

## Solvent reorganization around a "giant dipole" molecule

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The fluorescence risetimes of the  $^1L_a$  and  $^1L_b$  excited states of *p*-dimethylaminobenzonitrile (DMAB) in ethanol and methylcyclohexane following irradiation at room temperature by the fourth harmonic (2650 Å) of a Nd<sup>3+</sup> glass laser were measured directly using picosecond spectroscopy. The onset of  $^1L_b$  fluorescence, governed by prior vibronic relaxation in both polar and nonpolar solvents, occurs within 7–20 psec after the exciting pulse. The  $^1L_a$  fluorescence, characterized by a noticeably longer risetime of  $\sim 40$  psec at room temperature, yields directly the solvent orientational relaxation time in the field of the  $^1L_a$  state's large dipole moment ( $\sim 23$  D). This measured relaxation time is consistent with a modification of the Debye theory of viscosity-limited solvent reorganization.

## INTRODUCTION

Picosecond spectroscopy<sup>1</sup> has succeeded in illuminating a number of relaxation processes characterizing bound, electronically excited molecules in solution. These have included:

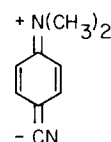
- (a) Electronic relaxation, which is unaffected by an inert solvent in the statistical limit.<sup>2,3</sup>
- (b) Redistribution of vibrational energy via intramolecular anharmonic coupling of the optically active vibrational modes with other vibrational modes.<sup>4</sup> Though this process also occurs in the isolated molecule, the medium may modify the intramolecular anharmonic terms.
- (c) Vibrational relaxation via coupling of the intramolecular vibrational modes with solvent modes (i. e. the nuclear motion of nearby solvent molecules).<sup>5,6</sup> This dissipates the intramolecular vibrations into "lattice" phonons.
- (d) Photochemical rearrangements<sup>7</sup> which may involve some or all of processes (a)–(c) in their intermediate stages.

By contrast, only meager direct information exists concerning solvent reorganization around an electronically excited state of a large molecule. Such intermolecular relaxation processes can originate from the following physical mechanisms:

- (1) In the case of extravalence excitation, short-range repulsions in the excited electronic state will prompt a radial expansion in the first solvent coordination layer.<sup>8,9</sup> Provided that this excited state is bound, a noticeable red Stokes shift will be observed between absorption and emission. Excited impurity states in ionic crystals (Tl doped alkali halides)<sup>10,11</sup> have exhibited this mechanism, as have solid and liquid rare gas alloys.<sup>12</sup>

- (2) Solvent reorientation due to polar interactions.<sup>13–15</sup> If an excitation of an intravalence electronic state from the ground state produces a large change of the molecular dipole moment, substantial solvent (angular) reorientation will follow, resulting in an appreciable Stokes shift between absorption and emission.

At present, most of the information concerning solvent reorientation has been inferred indirectly from spectral emission data in solution. In several classic works, Lippert *et al.*<sup>14,16</sup> reported dual fluorescences in *p*-dimethylaminobenzonitrile (DMAB) following excitation of its  $S_2$  state in solvents of varying polarity. While the lowest two electronic states  $S_0$ ,  $S_1$  of DMAB are nearly homopolar, the  $S_2$  state contains a large admixture of the intramolecular charge transfer state



characterized by a large dipole moment ( $\sim 23$  D).<sup>16</sup> In a nonpolar solvent, excitation of the  $S_2$  state will result in internal conversion to the  $S_1$  state, which will relax vibrationally before exhibiting  $S_1 \rightarrow S_0$  fluorescence (Fig. 1). In a very polar solvent, angular medium reorientation will lower the  $S_2$  state by  $\sim 1-2$  eV past the  $S_1$  state, resulting in  $S_2 \rightarrow S_0$  emission whose onset is controlled by orientational rather than vibrational relaxation.

As these dual fluorescences are well separated ( $\sim 350$  nm vs  $\sim 470$  nm) in wavelength, DMAB provides an ideal system for the study of polar solvent relaxation around a "giant" molecular di-

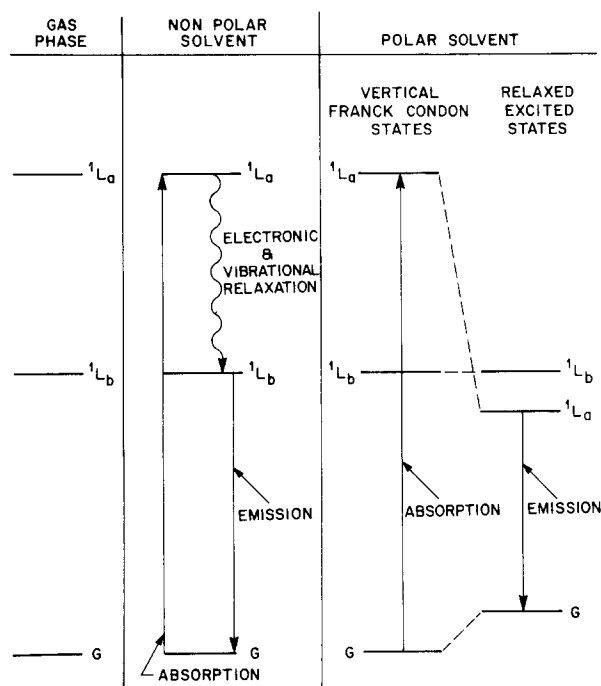


FIG. 1. Schematic energy level diagrams of DMAB in polar and nonpolar solvents.

pole. This paper presents an experimental study contrasting the picosecond time dependence of the emission spectra of DMAB in ethanol and methylcyclohexane.

#### EXPERIMENTAL

Samples of  $\sim 10^{-3} M$  *p*-dimethylaminobenzonitrile (Aldrich Chemical Co. used without further purifications) were dissolved in spectroscopic grade methylcyclohexane or absolute ethanol and excited to the  $^1L_a$  state by the fourth harmonic (2650 Å) of mode-locked pulse trains from a  $Nd^{3+}$  glass laser (average pulse width  $\sim 5$  psec as measured independently by three-photon fluorescence, separation  $\sim 7$  nsec). Eastman Kodak #9860 dye was used as the saturable absorber.

Mode-locking of the  $1.06 \mu$  laser fundamental was monitored with an ITT FW-114A photodiode (S-1 photocathode) and a Tektronix 519 oscilloscope. Phase matched KDP and temperature matched ADP crystals were used for successive frequency doubling (Fig. 2). The unconverted  $1.06 \mu$  fundamental was split from the sample interrogating beam for use as the trigger pulse which activated the  $CS_2$  optical shutter.<sup>17</sup> The length of the shutter cell was carefully chosen to provide a predetermined open time.<sup>18</sup> An echelon reflector<sup>19</sup> was used to generate a fixed stepped delay ( $\sim 7$  psec) between transversely separated

portions of the sample fluorescence. Thus, successive echelon segment images contained emission whose time spectra were consecutively delayed by an identical duration. Passage of this interrogating beam through the optical shutter (open time  $\sim 7$  and  $30$  psec for  $1$  cm and  $5$  cm  $CS_2$  cell lengths, respectively) subsequently produced an echelon image with segment intensities weighted according to the fluorescence time behavior. Simultaneous frequency selection was achieved with a Bausch and Lomb monochromator (dispersion  $\sim 75$  Å/mm) by aligning the echelon image along the length of the entrance slit. The transmitted fluorescence was amplified with an EMI 9693 image intensifier tube (intensity gain  $\sim 10^5$ ), and finally recorded on Polaroid 3000 speed film. Typical data are shown in Figs. 3–5.

Schott BG-18 and Corning 7-54 filters (F2 and F3, respectively, in Fig. 2) were located before and after the ADP doubling crystal to isolate the  $0.53$  and  $0.265 \mu$  laser harmonics, while a Schott BG-25 filter (F4) screened the residual  $0.53 \mu$  second harmonic pulses from the monochromator. The  $^1L_a \rightarrow ^1G$  fluorescence band centered at  $470$  nm in ethanol solution was isolated with a Corning 3-72 filter having a low wavelength cutoff at  $\sim 450$  nm. Most of the near-uv  $^1L_b$  emission from methylcyclohexane solution at  $\sim 350$  nm,<sup>16</sup> however, suffered considerable attenuation through the Polaroid butyrate-supported HNP-B optical shutter polarizers, and unpolarized transmission of the intense time-integrated fluorescence competed with the polarized transmission of time-resolved emission. This background was averted by selecting the longer wavelength fringe of the  $^1L_b$  fluorescence with a Corning 3-75 filter. Interfering light from the  $1.06 \mu$  trigger pulse was minimized by introduc-

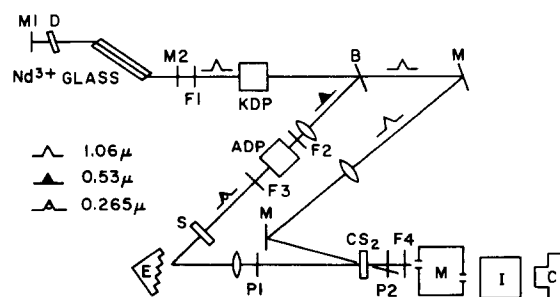


FIG. 2. Schematic diagram of apparatus used to determine fluorescence risetimes of DMAB in ethanol and methylcyclohexane. M1 and M2 denote the laser cavity mirrors, D the saturable dye absorber cell, B a beam splitter, F1–F4 filters, P1 and P2 polarizers, S the sample cell, and E the echelon. M, I, and C comprise the detector consisting of monochromator, image intensifier, and camera.

ing the trigger and interrogating beams at a very small angle ( $\lesssim 10^\circ$ ) into the  $\text{CS}_2$  cell. The absence of background due to filter fluorescence or solvent impurities was confirmed by blank runs using sample cells containing pure solvent.

#### RESULTS AND DISCUSSION

The fluorescence spectra reported by Lippert *et al.*<sup>14</sup> for DMAB in ethanol and methylcyclohexane were confirmed qualitatively with the use of color filters in conjunction with the monochromator. Time-resolved fluorescence data are presented for DMAB in ethanol solution in Figs. 3 and 4. In Fig. 3, the exciting pulse enters the optical shutter simultaneously with the emission in the fifteenth echelon segment from the right. Advancing the trigger pulse arrival by decreasing the optical path by  $\sim 50$  psec relative to the interrogating beam resulted in the data of Fig. 4, whose time

origin is thus shifted by this increment. It is evident here that the  $^1L_a$  emission reaches a constant level at  $t \sim 40-50$  psec after climbing from nearly zero intensity at  $t=0$ . Figure 4, which shows the filtered  $^1L_a$  fluorescence from  $\sim 50$  to 150 psec following the exciting pulse, indicates through its near uniformity in intensity that the  $^1L_a$  emission decay time is at least of the order of several hundred picoseconds. This behavior differs from the  $^1L_b$  emission from methylcyclohexane solution (Fig. 5), in which the exciting pulse coincides with the tenth segment to the left of the indicating arrow. It is evident here that the onset of the emission is preceded by vibronic relaxation from the fourth harmonic excited  $^1L_a$  manifold, and occurs between  $\sim 7$  and 20 psec. This observation is in agreement with previously observed rates for analogous relaxation in other systems.<sup>20</sup> Measurements of the  $^1L_a$  emission for later times, analogous to those

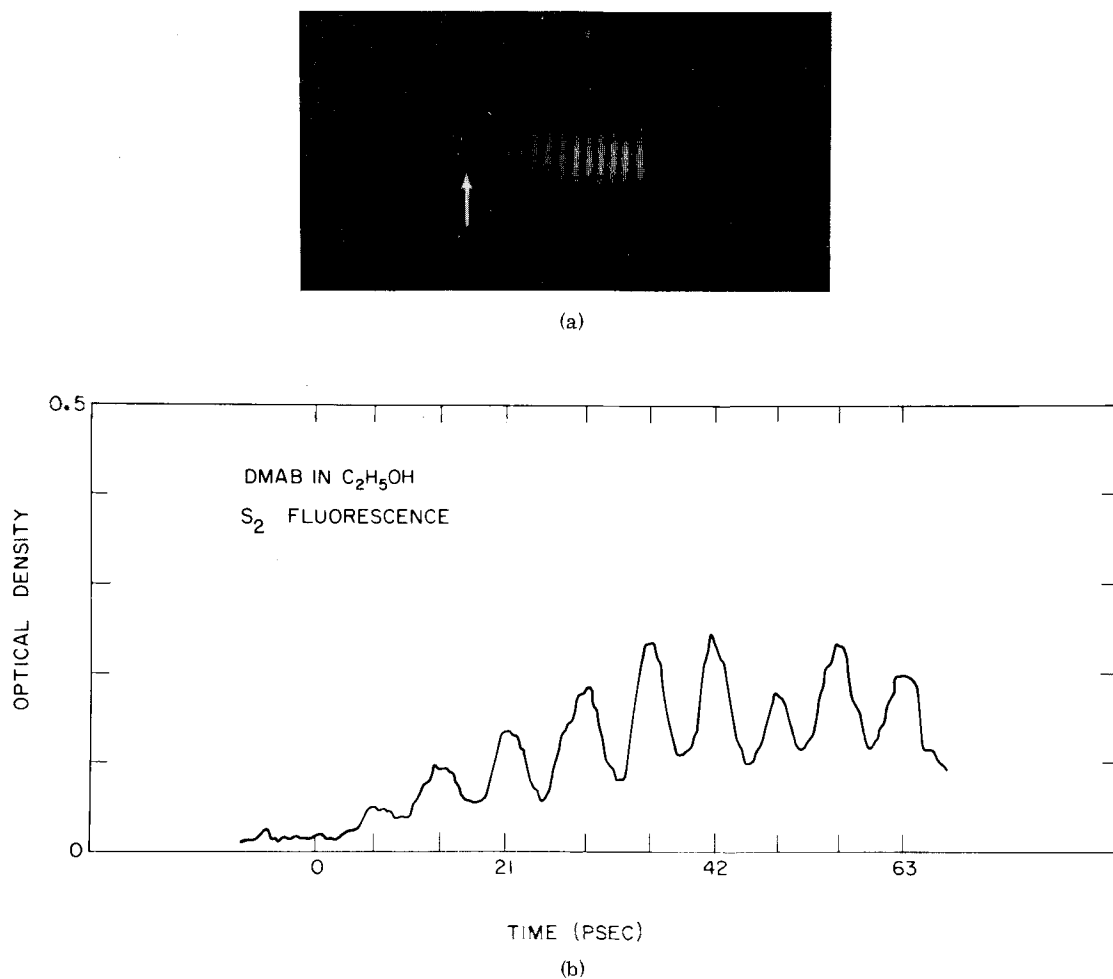


FIG. 3. (a) Photograph of time-resolved  $S_2-S_0$  emission of DMAB in ethanol solution. The time axis runs from left to right in 7 psec increments; the arrival of the exciting pulse coincides with segment indicated by the arrow. (b) Spectrodensitometer trace of (a).

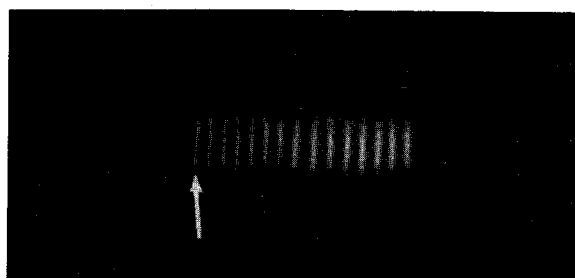
described for the  $^1L_b$  fluorescence (Fig. 4), indicate that its decay time is clearly greater than 200 psec.

We are thus led to conclude that the room temperature orientational relaxation of ethanol molecules following the sudden creation of the giant dipole is characterized by  $\tau \sim 40$  psec. There are no empirical dielectric relaxation times  $\tau_d$  for pure ethanol (which differ considerably from  $\tau_d$  of dilute solutions of ethanol in nonpolar solvents<sup>21</sup>) in the literature, though an order-of-magnitude estimate (following Wirtz<sup>22</sup>) for  $\tau_d \sim 2\pi\eta V/3kT$  in terms of the solvent viscosity  $\eta$  at 25 °C<sup>23</sup> and the molecular volume  $V \sim 20 \text{ \AA}^3$  yields  $\tau_d \sim 20$  psec.

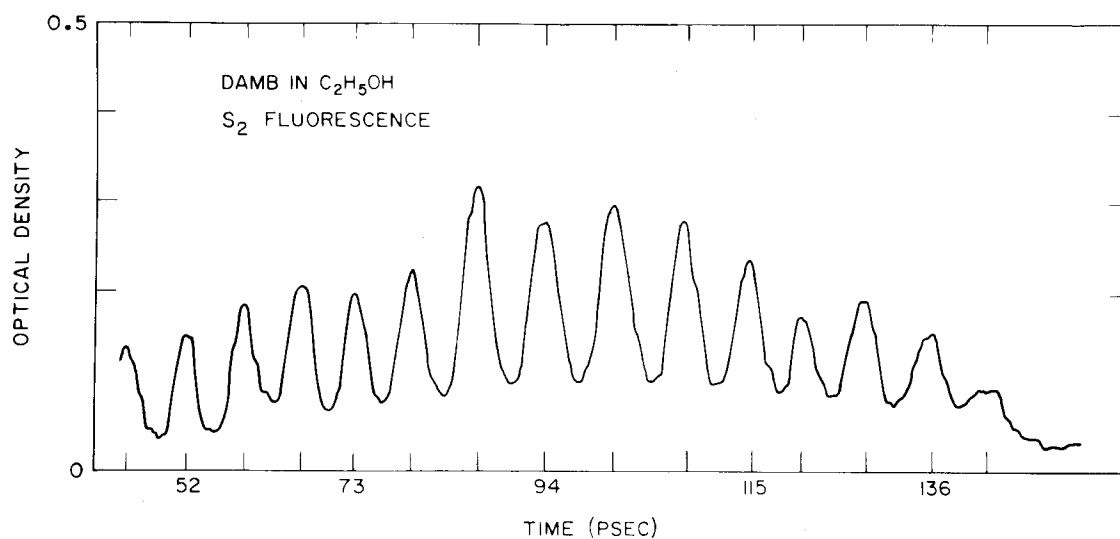
*Note added in proof:* We would like to emphasize at this point the fact that  $\tau \sim \tau_D$  provides a direct evidence for the original assumption<sup>14</sup> that the anomalous long wavelength ( $\sim 470$  nm) fluorescence of DMAB in polar solvents originates from solvent reorientation. As  $\tau$  was found to be concentration independent, the role of excimer emis-

sion suggested by McGlynn *et al.*<sup>24</sup> can be safely ruled out. Furthermore, recently it was reported by Rotkiewicz *et al.*<sup>25</sup> that the two emission bands are characterized by identical polarizations, ruling out the assignment<sup>14</sup>  $S_1 \equiv ^1L_b$  and  $S_2 \equiv ^1L_a$ . Although the energy levels of DMAB were not worked out theoretically, one can quite safely argue that the  $S_2$  state involves a large charge transfer component, while  $S_1$  is essentially a  $\pi \rightarrow \pi^*$  excitation. It was proposed<sup>25</sup> that the anomalous fluorescence may originate from an intramolecular conformational modification in the excited state. Our results do not concur with this conclusion.

Of particular interest is the variation of  $\tau$  with the solvent static dielectric constant  $\epsilon$  and temperature, which would reveal some relationship between the present process and the solvent  $\tau_d$  obtained by the usual<sup>21,26</sup> transient dielectric response studies. In the simplest approximation, the dipole moment of DMAB and  $\epsilon$  enter only in determining the  $^1L_a$  fluorescence red shift, given by<sup>15,16,27</sup>



(a)



(b)

FIG. 4. (a) Photograph of time-resolved  $S_2$ - $S_0$  emission of DMAB in ethanol solution, with the time axis commencing at  $\sim 50$  psec following the arrival of the exciting pulse. (b) Spectrodensitometer trace of (a).

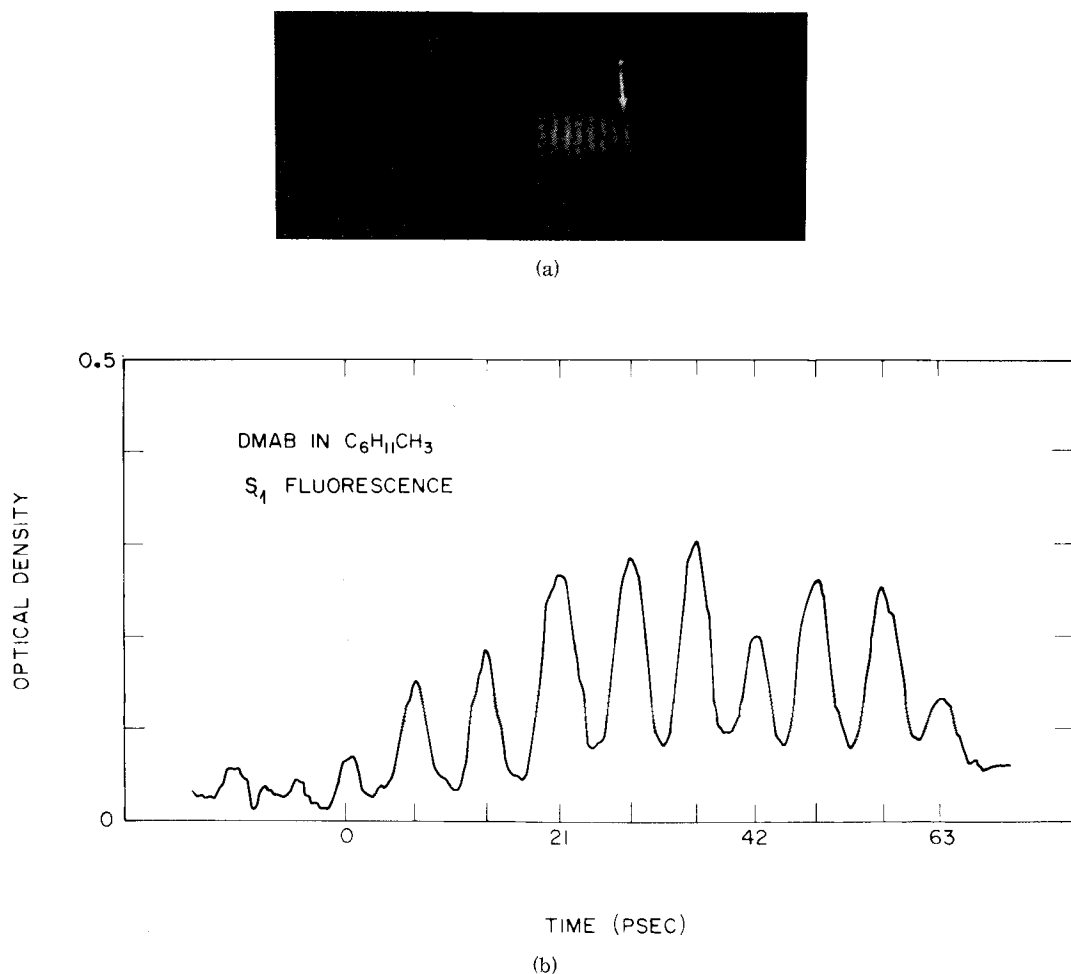


FIG. 5. Photograph of time-resolved  $S_1-S_0$  emission of DMAB in methycyclohexane solution. The exciting pulse arrives simultaneously with the tenth segment to the left of the arrow-indicated segment on the extreme right. (b) Spectrodensitometer trace of (a).

$$\Delta\nu = \frac{(\Delta\mu)^2}{V'} \left( \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 2}{2n^2 + 1} \right), \quad (1)$$

in which  $V'$  is the DMAB excluded volume,  $\Delta\mu$  is the  ${}^1G \rightarrow {}^1L_a$  increment in dipole moment, and  $n$  is the solvent refractive index. In this context, the relaxation times  $\tau$ , like  $\tau_a$ , reflect only the viscous rotational "drag" between neighboring solvent layers, and depend on temperature as  $\eta/T$ . Extensions of the present experiment are in progress to assess the dilation of  $\tau$  accompanying lowered temperatures, as well as explore the effects of solvent viscosity and dielectric constant.

The orientational relaxation of the solvent reaction field can be used as a means of controlling the output spectrum of several dye lasers.<sup>28-31</sup> The ratio of the associated relaxation time to the fluorescence lifetime has been inferred from spectral

shifts at various temperatures for 3-dimethylamino-6-methylamino-*N*-methylphthalimide in glycerine,<sup>28</sup> and detailed studies of orientational relaxation effects in the lasing characteristics of disubstituted fluorenes<sup>29</sup> have recently been carried out. The techniques of picosecond spectroscopy exhibit considerable potential to elucidate the underlying physical processes, which are also relevant to the solvation dynamics of zwitterions (characterized by dipole moments of  $\approx 20$  D for  $\beta$ - and  $\alpha$ -amino acids) as well as the kinetics of ionic reactions in aqueous solution.

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