Dynamics and phase transitions in solid ortho and para hydrogen and deuterium from an *ab initio* potential

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(Received 27 November 1989)

Starting from an *ab initio* H_2-H_2 potential that contains anisotropic short-range and dispersion terms, in addition to the quadrupole-quadrupole interactions, we have performed lattice-dynamics calculations for the orientationally disordered hexagonal (hcp) and ordered cubic ($Pa3$) phases of solid (ortho and para) hydrogen and deuterium. The method used is the time-dependent Hartree (TDH) formalism, with the explicit inclusion of translation-rotation coupling. By an anharmonic expansion of the potential through sixth order in the molecular displacements and the use of wave functions for the translational vibrations that are sufficiently flexible to adapt to this strong anharmonicity, we could avoid the usual (effective) Jastrow correction to the potential. The calculated phonon and roton or libron frequencies are in fairly good agreement with infrared, Raman, and neutron-scattering data, significantly better in general than the results from earlier (separate) phonon calculations and roton or libron calculations that have used empirical potentials. The transition pressure for ordering para-H_2 or ortho-D_2 appears to be dominated by the classical quadrupole-quadrupole interactions. It is significantly affected by the increase of the rotational constant and, especially, by the reduction of the quadrupole moment, which follows from a shortening of the intramolecular bond. Translation-rotation coupling yields the observed mixing of phonons and rotons at high pressure, but its effect on the transition pressure is minute. The remaining discrepancy between the calculated and observed transition pressures must be caused by three-body interactions and by correlations between the molecular motions that are beyond the TDH approximation.

I. INTRODUCTION

Although solid hydrogen is the simplest crystal from a chemical point of view, it shows many phenomena that make it interesting for experimental investigations and theoretical studies.[1-3] At extremely high pressures, estimated around 300 GPa,[4] it will probably undergo a transition from the molecular phase to an atomic and, possibly, metallic phase. Such pressures are becoming available to experimentalists in the near future.[5,6] But, even in the molecular phases, which are studied in this paper, a number of problems still remain to be solved. There is a large difference between the phase diagrams of para-hydrogen (p-H_2) and ortho-deuterium (o-D_2) on the one hand, and ortho-hydrogen (o-H_2) and para-deuterium (p-D_2) on the other. Because of the weakly anisotropic interactions and the large rotational constant, the free rotor states of the molecules practically do not mix at normal pressure. In p-H_2 and o-D_2 the ground state has $l=0$ and the molecules have no preferred orientation. Only at very high pressures the admixture of higher-l states caused by the anisotropic interactions is sufficiently large to induce a transition to an orientationally ordered state. In o-D_2 this transition has been found at a pressure of 27.8 GPa, while in p-H_2 it has still not been observed for pressures up to 54 GPa.[7] In o-H_2 and p-D_2 the rotational ground state has $l=1$ and the molecules crystallize in an orientationally ordered $Pa3$ structure. Because the splitting between the three states with

$l=1$ is small, there is an order-to-disorder transition already at very low temperature. The transition temperature found in o-H_2 is 2.8 K and in p-D_2 3.8 K.[8]

It will be clear that the standard harmonic lattice dynamics method is not at all applicable to the rotations in solid H_2 and D_2. Also the translational vibrations are strongly anharmonic because of the small mass of the molecules. Previous calculations on the lattice dynamics of p-H_2 and o-D_2 always treated the translational and rotational vibrations separately. Klein and Koehler used the self-consistent-phonon (SCP) method to calculate the translational phonon frequencies of hydrogen and deuterium[9] from an isotropic Lennard-Jones potential, while Mertens and Biem used the random-phase approximation (RPA).[10] In both calculations the intermolecular potential was modified by a Jastrow correction to account for the short-range correlation effects.

In the numerous calculations on the high-pressure ordering in p-H_2 and o-D_2 only the rotational motions of the molecules are considered. The first attempts to predict a critical density for the phase transition were made by Felsteiner and Friedman[11] and by England, Raich, and Etters.[12] These calculations used the mean-field approximation and gave densities that are considerably too small. Lagendijk and Silvera included the effect of orientational correlations by calculating the roton spectrum of p-H_2 and o-D_2 with the use of an electrostatic quadrupole-quadrupole potential.[13] Actually their roton Hamiltonian is identical to the RPA Hamiltonian, and it has been

shown[14,15] that the occurrence of soft rotons (i.e., zero or imaginary RPA eigenfrequencies) indicates the lack of stability of the mean-field solutions. They found that at the phase transition one roton in the spectrum becomes soft in a specific point of the Brillouin zone. But the calculated critical density still is too low.

Aviram et al.[16-18] used a variational Monte Carlo method to find the orientational ground state of the crystal. By the introduction of a Jastrow factor in the trial wave function the critical density in o-D_2 could be reproduced very well.[18] However, Sprik and Klein[19] point out that the Jastrow function used by Aviram et al. does not possess the correct symmetry and so these results must be treated with caution. Sprik and Klein conclude that a correct variational rotational wave function with Jastrow factor, in combination with an electrostatic quadrupole-quadrupole potential plus anisotropic exchange repulsions, cannot account for the observed critical density in o-D_2. They suggest that translation-rotation coupling and the decrease of the intramolecular bond length might play an important role. These effects are investigated in this paper. Another (variational and diffusion) quantum Monte Carlo study of the ground state in p-H_2 has been made by Ceperley and Alder,[4] who treat the electrons and the nuclei simultaneously. They estimate that orientational ordering in p-H_2 will occur at pressures around 100 GPa. Although they examined a number of crystal structures, the molecular hcp lattice was not included.

Theoretical studies on o-H_2 and p-D_2 are less numerous. They mostly concern pure translational phonons[9] and pure rotational motions (librons),[20] just as the studies on p-H_2 and o-D_2. Translation-rotation coupling is only included in the very complete RPA calculations on o-H_2 and p-D_2 by Mertens and Biem,[10] who have used an empirical anisotropic intermolecular potential.

In the lattice dynamics calculations presented in this paper we have used an *ab initio* potential of Schäfer and Meyer,[21] improved by Schäfer and Köhler[22] through a multiproperty analysis. In addition to the quadrupole-quadrupole interactions, this potential contains anisotropic exchange and dispersion terms and it is represented by a spherical expansion.[23] The potential anisotropy is fully included in the lattice dynamics calculations, the anharmonic expansion of the potential in the translational displacements is truncated only after the sixth power. We have first performed mean-field calculations on the translational vibrations and rotations separately and next we have introduced the correlation between the mean-field excitations as well as the effects of translation-rotation coupling by the time-dependent Hartree (TDH) method. At $T = 0$ K this method is identical to the RPA

method but, in contrast with the latter, it remains valid at higher temperature, when the thermal energy becomes comparable with the excitation energies of the system. By the TDH method we could calculate the phonon and roton dispersion curves for p-H_2 and o-D_2 and the phonon and libron dispersion curves for o-H_2 and p-D_2. Also the influence of the roton-phonon coupling on the high-pressure phase transition in p-H_2 and o-D_2 was studied, as well as the stability of the orientationally ordered ($Pa3$) and disordered fcc and hcp phases in o-H_2 and p-D_2.

II. THEORY

We consider a crystal that consists of molecules with their centers of mass at the positions $r_p = R_p + u_p$, where R_p are the equilibrium positions and u_p the displacements of the molecules p. The orientations of the molecules are described by a set of polar angles ω_p. The crystal Hamiltonian is then given by

$$H = \sum_p T(u_p) + \sum_p L(\omega_p) + \frac{1}{2} \sum_p \sum_{p' \neq p} \Phi_{pp'}(u_p, \omega_p, u_{p'}, \omega_{p'}) .$$

(1)

It contains the kinetic-energy terms for the translational and rotational motions of the molecules and the intermolecular potential.

The translational and rotational mean-field Hamiltonians are given by

$$H_p^T(u_p) = T(u_p) + \sum_{p' \neq p} \langle \Phi_{pp'}(u_p, \omega_p, u_{p'}, \omega_{p'}) \rangle^{L_p L_{p'} T_{p'}} ,$$

(2a)

$$H_p^L(\omega_p) = L(\omega_p) + \sum_{p' \neq p} \langle \Phi_{pp'}(u_p, \omega_p, u_{p'}, \omega_{p'}) \rangle^{L_{p'} T_p T_{p'}} ,$$

(2b)

where $\langle X \rangle^{K_p}$ means the thermodynamic average of X over the eigenstates of H_p^K with $K = T$ or L. From these equations it follows that the translational and rotational Hamiltonians are coupled and we have to solve them in an iterative way. The translational Hamiltonians are diagonalized in a basis of three-dimensional spherical harmonic-oscillator functions.[24] The basis for the molecular rotations consists of tesseral harmonics (real combinations of spherical harmonics).

The intermolecular potential is written in the form of a spherical expansion

$$\Phi_{pp'}(u_p, \omega_p, u_{p'}, \omega_{p'}) = \sum_l \phi_l(r_{pp'}) \sum_m \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{bmatrix} C_{m_1}^{l_1}(\omega_p) C_{m_2}^{l_2}(\omega_{p'}) C_{m_3}^{l_3}(\hat{r}_{pp'}) .$$

(3)

Here $r_{pp'} = (R_{p'} + u_{p'}) - (R_p + u_p)$ and $\hat{r}_{pp'}$ is the unit vector along $r_{pp'}$. The functions $C_m^l(\omega)$ are Racah spherical harmonics, the expression in large parentheses is a 3-j symbol[25] and the summations run over $l = \{l_1, l_2, l_3\}$ and $m = \{m_1, m_2, m_3\}$. The expansion coefficients $\phi_l(r_{pp'})$ reflect explicitly the anisotropy of the intermolecular potential.

In order to make this potential explicitly dependent also on the molecular displacements $\mathbf{u}_p$ and $\mathbf{u}_{p'}$, Briels et al.[26] made a Taylor expansion of the potential in both these displacements. Here, we derive the same expansion in a form that is amenable to much faster calculation.[27] First we expand the part of the potential that depends on the displacements as a Taylor series in $\mathbf{u}_{pp'} = \mathbf{u}_{p'} - \mathbf{u}_p$,

$$\phi_l(r_{pp'})C^{l_3}_{m_3}(\hat{\mathbf{r}}_{pp'}) = \sum_{\alpha=0}^{\infty} \frac{(\mathbf{u}_{pp'} \cdot \nabla)^\alpha}{\alpha!} \phi_l(R_{pp'})C^{l_3}_{m_3}(\hat{\mathbf{R}}_{pp'}) \ . \tag{4}$$

We can evaluate this expression by means of the gradient formula in spherical tensor form[25]

$$\mathbf{u}_{pp'} \cdot \nabla \phi_l(R_{pp'})C^{l_3}_{m_3}(\hat{\mathbf{R}}_{pp'}) = u_{pp'}\sum_{k_1} A_{l_3 k_1}(R_{pp'})\phi_l(R_{pp'})(-1)^{m_3} \sum_{n_1 n_2} \begin{bmatrix} 1 & k_1 & l_3 \\ n_1 & n_2 & -m_3 \end{bmatrix} C^1_{n_1}(\hat{\mathbf{u}}_{pp'})C^{k_1}_{n_2}(\hat{\mathbf{R}}_{pp'}) \ , \tag{5}$$

where the operator $A_{l_3 k_1}(R_{pp'})$ is given by

$$A_{l_3 k_1}(R_{pp'}) = (-1)^{l_3} \left[\delta_{k_1, l_3-1} \left[\frac{l_3(2l_3-1)}{2l_3+1} \right]^{1/2} \left[\frac{d}{dR_{pp'}} + \frac{l_3+1}{R_{pp'}} \right] - \delta_{k_1, l_3+1} \left[\frac{(l_3+1)(2l_3+3)}{2l_3+1} \right]^{1/2} \left[\frac{d}{dR_{pp'}} - \frac{l_3}{R_{pp'}} \right] \right] \ . \tag{6}$$

Using this relation in Eq. (4) gives

$$\phi_l(r_{pp'})C^{l_3}_{m_3}(\hat{\mathbf{r}}_{pp'}) = \sum_\alpha \frac{(u_{pp'})^\alpha}{\alpha!} \sum_{k_1 k_2} {}^l W^{(\alpha)}_{k_1 k_2}(R_{pp'}) \sum_{n_1 n_2} (-1)^{m_3} \begin{bmatrix} k_1 & k_2 & l_3 \\ n_1 & n_2 & -m_3 \end{bmatrix} C^{k_1}_{n_1}(\hat{\mathbf{u}}_{pp'})C^{k_2}_{n_2}(\hat{\mathbf{R}}_{pp'}) \ . \tag{7}$$

The coefficients ${}^l W^{(\alpha)}_{k_1 k_2}(R_{pp'})$ can be calculated with the following recursion relation:

$${}^l W^{(\alpha)}_{k_1 k_2}(R_{pp'}) = (2k_1+1)(-1)^{l_3+1} \sum_{j_1 j_2} \begin{bmatrix} j_1 & 1 & k_1 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} k_2 & k_1 & l_3 \\ j_1 & j_2 & 1 \end{Bmatrix} A_{j_2 k_2}(R_{pp'}) {}^l W^{(\alpha-1)}_{j_1 j_2}(R_{pp'}) \ , \tag{8}$$

with

$${}^l W^{(0)}_{k_1 k_2}(R_{pp'}) = \delta_{k_1, 0}\delta_{k_2, l_3}\sqrt{2l_3+1}\,\phi_l(R_{pp'}) \tag{9}$$

and the expression in curly braces being a 6-j coefficient.

Now we can split $(u_{pp'})^\alpha C^{k_1}_{n_1}(\hat{\mathbf{u}}_{pp'})$ in factors dependent on the molecular displacements $\mathbf{u}_p$ and $\mathbf{u}_{p'}$ (Ref. 28),

$$(u_{pp'})^\alpha C^{k_1}_{n_1}(\hat{\mathbf{u}}_{pp'}) = \sum_{\alpha_1=0}^{\alpha} \sum_{\lambda_1=0}^{\alpha_1} \sum_{\lambda_2=|k_1-\lambda_1|}^{min(k_1+\lambda_1,\alpha_2)} \sum_{\mu_1}\sum_{\mu_2} B^{\alpha k_1 n_1}_{\alpha_1\lambda_1\mu_1\alpha_2\lambda_2\mu_2}(u_p)^{\alpha_1}C^{\lambda_1}_{\mu_1}(\hat{\mathbf{u}}_p)(u_{p'})^{\alpha_2}C^{\lambda_2}_{\mu_2}(\hat{\mathbf{u}}_{p'}) \ , \tag{10}$$

where α_2 is given by $\alpha_2 = \alpha - \alpha_1$ and the coefficients are

$$B^{\alpha k_1 n_1}_{\alpha_1\lambda_1\mu_1\alpha_2\lambda_2\mu_2} = (-1)^{\lambda_1+n_1} \frac{(\alpha+k_1+1)!!(\alpha-k_1)!!(2\lambda_1+1)(2\lambda_2+1)}{(\alpha_1+\lambda_1+1)!!(\alpha_1-\lambda_1)!!(\alpha_2+\lambda_2+1)!!(\alpha_2-\lambda_2)!!} \begin{bmatrix} k_1 & \lambda_1 & \lambda_2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} k_1 & \lambda_1 & \lambda_2 \\ -n_1 & \mu_1 & \mu_2 \end{bmatrix} \ . \tag{11}$$

Introducing this into Eq. (3) and Eq. (7), the intermolecular potential reads

$$\Phi_{pp'}(\mathbf{u}_p,\omega_p,\mathbf{u}_{p'},\omega_{p'}) = \sum_{\Lambda_1}\sum_{\Lambda_2}(u_p)^{\alpha_1}C^{\lambda_1}_{\mu_1}(\hat{\mathbf{u}}_p)C^{l_1}_{m_1}(\omega_p)X_{\Lambda_1\Lambda_2}(R_{pp'})(u_{p'})^{\alpha_2}C^{\lambda_2}_{\mu_2}(\hat{\mathbf{u}}_{p'})C^{l_2}_{m_2}(\omega_{p'}) \ , \tag{12}$$

where Λ stands for the set of indices $\{\alpha,\lambda,\mu,l,m\}$ and $X_{\Lambda_1\Lambda_2}$ is given by

$$X_{\Lambda_1\Lambda_2}(R_{pp'}) = \sum_{l_3 m_3} \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{bmatrix} \sum_{k_1 k_2} {}^l W^{(\alpha_1+\alpha_2)}_{k_1 k_2}(R_{pp'}) \sum_{n_1}\sum_{n_2}(-1)^{m_3} \begin{bmatrix} k_1 & k_2 & l_3 \\ n_1 & n_2 & -m_3 \end{bmatrix} C^{k_2}_{n_2}(\hat{\mathbf{R}}_{pp'})B^{\alpha_1+\alpha_2 k_1 n_1}_{\alpha_1\lambda_1\mu_1\alpha_2\lambda_2\mu_2} \ . \tag{13}$$

This expansion is considerably simpler than that given in Ref. 26 because there is only one recurrence relation needed for the coefficients ${}^l W^{(\alpha)}_{k_1 k_2}(R_{pp'})$, instead of two.

Knowing the single-molecule eigenstates for the translations and the rotations, we can calculate the collective excitation energies of the crystal by using the time-dependent Hartree (TDH) method. This model is described in Refs. 26, 29, and 30; at zero temperature it is equivalent to the random-phase approximation. From the TDH method it follows that the lattice frequencies are the eigenvalues of the TDH matrix.

$$\underline{M}(\mathbf{q}) = \begin{bmatrix} \underline{\chi} - \underline{P}\underline{\Phi}(\mathbf{q}) & -\underline{P}\underline{\Phi}(\mathbf{q}) \\ \underline{P}\underline{\Phi}(\mathbf{q}) & -\underline{\chi} + \underline{P}\underline{\Phi}(\mathbf{q}) \end{bmatrix} .$$

(14)

The diagonal matrix $\underline{\chi}$ contains the mean-field excitation energies

$$\chi_{a,b,i,K;a',b',i',K'} = \delta_{aa'}\delta_{bb'}\delta_{ii'}\delta_{KK'}(\varepsilon_{i,K}^{(a)} - \varepsilon_{i,K}^{(b)}) ,$$

(15)

where $\varepsilon_{i,K}^{(a)}$ is the mean-field energy of excitation level a of a molecule of sublattice i; $K(=T$ or $L)$ labels the type of excitation (translational or rotational). We choose $\varepsilon^{(a)} > \varepsilon^{(b)}$, so elements of $\underline{\chi}$ are always positive. The matrix $\underline{P}$ is also diagonal and contains the population differences of the mean-field states

$$P_{a,b,i,K;a',b',i',K'} = \delta_{aa'}\delta_{bb'}\delta_{ii'}\delta_{KK'}(P_{i,K}^{(a)} - P_{i,K}^{(b)}) ,$$

(16)

with

$$P_{i,k}^{(a)} = \frac{\exp(-\beta\varepsilon_{i,K}^{(a)})}{\sum_a \exp(-\beta\varepsilon_{i,K}^{(a)})}$$

(17)

and $\beta = (kT)^{-1}$. The matrix $\underline{\Phi}(\mathbf{q})$ describes the interactions between the mean-field states of different molecules

$$\Phi_{a,b,i,K;a',b',i',K'}(\mathbf{q}) = \sum_n \exp(i\mathbf{q}\cdot\mathbf{R_n})\langle \psi_{i,K}^{(a)}\psi_{i',K'}^{(b')}|\langle \Phi_{\{0,i\}\{n,i'\}}\rangle^{i,K_c;i',K_c'}|\psi_{i,K}^{(b)}\psi_{i',K'}^{(a')}\rangle$$

$$+ \delta_{ii'}\delta_{KK_c'}\sum_{n''}\sum_{i''}\langle \psi_{i,K}^{(a)}\psi_{i,K_c}^{(b')}|\Phi_{\{0,i\}\{n'',i''\}}\rangle^{i'',K;i'',K_c}|\psi_{i,K}^{(b)}\psi_{i,K_c}^{(a')}\rangle ,$$

(18)

where $\psi_{i,K}^{(a)}$ is the mean-field state corresponding with $\varepsilon_{i,K}^{(a)}$, $\mathbf{q}$ is the wave vector, $\mathbf{n}$ labels the unit cells, and K_c is the complement of K. At the mean-field level the translations and rotations were treated separately, but from Eq. (18) it is clear that in the TDH matrix the rotations and translations are coupled by matrix elements with $K \neq K'$.

If we calculate the lattice frequencies in this way the frequencies of the acoustical phonons in the Γ point, which correspond with uniform translations of the lattice, are not exactly equal to zero. The correct translational invariance can be imposed on the TDH matrix. This implies that we have to recalculate the translational mean-field energies. If the difference between the recalculated and the original mean-field energies is small the calculation is consistent.

III. COMPUTATIONAL ASPECTS

The angular and distance dependence of the intermolecular potential is given by Eq. (3), with the expansion coefficients

$$\phi_l(R) = C_l^{sr}\exp(-a_l R - b_l R^2) + C_l^{mult}R^{-l_1-l_2-1}$$

$$+ C_l^{(6)}R^{-6} + C_l^{(8)}R^{-8} + C_l^{(10)}R^{-10} .$$

(19)

The first term represents the short-range interactions that decay exponentially, the second term the multipole-multipole interactions, and the last three terms the dispersion interactions. In each of the terms we include all anisotropic contributions up to $l_1, l_2 = 2$ inclusive; the only relevant multipole term is the quadrupole-quadrupole $(l_1, l_2, l_3 = 2, 2, 4)$ interaction. Schäfer and Köhler[22] have tabulated every term in the spherical expansion on a grid of R points. The short-range parame-

ters in Eq. (19) were obtained by fitting exponential functions to the short-range part of this intermolecular potential; the multipole and dispersion coefficients are explicitly given in Ref. 22.

Because of the relative weakness of the anisotropic interactions in the crystal a small basis for the calculation of the rotational mean-field states was sufficient. For p-H_2 and o-D_2 we included tesseral harmonics up to
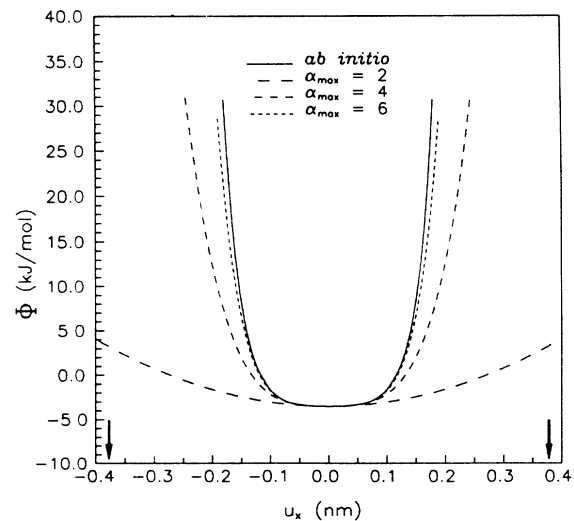

FIG. 1. Single-molecule potential in p-H_2 (normal pressure hcp phase) for displacements (u_x) along the crystallographic a direction. The dashed lines are Taylor expansions of this potential including all powers $(u_x)^\alpha$ for $\alpha \leq \alpha_{max}$. The arrows indicate the equilibrium positions of the nearest neighbors.

TABLE I. Nearest-neighbor distance, lattice free energy, and root-mean-square displacement of the molecules in p-H_2 and o-D_2 at normal pressure.

		R_{nn} (nm)	A (kJ/mol)	$\langle u^2 \rangle^{1/2}$ (nm)
p-H_2	Calculated $(T=0$ K$)$	0.3887	-0.56	0.059
	Experiment $(T=5$ K$)$	0.3789[a]	-0.75[a]	0.068[b]
o-D_2	Calculated $(T=0$ K$)$	0.3680	-0.99	0.045
	Experiment $(T=5$ K$)$	0.3605[a]	-1.10[a]	0.050[c]

[a]Reference 2.
[b]Reference 33.
[c]Reference 32.

$l_{max} = 2$ and for o-H_2 and p-D_2 up to $l_{max} = 3$. Because of the large anharmonicity in the translational motions the number of basis functions in the calculation of the translational states was much larger. Oscillator functions up to $n_{max} = 4$ were taken into account, which results in a basis of 35 functions. In these spherical harmonic oscillator functions there is a scaling parameter A which is used to optimize the basis.[26] In case of a harmonic Hamiltonian we should use $A = (M\omega/\hbar)^{1/2}$, with M being the molecular mass and ω the harmonic-oscillator frequency. For the anharmonic Hamiltonian we chose

$$A = [M(\varepsilon^{(1)} - \varepsilon^{(0)})/\hbar^2]^{1/2} ,$$

with $\varepsilon^{(1)} - \varepsilon^{(0)}$ being the first translational mean-field excitation energy.

In the calculations at normal pressure the maximum range of the intermolecular potential was set at 8.0 Å; in the hcp structure this corresponds with a lattice sum over six shells (56 molecules), in the fcc structure with four shells (54 molecules). For the higher pressures these lattice sums were extended to a maximum of 86 molecules.

It is well known that the potential wells for the molecules in solid hydrogen and deuterium are far from harmonic. So if we want a good representation of the potential as a power series in the molecular displacements we have to go beyond quadratic terms. In Fig. 1 the poten-

tial energy is given for a hydrogen molecule in the hcp lattice as a function of the displacement, while all other molecules were pinned to their equilibrium positions. From this figure it is clear that the expansion of the potential should not be truncated before the sixth-order terms. It is also made obvious why the harmonic approximation $(\alpha_{max} = 2)$ fails for solid hydrogen. If the translational wave function of the molecule consists of a single Gaussian, as assumed in the self-consistent phonon method[9] and in the RPA method of Mertens and Biem,[10] a Jastrow correlation factor had to be introduced to cut off the tail of this Gaussian.[31] Thus, the overlap of the wave functions of neighboring molecules is kept within reasonable limits. In our case, the translational wave functions are linear combinations of (up to) 35 harmonic-oscillator functions in which the tails can be canceled out. The tails of the resulting wave functions are indeed much smaller and thus a Jastrow function is not needed.

We have optimized the crystal structure by minimizing the free energy at the mean-field level. In Table I the nearest-neighbor distance, the lattice energy and the root mean square of the translational displacements are given at the optimum structure for the hcp lattices of p-H_2 and o-D_2. In both cases the optimized nearest-neighbor distance is somewhat too large and the root mean square of the translations is slightly too small. This is caused by the mean-field approximation. In the calculations of the

TABLE II. Phonon frequencies (in cm^{-1}) in the hcp phases at normal pressure.

		Experiment $(T=4.2$ and 5 K$)$	This work	Calculated $(T=0$ K$)$ SCP (Ref. 9)	RPA (Ref. 10)
p-H_2	E_{2g}	37.8[a]	45.4	40.5,[b] 35.7[c]	48.4
	B_{1g}	81.9[d]	96.8	118.3,[b] 87.5[c]	110.5
o-D_2	E_{2g}	38.3[a]	39.0	38.2,[b] 33.7[c]	45.2
	B_{1g}	81.6[d]	86.1	108.3,[b] 80.4[c]	97.8

[a]Reference 32.
[b]From the displacement-displacement correlation function (Ω_k).
[c]Eigenvalues of the dynamical matrix (ω_k).
[d]Reference 33.

TABLE III. Roton frequencies (in cm^{-1}) in the hcp phases at normal pressure.

| | p-H$_2$ | | o-D$_2$ | |
	This work ($T=0$ K)	Experiment (Ref. 35) ($T=2$ K)	This work ($T=0$ K)	Experiment (Ref. 35) ($T=2$ K)
E_{1u}	346.3		168.3	
E_{1g}	352.7	351.8	176.7	176.8
E_{2g}	354.8	353.8	179.6	179.4
E_{2u}	356.7		182.0	
A_{1g}	356.8	355.8	182.3	182.0
A_{1u}	365.6		193.4	

lattice frequencies we have used the optimized lattice parameters given in Table I. For the rotational constant of hydrogen we have taken $B = 0.7065$ kJ/mol$= 59.06$ cm^{-1} and for deuterium $B = 0.3570$ kJ/mol$= 29.83$ cm^{-1}.

IV. RESULTS

A. p-H$_2$ and o-D$_2$

At zero temperature and normal pressure p-H$_2$ and o-D$_2$ crystallize in the hcp structure (space group D^4_{6h}). The rotational states of the molecules are free rotor states with even l values. Because of the large rotational constants of H$_2$ and D$_2$ the excitation energy ($l = 0 \rightarrow l = 2$) for the rotational states is very large (≈ 360 and 180 cm^{-1}). Therefore, the coupling between the rotons and phonons is negligible at normal pressures.

In Table II the calculated optical phonon frequencies are compared with the experimental values[32,33] and the values calculated earlier by Klein and Koehler[9] and by Mertens and Biem.[10] In both these earlier calculations a Jastrow function was used to account for the short-range

correlation. In agreement with experiment[32-34] it is found that the phonon frequencies in p-H$_2$ and o-D$_2$ are almost the same, in spite of the mass difference. This indicates that the effective potential in H$_2$ is softer than in D$_2$, due to the averaging over the zero-point motions and the resulting extension of the lattice. Klein and Koehler have obtained lattice frequencies in two different manners: from the poles of the displacement-displacement correlation function (Ω_k) and from the eigenvalues of the dynamical matrix (ω_k). It is generally believed[32,33] that in self-consistent phonon calculations with the use of a Jastrow function the values Ω_k are more realistic. Klein and Koehler find, however, that their ω_k values agree considerably better with experiment. Table II shows that our calculated phonon frequencies are not as close to experiment as the ω_k values of Klein and Koehler, but are substantially better than their Ω_k values, and are also much better than the frequencies calculated by Mertens and Biem. In Table III our calculated roton frequencies are compared with the roton frequencies measured by Bhatnagar et al.[35] in Raman experiments. The agreement is perfect.

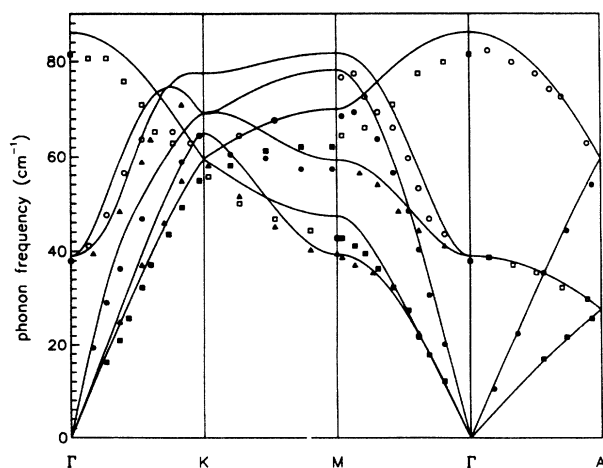In Fig. 2 the calculated phonon dispersion curves for

FIG. 2. Phonon dispersion curves for o-D$_2$ (normal pressure hcp phase) calculated at $T=0$ K. The dots are neutron scattering data (Refs. 33 and 34) at $T=4.2$ and 5 K.
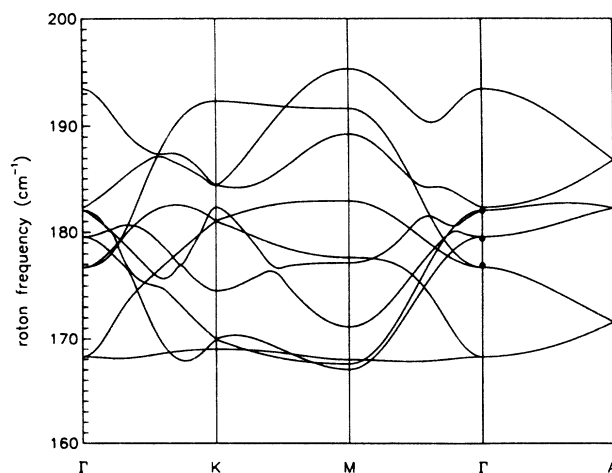

FIG. 3. Roton dispersion curves for o-D$_2$ (normal pressure hcp phase), calculated at $T=0$ K. The three dots at the Γ point are Raman results (Ref. 35) at $T=2$ K.
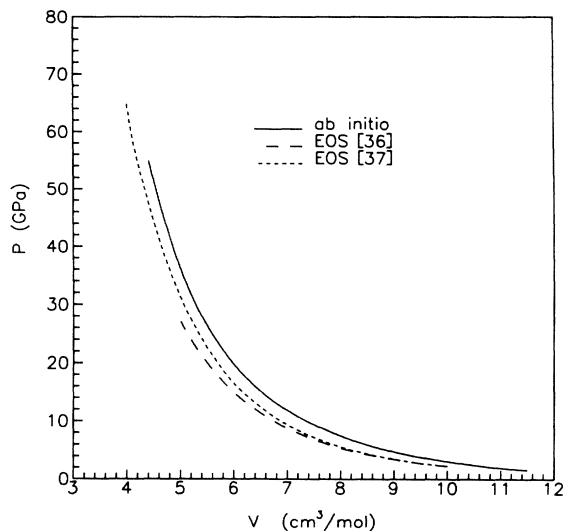
FIG. 4. p-V relation of p-H_2 (hcp phase) calculated *ab initio*, Eq. (20), and from (semi) empirical equations of state ($T = 0$ K).

FIG. 6. Roton dispersion curves for o-D_2 (hcp phase) calculated at the transition pressure. Note the occurrence of a soft roton at the M point.

o-D_2 are compared with neutron-scattering data from Nielsen and Møller.[33,34] The correspondence of the calculated curves with the experimental ones is very good and only for the higher frequencies the calculated curves are slightly too high. The roton dispersion curves for o-D_2 are plotted in Fig. 3.

The phonon and roton dispersion curves for p-H_2 closely resemble those of o-D_2 and are not given here. The roton frequencies are twice as high as for o-D_2, because of the factor of 2 in the rotational constants. For

the phonon frequencies of p-H_2 the agreement with experiment is somewhat less good than for o-D_2; the calculated frequencies are about 15% too high. Still, this is considerably better than the p-H_2 frequencies computed by Mertens and Biem, which were about 30% too high.

In order to predict the high-pressure phase transition in p-H_2 and to reproduce the observed transition pressure for o-D_2 we have calculated the lattice frequencies for different lattice constants. The pressure for a certain lattice constant was calculated from the Helmholtz free energy A at the mean-field level with the well-known relation

$$p = -\left[\frac{\partial A}{\partial V}\right]_T. \tag{20}$$
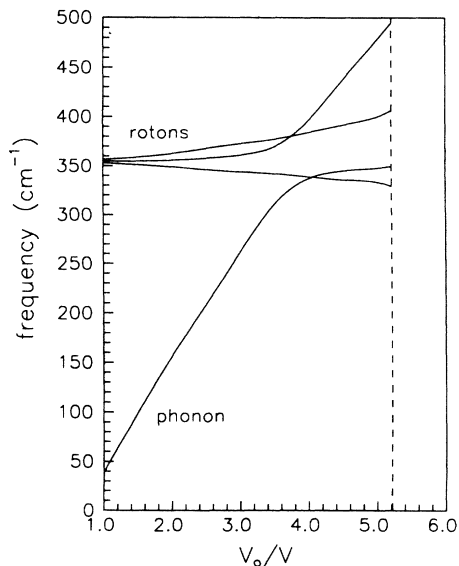

FIG. 5. Volume dependence of the Raman-active phonon and roton frequencies in p-H_2 (hcp phase) as calculated. The corresponding experimental curves are given in Fig. 1 of Ref. 7. The dashed line indicates the calculated transition volume and V_0 is the molar volume at zero pressure.
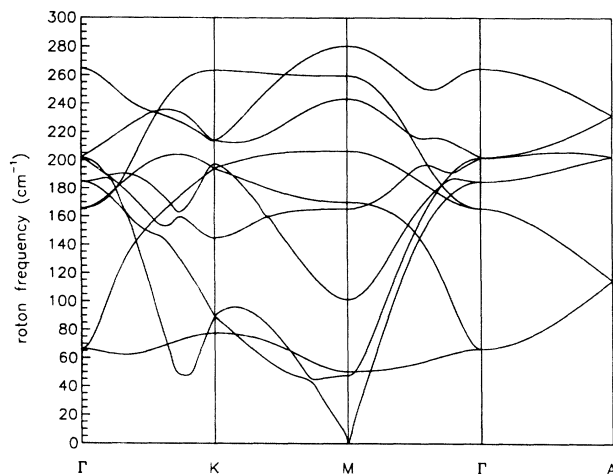
Thus, we have obtained the p-V curve completely *ab initio*. In Fig. 4 this p-V curve is compared with experimental[36] and semiempirical[37] equations of state. This figure shows that our equation of state yields too high pressures, which is probably due to the failure of the mean-field model. In the following discussion we use the *ab initio* equation of state, as well as an experimental one, to obtain the pressure belonging to the calculated molar volumes.

In Raman experiments Silvera and Wijngaarden[7,38] measured the phonon and roton frequencies of p-H_2 and o-D_2 as a function of the pressure. In Fig. 5 we present our calculated Raman frequencies as a function of the molar volume for p-H_2. The experimental results are given in Fig. 1 of Ref. 7. The correspondence is very good; the molar volume at which the avoided crossing between the roton and the phonon takes place is exactly the same as found in the experiment. In Fig. 1 of Ref. 7 we observe that all three roton frequencies slightly increase

TABLE IV. Volume and pressure of the orientational ordering transition in p-H_2 and o-D_2.

	Model[a]	V_t (cm^3/mol)	Calculated p_t^b (GPa)	p_t^c (GPa)	Experiment (Ref. 7) p_t (GPa)
p-H_2	I	4.35	60	42	
	II	4.44	64	39	
	III	4.26	76	44	
	IV	3.98	99	55	> 54
o-D_2	I	6.34	15	12	
	II	6.34	17	12	
	III	6.12	20	13	
	IV	5.78	25	16	27.8

[a]Model I: including rotons only. Model II: including rotons, phonons, and rotation-translation coupling. Model III: as II, corrected for H_2 bond-length shortening, effect on the rotational constant B only. Model IV: as III, effect on the rotational constant B and on the quadrupole moment Q.
[b]Obtained from V_t via *ab initio* equation of state, Eq. (20).
[c]Obtained from V_t via empirical equation of state (Ref. 36).

when the pressure is raised. This is probably due to the shortening of the intramolecular bond length, which leads to an increase of the rotational constant. In our calculations we have not included this effect so far, so the calculated roton frequencies do not show the overall raise with increasing pressure. We return to this point in the discussion of the phase transition pressure.

In order to calculate the volume at which the phase transition takes place we can compare the mean-field free energies of the disordered (hcp) phase and the ordered ($Pa3$) phase. Another way of observing a phase transition is by looking for the occurrence of soft lattice modes, throughout the Brillouin zone. It proves to be difficult to predict the transition volume by comparing the free energies, because of the extremely small differences in free energy between the two phases. The transition volume is therefore calculated by looking for a soft mode. In Fig. 6 the roton dispersion curves of o-D_2 are given at the transition volume $V_t = 6.34$ cm^3/mol. Only the rotational excitations of the molecules were considered in this calculation. The figure shows that at the M point in the Brillouin zone a roton becomes soft, which indicates that

there is a phase transition involving the orientations of the molecules.

The order parameter $\langle C_0^{(2)} \rangle$, which is a measure for the degree of localization of the molecules, shows an abrupt change at this phase transition. In the hcp phase, where the order parameter is defined as $\langle C_0^{(2)} \rangle$ with respect to the crystallographic c axis, the molecules are orientationally delocalized and the order parameter is very small ($\approx 5 \times 10^{-4}$). In agreement with experiment,[7,39] it is not equal to zero, however. So, the ground state of the molecules in the disordered phase has nearly $l = 0$, but there is very small admixture of the state with $l, m = 2, 0$. In the high-pressure fcc phase $\langle C_0^{(2)} \rangle$ is defined with respect to the [111] axis. Just above the phase transition it is equal to 0.3 and with increasing pressure there is a further rise of this order parameter.

We have also calculated the transition volume with the inclusion of both rotations and translations. Again, we find a soft roton at the M point in the Brillouin zone, but it proved that the rotation-translation coupling has little influence on the transition volume. In Table IV we have given the calculated transition volumes for both p-H_2 and

TABLE V. Phonon frequencies (in cm^{-1}) in the $Pa3$ phases at normal pressure.

		Experiment (Ref. 40) ($T = 1.3$ K)	Calculation ($T = 0$ K) This work	RPA (Ref. 10)
o-H_2	T_u	62.2	67.9	78.9
	E_u		68.0	79.1
	A_u	80.0	70.1	82.9
	T_u	93.0	97.0	115.4
p-D_2	T_u	57.4	59.5	70.3
	E_u		59.7	70.5
	A_u	74.5	61.3	73.7
	T_u	85	86.1	103.2

TABLE VI. Libron frequencies (in cm^{-1}) in the $Pa3$ phases at normal pressure.

		Experiment (Ref. 41) ($T=1.16$ K)	Calculated ($T=0$ K) This work	RPA (Ref. 10)
o-H$_2$	E_g	6.5	7.7	9.3
	T_g	8.2	10.3	12.5
	T_g	11.3	16.2	21.0
p-D$_2$	E_g	9.0	10.7	12.5
	T_g	11.2	14.1	16.9
	T_g	15.4	21.9	27.8

o-D$_2$ when calculated with only rotational excitations and with both rotational and translational excitations. The pressures given in Table IV are calculated using the equation of state obtained from the *ab initio* mean-field free energy, as well as from an empirical equation of state. This table shows that for o-D$_2$, and most probably also for p-H$_2$, the calculated transition pressures are too low compared with experiment.

From Fig. 1 of Ref. 7 it is clear that the approximation of the rotational constant being the same over the whole pressure range does not hold. Therefore, we have to consider the change in rotational constant as suggested by Sprik and Klein.[19] We did this by estimating the rotational constant from the frequency shift of the rotons in the Raman spectra[7] and using the following relation derived by Lagendijk and Silvera[13] to determine the nearest-neighbor distance at the phase transition:

$$R_{NN}^5 \sim \frac{Q^2}{B} . \qquad (21)$$

Here, Q is the molecular quadrupole moment and B is the rotational constant. It is justified to use this relation be-

cause the most relevant anisotropic interaction, the $l_1,l_2,l_3=2,2,4$ term, is dominated by the quadrupole-quadrupole interaction (with contributions of 98% and 99.5% at the phase transitions of p-H$_2$ and o-D$_2$, respectively). From relation (21) we can calculate the influence of the rotational constant on the nearest-neighbor distance and thus on the molar volume of the phase transition. The corrected transition volumes are also given in Table IV.

The change of the intramolecular bond length not only affects the rotational constant of the molecules but also their quadrupole moment. We can estimate the change in the quadrupole moment from calculations by Poll and Wolniewicz.[40] In Table IV the transition volumes are also given when calculated with the corrected rotational constant and quadrupole moment. It is clear that the effect of the change in quadrupole moment is larger than the effect of the change in rotational constant and that both corrections are certainly not negligible. For o-D$_2$ the transition pressure calculated in this way corresponds
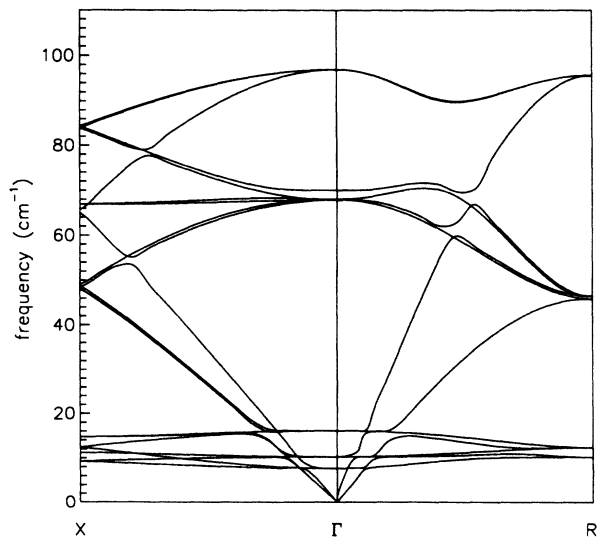

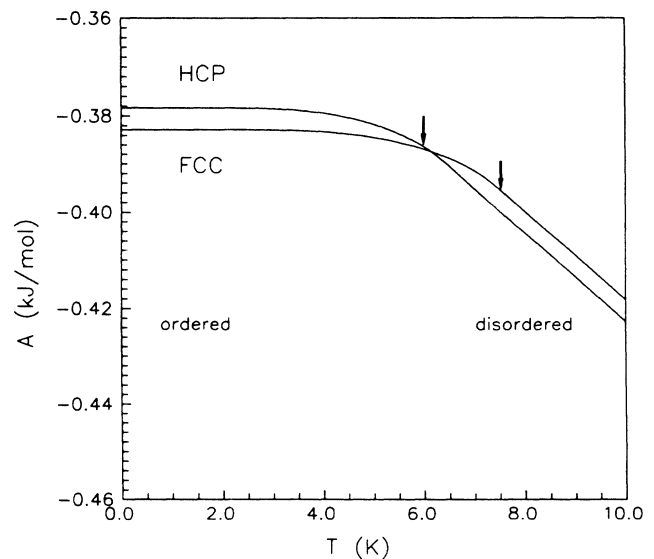FIG. 7. Phonon and libron dispersion curves for o-H$_2$ ($Pa3$ phase) calculated at $T=0$ K.

FIG. 8. Helmholtz free energy of the hcp and fcc phases of o-H$_2$ from mean-field calculations. The arrows indicate the disordering temperatures

very well to the transition pressure found in experiments, if we use the *ab initio* equation of state. This is probably fortuitous because we have to keep in mind that the pressure calculated from Eq. (20) is too high. Therefore, we have also estimated the pressures with the equation of state of Ref. 36 and we find, then, that the transition pressures are still substantially too low.

B. *o*-H$_2$ and *p*-D$_2$

In contrast with the excitations in *p*-H$_2$ and *o*-D$_2$, the phonons and librons in *o*-H$_2$ and *p*-D$_2$ are close together in energy and mixing between these excitations can occur at normal pressure. At very low temperature *o*-H$_2$ and *p*-D$_2$ crystallize in the cubic *Pa*3-phase (space group T_h^6). In Table V the calculated phonon frequences of *o*-H$_2$ and *p*-D$_2$ are compared with far-infrared measurements of Hardy *et al.*[41] and with earlier calculations by Mertens and Biem.[10] The calculated phonon frequencies are generally in good agreement with the experimental ones, somewhat better than those of Mertens and Biem. In the far-infrared measurements only three optical phonon frequencies were found, while group theoretical considerations yield four infrared-active phonon modes. From both our calculations and those of Mertens and Biem it is clear that the splitting between the T_u and the E_u phonon is indeed very small. However, the splitting between the A_u phonon frequency and the T_u and E_u frequencies, which is mainly caused by the quadrupole-quadrupole interactions, is much smaller in both calculations (it is only 2–3 cm^{-1}) than in the experiments (where it is 17.8 and 17.1 cm^{-1} for *o*-H$_2$ and *p*-D$_2$, respectively).

In Table VI the calculated libron frequencies are given together with the results of the calculations performed by Mertens and Biem and experimental frequencies from Raman measurements of Hardy *et al.*[42] The calculated libron frequencies are all somewhat too high, but considerably better than those of Mertens and Biem.

In Fig. 7 the phonon and libron dispersion curves for *o*-H$_2$ are plotted for the X and R directions in the Brillouin zone. The librons, which all have low frequencies (≈ 17 cm^{-1}), only mix with the acoustical phonons near the Γ point. The librons show little dispersion. Most of the phonon branches are split due to the quadrupole-quadrupole interaction. The phonon and libron dispersion curves of *p*-D$_2$ are not given here, because they closely resemble those of *o*-H$_2$.

Finally, we have considered the phase transition from the ordered cubic *Pa*3 phase to the orientationally disordered hcp phase in *o*-H$_2$ and *p*-D$_2$. The disordering temperatures and the free energies of both phases have been calculated by the mean-field method and displayed in Fig. 8. It is well known[1,2] that the mean-field approximation predicts disordering temperatures ($T = 7.5$ and 6 K for the fcc and hcp phases, respectively) which are considerably too high. The preferential stability of the fcc lattice for the ordered phase and the hcp lattice for the disordered phase is nicely illustrated by Fig. 8, but the calcu-

lated transition temperature, $T = 6.1$ K, is too high by a factor of 2 (experimentally $T = 2.8$ K for *o*-H$_2$).

V. CONCLUSIONS

From the agreement between the results of the lattice dynamics calculations and the experimental data we can conclude that the *ab initio* potential of Schäfer and Meyer is a good representation of the anisotropic H$_2$-H$_2$ interaction. By construction, this potential is a pure pair potential, which does not include any effective three-body interactions, as some of the empirical potentials.[36,37] In contrast with other lattice dynamics calculations on solid hydrogen[9,10] which replace the real potential by an effective one including a Jastrow correction, we have used the bare intermolecular potential. Thus, we avoid the truncated cluster expansion[31] of the Jastrow factor in the many-particle wave function which has to be made in order to arrive at the effective pair potential.[9,10] We have shown that this is realistic if the wave functions chosen for the translational vibrations of the molecules are sufficiently flexible, so that they can adapt to the strong anharmonicity of the potential (and thus avoid having long overlapping tails). The anharmonic expansion of the intermolecular potential in the molecular displacements had to be continued through sixth-order terms. At the mean-field level the correlation between the motions of the molecules is neglected and, therefore, the repulsion is still somewhat overestimated. This can be concluded from the root mean square of the translational displacements which is too small, from the optimized lattice parameter which is too large, and from the calculated equation of state which predicts too high pressures.

At the TDH level the correlation is partly restored. The calculated phonon frequencies for both the hexagonal and the cubic phases are in good agreement with the experimentally observed frequencies, considerably better than the frequencies calculated by Mertens and Biem[10] and the frequencies obtained from the displacement-displacement correlation function by Klein and Koehler.[9] Only the large observed splitting between the A_u-phonon peak and the lower peak in the *Pa*3 spectrum of *o*-H$_2$ and *p*-D$_2$ cannot be explained. The roton frequency splittings in the hexagonal phases match the experiments perfectly. The libron frequencies in the cubic phases are slightly too large; this is probably due to the strong correlation between the librational motions of the molecules[20] that cannot be fully taken into account at the TDH level. Still, the results are better than those calculated by Mertens and Biem[10]

In our calculations on the high-pressure phase transition in *p*-H$_2$ and *o*-D$_2$ it is demonstrated that the inclusion of rotation-translation coupling has only a small influence on the transition volume. The shortening of the intramolecular bond length, which changes the quadrupole moment and the rotational constant, cannot be neglected in attempts to predict the correct transition pressures and volumes. But these effects cannot fully account for the high value of the experimental transition pressure. We conclude that mainly three-body interactions and, to some extent, the correlation between the

molecular motions beyond the TDH model, must be responsible for the remaining discrepancy.

ACKNOWLEDGMENTS

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