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$\Delta J=4$ infrared transitions of solid D_2 and a Raman study of H_2, D_2, and HD in their liquid and solid phases

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Infrared spectra of solid D_2 are reported for the spectral regions around the $U_0(0)$ and $U_{1\leftarrow 0}(0)$ transitions. The measured integrated absorptions of these transitions arising from the hexadecapolar-induced dipole moment are in good agreement with theoretical calculations. Phonon branches and a double transition $Q_{1\leftarrow 0}(0)+U_0(0)$ accompanying the transitions have been seen and identified by their frequencies. Raman spectra of H_2, D_2, and HD in their liquid and solid phases are also reported. A new feature of the $S_{1\rightarrow 0}(0)$ transition in solid normal D_2, manifested as a marked asymmetry in its high-frequency wing, is identified by its position, width, and intensity as due to double Raman transitions of the type $Q_{1\rightarrow 0}(J)+S_0(0)$. These double Raman transitions arise from a near-resonant mixing of energy states due to quadrupole-quadrupole interaction and result in Raman emission that is comparable to the zero-phonon $S_{1\rightarrow 0}(0)$ transition, in contrast to the pure rotational band where double Raman transitions $S_0(J_1)+S_0(J_2)$ are several orders of magnitude weaker than the corresponding single $S_0(J)$ transitions.

I. INTRODUCTION

Studies of the isotopic varieties of molecular hydrogen in the condensed phases have, in both infrared absorption and Raman scattering, concentrated largely on the most abundant isotope H_2.[1,2] In this paper, we report the results of experiments on infrared absorption in solid ortho-D_2, and Raman scattering in normal H_2, D_2, and HD in their liquid and solid phases.

Previously, the infrared spectrum of the fundamental-band region of normal and enriched samples of orthodeuterium ($J=0$) have been studied by Crane and Gush.[3] These investigators have measured frequencies and integrated absorption coefficients for $Q_{1\leftarrow 0}(J)$ and $S_{1\leftarrow 0}(J)$ single transitions, and for $Q_{1\leftarrow 0}(J_1)+S_0(J_2)$ and $S_{1\leftarrow 0}(J_1)+S_0(J_2)$ double transitions. The present results extend these observations to the $U_0(0)$ and $U_{1\leftarrow 0}(0)$ transitions that arise from the hexadecapolar-induced dipole moment.

To keep matters in proper perspective, it is useful to clarify briefly the nomenclature, especially because of some slight differences between different publications on this subject. Energy states of molecular systems are characterized by specifying appropriate vibrational quantum numbers v and the rotational quantum numbers J. Ordinarily, in the infrared region one encounters transitions with $\Delta J=J'-J=-1,0,+1$ and they are referred to by the symbols P, Q, and R, respectively. Here the single prime refers to the upper state and the unprimed J to the lower state. The Raman selection rules $\Delta J=-2,0,+2$ give rise to O, Q, and S transitions. At the temperature of solid hydrogen (about 10 K) the lowest occupied J levels are $J=0$ for parahydrogen and $J=1$ for orthohydrogen and hence $\Delta J=-2$ transitions do not occur. The parenthetical entries following the symbols S, Q, and U above (U signifying $\Delta J=4$) give their lower-state J values. The parenthetical entries J_1 and J_2 give the lower-state J values for the two molecules involved in the double transition; J_1 is not necessarily equal to J_2. The subscripts associated with the symbols S, Q, and U give the final (v') and initial (v) vibrational quantum numbers v'-v of the levels involved in these transitions; the direction of the arrow specifies whether we are dealing with absorption ($\leftarrow$) as in the infrared data or inelastic scattering ($\rightarrow$) as in Raman spectra. In some previous articles, a subscript one has been used rather than identifying clearly the v'-v values 1 and 0 of the fundamental vibration-rotational transition. We feel that it would make matters unambiguous if we follow the nomenclature used in gas-phase studies and give the v'-v values rather than adopt a different convention. To be sure, we as well as other authors have followed the gas-phase notation for specifying the J values. The subscript zero indicates a pure rotational transition between the rotational levels of the ground vibrational state $v=0$.

The Raman spectrum of liquid hydrogen was first studied by McLennan and McLeod,[4] and that of solid normal hydrogen and parahydrogen ($J=0$) by Allin *et al.*[5] Bhatnagar and co-workers[6] later investigated the Raman spectra of solid H_2, D_2, and HD at higher resolution. They found that in solid parahydrogen the $S_0(0)$ transition appears as a completely resolved triplet,[7] whereas in solid orthodeuterium the three components are significantly overlapped. The overlapping of the three components is much greater in the spectrum of liquid ortho-D_2 and similarly for the $S_{1\to 0}(0)$ transition in solid para-H_2. In fact, in these latter spectra, the transitions appear as a single broad feature.

More recently, investigations of the pure rotational Raman spectra of solid H_2 and D_2 under higher pressure[8] (about 2 kbar) have revealed additional (normally forbidden) transitions corresponding to $\Delta J=4,6$ as well as double Raman transitions of the type $S_0(J_1)+S_0(J_2)$. These effects are small relative to the magnitudes of the $S_0(J)$ features and were attributed to the mixing of rotational states and the breakdown of the independent polarizability approximation.[8]

In the present work, we report new Raman spectra of the fundamental $S_{1\to 0}(0)$ region in solid normal H_2 and D_2. The feature in D_2 has a marked asymmetry in its high-frequency wing and we attribute that as due to double Raman transitions $Q_{1\to 0}(J)+S_0(0)$ arising primarily from a near-resonant mixing of vibration-rotational states that is much larger than the corresponding mixing of rotational states. The analogous effect in the fundamental band 1-0 of H_2 leads to double Raman transitions which are displaced further from the $S_{1\to 0}(0)$ feature and weaker by approximately an order of magnitude, in agreement with the experimental observations. Further discussion and comparisons between theory and experiment will be presented in Sec. III after a brief description of the experimental details in the following section. Conclusions drawn from the present work have been summarized in the final section of this article.

II. EXPERIMENTAL DETAILS

A Fourier transform spectrometer with a resolution of 0.04 cm^{-1} was used to record the induced-absorption spectrum of solid orthodeuterium in the wave number region 500—5000 cm^{-1}. The $U_0(0)$ and $U_{1\leftarrow 0}(0)$ transitions have been observed and have provided values for the integrated absorption coefficients which in turn led to values for the molecular hexadecapole moment matrix elements. In a second set of experiments, the vibration-rotational $S_{1\to 0}(J)$ transitions have been observed in liquid and solid H_2, D_2, and HD by Raman scattering. These transitions are shifted by about 1000—5000 cm^{-1} from the Rayleigh line and extend the Raman spectra obtained by earlier investigators.

For the present experiments, a 26-mm-long brass cell was used to contain either liquid or solid deuterium. The solid was grown by seeding on a copper needle, which protruded into the brass cell from below. The needle was cooled by suspension in liquid helium in a Janis Research Corporation Varitemp optical cryostat. Owing to the relatively low thermal conductivity ratio[9] of brass to copper ($k_{\text{brass}}=0.1$ $W\,cm^{-1}K^{-1}$, $k_{\text{copper}}=5$ $W\,cm^{-1}K^{-1}$ at 10 K), the needle served as a cold finger for crystal formation and growth.

The sample cells for the infrared and Raman experiments essentially differed in two ways. Firstly, two windows were used in infrared absorption, while the Raman cell had a third window at right angles to the first two for collection of the scattered light. Secondly, the window materials differed in the infrared and Raman experiments. It should be remembered that the windows have to withstand the strains of cooling to liquid-helium temperatures along with mechanical stresses that develop when they are pressed against an indium gasket to provide a vacuum seal. As pointed out before,[10] finding suitable window material for work at 6—20 μm had been a vexing problem because the commonly used crystals of KBr, NaCl, and CaF_2 cracked easily at low temperatures. After some experimentation, silver chloride windows had been found satisfactory in the earlier experiments on solid hydrogen. However, the windows needed to be replaced on a daily basis because of the corrosive reaction of silver chloride with both brass and indium.[11] In our experiments we found that this reaction could be minimized by deposition of a thick film (about 40 000 Å) of silver on the AgCl windows by sputtering.[12] The central part of the window not in contact with the indium gasket or brass was masked during sputtering to permit transmission of the infrared beam. The corrosive reaction of silver chloride was therefore delayed by the time it took for the chlorine ions to diffuse through the silver layer. This permitted the windows to provide a vacuum seal for several days. In Raman scattering, the incident and scattered light are both in the visible. It was therefore possible to use quartz windows on the sample cell. The Raman experiments were performed with a krypton ion laser at powers up to 500 mW and double grating (Spex) spectrometer with the solid kept at a temperature of about 2 K.

III. RESULTS AND DISCUSSION

A. Infrared studies

The main purpose of the infrared experiments in solid orthodeuterium was to identify and measure the integrated absorption coefficients of the U transitions. Figures 1 and 2 show the $U_0(0)$ and the $U_{1\leftarrow 0}(0)$ transitions recorded at 18 K. The observed wave numbers of the peaks are compared in Table I with the positions of the transitions

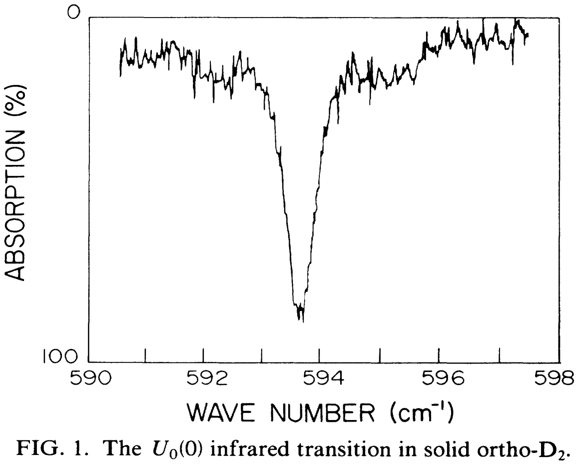

FIG. 1. The $U_0(0)$ infrared transition in solid ortho-D_2.

TABLE I. Wave numbers of rotational and vibration-rotational U transitions observed in solid deuterium.

Transition	Wave number (cm^{-1}) Gas-phase value (Ref. 13)	Observed
$U_0(0)$	593.63	593.6
$U_0(1)$	827.30	826.8
$U_{1\leftarrow 0}(0)$	3559.56	3559.4
$Q_{1\leftarrow 0}(0)+U_0(0)$	3580.58	3580.2

calculated using gas-phase data from Huber and Herzberg.[13] The small shifts in the wave numbers of the positions identifies these transitions.

The integrated absorption coefficient is defined by the relation

$$\tilde{\alpha}=c/Nl\int(1/\nu)\ln[I_0(\nu)/I(\nu)]d\nu \ , \qquad (1)$$

where c is the speed of light, N is the number of molecules per cm^3, l is the length of the crystal, ν is the wave number of the line (in cm^{-1}), and $I_0(\nu)$ and $I(\nu)$ are the intensities before and after absorption.

Assuming a rigid hcp crystal structure for solid orthodeuterium, it can be shown[12,14] that

$$\tilde{\alpha}=(175\pi^3Q_4^2\alpha^2S^2)/(48ha^{12}) \ . \qquad (2)$$

In Eq. (2), Q_4 and α are the appropriate rotational or vibration-rotational matrix elements of the hexadecapole moment and isotropic polarizability, respectively, h is Planck's constant, and a is the nearest-neighbor distance; S is a lattice sum which has been shown to be 5.1105 for an hcp lattice.[10] The experimental value of $\tilde{\alpha}(U_0(0))$ gives a value of Q_4 of 0.3593 a.u. compared to the theoretical value of 0.3269 a.u. given by Karl *et al.*[15] for an isolated molecule. For the $U_{1\leftarrow 0}(0)$ transition, the value of Q_4 obtained is 0.0985 a.u. compared to the theoretical value[15] of 0.1030 a.u.

Figure 3 shows the spectral region close to the $U_0(0)$ transition. The spectrum reveals a weak, broad feature centered around 630 cm^{-1}. The presence of such structure is consistent with the existence of phonon sidebands agreeing with the peak at ~45 cm^{-1} in the density of phonon states in solid D_2.[16] The $U_0(1)$ transition (not shown) has been observed as a weak feature that is caused by the presence of para impurities.

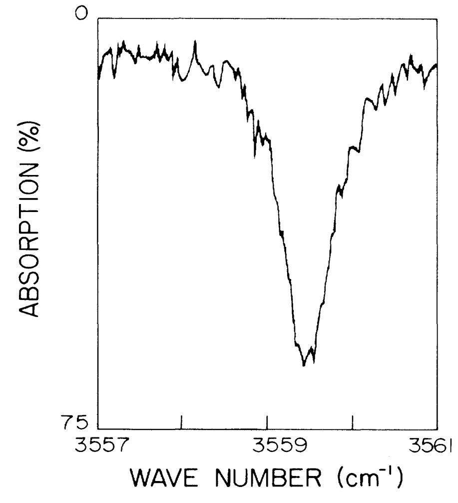

FIG. 2. The $U_{1\leftarrow 0}$ infrared transition in solid ortho-D$_2$.

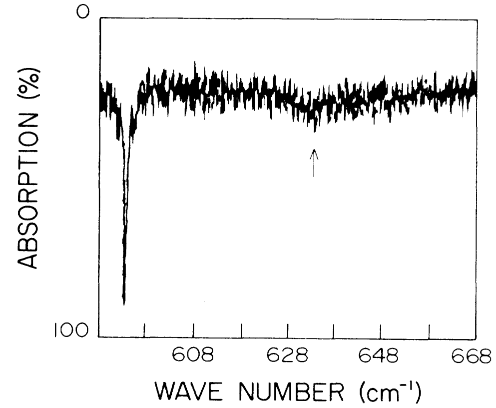

FIG. 3. Spectral region on the high-frequency side of $U_0(0)$ in solid D$_2$. The weak, broad structure is consistent with the peak in the density of phonon states.

The double transition $Q_{1\leftarrow 0}(0)+U_0(0)$ has been observed in solid ortho-D$_2$ at 3580.2 cm^{-1}, as shown in Fig. 4. It has a full width at half maximum (FWHM) of 0.8 cm^{-1} and is interpreted as due to a change of $\Delta v=0$, $\Delta J=4$ in one molecule accompanied by a change of $\Delta v=1$, $\Delta J=0$ in another molecule. Thus, the double transition is produced by absorption of a single quantum of light by excitations in two different deuterium molecules. The transition can be identified on the basis of frequency by adding the energies of the two transitions, using data from Huber and Herzberg.[13] The calculated and experimental wave numbers are shown in Table I and found to agree within reasonable limits. Unfortunately, the double transition lies within the phonon branch of the $U_{1\leftarrow 0}(0)$ transition; this is also the case in solid hydrogen.[17] In our study, we have been unable to observe the phonon branch of the $U_{1\leftarrow 0}(0)$ transition.

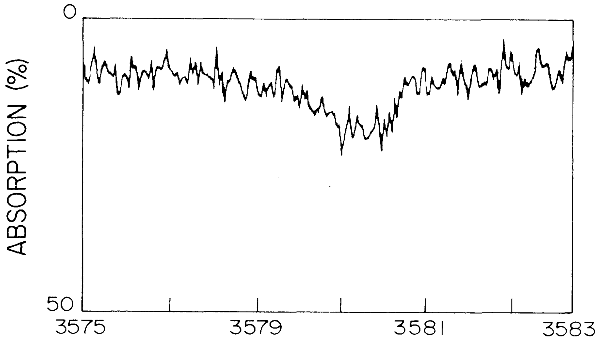

FIG. 4. The $Q_{1\leftarrow 0}(0)+U_0(0)$ infrared double transition in solid ortho-D$_2$.

B. Raman studies

As an extension of previous Raman studies of the isotopes of hydrogen in liquid and solid phases,[4–6] we have observed the vibration-rotational $S_{1\to 0}(J)$ transitions that extend up to 5000 cm^{-1} from the exciting line. In Figs. 5 and 6, we show the $S_{1\to 0}(0)$ and $S_{1\to 0}(1)$ transitions, respectively, in solid normal deuterium, and in Fig. 7, we show the corresponding weak $S_{1\to 0}(0)$ transition in solid HD. These transitions have not been observed in previous experiments by Raman scattering. The corresponding transitions in the liquid (not shown) occur at nearly the same positions and have approximately the same shapes.[12] The $S_{1\to 0}(1)$ transition is not observed in solid or liquid hydrogen deuteride. The reason for this is that owing to the absence of an ortho-para distinction, almost all the HD molecules at low temperature occupy the lowest ($J=0$) state. Table II lists the peak positions and FWHM of the vibration-rotational S transitions in liquid and solid D_2 and HD obtained in the present work by Raman scattering.

The $S_{1\to 0}(1)$ feature in solid normal H_2 (Fig. 8) displays a slight asymmetry which results from the almost complete overlapping of the three components that comprise the transition.[6,7] In contrast, the $S_{1\to 0}(0)$ feature in solid normal D_2 (Fig. 5) has an additional marked asymmetry in the high-frequency wing; we attribute this extra scattering to double Raman transitions of the type $Q_{1\to 0}(J)+S_0(0)$ that occur because of a near-resonant mixing of vibration-rotational states by the quadrupole-quadrupole interaction.

In the double transitions, two separate molecules of the normal solid are simultaneously excited by a single photon, a rotational-vibrational mode $Q_{1\to 0}(J)$ in one ortho or para molecule and a pure rotation $S_0(0)$ in another ortho molecule. The detailed theory for this effect will be published elsewhere,[18] but we note here that the ratio of the integrated intensity of the double transitions to that of the single $S_1(0)$ transition is of the order of $(E_{QQ}/\Delta E)^2$, were E_{QQ} is the quadrupole-quadrupole interaction energy and ΔE is the difference in energy between the two types of transitions. As mentioned in the Introduction,

TABLE II. Wave numbers and linewidths of some transitions observed in liquid and solid D_2 and HD observed in Raman spectra.

	Transition	Position (cm^{-1})	FWHM (cm^{-1})	Position in gas-phase in cm^{-1}, from Ref. 13
		Molecule in solid		
D_2	E_{2g}	35.5	3.0	
D_2	$S_{1\to 0}(0)$	3152.0	5.5	3159.66
D_2	$S_{1\to 0}(1)$	3270.0	7.0	3271.81
HD	E_{2g}	37.0	1.5	
HD	$S_{1\to 0}(0)$	3880.0		3880.48
		Molecule in liquid		
D_2	$S_{1\to 0}(0)$	3156.5	7.0	3159.66
D_2	$S_{1\to 0}(1)$	3272.5	4.0	3271.81
HD	$S_{1\to 0}(0)$	3882.0		3880.48

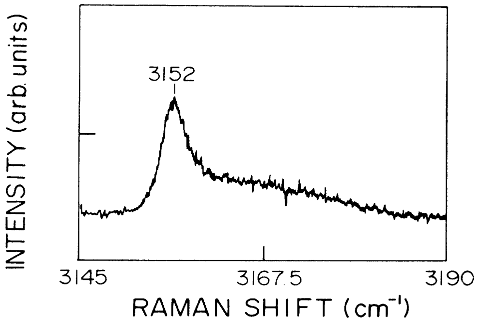

FIG. 5. The $S_{1\to 0}(0)$ vibration-rotational Raman transition in solid normal D_2. The asymmetry is due to $Q_{1\to 0}(J)+S_0(0)$ double Raman transitions.

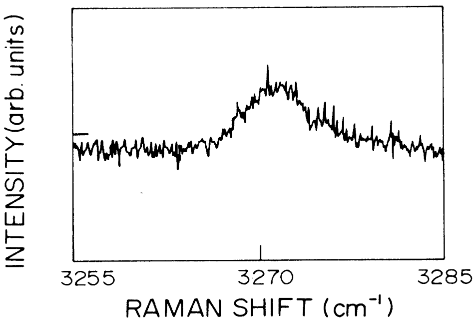

FIG. 6. The $S_{1\to 0}(1)$ vibration-rotational Raman transition in solid normal D_2.

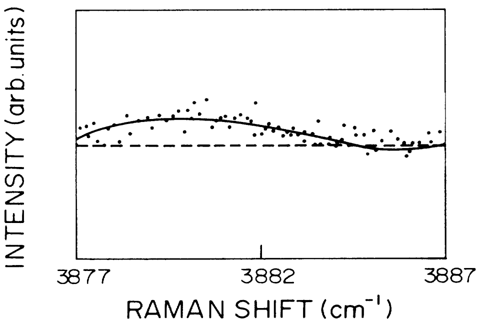

FIG. 7. The $S_{1\to 0}(0)$ vibration-rotational Raman transition in solid HD.

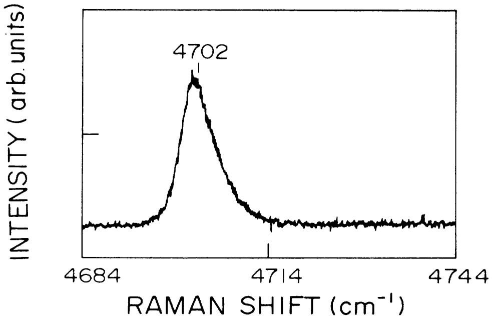

FIG. 8. The $S_{1\to 0}(1)$ vibration-rotational Raman transition in solid normal H_2.

the analogous effect for the $S_{1\to0}(0)$ transition in normal H_2 is smaller than that in normal D_2 by an order of magnitude; even so, this scattering is still an order of magnitude larger than previously identified[8] double rotational Raman transitions of the type $S_0(J_1)+S_0(J_2)$ observed in solid D_2 at about 1 kbar pressure.

In addition to the phonon bands accompanying the vibration-rotational transitions discussed above phonon sidebands to the pure rotational $S_0(0)$ transition were observed in solid hydrogen and deuterium.[12] The observation of these sidebands and of the E_{2g} phonon in all three solids was taken as an indication of the good quality of the crystal grown. In the case of polycrystal, multiphonon structures would be seen in the region between the E_{2g} phonon (~ 35 cm^{-1}) and the $S_0(0)$ transition.[19,20] No such structures were observed in any of the spectra obtained. Clarity and transparency of the solid were considered as addition checks on crystal quality. These tests on the quality of the crystal have been useful since no diffraction experiments were performed to verify crystal structure.

IV. CONCLUSIONS

In summary, the important features of this investigation are the following.

(1) The U transitions have been observed for the first time in solid ortho-D_2 by infrared absorption.

(2) The integrated absorption coefficients of the $U_0(0)$ and $U_{1\leftarrow0}(0)$ transitions yielded experimental values for the rotational and vibration-rotational hexadecapole moment matrix elements in good agreement with theoretical values.

(3) The Raman experiments led to the observations of the rotation-vibrational S transitions in solid and liquid D_2 and HD for the first time. These transitions occur at positions close to the positions predicted by theory for the gas phase.

(4) Double Raman transitions of the type $Q_{1\to0}(J)+S_0(0)$ have been identified for the first time; their intensity is several orders of magnitude larger than similar transitions in the infrared.

(5) Crystals of solid hydrogens of length 26 mm have been grown and maintained in a liquid-helium cryostat. This experience in crystal growth and maintainence can be applied to many other solids, as for example, solid nitrogen and solid oxygen.

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