Raman Spectroscopy of Hot Compressed Hydrogen and Nitrogen: Implications for the Intramolecular Potential

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Raman measurements of molecular hydrogen (H_2 and D_2) and nitrogen (N_2) have been made under simultaneous conditions of high temperature and high static pressure. Measurements have been made on H_2 and D_2 to 50 GPa and 1600 K, and on N_2 to 50 GPa and 2000 K. In all three materials the familiar molecular stretching mode (vibron) is accompanied in the high-temperature Raman spectra by one or more lower-frequency peaks due to transitions from excited vibrational states. We find that the frequency differences between these bands decreases with pressure, implying that the anharmonicity of the corresponding part of the intramolecular potential also decreases. This is accompanied by an increase in the measured linewidths of the bands that is consistent with a decrease of the depth of the potential and an approaching molecular dissociation.

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The atoms in diatomic homonuclear molecules are strongly bonded by covalent interaction. The dissociation energy of these materials is correspondingly high (consider that of N_2, for example, $\sim$9.7 eV). Nevertheless, when a collection of molecular oscillators is subjected to sufficiently high pressure, one can expect molecular dissociation and transformation to a monatomic system (e.g., [1]). This is a consequence of the electronic charge redistribution that follows from the increasing overlap of the molecular wave functions, the valence charge transfer, and the modification of the intramolecular potential. Elucidation of the detailed nature of these transformations represents one of the most important problems of condensed matter physics and has implications for the ongoing search for metallic hydrogen as well as new energetic materials.

At low and room temperatures molecular phases of hydrogen and nitrogen persist as orientationally ordered crystalline substances at surprisingly high pressure (at least in the range of several Mbar [2,3]), the corresponding compressional work ($\int PdV$) of which is comparable to the potential well depth [1] of the individual oscillators at 1 bar. Much less is known concerning the stability of molecular solid and liquid phases under *simultaneous* conditions of high pressure and temperature. Shock-wave compression experiments have been almost the sole way to obtain experimental data under such conditions. The dissociation of H_2 and N_2 molecules and the formation of metallic states during shock-wave compression has been reported [4,5]. Corresponding experiments under static conditions have been limited to below a few hundreds of degrees because of the difficulties of containing the sample, which becomes highly reactive and/or mobile [6–8]. Theoretical calculations were extensively used to explore the intramolecular bonding in H_2 under extreme conditions using a mean-field approach [1], and also effective potentials that include an electronic response [9]. These calculations show that although the change of frequency of the intramolecular stretching mode, or "vibron" is very moderate over a wide pressure range (which is qualitatively consistent with experimental observation), the intramolecular potential nevertheless weakens substantially at high densities (due to charge transfer), and the interactions between different proton pairs become important.

In this Letter we report Raman measurements of compressed H_2, D_2, and N_2 at temperatures above the corresponding melting curves. In contrast to previous investigations, we probe the intramolecular bonding by observing vibrational transitions not only from the ground to the first excited state but also from the excited states (which become populated due to thermal excitation) to higher excited states. The frequencies of these transitions are lower than that corresponding to the transition from the ground vibrational state, which is a consequence of the anharmonicity of the interatomic potential. We do, however, find that as the pressure is increased these differences in frequency become smaller, implying that this anharmonicity *decreases.* By contrast, we find that the corresponding bands *broaden* with pressure (we note that the expected temperature softening and broadening were also observed), consistent with a weakening of the potential as molecular dissociation is approached.

We have performed the experiments using the laser-heated diamond anvil cell (DAC) in the manner described previously [10,11]. N_2 was loaded into the DAC cryogenically along with an iridium square with side of length 40 μm, with thickness of 5–10 μm, and with a central hole of 5–10 μm. This square was used to absorb incident laser light and thus consequently to heat the sample material contained in the hole. In some experiments thin (<5 μm) alumina plates were positioned adjacent to the tips of the diamond anvils to function as thermal insulators, so thermal gradients through the sample were minimized.

Experiments with hydrogen isotopes were performed in two steps. First, thin aluminum metal plates ($< 20\ \mu$m) were loaded into the DAC along with liquid water (H_2O or D_2O), pressurized to between 5 and 20 GPa, and then laser heated to temperatures exceeding 2000 K. This procedure initiated a predictable chemical reaction that yielded H_2 or D_2 and alumina as reaction products. We found that hydrogen isotopes accumulated in vesicles near areas of unreacted aluminum, which thus permitted further laser heating. In the second stage of the experiment Raman spectra were collected as a function of temperature (typically to 1600 K). Thin iridium plates or powder were also occasionally included in the DAC cavity to enhance the laser heating efficiency. We found that the hydrogen isotopes often migrated during laser heating and that clathrates formed with unreacted water [12] upon cooling the samples. Clathrates were easily identified because the corresponding vibron frequency is larger than that of the free isotope and also because of the appearance of higher frequency sidebands similar to those that have been observed in other hydrogen containing van der Waals compounds [13]. We find that clathrates break down to release hydrogen when heated above approximately 1000–1200 K below 50 GPa, but remain stable at higher pressures and temperatures above 1500 K. This may be related to the triple point on the water phase diagram that has recently been identified [11].

The results presented in this work refer to temperatures measured radiometrically and also obtained from the ratio of the Stokes to anti-Stokes Raman intensities. These two estimates were consistent within the mutual uncertainties ($\sim$100 K). Pressure was measured at room temperature using a ruby manometer before and after experiment and was assumed to be temperature independent [10,11].

Figure 1 shows representative high-temperature Raman spectra. Prior to melting, the Raman spectrum of N_2 exhibits two major vibron bands (above 4 GPa) associated with molecules occupying nonequivalent crystallographic positions. Naturally, only one vibron branch is expected in the liquid state [6]. In addition to this main vibron band, the spectra of hot compressed N_2 reveal a number of additional lower-frequency peaks whose intensities decreased with decreasing frequency [Figs. 1(a) and 1(b)]. The frequency separations between these additional peaks were all approximately equal. We observed a single lower-frequency peak in hot H_2 and D_2 [Figs. 1(c) and 1(d)]. The intensities of these additional modes in all three materials increased with temperature according to the Boltzmann relation $I_{n,n+1} \sim (n+1)^{*} \exp(-\hbar\omega/kT)$, where n is the vibrational quantum number and ω is the vibrational frequency. It was encouraging to note that the application of this relation to the experimental intensities (Fig. 1) yielded temperatures that were in agreement with those obtained using the methods described earlier. This fact confirms the assignment of the additional modes to vibrational transitions from excited states [see also a coherent anti-Stokes Raman spectroscopy (CARS) study on N_2 [14,15]] and also implies that the temperature gradient across the relevant area of the sample (i.e., the area that was insulated from the anvils by the alumina plates) was small. The transitions up to and from the third excited level [the (3, 4) transition] were observed in N_2 while only the (1, 2) transition was observed in H_2 and D_2, in addition to the familiar (0, 1) transition that was observed in all three. This distinction may be accounted for by considering the sizable differences between the vibrational energy of N_2 and those of the hydrogen isotopes.

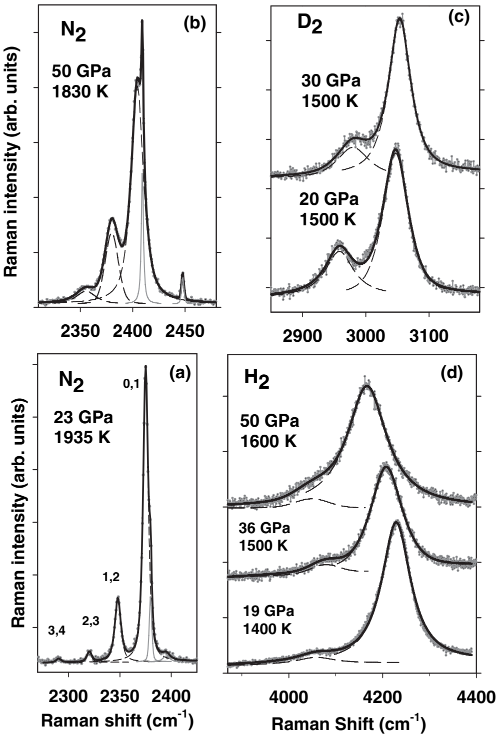

FIG. 1. High-temperature Raman spectra of hot N_2 (a),(b), D_2 (c), and H_2 (d) at different pressures. Dotted gray line, experiment; black thick line, phenomenological fit; dashed black and solid gray lines represent individual components used to fit the spectra. The spectra of N_2 (a),(b) show a small contribution from the cooler part of the sample that is adjacent to the diamond anvil tips (solid gray lines) and that is separated from the hot region by the alumina insulation.

Raman frequencies of the vibron modes of liquid N_2 (at temperatures between 1500 and 1900 K) show a monotonic dependence on pressure to at least 50 GPa [Fig. 2(a)]. Frequencies obtained using the CARS technique under static [15] and dynamic [14] conditions up to 20 GPa are mutually consistent but are slightly smaller than our values [Fig. 2(a)]. This discrepancy is unlikely to be a consequence of different experimental temperatures, since according to our results the temperature dependence of the N_2 vibron is weak. We also clearly observe that the anharmonic shifts of the vibron frequencies corresponding to

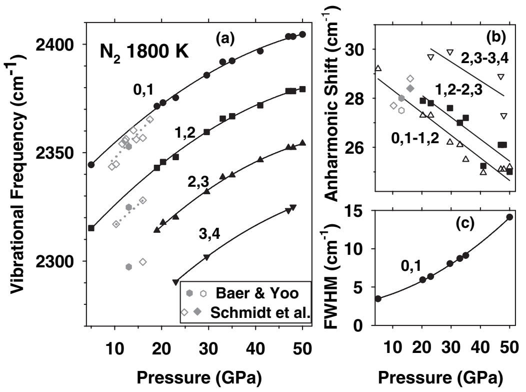

FIG. 2. (a) Pressure dependences of measured vibron frequencies in N_2 corresponding to transitions between vibrational levels n and $n + 1$ $(n, n + 1)$, where n is the vibrational quantum number; (b) anharmonic frequency shifts (see text); (c) linewidth of the (0, 1) transition. Gray symbols correspond to CARS data from Refs. [14,15] at 2000 and 655–2400 K, respectively.

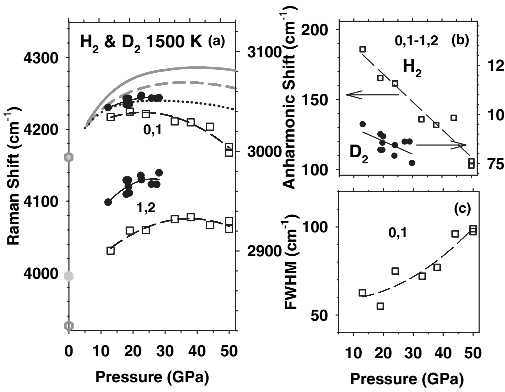

FIG. 3. Same as in Fig. 2 but for H_2 (open squares and dashed lines) and D_2 (filled circles and solid lines). The frequencies of the 0, 1 and 1, 2 transitions [Fig. 3(a)] of D_2 (right axis) have been uniformly scaled such that the frequencies of the 0, 1 transition are in agreement with those of H_2 (left axis) at 0 GPa. Gray lines in (a) show room temperature data [21]. Open and filled gray hexagons are vibrational quanta at ambient pressure for H_2 and D_2, respectively [22]. Dotted line in (a) corresponds to the vibron frequency of solid H_2 at the melting curve [8]. (b) compares the anharmonic frequency shifts for H_2 and D_2 scaled in the same manner as in Fig. 3(a).

transitions from excited states become smaller with pressure [Fig. 2(b)]—a new and unexpected observation. It is also worth noting that the vibron linewidth increases with pressure [Fig. 2(c)].

In H_2 and D_2 the temperature dependence of the vibron frequency and the linewidth is much stronger than in N_2 (Fig. 3). This may be accounted for by considering the relatively larger rotational anharmonic constant of the hydrogen isotopes, and the fact that the line broadening and softening are in part a consequence of an increasing population of thermally excited rotational levels. Moreover, these dependences become even stronger at higher pressure (see also [8]). We find that the vibron frequency depends strongly on temperature in the liquid state by comparing the vibron frequency just under the melting curve [8] with our measurements at higher temperature (Fig. 3). As a result, the frequency of the H_2 vibron at high temperature passes through a maximum that is located at lower pressure compared with that observed at room temperature. The pressure dependence of the (1, 2) transition is also nonmonotonic, the anharmonic shift, however, linearly decreases with pressure [Fig. 3(b)] and at a much faster rate than in the case of N_2. The spectral positions of the additional peak in H_2 and D_2 are in agreement with experiment and theoretical calculations in the limit of low densities [Fig. 3(a)]. The vibron linewidth also increases with pressure [Fig. 3(c)]. The results for D_2 are qualitatively similar, but the vibron softening and the rate of decrease of the anharmonic shift is smaller [Figs. 3(a) and 3(b)].

We now consider the implications for the intramolecular potential of the results just described. We assume that the effect of pressure on the potential is to increase the electronic kinetic energy by a value equal to the corresponding work done during the isothermal compression, A. This increase naturally tends to reduce the amount of energy required for molecular dissociation, D [1,16]. We have computed A using the equation of state of solids at ambient temperature [17,18] (we neglected the thermal expansion because no data are available). Compression to 50 GPa corresponds to approximately 0.8 and 1 eV per molecule additional electronic energy for N_2 and the hydrogen isotopes, respectively.

It has commonly been assumed that the overlap of individual oscillator wave functions remains small at moderate compression, although the parameters of the potential may be a function of density [1]. A particularly convenient and illustrative model potential to test this assumption is that proposed by Morse: $\Phi = D[\exp(-2\alpha(r - r_m)) - 2\exp(-\alpha(r - r_m))]$, where α is the range parameter and r_m is the position of the potential minimum. It has the advantage that it is analytically tractable [19].

We estimate the relevant parameters of the Morse potential for N_2 and the hydrogen isotopes as described below. We assume the potential depth at ambient pressure, D_0, to be that of the empirical Rydberg-Klein-Rees potential. Subtraction of our calculated value of A at each pressure from D_0 yields an estimate of D. To obtain α we note that for the Morse potential the frequency corresponding to the (0, 1) transition is given by $\hbar\omega_{0-1} = 2\alpha(D/2\mu)^{1/2} - \alpha^2/\mu$, where μ is the reduced mass. Experimentally determined frequencies together with our values for D are then used to determine α. Following [1,20] we also determine D and α for hydrogen independently by solving simultaneously the corresponding equations for each isotope. The results of these procedures are

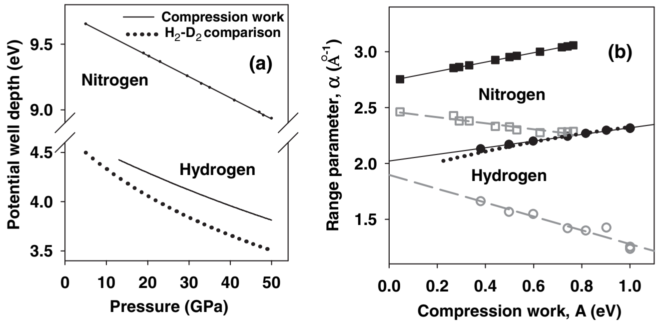

FIG. 4. Parameters of the model Morse potential under compression. (a) Potential well depth (D). Solid lines: results obtained from calculation of compressional work. Dotted line: results obtained independently by comparing vibron frequencies of H_2 and D_2 (see text). (b) Range parameter (α) as a function of compression work (A), Black symbols: α is determined from the frequency of the (0, 1) vibrational transition; gray symbols: α is determined from the anharmonic shift associated with the transition from the first excited energy level. The dotted line was obtained in the same way as for Fig. 4(a).

shown in Fig. 4. We note first that the assumption concerning the decrease of D with the increase of A is justified for hydrogen in light of the good agreement obtained for the two distinct approaches [Fig. 4(a)]. The range parameter α is seen to increase monotonically for both N_2 and the hydrogen isotopes [Fig. 4(b)], and again, in the case of H_2, the values obtained for α are consistent for the two approaches. Since the anharmonic shift of the vibrational transitions is $\hbar\Delta\omega = \alpha^2/\mu$, it is easy to see that an increasing α leads to an increasingly anharmonic potential. However, if we consider the *measured* anharmonic shift, we get precisely the opposite result that is that the potential becomes increasingly *harmonic* [Fig. 4(b)]. It is worth noting that at nearly ambient pressure both determinations of α yield nearly consistent results [Fig. 4(b)], implying that under this condition the Morse potential is satisfactory, as expected. The discrepancy at high pressure, however, must be due to the inadequacy of a single Morse function to model the effective intramolecular potential.

In conclusion, we have examined the intramolecular potentials of hot H_2, D_2, and N_2 to a pressure of 50 GPa. On the basis of measured transitions from the ground and excited states of the molecular vibron (that probe the potential further away from the equilibrium position), we have found that in all three cases the potential becomes less anharmonic. Concomitantly, the increase of the linewidth of the vibron band indicates that the potential barrier for molecular dissociation decreases with compression. These effects are most pronounced in hydrogen because of the relatively high vibron energy (with respect to the potential well depth). Theoretical calculations of the intramolecular potential function under conditions when the individual molecular oscillators cannot be considered independent are necessary to fully understand the observed behavior.

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