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Observation of U-branch transitions in the infrared fundamental band of solid hydrogen

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U-branch transitions corresponding to $5 \leftarrow 1$ and $4 \leftarrow 0$ in the rotational quantum number J of the H_2 molecule have been clearly observed in the infrared fundamental band with a 3.6-cm absorbing path of the solid at ~ 10 K. These transitions arise because of the hexadecapolar contribution to the intermolecular interaction, and this work represents the first observation of such absorption in solid H_2. A measurement of the absorption intensity was made for the case of high-purity parahydrogen.

I. INTRODUCTION

In this paper we report the results of an experimental study of the infrared fundamental absorption band of the H_2 molecule in the solid phase at ~10 K which yields the identification of sharp zero-phonon transitions $U_1(J)$ and $Q_1(J)+U_0(J)$, in which $U(J)$ corresponds to the rotational selection rule $\Delta J=4$, and of relatively broad phonon branches $U_R(J)$, for $J=0$ and 1.[1] The study also identifies the phonon branches which accompany the double transitions of the type $S_1(J)+S_0(J)$.

The infrared fundamental absorption band of solid hydrogen in the region 4000–5000 cm^{-1} has been investigated both experimentally[2] and theoretically.[3] As in the case of gaseous hydrogen[4] the observed spectrum of the solid is due to dipole moments induced by intermolecular interaction, and the $Q(\Delta J=0)$ and $S(\Delta J=2)$ branch features which have been observed in the solid to date are customarily divided into two groups of transitions each of which is associated with a specific type of interaction. These groups of transitions are the following: (i) The relatively sharp so-called zero-phonon transitions, which involve only the internal degrees of freedom of the molecules, are due to *quadrupolar interaction*. These include the single transitions $Q_1(J)$ and $S_1(J)$, as well as double transitions such as $Q_1(J)+S_0(J)$ and $S_1(J)+S_0(J)$. (ii) The phonon branches Q_R and S_R which contribute a major part of the intensity of the band are due to *overlap interaction*. These represent combination transitions involving both the internal degrees of freedom of the molecules and the lattice vibrations of the crystal and have characteristically very broad features with extended high-wave-number tails.

The next nonvanishing contribution to the induced moment is associated with *hexadecapolar interaction*. The hexadecapole-induced dipole is expected to give rise to the considerably weaker $U(J)$ transitions in accordance with the selection rule $\Delta J=4$. Recently a broad absorption feature corresponding to the $U(1)$ group of transitions was reported by Gibbs *et al.*[5] for the case of gaseous hydrogen at 195 K. In our present investigations of the fundamental band of the solid, the sharpness of the various features has made it possible to unambiguously identify the absorption associated with the $U_1(1)$ and $U_1(0)$ transitions. Our measurement of the intensity of the $U_1(0)$ absorption is of interest in view of the theoretical calculations of the matrix elements of the hexadecapole moment of H_2 by Karl *et al.*[6]

II. EXPERIMENTAL DETAILS

Transparent normal hydrogen and parahydrogen crystals suitable for observing the near-infrared absorption spectra were produced in a Pyrex glass absorption cell 3.6 cm long and 2.0 cm in diameter which was suspended over liquid helium in a glass cryostat. The cryostat which is schematically shown in Fig. 1 consists of two Pyrex Dewars, the inner one containing liquid helium and the outer one liquid nitrogen. The Dewars were provided with Pyrex windows near the bottom to allow the passage of radiation.

Nearly pure parahydrogen samples were produced by passing Matheson "ultrahigh-purity" normal hydrogen gas through a column of the paramagnetic catalyst APACHI-1 ($NiO.\ 2.5\ SiO_2$) (supplied by Houdry Process and Chemical Co., Philadelphia, Pa.) contained in the stem of the absorption cell (Fig. 1) and maintained at ~20 K by the cold helium vapor.

The temperature gradient necessary to grow the crystals was established in the vertical direction across the absorption cell which was maintained well above the surface of the liquid helium. When the crystals formed were not satisfactory, they were melted by passing an electrical current through a heating coil surrounding the absorption cell. It was found that in general parahydrogen crystals were clearer than the normal hydrogen ones.

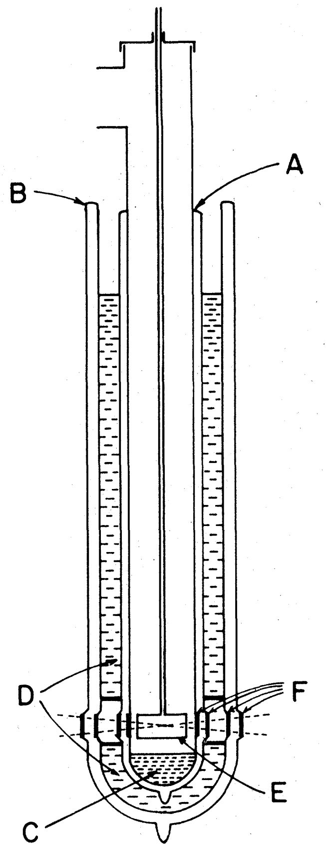

FIG. 1. Optical cryostat: *A*, liquid-helium Dewar; B, liquid-nitrogen Dewar; C, liquid helium; D, liquid nitrogen; E, Pyrex absorption cell; F, Pyrex windows fused to the walls of the cryostat.

Radiation from a General Electric FFJ quartz line projection lamp housed in a water-cooled brass jacket served as infrared continuum. The spectrometer used to record the absorption spectra consisted of a Perkin-Elmer model 99 monochromator equipped with a LiF prism and an uncooled PbS detector, a Dunn model LI-101 preamplifier and a Brower Laboratories model 101 lock-in voltmeter. The original 13-Hz chopper of the monochromator was replaced by a 260-Hz tuning fork chopper model L-40 supplied by American Time Products.

The wave-number region of the *U* transitions of the fundamental band of hydrogen is overlapped by atmospheric water vapor bands. In order to obtain accurate absorption spectra the atmospheric water vapor was removed from the entire optical path outside the cryostat by flushing with dry nitrogen gas during the experiments. Wave-number calibration of the spectral region was performed with the help of standard mercury emission lines and absorption peaks of atmospheric water vapor. The slit width maintained at 35 μm gave a spectral resolution of 6.6 cm^{-1} at 5500 cm^{-1}.

III. RESULTS

The spectra as shown in Fig. 2 cover the region 4900–6100 cm^{-1} and were recorded at a temperature of approximately 10 K. In this figure the results are presented as reproductions of the original strip-chart recordings in order to indicate as clearly as possible the actual conditions of observation. In particular we point out that, with the exception of the zero-offset spectrum of Fig. 2(a), the signal-to-noise ratio was limited only by the width of the recorder pen marking and is essentially as shown. In addition, the background spectra contain no absorption features which could interfere with the observations. All the sharp absorption features shown are superimposed upon the high-wave-number tail of the phonon branch associated with the $S_1(1)$ transition (at 4703 cm^{-1}). The wave numbers of the various absorption maxima measured in solid normal hydrogen and parahydrogen in the region 4800–5800 cm^{-1} are summarized in Table I. For comparison the wave numbers of the absorption maxima calculated from the observed Raman wave numbers of the $Q_1(0)$ and $Q_1(1)$ lines of solid normal H_2 and of the $Q_1(0)$ line of solid para-H_2 by Bhatnagar *et al.*[7] and the rotational constants determined for the low-pressure H_2 gas by Foltz *et al.*[8] are also given in the same table. This procedure is justified because the vibrational wave-number shifts from the low-pressure gaseous H_2 to its solid phase are larger [for the Raman $Q_1(0)$ and $S_1(0)$ lines these are 11.3 and 11.8 cm^{-1}, respectively] whereas the corresponding rotational wave-number shifts are small [for the Raman $S_0(0)$ line this shift is only 0.5 cm^{-1}].[7] It should be noted, however, that the difference between the measured and calculated wave numbers for any given transition in Table I does not represent the experimental error but represents to a greater extent the basic difference between the physical processes involved in induced absorption and scattering.

The grouping of the *U*-branch features is characteristic of the previous observations of the $S(0)$ and $S(1)$ groups.[9] In the case of normal (75% ortho) hydrogen the $U_1(1)$ line is readily identifiable and is accompanied at higher wave numbers by a double-peaked feature due to the associated $U_R(1)$ phonon branch and the $Q_1(1)+U_0(1)$ and $Q_1(0)+U_0(1)$ double transitions. It is to be noted here that, because the shift due to vibration-rotation interaction is approximately 80 cm^{-1}, the peak of the phonon branch is expected to occur on the *low*-wave-number side of the double-transition absorption [the

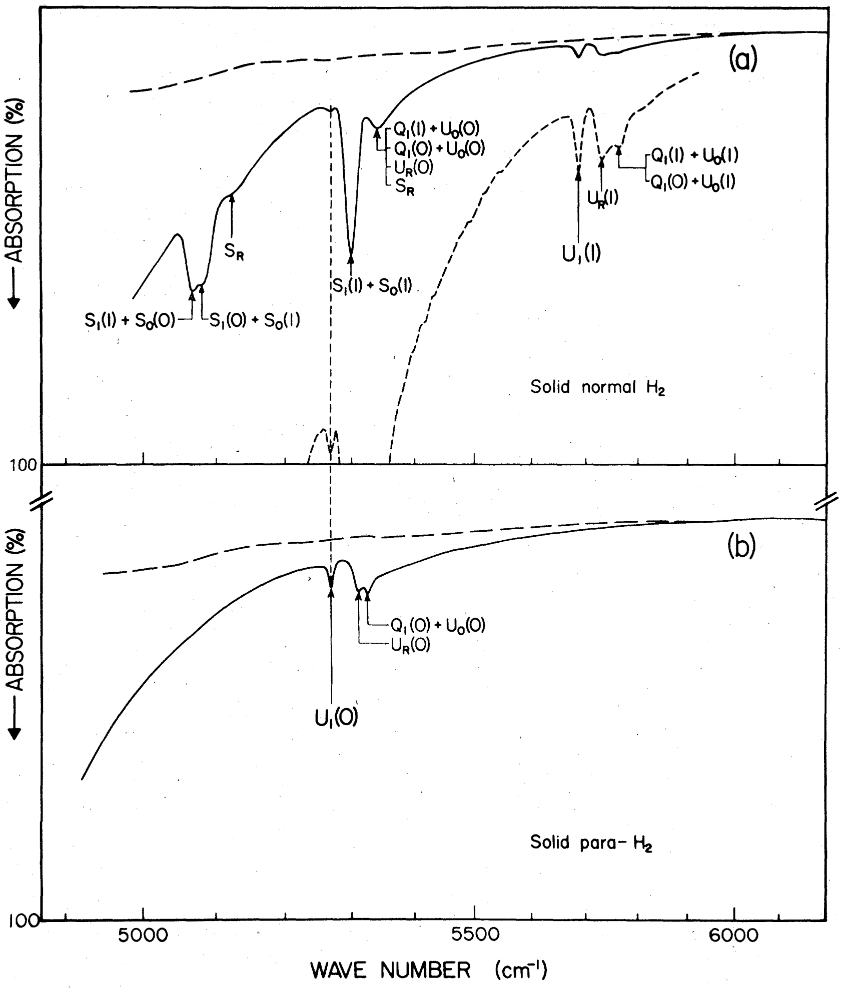

FIG. 2. Infrared fundamental band of solid hydrogen in the region 4900–6100 cm^{-1} with an absorption path length of 3.6 cm at ~10 K: (a) normal (75% ortho-) H_2 and (b) ~100% para-H_2. The curves are reproductions of actual strip-chart recordings. The upper dashed curves are the background traces obtained with the empty cell and represent zero-absorption. The solid curves are the absorption spectra of the samples. The lower dashed curve in (a) was taken with an offset of the zero-signal level to enhance the contrast.

reverse is the case for the $S_1(1)$ group, for example], and it is on this basis the assignments in Table I have been made. The observed U-branch spectrum of parahydrogen is very similar to that of normal hydrogen, and the $Q_1(0)+U_0(0)$ absorption is calculated to occur at about 60 cm^{-1} on the high-wave-number side of $U_1(0)$. On the basis of the previous theoretical work,[3] the U-branch double transitions should be associated with the creation of traveling rotational excitations (rotons). Since the widths of these roton energy bands are not known any assignments involving the U-branch double transitions must be treated as tentative at this point.

In this case of the parahydrogen spectrum no measurements of the orthohydrogen content were made, but it is apparent from Fig. 2(b) that the observations of the zero-phonon $U_1(0)$ line were not significantly affected by any orthohydrogen impurity. It is to be noted that of the two S-branch features shown in Fig. 2(a), the mixed (ortho-para) pair absorption corresponding to the $S_1(0)+S_0(1)$ and $S_1(1)+S_0(0)$ transitions is not detectable in Fig. 2(b). It can thus be argued that the ortho-ortho pair absorption due to $S_1(1)+S_0(1)$ transition must indeed be negligible in the parahydrogen spectrum, and therefore should have no effect upon the $U_1(0)$ feature which occurs in the same wave-number region.

The double rotational transitions of the types $S_1(J)+S_0(J)$, $J=0,1$, appear with more intensity in Fig. 2(a) than in the previous observations.[9] In the present spectra the phonon branches S_R accompanying these double transitions are also clearly identified.

A measurement of the integrated intensity of the $U_1(0)$ line was made by simply subtracting the contribution due to the underlying tail of the smoothly extended $S(1)$ phonon branch. The value obtained was 5×10^{-17} cm^3 s^{-1} which was calculated from the equation

$$\bar{\alpha}=\frac{c}{N_p l}\int \nu^{-1}\ln\left(\frac{I_0(\nu)}{I(\nu)}\right)d\nu ,$$

TABLE I. Wave numbers and assignments of the absorption maxima for the fundamental band of solid H_2 in the region 4800–5800 cm^{-1}.

	Measured wave number[a] (cm^{-1})	Assignments	Calculated wave number[b] (cm^{-1})
Normal H_2:			
	5066	$S_1(1)+S_0(0)$	5055
	5081	$S_1(0)+S_0(1)$	5076
	5124	S_R	...
	5266	$U_1(0)$	5262
	5298	$S_1(1)+S_0(1)$	5288
	5338	$Q_1(1)+U_0(0)$	5312
		$Q_1(0)+U_0(0)$	5321
		$U_R(0)$	...
		S_R	...
	5685	$U_1(1)$	5684
	5730	$U_R(1)$	...
	5764	$Q_1(1)+U_0(1)$	5765
		$Q_1(0)+U_0(1)$	5774
Para H_2:			
	4852	$S_1(0)+S_0(0)$	4841
	4894	S_R	...
	5266	$U_1(0)$	5260
	5310	$U_R(0)$	...
	5324	$Q_1(0)+U_0(0)$	5319

[a] Accuracy of measurement is $\sim\pm 2$ cm^{-1} for sharp maxima and less for broad ones.

[b] See text for details.

where c is the speed of light, N_p is the number of parahydrogen molecules per cm^3 (2.609×10^{22} cm^{-3}), l is the length of the absorption sample, ν is the wave number in cm^{-1}, $I_0(\nu)$ is the intensity of radiation incident on the sample, and $I(\nu)$ is the transmitted intensity. Because of the low intensity of $U_1(0)$ and also because it was undoubtedly not properly resolved by the prism spectrometer, we believe that the error involved in the quoted value of the integrated absorption coefficient will be $\sim\pm 20\%$. For para-H_2 at 2 K the absorption coefficient of the $S_1(0)$ determined experimentally by Gush[10] is $\tilde{\alpha}[S_1(0)] = 3.3\times 10^{-15}$ cm^3 s^{-1}. It will be interesting to obtain the ratio $\tilde{\alpha}[U_1(0)]/\tilde{\alpha}[S_1(0)]$ for solid para-H_2 which will give an idea of the relative magnitudes of the quadrupolar and hexadecapolar induction effects. As a matter of fact the intensity is proportional to the square of sum of the dipole moments induced by the quadrupolar or hexadecapolar field of the absorbing molecule in all the neighboring molecules. The ratio $\tilde{\alpha}[U_1(0)/\tilde{\alpha}[S_1(0)]^{10}$ is 1.5×10^{-2}. The theory for the integrated absorption of the zero-phonon U branches for solid H_2 has not yet been developed. When this is done one can compare the experimental result with theory by using the values of the matrix elements of the H_2 hexadecapole moment and polarizability calculated by Karl *et al.*[6] and Poll,[11] respectively. Further, a systematic study of the zero-phonon $U_1(J)$ branches of solid H_2 under higher resolution should reveal the structure of these branches. The results of such experiments, which are planned for the near future, will be presented in a subsequent paper.

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[1] In the conventional notation used here J refers to the ground-state rotational quantum number, which is 0 or 1 for solid H_2, and the subscripts refer to the change in the vibrational quantum number v.

[2] See, for example, S. A. Boggs, M. J. Clouter, and H. L. Welsh, Can. J. Phys. 50, 2063 (1972), and the references therein.

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