

## High-Resolution Infrared Spectroscopy of Solid Hydrogen

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A rich spectrum composed of hundreds of sharp features (HWHM  $\lesssim 20$  MHz) has been observed in the fundamental  $Q$  branch of solid  $H_2$ , representing the first case of solid phase linear spectroscopy in which the high-resolution capabilities of laser spectroscopy have been fully exploited. These features are interpreted as splittings of  $o$ - $H_2$  pairs based on the work by Hardy, Berlinsky, and Harris.

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Optical spectra of matter in condensed phases are usually quite broad due to homogeneous and inhomogeneous broadening caused by intermolecular interactions. The high resolution of laser spectroscopy is seldom applicable for studying such systems. In this paper we report our observation of extremely sharp infrared-absorption lines of solid hydrogen whose widths are an order of magnitude narrower than the Dicke-narrowed *gaseous* lines, representing the first case of solid phase spectroscopy in which the high-resolution capabilities of laser spectroscopy are fully exploited.

Because of the small molecular mass and relatively weak intermolecular interactions, the solid hydrogens (together with helium) form a class of solids called quantum crystals—crystals in which the mean amplitude of the zero-point lattice vibration is a sizable fraction ( $\sim 18\%$  in the case of  $H_2$ ) of the intermolecular distance, and the equilibrium positions of the molecules are unstable in the harmonic approximation.<sup>1,2</sup> Beginning with the initial infrared spectroscopic work by the Toronto group,<sup>3</sup> it has been well established that molecules in the solid hydrogens have well-defined vibrational and rotational quantum states and that their infrared spectrum has the vibration-rotational pattern resembling that for gaseous molecules but broadened into exciton bands and accompanied by double transitions and much broader phonon bands.

Patel and his colleagues were the first to utilize the high sensitivity afforded by laser spectroscopy to observe the weak overtone bands of solid hydrogen.<sup>4</sup> Transitions of the solid hydrogens are unusually sharp. For instance, the  $S_0(0)$  transition of  $H_2$  has a width of  $0.1\text{ cm}^{-1}$ .<sup>5,6</sup> Sierens *et al.*<sup>7</sup> found, in a time-resolved experiment, that this width is caused mainly by the dephasing time of the  $J=2$  roton. More recent high-resolution studies of higher-order  $\Delta J=4$  and  $\Delta J=6$  pure rotational and rovibrational transitions have shown sharper spectral lines due to narrower exciton bands.<sup>8-11</sup> In particular, our observation of the tetrahexacontapole- ( $2^6$ -pole-) induced  $\Delta J=6$  pure rotational  $W_0(0)$  transition<sup>10</sup> revealed the linewidth (HWHM) of  $\sim 90$  MHz reflecting the small magnitude of the  $2^6$ -pole- $2^6$ -pole interaction between

neighboring molecules which causes exciton hopping. This led us to the idea that we may be able to observe sharp spectral lines due to  $o$ - $H_2$  ( $J=1$ ) impurity in a crystal of predominantly  $p$ - $H_2$  ( $J=0$ ), since the energy mismatch of  $\sim 6.6\text{ cm}^{-1}$  between their pure vibrational transitions ( $Q$  branch) may localize the exciton (vibron) in the impurity molecules. It had been shown earlier that  $T_1$  and  $T_2$  relaxation times of the  $\nu=1$  vibron are quite long.<sup>12,13</sup> In the back of our minds was the beautiful work by Hardy and Berlinsky<sup>14</sup> in which they observed microwave transitions among the nine split orientational levels of a pair of  $o$ - $H_2$  with the linewidths of 6–100 MHz. The theory explaining the orientational splitting of the nine otherwise degenerate levels of a pair of  $J=1$   $o$ - $H_2$  by intermolecular electrostatic quadrupole-quadrupole (EQQ) interactions and other many-body interactions was worked out by Nakamura<sup>15</sup> and Harris.<sup>16</sup> We will call them *pair splittings*.

The cryostat and the preparation of 11.5-cm-long solid  $p$ - $H_2$  were described previously.<sup>11</sup> Optically transparent samples were made from either  $\sim 99.8\%$  or  $\sim 99.94\%$  para-enriched  $H_2$  gas. The crystals were examined through crossed polarizers. No grain boundaries were observed, but coloration was seen suggesting some mechanical strains. However, the consistency of the observed frequencies and spectral widths convinces us of the good spectroscopic quality of our samples. Our observations of the  $W_0(0)$  transition<sup>10</sup> and its crystal-field splitting<sup>11</sup> convince us that our sample is composed of hexagonal closed-packed crystallites. The sample was kept at  $\sim 4.2$  K while the spectrum was recorded.

Tunable infrared radiation with spectral purity of  $\Delta\nu \lesssim 2$  MHz was generated by a difference-frequency system.<sup>17</sup> Single-mode argon-ion laser radiation at 476 nm was mixed with tunable red radiation from a single-mode ring dye laser in a temperature-controlled  $LiNbO_3$  crystal. Tone-burst frequency modulation<sup>18</sup> was used to increase the sensitivity of detection. High power ( $\sim 30$  W) rf radiation in the range of 20–90 MHz was applied to an electro-optic modulator to generate rf sidebands on the 476-nm Ar laser radiation. The power of each sideband approached  $\sim 30\%$  of the Ar emission. These side-

bands were transferred to the infrared radiation by difference-frequency mixing. The sidebands were switched on and off at a frequency of 6 kHz and the signal was detected by an InSb detector and processed through a lock-in amplifier referenced at 6 kHz. This method gives second-derivative line shapes which emphasizes sharp features at the expense of broad features. The frequencies of the spectral lines were measured against the reference spectrum of  $\text{NO}_2$  gas.<sup>19</sup> The accuracy of the measurement was within  $0.0020 \text{ cm}^{-1}$ , limited by the accuracy of the reference spectrum, but the resolution was much better, on the order of  $0.0005 \text{ cm}^{-1}$ .

We have observed an extremely rich spectrum composed of about 200 sharp lines in the region of  $4140.5\text{--}4153.2 \text{ cm}^{-1}$ , corresponding to the fundamental ( $\nu=1\leftarrow 0$ )  $Q$  branch ( $\Delta J=0$ ) transitions of solid  $\text{H}_2$ . The linewidths are comparable to those of Hardy and Berlinsky's microwave spectrum<sup>14</sup> indicating that the hopping and quenching of vibrons do not occur rapidly enough to severely broaden the lines. However, the infrared spectral pattern is much more complicated than that of the microwave work.<sup>14</sup> The overall pattern is shown schematically in Fig. 1. The strongest center at  $4146.5606 \text{ cm}^{-1}$  is due to the  $Q_{1\leftarrow 0}(1)$  ( $\nu=1\leftarrow 0$ ,  $J=1\leftarrow 1$ ) transition of isolated  $J=1$  molecules in the  $p\text{-H}_2$  matrix. This line is accompanied by a great number of closely spaced satellite lines resulting mainly from

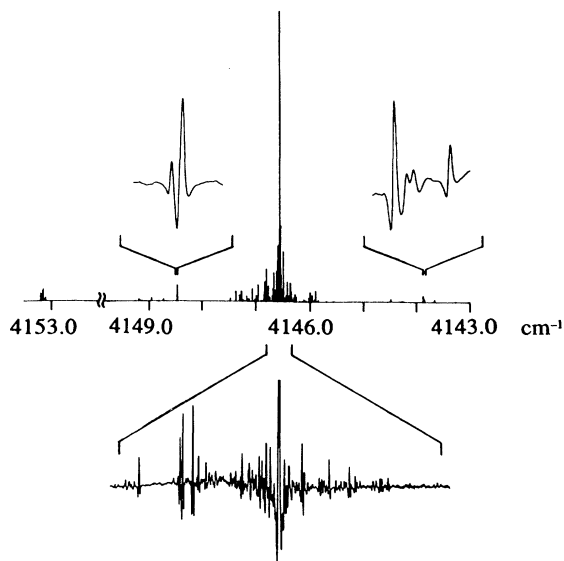


FIG. 1. A computer-generated stick spectrum and some observed lines of the experimental scan of solid hydrogen. The group of lines at the high-frequency end correspond to the  $Q_{1\leftarrow 0}(0)$  transitions of  $J=0$   $p\text{-H}_2$ . All the other lines are the  $Q_{1\leftarrow 0}(1)$  transitions of impurity  $o\text{-H}_2$  whose levels are split into pair levels due to anisotropic interactions. The frequency scan for the expanded central region is from  $4146.11$  to  $4146.97 \text{ cm}^{-1}$ .

the pair splittings of relatively distant  $o\text{-H}_2$  molecules and higher clusters. In effect, we have resolved the inhomogeneous broadening caused by the anisotropic EQQ interactions among the impurity  $o\text{-H}_2$  molecules. When the  $o\text{-H}_2$  concentration was reduced from  $\sim 0.2\%$  to  $\sim 0.06\%$ , the relative intensities of satellite lines to the central line were drastically reduced as expected.

On both sides of the highly congested central area, we observed many widely spaced spectral lines due to transitions between pair splittings of relatively close  $o\text{-H}_2$  pairs such as the nearest-neighbor (nn) and the next-nearest-neighbor (nnn) pairs. Two pairs of strong doublets at  $4143.9$  and  $4148.5 \text{ cm}^{-1}$  stand out. They are considerably stronger than the other lines and were already noticed as weak features by Balasubramanian *et al.*<sup>20</sup> in a lower-resolution spectrum. We assigned them to the pair transitions  $(1,1)'_{\pm} \leftarrow (2,1)_{\mp}$  and  $(2,1)'_{\pm} \leftarrow (1,1)_{\mp}$ , respectively, for the out-of-plane ortho pairs based on the intensity calculation and the earlier work by Hardy and Berlinsky.<sup>14</sup> Here we use the  $(F, |M|)_{\pm}$  notation for the pair levels adopted by other workers.<sup>1,14,21,22</sup> The quantum number  $F$  represents the total rotational angular momentum of the ortho pair and  $M$  is its projection on the pair axis; the  $\pm$  sign corresponds to the symmetric

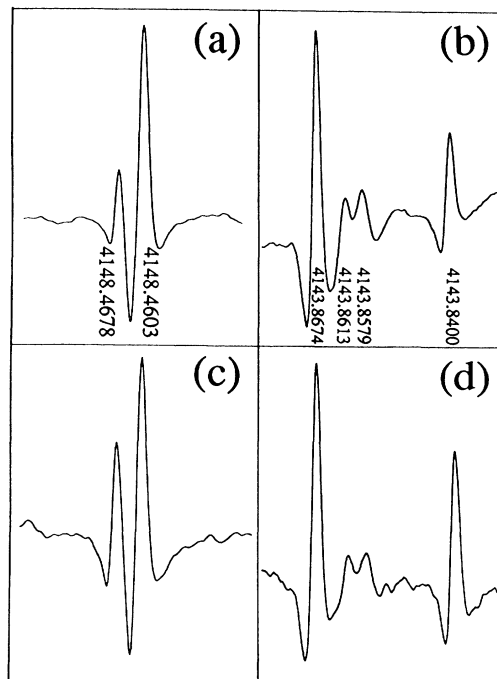


FIG. 2. Two pairs of strong doublets due to (a)  $(1,1)'_{\pm} \leftarrow (2,1)_{\mp}$  and (b)  $(2,1)'_{\pm} \leftarrow (1,1)_{\mp}$  transitions. The lower traces (c) and (d) show the same spectral lines taken with laser polarization perpendicular to that used for (a) and (b). The  $o\text{-H}_2$  concentration was  $0.06\%$ . Tone-burst modulation of  $40 \text{ MHz}$  was used. The time constant of detection was  $0.3 \text{ s}$ .

and antisymmetric combinations of the positive and negative  $|M\rangle$  states. The prime on  $(F, |M\rangle)$  indicates the  $v=1$  excited state. These two pairs of lines gain intensity due to addition of two different absorption mechanisms as discussed later. Typical traces of these spectral lines using different planes of infrared polarization are shown in Fig. 2. We measured their linewidths (HWHM) to be  $\sim 20$  MHz. The relative intensity of the components of the pair depends on the laser polarization indicating some orientation of the crystal. The spectral lines are reproducible in probing different parts of the crystal, different crystals, and crystals of different  $o$ -H<sub>2</sub> concentration.

The sharp doublet at  $4153.2 \text{ cm}^{-1}$  at the high-frequency end of Fig. 1 is the  $Q_{1-0}(0)$  transition due to  $J=0$   $p$ -H<sub>2</sub> molecules. This transition gets intensity from the presence of a nearby  $o$ -H<sub>2</sub> molecule.<sup>23</sup> The doublet appears at the high-frequency edge of the  $v=1$  exciton band. This situation is clearly shown in Fig. 3, where we compare a low-resolution spectrum using chopper modulation of the laser beam with a high-resolution spectrum. The mechanism of producing these sharp lines must be different from that for the impurity  $Q_{1-0}(1)$  transition since the vibration excitation of  $p$ -H<sub>2</sub> is not localized. The sharp lines may arise from the  $\Delta\mathbf{k}=0$  selection rule, where  $\mathbf{k}$  is the momentum vector of the exciton state. The observed splitting of 201 MHz must be caused either by the nonequivalent relative positions of the neighboring  $o$ -H<sub>2</sub> (in plane or out of plane) or by the simultaneous reorientation of the pair. The strongest doublet is accompanied by weaker features very likely due to  $J=0$  H<sub>2</sub> whose spectrum is induced by the presence of

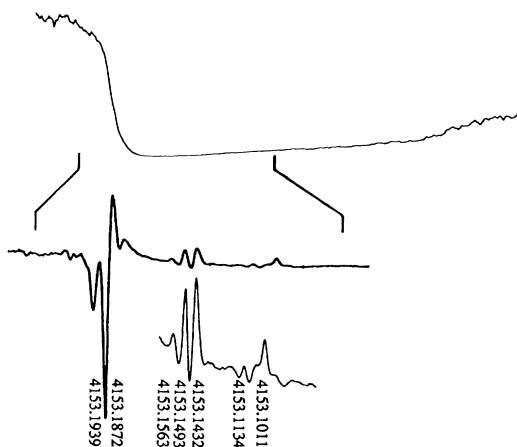


FIG. 3. Low-resolution spectrum (upper trace) and high-resolution spectrum (middle trace) of the  $Q_{1-0}(0)$  transitions. Part of the tone-burst spectrum is magnified in the bottom trace. The upper trace shows the entire exciton band. The sharp features appear at the high-frequency edge of this band. The frequency scan for the expanded central region is from  $4152.64$  to  $4153.28 \text{ cm}^{-1}$ .

nn and nnn  $o$ -H<sub>2</sub>.

While we are far from a good understanding of the rich spectrum, attempts have been made to assign the  $Q_{1-0}(1)$  spectral lines due to nn pairs, based on the observed frequencies and intensities. The pair splittings in the ground vibrational state were assumed to be identical to those reported by Hardy, Berlinsky, and Harris.<sup>14,21,22</sup> A complication arises in the excited state since a vibron in an ortho pair hops between two molecules of the pair. We used the simplest but perhaps crude assumption that the hopping is independent of the molecular orientations; in other words, we adopted the  $F_2(r_1, r_2, R)$  of Van Kranendonk.<sup>1</sup> This leads to symmetric ( $s$ ) and antisymmetric ( $a$ ) vibrational states separated by the hopping frequency of  $\sim 0.4 \text{ cm}^{-1}$  but with identical pair wave functions  $(F, |M\rangle)$  as the ground state. Each of the excited states possesses a pair-splitting pattern identical to that of the ground state except that the magnitude of the EQQ splitting is scaled by the ratio of the quadrupoles,  $Q(v=1)/Q(v=0) \sim 1.1$ . This model is similar to that by Balasubramanian *et al.*<sup>20</sup> except that we consider the  $s$  and  $a$  vibrational states separately.

Once this model is adopted, the intensity calculation is straightforward. An infrared photon excites an ortho pair through the vibrational dependence of the quadrupole moment  $Q_{10} \equiv |\langle v=1 | Q | v=0 \rangle|$ , or through that of the isotropic and anisotropic polarizability,  $\alpha_{10}$  and  $\gamma_{10}$ , respectively. We thus have three types of transition dipole moment operators with coefficients  $\alpha Q_{10}$ ,  $\alpha_{10}Q$ , and  $\gamma Q_{10} \pm \gamma_{10}Q$ , and angular dependences which are different for each of the four combinations of the  $s$  and  $a$  vibrational states and in-plane and out-of-plane pairs. The treatment of the  $\alpha Q_{10}$  term, which contains the lattice sum over the crystal, is analogous to that of the  $\alpha Q$  term by Harris, Berlinsky, and Hardy,<sup>21</sup> except that we calculate crystal-fixed dipole moments. The  $\alpha_{10}Q$  and  $\gamma Q_{10} \pm \gamma_{10}Q$  terms were calculated with respect to the pair axis and used to determine the crystal-fixed moment. The two strong doublets discussed earlier result from the addition of the  $\alpha Q_{10}$  and  $\alpha_{10}Q$  terms in the out-of-plane pairs.

Tentative assignments of stronger lines and their frequencies are listed in Table I. The majority of lines are still not assigned. We plan to unravel this problem using the method of infrared-microwave double resonance. If successful, such experiments will also provide information on the relaxation of the quantum states in the crystal. A complete table of spectral lines is available upon request.

While our study is still in a very primitive stage, the sharpness and the excellent signal-to-noise ratio of the observed lines indicate that we can explore further the following possibilities: (a) ultrahigh-resolution spectroscopy of other neutral and ionic impurity species embedded in cryogenic solids, (b) detailed studies of intermolecular interactions in solids, and (c) study of energy

TABLE I. Frequencies and assignments of some transitions (*o-p* denotes ortho-para).

Transition	Observed frequency (cm <sup>-1</sup> )
$Q_{1\leftarrow 0}(0)$ of <i>p</i> -H <sub>2</sub>	4153.1939
	4153.1872
	4153.1563
	4153.1493
	4153.1432
	4153.1134
4153.1011	
$s(1,1)'_{-} \leftarrow (2,1)_{+}$ of <i>o-p</i> pair	4148.4678
$s(1,1)'_{+} \leftarrow (2,1)_{-}$ of <i>o-p</i> pair	4148.4603
$Q_{1\leftarrow 0}(1)$ of isolated <i>o</i> -H <sub>2</sub>	4146.5606
$s(2,1)'_{-} \leftarrow (1,1)_{+}$ of <i>o-p</i> pair	4143.8674
$s(2,1)'_{+} \leftarrow (1,1)_{-}$ of <i>o-p</i> pair	4143.8400

transfer in solids.

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