Observation of $\Delta\nu = 4$ Vibrational Overtone Transitions in Solid hcp Parahydrogen

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The first observations of the third vibrational overtone of molecular hydrogen are reported. This overtone, long sought in high-pressure gaseous hydrogen studies, is important in the interpretation of some of the observed features in the spectra of outer giant planets. The observations carried out in hcp solid parahydrogen should provide the much needed incentive for increased theoretical understanding of the simplest of the molecular solids.

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Overtone absorption in hydrogen has played a very important role in the determination of H_2 in the atmospheres of the outer giant planets as observed by optical astronomy with ground-based optical telescopes.[1] Collision-induced optical absorption at the fundamental and the lower overtones of the vibrational bands of H_2 have been observed in laboratory studies.[2] While their comparison with the planetary optical spectral data provides quantitative information regarding the density of absorbing species in the atmospheres of the planets, there is a perceived need to be able to carry out similar analyses for the higher overtones. There is a reported observation[3] of an absorption feature at 642 nm in the spectra of Uranus and Neptune. This feature has been variously assigned[3,4] to H_2 and CH_4, and an unambiguous identification is difficult since the pressure-induced laboratory spectra of the third-overtone absorption in H_2 do not exist at the present time in spite of the extensive studies of gaseous molecular H_2 at densities as high as 37 amagats and with optical path lengths as long as 137 m at low temperatures.[2] In this Letter we report the first observations of the $\Delta\nu = 4$ vibrational-rotational transitions of molecular H_2 in hcp solid p-H_2 at $T \approx 10$ K. These first laboratory observations of the third overtone will provide much needed data for quantitative theoretical analyses of the overtone spectra of molecular solids and for the interpretations of visible-region planetary absorption spectra.

Solid H_2 is prototypical and the simplest of the molecular solids in which the H_2 molecules are subjected to the same type of intermolecular forces as found in high-pressure gaseous H_2 because of the large zero-point motion arising from the light mass of H_2 molecules. Additionally, the rotational degree of freedom is preserved in solid hcp H_2, and the rotational angular momentum is a good quantum number.[5] The narrowing of the vibrational overtone spectra in solid H_2 as opposed to the broad high-pressure gaseous H_2 spectra makes solid H_2 an ideal system for quantitative elucidation of the intermolecular forces. Low-pressure studies of gaseous H_2 have led to observation of the $\Delta\nu = 4$ quadrupole transition[6]—the $S_4(1)$ quadrupole transition. However, the collisions between H_2 molecules have been shown to be very important in inducing the forbidden vibrational transitions in H_2. The quadrupolar and the overlap interactions are shown to induce dipole moments, *albeit* weak ones, in the colliding molecules which allows one to observe the $\Delta\nu = 1$, 2, and 3 molecular transitions in high-pressure gaseous H_2 as well as in solid H_2. The small size of the induced dipole moment makes the observation of the optical absorption arising from the higher harmonics difficult in the high-pressure H_2 case, and it was felt that either higher pressures or longer optical path lengths would be necessary for the study of $\Delta\nu = 4$ transitions.[2] In dealing with solid hcp H_2, the luxury of using long optical path lengths does not exist, and hence, until recently, only the $\Delta\nu = 1$ and 2 molecular transitions were observed in solid H_2. Recently, we reported the first observation[7] of $\Delta\nu = 3$ transitions in hcp solid H_2 using a technique which is suitable for measurements of weak absorptions in condensed-phase materials over a wide range of temperatures and wavelengths.[8]

The measurements were carried out with the pulsed-laser piezoelectric-transducer (PULPIT) optoacoustic (OA) spectroscopy described earlier.[9] This technique consists of excitation of the sample with pulsed optical radiation and subsequent measurement of the acoustic pulses generated by nonradiative relaxation. Pulsed tunable laser radiation in the 560 to 630 nm region was obtained from a dye laser (Rh590 and

Rh610 dyes) pumped with a frequency doubled Nd-doped—yttrium-aluminum-garnet laser. Peak pulse energies as high as 90 mJ could be obtained (in pulse width $\tau_p \approx 7$ nsec) over the above-mentioned tuning range. However, typically pulse energies of only 1 mJ were used for the OA absorption measurements. The OA cell used for the present studies has been described by us briefly[7] and is unchanged. The optical path length was 8 mm. Details will be described in a forthcoming publication. Parahydrogen was prepared by liquefying ultrahigh-purity H_2 in a flow-through cell containing a paramagnetic catalyst.[10] The cell was cooled to temperatures below 20 K in another cryostat, and the transfer of catalyzed p-H_2 to the OA cell located within a Janis Varitemp Dewar was accomplished quickly to prevent conversion of p-H_2 to normal H_2. Parahydrogen was solidified in the OA cell by gently lowering its temperature to below 14 K. In the Varitemp Dewar the samples are cooled by effusing cold helium gas from the bottom, and thus the necessary temperature gradient to grow good hcp crystals of p-H_2 was naturally established in a vertical direction. Temperature stability of better than 0.1 K was routinely achieved by using an appropriate servo loop. Tunable dye-laser radiation traversed the OA cell and was measured to obtain a normalized OA signal[9] from the piezoelectric transducer in the cell. As seen from Eq. (1) of Ref. 7, the absorption coefficients α for the $\Delta v = 4$ transitions can be deduced from the measured normalized OA signal by scaling from the known absorption coefficients and the corresponding measured OA signals for the $\Delta v = 2$ and 3 transitions.[11]

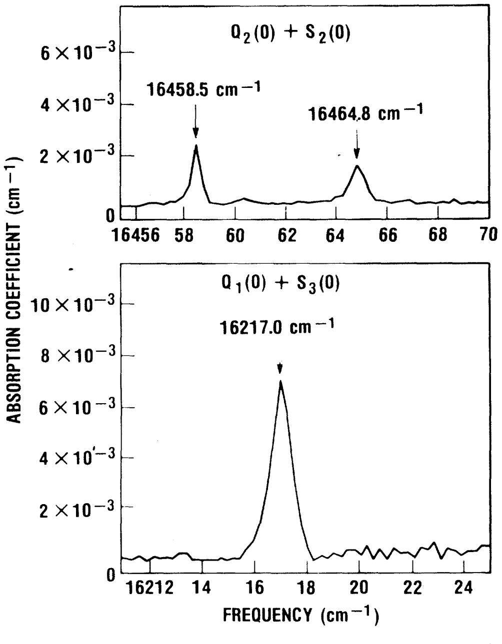

FIG. 1. Normalized optoacoustic spectra for $Q_1(0) + S_3(0)$ and $Q_2(0) + S_2(0)$ transitions.

Figure 1 shows the normalized OA spectra in the 16 200- and the 16 450-cm^{-1} regions. In the 16 200-cm^{-1} region the absorption feature at 16 217 cm^{-1} is identified as arising from the $Q_1(0)+S_3(0)$ transition. The free-molecule transition frequency calculated with the constants given by Foltz, Rank, and Wiggins[12] is 16 246 cm^{-1}, which is 29 cm^{-1} higher. The feature in the the 16 450-cm^{-1} region shows a multiplet structure which we assign to $Q_2(0)+S_2(0)$. The center of gravity of this multiplet is 16 461 cm^{-1}. The calculated free-molecule value[12] is 16 495-cm^{-1}, which is ~34 cm^{-1} higher than the observed value. These transitions are summarized in Table I together with their absolute absorption coefficients as determined by the scaling procedure as described earlier. Table I in addition lists the measured linewidths. These values are less than 1 cm^{-1} and are consistent with the linewidth of similar transitions measured for p-H_2 for the $\Delta v = 2$ and 3 bands.[11] The laser linewdith in all of these studies was ~0.2 cm^{-1} and hence the observed linewidth was determined by the computer-controlled step of the dye laser which was ~0.27 cm^{-1}. Thus the observed linewidths are real and less than the linewidths of ~1.0 cm^{-1} observed for hcp p-H_2 for the fundamental band by Allin *et al.*[13] but consistent with the results of Ivancic *et al.*[14] With the assumption that the observed linewidths are determined by nonradiative relaxation lifetimes (radiative relaxation being very slow), we estimate a lifetime of ~50–80 psec which would satisfy the conditions for OA detection as discussed earlier.[9] Notice that measurements of the $\Delta v = 3$ molecular transitions in solid normal

TABLE I. Observed frequencies, linewidths, and absorption coefficients of the third overtone of H_2.

Transition	Energy (cm^{-1})	Full width at half maximum (cm^{-1})	Abs. Coeff. (cm^{-1})
$Q_1(0)+S_3(0)$	16 217	0.74	$7.2\times10^{-3}\pm30\%$
$Q_2(0)+S_2(0)$	16 458.5	0.38	$2.4\times10^{-3}\pm30\%$
	16 464.8	0.64	$1.6\times10^{-3}\pm30\%$

H_2 (Ref. 7) (i.e., normal mixture of o-H_2 and p-H_2) yielded linewidths of the order of 8–10 cm^{-1} because of the anisotropic interactions from the o-H_2 molecules which lead to a significant inhomogeneous broadening of the vibrational overtones even when the excitation involves only p-H_2 molecules.

For the solid hcp H_2 data to be useful in the interpretation of observed planetary spectra arising from collision-induced dipole transitions, the important parameter is the line strength in absolute units. From a comparison of the measured optical absorption coefficient for $\Delta\nu = 2$ and 3 transitions with the normalized PULPIT optoacoustic signal [see Eq. (1) of Ref. 7] we deduce the absorption coefficient for the $\Delta\nu = 4$ transitions reported here. Figure 2 shows a plot of strongest absorption line α for $\Delta\nu = 2$, 3, and 4 molecular transitions in solid hcp p-H_2. From the absolute $\Delta\nu = 4$ line strength in the solid phase, it is possible, by knowing the density and intermolecular distance, to derive the line strength and band shape in the gas phase at specific temperatures. For a comparison we show in Fig. 2 the calculated[2] integrated absorption strengths of pressure-induced vibrational overtones (normalized to $\Delta\nu = 2$ value). The good correlation leads one to conclude that our measured values of $\Delta\nu = 4$ line strengths in solid hcp p-H_2 can be used for conversion of observed pressure-induced H_2 dipole lines in planetary spectra to a column density. Because of the extreme weakness, these absorption features, when unambiguously identified as arising from collision-induced H_2 dipole transitions, can be considered to be optically thin with no saturation problem and hence could yield good values for the H_2 column density on the outer giant planets.

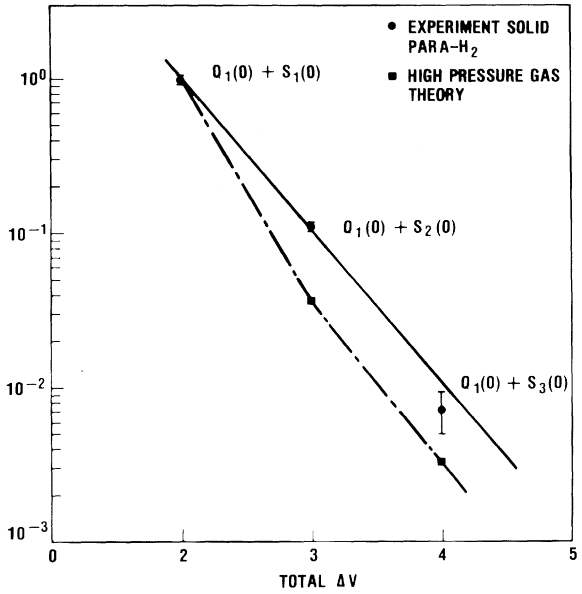

FIG. 2. The measured absolute absorption coefficients as a function of $\Delta\nu$ together with high-pressure gas calculations normalized to $\Delta\nu = 2$ measured values (Ref. 2).

As can be seen from Fig. 1, the signal-to-noise ratio seen for the $\Delta\nu = 4$ transitions is adequate but nowhere near as good as that seen from our PULPIT OA spectra of liquids[13] for similar absorption-coefficient situations. Further, our earlier data on cryogenic liquids indicate that there is no loss in the sensitivity of the piezoelectric transducers as the temperature is lowered from room temperatures to cryogenic temperatures.[8] We do not, at present, understand the reason behind this discrepancy. Further, as seen from Eq. (1) of Ref. 7, the normalized OA signal should vary as C_p^{-1}. Known values[15] of specific heat of solid hcp p-H_2 indicate that the OA signal should increase substantially as the temperature is lowered from 10 to 4.2 K. No such increase in signal was observed.

In agreement with the earlier observations in solid p-H_2 of $\Delta\nu = 1$ (Gush *et al.*[16]), and 2 and 3 (Ref. 11) double transitions are considerably stronger than the single molecular transitions. Single molecular transition occurs when the absorption of a photon results in the excitation of a single H_2 molecule to a $\nu = 4$ level. A double molecular transition results in simultaneous excitation of two molecules, one to a $\nu = 1$ level (say) and the second one to a $\nu = 3$ level as a result of the absorption of a single photon. In the present studies, no single transitions were observed in the third-overtone region of H_2.

Finally, we would like to point the reader's attention to the multiplet feature of the $\Delta\nu = 4$ spectra reported here. As can be seen in Fig. 1, we assign both peaks to the $Q_2(0) + S_2(0)$ transition. A multiplet with spacing of ~5 cm^{-1} is also seen[11] for the $Q_1(0) + S_1(0)$ molecular H_2 transition in the $\Delta\nu = 2$ spectra of solid hcp p-H_2. Similar doublet structure was also observed[11, 13] for the $S_1(0) + S_1(0)$ transition and was accounted for satisfactorily by the electric quadrupole-quadrupole (EQQ) interaction.[17] If we consider a pair of isolated H_2 molecules, the excited state $Q_2(0) + S_2(0)$ is tenfold degenerate. The degeneracy is removed by the EQQ interaction, and to a first approximation there are only three levels (two of them are still degenerate) of the manifold that are infrared active. The splitting is proportional to the quadrupole moment and the relative intensity is 3 to 2 for the doublet.[18] Calculations also show that the origin of the doublet should be at six-tenths of the splitting from the low-energy[11] component of the doublet. The first-order theoretical value for this splitting derived from the theoretical quadrupole moment is 8.17 cm^{-1},[19] whereas our observed value is 6.30 cm^{-1}. The discrepancy is believed to arise from the simplification of intermolecular forces in the calculations where the contribution from zero-point motion, many-body effects, charge overlap, and the dispersion-induced forces have been ignored.

In conclusion, we have reported the first observation of the $\Delta\nu = 4$ vibrational-rotational molecular H_2 transitions in solid hcp p-H_2. The data provide much needed information on the long sought after third vibrational overtone of H_2 which may have significant impact on the interpretation of some of the unidentified features in the optical spectra of Neptune and Uranus. Equally important are the observations of the frequencies, widths, and strengths of the spectra which should stimulate extensive theoretical work on this simplest of molecular solids.

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Coupling of Spin Waves with Zero Sound in Normal ^{3}He

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A scheme is proposed whereby a coupling can be achieved between the spin-wave and zero-sound modes in a neutral Fermi liquid; the technique should permit a detailed study of the spin-wave spectrum.

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Spin waves do not propagate in normal ^{3}He (Ref. 1); however, Silin[2] showed that in the presence of a finite magnetic field such modes do exist at sufficiently long wavelengths. The so-called Leggett-Rice effect[3] implies the existence of spin waves.[4] However, a systematic technique to directly study spin-wave dispersion has been absent to date.

In this Letter I propose a method to study spin waves, in detail, by observing the coupling