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Intensities of zero-phonon $U_v(0)$ and $Q_v(0)+U_{v'}(0)$ transitions in solid H_2, D_2, and HD

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Theoretical expressions are presented for the integrated intensities of zero-phonon $U_v(0)$ single, and $Q_v(0)+U_{v'}(0)$ double transitions in solid parahydrogen (p-H_2), orthodeuterium (o-D_2) and hydrogen deuteride. In H_2 and D_2, these transitions arise primarily through the hexadecapolar induction mechanism, while in HD there is an additional significant contribution from the shifted quadrupolar induction mechanism. The theoretical results are, for the most part, consistent with the available experimental data, but refinements such as more accurate vibration-rotational hexadecapole matrix elements and phonon renormalization factors are required for quantitative agreement.

I. INTRODUCTION

The first experimental observation of $U_v(J)$ transitions ($v,J+4\leftarrow 0,J$, where v and J are the vibrational and rotational quantum numbers, respectively) in H_2 was made in the gas by Gibbs *et al.*[1] Several years later, Prasad *et al.*[2] reported observations of the fundamental $U_1(0)$ and $U_1(1)$ zero-phonon lines, together with their associated $Q_1(0)+U_0(J)$ double transitions ($v=1,J=0\leftarrow v=J=0$ for molecule 1 and $v=0,J+4\leftarrow v=0,J$ for molecule 2) and phonon branches, in solid H_2. They obtained an approximate value of the integrated intensity, α, for the $U_1(0)$ transition ($\alpha=0.23$ cm^{-2}); a larger value ($\alpha=0.30$ cm^{-2}) obtained with a higher sensitivity spectrometer was reported by Ivancic *et al.*[3]

The pure rotational transition $U_0(0)$ in solid H_2 was first observed by Balasubramanian *et al.*[4] who reported a value $\alpha=(0.52\pm0.01)$ cm^{-2}; these authors also observed the crystal-field splitting of this transition and used their results to infer a phonon density of states in solid H_2. Much of this early work has been summarized by Rao *et al.*[5]

The $U_0(0)$ and $U_1(0)$ transitions in solid HD were first measured by Lo;[6,7] he obtained values of the integrated intensity $\alpha=1.04$ and 0.74 cm^{-2}, respectively, which are considerably higher than the corresponding results for H_2.

Recently, Baliga *et al.*[8] published results for solid D_2. They reported for α the values 0.60 and 0.17 cm^{-2} for the $U_0(0)$ and $U_1(0)$ transitions, respectively, which are similar to those for H_2. More recently, Lee[9] has remeasured the spectra of solid p-H_2, o-D_2, and HD and has obtained new values of α not only for the transitions mentioned above, but also for the $U_2(0)$, $Q_2(0)+U_0(0)$, and $Q_1(0)+U_1(0)$ transitions in the overtone region of the H_2 spectrum. These results will be discussed and compared with theory in Sec. III.

Paralleling the experimental advances, the theory of hexadecapolar induction has been developed. Poll and Tipping[10] have derived general expressions for calculating the integrated intensities of the zero-phonon $U_v(0)$ and $Q_v(0)+U_{v'}(0)$ transitions in p-H_2. These results are also applicable for o-D_2, but have to be modified for HD as discussed in Sec. II. Because of the existence of a more complete set of experimental data, it is now possible to assess the importance of some of the approximations made in deriving the theoretical expressions, and conclusions drawn from the present analysis are presented in Sec. III.

II. THEORY

The general theory for the intensity of induced lines in solid hydrogens was first given by Poll and Van Kranendonk.[11] They introduced the spherical components of the induced dipole moment of a pair of molecules, expanded in terms of appropriately coupled products of three spherical harmonics describing the orientations of the internuclear axes of the two molecules (ω_i) and the orientation of the vector connecting their centers of mass (Ω),[12]

$$\mu_\nu(\mathbf{r}_1\mathbf{r}_2\mathbf{R})=[(4\pi)^3/3]^{1/2}\sum_{\lambda_1\lambda_2\Lambda L}A_\Lambda(\lambda_1\lambda_2L;r_1r_2R)\times\sum_{\mu_1\mu_2M}C(\Lambda L1;\mu_1+\mu_2,M,\nu)C(\lambda_1\lambda_2\Lambda;\mu_1,\mu_2,\mu_1+\mu_2)Y_{\lambda_1\mu_1}(\omega_1)Y_{\lambda_2\mu_2}(\omega_2)Y_{LM}(\Omega)\ . \qquad (1)$$

In Eq. (1), r_i and R denote the internuclear and center-of-mass separations, respectively, and the C's are Clebsch-Gordan coefficients. The dipole coefficients $A_\Lambda(\lambda_1\lambda_2L;r_1r_2R)$ thus provide a coordinate-independent representation of the strengths of various induction mechanisms specified by the indices λ_1, λ_2, Λ, and L. For instance, the usual hexadecapolar induction primarily responsible for the $U_v(0)$ and $Q_v(0)+U_{v'}(0)$ transitions, respectively, in H_2 or D_2 is characterized by,[10]

$$\begin{aligned} A_4(405;r_1r_2R)&=\sqrt{5}H(r_1)\alpha(r_2)R^{-6}\ ,\\ A_4(045;r_1r_2R)&=-\sqrt{5}\alpha(r_1)H(r_2)R^{-6}\ , \end{aligned} \tag{2}$$

where $H(r_i)$ is the hexadecapole moment of molecule i, arbitrarily assumed to be the one making the $\Delta J=4$ transition, and $\alpha(r_j)$ is the isotropic polarizability of a neighboring molecule j making no transition in the single $U_v(0)$ case, or a pure vibrational transition in the $Q_v(0)+U_{v'}(0)$ case.

For HD, because the center of mass in a molecule does not coincide with the center of interaction, there are extra terms in the dipole-moment expansion arising from this shift of coordinates.[12,13] In particular, for each coefficient in Eq. (2), there is an extra term arising from the shifted quadrupolar induction, viz.,

$$\begin{aligned} A_4(405;r_1r_2R)&=\sqrt{5}[H(r_1)+r_1^2Q(r_1)/6]\alpha(r_2)R^{-6}\ ,\\ A_4(045;r_1r_2R)&=-\sqrt{5}[H(r_2)+r_2^2Q(r_2)/6]\alpha(r_1)R^{-6}\ , \end{aligned} \tag{3}$$

where $Q(r)$ is the quadrupole moment function. This extra term is responsible for the extra absorption in HD as noted in the Introduction.

From the theoretical standpoint, it is convenient to express the absorption in terms of a quantity $\tilde{\alpha}$ (cm^3/s) defined by

$$\tilde{\alpha}=(cV/Nl)\int\ln[I_0(\nu)/I(\nu)]\frac{d\nu}{\nu}\ , \tag{4}$$

in which N is the number of molecules in volume V, c is the speed of light, l the absorption path length, and $I_0(\nu)$ and $I(\nu)$ are the initial and final fluxes at wave number ν. In the present paper, we are interested in the zero-phonon transitions in which the lattice vibrational state does not change. In this case, the transitions are relatively sharp, and to a good approximation one can write

$$\tilde{\alpha}=(cV/N\nu_0)\alpha\ , \tag{5}$$

where α (cm^{-2}) is the usual integrated intensity of the line centered at wave number ν_0,

$$\alpha=\frac{1}{l}\int\ln[I_0(\nu)/I(\nu)]d\nu\ . \tag{6}$$

For pure p-H_2, o-D_2, or HD at the absolute zero of temperature, all molecules are in the $J=0$ state. According to the procedure discussed in Ref. 11, the intensity of the $U_v(0)$ single transitions is then given by

$$\tilde{\alpha}_0=(4\pi^2/3\hbar)\sum_{i,j}\sum_M\langle 0|F_{5M}(\mathbf{R}_i)|0\rangle\langle 0|F_{5M}(\mathbf{R}_j)^*|0\rangle\ , \tag{7}$$

where

$$F_{5M}(\mathbf{R}_i)=(4\pi/11)^{1/2}\times\langle 00;00|A_4(405;r_1r_2R_i)|v4;00\rangle Y_{5M}(\Omega_i)\ . \tag{8}$$

In these expressions, $|0\rangle$ denotes the ground state of the lattice, and the sums over i and j are over all neighbors of molecule 1; the subscript on $\tilde{\alpha}_0$ denotes the zero-phonon contribution. The vibration-rotational states for the pair $|v_1J_1;v_2J_2\rangle$ are taken to be simple product states; i.e., we do not consider any mixing of internal states by the anisotropic interaction. Such mixing can lead to additional effects such as double Raman transitions[8,14] as well as modify the line intensities. This mixing may be significant for HD, but because of current experimental uncertainties and other theoretical approximations, we ignore mixing in the present paper.

Using Eqs. (2), (7), and (8), we find for the intensity of the $U_v(0)$ lines in p-H_2 or o-D_2

$$\tilde{\alpha}_0=(20\pi^2H_{0v}^2\alpha_{00}^2/3\hbar a^{12})\xi_{65}^2\sum_{i,j}(a^2/a_ia_j)^6P_5(\cos\theta_{ij})\ , \tag{9}$$

where a is the nearest-neighbor distance, and the argument of the Legendre polynomial involves the angle subtended at the position of molecule 1 between the directions to molecules i and j in the equilibrium lattice; H_{0v} and α_{00} are the vibration-rotational matrix elements of the hexadecapole moment function and the isotropic polarizability function, respectively. The lattice sum in Eq. (9) is multiplied by a phonon renormalization factor ξ_{65}^2 which accounts for the zero-point motion of the lattice.[15] Various estimates of the analogous factor ξ_{54} arising from the renormalized quadrupole-quadrupole interaction energy indicate a value slightly less than unity,[16–18] and one would expect a similar magnitude to obtain for ξ_{65}.

For HD, one has to use Eq. (3) instead of Eq. (2), and we find for the intensities of $U_v(0)$ transitions

$$\begin{aligned} \tilde{\alpha}_0=(20\pi^2\alpha_{00}^2/3\hbar a^{12})&[H_{0v}^2+\tfrac{1}{36}(r^2Q)_{0v}^2\\ &+\tfrac{1}{18}(r^2Q)_{0v}H_{0v}]\xi_{65}^2\\ &\times\sum_{i,j}(a^2/a_ia_j)^6P_5(\cos\theta_{ij})\ , \end{aligned} \tag{10}$$

where $(r^2Q)_{0v}$ is the vibration-rotational matrix element of the twice shifted quadrupole-induced dipole moment. We note that in Eq. (10), the interference (cross term) between the two contributing mechanisms can be constructive or destructive depending on the signs of the corresponding matrix elements.

We now turn to the zero-phonon double transitions of the form $Q_v(0)+U_{v'}(0)$. The integrated intensities are given by expressions analogous to Eqs. (7) and (8), viz.,

$$\tilde{\alpha}_0=(4\pi^2/3\hbar)\sum_i\sum_M|\langle 0|F_{5M}(\mathbf{R}_i)|0\rangle|^2\ , \tag{11}$$

where

TABLE I. Comparison of experimental and theoretical values of α for the $U_v(0)$ and $Q_v(0)+U_{v'}(0)$ transitions in p-H_2, o-D_2, and HD.

Transition	Species	α (cm^{-2}) Expt.	Theor.
$U_0(0)$	p-H_2	0.52[a]	0.57
		0.50[b]	
	o-D_2	0.60[c]	0.53
		0.32[b]	
	HD	1.04[d]	1.70
		0.98[b]	
$U_1(0)$	p-H_2	0.23[e]	0.32
		0.30[f]	
		0.25[b]	
	o-D_2	0.17[c]	0.31
		0.20[d]	
	HD	0.74[d]	0.97
		0.64[b]	
$U_2(0)$	p-H_2	3.2×10^{-3}[b]	5.1×10^{-6}
$Q_1(0)+U_0(0)$	p-H_2	0.19[b]	0.083
	HD	0.32[b]	0.24
$Q_2(0)+U_0(0)$	p-H_2	1.78×10^{-3}[b]	1.33×10^{-3}
$Q_1(0)+U_1(0)$	p-H_2	2.4×10^{-2}[b]	1.8×10^{-2}

[a] Reference 4.
[b] Reference 9.
[c] Reference 8.
[d] Reference 6.
[e] Reference 2.
[f] Reference 3.

$$F_{5M}(\mathbf{R}_i)=(4\pi/11)^{1/2}\times\langle 00;00|A_4(045;r_1r_2R_i)|v0;v'4\rangle Y_{5M}(\Omega_i)\ . \tag{12}$$

The lattice sum in Eq. (11) is only a single sum over neighbors, and thus the double transitions are not affected by the "cancellation effect."[15] Again, using the hexadecapolar induction described by Eq. (2), we find for p-H_2 and o-D_2

$$\tilde{\alpha}_0=(20\pi^2H_{0v'}^2\alpha_{0v}^2/3\hbar a^{12})\xi_{60}^2\sum_i(a/a_i)^{12}\ , \tag{13}$$

and for HD,

$$\tilde{\alpha}_0=(20\pi^2\alpha_{0v}^2/3\hbar a^{12})[H_{0v'}^2+\tfrac{1}{36}(r^2Q)_{0v'}^2+\tfrac{1}{18}(r^2Q)_{0v'}H_{0v'}]\xi_{60}^2\sum_i(a/a_i)^{12}\ . \tag{14}$$

TABLE II. Lattice and molecular parameters for the solid hydrogens.

Parameter	p-H_2	o-D_2	HD
a (a.u.)[a]	7.1602	6.8125	6.8824
$N/V\times10^{-22}$ cm^{-3}[a]	2.600	3.019	2.928
$\sum_{i,j}(a^2/a_ia_j)^6P_5(\cos\theta_{ij})$	7.168	7.168	7.168
$\sum_i(a/a_i)^{12}$	12.132	12.132	12.132
α_{00} (a.u.)[b]	5.4138	5.3452	5.3823
α_{01} (a.u.)[b]	0.7392	0.6163	0.6853
α_{02} (a.u.)[b]	−0.0713	−0.0487	−0.0608
H_{00} (a.u.)[c]	0.3482	0.3269	0.3376
H_{01} (a.u.)[c]	0.1219	0.1030	0.1137
H_{02} (a.u.)[c]	-3.7×10^{-4}	1.5×10^{-3}	1.1×10^{-3}
$(r^2Q)_{00}$ (a.u.)[d]			1.0669
$(r^2Q)_{01}$ (a.u.)[d]			0.3548

[a] Reference 18.
[b] Reference 19.
[c] The hexadecapole moment matrix elements for H_2 and D_2 are from Ref. 20; for HD they are from Ref. 21.
[d] Reference 21.

TABLE III. Comparison of experimental and theoretical ratios of integrated intensities.

Ratio	p-H_2 Expt.	p-H_2 Theor.	o-D_2 Expt.	o-D_2 Theor.	HD Expt.	HD Theor.
$\frac{\alpha[U_1(0)]}{\alpha[U_0(0)]}$	0.50	0.55	0.63	0.60	0.65	0.57
$\frac{\alpha[Q_2(0)+U_0(0)]}{\alpha[Q_1(0)+U_1(0)]}$	0.074	0.074				

The phonon renormalization factor for the lattice sums in Eqs. (13) and (14), ξ_{60}, can be significantly different from that pertaining to the single $U_v(0)$ transitions. In fact, from theoretical considerations one would expect ξ_{60} to be larger than unity. This point will be discussed further in the next section, where we compare the values calculated from the theoretical expressions [Eqs. (9), (10), (13), and (14)] with the experimental values.

III. COMPARISON OF THEORY AND EXPERIMENT

The experimental values of α for the zero-phonon $U_v(0)$ and $Q_v(0)+U_{v'}(0)$ transitions in p-H_2, o-D_2, and HD are listed in Table I. Also given are the theoretical values obtained using the lattice and molecular parameters compiled in Table II. The theoretical values were calculated assuming $\xi_{65}=\xi_{60}=1$.

As can be seen from Table I, the largest discrepancy between the theoretical and experimental values of α is for the $U_2(0)$ transition in p-H_2. We attribute the major part of this difference to the inaccuracy of the $\langle 00|H|24\rangle$ matrix element.[20] The magnitude of this matrix element is of the same order as the uncertainty of the *ab initio* hexadecapole moment, thus it is not accurately known.

Although there are appreciable differences between independent experimental determinations of α for $U_v(0)$ transitions, it is generally found that the theoretical values are higher than the corresponding experimental ones. This is consistent with the expected magnitude of the phonon renormalization effect. One can, of course, consider ratios of α's, e.g., $\alpha[U_1(0)]/\alpha[U_0(0)]$, for which the ξ_{65} factors will drop out, and compare the experimental values with the theoretical result $(\nu_{01}H_{01}^2/\nu_{00}H_{00}^2)$. For the experimental data of Lee,[9] which are the most complete, the comparisons are presented in Table III. As can be seen from the table, the agreement is good for p-H_2 and o-D_2, but slightly less good for HD; this latter discrepancy may result from the expected greater importance of mixing of states in HD, neglected in the present paper.

By contrast, the theoretical values of α are smaller than the corresponding experimental values for the $Q_v(0)+U_{v'}(0)$ transitions. Ignoring the $Q_1(0)+U_0(0)$ transition in p-H_2 which is strongly overlapped by the U_R phonon branch and is therefore subject to a large experimental error, there is a consistent ratio $\alpha_{\text{expt}}/\alpha_{\text{theor}}\approx 1.3$. Neglecting any other sources of error, this would imply $\xi_{60}^2\approx 1.3$, a value not inconsistent with theoretical estimates. Again as in the single $U_0(0)$ transition, the double-shifted quadrupolar induction term, and more importantly the constructive interference with the hexadecapolar induction, contribute more than the hexadecapolar induction term alone to the intensity of the $Q_1(0)+U_0(0)$ transition in HD. Finally, one can consider the ratio of experimental and theoretical values of α for the two accurately measured double transitions in p-H_2. The result is given in Table III, where it can be seen that there is excellent agreement.

In summary, a detailed analysis of the zero-phonon intensities of the $U_v(0)$ and $Q_v(0)+U_{v'}(0)$ transitions reveals that in p-H_2 and o-D_2, the absorption can be interpreted as arising predominantly through the hexadecapolar mechanism provided one includes the effects of phonon renormalization. Mixing of states is not expected to play an important role in these solids. On the other hand, for HD there is a significant modification to the hexadecapolar induction by the twice-shifted quadrupolar induction. In addition, the experimental ratio $\alpha[U_1(0)]/\alpha[U_0(0)]$ is not in as good agreement with the theoretical prediction as for p-H_2 or o-D_2. Because of the stronger anisotropic interactions in solid HD (due to the same coordinate transformation that is responsible for the extra terms in the dipole moment expansion coefficients), the mixing of states is expected to be larger; further theoretical work, augmented by more accurate experimental determination of α for the $U_v(0)$ transitions, is required before definitive conclusions can be drawn. Finally, from the very large discrepancy between theory and experiment for the $U_2(0)$ transition in p-H_2, it is clear that more accurate hexadecapole matrix elements are desirable for the overtone transitions.

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