

Absorption intensities of the multipole-field-induced double transitions involving a homonuclear-heteronuclear pair of hydrogen molecules in condensed phase

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Theoretical expressions are derived for the integrated absorption coefficients of various zero-phonon double transitions involving a homonuclear-heteronuclear pair of hydrogen molecules in condensed phase. The formulas given in this paper can be applied to transitions in the absorption spectra of solid parahydrogen (or orthodeuterium, or solid HD, HT, etc.) matrices that contain a low concentration of impurity molecules which do not possess a permanent dipole moment (e.g., N_2).

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I. INTRODUCTION

Solid hydrogen and its isotopic variants are the simplest molecular quantum crystals and therefore provide unique opportunities for the study of lattice dynamics and intermolecular interactions in the condensed phase.¹⁻³ The study of absorption intensities in the spectra of solid hydrogens (H_2 , D_2 , HD, etc.) and comparisons between theory and experiment have been the subject of intensive research, due to the fundamental importance of solid hydrogens.¹⁻²² The gas phase property of quantized end-over-end molecular rotation persists in the solid hydrogens down to 0 K, with little change. This is a direct consequence of the extreme weakness of the anisotropic intermolecular forces, on the one hand, and the small moment of inertia of the molecules, on the other. The extremely weak intermolecular forces are the result of a nearly spherical molecular charge distribution and the large nearest-neighbor distances (3.6–3.8 Å) in the solid.¹ Due to very weak intermolecular forces, solid hydrogens have been recognized as unique cryogenic media for spectroscopic studies of molecular rotational-vibrational dynamics in the condensed phase.³ This has motivated, in recent years, high resolution infrared absorption studies of the rovibrational spectra of dopants embedded in solid hydrogens.²³⁻²⁶

Theoretically, it would be useful first to understand the spectra of solid hydrogen for a specific isotopomer that contains a small concentration of another isotopomer as a dopant. Recently, while developing intensity formulas for multipole-induced transitions in solid HD, HT, etc., we realized that most of the expressions for double transitions can be applied to *mixed* double transitions involving para- H_2 -HD or ortho- D_2 -HD pairs.²² The goal of this paper is to present intensity expressions derived for mixed isotopomer transitions involving ortho- H_2 or para- D_2 ($J=1$) in the molecular pair. Here J refers to the rotational quantum number of the molecule. Although mixed isotopomer transitions, where an HD molecule and an ortho- H_2 or para- D_2 molecule simultaneously take part in a transition, are observed experimentally and absorption intensities are measured for some of the lines,^{5,7,14} so far no theoretical analysis of the intensities of such transitions has been attempted. The formulas given in

this paper can be applied to the dopant-hydrogen combination transitions observed in the infrared spectra of solid para- H_2 (or ortho- D_2 , HD, HT, etc.) matrices containing a low concentration of impurity molecules.

II. THEORY

The absorption process in solid hydrogens results primarily from induced dipole moments. Details of the formalism used in the present work can be found in Refs. 16, 20 and 22. For any double transition, we first obtain the partial absorp-

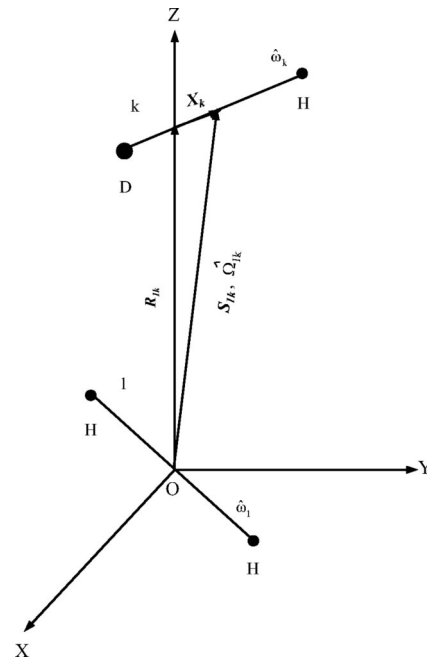


FIG. 1. Multipolar induction in a molecular pair (1,k) in a solid HD crystal that contains a small concentration of H_2 as impurity. Here HD and H_2 are representatives of, respectively, heteronuclear and homonuclear isotopomers. The origin 'O' of the laboratory coordinate system XYZ is placed at the c.m. of molecule 1, which is H_2 . k specifies an HD molecule, with center of mass located on the Z axis at $(0,0,R_{1k})$. The vector \mathbf{X}_k connects the c.m. of molecule k to its CC. The Z axis is directed along the hexagonal axis of the hcp lattice. $\omega_i (= \theta_i, \phi_i)$ defines the orientation of molecule i .

tion coefficient $\tilde{\alpha}(1,k)$ due to a pair of molecules 1 and k , and the net absorption coefficient is obtained by summing the pair absorption coefficients over k ,

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

The calculation of a partial absorption coefficient involves the matrix elements of the induced dipole moment μ_{ind} between initial and final states of the pair of molecules $(1,k)$. In order to calculate μ_{ind} , let us consider an isolated homonuclear-heteronuclear hydrogen molecular pair $(1,k)$ in a single crystal of, let us say, a heteronuclear solid hydrogen (HD, HT, or DT) at 0 K and assume a rigid hexagonal close packed (hcp) lattice. We label the lone homonuclear molecule (para- or ortho- H_2 , D_2 , etc.) substitutionally buried in the crystal as 1 and place its center at the origin of a laboratory fixed coordinate system XYZ (the Z axis pointing along the hexagonal axis) as shown in Fig. 1. The orientation of the intermolecular axis does not affect the value of $\tilde{\alpha}(1,k)$ for a double transition.^{20,22} We exploit this freedom to locate the center of mass (c.m.) of an arbitrary heteronuclear molecule, k , at $(0,0,R_{1k})$, that is, on the Z axis in Fig. 1. The c.m. of molecule k is specified by the position vector \mathbf{R}_{1k} ($=R_{1k}\hat{Z}$), while the center of charge (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 $\hat{\omega}_k(=\theta_k,\phi_k)$. Since, in the heteronuclear isotopomers, the c.m. does not coincide with the center of charge, one must express all of the relevant quantities in c.m. coordinates. The two relevant quantities required for the intensity calculations are the rovibrational matrix elements of the multipole moments and of the polarizability. The former matrix elements of these molecules have been reported by Mishra *et al.*²⁷ in the c.m. coordinates while the later matrix elements are available in the CC coordinate.^{22,28} In order to overcome the difficulty of two quantities being expressed in two different coordinate systems, one can make use of the relation between \mathbf{R}_{1k} and \mathbf{S}_{1k} illustrated by Fig. 1

$$\mathbf{S}_{1k} = \mathbf{R}_{1k} + \mathbf{X}_k \quad (2)$$

and expand the induced dipole moment as a Taylor series around \mathbf{R}_{1k} . For the above choice of location of molecule k (the c.m. on the Z axis as shown in Fig. 1), the spherical components $\mu_{\nu}^{\text{iso}}(l;1,k,\mathbf{S}_{1k})$ of the dipole moment induced in molecule k by the 2^l -pole field of molecule 1, through the isotropic and anisotropic parts of the polarizability of k , are given by²²

$$\begin{aligned} \mu_{\nu}^{\text{iso}}(l;1,k,\mathbf{S}_{1k}) &= [4\pi(l+1)]^{1/2} Q_l(r_1) \alpha(r_k) R_{1k}^{-(l+2)} (-)^{\nu} C(l,1,l+1;\nu,-\nu,0) Y_{l,\nu}(\hat{\omega}_1) + 4\pi[(l+1)(l+2) \\ &\quad \times (2l+3)/3]^{1/2} Q_l(r_1) X_k \alpha(r_k) R_{1k}^{-(l+3)} (-)^{\nu+1} \sum_n C(l,1,l+1;n-\nu,\nu,n) \\ &\quad \times C(l+1,1,l+2;n,-n,0) Y_{l,\nu-n}(\hat{\omega}_1) Y_{1,n}(\hat{\omega}_k) = \mu_{\nu}^{\text{iso}}(l;1,k)_I + \mu_{\nu}^{\text{iso}}(l;1,k)_{II}, \end{aligned} \quad (3)$$

$$\begin{aligned} \mu_{\nu}^{\text{an}}(l;1,k,\mathbf{S}_{1k}) &= [32\pi^2(l+1)/9]^{1/2} Q_l(r_1) \gamma(r_k) R_{1k}^{-(l+2)} \sum_m (-)^{l-m} C(2,1,1;\nu-m,m,\nu) C(l,1,l+1;m,-m,0) \\ &\quad \times Y_{l,m}(\hat{\omega}_1) Y_{2,\nu-m}(\hat{\omega}_k) + [128\pi^3(l+1)(l+2)(2l+3)/27]^{1/2} Q_l(r_1) X_k \gamma(r_k) R_{1k}^{-(l+3)} \\ &\quad \times \sum_{mn} (-)^{m+n} C(2,1,1;\nu-m-n,m+n,\nu) C(l,1,l+1;m,-m-n,-n) \\ &\quad \times C(l+1,1,l+2;n,-n,0) Y_{l,m}(\hat{\omega}_1) Y_{1,n}(\hat{\omega}_k) Y_{2,\nu-m-n}(\hat{\omega}_k) = \mu_{\nu}^{\text{an}}(l;1,k)_I + \mu_{\nu}^{\text{an}}(l;1,k)_{II}. \end{aligned} \quad (4)$$

In the above equations, $Q_l(r_1)$ is the 2^l -pole moment of molecule 1 in the c.m. coordinate, $\alpha(r_k)$ and $\gamma(r_k)$ are, respectively the isotropic and anisotropic parts of the polarizability of molecule k in the CC coordinate, X_k is the magnitude of the vector, \mathbf{X}_k , that connects the c.m. of molecule k to its CC, $Y_{L,M}$ is a spherical harmonic, C is a Clebsch-Gordan coefficient, and r_1 and r_k are the internuclear separations in the molecules specified by 1 and k . In Eqs. (3) and (4), only terms up to linear in X_k have been included. A

justification for truncation of the Taylor expansion at the linear term is given in Ref. 22.

Relations similar to Eqs. (3) and (4), supplemented by appropriate phase factors, describe dipole moments induced by the multipole of k on 1. Note that for centrosymmetric homonuclear molecules such as H_2 , D_2 , etc., Q_l is nonzero only for even values of $l \geq 2$. Also, for homonuclear molecules, the c.m. coincides with the CC, which means that $x_1=0$. Therefore, for induction by the multipole of k on 1,

TABLE I. Intensity formulas for homonuclear-heteronuclear double transitions in solid hydrogen, where the homonuclear molecule is in the $J=0$ rotational state (i.e., para- H_2 or ortho- D_2). In the intensity formulas, the matrix elements of the multipole moment, Q_l , are in the c.m. coordinate, whereas those of the polarizabilities, α and γ , are in the CC coordinate. The parts of $\mu_\nu(\text{pair}1,k)$ of Eq. (5), that yield a nonvanishing contribution to the transition, are also listed. Note that the formulas are valid for any homonuclear-heteronuclear combination: H_2 represents a homonuclear molecule while the HD stands for a heteronuclear molecule.

Transition	Parts of $\mu_\nu(\text{pair}1,k)$	Integrated absorption coefficient $\tilde{\alpha}/\text{cm}^3 \text{ s}^{-1}$
$Q_{v_{\text{HD}}}(0) + [\Delta J = l]_{v_{\text{H}_2}}(0)$	$\mu_\nu^{\text{iso}}(l; 1, k)_I$	$\frac{8\pi^3(l+1)}{3ha^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} 0 \alpha 00 \rangle^2 \langle v_{\text{H}_2} l Q_l 00 \rangle^2$
$R_{v_{\text{HD}}}(0) + [\Delta J = l]_{v_{\text{H}_2}}(0)$	$\mu_\nu^{\text{iso}}(l; 1, k)_{II} + \mu_\nu^{\text{an}}(l; 1, k)_{II}$	$\frac{8\pi^3(l+1)(l+2)(2l+3)}{9ha^{(2l+6)}} \xi_{l+3} S_{l+3} \langle v_{\text{H}_2} l Q_l 00 \rangle^2 [\langle v_{\text{HD}} 1 X \alpha 00 \rangle + \frac{1}{15} \langle v_{\text{HD}} 1 X \gamma 00 \rangle]^2$
$S_{v_{\text{HD}}}(0) + [\Delta J = l(\geq 4)]_{v_{\text{H}_2}}(0)$	$\mu_\nu^{\text{an}}(l; 1, k)_I$	$\frac{16\pi^3(l+1)}{27h(a^{(2l+4)})} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} 2 \gamma 00 \rangle^2 \langle v_{\text{H}_2} l Q_l 00 \rangle^2$
$S_{v_{\text{HD}}}(0) + S_{v_{\text{H}_2}}(0)$	$\mu_\nu^{\text{an}}(2; 1, k)_I + \mu_\nu^{\text{an}}(2; k, 1)_I$	$\frac{8\pi^3}{3ha^8} \xi_4 S_4 [\frac{2}{3} \langle v_{\text{HD}} 2 Q_2 00 \rangle^2 \langle v_{\text{H}_2} 2 \gamma 00 \rangle^2 + \frac{2}{3} \langle v_{\text{H}_2} 2 Q_2 00 \rangle^2 \times \langle v_{\text{HD}} 2 \gamma 00 \rangle^2 - \frac{4}{5} \langle v_{\text{HD}} 2 Q_2 00 \rangle \langle v_{\text{H}_2} 2 Q_2 00 \rangle \times \langle v_{\text{H}_2} 2 \gamma 00 \rangle \langle v_{\text{HD}} 2 \gamma 00 \rangle]$
$T_{v_{\text{HD}}}(0) + [\Delta J = l(\geq 4)]_{v_{\text{H}_2}}(0)$	$\mu_\nu^{\text{an}}(l; 1, k)_{II}$	$\frac{16\pi^3(l+1)(l+2)(2l+3)}{75ha^{(2l+6)}} \times \xi_{l+3} S_{l+3} \langle v_{\text{H}_2} l Q_l 00 \rangle^2 \langle v_{\text{HD}} 3 X \gamma 00 \rangle^2$
$Q_{v_{\text{H}_2}}(0) + [\Delta J = l(>1)]_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{iso}}(l; k, 1)_I$	$\frac{8\pi^3(l+1)}{3ha^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{H}_2} 0 \alpha 00 \rangle^2 \langle v_{\text{HD}} l Q_l 00 \rangle^2$
$S_{v_{\text{H}_2}}(0) + [\Delta J = l(\geq 4)]_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{an}}(l; k, 1)_I$	$\frac{16\pi^3(l+1)}{27ha^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} l Q_l 00 \rangle^2 \langle v_{\text{H}_2} 2 \gamma 00 \rangle^2$
$S_{v_{\text{H}_2}}(0) + T_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{an}}(2; 1, k)_{II} + \mu_\nu^{\text{an}}(3; k, 1)_I$	$\frac{64\pi^3}{3ha^{10}} \xi_5 S_5 [\frac{1}{5} \langle v_{\text{HD}} 3 Q_3 00 \rangle^2 \langle v_{\text{H}_2} 2 \gamma 00 \rangle^2 + \frac{21}{25} \langle v_{\text{H}_2} 2 Q_2 00 \rangle^2 \langle v_{\text{HD}} 3 X \gamma 00 \rangle^2 + \frac{2}{5} \langle v_{\text{HD}} 3 Q_3 00 \rangle \langle v_{\text{H}_2} 2 \gamma 00 \rangle \times \langle v_{\text{H}_2} 2 Q_2 00 \rangle \langle v_{\text{HD}} 3 X \gamma 00 \rangle]$

contributions arising from the second term of Eqs. (3) and (4) vanish. Thus the induced moment in the pair can be written as

$$\begin{aligned} \mu_\nu(\text{pair}1,k) = & \mu_\nu^{\text{iso}}(l; 1, k)_I + \mu_\nu^{\text{iso}}(l; 1, k)_{II} + \mu_\nu^{\text{an}}(l; 1, k)_I \\ & + \mu_\nu^{\text{an}}(l; 1, k)_{II} + \mu_\nu^{\text{iso}}(l; k, 1)_I + \mu_\nu^{\text{an}}(l; k, 1)_I. \end{aligned} \quad (5)$$

The induced moment in the pair given by Eq. (5), must in principle be summed over all possible l values. However, in practice, this is not necessary since not all values of l contribute to a given transition. Even for a given value of l , only some among the six terms given in Eq. (5) give nonzero matrix elements. Considering the lowest-order multipolar induction, in Tables I and II, we identify which of the terms in $\mu_\nu(\text{pair}1,k)$ give rise to nonvanishing contributions to a particular transition. The higher order multipoles contribute to

TABLE II. Intensity formulas for homonuclear-heteronuclear double transitions in solid hydrogen, where the homonuclear molecule is in the $J=1$ rotational state (i.e., ortho- H_2 or para- D_2). In the intensity formulas, the matrix elements of the multipole moment Q_l are in the c.m. coordinate, whereas those of the polarizabilities α and γ , are in the CC coordinate. The parts of $\mu_\nu(\text{pair}1,k)$ of Eq. (5) that yield a nonvanishing contribution to the transition, are also listed. Note that the formulas are valid for any homonuclear-heteronuclear combination: H_2 represents a homonuclear molecule while the HD stands for a heteronuclear molecule.

Transition	Parts of $\mu_\nu(\text{pair}1,k)$	Integrated absorption coefficient $\tilde{\alpha}/\text{cm}^3 \text{ s}^{-1}$
$Q_{v_{\text{HD}}}(0) + [\Delta J = l(\geq 2)]_{v_{H_2}}(1)$	$\mu_\nu^{\text{iso}}(l; 1, k)_I$	$\frac{8\pi^3(l+1)^2}{3h(2l+1)a^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} 0 \alpha 00 \rangle^2 \langle v_{H_2} l + 1 Q_l 01 \rangle^2$
$Q_{v_{\text{HD}}}(0) + Q_{v_{H_2}}(1)$	$\mu_\nu^{\text{iso}}(l=2; 1, k)_I$	$\frac{16\pi^3}{5ha^8} \xi_4 S_4 \langle v_{\text{HD}} 0 \alpha 00 \rangle^2 \langle v_{H_2} 1 Q_2 01 \rangle^2$
$Q_{v_{H_2}}(1) + [\Delta J = l(\geq 4)]_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{iso}}(l; k, 1)_I + \mu_\nu^{\text{an}}(l; k, 1)_I$	$\frac{8\pi^3(l+1)}{3ha^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} l Q_l 00 \rangle^2 \{ \langle v_{H_2} 1 \alpha 01 \rangle^2 + \frac{4}{45} \langle v_{H_2} 1 \gamma 01 \rangle^2 \}$
$Q_{v_{H_2}}(1) + R_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{iso}}(2; 1, k)_{II} + \mu_\nu^{\text{an}}(2; 1, k)_{II}$	$\frac{448\pi^3}{15ha^{10}} \xi_5 S_5 \langle v_{H_2} 1 Q_2 01 \rangle^2 [\langle v_{\text{HD}} 1 X \alpha 00 \rangle + \frac{1}{15} \langle v_{\text{HD}} 1 X \gamma 00 \rangle]^2$
$Q_{v_{H_2}}(1) + S_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{iso}}(2; k, 1)_I + \mu_\nu^{\text{an}}(2; k, 1)_I + \mu_\nu^{\text{an}}(2; 1, k)_I$	$\frac{8\pi^3}{3ha^8} \xi_4 S_4 \{ \langle v_{\text{HD}} 2 Q_2 00 \rangle^2 [3 \langle v_{H_2} 1 \alpha 01 \rangle^2 + \frac{4}{15} \langle v_{H_2} 1 \gamma 01 \rangle^2] + \frac{4}{15} \langle v_{H_2} 1 Q_2 01 \rangle^2 \langle v_{\text{HD}} 2 \gamma 00 \rangle^2 - \frac{8}{25} \langle v_{\text{HD}} 2 Q_2 00 \rangle \langle v_{H_2} 1 Q_2 01 \rangle \langle v_{\text{HD}} 2 \gamma 00 \rangle \times \langle v_{H_2} 1 \gamma 01 \rangle \}$
$Q_{v_{H_2}}(1) + T_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{iso}}(3; k, 1)_I + \mu_\nu^{\text{an}}(3; k, 1)_I + \mu_\nu^{\text{an}}(2; 1, k)_{II}$	$\frac{32\pi^3}{3ha^{10}} \xi_5 S_5 \{ \langle v_{\text{HD}} 3 Q_3 00 \rangle^2 [\langle v_{H_2} 1 \alpha 01 \rangle^2 + \frac{4}{45} \langle v_{H_2} 1 \gamma 01 \rangle^2] + \frac{84}{125} \langle v_{H_2} 1 Q_2 01 \rangle^2 \langle v_{\text{HD}} 3 X \gamma 00 \rangle^2 + \frac{8}{25} \langle v_{\text{HD}} 3 Q_3 00 \rangle \langle v_{H_2} 1 Q_2 01 \rangle \langle v_{\text{HD}} 3 X \gamma 00 \rangle \times \langle v_{H_2} 1 \gamma 01 \rangle \}$
$R_{v_{\text{HD}}}(0) + [\Delta J = l(\geq 2)]_{v_{H_2}}(1)$	$\mu_\nu^{\text{iso}}(l; 1, k)_{II} + \mu_\nu^{\text{an}}(l; 1, k)_{II}$	$\frac{8\pi^3(l+1)^2(l+2)(2l+3)}{9h(2l+1)a^{(2l+6)}} \xi_{l+3} S_{l+3} \langle v_{H_2} l + 1 Q_l 01 \rangle^2 \times [\langle v_{\text{HD}} 1 X \alpha 00 \rangle + \frac{1}{15} \langle v_{\text{HD}} 1 X \gamma 00 \rangle]^2$
$S_{v_{H_2}}(1) + [\Delta J = l(\geq 4)]_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{an}}(l; k, 1)_I$	$\frac{16\pi^3(l+1)}{45ha^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} l Q_l 00 \rangle^2 \langle v_{H_2} 3 \gamma 01 \rangle^2$
$S_{v_{\text{HD}}}(0) + [\Delta J = l(\geq 4)]_{v_{H_2}}(1)$	$\mu_\nu^{\text{an}}(l; 1, k)_I$	$\frac{16\pi^3(l+1)^2}{27h(2l+1)a^{(2l+4)}} \xi_{l+2} S_{l+2} \langle v_{\text{HD}} 2 \gamma 00 \rangle^2 \langle v_{H_2} l + 1 Q_l 01 \rangle^2$

TABLE II. (Continued.)

Transition	Parts of $\mu_\nu(\text{pair}l,k)$	Integrated absorption coefficient $\tilde{\alpha}/\text{cm}^3 \text{ s}^{-1}$
$S_{v_{\text{HD}}}(0) + S_{v_{\text{H}_2}}(1)$	$\mu_\nu^{\text{an}}(2;1,k)_I + \mu_\nu^{\text{an}}(2;k,1)_I$	$\frac{16\pi^3}{15ha^8} \xi_4 S_4 [\langle v_{\text{HD}}2 Q_2 00 \rangle^2 \langle v_{\text{H}_2}3 \gamma 01 \rangle^2 + \langle v_{\text{H}_2}3 Q_2 01 \rangle^2$ $\times \langle v_{\text{HD}}2 \gamma 00 \rangle^2 - \frac{6}{5} \langle v_{\text{HD}}2 Q_2 00 \rangle \langle v_{\text{H}_2}3 Q_2 01 \rangle$ $\times \langle v_{\text{H}_2}3 \gamma 01 \rangle \langle v_{\text{HD}}2 \gamma 00 \rangle]$
$T_{v_{\text{HD}}}(0) + [\Delta J = l(\geq 4)]_{v_{\text{H}_2}}(1)$	$\mu_\nu^{\text{an}}(l;1,k)_{II}$	$\frac{16\pi^3(l+1)^2(l+2)(2l+3)}{75h(2l+1)a^{(2l+6)}} \xi_{l+3} S_{l+3} \langle v_{\text{H}_2}l+1 Q_l 01 \rangle^2$ $\times \langle v_{\text{HD}}3 X \gamma 00 \rangle^2$
$S_{v_{\text{H}_2}}(1) + T_{v_{\text{HD}}}(0)$	$\mu_\nu^{\text{an}}(2;1,k)_{II} + \mu_\nu^{\text{an}}(3;k,1)_I$	$\frac{8\pi^3}{3ha^{10}} \xi_5 S_5 [\frac{8}{15} \langle v_{\text{HD}}3 Q_3 00 \rangle^2 \langle v_{\text{H}_2}3 \gamma 01 \rangle^2$ $+ \frac{504}{125} \langle v_{\text{H}_2}3 Q_2 01 \rangle^2 \langle v_{\text{HD}}3 X \gamma 00 \rangle^2$ $+ \frac{48}{25} \langle v_{\text{HD}}3 Q_3 00 \rangle \langle v_{\text{H}_2}3 \gamma 01 \rangle$ $\times \langle v_{\text{H}_2}3 Q_2 01 \rangle \langle v_{\text{HD}}3 X \gamma 00 \rangle]$

only some of the transitions (due to condition $J' + J'' \geq l$, where J' and J'' are, respectively, upper and lower state rotational quantum numbers) in Tables I and II. Also, restriction to the lowest order multipolar induction does not seriously compromise the accuracy of the intensity formulas. In fact, one can show that the relative contributions of Q_{l+1} and Q_l to the intensity of a particular transition scale as $[\langle Q_{l+1}(\text{a.u.}) / Q_l(\text{a.u.}) \rangle]^2 \times (a_0/R_k)^2 \sim (a_0/R_k)^2 \sim 0.02$, where a_0 is the Bohr radius and $R_k \sim 3.64 \text{ \AA}$ is the nearest-neighbor distance in solid HD. For homonuclear molecules Q_l is nonzero only for even values of l and the contribution of Q_{l+2} to the intensity relative to that of Q_l is $\sim 4 \times 10^{-4}$.

Next we need the matrix elements for the part of the induced dipole moment that contributes to the corresponding transition between the initial and final states of the pair of molecules. The rovibrational states for the pair can be written as simple product states

$$\begin{aligned}
 & |1v_1, J_1 M_1; kv_k, J_k M_k\rangle \\
 &= |1v_1, J_1, (r_1)\rangle |kv_k, J_k, (r_k)\rangle Y_{J_1, M_1}(\hat{\omega}_1) \\
 &\quad \times Y_{J_k, M_k}(\hat{\omega}_k),
 \end{aligned}$$

in which $|v, J, (r)\rangle$ refers to the radial part of the wavefunction of the vibrating rotator. From the matrix elements of the induced dipole moment, μ_{ind} , one can calculate the integrated absorption coefficient²⁹

$$\tilde{\alpha} = (8\pi^3/3h) \sum_{n_i n_f} |\langle fn_f | \mu_{\text{ind}} | in_i \rangle|^2 / d_i, \quad (6)$$

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 $\tilde{\alpha}$ is the experimentally measured quantity, defined as

$$\tilde{\alpha} = (c/Nl) \int \ln(I_0/I) d\nu/v. \quad (7)$$

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 . $N = N_{\text{homo}} \times N_{\text{hetero}} / (N_{\text{homo}} + N_{\text{hetero}})$ for the mixed isotopomer transitions.

III. RESULTS AND DISCUSSION

Tables I and II list the expressions for the integrated absorption coefficients for different types of zero-phonon double transitions involving homonuclear-heteronuclear isotopomers of hydrogen in condensed phase. In the intensity expressions, S and ξ are, respectively, the positive-definite lattice sums and phonon renormalization factor which corrects the rigid lattice sum to allow for zero-point motions.^{2,3,22} The lattice sums are defined as $S_{l+r} = \sum'_k (a/R_{1k})^{2l+2r}$, where a is the nearest neighbor distance in the crystal and the prime denotes exclusion of terms with $k=1$. In the notation of rovibrational transitions, 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, 0 or 1. Note that for heteronuclear molecules, the ortho-para distinction does not exist and practically all HD, HT, or DT molecules in solid phase are in the $J=0$ state, whereas homonuclear molecules exist in two metastable ortho- and para-modifications and H_2 or

TABLE III. Predicted intensities of some of the mixed isotopomer transitions in an HD crystal containing traces of ortho-H₂.

Transition	$\tilde{\alpha}/\text{cm}^3\text{s}^{-1}$	Transition	$\tilde{\alpha}/\text{cm}^3\text{s}^{-1}$
$Q_1(0)\text{HD} + S_0(1)\text{H}_2$	4.11×10^{-14a}	$Q_1(1)\text{H}_2 + S_0(0)\text{HD}$	6.74×10^{-14b}
$Q_2(0)\text{HD} + S_0(1)\text{H}_2$	3.20×10^{-16}	$Q_2(1)\text{H}_2 + S_0(0)\text{HD}$	7.43×10^{-16}
$Q_3(0)\text{HD} + S_0(1)\text{H}_2$	5.28×10^{-18}	$Q_1(1)\text{H}_2 + S_1(0)\text{HD}$	1.94×10^{-15}
$Q_1(0)\text{HD} + S_1(1)\text{H}_2$	1.06×10^{-15}	$Q_2(1)\text{H}_2 + S_1(0)\text{HD}$	1.88×10^{-17}
$Q_2(0)\text{HD} + S_1(1)\text{H}_2$	8.27×10^{-18}	$Q_1(1)\text{H}_2 + S_2(0)\text{HD}$	3.48×10^{-17}
$Q_1(0)\text{HD} + S_2(1)\text{H}_2$	2.42×10^{-17}	$Q_1(1)\text{H}_2 + Q_1(0)\text{HD}$	8.93×10^{-16c}
$Q_1(0)\text{HD} + U_0(1)\text{H}_2$	1.35×10^{-17}	$Q_2(1)\text{H}_2 + Q_1(0)\text{HD}$	1.46×10^{-17}
$Q_1(0)\text{HD} + U_1(1)\text{H}_2$	1.39×10^{-18}	$Q_3(1)\text{H}_2 + Q_1(0)\text{HD}$	2.96×10^{-19}
$Q_1(1)\text{H}_2 + U_0(0)\text{HD}$	6.34×10^{-17}	$Q_1(1)\text{H}_2 + Q_2(0)\text{HD}$	6.95×10^{-18}
$Q_1(1)\text{H}_2 + U_1(0)\text{HD}$	6.82×10^{-18}	$Q_2(1)\text{H}_2 + Q_2(0)\text{HD}$	1.13×10^{-19}
$Q_2(1)\text{H}_2 + U_0(0)\text{HD}$	5.55×10^{-19}	$Q_1(1)\text{H}_2 + Q_3(0)\text{HD}$	1.15×10^{-19}
$R_0(0)\text{HD} + S_0(1)\text{H}_2$	2.96×10^{-14}	$S_0(1)\text{H}_2 + U_0(0)\text{HD}$	6.14×10^{-17}
$R_0(0)\text{HD} + S_1(1)\text{H}_2$	6.47×10^{-16}	$S_0(1)\text{H}_2 + U_1(0)\text{HD}$	6.60×10^{-18}
$R_0(0)\text{HD} + S_2(1)\text{H}_2$	1.74×10^{-17}	$S_1(1)\text{H}_2 + U_0(0)\text{HD}$	4.35×10^{-18}
$R_1(0)\text{HD} + S_0(1)\text{H}_2$	1.64×10^{-15}	$S_0(1)\text{H}_2 + V_0(0)\text{HD}$	1.46×10^{-18}
$R_1(0)\text{HD} + S_1(1)\text{H}_2$	3.58×10^{-17}	$S_0(0)\text{HD} + U_0(1)\text{H}_2$	2.57×10^{-17}
$R_1(0)\text{HD} + S_2(1)\text{H}_2$	9.65×10^{-19}	$S_0(0)\text{HD} + U_1(1)\text{H}_2$	2.64×10^{-18}
$R_2(0)\text{HD} + S_0(1)\text{H}_2$	1.05×10^{-18}	$S_1(0)\text{HD} + U_0(1)\text{H}_2$	1.80×10^{-18}
$R_0(0)\text{HD} + U_0(1)\text{H}_2$	2.40×10^{-17}	$S_1(0)\text{HD} + U_1(1)\text{H}_2$	1.85×10^{-19}
$R_0(0)\text{HD} + U_1(1)\text{H}_2$	2.46×10^{-18}	$T_0(0)\text{HD} + U_0(1)\text{H}_2$	7.97×10^{-19}
$R_1(0)\text{HD} + U_0(1)\text{H}_2$	1.33×10^{-18}	$T_1(0)\text{HD} + U_0(1)\text{H}_2$	1.02×10^{-19}
$R_1(0)\text{HD} + U_1(1)\text{H}_2$	1.36×10^{-19}	$T_0(0)\text{HD} + S_0(1)\text{H}_2$	7.48×10^{-16}
$S_0(0)\text{HD} + S_0(1)\text{H}_2$	6.34×10^{-14}	$T_0(0)\text{HD} + S_1(1)\text{H}_2$	4.86×10^{-17}
$S_0(0)\text{HD} + S_1(1)\text{H}_2$	3.65×10^{-15}	$T_1(0)\text{HD} + S_0(1)\text{H}_2$	6.83×10^{-17}
$S_0(0)\text{HD} + S_2(1)\text{H}_2$	2.97×10^{-17}	$T_1(0)\text{HD} + S_1(1)\text{H}_2$	2.73×10^{-18}
$S_1(0)\text{HD} + S_0(1)\text{H}_2$	3.51×10^{-15}	$Q_1(1)\text{H}_2 + T_0(0)\text{HD}$	1.17×10^{-15}
$S_1(0)\text{HD} + S_1(1)\text{H}_2$	1.02×10^{-16}	$Q_1(1)\text{H}_2 + T_1(0)\text{HD}$	6.71×10^{-17}
$S_1(0)\text{HD} + S_2(1)\text{H}_2$	2.33×10^{-18}	$Q_2(1)\text{H}_2 + T_0(0)\text{HD}$	1.08×10^{-17}
$S_2(0)\text{HD} + S_0(1)\text{H}_2$	2.18×10^{-17}	$Q_1(1)\text{H}_2 + R_0(0)\text{HD}$	6.53×10^{-16}
$S_2(0)\text{HD} + S_1(1)\text{H}_2$	1.91×10^{-18}	$Q_1(1)\text{H}_2 + R_1(0)\text{HD}$	3.61×10^{-17}
$Q_2(1)\text{H}_2 + R_0(0)\text{HD}$	1.06×10^{-17}	$Q_2(1)\text{H}_2 + R_1(0)\text{HD}$	5.89×10^{-19}

^aExperimental value = $6.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ from Ref. 7.

^bExperimental value = $2.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ from Ref. 7.

^cExperimental value = $2.3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ from Ref. 7.

D₂ molecules in solid hydrogens can be in $J=0$ and $J=1$ states.

The intensity formulas for mixed isotopomer transitions involving para-H₂ or ortho-D₂ (with $J=0$) given in Table I summarize the results mentioned in Ref. 22. In that paper we predicted the intensities of many such transitions. Using the expressions given in Table II of this paper and the required multipole moments and polarizability matrix elements and other parameters from Refs. 22, 27, 28 and 30–32, we give, in Table III, theoretical values of integrated absorption coefficients for the various zero-phonon mixed isotopomer transitions in a HD crystal. Here, only mixed isotopomer transitions involving ortho-H₂ in solid HD are considered because, so far, the intensity of only three such transitions has been experimentally measured.⁷ One can calculate the intensities of any kind of mixed isotopomer transitions in the crystal of any particular solid hydrogen, by making use of these formu-

las and other available parameters.^{1,22,27,28,30–32} The experimental values of the absorption coefficient $\tilde{\alpha}$ in cm^3/s of the transitions given in the footnote to Table III are obtained from the integrated intensity α in cm^{-2} given by Lee,⁷ using the relation¹¹

$$\tilde{\alpha} = (c/N\nu_0)\alpha, \quad (8)$$

where ν_0 is the center of the absorption line (in cm^{-1}). The theoretical intensities for the transitions $Q_1(0)\text{HD} + S_0(1)\text{H}_2$, $Q_1(1)\text{H}_2 + S_0(0)\text{HD}$, and $Q_1(0)\text{HD} + Q_1(1)\text{H}_2$ are larger than the experimental values by approximately factors of 6, 3, and 4, respectively. Differences in experimental and theoretical intensities by factors of 3–6 can be due to (i) the phonon renormalization factor ξ is taken to be unity while calculating the theoretical intensities, (ii) uncertainty in the number of absorbing molecules per cm^3 N

(Lee has mentioned 3% H₂ impurities in the solid HD crystal and ortho-H₂ will be 75% in normal H₂ unless the solid sample is left for many days), (iii) the relation between α and $\tilde{\alpha}$ given by Eq. (8) is valid for sharp features, and (iv) experimental error. The mixed isotopomer transitions $Q_1(0)\text{HD} + S_0(1)\text{H}_2$ and $Q_1(1)\text{H}_2 + S_0(0)\text{HD}$ are also observed by Lo,⁵ but absolute intensities of the transitions is not reported. Similarly, Chan and Oka¹⁴ have observed the $Q_1(0)\text{HD} + S_0(1)\text{D}_2$ transition in solid D₂ crystal, but the absolute intensity of the transition is not measured. The theoretical intensity of this transition in solid D₂ crystal, according to our calculation, is 4.29×10^{-14} cm³/s.

Finally, one can make use of intensity formulas given in Tables I and II to calculate the intensity of para-H₂-dopant or ortho-D₂-dopant combination transitions where the dopant can be an ortho-H₂, or para-D₂, or any other molecule (which does not possess a permanent dipole moment) embedded in the crystal. In the intensity formulas, HD can be replaced by a dopant homonuclear (for which $X=0$) or heteronuclear molecule initially in the $J=0$ state, but H₂ can only be replaced by a homonuclear molecule which is initially in the same J state as H₂ molecule ($J=0$ or 1). Thus, seven of the formulas given in Table II of this paper reduce to the intensity formulas for double transitions involving the para-H₂-ortho-H₂ pair derived earlier in Ref. 20. In order to make use of these formulas, it is necessary that the dopant molecule in solid para-H₂ (or ortho-D₂) retain good rotational quantum numbers. Recently, such combination transitions have been observed by Hinde *et al.*²⁶ in the solid para-H₂ crystal doped with a low concentration of N₂. No absolute intensity measurement is reported. Intensity measurements of para-H₂-dopant transitions will provide useful information about the changes in the properties (such as multipole moments) of dopants due to crystal field effects. One cannot use the gas phase matrix elements of multipole moments and of polarizability of dopants in the solid phase,

unlike for hydrogen molecules for which solid state interactions are negligible.³³ Hinde *et al.*²⁶ has observed that the rotational constant B for N₂ in solid para-H₂ crystal is 10% lower than the B value in the gas phase due to crystal field effects. The formulas given in the present work are applicable to double transitions in which the dopant molecules are initially in the $J=0$ or 1 state. Dopant molecules having small B values can have significant populations in $J>1$ states. The present formalism, although the calculations may be quite involved, can be used to derive intensity formulas for combination transitions in which the dopant molecules are initially in a $J>1$ state.

IV. CONCLUSION

Closed form expressions are derived for the intensities of double transitions involving a homonuclear-heteronuclear pair of hydrogen molecules in condensed phase. These formulas can be applied to many combination transitions where a dopant molecule (with $J=0$ or 1) embedded in solid hydrogens together with a hydrogen molecule simultaneously take part in the absorption process. The same method, in principle, can be applied to predict the intensities of combination transitions in which the dopant molecules are initially in a $J>1$ state. With the results presented in this paper, theoretical intensities of all kinds of possible double transitions in the solid hydrogens can be calculated. New and accurate measurements of the infrared spectra of solid hydrogen of all isotopic variants are desirable. The results of the present paper would be useful to understand the dynamics of dopants embedded in solid hydrogen matrices.

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