

High-Resolution Infrared Spectroscopy of Solid Hydrogen: The Tetrahexacontapole-Induced $\Delta J = 6$ Transitions

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Weak new features in the absorption spectrum of solid hydrogen were observed by high-resolution infrared spectroscopy, and assigned as transitions with total change in angular momentum of $\Delta J = 6$. The tetrahexacontapole (64-pole)-induced rotational transition $W_0(0)$ was studied with a difference frequency laser spectrometer and found to be very narrow, with a linewidth of 0.003 cm^{-1} HWHM in 99.8% parahydrogen. Frequencies, linewidths, and integrated absorption strengths were measured for several pure rotational and rotation-vibration transitions from 1800 to 7000 cm^{-1} , and the tetrahexacontapole moment was determined.

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High-resolution absorption spectroscopy has rarely been a useful probe of molecular motion in the condensed phase, where rotational and vibrational transitions tend to be substantially broadened by intermolecular interactions. An important exception is solid hydrogen, the simplest molecular solid and a fundamental example of a quantum solid. The molecules are bound by very weak, slightly anisotropic forces, and rotate and vibrate nearly freely within the crystal.¹ In this paper we report our studies of the previously unobserved $\Delta J = 6$ rotational and rovibrational transitions in solid hydrogen by infrared-laser and Fourier-transform ir spectroscopy. We have observed lines with widths approaching those typically seen in gas-phase spectra, and our ability to detect these weak absorptions stems in part from their narrowness. Our results suggest that high-resolution techniques developed for gas-phase ir spectroscopy can be successfully applied to the study of solid hydrogen.

Although infrared transitions of H_2 in the gas phase are dipole forbidden, the solid possesses a rather strong infrared absorption spectrum, first observed by Allin, Hare, and MacDonald.² van Kranendonk has developed a beautiful theory which quantitatively describes the infrared and Raman spectra of solid hydrogen.^{1,3} The absorptions arise from intermolecular interactions: Dipole moments are induced by both multipole and overlap interactions between neighboring molecules. The multipole-induced dipole moment is responsible for the sharp zero-phonon absorption features, which lie close to corresponding gas-phase rovibrational transitions.⁴ The $\Delta J = 2$ transitions arise from quadrupole-induced dipole moments, and the rovibrational $S_{1 \leftarrow 0}(0)$ line (the subscripts refer to the vibrational transition, the number in parentheses to the initial value of J) was readily seen in the earliest infrared spectrum.² The $\Delta J = 4$ absorptions $U_0(0)$ and $U_{1 \leftarrow 0}(0)$ are hexadecapole-induced transitions, 2 orders of magnitude lower in intensity, and were first observed two decades later.^{5,6}

Many of the observed lines are sharp, and narrow significantly in nearly pure $J=0$ parahydrogen ($> 98\%$ $p\text{-H}_2$). The $S_0(0)$ transition has ir and Raman spectral widths of 0.1 cm^{-1} ,⁷⁻⁹ similar to the ir absorption width of the $U_0(0)$ line.^{6,10} From a time-resolved stimulated Raman experiment, Schoemaker and co-workers¹¹ have recently found that the dephasing time of the $S_0(0)$ Raman transition agrees well with the spectral width, showing that the linewidth in $p\text{-H}_2$ is nearly homogeneous. Linewidths can thus reveal dynamics of the $k \approx 0$ rotational exciton (roton). Of the many spectroscopic studies beginning in 1955, perhaps the most elegant were the microwave experiments of Hardy and co-workers.^{12,13} They observed very sharp transitions involving nearest-neighbor pairs of orthohydrogen ($J=1$, $o\text{-H}_2$) impurities in a crystal of 99.8% $p\text{-H}_2$. The impurity spectra had linewidths of 6 to 100 MHz.¹³

We have detected several weak rotational and rovibrational transitions with total changes in angular momentum of $\Delta J = 6$, by Fourier-transform infrared spectroscopy (FTIRS). We have found that the W -branch transitions, which arise from the dipole induced by the tetrahexacontapole (64-pole) moments of neighboring H_2 's, have instrument-limited linewidths, prompting us to examine the pure rotational transition $W_0(0)$ at high resolution by difference frequency laser spectroscopy.

Solid hydrogen was grown in a copper cell 11.5 cm long and 2 cm in diameter, attached to the bottom of the liquid-helium vessel of an Infrared Laboratories HD-3 Dewar. The cell had sapphire windows sealed with indium gaskets. The crystals were grown near 10 K by pulsing gas at 50 to 100 Torr into the cell, and after cooling to 4.2 K the samples were optically transparent but probably polycrystalline. Samples were prepared from Matheson ultrahigh purity hydrogen (99.999%). The gas was passed through a column of Appachi catalyst maintained at either 77 or 20 K to convert the normal hydrogen to 50% or 99.8% $p\text{-H}_2$, respectively.

Infrared spectra with an apodized resolution of 0.04 cm^{-1} were recorded using a Bomem DA2.026 Fourier-transform spectrometer with a globar source and InSb detector. For high-resolution spectroscopy, we used a difference frequency laser spectrometer¹⁴ in which we generated infrared radiation of 2-MHz spectral purity in a LiNbO_3 crystal by nonlinear mixing of radiation from a cw ring dye laser (Coherent 699-29) and a cw argon-ion laser (Coherent Innova 90-5). The laser light was either chopper modulated at 500 Hz, or tone-burst modulated at 60 kHz.¹⁵ The former gave a sensitivity of $\approx 100:1$. In the latter, we generated 30% radio-frequency sidebands on the argon-ion laser line at 514 nm in a potassium-dihydrogen-phosphate crystal, prior to infrared generation. The sidebands were square-wave modulated at 60 kHz; the ir signal was detected with a lock-in amplifier referenced to the 60-kHz modulation. This phase modulation enhanced the signal-to-noise ratio by 1 to 2 orders of magnitude relative to the chopper-modulated sensitivity.

Table I lists the new lines that were observed using the FTIR spectrometer, along with other previously observed single transitions. The new transitions that have been observed in this work are the $\Delta J=6$ single transitions $W_0(0)$ and $W_{1\leftarrow 0}(0)$, and the rovibrational double transitions $U_{1\leftarrow 0}(0)+S_0(0)$ and $U_0(0)+S_{1\leftarrow 0}(0)$ (in double transitions, two neighboring molecules are excited

simultaneously). The solid only weakly perturbs the transition frequencies, and the lines are thus readily assigned from the predicted gas-phase values.⁴ The $U_{1\leftarrow 0}(0)$ transition was remeasured, as previous work used higher $o\text{-H}_2$ concentrations.¹⁰ The linewidth is similar to those of the $U_0(0)$ and S -branch lines. Table I lists several other double transitions observed in 50% $p\text{-H}_2$.

The new transitions are approximately 2 to 3 orders of magnitude weaker than the previously observed $\Delta J=4$ transitions. The integrated intensities, defined as

$$\tilde{a} = \frac{c}{\rho l} \int \ln \left(\frac{I}{I_0} \right) \frac{1}{\nu} d\nu,$$

can be accurately calculated with the assumption of the multipole-induced dipole moment mechanism from the general expressions developed by Poll and van Kranendonk.^{16,17}

The hexatetracontapole (64-pole) moment of hydrogen has not been calculated. The integrated absorption coefficients for the W transitions can be used to find the value of this moment from the equation

$$\tilde{a} = \frac{28\pi(Q_{0v}^{(6)})^2 \alpha_{00}^2}{3\hbar a^{16}} \sum_{i,j} \xi_{87}^2 \left(\frac{a^2}{a_i a_j} \right)^8 P_7(\cos\theta_{ij})$$

derived by Ma, Tipping, and Poll.¹⁸ $Q_{0v}^{(6)}$ is the

TABLE I. Observed single and double transitions in solid hydrogen. All results are from this work with FTIR, unless noted. Resolution is 0.04 cm^{-1} for single transitions, 4 cm^{-1} for double transitions.

| Single transitions | ν_{obs} (cm^{-1}) | ν_{gas}^a (cm^{-1}) | Γ HWHM (cm^{-1}) | \tilde{a} ($\text{cm}^3 \text{ s}^{-1}$) | $J=1$ (%) |
|-------------------------------|--------------------------------------------|----------------------------------------------|---------------------------------------|-------------------------------------------------|--------------|
| $S_0(0)$ | 355.6(1) ^b | 354.37 | 0.1 ^c | 5.2×10^{-14} | 2 |
| $U_0(0)$ | 1167.10 ^d | 1168.80 | 0.125 | 5.1×10^{-16} | 0.2 |
| $W_0(0)$ | 2410.5384(20) ^e | 2414.896 | 0.003 | 3.3×10^{-19} | 0.2 |
| $Q_{1\leftarrow 0}(1)$ | 4146.54 | 4155.255 | 0.035 | | 0.2 |
| $S_{1\leftarrow 0}(0)$ | 4485.97 ^f | 4497.840 | 0.1 | 3.3×10^{-15} | 2 |
| $U_{1\leftarrow 0}(0)$ | 5261.28 | 5271.372 | 0.10 ^g | 6.6×10^{-17} | 0.2 |
| $W_{1\leftarrow 0}(0)$ | 6441.81(0.01) | 6454.38 | 0.04 ^h | 1.1×10^{-19} | 0.2 |
| Double transitions | ν_{obs} (cm^{-1}) | $J=1$ (%) | Double transitions | ν_{obs} (cm^{-1}) | $J=1$ (%) |
| $U_0(1)+S_0(1)$ | 1975 | 50 | $U_0(0)+S_{1\leftarrow 0}(1)$ | 5873 | 50 |
| $U_0(1)+S_0(0)$ | 2206 | 50 | $U_{1\leftarrow 0}(1)+S_0(0)$ | 6039 | 50 |
| $U_{1\leftarrow 0}(0)+S_0(0)$ | 5615 ⁱ | 0.2 | $U_0(1)+S_{1\leftarrow 0}(0)$ | 6107 | 50 |
| $U_0(0)+S_{1\leftarrow 0}(0)$ | 5654 ^j | 0.2 | $U_{1\leftarrow 0}(1)+S_0(1)$ | 6274 | 50 |
| $U_{1\leftarrow 0}(0)+S_0(1)$ | 5848 | 50 | $U_0(1)+S_{1\leftarrow 0}(1)$ | 6325 | 50 |

^aReference 4.

^bReference 7.

^cExtrapolated from instrument-limited value of 0.2 cm^{-1} at 2% $J=1$.

^dReference 6.

^eThis work, difference frequency laser.

^fReference 10.

^gIn good agreement with Ref. 10 which obtains $\Gamma=0.15 \text{ cm}^{-1}$ at 2% $J=1$.

^hDeconvoluted instrument-limited linewidth.

ⁱ $\tilde{a}=2.6 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$.

^j $\tilde{a}=1.6 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$.

hexatetracontapole-moment matrix element ($v=0$ and 1 for rotational and rovibrational transitions, respectively), α_{00} is the polarizability, a is the lattice spacing, 3.793 Å, a_i is the distance to molecule i , ξ_{87} is a renormalization constant (assumed to be unity here), and θ_{ij} is the angle between the vectors a_i and a_j . A formula yielding similar results has been derived by Balasubramanian, D'Souza, D'Cunha, and Rao.¹⁹ We find $Q_{00}^{(6)} = 0.26ea_0^6$ and $Q_{01}^{(6)} = 0.15ea_0^6$. These estimates assume that the multipole-induction mechanism, although weak, is still dominant. Ma, Tipping, and Poll have shown that the most likely alternative, mixing of different J levels, does not contribute significantly to the transition strength.¹⁸ Such a high-order moment should be rigorous test of any *ab initio* wave function of H₂.

The double transitions $U_0(0) + S_{1 \leftarrow 0}(0)$ and $U_{1 \leftarrow 0}(0) + S(0)$ involve lower-order multipole moments. The expression for the intensity $\tilde{\alpha}$ in units of $\text{cm}^3 \text{s}^{-1}$ is

$$\tilde{\alpha} = \frac{40\pi^2 \gamma_{0v}^2 (Q_{0v}^{(4)})^2}{27\hbar a^{12}} \sum_i \xi_i^2 \left(\frac{a}{a_i} \right)^{12},$$

where $Q_{0v}^{(4)}$ and γ_{0v} are the hexadecapole and anisotropic polarizability matrix elements, respectively, and the sum is over all neighbors. Using the *ab initio* values for the multipole moments,¹⁸ we obtain $\tilde{\alpha} = 1.8 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ and $\tilde{\alpha} = 1.3 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$, respectively, in good agreement with the observed results. There are no selection rules for k in double transitions, and the observed lines are thus very broad.

The linewidths of the W transitions were found to be instrument limited using the FTIR spectrometer. The $W_0(0)$ transition fell within the frequency coverage of the difference frequency laser, and we therefore examined this line at very high resolution by both chopper and tone-burst modulations. Figure 1 shows the tone-burst spectrum. The linewidth is 0.003 cm^{-1} HWHM, substantially narrower than the $U_0(0)$ or $S_0(0)$ widths listed in Table I. Shoulders are evident in the tone-burst spectrum, which is essentially a second-derivative spectrum. The tone-burst spectrum did not change when the side-band frequency was altered from 90 MHz to either 40 or 20 MHz, indicating no further resolvable structure in this line.

The most surprising aspect of these results is the narrowness of the single transitions. There are several plausible explanations for the observed width of the $W_0(0)$ transition.

Sierens *et al.*¹¹ find that the linewidths of the $S_0(0)$ transition are homogeneously broadened at low ortho concentrations. They attribute this to dephasing of the $k \approx 0$ rotons^{8,20} by the thermal fluctuations of the quadrupole-quadrupole (eQQ) interactions. Dephasing of the $J=6$ rotons excited in the W transition would occur as a result of the tetrahexacontapole-tetrahexacontapole interactions, and would be substantially slower. By generalizing van Kranendonk's expression for

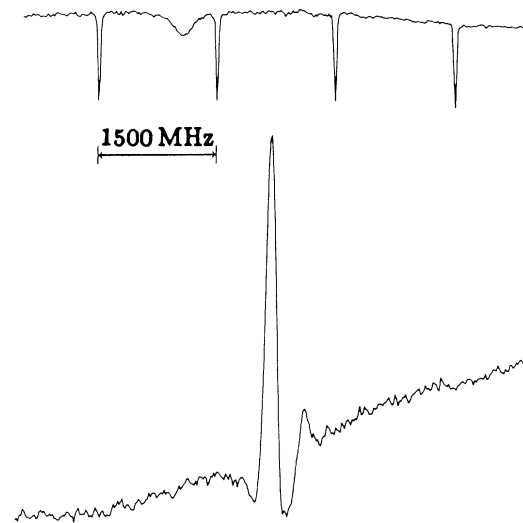


FIG. 1. Difference frequency laser spectrum of the $W_0(0)$ transition in p -H₂ solid by tone-burst modulation at 90 MHz. The peak is at $2410.5384 \text{ cm}^{-1}$, with a width 0.003 cm^{-1} HWHM. The path length is 11.5 cm, $T=4 \text{ K}$, and the o -H₂ concentration is 0.2%.

the $k=0$ exciton splitting,³ we find that the degenerate M_J levels of the $J=6$ exciton band will be split $< 10^{-4} \text{ cm}^{-1}$, a splitting closely related to the dephasing rate. From these considerations, we infer that homogeneous broadening is too narrow to account for the presently observed widths.

The presence of o -H₂ impurities (0.2%) will lead to inhomogeneous broadening. The $J=1$ H₂ have nonvanishing permanent quadrupole moments (unlike the $J=0$ molecules which have spherically symmetric wave functions), and there will be a random spatial distribution of neighboring $J=1$ molecules which will split and shift the M_J levels of the $J=6$ state through electrostatic interactions. Alternatively, this can be thought of as impurity scattering of the $J=6$ rotons.²¹ The observed linewidth is similar to that of the $Q_{1 \leftarrow 0}(1)$ impurity transition,²² for which the excitations are localized and the line is broadened by eQQ interactions. Statt and Hardy¹³ found that quadrupole-quadrupole interactions with neighboring o -H₂ impurities accounted for the widths observed in their microwave absorption spectra of o -H₂ pairs as well. By growing crystals with lower ortho impurities, we hope to investigate this mechanism.

Given the difficulties in growing a single crystal, strain broadening can also occur. The strength of this effect is difficult to predict.¹³ We do find, however, that the observed line is reproducible in different crystals. Our experiment on the $Q_{1 \leftarrow 0}(1)$ impurity transition²² sets the upper limit of the strain broadening to be $\approx 20 \text{ MHz}$. Further experiments are planned, using more controlled crystal-growth techniques. By reducing the inhomogeneous contributions, we hope to approach the natural width

of the W line.

In summary, we have observed several new rotational and rovibrational transitions in solid hydrogen. The surprising narrowness of the $W_0(0)$ transition means that we can exploit the spectral brightness of high-resolution lasers to gain sensitivity, opening several promising new directions in the study of solid hydrogen. These include detection of weaker transitions such as the Y ($\Delta J=8$) line, and study of impurities such as o -H₂. We also plan to explore the possibility of spectroscopy of other neutral and ionic impurities embedded in solid p -H₂.

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