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Intensities of $R_{v'}(0)$ transitions in solid HD

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Experimental values of the integrated intensity of the zero-phonon $R_2(0)$ and $R_3(0)$ transitions in solid HD are reported. Three distinct dipole components, the allowed dipole and the dipoles induced by the shifted, isotropic and anisotropic overlap mechanisms, in conjunction with their associated interferences, all play an important role in the absorption process. A two-parameter model describing the dependence of the induced dipoles on the internuclear separation is constructed. The parameters in this model are then determined by fitting to the previously observed $R_1(0)$ and the newly measured $R_2(0)$ intensities. The $R_3(0)$ transition intensity predicted by our model agrees well with the experimental value, and the present model also enables us to refine the theoretical calculation of the intensity of the $R_0(0)$ transition published previously.

I. INTRODUCTION

Because of its heteronuclear nature, the HD molecule has a dipole moment and correspondingly an allowed dipole spectrum in the gaseous, liquid, and solid phases.[1-3] It also has, through its interaction with other HD molecules, an induced dipole moment; this induced moment interferes with the allowed one and, in general, modifies both the intensity and shape of the $R_{v'}(J)$ and $P_{v'}(J)$ transitions.[4-9] The symbols $R_{v'}(J)$ and $P_{v'}(J)$ denote the transitions $v',J+1 \leftarrow v=0,J$ and $v',J-1 \leftarrow v=0,J$, where v and J are the vibrational and rotational quantum numbers, respectively.

The first high-resolution study of the spectrum of solid HD was reported by Crane and Gush.[10] They studied the fundamental region ($v'=1$) and reported a value for the integrated intensity of the $R_1(0)$ zero-phonon transition $\tilde{\alpha}[R_1(0)]=1.4\times10^{-15}$ cm^3 s^{-1}. Several years later, Trefler *et al.*[11] measured the pure-rotational spectrum ($v'=0$) and found $\tilde{\alpha}[R_0(0)]=4.3\times10^{-15}$ cm^3 s^{-1}. Because this latter value is less than that expected from the allowed dipole moment alone, it was suggested[5] that destructive interference between the allowed and induced dipole moments could reconcile this difference. However, using a recently calculated *ab initio* value of the induced dipole moment[12,13] (including its direction), Tipping and Poll[9] predicted a constructive interference and a theoretical intensity higher by more than a factor of four than that observed.[11] Recently, two independent experimental investigations corroborated this prediction.[14,15]

In this present paper, we report the first experimental determination of the integrated intensity of the zero-phonon $R_2(0)$ and $R_3(0)$ transitions in solid HD. These are discussed in Sec. II in which the details of the experiment are given. In Sec. III, we present a theoretical discussion of the intensities of the $R_{v'}(0)$ transitions. Using theoretical models for the functional form of the induced dipole moments, together with *ab initio* results and the experimental values of $\tilde{\alpha}$ for the $R_{v'}(0)$ ($v'=1,2$) transitions mentioned above, we determine the variation of the induced dipole-moment components with internuclear separation. Because this dependence was not considered in the *ab initio* calculation, no direct comparison with the empirical dipole parameters can be made at present. Finally in Sec. IV, we discuss some theoretical refinements and conclusions concerning this work.

II. EXPERIMENTAL DETAILS AND RESULTS

The gas used for growing the solid HD samples was purchased from Stohler Isotope Chemicals and had a nominal purity of 99%, with approximately 1% H_2 impurity. This gas was admitted to a temperature-controlled cell made mostly of copper and brass with a cold finger at the bottom on which the solid first condensed. The growth of the solid was monitored visually and if it was not clear, the growth procedure was repeated. No attempt was made to verify that the solid was a strain-free single crystal. After the solid was grown, the temperature of the cell was maintained approximately 17 K throughout the entire experiment.

Different window materials were necessary for the different spectral regions; in particular, for the overtone regions between 5000 cm^{-1} and 12 000 cm^{-1}, sapphire inner and quartz outer windows were used. The spectra were recorded using a commercial BOMEM (V 3.02) Fourier-transform spectrometer with a sample path length $l=1.08$ cm. For the first-overtone region ($v'=2$),

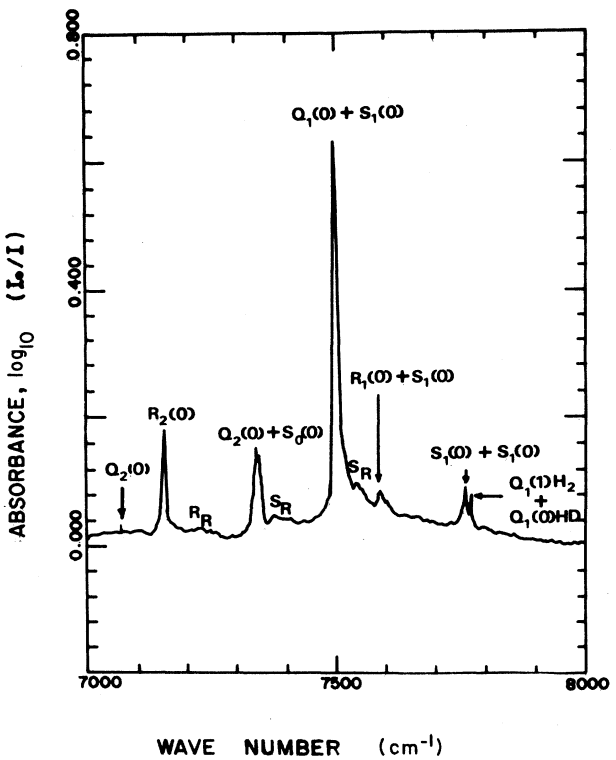

FIG. 1. The spectral region of solid HD around the $R_2(0)$ transition. The strongest single and double transitions as well as phonon bands are identified (Ref. 16).

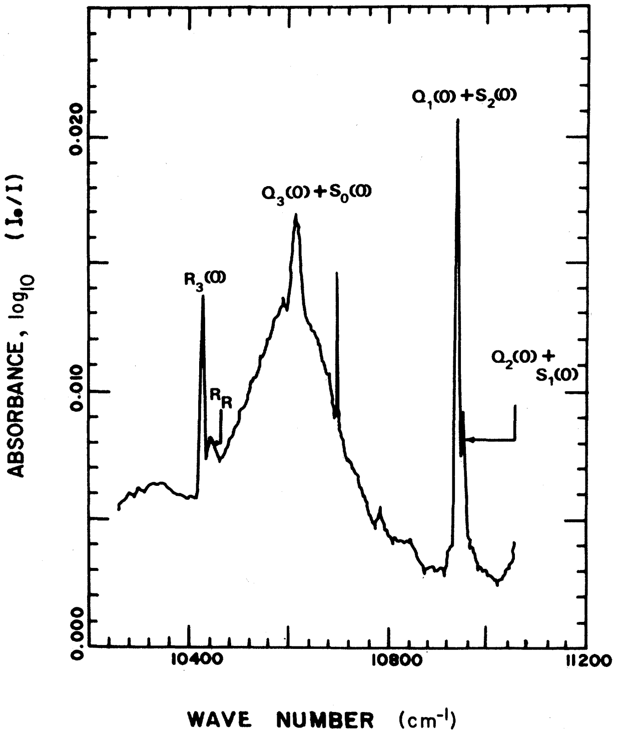

FIG. 2. The spectral region of solid HD around the $R_3(0)$ transition. The strongest single and double transitions as well as phonon bands are identified (Ref. 16).

$(v'=2)$, 100 scans were taken at a spectral resolution of 0.4 cm^{-1}, while for the second overtone $(v'=3)$, 500 scans with a resolution of 1.0 cm^{-1} were averaged to improve the signal-to-noise ratio. The spectral regions in which these transitions occur are shown in Figs. 1 and 2.

The integrated intensity of the individual transitions, $\tilde{\alpha}$ in $\mathrm{cm}^3\,\mathrm{s}^{-1}$, is defined by

$$\tilde{\alpha} \equiv \frac{c}{nl} \int \ln \left[\frac{I_0(\nu)}{I(\nu)} \right] \frac{d\nu}{\nu} , \qquad (1)$$

where c is the speed of light, n is the number density, and $I_0(\nu)$ and $I(\nu)$ are the incident and transmitted intensities at wave number ν, respectively. From the experimental spectra, we obtain for the zero-phonon $R_2(0)$ and $R_3(0)$ transitions the values of $\tilde{\alpha}^{\mathrm{expt}}$ listed in Table I. Integrated intensities obtained previously for other $R_{v'}(0)$ transitions are also listed. Some of these values are used in conjunction with the theoretical expressions discussed in Sec. III in order to obtain the variation of the induced dipole-moment components with internuclear separation.

TABLE I. Comparison between the allowed contribution and the experimental values of $\tilde{\alpha}$ ($\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$) for the $R_{v'}(0)$ zero-phonon transitions.

v'	$\tilde{\alpha}^{\mathrm{all}}$	$\tilde{\alpha}^{\mathrm{expt}}$
0	8.90×10^{-15}	$4.3\ \times10^{-15}$ [a]
		1.98×10^{-14} [b]
		1.95×10^{-14} [c]
1	4.05×10^{-17}	$1.4\ \times10^{-15}$ [d]
2	4.32×10^{-18}	1.97×10^{-16} [e]
3	1.00×10^{-18}	$5.6\ \times10^{-18}$ [e]

[a] Reference 11.
[b] Reference 14.
[c] Reference 15.
[d] Reference 10.
[e] Reference 16.

III. THEORY

As discussed elsewhere,[2] the components of the total dipole moment for a pair of molecules can be expressed in terms of the coordinate-independent coefficients $A_\Lambda(\lambda_1\lambda_2L;r_1r_2R)$ in which λ_1, λ_2, and L are the orders of the spherical harmonics describing the internal angular coordinates of molecules 1 and 2, and the angular coordinate of the vector separation between their centers of mass; r_1, r_2, and R are the corresponding radial coordinates. Because of the noncoincidence of the center of interaction and the center of mass in an HD molecule, one gets additional components for the collision-induced dipole moment of HD that have different angular symmetries from those of H_2 or D_2.[2,3,5] We refer to these components as "shifted dipoles" or "shifted components."[17]

The intensities of the zero-phonon $R_{v'}(0)$ single transitions can be expressed in terms of the spherical components of the dipole moment

$$\mu_\nu = A_1(100;r_1r_2R)\sqrt{4\pi/3}\,Y_{1\nu}(\omega_1)\ , \tag{2}$$

where $\omega_1 \equiv (\theta_1,\phi_1)$ specifies the angular orientation of the internuclear axis of molecule 1. The coefficient $A_1(100;r_1r_2R)$ has a contribution from the allowed dipole moment, $A_1(100;r_1)\equiv p^A$, and this by itself would lead to an integrated intensity denoted $\tilde{\alpha}^{\text{all}}$ given by the usual formula

$$\tilde{\alpha}^{\text{all}} = \frac{4\pi^2}{3\hbar}\sum_{i,f,\nu} P_i |\langle i|\mu_\nu^A|f\rangle|^2\ , \tag{3}$$

where the initial and final states of the transition are denoted by i and f, respectively, and P_i is a Boltzmann factor normalized according to $\sum_i P_i = 1$. Using the average of the *ab initio* allowed dipole-moment matrix elements calculated by different workers,[18–21] we obtain the values listed in Table I. As can be seen from these results, the allowed dipole contribution is largest for the pure-rotational transition where it is about 50% of the recently measured intensity; it is negligible for the fundamental and first-overtone transitions but contributes significantly to the intensity of the $R_3(0)$ transition.

As mentioned previously, there are two induced dipole contributions to the $A_1(100;r_1r_2R)$ coefficient, arising, respectively, from the shifted-isotropic- and shifted-anisotropic-overlap mechanisms.[2] The unshifted-isotropic-overlap dipole is described by the coefficient $A_0(001;r_1r_2R)$; traditionally, this has been represented by the form[2,5]

$$A_0(001;r_1r_2R) = ea_0A_0(r_1r_2)e^{-(R-\sigma)/\rho}\ , \tag{4}$$

where e is the electron charge, a_0 the Bohr radius, σ the molecular radius, and ρ is a range parameter. When this component is shifted,[22] we obtain

$$A_1^{\text{IO}}(100;r_1r_2R) = -\frac{ea_0r_1}{18}A_0(r_1r_2) \times \left[\frac{1}{\rho}-\frac{2}{R}\right]e^{-(R-\sigma)/\rho}\ . \tag{5}$$

Taking into account the symmetry relation[23]

$$A_0(001;r_1r_2R) = -A_0(001;r_2r_1R) \tag{6}$$

the dimensionless strength $A_0(r_1r_2)$ can be expanded about the expectation values of r_1 and r_2 in the ground state, r_e, in the form

$$A_0(r_1r_2) = [(r_1-r_2)/a_0] \times\{A_0' + A_0''[(r_1-r_e)/a_0 + (r_2-r_e)/a_0] + \cdots\}\ . \tag{7}$$

Because the dipoles induced in the 12 nearest neighbors of a given molecule are all independent, the effective absorbing dipole is given by

$$A_1^{\text{IO}}(100;r_1r_2a) = -\frac{2er_1}{3}(r_1-r_2)\{A_0' + A_0''[(r_1-r_e)/a_0 + (r_2-r_e)/a_0] + \cdots\}\left[\frac{1}{\rho}-\frac{2}{a}\right]e^{-(a-\sigma)/\rho}\ , \tag{8}$$

where a is the nearest-neighbor distance.

Similarly, the unshifted anisotropic overlap can be modeled by

$$A_2(201;r_1r_2R) = ea_0A_2(r_1r_2)e^{-(R-\sigma)/\rho}\ . \tag{9}$$

When shifted, this component becomes[22]

$$A_1^{\text{AO}}(100;r_1r_2R) = \frac{\sqrt{2}}{18}ea_0r_1A_2(r_1r_2)\left[\frac{1}{\rho}-\frac{2}{R}\right]e^{-(R-\sigma)/\rho}\ . \tag{10}$$

Expanding the dimensionless strength $A_2(r_1r_2)$

$$A_2(r_1r_2) = A_2(r_er_e) + A_2'[(r_1-r_e)/a_0 + (r_2-r_e)/a_0] + \cdots \tag{11}$$

and summing over the nearest neighbors, we obtain for this contribution the result

$$A_1^{\text{AO}}(100;r_1r_2a) = \frac{2\sqrt{2}ea_0r_1}{3}\{A_2(r_er_e) + A_2'[(r_1-r_e)/a_0 + (r_2-r_e)/a_0] + \cdots\}\left[\frac{1}{\rho}-\frac{2}{a}\right]e^{-(a-\sigma)/\rho}\ . \tag{12}$$

Combining all three contributions, the coefficient $A_1(100;r_1r_2a)$ can thus be written

$$\begin{aligned} A_1(100;r_1r_2a) &= A_1(100;r_1) + A_1^{\text{IO}}(100;r_1r_2a) + A_1^{\text{AO}}(100;r_1r_2a) \\ &= p^A + \frac{2er_1}{3}\{\sqrt{2}a_0A_2(r_er_e) - (r_1-r_2)A_0' + [\sqrt{2}A_2' - (r_1-r_2)A_0''/a_0] \\ &\quad \times[(r_1-r_e)+(r_2-r_e)] + \cdots\}\left[\frac{1}{\rho}-\frac{2}{a}\right]e^{-(a-\sigma)/\rho}\ . \end{aligned} \tag{13}$$

For the $R_{v'}(0)$ transitions, we need to consider vibration- rotational matrix elements of $A_1(100;r_1r_2a)$. Assuming simple product states $|v_1J_1;v_2J_2\rangle$, i.e., neglecting any mixing of internal states due to anisotropic interactions,[24,25] we find

$$\langle 00;00|A_1(100;r_1r_2a)|v'1;00\rangle = \langle 00|p^A|v'1\rangle + \frac{2ea_0^2}{3}\left[\frac{1}{\rho}-\frac{2}{a}\right]e^{-(a-\sigma)/\rho} \times\{[\sqrt{2}A_2(r_er_e)+A'x_e+A_0''(\overline{x^2}-2x_e^2)]\langle 00|x|v'1\rangle + [-A'+2A_0''x_e]\langle 00|x^2|v'1\rangle - A_0''\langle 00|x^3|v'1\rangle\}\ , \tag{14}$$

where we have introduced the definitions $x\equiv r/a_0$, $x_e\equiv r_e/a_0$, $\overline{x^2}\equiv\langle 00|x^2|00\rangle$, and $A'\equiv A_0'-2^{1/2}A_2'$. Using the following values[9,24] of the parameters in Eq. (14), $\rho/a_0=0.618$, $a/a_0=6.8824$, $\sigma/a_0=5.58$, $\overline{x^2}=2.1043$, and $x_e=1.4422$, we obtain for the theoretical expression of the vibration-rotational matrix elements of $A_1(100;r_1r_2a)$ in atomic units (a.u.):

$$\langle 00;00|A_1(100;r_1r_2a)|v'1;00\rangle = \langle 00|p^a|v'1\rangle + 0.108\,46\{[1.4142A_2(r_er_e)+1.4422A'-2.0556A_0'']\langle 00|x|v'1\rangle + [-A'+2.8844A_0'']\langle 00|x^2|v'1\rangle - A_0''\langle 00|x^3|v'1\rangle\}\ . \tag{15}$$

From the observed integrated intensities of the $R_{v'}(0)$ transitions, we obtain for the absolute values of the experimental vibration-rotational matrix elements of $A_1(100;r_1r_2a)$ in a.u. the results listed in Table II. Also listed are the average *ab initio* values of the allowed dipole-moment matrix elements[18–21] and the first three powers of x.[26]

As discussed elsewhere,[9] and as is easily verified from Eq. (15) and the values in Table II, the magnitudes of the coefficients of the contributions proportional to A' and A_0'' in the pure-rotational matrix element

$$\langle 00;00|A_1(100;r_1r_2a)|01;00\rangle$$

are very small. Therefore, unless, of course, one (or both) of these derivatives is abnormally large, the major contribution from the induced dipole moment to the $R_0(0)$ transition is described by the coefficient $A_2(r_er_e)$. From *ab initio* calculations of the anisotropic-overlap component of the induced dipole for an H_2-H_2 pair,[12,13] one can obtain the theoretical value $A_2(r_er_e)=-7.79\times10^{-4}$ by fitting Eq. (9) at separations R near the equilibrium lattice spacing of the solid; extrapolations to smaller separations (e.g., those important in the gas phase) will, of course, be somewhat uncertain. The minus sign implies the same polarity as the allowed dipole moment (H^+D^-) and consequently constructive interference.[9] Thus, ignoring the contributions from A' and A_0'', we find for the theoretical value of the pure-rotational matrix element -5.03×10^{-4} which is in good agreement with the experimental value $|4.94\times10^{-4}|$.

Therefore, assuming the theoretical value of $A_2(r_er_e)$, we can use Eq. (15) and the data in Table II for the fundamental and first overtone to infer values of A' and A_0''. These, in turn, should provide a reasonable theoretical prediction for the second-overtone result, although higher terms in the expansions, Eqs. (7) and (11), may contribute as well in this case.

For the four possible combinations of signs for the fundamental and first-overtone experimental matrix elements, we obtain the results listed in Table III. Also listed are the predicted values of the second-overtone matrix element,

$$\langle 00;00|A_1(100;r_1r_2a)|31;00\rangle\ ,$$

for the various choices of signs, and the pure-rotational matrix element refined by including the small contributions due to A' and A_0''.

TABLE II. Vibration-rotational matrix elements $\langle 00;00|O|v'1;00\rangle$ of various operators.

Operator \ v'	0	1	2	3
x	1.443	0.147	-1.87×10^{-2}	4.15×10^{-3}
x^2	2.107	0.444	-2.39×10^{-2}	2.64×10^{-3}
x^3	3.111	0.998	2.02×10^{-2}	-8.08×10^{-3}
p^A (10^5 a.u.)	-33.23	2.24	-0.733	0.353
$\|A_1(100;r_1r_2a)\|$ (10^5 a.u.)	49.4	13	5.0	0.83

TABLE III. Theoretical values of the induced dipole-moment expansion parameters, A' and A''_0, for the four possible choices of the signs of the fundamental- and first-overtone matrix elements, and the corresponding predicted values of the pure-rotational and second-overtone matrix elements.

Parameter	+,+	+,−	−,+	−,−
$10^3 A'$	−4.18	−5.73	6.29	4.74
$10^3 A''_0$	−9.85	8.58	−10.5	7.94
$\langle 00;00 \vert A_1 \vert 31;00\rangle$ (10^5 a.u.)	−0.61	0.76	−0.28	1.08
$\langle 00;00 \vert A_1 \vert 01;00\rangle$ (10^4 a.u.)	−4.92	−4.87	−5.23	−5.16

IV. DISCUSSION AND CONCLUSIONS

From the results listed in Table III, one can see that the best agreement with the experimental value of $\pm 0.83\times10^{-5}$ for the second-overtone matrix element occurs for the sign combination +, −; this implies that the signs of the $v'=1$, 2, and 3 matrix elements are +, −, and +, respectively. The other choices, however, cannot be completely ruled out, because the agreement, while not as good, is still reasonable taking into consideration both the approximations made in deriving Eq. (15) (i.e., truncation of the parametrized r dependence of the components of the induced dipole) and the choice of values for $A_2(r_e r_e)$ and the other molecular parameters. In addition, it should be pointed out that for the $R_1(0)$ transition, there is considerable mixing of translational and rotational states[27] which could modify the empirical value of the corresponding matrix element. This, in turn, would change the numerical values of the dipole-moment expansion parameters, $A'=-5.73\times10^{-3}$ and $A''_0=8.58\times10^{-3}$, obtained in the present analysis. Contributions from A' and A''_0 can also be included in the pure-rotational matrix element; the resulting values are listed in Table III. As suggested above, this refinement leads only to minor changes and the excellent agreement with experiment remains essentially the same.

From an analysis of the line shapes and intensities of the collision-induced fundamental band of gaseous hydrogens, Hunt and Poll[28] deduced a value of $|A'_0|=7\times10^{-3}$. Assuming this value and our result, $A'\equiv A'_0-\sqrt{2}A'_2=-5.73\times10^{-3}$, we obtain the value $A'_2=-1.1\times10^{-3}$. Although this latter value is very uncertain, its magnitude, roughly $\frac{1}{6}$ that of the corresponding isotropic-overlap quantity A'_0, is consistent with previous analyses of gas spectra.[28]

Before concluding, we note that one additional theoretical approximation has been tacitly made. In summing the induced dipole contributions from nearest neighbors in the lattice, we have assumed a rigid lattice. We have thus ignored the so-called "phonon renormalization" correction[3,24] which can have an effect on the lattice sums and consequently on the derived values of the parameters which describe the r dependence of the two overlap-induced dipole-moment components. However, in view of the very good agreement for the pure rotational $R_0(0)$ transition for which accurate *ab initio* information exists, one would not expect this modification to introduce appreciable error.

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