

Renormalized interactions in solid hydrogen and analysis of the ortho-pair level structure¹

S. LURYI AND J. VAN KRANENDONK

Department of Physics, University of Toronto, Toronto, Ont., Canada M5S 1A7

Received September 22, 1978

The orientational level structure of o-H₂ pairs in a solid p-H₂ matrix is studied theoretically, with particular attention paid to the phonon renormalization of the anisotropic interactions. For the two- and three-body multipolar and induction forces, this renormalization is performed analytically and the results are expressed in terms of a small number of lattice dynamical parameters describing the shape of the anisotropic distribution function, $g(\mathbf{u}_{12})$, of the relative zero-point displacement of a pair of molecules. A microscopic calculation of these parameters has revealed that the difficulties remaining in the theoretical analysis carried out by Harris, Berlinsky, and Hardy of the microwave spectra observed by Hardy, Berlinsky, and Harris stem from an incorrect parametrization of the deviations of $g(\mathbf{u}_{12})$ from cylindrical symmetry. Using our renormalization results, as well as a more convenient symmetry classification of the effective interactions in the solid, we arrive at an analysis of the microwave spectra which appears to be free of difficulties. From this analysis we obtain the following values of the effective anisotropic interaction constants in solid H₂ at normal pressure: the quadrupolar coupling constant $\tilde{\Gamma}_0 = 0.596 \text{ cm}^{-1}$, and the van der Waals coupling constants $\tilde{\epsilon}_0 = -0.013 \text{ cm}^{-1}$, $\tilde{\epsilon}_2 = 0.011 \text{ cm}^{-1}$, and $\tilde{\epsilon}_4 = -0.018 \text{ cm}^{-1}$.

On étudie théoriquement la structure orientationnelle les niveaux de paires o-H₂ dans une matrice de p-H₂ solide, en prêtant une attention particulière à la renormalisation des phonons des interactions anisotropes. Pour les forces multipolaires, à deux ou à trois corps, et pour les forces d'induction, cette renormalisation est faite analytiquement, et les résultats sont exprimés en terme d'un petit nombre de paramètres dynamiques du réseau qui décrivent la forme de la fonction anisotrope de distribution, $g(\mathbf{u}_{12})$, du déplacement relatif d'une paire de molécules. Un calcul microscopique de ces paramètres a révélé que les difficultés qui restent dans l'analyse théorique effectuée par Harris, Berlinsky et Hardy des spectres de micro-ondes observés par Hardy, Berlinsky et Harris proviennent d'une paramétrisation incorrecte des déviations de $g(\mathbf{u}_{12})$ de la symétrie cylindrique. En utilisant nos résultats de renormalisation de même qu'une classification plus commode des symétries des interactions effectives dans le solide, nous arrivons à une analyse des spectres de micro-ondes qui ne semble pas présenter de difficultés. À partir de cette analyse, nous obtenons les valeurs suivantes pour les constantes d'interaction anisotrope effective dans H₂ solide à pression normale: la constante de couplage quadrupolaire $\tilde{\Gamma}_0 = 0.596 \text{ cm}^{-1}$, et les constantes de couplage van der Waals $\tilde{\epsilon}_0 = -0.013 \text{ cm}^{-1}$, $\tilde{\epsilon}_2 = 0.011 \text{ cm}^{-1}$, $\tilde{\epsilon}_4 = -0.018 \text{ cm}^{-1}$.

Can. J. Phys., 57, 307 (1979)

[Traduit par le journal]

1. Introduction

The rotational level structure of pairs of nearest-neighbouring ortho molecules in a solid parahydrogen matrix has attracted considerable experimental investigation. This structure has been studied by nmr and specific heat techniques, and more directly by near infrared, neutron, and Raman scattering,

and microwave absorption experiments. References to these various experiments can be found in refs. 1 and 2. The microwave spectra of ortho pairs were first obtained by Hardy and Berlinsky (1), and then by Hardy, Berlinsky, and Harris (2). These experiments had far greater accuracy than all previous determinations of the pair spectra, and the relative positions of nearly all the pair levels were established to an accuracy on the order of 10^{-3} cm^{-1} . These results present a challenge since their interpretation

¹Supported by a grant from the National Research Council of Canada.

requires the introduction of the finer details of the anisotropic intermolecular interaction and of the interaction of the pair with the surrounding matrix.

The theory of the anisotropic interactions in solid hydrogen existing in 1975 was summarized by Harris (3). According to this theory, the general anisotropic interaction between a pair of ortho molecules in solid parahydrogen contains two types of terms: those which are invariant under simultaneous rotations of the two ortho molecules about the pair axis (axially symmetric terms) and those not invariant under such rotations. The most general interaction between two isolated hydrogen molecules belongs to the first category. In the presence of only the axially symmetric interaction, the nine-fold degenerate rotational level of two $J = 1$ ortho molecules splits into six levels of which three are doubly degenerate. This remaining degeneracy is removed by terms in the interaction of the second type, called "doublet-splitting" terms. The origin of these terms lies necessarily in the interaction with degrees of freedom other than the orientations of the two ortho molecules.

Two types of doublet-splitting terms were considered in ref. 3, the crystalline field and the three-body polarization interactions. The former were treated phenomenologically and include all the anisotropic interactions depending on the orientation of only one of the two molecules. The latter include the orientational polarizability effects as well as the dielectric screening effects which were also considered in ref. 4. Hardy and Berlinsky (1) attempted to interpret the microwave spectra on the basis of this theory but concluded that the theory was incomplete. The main difficulty concerned the fitting of the observed doublet splittings, and agreement with experiment could be obtained only by assigning a negative value to the static polarizability of the molecules. This difficulty was resolved in refs. 5 and 6 by introducing the doublet splitting interaction arising from the anisotropic renormalization of the EQQ interaction by the zero-point lattice vibrations. The magnitude of this effect is proportional to the non-axiality parameter, η , (cf. [56]), of the anisotropic distribution function of the relative displacements of the two interacting molecules. In ref. 5 this parameter was introduced phenomenologically and its values for in-plane (ip) and out-of-plane (op) pairs were obtained by fitting the microwave spectra reported in ref. 1. However, this fit required rather large values of the crystalline field parameters V_c and ΔB describing the effects of the local distortion of the lattice due to ortho impurities (7). This approach was criticized by Harris and Berlinsky (8), who compared the work (5) with the much more extensive analysis

of the pair level structure given in ref. 6. The latter work is superior to ref. 5 in that in addition to the η -effect it includes several other new effects such as the quadrupole-induced strain (mainly axial terms), admixtures of the $J = 3$ states of the ortho molecules by the EQQ interaction (axial), and the higher order polarization interactions which give a small doublet-splitting contribution. Nevertheless, the theory (6) is not entirely successful in that it fails to explain the observed splitting of the $F = 1$, $M = \pm 1$ doublet, where F , M refer to the total angular momentum of the ortho pair. As pointed out by Harris and Berlinsky (8), this is the main remaining problem in the interpretation of the microwave spectra whose resolution is unlikely to be found in a more exact treatment of the strain effects.

In our opinion, this problem arises in ref. 6 from an incorrect parametrization of the η -effect. According to ref. 6, the main contribution to η comes from the anisotropy in the immediate crystalline environment of the pairs, which is less axially symmetric for op than for ip pairs. This led the authors of refs. 2 and 6, henceforth referred to as HBH, to postulate that

$$[1] \quad \eta(\text{op})/\eta(\text{ip}) = 4$$

A discussion of the validity of [1] can be found in ref. 9. The main point is that another contribution to η exists, arising from the anisotropy of the phonon field associated with the uniaxial symmetry of the hcp lattice, which gives a larger contribution to $\eta(\text{ip})$ than to $\eta(\text{op})$. In ref. 9 we have calculated these contributions on the basis of a generalized Debye model in which the dependence of the phonon frequencies and polarization vectors on the direction of propagation is taken into account. In contrast to [1], these contributions have the ratio

$$[2] \quad \eta(\text{op})/\eta(\text{ip}) = -0.8$$

The theoretical values of η obtained in ref. 9 turn out to be in good agreement with the values required to describe the doublet splittings, as will be discussed in the present paper.

Another important feature of the present work is a unified treatment of the various phonon renormalization effects. Our treatment is based on the relation

$$[3] \quad 1 - \xi_{l,l-1} = \text{constant} \times l(l+1)$$

between the reduction factors, $\xi_{l,l-1}$, of the different multipolar interactions, (10, 11). The relation [3] can be derived by tensor algebra on the assumption that the distribution function of the relative displacements of two molecules in the solid is independent of

their angular momenta. This allows us to parameterize the phonon renormalizations of all the two- and three-body interactions whose dependence on the position variables of the interacting molecules is known accurately, by using only two lattice-dynamical parameters. These parameters are $\langle \mathbf{u}_{12} \cdot \mathbf{u}_{12} \rangle / R_0^2$ and ζ , cf. [77], [55], describing, respectively, the mean radius and eccentricity of the oblate ellipsoid associated with the pair correlation matrix, cf. ref. 9. We also correct an error appearing in ref. 6 in the renormalization of the second-order EQQ interaction between the two ortho molecules (the Γ^2/B terms). In ref. 6 it is assumed that this renormalization is given by the factor

$$[4] \quad f = (4\pi/9)R_0^{10} \langle [Y_{40}(\hat{\mathbf{R}}_{12})/R_{12}^5]^2 \rangle$$

which augments the interaction constants by about 30%. The correct renormalization factors, calculated in this paper, are different for the different two-body terms and lead to increases varying from 50 to 70%.

Finally we remark that we do not attempt here to include via a microscopic theory the strain effects, or in the terminology of ref. 7, the quasi-static distortion effects, which were discussed in ref. 8. Agreeing in principle that these effects contribute to all the different symmetry terms in the effective Hamiltonian, we feel that the inclusion of these effects, other than the EQQ-induced strain, at this stage requires the introduction of too many adjustable parameters. This situation will, of course, change once a reliable theory has been developed of the quasi-static distortion effect for ortho pairs.

The organization of this paper is as follows. In Sect. 2 we give the symmetry classification of the effective, anisotropic Hamiltonian in the manifold of rotational states of an ortho pair. This classification is different and, in our view, more convenient than that given in ref. 6. Each term in the effective Hamiltonian is a tensor operator irreducible under simultaneous rotations of the two ortho molecules. The products of such operators can be expanded in a Clebsch-Gordan series with coefficients given by an expression [36] involving no summations over the magnetic quantum numbers (12). In Sect. 3 we review the various contributions to the effective Hamiltonian in the rigid lattice. The renormalization of these interactions by the zero-point lattice vibrational motion is considered in Sect. 4. In Sect. 5 we use the theory to interpret the microwave absorption spectra (2), and to derive empirical values of certain parameters characterizing the anisotropic interactions in the solid. The paper concludes with a discussion of the results obtained here and a comparison with the work of HBH.

2. Symmetry Properties of the Effective Hamiltonian for a Pair of Ortho Molecules in Solid Parahydrogen

In the single-particle manifold, F , corresponding to a given value of the angular momentum, $\mathbf{J}^2 = F(F+1)$, the operators $|FM\rangle\langle FM'|$, $M, M' = F, F-1, \dots, -F$, form a complete set in the sense that any linear operator in F can be expressed as a linear combination of these operators. A set of linear combinations of the operators $|FM\rangle\langle FM'|$ with unitary coefficients also forms a complete set. For our purpose, a particularly convenient set is the one transforming irreducibly under rotations, obtained by using the Clebsch-Gordan coefficients and defined as

$$[5] \quad \hat{C}_{lm}(F) = \sum_{MM'} |FM\rangle C(FIF; M'mM) \langle FM'|$$

The operators [5] are defined in the full Hilbert space of the system but have non-vanishing matrix elements only within F , where they can be represented by explicit expressions in terms of the components of the angular momentum operator, \mathbf{J} . These so-called equivalent operators (13) will not be used here, because we need only the transformation properties of the operators [5]. For $F=1$, the operators [5] are proportional to the \mathcal{T}_l^m introduced in ref. 6,

$$[6] \quad \begin{aligned} \hat{C}_{2m} &= (8\pi/25)^{1/2} \mathcal{T}_2^m \\ \hat{C}_{1m} &= (2\pi/3)^{1/2} \mathcal{T}_1^m \\ \hat{C}_{00} &= \hat{1} = (4\pi)^{1/2} \mathcal{T}_0^0 \end{aligned}$$

In the two-particle manifold $F_1 \otimes F_2$, we choose as a complete set of operators the composite tensors

$$[7] \quad \begin{aligned} \hat{T}_{lm}^{(l_1 l_2)}(F_1, F_2) \\ = \sum_{m_1 m_2} C(l_1 l_2 l; m_1 m_2 m) \hat{C}_{l_1 m_1}(F_1) \hat{C}_{l_2 m_2}(F_2) \end{aligned}$$

which transform irreducibly under rotations generated by $\mathbf{J}_1 + \mathbf{J}_2$. Their reduced matrix elements in $F_1 \otimes F_2$ are given by (ref. 14, p. 152),

$$[8] \quad \begin{aligned} \langle F_1 F_2 F' | \hat{T}_{l_1 l_2}^{(l_1 l_2)} | F_1 F_2 F \rangle \\ = \Pi(F_1 F_2 F l) \begin{Bmatrix} F' & F & l \\ F_1 & F_2 & l_1 \\ F_1 & F_2 & l_2 \end{Bmatrix} \end{aligned}$$

where

$$[9] \quad \Pi(ab \dots) = [(2a+1)(2b+1) \dots]^{1/2}$$

and

$$[10] \quad \begin{aligned} |F_1 F_2 FM\rangle \\ = \sum_{M_1 M_2} C(F_1 F_2 F; M_1 M_2 M) |F_1 M_1\rangle |F_2 M_2\rangle \end{aligned}$$

The most general effective Hamiltonian in the manifold $(F_1 = 1) \otimes (F_2 = 1)$ of two ortho molecules in solid parahydrogen can be expressed in terms of the operators

$$\hat{T}_{lm}^{(l_1 l_2)}(1, 1) \equiv \hat{T}_{lm}^{(l_1 l_2)}$$

in the form

$$[11] \quad H = \sum_{lm} \sum_{l_1 l_2} H_{lm}^{(l_1 l_2)*} \hat{T}_{lm}^{(l_1 l_2)}$$

The coefficients $H_{lm}^{(l_1 l_2)}$ satisfy the following symmetry conditions (6). From the hermiticity of \hat{H} it follows that

$$[12] \quad H_{lm}^{(l_1 l_2)*} = (-)^{l_1 + l_2 + l + m} H_{lm}^{(l_1 l_2)}$$

whereas time reversal requires that terms with odd values of $l_1 + l_2$ drop out, assuming that velocity dependent interactions are absent,

$$[13] \quad H_{lm}^{(l_1 l_2)} = (-)^{l_1 + l_2} H_{lm}^{(l_1 l_2)}$$

Further restrictions arise from the symmetry properties of the lattice which is hcp (15). In the presence of ortho impurities, the anisotropic interactions distort the equilibrium configuration of the molecules, so that the lattice loses its periodicity. This would lead to the appearance of terms in [1] with no particular symmetry other than [12] and [13]. We treat these terms as corrections to the undistorted lattice in a phenomenological way.

To take advantage of the symmetry of the undistorted hcp lattice with two neighbouring ortho impurities, we define, following ref. 3, a local coordinate frame for each pair in such a way that both ortho molecules lie on the local z axis and the local xz plane is a plane of reflection symmetry. For the precise definition of the local frames, see refs. 3 and 9. The local frames used in HBH are slightly different. The conditions imposed on $H_{lm}^{(l_1 l_2)}$ by symmetry assume their simplest form in the appropriate local frame. First, the frames have been chosen such that

$$[14] \quad H_{lm}^{(l_1 l_2)} = H_{lm}^{(l_1 l_2)*}$$

is real. Next, for ip pairs the plane $\hat{z} \cdot \mathbf{R} = \frac{1}{2}$ is a reflection plane, giving

$$[15] \quad H_{lm}^{(l_1 l_2)}(\text{ip}) = (-)^{l+m} H_{lm}^{(l_1 l_2)}(\text{ip})$$

For op pairs, the midpoint between the two molecules is a centre of inversion symmetry,

$$[16] \quad H_{lm}^{(l_1 l_2)}(\text{op}) = (-)^l H_{lm}^{(l_1 l_2)}(\text{op})$$

There are no other symmetry elements in a hcp lattice with two neighbouring impurities. However, certain additional restrictions arise for those terms in [11] which depend on the variables of only one of

the ortho molecules ($l_1 = 0$ or $l_2 = 0$) when one considers the interactions common to ortho-ortho and ortho-para pairs. One can then use the full point symmetry of the hcp lattice and show that this contribution, ΔH , is symmetric about the c axis,

$$[17] \quad \Delta H_{2m}^{(02)} = \Delta H_{2m}^{(20)} = \delta_{m0} \Delta H_{20}^{(20)}$$

where m refers to the c axis. If the coefficient $\Delta H_{20}^{(20)}$ results from additive, pairwise interactions, it nearly vanishes in a close-packed lattice,

$$[18] \quad \Delta H_{20}^{(20)} = \sum_{j \neq 1} f(\mathbf{R}_{1j}) \cong 0$$

as first noted by Nakamura (16), cf. also ref. 9.

The symmetry conditions [12]–[17] leave 17 independent parameters in [11] for each type of pair corresponding to the coefficients $H_{lm}^{(l_1 l_2)}$ with the following values of $(l_1 l_2)$, where m refers to the respective pair frame,

$$[19] \quad \begin{pmatrix} 22 \\ 40 \end{pmatrix}, \begin{pmatrix} 22 \\ 20 \end{pmatrix}, \begin{pmatrix} 22 \\ 00 \end{pmatrix}, \begin{pmatrix} 20 \\ 20 \end{pmatrix}, \begin{pmatrix} 11 \\ 20 \end{pmatrix}, \begin{pmatrix} 11 \\ 00 \end{pmatrix}, \begin{pmatrix} 00 \\ 00 \end{pmatrix}$$

and

$$[20] \quad \begin{pmatrix} 22 \\ 44 \end{pmatrix}, \begin{pmatrix} 22 \\ 42 \end{pmatrix}, \begin{pmatrix} 22 \\ 22 \end{pmatrix}, \begin{pmatrix} 20 \\ 22 \end{pmatrix}, \begin{pmatrix} 11 \\ 22 \end{pmatrix}$$

for both types of pair, and

$$[21a] \quad \begin{pmatrix} 22 \\ 31 \end{pmatrix}, \begin{pmatrix} 22 \\ 33 \end{pmatrix}, \begin{pmatrix} 22 \\ 11 \end{pmatrix}, \begin{pmatrix} 20 \\ 11 \end{pmatrix}, \begin{pmatrix} 11 \\ 11 \end{pmatrix}, \quad \text{ip}$$

$$[21b] \quad \begin{pmatrix} 22 \\ 43 \end{pmatrix}, \begin{pmatrix} 22 \\ 41 \end{pmatrix}, \begin{pmatrix} 22 \\ 21 \end{pmatrix}, \begin{pmatrix} 20 \\ 21 \end{pmatrix}, \begin{pmatrix} 11 \\ 21 \end{pmatrix}, \quad \text{op}$$

A number of these parameters are eliminated by the perturbation scheme used (6) in the calculation of the ortho-pair states, which we also adopt. The axially symmetric interactions [19], of which the EQQ one is the most important term (16), are assumed to dominate over the interactions of the types [20] and [21]. The axial interactions split the nine-fold degenerate ortho-pair level into six levels three of which are doublets, cf. Fig. 1. The remaining interactions are included only to zeroth order, i.e., only within the remaining doublets. The only non-vanishing contributions come from the 'doublet-splitting' terms [20], and all the terms [21] which are neither axial nor doublet-splitting may be neglected.

3. Interactions in the Rigid Lattice

The interaction energy between two isolated H_2 molecules can be written in the form

$$[22] \quad V(\omega_1, \omega_2; \mathbf{R}_{12}) = \sum_{lm} \sum_{l_1 l_2} V_{lm}^{(l_1 l_2)*}(\mathbf{R}_{12}) T_{lm}^{(l_1 l_2)}(\omega_1, \omega_2)$$

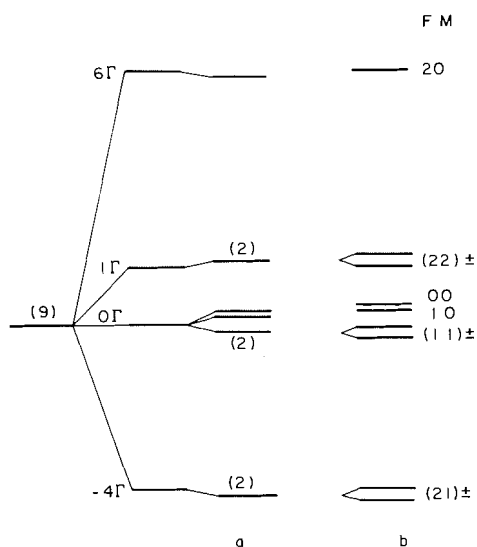


FIG. 1. Energy-level diagram for an ortho pair in solid hydrogen. (a) Including only the axial terms [19]. (b) Including the doublet-splitting terms [20]. The states $|FM\rangle$ are labelled by the eigenvalues of the total angular momentum of the pair, cf. eq. [10], and $\sqrt{2}|FM\rangle_{\pm} = |FM\rangle \pm |F\bar{M}\rangle$. The far left column represents the structure which results from including only the first order EQQ interaction.

where ω_1, ω_2 specify the orientations of the two molecules relative to a space-fixed frame, $\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1$, and

$$[23] \quad T_{lm}^{(l_1 l_2)}(\omega_1, \omega_2) = \sum_{m_1 m_2} C(l_1 l_2 l; m_1 m_2 m) C_{l_1 m_1}(\omega_1) C_{l_2 m_2}(\omega_2)$$

are the bipolar harmonics (14), which should be distinguished from the corresponding operators [7] in the $F_1 \otimes F_2$ manifold. The sum in [22] is restricted to even values of l_1, l_2 , and l . In the solid at normal densities, the anisotropic part of [22] is small compared to the spacing of the rotational levels of an H_2

molecule, and the effect of the interaction [22] on the states in the rotational manifold $F_1 \otimes F_2$ can therefore be treated by perturbation theory. The unperturbed Hamiltonian is

$$[24] \quad H_0 = B(J_1^2 + J_2^2)$$

To second order in the interaction [22], the perturbed energy levels belonging to the manifold $F_1 \otimes F_2$ are given by the eigenvalues of an effective Hamiltonian (17) which operates entirely within this manifold but which receives contributions from other manifolds. This Hamiltonian is of the form

$$[25] \quad \hat{H} = \hat{V}^{(1)} + \hat{V}^{(2)}$$

where

$$[26] \quad \hat{V}^{(1)} = P_{F_1} P_{F_2} V P_{F_1} P_{F_2}$$

$$[27] \quad \hat{V}^{(2)} = - \sum_{J_1 J_2} P_{F_1} P_{F_2} V P_{J_1} P_{J_2} V P_{F_1} P_{F_2} / \Delta E(J_1 J_2)$$

and

$$[28] \quad \Delta E(J_1 J_2) = B[J_1(J_1 + 1) + J_2(J_2 + 1) - F_1(F_1 + 1) - F_2(F_2 + 1)]$$

The interactions contributing to the anisotropic part of [22] include, besides the EQQ interaction, the valence, dispersion, and induction forces (18). Following HBH, we neglect the contributions of the non-EQQ interactions to the second-order term [27]. The effect of the non-EQQ interactions on the ortho-pair levels ($F_1 = F_2 = 1$) can then be described by a relatively small number of parameters, viz.,

$$[29] \quad \begin{aligned} V_{20}^{(20)}(R) &\equiv 2B(R) \\ V_{10}^{(22)}(R) &\equiv 5\alpha_1^{(22)}\epsilon_l(R) \end{aligned}$$

where $l = 0, 2, 4$ and

$$[30] \quad \begin{aligned} \alpha_0^{(22)} &= 5^{1/2}, & \alpha_2^{(22)} &= (7/2)^{1/2}, & \alpha_4^{(22)} &= 70^{1/2} \\ \alpha_0^{(11)} &= 3^{1/2}, & \alpha_2^{(11)} &= (3/2)^{1/2} \\ \alpha_0^{(20)} &= \alpha_0^{(02)} = -(2/5)^{1/2}, & \alpha_0^{(00)} &= 1 \end{aligned}$$

The most recent ab initio estimates of the parameters [29] are those of Raich *et al.* (19). The values they recommend at the nearest-neighbour separation (which they take to be $R_0' = 3.756 \text{ \AA}$) are given in Table 1. These estimates should be regarded as rather crude because of the large uncertainty in the calculation of the valence forces. The EQQ contribution to [22], which corresponds to $l_1 = l_2 = 2, l = 4$, is known very accurately. The fact that EQQ contributes only to $l = l_1 + l_2$ is characteristic for multipole interaction (20). With respect to an arbitrary frame, the EQQ interaction can be written in the form

$$[31] \quad V_{\text{EQQ}}(\omega_1, \omega_2; \mathbf{R}_{12}) = (25/6)\alpha_4^{(22)}\Gamma_0(R_0/R_{12})^5 \sum_m C_{4m}^*(\hat{\mathbf{R}}_{12})T_{4m}^{(22)}(\omega_1, \omega_2)$$

where $\Gamma_0 = (6e^2 Q^2 / 25R_0^5)$. For $v = 0, J = 1$ we have (21) $\langle 01|Q|01\rangle = 0.48529 \text{ au}$, and choosing R_0

$= 3.784 \text{ \AA}^2$ we get

$$[32] \quad \Gamma_0 = 0.6634 \text{ cm}^{-1}$$

and this is the value we will use.

The first-order part, $\hat{V}^{(1)}$, of the effective interaction between two $J = 1$ molecules is obtained from [22] by restricting the sum to $l_1, l_2 \leq 2$ and replacing the bipolar harmonics by the operators [7] using

$$[33] \quad P_{F_1} P_{F_2} T_{lm}^{(l_1 l_2)}(\omega_1, \omega_2) P_{F_1} P_{F_2} = C(F_1 l_1 F_1; 00) C(F_2 l_2 F_2; 00) \hat{T}_{lm}^{(l_1 l_2)}(F_1, F_2)$$

For $l_1 = l_2 = 2$ we obtain in this way

$$[34] \quad \hat{V}^{(1)} = \sum_{lm} A_{lm}^{(22)} \hat{T}_{lm}^{(22)}$$

where with respect to the pair frame

$$[35] \quad A_{lm}^{(22)} = 2\alpha_l^{(22)} [(5/6)\Gamma_0 \delta_{l4} + \epsilon_l] \delta_{m0}$$

The terms $l_1 = 2, l_2 = 0$ and $l_1 = 0, l_2 = 2$ will be considered separately, cf. [42].

To calculate the second-order contribution [27] due to the EQQ interaction, it is convenient to use the following expression (12) for the product of tensor operators with matrix elements restricted to parts of Hilbert space,

$$[36] \quad P_{F_1} P_{F_2} T_{kn}^{(k_1 k_2)}(\omega_1, \omega_2) P_{J_1} P_{J_2} T_{k'n'}^{(k'_1 k'_2)}(\omega_1, \omega_2) P_{F_1} P_{F_2} = X \sum_{lm} \sum_{l_1 l_2} \beta_{lm}^{(l_1 l_2)} \hat{T}_{lm}^{(l_1 l_2)}(F_1, F_2) C(kk'l; nn'm)$$

where

$$[37] \quad X = C(J_1 k_1 F_1; 00) C(J_2 k_2 F_2; 00) C(F_1 k_1' J_1; 00) C(F_2 k_2' J_2; 00) \Pi(J_1 J_2 k k')$$

and

$$[38] \quad \beta_{lm}^{(l_1 l_2)} = (-)^{l_1 + l_2} (2l_1 + 1)(2l_2 + 1) \begin{Bmatrix} k_1 k_1' l_1 \\ F_1 F_2 J_1 \end{Bmatrix} \begin{Bmatrix} k_2 k_2' l_2 \\ F_1 F_2 J_2 \end{Bmatrix} \begin{Bmatrix} k k' l \\ k_1 k_1' l_1 \\ k_2 k_2' l_2 \end{Bmatrix}$$

With the help of [36]-[38], we can express $\hat{V}_{\text{EQQ}}^{(2)} = \hat{V}^{(2)}$ in the form [11], viz.,

$$[39] \quad \hat{V}^{(2)} = \sum_{lm} \sum_{l_1 l_2} B_{lm}^{(l_1 l_2)} * \hat{T}_{lm}^{(l_1 l_2)}$$

where with respect to the pair frame we have

$$[40] \quad B_{lm}^{(l_1 l_2)} = \frac{13125}{4} \delta_{m0} (\Gamma_0^2 / B) [b_{l_1 l_2}^{(l_1 l_2)}(1, 3) + b_{l_1 l_2}^{(l_1 l_2)}(3, 1) + \frac{1}{2} b_{l_1 l_2}^{(l_1 l_2)}(3, 3)]$$

with

$$[41] \quad b_{l_1 l_2}^{(l_1 l_2)}(J_1, J_2) = (2l_1 + 1)(2l_2 + 1) C(44l; 00) [C(12J_1; 00) C(12J_2; 00)]^2 \begin{Bmatrix} 22l_1 \\ 11J_1 \end{Bmatrix} \begin{Bmatrix} 22l_2 \\ 11J_2 \end{Bmatrix} \begin{Bmatrix} 44l \\ 22l_1 \\ 22l_2 \end{Bmatrix}$$

Strictly speaking, the coefficients multiplying the three terms in [40] are Γ_0^2 , $\Gamma_0 \Gamma_0'$, and $\Gamma_0'^2$, where Γ_0' contains the quadrupole matrix element $\langle 01|Q|03 \rangle = 0.48790 \text{ au}$ (21), giving $\Gamma_0' = 0.6706 \text{ cm}^{-1}$ rather than [32], but we shall use the simplified form [40]. The resulting numerical values of the coefficients [40] are given in Table 2. These results are in agreement with those of HBH except that the top line in the right column of Table 5 in ref. 6 should read $-(837/6860)$ instead of $-(71145/514514)$.

The remaining contributions to the effective Hamiltonian [11] in the rigid lattice include the crystalline field, dielectric screening, and rotational polarization terms. These terms are discussed in detail in ref. 3, and we confine ourselves here to listing the resulting contributions to the parameters $H_{lm}^{(l_1 l_2)}$ of [11].

²R. L. Mills, private communication. This value has recently been confirmed by measurements of I. F. Silvera who obtains $R_0 = 3.788 \text{ \AA}$ (private communication).

The crystalline field contribution in the pair frame is of the form

$$[42] \quad C_{lm}^{(20)} = \alpha_2^{(20)} \left[-\frac{3}{5} V_c C_{2m}(\beta, \alpha) + 2\Delta B \delta_{m0} \right]$$

where β, α are the polar angles of the local z axis relative to the crystal frame. If the latter is chosen as in ref. 9, we have $(\beta, \alpha) = (\frac{1}{2}\pi, \frac{1}{2}\pi)$ for ip pairs, and $(\beta, \alpha) = (\beta_0, 0)$ for op pairs, where $\cos^2 \beta_0 = \frac{2}{3}$. The notations V_c and ΔB are in accordance with ref. 3. Both contributions are expected to be quite small in the rigid lattice, V_c being proportional to the deviation of c/a from the close-packed value, and ΔB to a difference between the coefficients $B(R)$ defined in [29] for ortho-ortho and ortho-para interactions (3).

The dielectric screening (3, 4) results from the quadrupole-induced dipole forces and its contribution is of the form

$$[43] \quad D_{lm}^{(22)} = 175(\Gamma_0 \rho) \left\{ \begin{matrix} 33l \\ 221 \end{matrix} \right\} \sum_{p \neq 1,2} (R_0/R_{1p})^4 (R_0/R_{2p})^4 T_{lm}^{(33)}(\hat{R}_{1p}, \hat{R}_{2p})$$

where $\rho = \alpha/R_0^3$, α being the isotropic H_2 polarizability (Table 1), and the sum extends over all para molecules. The dependence of α on the angular momentum of the molecule (22) leads to a small contribution to the crystalline field term ΔB , and the anisotropic part of the polarizability tensor contributes to the coefficients ϵ_l . However, the magnitude of these two corrections is well within the present uncertainty in these parameters, and these effects will therefore be neglected.

The orientational polarization terms (3) give the contributions

$$[44] \quad E_{lm}^{(22)} = -\frac{875}{3} \frac{\Gamma_0^2}{B} \left\{ \begin{matrix} 44l \\ 222 \end{matrix} \right\} \sum_{p \neq 1,2} (R_0/R_{1p})^5 (R_0/R_{2p})^5 T_{lm}^{(44)}(\hat{R}_{1p}, \hat{R}_{2p})$$

and

$$[45] \quad E_{2m}^{(20)} = -\alpha_2^{(20)} \frac{40625}{6048} \frac{\Gamma_0^2}{B} \sum_{p \neq 1,2} (R_0/R_{1p})^{10} C_{2m}(\hat{R}_{1p})$$

This last term is of the crystalline field type. In a perfect hcp lattice the sum in [45] evaluated in the pair frame gives $-\delta_{m0}$, so that

$$[46] \quad E_{2m}^{(20)} = \frac{40625}{6048} \frac{\Gamma_0^2}{B} \alpha_2^{(20)} \delta_{m0}$$

A similar term is contained in [40]. The resulting non-vanishing value of $E_{20}^{(20)} + B_{20}^{(20)}$ corresponds

TABLE 1. Various characteristics of solid parahydrogen at zero pressure

Equation	Symbol	Value and units	Reference
[24]	B	59.339 cm^{-1}	31
[31]	Q	0.48529 au	21
[29]	$\epsilon_0(R_0)$	-0.002 cm^{-1}	19
[29]	$\epsilon_2(R_0)$	-0.027 cm^{-1}	19
[29]	$\epsilon_4(R_0)$	-0.016 cm^{-1}	19
[29]	$B(R_0)$	-0.310 cm^{-1}	19
[31]	R_0	3.784 Å	^a
[43]	α	5.4138 au	22
[98]	$\langle u^2 \rangle$	0.48 Å ²	25
[31]	Γ_0	19.888 GHz	This work
[40]	Γ_0^2/B	0.222 GHz	This work
[43]	$\Gamma_0 \rho$	0.294 GHz	This work
[97], [102]	$A(1)/2R_0^2$	4.8×10^{-3}	This work
[97], [107]	$A(2)/2R_0^2$	5.6×10^{-3}	This work
[113]	g	8.5×10^{-4}	This work

^aR. L. Mills, private communication.

physically (5) to the difference between the orientational polarizabilities of para and ortho molecules ($J = 0 \rightarrow 2$ vs. $J = 1 \rightarrow 3$).

The lattice sums in [43] and [44] were evaluated

TABLE 2. Numerical values of the coefficients $B_{lm}^{(l_1 l_2)}$, eq. [40], and $G_{lm}^{(l_1 l_2)}$, eq. [112]. Tabulated are the values $[B_{l_0}^{(l_1 l_2)}/\alpha^{(l_1 l_2)}]$ in units of Γ_0^2/B and $[G_{l_0}^{(l_1 l_2)}/\alpha^{(l_1 l_2)}]$ in units of g

$l_1 l_2$ lm	B/α	G/α
22	$-\frac{279}{1372}$	-25
40	$-\frac{775}{2058}$	$-\frac{500}{9}$
22	$-\frac{31}{84}$	$-\frac{175}{3}$
00	$-\frac{25}{8}$	$-\frac{1750}{9}$
11	$-\frac{5}{2}$	$-\frac{700}{3}$
20	$-\frac{7}{4}$	175
00	$-\frac{77}{24}$	$-\frac{350}{3}$

TABLE 3. Numerical values of the coefficients $D_{lm}^{(22)}(s)$ (in units of $\Gamma_0\rho$) and $E_{lm}^{(22)}(s)$ (in units of Γ_0^2/B) characterising the three-body interactions, eqs. [43] and [44]. The contributions of the first ($s = 1$), the second ($s = 2$), and the residual ($s = r$) shells are tabulated separately with respect to the pair frame for each type of pair

lm	In-plane pairs			Out-of-plane pairs		
	$D(1)$	$D(2)$	$D(r)$	$D(1)$	$D(2)$	$D(r)$
00	19.566	-2.648	-1.832	19.566	-2.587	-1.846
20	-21.715	-5.963	-1.398	-21.715	-6.015	-1.371
22	-2.592	1.193	-0.048	-7.774	3.216	-0.066
40	-13.353	1.397	-0.161	13.353	1.334	-0.145
42	0.098	-0.189	0.038	0.295	-0.373	0.020
44	6.380	-0.769	-0.014	-8.203	1.152	0.014

lm	In-plane pairs			Out-of-plane pairs		
	$E(1)$	$E(2)$	$E(r)$	$E(1)$	$E(2)$	$E(r)$
00	16.758	3.083	-0.132	16.758	3.145	-0.150
20	-5.607	-5.462	-0.627	-5.607	-5.478	-0.612
22	-1.815	1.310	-0.055	-5.446	3.510	-0.088
40	-12.042	0.161	-0.075	-12.042	0.118	-0.066
42	-0.663	0.039	0.007	-1.989	0.178	0.002
44	5.071	-0.887	-0.039	-6.519	1.461	0.004

numerically (cf. the Appendix) and the results are given in Table 3 with respect to the pair frames. Only the independent coefficients are given, the others being deducible with the help of the symmetry relations [12]–[16]. We have tabulated separately the contributions from the four nearest neighbours common to the two ortho molecules (first shell), the remaining 14 nearest neighbours of the pair (second shell), and the net contributions from the more distant neighbours. The reason for separating these contributions is that they suffer different phonon renormalizations, as will be discussed in the next section.

It may be useful to indicate the relationship between the coefficients [43] and the lattice sums $g_{vv'}$ of ref. 3 (or, equivalently, the d_{mn} of ref. 4, which are related to the $g_{vv'}$ by $d_{mn} = (-)^m g_{\bar{v}\bar{v}'}$,

$$[47] \quad D_{lm}^{(22)} = -\frac{5}{64} \Gamma_0 \rho \sum_{vv'} C(22l; vv'm) g_{vv'}$$

Similarly, the $E_{lm}^{(22)}$ of [44] are related to the $h_{vv'}$ of (3) by

$$[48] \quad E_{lm}^{(22)} = -\frac{25}{13824} (\Gamma_0^2/B) \sum_{vv'} C(22l; vv'm) h_{vv'}$$

In ref. 3 only the first-shell contributions to the sums $g_{vv'}$ and $h_{vv'}$ were calculated. At an early stage of this work (5) we had computed these sums taking into account all neighbours, and found that the second and residual shells contribute appreciably, in some cases changing the order of magnitude or the sign of a particular sum. However, when combined in the form of irreducible tensors, the sums usually show a much faster convergence, as is evident from

Table 3. The result is that the first-shell contributions dominate the effects of both the dielectric screening and the rotational polarization on the ortho-pair levels, and that the residual-shell contributions are negligible.

4. Phonon Renormalization of the Intermolecular Interactions

Since we are interested in temperatures ($\lesssim 4$ K) low compared to the Debye temperature ($\gtrsim 100$ K), we may assume that the crystal is at 0 K. The effect of the lattice vibrations on the anisotropic interactions will be taken into account in the usual way by averaging the latter over the zero-point motion keeping the orientations of the molecules constant relative to space-fixed axes. This results in a significant renormalization of all the two- and three-body interactions introduced in Sect. 3. Because of the relatively large uncertainty in the functional dependence of the coefficients in [22] on R_{12} for the non-quadrupolar interactions, we shall not attempt to calculate the renormalization of these interactions from first principles. If the distribution function of the relative displacements of the two interacting molecules is assumed to be symmetric about the intermolecular axis, then the renormalization does not alter the form of the tensorial expansion [22] but only the magnitudes of the parameters [29]. The small anisotropy of the pair distribution function may be neglected for the non-EQQ interactions. We therefore simply replace the coefficients ϵ_l by renormalized coefficients, $\tilde{\epsilon}_l$, and treat the latter as adjustable parameters.

The renormalization of the multipole interactions, on the other hand, can be performed in detail if one

knows the pair distribution function. The renormalization of these interactions is very sensitive to the precise shape of the distribution function, inasmuch as a spherically symmetric distribution leads to no renormalization at all for multipole interactions. Effects associated with the anisotropy of the pair distribution function are considered in Sect. 4A. In Sect. 4B we consider the renormalization of the polarization interactions, such as the second-order effect [39] of the EQQ interaction and the three-body interactions [43] and [44], whose functional dependence on the position variables is known exactly.

In calculating these renormalization effects it is assumed that the lattice vibrations themselves are

not affected by the rotational motion of the molecules. In reality, the anisotropic forces due to the two ortho impurities slightly alter the zero-point motion of the lattice. The elastic energy of the resulting distortion (7) depends on the orientations of the molecules and thus gives rise to an additional effective interaction in the manifold of the ortho-pair states (7, 8). These dynamical effects are discussed in Sect. 4C.

A. Renormalization of the Multipole Interactions

The electrostatic interaction between a 2^{l_1} - and a 2^{l_2} -pole molecular charge distribution can be written in the form (20)

$$[49] \quad V_{l_1 l_2}(\omega_1, \omega_2; \mathbf{R}_{12}) = v_{l_1 l_2}(R_0) \sum_m f_{lm}^*(\mathbf{R}_{12}) T_{lm}^{(l_1 l_2)}(\omega_1, \omega_2)$$

where $l = l_1 + l_2$, $v_{l_1 l_2}(R_0)$ is the coupling constant, and

$$[50] \quad f_{lm}(\mathbf{R}) = (R_0/R)^{l+1} C_{lm}(\hat{\mathbf{R}})$$

The average of [49] over the zero-point lattice motion is of the form

$$[51] \quad \langle V_{l_1 l_2}(\omega_1, \omega_2; \mathbf{R}_{12}) \rangle = \int V_{l_1 l_2}(\omega_1, \omega_2; \mathbf{R}_0 + \mathbf{u}) g(\mathbf{u}) d\mathbf{u}$$

where $\mathbf{u} = \mathbf{u}_2 - \mathbf{u}_1$ is the relative displacement of the two molecules from their equilibrium positions, $\mathbf{R}_{12} = \mathbf{R}_0 + \mathbf{u}$, and $g(\mathbf{u})$ is the probability distribution of \mathbf{u} in the ground state. If $g(\mathbf{u})$ is spherically symmetrical, $g(\mathbf{u}) = g(u)$, we have

$$[52] \quad \langle V_{l_1 l_2}(\omega_1, \omega_2; \mathbf{R}_{12}) \rangle = V_{l_1 l_2}(\omega_1, \omega_2; R_0)$$

as follows from the fact that the average value of a harmonic function over the surface of a sphere is equal to its value at the centre of the sphere.

The renormalization of [49] thus depends on the deviation of $g(\mathbf{u})$ from spherical symmetry. We can express this effect in terms of the moments of $g(\mathbf{u})$ by expanding the function [50] in powers of \mathbf{u} ,

$$[53] \quad f_{lm}(\mathbf{R}_{12}) = f_{lm}(\mathbf{R}_0) + u_\alpha \nabla_\alpha f_{lm}(\mathbf{R}_0) + \frac{1}{2} u_\alpha u_\beta \nabla_\alpha \nabla_\beta f_{lm}(\mathbf{R}_0) + \dots$$

Averaging [53] over $g(\mathbf{u})$, we find up to second order

$$[54] \quad \langle f_{lm}(\mathbf{R}_{12}) \rangle = f_{lm}(\mathbf{R}_0) - \frac{1}{4} \zeta R_0^2 \nabla_z^2 f_{lm}(\mathbf{R}_0) + \frac{1}{4} \eta R_0^2 (\nabla_1^2 + \nabla_1'^2) f_{lm}(\mathbf{R}_0)$$

where

$$[55] \quad \zeta = \langle u_x^2 + u_y^2 - 2u_z^2 \rangle / R_0^2$$

and

$$[56] \quad \eta = \langle u_x^2 - u_y^2 \rangle / R_0^2$$

and where we have used the fact that $\Delta f_{lm} = 0$. The directions x, y, z refer to the principal axes of the quadratic form $\langle u_\alpha u_\beta \rangle$. For ip pairs these axes coincide with the pair frame, as follows from symmetry. For op pairs, the matrix $\langle u_\alpha u_\beta \rangle$ is not exactly diagonal in the pair frame, which leads to terms in the effective interaction [11] with $m = \pm 1$. Our calculations (9), as well as those in ref. 6, show that the non-vanishing off-diagonal element $\langle u_x u_z \rangle$ is small in the pair frame, and we shall neglect it (cf. also the discussion after [21]) by assuming that [54] is valid in the pair frames of ip and op pairs.

Using the gradient formula,

$$[57] \quad R_0 \nabla_\mu f_{lm}(\mathbf{R}) = -[(l+1)(2l+1)]^{1/2} C(l, 1, l+\mu; m\mu) f_{l+1, m+\mu}(\mathbf{R})$$

and the explicit expressions for the $3j$ -symbols (ref. 14, p. 36), we find that in the pair frame

$$[58] \quad \langle f_{lm}(\mathbf{R}_{12}) \rangle = \xi_{l+1, l} \delta_{m0} + \xi_{l+1, l}^{(2)} (\delta_{m2} + \delta_{m\bar{2}})$$

where

$$[59] \quad \xi_{l+1,l} = 1 - \zeta(l+1)(l+2)/4$$

and

$$[60] \quad \xi_{l+1,l}^{(2)} = \eta[(l-1)(l+1)(l+2)]^{1/2}/8$$

The result [58] is a generalization of the well-known quadrupolar reduction factor (10, 11). Since the relative motion of the molecules has smaller amplitude in the direction of their separation than in the transverse direction, we have generally $\zeta > 0$, and all multipole interactions are reduced by the zero-point lattice motion. The oblateness parameter, ζ , and the nonaxiality parameter, η , may be regarded as independent of the angular momenta of the two molecules, since the lattice vibrations are mainly determined by the isotropic intermolecular forces. It then follows that the reduction factors for the different multipole interactions satisfy simple algebraic relations. In particular, from [59] we obtain

$$[61] \quad \begin{aligned} (1 - \xi_{54})/(1 - \xi_{43}) &= 2/3 \\ (1 - \xi_{65})/(1 - \xi_{54}) &= 7/5 \end{aligned}$$

where

$$[62] \quad \xi_{54} = 1 - (15/2)\zeta$$

is the quadrupolar reduction factor.

The second term in [58] leads to an effective interaction with different tensorial properties. The existence of such an interaction is contingent upon a deviation of the pair distribution function from cylindrical symmetry about the pair axis. For the EQQ interaction we have (5, 6)

$$[63] \quad \xi_{54}^{(2)} = 3\sqrt{10}\eta/4$$

and the corresponding interaction term contributes to the splitting of the ground state doublet.

In a microscopic calculation of the parameters ζ and η one can distinguish two contributions. One can be expressed in terms of properties of the phonon dispersion relations, such as the difference between the longitudinal and transverse speeds of sound, and the dependence of the frequencies and polarization vectors on the angle between the direction of propagation and the crystal axis. These effects can be calculated on the basis of an anisotropic Debye model (9, 23). The other contribution is due to the short-range correlations between the motions of nearest neighbouring molecules, which can be taken into account in a perturbed Einstein or Hartree model (3, 6, 9). For the quadrupole reduction factor

$$[70] \quad C(44l; 00)B_{lm}^{(l_1 l_2)}(\mathbf{R}_{12}) = \sum_{m'm''} C(44l; m'm''m)f_{4m}(\mathbf{R}_{12})f_{4m''}(\mathbf{R}_{12})B_{l_0}^{(l_1 l_2)}(\mathbf{R}_0)$$

where $B_{l_0}^{(l_1 l_2)}(\mathbf{R}_0)$ is given by [40]. Averaging over the zero-point motion, we get

the short-range contribution gives

$$[64] \quad \xi_{54} = 0.93$$

for both types of pair. In the anisotropic Debye model the reduction factors for ip and op pairs are slightly different, the results being

$$[65] \quad \begin{aligned} \xi_{54}(\text{av}) &= \frac{1}{2}[\xi_{54}(\text{ip}) + \xi_{54}(\text{op})] = 0.98 \\ \Delta\xi_{54} &= \xi_{54}(\text{ip}) - \xi_{54}(\text{op}) = 0.01 \end{aligned}$$

cf. (9) with the set $[N]$ of elastic constants. Combining [64] and [65] we obtain

$$[66] \quad \xi_{54}(\text{av}) = 0.91$$

corresponding to the value $\zeta = 0.012$ of the oblateness parameter. This result agrees with that obtained in HBH, $\xi_{54} = 0.907$, on the basis of a self-consistent calculation including both the phonon anisotropic and the short-range correlations. However, the difference $\Delta\xi_{54}$ was not obtained in HBH.

The non-axiality parameter η was calculated in ref. 9 in the form

$$[67] \quad \eta = \eta_D + \eta_E$$

where η_D and η_E denote the contributions in the generalized Debye and perturbed Einstein models, respectively, which are given by

$$[68] \quad \begin{aligned} \eta_D(\text{ip}) &= 1.20 \times 10^{-3} \\ \eta_D(\text{op}) &= -0.95 \times 10^{-3} \end{aligned}$$

and

$$[69] \quad \eta_E(\text{ip}) = \frac{1}{3}\eta_E(\text{op}) \equiv \Delta < 0$$

The magnitude of Δ is quite uncertain and in the present work we shall treat Δ as an adjustable parameter. Our calculations in ref. 9 gave $\Delta = -0.77 \times 10^{-3}$, and the results of HBH correspond to $\Delta = -0.53 \times 10^{-3}$, agreeing in sign and order of magnitude.

B. Renormalization of the Polarization Interactions

As discussed in Sect. 3, the effective EQQ interaction in the manifold $F_1 \otimes F_2$ consists of a first- and a second-order part. It was suggested by HBH that the renormalization of the second-order part, [39], can be effected by multiplying the coefficients $B_{lm}^{(l_1 l_2)}$ by the factor f defined by [4]. As will now be explained, this approach is not completely correct and must be modified. With respect to an arbitrary frame which is fixed in space and does not follow the molecular motion, the coefficients in [39] can be shown to be given by

$$[71] \quad \langle B_{lm}^{(l_1 l_2)}(\mathbf{R}_{12}) \rangle = g_{lm} B_{l_0}^{(l_1 l_2)}(R_0)$$

where

$$[72] \quad C(44l; 00)g_{lm} = \sum_{m'm''} C(44l; m'm''m) \langle f_{4m}(\mathbf{R}_{12}) \hat{1} f_{4m''}(\mathbf{R}_{12}) \rangle$$

We can evaluate g_{lm} to second order in the displacements by putting $\hat{1} = \sum_n |n\rangle \langle n|$ in [72] and retaining only the zero- and one-phonon states $|n\rangle$ rather than all phonon states. In this way we obtain

$$[73] \quad g_{lm} = g_{lm}^{(0)} + g_{lm}^{(1)}$$

where

$$[74] \quad C(44l; 00)g_{lm}^{(0)} = \sum_{m'm''} C(44l; m'm''m) \langle 0 | f_{4m} | 0 \rangle \langle 0 | f_{4m''} | 0 \rangle$$

and

$$[75] \quad C(44l; 00)g_{lm}^{(1)} = \sum_{m'm''} C(44l; m'm''m) \langle \mathbf{u}_{12} \mathbf{u}_{12} \rangle : \nabla f_{4m}(\mathbf{R}_0) \nabla f_{4m''}(\mathbf{R}_0)$$

In evaluating [74], we neglect the non-axiality of the pair distribution function, and obtain

$$[76] \quad g_{lm}^{(0)} = \xi_{54}^2 \delta_{m0} \quad (l = 0, 2, 4)$$

Since the trace of the tensor $\nabla f_{4m} \nabla f_{4m''}$ in [75] does not vanish, we may replace the tensor $\langle \mathbf{u}_{12} \mathbf{u}_{12} \rangle$ by its isotropic part,

$$[77] \quad \langle \mathbf{u}_{12} \mathbf{u}_{12} \rangle_{\alpha\beta} = \frac{1}{3} \langle \mathbf{u}_{12}^2 \rangle \delta_{\alpha\beta}$$

Using [57], and the relation (ref. 14, p. 130)

$$[78] \quad \sum_m (-)^m \begin{pmatrix} 5 & 4 & 1 \\ 0 & m & \bar{m} \end{pmatrix} \begin{pmatrix} 5 & 4 & 1 \\ 0 & \bar{m} & m \end{pmatrix} \begin{pmatrix} 4 & 4 & l \\ m & \bar{m} & 0 \end{pmatrix} = - \begin{pmatrix} 55l \\ 000 \end{pmatrix} \begin{Bmatrix} 55l \\ 441 \end{Bmatrix}$$

we find that in the pair frame

$$[79] \quad C(44l; 00)g_{lm}^{(1)} = -165C(55l; 00) \begin{Bmatrix} 55l \\ 441 \end{Bmatrix} \delta_{m0} \langle \mathbf{u}_{12}^2 \rangle / R_0^2$$

Combining [76] and [79], we obtain

$$[80] \quad g_{lm} = \delta_{m0} [\xi_{54}^2 + \gamma_l \langle \mathbf{u}_{12}^2 \rangle / R_0^2]$$

where

$$[81] \quad \gamma_0 = 15, \quad \gamma_2 = 14, \quad \gamma_4 = 35/3$$

Using the values of ξ_{54} and $\langle \mathbf{u}_{12}^2 \rangle / R_0^2$ from [66] and [103], we get

$$[82] \quad g_{00} = 1.70, \quad g_{20} = 1.64, \quad g_{40} = 1.50$$

This means that the second-order EQQ interaction increases by 50–70%, depending on the value of l , when averaged over the zero-point motion. For comparison, we can treat the factor f of [4] in the same approximation, and we find

$$[83] \quad f = \xi_{54}^2 + \frac{25}{3} \langle \mathbf{u}_{12}^2 \rangle / R_0^2 = 1.31$$

Hence this factor is considerably too small and neglects the variation with l .

It should be noted that the same factors [80] describe the renormalization of the coefficient [46], so that its renormalized value is equal to

$$[84] \quad \tilde{E}_{20}^{(20)} = g_{20} E_{20}^{(20)}$$

This can be seen by noting that [46] describes the orientational polarization of the 'missing' para molecule at \mathbf{R}_2 by the quadrupole field of the ortho molecule at \mathbf{R}_1 .

The renormalization of the three-body interactions can be performed in a similar way. The instantaneous

values of these interactions can be regarded as given by [43] and [44], if in those equations we let $\mathbf{R}_{ip} = \mathbf{R}_{ip}^0 + \mathbf{u}_{ip}$, where $\mathbf{u}_{ip} = \mathbf{u}_p - \mathbf{u}_i$ is the relative displacement of the molecules i and p from their equilibrium positions, \mathbf{R}_i^0 and \mathbf{R}_p^0 , and $\mathbf{R}_{ip}^0 = \mathbf{R}_p^0 - \mathbf{R}_i^0$. The functions to be averaged depend on three position variables and are of the form

$$[85] \quad F_{lm}^j(\mathbf{R}_{1p}, \mathbf{R}_{2p}) = (R_0^2/R_{1p}R_{2p})^{j+1} T_{lm}^{(jj)}(\hat{\mathbf{R}}_{1p}, \hat{\mathbf{R}}_{2p})$$

where $j = 3, 4$ refers to the dielectric screening and orientational polarization interactions, respectively. Expressing [85] in terms of the harmonic functions $f_{jm}(\mathbf{R})$ and averaging, we get

$$[86] \quad \langle F_{lm}^j(\mathbf{R}_{1p}, \mathbf{R}_{2p}) \rangle = \sum_{m_1 m_2} C(jj; m_1 m_2 m) \langle 0 | f_{jm_1}(\mathbf{R}_{1p}) \hat{1} f_{jm_2}(\mathbf{R}_{2p}) | 0 \rangle$$

To second order in the displacements, only the zero- and one-phonon states need be retained in the expansion $\hat{1} = \sum_n |n\rangle \langle n|$, giving

$$[87] \quad \langle F_{lm}^j \rangle = \langle F_{lm}^j \rangle^{(0)} + \langle F_{lm}^j \rangle^{(1)}$$

In the zero-phonon term we assume that the distribution function of the relative displacements of molecules i and p is axially symmetric about \mathbf{R}_{ip}^0 , and that its deviation from spherical symmetry is appreciable only for nearest neighbours, for which $R_{ip}^0 = R_0$. Then we can write

$$[88] \quad \langle 0 | f_{jm}(\mathbf{R}_{ip}) | 0 \rangle = \xi_{j+1,j}(R_{ip}^0) f_{jm}(R_{ip}^0)$$

where

$$[89] \quad \xi_{j+1,j}(R_{ip}^0) = \begin{cases} \xi_{j+1,j} & \text{if } R_{ip}^0 = R_0 \\ 1 & \text{if } R_{ip}^0 > R_0 \end{cases}$$

where $\xi_{j+1,j}$ is given by [59]. Thus, the contribution of the zero-phonon term,

$$[90] \quad \langle F_{lm}^j(\mathbf{R}_{1p}, \mathbf{R}_{2p}) \rangle = \xi_{j+1,j}(R_{1p}^0) \xi_{j+1,j}(R_{2p}^0) F_{lm}^j(R_{1p}^0, R_{2p}^0)$$

to the renormalization of both types of the three-body interactions is expressed in terms of a single parameter, ζ , defined by [55]. In evaluating the lattice sums [43] and [44], we must multiply the contributions of the first, second, and residual shells by a different power (ξ^2 , ξ , and 1) of the appropriate reduction factor (5).

The one-phonon term in [87] can be written in the form

$$[91] \quad \langle F_{lm}^j \rangle^{(1)} = \sum_{m_1 m_2} C(jj; m_1 m_2 m) \mathbf{A} : \nabla f_{jm_1}(\mathbf{R}_{1p}^0) \nabla f_{jm_2}(\mathbf{R}_{2p}^0)$$

where the gradients are taken with respect to the position of particle p , and the matrix \mathbf{A} is given by

$$[92] \quad \mathbf{A} = \langle 0 | \mathbf{u}_{1p} \mathbf{u}_{2p} | 0 \rangle$$

Restricting ourselves to the isotropic part of \mathbf{A} ,

$$[93] \quad A_{\alpha\beta} = A \delta_{\alpha\beta}$$

using [57], and recombining the spherical harmonics to form bipolar harmonics, we get

$$[94] \quad \langle F_{lm}^j \rangle^{(1)} = AR_0^{-2} (j+1)(2j+1)(2j+3) \sum_{l'm'} (-)^{m'} F_{l'm'}^{j+1}(\mathbf{R}_{1p}^0, \mathbf{R}_{2p}^0) \\ \times \Pi(l'l') \sum_{m_1 m_2 \mu} (-)^{\mu} \begin{pmatrix} j & j & l \\ m_1 & m_2 & \bar{m} \end{pmatrix} \begin{pmatrix} j+1 & j & l \\ m_1 + \mu & \bar{m}_1 & \bar{\mu} \end{pmatrix} \begin{pmatrix} j+1 & j & l \\ m_2 - \mu & \bar{m}_2 & \mu \end{pmatrix} \begin{pmatrix} j+1 & j+1 & l' \\ m_1 + \mu & m_2 - \mu & \bar{m}' \end{pmatrix}$$

The last line of [94] can be evaluated with the help of a $6j$ -symbol, giving

$$[95] \quad (-)^{l+m+1} \delta_{ll'} \delta_{mm'} \begin{Bmatrix} j+1 & j+1 & l \\ j & j & l \end{Bmatrix}$$

Using an algebraic expression for the $6j$ -symbol (24), we finally obtain

$$[96] \quad \langle F_{lm}^j \rangle^{(1)} = -(A/2R_0^2) [(l+2j+2)(l+2j+3)(l-2j-2)(l-2j-1)]^{1/2} F_{lm}^{j+1}$$

which agrees with the expression given in HBH except for what is probably a misprint in eq. [A. 10] in ref. 6, which should read $\langle u_{12}^2 \rangle = (3/\bar{A})$.

The isotropic part of the matrix [92],

$$[97] \quad A = \frac{1}{3} \text{tr} \langle \mathbf{u}_p \mathbf{u}_p + \mathbf{u}_1 \mathbf{u}_2 - \mathbf{u}_1 \mathbf{u}_p - \mathbf{u}_p \mathbf{u}_2 \rangle$$

is described sufficiently accurately by the isotropic Debye model (7) in which the phonon frequencies are assumed to be independent of the polarization and propagation directions. In terms of this model we have

$$[98] \quad \langle \mathbf{u}_i \mathbf{u}_j \rangle_{\alpha\beta} = \frac{2}{3} \delta_{\alpha\beta} \langle \mathbf{u}^2 \rangle (1 - \cos q_D R_{ij}) (q_D R_{ij})^{-2}$$

where $\langle \mathbf{u}^2 \rangle$ refers to the single-particle distribution, and q_D is the radius of the Debye sphere. For a close-packed lattice, $q_D R_0 = (6\pi^2 \sqrt{2})^{1/3} = 4.375$, and the value of $\langle \mathbf{u}^2 \rangle$ in solid H_2 as measured by inelastic neutron scattering (25) is $\langle \mathbf{u}^2 \rangle = 0.48 \text{ \AA}^2$. As seen from [96]–[98], the one-phonon renormalization of the three-body interactions depends on the shape of the triangle formed by the three interacting molecules. However, the renormalization is appreciable only for nearest neighbours, and hence we need consider only the first two shells. We can then express [97] in the form

$$[99] \quad A = \frac{1}{6} \text{tr} \langle \mathbf{u}_{ip} \mathbf{u}_{ip} \rangle \equiv 1/6 \langle \mathbf{u}_{ip}^2 \rangle$$

where $i = 1$ or $i = 2$ and

$$[100] \quad \langle \mathbf{u}_{ip}^2 \rangle = 2 \langle \mathbf{u}^2 \rangle [1 - 2(1 - \cos q_D R_{ip}) (q_D R_{ip})^{-2}]$$

$R_{ip} = r_p R_0$ being the larger of R_{1p} and R_{2p} (cf. eq. [A2]). The ratio

$$[101] \quad \kappa = \langle \mathbf{u}_{ip}^2 \rangle / 2 \langle \mathbf{u}^2 \rangle$$

is appreciably different from 1 only for the molecules p in the first shell, as can be seen from Table A1 in the Appendix, where this ratio is given for all allowed values of r_p . Putting $\kappa = 1$ for all molecules p in the second shell, we obtain $A(2) = \frac{1}{3} \langle \mathbf{u}^2 \rangle$ for the contribution of this shell to A . For the contribution of the first shell we get from [99] and [100], $A(1) = 1.72 \langle \mathbf{u}^2 \rangle / 6$, giving

$$[102] \quad A(1)/2 R_0^2 = 4.8 \times 10^{-3}, \quad A(2)/2 R_0^2 = 5.6 \times 10^{-3}$$

and

$$[103] \quad \langle \mathbf{u}_{12}^2 \rangle / R_0^2 = 0.058$$

the quantity to be used in [80].

The resulting one-phonon contributions to the renormalized three-body interactions are given by

$$[104] \quad \delta D_{lm}^{(22)}(s) = -175 \Gamma_0 \rho \frac{A(s)}{2R_0^2} (l+10)(l+11)(10-l)(9-l) \left\{ \begin{matrix} 33l \\ 221 \end{matrix} \right\} S_{lm}^4(s)$$

for the dielectric screening, and

$$[105] \quad \delta E_{lm}^{(22)}(s) = \frac{875}{3} \frac{\Gamma_0^2}{B} \frac{A(s)}{2R_0^2} (l+12)(l+13)(12-l)(11-l) \left\{ \begin{matrix} 44l \\ 222 \end{matrix} \right\} S_{lm}^5(s)$$

for the orientational polarization. The index $s = 1, 2$ refers to the two shells, and the lattice sums are defined by

$$[106] \quad S_{lm}^j(s) = \sum_{p \in s} F_{lm}^j(\mathbf{R}_{1p}, \mathbf{R}_{2p})$$

These sums are easily evaluated with the help of the bipolar harmonics $T_{lm}^{(jj)}(\hat{\mathbf{R}}_{1p}, \hat{\mathbf{R}}_{2p})$ tabulated in the Appendix. Our results for the coefficients [104, 105] are presented in Table 4.

C. Self-energy Effects and Dynamical Renormalization of the Anisotropic Interactions

In addition to the renormalization effects discussed so far, the coupling between the rotational motion of the molecules and the lattice vibrations leads to a number of typical self-energy effects arising from the emission and reabsorption of virtual phonons (7). For single ortho impurities these effects are the main source of the crystalline field (7, 26). For ortho pairs, several additional effects appear in second-order perturbation theory, viz., the quadrupole induced strain (HBH), exchange of virtual phonons by the two ortho molecules, and cross terms between the ortho–ortho and ortho–para interactions. As pointed out in ref. 8, these effects contribute to all of the symmetry parameters [19, 20], and in general these contributions are

TABLE 4. Numerical values of the coefficients $\delta D_{lm}^{(22)}(s)$, eq. [104], in units of $[(\Gamma_0 \rho) A(s)/2R_0^2]$ and $\delta E_{lm}^{(22)}(s)$, eq. [105], in units of $[(\Gamma_0^2/B) A(s)/2R_0^2]$. The contributions of the first ($s = 1$) and the second ($s = 2$) shells are tabulated separately with respect to the pair frame for each type of pair

lm	In-plane pairs				Out-of-plane pairs			
	$\delta D(1)$	$\delta D(2)$	$\delta E(1)$	$\delta E(2)$	$\delta D(1)$	$\delta D(2)$	$\delta E(1)$	$\delta E(2)$
00	1134.3	208.7	-676.1	419.0	1134.3	212.9	-676.1	420.9
20	-394.1	-383.9	1570.5	-349.5	-394.1	-385.0	1570.5	-346.6
22	-127.6	92.0	90.2	22.3	-382.8	246.7	270.6	213.3
40	-954.3	12.7	-1068.3	-44.7	-954.3	9.4	-1068.3	-48.2
42	-52.5	3.1	-108.2	17.6	-157.6	14.1	-324.8	53.0
44	401.9	-70.3	-72.3	-50.0	-516.7	115.8	93.0	91.1

different for ip and op pairs. The difference in the lowering of the ortho pair levels due to the phonon self-energy effect is of particular importance in determining the relative position of the energy levels of ip and op pairs. Leaving a fuller treatment of these self-energy effects to another paper, we include here only the Q -induced strain which is also the only effect included in HBH. This interaction may be calculated by assuming that the relative displacement of the two ortho molecules has a spherical distribution and can be described by a simple Einstein model.

The unperturbed Hamiltonian of the two ortho molecules is thus given by

$$[107] \quad H_0 = \frac{1}{2m}(\mathbf{p}_1^2 + \mathbf{p}_2^2) + \frac{1}{2}m\omega_E^2(\mathbf{u}_1^2 + \mathbf{u}_2^2) + B(\mathbf{J}_1^2 + \mathbf{J}_2^2)$$

and the perturbation, V , is the potential of the average force between the two molecules due to the EQQ interaction,

$$[108] \quad V = \mathbf{u}_{12} \cdot \mathbf{h}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$$

where $\mathbf{u}_{12} = \mathbf{u}_2 - \mathbf{u}_1$ and

$$[109] \quad \mathbf{h}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = \langle \nabla V_{\text{EQQ}}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2; \mathbf{R}_{12}) \rangle = \xi_{65} \nabla V_{\text{EQQ}}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2; \mathbf{R}_0)$$

The factor ξ_{65} describing the reduction of the quadrupole induced force is related to ξ_{54} by [61]. To second order, the shifts in the energy levels due to the perturbation [108] are determined by the equivalent operator

$$[110] \quad \tilde{G} = -(\hbar\omega_E)^{-1} \langle 0 | \mathbf{u}_{12} \mathbf{u}_{12} | 0 \rangle : P_0 \mathbf{h} P_0 \mathbf{h} P_0$$

where P_0 is the projection operator onto the manifold $F_1 = F_2 = 1$. The intermediate states corresponding to $F_1 = 3$ or $F_2 = 3$ may be neglected since $10B \gg \hbar\omega_E$. Using [57], [36], and [78], we obtain

$$[111] \quad \tilde{G} = \xi_{65}^2 \sum_{lm} \sum_{l_1 l_2} G_{lm}^{(l_1 l_2)*} \hat{T}_{lm}^{(l_1 l_2)}$$

where, relative to the pair frame,

$$[112] \quad G_{lm}^{(l_1 l_2)} = 866250 \delta_{m0} g (2l_1 + 1)(2l_2 + 1) C(55l; 00) \begin{Bmatrix} 55l \\ 441 \end{Bmatrix} \begin{Bmatrix} 22l_1 \\ 111 \end{Bmatrix} \begin{Bmatrix} 22l_2 \\ 111 \end{Bmatrix} \begin{Bmatrix} 44l \\ 22l_1 \\ 22l_2 \end{Bmatrix}$$

and g is the dimensionless parameter

$$[113] \quad g = (\Gamma_0 / \hbar\omega_E) \langle \mathbf{u}_{12}^2 \rangle / R_0^2$$

The Einstein frequency can be estimated from the width of the single-particle distribution, eq. [52] of ref. 9, giving $\Gamma_0 / \hbar\omega_E = 1.3 \times 10^{-2}$. In the Einstein model, we have $\langle \mathbf{u}_{12}^2 \rangle = 2\langle \mathbf{u}^2 \rangle$, giving

$$[114] \quad \langle \mathbf{u}_{12}^2 \rangle / R_0^2 = 6.7 \times 10^{-2}$$

and hence

$$[115] \quad g = 8.5 \times 10^{-4}$$

which is the value we will use in Sect. 5.

5. The Effective Pair Hamiltonian and Frequency Fit of the Microwave Spectra

The coefficients in the effective Hamiltonian [11] of the ortho-pair system are given by

$$[116] \quad H_{lm}^{(l_1 l_2)} = (\tilde{A} + \tilde{B} + \tilde{C} + \tilde{D} + \tilde{E} + \tilde{G})_{lm}^{(l_1 l_2)}$$

where the nonvanishing contributions corresponding to the values [19] and [20] of $l_1 l_2 lm$ are given by

$$[117a] \quad \tilde{A}_{lm}^{(22)} = 2\alpha_l^{(22)}[\delta_{m0}\tilde{\epsilon}_l + \frac{5}{8}\Gamma_0\delta_{l4}(\xi_{54}\delta_{m0} + \xi_{54}^{(2)}\delta_{m,\pm 2})]$$

$$[117b] \quad \tilde{B}_{lm}^{(l_1 l_2)} = \delta_{m0}g_{l0}B_{l0}^{(l_1 l_2)}$$

$$[117c] \quad \tilde{C}_{lm}^{(20)} = \alpha_l^{(20)}[-\frac{3}{5}\tilde{V}_c C_{2m}(\beta, \alpha) + 2\delta_{m0}\tilde{\Delta}\tilde{B}]$$

$$[117d] \quad \tilde{D}_{lm}^{(22)} = [\xi_{43}^2 D(1) + \xi_{43} D(2) + D(r) + \delta D(1) + \delta D(2)]_{lm}^{(22)}$$

$$[117e] \quad \tilde{E}_{lm}^{(22)} = [\xi_{54}^2 E(1) + \xi_{54} E(2) + E(r) + \delta E(1) + \delta E(2)]_{lm}^{(22)}$$

$$[117f] \quad \tilde{E}_{2m}^{(20)} = \delta_{m0}g_{20}E_{20}^{(20)}$$

$$[117g] \quad \tilde{G}_{lm}^{(l_1 l_2)} = \delta_{m0}\xi_{65}^2 G_{l0}^{(l_1 l_2)}$$

The contribution of each term in [11] to the energy of the pair levels is found by using the Wigner-Eckart theorem (14) and the reduced matrix elements [8]. The resultant matrix elements are summarized in Table 5. Some of the parameters appearing in [117] are well established, viz.,

$$\Gamma_0, B_{l0}^{(l_1 l_2)}, D_{lm}^{(22)}(s), E_{lm}^{(22)}(s), E_{20}^{(20)}$$

whereas the values of the other parameters are less certain. The coefficients

$$g_{lm}, \xi_{j+1,j}, \xi_{54}^{(2)}, \delta D_{lm}^{(22)}, \delta E_{lm}^{(22)}$$

depend on the shape of the pair distribution function, $g(\mathbf{u})$, parameterized by ζ , η , and $\langle u_{12}^2 \rangle / R_0^2$. The parameters $\tilde{\epsilon}_l$, $l = 0, 2, 4$, are quite uncertain due to the crudeness of our knowledge of the functions $\epsilon_l(R_{12})$. Even larger uncertainties are associated with the crystal field parameters, \tilde{V}_c and $\tilde{\Delta}\tilde{B}$, whose nonvanishing values are due to the interaction between the rotational motion of the molecules and the lattice vibrations.

The experimental information obtained from the microwave spectra of nearest-neighbour pairs was summarized by HBH in eqs. [21] and [22] of ref. 2, which we reproduce here:

$$[118a] \quad \Delta^{\text{out}}(22) = -1.484$$

$$[118b] \quad \Delta^{\text{out}}(11) = -0.422$$

$$[118c] \quad \Delta^{\text{out}}(21) = 0.663$$

$$[118d] \quad \Delta^{\text{in}}(22) + \Delta^{\text{in}}(21) = 1.241$$

$$[118e] \quad \Delta^{\text{in}}(21) = 0.0$$

and

$$[119a] \quad E^{\text{out}}(22) - E^{\text{out}}(10) = 15.134$$

$$[119b] \quad E^{\text{out}}(10) - E^{\text{out}}(21) = 70.497$$

$$[119c] \quad E^{\text{out}}(11) - E^{\text{out}}(21) = 65.192$$

$$[119d] \quad E^{\text{in}}(22) - E^{\text{in}}(21) = 85.354$$

$$[119e] \quad E^{\text{in}}(00) - E^{\text{in}}(21) = 71.280$$

$$[119f] \quad E^{\text{in}}(10) - E^{\text{in}}(21) = 70.228$$

where $2\Delta(FM)$ denotes the splitting and $E(FM)$ the mean energy of the doublet (FM), and the numbers are the corresponding frequencies in gigahertz. Equations [118e] and [119f] follow from the assignment of the line B_2 as due to forbidden transitions between the $(21)_\pm$ and (10) levels of ip pairs. This assignment is less certain than that of the other lines. As pointed out by HBH, the intensity of B_2 is anomalously high and cannot be explained by an 'electric' violation of the selection rules (1) due to the anisotropic part of the polarizability. 'Mechanical' violation of the selection rules may account for the anomalous intensity, and HBH suggest a possible mixing of the states $|00\rangle$ and $|10\rangle$. However, an admixture of $|00\rangle$ into $|10\rangle$ would allow only transitions from the $(21)_-$ state, since the transition $(21)_+ \rightarrow (00)$ is also forbidden. Moreover, the interaction which would mix the (00) and (10) states must be of the form $\hat{T}_{l0}^{(l_1 l_2)}$ which is forbidden by the crystal symmetry, cf. [15]. Consequently, even though the interpretation of B_2 by HBH remains the most plausible one, we shall not use it on an equal footing with the other assignments.

Assuming that ξ_{54} and $\tilde{\epsilon}_l$ have the same value for the two types of pair, and adopting the theoretical value $\xi_{54} = 0.91$ for the quadrupolar reduction factor, we are left with eight adjustable parameters, viz.,

$$[120] \quad \tilde{\epsilon}_0, \tilde{\epsilon}_2, \tilde{\epsilon}_4, \tilde{V}_c(p), \tilde{\Delta}\tilde{B}(p), \Delta$$

the other parameters being fixed by [61], [67]–[69],

TABLE 5. Matrix elements of the basic operators within the ortho-pair manifold. Tabulated are the values of $\alpha^{(t_1 t_2)} \langle FM | \hat{T}_{im}^{(t_1 t_2)} | FM \rangle$ for the axially symmetric operators [19], and $\langle FM | T_{im}^{(t_1 t_2)} | FM \rangle$ for the doublet-splitting terms [20]^a

(a) Axially symmetric contributions

FM	$\alpha^{(t_1 t_2)} \langle FM \hat{T}_{im}^{(t_1 t_2)} FM \rangle$ for $(t_1 t_2) =$					
	$\begin{pmatrix} 22 \\ 40 \end{pmatrix}$	$\begin{pmatrix} 22 \\ 20 \end{pmatrix}$	$\begin{pmatrix} 22 \\ 00 \end{pmatrix}$	$\begin{pmatrix} 20 \\ 20 \end{pmatrix}$	$\begin{pmatrix} 11 \\ 20 \end{pmatrix}$	$\begin{pmatrix} 11 \\ 00 \end{pmatrix}$
20	18/5	1/10	1/10	1/5	-1/2	-1/2
2 ± 2	3/5	-1/10	1/10	-1/5	1/2	-1/2
2 ± 1	-12/5	1/20	1/10	1/10	-1/4	-1/2
10	0	-7/10	-1/2	-1/5	-1/2	1/2
1 ± 1	0	7/20	-1/2	1/10	1/4	1/2
00	0	0	1	0	0	1

(b) Doublet splittings

FM	$\langle FM T_{im}^{(t_1 t_2)} FM \rangle$ for $(t_1 t_2) =$				
	$\begin{pmatrix} 22 \\ 44 \end{pmatrix}$	$\begin{pmatrix} 22 \\ 42 \end{pmatrix}$	$\begin{pmatrix} 22 \\ 22 \end{pmatrix}$	$\begin{pmatrix} 20 \\ 22 \end{pmatrix}$	$\begin{pmatrix} 11 \\ 22 \end{pmatrix}$
22	3/5	0	0	0	0
11	0	0	$\frac{7}{10} \left(\frac{3}{7}\right)^{1/2}$	$-\frac{1}{2} \left(\frac{3}{5}\right)^{1/2}$	1
21	0	$-\frac{6}{5} \left(\frac{1}{7}\right)^{1/2}$	$-\frac{1}{10} \left(\frac{3}{7}\right)^{1/2}$	$\frac{1}{2} \left(\frac{3}{5}\right)^{1/2}$	1

^aNotation for the states, $|FM\rangle \equiv |11 FM\rangle$ is as defined by [10].

[80], [102], [103], and [115]. For Γ_0 , ρ , B , R_0 , and $\langle n^2 \rangle$ we take the values given in Table 1. We begin by fitting the theoretical expressions for the energy levels, [116], [117], and Table 5, to the experimental values, [118 *b, c, d*] and [119 *a, b, c, d, e*]. This yields eight independent equations in the eight unknowns [120], forming a linear system denoted by S_0 . At this point we are not using [118*e*] and [119*f*] resulting from the assignment of B_2 , nor [118*a*] because, given the value of ξ_{54} , the splittings $\Delta(22)$ contain no adjustable parameters.

The parameters [120] can be determined by solving S_0 . Alternatively, we can reduce the number of free parameters further by putting $\Delta = 0$, which amounts to assuming that η is given correctly by the Debye model result [68], and by letting $\tilde{V}_c(p) = \tilde{V}_c$ and $\Delta B(p) = 0$, which corresponds to neglecting the quasistatic distortion induced by the pair of impurities. By adjusting the remaining four parameters ($\tilde{\epsilon}_0$, $\tilde{\epsilon}_2$, $\tilde{\epsilon}_4$, \tilde{V}_c) we find that S_0 can then be satisfied to an accuracy of about 0.3 GHz, which is better than the fit in ref. 2 involving a larger number of free parameters. By relaxing the above constraints and solving S_0 exactly, we find $\Delta = -0.25 \times 10^{-3}$ which has the same sign as predicted by the Einstein model (9) and which results in

$$[121] \quad \begin{aligned} \eta(\text{ip}) &= 1.1 \times 10^{-3} \\ \eta(\text{op}) &= -1.2 \times 10^{-3} \end{aligned}$$

Next, we proceed to vary the assumed value of ξ_{54} , and for each value of ξ_{54} we solve the system S_0 exactly for the parameters [120]. For each value of ξ_{54} we can then calculate $\Delta^{\text{ip}}(21)$ and $\Delta^{\text{op}}(22)$. These calculated values are plotted as functions of the assumed value of ξ_{54} in Fig. 2. We have included the contributions to these doublet splittings of the higher-order, three-body polarization interactions calculated by HBH and scaled by Γ_0^3/B^2 , $\Gamma_0^2\rho/B$, and $\Gamma_0\rho^2$. These terms contribute mainly to $\Delta(22)$. Using the unrenormalized values $\Gamma_0^3/B^2 = 2.49 \times 10^{-3}$, $\Gamma_0^2\rho/B = 3.29 \times 10^{-3}$, and $\Gamma_0\rho^2 = 4.36 \times 10^{-3}$ GHz, we find the following values for these contributions to the doublet splitting, in gigahertz:

	$\Delta(22)$	$\Delta(11)$	$\Delta(21)$
[122] ip	-0.232	0.003	-0.030
op	0.304	0.015	-0.090

As seen from Fig. 2, both [118*a*] and [118*e*] are satisfied in the same region of values of ξ_{54} . The horizontal lines are the error bars for these equations which we assume to be established to an accuracy of ± 25 MHz. To this accuracy, both equations are satisfied for $0.89 \lesssim \xi_{54} \lesssim 0.91$, which agrees with the theoretical values of ξ_{54} . The best fit occurs at $\xi_{54} = 0.899$.

Once the system S_0 is satisfied, the frequency of the 'forbidden' transition $(21)_{\pm} \rightarrow (10)$ for ip pairs

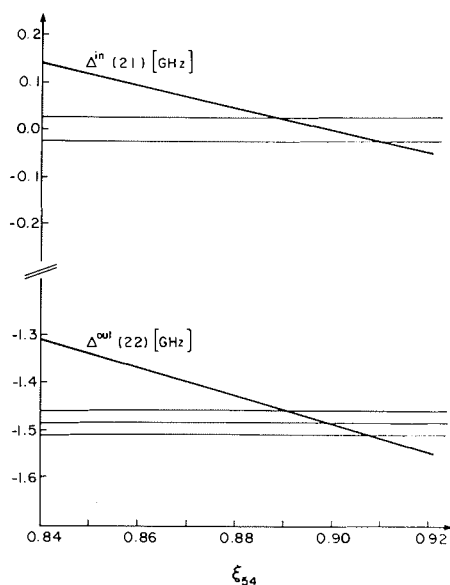


FIG. 2. Dependence of our theoretical predictions for the doublet splittings $\Delta^{in}(11)$ and $\Delta^{out}(22)$ on the assumed value of $\xi_{54}(av)$. The observed splittings along with their estimated error margins are indicated by horizontal lines.

is established *independently* of the assumed value of ξ_{54} . The predicted value, $E^{in}(10) - E^{in}(21) = 70.224$ GHz is in excellent agreement with $\nu(B_2) = 70.228$ GHz, eq. [119f]. If we maintain the assignment of B_2 proposed by HBH, this result implies that ξ_{54} is the same for ip and op pairs to the accuracy of 1 in 10^3 . This is illustrated in Fig. 3, where the predicted value of $E^{in}(10) - E^{in}(21)$ is plotted against an assumed difference $\Delta\xi = \xi_{54}(ip) - \xi_{54}(op)$. As mentioned earlier, the plot in Fig. 3 is independent of an assumed value of the average reduction factor $\xi_{54} = \frac{1}{2}[\xi_{54}(ip) + \xi_{54}(op)]$.

In the region of values defined by

$$[123] \quad 0.89 < \xi_{54} < 0.91, \quad |\Delta\xi| < 10^{-3}$$

all the 11 independent eqs. [118], [119] are satisfied with the following values of the adjusted parameters, in gigahertz:

$$[124a] \quad \tilde{\epsilon}_0 = -0.382 \pm 0.02$$

$$[124b] \quad \tilde{\epsilon}_2 = 0.333 \pm 0.06$$

$$[124c] \quad \tilde{\epsilon}_4 = -0.552 \pm 0.20$$

$$[124d] \quad \tilde{V}_c(ip) = -0.427 \pm 0.06$$

$$[124e] \quad \tilde{V}_c(op) = -0.170 \pm 0.12$$

$$[124f] \quad \tilde{\Delta B}(ip) = 0.157 \pm 0.06$$

$$[124g] \quad \tilde{\Delta B}(op) = -0.330 \pm 0.08$$

The first numbers in the right-hand side of [124] correspond to the 'exact fit' at $\xi_{54} = 0.899$ and

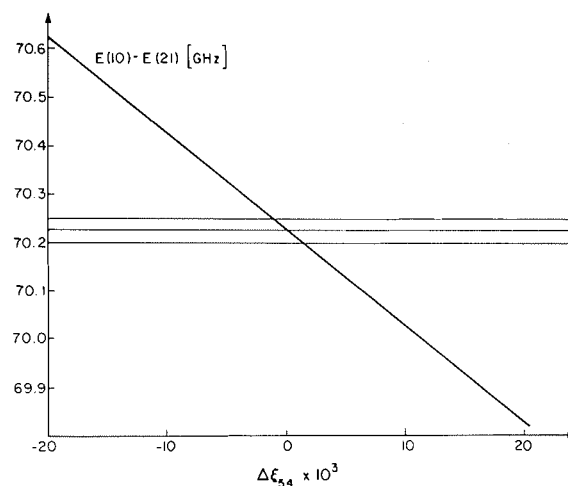


FIG. 3. Dependence of our theoretical predictions for the transition frequency between the (21) and (10) levels of ip pairs on the assumed value of $\Delta\xi_{54} = \xi_{54}(ip) - \xi_{54}(op)$. The horizontal lines indicate the frequency of the B_2 line and its estimated margin of error.

$\Delta\xi = 0$, and the error margins reflect the variations in the values of the parameters over the region [123]. The resulting orientational level structure is given in Table 6. The zero of energy chosen in Table 6 is arbitrary and does not coincide with the energy of two non-interacting ortho molecules. With the help of Table 6, we can predict the frequencies of the most important as yet unobserved lines, L_1, \dots, L_4 , viz.,

$$\begin{aligned}
 \nu(L_1) &= E^{in}(20) - E^{in}(00) = 91.99 \\
 \nu(L_2) &= E^{out}(20) - E^{out}(11)_- = 97.54 \\
 \nu(L_3) &= E^{out}(20) - E^{out}(11)_+ = 98.38 \\
 \nu(L_4) &= E^{in}(20) - E^{in}(21)_- = 163.27
 \end{aligned}
 \tag{125}$$

in gigahertz.

TABLE 6. Orientational level structure (in gigahertz) of an ortho pair^a

In-plane pairs	Level ^b	Out-of-plane pairs
95.943	(2, 0)	95.741
19.271	(2, 2) ₊	16.739
16.794	(2, 2) ₋	19.708
3.956	(0, 0)	3.969
2.903	(1, 0)	3.089
-2.477	(1, 1) ₊	-2.638
-1.749	(1, 1) ₋	-1.794
-67.319	(2, 1) ₊	-66.745
-67.324	(2, 1) ₋	-68.071

^aObtained from [11], [117], and Table 5, with the effective parameters as given by Table 1, [121], and [124]. The higher-order polarizability contribution [122] is included.

^bDesignation of the states, $\sqrt{2}|FM\rangle_{\pm} = |FM\rangle \pm |FM\rangle$, where $M > 0$, is in accordance with refs. 1, 2, 5, and 6.

We point out once more that our fit rests on the interpretation of the B_2 line, eq. [119f]. Without [119f] the experimental information is not sufficient to rule out a possible difference in the quadrupolar reduction factors for ip and op pairs. If we adopt the theoretical value $\Delta\xi = 0.01$ obtained (9) on the basis of the generalized Debye model, then [119f] is not satisfied, but all the other equations are satisfied perfectly with the following values of the effective parameters,

$$\begin{aligned}
 \tilde{\varepsilon}_0 &= -0.54, & \tilde{\varepsilon}_2 &= 0.55, & \tilde{\varepsilon}_4 &= -0.54 \\
 [126] \quad \tilde{V}_c(\text{ip}) &= -0.43, & \tilde{V}_c(\text{op}) &= -0.17 \\
 \tilde{\Delta B}(\text{ip}) &= 0.60, & \tilde{\Delta B}(\text{op}) &= -0.72
 \end{aligned}$$

The predicted frequencies of the lines L_1, \dots, L_4 in this case are

$$\begin{aligned}
 [127] \quad \nu(L_1) &= 93.4, & \nu(L_2) &= 96.6 \\
 \nu(L_3) &= 97.5, & \nu(L_4) &= 164.7
 \end{aligned}$$

The line L_4 has been observed in the Raman spectrum of solid hydrogen (27). The quoted frequency $\nu(L_4) = 5.51 \pm 0.1 \text{ cm}^{-1}$ or $\nu(L_4) = (165 \pm 3) \text{ GHz}$ agrees within the experimental uncertainty with both [125] and [127]. A high-resolution determination of any of the lines L_1, \dots, L_4 would clearly be of great interest.

6. Discussion and Conclusions

The values [124] of the effective interaction parameters obtained in our fit appear quite reasonable. The value of Γ_{eff} defined by

$$[128] \quad \Gamma_{\text{eff}} = \xi_{54}\Gamma_0 + (6/5)\tilde{\varepsilon}_4 = 17.22 \text{ GHz}$$

agrees well with the nmr data on dilute o- H_2 pairs in p- H_2 , (28), and our values for the $\tilde{\varepsilon}_i$ are in reasonable order-of-magnitude agreement with the theoretically calculated, unrenormalized, ε_i . The calculations of Raich *et al.* (19) give $\varepsilon_0 = -0.06$, $\varepsilon_2 = -0.81$, $\varepsilon_4 = -0.48 \text{ GHz}$. From the anisotropic potential given in (29) one can extract³ the values $\varepsilon_0 = -0.42$, $\varepsilon_2 = -0.57$, $\varepsilon_4 = -0.91 \text{ GHz}$, where only the R^{-6} and R^{-8} contributions are included. The main disagreement between these values and [124] is in the sign of ε_2 and this may be related to our incomplete inclusion of the quasi-static distortion effect. The values obtained for $\tilde{\varepsilon}_0$ and $\tilde{\varepsilon}_2$ in ref. 2 are similar to ours, although in other respects the results of our fit are quite different. The values of the crystalline field parameters \tilde{V}_c and $\tilde{\Delta B}$ in [124] are different for ip and op pairs, and are not directly comparable to the crystalline field measured at the site of a single ortho molecule, for which the upper limit is $|V_c| \lesssim$

0.58 GHz with the sign uncertain (30). If the sign of V_c for single ortho molecules is assumed to be the same as the signs of the parameters $\tilde{V}_c(p)$ given in [124], one obtains $V_c < 0$, implying that the ground state of a single ortho impurity corresponds to $m = \pm 1$. However, in our view it is more likely that no simple relation exists between V_c and the pair parameters $\tilde{V}_c(p)$.

The main difference between our work and that of HBH lies in the treatment of the phonon renormalization effects. In analyzing the doublet splittings, $\Delta(FM)$, HBH used two adjustable parameters, V_c and T_p , which are essentially equivalent to our \tilde{V}_c and η , respectively. It was assumed in HBH that $V_c(\text{ip}) = V_c(\text{op}) \equiv V_c$ and $T_p(\text{op}) = 4T_p(\text{ip}) \equiv T_p$, cf. eq. [1]. It is the latter assumption which we feel leads to difficulties, as discussed in ref. 9. Adoption of [1] forces a positive value on V_c when the theoretical values are fitted to the data [118]. As a result, the splitting $\Delta^{\text{out}}(11)$, which is one of the best known experimental values, is not given correctly and in fact has the wrong sign, and in this respect our approach based on [67]–[69] is clearly more acceptable. With the three adjustable parameters $\tilde{V}_c(\text{ip})$, $\tilde{V}_c(\text{op})$, and Δ , we are able to fit the data [118] exactly. Moreover, by putting $\Delta = 0$, and even $\tilde{V}_c(p) = \tilde{V}_c$, i.e., using \tilde{V}_c as the only free parameter, we obtain better agreement with the observed splittings, than obtained in ref. 2. Thus, the most important difference between this work and HBH lies in the treatment of the axial asymmetry of the pair distribution function, i.e., in the use of [67]–[69] for the parameters $\eta(p)$, leading to the values [121], rather than [1].

The other differences between the two theories do not seriously affect the quality of the overall fit, but they do lead to appreciably different values for the effective parameters. For example, the parameter f , chosen in HBH to describe the renormalization of the second-order EQQ interaction, was assigned the value $f = 1$. In view of our result [82] for the corresponding renormalization factors [80], this means that the effect of the two-body terms involving Γ_0^2/B was underestimated in HBH by amounts varying from 50 to 70%. The effective quadrupolar reduction factor, $\Gamma_{\text{eff}}/\Gamma_0$, is varied in HBH independently of the renormalization of the polarization interactions and of the EQQ-induced strain, whereas in our theory the relations between these effects are taken into account, cf. Sect. 4.

The EQQ-induced strain is treated in HBH on the basis of a more sophisticated model than the one used in Sect. 4C. However, the main effect is contained in [112], and the two theories give similar results if one identifies our parameter g , [113], with

³W. N. Hardy, private communication.

the parameter ($3G_0^0 \Gamma_0/E_D$) of HBH. The results of a self-consistent, lattice dynamical calculation of Goldman, quoted in ref. 6, give

$$[129] \quad 3G_0^0 \Gamma_0/E_D = 8.46 \times 10^{-4}$$

which agrees very well with our result, $g = 8.5 \times 10^{-4}$. The Einstein model we used describes the EQQ-induced strain adequately because this effect does not depend on the detailed shape of the pair distribution function. One can regard the result [115], [129] as one of the better established numbers in the theory. In HBH this parameter is varied and the result obtained for it by fitting the spectrum, 4.8×10^{-4} , should be regarded as a renormalized value, comparable to our result

$$[130] \quad \xi_{65}^2 g = 6.3 \times 10^{-4}$$

Finally, we want to comment on the result obtained empirically by HBH that the effective coupling constant $\bar{\Gamma}$ is different for ip and op pairs. The difference found from the fit in ref. 2,

$$[131] \quad \bar{\Gamma}(\text{ip}) - \bar{\Gamma}(\text{op}) = 0.02 \text{ GHz}$$

is of the same sign as predicted by the generalized Debye model (9) and corresponds to $\Delta\xi_{54} = 1 \times 10^{-3}$. As discussed in ref. 9, a difference of this magnitude does not imply a departure from the c/a ratio from the ideal hcp value, as claimed in HBH. The result [131] is rather a consequence of the single positive value for V_c resulting from a somewhat arbitrary fit of [118], as discussed above.

1. W. N. HARDY and A. J. BERLINSKY. Phys. Rev. Lett. **34**, 1520 (1975).
2. W. N. HARDY, A. J. BERLINSKY, and A. B. HARRIS. Can. J. Phys. **55**, 1150 (1977).
3. A. B. HARRIS. Phys. Rev. B, **1**, 1881 (1970).
4. J. NOOLANDI. Can. J. Phys. **48**, 2032 (1970).
5. S. LURYI, J. VAN KRANENDONK, and J. NOOLANDI. Phys. Rev. Lett. **38**, 418 (1977).
6. A. B. HARRIS, A. J. BERLINSKY, and W. N. HARDY. Can. J. Phys. **55**, 1180 (1977).
7. J. VAN KRANENDONK and V. F. SEARS. Can. J. Phys. **44**, 313 (1966).
8. A. B. HARRIS and A. J. BERLINSKY. Solid State Commun. **24**, 159 (1977).
9. S. LURYI and J. VAN KRANENDONK. Can. J. Phys. **57**, 136 (1979).
10. A. B. HARRIS. Int. J. Quantum Chem., **II** Symp. 347 (1968).
11. J. NOOLANDI and J. VAN KRANENDONK. Phys. Lett. A, **30**, 258 (1969).
12. S. LURYI. Can. J. Phys. This issue.
13. K. W. H. STEVENS. Proc. Phys. Soc., London, Sect. A, **65**, 209 (1952).
14. D. M. BRINK and G. R. SATCHLER. Angular momentum, 2nd ed., (reprinted 1971 with corrections). Clarendon Press, Oxford, England, 1968.
15. J. VAN KRANENDONK and H. P. GUSH. Phys. Lett. **1**, 22 (1962).
16. T. NAKAMURA. Progr. Theor. Phys. **14**, 135 (1955).

17. M. H. L. PRYCE. Proc. Phys. Soc. A, **63**, 25 (1950).
18. J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD. Molecular theory of gases and liquids. Wiley, New York, NY, 1954.
19. J. C. RAICH, A. B. ANDERSON, and W. ENGLAND. J. Chem. Phys. **64**, 5088 (1976).
20. C. G. GRAY. Can. J. Phys. **46**, 135 (1968).
21. A. BIRNBAUM and J. D. POLL. J. Atmos. Sci. **26**, 943 (1969).
22. J. D. POLL. Planetary atmospheres. I.A.U. Symposium #40, Edited by Sagan *et al.* 1971. p. 384.
23. J. NOOLANDI and J. VAN KRANENDONK. Can. J. Phys. **48**, 675 (1970).
24. M. ROTENBERG, R. BIVINS, N. METROPOLIS, and J. K. WOOTEN, JR. The 3- j and 6- j symbols. Technology Press, MIT, Cambridge, MA, 1959.
25. M. NIELSEN. Phys. Rev. B, **7**, 1626 (1973).
26. J. C. RAICH and L. B. KANNEY. J. Low Temp. Phys. **28**, 95 (1977).
27. I. F. SILVERA, W. N. HARDY, and J. P. MCTAGUE. Phys. Rev. B, **4**, 2724 (1971).
28. A. B. HARRIS, L. I. AMSTUTZ, H. MEYER, and S. M. MYERS. Phys. Rev. **175**, 603 (1968).
29. W. MEYER. Chem. Phys. **17**, 27 (1976).
30. R. F. BUZERAK, M. CHAN, and H. MEYER. J. Low Temp. Phys. **28**, 415 (1977).
31. B. P. STOICHEFF. Can. J. Phys. **35**, 730 (1957).

Appendix

We wish to tabulate the values of the bipolar harmonics involved in the calculation of the three-body lattice sums [43], [44], [104], and [105] for all possible angles \hat{R}_{1p} , \hat{R}_{2p} occurring in the first two shells of neighbours of the pair. The functions $T_{lm}^{(jj)}(\hat{R}_{1p}, \hat{R}_{2p})$ defined by [23] are evaluated in the 'triangle' frame (6) in which the z -axis is along R_{12} and the x -axis in the plane of the three molecules 1, 2, and p . In this frame the functions $T_{lm}^{(jj)}$ are real and of the form

$$[A1] \quad T_{lm}^{(jj)}(\hat{R}_{1p}, \hat{R}_{2p}) = T_{lm}^{(jj)}(\theta_{1p}, \theta_{2p})$$

where $\theta_{ip} = \arccos(\tau \cdot \hat{R}_{ip})$. For the molecules p of the first two shells, the value of [A1] depends only on the magnitude of the largest side in the isosceles triangle (R_{1p} , R_{2p} , R_0). Putting

$$[A2] \quad r_p = \max(R_{1p}/R_0, R_{2p}/R_0)$$

and using the fact that

$$[A3] \quad T_{lm}^{(jj)}(\pi - \theta_{2p}, \pi - \theta_{1p}) = (-)^{l+m} T_{lm}^{(jj)}(\theta_{1p}, \theta_{2p})$$

we find that for even $l+m$ (i.e., for all l and m occurring in [19] and [20])

$$[A4] \quad T_{lm}^{(jj)} = T_{lm}^{(jj)}(r_p)$$

independently of whether R_{1p} or R_{2p} is the largest side. The values of [A4] are tabulated in Table A1 for all possible r_p .

With the help of Table A1 we can easily compute

TABLE A1. The possible values of r_p , eq. [A2], for the molecules p belonging to the first two shells, and the corresponding values of κ , eq. [101], and $T_{lm}^{(jj)}$, eq. [A4]

r_p	$r_p = 1$ $\kappa = 0.86$	$r_p = (2)^{1/2}$ $\kappa = 1.00$	$r_p = (8/3)^{1/2}$ $\kappa = 0.99$	$r_p = (3)^{1/2}$ $\kappa = 0.98$	$r_p = (11/3)^{1/2}$ $\kappa = 0.96$	$r_p = 2$ $\kappa = 0.95$
$T_{00}^{(33)}$	0.16536	0.06682	-0.05143	-0.12275	-0.28648	$-(1/7)^{1/2}$
$T_{20}^{(33)}$	-0.22163	-0.25074	-0.14848	-0.05315	0.23722	$(4/21)^{1/2}$
$T_{22}^{(33)}$	-0.23803	-0.16536	-0.09699	-0.06510	-0.01510	0
$T_{40}^{(33)}$	-0.27008	-0.02137	0.19007	0.21917	-0.07246	$-(18/77)^{1/2}$
$T_{42}^{(33)}$	0.01792	0	-0.10981	-0.15517	-0.12495	0
$T_{44}^{(33)}$	0.21332	0.08939	0.03058	0.01368	0.00056	0
$T_{00}^{(44)}$	-0.09635	-0.13542	-0.06019	0.00781	0.20457	1/3
$T_{20}^{(44)}$	0.04303	0.18993	0.17411	0.11129	-0.15877	$-(100/693)^{1/2}$
$T_{22}^{(44)}$	0.12540	0.20354	0.17016	0.13630	0.04840	0
$T_{40}^{(44)}$	0.24318	0.07753	-0.12644	-0.18111	0.02486	$(162/1001)^{1/2}$
$T_{42}^{(44)}$	0.12051	0.03092	0.04875	0.07192	0.07159	0
$T_{44}^{(44)}$	-0.16928	-0.16070	-0.08917	-0.05387	-0.00653	0
$T_{00}^{(55)}$	-0.02709	0.11326	0.11283	0.06732	-0.13607	$-(1/11)^{1/2}$
$T_{20}^{(55)}$	0.08768	-0.09430	-0.16260	-0.14032	0.09470	$(50/429)^{1/2}$
$T_{22}^{(55)}$	0.04532	-0.14321	-0.18492	-0.17186	-0.07793	0
$T_{40}^{(55)}$	-0.17480	-0.12152	0.06572	0.14373	0.01245	$-(18/143)^{1/2}$
$T_{42}^{(55)}$	-0.15942	-0.07438	-0.02757	-0.02562	-0.03174	0
$T_{44}^{(55)}$	-0.01957	0.11479	0.09538	0.06653	0.01023	0

TABLE A2. Numerical values of the lattice sums $S_{lm}^j(s)$ defined by eq. [106] for $j = 3, 4$, and 5. Tabulated are the values of $10^3 \times S_{lm}^j(s)$ for $s = 1$ (first shell) and $s = 2$ (second shell), calculated with respect to the pair frame for each type of pair

lm	$S_{lm}^j(s)$ for $js =$					
	31	32	41	42	51	52
In-plane pairs						
00	661.44	880.69	-385.40	-70.92	-108.36	67.16
20	-886.52	902.22	172.12	167.67	350.72	-78.06
22	-105.79	-22.16	55.73	-40.20	20.14	4.99
40	-1080.32	884.21	972.72	-12.98	-699.20	-29.26
42	7.96	-32.92	53.56	-3.19	-70.85	11.55
44	516.18	-87.69	-409.62	71.66	-47.35	-32.72
Out-of-plane pairs						
00	661.44	445.21	-385.40	-72.33	-108.36	67.46
20	-886.52	438.10	172.12	168.18	350.72	-77.40
22	-317.37	-292.28	167.20	-107.75	60.43	47.64
40	-1080.32	393.54	972.72	-9.56	-699.20	-31.52
42	23.89	-289.91	160.68	-14.40	-212.56	34.66
44	-663.66	303.54	526.65	-118.05	60.88	59.63

the lattice sums S_{lm}^j defined by [106], where now

$$[A5] \quad F_{lm}^j(\mathbf{R}_{1p}, \mathbf{R}_{2p})$$

$$= T_{lm}^{(jj)}(r_p) \exp(-im\phi_p) / r_p^{j+1}$$

the angle ϕ_p being the azimuthal angle of molecule p . The numerical values of the sums $S_{lm}^j(s)$ for $j = 3, 4, 5$ and $s = 1, 2$ are given in Table A2.