\(^{-1}\). Very little weight loss was observed before decomposition, confirming the fact that these ILs have negligible vapor pressures.
Table 3.2 Calorimetric data. $T_g$ is the glass transition temperature measured upon cooling as the midpoint of the transition (see Figure 3.2). $T_{cr}$, $\Delta_{cr}H$, $T_{fus}$, and $\Delta_{fus}H$ are the temperatures and enthalpies of crystallization and fusion, measured upon heating (Figure 3.2). $T_{dcp}$ is the decomposition temperature measured as the onset of decomposition (~10% mass loss) using TGA for a few selected ILs. Uncertainties in the temperatures are estimated to be on the order of ±1-2 K, uncertainties in the enthalpies ±20%. DSC Notes: (a) Upon heating a second transition was observed roughly 10 K below the melting point. $\Delta_{fus}H$ here is the sum of the enthalpies of the two transitions. (b) Sample crystallized upon cooling at 224 K and three exotherms at 238, 246, and 280 K were observed upon warming. (c) 3 exotherms of unknown origin were observed at 247, 259, and 298 K. “?” indicates that the presence of multiple peaks rendered assignments unclear.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>$T_g$ /K</th>
<th>$T_{cr}$ /K</th>
<th>$\Delta_{cr}H$ /kJ mol$^{-1}$</th>
<th>$T_{fus}$ /K</th>
<th>$\Delta_{fus}H$ /kJ mol$^{-1}$</th>
<th>DSC Notes</th>
<th>$T_{dcp}$ /K</th>
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</thead>
<tbody>
<tr>
<td>1 [Im$_{41}$]$^+$[BF$_4^-$]</td>
<td>188</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2 [Im$_{41}$]$^+$[PF$_6^-$]</td>
<td>191</td>
<td>230</td>
<td>7</td>
<td>282</td>
<td>12</td>
<td>(a)</td>
<td>--</td>
</tr>
<tr>
<td>3 [Im$_{41}$]$^+$[Tf$_2$N$^-$]</td>
<td>186</td>
<td>232</td>
<td>17</td>
<td>271</td>
<td>21</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4 [Im$_{41}$]$^+$[Tf$_2$C$^-$]</td>
<td>208</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5 [Pr$_{31}$]$^+$[Tf$_2$N$^-$]</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>283</td>
<td>11</td>
<td>--</td>
<td>707</td>
</tr>
<tr>
<td>6 [Pr$_{61}$]$^+$[Tf$_2$N$^-$]</td>
<td>186</td>
<td>220</td>
<td>11</td>
<td>255</td>
<td>11</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7 [Pr$_{61}$]$^+$[Tf$_2$N$^-$]</td>
<td>190</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>703</td>
</tr>
<tr>
<td>8 [Pr$_{10,1}$]$^+$[Tf$_2$N$^-$]</td>
<td>191</td>
<td>221</td>
<td>12</td>
<td>283</td>
<td>8</td>
<td>(a)</td>
<td>696</td>
</tr>
<tr>
<td>9 [N$_{ip311}$]$^+$[Tf$_2$N$^-$]</td>
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<td>230</td>
<td>10</td>
<td>290</td>
<td>14</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10 [N$_{ip411}$]$^+$[Tf$_2$N$^-$]</td>
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<td>269</td>
<td>10</td>
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<td>10</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
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<td>192</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>12 [N$_{ip10,11}$]$^+$[Tf$_2$N$^-$]</td>
<td>192</td>
<td>239</td>
<td>20</td>
<td>276</td>
<td>26</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>13 [Im$_{21}$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>192</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>14 [Pr$_{31}$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>?</td>
<td>?</td>
<td>(b)</td>
<td>679</td>
</tr>
<tr>
<td>15 [N$_{ip211}$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>189</td>
<td>241</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>(c)</td>
<td>--</td>
</tr>
<tr>
<td>16 [Pr$_{31}$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>223</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>645</td>
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</table>
Figure 3.2 Representative DSC thermogram (warming cycle, 10 K min\(^{-1}\)) of \([N_{p311}^+][Tf_2N]\) illustrating the measurement of the glass transition, \(T_g\), crystallization, \(T_{cr}\), and melting, \(T_{fus}\), temperatures.
3.3.3 Static Properties

Table 3.3 summarizes a number of physical properties and solvatochromic parameters measured at 25 °C. Also provided are representative values of the water contents of the samples used. The bottom row of Table 3.3 indicates the extent to which the measured properties vary over the set of liquids considered. By far the most variable property among these ILs is the molar volume, which ranges between 190 cm$^3$/mol and 433 cm$^3$/mol as a result of both variations in the amino-alkyl chain lengths of the cations and the variations in anion size. In contrast, the refractive index is remarkably constant, with $n_D$ varying by only 0.03 (6% of $n_D$-1) over this collection of solvents. In the few liquids for which literature comparisons are available the densities and refractive indices measured here are in good agreement with published data\textsuperscript{15,17,20,23,63-68}. By comparing the measured molar volumes to the van der Waals volumes of the ions from Table 3.1 we find the packing fractions $f = V_{vdW}/V_m$ in these ionic liquids are relatively constant at $f = 0.63\pm0.02$. These values are substantially higher than the packing fractions found in most conventional liquid solvents,\textsuperscript{09} 0.54±0.03, in keeping with the smaller isothermal compressibilities of ILs\textsuperscript{19}.

Surface tension is of interest because of its well-known connection to the cohesive energies of liquids\textsuperscript{70,72}. Although several recent reports have employed surface tensions in the estimation of vaporization quantities\textsuperscript{73,74} relatively few systematic studies of surface tension are yet available\textsuperscript{15,16,75-77} and the values reported by different groups are often inconsistent. The only comparisons we can make with published data are for the imidazolium liquids #1-3. Our values appear to be in good agreement with the recent work of Deetlefs et al.\textsuperscript{16}. Table 3.3 shows that the surface tensions of the ILs studied here vary over a significant range. As illustrated in Figure 3.3, if one neglects the hydroxylic liquids (open symbols), the surface tensions observed here are inversely correlated to molar volume. Also shown in Figure 3.3 are the surface tensions of
Table 3.3 Static properties. $c_{\text{water}}$ is a representative value of the weight % of water, $d$ the mass density (±1%), $V_m$ the molar volume (±1%), $n_D$ the refractive index (±0.001), $\gamma$ the surface tension (#1-12 ± 2%; #13-16 ± 10%), “Est. $\delta_H$” the estimated Hildebrand solubility parameter, $\pi_{NR}$ the Nile Red polarity measure (±0.03), and $\delta_F$ the $^{19}\text{F}$ chemical shift of the Tf$_2$N$^-$ anion relative to neat CF$_3$COOH (±0.03). $\lambda_{C153}$ and $\Delta G_{C153}$ are the solvent reorganization energy and solvation free energy change associated with the $S_0 \rightarrow S_1$ transition of coumarin 153 (±1-2 kJ/mol; from Ref. 29). The last row shows the value $(P_{\text{max}} - P_{\text{min}}) / \left| P_{\text{average}} \right|$ for each property $P$. In the case of $n_D$, the average value used for comparison is $n_D - 1$ rather than $n_D$. 

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>$c_{\text{water}}$ / ppm</th>
<th>$d$ / g cm$^{-3}$</th>
<th>$V_m$ / cm$^3$ mol$^{-1}$</th>
<th>$n_D$</th>
<th>$\gamma / 10^{-3}$ N m$^{-1}$</th>
<th>Est. $\delta_H$</th>
<th>$\pi_{NR}$</th>
<th>$\lambda_{C153}$ / kJ mol$^{-1}$</th>
<th>$\Delta G_{C153}$ / kJ mol$^{-1}$</th>
<th>$\delta_F$ / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 [Im$_4^+$][BF$_4^-$]</td>
<td>61</td>
<td>1.19</td>
<td>190</td>
<td>1.420</td>
<td>44.0</td>
<td>26.5</td>
<td>1.01</td>
<td>12.9</td>
<td>44.1</td>
<td>--</td>
</tr>
<tr>
<td>2 [Im$_4^+$][PF$_6^-$]</td>
<td>45</td>
<td>1.37</td>
<td>208</td>
<td>1.409</td>
<td>40.9</td>
<td>25.1</td>
<td>0.94</td>
<td>12.8</td>
<td>45.6</td>
<td>--</td>
</tr>
<tr>
<td>3 [Im$_4^+$][Tf$_2$N$^-$]</td>
<td>12</td>
<td>1.42</td>
<td>295</td>
<td>1.427</td>
<td>33.0</td>
<td>21.3</td>
<td>0.95</td>
<td>10.8</td>
<td>43.5</td>
<td>4.88</td>
</tr>
<tr>
<td>4 [Im$_4^+$][Tf$_2$C$^-$]</td>
<td>27</td>
<td>1.56</td>
<td>352</td>
<td>1.436</td>
<td>35.1</td>
<td>21.4</td>
<td>0.94</td>
<td>12.0</td>
<td>42.8</td>
<td>--</td>
</tr>
<tr>
<td>5 [Pr$_{31}^+$][Tf$_2$N$^-$]</td>
<td>61</td>
<td>1.40</td>
<td>291</td>
<td>1.420</td>
<td>34.4</td>
<td>21.8</td>
<td>0.95</td>
<td>12.9</td>
<td>42.9</td>
<td>4.71</td>
</tr>
<tr>
<td>6 [Pr$_{31}^+$][Tf$_2$N$^-$]</td>
<td>42</td>
<td>1.39</td>
<td>317</td>
<td>1.423</td>
<td>33.0</td>
<td>21.1</td>
<td>0.91</td>
<td>12.9</td>
<td>42.2</td>
<td>4.66</td>
</tr>
<tr>
<td>7 [Pr$_{31}^+$][Tf$_2$N$^-$]</td>
<td>42</td>
<td>1.32</td>
<td>342</td>
<td>1.425</td>
<td>31.7</td>
<td>20.4</td>
<td>1.03</td>
<td>10.9</td>
<td>43.2</td>
<td>4.55</td>
</tr>
<tr>
<td>8 [Pr$_{10,1}^+$][Tf$_2$N$^-$]</td>
<td>20</td>
<td>1.25</td>
<td>406</td>
<td>1.431</td>
<td>31.4</td>
<td>19.8</td>
<td>0.96</td>
<td>10.9</td>
<td>40.5</td>
<td>4.40</td>
</tr>
<tr>
<td>9 [N$_{ip31}^+$][Tf$_2$N$^-$]</td>
<td>15</td>
<td>1.40</td>
<td>294</td>
<td>1.416</td>
<td>34.3</td>
<td>21.8</td>
<td>1.02</td>
<td>13.0</td>
<td>43.2</td>
<td>4.55</td>
</tr>
<tr>
<td>10 [N$_{ip41}^+$][Tf$_2$N$^-$]</td>
<td>20</td>
<td>1.36</td>
<td>311</td>
<td>1.419</td>
<td>32.8</td>
<td>21.1</td>
<td>1.15</td>
<td>12.6</td>
<td>43.9</td>
<td>4.51</td>
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<td>339</td>
<td>1.422</td>
<td>31.4</td>
<td>20.4</td>
<td>1.01</td>
<td>12.4</td>
<td>41.8</td>
<td>4.40</td>
</tr>
<tr>
<td>12 [N$_{ip10,11}^+$][Tf$_2$N$^-$]</td>
<td>36</td>
<td>1.18</td>
<td>433</td>
<td>1.429</td>
<td>31.3</td>
<td>19.6</td>
<td>0.90</td>
<td>12.1</td>
<td>40.0</td>
<td>4.23</td>
</tr>
<tr>
<td>13 [Im$_2$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>40</td>
<td>1.51</td>
<td>269</td>
<td>1.429</td>
<td>34.2</td>
<td>22</td>
<td>1.24</td>
<td>--</td>
<td>--</td>
<td>4.92</td>
</tr>
<tr>
<td>14 [Pr$_{21}$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>130</td>
<td>1.51</td>
<td>271</td>
<td>1.427</td>
<td>38</td>
<td>23</td>
<td>1.24</td>
<td>--</td>
<td>--</td>
<td>4.73</td>
</tr>
<tr>
<td>15 [N$_{ip21}$(OH)$^+$][Tf$_2$N$^-$]</td>
<td>30</td>
<td>1.48</td>
<td>279</td>
<td>1.421</td>
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<td>23</td>
<td>1.40</td>
<td>--</td>
<td>--</td>
<td>4.59</td>
</tr>
<tr>
<td>16 [Pr$_{10,11}$(OH)$_3^+$][Tf$_2$N$^-$]</td>
<td>2400</td>
<td>1.61</td>
<td>273</td>
<td>1.434</td>
<td>--</td>
<td>--</td>
<td>1.55</td>
<td>--</td>
<td>--</td>
<td>4.63</td>
</tr>
</tbody>
</table>

range / average: 32% 80% 6% 43% 32% 60% 19% 13% 15%
molten alkali halides at their melting temperatures (820-1270 K). Although there is a large gap between the smallest ionic liquid studied here and the largest alkali halide, these two classes of liquids appear to share a common relationship between surface tension and molar volume. As noted in an early study of tetraalkylammonium ILs, this dependence on molar volume or ion size is roughly what is predicted by simple theories of the surface tension of molten salts.

To gain additional perspective on their solvating characteristics, we have used the measured values of surface tension and molar volume to estimate values of the Hildebrand solubility parameters of these ILs. The solubility parameter is defined as the square root of the cohesive energy density of a liquid,

$$\delta_H = \left( \frac{\Delta_{vap} U}{V_m} \right)^{1/2} \equiv \left( \frac{\Delta_{vap} H - RT}{V_m} \right)^{1/2} \quad (3.6)$$

where $\Delta_{vap} U$ and $\Delta_{vap} H$ are the internal energy and enthalpy of vaporization and $R$ is the gas constant. A variety of correlations between surface tension and $\delta_H$, or equivalently $\Delta_{vap} H$ and $V_m$, have been proposed, the simplest being $\delta_H^2 = A \gamma / V_m^{1/3}$ with $A$ an empirical constant.

In Figure 3.4 we plot measured values of $\delta_H$ versus the factor $\gamma / V_m^{1/3}$ using collected data in various types of conventional solvents (25 °C from Ref. 69), molten alkali halides at their melting points and in room temperature ionic liquids. The latter values, shown as the large open symbols, were calculated using recent reports of $\Delta_{vap} H$ (extrapolated to 25 °C) from direct calorimetric measurements or vapor pressure determinations and independent surface tension measurements. Note that there are only 6 ILs, $[\text{Im}_{n1}^+] [\text{Tf}_2N]^{-}$, $n=2, 4, 6, 8$, $[\text{Im}_{n1}^+] [\text{BF}_4^{-}]$ and $[\text{Im}_{n1}^+] [\text{PF}_6^{-}]$, for which both $\Delta_{vap} H$ and $\gamma$ have been determined, but because there is currently some uncertainty in both types of data, we have used $\Delta_{vap} H$ and $\gamma$ to arrive at the 17 points shown in this figure. The IL data and the dashed lines showing the proportionality $\delta_H^2 \propto \gamma / V_m^{1/3}$ are
Figure 3.3 Surface tensions $\gamma$ of the ionic liquids studied here (see legend) and alkali halides at their melting points$^{78,79}$ (filled diamonds) plotted versus molar volume $V_m$. Ionic liquids designated with open symbols contain hydroxylic cat ions. The curve is a fit to all of the data excluding the hydroxylic ILs to the relation

$$\gamma / \text{mN m}^{-1} = 22.77 + 3.82 \times 10^3 \text{ (cm}^3 \text{ mol}^{-1} / V_m) - 1.09 \times 10^3 \text{ (cm}^3 \text{ mol}^{-1} / V_m)^2.$$
Figure 3.4 Hildebrand solubility parameters $\delta_H$ versus the correlating factor $\gamma/V_m^{1/3}$. For clarity, the different categories of liquids are shown on shifted vertical axes. Data in conventional organic solvents (small filled symbols) are all taken from the compilations of Marcus. The liquids included in each grouping are as follows: #1 – “alcohols and amides” includes aliphatic and aromatic mono- and poly-alcohols and protic amides. #3 – “polar aprotics” includes a wide variety of functional groups without significant hydrogen bond donating ability. #4 – “alkanes and halogenated” includes both aliphatic and aromatic hydrocarbons and halogenated hydrocarbons of low to moderate polarity. The alkali halide data (all Li$^+$-Cs$^+$ and F-I pairs at their melting temperatures) are from Refs. Room temperature ionic liquid data from Refs. are shown as large open circles. The polar aprotic data are shown with the correct values of $\delta_H$, remaining data have been shifted by factors of 4. IL data along with dashed lines proportional to $\gamma/V_m^{1/3}$ passing through the average of these data are repeated to provide comparisons with data sets #1-4. The solid lines through data sets 1-4 are fits to $\delta_H^2 = A(\gamma/V_m^{1/3})^p$. The inset table shows the number of liquids included in each category (#), the fit parameters $A$ and $p$, and the standard error of the fit ($s_{fit}$).
reproduced four times and offset vertically in Figure 3.4 in order to compare to values in other classes of liquids. As illustrated in this figure, within sets of liquids having similar intermolecular interactions, \( \delta_H \) is reasonably correlated using only \( \gamma / V_m^{1/3} \), although the relationship is not a simple proportionality. Functions with one more adjustable parameter such as

\[
\delta_H^2 = A(\gamma / V_m^{1/3})^p,
\]

shown here by the solid lines, or \( \delta_H^2 = A(\gamma / V_m^{1/3}) + B \) provide reasonable fits to each set of data but the fits differ with the type of liquid considered. For example, for a given value of \( \gamma / V_m^{1/3} \) the solubility parameters of associated liquids such as the alcohols and amides are significantly higher than those of polar aprotic solvents. The more specific the interactions (alcohols) or the more varied the functional groups involved (polar aprotic solvents) the greater the deviations from these two-parameter correlations. Such complications aside, it appears that these correlations are accurate enough to provide useful estimates of \( \delta_H \) (or \( \Delta_{\text{vap}} H \)) of ionic liquids in cases where direct measurements are not available. In particular, we note that both the alcohol + amide and the alkali halide correlations pass through the available IL data. For the liquids studied here, values of \( \delta_H \) predicted by these two correlations differ by at most 6% and for the present we use the average of these two predictions as the best estimates shown in Table 3.3.

The solubility parameters estimated in this manner fall in the range 20-26 \( J^{1/2} \text{cm}^{-3/2} \), the same range spanned by the values of \( \delta_H \) of imidazolium ILs available using measured values of \( \Delta_{\text{vap}} H \). These values can be compared to values in conventional liquids\(^69\): \( n \)-hexane (15.0), benzene (18.8), acetone (22.1), acetonitrile (24.1), dimethylsulfoxide (26.6), methanol (29.3), and water (47.9). For an IL such as \([\text{Im}^{+}\text{][BF}_4^-]\) regular solution theory predicts complete miscibility for solvents roughly in the range \( 19.4 \leq \delta_H \leq 33.4 \text{ J}^{1/2} \text{cm}^{-3/2} \) at room temperature\(^87\). Although one cannot expect regular solution theory to be accurate here, this prediction is roughly consistent with experimental observations\(^88,89\). Similar conclusions concerning the relative cohesive
energies of tetraalkylammonium ILs and dipolar solvents were made some time ago by Gordon\textsuperscript{80}. Finally, we note that the solubility parameters obtained here are significantly smaller than values deduced from measurements of reaction rates\textsuperscript{91} and intrinsic viscosities\textsuperscript{92}. Direct comparisons are: $\text{[Im}_{4}\text{]+}[\text{BF}_4]$ 26.4 here versus 31.6\textsuperscript{91}, $\text{[Im}_{4}\text{]+}[\text{PF}_6]$ 25.1 here versus 30.2\textsuperscript{91} and 29.8\textsuperscript{92}, and $\text{[Im}_{4}\text{]+}[\text{Tf}_2\text{N}]$ 21.2 here versus 25.5\textsuperscript{91} and 26.7\textsuperscript{92}.

Three solvatochromic measures of solvent polarity are listed in Table 3.3. $\pi_{\text{NR}}$ is measured from the shift in the absorption spectrum of Nile Red\textsuperscript{93,94}, a probe used previously in a number of studies of ionic liquids\textsuperscript{6,95-98}. We chose Nile Red here instead of the more popular Reichardt’s dye\textsuperscript{99} because we found protonation of the latter probe to be problematic in the hydroxylic liquids studied. The absorption maxima measured for ILs #1-3 agree well with those reported by Carmichael et al.\textsuperscript{98}. Rather than reporting absorption maxima, we employ a normalized polarity scale defined by

$$\pi_{\text{NR}}(x) = \frac{\overline{\nu}_x - \overline{\nu}_{\text{chex}}}{\overline{\nu}_{\text{DMSO}} - \overline{\nu}_{\text{chex}}}$$

(3.7)

where $\overline{\nu}_x$ is the average\textsuperscript{100} frequency of the absorption spectrum in solvent $x$. The scale is defined, in analogy to the $\pi^*$ scale\textsuperscript{101}, such that $\pi_{\text{NR}} = 0$ in cyclohexane (chex) and 1.00 in dimethylsulfoxide (DMSO). All of the non-hydroxylic ILs exhibit values of $\pi_{\text{NR}}$ close to 1.0, indicating that Nile Red senses a “polarity” close to that of the highly polar aprotic solvent DMSO. Compared to the range of values of $\pi_{\text{NR}}$ found in conventional aprotic solvents the variation observed in these solvents is remarkably small. A similarly narrow solvatochromic range, 1.01±0.05, is found using the Nile Red shifts compiled by Poole on 15 imidazolium liquids with a variety of anions\textsuperscript{6}. The hydroxylic ILs studied here possess higher values of $\pi_{\text{NR}}$, which lie in the range 1.24-1.55. These higher values presumably reflect the sensitivity of the electronic spectrum of Nile Red to solvent hydrogen bond donation. This sensitivity was analyzed by Moog
et al.\textsuperscript{93} in conventional solvents using a Kamlet-Taft analysis\textsuperscript{101}. In dipolar solvents, they found the relative contributions to $\pi_{NR}$ could be reproduced by a 2:1 mix of $\pi^*$ (polarity/polarizability) and $\alpha$ (hydrogen-bond donating ability), or in our notation, $\pi_{NR} = 1.00\pi^* + 0.52\alpha$. Assuming negligible hydrogen bond donation in the other ILs, such a decomposition together with the values in Table 3.3 imply values of $\alpha$ for the hydroxylic ILs studied here in the range of 0.2-0.6, much smaller than those of normal alcohols (in methanol $\alpha = 0.98$ and in n-decanol $\alpha = 0.70$\textsuperscript{69}). Given the much lower density of OH groups in these ILs compared to the alcohols, such a result seems reasonable\textsuperscript{102}.

For completeness, Table 3.3 also lists values of the solvent reorganization energy $\lambda_{C153}$ and the solvation free energy change $\Delta G_{C153}$ measured from absorption and emission spectra of coumarin 153 as described in Ref.\textsuperscript{29}. In that previous work, we showed that $\lambda_{C153}$ and to a lesser extent $\Delta G_{C153}$ increases in magnitude as the molar volume or the mean separation between ions of the IL increases. In the non-hydroxylic solvents studied here these energy values tell much the same story as $\pi_{NR}$. Variations in either the “nuclear” polarizability sensed by $\lambda_{C153}$ or the total (nuclear plus electronic) polarizability sensed by $\Delta G_{C153}$ are comparable to those in highly polar solvents and vary relatively little among this collection of ILs.

The final solvatochromic data contained in Table 3.3 are $^{19}$F chemical shifts of the CF\textsubscript{3} group of Tf$_2$N\textsuperscript{-} in the ILs containing this anion. Fluorine chemical shifts are well known to be sensitive probes of both bonding and intermolecular environment\textsuperscript{103,104}. The solvent dependence of the $^{19}$F shift is believed to reflect both dispersion and electrostatic interactions\textsuperscript{105-113}. The same is true of electronic spectral shifts, but we conjectured that these chemical shifts might provide a rather different perspective on the interactions. As seen from the data in Table 3.3, the $^{19}$F chemical shifts of Tf$_2$N\textsuperscript{-} studied here span a modest range of 0.7 ppm. For comparison, the range of $^{19}$F shifts of fluorobenzene in a range of common solvents is about 4 ppm\textsuperscript{113} and that of BF$_4$ is
about 6 ppm\textsuperscript{110}. Like the electronic shifts in Nile Red, this modest variation suggests rather similar solvation of the Tf\textsubscript{2}N\textsuperscript{-} anion in the range of ILs studied. But, in contrast to the Nile Red case, hydrogen bonding does not appear to affect the chemical shifts.

To discern possible inter-relationships among the various static quantities measured here, we performed a correlation analysis on the data in Table \ref{tab:3.3}. The strongest non-trivial correlations found were between the molar volume and a number of other properties such as the refractive index, surface tension, and \textsuperscript{19}F chemical shift. Linear correlation coefficients between \(V_m\) and these other properties are: \(n_D (0.54, 0.74), \gamma (-0.64, -0.85),\) and \(\delta (-0.80, -0.82),\) where the first value corresponds to use of all data and the second value to only the non-hydroxylic liquids. Interestingly, the mass density, from which \(V_m\) is derived, is not significantly correlated to the other properties in Table \ref{tab:3.3}.

In contrast to these modest correlations within the data set as a whole, much clearer trends are found when one ion is maintained constant and the other varied in some systematic manner. For example, as expected, when either the cation or the anion is varied with a constant counter ion, the molar volume is linearly related to either the mass or the van der Waals volume of the variable ion (not shown). Some less obvious trends observed upon cation variation are displayed in Figure \ref{fig:3.5}. Figure \ref{fig:3.5} shows that the refractive index is a nearly linear function of the cation mass in each of the series \([\text{Pr}_{n1}^+]\) and \([\text{Nip}_{n11}^+]\), \(n = 3, 4, 6, 10\). The surface tension (not shown) and the Hildebrand solubility parameter derived from it (Figure \ref{fig:3.5}) also vary systematically in these homologous series. Substitution of a CH\textsubscript{3} group for an OH group, as in \([\text{Pr}_{31}^+]\rightarrow[\text{Pr}_{21}(\text{OH})^+]\) and \([\text{Nip}_{3311}^+]\rightarrow[\text{Nip}_{21}(\text{OH})^+]\) leads to departures from what is observed with the purely aliphatic R groups. The \textsuperscript{19}F chemical shift is also approximately linearly related to the cation mass in the \([\text{Pr}_{n1}^+]\) and \([\text{Nip}_{n11}^+]\) series. However, as already mentioned, in contrast to most other properties, Figure \ref{fig:3.5} shows that \(\delta_F\) is insensitive to CH\textsubscript{3} \(\rightarrow\) OH substitutions. (The same insensitivity appears to be true of the analogous substitution \([\text{Im}_{n1}^+]\) \(\rightarrow\) \([\text{Im}_{n1}(\text{OH})^+]\), but here we
Figure 3.5 Trends in the refractive index $n_D$, the Hildebrand solubility parameter $\delta_H$, and the $^{19}$F chemical shift of the Tf$_2$N$^-$ anion $\delta_F$ plotted against cation mass for the Tf$_2$N$^-$ ionic liquids. The filled circle denotes [Im$_{41}$$^+$][Tf$_2$N$^-$] and the filled squares and triangles denote the [Pr$_{n1}$$^+$][Tf$_2$N$^-$] and [N$_{p,n1}$$^+$][Tf$_2$N$^-$] series. The open circle, square, and triangle denote the mono-hydroxy imidazolium, pyrrolidinium, and ammonium ILs and the open diamond [Pr$_3$(OH)$_2$$^+$][Tf$_2$N$^-$]. Curves drawn here are only guides to the eye.
do not have a strict comparison.)

Finally, it is of interest to consider the interpretation of the $^{19}$F chemical shifts measured here in more detail. Although $^{19}$F shifts have long been used to probe environmental effects in simple solutions$^{105-109}$, heterogeneous media$^{114}$, and proteins$^{115,116}$, the precise origin of the environmental effect is still a matter of debate. Electronic structure calculations and modeling studies in proteins$^{111,112,115,116}$ indicate that the strength of electric fields at the $^{19}$F nucleus dominates in determining $\delta_F$, but most early empirical studies$^{105-108}$ and some more recent studies in homogeneous solution$^{113}$ suggest that electrical interactions are of minor importance compared to the primary effect of dispersion interactions. In Figure 3.6 we replot the $\delta_F$ data from Table 3.3 along with data from 9 additional Tf$_2$N$^-$ ILs as a function of $V^{-1/3}_m$, an approximate measure of the relative ion-ion separations in these liquids. The addition of several much larger cations (for example [P$_{14,666}$]$^+$) in this expanded data set broadens the range of chemical shifts observed to over 1 ppm, but this range is still relatively modest compared to the range of shifts observed in other systems. The inset to Figure 3.6 illustrates the effect of diluting a neat IL, [N$_{ip411}$]$^+${Tf$_2$N$^-$}, with dimethylsulfoxide. The $^{19}$F chemical shift of the Tf$_2$N$^-$ anion in ILs is between 1-2 ppm greater than it is in this highly polar and polarizable conventional solvent. The approximately linear trends of the IL data with $V^{-1/3}_m$ displayed in Figure 3.6 suggest an electrical origin for much of the shift found in the ILs. The fact that different classes of ILs follow slightly different correlations indicates that other factors are also involved. For example, in the case of the imidazolium ILs, part of the difference from the remaining ILs is likely to reflect the additional shift caused by aromatic ring currents (the “ASIS” effect$^{117}$). However, it should be noted that we have not accounted for variations in the bulk diamagnetic susceptibility in these chemical shifts, and such variations might also give rise to some of the differences observed$^{118}$. 
Figure 3.6 $^{19}$F chemical shifts plotted versus “mean ion separation” $V_m^{-1/3}$. The large symbols denote data for the ILs studied here. The smaller symbols denote data from additional Tf$_2$N-ILs. In order of increasing molar volume, these liquids contain the following cations: N$_{2220}^+$, Im$_{21}^+$, N$_{3330}^+$, N$_{4440}^+$, N$_{4441}^+$, N$_{6444}^+$, N$_{8881}^+$, P$_{14,666}^+$ where the subscripts denote the numbers of C atoms ($n$) in pendant $n$-alkane groups and $n = 0$ denotes a hydrogen atom. “P” here stands for phosphorous (diamond symbol). The inset reproduces the data from the main panel as small open symbols together with data on the effect of diluting [N$_{ip41}^+$][Tf$_2$N] with dimethylsulfoxide (filled diamonds). In all cases the lines shown here are only guides to the eye.
3.3.4 Dynamical Properties

To characterize some dynamical properties of these ionic liquids we have measured viscosities as functions of temperature as well as conductivities and cation self-diffusion constants at a single temperature. These results are summarized in Table 3.4 and representative viscosity data are provided in Figure 3.7. As is commonly observed\(^{17,23}\), the viscosities exhibit a non-Arrhenius temperature dependence, even over the limited (60 K) temperature range studied here. The data are instead well represented by a Vogel-Fulcher-Tamman dependence of the form,

\[
\ln(\eta / \text{mPa s}) = A + \frac{B}{T - T_0}
\]  

(3.8)

In cases where the glass transition temperature is known, we follow the practice of Angell and coworkers\(^{119}\) in including a point at \(\eta(T_g) = 10^{13} \text{ cP}\) in these fits, in order to provide more meaningful values of the parameters. Like the glass transition temperatures (Table 3.2), the divergence temperatures \(T_0\) fall in a narrow range, and we find \(T_0/T_g = 30 \pm 3 \text{ K} \) (or \(T_0/T_g = 0.84 \pm 0.02\)) for the present liquids. Comparison of these data to the viscosity-temperature relationships of other glass-forming materials\(^{119}\) classifies these ILs as fragile liquids, comparable in fragility to ethanol or glycerol.

It is interesting to examine the variations in viscosities of these liquids at 25 °C. No systematic variation is observed upon increasing the size of the anion in the Im\(_4^+\) series #1-4. Within the homologous series of Pr\(_{n1}^+\) and N\(_{lpn1}^+\) liquids, \(\eta(25 \text{ °C})\) increases systematically with \(n\). Most interesting are the differences observed between these two series. Table 3.1 shows that the masses, volumes, and even the shapes of Pr\(_{n1}^+\) and N\(_{lpn1}^+\) ions are very similar for a given value of \(n\), yet for small \(n\) the viscosities of the Tf\(_2^+\)N\(^-\) liquids containing these ions are quite different. At \(n = 3\) the difference is nearly a factor of 2. The difference decreases systematically
<table>
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<th>#</th>
<th>Ionic Liquid</th>
<th>c&lt;sub&gt;water&lt;/sub&gt; / ppm</th>
<th>Α / K</th>
<th>B / K</th>
<th>T&lt;sub&gt;0&lt;/sub&gt; / K</th>
<th>η(25 °C) / mPa s</th>
<th>E&lt;sub&gt;η&lt;/sub&gt;(25 °C) / kJ mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Λ(22 °C) / S cm&lt;sup&gt;2&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>D&lt;sub&gt;+&lt;/sub&gt;(25 °C) / 10&lt;sup&gt;-12&lt;/sup&gt; m&lt;sup&gt;2&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>R&lt;sub&gt;H&lt;/sub&gt;/R&lt;sub&gt;+&lt;/sub&gt;</th>
<th>Λ&lt;sub&gt;obs&lt;/sub&gt;/Λ&lt;sub&gt;est&lt;/sub&gt;</th>
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<td>114&lt;sup&gt;102&lt;/sup&gt;</td>
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<td>157.3</td>
<td>196(9)</td>
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<td>0.42</td>
<td>0.76</td>
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<td>158</td>
<td>54&lt;sup&gt;102&lt;/sup&gt;</td>
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<td>42</td>
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<td>-2.265</td>
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<td>159.3</td>
<td>150&lt;sup&gt;100&lt;/sup&gt;</td>
<td>18</td>
<td>0.28</td>
<td>7.5</td>
<td>0.47</td>
<td>0.55</td>
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<td>[N&lt;sub&gt;ip311&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;][Tf&lt;sub&gt;2&lt;/sub&gt;N]&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>1007.84</td>
<td>160.9</td>
<td>147(7)</td>
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<td>[N&lt;sub&gt;ip10.1.1&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;][Tf&lt;sub&gt;2&lt;/sub&gt;N]&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>1062.52</td>
<td>159.9</td>
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<tr>
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<td>[Im&lt;sub&gt;21&lt;/sub&gt;(OH)&lt;sup&gt;+&lt;/sup&gt;][Tf&lt;sub&gt;2&lt;/sub&gt;N]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>40</td>
<td>-2.449</td>
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<td>163.0</td>
<td>91(3)</td>
<td>17</td>
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<tr>
<td>14</td>
<td>[Pr&lt;sub&gt;31&lt;/sub&gt;(OH)&lt;sup&gt;+&lt;/sup&gt;][Tf&lt;sub&gt;2&lt;/sub&gt;N]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>90</td>
<td>-0.9130</td>
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<td>179.6</td>
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<td>15</td>
<td>0.54</td>
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<td>[N&lt;sub&gt;ip211&lt;/sub&gt;(OH)&lt;sup&gt;+&lt;/sup&gt;][Tf&lt;sub&gt;2&lt;/sub&gt;N]&lt;sup&gt;-&lt;/sup&gt;</td>
<td>100</td>
<td>-2.699&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1166.39&lt;sup&gt;a&lt;/sup&gt;</td>
<td>153.2&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>1500(130)</td>
<td>22</td>
<td>0.02</td>
<td>1.2</td>
<td>0.35</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 3.4 Dynamic properties. c<sub>water</sub> is the weight % of water of samples used for viscosity measurement. A, B, T<sub>0</sub> are parameters in the fit of viscosity data to eq. 3.8. Viscosity data were collected in 5 K increments over the range 5 - 65 °C, with the exception of [Im<sub>4</sub><sup>+</sup>][Tf<sub>2</sub>C]<sup>-</sup> (20-65 °C). η is the viscosity, E<sub>η</sub> is the viscosity activation energy (25 °C; eq 3.9), Λ the molar conductivity, (±10%) and D<sub>+</sub> the cation diffusion coefficient (±10%) at the indicated temperatures. Values of η are derived from the temperature-dependent fits with the standard error of the fit of these values indicated in parenthesis. The actual uncertainty in viscosities is probably closer to ±10%. R<sub>H</sub>/R<sub>+</sub> is the ratio of hydrodynamic radius determined from D<sub>+</sub> according to eq 3.10 to the calculated cation radius from Table 3.1. Λ/Λ<sub>est</sub> is an estimate of the ratio of the observed molar conductivity to the value calculated using the Nernst-Einstein equation via eq 3.12. (a) Values fit without use of the (unknown) value of T<sub>g</sub>. 
Figure 3.7 Example viscosity data (points) and fits to eq 3.8 (curves). The top panel shows data for the series of pyrrolidinium ILs [Pr$_{n1}$][Tf$_2$N] with the values of $n$ as indicated. The bottom panel shows data in the mono-hydroxy ionic liquids [Im$_{21}$(OH)$^+$][Tf$_2$N], [Pr$_{21}$(OH)$^+$][Tf$_2$N], and [N$_{ip211}$(OH)$^+$][Tf$_2$N].
with \( n \) until at \( n = 10 \) the viscosities are the same to within uncertainties. Some subtle difference in liquid-state packing or interactions must account for this difference in viscosities. We note that the packing fractions of the \( N_{i=11}^{+} \) liquids are slightly higher than those of the \( Pr_{i=1}^{+} \) series (averages over the set \( n = 3-6 \) are \( f = 0.64 \) and \( 0.61 \), respectively) but it is not clear whether the calculated ion sizes are sufficiently accurate to trust such small differences. Comparing the pairs of ILs in which a single substitution \( CH_{3} \rightarrow OH \) is made, one finds that the presence of an OH group leads to an increase in viscosity by as much as a factor of 2 in the case of \( [N_{i=11}{^{+}}] \rightarrow [N_{i=21}(OH)^{+}] \), with lesser differences in the case of the \( Pr_{i=1}^{+} \) and \( Im_{i=1}^{+} \) comparisons.

Much more dramatic is the effect of having two OH groups in the molecule, as illustrated by the case of \([Pr_{i=1}(OH)_{2}^{+}][Tf_{2}N]^{-}\). Here the viscosity is \(~10\)-fold higher than in the unsubstituted \([Pr_{i=1}^{+}]\) liquid. This effect is analogous to what is observed when one compares (uncharged) normal alcohols to diols, for example in n-propanol versus 1,2-propanediol where \( \eta(25 \, ^{\circ}C) = 1.9 \) and \( 42 \) mPa s, respectively.\(^{69}\) Also shown in Table 3.4 are viscosity activation energies (25 \(^{\circ}C\)), defined by

\[
E_{\eta} = \frac{1}{R} \frac{d \ln \eta}{d(1/T)}
\]  

(3.9)

As already mentioned viscosities are non-Arrhenius, and we provide these activation energies simply as a measure of how rapidly viscosities change with temperature near room temperature. In the non-hydroxylic and mono-hydroxy ILs these activation energies average \( 17 \pm 3 \, kJ/mol \), making their rates of change comparable to what is found in short-chain alcohols such as 1-propanol.\(^{69}\)

In Fig. 3.8 we compare the cation diffusion coefficients \( D_{+} \) and molar conductivities \( \Lambda \) of the various ILs by plotting these quantities versus viscosity. As illustrated here, the variations in \( D_{+} \) and \( \Lambda \) among the different liquids are largely accounted for by differences in viscosity. The
Figure 3.8 Cation diffusion coefficients (25 °C) and molar conductivity (22 °C) plotted as functions of viscosity. Circles, squares, and triangles represent Im⁴⁺, Pr⁴⁺, and Nip⁴⁺ liquids, respectively. Open symbols denote hydroxylic cations. The lines indicate an inverse proportionality to viscosity.
lines in Figure 3.8 indicate proportionality to viscosity and, at least in first approximation, the diffusion coefficients and conductivities vary in proportion to viscosity. The scatter in these data, which is larger than their uncertainties, indicates that factors other than simply viscosity control the liquid-to-liquid variations in \( D \) and \( \Lambda \). (Nevertheless, within a single liquid, the more extensive temperature-dependent measurements reported by other groups\textsuperscript{11,20,23,24} suggests that the \( \eta(T) \) parameterizations in Table 3.3 should suffice to predict the temperature dependence of these other quantities with reasonable accuracy.) One expected source of according to hydrodynamic models is the differences in the cation (and anion) sizes in the different ILs. To examine the influence of ion size we have tabulated “hydrodynamic radii” \( R^H_+ \) determined from the cation diffusion coefficients using the relation

\[
R^H_+ = \frac{k_B T}{6\pi D_+\eta} \tag{3.10}
\]

Values of \( R^H_+ \) are listed in Table 3.4 normalized by the cation radii calculated from molecular volumes (Table 3.1). The values of \( R^H_+ / R_+ \) observed here range between 0.33-0.60, and for the non-hydroxylic ILs \( R^H_+ / R_+ = 0.45\pm0.08 \). These values are consistent with the values calculated from the data of Watanabe and coworkers for imidazolium ILs at room temperature, 0.53\pm0.06\textsuperscript{20,23,24}. For a spherical species one expects \( R^H_+ / R_+ =1 \) for stick boundary conditions and \( R^H_+ / R_+ =2/3 \) for slip boundary conditions. Thus, the observed values tend to be slightly below slip values for a sphere, similar to what is observed for self-diffusion of nonionic molecules in conventional solvents of comparable size\textsuperscript{120,121}. Tokuda et al.\textsuperscript{21} and Every et al.\textsuperscript{11} have suggested that a useful gauge of the extent of ion association in ILs can be obtained by comparing measured values of the conductivity to
conductivities calculated assuming independent cation and anion diffusion via the Nernst-Einstein equation,

$$\Lambda_{NE} = \frac{F^2}{RT} (D_+ + D_-) \tag{3.11}$$

In this expression $D_-$ is the anion self diffusion coefficient and $F$ is the Faraday constant. Because we have not measured $D_-$ we cannot calculate $\Lambda_{NE}$ exactly. However, the accumulated data of Watanabe and coworkers in 13 imidazolium and related ILs show that $D_-$ and $D_+$ are very often nearly equal, with $D_- = (0.79 \pm 0.13) D_+$ at 30 °C.\textsuperscript{21} With this similarity in mind, we have calculated approximate values of $\Lambda_{NE}$ of the ILs studied here assuming that $D_- = 0.79 D_+$ by using the relation

$$\Lambda_{est} = \frac{1.79 F^2 D_+}{RT} \tag{3.12}$$

Values of $\Lambda/\Lambda_{est}$ are listed in the final column of Table 3.4. With the exception of $\text{[Pr}_{31}(\text{OH})_2^+\text{][Tf}_2\text{N}]$, the values so determined average 0.8 ± 0.1. Although not accurate, these approximate values suffice to indicate the similarity of the present ILs and those studied by Watanabe and coworkers\textsuperscript{21}.
3.4 Summary & Conclusions

In this work we have calculated single ion characteristics and measured a number of physical properties of 16 ionic liquids. The majority of the results reported here concern many of the same quantities and exhibit similar trends that have been previously reported in studies of this sort\textsuperscript{11-24}. The present results simply add useful data on a number of new and easily synthesized ILs to the growing database on ionic liquid properties, a database which is essential for the many applications of these liquids currently under exploration. We have also, for the first time, estimated dielectric constants from calculated dipole moments, showed that Hildebrand solubility parameters can be reliably estimated from measured values of surface tension and density, and examined the utility of \textsuperscript{19}F chemical shifts as a probe of ion solvation in ILs. These more novel aspects of this work should be of more general interest and will hopefully spur further work on such properties.
References and Notes

6 Poole, C. F. J. Chromatogr., A 2004, 1037, 49.


Hu, Y. F.; Xu, C. M. Chem. Rev. 2006, ASAP Article; DOI: 10.1021/cr0502044 (withdrawn by Editor).


We note that the geometries and relative energies of the conformers of $\text{Tl}_2\text{N}^-$ calculated here are in good agreement with the recent calculations of Lopes and Padua who reported a global energy minimum at $\angle\text{C-S-N-S} \approx 93^\circ$ and a secondary minimum at $\approx 3.5$ kJ/mol and $\approx 230^\circ$ using MP2/cc-pVTZ(-f)/HF/6-31G(d) calculations.

81 Becher, P. J. Colloid Interface Sci. 1972, 38, 291.
82 Beaberower, A. J. Colloid Interface Sci. 1971, 35, 126.


Calculations assumed the standard expression for the excess Gibbs chemical potential, an ideal entropy of mixing that accounts for the distinguishability of the cation and anion components of the IL, and a typical molar volume of the liquid component of 80 cm$^3$/mol.


We follow Moog et al. in using the average of the frequencies at the low and high half-height points of the absorption band for determining the characteristic frequency for comparison. This method is preferable to using the peak frequency when vibronic structure is present in some solvents, as is the case of Nile Red in the nonpolar reference solvent cyclohexane.


When the probe solutes originally designed for Kamlet-Taft analysis or combinations of other probes are used to measure $\alpha$ in ionic liquids, much larger values have often been obtained.


Based on the dependence of diamagnetic susceptibilities with molar refraction found in conventional solvents and in ionic crystals we estimate that the basic trends displayed in Fig. 6 will not be altered by such corrections.
Chapter 4

Solvational and Rotational Dynamics of Ionic Liquids

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Co-author’s contributions:

This chapter has been reproduced from above publication with modifications. I acknowledge my co-author’s contributions to this work, which include viscosity measurements by Jing Dong and Kerr-gated measurements by Sergei Arzhantsev.
4.1 Introduction

Research exploring the uses of room temperature ionic liquids is growing at an exponential pace. A recent news article lists the use of ionic liquids as solvents for nucleoside chemistry and biosensing, as liquid rocket propellants, high-temperature lubricants and index matching fluid as just some of the newest applications\(^1\). In parallel with these developing applications, much recent work has focused on characterizing the physical properties of ionic liquids and how they differ from those of conventional organic solvents\(^2-5\). One important aspect of the latter work involves attempts to understand the unique features of solvation in ionic liquids, using both thermodynamic\(^6-11\) and spectroscopic methods\(^8,11-13\). In addition to equilibrium aspects of solvation, a number of groups have applied various techniques to measure dynamical aspects of solvation such as translational\(^14-16\) and rotational\(^17-29\) diffusion of solutes and measurements of solvation dynamics, the time-dependent response to a solute perturbation\(^30,31\). Study of the latter dynamics has been especially popular\(^18-22,26-29,32-45\) and several papers have just been published reviewing the status of this area\(^45-47\).

**SCHEME 1**

In the present paper we add to the growing literature on solvation in ionic liquids through spectroscopic measurements on the solvatochromic probe coumarin 153 (C153; Scheme 1) in a diverse collection of 21 ionic liquids. This work collects data previously reported by our group
on a number of imidazolium$^{19,21}$ and phosphonium$^{20}$ ionic liquids together with new data on two homologous series of ammonium and pyrrolidinium ionic liquids. In addition to summarizing the ionic liquid results, a focus of the present work is to compare the solvation of C153 in ionic liquid and conventional dipolar solvents. We use steady-state absorption and emission data to measure solvent contributions to the free energy difference and reorganization energy associated with the $S_0 \leftrightarrow S_1$ transition of C153. In conventional dipolar solvents these equilibrium solvation quantities are well described by dielectric continuum models of solvation. Based on the data currently available on the dielectric constants of ionic liquids$^{48-50}$, it appears that the same models are not useful for predicting the energetics in these solvents. Reasonable correlations are, however, observed for these energies with ion size. Time-resolved anisotropy measurements made with the time-correlated single photon counting (TCSPC) method are used to measure the reorientation of C153. In both conventional solvents and in ionic liquids the rotation times follow simple hydrodynamic predictions reasonably. We find no evidence for the frictional coupling between this dipolar solute and its environment to be qualitatively different in ionic liquids compared to conventional dipolar solvents. Finally, TCSPC measurements of the dynamic Stokes shift of C153 are used to quantify solvation dynamics in ionic liquids. It has been recognized for some time$^{18}$ that, despite the fact that slow dynamics are often observed, a substantial fraction of the solvation response is missed in such experiments, which are limited in our case by a 25 ps instrument response time. Fortunately, recent work with higher time resolution$^{45}$ indicates that the integral solvation times measured in this way provide good estimates of the non-inertial portions of the dynamics. Comparisons of these times measured in ionic liquids with the equivalent times in dipolar solvents reveals a single overall correlation between solvation time and solvent viscosity, albeit a very crude one. In ionic liquids, the connection between viscosity and solvation time appears to be much closer, especially if some account is made for ion size.
4.2 Materials and Experimental Methods

The 21 ionic liquids surveyed in this work are listed in Table 4.1. Structural formulas of the ions involved and the designations we employ for them are described in Figure 4.1. 1-butyl-3-methylimidazolium chloride [Im$_{41}^+$][Cl$^-$], 1-butyl-3-methylimidazolium hexafluorophosphate [Im$_{41}^+$][PF$_6$], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide [Im$_{41}^+$][Tf$_2$N], 1-butyl-3-methylimidazolium tris(trifluoromethylsulfonylimethide [Im$_{41}^+$][Tf$_3$C$^-$], and 1-propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonylimide [mIm$_{31}^+$][Tf$_2$N] were obtained from Covalent Associates (electrochemical grade, >99.5%, <50 ppm H$_2$O) and used as received. 1-butyl-3-methylimidazolium tetrafluoroborate [Im$_{41}^+$][BF$_4$] was obtained from Sigma-Aldrich (97%). It was dissolved in acetonitrile and treated with activated carbon after which the solvent was removed and the sample dried under vacuum for 36 hours at 60 °C.

Methyl(tributyl)ammonium bis(trifluoromethylsulfonylimide [N$_{4441}^+$][Tf$_2$N] was provided by Pedatsur Neta and was synthesized according to the procedure described in Ref. 51. All liquids containing the trihexyl(tetradecyl)phosphonium (P$_{14,666}^+$) cation (~94%) were prepared by Cytec Canada 52. The two series of liquids consisting of N-methyl(N-alkyl)pyrrolidinium (Pr$_{n1}^+$) and (dimethyl)(isopropyl)(alkylammonium) (N$_{ipn1}^+$) cations and the bis(trifluoromethylsulfonylimide anion were synthesized according to published methods 53 and purified as detailed in Ref. 54. Coumarin 153 (laser grade) was purchase from Exciton and used as received.

The physical properties and water contents of many of these ionic liquids will be detailed in a separate publication 54. In most cases spectroscopic measurements were made on initially dried samples that were stored in a dry atmosphere but were not dried immediately prior to measurement. Such treatment means that the water content of most of the samples reported here varies between 100 – 500 ppm by weight. Exceptions are the phosphonium ionic liquids which...
Figure 4.1 Structures of the ionic liquids surveyed and the designations employed in this work.
<table>
<thead>
<tr>
<th>#</th>
<th>Ionic Liquid</th>
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<th>$R_-$ /Å</th>
<th>MW /g mol$^{-1}$</th>
<th>$V_{sdw}$ /Å$^3$</th>
<th>$V_m$ /Å$^3$</th>
<th>η /cP</th>
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<td>284</td>
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Table 4.1 Ionic liquids studied and some of their characteristics.
contained up to as much as 0.8% water (see Ref. 20) and the imidazolium chlorides which contained 1-2% water. These higher amounts of water can significantly alter some physical properties such as viscosity. However, as discussed previously20, we have found that the spectra of C153 are not specifically sensitive to the presence of water, and the influence of water on the dynamics measured with C153 appear to be accounted for by viscosity changes alone. In all of the dynamical comparisons we therefore use viscosities measured using the same ionic liquids used for the time-resolved spectroscopic measurements.

The instrumentation and procedures for measuring steady-state and time-resolved spectral data are essentially the same as described in Ref. 20. Absorption spectra (1 nm resolution) were recorded using a Hitachi U-3000 UV/Vis spectrometer and steady-state emission spectra with a Spex Fluorolog 212 spectrometer (2 nm resolution). Emission spectra were corrected for instrument responsivity calibrated against a series of dyes as described in Ref. 56. Time-resolved emission decays were measured using a time-correlated single photon counting instrument57 based on a fs-Ti:sapphire laser (Coherent Mira). The doubled output of this laser at 410 nm (~200 fs, 76 MHz) was used in the present measurements. Instrumental parameters were typically chosen to collect data at intervals of 4.8 ps over a total time of 20 ns and data accumulated until a maximum of 1000-4000 counts were collected in the peak channel. To obtain time-resolved spectra, 14-16 decays at wavelengths spanning the emission spectrum (450-650 nm) were recorded at magic angle through a monochromator with 8 nm resolution. The effects of instrumental broadening were partially removed from the data by independently fitting each decay to a sum of 3-4 exponentials using an iterative reconvolution scheme and an instrument response function (~25 ps FWHM) obtained from a scattering solution. Time-resolved spectra were then reconstructed from these fitted decays by normalizing to steady state emission spectra in the usual manner58. Information about reorientational dynamics was obtained from a set of 3 decays measured near to the peak of the steady-state emission and recorded with
parallel, perpendicular, and magic angle polarizations. The parallel and perpendicular decays were simultaneously fit using an iterative reconvolution algorithm\(^\text{59}\) to model functions including a multi-exponential population decay and a multi-exponential or stretched-exponential anisotropy. All measurements were made in tightly sealed 1 cm quartz cuvettes using probe concentrations chosen to give optical densities near 0.1. Sample temperatures (± 0.1 K) were controlled using circulating water from thermostated baths (Neslab).
4.3 Results and Discussion

4.3.1 Solvation Energies

Many workers have already attempted to characterize the polarity of ionic liquids using the spectral shifts of popular solvatochromic probes. In most cases electronic absorption has been used for this purpose\(^3,8\) on such well-known probes as betaine-\(^30\)\(^{13,60}\), the nitrobenzene derivatives used for the \(\pi^*\) scale\(^61,62\), Nile Red\(^54,63,64\) and others\(^65,66\). C153 is in some ways a superior probe, because the possibility of measuring both absorption and emission shifts enables a finer definition of what is meant by solvent polarity. In particular, the Stokes shift of C153 has been shown to provide a direct measure of the “nuclear polarizability” of a solvent, i.e. that part of the solvent response due to positional and orientational reorganization of the permanent charge distributions of solvent molecules\(^31,67\).

Figure 4.2 provides a comparison of the absorption and emission spectra of C153 in a series of dipolar aprotic solvents of increasing polarity (2-methylbutane to dimethylsulfoxide) and in a representative ionic liquid, \([\text{Pr}\(_{31}\)]\)[Tf\(_2\)N\(-\)]. As noted previously with respect to a number of other probes\(^18,68\), there is nothing distinctive about the spectra of C153 in ionic liquids. As illustrated by the \([\text{Pr}\(_{31}\)]\)[Tf\(_2\)N\(-\)] spectra here, the shift and broadening of the spectra of C153 in ionic liquids is indistinguishable from what pertains in strongly dipolar solvents. The example in Figure 4.2 is also typical in showing spectra that fall in the polarity range between acetone and dimethylsulfoxide.

Frequency data for all of the ionic liquids studied here are summarized in Table 4.2. This table contains peak frequencies of the absorption and steady-state emission spectra \((\nu^\text{pk}_{\text{abs}}, \nu^\text{pk}_{\text{em}})\) as well as estimates of the peak frequency of the “time-zero”, \(\nu^\text{pk}(0)\), and fully relaxed spectra, \(\nu^\text{pk}(\infty)\). Time-zero spectra were derived from an analysis of the shift and broadening of the
Table 4.2 C153 spectral frequencies and energy estimates(a). $\nu_{abs}^{pk}$ and $\nu_{em}^{pk}$ are peak frequencies ($\pm$100 cm$^{-1}$) of the steady-state $S_1$ absorption and emission bands. $\nu_{est}^{pk}(0)$ is the estimated peak frequency of the “time-zero” spectrum, the spectrum expected prior to solvent relaxation calculated via comparison of the absorption spectrum to the spectrum in a nonpolar reference solvent. $\nu_{est}^{pk}(\infty)$ is the peak frequency of the fully relaxed spectrum, obtained by extrapolating time resolved data to infinite time, and $\Delta \nu_{est}^{pk} = \nu_{est}^{pk}(0) - \nu(\infty)$. Uncertainties in the latter frequencies are estimated to be $\pm$200 cm$^{-1}$. $\lambda_{sol}$ and $\Delta_{sol}G$ ($\pm$1-2 kJ/mol) are the solvent contributions to the reorganization energy and free energy change associated with the $S_0 \rightarrow S_1$ transition, calculated from frequency data as described in the text.

(a) Most data were recorded at 298 K. Data in [Im$_4^+$][Cl$^-$] and the [P$_{14,666}^+$] ionic liquids are at 343 K.

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<th>$\nu_{em}^{pk}$ /10$^3$ cm$^{-1}$</th>
<th>$\nu_{est}^{pk}(0)$ /10$^3$ cm$^{-1}$</th>
<th>$\nu_{est}^{pk}(\infty)$ /10$^3$ cm$^{-1}$</th>
<th>$\Delta \nu_{est}^{pk}$ /10$^3$ cm$^{-1}$</th>
<th>$\lambda_{sol}$ /kJ mol$^{-1}$</th>
<th>$\Delta_{sol}G$ /kJ mol$^{-1}$</th>
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Figure 4.2 Absorption and emission spectra of C153 in representative conventional solvents (solid curves, data from Ref.31) and in the ionic liquid \([\text{Pr}_{31}^+][\text{Tf}_2\text{N}^-]\) (dashed curves, 25 °C). All spectra are normalized to unit height. The conventional solvents are from right to left: 2-methylbutane (2MB), diethyl ether, ethyl acetate, acetone, and dimethylsulfoxide (DMSO).
absorption spectrum in a given ionic liquid relative to the spectrum in a nonpolar reference solvent, 2-methylbutane, as described in Ref. 69. Such spectra provide estimates of the emission prior to any solvent motion. Estimates of the spectra expected after full solvent relaxation were obtained by extrapolating the time-dependent data discussed in Sec. 4.3.3. We note that solvation in many of the ionic liquids is sufficiently slow compared to the ~6 ns emission lifetime of C153 that \( \nu^\text{em} \) is significantly larger than \( \nu^\text{ph} (\infty) \), i.e. the steady-state emission spectrum does not provide a quantitative reflection of their equilibrium polarity. On average the difference is about 300 cm\(^{-1}\).

From frequency data such as these we compute two solvation characteristics of the 
\( S_0 \leftrightarrow S_1 \) transition of C153, the solvation free energy difference

\[
\Delta_{\text{sol}} G = \frac{1}{2} h \{ \nu_{\text{abs}} + \nu(\infty) \} - \Delta G_0 \tag{4.1}
\]

and the reorganization energy,

\[
\lambda_{\text{sol}} = \frac{1}{2} h \{ \nu(0) - \nu(\infty) \} \tag{4.2}
\]

By subtracting an approximate gas-phase value of \( \Delta G_0 \approx 295.9 \text{ kJ/mol} \) in eq 4.1 (estimated from a dielectric extrapolation in conventional solvents) \( \Delta_{\text{sol}} G \) represents the difference in solvation free energies of the \( S_1 \) and \( S_0 \) states of C153. Similarly, \( \lambda_{\text{sol}} \) provides an approximate measure of the solvent contribution to the nuclear reorganization energy accompanying the 
\( S_0 \leftrightarrow S_1 \) transition. Values of \( \Delta_{\text{sol}} G \) and \( \lambda_{\text{sol}} \) provided in Table 4.2 reflect weighted averages obtained by using both the peak frequencies listed there and also the first-moment frequencies (not tabulated) in eqs. 4.1-4.2.

Figures 4.3 and 4.4 summarize these solvation energies and compare them to what is observed in conventional dipolar solvents. The energetics of C153 in dipolar solvents are well accounted for using simple continuum dielectric models of solvation\(^{31,67}\). This fact is illustrated by Figure 4.3, which shows that \( \Delta_{\text{sol}} G \) in dipolar solvents is approximately proportional to the
Figure 4.3 Solvation free energy differences ($S_1 - S_0$) of C153 in conventional dipolar liquids and in ionic liquids. The left panel shows data in 30 conventional dipolar solvents calculated using data from Refs. 31, 67. The regression shown here is $\Delta_{sol} G / \text{kJ mol}^{-1} = -46.5 f (\varepsilon_r)$ ($r^2=0.995$; standard error = 2.6). The right panel shows ionic liquid data plotted versus the inverse of the mean ionic separation, $1/d = V_m^{-1/3}$. The line here is a fit to the ionic liquid data excluding the phosphonium liquids ($N = 16, r^2=0.84$).
Figure 4.4 Solvent reorganization energies of C153 in conventional dipolar liquids and in ionic liquids. The left panel shows data in 30 conventional dipolar solvents calculated using data from Refs. 31,67. These data are plotted versus the function $f(\varepsilon_r, n)$ defined by eq 4.3. The regression shown here is $\lambda_{sol} / \text{kJ mol}^{-1} = 17.5 f(\varepsilon_r, n)$ ($r^2=0.98$; standard error = 1.2). The right panel shows ionic liquid data plotted versus the inverse of the mean ionic separation, $1/d = V_m^{-1/3}$. The regression here is $\lambda_{sol} / \text{kJ mol}^{-1} = 94.2(\text{Å} / d)$ ($N = 21$, $r^2=0.74$; standard error = 0.9).
reaction field factor \( \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \), where \( \varepsilon_r \) is the relative permittivity of the solvent. To a good first approximation, the single parameter, \( \varepsilon_r \), captures the net (nuclear + electronic) polarizabilities of conventional dipolar solvents relevant for determining \( \Delta_{\text{sol}} G \). It is noteworthy that there is no distinction between the behavior of protic and aprotic solvents in Figure 4.3 (or Figure 4.4), which indicates that the \( S_0 \leftrightarrow S_1 \) transition of C153 primarily senses the strength of nonspecific polar interactions and is insensitive to hydrogen bonding.

The values of \( \Delta_{\text{sol}} G \) in the ionic liquids studied here all fall within a relatively narrow range between 40-50 kJ/mol. This modest spread, a factor of 5 smaller than observed in dipolar solvents, is surprising given the variety of ionic liquids included in this study. To date, the relative permittivities of only five of these ionic liquids \( \leq 4, 3, 4, 7, 9 \) have been determined \( \leq 48, 70 \), and they too fall within a remarkably narrow range, \( 11.1 \leq \varepsilon_r \leq 11.9 \). However, these values of \( \varepsilon_r \) are all smaller than would be expected if the same correlation found in dipolar liquids were to apply to ionic liquids, which would imply values in the range \( 19 \leq \varepsilon_r \leq \infty \). Given the different character of the electrostatics, it is not surprising that the same correlation does not apply to both classes of liquids. In fact, one might anticipate that \( \varepsilon_r \), which monitors dipolar interactions, would fail to account for the most important aspects of the electrostatic interactions present in ionic liquids, in much the same way that fails in quadrupolar solvents \( \leq 67, 72 \).

In the absence of any theory of dipolar solvation in ionic liquids, we have plotted the observed values of \( \Delta_{\text{sol}} G \) in ionic liquids versus the inverse of the average ion-ion separation, calculated from the experimental molar volumes using \( 1/d = V_m^{-1/3} \). We adopt this particular parameter as a measure of the strength of electrical interactions by analogy to its appearance in the Born-Lande expression for lattice energies of ionic crystals. More generally, \( V_m \) has been found to correlate both energetic and entropic properties of ionic substances \( \leq 73 \). As indicated by
the solid line in Figure 4.3, some correlation seems to exist between $1/d$ and $\Delta_{sol}G$ in the majority of the ionic liquids studied here, but this correlation does not extend to the liquids containing the large $P_{14,666}^+$ cation. One might imagine electronic polarizability to also be important in determining $\Delta_{sol}G$. But attempts to include electronic polarizability using the refractive indices of the ionic liquids$^{34}$ did not provide better results.

Figure 4.4 shows an analogous presentation of solvent reorganization energies, $\lambda_{sol}$. In dipolar solvents, the reorganization energies of C153 are approximately proportional to dielectric measures of nuclear solvent polarizability such as

$$f(\varepsilon_r, n) = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2}$$  \hspace{1cm} (4.3)

As was the case with $\Delta_{sol}G$, hydrogen bonding in conventional solvents does not appear to affect these energies. The values of $\lambda_{sol}$ observed in ionic liquids cover a greater fraction of the range spanned by dipolar solvents than did the $\Delta_{sol}G$ values. If the same correlation with $\varepsilon_r$ found in dipolar solvents were to pertain to the ionic liquids, the range of dielectric constants implied would be $10 \leq \varepsilon_r \leq \infty$. For the collection of ionic liquids mentioned above whose relative permittivities have been measured to be 11.5±.4, the observed values of $\lambda_{sol}$ imply $\varepsilon_r \geq 65$. Thus, here too, if any simple relationship between $\lambda_{sol}$ and $\varepsilon_r$ exists, it must differ from that applicable to conventional solvents. However, as illustrated in Figure 4.4, the parameter $1/d$ does correlate the reorganization energies of ionic liquids to within their expected uncertainties. Thus, it appears that it should be possible to model solvent reorganization energies in ionic liquids in a manner comparable to dielectric continuum models in conventional solvents by using some parameter like $1/d$, related to ion densities or molar volumes.
4.3.2 Rotational Dynamics

Figure 4.5 displays a representative set of anisotropy data recorded for C153 in [Pr$_{31}$][Tf$_2$N$^-$. As is the case here, we mainly collect anisotropy information near to the peak of the steady-state emission spectrum, where magic angle or population decays “K(t)” are usually close to a single exponential function of time. The simplicity of the decays in this spectral region facilitates accurate anisotropy fits. We have also examined anisotropies at wavelengths on the blue and red edges of the steady-state emission spectrum in a number of liquids and find the same anisotropy decays r(t) to within anticipated uncertainties. In addition, in the particular liquid, [N$_{ip311}$][Tf$_2$N$^-$], we measured anisotropy data at a number of excitation wavelengths and observed no dependence upon excitation wavelength$^{74}$. Thus, at least for many of the ionic liquids studied here, we do not find any clear evidence for heterogeneity in the rotational dynamics of C153.

We fit anisotropy decay data to both stretched exponential,

\[ r(t) = r_0 \exp\left\{-\left(t / \tau_{rot}\right)^\beta\right\} \]

and bi-exponential functions of time, using a fixed value of the initial anisotropy $r_0 = 0.375^{75}$. As in the example shown in Figure 4.5, the stretched exponential representation typically afforded good fits to such data. In only a few cases did the additional fitting parameter available with a bi-exponential function provide better fits, at least at the signal-to-noise levels used in the present study. However, we note that recent work by Castner and coworkers$^{29}$ on C153 in comparable ionic liquids has shown that when data are collected over a wider time window (>50 ns) and with higher signal-to-noise, 3- or even 4-exponential representations may be needed to fit anisotropy data. For this reason we do not ascribe any meaning to the stretched exponential function or its parameters here, but we use it as a convenient way to approximately represent the data.

Table 4.3 contains a summary of the parameters $\tau_{rot}$ and $\beta_{rot}$ from stretched exponential fits as well as rotational correlation times $<\tau_{rot}>$ (the integral of $r(t)/r_0$) determined by averaging
Figure 4.5 Representative anisotropy decay data in $[\text{Pr}_{31}^+][\text{Tf}_2\text{N}]$ at 313 K ($\lambda_{\text{em}} = 530$ nm; $\lambda_{\text{exc}} = 410$ nm). The bottom panel shows data (points) recorded with the analyzing polarizer parallel (||) and perpendicular (⊥) excitation polarization direction as well as fits to these data (solid curves). The curve labeled “IF” is the instrument response function. The top panels show the weighted residuals of the fit and the parameters of the bi-exponential fit to the population decay function $K(t)$ and a stretched exponential fit to the anisotropy decay function $r(t)$ are shown. $g$ is the parallel perpendicular sensitivity factor, $N$ the total number of points in the fit, and $\chi^2_v$ the goodness of fit parameter. Residuals have been thinned by a factor of 2 and data points by a factor of 10 for clarity.
values obtained from both stretched-exponential and bi-exponential fits. The uncertainties listed
in $<\tau_{\text{rot}}>$ partially reflect the differences in the times obtained by these two fitting methods. In
general, the values of $\beta_{\text{rot}}$ observed here indicate a significantly non-exponential character to the
reorientational correlation functions. This non-exponentiality is somewhat unusual in the sense
that hydrodynamic modeling\textsuperscript{76} predicts exponential anisotropies and, at least in low-viscosity
solvents, C153 does rotate exponentially. However, studies in conventional solvents have shown
that reorientational correlation functions of C153 are often non-exponential in slowly relaxing
solvents like the normal alcohols\textsuperscript{76,77}. We conjectured previously that such non-exponential
dynamics reflect the non-Markovian character of rotational friction in slowly relaxing solvents\textsuperscript{76}. Such an explanation is also plausible in these highly sluggish solvents, but dynamic heterogeneity
might also be the source of this behavior, at least in some instances.

There is a significant difference in the degree of non-exponentiality of the rotational
anisotropy decays observed in the phosphonium ionic liquids compared to all of the other liquids
studied. The distinction is most obvious in the cation-averaged data shown in Table 4.4. Here we
list $\beta_{\text{rot}}$ values averaged over data for the four different types of cations examined. It is clear from
this summary that liquids incorporating the large phosphonium cation $\text{P}^{14,666+}$ stand out as being
markedly more non-exponential than the remaining types of liquids (see also Figure 4 of Ref.\textsuperscript{20}).
The values of $\beta_{\text{rot}} \sim 0.7$ in the other ionic liquids indicate a degree of non-exponentiality that is
roughly comparable to what was found for C153 in normal alcohol solvents\textsuperscript{76,77}. The fact that we
have failed to observe an excitation wavelength dependence to the rotation times of C153 in
$[\text{N}_{\text{ip311}}][\text{Tf}_2\text{N}^-]$ (298 K, $\beta_{\text{rot}} = 0.72\pm0.01$ for $\lambda_{\text{exc}} = 410-460$ nm) suggests that in the majority of the
ionic liquids studied here heterogeneity is not the main source of the non-exponential rotations.
In the phosphonium liquids, on the other hand, rotational motion is highly dispersive ($\beta_{\text{rot}} \sim 0.5$
and similar to what is observed near the glass transition of fragile glass-forming liquids when the
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<th>$\beta_{rot}$</th>
<th>$\langle \tau_{ro}\rangle$ /ns</th>
<th>$C_{rot}$ /10$^3$ cm$^{-1}$</th>
<th>$f_{obs}$</th>
<th>$\tau_{br}$ /ns</th>
<th>$\beta_{obs}$</th>
<th>$\langle \tau_{obs}\rangle$ /ns</th>
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Table 4.3: Summary of dynamical quantities. Viscosities $\eta$ were calculated from parameterizations of temperature-dependent data reported in$^4$ or in the earlier references cited. $\tau_0$, and $\beta_{\text{rot}}$, are from stretched exponential fits of anisotropy data (eq 4.4); $\langle \tau_{\text{rot}} \rangle$ is the rotational correlation time determined as an average of the results from both stretched exponential and bi-exponential fits. $C_{\text{rot}}$ is the rotational coupling factor defined by eq 4.6. $\Delta \nu$, $\tau_{\text{sol}}$, and $\beta_{\text{solv}}$, are the parameters of eq 4.7, averaged over $\nu(t)$ measured using both the peak and first moment measures of frequency. The integral solvation time $\langle \tau_{\text{solv}} \rangle$ is related to these values by $\langle \tau \rangle = \tau_{\text{0}} \Gamma(\beta^{-1})/\beta$ where $\Gamma$ is the gamma function. $f_{\text{obs}}$ (±1) is the fraction of the expected solvation shift actually observed, $f_{\text{obs}} = \{\nu(0) - \nu(\infty)\}/\{|\nu_{\text{est}}(0) - \nu(\infty)|\}$.

(a) Data from Ref.$^{21}$
(b) Data from Ref.$^{19}$
(c) Data from Ref.$^{20}$

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<td>1.98±11</td>
</tr>
<tr>
<td>20</td>
<td>[P$_{14,666}$$^{-}$][N(CN)$_2$$^{-}$]$^{(c)}$</td>
<td>343</td>
<td>31</td>
<td>0.91</td>
<td>0.54</td>
<td>1.60±24</td>
<td>0.58</td>
<td>1.42</td>
<td>0.93</td>
<td>0.36</td>
<td>0.48</td>
<td>0.78±05</td>
</tr>
<tr>
<td>21</td>
<td>[P$_{14,666}$$^{-}$][Tf$_2$N]$^{(c)}$</td>
<td>298</td>
<td>277</td>
<td>7.5</td>
<td>0.46</td>
<td>18±4</td>
<td>0.63</td>
<td>1.60</td>
<td>1.06</td>
<td>3.7</td>
<td>0.42</td>
<td>10.6±6</td>
</tr>
<tr>
<td>21</td>
<td>[P$_{14,666}$$^{-}$][Tf$_2$N]$^{(c)}$</td>
<td>318</td>
<td>102</td>
<td>2.8</td>
<td>0.50</td>
<td>5.5±8</td>
<td>0.56</td>
<td>1.54</td>
<td>1.03</td>
<td>1.3</td>
<td>0.44</td>
<td>3.52±23</td>
</tr>
<tr>
<td>21</td>
<td>[P$_{14,666}$$^{-}$][Tf$_2$N]$^{(c)}$</td>
<td>343</td>
<td>39</td>
<td>1.00</td>
<td>0.56</td>
<td>1.7±3</td>
<td>0.49</td>
<td>1.43</td>
<td>0.97</td>
<td>0.44</td>
<td>0.47</td>
<td>0.99±06</td>
</tr>
</tbody>
</table>
Table 4.4 Dynamic characteristics averaged over cation classes. 

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$\beta_{rot}$</th>
<th>$C_{obs}$</th>
<th>$\beta_{solv}$</th>
<th>$I_{obs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Im$^+$</td>
<td>12/18</td>
<td>0.71±0.05</td>
<td>0.58±0.15</td>
<td>0.60±0.13</td>
<td>0.62±0.13</td>
</tr>
<tr>
<td>Pr$^+$</td>
<td>6/6</td>
<td>0.71±0.06</td>
<td>0.48±0.11</td>
<td>0.61±0.05</td>
<td>0.65±0.11</td>
</tr>
<tr>
<td>N$^+$</td>
<td>5/6</td>
<td>0.71±0.06</td>
<td>0.57±0.10</td>
<td>0.58±0.10</td>
<td>0.77±0.16</td>
</tr>
<tr>
<td>P$^+$</td>
<td>9/9</td>
<td>0.46±0.07</td>
<td>0.46±0.12</td>
<td>0.44±0.04</td>
<td>0.98±0.05</td>
</tr>
</tbody>
</table>

$\beta_{rot}$, $C_{obs}$, $\beta_{solv}$, and $I_{obs}$ are the average over the cation class ± the standard deviation of each set. In computing the rotational averages data from liquids #6 and 16 have been omitted because of their much larger uncertainties.
solute / solvent size ratio is small\textsuperscript{22,78,79}. We conjecture that in these latter ionic liquids, the large size of the cation relative to the solute \((V_p / V_{C153} \sim 2.6)\) might produce dynamicheterogeneity similar to what is observed in conventional glass-forming liquids. Alternatively, the heterogeneity might result from the domain-like structures observed in simulations of ionic liquids with long alkyl chains\textsuperscript{80,81}. Whatever the origin, the character of the rotational correlation functions in the phosphonium liquids is decidedly different from that in the other liquids studied.

We now turn to the rotational correlation times of C153, \(<\tau_{rot}> = \int_0^\infty r(t)dt\). Figure 4.6 displays the results measured in ionic liquids and conventional solvents. Rotation times are plotted against \(\eta / T\) (viscosity/temperature), the scaling expected from hydrodynamic models. The smaller points in Figure 4.6 are data in 27 dipolar solvents at room temperature, taken from Ref.\textsuperscript{76}. The solid line in this figure shows that in dipolar solvents, both protic and aprotic and including the n-alcohols, rotation times of C153 conform to the expected proportionality to \(\eta / T\), albeit with some scatter. The rotation times in ionic liquids show greater scatter, but nevertheless also follow essentially the same correlation established by the dipolar solvents. The dashed lines in Figure 4.6 are the predictions of hydrodynamic models, made by assuming a solute of ellipsoidal shape with semi-axis dimensions of 2.0, 4.8, and 6.1 Å\textsuperscript{76} and the relation:

\[
\tau^{(2)} = \frac{V\eta}{k_B T} fC
\]

(4.5)

where \(V\) is the solute volume (246 Å\(^3\)), \(f\) a shape factor (1.71) and \(C\) a “rotational coupling factor”. For stick boundary conditions \(C = 1\) and for slip boundary conditions \(C = 0.24\textsuperscript{76}\). Virtually all of the rotation times, both in dipolar and ionic liquids, fall between these two limiting predictions.
Figure 4.6 Rotational correlation times of C153 in 27 dipolar solvents at room temperature (small symbols, data from Ref. 76) and in ionic liquids (larger symbols with error bars) plotted versus $\eta/T$. The solid line shows the best fit of the dipolar liquid data to the proportionality $\langle \tau_{\text{rot}} \rangle = A(\eta/T)$ with $A = 1.73 \times 10^{-8}$ s·K·cP$^{-1}$. The dashed lines show the predictions of hydrodynamic calculations using slip and stick boundary conditions.
A convenient way to examine deviations from hydrodynamic predictions is to calculate
an empirical value of the coupling factor

\[ C_{\text{rot}} = \frac{k_B T}{V \eta f} = \frac{\langle \tau_{\text{rot}} \rangle}{\tau_{\text{stk}}^{(2)}} \]  \hspace{1cm} (4.6)

where \( \tau_{\text{stk}}^{(2)} \) is the stick hydrodynamic prediction. In dipolar solvents we find \( C_{\text{rot}} = 0.57 \pm 0.09 \).

Values of this factor in the ionic liquids are listed in Tables 4.3 and 4.4 and plotted in Figure 4.7. Neglecting liquids #6 and #16 whose long rotation times make the data highly uncertain, the average value of \( C_{\text{rot}} \) is 0.53 ± 0.13, close to the dipolar liquid value. Although there are several cases, for example [P\(_{14,111}\)][Cl\(^-\)] and [P\(_{14,111}\)][Br\(^-\)]\(^{17,18}\), where the deviations of \( C_{\text{rot}} \) from the dipolar liquid values are greater than the estimated uncertainties, most values of \( C_{\text{rot}} \) measured in the ionic liquids fall within the scatter of the dipolar liquid data (denoted by the dashed lines in Figure 4.7). Overall, these results indicate that there is no obvious difference between the way in which rotation of C153 is coupled to bulk viscosity in ionic liquids and in conventional dipolar solvents. Also, unlike \( \beta_{\text{rot}} \), there is no clear distinction among the values of \( C_{\text{rot}} \) in the different cation classes (Table 4.4).

Finally it is worth mentioning how the present data compare to other data on rotation in the literature. Although there are few direct comparisons possible\(^8\), we can compare the general trends observed here to the recent data of Castner and coworkers\(^{29}\) who measured rotation times of C153 in two ammonium and two pyrrolidinium ionic liquids at five temperatures between 278-353 K. In the two pyrrolidinium liquids these authors observed small-amplitude components with time constants of greater than 100 ns which we would not be able to detect in the present experiments. If these slow components of uncertain origin are neglected, the correlation times measured by Castner and coworkers\(^{29}\) fall nicely on the correlation with \( \eta/T \) established here. For their set of 20 data points we find \( C_{\text{rot}} = 0.46 \pm 0.06 \), just slightly lower than
Figure 4.7 Rotational coupling factors of C153 measured in ionic liquids. The solid and dashed horizontal lines in this figure indicate the average and standard deviation of $C_{rot}$ observed in the sample of dipolar liquids. The error bars here include the estimated uncertainties in both the rotation time and the viscosity (assumed to be $\pm 10\%$). Numbers designate ionic liquids according to Table 4.1.
our average ionic liquid value.

4.3.3 Solvation Dynamics

Representative time-resolved spectra of C153 in \([\text{N}_{\text{ip}311}^+]\text{[Tf}_2\text{N}^-]\) are shown in Figure 4.8. Unnormalized spectra in a wavelength representation are plotted in the upper panel. The spectra decrease in overall intensity due to the ~6 ns lifetime of C153 and simultaneously shift to the red in a manner characteristic of solvation dynamics. In the bottom panel these spectra have been normalized and fit to a log-normal line shape function\(^{58}\) in order to illustrate the fact that there is little change in spectral width or shape with time. The dashed curve labeled “est. \(t=0\)” is the estimated time-zero spectrum\(^{69}\) discussed in Sec. 4.3.1 and “obs. \(t=0\)” is what is observed from deconvolution analysis of the time-resolved data. The displacement between these two curves indicates that some portion (~40%) of the solvation response is missed in these experiments, due to the finite response time of the TCSPC experiment (25 ps FWHM). As will be discussed more later, recent experiments having greater time resolution\(^{37,45}\) have shown that this missing portion of the dynamics contains both sub-picosecond inertial contributions as well as components relaxing on the 1-10 ps time scale. For now we note that in many of the ionic liquids studied here, we can only partially characterize the solvation response with the present approach.

Quantitative information about the solvation response is derived from the time-dependence of characteristic frequencies of the time-evolving spectra. Figure 4.9 shows the time-evolution of the peak frequency \(\nu_{pk}(t)\) of the fitted spectra of C153 in the two homologous series \([\text{Pr}_{n1}^+]\text{[Tf}_2\text{N}^-]\) and \([\text{N}_{\text{ip}n11}^+]\text{[Tf}_2\text{N}^-]\) with \(n=3, 4, 6,\) and 10. These plots serve to illustrate the quality of the data recorded here. Assuming that it is reasonable to expect all features of these data to vary systematically with \(n\), the fact that there is some crossover of the curves at long times
Figure 4.8 Time resolved spectra of C153 in \([\text{Nip311}^+][\text{TeN}^-]\) at 298 K. The top panel contains reconstructed spectra at the times indicated. The bottom panel shows fits of these spectra in a frequency representation to log-normal line shape functions (smooth solid curves). The actual data at \(t=0\) and 20 ns are shown as filled and open symbols respectively. The dashed curves labeled “ss” and “est. \(t=0\)” are the steady state and estimated “time-zero” spectra. In the bottom panel, spectra at 5 and 10 ns have been omitted for clarity.
Figure 4.9 Representative peak frequency data $\nu_{pk}(t)$ obtained from log-normal fits of time-resolved spectra in the $[\text{Pr}_{n1}^+]$[$\text{Tf}_2\text{N}^{-}$] and $[\text{N}_{ip,n11}^+]$[$\text{Tf}_2\text{N}^{-}$] series at 298 K. Points are the actual data and the smooth curves are stretched exponential fits (eq 4.7) to these data.
suggests a precision of roughly ±100 cm\(^{-1}\) in \(\nu_{pk}(t)\). Repeated runs on the same liquid suggest similar uncertainties. The curves in Figure 4.9 are fits of the logarithmically spaced data (symbols) to a stretched exponential time dependence

\[
\nu(t) = \nu(\infty) + \Delta \nu \exp\left\{-\left(t / \tau_{0s}\right)^{\beta_{solv}}\right\}
\]

(4.7)

As illustrated here, this functional form is able to reproduce the data to well within the anticipated accuracy. Although deviations in some data sets are larger than those shown in Figure 4.9, we find that such fits adequately capture the dynamics of \(\nu(t)\) in all of the ionic liquids studied here. Multi-exponential representations, preferred by most other authors\(^{29,40,47}\), do fit some data sets more accurately, but they do so only at the expense of introducing additional fitting parameters which we find unnecessary.

In Table 4.3 we summarize all of the solvation dynamics measurements by listing quantities derived mainly from stretched exponential fits to \(\nu(t)\) data. \(\Delta \nu\), \(\tau_{0s}\), and \(\beta_{solv}\), are the values of the parameters in eq 4.7 averaged over fits to \(\nu(t)\) data using both the peak and first moment frequencies of the spectra. The integral solvation time \(<\tau_{solv}>\) is related to these values by

\[
\langle \tau \rangle = \tau_{0s} \Gamma(\beta^{-1}) / \beta
\]

where \(\Gamma\) is the gamma function, and \(f_{obs}\) is the fraction of the expected solvation shift actually observed, \(f_{obs} = \Delta \nu / \{\nu_{ext}(0) - \nu(\infty)\}\). Cation-averaged values of \(\beta\) and \(f_{obs}\) are also provided in Table 4.4.

The magnitudes of the Stokes shifts \(\Delta \nu\) observed in these experiments range between approximately 1000 and 2000 cm\(^{-1}\). The fraction of the total solvation response represented by these Stokes shifts varies from about 0.5 to 1 depending on solvent. As highlighted in Table 4.4, virtually all of the dynamics are observed in the \(P_{14,111}^x\) liquids whereas successively less and less of the response is observed in the ammonium, pyrrolidinium, and imidazolium ionic liquids.

Crudely speaking, these trends in \(f_{obs}\) are inversely related to the speed of the observed solvation
response in the manner expected. Comparing values of $\beta_{solv}$ and $\beta_{rot}$ shows that generally $\beta_{solv} < \beta_{rot}$ – the observed solvation response functions are usually farther from single-exponential functions than are the rotational correlation functions in a given liquid. This observation is consistent with the behavior noted by Ito and Richert in two ionic liquids near to their glass transitions.\textsuperscript{26,27} Table 4.4 also suggests a significant difference in the degree of non-exponentiality ($\beta_{solv}$) among the different classes of ionic liquids, with the phosphonium liquids again being distinct in their larger departure from exponential time dependence. However, this last observation is probably an artifact related to the insufficient time resolution in the experiments. Values of $\beta_{solv}$ are clearly correlated to $f_{obs}$ (the set of all data show linear correlation coefficient 0.75) such that the smaller the fraction of the response observed, the more exponential the response appears to be. (See, for example, the temperature dependent series in the [mIm$_{31}$][Tf$_2$N] liquid in Table 4.3.)

Data collected with sufficient time resolution to observed the entire solvation response\textsuperscript{37,45} show that the nonexponentiality of even the non-inertial component of the response is systematically under-estimated by TCSPC experiments when $f_{obs}$ is significantly less than unity. Thus, values of $\beta_{solv}$ reported here are probably best viewed as upper limits to the correct values. Values of $\tau_0$ measured by TCSPC were also found to be systematically too large when $f_{obs}$ is much less than unity.\textsuperscript{45} Luckily, the systematic biases created in $\beta_{solv}$ and $\tau_0$ as a result of insufficient time resolution work in opposite directions and partially cancel when the correlation time $<\tau_{solv}>$ is considered. At least in the set of six ionic liquids fully resolved to date,\textsuperscript{2,6,8} the values of $<\tau_{solv}>$ measured with TCSPC are found to deviate only by an average of 20% from values associated with the non-inertial component of the dynamics.\textsuperscript{45} We therefore focus solely on $<\tau_{solv}>$ in the remaining discussion.

In Figure 4.10 we compare values of $<\tau_{solv}>$ measured in ionic liquids to values
Figure 4.10 Integral solvation times $<\tau_{\text{solv}}>$ in conventional dipolar solvents and in ionic liquids plotted versus solvent viscosity. The dipolar solvent data (small symbols and numerals) are from Refs. 31,67. Numerals $n$ denote normal alcohols $\text{C}_n\text{H}_{2n+1}\text{OH}$. The ionic liquid data (large symbols with error bars) represent observed values of $<\tau_{\text{solv}}>$. The upper limits of the error bars are estimated uncertainties whereas the lower limits denote $f_{\text{obs}}<\tau_{\text{solv}}>$ in recognition of the unobserved dynamics in these systems. (If the uncertainty is larger than $(1-f_{\text{obs}})<\tau_{\text{solv}}>$ the uncertainty is plotted instead.) The line shown here is the fit

$$\ln(<\tau_{\text{solv}}>/s) = -26.40 + 1.20\ln(\eta/\text{cP})$$

($N=66$, $R^2 = .91$, $\sigma_{\text{fit}} = 0.95$). The asterisk indicates data in $[\text{Nip10,11}^+[\text{Tf}_2\text{N}]]$. 
previously measured in conventional dipolar solvents at room temperature\textsuperscript{31,67}. With the exception of the normal alcohols ($n$ in Figure 4.10 denotes an alcohol with $n$ C atoms) solvation times in most conventional solvents fall in the 1-10 ps range. The times observed in ionic liquids are much longer, typically in the 0.1-10 ns range. These longer solvation times can be partially understood in terms of the much larger viscosities of ionic liquids compared to conventional solvents. The solid line in Figure 4.10 shows a fit of all of the data to $<\tau_{\text{solv}}>/\eta^p$ with $p = 1.2$. Clearly, viscosity differences rationalize the $>10^4$-fold variations in solvation times of C153, at least in a crude way. But the considerable scatter (10-fold differences for a given value of $\eta$) indicate that viscosity is not the only factor involved.

Solvation dynamics in conventional dipolar solvents has been studied for many years and is well understood\textsuperscript{30,31,83,84}. There are two main reasons for the poor correlation between $<\tau_{\text{solv}}>$ and $\eta$ in such solvents. First, in many small-molecule dipolar solvents a substantial fraction of the total response comes from inertial contributions and these contributions are not expected to be proportional to solvent viscosity. More importantly, dipolar solvation is a collective process whose time scale is determined both by the rate of individual solvent molecule motions, primarily rotation, and by the strength of the solvent-solvent coupling, or “polarity”\textsuperscript{30,85}. Because polarity is uncorrelated to solvent viscosity, except in homologous series such as the normal alcohols, solvent viscosity alone is unable to account for the variations in solvation times observed. But all of these factors are captured in the dielectric response, $\varepsilon(\omega)$, of dipolar solvents, and solvation times of C153 in all of the dipolar solvents included in Figure 4.10 can be predicted with surprising accuracy from $\varepsilon(\omega)$ and simple continuum models of solvation\textsuperscript{31,86}.

Some authors have suggested that these same dielectric approaches might also be used to calculate solvation times in ionic liquids\textsuperscript{26,27,42}. $\varepsilon(\omega)$ data has been recently been reported on a few ionic liquids\textsuperscript{26,27,49,87-89}, and we have been able to make three detailed comparisons to date\textsuperscript{45,90}.
Like the solvation energy - $\varepsilon_r$ comparisons in Sec. 4.3.1, the few available comparisons suggest that if any direct relationship exists between the solvation response and $\varepsilon(\omega)$ in ionic liquids, it is not the same as in dipolar liquids. In the absence of simple models and more dielectric data, we can at present only explore what correlations might exist between $<\tau_{solv}>$ and other properties of these solvents.

The viscosity correlation shown in Figure 4.10 indicates the ionic liquid data fall into two main groupings. The solvation times of the majority (15) of the ionic liquids relate to viscosity in a way that is distinct from the 5 ionic liquids containing the $\text{P}_{14}^{+}$ cation. The single liquid $[\text{N}_{ip10,11}][\text{TF}_{2} \text{N}]$ (marked with an asterisk in Figure 4.10) occupies an ambiguous position between these two groups. We note that this particular solvent exhibited considerably higher background emission than the other liquids studied and we suspect that these points may be significantly affected by this background, which could not be entirely eliminated.

Notwithstanding these errant points, we note that within either of the two main groups of solvents the correlation to viscosity is much better than it is in conventional solvents. For a given viscosity, however, the solvation times in the phosphonium liquids are about a factor of 5 slower than those in the main group of solvents. Another distinguishing feature of the dynamics in the phosphonium liquids is that essentially all of the solvation dynamics is observed ($f_{obs} \geq 93\%$). In most of the other liquids, even ones in which $<\tau_{solv}>$ is greater than those of many of the phosphonium liquids, $f_{obs}$ is much smaller. Thus, in contrast to most of the other liquids, those liquids containing the $\text{P}_{14}^{+}$ cation must lack substantial dynamics on the $<25$ ps time scale. We note that when the unresolved solvation components are considered, the distinction between the two groups of liquids becomes larger. This fact can be appreciated from the lower error bounds shown in Figure 4.10, which are the products $f_{obs} <\tau_{solv}>$. Whereas the points indicate measured values of $<\tau_{solv}>$, which we take as best estimates of the integral time of the diffusive component
of the dynamics, the product $f_{obs} <\tau_{solv}>$ is a lower limit to the integral time expected for the total response, including the inertial solvation component.

The most obvious characteristic that distinguishes the two groups of ionic liquids is cation size. As indicated by the ion radii ($R_+, R_-$) in Table 4.1, the $P_{14,666}$ ion much larger than all of the other ions studied here. To investigate how ion size and other factors might control the observed solvation times, we have performed multi-linear correlations of the logarithms of the solvation times to various measured and computed properties (viscosity, mass density, molar volume, molar refraction, and ion sizes) of these liquids. The best correlation we have found is reproduced in Figure 4.11, which shows the relation $<\tau_{solv}> \propto (\eta/T)^p R_+^q$ with $p = 1.04 \pm 0.04$ and $q = 4.1 \pm 2$. This correlation is reasonably accurate, with a standard error of $\pm 23\%$ and only two points, one of the $[N_{10,11}]^{1+}[Tf_2N]$ points $^{15}$ and the lowest temperature datum in $[mIm_{31}]^{1+}[Tf_2N]$ $^7$, showing deviations of more than $50\%$. Because a number of related correlations provide comparable fits to the one shown here, we do not wish to place much significance on the specific quantities ($\eta/T$) and $R_+$. For example, correlations with $\eta$ rather than $\eta/T$, and with $R_{max}$, the radius of the largest ion, rather than $R_+$, are of similar quality. What is clear from these analyses is that viscosity is the primary factor controlling the solvation time but that some measure of ion size ($R_+$ or $R_{max}$) is also needed to account for the split grouping shown in Figure 4.10. We find that ion size is better able to account for this split than are bulk properties such as molar volume (equivalent to the $1/d$ used in Sec. 4.3.1) or density, and that the anion size $R_-$ has virtually no effect on the quality of the correlations.

The interpretation of these correlations is not obvious. A relationship of the form $<\tau_{solv}> \propto (\eta/T)R_+^3$ might be interpreted in terms of cation or largest ion reorientation or translational diffusion of the cation or the largest ion over some fraction of its size $^{91}$. But an even stronger dependence on ion size than implied by such models, approximately $R_+^4$, is found here.
Figure 4.11 Correlation of the observed solvation times in ionic liquids $\langle \tau_{solv} \rangle$ with $\eta/T$ and the cation radius $R_+$. Error bars are as in Figure 4.10. The correlation shown here represents the fit:

$$\ln(\langle \tau_{solv} \rangle / \text{s}) = \ln A + p \ln \left( \frac{\eta / \text{cP}}{T / \text{K}} \right) + q \ln(R_+ / \text{Å})$$

with $A = -25.15$, $p = 1.04$, $q = 4.97$ ($N = 39$, $R^2 = .97$, $\sigma_{fit} = 0.23$).
Based on the important role of “polarity” via dipolar correlations in determining solvation times in dipolar solvents, it is plausible that this additional dependence on ion size reflects some analogous influence of charge density in ionic liquids. But, if one neglects the ambiguous \([\text{Nip}]^{+}\)[Tf$_2$N$^-$] data and simply treats the phosphonium liquids and all of the remaining ionic liquids as two distinct sets of data, the data within each set is accounted for with equivalent accuracy without any explicit consideration of ion size. Thus, instead of attempting to rationalize the size dependence, it might be more profitable to assume that some qualitative distinction exists between the liquids incorporating the large \(\text{P}_{14,666}^+\) cation and the remaining ionic liquids. As already noted, the phosphonium ionic liquids also show some distinctive behavior both with respect to the energies $\Delta_{\text{sol}}G$ (Figure 4.3) and with respect to the non-exponentiality of C153 reorientations ($\beta_{\text{rot}}$; Table 4.4). We conjecture that the long 14-carbon chain of \(\text{P}_{14,666}^+\) might lead to extensive polar/nonpolar domain formation of the sort uncovered in computer simulations. Support for such structures comes from previous studies which show that phosphonium ionic liquids with long alkyl chains tend to form layered crystals and liquid crystalline phases in which ionic and nonpolar domains segregate into planar arrays. The slower than expected solvation of C153 in phosphonium ionic liquids might be associated with slow domain relaxation kinetics or possibly solute diffusion among different domains. Clearly more study of the phosphonium liquids is required to decide the correctness of this idea.
4.4 Summary and Conclusions

We have used steady-state and time-resolved emission spectroscopy to measure static and dynamic aspects of the solvation of C153 in 21 different ionic liquids and compared these results to what is observed in conventional dipolar solvents. In keeping with the findings of many prior studies of solvatochromism in ionic liquids, the electronic shifts of C153 report “polarities” of the ionic liquids studied here to be comparable to those in highly polar conventional solvents. This polarity, as reported by the energetic quantities $\Delta_{\text{sol}}G$ and $\lambda_{\text{sol}}$, is not simply related to solvent permittivity $\varepsilon$, as it is in conventional solvents. These quantities instead appear to be correlated to some measure of ion density or mean ion separation. It seems likely that simple models akin to dielectric continuum models for dipolar solvents can be developed to understand dipole solvation in ionic liquids.

Beyond the considerable reduction in rotation rates caused by the larger viscosities of ionic liquids, rotation of C153 appears much the same in ionic liquids and conventional solvents. The rotation times of C153 in ionic liquids follow the expected $\eta/T$ dependence and show comparable frictional coupling in ionic liquids and conventional dipolar solvents. Rotational correlation functions in ionic liquids are usually not single exponential functions of time as they often are in low-viscosity conventional solvents. However, in most cases we suspect that this difference can be attributed to non-Markovian of friction effects that are more evident in ionic liquids because of their higher viscosities, rather than to any special features of the ionic liquid environment. An exception might be in the phosphonium ionic liquids, where the non-exponentiality of the rotational correlation functions is much greater than is observed in the remaining liquids. It is interesting to note that even in these latter liquids, the rotational correlation times observed are close to what is expected based on stick hydrodynamic calculations. This observation is consistent with the rotation times of a number of different
fluorescence probes in [Im$_4^+$][PF$_6^-$]$^{21}$ and other liquids$^{17,22-29}$. It stands in marked contrast to emerging dielectric$^{88,96}$ and NMR results$^{97}$ of rotation times of the ionic liquid constituents themselves, which have been interpreted as indicating 20-50 times faster rotation of imidazolium cations compared to hydrodynamic expectations.

Solvation dynamics of C153 in ionic liquids occurs over a broad range of time scales and for this reason, only a portion of the total response can typically be captured using TCSPC$^{37}$. Nevertheless, use of TCSPC is expected to provide reliable values for the integral solvation times associated with the non-inertial component of solvation$^{45}$. The survey of such times presented here shows that a single parameter, the solvent viscosity, suffices to correlate solvation times in the majority of the ionic liquids studied with an average accuracy of about 25%. This connection to viscosity has been noted in a number previous studies$^{18,19,36,40}$, but given the variety of cations and anions included in the present data set (15 ionic liquids) the quality of this single-parameter correlation is remarkable. We note that a number of other groups have measured solvation times of C153 in solvents other than those studied here$^{29,33,34,39,40,47}$. In light of the variability of samples and analysis methods among different laboratories$^{21,39}$ we have not attempted to include any of these data in the present compilations. However, it is worth mentioning that the recent data of Castner and coworkers$^{29}$ in two ammonium and two pyrrolidinium ionic liquids at 6 temperatures follow the same correlation with viscosity as do the majority of ionic liquids studied here$^{98}$. The only clear deviations we find from this general correlation with viscosity are in ionic liquids containing the large P$_{14,666}^+$ cation. Within this set of solvents there is also a good correlation between solvation times and viscosity, but here the solvation times are about 5-fold slower for a given viscosity than in the remaining liquids. This dichotomy can be viewed as a result of an either explicit cation size dependence of the solvation dynamics or as the result of some qualitative difference in these phosphonium ionic liquids. We favor the latter viewpoint...
and propose that some domain-like structure, induced by the long C14 chain of the cation, and leads to distinctive behavior in both the solvation and rotation of C153 in these liquids.
References and Notes

We had available one of the phosphonium ionic liquids, \([\text{P}_{14,666}^+][\text{Tf}_2\text{N}]\), used for making the measurements reported in Ref. 20. Because our ability to dry and measure water content has improved significantly since that earlier work, we dried the \([\text{P}_{14,666}^+][\text{Tf}_2\text{N}]\) (to <30 ppm water) and re-measured the solvation dynamics at 298 K. The results obtained with this drier sample were well within experimental uncertainties of the earlier results.


It should be noted that Wu and Stark⁵⁰ have reported a value of 69.9 ± 0.7 for [Im₄⁺][BF₄⁻] using a new method they propose for measuring permittivities of conducting materials. This value differs greatly from the value of 11.7 of Weingärtner and coworkers⁴⁸, which we take to be more reliable.


In an attempt to observe kinetic heterogeneity we measured anisotropies of C153 in [Nᵢₙ₃⁺][Tf₂N] at 298 K using excitation wavelengths of 410, 420, 430, 440, 450, and 460 nm (emission observed near steady-state emission maximum). We found the integral rotation times to be 6.0 ± 0.2 ns with no systematic variation in the times or the non-exponentialities (β_rot) of the decays.

Allowing this parameter to vary in the fitting procedure typically yielded values between 0.36-0.38. However, in some cases allowing this parameter to vary lead to significantly different values. For consistency we therefore fixed the value to 0.375 which was determined from the value in a glassy medium determined in Ref.⁷⁶.


Three direct comparisons can be made. In [Im₄⁺][PF₆⁻] at 298 K, Sarkar and coworkers reported C153 rotation times of 4.7²⁴ and 3.57 ns²² (τ₀=-.25), much shorter times than the 12 ± 2 ns measured here. The reason for this large difference is unclear. Funston et al.²⁹ measured temperature dependent rotation times of C153 in [N₄₄₄⁺][Tf₂N] and [Pr₄⁺][Tf₂N]. Interpolating their data to 298 K provides values of 28 ns in both cases.
Our value of 51±25 ns in [N_4441]^+\text{[Tf}_2\text{N}^-] at 298 K is poorly defined, but in general agreement with their more accurate determination. In [Pr_{14668}]^+\text{[Tf}_2\text{N}^-] we measure 3.4±0.5 ns which is quite far from their correlation time of 28 ns. However, their large correlation time reflects the presence of a ~200 ns component whose reality is presently uncertain, and which would be impossible to detect in our experiments. If this component is neglected their time reduces to 3.8 ns, in agreement with our value.

90 Halder *et al.* have made a similar comparison in a fourth ionic liquid with apparently more satisfactory agreement between experiment and dielectric continuum calculations. However, their calculations ignore the missing fast components of \(\varepsilon(\omega)\). Although the dielectric measurements they employ extend to 90 GHz, even here when unobserved components in \(\varepsilon(\omega)\) are accounted for in the approximate manner described in Ref.\(^{46}\), the level of agreement between the calculated and observed solvation response is significantly degraded.
91 More specifically diffusion of a cation over a time \(t\) leads to an average squared displacement of \(\langle r_c^2 \rangle = 6D_c t\) with \(D_c = k_BT / 6\pi\eta R_c\). The time required to diffuse a distance proportional to the size of a cation is therefore proportional to \((\eta/T)R_c^3\).
95 On the basis of observing anomalously small activation energies for rotation of an ESR probe Evans *et al.* suggested that such a bilayer structure exits in [P_{14668}]^+\text{[Tf}_2\text{N}^-] and a
related $\text{P}_{14,666}^+$ ionic liquid. The simple volumetric behavior observed of $[\text{P}_{14,666}^+][\text{Tf}_2\text{N}]$ and other $\text{P}_{14,666}^+$ liquids$^{100}$ would seem to argue against anything so highly organized. It could be that the unusual behavior observed by Evans et al.$^{99}$ might result from the reorientation being highly non-exponential in these liquids which could invalidate the lineshape analysis used.


The collected data of Funston et al.$^{29}$ as a function of viscosity show roughly the same amount of scatter as the majority grouping of solvents in Figure 4.10. The only clear deviation occurs for the two highest viscosity points ($\eta > 3000$ cP) where the times they report (~10 ns) are roughly a factor of 3 faster than expected.


Chapter 5

Heterogeneous Solute Dynamics in Ionic Liquids

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Co-author’s contributions:

This chapter has been reproduced from above publication with only minor modification. I acknowledge my co-author’s contributions to this work, which include measurement of CVL intramolecular electron transfer reaction and DMASBT isomerization reaction by Xiang Li, and Kerr-gated measurement by Sergei Arzhantsev.
5.1 Introduction

A number of recent studies of both solvent\textsuperscript{1,2} and solute dynamics\textsuperscript{3-6} in room-temperature ionic liquids ("ILs") have pointed to the dispersive nature of kinetics in these systems. For example, we have observed that the time-dependent response to a solute electronic perturbation in several imidazolium ionic liquids extends over 3 or more decades in time, exhibiting a time evolution that can be reasonably represented by a stretched exponential function with a stretching parameter of $\beta \sim 0.4$. Such kinetics resemble those typically found in fragile liquids in the supercooled regime, despite the fact that most ionic liquids near room temperature are above (but close to\textsuperscript{7}) their melting points and roughly 100 K away from their glass transition temperatures\textsuperscript{8}.

In the case of conventional supercooled liquids, it is generally agreed that dispersive kinetics are the result of dynamic heterogeneity – the fact that molecules in different local environments relax at significantly different rates\textsuperscript{9,10}. The meaning of dynamic heterogeneity is illustrated in Figure 5.1\textsuperscript{11,12}, where two possibilities for the origin of dispersive kinetics are proposed. The left part in the left panel is a homogeneous scenario in which all local subensembles have the same intrinsic non-exponentiality as the ensemble-averaged dynamics. The right side refers to dynamic heterogeneity, in which every local relaxation is associated with purely exponential dynamics but there is a spatial distribution of different time constants that upon averaging leads to a complex decay. In the right panel an example of dynamic heterogeneity is provided from MD simulations of 2D fluid.

It is reasonable to suppose that dynamic heterogeneity also underlies the dispersive kinetics observed in room-temperature ionic liquids. An obvious prerequisite is variability of the instantaneous local structures and energetics encountered by a molecule, which we term "static heterogeneity". The presence of static heterogeneity in ionic liquids has been clearly demonstrated both experimentally\textsuperscript{13-16} and in computational studies\textsuperscript{17-20}. However, whereas
Figure 5.1 Schematic representations of two different sources of non-exponential correlation decays. The left part in the left panel\textsuperscript{11} shows a homogeneous relaxation scenario. The right side\textsuperscript{12} refers to heterogeneous dynamics, and two different local dynamics correspond to two different regions from a 2d simulation picture in the right panel.
computer simulations have shown how such static heterogeneity translates into dynamic heterogeneity of solvent\textsuperscript{19} and solute\textsuperscript{21} motions, experimental evidence for dynamic heterogeneity in room temperature ionic liquids is lacking. The purpose of this research is to provide such evidence based on the kinetics of several probe solutes.

We do so by observing differences in the time-dependent emission of a solute produced by the site (energy) selection afforded by red-edge excitation\textsuperscript{22,23}. Because of the asymmetric nature of vibronic structure, excitation near the peak or on the blue side of an electronic absorption tends to excite a broad distribution of energetically different solute - solvent environments. In contrast, excitation on the red edge of an absorption band preferentially selects a narrowed and red-shifted subset of the overall distribution. For polar solvatochromic probes of the sort examined here, red-edge excitation is capable of selecting subpopulations that are energetically stabilized by \( \sim 2000 \text{ cm}^{-1} \) (10 \( k_B T \) at room temperature) compared to the average solvation state.\textsuperscript{24} The ability of red-edge excitation to select different distribution is illustrated in Figure 5.2. Samanta and coworkers\textsuperscript{15} have also demonstrated that site-selection is possible in room-temperature ionic liquids by monitoring the shifts in steady-state emission of short-lived solutes caused by red-edge excitation\textsuperscript{25}. Here we extend this approach to explore the extent to which red-edge excitation leads to different kinetics from those observed upon non-selective excitation, which will provide solid evidence for dynamic heterogeneity in ILs. The solute kinetics examined here include solvation and rotational dynamics of Coumarin 153 (C153), isomerization of two malononitriles p-(dimethylamino)benzylidene malononitrile (DMN) and julolidine malononitrile (JDMN), isomerization of trans-2-[4-(dimethylamino)styryl]benzothiazole (DMABST), and intramolecular electron transfer in crystal violet lactone (CVL). Isomerization of malononitriles in conventional solvents at room temperature and at low temperature is also measured to compare with the results in ILs.
Figure 5.2 Illustration of spectral shift distributions selected by different excitation frequencies across absorption spectrum. In the upper panel, $S_0$ and $S_1$ stand for the potential surfaces of the ground and first excited state. Vertical arrows with different colors are different excitation frequencies: 20, 21, 22, 23.5, 25, and 27 km$^{-1}$ from red to purple. In the lower panel, site distributions $P(\delta)$ are selected excited-state distribution calculated as described in ref$^{26}$. These distributions are calculated using Coumarin 153 as the solute in a representative IL [N$_{ip311}$]$^+$[Tf$_2$N$^-$].
5.2 Material and Methods

We will mainly focus on dynamics in the ionic liquid, dimethyl-isopropyl-propyl-
ammonium *bis*(trifluoromethylsulfonyl)imide [N*ip311*]^[Tf2N] (Scheme 1) at 25 °C.

[N*ip311*]^[Tf2N] was chosen for the present study because it exhibits the least impurity emission out of all of the ILs in our collection, an important consideration for edge excitation experiments. Beyond this optical purity, it is in no way distinctive compared to other short chain, non-functionalized ionic liquids we have studied. The features observed with this particular IL should therefore be representative of most of the ILs in common use today. For comparison purposes, some physical properties of [N*ip311*]^[Tf2N] (25 °C) are: glass and fusion temperatures \( T_g = 189 \text{ K}, T_{ fus } = 290 \text{ K} \); density \( d = 1.40 \text{ g cm}^{-3} \); refractive index \( n_D = 1.42 \); viscosity \( \eta = 113 \text{ cP} \). In one example, we instead use the closely related ionic liquid \( N\)-propyl-\( N\)-methylpyrrolidinium *bis*(trifluoromethylsulfonyl)imide \([\text{Pr31}^+][\text{Tf2N}^−]\) \( (T_{ fus } = 283 \text{ K}; d = 1.40 \text{ g cm}^{-3}; n_D = 1.42; \eta = 54 \text{ cP})\). Another interesting ionic liquid used for comparison is trimethyldecylammonium *bis*(pentafluoroethylsulfonyl)imide \([\text{N10,111}^+][\text{Bet}^−]\), which shows unusual coexisting glass and crystal structures at 25 °C and a normal liquid state at 45 °C.

In the experiments reported here we employ either steady-state absorption and emission measurements or time-correlated single-photon counting (TCSPC) using the instruments and methods detailed in reference. Absorption spectra (1 nm resolution) were recorded using a Hitachi-U-3000 UV/Vis spectrometer and steady-state emission spectra with a SPEX Fluorolog.
212 spectrometer (2 nm resolution). The short lifetime of malononitriles (DMN and JDMN) makes the polarization of emission an important issue when determining fluorescence quantum yields of these spectra. So the steady-state emission spectra of malononitriles are taken using a polarized setup (vertical excitation and magic detection) as described in detail in section 6.2.2. We also remark that the TCSPC instrument used here has a response time of 25 ps FWHM, which means we poorly sample or entirely miss dynamics taking place at times earlier than ~10 ps.
5.3 Results and Discussion

5.3.1 C153 Rotational and Solvational Dynamics

The first solute to be considered is the well-known solvatochromic probe coumarin 153 (C153; Figure 5.3). The top panel of Figure 5.3 shows the excitation frequency dependence of the steady-state emission (filled symbols; “SS”) of C153. Here and in later figures we represent various observables by normalized differences from the values observed when excited at the absorption maximum. Actual values are provided in the tables. In the case of frequencies we plot $2(\nu - \nu_0)/\Gamma_0$ where $\nu$ is the 1st moment of the emission band and $\nu_0$ and $\Gamma_0$ are the (1st moment) frequency and full width of the emission band excited at the absorption maximum. As previously noted by Mandal et al.\textsuperscript{15}, the steady-state emission of C153 is relatively insensitive to excitation frequency. Over the range of excitation wavelengths employed the shift of the steady-state spectrum is a mere 4% (140 cm\(^{-1}\)) of its width $\Gamma_0$ (3440 cm\(^{-1}\)). This insensitivity is expected\textsuperscript{15,22,23} given that the emission lifetime of C153 is 6 ns whereas the majority of the spectral dynamics of C153 in [Nip311][Tf2N-] take place at sub-nanosecond times\textsuperscript{4}. Also shown in the top panel of Figure 5.3 (labeled “t=0”) are the frequencies expected in the absence of solvent relaxation, i.e. when the solvent is immobile on the emission time scale, which is identical to the spectrum expected immediately after excitation. These “time-zero” frequencies are calculated using estimates of the polar solvent contribution to the inhomogeneous broadening of the absorption spectrum as described in Refs.\textsuperscript{24,26}. Such calculations for C153 accurately reproduce the red-edge excitation shifts observed at low temperatures\textsuperscript{24} and the earliest spectra in dynamic Stokes shift experiments when performed with high time resolution\textsuperscript{28}. In contrast to the small steady-state shifts, the time-zero frequencies estimated in Figure 5.3 shift by 30% of the spectral width (1000 cm\(^{-1}\)). This sizeable shift demonstrates that significant site (energy) selection is
Figure 5.3 Excitation frequency dependence of the emission frequencies, rotation times, and solvation times of C153 in [N<sub>p311</sub>][Tf<sub>2</sub>N] at 25 °C. The smooth curves in all three panels show the normalized absorption spectrum. Points display various quantities relative to their values observed when excitation is at the absorption maximum. Emission frequencies measured as the 1<sup>st</sup> moment of the emission band are represented by 

\[ 2\Delta \nu/\Gamma_0 = 2(\nu - \nu_0)/\Gamma_0 \]

where \( \nu_0 \) and \( \Gamma_0 \) are the frequency and full width at half maximum of the emission excited at the absorption maximum (\( \Gamma_0 = 3440 \text{ cm}^{-1} \)). Rotation and solvation times are represented by

\[ \Delta \tau/\tau_0 = (\tau - \tau_0)/\tau_0 \]

where \( \tau_0 \) is the time observed when exciting at the absorption maximum. Rotation times are integral times derived from stretched exponential fits of the anisotropy data (\( \tau_0 = 6.0 \text{ ns} \)). Solvation times shown as the open triangles are integral times of the observed \( \nu(t) \) data (\( \tau_0 = 0.52 \text{ ns} \)) and those shown as filled circles are the \( 1/e \) times of the spectral response functions (\( \tau_0 = 0.12 \text{ ns} \)) after approximately accounting for the (~50 %) fast component not observed in these experiments (see Ref. 4). For clarity, the two sets of points in the bottom panel are horizontally offset by a small amount.
Table 5.1 Emission frequencies of C153 in [N_{p311}]{+}[Tf_2N] at 25 °C Here and in the following tables $\lambda_{exc}$ and $\nu_{exc}$ are the excitation wavelength and frequency, and $\nu_{em}$ and $\nu_{t=0}$ are the 1st moments of the steady-state emission and the time-zero emission spectrum. Uncertainties in the measured frequencies are expected to be about ±100 cm$^{-1}$.

<table>
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<th>$\lambda_{exc}$/nm</th>
<th>$\nu_{exc}$/10$^3$ cm$^{-1}$</th>
<th>$\nu_{em}$/10$^3$ cm$^{-1}$</th>
<th>$\lambda_{exc}$/nm</th>
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<td>21.74</td>
<td>18.04</td>
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provided by the range of excitation frequencies accessible in these experiments. We note that if C153 had a much shorter lifetime, as do several of the other solutes examined later, we would observe much larger shifts of the steady-state spectra than we do. But observation of an excitation dependent shift of the emission spectrum only indicates the presence of a static heterogeneity, which is a necessary but not a sufficient condition for the dynamic heterogeneity of interest here.

The first dynamical property we examine is the rotation of C153. In previous work, it has been noted that the rotational correlation functions of C153 in most ionic liquids such as [N\text{ip3\text{11}}\text{+}][\text{Tf}_2\text{N}^-] are non-exponential\textsuperscript{4,6,29} Although there is some disagreement on the best description of such data, we find that stretched exponential functions of time with stretching exponents $\beta$ in the range 0.6-0.8 provide reasonable fits\textsuperscript{4}. Figure 5.4 is a representative anisotropy decay data of C153 in [N\text{ip3\text{11}}\text{+}][\text{Tf}_2\text{N}^-] and the $\beta$ value clearly shows the non-exponential character. One might suppose that this nonexponentiality reflects heterogeneity of the rotation dynamics, and if so, one might expect to observe an excitation wavelength dependence to the rotation times. In the middle panel of Figure 5.3 we plot the rotational correlation times of C153 in [N\text{ip3\text{11}}\text{+}][\text{Tf}_2\text{N}^-] measured from fits to emission anisotropy data collected at 8 excitation frequencies. At these frequencies we find anisotropy decays that are the same to within uncertainties, with $\langle \tau \rangle = 6.0 \pm 0.1$ ns and $\beta = 0.72 \pm 0.01$ ($\pm 1 \sigma$). This lack of excitation dependence could be interpreted to mean that rotations are homogeneous, i.e. that all solutes undergo the same non-exponential rotational motion independent of their particular solvent environment. Given that much of the solvation response in [N\text{ip3\text{11}}\text{+}][\text{Tf}_2\text{N}^-] (discussed below) is 10-fold faster than these rotation times, such rotational homogeneity might be expected\textsuperscript{30}. As discussed in Ref.\textsuperscript{4}, this is our current interpretation, that rotation of C153 is not significantly heterogeneous in most ILs. We suggest that the non-exponential rotational
Figure 5.4 Representative anisotropy decay data of C153 in [N\textsubscript{6311}][Te\textsubscript{2}N\textsubscript{2}] at 25 °C (\(\lambda_{\text{em}} = 530\) nm; \(\lambda_{\text{ex}} = 410\) nm). The bottom panel shows data (points) recorded with the analyzing polarizer parallel (\(\parallel\)) and perpendicular (\(\perp\)) emission polarization direction as well as fits to these data (solid curves). The curve labeled IF is the instrumental response function. The top panels show the weighted residuals of the fit and the parameters of the stretched-exponential fit to the population decay are shown.

\[ r(t) = r_0 \exp\left\{-\left(\frac{t}{\tau_0}\right)^\beta\right\} \]

\[ \tau_0 = 4.8 \text{ ns}; \beta = .71 \]
Table 5.2 Rotation times of C153 in [N_{p31}][Tf_2N] at 25 °C. Integral rotational correlation times $\langle \tau_{rot} \rangle$ and stretching parameters $\beta$ obtained from stretched exponential fits to emission anisotropy data. See Ref.¹ for details.
correlation functions observed instead reflect the non-Markovian nature of friction in these slowly
relaxing solvents\textsuperscript{31}. However, another explanation should also be considered. The primary
friction on rotation of C153 results from short-range repulsive interactions with surrounding
solvent molecules\textsuperscript{31} whereas the electronic spectral shifts used for site selection are dominated by
electrostatic interactions. Given that there might be little or no correlation between the
magnitudes of these two types of interactions, the present experiments might not select molecules
in a manner relevant to rotational motion. The distinction between what is selected for via edge
excitation and its correlation to the dynamics of interest must always be kept in mind when using
such experiments to explore dynamic heterogeneity.

Finally, the bottom panel of Figure 5.3 contains data on the excitation dependence of the
solvation response of C153 as monitored by its dynamic Stokes shift. Representative time-
resolved spectra, from which these results were derived, are shown in Figure 5.5(a). In contrast
to the situation with rotation, what is being observed here is the relaxation of the emission
frequency and, assuming the absorbing and emitting transitions are identical\textsuperscript{32}, the selection
process is performed directly on the coordinate of interest. It is expected that changing the
excitation frequency will change the initial position of the relaxing spectrum and therefore the
total extent of the Stokes shift observed will also change\textsuperscript{23,24,26}. As illustrated in the peak
frequency versus time data in Figure 5.5(b), the expected variations are indeed observed in the
experimental spectra. But, as shown by the estimated time-zero spectrum in Figure 5.5(a), due to
the limited time resolution of the experiment, we fail to observe a significant fraction of the initial
spectral relaxation. This shortcoming complicates the interpretation of the kinetics slightly. If we
examine the times associated with the peak (Figure 5.5(a)) or first moment frequencies of the
spectra (not shown) we find times which decrease with increasing $\nu_{exc}$. The open symbols in the
bottom panel of Figure 5.3 are the integral times associated with these observed $\nu(t)$ data.\textsuperscript{33} There
is a systematic variation with excitation wavelength which amounts to 15-20\% about the central
Figure 5.5 (a) Time-resolved emission spectra of C153 in [N₆₃]⁺[TF₅N⁻] at 25 °C excited at 380 nm = 26,300 cm⁻¹. Points show actual data at 0 (circles) and 10 ns (triangles). The smooth solid curves are log-normal fits to the data at 0, 10, 20, 50, 100, 200, 500 ps, and 1, 2, and 10 ns (later times correspond to lower frequencies). The dashed curves show the estimated time-zero spectra. (b) Peak frequencies versus time derived from log-normal fits to such spectra.
Table 5.3 Integral solvation times of C153 in [N_{ip}311]^+|[Tf_2N]^- at 25 °C. “<\mathcal{\nu}(t)>” denotes the integral time of the \mathcal{\nu}(t) evolution observed with TCSPC. The values here come from (2:1) weighted averages of values obtained from stretched exponential fits to the time evolution of the peak and average frequencies of log-normal fits to the spectra. “t_{1/\mathcal{e}} S(t)” denotes the 1/e time of the solvation response function, S(t) = \{\mathcal{\nu}(t) - \mathcal{\nu}(\infty)\}/\{\mathcal{\nu}(0) - \mathcal{\nu}(\infty)\}. Such functions were constructed from observed \mathcal{\nu}(t) data using both peak and 1st moment frequencies of the time-resolved spectra and values of \mathcal{\nu}(0) obtained from estimates of the time-zero spectra\(^{26}\). The final values shown here are also (2:1) weighted averages of the times obtained from the peak and 1st moment frequencies. In both cases the uncertainties reflect the differences obtained using these two frequency measures.

<table>
<thead>
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<th>\lambda_{exc} /nm</th>
<th>\nu_{exc} /10^3 \text{ cm}^{-1}</th>
<th>&lt;\mathcal{\nu}(t)&gt; /ns</th>
<th>t_{1/\mathcal{e}} S(t) /ns</th>
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value of $\tau_0 = 0.52$ ns. The trend is such that $\nu(t)$ decays more slowly as $\nu_{\text{exc}}$ is decreased and the magnitude of the Stokes shift decreases. Although these variations appear significant compared to the uncertainties in the data, they are small and one could question whether they might not be an artifact of the insufficient time resolution employed here. (For example, we have previously found that the larger the Stokes shift, the easier it is to detect fast relaxation components and therefore the faster the observed response in TCSPC experiments\(^3\).) To ascertain whether such an artifact might be responsible for the variations observed, we also calculated normalized response functions, $S(t) = (\nu(t) - \nu(\infty)) / (\nu(0) - \nu(\infty))$, using values of $\nu(0)$ obtained from estimates of the time-zero spectra\(^26\) and a common value of $\nu(\infty)$ for all $\nu_{\text{exc}}$. The $1/e$ times of these $S(t)$ functions are shown as the filled symbols in the bottom panel of Figure 5.3. Despite their large uncertainties, these times exhibit a clear and much larger dependence on $\nu_{\text{exc}}$. The variation is $\pm 35\%$ about the peak value, $\tau_0 = 0.12$ ns. Thus, although the present experiments do not resolve all of the dynamics, they provide clear evidence that the solvation response in $[N_{ip311}^+][\text{Tf}_2\text{N}]$ is site or solvation energy dependent, i.e. that the solvation dynamics is heterogeneous.

We note that whereas the excitation dependence of the dynamic Stokes shift has only rarely been studied in simple solvents\(^23\), it has recently been finding increasing use in studies of organized assemblies such as micelles\(^34\). In simple solvents, heterogeneity in solvation dynamics has mainly been inferred from the presence of a maximum in the dynamic spectral width that can sometimes be detected in experiment\(^10,35\) and simulation\(^36,37\). Although data such as those shown in Figure 5.5(a) do not reveal any pronounced width variations, examination of a large collection such data, recorded with C153 and with the alternative solvation probe 4-dimethylamino-4'-cyanostilbene, suggests that the non-monotonic variation expected for heterogeneous dynamics\(^38\) is present in ionic liquids but is difficult to observe given the spectral and time-resolution typically available. It should also be noted that heterogeneity of solvation dynamics in ionic
liquids is to be expected based on the molecular descriptions of solvation dynamics provided by recent computer simulations\textsuperscript{39-42}. As discussed in Ref.\textsuperscript{3}, simulations show that the solvation energy relaxes primarily via collective small-amplitude translational motions of ions near to the solute. The nature of this motion is such that the majority of the solvation energy is relaxed before any significant reorganization of the solvation structure can occur. Assuming the solvation time to depend on initial solvation structure, the disparity between solvation structure relaxation times and solvation energy relaxation times leads to heterogeneous solvation dynamics.

5.3.2 Malononitrile Isomerization

Another example of dynamic heterogeneity is found in the excited-state decay of the so-called “molecular rotors”, p-(dimethylamino)benzyldene malononitrile (DMN) and julolidine malononitrile (JDMN) (see Figure 5.6). The fluorescence quantum yields of these molecules are sensitive to solvent fluidity, and, for this reason, they have long been used as “microviscosity” probes in conventional solvents\textsuperscript{43}, polymers\textsuperscript{44} and biological systems\textsuperscript{45}, and recently in ionic liquids\textsuperscript{46,47}. Femtosecond experiments and electronic structure calculations show that the $S_1$ lifetimes of these molecules are on the order of a few picoseconds in conventional solvents at room-temperature due to internal conversion via a barrierless isomerization about the double bond\textsuperscript{48}. There is also a large ($\sim10$ D\textsuperscript{49}) increase in dipole moment between $S_0$ and $S_1$ which renders these molecules highly solvatochromic; however, no clear connection between solvent polarity and the isomerization rates has yet been discerned. In ionic liquids such as $[\text{N}_{\text{iop}}][\text{Tf}_2\text{N}]$, emission decays measured with TCSPC are non-exponential, consisting of components having time constants in the 10-50 ps range. But a significant portion of the decay is too rapid to observe with such experiments. We therefore estimate $S_1$ lifetimes and thus isomerization rates indirectly, using measured quantum yields ($2-6 \times10^{-3}$) and radiative rates
Figure 5.6 Excitation wavelength dependence of the emission frequencies and lifetimes of DMN and JDMN in [Ni₃][Tf₂N] at 25 °C. Frequencies $\nu$ are the average (first moment) frequencies of the emission bands and the lifetimes $\tau$ are estimated from the quantum yields as described in the text. The values used for normalizing the DMN data are $\Gamma_0 = 2825$ cm$^{-1}$ and $\tau_0 = 8.0$ ps and for JDMN the values are $\Gamma_0 = 2335$ cm$^{-1}$ and $\tau_0 = 16.9$ ps.
Table 5.4 Emission frequencies, quantum yields, and estimated isomerization times of DMN in [N_i_{p3}][Tf_{2}N] at 25 °C. $\nu_{\text{em}}$ is the 1st frequency moment of the emission spectrum (±100 cm$^{-1}$), $\phi_{\text{em}}$ the emission quantum yield (±10%) and $\tau$ the estimated isomerization time (±10%). The latter is estimated using the relation $\tau = (\phi_{\text{em}} / k_{\text{rad}}) (\nu_{\text{em}}^p / \nu_{\text{em}})^{3}$ where $\nu_{\text{em}}^p$ and $\nu_{\text{em}}$ refer to the first moment frequencies excited at the peak and at an arbitrary excitation frequency and $k_{\text{rad}}$ is the reference radiative rate taken to be 2.8×10$^8$ s$^{-1}$.50,51.

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Table 5.5 Emission frequencies, quantum yields, and estimated isomerization times of JDMN in [Nip$_{311}^+$][Tf$_2$N] at 25 °C. $\nu_{\text{em}}$ is the 1$^{st}$ frequency moment of the emission spectrum (±100 cm$^{-1}$), $\phi_{\text{em}}$ the emission quantum yield (±10%) and $\tau$ the estimated isomerization time (±10%). The latter is estimated using the relation $\tau = (\phi_{\text{em}} / k_{\text{rad}})^{\nu_{\text{em}}^\nu_{\text{em}}^\nu_{\text{em}}}$, where $\nu_{\text{em}}$ and $\nu_{\text{em}}$ refer to the first moment frequencies excited at the peak and at an arbitrary excitation frequency and $k_{\text{rad}}$ is the reference radiative rate taken to be 2.8×10$^8$ s$^{-1}$.\textsuperscript{50,51}.
\((-2.8 \times 10^9 \text{ s}^{-1})^{50,51,52}\) as described in detail in Chapter 6.

The results are summarized in Figure 5.6. The lifetimes of DMN and JDMN upon peak excitation are 8 ps and 17 ps, respectively. These times are much shorter than the solvation response of \([N_{ip311}^+]\text{[Tf}_2\text{N}^{-}]\) so that, unlike C153, both solutes exhibit pronounced red-edge excitation shifts of their emission spectra. The observed shifts are more than half of the widths of the respective emission spectra, or roughly 700 cm\(^{-1}\) in DMN and 1000 cm\(^{-1}\) in JDMN. These shifts are a sizeable fraction of what is predicted should be observed in frozen solvents. More importantly, the estimated isomerization times depend strongly on excitation wavelength. These times are \(~50\%\) (JDMN) and \(~70\%\) (DMN) slower when excited on the red edge compared to excitation at the absorption peak. These data provide unequivocal evidence for the presence of dynamic heterogeneity on the tens of picoseconds time scale in \([N_{ip311}^+]\text{[Tf}_2\text{N}^{-}]\). Given the slow dynamics in ionic liquids, finding such rapid reactions to be heterogeneous is perhaps not surprising. But it should be noted again that even for such fast reactions one would not observe an excitation dependence unless the environmental factors affecting the reaction rate and the absorption shift are correlated. The fact that we do observe a clear excitation effect implies that the electrical interactions selected for by the spectroscopy influence the effective potential on which the isomerization occurs, via either energetic or frictional means.

Decay times of DMN and JDMN in \([N_{ip311}^+]\text{[Tf}_2\text{N}^{-}]\) with different excitations were also measured by TCSPC (25 ps instrumental response time) and the Kerr-gated technique (450 fs instrumental response time). Quantum yields of DMN and JDMN in the polar solvent dimethyl sulfoxide (DMSO) and nonpolar solvent cyclohexane (CHEX) were measured to compare with the results in ILs. These comparisons are shown in Figure 5.7 for DMN and in Figure 5.8 for JDMN. As shown in these figures, the excitation dependence of decay times measured directly with TCSPC parallel the time deduced from quantum yield measurements, but the TCSPC times are uniformly longer due to the presence of components too fast to observe with this method.
Figure 5.7 Comparison of DMN in $[\text{Nip}_{311}^{+}][\text{Tf}_2\text{N}]$, DMSO and CHEX. The upper panel shows how the decay times changes with excitation and the lower panel shows how the averaged frequency changes with excitation. Normalized excitation is used to show the excitation wavelength peak on the absorption spectrum. The peak of the absorption spectrum is defined to be zero and the intensity is $A_{\text{max}}$. The blue side of the absorption spectrum is negative and calculated by $(A/A_{\text{max}}) - 1$ while the red side of the spectrum is positive and calculated by $1 - (A/A_{\text{max}})$. For example, for normalized excitation 0.1, we excite at the red side of the absorption spectrum where the intensity has decreased to 10% of $A_{\text{max}}$. The open circles stand for time-resolved measurement by TCSPC and Kerr-gated technique. The closed circles, down triangles and up triangles are results for DMN in $[\text{Nip}_{311}^{+}][\text{Tf}_2\text{N}]$, DMSO and CHEX by steady-state emission measurements.
Figure 5.8 Comparison of JDMN in \([N_{p311}^+][Tf_2N^−]\) and DMSO. The upper panel shows how the decay times changes with excitation and the lower panel shows how the averaged frequency changes with excitation. Normalized excitation is used to show the excitation wavelength peak on the absorption spectrum. The peak of the absorption spectrum is defined to be zero and the intensity is \(A_{\text{max}}\). The blue side of the absorption spectrum is negative and calculated by \((A/A_{\text{max}})-1\) while the red side of the spectrum is positive and calculated by \(1-(A/A_{\text{max}})\). For example, for normalized excitation 0.1, we excite at the red side of the absorption spectrum where the intensity has decreased to 10% of \(A_{\text{max}}\). The open circles stand for time-resolved measurement by TCSPC and Kerr-gated technique. The closed circles, down triangles and up triangles are results for JDMN in \([N_{p311}^+][Tf_2N^−]\), DMSO and CHEX by steady-state emission measurements.
DMN shows a clear excitation dependence in [N$_{ip311}$]$^+$$^+$$][Tf$_2$N$^-$], a mild excitation dependence in DMSO and no excitation dependence in CHEX. This observation parallels the degree of non-exponentiality observed from Kerr-gate experiments when the integrated emission intensities in Kerr-gated experiments are fitted to stretched exponential functions. The $\beta$ value for DMN in [N$_{ip311}$]$^+$$^+$$][Tf$_2$N$^-$], DMSO and CHEX are 0.63, 0.79 and 1 respectively, which follows the trend on the extent of dynamic heterogeneity seen in Figure 5.7. Similar results for JDMN as described for DMN can also be seen in Figure 5.8. JDMN shows a clear excitation dependence in [N$_{ip311}$]$^+$$^+$$][Tf$_2$N$^-$] and a mild excitation dependence in DMSO. The lower panels of Figure 5.7 and 5.8 show how the averaged emission frequencies change with excitation. The average emission frequencies of both DMN and JDMN show clear dependencies on excitation wavelength in [N$_{ip311}$]$^+$$^+$$][Tf$_2$N$^-$] and DMSO, which is red-edge effect (REE). REE demonstrates energetic (static) heterogeneity that persists for times longer than emission lifetime, but REE is not a sufficient evidence for dynamic heterogeneity.

Another interesting IL we studied is [N$_{10,111}$]$^+$$^+$$][Beti$^-$]. This IL has coexisting structures of glass and crystal at 25 °C but reaches a normal viscous liquid state after heating to 45 °C. We expect [N$_{10,111}$]$^+$$^+$$][Beti$^-$] to show a larger extent of dynamic heterogeneity than [N$_{ip311}$]$^+$$^+$$][Tf$_2$N$^-$]. We do observe very dramatic heterogeneous dynamics of DMN in [N$_{10,111}$]$^+$$^+$$][Beti$^-$] (Figure 5.9). The change of DMN lifetimes estimated from quantum yield measurements from peak excitation to reddest excitation is 300% at 25 °C and 180% at 45 °C, much larger than the 70% we observed in [N$_{ip311}$]$^+$$^+$$][Tf$_2$N$^-$] at 25 °C. The emission frequencies also show pronounced REE as expected (1600 cm$^{-1}$ at 25°C and 1400 cm$^{-1}$ at 45 °C). The fact that we do observe a more dramatic excitation effect in [N$_{10,111}$]$^+$$^+$$][Beti$^-$] confirms again that for the malononitrile isomerization reaction the environmental factors affecting reaction rate and the absorption shift are correlated and thus malononitriles are good candidate solutes to probe dynamic heterogeneity using different
Figure 5.9 Excitation wavelength dependence of the emission frequencies and lifetimes of DMN in [N_{10,11}][BetI] at 25 °C and 45 °C. Frequencies $\nu_{\text{em}}$ are the average (first moment) frequencies of the emission bands and the lifetimes $\tau$ are estimated from the quantum yields as described in the text. The solid line without symbols is absorption spectrum, the triangles the lifetimes, and the circles the emission frequencies. The closed symbols are data collected at 25 °C, the open symbols are data collected at 45 °C.
excitation. Another thing worth mentioning is that although \( \text{[N}_{10,111}^+][\text{Beti}^-] \) is a glass at room-temperature, the reaction time is not much slower than in other ILs. This supports the idea that non-radiative deactivation of malononitrile is controlled by free volume and \( \text{[N}_{10,111}^+][\text{Beti}^-] \) has heterogeneous domains due to its long alkyl chain.

Although we observe much stronger excitation dependence in ILs compared to conventional polar solvents, dynamic heterogeneity is not unique to ILs. In addition to the many reports of dynamic heterogeneity in supercooled liquids\(^9,10\), we observe a small excitation dependence of the kinetics of malononitriles even in DMSO at room temperature. The small size of the effect is easy to understand because the fast relaxation time of DMSO will average heterogeneous dynamics and decrease the extent of observed dynamic heterogeneity. If the relaxation time can be slowed down, much larger excitation dependence should be observed even in conventional polar solvents. As a demonstration the excitation dependence of DMN in 1-PrOH at 135K was measured and the results are shown in Figure 5.10. The change of DMN lifetimes from peak excitation to red excitation is 140% and the emission frequencies also show pronounced REE (1200 cm\(^{-1}\)). Observation of similar behavior of DMN in 1-PrOH at low temperature confirms again that ILs are not qualitatively different from highly polar conventional solvents, except that they have very high viscosities.

### 5.3.4 DMASBT Isomerization

We also observed evidence of heterogeneous dynamics in another probe DMASBT (Figure 5.11). Similarly to the malononitriles, DMASBT goes through an internal conversion via isomerization around the double bond, and thus the fluorescence intensity is sensitive to the solvent fluidity. Kabac\(^53\) studied DMASBT in conventional solvents and polymers, and showed that there is a large dipole moment change (6 D\(^53\)) of DMASBT between the ground and excited
Figure 5.10  Excitation wavelength dependence of the emission frequencies and lifetimes of DMN in 1-PrOH at 135 K (-102 °C). Frequencies $\nu_{em}$ are the average (first moment) frequencies of the emission bands and the lifetimes $\tau$ are estimated from the quantum yields as described in the text. The solid line without symbols is the absorption spectrum, the triangles the lifetimes, and the circles the emission frequencies.
Figure 5.11 Excitation wavelength dependence of the emission frequencies and lifetimes of DMASBT in $[N_{ip311}^+]$[$Tf_2N^-$] at 25 °C. Frequencies $\nu_{em}$ are the average (first moment) frequencies of the emission bands and the lifetimes $\tau$ are estimated from the relative quantum yields comparing steady-state fluorescence intensity and the decay time measured by time-resolved spectra at peak excitation as standard. The solid line without symbols is the absorption spectrum, the triangles the lifetimes, and the circles the emission frequencies.
states. The quantum yield of DMASBT is about ten times larger than DMN and JDMN, and their lifetimes are also longer than those of DMN and JDMN. The excitation dependence measurement of DMASBT provides useful perspective on how the time scale of the dynamics affects the extent of dynamic heterogeneity observed. We also observe clear excitation dependence for DMASBT and the results are shown in Figure 5.11. The change of DMASBT lifetimes from peak excitation to red edge excitation is 70% and the emission frequencies also show REE (500 cm$^{-1}$). Although the lifetimes of DMABST in ILs (~200 ps) are much longer than DMN (~10 ps), the extent of dynamic heterogeneity we observe here is very similar (~70% change). These results suggest more generally that dynamic processes taking place on the sub-nanosecond time scale in ILs, which is faster than typical solvent relaxation times in ILs, are likely to be heterogeneous in character.

5.3.3 CVL Intramolecular Charge Transfer Reaction

We have also observed signs of dynamic heterogeneity in several ultrafast intramolecular electron transfer reactions in ionic liquid solvents. As a last example we present results on the dual fluorescent solute CVL (Figure 5.12). Karpiuk$^{54}$ has shown that excitation into the S$_1$ state of CVL produces a polar excited state ("LE"; $\mu$ ~ 11 D) localized on the aminophthalide ring which subsequently transforms into a more polar charge-transfer state ("CT": $\mu$ ~ 25 D) in which an electron is transferred from one of the dimethylaniline donor groups to the aminophthalide acceptor. We have recently begun investigating the LE $\rightarrow$ CT process of CVL and its connection to solvation dynamics in conventional dipolar solvents. We have found that in strongly polar and highly fluid solvents like acetonitrile, the emission dynamics observed are those expected for a
Figure 5.12 Top panel: Steady-state emission spectra of CVL in [Pr3+][Tf2N−] at 25 °C at excitation frequencies of 25.0, 25.6, 26.3, 27.0, 27.8 and 28.6 × 10^3 cm⁻¹. Points show actual data for the two extreme values of ν_ex and the smoothed curves are fits to these data. The dashed curves are the decomposition into LE and CT components for ν_ex = 25,000 cm⁻¹. These spectra have been normalized to equal areas (of fitted spectra) in order to best display the relative intensities of the LE and CT bands. Bottom panel: Normalized values of the peak LE emission frequency (ν, filled circles, ν₀ = 22,9400 cm⁻¹, Γ₀ = 3780 cm⁻¹) and the ratio of the LE to the CT band areas (r, open triangles, r₀ = 0.90) determined from these spectra. The absorption spectrum is also shown for reference.
Table 5.6 Characteristics of the emission of CVL in [Pr$_{31}^+$][Tf$_2$N$^-$] at 25 °C. Characteristics of the component bands of the spectra determined using a least squares fit of the experimental spectra to a model assuming the bands to result from a shifting and convolution of a vibronic lineshape function with an inhomogeneous distribution of solvent-induced shifts. The lineshape function used was derived from a spectrum of CVL in hexane (assumed to be the same for the LE and CT bands. $\delta\nu$ is the shift and $\Gamma$ the broadening (FWHM of Gaussian broadening function) required to fit the component bands and $f(\text{CT})$ is the fractional area of the CT band. Uncertainties are estimated to be about 100 cm$^{-1}$ in the shifts and widths and 5% in $f(\text{CT})$. 

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reversible 2-state interconversion. Equilibrium constants are in the range 50 - 100 and reaction times are 10 - 30 ps, similar to what is observed in alkylaminobenzonitriles. In ionic liquids, the interconversion is much slower (> 100 ps) and highly non-exponential. Available data indicates that reaction times roughly track the viscosity of the ionic liquid, suggesting that solvation dynamics or large-amplitude intramolecular motions (or both) play an important role in the charge transfer. Because the time scales of solvation, reaction, and excited-state decay of CVL in ionic liquids are all comparable, analysis of the observed kinetics is complicated. For this reason we simply use the steady-state spectra shown in Figure 5.12 to provide a qualitative demonstration of dynamic heterogeneity in this reaction. We show data collected in [Pr$_{31}^+$][Tf$_2$N$^-$] at 25 °C because the variations in the steady-state spectra are much more pronounced in this liquid that in [N$_{ip31}^+$][Tf$_2$N$^-$]. The same qualitative features are observed for CVL in [N$_{ip31}^+$][Tf$_2$N$^-$], but the 2-fold smaller viscosity of [Pr$_{31}^+$][Tf$_2$N$^-$] modifies the relative rates of reaction and excited-state decay so as to greatly enhance the edge excitation effects on the steady-state spectra. As shown in the bottom panel of Figure 5.12, there is a significant shift (~350 cm$^{-1}$) of the LE band with excitation frequency. Much more striking is the dramatic variation in the relative intensities of the LE and CT bands, measured by the ratio $r = I_{CT} / I_{LE}$. As shown in the bottom panel of Figure 5.12, $r$ increases by nearly a factor of 2.5 ($\Delta r / r_0 = 1.5$) between peak excitation and the reddest excitation employed. Given that the equilibrium lies far to the CT side of the reaction, this variation in band area reflects a large increase in the net LE $\rightarrow$ CT interconversion during the ~1 ns lifetime of the excited state and thus in the reaction rate with excitation frequency. Quantitative estimates of $\Delta \tau \tau_0$ of the sort made for the malononitriles will require a more detailed analysis, but it is not unreasonable to assume factors of 2 or more will be found based on these steady-state results. Thus, for this charge transfer process in which there is
a small but significant barrier to reaction, the effects of environmental heterogeneity appear to be quite large.
5.4 Summary and Conclusions

To summarize, we have used the site selection provided by red-edge excitation of solutes to look for experimental evidence of dynamic heterogeneity in the representative ionic liquids $[\text{N}_{\text{ip311}}^+][\text{Tf}_2\text{N}^-]$, $[\text{N}_{10,111}^+][\text{Tf}_2\text{N}^-]$ and $[\text{Pr}_{31}^+][\text{Tf}_2\text{N}^-]$. Such heterogeneity is anticipated for processes that are faster than the lifetime of a typical solvation environment. The solvation response, as measured by the dynamic Stokes shifts of a solute such as C153, provides one estimate of this environment lifetime $^{30}$. In $[\text{N}_{\text{ip311}}^+][\text{Tf}_2\text{N}^-]$ at 25 °C, solvation occurs over a broad time window: roughly 50% of the solvation response is complete in 10 ps, 75% in 300 ps, 90% in 1 ns and >98% in 10 ns. Given this characterization, it is not surprising that we do not observe any excitation dependence to the rotation of C153, which is a relatively slow process, $<\tau_{\text{rot}}> = 6$ ns. But the rates of all of the other processes investigated here, such as the solvation of C153 itself, the barrierless isomerization of the fluidity probes DMN and JDMN (7-25 ps), the isomerization of DMASBT (200 ps) and the low-barrier LE→CT intramolecular charge transfer in CVL (100-500 ps) do all vary significantly as functions of excitation wavelength (Table 5.7).

Although these examples provide the first clear experimental evidence for dynamic heterogeneity in room temperature ionic liquids, we do not consider such behavior to be unusual. Given the sluggish and broadly distributed solvation response of these solvents, we anticipate that heterogeneous kinetics will be the norm rather than the exception for processes that occur in the sub-nanosecond time regime. Similar heterogeneous dynamics observed in low temperature polar conventional solvent indicates dynamic heterogeneity is not a unique character of ILs. It will be important to recognize this heterogeneity when attempting to model fast kinetics in ionic liquids.

Finally, some comment on the nature of the static heterogeneity underlying the heterogeneous dynamics observed here may be useful. Dynamic heterogeneity can be produced by subtle differences in local packing even in model liquids comprised of spherical molecules $^{56}$. 
Table 5.7 Summary of dynamic heterogeneity observed by experiments. $t$ is the time scale of measured dynamical processes, $\Delta t/t$ the changes of measured times for those dynamical processes from peak excitation to reddest excitation.

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<td>~0</td>
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<tr>
<td>CVL</td>
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<td>low-barrier ET</td>
<td>300</td>
<td>?</td>
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</tbody>
</table>
In the case of ILs the ions comprising the liquid of are themselves “heterogeneous” in that they are often conformationally flexible and amphiphilic in character, which can lead to other sorts of structural heterogeneity and even to local polar / nonpolar domain segregation\textsuperscript{13,17,18}. While these latter sources of static heterogeneity cannot be excluded in the present systems, we note that solvatochromic measurements of the solutes examined here as well as others\textsuperscript{57,58} indicate that the extent of the energetic heterogeneity in these liquids is not significantly different from that found in simple dipolar solvents having comparable solvation energies. On this basis, we conjecture that dynamic heterogeneity of the sort measured here is readily observable in room temperature ionic liquids primarily because of their much slower relaxation compared to conventional solvents\textsuperscript{4}, rather than to any special structural features they might also possess. But, further experiments and computer simulations of solute spectra and dynamics\textsuperscript{20,41} are needed to define the origins of dynamic heterogeneity in ionic liquids and explore its effect on chemical processes carried out in them.
7 We note that Hamaguchi and coworkers\textsuperscript{59} some workers have suggested the existence of solid-like regions within ionic liquids, and if this suggestion is correct, proximity to the melting point may have some relevance to the liquid dynamics.
23 Nemkovich, N. A.; Rubinov, A. N.; Tomin, V. I. Inhomogeneous Broadening of Electronic Spectra of Dye Molecules in Solutions. In \textit{Topics in Fluorescence}


25 Pronounced red-edge excitation shifts in the emission of neat ionic liquids have also been well documented by Samanta and coworkers$^{14,60-62}$. Fee, R. S.; Maroncelli, M. Chem. Phys. 1994, 183, 235.


33 The data labeled $\nu(t)$ in Figure 5.3 are weighted averages of the integral correlation times obtained from stretched exponential fits of the peak and first moment frequencies of the spectra. No account of the unobserved portion of the spectra is made in these fits. Ghosh, S.; Mandal, U.; Adhikari, A.; Dey, S.; Bhattacharyya, K. Int. Rev. Phys. Chem. 2007, 26, 421.


Accurate measurements of quantum yields for these molecules require that one account for the fact that their emission in most solvents is not depolarized. This means that the polarization properties of the quantum yield reference and the polarization sensitivity of the detection system must be considered. Here all emission spectra and emission responsivity correction factors were measured using magic angle detection. Radiative rates were assumed to vary as $\nu^3$ (i.e. emission transition moments were assumed constant) and lifetimes calculated as $\tau = (\phi / k_{ref}^{rad}) (\nu_{em}^{pk} / \nu_{em}^{ref})^3$ where $\nu_{em}^{pk}$ and $\nu_{em}^{ref}$ refer to the first moment frequencies excited at the peak and at an arbitrary excitation frequency and $k_{rad}^{ref}$ is the reference radiative rate taken to be $2.8 \times 10^8$ s$^{-1}$ for both DMN and JDMN$^{50,51}$. 


Chapter 6

Non-Radiative Deactivation of Malononitriles

6.1 Introduction

Push-pull molecules (scheme 1) 4-N,N-dimethylamino-benzylidenemalononitrile (DMN) and joulolidine-malononitrile (JDMN) have long been examined for their nonlinear optical properties\textsuperscript{1-3} and as microviscosity probes in conventional solvents\textsuperscript{4-6}, polymers\textsuperscript{7-10}, biological systems\textsuperscript{11-13} and recently ILs\textsuperscript{14,15}. DMN and JDMN are disubstituted benzenes with donor and acceptor groups. Their large nonlinear optical coefficients arise from the intramolecular charge transfer character of their $S_0 \rightarrow S_1$ absorptions, as revealed by large dipole moment changes of approximately 9 D\textsuperscript{16}. Sensitivity of the emission quantum yields of these molecules to viscosity makes them very useful as microviscosity probes\textsuperscript{5,6}. In glycerol, decay times of 60 and 120 ps have been reported\textsuperscript{17}. In more typical solvents with low viscosity, lifetimes in the 1-10 ps range\textsuperscript{4,6} have been deduced from quantum yield measurements and radiative lifetimes (~ 3.6 ns) either estimated from absorption spectra\textsuperscript{4,18,19} or measured by TCSPC at 77 K\textsuperscript{5}. Whereas quantum yields in common solvents are loosely correlated to solvent viscosity, temperature-dependent measurements show that emission yields correlate with $(\eta/T)^p$ with $p$ in the range 0.4-1\textsuperscript{5,6}. Such fractional power law dependence on viscosity is predicted by free volume theory\textsuperscript{20}.

The mechanism behind the short lifetime of malononitriles is only partially understood. Studies on malononitriles also want to elucidate the origins of the ultrafast lifetime. No phosphorescence is observed at low temperature, which excludes the possibility that deactivation occurs by intersystem crossing\textsuperscript{4,5,21}. The quantum yields of malononitrile increase with increasing solvent viscosity and decreasing temperature. Loutfy\textsuperscript{4} reported quantum yields near
Scheme 1 Structures of DMN and JDMN. Their possible deactivation motions are shown by arrows (a and b are rotations around the single bonds connecting donor and acceptor moiety, and c is isomerization around the double bond).
unity for DMN and JDMN in MTHF at 77 K where the rigid matrix restricts motions. These and other observations have led to the conclusion that non-radiative deactivation is due to an internal conversion process that requires some large amplitude torsional motion\textsuperscript{17-19}. Environments that resist such internal motions lead to decreases non-radiative deactivation and thus increased quantum yields and lifetimes. The precise nature of the motion has not been clearly established. Rotations around the single bond connecting donor and acceptor groups and isomerization around the double bond are all possible deactivation motions\textsuperscript{17-19}. The activation energies of the lifetimes estimated from temperature-dependence experiments are usually smaller than the solvent viscosity activation energy\textsuperscript{4,5,21}, which suggests a barrierless torsional motion. Finally although the absorption and emission spectra of malononitriles are strongly solvatochromic, the effect of solvent polarity on the deactivation is unclear\textsuperscript{22,23}.

Despite these uncertainties, malononitriles provide a unique window on solvent friction. Their non-radiative decay is sensitive to local environment and even to the distributions of environments present in a system\textsuperscript{24}. In the previous chapter we used malononitriles to demonstrate the presence of dynamic heterogeneity in ILs\textsuperscript{25}. In the present chapter, we focus on understanding more about the basis of this non-radiative deactivation. Malononitriles are studied in a collection of conventional room-temperature solvents with different viscosities and polarities using both steady-state and time-resolved emission spectroscopy. With the exception of one early crude measurement\textsuperscript{17}, the results reported here are the only time-resolved data for malononitriles. Temperature dependent data of malononitriles in 2-methyltetrahydrofuran and 1-propanol over wide temperature ranges are also presented. Such work, combined with computational studies that are currently in progress, should provide a solid foundation for using the malononitriles to probe solvent friction in unusual environment such as ILs, polymers, biological systems, and nanostructured environments.
6.2 Material and Methods

6.2.1 Materials and Experimental Methods

The fluorescence probes Coumarin 153 (C153) from Exciton, DMN from Sigma-Aldrich, and JDMN from Fluka were used as received. The solvents acetonitrile (ACN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), polyethylene carbonate (PC), ethyl acetate (EA), cyclohexanone (CHEXO), tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), suqalene (SQL), 1,1,2-trichloro-1,2,2-trifluorethane (TCTFE), diisopropyl ether (IPE), 1,2,3-triacetoxypropane (Triacetin), methyl acetate (MA), hexamethylphosphoramide (HMPA), 1,4-dioxane (Dioxane), benzene, trichloromethane (Chloroform), hexane (HEX), cyclohexane (CHEX), decahydronaphthalene (decalin), methanol (MEOH), n-propanol (PrOH), n-butanol (n-BuOH), and ethylene glycol (EG) were Sigma-Aldrich spectroscopic or HPLC grade. Some solvents were dried over molecular sieves, but otherwise these solvents were used as received.

The instrumentation and procedures for measuring steady-state and time-resolved spectral data are essentially the same as described in previous chapters and in ref\textsuperscript{26}. Absorption spectra (1 nm resolution) were recorded using a Hitachi U-3000 UV/Vis spectrometer and steady-state emission spectra with a Spex Fluorolog 212 spectrometer (2 nm resolution). In all cases solvent backgrounds were subtracted from the spectra. Time-resolved emission decays were measured using a time-correlated single photon counting instrument\textsuperscript{27} based on a fs-Ti:sapphire laser (Coherent Mira). The doubled output of this laser at 380-460 nm (~200 fs, 76 MHz) was used in the present measurements. Instrumental parameters were typically chosen to collect data over intervals of at least three probe lifetimes and data accumulated until a maximum of 1000-8000 counts were collected in the peak channel. To obtain time-resolved spectra, 14-16 decays at wavelengths spanning the emission spectrum were recorded at magic angle through a monochromator with 8 nm resolution. The effects of instrumental broadening were partially removed from the data by independently fitting each decay to a sum of 3-4 exponentials using an
iterative reconvolution scheme and an instrument response function (~25 ps FWHM) obtained from a scattering solution. Time-resolved spectra were then reconstructed from these fitted decays by normalizing to steady state emission spectra in the usual manner\textsuperscript{28}.

All measurements were made on samples contained in tightly sealed 1 cm quartz cuvettes (NSG) using probe concentrations chosen to give optical densities near 0.1 (for C153) or 0.1 - 0.25 (for DMN and JDMN). Unless otherwise stated, samples are measured at 25 °C ± .1 °C. Samples measured above 20 °C (± 0.1 K) were temperature-controlled using circulating water from thermostated baths (Neslab). For low-temperature measurements, vacuum-sealed cryogenic cuvettes (NSG) with removable Teflon fittings were enclosed in a copper block mounted on the cold finger of an APD liquid N\textsubscript{2} cryostat (Oxford Instrument DN1754). With this cooling system, temperatures between 85 and 300 K could be maintained constant to within ± 2 K.

The peak extinction coefficients of DMN and JDMN were measured in three different solvents: ACN as polar solvent, MeOH as protic solvent, and hexane as nonpolar solvent. Certain masses of DMN or JDMN were weighed and dissolved in solvents in volumetric flasks to make concentrated stock solutions with known concentration. Then this stock solution was diluted to five solutions with different concentrations. Peak absorbances measured from these solutions were correlated with solution concentrations to determine the peak extinction coefficients.

6.2.2 Quantum Yield Measurement of Malononitriles

Actually measuring the quantum yield of malononitriles is difficult. Determination of the quantum yield is generally accomplished by comparison of the integrated intensity of the sample to that of a reference standard using following equation:

\[
Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}
\]  

(6.1)
where $Q_R$ is the quantum yield of the standard, $I$ and $I_R$ the integrated intensity of sample and standard emission spectra, $OD$ and $OD_R$ the optical density of sample and standard respectively, and $n$ the solvent refractive index. The quantum yield standard used for in these experiments is C153 in MeOH at 25 °C, with a quantum yield = 0.42\textsuperscript{29}. Due to very low quantum yield and thus low fluorescence intensity of malononitriles, the optical densities of malononitrile samples were usually between 0.15 - 0.25. The inner-filter effect on the fluorescence emission due to these high optical densities was corrected using $I_{\text{real}}(\lambda_{\text{em}}) = I_{\text{measured}}(\lambda_{\text{em}}) \times 10^{0.5A_(\lambda_{\text{exc}})}$. Optical densities used to calculate quantum yields were also corrected for the inner-filter effect by using $1 - 10^{-A(\lambda_{\text{exc}})}$ instead of $A(\lambda_{\text{exc}})$.

More importantly, emission polarization conditions have a significant effect on the quantum yields measured for malononitriles. The reason is that the observed fluorescence intensity can be dependent upon the polarization displayed by emission. The extent to which emission is polarized depends on the ratio of the lifetime $\tau$ and rotation time $\theta$ of fluorophores, which is expressed by Perrin equation.

$$\frac{r}{r_0} = 1 + \frac{\tau}{\theta} \quad (6.2)$$

where $\tau$ is fluorophore lifetime, $\theta$ is fluorophore rotation time, and $r$ and $r_0$ are the measured and fundamental anisotropy respectively. Take C153 as an example, the lifetime of C153 is usually around 6 ns, and the rotation time in conventional solvents is in the range of $10-100$ ps and $r_0=0.375$. So the measured steady-state anisotropy will be close to zero, which means depolarized emission light. For DMN and JDMN, the lifetime is about 1-10 ps, and the measured anisotropy then will be around 0.3 assuming $r_0=0.4$ and similar rotation time as above in conventional solvents. So unlike C153, the common unpolarized emission collection setup of our fluorometer will not measure the fluorescence intensity of malononitriles correctly. In order to get rid of the emission polarization effect, two polarizers are added to the normal setup before excitation and emission light to achieve vertical excitation and magic emission detection.
In order to properly collect spectra at magic angle, new correction file need to be created under this polarized setup. The details for making emission correction file can be found in the Appendix. This new correction file is used for recording emission spectra with the polarized setup. Figure 6.1 compares the correction files for unpolarized and polarized setups. There are some small differences between these two correction files but overall they are very similar. Quantum yields of DMN and JDMN in several different conventional solvents are measured under both polarized and unpolarized setup, and the results confirm the differences between two setups (Table 6.1). It is also worth mentioning that although the fluorescence intensity (quantum yield) changes between polarized and unpolarized setup, the spectral shape does not change much (Figure 6.2).
Figure 6.1 Comparison of unpolarized and polarized correction files.
<table>
<thead>
<tr>
<th></th>
<th>$Q_{\text{unpolarized}} \times 10^3$</th>
<th>$Q_{\text{polarized}} \times 10^3$</th>
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<td></td>
</tr>
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</tr>
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<td></td>
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<td>PrOH</td>
<td>1.24</td>
<td>1.82</td>
<td>1.47</td>
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Table 6.1 Comparisons of quantum yields measured with unpolarized and polarized setups. The factors show the ratio between quantum yields of polarized and unpolarized setup. The uncertainties of quantum yields measured here are estimated as $\pm 15\%$. 
Figure 6.2 Comparison of malononitrile spectra measured with the unpolarized and polarized setups. In the upper panel intensities are normalized and in the lower panel the intensities are shown relative to the C153 standard.
6.3 Results and Discussion

6.3.1. Solvatochromism of Malononitriles

Figure 6.3 shows representative spectra of malononitriles in DMSO solvent. Table 6.2 summarizes spectral data on malononitriles in a collection of conventional solvents at 25 °C. These solvents were chosen to provide a wide range of polarities and viscosities. The first thing we examine is the correlation between steady-state absorption and emission spectral shifts and solvent dielectric properties.

To determine spectral frequencies and widths, models described as follows are used. If we denote the intrinsic line shape function of malononitriles for absorption as \( g_1(\nu) \) and the distribution of spectral shift \( \delta \) caused by the distribution of solvent environment \( p(\delta) \), then the absorption spectrum in a polar solvent can be expressed by

\[
A_p(\nu) \propto \nu \int g(\nu - \delta)p(\delta) d\delta
\]

(6.3a)

Similarly, denoting the emission line shape by \( f(\nu) \), the emission spectrum is given by

\[
F_p(\nu) \propto \nu^3 \int f(\nu - \delta)p(\delta)d\delta
\]

(6.3b)

The line shape functions are assumed to be related to the absorption and steady-state emission spectra observed in a nonpolar reference solvent (HEX) via

\[
g(\nu) \propto \nu^{-1}A_{np}(\nu)
\]

(6.4a)

and

\[
f(\nu) \propto \nu^{-3}F_{np}(\nu)
\]

(6.4b)

The distribution function is assumed to be a Gaussian function,

\[
p(\delta) = (2\pi\sigma^2)^{-1/2}\exp\left[-(\delta - \delta_0)^2/2\sigma^2\right]
\]

(6.5)

The parameters of \( \delta_0 \) and \( \sigma \) are determined by iterative fittings of the polar spectrum to eq 6.3a and 6.3b. Here we report \( \delta_0 \) as spectra shift \( \Delta\nu \) and \( \sigma \) as additional bandwidths \( \Gamma \) by relation

\[
\Gamma_{FWHM} = \sqrt{8\ln 2}\sigma.
\]
Figure 6.3 Representative absorption and steady-state emission spectra of malononitriles in DMSO.
Table 6.2 Spectral data summary. $\varepsilon$ is the solvent dielectric constant, $n$ the solvent refractive index, and $d_{0.25}(n^2)$ and $d_{0.25}(\varepsilon-n^2)$ the reaction fields defined in eq 6.6. Spectral shifts $\Delta \nu$ and bandwidths $\Gamma$ are in units of $10^3$ cm$^{-1}$. Data were recorded at 25±1°C. Dielectric constants and refractive indices are from ref$^{31}$. The frequencies $\nu$ (1st moment) and bandwidths $\Gamma$ (2nd moment) in km$^{-1}$ for DMN in HEX are $\nu_{\text{abs}} = 25.79$, $\Gamma_{\text{abs}} = 3.18$, $\nu_{\text{em}} = 21.86$, $\Gamma_{\text{em}} = 3.14$. For JDMN in HEX, $\nu_{\text{abs}} = 24.37$, $\Gamma_{\text{abs}} = 2.99$, $\nu_{\text{em}} = 21.41$, $\Gamma_{\text{em}} = 2.60$. Spectra in some solvents listed here are from previous measurements in our group. Spectra data are averaged when we have repeated measurements.

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<th>$n$</th>
<th>$d_{0.25}(n^2)$</th>
<th>$d_{0.25}(\varepsilon-n^2)$</th>
<th>$\Delta \nu_{\text{abs}}$</th>
<th>$\Gamma_{\text{abs}}$</th>
<th>$\Delta \nu_{\text{em}}$</th>
<th>$\Gamma_{\text{em}}$</th>
<th>$\Delta \nu_{\text{abs}}$</th>
<th>$\Gamma_{\text{abs}}$</th>
<th>$\Delta \nu_{\text{em}}$</th>
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<td></td>
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The dielectric properties we use here are based on a simple dielectric continuum model where the solute is treated as a spherical point dipole and the solvents as a continuum fluid characterized by solvent dielectric constant and refractive index. These reaction field factors are expressed in eq 6.6a to 6.6c.

\[ d_\varepsilon(\varepsilon) = \frac{\varepsilon^{-1}}{2(1-c)\varepsilon + (1+2c)} \]  
(6.6a)

\[ d_\varepsilon(n^2) = \frac{n^2-1}{2(1-c)n^2 + (1+2c)} \]  
(6.6b)

\[ d_\varepsilon(\varepsilon - n^2) = \frac{\varepsilon^{-1}}{2(1-c)\varepsilon + (1+2c)} - \frac{n^2-1}{2(1-c)n^2 + (1+2c)} \]  
(6.6c)

where \( \varepsilon \) is the solvent dielectric constant, \( n \) is the solvent refractive index, and \( c \) is a solvent-independent parameter \( 0 \leq c \leq 1 \). Different values of \( c \) reflect different possible choices for the solute polarizability. Whereas any value of \( c \) in this range correlates the experimental data equally well, we prefer an intermediate value \( c = 0.25 \). Correlations between the spectral shift and reaction field \( d_{0.25}(n^2) \) and \( d_{0.25}(\varepsilon - n^2) \) are shown in Figure 6.4 and Figure 6.5.

Regression coefficients obtained from fitting observed spectral shift to the relation \(-\Delta \nu = \nu_0 - Ad_{0.25}(n^2) - C d_{0.25}(\varepsilon, n^2)\) are provided in those figures. Among all the solvents listed, benzene and dioxane are excluded because their zero dipole moment but substantial quadrupole moments cannot be modeled by dielectric continuum model. Absorption and emission shift of DMN and JDMN can be reasonably approximated as linear function of \( d_{0.25}(n^2) \) and \( d_{0.25}(\varepsilon - n^2) \). The fitting parameters are comparable between absorption and emission spectra, and they are also comparable between DMN and JDMN. The fitting parameters we obtained here are useful for deriving dipole moment for first excited state, as described in the follows.

First method we use to derive dipole moment is independent state (IS) model\(^{33}\). This model assumes electronic properties important to solvatochromism relevant properties of the solute, the cavity radius, the (gasphase) dipole moments \( \mu_0 \) and \( \mu_1 \) in the \( S_0 \) and \( S_1 \) states, and the polarizability \( \alpha \) are considered to be characteristics of the isolated solute and to be independent of the solvent. This type of model is most often used to derive solute dipole moments from
Figure 6.4 Comparison between observed and calculated spectral shifts of DMN. The equations shown in figures are correlation function between spectral shifts and reaction field factors, based on which the calculated shifts are obtained. Dash lines are 1:1 line. Blue circles are data of DMN in aprotic solvents, green circles the alcohols, and red circles non-dipolar solvents.
Figure 6.5 Comparison between observed and calculated spectral shifts of JDMN. The equations shown in figures are correlation function between spectral shifts and reaction field factors, based on which the calculated shifts are obtained. Dash lines are 1:1 line. Blue circles are data of JDMN in aprotic solvents, green circles the alcohols, and red circles non-dipolar solvents.
solvatochromic data of the sort shown in Figure 6.3 and Figure 6.4. Such a model predicts that
the absorption and emission frequencies should be linearly related to the reaction field functions
defined in eq 6.6 via
\[ h\nu_{abs} = h\nu_{0,abs} + A_{abs}d_c(n^2) + C_{abs}d_c(\varepsilon - n^2) \] (6.7a)
\[ h\nu_{em} = h\nu_{0,em} + A_{em}d_c(n^2) + C_{em}d_c(\varepsilon - n^2) \] (6.7b)
We use \( c \equiv \alpha/a^3 \) and define \( \gamma = (h\alpha^3)^{-1} = (0.1984a^3)^{-1} \), then
\[ A_{abs} = -(\mu_1^2 - \mu_0^2)\gamma \quad \quad \quad \quad \quad \quad \quad C_{abs} = -2\mu_0(\mu_1 - \mu_0)\gamma \] (6.8a)
\[ A_{em} = -(\mu_1^2 - \mu_0^2)\gamma \quad \quad \quad \quad \quad \quad \quad C_{em} = -2\mu_1(\mu_1 - \mu_0)\gamma \] (6.8b)
if we assume that \( \mu_0 \) and \( \mu_1 \) are parallel and \( \mu_0 \) and \( \gamma \) are known, then we can calculate \( \mu_1 \) via:
\[ \mu_1 = \pm \sqrt{\mu_0^2 - A_{abs}/\gamma} \quad \quad \quad \quad \quad \quad \quad \mu_1 = \frac{1}{2}(\mu_0 \pm \sqrt{\mu_0^2 - 2C_{em}/\gamma}) \] (6.9a)
In this work, \( c \) is chosen to be 0.25. \( \mu_0 \) for DMN and JDMN are reported to be 8.7 D and 9.6 D in
dioxane\(^1\), and 8.7 D and 9.4 D in benzene\(^3\). Note that the \( \mu_0 \) in eq 6.9 are gas phase moments.
So the experimental solution phase moments are corrected by relationship \( \mu(\varepsilon) = \frac{\mu}{1 - 2cd_0(\varepsilon)} \) with
d_0(\varepsilon) = \frac{\varepsilon^{-1}}{2\varepsilon + 1}. 7.7 D for DMN and 8.5 D for JDMN are used for gas phase ground dipole
moments. The van der Waals volumes and radii are 147.7 Å\(^3\), 3.28 Å for DMN and 239.1 Å\(^3\),
3.85 Å for JDMN. The sensible cavity radii would be about 1.5 Å larger than these values. 4.78
Å for DMN and 5.35 Å JDMN are used for cavity radii \( a \).
Another method to analyze solvent-induced frequency shifts is according to the
following equations from ref\(^4\). The cavity is assumed as an ellipsoid instead of a sphere.
\[ \nu_{abs} - \nu_{em} = \frac{2}{h\alpha^3}(\mu_1 - \mu_0)^2 f(n, \varepsilon) + \text{constant} \] (6.10a)
\[ \frac{\nu_{abs} + \nu_{em}}{2} = -\frac{2}{h\alpha^3}(\mu_1^2 - \mu_0^2) \left\{ \frac{f(n,\varepsilon)}{2} + f(n) \right\} + \text{constant} \] (6.10b)
where \( \nu_{abs} \) and \( \nu_{em} \) are spectral frequencies of absorption and steady-state emission, \( a \) is cavity
radius, and \( f(n,\varepsilon) \) and \( f(n) \) are reaction field factors defined as following equations.
If the $\mu_0$ is known, then $\mu_1$ can be calculated from the slope ratio of eq 6.10a and 6.10b without knowing $a$.

Table 6.3 shows the summary of $\mu_1$ from different source. Averaged $\mu_1$ from all four calculations via equation 6.9a and 6.9b are 15.3 D for DMN and 16.9 D for JDMN. If we only use correlation parameters for absorption spectra considering better correlation quality, the averaged $\mu_1$ are 15.9 D and 17.6 D for DMN and JDMN respectively. $\mu_1$ derived from equation 6.10 are 15.2 D and 16.6 D for DMN and JDMN respectively. Values from these two different methods are comparable and they are also comparable to values from electrochromic data from ref 16 and electronic structure calculations from our group.

6.3.2 Transition Moments and Radiative Rates

Transition moments and radiative rates can be obtained from absorption spectra and steady-state emission spectra. This information is useful for both testing electronic structure computations and providing radiative rates necessary to obtain non-radiative decay rates from observed quantum yields. The transition moment represents the transient dipole resulting from the displacement of charges during the electronic transitions. The transition moments corresponding to absorption and emission transitions are absorption transition moment and emission transition moment. When there is no significant change in the character of the electronic states of the excited state molecules, similar transition moments are expected for both absorption and emission transition moments.

We can estimate the transition moment of DMN and JDMN from the absorption spectra and the peak extinction coefficients using the following equations\(^{35}\).
Table 6.3 Summary of first excited state dipole moments $\mu_1$ of malononitriles. $\mu_1^a$ is averaged value from all four calculations via eq 6.9a and 6.98b of IS model. $\mu_1^b$ is averaged value from two calculations via eq 6.9a of IS model. $\mu_1^c$ is value derived from eq 6.10. $\mu_1^d$ is value from electronic structure calculation using RICC2/TZVP and $\mu_0 = 9.8$ from same calculation. $\mu_1^e$ is value derived from electrochromic data from ref\textsuperscript{16}, corrected to gas-phase moments.

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<td>16.6</td>
<td>15.9</td>
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\[ M_{01} = 9.584 \times 10^{-2} \left[ \int_{\nu_{S1}}^{\nu_{S0}} \frac{\varepsilon(\nu)}{\nu} d\nu \right]^{\frac{1}{2}} \]  
(6.12)

where \( M_{01} \) is the absorption transition moment from ground state to first excited state, \( n \) the refractive index and \( \int \frac{\varepsilon(\nu)}{\nu} \) is calculated by following equation using Beer’s law.

\[
\int \frac{\varepsilon(\nu)}{\nu} = \int \left[ \frac{A(\nu)}{\nu} \right] / C
\]

(6.13)

where \( A(\nu) \) is the absorption spectrum and \( C \) is the concentration of the solution in M which will be calculated by peak absorbance and peak extinction coefficients via Beer's law.

In order to estimate the absorption transition moment, peak extinction coefficients were determined. The peak extinction coefficients of DMN in ACN, MeOH and HEX are 53 ± 3, 56 ± 4, and 57 ± 5 \( \times 10^3 \) M\(^{-1}\)cm\(^{-1}\), and the peak extinction of JDMN in ACN, MeOH and HEX are 63 ± 3, 66 ± 5, and 68 ± 6 \( \times 10^3 \) M\(^{-1}\)cm\(^{-1}\) respectively. The literature values\(^4\) are smaller than our measured value: 47 - 51 \( \times 10^3 \) M\(^{-1}\)cm\(^{-1}\) for DMN and 57 - 63 \( \times 10^3 \) M\(^{-1}\)cm\(^{-1}\) for JDMN in different solvents. The value of extinction coefficient measured in ACN, MeOH and HEX are used for all polar, protic and nonpolar solvents respectively in later absorption transition moment calculations.

Determination of absorption transition moment involves integration over only the \( S_0 \rightarrow S_1 \) absorption band. Typical absorption spectra are shown in Figure 6.3. Although the first absorption band appears to be well isolated from high-energy bands, we choose the upper frequency limit of the integration to be the minimum intensity between the first absorption band and higher transitions.

We found that the absorption transition moments of DMN and JDMN in different solvents are very close to each other (Table 6.4 and Table 6.5). The transition moment ranges 5.9-7.1 D with average value 6.6 D for DMN and 5.8-7.4 D with average value 6.8 D for JDMN. Those results are comparable but smaller than literature value 7.5 D for both DMN and JDMN\(^{16} \).
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Table 6.4 DMN absorption transition moment and radiative rate summary. $A_{\text{max}}$ is the peak intensity of absorption spectrum, $\bar{v}$ the average frequency of emission spectrum, $n$ the refractive index of the solvent from ref$^{31}$, $M_{01}$ the transition moment from ground state to excited state, and $k_{\text{rad}}$ the radiative rate.
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</tbody>
</table>

Table 6.5 JDMN transition moment and radiative rate summary. $A_{\text{max}}$ is the peak intensity of absorption spectrum, $\bar{v}$ the average frequency of emission spectrum, $n$ the refractive index of the solvent from ref\textsuperscript{31}, $M_{01}$ the transition moment from ground state to excited state, and $k_{\text{rad}}$ the radiative rate.
and 7.9 D for DMN and 7.8 D for JDMN from electronic structure calculations by Dr. Chet Swalina in our group.

If we assume equal absorption and emission transition moments, we can also calculate the radiative rate $k_{rad}$ using the following equation:

$$M_{10} = 1.7857 \times 10^3 \left[ \frac{1}{n^3} \frac{k_{rad}}{\bar{\nu}} \right]^{1/2}$$  \hspace{1cm} (6.14)

where $n$ is solvent refractive index, and $\bar{\nu}$ is averaged frequency ($\text{cm}^{-1}$) of emission spectrum.

The calculated $k_{rad}$ is in the range of 0.28-0.40 ns$^{-1}$ with average value 0.32 ns$^{-1}$ for DMN and in the range of 0.29-0.37 ns$^{-1}$ with average value 0.31 ns$^{-1}$ for JDMN (Table 6.4 and Table 6.5). These results are comparable to literature values which are 0.29 ns$^{-1}$ for DMN and 0.28 ns$^{-1}$ or 0.27 ns$^{-1}$ for JDMN.

### 6.3.3 Quantum Yield and Lifetime

Quantum yield $Q$ is the ratio of the number of photons emitted to the number absorbed and can be defined as $Q = \frac{k_{rad}}{k_{rad} + k_{nr}}$ where $k_{rad}$ and $k_{nr}$ are radiative and non-radiative rates. Lifetime $\tau$ can be calculated by the relation $\tau = \frac{1}{k_{rad} + k_{nr}} = \frac{Q}{k_{rad}}$. We can estimate the lifetime of malononitriles by measured quantum yield and radiative rate.

Table 6.6 shows different radiative rates from our own experimental methods and literature values. We can see that radiative rates estimated using different methods are within uncertainties of literature values except those estimated using lifetime data from Kerr-gated emission measurements. But the latter values are much more scattered for reasons that are unclear at present. Although we expect the radiative rates depend on emission frequency, the variation with solvent is very small. To estimate lifetimes we therefore use the average values of 0.32 ns$^{-1}$ for DMN and JDMN for simplicity.
Table 6.6 Radiative rates of malononitriles. $k_{\text{rad,ss}}$ are averaged values from 17 solvents in Table 6.4 and Table 6.5. $k_{\text{rad,TCSPC}}$ are calculated by lifetimes from TCSPC and quantum yields from steady-state emission of DMN in MTHF at 90 K. $k_{\text{rad,Kerr-gated}}$ are calculated by lifetimes from Kerr-gated emission measurements and quantum yields from steady-state emission.

<table>
<thead>
<tr>
<th></th>
<th>DMN ns$^{-1}$</th>
<th>JDMN ns$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature$^{5,19}$</td>
<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>$k_{\text{rad,ss}}$</td>
<td>0.32±0.04</td>
<td>0.31±0.03</td>
</tr>
<tr>
<td>$k_{\text{rad,TCSPC}}$</td>
<td>0.32±0.03</td>
<td>0.33±0.03</td>
</tr>
<tr>
<td>$k_{\text{rad,Kerr-gated}}$</td>
<td>0.6±0.4</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6.7 is the quantum yield and lifetime summary of malononitriles. We note that the estimated lifetimes of JDMN are always longer than those of DMN, as a result of the larger quantum yields of JDMN. This difference might be expected considering the internal conversion to involve torsional motion. The structural difference between JDMN and DMN blocks one of the possible deactivation motions (a in scheme 1), and thus the quantum yield increases and so does the lifetime of JDMN.

Next we examine the correlation between the lifetimes of malononitriles and solvent viscosities. These correlations are shown in Figure 6.6. Both graphs show a power-law correlation with viscosity but the correlation shows considerable scatter. These data indicate that the quantum yields and lifetimes of malononitriles are sensitive to solvent viscosity but the connection is not simple one. Figure 6.6 also shows that the lifetimes of JDMN and to a lesser extent DMN are similar in polar and nonpolar solvents with comparable viscosities. Apparently polarity does not have a large effect on quantum yields and lifetime. The quantum yields and lifetimes in alcohols seem to be larger than in other aprotic solvents with similar viscosities, which might be the result of hydrogen-bonding interactions between the probes and solvents.

In Table 6.7 we also summarize the available literature values for quantum yields of malononitriles. Our results often differ significantly from literature values, but literature values from different laboratories also differ widely. As we already discussed in section 6.2.2, the measurement of the quantum yields of malononitriles is not an easy job and experimental details are very important. We are confident that our quantum yield measurement should be reliable with ±20%. We also measure decay times using the Kerr-gated technique with high time-resolution (450 fs) and the results are listed in Table 6.8. Our results are mostly comparable to Kerr-gated measurements except for CHEX and the more viscous solvent BuOH and EG. The averaged lifetime from Kerr-gated measurements is usually smaller than estimated life time from quantum yields measurement. This might be the result of Kerr-gated measurement missing some of the longer time component of the decay, which also explains those big differences for BuOH.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>η[cP]</th>
<th>(Q\times10^{-3})</th>
<th>(Q_{\text{lit}}\times10^{-3})</th>
<th>(\tau) [ps]</th>
<th>(\tau) [ps]</th>
<th>D/J ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX</td>
<td>0.29</td>
<td>0.62</td>
<td>2.21</td>
<td>1.09</td>
<td>3.89</td>
<td>0.57</td>
</tr>
<tr>
<td>CHEX</td>
<td>0.90</td>
<td>0.18</td>
<td>0.65</td>
<td>1.10</td>
<td>3.93</td>
<td>0.56</td>
</tr>
<tr>
<td>Decalin</td>
<td>2.42</td>
<td>0.70</td>
<td>2.50</td>
<td>1.41</td>
<td>5.04</td>
<td>0.50</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.94</td>
<td>0.58</td>
<td>2.07</td>
<td>1.59</td>
<td>5.68</td>
<td>0.36</td>
</tr>
<tr>
<td>EA</td>
<td>0.43</td>
<td>0.82</td>
<td>0.89</td>
<td>2.93</td>
<td>1.18</td>
<td>3.07</td>
</tr>
<tr>
<td>THF</td>
<td>0.46</td>
<td>0.81</td>
<td>1.54</td>
<td>2.92</td>
<td>1.19</td>
<td>3.34</td>
</tr>
<tr>
<td>CHEXO</td>
<td>2.00</td>
<td>0.93</td>
<td>3.32</td>
<td>1.39</td>
<td>4.96</td>
<td>0.67</td>
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<tr>
<td>HMPA</td>
<td>3.10</td>
<td>1.06</td>
<td>3.79</td>
<td>1.73</td>
<td>6.18</td>
<td>0.61</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.99</td>
<td>0.98</td>
<td>3.51</td>
<td>1.16</td>
<td>4.14</td>
<td>0.82</td>
</tr>
<tr>
<td>DMF</td>
<td>0.80</td>
<td>0.81</td>
<td>2.89</td>
<td>0.87</td>
<td>3.11</td>
<td>0.93</td>
</tr>
<tr>
<td>PC</td>
<td>2.53</td>
<td>1.02</td>
<td>3.64</td>
<td>1.16</td>
<td>4.14</td>
<td>0.88</td>
</tr>
<tr>
<td>ACN</td>
<td>0.30</td>
<td>0.59</td>
<td>1.14</td>
<td>2.11</td>
<td>0.77</td>
<td>1.54</td>
</tr>
<tr>
<td>BuOH</td>
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<td>1.98</td>
<td>7.07</td>
<td>2.13</td>
<td>1.04</td>
<td>7.61</td>
</tr>
<tr>
<td>PrOH</td>
<td>1.94</td>
<td>1.34</td>
<td>4.79</td>
<td>1.82</td>
<td>2.91/0.95</td>
<td>6.50</td>
</tr>
<tr>
<td>EG</td>
<td>17.3</td>
<td>2.27</td>
<td>8.11</td>
<td>3.29</td>
<td>11.11</td>
<td>11.8</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.55</td>
<td>1.06</td>
<td>0.96</td>
<td>3.78</td>
<td>1.72</td>
<td>2.24/0.70</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.55</td>
<td>0.58</td>
<td>0.75</td>
<td>2.07</td>
<td>0.78</td>
<td>3.07</td>
</tr>
<tr>
<td>Dioxane</td>
<td>1.19</td>
<td>0.45</td>
<td>1.61</td>
<td>1.29</td>
<td>4.61</td>
<td>0.42</td>
</tr>
<tr>
<td>([N_{\text{ii1}}^+][\text{Tf}_2\text{N}^-])</td>
<td>111</td>
<td>2.10</td>
<td>7.49</td>
<td>4.70</td>
<td>16.8</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table 6.7 Quantum yield and lifetime summary of malononitriles. \(Q\) and \(Q_{\text{lit}}\) are quantum yield from experiment and references, \(\tau\) the estimated lifetime, ratio is the quantum yields ratio between DMN and JDMN. Data were recorded using excitation at absorption peak at 25±1°C.
Figure 6.6 Correlations between malononitrile lifetime and solvent viscosity. The blue circles are the polar solvents, cyan circles the non-polar solvents, pink triangles the alcohols, and red diamonds ionic liquid. The solid line is the power-law regression of the data and the dash line is the regression of the other malononitrile for comparison. The correlating equations are $\tau = 2.8 \times \eta^{0.23}$ for DMN and $\tau = 4.1 \times \eta^{0.30}$ for JDMN.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$Q \times 10^3$</th>
<th>$\tau_{em}$ (ps)</th>
<th>$\tau_{Kerr}$ (ps)</th>
<th>$d$ (%)</th>
<th>$k_{rad}$ (ns$^{-1}$)</th>
<th>$M_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN</td>
<td>0.50</td>
<td>1.79</td>
<td>1.61</td>
<td>11</td>
<td>0.37</td>
<td>7.7</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.32</td>
<td>4.71</td>
<td>3.44</td>
<td>37</td>
<td>0.28</td>
<td>6.2</td>
</tr>
<tr>
<td>EA</td>
<td>0.68</td>
<td>2.44</td>
<td>1.68</td>
<td>46</td>
<td>0.49</td>
<td>8.7</td>
</tr>
<tr>
<td>HEX</td>
<td>0.18</td>
<td>0.64</td>
<td>0.64</td>
<td>1.0</td>
<td>0.97</td>
<td>10.6</td>
</tr>
<tr>
<td>CHEX</td>
<td>0.34</td>
<td>1.21</td>
<td>0.69</td>
<td>75</td>
<td>0.90</td>
<td>9.8</td>
</tr>
<tr>
<td>Decalin</td>
<td>0.29</td>
<td>1.02</td>
<td>0.90</td>
<td>14</td>
<td>0.78</td>
<td>8.6</td>
</tr>
<tr>
<td>BuOH</td>
<td>1.24</td>
<td>4.44</td>
<td>1.54</td>
<td>188</td>
<td>1.29</td>
<td>13.5</td>
</tr>
<tr>
<td>EG</td>
<td>2.42</td>
<td>8.64</td>
<td>4.76</td>
<td>81</td>
<td>0.48</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Table 6.8 Comparison between steady-state measurements and Kerr-gated measurements of DMN. $Q$ is quantum yield recorded at same 387 nm excitation as Kerr-gated measurement. $\tau_{em}$ is the estimated lifetime, $\tau_{Kerr}$ the decay time by Kerr-gated measurement and $d$ the percentage difference between them. $k_{rad}$ is the radiative rates calculated by $\tau_{Kerr}$ and $Q$, and $M_{10}$ is transition moment from emission calculated by eq 6.14.
and EG with longer lifetimes. We can also calculate again the $k_{rad}$ from Kerr-gated averaged lifetime and measured quantum yields and then the emission transition moment from eq 6.14. Those values are also listed in Table 6.9. Emission transition moment $M_{10}$ are comparable in different solvents (BuOH excluded), ranging 6.2-10.6 D with averaged value 8.6 D.

### 6.3.4 Temperature Dependence

Measuring the temperature dependence of the emission of malononitriles provides a useful complement to the solvent dependence discussed previously. Temperature dependence experiment provides a wide and systematic widow for monitoring the viscosity effects on the reaction. The slower reaction times present at lower temperatures mean that the dynamics can be more easily measured using TCSPC. Near to or below the glass transition temperature, the non-radiative deactivation should be blocked so that the radiative rate can then be obtained.

MTHF ($T_g = 91\text{K}^{36}$ and $T_{fus} = 137\text{K}^{37}$) and PrOH ($T_g = 98\text{K}^{31}$ and $T_{fus} = 147\text{K}^{37}$) both easily form glasses. The large liquid temperature ranges of these solvents make them useful for kinetic studies over large ranges of viscosities. To analyze such experiments, we need viscosity data for correlation with reaction times and density data for the refractive index correction of the quantum yields. Several literature reports have provided these data at some low temperatures but there are no data for the specific temperatures we use for experiment. So different correlation equations are used to compare with measured data and estimate the data needed.

For MTHF, viscosities data from ref$^{36,38,39}$ are correlated by two distinct equations in different temperature ranges:

\begin{align}
90 - 115\text{K} : \log(\eta_{\text{cP}}) &= \frac{4930}{(T / \text{K})} - 41.1 \\
115 - 298\text{K} : \ln(\eta_{\text{cP}}) &= \frac{896.8}{(T / \text{K})} - 3.635
\end{align}

(6.15a)

(6.15b)

Densities from ref$^{38,39}$ are correlated using the equation:
\[
\frac{d}{\text{g cm}^{-3}} = 1.138 - 9.56 \times 10^{-4} \times (T / K) \quad (6.16)
\]

For PrOH, viscosity data from ref\textsuperscript{39,40} are correlated using

\[
90 - 130 \text{K} : \log\left(\frac{\eta}{\text{cP}}\right) = \frac{2863}{(T / K)} - 15.7 \quad (6.17a)
\]

\[
130 - 298 \text{K} : \log\left(\frac{\eta}{\text{cP}}\right) = \frac{1091.5}{(T / K)} - 3.48 \quad (6.17b)
\]

Densities from ref\textsuperscript{39} are correlated by:

\[
\frac{d}{\text{g cm}^{-3}} = 1.035 - 7.92 \times 10^{-4} \times (T / K) \quad (6.18)
\]

Figures 6.7 and 6.8 show MTHF and 1-PROH viscosity and density data and these correlations.

First we measured the absorption spectra of DMN in MTHF from 90 K to 298 K as well as absorption spectra of the reference probe C153 over same temperature ranges. Figure 6.9 shows representative absorption spectra of DMN in MTHF at different temperatures. We can see that the peak absorbance from 90 K to 298 K changes by a factor of 1.6 while the absorbance at the excitation wavelength used below remains nearly constant. In later quantum yield calculations, optical densities at different temperatures are sometimes assumed to be the same when no real absorption spectra are taken which makes this invariance convenient. Using the absorption spectrum at the lowest temperature, 90 K, as a reference, we can obtain the spectral shifts and additional bandwidths of DMN in MTHF at different temperatures using similar methods to those described in section 6.3.1. These results are listed in Table 6.9 and shown in Figure 6.10. Figure 6.10 shows with increasing temperature the absorption spectra shift to the blue due to the decreasing density and thus decreasing polarity of the solvent. We also note that the absorption spectra broaden monotonically with increasing temperature due to inhomogeneous broadening. Both the spectra shifts and widths of DMN change more dramatically with temperature than C153 and the values are always larger than C153.
Figure 6.7 Viscosities of MTHF and 1-PROH at different temperatures and their correlations. Points are from references and solid lines are correlations.
Figure 6.8 Densities of MTHF and 1-PROH at different temperatures and their correlations. Points are from references and solid lines are correlations.
Figure 6.9 Representative absorption spectra of DMN in MTHF at different temperatures.
<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta v_{C153}$ ($10^3$cm$^{-1}$)</th>
<th>$\Gamma_{C153}$ ($10^3$cm$^{-1}$)</th>
<th>$\Delta v_{DMN}$ ($10^3$cm$^{-1}$)</th>
<th>$\Gamma_{DMN}$ ($10^3$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>100</td>
<td>0.005</td>
<td>0.108</td>
<td>0.012</td>
<td>0.108</td>
</tr>
<tr>
<td>125</td>
<td>0.006</td>
<td>0.113</td>
<td>0.050</td>
<td>0.164</td>
</tr>
<tr>
<td>150</td>
<td>0.056</td>
<td>0.111</td>
<td>0.096</td>
<td>0.341</td>
</tr>
<tr>
<td>175</td>
<td>0.093</td>
<td>0.160</td>
<td>0.208</td>
<td>0.565</td>
</tr>
<tr>
<td>200</td>
<td>0.176</td>
<td>0.512</td>
<td>0.283</td>
<td>0.678</td>
</tr>
<tr>
<td>225</td>
<td>0.243</td>
<td>0.646</td>
<td>0.379</td>
<td>0.806</td>
</tr>
<tr>
<td>250</td>
<td>0.328</td>
<td>0.754</td>
<td>0.473</td>
<td>0.912</td>
</tr>
<tr>
<td>275</td>
<td>0.418</td>
<td>0.897</td>
<td>0.587</td>
<td>1.057</td>
</tr>
<tr>
<td>298</td>
<td>0.493</td>
<td>0.954</td>
<td>0.753</td>
<td>1.190</td>
</tr>
</tbody>
</table>

Table 6.9 Spectral data summary of C153 and DMN in MTHF at different temperatures. $\Delta v$ is the frequency shift and $\Gamma$ is the additional bandwidth relative to reference spectra recorded at the lowest temperatures.
Figure 6.10 Comparison of the absorption shifts and bandwidths of C153 and DMN in MTHF at different temperatures.
Figure 6.11 shows representative steady-state emission spectra of DMN in MTHF at different temperatures from 90 K to 298 K. Emission spectra of JDMN in same solvent MTHF, the reference solute C153 in same solvent MTHF, and DMN in a more complicated solvent 1-PrOH were also recorded for comparison. The emission spectra of malononitriles at low temperatures show vibronic structure and this structure disappears when temperature is higher than 140 K. The emission spectral widths increase monotonically with increasing temperature due to inhomogeneous broadening. Figure 6.12 shows how the spectral shift changes with temperature. We note that for both DMN and JDMN in MTHF, the emission spectra shift to the red until around 140 K and then slowly shift back to the blue with increasing temperature until 298 K. On contrast the spectra shift monotonically to the red for DMN in 1-PrOH. These trends are somehow unusual compared to the S-curve normally observed similar to C153 in MTHF in Figure 6.12. Table 6.10 tabulates spectral shifts and additional bandwidths at different temperatures for all four sets of temperature dependence measurements. The spectral shift of DMN in PrOH increases monotonically with temperature, which differs from both S-curve behavior and DMN/JDMN in MTHF. All these varying temperature dependences result from the variations of solvation times versus fluorescence lifetimes with T. Detailed modeling to explain these shifts will be discussed in section 6.3.5.

The fluorescence intensity of malononitriles increases dramatically with decreasing temperature especially below 140 K and reaches a maximum when approaching $T_g$. Quantum yields of malononitriles at different temperatures are calculated using the quantum yield at 298 K as the standard and the results are tabulated in Table 6.10. The refractive index corrections are done using known densities at different temperatures and assuming that density is proportional to $n^2 + 2 \over n^2 - 1$ where n is the refractive index. Lifetimes of malononitriles are estimated using measured quantum yields and $k_{rad}$ as described previously.
Figure 6.11 Representative emission spectra of DMN in MTHF at different temperatures. The lower panel shows the raw spectra at different temperatures with an insert of the spectra at the three highest temperatures. The upper panel shows normalized spectra at different temperatures. For clarity, the spectra at three highest temperatures are fitted spectra by log-normal fits to the spectra.
Figure 6.12 Spectral shifts of malononitriles and C153 at different temperatures.
Lifetimes of malononitriles in MTHF at different temperatures were also measured using the TCSPC technique. The sample is excited at the absorption peak and emission is recorded at the steady-state emission peak and at the half intensity point on the red-edge to see if the lifetimes are emission-wavelength dependent. The decays can be fit to single exponential function below 130 K but above this temperature double exponential fits were required, probably as a result from heterogeneous dynamics. Detailed fitting parameters are listed in Table 6.11. The decay times measured at the steady-state emission peak and at the half red-edge is also tabulated in Table 6.11. A comparison of the lifetimes measured using TCSPC and the lifetimes estimated from steady-state quantum yields is shown in Figure 6.13. We can see that estimated lifetimes from steady-state emission measurements and decay times from TCSPC measurements are comparable except for lifetimes below 10 ps, which are not measured accurately with TCSPC time resolution (25 ps instrumental response time).

As discussed previously, the quantum yields of malononitriles increase dramatically with decreasing temperature, especially below 140 K, and reach maximum values when approaching $T_g$. This temperature dependence can be explained by changes in solvent viscosity. Viscosities increase when temperature decreases and increase dramatically to infinity when the temperature approaches $T_g$. The increasing viscosities decrease the deactivation rates and thus the quantum yields and fluorescence intensities are increased. When the temperature reaches $T_g$, all motions will be blocked and the quantum yield and fluorescence intensity reach maximum values.

In order to see the viscosity effect on the torsional deactivation motions, we assume that the derived decay rate $k_d$ is the sum of the deactivation rate related to all orientational motions $k_{or}$ and the radiative rate $k_{rad}$.

$$k_d = k_{or} + k_{rad} \quad (6.19)$$

Then we can calculate the relaxation time $\tau_{or}$ related to all orientational motions by
Table 6.10 Summary of emission spectra at different temperatures. $\Delta \nu$ is the spectral shift and $\Gamma$ is additional bandwidth relative to spectrum at lowest temperature, and $Q$ the quantum yield. Samples are all excited at the wavelength of the absorption peak at 298K.
**Table 6.11** Summary of fits to TCSPC data on DMN and JDMN in MTHF. Fluorescence decays are fit to $I(t) = a_0 + a_1 \exp(-t/\tau_1) + (1 - a_4)\exp(-t/\tau_2)$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$a_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
<th>$a_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
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<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
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</thead>
<tbody>
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<td>998</td>
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<td>1404</td>
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<td>2379</td>
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<td>2322</td>
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<td>2704</td>
<td>1</td>
</tr>
<tr>
<td>125</td>
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<td>1168</td>
<td>388</td>
<td>998</td>
<td>0.71</td>
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<td>367</td>
<td>0.61</td>
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<td>101</td>
<td>0.68</td>
<td>391</td>
<td>143</td>
<td>312</td>
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<td>158</td>
<td>52.4</td>
<td>105</td>
<td>0.61</td>
<td>143</td>
<td>36.3</td>
<td>101</td>
<td>0.68</td>
<td>391</td>
<td>143</td>
<td>312</td>
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<td>9.78</td>
<td>47.6</td>
<td>38.2</td>
<td>0.53</td>
<td>72.5</td>
<td>14.8</td>
<td>45.6</td>
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<td>7.67</td>
<td>36.4</td>
<td>13.1</td>
<td>0.78</td>
<td>8.45</td>
<td>36.7</td>
<td>14.8</td>
<td>0.11</td>
<td>38.6</td>
<td>11.4</td>
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<td>0.92</td>
<td>6.26</td>
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<td>0.96</td>
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<td>0.98</td>
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<td>3.63</td>
<td>1</td>
<td>1.39</td>
<td>1.39</td>
<td>1</td>
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Figure 6.13 Comparison between lifetimes measured using TCSPC and estimated from emission quantum yields. Circles are data of DMN in MTHF, and triangles the data of JDMN in MTHF. Points in black color are recorded at peak emission and points in red color are recorded at half red-edge emission. The dash line separates lifetimes below and above 10 ps.
\[
\tau_{or} = \frac{1}{k_{or}} = \frac{\tau_{rad} \times \tau_d}{\tau_{rad} - \tau_d}
\]  

(6.20)

where \( \tau_{rad} \) is the radiative lifetime and \( \tau_d \) is the measured lifetime.

Figure 6.14 shows the correlation between \( \tau_{or} \) and \( \eta/T \) from four sets of experiments.

All of the data can be well fit to power law relations of the form \( \tau_{or} = A(\eta/T)^\beta \). The fitting parameters are tabulated in Table 6.12. From Table 6.12, we can see that \( \beta \) is close to 1 for both DMN and JDMN in MTHF, whereas for DMN in PrOH and \([N_{ip311}^+][Tf_2N] \) values are 0.59 and 0.44, much smaller than 1. Loutfy and coworkers\(^5\) also reported small \( \beta \) values of 0.43 and 0.69 for DMN in dimethylphthalate and glycerol respectively. For MTHF as a solvent with simple interactions, \( \beta \) values close to 1 indicate that the deactivation motions are totally controlled by viscosity. While for protic solvent PrOH, interactions between solvents and solutes become complicated due to hydrogen-bonding. When it comes to ionic liquids, these interactions are even more complicated resulting from strong electrostatic interactions from ions. All these interaction complicates the dynamics and the correlation between deactivation motions and viscosity is not simple linear correlation anymore, which is indicated by the small \( \beta \) value in PrOH and \([N_{ip311}^+][Tf_2N] \).

### 6.3.5 Modeling the Observed Spectral Shift

In order to explain the unusual spectra shifts we observed from malononitriles at different temperatures, a mathematical model called S-curve method\(^41\) is used. The S-curve method was developed to estimate solvation times from steady-state emission spectra, but here we will use equations from this method to model the observed steady-state spectral shift. The fractional shift \( \rho \) is defined as the fraction of total Stokes shift observed in steady-state spectra.
Figure 6.14 Correlations between $\tau_{\alpha r}$ and $\eta/T$. The blue, red and green circles are data for DMN in MTHF, PrOH [N$_{ip311}^+$][Tf$_2$N$^-$], and black triangles the data for JDMN in MTHF. The solid lines in same color are regression lines fitted to $\tau_{\alpha r} = A(\eta/T)^\beta$. The uncertainty for $\tau_{\alpha r}$ and $\eta/T$ are estimated as $\pm 20\%$ shown by error bars.
<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>$T$ range</th>
<th>$A$</th>
<th>$\beta$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMN</td>
<td>MTHF</td>
<td>150-298K</td>
<td>2320</td>
<td>1.1</td>
<td>0.997</td>
</tr>
<tr>
<td>JDMN</td>
<td>MTHF</td>
<td>175-298K</td>
<td>1790</td>
<td>1.0</td>
<td>0.997</td>
</tr>
<tr>
<td>DMN</td>
<td>PrOH</td>
<td>175-298K</td>
<td>63.8</td>
<td>0.60</td>
<td>0.999</td>
</tr>
<tr>
<td>DMN</td>
<td>[N_{ip311}][Tf$_2$N']</td>
<td>268-338K</td>
<td>8.12</td>
<td>0.44</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 6.12 Fitting parameters of fits to the relation $\tau_{or} = A(\eta / T)^\beta$. $[N_{ip311}][Tf_2N']$ crystallizes before forming a glass, so the data are recorded only between 268 and 338 K at 10 K intervals.
\[ \rho = \frac{\nu - \nu_{\infty}}{\nu_0 - \nu_{\infty}} \]  

(6.21)

where \( \nu, \nu_0, \) and \( \nu_{\infty} \) are emission frequencies from steady-state, time-zero and time-infinity spectra respectively. The spectral shift \( \Delta \nu_{\text{obs}} \) we observed can be expressed by

\[ \Delta \nu_{\text{obs}} = \nu_0 - \nu = (1 - \rho)(\nu_0 - \nu_{\infty}) \]  

(6.22)

and fraction shift \( \rho \) can be calculated by

\[ \rho = \frac{1}{\tau_f} \sum a_i \tau_i \left( \frac{1}{1 + \tau_i / \tau_f} \right) \]  

(6.23)

or in terms of a simple average solvation time using the approximation \( 1 + \tau_i / \tau_{fl} \approx 1 + (\tau) / \tau_{fl} \)

\[ \rho = \frac{\langle \tau \rangle / \tau_{fl}}{1 + \langle \tau \rangle / \tau_{fl}} \]  

with \( \langle \tau \rangle = \sum_i a_i \tau_i \)  

(6.24)

We calculated \( \rho \) from both averaged solvation times and multi-exponential solvation functions obtained from the literature\(^{42}\) and fluorescence lifetimes from our measurements or a fixed 6 ns lifetime in the case of C153. The total Stokes-shift used here are 840 cm\(^{-1}\) for DMN, 570 cm\(^{-1}\) for JDMN and 2000 cm\(^{-1}\) for C153 respectively. Comparisons between calculated and observed spectra shifts are shown in Figure 6.15. We can see that this S-curve method works well to reproduce different spectral shift behavior we observed from experiments. Calculated results using multi-exponential solvation times are more accurate than those using averaged solvation times. The improvement when using multi-exponential solvation time is more dramatic for PrOH because solvation dynamics of PrOH has four exponential decay times.
6.3.6 Spectral Dynamics at Low Temperature

Decays of DMN in MTHF at 140 K and DMN in PrOH at 135 K were measured by TCSPC using absorption peak excitation and different emission wavelengths in order to reconstruct the time-resolved spectra. Time-resolved spectra of C153 in MTHF at 140K were also measured for comparison. These time-resolved spectra are shown in Figure 6.16. Three sets of time-resolved spectra show very different behavior due to the different time scales of solvation dynamics and reaction dynamics. For DMN in MTHF at 140 K, the solvation time (330 ps) and reaction time (330 ps) are comparable, which is reflected by simultaneously fast intensity decay and time-dependent spectral shift. In C153 in MTHF at 140 K, spectral evolution results only from solvation dynamics. In DMN in PrOH at 135K, solvation (estimated to be around 300 ns) becomes much slower, and the isomerization reaction (1.1 ns) dominates. As a result, the intensity decays very quickly while the spectra do not shift much. The time dependent peak frequencies and the integrated intensities are shown in Figure 6.17. The peak frequency of DMN in MTHF at 140 K shifts to the red and the shift is bigger than C153 as a result of both solvation dynamics and non-radiative deactivations.

The solvation response function can be fit well by stretched exponential functions.

\[ \nu_{\text{peak}} = \nu_{\infty} + \Delta \nu \exp \left( -\frac{t}{\tau} \right)^\beta \]  (6.25)

And for the integrated intensity decay, we fit it to double exponential functions.

\[ I(t) = a_1 \exp \left( -\frac{t}{\tau_1} \right) + (1 - a_1) \exp \left( -\frac{t}{\tau_2} \right) \]  (6.26)

The fitting parameters are listed in Table 6.13. The solvation response of DMN in 1-PrOH at 135 K cannot be fit well because time window is not long enough for observing whole solvation dynamics.
Figure 6.15 Modeling observed spectral shifts. Points are experimental data, dash lines the results calculated using eq 6.24, and solid lines the results calculated using eq 6.23.
Figure 6.16 Time-resolved spectra. The upper panel is DMN in MTHF at 140 K, middle panel the DMN in PrOH at 135 K, and lower panel C153 in MTHF at 140 K. Points are the real data, and solid lines are the log-normal fits to these points. Dash lines connect the peak frequencies of emission spectra at different times.
Figure 6.17 Peak frequencies and integrated intensity change with time. The upper panel is peak frequency at different times; points are data thinned by a factor of 5 and solid lines are fitted to relation $\nu_{\text{peak}} = \nu_{\infty} + \Delta \nu \exp \left( -\frac{t}{\tau} \right)$. The lower panel is normalized integrated intensity at different times; points are data thinned by a factor of 3 and solid lines fits to relation $I(t) = a_1 \exp \left( -\frac{t}{\tau_1} \right) + (1 - a_1) \exp \left( -\frac{t}{\tau_2} \right)$. Black color is the data of C153 in MTHF at 140 K, red color the data of DMN in MTHF at 140 K, and green color the data of DMN in PrOH at 135 K.
<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>$\nu_0$ $10^3$cm$^{-1}$</th>
<th>$\Delta\nu$ $10^3$cm$^{-1}$</th>
<th>$\tau$ ns</th>
<th>$\beta$ ns</th>
<th>$&lt;\tau&gt;$ ns</th>
<th>$a_1/a_2$</th>
<th>$\tau_1$ ns</th>
<th>$\tau_2$ ns</th>
<th>$&lt;\tau&gt;$ ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>C153</td>
<td>MTHF</td>
<td>19.3</td>
<td>0.71</td>
<td>0.25</td>
<td>0.80</td>
<td>0.29</td>
<td>0.12</td>
<td>0.05</td>
<td>6.50</td>
<td>5.81</td>
</tr>
<tr>
<td>DMN</td>
<td>MTHF</td>
<td>20.7</td>
<td>0.96</td>
<td>0.15</td>
<td>0.78</td>
<td>0.17</td>
<td>0.71</td>
<td>0.07</td>
<td>0.54</td>
<td>0.34</td>
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<tr>
<td>DMN</td>
<td>PrOH</td>
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<td></td>
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<td>0.24</td>
<td>1.66</td>
<td>1.14</td>
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</table>

Table 6.13 Fitting parameters for correlations of peak frequency and integrated intensity with time using eq 6.25 and eq 6.26.
6.4 Summary and Conclusions

To summarize, we have studied two push-pull malononitrile molecules DMN and JDMN in a series of conventional solvents and at different temperatures. Both the absorption and emission spectra of DMN and JDMN show large shifts with solvent polarity and these shifts are reasonably correlated to dielectric properties. The quantum yields of malononitriles are sensitive to solvent viscosity but the relationship is not simple. The quantum yields of malononitriles do not seem to be sensitive to solvent polarity. Our quantum yields do not agree with previous reported values, but the decay times deduced from them are consistent with time-resolved measurements from TCSPC and at least in some cases the Kerr-gated emission technique.

The temperature dependence of the emission of malononitriles in MTHF and PrOH provides further information about the non-radiative deactivation. Reaction times follow the relation \((\eta/T)^p\) with \(p\) values of 1.0, 0.60 and 0.44 for MTHF, PrOH and [Nip311][Tf2N] respectively. It seems that complicated interactions will decouple the correlation between deactivation motions and viscosity, which is indicated by the small \(\beta\) values in PrOH and [Nip311][Tf2N]. We observe nonmonotonic trends of the spectral shifts with temperature in some solvents, which result from different temperature dependence of the solvation time and lifetime. These results can be reproduced by S-curve model. Spectral dynamics of DMN at low temperature are influenced by from both solvation dynamics and reaction dynamics.
References and Notes

38 DOE technical report SAND-78-1414.
39 *TRC thermodynamic tables*.
41 Fee, R. S., Pennsylvania State University, 1994.
Appendix

Making Correction Files for the SPEX Fluorometer

Details for making emission correction file can be found in ref\(^1\). The following table shows probes and solvents used for correction file measurement.

<table>
<thead>
<tr>
<th>#</th>
<th>Probe</th>
<th>Solvent</th>
<th>Excitation</th>
<th>Emission</th>
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</thead>
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<td>1</td>
<td>Trypotophan</td>
<td>Water</td>
<td>265 nm</td>
<td>310-428 nm</td>
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<tr>
<td>2</td>
<td>α-NPO</td>
<td>MeOH</td>
<td>315 nm</td>
<td>364-486 nm</td>
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<tr>
<td>3</td>
<td>TPB</td>
<td>CHEX</td>
<td>340 nm</td>
<td>390-570 nm</td>
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<tr>
<td>4</td>
<td>C153</td>
<td>MeOH</td>
<td>400 nm</td>
<td>486-678 nm</td>
</tr>
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<td>6</td>
<td>LDS751</td>
<td>MeOH</td>
<td>550 nm</td>
<td>646-844 nm</td>
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</table>

Experimental Details and Procedures

1. Water used as solvent should be deionized water.
2. The optical density of each sample should be smaller than 0.1.
3. When recording emission spectra, record signal only (S) using 2 nm steps. Record the emission spectra twice for each sample and solvent blank.
4. Average the spectra, and subtract the solvent background from sample.
5. Normalize the probe emission spectra and record the normalization factor for later use.
6. Input spectra to preformatted Excel worksheet where the correction file will be automatically generated.

The Excel file is available at:

http://research.chem.psu.edu/maroncelli/supporting_material/57_Emission%20Calibration.xls
Procedures for Reading the Correction File into SPEX Software

1. Prepare the correction file as an XY .txt file (wavelength ranges from 310-845 nm, increment = 5 nm), then change the .txt file to a .prn file.

2. Open C:\DATAMAX\ISAMAIN.EXE
   Use File→Open, change file type to ASCII XY data pair format, then read the previous .prn file. Use File→Save As to save the correction file as a .SPC file.

3. Open E:\DATAMAX\ISAMIN.EXE
   Read .SPC file, and open File→File Information→Audit Log
   Input the following command:
   [Scan Param]
   Start=300.0
   End=850.0
   Increment=5.0
   wld_units=1
   Use File→Save to save it.

4. Before collecting data, read the .SPC correction file from correction file menu. Save the experiment method.

References

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American Chemical Society