

Observation of the $\Delta J = 4$ Pure Rotational Transitions in Solid H_2 and the Inference of the Phonon Density of States

T. K. Balasubramanian,^(a) Chen-Hsin Lien, K. Narahari Rao, and J. R. Gaines
Department of Physics, Ohio State University, Columbus, Ohio 43210

(Received 20 July 1981)

A pure rotational U -type transition ($\Delta J = 4$) in solid parahydrogen has been recorded by using a high sensitivity infrared spectrometer. On the assumption of a rigid lattice, the measured intensity led to a value of 0.335 (in atomic units) for the hexadecapole moment of molecular hydrogen. Electric quadrupole-quadrupole interaction effects have been identified in the spectra. It appears possible to extract the phonon density of states in solid H_2 from the phonon branch $U_0^R(J)$.

PACS numbers: 33.20.Ea, 63.20.Dj, 67.80.Cx

We report here the first observation of pure rotational U transitions in solid hydrogen (p - H_2 and n - H_2) at 6 – 9 μm in the infrared. The symbol U signifies that $\Delta J = J' - J'' = 4$ where J' represents the rotational angular momentum of the molecule in the upper state and J'' its value in the lower state. Since H_2 has no permanent dipole moment, the spectrum is a "collision-induced spectrum" with the transitions studied here arising from the part of the dipole moment induced by the hexadecapolar interaction. Transitions with $\Delta J = 4$ were first observed in H_2 gas at high pressures¹ and later seen in the solid in the vibration-rotation spectra.² The possibility of observing a pure rotational $\Delta J = 4$ transition was indicated in recent experiments done in this laboratory³ on the vibration-rotation spectrum of H_2 solid employing modern high-sensitivity technology in the infrared.

In the present experiments, finding suitable windows had been a vexing problem. This is because they had to withstand the strains of liquid-helium temperatures on the top of mechanical stresses that develop when they are pressed against gasket material (indium in this case) to provide a vacuum seal. Sapphire windows used earlier do not transmit in the region 6 – 9 μm and were therefore unsuitable in the present study. Windows made out of silver chloride provided a satisfactory answer ultimately. A 26-mm-long sample of solid hydrogen contained between AgCl windows sealed to a brass cell was placed in the optical path of a Fourier transform spectrometer. Liquid helium flowing through a copper box thermally anchored to the brass cell brought about the required cooling. Calibrated diodes attached to the top and bottom of the cell were used to measure the temperature. The spectra reported here are appropriate to zero sample pressure and a temperature of 13 K.

The spectral line resulting from a transition from $J'' = 0$ to $J' = 4$ for a p - H_2 molecule in the ground electronic and vibrational state (with no change in vibrational quantum number) is shown in Fig. 1. Using the gas-phase ground-state constants for H_2 quoted by Herzberg and Huber,⁴ we calculate 1168.75 cm^{-1} for the wave number of $U_0(0)$, in good agreement with the observed wave number of 1167.10 cm^{-1} . Thus the identification of this line as $U_0(0)$ is made solely on the basis of its wave number. The line is relatively sharp with the full width at half maximum (FWHM)

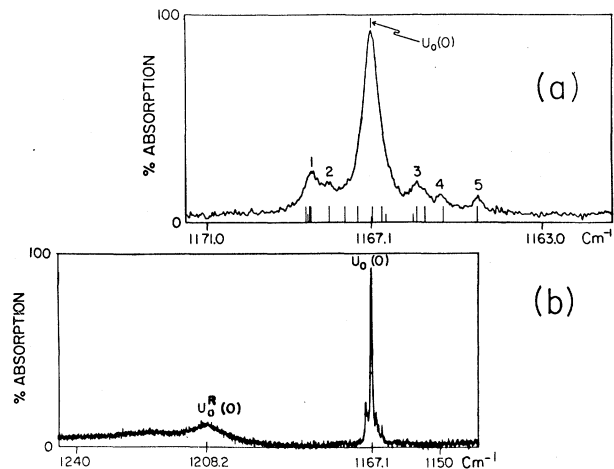


FIG. 1. $U_0(0)$ transition in solid parahydrogen at 13 K for a crystal of length 26 mm is plotted versus wave number. A Fourier-transform spectrometer having a spectral resolution of 0.04 cm^{-1} has been used to record the data. The satellite structure with serial numbers 1–5 observed, respectively, at 1168.49 , 1168.13 , 1165.98 , 1165.44 , and 1164.57 cm^{-1} was interpreted as due to orthoimpurity in the sample. The vertical lines drawn in this structure represent the calculated locations of these satellite lines. This figure shows a composite of the $U_0(0)$ transition and its associated phonon branch located at 1208.2 cm^{-1} .

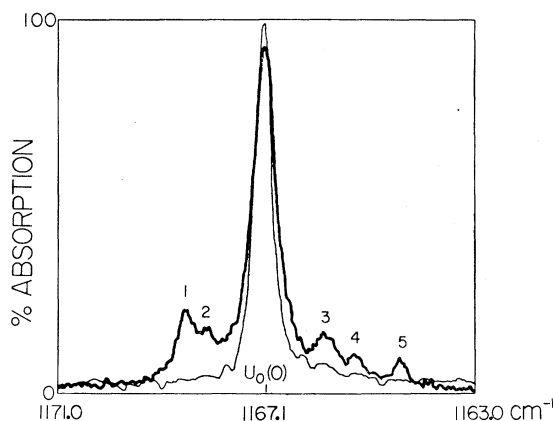


FIG. 2. The $U_0(0)$ line is shown for two ortho H_2 impurity concentrations. The line showing structure labeled 1, 2, 3, 4, and 5 has an $o-H_2$ concentration between 1 and 2%. The thin line is a spectrum made with $o-H_2$ concentration of 0.2%. The sample temperature was 13 K.

being 0.25 cm^{-1} as are the other zero-phonon single transitions $U_{1\rightarrow 0}(0)$,³ $S_{1\rightarrow 0}(0)$,⁵ and $S_0(0)$.⁶

A weak satellite structure surrounds the main peak in Fig. 1(a). This sample contained between 1% and 2% orthohydrogen ($o-H_2$) impurity. A subsequent experiment on a sample containing about 0.2% $o-H_2$ gave the spectrum shown in Fig. 2 confirming that the satellite structure was due to the $J=1$ $o-H_2$ impurity. This point will be discussed later.

One very interesting aspect of this spectrum is the weak, broad feature located at 1208.2 cm^{-1} in Fig. 1(b). By analogy with the phonon branches that accompany the zero phonon lines in the region of the vibration-rotation fundamental, we identify this feature as the phonon branch $U_0^R(0)$. The peak is shifted from the center of $U_0(0)$ by 41 cm^{-1} . A similar feature was observed when $n-H_2$ (75% $o-H_2$) was studied. The calculated position⁴ of $U_0(1)$ was 1621.59 cm^{-1} whereas the observed wave number was 1619.8 cm^{-1} . The peak of the

TABLE I. $\Delta J=4$ transitions in solid hydrogen. $\bar{\alpha}$ is the integrated absorption coefficient.

Species	Spectral location (cm^{-1} vac.)		Assign- ment	$10^6 \bar{\alpha}$ (cm^3/sec)
	Obs.	Calc.		
$p-H_2$	1167.10	1168.75	$U_0(0)$	5.1
	1208.2		$U_0^R(0)$	
$n-H_2$	1619.8	1621.59	$U_0(1)$	2.7
	1663		$U_0^R(1)$	

corresponding phonon branch $U_0^R(1)$ was observed at 1663 cm^{-1} about 43 cm^{-1} to the large wave number side of $U_0(1)$. Tables I and II summarize all the experimental data related to the $\Delta J=4$ transitions in solid hydrogen.

The integrated absorption coefficient is defined by the relation

$$\bar{\alpha} = \frac{c}{Nl} \int \frac{1}{\nu} \ln \left(\frac{I_0}{I} \right) d\nu, \quad (1)$$

where c is the speed of light, N is the number of hydrogen molecules per cm^3 , l is the length of the crystal, ν is the wave number of the line (in cm^{-1}), and I is the intensity. Assuming a rigid hcp crystal structure for solid parahydrogen, it can be shown that⁷

$$\bar{\alpha} = \frac{175 \pi^3 Q_4^2 p^2 S^2}{48 h R^{12}}. \quad (2)$$

In Eq. (2), Q_4 is the appropriate rovibrational matrix element $\langle \nu=0, J=0 | Q_4(\text{op}) | \nu', J'=4 \rangle$ of the hexadecapole moment operator, p is the isotropic polarizability, h is the Planck's constant, and R is the nearest-neighbor distance; S is a lattice sum which has been calculated by us to be 5.1105 for an hcp lattice. With the experimental value for $\bar{\alpha}[U_0(0)]$ a value of $Q_4 = 0.335 \pm 0.008$ in atomic units results from expression (2). This compares well with the theoretical value of $Q_4 = 0.3482$ (in atomic units) given by Karl, Poll, and Wolniewicz⁸ for an isolated molecule.

An expression similar to (2) was derived earlier by Poll and Tipping.⁹ It incorporates a "reduction factor" ξ ($=0.8$) as a means of allowing for the nonrigidity of the real lattice, but leads to intensities that are smaller by almost the factor 0.6 both for the $U_0(0)$ studied presently and the $U_{1\rightarrow 0}(0)$ studied earlier in our laboratory.³ In Table II the theoretical and experimental in-

TABLE II. Comparison of theoretical and experimental intensities of $\Delta J=4$ transitions in solid hydrogen.

Transition	Experimental $\bar{\alpha} \times 10^{17} \text{ cm}^{-3} \text{ sec}$	Theoretical $\bar{\alpha} \times 10^{17} \text{ cm}^{-3} \text{ sec}$	
		Eq. (2)	Ref. 9
$U_{1\rightarrow 0}(0)$	6.6 ± 0.6^a	6.8	3.9
$U_0(0)$	51 ± 2.5^b	55	32

^aRef. 3.

^bSee Table I.

tensities are compared. It is important to note that the presently measured $\bar{\alpha}[U_0(0)]$ and the $\bar{\alpha}[U_{1-o}(0)]$ measured previously³ are internally consistent. This was shown by forming the ratio $\bar{\alpha}[U_{1-o}(0)]/\bar{\alpha}[U_0(0)]$. From the experimental $\bar{\alpha}$ values this ratio is 0.129 ± 0.019 . Theoretically this ratio should equal $[\langle 00|Q_4|14\rangle/\langle 00|Q_4|04\rangle]^2 = 0.123$, from the matrix elements given in Ref. 8.

Quantitative evaluations of the satellite structure seen in Fig. 1(a) (with lines labeled 1 through 5) were made by assuming the dominant cause to be the electric quadrupole-quadrupole (EQQ) interaction between a para H_2 molecule in the excited $J=4$ level and a near neighbor ortho H_2 in the state $J=1$. The EQQ interaction partially lifts the 27-fold degeneracy and solution of the secular equation leads to a total of fifteen energy levels of which twelve are still doubly degenerate. These levels are indicated in Fig. 1(a) by the vertical lines, a value of $\Gamma = 0.559 \text{ cm}^{-1}$ having been used to obtain the maximum splitting (separation of lines 1 and 5) of the spectrum.¹⁰ The width of the line $U_0(1)$ observed in $n\text{-}H_2$ is also attributed to this same EQQ interaction; however, at this much higher $J=1$ concentration one has so many $o\text{-}H_2$ neighbors that the mean square value of this EQQ energy is more meaningful.¹¹

The phonon branch of the spectrum actually involves a product of a transition matrix element with the phonon density of states. To the extent that the matrix element is independent of frequency, the spectrum $U_0^R(0)$ is simply proportional to the phonon density of states. The data of Fig. 1(b), smoothed to remove the high-frequency noise, are plotted in Fig. 3 along with a phonon spectrum actually measured using neutron-diffraction techniques¹² on an hcp crystal. The similarity of the gross features such as location of the peak and general shape make this a very promising alternative technique for extracting the phonon spectrum in all of the solid hydrogens. Measurement of the phonon spectrum was not the primary objective of this initial study. The present data were accumulated as a result of 1000 scans covering 4 h so that with suitable modifications to the apparatus it would be possible to significantly improve the signal to noise ratio of $U_0^R(0)$ making a much more precise determination of the phonon spectrum possible. In summary, the important features of this work are the following:

(1) The $\Delta J=4$ transitions in the pure rotational spectrum of solid H_2 have been observed for the first time. Both the $p\text{-}H_2$ ($J=0$) and $o\text{-}H_2$ ($J=1$)

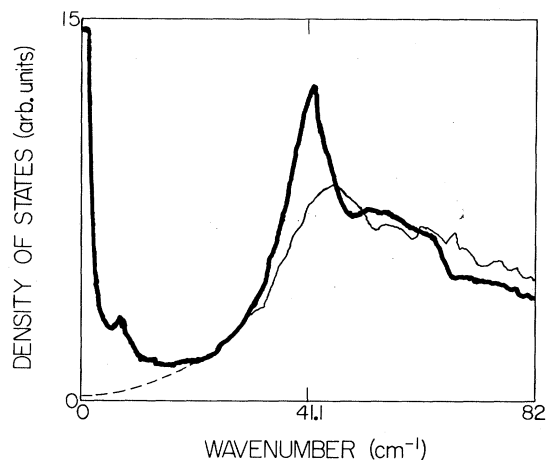


FIG. 3. An expanded view of the branch $U_0^R(0)$, with the high-frequency noise smoothed, is plotted against wave number. The thin curve gives the phonon density of states obtained by neutron diffraction from Ref. 12, the dotted line indicates an extrapolation to zero wave number. No such extrapolation was made on the data here. The increase in the observed data near the zero is due to the $U_0(0)$ absorption.

ground states have been used as the initial state resulting in the lines $U_0(0)$ and $U_0(1)$.

(2) The presence of other $J=1$ molecules in the solid contributes significantly to the width of the $U_0(J)$ transition. In $p\text{-}H_2$, the line is narrow whereas in $n\text{-}H_2$ the line is broad.

(3) The observed line positions in this research are displaced to lower wave number from the calculated positions by 1.65 and 1.8 cm^{-1} . For the $S_0(0)$ line, the observed line is 1.5 cm^{-1} above the calculated position.

(4) The integrated absorption coefficient yields an experimental value for the molecular hexadecapole moment of 0.335 atomic units, in good agreement with the theoretical value. A reduction factor smaller than 0.95 would be inconsistent with these data and the theoretical value.

(5) The spectral region near 1167 cm^{-1} in H_2 is very clean permitting observation of the weak U transitions. The peak of the phonon branch is roughly 41 cm^{-1} away from the zero-phonon line. This may possibly be an extremely useful method of obtaining the phonon spectrum in solid hydrogen which is very difficult to extract by any other means.

The authors would like to thank Dr. P. C. Souers of Lawrence Livermore National Laboratory for his useful comments on the manuscript. The partial support of the National Sci-

ence Foundation Grant No. DMR-81-06166 is gratefully acknowledged.

^(a)Permanent address: Spectroscopy Division, Bhabha Atomic Research Center, Modular Laboratories, Trombay, Bombay 400085, India.

¹P. W. Gibbs, C. G. Gray, J. L. Hunt, S. P. Reddy, R. H. Tipping, and K. S. Chang, *Phys. Rev. Lett.* **33**, 256 (1974).

²R. D. G. Prasad, M. J. Clouter, and S. P. Reddy, *Phys. Rev. A* **17**, 1690 (1978).

³W. Ivancic, T. K. Balasubramanian, J. R. Gaines, and K. Narahari Rao, *J. Chem. Phys.* **74**, 1508 (1981); T. K. Balasubramanian, Chen-Hsin Lien, J. R. Gaines, K. Narahari Rao, E. K. Damon, and R. J. Nordstrom, to be published.

⁴K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

⁵H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **38**, 176 (1960).

⁶M. Treffler, A. M. Cappel, and H. P. Gush, *Can.*

J. Phys. **47**, 2115 (1969).

⁷Chen-Hsin Lien, unpublished.

⁸G. Karl, J. D. Poll, and L. Wolniewicz, *Can. J. Phys.* **53**, 1781 (1975).

⁹J. D. Poll and R. H. Tipping, *Can. J. Phys.* **56**, 1165 (1978).

¹⁰If Γ is the EQQ coupling constant for the pair ($v = 0, J = 4$) and ($v = 0, J = 1$) and Γ' is the coupling constant for a pair in the $J = 1$ state, then the ratio of Γ to Γ' is equal to the ratio of the state average of the quadrupole moment over the appropriate initial and final states. Extrapolating the matrix elements of G. Karl and J. D. Poll [*J. Chem. Phys.* **46**, 2944 (1967)] to the $v = 0, J = 4$ state and using $\Gamma' = 0.54 \text{ cm}^{-1}$ given by S. A. Boggs and H. L. Welsh [*Can. J. Phys.* **51**, 1910 (1971)], we obtain $\Gamma = 0.55 \text{ cm}^{-1}$ in close agreement with the value of 0.559 cm^{-1} used in this analysis.

¹¹If we use $9E_{\text{QQ}}^2$ as an estimate of the second moment, assume a Gaussian lineshape, and compute E_{QQ}^2 for a pair of molecules in the $J = 1$ and $J = 5$ states, we obtain a FWHM of 9.6 cm^{-1} . The observed FWHM is 8.3 cm^{-1} .

¹²H. Stein, H. Stiller, and R. Stockmeyer, *J. Chem. Phys.* **57**, 1726 (1972).

Developments in the $\text{H}^+ - \text{H}^-$ Problem

V. Sidis^(a) and C. Kubach

Laboratoire des Collisions Atomiques et Moléculaires, Université Paris-Sud, F-91405 Orsay, France

and

D. Fussen

Université Catholique de Louvain, Institut de Physique Corpusculaire, B-1348 Louvain La Neuve, Belgium

(Received 4 May 1981)

A one-electron treatment of the $\text{H}^+ - \text{H}^-$ collision is proposed which is not restricted to neutralization into $\text{H}(n=2) + \text{H}$, is free from two-state-crossing models, and involves an electron translation factor. Diabatic states are found to differ from those conventionally invoked. Neutralization into $\text{H}(n=3) + \text{H}$ is put forward and detachment is interpreted as a dynamic polarization effect. Agreement with available experiments is found above 200 eV (c.m.). Below this energy puzzling discrepancies persist.

PACS numbers: 34.70.+e

The conventional treatment of the $\text{H}^+ + \text{H}^-$ mutual neutralization into $\text{H}^*(n) + \text{H}$ assumes transitions around crossings of the *Coulombic* ionic energy curve with *horizontal* covalent curves. Following Bates and Lewis¹ it has been agreed by some authors² that, according to the Landau-Zener (LZ) model,³ mutual neutralization at low energy ($E_{\text{c.m.}} < 20 \text{ eV}$) occurs predominantly into $\text{H}^*(n=3) + \text{H}$, whereas at moderate energies ($50 \text{ eV} \lesssim E_{\text{c.m.}} \lesssim$ a few kiloelectronvolts) *neutralization into $\text{H}^*(n=2) + \text{H}$ prevails*. Most of the theoretic-

cal efforts to date have been devoted to the improvement of either the LZ curve-crossing parameters⁴ or the LZ model itself.⁵ Agreement with experiments was found accidentally when either incorrect LZ parameters or *ad hoc* adjustments were used.⁶ Dalgarno, Victor, and Blanchard⁷ were the first to abandon the simplistic LZ point of view and considered the $\text{H}^*(n=2 \text{ and } 3) + \text{H}$ channels within an *ab initio* close-coupling treatment. Unfortunately their calculations suffered from an inaccurate H^- binding energy