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Absorption intensities of multipole-field-induced double transitions involving orthohydrogen pairs in a solid parahydrogen crystal

Adya P. Mishra,* Richard D'Souza,† and T. K. Balasubramanian‡
Spectroscopy Division, Modular Laboratories, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

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Orthohydrogen molecules exhibit quantum diffusion through a solid parahydrogen lattice. At very low orthohydrogen concentrations ($\sim 1\%$), stable and isolated ortho-H_2 pairs are formed in the para-H_2 crystal. In this paper, theoretical expressions are derived for the integrated absorption coefficients of various multipole-field-induced zero-phonon double transitions in an isolated pair of ortho-H_2 molecules embedded in para-H_2 crystal. Although, the double transitions involving ortho-H_2 pairs consist entirely of fine structures (FS), the intensity formulas derived here are for the line as a whole, except for $Q_{v_1}(1)+Q_{v_k}(1)$ transition in which the individual components are separately treated. Since the $J=1$ rotational state pair splittings of various ground state FS components are well known, experimentalists can compare the observed intensities to the theoretical calculations for the line as a whole (given in units of per molecular-pair) by reducing the observed intensities of each FS components to per molecular pair and summing them together. The formulas given in this paper can be applied to double transitions involving a pair of $J=1$ dopant molecules (with zero permanent dipole moment) embedded in solid parahydrogen (or orthodeuterium) matrices. Furthermore, it is shown that the intensity formulas given for an isolated pair, after generalization, provide good estimates of the intensities of double transitions in a nearly pure ortho-H_2 crystal.

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I. INTRODUCTION

Solid hydrogen is a molecular quantum crystal, in which the individual molecules undergo almost free rotation and vibration.[1] H_2 molecules in solid hydrogen at liquid helium temperature can be in $J=0$ or $J=1$ rotational states. In solid parahydrogen crystal, nearly all the H_2 molecules are in a spherically symmetric $J=0$ state with zero average electrostatic multipole moments. This results in extremely weak (isotropic) intermolecular forces inside the parahydrogen crystal. Due to very weak intermolecular interactions and a large lattice constant (~ 3.8 Å) the solid parahydrogen crystal has proven to be a nearly ideal matrix medium for spectroscopic studies of molecular vibrational-rotational dynamics in the condensed phase.[2] In the last decade, spectra of a variety of impurities, such as, various isotopomers and nuclear spin modifications of hydrogen, stable neutral molecules, free radicals and molecular ion clusters, embedded in this crystal have been studied.[2–9] Parahydrogen solids containing low concentration of $J=1$ orthohydrogen "rotational impurities" have been the subject of many investigations due to various reasons. The ortho-H_2 impurity in a parahydrogen crystal is known to exhibit quantum diffusion.[10–12] The observations made by Amstutz *et al.*[10] from the NMR spectral study indicated for the first time that ortho-H_2 molecules (strictly, $J=1$ rotons) quantum diffuse through the para-H_2 lattice to form relatively stable ortho-H_2 pairs. The direct observation of orthohydrogen pair splittings by Silvera *et al.*[13] using Raman spectroscopy and by Boggs and Welsh[11,12] using infrared spectroscopy in para-H_2 crystal (containing trace ortho-H_2 molecules) further strengthened the idea of ortho-H_2-pair formation. Later, Hardy and Berlinsky[14] obtained detailed information about the $J=1$ pair splittings by observing the well resolved microwave transitions between the split levels of the ortho-H_2 pair in nearly pure parahydrogen crystal. Oka and his colleagues,[6] in recent years, performed high resolution laser spectroscopic studies and observed hundreds of sharp lines due to the pairs and higher-order clusters of ortho-H_2, accompanying the $Q_1(1)$ ($v=1 \leftarrow 0$, $J=1 \leftarrow 1$) single molecule transition.

The infrared spectrum of hydrogen in the condensed phase is characterized by single and double transitions, primarily caused by multipolar induction mechanism.[1,2] Although double transitions involving an ortho-H_2-pair have been observed experimentally,[15–21] and absolute intensities have been measured for some of the lines, so far no theoretical analysis of the intensities of such transitions has been attempted. The double transitions involving ortho-H_2-pair in predominantly parahydrogen crystals are interesting because they consist entirely of fine structures (FS).[20] This calls for the highest resolution infrared techniques to be applied for their characterization. The intensity as well as FS separations carry important signatures of the crystalline environment. Therefore, through a careful theoretical analysis of FS and correlation to experiments one can gain insight into the structure and dynamics of quantum solids. The goal of this paper is to present intensity expressions for multipole-field-induced zero-phonon double transitions of various kinds in well isolated ortho-H_2 pairs in the parahydrogen crystal. As an illustration, we present explicit expressions for the intensities of all the FS components of $Q_{v_1}(1)+Q_{v_k}(1)$ double transition. A good agreement between theoretical and experimental intensities of different FS components of this kind of transition is found. The intensity formulas for other types of transitions are for the line as a whole. Since the theoretical intensities given here are expressed in units of per molecular-pair per unit volume (in cm^3 s^{-1}), one can compare the observed intensities to the theoretical predictions given in this paper by reducing the observed intensities of each FS components to single molecular pair and summing them together. This is easily possible because the ground state ortho-pair splittings are well known and one can calculate the Boltzmann distribution of the populations in the various FS components from the temperature of the crystal. The formulas derived in the present paper would also be useful to predict the intensities of double transitions involving a pair of $J=1$ state dopants, with zero permanent dipole moment, such as N_2, in parahydrogen crystal.

II. THEORY

The derivation of intensity formulas in this section is based on the assumption that each pair of (e.g., nearest neighbor) ortho-H_2 molecules is well isolated from other orthohydrogen molecules in the parahydrogen crystal. This situation can be realized in the parahydrogen crystal containing trace amount of ortho-H_2 impurity ($\sim$1% or smaller) after the diffusion process is complete. The absorption processes in solid hydrogen are due to induced dipole moments. For any double transition, the calculation of absorption coefficient involves the matrix elements of the induced dipole moment, $\boldsymbol{\mu}_{\text{ind}}$, between the initial and final states of the pair of molecules $(1,k)$. The orientation of the intermolecular axis does not affect the value of absorption coefficient, $\tilde{\alpha}(1,k)$, for a double transition.[22–24] We exploit this freedom to locate a laboratory fixed coordinate system XYZ whose origin is at the center of mass (CM) of molecule 1 and the Z axis passes through the CM of the lone ortho-H_2 molecule k, say, nearest neighbor. Thus the location of the CM of molecule k is specified by the position vector $\mathbf{R}_{1k}=\hat{\mathbf{k}}R_{1k}$ ($R_{1k}=a$, lattice constant, $\hat{\mathbf{k}}$ unit vector along Z axis). Let the orientations of the axes of the two molecules be $\hat{\omega}_1$ $(=\theta_1,\phi_1)$ and $\hat{\omega}_k(=\theta_k,\phi_k)$. For the above choice of location of the molecular pair $(1,k)$, the spherical components $\mu_\nu(\ell;1,k)$ 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 by[22]

$$\mu_\nu^{\text{iso}}(\ell;1,k)=[4\pi(\ell+1)]^{1/2}Q_\ell(r_1)\alpha(r_k)\times R_{1k}^{-(\ell+2)}(-)^\nu C(\ell,1,\ell+1;\nu,-\nu,0)Y_{\ell,\nu}(\hat{\omega}_1), \tag{1}$$

$$\mu_\nu^{an}(\ell;1,k)=[32\pi^2(\ell+1)/9]^{1/2}Q_\ell(r_1)\gamma(r_k)R_{1k}^{-(\ell+2)}\sum_m(-)^{1-m}\times C(2,1,1;\nu-m,m,\nu)\times C(\ell,1,\ell+1;m,-m,0)Y_{\ell,m}(\hat{\omega}_1)Y_{2,\nu-m}(\hat{\omega}_k). \tag{2}$$

In the above equations, $Q_\ell(r_1)$ is the 2^ℓ-pole moment of molecule 1, $\alpha(r_k)$ and $\gamma(r_k)$ are, respectively, the isotropic and anisotropic parts of the polarizability of molecule k, $Y_{L,M}$ 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. Relations similar to Eqs. (1) and (2), supplemented by appropriate phase factors, $(-)^{\ell+1}$, describe the dipole moment components induced by the multipole of k on 1. Thus the induced moment in the pair can be written as,

$$\mu_\nu(\text{pair}1,k)=\mu_\nu^{iso}(\ell;1,k)+\mu_\nu^{an}(\ell;1,k)+\mu_\nu^{iso}(\ell;k,1)+\mu_\nu^{an}(\ell;k,1). \tag{3}$$

The induced moment in the pair given by Eq. (3), must in principle be summed over all possible ℓ values. However, we restrict ourselves here to the lowest order multipolar induction that yields nonzero matrix elements between given initial and final states. This restriction does not seriously compromise the accuracy of the intensity formulas. For homonuclear molecules, like H_2, Q_ℓ is nonzero only for even values of $\ell(\geqslant 2)$ and one can show[22] that the relative contributions of $Q_{\ell+2}$ and Q_ℓ to the intensity of a particular transition scale as $[Q_{\ell+2}(\text{a.u.})/Q_\ell(\text{a.u.})]^2\times(a_0/R_{1k})^4\sim(a_0/a)^4\sim 4\times 10^{-4}$, where a_0 is the Bohr radius and $a\sim 3.8$ Å is the nearest neighbor distance in solid H_2.

Theoretically, the integrated absorption coefficient, $\tilde{\alpha}(1,k)$, is related to the induced dipole moment, $\boldsymbol{\mu}_{\text{ind}}$ as[25]

$$\tilde{\alpha}=(8\pi^3/3h)\sum_{n_in_f}|\langle fn_f|\boldsymbol{\mu}_{\text{ind}}|in_i\rangle|^2/d_i, \tag{4}$$

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 is the initial state degeneracy. Thus to calculate the intensity of a transition, we need the matrix elements for the part of the induced dipole moment in the ortho-pair given by Eq. (3), which contributes to the corresponding transition between the initial and final states of the *pair* of molecules. The unsplit rovibrational states for the pair, if we neglect the mixing of rotational states of individual molecules by the anisotropic interaction present in the crystal, can be written as simple product states,

$$|1v_1,J_1M_1;kv_k,J_kM_k\rangle=|1v_1,J_1,(r_1)\rangle|kv_k,J_k,(r_k)\rangle\times Y_{J_1,M_1}(\hat{\omega}_1)Y_{J_k,M_k}(\hat{\omega}_k), \tag{5}$$

in which $|v,J,(r)\rangle$ refers to the radial part of the wave function of the vibrating rotor. Table I lists the formulas for the integrated absorption coefficients, obtained after insertion of matrix elements in Eq. (4), for different types of zero-phonon double transitions involving isolated ortho-H_2-pairs in the parahydrogen crystal. Considering the lowest-order multipolar induction, the terms in $\mu_\nu(\text{pair}1,k)$, which give rise to nonzero contributions to the intensity of a particular transition, are also listed. In Table I, the symbols Q, S, etc. are used to denote, respectively, rotational transitions with $\Delta J=J'-J''=0$, 2, etc. The subscript to the symbols Q, S, etc. 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, which is 1 for an ortho-H_2 molecule. It would be useful to mention that the intensity formulas for the $Q(1)+S(1)$ and $S(1)+S(1)$ transitions embody an interference term which arises when the roles of the molecules 1 and k in the pair are interchanged. Furthermore, molecules 1 and k, both being ortho-H_2, their rotation-vibration energy level structures are obviously iden-

TABLE I. Intensity formulas for double transitions involving isolated pairs of orthohydrogen molecules in solid parahydrogen crystal. The parts of $\mu_\nu(\text{pair } 1,k)$ of Eq. (3) that yield a nonvanishing contribution to the transition, are also listed.

Transition	Parts of $\mu_\nu(\text{pair } 1,k)$	Integrated absorption coefficient $\tilde{\alpha}/\mathrm{cm}^3\, s^{-1}$
$Q_{v_1}(1)+Q_{v_k}(1)(v_1\neq v_k)$	$\mu_\nu^{\mathrm{iso}}(2;1,k)+\mu_\nu^{\mathrm{iso}}(2;k,1)$ $+\mu_\nu^{an}(2;1,k)+\mu_\nu^{an}(2;k,1)$	$\frac{32\pi^3}{5hR_{1k}^8}\{\langle 01\vert Q_2\vert v_1 1\rangle^2[\langle 01\vert\alpha\vert v_k 1\rangle^2+\frac{4}{45}\langle 01\vert\gamma\vert v_k 1\rangle^2]$ $+\langle 01\vert Q_2\vert v_k 1\rangle^2[\langle 01\vert\alpha\vert v_1 1\rangle^2+\frac{4}{45}\langle 01\vert\gamma\vert v_1 1\rangle^2]-\frac{8}{75}\langle 01\vert Q_2\vert v_1 1\rangle$ $\times\langle 01\vert Q_2\vert v_k 1\rangle\langle 01\vert\gamma\vert v_k 1\rangle\langle 01\vert\gamma\vert v_1 1\rangle\}$
$Q_v(1)+Q_v(1)$	$\mu_\nu^{\mathrm{iso}}(2;1,k)+\mu_\nu^{\mathrm{iso}}(2;k,1)$ $+\mu_\nu^{an}(2;1,k)+\mu_\nu^{an}(2;k,1)$	$\frac{32\pi^3}{5hR_{1k}^8}\langle 01\vert Q_2\vert v1\rangle^2\{\langle 01\vert\alpha\vert v1\rangle^2+\frac{8}{225}\langle 01\vert\gamma\vert v1\rangle^2\}$
$Q_{v_1}(1)+[\Delta J=\ell(\geqslant 4)]_{v_k}(1)$	$\mu_\nu^{\mathrm{iso}}(\ell;k,1)+\mu_\nu^{an}(\ell;k,1)$	$\frac{16\pi^3(\ell+1)^2}{3hR_{1k}^{(2\ell+4)}(2\ell+1)}\langle 01\vert Q_\ell\vert v_k\ell+1\rangle^2\{\langle 01\vert\alpha\vert v_1 1\rangle^2+\frac{4}{45}\langle 01\vert\gamma\vert v_1 1\rangle^2\}$
$S_{v_1}(1)+[\Delta J=\ell(\geqslant 4)]_{v_k}(1)$	$\mu_\nu^{an}(2;1,k)$	$\frac{32\pi^3(\ell+1)^2}{45hR_{1k}^{2\ell+4}(2\ell+1)}\langle 01\vert Q_\ell\vert v_k\ell+1\rangle^2\langle 01\vert\gamma\vert v_1 3\rangle^2$
$Q_{v_1}(1)+S_{v_k}(1)$	$\mu_\nu^{\mathrm{iso}}(2;k,1)+\mu_\nu^{an}(2;1,k)$ $+\mu_\nu^{an}(2;k,1)$	$\frac{16\pi^3}{15hR_{1k}^8}\{9\langle 01\vert Q_2\vert v_k 3\rangle^2\langle 01\vert\alpha\vert v_1 1\rangle^2+\frac{4}{5}\langle 01\vert Q_2\vert v_k 3\rangle^2\langle 01\vert\gamma\vert v_1 1\rangle^2$ $+\frac{4}{5}\langle 01\vert Q_2\vert v_1 1\rangle^2\langle 01\vert\gamma\vert v_k 3\rangle^2-\frac{24}{25}\langle 01\vert Q_2\vert v_k 3\rangle\langle 01\vert Q_2\vert v_1 1\rangle$ $\times\langle 01\vert\gamma\vert v_1 1\rangle\langle 01\vert\gamma\vert v_k 3\rangle\}$
$S_{v_1}(1)+S_{v_k}(1)(v_1\neq v_k)$	$\mu_\nu^{an}(2;1,k)+\mu_\nu^{an}(2;k,1)$	$\frac{32\pi^3}{25hR_{1k}^8}\{\langle 01\vert Q_2\vert v_1 3\rangle^2\langle 01\vert\gamma\vert v_k 3\rangle^2+\langle 01\vert Q_2\vert v_k 3\rangle^2\langle 01\vert\gamma\vert v_1 3\rangle^2$ $-\frac{6}{5}\langle 01\vert Q_2\vert v_1 3\rangle\langle 01\vert Q_2\vert v_k 3\rangle\langle 01\vert\gamma\vert v_1 3\rangle\langle 01\vert\gamma\vert v_k 3\rangle\}$
$S_v(1)+S_v(1)$	$\mu_\nu^{an}(2;1,k)+\mu_\nu^{an}(2;k,1)$	$\frac{64\pi^3}{125hR_{1k}^8}\langle 01\vert Q_2\vert v3\rangle^2\langle 01\vert\gamma\vert v3\rangle^2$

tical. Consequently, there are degeneracies involved in the final composite rovibrational state. Considering only the radial part of $|f\rangle$ we find that $|1v_1,J_1;kv_k,J_k\rangle$ and $|1v_k,J_k;kv_1,J_1\rangle$ are doubly degenerate whenever $v_1\neq v_k$ and/or $J_1\neq J_k$. However, when $v_1=v_k$ and $J_1=J_k$, there is no degeneracy.[23,24] These features have been kept track of in the intensity derivation.

The intensity formulas of Table I are derived for the line as a whole, without considering the details of fine structure components. As an illustration, we now derive expressions for the intensity of different fine structure components of $Q_{v_1}(1)+Q_{v_k}(1)$ transition. The largest interaction responsible for the splittings of the levels of the ortho-H_2 pair in solid hydrogen is the electric-quadrupole-quadrupole (EQQ) interaction. The resulting FS states can be written in terms of the unsplit pair basis states given by Eq. (5), as

$$|F,M\rangle=\sum_{M_1}C(J_1,J_k,F;M_1,M-M_1,M)$$
$$\times|1v_1,J_1,(r_1)\rangle|kv_k,J_k,(r_k)\rangle Y_{J_1,M_1}(\hat{\omega}_1)Y_{J_k,M-M_1}(\hat{\omega}_k),$$

where F and M are quantum numbers corresponding, respectively, to the total rotational angular momentum $\mathbf{F}=\mathrm{J}_1+\mathrm{J}_k$ of the pair and its projection on the Z axis. For an ortho–ortho pair in solid hydrogen with both molecules in the $J=1$ state, the first order EQQ interaction leaves the four states with $F=1(M=0,\pm 1)$ and 0 unshifted and degenerate, while the five substates with $F=2$ split into three levels with $M=0$, ±1, ±2. These degeneracies are further lifted by second-order EQQ and other interactions. Six well resolved levels denoted by: (i) $|2,1\rangle_\pm$, (ii) $|1,1\rangle_\pm$; (iii) $|1,0\rangle$, and $|0,0\rangle$ (degenerate); (iv) $|2,2\rangle_+$, (v) $|2,2\rangle_-$, and (vi) $|2,0\rangle$ in the nearest-neighbor ortho-hydrogen pair have been identified.[20,26] States with $M\neq 0$ are expressed as

$$|F,M\rangle_\pm=\frac{|F,M\rangle\pm|F,-M\rangle}{\sqrt{2}},$$

where ± represent eigenfunctions symmetric (+ve sign) or antisymmetric (−ve sign) with respect to reflection in the XZ symmetry plane. The excited state of the transition $Q_{v_1}(1)+Q_{v_k}(1)$ will have a splitting pattern similar to that of the ground state. One can therefore expect $6\times 6=36$ FS components in the $Q_{v_1}(1)+Q_{v_k}(1)$ transition. However, selection rules for nonvanishing quadrupole induced dipole matrix elements allow: (i) $\Delta F=0,\pm 1,\pm 2$, with restriction $F'+F''\geqslant 2$, and (ii) $\Delta M=0,\pm 1$. This limits the number of the FS components to 28. As shown in the second column of Table I, all four terms in μ_ν (pair 1, k) give a nonzero contribution to the intensity of this transition, which results in interference effects. Details of our calculations show that the matrix elements $M_\nu(2;1,k)$ $(=\langle F',M'|\mu_\nu(2;1,k)|F'',M''\rangle)$ and $M_\nu(2;k,1)$ of the isotropic and anisotropic parts of the induced dipole moment differ by a phase factor $(-)^{F'+F''+1}$, which implies negative interference for $F'+F''=$even and positive interference for $F'+F''=$odd. For $v_1=v_k$, negative interference leads to zero intensity for all $F'+F''=$even components, resulting in only ten observable transitions. In other cases, the matrix elements $M_\nu(2;1,k)$ and $M_\nu(2;k,1)$ are nearly equal. As a result, the intensity of the FS components involving negative interference is two orders of magnitude smaller compared to the FS components with positive interference. Therefore, in Table II, we give intensity formulas, obtained after insertion of matrix elements in Eq. (4), only for the ten components with $F'+F''=$odd. These formulas are valid for $v_1\neq v_k$. As mentioned in the previous paragraph, substitution $v_1=v_k=v$ yields an extra factor of 2 on account of the double degeneracy that exists for $v_1\neq v_k$ and division by 2 is required to obtain the final expressions. Here it is important to emphasize that the formulas of Tables I and II need to be supplemented by suitable phonon-renormalization factors[1] to correct the rigid lattice values of R_{1k} for the dynamical state of the crystal.

III. RESULTS AND DISCUSSION

The intensity formulas for double transitions involving two isolated ortho-H_2 molecules separated by a distance R_{1k}

TABLE II. Intensity formulas for different fine structure (FS) components of $Q_{v_1}(1)+Q_{v_k}(1)(v_1 \neq v_k)$ transitions in solid parahydrogen. For $v_1=v_k=v$, division by 2 is required to get the intensity expressions.

FS component	Integrated absorption coefficient $\tilde{\alpha}/\mathrm{cm}^3\,\mathrm{s}^{-1}$ (per ortho pair)
$\vert 1,1\rangle_{\pm} \leftarrow \vert 2,0\rangle$	$\frac{32\pi^3}{9hR_{1k}^8}\big[\langle 01\vert Q_2\vert v_1 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_k 1\rangle+\frac{2}{25}\langle 01\vert\gamma\vert v_k 1\rangle\big)+\langle 01\vert Q_2\vert v_k 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_1 1\rangle+\frac{2}{25}\langle 01\vert\gamma\vert v_1 1\rangle\big)\big]^2$
$\vert 2,1\rangle_{\pm} \leftarrow \vert 1,1\rangle_{\pm}$	$\frac{216\pi^3}{225hR_{1k}^8}(\langle 01\vert Q_2\vert v_1 1\rangle\langle 01\vert\alpha\vert v_k 1\rangle+\langle 01\vert Q_2\vert v_k 1\rangle \times\langle 01\vert\alpha\vert v_1 1\rangle)^2$
$\vert 1,1\rangle_{\pm} \leftarrow \vert 2,1\rangle_{\pm}$	same as above
$\vert 2,0\rangle \leftarrow \vert 1,1\rangle_{\pm}$	$\frac{32\pi^3}{9hR_{1k}^8}\big[\langle 01\vert Q_2\vert v_1 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_k 1\rangle+\frac{2}{25}\langle 01\vert\gamma\vert v_k 1\rangle\big)+\langle 01\vert Q_2\vert v_k 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_1 1\rangle+\frac{2}{25}\langle 01\vert\gamma\vert v_1 1\rangle\big)\big]^2$
$\vert 1,1\rangle_{\pm} \leftarrow \vert 2,2\rangle_{+}$	$\frac{32\pi^3}{27hR_{1k}^8}\big[\langle 01\vert Q_2\vert v_1 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_k 1\rangle-\frac{1}{25}\langle 01\vert\gamma\vert v_k 1\rangle\big)+\langle 01\vert Q_2\vert v_k 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_1 1\rangle-\frac{1}{25}\langle 01\vert\gamma\vert v_1 1\rangle\big)\big]^2$
$\vert 1,1\rangle_{\pm} \leftarrow \vert 2,2\rangle_{-}$	same as above
$\vert 2,2\rangle_{+} \leftarrow \vert 1,1\rangle_{\pm}$	same as above
$\vert 2,2\rangle_{-} \leftarrow \vert 1,1\rangle_{\pm}$	same as above
$\vert 2,1\rangle_{\pm} \leftarrow \vert 0,0\rangle, \vert 1,0\rangle$	$\frac{32\pi^3}{27hR_{1k}^8}\big[\big[\langle 01\vert Q_2\vert v_1 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_k 1\rangle-\frac{4}{25}\langle 01\vert\gamma\vert v_k 1\rangle\big)+\langle 01\vert Q_2\vert v_k 1\rangle\big(\frac{3}{10}\langle 01\vert\alpha\vert v_1 1\rangle-\frac{4}{25}\langle 01\vert\gamma\vert v_1 1\rangle\big)\big]^2+\frac{6}{25}\big[\langle 01\vert Q_2\vert v_1 1\rangle\big(\langle 01\vert\alpha\vert v_k 1\rangle+\frac{1}{15}\langle 01\vert\gamma\vert v_k 1\rangle\big)+\langle 01\vert Q_2\vert v_k 1\rangle\big(\langle 01\vert\alpha\vert v_1 1\rangle+\frac{1}{15}\langle 01\vert\gamma\vert v_1 1\rangle\big)\big]^2\big]$
$\vert 1,0\rangle, \vert 0,0\rangle \leftarrow \vert 2,1\rangle_{\pm}$	same as above

in parahydrogen crystal are given in Table I. The derivation of these formulas relies on the assumption that the level of ortho-H_2 impurity in the sample is extremely low. As a result, possibility of formation of many ortho-H_2 clusters and the mixing of rotational states of individual molecules by anisotropic interaction can be neglected. The dominant anisotropic interaction between two ortho-H_2 molecules is the EQQ interaction.[1] The separation of lowest and uppermost FS components of the ortho-pair due to EQQ interaction is $\sim 5.8\ \mathrm{cm}^{-1}$ for nearest neighbor,[26] whereas the first rotationally excited ortho $(J=3)$ state lies at $\sim 587\mathrm{cm}^{-1}$. This justifies neglect of the mixing of rotational states of individual molecules, underlying the derivation above.

Using the expressions given in Table I and the required multipole moments and polarizability matrix elements from Refs. 27 and 28, we give, in Table III, theoretical values of integrated absorption coefficients $\tilde{\alpha}(1,k)$, for the various zero-phonon double transitions involving an isolated pair of (nearest-neighbor) ortho-H_2 molecules in a para-H_2 crystal. The corresponding experimentally measured quantity $\tilde{\alpha}(1,k)$ is defined as:

$$\tilde{\alpha} = (c/Nl)\int \ln(I_0/I)d\nu/\nu. \tag{6}$$

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, l is the sample length, and N is the number of absorbing species per cm^3. Note that here the absorbing species are isolated pairs of ortho-H_2 molecules, hence the number density $N=N_{\mathrm{ortho}}/2$, under the assumption that the diffusion process driving the ortho molecules to form pairs is complete. This will be the case several hours after the crystal has been formed, and thus represents one extreme. However, initially, just before the diffusion process sets in the random distribution of ortho-pairs density is given by[1] $N=6N'X^2(1-X)$,[18] where N' is the number density of sites in the crystal and $X(=N_{\mathrm{ortho}}/N' \ll 1)$ is the *a priori* probability of occupancy of an ortho-molecule at a random site. This value of N represents the other extreme of the experimental measurement and should be used in Eq. (6). Experimentally, intensity of only two such transitions, namely, $Q_1(1)+Q_1(1)$[20] and $Q_1(1)+Q_2(1)$,[21] have been measured. It has been pointed out by Mishra *et al.*[29] in a recent paper that the ortho-H_2 concentrations have been underestimated in Refs. 20 and 21 by a factor 1.85; the experimental values given in the footnote of Table III are therefore corrected for orthohydrogen concentration by dividing the observed intensities of Refs. 20 and 21 by 1.85. As can be seen from this table, there is a reasonably good agreement between the theoretical and experimental intensity for $Q_1(1)+Q_1(1)$ and $Q_1(1)+Q_2(1)$ transitions. One should note that the experimental intensity reported in Refs. 20 and 21 is the sum of only two prominent FS components of these two transitions. Agreement between experimental observations and theory remains good if we sum the theoretical intensities of only the two experimentally observed FS components $\vert 2,1\rangle_{\pm} \leftarrow \vert 1,1\rangle_{\pm}$ and $\vert 1,1\rangle_{\pm} \leftarrow \vert 2,1\rangle_{\pm}$. The theoretical intensities (in units of per ortho-pair) of different FS components of $Q_{v_1}(1)+Q_{v_k}(1)$ transitions, using the formulas of Table II, are given in Table IV. The intensities of Table IV are calculated for a nearest-neighbor pair in the rigid-lattice approximation by setting $R_{1k}=a=3.793$ Å. The formulas given in Table II are valid for any pair separated by R_{1k} for the given initial and final states in each formula. However, if higher-order neighbors are considered, the intensities would be much smaller while the overall FS

TABLE III. Predicted intensities of some of the ortho-H_2-ortho-H_2 double transitions in parahydrogen crystal containing traces of ortho-H_2.

Transition	$\tilde{\alpha}/\mathrm{cm}^3\,\mathrm{s}^{-1}$ (per ortho pair)	Transition	$\tilde{\alpha}/\mathrm{cm}^3\,\mathrm{s}^{-1}$ (per ortho pair)
$Q_1(1)+Q_1(1)$	1.20×10^{-16}[a]	$Q_1(1)+U_1(1)$	1.74×10^{-19}
$Q_1(1)+Q_2(1)$	3.10×10^{-18}[b]	$Q_2(1)+U_0(1)$	1.48×10^{-20}
$Q_1(1)+Q_3(1)$	6.42×10^{-20}	$S_0(1)+S_0(1)$	2.22×10^{-15}
$Q_2(1)+Q_2(1)$	1.78×10^{-20}	$S_0(1)+S_1(1)$	2.53×10^{-16}
$Q_1(1)+S_0(1)$	5.63×10^{-15}	$S_0(1)+S_2(1)$	2.11×10^{-18}
$Q_1(1)+S_1(1)$	1.25×10^{-16}	$S_0(1)+S_3(1)$	1.48×10^{-19}
$Q_1(1)+S_2(1)$	3.33×10^{-18}	$S_1(1)+S_1(1)$	3.45×10^{-18}
$Q_1(1)+S_3(1)$	1.11×10^{-19}	$S_1(1)+S_2(1)$	1.70×10^{-19}
$Q_2(1)+S_0(1)$	5.16×10^{-17}	$S_1(1)+S_3(1)$	9.03×10^{-21}
$Q_2(1)+S_1(1)$	1.21×10^{-18}	$S_0(1)+U_0(1)$	1.64×10^{-18}
$Q_2(1)+S_2(1)$	2.98×10^{-20}	$S_1(1)+U_0(1)$	1.16×10^{-19}
$Q_3(1)+S_0(1)$	1.06×10^{-18}	$S_0(1)+U_1(1)$	1.68×10^{-19}
$Q_3(1)+S_1(1)$	2.58×10^{-20}	$S_1(1)+U_1(1)$	1.19×10^{-20}
$Q_1(1)+U_0(1)$	1.69×10^{-18}		

[a] Experimental value $=(1.0\pm0.2)\times10^{-16}$ $\mathrm{cm}^3\,\mathrm{s}^{-1}$ from Ref. 20, after incorporating correction to ortho-H_2 concentration. The experimental value is sum of the absorption coefficient of two major components only.

[b] Experimental value $=(3\pm1)\times10^{-18}$ $\mathrm{cm}^3\,\mathrm{s}^{-1}$ from Ref. 21, after incorporating correction to ortho-H_2 concentration. The experimental value is sum of the absorption coefficient of two major components only.

width would shrink. For example, the intensity of a FS component due to a next-nearest-neighbor pair ($R_{1k}=1.414a$) would be $(a/1.414a)^8\sim0.06$ times that of the corresponding nearest-neighbor pair. The FS splittings (which vary as R_{1k}^{-5}) would fall within a span of $\sim5.8\times(a/1.414a)^5\sim1.0$ cm^{-1} in this case.[6] As can be noticed, the sum of the intensities of all ten components of transitions for $v_1\neq v_k$ in Table IV is slightly smaller [3.5% for $Q_1(1)+Q_2(1)$ and 8.3% for $Q_1(1)+Q_3(1)$] compared to the intensity of the corresponding unsplit transition in Table III. This is because, as pointed out in Sec. II, for $v_1\neq v_k$, 18 additional weak FS components, which involve negative interference due to two nearly equal terms, also contribute.

Finally, one can make use of the intensity formulas given in Tables I and II to calculate the intensity of double transitions involving a pair of dopant molecules (such as N_2) in para-H_2 or ortho-D_2 crystal, where both the dopant molecules are in the $J=1$ rotational state and do not possess a permanent dipole moment. Furthermore, the formulas given in Table I can easily be extended to provide an order-of-magnitude estimate of the intensity of double transitions in a nearly pure ortho-H_2 crystal (or for that matter even an n-H_2 crystal). The net absorption coefficient, $\tilde{\alpha}$ per molecule, in this case is obtained by summing the pair absorption coefficient $\tilde{\alpha}(1,k)$ over k. The resulting formulas are similar to those in Table I with $1/R_{1k}^{(2\ell+4)}$ replaced by $S_{\ell+2}\xi_{\ell+2}/2a^{(2\ell+4)}$. Here, $S_{\ell+2}=\Sigma_{k\neq1}(a/R_{1k})^{2\ell+4}$ (≈12) are positive definite lattice sums and $\xi_{\ell+2}(\sim1)$ are the phonon renormalization factors which correct the rigid-lattice sums to allow for zero-point motions.[22–24] The exact values of $S_{\ell+2}$ can be found in Table I of Ref. 23 for a hexagonal close-packed lattice. Note also that a division by 2 of the expressions is required to allow for overcounting since, here, we need the absorption coefficient $\tilde{\alpha}$ per molecule rather than for an isolated pair. No more than order-of-magnitude agreement with the observations can be expected. Higher-order clustering of orthomolecules and strong mixing of rotational states of different molecules in the anisotropic environment that exists in a nearly pure ortho-H_2 crystal can lead to considerable line broadening. Nevertheless, the comparison of observed and estimated intensity may be useful to gain insight into the strength of the interaction in the ortho-H_2 crystal. In Table V, we show a comparison of the experimental and theoretical intensities of some of the double transitions involving a pair of ortho-H_2 molecules in normal-H_2 crystal (75% ortho-H_2). The agreement between experimental and estimated theoretical intensities varies from a few percent to a factor of ~2.

TABLE IV. Predicted intensities of different fine structure components of some of the $Q_{v_1}(1)+Q_{v_k}(1)$ transitions in parahydrogen crystal containing traces of ortho-H_2

	$\tilde{\alpha}/\mathrm{cm}^3\,\mathrm{s}^{-1}$ (per ortho pair)			
FS component	$Q_1(1)+Q_1(1)$	$Q_1(1)+Q_2(1)$	$Q_1(1)+Q_3(1)$	$Q_2(1)+Q_2(1)$
$\lvert1,1\rangle_\pm\leftarrow\lvert2,0\rangle$	1.75×10^{-17}	3.87×10^{-19}	6.59×10^{-21}	1.95×10^{-21}
$\lvert2,1\rangle_\pm\leftarrow\lvert1,1\rangle_\pm$	3.53×10^{-17}	8.84×10^{-19}	1.75×10^{-20}	5.32×10^{-21}
$\lvert1,1\rangle_\pm\leftarrow\lvert2,1\rangle_\pm$	3.53×10^{-17}	8.84×10^{-19}	1.75×10^{-20}	5.32×10^{-21}
$\lvert2,0\rangle\leftarrow\lvert1,1\rangle_\pm$	1.75×10^{-17}	3.87×10^{-19}	6.59×10^{-21}	1.95×10^{-21}
$\lvert1,1\rangle_\pm\leftarrow\lvert2,2\rangle_+$	3.10×10^{-18}	8.44×10^{-20}	1.82×10^{-21}	5.64×10^{-22}
$\lvert1,1\rangle_\pm\leftarrow\lvert2,2\rangle_-$	3.10×10^{-18}	8.44×10^{-20}	1.82×10^{-21}	5.64×10^{-22}
$\lvert2,2\rangle_+\leftarrow\lvert1,1\rangle_\pm$	3.10×10^{-18}	8.44×10^{-20}	1.82×10^{-21}	5.64×10^{-22}
$\lvert2,2\rangle_-\leftarrow\lvert1,1\rangle_\pm$	3.10×10^{-18}	8.44×10^{-20}	1.82×10^{-21}	5.64×10^{-22}
$\lvert2,1\rangle_\pm\leftarrow\lvert0,0\rangle,\lvert1,0\rangle$	1.22×10^{-18}	5.65×10^{-20}	1.70×10^{-21}	4.85×10^{-22}
$\lvert0,0\rangle,\lvert1,0\rangle\leftarrow\lvert2,1\rangle_\pm$	1.22×10^{-18}	5.65×10^{-20}	1.70×10^{-21}	4.85×10^{-22}

TABLE V. Comparison of the experimental and theoretical integrated absorption coefficient $\tilde{\alpha}$ (per molecule) of some zero-phonon ortho-H_2-ortho-H_2 double transitions in normal-H_2 crystal (75% ortho-H_2).

	$\tilde{\alpha}/\mathrm{cm}^3\,\mathrm{s}^{-1}$ (per molecule)		
Transition	Theory	Experiment	Measured by (Reference)
$Q_1(1)+Q_2(1)$	1.99×10^{-17}	1.45×10^{-17}	19
$Q_1(1)+S_2(1)$	2.13×10^{-17}	1.41×10^{-17}	19
$S_0(1)+S_0(1)$	1.42×10^{-14}	$(1.46\pm0.05)\times10^{-14\mathrm{a}}$	18
$S_0(1)+S_1(1)$	1.62×10^{-15}	$(3.18\pm0.10)\times10^{-15\mathrm{b}}$	17
$S_1(1)+S_1(1)$	2.21×10^{-17}	9.48×10^{-18}	19

[a] Deduced from the spectrum given in Ref. 18. The error margin reflects the uncertainty in the evaluated area.

[b] Deduced from the spectrum given in Ref. 17. The error margin reflects the uncertainty in the evaluated area.

IV. CONCLUSION

Closed form theoretical expressions are derived for the integrated absorption coefficients of various multipole-field-induced zero-phonon double transitions in an isolated pair of ortho-H_2 molecules embedded in para-H_2 crystal. These formulas can be applied to double transitions of dopant molecules, with zero permanent dipole moment and both molecules in $J=1$ initial rotational state, embedded in solid parahydrogen matrix. The intensity of different FS components have been calculated for $Q_{v_1}(1)+Q_{v_k}(1)$ transition. Following the same method one can calculate the intensities of FS components of other transitions. Intensity formulas given for an isolated pair, with minor modifications, can be used to estimate the intensities of double transitions in nearly pure ortho-H_2 crystal, which would provide useful information about the mixing of rotational states of different molecules due to strong anisotropic interaction present inside the ortho-H_2 crystal.

The detailed calculations of theoretical absorption coefficients presented here can help advance one's understanding of the absorption phenomena in solid hydrogen by stimulating new experiments on transitions that are relatively strong such as $Q_1(1)+S_0(1)$ and $S_0(1)+S_0(1)$. The related matrix elements that go into the calculations for these transitions are also known quite accurately.[27] The discrepancies that are observed between experimental results and theoretical predictions can be attributed to: (a) the experiments are usually performed at times intermediate between the two extreme cases, either just when the crystal is formed, or when the diffusion process is complete, so much so, there is an inherent uncertainty in the ortho-pair concentration N that should be used in Eq. (6) and (b) the phonon renormalization factors are not easily amenable for calculation, *a priori* and it is customary to set them equal to unity (rigid lattice approximation). Once the experimental uncertainties are reduced, the result presented here can, in fact, be used to deduce magnitudes of the renormalization factors involved in the various transitions which would lead to significant new results in the field of molecular quantum solids.

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*Electronic address: amishra@apsara.barc.ernet.in
†Electronic address: rdsouza@apsara.barc.ernet.in
‡Retired from Spectroscopy Division, BARC. Present address: A-21, Parmanu Nagar, Vashi, Navi Mumbai 400 703, India.

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