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Collective excitations in liquid para-H_2 observed by neutron inelastic scattering

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Inelastic-neutron-scattering studies of liquid H_2 enriched in para-H_2 molecules show the existence of a damped mode, interpreted as a phononlike collective excitation whose wave-vector dependence is established for $0.6 \leqslant Q \leqslant 2.0$ Å^{-1}. Our result, in marked disagreement with previous observations in this system, is in qualitative agreement with theoretical variational calculations. A comparison with liquid normal D_2 is made. The crossover from collective to single molecule response in both the solid and the liquid phases has also been determined. [S0163-1829(97)04242-2]

I. INTRODUCTION

Interest in the observation of collective excitations in molecular liquids has been focused in the liquid hydrogens both as a consequence of their significant proximity to the quantum limit and of their deviations from the corresponding-states laws followed by most liquids formed by few-atom molecules. Neutron-inelastic-scattering studies using a triple-axis spectrometer carried out in the early 1970's by Carneiro *et al.*[1] are often quoted as the strongest direct experimental evidence for the existence of well-defined collective excitations far from the hydrodynamical regime in molecular liquids. Those studies, complementary to the ones conducted by Schott[2] using neutron time-of-flight spectroscopy, deal with the observation of the collective excitations in liquid hydrogen samples enriched in para-H_2 molecules. Hydrogen exists in two modifications: para-H_2 molecules have even rotational quantum number, J, and antisymmetric nuclear molecular spin state, $I=0$, while ortho-H_2 molecules have odd values of J and symmetric nuclear molecular spin states, $I=1$. Neutrons with energies lower than the para-ortho conversion threshold ($E_{01}=14.7$ meV) scatter coherently from para-H_2, while for higher neutron energies the incoherent scattering dominates due to the much larger incoherent cross section. In ortho-H_2, the incoherent scattering is always dominating. Collective excitations, seen through the coherent scattering, can therefore be observed in para-H_2 enriched samples using low-energy incident neutrons. On this basis, Carneiro *et al.* reported the observation of well-defined spectral features near a neutron energy transfer of $E=7.5$ meV for wave vectors 1.1 Å$^{-1} \leqslant Q \leqslant 3.1$ Å^{-1}, which they attributed to collective excitations of longitudinal-acoustic character. From their published spectra it appears as if these sharp features show a very small degree of dispersion. Additional features at lower values of E were attributed to modes of transverse-acoustic character. A more extensive account of their work is contained in Ref. 3, including a reevaluation of the spectra to obtain a revised value for the mean square displacement $\langle u^2 \rangle$, via the Ambegaokar, Conway, and Baym (ACB) sum rule. In particular, Ref. 3 contains details of the work on the normal mixture (n-H_2 is 75% para-H_2 and 25% ortho-H_2), which scatters mostly incoherently and thus yields information predominantly on $S_s(Q,E)$, the self-part of the scattering function. From these measurements information was derived on the generalized density of collective excitations, i.e., the Fourier transform of the velocity autocorrelation function, dealt with in Ref. 4, for liquid hydrogen. More recent neutron inelastic-scattering experiments in these liquids have focused on higher incident neutron energies in order to study the single-molecule response at Q values high enough for the impact approximation to be valid at the molecular level.[5,6] In these studies, for values of $Q \geqslant 5$ Å^{-1}, the position of the rotational transitions is consistent with a single-molecule response already in the impact approximation in both para-H_2 and n-H_2, and in the liquid and solid phases. From the broadening of the corresponding peaks the mean kinetic energies are determined for the molecules in both phases. Further work at even higher wave vectors has concentrated recently on the single-atom response yielding information either in real space[7] or in reciprocal space.[8] This experimental situation contrasts vividly with the availability of a variational theoretical estimate for the dispersion relation of the collective excitations in liquid H_2, within the single-mode approximation.[9] This prediction, prompted by the interest in the search for a superfluid phase of H_2, bears a remarkable qualitative similarity to the dispersion curve for the collective modes in liquid ^{4}He and implies noticeable dispersion of the collective modes, which should be experimentally accessible in most of the Q range with neutron-inelastic-scattering measurements. Moreover, a similar set of predictions for liquid D_2 in various thermodynamic states in the liquid range have been found to account qualitatively for the observed dispersion relations in n-D_2.[10,11]

With these elements in mind, we have performed neutron-scattering measurements of the inelastic response of liquid H_2 enriched in para-H_2 molecules using a triple-axis spectrometer. The collective excitations and their dispersion were probed by neutrons with low energies (below the para-ortho conversion threshold). Higher-energy neutrons were used at $Q=4$ Å^{-1} to locate the transition from the collective to the single-molecule response in both the liquid and the solid phases.

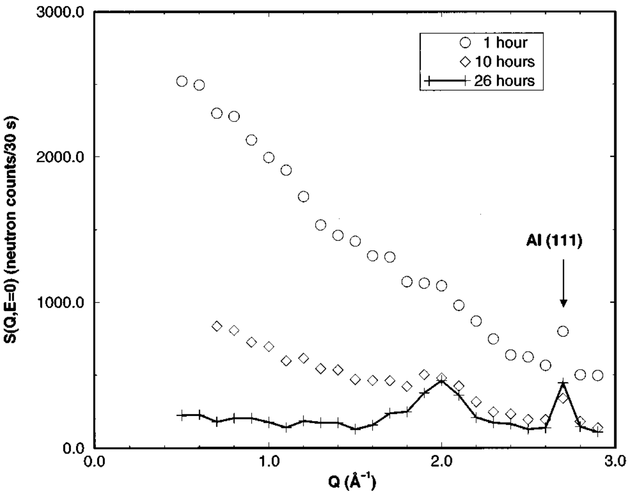

FIG. 1. Measured $S(Q,E=0)$ at three occasions after sample condensation. This time evolution is due to ortho-para conversion. Empty circles correspond to 1 h after sample condensation, empty diamonds to 10 h after condensation and crosses linked by a continuous line to 26 h after condensation. No background subtraction has been performed as evidenced by the Al (111) Bragg reflection.

II. EXPERIMENTAL DETAILS

The experiments reported in this paper were performed on the triple-axis spectrometer DN1 at the Siloé reactor of CEA/Grenoble. The spectrometer was operated in the ''W'' configuration and constant-Q scans were performed at constant neutron incident energy using the (002) reflections from a vertically focused pyrolitic graphite (PG) monochromator and a flat analyzer. A PG filter was inserted in the incident beam to reduce the higher-order contamination. Two different incident energies were used: $E_i=$ 14.2 meV and E_i $=$ 33.4 meV.

The H_2 sample enriched in para-H_2 was prepared as follows. High-purity commercially available (Alphagaz N99) H_2 gas was condensed over ferric oxide powder at a temperature of 15 K in a sample container designed for these experiments. The catalyst accelerates the conversion process of the initially normal mixture of H_2 to a composition close to the equilibrium concentration at the experimental temperature (99.98 % para-H_2). This process was monitored regularly by measuring the elastic structure factor $S(Q,E=0)$. Figure 1 shows the temporal evolution of this magnitude for one of the two samples in our study. As can be seen in the figure, 26 h after condensation the shape of $S(Q,E=0)$ clearly resembles what is expected for a molecular liquid scattering mostly coherently. Repeated checks for changes in $S(Q,E=0)$ over the available range of Q were performed throughout the duration of the experiments. These were particularly relevant in establishing the absence of any after-condensation effects which could temporarily alter the composition of the liquid mixture being examined and thus increase the proportion of molecules contributing to the incoherent scattering. This was detected at one occasion during the low-energy experiment and the data for that time period were not used. All measurements were performed at a temperature of 15 K under saturated vapor pressure, and the corresponding density was 0.0377 mol/cm^3.[12] In order to reduce multiple scattering, the cylindrical cell (1.5 cm diameter, 5 cm height) was divided into five sectors of approximately 1 cm height by means of the insertion of Cd spacers lying parallel to the instrument scattering plane. Monte Carlo simulations using the DISCUS code[13] show that combined absorption and multiple-scattering corrections in our case are negligible. The ferric oxide catalyst was masked by means of a Cd strip attached to the bottom of the cell. The scattering from the empty cell was measured at low temperatures and subtracted from the data. As the spectrometer was operated with a fixed incident energy, the data were corrected by the instrumental factor $(k_f^3 \cot \theta_A)^{-1}$,[14] where k_f is the final wave vector and θ_A the analyzer Bragg angle. The instrumental energy resolution determined from the incoherent scattering of vanadium was (Gaussian full width at half maximum) 0.68 meV at $E_i=$ 14.2 meV and 1.92 meV at $E_i=$ 33.4 meV.

A. Study below the conversion energy threshold

Our first study was conducted with an incident energy $E_i=$ 14.2 meV. The values of the horizontal in-pile-monochromator, monochromator-sample, sample-analyzer, and analyzer-detector collimations were, respectively, 25, 30, 60, and 30 arc min. The main experimental problem was due to the contamination from higher-order harmonics from the monochromator, which despite the use of a PG filter in the incident beam was not sufficiently suppressed. These higher-order neutrons (mostly second order) have sufficiently high energy that they can excite a rotational level, hence converting para-H_2 into ortho-H_2 (i.e., $J=0 \rightarrow J=1$). The cross section for this process is so strong that a substantial number of these neutrons can (again) be scattered in second order (or higher) by the analyzer. This gives a spurious peak at an apparent energy transfer of $E/n^2=3.7$ meV, where E is the real energy transfer (here E_{01}) and $n=2$ is the order of the scattering. This dispersionless peak is clearly seen in all spectra shown in Fig. 2. An analysis of these data is given in Sec. IV A.

B. Study above the conversion energy threshold

A second study was performed using a higher incident energy ($E_i=$ 33.4 meV), horizontal collimations of 25, 30, 30, and 30 arc min, and a PG filter in the incident beam. Due to the characteristics of the energy spectra of the neutrons from the radial beam tube at the Siloé reactor, the amount of higher-order contamination is considerably lower at this energy, and no spurious peaks were observed. Data at $Q=4.0$ Å^{-1} were taken for both the liquid phase at T = 15 K and in the solid at T = 6 K (fully corrected spectra for $Q=2.0$ and 4.0 Å^{-1} are shown in Fig. 3). The $S(Q,0)$ measurement in the solid phase is consistent with an hcp structure, with parameters compatible with those reported by Ishmaev *et al.*[15]

III. THEORETICAL BACKGROUND AND MODELS FOR DATA ANALYSIS

The neutron incident wavelengths employed in our studies are sufficiently close to the value of the internuclear distance in the H_2 molecule, $d=0.74$ Å, to require a theoretical treatment that takes into account the phase differences in the

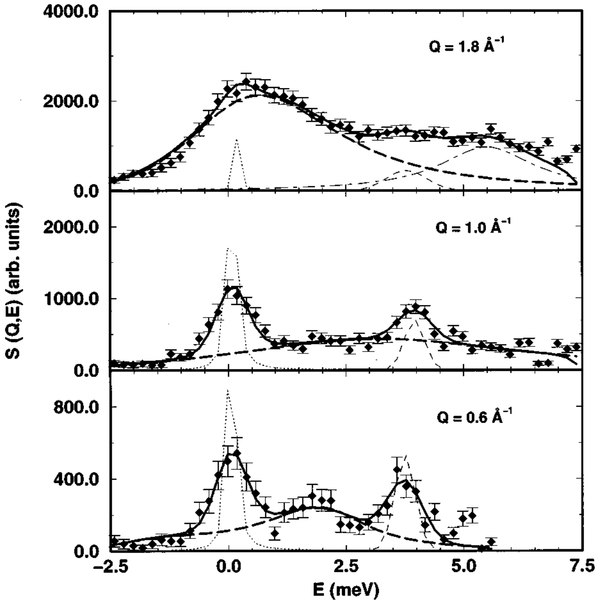

FIG. 2. Representative spectra at three wave vectors with $E_i = 14.2$ meV. Filled diamonds are fully corrected experimental data. The continuous line represents the best fit to these data, consisting of the convolution with the instrumental resolution of the following model components: a central Lorentzian (dotted line), a Gaussian near 3.7 meV representing the second-order contamination (thin dashed line), a damped harmonic oscillator (thick dashed line) representing the collective mode, and an additional damped harmonic oscillator (dot-dashed line) for $Q \geqslant 1.6$ Å^{-1}.

scattering amplitudes corresponding to the two protons in the molecule. One treatment is due to Young and Koppel[16] and is based on the assumption that collective modes are not coupled to the molecular nuclear-spin states. This assumption is quite severe since the anisotropy terms in the intermolecular potential in H_2 depend strongly on the complete molecular wave function, which, restricting ourselves to the fundamental electronic and vibrational states, implies a strong dependence on the rotational-nuclear quantum numbers and more specifically on the ortho-para ratio. For solids, the coupling of the libron and phonon bands in ortho-H_2 rich mixtures has been treated by Bickermann *et al.*[17] Since we are dealing with a mixture poor in $J=1$ molecules, we assume that the collective modes are totally decoupled from the molecular states. Therefore, we consider that the scattering described by the formulas developed in Ref. 16, strictly valid only for a low pressure gas, will be weighted by the collective contributions in the liquid phase in each point of (Q,E) space. For ease of reference, we summarize here the results of Young and Koppel treatment specialized to our case,

$$S_{\mathrm{para}}(Q,E)=c_{\mathrm{para}}[\sigma_{\mathrm{coh}} j_0^2(Qd/2) S_{\mathrm{coh}}(Q,E) + 3\sigma_{\mathrm{incoh}} j_1^2(Qd/2) S_{\mathrm{incoh}}(Q,E-E_{01})], \tag{1}$$

$$S_{\mathrm{ortho}}(Q,E)=c_{\mathrm{ortho}}\left(\sigma_{\mathrm{coh}} S_{\mathrm{coh}}(Q,E)+\frac{2}{3}\sigma_{\mathrm{incoh}} S_{\mathrm{incoh}}(Q,E)\right) \times[j_0^2(Qd/2)+2j_2^2(Qd/2)]. \tag{2}$$

In the above formulas, c_{para} and c_{ortho} are the fractional composition of those types of molecules, $\sigma_{\mathrm{coh}} = 2.05$ b and $\sigma_{\mathrm{incoh}} = 78.7$ b, and $j_l(x)$ are spherical Bessel functions of order l. It should be remembered that, in terms of the self- and distinct-scattering functions,

$$S_{\mathrm{coh}}(Q,E)=S_d(Q,E)+S_s(Q,E), \tag{3}$$

while

$$S_{\mathrm{incoh}}(Q,E)=S_s(Q,E). \tag{4}$$

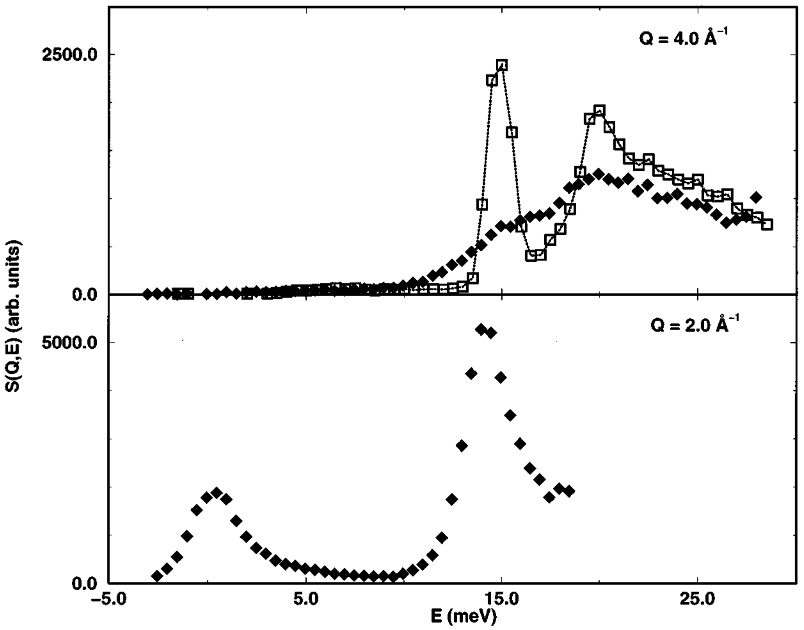

FIG. 3. Fully corrected spectra taken at $E_i = 33.4$ meV. Filled diamonds are the data for the liquid at $T = 15$ K. At $Q = 4.0$ Å^{-1}, the empty squares joined by a dotted line correspond to the solid sample studied at $T = 6$ K.

$S_d(Q,E)$ can be adequately modeled by a sum of damped harmonic oscillator (dho) terms, each corresponding to the individual collective modes presumed to contribute to the spectra:

$$S_d(Q,E)=[n(E)+1]\sum_{i=1}^{N} Z_i(Q)\frac{4EE_{i,Q}\Gamma_{i,Q}}{(E^2-\Omega_{i,Q}^2)^2+4E^2\Gamma_{i,Q}^2}, \tag{5}$$

where $E_{i,Q}$ stands for the bare energy of oscillator i, $\Gamma_{i,Q}$ stands for the damping parameter in energy units, the renormalized energy is given by $\Omega_{i,Q}=(E_{i,Q}^2+\Gamma_{i,Q}^2)^{1/2}$, $Z_i(Q)$ is an intensity parameter and $[n(E)+1]=[1-\exp(-E/(k_BT))]^{-1}$ is the Bose occupation factor. $S_s(Q,E)$ requires at least two contributions that have different relative weights depending on the Q value. For low Q values, the classical interaction time of the neutron and the system is sufficiently long to allow the observation of the diffusive motion of the molecules and $S_s(Q,E)$ can be adequately described by a Lorentzian component of intensity $H(Q)$ whose width, $\Gamma_{Q,L}$, depends on the translational diffusion coefficient,

$$S_s(Q,E)=[n(E)+1]H(Q)\frac{E\Gamma_{Q,L}}{E^2+\Gamma_{Q,L}^2}. \tag{6}$$

For intermediate values of Q the situation is more complex since $S_s(Q,E)$ will contain a projection of the collective motions on the single-particle (molecule) dynamics in addition to a contribution from the broadened rotational modes. Assuming that there is no coupling between the two sets of modes, $S_{\mathrm{incoh}}(Q,E)$ can be related to the density of states, $G(E)$. To obtain an estimate of the density of states from $S_{\mathrm{incoh}}(Q,E)$ in the liquid phase we assume that the expression for a polycrystalline sample can be used without further justification. Thus,

$$G(E)\propto\frac{ES_{\mathrm{incoh}}(Q,E)}{n(E)+1}. \tag{7}$$

For sufficiently high Q values, however, the possibility of the neutron creating multiple excitations has to be taken into account in the corresponding evaluations. In this circumstance, the simple proportionality does not hold unless $G(E)$ is replaced by an effective multiexcitation expansion, similar to what is done in periodic media.[18] Finally, we mention here that in order to compare the model predictions with the observed intensities, it is necessary to convolve the former with the known Gaussian instrumental resolution function.

IV. RESULTS AND DISCUSSION

A. Dispersion relation of the collective modes

A first approach to the low incident energy spectra is their evaluation in terms of a single-mode model [$N=1$ in Eq. (5)], suggested by results in similar systems and theoretical predictions.[9] The collective contribution, emerging through $S_d(Q,E)$, is described by a damped harmonic oscillator term. This contribution is supplemented by a quasielastic Lorentzian centered at $E=0$ meV to account for the diffusionlike motions observed in $S_s(Q,E)$ and a Gaussian (centered near $E=4$ meV) for the spurious peak due to higher-order scattering. This model describes satisfactorily the observations below $Q=$ 1.6 Å^{-1} but it is not adequate for spectra at higher Q values. For $Q\geq 1.6$ Å^{-1}, the fits improve significantly by using two dho terms ($N=2$), the second being necessary to describe a fraction of the observed intensity at higher energies. Figure 2 illustrates the good agreement between observed and calculated spectra in both Q ranges obtained after least-squares fitting of the parameters contained in the corresponding model. The Q dependence of the extracted parameters is shown in Fig. 4. Due to the broad instrumental resolution, the $E=0$ part of the spectra cannot be used to obtain information on diffusion processes.

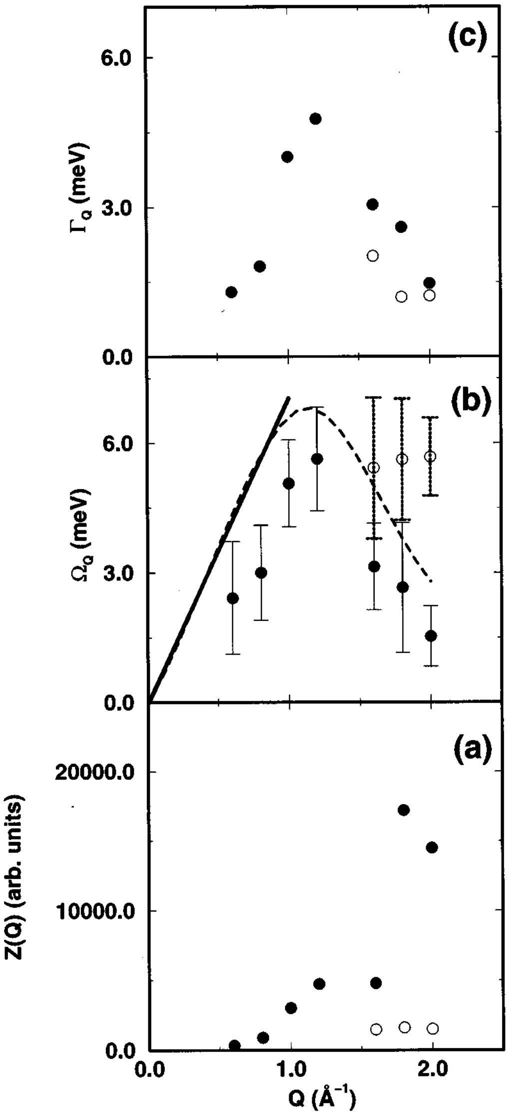

FIG. 4. Q dependence of the best-fit model parameters. Filled circles refer to the first damped harmonic oscillator and empty circles to the second one. The $Z_i(Q)$ intensity parameters are shown in (a). Renormalized energies are shown in (b) where the continuous line represents the extrapolation of the hydrodynamic sound regime, and the dashed line the results from the variational correlated density-matrix calculation. The damping coefficients are shown in (c).

The interpretation of the Q dependence shown by the parameters corresponding to the single– and the two-mode models is by no means unique. In fact, Fig. 4 has been drawn under the assumption that for $Q \geqslant 1.6$ Å^{-1}, the dho term yielding the lower renormalized energy ($i=1$ with $N=2$) represents a continuation of the single mode identified in the lower Q region ($i=1$ with $N=1$). This interpretation is suggested by the dispersion relation obtained from variational calculations and further reinforced by the obtained Q dependence for the dho intensity parameter, $Z_1(Q)$, which resembles the static structure factor for the center-of-mass of a classical diatomic liquid exhibiting a first peak near $Q=2$ Å^{-1}. This mode would then correspond to collective excitations of longitudinal-acoustic character. The nature of the second mode at higher energies and Q values is more difficult to interpret. We note the small Q dependence of the renormalized energy and the low values for the intensity parameter, $Z_2(Q)$. These characteristics are compatible with two possible origins for the observed scattering. First, collective modes of optical character cannot be excluded in view of the presence of several of these branches in the solid lying particularly low towards the center of the Brillouin zone.[19] Molecular-dynamics simulation of other molecular liquids have identified these optical modes as responsible for the observed neutron-scattering spectra at Q values close to the first maximum in the static structure factor.[20] Second, the scattering could also be due to the density of states or self-part of $S(Q,E)$, whose contribution will increase with increasing Q due to the j_1 Bessel function. Without recourse to polarization analysis, there is no way to circumvent this inherent limitation of our experimental approach.

In the context of the first interpretation, the renormalized energies for the *first* dho ($i=1$ with $N=1,2$) should be compared both with the results from Carneiro *et al.* and with those from variational calculations [see Fig. 4(b)]. Our spectra show a clear discrepancy with those reported by Carneiro *et al.*[1,3] More specifically, our measurements do not show any trace of the strong nearly dispersionless spectral feature reported by those authors near $E=7$ meV. It should be noted that the extrapolation of the hydrodynamic limit reported in Fig. 2 of Ref. 1 and in Fig. 6 of Ref. 3 does not correspond to the normally quoted values for the speed of sound in liquid para-H$_2$. At the lower Q values covered in our experiment, the renormalized energies are lower than the extrapolation of the hydrodynamic limit with an isothermal speed of sound of $v_T=1029$ m/s (derived from the adiabatic speed of sound of $v_Q=1235$ m/s using $v_T=v_Q/\sqrt{\gamma}$, where $\gamma=C_p/C_V$ is the ratio of the specific heats at constant pressure and constant volume and has been taken as 1.44 at the experimental temperature[12]). Our results are also consistently lower than those from the variational calculations.[9] However, a quantitative comparison between our experimental results and the calculations is particularly unfair to the latter since at the present time many known ingredients of the system (such as backflow effects and the finite lifetime of the excitations) are not included in the theoretical approach. In particular, it is recognized that neglecting backflow overestimates the excitation energies by a factor of 2–3 near $Q=2$ Å^{-1}. As shown in Fig. 4(c), the damping coefficient for the *first* dho is not greater than the renormalized energy except for $Q \geqslant 1.6$ Å^{-1}. This implies that the observed excitations at low Q values ($Q \leqslant 1.2$ Å^{-1}), although corresponding to a damped collective mode are not in the overdamped regime ($\Gamma_Q^2 > \Omega_Q^2$).[21]

The above comparison with measured sound velocities in the hypersonic and ultrasonic regimes indicates negative dispersion. This is at a striking difference with the observations made in liquid n-D$_2$,[10,11] where strong positive dispersion is observed. This difference is clearly not related to any coupling with the rotational level, since this level is much closer to the collective mode in liquid D$_2$ than in liquid H$_2$. The most likely origin for the effect is in terms of the intermolecular potential, which could favor anomalous dispersion in liquid D$_2$. In fact, the measurements on liquid D$_2$ were made on samples of n-D$_2$. These mixtures contain one out of every three molecules in para-D$_2$ states with $J=1$. The molecules in this excited state contribute with anisotropic terms to the intermolecular potential. This is also seen as differences in the position of the first maximum of the single differential neutron cross sections of liquid mixtures enriched in ortho- and para-D$_2$, as reported by Talhouk *et al.*,[22] and can be related to changes in the nearest-neighbor distance and effective coordination number, probably arising from the better packing of the $J=1$ molecules. The data reported in this paper can only point out to this anomalous comparative behavior of para-H$_2$ and n-D$_2$ in the liquid state near their triple points, but given the readiness with which liquid samples enriched in ortho-D_2 can be prepared, an experimental approach to the dynamics of this liquid is perhaps in order.

B. Crossover to the single-molecule response regime

Instead of attempting an independent analysis of the spectra in the liquid and solid phases for $Q=4$ Å^{-1} with incident energy above the conversion threshold, we have followed an alternative procedure for a comparative analysis of both phases. We start by noting that in the solid phase a narrow spectral feature appears centered at $E=14.7$ meV (see Fig. 3). Given the value of energy transfer at which it appears and the fact that it is only broadened by the instrumental resolution, it can be easily assigned as the $\Delta J=1$ transition corresponding to the para-ortho conversion and we can safely establish that the system response is far from the domain of validity of the impact approximation. In the impact approximation, a Gaussian centered at $E_{JJ'}+E_r$ ($=30.7$ meV at $Q=4$ Å^{-1}) with a width of $\sigma_E=\sqrt{\frac{3}{4}E_rE_K}$ should have been observed, where $E_r=\hbar^2Q^2/2M_{\mathrm{mol}}$ is the recoil energy at momentum transfer Q of a free molecule of mass M_{mol} and E_K is the kinetic energy of the molecule. An alternative assignment of the spectral feature as arising from nearly-free molecule recoil-shifted $\Delta J=0$ transitions can be dismissed on the basis of the expected line broadening (using for E_K the value of 6.5 ± 0.8 meV obtained for solid para-H$_2$ at 10 K by Langel *et al.*,[6] we should obtain for $M_{\mathrm{mol}}=2$ a.m.u. a broadening much in excess of that observed). Also, in this Q range, $\Delta J=0$ transitions possess considerably less intensity than $\Delta J=1$ transitions, since the intramolecular structure factor for the former is small for this value of Q, while that for $\Delta J=1$ is close to its maximum value (see Fig. 5). Additional support for that the impact approximation is not

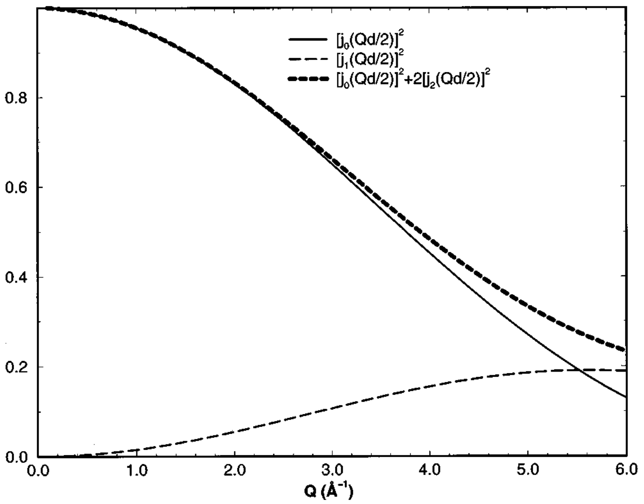

FIG. 5. Spherical Bessel functions entering the neutron-scattering cross sections for H_2 in our experimental range of energy and wave-vector transfers. The internuclear distance in the molecule is taken to be $d=0.74$ Å.

reached for $Q=4$ Å^{-1} in solid para-H_2 comes from the observation of inelastic scattering at higher values of E, reminiscent of a fairly structured density of states. We conclude that at this Q value we are well into the domain of validity of the incoherent approximation but far from realizing the impact approximation.

We turn now our attention to the liquid sample, where the most striking difference found with respect to the solid is the absence of any narrow rotational contribution. Presumably, this contribution is smeared out by Doppler broadening in the liquid and gives rise to the broad spectral feature around $E=$ 15 meV, which overlaps substantially with the more intense feature found at higher energies. The latter is rather similar to the density-of-states contribution in the solid. It is clear that the observed spectrum deviates strongly from the Gaussian line-shape characteristic of the impact approximation, and as the intramolecular form factor argument mentioned above for the solid is equally applicable to the liquid, we conclude that the spectrum actually corresponds to the observation of rotational and collective modes of the liquid phase through the incoherent scattering arising from $\Delta J=1$ transitions. Hence, for both studied phases at $Q=4$ Å^{-1} we find that the response is not yet in the single-particle (molecule) regime. By contrast, both triple-axis and time-of-flight spectrometry results at $Q=5$ Å^{-1} signify the validity of the impact approximation, at the single-molecule level, for samples under similar thermodynamic conditions.[5,6] We conclude that in both phases, the crossover from the collective to the single-molecule response to neutrons seems to be localized between $Q=4$ and $Q=5$ Å^{-1}. The values of the free molecule recoil energy, $E_r=\hbar^2Q^2/2M_{\mathrm{mol}}$, corresponding to these Q values, 16 and 25 meV, can then be employed to locate the effective binding energies of the molecules in each of the two phases. In the solid phase, it is noteworthy that the value for the activation energy of the thermally induced diffusion coefficient is 16.97 meV,[23] reinforcing the classical image in which neutron scattering with wave-vector transfer of $Q>4$ Å^{-1} leaves the molecules with an excess of translational energy with respect to the thermal mean value which enables them to move freely out of their equilibrium position in the lattice. The corresponding image in the liquid phase is much harder to establish.

A more quantitative approach to our spectra can be tried under two strong hypotheses. First, we assume that multiphonon contributions will affect with equal weight the observed spectra in the two phases and that they can be canceled by considering relative quantities. Second, we assume that the ACB sum rule can be applied to the liquid phase. Since the instrumental setup is the same, and only the sample thermodynamic conditions change we can express the ratio of the observed integrated intensities near E_{01}, $I_{s,\alpha}$, $\alpha=S$(solid), L(liquid) in the two phases as a function of their corresponding Debye-Waller factors, $\exp[-2W_\alpha]$, $\alpha=S,L$ and mean-square displacements as

$$\frac{I_{s,S}}{I_{s,L}}=\exp[-2(W_S-W_L)]\frac{\langle u^2\rangle_S}{\langle u^2\rangle_L}. \tag{8}$$

For $\langle u^2\rangle_S$, it is possible to get an independent estimate of 0.46 ± 0.02 Å^2 from the evaluations made by Nielsen[19] and Bickermann *et al.*[24] In computing I_s in the two phases, after correcting for the two different temperature factors, we have subtracted the rotational contribution: in the solid we have fitted and subtracted the clearly defined peak. In the liquid, we have subtracted a Gaussian feature of the same integrated intensity and center as in the solid phase but with a width adjusted to account for the observed slope for E values smaller than E_{01}. With these approximations we obtain an estimate, after linearizing, of $\langle u^2\rangle_L=0.58$ Å^2. A consistency test for this value can be performed by translating this mean amplitude into the mean quantity for the corresponding momentum distribution,[25] $p_0=\sqrt{3}/\langle u^2\rangle_L^{1/2}$. From this quantity, we can estimate the mean kinetic energy for a single molecule $E_K=\hbar^2p_0^2/2M_{\mathrm{mol}}$ of 60 K, which agrees well with the value reported in Ref. 6 of 63±6 K. Consequently, the Debye-Waller factors for the two phases at $Q=4$ Å^{-1} are both smaller than unity and, as in the case of solid ^{4}He,[26] seem to offer a more stringent criteria than the recoil energy for the crossover to the single-molecule response.

V. CONCLUSIONS

Our experimental study on para-H_2-enriched samples in the liquid phase based on conventional triple-axis neutron spectrometry and a partition of the observed scattering into model contributions has revealed the existence of spectral features which are consistent with collective excitations of longitudinal-acoustic character. These excitations are damped up to wave vectors of about 1.2 Å^{-1}, and overdamped at higher wave vectors. The dispersion seems to follow the qualitative trend of variational calculations, although the energies are considerably lower than the extrapolation of the hydrodynamic sound velocity. This situation is in contrast to the observations made in liquid n-D_2, where a strong anomalous (upward) dispersion is observed at low Q values. We suggest that this may be due to the difference in the degree of anisotropy of the intermolecular potential in the studied samples. At higher wave vectors, near the maximum in $S(Q,E=0)$, additional scattered intensity is found whose origin cannot be definitively established, but which may point to low-lying collective excitations of optical character or to a density-of-states contribution. From a comparison of spectra at relatively high wave vectors, $Q=4$ Å^{-1}, in the solid and liquid phase with those of earlier work, we have established that the crossover from collective to single-molecule response takes place with recoil energies in excess of 16 meV, although a better signal for this transition seems to be, for both phases, the small value of the Debye-Waller factor. Finally, we mention that our conclusions for the characteristics of the collective excitations are based on a model interpretation of the observed intensities. Neutron polarization analysis can offer an experimental separation of the scattering into coherent and incoherent nuclear-scattering components, from which a direct validation of our present models can be performed.

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