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Brillouin and Raman scattering of fluid and solid hydrogen at high pressures and temperatures

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Abstract

The Brillouin and Raman scattering spectra of fluid and solid hydrogen at high pressures (2–14 GPa) and temperatures (293–520 K) were measured to investigate the intermolecular interaction in the fluid and solid states. A Benedict type of equation of state was determined in $P \leq 15$ GPa, $T \leq 550$ K for fluid hydrogen with an average deviation of 1.0% from existing experimental data. We examined three types of intermolecular potential, and found that the Hemley–Silvera–Goldman potential gives superior fits to experimental data over a wide temperature range above 5 GPa. It was also found that the effect of intrinsic mode anharmonicity becomes significant at high temperatures for solid hydrogen.

1. Introduction

Most experimental studies on fluid and solid hydrogen have been carried out at and below room temperature except for those by shock compression. The P – V equation of state (EOS) of solid hydrogen has been obtained experimentally up to 150 GPa at room temperature [1]. However, the P – V – T EOS of hydrogen derived from static compression experiments on the fluid state is limited to $P \leq 2$ GPa and $T \leq 300$ K [2]. The EOS and the behaviours of vibrons at higher pressures and temperatures are needed in order to discuss the intermolecular interaction and potential for fluid and solid hydrogen.

In the present study, we measured the Brillouin and Raman scattering of fluid and solid hydrogen (n -H₂) at high pressures (2–14 GPa) and temperatures (293–520 K) to investigate the intermolecular interaction in the fluid and solid states through the temperature dependences of the sound velocity and the vibron frequency at high pressures.

2. Experimental details

Experiments were carried out in an internally heated Mao–Bell diamond-anvil cell, using Brillouin (90° scattering geometry) and Raman (45° scattering geometry) techniques with excitation by the $\lambda_0 = 514.5$ nm line from an Ar⁺ laser. Raman and Brillouin measurements were performed simultaneously using the same excitation to allow us to discuss consistently both vibrational and elastic properties. The compressional (longitudinal) sound velocity U was obtained from $U = v\lambda_0/\sqrt{2}$, where v is the Brillouin frequency shift. Temperature was measured with a Pt–Pt/10% Rh thermocouple placed very close to the sample chamber in rhenium gaskets, and pressure was calibrated using the pressure and temperature scale of ruby fluorescence. The temperature-induced shift of the R₁ line was calculated, based on a model of a two-phonon Raman process with $\alpha = -400$ cm⁻¹, $T_D = 760$ K and $\beta_{12} = 0$ [3].

3. Results and discussion

We determined a Benedict type of P – V – T EOS;

$$V = \sum_{m=1}^3 \sum_{n=-2}^2 A_{n,m} T^{\frac{n}{2}} P^{-\frac{m}{3}}, \quad (1)$$

for fluid hydrogen for $P \leq 15$ GPa, $T \leq 550$ K by a least-squares fitting made simultaneously to the compressional sound velocity data which were obtained from Brillouin spectra in the present study and to the volume and ultrasonic velocity data available over the ranges $75 < T < 600$ K and $0.07 < P < 2$ GPa [2, 4–8]. In this fitting procedure, the compressional sound velocity U was calculated from the volume V given by equation (1) using the thermodynamic equation

$$U = V \left[-M \left\{ \left(\frac{\partial V}{\partial P} \right)_T + \frac{T \left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2}{C_P} \right\} \right]^{-\frac{1}{2}}, \quad (2)$$

where M is the molecular weight. Here, we calculated the heat capacity at constant pressure, C_P , using the formula

$$C_P = C_{P_0}(T) - T \int_{P_0}^P \left(\frac{\partial^2 V}{\partial T^2} \right)_P dP, \quad (3)$$

where we used $C_{P_0}(T) = 0.1084T - 7.4519T^{0.5} + 205.774 - 1617.14T^{-0.5} + 4394.09T^{-1}$ (J mol⁻¹ K⁻¹) which was obtained by fitting to the heat capacity data in 80–800 K at $P_0 = 0.1$ GPa [7]. The best-fit parameters obtained, $A_{n,m}$, in equation (1), are tabulated in table 1. The best fits to the sound velocity data of the Benedict-type EOS are shown in figure 1. Our EOS for fluid hydrogen is found to be within an average deviation of 0.95% from the existing volume data and 1.09% from the existing sound velocity data in this P – T range. It should be noted that our sound velocity data for fluid hydrogen at $T = 293$ – 520 K above 5 GPa deviate significantly from the extrapolation of the P – V – T EOS derived for fluid hydrogen for $75 < T < 307$ K and $0.2 < P < 2$ GPa reported previously by Mills *et al* [2]. In other words, fluid hydrogen is much softer than is predicted by the P – V – T EOS at $P < 2$ GPa and $T < 307$ K. This is consistent with the finding for solid hydrogen by Hemley *et al* [10, 11] and Loubeyre *et al* [1] that the intermolecular potentials derived from low-pressure properties of hydrogen ($P < 2.5$ GPa) could not explain the higher-pressure properties, indicating that solid hydrogen is more compressible than is predicted using previously proposed intermolecular potentials. Using our EOS, we calculated the pressure and temperature dependences of thermodynamic quantities such as thermal expansion coefficient, isothermal and adiabatic

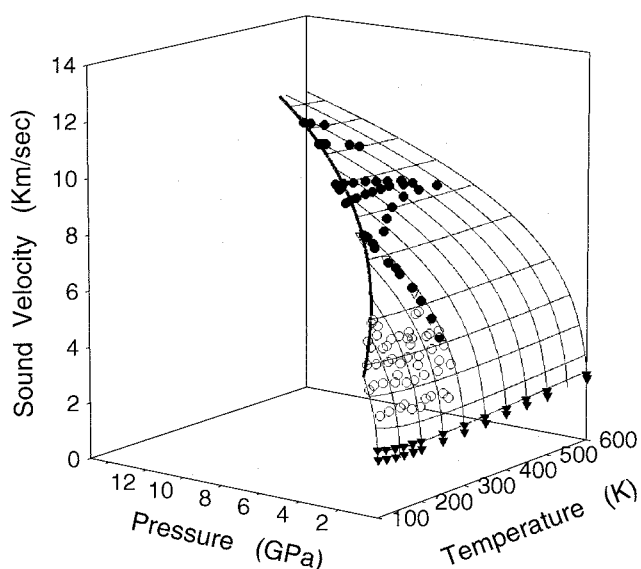


Figure 1. Temperature and pressure dependence of sound velocity of fluid hydrogen. The solid curves represent the nonlinear least-squares fits to the data using the Benedict-type EOS. The thick solid curve denotes the melting curve. ●, present study; ○, [2] and [4]; ▽, [9]; and ▼, [7].

Table 1. Values of the best-fit parameters in the Benedict-type P - V - T EOS given by equation (1) for fluid hydrogen. The units cm^{-3} /mole, kbar and K are used for V , P and T respectively in equation (1).

n	$A_{n,1}$	$A_{n,2}$	$A_{n,3}$
-2	0	0	943.191
-1	89.538 7	0	-307.938
0	31.964	-38.715	36.215 3
1	0	0	0
2	-0.009 351 32	0.068 021 8	0.010 509 3

compressibilities, heat capacities at constant volume C_V and at constant pressure C_p , and heat capacity ratio $\gamma = C_p/C_V$.

Then, three types of intermolecular potential, which had been proposed for hydrogen, were examined by comparing our EOS with the volume calculated using those potentials using fluid perturbation theory [12]. As shown in figure 2, we have found that the Silvera–Goldman (SG) [13] and the Ross–Ree–Young (RRY) [14] potentials cannot reproduce our EOS at high temperature and in the high-pressure range, though they give fairly good fits at low temperatures and low pressures. On the other hand, the Hemley–Silvera–Goldman (HSG) potential [10, 11] gives superior fits over a wide temperature range above 5 GPa, suggesting that the HSG potential is a useful description of the intermolecular potential for fluid hydrogen in this P - T range. However, it should be noticed that none of them can reproduce satisfactorily our experimental EOS in the high-temperature range at low pressures, providing another constraint on determination of the intermolecular potential.

In figures 3(a) and (b), the compressional sound velocity and the frequency of the vibron, respectively, which are normalized with the values at room temperature, are plotted as a function of temperature for solid and fluid hydrogen for each pressure. Here, it should be

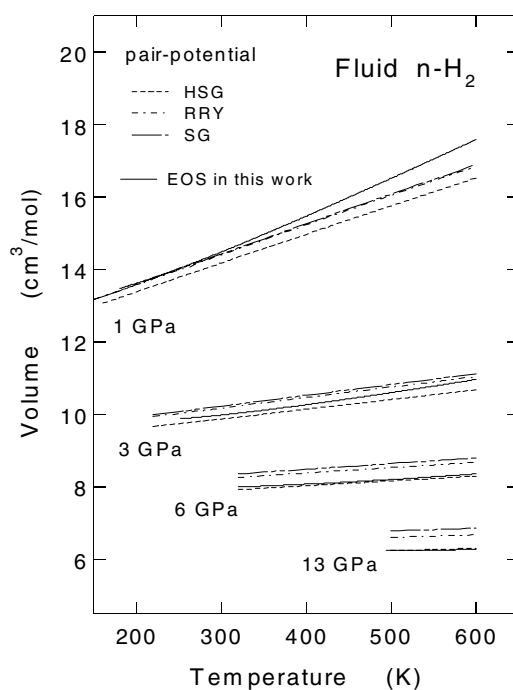


Figure 2. Temperature dependence of volume at constant pressures, which was calculated using the SG, RRY, and HSG potentials using fluid perturbation theory. The solid curves are obtained from the Benedict-type EOS derived experimentally for fluid hydrogen in the present study.

stated that the sound velocity of fluid hydrogen is normalized with the aggregate bulk sound velocity obtained from the single-crystal Brillouin data at room temperature [15], since the aggregate bulk sound velocity gives a fairly good extrapolation for the compressional sound velocity of fluid hydrogen at room temperature. Both sound velocity and vibron frequency decrease significantly with increase in temperature for solid hydrogen, while they show little change with temperature for the fluid state. The result demonstrates that the effects of intrinsic mode anharmonicity (i.e. the variations in mode frequencies with temperature at constant volume) become important at high temperatures for solid hydrogen. This leads us to suggest that the quasiharmonic treatment so far used to estimate the thermal correction to the EOS of solid hydrogen would become inaccurate at high temperatures where the mode anharmonicity becomes significant.

4. Conclusions

We have investigated the temperature dependences of the sound velocity and the vibron frequency of fluid and solid hydrogen ($n\text{-H}_2$) from Brillouin and Raman scattering measurements at high pressures (2–14 GPa) and temperatures (293–520 K). From the sound velocity data together with existing volume and ultrasonic velocity data at low pressures and temperatures, we determined a Benedict type of P - V - T EOS in $P \leq 15$ GPa, $T \leq 550$ K for fluid hydrogen with an average deviation of 1.0% from existing experimental data. Comparison of the EOS with the volume calculated using three types of intermolecular potential leads us to conclude that the HSG potential is the best description of the intermolecular potential for fluid

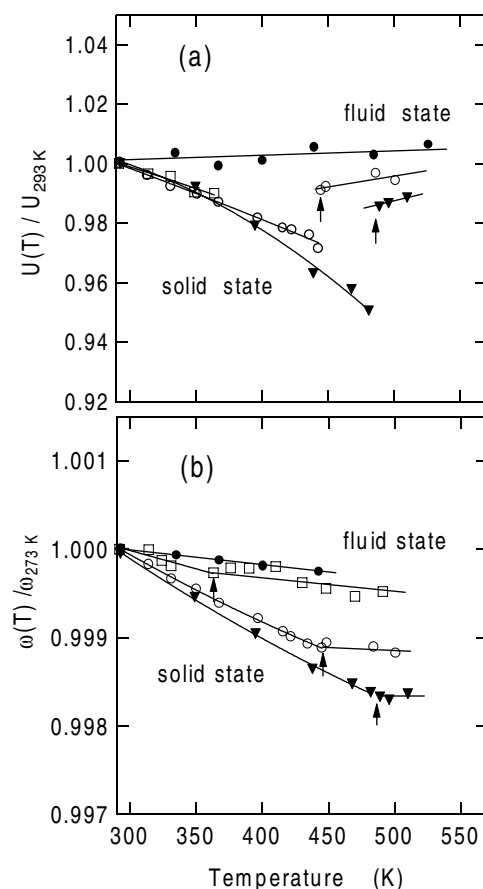


Figure 3. (a) Compressional sound velocity, and (b) vibron frequency, as a function of temperature for solid and fluid hydrogen at each pressure; ●, 4.6 GPa; □, 8.0 GPa; ○, 10.3 GPa; and ▼, 12.7 GPa. The data are normalized with the values at room temperature. The arrows indicate the melting points. The solid curves are drawn as a guide to eye.

hydrogen among them in this P - T range. However, the discrepancy that was found in the high-temperature range at low pressures would provide another constraint on determination of the intermolecular potential. For solid hydrogen, we have found that the effect of intrinsic mode anharmonicity becomes significant at high temperatures, based on the temperature dependences of sound velocity and vibron frequency in the solid.

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