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Photoisomerization of cyanine derivatives in 1-butyl-3-methylimidazolium hexafluorophosphate and aqueous glycerol: Influence of specific interactions

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Photoisomerization of two cyanine derivatives, 3,3′-diethyloxadicarbocyanine iodide (DODCI) and merocyanine 540 (MC 540), has been investigated in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate and aqueous glycerol (93 wt % glycerol +7 wt % water) by measuring fluorescence lifetimes and quantum yields. The aim of this work is to understand how the rates of photoisomerization of DODCI and MC 540 are influenced by specific solute-solvent interactions besides the viscosity of the medium. For DODCI, it has been observed that the nonradiative rate constants, which represent the rates of photoisomerization, are almost identical in the ionic liquid and aqueous glycerol at given temperature, indicating that viscosity is the sole parameter that governs the rate of photoisomerization. In contrast, the photoisomerization rate constants of MC 540 have been found to be a factor of 2 higher in aqueous glycerol compared to the ionic liquid. The observed behavior is due to the zwitterionic character of MC 540, a consequence of which, the twisted state gets stabilized by the solute-solvent hydrogen bonding interactions in aqueous glycerol, thus lowering the barrier for isomerization. © *2008 American Institute of Physics.*
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I. INTRODUCTION

It is a well-known fact that solvent polarity and solute-solvent interactions play an important role in governing rates of chemical reactions in solutions.[1] Friction dependent processes such as rotational diffusion and photoisomerization in liquids have been found to be significantly influenced by specific and nonspecific solute-solvent interactions in addition to the viscosity and polarity of the medium.[2–6] The above-mentioned processes were extensively studied in organic solvents, and a reasonable mastery of the subject has been achieved in conjunction with theoretical models. However, efforts to understand these processes, especially the photoisomerization of olefins and polyenes in ionic liquids, have begun only recently.[7–9] In addition to photoisomerization studies, numerous reports dealing with solvatochromism, solute rotation, and solvation dynamics in ionic liquids are also available in literature.[10–22] Nevertheless, the effect of high viscosities of these ionic liquids, which arises due to the strong interactions between the cations and anions that constitute them, on photoisomerization has not been addressed explicitly. Moreover, specific interactions between the solute undergoing isomerization and the solvent are also known to facilitate isomerization by lowering the barrier height. In the present work, we address how the specific solute-solvent interactions beside the viscosity and polarity of the medium govern the rates of photoisomerization by carrying out investigations on two cyanine derivatives in an ionic liquid and compare the results obtained with those in a conventional organic solvent, which is isoviscous.

Photoisomerization of olefins and polyenes such as stilbene and its analogues,[4] diphenylbutadienes[23–28] and carbocyanines,[29–38] has been thoroughly investigated in organic solvents in the recent past. The findings of these studies reveal that the excited state isomerization of these systems essentially involves an activated twist motion about the double bond/bonds to an intermediate geometry. In the twisted geometry, the excited state becomes close in energy to the ground state, thus it rapidly decays to the twisted ground electronic state by internal conversion. Once on the ground state surface, branching between the isomer and the normal form occurs. The nonradiative process is dominated by the barrier crossing or the twisting motion because the internal conversion from the twisted excited state is very rapid. In essence, the nonradiative rate has been identified as the rate of photoisomerization in these systems. Since a large amplitude motion is involved in the barrier crossing, the nonradiative rate depends on solute-solvent frictional coupling. In other words, isomerization rate constants are sensitive to the viscosity of the medium. However, when the solute is solubilized in a very high viscous medium such as a polymer matrix, the twisting motion gets inhibited and internal conversion becomes the main nonradiative process.[31] Besides the viscosity of the medium, solute-solvent dielectric interactions also govern the photoisomerization rate due to the polar nature of the transition state. Kramers' theory[39] has been widely applied to understand the isomerization rates in terms of barrier heights.[3–5] Although Kramers' theory has been quite successful, systematic deviations from Kramers'

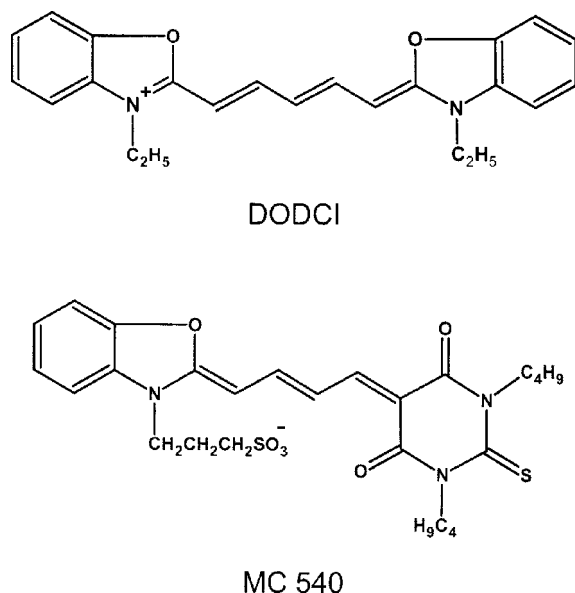[a)]Electronic mail: gbdutt@barc.gov.in.

DODCI

MC 540

FIG. 1. Molecular structures of DODCI and MC 540.

model were observed, which have been rationalized on the basis of microscopic friction being different from the bulk viscosity of the solvent, frequency-dependent frictional effects in which solute-solvent couplings depend on the relative time scales of the solute and solvent isomerization motions and inadequacy of the one-dimensional model.

As mentioned earlier, preliminary studies carried out in ionic liquids[7–9] do not address the role of specific solute-solvent interactions and the viscosity of the medium on the rates of photoisomerization. To this effect, photoisomerization of two cyanine derivatives, 3,3′-diethyloxadicarbocyanine iodide (DODCI) and merocyanine 540 (MC 540) has been studied in the temperature range of 293–343 K. Figure 1 gives molecular structures of the two probes, and it is evident from the figure that DODCI is a cationic solute whereas MC 540 is anionic. The solvents chosen for the present study are the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}^+][\text{PF}_6^-]$) and aqueous glycerol (93 wt % glycerol +7 wt % water). These solvents were chosen as they have similar viscosities but different polarities. Moreover, because of the distinct chemical nature of these solvent molecules, their ability to experience specific interactions with the probes will not be the same, which can also influence the photoisomerization rates significantly. The strategy, which will be adopted here, is to measure the fluorescence lifetimes (τ_f) and quantum yields (ϕ_f) of DODCI and MC 540 in the two solvents and determine the nonradiative constants (k_{nr}). Since the nonradiative rate constant has been identified as the rate of photoisomerization for these systems, it would be interesting to find out how the k_{nr} values of DODCI and MC 540 compare in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol.

II. EXPERIMENT

The probes DODCI (laser grade) and MC 540 (90% pure) were obtained from Exciton and Aldrich, respectively. The solvents $[\text{bmim}^+][\text{PF}_6^-]$ and glycerol are from Lancaster

and S. D. Fine-Chem Ltd., respectively. The purity of the ionic liquid is 99% and the water content is less than 100 ppm. De-ionized water from Millipore A-10 was used in the preparation of aqueous glycerol. MC 540 was purified by repeated recrystalization from ethanol, and the purity of the sample was assessed from the lifetime measurements. The rest of the chemicals were used without further purification.

Absorption and fluorescence spectra were recorded using Chemito Spectrascan UV 2600 spectrophotometer and Hitachi F-4010 spectrofluorometer, respectively. For the purpose of quantum yield measurements, samples containing the probe DODCI were excited at 555 nm, whereas the wavelength of excitation for the ones with MC 540 was 545 nm. The absorbance (A) of the sample and the reference were matched up to the third decimal, and it was ensured that these values did not exceed 0.1 at the wavelength of excitation. Corrected emission spectra were recorded from 570 to 700 nm for DODCI and the spectral range was 550–700 nm for MC 540. The integrated areas (I) of these regions were calculated and compared with that of a reference. The quantum yields of the samples were obtained with the aid of the following equation.[40]

$$\phi_f^{\text{sample}} = \phi_f^{\text{reference}}\left[\frac{I}{I_{\text{reference}}} \times \frac{A_{\text{reference}}}{A} \times \frac{n^2}{n_{\text{reference}}^2}\right]. \quad (1)$$

In the above equation, n is the refractive index of the solvent. For both DODCI and MC 540, the respective quantum yield values in ethanol were used as the standards. The reported ϕ_f values of DODCI and MC 540 in ethanol are 0.42 and 0.20, respectively, at 298 K.[37,38] The refractive index measurements were carried out with Mettler Toledo RE 50 refractometer and the viscosity (η) measurements with Physica MCR 101 rheometer.

Steady-state anisotropy measurements were carried out with the above-mentioned spectrofluorometer in the temperature range of 313–343 K, and the details have been mentioned in our earlier publication.[41] The samples containing DODCI and MC 540 were excited at 575 and 600 nm, respectively, and the emission was monitored in the wavelength region of 615–665 nm. Fluorescence decays were measured using single-photon counting[42] facility at the Tata Institute of Fundamental Research, Mumbai, and details of the system have been described elsewhere.[43] The only modification that has been carried out to the earlier system is the replacement of the pump laser with a newer one, which is Spectra Physics (Vanguard) cw mode-locked neodymium doped yttrium aluminum garnet laser with a repetition rate of 80 MHz. The frequency doubled and attenuated (from 2 to 0.6 W) output of this laser was used to pump the dye laser. The samples were excited at 575 nm and the emission was monitored at 600 nm. For fluorescence decay measurements, 10 000 peak counts were collected in 512 channels with a time increment of 20 ps/channel and each measurement was repeated two to three times. In both time-resolved and steady-state equipments, the desired sample temperature (T) was achieved with the help of a thermocouple based temperature controller, which is regulated by a microprocessor (Eurotherm). The measured fluorescence decays were analyzed using the iterative reconvolution method with the
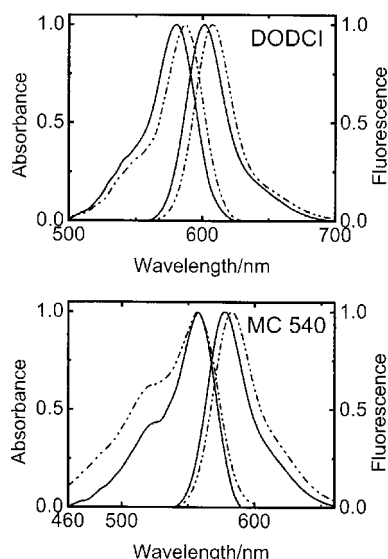
FIG. 2. Absorption and emission spectra of DODCI and MC 540 in $[bmim^+][PF_6^-]$ (solid lines) and aqueous glycerol (broken lines) at room temperature.

TABLE I. Viscosities and refractive indices of $[bmim^+][PF_6^-]$ and aqueous glycerol as a function of temperature.

Temperature/K	$[bmim^+][PF_6^-]$		Aqueous glycerol	
	η/mPa s	n	η/mPa s	n
293	282.6	1.410	304.8	1.462
298	213.2	1.409	208.8	1.461
303	160.6	1.408	148.1	1.460
308	124.3	1.407	108.0	1.459
313	95.7	1.405	81.0	1.458
323	62.7	1.403	45.8	1.455
333	43.5	1.401[a]	29.6	1.453[a]
343	30.6	1.398[a]	19.8	1.451[a]

[a]Refractive indices at these temperatures were obtained by extrapolation.

aid of Marquardt algorithm as described by Bevington.[44] The criteria for a good fit were judged by statistical parameters such as the reduced χ^2 being close to unity and the random distribution of the weighted residuals. To compare our results with those available in literature[9] DODCI was excited with 408 nm light. For this purpose, 408 nm diode laser (IBH, UK) with a repetition rate of 1 MHz was used as the excitation source. The fluorescence was detected with a special Hamamatsu photomultiplier tube, and the details of the system have been described elsewhere.[45]

III. RESULTS AND DISCUSSION

The absorption and emission spectra of DODCI and MC 540 in $[bmim^+][PF_6^-]$ and glycerol are displayed in Fig. 2. In case of DODCI, both absorption and emission spectra are red shifted in aqueous glycerol compared to $[bmim^+][PF_6^-]$, whereas for MC 540, only the emission spectrum is red shifted. The observed red shifts in aqueous glycerol are due to its higher polarity compared to the ionic liquid. However, solvatochromic studies indicate that the polarity of $[bmim^+]\times[PF_6^-]$ is similar to that of lower alcohols and 90 wt % glycerol in water.[10,11] But a more direct microwave dielectric spectroscopic investigation[46] reveals that the dielectric constant of $[bmim^+][PF_6^-]$ is only 11.4 at 298 K, which is much lower compared to aqueous glycerol. Even though the spectra of DODCI are red shifted in aqueous glycerol, the Stokes shift (S) values in both these solvents are comparable; 602 and 572 cm^{-1}, respectively, in $[bmim^+][PF_6^-]$ and aqueous glycerol. In contrast, for MC 540 the S values are 615 and 814 cm^{-1}, respectively, in $[bmim^+][PF_6^-]$ and aqueous glycerol, indicating that the solvation energy is greater in the latter.

Since the viscosity of the medium is an important parameter in controlling the rate of photoisomerization, viscosities of the two solvents were measured in the temperature range of 293–343 K and are given in Table I along with the refractive indices, which are needed for the estimation of

quantum yields. To find out how the measured viscosities of $[bmim^+][PF_6^-]$ compare with those available in literature, the following procedure was adopted. The viscosity of $[bmim^+]\times[PF_6^-]$ reported in literature is in the range of 207–273 mPa s at 298 K,[12,15,47–49] and this variation is more than 30%. The spread in the values of η has been attributed to varying amounts of water present in the system. In view of this, data from literature[12,15,47–49] in the temperature range of 283–363 K were plotted as $\ln(\eta)$ versus $1/T$ and the following empirical relation has been obtained:

$$\ln(\eta) = (4.757) - (4.711 \times 10^3/T)$$
$$+ (1.467 \times 10^6/T^2) \quad (N = 39, R = 0.98). \quad (2)$$

In the above equation, N and R are the number of data points and the regression coefficient, respectively. It is evident from Table I that the measured viscosities in the temperature range of 293–343 K match with those obtained from Eq. (2) within the range of 7%–12%. Inspection of Table I also reveals that the viscosities of both $[bmim^+][PF_6^-]$ and aqueous glycerol at a given temperature are almost identical in the temperature range of 293–303 K, but from 308 to 343 K the decrease in the viscosity of aqueous glycerol is steeper compared to $[bmim^+][PF_6^-]$. In other words, the viscosity of $[bmim^+][PF_6^-]$ is 1.2 times higher than aqueous glycerol at 308 K, and this factor increases to 1.5 at 343 K. Thus, despite choosing two solvents of identical viscosities, isoviscous conditions could not be maintained at higher temperatures due to the dissimilarities in the variation of the respective solvent viscosities. It remains to be seen how these differences in the viscosities of the two solvents at higher temperatures are going to influence isomerization rate constants of the two solutes.

Figure 3 gives variation of fluorescence quantum yield with temperature for DODCI and MC 540 in $[bmim^+][PF_6^-]$ and aqueous glycerol. The measured quantum yields of DODCI in $[bmim^+][PF_6^-]$ and aqueous glycerol at a given temperature are more or less identical within the limits of experimental error. In contrast, the quantum yields of MC 540 in ionic liquid are higher by a factor of 1.3–1.8 compared to aqueous glycerol. Considering the fact that the uncertainties associated with these numbers are about 10%, the photoisomerization of MC 540 appears to proceed faster in aqueous glycerol and the fluorescence lifetime data will pro-
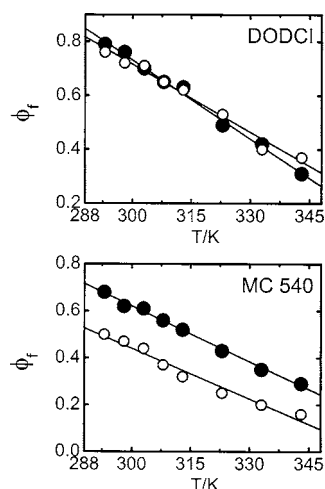
FIG. 3. Plots of quantum yield vs temperature for DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ (●) and aqueous glycerol (○). The lines passing through the data points were obtained by linear least-squares fit.

vide further evidence for this conjecture. Fluorescence decays of DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol could be adequately fitted with a single exponential function throughout the temperature range used in this study. The experimentally measured fluorescence decays of both DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol at 298 K are given in Fig. 4. It is evident from the figure that the fluorescence of DODCI decays with almost identical lifetimes in both the solvents, whereas that of MC 540 is faster in aqueous glycerol compared to $[\text{bmim}^+][\text{PF}_6^-]$. The lifetimes of DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol as function of temperature are given in Tables II and III, respectively.

It has been well established that the photophysics of carbocyanines and other polymethine dyes is dominated by a very fast isomerization process, which takes place from the first excited singlet state.[29–38] Upon optical excitation, the
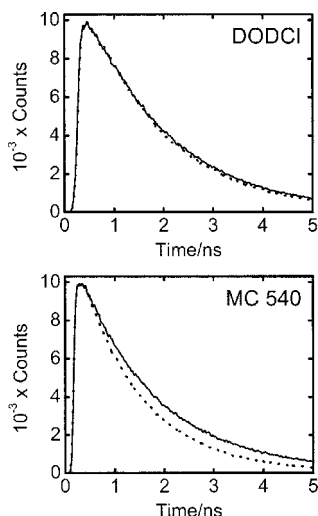

FIG. 4. Fluorescence decays of DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ (solid lines) and aqueous glycerol (dotted lines) at 298 K. Notice that the decays of DODCI are almost identical in both the solvents, whereas the decay of MC 540 in aqueous glycerol is faster compared to that in $[\text{bmim}^+][\text{PF}_6^-]$ (see text, for details).

bond order in one of the double bonds along the polymethine chain gets reduced, and as a consequence the molecule can twist in the excited state to form an intermediate geometry. As mentioned earlier, the twisted state rapidly undergoes internal conversion to ground electronic state, where branching between the isomer and normal forms takes place. Typically, once on the ground state surface the molecule goes to the thermodynamically stable all-*trans* form. In this investigation, the isomerization rate constants have been obtained from the nonradiative rate constants. However, such calculation can be flawed because of the presence of other nonradiative channels such as internal conversion and intersystem crossing. Nonetheless, all the nonradiative pathways have been characterized for both DODCI and MC 540. It has been established from the flash photolysis studies that isomerization is the dominant pathway for nonradiative decay for these molecules,[31,34–36] and this can be understood as follows. The triplet quantum yields of these molecules are typically very small so that k_{isc} can be neglected compared to $(k_{\text{ic}}+k_{\text{iso}})$. Moreover, these studies also indicate that the photoisomer directly arises from the first excited singlet state. The outcome of these investigations reveals that internal conversion is not a major pathway for the nonradiative decay in these systems.[31,34–36] Therefore, one can essentially equate the nonradiative rate to the rate of photoisomerization ($k_{\text{nr}} = k_{\text{iso}}$).

Thus, to comprehend the photoisomerization process of these systems, the nonradiative rate constants were obtained

TABLE II. Variation of fluorescence lifetimes and nonradiative rate constants of DODCI in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol with temperature. The excitation wavelength was 575 nm.

Temperature/K	$[\text{bmim}^+][\text{PF}_6^-]$		Aqueous glycerol	
	τ_f/ns	$k_{\text{nr}} \times 10^{-9}$/s^{-1}	τ_f/ns	$k_{\text{nr}} \times 10^{-9}$/s^{-1}
293	1.74	0.12	1.65	0.15
298	1.67	0.14	1.59	0.18
303	1.59	0.19	1.52	0.19
308	1.51	0.23	1.45	0.24
313	1.41	0.26	1.37	0.28
323	1.23	0.42	1.19	0.40
333	1.03	0.56	0.99	0.60
343	0.84	0.82	0.80	0.79

TABLE III. Variation of fluorescence lifetimes and nonradiative rate constants of MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol with temperature. The excitation wavelength was 575 nm.

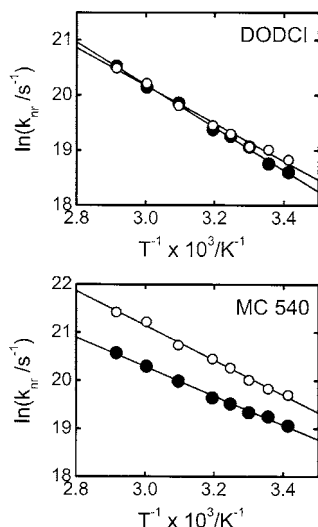| Temperature/K	$[\text{bmim}^+][\text{PF}_6^-]$		Aqueous glycerol	
	τ_f/ns	$k_{\text{nr}} \times 10^{-9}$/s^{-1}	τ_f/ns	$k_{\text{nr}} \times 10^{-9}$/s^{-1}
293	1.72	0.19	1.39	0.36
298	1.65	0.23	1.28	0.41
303	1.56	0.25	1.14	0.49
308	1.49	0.30	1.01	0.63
313	1.39	0.34	0.89	0.76
323	1.20	0.48	0.71	1.05
333	1.01	0.65	0.54	1.49
343	0.82	0.86	0.42	2.01

FIG. 5. Plots of $\ln(k_{nr})$ versus $1/T$ for DODCI and MC 540 in $[\text{bmim}^+]$ $\times[\text{PF}_6^-]$ ($\bullet$) and aqueous glycerol ($\circ$). The lines passing through the data points were obtained by linear least-squares fit.

in the following manner. Fluorescence quantum yield and lifetime are related to radiative (k_r) and nonradiative rates by the following relations:[40]

$$\phi_f = \frac{k_r}{k_r + k_{nr}}, \qquad (3)$$

$$\tau_f = \frac{1}{k_r + k_{nr}}. \qquad (4)$$

Radiative rate constants were obtained from the measured quantum yields and lifetimes using Eqs. (3) and (4). Nonradiative rate constants of DODCI and MC 540, which were obtained using the parameters k_r and τ_f, are also given in Tables II and III, respectively. Since the variation of photoisomerization rate constant with temperature follows Arrhenius-type relation, the parameters $\ln(k_{nr})$ and $1/T$ were plotted as ordinate and abscissa, respectively, in Fig. 5 for DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol.

Inspection of Table II and Fig. 5 reveals that k_{nr} values of DODCI are almost identical in aqueous glycerol and $[\text{bmim}^+][\text{PF}_6^-]$ over the temperature range of 293–343 K. This result indicates that the viscosity is the sole parameter responsible for controlling the rate of photoisomerization of DODCI in these two solvents. It must also be noted that despite having vastly different polarities and chemical nature, both aqueous glycerol and $[\text{bmim}^+][\text{PF}_6^-]$ offer identical friction to the photoisomerization process of DODCI. At this juncture, it is imperative to compare the results obtained by Chakrabarty et al.[9] for the isomerization of DODCI in $[\text{bmim}^+][\text{PF}_6^-]$. In their study, the lifetimes and quantum yields of DODCI in $[\text{bmim}^+][\text{PF}_6^-]$ were measured with varying amounts of water, and it has been observed that the rate of photoisomerization increases with an increase in the water content, which has been ascribed to the decrease in the viscosity of the medium upon the addition of water. However, addition of water to $[\text{bmim}^+][\text{PF}_6^-]$ also increases the polarity of the medium besides decreasing the viscosity. A quick glance at the data presented for DODCI in $[\text{bmim}^+][\text{PF}_6^-]$ at
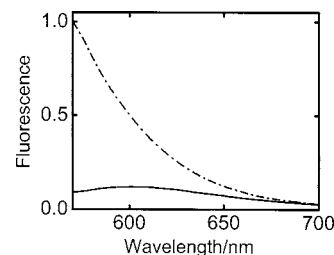

FIG. 6. Normalized emission spectra of neat $[\text{bmim}^+][\text{PF}_6^-]$ at room temperature upon excitation at 408 nm (broken line) and 555 nm (solid line).

298 K reveals that the quantum yield values reported in the two studies are comparable, $\phi_f=0.93$ (Ref. 9) and $\phi_f=0.76$ (this work). In contrast, the lifetimes reported for DODCI in these two studies are vastly different. Chakrabarty et al.[9] reported a value of 3.64 ns for DODCI in $[\text{bmim}^+][\text{PF}_6^-]$ at 298 K, whereas our measurements gave a value of 1.67 ns. What are the reasons for this anomaly? The probable reasons are the purity of $[\text{bmim}^+][\text{PF}_6^-]$ used in the two studies and the choice of the excitation wavelength. As mentioned in Sec. II, the stated purity and water content of the sample used in this study are 99% and less than 100 ppm, respectively. Under these circumstances, the likely impurities present in $[\text{bmim}^+][\text{PF}_6^-]$ are the pyrolysis by-products of 1-methylimidazole, and also traces of unreacted 1-methylimidazole. The presence of pyrolysis products of 1-methylimidazole in $[\text{bmim}^+][\text{PF}_6^-]$ can be easily detected from the color of the sample. These impurities impart yellow color to the ionic liquid. However, the $[\text{bmim}^+][\text{PF}_6^-]$ sample used in our studies is a colorless liquid. Thus, the presence of pyrolysis products of 1-methylimidazole can be ruled out. As discussed earlier, the presence of large amounts of water decreases the viscosity of $[\text{bmim}^+][\text{PF}_6^-]$ significantly. Nevertheless, the viscosities of the sample measured in the temperature range of 293–343 K are comparable to those reported in literature.

Now turning our attention to the excitation wavelengths employed in the two studies; DODCI was excited at 575 nm in this study, whereas the wavelength of excitation used by Chakrabarty et al.[9] is 408 nm. It has been reported in literature[50] and we have also noticed during our experiments that $[\text{bmim}^+][\text{PF}_6^-]$ displays weak emission in the wavelength region of 300–600 nm and the emission maxima shifts to longer wavelengths with an increase in the excitation wavelength. This kind of emission is observed even from rigorously purified samples, which has been ascribed to various associated forms of imidazolium ions.[50] To find out if the different excitation wavelengths employed in the two studies are indeed the reason for the discrepancies observed, we have recorded the emission spectra of neat $[\text{bmim}^+][\text{PF}_6^-]$ in the wavelength range of 570–700 nm by exciting at 408 as well as 555 nm, and the results are presented in Fig. 6. It is evident from the figure that the integrated area of the spectrum when excited at 408 nm is 3.7 times larger compared to the one obtained at 555 nm excitation. Moreover, at 600 nm, where the emission was monitored for the lifetime measurements, the emission intensity of $[\text{bmim}^+][\text{PF}_6^-]$ is a factor of 4.2 higher when the ionic liquid was excited at 408 nm com-

pared to 555 nm excitation. It must also be noted that 555 nm excitation was employed only for the quantum yield measurements of DODCI and for the lifetime measurements 575 nm excitation was used. The emission intensity of $[\text{bmim}^+][\text{PF}_6^-]$ at 600 nm is higher by a factor of 8 when excited at 408 nm compared to 575 nm. In other words, when 408 nm was employed to excite DODCI in $[\text{bmim}^+]$ $\times[\text{PF}_6^-]$, emission from the ionic liquid strongly interferes with the emission of the probe. Besides, the absorbance of DODCI in $[\text{bmim}^+][\text{PF}_6^-]$ at 408 nm is lower by more than a factor of 10 compared to the one at 575 nm. Hence, a combination of these two factors increases the emission contribution from the ionic liquid by a factor of 80 upon excitation with 408 nm compared to 575 nm. To substantiate our arguments, we have measured the lifetime of DODCI in $[\text{bmim}^+][\text{PF}_6^-]$ by exciting the sample at 408 nm, which gave a value of 4.0 ns, and this number is close to the one reported by Chakrabarty et al.[9] Thus, the observed discrepancies between our work and those reported in Ref. 9 are a consequence of different excitation wavelengths employed in the two studies. In essence, the vast amount of literature available on the photophysical studies involving DODCI and also the arguments presented here indicate that 550–600 nm region is appropriate for its excitation, especially in $[\text{bmim}^+]$ $\times[\text{PF}_6^-]$.

A quick glance at Table III points to the fact that k_{nr} values of MC 540 in aqueous glycerol are about a factor of 2 higher compared to the ones in ionic liquid throughout the temperature range studied (also see Fig. 5), which is in contrast to the results obtained for DODCI. This result is surprising considering the fact that both DODCI and MC 540 are ionic polyenes, but only the latter shows marked differences in the isomerization rate constants in the two solvents. A similar result has been obtained by Onganer et al.[37] who observed that the isomerization rate constant of MC 540 is a factor of 5 higher in 1-propanol compared to nonanenitrile at 298 K despite identical viscosities of both the solvents. This result indicates that solvent polarity plays an important role in the photoisomerization of MC 540. Since the polarity of aqueous glycerol is considerably higher than $[\text{bmim}^+][\text{PF}_6^-]$,

photoisomerization of MC 540 proceeds faster in aqueous glycerol. To understand the effect of solute-solvent frictional coupling on photoisomerization rates, the following relation has often been used:

$$k_{\text{iso}} = F(\zeta)\exp(-E_0/RT). \tag{5}$$

In the above equation, E_0 is the intrinsic barrier height and R is the universal gas constant. The term $F(\zeta)$ is a dynamical quantity that depends on solute-solvent frictional coupling.[37] The solute-solvent frictional effects and the viscosity dependence of the isomerization rates are usually compared to theoretical models for $F(\zeta)$. Even though $\ln(k_{\text{nr}})$ versus $1/T$ plots are given in Fig. 5, the activation energies or barrier heights of the reaction cannot be estimated from such plots because of the expected influence of temperature on viscosity. For this purpose, isoviscous plots in a homologous series of solvents are often employed. Since the transition states involved in isomerization of DODCI and MC 540 have a polar character, solvent polarity also influences isomerization rate constants. To disentangle the effects of viscosity and polarity on isomerization rate constants and obtain the activation energies of the reaction, nonradiative rate constants were measured under isoviscous and isodielectric conditions and modified Kramers' equation has been employed.[5] However, in the present study, only two solvents of different nature were used, and hence the application of theoretical models to understand solute-solvent frictional coupling is not possible. Despite this limitation, the significant differences observed in the photoisomerization rate constants of MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol can be understood in a qualitative manner with the help of static solvation effects such as the solute-solvent hydrogen bonding.

Apart from the structure given in Fig. 1, MC 540 exists in zwitterionic resonance structures, as shown below.[37] Hydrogen bonding between the hydroxyl groups of aqueous glycerol and the carbonyl groups stabilizes the negative charge on the carbonyl oxygens, which lowers the energy of the zwitterionic structures and hence the barrier for isomerization is decreased.
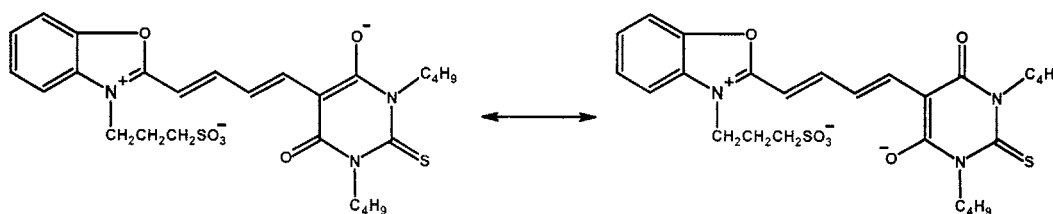
This explanation is consistent with the one given by Onganer et al.[37] while rationalizing the higher isomerization rate constants obtained for MC 540 in alcohols compared to nitriles. Although the results obtained for DODCI and MC 540 in a hydroxyl solvent such as aqueous glycerol appear to be along the expected lines, it was not evident whether or not these

two probes experience specific interactions with ions that constitute the ionic liquid, $[\text{bmim}^+][\text{PF}_6^-]$. From this study, it has been established that both DODCI and MC 540 do not experience specific interactions with $[\text{bmim}^+][\text{PF}_6^-]$, and the photoisomerization of these probes is solely governed by the viscosity of the medium.

To find an experimental evidence for this hypothesis, rotational diffusion measurements of the two solutes in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol were performed. Due to the high viscosities of the solvents used in this study, the reorientation times τ_r of both DODCI and MC 540 are significantly longer than their respective lifetimes. In view of the prevailing situation, time-resolved anisotropy measurements could not be employed, instead, the reorientation times were obtained from the measured steady-state anisotropies ($\langle r \rangle$) and lifetimes using Eq. (6).[40]

$$\tau_r = \frac{\langle r \rangle}{[r_0 - \langle r \rangle]} \tau_f. \tag{6}$$

In the above equation, r_0 is the limiting anisotropy and this parameter was obtained from the low temperature steady-state anisotropy measurements in glycerol. The respective r_0 values for DODCI and MC 540 were found to be 0.372 ± 0.006 and 0.374 ± 0.004. It must be noted that the above relation is valid only when the decay of fluorescence and the decay of anisotropy can be represented by single exponential functions. In the case of DODCI and MC 540, it has been established that both these conditions are fulfilled in conventional solvents.[51,52] However, whether the same conditions hold in the case of an ionic liquid such as $[\text{bmim}^+]$ $\times[\text{PF}_6^-]$ is debatable. This is due to the fact that quite a few studies available in literature indicate that anisotropy decays of dipolar organic solutes such as coumarin 153 (C153) in ionic liquids can only be described by stretched[14,15] or multiexponential[22] functions. Nonetheless, it must be noted that Horng *et al.*[53] have observed biexponential anisotropy decays for C153 even in conventional dipolar solvents. In contrast, anisotropy decays of other dipolar and nondipolar solutes such as 4-aminophthalimide, rhodamine 110 (at 348 K), 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP), and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) in $[\text{bmim}^+][\text{PF}_6^-]$ have been described by single exponential functions.[13,18,19] Despite these arguments and counterarguments, in the absence of direct time-resolved anisotropy measurements, the assumed single exponential functional form for the anisotropy decays of DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ is only circumstantial. It must also be borne in mind that the measurement of anisotropy decays when $\tau_r \gg \tau_f$ is not entirely impossible. In a recent study, Funston *et al.*[22] could measure anisotropy decays of C153 in a number of ionic liquids under similar circumstances. For this purpose, they collected very high peak counts over a large time window and employed better data analysis methods. However, with the resources available at our disposal, such an endeavor could not be undertaken in the present study.

For both the solutes at ambient temperatures, it was noticed that the measured values of $\langle r \rangle$ are close to r_0, thus the reorientation times could only be measured from 313 K. The measured reorientation time of a solute molecule in a given solvent can be described by the Stokes–Einstein–Debye (SED) hydrodynamic theory, as indicated below.[3]
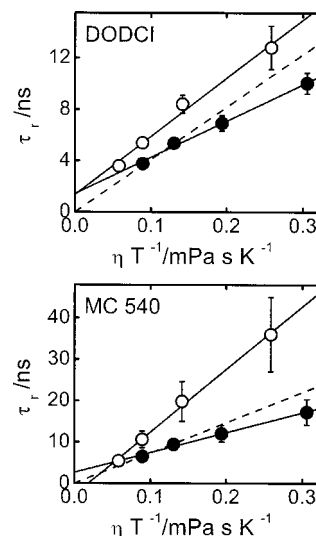

FIG. 7. Plots of τ_r vs η/T for DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ (●) and aqueous glycerol (○). The lines passing through the data points were obtained by linear least-squares fit. The dashed lines are the calculated ones using SED theory with stick boundary condition.

$$\tau_r = \frac{\eta V_h}{kT}, \tag{7}$$

where V_h is the hydrodynamic volume of the solute and k is the Boltzmann constant. Since the SED theory predicts a linear relationship between the solute reorientation time and solvent viscosity, τ_r versus η/T for DODCI and MC 540 in the two solvents are plotted in Fig. 7. The SED lines with stick boundary condition are also displayed in the figure. The hydrodynamic volumes of the two solutes obtained from the slopes of the plots of τ_r versus η/T in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol along with the ones calculated using the SED theory with stick boundary condition are given in Table IV. It is evident from the table that the hydrodynamic volume of DODCI in aqueous glycerol is larger by a factor of 1.5 compared to that in $[\text{bmim}^+][\text{PF}_6^-]$. It has been established that solvent attachment does not play an important role in the rotational diffusion of DODCI.[51] Thus the observed slower rotation of DODCI in aqueous glycerol compared to $[\text{bmim}^+][\text{PF}_6^-]$ is a consequence of the smaller size of glycerol compared to the ionic liquid. It must be noted that, in the absence of specific solute-solvent interactions, an

TABLE IV. Comparison of experimentally obtained and theoretically calculated hydrodynamic volumes of DODCI and MC 540 in $[\text{bmim}^+][\text{PF}_6^-]$ and aqueous glycerol. The probes DODCI and MC 540 were excited a 575 and 600 nm, respectively, and the emission was monitored in the range of 615–665 nm.

Solute-solvent system	$V_h/\text{Å}^3$	
	Experimental	Theoretical
DODCI/$[\text{bmim}^+][\text{PF}_6^-]$	391 ± 18	563^a
DODCI/aqueous glycerol	625 ± 50	563^a
MC 540/$[\text{bmim}^+][\text{PF}_6^-]$	662 ± 40	1010^b
MC 540/aqueous glycerol	2092 ± 83	1010^b

^{a}From Ref. 51.
^{b}From Ref. 52.

increase in the solvent size reduces the friction experienced by the rotating solute molecule, leading to a faster rotation. This aspect has been theoretically predicted[54,55] and experimentally verified in the case of a number of nonpolar solutes in nonpolar and/or dipolar solvents[6,56–61] and also in $[bmim^+][PF_6^-]$.[19] Even though the reorientation times of DODCI could not be measured below 313 K due to the reasons mentioned above, the values reported by us in the temperature range of 313–343 K are longer than the one reported by Chakrabarty *et al.*[9] at 298 K. This discrepancy again appears to be due to the differences in the excitation wavelengths employed in the two studies.

In contrast to DODCI, the hydrodynamic volume of MC 540 obtained in aqueous glycerol is larger by over a factor of 3 compared to that in the ionic liquid. This observation indicates that specific solute-solvent interactions are playing a significant role in the rotational diffusion of MC 540. Thus, the rotational diffusion studies carried out in this manner provide evidence to the hypothesis that in the case of MC 540 in aqueous glycerol, specific solute-solvent interactions are indeed stabilizing the zwitterionic structures of the solute, thereby lowering the barrier for isomerization. Apart from lowering the barrier height, specific solute-solvent interactions also increase the friction for rotational diffusion as well as twisting motion. It is a well-established fact that in the intermediate and high friction regimes, the rate constant for isomerization decreases as the friction increases.[4,5] However, in the case of MC 540 in aqueous glycerol, the effect of an increase in the friction on the isomerization rate constant is more than compensated by the lowering of the barrier height due to specific solute-solvent interactions.

IV. CONCLUSIONS

From the temperature-dependent isomerization study of two cyanine derivatives in $[bmim^+][PF_6^-]$ and aqueous glycerol, the following conclusions can be drawn. The nonradiative rate constants of DODCI measured under isoviscous conditions are more or less identical in both the solvents, indicating that viscosity alone controls the rate of photoisomerization. On the other hand, the nonradiative rate constants of MC 540 are found to be a factor of 2 higher in aqueous glycerol compared to $[bmim^+][PF_6^-]$. In the case of MC 540 in aqueous glycerol, the twisted state gets stabilized by the solute-solvent hydrogen bonding interactions due to its zwitterionic character, thus the barrier for isomerization is lowered. Further evidence for this hypothesis is provided by the rotational diffusion measurements, which indicate that the specific solute-solvent interactions are indeed stabilizing the zwitterionic structures of MC 540 in aqueous glycerol. The outcome of this study essentially reveals that both $[bmim^+][PF_6^-]$ and aqueous glycerol merely act as viscous liquids pertaining to the photoisomerization of DODCI, whereas in the case of MC 540, the chemical nature of aqueous glycerol and its ability to form hydrogen bonds with the solute have a profound bearing on the isomerization rates.

[1] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed. (VCH, New York, 1988).
[2] D. Kivelson, in *Rotational Dynamics of Small and Macromolecules*, edited by Th. Dorfmüller and R. Pecora (Springer-Verlag, Berlin, 1987).
[3] G. R. Fleming, *Chemical Applications of Ultrafast Spectroscopy* (Oxford University Press, New York, 1986) and references therein.
[4] D. H. Waldeck, Chem. Rev. (Washington, D.C.) **91**, 415 (1991) and references therein.
[5] D. H. Waldeck, in *Conformational Analysis of Molecules in Excited States*, edited by J. Waluk, (Wiley-VCH, New York, 2000), pp. 113–176.
[6] G. B. Dutt, ChemPhysChem **6**, 413 (2005).
[7] R. Ozawa and H. Hamaguchi, Chem. Lett. **2001**, 736.
[8] C. Lee, G. Mamantov, and R. M. Pagni, J. Chem. Research, 122 (2002).
[9] D. Chakrabarty, A. Chakraborty, P. Hazra, D. Seth, and N. Sarkar, Chem. Phys. Lett. **397**, 216 (2004).
[10] S. N. V. K. Aki, J. F. Brennecke, and A. Samanta, Chem. Commun. (Cambridge) **2001**, 413.
[11] K. A. Fletcher, I. A. Storey, A. E. Hendricks, S. Pandey, and S. Pandey, Green Chem. **3**, 210 (2001).
[12] S. N. Baker, G. A. Baker, M. A. Kane, and F. V. Bright, J. Phys. Chem. B **105**, 9663 (2001).
[13] J. A. Ingram, R. S. Moog, N. Ito, R. Biswas, and M. Maroncelli, J. Phys. Chem. B **107**, 5926 (2003).
[14] N. Ito, S. Arzhantsev, M. Heitz, and M. Maroncelli, J. Phys. Chem. B **108**, 5771 (2004).
[15] N. Ito, S. Arzhantsev, and M. Maroncelli, Chem. Phys. Lett. **396**, 83 (2004).
[16] D. Chakrabarty, A. Chakraborty, D. Seth, P. Hazra, and N. Sarkar, Chem. Phys. Lett. **397**, 469 (2004).
[17] D. Chakrabarty, A. Chakraborty, D. Seth, and N. Sarkar, J. Phys. Chem. A **109**, 1764 (2005).
[18] K. S. Mali, G. B. Dutt, and T. Mukherjee, J. Chem. Phys. **123**, 174504 (2005).
[19] K. S. Mali, G. B. Dutt, and T. Mukherjee, J. Chem. Phys. **128**, 054504 (2008).
[20] A. Samanta, J. Phys. Chem. B **110**, 13704 (2006).
[21] A. Paul and A. Samanta, J. Phys. Chem. B **111**, 4724 (2007).
[22] A. M. Funston, T. A. Fadeeva, J. F. Wishart, and E. W. Castner, Jr., J. Phys. Chem. B **111**, 4963 (2007).
[23] S. P. Velsko and G. R. Fleming, J. Chem. Phys. **76**, 3553 (1982).
[24] K. M. Keery and G. R. Fleming, Chem. Phys. Lett. **93**, 322 (1982).
[25] M. Lee, A. J. Bain, P. J. McCarthy, C. H. Han, J. N. Haseltine, A. B. Smith III, and R. M. Hochstrasser, J. Chem. Phys. **85**, 4341 (1986).
[26] M. Lee, J. N. Haseltine, A. B. Smith, and R. M. Hochstrasser, J. Am. Chem. Soc. **111**, 5044 (1989).
[27] R. M. Anderton and J. F. Kauffman, J. Phys. Chem. **98**, 12125 (1994).
[28] R. M. Anderton and J. F. Kauffman, J. Phys. Chem. **99**, 14628 (1995).
[29] C. Rullière, Chem. Phys. Lett. **43**, 303 (1976).
[30] V. Sundström and T. Gillbro, J. Phys. Chem. **86**, 1788 (1982).
[31] S. P. Velsko and G. R. Fleming, Chem. Phys. **65**, 59 (1982).
[32] S. P. Velsko, D. H. Waldeck, and G. R. Fleming, J. Chem. Phys. **78**, 249 (1983).
[33] K. Hara and S. Akimoto, J. Phys. Chem. **95**, 5811 (1991).
[34] M. Hoebeke, J. Piette, and A. V. Vorst, J. Photochem. Photobiol., B **4**, 273 (1990).
[35] P. F. Aramendía, M. Kreig, C. Nitsch, E. Bittersmann, and S. E. Braslavsky, Photochem. Photobiol. **48**, 187 (1988).
[36] P. F. Aramendía, R. Duchowicz, L. Scaffardi, and J. O. Tocho, J. Phys. Chem. **94**, 1389 (1990).
[37] Y. Onganer, M. Yin, D. R. Bessire, and E. L. Quitevis, J. Phys. Chem. **97**, 2344 (1993).
[38] P. F. Aramendía, R. M. Negri, and E. S. Román, J. Phys. Chem. **98**, 3165 (1994).
[39] H. A. Kramers, Physica (Amsterdam) **7**, 284 (1940).

[40] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed. (Plenum, New York, 1999).

[41] G. B. Dutt, V. J. P. Srivatsavoy, and A. V. Sapre, J. Chem. Phys. **110**, 9623 (1999).

[42] D. V. O'Connor and D. Phillips, *Time-Correlated Single Photon Counting* (Academic, London, 1984).

[43] N. Perisamy, S. Doraiswamy, G. B. Maiya, and B. Venkataraman, J. Chem. Phys. **88**, 1638 (1988).

[44] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).

[45] M. Kumbhakar, J. Phys. Chem. B **111**, 12154 (2007).

[46] C. Wakai, A. Oleinikova, M. Ott, and H. Weingärtner, J. Phys. Chem. B **109**, 17028 (2005).

[47] *Clean Solvents: Alternative Media for Chemical Reactions and Processing*, edited by M. A. Abraham and L. Moens (American Chemical Society, Washington, D.C., 2002).

[48] A. G. Fadeev and M. M. Meagher, Chem. Commun. (Cambridge) **2001**, 295.

[49] S. V. Dzyuba and R. A. Bartsch, ChemPhysChem **3**, 161 (2002).

[50] A. Paul, P. K. Mandal, and A. Samanta, Chem. Phys. Lett. **402**, 375 (2005).

[51] G. R. Fleming, A. E. W. Knight, J. M. Morris, R. J. Robbins, and G. W. Robinson, Chem. Phys. Lett. **49**, 1 (1977).

[52] D. R. Bessire and E. L. Quitevis, J. Phys. Chem. **98**, 13083 (1994).

[53] M.-L. Horng, J. A. Gadecki, and M. Maroncelli, J. Phys. Chem. A **101**, 1030 (1997).

[54] A. Gierer and K. Wirtz, Z. Naturforsch. A **8**, 532 (1953).

[55] J. L. Dote, D. Kivelson, and R. N. Schwartz, J. Phys. Chem. **85**, 2169 (1981).

[56] D. Ben-Amotz and J. M. Drake, J. Chem. Phys. **89**, 1019 (1988).

[57] M. Roy and S. Doraiswamy, J. Chem. Phys. **98**, 3213 (1993).

[58] R. M. Anderton and J. F. Kauffman, J. Phys. Chem. **98**, 12117 (1994).

[59] S. De Backer, G. B. Dutt, M. Ameloot, F. C. De Schryver, K. Müllen, and F. Holtrup, J. Phys. Chem. **100**, 512 (1996).

[60] J. Benzler and K. Luther, Chem. Phys. Lett. **279**, 333 (1997).

[61] G. B. Dutt and G. R. Krishna, J. Chem. Phys. **112**, 4676 (2000).