Observation of the $U_{1-0}(1)$ transition of solid deuterium

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Infrared absorption in the 3 μm region of normal and ortho enriched solid deuterium samples at 4.2 K has been restudied with improved signal-to-noise ratio using a Bomem FTIR spectrometer. The zero-phonon $U_{1-0}(1)$ transition of deuterium was observed for the first time in the spectrum of normal D_2. In addition, we also observed the phonon branches $U_R(0)$ [of the $U_{1-0}(0)$ transition] and $U_R(1)$ [of the $U_{1-0}(1)$ transition], which were not seen in previous work. The analysis of the spectra and the effect of p-D_2 molecules on the intensities and linewidths of the transitions are discussed. The hexadecapole moment of the $U_{1-0}(0)$ transition was estimated to be 0.121 ea_0^4 from the experimental integrated intensity.

INTRODUCTION

Solid molecular hydrogen and its isotopic species form a special class of crystals in solid state physics. Because of the weak intermolecular interactions, the hydrogen molecules are only slightly perturbed in solid state. As a result, most of the solid properties can be derived from first principles.[1] Molecules in the solid have nearly free rotation and vibration even at very low temperature. The properties of solid hydrogen have been extensively studied by theorists and experimentalists.[2,3] Since the first observation of the Q ($\Delta J = 0$) and S ($\Delta J = 2$) branches of its fundamental band by Allin, Hare, and MacDonald[4] and the subsequent more complete study by Gush, Hare, Allin, and Welsh at Toronto,[5] the infrared spectroscopy of solid hydrogen has aroused much interest from spectroscopists.[1] Similar to the case of collision-induced absorption of gaseous H_2, the observed spectrum is ascribed to the electric dipole moment induced by the multipolar interactions of the molecules in the solid. These induced transitions can have various ΔJ (change of rotational quantum number between the initial and final states) depending on the order of the multipole moment, and weaker intensities are predicted for those transitions with larger ΔJ. Because of the weakness, the hexadecapole-induced[6] rovibrational U branch ($\Delta J = 4$) transitions were observed more than two decades later by Prasad, Clouter, and Reddy.[7] The much weaker tetrahexacontapole-induced[6] W ($\Delta J = 6$) transitions of solid H_2 have been reported very recently using high resolution infrared laser spectroscopy.[8] However, relatively little work has been done on solid deuterium. Crane and Gush reported the observation of the fundamental band, covering the Q and S branches, of normal and ortho enriched solid D_2 in 1966.[9] Baliga, Sooryakumar, Rao, Tipping, and Poll extended the observation to the $U_{1-0}(0)$ transition in the 3 μm region in 1987.[10] In this paper we report our studies of the $U_{1-0}(1)$ transition of solid deuterium.

The notations used for the transitions in this paper follow the conventions of Ivancic *et al.*[11] The symbols Q, S, U, and W indicate the change of rotational quantum number by 0, $+2$, $+4$, and $+6$, respectively. The subscript signifies the change of vibrational quantum number; subscripts $1\leftarrow0$, 0, and R represent the vibrational, pure rotational, and the corresponding phonon branches of the transitions, respectively. The quantity in the parentheses corresponds to the initial J value of the transition. For instance, $U_{1-0}(1)$ stands for the rovibrational excitation with $v = 1\leftarrow0$ and $\Delta J = +4$ starting from the $J = 1$ level in the ground vibrational state.

EXPERIMENTAL

The apparatus was similar to that used for the study of W transitions of solid H_2.[8] A copper sample cell 1 cm long and 2 cm in diameter was attached to the cold surface of the Infrared Laboratories HD-3 liquid helium Dewar. CsI windows were sealed onto the cell using cryogenic epoxy D.E.R. 331 from Union Carbide. The sample of solid D_2 was made by pulsing the gas into the cell at about 60 to 110 Torr.[8] The D_2 samples prepared in this way are normally optically transparent with few fractures. The infrared beam was adjusted to probe the clear part of the solid. Chemically pure grade deuterium from Matheson was passed through a liquid N_2 trap to remove impurities prior to use. Ortho (molecules of even J value) enriched ($\sim97\%$) D_2 gas was produced by passing the normal gas through a column of Appachi catalyst equilibrated at the liquid hydrogen temperature. Spectra at 0.1 and 4.0 cm^{-1} resolution of the solid samples at 4.2 K were recorded using a Bomem DA2.026 FTIR spectrometer with a CaF$_2$ beam splitter and a globar source. The signal was detected using a liquid nitrogen cooled InSb detector. The optical path was purged with dry N_2 to minimize the background absorption due to atmospheric H_2O.

ANALYSIS OF SPECTRA

The concentration of paradeuterium (p-D_2) in the ortho enriched sample was estimated from the integrated intensity of the $Q_{1-0}(1)$ transition. The spectra of normal deuterium (n-D_2) and $\sim97\%$ orthodeuterium (o-D_2) in the 3 μm region at 4.0 cm^{-1} resolution are shown in Fig. 1. The transition frequencies and assignments are listed in Table I. The observed transitions were assigned to be zero-phonon single and double transitions (for double transitions, two interacting molecules, behaving as a single system, change their quantum states "simultaneously" by absorbing
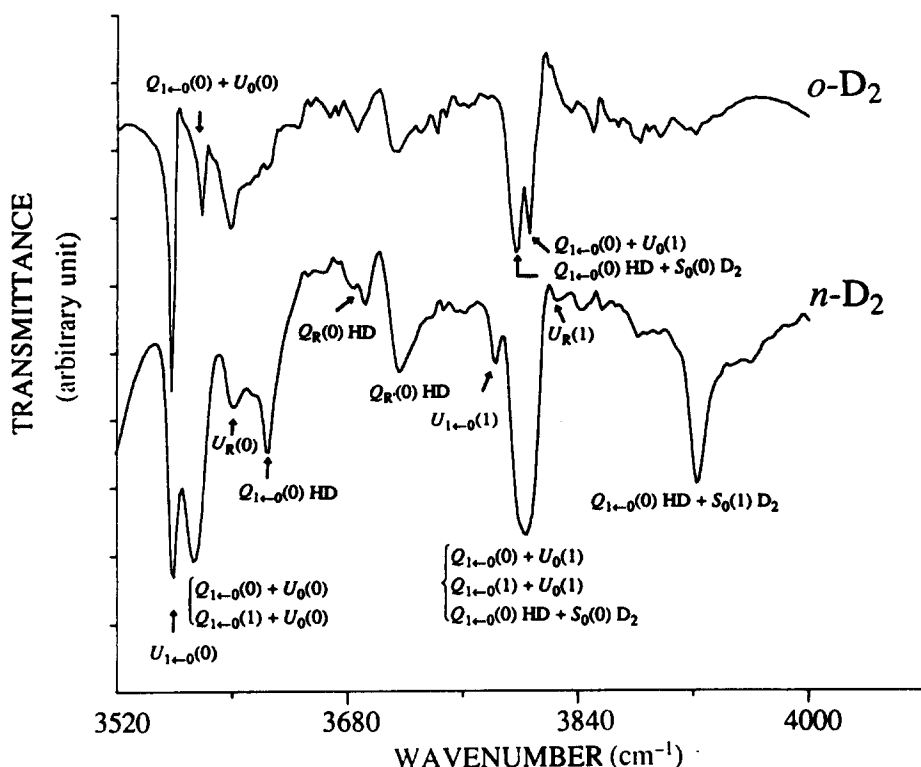
FIG. 1. Spectra of normal (lower trace) and ortho enriched (upper trace) deuterium at 4 cm^{-1} resolution in the 3 μm region.

a photon) as well as the phonon branches of these transitions. In addition to the previously observed $U_{1-0}(0)$ and $Q_{1-0}(0) + U_0(0)$ transitions of deuterium,[10] we also observed the $U_{1-0}(1)$ transition in the spectrum of n-D$_2$. Furthermore, the combined D$_2$–HD double transitions and the single transition $Q_{1-0}(0)$ of HD were observed in the same region because of the HD impurity ($\sim0.4\%$) in the commercial D$_2$ gas.

The $U_{1-0}(0)$ and $Q_{1-0}(0) + U_0(0)$ transitions were observed at 3559.2 and 3580.2 cm^{-1}, respectively, in the sample of o-D$_2$, in good agreement with the work of Baliga *et al.*[10] Because of the improved signal-to-noise ratio in our experiment, we were able to observe the phonon branch of the $U_{1-0}(0)$ transition at 3599.5 cm^{-1}. Its shift from the zero-phonon transition $U_{1-0}(0)$ is consistent with the predicted peak position of the density of phonon states in solid deuterium.[12] The phonon branch of the $Q_{1-0}(0) + U_0(0)$ transition was not seen clearly because it partially overlaps with the more prominent $Q_{1-0}(0)$ transition of the HD impurity.

The newly observed $U_{1-0}(1)$ transition appearing at 3782.7 cm^{-1} in the spectrum of n-D$_2$ was shifted by ~7 cm^{-1} from the gas phase value.[13] The phonon branch $U_R(1)$ of this transition was observed at 3825.1 cm^{-1}. These transitions were too weak to be observed in o-D$_2$, in which the concentration of p-D$_2$ molecules was reduced to $\sim3\%$. However, the $Q_{1-0}(0) + U_0(1)$ double transition still appeared with strong intensity in the same sample. The substantial difference between the intensities of the $U_{1-0}(1)$ and $Q_{1-0}(0) + U_0(1)$ transitions in o-D$_2$ can be explained by the fact that the cancellation effect of the transition intensity due to the crystal symmetry[1,5,14] applies only to single transitions. This effect, in addition to the concentration factor, makes the $U_{1-0}(1)$ transition in the o-D$_2$ sample unobservable.

In the spectrum of n-D$_2$, the $Q_{1-0}(0) + U_0(1)$ transition overlaps with two other double transitions,

TABLE I. Observed transitions in solid deuterium. Resolution is 4 cm^{-1}, unless noted.

| | Wave number (cm^{-1}) | | |
Transitions	n-D$_2$	o-D$_2$	Calc.[a]
D$_2$			
$U_{1-0}(0)$	3559.2	3559.29[b]	3566.2
$Q_{1-0}(1) + U_0(0)$	3573.5[c]	$\cdots$	3578.4
$Q_{1-0}(0) + U_0(0)$	3573.5[c]	3580.2	3580.4
$U_R(0)$	3600.5	3599.5	$\cdots$
$U_{1-0}(1)$	3782.7	$\cdots$	3789.9
$Q_{1-0}(1) + U_0(1)$	3803.9[d]	$\cdots$	3811.6
$Q_{1-0}(0) + U_0(1)$	3803.9[d]	3806.8	3813.6
$U_R(1)$	3825.1	$\cdots$	$\cdots$
HD			
$Q_{1-0}(0)$	3624.6	3627.5	
$Q_R(0)$	3684.3	3689.2	
	3692.1		
$Q_R{}'(0)$	3717.1	3713.3	
		3720.0	
D$_2$–HD			
$Q_{1-0}(0)$HD + $S_0(0)$D$_2$	3803.9[d]	3799.1	
$Q_{1-0}(0)$HD + $S_0(1)$D$_2$	3922.5	$\cdots$	

[a] Single transitions were calculated using the gas phase data from Ref. 13. Double transitions were calculated by summing the frequencies of the corresponding single transitions in solid D$_2$.

[b] At 0.1 cm^{-1} resolution, in good agreement with Baliga *et al.* (1987) their value is 3559.4 cm^{-1}.

[c] These two transitions are unresolved.

[d] These three transitions are unresolved.

$Q_{1-0}(1) + U_0(1)$ and $Q_{1-0}(0)$ HD $+ S_0(0)$ D$_2$, and appears as a broad feature at 3803.9 cm^{-1}. They were not resolved because of the broadening effect from p-D$_2$ molecules. This broad feature was resolved into two peaks with a separation of 7.7 cm^{-1} in o-D$_2$. They were assigned to be $Q_{1-0}(1) + U_0(1)$ at 3806.8 cm^{-1} and $Q_{1-0}(0)$ HD $+ S_0(0)$ D$_2$ at 3799.1 cm^{-1}, respectively. The $Q_{1-0}(0) + U_0(1)$ transition, involving two p-D$_2$ molecules, was not observed clearly in o-D$_2$ due to the low probability of two impurity molecules being close enough to induce an electric dipole for the transition. We also observed another combined D$_2$–HD double transition $Q_{1-0}(0)$ HD $+ S_0(1)$ D$_2$ at 3922.5 cm^{-1} in n-D$_2$. For the same reason, it was much weaker in the spectrum of o-D$_2$.

Based on the observation of Crane and Gush,[9] we assigned the zero-phonon $Q_{1-0}(0)$ transition of HD impurity at 3624.6 cm^{-1}. The characteristic shape of the corresponding phonon branches $Q_R(0)$ and $Q_{R'(0)}$[15,16] also serve as fingerprints for identifying this transition. Figure 1 shows an appreciable difference in the intensities of the zero-phonon $Q_{1-0}(0)$ transition of HD in the spectra of o-D$_2$ and n-D$_2$. According to Sears and Van Kranendonk,[17] the $Q_{1-0}(0)$ transition is forbidden in the absence of $J = 1$ molecules. In the presence of nearby $J = 1$ molecules, this transition can occur with a simultaneous reorientation of a $J = 1$ molecule. It is thus expected that the intensity of $Q_{1-0}(0)$ of HD will be much stronger in n-D$_2$, which contains $\sim 33\%$ of p-D$_2$.

Table II lists the integrated absorption intensities $\tilde{\alpha}$, defined as

$$\tilde{\alpha} = \frac{c}{nl} \int \ln\left[\frac{I_0}{I}\right] \frac{d\nu}{\nu},$$

of the deuterium transitions. c is the speed of light, n is the number density of the molecules (in cm^{-3}), l is the optical path length of the sample, ν is the wave number of the line, and I_0 and I are the infrared intensity before and after the sample, respectively. From the integrated intensity of the $U_{1-0}(0)$ transition and assuming a hexadecapole-induction mechanism for this transition, we can estimate the transition hexadecapole moment

$$|Q_{01}^{(4)}(0)| \equiv |\langle v=1, J=4|\hat{Q}^{(4)}|v=0, J=0\rangle|$$

from the equation

$$\tilde{\alpha} = \frac{20\pi^2 |Q_{01}^{(4)}(0)|^2 \alpha_{00}^2}{3\hbar a^{12}} \xi_{65}^2 \sum_{i,j} \left[\frac{a^2}{a_i a_j}\right]^6 P_5(\cos\theta_{ij})$$

TABLE II. Measured integrated intensity $\tilde{\alpha}$ of zero-phonon transitions in solid deuterium.

Transitions	$10^{16}\,\tilde{\alpha}$ (in cm^3 s^{-1})
$U_{1-0}(0)$	1.2 ± 0.2[a]
$Q_{1-0}(0) + U_0(0)$	0.27[a,c]
$U_R(0)$	1.9[a,c]
$U_{1-0}(1)$	0.66[b,c]
$U_R(1)$	0.65[b,c]

[a] Measured from the $\sim97\%$ o-D$_2$ sample.
[b] Measured from the n-D$_2$ sample.
[c] Due to the overlapping of transitions, the uncertainty of measurement is $\sim30\%$.

derived by Poll and Tipping.[18] α_{00} is the isotropic polarizability, a is the lattice constant, a_i is the distance to molecule i, ξ_{65} is the renormalization constant due to lattice vibration (assumed to be unity here), and θ_{ij} is the angle between the vectors $\mathbf{a}_i$ and $\mathbf{a}_j$. We obtained $|Q_{01}^{(4)}(0)| = 0.121 \pm 0.01ea_0^4$, a factor of about 1.2 larger compared with the value of 0.0985 ea_0^4 given by Baliga et al.[10]

The linewidths Γ (HWHM) of the $U_{1-0}(0)$ and $U_{1-0}(1)$ transitions in n-D$_2$ are about 5.4 and 4.8 cm^{-1}, respectively. In $\sim97\%$ o-D$_2$, the $U_{1-0}(0)$ transition is much sharper, with a linewidth of about 0.32 cm^{-1} (Fig. 2). As shown in Fig. 1, the double transitions also appear to be sharper in o-D$_2$. The line broadening effect is expected to be mainly due to p-D$_2$ molecules and thus the difference in the linewidth in the two spectra can be attributed to the difference in p-D$_2$ concentration. The narrowing of the double transitions involving p-D$_2$ molecules in the o-D$_2$ sample may also be explained by the suppression of the exciton band formation due to different energy separations of the p-D$_2$ molecule and the surrounding o-D$_2$ molecules. The measured linewidth of the transitions are listed in Table III.

DISCUSSION

The spectra reported in this paper demonstrate a variety of interesting phenomena (e.g., double transitions, cancellation effect, the intensity of the Q branch, the broadening mechanism, etc.) of the spectroscopy of solid hydrogen and its isotopic species which were extensively discussed by Van Kranendonk in his comprehensive treatise.[1] As the experimental accuracy improves, more precise theoretical models are required to explain the experimental observations. The transition hexadecapole moment $|Q_{01}^{(4)}(0)|$ for an isolated deuterium molecule was calculated to be 0.1030 ea_0^4 by Karl, Poll, and Wolniewicz.[19] This value is $\sim85\%$ of our observed value for solid D$_2$. A higher experimental value for the hexa-
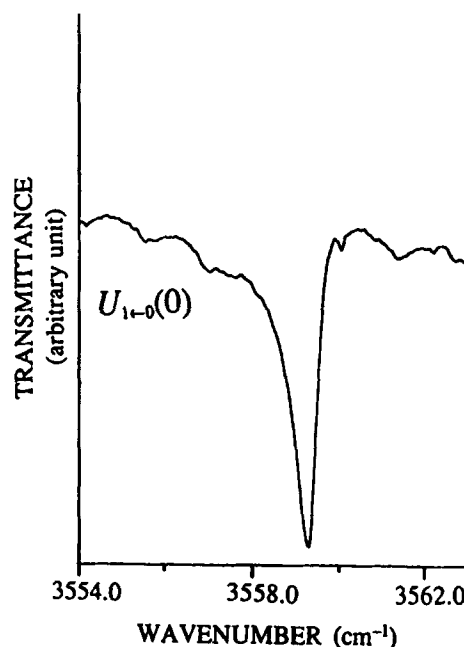

FIG. 2. The $U_{1-0}(0)$ transition in o-D$_2$ sample. The measured linewidth (HWHM) is 0.32 cm^{-1} at 0.1 cm^{-1} resolution.

TABLE III. Measured linewidths Γ (HWHM) of zero-phonon transitions in solid deuterium from the spectra at 4 cm^{-1} resolution, unless noted.

Transitions	Γ (in cm^{-1})	
	n-D$_2$	o-D$_2$
D$_2$		
$U_{1-0}(0)$	5.4	0.32[a]
$Q_{1-0}(0) + U_0(0)$	9.6[b]	0.50[a]
$Q_{1-0}(1) + U_0(0)$	9.6[b]	...
$U_{1-0}(1)$	4.8	...
$Q_{1-0}(0) + U_0(1)$	10.2[c]	5.2
$Q_{1-0}(1) + U_0(1)$	10.2[c]	...
HD		
$Q_{1-0}(0)$	3.4	2.5
D$_2$-HD		
$Q_{1-0}(0)$HD $+ S_0(0)$D$_2$	10.2[c]	6.2
$Q_{1-0}(0)$HD $+ S_0(1)$D$_2$	11.3	[d]

[a] Measured from spectrum at 0.1 cm^{-1} resolution.
[b] Transitions unresolved, combined linewidth.
[c] Transitions unresolved, combined linewidth.
[d] Too weak for linewidth measurement.

decapole moment of the $U_{1-0}(0)$ transition was also reported in solid p-H$_2$.[7,11] The discrepancy between the experimental result and the calculated value may be ascribed to the stronger intermolecular interactions in solid state which were not taken into account in the theoretical model. The values of higher multipole moments are more sensitive than that of the quadrupole moment to the distribution of electrons far from the center of the molecule and consequently more likely to be affected by solid state perturbations. The experimental values of the high-order moments provide crucial tests for the *ab initio* wave function of hydrogen as well as the model of interactions in solid hydrogen.

From what we observed in this experiment, the concentration of $J = 1$ molecules is very critical in high resolution spectroscopy of solid hydrogen and deuterium. Paradeuterium molecules not only broaden the infrared transitions but also change the intensities of transitions. It is not surprising that the linewidth for the $U_{1-0}(0)$ transition in 97% o-D$_2$ is significantly broader than that in 99.8% p-H$_2$.[8,11] The existence of $J = 1$ molecules and isotopic impurities introduce strain and quadrupolar broadening (from $J = 1$ molecules) to the transitions.[20] This effect is more serious in the case of o-D$_2$ ($\sim$3% of p-D$_2$ and $\sim$0.4% of HD) than p-H$_2$ ($\sim$0.2% of o-H$_2$ and $\sim$300 ppm of HD). Because of the higher triple point and smaller rotational constant of deuter-

ium, it is technically more difficult to make highly pure o-D$_2$ for linewidth studies. Another approach to the problem is to use p-H$_2$ as a matrix for studying deuterium impurity transitions. Attempts along this direction are underway.[21]

ACKNOWLEDGMENTS

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