

Pressure dependence of the vibron in solid hydrogen and deuterium up to 600 kbar

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We have studied the $Q_1^+(0)$ intramolecular vibrational transition in solid molecular hydrogen and deuterium by means of Raman scattering for pressures up to 600 kbar and temperatures down to 5 K in a diamond anvil cell. We present a semiempirical model developed to describe the pressure dependence of the transition frequency. The agreement between theory and experiment is surprisingly good up to about 200 kbar. Deviations at higher pressures cannot be explained in terms of this simple mean-field model.

I. INTRODUCTION

In the solid state, molecular hydrogen has three types of lattice modes: phonons, rotational modes, and internal molecular vibrational modes called vibrons. In this paper we study the pressure dependence of the transition frequency of the Raman-active $Q_1^+(0)$ vibron for which we have made a preliminary report.¹ This mode corresponds to the transition $v, J=0, 0 \rightarrow 1, 0$, where v and J are the vibrational and rotational quantum numbers; the + refers to the even symmetry of this lattice mode. We shall refer to this mode as the "vibron." In the free molecule the vibrational frequency is 4161.134 and 2993.548 cm^{-1} for hydrogen and deuterium, respectively.² Since these frequencies are much higher than the other lattice modes and since the interatomic forces are much stronger than the intermolecular forces, the vibron is only weakly coupled to the other modes of the lattice. Its frequency decreases by $\sim 0.3\%$ in going from the rarefied gas phase to the solid. With increasing pressure the transition frequency increases up to about 350 kbar and then starts to decrease. At our highest pressures of 600 kbar the transitions remain narrow and well defined, enabling an accurate study.

Sharma *et al.* observed vibrational transitions in normal hydrogen^{3,4} and deuterium⁵ at room temperature to pressures of several hundred kilobar. The interpretation of these data is rather difficult because the molecules are in different rotational states. In our study at $T=5$ K all molecules are in the $J=0, v=0$ ground state and we study the pure $v=0 \rightarrow 1$ transition.

In Sec. II we describe our experimental techniques. Section III presents a model to interpret the pressure dependence; this is followed by a discussion and conclusion.

II. EXPERIMENTAL

Samples of 98.5% *para*-H₂ and 98.5% *ortho*-D₂ were prepared by catalytic conversion in the liquid state. Pressure was applied in our diamond anvil cell, which is operated in a ⁴He cryostat, enabling temperature control in the range 1.1–300 K. Samples were confined in a cylindrical chamber in a T301 steel gasket. The typical sample size was 100- μm diameter and ~ 20 - μm thick. Present experimental data were obtained in a few runs on both isotopes. The $Q_1^+(0)$ vibron was observed in a Raman backscattering geometry. An argon-ion laser with power up to 500 mW in the 5145- \AA line was employed. Pressure was determined from the luminescence spectrum of a few grains of ruby enclosed with the sample. Below 350 kbar the 5145- \AA line was used to excite this fluorescence, but above 350 kbar it proved to be necessary to use the 4880- \AA line for excitation. The pressure calibration of Mao *et al.*⁶ was used. At the beginning of each experimental run the zero-pressure frequency of the fluorescence line was determined at 5 K. This zero-pressure frequency was used when applying the formula of Mao *et al.* Our experimental results are presented in Fig. 1, which includes low-pressure points by Bhatnagar *et al.*⁷ and Lassche *et al.*⁸ We note that the data of Bhatnagar *et al.* on deuterium refer to a purity of 80% *ortho*-D₂ only. We see that for both isotopes the transition frequency increases to about 350 kbar and then starts to turn down. A similar behavior was observed by Sharma *et al.*^{3–5} However, a detailed comparison of our spectra and theirs cannot be made directly since the experiments were done on quite different samples (normal versus pure $J=0$) and since different transitions were studied: $Q_1^+(1)$ and $Q_1^+(2)$ vs $Q_1^+(0)$. Also the temperature of the samples was different (300 vs 5 K).

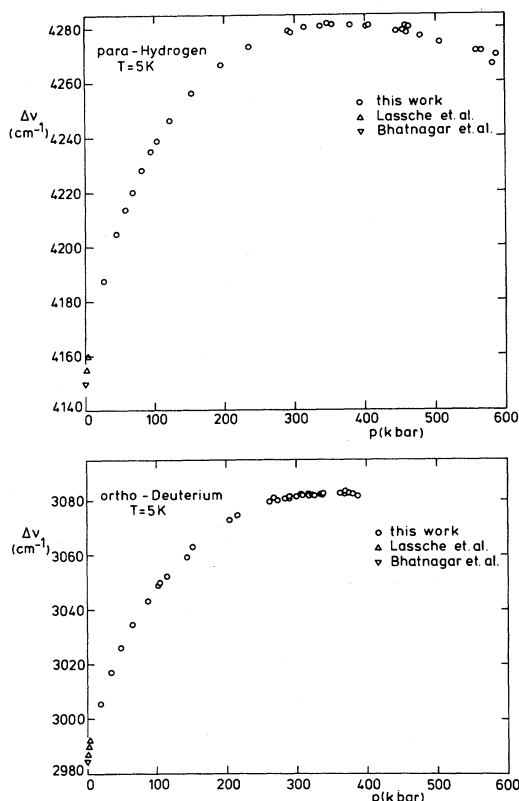


FIG. 1. Frequency of the $Q_1^+(0)$ transition as a function of pressure. Low-pressure points by Bhatnagar *et al.* (Ref. 7) and Lassche *et al.* (Ref. 8) are also included.

We want to emphasize that the transition observed by Sharma *et al.* in H_2 was identified by them as a transition of the $J=1$ molecule, which is present in our samples as a contamination only.

III. INTERPRETATION

In this section we develop a simple model to describe the behavior under pressure of the $Q_1^+(0)$ vibron. We first consider the problem of finding the vibrational energy levels of an atom once the potential is known. We consider the hydrogen molecule as a rotating vibrator. The proper Hamiltonian is

$$H = \frac{1}{m} \left[\vec{p}_r^2 + \frac{\vec{J}^2}{r^2} \right] + V(r), \quad (1)$$

where $m = \frac{1}{2}(2m_a)$ is the reduced mass, m_a is the mass of the atom, \vec{p}_r is the momentum operator, and \vec{J} is the angular momentum operator. By using the wave function

$$\psi(r, \theta, \phi) = \chi_J(r) Y_J^m(\theta, \phi),$$

where $\chi_J(r)$ is the radial part and the spherical harmonic $Y_J^m(\theta, \phi)$ is the rotational part, we obtain the following Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} y_J(r) + \frac{\hbar^2 J(J+1)}{2mr^2} y_J(r) + [V(r) - E] y_J(r) = 0 \quad (2)$$

with $y_J(r) = r\chi_J(r)$. This is equivalent to

$$\frac{d^2 \psi_J(\xi)}{d\xi^2} + \frac{2mr_e^2}{\hbar^2} \left[E - V(\xi) - \frac{\hbar^2 J(J+1)}{2mr_e^2(1+\xi^2)} \right] \psi_J(\xi) = 0. \quad (3)$$

Here $\xi = (r - r_e)/r_e$, r_e is the equilibrium nuclear separation. For the special case where $V(\xi)$ can be written as a polynomial

$$V(\xi) = hca_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + \dots). \quad (4)$$

Dunham⁹ has solved Eq. (3) analytically. The eigenvalues he finds are given by

$$\frac{E_{\nu J}}{hc} = \sum_{l, j} y_{lj} \left(\nu + \frac{1}{2} \right)^l J^j (J+1)^j,$$

where ν and J are the vibrational and rotational quantum numbers, respectively. The coefficients y_{lj} (not spherical harmonics) have been calculated by Dunham and are expressed in terms of B_e , ω_e , and a_i , where ω_e is the classical frequency for small oscillations, B_e is the classical rotational constant $\hbar^2/(8\pi^2 m r_e^2 c)$ and $a_0 = \omega_e^2/4B_e$. We will use the following scheme to calculate the vibrational frequencies in the solid:

- (1) Write the atom-atom potential in the gas in the form of Eq. (4).
- (2) Modify this potential to incorporate the effect of the surrounding lattice.
- (3) Calculate the vibrational frequencies from this

TABLE I. Coefficients (in cm^{-1}) for Eq. (4) for the free hydrogen atom according to van Kranendonk and Karl (Ref. 10); the value for a_0 is from Stoicheff *et al.* (Ref. 2).

a_0	= 79566
a_1	= -1.607
a_2	= 1.898
a_3	= -2.060
a_4	= 1.965
a_5	= 0.11

modified potential.

The problem of writing the atom-atom potential in the polynomial form of Eq. (4) has been solved by van Kranendonk and Karl.¹⁰ Their coefficients are calculated precisely for the purpose of fitting spectroscopic data and are given in Table I.

To calculate the atom-atom potential in the solid, V_s , we assume this to be the sum of the gas-phase atom-atom potential V_g and a lattice contribution potential V_l due to the surrounding molecules:

$$V_s = V_g + V_l. \quad (5)$$

The lattice potential is calculated by considering one molecule j and summing an atom-molecule potential V_{am} over the whole lattice

$$V_l(\xi) = \sum_{\substack{i \\ i \neq j}} V_{am}(\vec{R}_i - \vec{r}_j, \xi), \quad (6)$$

where \vec{R}_i is the position vector of molecule i and \vec{r}_j is the position vector of atom j . The index j has been omitted on the left-hand side because we are going to calculate the vibrational frequencies in hcp solid hydrogen for which potential (6) is the same for all atoms. To perform the actual calculation we used the H-H₂ atom-molecule potential of Gengenbach *et al.*¹¹ This was summed over 15 subshells (maximum radius of the sphere was thus $3R$) and

averaged over the orientation of molecule j . This orientational average is directly built into the calculation since the potential of Gengenbach *et al.* already contains the average over all orientations of the molecule. Correlations between the rotations of the molecules were taken to be zero. After substituting the potential of Gengenbach *et al.* in Eq. (6) we expanded this equation into a polynomial. The constant term of this polynomial can be neglected as it does not influence the results of the present calculation. The total solid-state potential is calculated using Eq. (5). Because V_g was already given in polynomial form, the total solid-state potential is now expressed in polynomial form. The presence of a linear term in the potential indicates that the equilibrium distance is different from r_e . By choosing a new r_e' , the linear term can be eliminated, and V_s can be written as Eq. (4), but with different coefficients a_i^s . We must stress here that the use of an average atom-molecule potential for the interactions between a molecule and an atom that is part of a covalent molecule is a gross simplification. This procedure is only justified by the fact that no other simple approach was available and by the reasonable agreement that is obtained with experimental data.

We can now directly find the frequencies of the vibrational transitions by substituting the new coefficients a_i^s in Dunham's formulas. For instance,

TABLE II. Comparison between calculated and measured values for the $Q_1^+(0)$ frequency. For the calculation, see text. Unless otherwise noted, "measurement" data points were obtained by interpolation of the data obtained in this work.

R (Å)	Hydrogen		Deuterium			
	p (kbar)	$Q_1^+(0)$ calc. (cm ⁻¹)	$Q_1^+(0)$ meas. (cm ⁻¹)	p (kbar)	$Q_1^+(0)$ calc. (cm ⁻¹)	$Q_1^+(0)$ meas. (cm ⁻¹)
3.789	gas	4159.87	4161.134 ^a	gas	2991.80	2993.548 ^a
3.605	0	4162.65	4149.81 ^b	0	2995.15	2984.79 ^b
3.499	1	4165.83	4155.1 ^c	0.4	2995.96	
3.380	2	4167.49		1.2	2997.11	2987.8 ^c
3.200	5	4170.72		3.7	2999.33	
3.050	10	4174.66		8.0	3002.04	
2.895	20	4183.57	4180	17	3008.23	3004
2.686	50	4204.32	4210	45	3022.61	3024
2.530	100	4230.43	4238	92	3040.77	3046
2.376	200	4270.22	4270	188	3068.47	3070
2.288	300	4302.92	4279	284	3091.06	3081
2.180	500	4354.93	4276	480	3127.29	
2.038	1000	4449.53		970	3193.25	

^aFrom Stoicheff *et al.* (Ref. 2).

^bFrom Bhatnagar *et al.* (Ref. 14).

^cFrom Lassche *et al.* (Ref. 8).

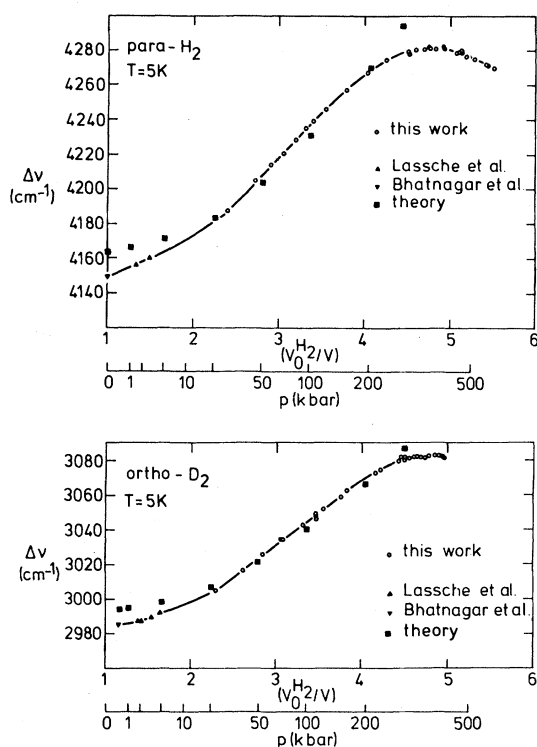


FIG. 2. Frequency of the $Q_1^+(0)$ transition as a function of relative density; the full squares indicate the results of the calculation discussed in the text. Low-pressure points by Bhatnagar *et al.* (Ref. 7) and Laasche *et al.* (Ref. 8) were also included. The density is scaled to the zero-pressure volume, $V_0^{H_2} = 23.14 \text{ cm}^3/\text{mol}$.

$$\begin{aligned}
 \nu\{Q_1^+(0)\} &= y_{1,0} + 2y_{2,0} + 3\frac{1}{4}y_{3,0} + \dots, \\
 \nu\{Q_1^+(1)\} &= y_{1,0} + 2y_{2,0} + 3\frac{1}{4}y_{3,0} \\
 &\quad + 2y_{1,1} + 4y_{2,1} + \dots, \\
 \nu\{Q_1^+(2)\} &= y_{1,0} + 2y_{2,0} + 3\frac{1}{4}y_{3,0} \\
 &\quad + 6y_{1,1} + 12y_{2,1} + \dots.
 \end{aligned} \tag{7}$$

These frequencies were calculated for various values of the lattice parameter. Table II shows the results for $Q_1^+(0)$. Since the calculations are done as a function of lattice parameter or density we must use an equation of state to compare with experiment. The pressure scale in this table is based on the equation of states (EOS) of Silvera and Goldman¹² and should be modified as our knowledge of the EOS improves. Figure 2 summarizes the calculational results.

IV. DISCUSSION

The calculations incorrectly predict that the gas to solid phase frequency shift is a small blue shift,

whereas in reality it is a 10-cm^{-1} red shift. The same problem was encountered by Helmy and Etters¹³ in a similar calculation on CO_2 and N_2 . However, using a slightly different model, Bhatnagar *et al.*¹⁴ correctly predict this shift with a Lennard-Jones potential. When put into our own model their potential still correctly predicts the gas-solid frequency shift but yields quite unrealistic frequencies at higher pressures. We therefore conclude that the difficulties in predicting the gas-solid shift are not inherent in the model but must be attributed to the potential used. It may well be that the Lennard-Jones potential gives a better description of the zero-pressure behavior whereas the potential of Gengenbach *et al.*¹¹ is better suited for the high-pressure region. In this respect it seems appropriate to note that Gengenbach *et al.* claim an accuracy in the well region of 30% whereas their accuracy increases up to 1% in the repulsive core. In our calculation zero-point motion (ZPM) was not taken into account. The effect of ZPM would be to yield a slight increase of the blue shift, itself decreasing with increasing pressure.

The phase transition discussed in Ref. 1 causes a downward jump of $\sim 2 \text{ cm}^{-1}$ at 290 kbar in deuterium and does not yet occur in hydrogen for the pressure range investigated. An extension of our model which takes into account the effect of the quadrupole moments of the molecules was used to calculate this jump. If we take the zero-pressure EQQ moment from Ref. 15 and scale this with R^{-5} for molecules fixed on a $Pa3$ structure, which is predicted for the orientationally ordered phase, a change in frequency of $\sim -5 \text{ cm}^{-1}$ is found. This is in reasonably good agreement with experiment, considering the simplicity of the model. The turning over of frequency with increasing pressure also occurs in hydrogen and thus cannot be attributed to the phase transition.

It is illustrative to compare all existing measurements on hydrogen and deuterium with respect to the bending over of the frequency at high pressure (see Fig. 3). To make the comparison we must know the expressions for the vibron frequencies in the solid state. These frequencies are given¹⁰ by subtracting $6\epsilon'$ from the frequencies given in Eq. (7), where ϵ' is an energy contribution due to the effective vibron-vibron coupling. The magnitude of ϵ' at zero pressure can be obtained by comparing ir and Raman measurements on hydrogen, and one then obtains¹⁰ $\epsilon' \approx 0.5 \text{ cm}^{-1}$. Alternatively, comparing the zero-pressure Raman measurements⁷ on hydrogen and deuterium, a better agreement is found if $\epsilon' \approx 0 \text{ cm}^{-1}$. It can be shown that ϵ' de-

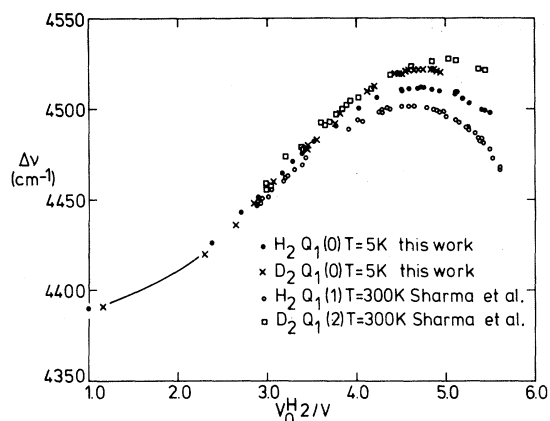


FIG. 3. Scaled vibron frequencies as a function of pressure. Scaling is done such that, apart from thermal effects, all curves should coincide. Data points of Sharma *et al.* were taken from their plots in Refs. 3–5. The density is scaled to the zero-pressure volume $V_0^{H_2} = 23.14 \text{ cm}^3/\text{mol}$.

creases with increasing pressure. For these reasons we take $\epsilon' \equiv 0$ in the following analysis. The comparison is still made with a slight degree of delicacy due to the fact that we measured the $Q_1^+(0)$ transition in H_2 and D_2 and Sharma *et al.*^{3–5} measured the $Q_1^+(1)$ in H_2 and $Q_1^+(2)$ in D_2 , especially because these frequencies are composed of different contributions [as indicated by Eq. (7)] and these contributions have different dependences on the mass m . For example, $y_{1,0} \propto m^{-1/2}$, $y_{2,0} \propto m^{-1}$, and $y_{3,0} \propto m^{-3/2}$.

All frequencies were transformed to a mass-independent value by the following procedure. First we note that the first three terms in the expressions for $Q_1^+(0)$, $Q_1^+(1)$, and $Q_1^+(2)$ are the same [Eq. (7)]; these expressions differ, however, in the higher-order contributions. The value of $y_{2,0}$ was calculated at the appropriate pressure along the lines discussed previously in this section. The term $2y_{2,0}$ is 5% of $y_{1,0}$, and $y_{2,0}$ itself was found to change only 7% over the investigated pressure range. Higher-order terms contributing to the vibrational frequencies were taken to be pressure independent and equal to their zero-pressure values as given by van Kranendonk and Karl.¹⁰ For deuterium these values were appropriately scaled with

mass. From the experimental frequencies all terms in Eq. (7) except $y_{1,0}$ were subtracted according to this calculation and the result was multiplied by \sqrt{m} thus yielding a mass-independent “experimental” value for $\sqrt{m}y_{1,0}$. These values are plotted in Fig. 3. If our application of the Dunham theory remains valid all data points should follow one curve. We note that in the experiments by Sharma *et al.*, at room temperature, a distribution of $Q_1^+(J)$ transitions may have been measured due to the fact that not all molecules are in the rotational ground state and that they use a normal *ortho-para* mixture. They observe broadening of the vibrational lines.^{3–5} The fact that the different curves diverge in the region where the turning over starts and also the different points of maximum frequency may provide insight into the mechanism responsible for the turning over.

V. CONCLUSION

The model used to describe pressure dependence of the vibron frequencies is in reasonable agreement with experimental data up to pressures of ~ 200 kbar. The low-pressure deviations may point to a possible inaccuracy in the potential of Gengenbach *et al.* The fact that above ~ 350 kbar the vibron frequency starts to decrease with increasing pressure cannot be described by the present analyses. This and the fact that the curves for the experimental values of $\sqrt{m}y_{1,0}$ no longer coincide in this region point to new phenomena becoming involved here, for instance, charge transfer and electron-correlation effects, which may be a precursor to the solid becoming metallic. One might also speculate that the bending over is a precursor of a soft vibron model which would eventually lead to an atomic instead of a molecular solid. However, this requires a careful theoretical investigation.

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