

The Effects of Pressure on the Intramolecular Proton Transfer and Charge Transfer of 4'-*N*-Dimethylamino-3-hydroxyflavone[†]

A. Zhu, B. Wang, J. O. White,* and H. G. Drickamer

School of Chemical Sciences and The Frederick Seitz Materials Research Laboratory,
University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, Illinois 61801-3792

Received: August 5, 2003; In Final Form: November 4, 2003

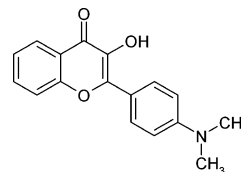
We report the effect of pressure on the intramolecular proton transfer and charge transfer of 4'-*N*-(dimethylamino)-3-hydroxyflavone(I) in five polymeric solvents (PAA, CAC, PAN, PMMA, and PVC). The intramolecular proton transfer and charge transfer are dependent on solvent, excitation wavelength, and pressure. The abnormal absorption and fluorescence spectra of I in PAA and PAN are explained by an interaction between the *N,N*-dimethylamino group and solvent molecules. The calculated proton-transfer rates show that excited-state intramolecular proton transfer is suppressed by pressure in all five polymers, but to different degrees. The effect of pressure on the fluorescence quantum yield of the normal state is quite different at different excitation wavelengths. When excited at 325 nm, the fluorescence quantum yield of the normal state increases with pressure, then decreases gradually. When excited at 441.6 nm, the fluorescence quantum yield of the normal state decreases with pressure.

Introduction

Excited-state intramolecular proton transfer (ESIPT) has attracted extensive attention because it yields unusual photo-physical properties.^{1–4} One of the striking model compounds is 3-hydroxyflavone.^{5–9} Like 3-hydroxyflavone, the fluorescence spectrum of 4'-*N*-alkylamino-3-hydroxyflavone exhibits two emission bands; one corresponds to the emission of the normal form (N*), the other to the phototautomer (T*).^{10–15} However, with the introduction of a strong electron donor, 4'-*N*-alkylamino, the normal form of 4'-*N*-alkylamino-3-hydroxyflavone also displays a significant intramolecular charge transfer (ICT) character, resulting in non-negligible normal emission even in alkane solvents. So the question arises whether there is competition between ESIPT and ICT. The reversal of the excitation behavior of ESIPT and ICT in 4'-*N*-alkylamino-3-hydroxyflavone by solvent dielectric perturbation has been investigated by Chou et al.¹⁰ Rettig et al. have observed the same behavior;¹² however, they suggest that the reason for the fluorescence change is a transformation between the TICT (twisted intramolecular charge transfer) state and the ESIPT state.

Pressure as a perturbing variable provides a way to change the environment of molecules in a continuous and controlled fashion. One can select a single matrix and vary its density and dielectric properties without altering its chemical composition.¹⁶ We have previously studied the effect of high pressure on the proton transfer in 3-hydroxyflavone and polyhydroxyflavones.¹⁷ Continuing our work in this paper, we report on the effect of pressure on ESIPT and ICT in 4'-*N*-(dimethylamino)-3-hydroxyflavone(I). The structure of I is shown in Scheme 1.

SCHEME 1: Structure of 4'-*N*-(Dimethylamino)-3-hydroxyflavone



Experimental Section

2'-Hydroxyacetophenone and 4-*N,N*-dimethylaminobenzaldehyde were purchased from Aldrich. 4'-*N*-(dimethylamino)-3-hydroxyflavone was synthesized by the modified Algar–Flynn–Oyamada reaction^{12,17} and then purified by repeated recrystallization from methanol until the elemental analysis was satisfactory. (Anal. calcd for C₁₇H₁₅NO₃: C 72.58%, H 5.37%, N 4.98%; found: C 72.24%, H 5.25%, N 5.00%).

Poly(acrylonitrile), $M_w = 150\,000$, density = 1.19) was purchased from Polysciencies, Inc. Poly(methyl methacrylate) (PMMA, medium molecular weight), poly(acrylic acid) (PAA, $M_w = 250\,000$, $T_g = 106\,^{\circ}\text{C}$), cellulose acetate (CAC, acetyl content 39.8%), and poly(vinyl chloride) (PVC, $M_w = 95\,000$, density = 1.40) were all Aldrich products. The polymers were used without further purification, because they do not emit when irradiated at the excitation wavelength.

The preparation of samples followed the procedure reported in previous papers.¹⁷ All the solvents used in the experiment were photometric grade. The samples were dried and stored in a vacuum oven. The concentration of 4'-*N*-(dimethylamino)-3-hydroxyflavone was 0.05 wt % in all cases.

The operation of the high-pressure diamond anvil cell has been described in detail elsewhere.^{18–20} For steady-state measurements, the emission spectra were obtained via excitation with the 441.6 and 325 nm lines of a HeCd laser. The absorption apparatus utilized light from a Xenon lamp, which was transmitted to and from the surface of the diamonds by optical

[†] This work was supported in part by the U.S. Department of Energy, Division of Materials Science Grant DEFG02-91ER45439 through the University of Illinois at Urbana-Champaign, Frederick Seitz Materials Research Laboratory.

* To whom correspondence should be sent. E-mail: white@MRL.uiuc.edu.

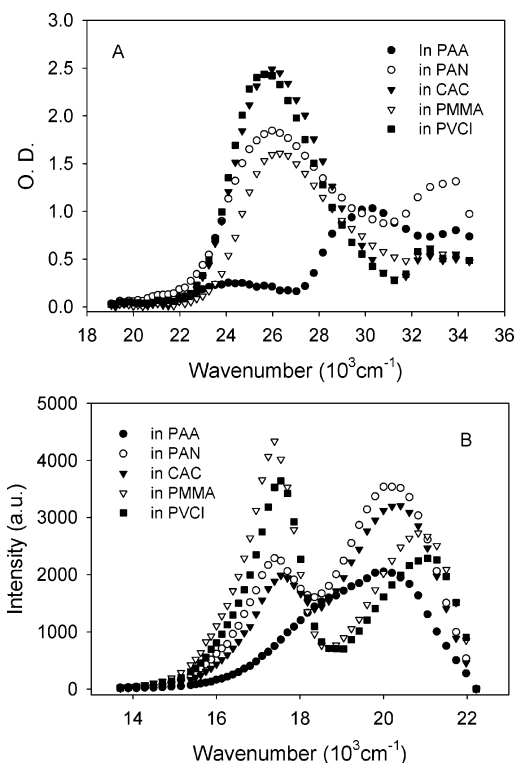


Figure 1. (A) Absorption spectra of I in five polymers at atmospheric pressure. (B) Fluorescence spectra, with excitation at 441.6 nm.

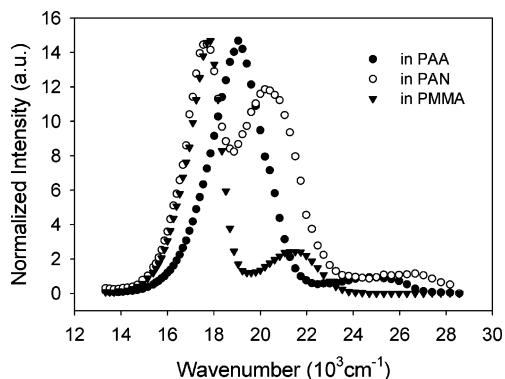


Figure 2. Fluorescence spectra of I in PAA, PAN, and PMMA, with excitation at 325 nm.

fibers. For the time-dependent measurements, the samples were excited by 100 fs pulses from an 80 MHz mode-locked Ti:Sapphire laser, after frequency doubling to 420 nm with a BBO crystal. The detection system involved an Acton 0.3 m monochromator, a Tennelec 863 time-to-amplitude converter, an Ortec 582 discriminator, and a Hamamatsu R1564 micro-channel plate photomultiplier.

Results and Discussion

1. Steady State. Solvent Dependence and Excitation Wavelength Dependence. The absorption and emission spectra of I at atmospheric pressure were taken in five polymeric solvents with different polarity: PAA, PAN, CAC, PMMA, and PVCl. The absorption and fluorescence spectra (excited by 441.6 and 325 nm) are presented in Figure 1 and Figure 2, respectively. The fluorescence peak positions and the ratios of the emission intensity of the excited normal state and the excited tautomer state are summarized in Table 1.

As shown in Figure 1B and Table 1, the ratio of the normal/tautomer fluorescence intensities increases with increasing

TABLE 1: Peak Positions and the Ratios of Dual Emission Intensities (N^*/T^*) of I in Five Polymers

polymer	ν_{\max} of normal state (cm^{-1})		ν_{\max} of tautomer (cm^{-1})		ratios of intensities (N^*/T^*)	
	325 nm	441.6 nm	325 nm	441.6 nm	325 nm	441.6 nm
PAA	24940	20510	19000	18940	0.07	0.76
PAN	20240	20150	17520	17430	0.80	1.85
CAC	20540	20300	17620	17580	0.77	1.86
PMMA	21280	20930	17690	17530	0.19	0.67
PVCl	21160	21000	17580	17410	0.27	0.68

polymer polarity, except in PAA. The tautomer emission is not very sensitive to the polarity of solvents, but the maximum of the normal emission is red shifted drastically with increasing solvent polarity. This result matches well with the typical solvatochromic effect of ICT. The absorption and emission spectra of I in PAA (I:PAA) differ substantially from those in other polymers. First, the normal and tautomer emission overlap in I:PAA, giving rise to a single broad emission band. Second, the low-energy absorption of I:PAA is much weaker, so that the main absorption band is at $\sim 30000 \text{ cm}^{-1}$. This explains why the tautomer emission intensity of I:PAA, excited at 441.6 nm, is lower than in other polymers.

In addition to the solvent polarity, the hydrogen bond between solute and solvent is another important factor to determine the balance between the charge transfer and proton transfer reaction. PAN is a strong H-bond acceptor; PMMA is a weak H-bond acceptor; CAC and PAA can act as both a H-bond donor and acceptor; PVCl cannot form a H-bond with I. ESIPT usually occurs across a preexisting intramolecular H-bond. Rupture of the *intermolecular* H-bond must occur prior to formation of an intramolecular H-bond. Strong intermolecular H-bonds can effectively suppress the ESIPT, while ICT is insensitive to hydrogen-bonding behavior. This is the reason that normal:tautomer ratios of fluorescence intensities in CAC and PAN are much higher than those in PVCl and PMMA.

Even the combination of solvent polarity and *intermolecular* hydrogen bonding cannot account for the anomalous behavior of I:PAA. Compared to other polymers, the tautomer and normal emission of I:PAA are blue-shifted to 19000 and 22940 cm^{-1} (Figure 2). The emission spectrum is identical to that of 3-hydroxyflavone.^{17a} This result can be explained by the covalent interaction between PAA and the dimethylamino substituent, which prohibits the ICT reaction. Chou et al. observed similar behavior for 4'-N-diethylamino-3-hydroxyflavone in CHCl_3 saturated with HCl gas.¹⁰

On the basis of the strong high-energy absorption at $\sim 33470 \text{ cm}^{-1}$ (Figure 1A) and the high-energy emission tail at $\sim 26500 \text{ cm}^{-1}$ (Figure 2), we can conclude that in addition to the H-bonds, PAN may have other interactions with the solute molecule. PAN is not likely to covalently bind to I. However, intermolecular charge transfer between the strong electron donor ($-\text{N}(\text{CH}_3)$) and the strong electron acceptor ($-\text{CN}$) is possible. So, the intermolecular charge transfer perturbs the intramolecular charge transfer, resulting in the appearance of the new emission band centered at 26650 cm^{-1} and the low fluorescence efficiency of I:PAN. The fluorescence intensity in PAN is only one-third of that in PMMA (25% of that in PAA).

In each polymer, the choice of excitation wavelength does not affect the tautomer fluorescence peak position. However, the choice of excitation wavelength does effect the ratio of normal and tautomer intensity. The tautomer emission is favored with excitation at 325 nm, while the normal emission is favored at 441.6 nm. Therefore, the competition between ICT and ESIPT is excitation wavelength dependent. These results can be

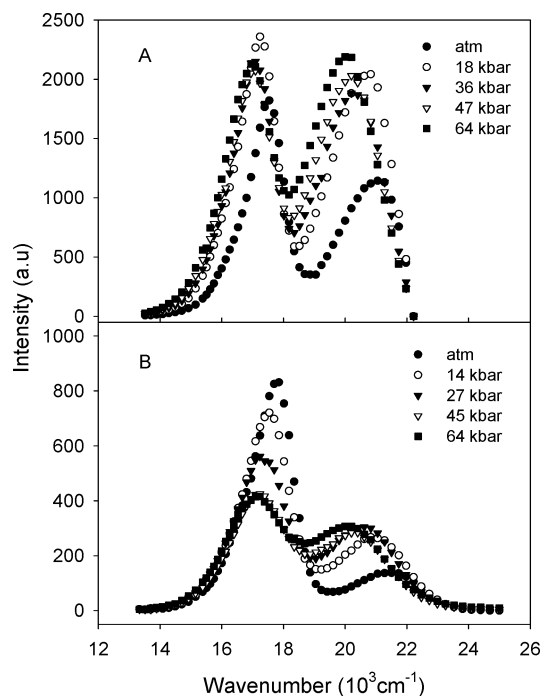


Figure 3. The effect of pressure on the fluorescence of I:PMMA. (A) Excited with 441.6 nm. (B) Excited with 325 nm.

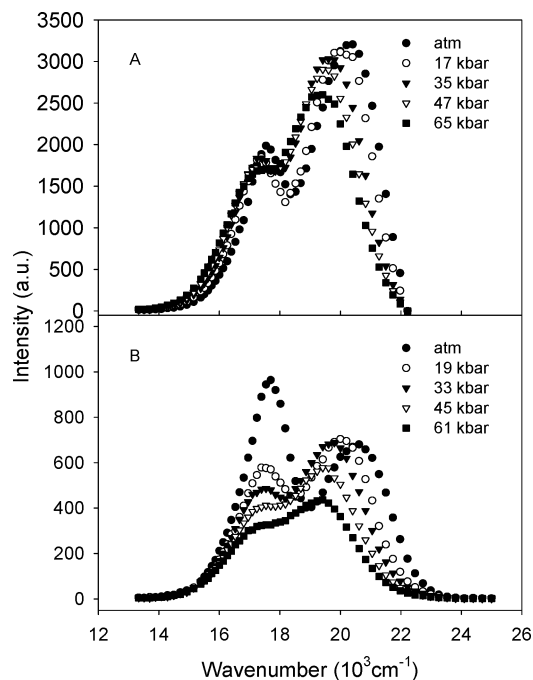


Figure 4. The effect of pressure on the fluorescence of I:CAC. (A) Excited with 441.6 nm. (B) Excited with 325 nm.

explained on the basis of the absorption spectra in Figure 1A. The low-energy peak is the ICT absorption, while the high-energy peak is from the benzopyrone structure. So, excitation at 441.6 nm favors the normal excited state, while excitation at 325 nm favors the phototautomer excited state.

Pressure Effect. Figure 3 shows the fluorescence spectra of I in PMMA at different pressures with excitation at 441.6 and 325 nm. Figure 4 shows the analogous results for CAC. The results for PVCl and PAN are not shown because they are similar to those for PMMA and CAC.

For I:PMMA, with increasing pressure, the normal state fluorescence intensities increase drastically at low pressures, and

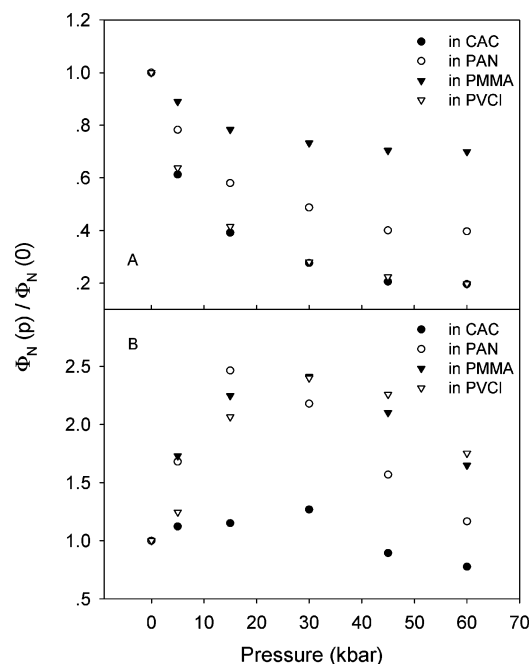


Figure 5. The effect of pressure on the normal state fluorescence quantum yield. (A) Excited with 441.6 nm. (B) Excited with 325 nm.

the fluorescence maxima red-shift remarkably. These trends are present at both excitation wavelengths. However, the effect of pressure on the tautomer luminescence is wavelength dependent. For excitation at 441.6 nm (Figure 3A), the tautomer fluorescence intensity is not very sensitive to pressure; after a larger red shift in the low-pressure range, the fluorescence maximum shifts only slightly. For excitation at 325 nm (Figure 3B), the tautomer fluorescence decreases gradually, while the normal fluorescence increases. There exists an isoemissive point.

For I:CAC, with increasing pressure, the normal state fluorescence intensity decreases for both excitation wavelengths; the fluorescence peaks shift to lower energy, as in PMMA. The tautomer fluorescence intensity does not show much dependence on pressure for excitation at 441.6 nm (Figure 4A). However, for excitation at 325 nm (Figure 4B), the tautomer fluorescence exhibits identical behavior to that in PMMA: the intensity decreases with increasing pressure, and there is an isoemissive point, which implies that there exists an equilibrium between the normal and tautomer states. Above 60 kbar, the measured fluorescence intensity may decrease because the hole in the gasket expands.

To quantitatively analyze the effect of pressure on the ICT and ESIPT, we fit each fluorescence spectrum with two Gaussian peaks. The relative fluorescence quantum yield of the normal state is given by

$$\frac{\Phi_N(p)}{\Phi_N(0)} = \frac{OD(0)A(p)}{OD(p)A(0)} \quad (1)$$

Φ_N is the normal state fluorescence quantum yield, OD is the optical density at the excitation wavelength, A is the area under the corresponding fluorescence band, and 0 and p correspond to atmospheric pressure and higher.

Because the cation and neutral molecules coexist in PAA, eq 1 is not applicable in this case. We present the calculated results for the other four polymers in Figure 5.

The relative fluorescence quantum yield decreases with pressure in all polymers for excitation at 441.6 nm (Figure 5A).

For excitation at 325 nm, the relative fluorescence yield in all polymers first increases with pressure and then decreases.

2. Time-Dependent Results. The time-dependent fluorescence curves can be better fitted by a double exponential decay for normal state and phototautomer; therefore, we apply Birks' scheme²¹ to describe the ESIPT process. The ratio of fluorescence quantum yields is given by

$$\frac{\Phi_T}{\Phi_N} = \frac{k_{PT}k_T^r}{k_N^r\tau_T} \quad (2)$$

Where Φ_N and Φ_T are the fluorescence quantum yield of the normal and tautomer state; τ_T is the slower of the two tautomer lifetimes; k_{PT} is the ESIPT rate; k_N^r and k_T^r are radiative rates for the normal and tautomer.

Solving for k_{PT} , we have

$$k_{PT} = \frac{k_N^r\Phi_T}{k_T^r\Phi_N\tau_T} = \frac{k_N^rA_Tn_T^2}{k_T^rA_N\tau_Tn_N^2} \quad (3)$$

Where n is the refractive index of the matrix and A_T and A_N are areas under the tautomer and normal fluorescence bands. In general, the radiative rate of aromatic molecules in a solid polymer is described by a single exponential and shows a negligible pressure dependence.²¹ Concerning I in solid polymers, our results show that τ_N and τ_T have a negligible pressure dependence. So, it is reasonable to make an approximation: k_N^r/k_T^r and τ_T are pressure independent.

Because we investigated the normal and tautomer states in the same media, $n_T^2/n_N^2 = 1$, the relative rates of proton transfer can be expressed as follows:

$$\frac{k_{PT}(p)}{k_{PT}(0)} = \frac{A_T(p)A_N(0)}{A_N(p)A_T(0)} \quad (4)$$

For all polymers and excitation at 325 nm, $k_{PT}(p)/k_{PT}(0)$ decreases rapidly with pressure reaching ~30% at 60 kbar (Figure 6B). On the other hand, with excitation at 441.6 nm, the variation of $k_{PT}(p)/k_{PT}(0)$ with pressure is matrix dependent. In PAN and CAC, $k_{PT}(p)/k_{PT}(0)$ first decreases until 25 kbar and then increases. However, in PMMA and PVCl, the ratios decrease monotonically, albeit less than in Figure 6B.

Conclusions

We have investigated the effect of pressure on ESIPT and ICT in 4'-N-(dimethylamino)-3-hydroxyflavone dissolved in polymeric matrixes. We can draw the following conclusions:

1. ESIPT and ICT depend on solvent, excitation wavelength, and pressure.
2. The abnormal photophysical properties of I:PAA are the result of protonation of the *N,N*-dimethylamino group.
3. Pressure suppresses the ESIPT to some extent in all of the polymers we investigated and at both excitation wavelengths.
4. The fluorescence quantum yield of the normal state depends on excitation wavelength and pressure. The fluorescence quantum yield of the normal state decreases with pressure when the excitation is at 441.6 nm but increases with pressure when the excitation is at 325 nm.

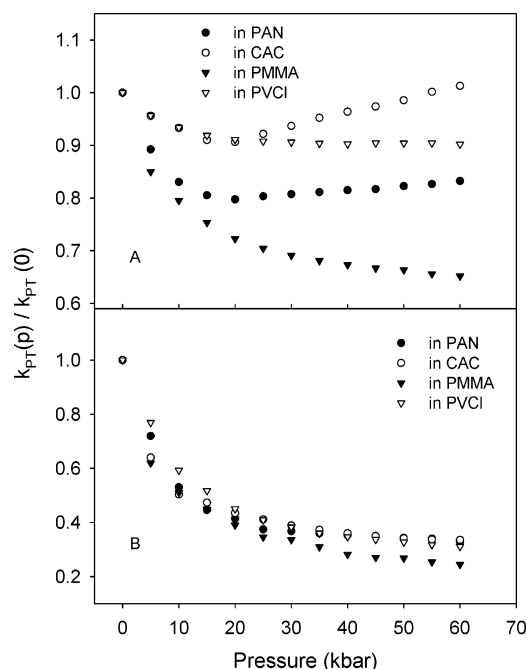


Figure 6. Relative proton-transfer rate $k_{PT}(p)/k_{PT}(0)$ vs pressure. (A) Excited with 441.6 nm. (B) Excited with 325 nm.

Acknowledgment. The authors wish to thank the U.S. Department of Energy, Division of Materials Science for continuing support under Grant DEFG 02-91ER45439 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign.

References and Notes

- (1) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.
- (2) Kasha, M. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2379.
- (3) Ormson, S. M.; Brown, R. G. *Prog. React. Kinet.* **1994**, *19*, 45.
- (4) Le Gourrieree, D.; Ormson, S. M.; Brown, R. G. *Prog. React. Kinet.* **1994**, *19*, 211.
- (5) Sengupta, P. K.; Kasha, M. *Chem. Phys. Lett.* **1979**, *68*, 382.
- (6) Strandjord, A. J. G.; Courtney, S. H.; Friedrich, D. M.; Barbara, P. F. *J. Phys. Chem.* **1983**, *87*, 1125.
- (7) Dick, B.; Ernsting, N. P. *J. Phys. Chem.* **1987**, *91*, 4261.
- (8) Schwarz, B. J.; Peteanu, L. A.; Harris, C. B. *J. Phys. Chem.* **1992**, *96*, 3190.
- (9) Bader, A. N.; Ariese, F.; Gooijer, C. *J. Phys. Chem.* **2002**, *106*, 2844.
- (10) Chou, P.-T.; Martinez, M. L.; Clements, J. H. *J. Phys. Chem.* **1993**, *97*, 2618.
- (11) Sytnik, A.; Gormin, D.; Kasha, M. *J. Fluoresc.* **1994**, *91*, 11968.
- (12) Ormson, S. M.; Brown, R. G.; Vollmer, F.; Rettig, W. *J. Photochem. Photobiol. A* **1994**, *81*, 65.
- (13) Roshal, A. D.; Grigorovich, A. V.; Doroshenko, A. O.; Pivovarenko, V. G.; Demchenko, A. P. *J. Phys. Chem. A* **1998**, *102*, 5907.
- (14) Nemkovich, N. A.; Baumann, W.; Pivovarenko, V. G. *J. Photochem. Photobiol. A* **2002**, *153*(1-3), 19.
- (15) Itoh, M.; Sumitani, F. M.; Yoshihara, K. *J. Phys. Chem.* **1986**, *90*, 5672.
- (16) Weber, G.; Drickamer, H. G. *Annu. Rev. Biophys.* **1983**, *16*, 89.
- (17) (a) Zhu, A.; Wang, B.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. B* **2003**, *107*, 9973. (b) Zhu, A.; Wang, B.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. A* **2003**, *107*, 6932.
- (18) Yang, G.; Dreger, Z. A.; Drickamer, H. G. *J. Phys. Chem. B* **1997**, *101*, 4218.
- (19) Dreger, Z. A.; Yang, G.; White, J. O.; Drickamer, H. G. *J. Phys. Chem. B* **1997**, *101*, 9511.
- (20) Yang, G.; Dreger, Z. A.; Li, Y.; Drickamer, H. G. *J. Phys. Chem. A* **1997**, *101*, 7948.
- (21) Birks, J. B. *Photophysics of Aromatic Molecular*; Wiley-Interscience: New York, 1970.