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

Robert M. Dickson* and Takeshi Oka
Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637
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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 $\Delta B$ and $\epsilon_{2c}$ upon the $v = 3 \Diamond 0$ 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 paper 1 (which will be referred to as paper I hereafter) on the high-resolution spectroscopy of the $Q_1(0)$ transition ($v = 3 \diamond 0, \ J = 0 \diamond 0$) 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.\textsuperscript{2,3} on the $Q_1(0)$ transitions ($v = 1 \diamond 0, \ J = 0 \diamond 0$) 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 (vibrations) in those systems, and the analysis of the well resolved structure has given a most decisive confirmation of the mechanism of the $Q_1(0)$ transitions initially proposed by Sears and VanKranendonk.\textsuperscript{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 $J = 1, M' \pi J = 1, M$ 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.\textsuperscript{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

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

where $C_{20}(\Omega)$ and $C_{20}(\omega)$ are Racah spherical harmonics\textsuperscript{5} with angle variables $\Omega$ and $\omega$ 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 $\epsilon_{2c}$ and $\Delta B$ based on Eq. (1) are listed in Table I. Values for $D_2$ and HD impurity transitions reported by Weliky et al.,\textsuperscript{2} are also listed for comparison. If the two simplifying assumptions (a) and (c) mentioned above are valid to good approximations, the value of $\epsilon_{2c}$ 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>
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<tr>
<th>Quantum state</th>
<th>Pair type</th>
<th>$\Delta B$ (cm$^{-1}$)</th>
<th>$\epsilon_{2c}$ (cm$^{-1}$)</th>
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<td></td>
</tr>
<tr>
<td>$v = 1 \ D_2$</td>
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<td>-0.0128</td>
</tr>
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<td>$NN$ op</td>
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<tr>
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</tr>
<tr>
<td>$NN$ op</td>
<td>-0.3292</td>
<td>-0.0160</td>
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Q_3(0) transition of H_2, for example, all \( \varepsilon_{2c} \) values in the \( v = 3 \) excited state are larger in magnitude than is the \( \varepsilon_{2c} \) in the ground state. \( \varepsilon_{2c} \) 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 \( \varepsilon_{2c} \) of similar magnitude were noted upon isotopic substitution and vibrational excitation for the \( Q_3(0) \) transitions of D_2 and HD impurities and were ascribed by Weliky et al.\(^5\) 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 \( \varepsilon_{2c} \) changes drastically because the small value of \( \varepsilon_{2c} \) 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 \( \varepsilon_{2c} \). Using this idea, Weliky was able to qualitatively explain the trends of \( \varepsilon_{2c} \) 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 \( \varepsilon_{2c} \) upon the vibrational excitation \( v = 3 \rightarrow 0 \) 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.\(^8\) 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 \( \varepsilon_{2c} \) upon vibrational excitation alone.

In studying the variation of intermolecular interactions upon vibrational excitation, recent extensive high-resolution spectroscopy of hydrogen dimers by McKellar\(^2\) 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 \emph{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 renormalization\(^11\) 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 \emph{ab initio} potential.

II. THEORETICAL MODEL

A. Anisotropic intermolecular interaction

We base our calculation on the \emph{ab initio} anisotropic intermolecular potential reported by Mulder and co-workers\(^10\) 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

\[
V(\omega_1, \omega_2, R) = -\sum_{n} \sum_{i_1, i_2, m} \gamma_{i_1, i_2, m}^n C_n R^{-n} P_{i_1}^m(\cos \theta_1) \\
\times P_{i_2}^m(\cos \theta_2) \cos[m(\phi_1 - \phi_2)],
\]

where the \( P_i^m(\cos \theta) \) are associated Legendre polynomials, \( R \) is the intermolecular distance, \( \gamma \) 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

\[
V(\omega_1, \omega_2, R) = -\sum_{n} \gamma_{n}^{200} C_n R^{-n} C_{20}(\omega) = B(R) C_{20}(\omega),
\]

where \( \omega \) represents the angle variables of \( J = 1 \) H_2 with respect to the pair axis. Mulder \emph{et al.} have given numerical values of \( C_n \) and \( \gamma_{n}^{200} \) 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

\[
-B(R) = 2.249 \left( \frac{R_0^3}{R} \right)^6 + (1.553 + 0.073) \left( \frac{R_0^3}{R} \right)^8 \\
+ (0.720 + 0.026) \left( \frac{R_0^3}{R} \right)^{10},
\]

where \( R_0 = 3.783 \) Å (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 Å, is much larger than the equilibrium distance in the isotropic pair potential, 3.41 Å.\(^16,17\)

(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 Koshenev\(^19\) 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,

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

where \( \alpha \) (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. This formula gives the induction portion of the anisotropy to be $-0.098 C_{20}(\omega)$, in agreement with $-0.099 C_{20}(\omega)$ 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

$$V_{\text{EEQQ}} = \frac{Q_1^2 Q_2^2}{5R^6} \sum_{i,j=1}^{1,3} \sum_m \left( \frac{4}{2 + m} \right)^2 \times \frac{|C_{2m}(\omega)|^2 |J, M-m\rangle \langle J, M-m| C_{2m}(\omega)|}{[2 - (J + 1)] B_1 - 6B_2},$$

where $Q$ and $B$ are the electric quadrupole moment and the rotational constant, respectively, and $(2 + m)$ is the binomial factor $4!/(2 + m)!/(2 - m)!$. $\omega$ 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, $11.758$ cm$^{-1}$, 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. It is convenient to use the extended London formula reported by Buckingham for the interaction between two linear molecules, the relevant part of which is written as

$$V_{\text{disp}} = -\frac{3I_1 I_2}{2(I_1 + I_2)} \gamma \left[ \alpha_1 \alpha_2 + \frac{1}{3} \gamma_1 \alpha_2 C_2(\omega) + \cdots \right],$$

where $I$ (15.43 eV) and $\gamma$, the difference between the parallel and perpendicular polarizabilities (2.024 a.u.), 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. Upon the vibrational excitation $v = 3 \rightarrow 0$, the isotropic polarizability of the $J = 0$ H$_2$, $\alpha_0$, increases by 27% 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, $V_{\text{ind}},$ is simply due to the 27% increase of the isotropic polarizability, $\alpha$. The variation of the second-order EQQ interaction $V_{\text{EEQQ}}$ 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 $S_3(0)$ transition and the $Q_2(0)$ transition.

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. While the former 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 data on hydrogen dimers gives helpful insight. The rotational constants of H$_2$-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 $v = 1 \rightarrow 0$ of H$_2$ and HD, respectively, indicating that the dimers contract upon the vibrational excitations. Since McKellar does not report data for H$_2$-H$_2$ and his data for HD-HD and D$_2$-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 $\varepsilon_{2c}$ 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 $\Omega_{1i}$, then $\Delta R_{1i} = 0$.

2. Only the equilibrium positions of the nearest neighbors change 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 $\varepsilon_{2c}$. We first calculate $\varepsilon_{2c}$ and $\Delta B$ using the zeroth-order approximation on the lattice, that is, no distortion. We then calculate $\varepsilon_{2c}$ 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 = ±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 Koshenev 19 puts M = ±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 → 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 ε₂c 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, ε₂c is simply calculated by

\[ ε₂c = \sum_{i=2}^{N} B(R_{i1}) C_{20}(Ω_{i1}) = \sum_{n=6,8,10} a_n S_{20}^n, \tag{8} \]

where the aₙ are identical to the three coefficients of Eq. (4) and the crystal sums, S₂₀ = Σₙ (Rₙ/R₀)ⁿ C₂₀(Ω₁), 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 ε₂c as listed in Table II. The contributions of the second-order EQQ interaction are calculated by averaging ΣEQQ of Eq. (6) with |M| and dividing the splitting between M = ±1 and M = 0 levels by 0.6. The total of these values, 0.00115 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 paper 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 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, ΔB = B(R) - B(R₀) 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 → 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/R₀, 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 ε₂c upon crystal distortion is

\[ Δε₂c = \sum \nabla_i ε₂c \cdot r_i + 0[(r/R₀)^2], \tag{9} \]

where rᵢ (||rᵢ|| = r) is the displacement of the i-th molecule and \( \nabla_i ε₂c \) is the gradient, \( \partial ε₂c / \partial r_i \). 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 ε₂c 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 i-pair, for example, with the choice of the coordinate system shown in the figure caption, \( \partial ε₂c / \partial x \) and \( \partial ε₂c / \partial z \) vanish because of the symmetry of the lattice surrounding the J = 1 H₂ with

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

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<th>ΔBNN</th>
<th>ΔBNN</th>
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<th></th>
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</tbody>
</table>

r/R = 0.003 68
The 11 H₂ molecules are calculated individually using a straightforward calculation gives 

\[ \Delta e_{2c} = 10.65 \frac{r}{R} \quad \text{for in-plane pairs, and} \]

\[ \Delta e_{2c} = -11.23 \frac{r}{R} \quad \text{for out-of-plane pairs.} \]

For both cases, the first terms of Eqs. (11) and (12) due to the four \( J=0 \) H₂ that are common nearest neighbors of the vibrationally excited \( J=0 \) H₂ and the \( J=1 \) H₂ give the dominant contributions amounting to 87% and 82% of the total values. The opposite signs of \( \Delta e_{2c} \), 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 in and out pairs, we obtain as the most consistent value \( r/R = 0.00368 \). The values of \( \Delta e_{2c} \) 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 \( \Delta B \) and \( e_{2c} \) 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 \( \Delta e_{2c} \) is a sensitive indicator of local lattice distortion. Since the small value of \( e_{2c} \) is due to cancellation of large terms in the crystal summation, any small lattice distortion that breaks the lattice symmetry around the \( J=1 \) H₂ destroys the cancellation effect, resulting in a \( \Delta e_{2c} \) whose magnitude is higher than \( e_{2c} \) itself. Our observed fine structure of the \( Q(0) \) transition in para-hydrogen crystals provides clean information for which this idea is applicable. By employing a simple model of lattice distortion around the vibrationally excited \( J=0 \) H₂, 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 \( \Delta B \). 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 \( e_{2c} \) for the next-nearest-neighbor pairs. The dominant effect due to common nearest neighbors corresponding to the first terms of Eqs. (11) and (12) vanishes under our assumptions leading to a small value of \( \Delta e_{2c} \) that is clearly in contradiction to the large observed value of \( \Delta e_{2c}=0.0287 \text{ cm}^{-1} \). 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 $D_B = 0$ in the ground state and also for $D_B \approx \varepsilon_{2c}$ for nearest-neighbor pairs. If $D_B$ and $\varepsilon_{2c}$ 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.

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9Present address: Department of Chemistry, Mail Code 0340, University of California at San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0340.


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