

Brillouin Measurements of Solid $n\text{-H}_2$ and $n\text{-D}_2$ to 200 kbar at Room Temperature

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Using a five-pass interferometric Brillouin spectrometer, we have measured the pressure dependence of longitudinal- and transverse-acoustic velocities and refractive index of solid $n\text{-H}_2$ and $n\text{-D}_2$ at room temperature in a diamond-anvil cell up to 200 kbar. The equations of state have been determined ($55 \leq P \leq 200$ kbar: $\rho = 0.0734P^{0.334} - 0.0214$ for solid $n\text{-H}_2$, and $\rho = 0.148P^{0.334} - 0.0627$ for solid $n\text{-D}_2$, with P in kbar and ρ in g/cm^3).

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High-density properties of molecular hydrogen and its isotope deuterium have been the subject of recent studies in which ultrasonic measurements have been made in the range 75 to 300 K and 2 to 20 kbar (1 kbar = 0.1 GPa) for $n\text{-H}_2$ and $n\text{-D}_2$,¹⁻⁴ visual observations by using a microscope at 300 K up to 500 kbar for $n\text{-H}_2$,⁵ and Raman measurements at 5 K up to 150 kbar for $o\text{-D}_2$,⁶ and at 300 K up to 630 kbar for $n\text{-H}_2$.⁷ However, very little is known about Brillouin scattering⁸ which can ascertain the fundamental thermodynamic relation between pressure and density, that is, the equation of state (EOS).

In this paper we report the first Brillouin measurements of solid $n\text{-H}_2$ and $n\text{-D}_2$ (including fluid-solid phase transition) in a diamond-anvil cell up to 200 kbar at 300 K. The pressure dependence of longitudinal and transverse acoustic phonon velocities and refractive index was obtained to determine EOS and the pressure dependence of elastic moduli and polarizability.

A five-pass interferometric Brillouin spectrometer, described previously,⁹ was used. The $\lambda_0 = 514.5$ nm Ar⁺-laser line with single longitudinal mode was used for excitation at power levels from 300 to 600 mW input. Since a variation of acoustic sound velocity with incident laser power was not observed, sample heating effects were unimportant. The 90° scattering geometry was used principally to determine the adiabatic sound velocity (U_s). The Brillouin frequency shift between the scattered and incident frequencies, $\nu_s - \nu_i = \pm \nu_1$, is related to U_s by the expression $U_{s1} = \nu_1 \lambda_0 / \sqrt{2}$, which is independent of refractive index of a medium.¹⁰ The wave vector of the acoustic phonon is parallel to interfaces of the input and output diamonds crossed by the laser beam.

There is also a laser beam reflected from the

output diamond anvil that serves as incident light, giving a backscattered signal. In this case the Brillouin shift ν_2 is related to U_s by the expression $U_{s2} = \nu_2 \lambda_0 / (2n)$, where the refractive index n of the medium is assumed to be homogeneous. The wave vector of this acoustic phonon is not parallel to diamond interfaces. For an isotropic medium, the ratio of ν_1 to ν_2 , $\nu_1/\nu_2 = 1/(\sqrt{2}n)$ determines the value of n . Furthermore, 60° and 120° scattering geometries¹¹ were used in order to estimate the direction dependence of U_s , that is, the anisotropy in solid $n\text{-H}_2$ and $n\text{-D}_2$.¹²

The high-pressure cell used was a modified version that could be operated at cryogenic temperatures for filling the chamber with liquefied gas.¹³ The sample chamber was a small cylindrical hole (diam, 0.2 mm; depth, 10 μm) drilled in stainless steel. Small ruby crystals (10 μm) for pressure calibration were placed inside the sample chamber prior to filling with $n\text{-H}_2$ and $n\text{-D}_2$. Fluid $n\text{-H}_2$ and $n\text{-D}_2$ were sealed in the sample chamber by operating the cell in a liquid He cryostat. The samples were pressurized to 10–50 kbar before the cell was removed from the cryostat. After removal, the cell was warmed to room temperature. The pressure was determined by measuring the shift in wavelength of the R_1 fluorescence from the ruby crystal; $P(\text{kbar}) = 3808[(\lambda/\lambda_0)^5 - 1]$, where λ_0 is the wavelength of the $R(1)$ line at 1 bar, and λ the wavelength at pressure P .¹⁴ The pressure was measured before and after the Brillouin spectrum was obtained. No systematic variation between these two measurements has been observed. Both fluid $n\text{-H}_2$,⁵ and $n\text{-D}_2$ transform to transparent solids at about 55 kbar and 300 K.^{5,15} In our present experiments we did not find whether solid $n\text{-H}_2$ and $n\text{-D}_2$ are single crystalline¹⁶ or polycrystalline.

Figure 1 shows the pressure dependence of sound velocity determined from the normal frequency shift at 90° scattering geometry. The vertical scale for $n\text{-H}_2$ sound velocity is $\sqrt{2}$ times that for the $n\text{-D}_2$ sound velocity. Lattice dynamics suggest that $U_s(n\text{-H}_2)/U_s(n\text{-D}_2) = (M_{n\text{-D}_2}/M_{n\text{-H}_2})^{1/2} = \sqrt{2}$, where $M_{n\text{-D}_2}$ and $M_{n\text{-H}_2}$ are the molecular weights of $n\text{-D}_2$ and $n\text{-H}_2$, respectively. This relation is approximately obeyed at all pressures. At the fluid-solid phase transition point ($P=55$ kbar), sound velocities of both $n\text{-H}_2$ and $n\text{-D}_2$ in their fluid phases show a discontinuous change to longitudinal acoustic (LA) and transverse acoustic (TA) velocities in their solid phases. As shown in Fig. 2 the intensity of TA mode (ν_t) is weak in comparison with that of LA mode (ν_l) for solid $n\text{-H}_2$ and $n\text{-D}_2$. The linear behavior of plots of $\log U_s$ vs $\log P$ in the solid phase gives the pressure dependence of each velocity which can be represented by power laws,

$$U_s(n\text{-H}_2, \text{LA}) = 2.68 P^{0.333} \quad (1a)$$

$$U_s(n\text{-H}_2, \text{TA}) = 1.52 P^{0.333} \quad (1b)$$

$$U_s(n\text{-D}_2, \text{LA}) = 1.89 P^{0.333} \quad (2a)$$

$$U_s(n\text{-D}_2, \text{TA}) = 1.08 P^{0.333} \quad (2b)$$

with P in kbar and U_s in km/sec.

Figure 2 shows a typical Brillouin spectrum of solid $n\text{-D}_2$ at 200.6 kbar and 300 K. Backscattered signals of ν_{l2} on the left and right sides of the Rayleigh peak belong to the previous and the

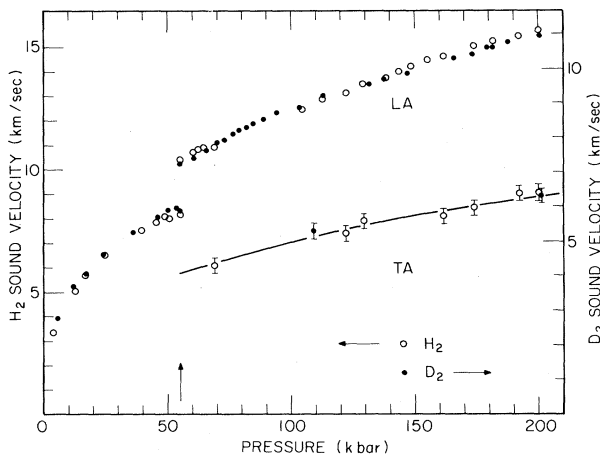


FIG. 1. Sound velocity of $n\text{-H}_2$ and $n\text{-D}_2$ with pressure. Open circles, $n\text{-H}_2$; solid circles, $n\text{-D}_2$. The vertical scale for $n\text{-H}_2$ sound velocity is $\sqrt{2}$ times that for the $n\text{-D}_2$ sound velocity. LA, longitudinal acoustic mode; TA, transverse acoustic mode. Vertical arrow indicates the fluid-solid phase transition point (55 kbar).

next-order Rayleigh peaks, respectively. The value of n can be estimated by the relation of $\nu_{l1}/\nu_{l2} = 1/(\sqrt{2}n)$. To estimate whether solid $n\text{-H}_2$ and $n\text{-D}_2$ are acoustically isotropic or anisotropic, we measured the direction dependence of the sound velocity at 60°, 90°, and 120° scattering geometries at 136 kbar and at room temperature: For each optical geometry the spectra were taken for two configurations of the diamond-anvil cell by rotating by 90° about the anvil axis. Within the experimental error ($\pm 1.5\%$ in velocity) all velocities for different phonon directions have the same values under the assumption of homogeneous refractive index; that is, all data of velocity and refractive index are consistent with isotropy. Therefore, for our Brillouin study, solid $n\text{-H}_2$ and $n\text{-D}_2$ are treated as acoustically isotropic crystals at room temperature. Figure 3 shows the pressure dependence of refractive index of $n\text{-H}_2$ and $n\text{-D}_2$ obtained from the ratio of normal and backscattering frequency shifts at 90° scattering geometry. The values of n for $n\text{-H}_2$ and $n\text{-D}_2$ are almost the same and increase sharply with pressure. There is a small change at the fluid-solid phase transition point.

The density ρ at pressure P can be calculated from the present data with the expression

$$\rho(P_B) - \rho(P_A) = \int_{P_A}^{P_B} (\gamma/U_s^2) dP, \quad (3)$$

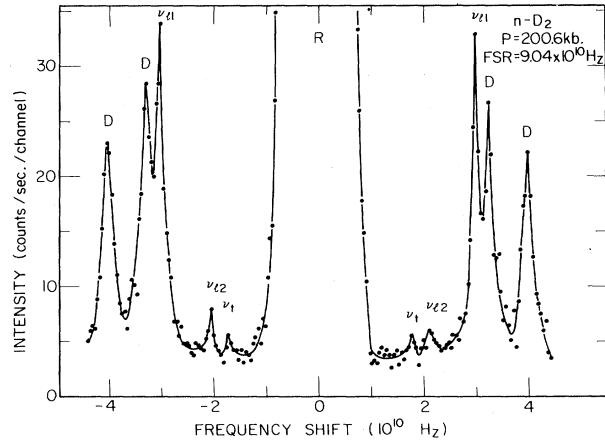


FIG. 2. Brillouin spectrum of solid $n\text{-D}_2$ at 200.6 kbar and 300 K. ν_{l1} and ν_t are Brillouin-shifted signals from longitudinal and transverse acoustic modes, respectively. ν_{l2} is the backscattered signal from LA mode; signals of ν_{l2} on the left and right sides of Rayleigh peak belong to the previous and the next order Rayleigh (R) peaks, respectively. D is the Brillouin-shifted signal from the diamond anvil.

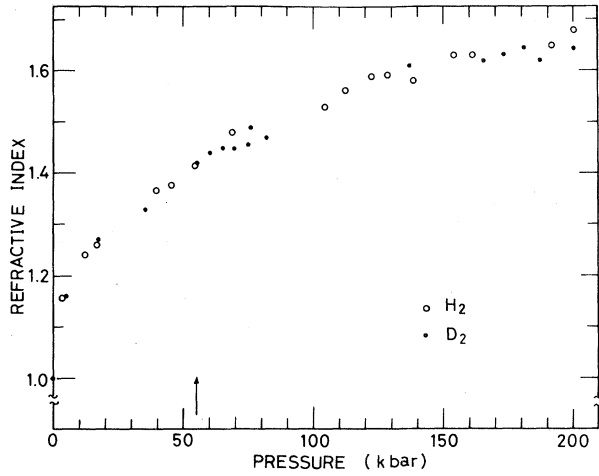


FIG. 3. Refractive index of $n\text{-H}_2$ and $n\text{-D}_2$ as a function of pressure. Open circles, $n\text{-H}_2$; solid circles, $n\text{-D}_2$.

where $\gamma = C_p/C_v$ is the ratio of the specific heats at constant pressure and volume.¹⁷ The value of ρ to 50 kbar in the fluid phase has been very recently calculated⁸ by using Eq. (3) and constant $\bar{\gamma} = 1.07$ for $n\text{-H}_2$ and $\bar{\gamma} = 1.10$ for $n\text{-D}_2$.¹⁸ The resulting equations of state at P in the fluid phase are $\rho(P) = 0.0577 P^{0.366} - 0.0006$ for $n\text{-H}_2$ and $\rho(P) = 0.126 P^{0.336} + 0.0048$ for $n\text{-D}_2$. The calculated values of fluid $n\text{-H}_2$ are plotted as open circles in Fig. 4. These values are almost the same as half of $\rho(P)$ for fluid $n\text{-D}_2$ at each pressure within 1.5%. We cannot estimate the expected isotope effect² on this system because of the accuracy of about $\pm 1.5\%$ in ρ . At the fluid-solid phase transition point, a small jump in ρ is expected.³ Since we could not measure its change by our method, we used Liebenberg's formula for the density change at the freezing point,³ which was extrapolated to room temperature from 164 K. The calculated density change is about 3.5% of the fluid density (see Fig. 4).

In an isotropic solid phase the adiabatic sound velocity U_s is represented by the expression

$$U_s = (U_{LA}^2 - \frac{4}{3} U_{TA}^2)^{1/2}, \quad (4)$$

where U_{LA} and U_{TA} are the longitudinal and transverse sound velocities. Using Eqs. (1a), (1b), (2a), (2b), and (4) we obtain, for solid $n\text{-H}_2$ and $n\text{-D}_2$,

$$U_s(n\text{-H}_2) = 2.02 P^{0.333}, \quad (5a)$$

$$U_s(n\text{-D}_2) = 1.42 P^{0.333}. \quad (5b)$$

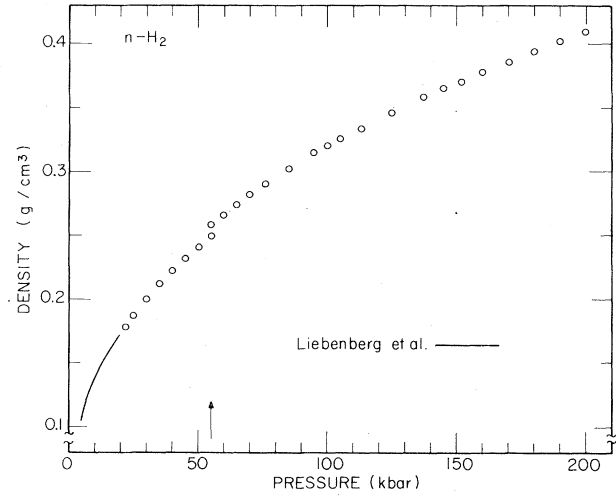


FIG. 4. Density of $n\text{-H}_2$ as a function of pressure. Open circles show the present result and solid line shows the result by Liebenberg *et al.* (Ref. 4).

Moreover, with Eqs. (3), (5a), and (5b), and constant $\bar{\gamma} = 1^{19}$ for $n\text{-H}_2$ and $n\text{-D}_2$ in their solid phases, the equations of state are obtained as follows ($55 \leq P \leq 200$ kbar):

$$\rho(P) = 0.0734 P^{0.334} - 0.0214 \text{ for solid } n\text{-H}_2, \quad (6a)$$

$$\rho(P) = 0.148 P^{0.334} - 0.0627 \text{ for solid } n\text{-D}_2. \quad (6b)$$

The calculated values of Eq. (6a) for solid $n\text{-H}_2$ are plotted as open circles in Fig. 4. The ρ increases sharply with pressure and has the value of about 0.4 g/cm^3 at 200 kbar. The molar volume ($= M/\rho$) of $n\text{-H}_2$ calculated from Eq. (6a), in contradiction to the expected isotope effect,^{2,20} shows the value about 2% smaller than that of $n\text{-D}_2$ from Eq. (6b) at each pressure, but this difference is within the experimental error of $\pm 1.5\%$ in the molar volume. Therefore, we cannot discuss the isotope effect from Eqs. (6a) and (6b). Within the error of our experiment, the molar volumes of solid $n\text{-H}_2$ and $n\text{-D}_2$ are almost the same at room temperature and at each pressure. It is interesting to note that if the extrapolation of Eq. (6a) for $n\text{-H}_2$ is possible to higher pressures, it yields $\rho = 0.80 \text{ g/cm}^3$ at $P = 1.38 \text{ Mbar}$.

Using $\rho(P)$ and LA and TA velocities we can calculate ρU_{LA}^2 and ρU_{TA}^2 corresponding to elastic moduli. The values of ρU_{LA}^2 and ρU_{TA}^2 for both solid $n\text{-H}_2$ and $n\text{-D}_2$ near 95 kbar are close to the values $C_{11} = 4.82 \times 10^{11} \text{ dyn/cm}^2$ and $C_{44} = 1.27 \times 10^{11} \text{ dyn/cm}^2$ of NaCl at 1 bar.¹⁰ Therefore, $n\text{-H}_2$ and $n\text{-D}_2$ are soft solids. The pressure dependence of ρU_{LA}^2 and ρU_{TA}^2 shows linear change with pres-

sure to 200 kbar: $\partial(\rho U_{LA}^2)/\partial P = 5.1$ and $\partial(\rho U_{TA}^2)/\partial P = 1.6$.

To calculate the polarizability the Lorenz-Lorentz relation was used²¹: $(n^2 - 1)/(n^2 + 2) = (4\pi/3) \times (N\alpha/V)$, when n is the refractive index, N Avogadro's number, V the molar volume ($= M/\rho$), and α the polarizability. Using the present results of $n(P)$ and $V(P)$, we can estimate the pressure dependence of α for n -H₂ and n -D₂. In their fluid phases α has pressure insensitive and constant value of 8.17×10^{-25} cm³.⁸ However, α shows a discontinuous decrease of about 4.5% at 55 kbar and, moreover, decreases gradually to the value of 7.12×10^{-25} cm³ at 200 kbar in their solid phases. Interpreting a decreasing α with a decrease in the volume of a molecule means that in solid n -H₂ and n -D₂ the molecules are compressed and become harder to deform or displace at these pressures.

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At low temperature and low pressure, solid n -H₂ undergoes a structural phase transition from a hexagonal close-packed lattice to a face-centered cubic one with increasing pressure.

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¹⁹Since the value of γ is unknown in the solid phase, the average value of $\bar{\gamma} = 1$ is assumed on the basis of Mills *et al.* (Refs. 1 and 2). γ tends to decrease with increasing pressure.

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