Z. Phys. Chem. **222** (2008) 1551–1558 / **DOI** 10.1524/zpch.2008.5414

Collective High Frequency Motions in Liquid Deuterium Fluoride

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(Received May 19, 2008; accepted July 23, 2008)

Hydrogen Bonding / Liquid Dynamics / Neutron Spectroscopy

The collective motions in liquid deuterium fluoride (DF) have been investigated by neutron scattering motivated by a MD simulation, which predicted an optic-type mode at small momentum transfers. Spectra of the measured longitudinal current correlation function show two modes. The lower frequency one originates from acoustic-type movements. The intensity of the higher frequency excitation can be attributed to an out of phase motion of neighboring DF molecules, an optic-type mode. Both, the frequencies and the intensity distribution in momentum space agree well with the MD simulation. The widths of the experimental spectra exceed the widths from the MD simulation and indicate missing relaxation processes in the simulation.

1. Introduction

Hydrogen bonding (HB) is one of the most important interactions in biology and chemistry. The structure of DNA, protein conformation and of course water are the seminal examples for the influence of this directional interaction. Nevertheless, the very nature of the bonding still remains elusive after many decades of its discovery [1]. The bonds are rather dynamical in their nature, which ultimately enables functioning in biological systems, e.g. folding and unfolding [2], and hence it is appropriate to investigate the dynamical response of hydrogen bonded liquids. Hydrogen fluoride has an even stronger hydrogen bond than water and is therefore an ideal model system to study HB. This strong interaction is the reason for a lot of structural arrangements in the different phases. In vapor, hydrogen fluoride forms clusters with rings or chains of $(HF)_n$ [3]. In the crystal-

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line state hydrogen fluoride develops zigzag chains with an FFF angle of 120° [4]. For the liquid state calculations with *ab initio* methods indicate that HF consists of winding hydrogen bonded chains, quite similar to the solid structure, and with about two nearest neighbor molecules [5]. Results from neutron diffraction experiments are consistent with the picture of chains in the liquid state [6]. In contrast, water forms a three dimensional network with four nearest neighbors. This difference in bonding geometry is probably the reason for the difference in viscosity which is much lower in hydrogen fluoride compared to water. This might be due to the ease of movement of the weakly connected chains in the liquid and indicates differences in the dynamics of both systems [7]. The structural feature of chains in the liquid state is responsible for a richer collective dynamical response compared to simple liquids. A MD simulation on liquid HF, based on a classical effective pair potential, revealed an acoustic-like mode in the spectra of the longitudinal current correlation function and a further non dispersing mode at high frequencies [8]. Resulting from a normal mode analysis this high frequency mode consists of out of phase particle movements of nearest neighbors and was therefore called an optic-type mode [9].

Due to the toxic and reactive nature of hydrogen fluoride there are only a few experimental studies on the dynamical properties, in particular, of the liquid state. Raman and infrared studies on crystalline HF and DF revealed a bending mode near 70 meV in HF, which shifts to 50 meV in DF [10, 11]. This mode was assigned to an out of plane bending mode of the hydrogen atoms, which explains the isotope effect. Furthermore, lines at 25 and 30 meV could be identified which have been related to in plane translational movements. By neutron scattering an inelastic mode at 67 meV and at 27 meV was observed in solid HF [12]. In the liquid state the high energy mode remained, but the lower one seems to disappear to a weak shoulder. A later neutron study was concerned with the quasielastic broadening by rotational diffusion, which supported the idea of chain structures in the liquid [13]. The excitation at about 70 meV was also found in an *ab initio* simulation on liquid HF [5]. With inelastic X-ray scattering the acoustic-type excitations have been identified and the structural relaxation process has been related to the number of hydrogen bonds [14]. Recently a neutron scattering study on liquid deuterium fluoride showed an inelastic excitation at about 30 meV energy transfer, but at large momentum transfers, $Q \approx 12$ Å^{-1} [15]. These momentum transfer values are far beyond the predicted intensity maximum from the MD simulation, $Q \approx 1.5$ Å^{-1}. Here we present the coherent response of liquid DF, obtained by neutron scattering, which demonstrates an excitation in the current spectra at about 27 meV at the predicted small Q-vectors. The energy and the intensity distribution in momentum space agree with the results of the MD-simulation for an optic-type mode in liquid hydrogen fluoride [8].

2. Experiment

The neutron scattering experiment has been performed on the instrument IN4C, the most intense thermal time of flight spectrometer, at the ILL, Grenoble. For the experiment an incoming energy of 67 meV (energy resolution FWHM = 3.4 meV) with the pyrolytic graphite monochromator was used. The smallest achievable scattering angle was 13°, which corresponds to a minimum in momentum transfer of Q = 1.3 Å^{-1} at energy transfer zero. The sample cell was a copper plate geometry. Deuterium fluoride with a purity of 99.99 % was purchased from ABCR Chemicals (Karlsruhe, Germany). To ensure anhydrous conditions the experimental equipment was evacuated and heated. In order to prevent the formation of deuterium gas during the filling process, the sample cell was first passivated with hydrogen fluoride. As no further hydrogen development was observed, the passivation of the cell was assumed to be complete. In the next step the cell was filled with DF and the sample cell was pinched off from the vacuum line at the copper tubes with a pinch tool. The cell plates had a thickness of 0.6 mm and the sample thickness was 1.9 mm, which corresponds to a 10 % scatterer. The cell was installed under a 45° orientation to the incoming beam in a cryostat with a temperature stability of better than 1 K during the measurement time. In total we collected for about 24 hours sample data as well as empty cell data. The measurement temperature was 200 K, well above the melting point of DF, 190 K. The liquid was in equilibrium with its vapor at this temperature. An empty cell subtraction was performed with appropriate energy and angle dependent correction factors, which were calculated according to the procedure of Paalman and Pings [16]. Absolute calibration was achieved by normalisation with a flat vanadium standard. Multiple scattering was treated and subtracted by using the MSCAT program [17]. In the elastic region multiple scattering amounts to a few percent only and increases typically to about 20–30% at energy transfers of 20–30 meV, in the interesting wave vector range of about 2 Å^{-1}. To correct for detailed balance the resulting spectra are symmetrised by multiplication with $\exp(-(\hbar\omega/2k_B T))$. From the $S(Q, \omega)$ spectra we obtained constant Q spectra by searching and averaging within a grid of Q and ω values, which is 0.5 meV and 0.1 Å^{-1} wide. Then current spectra $j(Q, \omega) = \frac{\omega^2}{Q^2} S(Q, \omega)$ have been calculated. These are the Fourier transformed correlation functions of the longitudinal currents $J_L(Q, t)$ [18]: $J_L(Q, t) = \frac{1}{\sqrt{N}} \sum v_{iQ}(t) exp(iQr_i(t))$. Herein v_{iQ} denotes the velocity projection of particle i onto the direction of the momentum transfer vector Q and hence these currents describe the flow of the particles parallel or antiparallel to the wave vector. A positive contribution to the autocorrelation function of these currents can be obtained by e.g. an out of phase motion of neighboring molecules or by an in phase acoustic-type motion. Both positive interferences will result in peaks in the spectra. Spectra of current correlation

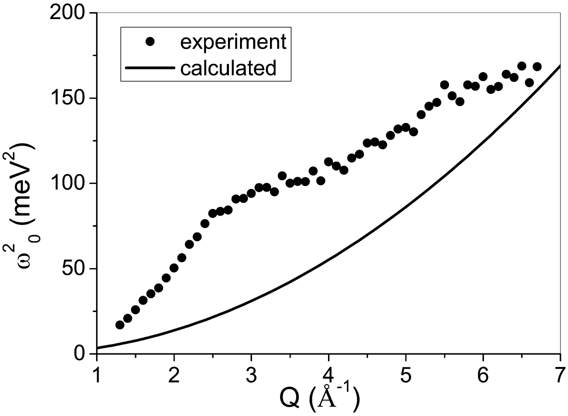

Fig. 1. The calculated second frequency moment from theory and from the measurement is shown.

functions have been obtained in the MD-simulation and along these we shall analyze our data.

3. Results and Discussion

In Fig. 1 the second frequency moment of the $S(Q, \omega)$ spectra is depicted, calculated by integrating up to the maximum available energy transfer: $\omega^2_0 = \int_{-50}^{+50} \omega^2 S(Q, \omega) d\,\omega$. Moments are describing the broadening of the dynamical response and are related to the short time evolution of the intermediate scattering function. According to liquid theory the second frequency moment of simple monatomic liquids is given by: $\omega_0^2 = \frac{k_B T}{M} Q^2$ [18]. It is obvious from the figure that there is a general trend to increase considerably with rising momentum transfer consistent with the theoretical prediction. The approach of both curves at smaller Q vector is probably related to a reduced energy range for integration at smaller Q vectors due to kinematic restrictions. However, the experimentally obtained second moment exceeds the calculated one. Simple liquids, like alkali metals, exhibit a good agreement [19] and we conclude an already much more emphasized inelastic response around $Q \approx 2.0$ Å^{-1} in that associated liquid, which seems to be not covered by the second moment.

Fig. 2 shows a (Q, ω)-map of the obtained current spectra $j(Q, \omega)$. The intensity around 50–60 meV can be attributed to an isotopically shifted librational mode, which was already observed in the early measurements on HF [12]. The second obvious part is the region of intensity in the small wave vector range up to $Q \approx 2.5$ Å^{-1}. A band of intensity between 5 and 10 meV extends even to larger Q vectors. A large part of the intensity is distributed at energy transfers between 20 and 30 meV, which diminishes rapidly with increasing Q vector. The measured intensity map is quite similar to the one predicted by the MD simulation [8]. Therein, the intensity at low energy transfers is attributed to an acoustic-type motion and a further peak near 30 meV was assigned to an optic-type motion. Fig. 1 of Ref [8] shows that the intensity maximum at this high energy transfer appears around a momentum transfer of $Q = 1.5$ Å^{-1}, a value outside the kinematic region of our experiment. Nevertheless, the chosen setup with a high incoming energy allowed to detect a large part of the excitation.

In Fig. 3 we display several constant Q cuts of the current spectra. With decreasing Q vector inelastic intensity is built up around 20–30 meV energy transfer. A comparison with cuts from the MD simulation shows a good agreement with the vanishing intensity beyond Q vectors of $Q \approx 3.0$ Å^{-1} [20]. However, the well separated peaks in the simulation are much more broadened and overlapping in the experimental data, in particular towards smaller Q vectors. The rotational contributions are not included in the figure of the MD simulation and therefore the librational type of motion does not appear in their spectra, whereas the experimental data show them distinctly at 50 meV and beyond. Figure 4 shows the spectrum at $Q = 2.2$ Å^{-1} with a fit of Lorentzians to the inelastic peaks. The resulting peak positions of the current spectra are represented in Fig. 5. The low energy branch is in very good agreement with the predictions of the MD simulation. Furthermore, our results for these acoustic-type excitations are in good accord with the derived frequencies of the inelastic X-ray scattering work compared at the respective wave vectors (see Fig 5 in Ref [14]). The higher energy branch shows slightly smaller values compared to the simulation, which at least partly can be understood due to the difference in mass between simulation and experiment. An instantaneous normal mode analysis demonstrated that the nearest neighbors have opposite phases in the frequency range around 30 meV and move preferentially along the chain axis [9]. Hence, this movement can be assigned an optic-type character. Even a weak dispersion could be supposed, although the restricted kinematic region might deviate the peak positions at smaller Q vectors. From the dispersive character one can conclude that the mode might extend beyond only nearest neighbors. For molten salts MD simulation predicted a dispersive optic mode, which has been evidenced recently by inelastic X-ray scattering [21]. The fit at $Q = 2.2$ Å^{-1} in Fig. 4 delivers a half width at half maximum height of the high frequency excitation of $\Gamma = 10$ meV, corresponding to a lifetime of about $\hbar / \Gamma = 0.07$ ps. The experimental spectra are broader than the spectra from the simulation. Both points, the indication of dispersion and the widths of the spectra, exhibit differences to the simulation obtained from a classical potential. It seems that further relaxation processes occur in liquid deuterium fluoride which are not described by the potential.

Our results confirm the viability of the potential to predict not only some structural features but also at least some important parts of the dynamics. The appearance of this optic-type mode is strongly linked to the topology of liquid DF, the chain structure. Such a type of motion, at lower energy, was also pre-

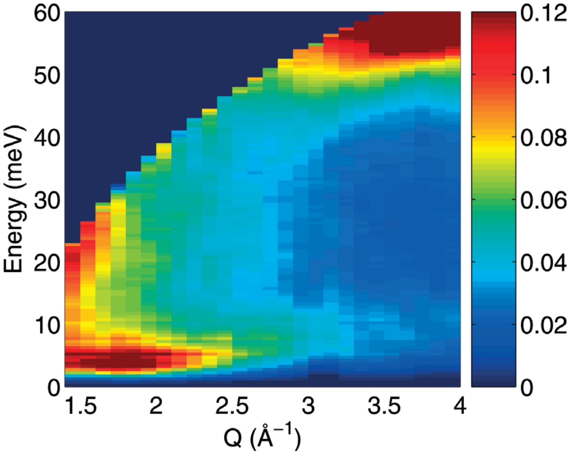

Fig. 2. A map of the current spectra $j(Q, \omega)$ is shown. At small Q vectors two inelastic regions can be identified near 5 meV and around 30 meV. The colored area marks the accessed (Q,ω)-region of the experiment.

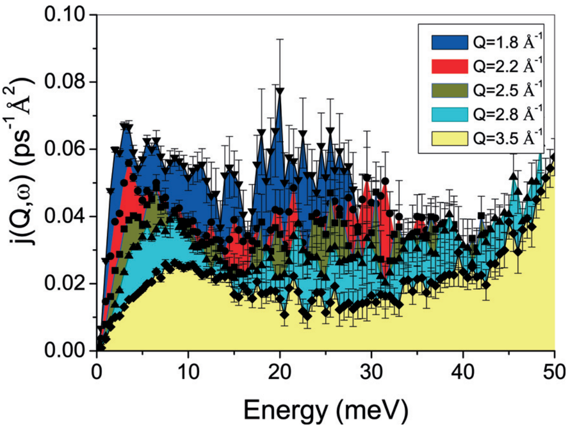

Fig. 3. Several constant Q cuts of the current spectra are depicted. With decreasing Q vector an increasing intensity shows up at about 25 meV energy transfer.

dicted for liquid methanol, which is only weakly connected linearly [22]. It might be that in more linear bonded systems such a movement could occur.

4. Conclusion

We presented results from an inelastic neutron scattering experiment on liquid deuterium fluoride. The obtained spectra exhibit inelastic peaks in accord with

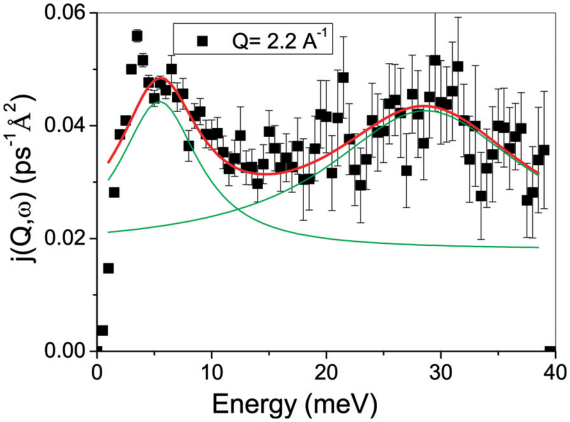

Fig. 4. The figure shows the spectrum at $Q = 2.2\ \text{Å}^{-1}$ with Lorentzian fits to the excitations.

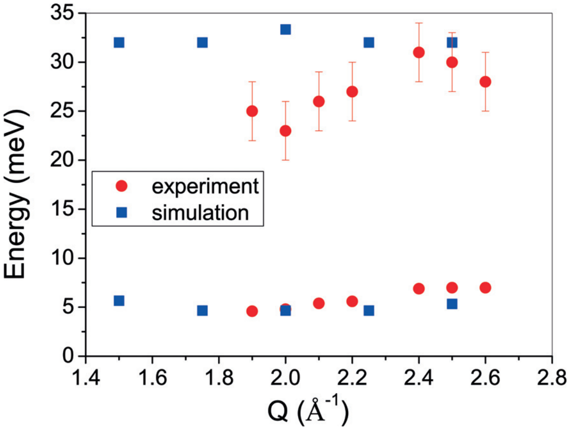

Fig. 5. The derived dispersion from the peaks in the current spectra (circles) is compared with the results from the MD-simulation (squares) [8].

predictions of a MD simulation. The anticipated optic-type motion was experimentally observed in liquid DF. The agreement is not only restricted to the frequency but also the intensity distribution in momentum transfer corresponds well. An extension of the measurement range to smaller momentum transfers is desirable. Widths and a weak dispersion indicate limits of the used classical potential.

Acknowledgement

The authors gratefully acknowledge the DFG (Deutsche Forschungsgemeinschaft) for financial support.

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