Interactions between Molecules in Solid Hydrogen*

A. BROOKS HARRIS†

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 2 September 1969)

The interactions between molecules in solid H_2 and D_2 are discussed with emphasis on those features which are of importance for the orientational properties. It is shown that pseudo-three-body interactions split by 0.1 cm^{-1} the rotational levels of a pair of $J = 1$ molecules which are degenerate when only pairwise interactions are considered. The dielectric screening of quadrupole interactions due to these terms is also estimated. The static and dynamic renormalizations of the electric quadrupole-quadrupole interaction constant Γ due to phonon interactions are studied using the theory of quantum crystals and treating the dynamical interaction between phonons and rotations perturbatively. For H_2 and D_2 in the fcc phase, a reduction in Γ of about 12% is found therefrom, where as in the dilute $J = 1$ solid practically no renormalization is expected. By comparing the author's calculations with experimental data, it is infered that perhaps the static renormalization has been underestimated as a result of the crude description of the phonon modes. However, the differing renormalizations for the dilute and concentrated $J = 1$ systems are confirmed by experiment. Finally, the indirect interaction between distant $J = 1$ molecules analogous to the Suhl-Nakamura interaction is discussed. It is shown that the NMR T_2 data place a bound on this interaction which can only be understood using rather small values of certain intermolecular interaction coefficients which are renormalized to take account of short-range correlations. Harmonic renormalization leads to anomalously large indirect interactions in disagreement with T_2 data.

I. INTRODUCTION

THIS paper is the first in a series of papers whose ultimate objective is a quantitative understanding of the orientational state of solid hydrogen.[1] These systems have been widely studied, both experimentally and theoretically, in recent years. The importance of this problem is due to the possibility in the foreseeable future of a first-principles calculation of the properties of the solids in which no *ad hoc* parameters are introduced.

Within the approximation of considering the system of nuclei and electrons as forming constituent molecules, one is naturally led to a discussion of the interaction between molecules. For our purposes, we need consider only the orientationally dependent interactions of which the largest is the electric quadrupole-quadrupole (EQQ) interaction.[2] Thus far this aspect of the problem has not been treated in a fundamentally satisfying way, although such calculations can be anticipated in the near future. Accordingly, in Sec. II a discussion is given of these orientationally dependent interactions based

partly on theoretical considerations and partly on experimental indications with particular emphasis on effects which are important in the solid. In Sec. III it is shown how pseudo-three-body forces remove the degeneracy associated with the higher symmetry of the pairwise interactions for the case of an isolated pair of $J = 1$ molecules in an otherwise pure solid of $J = 0$ molecules. These pseudo-three-body interactions produce energy-level splittings of the order of 0.1 cm^{-1}. The observation of such splittings which are inconsistent with the symmetry of pairwise interactions would be a dramatic manifestation of pseudo-three body interactions. Here it is also estimated that the effect of dielectric screening on EQQ interactions is to reduce the effective coupling constant Γ_{eff} by about 5%.

In Secs. IV and V, the renormalizations, both static and dynamic, of the EQQ interaction due to the presence of the large zero-point motion of the phonon system are studied. Using the quantum crystal wave functions of Nosanow,[3] we find static and dynamic reductions in the EQQ coupling constant Γ_{eff} of respectively 7 and 6% for fcc ordered H_2 and similar results for D_2 are found. In order to discuss the case of dilute $J = 1$ hydrogen we also consider the case of isolated pairs of $J = 1$

[1] The word "hydrogen" will be used to refer to all isotopic species. Specific species are denoted as usual, H_2, D_2, etc.

[2] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).

[3] L. H. Nosanow (private communication).

TABLE I. Some constants for free hydrogen molecules.

Symbol	Equation	H_2	D_2	Reference
B_J	(2.1)	59.34 cm^{-1}	29.91 cm^{-1}	12
Q	after (2.5)	0.4883 a_0^2	0.4783 a_0^2	13
d	(7.1)	57.67 kHz	25.24 kHz	14

molecules. Here we find the same static renormalization but in this case the dynamic interaction leads to an increase in Γ_{eff} which nearly cancels the static reduction. We explain our differing conclusions for the concentrated and dilute cases as being due to the possibility of strains in the latter case, whereas in the former case this possibility is inconsistent with cubic symmetry. In Sec. VI we show that distant $J=1$ molecules interact with one another via the virtual emission and absorption of phonons, an effect which is analogous to the Suhl-Nakamura[4,5] indirect interaction in magnetic materials. Using NMR T_2 measurements[6,7] we are able to place a bound on the size of this indirect interaction which is consistent with the most reliable estimates of the potential coefficients[8] describing the interaction between hydrogen molecules, providing these potentials are renormalized according to the theory of quantum crystals.[9,10] The harmonically renormalized potentials[11] lead to anomalously large interactions. Finally, in Sec. VII, we compare the results of our calculations of the phonon renormalizations with experimental data. On the whole, the experimental data agree reasonably well with our calculations. In particular, the prediction that the observed value of Γ should be about 10% larger in the dilute $J=1$ system than in the concentrated system seems to be verified. In order to achieve a more precise agreement with experimental data it would be necessary to employ a better description of the phonon system. The method of calculation in which the interactions between the phonons and the molecular rotations are treated perturbatively does seem to be reliable considering the smallness of the effects involved.

Later papers in this series will discuss the interpretation of (a) infrared and Raman spectra of $J=0$ H_2, (b) the specific heat of hydrogen at high temperatures or at extreme dilution of $J=1$ molecules, and (c) the NMR properties of solid hydrogen in various regimes. The objective of this program is to be able to discuss in more detail the consistency of the values of Γ as determined from various experiments.

[4] H. Suhl, Phys. Rev. 109, 606 (1958).
[5] T. Nakamura, Progr. Theoret. Phys. (Kyoto) 20, 542 (1958).
[6] W. Hardy and J. R. Gaines, Bull. Am. Phys. Soc. 12, 1047 (1967); Phys. Rev. Letters 17, 1278 (1968). See also the data reported in Ref. 7.
[7] C. C. Sung, Phys. Rev. 167, 271 (1968).
[8] W. D. Davison, Disc. Faraday Soc. 33, 71 (1962).
[9] L. H. Nosanow, Phys. Rev. 146, 120 (1966).
[10] F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. 162, 824 (1967).
[11] J. Van Kranendonk and V. F. Sears, Can. J. Phys. 44, 313 (1966).

II. INTERACTIONS BETWEEN MOLECULES IN A RIGID LATTICE

The first step in understanding the orientational effects in solid H_2 and D_2 is, of course, to calculate from first principles the interactions between molecules. As we have mentioned, although it is hoped that such a calculation will be possible in the near future, at present we are limited to phenomenological treatments. The purpose of this section is to correlate the available information about the intermolecular potential, emphasizing those features which are most influential in determining the orientational state of solid hydrogen. For this purpose we will not consider the electronic or vibrational degrees of freedom explicitly. We will consider the hydrogen molecule to be a rigid rotator whose dielectric properties can be parametrized in the usual way. As is well known, the energy levels of a rigid rotator are

$$E_J = B_J J(J+1),   (2.1)$$

where the values of the rotational constant B_J for H_2 and D_2 are given in Table I.[12-14] The Pauli principle requires that an odd (even) rotational level be combined with an even (odd) nuclear spin function for H_2 and with an odd (even) nuclear spin function for D_2, since these molecules have nuclei with spin $\frac{1}{2}$ and 1, respectively. At low temperatures only the lowest J manifold of a given symmetry, i.e., either $J=0$ or $J=1$, is occupied. Thus for H_2 one has ortho molecules with $J=1$, $I=1$ or para molecules with $I=0$, $J=0$, and for D_2 there exist ortho molecules with $J=0$, $I=0$ or $I=2$ and para molecules with $J=1$, $I=1$, where I is the total nuclear spin of the molecule. The angular-dependent part of the intermolecular interaction is much smaller than B_J, so that J is essentially a good quantum number. Consequently, we need only consider matrix elements of the intermolecular potential which are diagonal with respect to J. Matrix elements off-diagonal in J can be taken into account perturbatively via a canonical transformation, if need be.

We shall primarily be interested in describing the orientational state of mixtures of $J=0$ and $J=1$ molecules as a function of the concentration x of $J=1$ molecules. Accordingly, if the intermolecular potential is expanded in terms of spherical harmonics,[15] $Y_L^M(\theta,\varphi)$, it is not necessary to include terms with $L>2$, since their matrix elements vanish within the $J=0$ and $J=1$ manifolds. Therefore, we write the intermolecular potential as

$$V = A(R) + (16\pi/5)^{1/2} B(R) [Y_2^0(\omega_1) + Y_2^0(\omega_2)]$$
$$+ 4\pi \sum_M C_M(R) Y_2^M(\omega_1) Y_2^{-M}(\omega_2),   (2.2)$$

[12] B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).
[13] G. Karl and J. D. Poll, J. Chem. Phys. 46, 2944 (1967).
[14] N. F. Ramsey, Molecular Beams (Oxford University Press, Oxford, 1956), pp. 235 and 238.
[15] Note that we use the phase convention for spherical harmonics of Rose; see Ref. 17.

where $\omega_1 \equiv \theta_1$, φ_1 and $\omega_2 \equiv \theta_2$, φ_2 specify the orientations of the molecules relative to R, the vector connecting their centers of gravity. Note that the last term involves three independent parameters, since $C_M(R) = C_{-M}(R)$. An alternative formulation due to Van Kranendonk[16] is often convenient:

$$\sum_M C_M(R) Y_2{}^M(\omega_1) Y_2{}^{-M}(\omega_2)$$
$$= \sum_{j\mu} \epsilon_j(R)\alpha_j C(22j; \mu, -\mu) Y_2{}^\mu(\omega_1) Y_2{}^{-\mu}(\omega_2), \quad (2.3)$$

where $C(L_1, L_2, L_3; M_1, M_2)$ is a Clebsch-Gordan coefficient,[17] and $\alpha_4 = \sqrt{70}$, $\alpha_2 = \sqrt{\frac{7}{2}}$, and $\alpha_0 = \sqrt{5}$. The physical interpretation of this formula is that $\epsilon_j(R)\alpha_j$ measures the strength of the coupling between the two angular momenta so as to form a resultant angular momentum j. The coefficients $C_M(R)$ and $\epsilon_j(R)$ are related by

$$\epsilon_j(R)\alpha_j = \sum_M C_M(R) C(22j; M, -M), \quad (2.4)$$

from which it follows that $\epsilon_j(R)\alpha_j$ vanishes for odd j. Although all these coefficients are not known accurately, some idea of their magnitude can be given.

As Nakamura[2] has discussed, $C_M(R)$, and hence $\epsilon_4(R)$, is dominated by the EQQ interactions. Neglecting other interactions one has

$$C_M(R) = \tfrac{5}{6}\Gamma_0 (70)^{1/2} C(224; M, -M)(R_0/R)^5. \quad (2.5)$$

As a matter of arbitrary convenience we will define $R_0 = 3.755$ Å for H_2 and $R_0 = 3.59$ Å for D_2, and then $\Gamma_0 = 6e^2 Q^2/25 R_0{}^5$ is the EQQ coupling constant, where eQ is the quadrupole moment of the molecule. This value of the intermolecular separation R_0 for H_2 is quite close to that observed for the solid at essentially zero temperature and atmospheric pressure for para H_2,[18] normal H_2 in the ordered fcc phase,[19] or normal H_2 in the disordered hcp phase.[19] Similarly the value of R_0 for D_2 is essentially that obtained for normal D_2,[20] or for para enriched D_2 in either the ordered fcc or disordered hcp phase.[20] Thus we will reduce all experimental determinations of Γ to these standard nearest-neighbor separations. The electric-quadrupole moment of the molecule in the solid will be assumed not to differ significantly from that of the free molecule. As Van Kranendonk and Karl[21] discuss, this assumption is

probably a good one. The quadrupole moment of the free molecule has been calculated by Karl and Poll[13] and also by Wolniewicz.[22] The principal difference between their results lies in their respective estimates of nonadiabatic effects. Combining the estimates of Karl and Poll for these effects with their value of the quadrupole moment in the $J = 1$ rotational state, we obtain $Q = 0.4883 \, a_0{}^2$ for H_2, where a_0 is the Bohr radius, and $Q = 0.4783 a_0{}^2$ for D_2. To obtain this latter value it was necessary to scale Eqs. (9), (18), and (23) in Ref. 13 to take account of the larger mass of the D_2 molecule. Using the values of the quadrupole moments we find $\Gamma_0 = 0.698$ cm^{-1} for H_2 and $\Gamma_0 = 0.839$ cm^{-1} for D_2 or $\Gamma_0/k_B = 1.005°$K for H_2 and $\Gamma_0/k_B = 1.206°$K for D_2. In later sections we shall discuss several effects which will effectively change these rigid lattice values.

The coefficients $\epsilon_2(R_0)$ and $\epsilon_0(R_0)$ are smaller, being in part the result of anisotropic van der Waals and valence forces.[23,24] The calculations of Margenau[23] and de Boer[24] would indicate that these coefficients are, in Nakamura's notation,

$$\epsilon_2(R_0) = -\frac{4}{105}\frac{R}{r_0{}^6} - \frac{40}{7}\lambda_2{}^2 V e^{-r_0/\rho} \approx -0.11 \text{ cm}^{-1}, \quad (2.6a)$$

$$\epsilon_0(R_0) = -\frac{2}{75}\frac{R}{r_0{}^6} + 4\lambda_2{}^2 V e^{-r_0/\rho} \approx 0.06 \text{ cm}^{-1}. \quad (2.6b)$$

However, due to the crudeness of the calculations these values must be regarded as being quite uncertain. At present we are reanalyzing the infra red[25] and Raman spectra[26] in order to give empirical estimates of these parameters which may be more reliable than the theoretical values of Eq. (2.6). Hopefully a satisfactory first-principles calculation of these terms will be performed in the near future.

There are varying estimates of $B(R)$. Nakamura[2] and others[11,27,28] have used the early theoretical estimates of Margenau[23] and de Boer.[24] However, more recently Davison[8] has shown from an analysis of ultrasonic dispersion data[29] that these estimates are unreasonably large. He assumes $B(R)$ to be of the form

$$B(R) = \beta_1 e^{-2\alpha'(R-R_0)} - \beta_2 (R_0/R)^6. \quad (2.7)$$

Since the theoretical calculations[30] of the long-range forces are more reliable than those for the short-range term β_1, he used the theoretical value of β_2 and an estimated value of α'. He was then able to determine β_1

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[18] W. H. Keesom, J. de Smedt, and H. H. Mooy, Commun. Kamerlingh Onnes Lab., Univ. Leiden **19**, 209d (1930).

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[22] L. Wolniewicz, J. Chem. Phys. **45**, 515 (1966).

[23] H. Margenau, Phys. Rev. **64**, 131 (1943).

[24] J. de Boer, Physica **9**, 363 (1942).

[25] H. P. Gush and J. Van Kranendonk, Can. J. Phys. **40**, 1461 (1962).

[26] V. Soots, E. J. Allin, and H. L. Welsh, Can. J. Phys. **43**, 1985 (1965).

[27] W. H. Orttung, J. Chem. Phys. **36**, 652 (1962).

[28] A. B. Harris, Int. J. Quantum Chem. **IIS**, 347 (1968).

[29] J. E. Rhodes, Jr., Phys. Rev. **70**, 932 (1946).

[30] F. R. Britton and D. J. W. Bean, Can. J. Phys. **33**, 668 (1955).

from a one-parameter fit to the experimental data. His values, $\beta_1 = 0.47$ cm^{-1} and $\beta_2 = 0.69$ cm^{-1}, are much smaller then those used by Nakamura[2] based on the work of Margenau[23] and de Boer[24]: $\beta_1 = 1.8$ cm^{-1} and $\beta_2 = 1.1$ cm^{-1}. Consequently the estimates of the effects of the linear phonon coupling due to this term given by Van Kranendonk and Sears,[11] and by Harris,[28] are grossly in error. Thus it is not surprising, for instance, that the crystalline field of an isolated $J=1$ molecule in otherwise pure $J=0$ H$_2$ is much smaller than predicted in Ref. 11. In Sec. VI we will show that experimental results for the nuclear spin-spin relaxation time tend to corroborate Davison's estimates.

Since the details of the mechanism responsible for the crystalline field are at present uncertain, we will only assume it to be of the form appropriate to the symmetry of the lattice. For hcp H$_2$ or D$_2$ this means that the crystal-field Hamiltonian H_c is of the form

$$H_c = V_c[(\mathbf{J}\cdot\hat{n})^2 - \tfrac{2}{3}], \qquad (2.8)$$

where $\hat{n}$ is a unit vector parallel to the crystal c axis. The result of Hardy and Gaines[31] and also of Gaines, Hartzler, and Kaeck[32] that $|V_c| \leq 0.006$ cm^{-1} may apply directly only to the case of isolated $J=1$ molecules in otherwise pure $J=0$ H$_2$. The crystalline field for an isolated pair of $J=1$ molecules might be somewhat different due both to local strains and to the different sizes of $J=0$ and $J=1$ molecules. Although these effects would not change the form of Eq. (2.2), they would cause the coefficient $B(R)$ to depend on the angular momenta of the interacting molecules. It is known[2] that the crystal-field term involving $B(R)$ in Eq. (2.2) vanishes when summed over nearest neighbors in a rigid hcp lattice. Using this fact it is clear that if one allows $B(R)$ to be slightly dependent on angular momenta of the interacting molecules, one thereby obtains for isolated pairs of $J=1$ molecules in otherwise pure $J=0$ H$_2$ a crystalline field Hamiltonian of the form

$$H_c' = \sum_i V_c[(\mathbf{J}_i\cdot\hat{n})^2 - \tfrac{2}{3}] - (6/5)\Delta B[(\mathbf{J}_i\cdot\hat{R})^2 - \tfrac{2}{3}], \quad (2.9)$$

where $\hat{R}$ is a unit vector along the pair axis and ΔB is the difference between $B(R)$ for a pair of $J=1$ molecules and $B(R)$ when the interacting molecules have J values 0 and 1. Since this effect depends either on the smaller explicit dependence of $B(R)$ on the angular momenta, or on the existence of strains, we may expect H_c' to be quite small in general.

Finally let us note that it is often convenient to use the operator equivalents as Nakamura has done. Within the manifold of constant J one has

$$(Jm| Y_L^M(\theta,\varphi) |Jm') = \alpha_{LJ}(Jm| \mathcal{G}_L^M(J) |Jm'), \qquad (2.10)$$

where $\alpha_{21} = -\tfrac{2}{5}$ and

$$\mathcal{G}_2^{\pm 2}(J) = (\tfrac{15}{32}\pi)^{1/2} J_{\pm}{}^2, \qquad (2.11a)$$

$$\mathcal{G}_2^{\pm 1}(J) = \mp(\tfrac{15}{32}\pi)^{1/2}(J_{\pm}J_z + J_z J_{\pm}), \qquad (2.11b)$$

$$\mathcal{G}_2^0(J) = (\tfrac{5}{16}\pi)^{1/2}(3J_z{}^2 - 2). \qquad (2.11c)$$

Accordingly we shall use the spherical harmonics $Y_L^M(\theta,\varphi)$ and the tensor operators $\mathcal{G}_L^M(J)$ interchangeably when J is constant.

III. PSEUDO-THREE-BODY INTERACTIONS

In the previous section we made some general remarks about the pairwise interactions between hydrogen molecules in the solid. In this section we shall consider possible new effects due to pseudo-three-body forces. Specifically, we shall first investigate polarizability effects such as are responsible for dielectric shielding. Then, using perturbation theory, we shall examine the effects of pairwise orientational interactions which are not diagonal in J.

A. Dilute $J=1$ Systems: Isolated $J=1$ Pairs

In this subsection we shall treat the case of isolated pairs of $J=1$ molecules in otherwise pure $J=0$ hydrogen. The specific mechanism we shall investigate is that which is responsible for dielectric screening between widely separated molecules. While it is generally agreed that dielectric screening is important as far as distant interactions are concerned,[31] there is some uncertainty as to the role of this effect for short range interactions. We shall study this effect in a simple approximation, although a more rigorous treatment of these three-body interactions is possible.[33] The energy term ΔE we consider is that of a third molecule at position $\mathbf{r}$ due to the electric field created by molecules at $\mathbf{r}_1$ and $\mathbf{r}_2$, which are nearest-neighboring lattice sites:

$$\Delta E = -\tfrac{1}{2}\alpha[\nabla\varphi_1(\mathbf{r}) + \nabla\varphi_2(\mathbf{r})]^2. \qquad (3.1)$$

Here we neglect the small anisotropy of the polarizability,[34] α, in order to obtain an order-of-magnitude calculation. The two-body terms contribute to the crystal-field interaction whose calculation is extremely delicate and will not be pursued here. Here we consider only the three-body term:

$$V_3 = -\alpha \sum_{\mathbf{r}} \nabla\varphi_1(\mathbf{r})\cdot\nabla\varphi_2(\mathbf{r}), \qquad (3.2)$$

where we now sum over all positions of a third molecule. Physically this energy describes the following process: The quadrupole moment of molecule one causes an electric field which polarizes the molecular at $\mathbf{r}$. Then V_3

[31] W. Hardy and J. R. Gaines, Phys. Rev. Letters 19, 1417 (1967).

[32] J. R. Gaines, E. A. Hartzler, and J. A. Kaeck, in Proceedings of the Eleventh International Conference on Low Temperature Physics, Vol. I, p. 615 (unpublished).

[33] A. Dalgarno and W. D. Davison, Advances in Atomic and Molecular Physics (Academic Press Inc., New York, 1966), Vol. 2, p. 1.

[34] D. W. Davies, The Theory of the Electric and Magnetic Properties of Molecules (John Wiley & Sons, Inc., New York, 1967), p. 95 ff.
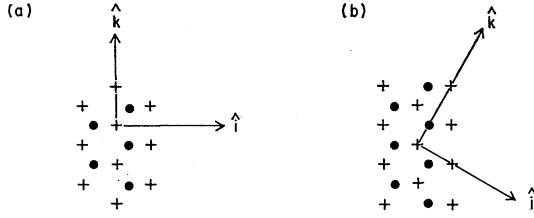
FIG. 1. Coordinate axes for type (a) pairs (left) and type (b) pairs (right). The crosses and dots denote sites in adjacent basal planes of the hcp lattice. For type (a) pairs $\hat{\imath}$ and $\hat{k}$ lie in the basal plane as shown, and $\hat{\jmath}=\hat{k}\times\hat{\imath}$. For type (b) pairs $\hat{\jmath}$ lies in the basal plane, $\hat{k}$ lies along r_{12}, and $\hat{\imath}=\hat{\jmath}\times\hat{k}$.

TABLE II. Values of $g_{\nu\nu'}$ and $h_{\nu\nu'}$.

ν	ν'	$g_{\nu\nu'}{}^{(a)}$	$g_{\nu\nu'}{}^{(b)}$	$h_{\nu\nu'}{}^{(a)}$	$h_{\nu\nu'}{}^{(b)}$
2	-2	57	57	-1691	-1691
2	-1	$-47(\sqrt{3})/3$	0	$-175(\sqrt{3})/3$	0
2	0	$7\sqrt{6}$	$21\sqrt{6}$	$865(\sqrt{6})/3$	$865\sqrt{6}$
2	1	$115(\sqrt{3})/9$	0	$10925(\sqrt{3})/9$	0
2	2	$-245/3$	105	$-25235/9$	3605
1	-1	268	268	8156	8156
1	0	$-9\sqrt{2}$	0	$-1225\sqrt{2}$	0
1	1	$-68/3$	-68	-380	-1140
0	0	-138	-138	-1026	-1026

is the energy of the induced dipole moment in the electric field of the quadrupole moment of molecule two. The splittings caused by V_3 may be different for the case when (a) $\mathbf{r}_1$ and $\mathbf{r}_2$ lie in the same basal plane, or when (b) $\mathbf{r}_1$ and $\mathbf{r}_2$ lie in different basal planes.

The potential at r due to the quadrupole moment of molecule i can be written as

$$\varphi_i(\mathbf{r})=\frac{4\pi eQ}{5}\sum_\nu Y_2{}^\nu(\Omega_i)Y_2{}^\nu(\omega_i)^*|\mathbf{r}-\mathbf{r}_i|^{-3},\quad (3.3)$$

where ω_i and Ω_i specify, respectively, the orientation of the molecule at $\mathbf{r}_i$ and the orientation of the vector $\mathbf{r}-\mathbf{r}_i$ with respect to the quantization axis, which for later convenience is taken along the pair axis, $\mathbf{r}_1-\mathbf{r}_2 = \mathbf{r}_{12}$. Using spherical components for vectors,

$$V^{\pm1}=\mp2^{-1/2}(V_x\pm iV_y),\quad (3.4a)$$

$$V^0=V_z,\quad (3.4b)$$

we have

$$\nabla^\mu Y_2{}^\nu(\Omega_i)|\mathbf{r}-\mathbf{r}_i|^{-3}$$
$$=-5(3/7)^{1/2}Y_3{}^{\mu+\nu}(\Omega_i)|\mathbf{r}-\mathbf{r}_i|^{-4}C(123;\mu\nu),\quad (3.5)$$

so that

$$V_3=-(\alpha R_0{}^{-3})\left(\frac{6e^2Q^2}{25R_0{}^5}\right)\left(\frac{\pi}{40}\right)$$
$$\times\sum_{\nu\nu'}\mathcal{G}_2{}^\nu(J_1)^\dagger\mathcal{G}_2{}^{\nu'}(J_2)^\dagger g_{\nu\nu'},\quad (3.6)$$

where

$$g_{\nu\nu'}=\frac{1280\pi}{7}\sum_{\mathbf{r}\mu}(-1)^\mu\left|\frac{R_0}{\mathbf{r}-\mathbf{r}_1}\right|^4\left|\frac{R_0}{\mathbf{r}-\mathbf{r}_2}\right|^4 Y_3{}^{\mu+\nu}(\Omega_1)$$
$$\times Y_3{}^{-\mu+\nu'}(\Omega_2)C(123;\mu\nu)C(123;-\mu\nu').\quad (3.7)$$

For convenience we choose the coordinate axes as shown in Fig. 1. That is, for type (a) pairs we take

$$\hat{\imath}=(1,0,0),\quad (3.8a)$$

$$\hat{\jmath}=(0,0,-1),\quad (3.8b)$$

$$\hat{k}=(0,1,0),\quad (3.8c)$$

where the coordinates (x,y,z) refer to axes in which z

coincides with the crystal c axis, as in Fig. 1. For type (b) pairs we take

$$\hat{\imath}=(-1/\sqrt{6},\,-1/\sqrt{2},\,1/\sqrt{3}),\quad (3.9a)$$

$$\hat{\jmath}=(\tfrac{1}{2}\sqrt{3},\,-\tfrac{1}{2},\,0),\quad (3.9b)$$

$$\hat{k}=(\tfrac{1}{6}\sqrt{3},\tfrac{1}{2},\sqrt{\tfrac{2}{3}}).\quad (3.9c)$$

Note that for both type (a) and type (b) pairs the i,k plane is a reflection plane. This assures that the coefficients $g_{\nu\nu'}$ are real. Using this reality property, one also deduces that

$$g_{\nu\nu'}=(-1)^{\nu+\nu'}g_{-\nu,-\nu'}.\quad (3.10a)$$

Also note that for type (a) pairs the plane $\mathbf{r}\cdot\hat{k}=\tfrac{1}{2}$, which is the plane perpendicularly bisecting the bond r_{12}, is a reflection plane. Use of this symmetry property yields

$$g_{\nu,\nu'}{}^{(a)}=g_{\nu',\nu}{}^{(a)}(-1)^{\nu+\nu'},\quad (3.10b)$$

where the superscript indicates the type of pair. For type (b) pairs the midpoint of the bond r_{12} is a center of inversion symmetry, from which one deduces

$$g_{\nu,\nu'}{}^{(b)}=g_{\nu',\nu}{}^{(b)}.\quad (3.10c)$$

The independent coefficients are given in Table II within the approximation that the summation in Eq. (3.7) is extended only over the four values of $\mathbf{r}$ such that $(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)$ form an equilateral triangle.

Before discussing the effect of these terms on the energy levels of a pair of $J=1$ molecules, let us examine those terms which describe the possibility that neighboring $J=0$ molecules are slightly oriented in the quadrupolar fields of molecules one and two. In contrast to the preceding calculation where the electronic structure of the molecule was distorted, here we distort the $J=0$ rotational ground state without disturbing the electron wave function. We obtain the corresponding effective Hamiltonian by considering the effect of two-body terms which are off diagonal in J in second-order perturbation theory. The effective Hamiltonian H_{eff} we consider arises from terms which are diagonal in J_1 and J_2 but are off-diagonal in $J_\mathbf{r}$, these being the rotational quantum numbers of the $J=1$ molecules at $\mathbf{r}_1$ and $\mathbf{r}_2$ and the even J molecules, i.e., para H_2 or ortho D_2, at

TABLE III. Energy levels of an isolated pair of $J=1$ molecules.

State[a]	EQQ energy	Total energy[b]
$(\frac{1}{6})^{1/2}[\,|1\bar{1}\rangle+2\,|00\rangle+|\bar{1}1\rangle\,]=\Phi_1$	$6\Gamma_0$	$6\Gamma_0+\frac{1}{5}(\epsilon_0+\epsilon_2)+\frac{4}{5}\Delta B$
$\|11\rangle \qquad =\Phi_2$	Γ_0	$\Gamma_0+\frac{1}{5}(\epsilon_0-\epsilon_2)-\frac{4}{5}\Delta B$
$\|\bar{1}\bar{1}\rangle \qquad =\Phi_3$		
$(\frac{1}{3})^{1/2}[\,|1\bar{1}\rangle-|00\rangle+|\bar{1}1\rangle\,]=\Phi_4$	0	$2\epsilon_0$
$(\frac{1}{2})^{1/2}[\,|10\rangle-|01\rangle\,]=\Phi_5$	0	$(7/10)\epsilon_2-\epsilon_0+\frac{2}{5}\Delta B$
$(\frac{1}{2})^{1/2}[\,|\bar{1}0\rangle-|0\bar{1}\rangle\,]=\Phi_6$		
$(\frac{1}{2})^{1/2}[\,|1\bar{1}\rangle-|\bar{1}1\rangle\,]=\Phi_7$	0	$-(7/5)\epsilon_2-\epsilon_0-\frac{4}{5}\Delta B$
$(\frac{1}{2})^{1/2}[\,|10\rangle+|01\rangle\,]=\Phi_8$	$-4\Gamma_0$	$-4\Gamma_0+\frac{1}{10}(\epsilon_2+2\epsilon_0)+\frac{2}{5}\Delta B$
$(\frac{1}{2})^{1/2}[\,|\bar{1}0\rangle+|0\bar{1}\rangle\,]=\Phi_9$		

[a] Here $\bar{1}\equiv-1$.
[b] Here we include the second (but not the first) term in the crystal-field Hamiltonian of Eq. (2.9).

r, respectively. Thus we obtain

$$H_{\rm eff}=-\sum_{re}\{H_{1r}|e\rangle E_e^{-1}\langle e|H_{2r}$$
$$+H_{2r}|e\rangle E_e^{-1}\langle e|H_{1r}\}, \quad (3.11)$$

where H_{1r} is the quadrupole interaction

$$H_{1r}=\frac{20\pi\Gamma_0}{9}\sum_{\mu\nu}C(224;\mu\nu)\left|\frac{R_0}{\mathbf{r}-\mathbf{r}_1}\right|^5$$
$$\times Y_2^\mu(\omega_1)Y_2^\nu(\omega_r)Y_4^{\mu+\nu}(\Omega_{1r})^*, \quad (3.12)$$

and similarly for H_{2r}. In Eq. (3.11) the sum is over excited states $|e\rangle$ for which $J_r=2$ and all the other molecules are in their initial rotational multiplet: $J_1=J_2=1$, $J_{r'}=0$, for $\mathbf{r}'$ not equal to $\mathbf{r}_1$, $\mathbf{r}_2$, or $\mathbf{r}$, and E_e is the excitation energy between the excited state and the initial state $|i\rangle$. We set $E_e=6B$ and compute the sum over $|e\rangle$ by closure:

$$\langle i|Y_2^\nu(\omega_r)Y_2^{-\nu}(\omega_r)|i\rangle=(-1)^\nu(4\pi)^{-1}. \quad (3.13)$$

Now we can also replace the spherical harmonics by their operator equivalents. In this way we obtain

$$H_{\rm eff}=\frac{-\pi}{1728}\frac{\Gamma_0^2}{B}\sum_{\nu\nu'}h_{\nu\nu'}\mathcal{J}_2^\nu(J_1)\mathcal{J}_2^{\nu'}(J_2), \quad (3.14)$$

where

$$h_{\nu\nu'}=(70\pi)\frac{1024}{9}\sum_{r\rho}C(224;\nu,\rho)C(224;\nu',-\rho)\left|\frac{R_0}{\mathbf{r}-\mathbf{r}_1}\right|^5$$
$$\times\left|\frac{R_0}{\mathbf{r}-\mathbf{r}_2}\right|^5 Y_4^{\nu+\rho}(\Omega_{1r})^*Y_4^{\nu'-\rho}(\Omega_{2r})^*(-1)^\rho. \quad (3.15)$$

The symmetry properties of $h_{\nu\nu'}$ can be discussed in strict analogy with those of $g_{\nu\nu'}$ and so we only cite the results: $h_{\nu\nu'}$ is real and

$$h_{\nu,\nu'}=(-1)^{\nu+\nu'}h_{-\nu,-\nu'}, \quad (3.16a)$$

$$h_{\nu,\nu'}{}^{(a)}=h_{\nu'\nu}{}^{(a)}(-1)^{\nu+\nu'}, \quad (3.16b)$$

$$h_{\nu,\nu'}{}^{(b)}=h_{\nu',\nu}{}^{(b)}, \quad (3.16c)$$

where again the superscripts indicate the type of pair. We have evaluated these coefficients within the approximation that the summation in Eq. (3.15) is extended only over the four values of $\mathbf{r}$ such that $(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)$ form an equilateral triangle, and the results are given in Table II.

The pseudo-three-body interactions of Eq. (3.6) are governed by the coupling constant $\Gamma_0\rho$, where $\rho=\alpha R_0^{-3}\approx0.02$, whereas those of Eq. (3.14) are scaled by the coupling constant Γ_0^2/B. Anticipating the results of the next section we use the renormalized values of Γ_0. That is, we replace $\Gamma_0\rho$ by $\Gamma_0\rho[\xi_{43}{}^{(a)}]^2$ and Γ_0^2/B by $[\Gamma_0\xi_{54}{}^{(a)}]^2/B$. The values of these coupling constants are given in Table IV, below. Clearly it does not make sense to worry about such interactions if larger ones, such as valence[2] or anisotropic van der Waals,[2] are neglected. Accordingly, let us discuss the energy-level scheme of an isolated pair of $J=1$ molecules in otherwise pure $J=0$ solid hydrogen. The energy levels of this system assuming only EQQ interactions are well known and are given in Table III. These energy levels correspond to taking $\epsilon_0(R_0)=\epsilon_2(R_0)=0$ in Eq. (2.3). More generally, when these constants are nonvanishing we obtain the results given in column 3 of Table III. Here we have also included the effect of the second term of Eq. (2.9). The first term in Eq. (2.9) will be treated perturbatively later on. We conclude that in the presence of the most general pairwise interactions allowed by symmetry the energy-level scheme consists of three singlets and three doublets. In the solid these doublets can be split by the first term in the crystalline field potential of Eq. (2.9) and by the pseudo-three-body interactions.

Let us now calculate the splittings of the three doublets, which we denote in order of increasing average energy as Δ_3, Δ_2, Δ_1, respectively, assuming the smaller interactions scaled by $\epsilon_0(R_0)$, $\epsilon_2(R_0)$, and ΔB have removed the accidental degeneracies. Then we find the splittings of the three doublets due to the pseudo-three-body interactions and the crystalline field to be

$$E^+(\Gamma_0)-E^-(\Gamma_0)\equiv\Delta_1$$
$$=\left|\frac{3}{32}\Gamma_0\rho g_{22}+\frac{5}{2304}\frac{\Gamma_0^2}{B}h_{22}\right|, \quad (3.17a)$$

$$E^+(0)-E^-(0)\equiv\Delta_2$$
$$=\left|\frac{3}{64}\Gamma_0\rho(g_{11}-\frac{2}{3}\sqrt{6}g_{20})\right.$$
$$\left.+\frac{5}{4608}\frac{\Gamma_0^2}{B}(h_{11}-\frac{2}{3}\sqrt{6}h_{20})-V_c\sin^2\psi\right|, \quad (3.17b)$$

$$E^+(-4\Gamma_0)-E^-(-4\Gamma_0)\equiv\Delta_3$$
$$=\left|\frac{3}{64}\Gamma_0\rho(g_{11}+\frac{2}{3}\sqrt{6}g_{20})\right.$$
$$\left.+\frac{5}{4608}\frac{\Gamma_0^2}{B}(h_{11}+\frac{2}{3}\sqrt{6}h_{20})+V_c\sin^2\psi\right|, \quad (3.17c)$$

where $E^{\pm}(E)$ are the energies of the upper (+) and lower (−) states of the doublet near energy E and ψ is the angle between the pair axis and the crystal c axis. We take V_c to be about 0.006 cm^{-1}, although we do not know its sign.[31,32] For concreteness we shall assume it to be positive. Using the renormalized values of the parameters from Table IV we find

$$\Delta_1 = 0.17 \text{ cm}^{-1}, \tag{3.18a}$$

$$\Delta_2 = 0.12 \text{ cm}^{-1}, \tag{3.18b}$$

$$\Delta_3 = 0.02 \text{ cm}^{-1}, \tag{3.18c}$$

for type (b) pairs of H_2 $J=1$ molecules. For H_2 we see from Eq. (3.17) that the dominant contributions to Δ_1 and Δ_2 are from the static pseudo-three-body terms scaled by ρ which describe polarizability effects. In D_2, where Γ_0^2/B is much larger, these polarizability terms are only slightly more important than the orientational terms. If the resonance between the ground state and the excited states of the pair system could be observed, these splittings would be a dramatic manifestation of pseudo-three-body interactions. Also note that any arguments based on the exact placement of EQQ energy levels is suspect as these smaller perturbations are not negligible.

Finally we give the shifts in the center of gravity of the EQQ pair levels due to the pseudo-three-body interactions. We find

$$\Delta E(6\Gamma_0)$$
$$= -(\Gamma_0\rho/128)[2g_{2,-2}+4g_{1,-1}+3g_{00}]$$
$$\quad -(5\Gamma_0^2/27{,}648B)[2h_{2,-2}+4h_{1,-1}+3h_{00}], \tag{3.19a}$$

$$\Delta E(\Gamma_0) = -\Gamma_0\rho g_{00}/128 - 5\Gamma_0^2 h_{00}/27{,}648B, \tag{3.19b}$$

$$\Delta E(0)$$
$$= (\Gamma_0\rho/512)(2g_{2,-2}-2g_{1,-1}+g_{00})$$
$$\quad + (5\Gamma_0^2/110{,}592B)(2h_{2,-2}-2h_{1,-1}+h_{00}), \tag{3.19c}$$

$$\Delta E(-4\Gamma_0)$$
$$= (\Gamma_0\rho/128)(3g_{1,-1}+2g_{00})$$
$$\quad + (5\Gamma_0^2/27{,}648B)(3h_{1,-1}+2h_{00}), \tag{3.19d}$$

where $\Delta E(E)$ is the average shift in the levels with EQQ energy E. Since the experimental determination of Γ_0 at low concentration depends mainly on the separation from the ground doublet to the excited quartet states, we estimate the correction to this quantity due to the perturbations considered:

$$\Delta E(0) - \Delta E(-4\Gamma_0) = -0.10 \text{ cm}^{-1} \text{ for } H_2, \tag{3.20a}$$

$$\Delta E(0) - \Delta E(-4\Gamma_0) = -0.18 \text{ cm}^{-1} \text{ for } D_2, \tag{3.20b}$$

which constitute corrections of 4 and 6%, respectively.

B. Concentrated $J=1$ Systems: Cubic Phase

We now discuss briefly these effects for concentrated $J=1$ hydrogen in the cubic phase. First let us consider

TABLE IV. Potential coefficients.

Equation	Symbol	H$_2$	D$_2$	References
(2.5)	Γ_0	0.698 cm^{-1}	0.839 cm^{-1}	13
(2.7)	β_1	0.467 cm^{-1}	0.467 cm^{-1}	8
(2.7)	β_2	0.694 cm^{-1}	0.694 cm^{-1}	8
(2.7)	α'	1.77 Å^{-1}	1.77 Å^{-1}	8
(2.8)	V_c	0.006 cm^{-1}		31
(3.1)	$\rho \equiv \alpha R_0^{-3}$	0.02	0.02	34
(3.6)	$\Gamma_0\rho[\xi_{43}^{(a)}]^2$	0.013 cm^{-1}	0.015 cm^{-1}	a
(3.14)	$[\Gamma_0\xi_{54}^{(a)}]^2 B^{-1}$	0.007 cm^{-1}	0.020 cm^{-1}	a
(4.3)	ϵ	25.7 cm^{-1}	25.7 cm^{-1}	41
(4.3)	σ	2.93 Å	2.93 Å	41
(4.4a)	AR_0^2	46.5	60.5	3
(4.4b)	K	0.2406	0.2406	3
(4.19)	$\tilde{\Gamma}/\Gamma_0$	0.92	0.92	a
(4.29)	Γ_{ph}/Γ_0	0.85	0.80	a
(5.24)	$M\omega_D^2 R_0^2$	6600 cm^{-1}	8400 cm^{-1}	42, 43
(5.24)	$\hbar\omega_D$	89 cm^{-1}	73 cm^{-1}	42, 43
(5.41)	Γ_{eff}/Γ_0	0.84	0.84	a
(5.48)	$\Gamma_{eff}^{pairs}/\Gamma_0$	0.94	0.92	a
	$\Gamma_{eff}(kT\gg\Gamma_0)/\Gamma_0$	0.87	0.88	a

a This work.

the screening of nearest-neighbor EQQ interactions. Again for the geometry of the fcc lattice each nearest-neighboring pair of molecules has four mutual nearest neighbors. Hence the term scaled by $\Gamma_0\rho$ will be about the same as for the dilute case. On the other hand, the term scaled by Γ_0^2/B will be only about one-half as big because the $J=1$ to $J=3$ excitation energy is almost twice as large as the $J=0$ to $J=2$ excitation energy. By this crude argument we estimate a 4% reduction in Γ_0 due to dielectric screening for concentrated $J=1$ H_2 and a 5% reduction for concentrated $J=1$ D_2.

More interesting is the case of next nearest neighbors. As Berlinsky et al.[35] point out, these smaller interactions have a surprisingly large effect on the $k=0$ libron energies. We shall investigate the dielectric screening of next nearest neighbors in concentrated $J=1$ hydrogen in the following simple way. We shall calculate the contribution of these pseudo-three-body terms to the effective field acting on each molecule.

What we are interested in is to determine the contribution to the effective field from V_3 of Eq. (3.6) when molecules 1 and 2 are next nearest neighbors. To do this we need to express $\mathcal{J}_2^m$ in terms of libron creation and destruction operators[36] and then extract the term proportional to $n_1 = a_1^\dagger a_1$, where $a_1^\dagger$ creates a $J_z = +1$ excitation on molecule 1. For this program we need to express the rotation operators relative to a quantization axis appropriate to the particular sublattice involved, i.e., along one of the [111] directions. It simplifies the calculation that next nearest neighbors belong to the

[35] A. J. Berlinsky, A. B. Harris, and C. F. Coll, III, Solid State Commun. **7**, 1491 (1969).

[36] J. C. Raich and R. D. Etters, Phys. Rev. **168**, 425 (1968).

same one of the four inequivalent sublattices. Taking the [111] direction as the quantization axis we write Eq. (3.6) as

$$V_3 = -\rho\Gamma_0\frac{\pi}{40}\sum_{\nu\nu',\sigma\sigma'} g_{\nu\nu'}D_{\nu\sigma}^{(2)}(\hat{r}_{12})D_{\nu'\sigma'}^{(2)}(\hat{r}_{12})$$
$$\times \mathcal{G}_2^{\sigma}(J_1)^{\dagger}\mathcal{G}_2^{\sigma'}(J_2)^{\dagger}, \quad (3.21)$$

where $D_{mm'}^{(2)}(\hat{n})$ is the rotation matrix.[17] It is readily seen that terms proportional to n_1 arise only from the terms in Eq. (3.21) for which $\sigma = \sigma' = 0$. We note that

$$\mathcal{G}_2^0(J_1) = \left(\frac{5}{16\pi}\right)^{1/2}(3J_{1z}^2 - 2) \quad (3.22a)$$

$$\sim \left(\frac{5}{16\pi}\right)^{1/2}(-2 + 3n_1). \quad (3.22b)$$

Thus we obtain the dependence of V_3 upon n_1 as

$$V_3 = n_1 \frac{3\pi}{80}\Gamma_0\rho \sum_{\nu\nu'} g_{\nu\nu'} Y_2^{\nu}(\hat{r}_{12})^* Y_2^{\nu'}(\hat{r}_{12})^*. \quad (3.23)$$

To obtain the effective field on molecule 1 we should sum V_3 over next nearest neighbors r_2. By symmetry $\nu + \nu'$ is required to be even and a multiple of three, so $\nu + \nu' = 0$ and all next nearest neighbors give identical contributions. Thus we find the effective-field contribution Δ_1^{eff} to be

$$\Delta_1^{eff} \equiv \frac{dV_3}{dn_1} = \frac{9\pi}{40}\Gamma_0\rho \sum_{\nu} g_{\nu,-\nu'}|Y_2^{\nu}(\hat{r}_{12})|^2(-1)^{\nu}, \quad (3.24)$$

which gives numerically

$$\Delta_1^{eff} = -(33/2)\Gamma_0\rho \approx -\tfrac{1}{3}\Gamma_0. \quad (3.25)$$

But the effective field splitting due to next nearest neighbors is about $2\Gamma_0$,[37] so that dielectric screening reduces next-nearest-neighbor interactions by about 15%.

This result is quite reasonable because next nearest neighbors are the closest neighbors having intervening molecules strongly screening the EQQ interactions. Thus we can understand in a naive way screening factors 0.95, 0.85, and 0.75 for distances, r_{12}/R_0, of 1, $\sqrt{2}$, and ∞, respectively.

IV. STATIC PHONON RENORMALIZATION OF ORIENTATIONAL INTERACTIONS

As we have indicated, the dominant interaction which depends on the orientations of the molecules is due to the EQQ interaction which can be calculated quite accurately assuming a rigid lattice. However, H_2, and to a lesser extent D_2, are quantum crystals displaying large zero-point motion of the molecules. We now

investigate how this zero-point motion affects the EQQ or similar orientational interactions.[38,39]

We present here a rudimentary treatment based on the theory of quantum crystals as developed by Nosanow[9] and others.[10] Their theory is designed to overcome the fact that the usual harmonic approximation leads to an unstable lattice.[40] The stability of the lattice in the theory of quantum crystals comes from a better treatment of short-range correlations. Whereas in the harmonic approximation the molecules can move into the region of the hard core, the improved theory prevents this by inclusion of terms in the wave function which depend on the relative coordinates. Thus a starting approximation for the crystal wave function is

$$\psi = \pi_i \, \varphi(|r_i - R_i^0|) \, \pi_{j<k} \, f(r_{jk}), \quad (4.1)$$

where r_i is the position of the ith molecule, $r_{jk} = r_j - r_k$, and R_i^0 is the equilibrium position of the ith molecule. Evaluating the ground-state energy by a cluster expansion, Nosanow finds that the molecules behave as if they interacted via an effective potential $v_{eff}(r)$, rather than the original hard-core interaction $v(r)$. Explicitly $v_{eff}(r)$ is given by

$$v_{eff}(R_1 - R_2)$$
$$= \int d r_1 \int d r_2 \, \varphi^2(|r_1 - R_1|)\varphi^2(|r_2 - R_2|)f^2(r_{12})v(r_{12}) \Big/$$
$$\int d r_1 \int d r_2 \, \varphi^2(|r_1 - R_1|)\varphi^2(|r_2 - R_2|)f^2(r_{12}). \quad (4.2)$$

Here $v(r)$ is taken to be the Leonard-Jones potential,

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (4.3)$$

and the functions $\varphi(r)$ and $f(r)$ are chosen for convenience to be

$$\varphi(r) = (A/\pi)^{3/4}\exp(-\tfrac{1}{2}Ar^2), \quad (4.4a)$$

$$f(r) = \exp-\{K[(\sigma/r)^{12} - (\sigma/r)^6]\}. \quad (4.4b)$$

The parameters A and K were determined by Nosanow[3] to minimize the ground-state energy. The various parameters appearing in the potential function are listed in Table IV.[41-43] Using the effective potential $v_{eff}(r)$,

[37] H. M. James and J. C. Raich, Phys. Rev. **162**, 649 (1967).

[38] These calculations have been partially described previously in Refs. 28 and 39.
[39] A. B. Harris, in Proceedings of the Eleventh International Conference on Low Temperature Physics, Vol. I, p. 608 (unpublished).
[40] F. W. de Wette and B. R. A. Nijboer, Phys. Letters **18**, 19 (1965).
[41] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1083.
[42] G. Ahlers, J. Chem. Phys. **41**, 86 (1964).
[43] R. W. Hill and O. Lounasmaa, Phil. Mag. **4**, 786 (1959).

one can then determine the phonon frequencies from the dynamical matrix in which $v(\mathbf{r})$ is replaced by $v_{\text{eff}}(\mathbf{r}) - (\hbar^2/m)f^{-1}(r)\nabla^2 f(r)$. Having obtained a self-consistent description of phonons one can then evaluate averages over the zero-point motion. In particular, one can evaluate averages of $B(r)$ and $C_M(r)$ over the zero-point motion. Since the above-mentioned program has not actually been carried out for H_2 or D_2, we shall content ourselves with a more primitive calculation, which, however, should indicate the order of magnitude of the effect involved. That is, we shall average the orientational interactions over the wave functions of Eq. (4.1) using values of the parameters A and K for H_2 as determined variationally by Nosanow and for D_2 as obtained by a simple scaling procedure. Thus we assume K to be roughly independent of isotopic mass as is true[44] for He^3 and He^4 whereas A^2 is proportional to the isotopic mass.

In so doing, one should not simply average $1/r^5$, for instance, to treat the EQQ interaction. To see this consider the probability distribution for one molecule relative to its neighbor. If this distribution is spherically symmetric, then by Gauss's law there will be no change in any multipole moment of the molecule. On the other hand, use of the wave function of Eq. (4.1) implies a correlated motion, so that the probability distribution is asymmetric, the two molecules tending to avoid one another. Thus we are led to expect that the zero-point motion will tend to reduce the strength of the EQQ interaction. To see this quantitatively we rewrite the EQQ interaction between molecules i and j with the quantization axis along the equilibrium separation $\mathbf{R}_i{}^0 - \mathbf{R}_j{}^0 \equiv \mathbf{R}_{ij}{}^0$. Then

$$H_{\text{EQQ}} = \frac{20\pi\Gamma_0}{9}(70\pi)^{1/2}(R_0/R_{ij})^5 \sum_{mn} C(224; mn)$$
$$\times Y_2{}^m(\omega_i)Y_2{}^n(\omega_j)Y_4{}^{m+n}(\hat{R}_{ij})^*. \quad (4.5)$$

In the rigid-lattice approximation we have

$$Y_4{}^{m+n}(\hat{R}_{ij})^* = \delta_{m+n,0}\left(\frac{9}{4\pi}\right)^{1/2}. \quad (4.6)$$

To allow for the motion of the molecules it is necessary to average the function $R_{ij}{}^{-5}Y_4{}^{m+n}(\hat{R}_{ij})^*$ over the ground-state wave function of Eq. (4.1).[45-47]

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[44] J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, Phys. Rev. **154**, 175 (1967).

[45] Since the phonon energies are much larger than the energy spread of the $J=1$ levels, one should take account of the zero-point motion by averaging the orientational Hamiltonian over the phonon coordinates as is done here rather than average the calculated quantities over the phonon motion as was done in Ref. 46. This argument is familiar from NMR theory, see Ref. 47.

[46] R. J. Elliott and W. M. Hartmann, Proc. Phys. Soc. (London) **90**, 671 (1967).

[47] A. Abragam, *Principles of Nuclear Magnetic Resonance* (Oxford University Press, Oxford, 1961), p. 425.

A. Renormalized Potentials

Let us now consider this question in greater detail. For any interaction $v(\mathbf{r}_1,\mathbf{r}_2)$ we define $\langle v(\mathbf{R}) \rangle$ as

$$\langle v(\mathbf{R}) \rangle \equiv \int \varphi^2(|\mathbf{r}_1|)\varphi^2(|\mathbf{r}_2+\mathbf{R}|)$$
$$\times v(\mathbf{r}_1,\mathbf{r}_2)f^2(r_{12})d\mathbf{r}_1 d\mathbf{r}_2, \quad (4.7)$$

so that we may write Eq. (4.2) as

$$v_{\text{eff}}(\mathbf{R}) = \langle v(\mathbf{R}) \rangle / \langle 1 \rangle. \quad (4.8)$$

Let us consider the case when $v(\mathbf{r}_1,\mathbf{r}_2) = v_{nm}(\mathbf{r}_1,\mathbf{r}_2) = V(r_{12})Y_n{}^m(\Omega_{12})$, where $\Omega_{12} = (\theta_{12},\varphi_{12})$ and where θ_{12} and φ_{12} specify the orientation of $\hat{r}_{12}$ with respect to $\hat{R}_{ij}{}^0$. Then we have

$$\langle v_{nm}(\mathbf{R}) \rangle = (A/\pi)^3 \int e^{-Ar_1{}^2 - A|\mathbf{r}_1 - \mathbf{r}_{12} + \mathbf{R}|^2}\tilde{V}(r_{12})$$
$$\times Y_n{}^m(\Omega_{12})d\mathbf{r}_1 d\mathbf{r}_2 \quad (4.9a)$$

$$= (A/2\pi)^{3/2} \int d\mathbf{r}_{12}e^{-(A/2)|\mathbf{r}_{12} - \mathbf{R}|^2}\tilde{V}(r_{12})$$
$$\times Y_n{}^m(\Omega_{12}), \quad (4.9b)$$

where

$$\tilde{V}(r_{12}) = V(r_{12})f^2(r_{12}). \quad (4.10)$$

We now express $Y_n{}^m(\Omega_{12})$ in terms of $\Omega_{21}' \equiv (\theta_{21}',\varphi_{21}')$, where θ_{21}' and φ_{21}' are the angles of $\mathbf{r}_{12}$ with respect to $\mathbf{R}$ and $\chi = (\alpha_0,\beta_0,\gamma_0)$, where α_0, β_0, and γ_0 are the Eulerian angles[16] specifying the orientation of the $\mathbf{R}$ coordinate system with respect to the $\mathbf{R}_{ij}{}^0$ coordinate system. Thus we write

$$Y_n{}^m(\Omega_{12}) = \sum_{m'} D_{mm'}{}^{(n)}(\chi)^* Y_n{}^{m'}(\Omega_{21}'), \quad (4.11)$$

where $D_{mm'}{}^{(n)}(\chi)$ is the rotation matrix.[17] Only the term with $m'=0$ survives the φ' integration in Eq. (4.9b), so that

$$\langle v_{nm}(\mathbf{R}) \rangle = 2\pi(A/2\pi)^{3/2}\int_0^\infty r_{12}{}^2 dr_{12}\int_{-1}^1 dx P_n(x)$$
$$\times \tilde{V}(r_{12})Y_n{}^m(\beta_0,\alpha_0)e^{-(1/2)A^2[r_{12}{}^2 + R^2 - 2Rr_{12}x]}, \quad (4.12)$$

where we have used

$$D_{m0}{}^{(n)}(\chi)^* = \left(\frac{4\pi}{2n+1}\right)^{1/2}Y_n{}^m(\beta_0,\alpha_0). \quad (4.13)$$

Thus $\langle v_{nm}(\mathbf{R}) \rangle$ is of the form

$$\langle v_{nm}(\mathbf{R}) \rangle = \tilde{v}_n(R)Y_n{}^m(\beta_0,\alpha_0), \quad (4.14)$$

from which result we see that renormalization does not change the angular dependence of the interaction, but

TABLE V. Renormalization coefficients for H_2. $\xi_{-1,1}^{(a)} = 1.003$.

n/m	$\xi_{n,m}^{(a)}$					
	0	1	2	3	4	5
3	1.035	1.01	0.97	0.92	0.82	0.74
4	1.09	1.06	1.01	0.95	0.86	0.77
5	1.16	1.14	1.08	1.01	0.93	0.82
6	1.27	1.24	1.18	1.10	1.00	0.88
7	1.40	1.37	1.30	1.21	1.10	0.98
8	1.58	1.54	1.47	1.36		

n/m	$\xi_{n,m}^{(b)}$			
	0	1	2	3
-1	2.30	2.26	2.17	2.00
0	2.74	2.66	2.53	2.34
1	3.30	3.21	3.04	2.81
2	4.02	3.91	3.71	3.42

does replace the radial function $V(r_{12})$ by $V_{\text{eff}}(R)$:

$$V_{\text{eff}}{}^n(R) = \tilde{v}_n(R)/\langle 1 \rangle \equiv \xi_n V(r_{12}). \qquad (4.15)$$

For the static renormalization of the orientational interactions we evaluate this for $R = R_{ij}{}^0$:

$$\langle v_{nm}(\mathbf{R}_{ij}{}^0) \rangle = \delta_{m0} \left(\frac{2n+1}{4\pi} \right)^{1/2} \tilde{v}_n(R_{ij}{}^0). \qquad (4.16)$$

We have evaluated $V_{\text{eff}}{}^n(R_0)$ for various functions $V(r_{12})$ and for several choices of n. In Tables V and VI we give numerical values of the renormalization coefficients $\xi_{ln}^{(a)}$ and $\xi_{ln}^{(b)}$ for H_2 and D_2. These coefficients are defined by

$$\xi_{ln}^{(a)} = \langle 1 \rangle^{-1}(AR_0{}^2/2\pi)^{1/2} \int_0^\infty s^{1-l} ds f^2(sR_0)$$

$$\times e^{-(1/2)AR_0{}^2(1-s)^2} G_n(AR_0{}^2 s), \qquad (4.17a)$$

$$\xi_{ln}^{(b)} = \langle 1 \rangle^{-1}(AR_0{}^2/2\pi)^{1/2} \int_0^\infty s^{1-l} ds f^2(sR_0)$$

$$\times e^{\alpha(1-s)} e^{-(1/2)AR_0{}^2(1-s)^2} G_n(AR_0{}^2 s), \qquad (4.17b)$$

where

$$G_n(q) = \int_{-2q}^0 e^{u P_n(1+u/q)} du \qquad (4.18a)$$

$$\approx \int_{-\infty}^0 e^{u P_n(1+u/q)} du. \qquad (4.18b)$$

Here $\xi_{ln}^{(a)}$ is the value of ξ_n corresponding to the radial function $V(r_{12}) = (R_0/r_{12})^l$ and $\xi_{ln}^{(b)}$ is the value of ξ_n corresponding to the radial function $V(r_{12}) = (R_0/r_{12})^l \times e^{\alpha'(R_0 - r_{12})}$.

Using these tables we can immediately determine the renormalization of various interactions. According to Eq. (4.16) the potential $r^{-l} Y_n{}^m(\theta_{12}, \varphi_{12})$ should be replaced by an effective potential $\xi_{ln}^{(a)} R_0{}^{-l} [(2n+1)/(4\pi)]^{1/2} \delta_{m0}$ and similarly the potential $e^{-\alpha'(r - R_0)} r^{-l} Y_n{}^m \times (\theta_{12}{}^0, \varphi_{12}{}^0)$ should be replaced by the potential

$$\xi_{ln}^{(b)} R_0{}^{-l} [(2n+1)/(4\pi)]^{1/2} \delta_{m0}.$$

As a special case consider the EQQ interactions. From what we have said it is clear that $(R_0/R_{ij})^5 Y_4{}^{m+n}(\hat{R}_{ij})^*$ in Eq. (4.5) should be replaced by $\xi_{54}^{(a)}(9/4\pi)^{1/2} \delta_{n+m,0}$. Thus we see that averaging over the zero-point motion effectively renormalizes the EQQ coupling constant Γ to the new value

$$\tilde{\Gamma} = \xi_{54}^{(a)} \Gamma_0, \qquad (4.19)$$

but otherwise does not change the form of the interaction. As a second example let us consider the renormalization of the dipole-dipole interaction between the nuclear spins of different molecules. Clearly, only nearest-neighbor interactions will be significantly renormalized. We write this interaction as

$$H_{dd} = -\gamma_{dd} \sum_{mn} C(112; mn) \mathcal{J}_1{}^m(I_i) \mathcal{J}_1{}^n(I_j)$$

$$\times Y_2{}^{m+n}(\hat{R}_{ij})^* (R_0/R_{ij})^3, \qquad (4.20)$$

where the quantization axis is taken along $\mathbf{R}_{ij}{}^0$ and $\gamma_{dd} = (6\pi/5)^{1/2} g_N{}^2 \beta_N{}^2 R_0{}^{-3}$ in the usual notation. Here $\mathcal{J}_1{}^m(I)$ are the irreducible tensor operators: $\mathcal{J}_1{}^{\pm 1}(I) = \mp(\sqrt{\frac{1}{2}})I^\pm$, $\mathcal{J}_1{}^0(I) = I_z$. According to Eq. (4.16) averaging over the zero-point motion of the nuclei leads to the renormalized interaction

$$H_{dd,\text{eff}} = -\xi_{32}\gamma_{dd} \left(\frac{5}{4\pi} \right)^{1/2} \sum_m C(112; m, -m)$$

$$\times \mathcal{J}_1{}^m(I_i) \mathcal{J}_1{}^{-m}(I_j). \qquad (4.21)$$

Again the result is that the renormalized interaction has the same form as the original interaction except that the coupling constant is now $\xi_{32}\gamma_{dd}$ instead of γ_{dd}. Since the second moment of the NMR spectrum due to intermolecular dipolar interactions is dominated by the nearest-neighbor interactions, one sees using the values of Table V that our theory predicts a 6% reduction in the second moment due to phonon renormalizations. The experimental results of Amstutz et al.[48] show a 10% reduction in the second moment at high concentration of $J = 1$ molecules.

B. Derivatives of Renormalized Potentials

Before proceeding with the calculations let us make a few general remarks. If renormalization were a linear operation, then there would be no distinction between the derivative of the renormalized potential and the renormalized potential gradient. However, according to Eq. (4.2) one sees that these quantities are not identical because of the appearence in the former of derivatives of the denominator in that equation. To the extent that this difference is important the renormalization procedure is suspect. In this connection we note that the EQQ interaction itself is the second derivative of a

[48] L. I. Amstutz, H. Meyer, S. M. Myers, and D. C. Rorer, Phys. Rev. 181, 589 (1969).

simple $1/r$ potential. We have renormalized the EQQ interaction by renormalizing this second derivative instead of renormalizing a $1/r$ potential and subsequently differentiating the result twice.[49] Thus, our renormalizations are not really well defined. Fortunately, however, they are of order 10%, so that these ambiguities are not too serious.

We now return to the evaluation of the derivatives of the renormalized potentials. According to Eqs. (4.8) and (4.15) we have

$$R\nabla^\rho V_{\text{eff}}(R) = R\nabla^\rho V_{\text{eff}}{}^n(R) Y_n{}^m(\hat{R}),\qquad (4.22)$$

using spherical components for vectors. We evaluate the gradient using the convenient formula of Poll and Van Kranendonk[50]:

$$R_0\nabla^\rho V_{\text{eff}}{}^n(R_0) Y_n{}^m(\hat{R}_0)$$

$$=\left(\frac{n+1}{2n+3}\right)^{1/2} C(1, n, n+1; \rho, m) Y_{n+1}{}^{m+\rho}(\hat{R}_0)$$

$$\times\left(R_0\frac{d}{dR_0}-n\right)V_{\text{eff}}{}^n(R_0)$$

$$-\left(\frac{n}{2n+1}\right)^{1/2} C(1, n-1, n; \rho, -\rho-m) Y_{n-1}{}^{m+\rho}(\hat{R}_0)$$

$$\times\left[R_0\frac{d}{dR_0}+n+1\right]V_{\text{eff}}{}^n(R_0). \quad (4.23)$$

It only remains to evaluate the radial derivatives, $R_0(d/dR_0)V_{\text{eff}}{}^n(R_0)$, which can be done from Eq. (4.12):

$$R_0\frac{dV_{\text{eff}}{}^n}{dR_0}(R_0)$$

$$=R_0\frac{d}{dR_0}[\tilde{v}_n(R_0)/\langle 1\rangle]$$

$$=AR_0^2\left[\tilde{v}_{n+1}{}^+(R_0)\frac{n+1}{2n+1}\right.$$

$$\left.+\tilde{v}_{n-1}{}^+(R_0)\frac{n}{2n+1}-\tilde{v}_n{}^+(R_0)\xi_{-1,1}{}^{(a)}\right]\bigg/\langle 1\rangle, \quad (4.24)$$

where $\tilde{v}_n{}^+(R)$ is defined in analogy with $\tilde{v}_n(R)$ except that $V(r_{12})$ is replaced by $V(r_{12})(r_{12}/R_0)$. For the potentials we have considered in Eq. (4.17) all the quantities involved in Eq. (4.24) can be related to the renormalization coefficients defined in Eq. (4.17) and given in our

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[49] The latter method would be much more complicated and hence we do not consider it further.

[50] J. D. Poll and J. Van Kranendonk, Can. J. Phys. **40**, 163 (1962).

TABLE VI. Renormalization coefficients for D_2. $\xi_{-1,1}{}^{(a)}=1.005$.

n/m	0	1	$\xi_{n,m}{}^{(a)}$ 2	3	4	5
3	1.02	1.00	0.97	0.92	0.86	0.79
4	1.06	1.04	1.00	0.95	0.89	0.82
5	1.11	1.09	1.06	1.00	0.93	0.85
6	1.19	1.16	1.12	1.06	0.99	0.91
7	1.28	1.26	1.21	1.15	1.07	0.99
8	1.40	1.38	1.33	1.26		
	0	1	$\xi_{n,m}{}^{(b)}$ 2	3		
-1	2.08	2.02	1.95	1.86		
0	2.37	2.32	2.23	2.11		
1	2.76	2.71	2.60	2.45		
2	3.25	3.19	3.06	2.88		

tables. Thus we find

$$R_0\frac{dV_{\text{eff},a}{}^{nl}(R_0)}{dR_0}=AR_0^2\left[\xi_{l-1,n+1}{}^{(a)}\frac{n+1}{2n+1}\right.$$

$$\left.+\xi_{l-1,n-1}{}^{(a)}\frac{n}{2n+1}-\xi_{l,n}{}^{(a)}\xi_{-1,1}{}^{(a)}\right], \quad (4.25a)$$

$$R_0\frac{dV_{\text{eff},b}{}^{nl}(R_0)}{dR_0}=AR_0^2\left[\xi_{l-1,n+1}{}^{(b)}\frac{n+1}{2n+1}\right.$$

$$\left.+\xi_{l-1,n-1}{}^{(b)}\frac{n}{2n+1}-\xi_{l,n}{}^{(b)}\xi_{-1,1}{}^{(a)}\right], \quad (4.25b)$$

corresponding to the choices $V(r_{12})=(R_0/r_{12})^l$ and $V(r_{12})=(R_0/r_{12})^l \exp[\alpha'(R_0-r_{12})]$, respectively. Using these evaluations in Eq. (4.23) we find

$$-R_0\nabla^\rho V_{\text{eff},a}{}^{nl}(R_0) Y_n{}^m(\hat{R}_0)$$

$$=\left\{\left(\frac{n+1}{4\pi}\right)^{1/2} C(1, n, n+1; \rho, m)\gamma_1{}^{(a)}\right.$$

$$+\gamma_2{}^{(a)}\left[\frac{n}{2n+1}\frac{(2n-1)}{4\pi}\right]^{1/2}$$

$$\left.\times C(1, n-1, n; \rho, -\rho-m)\right\}\delta_{m+\rho,0} \quad (4.26a)$$

and

$$-R_0\nabla^\rho V_{\text{eff},b}{}^{nl}(R_0) Y_n{}^m(\hat{R}_0)$$

$$=\left\{\left(\frac{n+1}{4\pi}\right)^{1/2} C(1, n, n+1; \rho, m)\gamma_1{}^{(b)}\right.$$

$$+\gamma_2{}^{(b)}\left(\frac{n}{2n+1}\frac{2n-1}{4\pi}\right)^{1/2}$$

$$\left.\times C(1, n-1, n; \rho, -\rho-m)\right\}\delta_{m+\rho,0}, \quad (4.26b)$$

where

$$\gamma_1^{(a)} = n\xi_{l,n}^{(a)} - AR_0^2\left[\xi_{l-1,n+1}^{(a)}\frac{n+1}{2n+1}\right.$$

$$\left. + \xi_{l-1,n-1}^{(a)}\frac{n}{2n+1} - \xi_{l,n}^{(a)}\xi_{-1,1}^{(a)}\right], \quad (4.27a)$$

$$\gamma_2^{(a)} = (n+1)\xi_{l,n}^{(a)} + AR_0^2\left[\xi_{l-1,n+1}^{(a)}\frac{n+1}{2n+1}\right.$$

$$\left. + \xi_{l-1,n-1}^{(a)}\frac{n}{2n+1} - \xi_{l,n}^{(a)}\xi_{-1,1}^{(a)}\right], \quad (4.27b)$$

$$\gamma_1^{(b)} = n\xi_{ln}^{(b)} - AR_0^2\left[\xi_{l-1,n+1}^{(b)}\frac{n+1}{2n+1}\right.$$

$$\left. + \xi_{l-1,n-1}^{(b)}\frac{n}{2n+1} - \xi_{ln}^{(b)}\xi_{-1,1}^{(a)}\right], \quad (4.27c)$$

$$\gamma_2^{(b)} = (n+1)\xi_{ln}^{(b)} + AR_0^2\left[\xi_{l-1,n+1}^{(b)}\frac{n+1}{2n+1}\right.$$

$$\left. + \xi_{l-1,n-1}^{(b)}\frac{n}{2n+1} - \xi_{ln}^{(b)}\xi_{-1,1}^{(a)}\right]. \quad (4.27d)$$

To illustrate these results we consider first EQQ interactions. For this purpose we evaluate Eq. (4.26a) with $l=5$ and $n=4$. We find

$$\gamma_1^{(a)} = 7.67, \quad \gamma_2^{(a)} = 0.70, \quad \text{for } H_2 \quad (4.28a)$$

$$\gamma_1^{(a)} = 7.17, \quad \gamma_2^{(a)} = 1.20, \quad \text{for } D_2 \quad (4.28b)$$

compared to the unrenormalized values $\gamma_1^{(a)} = 9$, $\gamma_2^{(a)} = 0$. Since $\gamma_2^{(a)} \ll \gamma_1^{(a)}$ we shall neglect $\gamma_2^{(a)}$ so that in the linear phonon coupling due to EQQ interactions we should replace Γ_0 by Γ_{ph} where

$$\Gamma_{ph} \equiv \gamma_1^{(a)}\Gamma_0/9. \quad (4.29)$$

We can compare our results to those obtained by Van Kranendonk and Sears[11] using the harmonic approximation with the experimental value of the Debye theta. They found for H_2 $\xi_{02}^{(b)} = 3.0$ and $\xi_{62}^{(a)} = 1.25$, both of which are somewhat larger than we found. From their Eqs. (89) and (90) one can also deduce a value of their renormalized derivatives from which they generated the linear phonon coupling with the molecular rotations. In our notation their results for $l=6$ and $n=2$ (dispersion forces) are

$$\gamma_1^{(a)} = (5/3)^{1/2}8.5 = 11.0, \quad (4.30a)$$

$$\gamma_2^{(a)} = (\tfrac{5}{2})^{1/2}3.1 = 4.9, \quad (4.30b)$$

whereas our values are

$$\gamma_1^{(a)} = 8.03(8.0), \quad (4.31a)$$

$$\gamma_2^{(a)} = 2.13(3.0). \quad (4.31b)$$

For comparison we give the unrenormalized values in parentheses. A similar comparison can be made for the valence forces for which $l=0$ and $n=2$. Van Kranendonk and Sears obtain

$$\gamma_1^{(b)} = (5/3)^{1/2}36 = 46.4, \quad (4.32a)$$

$$\gamma_2^{(b)} = (\tfrac{5}{2})^{1/2}19.6 = 31.0, \quad (4.32b)$$

whereas our values are

$$\gamma_1^{(b)} = 25.9(15.3), \quad (4.33a)$$

$$\gamma_2^{(b)} = 12.2(10.3), \quad (4.33b)$$

and the unrenormalized values are in parentheses. They do not estimate any corrections for the EQQ interactions because an isotropic wave function such as theirs will have no effect on these interactions. Since theories invariably involve the square of the linear phonon coupling, the differences between Eqs. (4.30) and (4.31) or between (4.32) and (4.33) are quite significant.

C. Discussion

We should say a word or two about the reliability of our results. Our calculations are physically more reasonable than those of Van Kranendonk and Sears,[11] because the wave functions we use prevent the molecules from sampling the anomalously large potential available in the hard-core region. This effect is naturally the smallest for potentials which do not increase rapidly as one goes into the forbidden hard-core region. Note that potentials which vary as large negative powers of the displacement or those which vary exponentially must be treated carefully. With such potentials it is clearly important to get the exact shape of the wave function near the hard-core region correctly. This same problem arises in calculating the exchange integral[51] in He^3. Thus we would estimate that our results are least reliable when the renormalization factors are large, because then the molecules are beginning to sample the hard-core region which we are not describing quantitatively correctly by Eq. (4.1). Similarly, as one goes to higher spherical harmonics the exact details of the shape of the wave function become progressively more important and again our calculations become correspondingly less accurate. Of particular interest would be an *ab initio* calculation of the parameters A and K for D_2, to see if they really do scale as we have assumed them to.

V. DYNAMICAL PHONON RENORMALIZATIONS OF EQQ INTERACTION

In the preceding section we indicated that it was necessary to average the orientational interactions over the large zero-point motion of the phonon system. This effect is a static one, merely leading to a renormaliza-

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[51] L. H. Nosanow, in Proceedings of the Eleventh International Conference on Low Temperature Physics, Vol. I, p. 329 (unpublished).

tion of the EQQ coupling constant Γ_0. As we have pointed out previously, one can also expect dynamical effects. One can understand these physically as follows. If we picture the phonons as particles, then the molecules are continually being bombarded by phonon particles. Thus we expect an increased zero-point motion of the molecular rotations and also a modification of their excitation spectrum. Alternatively, we can reason in analogy with a system of particles whose low energy excitation mode is characterized by an effective mass. Due to the interaction via second-order perturbation theory, these excitations carry with them some admixture of high-energy excitation, so that their effective mass is increased. Similarly, here the true modes consist of a mixture of rotational motion and phonon excitations, leading to an increased effective mass of the rotational modes. There is also the possibility of local distortions because of the additional EQQ interaction between $J=1$ molecules. We shall neglect this possibility for the cubic phase, as it is forbidden by symmetry for $x=1$ within the approximations we will use. For the case of isolated pairs of $J=1$ molecules this effect is not negligible and, as we shall show, tends to offset the reduction in Γ due to other mechanisms. To study these effects one must insert a phonon coupling into second-order perturbation theory. Since the expansion parameter involves the ratio of the orientational energies to the Debye energy, we need consider only a linear phonon coupling. In oure previous work,[28] we obtained this coupling term by expanding the term $B(R)$ in Eq. (2.2) in terms of displacements. This calculation is completely misleading, as we have said, because we grossly over-estimated the value of $B(R)$. However, as we mentioned, the effect is strongly suggested by various experimental data. Accordingly, we now turn our attention towards the modulation of the EQQ interaction by phonon emission and absorption.

A. Orientationally Ordered Phase

First we shall calculate the effect of phonon interactions for the orientationally ordered fcc phase. The quantities we shall calculate are (a) $\langle (3(J_i^z)^2-2)_i \rangle$, which measures the degree to which the system is ordered, and (b) $\tilde{\Delta}(T)$, the temperature-dependent excitation energy. Here and below the outermost subscript i indicates that the quantization axis is taken along the local symmetry direction of the ith sublattice $\hat{n}_i$ which lies along the various [111] directions for the different sublattices. The values of $\hat{n}_i$ are[37,52]

$$\hat{n}_1 = 3^{-1/2}(1,1,1), \qquad \tau_1 = (0,0,0), \qquad (5.1a)$$

$$\hat{n}_2 = 3^{-1/2}(-1,1,1), \qquad \tau_2 = 2^{1/2}R_0(\tfrac{1}{2},\tfrac{1}{2},0), \quad (5.1b)$$

$$\hat{n}_3 = 3^{-1/2}(1,1,-1), \qquad \tau_3 = 2^{1/2}R_0(\tfrac{1}{2},0,\tfrac{1}{2}), \quad (5.1c)$$

$$\hat{n}_4 = 3^{-1/2}(1,-1,1), \qquad \tau_4 = 2^{1/2}R_0(0,\tfrac{1}{2},\tfrac{1}{2}), \quad (5.1d)$$

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[52] J. Felsteiner, Phys. Rev. Letters **15**, 1025 (1965).

where τ_i is the position of the ith molecule in the unit cell. Due to the algebraic complexities we will adopt a crude model using the Hamiltonian

$$H = H_0^{\text{rot}} + H_0^{\text{ph}} + V. \qquad (5.2)$$

For the unperturbed Hamiltonian of the rotational system, we take

$$H_0^{\text{rot}} = -\frac{1}{72} \sum_{i<j} \Delta^0 \mathcal{O}_i \mathcal{O}_j + y \sum_i \mathcal{O}_i, \qquad (5.3)$$

where $\mathcal{O}_i \equiv [3(J_i^z)^2 - 2]_i$. The first term in Eq. (5.3) is the diagonal part of the EQQ interaction and Δ^0 is the energy gap at zero temperature[37]:

$$\Delta^0 = 19\Gamma_0. \qquad (5.4)$$

We introduce the second term in Eq. (5.3) in order to generate the average $\langle \mathcal{O}_i \rangle$ by differentiation with respect to the parameter y which is set equal to zero thereafter. The approximation of taking only the diagonal part of H_{EQQ} is a reasonable one because the band width of the rotational excitations is much less than their average energy.[36,53,54] Hence this Ising-like model[55] should have qualitative validity except perhaps near the phase transition. This simplification allows us to perform calculations in terms of single-particle states. It is clear that a reasonable way to take account of the normal modes is to assume that the libron energies $\omega_{\mathbf{k}\tau}$ are renormalized like our $\tilde{\Delta}(T)$ (see below) independent of $\mathbf{k}$. A more detailed calculation is not worth undertaking at present considering the uncertainties in the phonon coupling constants. For the phonon system we take the Hamiltonian to be

$$H_0^{\text{ph}} = \sum_{\mathbf{k}\tau} N_{\mathbf{k}\tau} E_{\mathbf{k}\tau}, \qquad (5.5)$$

where $N_{\mathbf{k}\tau} = a_{\mathbf{k}\tau}^\dagger a_{\mathbf{k}\tau}$, where $a_{\mathbf{k}\tau}^\dagger$ creates a phonon of wave vector $\mathbf{k}$ in the τth excitation branch. This approximation has been shown by de Wette et al.[10] to be a good one for quantum crystals providing the $E_{\mathbf{k}\tau}$ are suitably chosen. In this connection we note that the EQQ interaction and its derivatives should be renormalized as described in the preceding section.

The interaction term V will be taken to be the linear coupling between the phonons and molecular rotations as obtained by expanding H_{EQQ} to first order in the displacements.[3] For this purpose we write H_{EQQ} as

$$H_{\text{EQQ}} = \frac{16\pi\Gamma_0}{45}(70\pi)^{1/2} \sum_{mn} C_{mn}(-1)^{m+n} \mathcal{J}_2^m(J_i)_i$$

$$\times \mathcal{J}_2^n(J_j)_i Y_4^{-m-n}(\Omega_{ij})_i (R_0/R_{ij})^5, \quad (5.6)$$

where $C_{mn} \equiv C(224; mn)$. We now express $\mathcal{J}_2^n(J_j)_i$ in

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[53] H. Ueyama and T. Matsubara, Progr. Theoret. Phys. (Kyoto) **38**, 784 (1967).

[54] S. Homma, K. Okada, and H. Matsuda, Progr. Theoret. Phys. (Kyoto) **38**, 767 (1967).

[55] A. B. Harris, Solid State Commun. **6**, 149 (1968).

terms of operators relative to a quantization axis along $\hat{n}_j$:

$$\mathcal{G}_2{}^n(J_j)_i = \sum_\rho D_{n\rho}{}^{(2)}(\psi_{ij})^* \mathcal{G}_2{}^\rho(J_j)_j, \qquad (5.7)$$

where $\psi_{ij} \equiv (\alpha_{ij}, \beta_{ij}, \gamma_{ij})$ is the triad of Euler angles which take the coordinate system relative to $\hat{n}_i$ into that relative to $\hat{n}_j$. The linear phonon coupling is generated by expanding $Y_4{}^{-m-n}(\Omega_{ij})_i(R_0/R_{ij})^5$ to first order in the displacements as:

$$Y_4{}^{-m-n}(\Omega_{ij})_i(R_0/R_{ij})^5 = Y_4{}^{-m-n}(\Omega_{ij}{}^0)_i \\ + \mathbf{u}_{ij} \cdot \nabla Y_4{}^{-m-n}(\Omega_{ij})_i(R_0/R_{ij})^5 \cdots, \qquad (5.8)$$

where $\Omega_{ij}{}^0$ is the orientation of $\hat{R}_{ij}{}^0$ and the gradient is with respect to R_{ij}. We evaluate the gradient as

$$R_0\Gamma_0 \nabla^{-\lambda} Y_4{}^{-\rho}(\Omega_{ij})(R_0/R_{ij})^5 \\ = -9\Gamma_{\mathrm{ph}}(5/11)^{1/2} C'(-\lambda, -\rho) Y_5{}^{-\rho-\lambda}(\Omega_{ij}{}^0), \quad (5.9)$$

where $C'(\lambda,\rho) \equiv C(1,4,5;\lambda,\rho)$. We have used the results of the last section to replace Γ by the renormalized coefficient Γ_{ph}. According to Eq. (4.25) we have $\Gamma_{\mathrm{ph}} = \gamma_1{}^{(\mathrm{a})}\Gamma_0/9 \approx 0.85\Gamma_0$ and H_2 and $\Gamma_{\mathrm{ph}} = 0.80\Gamma_0$ for D_2. Thus the linear coupling between the phonons and the molecular rotations takes the form

$$V = -16\pi\Gamma_{\mathrm{ph}}(14\pi/11)^{1/2} \sum_{i<j,mn\rho\lambda} C_{mn}C'(\lambda, m+n) \\ \times \mathcal{G}_2{}^m(J_i)_i\mathcal{G}_2{}^\rho(J_j)_j D_{n,\rho}{}^{(2)}(\psi_{ij})^*(u_{ij}{}^\lambda)_i \\ \times Y_5{}^{-n-m-\lambda}(\Omega_{ij}{}^0)_i R_0{}^{-1}(-1)^{n+m+\lambda}. \quad (5.10)$$

Before carrying out the detailed calculations let us describe the general approach. We will carry the calculations to lowest order in V, i.e., we will use second-order perturbation theory. Thus we obtain the free energy F as

$$F = F^{(0)} + F^{(2)}, \qquad (5.11)$$

where $F^{(n)}$ is the contribution to the free energy from the nth order perturbation terms. We shall then find $\langle \mathcal{O}_i \rangle$ as

$$\langle \mathcal{O}_i \rangle = N^{-1} \partial F/\partial y. \qquad (5.12)$$

To find the temperature-dependent excitation energy we use a canonical transformation to eliminate V and obtain an effective Hamiltonian for the rotational system in the form

$$H' = -\frac{\Delta^0}{72} \sum_{i<j} \mathcal{O}_i\mathcal{O}_j + \sum_i V_i\mathcal{O}_i + \frac{1}{2} \sum_{i\neq j} V_{ij}\mathcal{O}_i\mathcal{O}_j \\ + \frac{1}{6} \sum_{i,j,k\neq} V_{ijk}\mathcal{O}_i\mathcal{O}_j\mathcal{O}_k, \quad (5.13)$$

where $ijk\neq$ indicates that all the indices must be distinct. Then we find $\tilde{\Delta}(T)$ as

$$\tilde{\Delta}(T) = 3\left\langle \frac{\delta H'}{\delta \mathcal{O}} \right\rangle, \qquad (5.14)$$

so that

$$\tilde{\Delta}(T) = \Delta^0(T) + 3\Big[V_i + \sum_{j\neq i} V_{ij}\langle\mathcal{O}_j\rangle \\ + \frac{1}{2} V_{ijk,jk\neq i}\langle\mathcal{O}_j\mathcal{O}_k\rangle \cdots\Big]. \quad (5.15)$$

If Eq. (5.13) were an equation involving occupation numbers, then Eq. (5.15) would indeed follow.[56] This formula may not be rigorously true for angular momentum operators, although at low temperatures when a boson formalism becomes valid it reduces to the familiar equation in terms of occupation numbers for many body systems. In reality one should relate the excitation energy to the energy shift of a resonance in a response function. However, such a procedure would be much more complicated than the one used here and would probably not change the results qualitatively.

Some further approximations will be introduced to lighten the calculations. Firstly, we remark that the temperature is very small compared to the Debye temperature: $T/\Theta_D \leq 0.02$. Accordingly, we shall neglect the presence of thermal phonons. Secondly, the energy gap for rotational excitations is also much smaller than $k\Theta_D : \Delta^0(T)/k\Theta_D \approx 0.15$. Therefore we shall neglect $\Delta^0(T)$ in comparison to $E_{k\tau}$ in the energy denominators. Thirdly, we shall neglect correlations between different molecules in that we assume

$$\langle \mathcal{G}_2{}^\rho(J_i)_i \mathcal{G}_2{}^\lambda(J_j)_j \rangle = (5/16\pi)\delta_{\rho 0}\delta_{\lambda 0}\langle\mathcal{O}\rangle^2, \quad i\neq j \quad (5.16)$$

where $\langle \mathcal{O}_i \rangle \equiv \langle \mathcal{O} \rangle$ independent of i. Finally, since we did not take account of the bandwidth of rotational excitations in Eq. (5.3), there is no point in retaining terms like

$$V_{ij}{}^{\mu\nu}\mathcal{G}_2{}^\mu(J_i)_i\mathcal{G}_2{}^\nu(J_j)_j, \quad \mu, \nu\neq 0 \qquad (5.17)$$

which should appear in Eq. (5.13). These terms mainly affect the propagation of excitations but do not appreciably affect the average excitation energy $\tilde{\Delta}(T)$, which we are calculating. These approximations have been made in the interest of simplicity. After the phonon spectrum of solid hydrogen has been determined, it would be worthwhile to undertake a more elaborate calculation without these approximations.

It is convenient to rewrite Eq. (5.10) in the form

$$V = \sum_{im} V_i{}^m \mathbf{T}_2{}^m(J_i)_i + \sum_{i<j} V_{ij}{}^{mn} \mathbf{T}_2{}^m(J_i)_i \mathbf{T}_2{}^n(J_j)_j, \quad (5.18)$$

where

$$\mathbf{T}_2{}^m(J_i)_i \equiv \mathcal{G}_2{}^m(J_i)_i - \langle \mathcal{G}_2{}^m(J_i)_i \rangle, \qquad (5.19)$$

and the phonon operators are implicit in $V_i{}^m$ and $V_{ij}{}^{mn}$. Note that there are no terms linear in the phonon operators which are nonvanishing when averaged over the rotational degrees of freedom. Such a linear term in the displacements is forbidden by the inversion symmetry of

[56] T. D. Lee and C. N. Yang, Phys. Rev. 117, 22 (1960).

the four sublattice structure.[57,58] By the use of Eq. (5.18) rather than (5.10) we also eliminate cross terms and unlinked terms in the free energy in a convenient way.

Substituting Eq. (5.18) into Eq. (5.12) we find $\langle \Theta_i \rangle$ as

$$\langle \Theta_i \rangle = \langle \Theta_i \rangle^o - \sum_{mn\rho} p_n{}^o (E_n{}^{\mathrm{ph}} - E_m{}^{\mathrm{ph}})^{-2}$$

$$\times \langle n | (V_i{}^\rho)^\dagger \mathbf{T}_2{}^\rho(J_i)_i{}^\dagger | m \rangle \langle m | V_i{}^\rho [\mathbf{T}_2{}^\rho(J_i)_i, \Theta_i] | n \rangle$$

$$- \sum_{mn\rho\lambda j} p_n{}^o \langle n | (V_{ij}{}^{\rho\lambda})^\dagger \mathbf{T}_2{}^\rho(J_i)_i{}^\dagger \mathbf{T}_2{}^\lambda(J_j)_j{}^\dagger | m \rangle$$

$$\times \langle m | [\mathbf{T}_2{}^\rho(J_i)_i, \Theta_i] \mathbf{T}_2{}^\lambda(J_j)_j V_{ij}{}^{\rho\lambda} | n \rangle. \quad (5.20)$$

Here the superscript o on $\langle \Theta_i \rangle$ and p_n denotes unperturbed values, where p_n is the canonical probability of the state $| n \rangle$. Henceforth we set $y = 0$. Similarly, use of Eq. (5.18) permits us to write the effective Hamiltonian H' for the rotational degrees of freedom as

$$H' = H_0{}^{\mathrm{rot}} - \sum_{i\rho} \langle\langle (V_i{}^\rho)^\dagger \mathbf{T}_2{}^\rho(J_i)_i{}^\dagger (H_0{}^{\mathrm{ph}})^{-1} V_i{}^\rho \mathbf{T}_2{}^\rho(J_i)_i \rangle\rangle$$

$$- \tfrac{1}{2} \sum_{ij\rho\mu} \langle\langle (V_{ij}{}^{\rho\mu} \mathbf{T}_2{}^\rho(J_i)_i \mathbf{T}_2{}^\mu(J_j)_j)^\dagger$$

$$\times (H_0{}^{\mathrm{ph}})^{-1} V_{ij}{}^{\mathrm{ph}} \mathbf{T}_2{}^\rho(J_i)_i \mathbf{T}_2{}^\mu(J_j)_j \rangle\rangle$$

$$- \sum_{ij\rho} \{ \langle\langle (V_i{}^\rho \mathbf{T}_2{}^\rho(J_i)_i)^\dagger (H_0{}^{\mathrm{ph}})^{-1}$$

$$\times V_{ij}{}^{\rho 0} \mathbf{T}_2{}^\rho(J_i)_i \mathbf{T}_2{}^0(J_j)_j \rangle\rangle + \mathrm{H.c.} \}, \quad (5.21)$$

where $\langle\langle\ \rangle\rangle$ indicates an average over the phonon variables in the zero-phonon state, and H.c. stands for the Hermitian conjugate of the preceding term. Terms involving three different molecules will not contribute to $\tilde{\Delta}(T)$ by virtue of Eqs. (5.19) and (5.16).

It is apparent that we need averages over the zero-phonon states of the types

$$G_{ij;s}{}^{\alpha\beta} = \langle\langle u_{ji}{}^\alpha (H_0{}^{\mathrm{ph}})^{-s} u_{ji}{}^\beta \rangle\rangle, \quad (5.22a)$$

$$G_{ijk;s}{}^{\alpha\beta} = \langle\langle u_{ji}{}^\alpha (H_0{}^{\mathrm{ph}})^{-s} u_{jk}{}^\beta \rangle\rangle, \quad (5.22b)$$

where ij and ik are nearest-neighboring pairs. To estimate these correlation functions we assume an isotropic Debye spectrum with identical longitudinal and transverse sound speeds. In so doing we treat the solid as if it were a Bravais lattice, ignoring the fact that there are really four molecules per unit cell. Also we use the long-wavelength approximation which probably compensates somewhat for the incorrectness of the Debye spectrum. Thus we set

$$u_{ji}{}^\rho \approx i N^{-1/2} \sum_{\mathbf{k}\tau} e^{i\mathbf{k}\cdot\mathbf{R}_{i0}} (\mathbf{k}\cdot\mathbf{R}_{ij}{}^0) \hat{\epsilon}_{\mathbf{k}\tau}{}^\rho$$

$$\times \left(\frac{\hbar}{2M\omega_{\mathbf{k}}}\right)^{1/2} (a_{\mathbf{k}\tau}{}^\dagger + a_{-\mathbf{k}\tau}), \quad (5.23)$$

where $\hat{\epsilon}_{\mathbf{k}\tau}$ is the polarization vector of the τth mode, $\tau = 1, 2, 3$. Thus

$$G_{ij;s}{}^{\alpha\beta} = (-1)^\alpha \delta_{\alpha+\beta,0} \frac{R_0{}^2}{6} \frac{(k_0 R_0)^2}{M\omega_D{}^2 R_0{}^2}$$

$$\times (\hbar\omega_D)^{1-s} \frac{1}{N} \sum_{\mathbf{k}} \left(\frac{\omega_D}{\omega_{\mathbf{k}}}\right)^{s-1}. \quad (5.24)$$

Here we used

$$\omega_{\mathbf{k}}/\omega_D = k/k_0, \quad (5.25)$$

where ω_D is the Debye frequency and

$$k_0{}^3 v = 6\pi^2, \quad (5.26)$$

where v is the volume per molecule: $v = R_0{}^3 2^{-1/2}$. Likewise

$$G_{ijk;s}{}^{\alpha\beta} = (-1)^\alpha \delta_{\alpha+\beta,0} \frac{\mathbf{R}_{ij}{}^0 \cdot \mathbf{R}_{ik}{}^0}{6} \frac{(k_0 R_0)^2}{M\omega_D{}^2 R_0{}^2}$$

$$\times (\hbar\omega_D)^{1-s} N^{-1} \sum_{\mathbf{k}} \left(\frac{\omega_D}{\omega_{\mathbf{k}}}\right)^{s-1}. \quad (5.27)$$

Crudely, $N^{-1} \sum_{\mathbf{k}} (\omega_D/\omega_{\mathbf{k}}) \approx 2$ and also $(k_0 R_0)^2 \approx 20$.[59]

We must compute V as in Eq. (5.18) and substitute the appropriate terms into Eqs. (5.20) and (5.21). From Eq. (5.10) we have

$$V_i{}^m = -8\pi\Gamma_{\mathrm{ph}} \left(\frac{14\pi}{11}\right)^{1/2} \sum_{jn\lambda} C_{mn} C'(\lambda, m+n) \langle \Theta \rangle Y_2{}^n(\psi_{ij})$$

$$\times (u_{ij}{}^\lambda)_i R_0{}^{-1} Y_5{}^{-n-m-\lambda}(\Omega_{ij})_i (-1)^{n+m+\lambda}, \quad (5.28)$$

and also

$$V_{ij}{}^{\mu\nu} = -16\pi\Gamma_{\mathrm{ph}} \left(\frac{14\pi}{11}\right)^{1/2} \sum_{n\lambda} C_{\mu n} C'(\lambda, \mu+n) D_{n\nu}{}^{(2)}(\psi_{ij})^*$$

$$\times (-1)^{n+\mu+\lambda} (u_{ij}{}^\lambda)_i Y_5{}^{-n-\mu-\lambda}(\Omega_{ij})_i R_0{}^{-1}. \quad (5.29)$$

Substituting these expressions into Eq. (5.20) we find

$$\langle \Theta_i \rangle = \langle \Theta_i \rangle^o [1 - \xi_1 - \xi_2], \quad (5.30)$$

where ξ_1 and ξ_2 pertain to the second and third terms on the right-hand side of Eq. (5.20). We find

$$\xi_1 = \frac{1}{216} [\langle \Theta_i \rangle^o]^2 (k_0 R_0)^2 (\Gamma_{\mathrm{ph}}/\hbar\omega_D)(\Gamma_{\mathrm{ph}}/M\omega_D{}^2 R_0{}^2)$$

$$\times \langle \omega_D/\omega_{\mathbf{k}} \rangle \sum_\rho |G_{\rho 1}|^2, \quad (5.31)$$

where

$$G_{\rho\mu} = 36\pi \left(\frac{70}{11}\right)^{1/2} \sum_{nj} Y_2{}^n(\psi_{ij}) C_{\mu n} C'(\rho, \mu+n)(-1)^n$$

$$\times Y_5{}^{-\rho-\mu-n}(\hat{R}_{ij}{}^0)_i \hat{R}_{ij0}{}^{\mu+\rho}, \quad (5.32)$$

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[57] A small uniform strain is quite likely. See Ref. 58.

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

[59] These approximate evaluations, Eq. (5.24) and (5.27), probably constitute the most serious shortcoming of our theory. It would not be difficult to incorporate the results of a quantum crystal calculation of these correlation functions into the framework of our theory. Judging by our results, we may have underestimated the size of these correlation functions by up to 50%.

TABLE VII. Values of $G_{\sigma\rho}$.[a]

σ^ρ	2	1	0	-1	-2
1	0	0	$120\,\mu$	$-15\sqrt{3}$	$20(\sqrt{6})\mu^*$
0	0	$80(\sqrt{3})\mu$	-45	$80(\sqrt{3})\mu^*$	0
-1	$20(\sqrt{6})\mu$	$-15\sqrt{3}$	$120\,\mu^*$	0	0

[a] $\mu = 1 - 5(\sqrt{3})i/24$.

where $\hat{R}_{ij0}{}^\mu$ is the μth spherical component of $\hat{R}_{ij}{}^0$. The values of $G_{\rho\mu}$ are given in Table VII. Also

$$\xi_2 = 75(k_0R_0)^2(\Gamma_{\rm ph}/\hbar\omega_D)(\Gamma_{\rm ph}/M\omega_D{}^2R_0{}^2)\langle\omega_D/\omega_k\rangle$$

$$\times\sum_\sigma \{1 - \tfrac{1}{2}\delta_{\sigma0}[\langle\Theta_i\rangle^o]^2 + \tfrac{7}{8}C(222;\sigma\Theta)\langle\Theta_i\rangle^o\}W_{\sigma1}, \quad (5.33)$$

where

$$W_{\sigma\rho} = \sum_{j\lambda} |H_{j\lambda}{}^{\sigma\rho}|^2, \quad (5.34)$$

with

$$H_{j\lambda}{}^{\sigma\rho} = \left(\frac{14\pi}{11}\right)^{1/2} \sum_n C_{\rho n}C'(\lambda, \rho+n)$$

$$\times D_{n\sigma}{}^{(2)}(\psi_{ij})^* Y_5{}^{n+\rho+\lambda}(\Omega_{ij}{}^0)_i{}^*. \quad (5.35)$$

We have evaluated $W_{\sigma\rho}$ and the results are given in Table VIII. These evaluations were checked via the sum rule

$$\sum_{\sigma\rho} W_{\sigma\rho} = 42, \quad (5.36)$$

which follows from the orthonormality properties of the rotational matrices, the Clebsch-Gordan coefficients, and the spherical harmonics.[17] At zero temperature, when $\langle\Theta_i\rangle^o = -2$, we find

$$\langle\Theta_i\rangle/\langle\Theta_i\rangle^o = 0.98 \quad \text{for } H_2, \quad (5.37a)$$

$$\langle\Theta_i\rangle/\langle\Theta_i\rangle^o = 0.98 \quad \text{for } D_2. \quad (5.37b)$$

We shall compare these values to experimental data in a later section.

Let us now turn to the evaluation of $\tilde{\Delta}(T)$. We have evaluated Eq. (5.21) and write the result for $\tilde{\Delta}(T)$ using Eq. (5.14) as

$$\tilde{\Delta}(T) = \Delta^0(T) - \Delta^0(0)[\xi_3 + \xi_4 + \xi_5], \quad (5.38)$$

where ξ_3, ξ_4, and ξ_5 are the respective contributions to $\tilde{\Delta}(T)$ when the three perturbative terms in Eq. (5.21)

TABLE VIII. Values of $W_{\sigma\rho}$.

σ^ρ	2	1	0	-1	-2
2	1.920	3.120	2.256	0.918	0.244
1	3.120	1.386	1.398	1.344	0.918
0	2.256	1.398	1.446	1.398	2.256
-1	0.918	1.344	1.398	1.386	3.120
-2	0.244	0.918	2.256	3.120	1.920

are written as in Eq. (5.13). Explicitly we have

$$\xi_3 = \tfrac{1}{4}\langle\Theta_i\rangle^o(k_0R_0)^2(\Gamma_{\rm ph}/M\omega_D{}^2R_0{}^2)\frac{1}{1539}$$

$$\times\sum_m \{\tfrac{1}{4}\sqrt{(14)}C(222; m0)\langle\Theta_i\rangle^o$$

$$-\delta_{m0}[\langle\Theta_i\rangle^o]^2\} \sum_\lambda |G_{\lambda m}|^2, \quad (5.39a)$$

$$\xi_4 = \frac{50}{19}(k_0R_0)^2(\Gamma_{\rm ph}/M\omega_D{}^2R_0{}^2)$$

$$\times\sum_{\mu\nu} W_{\mu\nu}\{\tfrac{1}{4}\sqrt{(14)}C(222; \mu0) - \delta_{\mu0}\langle\Theta_i\rangle^o\}$$

$$\times\{1 + (\tfrac{7}{8})^{1/2}C(222; \nu0)\langle\Theta_i\rangle^o$$

$$-\tfrac{1}{2}\delta_{\nu0}[\langle\Theta_i\rangle^o]^2\}, \quad (5.39b)$$

$$\xi_5 = \frac{1}{3078}\langle\Theta_i\rangle^o(\Gamma_{\rm ph}/M\omega_D{}^2R_0{}^2)(k_0R_0)^2$$

$$\times\sum_\mu \{1 + (\tfrac{7}{8})^{1/2}C(222; \mu0)\langle\Theta_i\rangle^o$$

$$-\tfrac{1}{2}\delta_{\mu0}[\langle\Theta_i\rangle^o]^2\} \sum_\lambda |G_{\lambda\mu}|^2. \quad (5.39c)$$

Each of these terms has a physical significance which is most easily described in terms of scattering diagrams. The first term in Eq. (5.21) clearly represents a single phonon being created or absorbed while a libron is created or absorbed as shown in Fig. 2(a). This term then describes linear phonon-libron coupling. The second term in Eq. (5.21) describes a higher-order process in which besides phonon absorption or creation there is libron scattering. Finally, the last term in Eq. (5.21) describes a higher-order scattering which leads to a renormalized libron potential quadratic in libron amplitudes. We have evaluated these expressions numerically for $T=0$ taking $\langle\Theta_i\rangle^o = -2$ and find

$$19\Gamma' \equiv \tilde{\Delta}(T=0) = 19\Gamma_0(1-0.06) \quad \text{for } H_2, \quad (5.40a)$$

$$\tilde{\Delta}(T=0) = 19\Gamma_0(1-0.05) \quad \text{for } D_2, \quad (5.40b)$$

so that due to dynamical phonon renormalization the energy gap is reduced further by 6% for H_2 and 5% for D_2. We thus conclude that the orientational properties of fcc hydrogen should be calculated using a coupling constant $\Gamma_{\rm eff}$, renormalized both by static and dynamical phonon interactions and by dielectric screening:

$$\Gamma_{\rm eff} = 0.96\xi_{54}\Gamma' = 0.84\Gamma_0 \quad \text{for } H_2, \quad (5.41a)$$

$$\Gamma_{\rm eff} = 0.95\xi_{54}\Gamma' = 0.84\Gamma_0 \quad \text{for } D_2, \quad (5.41b)$$

where the factors 0.96 and 0.95 result from dielectric screening as is discussed in Sec. III. Note that neither the static nor the dynamic effect is significantly different for D_2 than for H_2. This surprising result occurs because here the expansion parameter is $\Gamma_{\rm ph}/M\omega_D{}^2R_0{}^2$ which is roughly the same for both solids. We shall discuss the experimental verification of these results in a later section.

B. Isolated Pairs of $J=1$ Molecules

Let us now investigate the effects of phonon coupling on the energy levels of a nearest-neighboring pair of $J=1$ molecules in otherwise pure $J=0$ hydrogen. Here the calculations are much simpler algebraically because of the symmetry of the interactions with respect to the intermolecular axis R_{12}. If the EQQ Hamiltonian is expanded to first order in the displacements, one finds the linear phonon coupling $H_{\text{EQQ}}^{(1)}$

$$H_{\text{EQQ}}^{(1)} = -16\pi\Gamma_{\text{ph}}\left(\frac{14\pi}{11}\right)^{1/2} \sum_{mn\rho} C_{mn}C'(\rho, m+n)$$

$$\times \mathcal{J}_2{}^m(J_i)\mathcal{J}_2{}^n(J_j)u_{ij}{}^\rho Y_5{}^{m+n+\rho}(\hat{R}_{ij}{}^0)^*(R_{ij}{}^0)^{-1}. \quad (5.42)$$

Taking the quantization axis along $R_{12}{}^0$, the equilibrium value of R_{12}, we write this as

$$H_{\text{EQQ}}^{(1)} = -\frac{\Gamma_{\text{ph}}}{\Gamma_0}\frac{5H_0}{R_0}u_{\delta 0}{}^0 - \frac{5\Gamma_{\text{ph}}\sqrt{2}}{4R_0}[u_{\delta 0}{}^{-1}Q+\text{H.c.}]$$

$$(5.43)$$

using spherical components for the vector $u_{\delta 0}$ and where H_0 is the rigid lattice EQQ Hamiltonian. Here the operator Q is

$$Q \equiv (J_1{}^-J_1{}^z+J_1{}^zJ_1{}^-)(J_2{}^+)^2+(J_2{}^-J_2{}^z+J_2{}^zJ_2{}^-)(J_1{}^+)^2$$
$$-2(3(J_1{}^z)^2-2)(J_2{}^+J_2{}^z+J_2{}^zJ_2{}^+)$$
$$-2(3(J_2{}^z)^2-2)(J_1{}^+J_1{}^z+J_1{}^zJ_1{}^+). \quad (5.44)$$

In terms of the pair eigenstates of Table III the only nonvanishing matrix elements of Q are

$$\langle 2|Q|8\rangle = -4, \quad (5.45a)$$

$$\langle 1|Q|9\rangle = -4\sqrt{6}, \quad (5.45b)$$

$$\langle 9|Q|3\rangle = 4, \quad (5.45c)$$

$$\langle 8|Q|1\rangle = 4\sqrt{6}. \quad (5.45d)$$

The quartet state of E_{EQQ} with zero energy spanned by $|4\rangle$, $|5\rangle$, $|6\rangle$, and $|7\rangle$ thus suffers no perturbation from the linear phonon coupling. The ground doublet at energy -4Γ spanned by $|8\rangle$ and $|9\rangle$ is depressed to a new energy $E_0{}'$ given by

$$E_0{}' = -4\Gamma_0-750\Gamma_{\text{ph}}{}^2G_{ij;1}{}^{00}R_0{}^{-2} \quad (5.46a)$$

$$\equiv -4\Gamma_0(1+\xi_6), \quad (5.46b)$$

with

$$\xi_6 = 375(k_0R_0)^2\Gamma_{\text{ph}}{}^2/12M\omega_D{}^2R_0{}^2\Gamma_0 \quad (5.47a)$$

$$\approx 0.05 \quad \text{for } H_2 \quad (5.47b)$$

$$\approx 0.04 \quad \text{for } D_2. \quad (5.47c)$$

Thus for isolated $J=1$ pairs the dynamical effect tends to increase Γ_0. Combining these estimates with those of Eq. (4.19) for the static effect we find

$$\Gamma_{\text{eff}}{}^{\text{pairs}}/\Gamma_0 = 0.96\xi_{54}(1+\xi_6) = 0.94 \quad \text{for } H_2 \quad (5.48a)$$

$$= 0.95\xi_{54}(1+\xi_6) = 0.92 \quad \text{for } D_2, \quad (5.48b)$$

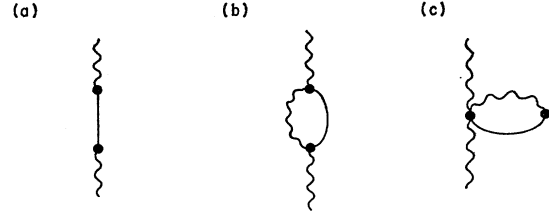
FIG. 2. Diagrams describing second-order corrections to libron energies. Here wiggly lines indicate librons and smooth lines phonons. Each vertex represents an interaction. Diagram (a) represents linear phonon-libron mixing. Diagram (b) represents anharmonicity cubic in phonon-libron amplitudes. Diagram (c) shows a contribution to the static libron potential due to phonon-libron interactions.

where again we have included the screening factors of Sec. III. We can also calculate the quantity $\langle 3J_z{}^2-2\rangle$, which in the ground state has the value $-\frac{1}{2}$. This computation is performed by including in the unperturbed Hamiltonian a term $\sum_i \rho\Theta_i$ and using

$$2\langle\Theta_i\rangle = \partial E_0/\partial\rho. \quad (5.49)$$

The calculation follows along similar lines to the above ones and we quote only the final result:

$$\langle\Theta_i\rangle = -\frac{1}{2}(1+\xi_7), \quad (5.50)$$

with

$$\xi_7 = 150G_{ij;2}{}^{00}\Gamma_{\text{ph}}{}^2R_0{}^{-2}$$

$$= 25(k_0R_0)^2\left(\frac{\Gamma_{\text{ph}}}{m\omega_D{}^2R_0{}^2}\right)\left(\frac{\Gamma_{\text{ph}}}{\hbar\omega_D}\right)\left\langle\frac{\omega_D}{\omega_k}\right\rangle, \quad (5.51)$$

which gives $\xi_7 \approx 10^{-3}$ which is negligible.

C. Summary

The differing conclusions for the case of the isolated pair and for the ordered system can be partly understood in a simple way. Basically there are two distinct effects on the orientational interactions due to their interactions with the phonons. The first of these can be visualized as follows. Phonon particles continually bombard the molecules thus inevitably creating some disorder in the orientation of the molecules. This disorder can be described by a reduction in the rigid-lattice orientational interactions. This mechanism is operative for both the pair system and the ordered phase and has the effect of reducing the coupling constant and the order parameter, $\langle 3J_z{}^2-2\rangle$. The second mechanism depends on the extra attraction or repulsion which two $J=1$ molecules have for one another depending on their relative orientations. This effect arises from the term linear in the displacements which is diagonal in the rotational operators. This term clearly vanishes for the ordered fcc phase because of the inversion symmetry of that structure. For the isolated pair system this term becomes important. The effect of this term is to increase the orientational interaction because the $J=1$ molecules

are attracted to one another[60] and the resulting value of R tends to increase Γ. The resulting stronger interaction also leads to an increase in the order parameter $\langle 3J_z{}^2 - 2 \rangle$. Finally, the fact that for the pairs there is a much smaller effect on the order parameter and that the dynamical reduction is less important is readily traced to the fact that these quantities are second order in the phonon coupling divided by the Debye energy. For the ordered state the phonon coupling is larger by a factor of z than for the case of pairs, where $z = 12$, z being the number of nearest neighbors. These arguments also imply that at high temperatures, when the orientational energy is essentially thermally averaged to zero, the dynamical effects become unimportant. In that case we estimate Γ_{eff}, denoted $\Gamma_{eff}(kT \gg \Gamma_0)$, to reflect only static phonon and dielectric screening effects. The results of our calculations for Γ_{eff} are summarized in Table IV and are compared with corresponding experimental values in Table IX, below. A discussion of this comparison is given in Sec. VII.

We should emphasize that more refined treatments can be generated using our work. In particular, one can incorporate a better treatment of the phonon spectrum when it becomes available by replacing Eq. (5.24) and (5.17) by the results of detailed calculations. At the same time one should also take account of the rotational energies along with the phonon energies in the energy denominators.

VI. INDIRECT INTERACTION BETWEEN $J=1$ MOLECULES AT LARGE SEPARATIONS

There is another way in which phonons can affect the interactions between molecules. They can give rise to an indirect interaction which is quite analogous to the Suhl-Nakamura interaction[4,5] between widely separated nuclear spins in an ordered magnetic material. The mechanism is thus the following: As molecule A rotates, its interaction with the phonon system produces disturbances in the lattice. These excitations can propagate and can be absorbed by molecule B which may be very far from molecule A. Absorption of a phonon causes molecule B to rotate thereby interacting indirectly with molecule A. Clearly, this type of interaction will dominate at sufficiently large separations because it falls off as a lower power (viz. r^{-3}) of separation than do the EQQ interactions. Hence the calculation we are about to perform will have some relevance for studies of hydrogen at very low $J=1$ concentrations.

As we shall see, the rotational and phonon degrees of freedom are coupled together via a term of the form

$$V_{INT} = \sum_{kjR} \mathcal{O}_{kj}(J_R)(a_{kj}{}^\dagger + a_{-kj})e^{i\mathbf{k}\cdot\mathbf{R}}. \quad (6.1)$$

Here $a_{kj}{}^\dagger$ creates a phonon of wave vector $\mathbf{k}$ and polarization along the unit vector ϵ_j, j is summed over the three polarization indices, $\mathbf{R}$ is summed over the posi-

[60] L. I. Amstutz, J. R. Thompson, and H. Meyer, Phys. Rev. Letters 21, 1175 (1968).

tions of all $J=1$ molecules, and $\mathcal{O}_{kj}(J_R)$ is an operator in the $J=1$ manifold of the molecule at $\mathbf{R}$ and is dependent on $\mathbf{k}$ and j. From second-order perturbation theory or better, using a canonical transformation, one shows that V_{INT} can be replaced by an effective interaction V_{SN} between $J=1$ molecules:

$$V_{SN} = -\sum_{kjRR'} \mathcal{O}_{kj}(J_R)\mathcal{O}_{-kj}(J_{R'})e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R'})}(\hbar\omega_{kj})^{-1}. \quad (6.2)$$

Thus, a calculation of $\mathcal{O}_{kj}(J_R)$ will enable us to estimate the indirect interaction between distant $J=1$ molecules.

To obtain an interaction between molecules of the type of Eq. (6.1), we must use the second term of Eq. (2.2):

$$V = \sum_{R,\delta} B(|\mathbf{r}_R - \mathbf{r}_{R+\delta}|)Y_2{}^0(\omega_{R\delta})\left(\frac{16\pi}{5}\right)^{1/2}. \quad (6.3)$$

Here $\mathbf{r}_R$ is the instantaneous position of the molecule at $\mathbf{R}$:

$$\mathbf{r}_R \equiv \mathbf{R} + \mathbf{u}_R, \quad (6.4)$$

and $\omega_{R\delta}$ is the angle between the molecular axis at $\mathbf{R}$ and $\mathbf{r}_R - \mathbf{r}_{R+\delta}$. The sum over $\mathbf{R}$ is carried over all $J=1$ molecules and δ is summed over all nearest-neighbor vectors. We write

$$Y_2{}^0(\omega_{R\delta}) = \frac{8\pi}{5}\sum_m Y_2{}^m(\omega_{RC})Y_2{}^m(\Omega_{R\delta})^*. \quad (6.5)$$

Here ω_{RC} is the angle between the molecular axis at $\mathbf{R}$ and the crystal axis and $\Omega_{R\delta}$ is the angle between $\mathbf{r}_R - \mathbf{r}_{R+\delta}$ and the crystal axis. Thus the linear phonon coupling is

$$\delta V = -\frac{16\pi}{25}\sum_{R\delta m} \mathcal{G}_2{}^m(J_R)(\mathbf{u}_{R+\delta} - \mathbf{u}_R)$$
$$\cdot \nabla_\delta[B(\delta)Y_2{}^{-m}(\hat{\delta})](-1)^m, \quad (6.6)$$

where the quantization axis is taken to coincide with the crystal c axis. As we have mentioned in Sec. IV, we should interpret $B(r)$ as an effective renormalized potential.

To obtain an approximate calculation of V_{SN} it suffices to assume an isotropic Debye spectrum. We shall allow for different transverse and longitudinal sound speeds, however. Thus we write

$$u_{R+\delta}{}^\alpha - u_R{}^\alpha = N^{-1/2}\sum_{kj} e^{i\mathbf{k}\cdot\mathbf{R}}(e^{i\mathbf{k}\cdot\delta} - 1)$$
$$\times (\hbar/2M\omega_{kj})^{1/2}(a_{kj}{}^\dagger + a_{-k,j})\hat{\epsilon}_j{}^\alpha, \quad (6.7)$$

where we use spherical components of vectors. Then we find

$$V_{INT} = -\left(\frac{16\pi}{25}\right)\left(\frac{\hbar}{2MN}\right)^{1/2} i \sum_{m\delta R\mu\rho j} (-1)^{m+\mu+\rho}\mathcal{G}_2{}^m(J_R)$$
$$\times k^\rho \delta^{-\rho}e^{i\mathbf{k}\cdot\mathbf{R}}\omega_{kj}{}^{-1/2}(a_{kj}{}^\dagger + a_{-kj})\hat{\epsilon}_j{}^\mu$$
$$\times \nabla_\delta{}^{-\mu}[B(\delta)Y_2{}^{-m}(\hat{\delta})]. \quad (6.8)$$

According to Eq. (6.2) this potential leads to the following effective interaction:

$$V_{\rm SN} = -\frac{16\pi}{5}(16\pi/250mN)$$

$$\times \sum_{m\delta\mathbf{R}k\mu\rho, m'\delta'\mathbf{R}'\mu'\rho'j}(-1)^{m+m'+\mu+\mu'+\rho+\rho'}\mathcal{J}_2{}^m(J_{\mathbf{R}})$$

$$\times \mathcal{J}_2{}^{m'}(J_{\mathbf{R}'})e^{i\mathbf{k}\cdot\mathbf{R}-\mathbf{R}'}k^\rho k^{\rho'}\delta^{-\rho}\delta'^{-\rho'}\omega_{kj}{}^{-2}\hat\epsilon_j{}^\mu\hat\epsilon_j{}^{\mu'}$$

$$\times\nabla_\delta{}^{-\mu}[B(\delta)Y_2{}^{-m}(\hat\delta)]\nabla_{\delta'}{}^{-\mu'}[B(\delta')Y_2{}^{-m'}(\hat\delta')]. \quad (6.9)$$

To obtain $V_{\rm SN}$ at large separation, i.e., in the wave zone, we need only treat the summand correctly for small k. Hence we set $\omega_{kj}=c_jk$. Furthermore we shall assume that there exist only purely transverse and longitudinal phonons with sound speeds, $c_\perp$ and $c_{\rm ll}$, respectively.[61] Then we write

$$V_{\rm SN}=V_{\rm SN}{}^{(1)}+V_{\rm SN}{}^{(2)}, \quad (6.10)$$

where

$$V_{\rm SN}{}^{(1)}=-\frac{16\pi}{5}(16\pi/250MNc_\perp{}^2)$$

$$\times\sum_{mm'\mathbf{R}\mathbf{R}',k\rho\rho'\mu}(-1)^{m+m'+\rho+\rho'+\mu}e^{i\mathbf{k}\cdot\mathbf{R}-\mathbf{R}'}\mathcal{J}_2{}^m(J_{\mathbf{R}})$$

$$\times\mathcal{J}_2{}^{m'}(J_{\mathbf{R}'})\hat k^\rho\hat k^{\rho'}\sum_\delta \delta^{-\rho}\nabla_\delta{}^{-\mu}[B(\delta)Y_2{}^{-m}(\hat\delta)]$$

$$\times\sum_{\delta'}\delta'^{-\rho'}\nabla_{\delta'}{}^\mu[B(\delta')Y_2{}^{-m'}(\hat\delta')], \quad (6.11a)$$

$$V_{\rm SN}{}^{(2)}=-\frac{16\pi}{5}(16\pi/250MN)(c_{\rm ll}{}^{-2}-c_\perp{}^{-2})$$

$$\times\sum_{mm'\mathbf{R}\mathbf{R}'k,\rho\rho'\mu\mu'}(-1)^{m+m'+\rho+\rho'+\mu+\mu'}e^{i\mathbf{k}\cdot\mathbf{R}-\mathbf{R}'}$$

$$\times\mathcal{J}_2{}^m(J_{\mathbf{R}})\mathcal{J}_2{}^{m'}(J_{\mathbf{R}'})\hat k^\rho\hat k^{\rho'}\hat k^\mu\hat k^{\mu'}$$

$$\times\sum_\delta \delta^{-\rho}\nabla_\delta{}^{-\mu}[B(\delta)Y_2{}^{-m}(\hat\delta)]$$

$$\times\sum_{\delta'}\delta'^{-\rho'}\nabla_{\delta'}{}^{-\mu'}[B(\delta')Y_2{}^{-m'}(\delta')]. \quad (6.11b)$$

Using the symmetry of the hcp lattice one sees that the sums over $\boldsymbol\delta$ and $\boldsymbol\delta'$ vanish in Eq. (6.11a) unless $\rho+m+\mu=\rho'+m'+\mu=0$ and in Eq. (6.11b) unless $\rho+m+\mu=\rho'+m'+\mu'=0$. We have simplified these expressions using the following relations:

$$\hat k^\rho\hat k^{\rho'}=\tfrac{1}{3}\Delta_{\rho+\rho',0}(-1)^\rho$$

$$+(8\pi/15)^{1/2}C(112;\rho\rho')Y_2{}^{\rho+\rho'}(\hat k), \quad (6.12a)$$

$$N^{-1}\sum_k Y_J{}^M(\hat k)e^{i\mathbf{k}\cdot\mathbf{R}}$$

$$\approx(3V/4\pi NR_0{}^3)\gamma_J Y_J{}^M(\hat R)(R/R_0)^3, \quad (6.12b)$$

where $\Delta_{\alpha,\beta}$ is a Kronecker δ and the constants γ_J are $\gamma_0=0$, $\gamma_1=-1$, and $\gamma_2=5/4$. The relation Eq. (6.12b)

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[61] In Ref. 10 this was shown to be an excellent approximation.

is the asymptotic expansion for large separation. Also we define

$$g_{m\mu}=\sum_\delta \delta^{m+\mu}\nabla_\delta{}^{-\mu}[B(\delta)Y_2{}^{-m}(\hat\delta)]. \quad (6.12c)$$

Explicitly we find

$$g_{m\mu}=\psi'\delta^3C(112; m+\mu, -\mu)(8\pi/15)^{1/2}$$

$$\times\sum_\delta Y_2{}^m(\hat\delta)Y_2{}^{-m}(\hat\delta)+\psi\delta^2C(112; m+\mu, -\mu)$$

$$\times(15/2\pi)^{1/2}\sum_\delta \hat\delta^{m+\mu}\hat\delta^{-m-\mu}(-1)^\mu, \quad (6.13)$$

where $\psi(\delta)\equiv B(\delta)\delta^{-2}$. If we make the slight approximation that

$$\sum_\delta Y_2{}^{-m}(\hat\delta)Y_2{}^m(\hat\delta)=(-1)^m3/\pi, \quad (6.14)$$

then we obtain

$$g_{m\mu}=(4/5)(-1)^m(15/2\pi)^{1/2}C(112; m+\mu, -\mu)$$

$$\times[3B(\delta)+\delta B'(\delta)]. \quad (6.15)$$

Carrying out the algebra in a straightforward way we find the result,

$$V_{\rm SN}=\tfrac{1}{2}(4\pi)^{1/2}\sum_{\mathbf{R}\mathbf{R}'}\sum_{Jmm'}\alpha_J C(22J; mm')\mathcal{J}_2{}^m(J_{\mathbf{R}})$$

$$\times\mathcal{J}_2{}^{m'}(J_{\mathbf{R}'})Y_J{}^{m+m'}(\Omega_{\mathbf{R}\mathbf{R}'})^*\left|\frac{R_0}{\mathbf{R}-\mathbf{R}'}\right|^3, \quad (6.16)$$

where $\Omega_{\mathbf{R}\mathbf{R}'}$ is the angle between $\mathbf{R}-\mathbf{R}'$ and the crystal c axis and

$$\alpha_2=\frac{-48}{4375}[3B(\delta)+\delta B'(\delta)]^2$$

$$\times\left(\frac{V}{MNR_0{}^3\pi}\right)\left(\frac{14}{5}\right)^{1/2}\left[\frac{5}{c_\perp{}^2}+\frac{2}{c_{\rm ll}{}^2}\right], \quad (6.17a)$$

$$\alpha_4=\frac{-24}{875}[3B(\delta)+\delta B'(\delta)]^2$$

$$\times\left(\frac{V}{MNR_0{}^3\pi}\right)\left(\frac{14}{5}\right)^{1/2}\left[\frac{1}{c_{\rm ll}{}^2}-\frac{1}{c_\perp{}^2}\right], \quad (6.17b)$$

$$\alpha_0=\alpha_1=\alpha_3=0. \quad (6.17c)$$

The form of the result, Eq. (6.16), is as expected, since with the approximation of Eq. (6.14) one has the same $g_{m\mu}$ as for spherical symmetry. Then $V_{\rm SN}$ must be formed from expressions which are both rotationally invariant and symmetric with respect to interchange of $\mathbf{R}$ and $\mathbf{R}'$. Consequently, Eqs. (6.16) and (6.17c) follow. If furthermore $c_{\rm ll}=c_\perp$, then we have

$$\alpha_J=0, \quad J\neq 2 \quad (6.18a)$$

$$\alpha_2=-0.56[3B(\delta)+\delta B'(\delta)]^2/M\omega_D{}^2R_0{}^2. \quad (6.18b)$$

TABLE IX. Experimental values of Γ_{eff}.

$\Gamma_{\mathrm{eff}}/\Gamma_0$	Method	References
	Dilute $J=1$ H_2	
0.82	NMR, $J=1$ pairs	64
0.82	$\dfrac{\partial p}{\partial T}\bigg)_v$ for $x\leq0.07$	65, 66
0.79	Neutron scattering	63, 46
	Concentrated $J=1$ H_2	
0.82	EQQ pressure	65, 67
0.75	Neutron scattering	63, 46
0.69	Raman spectrum	58, 35
	Dilute $J=1$ D_2	
0.88	$\dfrac{\partial p}{\partial T}\bigg)_v$ for $x\leq0.07$	68, 66
	Concentrated $J=1$ D_2	
0.81	Raman spectrum	58, 35
0.79	$\dfrac{\partial p}{\partial T}\bigg)_v$ for $x\geq0.83$	68, 69, 36, 53
0.83	Specific heat for $T\geq7°K$	70, 71

We shall now consider the importance of our result with respect to the interpretation of experimental data. Clearly such interactions can only become important at very low concentration x of $J=1$ molecules. In this regime the NMR relaxation time T_2 is a sensitive measure of interactions between distant molecules. As Sung[7] has shown, one can attribute the $x^{5/3}$ variation of T_2[6,7] to the EQQ interactions between distant molecules. This analysis will be valid as long as the root mean square EQQ energy is larger than other energies. In particular this behavior implies that in the concentration range covered the root mean square EQQ energy $\langle E_{\mathrm{EQQ}}\rangle$ is larger than the root mean square energy $\langle E_{\mathrm{SN}}\rangle$ from the indirect interactions. From Table II we find the former to be

$$\langle E_{\mathrm{EQQ}}\rangle=\left(\frac{70}{9}\right)^{1/2}\Gamma_0(R_0/R)^5 \qquad (6.19a)$$

$$\approx2\Gamma x^{5/3}, \qquad (6.19b)$$

where we took account of dielectric screening and also we assumed the separation between molecules to be of order $R=R_0x^{-1/3}$, where x is the concentration of $J=1$ molecules. From Eq. (6.16) we find $\langle E_{\mathrm{SN}}\rangle$ as

$$\langle E_{\mathrm{SN}}\rangle^2=\tfrac{1}{9}\,\mathrm{Tr}V_{\mathrm{SN}}^2 \qquad (6.20a)$$

$$=\left(\frac{5}{8\pi}\right)^2\sum_J \alpha_J^2(2J+1)(R_0/R)^6. \qquad (6.20b)$$

For an order-of-magnitude estimate of this quantity we use Eq. (6.18) from which we find

$$\langle E_{\mathrm{SN}}\rangle\approx2.4\times[3B(R_0)+R_0B'(R_0)]^2/M\omega_D^2R_0^2. \qquad (6.21)$$

As we have mentioned, we substitute into this expression not the potential of Eq. (6.7), but rather the renormalized potential. Thus, using the results of Sec. IV, we replace the square bracket in Eq. (6.21) by the factor

$$\beta_1[3\xi_{02}^{(b)}+AR_0^2(\tfrac{3}{5}\xi_{-1,3}^{(b)}+\tfrac{2}{5}\xi_{-1,1}^{(b)}+\xi_{-1,1}^{(a)}\xi_{02}^{(b)})]$$
$$-\beta_2[3\xi_{62}^{(a)}+AR_0^2(\tfrac{3}{5}\xi_{5,3}^{(a)}+\tfrac{2}{5}\xi_{5,1}^{(a)}+\xi_{-1,1}^{(a)}\xi_{6,2}^{(a)})]$$
$$(6.22a)$$

$$=\beta_1\gamma_2^{(b)}-\beta_2\gamma_2^{(a)}, \qquad (6.22b)$$

where these coefficients are evaluated in Eq. (4.27b) and (4.27d). In this way we find the renormalized value

$$3B(\delta)+R_0B'(R_0)=12.2\beta_1-2.13\beta_2. \qquad (6.23)$$

From the data of Hardy and Gaines[6,7] we see that the $x^{5/3}$ behavior in T_2 persists down to a concentration $x=0.003$. The condition that the EQQ energy be larger than the indirect interaction energy at this concentration becomes

$$\Delta E_{\mathrm{SN}}/x\leq0.03\ \mathrm{cm}^{-1}, \qquad (6.24)$$

in comparison to which Eq. (6.23) with our values of β_1 and β_2 gives

$$\Delta E_{\mathrm{SN}}/x=0.022\ \mathrm{cm}^{-1}. \qquad (6.25)$$

In contrast the anomalously large values of β_1 and β_2, i.e., $\beta_1=5.0$ cm^{-1} and $\beta_2=3.7$ cm^{-1}, used by Van Kranendonk and Sears[11] give[62]

$$\Delta E_{\mathrm{SN}}/x=0.09\ \mathrm{cm}^{-1}. \qquad (6.26)$$

Clearly the T_2 data rules out such large values of the potential coefficient $B(R)$. For this reason measurements at even lower concentration would be of interest.

VII. DISCUSSION

In this section we shall discuss the experimental values of Γ_{eff} in order to see whether our theoretical predictions are in accord with experiment. The most direct determinations include these by Raman scattering,[58] neutron scattering,[63] nuclear magnetic resonance[64] and thermodynamic measurements such as the pressure due to EQQ interactions[36,53,65–69] and the corresponding specific heat.[70,71] Several other methods of determining

[62] Using the values of β_1 and β_2 from Ref. 11 and also using their renormalization procedure yields the value $\Delta E_{\mathrm{SN}}/x=0.75$ cm^{-1}.

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Γ are possible. However, they seem to be less reliable at present due to uncertainties in either or both the experiment or the theory. Among these are determinations of Γ_{eff} based on the high-temperature specific heat of H_2,[72] the NMR spin-lattice relaxation time at high $J=1$ concentration in the disordered hcp phase,[73-78] the dependence of the saturated vapor pressure on $J=1$ concentration,[28,79,80] the NMR relaxation time at very low $J=1$ concentrations,[6,7,78] and the infrared and Raman spectra of nearly pure $J=0$ H_2.[21,25] Within the current resolution of the above techniques and the state of the theoretical models, these experiments can be understood using values of Γ_{eff} comparable to those in Table IX. We shall discuss here only those determinations cited in Table IX.

A. Dilute $J=1$ H_2

For dilute $J=1$ systems one can determine Γ_{eff} by essentially observing isolated pairs of $J=1$ molecules. Corrections for interactions between distant molecules are negligible for $x \leq 0.07$, say. For the value obtained from neutron scattering we modified the analysis of Elliott and Hartmann[46] in that we did not use the average of R_{ij}^{-10} for reasons explained above.[45] The value obtained using the data of Schott et al.[63] corroborates our renormalization as contrasted to that of Ref. 46 which predicts $\Gamma_{\text{eff}}/\Gamma_0 \approx \frac{4}{3}$.

B. Concentrated $J=1$ H_2

Here it is vital to analyze the Raman spectrum[58] taking account of next nearest neighbors.[35] This effect leads to a reduction in Γ_{eff} of between 15 and 20%. We note that the value obtained from the EQQ pressure[65] which is directly related to the EQQ energy[67] may be uncertain due to the assumption that the lattice pressure is independent of $J=1$ concentration. Accordingly, we believe the other two values of Γ_{eff} to be more reliable. In particlular note that Γ_{eff} for the concentrated $J=1$ system is 5% less than that for the dilute $J=1$ system. The accuracy of these determinations of Γ_{eff} is such that this difference is not conclusive. However, the trend is certainly in the direction predicted by our calculations which give Γ_{eff} 10% smaller in the concentrated than in the dilute $J=1$ systems. The fact that we obtain

theoretical values of Γ_{eff} which are too large in both cases suggests that our static renormalizations underestimate the reduction in Γ_{eff} due to averaging the EQQ interaction over the phonon ground state.

Note added in proof: Recently C. F. Coll, III, and the author have studied the effect of anharmonic libron-libron interactions in a rigid lattice and find surprisingly large, viz. $\sim 15\%$, shifts in the libron energies therefrom. This result will modify the interpretation of data in the ordered phase.

C. D_2

Most of the above comments apply to the D_2 data as well. For D_2 one has the more extensive specific-heat data of Grenier and White,[70] whose data gives quite an anomalously small value of Γ_{eff} ($\Gamma_{\text{eff}} \approx 0.50$ cm^{-1}) when fit to a $1/T^2$ law. In order to resolve this difficulty[71] it is necessary to keep several higher-order terms, even at temperatures above $10°$K. The fit obtained using Padé approximants is reasonable, but this determination is only reliable to within 10% due to the slow convergence of the high-temperature expansion. For D_2 we see that the concentration dependence of Γ_{eff} is more obvious than for H_2. For D_2 we would claim that the present data substantiates our phonon renormalization mechanism, although as for H_2, our static renormalizaion is probably not so reliable.

D. Order Parameter

Lastly, we can compare our calculations with the value of the order parameter $\langle 3 \cos^2\theta - 1 \rangle_T$ as deduced from NMR experiments. This determination is based on observation of the frequency splitting of the Pake doublet in powdered samples of H_2 or D_2. This splitting is given by a slight generalization of the formula used by Reif and Purcell[81] as

$$\Delta\nu = (15/4)d\langle 3 \cos^2\theta - 1 \rangle_T, \qquad (7.1)$$

where $\langle \ \rangle_T$ indicates a thermodynamic average over the rotational motion, and d is a constant describing the intramolecular interactions of the nuclear spins. The values of d have been determined by Ramsey and co-workers for free molecules[14] and are given in Table I. From the analysis of Van Kranendonk and Karl[21] it is clear that the internuclear separation of the hydrogen molecules is very little different for the free molecules as compared to those in the solid. Hence the value of d in the solid differs from that in the gas by at most a few tenths of a percent. Thus a measurement of $\Delta\nu$ gives directly a value of the order parameter.

Using the equivalent Ising model we have shown elsewhere[28] that the order parameter in the ordered state is slightly affected by perturbations off diagonal in J. Thus

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we found

$$\langle 3\cos^2\theta-1\rangle_{T=0}=\tfrac{4}{5}[1+(171)(1.1)\Gamma/70B]\quad(7.2\text{a})$$

$$\approx\tfrac{4}{5}[1+0.032x]\quad\text{for }H_2\quad(7.2\text{b})$$

$$\approx\tfrac{4}{5}[1+0.076x]\quad\text{for }D_2.\quad(7.2\text{c})$$

One can also take account of the zero-point rotational motion caused by the fact that the ordered state is not an exact eigenstate of the EQQ Hamiltonian. We use the calculations of Raich and Etters[36] for the zero-point reduction in the order parameter which we scale with $1/x$ in analogy with the Heisenberg antiferromagnet where this quantity is known to be inversely proportional to the number of nearest neighbors.[82] Thus we obtain

$$\Delta\nu=173.0(1+0.032x-0.02/x)\text{ kHz}\quad\text{for }H_2,\quad(7.3\text{a})$$

$$\Delta\nu=75.72(1+0.076x-0.02/x)\text{ kHz}\quad\text{for }D_2.\quad(7.3\text{b})$$

In normal ($x=0.75$) H_2 after the correction for frequency pulling due to intermolecular dipolar interactions has been made one finds the experimental[48,81] and theoretical values of $\Delta\nu$ to be

$$\Delta\nu_{\text{expt}}=164.1\text{ kHz},\quad\Delta\nu_{\text{th}}=172.5\text{ kHz},\quad(7.4\text{a})$$

whereas for D_2 with $x=0.81$ the results are[83]

$$\Delta\nu_{\text{expt}}=76.8\text{ kHz},\quad\Delta\nu_{\text{th}}=79.0\text{ kHz}.\quad(7.4\text{b})$$

We attribute such a difference to the additional zero-point motion in the rotational system induced by dynamical interactions with the phonon system as calculated in Eq. (5.37). For the case of isolated pairs of $J=1$ molecules all these corrections are negligible and one should expect to observe a frequency splitting $\Delta\nu=\tfrac{3}{8}d$ ≈43.3 kHz. The actually observed value[64] is some 5% less than this for reasons which we do not understand at present.

E. Summary

We can summarize our work as follows. We have calculated the effects of phonon-libron interactions and

dielectric screening on the EQQ interactions. These effects lead to a renormalization, so that the EQQ interaction constant Γ_0 is replaced by Γ_{eff}. Our calculations show that $\Gamma_{\text{eff}}/\Gamma_0\approx0.84$ for ordered $J=1$ systems and $\Gamma_{\text{eff}}/\Gamma_0\approx0.93$ for dilute $J=1$ systems, and $\Gamma_{\text{eff}}/\Gamma_0\approx0.88$ when $kT\gg\Gamma_0$, the results being about the same for both H_2 and D_2. The concentration dependence of $\Gamma_{\text{eff}}/\Gamma_0$ is due to the concentration dependence of the dynamical phonon renormalization. At low concentration this reflects the presence of strains around clusters of $J=1$ molecules which tends to increase Γ_{eff}. At high concentration one has a reduction in Γ_{eff} because strains are forbidden by symmetry for $x=1$ and then interactions mixing phonons and librons become important. These mechanisms seem to be verified by the experimentally observed concentration dependence of Γ_{eff}. From the concentration-independent discrepancy between theoretical and experimental values of $\Gamma_{\text{eff}}/\Gamma_0$ we infer that a more sophisticated treatment of the static phonon renormalization is needed, from which presumably larger reductions in Γ_{eff} would be found. This supposition is supported by the fact that also the observed renormalization of the nuclear spin-spin interactions is more severe than we predict. Further evidence that our renormalized potentials are qualitatively correct comes from NMR T_2 data. There use of unrenormalized potentials leads to a very much larger interaction between molecules than is indicated by the rotational correlation times implied by T_2 at very low $J=1$ concentration in H_2. As is apparent, we have a reasonable understanding of the orientational interactions and their interactions with phonons. It will be interesting to see whether more sophisticated phonon calculations lead to a better agreement between experimental and theoretical values of Γ_{eff}.

ACKNOWLEDGMENTS

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