Observation of Fourth Vibrational Overtone of Hydrogen

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We report the first observation of the fourth vibrational overtone ($\Delta v = 5$) transition of molecular hydrogen in solid parahydrogen at 19 062 cm^{-1}. We also report the first measurements of an almost complete set of the third vibrational overtone ($\Delta v = 4$) transitions.

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Spectroscopic observations of solar radiation reflected from planetary surfaces have traditionally provided important information about the constituents and conditions of the atmospheres of these planets. These data have been used for obtaining information about the column density of hydrogen in the atmospheres of Uranus and Neptune.[1,2] The interpretations crucially depend upon having laboratory data on the line positions and strengths of vibrational overtones of hydrogen. These overtones are forbidden in electric dipole approximation and are weakly allowed in quadrupole approximation. Recently, laboratory observation of the $S_4(1)$ quadrupole transition has been reported by Brault and Smith.[3] Quadrupolar interaction between hydrogen molecules during collisions induces dipole moments which make possible infrared absorption on the vibrational overtones. The earliest explanation of the observed spectra of Uranus involved their assignment to the first overtone of hydrogen and relied heavily on laboratory data.[2] Laboratory data on high-pressure hydrogen gas for the second overtone are available.[4] Similar data on higher overtones are not available because of their extreme weakness. At the same time the higher overtones are important because these fall in the optical region where the Earth's atmosphere is relatively free of water-vapor absorption lines and is therefore transparent. Further, the long absorption paths encountered on the giant planets often lead to the complication of line saturation for the lower overtones. The higher overtones, because of their weakness, could have an inherent advantage due to the ease of interpretation of the observed data.

In this Letter we report the first observation of a vibrational-rotational transition belonging to the fourth overtone ($\Delta v = 5$) of hydrogen at ~ 524.6 nm. Further, we report measurements of an (almost) complete set of third overtone transitions of parahydrogen. These include data on the $S_4(0)$ transition which was, at one time, thought to have been observed[5] in the spectrum of Uranus. Subsequent interpretations have ruled out this identification.[6,7] From our recent observations of a set of second overtone transitions[8] and two transitions of the third overtone[9] of molecular hydrogen in solid hydrogen we have indicated that there is a one-to-one correlation between observed line strengths in the gas phase and the solid phase. The line positions for isolated hydrogen molecules derived from our data should be of significant help in delineating ranges in the 530 and 580–650 nm regions where planetary spectroscopic observations of the fourth and the third overtones of hydrogen can be fruitfully carried out.

Our earlier studies of overtone absorption in hydrogen were carried out by means of pulsed optoacoustic spectroscopy.[10] The present studies of the fourth overtone (and third overtone) were carried out with a Fourier-transform spectrometer (FTS). The solid-hydrogen cell was similar to the one described in Ref. 8, and had a path length of 50 mm. Normal hydrogen was converted to parahydrogen by use of APACHI catalyst[11] at ~ 18 K.

Figure 1 shows absorption data of solid hydrogen at ~ 11 K in the 18 950 to 19 150 cm^{-1} region (~ 530 nm). The data represent coaddition of 24 000 scans of the FTS taken with a spectral resolution of 2 cm^{-1}. A well-defined absorption peak at 19 061.9 cm^{-1} stands out, and is identified as arising from the $S_5(0)+S_0(0)$ transition of molecular hydrogen in solid parahydrogen. The observed linewidth of the transition is 2.5 ± 0.4 cm^{-1}. A deconvolution of the observed linewidth with the instrumental width of 2 cm^{-1} yields

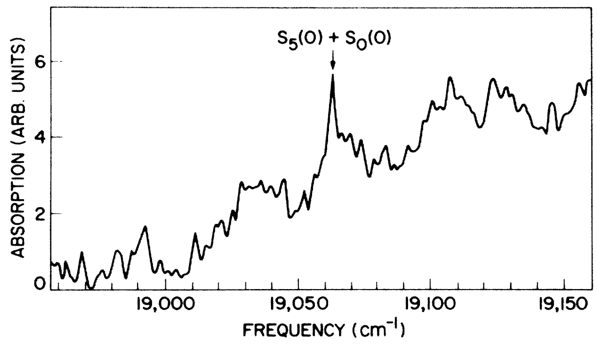

FIG. 1. Solid-parahydrogen absorption data in the fourth overtone ($\Delta v = 5$) region.

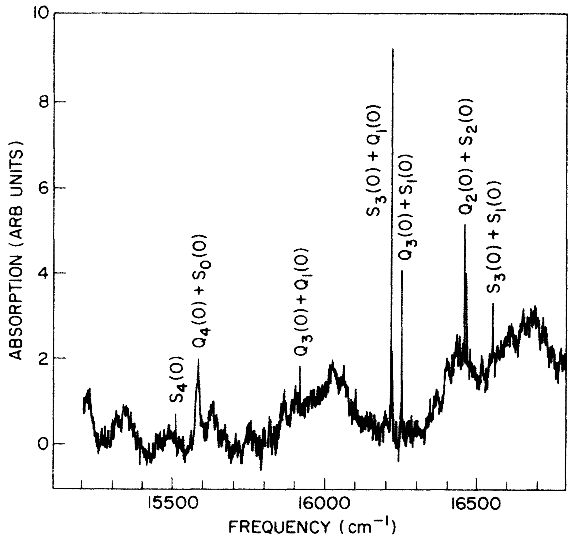

FIG. 2. Solid-parahydrogen absorption data in the third overtone ($\Delta v = 4$) region.

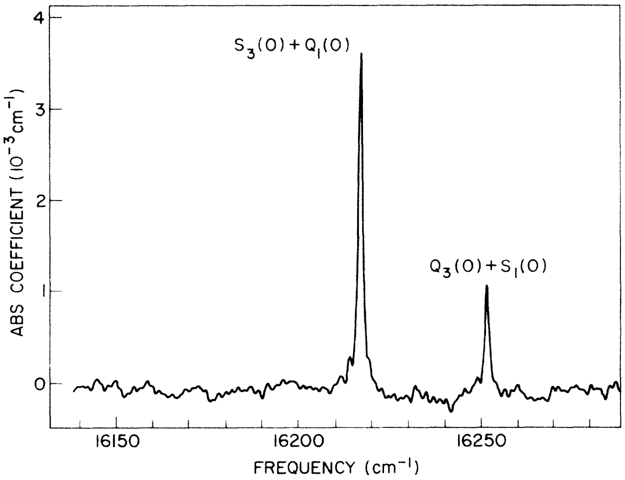

FIG. 3. Selected region from Fig. 2 expanded to show two of the $\Delta v = 4$ transitions in detail.

an intrinsic linewidth of 1.4 ±0.6 cm^{-1}, which is consistent with linewidths of transitions belonging to lower vibrational overtones of H_2 in solid parahydrogen. The observed absorption coefficient is $(2.5 \pm 0.5) \times 10^{-4}$ cm^{-1}. This will be discussed later. The identification of the observed line at 19061.9 cm^{-1} with the $S_5(0)+S_0(0)$ transition of the H_2 molecule requires us to ascribe the discrepancy between the gas-phase value[12] of 19124 cm^{-1} and our observed value to solid-state effects associated with the embedding of molecular hydrogen in the solid-hydrogen lattice.

Figure 2 shows a typical absorption spectrum of solid parahydrogen at 12 K in the region from 15100 to 16800 cm^{-1}. Figure 3 shows an expanded region in the vicinity of 16150–16300 cm^{-1}. The nominal resolution of the FTS was 1.0 cm^{-1} and 4000 scans have been coadded to produce the results. In addition to the transitions at 16217 cm^{-1} and the doublet at 16424 cm^{-1}, which were reported earlier,[9] we see all but four of the possible single and double transitions in parahydrogen. [Single transitions involve absorption of one photon leading to the excitation of a single hydrogen molecule through a change in its vibrational

TABLE I. Fourth and third overtone transitions of parahydrogen.

Transition	Calculated frequency (cm^{-1})	Observed frequency (cm^{-1})	Difference (cm^{-1})	Linewidth (cm^{-1})	Absorption coefficient (cm^{-1})
		Fourth overtone			
$S_5(0)+S_0(0)$	19124	19062	62	1.4 ±0.6	2.5×10^{-4}
		Third overtone			
$Q_4(0)$	15252	No			
$S_4(0)$	15537.4	15509.2	28.2	1.3	2×10^{-4}
$Q_4(0)+S_0(0)$	15606.5	15582.6	23.9	18 ±3	4×10^{-4}
		15578.0	28.5		
$S_4(0)+S_0(0)$	15892	No			
$Q_3(0)+Q_1(0)$	15943.6	15915.8	27.8	2.5 ±1	2×10^{-4}
$Q_2(0)+Q_2(0)$	16174	No			
$S_3(0)+Q_1(0)$	16246	16216.4	29.6	1.4 ±0.03	3.6×10^{-3}
$Q_3(0)+S_1(0)$	16280.2	16249.6	30.6	1.6 ±0.03	1.2×10^{-3}
$Q_2(0)+S_2(0)$	16493.4	16458.5	34.9	1.3 ±0.03	8×10^{-4}
		16464.7	28.7	1.6 ±0.03	6×10^{-4}
$S_3(0)+S_1(0)$	16582.4	16551.6	30.8	4 ±2.9	2×10^{-4}
$S_2(0)+S_2(0)$	16812.6	No			

quantum number $\Delta v = n$. Double transitions involve the absorption of a single photon resulting in simultaneous excitation of two hydrogen molecules to $H_2(v_1)$ and $H_2(v_2)$ such that $v_1 + v_2 = n$.] Table I lists the observed transitions for the $\Delta v = 5$ and $\Delta v = 4$ overtone bands, their vacuum wave numbers, identifications, and the corresponding free-hydrogen-molecule values derived from the work of Foltz *et al.*[12] Several features need to be examined and these are given below.

First, the observed solid-hydrogen absorption features occur at frequencies signficantly lower than the calculated free-hydrogen values. The set of such differences obtained for the $\Delta v = 5$ and for $\Delta v = 4$ transitions follow the trend observed in our earlier studies, i.e., the measured differences increase progressively with Δv irrespective of whether we are considering a single or a double transition. The value of the difference for the $\Delta v = 5$ transition is 62 cm^{-1}. For $\Delta v = 4$ transitions, the average value of the differences is 30 cm^{-1}. Figure 4 shows the average values of differences for $\Delta v = 1$ (taken from Ref. 13), $\Delta v = 2$ (taken from Ref. 8), $\Delta v = 3$ (taken from Ref. 8 and this work), and $\Delta v = 4$ and 5 as reported in this work. While calculations exist for the first vibrational overtone of hydrogen,[14] no similar data exist for the higher overtones. The trend of increasing differences between solid-hydrogen and isolated-hydrogen transition values is quite clear and should provide the theorists with incentive to extend the calculations to higher overtones.

Table I also shows the measured absorption coefficients for the observed $\Delta v = 4$ and 5 transitions. As with the lower overtones, the single transitions are significantly weaker than the double transitions. For example the $S_4(0)$ transition observed at 15 509.2 cm^{-1} in solid parahydrogen has a measured absorption coefficient of 2.0×10^{-4} cm^{-1}, while the strongest of the double transitions is seen to have an absorption coefficient of 3.6×10^{-3} cm^{-1}. This observation is consistent with our observations for lower overtones.

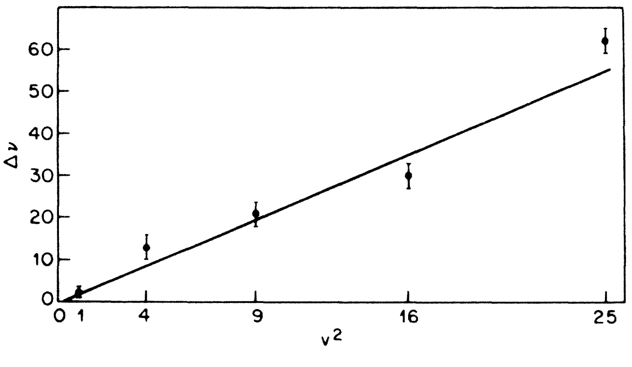

FIG. 4. Differences between the measured line positions and those calculated for a free hydrogen molecule as a function of the square of the vibrational quantum number.

The observed linewidths range from ~1 to 20 cm^{-1}, depending upon the complexity of the transitions. The $S_4(0)$ transition which has no degeneracy is expected to exhibit the narrowest linewidth, while the $Q_4(0) + S_0(0)$ at 15 578 cm^{-1} shows an effective linewidth of ~18 cm^{-1}. Such broad line shapes have been observed in $\Delta v = 1$, 2, and 3 overtones when one of the double transitions is $S_0(0)$ (Refs. 8 and 15). The structure and the width are likely to be determined by density-of-states factors of the particular double transition but no calculations exist.[15]

In conclusion, we have reported first observations of a number of vibrational overtone transitions of molecular hydrogen for $\Delta v = 4$ and 5. These data should be of significant interest for an increased understanding of the simplest of the molecular solids, and for identifying wavelength regions in the visible for spectroscopic observations of molecular hydrogen absorption in the atmospheres of the giant planets.

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