

# High resolution infrared spectroscopy of deuterium in *p*-H<sub>2</sub> matrix

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Solid hydrogen, being the simplest molecular solid and a quantum crystal,<sup>1</sup> has been studied by spectroscopists for more than three decades.<sup>2</sup> Since the first observation of the multipole-induced dipole transitions of solid hydrogen by Allin, Hare, and MacDonald in 1955,<sup>3</sup> subsequent experimental efforts have been mainly concentrated on the search for weaker features induced by higher order multipole moments.<sup>4-8</sup> Unlike the case of other solid materials in which the transitions are seriously broadened by intermolecular interactions, spectral lines in solid hydrogens can be very sharp.<sup>6-12</sup> In particular, transitions with widths much narrower than those typically seen in gas phase spectra have recently been observed in samples of highly pure ( $\geq 99.8\%$ ) parahydrogen (*p*-H<sub>2</sub>) in our laboratory using high resolution laser spectroscopy.<sup>8,11,12</sup> The narrowness of the transitions allows us to uncover a wealth of previously unobserved information, such as the triplet structure of the  $\Delta J = 6$  pure rotational  $W_0(0)$  transition of H<sub>2</sub> resulting from crystal field interactions<sup>12</sup> and numerous sharp features in the fundamental *Q* branch of solid H<sub>2</sub> due to interactions among *o*-H<sub>2</sub> impurity molecules.<sup>11</sup> These observations not only provide new information on the structure and dynamics of solid hydrogen but also suggest the possibility of high resolution matrix spectroscopy in solid *p*-H<sub>2</sub> despite the fact that hydrogen has rarely been used as a matrix material. In this letter we report our observation of deuterium impurity in *p*-H<sub>2</sub>. This observation represents the first attempt of high resolution spectroscopy in *p*-H<sub>2</sub> matrix.

As pointed out by Van Kranendonk,<sup>2,13</sup> infrared transitions of solid H<sub>2</sub> and its isotopic species arise mainly from the electric dipole moments induced in the solid by the multipolar interactions among the molecules. These dipoles, which are induced coherently on each molecule, cause infrared transitions by interacting with the radiation field through many-body effects. Transitions of solid H<sub>2</sub> induced by various multipoles have been reported, including quadrupole-induced  $Q(\Delta J = 0)$  and  $S(\Delta J = 2)$  lines,<sup>3,4,7,10,11,14</sup> hexadecapole-induced  $U(\Delta J = 4)$  lines,<sup>5,6,9,10</sup> and tetrahexacontapole (64-pole)-induced  $W(\Delta J = 6)$  lines.<sup>8,12</sup> Since Crane and Gush observed the *Q* and *S* branches of the fundamental band in the first spectrum of solid D<sub>2</sub> in 1966,<sup>15</sup> the *U* transitions have been reported recently.<sup>16,17</sup> Although the spectroscopy of various isotopic hydrogens has been extensively investigated, mixtures of isotopic hydrogens have seldom been studied.<sup>15,18</sup>

As a starting point for high resolution matrix spectroscopy in solid parahydrogen, the fundamental band of D<sub>2</sub>

impurity was studied using difference frequency laser spectroscopy. We expected that the large energy mismatch between the D<sub>2</sub> molecule and the surrounding *p*-H<sub>2</sub> molecules ( $\sim 180 \text{ cm}^{-1}$  in rotational energy and  $\sim 1100 \text{ cm}^{-1}$  in vibrational energy) may localize the excitation energy on D<sub>2</sub> and give rise to sharp spectral features. This situation is similar to the case of *o*-H<sub>2</sub> impurity in solid *p*-H<sub>2</sub>, in which transitions as sharp as  $\sim 20 \text{ MHz}$  half-width at half maximum (HWHM) have been observed in the fundamental *Q* branch as a result of a mismatch of  $6 \text{ cm}^{-1}$  between the  $\nu = 1$  vibron energies of *o*-H<sub>2</sub> and *p*-H<sub>2</sub>.<sup>11</sup> We have observed the pure vibrational *Q* branch and the rovibrational *S* branch of D<sub>2</sub> in the  $3 \mu\text{m}$  region. Attempts to observe the rovibrational *U* branch were not successful due to the weak intensity of the transitions.

The experimental apparatus was described in our previous reports.<sup>8,11,12,17</sup> A gas mixture containing about 0.4% *o*-D<sub>2</sub>, 0.2% *p*-D<sub>2</sub>, 0.06% *o*-H<sub>2</sub>, and 99.3% *p*-H<sub>2</sub> was generated by mixing normal deuterium gas with  $\sim 99.94\%$  para-enriched H<sub>2</sub> gas in a stainless steel vessel. A solid sample with 11.5 cm optical path was prepared by pulsing the gas mixture into a copper cell fitted with sapphire windows and maintained at  $\sim 4.2 \text{ K}$  in a liquid helium cryostat as described before. Optically transparent samples can usually be obtained using this method. The spectra were recorded using a difference frequency laser spectrometer<sup>19</sup> with either chopper modulation at 1 kHz or radiofrequency (at 7–20 MHz) tone-burst modulation<sup>20</sup> at 6 kHz.

The  $Q_{1-0}(0)$  transition of D<sub>2</sub> near  $2987 \text{ cm}^{-1}$  was resolved into three groups of lines, a quartet at  $2986.97 \text{ cm}^{-1}$ , a triplet at  $2986.95 \text{ cm}^{-1}$ , and another triplet at  $2986.85 \text{ cm}^{-1}$  (Fig. 1). According to Sears and Van Kranendonk, the  $Q_{1-0}(0)$  transition occurs only with a simultaneous reorientation of nearby  $J = 1$  molecule(s).<sup>21</sup> Both *o*-H<sub>2</sub> and *p*-D<sub>2</sub> in this system can induce the  $Q_{1-0}(0)$  line with slightly different transition frequencies. To identify the transitions due to *o*-H<sub>2</sub> and understand the cause of the quartet and triplet splittings of the spectrum, more systematic surveys, including the study of a sample containing *only o*-D<sub>2</sub> impurity in highly pure *p*-H<sub>2</sub> matrix, have to be done.

The pattern of the  $Q_{1-0}(1)$  line of D<sub>2</sub> was very similar to the corresponding transition of *o*-H<sub>2</sub> observed in para-enriched hydrogen<sup>11</sup>—a strong central peak at  $2984.8301 \text{ cm}^{-1}$  due to single *p*-D<sub>2</sub> impurities is accompanied by many satellite lines as a result of interactions among the  $J = 1$  molecules (including *o*-H<sub>2</sub> and *p*-D<sub>2</sub>) in the solid. However, the satellite lines are much weaker in the case of D<sub>2</sub>, making the identification difficult. More sensitive

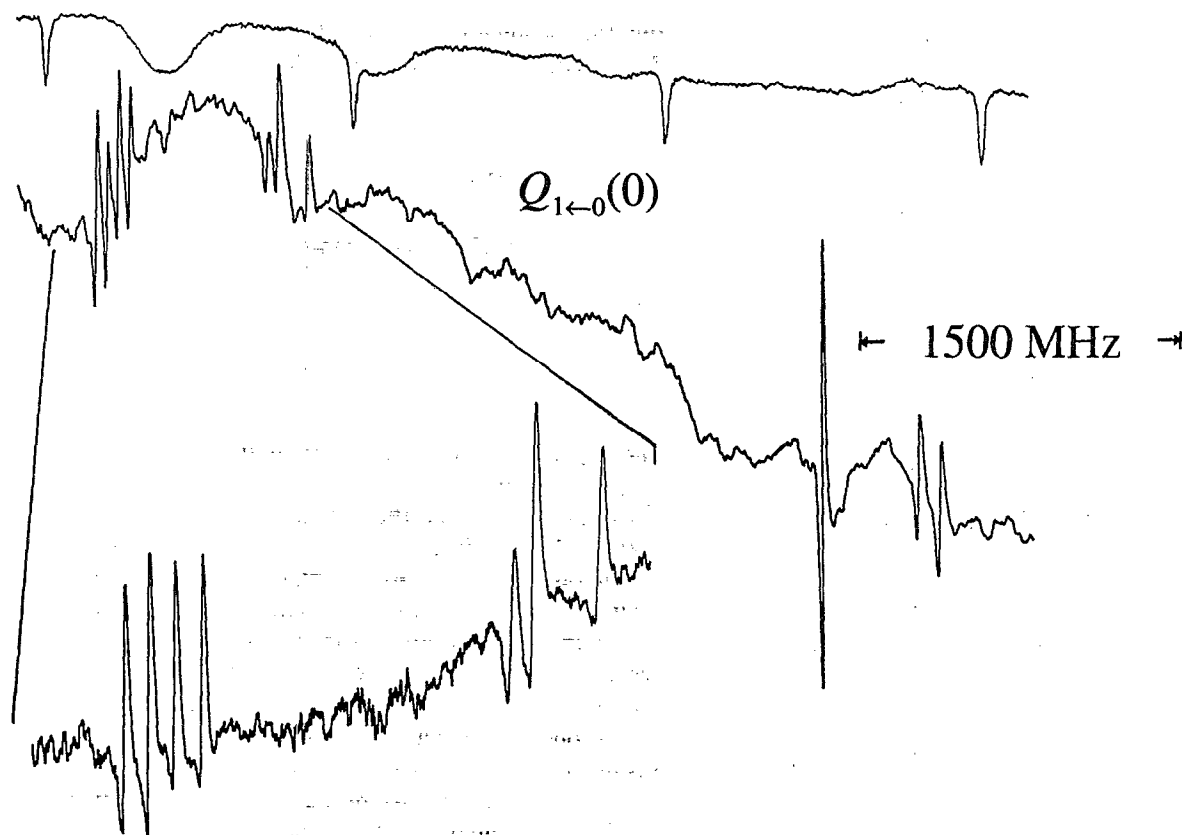


FIG. 1. Difference frequency spectrum of the  $Q_{1\leftarrow 0}(0)$  transition of *o*-D<sub>2</sub> impurity in para-enriched (~99.3%) H<sub>2</sub>. Three groups of lines were observed. Typical linewidths were  $\lesssim 10$  MHz HWHM. Part of the spectrum in expanded frequency scale is shown in the bottom trace. The optical path was 11.5 cm and the RF modulation frequency was 7 MHz.

modulation/detection technique is necessary before we can study this transition further.

The typical linewidth of the  $Q$ -branch transitions is  $\lesssim 10$  MHz (HWHM). In particular, the quartet in the  $Q_{1\leftarrow 0}(0)$  region showed an instrument-limited linewidth of 7 MHz. The extremely sharp D<sub>2</sub> transitions indicate that the  $\nu = 1$  vibron is highly localized, and its relaxation due to interaction between D<sub>2</sub> and the surrounding H<sub>2</sub> is very slow, as expected from the large energy mismatch ( $\sim 1100$  cm<sup>-1</sup>) between the  $\nu = 1$  vibrons of D<sub>2</sub> and H<sub>2</sub>.

In contrast to the extremely sharp  $Q$ -branch lines, both the  $S_{1\leftarrow 0}(0)$  and  $S_{1\leftarrow 0}(1)$  lines of D<sub>2</sub> impurity have a spectral width of  $\sim 0.07$  cm<sup>-1</sup> (HWHM) in the spectra shown in Fig. 2 using chopper modulation. Neither of these broad lines was detected in the tone-burst spectrum, indicating that no sharp feature exists in the broad profile. Based on group theoretical considerations of molecules isolated in a solid *p*-H<sub>2</sub> matrix,<sup>12,22</sup> the  $S_{1\leftarrow 0}(0)$  line has only one allowed component corresponding to the  $|M| = 2 \leftarrow 0$  transition whereas the  $S_{1\leftarrow 0}(1)$  line has five components corresponding to  $|M| = 3 \leftarrow 0, 2 \leftarrow 1, 2 \leftarrow 0, 3 \leftarrow 1, \text{ and } 1 \leftarrow 1$ . The absence of fine structure in the  $S_{1\leftarrow 0}(1)$  line indicates that the  $M$  splitting is smeared out by broadening.

Although the complete spectrum has yet to be assigned, an interesting phenomenon is noticeable: it came as a surprise that the  $S$ -branch lines are more than 200 times

broader than the  $Q$ -branch lines. Since both the  $Q$  and  $S$  branches were studied using the same sample, the inhomogeneous broadening should be similar for both branches. The linewidth difference must be due to the difference in the homogeneous broadening for different types of transitions. The qualitative difference between the  $Q$  and  $S$  transitions is that in the former only a  $\nu = 1$  vibron is excited whereas in the latter a roton is excited in addition to the  $\nu = 1$  vibron. The different linewidths in the  $Q$  and  $S$  branches must result from the different relaxation rates between the  $\nu = 1$  vibron and the  $J = 2$  roton [ $J = 3$  roton for  $S(1)$  line].

The vibron population relaxation ( $T_1$ ), involving multiphonon scattering processes, has been shown to be very slow ( $\sim 150$  ns), due to the mismatch between the exciton energy and the Debye frequency ( $\sim 90$  cm<sup>-1</sup>), and has little effect on the linewidths of  $Q$ -branch transitions.<sup>23,24</sup> On the other hand, the population relaxation of  $J = 2$  rotons (or  $J = 3$  rotons) of D<sub>2</sub> may contribute more significantly to the linewidth of the  $S$ -branch lines, since the gap between the roton energy of D<sub>2</sub> and Debye frequency is much smaller. However, its actual importance has yet to be studied.

In comparing the phase relaxation ( $T_2$ ) of the  $\nu = 1$  vibron and the  $J = 2$  roton [ $J = 3$  roton for  $S(1)$  line], we assumed that phonon-assisted dephasing occurs during the

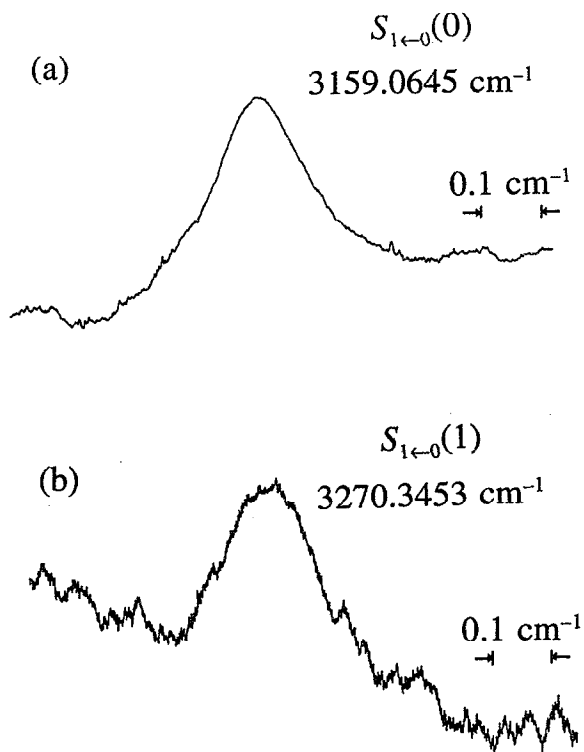


FIG. 2. The chopper-modulated spectra of (a) the  $S_{1\leftarrow 0}(0)$  transition of  $o$ - $D_2$  impurity and (b) the  $S_{1\leftarrow 0}(1)$  transition of  $p$ - $D_2$  impurity in para-enriched ( $\sim 99.3\%$ )  $H_2$ . The linewidths were  $0.07\text{ cm}^{-1}$  HWHM, and the optical path was  $11.5\text{ cm}$ . Both lines were not observed in the tone-burst spectrum. The absence of fine structure in (b) indicates that the  $M$  splitting due to crystal field interactions may be obscured by broadening.

resonance hopping of the exciton energy due to the dependence on the phonon coordinates of the hopping Hamiltonian. A faster dephasing is expected from a stronger hopping interaction. The exciton hopping from a  $D_2$  impurity molecule to the surrounding  $H_2$  molecules is unlikely to happen because of the large energy mismatch. The excitation energy of a  $D_2$  molecule can only hop to another  $D_2$  molecule, which is normally far apart because of the low  $D_2$  concentration. For less than  $1\%$   $D_2$  concentration, the average separation  $R$  is estimated to be  $\gtrsim 3R_0$ , where  $R_0$  is the nearest neighboring distance ( $3.793\text{ \AA}$ ) in solid  $H_2$ . According to Van Kranendonk,<sup>2,13</sup> the vibron hopping is due to isotropic dispersion interaction, which has an  $R^{-6}$  dependence. To estimate the effect of the larger separation between  $D_2$  molecules on the hopping process, we scale the vibron hopping Hamiltonian as

$$\epsilon'_R(D_2) = \frac{\epsilon'_0(H_2)}{\sqrt{2}} \left(\frac{R_0}{R}\right)^6, \quad (1)$$

where  $\epsilon'_0(H_2) \sim 0.4\text{ cm}^{-1}$  is the interaction between the nearest-neighboring  $H_2$  pairs, and the factor  $\sqrt{2}$  comes from the vibrational frequency ratio between  $H_2$  and  $D_2$  molecules. On the other hand, the hopping of a  $J=2$  roton (or  $J=3$  roton) involves the anisotropic electrostatic

quadrupole-quadrupole (EQQ) interaction, which has an  $R^{-5}$  dependence. The scaled EQQ interaction gives the form

$$\mathcal{H}_{\text{EQQ}} = \epsilon_{22} \sum_{mn} C(224; m n m + n) \times C_{2m}(\Omega_1) C_{2n}(\Omega_2) C_{4m+n}^*(\Omega_{12}), \quad (2)$$

where

$$\epsilon_{22} = \sqrt{70} \frac{\mathcal{Q}^2}{R_0^5} \left(\frac{R_0}{R}\right)^5 \sim 22.1\text{ cm}^{-1} \left(\frac{R_0}{R}\right)^5, \quad (3)$$

and  $\Omega_1$ ,  $\Omega_2$ , and  $\Omega_{12}$  are the orientation of the two interacting quadrupoles  $\mathcal{Q}$  and  $R$ , respectively. It is seen from Eqs. (1) and (3) that the ratio between  $\epsilon_{22}$  and  $\epsilon'_R$  is about 230 for  $R \sim 3R_0$ , in good agreement with the observed linewidth ratio of the  $S$  and  $Q$  branches. Scaling the bandwidths of the  $\nu=1$  vibron ( $\sim 1\text{ cm}^{-1}$ ) and the  $J=2$  roton ( $\sim 25\text{ cm}^{-1}$ ) in parahydrogen based on Eqs. (1) and (3), we estimated the corresponding vibron and roton bandwidths of  $D_2$  to be  $\sim 30\text{ MHz}$  and  $\sim 0.1\text{ cm}^{-1}$ , very close to the observed linewidths of  $Q$  and  $S$  transitions. These results suggest that the dephasing may still be the major source of homogeneous broadening for  $D_2$  impurity in solid  $H_2$ . Systematic study of the transitions with various  $\Delta J$  would be useful in determining the relative contribu-

TABLE I. Observed transitions of deuterium in solid  $p$ - $H_2$  matrix.

Transitions	Frequency ( $\text{cm}^{-1}$ )	Typical HWHM ( $\text{cm}^{-1}$ )
$Q_{1\leftarrow 0}(1)^a$	2984.7672	0.0003
	2984.7873	
	2984.7938	
	2984.8077	
	2984.8251	
	2984.8277	
	2984.8301 <sup>b</sup>	
	2984.8319	
	2984.8356	
	2984.8679	
	2984.8700	
	2984.9107	
	$Q_{1\leftarrow 0}(0)^c$	
2986.8475		
2986.8628		
2986.9463		
2986.9509		
2986.9525		
$S_{1\leftarrow 0}(0)$	2986.9742	0.07
	2986.9761	
	2986.9779	
	2986.9797	
	3159.0645	
	3270.3453	
$S_{1\leftarrow 0}(1)$	3270.3453	0.07

<sup>a</sup>Only stronger transitions are listed.

<sup>b</sup>The strongest transition, due to isolated single  $p$ - $D_2$ .

<sup>c</sup>Transitions are separated into three groups of lines.

tions of the phase and population relaxation to the homogeneous spectral linewidths.

Although this simple consideration leads to a qualitative rationalization of the linewidths in the fundamental band of D<sub>2</sub> impurity, a more detailed theory on the linewidths of various transitions in solid hydrogen based on first principles remains to be studied. A list of observed transitions and linewidths is given in Table I.

In summary, we have observed the high-resolution spectrum of D<sub>2</sub> impurity in solid *p*-H<sub>2</sub>, which provides information on the relaxation of vibrons and rotons in solid hydrogen. These results suggest the possibility of studying homogeneous broadening and relaxation processes of other impurity molecules in *p*-H<sub>2</sub> matrix. These studies form a very interesting topic in the high resolution spectroscopy of solid phase matter.

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