which is reduced for large M to

$$M^{1/2}\epsilon_e^{-1}\int_{-\infty}^{\infty} e^{-(M/2)|Y''(\epsilon_e)|(\epsilon-\epsilon_e)^2}d\epsilon.$$

Therefore we have

$$\lim_{M\to\infty} J_M=\epsilon_e^{-1}[2\pi/|Y''(\epsilon_e)|]^{1/2}. \quad \text{(B7)}$$

Then, using Eq. (B3), we have the asymptotic form

$$I_M\sim\epsilon_e^{-1}\left[\frac{2\pi X(\epsilon_e)}{|X''(\epsilon_e)|}\right]^{1/2}M^{-1/2}[X(\epsilon_e)]^M. \quad \text{(B8)}$$

Now we find that the factor $\epsilon_e^{-1}[2\pi X(\epsilon_e)/|X''(\epsilon_e)|]^{1/2}$ is neglected in the expression of Eq. (2.12).

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One-Phonon Excited States of Solid H_2 and D_2 in the Ordered Phase*†

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Optical-phonon frequencies of ordered solid H_2 and D_2 have been calculated using a Lennard-Jones intermolecular potential derived from measurements of gas-phase properties. Good agreement with experiment is obtained. Density-of-states functions and phonon dispersion curves in three directions have also been computed.

INTRODUCTION

THE lattice dynamics of solid hydrogen and deuterium cannot be treated by the traditional harmonic approximation.[1] The molecules are so light and the intermolecular forces so weak that the zero-point kinetic energy is equal to about half of the sublimation energy,[2] and the harmonic approximation, when attempted, gives imaginary energies of excitation.[3]

Nosanow and Werthamer[4] have developed a means of treating the lattice dynamics of such crystals and have reported reasonable agreement between calculated and experimental sound velocities in solid ^{3}He and ^{4}He. We report here the application of this method to the calculation of phonon frequencies and density-of-states functions for the fcc phases of orthohydrogen and paradeuterium. A similar calculation has recently been done for hexagonal hydrogen by Mertens and Biem.[5]

The approach of Nosanow and Werthamer assumes a ground-state wave function of the form

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)=\prod_i \phi_0(\mathbf{r}_i-\boldsymbol{\tau}_i)\prod_{k<1} f(|\mathbf{r}_k-\mathbf{r}_1|), \quad (1)$$

where $\phi_0(\mathbf{r}-\boldsymbol{\tau})$ is a function of one molecule at $\mathbf{r}$, the equilibrium position of which is a lattice point $\boldsymbol{\tau}$, and the short-range correlation functions $f(\rho)=\exp(-K[(\sigma/\rho)^{12}-(\sigma/\rho)^6])$. Here K is a variational parameter and the intermolecular potential $v(\rho)=4\epsilon[(\sigma/\rho)^{12}-(\sigma/\rho)^6]$, with[6] $\epsilon=37.00$°K and $\sigma=2.928$ Å. An approximate treatment[7] has shown that for solid helium an appropriate ground-state one-particle function is

$$\phi_0(\mathbf{r})=(A/\pi)^{3/4}e^{-Ar^2/2}. \quad (2)$$

The effect of the short-range correlations may be looked upon as a replacement of the assumed intermolecular potential $v(\rho)$ by an effective potential[4]

$$W(\rho)\cong[v(\rho)-(\hbar^2/2\mu)\nabla^2\ln f(\rho)]f^2(\rho), \quad (3)$$

where μ is the molecular mass. By using linear response theory and several approximations, it is found that the

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* Work at Minnesota supported in part by the U. S. Atomic Energy Commission.

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).
[2] E. S. Borovik, S. F. Grishin, and E. Ya. Grishina, Zh. Tekhn. Fiz. **30**, 539 (1960) [English transl.: Soviet Phys.—Tech. Phys. **5**, 506 (1960)].
[3] F. W. deWette and B. R. A. Nijboer, Phys. Letters **18**, 19 (1965).
[4] L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).
[5] F. G. Mertens and W. Biem (unpublished).
[6] J. O. Hirschfelder, E. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1110.
[7] L. H. Nosanow, Phys. Rev. **146**, 120 (1966).

TABLE I. Constants used in calculation and ground-state energy.

Crystal	ϵ[a]	σ[a]	d_0[b]	A	$K/4\epsilon$	E_0 (calc)	E_0[c] (expt)
H_2	37.00°K	2.928 Å	3.757 Å	3.319 Å^{-2}	0.2404	−152.4 cal mole^{-1}	−248 cal mole^{-1}
D_2	37.00°K	2.928 Å	3.592 Å	5.7099 Å^{-2}	0.2856	−261.0 cal mole^{-1}	

[a] Reference 6.
[b] Reference 8.
[c] Reference 2.

phonon frequencies are roots of the equation[4]

$$\det\left|\mu\omega^2\delta_{\zeta\zeta'}\delta_{qq'}-\sum_p{}'\exp\{i\mathbf{k}\cdot[\tau(p,q')-\tau(0,q)]\}\times\frac{\partial^2\langle 00|W(|\mathbf{r}(p,q')-\mathbf{r}(0,q)|)|00\rangle}{\partial\tau_\zeta(p,q')\partial\tau_{\zeta'}(0,q)}\right|=0, \quad (4)$$

where $\zeta=x, y, z$; p labels the unit cell; and q, q' label the site in the unit cell. Equation (4) is the same equation as that obtained from the harmonic approximation, except that the average of the effective potential $W(\rho)$ over the ground-state distribution of the two interacting molecules has been substituted for the intermolecular potential $v(\rho)$. When this substitution is made, the roots of the secular equation are all positive and the frequencies real.

At low temperatures, orthohydrogen and paradeuterium (the species with $J=1$) crystallize in an fcc lattice.[8,9] Neutron-diffraction experiments[9] on deuterium indicate that the space group is $Pa3$ (T_h^6); o-hydrogen is assumed to have the same space group. This structure contains four molecules per primitive unit cell arranged in an fcc array, but with the molecules differentiated by orientational ordering. Optical phonons have been observed by far-infrared absorption spectroscopy[10] proving there is more than one molecule per primitive unit cell. The quadrupole-quadrupole interaction between hydrogen molecules is thought to be the origin of this ordering.[11] However, this interaction has a small effect on the phonon frequencies and has been neglected in this calculation, so that the potential function used is spherically symmetric. This means that the potential cannot distinguish the different sites in the unit cell and the effective space group is, therefore, $Fm3m$ (O_h^5).

Since the wave functions used for the ground and first-excited states have the same symmetry properties as harmonic-oscillator functions, the group-theoretical treatments of this problem and of the harmonic approximation are exactly alike.

CALCULATION

The parameters ϵ and σ in the Lennard-Jones potential function are those obtained from the second virial coefficients of gaseous H_2 and D_2.[6] The nearest-neighbor distances d_0 are taken from the x-ray data of Mills and Schuch.[8]

The energy of the ground state is approximated by the

TABLE II. Dynamical matrix.

	x_1	y_1	z_1	x_2	y_2	z_2	x_3	y_3	z_3	x_4	y_4	z_4
x_1	$2X+Z$[a,b]	0	0	$-XC(u)$[c]	$-VS(u)$[d,e]	0	$-ZC(v)$[f]	0	0	$-XC(w)$[g]	0	$-VS(w)$[h]
		$2X+Z$	0	$-VS(u)$	$-XC(u)$	0	0	$-XC(v)$	$-VS(v)$[i]	0	$-ZC(w)$	0
			$2X+Z$	0	0	$-ZC(u)$	0	$-VS(v)$	$-XC(v)$	$-VS(w)$	0	$-XC(w)$
				$2X+Z$	0	0	$-XC(w)$	0	$-VS(w)$	$-ZC(v)$	0	0
					$2X+Z$	0	0	$-ZC(w)$	0	0	$-XC(v)$	$-VS(v)$
						$2X+Z$	$VS(w)$	0	$-XC(w)$	0	$-VS(v)$	$-XC(v)$
							$2X+Z$	0	0	$-XC(u)$	$-VS(u)$	0
								$2X+Z$	0	$-VS(u)$	$-XC(u)$	0
									$2X+Z$	0	0	$-ZC(u)$
										$2X+Z$	0	0
											$2X+Z$	0
												$2X+Z$

[a] $X=Z+2[\partial^2V_{\rm eff}/\partial R^2|_{R=d_0}-(1/d_0)\partial V_{\rm eff}/\partial R|_{R=d_0}]=210.558$ erg cm^{-2}.
[b] $Z=(4/d_0)\partial V_{\rm eff}/\partial R|_{R=d_0}=8.35356$ erg cm^{-2}.
[c] $C(u)=\cos(\frac{1}{2}k_xa_0)\cos(\frac{1}{2}k_ya_0)$.
[d] $V=-2[\partial^2V_{\rm eff}/\partial R^2|_{R=d_0}-(1/d_0)\partial V_{\rm eff}/\partial R|_{R=d_0}]=-208.470$ erg cm^{-2}.
[e] $S(u)=\sin(\frac{1}{2}k_xa_0)\sin(\frac{1}{2}k_ya_0)$.
[f] $C(v)=\cos(\frac{1}{2}k_ya_0)\cos(\frac{1}{2}k_za_0)$.
[g] $C(w)=\cos(\frac{1}{2}k_za_0)\cos(\frac{1}{2}k_xa_0)$.
[h] $S(w)=\sin(\frac{1}{2}k_za_0)\sin(\frac{1}{2}k_xa_0)$.
[i] $S(v)=\sin(\frac{1}{2}k_ya_0)\sin(\frac{1}{2}k_za_0)$.

[8] R. L. Mills and A. F. Schuch, Phys. Rev. Letters **15**, 722 (1965); **16**, 616 (1966); A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. **165**, 1032 (1968).
[9] K. F. Mucker, S. Talhouk, P. M. Harris, D. White, and R. A. Erickson, Phys. Rev. Letters **16**, 799 (1966).
[10] W. N. Hardy, I. F. Silvera, K. N. Klump, and O. Schnepp, Phys. Rev. Letters **21**, 291 (1968).
[11] J. C. Raich and H. M. James, Phys. Rev. Letters **16**, 173 (1966).

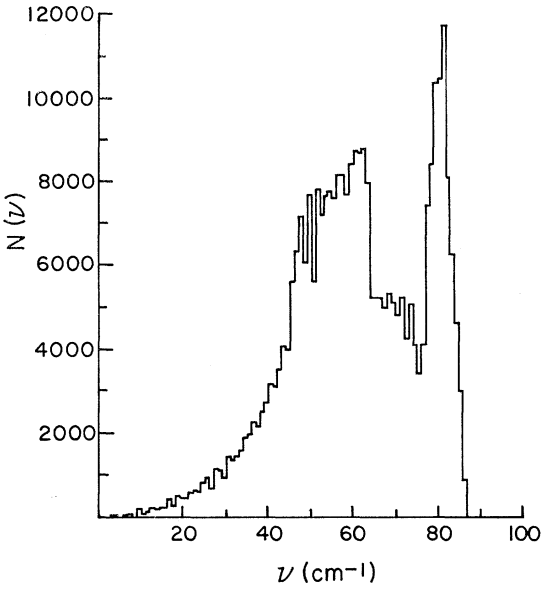

FIG. 1. Density-of-states function for hydrogen.

first two terms of a cluster expansion of $\langle\psi_0|H|\psi_0\rangle$:

$$E_0 \simeq \frac{3h^2A}{4M} + \sum_j \frac{\langle\phi_0(0)\phi_0(j)|W(|\mathbf{r}_0-\mathbf{r}_j|)|\phi_0(0)\phi_0(j)\rangle}{\langle\phi_0(0)\phi_0(j)|f^2(|\mathbf{r}_0-\mathbf{r}_j|)|\phi_0(0)\phi_0(j)\rangle}. \quad (5)$$

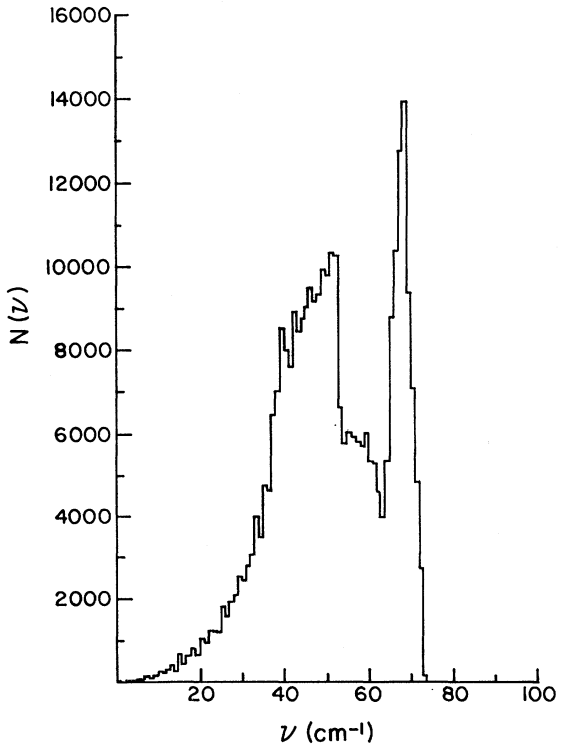

FIG. 2. Density-of-states function for deuterium.

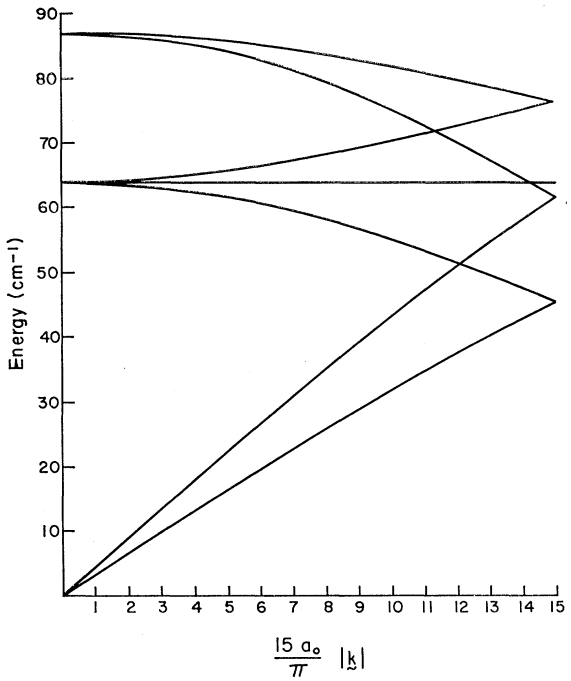

FIG. 3. Hydrogen phonon dispersion curve [100].

Minimizing E_0 gives values for A and K. The parameters used are shown, with the calculated E_0, in Table I.

The values of A and K so obtained are used to compute $\partial V_{\text{eff}}/\partial R$ and $\partial^2 V_{\text{eff}}/\partial R^2$, where $V_{\text{eff}}=\langle\phi_0(i)\phi_0(j)|W(|\mathbf{r}_i-\mathbf{r}_j|)|\psi_0(i)\phi_0(j)\rangle$ and $R=|\tau_0-\tau_j|$. Although in the computation of E_0, the sum over j must be an

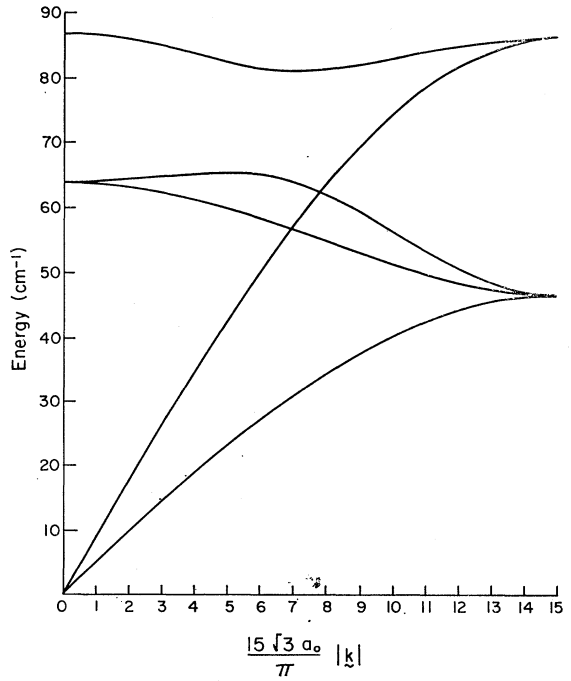

FIG. 4. Hydrogen phonon dispersion curve [111].

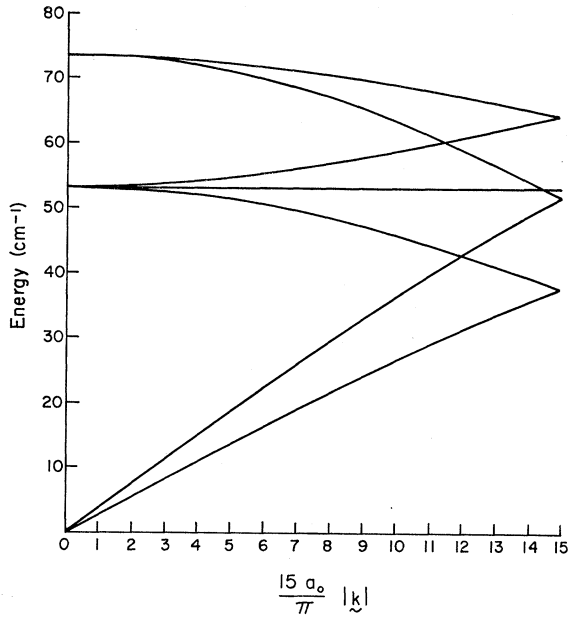

FIG. 5. Deuterium phonon dispersion curve [100].

extensive lattice sum, the phonon frequencies are given with an error of less than 3% by a sum over nearest neighbors only. In the present paper, the dynamical matrix has been computed by neglecting all but nearest-neighbor interactions. The only difference between the form of this matrix and that of an fcc atomic lattice in the harmonic approximation is that we have not assumed that $\partial V_{\text{eff}}/\partial R=0$. This quantity is small however. The dynamical matrix is shown in Table II.

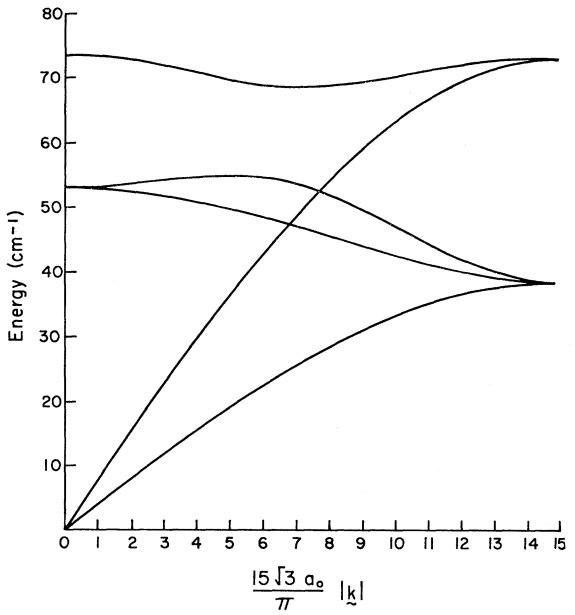

FIG. 6. Deuterium phonon dispersion curve [111].

TABLE III. Frequencies of optical phonons.

Crystal	Calc $\tilde{\nu}$(cm^{-1})	Symmetry species	Obs $\tilde{\nu}$(cm^{-1})[a]
H_2	63.8	T_u,A_u,E_u	62.2
	87.0	T_u	80
			93
D_2	53.1	T_u,A_u,E_u	57.4
	73.4	T_u	74.5
			85

[a] Reference 10.

This matrix is computed and diagonalized by computer at each of 816 points in that section of the first Brillouin zone bounded by the planes $k_z=0$, $k_x=k_y$, $k_y=k_z$, and $k_x=\pi/a_0$, where a_0 is the lattice constant. This[12] comprises 1/48 of the zone. The other parts are obtained by symmetry, so that frequencies are computed at 27 000 points in the first Brillouin zone for the simple-cubic primitive cell of $T_h^6(Pa3)$.

RESULTS

The computed density-of-states functions are shown in Figs. 1 and 2; the dispersion curves in the [100] and [111] directions in Figs. 3–6.

The calculated and experimental[10] frequencies of the optical phonons are given in Table III. The calculation and experiment are in very good agreement. There are four optical phonons: two of T_u symmetry, which are optically active, and one each of A_u and E_u symmetry, which are optically forbidden. However, in the absence of an angle-dependent term in the potential, the A_u, E_u, and lower frequency T_u phonons are all degenerate. We are unable to explain the experimental observation of three absorption bands.[10] We suppose that the extra band arises from two-quantum excitations of some kind. A structural mechanism has also been proposed.[13]

[12] J. Grindley and R. Howard, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen 1963*, edited by R. F. Wallis (Pergamon Press, Ltd., Oxford, 1965), p. 129; O. Schnepp and A. Ron, Discussions Faraday Soc. (to be published).

[13] W. N. Hardy, I. F. Silvera, and J. P. McTague, Phys. Rev. Letters **22**, 297 (1969).