

# Solute Rotation and Solvation Dynamics in a Room-Temperature Ionic Liquid

J. A. Ingram and R. S. Moog

Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17604

N. Ito, R. Biswas,<sup>†</sup> and M. Maroncelli\*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received: January 29, 2003; In Final Form: April 7, 2003

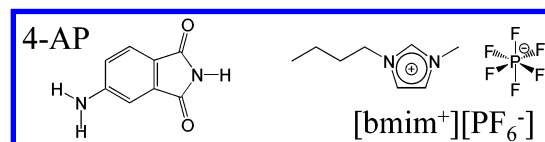
Steady-state spectra, rotation times, and time-resolved emission spectra of the probe 4-aminophthalimide (4-AP) in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>]) were measured over the temperature range 298–355 K. The steady-state spectroscopy indicates that the solvation energetics of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] are comparable to those of 4-AP in highly polar but aprotic solvents such as dimethylformamide and acetonitrile ( $\pi^* \sim 0.8$ ,  $E_T^N \sim 0.4$ ). The rotation of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] and in more conventional aprotic solvents generally conforms to the expectations of simple hydrodynamic models. Other than the fact that [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] is highly viscous, nothing distinguishes the rotation of 4-AP in this ionic liquid from its rotation in more conventional polar aprotic solvents. Time-dependent emission spectra, recorded with an instrumental response of 25 ps, indicate that solvation dynamics in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] occur in two well-separated time regimes. Near to room temperature, the observable response takes place in the 0.1–2 ns time range. This component can be described by a stretched exponential time dependence with an exponent of 0.6–0.7, indicative of strongly nonexponential relaxation. The integral time of the observed component of solvation is proportional to the rotation time of 4-AP and to solvent viscosity, suggesting the involvement of substantial solvent rearrangement. In addition to this relatively slow component, more than half of the solvation response in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] is faster than can be detected in these experiments, that is, takes place in <5 ps.

## I. Introduction

Room-temperature ionic liquids<sup>1,2</sup> are actively being explored as possible “green” (or at least “greener”<sup>3</sup>) substitutes for conventional organic solvents in a variety of electrochemical,<sup>4</sup> synthetic,<sup>5,6</sup> and separation<sup>7,8</sup> processes. In addition to their tremendous potential in such applications, ionic liquids offer fascinating possibilities for fundamental studies of solvation and its effects on chemical reactions. Because of the relative newness of air- and water-stable ionic liquids,<sup>6</sup> many of the basic physical properties of these liquids are just beginning to be characterized.<sup>9–12</sup> Exploration of the nature of solvation in these liquids is also in the earliest stages. Thus far, several groups have attempted to quantify the polarity of ionic liquids using the same solvatochromic probes and polarity scales that have long been used to characterize conventional solvents.<sup>13–20</sup> The consensus emerging from this work is that the most popular imidazolium-based ionic liquids are comparable to highly polar solvents such as acetonitrile or methanol in the strength of their interactions with polar solutes. However, a solvent’s “polarity” or “solvation strength” is a multidimensional property even in conventional liquids. It is likely that the addition of a new dimension, charge density, to the mix will require new concepts and polarity measures before the equilibrium aspects of solvation in ionic liquids can be adequately understood.

The dynamical nature of ionic liquids in the neat state<sup>21,22</sup> and as solvents<sup>23–26</sup> is also beginning to be explored. Quitevis and co-workers<sup>22</sup> and Weingärtner et al.<sup>21</sup> have respectively

## SCHEME 1



measured the (fs) polarizability and (ps) dielectric responses of several neat ionic liquids. Of most interest to the present work, two groups have already reported measurements of the dynamics of solvation of probe solutes in ionic liquid solvents. Prior to the availability of room-temperature ionic liquids, Huppert and co-workers measured time-dependent Stokes shifts of several probe solutes in liquid<sup>23,24</sup> (and even solid<sup>27</sup>) tetraalkylammonium salts at elevated temperatures. These authors reported a biphasic solvation response that is much slower than what is observed in typical liquid solvents.<sup>28,29</sup> More recently, Karmakar and Samanta<sup>25,26</sup> made similar measurements on two of the newer ionic liquids at room temperature using two different probe solutes. They too reported biphasic dynamics occurring on the ps and ns time scales and interpreted these dynamics analogously to Huppert and co-workers. The solvation dynamics measured in the present work share much in common with these earlier reports as will be discussed later.

In the present study, we seek to further characterize the dynamical aspects of solvation in ionic liquids by measuring the temperature dependence of both the rotational times and the solvation response of a dipolar solute, 4-aminophthalimide<sup>30–34</sup> (4-AP; Scheme 1), in the room-temperature ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>]). 4-AP was chosen for this study because it has a longer

\* Address correspondence to this author.

<sup>†</sup> Current address: S. N. Bose National Center for Basic Sciences, Kolkata, India.

fluorescence lifetime ( $\sim 20$  ns) than most solvation probes, which is advantageous for measuring the slow relaxation dynamics in ionic liquids. [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] was selected because it is, at this time, the best characterized room-temperature ionic liquid, and because it is commercially available in pure, dry form.

## II. Experimental Section

4-AP (4-aminophthalimide) was purchased from Aldrich (stated purity 98%) and was recrystallized four times from a 50% (by volume) methanol + water mixture. Electrochemical grade [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] (1-*n*-butyl-3-methylimidazolium hexafluorophosphate) was purchased from Covalent Associates (stated purity >99%; <50 ppm H<sub>2</sub>O; packaged under Ar) and stored under a nitrogen atmosphere in the dark. Other solvents were obtained from Aldrich and were the highest grade available (typically spectral grade, >99%).

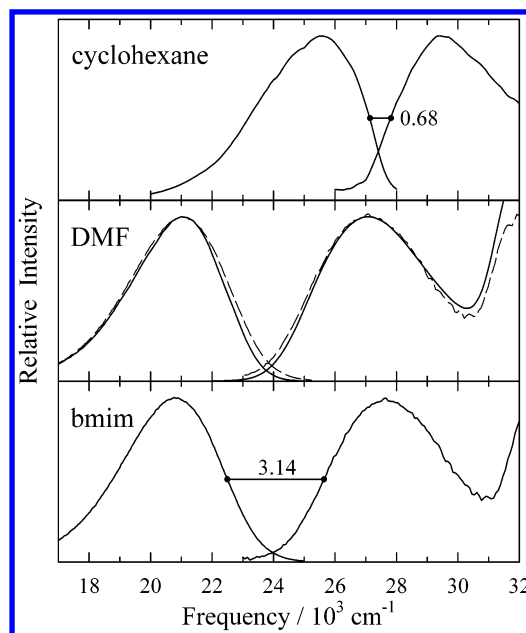
Samples of 4-AP at concentrations providing optical densities of <0.1 for 1-cm path lengths were prepared in quartz cuvettes. When [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] was used as the solvent, the probe was initially dissolved in methanol and placed in a vial. After removal of the methanol under vacuum, the vial was filled with 2 mL of solvent under a nitrogen atmosphere in a glovebag and stirred for at least 15 min. Samples prepared in this manner and stored in the dark under nitrogen atmosphere were spectroscopically stable for at least several weeks.

Steady-state absorption spectra were measured using a Hitachi U-3000 UV/vis spectrophotometer and emission spectra with a Spex Fluorolog 212 fluorimeter. Emission spectra were corrected for emission responsivity.<sup>35</sup> Time-resolved emission measurements were made using a time-correlated single-photon-counting system previously described.<sup>36</sup> The system employed the doubled output of a mode-locked Ti:sapphire laser (Coherent Mira 900F) for excitation ( $\sim 390$  nm) and had an overall response time of 25 ps (fwhm) as measured by a scattering solution. Emission was collected through a single monochromator (ISA H10) with an 8-nm band-pass over time ranges of 5–20 ns, depending on the slowest part of the dynamics being observed. Emission decays were fit together with instrument response functions using an iterative reconvolution least-squares algorithm<sup>37</sup> which enhances the effective time resolution to  $\sim 5$  ps. Rotational dynamics were observed by measuring emission decays polarized parallel and perpendicular to the excitation polarization in the usual manner.<sup>37</sup> These polarized decays were tail-matched and simultaneously fit, together with a decay measured at “magic angle” polarization, to single or multiexponential anisotropy and population decay models as needed.

Time-resolved emission spectra were constructed from a series of 9–11 magic angle decays recorded at wavelengths spanning the emission spectrum. Decays were individually fit to multiexponential functions of time and spectra were then reconstructed from these fits by normalizing to the steady-state emission spectrum.<sup>38</sup> Triple exponential functions were adequate to represent the data to within statistical uncertainties, even after constraining the longest time constant, which represents the overall population decay ( $\sim 20$  ns), to be the same for all wavelengths. For most temperatures studied, only a single series of wavelengths were recorded (in random order) to monitor the spectral dynamics. At 41 °C, two series of decays were measured several weeks apart on different samples and the results were found to be virtually indistinguishable.

## III. Results and Discussion

**Steady-State Spectroscopy.** As illustrated by the representative spectra in Figure 1, the S<sub>1</sub> absorption and emission of 4-AP



**Figure 1.** Room-temperature absorption and emission spectra of 4-AP in cyclohexane, dimethyl formamide (DMF), and [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] (bmim). The solid lines in the middle panel are spectra in DMF, whereas the dashed lines are the bmim spectra shifted slightly to facilitate comparison of lines shapes. The values 0.68 and 3.14 ( $10^3 \text{ cm}^{-1}$ ) are the differences between the low-frequency absorption and high-frequency emission half-intensity points,  $\nu_{\text{abs}}^{(-)} - \nu_{\text{em}}^{(+)}$ . The difference between these values in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] and cyclohexane is approximately the magnitude expected for the time-dependent Stokes shift due to solvation.

in typical organic solvents are broad and featureless. Apart from a frequency shift, the spectra in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] are similar to spectra observed in a polar solvent such as dimethylformamide (DMF). As shown by the middle panel of Figure 1, the only difference in the line shapes of 4-AP in typical organic solvents as opposed to [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] is that the latter spectra are slightly broader. Correlations of the frequencies of 4-AP in a series of 11 polar aprotic solvents to the popular  $\pi^*$  and  $E_T^N$  scales of solvent polarity<sup>39,40</sup> places the polarity of [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] in the range  $\pi^* = 0.7\text{--}0.9$  and  $E_T^N = 0.3\text{--}0.5$ . (In both cases the lower value is obtained from absorption frequencies and the higher value from emission frequencies.) Given that polarity is a composite property, these values are only meant to provide a qualitative indication that, as far as 4-AP is concerned, [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] is about as interactive as strongly dipolar solvents such as DMF and acetonitrile. This assessment is consistent with what has previously been deduced from a variety of solvatochromic probes;<sup>13,14,16,41,20</sup> however, the actual value of  $E_T^N$  measured using the original  $E_T(30)$  indicator differs somewhat.  $E_T^N$  has been measured to be in the range 0.67–0.75 using Reichardt's dye.<sup>15,14,41,19</sup>

The behavior of 4-AP also contradicts past studies that have characterized [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] as possessing substantial hydrogen bond donating ability. Two previous analyses determined values of the hydrogen bond donating parameter  $\alpha^{\text{HBD}}$  to be 0.77<sup>20</sup> and 0.76,<sup>19</sup> values characteristic of branched alcohols.<sup>43</sup> However, the absorption and, especially, emission of 4-AP are sensitive to hydrogen bond donation, and in solvents with a high H-bond donating capacity, the Stokes shift of 4-AP is markedly larger than in polar aprotic solvents.<sup>30,44,33</sup> Such a large Stokes shift is not observed in [bmim<sup>+</sup>][PF<sub>6</sub><sup>−</sup>]. In addition, the peaks of the spectra of 4-AP in a series of typical organic solvents (including

TABLE 1: Summary of Rotation Data

solvent	T/K	$\eta/\text{cP}^a$	$r_0$	$\tau_{\text{rot}}/\text{ns}$
[bmim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	298	207	0.31	$8.7 \pm 0.9$
[bmim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	314	87	0.30	$3.7 \pm 0.4$
[bmim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	332	41	0.31	$1.8 \pm 0.3$
[bmim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	355	21	(0.31)	$0.52 \pm 0.10$
triacetin	283	54	0.31	$2.0 \pm 0.2$
triacetin	293	24	0.32	$0.98 \pm 0.08$
triacetin	303	13	0.34	$0.55 \pm 0.04$
triacetin	313	7.9	0.33	$0.35 \pm 0.04$
1-propanol	295	2.1	0.32	$0.30 \pm 0.03$
dimethyl sulfoxide	295	2.1	0.30	$0.17 \pm 0.02$
methanol	295	0.58	(0.31)	$0.066 \pm 0.010$
benzene	295	0.63	(0.31)	$0.024 \pm 0.004$
acetone	295	0.31	(0.31)	$0.024 \pm 0.005$

<sup>a</sup>  $\eta$  is the solvent viscosity,  $r_0$  the initial anisotropy, and  $\tau_{\text{rot}}$  the rotation time.  $r_0$  values in parentheses were fixed during the fitting process. Viscosities in triacetin (1,2,3-propanetriol triacetate) were determined from the following parametrization of literature data:<sup>59–63</sup>

$$\ln(\eta/\text{cP}) = 44.19 - 30.22 \times 10^3(\text{K}/T) + 5.333 \times 10^6(\text{K}/T)^2$$

The values for the remaining conventional solvents are determined from the data in ref 43.

both aprotics and alcohols) can be reasonably well fit to Taft–Kamlet solvatochromic equations:<sup>42</sup>

$$\nu_{\text{abs}} = 29.65 - 1.74 \pi^* - 0.77\alpha - 1.52\beta$$

$$(n = 14; r^2 = 0.995)$$

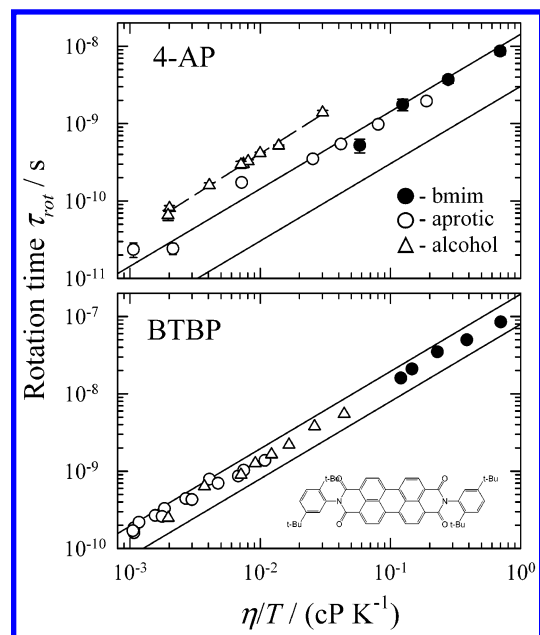
$$\nu_{\text{em}} = 25.45 - 3.35 \pi^* - 3.48\alpha - 2.46\beta$$

$$(n = 15; r^2 = 0.979)$$

These relations typically predict the relevant peak energies to within 100 cm<sup>-1</sup> for absorption and a few hundred cm<sup>-1</sup> for emission in organic solvents. However, if the reported values<sup>20,19</sup> for  $\pi^*$ ,  $\alpha$ , and  $\beta$  (derived from measurements on the indicators used to establish the scales) are used to predict the positions of the absorption and emission peaks of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], the estimates are significantly more discrepant, with the predictions for the emission peak being well over 1000 cm<sup>-1</sup> too low. An alternative method for determining  $\pi^*$ ,  $\alpha$ , and  $\beta$  for ionic liquids (using solvatochromic equations for numerous highly dipolar probes) provides much better agreement with the observed absorption and emission energies, with the following solvatochromic parameters:  $\pi^* = 0.86$ ;  $\alpha = 0.40$ ;  $\beta = 0.18$ .<sup>45</sup> Thus, using a different set of probes to evaluate the solvatochromic parameters, the value of  $\alpha$  is also substantially lower than previous estimates. These discrepancies highlight the difficulty of characterizing the nature of polarity in ionic liquids using methods developed for conventional solvents.

A final important aspect of Figure 1 concerns the magnitude of the Stokes shift in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]. The solvent component of the Stokes shift, which is of interest in studies of solvation dynamics, is approximately given by the difference between the Stokes shifts in polar and nonpolar solvents.<sup>46</sup> As illustrated by the values marked on the tie bars in Figure 1, the magnitude of the dynamic Stokes shift in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] is expected to be greater than 2000 cm<sup>-1</sup>. It will be important to keep this expectation in mind when the time-dependent spectra observed in this system are examined.

**Rotational Dynamics.** A summary of the rotation times of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] and in conventional solvents is provided in Table 1 and in Figure 2. In nearly all cases studied, the emission anisotropies could be fit to single-exponential functions of time. (In [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] and triacetin at the highest temperatures a biexponential anisotropy yielded a slightly better fit to



**Figure 2.** Rotation times of 4-AP (top panel) and BTBP (bottom panel) in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] (filled circles) conventional polar aprotic solvents (open circles) and alcohols (open triangles). The 4-AP data are those listed in Table 1 with the addition of the alcohol data of Yeh<sup>48</sup> (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, and 1-octanol). BTBP data are from refs 18 and 51. The solid lines are predictions of slip (lower) and stick (upper line) hydrodynamics for ellipsoidal representations of the solutes, as described in the text.<sup>47</sup>

the data, but the average times obtained from such fits are equal to the single-exponential times reported in Table 1.) In most cases, anisotropy data were recorded at the peak of the steady-state emission spectrum, where the magic angle decay is not greatly affected by solvation dynamics. However, anisotropies were also measured at emission wavelengths on the blue and red sides of the steady-state emission and no significant differences were found. The initial anisotropies  $r_0$  (Table 1) are in the range 0.30–0.34, lower than the limiting value of 0.4, but consistent with the steady-state anisotropy of 0.28–0.36 observed in frozen ethanol solution.<sup>34</sup> Thus, all of the rotational motion of 4-AP is probably being observed in these measurements.

Hydrodynamic theories predict that rotation times should be proportional to viscosity and inversely proportional to temperature ( $\tau_{\text{rot}} \propto \eta/T$ ). The viscosities of [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] have been reported by several laboratories<sup>18,8,10</sup> and these data can be parametrized:

$$\ln(\eta/\text{cP}) = 7.043 - 5.931 \times 10^3(\text{K}/T) + 1.617 \times 10^6(\text{K}/T)^2 \quad (1)$$

(30 data points; standard error of 15% in  $\eta$ ). Using these viscosities, rotation times can be represented by  $\tau_{\text{rot}}/\text{ns} = 12.6 \cdot (\eta/\text{cP})/(T/\text{K})$  nearly to within the estimated uncertainties in the data. Thus, we find that the rotation times of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] conform to hydrodynamic expectations. Furthermore, as shown in Figure 2, the rotation times in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] correlate with the rotation times of 4-AP in conventional polar aprotic solvents. The solid lines drawn in this figure are the predictions of hydrodynamic calculations with stick (upper line) and slip (lower line) boundary conditions, estimated by considering 4-AP to be an ellipsoid with semiaxis lengths of 2.0, 3.0, and 5.0 Å and with the emission transition moment along the longest axis.<sup>47</sup> The observed rotation times

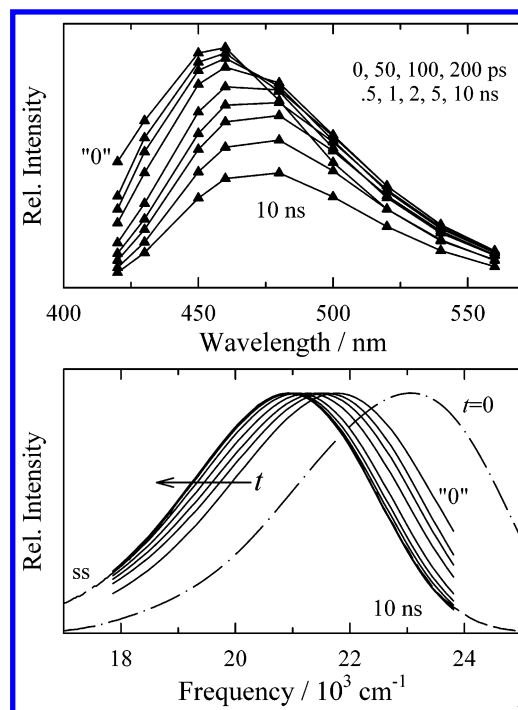


of 4-AP are close to the stick estimates in  $[\text{bmim}^+][\text{PF}_6^-]$  and in polar aprotic solvents. Thus, as far as the rotation of 4-AP is concerned, there is nothing to distinguish this ionic liquid from more conventional polar aprotic solvents. It is interesting that rotation of 4-AP in alcohol solvents (triangles, data from Yeh<sup>48</sup>) is systematically slower than expected on the basis of the correlation established by the other solvents. This “superstick” behavior is often seen when strong hydrogen bonding between the solute and solvent is possible,<sup>49</sup> a behavior which probably reflects long-lived attachment of one or more alcohol molecules to the solute. The fact that the rotation times in  $[\text{bmim}^+][\text{PF}_6^-]$  do not deviate from the more general correlation suggests the absence of any strong solvent-to-solute hydrogen bonding in the 4-AP  $[\text{bmim}^+][\text{PF}_6^-]$  system and is consistent with the idea that the value of  $\alpha$  for this liquid should be much lower than that of the normal alcohols.

The present conclusions concerning rotational dynamics in  $[\text{bmim}^+][\text{PF}_6^-]$  seem rather different from another study recently published on this ionic liquid. Bright and co-workers measured the rotation times of the large solute “BTBP” (see inset to Figure 2) as a function of temperature in  $[\text{bmim}^+][\text{PF}_6^-]$ .<sup>18</sup> They reported that the apparent volume deduced from these rotation times was roughly 3-fold larger than the actual molecular volume of BTBP and interpreted this difference to imply the presence of a layer of  $[\text{bmim}^+]$  or  $[\text{PF}_6^-]$  ions rotating with the solute. However, as shown in the bottom panel of Figure 2, if the same analysis we have used for 4-AP is applied to BTBP, no such solvent association is indicated.<sup>50</sup> The rotation times of BTBP in  $[\text{bmim}^+][\text{PF}_6^-]$  measured by Bright and co-workers<sup>18</sup> correlate nicely with rotation times of this solute measured in conventional organic solvents.<sup>51</sup> Moreover, all of these times are consistent with a hydrodynamic description in which the proportionality between  $\tau_{\text{rot}}$  and  $\eta/T$  is close to what would be predicted from an ellipsoidal solute representation and stick boundary conditions<sup>47</sup> (upper line). On the basis of these comparisons, we would conclude that the rotational dynamics of BTBP in  $[\text{bmim}^+][\text{PF}_6^-]$ , like those of 4-AP, reflect nothing more than the behavior expected for rotation in a highly viscous medium.

**Solvation Dynamics.** Representative time-resolved emission spectra of 4-AP in  $[\text{bmim}^+][\text{PF}_6^-]$  are shown in Figure 3. The top panel contains a series of spectra obtained via spectral reconstruction.<sup>38,52</sup> The bottom panel shows log-normal fits<sup>38</sup> to these spectra after normalization and conversion to a frequency representation. The main feature of the time evolution displayed here is a continuous redshift of the spectrum with time. Except for the fact that this shift is much slower, the evolution is comparable to what has been observed in conventional polar solvents<sup>28,53,44,32</sup> and attributed to polar solvation dynamics. Although the precise solvent (and possibly solute) motions involved are likely to be different from those in polar liquids, by analogy we attribute the spectral dynamics observed here to nonspecific solvation dynamics.

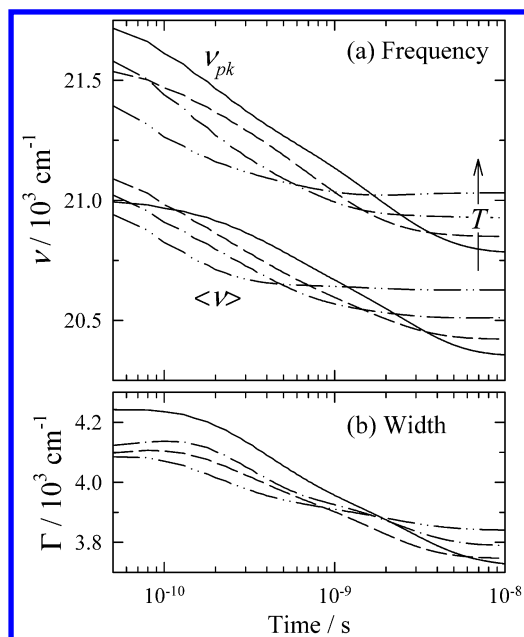
An important feature of the present data is that although the *observed* dynamics are slow, a substantial portion of the spectral response is apparently missed as a result of limited time resolution. Two observations suggest that the extent of the dynamic Stokes shift should be  $>2000\text{ cm}^{-1}$ . First, the steady-state Stokes shift of 4-AP in  $[\text{bmim}^+][\text{PF}_6^-]$  is  $\sim 2450\text{ cm}^{-1}$  larger than in cyclohexane (Figure 1). The more sophisticated estimate of the “time-zero” spectrum<sup>46</sup> (labeled “ $t = 0$ ” in Figure 3) also indicates a value of  $\sim 2200\text{ cm}^{-1}$  for the total shift. The dynamic shift captured in the present experiments is only  $\sim 1000\text{ cm}^{-1}$ , meaning that less than half of the total spectral shift is



**Figure 3.** Examples of time-resolved emission spectra of 4-AP in  $[\text{bmim}^+][\text{PF}_6^-]$  at 332 K. The top panel shows the spectra as reconstructed from fitted decays at various wavelengths (points) and the times indicated. The bottom panel shows the log-normal fits to these data in a frequency representation. The dashed curve labeled ss is the steady-state emission spectrum and the dashed-dot curve labeled  $t = 0$  is an estimate of spectrum prior to solvent relaxation (see text).

being observed here. The missing dynamics must be substantially faster than the components that are observed. For example, in the individual wavelength decays used to construct the spectra in Figure 3, there are no decay components observed with time constants less than 150 ps. In a search of the most sensitive, blue edge of the spectrum, we could detect no faster decay components, which implies that the missing dynamics must occur with time constants faster than  $\sim 5\text{ ps}$ . Thus, the solvation dynamics in this ionic liquid proceeds on two highly disparate time scales, with roughly half of the dynamics being undetectably rapid, perhaps subpicosecond, and the remainder taking place on the 100 ps to 1 ns time scale.

To analyze the observable portion of the dynamics, we utilize the parameters derived from log-normal fits to the spectra: the peak frequency  $\nu_{\text{pk}}(t)$ , the first frequency moment  $\langle \nu(t) \rangle$ , and the full width of the spectrum  $\Gamma(t)$ . These characteristics are plotted in Figure 4 and summarized in Table 2. The frequencies of the fully relaxed spectra  $\nu(\infty)$  increase systematically with increasing temperature, as do the frequencies of the steady-state emission spectra. The changes in  $\nu(\infty)$  are relatively small,  $<10\%$  of the spectral width, and they presumably reflect a decrease in solvent polarity with increasing temperature. The effective time-zero frequency and the dynamic Stokes shift magnitude  $\Delta\nu$  are less accurately determined by the data. In all cases, the observed Stokes shift is less than  $1000\text{ cm}^{-1}$ .  $\Delta\nu$  appears to be approximately constant (or to slightly decrease with increasing  $T$ ) except at the highest temperature where it is significantly smaller than at the remaining temperatures. This change may simply reflect that more of the dynamics is being missed because of insufficient time resolution at this temperature. The widths of the spectra (Figure 4b) decrease with time, possibly going through a maximum before approaching steady-state values.



**Figure 4.** (a) Frequencies and (b) widths of the time-evolving spectra of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] at various temperatures (solid = 298 K, dashed = 314 K, dash-dot = 332 K, and dash-dot-dot = 355 K.)  $\nu_{pk}$ ,  $\langle \nu \rangle$ , and  $\Gamma$  are the peak frequency, first moment frequency, and full width at half-height of the spectra determined from the log-normal fits. Data plotted for 314 K are the averages over two independent experiments.

**TABLE 2: Summary of Spectral Shift Parameters<sup>a</sup>**  
Stretched Exponential Fits (Eq 2)

T/K	$\nu(\infty)/10^3 \text{ cm}^{-1}$	$\Delta\nu/10^3 \text{ cm}^{-1}$	$\tau_0/\text{ns}$	$\beta$	$\langle \tau \rangle_{\text{solv}}/\text{ns}$
298	20.55	0.91	1.15	0.65	$1.6 \pm 0.3$
314	20.64	0.78	0.56	0.70	$0.71 \pm 0.11$
314	20.63	0.87	0.51	0.68	$0.71 \pm 0.11$
332	20.72	0.84	0.21	0.63	$0.30 \pm 0.04$
355	20.83	0.59	0.11	0.80	$0.13 \pm 0.04$

Biexponential Fits (Eq 3)

T/K	$\nu(\infty)/10^3 \text{ cm}^{-1}$	$\Delta\nu/10^3 \text{ cm}^{-1}$	$f_1$	$\tau_1/\text{ns}$	$\tau_2/\text{ns}$	$\langle \tau \rangle_{\text{solv}}/\text{ns}$
298	20.57	0.88	0.36	0.26	2.00	$1.4 \pm 0.5$
314	20.64	0.75	0.48	0.25	1.21	$0.74 \pm 0.11$
314	20.64	0.87	0.43	0.18	1.12	$0.66 \pm 0.10$
332	20.72	0.81	0.60	0.11	0.61	$0.31 \pm 0.05$
355	20.83	0.59	0.78	0.08	0.69	$0.15 \pm 0.03$

Values listed here are the averages of the values obtained using the two measures of spectral frequency, the peak frequency  $\nu_{pk}$  and the first frequency moment  $\langle \nu \rangle$ .  $\langle \tau \rangle_{\text{solv}}$  is the integral response time, eq 4 in the stretched exponential fits and  $\langle \tau \rangle_{\text{solv}} = f_1 \tau_1 + (1 - f_1) \tau_2$  in the biexponential fits.

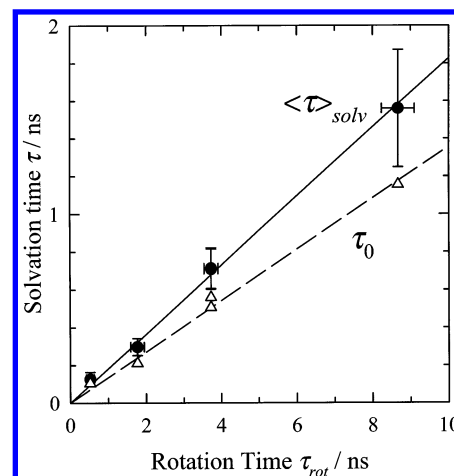
The quantities most closely related to the dynamics of solvation are the frequency changes  $\nu(t)$ . In all cases, frequencies could be adequately represented using either a stretched exponential

$$\nu(t) = \nu(\infty) + \Delta\nu \exp\{-(t/\tau_0)^\beta\} \quad (2)$$

or biexponential

$$\nu(t) = \nu(\infty) + \Delta\nu \{f_1 \exp(-t/\tau_1) + (1 - f_1) \exp(-t/\tau_2)\} \quad (3)$$

time dependence. Parameters derived from fitting the  $\nu(t)$  data (both  $\nu_{pk}(t)$  and  $\langle \nu(t) \rangle$ ) to these functional forms are summarized in Table 2. In the absence of theories justifying either form, we use these fits as convenient ways to summarize the experimental data. By virtue of its having one less fitting



**Figure 5.** Characteristic times of the spectral (solvation) dynamics plotted versus solute rotation times for 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>].  $\tau_0$  (open triangles) and  $\langle \tau \rangle_{\text{solv}}$  (filled circles) are defined by eqs 2 and 4, respectively. The lines show the proportionalities,  $\langle \tau \rangle_{\text{solv}} \cong 0.18\tau_{\text{rot}}$  (solid) and  $\tau_0 \cong 0.14\tau_{\text{rot}}$  (dashed).

parameter, we prefer the stretched exponential representation and therefore discuss the dynamics in terms of eq 2. (The biexponential representation is provided for ease of comparison to prior results which have been fit to such a form.) With the exception of the 355 K data, values of the exponent  $\beta$  mainly lie in the range 0.6–0.7. Such values indicate that the solvent relaxation deviates substantially from the single-exponential time dependence seen for simple rate processes. The fact that the exponents are all roughly the same indicates that, at least to a first approximation, the effect of temperature is merely to alter the overall time scale of the relaxation, that is, produce an overall horizontal shift in the  $\nu(t)$  curves in Figure 4. It is not clear whether the larger value of  $\beta$  at 355 K indicates a real change in the form of the relaxation, or like the decrease in  $\Delta\nu$ , it signals that some additional part of the dynamics has dropped below the effective time resolution of the experiment.

To characterize the time scale of the solvation response we use the integral response time

$$\langle \tau \rangle_{\text{solv}} = \frac{1}{\Delta\nu} \int_0^\infty \{\nu(t) - \nu(\infty)\} dt = \frac{\tau_0}{\beta} \Gamma(\beta^{-1}) \quad (4)$$

where  $\Gamma(x)$  is the gamma function. (The average times obtained from biexponential fits, listed in Table 2, are nearly identical to these times.)  $\langle \tau \rangle_{\text{solv}}$  is plotted in Figure 5, along with  $\tau_0$  for comparison as a function of the observed rotation time. Figure 5 shows that the integral solvation time observed here is approximately proportional to the solute rotation time:  $\langle \tau \rangle_{\text{solv}} \cong 0.2\tau_{\text{rot}}$ . Given that a comparably good correlation is also observed between  $\langle \tau \rangle_{\text{solv}}$  and solvent viscosity (or  $\eta/T$ ), this correlation does not imply a direct link between solvation dynamics and solute rotation. Rather, these observations indicate that the observable component of solvation dynamics and solute rotation sense the fluidity of the environment in comparable ways.

Table 3 compares the solvation dynamics measured with 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] to what has been measured in other ionic liquid/probe solute combinations. The only other room-temperature data we are aware of is the work of Karmakar and Samanta,<sup>26,25</sup> who measured dynamic Stokes shifts of coumarin 153 and “Prodan” (6-propionyl-2-dimethylaminonaphthalene) in the ionic liquids [emim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] (1-ethyl-3-methylimidazolium tetrafluoroborate) and [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], using instrumenta-

**TABLE 3: Summary of Observed Ionic Liquid Solvation Times<sup>a</sup>**

ionic liquid	solute	$\eta/\text{cP}$	$\Delta\nu_{\text{obs}}/\text{cm}^{-1}$	$f_{\text{obs}}$	$\langle\tau\rangle_{\text{solv}}/\text{ns}$	ref
[emim <sup>+</sup> ][BF <sub>4</sub> <sup>-</sup> ]	C153	66	$\sim 900^c$	$\sim 0.5$	0.44	25
[emim <sup>+</sup> ][BF <sub>4</sub> <sup>-</sup> ]	Prodan	66	$\sim 1200^c$	$?^d$	0.68	25
[bmim <sup>+</sup> ][BF <sub>4</sub> <sup>-</sup> ]	C153	154	900	0.5	2.13	26
[bmim <sup>+</sup> ][BF <sub>4</sub> <sup>-</sup> ]	Prodan	154	$\sim 1500^c$	$?^d$	1.44	25
[bmim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	4-AP	207	900	0.4	$1.4 \pm 0.3$	this work
[bmim <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	C102 <sup>b</sup>	207	1000	$\sim 0.5$	$1.8 \pm 0.4$	this work

C153 and C102 denote the dyes coumarin 153 and 102. Prodan denotes 6-propionyl-2-dimethylaminonaphthalene.  $\eta$  is the solvent viscosity,  $\Delta\nu_{\text{obs}}$  the observed Stokes shift,  $f_{\text{obs}}$  an estimate of the fraction of the spectral shift observed, and  $\langle\tau\rangle_{\text{solv}}$  the integral solvation time of the observed portion of the dynamics. Data correspond to 25 °C (4-AP and C102) and room temperature (C153 and Prodan). <sup>b</sup> Preliminary results from this laboratory. <sup>c</sup> Total Stokes shifts estimated from plots of time-resolved spectra and reported values of  $\langle\tau\rangle_{\text{solv}}$ . <sup>d</sup> It is not possible to reliably estimate the position of the  $t = 0$  of Prodan because of the presence of overlapping absorption bands.

tion and analysis methods quite similar to ours. These ionic liquids differ only slightly from [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], with the main difference being that [emim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] is substantially less viscous and [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] slightly less viscous than [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] at room temperature (Table 3). Also included in Table 3 is a preliminary measurement we have made using the probe coumarin 102 in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]. Apart from the overall solvation time, represented by  $\langle\tau\rangle_{\text{solv}}$ , the observed spectral dynamics are similar in all of the cases studied. All of these well-known dipolar probes report polarities in ionic liquids which are comparable to highly polar aprotic solvents such as acetonitrile.<sup>25</sup> All of the values of  $\Delta\nu_{\text{obs}}$  lie in the range 900–1500 cm<sup>-1</sup>. Where reliable estimates of the expected Stokes shift can be made, they imply that roughly one-half of the total dynamics have been missed because of insufficient time resolution. The dynamics that are observed are highly nonexponential in all cases. Karmakar and Samanta<sup>26,25</sup> chose to fit their data to biexponential functions of time. Their fits consist of two components of comparable amplitude and with time constants that differ by roughly an order of magnitude. The present data yield similar fits to biexponential functions (Table 2). Similar response functions were also observed in the higher-temperature ionic liquids studied by Huppert and co-workers.<sup>23,24</sup> In addition, the observed solvation times in Tables 2 and 3 appear to be simply related to solvent viscosity. For example, if the times of all nine solute + solvent combinations are fit to the relation  $\langle\tau\rangle_{\text{solv}} = c\eta$ , one finds  $c = 8.5$  ps/cP with a correlation coefficient of  $R = 0.90$ . (Omission of the one apparent outlier, C153 in [bmim<sup>+</sup>][BF<sub>4</sub><sup>-</sup>], leads to  $c = 9.4$  ps/cP with  $R = 0.98$ .)

Finally, it is interesting to speculate on the molecular basis of the solvation response in these room-temperature ionic liquids. The most striking feature of the response is that it is divided (approximately equally) into two components which differ markedly in time scale: an unobserved rapid component that occurs in the  $<5$  ps (perhaps  $<1$  ps) time domain and the observed component which is in the 100 ps to 1 ns range. Whereas the former dynamics is apparently not strongly hindered by the high viscosities of these liquids, the latter dynamics is directly coupled to viscosity in some manner, a dichotomy reminiscent of the  $\beta$  and  $\alpha$  relaxation process in molecular glasses.<sup>54</sup> It seems reasonable to interpret the fast dynamics as reflecting small-amplitude motions of the solute or solvent molecules which can be effected without significant rearrangement of neighboring molecules. The solvation response consists of whatever motions can bring about a change in the

average electric field (the so-called reaction field) acting upon the dipolar solute. Although the [bmim<sup>+</sup>] and [emim<sup>+</sup>] cations possess significant dipole and higher electrical moments which enable some relaxation via reorientation, it is likely that translational motion of both cations and anions will be more effective in relaxing the solvation energy. We therefore conjecture that the fast response mainly involves small translational adjustments of ions within the solvation structure present at the time of solute excitation. (Such motions are manifest in the femtosecond optical Kerr response measured by Quitevis and workers,<sup>22</sup> but inter-relating the solvation and Kerr dynamics<sup>55</sup> in these systems will be a difficult task.)

The slower portion of the dynamics, which is linked to the bulk solvent viscosity, presumably involves larger-scale rearrangements of the solvation structure. In envisioning the latter dynamics, Huppert and co-workers<sup>23,24</sup> and Karmakar and Samanta<sup>26,25</sup> focused on the fact that the spectral shifts can be represented as biexponential functions of time. They postulated that the two times are associated with motions of the cations and anions which, because of their differing sizes, occur on distinct time scales. The present analysis shows that it is not necessary to view the slow dynamics as being “biphasic” in this manner. Instead, we prefer to view this observable portion of the dynamics as simply nonexponential in time (presumably reflecting coupled reorganization of both cations and anions). Such a representation is at least consistent with the distributed relaxation description of the dielectric response of a room-temperature ionic liquid in the ps–ns time domain.<sup>21</sup>

#### IV. Summary and Conclusions

We have presented results of steady-state and time-resolved emission measurements of the probe 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] designed to help better understand the dynamical nature of solvation in room-temperature ionic liquids. The main results can be summarized as follows. Rotation of 4-AP in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] shows no unusual features. Although rotation in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] is much slower than in most conventional solvents, the difference is completely accounted for by the high viscosity of this solvent. Although initially reported otherwise, we find that the same conclusion also pertains to the much larger solute BTBP, whose rotation times in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] were also recently measured.<sup>18</sup> Solvation dynamics in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] occurs on two distinct time scales. Roughly half of the solvation response is very rapid ( $<5$  ps), so rapid that it is undetected in the present experiments. The remainder of the response is much slower, generally taking place in the 100 ps to 10 ns time range. This latter dynamics is highly nonexponential in character. The average times of this slow component are strongly correlated to solute rotation times and solvent viscosity. These observations concerning solvation dynamics apply not only to the 4-AP/[bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] system studied here but also to the other probe/ionic liquid data recently reported by Karmakar and Samanta.<sup>26,25</sup> Finally, we conjecture that both the fast and slow components of solvation dynamics involve primarily translational motions of both cations and anions. The fast component presumably entails motions that do not require significant structural rearrangements, whereas the slow component does. Several groups have begun computer simulations using relatively realistic models of ionic liquids,<sup>56–58</sup> and such simulations will undoubtedly soon provide further insight into these dynamics.

**Acknowledgment.** We would like to acknowledge the help of Kevin Dahl, Jeremy Evans, and Christina Palladino in carrying out some of the measurements reported here. This



research was supported by grants from the Office of Basic Energy Sciences of the U.S. Department of Energy (M.M.) and the Hackman Scholars program of Franklin and Marshall College (R.S.M.).

## References and Notes

- (1) *Ionic Liquids, Industrial Applications for Green Chemistry*; Rodgers, R., Seddon, K., Eds.; American Chemical Society: Washington, DC, 2002; Vol. 818.
- (2) Brennecke, J. F.; Maginn, E. J. *AIChE J.* **2001**, *47*, 2384.
- (3) Nelson, W. Are Ionic Liquids Green Solvents? In *Ionic Liquids, Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002; p 30.
- (4) Wilkes, J. Ionic Liquids in Perspective: The Past with an Eye toward the Industrial Future. In *Ionic Liquids, Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002; p 214.
- (5) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.
- (6) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- (7) Visser, A. E.; Reichert, W.; Swatoski, R. P.; Willauer, H.; Huddleston, J. G.; Rogers, R. D. Characterization of Hydrophilic and Hydrophobic Ionic Liquids: Alternatives to Volatile Organic Compounds for Liquid-Liquid Separations. In *Ionic Liquids, Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002; p 289.
- (8) Brennecke, J. F.; Blanchard, L.; Anthony, J.; Gu, Z.; Zarraga, I.; Leighton, D. Separation of Species from Ionic Liquids. In *Clean Solvents*; Abraham, M., Moens, L., Eds.; American Chemical Society: Washington, DC, 2002; Vol. 819, p 82.
- (9) Huddleston, J. G.; Visser, A.; Reichert, W.; Willauer, H.; Broker, G.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.
- (10) Seddon, K.; Stark, A.; Torres, M. Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids. In *Clean Solvents*; Abraham, M., Moens, L., Eds.; American Chemical Society: Washington, DC, 2002; Vol. 819, p 34.
- (11) Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont, J. *J. Chim. Phys.* **1998**, *95*, 1626.
- (12) Gu, Z.; Brennecke, J. *J. Chem. Eng. Data* **2002**, *47*, 339.
- (13) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, *13*, 591.
- (14) Aki, S. N. V. K.; Brennecke, J.; Samanta, A. *Chem. Commun.* **2001**, 2001, 413.
- (15) Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2001, 433.
- (16) Fletcher, K. A.; Storey, I. A.; Hendricks, A. E.; Pandey, S.; Pandey, S. *Green Chem.* **2001**, *3*, 210.
- (17) Fletcher, K. A.; Pandey, S.; Storey, I. K.; Hendricks, A. E.; Pandey, S. *Anal. Chim. Acta* **2002**, *453*, 89.
- (18) Baker, S. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. *J. Phys. Chem. B* **2001**, *105*, 9663.
- (19) Baker, S. N.; Baker, G. A.; Bright, F. V. *Green Chem.* **2002**, *4*, 165.
- (20) Huddleston, J. G.; Broker, G.; Willauer, H.; Rogers, R. D. Free-Energy Relationships and Solvatochromic Properties of 1-Alkyl-3-methylimidazolium Ionic Liquids. In *Ionic Liquids, Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002; p 270.
- (21) Weingartner, H.; Knocks, A.; Schrader, W.; Kaatz, U. *J. Phys. Chem.* **2001**, *105*, 8646.
- (22) Hyun, B. R.; Dzyuba, S. V.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem. A* **2002**.
- (23) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, *98*, 3295.
- (24) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, *98*, 10819.
- (25) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 6670.
- (26) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447.
- (27) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1995**, *99*, 9253.
- (28) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
- (29) Maroncelli, M. *J. Mol. Liq.* **1993**, *57*, 1.
- (30) Wetzler, D. E.; Chesta, C.; Fernandez-Prini, R.; Aramendia, P. F. *J. Phys. Chem. A* **2002**, *106*, 2390.
- (31) Soujanya, T.; Fessenden, R. W.; Samanta, A. *J. Phys. Chem.* **1996**, *100*, 3507.
- (32) Harju, T. O.; Huizer, A. H.; Varma, C. A. G. O. *Chem. Phys.* **1995**, *200*, 215.
- (33) Noukakis, D.; Suppan, P. *J. Lumin.* **1991**, *47*, 285.
- (34) Azarov, V. Y.; Nurmukhametov, R. N.; Khalbaev, B. K.; Misurkin, I. A. *Zh. Prik. Spektrosk.* **1984**, *40*, 131.
- (35) Gardecki, J. A.; Maroncelli, M. *Appl. Spectrosc.* **1998**, *52*, 1179.
- (36) Heitz, M. P.; Maroncelli, M. *J. Phys. Chem. A* **1997**, *101*, 5852.
- (37) Birch, D. J. S.; Imhof, R. E. Time-Domain Fluorescence Spectroscopy using Time-Correlated Single-Photon Counting. In *Topics in Fluorescence Spectroscopy, Vol. 1: Techniques*; Lakowicz, J. R., Ed.; Plenum: New York, 1991; p 1.
- (38) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221.
- (39) Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807.
- (40) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
- (41) Fletcher, K. A.; Pandey, S. *Appl. Spectrosc.* **2002**, *56*, 266.
- (42) Kamlet, M. J.; Abboud, J. L. M.; Taft, W. R. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.
- (43) Marcus, Y. *The Properties of Solvents*; Wiley: New York, 1998.
- (44) Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 4811.
- (45) Ingram, J. A.; Moog, R. S. manuscript in preparation.
- (46) Fee, R. S.; Maroncelli, M. *Chem. Phys.* **1994**, *183*, 235.
- (47) These ellipsoid dimensions are chosen to reproduce the van der Waals volume of 4-AP ( $\sim 126 \text{ \AA}^3$ ), its longest dimension ( $\sim 10 \text{ \AA}$ ), and the thickness of the planar aromatic system ( $\sim 4 \text{ \AA}$ ). They provide shape factors  $f_{\text{slip}} = 0.33$ ,  $f_{\text{stick}} = 1.57$ , which relate the rotation time to that of the sphere of the same dimensions,  $\tau_{\text{sphere}} = V\eta/k_B T$ . (See, for example, Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford: New York, 1986; Chapter 6.) At 298 K and  $\eta = 1 \text{ cP}$ ,  $\tau_{\text{sphere}} = 30.7 \text{ ps}$ . In BTBP, we assume ellipsoid semiaxes of 2.0, 6.2, and  $13.8 \text{ \AA}$  and the transition moment along the longest axis, which provides factors  $f_{\text{slip}} = 1.53$ ,  $f_{\text{stick}} = 3.74$ , and  $\tau_{\text{sphere}} = 175 \text{ ps}$  (298 K,  $1 \text{ cP}$ ).
- (48) Yeh, S. Picosecond time-resolved emission studies. I. Real-time measurements of solvent-solute interactions. II. Kinetics of energy flow in a photosynthetic antenna system. Ph.D. Thesis, University of California, Berkeley, 1985.
- (49) Williams, A. M.; Jiang, Y.; Ben-Amotz, D. *Chem. Phys.* **1994**, *180*, 119.
- (50) The conclusions of Bright and co-workers<sup>18</sup> concerning the rotational volume of BTBP apparently resulted from assuming a spherical shape for the molecule.
- (51) Ben-Amotz, D.; Drake, J. M. *J. Chem. Phys.* **1988**, *89*, 1019.
- (52) Gardecki, J. A.; Maroncelli, M. *J. Phys. Chem. A* **1999**, *103*, 1187.
- (53) Nagarajan, V.; Brearley, A. M.; Kang, T. J.; Barbara, P. F. *J. Chem. Phys.* **1987**, *86*, 3183.
- (54) Ediger, M. D.; Angell, C. A.; Nagel, S. R. *J. Phys. Chem.* **1996**, *100*, 13200.
- (55) Castner, E. W., Jr.; Maroncelli, M. *J. Mol. Liq.* **1998**, *77*, 1.
- (56) Hanke, C.; Price, S.; Lynden-Bell, R. M. *Mol. Phys.* **2001**, *99*, 801.
- (57) Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B* **2002**, *106*, 12807.
- (58) Znamensky, V. S.; Kobrak, M. N. Abstracts of Papers, 225th National Meeting of the American Chemical Society, New Orleans, LA, 2003.
- (59) Rodriguez, M.; Galan, M.; Munoz, M.; Martin, R. *J. Chem. Eng. Data* **1994**, *39*, 102.
- (60) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; West, C. J., et al., Eds.; McGraw-Hill: New York, 1930.
- (61) Lueck, H.; Windsor, M. W.; Rettig, W. *J. Phys. Chem.* **1990**, *94*, 4550.
- (62) Linde, D. *Handbook of Organic Solvents*; CRC Press: Boca Raton, FL, 1995.
- (63) von Salis, G. A.; Labhart, H. *J. Phys. Chem.* **1968**, *72*, 752.