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Evidence of the Presence of Opticlike Collective Modes in a Liquid from Neutron Scattering Experiments

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Inelastic neutron scattering data from liquid DF close to the melting point show, in addition to spectra comprising quasielastic and heavily damped acoustic motions, an intense, nondispersive band centered at about 27 meV along with a broader higher energy feature. Observation of the former band provides the first direct verification of the existence within the liquid state of collective opticlike excitations as predicted by molecular dynamics simulations. The latter corresponds to mainly reorientational motions assigned from mode eigenvector analysis carried out by computer simulations.

Fundamental interactions within condensed bodies where a large proportion of the cohesion energies arise from hydrogen bonds are known to be governed by strong directional forces of electrostatic nature. Such materials significantly differ from ionic solids in the sense that the heavy atoms to which hydrogen bonds bridge approach each other at shorter distances than what is expected given their ionic radii. Also, these systems are known to exhibit strong cooperative behavior as observed by the gas-phase structures of small clusters [1] and by calculations on infinite hydrogen-fluoride chains. Furthermore, they constitute optimal benchmarks for the study of nonlinear dynamic phenomena leading to solitonic proton transport that is facilitated by the existence of a doubly degenerate ground state [2] where all the protons of the hydrogen bonds are closer to one or the other of their two nearest neighbors.

Hydrogen fluoride is known to be the system having the strongest as well as the simplest hydrogen bond. However, the aggressive nature of the material has largely prevented the experimental investigation of many of its properties. Particular consideration merits the investigation of liquid HF as it constitutes a reference system to which the behavior of more complex liquids such as water can be referred [3]. Given the dearth of experimental data and the archetypal nature of HF, to which we and others have referred to elsewhere, a comprehensive knowledge of its structure and properties have only recently begun to emerge. In fact, structural reports on liquid HF are scarce, where only one reports the structure at the pair correlation function level [4].

At 4 K and ambient pressure HF crystallizes in the $C_{2v}^{12}(Bm2_1b)$ space group where the structure is comprised of parallel zigzag chains which align parallel to the b axis [5]. Each molecule binds to its two nearest neighbors

through hydrogen bonds and the lattice structure is stabilized by interchain van der Waals interactions believed to be between 1 or 2 orders of magnitude weaker than the bonds which hold the chains together. Contrary to other halides, the crystal structure described above is retained at all explored temperatures. Studies concerning the dynamics within the solid state mostly arise from optical spectroscopy [6,7] as well as the pioneering work due to Axmann *et al.* [8]. In the liquid the dynamical properties have been previously studied by neutron measurements carried out several decades ago [9], where the resolution in energy transfers achieved at the time gave no estimate for the diffusion coefficients. Later, Ring [9] analyzed the inelastic neutron scattering of liquid and solid HF by considering the vibrational modes of hydrogen-bonded chains and concluded that the features found in the spectra could not be accounted for by the chain modes alone; therefore, there must be some other motion or structural feature that is responsible for the remaining scattering. More recent reports [10] using inelastic x-ray scattering—achieving a resolution of energy transfers of 1.6 meV—lump together all the inelastic intensity below some 20 meV into a single ''acoustic mode'' whose high-frequency phase velocity comes close to double the value of the hydrodynamic result. Finally, indirect inferences about the presence within the liquid of various short-lived polymeric cluster have been derived from analysis of the infrared spectrum [11].

Molecular dynamics simulations, providing calculated properties which are sensitive to details of the model potential [12], depict the microscopic dynamics within the liquid to be substantially more intricate than that exhibited by simple liquids such as the molten alkali metals [13] where all of the observed intensity can be attributed to collective density oscillations. In fact, detailed analysis of

the frequency spectrum [14], as well as the spectrum of collective dynamics [15] and the decomposition of the generalized spectrum in terms of instantaneous normal modes (INMs) [16] in liquid HF, all reveal well-defined features not accountable in terms of acousticlike excitations. In addition, the frequency spectrum shows a translational component which, apart from a low-frequency peak mostly arising from heavily damped acoustic modes that are bounded below 6.5 meV [16], displays a clear second maximum at about 30 meV. In turn, a broad rotational component spanning a frequency region of about 30–150 meV is also seen. In view of the rather disparate results derived from experiment or simulational means, as well as the special importance of the material as an epitome of hydrogen-bonded systems, we have carried out a comprehensive study by means of neutron scattering using a state-of-the-art spectrometer combined with recent advances in sample handling and containment procedures [4].

The measurements were carried out using the MARI spectrometer at the ISIS pulsed neutron source. A set of four different incident energies ranging from $E_0 = 15$ meV up to $E_0 = 400$ meV was employed. This has enabled the exploration of different portions of the $S(Q, \omega)$ dynamic structure factor achieving resolutions in energy transfer ranging from $\Delta E_0 = 0.3$ meV (FWHM) to $\Delta E_0 = 10$ meV. Here we focus on results pertaining to high frequencies, which provides a wealth of dynamic information without needing to resort to model fits of the inelastic intensities, as usually is the case for lower energy phenomena.

A 20 g sample of DF (Fluorochem, U.K.) was cryogenically distilled into a 316 stainless steel Swagelok single cylinder equipped with a needle valve. The DF was transferred onto 10 g of K_2NiF_6 in order to remove any aqueous contamination before being transferred into the sample cell. A sample consisting of 5 g of anhydrous DF was loaded into an annular geometry sample cell manufactured from monel (alloy 400) which had previously been surface passivated under an atmosphere of fluorine [17]. An annular geometry of 1 mm was used to minimize absorption and multiple scattering effects. The sample was cooled to 200 K using a He exchange gas cryostat.

The measured intensities, once corrected for background and other instrumental effects, were transformed into a $Q - \omega$ grid. Images were then reconstructed from measured data by means of a recently described purpose-built algorithm [18] which avoids introducing substantial correlation between adjacent pixels as smoothing algorithms usually do.

A color plot depicting the inelastic intensity over the whole $Q - \omega$ region explored using the highest employed incident energy (400 meV) is shown in Fig. 1. The graph shows three well differentiated regions: a strong intensity along the elastic or quasielastic line, a brownish stripe centered at around 27 meV which becomes more visible
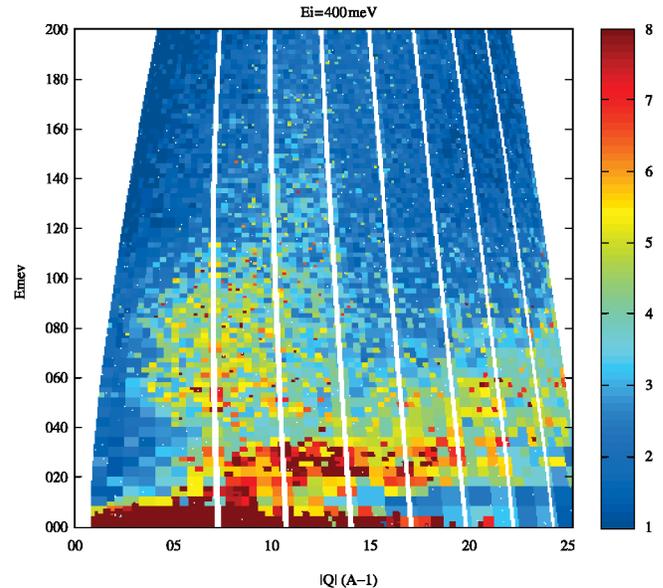

FIG. 1 (color). Intensity plot showing the accessible range of energy and momentum transfers. Color codes are shown by the vertical bar. White stripes show separators between different detector banks.

at Q values above 6 Å^{-1}, and a more diffuse (yellow) region spanning frequencies between 20 and 160 meV within a range of wave vectors between 2 and 12 Å^{-1}.

A more detailed view is provided by plots at constant wave vector and constant energy that are shown in Figs. 2 and 3. Data shown in Fig. 2 display a rather well-defined feature at finite frequencies centered at about 27 meV having a width of ≈ 15 meV. The center frequency of such a feature as well as its width shows no significant dependence on the wave vector. In contrast, its amplitude follows a well-defined modulation within reciprocal space and it is shown in Fig. 3. Such a graph defines an inelastic form factor, which provides valuable information about the relative phases of the particles in motion.

As far as the higher-frequency feature is concerned, its energy spectrum as well as its inelastic form-factor are depicted in Figs. 2 and 3. The excitation here corresponds to heavily damped motions having an average frequency of 80 meV and a comparable linewidth.

In order to assign the feature centered at about 27 meV, several simulation studies were considered [14–16] that show the presence of such an excitation in both collective (longitudinal and transverse) current correlations and single-molecule correlation functions. The former quantities amount to $\omega^2 S_{L,T}(Q, \omega)/Q^2$, where the subscripts indicate longitudinal and transverse components, and show, above 1 Å^{-1}, a peak with a center frequency with no wave vector dependence even at large values of Q. In addition, a detailed analysis of the relative phases of atomic motions, which take place at such frequencies carried out within the INM framework, shows purely out-
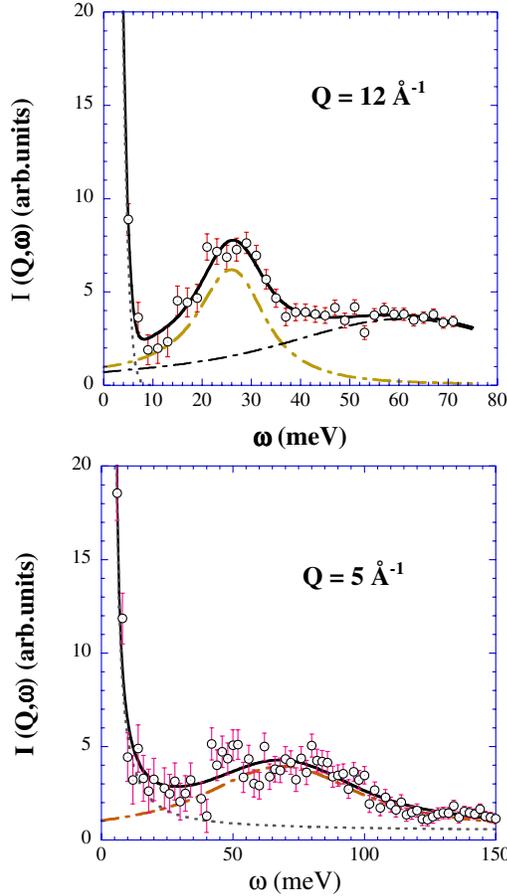
FIG. 2 (color online). Cuts made at constant momentum transfers given as insets corresponding to the main features shown in Fig. 1. The contribution of both low- and high-frequency features is clearly visible in the upper panel. The model fit (solid line) comprises a central Lorentzian component (dots), a damped harmonic oscillator (dash-dotted line), plus a constant background. The upper panel shows the two oscillators needed to account for both excitations.
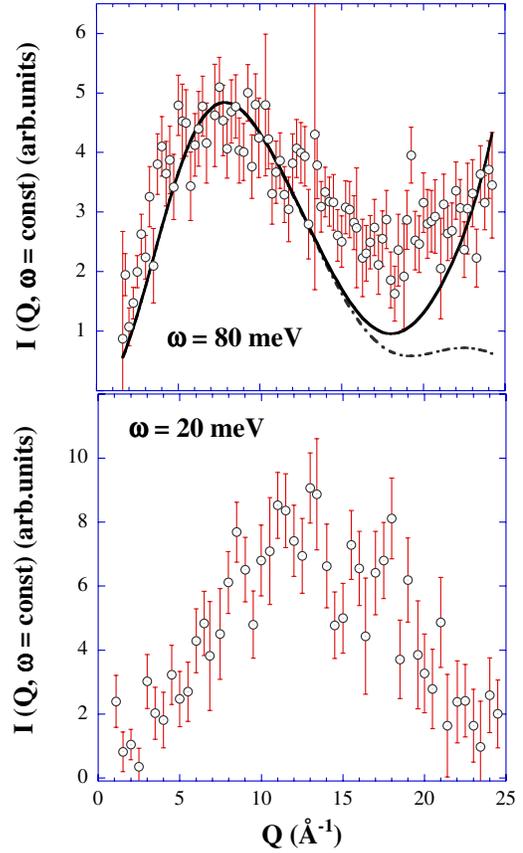

FIG. 3 (color online). Cuts made at constant energy transfers that correspond to the broad rotational feature as well as to the opticlike strip. The solid line represents a calculated model (solid line) for small reorientational motions (dashed line) supplemented with a calculated multiexcitation background [21].

of-phase motions suggestive of those characterizing vibrational excitations along the extended zigzag chains within the crystalline solid [6,7]. In fact, the liquid at low temperatures retains long-lived hydrogen-bonded chains with a low degree of branching [4] and a local geometry reminiscent of that found for the crystalline solid. However, the wave vector dependence of such an excitation shown in Fig. 3 warns against any oversimplified interpretation of such a feature in terms of "hydrogen-bond stretching." In fact, its broad shape centered at about 12 Å^{-1} suggests that many vibrational displacements in and out of planes formed by short chain structures participate in these motions. Such a picture is also supported by the available neutron data for the crystal [8] which was at that time analyzed in terms of a three-dimensional crystal model encompassing a total of seven intra- and interchain force constants [8]. Purely acoustic phonon branches were found to be confined below 15 meV for the main symmetry

directions, and a peak covering a region within 20–35 meV was found in the experimentally derived crystal frequency distribution. The lattice dynamics results yield mode eigenvectors for some three dispersion branches that yield intensities within such frequency range. This served to identify such features as translational librational in character, involving a concerted translation and small angle reorientations of atoms within a chain as well as a pure antiphase motion of atoms in a direction perpendicular to the chains.

The higher-frequency region can also be assigned on the basis of previous simulation data [16]. Its associated form factor shown in Fig. 3 shows some noticeable modulation. In the absence of an adequate theoretical recipe to treat such a strongly interacting system, we have used the partial-wave expansion of the rotational cross section [19],

$$F_{rot}(Q) \propto \sum_{l=0}^{\infty}(2l+1)a_l^2 j_l(Qd/2)^2 + \text{m.p.}, \quad (1)$$

with $a_l^2 = 4b_{coh}^2 + 2b_{inc}^2$ for even l and $2b_{inc}^2$ for odd l, and $b_{coh,inc}$ is taken as the average coherent and incoherent

scattering lengths for F and D. Here d is taken as a distance that characterizes the reorientational motion and m.p. are the multiphonon terms. The approximation shown in the upper panel of Fig. 3 has been calculated using a value for d of 0.75 Å, which is significantly shorter than the characteristic intramolecular covalent bond ($\sim$1 Å), but certainly larger than the average particle mean-square displacement of 0.46 Å reported for the crystal [8]. The result is thus suggestive of relatively large amplitude librational motions taking place at such frequency scales rather than fully developed whole molecule reorientations. Such a view is also grounded in lattice dynamics and optical spectroscopy results for crystalline DF [6,7] that show three librational Raman-active modes at $\approx$50, 63, and 70 meV [7], and indeed, early calculations of the frequency distribution for the DF bond showed the librational region of the spectrum to be within 30–90 meV. In addition, neutron data for the crystal reveal a broad band centered at about 70 meV identified as arising from atomic librations within the chains.

In summary, opticlike excitations of collective nature, as predicted on the grounds of molecular dynamics simulations, have been directly evidenced by experimental means without recourse to modeling the inelastic intensities. Additionally, their relatively narrow linewidth portrays these excitations as having relatively long lifetimes as given by $2\pi/\Delta\omega$ on the order of 0.3 ps, and their wave-vector–independent character also points towards localized intermolecular modes. In addition, well-defined librational excursions are also shown to be present, albeit having a significantly shorter lifetime. Microscopically, both features arise as a direct consequence of the presence within the liquid state of remnants of chain structures similar to those from the crystal, as recently shown by diffraction measurements [4]. To our knowledge, this study marks the first direct observation of collective modes of nonacoustic nature by purely experimental methods. Although evidence of these modes have been actively sought [20,22], until now such results relied upon parametric fits to spectra devoid of clear features. Furthermore, these modes have been predicted by various simulations prior to experiment [14–16], which provides a direct test of calculational methods on a prototypical hydrogen-bonded system. The importance of this result cannot be overstated, given the difficulty of modeling the HF system in the absence of a large body of experimental data.

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