Absorption intensities of the multipole-field-induced zero-phonon transitions in solid HD, HT, and DT

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Closed-form theoretical expressions are derived for the integrated absorption coefficient of various zero-phonon single and double transitions in heteronuclear isotopic variants of hydrogen in condensed phase. Theoretical analysis predicts a different kind of double transition in the spectra of solid HD, HT, and DT, where the rotational energy of one molecule changes by three quanta and the rotational energy of another molecule simultaneously changes by at least three quanta. The expressions for double transitions given in this paper may, for example, be applied to double transitions involving $para$-H_2–HD or $ortho$-D_2–HD pairs.

I. INTRODUCTION

Solid hydrogen as the archetypical molecular quantum crystal provides opportunities and challenges to experimentalists and theorists alike.[1] The absorption process in solid hydrogens (H_2, D_2, HD, etc.) results primarily from induced dipole moments, although the small nonadiabatic permanent dipole contributes to the R- and P-branch transitions for heteronuclear isotopomers. General and special expressions for the integrated absorption coefficients of all types of zero-phonon single and double transitions in solid H_2 have been derived by various groups.[2–7] These expressions would also be valid for D_2 and T_2, but the definitions of ortho and para modifications with respect to J (rotational quantum number) will be different. For heteronuclear molecules, the ortho-para distinction does not exist and nearly all molecules in solid HD, HT, and DT are in the $J=0$ state, thus simplifying the infrared spectrum and the theoretical analysis. However, complications arise due to the noncoincidence of the center of charge with the center of mass of the molecule. Further, since these molecules are not perfectly centrosymmetric, odd ΔJ transitions are allowed in addition to even ΔJ transitions, which are the only allowed transitions in homonuclear counterparts such as H_2.

Although theoretical expressions for the intensities of certain transitions in HD are derived by Poll and co-workers,[8–10] so far no attempt is made to give general expressions that are valid for all transitions of a similar type. In the present paper, our concern is to derive closed-form expressions for the absorption intensities of zero-phonon single and double transitions in solid HD, HT, and DT. The general expressions derived here for the single and double transitions reduce to the special cases of Refs. 8–10. In addition, our theoretical analysis predicts a different kind of double transition $T_v(0)+[\Delta J=\ell\geqslant3]_{v'}(0)$ in solid HD, HT, and DT. The intensity formulas for this kind of transition are also derived, and the predicted intensities imply that these transitions are relatively strong. Here the symbols Q, R, S, etc., are used to denote, respectively, rotational transitions

with $\Delta J=0,1,2$, etc. The subscript specifies the change in the vibrational quantum number (the lower state always being $v=0$) whereas the number in parentheses represents the lower-state J value. The symbol ℓ denotes the order of the multipole.

Experimentally, among the three heteronuclear isotopomers of hydrogen, most infrared measurements of the multipole-induced spectrum in the solid phase have been on HD (Refs. 11–13), however, these measurements are not as extensive as those for H_2. In solid HD, the pure rotational as well as rovibrational transitions up to $\Delta J=5$ (induced by the 2^5-pole moment) have been observed, while in the case of HT, only the quadrupole-induced transitions have been reported[14,15] and, to our knowledge, no spectroscopic studies have been performed in solid DT. For some of the transitions in HD for which absorption intensities are measured, theoretical intensities are not yet available. Also, given the fundamental importance of the spectroscopy of the hydrogens in the condensed phase, it seems likely that important results on the heteronuclear hydrogens will be reported. One would then require theoretical absorption intensities to correlate with the experimental findings. In this paper, we provide predicted intensities of transitions up to $\Delta J=11$ (induced by the 2^{11}-pole moment) in solid HD. For other isotopomers, the intensities can be calculated with the available data. The theoretical approach adopted here is simple and extension of the results to "mixed isotopomer transitions," such as $R_v(0)\mathrm{HD}+[\Delta J=\ell]_{v'}(0)\mathrm{H_2}$, $S_v(0)\mathrm{HD}+[\Delta J=\ell]_{v'}(0)\mathrm{D_2}$, etc., is straightforward. Although mixed isotopomer transitions, where a HD molecule and a H_2 or D_2 molecule simultaneously take part in a transition, are observed experimentally,[11,13,16] and absorption intensities are measured for some of the lines, so far no theoretical analysis of intensities of such transitions has been attempted.

II. THEORY

The basic formalism for the absorption intensities of multipolar-induced transitions in solid hydrogens was first developed by VanKranendonk[2] and others.[17] They expressed

the intensity in terms of the matrix elements of the spherical components of the induced dipole moment of a pair of molecules. The dipole components were expanded in terms of appropriately coupled products of three spherical harmonics, $Y_{\ell,m}$, describing the orientations of the internuclear axes of the two individual molecules in the pair, $\mathbf{r}_1$ ($=r_1,\omega_1$) and $\mathbf{r}_2$ ($=r_2,\omega_2$), and of the vector separation between their centers of mass $\mathbf{R}$ ($=R,\Omega$). Balasubramanian and co-workers[4–6] adopted a slightly different approach to obtain closed-form expressions for the intensities of single and double transitions in solid hydrogen. The latter method is followed in this paper.

The basic experimental quantity that is directly relatable to theory is the integrated absorption coefficient defined as

$$\tilde{\alpha} = (c/Nl)\int \ln(I_0/I)d\nu/\nu. \tag{1}$$

Here c is the speed of light, I_0 and I are, respectively, the incident and transmitted intensities, ν is the wave number of the line (in cm^{-1}), l is the sample length, and N is the number of absorbing molecules per cm^3. Theoretically, $\tilde{\alpha}$ is related to the matrix elements of the induced dipole moment μ_{ind}[18]

$$\tilde{\alpha} = (8\pi^3/3h)\sum_{n_i n_f} |\langle fn_f|\mu_{ind}|in_i\rangle|^2/d_i, \tag{2}$$

where $|in_i\rangle$ and $|fn_f\rangle$ are the initial and final states, n_i and n_f are the labels of the respective degenerate components, and d_i ($=2J''+1$) is the initial-state degeneracy. The task of developing an expression for $\tilde{\alpha}$ for any specifiable transition thus reduces to one of evaluating the appropriate expression for the induced dipole moment.

In order to calculate μ_{ind}, let us consider an isolated molecular pair 1 and k in a single crystal of solid HD, HT, or DT at 0 K and assume a rigid hexagonal close-packed (hcp) lattice. Since, in the heteronuclear isotopomers, the center of mass (CM) does not coincide with the center of charge (CC), one must express all of the relevant quantities in CM coordinates. We take advantage of the recent computation of rovibrational matrix elements of the multipole moments of these molecules in CM coordinates,[19] and, as shown in Fig. 1, place the CM of molecule 1 at the origin of a laboratory fixed coordinate system XYZ (the Z axis pointing along the hexagonal axis). The CM of the molecule k is located by the position vector $\mathbf{R}_{1k}$ ($=R_{1k},\hat{\Omega}_{1k}$), while the CC of this molecule is given by $\mathbf{S}_{1k}$ ($=S_{1k},\hat{\Omega}'_{1k}$). The orientations of the axes of the two molecules are given by $\hat{\omega}_1(=\theta_1,\phi_1)$ and $\hat{\omega}_2(=\theta_2,\phi_2)$. The electric field at molecule k, due to the
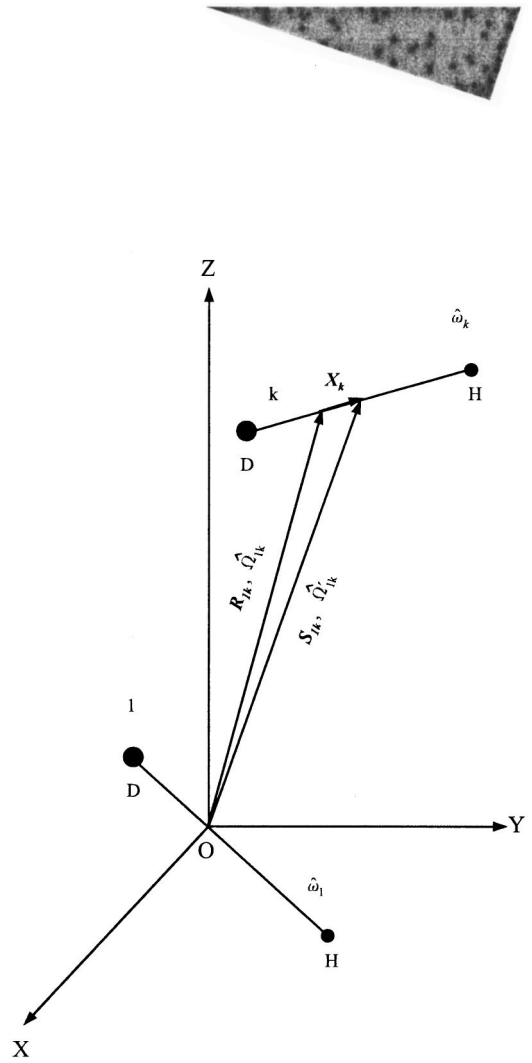

FIG. 1. Multipolar induction in a molecular pair $(1,k)$ in solid HD, representative of heteronuclear isotopomers. The origin "O" of the laboratory coordinate system XYZ is placed at the CM of molecule 1. The vector $\mathbf{X}_k$ connects the CM of molecule k to its CC. The Z axis lies along the hexagonal axis of the hcp lattice. ω_i ($=\theta_i,\phi_i$) defines the orientation of the molecule.

2^ℓ-pole moment of molecule 1 polarizes k to produce in it an induced dipole moment $\mu_{ind}(\ell;1,k)$. This has an isotropic component μ^{iso} parallel to the field and an anisotropic part μ^{an}, which is dependent on the orientation of k. The polarizability matrix elements are available in the CC coordinate and hence spherical components $\mu_\nu(\ell;1,k)$ of the two parts of the multipole-induced dipole moment as a function of $\mathbf{S}_{1k}$ can be written as[5,17]

$$\mu_\nu^{iso}(\ell;1,k,\mathbf{S}_{1k}) = 4\pi[(\ell+1)/(2\ell+3)]^{1/2}Q_\ell^{CM}(r_1)\alpha^{CC}(r_k)S_{1k}^{-(\ell+2)}\sum_m (-)^m C(\ell,1,\ell+1;m,\nu,m$$

$$+\nu)Y_{\ell,-m}(\hat{\omega}_1)Y_{\ell+1,m+\nu}(\hat{\Omega}'_{1k}), \tag{3}$$

$$\mu_\nu^{an}(\ell;1,k,\mathbf{S}_{1k})=(-)^{\ell+1}[128\pi^3(\ell+1)/27]^{1/2}Q_\ell^{CM}(r_1)\gamma^{CC}(r_k)S_{1k}^{-(\ell+2)}\sum_{mM}C(2,1,1;\nu-M-m,M+m,\nu)$$

$$\times C(\ell,\ell+1,1;m,M,M+m)Y_{\ell,m}(\hat{\omega}_1)Y_{2,\nu-M-m}(\hat{\omega}_k)Y_{\ell+1,M}(\hat{\Omega}'_{1k}). \tag{4}$$

In the above equations $Q_\ell^{CM}(r_1)$ is the 2^ℓ-pole moment of molecule 1 in the CM coordinate, $\alpha^{CC}(r_k)$ and $\gamma^{CC}(r_k)$ are, respectively, the isotropic and anisotropic parts of the polarizability of molecule k in the CC coordinate, C is a Clebsch-Gordan coefficient, and r_1 or r_k is the internuclear separation in the corresponding molecule. In order to express the induced dipole moment as a function of $\mathbf{R}_{1k}$, we make use of the relation between $\mathbf{R}_{1k}$ and $\mathbf{S}_{1k}$ illustrated by Fig. 1,

$$\mathbf{R}_{1k}=\mathbf{S}_{1k}-\mathbf{X}_k, \tag{5}$$

and expand $\mu_\nu(\ell;1,k,\mathbf{R}_{1k})$ as a Taylor series:

$$\mu_\nu(\ell;1,k,\mathbf{R}_{1k})=\mu_\nu(\ell;1,k,\mathbf{S}_{1k})-\mathbf{X}_k\cdot\boldsymbol{\nabla}_{S_{1k}}\mu_\nu(\ell;1,k,\mathbf{S}_{1k})$$

$$+\tfrac{1}{2}\mathbf{X}_k\cdot\mathbf{X}_k:\boldsymbol{\nabla}_{S_{1k}}\boldsymbol{\nabla}_{S_{1k}}\mu_\nu(\ell;1,k,\mathbf{S}_{1k})+\cdots. \tag{6}$$

Using the gradient formula[20] and Eqs. (3), (4), and (6), the μ^{iso} and μ^{an} expressed as functions of $\mathbf{R}_{1k}$ can be written as [retaining only the first two terms in Eq. (6), i.e., terms up to linear in X_k, in each case]

$$\mu_\nu^{iso}(\ell;1,k,\mathbf{R}_{1k})=\mu_\nu^{iso}(\ell;1,k,\mathbf{S}_{1k})+4\pi[4\pi(\ell+1)(\ell+2)(2\ell+3)/3(2\ell+5)]^{1/2}Q_\ell^{CM}(r_1)x_k\alpha^{CC}(r_k)S_{1k}^{-(\ell+3)}$$

$$\times\sum_{mn}(-)^{m+n}C(\ell,1,\ell+1;m,\nu,m+\nu)C(\ell+1,1,\ell+2;m+\nu,-n,m+\nu$$

$$-n)Y_{\ell,-m}(\hat{\omega}_1)Y_{1,n}(\hat{\omega}_k)Y_{\ell+2,m+\nu-n}(\hat{\Omega}'_{1k}), \tag{7}$$

$$\mu_\nu^{an}(\ell;1,k,\mathbf{R}_{1k})=\mu_\nu^{an}(\ell;1,k,\mathbf{S}_{1k})+(-)^{\ell+1}\frac{16\pi^2(2\ell+3)}{9}[2(\ell+1)(\ell+2)/(2\ell+5)]^{1/2}Q_\ell^{CM}(r_1)x_k\gamma^{CC}(r_k)$$

$$\times S_{1k}^{-(\ell+3)}\sum_{mnM}C(2,1,1;\nu-M-m,M+m,\nu)C(\ell,\ell+1,1;m,M,M+m)C(\ell+1,1,\ell$$

$$+2;M,-n,M-n)Y_{\ell,m}(\hat{\omega}_1)Y_{1,n}(\hat{\omega}_k)Y_{2,\nu-M-m}(\hat{\omega}_k)Y_{\ell+2,M-n}(\hat{\Omega}'_{1k}), \tag{8}$$

where x_k is the magnitude of the vector $\mathbf{X}_k$ that connects the CM of molecule k to its CC. As a small digression, let us return to Eq. (6) to estimate the order of magnitude of the relative contribution to μ_ν from the quadratic and the linear terms. From Eq. (6), we have

$$\frac{T_{quad}}{T_{lin}}\approx\left|\frac{\mathbf{X}_k\cdot\mathbf{X}_k:\boldsymbol{\nabla}_{S_{1k}}\boldsymbol{\nabla}_{S_{1k}}\mu_\nu(\ell;1,k,\mathbf{S}_{1k})}{\mathbf{X}_k\cdot\boldsymbol{\nabla}_{S_{1k}}\mu_\nu(\ell;1,k,\mathbf{S}_{1k})}\right|.$$

From Eqs. (3) or (4) this reduces to

$$\frac{|\mathbf{X}_k|^2S_{1k}^{-(\ell+4)}}{|\mathbf{X}_k|S_{1k}^{-(\ell+3)}}=\frac{x_k}{S_{1k}}.$$

In HD, for instance, $x_k=r_e/6$, where $r_e=0.74$ Å is the equilibrium bond distance. For S_{1k} if we substitute the nearest-neighbor distance of 3.64 Å, appropriate for solid HD at 0 K,

the above ratio becomes 0.034. This justifies the truncation of the Taylor expansion [Eq. (6)] at the linear term.

The expressions (3), (4), (7), and (8) restrict the rotational transitions that the individual molecules in the pair can undergo. However, there is no restriction on the vibrational transitions. This makes it possible to observe pure rotational as well as rovibrational transitions in the fundamental and overtone regions. It is clear that the first term of μ^{iso} in Eq. (7), which is given by Eq. (3), can cause a rovibrational transition in molecule 1 that obeys the selection rule $\Delta J\leq\ell$ (with restriction $J'+J''\geq\ell$). This rotational transition may occur with or without a simultaneous pure vibrational transition in molecule k. The former possibility results in a double transition of the type $[\Delta J=\ell]_{v_1}(0)+Q_{v_k}(0)$ while, in the latter case, we have a single transition $[\Delta J=\ell]_{v_1}(0)$. On the other hand, the second term of μ^{iso} in Eq. (7) implies the possibility of another type of double transition $[\Delta J=\ell]_{v_1}(0)+R_{v_k}(0)$. Equation (4) implies that the

first term of μ^{an} in Eq. (8) permits a different kind of double transition in which both molecules in the pair $(1,k)$ can change their rotational states with $\Delta J_1 \leqslant \ell$ (with restriction $J'_1 + J''_1 \geqslant \ell$) and $\Delta J_k \leqslant 2$ (with restriction $J'_k + J''_k \geqslant 2$), which corresponds to a double transition of the type $[\Delta J = \ell]_{v_1}(0) + S_{v_k}(0)$. The spherical harmonic product rule[20] results in a sum of first-order and third-order spherical harmonics, $Y_{1,m'}(\hat{\omega}_k)$ and $Y_{3,m''}(\hat{\omega}_k)$, in the second term of Eq. (8); hence this term of μ^{an} gives rise to $[\Delta J = \ell]_{v_1}(0) + R_{v_k}(0)$ and $[\Delta J = \ell]_{v_1}(0) + T_{v_k}(0)$ types of double transitions.

It is evident how the formalism adopted in this paper to derive intensity formulas for induced transitions in the heteronuclear molecules has advantages over the one developed by Poll, Tipping, and others.[8–10] The forms of the parts of the induced dipole moment mentioned above, which contribute to a single transition $[\Delta J = \ell]_{v_1}(0)$ and to double transitions $[\Delta J = \ell]_{v_1}(0) + Q_{v_k}(0)$ and $[\Delta J = \ell]_{v_1}(0) + S_{v_k}(0)$ in solid HD, HT, and DT are similar to those applicable to solid *para*-H_2 and the derivation of intensity formulas for these types of transitions is straightforward. Considering only lower-order multipolar induction, one can write the intensity expressions for the heteronuclear isotopomers as[4,5]

$$\tilde{\alpha}\{[\Delta J=\ell]_v(0)\}=\frac{8\pi^3(\ell+1)}{3ha^{(2\ell+4)}}\langle 00|\alpha^{CC}(r)|00\rangle^2\langle v\ell|Q_\ell^{CM}(r)|00\rangle^2\xi_{\ell+1}S_{\ell+1}, \tag{9}$$

$$\tilde{\alpha}\{[\Delta J=\ell]_{v_1}(0)+Q_{v_k}(0)\}=\frac{8\pi^3(\ell+1)}{3ha^{(2\ell+4)}}\langle v_k0|\alpha^{CC}(r)|00\rangle^2\langle v_1\ell|Q_\ell^{CM}(r)|00\rangle^2\xi'_{\ell+2}S'_{\ell+2}, \tag{10}$$

$$\tilde{\alpha}\{[\Delta J=\ell(\geqslant4)]_{v_1}(0)+S_{v_k}(0)\}=\frac{16\pi^3(\ell+1)}{27ha^{(2\ell+4)}}\langle v_k2|\gamma^{CC}(r)|00\rangle^2\langle v_1\ell|Q_\ell^{CM}(r)|00\rangle^2\xi'_{\ell+2}S'_{\ell+2}, \tag{11}$$

$$\tilde{\alpha}\{S_{v_1}(0)+S_{v_k}(0)\}=\frac{8\pi^3}{3ha^8}\xi'_4S'_4\{\tfrac{2}{3}\langle v_12|Q_2^{CM}(r)|00\rangle^2\langle v_k2|\gamma^{CC}(r)|00\rangle^2+\tfrac{2}{3}\langle v_12|\gamma^{CC}(r)|00\rangle^2\langle v_k2|Q_2^{CM}(r)|00\rangle^2$$
$$-\tfrac{4}{5}\langle v_12|Q_2^{CM}(r)|00\rangle\langle v_k2|Q_2^{CM}(r)|00\rangle\langle v_12|\gamma^{CC}(r)|00\rangle\langle v_k2|\gamma^{CC}(r)|00\rangle\}, \tag{12}$$

$$\tilde{\alpha}\{S_v(0)+S_v(0)\}=\frac{32\pi^3}{45ha^8}\xi'_4S'_4\langle v2|\gamma^{CC}(r)|00\rangle^2\langle v2|Q_2^{CM}(r)|00\rangle^2, \tag{13}$$

where $S_{\ell+1}=\Sigma'_{jk}(a^2/R_{1j}R_{1k})^{\ell+2}P_{\ell+1}(\cos\theta_{jk})$ and $S'_{\ell+2}=\Sigma_k'(a/R_{1k})^{2\ell+4}$ are the positive-definite lattice sums (their values are given in Table I) and a is the nearest-neighbor distance in the crystal. The prime denotes exclusion of terms with $j=1$ or $k=1$. The additional term ξ, described as the phonon renormalization factor, corrects the rigid-lattice sum to allow for zero-point motions.[1–5,8–10] The expressions (9) and (10) are not valid for $\ell=1$, because for a $\Delta J=1$ transition the transition amplitude arising from the induced dipole moment interferes with that from the permanent dipole moment of the heteronuclear molecule and the intensities are modified by this interference effect. A detailed theoretical discussion of the intensities of the $R_v(0)$ transitions is given in Ref. 21. The specific expressions (12) and (13) for the double transitions of the type $S(0)+S(0)$ embody an interference term which arises when the roles of the molecules 1 and k in the pair are interchanged. Further, for $v_1=v_k=v$, the two normally distinct doubly degenerate states $|1v_1,2;kv_k,2\rangle$ and $|1v_k,2;kv_1,2\rangle$ become a single

composite state and division by 2 is required to get the final expression (13).[4]

We turn now to the intensity formulas for double transitions of types $[\Delta J=\ell]_{v_1}(0)+R_{v_k}(0)$ and $[\Delta J=\ell]_{v_1}(0)+T_{v_k}(0)$. For any double transition, we first obtain the partial absorption coefficient $\tilde{\alpha}(1,k)$ due to the molecular pair $(1,k)$ and the net absorption coefficient is obtained by summing the pair absorption coefficients over k,

$$\tilde{\alpha}=\sum_k\tilde{\alpha}(1,k). \tag{14}$$

As pointed out in Ref. 6, the orientation of the intermolecular axis (the angular coordinates $\hat{\Omega}_{1k}$ in Fig. 1) does not affect the value of $\tilde{\alpha}(1,k)$. We exploit this freedom to locate the center of charge of molecule k at $(0,0,S_k)$, that is, on the Z axis in Fig. 1, which simplifies the algebra considerably. For this choice, the second terms of μ^{iso} in Eq. (7) and μ^{an} in

TABLE I. Numerical values of various lattice sums needed for the calculation of absorption intensities of transitions in solid hydrogens. The values for $\ell = 7$ and 9–11 have not been reported previously. The computation assumes R_{1j} and R_{1k} as the distances between the centers of charge of two molecules. a is the nearest-neighbor distance.

ℓ	$\Sigma'_{jk}(a^2/R_{1j}R_{1k})^{\ell+2}P_{\ell+1}(\cos\theta_{jk})$	$\Sigma'_k(a/R_{1k})^{2\ell+4}$
1	2.5464	14.4544
2	0.3062	12.8028
3	0.8129	12.3119
4	7.1414	12.1323
5	31.3581	12.0592
6	14.3510	12.0275
7	15.4048	12.0131
8	2.9352	12.0063
9	6.1809	12.0031
10	2.2565	12.0015
11	33.8280	12.0008

Eq. (8), responsible for the occurrence of the above-mentioned transitions, reduce, respectively, to

$$4\pi[(\ell+1)(\ell+2)(2\ell+3)/3]^{1/2}Q_\ell^{CM}(r_1)x_k\alpha^{CC}(r_k)$$

$$\times S_{1k}^{-(\ell+3)}(-)^\nu\sum_n C(\ell,1,\ell+1;n-\nu,\nu,n)$$

$$\times C(\ell+1,1,\ell+2;n,-n,0)Y_{\ell,\nu-n}(\hat{\omega}_1)Y_{1,n}(\hat{\omega}_k),$$

and

$$[128\pi^3(\ell+1)(\ell+2)(2\ell+3)/27]^{1/2}$$

$$\times Q_\ell^{CM}(r_1)x_k\gamma^{CC}(r_k)S_{1k}^{-(\ell+3)}\sum_{mn}(-)^{m+n+1}$$

$$\times C(2,1,1;\nu-m-n,m+n,\nu)$$

$$\times C(\ell,1,\ell+1;m,-m-n,-n)C(\ell+1,1,\ell+2;n,$$

$$-n,0)Y_{\ell,m}(\hat{\omega}_1)Y_{1,n}(\hat{\omega}_k)Y_{2,\nu-m-n}(\hat{\omega}_k).$$

The contributions of molecule k to R- or T-branch transitions due to an anisotropic interaction can be isolated by making use of product rule for spherical harmonics,[20]

$$Y_{1,n}(\hat{\omega}_k)Y_{2,\nu-m-n}(\hat{\omega}_k)=\sum_M -(1/2\pi)^{1/2}C(1,2,1;n,\nu-m$$

$$-n,M)Y_{1,M}(\hat{\omega}_k)$$

$$+(9/28\pi)^{1/2}C(1,2,3;n,\nu-m$$

$$-n,M)Y_{3,M}(\hat{\omega}_k). \quad (15)$$

Next we need the matrix elements for the part of induced dipole moment that contributes to the corresponding transition between the initial and final states of the pair of molecules. Throughout this paper, any mixing of rotational states of individual molecule by the anisotropic interaction present in the crystal is neglected and the rovibrational states for the pair are taken as simple product states

$$|1v_1,J_1M_1;kv_k,J_kM_k\rangle=|1v_1,J_1,(r_1)\rangle|kv_k,J_k,(r_k)\rangle$$

$$\times Y_{J_1,M_1}(\hat{\omega}_1)Y_{J_k,M_k}(\hat{\omega}_k),$$

in which $|v,J,(r)\rangle$ refers to the radial part of the wave function of the vibrating rotator. The initial state $|i\rangle$ $=|10,00;k0,00\rangle=|10,0,(r_1)\rangle|k0,0,(r_k)\rangle Y_{0,0}(\hat{\omega}_1)Y_{0,0}(\hat{\omega}_k)$ is the same for all transitions considered. The final state $|f\rangle$, reached by the molecular pair subsequent to absorption, for the transitions $[\Delta J=\ell]_{v_1}(0)+R_{v_k}(0)$ and $[\Delta J=\ell]_{v_1}(0)+T_{v_k}(0)$ are, respectively,

$$|1v_1,\ell M_1';kv_k,1M_k'\rangle=|1v_1,\ell,(r_1')\rangle|kv_k,1,(r_k')\rangle$$

$$\times Y_{\ell M_1'}(\hat{\omega}_1)Y_{1,M_k'}(\hat{\omega}_k)$$

and

$$|1v_1,\ell M_1';kv_k,3M_k'\rangle=|1v_1,\ell,(r_1')\rangle|kv_k,3,(r_k')\rangle$$

$$\times Y_{\ell M_1'}(\hat{\omega}_1)Y_{3,M_k'}(\hat{\omega}_k).$$

Insertion of the matrix elements in Eq. (2) and summation over the lattice in Eq. (14) yield

$$\tilde{\alpha}\{[\Delta J=\ell(>1)]_{v_1}(0)+R_{v_k}(0)\}=\frac{8\pi^3(\ell+1)(\ell+2)(2\ell+3)}{9ha^{(2\ell+6)}}\langle v_1\ell|Q_\ell^{CM}(r)|00\rangle^2\xi_{\ell+3}''S_{\ell+3}''\left\{\langle v_k1|x\alpha^{CC}(r)|00\rangle^2\right.$$

$$\left.+\frac{1}{225}\langle v_k1|x\gamma^{CC}(r)|00\rangle^2+\frac{2}{15}\langle v_k1|x\alpha^{CC}(r)|00\rangle\langle v_k1|x\gamma^{CC}(r)|00\rangle\right\}, \quad (16)$$

$$\tilde{\alpha}\{[\Delta J=\ell(>3)]_{v_1}(0)+T_{v_k}(0)\}=\frac{16\pi^3(\ell+1)(\ell+2)(2\ell+3)}{75ha^{(2\ell+6)}}\langle v_1\ell|Q_\ell^{CM}(r)|00\rangle^2\langle v_k3|x\gamma^{CC}(r)|00\rangle^2\xi_{\ell+3}''S_{\ell+3}'', \quad (17)$$

TABLE II. Computed values for rovibrational matrix elements $\langle v'J'|\hat{O}|00\rangle$ of various operators $\hat{O}$ involving polarizability and x for HD, HT, and DT. The parameter x stands for the distance between the centers of charge and mass. The matrix elements are valid in the center of charge coordinate system. The algebraic sign of the matrix elements is determined by the phase convention that each radial wave function is real and positive at its outermost extremum. This means that the innermost wave function lobe is positive for even levels ($v=0,2,4,\ldots$) and negative for odd levels ($v=1,3,5,\ldots$).

| J' | $\hat{O}$ | $v'=0$ | | | $v'=1$ | | | $v'=2$ | | |
		HD	HT	DT	HD	HT	DT	HD	HT	DT
0	$\alpha(r)$	5.38552	5.37394	5.33407	0.68551	0.66469	0.58799	−0.06051	−0.05671	−0.04391
1	$x\alpha(r)$	1.31311	1.95839	0.76878	0.30382	0.44078	0.15479	−0.00873	−0.01201	−0.00344
1	$x\gamma(r)$	0.49572	0.73613	0.28466	0.19157	0.27669	0.09565	0.01065	0.01526	0.00502
2	$\gamma(r)$	2.00763	1.99563	1.95494	0.53109	0.51524	0.45651	−0.01598	−0.01426	−0.00915
3	$x\gamma(r)$	0.50043	0.74239	0.28620	0.17912	0.25973	0.09101	0.00607	0.00919	0.00352

where $S''_{\ell+3}$ stands for the lattice sum $\Sigma_k'(a/R_{1k})^{2\ell+6}$ and $\xi''_{\ell+3}$ is the corresponding reduction factor. In the absorption intensity Eq. (17), the restriction $\ell > 3$ is imposed to preclude use of this expression to calculate the intensities of transitions of types $R+T$, $S+T$, and $T+T$. The intensity contribution to the $R+T$ transitions from Eq. (17) is negligible relative to that from Eq. (16). (The former contribution is due to the induced dipole that arises from the very weak permanent dipole moment of molecule 1 and the anisotropic polarizability of molecule k. In contrast, the latter contribution originates from a relatively strong induced dipole moment, due to the 2^3-pole moment of molecule 1 and the polarizability of molecule k.) For $T+T$ transitions the role of molecules 1 and k can be interchanged, which gives rise to an interference effect, and a lengthy derivation leads to

$$\tilde{\alpha}\{T_{v_1}(0)+T_{v_k}(0)\}$$

$$=\frac{192\pi^3}{ha^{12}}\xi''_6 S''_6\{\tfrac{1}{5}\langle v_1 3|Q_3^{CM}(r)|00\rangle^2\langle v_k 3|x\gamma^{CC}(r)|00\rangle^2$$

$$+\tfrac{1}{5}\langle v_1 3|x\gamma^{CC}(r)|00\rangle^2\langle v_k 3|Q_3^{CM}(r)|00\rangle^2$$

$$-\tfrac{2}{7}\langle v_1 3|Q_3^{CM}(r)|00\rangle\langle v_k 3|Q_3^{CM}(r)|00\rangle$$

$$\times\langle v_1 3|x\gamma^{CC}(r)|00\rangle\langle v_k 3|x\gamma^{CC}(r)|00\rangle\}, \qquad (18)$$

$$\tilde{\alpha}\{T_v(0)+T_v(0)\}=\frac{384\pi^3}{35ha^{12}}\xi''_6 S''_6\langle v3|x\gamma^{CC}(r)|00\rangle^2\langle v3|$$

$$\times Q_3^{CM}(r)|00\rangle^2. \qquad (19)$$

Here it is important to mention that the substitution $v_1=v_k$ in Eq. (18) does not automatically lead to Eq. (19). Instead it yields an extra factor of 2 because of the double degeneracy that exists for $v_1 \neq v_k$. One final special case must be addressed. The $S+T$ transition types derive intensity from Eq. (11) as well as from Eq. (17). Again, an interference effect plays an important role and further calculation yields

$$\tilde{\alpha}\{S_{v_1}(0)+T_{v_k}(0)\}$$

$$=\frac{64\pi^3}{3ha^{10}}\xi S\{\tfrac{21}{25}\langle v_1 2|Q_2^{CM}(r)|00\rangle^2\langle v_k 3|x\gamma^{CC}(r)|00\rangle^2$$

$$+\tfrac{1}{9}\langle v_1 2|\gamma^{CC}(r)|00\rangle^2\langle v_k 3|Q_3^{CM}(r)|00\rangle^2$$

$$+\tfrac{2}{5}\langle v_1 2|Q_2^{CM}(r)|00\rangle\langle v_k 3|Q_3^{CM}(r)|00\rangle$$

$$\times\langle v_1 2|\gamma^{CC}(r)|00\rangle\langle v_k 3|x\gamma^{CC}(r)|00\rangle\}, \qquad (20)$$

where S stands for the lattice sum $\Sigma_k'(a/R_{1k})^{10}$ and ξ is the phonon renormalization factor.

III. RESULTS AND DISCUSSION

Equations (9)–(13) and (16)–(20) give the integrated absorption coefficients for different types of zero-phonon single and double transitions in the heteronuclear isotopomers of hydrogen in condensed phase. Of these, some special cases for solid HD, namely, $T_v(0), U_v(0), V_v(0), S_v(0)+R_{v'}(0), S_v(0)+T_{v'}(0)$, and $U_v(0)+Q_{v'}(0)$, have been treated previously.[8,9] Also, in Ref. 10, Poll *et al.* give some selected dipole coefficients for HD, $A_\Lambda^{(n)}(\lambda_1\lambda_2 L;r_1r_2R)$, which arise from "$n$-shifted" [obtained through n repeated applications of an operation, which is used to get first-order shifted coefficients (for details see Ref. 10)] multipolar-induced dipoles $A_\lambda(\lambda_1\lambda_2 L;r_1r_2R)$ of H_2 (homonuclear) molecule. These $A_\Lambda^{(n)}$ functions can be used to calculate the intensities of special case transitions in solid HD. In order to calculate $(n+1)$-shifted induced dipoles by this method, one needs prior knowledge of n-shifted dipoles. Moreover, a generalization of the results seems to be impossible. Using the transformation of multipole moments from one coordinate system to another,[19,22]

$$Q_\ell^{CM}(r)=Q_\ell^{CC}(r)+\sum_{\ell_1=0}^{\ell-1}\frac{(-)^{\ell-\ell_1}\ell!}{\ell_1!(\ell-\ell_1)!}x^{\ell-\ell_1}Q_{\ell_1}^{CC}(r),$$

and setting the distance between the CM and the CC, $x=r/6$ for HD, it can easily be shown that the general intensity formulas given in this paper reduce to the theoretical expressions for the special cases reported in Refs. 8–10. Thus, the present derivation of general expressions via a dif-

TABLE III. Predicted integrated absorption coefficients of typical zero-phonon single and double transitions in solid HD. Also included are experimental and earlier theoretical values, wherever data are available.

| Transition | Integrated absorption coefficient $\tilde{\alpha}$/cm^3 s^{-1} | | | | Transition | Integrated absorption coefficient $\tilde{\alpha}$/cm^3 s^{-1} | | | |
| | Experiment | | Theory | | | Experiment | | Theory | |
	Lo (Ref. 11)	Lee (Ref. 13)	Tipping and co-workers (Refs. 8–10)	This work		Lo (Ref. 11)	Lee (Ref. 13)	Tipping and co-workers (Refs. 8–10)	This work
$T_0(0)$			4.1×10^{-15}	3.94×10^{-15}	$R_0(0)+T_1(0)$				6.47×10^{-17}
$U_0(0)$	1.2×10^{-15}	1.1×10^{-15}	2.0×10^{-15}	1.86×10^{-15}	$R_0(0)+U_1(0)$				9.46×10^{-18}
$V_0(0)$	1.1×10^{-16}	8.9×10^{-17}	2.1×10^{-16}	1.96×10^{-16}	$R_0(0)+V_1(0)$				4.90×10^{-19}
$W_0(0)$			3.6×10^{-18}	2.88×10^{-18}	$R_0(0)+W_1(0)$				2.96×10^{-20}
				9.8×10^{-20}					
$X_0(0)$				8.36×10^{-20}	$R_1(0)+S_1(0)$	7.2×10^{-17}	6.5×10^{-17}		6.32×10^{-17}
$Y_0(0)$				4.67×10^{-22}	$R_1(0)+T_1(0)$				3.52×10^{-18}
$Z_0(0)$				2.82×10^{-23}	$R_1(0)+U_1(0)$				5.12×10^{-19}
$\Delta[J=10]_0(0)$				3.07×10^{-25}	$R_1(0)+V_1(0)$				2.65×10^{-20}
$\Delta[J=11]_0(0)$				1.39×10^{-25}	$R_1(0)+W_1(0)$				1.60×10^{-21}
$T_1(0)$			2.4×10^{-16}	2.26×10^{-16}	$S_0(0)+S_0(0)$				5.10×10^{-14}
$U_1(0)$	1.7×10^{-16}	1.5×10^{-16}	2.2×10^{-16}	2.00×10^{-16}	$S_0(0)+S_1(0)$	2.5×10^{-15}			5.71×10^{-15}
$V_1(0)$	2.1×10^{-17}		3.8×10^{-17}	3.32×10^{-17}	$S_1(0)+S_1(0)$	6.3×10^{-17}			8.46×10^{-17}
$W_1(0)$				6.98×10^{-19}	$S_0(0)+S_2(0)$				3.72×10^{-17}
$X_1(0)$				2.70×10^{-20}	$S_1(0)+S_2(0)$				2.96×10^{-18}
$Y_1(0)$				1.92×10^{-22}	$S_2(0)+S_2(0)$				1.37×10^{-21}
$T_2(0)$				1.45×10^{-19}	$S_0(0)+T_0(0)$	3.1×10^{-16}	1.2×10^{-15}		1.20×10^{-15}
$U_2(0)$				1.70×10^{-18}	$S_0(0)+U_0(0)$		6.9×10^{-17}		9.76×10^{-17}
$V_2(0)$				7.42×10^{-19}	$S_0(0)+V_0(0)$				2.32×10^{-18}
$W_2(0)$				2.76×10^{-20}	$S_0(0)+W_0(0)$				7.44×10^{-20}
$Q_1(0)+S_0(0)$				6.68×10^{-14}	$S_1(0)+T_0(0)$		7.7×10^{-17}		7.52×10^{-17}
$Q_1(0)+S_1(0)$		1.1×10^{-15}		1.59×10^{-15}	$S_1(0)+U_0(0)$		5.6×10^{-18}		6.83×10^{-18}
$Q_1(0)+S_2(0)$		1.6×10^{-17}		2.84×10^{-17}	$S_1(0)+V_0(0)$				1.63×10^{-19}
$Q_2(0)+S_0(0)$		3.3×10^{-16}		5.21×10^{-16}	$S_1(0)+W_0(0)$				5.21×10^{-21}
$Q_2(0)+S_1(0)$		5.2×10^{-18}		1.24×10^{-17}	$S_0(0)+T_1(0)$		1.2×10^{-16}		1.19×10^{-16}
$Q_2(0)+S_2(0)$				2.22×10^{-19}	$S_0(0)+U_1(0)$		7.0×10^{-18}		1.05×10^{-17}
$Q_3(0)+S_0(0)$		4.9×10^{-18}		8.59×10^{-18}	$S_0(0)+V_1(0)$				3.94×10^{-19}
$Q_3(0)+S_1(0)$				2.04×10^{-19}	$S_0(0)+W_1(0)$				1.81×10^{-20}
$Q_1(0)+T_0(0)$			9.9×10^{-16}	9.66×10^{-16}	$S_1(0)+T_1(0)$				4.42×10^{-18}
$Q_1(0)+U_0(0)$		7.3×10^{-17}	5.5×10^{-17}	5.12×10^{-17}	$S_1(0)+U_1(0)$				7.35×10^{-19}
$Q_1(0)+V_0(0)$			1.3×10^{-18}	1.22×10^{-18}	$S_1(0)+V_1(0)$				2.76×10^{-20}
$Q_1(0)+W_0(0)$			4.9×10^{-20}	3.90×10^{-20}	$T_0(0)+T_0(0)$				1.10×10^{-17}
			1.3×10^{-21}						
$Q_1(0)+X_0(0)$				1.06×10^{-21}	$T_0(0)+T_1(0)$				2.43×10^{-18}
$Q_1(0)+Y_0(0)$				3.10×10^{-23}	$T_1(0)+T_1(0)$				8.10×10^{-20}
$Q_1(0)+T_1(0)$				5.54×10^{-17}	$T_0(0)+T2(0)$				3.04×10^{-20}
$Q_1(0)+U_1(0)$				5.51×10^{-18}	$T_0(0)+U_0(0)$				2.51×10^{-19}
$Q_1(0)+V_1(0)$				2.07×10^{-19}	$T_0(0)+U_1(0)$				2.70×10^{-20}
$Q_1(0)+W_1(0)$				9.47×10^{-21}	$T_1(0)+U_0(0)$				3.22×10^{-20}
$R_0(0)+S_0(0)$				4.81×10^{-14}	$T_1(0)+U_1(0)$				3.47×10^{-21}
$R_0(0)+T_0(0)$			1.2×10^{-15}	1.13×10^{-15}	$T_0(0)+V_0(0)$				8.28×10^{-21}
$R_0(0)+U_0(0)$				8.80×10^{-17}	$T_0(0)+V_1(0)$				1.4×10^{-21}
$R_0(0)+V_0(0)$				2.89×10^{-18}	$T_1(0)+V_0(0)$				1.06×10^{-21}
$R_0(0)+W_0(0)$				1.22×10^{-19}	$T_1(0)+V_1(0)$				1.80×10^{-22}
$R_0(0)+S_1(0)$				1.14×10^{-15}					

TABLE IV. Predicted intensities of some of the mixed isotopomer transitions in a HD crystal.

Transition	$\widetilde{\alpha}/\text{cm}^3\ \text{s}^{-1}$	Transition	$\widetilde{\alpha}/\text{cm}^3\ \text{s}^{-1}$
$Q_1(0)\text{HD}+S_0(0)\text{H}_2$	6.79×10^{-14}	$Q_1(0)\text{H}_2+W_1(0)\text{HD}$	1.10×10^{-20}
$Q_1(0)\text{HD}+U_0(0)\text{H}_2$	4.46×10^{-16}	$Q_2(0)\text{H}_2+S_0(0)\text{HD}$	7.18×10^{-16}
$Q_1(0)\text{HD}+W_0(0)\text{H}_2$	8.45×10^{-18}	$R_0(0)\text{HD}+S_0(0)\text{H}_2$	4.89×10^{-14}
$Q_1(0)\text{HD}+S_1(0)\text{H}_2$	1.77×10^{-15}	$R_0(0)\text{HD}+U_0(0)\text{H}_2$	4.06×10^{-17}
$Q_1(0)\text{HD}+U_1(0)\text{H}_2$	2.87×10^{-18}	$R_0(0)\text{HD}+W_0(0)\text{H}_2$	2.01×10^{-20}
$Q_1(0)\text{HD}+W_1(0)\text{H}_2$	1.66×10^{-21}	$R_0(0)\text{HD}+S_1(0)\text{H}_2$	1.27×10^{-15}
$Q_2(0)\text{HD}+S_0(0)\text{H}_2$	5.30×10^{-16}	$R_0(0)\text{HD}+U_1(0)\text{H}_2$	4.93×10^{-18}
$Q_1(0)\text{H}_2+S_0(0)\text{HD}$	7.79×10^{-14}	$R_1(0)\text{HD}+S_1(0)\text{H}_2$	7.05×10^{-17}
$Q_1(0)\text{H}_2+T_0(0)\text{HD}$	1.13×10^{-15}	$R_1(0)\text{HD}+U_1(0)\text{H}_2$	2.67×10^{-19}
$Q_1(0)\text{H}_2+U_0(0)\text{HD}$	5.97×10^{-17}	$S_0(0)\text{HD}+S_0(0)\text{H}_2$	1.04×10^{-17}
$Q_1(0)\text{H}_2+V_0(0)\text{HD}$	1.42×10^{-18}	$S_0(0)\text{HD}+U_0(0)\text{H}_2$	4.51×10^{-17}
$Q_1(0)\text{H}_2+W_0(0)\text{HD}$	4.55×10^{-20}	$S_0(0)\text{HD}+S_1(0)\text{H}_2$	6.63×10^{-19}
$Q_1(0)\text{H}_2+S_1(0)\text{HD}$	1.85×10^{-15}	$S_1(0)\text{HD}+S_0(0)\text{H}_2$	5.80×10^{-19}
$Q_1(0)\text{H}_2+T_1(0)\text{HD}$	6.46×10^{-17}	$S_0(0)\text{HD}+U_1(0)\text{H}_2$	5.47×10^{-18}
$Q_1(0)\text{H}_2+U_1(0)\text{HD}$	6.42×10^{-18}	$T_0(0)\text{HD}+U_0(0)\text{H}_2$	1.16×10^{-19}
$Q_1(0)\text{H}_2+V_1(0)\text{HD}$	2.41×10^{-19}		

ferent route provides an independent confirmation of the results in Refs. 8–10 and vice versa. The factor 1/18 that appears in Eqs. (10) and (14) of Ref. 9 should in fact be replaced by 1/3.

The intensity expressions in the present paper are more compact than those in Refs. 8–10 and contain rovibrational matrix elements of the multipole moments in the CM coordinate system and of $\alpha(r)$, $\gamma(r)$, $x\alpha(r)$, and $x\gamma(r)$ in the CC coordinate system. While the required rotational-vibrational matrix elements for the multipole moments up to order 11 are reported for all heteronuclear isotopomers,[19] for other operators the required matrix elements are only available for HD.[10] In Table II, we list the necessary rovibrational matrix elements of $\alpha(r)$, $\gamma(r)$, $x\alpha(r)$, and $x\gamma(r)$ for all heteronuclear isotopomers, including HD, as we believe these matrix elements are more accurate than the results given in Ref. 10. A comprehensive listing of different matrix elements may be obtained from the authors on request. These matrix elements are computed using the r-dependent polarizability functions given by Rychlewski,[23] potentials of Ref. 24, and the computer program "LEVEL 6.0" obtained from Le Roy.[25] Finally, using the data given in Tables I and II, and the expressions derived in this paper, we give in Table III theoretical values of integrated absorption coefficients for the various zero-phonon transitions in solid HD. A comparison of the present results with other theoretical works and the experimental observations is also made, wherever the data are available. The theoretical calculations assume that the phonon renormalization factors are equal to 1. The value for the nearest-neighbor distance a is taken as 6.8824 a.u. from Ref. 26. In general, there is good agreement among the present work, the experimental observations, and the previous theoretical estimates. Our theoretical intensities for single and double transitions differ by 2–30 % from the intensities predicted by Tipping co-workers.[8–10] In fact, for most cases, our values are closer to experimental observations. This is due to the fact that the various rovibrational matrix elements used in our calculations, particularly of higher-order multipole moments, are more accurate. Poll *et al.*[10] have predicted two possibilities for intensities of the transitions $W_0(0)$ and $Q_1(0)+W_0(0)$ dependent upon the sign of $\langle 06|Q_6|00\rangle$ for the H_2 molecule, which is obtained from the observed intensity of the $W_0(0)$ transition.[27] Our predicted intensity is close to the value obtained for the positive sign of the matrix element, in agreement with the computed Q_6 matrix element for the H_2 molecule.[28] For $S_{v_1}(0)+T_{v_k}(0)$ type transitions an experimental intensity is available only for one transition, $S_0(0)+T_0(0)$, and our value as well as the Ref. 8 theoretical value are approximately a factor of 4 larger than the experimental result. Accurate measurements of the intensity of this transition and other transitions of this type are therefore required to validate Eq. (20). Intensities of, hitherto unobserved, double transitions of $T+\Delta J\geqslant 3$ type and of transitions involving $\Delta J\geqslant 7$ are predicted here to the best of our knowledge. New infrared measurements with high sensitivity, as have been demonstrated by Okumura *et al.*[27] and Winnewisser and co-workers[29] in their observations of W and Y transitions in solid H_2, could test the reliability of the present results for higher-order multipole-induced transitions (W,X,Y, etc.) and for the predicted double transitions of types $T+T,T+U,T+V$, etc.

One can also make use of the intensity formulas for double transitions given in this work to calculate the intensity of mixed isotopomer transitions, where both molecules are initially in the $J=0$ rotational state. All expressions for double transitions, except Eqs. (13) and (19), are applicable to mixed double transitions when both molecules are heteronuclear. Equations (12) and (18), rather than Eqs. (13) and (19), are the correct formulas for $v_1=v_k=v$. When one molecule of the pair undergoing simultaneous transitions is homonuclear (*para*-H_2 or *ortho*-D_2), then ℓ is restricted to even values and, in the intensity expressions, v_1 and v_k should, respectively, be associated with homonuclear and

heteronuclear molecules. For example, the expression for the intensity of the $R_v(0)\text{HD}+[\Delta J=\ell]_{v'}(0)\text{H}_2$ transition is

$$\tilde{\alpha}\{[\Delta J=\ell]_{v'}(0)\text{H}_2+R_v(0)\text{HD}\}$$

$$=\frac{8\pi^3(\ell+1)(\ell+2)(2\ell+3)}{9ha^{(2\ell+6)}}$$

$$\times\langle v'\ell|Q_\ell^{\text{H}_2}(r)|00\rangle^2\xi_{\ell+3}''S_{\ell+3}''$$

$$\times\left\{\langle v1|x\alpha^{\text{HD}}(r)|00\rangle^2+\frac{1}{225}\langle v1|x\gamma^{\text{HD}}(r)|00\rangle^2\right.$$

$$\left.+\frac{2}{15}\langle v1|x\alpha^{\text{HD}}(r)|00\rangle\langle v1|x\gamma^{\text{HD}}(r)|00\rangle\right\}.$$

Note that for homonuclear molecules the center of mass coincides with the center of charge. When calculating the intensities of transitions of the type $S_v(0)\text{H}_2+T_{v'}(0)\text{HD}$, Eq. (11) rather than Eq. (20) should be used. Again, for transitions $S_v(0)\text{H}_2+S_v(0)\text{HD}$, Eq. (12) and not Eq. (13) should be applied. In Table IV, we give the predicted intensities of some mixed isotopomer transitions. However, most such experimentally measured transitions involve *ortho*-H_2, and the present formalism can be applied to develop expressions for the transitions involving $J=1$.

IV. CONCLUSION

Closed-form formulas are derived for the intensities of single and double transitions in solid HD, HT, and DT. These formulas can be applied to many mixed isotopomer transitions and the same method can be applied to predict the intensities of other kinds of mixed isotopomer transitions. In this paper, we provide tests of fundamental concepts for the prototype systems of solid hydrogens. We hope to stimulate further studies, both experimental and theoretical, of other molecular solids. In view of the availability of very accurate rovibrational matrix elements of multipole moments[19,28,30,31] up to rank 11 for all isotopomers of hydrogen and the high sensitivity recently achieved in absorption experiments,[27,29] together with the ease of growing high optical quality hydrogen crystals by the rapid vapor deposition method,[32] new and accurate measurements of the infrared spectra of solid hydrogen of all isotopic variants are desirable.

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