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# Ultrafast Optical Kerr Effect and Solvation Dynamics of Liquid Aniline

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Femtosecond optically heterodyne detected optical Kerr effect (OHD-OKE) measurements have been made on liquid aniline. These are contrasted with solvation dynamics measurements made earlier. The OHD-OKE data in the frequency domain can be analyzed in terms of three components: a low-frequency diffusional part; a collisional part; an underdamped intermolecular mode. The latter is quite intense, suggesting strong intermolecular interactions and a relatively high degree of structure in liquid aniline. When the solvation dynamics calculated from the pure liquid data are compared with those measured directly, the agreement beyond 1 ps is good. This result suggests that it is possible to use experimental data obtained on the pure solvent dynamics to model the solvation dynamics response. However, the agreement is not as good at very early times. While this may simply reflect the lower time resolution of solvation dynamics experiments compared to OHD-OKE experiments, we speculate that the differences could also result from either fundamental differences in the measured solvation dynamics and those calculated from OHD-OKE data or a perturbation of the intermolecular interactions in liquid aniline by the solute.

## 1. Introduction

The ultrafast dynamics of numerous pure liquids have been measured in femtosecond optically heterodyne detected optical Kerr effect (OHD-OKE) experiments.[1−13] The connection between such experiments and ultrafast solvation dynamics, observed in time-resolved fluorescence shift experiments,[14−16] has been the subject of much recent discussion.[1,6−9,17,18] In the following we will describe OHD-OKE measurements on liquid aniline (AN) and contrast these results with solvation dynamics reported earlier.[19] Liquid AN itself has attracted much recent attention in diffusionless electron transfer experiments where it serves the dual role of solvent and electron donor.[20−23] Given the predicted connection between solvent dynamics and rate of electron transfer reaction,[24,25] it is clearly desirable to have a clearer picture of the liquid dynamics of AN.

One of the earliest studies of the connection between femtosecond OHD-OKE and solvation dynamics was by Cho *et al.*[17] They showed that both the ultrafast solvation dynamics of LDS-750 in acetonitrile and the pure liquid's OHD-OKE signal could be simulated with a common set of parameters. At the same time Maroncelli and co-workers made the interesting proposal that, in the limit of a linear response, the relationship between solvation dynamics and pure liquid dynamics could be described approximately by[18]

$$C_v(t) \cong \{C_1(t)\}^{\alpha_S} \tag{1}$$

where $C_v(t)$ is an equilibrium time correlation function of solvation, $C_1(t)$ is the dipole autocorrelation function $\langle\mu\cdot\mu\rangle/\mu^2$, and $\alpha_S$ is a function related to the solvent dipole density:

$$\alpha_S = \left(\frac{4\pi\rho\mu^2}{3k_BT}\right)\Big/\left(\frac{9\epsilon_\infty}{(\epsilon_\infty + 2)^2}\right)\left(1 - \frac{\epsilon_\infty}{\epsilon_0}\right) \tag{2}$$

This relationship has been supported by a recent theoretical models[26] and a number of molecular dynamics simulations.[27−29] Quite recently Chang and Castner developed an approximate method for the derivation of $C_1(t)$ from OHD-OKE data and applied it to a number of pure liquids to obtain $C_v(t)$.[6−9] However, there has not, since the original work of Cho et al.,[17] been (as far as we are aware) any detailed comparison of the data obtained from OHD-OKE measurements and experimental measurements of solvation dynamics. In the following sections the data of ref 19 are contrasted with the solvation dynamics predicted by our OHD-OKE study of AN. The differences (particularly at early times) and similarities are discussed. These experiments represent a first effort at testing the relationship of eq 1 in polar solvents other than acetonitrile. It may however be noted that femtosecond OHD-OKE data have recently been used as characteristic of solvent effects in studies of vibrational relaxation and two-pulse photon echoes in solution.[30,31]

## 2. Experimental Section

The laser source was a mode-locked titanium sapphire laser operating at 813 nm at a repetition rate of 100 MHz (Clark MXR). The autocorrelation width measured at the sample position was 75 fs. The autocorrelation was not well described by either Gaussian or sech$^2$ profiles but was intermediate between the two. The observed bandwidth of 17 nm was below the transform limit for Gaussian pulses and 1.25 times the limit for a sech$^2$ profile.

The experimental arrangement for the OHD-OKE measurement was based on published designs[1] and will be described in more detail elsewhere.[32] Important parameters were: pump and probe energy 330 and 2 mW respectively, focused onto the sample by a 150 mm lens; pump and probe linearly polarized, probe at 45° with respect to pump; the probe beam passed a polarizer, quarter wave plate, the sample, and a second polarizer; attenuation between the polarizers, with the sample cell in place, was $10^6$ times. To obtain a heterodyne signal the first polarizer is rotated by 1°, yielding an in-phase local oscillator, so that

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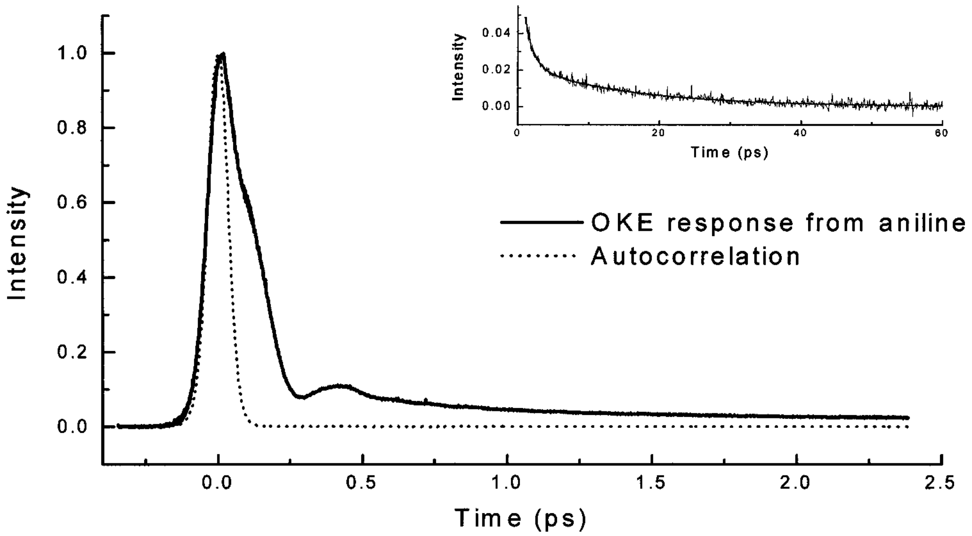

**Figure 1.** OHD-OKE data for liquid AN recorded at 1.33 fs per point. The laser cross-correlation function is shown as the dashed line. Inset is the data recorded between 1.0 and 60 ps, fit to a biexponential function.

the real (birefringence) part of the nonlinear response is recorded. Detection was by a photodiode and lock-in amplifier. For the highest time resolution scans, data points were recorded at 1.3 fs intervals. For long time data, measurements were made out to 60 ps (with a larger step size).

The AN sample was distilled under vacuum and injected into the 3 mm path length cuvette *via* a 0.2 $\mu$m filter. All measurements were made at 294 K.

The experimental apparatus and methodology used in the determination of the solvation dynamics of coumarin 102 in AN have been described in detail elsewhere.[19–23]

## 3. Results and Discussion

The OHD-OKE data for AN are displayed in Figure 1. In common with most such studies of polar liquids, the data reveal an instantaneous response due to the electronic hyperpolarizability and a noninstantaneous response due to the nuclear dynamics of principal interest. The nuclear component shows a rapid rise and decay followed by a strong oscillatory feature and a slower, nonexponential decay. Such a strong oscillatory feature has only been observed in a few liquids and is characteristic of strong intermolecular interactions and a structured liquid.[13] Also present, but not discernible in the figure, is a weak relatively long lived high frequency oscillation of intramolecular origin (this is seen more clearly in the frequency domain).[32]

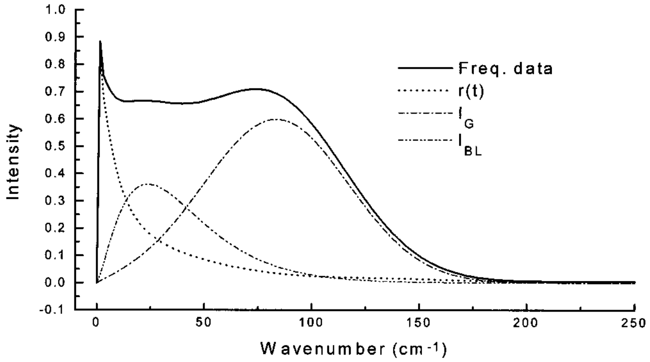

**Figure 2.** Imaginary part of the frequency domain representation of the data in Figure 1 after deconvolution. Also shown is the spectral deconstruction of the data into, with increasing frequency, a diffusional part, a collisional-induced part, $I_{\rm BL}$, and an antisymmetrized Gaussian.

Nuclear dynamics are most easily discussed on conversion to the frequency domain, where the identity of the OHD-OKE experiment with the low-frequency depolarized Raman scattering is clear.[33] The transformation methods, developed by McMorrow and Lotshaw, have been described in detail.[1–5] Essentially taking the imaginary part of the ratio of the Fourier transforms of the data and excitation function (also shown in Figure 1) yields the low-frequency depolarized Raman scattering spectrum of the liquid (modified by a Bose-Einstein occupation factor), Im[$R(\omega)$], uncontaminated by the instantaneous electronic response. This spectrum, up to 200 cm$^{-1}$, is shown in Figure 2. Beyond 200 cm$^{-1}$ a weak narrow feature of intramolecular origin was observed.[32] This spectrum can then be back-transformed to the time domain to yield the pure nuclear dynamics. It is however convenient to analyze the data in the frequency domain. First it is possible to separate the contributions to Im[$R(\omega)$] into a low-frequency, diffusive band and a higher frequency band of intermolecular modes. The low-frequency part is most readily obtained in the time domain by a fit of the long time (>1 ps) data to the function[6–9]

$$r(t) = [a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)][1 - \exp(-2\omega_0 t)] \tag{3}$$

where $\omega_0$ is the mean frequency of the intermolecular band and the time constants and preexponents are fitting parameters. The long time data for AN are clearly not exponential but are well described by the two-component fitting function (eq 3) with $\tau_1 = 1.2$ ps and $\tau_2 = 14.8$ ps. This function can be subtracted from the spectrum in the frequency domain to yield the pure intermolecular response. Such a separation into two bands, while approximate, has at least been shown to have some basis in simulations of liquid dynamics.[34] Rather less certain is the analysis of the complex line shape of the intermolecular response. Chang and Castner have shown that for a very wide range of liquids this portion of Im[$R(\omega)$] can be fitted to a sum of two functions:[9] first, an asymmetric line shape introduced by Bucaro and Litovitz,[34] $I_{\rm BL}(\omega) \approx \omega^{\alpha} \exp(-\omega/\omega_{\rm BL})$, peaked at $\omega_{\rm BL}$; secondly the librational intermolecular motion may be represented by an antisymmetrized Gaussian line shape.[9] Although the justification for fitting this broad band to two distinct functions is slight and the isolated binary collision model which leads to $I_{\rm BL}$ is unlikely to be applicable to AN, it has to be admitted that data for a wide range of liquids are well described by these two functions; AN may be added to this list

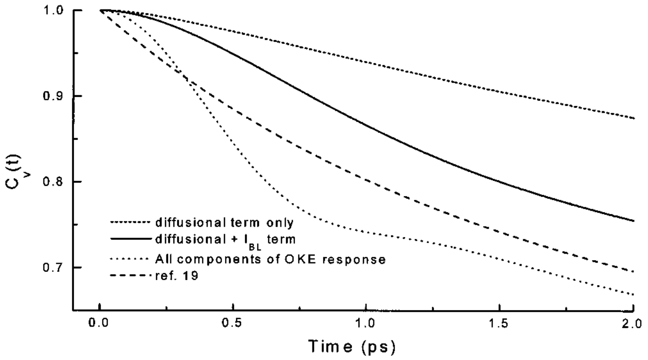

**Figure 3.** Solvation time correlation function calculated from the OHD-OKE data using eq 1. (a, ···) The entire data set has been included in the calculation; (b, —) the calculation is made omitting the anti-symmetrized Gaussian part of the OHD-OKE response; (c, - - -) only the diffusional part is included in the calculation. Also included (d, — — —) for comparison are the solvation dynamics measured by the time-resolved fluorescence method.[19]

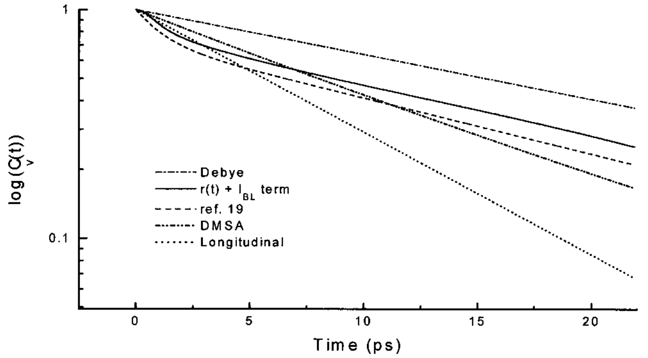

**Figure 4.** Long time behavior of (c) and (d) from Figure 4 compared and contrasted with various theoretical models of solvation dynamics.

(Figure 2). Further discussion of the parameters obtained from the fit is postponed to a more detailed study of AN and its derivatives.[32] The main objective here is to compare the data of Figure 2 with the solvation dynamics.[19]

The inverse transform of the data in Figure 2 yields either the complete nuclear response in the time domain or its separate components: diffusive, collisional, and librational. These data were converted to the polarizability correlation function, $C_2(t)$, using the method of Chang and Castner[6−9]

$$C_2(t) = 1 - \left[\int_0^t r(t)\,\mathrm{d}t \Big/ \int_0^\infty r(t)\,\mathrm{d}t\right]$$

Several models of orientational relaxation in liquids make the prediction $C_1(t) = [C_2(t)]^{1/3}$.[26,36,37] This relationship has been tested and found approximately true at least for the rotational diffusion time of several liquids.[37] By these means it is possible to construct the solvation time correlation function from eqs 1 and 2 and the OHD-OKE data, where $\alpha_S = 1.8$ for AN. The results are plotted in Figures 3 and 4. Also shown in these figures are the solvation dynamics data measured previously by Pal *et al.*[19]

First we consider the data over the first picosecond (Figure 3). The $C_v(t)$ calculated from the complete OHD-OKE data show an initial rapid nonexponential component of the Gaussian profile, a weak oscillation around 0.2 ps, followed by a longer nonexponential decay. An ultrafast feature of Gaussian profile in $C_v(t)$ is expected; it arises from the inertial motion of the solvent molecules, as has been discussed in numerous publications.[6−9,15,27,38] Such an inertial component has been observed in simulations of solvation dynamics[27,28] and in high time resolution fluorescence up-conversion experiments.[39] Thus the absence of an ultrafast Gaussian component in the measured solvation dynamics, Figure 3 and ref 19, deserves some comment. This component has proved elusive in some earlier experimental measurements, but this was ascribed to the limited (200 fs) resolution of the experiments.[27] Further, in those cases it was found that extrapolation of the shift with time of the fluorescence spectrum back to time zero did not reproduce the time zero spectrum predicted from experiments in nonpolar solvents.[27] For the AN spectra this extrapolation produced much closer agreement with the predicted time zero spectrum.[19] For this reason it seems necessary, in the case of AN, to seek explanations beyond limited time resolution for the absence of an ultrafast component in the solvation dynamics. Two explanations will be considered, one of which highlights the differences between solvation dynamics as embodied by eq 1, actual solvation dynamics, and OHD-OKE measurements; this subject has been addressed in theoretical and simulation studies by Ladyani and co-workers.[29,40] The second explanation concerns the molecular features of the AN−solute system.

An important approximation invoked in writing eq 1 is that the solvation dynamics are dominated by the rotational dynamics of the solvent. This approximation has been supported by simulations with both model and realistic solvent−solute systems.[38] However, it has been pointed out that the translational dynamics of the solvent may also contribute to the solvation.[29,40] It has also been shown that both translational and orientational dynamics are important in the polarization relaxation observed in OHD-OKE experiments.[40] However the relative importance of orientational and translational relaxation in the two measurements is not in general the same. In this sense it should not be expected that the measured OHD-OKE trace will, when treated by the methods described above, yield the observed solvation dynamics in every case. Ladyani and Klein have previously pointed out that in the much studied case of water as a solvent the solvation dynamics are mainly rotational in character, while the polarization relaxation occurs primarily through translation. Unfortunately the role of these different contributions is most easily assessed through molecular dynamics simulations, and these have not yet been attempted for the coumarin−AN system.

The second explanation for the differences reported in Figure 3 lies in the nature of the intermolecular interactions in AN. A second assumption made in writing eq 1 is that the solute has a negligible effect on the solvent dynamics. However, it can be seen (Figure 3) that the fast component in the calculated $C_v(t)$ arises almost exclusively from the intense and unusually high-frequency (85 cm$^{-1}$) component of [Im$R(\omega)$]. This mode has been assigned to a strong underdamped intermolecular mode of liquid AN. The frequency is higher than that found for methylated anilines[32] and for other polar aromatic liquids.[12] This mode in AN may be associated with the parallel H-bonded dimer of AN observed in the gas phase.[41] It seems reasonable to propose that such an intermolecular mode may be particularly sensitive to disruption by an adjacent solute molecule. Since the first solvation shell often makes the dominant contribution to solvation, it is likely that a strong perturbation of this mode would lead to an attenuation of the ultrafast component. Calculations with simulated data show that when the Gaussian component of Figure 2 is artificially broadened and attenuated by a factor of 2 (somewhat crudely representing an increased contribution of inhomogeneous broadening) an excellent agreement is obtained between the resulting $C_V(t)$ and the measured solvation dynamics. This proposition can be tested by further comparisons of solvation and OHD-OKE data; such measurements are planned.

**TABLE 1**

| model | exptl[19] [a] | OKE[a] | DMSA[2] [b] | Debye | longitudinal |
|---|---|---|---|---|---|
| $\tau_{\mathrm{rel}}$ | 17.8 | 19.75 | 12.25 | 22.2 | 8.11 |

[a] $\tau_{\mathrm{rel}}$ from a fit of 1 exponential to the long time ($t > 5$ ps) part of the decay. [b] Weighted mean lifetime.

In Figure 3 it can also be seen that the diffusional dynamics alone (as obtained from eq 3 and the procedures described above) cannot account for the solvation dynamics; the initial decay is too slow. However, if both the diffusional and collisional ($I_{\mathrm{BL}}$) parts of the OHD-OKE response are included in the calculation of $C_{\mathrm{v}}(t)$, a reasonable fit to the early time data is obtained, although the amplitude of the initial decay in the OHD-OKE data is a little too small. It is interesting to note that Cho *et al.* were able to simulate the solvation data for LDS 750 in acetonitrile including only the diffusional dynamics and an ohmic line shape (equivalent to $I_{\mathrm{BL}}$ with $\alpha = 1$).[17]

The data measured or calculated over a 20 ps time window are shown in Figure 4. Some theoretical models of solvation dynamics are included for comparison. The data are shown on a logarithmic scale, which allows a simple comparison of the slow exponential relaxation. The relaxation time recovered is shown in Table 1. Firstly we compare the solvation dynamics measured by the fluorescence shift method with $C_{\mathrm{V}}(t)$ obtained from OHD-OKE, analyzed in the manner described above. It is easy to see (Figure 4 and Table 1) that the agreement beyond 3 ps is very good indeed. This is an important result as it suggests that the OHD-OKE data, analyzed by the methods detailed,[6−9] provide, when used in combination with eq 1, an accurate representation of $C_{\mathrm{V}}(t)$, at least for the long time data.

In Figure 4 the experimental data are contrasted with the predictions of simple continuum models of solvation dynamics and of the dynamical mean spherical approximation. As input for these data the microwave absorption measurements of Garg and Smyth are used.[41] These authors found two dielectric relaxation times for AN, a minor one of 0.9 ps and a major one of 22.2 ps. For the purpose of calculation, given that the two relaxation times are so different, we use only the longer Debye time, $\tau_{\mathrm{D}}$. From this the longitudinal relaxation time can be calculated, $\tau_{\mathrm{L}} = (\epsilon_{\infty}/\epsilon_0)\tau_{\mathrm{D}}$. The simplest continuum theory of solvation dynamics predicts that $\tau_{\mathrm{L}}$ is equal to the solvation time.[15,16] This is clearly not the case for AN, where the measured solvation time lies between $\tau_{\mathrm{D}}$ and $\tau_{\mathrm{L}}$. An attempt has been made to model the solvation dynamics using the DMSA.[42] This requires as input both the dielectric parameters of the solvent and a parameter, $x$ in ref 41, describing the relative size of solvent and solute. In Figure 4 $x = 0.5 = R_{\mathrm{i}}^*/2R_{\mathrm{d}}$ where $R_{\mathrm{i}}^*$ is a scaled radius of a dipolar dumbbell representation of the solute and $R_{\mathrm{d}}$ represents the solvent radius.[42] As can be seen the DMSA model provides a better representation of the solvation dynamics in AN than does the simplest continuum model. It has been found previously that the DMSA provides a reasonable approximation to the measured solvation dynamics.

## 4. Conclusion

Liquid AN has been studied by means of femtosecond OHD-OKE measurements. These data, analyzed in the frequency domain, show high-frequency components which can be analyzed in terms of a collision-induced part and an underdamped intermolecular mode, as well as diffusional dynamics.

The OHD-OKE data have been used to construct the solvation time correlation function. The result has been directly compared with an experimental measurement of solvation dynamics in AN, the first time such a comparison has been attempted for liquids more complex than acetonitrile. At early times the agreement is not particularly good. It is found that attenuation or omission of the intermolecular mode's contribution to the solvation dynamics results in much better agreement. This can be accounted for if the presence of the solute were sufficient to disrupt the local structure of the solvent. Alternatively the differences between measured and calculated $C_{\mathrm{V}}(t)$ may imply that some of the approximations made in the analysis are inappropriate for AN solvents.

On a longer time scale (>1 ps) the agreement between the solvation time calculated from the OHD-OKE data and that measured in fluorescence experiments is much better, lending support to the idea that pure solvent dynamics can be used to estimate the solvation time. The solvation time, calculated or measured, is not well represented by the longitudinal relaxation time of AN, but a calculation using the DMSA provides much better agreement.

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