Synchrotron Infrared Spectroscopy at Megabar Pressures: Vibrational Dynamics of Hydrogen to 180 GPa

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(Received 6 January 1992)

We have developed new techniques for measuring infrared spectra at megabar pressures using synchrotron radiation and applied them to study the $Q_1(1)$, $Q_1(1)+S_1(0)$, and $Q_R(J)$ vibrational transitions of solid hydrogen to 180 GPa. The frequency difference between the $Q_1(1)$ infrared and Raman vibrons increases from 3 cm^{-1} (zero pressure) to 510 cm^{-1} (180 GPa), indicating a dramatic increase in intermolecular coupling with pressure. A negative frequency shift is observed for the infrared vibron above 140 GPa. A significant increase in frequency and LO-TO splitting of the lattice phonon is also documented.

PACS numbers: 78.30.Hv, 62.50.+p, 63.20.−e

The density dependence of intermolecular and intramolecular interactions in solid hydrogen is fundamental to understanding the range of structure, dynamics, and phase transitions in this material, from quantum-solid behavior of the low-density molecular solid to theoretically predicted monatomic phases at ultrahigh pressures [1]. One of the critical issues is the mechanism responsible for the decrease in the frequency of the Raman-active (intramolecular) vibron at 30 GPa in hydrogen and 50 GPa in deuterium [2-4]. The negative pressure shift continues to higher pressures above 100 GPa [5-7]. This result has been ascribed to the development of increasing intermolecular and decreasing intramolecular bonding with pressure, and has been regarded as a possible precursor to dissociation. In the megabar range (> 100 GPa), profound changes in interactions are expected due to the onset of band-overlap metallization and related transitions [8]. Further evidence for changes in intermolecular forces with pressure has been obtained from calculations of pressure-volume relations using gas-phase (or low-density) intermolecular potentials for hydrogen [9], which show a significant departure from accurate equations of state determined by diffraction techniques [10]. Moreover, the phonon frequencies calculated from such potentials differ significantly from direct measurements by Raman spectroscopy [8,11]. These results demonstrate that although appreciable increases in intermolecular interactions occur with increasing density, the form of the potentials and a quantitative understanding of the vibrational dynamics in the high-density solid are not yet in hand.

Additional types of vibrational spectroscopic measurements are required to evaluate separately the intramolecular and intermolecular interactions. Raman studies of H_2 and D_2 molecules isolated in rare-gas matrices and of hydrogen isotopic mixtures provide such information, but these have been limited to moderate pressures [12,13]. The infrared absorption spectrum of solid hydrogen consists of vibrational and rotational transitions induced by fluctuating dipole moments that arise from intermolecular interaction in condensed phase [1]. The infrared absorption spectrum of solid hydrogen at ambient pressure has been measured in detail by Gush *et al.* [14]. Because of the sensitivity of the spectra to the range and extent of intermolecular interactions [1], infrared measurements of hydrogen as a function of pressure assume a critical role for determining the variation in such interactions with density. Such measurements have been performed to moderate pressures [15,16], but none has yet been conducted in the megabar range (> 100 GPa).

Infrared measurements at high densities are complicated by the extremely small sample sizes needed for reaching the highest pressures (< 10 picoliter at > 100 GPa). The consequence of these small sample sizes is the reduced aperture (< 20 μm diameter) through which the transmission measurement is made. These measurements have not been possible with conventional light sources, in particular, if higher spectral resolution compared to previous studies [17] is needed. Synchrotron radiation, with its high brilliance, is an ideal source for measurements on ultrasmall samples [18]. We have developed new techniques for the use of synchrotron radiation for infrared spectroscopy at megabar pressures (> 100 GPa). Here we apply these to study vibrational transitions in solid molecular hydrogen as a function of pressure to 180 GPa. The data document the existence of extensive intermolecular coupling in high-density hydrogen and uncover the origin of the turnover of the Raman-active vibron. In addition, the measurements show a significant increase in the LO-phonon frequency and LO-TO splitting with pressure. Further, knowledge of the contributions of vibrational transitions to the infrared absorption of hydrogen is necessary to determine the changes in the infrared caused by electronic excitations (e.g., associated with metallization) [17].

Hydrogen samples were loaded in modified megabar (Mao-Bell) diamond cells using techniques described in detail previously [8,11]. The measurements were performed on the U4-IR beam line [18] at the National Synchrotron Light Source, Brookhaven National Laboratory,

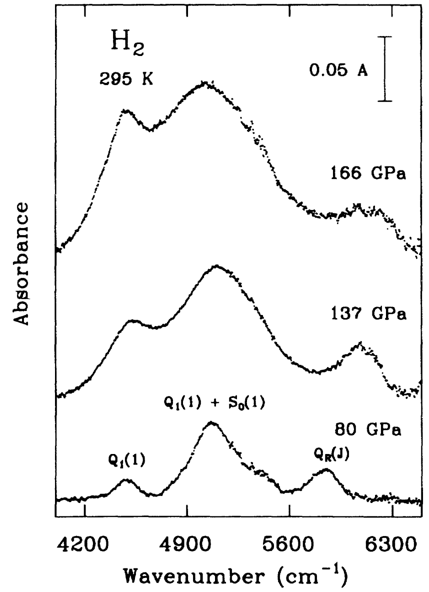

FIG. 1. Representative absorption spectra of hydrogen at 80, 137, and 166 GPa (295 K). The intensity in absorbance is given by the vertical scale bar and is identical for the three spectra. A background signal is subtracted from each spectrum to give a constant absorbance at 4000 and 6800 cm^{-1} in order to bring out the discrete vibrational peaks analyzed in the present study.

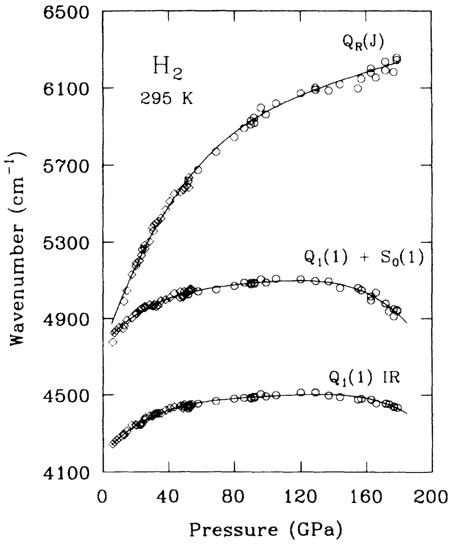

FIG. 2. Pressure dependence of the frequencies of the principal mid-infrared absorption bands. Circles, this study; diamonds, Mao, Xu, and Bell [16].

using a Nicolet 740 Fourier transform spectrometer. The optical system was extensively modified for megabar diamond-cell experiments and will be described in detail elsewhere [19]. Two experiments at 295 K were performed. The pressures were determined from both the ruby R_1 line and the frequency of the Raman vibron, which has been precisely calibrated against ruby [8].

Infrared absorption spectra of hydrogen at different pressures are presented in Fig. 1. Three bands are well resolved in the frequency range 4000-6500 cm^{-1}. Comparisons with low-pressure measurements [14-16] show that the first band arises from the excitation of a $Q_1(1)$ intramolecular stretching mode (vibron). The second band $[Q_1(1)+S_1(0)]$ is due to the simultaneous creation of a $Q_1(1)$ vibron and a $S_1(0)$ rotational excitation (roton), while the third band $[Q_R(J)]$ arises from the excitation of a vibron and a lattice mode (phonon). The intensity of the $Q_1(1)$ and $Q_1(1)+S_1(0)$ bands increases with pressure approximately as ρ^2, as noted in previous measurements to 54 GPa by Mao, Xu, and Bell [16]. The results are also consistent with earlier low-resolution measurements of Hanfland, Hemley, and Mao [17] over the same pressure range. The improved resolution and signal/noise of the new spectra show that vibrational transitions form a major contribution to the near-infrared absorption. This possibility was discussed in Ref. [17]. The pressure dependencies of the frequencies of the three bands are shown in Fig. 2 together with the results of the previous low-pressure study [16]. The frequency of the $Q_1(1)$ vibron increases with pressure, but passes through a broad maximum at 100-145 GPa. The pressure dependence of the $Q_1(1)+S_0(1)$ roton-vibron combination band is very similar to that of the vibron. In contrast, the frequency of the $Q_R(J)$ phonon-vibron combination band increases steeply with pressure; this is due to the large pressure shift of the phonon [11].

The results may be understood within the framework of the theory developed by van Kranendonk [1] for the low-density solid. The $Q_1(1)$ vibrational excitations of solid hydrogen form a band with a width of $\sim 8\varepsilon'$, where ε' is the nearest-neighbor vibrational coupling parameter [1]. The vibron frequency measured by infrared absorption is close to the band origin $\nu_{\mathrm{IR}} \approx \nu_0$, whereas that measured by Raman corresponds to the bottom of the vibron band, $\nu_R = \nu_0 - 6\varepsilon'$ [1,20]. A comparison of the infrared and Raman-active vibrons provides detailed information on the increase in intermolecular interaction with pressure or density. Figure 3 shows the density dependence of $\nu[Q_1(1)_{\mathrm{IR}}]$ and $\nu[Q_1(1)_R]$, and their difference $\Delta\nu = \nu[Q_1(1)_{\mathrm{IR}}] - \nu[Q_1(1)_R]$. The maximum in the frequency of the Raman mode at $\rho/\rho_0 \approx 5$ (30 GPa) and marked decrease at higher density is indicated. Although the shift of $Q_1(1)_{\mathrm{IR}}$ is significantly steeper than that of $Q_1(1)_R$ [16], the present measurements establish that at $\rho/\rho_0 \approx 8.9$ (~ 140 GPa), the infrared vibron also undergoes a turnover. At $\rho/\rho_0 = 1$ (zero pressure and 4 K), $\Delta\nu$ ($\approx 6\varepsilon'$) is 3 cm^{-1} [14]. The difference increases markedly with density such that $\Delta\nu = 510$ cm^{-1} at $\rho/\rho_0 \approx 9.9$ (180 GPa). Within the van Kranendonk model, the vibron bandwidth $8\varepsilon'$ thus reaches 680 cm^{-1}. Daniels and Brown [12] and Loubeyre, Letoullec, and Pinceaux [13] determined $6\varepsilon'$ to 60 and 40 GPa ($\rho/\rho_0 \approx 6.4$ and 5.5), respectively, by measuring the Ra-

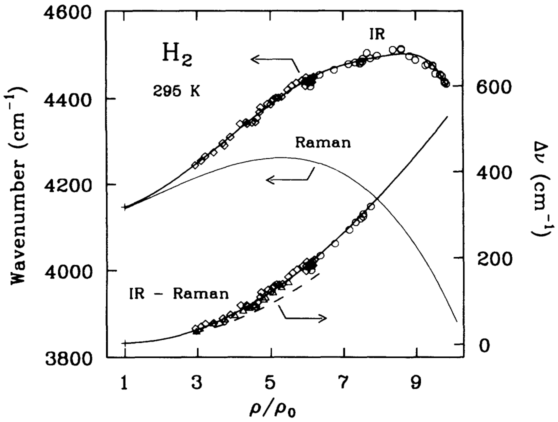

FIG. 3. Density dependence of the Raman [2,8] and infrared vibron frequencies and of their difference $\Delta\nu$, which is close to effective nearest-neighbor coupling constant $\sim 6\varepsilon'$ of the van Kranendonk model [1,20]. The circles are from this study and correspond to direct measurements of both the infrared and Raman-active vibron peaks on the same sample and the same pressure. The crosses are the zero-pressure values of Gush *et al.* [14], and the diamonds are the results of the low-pressure infrared study of Mao, Xu, and Bell [16]. The results of Raman studies of isotopic mixtures by Daniels and Brown [12] and by Loubeyre and co-workers [13] are given by the dashed line and triangles, respectively.

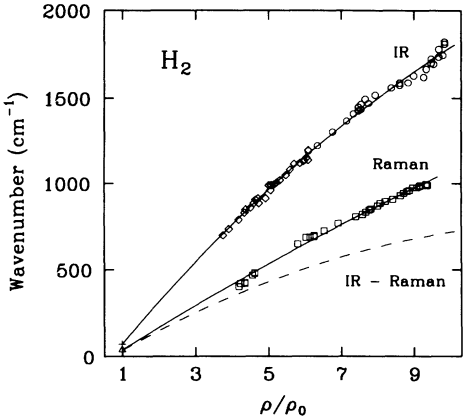

FIG. 4. Density dependence of the phonon frequencies obtained from the infrared and Raman measurements. Infrared: cross, Gush *et al.* [14]; circles, this study; diamonds, Mao, Xu, and Bell [16]. Raman: see Hemley, Mao, and Shu [11] and references therein. The dashed line shows the difference between the IR and Raman phonon frequencies.

man frequency of H_2 molecules isolated in D_2 matrices. The results of these experiments, also shown in Fig. 3, agree well with our data in the lower-density range (particularly those of Ref. [13]).

These results have direct implications for the determination of effective potentials from high-pressure vibrational spectra, and provide the means for resolving the problem of predicting the pressure dependence of the vibron frequency. Chakravarty *et al.* [21] used local-density methods to calculate the frequency of the intramolecular stretching mode and found it to increase monotonically with pressure (no turnover). A similar result was obtained by Wijngaarden, Lagendijk, and Silvera [4] who calculated the pressure dependence of the Raman mode using an effective intramolecular potential. In these calculations [4], it was assumed that $6\varepsilon'$ can be neglected at high pressure (i.e., < 3 cm^{-1} [14]). In contrast, the present measurements demonstrate that the vibrational coupling increases markedly with pressure: $6\varepsilon' \approx \Delta\nu = 120$ cm^{-1} at 30 GPa (pressure of the turnover of the Raman vibron in H_2, $\rho/\rho_0 \approx 5$) and reaches 510 cm^{-1} at 180 GPa ($\rho/\rho_0 \approx 9.9$).

Ashcroft [22] modeled the turnover with a simple volume-dependent Morse potential that was fitted to the Raman frequencies for H_2 and D_2 to 147 GPa [5]. According to this model, both the frequency turnover and the pronounced isotope effect on the vibron frequency [3-5] result from increasing anharmonicity in the molecular bond with compression. The present results reveal that the potential obtained from such a fit is actually an effective potential for coupled, in-phase (Raman-active) intramolecular motion, which differs strongly from that of uncoupled (or out-of-phase) intramolecular motion. Further, the anharmonicity obtained from such a fit arises from the lowering of an effective dissociation energy (saddle point) where the two bare molecule potentials cross. At the saddle point the bare molecule potential goes as R^{-6}, the leading term of a van der Waals interaction [23]. Fitting our data, we find that the force constant for vibrational coupling $k = \nu[Q_1(1)_{\rm IR}]^2 - \nu[Q_1(1)_R]^2$ varies as $R^{-6.89(5)}$, where R is the intermolecular distance in hcp hydrogen determined from the experimental equation of state [9]. This dependence is close to that determined by Loubeyre, Letoullec, and Pinceaux [13] to 40 GPa. The results show that the principal origin of the coupling, and hence the anharmonicity in the effective intramolecular potential, may be a van der Waals-type (induced dipole) interaction; however, the measured dependence is steeper than the leading term in such an expansion.

Additional information is obtained from the pressure dependence of the higher frequency $Q_R(J)$ band. The difference $\nu_{\rm IR} = \nu[Q_R(J)] - \nu[Q_1(1)_{\rm IR}]$ is essentially the frequency of the longitudinal-optical (LO) phonon of hexagonal-closed-packed (hcp) hydrogen. The LO-phonon frequency determined by inelastic neutron scattering is 82 cm^{-1} near $\rho/\rho_0 = 1$ [24]. Zero-pressure infrared measurements [14] give $\nu_{\rm IR} = 76.5$ cm^{-1}. Figure 4 shows that this quantity increases to 1800 cm^{-1} at $\rho/\rho_0 \approx 9.9$ (180 GPa). The transverse-optical (TO) phonon of hcp hydrogen is Raman-active and its density dependence, which has been studied to $\rho/\rho_0 > 9.1$ (150 GPa) [11], is also shown in Fig. 4. A significant increase in the LO-TO splitting is observed ($\nu_{\rm IR} - \nu_R = 715$ cm^{-1} at 180 GPa). Further, the uniform shifts of the phonon and rotational bands observed in both IR and Raman argue strongly for continuity of a structure close to hcp to these high densities [8,11].

In conclusion, new synchrotron radiation techniques have been developed for measurement of infrared spectra of samples at ultrahigh (megabar) pressures and have been used to study vibrational transitions in solid hydrogen to 180 GPa. Analysis of the spectra shows that the vibrational coupling increases by over 2 orders of magnitude with pressure over this range ($\rho/\rho_0 > 9$). The results reveal that the origin of vibron turnover, now observed in both the Raman and infrared branches, is due to the combination of increasing intermolecular and decreasing intramolecular interactions. The increase in intermolecular interaction arises from increasing charge redistribution associated with intramolecular vibrations, analogous to electronic "orbital following" effects in coupled stretching vibrations in conjugated chains [25]. The changes eventually force a decrease in the infrared vibron frequency (band origin), which is indicative of a gradual bond weakening, behavior expected at an electronic delocalization transition or as a precursor of molecular dissociation. Finally, this study demonstrates intrinsic advantages of infrared measurements over the Raman technique, which has been the predominant method for characterizing structural and vibrational properties of hydrogen at megabar pressures. Specifically, the infrared measurements are not complicated by interference from visible absorption and fluorescence of the stressed diamond anvils, and they reveal well-defined vibron, phonon, and rotational excitations. The present techniques should be useful for investigations of a wide variety of materials at megabar to multimegabar pressures.

We thank W. B. Daniels for very useful discussions, and P. Loubeyre for communicating results prior to publication. This work was supported by NSF (DMR-8912226, EAR-8920239), NASA (NAGW1722), and DOE (DE-AC-2-76CH00016).

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