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Predicted intensities for new Raman transitions in solid HD

M. Attia, M. Ali, and R. H. Tipping
Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama 35487-0324

J. D. Poll
Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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The scattering efficiencies for the zero-phonon and phonon branches associated with predicted new Raman transitions in solid HD are calculated. These transitions arise from the interaction-induced polarizability of a pair of molecules expressed in terms of the vector separation between the centers of mass and satisfy different rotational selection rules from those of allowed Raman transitions. For single transitions in which only one molecule of the pair is excited by the incoming photon, one expects an R branch, while, for double transitions in which both molecules are excited, one expects $R+S$ and $T+S$ branches with progressively less intensity. A previously obtained experimental Raman spectrum of solid HD does have spectral features similar in shape and intensity to those predicted for the R_R phonon branch, although this feature was tentatively assigned as a two-phonon Raman-active transition. We conclude that a new Raman study of solid HD carried out with higher sensitivity and over a greater frequency region would be of interest to determine the correct assignment of this feature and to look for other predicted transitions resulting from the interaction-induced polarizability.

I. INTRODUCTION

Traditionally, Raman scattering and infrared absorption spectroscopy have been complementary tools for the study of molecular structure and molecular interactions. For instance, for isolated homonuclear diatomic molecules that do not have an infrared dipolar spectrum, Raman spectroscopy has provided a wealth of structural data.[1] However, as is well known, when such molecules (e.g., H_2) collide, a transient induced dipole is created, which when modulated by the translational, rotational and/or vibrational motions leads to infrared absorption.[2,3] The strongest transitions in these interaction-induced spectra obey the rotational selection rules $\Delta J \equiv J'-J=0,\pm 2$ (where J and J' are the initial- and final-state rotational quantum numbers, respectively); these are identical to those obeyed in ordinary Raman scattering, arising from dipoles induced by the electric fields of the incoming photons through the molecular polarizability tensor. Weaker infrared transitions arising from hexadecapolar induction[4,5] satisfying the selection rule $\Delta J=4$ have also been observed in gas-phase H_2 (Refs. 6 and 7) and in solid H_2,[8,9] D_2,[10] and HD.[11] These transitions would be analogous to those arising from hyper Raman scattering[12] (i.e., scattering from the molecular hyperpolarizability tensor[13]). Recently, transitions satisfying $\Delta J=6$ arising from the tetrahexacontapole-induced dipole[14,15] have been observed in the absorption spectrum of solid H_2. Similar transitions in Raman scattering due to higher-order hyperpolarizabilities have not, to our knowledge, been observed.

For heteronuclear diatomic molecules in general, and for the isotopically heteronuclear species HD in particular, infrared transitions having odd values of ΔJ have been observed in the gas,[16–18] liquid,[19] and solid[20–22] phases. Those satisfying $\Delta J=\pm 1$ (R- and P-branch transitions, respectively) arise not only from the weak allowed (nonadiabatic) dipole moment, but also from an interaction-induced dipole moment of the same symmetry.[23,24] The interference between these two dipoles can have a profound influence on both the shapes[25] and intensities[26–28] of these transitions. Transitions corresponding to $\Delta J=3$ and 5, arising for the most part, through interaction-induced dipoles of the requisite symmetry have also been reported.[22,29]

As discussed elsewhere in detail,[23] the induced-dipole moment of a pair of HD molecules can be related to that of the homonuclear counterpart, H_2 or D_2, by a coordinate transformation from the vector between the centers of interaction to that between the centers of mass. This transformation introduces additional ("shifted") dipole components having different angular symmetries. In an analogous way, the polarizability tensor for a pair of interacting HD molecules, including the interaction-induced part calculated within the dipole–induced-dipole (DID) approximation, can be obtained, and this contains shifted components which give rise to Raman scattering at frequencies corresponding to odd values of ΔJ.

In Sec. II we first discuss the polarizability tensor for a pair of interacting H_2 molecules and carry out the transformation mentioned earlier to compute the shifted components. In Sec. III, we apply these results to calculate the Raman scattering efficiency for zero-phonon transitions for solid HD, satisfying the selection rule $\Delta J=1$ [designated $R_v(0)$, where the subscript indicates the vibrational quantum number of the final state]. We also consider the intensities of two double Raman transitions[10,30,31] in which both molecules in a pair are simultaneously excited by the same incoming photon.

In Sec. IV we consider the phonon branches accompanying the odd ΔJ transitions. As discussed previously for the R_R branch,[32] these phonon spectra are similar to those observed in infrared absorption spectra and can be treated using a straightforward generalization of the formalism developed for calculating the intensities resulting from multipolar-induced dipoles.

In Sec. V we present numerical values for the scattering efficiencies, and discuss the existing Raman spectra of solid HD (Refs. 33 and 34) in light of the theory developed in Secs. III and IV. We suggest specific new Raman scattering experiments which, if carried out at higher sensitivity and over a wider frequency region, would be of interest to verify the predictions made in the present treatment.

II. POLARIZABILITY OF A PAIR OF INTERACTING HD MOLECULES

The irreducible components of the polarizability tensor referred to a space-fixed coordinate system can, for a pair of interacting H_2 molecules, be written in the form

$$\alpha_{\lambda\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})=\alpha_{\lambda\mu}(\mathbf{r}_1)+\alpha_{\lambda\mu}(\mathbf{r}_2)+\alpha_{\lambda\mu}^{(\mathrm{ind})}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R}) , \tag{1}$$

where $\mathbf{r}_1=(r_1,\omega_1)$ and $\mathbf{r}_2=(r_2,\omega_2)$ refer to the internuclear separation and orientation of molecules 1 and 2, respectively, and $\mathbf{R}=(R,\Omega)$ is the vector between the centers of mass of the two molecules; $\alpha_{\lambda\mu}(\mathbf{r}_i)$ are the polarizabilities of the isolated molecules, and $\alpha_{\lambda\mu}^{(\mathrm{ind})}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$ is the induced contribution. The anisotropic part of the interaction-induced polarizability, $\alpha_{2\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$, can in analogy to the interaction-induced dipole moment function[32] be expanded in terms of products of three appropriately coupled spherical harmonics:

$$\begin{aligned}\alpha_{2\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})=[(4\pi)^3/5]^{1/2}\sum_{\lambda_1\lambda_2\Lambda L}P_{\Lambda}^{(2)}(\lambda_1\lambda_2L;r_1r_2R)\\ \times\sum_{\mu_1\mu_2M}C(\lambda_1,\lambda_2,\Lambda;\mu_1,\mu_2,\mu_1+\mu_2)\\ \times C(\Lambda,L,2;\mu_1+\mu_2,M,\mu)Y_{\lambda_1\mu_1}(\omega_1)\\ \times Y_{\lambda_2\mu_2}(\omega_2)Y_{LM}(\Omega) ,\end{aligned} \tag{2}$$

where the coefficients,

$$P_{\Lambda}^{(2)}(\lambda_1\lambda_2L;r_1r_2R) ,$$

provide a unique, coordinate-independent representation of the induced polarizability specified by the indices λ_1, λ_2, Λ, and L, and the C's are Clebsch-Gordan coefficients. The polarizability coefficients satisfy the symmetry relation

$$P_{\Lambda}^{(2)}(\lambda_1\lambda_2L;r_1r_2R)=(-1)^{\lambda_1+\lambda_2-\Lambda+L}P_{\Lambda}^{(2)}(\lambda_2\lambda_1L;r_2r_1R) \tag{3}$$

and can be easily obtained within the dipole–induced-dipole (DID) model;[35,36] the results are listed in Table I in terms of the usual isotropic $\alpha=(\alpha_{\parallel}+2\alpha_{\perp})/3$ and anisotropic $\gamma=(\alpha_{\parallel}-\alpha_{\perp})$ molecular polarizabilities.

As discussed elsewhere in detail,[23] because of the noncoincidence of the vectors between the centers of interaction, $\mathbf{S}$, and centers of mass, $\mathbf{R}$, for a pair of interacting HD molecules, one can expand the corresponding anisotropic induced polarizability in a Taylor series

$$\begin{aligned}\alpha_{2\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{S})=\alpha_{2\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\\ +(\mathbf{x}_1-\mathbf{x}_2)\cdot\nabla_R\,\alpha_{2\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})+\cdots ,\end{aligned} \tag{4}$$

where $\mathbf{x}_i=\mathbf{r}_i/6$. The terms proportional to $\mathbf{x}_i$ can be written in the same form as Eq. (2) and the resulting coefficients are given by

$$\begin{aligned}P_{\lambda}^{(2)}(\delta\lambda_2L+1;r_1r_2R)=x_1[(d/dR-L/R)P_{\Lambda}^{(2)}(\lambda_1\lambda_2L;r_1r_2R)](-1)^{L+\lambda}[(2\lambda_1+1)(2\Lambda+1)(2L+1)(2\lambda+1)]^{1/2}\\ \times C(1\lambda_1\delta;000)C(1LL+1;000)W(1\delta\Lambda\lambda_2;\lambda_1\lambda)W(L+1L\lambda\Lambda;12)\end{aligned} \tag{5a}$$

and

$$\begin{aligned}P_{\lambda}^{(2)}(\lambda_1\delta L+1;r_1r_2R)=x_2[(d/dR-L/R)P_{\Lambda}^{(2)}(\lambda_1\lambda_2L;r_1r_2R)](-1)^{\Lambda+L}[(2\lambda_2+1)(2\Lambda+1)(2L+1)(2\lambda+1)]^{1/2}\\ \times C(1\lambda_2\delta;000)C(1LL+1;000)W(1\delta\Lambda\lambda_1;\lambda_2\lambda)W(L+1L\lambda\Lambda;12) .\end{aligned} \tag{5b}$$

In these expressions, the W's are Racah coefficients,[37] and the new polarizability coefficients obtained by the application of Eq. (5a) or (5b) are referred to as the "shifted components."

Applying Eq. (5a), we obtain the shifted components listed explicitly in Table II; coefficients related by the symmetry relation, Eq. (3), which one could obtain by applying Eq. (5b), are not listed. We also note that one could apply Eqs. (5a) and (5b) to the shifted coefficients to obtain "twice-shifted" components (aside from a factor of $\frac{1}{2}$ from the Taylor series expansion). These, of course, would have different angular symmetries from those listed in Tables I and II and would give rise to other Raman transitions, but these components are not considered in the present paper.

III. ZERO-PHONON TRANSITIONS

In this section, we apply the shifted polarizability components to calculate the scattering efficiencies of zero-phonon transitions corresponding to the $R_v(0)$ single transitions and to the $R_v(0)+S_{v'}(0)$ and $T_v(0)+S_{v'}(0)$

TABLE I. Interaction-induced anisotropic polarizability components, $P_\Lambda^{(2)}(\lambda_1\lambda_2L;r_1r_2R)$, for a pair of H_2 molecules calculated within the DID approximation.

λ_1	λ_2	Λ	L	$P_\Lambda^{(2)}(\lambda_1\lambda_2L;r_1r_2R)$
0	0	0	2	$2\sqrt{6}\alpha(r_1)\alpha(r_2)R^{-3}$
0	2	2	2	$-\frac{2\sqrt{105}}{15}\alpha(r_1)\gamma(r_2)R^{-3}$
2	0	2	2	$-\frac{2\sqrt{105}}{15}\gamma(r_1)\alpha(r_2)R^{-3}$
2	2	0	2	$\frac{2\sqrt{30}}{225}\gamma(r_1)\gamma(r_2)R^{-3}$
2	2	2	2	$-\frac{2\sqrt{6}}{45}\gamma(r_1)\gamma(r_2)R^{-3}$
2	2	4	2	$\frac{4\sqrt{30}}{25}\gamma(r_1)\gamma(r_2)R^{-3}$

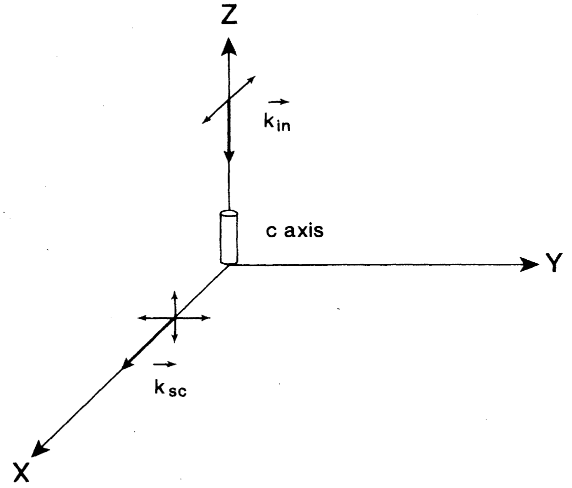

FIG. 1. Scattering geometry used for calculating the scattering efficiency of the Raman R_R phonon branch of solid HD. The polarizations are XY and XZ, where the first index denotes the polarization of the incident field and the second index that of the scattered field. The molecular c axis is parallel to the laboratory Z axis.

double transitions in solid HD. We note that the unshifted components listed in Table I will not contribute significantly to single transitions because the corresponding lattice sum for nearest neighbors vanishes,[32] but they do lead to transitions of the form $S_v(0)+S_{v'}(0)$, which have been discussed previously and observed experimentally.[30,31]

The integrated Raman scattering efficiency (i.e., the fraction of the incoming photons scattered per unit solid angle and per unit length of the crystal) for solid HD can be written in the form[34]

$$I_{IJ}=(4\omega_0\omega_s^3/c^4)\rho\sum_f|\langle f|\alpha_{IJ}|i\rangle|^2\,, \tag{6}$$

where ω_0 and ω_s are the frequencies of the incoming and scattered photons, ρ is the number density of the crystal, and α_{IJ} are the Cartesian components of the polarizability tensor.[38]

Because of the absence of the ortho-para distinction in HD, we assume that the initial (ground) state is specified by

$$|i\rangle\equiv|v_1J_1m_1;\ v_2J_2m_2;n_\lambda\rangle=|000;000;0\rangle\,,$$

where n_λ labels the phonon states such that $\sum_\lambda^{(n)}n_\lambda=n$, n being the number of phonons.[39] For the zero-phonon $R_v(0)$ single transition, the final state is $\langle f|=\langle v1m;000;0|$, while for the zero-phonon double transitions, $R_v(0)+S_{v'}(0)$ and $T_v(0)+S_{v'}(0)$, the final states are $\langle v1m;v'2m';0|$ and $\langle v3m;v'2m';0|$, respectively.

In this paper, we consider only one scattering geometry where both the crystal c axis and incoming wave vector are parallel to the laboratory Z axis (cf. Fig. 1), with the

TABLE II. Shifted interaction-induced anisotropic polarizability components, $P_\Lambda^{(2)}(\lambda_1\lambda_2L;r_1r_2R)$, for a pair of HD molecules calculated within the DID approximation.

λ_1	λ_2	Λ	L	$P_\Lambda^{(2)}(\lambda_1\lambda_2L;r_1r_2R)$
1	0	1	3	$\frac{\sqrt{30}}{3}r_1\alpha(r_2)[\alpha(r_1)+\gamma(r_1)/15]R^{-4}$
1	2	1	3	$-\frac{\sqrt{15}}{45}r_1\gamma(r_2)[\alpha(r_1)+\gamma(r_1)/15]R^{-4}$
1	2	2	3	$-\frac{\sqrt{6}}{9}r_1\gamma(r_2)[\alpha(r_1)+\gamma(r_1)/15]R^{-4}$
1	2	3	3	$-\frac{2\sqrt{10}}{15}r_1\gamma(r_2)[\alpha(r_1)+\gamma(r_1)/15]R^{-4}$
3	2	1	3	$\frac{2\sqrt{10}}{525}r_1\gamma(r_1)\gamma(r_2)R^{-4}$
3	2	2	3	$-\frac{2\sqrt{6}}{315}r_1\gamma(r_1)\gamma(r_2)R^{-4}$
3	2	3	3	$-\frac{\sqrt{210}}{525}r_1\gamma(r_1)\gamma(r_2)R^{-4}$
3	2	4	3	$\frac{\sqrt{30}}{105}r_1\gamma(r_1)\gamma(r_2)R^{-4}$
3	2	5	3	$\frac{2\sqrt{330}}{105}r_1\gamma(r_1)\gamma(r_2)R^{-4}$

incident polarization along the X axis. For unpolarized detection along the X axis, only the α_{XY} and α_{XZ} polarizability tensor components contribute to the scattering efficiency.[38] These can be expressed in terms of the irreducible components given in Eq. (2) by

$$\alpha_{XY}=-(i/2)[\alpha_{22}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})-\alpha_{2-2}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})] \tag{7a}$$

and

$$\alpha_{XZ}=-(\tfrac{1}{2})[\alpha_{21}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})-\alpha_{2-1}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})]\ . \tag{7b}$$

The $R_v(0)$ transitions are described by the shifted component $P_1^{(2)}(103;r_1r_2R)$. Thus, using the result given in Table II and Eq. (2), we can write

$$\begin{aligned}\alpha_{2\mu}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})=&[4\pi\sqrt{6}\alpha(r_2)/3]\\ &\times[r_1\alpha(r_1)+r_1\gamma(r_1)/15]R^{-4}\\ &\times\sum_{\mu_1}C(132;\mu_1,\mu-\mu_1,\mu)\\ &\times Y_{1\mu_1}(\omega_1)Y_{3,\mu-\mu_1}(\Omega)\ .\end{aligned} \tag{8}$$

Noting that because of crystal symmetry only the α_{XY} component contributes to the zero-phonon intensity, and carrying out the integrations over the internal coordinates of molecules 1 and 2, we can rewrite Eq. (6) in a form analogous to that given previously for infrared transitions,[39]

$$\begin{aligned}I_{XY}=&(4\omega_0\omega_S^3/c^4)\rho\sum_{jj'}\sum_{M}\langle 0|F_{3M}(\mathbf{R}_j)|0\rangle\\ &\times\langle 0|F_{3M}(\mathbf{R}_{j'})^*|0\rangle\ ,\end{aligned} \tag{9}$$

where

$$\begin{aligned}F_{3M}(\mathbf{R}_j)=&(4\pi/7)^{1/2}\{\sqrt{5/6}(\alpha)_{00}[(r\alpha)_{v1}+(r\gamma)_{v1}/15]\}\\ &\times Y_{3M}(\Omega_j)R_j^{-4}\ .\end{aligned} \tag{10}$$

In this expression, the double subscripts on the polarizability matrix elements denote the final-state vibrational and rotational quantum numbers, respectively; numerical values[40] for these are listed in Table III. Using Eqs. (9) and (10), we can write the scattering efficiency for the $R_v(0)$ transition in the form

$$I_{XY}(R_v(0))=(4\omega_0\omega_s^3/c^4)\rho\left[[5(\alpha)_{00}^2/6a^8][(r\alpha)_{v1}+(r\gamma)_{v1}/15]^2\sum_{jj'}\left[\frac{a^2}{a_ja_{j'}}\right]^4P_3(\cos\theta_{jj'})\right]\ . \tag{11}$$

In the lattice sum, the angle $\theta_{jj'}$, in the argument of the Legendre polynomial P_3, is the angle between the vectors $\mathbf{R}_j$ and $\mathbf{R}_{j'}$, and $a=6.8824a_0$ is the lattice constant for the hcp crystal.

Using the shifted components $P_\Lambda^{(2)}(123;r_1r_2R)$ and $P_\Lambda^{(2)}(323;r_1r_2R)$, respectively, together with Eqs. (2) and (6), one can obtain the Raman scattering efficiences for the $R_v(0)+S_{v'}(0)$ and $T_v(0)+S_{v'}(0)$ transitions. In contrast to the single transition case, both polarizations contribute, and one can write the results in the following form:

$$I_{XY+XZ}(R_v(0)+S_{v'}(0))=(4\omega_0\omega_s^3/c^4)\rho\left[[(\gamma)_{v'2}(r\alpha)_{v1}/a^4+(\gamma)_{v'2}(r\gamma)_{v1}/15a^4]^2\sum_{L=0}^{2}c_L^{RS}\sum_j(a/a_j)^8P_{2L}(\cos\theta_j)\right] \tag{12}$$

and

$$I_{XY+XZ}(T_v(0)+S_{v'}(0))=4(\omega_0\omega_s^3/c^4)\rho\left[[(r\gamma)_{v3}(\gamma)_{v'2}/a^4]^2\sum_{L=0}^{2}C_L^{TS}\sum_j(a/a_j)^8P_{2L}(\cos\theta_j)\right]\ . \tag{13}$$

Numerical values of the coefficients C_L^{RS}, C_L^{TS}, and the corresponding lattice sums are listed in Table III. For double transitions, as in the infrared case,[39] these lattice sums are over a single summation index and are thus not reduced by the so-called "cancellation effect." As a consequence, the scattering intensity for zero-phonon $R_0(0)+S_0(0)$ double transitions is approximately $\frac{1}{3}$ that of the $R_0(0)$ transition, although that of the $T_0(0)+S_0(0)$ is considerably less, as will be discussed in greater detail in Sec. V.

IV. PHONON BRANCHES

As discussed elsewhere,[32] all the polarizability coefficients, $P_\Lambda^{(2)}(\lambda_1\lambda_2L;r_1r_2R)$, listed in Table II have the same functional dependence on the lattice variables as the quadrupole-induced dipole moment [i.e., $Y_{3M}(\Omega)R^{-4}$]. Thus, one can calculate the scattering efficiencies for the phonon branches accompanying the Raman transitions by a straightforward generalization of the formalism developed previously to calculate the phonon branches in induced infrared spectra.[39] For instance, for the R_R branch associated with the $R_v(0)$ transitions, one can write

$$I_{XY}=(4\omega_0\omega_s^3/c^4)\rho\sum_{jj'}\sum_{M}\sum_{n_\lambda}^{(n)}\langle 0|F_{3M}(\mathbf{R}_j)|n_\lambda\rangle\langle n_\lambda|F_{3M}(\mathbf{R}_{j'})^*|0\rangle\ , \tag{14}$$

where $F_{3M}(\mathbf{R}_j)$ is given by Eq. (10). Poll and Van Kranendonk[39] calculated the lattice matrix elements appearing in Eq. (14) within an isotropic Debye model. They introduced a dimensionless average square displacement from equilibrium $\Delta=\langle u_{j\alpha}^2\rangle/a^2$, and found that they could get good agreement with experiment for the infrared S_R phonon branches in solid H_2 by choosing $\Delta=1.0\times10^{-2}$. For HD, the choice $\Delta=0.8\times10^{-2}$ gives

TABLE III. Molecular matrix elements, intensity coefficients, C_L, and lattice sums for solid HD.

$(\alpha)_{00}=5.3855\ a_0^3$	$(\gamma)_{02}=2.0077\ a_0^3$	$(\gamma)_{12}=0.5311\ a_0^3$
$(r\alpha)_{01}=7.8839\ a_0^4$	$(r\alpha)_{11}=1.8241\ a_0^4$	$(r\gamma)_{01}=2.9763\ a_0^4$
$(r\gamma)_{11}=1.1503\ a_0^4$	$(r\gamma)_{03}=3.0046\ a_0^4$	$(r\gamma)_{13}=1.0755\ a_0^4$
$C_0^{RS}=7/135$	$C_1^{RS}=1/315$	$C_2^{RS}=-1/315$
$C_0^{TS}=584/23\,625$	$C_1^{TS}=-454/165\,375$	$C_2^{TS}=-4/18\,375$

$$\sum_{jj'}\left[\frac{a^2}{a_j a_{j'}}\right]^4 P_3(\cos\theta_{jj'})=0.306 \qquad \sum_{j}\left[\frac{a}{a_j}\right]^8 P_0(\cos\theta_j)=12.8$$

$$\sum_{j}\left[\frac{a}{a_j}\right]^8 P_2(\cos\theta_j)=2.2\times10^{-3} \qquad \sum_{j}\left[\frac{a}{a_j}\right]^8 P_4(\cos\theta_j)=1.06$$

good agreement[32] and is used in the present calculations. As noted previously,[32] because of the large cancellation effect for the lattice sum in single transitions, the R_R phonon branches are an order of magnitude larger than the corresponding $R_v(0)$ transitions.

For the double Raman transitions, one can calculate the scattering efficients from the expression[39]

$$I_{XY+XZ}=(4\omega_0\omega_s^3/c^4)\rho\sum_j\sum_M\sum_{n_\lambda}^{(n)}|\langle 0|F_{LM}(\mathbf{R}_j)|n_\lambda\rangle|^2\ , \tag{15}$$

where the functions $F_{LM}(\mathbf{R}_j)$ can be expressed in terms of the shifted polarizability coefficients. Numerical results for the scattering efficiencies of the phonon branches for the three new Raman transitions considered earlier are discussed in Sec. V.

V. NUMERICAL RESULTS AND DISCUSSION

Raman scattering efficiencies for the $R_v(0)$, $R_v(0)+S_{v'}(0)$, and $T_v(0)+S_{v'}(0)$ zero-phonon transitions can be calculated from Eqs. (11), (12), and (13), respectively, and the data in Table III. Similarly, the phonon branch scattering efficiencies can be obtained starting from Eqs. (14) and (15), using the isotropic Debye model previously developed for infrared transitions. The results for the pure rotational band ($v=v'=0$) are presented in Table IV in terms of ratios of the phonon branches to the corresponding zero-phonon transitions and ratios of the phonon branches to the allowed $S_0(0)$ transition. Results for the vibrational bands can be calculated simply by using the vibrational molecular matrix elements in place of the pure rotational ones used in the present calculations.

As one can see from Table IV, the scattering efficiency for the R_R branch is small compared to that of the allowed $S_0(0)$ transition, but is an order of magnitude larger than the corresponding zero-phonon transition. This disparity does not apply to the double transitions, for which the zero-phonon and phonon branches are comparable in intensity.

Early Raman spectra of solid HD, obtained with conventional light sources and limited sensitivity,[33] showed only the strongest allowed scatterings at the $S_v(0)$ and $Q_v(0)$ single transitions. More recent measurements obtained with laser sources and improved sensitivity,[34] revealed not only a Raman-active phonon transition, but also a weak, broad structure with the expected shape and frequency spectrum corresponding to the R_R branch. However, no other sharp transitions were observed. The

TABLE IV. Numerical values for ratios of scattering efficiencies for new Raman transitions in solid HD, and relative magnitudes of the n-phonon contributions.

$$\frac{I_{XY}(R_R)}{I_{XY}(R_0(0))}=14.7 \qquad \frac{I_{XY}(R_R)}{I_{XY+XZ}(S_0(0))}=2.6\times10^{-3}$$

$$\frac{I_{XY+XZ}(R_R+S_R)}{I_{XY+XZ}(R_0(0)+S_0(0))}=0.539 \qquad \frac{I_{XY+XZ}(R_R+S_R)}{I_{XY+XZ}(S_0(0))}=3.5\times10^{-5}$$

$$\frac{I_{XY+XZ}(T_R+S_R)}{I_{XY+XZ}(T_0(0)+S_0(0))}=0.535 \qquad \frac{I_{XY+XZ}(T_R+S_R)}{I_{XY+XZ}(S_0(0))}=2.3\times10^{-6}$$

	Relative phonon-branch contributions		
n	R_R	R_R+S_R	T_R+S_R
0	1.000	1.000	1.000
1	7.904	0.374	0.373
2	4.412	0.117	0.114
3	1.707	0.035	0.035
4	0.468	0.011	0.009
5	0.150	0.003	0.003

broad structure was tentatively identified as due to a Raman-active two-phonon transition, although the possibility of the R_R branch was mentioned. The observations are consistent with the interpretation of this feature as the R_R phonon branch because it is expected to be more than an order of magnitude stronger than the corresponding zero-phonon single transition. Notwithstanding, we note that the $R_0(0)$ transition may still be observable with the current state-of-the-art Raman equipment because of its much narrower linewidth. This linewidth would be due, for the most part, to the delocalization of the $J=1$ roton in the solid.[38] Because the scattering of the $R_0(0)+S_0(0)$ double Raman transition is comparable to that of the $R_0(0)$ single transition, it would also be of interest to look for Raman scattering at this frequency as well. If these transitions were observed with the expected intensity ratios, one would be able to assign unambiguously the scattering observed previously[34] to the R_R branch.

Finally, we note that the new Raman transitions discussed in the present paper occur only because of the breakdown of the independent polarizability approximation; thus, in contradistinction to the situation in the gas where effects due to the interaction-induced polarizability (generically referred to as collision-induced light scattering[41]) are manifested only by small changes in the shapes and intensities of allowed transitions, the study of the Raman spectrum of solid HD could provide an excellent opportunity to understand better some of the subtleties of molecular interactions.

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