Ultrafast Dynamics of Liquid Anilines Studied by the Optical Kerr Effect

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The femtosecond dynamics of liquid aniline, its N-methylated derivatives, two deuterium isotopes, and some mixtures are studied by means of the optically heterodyne detected optical Kerr effect. All data can be effectively described by three contributions: an oscillatory response associated with librational motion which is most significant at early times, a dual exponential relaxation occurring on the picosecond time scale, and a response at intermediate times which is fit to a model describing collisional dynamics, but is of uncertain origin in these complex liquids. The frequency of the librational response of aniline itself is anomalous and is interpreted in terms of a dimer like structure in the liquid. The librational response for the methylated derivatives is typical of that found in other aromatic liquids. The slowest relaxation times are not well described by simple diffusional rotational reorientation models. It is proposed that some structural relaxation may make a nonhydrodynamic contribution to the slow relaxation. For both fast and slow relaxation components the effect of deuteration is slight. The electronic hyperpolarizability is also determined from the data and increases with increasing degree of methylation. The measured pure liquid dynamics are used to calculate the solvation time correlation function, which is compared with earlier measurements of the solvation dynamics on anilines. The calculation of the solvation dynamics from the pure liquid dynamics (as measured by OHD-OKE) is not particularly successful for this class of weakly polar liquids.

1. Introduction

The ultrafast dynamics of liquids have attracted a great deal of attention in recent years. One reason for this is the proposal that the dynamics of pure liquids can have a controlling influence on the dynamics of chemical reactions in solution. Much of this attention has focused on the dynamics of dipolar solvation,[1] which is often observed experimentally through the time dependence of the fluorescence spectrum.[1,2] Maroncelli *et al.*[3] made the important proposal that solvation dynamics could, under certain assumptions, be calculated from a measurement of the pure solvent's dipole correlation function. This proposition was subsequently derived in a more rigorous fashion by Raineri and Friedman.[4] The model was tested by comparing the results of molecular dynamics (MD) simulations of solvation with either experimental measures of solvation or calculations of pure liquid dynamics.[3,5] One of the main results of the MD calculations was the prediction that a substantial part of the solvation occurred on a subpicosecond time scale, much faster than the longitudinal relaxation time of the solvent.[5,6] This ultrafast solvation could be assigned to the inertial and librational dynamics of the liquid. It has only recently become possible to observe this effect in experimental measurements of solvation dynamics, following the improvement in the time resolution of the fluorescence up-conversion experiment to the sub 100 fs time scale.[2] In spite of this continuing progress in the understanding of the molecular basis of solvation there have so far been relatively few direct comparisons of measured solvation dynamics with measured liquid dynamics.[7] This is undertaken here for liquid anilines in section 4.5, using solvation dynamics data recorded earlier.

There are several reasons why the dynamics of liquid anilines are of particular interest. In the first place they represent an interesting series of aromatic liquids in which the extent of intermolecular H-bonding is modulated by methylation of the N atom. Second, anilines have recently been prominent in the study of ultrafast electron-transfer reactions, where the aniline acts as both the electron donor and the solvent.[8−10] It has been proposed that the pure liquid dynamics can be a controlling factor in the rate of electron-transfer reactions in solution.[11] This was investigated experimentally by Nagasawa et al., who found that the electron transfer between dimethylaniline and oxazine occurred faster than the rate of solvation.[8] This result was explained by an important effect of intramolecular vibrational nuclear motion on the rate of the electron transfer.[8,9] However, electron transfer reactions in anilines continue to be studied, so a knowledge of their nuclear dynamics is likely to be of importance.[10] Finally, the few MD calculations and experiments which directly test the predicted relationship between pure liquid dynamics and solvation dynamics have tended to focus on somewhat idealized, strongly polar, solvents.[5,6] The weakly polar H-bonding anilines are in this respect less than ideal, so it is of interest to see how robust is the prediction of a relationship between solvation dynamics and liquid dynamics in this case.

Among the most popular methods of determining the ultrafast dynamics of liquids are those which monitor the relaxation of the polarizability anisotropy. Historically this was achieved in the frequency domain by Rayleigh wing measurements[12] and in the time domain by the optical Kerr effect (OKE).[13] These early measurements had limitations in their particular domains, but recent years have seen considerable progress in experimental

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methods. In the frequency domain Friedman and co-workers[14] introduced the stimulated Raman gain method, while in the time domain McMorrow, Lotshaw, and co-workers introduced femtosecond optically heterodyne detected (OHD) OKE measurements[15] and Fayer, Nelson and their co-workers[16] pioneered the impulsive stimulated scattering (ISS) technique. The method employed here in the study of liquid anilines was the OHD-OKE, which provides the high signal-to-noise ratio and linear response characteristic of heterodyne detected methods, while requiring only a low power femtosecond laser source. In general the ISS methods are perhaps more flexible, but have lower signal-to-noise and yield a quadratic response. Recent OHD-ISS methods seem to preserve the best features of both experiments.[17]

The Fourier transform analysis of OHD-OKE data to yield the sample spectral density has been described in detail by McMorrow and Lotshaw;[15] these methods are outlined for completeness in section 3. The relationship between the spectral density recovered and the Raman spectrum has been demonstrated experimentally and theoretically on several occasions.[15,18] From this result it is straightforward to obtain the nuclear dynamics of the liquid in the time domain.[15] For the case of anilines these results are described and analyzed in section 4.1, while the results for liquid mixtures and deuterated derivatives are described in sections 4.2 and 4.3, respectively.

The connection between the OHD-OKE data and the solvation dynamics was discussed by Cho *et al.*[7] and McMorrow and Lotshaw,[15b] but the detailed route to their calculation was first set out in detail by Chang and Castner.[19] These authors calculated the solvation response for a number of liquids, based on their OHD-OKE data. The main features of the model employed was also derived later in the paper of Rainieri and Friedman.[4] This model is followed here for the liquid anilines, and we are able to compare our calculated data with previously measured solvation dynamics.[20] Preliminary results were presented earlier.[21]

2. Experimental Section

The experimental arrangement for the OHD-OKE measurements described below was based on published designs.[15a,b,19a] The advantages of the heterodyne detected method, greatly improved signal-to-noise ratio and a linear relationship between signal intensity and probe intensity, have been described in great detail elsewhere.[15,19] The laser source used here was a Kerr lens mode-locked titanium sapphire laser (Clark-MXR) operating at 812 nm with a repetition frequency of 100 MHz. The output power was 330 mW when the laser was pumped by 3.5 W (all lines) from an argon ion laser via a dual axis pointing stabilizer.

To compensate for the group velocity dispersion introduced by the optics in the pump−probe spectrometer, the laser output was first routed through a dispersive delay line consisting of a pair of SF10 equilateral prisms separated by approximately 50 cm. After the delay line the laser pulses are incident on a beam splitter to produce pump and probe beams with an intensity ratio of 99:1. The pump beam is routed through a fixed optical path, a half-wave plate (all waveplates were of the broad band type) and a polarizer transmitting vertically polarized light just prior to the focusing lens. The beam intensity was modulated by a mechanical chopper at a frequency of 1 kHz. The probe beam is routed through a variable delay line (accuracy 0.2 micron), a 1% reflecting beam splitter, a half-wave plate and polarizer to give a final polarization 45° to the vertical, and then via a quarter-wave plate to the lens. With this arrangement the dispersion in the pump and probe beams is exactly balanced. The two beams were focused onto the sample with a 150 mm focal length achromatic lens and recollimated with an identical lens. The pump beam was blocked while the probe was routed through a second polarizer just prior to the detector. With all optics and sample cell in place the extinction between the two polarizers in the probe beam was measured as 10^6 times after careful adjustment of the quarter-wave plate and polarizers.[15b] To achieve heterodyne detection, an out of phase local oscillator was introduced by rotating the input polarizer by 1° away from the homodyne orientation. The OHD-OKE signal was recorded as a function of pump−probe delay by an amplified photodiode and recorded by a digital lock-in amplifier referenced to the chopper frequency. Both delay stage and lock in were under computer control. For high time resolution scans data were recorded at 1.33 fs intervals. For low time resolution measurements a step size of 67 fs was used, and data were recorded out to 60 ps.

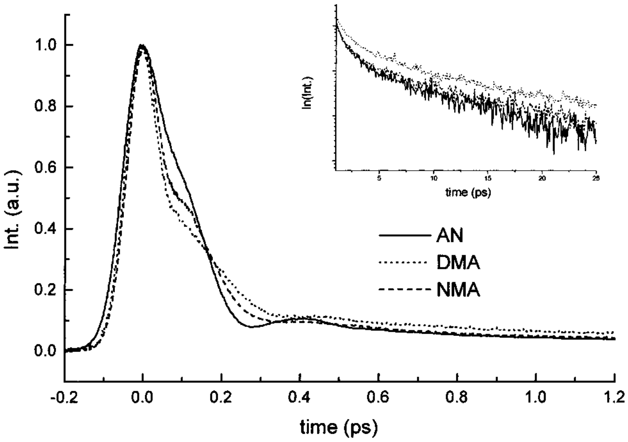

Figure 1. OKE data for aniline (AN), *N*-methylaniline (NMA), and *N*,*N*′-dimethylaniline (DMA). Inset shows low time resolution data out to 25 ps.

The second-order laser pulse autocorrelation function, $G_2(t)$, required for the data analysis procedure described below, was measured in a conventional background-free autocorrelation with a 200 micron thick KDP crystal placed in the sample position. When the prism pair was properly aligned to compensate for the group velocity dispersion of the optical path, a pulse width of 48 fs was measured, assuming a sech^2 pulse shape. The measured bandwidth was 17 nm, suggesting a time bandwidth product of 1.2 times the transform limit (again assuming a sech^2 pulse shape).

The fused silica sample cell, selected for low birefringence, had a path length of 3 mm. All liquids (aniline, AN, *N*-methylaniline, NMA, and *N*,*N*′-dimethylaniline, DMA) were distilled under vacuum before being injected into the sample cell via a 0.2 micron PTFE filter (PhaseSep). The deuterated analogues, AN-d_2 and NMA-d were prepared by shaking with and distillation from D_2O. All measurements were made at 294 ± 1 K.

3. Data Analysis

In the OHD-OKE experiment the macroscopic sample polarization change induced and detected by the femtosecond laser pulses results from an interaction between the third-order molecular nonlinear response and the electric field.[22] Experimental measurements of the OHD-OKE signal for three of the liquids studied are shown in Figure 1. The analysis of the measured optically induced Kerr effect signal has been described previously by McMorrow and co-workers and others.[15] The Kerr response contains both an instantaneous electronic hyperpolarizability contribution, $\sigma(t)$, and a sum of nuclear contributions, $r_i(t)$

$$R(t) = \sigma(t) + \sum_i r_i(t) \tag{1}$$

However as the femtosecond pulses themselves are not instantaneous the measured signal, $T(\tau)$, is a convolution of the true response with the second-order intensity cross correlation function, $G_2(t)$

$$T(\tau) = \int_{-\infty}^{\infty} G_2(t) R(\tau - t)\, \mathrm{d}t \tag{2}$$

Both the convolution and the electronic response can be separated out from the data by taking the imaginary part of the ratio of the Fourier transforms of $T(\tau)$ and $G_2(t)$ to yield the nuclear dynamics in the frequency domain.

$$\mathrm{Im}[D(\omega)] = \mathrm{Im}\left\{\frac{F^{+}[T(\tau)]}{F^{+}[G_2(\tau)]}\right\} \tag{3}$$

The resulting frequency domain spectrum, the spectral density, is equivalent to the low-frequency depolarized Rayleigh spectrum times a Bose thermal occupation factor.[5b,19b] The real part of the division in eq 3 also contains information on the magnitude of the electronic hyperpolarizability (discussed in section 4.4).[15d,23]

To achieve a sufficient number of data points to obtain a reasonable spectrum it is necessary to extend the high time resolution data of Figure 1 over a longer time range than it is practical to record. To achieve this the low time resolution, data (Figure 1 inset) are fit to the following function[15c,19]

$$r_1(t) = a_1 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right)[1 - \exp(-2\omega_0 t)] \tag{4}$$

and the data set is extended to 32 768 points with a time step of 1.33 fs, yielding approximately 0.76 cm^{-1}/data point in the spectrum. Equation 4 was initially introduced by McMorrow and co-workers to describe the long time response of the OHD-OKE signal, which was typically assigned to orientational diffusional relaxation. The term ω_0 reflects an inertial rise time and is chosen to be equal to the mean frequency of the high-frequency part of the spectrum; however, the choice of ω_0 is not critical.

Further analysis of the spectrum takes place in the frequency domain. The Fourier transform of (4) can be subtracted from the spectrum to isolate the higher frequency components. This subtraction can also be made directly in the time domain,[15b,c] though strictly speaking eq 4 should first be convoluted with $G_2(t)$. We find that the two methods yield nearly identical results. The long time response of eq 4 is found to account entirely for the low-frequency peak observed in the spectrum (see below). The remaining higher frequency band reveals, at least in the case of the liquids studied here, a somewhat structured spectrum. This encourages the fitting of the spectrum to two or more distinct functions,[19] and we will follow this procedure in the following section. First, the higher frequency part can be accounted for by one or more broad antisymmetrized Gaussians[19b]

$$I_{\mathrm{G}}(\omega) = g_1 \exp\left[-\frac{2(\omega - \omega_1)^2}{\Delta\omega^2[2\ln(2)]^{-1}}\right] - g_1 \exp\left[-\frac{2(\omega + \omega_1)^2}{\Delta\omega^2[2\ln(2)]^{-1}}\right] \tag{5}$$

where ω_1 is the maximum and $\Delta\omega$ is the width (fwhm) of $I_{\mathrm{G}}(\omega)$. This is usually taken to represent the presence of a Raman active inhomogeneously broadened intermolecular librational mode (further Gaussian terms are required if intramolecular modes are present in this frequency range). The intermediate frequency part of the spectrum can be fit to the following function

$$I_{\mathrm{BL}}(\omega) = b\omega^{\alpha} \exp(-(\omega/\omega_{\mathrm{BL}})) \tag{6}$$

which was originally introduced by Bucaro and Litovitz to describe the dynamic light scattering spectra of simple liquids.[24] The function accounts in that case for the collision-induced contribution to the spectrum and is derived from an isolated binary collision model. A function equivalent to eq 6 with $a = 1$, the Ohmic line shape, has a more general origin.[25] Here α is treated as a fitting parameter. It was observed that there was a strong correlation between α and ω_{BL}, i.e., different pairs could provide almost equally good descriptions of $\mathrm{Im}[D(\omega)]$. In all cases a combination of eqs 4−6 gave a good description of our spectra. The significance of the resulting parameters will be discussed in the following section (4.1).

Finally, the measured solvation dynamics, $C_{\mathrm{V}}(t)$, obtained from the time-resolved fluorescence method, will be compared with those calculated from the OHD-OKE measurements.[19] A simple connection between the solvation dynamics and the pure liquid dipole autocorrelation function was proposed by Maroncelli et al.[3]

$$C_{\mathrm{V}}(t) = \{C_1(t)\}^{\alpha_{\mathrm{s}}} \tag{7}$$

where α_{s} is a function related to the solvent dipole density and dielectric constant.[3,4,19] The key approximations made in this model are (1) a linear solvent response and (2) that orientational motions of the solvent make a dominant contribution to the solvation dynamics. Computer simulations for both model and simple but realistic systems suggest these approximations are largely valid. In addition, it is further assumed that the presence of a solute molecule does not greatly disturb the dynamics of the surrounding liquid. This equation was later derived more rigorously but with similar approximations by Raineri and Friedman.[4] From the OHD-OKE data the $r(t)$ can be determined from an inverse complex transform of $\mathrm{Im}[D(\omega)]$. The $r(t)$ so obtained can be related to $C_2(t)$, the polarizability autocorrelation function, using the methods introduced by Chang and Castner.[19]

$$C_2(t) = \left\{1 - \frac{\int_0^t r(t)\, \mathrm{d}t}{\int_{-\infty}^{\infty} r(t)\, \mathrm{d}t}\right\} \tag{8}$$

Finally, to obtain $C_1(t)$ use is made of the relations between different rank reorientational correlation functions, $C_l(t)$ ($l = 1, 2, ...$) given by simple models of liquid dynamics,[26] which yields

$$C_1(t) = \{C_2(t)\}^{1/3} \tag{9}$$

This was also derived by Rainieri and Friedman.[4] Thus from

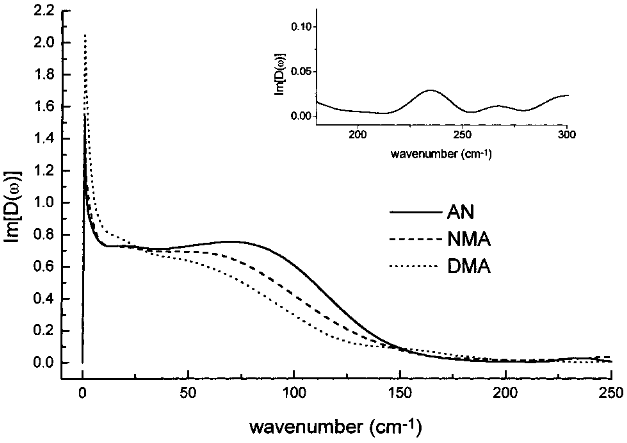

Figure 2. Frequency domain representation of nuclear dynamics for AN, NMA, and DMA. Inset shows intramolecular mode of AN at 235 cm^{-1}.

TABLE 1: Analysis of Long-Time OKE Data for Anilines (Eq 4)

	AN	NMA	DMA
a_1	0.053	0.048	0.049
τ_1 (ps)	1.45 ± 0.18	1.84 ± 0.12	2.77 ± 0.18
a_2	0.020	0.019	0.020
τ_2 (ps)	16.8 ± 0.9	23.8 ± 0.1	32.8 ± 1.5
ω_0 (ps^{-1})	15.8	11.8	11.3

the data of Figure 1 the solvation dynamics can be calculated, and finally compared with the experimental results (section 4.5).

4. Results and Discussion

4.1. Nuclear Dynamics of AN, NMA, and DMA. The femtosecond OHD-OKE data for AN, NMA, and DMA are shown in Figure 1. The main plot shows the measured high time resolution data up to the first picosecond while the inset shows the long time data out to 25 ps, fit to eq 4. All three plots show a sharp rise followed by an initial decay which appears faster in the methylated derivatives. This apparently faster relaxation is due to the larger electronic response of these derivatives (see below). For AN there is a strong damped oscillatory feature (a shoulder at *ca.* 150 fs and a peak at 400 fs) superimposed on the fast decay. Similar but weaker and less well resolved features are found for NMA and DMA. Finally, the OHD-OKE data reveal a long-lived nonexponential relaxation. The long relaxation was well described by eq 4 for all three liquids, and the resulting fit parameters are shown in Table 1. In each case, a component of a few picoseconds and a component longer than 15 ps are observed. Both components become longer as the degree of methylation increases. The relative amplitudes of the two components remain approximately constant for the three liquids. The absolute amplitude is largest for DMA (Figure 1).

In Figure 2 the nuclear dynamics of the three liquids are shown in the frequency domain representation of eq 3. There are again common features to all Im[$D(\omega)$] spectra: a narrow feature near zero frequency, most intense in DMA; a broad band at higher frequencies, which diminishes in intensity and shifts to lower frequency between AN and NMA or DMA; a weak shoulder near 25 cm^{-1}, largely obscured by the other components. Also seen for AN alone (inset) is a narrow feature at 235 cm^{-1}. This peak shifts to 225 cm^{-1} on deuteration. This can be assigned to an intramolecular mode, specifically the out-of-plane bend of the substituent, reported to yield a depolarized Raman band at 233 cm^{-1} for AN and 228 cm^{-1} for AN-d_2.[27] For DMA a broad feature is found near 170 cm^{-1} which is not present in the other liquids. We are unable to assign this band, but it may also be of intramolecular origin; a number of substituent or substituent-sensitive ring modes may occur in this region of the spectrum.

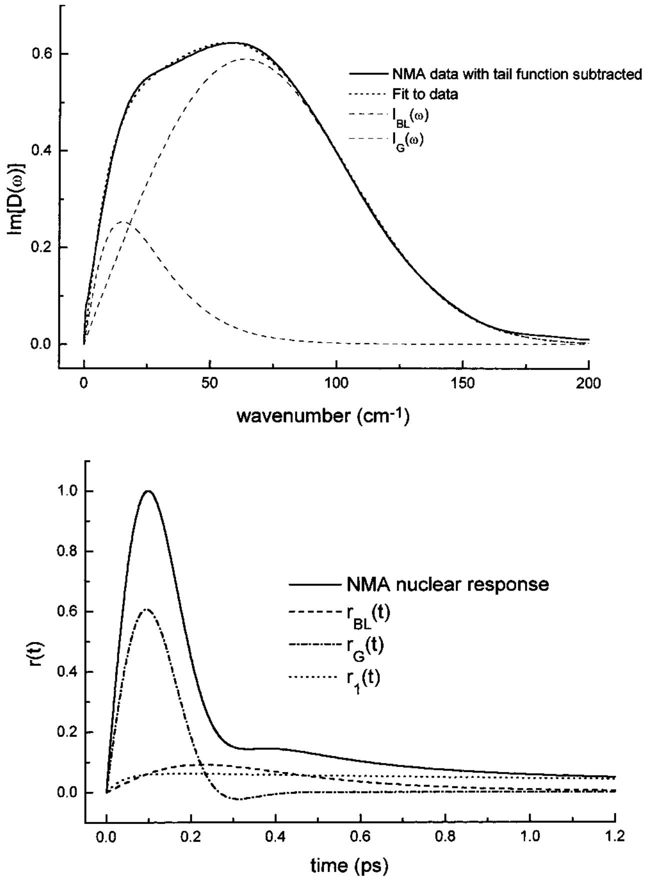

Figure 3. (a, top) Analysis of NMA frequency domain data in terms of eqs 5 and 6. (b, bottom) Pure nuclear response of NMA including rotational [$r_1(t)$], librational [$r_G(t)$] and collisional [$r_{BL}(t)$] components.

Further analysis of the spectrum below 150 cm^{-1} requires some model assumptions to be made. Following the procedure developed by McMorrow and Lotshaw, the low-frequency peak is subtracted from the spectrum in the manner described in section 3. This contribution to the spectrum is tentatively assigned to the orientational diffusion part of the liquid dynamics (see discussion below). The remaining intensity is fit to an antisymmetrized Gaussian (eq 5) and the Bucaro−Litovitz function (eq 6). The former is taken to represent intermolecular librational dynamics while the latter accounts for collisional or interaction induced liquid dynamics.

An example of the fit of this model to the data is shown in Figure 3a for NMA (for AN see ref 21). The quality of the fit is good. The nuclear dynamics in the time domain, undistorted by the electronic response and the convolution, are obtained through the inverse Fourier transform

$$r(t) = 2F^{-}\{\mathrm{Im}[D(\omega)]\}H(t) \qquad (10)$$

where $H(t)$ is the Heaviside function; this is shown in 3b, separated into the three components. From Figure 3, a and b, it can be seen that the analysis employed represents a somewhat arbitrary separation of the spectrum into collision induced (eq 6) and librational (eq 5) contributions. In the time domain this is equivalent to suggesting a separation of time scales for these two relaxation mechanisms. Recent MD calculations suggest that such a separation should not be taken too literally. In those calculations it was found that collision-induced relaxation can

TABLE 2: Analysis in the Frequency Domain of Anilines Using Eqs 5 and 6

	AN	NMA	DMA
b	0.045	0.029	0.027
ω_{BL} (cm^{-1})	23.5 ± 0.6	12.2 ± 0.5	11.4 ± 0.3
α	1.05	1.25	1.38
g_1	0.565	0.594	0.485
ω_1 (cm^{-1})	83.9 ± 0.3	62.4 ± 0.6	60.1 ± 0.6
$\Delta\omega_1$ (cm^{-1})	75.6 ± 3.41	97.8 ± 4.42	83.6 ± 5.17
g_2			0.057
ω_2 (cm^{-1})			156.7 ± 1.2
$\Delta\omega_2$ (cm^{-1})			46.7 ± 5.70

occur over a wide range of time scales.[28] This might suggest that the present analysis is somewhat artificial. On the other hand, the justification for using the present analysis is that it is very successful in describing the Im[$D(\omega)$] response of numerous liquids, as has been shown by Chang and Castner.[19] Thus the model provides a simple basis on which to discuss contributions to the complex dynamics of polar liquids. In addition the main features of the model are consistent with several theoretical models and simulations of liquid dynamics.[26,28]

The results from the fitting procedure are displayed in Table 2. First we consider the librational response, represented by the antisymmetrized Gaussian (eq 5). For DMA and NMA the spectral maxima are similar while that for AN is some 35% higher in energy. The results for DMA and NMA are in good agreement with the librational response observed for a wide range of substituted benzenes. The remarkable similarity, independent of intermolecular interaction, of the librational frequencies (60 ± 5 cm^{-1}) and widths of liquids as diverse as benzene,[15d] benzyl alcohol,[19b] and benzonitrile[29,19b] has been pointed out by Cong et al.[29] This result was discussed in terms of a competition between the anisotropy of the intermolecular potential and the moments of inertia.[29] The small differences between NMA and DMA are consistent with the effect of an increased moment of inertia for similar intermolecular interaction strength. However, the fact that a second Gaussian band was required in the description of the DMA spectrum makes a quantitative discussion of small frequency shifts difficult. All that can properly be concluded is that a librational band around 60 cm^{-1} appears characteristic of substituted benzenes. The remarkable result from Table 2 is that the frequency for the librational motion in AN is so high. We are aware of only one similar result, the 103 cm^{-1} librational frequency observed by Wynne et al. for liquid pyrrole.[30] This was assigned to the excitation of a mode associated with the T-shaped dimer which had been predicted to exist in the condensed phase.[30] We also interpret the anomalous result for AN in terms of the relaxation of transient structures in the liquid state. While there are no calculations of such structures in the condensed phase of AN, the AN dimer has been observed in gas-phase spectroscopy, and calculations suggest a staggered dimer structure, with the NH_2 groups of one partner interacting with the π ring of the other.[31] Some such strong interaction would be required in the liquid state of AN to give the observed high-frequency librational response. It is easy to see that replacement of an H atom by a methyl group would lead to the disruption of a sandwich type dimer structure and a more normal substituted benzene like librational response, as found for NMA and DMA.

The parameters for the fit to eq 6 are also shown in Table 2. The value of α is in general closer to 1 than 12/7, predicted for molecular liquids in the Bucaro−Litowitz model.[24] The function is thus closer to the Ohmic line shape.[25] For the reasons outlined above it is not clear that this function should be associated exclusively with the collision-induced contribution to the spectrum, and is therefore much more difficult to assign than the librational contribution. We simply note that the maximum value of eq 6, $\alpha\omega_{BL}$, is also higher for AN than the methylated derivatives, pointing once again to some unique interaction in AN.

TABLE 3: Static Constants of Anilines[a]

	AN	NMA	DMA
α_s	2.2	2.4	2.2
dipole moment (D)	1.51	1.65	1.61
dielectric constant	6.89	5.97	5.01
refractive index	1.586	1.568	1.558
viscosity (cP)	3.77	1.79	1.29
density (g/cm^3)	1.02	0.99	0.96

[a] Data from: McClellan and Aubrey. *Tables of experimental dipole moments*, 2nd ed.; Rahara Enterprises, 1974; *CRC Handbook of Physics and Chemistry*, 55th ed., 1974; and *Lange's Handbook of Chemistry*; 1992. α_s, related to solvent dipole density, is calculated according to ref 19.

The long time “orientational diffusion” component of the OHD-OKE signal was analyzed in the time domain according to eq 4. The results are presented in Table 1. The data are well described by the two exponential function between 1.5 and 60 ps. Similar biexponential behavior has been observed for other substituted benzenes.[19b,29] In benzonitrile this was assigned to rotation about different molecular axes.[29] Chang and Castner pointed out that, on the basis of the similar rotational constants for a series of aromatic and nonaromatic ring liquids, a nonexponential rotational relaxation need not be expected for substituted benzenes and that the origin of the nonexponentiality might lie in the strong intermolecular interactions.[19b] In the case of aniline internal motion, either internal rotation or inversion could be another contributing factor to the nonexponential relaxation. The observed non-Debye dielectric function for AN was ascribed to the AN inversion mode.[32] It is not clear to what extent this intermolecular motion would influence the polarization relaxation observed in OHD-OKE. However, both the fact that there is a relatively weak dependence of τ_1 on substitution and the nonexponential relaxation is also found in the rigid benzonitrile molecule suggest a reorientational rather than intramolecular origin for the nonexponential relaxation.

Much more surprising than the nonexponential relaxation is the trend in the reorientational relaxation times between the different anilines. The measured relaxation time approximately doubles between AN and DMA. This is true for both long and short components. This result can be contrasted with some of the static data for the anilines presented in Table 3. The most marked difference between the three liquids is in the shear viscosity which *decreases* between AN and DMA, presumably as a result of the decreasing degree of H bonding. The observed trend in relaxation time is then the *opposite* of what is expected from a simple Stokes−Einstein−Debye analysis, where the single-particle relaxation time is

$$\tau_s = \eta VF/k_B TS \tag{11}$$

and V is the molecular volume, S a shape factor, and F the friction factor which is 1 for “slip” rotational motion and less than 1 for “stick” conditions.[33] Assuming a similar molecular shape for the three derivatives τ_s should scale as ηVF. An increase in volume is calculated, as expected, between AN and DMA, but the effect is weaker than the decreasing viscosity. It seems unreasonable to propose that the H-bonding AN rotates under slip conditions while DMA shows stick behavior. For these reasons it is difficult to interpret the relaxation times reported in Table 1 simply on the basis of eq 11, and other explanations must be sought.

In the OHD-OKE experiment the relaxation which is observed is the *collective* orientational relaxation time, τ_c

$$\tau_c = (g_2/j_2)\tau_s \qquad (12)$$

In dense fluids this may differ from the single particle reorientation due to static and dynamic orientational correlation between pairs of molecules.[34] In eq 12 g_2 is the static and j_2 the dynamic orientational correlation parameters. It is certainly possible to adjust g_2 (j_2 is usually taken to be close to unity) to obtain reasonable agreement between τ_c and the measured relaxation time, by requiring g_2 to be larger for DMA than AN. This could be tested in further experiments, by studying the viscosity and temperature dependence of the relaxation time for the anilines in solution.[35] It seems, however, difficult to argue that g_2 is largest for the neat liquid with the weaker intermolecular interaction.

A second possibile explanation for this anomalous viscosity dependence is that a longer component in the OHD-OKE experiment on AN has simply been missed. However, the data of Figure 1 show that the short component dies out rather quickly (e.g. $\tau_1 = 1.45$ ps for AN) and the remaining data between 5 and 60 ps are well described by a single-exponential function. Any undetected component must be either close to the 16 ps value measured such that it might not appear as a well-resolved second exponential or of very low amplitude. This would not then be sufficient to account for the differences between AN and DMA.

Another explanation is that the dynamics observed may contain contributions from relaxation processes other than collective orientational diffusion. One possibility is that there remains on the picosecond time scale an interaction-induced contribution from translational motion to the polarizability anisotropy relaxation in anilines. As already noted, the assumption that translational and orientational polarizability relaxation occur on separate time scales is not supported by some recent MD calculations.[28] Under these conditions, the analysis in terms of eqs 11 and 12 would not be expected to be appropriate. It is noted, however, that the anomalous behavior seen here is also observed in dielectric relaxation and solvation dynamics measurements (see below), both of which are less sensitive to translational dynamics than OHD-OKE.

Finally, the existence of transient H-bonded structures in AN (and possibly NMA) may contribute to a faster than expected orientational relaxation. If the formation and decay of the transient structure is faster than the rate of diffusional orientational relaxation, then dissociation may leave one partner with excess thermal energy. This can lead to faster than expected orientational relaxation, until the excess energy has dissipated and the structure reforms. Such a model was first outlined by Matsumoto and Gubbins in their MD simulation of liquid methanol.[36] Both Fayer and co-workers[37] and Wynne *et al.*[30] invoked similar models in which the relaxation dynamics of local structures in the liquid accounted for their observations of nonhydrodynamic orientational relaxation. Similarly, the idea of Chang and Castner[19b] that the very long (63 ps) orientational relaxation time observed in benzyl alcohol is associated with long-lived H-bond complexes in the liquid is related to the above model. In light of these results it seems possible that the lifetimes of local liquid structures can often contribute to the observation of nonhydrodynamic orientational relaxation. These ideas can be tested further by recording temperature-dependent OHD-OKE data; such measurements are planned.

In summary, the pure nuclear dynamics for AN, NMA, and DMA are well described in the frequency domain by eqs 4, 5, and 6, in common with a number of other polar liquids.[19] However, the significance of the intermediate frequency component eq 6 remains unclear. The fast librational dynamics for AN reveal an anomalously high frequency, which is tentatively assigned to the existence of an H-bonded dimer structure in the liquid. The other derivatives fit well with the data for a number of substituted benzene derivatives. The long time part of the OHD-OKE data for this series of anilines could not be accounted for by simple hydrodynamic models of orientational relaxation. It is suggested that there is a contribution to this long time relaxation from intermolecular structural relaxation in the liquid.

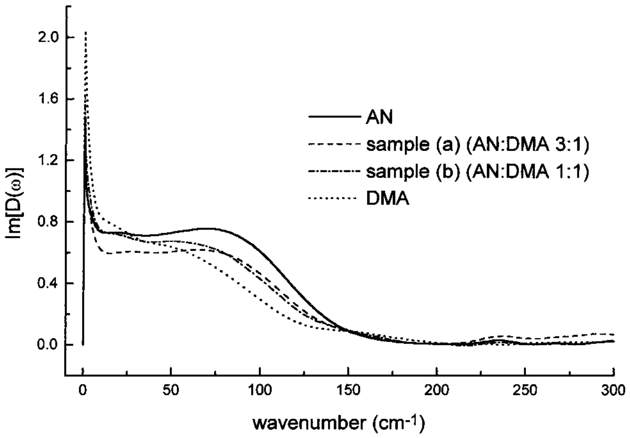

Figure 4. Frequency domain representation of nuclear dynamics for mixtures, compared to the pure liquids: sample (a) (AN:DMA 3:1), sample (b) (AN:DMA 1:1) and DMA.

TABLE 4: Analysis in Frequency Domain of Mixed Samples (AN:DMA) (a and b) Using Eqs 5 and 6

	sample a [3:1]	sample b [1:1]	AN-d_2	NMA-d
b	0.01	0.01	0.04	0.038
ω_{BL}	18.6 ± 0.3	10.8 ± 0.3	30.3 ± 0.6	14.67 ± 0.6
α	1.48	1.76	1.02	1.09
g_1	0.46	0.58	0.434	0.555
ω_1	82.3 ± 0.2	68.7 ± 0.4	85.9 ± 0.3	63.1 ± 1.5
$\Delta\omega_1$	75.6 ± 2.0	87.7 ± 3.0	67.7 ± 1.8	90.6 ± 3.3
g_3	0.02	0.03		
ω_2[a]	156.7	156.7		
$\Delta\omega_2$[a]	46.7	46.7		

[a] These data, taken from Table 2, were fixed in the current analysis.

4.2. Dynamics of Mixtures. To address further the origin of the high-frequency librational spectrum in AN the OHD-OKE data were recorded for mixtures of AN and DMA. The Im[$D(\omega)$] data are shown in Figure 4 for molar ratios (AN:DMA) of (a) 3:1 and (b) 1:1. It can be seen that there is an initial decrease in the intensity of the 84 cm^{-1} band (sample a) followed by a shift to lower frequency (sample b). This is accompanied by an increase in the intensity below 40 cm^{-1}. The details of the spectral analysis are shown in Table 4. Attempts to simulate the measured spectra by adding together the appropriate amount of the individual components were not successful. For the 3:1 mixture the attenuation of the Gaussian component is larger than predicted by a sum of the individual components. For the 1:1 mixture the agreement between measured and simulated data is good above 30 cm^{-1}, but poor at lower frequency. The nonadditive form of the measured spectra suggests specific intermolecular interactions. The observed attenuation and shift of the high-frequency librational peak of AN is consistent with an assignment to a specific intermolecular aniline mode.

The OHD-OKE data were also recorded out to 60 ps, but mainly to improve the quality of the Fourier transform analysis

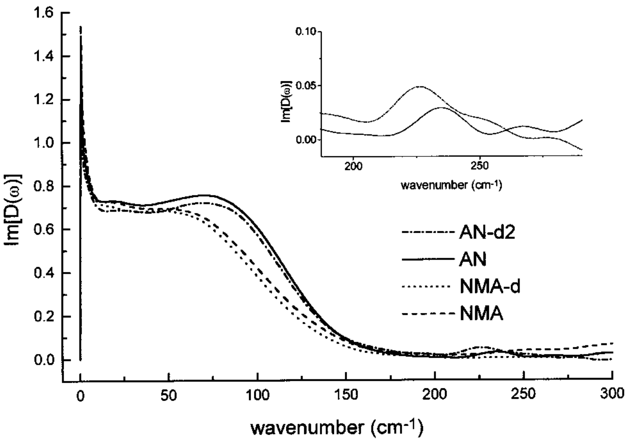

Figure 5. Frequency domain representation of AN, AN-d_2, NMA, and NMA-*d*. Inset shows shift to lower frequency (225 cm^{-1}) of intramolecular mode with deuteration of AN.

(see section 3). The slowest relaxation was observed to increase in relaxation time and amplitude with increasing amounts of DMA. This is as one might expect from the data of Table 1, and the result is not helpful in ascertaining the role of pair correlation (g_2) in the slow dynamics. For that the dilution should be in a solvent which has a weak OKE response.

4.3. Deuterium Isotope Effects. The effect of exchanging the amino hydrogens for deuterium was studied for AN and NMA. The results are shown in Figure 5 and Table 4. A small shift to higher frequency and narrowing of the librational response are detected on deuteration which is suggestive of a role for H bonding in both spectra. The time domain data were recorded out to 40 ps, but no effect of deuteration on the slow relaxation was detected within experimental error. Further interpretation of this result would require a knowledge of the viscosity of the deuterated sample, which is currently unavailable. The other effect of deuteration is the shift in the intramolecular vibrational mode (to 224 cm^{-1}) already discussed. Overall the effect of deuteration on the nuclear dynamics is slight apart from a small increase in the strength of the intermolecular interaction leading to the librational response.

4.4. Hyperpolarizability of Methylated Anilines. The real part of the OHD-OKE response contains both the nuclear dynamics and the electronic response due to the molecular third-order hyperpolarizability, γ. This appears as a constant level as a function of frequency, from which a relative value for γ can be obtained. The results for the three derivatives, normalized to the AN result, are 1.0 (AN), 1.27 (NMA), and 1.43 (DMA). Thus there is a clear trend of increasing hyperpolarizability with increasing degree of methylation. The trend is in good agreement with that found in nonresonant third harmonic generation experiments.[38] This result is consistent with a more extensive delocalization of the amino lone pair into the aromatic ring in the methylated derivatives, which is in turn consistent with a more planar configuration for these derivatives.

4.5. Solvation Dynamics in Anilines. As discussed in section 3 the solvation time correlation function can, under certain approximations, be calculated from the OHD-OKE data.[3,4,19] The results of an analysis of the data of Figure 2 in terms of eqs 7−9 are shown in Figure 6, where α_s was calculated using the data of Table 3. For all three derivatives a fast component in the solvation dynamics is predicted (Figure 6, inset) which accounts for between 10 and 20% of the complete solvation response. The amplitude of this component decreases in the order AN ≈ NMA > DMA. The initial part of this component is not exponential but has an apparent Gaussian shape. This early time Gaussian contribution is associated with the librational response of the liquids, as can be shown by omitting this component from the inverse Fourier transform (eq 10).[21] The main part of $C_V(t)$, between 1 and 20 ps, is well described by a sum of exponentials function, the data being given in Table 5.

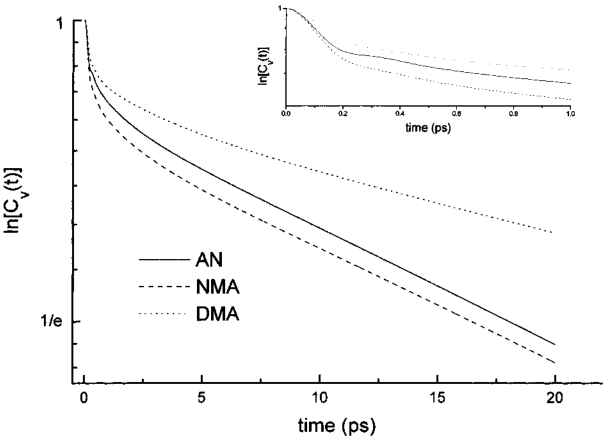

Figure 6. Calculated solvation dynamics [$C_V(t)$] for AN, NMA, and DMA. Inset shows Gaussian relaxation at early times (<200 fs) which is not observed experimentally.

TABLE 5: Biexponential Fits to Calculated and Measured $C_V(t)$

	AN		NMA		DMA	
	calc	expt[a]	calc	expt	calc	expt[a]
a_1	0.16	0.28	0.13	0.25	0.13	0.35
τ_1	1.32 ± 0.1	1.2	1.51 ± 0.1	2.0	2.99 ± 0.1	3.8
a_2	0.84	0.72	0.87	0.75	0.73	0.65
τ_2	22 ± 2	17.8	27 ± 2	16.2	53 ± 5	22.6
$\langle\tau\rangle$	18.7	13.2	22.8	12.7	39.1	16.0

[a] Pal, H., et al. *J. Chem. Phys.* **1995**, *19*, 7758. $\langle t\rangle = a_1\tau_1 + a_2\tau_2$.

For comparison, the solvation dynamics data (measured with 200 fs time resolution) for the solute coumarin 102 in the three different aniline solvents are also shown in Table 5. The data for AN and DMA (measured by both the spectral shift and the single-wavelength method[39]) have been presented elsewhere.[20] (The agreement between the two methods was better than 10%.) The data for NMA, measured by the single-wavelength method, are presented here for the first time.

Comparing first the long-time data in calculated and measured solvation dynamics (Table 5), it is observed that the anomalous trend in the long relaxation time observed in the OHD-OKE experiments discussed above is also observed in the measured solvation dynamics. This means that the nonhydrodynamic relaxation mechanism operating in OHD-OKE, which we assigned to a structural relaxation of the liquid, rather than simple diffusive reorientation, is also effective in dipole solvation. The same trend is also observed in the dielectric relaxation data of Garg and Smyth.[32] Since the same effect, increasing relaxation time with decreasing viscosity, is observed in both dipolar and collective polarizability relaxation measurements, the explanation, mentioned above, of a contribution from translational dynamics in the long-time relaxation is unlikely to be the origin of the anomalous behavior.

In an earlier paper[21] the similarity of the calculated and measured solvation dynamics beyond 1 ps for AN was discussed. It can be seen from Table 5 that the success of the calculation is not so obvious when all three derivatives are considered. Specifically, the calculated data predict an appreciably longer long relaxation time and reveal a weaker and shorter fast component than is measured experimentally. The measured data appear to sense some average of the response calculated from the pure liquid dynamics; the measured short component is longer than the calculated one, while the opposite is true for the long components. The origin of this behavior is not clear, but it can be concluded that there is no quantitative agreement between the calculated (through eqs 7−9) and measured solvation dynamics for these weakly polar liquids. Clearly for a more detailed test of these calculation methods a wider range of liquids should be studied.

It was noted in the earlier study of AN alone that there is no quantitative agreement between the calculated and measured solvation data in the subpicosecond region;[21] this is also observed for NMA and DMA; in particular the experimental solvation data (resolution 200 fs) do not reveal an ultrafast Gaussian component, which is predicted both by the calculated data (Figure 6, inset) and numerous MD simulations of solvation dynamics[6] and observed in some recent experiments in strongly polar solvents.[2]

One possible origin for the absence of the Gaussian component from the measured $C_V(t)$ is simply that the 200 fs time resolution up conversion data cannot resolve the fast component predicted from the OHD-OKE (which are undistorted by convolution with the laser pulse). For this reason the solvation dynamics of AN were reinvestigated using an up-conversion spectrometer with a 100 fs time resolution,[40] and the dye molecule LDS-750 as the solute.[41] Faster components were isolated in the solvation response; specifically a shortest relaxation component of lifetime 350 fs with a weight of 25%, but once again the dynamics were well described by a sum of exponentials function, with no observable Gaussian component. The interpretation of this result is complicated by the fact that LDS-750 may not report exclusively the solvation dynamics,[42] but if the observed fast relaxation is of intramolecular origin this merely emphasizes the disagreement between calculated and experimental solvation data. This point is discussed further elsewhere.[41] It is concluded here that a Gaussian component is not observed in the solvation dynamics of liquid anilines, although it is predicted on the basis of OHD-OKE data and the analysis of eqs 7−9.

Possible reasons for the failure of the analysis of eqs 7−9 to reproduce the experimental solvation dynamics at early times in anilines have been discussed elsewhere.[21] First, the relaxation of the polarizability anisotropy observed in OHD-OKE need not always reflect the same dynamics as solvation. This was discussed in detail by Ladanyi and Klein[28] who pointed out that in, for example, water the OHD-OKE mainly reports (for reasons of symmetry) translational dynamics, while the solvation is most influenced by rotational reorientation. At present we are unable to assess the relative importance of translational and rotational dynamics in the OHD-OKE measurements on anilines. In a similar way the transformation between the $l = 1$ and $l = 2$ correlation functions (eq 9) is normally derived on the basis of reorientational dynamics[26] and may not be appropriate for the complete OHD-OKE data. Second, the assumption that the solvation dynamics will be independent of solute seems unrealistic for many systems. It is suggested[21] that the intermolecular librational modes which make such a strong contribution to $\mathrm{Im}[D(\omega)]$ in aromatic liquids (Figure 2) may be particularly sensitive to solvent solute interactions in the first solvation shell. Indeed recent semiempirical calculations suggest some specific interactions exist between aniline's amino group and the π ring of the dye oxazine 1.[43] Such specific interactions may perturb the dynamics of the liquid in the solvation shell to the extent that the pure liquid dynamics may not exactly reproduce the solvation dynamics. Finally, eq 7 is expected to be most appropriate for polar solvents ($\alpha_s \geq 5$). For less polar solvents molecular contributions to α_s may be important, making the continuum based approximation[3,19] employed here less suitable. In light of these considerations it is perhaps surprising that the agreement between measured and calculated solvation dynamics is as good as it is for AN solutions.[44] A more detailed comparison of measured and calculated data in a range of solvents is in progress.[45]

The solvation dynamics of coumarin 102 in AN and AN-d_2 have been reported, and a significant deuterium isotope effect was reported.[20] The $C_V(t)$ data cannot be calculated directly from the OHD-OKE data (section 4.3) because the static data for the calculation of α_s are not available. However, the fact that the effect of deuteration on OHD-OKE was small on the short-time data and negligible beyond 2 ps suggests that the isotope effect observed in solvation dynamics does not arise from changes in the pure liquid dynamics. This is an indication that the effect of the deuteration of aniline on the solvation dynamics may arise from specific solvent−solute interactions, even though there are no indications of such interactions in the steady-state electronic spectra.[20] It is noteworthy that the observation of an isotope effect on the electron-transfer rate when AN (or AN-d_2) was the solvent donor was also explained in terms of a specific interaction.[46]

5. Summary

The femtosecond dynamics of liquid AN and its methylated derivatives have been measured. The data are well described by an instantaneous electronic response, and a sum of a librational component, an ohmic line shape, and a biexponential long-time relaxation. This analysis, while approximate and invoking a somewhat unrealistic separation of the complex band shape into distinct contributions, is very successful in describing the dynamics of the three anilines as well as a number of other polar liquids. A more detailed interpretation of the dynamics awaits further theoretical progress. The librational bands of DMA and NMA are at around 60 cm^{-1}, a feature that appears to be characteristic of substituted benzenes. For AN the librational band is at an appreciably higher frequency which has been assigned to a stronger intermolecular interaction in this liquid, probably associated with an AN dimer like structure. This interpretation is supported by measurements in mixed solvents. The origin of the ohmic line shape is less clear, but it is also shifted to higher frequency in AN. The electronic hyperpolarizability part of the OHD-OKE response has been measured; it increases with methylation, in line with expectations.

The slowest nonexponential relaxation could not be interpreted in terms of simple hydrodynamic models. It has been suggested that there is a contribution to this slow component from a structural relaxation in the liquid, distinct from single particle reorientation. This relaxation may be associated with the dynamics of the H-bonded structures in the liquid, but their is no conclusive evidence to support this; more definite conclusions on the mechanism of the slow relaxation in anilines requires measurements as a function of temperature and concentration. Such measurements are planned.

The solvation dynamics time correlation function has been constructed from the OHD-OKE data following the model of Chang and Castner and Maroncelli *et al.*[3,19] There was no quantitative agreement between the calculated dynamics and those measured in time-resolved fluorescence experiments. On the short time scale the solvation dynamics fail to reproduce the Gaussian form predicted from OHD-OKE data. This suggests that a direct transformation from pure liquid dynamics (or at least those measured by OHD-OKE) to solvation dynamics is not appropriate for this particular class of weakly polar liquids. Possible reasons for the failure of the model were discussed. A more detailed picture of the limitations of the model set out in eqs 7−9 requires the study of a much wider range of liquids.

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