

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231658234>

# Relaxation Dynamics of Water and HCl Aqueous Solutions Measured by Time-Resolved Optical Kerr Effect

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · SEPTEMBER 1997

Impact Factor: 2.69 · DOI: 10.1021/jp962760v

---

CITATIONS

31

---

READS

19

5 AUTHORS, INCLUDING:



Paolo Foggi

Università degli Studi di Perugia

119 PUBLICATIONS 1,641 CITATIONS

SEE PROFILE



Roberto Righini

University of Florence

171 PUBLICATIONS 4,040 CITATIONS

SEE PROFILE

# Relaxation Dynamics of Water and HCl Aqueous Solutions Measured by Time-Resolved Optical Kerr Effect

Paolo Foggi,<sup>†</sup> Marco Bellini, Dany P. Kien, Isabelle Vercuque,<sup>‡</sup> and Roberto Righini<sup>\*,§</sup>

LENS (European Laboratory for Nonlinear Spectroscopy), University of Florence,  
L.go E. Fermi 2, 50125 Florence, Italy

Received: September 9, 1996; In Final Form: June 17, 1997<sup>®</sup>

Fast relaxation processes in water and HCl–water solutions are measured by time-resolved heterodyne detected optical kerr effect. The decay of the signal, observed after 500 fs, is well fitted by a biexponential. The temperature dependence of the two decay time constants and the relative weights of the two exponentials, for water and for samples of different HCl concentration, are consistent with a picture in which the hydrogen bonds dominate the dynamics and the optical response of the system: the fast decay time is closely related to the mean lifetime of individual H bonds, while the slow time constant is attributed to collective relaxation of structured regions of the liquid.

## Introduction

The dynamics, on a molecular scale, of liquid water and of aqueous solutions has been in the recent past the subject of a large number of theoretical<sup>1–3</sup> and experimental<sup>4–14</sup> papers. Not surprisingly, the general picture that can be extracted is that of a complex dynamics, characterized by different time constants. For instance, recent papers<sup>12–14</sup> reported on femtosecond time resolved optical Kerr effect (OKE) experiments investigating the dynamics of liquid water in the ultrafast regime, i.e., in a time scale well below 1 ps. This very fast dynamics is of course strictly related to the first events of the solvation processes in aqueous solutions and is then of primary importance for many chemical reactions. The very early step of relaxation in water is essentially nondiffusive in nature, being associated with vibrational and librational motions of the molecules. The same time resolved optical experiments have also shown quite clearly the appearance of a relaxation tail at longer times, extending up to about 15 ps at room temperature. Although evidence for such a “slow” relaxation dynamics in water has already been reported by several authors employing different experimental techniques,<sup>5–8,10</sup> still its characterization is far from being complete. At the same time, the renewed interest in proton-transfer processes claims for a better understanding of the diffusion-governed processes in aqueous solutions. In a recent paper<sup>11</sup> different contributions to the delayed OKE signal of different ionic aqueous solutions have been analyzed in details. In the present paper we present the results of the time-resolved OKE experiments performed at different temperatures on pure water and on HCl–water solutions. Changing over a large extent the concentration of H<sup>+</sup> ions in fact is expected to have a large influence on the hydrogen-bond network, which of course determines most of the dynamical properties of water and of aqueous solutions.

## Experimental Section

Triply distilled water (water p.a.) and concentrated (37%) HCl from Merck were used for the preparation of the samples.

<sup>†</sup> Also: Department of Chemistry, University of Florence, Via G. Capponi 9, 50121 Florence Italy.

<sup>‡</sup> From: LASIR, CNRS UPR A2631L, University Sci. et Techn. de Lille, 59655, Villeneuve d'Ascq, France

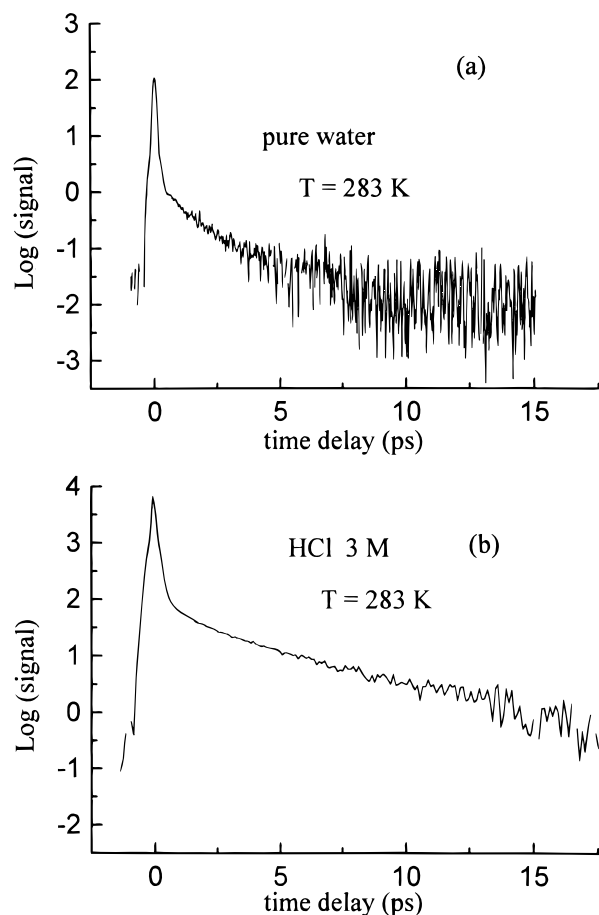
<sup>§</sup> Also: Department of Chemistry, University of Basilicata, Via N. Sauro 85, 85100 Potenza, Italy.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, August 15, 1997.

Repeated filtrations through cellulose acetate filters (pore size 0.22  $\mu\text{m}$ ) reduced the amount of scattering particles to a negligible level. The 1 cm, hermetically closed quartz cuvette used for the experiments was especially selected for minimum depolarization of light. The cuvette was placed in a copper holder, whose temperature was controlled by internal circulation of a thermostated liquid. The sample temperature was thus regulated within  $\pm 0.1$  K.

The laser system consisted of a Ti–sapphire oscillator (Spectra Physics Tsunami), pumped by a argon ion laser (Spectra Physics 2060), producing a train of mode-locked 80 fs pulses at 800 nm, with a repetition rate of 82 MHz, and average power of 1 W.

Heterodyne detection (HD) technique was used for measuring the time decay of the OKE signal. The technique has been described in several papers<sup>13,15,16</sup> and its advantages discussed. In the present case we adopted the HD technique because of the much higher sensitivity, compared to the homodyne detection. The experimental setup for the time-resolved OKE measurements was based on a standard scheme: the output of the Ti–sapphire laser was passed through a calcite polarizer and focused on the sample by a thin quartz lens ( $f = 100$  mm). About 10% of the pump beam was split off before the polarizer and sent to a computer controlled (0.1  $\mu\text{m}$  resolution) delay line. In view of the rather low Kerr response of the aqueous solutions, to increase the sensitivity of the detection and to exclude any possible background contribution from the pump, the probe beam was frequency doubled in a 600  $\mu\text{m}$  thick BBO crystal, placed after a calcite polarizer making an angle of 45° with the polarization plane of the pump beam. A second polarizer placed after the sample, adjusted for complete extinction of the probe beam in the absence of the pump, acted as an analyzer. The HD detection was realized by rotating the polarization direction of the entering probe beam by about 2°, thus generating the local oscillator. The throughput of the analyzing polarizer was sent to a monochromator (50 nm band-pass) to filter out any residual pump light, and detected by a photomultiplier. The heterodyne signal was measured by means of a lock-in amplifier, coupled to a mechanical chopper (3 kHz chopping rate) placed on the pump beam. The HDOKE signal time profiles shown in Figure 1 are obtained as the average of 20 repeated scans. The time resolution of the setup was tested by measuring the HDOKE signal of a thin quartz plate, whose



**Figure 1.** Time-resolved heterodyne detected OKE signal (semilog scale) of (a) pure water,  $T = 283$  K and (b) 3 M HCl aqueous solution at 283 K.

delayed optical response is practically negligible. A pair of LaKL21 glass Brewster angle prisms were placed at the output of the Ti-sapphire laser, and their relative distance adjusted in order to minimize the pulse duration on the sample; in the final setup used for the experiments, the fwhm of the heterodyne detected OKE signal from the quartz plate was 100 fs.

In principle heterodyne detected signals may contain also a small homodyne contribution; the tests that we performed in homodyne configuration on the different samples shown that this contribution is absolutely undetectable outside the  $t = 0$  electronic peak.

## Results

Figure 1 shows the heterodyne detected OKE signal measured in pure water and in 3 M HCl solution at 283 K. The shape of the time-resolved HDOKE signal of pure water was already discussed in detail in two recent papers:<sup>12,13</sup> it consists of (i) an intense peak at zero delay time, due to the purely electronic (instantaneous) response; (ii) a very fast (approximately within the first 500 fs) delayed contribution, that has been shown<sup>12,13</sup> to carry information on the inertial and vibrational dynamics of the water molecules; (iii) a rather weak tail, extending over a few picoseconds, associated with the relaxation dynamics of water. In both those papers this last contribution was interpreted as a biexponential decay.

Our results fully confirm those findings; more importantly, the same general structure of the signal, consisting of the three contributions at points i–iii is obtained also from the HCl solutions of different concentrations. In fact, the increase of the HCl concentration affects the intensity of the OKE signal, which increases strongly with the acidity of the solution, without changing the structure of the signal itself.

In refs 12–14 the contribution of point ii was discussed in great detail; here instead we focus our attention on the relaxational component of point iii, which gives rise to the long time tail of the signal.

We already noticed that the same authors interpreted this last contribution as a biexponential decay. This interpretation is fully consistent with the results of a number of frequency domain experiments<sup>5–7,9,10,17,18</sup> in which the depolarized light-scattering spectrum of water results as the superposition of two Lorentzians of different line widths.

It is well-known<sup>19</sup> that the depolarized Rayleigh scattering measures the power spectrum of the time correlation function of the first-order susceptibility  $\chi$ . On the other hand, an OKE experiment probes the third-order nonlinear susceptibility of the sample. For a molecular system, within the Born–Oppenheimer approximation, this quantity consists of two terms:<sup>20</sup>

(a) A purely electronic, essentially instantaneous contribution, described by a fourth-rank tensor  $\sigma$ , obtained as the quantum average of the molecular hyperpolarizability:

$$\sigma_{ijkl} \equiv \langle \gamma_{ijkl} \rangle \quad (1)$$

(b) A nuclear contribution  $d$ , which is proportional to the quantum average:

$$d_{ijkl} \equiv \frac{1}{2} \hbar^{-1} \langle [\chi_{ij}(t), \chi_{kl}(0)] \rangle \quad (2)$$

where the quantity in the brackets is the commutator of the linear susceptibility operator at different times.<sup>20</sup> This term is responsible for the delayed OKE signal, and it carries information on the dynamics of the molecular system.

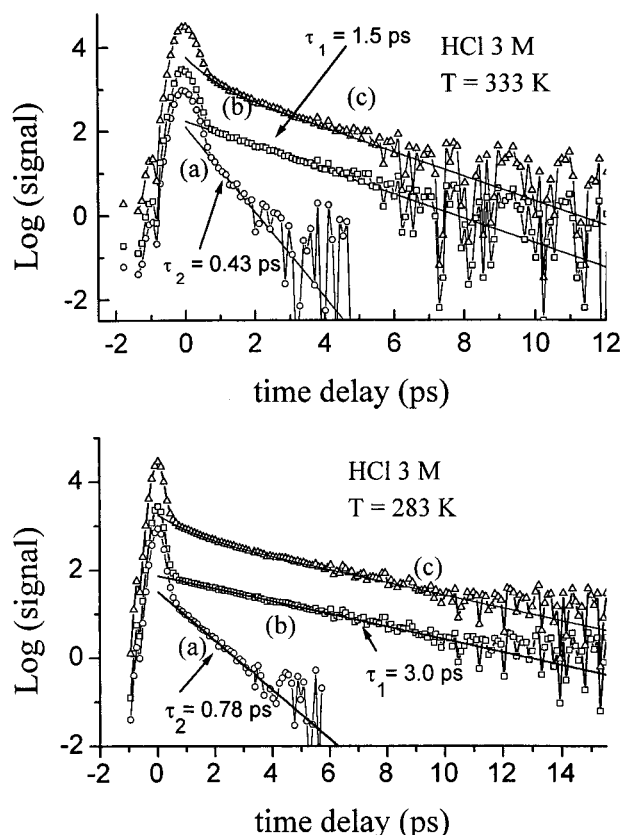
It has been shown<sup>21</sup> that the nuclear contribution of eq 2 corresponds to the time derivative of the classical time correlation function of the linear susceptibility. The superposition of two Lorentzians in a frequency spectrum then corresponds to a biexponential HDOKE decay function of the type

$$S(t) = \frac{A_1}{\tau_1} \exp(-t/\tau_1) + \frac{A_2}{\tau_2} \exp(-t/\tau_2) \quad (3)$$

This is then the form of the fitting function that we adopted in the analysis of the long-time tail of the HDOKE signal.

Actually we found that the response function in eq 3 reproduces very satisfactorily our experimental data of pure water and of the HCl solutions of different concentrations in the entire temperature range considered. Figure 2 illustrates the fitting procedure adopted. The choice of a biexponential function to reproduce the observed decay, although supported by the results of many previous independent experiments, is not obvious and deserves some further consideration. The existence of a quasi-glassy phase deep in the supercooled region (near 220 K) prompted us to test the ability of a stretched exponential function (often adopted for glass-forming liquids) of the form  $\exp(-(t/\tau)^\beta)$  to fit our experimental OKE decay curves. Several attempts in this direction allowed us to definitely rule out this possibility. In fact, as Figure 2 clearly shows, the long time tail of the decay is linear in the semilog plot: this requires a  $\beta$  exponent very close to unity ( $\beta \sim 0.95$ ), a value absolutely incompatible with the steep increase of the slope at short delays (Figure 2). We can conclude that the optically induced birefringence shows, in the temperature interval considered, an essentially bimodal relaxation; the biexponential form (3) is the simplest function that reproduces satisfactorily our experimental results.

The procedure adopted to evaluate the parameters in the biexponential function (3) is the following: zero-order values of the longer time constant  $\tau_1$  and of the relative weight  $A_1$  are



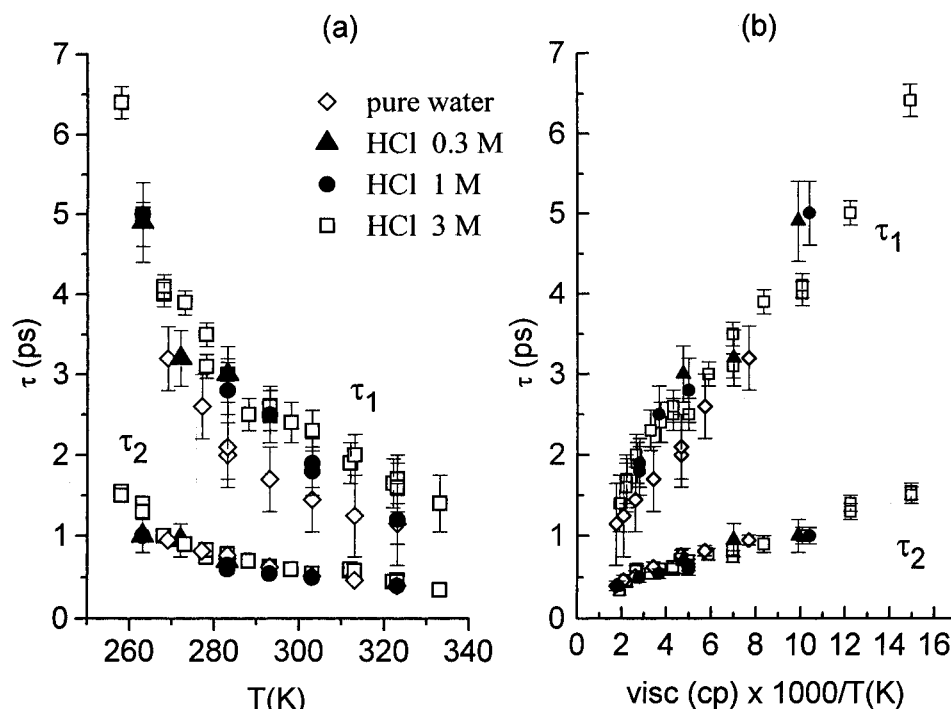
**Figure 2.** Procedure used to extract the decay times. The open circles of curve (a) represents the experimental data of Figure 1a after subtraction of the contribution from the slow decay; the solid line is the fit to a single exponential ( $\tau_2$ ). The squares of curve (b) represent the experimental data after the subtraction of the fast decay (obtained from curve (a)); the solid line is the fit to a single exponential ( $\tau_1$ ). Curve (c) shows the resulting fit of the biexponential decay function to the experimental data. The three curves have been offset along the vertical axis for better visibility.

directly extracted from the long time tail of the decay. The exponential function  $A_1/\tau_1 \exp(-t/\tau_1)$  is then subtracted from

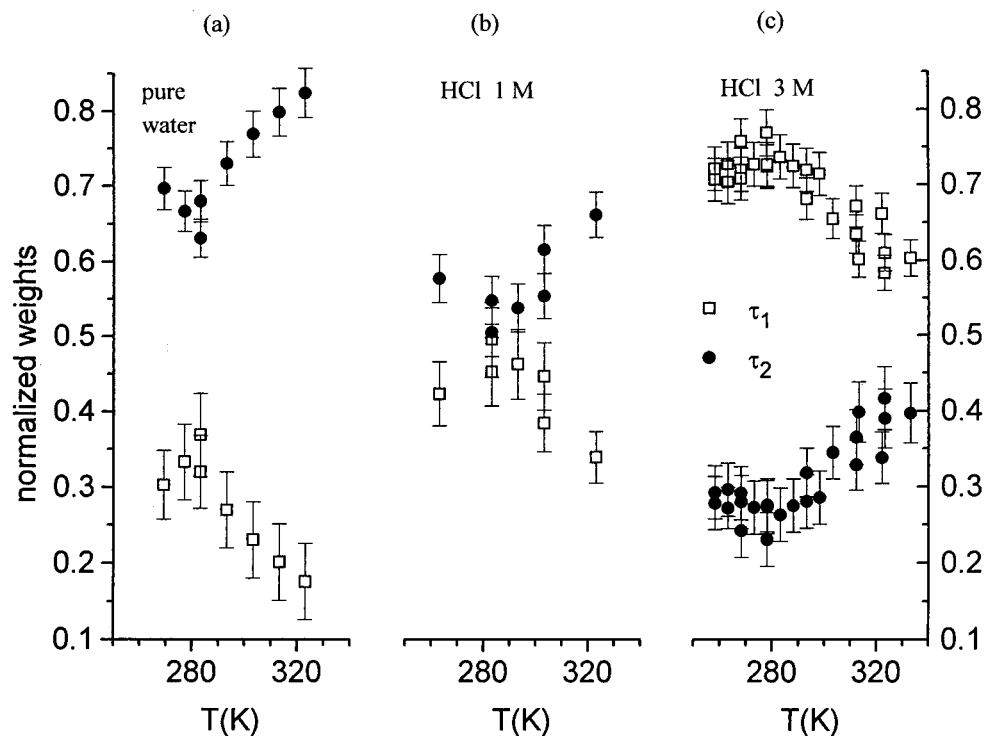
the experimental HDOKE time profile, and the parameters  $A_2$  and  $\tau_2$  are then obtained from the remaining signal. The biexponential function thus obtained is used as the starting function in an overall least-squares fitting of the full experimental profile.

Figure 2 demonstrates the quality of the fitting for 3 M HCl aqueous solution at 283 and 333 K. In this case, the presence of a very fast contribution due to the inertial and vibrational dynamics, which appears as a weak shoulder on the purely electronic peak, does not affect the fitting. Also at high temperature, when the short relaxation time becomes less than 500 fs, the method adopted allows for a clear identification of the two exponential components. Only for pure water, whose OKE intensity is much lower, we followed, for temperatures higher than 310 K, a deconvolution procedure to extract the correct value of  $\tau_2$ . In the deconvolution we took advantage of the detailed knowledge of the very fast dynamics derived from refs 12–14. Auto- and cross-correlation traces gave a Gaussian form for the pump and probe pulses, with a duration of 75 fs; a very fast exponential decay (100 fs time constant) was added to account for the relaxation of the Raman-induced inertial and vibrational term, which contribute to the signal in the first 500 fs. We notice here that duration of the pulses used in our experiments is longer than that used in refs 12–14 (30% and 80%, respectively); for this reason the Raman-induced term is much less effectively excited in our experiments, and its fine structure cannot be resolved.

In Figure 3a the  $\tau_1$  (slow decay) and  $\tau_2$  (fast decay) relaxation times measured at different temperatures are collected. The error bars are obtained from the distribution of the fitting parameters obtained from different sets of data, and from the standard deviation provided by the refinement procedure. It is apparent that the behavior of the two time constants is quite similar for the different solutions, the main difference consisting of a slight increase of the relaxation times with the HCl concentration. The similarity is even more striking if the data are corrected for the value of the bulk viscosity of the liquids. As shown in Figure 3b, both  $\tau_1$  and  $\tau_2$  of all the different HCl solutions and of pure water coincide within the experimental



**Figure 3.** Measured decay times  $\tau_1$  and  $\tau_2$  for pure water and for three aqueous solutions of HCl of different concentrations. In Figure 3a the relaxation times are shown vs the absolute temperature; in Figure 3b the same values are given vs the viscosity divided by the temperature.



**Figure 4.** Weights  $A_1$  and  $A_2$  of the  $\tau_1$  and  $\tau_2$  contributions to the OKE signal (see eq 1 in the text) for (a) pure water, (b) 1 M HCl, and (c) 3 M HCl. For each temperature the sum of the two weights is normalized to 1.

error, when plotted against the viscosity  $\eta$  (from ref 22) divided by the temperature. This way of presenting the data is suggested by the Debye–Stokes–Einstein relation:

$$\tau = V_{\text{eff}}\eta/KT \quad (4)$$

that is commonly used, in a simple hydrodynamic approach,<sup>19</sup> to describe the temperature dependence of the rotational relaxation of a molecule in a continuum medium. We will return later to the meaning and implications of eq 4 in the present case.

Figure 4 shows that the temperature dependence of the amplitudes  $A_1$  and  $A_2$  (normalized to unity; see eq 3) is essentially unchanged in the different samples. On the contrary, the relative values of  $A_1$  and  $A_2$  at each temperature are strongly dependent on the HCl concentration: the contribution of the slow ( $\tau_1$ ) process increases roughly by a factor five, compared to the fast ( $\tau_2$ ) process, on going from pure water to 3M HCl solution.

We already mentioned that the relaxation dynamics of pure water was the subject of several depolarized light-scattering experiments, from which the line shape results as the superposition of two Lorentzians. The corresponding relaxation times  $\tau_1$  and  $\tau_2$  available from those experiments are rather scattered over the temperature range considered here; however, they are in generally good agreement with our values, given in Figure 3a. Under this respect, we find of special relevance, in view of the completeness of those data, the agreement with the results by Conde and Teixeira<sup>5</sup> and Montrose et al.<sup>17</sup>

In the two recent time-resolved OKE papers on water the long time decay of the signal was equally interpreted as a biexponential relaxation: our values for the relaxation times coincide closely with the time constants obtained by Palese et al.<sup>13</sup> in their room-temperature experiment, while they are about 30% higher than those obtained by Castner et al.<sup>12</sup> at the same temperature.

In conclusion, the following points summarize the main features of our results:

(1) In the entire temperature range considered and for all the different samples investigated, the decay of the delayed HDOKE signal is well reproduced by a biexponential function. In respect our data agree completely with the results of several previous depolarized light-scattering and time-resolved OKE experiments on pure water. If the effect of viscosity is taken into account, the curves representing the temperature dependence of  $\tau_1$  and  $\tau_2$  for the HCl solutions of different concentrations and for pure water overlap within the experimental error.

(2) For all the liquids investigated, the relative contribution of the slow decay to the overall relaxation increases with decreasing temperature, while the opposite behavior is shown by the slow decay (Figure 4).

(3) The relative weight of the slow decay increases with increasing HCl concentration (Figure 4).

## Discussion

The first point we want to stress is that the main features of the HDOKE signal decay are maintained, throughout the entire temperature range, on going from pure water to the HCl solutions. The only relevant difference concerns the overall intensity of the signal, which increases substantially with the HCl concentration, and the relative intensity of the fast and slow contributions to the decay. It is then a reasonable assumption that the structural and dynamical properties that determine the observed relaxation are essentially the same in pure water and in HCl solutions; actually, the differences that we already noticed among the various samples can provide important information on those properties.

With this idea in mind, on proposing an interpretation of the ensemble of the experimental results, we find it more convenient to start from the HCl solutions. The following discussion is greatly based on the paper by Danninger and Zundel,<sup>18</sup> who investigated the depolarized light-scattering spectra of HCl solutions, providing a very illuminating picture of the relation between the microscopic dynamics of those systems and their optical properties. Both depolarized Rayleigh scattering and time-resolved OKE measure the time correlation function of

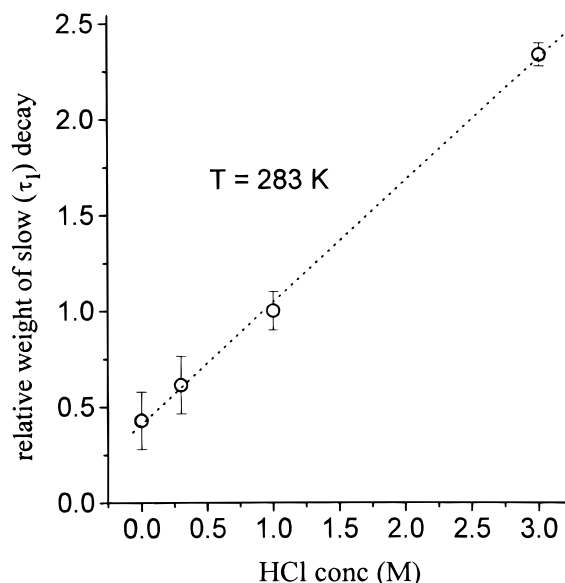
the linear susceptibility. The simplest approach, quite frequently used, is that of expressing the macroscopic susceptibility as the sum of the individual molecular polarizability:

$$\chi_{ij} = \sum_n \alpha_{ij}(n) \quad (5)$$

However, this simple assumption does not seem acceptable for water and aqueous solutions. In fact, the polarizability of an isolated water molecule is essentially isotropic, as already noted by several authors,<sup>17,18,23,24</sup> so that its contribution to the OKE signal (and equally to the depolarized light scattering) would be absolutely negligible. This leads to the conclusion that the origin of the observed delayed OKE response and of the depolarized light scattering is essentially intermolecular in nature.<sup>17,18</sup>

Water and aqueous solutions are characterized by a high degree of intermolecular connectivity, as a result of the ability of forming up to four hydrogen bonds per molecule. Under this respect acid solutions differ remarkably from pure water: the formation of protonated complexes  $(\text{H}_2\text{O})_n\text{H}^+$  (the value of  $n$  may vary,  $n = 4$  appearing as the most probable) produces strongly bonded molecular clusters, characterized by a strengthening of the hydrogen bonds in the vicinity of the ion. In particular, theoretical<sup>2,3</sup> and experimental<sup>4,18,25</sup> investigation show that adding HCl to water has a large effect on the average  $\text{O}\cdots\text{H}\cdots\text{O}$  distance: its value in fact decreases from 2.85 Å in pure water to 2.52 Å in 13.8 M HCl.<sup>25</sup> This is of particular relevance with respect to the observed increase of the OKE signal intensity with increasing acidity. In fact, the shortening of the inter-oxygen distance is accompanied by a large modification of the intermolecular potential along that coordinate: the double-well potential passes from a largely asymmetric geometry to a quasi-symmetric configuration. In this latter geometry the barrier to proton exchange becomes very small, and the situation closely resembles that of a charged particle in an unidimensional box. As a consequence, the polarizability of the H-bond network increases dramatically. The  $\text{O}\cdots\text{H}\cdots\text{O}$  being group quasi-unidimensional, its polarizability is highly directional: this means large anisotropy of the polarizability per unit volume of the liquid, and hence large contribution to the OKE signal and to the depolarized light-scattering intensity. This picture provides a fully satisfactory explanation of the large increase of the intensity of the OKE signal (this work), of the depolarized Rayleigh scattering,<sup>18</sup> and of the Raman scattering<sup>4</sup> with the concentration of HCl.

Of course at HCl concentrations  $\leq 3$  M not all water molecules are engaged in the molecular aggregates around the positive ions: there is a continuous exchange of molecules between those aggregates and the bulk of more loosely bound molecules, involving breaking and formation of hydrogen bonds. The susceptibility of the sample is then modulated at a high rate by the breaking and formation of H-bonds involving the “free” molecules. Here is the origin of the biexponential relaxation observed. The lifetime of the strongly bound groupings is of course longer than that of the individual hydrogen bonds with the neighboring water molecules and between them; the relaxation of those structures is then responsible for the long ( $\tau_1$ ) relaxation time observed in our experiments. It is instead the high-frequency modulation of the overall susceptibility, produced by the breaking and formation of H-bonds with and within external water molecules, which causes the relaxation process resulting in the fast decay ( $\tau_2$ ) of the OKE signal. This interpretation is fully confirmed by the temperature and concentration dependence of the relative amplitudes  $A_1$  and  $A_2$  shown in Figure 4: as the HCl concentration increases, the relative weight  $A_1$  of the collective relaxation



**Figure 5.** Ratio  $A_1/A_2$  ( $A_1$  = weight of the slow decay;  $A_2$  = weight of the fast decay, see eq 1 in the text) for different concentrations of HCl, obtained from experiments performed at 283 K.

increases with respect to that of the “free” molecules. Figure 5 shows that this increase is linear in the HCl concentration. It is not surprising that the corresponding increase of the slow relaxation time  $\tau_1$  parallels that of the viscosity (Figure 3a,b): both properties are in fact largely dependent on the size, number and stability of the H-bonded groupings discussed above. In this sense then the use of eq 4 to normalize the relaxation time is not arbitrary.

Clearly the size and the stability of those aggregates increases at low temperature: this explains the increasing value of the ratio  $A_1/A_2$  with decreasing temperature observed for all the different solutions (Figure 4).

The experimental evidence then points to the following picture:

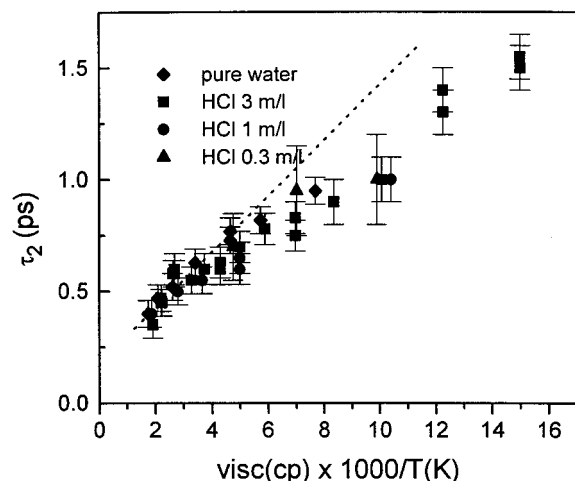
- (1) The fast decaying contribution to the delayed OKE signal is attributed to the modulation of the susceptibility of the liquid due to breaking and formation of individual hydrogen bonds.
- (2) The slow decay is due to the collective relaxation of highly connected H-bonded molecular groupings, whose relative weight increases at high HCl concentration and at low temperature.

The essentially “local” nature of the  $\tau_2$  relaxation is confirmed by Figure 6: it is evident that, at low temperature, this relaxation time does not follow the temperature dependence of the viscosity, represented by the dotted line (from ref 5). In this sense the normalization of the  $\tau_2$  times with the viscosity of Figure 3b is not fully justified. The error introduced by this correction is however quite small: the maximum divergence of  $\tau_2$  from the linear dependence on  $\eta$  is in fact about 15% (see Figure 6).

In Figure 7 the values of  $\tau_1$  and  $\tau_2$  are reported in an Arrhenius plot. The activation energy of the fast relaxation in the different samples (2.7–2.8 kcal/mol, see Table 1) is a further confirmation of the connection of this process with hydrogen bond lifetime. In fact, its value is very close to that obtained by Montrose et al. (3.0 kcal/mol, ref 17) and by Conde and Teixeira (2.7 kcal/mol, ref 5), and it corresponds to the energy difference

**TABLE 1: Activation Energies (kcal/mol) from the Arrhenius Plots of Figure 7**

	$E_a(\tau_1)$	$E_a(\tau_2)$
H <sub>2</sub> O	$3.2 \pm 0.2$	$2.8 \pm 0.1$
1 M HCl	$3.6 \pm 0.4$	$2.7 \pm 0.2$
3 M HCl	$3.5 \pm 0.1$	$2.7 \pm 0.1$



**Figure 6.** Fast relaxation time  $\tau_2$  vs the viscosity divided by the temperature. The dotted line corresponds to a linear relation of  $\tau_2$  and  $\eta/T$  (from ref 5).

(2.5–3 kcal/mol) between bonded–unbonded configurations in water, obtained in previous experimental<sup>4,26,27</sup> and theoretical<sup>28,29,30,31</sup> work. Note that, in all cases, this value is definitely less than the generally accepted depth of the individual hydrogen bond potential well ( $V_{HB} = 3.5$ –4.5 kcal/mol). This can be easily understood on the basis of the stochastic approach of ref 28. In fact, the rate constant is given by

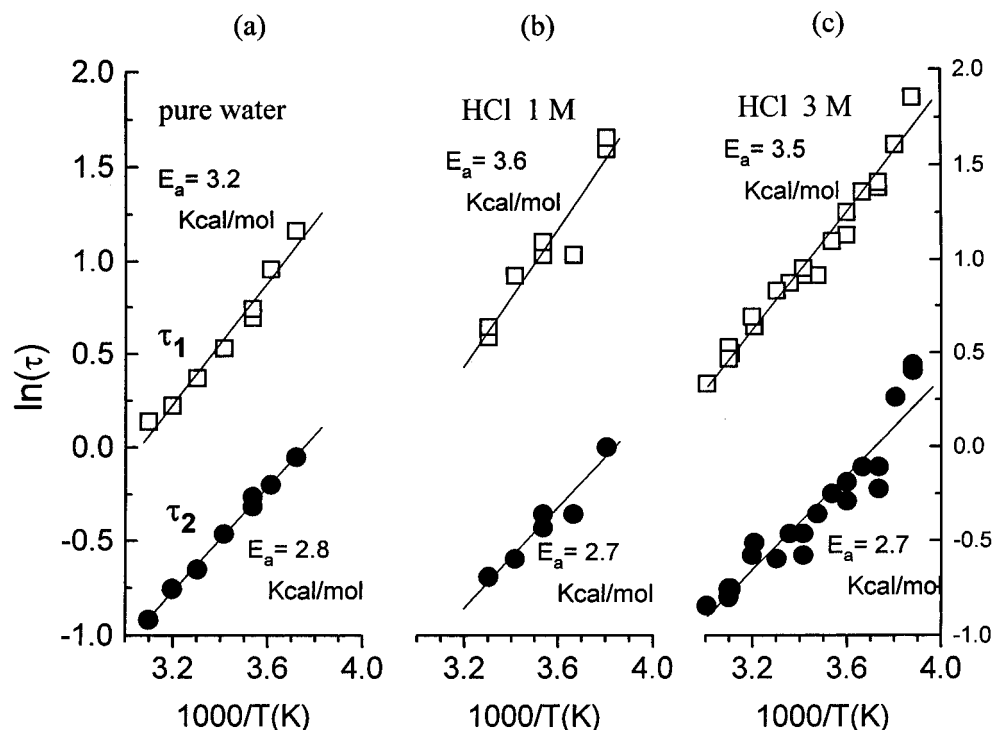
$$k(T) = \frac{1 - p_B(T)}{p_B(T)} = Ae^{-E_a/KT} \quad (6)$$

according to the authors,<sup>28</sup> with the choice  $V_{HB} = 3.5$  kcal/mol, the probability  $p_B$  that an hydrogen bond is intact varies almost linearly between 260 K ( $p_B \sim 0.7$ ) and 340 K ( $p_B \sim 0.5$ ), yielding for the activation energy  $E_a$  the value of 2.4 kcal/mol.

On accepting the interpretation of the slow  $\tau_1$  process as an essentially collective relaxation, one would expect that, in

contrast with the “local”  $\tau_2$  process, it follows the same temperature dependence of typical transport properties, such as, for instance, viscosity. It is well-known that the viscosity of water does not follow an Arrhenius behavior, its activation energy increasing with decreasing temperature.<sup>32</sup> However, the divergence of different transport properties of water is evident only at temperatures below about 270 K.<sup>5</sup> Very likely, our measurements do not extend low enough in temperature to clearly observe, also because of the experimental error of the data, the appearance of such a critical behavior of the slow relaxation. It may be of some interest that, if we pretend to fit the viscosity data of ref 32 with an Arrhenius law between 263 and 333 K, we obtain a value of about 3.7 kcal/mol for the mean activation energy in that range. This value is not far from our findings for  $\tau_1$  (see Figure 7).

It is quite clear that in this picture pure water represents just the limiting case of vanishingly low HCl concentration. The interpretation, extended to pure water, of  $\tau_1$  as a collective relaxation time, and of  $\tau_2$  as closely connected to the lifetime of the hydrogen bond coincides with the prediction of the stochastic treatment by Bertolini et al.:<sup>28</sup> in their picture the relaxation of liquid water is biexponential, the longer time constant “being... the time of residence in the structured region” of water. The setup of a dynamic equilibrium between highly disordered regions and tetrahedrally bonded, icelike structures in water has been invoked by several authors. Rousset et al.,<sup>6</sup> for instance, estimated from the Raman spectra a correlation radius for those aggregates of 11 Å at 293 K and of 27 Å at 268 K. Of course the hydrogen bonds in those structured regions do not differ substantially from those in the disordered regions of the liquid (differently from what happens in acidified water): the susceptibility is then definitely lower than that of HCl solutions, and the relative weight of the collective relaxation is much smaller (Figure 5). At the same time, also the stability of those structures is lower than in the HCl solutions, and the  $\tau_1$  relaxation is correspondingly faster. Not surprisingly, its dependence on concentration parallels that of the viscosity (Figure 3b). The temperature dependence of the ratio  $A_1/A_2$



**Figure 7.** Arrhenius plot of  $\tau_1$  and  $\tau_2$  for (a) pure water; (b) 1 M HCl, and (c) 3 M HCl. The activation energies  $E_a$  obtained from a linear fit are shown.

(Figure 4) also for pure water is due to the strongly correlated, tetrahedrally connected molecular structures, whose size and number increase at low temperature.<sup>33</sup>

The appearance of a contribution of collective dynamics to the relaxation of birefringence in liquids is not an isolated case: there is, in fact, clear experimental evidence that in liquids characterized by strong intermolecular correlation, a single-molecule picture cannot explain the experimental data. This is the case for instance of the isotropic phase of liquid crystals: even 50 °C above the nematic transitions, experiments (time-resolved OKE<sup>34</sup> and light scattering<sup>35</sup>) show that, in addition to what is interpreted as single-molecule relaxation, a slower relaxation is present with a relative weight that increases when the temperature is lowered. This slow decay is attributed to collective dynamics of the correlated molecules.

Obviously acid aqueous solutions contain also a relevant amount of Cl<sup>-</sup> ions; to verify the possible effects of the presence of the negative counterions, we performed OKE measurements on NaCl solutions of different concentrations up to 3 M: the results agree with previous findings from our group,<sup>11</sup> showing no significant difference from pure water. We can thus confirm previous indications<sup>24,25</sup> that the Cl<sup>-</sup> ions in moderate concentrations, do not perturb noticeably the dynamic behavior of water or, at least, that part of the dynamics that can be investigated by OKE or by depolarized light scattering.

## Conclusions

The picture of liquid water and of HCl solutions that emerges from the body of experimental results given here is that of systems whose delayed optical response in an OKE experiment is largely dominated by the hydrogen-bond network. The relaxation dynamics revealed by this time resolved technique then is essentially that of the H-bonds. It is characterized by a biexponential decay: the fast process (0.3–1.2 ps, depending on the temperature) is closely related to the mean lifetime of the individual hydrogen bonds. The temperature dependence of the fast decay time corresponds to an activation energy (2.7 kcal/mol) that equals the energy required for breaking an H-bond in water. Consistently with its "local" nature, the fast relaxation process is only slightly affected by the addition of HCl.

The relative weight of the slow (1.2 ps to about 6 ps at low temperature) relaxation instead increases markedly with the concentration of HCl. The corresponding time constants, once corrected for the value of the bulk viscosity of the different solutions, are instead practically independent of the HCl concentration, showing an activation energy higher than that of the fast process. This slowly relaxing contribution to the OKE signal is attributed to structured regions of the liquid, whose number and size increases at low temperature. The corresponding decay time then measures the mean lifetime of those strongly correlated structures. The relative simplicity of the picture for the relaxation of simple aqueous solutions that emerges from the present results and from those of several other authors<sup>5–7,10–14,17,18,28</sup> may appear in contrast with the great complexity (in terms of interactions and degrees of freedom) of such highly connected liquids. The fact is that, according to our interpretation based on the Zundel picture of the susceptibility of aqueous solutions,<sup>18</sup> the optical birefringence is induced in the sample through the polarization of the H-bond network; in other words, the OKE signal and, equally, the depolarized light scattering, are only sensitive to that part of the dynamics directly involving this specific interaction.

Other liquids of small molecules (alcohols, carboxylic acids, for instance) are characterized by strong hydrogen bonds, with geometrical and energetic characteristics quite different from those of water: we intend to extend our investigation to some

of these liquids. At the same time, quantum molecular dynamics calculations on water and water solutions, primarily aimed to the investigation of the collective dynamics of the liquid, would provide a fundamental contribution to a better understanding of the dynamical properties of these ubiquitous molecular liquids.

**Acknowledgment.** This work was supported by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and by the Commission of the European Communities under Contract No. GE1-CT92-0046. D.P.K. gratefully acknowledges the financial support under the HCM Contracts CHRX-CT930282 and CHRX-CT940561.

## References and Notes

- (1) Stanley, H. E.; Teixeira, J. J. *Chem. Phys.* **1980**, *73*, 3404.
- (2) Moore Plummer, P. L. *J. Mol. Struct.* **1990**, *237*, 47.
- (3) Tuckerman, M.; Laasonen, K.; Spick, M.; Parrinello, M. *J. Phys. Chem.* **1995**, *99*, 5749.
- (4) Walrafen, G. E.; Chu, Y. C.; Carlon, H. R. In: *Proton Transfer in Hydrogen Bonded Systems*; Bountis, T., Ed.; Plenum Press: New York, 1992.
- (5) Conde, O.; Teixeira, J. J. *Phys.* **1983**, *44*, 525.
- (6) Rousset, J. L.; Duval, E.; Boukenter, A. *J. Chem. Phys.* **1990**, *92*, 2150.
- (7) Mizogouchi, K.; Hori, Y.; Tominaga, Y. *J. Chem. Phys.* **1992**, *97*, 1961.
- (8) Bertolini, D.; Cassettari, M.; Salvetti, G. *J. Chem. Phys.* **1982**, *76*, 3285.
- (9) Sobron, F.; Puebla, F.; Rull, F.; Faurskov Nielsen, O. *Chem. Phys. Lett.* **1991**, *185*, 393.
- (10) Sokolov, A. P.; Hurst, J.; Quitman, D. *Phys. Rev.* **1995**, *B51*, 12865.
- (11) Santa, I.; Foggi, P.; Righini, R.; Williams, J. H. *J. Phys. Chem.* **1994**, *98*, 7692.
- (12) Castner, E. W., Jr.; Chang, Y. J.; Chu, Y. C.; Walrafen, G. E. *J. Chem. Phys.* **1995**, *102*, 653.
- (13) Palese, S.; Shilling, L.; Miller, R. J. D.; Staver, P. R.; Lotshaw, W. T. *J. Phys. Chem.* **1994**, *98*, 6308.
- (14) Palese, S.; Mukamel, S.; Miller, R. J. D.; Lotshaw, W. T. *J. Phys. Chem.* **1996**, *100*, 10380.
- (15) Eesley, G. L.; Levenson, M. D.; Tolles, W. M. *IEEE J. Quantum Electron.* **1978**, *14*, 45.
- (16) McMorro, D.; Lotshaw, W. T.; Kenney-Wallace, G. A. *IEEE J. Quantum Electron.* **1988**, *24*, 443.
- (17) Montrose, C. J.; Bucaro, J. A.; Marshall-Coakley, J.; Litovitz, T. A. *J. Chem. Phys.* **1974**, *60*, 5025.
- (18) Dunninger, W.; Zundel, G. *J. Chem. Phys.* **1981**, *74*, 2769.
- (19) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley: New York, 1976.
- (20) Hellwarth, R. W. *Prog. Quantum Electron.* **1977**, *5*, 1.
- (21) Wang, C. H. *Spectroscopy of condensed media, dynamics of molecular interactions*; Academic Press: London, 1985. Yan, Y. X.; Nelson, K. A. *J. Chem. Phys.* **1987**, *87*, 6257. Ruhman, S.; Joly, A. G.; Nelson, K. A. *IEEE J. Quantum Electron.* **1988**, *24*, 460.
- (22) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boston, 1990.
- (23) Orttung, W. H.; Meyer, J. A. *J. Phys. Chem.* **1963**, *67*, 1905.
- (24) Zhu, Sheng-Bai; Sing, S.; Robinson, G. W. In: *Modern Nonlinear Optics*, Part 3; Evans, M., Kielich, S., Eds.; *Adv. Chem. Phys. Series*; Wiley: New York, 1994; Vol. 85, p 627.
- (25) Triolo, R.; Narten, A. H. *J. Chem. Phys.* **1975**, *63*, 3624.
- (26) Davis, C. M.; Litovitz, T. A. *J. Chem. Phys.* **1965**, *42*, 2563.
- (27) Worley, J. D.; Klotz, I. M. *J. Chem. Phys.* **1966**, *45*, 2868.
- (28) Bertolini, D.; Cassettari, M.; Ferrario, M.; Grigolini, P.; Salvetti, G. In: *Memory Function Approaches to Stochastic Problems in Condensed Matter*; Evans, M. W., Grigolini, P., Pastori Parravicini, G., Eds.; in *Adv. Chem. Phys. Series*; Wiley: New York, 1985; Vol. 62, p 277.
- (29) Rahman, A.; Stillinger, F. H. *J. Chem. Phys.* **1971**, *55*, 336.
- (30) Rapaport, D. C. *Mol. Phys.* **1983**, *50*, 1151.
- (31) Geiger, A.; Mausbach, P.; Shnikter, J.; Blumberg, R. L.; Stanley, H. E. *J. Phys. (Paris)* **1984**, *C7*, 31.
- (32) Hallet, J. *Proc. Phys. Soc.* **1963**, *82*, 1046.
- (33) Stanley, H. E.; Teixeira, J. J. *Chem. Phys.* **1980**, *73*, 3404.
- (34) Stankus, J. J.; Torre, R.; Marshall, C. D.; Greenfield, S. R.; Sangupta, A.; Tokmakoff, A.; Fayer, M. D. *Chem. Phys. Lett.* **1992**, *193*, 213. Stankus, J. J.; Torre, R.; Fayer, M. D. *J. Phys. Chem.* **1993**, *97*, 9480.
- (35) Torre, R.; Santa, I.; Righini, R. *Chem. Phys. Lett.* **1993**, *212*, 90. Torre, R.; Ricci, M.; Saielli, G.; Bartolini, P.; Righini, R. *Mol. Cryst. Liq. Cryst.* **1995**, *262*, 391.
- (36) Stinson, T. W.; Lister, J. D.; Clark, N. A. *J. Phys., Paris* **1972**, *33*, C1–69.