PHYSICAL REVIEW B, VOLUME 64, 212102

Molecular vibrational spectroscopy by inelastic x-ray scattering: Experimental determination of the absolute vibrational cross section in liquid nitrogen

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(Received 5 September 2001; published 12 November 2001)

Inelastic x-ray scattering (IXS) is used to measure the vibrational spectrum of liquid nitrogen at a temperature of 76 K and a pressure of 1 bar as a function of wave vector q in the 1.45–11.8 A^{-1} range. The absolute IXS cross section for the vibrational excitation is determined in the explored q range. Its comparison with a theoretical calculation is very satisfactory, and leads to a precise determination of the intramolecular distance and the vibrational root-mean-square displacement. This demonstrates that the IXS technique can provide accurate information on the vibrational dynamics in molecular systems. The peculiarities of IXS with respect to other vibrational spectroscopies are briefly discussed.

DOI: 10.1103/PhysRevB.64.212102 PACS number(s): 61.10.Eq, 33.70.−w, 63.50.+x, 78.70.Ck

Nowadays, the inelastic x-ray scattering (IXS) technique is successfully used to study the atomic dynamics in the meV range.[1] Much of this success is due to the fact that the IXS cross-section per unit exchanged frequency (ω) and unit solid angle (Ω) has a very simple expression which, for a monatomic system, reads[2]

$$\frac{\partial^2\sigma}{\partial\omega\partial\Omega}=r_o^2|\boldsymbol{\epsilon}_i\cdot\boldsymbol{\epsilon}_f|^2\frac{k_i}{k_f}|f(q)|^2\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\omega t}F(q,t)dt. \tag{1}$$

Here r_o is the classical electron radius, $\boldsymbol{\epsilon}_\alpha$ and $\mathbf{k}_\alpha$ are the polarization and the wave vector of the incident (subscript i) and scattered (subscript f) x-ray beam, q is the wave vector exchanged by the incident photon in the scattering process, $f(q)$ is the atomic form factor (given by the space Fourier transform of the atomic electronic density distribution), and $F(q,t)$ is the intermediate scattering function (given by the space Fourier transform of the atomic density-density correlation function), namely,

$$F(q,t)=\left\langle\sum_{i,j}\exp(-i\mathbf{q}\cdot\mathbf{R}_i(t))\exp(-i\mathbf{q}\cdot\mathbf{R}_j(0))\right\rangle. \tag{2}$$

Here $\mathbf{R}_i(t)$ is the position operator of the ith atom at time t, and $\langle\cdots\rangle$ indicates the ensemble average. Thus, although the scattering process is determined by the electromagnetic coupling between the incident photons and the electrons of the target system, it is essentially the atomic dynamics that, as a consequence of the adiabatic coupling between electrons and nuclei, is probed at low exchanged energies.

Among all the processes affecting the density-density correlation function, the ones which spectrally contribute the most in fluid systems are the collective, acousticlike excitations, and in fact much work has been reported on this topic.[1] In this paper, conversely, we report on the measurement of the absolute IXS cross section for a process which is spectrally much weaker, i.e., the scattering from a high-energy vibrational excitation. Specifically, we present here the measurement of the absolute IXS cross section for the vibrational excitation in liquid nitrogen as a function of q. The quality of the experimental data allows us to precisely determine parameters like the interatomic distance and the vibrational mean-square displacement, and shows the potentialities of IXS as a vibrational spectroscopy.

The experiment has been carried out at the beamline ID16 of the European Synchrotron Radiation Facility situated in Grenoble, France. The monochromatic x-ray beam at the sample position was characterized by an energy of $\approx 13\,840$ eV, a spot of 250×250 $\mu\mathrm{m}^2$ horizontal by vertical size, and a flux of $\approx 3\times10^9$ photons/s. The photons scattered by the sample were collected in a 2.6 m long spectrometer arm where a spherical silicon crystal is used to perform the energy analysis.[3] Energy scans are accomplished by varying the relative temperature between the monochromator and the analyzer crystals. The spectrometer can be rotated in the vertical scattering plane, thus allowing for the selection of the momentum transfer, $q=2k_i\sin(\theta_s/2)$, where θ_s is the scattering angle. The q values investigated here have been selected to be between 1.45 and 11.8 A^{-1}; at each considered q value an energy scan in the range -40–400 meV has been performed. The q resolution, defined by two slits placed in front of the analyzer, varied from 0.3 A^{-1} at $q=1.45$ A^{-1} to 0.1 A^{-1} at $q=11.8$ A^{-1}. The energy resolution function was q independent with a value of ≈ 10 meV at full width at half maximum. The sample container was a 7 mm internal diameter 1 mm thick teflon tube, the inner diameter of which was chosen to be comparable with the photoabsorption length of nitrogen at the incoming beam energy. The nitrogen sample was kept at a temperature of 76 ± 0.2 K and at a pressure of 1 ± 0.1 bar. A typical scan of the entire -40–400 meV energy range took about 7 h, and at each q value two scans were usually performed. However, three or four scans were additionally added up on the weak spectral energy tails in order to accumulate sufficient statistics, with a final average integration time of ≈ 6 min/channel. Empty container spectra were also recorded and subtracted in order to obtain the final spectra. This subtraction is not critical since, in the adopted experimental configuration, the empty container contribution amounts at most to a few percent of the total signal; in par-

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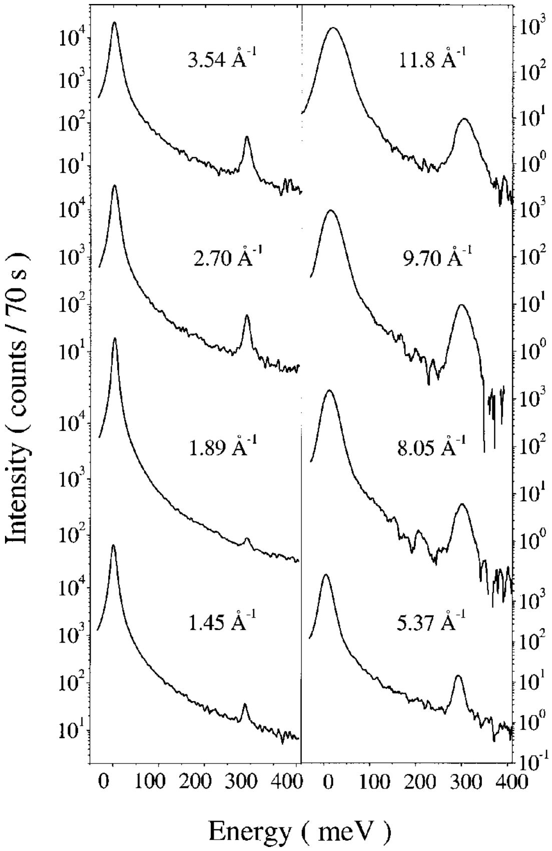

FIG. 1. Evolution with q of the IXS spectrum of liquid nitrogen on a semilog scale. Each spectrum has been reported on a 70 s integration time y scale, but much longer integration times (typically 6 min/channel) have been used in the spectral wings in order to reach the statistical quality presented here.

ticular, for $q > 4.5\ \text{A}^{-1}$ the empty container spectra are indistinguishable from the flat electronic detector background of 0.5 counts/min.

The final spectral intensities, reported on a semilog scale in Fig. 1, are characterized by two distinct features: a central band and a much weaker band at high energy. The peak position of the latter band corresponds to the stretching energy of the nitrogen molecule at 289 meV,[4] while the former band is due to the rototranslational dynamics of the molecule. As a general consideration, the capability of IXS to access the vibrational dynamics in the condensed phase—shown in pioneering experiments which used a second generation synchrotron source[5] and recently demonstrated at one q value for the case of the O-H stretching band in liquid water[6]—is here clearly confirmed for the case of liquid nitrogen.

The spectra of Fig. 1 show prominent changes with increasing q: (i) both the central and the vibrational bands become broader, (ii) the intensity of the vibrational band, as compared to that of the central one, shows a general trend to increase, and (iii) both the central and the vibrational bands move towards larger energy shifts. All these features can be understood in terms of an impulse approximation approach for the intermediate atomic scattering function,[7] and a detailed analysis of such a spectral evolution will be presented in a forthcoming publication. In the following, we will concentrate our attention only on the integrated intensity behavior of the vibrational band.

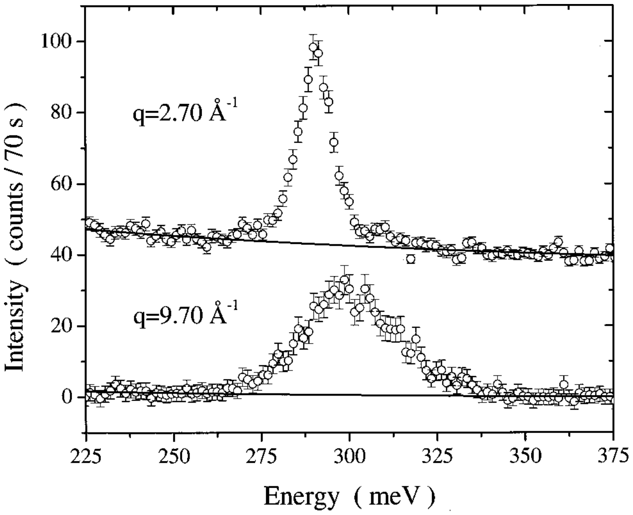

FIG. 2. Detail of the vibrational band region for two selected q values. For clarity, the $q = 2.7\ \text{A}^{-1}$ spectrum has been vertically shifted by 35 counts/70 s. In the energy range considered here, the spectra consist of the sum of the vibrational band and the tail of the central band. Such a tail can be simply fitted by a smooth curve (full line). The pure vibrational contribution is then obtained as the difference between the measured spectrum and the base line.

The intensity of the vibrational band can be readily obtained from the spectra of Fig. 1. In fact, as shown in Fig. 2, the tail of the central band around the vibrational position can be easily fitted, using a low-order polynomial, and then subtracted from the spectrum in order to determine the pure spectral contribution of the single vibrational excitation. The integrated intensity of this contribution, relative to the total integrated intensity, is given by the ratio $S_v(q)/S(q)$, where $S(q)$ is the atomic structure factor, i.e., the total integral over energy of the spectra that we measure, and $S_v(q)$ is the contribution to $S(q)$ which is due to the vibrational dynamics alone.[8] For the case of nitrogen in the thermodynamic condition considered here, very detailed $S(q)$ data are available in the literature[9] [see Fig. 3(a)]. It is therefore straightforward to obtain absolute values for $S_v(q)$ from the experimental results. These data, reported in Fig. 3(b), show an oscillating increase with increasing q, and can be compared with a simple theoretical prediction. In particular, although even more general quantum results for the dynamics of diatomic molecules are available,[10,11] we will compare our results with a semiclassical calculation for the integrated intensity of the vibrational band of a homonuclear diatomic molecule neglecting correlations among translational, rotational, and vibrational degrees of freedom. This approximation, which is very well suited for the case of liquid nitrogen,[4] for the single vibrational contribution $F_v(q,t)$, i.e., for the leading term in the expansion of $F(q,t)$ in powers of the internal relative interatomic coordinate $\rho(t)$, yields the following expression:

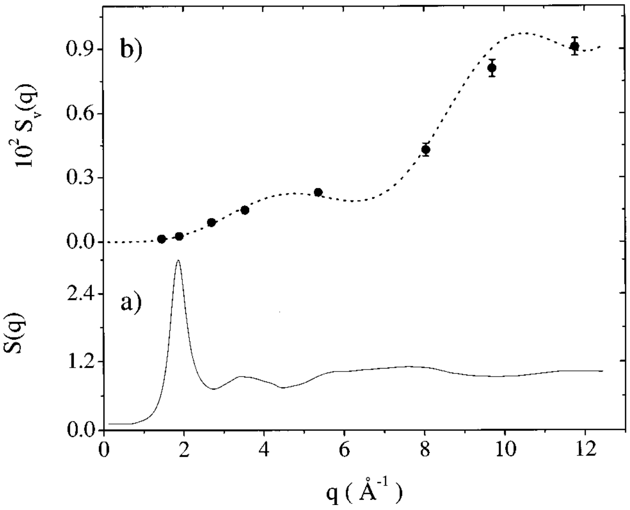

FIG. 3. (a) $S(q)$ data of liquid nitrogen at the temperature of 76 K and at ambient pressure, from Ref. 9. (b) q dependence of the vibrational structure factor $S_v(q)$ (full circles) obtained from the ratio of the vibrational intensity contribution relative to the total spectral intensity and from the $S(q)$ data reported in (a). The experimental $S_v(q)$ data are compared with the theoretical expression calculated following Eq. (4) (dotted line).

$$F_v(q,t)=2F_{CC}^{self}(q,t)\langle\rho(t)\rho(0)\rangle_v \times\left\langle \sin\left(\mathbf{q}\cdot\frac{r_{NN}}{2}\mathbf{u}(t)\right)\frac{\mathbf{q}\cdot\mathbf{u}(t)}{2} \times\sin\left(\mathbf{q}\cdot\frac{r_{NN}}{2}\mathbf{u}(0)\right)\frac{\mathbf{q}\cdot\mathbf{u}(0)}{2}\right\rangle_{or}. \tag{3}$$

Here $F_{CC}^{self}(q,t)$ is the self part of the molecular center-of-mass intermediate scattering function, r_{NN} the intramolecular nitrogen-nitrogen distance, $\mathbf{u}(t)$ is the unit vector specifying the molecular orientation, and $\langle\cdots\rangle_{or}$ and $\langle\cdots\rangle_v$ stand for averages over the orientational and vibrational variables, respectively. The first order vibrational contribution to the integrated intensity can be directly obtained setting $t=0$ in the equation above, which yields

$$S_v(q)=2l_{NN}^2\left\langle\left(\frac{\mathbf{q}\cdot\mathbf{u}}{2}\right)^2\sin^2\left(\mathbf{q}\cdot\frac{r_{NN}}{2}\mathbf{u}\right)\right\rangle_{or} =\frac{q^2}{12}l_{NN}^2[1-j_o(qr_{NN})+2j_2(qr_{NN})]. \tag{4}$$

Here, $j_k(r)$ is the kth spherical Bessel function, and $l_{NN}^2=\langle|\rho|^2\rangle_v$.

Equation (4) can now be readily compared with the experimental results reported in Fig. 3(b). Actually, we have fitted Eq. (4) to the experimental results for $S_v(q)$ leaving both r_{NN} and l_{NN} as free parameters. The result of this fit is reported in Fig. 3(b) (dotted line), and shows a nice agreement between the data and the calculation. The values of the free parameters that we get from this fitting exercise are reported in Table I, and they show a fair agreement with those obtained with other experimental methods. This result is interesting for two reasons: (i) it shows the good accuracy which is currently obtainable with IXS for the determination of the absolute intensities of vibrational bands, and (ii) it shows how direct the comparison between experimental data and theoretical calculation can be, given the simplicity of the expression for the cross section [Eq. (1)].

TABLE I. Intramolecular distance r_{NN} and associated root-mean-square displacement l_{NN} for nitrogen.

r_{NN} (Å)	l_{NN} (Å)	Method
1.11 ± 0.02	0.030 ± 0.002	IXS, this work
1.100 ± 0.011	0.031 ± 0.025	x-ray diffraction[a]
1.099 ± 0.002	0.031 ± 0.002	electron diffraction[b]
1.0976 ± 0.0001		Raman scattering[c]

[a] Reference 12.
[b] Reference 13
[c] Reference 14.

The same data of Fig. 3(b) can also be used, via Eq. (1), to determine the absolute scattering cross-section per unit solid angle for the vibrational band, $\partial\sigma_v/\partial\Omega=r_o^2f_q^2S_v(q)$, where values for f_q are available in the literature.[15] The cross-section values obtained in this way are reported in Fig. 4, and, for $q>1\,\mathrm{A}^{-1}$, show an oscillatory behavior around 10^{-27} cm^2 sr^{-1} molecule^{-1} which, keeping in mind the typical incident-beam fluxes available for IXS, can be considered a fairly high value. This result clearly shows the possibility of exploiting IXS, using third generation synchrotron-radiation sources, to measure the vibrational spectra of many different systems.

Given this picture, we can make some comments on the role of the IXS vibrational spectroscopy in a more general context. Indeed, the vibrational properties of condensed matter are routinely studied using Raman scattering (RS) and

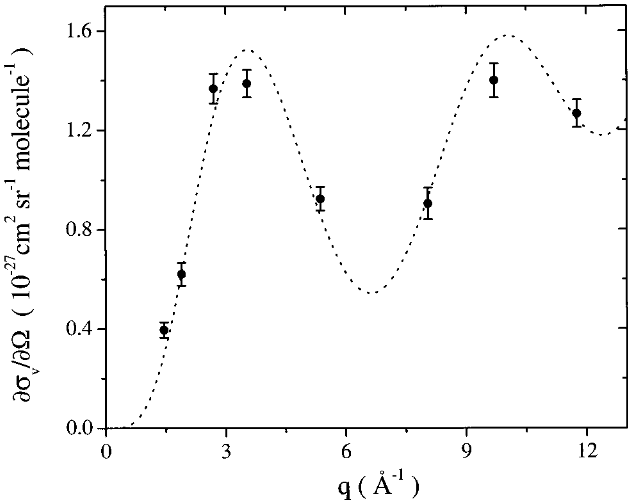

FIG. 4. The absolute cross-section-per-unit solid angle for the vibrational band obtained from the data of Fig. 3(b) using Eq. (1) (full circles). The corresponding result for the theoretical expression calculated following Eq. (4) is also reported (dotted line).

infrared-absorption (IRA) techniques, which generally ensure a high signal-to-noise ratio together with a high resolution. It is then generally easy with these spectroscopies to obtain precise information on the frequency position of the vibrational bands and then to compare them with theoretical models. Nonetheless there are cases in which additional information is required in order to interpret correctly the vibrational spectrum. One example is given by those situations where it is the knowledge of the spectral intensity of the vibrational excitations, besides their frequency position, that is needed in order to allow for a definite assignment. This is a task which is often difficult to achieve with RS and IRA since with these techniques the amplitude of the vibrational bands is determined by strongly model-dependent quantities such as the molecular polarizability derivatives and the electrical dipole moment derivatives. Another example is given by those situations where the q dependence of the vibrational excitations is important, e.g., those situations where the energy of a certain vibration depends on q as a result of an interaction with other degrees of freedom. In these cases one clearly needs a spectroscopic technique which is able to probe finite q values. In cases like those cited above, the neutron-scattering (NS) technique has already proven to be an important tool because NS has access to finite q values and the neutron cross section is susceptible to a straightforward comparison with theoretical results.[16] We have shown here that IXS offers basically the same advantages as NS, and thus it as well can be useful in similar situations. Furthermore since the IXS and the NS cross sections are both proportional to the atomic density-density correlation function with different weighting factors (the atomic form factor for the case of IXS and the scattering length for the case of NS), their combined use can be of great help in understanding the vibrational properties in polyatomic molecules. In practice, a joint use of IXS and NS can now be used to clarify the vibrational dynamics of complex systems much like neutron and x-ray diffraction can be complementary in understanding structural properties.

In conclusion, we have presented here IXS vibrational spectra of liquid nitrogen at a temperature of 76 K and a pressure of 1 bar. These spectra cover a large energy range which allows us to detect, besides the central band which reflects the rototranslational dynamics, the first-order Stokes vibrational band. The most important information which can be obtained by IXS on vibrational bands is, as in the case of NS, their absolute intensity, or cross section. This information has been demonstrated here to be achievable with good accuracy, as shown by the precise determination of the intramolecular distance and the vibrational root-mean-square displacement of liquid nitrogen. This shows that IXS can now be considered an important method to study the molecular vibrations, complementary to other established techniques.

We acknowledge C. Henriquet for the construction of the sample container used for the measurements, and R. Angelini for her help during the IXS measurements.

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