

Variation of intermolecular interaction and local lattice distortion of parahydrogen crystals upon vibrational excitation

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When a hydrogen molecule in a parahydrogen crystal is excited to a high vibrational overtone state, its electronic properties vary significantly since the energy of excitation is a sizable fraction of the energies of the excited electronic states. Thus the vibrational excitation leads to a significant variation of the intermolecular potential and resultant local distortion of the crystal lattice. Such an effect is sensed by the variation of the splitting of M sublevels of the $J=1$ H_2 impurity that causes the overtone transition. In this paper we attempt to theoretically explain the observed large variations of the pair and crystal-field splitting parameters ΔB and ε_{2c} upon the $v=3\leftarrow 0$ vibrational excitation. Using the *ab initio* anisotropic intermolecular pair potential and simplified models on the vibrational dependence of the potential and crystal distortion, observed values are well explained. [S0163-1829(98)04901-7]

I. INTRODUCTION

In the preceding paper¹ (which will be referred to as paper I hereafter) on the high-resolution spectroscopy of the $Q_3(0)$ transition ($v=3\leftarrow 0$, $J=0\leftarrow 0$) in para- H_2 crystals, a group of sharp spectral lines with an intricate structure is observed. Groups of sharp spectral lines with similar structure were also reported by Weliky *et al.*^{2,3} on the $Q_1(0)$ transitions ($v=1\leftarrow 0$, $J=0\leftarrow 0$) of D_2 and HD impurities in para- H_2 crystals. The sharpness of these spectral lines demonstrated the highly localized nature of the vibrational excitations (vibrons) in those systems, and the analysis of the well resolved structure has given a most decisive confirmation of the mechanism of the $Q_v(0)$ transitions initially proposed by Sears and VanKranendonk.⁴ In their theory the averaged quadrupolar electric field of a $J=1$ orthohydrogen “impurity,” which remains in the otherwise pure para- H_2 crystal, induces a small dipole moment in the surrounding $J=0$ para- H_2 molecules. One of the $J=0$ H_2 is excited to the vibrationally excited state via the induced dipole moment, and the $J=1$ H_2 makes a simultaneous orientational transition $J=1$, $M'\leftarrow J=1$, M between M sublevels of the $J=1$ rotational state. These M sublevels are degenerate in free space but are split in the crystal and thus cause the observed fine structure.

In analyzing the splitting of the M sublevels we used a simplified model based on the following three assumptions: (a) We treat the total interaction in the crystal as the assembly of pairwise intermolecular interactions. (b) Anisotropic dispersion is the main interaction giving rise to the observed splittings. This is valid owing to the fact that dispersion provides the major binding energy of the crystal, and that in the solid, the molecules interact on a point that is beyond the point of inflection of the intermolecular potential, thus attractive dispersion is still the major force governing intermolecular interactions.⁵ (c) We assume as the zeroth order approximation that the positions of lattice sites do not vary upon vibrational excitation. Under these assumptions the angle-dependent interaction between the crystal field and

a $J=1$ H_2 is expressed by a two parameter Hamiltonian^{1,2}

$$H = \varepsilon_{2c} C_{20}(\Omega) + \Delta B C_{20}(\omega), \quad (1)$$

where $C_{20}(\Omega)$ and $C_{20}(\omega)$ are Racah spherical harmonics⁵ with angle variables Ω and ω of the $J=1$ H_2 with respect to the crystal c axis and the pair axis, respectively. The first term represents the anisotropy of the crystal field while the second term represents the breakdown of the D_{3h} symmetry of the system due to vibrational excitation on one of the $J=0$ H_2 surrounding the $J=1$ H_2 .

Experimentally determined anisotropic parameters ε_{2c} and ΔB based on Eq. (1) are listed in Table I. Values for D_2 and HD impurity transitions reported by Weliky *et al.*² are also listed for comparison. If the two simplifying assumptions (a) and (c) mentioned above are valid to good approximations, the value of ε_{2c} should not change upon vibrational excitation or isotopic substitution. The data summarized in Table I clearly demonstrate that this is not the case. For the

TABLE I. Experimentally determined pair and crystal-field parameters using Eq. (1).

| Quantum state | Pair type | ΔB (cm ⁻¹) | ε_{2c} (cm ⁻¹) |
|--------------------------------------|-----------|--------------------------------|--|
| $Q_3(0)$ Transitions in H_2 | | | |
| $v=0$ H_2 | | 0 | -0.0118 |
| $v=3$ H_2 | NN ip | -0.8037 | +0.0250 |
| | NN op | -0.7730 | -0.0562 |
| | NNN | -0.0428 | -0.0298 |
| $Q_1(0)$ Transitions in D_2 and HD | | | |
| $v=0$ D_2 | NN ip | -0.2042 | -0.0160 |
| | NN op | -0.2269 | +0.0400 |
| $v=1$ D_2 | NN ip | -0.3923 | -0.0128 |
| | NN op | -0.4075 | +0.0175 |
| $v=0$ HD | NN ip | -0.1052 | -0.0128 |
| | NN op | -0.1194 | +0.0189 |
| $v=1$ HD | NN ip | -0.3300 | -0.0097 |
| | NN op | -0.3292 | -0.0160 |

$Q_3(0)$ transition of H_2 , for example, all ε_{2c} values in the $v=3$ excited state are larger in magnitude than is the ε_{2c} in the ground state. ε_{2c} even changes sign depending on whether the $J=1$ H_2 and the vibrationally excited nearest-neighbor $J=0$ H_2 are in the same hexagonal plane (in plane denoted by ip) or out of the hexagonal plane (op). Variations in ε_{2c} of similar magnitude were noted upon isotopic substitution and vibrational excitation for the $Q_1(0)$ transitions of D_2 and HD impurities and were ascribed by Weliky *et al.*² to the breakdown of the third assumption (c). The introduction of heavy isotopes at a lattice site causes a local lattice distortion. Although the magnitude of the distortion is very small, the value of ε_{2c} changes drastically because the small value of ε_{2c} results from the ‘‘accidental’’ exact cancellation of the large pair interactions for the nearest neighbor and next-nearest-neighbor shells in a hcp crystal.^{6,7} A small lattice distortion off balances this cancellation effect and appears as a large relative variation of ε_{2c} . Using this idea, Weliky was able to qualitatively explain the trends of ε_{2c} variation upon vibrational excitation of the hydrogenic isotopes.

The purpose of our present paper is to study the effect of vibrational excitation on local lattice distortion and to explain quantitatively the variation of the crystal-field splitting parameter ε_{2c} upon the vibrational excitation $v=3 \leftarrow 0$ in $J=0$ H_2 . This system is much simpler than are the systems with D_2 or HD impurities since the mass of its constituents is homogeneous and no static or dynamic distortion effects caused by mass differences are involved. The ground state retains the D_{3h} symmetry around the $J=1$ H_2 , and the splitting between $M=\pm 1$ and $M=0$ sublevels is exactly determined.⁸ This allows us to concentrate on the symmetry-breaking local lattice distortion and the variation of ε_{2c} upon vibrational excitation alone.

In studying the variation of intermolecular interactions upon vibrational excitation, recent extensive high-resolution spectroscopy of hydrogen dimers by McKellar⁹ lends very useful insight. The accurate rotational constants determined for each of the possible isotopic dimer pairs except $(H_2)_2$ reflect subtle changes of the intermolecular potential and distance upon vibrational excitation. We also heavily rely on the anisotropic intermolecular potential given by the *ab initio* calculation of Mulder, van der Avoird, and Wormer,¹⁰ as modified by VanKranendonk.⁵

We use a static model in the calculation of level splittings; neither phonon renormalization¹¹ nor dynamical phonon effects^{12,13} are considered. This is due to our experience that the level splitting for $J=1$ (Ref. 8) and $J=6$ (Ref. 14) rotational states in the ground vibrational state were explained very well by the static model employing the *ab initio* potential.

II. THEORETICAL MODEL

A. Anisotropic intermolecular interaction

We base our calculation on the *ab initio* anisotropic intermolecular potential reported by Mulder and co-workers¹⁰ and modified slightly by VanKranendonk (Ref. 5, p. 41). The angle-dependent intermolecular potential between two hydrogen molecules 1 and 2 is expressed in the general form as

$$V(\omega_1, \omega_2, R) = - \sum_n \sum_{l_1, l_2, m} \gamma_n^{l_1, l_2, m} C_n R^{-n} P_{l_1}^m(\cos \theta_1) \times P_{l_2}^m(\cos \theta_2) \cos[m(\phi_1 - \phi_2)], \quad (2)$$

where the $P_l^m(\cos \theta)$ are associated Legendre polynomials, R is the intermolecular distance, γ and C are constants, and $n=6, 8, 10$. For the discussion of anisotropic interactions between $J=1$ H_2 and $J=0$ H_2 , the only relevant terms of Eq. (2) are

$$V(\omega_1, \omega_2, R) = - \sum_n \gamma_n^{200} C_n R^{-n} C_{20}(\omega) \equiv B(R) C_{20}(\omega), \quad (3)$$

where ω represents the angle variables of $J=1$ H_2 with respect to the pair axis. Mulder *et al.* have given numerical values of C_n and γ_n^{200} separately for dispersion ($n=6, 8, 10$) and induction ($n=8, 10$) interactions. VanKranendonk modified the values of C_n slightly so that they agree better with experimental and other theoretical results [see Eq. (2.64) of Ref. 5]. We use this modified potential in which the coefficient $B(R)$ in cm^{-1} is expressed as

$$-B(R) = 2.249 \left(\frac{R_0}{R} \right)^6 + (1.553 + 0.073) \left(\frac{R_0}{R} \right)^8 + (0.720 + 0.026) \left(\frac{R_0}{R} \right)^{10}, \quad (4)$$

where $R_0 = 3.783 \text{ \AA}$ (Ref. 15) is the equilibrium nearest-neighbor distance and the two numbers in parentheses are for dispersion and induction interactions, respectively. This potential best represents the long-range attractive part of the intermolecular interaction but its use for our problem is justified for the following three reasons.

(i) The equilibrium intermolecular distance in para- H_2 crystals, 3.783 \AA , is much larger than the equilibrium distance in the isotropic pair potential, 3.41 \AA .^{16,17}

(ii) The average intermolecular distance in the solid corresponds to an attractive point in the intermolecular potential where attractive dispersion is the dominant intermolecular force as described in the Introduction.

(iii) The intermolecular interaction between $J=1$ H_2 and $J=0$ H_2 is not fully anisotropic, that is, it does not depend on the angular variables of both molecules. In addition to the attractive part of the potential, molecules also sense the repulsive part of the potential due to their large mean amplitude within the lattice phonons, indicative of a quantum crystal.¹⁸ Renormalization treatments of this effect such as that reported by Koshenev¹⁹ are outside the scope of this paper.

The two numbers in parentheses of Eq. (4) clearly show that dispersion is the dominant interaction causing the anisotropy. The small effect of induction may be expressed by the less accurate but more explicit classical formula,

$$V_{\text{ind}} = - \frac{12}{5} \frac{\alpha Q^2}{R^8} C_{20}(\omega), \quad (5)$$

where α (5.414 a.u.) is the isotropic polarizability and Q (0.4835 a.u.) is the permanent electric quadrupole moment of

H_2 in the ground rovibrational state, $v=J=0$, both of which were theoretically calculated by Kolos and Wolniewicz.²⁰ This formula gives the induction portion of the anisotropy to be $-0.098C_{20}(\omega)$, in agreement with $-0.099C_{20}(\omega)$ given in Eq. (4), which we use in our analysis.

Other than the dispersion interaction, the electric quadrupole-quadrupole interaction between H_2 molecules is the largest angle-dependent Hamiltonian in the analysis of many transitions. For the pair of $J=1$ H_2 and $J=0$ H_2 , however, this term does not contribute in first order and its second-order energy is on the order of the induction energy. For completeness, we write this energy in an operator form to be averaged by $|1M\rangle$ as

$$V_{\text{EQQ}} = \frac{Q_1^2 Q_2^2}{5R^{10}} \sum_{J=1,3} \sum_m \binom{4}{2+m}^2 \times \frac{|C_{2m}(\omega)\langle J, M-m \rangle \langle J, M-m | C_{2\bar{m}}(\omega)|}{[2-J(J+1)]B_1 - 6B_2}, \quad (6)$$

where Q and B are the electric quadrupole moment and the rotational constant, respectively, and $\binom{4}{2+m}$ is the binomial factor $4! / [(2+m)!(2-m)!]$. ω in Eq. (6) represents the angle variables of $J=1$ H_2 as in Eqs. (3)–(5).

B. Variation of the intermolecular potential upon vibrational excitation

When the $J=0$ H_2 is excited from the ground state to the $v=3$ state, various molecular constants change significantly since the energy of the vibrational excitation, $11\,758\text{ cm}^{-1} \sim 1.46\text{ eV}$, is a sizable fraction of the electronic energy. This leads to a considerable variation of the intermolecular potential and distance. The variations of the interactions discussed above are estimated as follows.

We estimate the variation of the most dominant dispersion by using London's approximate formula.²¹ It is convenient to use the extended London formula reported by Buckingham²² for the interaction between two linear molecules, the relevant part of which is written as

$$V_{\text{disp}} = -\frac{3I_1 I_2}{2(I_1 + I_2)} \frac{1}{R^6} \left[\alpha_1 \alpha_2 + \frac{1}{3} \gamma_1 \alpha_2 C_2(\omega) + \dots \right], \quad (7)$$

where I (15.43 eV) and γ , the difference between the parallel and perpendicular polarizabilities (2.024 a.u.),² are the ionization potential and the anisotropic polarizability, respectively. London's formula significantly underestimates the absolute value of the dispersion energy, but we assume that it reproduces relative variations more accurately.²³ Upon the vibrational excitation $v=3 \leftarrow 0$, the isotropic polarizability of the $J=0$ H_2 , α_2 , increases by 27.0% from 5.414 to 6.878 a.u. (Ref. 20) and the ionization potential I_2 decreases by 9.4% from 15.43 to 13.97 eV resulting in the overall increase by 22.3% of the dispersion energy for both the first (isotropic) and the second (anisotropic) terms of Eq. (7).

The explicit formulas, Eqs. (5) and (6), allow us to estimate the variation of these interactions more directly. The variation of the induction energy, V_{ind} , is simply due to the 27% increase of the isotropic polarizability, α . The variation of the second-order EQQ interaction V^{EQQ} is due to the

31.4% increase of the quadrupole moment Q_2 from 0.4841 to 0.6362 a.u. (Ref. 24) and the 15.5% decrease of the rotational constant B_2 from 59.25 to 50.06 cm^{-1} ; the latter value was determined from our observed frequencies of the $S_3(0)$ transition²⁵ and the $Q_3(0)$ transition.¹

C. Local lattice distortion upon vibrational excitation

The 22.3% increase of the isotropic dispersion energy [the first term in Eq. (7)] increases the attraction between the excited $v=3$ $J=0$ H_2 and the surrounding molecules and distorts the local lattice. [We ignore the similar effect by the $J=1$ H_2 since the difference between isotropic polarizabilities of $J=1$ and $J=0$ H_2 is only 0.18% (Ref. 2)]. There is a reverse effect due to the increased molecular size and mean amplitude of vibration upon vibrational excitation which, with the repulsive part of the potential, tends to *repel* the surrounding H_2 molecules away from the vibrationally excited H_2 . While the former effect contracts the local lattice sites, this latter effect will expand the crystal. We do not know which of the two effects is stronger. Here McKellar's experimental data⁹ on hydrogen dimers gives helpful insight. The rotational constants of $H_2\text{-D}_2$ and HD-D_2 dimers increase by 1.0% (from 0.685 to 0.692 cm^{-1}) and 0.7% (from 0.569 to 0.573 cm^{-1}) upon vibrational excitations $v=1 \leftarrow 0$ of H_2 and HD, respectively, indicating that the dimers contract upon the vibrational excitations. Since McKellar does not report data for $H_2\text{-H}_2$ and his data for HD-HD and $\text{D}_2\text{-D}_2$ do not show meaningful variation, we cannot conclude contraction simply from his data. Moreover, the many-body nature of molecular interactions in solids and the large difference in intermolecular distance between the solid and gas make such arguments tentative. Nevertheless, McKellar's results suggest that contraction does occur upon vibrational excitation.

Here we theoretically calculate the variation of our crystal-field parameter ε_{2c} upon vibrational excitation and let our experimentally determined $\Delta\varepsilon_{2c}$ discriminate between contraction or expansion of the local lattice. We assume the following simplified model of the lattice distortion:

(1) The positions of H_2 around the vibrationally excited $J=0$ H_2 contract or expand radially. That is, if we specify the positions of the surrounding molecules with respect to the excited molecule by intermolecular distance R_{1i} and angle variable Ω_{1i} , then $\Delta\Omega_{1i}=0$.

(2) Only the equilibrium positions of the nearest neighbors change and by equal amounts; equilibrium positions of all other molecules stay the same. That is, $\Delta R_{1i}=r \neq 0$ only if i is a nearest neighbor of the vibrationally excited molecule. The first assumption is based on the pairwise nature of the intermolecular interactions and the second is based on the short range of the intermolecular interaction. Because the contraction is about the vibrationally excited parahydrogen molecule, the $J=1$ molecule experiences an anisotropic distortion of the lattice, thus allowing for a variation of ε_{2c} . We first calculate ε_{2c} and ΔB using the zeroth-order approximation on the lattice, that is, no distortion. We then calculate ε_{2c} using the first-order distortion of the crystal defined above.

III. RESULTS

The experimentally derived crystal field splitting parameters listed in Table I, of course, include all effects mentioned; we only presume to calculate the major effect using the simplified model introduced in Sec. II. The three major steps we have taken are (1) neglect of static and dynamic phonon renormalization, (2) use of the approximate London formula for scaling pair interactions, and (3) neglect of lattice site distortion other than that at the nearest-neighbor positions of the excited molecule. The inadequacy of the first assumption for the cases of the HD and D₂ spectra is immediately realized when we calculate the values of ΔB in the ground state due to the isotopic substitutions. Since the polarizabilities of HD (5.382 a.u.) and D₂ (5.345 a.u.) (Ref. 2) are smaller than that of H₂ (5.414 a.u.), ΔB due to the variation of the polarizability should be positive and that the $M = \pm 1$ levels should lie *below* the $M=0$ level. The well established experimental results are opposite to this and suggest that phonon renormalization may be the dominant effect in producing the anisotropy. Indeed the theoretical work by Koshenev¹⁹ puts $M = \pm 1$ levels above the $M=0$ level although his calculated splitting on the order of 1 cm⁻¹ is much higher than the experimental values in Table I. More theoretical work is awaited on this problem. In the case of the $v=3 \leftarrow 0$ excitation of H₂ considered in this paper, however, the effect of phonon renormalization is expected to be much smaller due to the homogeneity of mass, and we believe that the assumed static model gives a good approximation. The reasonable agreement between the calculated and observed crystal-field splittings for $J=1$ (Ref. 8) and $J=6$ (Ref. 14) levels lends support to this belief. In the following we report results of our calculation based on the static model (nonrenormalized) without and with the local lattice distortion described above.

A. Calculations in an undistorted hcp lattice

For an undistorted lattice, the crystal-field parameter ε_{2c} remains constant upon vibrational excitation since the effect is completely absorbed by the term with ΔB . This results from the separation of variables in our pairwise additive model used in paper I, Ref. 2, and in this paper. In this approximation, ε_{2c} is simply calculated by

$$\varepsilon_{2c} = \sum_{i=2}^N B(R_{1i}) C_{20}(\Omega_{1i}) = \sum_{n=6,8,10} a_n S_n^{20}, \quad (8)$$

where the a_n are identical to the three coefficients of Eq. (4) and the crystal sums, $S_n^{20} \equiv \sum_i (R_0/R_i)^n C_{20}(\Omega_{1i})$, are 0.00305, 0.00216, and 0.00133 for $n=6, 8,$ and 10 , respectively.²⁶ These values give the contributions of the dispersion and induction interactions to ε_{2c} as listed in Table II. The contributions of the second-order EQQ interaction are calculated by averaging V_{EQQ} of Eq. (6) with $|1M\rangle$ and dividing the splitting between $M = \pm 1$ and $M=0$ levels by 0.6. The total of these values, -0.0115 cm^{-1} agrees well with the experimental value for the ground state of -0.0118 cm^{-1} . The difference between our calculated values in our earlier paper⁸ and this work is due to our use of VanKranendonk's modification of the *ab initio* potential of Mulder, *et al.* This agreement supports our neglect of the

TABLE II. Calculated pair and crystal-field interaction parameters (in cm⁻¹).

| Undistorted lattice | | | |
|---------------------|--------------------|-----------------|------------------|
| | ε_{2c} | ΔB^{NN} | ΔB^{NNN} |
| Dispersion | -0.0112 | -1.008 | -0.089 |
| Induction | -0.0002 | -0.027 | -0.001 |
| EQQ | -0.0001 | -0.009 | -0.000 |
| Total | -0.0115 | -1.044 | -0.090 |
| Experimental | -0.0118 | -0.804 (ip) | -0.730 (op) |

| Slightly distorted lattice in excited state | | | $r/R = 0.00368$ |
|---|-----------------------------------|--|-----------------------------------|
| | $\Delta \varepsilon_{2c}^{NN}$ ip | | assumed |
| Dispersion | 0.0384 | | $\Delta \varepsilon_{2c}^{NN}$ op |
| Induction | 0.0008 | | -0.0405 |
| EQQ | 0.0003 | | -0.0008 |
| Total | 0.0395 | | -0.0005 |
| Experimental | 0.0368 | | -0.0418 |

static and dynamic phonon effects and the distortion of the hcp crystal lattice due to the presence of the $J=1$ H₂ (Ref. 27) that were perhaps overemphasized in the past.

The variation of $B(R)$ upon vibrational excitation, $\Delta B = B(R)^* - B(R)$ is calculated from the values given in Sec. II B. Again, the dispersion is the dominant interaction which changes by 22.3% upon the vibrational excitation $v=3 \leftarrow 0$. Calculated values are listed in Table II together with observed values.

B. Calculations in a slightly distorted hcp lattice

The model of small local lattice distortions introduced in Sec. II C is illustrated schematically in Fig. 1. The vibrationally excited $J=1$ H₂, labeled as v , distorts the surrounding nearest-neighbor sites radially by an amount $r \ll R_0$, including the $J=1$ H₂ labeled as J . The direction of distortion is not known initially but the figure shows the case of contraction. The variation of ε_{2c} upon crystal distortion is

$$\Delta \varepsilon_{2c} = \sum_i \nabla_i \varepsilon_{2c} \cdot \mathbf{r}_i + 0[(r/R_0)^2], \quad (9)$$

where \mathbf{r}_i ($|\mathbf{r}_i|=r$) is the displacement of the i th molecule and $\nabla_i \varepsilon_{2c}$ is the gradient, $\partial \varepsilon_{2c} / \partial \mathbf{r}_i$. The second term represents the second-order variation that is less than 0.1% of the first-order variation and is neglected in this treatment. The summation over i extends over the 12 nearest neighbors of the vibrationally excited $J=0$ H₂. They are decomposed into two qualitatively different effects, that is, the variation of ε_{2c} due to the displacement of the $J=1$ H₂ itself with respect to the rest of the crystal and that due to the displacement of the remaining nearest-neighbor molecules with respect to the $J=1$ H₂. The calculation is simplified because the former effect that involves an infinite number of pairs is shown to be identically equal to zero. This is seen by straightforward calculation but also from symmetry considerations. For ip pair, for example, with the choice of the coordinate system shown in the figure caption, $\partial \varepsilon_{2c} / \partial x$ and $\partial \varepsilon_{2c} / \partial z$ vanish because of the symmetry of the lattice surrounding the $J=1$ H₂ with

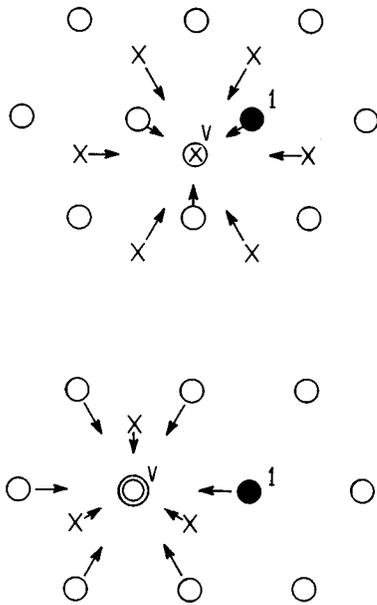


FIG. 1. Schematic diagram showing the assumed local lattice contraction upon the vibrational excitation. Molecules in the same hexagonal plane as the $J=1$ H_2 (indicated by a black circle with 1) are shown with white circles, while molecules above and below the plane are shown by X. When a $J=0$ H_2 is vibrationally excited (shown with a circled X and a double circle with V) 12 nearest-neighbor molecules are attracted radially by the same amount. The top figure shows the op configuration while the bottom figure shows the ip configuration. The pair fixed axes are chosen such that the z axis is along the pair axis and the y axis is along the C_2 axis. The magnitude of contraction is exaggerated by two orders of magnitude.

respect to the $\sigma(yz)$ and $\sigma(xy)$ planes and $\partial\epsilon_{2c}/\partial y$ because of the C_3 axis. The values of $\Delta_i\epsilon_{2c}$ due to displacements of the 11 H_2 molecules are calculated individually using

$$\Delta_i\epsilon_{2c} = -3 \cos \theta_i B(R_i)(z_i - \delta R_i \cos \theta_i)/R_0 + \frac{1}{2}(3 \cos^2 \theta_i - 1) \delta R_i B'(R_i), \quad (10)$$

where z_i is the z component of \mathbf{r}_i , $B'(R) \equiv dB(R)/dR$, and $\delta R_i \equiv (\mathbf{R}_i \cdot \mathbf{r}_i)/R_0$. A straightforward calculation gives

$$\Delta\epsilon_{2c} = - \left[2B(R) + B(\sqrt{2}R) + \frac{2}{3}B(\sqrt{3}R) - \frac{2}{\sqrt{3}}RB'(\sqrt{3}R) - \frac{1}{2}RB'(2R) \right] \frac{r}{R} \quad (11)$$

for the in-plane pair [Fig. 1(a)], and

$$\Delta\epsilon_{2c} = \left[2B(R) + B(\sqrt{2}R) + 3B(\sqrt{8/3}R) + \frac{2}{3}B(\sqrt{3}R) - \sqrt{\frac{2}{3}}RB'(\sqrt{8/3}R) + \frac{1}{2\sqrt{3}}RB'(\sqrt{3}R) - \frac{13}{2\sqrt{33}}RB'\left(\sqrt{\frac{11}{3}}R\right) \right] \frac{r}{R} \quad (12)$$

for the out-of-plane pair [Fig. 1(b)], where R now denotes R_0 . The sign of r is chosen such that $r > 0$ corresponds to contraction. Using the expression of $B(R)$ in Eq. (4), we obtain

$$\Delta\epsilon_{2c} = 10.65 \frac{r}{R} \quad \text{for in-plane pairs, and} \quad (13)$$

$$\Delta\epsilon_{2c} = -11.23 \frac{r}{R} \quad \text{for out-of-plane pairs.} \quad (14)$$

For both cases, the first terms of Eqs. (11) and (12) due to the four $J=0$ H_2 that are common nearest neighbors of the vibrationally excited $J=0$ H_2 and the $J=1$ H_2 give the dominant contributions amounting to 87% and 82% of the total values. The opposite signs of $\Delta\epsilon_{2c}$ for in-plane and out-of-plane pairs are in accord with experimental observations, and their absolute signs clearly demonstrate that the distortion is a contraction. Assuming that the fractional distortion is the same for ip and op pairs, we obtain as the most consistent value $r/R = 0.00368$. The values of $\Delta\epsilon_{2c}$ based on this value are listed in Table II.

IV. DISCUSSION

The results of this paper together with those in Ref. 2 demonstrate that the pair and crystal-field splitting parameters ΔB and ϵ_{2c} provide good insight into the variation of intermolecular interactions upon vibrational excitation and isotopic substitution. In addition, the results of the present paper show that the variation of the crystal-field splitting parameter $\Delta\epsilon_{2c}$ is a sensitive indicator of local lattice distortion. Since the small value of ϵ_{2c} is due to cancellation of large terms in the crystal summation, any small lattice distortion that breaks the lattice symmetry around the $J=1$ H_2 destroys the cancellation effect, resulting in a $\Delta\epsilon_{2c}$ whose magnitude is higher than ϵ_{2c} itself. Our observed fine structure of the $Q_3(0)$ transition in parahydrogen crystals provides clean information for which this idea is applicable. By employing a simple model of lattice distortion around the vibrationally excited $J=0$ H_2 , the correct relative signs and magnitudes of all parameters are reproduced lending solid physical insight that the local lattice sites contract upon the vibrational excitation.

Our model has limitations, however. First, although not explicitly considered here, as discussed at the beginning of Sec. III, the variation of the intermolecular interaction upon isotopic substitution due to the different electronic properties alone cannot explain even the sign of ΔB . Mass effects must play the dominant role in those cases. Our result of this paper will help to isolate the mass effects in the isotopic vibrational splittings. Second, our model calculation does not explain the variation of ϵ_{2c} for the next-nearest-neighbor pairs. The dominant effect due to common nearest neighbors corresponding to the first terms of Eqs. (13) and (14) vanishes under our assumptions leading to a small value of $\Delta\epsilon_{2c}$ that is clearly in contradiction to the large observed value of $\Delta\epsilon_{2c} = 0.0287 \text{ cm}^{-1}$. We can reproduce this observed value if we change the assumption (2) in Sec. II C and extend the distortion to the next-nearest neighbors, but such a compromise is clearly unsatisfactory. Finally, there is the problem of

the validity of the two parameter model itself. This model assumes D_{3h} symmetry of the hypothetical crystal field in which the effect of the symmetry-breaking pair interaction is subtracted, and cylindrical symmetry for the pair interaction. Those assumptions are good of course for $\Delta B=0$ in the ground state and also for $\Delta B \gg \epsilon_{2c}$ for nearest-neighbor pairs. If ΔB and ϵ_{2c} are comparable as for the next-nearest pairs in the $v=3$ state (Table I), the assumptions are not good and we need to consider other angle dependences

$C_{2m}(\Omega)$ or $C_{2m}(\Omega)$ with $m \neq 0$. It is difficult to determine these angle dependences experimentally since $J=1$ sublevels provide at most two independent parameters, but these may be treated theoretically.

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