Raman Measurements of Hydrogen in the Pressure Range 0.2–630 kbar at Room Temperature

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Raman spectra of fluid hydrogen at room temperature include rotational, $S_0(J)$, and vibrational bands, $Q_1(J)$. The rotational bands become diffuse between 0.2 and 55 kbar, the solidification point at 22°C. Between 55 and 630 kbar, only $Q_1(1)$ was resolved. This band increases in frequency to 360 kbar, but the frequency decreases between 360 and 630 kbar. These phenomena are consistent with the softening of the molecular bond at high pressure.

Hydrogen is solid under cryogenic conditions, but does not solidify at room temperature unless the pressure is raised above approximately 55 kbar, a value that had until recently[1-3] been above the upper working pressure limit[4] because of experimental difficulties. The recent high-pressure experiments with hydrogen were conducted at 25 °C to 500 kbar (Ref. 1) although detailed studies of the properties of the phases of hydrogen still are available only at low temperatures (below 175 K).[4-6]

In the present experiments the Raman spectra of hydrogen were measured at pressures between 200 bars and 630 kbar at 25°C. The data were obtained to characterize fluid and solid hydrogen, and specifically to observe the behavior of hydrogen that may be precursory to its eventual transformation to the metallic state.[7-9]

The diamond-window high-pressure cell used was a modified version that could be operated at cryogenic temperatures for filling the chamber with liquefied gas. Descriptions of this apparatus are reported in detail elsewhere.[1]

In these experiments the sample chamber was a small cylindrical hole (diameter, 0.4 and 0.1 mm for low- and high-pressure experiments; depth, 20 and 10 μm) drilled in work-hardened stainless steel. Small ruby crystals (10-μm diameter) were placed inside the sample chamber prior to filling with hydrogen. Liquid hydrogen at 17 K was sealed in the sample chamber by operating the cell in a liquid He cryostat.[1] 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 on the sample at room temperature was determined by observing the R_1 fluorescence line of the ruby crystal. Primary pressure calibration of this system is based on simultaneous measurement of pressure/volume functions of four metals (Cu, Mo, Pd, and Ag),[2] and independently on absolute measurements[3] which form the basis of the relation

$$P(\text{Mbar}) = 3.808[(\lambda/\lambda_0)^5 - 1],$$

where λ_0 is the wavelength of the ruby R_1 line at 1 bar, and λ the wavelength at pressure P.

Data on hydrogen were obtained with the modified diamond-window high-pressure cell, coupled to a Raman spectrometer. Scattered radiation was collected in the forward direction (0°), with a 90° off-axis ellipsoidal mirror.[10,11]

The positions of the four Q-branch lines $[Q_1(J)$ $(\Delta v = 1;\ \Delta J = 0;\ J = 0,\ 1,\ 2,\ 3)]$ of the vibrational bands of hydrogen observed at 200 bars (Table I) are in good agreement with previously reported values.[12,13] The bands are relatively narrow because Doppler broadening effects were minimized in the forward-scattering geometry.[14-16]

At pressures above 9 kbar, an intense, well reserved H-H stretching band $[Q_1(1)]$ was observed (Fig. 1). The width of this vibrational band varies significantly with pressure. When hydrogen is fluid, the band broadens with increasing pressure up to the solidification point (55 kbar), where it suddenly becomes relatively sharp. The decrease in the half-width of the $Q_1(1)$ band from 15 to 5.6 cm^{-1} at the solidification point (Fig. 1) is a result of reduction of collision-induced broadening in the solid. This large decrease in half-width can be used as an indication of the transition.

In solid hydrogen, the band sharpens further with increasing pressure to about 175 kbar, where it gradually broadens again and the half-width increases rapidly above 545 kbar (Fig. 1) ($\omega = 6.1$ cm^{-1} at 545 kbar and $\omega = 7.6$ at 626 kbar). Figure 2 is a plot of the major shift of this band from 200 bars to 630 kbar. The following relationship is a polynomial least-squares fit to the observed data points in fluid hydrogen:

$$\Delta\nu = 1.55P - 0.0115P^2,$$

TABLE I. Frequencies in inverse centimeters of Raman bands of hydrogen at various pressures and room temperature (*vw*, very weak; *w*, weak; *m*, medium; bd, broad; sh, shoulder; ω, full width at half maximum height).

	Pure rotational bands				Vibrational bands			
Pressure	$S_0(0)$	$S_0(1)$	$S_0(2)$	$S_0(3)$	$Q_1(0)$	$Q_1(1)$	$Q_1(2)$	$Q_1(3)$
1–2 bars[a]	354.381	587.055	814.406	1034.651	4161.134	4155.201	4143.387	4125.832
200 bars[b]	354.8,*m*	588.4,*s*	814.5,*w*	1034.2,*w*	4161.6,*w*	4155.9,*m*	4144.2,*w*	4126.6,*w*
5 kbar	355.0,*m* (ω = 12.0)	590.8,*s* (ω = 13.0)	817.4,*w* (ω = 11.6)	1036.3,*w* (ω = 10.6)	. . .[c]	4163.3,*m*	. . .[c]	. . .[c]
9 kbar	357.0,*m* (ω = 12.1)	592.4,*s* (ω = 28.8)	820.9,*w* (ω = 20.2)	1040.0,*w* (ω = 20.7)	. . .[c]	4165.5,*m*	. . .[c]	. . .[c]
24 kbar	354.8,*m*; 369.0,*vw*(sh	529.5,*w*; 564.5,*vw*(sh); 596.2,*s*	824.7,*w* (ω = 22.7)	1044.4,*w* (ω ~ 20)	. . .[c]	4183.8,*m* (ω = 13.1)	. . .[c]	. . .[c]
40 kbar	360.7 (ω = 27.3)	601.5,*s* (ω = 51.5)	832.0,*w* (ω = 33.8)	1051.2 (ω = 32.3)	. . .[c]	4200.7,*m* (ω = 14.1)	. . .[c]	. . .[c]
55 kbar	*vw*,bd	~ 602,*w*,bd	~ 832,*vw*,bd	*vw*,bd	. . .[c]	4205.0,*m* (ω = 5.7)	. . .[c]	. . .[c]

[a] From Stoicheff (Ref. 10); the positions of rotational bands within ± 0.02 cm^{-1} and of Q-branch vibrational bands within ± 0.05 cm^{-1}.

[b] Measurement accuracy ± 0.5 cm^{-1}.

[c] Bands not detected.

where $\Delta\nu$ is the frequency shift in wave numbers (in inverse centimeters) for $Q_1(1)$, P is the pressure in the fluid in kilobars. In the solid phase (55–630 kbar) a similar relationship is

$$\Delta\nu = 14.6 + 0.780P - 0.229\times10^{-2}P^2 + 0.296\times10^{-5}P^3 - 0.165\times10^{-8}P^4.$$

The positions of the four pure rotational lines [$S_0(J)$ ($\Delta v = 0$; $J = 0, 1, 2, 3$)] of hydrogen observed at 200 bar (Table I) are in agreement with previously reported values.[12,13] The observed spectral region of the rotational bands at higher pressures is shown in Fig. 3. The bands broaden and become diffuse with increasing pressure to 55 kbar, the solidification point at 22 °C. At 55 kbar the rotational bands become more diffuse (Fig. 3). Where the fluid phase is stable, the intensity of the tail of the Rayleigh scattering increases at high pressure and merges with the rotational bands because of broadening,[15,16] as can be seen in Fig. 3.

In solid hydrogen the intensity of Rayleigh scattering increases significantly in these experi-

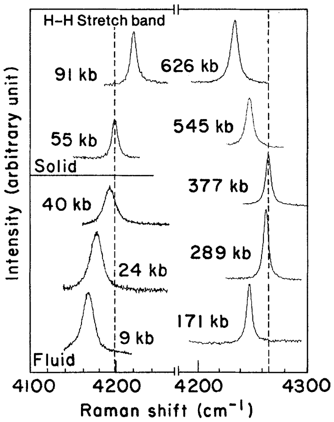

FIG. 1. Spectra of the $Q_1(1)$ Raman mode of hydrogen at selected pressures, 9–626 kbar. Instrumental: excitation, Ar-laser line 488.0 nm, 400 mW; spectral slit, width 5 cm^{-1} for fluid phase and 3.5 cm^{-1} for solid phase.

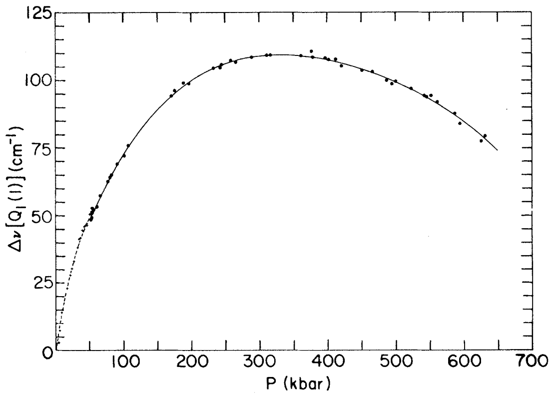

FIG. 2. The frequency shift ($\Delta\nu$) of the $Q_1(1)$ Raman line in hydrogen as a function of pressure at room temperature (26° ± 4°C).

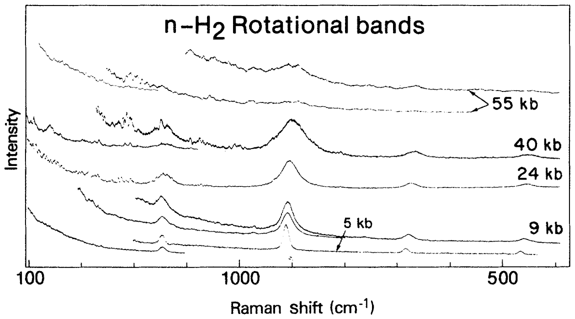

FIG. 3. Raman spectra of hydrogen in the region of the rotational modes; $P = 5-55$ kbar and $T = 22°C$. Instrumental: excitation, Ar-laser line 488.0 nm, 200 mW; spectral slit, 10 cm^{-1}; where two traces are shown for a given pressure, the lower trace has an amplification of × 0.5. The slit width for the lowest and the middle traces at 55 kbar was 5 cm^{-1}, and these were recorded with amplification of ×0.5 and ×1, respectively.

ments so that it was necessary to adjust the spectral slit width from 10 to 5 cm^{-1} resolve scattered radiation below 200 cm^{-1} (Fig. 1). No well-defined lattice mode was detected. The presence of strong continuous background at low frequency is possibly due to parasitic scattering from macroscopic inhomogenities in the solid sample, and may also be due to anharmonic broadening of a one-phonon transition due to the relatively high temperature of the measurement. High temperature, and in addition, random distribution of orthohydrogen and parahydrogen molecules in the solid n-H_2 contribute to the broadening of the rotation modes. Bhatnager, Allin, and Welsh[17] showed that even at low temperature, the presence of 20% p-D_2 causes serious broadening of the $S_0(0)$ line.

The observations can be summarized as follows. The freezing pressure at 298 K (57 kbar) is close to the value extrapolated from measurements at 175 K. Molecular rotation of hydrogen molecules is predicted to cease by approximately 375 kbar.[18] The notion that changes in the molecular state of solid hydrogen begin to occur at lower pressure is supported by the observation that the frequency-shift curve begins to flatten at approximately 200 kbar (Fig. 2). In the present experiments the bands attributed to this rotation $[S_0(J)]$ become diffuse and disappear slightly above the freezing pressure at 298 K, well below 375 kbar. The decrease in the half width of the $Q_1(1)$ at 175 kbar probably indicates the lessening of rotation of hydrogen molecules.

The behavior of the observed Raman band assigned to H-H stretching $[Q_1(J)]$ gives a strong indication that bonding changes begin to occur at pressures above 330 kbar. The initial increase in frequency is a result of compression of the molecular bond.[19] As pressure is increased further, the increase in frequency becomes less and finally decreases at approximately 330 kbar, as the molecular bonds are weakening. Eventually when molecular hydrogen transforms to the predicted atomic (metallic) state, the molecular bonds will be broken and the intermolecular bonds will be strengthened. The present observations lead to the view that the solid-hydrogen structure is tending toward the start or onset of such a change at higher pressure.

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