PHYSICAL REVIEW B **73**, 174301 (2006)

Anisotropic interactions between HD molecules

Mikhail A. Strzhemechny
Verkin Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine
and Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

(Received 19 January 2006; revised manuscript received 17 March 2006; published 1 May 2006)

The anisotropic interactions between molecules in the heteronuclear hydrogen solids are discussed with stress on their properties of importance for the orientational and translational lattice dynamics. A specific interaction component for homonuclear species, which originates from crystal-field interactions, is suggested and evaluated, in addition to the well-known similar specific component that originates from the isotropic potential due to the shift of the center of mass respective to the charge distribution center. The energy parameters of both specific interaction components have been accurately evaluated and renormalized to account for zero-point translational vibrations. The dispersion laws of the $J=1$ roton excitation in solid HD and DT have been calculated. The bandwidths of the $J=1$ roton excitation are 1.16 cm^{-1} in HD and 0.59 cm^{-1} in DT.

DOI: 10.1103/PhysRevB.73.174301 PACS number(s): 71.70.Gm, 34.20.Mq, 34.50.Gb

I. INTRODUCTION

Hydrogen is perhaps the most studied element. Finest details of molecular interactions have been elucidated in experimental and theoretical studies.[1–3] Yet, among the molecular hydrogen isotopomers, the heteronuclear species HD and DT (especially, the latter) are by far less studied than their homonuclear counterparts. In particular, this concerns the anisotropic components of the interactions between the heteronuclear species. Although the interaction potential, if referred to the axis between the centers of electron charge distributions, is basically the same for any two isotopic molecular species,[4] the rotational and translational dynamics of interacting heteronuclear molecules in the solid are appreciably affected by the asymmetry of the species involved. This asymmetry entails, in particular, specific anisotropic intermolecular forces, nonexistent between homonuclear species. One of such specific anisotropic interactions was suggested and theoretically studied by Van Kranendonk.[1] However, his consideration lacks completeness, which would not allow the effects that are determined by those specific interactions to be fully investigated. In addition, the energy parameters even of the known[1] specific interaction have not been evaluated, even without quantum-crystal renormalization. These specific interactions play an important role in many unusual properties of the heteronuclear hydrogen solids. In particular, these specific interactions determine the unusual shape of the pure rotational IR and Raman bands in the heteronuclear HD and DT solids.[5,6] The aim of this paper is to present a complete set of these specific interactions and their possible role in solid-state effects inherent only in the isotopic hydrogen crystals made of heteronuclear species.

The paper is structured as follows. Section II presents concisely a general theory of the interactions between HD molecules, including the specific anisotropic components. Here we derive a specific interaction component, which originates from the rank-2 crystal field energy. The relevant technical details of the pertaining expansions can be found in Appendix A. In Sec. III, for the purpose of solid-state applications, we evaluate the relevant interaction energy parameters with account of zero-point lattice vibrations. Again, the pertaining technical details can be found in Appendix B, where we extend the approach suggested by Harris[7] to obtain an explicit analytical expression for the renormalization of the second derivatives of effective angle-dependent potentials. We further consider the spectrum of the $J=1$ roton excitation, which exists only in heteronuclear hydrogen solids. Hereinafter, for the sake of brevity we will focus on HD, adding where needed remarks about DT.

II. ANISOTROPIC INTERACTIONS

As mentioned above, the interaction between any hydrogen isotope molecules does not depend on the species involved, which is a consequence of the fact that the chemical forces that bind any two hydrogen isotope atoms into a molecule are strong enough to suppress the internal quantum nature of the nuclei in the intramolecular-vibration ground state. As a result, the electron charge distribution around the molecule is for all practical purposes the same irrelevant of the species. This distribution has an ellipsoidal symmetry with respect to the midpoint of the internuclear axis. On the other hand, both rotational and translational dynamics are naturally referred to the center of mass, which is shifted from the charge distribution center by s (see Fig. 1), equal to $r_e/6$ in the HD molecule and $r_e/10$ in the DT molecule where $r_e=0.74116$ Å is the equilibrium internuclear spacing in the

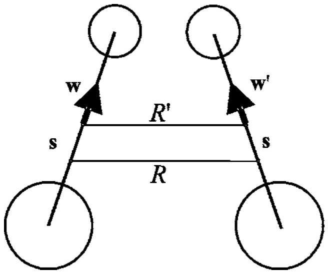

FIG. 1. Two interacting HD molecules. The center of mass distance vector **R** is dynamically meaningful; the vector between geometric centers, **R**′, is the reference axis for the basic potential; the shifts **s** are oriented as the respective molecular axes **w** and **w**′.

hydrogen molecule in its vibron ground state. Although measured for the H_2 molecule,[8] r_e is virtually the same in any isotopic species for the reason above. Making use of Van Kranendonk's reasoning[1] and knowing the basic intermolecular potential V referred to the axis connecting the geometrical centers of the two electron charge distribution ellipsoids, we can expand V in s/R, where R is the distance between the centers of mass (see Fig. 1).

The basic potential, referred to the axis through ellipsoid midpoints, can be divided in the standard way

$$V = v(R') + V_{\rm an}(\mathbf{R}', \mathbf{w}_1, \mathbf{w}_2), \tag{1}$$

where $\mathbf{R}' \equiv R'\mathbf{n}'$ is the vector connecting the symmetry centers of the interacting molecules; $v(R')$ is the central (isotropic) part of the interaction potential; and $\mathbf{w}_i$ are the unit vectors along the molecular axes. The anisotropic part of the potential

$$V_{\rm an}(\mathbf{R}', \mathbf{w}_1, \mathbf{w}_2) = V_1(\mathbf{R}', \mathbf{w}_1) + V_1(\mathbf{R}', \mathbf{w}_2) + V_2(\mathbf{R}', \mathbf{w}_1, \mathbf{w}_2) \tag{2}$$

includes the terms V_1, which are functions of the angle variables of only one of the interacting molecules, and the term V_2 which depends on both sets of angle variables. The latter term can be represented in the form

$$V_2(\mathbf{R}', \mathbf{w}_1, \mathbf{w}_2) = \sum_N \varepsilon_N(R')(\{\mathbf{C}_2(\mathbf{w}_1) \otimes \mathbf{C}_2(\mathbf{w}_2)\}_N \cdot \mathbf{C}_N(\mathbf{n}')). \tag{3}$$

Here $\varepsilon_N(R')$ are the respective energy parameters which are functions of R'; $C_{Mm}(\mathbf{a})$ are the spherical harmonics in Racah's representation; the direct and scalar products of irreducible tensors (such as spherical harmonics) are defined as usual[9]

$$\{\mathbf{C}_K(\mathbf{a}) \otimes \mathbf{C}_L(\mathbf{b})\}_{Mm} \equiv \sum_{klm} C^{Mm}_{Kk,Ll} C_{Kk}(\mathbf{a}) C_{Ll}(\mathbf{b}), \tag{4}$$

$$(\mathbf{C}_K(\mathbf{a}) \cdot \mathbf{C}_K(\mathbf{b})) \equiv \sum_k C_{Kk}(\mathbf{a}) C^*_{Kk}(\mathbf{b}) = P_K(\mathbf{a} \cdot \mathbf{b}), \tag{5}$$

where $C^{Mm}_{Kk,Ll}$ are the Clebsch-Gordan coefficients and P_K is the Legendre polynomial. Among the energy parameters $\varepsilon_N(R')$, the one with $N=4$ is almost entirely due to the electrical quadrupole-quadrupole (EQQ) interaction. The other parameters $\varepsilon_0(R')$, $\varepsilon_2(R')$ as well as the non-EQQ part of $\varepsilon_4(R')$ are one to three orders of magnitude smaller compared to the EQQ part of $\varepsilon_4(R')$. The values of $\varepsilon_N(R')$ as functions of R' can be found in Van Kranendonk's book.[1]

Each of the "crystal-field" terms V_1 in Eq. (2) has the form

$$\begin{aligned} V_{\rm cf} &\equiv V_1(\mathbf{R}', \mathbf{w}_1) + V_1(\mathbf{R}', \mathbf{w}_2) \\ &= B(R')(P_2(\mathbf{n}' \cdot \mathbf{w}_1) + P_2(\mathbf{n}' \cdot \mathbf{w}_2)). \end{aligned} \tag{6}$$

The energy parameter $B(R')$ has two contributions, from the short-range repulsive and long-range attractive forces. The most consistent analysis of the parameter $B(R')$ and the relevant estimates of the contributions can also be found in Van Kranendonk's book.[1]

For the case of heteronuclear molecules we need to refer the whole potentials to the axis which goes through both molecular centers of mass (see Fig. 1). Then the potential in Eq. (1) in the new frame can be expanded in the ratio s/R. Expansion is convenient to perform using the so-called gradient formula, see Appendix A, Eq. (A2). If only the first, isotropic term $v(R')$ in Eq. (1) is taken, this expansion to the second order in s/R is[1]

$$\begin{aligned} v(R') \simeq v(R) &+ \frac{s^2}{3}\left(v'' + \frac{2v'}{R}\right) + V_{11} + \frac{s^2}{3}\left(v'' - \frac{v'}{R}\right) \\ &\times [P_2(\mathbf{n} \cdot \mathbf{w}_1) + P_2(\mathbf{n} \cdot \mathbf{w}_2)] \\ &- sv'[(\mathbf{n} \cdot \mathbf{w}_1) - (\mathbf{n} \cdot \mathbf{w}_2)], \end{aligned} \tag{7}$$

where the prime means differentiation with respect to R and $\mathbf{n}$ denotes the unit vector along the vector between the molecular centers of mass $\mathbf{R} \equiv R\mathbf{n}$. The two first terms in Eq. (7) represent the corrected isotropic potential; the terms in the second and third lines are the crystal-field interactions, respectively, of rank 2 and 1, the former being a correction to the main rank-2 crystal field interaction of Eq. (6). The term V_{11}, which ensures hopping from site to site, can be written as

$$V_{11} = \sum_{N=0,2} \gamma_N(R)(\{\mathbf{C}_1(\mathbf{w}_1) \otimes \mathbf{C}_1(\mathbf{w}_2)\}_N \cdot \mathbf{C}_N(\mathbf{n})). \tag{8}$$

Here the energy parameters $\gamma_N(R)$ are[1] [we introduce the superscript (V) to distinguish from another contribution to the hopping Hamiltonian]

$$\gamma_0^{(V)}(R) = \frac{s^2}{\sqrt{3}}\left(v'' + \frac{2v'}{R_0}\right), \tag{9}$$

$$\gamma_2^{(V)}(R) = s^2\sqrt{\frac{2}{3}}\left(-v'' + \frac{v'}{R_0}\right). \tag{10}$$

Notice that the same combinations of $v(R)$ and v' appear in the other second-order parts of the expansion in Eq. (7).

The heteronuclear hydrogen molecules have nonzero static electric dipole moments and the corresponding dipole-dipole interaction has the same form as the $N=2$ term in Eq. (8). The experimental value of the HD dipole moment μ, as derived from pure rotational spectra of gaseous HD, is[10] $\mu = 8.47 \times 10^{-4}$ D. Theory[11] gives a close value of 8.51×10^{-4} D. The dipole moment evaluated[11] for DT is even smaller (2.83×10^{-4} D). This means that the magnitude of the parameter $\gamma_2^{(\mu)} \sim \mu^2/R^3$ in the respective analog of Eq. (8) is of the order of 10^{-3} cm^{-1}, which, as will be shown below, is three orders of magnitude smaller than that estimated from Eq. (10).

When applied to the EQQ interaction in Eq. (3), the same procedure does not result in terms like Eq. (8). This is because the EQQ Hamiltonian has a special (multipole) form of the type $C_{Nn}(\mathbf{n})/R^{N+1}$. Indeed, as can be verified with the aid of Eq. (A2), expansion of the EQQ interaction leads only to increasing ranks of the spherical harmonics of both arguments $\mathbf{w}_1$ and $\mathbf{w}_2$.

Let us examine the basic rank-2 crystal-field potential of Eq. (6). The energy V_1 itself was, in principle, obtained as a result of an expansion of the isotropic potential in the ratio d/R, where d is half of the internuclear separation r_s in the molecule. The expansion in s/R, considered here, is an independent one and, as such, should be applied to all terms of the expansion in d/R. Contrary to the statement of Van Kranendonk,[12] expansion of this potential $V_{\mathrm{cf}}(\mathbf{R}')$ does result, in particular, in an interaction of the same algebraic type as V_{11} in Eq. (8). Within the frame of our approach we should also include a contribution, which comes from the fourth-order term of the expansion of $V(R')$ in d/R. Our estimates, however, show that these terms result in 3–9% corrections to $\gamma_N^{(V)}$ for HD and therefore may be neglected.

A complete formula for the expansion of Eq. (6) up to second order terms in s/R is given in Appendix A. In this paper we are especially interested in the contribution that is algebraically similar to the hopping interaction V_{11} in Eq. (8). The pertaining energy parameters, defined similarly as in Eqs. (9) and (10), are [we mark them with the superscript (B)]

$$\gamma_0^{(B)} = -\frac{4s^2}{5}\sqrt{\frac{2}{3}}\left(B'' + \frac{2B'}{R_0} - \frac{6B}{R^2}\right), \tag{11}$$

$$\gamma_2^{(B)} = \frac{4s^2}{5\sqrt{3}}\left(B'' + \frac{5B'}{R_0} + \frac{3B}{R^2}\right). \tag{12}$$

Here we note that the contributions to the above and similar quantities from the other terms of the anisotropic interaction potential V_2 in Eq. (3) are nonzero but negligible compared to the respective parameters $\gamma_N^{(V)}$ or $\gamma_N^{(B)}$. Therefore we ignore them in our further considerations.

The parameters $\gamma_N^{(B)}$ in Eqs. (11) and (12) should be summed with the similar quantities that originate from the isotropic potential, Eqs. (9) and (10), to yield the net values of the total γ parameters:

$$\gamma_N = \gamma_N^{(V)} + \gamma_N^{(B)}; \quad N = 0,2. \tag{13}$$

The values of γ_N for HD are given in Table I, both nonrenormalized and renormalized for zero-point lattice vibrations (see Sec. III). One can see that the contribution from the crystal-field interaction, Eq. (6), is quite appreciable and cannot be disregarded.

III. QUANTUM-CRYSTAL RENORMALIZATION OF ENERGY PARAMETERS

In quantum crystals such as any isotopic hydrogen solid the quantities appearing as energy parameters in Hamiltonians should be averaged over zero-point vibrations. We will use the approach suggested by Harris[7] for the evaluation of the operating values of similar energy parameters in solid H_2 and D_2. This approach is based on Nosanow's idea that when calculating the cluster-expansion ground-state energy the exact dynamic problem can be solved to a good approximation by assuming that the particles interact via an effective potential $V_{\mathrm{eff}}(\mathbf{R})$, which can be constructed from the true "bare" potential $V(\mathbf{R})$ as follows:

TABLE I. Renormalized and nonrenormalized values of the energy parameters and renormalization ratios for solid HD. All energies are in cm^{-1}.

Energy parameter	Renormalized	Nonrenormalized	Ratio
V_0	−14.363	−20.682	0.694
RV_0'	−13.673	63.298	−0.216
R^2V_0''	248.829	668.841	0.372
B	1.699	−0.0731	−23.235
RB'	−24.029	−14.207	1.691
R^2B''	404.401	217.683	1.858
$\gamma_0^{(V)}$	0.413	0.241	1.709
$\gamma_2^{(V)}$	−0.621	−0.169	3.679
$\gamma_0^{(B)}$	−0.252	−0.138	1.825
$\gamma_2^{(B)}$	0.149	0.075	1.976
γ_0	0.161	0.103	1.554
γ_2	−0.472	−0.093	5.052

$$V_{\mathrm{eff}}(\mathbf{R}) \equiv \frac{\langle V(\mathbf{R})\rangle}{\langle 1\rangle}, \tag{14}$$

where the averaging operator is defined as

$$\langle\cdots\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \cdots \phi^2(|\mathbf{r}_1 - \mathbf{R}'|)\phi^2(|\mathbf{r}_2 - \mathbf{R} + \mathbf{R}'|)f^2(r_{12}) \tag{15}$$

(see Fig. 1). The functions in Eq. (15) are chosen in the form

$$\phi(r) = (A/\pi)^{3/4}\exp(-Ar^2/2), \tag{16}$$

$$f(r) = \exp[-\kappa V(r)], \tag{17}$$

where the function $\phi(r)$ accounts for the spread of the wave function and $f(r)$ does not allow the isotropic potential to become unphysically large as r tends to zero. The constants A and κ have been found[13] for H_2 and D_2 by minimizing the ground-state energy of the crystal. We note here that the constant κ may be considered[7] independent of the hydrogen molecule species. However, since we use an interaction potential[14] different from the Lennard-Jones one used by Harris, we put in Eq. (17) the constant κ instead of K used by Harris assuming a Lennard-Jones potential. The constant κ, which is expected to vary but slightly from one isotopomer to another, has been recalculated from the $K=0.2406$ value:

$$\kappa = \frac{K}{4\varepsilon} = 0.0023405, \tag{18}$$

where ε is the Lennard-Jones energy constant for the hydrogen molecule. The parameters A in Eq. (16) for HD ($AR^2=52.51$) and DT ($AR^2=69.44$) were chosen assuming the quantity $RA^{-1/2}$ to be a linear function of the molecular mass and based on the respective values[7] $AR^2=46.5$ for H_2 and 60.5 for D_2. Variation of A within a reasonable interval does not change qualitatively the final results. The equilibrium spacing R in zero-temperature zero-pressure solid HD with

TABLE II. Renormalized and nonrenormalized values of the energy parameters and renormalization ratios for solid DT. All energies are in cm^{-1}.

Energy parameter	Renormalized	Nonrenormalized	Ratio
V_0	−15.768	−22.766	0.693
RV_0'	−32.27	44.819	−0.720
R^2V_0''	955.331	648.51	1.473
B	2.353	0.627	3.755
RB'	−31.996	−23.436	1.365
R^2B''	698.846	313.403	2.230
$\gamma_0^{(V)}$	0.222	0.184	1.207
$\gamma_2^{(V)}$	−0.349	−0.213	1.636
$\gamma_0^{(B)}$	−0.175	−0.074	2.362
$\gamma_2^{(B)}$	0.109	0.0396	2.756
γ_0	0.0471	0.110	0.428
γ_2	−0.240	−0.174	1.381

account of the 1% deviation from $\sqrt{8/3}$ of the c/a ratio at zero temperature was chosen to be an average of two values[15] (in-plane and out-of-plane shortest distances) $R = 3.701$ Å. The nearest-neighbor distance for solid DT, $R = 3.564$ Å, was estimated from the DT molar volume as quoted by Souers.[16]

In our calculations we employed the energy parameters of the isotropic interaction potential as suggested by Silvera and Goldman.[14] Estimates obtained with a more accurate recent isotropic potential[17] do not deviate significantly from all the relevant values shown in Tables I and II. The energy parameters for the function $B(R)$ in Eq. (6) were taken from Ref. 1. Details of the renormalization procedure can be found in Appendix B.

In Tables I and II we compare the nonrenormalized and renormalized values of the basic energy functions $V(R)$ and $B(R)$ as well as their first and second derivatives for HD and DT, respectively. The general conclusion is that the renormalization ratios are appreciable for both isotopes and for all the energy parameters considered. For RV' and B in HD and for RV' in DT the renormalized values even have an opposite sign. This is because those quantities are close to zero for the respective equilibrium R values; the averaging procedure with a comparatively broad probability function $\phi(R)$ brings in contributions of the predominantly opposite sign from the region (with $r<R$) where both functions are steeper than left of the point R. The contributions $\gamma_N^{(B)}$ from the crystal-field energy to the total γ_N are in all cases opposite in sign to $\gamma_N^{(V)}$.

Knowing γ_N, we can calculate the dispersion law for the $J=1$ roton excitation. The wave function of the rotational ground state of solid HD can be written as a product of the individual $J=0$ single-particle wave functions

$$\Psi_{\mathrm{GS}} = \prod_i |0,i\rangle, \tag{19}$$

where i numerates the molecules. Let $|1m,j\rangle$ denote the state in which molecule j is in the excited state with $J=1$ and $J_z = m$ where $m=1,0,-1$. If no coupling between rotational momenta is present, the total state with a single $J=1$ excitation at j is described by the wave function

$$\Psi_{\mathrm{EX}} = |1m,j\rangle \prod_{i\neq j} |0,i\rangle. \tag{20}$$

In the presence of the anisotropic interaction V_{11} like that in Eq. (8) with γ_N as in Eq. (13), the correct delocalized excited state $|1m\rangle$ can be written as

$$|1m\rangle \Rightarrow \sum_{i,\alpha} \sum_{m=-1}^{1} U_m(\mathbf{R}_{i\alpha})|1m,\mathbf{R}_{i\alpha}\rangle. \tag{21}$$

Here $U_m(\mathbf{R}_{i\alpha})$ is the wave function describing the hopping motion of the $J=1$ excitation through the crystal and we took explicitly into account the actual (hcp) structure of both HD and DT by virtue of which the lattice vector carries the elementary cell number J and the sublattice label α. According to Bloch's theorem the wave function U can be written in the form

$$U_m(\mathbf{R}_{j\alpha}) = A_{m\alpha}(\mathbf{k})e^{i(\mathbf{k}\cdot\mathbf{R}_{j\alpha})}. \tag{22}$$

The amplitudes A are the solutions to the set of secular equations[1]

$$\sum_{m'\alpha'} H_{m\alpha,m'\alpha'}(\mathbf{k})A_{m'\alpha'}(\mathbf{k}) = E(\mathbf{k})A_{m\alpha}(\mathbf{k}), \tag{23}$$

where

$$H_{m\alpha,m'\alpha'}(\mathbf{k}) = \sum_j \langle 1m,\mathbf{R}_{0\alpha}|V_{11}|1m',\mathbf{R}_{j\alpha'}\rangle e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_0)} \tag{24}$$

with V_{11} from Eq. (8). In the nearest-neighbor approximation we have

$$H_{m\alpha,m'\alpha'}(\mathbf{k}) = \frac{1}{3}\sum_j e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_0)} \times \left[\gamma_2(-1)^{m'} C^{2m-m'}_{1m1m'} C^*_{2m-m'}(\mathbf{n}_{j\alpha}) - \frac{\gamma_0}{\sqrt{3}}\Delta(m-m')\right]. \tag{25}$$

This matrix element simplifies for the case $\mathbf{k}\| z$. Then

$$H_{m\alpha,m'\alpha'}(\mathbf{k}) = \Delta(m-m')h_{m\alpha,m'\alpha'}, \tag{26}$$

where $(\beta\neq\alpha)$

$$h^{(m)}_{\alpha\alpha} = -\frac{2\gamma_0}{\sqrt{3}} - \frac{\gamma_2}{\sqrt{6}}\frac{3(-1)^m+1}{2}, \tag{27}$$

$$h^{(m)}_{\alpha\beta} = \left[-\frac{2\gamma_0}{\sqrt{3}} + \frac{\gamma_2}{\sqrt{6}}\frac{3(-1)^m+1}{2}\right]\Phi(k_z). \tag{28}$$

Here $\Phi(k_z) = \cos k_z c/2$ and c is the lattice parameter along axis z. Now the dispersion law can be found in analytical form:

$$E_0^{(+)} = -\frac{2}{\sqrt{3}}\left[\left(\gamma_0 + \frac{\gamma_2}{\sqrt{2}}\right) - \left(\gamma_0 - \frac{\gamma_2}{\sqrt{2}}\right)\Phi(k_z)\right], \tag{29}$$

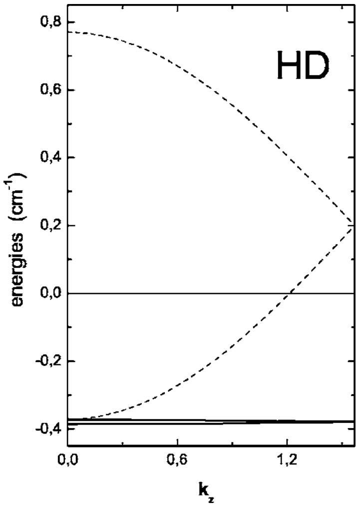

FIG. 2. The dispersion curve for the $J=1$ roton excitation in solid HD. The wave vector $\mathbf{k}$ is parallel to the crystallographic axis c. The thick lines are for twofold degenerate modes; the dot lines are for nondegenerate modes.

$$E_{\pm1}^{(+)} = -\frac{1}{\sqrt{3}}\left[\left(2\gamma_0 - \frac{\gamma_2}{\sqrt{2}}\right) - \left(2\gamma_0 + \frac{\gamma_2}{\sqrt{2}}\right)\Phi(k_z)\right], \tag{30}$$

$$E_{0}^{(-)} = -\frac{2}{\sqrt{3}}\left[\left(\gamma_0 + \frac{\gamma_2}{\sqrt{2}}\right) + \left(\gamma_0 - \frac{\gamma_2}{\sqrt{2}}\right)\Phi(k_z)\right], \tag{31}$$

$$E_{\pm1}^{(-)} = -\frac{1}{\sqrt{3}}\left[\left(2\gamma_0 - \frac{\gamma_2}{\sqrt{2}}\right) + \left(2\gamma_0 + \frac{\gamma_2}{\sqrt{2}}\right)\Phi(k_z)\right]. \tag{32}$$

Here the subscript denotes the cyclic z-projection of the rotational momentum; the superscript denotes the parity under the inversion in the midpoint between two nearest neighbors from different adjacent hexagonal planes. The positive-parity mode is triply degenerate at $\mathbf{k}=0$. The infrared active negative-parity excitation with $E_{\pm1}^{(-)}$ was observed[18–20] in IR spectra of solid HD, the absorption coefficient agreeing well with theoretical estimates.[21] The combination

$$2\gamma_0 + \frac{\gamma_2}{\sqrt{2}}$$

proves for HD to be two orders of magnitude smaller compared to the other three combinations in Eqs. (29)–(32), which results in two doubly degenerate virtually dispersionless branches (see Fig. 2). The dispersion curves lie (Fig. 2) between the two $\mathbf{k}=0$ extremes, $E_0^{(+)}(0)$ and $E_0^{(-)}(0)$, i.e., the density of states is concentrated around the center of the band. The width of the $J=1$ roton band, δE, for HD is

$$\delta E = |E_0^{(-)}(0) - E_0^{(-)}(\pm 1)| = \sqrt{6}\gamma_2, \tag{33}$$

which amounts to 1.16 cm^{-1} in solid HD. The $J=1$ roton bandwidth in solid DT is almost twice as narrow (about 0.59 cm^{-1}). It is interesting that the energy position of the IR-active mode $E_{\pm1}^{(-)}$ equal in solid HD to -0.385 cm^{-1} is in qualitative agreement with the negative shift (-0.28 cm^{-1}) suffered by the infrared line $R(0)$ when crossing the melting point from liquid to crystal.[20]

IV. CONCLUSIONS

It is shown that a substantial contribution to the specific anisotropic interaction components, caused by the asymmetry of HD and DT molecules and which are important for the rotational (orientational) and translational dynamics of these solids, comes from the crystal field of rank 2. The relevant energy parameters for both specific anisotropic interaction components have been evaluated and renormalized to account for zero-point translational vibrations in these quantum crystals. The renormalized values of all energy constants (parameters) differ substantially from the initial nonrenormalized values. Exemplary dispersion curves have been calculated for the $J=1$ roton excitation for solid HD and DT; the corresponding bandwidths are found to be 1.16 cm^{-1} for HD and 0.59 cm^{-1} for DT.

ACKNOWLEDGMENTS

The author thanks R. J. Hemley for drawing his attention to the unusual optical properties of the heteronuclear hydrogen solids and for stimulating discussions. Financial support of CRDF (Grant No. UP2-2445-KH-02) and NSF is acknowledged.

APPENDIX A: EXPANSIONS

Since we deal with Hamiltonians, that is, scalars or tensors of rank 0, it is convenient to transform the known gradient formula[9,22] to another form. Algebraically, in virtue of being a scalar, any Hamiltonian can be represented as a sum of the following terms:

$$H = F(r)(\mathbf{C}_l(\mathbf{m}) \cdot \mathbf{T}_l), \tag{A1}$$

where $\mathbf{r}=r\mathbf{m}$ is the distance radius vector and $\mathbf{T}_l$ is a rank-l irreducible tensor independent of $\mathbf{r}$. In our case (see definitions in Sec. II) $\mathbf{r}=\mathbf{R}'=\mathbf{R}+\mathbf{a}$ where the vector $\mathbf{a}=s(\mathbf{w}_2-\mathbf{w}_1)$ is small. Application of the standard gradient formula[8] to H in Eq. (A1) gives for the first-order correction

$$\begin{aligned}\sum_{\mu} a_\mu (\nabla H)^\mu = {} & \sqrt{\frac{l+1}{2l+1}}\left(F' - \frac{l}{R}F\right)(\mathbf{C}_{l+1}(\mathbf{n}) \cdot \{\mathbf{a} \otimes \mathbf{T}_l\}_{l+1}) \\ & - \sqrt{\frac{l}{2l+1}}\left(F' + \frac{l+1}{R}F\right) \\ & \times (\mathbf{C}_{l-1}(\mathbf{n}) \cdot \{\mathbf{a} \otimes \mathbf{T}_l\}_{l-1}),\end{aligned} \tag{A2}$$

where μ denotes cyclic coordinates. Further expansion can be performed by applying the same formula.

The relevant expansion[12] for the isotropic interaction energy $v(R')$ is given above in Eq. (7). Expansion of the crystal-field energy, Eq. (6), can be performed in a similar way with the aid of the gradient formula, Eq. (A2). After some algebra we obtain the following expression:

$$V_{\mathrm{cf}}(R') = V_{\mathrm{cf}}^{(0)} + V_{\mathrm{cf}}^{(1)} + V_{\mathrm{cf}}^{(2)}. \tag{A3}$$

Here $V_{\mathrm{cf}}^{(0)} = V_{\mathrm{cf}}(R)$, where R is the nearest-neighbor distance (between centers of mass). The other two terms are the first-order and second-order corrections in s/R. The former can be represented in the form

$$V_{\mathrm{cf}}^{(1)} = \sum_{N=1,3} \epsilon_N^{(1)} (\mathbf{T}_N^{(1)}(\mathbf{w}_1,\mathbf{w}_2) \cdot \mathbf{C}_N(\mathbf{n})), \tag{A4}$$

where

$$\epsilon_1^{(1)} = -\sqrt{\frac{2}{5}}\frac{s}{R}(RB' + 3B), \tag{A5}$$

$$\epsilon_3^{(1)} = \sqrt{\frac{3}{5}}\frac{s}{R}(RB' - 2B), \tag{A6}$$

and

$$\mathbf{T}_3^{(1)}(\mathbf{w}_1,\mathbf{w}_2) = \{\mathbf{C}_2(\mathbf{w}_1) \otimes \mathbf{w}_2\}_3 - \{\mathbf{C}_2(\mathbf{w}_2) \otimes \mathbf{w}_1\}_3 + \sqrt{3/5}[\mathbf{C}_3(\mathbf{w}_2) - \mathbf{C}_3(\mathbf{w}_1)], \tag{A7}$$

$$\mathbf{T}_1^{(1)}(\mathbf{w}_1,\mathbf{w}_2) = \{\mathbf{C}_2(\mathbf{w}_1) \otimes \mathbf{w}_2\}_1 - \{\mathbf{C}_2(\mathbf{w}_2) \otimes \mathbf{w}_1\}_1 - \sqrt{2/5}[\mathbf{w}_2 - \mathbf{w}_1]. \tag{A8}$$

The second-order term $V_{\mathrm{cf}}^{(2)}$ is more complicated than $V_{\mathrm{cf}}^{(1)}$ or the second-order term in the expansion of the isotropic interaction potential, Eqs. (7) and (8). We give below $V_{\mathrm{cf}}^{(2)}$ in complete form without separating it into irreducible tensor components:

$$V_{\mathrm{cf}}^{(2)} = \sum_{M=1,3;\ N=0,2,4} \Phi_{MN}(R) T_{MN}(\mathbf{w}_1,\mathbf{w}_2). \tag{A9}$$

Here

$$T_{MN} = (\{\{\mathbf{C}_2(\mathbf{w}_1) + \mathbf{C}_2(\mathbf{w}_2) \otimes \mathbf{a}\}_M \otimes \mathbf{a}\}_N \cdot \mathbf{C}_N(\mathbf{n})), \tag{A10}$$

where, again, $\mathbf{a}=s(\mathbf{w}_2-\mathbf{w}_1)$ and the following R-dependent components are nonzero:

$$\Phi_{10}(R) = \sqrt{\frac{1}{30}}s^2\left(B'' + \frac{5B'}{R} + \frac{3B}{R^2}\right); \tag{A11}$$

$$\Phi_{12}(R) = -\sqrt{\frac{1}{15}}s^2\left(B'' + \frac{2B'}{R} - \frac{6B}{R^2}\right); \tag{A12}$$

$$\Phi_{32}(R) = -\sqrt{\frac{9}{140}}s^2\left(B'' + \frac{2B'}{R} - \frac{6B}{R^2}\right); \tag{A13}$$

$$\Phi_{34}(R) = \sqrt{\frac{3}{35}}s^2\left(B'' - \frac{5B'}{R} + \frac{8B}{R^2}\right). \tag{A14}$$

Separation of the relevant hopping Hamiltonian of the form similar to that in Eq. (8) is performed routinely to yield the energy parameters as given in Eqs. (11) and (12).

APPENDIX B: DERIVATIVES OF EFFECTIVE POTENTIALS

The potential energy of a molecular crystal, which is a scalar, can be represented in the form

$$E(\{\mathbf{R}\}) = 1/2\sum_{ij}\sum_{Ll} T_{Ll}^{*}(\{\mathbf{a}\}) V_L(R_{ij}) C_{Ll}(\mathbf{n}_{ij}), \tag{B1}$$

where $\mathbf{R}_{ij}=R_{ij}\mathbf{n}_{ij}$ is the intermolecular radius vector and $T_{Ll}^{*}(\{\mathbf{a}\})$ is an l-component of a tensor of rank L and neither T nor its vector arguments $\mathbf{a}$ depend on the intermolecular distance. As shown by Harris,[7] application of the averaging procedure of Eqs. (15)–(17) to any term from Eq. (B1) with different L and l, namely, $V_L(R)C_{Ll}(\mathbf{n})$ results in an effective quantity of the form

$$U_{\mathrm{eff}}(\mathbf{R}) = \widetilde{V}_L(R) C_{Ll}(\mathbf{n}) \tag{B2}$$

with

$$\widetilde{V}_L(R) = \langle 1\rangle^{-1}\hat{M}_L[V(R)]. \tag{B3}$$

The operation

$$\hat{M}_N[\cdots] = \frac{A^{3/2}}{\sqrt{2\pi}}\int_0^\infty r^2 dr f^2(r) \times \int_{-1}^{1} P_N(x)\cdots \exp\left[-\frac{1}{2}A^2(r^2+R^2-2Rrx)\right], \tag{B4}$$

where $P_N(x)$ is the Legendre polynomial, was derived by proceeding[7] from Eqs. (15)–(17). Notice that in Eq. (B2) the averaging with the weight functions specified above does not affect the angular dependence of the anisotropic interaction, if it is represented by an irreducible tensor of a unique rank.

Following Harris' reasonings,[7] the effective derivatives of the potentials are to be found as derivatives of the effective potential in Eq. (B2) rather than applying a similar averaging procedure to the derivatives of the source, nonrenormalized potential in Eq. (B1). Then, by applying the gradient formula to the effective potential we can obtain the corresponding expression where only functions of R should be averaged in a proper way, like in Eq. (B2). We thus arrive at the following expression for the first derivative (Harris' formula[7] in a different representation)

$$R\frac{\partial\widetilde{V}_n(R)}{\partial R} = \frac{AR^2}{\langle 1\rangle}\left\{\frac{n+1}{2n+1}\hat{M}_{n+1}\left[\frac{r}{R}V_n\right] + \frac{n}{2n+1}\hat{M}_{n-1}\left[\frac{r}{R}V_n\right] - \widetilde{V}_n(R)\hat{M}_1\left[\frac{r}{R}\right]\right\}. \tag{B5}$$

Here A is defined in Eq. (16); V_n is the R-dependent parameter appearing in the initial (nonrenormalized) potential together with the rank-n spherical harmonic.

Then, continuing the procedure, we derive the expression for the second derivative of the effective potential in the same way as the first derivative above

$$R^2\frac{\partial^2\widetilde{V}_n(R)}{\partial R^2} = \frac{A^2R^4}{\langle 1\rangle}\left\{\frac{(n+1)(n+2)}{(2n+1)(2n+3)}\hat{M}_{n+2}[(r/R)^2V_n] + \frac{2n^2+2n-1}{(2n-1)(2n+3)}\hat{M}_n[(r/R)^2V_n]\right\} + \frac{A^2R^4}{\langle 1\rangle}\frac{n(n-1)}{(2n+1)(2n-1)}\hat{M}_{n-2}[(r/R)^2V_n] - \frac{AR^2}{\langle 1\rangle}\hat{M}_1[(r/R)]R\frac{\partial\widetilde{V}_n(R)}{\partial R} - \frac{A^2R^4}{3\langle 1\rangle^2}\widetilde{V}_n(R)\{2\hat{M}_2[(r/R)^2]+\hat{M}_0[(r/R)^2]\}. \qquad \text{(B6)}$$

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