Properties of H_2 under Strong Compression in a Ne Matrix

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The vibron frequencies of H_2 and D_2 molecules compressed in a Ne matrix have been measured up to 45 GPa in a diamond-anvil cell. This evolution with pressure is seen to be very different from that measured previously in pure H_2 and D_2 solids: The vibron frequency displays a strong monotonic increase with pressure. The effect of pressure on the bond length of the isotopic H_2 molecules is then extracted from the Raman data with two analyses: A strong decrease is shown.

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With the advent of the diamond-anvil cell, great progress has been made during the past ten years in the physics of simple molecular systems at very high densities [1]. As an outstanding example, H_2 has been recently pressurized up to 250 GPa and one can say that its metallization is now within experimental reach [2]. Knowledge of the electronic properties of the H_2 molecule in various highly compressed systems ranging from fluid to eventually metal constitutes a valuable data basis set for testing physical-chemistry theories at high pressures. Among them, the quantum-mechanics calculation of $H_2{}^+$ or H_2 molecules imprisoned in a spheroidal box of shrinking volume has long served as a compelling model for the study of electronic perturbation induced by pressure [3]. But the hypotheses of this cornerstone theory are too simple for giving a correct analysis of the experimental situation in dense solid H_2, mainly because in this case the coupling between the electronic properties of the H_2 molecule and that of its surrounding H_2 neighbors is very important, as will be demonstrated below. On the other hand, the situation of an H_2 molecule embedded in a rare-gas matrix should directly probe the pure effect of compression which is described by the box model.

Since the pioneering work of May *et al.* [4], several Raman studies have been devoted to measure the properties of isotopic H_2 molecules perturbed by rare gases but they were all performed at low pressures [5]. We present here the Raman measurements of the vibron frequencies of H_2 and D_2 in a Ne matrix up to 45 GPa; the frequency shift with pressure is in striking contrast to that measured in solid H_2 (D_2), which presents a maximum around 30 GPa (50 GPa) [6].

Among the rare gases Ne is the most appropriate matrix host for H_2, since the thermodynamical properties of their corresponding dense systems, such as the melting line or the equation of state, are very similar at least below 30 GPa [1]. As a direct consequence, H_2 concentration as high as 5 mole% can be incorporated into solid Ne, whereas in the case of solid He and solid Ar an almost total immiscibility, less than 0.5 mole%, has been observed at room temperature [7]. Also, the H_2 molecule should sit on a substitutional site of the fcc solid Ne with very small distortion of the surrounding. The present measurements were done on H_2-Ne and D_2-Ne mixtures of 1 mole% H_2 (or D_2). This concentration is low enough to satisfy matrix isolation criteria and high enough to give a measurable Raman signal. These mixtures were loaded in the diamond-anvil cell, MDAC [8], at room temperature with a BeCu gasket. Because of the small sample volume (100 μm diameter and 20 μm thickness) and small H_2 concentration, the Raman signals were weak. Relatively high-power conditions (300 mW) of the exciting 488-nm Ar^+ laser line were employed but no measurable heating effects could be detected when the power was varied by a factor of 2. The Raman peaks were measured with a triple T800 Coderg spectrometer and the pressures were determined with the ruby fluorescence technique [9]. As seen in Fig. 1, the molecular vibron of H_2 and D_2 in a Ne matrix is clearly measurable in the Raman spectra over the whole pressure range investigated here. It is observed that the vibron line of D_2 in a Ne matrix is narrower and more intense than the one of H_2 in a Ne matrix.

The evolution of the vibron frequency of H_2, ω_{H_2}, in dense Ne is shown in Fig. 2. There is a strong blueshift of the frequency with pressure in qualitative agreement with the calculation of an H_2 molecule in a box of shrinking volume [10] and with the perturbation calculation of H_2 in an Ar matrix [11]. The positive discontinuity ob-

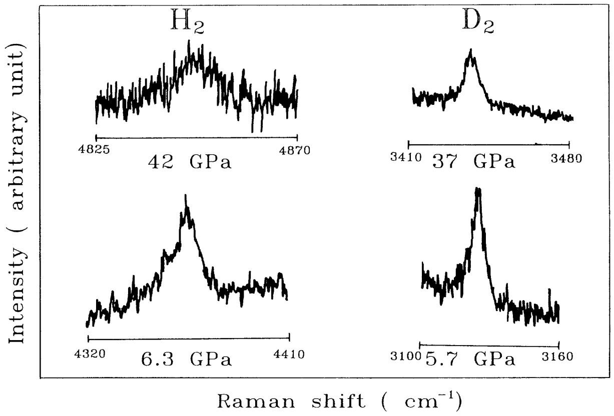

FIG. 1. Typical room-temperature Raman spectra of the vibron mode of H_2 and D_2 molecules in a Ne matrix (instrumental resolution, 4 cm^{-1}).

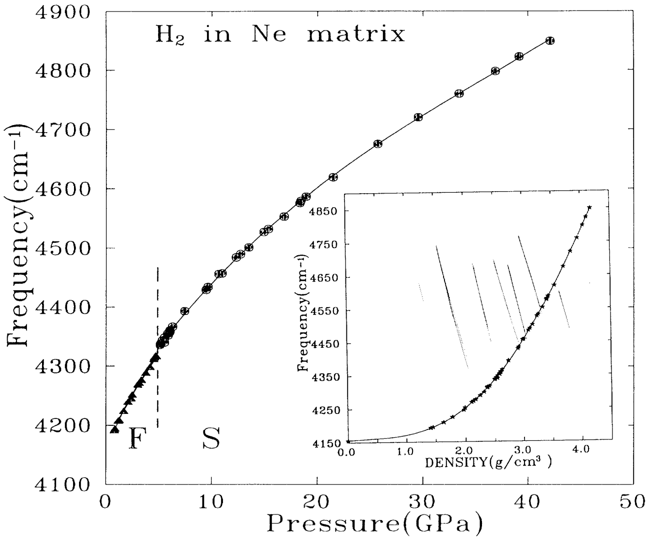

FIG. 2. Room-temperature frequency of the vibron mode of H_2 in a Ne matrix. The triangles identify the measurements in the fluid phase and the dots identify the ones in the solid phase. Inset: The vibron frequency expressed as a function of the density of the Ne matrix; the solid line represents the fourth-order polynomial fit.

served at 4.75 GPa is directly related to the density discontinuity at melting. It is more useful for theoretical analysis or extrapolation to express ω_{H_2} as a function of the density of the surrounding Ne medium which has been measured at $T=300$ K in the liquid phase [12] and in the solid phase up to 110 GPa [13]. The data, ω_{H_2} (cm^{-1}), are very well represented by the following polynomial in the density, ρ (g/cm^3), as seen in the inset of Fig. 2:

$$\omega_{H_2}=4155.2+17.3995\rho-23.8369\rho^2+24.5525\rho^3-2.4711\rho^4. \qquad (1)$$

The Raman measurements were also done for D_2 in dense Ne over the same pressure range. The data, ω_{D_2} (cm^{-1}), are also very well represented by a fourth-order polynomial:

$$\omega_{D_2}=2987.3+16.104\rho-18.248\rho^2+17.2072\rho^3-1.7005\rho^4. \qquad (2)$$

As seen in Fig. 3, ω_{H_2} and ω_{D_2} at a given pressure do not simply scale with the isotopic masses since the relative frequency shift $\Delta\omega/\omega$ for H_2 is slightly bigger than the one for D_2. This is in qualitative agreement with the perturbational calculation of H_2 and D_2 molecules in an Ar matrix [11] and it indicates that the anharmonicity of the intramolecular potential is significant. Furthermore, the two measurements do not correspond to the same vibron mode [14], $Q_1(1)$ in the case of H_2 and $Q_1(2)$ in the case of D_2, which differ slightly by the vibration-rotation coupling term. It should be noted, however, that this isotopic shift is of the opposite sign to the one observed between the Raman measurements in pure solid H_2 and D_2 [15, 16].

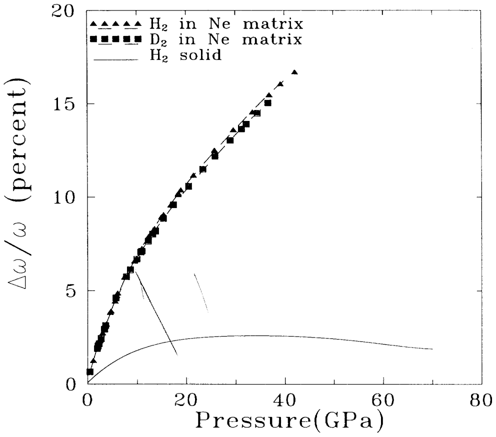

FIG. 3. Room-temperature Raman shift of the vibron mode of isotropic H_2 molecules: The triangles correspond to H_2 in a Ne matrix, the squares to D_2 in a Ne matrix, and the solid line is the fit of the measurements in solid H_2 [16]. The dashed lines interpolate between the experimental points.

In Fig. 3, the relative shift with pressure of the vibron frequency of H_2 in a Ne matrix is also compared to the one in solid H_2 [16]: Large differences between these two curves are observed. Taking into account the fact that the H_2-H_2 pair potential [17] is not very different from that of Ne-Ne [13], these results demonstrate that the turnover of the vibron frequency in solid H_2 is related to neither a pure compressional effect, such as the weakening of the intramolecular potential due to the increase of the kinetic energy of the electrons, nor, as it was recently proposed, the relative effects of density increase on anharmonicity and intramolecular and intermolecular spring constants [18]. It corroborates a recent calculation of Pucci, March, and Siringo [19] that qualitatively shows that the maximum of the vibrational frequency of H_2 is a balance between pure compressional effects and an increased dielectric constant of the surrounding medium, which in fact is the mean-field expression of the collective electronic properties of the H_2 molecules.

The determination of the change with compression of the intramolecular distance of the H_2 molecule is crucial for detailing the evolution of its electronic properties. We have recently presented a spectroscopic determination of the bond length of H_2 in its dense solid [20]. Unfortunately, such a spectroscopic determination was not possible here because the weak rotational lines were almost hidden by the fluorescence of the diamond anvils and furthermore this would have required very-low-temperature measurements. However, following Ashcroft [21], we have tried to extract this valuable information from the present Raman data. We just outline below the steps

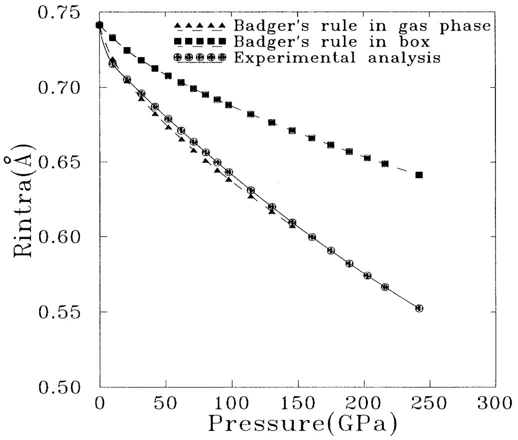

FIG. 4. Variation with pressure of the intramolecular distance of H_2 in a Ne matrix. The dots are obtained from the Raman results as described in the text. The dashed line with squares and the dashed line with triangles correspond to assuming a semilogarithmic correlation between force constant and bond length, known as the Badger's rule, to infer changes in bond length from changes in the measured harmonic vibrational frequency, respectively, with the slopes given by the box-model calculation [10] and the gas-phase spectroscopy [25].

of this simple analysis. In dense Ne, the two protons (or deuterons) are supposed to be bound by an effective intramolecular potential chosen to be of the Morse type: $\Phi_P(r) = D(e^{-a(r-r_m)} - 1)^2 + E$. This function is known to be a very satisfactory approximation of the intramolecular potential of the free H_2 molecule and moreover the vibrational solutions of this central field interaction are well known [22]. The present measurements for both H_2 and D_2 isolated in a Ne matrix allow the determination of the parameters a and D. The variation of the electronic energy E is assumed to be essentially equal to the compressional work on a substitutional lattice site, evaluated with the experimental Ne equation of state [13]. The values of interest here, $r_m(P)$, are then chosen in order to give coincidence of the short-range parts of the potentials Φ_P at various pressures. This property appears as a result of the calculation of H_2 in a box [10], but a clear demonstration of it has recently been given by Ashcroft with the use of the cusp theorem [21]. This determination of $r_m(P)$ is reported as dots in Fig. 4. We have also inferred changes in the bond length of the H_2 molecule from changes in the harmonic vibrational frequencies of isotopic H_2 molecules isolated in dense Ne, by assuming either a box-type or a gas-phase Badger's rule evolution. In various box models, hard box [10] or padded box [23], evidence is presented for a semilogarithmic correlation between the equilibrium bond length r_m and the quadratic vibrational force constant k_2, viz., $\ln k_2 = ar_m + b$. Following these theoretical papers, we may identify this relation as an example of Badger's rule, although originally the empirical formula was a power relation [24]. The slope of this relation was found to be independent of the stiffness of the box model, with $a = -3.3448$ Å^{-1}, and to hold over a very large range of pressure. The slope of this relation derived from gas-phase spectroscopy [25] is $a = -1.8519$ Å^{-1}. As expected, our above-described determination is bounded by these two trends, however, being interestingly very close to the gas-phase one.

The major indication of these analyses is that the bond length of the H_2 molecule in a Ne matrix is seen to be a strongly decreasing function of pressure, in contrast with the situation in pure solid H_2 where a minimum around 30 GPa has been reported [20]. Further experimental and theoretical work is now needed in order to settle this result more quantitatively. Finally, the present work has clearly shown that the measurements of the properties of H_2 isolated in matrices can bring insight for a better understanding of pure solid H_2 at very high pressure.

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