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Pressure dependence of the vibron modes in solid hydrogen and deuterium

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It has long been speculated that the high-pressure softening of the Raman-active vibron in hydrogen is a precursor of metallization. We use data for hydrogen, our new results for deuterium, and an established theory of the infrared- and Raman-active modes, to show that the softening of the Raman mode is due to the intermolecular potential and that it is the behavior of the ir mode which is crucial in considerations of metallization.

The Raman-active vibron mode (internal molecular vibration) of solid hydrogen and deuterium has been extensively studied as a function of pressure and temperature into the megabar (100-GPa) range.[1-6] For hydrogen the mode frequency rises with pressure to about 36 GPa and then turns over and decreases with further increase in pressure, shown in Fig. 1; a similar result is observed for deuterium. This turnover in frequency has been hypothesized as being due to charge transfer and called a possible precursor of dissociation of the molecular bond leading to the atomic metallic phase of hydrogen,[6] although a detailed theoretical model with such an interpretation did not exist. Pucci, March, and Siringo,[7] inspired by the turnover of the Raman-active vibron, presented a general analysis of the vibron frequency maximum in terms of the intramolecular potential but were unable to relate the turnover to the insulator-metal (IM) transition. Silvera[8] has stated that the frequency turnover of the Raman mode "is an interesting 'red herring' with regard to the IM transition." Ashcroft[9] has utilized the experimental pressure dependence of the frequency of the Raman-active mode to determine a density-dependent *intramolecular* hydrogen potential.

In this paper we argue that the turnover of the Raman-active vibron at intermediate pressures is primarily due to *intermolecular* interactions, rather than being a result of weakening of the *intramolecular* interaction and a precursor of metallization; it is mainly the ir mode that should be used to determine the intramolecular potential in the solid. This is seen from a vibron normal mode analysis and is clearly demonstrated by experimentally studying both the Raman- and ir-active vibron modes; the frequency of the ir mode continues to rise with pressure to 55 GPa, the highest pressure of study. A similar interpretation has also been reached recently by Loubeyre, LeToullec, and Pinceaux[10] from studies of hydrogen embedded in a neon lattice.

We present measurements of the ir vibron in deuterium at high pressure. Deuterium was pressurized in a diamond-anvil cell and studied at liquid-helium temperatures; the experimental system has been described elsewhere.[11] Pressurized samples of deuterium were allowed to convert to the equilibrium ortho-para concentration at $T=5$ K, essentially pure ortho-deuterium (even rotational states). Infrared vibron spectra were measured using a computer controlled tuneable Burleigh ir color center laser. At low pressures the intensity of the ir-active vibron mode is zero in a pure ortho-deuterium sample as it depends on a $j=1$ impurity induction mechanism.[12]

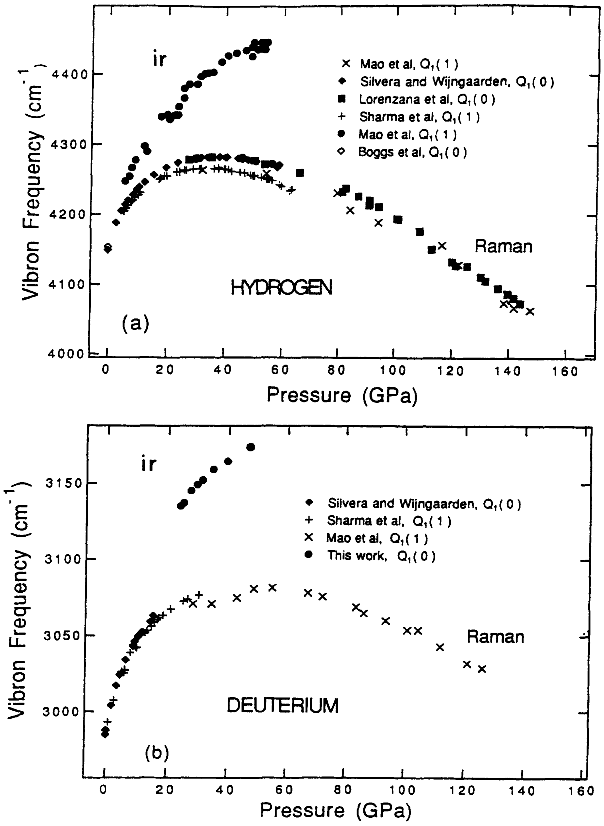

FIG. 1. Pressure dependence of the infrared and Raman active vibrons in hydrogen. The modes of Silvera and Wijngaarden, Lorenzana *et al.*, and Boggs *et al.* are helium temperatures; the rest are at higher temperatures.

However, at higher pressures when the sample has gone into the broken-symmetry phase[13,14] (BSP) the lattice site symmetry is changed, and the vibron intensity is then nonzero. Our results for ir vibron frequencies are shown in Fig. 1, as well as those of Mao, Xu, and Bell[15] for room-temperature equilibrium hydrogen. We now explain the differences in the pressure dependence of the Raman and ir vibron frequencies.

For an isolated molecule in its ground state, the internal vibrational frequency is determined by the reduced molecular mass μ and the intramolecular potential $\phi_0(u)$, where $u=r-r_e$ is the deviation of the proton separation r from its equilibrium position r_e. In order to determine a density-dependent intramolecular potential, Ashcroft modeled ϕ_0 as a density-dependent Morse potential

$$\phi_0(u,R)=D(e^{-2au}-2e^{-au}) , \tag{1}$$

where R is the intermolecular separation in the solid. The depth parameter D, the range parameter a, and $u=r-r_e$ are all R or density dependent. Ashcroft used the experimental Raman frequencies of hydrogen and deuterium in an attempt to determine an effective intramolecular potential for each density. This analysis elegantly extracts information about the solid's intramolecular potential. Here we show that the turnover in frequency of the Raman mode at 36 GPa is due mainly to the intermolecular potential, and that such analyses should focus on the ir mode.

We shall first briefly review the theory of the vibron frequency in solid hydrogen, developed by Van Kranendonk,[16] and whose notation we shall follow. For a pair of molecules separated by distance R_{12}, the potential is $\phi_0(u_1)+\phi_0(u_2)+V(u_1,u_2,R_{12})$, where $V(u_1,u_2,R_{12})$ is the intermolecular potential. V can be decomposed into several parts:

$$\begin{aligned} V(u_1,u_2,R_{12})=V_0(R_{12})&+A(\omega_1,\omega_2,R_{12}) \\ &+F(u_1,u_2,R_{12})+\cdots , \end{aligned} \tag{2}$$

where V_0 is the isotropic part, A is the anisotropic part, and F is the vibrational part of the potential. For our purposes it is sufficient to consider only the vibrational term,

$$\begin{aligned} F(u_1,u_2,R_{12})=F_1(u_1,R_{12})&+F_1(u_2,R_{12}) \\ &+F_2(u_1,u_2,R_{12}) , \end{aligned}$$

which has a single-molecule and a two-molecule part. These potentials can be expanded in terms of intramolecular displacements:

$$F_2(u_1,u_2,R_{12})=g(R_{12})u_1u_2+\cdots .$$

We incorporate the single-molecule part F_1 into ϕ_0 so that our reduced pair potential is

$$\phi_0(u_1,R_{12})+\phi_0(u_2,R_{12})+g(R_{12})u_1u_2 ,$$

keeping only the harmonic terms. $\phi_0(u_i,R_{ij})$ thus becomes the density-dependent intramolecular potential in the solid and $g(R_{12})u_1u_2$ is the harmonic part of the intermolecular potential.

In the low-density solid the potential can be taken as a sum over all of the single molecule and pair potentials, and we shall assume this to be valid for higher densities. In the case of the vibrons,

$$\phi_{\text{tot}}=\sum_i \phi_0(u_i,R_0)+\tfrac{1}{2}\sum_{i,j} g(R_0)u_iu_j , \tag{3}$$

where R_0 is the nearest-neighbor distance, and we have assumed that ϕ_{tot} depends only on nearest neighbors.

The vibrational frequency of an isolated hydrogen molecule is 4161.2 cm^{-1}.[12,17] This is shifted down several cm^{-1} when condensed in the zero-pressure solid; however, with increasing pressure the frequency increases by about 100 cm^{-1}. Since this shift is small relative to the frequency, F_1 and F_2 can be treated as perturbations on the vibrational energies.

In an ordered solid the collective vibrational excitations are called vibrons and the frequencies of the modes depend upon the lattice structure. Hydrogen has the hexagonal close packed (hcp) structure for the conditions of interest in this article.[18] We shall show that the Raman frequency is affected by both F_1 and F_2, whereas the ir frequency depends mainly on F_1. In the following we call ν_{intra} the part of the vibrational frequency due to the intramolecular part of the potential $\phi_0(u_i,R_0)$. Due to the intermolecular part of the potential F_2, the Raman vibrational energy is shifted by $-\varepsilon'/2$ (the matrix element of the perturbation between the vibrational eigenstates of a pair of molecules). This has the value $\varepsilon'=-ag(R_{ij})/\mu^{1/2}$, where a is a numerical factor, so that ε' depends on the intermolecular separation and is inversely proportional to the square root of the reduced mass. For the hcp lattice there are two vibron modes with experimental peak energies at[19]

$$E_{\text{Raman}}=h\nu_{\text{intra}}-6\varepsilon', \quad E_{\text{ir}}=h\nu_{\text{intra}}+0.6\varepsilon' . \tag{4}$$

We thus see that it is the infrared mode, not the Raman mode, which is more appropriate for determining the intramolecular potential.[20]

In Fig. 1 we show the experimental data for the Raman and ir vibron frequencies as a function of pressure in solid hydrogen and deuterium. Room-temperature modes have been identified as the $Q_1(1)$ mode.[17] The identification is unclear, since these samples were equilibrium hydrogen (25% para, 75% ortho).[21] Although there are differences in the measured Raman frequencies reported by different experimenters (studies performed at different temperatures), these are not important for the purposes of this paper. Since the ir modes depend mainly on the intramolecular potential and there is no turnover, it is clear from experiment that the turnover of the Raman modes is due to the intermolecular potential and both frequencies should be used to determine the intramolecular potential.

Using Eqs. (4), we can isolate the potential parameter ε', shown in Fig. 2. Here we have plotted $\Delta\nu=\nu_{\text{ir}}-\nu_{\text{Raman}}=6.6\varepsilon'$ as a function of density, ρ.[22] The experimental data were fit to polynomials to facilitate the analysis, so that the points in the figure represent smoothed data. Van Kranenonk[12] found that at low-

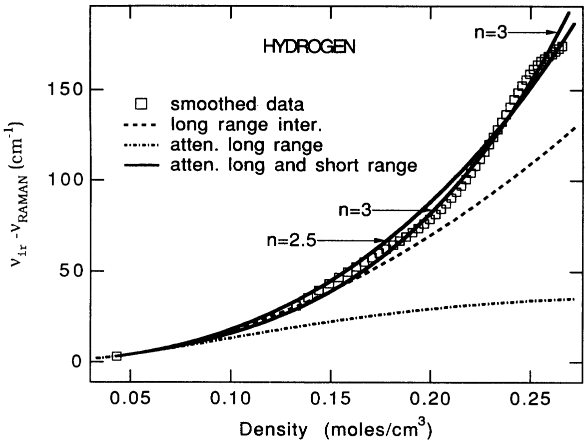

FIG. 2. The difference in the vibron frequencies as a function of density shown as smoothed data, along with the fits discussed in the text.

pressure ε′ originates from dispersion forces and varies as R^{-6} so that the dependence on density is ρ^2. At low density we expect the intermolecular potential to be dominated by this term, and since there appears to be close agreement with theory at zero pressure,[19] we have fit the difference in the vibron frequency at zero pressure, $\Delta\nu = \nu_{\text{ir}} - \nu_{\text{Raman}}$, and find $\Delta\nu_{\text{fit}} = 1724\rho^2$,[23] with the frequency in cm^{-1} when density is in mol/cm^3. We see in Fig. 2 that agreement is good at low density but deviates substantially at higher density.

It would be useful to fit the data and extrapolate to higher densities to understand how one might expect the infrared vibron to shift at high pressure. At high density F_2 or ε′ is probably dominated by overlap interactions and charge transfer for which there currently exists no theoretical analyses. Although the overlap depends exponentially on separation, we do not expect F_1 or F_2 to have such a dependence. In order to understand how the potentials might vary with intermolecular separation we consider the work of Ree and Bender[24] who studied the intramolecular forces for a pair of hydrogen molecules as a function of intermolecular separation R and proton separation r. Their study reveals only the behavior of F_1. We shall assume that F_1 and F_2 both have similar density dependences and now consider the dependence of F_1. For each value of R we fit the Ree-Bender potential to a harmonic potential of the form $K(R)u^2$ to find the R dependence of K. With increasing density ($\rho \propto R^{-3}$), K remains constant until approximately the density corresponding to the zero-pressure nearest-neighbor distance ($R = 3.79$ Å, $\rho = 0.043$ mol/cm^3) and then increases as a low-power n (n of order 1–3) of the increase in density.

Thus, for low density, F_2 varies as ρ^2 and then goes over to the short-range behavior, similar to F_1. We use a fitting curve of the form

$$\Delta\nu_{\text{fit}} = 1777\rho^2 fc, \quad \rho < 0.043 , \tag{5a}$$

$$\Delta\nu_{\text{fit}} = 1777\rho^2 fc + \kappa(\rho - 0.043)^n, \quad \rho \geq 0.043 . \tag{5b}$$

Here κ is a fitting parameter, which was optimized for powers of n between 1 and 3, and f_c is a short-range attenuation function of the form that Silvera and Goldman[25] used to attenuate the dispersion forces in determining the isotropic intermolecular potential of hydrogen:

$$\begin{aligned} fc &= \exp[-(3.3135\rho^{1/3} - 1)^2], \quad \rho \geq 0.0275 , \\ fc &= 1, \quad \rho < 0.0275 . \end{aligned} \tag{6}$$

In the above, density is in the units of mol/cm^3. The cutoff fc has the effect of gently turning off the long-range dipole interactions at short range. This is shown in Fig. 2 along with the fit to the data, using the attenuated plus short-range interactions (solid lines). We found the best fits for the following values of n and κ: $n = 3$, $\kappa = 12\,500$; $n = 2.5$, $\kappa = 6000$. With these values the frequency is given in wave numbers. We plot all of the data as a function of density in Fig. 3, along with the fits and their extrapolations to high density. The fit to the deuterium data uses the fit to the hydrogen data, scaled by $\mu^{-1/2}$, as predicted by theory, and agrees reasonably well with the data. This is a result of the dynamics and does not necessarily support the form of the potential that has been used. However, it may support our supposition that the BSP phase of deuterium has an hcp lattice for the molecular centers.[18] The extrapolated fits feature the interesting prediction that for the $n = 2.5$ power, the ir frequency of hydrogen should turn over at a pressure of about

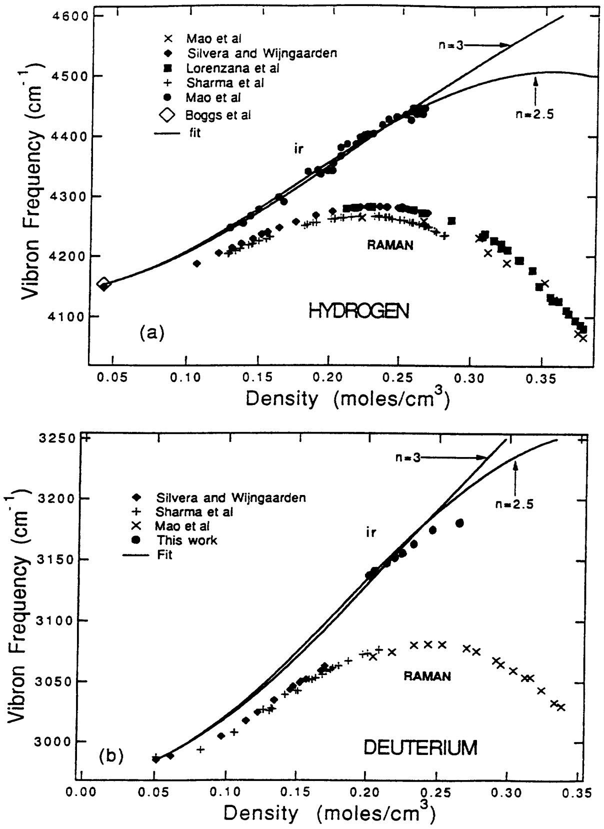

FIG. 3. The infrared and Raman active vibrons as a function of density, along with the fits discussed in the text.

100 GPa. From our scaling we expect the turnover for deuterium to be at a higher pressure than for hydrogen. However, it is clear from the figure that the high-density behavior depends sensitively on the power of the fitting function.

We conclude that information about the intramolecular potential of hydrogen and its isotopes is mainly contained in the ir vibron frequency, not the Raman vibron frequency. Unfortunately there is as yet no megabar pressure data on the ir vibron frequency, so we have attempted to fit the experimental data to be able to extrapolate this. It is quite possible that the ir vibron frequency may have a turnover at higher pressures. This, by itself is still no precursor of metallization although it may imply that charge transfer out of the molecular bond is gradually taking place. Ultrahigh pressure measurements of the ir vibron would be a welcome asset in trying to understand the path to metallization of solid hydrogen.

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[1] S. K. Sharma, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **44**, 886 (1980).

[2] I. F. Silvera and R. J. Wijngaarden, Phys. Rev. Lett. **47**, 39 (1981).

[3] R. J. Wijngaarden, A. Lagendijk, and I. F. Silvera, Phys. Rev. B **26**, 4957 (1982).

[4] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[5] H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, Phys. Rev. Lett. **64**, 1939 (1990).

[6] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[7] R. Pucci, N. H. March, and F. Siringo, J. Phys. Chem. Solids **47**, 231 (1986).

[8] I. F. Silvera, in *Simple Molecular Systems at Very High Density*, edited by A. Polian and P. Loubeyre (Plenum, New York, 1989), p. 33.

[9] N. W. Ashcroft, Phys. Rev. B **41**, 10963 (1990).

[10] P. Loubeyre, R. LeToullec, and J. P. Pinceaux, Phys. Rev. Lett. **67**, 3271 (1991).

[11] I. F. Silvera and R. J. Wijngaarden, Rev. Sci. Instrum. **56**, 121 (1985).

[12] See, for example, J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

[13] I. F. Silvera and R. J. Wijngaarden, Phys. Rev. Lett. **47**, 39 (1981).

[14] See Ref. 8 for a discussion of the structure. The structure of the high-pressure ordered phases of ortho-deuterium and para-hydrogen (BSP phases) are not known, but the small frequency shifts of the vibron at the transition indicate that the underlying lattice of molecular centers is probably hexagonal or fcc.

[15] H. K. Mao, J. Xu, and P. M. Bell, *High Pressure in Science and Technology*, edited by C. Homan, R. K. MacCrone, and E. Whalley (North-Holland, Amsterdam, 1984), Pt. III, p. 327.

[16] J. Van Kranendonk, Physica **25**, 1080 (1959).

[17] This is for the $Q_1(0)$ mode. The notation $Q_v(J)$ refers to the pure vibrational excitation of the vth vibrational quantum number with the molecule in the Jth rotational state.

[18] See Ref. 8 for a discussion of the structure. The structure of the high-pressure ordered phases of ortho-deuterium and para-hydrogen (BSP transition) are not known, but the small frequency shifts of the vibron at the transition indicate that the underlying lattice of molecular centers is probably hexagonal or fcc.

[19] J. Van Kranendonk and G. Karl, Rev. Mod. Phys. **40**, 531 (1968).

[20] From Eqs. (4) we see that $h\nu_{\rm intra}=(10E_{\rm ir}+E_{\rm Raman})/11$.

[21] It has been observed that the $Q_1(1)$ and $Q_1(0)$ Raman frequencies merge together at modest pressures [R. J. Wijngaarden and I. F. Silvera (unpublished data)].

[22] To convert to density we have used the equation of state of J. van Stratton and I. F. Silvera, Phys. Rev. B **37**, 1989 (1988), and its extrapolation to pressures higher than the experimental maximum of 37 GPa. The extrapolated equation of state of R. J. Hemley, H. K. Mao. L. W. Finger, A. P. Jephcoat, R. M. Horen, and C. S. Zha, Phys. Rev. B **42**, 6458 (1990), determined to lower pressures, gives similar results.

[23] We use the $Q_1(0)$ mode. At zero pressure we use the value 4149.7 cm^{-1} for the Raman mode from W. C. Prior and E. J. Allin, Can. J. Phys. **51**, 1935 (1973), and 4153.0 cm^{-1} for the ir mode from S. A. Boggs, M. J. Clouter, and H. L. Welsh, Can. J. Phys. **50**, 2063 (1972). This differs substantially from the value quoted in Ref. 1, which is actually the free-molecule frequency.

[24] F. H. Ree and F. Bender, J. Chem. Phys. **71**, 5362 (1979).

[25] I. F. Silvera and V. V. Goldman, J. Chem. Phys. **69**, 4209 (1978).