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Equation of state and Raman-active E_{2g} lattice phonon in phases I, II, and III of solid hydrogen and deuterium

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We present results of lattice dynamics calculations of the P-V equation of state and the pressure dependence of the Raman-active E_{2g} lattice phonon for p-H_2 and o-D_2 in a wide pressure range up to ~2 Mbars using our recently developed semiempirical many-body potential, and density-functional theory (DFT). Comparison with the existing body of experimental and theoretical results showed that the employed many-body potential is a reliable basis for high-precision calculations for phases I and II. For phase III it still works satisfactorily but the use of the DFT is preferable. The decomposition of the total energy and pressure into contributions from pair forces, three-body forces, and zero-point motion is presented.

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An accurate determination of the equation of state (EOS) of solid hydrogens has been an important research objective for decades. Systematic high-pressure studies were started in the 1970s[1–3] (see reviews[4–6] and references therein), and at present they reach pressures up to ~2 Mbars[7–13] and temperatures up to 1000 K. The highest compression reached in the EOS experiments was 10.4 for solid H_2 (Ref. 13) [7.6 for solid D_2 (Ref. 12)], higher than for solid helium (8.4).[14] The EOS data provide a fundamental basis for examining intermolecular interactions, testing *ab initio* theories, and developing model intermolecular potentials.[15,16] Another experimental technique which provides direct information on intermolecular interactions and vibrational dynamics is Raman scattering. The hcp structure has a Raman-active optical mode (E_{2g} symmetry) in the phonon spectrum which corresponds to the out-of-phase shear motions in the *ab* plane. The frequency range of this Raman mode is extremely large, from 36 cm^{-1} at zero pressure[17–22] to 1100 cm^{-1} at 250 GPa. These measurements show that hcp-based structures are stable in this pressure range. The E_{2g} Raman frequency $\nu(P)$ calculated using various empirical potentials[5] is highly sensitive to details of the potential used, making it a hard test for any empirical potential [or for any other theoretical method, e.g., density-functional theory (DFT)]. It is essential that these properties are sensitive to different characteristics of the intermolecular potential: while EOS is sensitive to the potential well depth, the E_{2g} Raman frequency probes the second derivative of the potential at the minimum. In our recent paper[23] we proposed semiempirical (SE) many-body potentials for H_2 and D_2. Unlike the previous potentials[10,15,16,24] they include not only pair forces, but triple forces as well. The reason for using SE potentials at all for H_2 and D_2 is twofold. First, they work better for low pressures compared to most other theoretical methods, including DFT. In particular SE potentials have no problem describing quantum rotors representing spherically symmetric H_2 molecules of phase I, and the distinction between ortho- and para-hydrogen. Second, SE calculations are time efficient, which becomes important for methods like Molecular Dynamics (MD) or Path Integral Molecular Dynamics (PIMD).

The goal of the present paper is to perform detailed calculations of the EOS and pressure dependence of E_{2g} Raman frequencies for H_2 and D_2 using our SE many-body potentials and to compare the results to experimental data and theoretical results for a wide pressure range which spans phases I, II, and III of solid p-H_2 and o-D_2.

As mentioned above, our potential includes pair (U_p) and triple (U_{tr}) intermolecular forces. It is similar to the potential for solid helium.[25,26] It has the form of a sum of the pair Silvera-Goldman (SG) potential[15] (discarding the R^{-9} term) and three-body terms which include the long-range Axilrod-Teller dispersive interaction and a short-range three-body exchange interaction in the Slater-Kirkwood form.[25,26] An explicit form and parameters of our potential are given in Ref. 23. All our calculations are done for $T = 0$ K with our own computer code. The static contributions of pair and triple forces were calculated by summation over 51 spheres of neighbors (five lattice constants) on hcp lattice; the zero-point energy was taken into account using the cell model within the Einstein approximation. The quantum-crystal pressure range (<0.5 GPa) was excluded from consideration. The effect of the orientational order on the EOS and Raman frequencies is very small. This follows from both theoretical estimates, and from the fact that there is no features at the I-II and II-III transition points in the experimental EOS[13] and Raman[18,21] curves. Since we are only interested in EOS and the E_{2g} frequency in the present paper, we included only the orientation-independent terms of the potentials in the present calculations. The problem of the orientational ordering is beyond the scope of the present paper since it has been already studied extensively within the SE approach (Ref. 23, for example).

The decomposition of the total ground-state energy $E_{\mathrm{g.s.}}$ and EOS (inset) into contributions from the pair forces (E_p), triple forces (E_{tr}), and the zero-point motion (E_{zp}) is presented in Fig. 1. As can be seen, the interplay between these three contributions is rather complicated and different for different regions of the molar volume. At relatively small compressions $V_0/V < 2$ (V_0 is the molar volume at $T = 0$ and $P = 0$, 23.15, and 19.95 $\mathrm{cm}^3/\mathrm{mol}$ for p-H_2 and o-D_2, respectively), the zero-point term E_{zp} dominates. The relative contribution $E_{\mathrm{zp}}/E_{\mathrm{g.s.}}$ decreases with rising compression, but it remains significant up to 250 GPa. At the ten-fold compression, $E_{\mathrm{zp}}/E_{\mathrm{g.s.}}$ remains as high as 20%. It is interesting

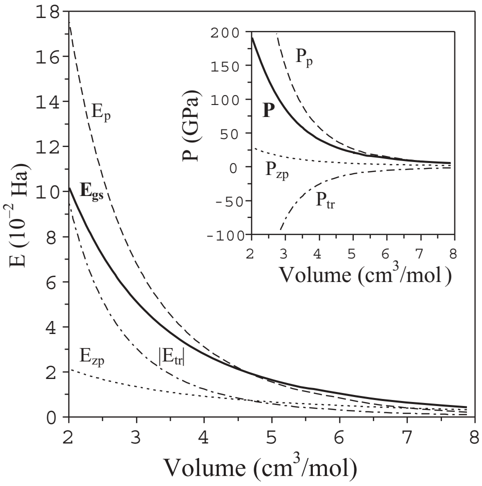

FIG. 1. Contributions of the pair E_p and triple E_{tr} forces, and zero-point energy E_{zp} to the total ground-state energy $E_{g.s.}$ for solid p-H_2. (Notice that E_{tr} is always negative.) The inset shows the respective contributions to EOS.

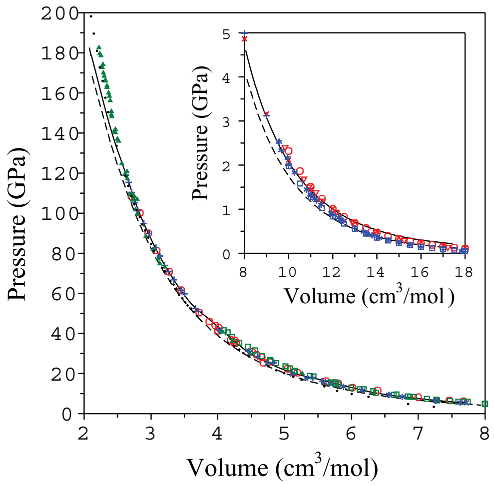

FIG. 2. (Color online) Calculated and experimental pressure-volume relations for solid H_2 and D_2. Semiempirical calculations for many-body potential (this work): p-H_2 (solid line), o-D_2 (dashed line); DFT-GGA calculations (dotted lne).[27] Experiment (reduced to 0 K): [H_2: ▲ (Ref. 13), ○ (Ref. 12), □ (Ref. 5)]; (D_2: + (Ref. 12), × (Ref. 11), ∗ (Ref. 5)]; the inset shows the low-pressure range. Experiment (reduced to 0 K): [H_2: ○ (Ref. 3), × (Ref. 9), ▽ (Ref. 7)]; [D_2: □ (Ref. 3), + (Ref. 9), ∗ (Ref. 8)].

to note that for the eight-fold compression, $E_{zp}/E_{g.s.}$ coincides with that for solid ^{4}He, but for helium it increases with decreasing compression more steeply and already at three-fold compression it dominates in the ground-state energy.[14] For solid hydrogen the three-body attraction becomes appreciable at the compressions higher than two-fold which corresponds to pressures about 2 GPa. The relative contribution of the three-body forces $|E_{tr}|/E_p$ (it should be remembered that E_{tr} is always negative!) monotonically increases with pressure and for the eight-fold compression it reaches 0.5.

There have been many attempts to propose effective pair potentials which would have the same softening effect as attractive many-body forces.[10,16,24] To account for these effects Hemley *et al.*[10,24] modified the SG potential[15] with a short-range correcting term. This Hemley-Silvera-Goldman (HSG) effective potential was shown to fit EOS up to 40 GPa, but at higher pressures, $P(V)$ calculated with this effective pair potentials increases far more rapidly than in experiment.[12]

The calculated equations of state $P(V)$ for solid hydrogen and deuterium are shown in Fig. 2 in comparison with DFT generalized gradient approximation (GGA) calculations[27] and the experimental results from Refs. 3,5,7–10,12,13, and 24. As can be seen, the SE calculation with the proposed many-body potential is in excellent agreement with experiment in the pressure range 1–140 GPa (phases I and II).[28] These results can be compared favorably with recently published EOS calculations.[29] From 140 GPa onward, the theoretical $P(V)$ curve lies slightly below the experimental one, and at the highest reached pressures of 180 GPa (Phase III) the difference amounts up to about 10%. The reason for this is the neglect of the higher order ($n > 3$) terms in the n-body expansion. The effect of the large-n terms increases with pressure, and at the metallization point the n-body expansion would converge extremely slowly. Methods based on the DFT using the local-density approximation (LDA) and GGA functionals are somewhat opposite to the empirical potentials method. Indeed, the accuracy of the EOS from DFT-GGA[27] improves with the increase of pressure: in the pressure range 70–180 GPa the EOS from GGA practically coincides with the experimental one and for $P > 140$ GPa the agreement is better than for our empirical potentials; but at lower pressures the *ab initio* results progressively underestimate the pressure, and GGA gives a strongly underestimated equilibrium volume of about 8 cm^3/mol. The reason for this is twofold: first, GGA gives a poor description of the van der Waals forces, and second, DFT calculations ignore all quantum zero-point motions of nuclei, including the distinction between ortho- and para-species. We also compare theoretical and the experimental values for the isotopic shift $\Delta P(V) \equiv P_{D_2}(V) - P_{H_2}(V)$. Loubeyre *et al.*[12] found that the isotopic shift in the EOS is markedly smaller than that calculated with the effective pair potential[10,24] within the Debye model. We obtained similar results with our many-body potential within the Einstein model. While the values of the isotopic shift are slightly different for different models the order of magnitude is the same and experiment is overestimated by a factor of 3. This could be an unharmonic effect.

The comparison between theoretical and experimental pressure dependencies $\nu(P)$ of the E_{2g} optical phonon Raman-active mode is presented in Fig. 3. Since we could not find any DFT data of this mode in the literature, we have also calculated the E_{2g} Raman frequency of solid H_2 and D_2 in the Pca2$_1$ structure—one of the plausible candidates for the orientational structure of phases II and III—using the DFT-LDA approximation. Our calculations were done using the full-potential linear muffin-tin orbital (FP-LMTO) code RSPt.[30]

Comparing the theoretical results with experiment we see that, similar to the results we had for the EOS at pressures lower than ∼150 GPa, the SE curves agree with experiment better than DFT calculations; but at higher pressures, the situation is reversed. The limiting pressures at which the SE approach still works are ∼175 GPa while LDA has a fine agreement with the experiment for H_2 and with frequencies

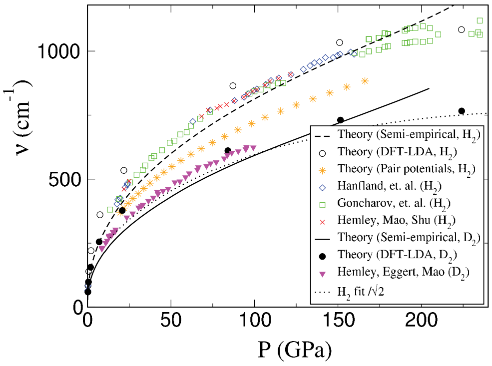

FIG. 3. (Color online) Calculated and experimental Raman frequencies vs pressure for solid hydrogen and deuterium. SE calculations for many-body potential (this work): p-H_2 (dashed line), calculations for the SG potential $*$ (Ref. 5); o-D_2 (solid line). DFT-LDA theory (this work): H_2 ○, D_2 ●. Experiment: [H_2: ◇ (Ref. 18), × (Ref. 19), □ (Refs. 20 and 21)]; [D_2: ▽ (Ref. 22)].

obtained for D_2 with the help of the harmonic ratio of $\sqrt{2}$ from 150 GPa up to the highest considered pressures ~230 GPa. The frequencies calculated from the SG potential[15] deviate from experiment even for very low pressures. The same is true[5] for the effective HSG pair potential.[10,24] Thus we have shown that while effective pair potentials work reasonably well for EOS up to 40 GPa, they fail for the dynamical properties like Raman spectrum, where the explicit inclusion of the three-body forces is necessary.

In conclusion, we have calculated the EOS and the pressure dependence of the Raman-active E_{2g} mode using our recently proposed many-body potential[23] and compared the results to experiment and previous SE and DFT calculations. Also, DFT-LDA calculations of the Raman frequency were performed. For phases I and II ($P < 150$ GPa) the proposed many-body potential gives excellent agreement with experiment, markedly better than any previous calculations. It proves that this potential is a reliable basis for high-precision calculations of structure and dynamics of H_2 and D_2. In particular, it provides a considerable improvement over any effective two-body potentials, stressing the importance of including the three-body forces. For phase III it still works well; but as pressure increases, the use of the DFT approach is more and more preferable. Finally, the decomposition of the total energy and pressure into contributions from pair forces, three-body forces, and zero-point motion is presented.

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