Relaxation dynamics in (HF)$_x$(H$_2$O)$_{1-x}$ solutions

R. Angelini, P. Giura, and G. Monaco
European Synchrotron Radiation Facility, B.P. 220, F-38043, Grenoble Cedex, France

G. Ruocco
Università di Roma “La Sapienza” and Istituto Nazionale di Fisica della Materia, I-00185, Roma, Italy

F. Sette
European Synchrotron Radiation Facility, B.P. 220, F-38043, Grenoble Cedex, France

(Received 6 April 2005; accepted 16 May 2005; published online 22 July 2005)

The high-frequency dynamics of (HF)$_x$(H$_2$O)$_{1-x}$ solutions has been investigated by inelastic x-ray scattering. The measurements have been performed as a function of the concentration in the range $x=0.20–0.73$ at fixed temperature $T=283$ K. The results have been compared with similar data in pure water ($x=0$) and pure hydrogen fluoride ($x=1$). A viscoelastic analysis of the data highlights the presence of a relaxation process characterized by a relaxation time and a strength directly related to the presence of a hydrogen-bond network in the system. The comparison with the data on water and hydrogen fluoride shows that the structural relaxation time continuously decreases at increasing concentration of hydrogen fluoride passing from the value for water to the one for hydrogen fluoride $\tau_{\text{HF}}$, which is three times smaller. This is the consequence of a gradual decreasing number of constraints of the hydrogen-bond networks in passing from one liquid to the other.


I. INTRODUCTION

The study of the high-frequency dynamics of liquids presents many open and debated topics related to the propagation of the density fluctuations. One of the most important concerns is the understanding of the relaxation processes at a microscopic level and of the associated physical mechanisms which affect the dynamics of the density fluctuations. For instance, the dynamics of glass-former liquids is strongly dominated by the structural ($\alpha$) relaxation process with a characteristic time ($\tau_\alpha$) which is strongly temperature dependent. At the glass transition $\tau_\alpha$ becomes of the order of hundreds of seconds. The $\alpha$ process is not the only one present in liquids. The presence of more than one relaxation process affecting the dynamics of density fluctuations is well documented for different classes of samples: in simple Lennard-Jones liquids the evidence comes from molecular-dynamics simulations; in molecular liquids, relaxation processes associated with the internal degrees of freedom of the molecules may be observed; if in liquid metals the experimental evidence of two distinct relaxation processes has been recently found in studying the dynamic structure factor $S(Q, \omega)$ (Ref. 5) by inelastic x-ray scattering (IXS). In the IXS studies, the two relaxation processes which affect the high-frequency dynamics are referred to as the $\alpha$ process and the microscopic or the $\mu$ process. While the $\alpha$ relaxation is associated with the structural rearrangement of the particles in the liquid, the $\mu$ process takes its origin from the oscillatory motion of a particle in the cage of its nearest neighbors before escaping. Since the instantaneous liquid structure is “disordered,” the collective oscillation of the atoms/molecules around their equilibrium position is not described by a “plain wave” and this produces a decay (a relaxation) of the energy stored in the density fluctuation with a well-defined $Q$ vector. The two relaxations are characterized by two well-distinct time scales such that the characteristic time $\tau_\mu$ associated with the microscopic process is shorter than $\tau_\alpha$ by at least one order of magnitude. Besides glass-former liquids and liquid metals, another important class of systems, the dynamics of which is affected by relaxation processes, are the hydrogen-bonded liquids. In these systems it has been found that the $\mu$ process is very fast and its decay, “instantaneous” on the time scale of the sound wave propagation, has been represented by a delta function in the time domain. On the contrary the slower $\alpha$ process that is thought to be directly related to the dynamical organization of the hydrogen-bond network of the system has a relaxation time $\tau_\alpha(T)$ that, in the normal liquid phase, lies in the subpicosecond time scale and follows an Arrhenius law. In these systems the highly directional hydrogen bond plays a crucial role in the determination of the microscopic properties. These are mainly affected by the hydrogen-bond strength, the spatial network arrangement of the hydrogen bonds, and the number of hydrogen bonds per molecule. In order to better understand the dynamics of high associated liquids, we decided to compare the high-frequency dynamics of water with that of HF. Moreover, the collective dynamics of (HF)$_x$(H$_2$O)$_{1-x}$ solutions is investigated with the aim to describe the transition from the dynamics of one liquid to the other. Several investigations have been performed to provide an insight into the microscopic interactions which affect the structure and the dynamics of this system. Here we report IXS measurements on (HF)$_x$(H$_2$O)$_{1-x}$ solutions as a function of the concentration in the range $x=0.20–0.73$ at fixed temperature $T=283$ K. The
II. EXPERIMENTAL DETAILS

Commercial solutions of water and hydrogen fluoride (HF),(H₂O)ₓ−, with x=0.40 and x=0.73 nominal value have been purchased from Fluka, while the one at x=0.20 has been prepared by diluting with demineralized water the solution at x=0.40. The sample environment is composed of a sample cell of cylindrical shape made of Teflon. Its diameter, ~1 cm, was comparable to the x-ray photoabsorption length of (HF),(H₂O)ₓ− solutions at E=21.7 keV at each x value. The Teflon container, inserted in a copper holder, was cooled at T=283 K using a liquid flux cryostat DC50-K75 Haake. Further details on the sample cell are reported in Ref. 17. The inelastic x-ray scattering experiment has been carried out at the very high energy resolution IXS beamline ID16 at the European Synchrotron Radiation Facility. The instrument consists of a backscattering monochromator and five independent analyzers operating at the (11 11 11) Si Bragg reflection. They are held such that one is next to the other with a constant angular offset on a 6.5-m-long analyzer arm. The used configuration18 gives an instrumental energy resolution of 1.6-meV full width at half maximum (FWHM) and a Q offset of 3 nm⁻¹ between two neighbor analyzers. The momentum transfer Q is selected by rotating the analyzer arm. The spectra at constant Q and as a function of energy were measured with a Q resolution of 0.40-nm⁻¹ FWHM. The energy scans were performed varying the backscattering monochromator temperature with respect to that of the analyzer crystals. Further details on the beamline are reported elsewhere.19 Each scan took about 180 min and each spectrum at fixed Q was obtained by summing up to three scans. The measurements have been performed along the liquid–vapor coexistence line and at fixed temperature T=283 K.

III. DATA ANALYSIS

The IXS data have been collected as a function of the wave-vector Q in the range 1–15 nm⁻¹. The data have been normalized to the intensity of the incident beam. The empty-cell contribution, due to the scattering of the Teflon walls of the cylindrical cell (1-mm total thickness), has been subtracted from the total scattered intensity. A selection of IXS spectra at low-Q values is reported in Fig. 1; they are compared with those of pure HF from Ref. 8. The IXS line shape shows a concentration dependence visible already in the raw data passing gradually from a situation in which a peak cen-
tered at zero energy transfer is present (pure HF) to the case in which the inelastic peaks become clearly distinguishable above the tail of the elastic peak. The spectra have been analyzed using the memory-function approach according to which the dynamic structure factor \( S(Q,\omega) \) is written as

\[
S(Q,\omega) = \frac{S(Q)}{\pi} \frac{\omega_0(Q)^2 M'(Q,\omega)}{\omega^2 - \omega_0(Q)^2 - \omega M''(Q,\omega)^2 + \omega M'(Q,\omega)^2},
\]

(1)

where \( \omega_0(Q)^2 = (k_BT/mS(Q))Q^2 \) is the normalized second frequency moment of \( S(Q,\omega) \), \( k_B \) is the Boltzmann constant, \( m \) is the mass of the molecule, and \( M'(Q,\omega) \) and \( M''(Q,\omega) \) are the real and the imaginary parts of the Laplace transform of the memory function \( M(Q,t) \), respectively. The models for \( M(Q,t) \) are discussed in Sec. II. To fit the spectra of Fig. 1 we used a function given by the convolution of the experimentally measured energy resolution \( R(\omega) \) and the classic dynamic structure factor \( S(Q,\omega) \) corrected in order to satisfy the detailed balance;

\[
I(Q,\omega) = I_0 R(\omega) \otimes [\beta h \omega/(1 - e^{-\beta h \omega}) S(Q,\omega)],
\]

(2)

where \( I_0 \) is a normalization factor and \( \beta = 1/k_BT \).

### A. Markovian approach

As discussed in detail in the case of pure HF, a preliminary analysis of the spectra has been done by fitting the data within the Markovian approximation. This approach assumes an instantaneous memory function and Eq. (1) simplifies into the sum of a damped harmonic-oscillator (DHO) spectrum with characteristic frequency \( \Omega(Q) \) and damping \( \Gamma(Q) \) and of a \( \delta \) function for the elastic peak. Specifically one supposes that the time scale of density fluctuations \([1/\Omega(Q)]\) is much faster than the relaxation time \([\tau(Q)]\) associated with any relaxation process active in the system \([\Omega(Q)\tau(Q) \ll 1]\). Albeit this analysis has no meaning whenever a relaxation process such that \( \Omega(Q)\tau(Q) \sim 1 \) is present, however, it allows to extract the energy position of the inelastic excitations \( \Omega(Q) \) and to get information on the apparent sound velocity \( c(Q) = \Omega(Q)/\tau(Q) \). The proper analysis, the viscoelastic one, will be presented in the next paragraph. In Fig. 2 we report the results of the fit with \( M(Q,t) \) within the Markovian approximation superimposed to the data for a selected \( Q \) value \((Q = 4 \text{ nm}^{-1})\). The quasielastic and inelastic contributions are individually shown. The main fit parameter \( \Omega(Q) \) provides an estimate of the current maxima. The \( \Omega(Q) \) values are reported in Fig. 3 as a function of \( Q \) in the range 1–7 nm\(^{-1}\) at the investigated concentrations. The dispersion curves are compared with the respective adiabatic sound velocities. From these plots it is evident that the sound velocity undergoes a transition from the hydrodynamic values (low \( Q \)) to the high-frequency one (high \( Q \)). It is also evident that passing from pure hydrogen fluoride (top) to pure water, the transition of the apparent sound velocity \( \Omega(Q)/\tau(Q) \) takes place at decreasing \( Q \) with decreasing concentration of HF. Specifically, this transition falls in the region \( Q \approx 1 \text{ nm}^{-1} \) for the 40% and 20% HF solutions. In these last two cases a linear fit in the 1–7 nm\(^{-1}\)\( Q \) range provides a value of the sound velocity substantially higher than the adiabatic one. In the case of pure HF and 73% HF solutions, the dispersion curves show a linear dependence for \( Q \) between 4 and 7 nm\(^{-1}\) with a slope corresponding to a sound velocity higher than the adiabatic one. Furthermore, in the 1–4 nm\(^{-1}\)\( Q \) region, the data show a transition of the sound velocity \( c(Q) \) from the low-frequency value to the higher one. This means that, as in the case of pure HF at different temperatures, the structural or \( \alpha \) relaxation is active in the investigated frequency windows at higher concentrations of HF. In addition, it may be noted that the high-frequency sound velocity \( c_{\alpha,\text{HF}} \) decreases at increasing concentration of hydrogen fluoride.

### B. Viscoelastic analysis

Whenever a relaxation process is present (as in the case reported in Fig. 3) the decay of the density fluctuations is characterized by a relaxation time \( \tau \) in the range of the probed sound waves (i.e., \( \Omega(Q)\tau(Q) \sim 1 \)) and the memory function \( M(Q,t) \) must be characterized by a decay time scale. In this case a more appropriate analysis of the spectra is performed in terms of the viscoelastic approach. In liquids usually two relaxation processes are present and the memory function \( M(Q,t) \) is expressed by the sum of two exponential decay contributions:

![FIG. 2. IXS spectra of (HF)\(_{x}\)(H\(_2\)O)\(_{1-x}\) solutions with \( x = 0.20, 0.40, \) and 0.73, \( T = 283 \text{ K} \), and \( Q = 4 \text{ nm}^{-1} \) compared with that of pure HF \((x = 1)\) from Ref. 8. The DHO model fit is superimposed to the data; the two distinct quasi elastic (dashed lines) and inelastic (full lines) contributions are individually shown.](https://jcp.aip.org/jcp/copyright.jsp)
We observe that in the case of 20% and 40% HF solutions the slope of the lower dashed lines corresponds to the adiabatic sound velocity. The upper full lines correspond to the linear fits to the higher-Q concentrations and together with the apparent sound velocity $c_T$ the hypothesis of the presence, in the investigated frequency range, of the $\alpha$ relaxation in both cases. The $Q$ dependence of $\tau_\alpha(Q)$ is shown in Fig. 5 at all the investigated concentrations. It is worthwhile to note that the values of $\tau_\alpha(Q)$ increase with increasing the content of water, which means that in hydrogen fluoride the structural relaxation is quicker than in water. This can be attributed to the fact that the chainlike structures of HF molecules are “more free” with respect to the three-dimensional clusters of water. The last parameter related to the strength of the microscopic relaxation process $\Gamma_\mu(Q)$ is reported as a function of $Q$ at all the investigated concentrations in Fig. 6. As already observed in pure HF, it follows a quadratic behavior:

$$\Gamma_\mu(Q) = DQ^2.$$  

We discuss in Sec. IV the dependence of $D$, as well as of the other fitting parameters, on the concentration.

**IV. DISCUSSION**

This section is dedicated to analyze the concentration dependence of the fit parameters in the low-$Q$ limit. A comparison between the high-frequency sound velocity $c_{ad}$, as obtained by the linear fit to the data reported in Fig. 3, and the adiabatic sound velocity, as obtained from Ref. 20, is reported in Fig. 7(a). Changing the concentration, the $c_{ad}/c_0$ ratio shown in Fig. 7(b) is always close to 2 as for the two limit compounds, water and HF. The concentration dependence of $\Gamma_\mu(Q)$ in the low-$Q$ limit is given by the parameter $D$ coming from the fit done with the parabolic function of Eq. (5). The values of $D$ are plotted in Fig. 8 as a function of

---

**FIG. 3.** Dispersion curves for (HF)$_x$(H$_2$O)$_{1-x}$ solutions at the indicated concentrations and $T=283$ K compared with that of pure HF ($x=1$) from Ref. 8. The upper full lines correspond to the linear fits to the higher-$Q$ data. The slope of the lower dashed lines corresponds to the adiabatic sound velocity (Ref. 20).

$$M(Q,t) = \Delta_\alpha^2(Q) e^{-i\tau_\alpha(Q)} + \Delta_\mu^2(Q) e^{-i\tau_\mu(Q)},$$  

where $\Delta_\alpha^2(Q) = [c_{ad}(Q)^2 - c_0(Q)^2]Q^2$ and $\Delta_\mu^2(Q) = [c_{ad}(Q)^2 - c_{ad}(Q)^2]Q^2$ are the strengths of the two processes. In (HF)$_x$(H$_2$O)$_{1-x}$ solutions as in the two limit cases, water$^6$ and pure HF$^3$ one expects that the $\mu$ process is very fast with respect to the investigated time scale and the second term is approximated by a $\delta$ function:

$$M(Q,t) = \Delta_\alpha^2(Q) e^{-i\tau_\alpha(Q)} + \Gamma_\mu(Q) \delta(t),$$

with $\Gamma_\mu(Q) = \Delta_\mu^2 \tau_\mu(Q)$. The fit to the data is therefore performed using Eq. (4) as a model for the memory function.

We report in the following the $Q$ dependence of the main fit parameters $c_{ad}(Q)$, $c_0(Q)$, $\tau_\alpha(Q)$, and $\Gamma_\mu(Q)$ at all the investigated concentrations. In Fig. 4 $c_{ad}(Q)$ and $c_0(Q)$ are reported together with the apparent sound velocity $c(Q) = \Omega(Q)/Q$ obtained from the dispersion curves $\Omega(Q)$ of Fig. 3. We observe that in the case of 20% and 40% HF solutions the $c(Q)$, found with the DHO analysis, lies completely on the $c_{ad}$ points except for $Q=1$ nm$^{-1}$; this reinforces the idea that in these two cases the transition of the sound velocity $c(Q)$ occurs at lower $Q$'s and that the system is unrelaxed. With increasing concentration of HF and, in particular, for the 73% HF solution and pure HF a transition of $c(Q)$ takes place between the values of $c_0(Q)$ and $c_{ad}(Q)$, supporting the hypothesis of the presence, in the investigated frequency window, of the $\alpha$ relaxation in both cases. The $Q$ dependence of $\tau_\alpha(Q)$ is shown in Fig. 5 at all the investigated concentrations.
the concentration. While in the case of pure HF (Ref. 8) $D$ turned out to be temperature independent, it shows a dependence on the concentration in the case of HF/H$_2$O$_{1-x}$ solutions, in particular, we observe that the ratio $D_{HF}/D_{HF}$ at $T=283$ K. The fit has provided values of $c_{\infty}/c_0$, plotted in Fig. 9(a), which show a good agreement with those of water and HF coming from Refs. 6 and 8, respectively. The low-$Q$ values of the four viscoelastic fit parameters $c_0(0), c_{\infty}(0), \Gamma(0)$, and $\tau(0)$ are related among them through the expression $21$

FIG. 5. $Q$ dependence of the relaxation time $\tau_\alpha(Q)$ from a viscoelastic analysis in (HF)$_x$(H$_2$O)$_{1-x}$ solutions at $T=283$ K. The data are compared with the pure HF results from Ref. 8.

FIG. 6. $Q$ dependence of the parameter $\Gamma_\alpha(Q)$ (full circles) in the low-$Q$ region from a viscoelastic analysis in (HF)$_x$(H$_2$O)$_{1-x}$ solutions at $T=283$ K. The full lines represent the parabolic fits to the low-$Q$ data.

FIG. 7. (a) Behavior of the sound velocity in (HF)$_x$(H$_2$O)$_{1-x}$ solutions as a function of the concentration at $T=283$ K compared with the two limit cases, $x=0$ at $T=300$ K from Ref. 6 and $x=1$ from Ref. 8: $c_0$ (full squares), $c_{\infty}$ (full circles). (b) Sound velocity ratios $c_{\infty}/c_0$.

FIG. 8. Dependence on the concentration of HF of the parameter $D$ in (HF)$_x$(H$_2$O)$_{1-x}$ solutions at $T=283$ K. The values are compared with the two limit cases, $x=0$ from Ref. 6 and $x=1$ from Ref. 8.
The comparison of the theoretical law water presents a three-dimensional tetraedric structure with relaxation process is related to that of the H bond. If, in fact, experimental points with hence we cannot extract the activation energies as in Ref. 8 experiment we have no data as a function of the temperature, 034502-6 Angelini et al. here we have experimental values for the two pure liquids. Here we have addition, the data are compared with the validation of HF and still we observe a good agreement with the Arrhenius plot of 23 Finally, we compare in Fig. 10 the values of similar mass as recently reported for different liquid solutions. In particular, in the case of water we use the values of the parameter which in Ref. 6 is referred as \( \tau_M \). In this experiment we have no data as a function of the temperature, hence we cannot extract the activation energies as in Ref. 8 for the pure liquids. Anyway, it is useful to see that the experimental points with \( x=0.20, 0.40, \) and 0.73 at \( T=283 \) K fall in between those for water and HF, reinforcing the hypothesis that the activation energy for the structural relaxation process is related to that of the H bond. If, in fact, water presents a three-dimensional tetraedric structure with four H bonds per molecule and HF forms linear chains with two H bonds, then (HF)\(_x\)(H\(_2\)O)\(_{1-x}\) solutions are in an intermediate situation in which H bonds are formed among molecules of water and HF.

\[
\nu_L = \tau_a(0)(c_{x,a}^2(0) - c_0^2(0)) + \frac{D}{2},
\]

which allows to calculate the kinematic longitudinal viscosity \( \nu_L \). In Fig. 9(b) we report \( \nu_L \) as a function of concentration of HF and still we observe a good agreement with the results for pure HF and water coming from different IXS experiments. In addition, the data are compared with the values predicted by the linear relationship

\[
\nu_L = (1 - x)\nu_{H_2O} + x\nu_{HF},
\]

where \( x \) is the concentration of HF and \( \nu_{H_2O} \) and \( \nu_{HF} \) are the experimental values for the two pure liquids. Here we have used \( \nu_{HF} = 3 \times 10^{-3} \) cm\(^2\)/s\(^8\) and \( \nu_{H_2O} = 4.2 \times 10^{-2} \) cm\(^2\)/s\(^8\).

The comparison of the theoretical law (7) (dashed line) with the data reported in Fig. 9(b) shows a good agreement. This result for (HF)\(_x\)(H\(_2\)O)\(_{1-x}\) solutions seems to confirm that no deviation from the ideal linear model is present for species of similar mass as recently reported for different liquid mixtures. Finally, we compare in Fig. 10 the values of \( \tau_a(0) \) at \( T=283 \) K and \( x=0.20, 0.40, \) and 0.73 with the Arrhenius plot of \( \tau_a(0) \) at different temperatures for water \( (x=0) \) and HF \( (x=1) \) coming from Refs. 6 and 8, respectively. In particular, in the case of water we use the values of the parameter which in Ref. 6 is referred as \( \tau_M \). In this experiment we have no data as a function of the temperature, hence we cannot extract the activation energies as in Ref. 8 for the pure liquids.
Relaxation dynamics in (HF)$_x$(H$_2$O)$_{1-x}$ solutions


20 http://www.mesalabs.com/nusonics/hydrofluoric_acid_analyzer_appli.shtml
22 G. Castellan, Physical Chemistry (Addison-Wesley, Reading, Massachusetts, 1971).