Dipole Correlation Functions in Liquid Benzenes Measured with Terahertz Time Domain Spectroscopy

S. R. Keiding

Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Received: February 18, 1997; In Final Form: May 15, 1997[⊗]

We report an experimental investigation of the dynamics of the dipole correlation functions in selected liquid benzenes (C_6H_{12}, C_6H_6, C_6D_6, $C_6H_3F_3$, and C_6F_6). Using terahertz time domain spectroscopy, we have measured the complex frequency response, i.e., both index of refraction and absorption, in the range from 0 to 2.5 THz (0 to 83 cm^{-1}), where the response is dominated by collective collision-induced processes. We have analyzed the data using the Mori memory function formalism and obtained dipole correlation function dominated by a simple exponential decay for all the substituted benzenes. The observed decay times are shorter than typical reorientation times and proportional to the free rotation time of the molecules. This indicates that small angle librational motion is responsible for the dipolar absorption observed.

Introduction

As the theoretical and experimental methods in chemistry advance, there is a growing interest in understanding the detailed microscopic mechanisms controlling chemical reactivity in the liquid phase.[1] A central theme in these efforts is the understanding of the ultrafast energy exchange between solvent and solute.[2−4] An obvious problem is the formulation of a molecular theory in the liquid phase where the degrees of freedom are numerous. This has led to the description of liquids based on macroscopic variables, such as the dielectric function in the frequency domain or equivalently the dipole correlation function in the time domain. The dipole correlation function, $C_1(t)$, describes the correlation between the macroscopic polarization, M, of a sample at time $t = 0$ and the same polarization at later times t.

$$C(t) = \langle M(0)M(t)\rangle = \langle \sum_{i=1}^{N}\mu(0) \sum_{i=1}^{N}\mu(t)\rangle \tag{1}$$

The correlation function is obtained from the single molecule correlation function ($i = j$) and cross terms correlating dipole moments on one molecule with dipole moments on other molecules ($i \neq j$). The correlation function describes how an induced polarization is dissipated in the liquid, *i.e.*, in other words, a description of the dynamics of solvation. This is illustrated in the observation of dynamical Stokes shifts observed in time-resolved fluorescence spectroscopy. The ultrafast solvation of an excited state dipole moment is described using the correlation function. Both experiments and theory show that 60−90% of the solvent relaxation occurs within the first 25−200 fs,[2−4] corresponding to the inertial motion of the (small) solvent molecules studied. Theoretical correlation functions have been calculated using molecular dynamics simulations, but until recently there were no experimental techniques suitable for direct measurements of dipole correlation functions.

The reason for this can be understood by considering the spectral response of the correlation functions. With solvatization times ranging from below 25 fs to picoseconds, the spectral response of a liquid is in the tetrahertz (THz), or far-infrared (FIR), part of the electromagnetic spectrum. Very few bright and broad-band sources exist in the THz range, and furthermore detection of the radiation requires cryogenic equipment. Consequently, spectroscopy in the 0−100 cm^{-1} range has been a very challenging experimental task. This situation recently changed with the introduction of THz time domain spectroscopy (TDS).[5,6] This technique, in brief, consists of a bright ultrabroad-band pulsed THz emitter and a highly sensitive room temperature detector, both driven by a femtosecond optical pulse. In addition to advantages in sensitivity and bandwidth, the THz−TDS technique allows for the measurement of both index of refraction and absorption coefficient simultaneously, a prerequisite if one wants to obtain the dipole correlation function.

We report an investigation of the far-infrared properties of liquid benzenes, focusing on the dipole correlation functions, investigated using THz time domain spectroscopy. The absorption of liquids is different in nature for polar and nonpolar liquids.[7−10] Absorption in polar liquids is (mainly) due to the interaction with the permanent dipole moments of the individual molecules. The electric field from the THz pulse (or another source) partly aligns the dipoles, and subsequently intermolecular collisions remove the orientational order (Debye relaxation). This relaxation takes place with a time constant (τ_D) ranging from 0.1 to 40 ps and gives rise to a strong absorption in the THz range, peaking at $\omega = 1/\tau_D$. For nonpolar molecules, the much weaker absorption originates both in the transient dipole moments induced via collisions in the liquid and in the interaction between higher moments, typically quadrupole−quadrupole and quadrupole−induced-dipole interactions. In the present case for the substituted benzenes, the quadrupole−quadrupole interactions can be very strong, even comparable to the dipole−dipole interactions, due to the high polarity of the individual C−H and C−F bonds. On the basis of measurements of dynamical Stokes shifts and solvatochromatic shifts, it has recently been demonstrated that the distinction between polar or nonpolar solely based on the presence of a permanent dipole moment is not valid for pure and halogenated benzenes.[11,12] There is also speculation that pair formation between some of the molecules can play a role. For 1,3,5-trifluorobenzene a dimer structure, with the benzene ring rotated by 60° thereby allowing the F atoms on one molecule to make a strong hydrogen bond with a second molecule, has been suggested.[13−17] For a 1:1 mixture of benzene and hexafluo-

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

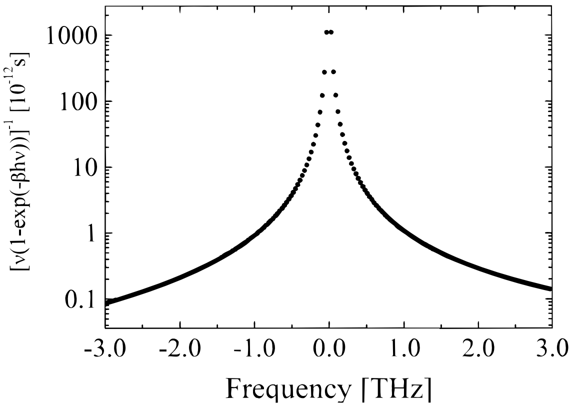

Figure 1. Thermal population factor used in the determination of the correlation function, shown as function of the frequency. Only a narrow frequency range around ±2 THz effectively contributes to the correlation function. At zero frequency the thermal population factor is infinite, and the curve is only shown for frequencies larger than 0.03 THz. Note also the slight asymmetry in the curve, most visible at higher frequencies where $h\nu \approx kT$. The asymmetry makes the correlation function complex, provided that the frequency spectrum of a extends to higher frequencies.

robenzene this pair- formation can be so strong that the mixture solidifies at room temperature.[17]

Theoretical Background

Before describing the results, we briefly outline the relationship among the time domain representation of the molecular dynamics, the correlation function, and the frequency domain description of the molecular properties, corresponding to the index of refraction and absorption coefficient.[18] In the frequency domain, the absorption coefficient can be calculated as the Fourier transform of the dipole correlation function, multiplied with a frequency-dependent prefactor. In eq 2, $\alpha(\omega)$ and $n(\omega)$ are the absorption coefficient and index, respectively, $C(t)$ is the dipole correlation function, and β is the inverse of the thermal energy $1/kT$.

$$\alpha(\omega) = \frac{2\pi\omega(1 - \exp(-\beta\hbar\omega))}{\hbar n(\omega)c}\int_{-\infty}^{\infty} C(t)\exp(-i\omega t)\,\mathrm{d}t \qquad (2)$$

It is straightforward to invert eq 2 and instead obtain an expression for the dipole correlation function, based solely on the measurable quantities $\alpha(\omega)$ and $n(\omega)$.

$$C(t) = \int_{-\infty}^{\infty} \frac{\alpha(\omega)\, n(\omega)c\hbar}{2\pi\omega(1 - \exp(-\beta\hbar\omega))}\exp(i\omega t)\,\mathrm{d}\omega \qquad (3)$$

In the literature[18] the integrand in eq 3 is often denoted the spectral function or the line shape function, $I(\omega)$,

$$I(\omega) = \frac{\hbar c}{2\pi}\frac{1}{\omega(1 - \exp(-\beta\hbar\omega))}\alpha(\omega)\, n(\omega) \qquad (4)$$

The dipole correlation function is then simply obtained as the Fourier transform of the spectral function,

$$C(t) = \int_{-\infty}^{\infty} I(\omega)\exp(i\omega t)\,\mathrm{d}\omega \qquad (5)$$

The presence of the thermal population factor, equal to $[\omega(1 - \exp(-\beta\hbar\omega))]^{-1}$, related to the Bose factor used in light scattering experiments,[19] is crucial in selecting a limited frequency interval from 0 to 2 THz effectively determining the time dependence of the correlation function.[20] In Figure 1 we plot the thermal population factor as function of frequency $\nu = \omega/2\pi$. For small frequencies, the weight factor is proportional to ν^{-2} and symmetric around the divergence point at zero frequency. As the frequency increase and approach kT/h, the thermal population function becomes asymmetric. Conventional far-infrared Fourier transform techniques have a practical lower limit around 50 cm^{-1} (1.5 THz), and typical microwave spectrometers have an upper limit around 0.15 THz. THz−TDS, however, seems to be a well-suited technique for liquids. The spectral coverage is perfect; both index and absorption are obtained, and the experimental procedures and requirements are quite simple.

As evident from eq 3 and Figure 1, there is a problem associated with the singularity a zero frequency in the thermal population function. The absorption coefficient goes to zero as the frequency goes to zero, but in a measurement, the finite signal-to-noise ratio will introduce noise around zero frequency, which potentially can alter the dipole correlation function obtained. In order to circumvent this problem, we have fitted the measured absorption curve to an analytical expression for the absorption coefficient and use the smooth analytical curve to calculate the correlation function.

It has previously been demonstrated[7,10] that the memory function formalism is very successful in reproducing the detailed shape of the far-infrared absorption curves for nonpolar liquids. Using a second-order memory function, one obtains the following expression for the absorption coefficient.

$$\alpha(\omega) = \frac{E\omega^2\gamma K_0 K_1}{\gamma^2[K_0 - \omega^2]^2 + \omega^2[\omega^2 - K_0 - K_1]^2} \qquad (6)$$

The memory function is very efficient in reproducing the experimental data, but a drawback of the approach is that one cannot directly related the parameters E, γ, K_0, and K_1 to molecular parameters. Only in certain approximate models can one associate the memory function parameters directly to molecular parameters.[21] As an example of this type of approach, we will analyze the THz−TDS spectra of some substituted benzenes in the following.

Results and Discussion

In Figure 2 we have shown the experimental results for index and absorption coefficients, obtained from transmission measurements as described in detail in refs 5 and 7. The uncertainty in the absolute value of the measured index of refraction is determined by the uncertainty in the measurement of the cell thickness determining the sample length. We estimate this uncertainty to ±0.0025 on the absolute value of the indices. The uncertainty on the shape of the index curve, the dispersion, is an order of magnitude lower. The uncertainty in the absorption measurements is determined by the stability of the entire THz setup during the two scans with and without liquid sample. On the basis of the reproducibility of the results, we estimate uncertainty of $\alpha(\nu)$ to be ±2.5% at 1 THz with a slightly higher uncertainty at the high- and low-frequency wings of the spectrum.

The measured absorption data were fitted to the second-order memory function, and the parameters obtained are summarized in Table 1. We have included previously published[7] data on cyclohexane and benzene in Table 1 for completeness. Implicit in the memory function formalism are a set of sum rules relating the parameters K_0 and K_1 to the expressions involving the moment of inertia and kT.[21] In Table 1 we have included two entries, where the sum rules were used in an attempt to bring the parameters K_0 and K_1 on a common scale. The fact that this is not possible indicates that the memory formalism, as expressed in eq 6, is mainly a fitting expression, where it is difficult to relate the individual parameters to molecular properties. Using the fitted memory function, we have con-

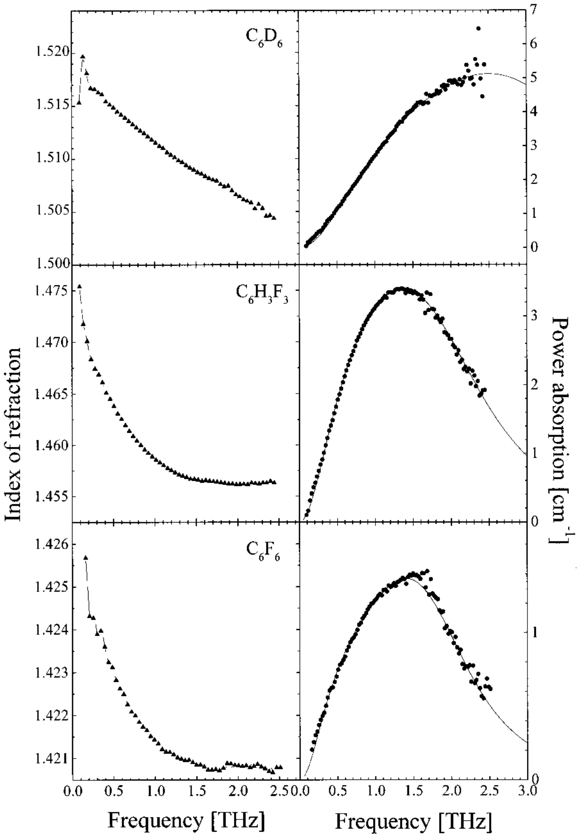

Figure 2. Index of refraction and absorption coefficient for the substituted nonpolar benzenes C_6D_6, $C_6H_3F_3$, and C_6F_6.

TABLE 1: Fitting Parameters for the Mori Function Shown in Eq 6[a]

		C_6H_{12}[b]	C_6H_6[b]	C_6D_6[c]	$C_6H_3F_3$[c]	C_6F_6[c]
E,	ps cm^{-1}	0.081	0.72	0.75	0.989(8)	0.45
γ,	ps^{-1}	50	19	31	20.1(4)	15
K_0,	ps^{-2}	80	71	99	31.2(4)	25
K_1,	ps^{-2}	1000	250	551	211(4)	154
τ_{DCF},	ps	0.22	0.16	0.16	0.29	0.36
$C(0)$[d,e]		0.07	0.81	0.81	1	0.44
I_{eff},[f]	10^{45} kg m^2	2.3	2.92	3.35	9.76	16.8
τ_{fr},[g]	ps	0.54	0.61	0.65	1.1	1.5
$K_0\tau^2_{fr}$[e]		0.61	0.68	1.1	1	1.47
$K_1\tau^2_{fr}$[e]		1.15	0.36	0.91	1	1.36
τ_{DCF}/τ_{fr}		2.5	3.8	4.0	3.7	3.5

[a] For the best fit, $C_6H_3F_3$, we have included the uncertainty of the parameters, given as one standard deviation. Note also that in the original publication[7] K_0 was incorrectly given as 800 for cyclohexane. [b] Reference 7. [c] This work. [d] The amplitude of the real part of the correlation function at $t = 0$. [e] Normalized to $C_6H_3F_3$. [f] Calculated using Gauss92. [g] $\tau_{fr} = (2\pi/9)(I_{eff}/kT)^{1/2}$.

verted the measured index and absorption data to the line shape function $I(\omega)$ using eq 4, and by Fourier transformation this is used to obtain the dipole correlation functions as shown in Figures 3 and 4.

For all the correlation functions, there is a weak imaginary component corresponding to the quantum contribution, as shown in Figure 4. This contribution originates in the asymmetry in the thermal population function for frequencies where $h\nu > kT$. The imaginary contribution to the correlation functions are 6−7% for the lightest molecules (C_6H_6, C_6H_{12}, C_6D_6) and smaller, ∼3%, for the fluorinated benzenes (C_6F_6, $C_6H_3F_3$). In the remainder of the work we will neglect the small imaginary part of the correlation function. The real part of the correlation function, shown in Figure 4 is characterized by a single-exponential decay for times longer than roughly 100 fs. We have fitted the correlation functions to a single-exponential decay, $C(t) = C(0)\exp(-t/\tau_{DCF})$, and the decay times for the benzenes are summarized in Table 1. For cyclohexane, with the smallest moment of inertia, we obtain a decay time of 0.22 ps whereas the fluorinated benzenes, with larger moments of inertia, the decay time is 0.30 ps (1,3,5-trifluorobenzene) and 0.36 ps (hexafluorobenzene). In Table 1 we also included the peak amplitude of the correlation functions, indicating the magnitude of the collision-induced dipole moments. It is interesting to note that although both the dipole moment and the quadrupole moment of $C_6H_3F_3$ are near zero, this molecule still have the largest dipolar correlation function of the molecules studied.[13] The observation of almost pure exponential correlation functions for the induced absorption in the nonpolar benzenes constitutes the main result of this work, and in the

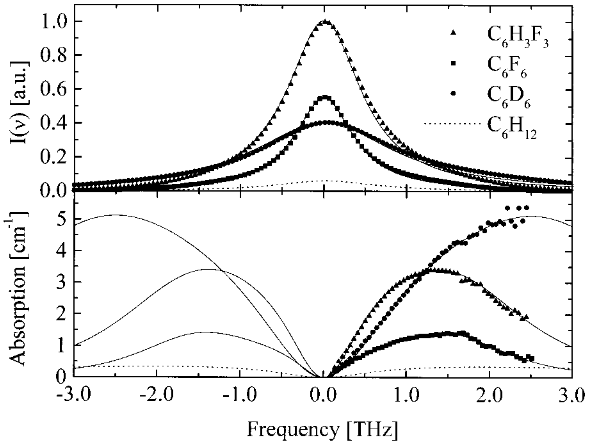

Figure 3. Lower part of the Figure shows the measured absorption coefficient (points), and the fitted curves, corresponding to eq 6 are shown as dashed lines. The upper part of the Figure shows the normalized spectral function I(ν) (points) obtained from eq 4 using the measured index of refraction and absorption coefficient. The full line corresponds to a Lorentz curve. Note the weak asymmetry of the spectral function. This asymmetry is responsible for the nonzero imaginary part of the dipole correlation function shown in Figure 4.

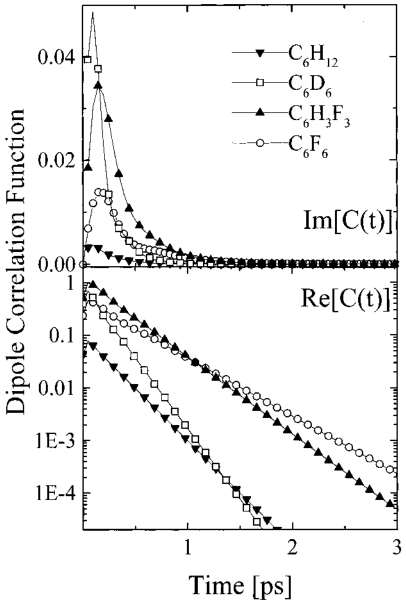

Figure 4. Real part and imaginary parts of the dipole correlation functions, obtained by Fourier transforming the line shape functions shown in Figure 3. We have included the data for cyclohexane previously published in ref 7. The correlation functions have all been normalized to the amplitude of the real part of the correlation function for $C_3H_3F_3$. The full line is a single-exponential decay fitted to the real part of the correlation function.

following, we will try to provide a framework for understanding these results.

In general, one can expect two types of contributions to the dipole correlation function. Since the individual molecular dipole moments are transient or interaction induced, the correlation function will decay as the induced dipole moments decay. This posses a complicated quantum mechanical problem of calculating the interaction between the higher-order moments on one molecule with the polarizable neighbor molecule(s) as a function of both distance and orientation. For the molecules studied in this work the interactions cannot be evaluated using simple point multipoles since the molecules, although nonpolar, contain highly polar and polarizable bonds. Instead, the interactions must be evaluated using the detailed charge distribution of the molecules, taking into account the local polar C−H and C−F bonds.[12,13] In addition, there is the orientational decay (Debye relaxation) of the molecules, as formulated in a statistic mechanical theory for orientational diffusion of the molecular frame in the liquid phase. This simple division is highly questionable, since the collisions responsible for the orientational dephasing are exactly the same collisions responsible for the induced dipole moments, and gives a good example of the difficulties associated with understanding and predicting the properties of the liquid phase.

The simplest model to describe the orientational diffusion is the free rotation model, where the oriental decay time scales as the square root of the moment of inertia,[22]

$$\tau_{\mathrm{FR}} = \frac{2\pi}{9}\sqrt{\frac{I_{\mathrm{eff}}}{kT}} \tag{7}$$

where I_{eff} is the average moment of inertia, corresponding to an average rotational constant $B_{\mathrm{eff}} = (A + B + C)/3$. The free rotation time, τ_{FR}, summarized in Table 1, corresponds to the free inertial (*i.e.*, gas phase) rotation of the molecules and is considered the short time limit for rotation of the molecular frame in the liquid phase. The free rotation time ranges from 0.5 ps for cyclohexane to 1.5 ps for the trifluorobenzene. In this simple picture, the pure free rotation model can be considered a single particle model, where the motion of the solvent molecule is independent of any interaction with its nearest neighbors.[1] Consequently, the correlation function for this type of inertial motion is expected to be Gaussian, with $C(t) = C(0)\exp(-(\Delta_g t)^2)$. In our experiments, we observe a purely exponential correlation function.

In liquids where the time between two collisions is shorter than or comparable to the free rotation time, the orientational diffusion process will depend on the viscosity of the liquid, as given for example in the Debye−Einstein−Stokes expression for the rotational diffusion time τ_θ,[22]

$$\tau_\theta = 4\pi r^3 \eta / kT \tag{8}$$

where r is the hydrodynamic radius of the rotating molecule and η is the viscosity of the solvent. In the Debye−Einstein−Stokes model, the correlation function is expected to be exponential with $C(t) = C(0)\exp(-t/\tau_\theta)$. The rotational diffusion time, τ_θ, is longer than the inertial rotation time and can be estimated from NMR spin−lattice relaxation times. For 1,3,5-trifluorobenzene-d_3 in different aromatic solvents a decay time of $\tau_\theta \approx 3.0{-}3.3$ ps was reported.[15] Similar time scales for rotational diffusion of the molecular frame have been observed in OHD-RIKES/OKE experiments[23−25] for benzene and most recently also C_6F_6[17] where the reorientation time is longer. In the OHD−RIKES experiments the correlation function for the polarizability is measured, $C_2(t) \propto \langle \alpha(0)\, \alpha(t) \rangle$, where $\alpha(t)$ is the macroscopic polarizability of the sample at time t. The measured decay is in general divided into two parts: a fast initial decay within the first picosecond, followed by a slower decay corresponding to the rotational diffusion process. With this assumption, the rotational diffusion time in cyclohexane, benzene, and hexafluorobenzene is 1.7, 2.53, and 13.5 ps, respectively, in the OHD−RIKES experiments. For dipolar liquids, with strong dipole−dipole interactions, the dipole correlation function and the polarizability correlation function are related through[25] $C_1(t) = [C_2(t)]^{1/3}$, and thus the oriental decay times for the dipole correlation functions are expected to be longer than the orientational decay times observed in OHD−RIKES experiments. Since the dipole correlation decay time obtained from our measurements are much shorter than the measured/estimated rotational diffusion decay times, we can conclude that the observed decay of the dipole correlation function is not related to the rotational diffusion of the liquid molecules.

Instead of the relaxational response, one could also consider resonance absorption by the librational modes of the liquids. If the intermolecular forces are strong enough to prevent free rotation of the molecules, these will instead perform a periodic pendulum-like small-angle motion. Consequently, librations are most often evoked to explain the behavior of polar liquids, where the strong dipole−dipole interactions are responsible for the reversal of the angular momentum leading to the periodic motion instead of the free rotational relaxation. For the substituted benzene studied in this work, the intermolecular interactions resulting from the highly polar bonds can be of substantial magnitude and thus cause the "caging" of the molecular rotation. Based on recent OHD-RIKES data,[17] the libration frequency in benzene and hexafluorobenzene was estimated to be 69 and 33 cm^{-1}. For benzene, the OHD−RIKES was fitted assuming an inhomogeneous (Gaussian) dephasing mechanism for the librational decay, with a decay constant of $\Delta_g = 3.9\ \mathrm{ps}^{-1}$. For hexafluorobenzene a more homogeneous (exponential) dephasing mechanism was used to represent the data, and an exponential decay time of 0.6 ps was observed. Assuming that the librational frequencies observable in OHD−RIKES and in FIR spectroscopy are directly comparable, we thus find that the librational response as observed in OHD−RIKES experiments is too slow to account for the present FIR observation. We cannot, however, exclude librational motion as being responsible for the observed FIR spectra. It is interesting to note the constant ratio existing between the free rotation time, τ_{FR}, and the dipole correlation time, τ_{DCF}, as shown in Table 1. For all molecules, apart from cyclohexane, this ratio is within 10% of 3.75. The free rotation time is proportional to the square root of the moment of inertia and will thus in a simple picture also be proportional to the libration period. In addition, the exponential character of the dipole correlation function also could indicate a homogeneously damped (overdamped) resonance motion.

For a more quantitative understanding of the observed FIR absorption in the substituted benzenes, it is necessary not only to consider the molecular motion but also to consider to what extent the individual motion is "infrared-active",[26] *i.e.*, gives rise to an induced dipole moment. By use of instantaneous normal mode (INM) theory, it might be possible to obtain a better understanding of the very rapid decay of the dipole correlation functions observed in this work. Briefly, the INM theory[1,26,27] assumes a set of inter- and intramolecular coordinates and expands the dipole moment and polarizability in these coordinates. The nuclear motion is then modeled using a Brownian oscillator model driven by a random Gaussian force and damped by a time-dependent friction coefficient. The instantaneous normal mode theory has recently been used to model several different ultrafast experiments,[28,29] including OHD−RIKES, OHD−ISRS, and dynamic Stokes shift. A key parameter in this theory is the spectral density of the active normal modes, corresponding to the FIR spectrum, the Raman spectrum, or the modes active in the process of solvation. The relationship between the different spectra,[30] as calculated from the INM model normal, has not yet been investigated in detail. It is likely that for example the spectrum associated with collision-induced absorption will be comparable to the spectral density calculated in dynamical Stokes shift experiments. Molecular dynamics simulations of solvent−solute interaction[2−4] have indicated that small angular displacements (librations) can account for most of the ultrafast (∼100 fs) relaxation observed in dynamical Stokes shift experiments. Similarly, we believe that the rapid decay of the collision-induced dipole correlation function has its origin in the librational motion of the solvent molecules. The instantaneous normal mode theory also offers more insight the short-time ($\tau \sim 100$ fs) dynamics of molecular motion.[1] At short times the description of solvation based on collective or single particle motion is equally valid. At short times the liquid normal modes are in-phase, and the collective motion is just the sum of the motion of the individual molecules. In the INM description of solvation each mode is given a weight depending on the modes ability to influence the solute.[1] To describe the observed FIR spectra, the solvation weight function should be replaced by a weight function describing the collision-induced dipole moments. The rapid decay observed in this work, indicates that the dynamics of the collision-induced dipole moments are more related to the dynamics of solvation than to the dynamics of the polarizability as measured in OHD−RIKES and Raman scattering experiments.

Conclusion

In conclusion, we have demonstrated that THz−TDS in the transmission mode is a very useful tool in the investigation of the ultrafast dynamics of nonpolar liquids. The advantage of the THz technique is the ability to measure both index and absorption with high precision in the FIR/THz range. From the data we have extracted the dipole correlation functions. For all the substituted benzenes studied in this work, we observe a Lorentzian spectral function corresponding to an exponential decay of the dipole correlation function. The decay times scales with the moment of inertia of the molecules, indicating that librational motion could be responsible for the observed dynamics. The decay times are substantially faster than simple reorientation times corresponding to free rotation of the molecular frame, and it is suggested that the dynamics is caused by the dephasing of the liquid normal modes, similarly to the fast dynamics observed in dynamical Stokes shift measurements.

Acknowledgment. The author thanks O. F. Nielsen for suggesting to study the fluorinated benzenes, J. E. Pedersen and A. Mortensen for excellent assistance in obtaining the data, and K. Sylvester-Hvid for calculating the moments of inertia given in Table 1. In addition, the author thanks both referees for valuable and constructive suggestions. This work was supported by the SNF-Center for Molecular Reaction Dynamics and Laser Chemistry.

References and Notes

(1) Stratt, R. M.; Cho, M. *J. Chem. Phys.* **1994**, *100*, 6700.
(2) Rosenthal, S. J.; Xie, X.; Du, M.; Fleming, *J. Chem. Phys.* **1991**, *95*, 4715.
(3) Maroncelli, M. *Chem. Phys.* **1991**, *94*, 2085.
(4) Jimenez, R.; Flemming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471.
(5) Grischkowsky, D. R.; Keiding, S. R.; van Exter, M.; Fattinger, Ch. *J. Opt. Soc. Am. B* **1990**, *7*, 2006.
(6) van Exter, M.; Fattinger, Ch.; Grischkowsky, D. R.; *Opt. Lett.* **1989,** *14*, 1128.
(7) Pedersen, E.; Keiding, S. R. *IEEE J. Quantum Electron.* **1992**, *28*, 2518.
(8) Thrane, Jacobsen, R. H.; Jepsen, P. U.; Keiding, S. R. *Chem. Phys. Lett.* **1995**, *240*, 330.
(9) Kindt, J. T.; Schmuttenmaer, C. A. *J. Phys. Chem.* **1996**, *100*, 10373.
(10) Flanders, B. N.; Cheville, R. A.; Grischkowsky, D.; Scherer, N. F. *J. Phys. Chem.* **1996**, *100*, 11824.
(11) Horng, M. L.; Gadecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.
(12) Reynolds, L.; Gadecki, J. A.; Frankland, S. J. V.; Horng, M. L.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 10337.
(13) Del Campo, N.; Besnard, M.; Yarwood, J. *Chem. Phys. Lett.* **1990**, *142*, 91.
(14) Zoidis, E. *Chem. Phys.* **1996**, *205*, 407.
(15) Lee, D. H.; Mcclung, R. E. D. *Chem. Phys.* **1987**, *116*, 101.
(16) Tassaing, T.; Danten, Y.; Besnard, M.; Zoidis, E.; Yarwood, J. *Chem. Phys. Lett.* **1994**, *184*, 225.
(17) Neelakandan, M.; Pant, D.; Quitevis, E. L. *Chem. Phys. Lett.* **1997**, *265*, 283.
(18) McQuarrie, D. A. *Statistical Mechanics*; Harper and Row: New York, 1973; Chapter 21.
(19) Nielsen, O. F. *Annu. Rep. Prog. Chem., Sect. C, Phys. Chem.* **1993**, *90*, 3.
(20) Thrane, L.; Larsen, I. W.; Jacobsen, R. H.; Uhd Jepsen, P.; Keiding, S. R. *Femtochemistry*; Chergui M. Ed.; World Scientific: Singapore, 1996.
(21) Kamykov, Y. P.; Titov, S. V. In *Advances in Chemical Physics;* Prigogine, I., Rice, S. A., Eds.; J. Wiley and Sons: New York, 1994; Vol. 87, pp 31-123.
(22) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy;* Oxford University Press: New York, 1986.
(23) McMorrow, D.; Lotshaw, W. T. *Chem. Phys. Lett*. **1993**, 201.
(24) Vöhringer, P.; Scherer, N. F. *J. Phys. Chem.* **1995**, *99*, 2684.
(25) Chang, Y. J.; Castner, E. W., Jr. J. *Phys. Chem.* **1996**, *100*, 3330.
(26) Goodyear, G.; Stratt, R. M. *J. Chem. Phys.* **1996**, *105*, 10050.
(27) Keyes, T. *J. Chem. Phys.* **1997**, *106*, 46.
(28) Cho, M.; Du, M.; Scherer, N. F.; Fleming, G. R.; Mukamel, S. *J. Chem. Phys.* 99, 2410.
(29) Cho, M.; Rosenthal, S. J.; Scherer, N. F.; Ziegler, L. D.; Fleming, G. R. *J. Chem. Phys.* **1992**, *96*, 5033.
(30) Kinoshita, S.; Kai, Y.; Yamaguchi, M.; Yagi, T. *Chem. Phys. Lett.* **1995**, *236*, 259.