while 1-naphthol-2-sulfonic acid fits the four-water scheme very well,<sup>10</sup> various other polysubstituted -OH and -SO<sub>3</sub><sup>-</sup> naphthalenes do not. In some of these cases, it is clear that there is an interference between inter- and intramolecular proton transfer.46 Certain other acids that seem very far removed from the ROH\* hierarchy also appear not to fit the four-water scheme very well. Examples<sup>47,48</sup> are 8-hydroxypyrene-1,3,6-trisulfonate and protonated 1-aminopyrene. In the former, complications from the polysubstituted nature of the molecule may play some as yet unknown role. In the latter molecule, not only is the  $pK_a$  very close to zero, but the cationic nature of this acid could cause a

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prepolarization of nearby water molecules, thus distorting the need for the four-water cluster. Certainly, more ultrafast dynamics work needs to be done on a variety of photon-initiated acid types, now becoming available,<sup>49</sup> before a complete picture is obtained. It would also help in the understanding of these processes if more extensive data on ground-state acid thermodynamics ( $\Delta S^{\circ}$  and  $\Delta H^{\circ}$ ) were available for nonaqueous, mixed aqueous, and deuterated solvents.

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## Femtosecond Studies of Excited-State Proton and Deuterium Transfer in Benzothiazole Compounds

#### Wilhelm Frey, Franz Laermer, and Thomas Elsaesser\*

Physik Department E 11, Technische Universität München, D-8000 München 2, Federal Republic of Germany (Received: March 27, 1991)

Intramolecular proton and deuterium transfer in the excited state of 2-(2'-hydroxyphenyl)benzothiazole (HBT) is investigated on the femtosecond time scale. The reaction steps occurring immediately after photoexcitation are temporally resolved in pump and probe measurements, where the onset of emission of the reaction product is monitored. For HBT in nonpolar solvents, the transfer of the proton occurs with a time constant of  $160 \pm 20$  fs. The deuterated analogue DBT undergoes a similar reaction with a transfer time of the deuterium of  $150 \pm 20$  fs. In polar solvents, the hydroxylic proton of HBT is shifted within the molecules on a time scale between 80 and 250 fs. The experimental results point to an essentially barrierless potential energy surface of the reaction in the excited state. The measured time constants correspond to the period of molecular vibrations of low frequency, suggesting proton and deuterium transfer via large-amplitude motions.

## Introduction

Intramolecular proton transfer in the electronically excited state represents an elementary photochemical reaction that has been studied in a large number of compounds.<sup>1-4</sup> Proton transfer often results in drastic changes of the electronic spectra, e.g., a large Stokes shift of the fluorescence of the reaction product relative to the absorption band of the original molecules. These spectra, which are related to changes of the molecular chromophore ( $\pi$ electron system), have been studied in steady state as well as time-resolved experiments to elucidate the pathway and the speed of the reaction. Proton-transfer times vary over a broad range from 100 fs<sup>5,6</sup> to microseconds<sup>7</sup> for different compounds. Specific information on the molecular geometry formed by proton transfer is available from time-resolved infrared measurements, where the vibrational bands of the relevant groups are monitored in the excited state.8.9

Here we address the photophysics of 2-(2'-hydroxyphenyl)benzothiazole (HBT) and its deuterated analogue 2-(2'deuterioxyphenyl)benzothiazole (DBT). In nonpolar solvents, the

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enol tautomer of HBT (I) represents the predominant ground-state species with a strong intramolecular hydrogen bond between the hydroxylic proton and the nitrogen atom.<sup>10,11</sup> Excitation of this



species via the  $S_0 \rightarrow S_1$  absorption band leads to the rapid formation of the keto tautomer (II) with N-H and C=O groups. In the excited keto tautomer, these new groups are linked by a strong intramolecular hydrogen bond, as is obvious from picosecond infrared studies of the respective stretching vibrations.<sup>8</sup> The keto species shows a strongly Stokes shifted fluorescence emission with maximum around 540 nm and a temperature- and solvent-dependent quantum yield.<sup>12-16</sup> In nonpolar solution at room temperature, the quantum yield and the lifetime of the excited state have respective values of several percent and several

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hundreds of picoseconds. Radiationless internal conversion to the keto ground state, intersystem crossing to the triplet manifold, and-possibly-cis-trans isomerization contribute to the deactivation of the excited keto molecules.<sup>14-16</sup> The reaction cycle of HBT is completed by the keto  $\rightarrow$  enol back-transfer, proceeding mainly via the electronic ground state.

In the present paper, we concentrate on the very fast end  $\rightarrow$ keto reaction in the excited state. Picosecond experiments, where the onset of the keto emission was monitored, gave an upper limit of the proton-transfer time of 4 ps, even at temperatures as low as 4 K.<sup>8,12,17</sup> The transfer reaction was temporally resolved in recent pump-probe studies with femtosecond pulses at two fixed wavelengths.<sup>5</sup> The formation time of the keto tautomer of 170  $\pm$  20 fs was measured with HBT dissolved in nonpolar tetrachloroethylene, suggesting a barrierless transfer of the proton in the excited singlet states. Further studies with tunable femtosecond pulses are necessary to obtain a more detailed picture of the reaction mechanism. In the following, we present new femtosecond data on proton and deuterium transfer in benzothiazole compounds. A proton-transfer time of 160 fs is measured in nonpolar solvents. Excited-state deuterium transfer, which is studied for the first time with femtosecond time resolution, occurs with practically identical time constants, confirming the barrierless shape of the potential energy surface relevant for the reaction. In polar solution, intramolecular proton transfer is observed on a time scale between 80 and 250 fs. The measured time constants suggest that low-frequency vibrations of large amplitude are involved in the intramolecular transfer reactions.

## **Experimental Section**

Commercially available HBT (Aldrich) was purified by liquid-phase chromatography. For H/D exchange of the hydroxylic proton, HBT was dissolved in a mixture of deuterated ethanol and  $D_2O$  at temperature of 330 K. After the deuterated molecules were separated by evaporating the alcohol, a large amount of tetrachloroethylene  $(C_2Cl_4)$  was added to dissolved DBT in the nonpolar solvent. Finally, the remaining D<sub>2</sub>O was removed.

The fraction of deuterated molecules in the sample was determined by vibrational spectroscopy. First, the extinction coefficient of the O-H stretching band of HBT dissolved in C<sub>2</sub>Cl<sub>4</sub> (concentration  $c = 5 \times 10^{-3}$  M) was measured.<sup>8</sup> The infrared spectrum of the deuterated sample of an identical concentration exhibits a strong O-D stretching band of DBT around 2250 cm<sup>-1</sup> and a weak residual O-H absorption due to nondeuterated (HBT) molecules. The concentration of the latter species amounts to 9  $\times$  10<sup>-4</sup> M, as estimated with the help of the known O-H extinction coefficient. The ratio of the two concentrations corresponds to a fraction of deuterated (DBT) molecules of approximately 80%. Samples for the femtosecond measurements were prepared with spectrograde tetrachloroethylene, benzyl alcohol, pyridine and acetonitrile as the solvents. The concentrations of HBT and DBT were in the range between  $10^{-4}$  and  $5 \times 10^{-3}$  M.

The pump and probe technique was applied in the femotsecond experiments. The samples were excited by an intense pump pulse in the ultraviolet region, and the resulting change of transmission was monitored by weak tunable probe pulses as a function of delay time. The time-dependent change of transmission gives direct information on the kinetics of photoinduced processes in the molecules.

Intense femtosecond pulses at 620 nm are generated in a colliding pulse mode-locked (CPM) dye laser and a six-pass dye amplifier that was pumped by a XeCl excimer laser. Details of this system have been published in ref 18. The energy and the duration of the amplified pulses have values of 20  $\mu$ J and 70 fs, respectively. Excitation pulses at a wavelength of 310 nm are produced by frequency doubling of part of the amplifier output in a thin KDP crystal (thickness l = 0.1 cm). The duration of



Figure 1. Absorption (lhs) and emission (rhs) spectra of HBT and DBT dissolved in  $C_2 Cl_4. \ The S_0 \rightarrow S_1$  absorption bands of the protonated and of the deuterated molecules are identical with a maximum extinction coefficient of 12600 M<sup>-1</sup> cm<sup>-1</sup>. The emission spectra with maxima in the green spectral range are Stokes shifted by approximately 11 000 cm<sup>-1</sup>.

the ultraviolet pulses amounts to 160 fs. The second part of the amplifier output is focused onto a jet of ethylene glycol to generate a femtosecond white light continuum containing wavelength components from 400 to 850 nm. A tunable dichroic filter selects a well-defined part of the continuum that serves as a probe pulse of a duration of 90 fs. The energy of the probe pulses is less than 2% of the pumping energy. The polarization vectors of pump and probe enclose the ("magic") angle of 54.7° to suppress the influence of rotational relaxation on the measured transmission changes.

The time resolution and the delay zero are determined with the help of laser dyes showing an excited-state lifetime of several hundred picoseconds.  $S_0 \rightarrow S_n$  transitions of the dye molecules are excited by the pump pulse at 310 nm. The instantaneous depletion of the ground state is monitored by probe pulses in the spectral range of the strong  $S_0 \rightarrow S_1$  absorption band. For weak excitation, the population decrease of  $S_0$  follows the time integral over the excitation pulse, since the  $S_1$  lifetime is much longer than the pulse duration. The transmission change monitored by the probe pulse is proportional to the convolution of this kinetics with the probe pulse envelope; i.e., the temporally integrated crosscorrelation function is measured.<sup>18</sup>

#### Results

Proton and Deuterium Transfer in Nonpolar Solution. Absorption and emission spectra of HBT and DBT dissolved in C<sub>2</sub>Cl<sub>4</sub> are summarized in Figure 1. The normalized  $S_0 \rightarrow S_1$  bands of the enol species I and III are plotted on the left-hand side. The maximum extinction coefficient at 340 nm has an absolute value of 12600  $M^{-1}$  cm<sup>-1</sup>. The spectral position and the shape of the two absorption spectra in Figure 1a,b are identical.

HBT as well as DBT shows a strongly Stokes shifted fluorescence band due to the respective keto tautomers (rhs of Figure 1). The emission maximum of DBT occurs at slightly longer wavelengths than that of HBT. The fluorescence quantum yield of both HBT and DBT dissolved in C<sub>2</sub>Cl<sub>4</sub> amounts to approximately 2% with identical fluorescence decay times of 300 ps.<sup>13</sup> This finding demonstrates that the yield of *formation* of excited keto tautomers is not affected by deuteration. The decay time of the emission is substantially shorter than the radiative lifetime of the keto  $S_1$  level of 15 ns,<sup>13,19</sup> pointing to a predominantly radiationless decay of the emitting keto levels.

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**Figure 2.** (a) Femtosecond ground-state bleaching of rhodamine 101 in ethanol (excitation wavelength 310 nm, probe wavelength 570 nm). The data give the time-integrated cross-correlation function of pump and probe pulses. (b, c) Emission kinetics of HBT in  $C_2Cl_4$  for different wavelengths  $\lambda_{pr}$  in the emission band (points, excitation wavelength 310 nm). The gain  $G = \ln (I/I_0)$  is plotted versus the delay time between pump and probe pulses. The delayed onset of stimulated emission reveals the delayed formation of the keto species by excited-state proton transfer. The solid lines are calculated from a rate equation model as explained in the text. The theoretical analysis gives a proton-transfer time of 160 fs.

We now present results of our femtosecond experiments. The data in Figure 2a, which serve for a calibration of delay zero, represent the time-dependent absorption change  $\Delta A = -\ln (T/T_0)$  of a dye solution (rhodamine 101 in ethanol) for a probe wavelength  $\lambda_{pr} = 570$  nm, after excitation by an ultraviolet pulse at 310 nm ( $T_0$  and T are the transmission of the sample before and after excitation). The time evolution of  $\Delta A$  is determined by the ground-state bleaching of the dye molecules that follows the time integral of the correlation function of pump and probe pulses. The solid line through the experimental points gives the temporally integrated cross correlation of two sech<sup>2</sup> pulses with a duration of 160 and 90 fs and is in good agreement with the experimental result.

Data measured with HBT dissolved in  $C_2Cl_4$  are plotted in Figure 2b,c for probe wavelengths of 540 and 570 nm, respectively. At these spectral positions in the keto emission band, the probe pulses are amplified by interaction with the excited molecules in the sample. The probe light induces transitions from the fluorescent excited state to the ground state of the keto tautomer. In Figure 2b,c, the gain  $G = \ln (I/I_0)$  is plotted versus delay time;  $I_0$  and *I* represent the intensities of the incident and the amplified probe pulses. The signal has a maximum value of  $G \simeq 0.01$ , corresponding to small signal amplification. Here, the gain *G* is proportional to  $(N_{S_1'} - N_{S_0'})\sigma_{em}l$ , where  $N_{S_0'}$  and  $N_{S_1}'$  represent the population densities of the keto ground  $(S_0')$  and excited state  $(S_1')$ , respectively;  $\sigma_{em}$  is the emission cross section and *l* the thickness of the sample. Prior to excitation, the keto ground state is not populated:  $N_{S_0'} = 0$ . Consequently, the time evolution of the gain is determined by the population kinetics of the excited keto state formed by intramolecular proton transfer.

The rise of the gain in Figure 2b,c exhibits a substantial delay in relation to delay zero and is temporally broadened compared to the kinetics plotted in Figure 2a. This observation gives direct evidence of the delayed formation of the emitting keto molecules.



**Figure 3.** Gain kinetics of (a) HBT and (b) the deuterated analogue DBT dissolved in  $C_2Cl_4$ . The samples are excited at  $\lambda_{ex} = 310$  nm, and the time-dependent gain is monitored by probe pulses at  $\lambda_{pr} = 540$  nm (points). The solid lines represent results of a numerical simulation, where risetimes of 160 and 150 fs were used for HBT and DBT, respectively.

It is important to note that the onset of amplification occurs with similar delay times at all probe wavelengths between 520 and 630 nm;<sup>5</sup> i.e., the different components of the emission spectrum build up simultaneously. On a slower picosecond time scale, the gain decreases with a time constant of 300 ps, the lifetime of the emitting levels. This behavior is in good agreement with the fluorescence decay observed in earlier picosecond experiments.<sup>13</sup>

The deuterated compound DBT was also investigated in nonpolar solution. The experimental parameters, i.e., the concentration of the solution and the intensity of the excitation pulses, were identical with the measurements with HBT. The gain kinetics of DBT observed at a probe wavelength of  $\lambda_{pr} = 540$  nm is plotted in Figure 3b. The buildup of the gain in the deuterated molecules shows a delay time that is close to the rise time of the emission of HBT at the same  $\lambda_{pr}$ ; i.e., the formation rate of the keto species is quite insensitive to a H/D exchange. This behavior suggests a barrierless potential energy surface of excited-state proton and deuterium transfer, as will be discussed in the next section.

The solid lines in Figures 2 and 3 were calculated from a rate equation model, comprising the following four levels: the ground state  $S_0$  and the excited state  $S_1$  of the enol tautomer and the corresponding states  $S_0'$  and  $S_1'$  of the keto species. The different photophysical processes are simulated by exponential kinetics which are characterized by time constants  $\tau_i$ . After excitation of the  $S_1$  state by the femtosecond pump pulse, the proton (deuterium) transfer leads to the population of the keto  $S_1'$  level (time constant  $\tau_1$ ). The excited keto state decays with a slower picosecond kinetics (time constant  $\tau_2$ ) to S<sub>0</sub>'. The keto ground state is depopulated by the keto  $\rightarrow$  enol back-reaction, which proceeds on an even slower time scale. Contributions of the  $S_1$ deactivation and of the back-reaction to the subpicosecond behavior of the molecules are negligible. The calculated signal is taken proportional to the difference of the populations of the  $S_1'$  and of the  $S_0'$  state,  $N_{S_1'} - N_{S_0'}$ , and is convoluted with the envelope of the probe pulses. The solid lines in Figure 2b,c, which are in good agreement with the data points, were calculated with  $\tau_1 =$ 160 fs and  $\tau_2 = 300$  ps. For the deuterated molecule DBT (Figure 3b), a similar value of  $\tau_1 = 150$  fs was found. Within the experimental uncertainty of  $\pm 20$  fs, the transfer times of proton and deuterium are identical.

**Proton Transfer in Polar Solvents.** The vibrational spectra of HBT in polar solvents suggest that the strong intramolecular hydrogen bond formed in nonpolar solution (structure I) is either replaced by a H bridge to solvent molecules, e.g., in pyridine and alcoholes, or cleaved like in acetonitrile.<sup>13,20</sup> The electronic



Figure 4. Gain kinetics of HBT dissolved in (a) pyridine, (b) acetonitrile, and (c) benzyl alcohol (BA) (points). The excitation and probe wavelengths are  $\lambda_{ex}$  = 310 nm and  $\lambda_{pr}$  = 540 nm, respectively. A delayed nonexponential rise of emission is observed.

absorption and fluorescence bands in polar solution suggest an intramolecular proton transfer of the excited molecules, similar to the behavior in nonpolar solvents. The keto emission in polar environment, which was studied in picosecond experiments, rises within 4 ps after excitation, even for the modified geometry of the O-H proton donor.<sup>12,13</sup> More detailed information on the reaction kinetics is obtained from femtosecond measurements we discuss now.

In Figure 4, the buildup of the keto emission at  $\lambda_{pr} = 540$  nm is plotted for HBT in (a) pyridine, (b) acetonitrile, and (c) benzyl alcohol (BA). In all cases, the rise of the gain is shifted to positive delay times by up to 250 fs, similar to the results in the nonpolar solvent (Figures 2 and 3). This observation demonstrates that the enol  $\rightarrow$  keto reaction rates of HBT molecules without internal hydrogen bond are of the same order of magnitude as for the species with the N-H-O bridge. In contrast to the data in Figures 2 and 3, however, the rise of the signals in Figure 4 does not follow a simple monoexponential behavior. The slope of the experimental curves measured in polar solution is considerably higher than calculated from a kinetics with transfer times  $\tau_1$  that are estimated from the overall shift of the data points to positive delay times. The nonexponential onset of gain may be related to solvent effects during proton transfer, e.g. polar solvation.<sup>21</sup> Further experimental studies, where transient emission spectra are recorded, are required to clarify this problem.

The emission decays in the picosecond regime with time constants of 20 ps for HBT in pyridine, 12 ps in acetonitrile, and approximately 50 ps in BA. These values agree with the results of previous picosecond measurements of the fluorescence kinetics.<sup>13</sup>

#### Discussion

We first discuss the mechanisms of the excited-state enol  $\rightarrow$ keto transformation of HBT. In our experiments, the femtosecond

pump pulse at 310 nm populates vibronic  $S_1$  states of the enol tautomer via a vertical transition; i.e., the nuclear configuration of the molecules remains unchanged during excitation. The redistribution of electronic charge occurring immediately after absorption of the ultraviolet photon establishes a new potential energy surface of the hydroxylic proton with a minimum for the keto configuration of the molecule. Quantum chemical calculations indicate a strong increase of electron density on the nitrogen atom of the thiazole moiety, whereas the covalent bond of the proton to the oxygen atom is weakened.<sup>22</sup> This process occurs on a time scale much faster than 70 fs, the temporal resolution of the experiment. Some of the normal modes of enol HBT are now displaced from their new equilibrium positions, which are defined by the new potential. Consequently, those degrees of freedom evolve temporally until the final keto configuration is reached. The delayed onset of keto emission observed in the different measurements is due to the motion of the proton on the excited-state potential, characterized by time constants between 80 and 250 fs.

The geometry of the hydrogen-bonded O-H group, which acts as the proton donor, is markedly different in nonpolar and polar solvents as explained above. Nonetheless, the keto emission rises with similar delay times in all cases investigated (cf. Figures 2 and 4). This observation suggests that the potential energy surface is mainly determined by the intramolecular charge redistribution. Solvent-induced changes of the hydrogen-bonding geometry seem to be of secondary importance.

Qualitative information on the shape of the potential energy surface in the excited state is obtained from the data on HBT and DBT in nonpolar solvents, which demonstrate nearly identical rise times of the keto emission. The absence of an H/D isotope effect demonstrates that tunneling through a potential well between an enol and a keto minimum can be ruled out as a transfer mechanism. This process would result in a much slower motion of the deuterium than of the proton. Obviously, the transfer reaction proceeds on a barrierless surface with a substantial slope, i.e., driving force, for the enol configuration and a broad keto minimum. The time scale of motion is determined by the period of vibrations that are displaced after electronic excitation. Here the O-H or O-D stretching vibrations with a period between 30 and 50 fs are of minor relevance, as suggested by the lack of a deuterium effect and the substantially longer time constants of 80-250 fs found in the different experiments. The latter values correspond to large-amplitude vibrations in the frequency range between 50 and 200 cm<sup>-1</sup>. Thus, vibrational degrees of freedom showing practically no deuterium shift of their low frequency are involved in proton and deuterium transfer. Two types of structural change have to be considered: (i) The separation of the oxygen donor atom and the accepting nitrogen atom could be fixed during the reaction, and the proton (deuterium) is shifted over a relatively long distance from its original to its final location. (ii) In addition to proton (deuterium) motion, a reorientation of the remainder molecule could participate in forming the keto species. The second mechanism involves additional degrees of freedom of the thiazole and the phenyl parts of the molecular structure, which are expected to lie in the same frequency range of 50-200 cm<sup>-1</sup>. Both mechanisms are consistent with our present data and further experiments, e.g., with sterically fixed derivatives, are necessary to identify the dominating low-frequency motions.

After femtosecond excitation of the enol tautomer, vibronic relaxation of modes not involved in proton transfer occurs on a similar time scale as the chemical reaction.<sup>18,23</sup> The excess energy supplied by the excitation pulse is redistributed over many vibrations, and an equilibrium distribution of elevated vibrational temperature is established in the molecules. Nonequilibrium populations of higher lying vibrational modes should result in a transient enhancement of the short-wavelength edge of the emission spectrum.<sup>24</sup> However, the simultaneous onset of keto

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emission over a broad spectral range suggests an essentially equilibrated vibrational system of the keto species produced by proton transfer.

The vibrationally hot molecules cool down by collisional interaction with the surrounding solvent on a time scale of 10-50 ps.<sup>23</sup> In the femtosecond measurements, a broad interval of vibronic  $S_1$  states in the range of the keto minimum contributes to stimulated emission at a specific probe wavelength. Even for high transient temperatures of the molecules of 500-1000 K, the population density of those states is very large compared to that of levels on the high-energy tail of the distribution. As a result, the gain is not very sensitive to changes of the vibrational temperature. The cooling kinetics makes no significant contribution to the measured signal; i.e., the measured time constants are identified as proton- and deuterium-transfer times.

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## Conclusions

We have studied proton and deuterium transfer in the first excited singlet state of benzothiazole compounds by femtosecond pump-probe spectroscopy. In nonpolar solvents, proton- and deuterium-transfer times of 160 and 150 fs have been found. Intramolecular proton transfer in polar solution occurs on a similar femtosecond time scale. These results suggest a barrierless potential energy surface of the excited-state reaction with a rate determined by the period of low-frequency vibrations of large amplitude. Our recent studies of benzotriazoles<sup>6</sup> reveal similar femtosecond kinetics of proton transfer. Thus, the reaction scheme reported here may be valid for a larger class of aromatic molecules.

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Registry No. DBT (keto tautomer), 136067-11-3; DBT (enol tautomer), 30612-16-9; HBT (keto tautomer), 67294-91-1; HBT (enol tautomer), 3411-95-8; D2, 7782-39-0.

# Intermolecular Dynamics in Acetonitrile Probed with Femtosecond Fourier Transform Raman Spectroscopy

## Dale McMorrow\*

Naval Research Laboratory, Code 4613, Washington, D.C. 20375

## and William T. Lotshaw\*

G.E. Research and Development, P.O. Box 8, Rm. KWD-270, Schenectady, New York 12301 (Received: March 27, 1991)

We present femtosecond optical heterodyne detected optical Kerr effect measurements of the transient birefringence of neat acetonitrile liquid. Using a recently developed Fourier transform analysis, the transient data are presented in both the timeand frequency-domain representations. The nuclear contributions to the transients, free from any distortions introduced by the electronic response, are generated from the frequency-domain data. The focus of this work is on the high-frequency dynamics associated with intermolecular vibrational degrees of freedom. We observe markedly nonexponential dynamics at short times, with the long-time relaxation characterized by an  $\sim$ 1.4-ps exponential time constant. The femtosecond dynamics exhibit characteristics of rapid inhomogeneous dephasing, which accounts for  $\sim 80\%$  of the signal decay, as well as evidence for contributions from lower frequency, overdamped oscillators. The NLO intermolecular vibrational spectrum of acetonitrile exhibits a broad resonance with a band maximum of  $\sim 55$  cm<sup>-1</sup> and a bandwidth of  $\sim 100$  cm<sup>-1</sup>. The femtosecond transients emphasize the role of the (microscopic) intermolecular potential energy surfaces in shaping the short-time vibrational aspects of the intermolecular dynamics in this liquid. The possible role of similar considerations in the short-time aspects of dynamic solvation phenomena is discussed. The manifestations of intermolecular vibrational motion in solvation transients have not yet been observed experimentally but are revealed clearly in recent molecular dynamics simulations. The correspondence between certain aspects of the two experiments is noted, and experimental questions associated with the observation of intermolecular vibrational modulation of solvation transients are discussed.

## I. Introduction

Acetonitrile can be regarded as the prototypical polar aprotic molecule, with acetonitrile liquid representing the best approximation available to an ideal dipolar fluid. Because of its large  $(3.92 D)^1$  permanent dipole moment, and lack of specific (e.g., hydrogen-bonding) interactions, the dynamics of acetonitrile liquid are of tremendous theoretical, experimental, and practical importance. In this paper we utilize femtosecond nonlinear-optical (NLO) methods to observe directly the dynamics of intermolecular motion in acetonitrile liquid. The molecular dynamics of acetonitrile have been studied extensively for more than two decades utilizing numerous techniques.<sup>1-12</sup> We focus here on the high-

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frequency dynamics that occur on a time scale of less than  $\sim 500$ fs, although the longer time dynamics are revealed as well. The transients detected in this study are closely related to depolarized light-scattering (LS) spectra, 6.7, 10, 13-16 with the ultrafast dynamics

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