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Pressure dependence of the optical phonon in solid hydrogen and deuterium up to 230 kbar

Rinke J. Wijngaarden, Victor V. Goldman, and Isaac F. Silvera*

*Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65,
1018-XE Amsterdam, The Netherlands*

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We have studied the E_{2g} transverse-optical phonon by means of Raman scattering in solid molecular hydrogen and deuterium at pressures up to 230 kbar at 5 K in a diamond anvil cell. With the use of a self-consistent phonon calculation which incorporates anharmonic corrections to the self-energy, phonon frequencies were calculated using an isotropic intermolecular pair potential. Deviations between theory and experiment point to deficiencies in the potential. The present experimental data can be used as a test on the isotropic part of the intermolecular potential of the solid.

I. INTRODUCTION

Solid molecular hydrogen and deuterium are the simplest molecular solids. A great deal is known about their interaction potentials, equations of state, and dynamical properties for both the even-rotational-state species (para- H_2 , ortho- D_2) and the odd-rotational-state species (ortho- H_2 , para- D_2). In this paper we confine our attention to para- H_2 and ortho- D_2 for which the molecules are in the spherical $J=0$ state (J is the rotational quantum number) at low pressure. The crystal structure of the solid is hexagonal close packed (hcp) and is not complicated by an orientational-order phase transition such as that which occurs in the odd- J species at low pressure.

The lattice excitations in order of descending energy are the vibrons (coupled internal vibrational modes), the rotons ($J=2$ rotational excitations), and the phonons. All of these lattice modes vary in energy with crystal density (pressure). The mode-Grüneisen constant is by far the largest for the phonon so that by increasing density (pressure), the phonon energy will eventually cross and exceed that of the rotons. Since the energy is directly related to the intermolecular potential and its derivatives, a study of its density dependence can be used to assess the quality of intermolecular potentials currently in use. Such a study has at least two operational difficulties. First, at low pressure the phonons are highly anharmonic, requiring the sophisticated calculational techniques developed for quantum solids. These techniques are used in this paper. However, with increasing density, the self-consistent phonon approximation improves due to decreasing anharmonicity, so that the validity of the theoretical approximations

increases with density. Second, the Raman-active phonon studied has a level anticrossing with one of the roton bands, severely distorting the density dependence in the crossing region. However, we feel confident in our understanding of this crossing phenomenon so that we can use standard theory to correct the phonon frequency to correspond to its value in the limit of zero roton-phonon coupling. Moreover, these corrections are only important in the region of the crossing.

In the hcp crystal structure there are three zone-center optical phonons. Of these, the doubly degenerate transverse-optic (TO) phonons are polarized within the hexagonal planes and are Raman active with a symmetry E_{2g} . This phonon mode was first observed by Silvera *et al.*^{1,2} at zero pressure and later by Nielsen,³ Thiéry *et al.*,⁴ and Berkhout and Silvera⁵ for pressures up to 10 kbar. In this paper we present the experimental phonon frequencies of the TO E_{2g} mode in hydrogen and deuterium for pressures up to 230 kbar. These are compared to self-consistent phonon calculations using an intermolecular pair potential that has been developed earlier to fit the P - V equation of state data of H_2 and D_2 .

II. EXPERIMENTAL OBSERVATIONS

Samples of 98.5% para- H_2 and 98.5% ortho- D_2 were prepared by catalytic conversion in the liquid state. Pressure was applied in our diamond anvil cell (with a pressure range up to 600 kbar) which is operated in a ^4He cryostat enabling temperature control in the range 1.1–300 K. Samples were confined in a steel T301 gasket; the typical sample size had a 100- μm diam. and was $\sim 20 \mu\text{m}$ thick. Present ex-

perimental data were obtained in several runs on both isotopes. The lattice excitations were observed in a Raman backscattering geometry. An argon-ion laser with power up to 500 mW in the 5145-Å line was employed. Pressure was determined from the luminescence spectrum of a few grains of ruby enclosed with the sample which was also excited with the 5145-Å line. The pressure calibration of Mao *et al.*⁶ was used. At the beginning of each experimental run the zero-pressure frequency of the fluorescence line was determined at 5 K. This zero-pressure frequency was used when applying the formula of Mao *et al.*

Owing to our small sample size, phonon intensities were generally too weak to detect. However, in the pressure region where the phonon has about the same frequency as the roton, a much higher intensity is observed due to hybridization of these two modes.^{7,8} In this pressure region the phononlike branch was measured. The effect of hybridization on frequencies is given by

$$\omega_h^\pm = \frac{1}{2}(\omega_r + \omega_p) \pm \frac{1}{2}[(\omega_r - \omega_p)^2 + 4c^2]^{1/2}. \quad (1)$$

Here ω_r and ω_p are the unperturbed roton and phonon frequencies, ω_h^\pm are the hybridization frequencies, and c is the coupling constant which at the crossover point has the experimental value^{7,8}

$$\begin{aligned} c/2\pi &= 12 \pm 2 \text{ for H}_2, \\ c/2\pi &= 6 \pm 1 \text{ for D}_2, \end{aligned} \quad (2)$$

measured in cm^{-1} . In the crossover region measured phonon frequencies $\omega_h/2\pi$ were converted back to unperturbed phonon frequencies $\omega_p/2\pi$, using Eq. (1) and the measured roton frequencies. In Fig. 1 we present our thus corrected data. We plot $\ln(\nu/\nu_0)$ vs $\ln(V/V_0)$, where ν denotes the phonon frequency and V the molar volume and the zero subscript denotes zero pressure. The negative slope of this plot is the (mode) Grüneisen parameter, $\gamma = -\partial \ln \nu_{\text{TO}} / \partial \ln V$. Our data together with those of Berkhout and Silvera⁵ were fitted to a polynomial of degree 2 by means of a least-squares method. All measurements were given the same weight. We find for hydrogen

$$\begin{aligned} \ln(\nu/\nu_0^{\text{H}}) &= -0.012(10) - 2.17(5) \ln(V/V_0^{\text{H}}) \\ &\quad - 0.28(3) \ln^2(V/V_0^{\text{H}}) \end{aligned} \quad (3)$$

with $\nu_0^{\text{H}} = 36.79 \text{ cm}^{-1}$ and $V_0^{\text{H}} = 23.14 \text{ cm}^3/\text{mol}$. For deuterium

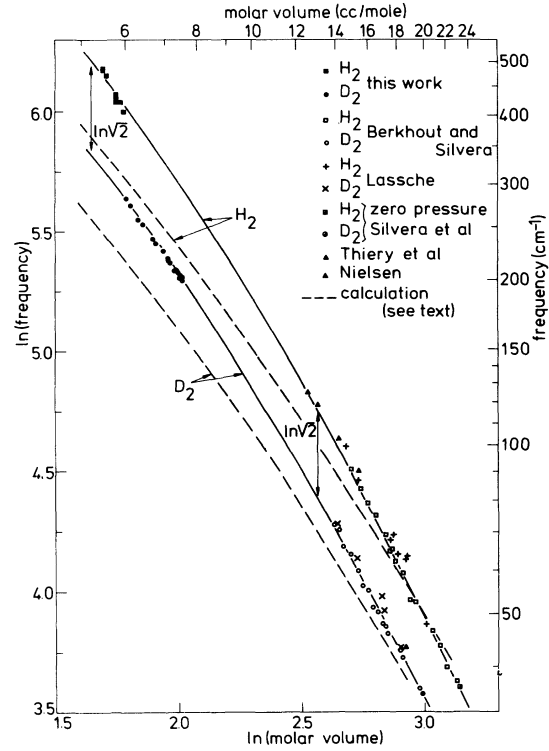


FIG. 1. Phonon frequencies plotted on a double logarithmic scale. The slope is the Grüneisen parameter. Measurements by Berkhout and Silvera (Ref. 5), Lassche *et al.* (Ref. 16), Silvera *et al.* (Ref. 2), Nielsen (Ref. 3) and Thiery *et al.* (Ref. 4) are also included. The dashed line is the calculation discussed in Sec. III; the solid line is a least-squares fit to the data.

$$\begin{aligned} \ln(\nu/\nu_0^{\text{D}}) &= -0.017(5) \\ &\quad - 2.05(3) \ln(V/V_0^{\text{D}}) \\ &\quad - 0.27(2) \ln^2(V/V_0^{\text{D}}), \end{aligned} \quad (4)$$

with $\nu_0^{\text{D}} = 35.83 \text{ cm}^{-1}$ and $V_0^{\text{D}} = 19.95 \text{ cm}^3/\text{mol}$. These fits are indicated by the solid lines in Fig. 1. For the (mode) Grüneisen parameter we find, for hydrogen

$$\gamma_{\text{H}} = 2.17(5) + 0.56(6) \ln(V/V_0^{\text{H}}). \quad (5)$$

For deuterium

$$\gamma_{\text{D}} = 2.05(3) + 0.54(4) \ln(V/V_0^{\text{D}}). \quad (6)$$

The dependence of the Grüneisen parameter on molar volume is plotted in Fig. 2.

III. THEORETICAL CONSIDERATIONS

The phonon frequencies were calculated starting from a self-consistent phonon basis corrected by the

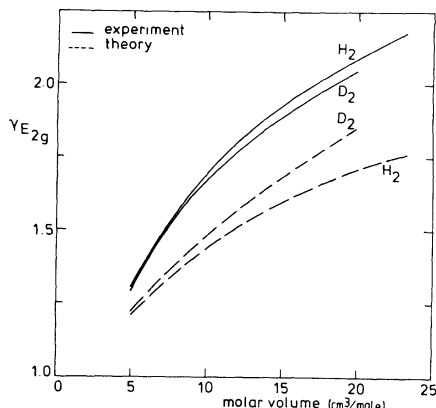


FIG. 2. E_{2g} mode-Grüneisen parameter as a function of molar volume [from Eqs. (5) and (6)]. Solid line: experiment; dashed line: calculation.

three-phonon anharmonic processes in the manner described by Goldman *et al.*⁹ The hcp Γ optical phonons calculated including terms up to the *pure* three-phonon process were found to differ only marginally from similarly calculated (Ref. 10) L phonons in fcc H_2 and D_2 . For computational economy, terms in the self-energy of Ref. 9 going beyond the pure three-phonon process were evaluated for the fcc L-phonon case. We believe that this procedure does not introduce any appreciable error. In Ref. 10 it was shown that these higher-order corrections can be neglected in H_2 and D_2 for densities higher than $10 \text{ cm}^3/\text{mol}$. The intermolecular potential used was that of Silvera and Goldman¹¹ which is an isotropic effective pair potential, which includes three-body effects of the Axilrod-Teller-Muto type.

In Fig. 1 we show the results of this calculation together with the experimental points. We note that the calculated values are systematically lower than the observed values. The same sort of discrepancy was also observed for the pressure dependence of ir frequencies measured by Jochemsen *et al.*¹² and for the density dependence of Debye temperatures.¹³ Since anharmonic effects become relatively smaller at higher densities we believe the disagreement to be due to the potential used in the calculation. This can originate from effects such as the inadequacy of the pair potential itself as well as the increasing importance of many-body forces other than those accounted for in Ref. 11 in the high-pressure regime. The calculated E_{2g} Grüneisen parameters are shown in Fig. 2. Although the agreement with experiment improves with increasing density, the calculated isotopic behavior is qualitatively different from the observed one. This anharmonic effect may point to the necessity of including higher-order terms in the

phonon self-energy.

The pair potential of Ref. 11 was determined principally by fitting the equation of state (EOS) data for pressures up to 25 kbar. The phonons here extend to 230 kbar, an order of magnitude higher. Recently, van Straaten *et al.*¹⁴ have extended the EOS to about 400 kbar. Their EOS is slightly softer than that derived using the potential of Ref. 11 in this region. On the other hand, we would expect a softer potential to give lower calculated frequencies. This possible correction apparently works in the wrong direction and would not improve the agreement. We also point out that calculated phonon frequencies involve higher derivatives of the potential than appear in the EOS and thus are a much more stringent test of the quality of a potential.

Finally, we wish to mention that the present measurements can be used to estimate the Debye temperature for H_2 and D_2 at high pressures. This can be done by scaling the calculated Debye temperature¹⁰ with the ratio of the measured E_{2g} frequency and the calculated E_{2g} frequency. The results of this are shown in Fig. 3. This procedure would also yield the Grüneisen parameter for the Debye temperature (which would presumably be different from the mode-Grüneisen constant given in the experimental section). Furthermore, the Debye temperature and its Grüneisen parameter could be used in extending the low-temperature equation of state¹¹ to higher temperatures via the Mie-Grüneisen scheme as was done by Driessen *et al.*¹⁵ in the low-pressure regime.

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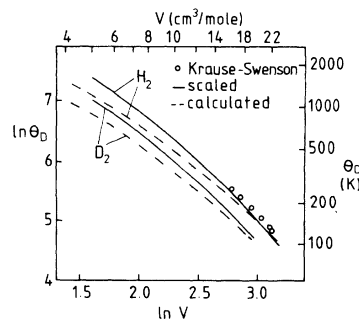


FIG. 3. Logarithmic plot of Debye temperature vs molar volume. The dashed curve represents the direct calculation. The solid curve is scaled with phonon frequency ratio (see text). Experimental points are from Krause and Swenson (Ref. 17).

*Current address: Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138.

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