High resolution infrared spectroscopy of deuterium in p-H₂ matrix

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Solid hydrogen, being the simplest molecular solid and a quantum crystal, has been studied by spectroscopists for more than three decades. Since the first observation of the multipole-induced dipole transitions of solid hydrogen by Allin, Hare, and MacDonald in 1955, subsequent experimental efforts have been mainly concentrated on the search for weaker features induced by higher order multipole moments. Unlike the case of other solid materials in which the transitions are seriously broadened by intramolecular interactions, spectral lines in solid hydrogens can be very sharp. In particular, transitions with widths much narrower than those typically seen in gas phase spectra have recently been observed in samples of highly pure (≳99.8%) parahydrogen (p-H₂) in our laboratory using high resolution laser spectroscopy. The narrowness of the transitions allows us to uncover a wealth of previously unobserved information, such as the triplet structure of the fundamental band of D₂ in the 3 μm 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. A gas mixture containing about 0.4% o-D₂, 0.2% p-D₂, 0.06% o-H₂, and 99.3% p-H₂ was generated by mixing normal deuterium gas with para-enriched H₂ 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 −4.2 K in a liquid helium cryostat.

The Q₁olesterol of D₂ near 2987 cm⁻¹ was resolved into three groups of lines, a quartet at 2986.97 cm⁻¹, a triplet at 2986.95 cm⁻¹, and another triplet at 2986.85 cm⁻¹ (Fig. 1). According to Sears and Van Kranendonk, the Q₁俐(0) transition occurs only with a simultaneous reorientation of nearby J = 1 molecule(s). Both o-H₂ and p-D₂ in this system can induce the Q₁俐(0) line with slightly different transition frequencies. To identify the transitions due to o-H₂ 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-D₂ impurity in highly pure p-H₂ matrix, have to be done.

The pattern of the O₁俐(1) line of D₂ was very similar to the corresponding transition of o-H₂ observed in para-enriched hydrogen—a strong central peak at 2984.8301 cm⁻¹ due to single p-D₂ impurities is accompanied by many satellite lines as a result of interactions among the J = 1 molecules (including o-H₂ and p-D₂) in the solid. However, the satellite lines are much weaker in the case of D₂, making the identification difficult. More sensitive
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 \( Q_{1-0}(0) \) region showed an instrument-limited linewidth of 7 MHz. The extremely sharp D_2 transitions indicate that the \( v = 1 \) vibron is highly localized, and its relaxation due to interaction between D_2 and the surrounding H_2 is very slow, as expected from the large energy mismatch (\(-1100 \text{ cm}^{-1}\)) between the \( v = 1 \) vibrons of D_2 and H_2.

In contrast to the extremely sharp Q-branch lines, both the \( S_{1-0}(0) \) and \( S_{1-0}(1) \) lines of D_2 impurity have a spectral width of \(-0.07 \text{ cm}^{-1}\) (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_2 matrix,\(^{12,22}\) the \( S_{1-0}(0) \) line has only one allowed component corresponding to the \( |M| = 2 \leftarrow 0 \) transition whereas the \( S_{1-0}(1) \) line has five components corresponding to \( |M| = 3 \leftarrow 0, 2 \leftarrow 1, 2 \leftarrow 0, 3 \leftarrow 1, \) and \( 1 \leftarrow 1 \). The absence of fine structure in the \( S_{1-0}(1) \) 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 \( v = 1 \) vibron is excited whereas in the latter a roton is excited in addition to the \( v = 1 \) vibron. The different linewidths in the Q and S branches must result from the different relaxation rates between the \( v = 1 \) vibron and the \( J = 2 \) roton \([J = 3 \text{ roton for } S(1) \text{ line}]\).

The vibron population relaxation \( (T_1) \), involving multiphonon scattering processes, has been shown to be very slow (\(-150 \text{ ns}\)), due to the mismatch between the exciton energy and the Debye frequency (\(-90 \text{ cm}^{-1}\)), and has little effect on the linewidths of Q-branch transitions.\(^{23,24}\) On the other hand, the population relaxation of \( J = 2 \) rotons (or \( J = 3 \) rotons) of D_2 may contribute more significantly to the linewidth of the S-branch lines, since the gap between the roton energy of D_2 and Debye frequency is much smaller. However, its actual importance has yet to be studied.

In comparing the phase relaxation \( (T_2) \) of the \( v = 1 \) vibron and the \( J = 2 \) roton \([J = 3 \text{ roton for } S(1) \text{ line}]\), we assumed that phonon-assisted dephasing occurs during the
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 $\gtrsim 3 R_0$, where $R_0$ is the nearest neighboring distance ($3.793$ Å) in solid H$_2$. According to Van Kranendonk, 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

$$
\epsilon_R(D_2) = \epsilon_0(H_2) \frac{R_0^6}{R^6},
$$

where $\epsilon_0(H_2) \approx 0.4$ cm$^{-1}$ is the interaction between the nearest-neighbor 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

$$
\mathcal{H}_{EQQ} = \sum_{m n} C(224, m n m + n) \epsilon_{22} \frac{C_{2n}^m(\Omega_1) C_{2n}^m(\Omega_2) C_{4m+n}(\Omega_{12})}{R^5},
$$

where

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

and $\Omega_1$, $\Omega_2$, and $\Omega_{12}$ are the orientation of the two interacting quadrupoles $\mathcal{Q}$ and $\mathcal{R}$, respectively. It is seen from Eqs. (1) and (3) that the ratio between $\epsilon_{22}$ and $\epsilon_0$ 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 ($\sim 1$ cm$^{-1}$) and the $J=2$ roton ($\sim 25$ cm$^{-1}$) in parahydrogen based on Eqs. (1) and (3), we estimated the corresponding vibron and roton bandwidths of D$_2$ to be $\sim 30$ MHz and $\sim 0.1$ 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>
<thead>
<tr>
<th>Transitions</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Typical HWHM (cm$^{-1}$)</th>
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<tr>
<td>$Q_{1-0}(1)^a$</td>
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<tr>
<td>$S_{1-0}(1)$</td>
<td>3270.3453</td>
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</table>

$^a$Only stronger transitions are listed.
$^b$The strongest transition, due to isolated single p-D$_2$.
$^c$Transitions are separated into three groups of lines.
tions of the phase and population relaxation to the heterogeneous spectral linewidths.

Although this simple consideration leads to a qualitative rationalization of the linewidths in the fundamental band of D₂ 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 D₂ impurity in solid p-Η₂, 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-Η₂ matrix. These studies form a very interesting topic in the high resolution spectroscopy of solid phase matter.

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