Intensities of multipole-induced zero-phonon transitions in solid parahydrogen

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(Received 7 July 1988)

Theoretical expressions are given for the intensities of zero-phonon single and double transitions in solid parahydrogen arising from the isotropic 2^l multipole induction mechanism. Comparisons between theory and experiment for $l=2$ and 4 [corresponding to $S_{v'}(0)$ and $S_{v'}(0)+Q_{v''}(0)$ and $U_{v'}(0)$ and $U_{v'}(0)+Q_{v''}(0)$ transitions, respectively] have been given previously, and the results are in reasonably good agreement. A direct comparison is not possible for the recently observed $l=6$ [$W_{v'}(0)$ and $W_{v'}(0)+Q_{v''}(0)$] transitions because of the unavailability of *ab initio* values of the vibration-rotational matrix elements of the 64-pole moment function, or for the as yet unobserved $l=8[Y_{v'}(0)$ and $Y_{v'}(0)+Q_{v''}(0)]$ transitions. Modifications of the intensities of the $W_{v'}(0)$ transitions due to the mixing of rotational levels by the quadrupole-quadrupole interaction have been calculated, and they contribute less than 1%. These corrections are smaller than those due to phonon renormalization and thus will not appreciably affect the magnitudes of the 64-pole moment matrix elements deduced from the experimental intensities.

I. INTRODUCTION

The spectrum of pure solid parahydrogen (p-H$_2$) is particularly simple for a number of reasons. Only transitions originating from the ground rotational level ($J=0$, where J is the rotational quantum number of an isolated molecule) are observed, and the absorption is, for the most part, dominated by the long-range multipolar induction mechanism.[1,2] Because of the inversion symmetry of H$_2$ and its large rotational constant, only even multipole moments exist and the corresponding absorption features are widely separated in frequency. Also, as is well known, the rotational motion of the molecules in the solid lattice is almost free, thus enabling one to identify the spectral features directly from their positions as calculated from parameters obtained from gaseous spectra.

From the theoretical standpoint, solid hydrogen is important not only because it is the simplest molecular solid, but also because one is able to compare accurate *ab initio* quantities (e.g., induced-dipole-moment functions[3,4] and multipole-moment matrix elements[5−7]) directly with the corresponding experimental values.

In the present paper, we consider the integrated intensities of the zero-phonon single and double transitions in solid p-H$_2$ arising from the isotropic induction due to the 2^l multipole moments of the individual hydrogen molecules. Previously, explicit expressions have been given for quadrupole ($l=2$) induction[8] leading to $S_{v'}(0)$ ($v=J=0\rightarrow v',J+2$, where v is the vibrational quantum number) and $S_{v'}(0)+Q_{v''}(0)$ ($v=J=0\rightarrow v',J+2$ for molecule one and $v=J=0\rightarrow v'',0$ for molecule two) transitions, and for hexadecapolar ($l=4$) induction[9] lead-

ing to $U_{v'}(0)$ ($v=J=0\rightarrow v',J+4$) and $U_{v'}(0)+Q_{v''}(0)$ ($v=J=0\rightarrow v',J+4$ for molecule one and $v=J=0\rightarrow v'',0$ for molecule two) transitions. Comparisons between experiment and theory for these transitions for which all the theoretical parameters (except for values of phonon renormalization factors which are discussed in more detail below) are available from other sources have been presented elsewhere[10,11] and will not be repeated here. Suffice it to say that the overall agreement leads one to the conclusion that these features can be successfully interpreted in terms of isotropic multipolar induction.

Recently, $W_{v'}(0)$ transitions for $v'=0$ and 1 have been reported.[12] Unfortunately, no *ab initio* values of vibration-rotational matrix elements of the 64-pole moment function have as yet been calculated. One can, of course, use the theoretical expression and the experimental intensities to deduce experimental values for these quantities providing that other effects (e.g., mixing of levels and phonon renormalization) are not important. To investigate this assumption, we have calculated the effect on the intensities of the $W_{v'}(0)$ transitions due to the mixing of rotational levels by the quadrupole-quadrupole interaction and find that in the present case such mixing does not lead to appreciable changes. This is in contrast to other cases in which mixing does play a significant role.[13]

The next higher ($l=8$) multipolar transitions have not yet been observed; their intensities are expected to be smaller than the $l=6$ transitions by approximately 3–4 orders of magnitude. However, because of their narrow width[12] and known positions, it may be possible in the future to observe these features if one can grow sufficiently large crystals of solid hydrogen.

II. THEORY

The general theory for the integrated intensity of the induced lines in solid hydrogens was first given by Poll and Van Kranendonk.[8] They considered the spherical components of the induced dipole moment of a pair of molecules and expressed the intensity in terms of matrix elements of this dipole. The dipole components were expanded in terms of appropriately coupled products of three spherical harmonics, Y_{lm}, describing the orientations of the individual internuclear axes, $\mathbf{r}_1 \equiv (r_1, \omega_1)$ and $\mathbf{r}_2 \equiv (r_2, \omega_2)$, and the orientation of the vector separation between their centers of mass, $\mathbf{R} \equiv (R, \Omega)$,

$$\mu_\nu(\mathbf{r}_1\mathbf{r}_2\mathbf{R}) = [(4\pi)^3/3]^{1/2} \sum_{\lambda_1\lambda_2\Lambda L} A_\Lambda(\lambda_1\lambda_2 L; r_1 r_2 R)$$

$$\times \sum_{\mu_1\mu_2 M} C(\Lambda L 1; \mu_1 + \mu_2, M, \nu) C(\lambda_1\lambda_2\Lambda; \mu_1, \mu_2, \mu_1 + \mu_2) Y_{\lambda_1\mu_1}(\omega_1) Y_{\lambda_2\mu_2}(\omega_2) Y_{LM}(\Omega) . \quad (1)$$

In this expression, the C's are Clebsch-Gordan coefficients, and the dipole coefficients $A_\Lambda(\lambda_1\lambda_2 L; r_1 r_2 R)$ provide a unique coordinate-independent representation of the strength of the various induction mechanisms specified by the indices λ_1, λ_2, Λ, and L. The isotropic multipolar induction of order l is described by the two coefficients[14]

$$A_l(l0l + 1; r_1 r_2 R) = (-1)^l \sqrt{l+1} Q^{(l)}(r_1) \alpha(r_2) R^{-(l+2)}$$
$$(2)$$

and

$$A_l(0ll + 1; r_1 r_2 R) = -\sqrt{l+1} \alpha(r_1) Q^{(l)}(r_2) R^{-(l+2)} .$$
$$(3)$$

In these expressions, $Q^{(l)}(r)$ and $\alpha(r)$ are the multipole moment and polarizability functions, respectively. The coefficients in Eq. (2) lead to single transitions while those in Eq. (3) lead to double transitions.

The integrated intensity $\tilde{\alpha}$ (in units of cm^3/s) is defined according to

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

where N is the number of molecules in volume V, c is the speed of light, L is the absorption pathlength, and $I_0(\nu)$ and $I(\nu)$ are the initial and final fluxes at wave number ν. For sharp transitions centered at wave number ν_0, this quantity is related to the usual experimentally determined intensity α (in cm^{-2}) by

$$\alpha \equiv \frac{1}{L} \int \ln[I_0(\nu)/I(\nu)] d\nu = \frac{N\nu_0\tilde{\alpha}}{cV} . \quad (5)$$

Following the theory outlined in Ref. 8, we obtain the following expressions for the zero-phonon single and double transitions, respectively,

$$\tilde{\alpha}_0[X_\nu^{(l)}(0)] = \frac{4\pi^2(l+1)Q_{0\nu'}^{(l)2}\alpha_{00}^2}{3\hbar a^{2(l+2)}} \xi_{l+2,l+1}^2$$

$$\times \sum_{i,j} \left[\frac{a^2}{a_i a_j}\right]^{l+2} P_{l+1}(\cos\theta_{ij}) \quad (6)$$

and

$$\tilde{\alpha}_0[X_\nu^{(l)}(0) + Q_{\nu''}(0)] = \frac{4\pi^2(l+1)\alpha_{0\nu''}^2 Q_{0\nu'}^{(l)2}}{3\hbar a^{2(l+2)}}$$

$$\times \xi_{l+2,0}^2 \sum_i \left[\frac{a}{a_i}\right]^{2(l+2)} . \quad (7)$$

The symbol $X^{(l)}$ is a generic spectroscopic designation (i.e., $X^{(2)} = S$, $X^{(4)} = U$, etc.), and the double subscripts on α and $Q^{(l)}$ denote the corresponding vibration-rotational matrix elements. In the lattice sums, a is the nearest-neighbor distance of the rigid (hcp) lattice ($a = 7.1602$ a.u.), and the argument of the Legendre polynomial involves the angle subtended at the position of molecule 1 between the directions to molecule i and j. These lattice sums are multiplied by an appropriate phonon renormalization factor ξ to account for the zero-point motion in the lattice.[1,15–17] Note that the lattice sum for the double transitions contains only a single sum over neighbors and thus there is no reduction of intensity due to the "cancellation effect"[1] as there is in the case of single transitions. Theoretical expressions equivalent to those in Eqs. (6) and (7) have been derived independently by Balasubramanian et al. for the $l = 6$ case.[18]

It is clear from Eqs. (5)–(7) that one can calculate a theoretical value of α for the various transitions provided one knows the values of the vibration-rotational matrix elements and the phonon renormalization factors. However, in deriving these results, we have tacitly assumed that J is a good quantum number (i.e., that there is no mixing of rotational levels in the solid due to anisotropic interactions[13]). To investigate the validity of this approximation, we have calculated the effects of mixing on the intensity of the $W_{\nu'}(0)$ transitions due to the quadrupole-quadrupole interaction ϕ_{EQQ}.[17] In this case, the perturbed levels in first-order perturbation theory are connected to the unperturbed levels by the anisotropic hexadecapolar contribution to the induced dipole described by the coefficients $A_\Lambda(425; r_1 r_2 R)$, $\Lambda = 4, 5$, and 6, in Eq. (1), thus modifying the theoretically predicted intensity. The magnitude of this change is, however, less than 1%; similar changes would obtain for the other transitions considered in the present paper. Because these changes are smaller than those expected from the phonon renormalization factors and from uncertainties in the vibration-rotational matrix elements and lattice constant, they will not affect the validity of Eqs. (6) and (7) significantly.

TABLE I. Numerical values of vibration-rotational matrix elements (a.u.) and lattice sums.

Parameters	l			
	2	4	6	8
$\langle 00 \lvert Q^{(l)} \rvert 0l \rangle^{\mathrm{a}}$	0.4852	0.3482		
$\langle 00 \lvert Q^{(l)} \rvert 1l \rangle^{\mathrm{a}}$	0.0784	0.1219		
$\langle 00 \lvert \alpha \lvert \frac{l-2}{2}, 0 \rangle^{\mathrm{b}}$	5.4138	0.7392	-0.0713	0.0099
$\sum_{i,j} \left[\dfrac{a^2}{a_i a_j} \right]^{(l+2)} P_{l+1}(\cos\theta_{ij})$	0.306	7.141	14.351	2.935
$\sum_i \left[\dfrac{a}{a_i} \right]^{2(l+2)}$	12.803	12.132	12.027	12.006

[a]References 6 and 7.
[b]Reference 7.

III. DISCUSSION AND CONCLUSIONS

The analysis of experimental intensity data based on Eqs. (6) and (7) for quadrupole and hexadecapolar induction has been presented elsewhere[10,11] and is not considered here. We do remark, however, that the phonon renormalization for the single $S_{v'}(0)$ transitions can dramatically alter the corresponding lattice sum,

$$\sum_{i,j} \left[\frac{a^2}{a_i a_j} \right]^4 P_3(\cos\theta_{ij}) = 0.306$$

listed in Table I together with other lattice sums and vibration-rotational matrix elements. This is because renormalization affects primarily only the contributions from nearest neighbors. These have a magnitude of 0.833 for the rigid lattice, while the remaining contributions from the more distant neighbors are negative (-0.527). Therefore, because of the large cancellation, the lattice sum is sensitively dependent on renormalization. In fact, an accurate experimental determination of the intensity of the zero phonon $S_{v'}(0)$ transitions would provide tight bounds on the magnitude of this effect.

As mentioned previously, intensities for $W_{v'}(0)$ transitions have been reported.[12] Using these values, $\tilde{\alpha}_0(W_0(0)] = 3.3 \times 10^{-19}$ cm^3/s and $\tilde{\alpha}_0[W_1(0)] = 1.1 \times 10^{-19}$ cm^3/s, together with the data in Table I, and assuming $\xi_{8,7} = 1$, we obtain for the values of the 64-pole matrix elements $\lvert \langle 0 \lvert Q^{(6)} \rvert 06 \rangle \rvert = 0.26$ a.u. and $\lvert \langle 00 \lvert Q^{(6)} \rvert 16 \rangle \rvert = 0.15$ a.u., respectively. Because the cancellation in the lattice sum in this case is not nearly as complete as that in the case of quadrupolar induction, these values would not be markedly changed by phonon renormalization. Furthermore, the ratio $\tilde{\alpha}_0[W_0(0)]/\tilde{\alpha}_0[W_1(0)]$ would not depend at all on renormalization and can be compared directly with future *ab initio* calculations.

Finally, we consider the ratios of the intensities of $l = 8$ to $l = 6$ single and double transitions. Using Eq. (6) and the data in Table I, we find, neglecting phonon renormalization

$$\frac{\tilde{\alpha}_0[Y_{v'}(0)]}{\tilde{\alpha}_0[W_{v'}(0)]} = 1.0 \times 10^{-4} \left[\frac{Q_{0v'}^{(8)}}{Q_{0v'}^{(6)}} \right]^2$$

and

$$\frac{\tilde{\alpha}_0[Y_{v'}(0) + Q_{v''}(0)]}{\tilde{\alpha}_0[W_{v'}(0) + Q_{v''}(0)]} = 4.9 \times 10^{-4} \left[\frac{Q_{0v'}^{(8)}}{Q_{0v'}^{(6)}} \right]^2 .$$

Using the experimental values of $Q_{00}^{(6)}$ and $Q_{01}^{(6)}$, we find

$$\tilde{\alpha}_0[Y_0(0)]/\tilde{\alpha}_0[W_0(0)] = 1.5 \times 10^{-3}(Q_{00}^{(8)})^2,$$

$$\tilde{\alpha}_0[Y_1(0)]/\tilde{\alpha}_0[W_1(0)] = 4.4 \times 10^{-3}(Q_{01}^{(8)})^2,$$

$$\tilde{\alpha}_0[Y_0(0) + Q_{v''}(0)]/\tilde{\alpha}_0[W_0(0) + Q_{v''}(0)]$$

$$= 7.2 \times 10^{-3}(Q_{00}^{(8)})^2,$$

and

$$\tilde{\alpha}_0[Y_1(0) + Q_{v''}(0)]/\tilde{\alpha}_0[W_1(0) + Q_{v''}(0)]$$

$$= 2.2 \times 10^{-2}(Q_{01}^{(8)})^2,$$

respectively. Whether or not it is feasible to detect these transitions depends somewhat on the magnitudes of the vibration-rotational matrix elements of the 128-pole moment function as well as on the ability to grow crystals of sufficient dimensions so as to make long-path multipass experiments possible.

ACKNOWLEDGMENTS

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