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Interference effects in the $R_0(0)$ transition of solid HD

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A detailed theoretical analysis of the pure rotational $R_0(0)$ transition in solid HD is given. Although the shape of the zero-phonon line is experimentally observed to be (approximately) symmetric, the integrated absorption coefficient contains contributions not only from the allowed and induced dipole moments, but also from an important interference between these components. Using accurate *ab initio* values of the dipole moments, the interference is found to be constructive, leading to a theoretical absorption coefficient significantly larger than the reported experimental value. A similar constructive interference has been observed for the $R_0(0)$ transition in the liquid phase and in the gas at 77 K. We conclude that the discrepancy between theory and experiment for the intensity of the $R_0(0)$ line in solid HD cannot, within the context of our present understanding, be reconciled by destructive interference and suggest that in view of the importance of a quantitative understanding of this spectrum, a remeasurement of the intensity of the $R_0(0)$ zero-phonon line and its associated phonon structure be carried out.

I. INTRODUCTION

Because of the absence of a center of inversion symmetry in the molecule, the spectrum of gaseous HD is more complicated than that of H_2 or D_2.[1-5] Additional absorptions in HD arise from allowed dipole transitions and from interferences[6-9] between the allowed (nonadiabatic) dipole moment and the transient dipole moment induced in a pair of colliding molecules (collision-induced dipole moment), and between dipole moments induced in successive collisions. These latter effects are manifested as dramatic changes in both the intensities and the shapes of the fundamental $R_1(J)$ transitions as the density varies.[2,10] Much less drastic changes in the pure rotational lines of gaseous HD have also been reported.[11-14] The notation $R_{v'}(J)$ designates the transition $v=0,J \rightarrow v',J'=J+1$, where v,J and v',J' are the vibrational and rotational quantum numbers of the initial and final states, respectively. Pure rotational transitions ($v'=0$) are indicated by the subscript 0 and pure vibrational transitions ($0,J \rightarrow v',J$) are designated by the symbol $Q_{v'}(J)$.

In contrast, because of the absence of the ortho-para distinction, the spectrum of solid HD is simpler than that of normal H_2 or D_2 since virtually all of the HD molecules are in the $J=0$ level. (Of course, it is possible to prepare solid samples of nearly pure para-hydrogen or ortho-deuterium in which most of the molecules are in the $J=0$ level; in these solids, transitions originating from excited rotational levels as well as complications arising from crystal-field splittings due to quadrupole-quadrupole interaction are both greatly reduced.[15-17]) There are also theoretical considerations that make the analyses of the spectra of solids simpler than those of the corresponding liquids or gases. For instance, all of the spectral features are narrower and the zero-phonon lines are well separated from their associated phonon structures; the necessary averaging over perturbers reduces to lattice sums that can be calculated easily if one neglects the small effects due to anharmonicity and renormalization;[18-20] some components of the induced dipole moment vanish because of lattice symmetry, etc.

In the present work, we consider the zero-phonon $R_0(0)$ transition in solid HD.[21] Even though the pure rotational spectrum is relatively simple and the $R_0(0)$ feature is well separated from other features, the integrated absorption exhibits a large interference between the allowed dipole moment and the shifted anisotropic overlap component of the induced moment.[22] Both of these dipole moments have been calculated by *ab initio* methods,[23-27] so that there are no unknown parameters in our calculation of the integrated absorption. The interference in the pure rotational $R_0(0)$ transition in solid HD is constructive, in contradistinction to several lines in the fundamental vibration-rotational band of gaseous HD, where interference has been found experimentally to be destructive.[2] There is similar experimental evidence for constructive interference in the $R_0(0)$ transition in the liquid[28] and in the gas[13] at 77 K. Moreover, the shape of the $R_0(0)$ transition in all three phases is (approximately) symmetric and does not exhibit the Fano shape that characterizes the lines in the fundamental.

Further discussion of the specific results for $R_0(0)$ in solid HD, and implications for similar calculations of the integrated absorption of other $R_0(J)$ lines are presented in Sec. III, after the details of the present theoretical calculation are described in Sec. II.

II. THEORY

In order to investigate the zero-phonon $R_0(0)$ transition in solid HD, we first consider the various components of the dipole moment that could conceivably contribute to this line. Our main purpose is the evaluation of the integrated absorption coefficient, not the line shape; a theoretical discussion of the line shape as well as the observed interference[29] in the phonon branch associated with the $Q_1(0)$ transition has been published previously.[30]

As discussed elsewhere,[22] 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 coordinates of the vector separation between their centers of mass; r_1, r_2, and R are the corresponding radial coordinates. As is well known,[6,7,22] because of the separation between the center of interaction and the center of mass in an HD molecule, one gets additional components for the collision-induced dipole moment that have different angular symmetries from those for H_2 or D_2. We refer to these components as "shifted dipoles."

The spherical components of the allowed dipole moment of a molecule can also be represented in terms of an A coefficient, viz.,

$$\mu_\nu^A = A_1(100;r_1)\sqrt{4\pi/3}\,Y_{1\nu}(\omega_1)\ . \tag{1}$$

The integrated intensity S associated with an allowed dipolar transition from an initial state i to a final state f is

$$\begin{aligned} S &\equiv \int \frac{\alpha(\omega)}{\omega}\,d\omega \\ &= n\frac{4\pi^2}{3\hbar c}\sum_{i,f,\nu} P_i\,|\langle i\,|\,\mu_\nu^A\,|\,f\rangle|^2\ , \end{aligned} \tag{2}$$

where $\alpha(\omega)$ is the absorption coefficient at wave number ω, n is the number of absorbing molecules per unit volume, and P_i is a Boltzmann factor normalized according to $\sum_i P_i = 1$. Using n $(=2.928\times 10^{22}\ \text{cm}^{-3})$ as calculated from the molar volume,[31] and the average of the four *ab initio* calculations[23-26] for the $R_0(0)$ matrix element $(\langle 00\,|\,A_1(100;r_1)\,|\,01\rangle = -8.446\times 10^{-4}$ D, the negative sign indicating the polarity H^+D^-), we find $S = 8.69\times 10^{-3}\ \text{cm}^{-1}$. Noting that for narrow lines, one can approximate the integrated absorption coefficient α by

$$\alpha = \int \alpha(\omega)\,d\omega \cong S\omega_0\ , \tag{3}$$

where ω_0 $(=88.6\ \text{cm}^{-1})$ is the wave number of the $R_0(0)$ transition, we find $\alpha = 0.77\ \text{cm}^{-2}$ which is more than a factor of 2 larger than the observed value[21] $\alpha = 0.37\ \text{cm}^{-2}$.

Because the observed $R_0(0)$ transition is accompanied by a phonon branch, we know that there is also a collision-induced contribution to the zero-phonon line. To determine this contribution and to ascertain whether a destructive interference between the allowed and induced moments can reconcile the factor of 2 difference obtained above, we now consider the induced dipole components that could possibly contribute to the $R_0(0)$ transition. There are four such candidates: (1) dipole-induced dipole; (2) shifted quadrupole-induced dipole; (3) shifted isotropic overlap dipole; (4) shifted anisotropic overlap dipole.

The dipole-induced dipole moment is characterized by the coefficients $A_1(102;r_1r_2R)$ and $A_1(012;r_1r_2R)$. Both of these are nonzero but small due to the nonadiabatic nature of the permanent dipole moment. In addition, in summing the contributions from the neighboring molecules, the corresponding lattice sum vanishes and therefore there is no contribution from this component.

The quadrupole-induced dipole resulting from the isotropic polarizability is represented by $A_2(203;r_1r_2R)$ and $A_2(023;r_1r_2R)$. The shifted dipole from the long-range (multipolar) part of either of these coefficients does indeed have a contribution that leads to $\Delta J = 1$ transitions; however, the vibration-rotational matrix element appropriate to the $R_0(0)$ transition vanishes. We note though, that for other $R_0(J)$ transitions $(J\neq 0)$, this induced dipole can contribute to the corresponding intensity. The shifted short-range (nonmultipolar) part, although small,[27] would have an additional contribution of the same symmetry as the dipole-induced dipole but this too would vanish because of the lattice sum.

In our previous analysis of spectral lines in the fundamental band of gaseous HD,[7] we have shown that the shifted isotopic overlap component $A_0(001;r_1r_2R)$ was the dominant induced dipole leading to interference in that case. For pure rotational transitions, however, this component is zero or at least very small because of symmetry considerations[32] and we do not consider it further.

The anisotropic overlap contributions to the induced dipole are characterized by $A_2(201;r_1r_2R)$ and $A_2(021;r_1r_2R)$. As described elsewhere,[7] the shifted component of $A_2(201;r_1r_2R)$ that will interfere with the allowed dipole given in Eq. (1) is

$$A_1(100;r_1r_2R) = A_2(r_1r_2)\frac{\sqrt{2}}{18}r_1\left[\frac{1}{\rho}-\frac{2}{R}\right]e^{-(R-\sigma)/\rho}\ , \tag{4}$$

where we have assumed an exponential model for the dependence of the anisotropic overlap on the separation R

$$A_2(201;r_1r_2R) = A_2(r_1r_2)e^{-(R-\sigma)/\rho}\ . \tag{5}$$

In these formulas, σ is the molecular diameter and ρ is the range of the dipole moment. Meyer,[27] using accurate *ab initio* wave functions, has calculated this component of the dipole moment for an H_2-H_2 pair as a function of R with r_1 and r_2 fixed at their average values $(\bar{r}_1 = \bar{r}_2 = 1.449a_0)$. This result should also be valid for HD if one uses the appropriate values of $\sigma = 5.63a_0$ (Ref. 31) and $\rho = 0.618a_0$ (Ref. 7). By fitting Eq. (5) to the *ab initio* results, we obtain (in Debye)

$$A_2(201;\bar{r}_1\bar{r}_2R) = -1.8\times 10^{-3}e^{-(R-\sigma)/\rho}\ . \tag{6}$$

The negative sign indicates that the polarity of this dipole is the same as that of the allowed dipole, while the magnitude is considerably smaller than that previously assumed in the calculations for pure rotational transitions in gaseous HD.[7]

The shifted component, Eq. (4), is accordingly,

$$A_1(100;\bar{r}_1\bar{r}_2R) = -2.5\times 10^{-4}e^{-(R-\sigma)/\rho}\ . \tag{7}$$

Summing over the neighboring molecules in the hcp lattice (only the 12 nearest neighbors contribute significantly in view of the exponential decrease with R), we finally obtain for the induced dipole moment in Debye

$$\mu_\nu^I = -3.8\times 10^{-4}\sqrt{4\pi/3}\,Y_{1\nu}(\omega_1)\ . \tag{8}$$

The magnitude of this dipole is almost one-half that of the allowed (-8.446×10^{-4} D) and has the same symmetry and sign. Thus, in calculating the integrated intensity (proportional to the square of the total dipole moment), one obtains significant contributions from both the square of μ^I and the interference term $\mu^I\mu^A$. Accordingly, we find for the integrated absorption coefficient for the $R_0(0)$ transition the value $\alpha = 1.6$ cm^{-2} which is considerably higher than the experimental value[21] $\alpha = 0.37$ cm^{-2}.

III. DISCUSSION AND CONCLUSIONS

Because the magnitude of the integrated absorption coefficient α for the $R_0(0)$ transition in solid HD calculated with the allowed dipole alone is larger than the experimental value, and because there is experimental evidence of the existence of a significant induced dipole contribution (phonon structure), we sought to reconcile these data through a destructive interference. However, as discussed in the preceding section, although the magnitude of the shifted anisotropic overlap component of the induced-dipole moment for HD is indeed calculated to be almost half as large as that of the allowed dipole, it has the same polarity. As a result, the interference is constructive, and both the square of the induced dipole and the cross product increase the calculated integrated absorption coefficient. Other possible induced-dipole components are either small or do not contribute to the $R_0(0)$ transition. Therefore, we conclude that the discrepancy cannot be resolved within the limitations of the present theory.

In the Introduction, we mentioned experimental measurements of the intensities of the $R_0(0)$ transition in gaseous[13] and in liquid[28] HD. The gas measurements show only a very slight constructive interference, while the liquid results, carried out at much higher densities, show appreciable constructive interference. These results are consistent with the present theoretical calculations, since the interference results from the cross terms which lead to relatively sharp absorption that scales as the density squared. (The absorption due to the allowed dipole moment scales linearly with the density.) There is no *a priori* reason to expect qualitatively different results for the solid.

Experimental results for other lines in the pure rotational spectrum of gaseous HD at room temperature[14] indicate the interference effects (sign as well as magnitude) depend on the rotational quantum number J. Similar results obtain for lines in the fundamental band.[2] Theoretically, as discussed in the preceding section, there are other induced components that will interfere in these cases, as well as additional effects (e.g., double transitions, near-resonant mixing of vibration-rotational levels,[33] etc.) that must be taken into account.

There is one final point that we would like to make concerning the experimental spectrum of solid HD.[21] The measured absorption coefficient for the $S_0(0)$ transition in this case was also found to be much smaller (by more than a factor of 3) than the theoretical value; this discrepancy far exceeds those typical of later measurements, even for much weaker absorption features.[16,17]

In light of the results of the present calculation and the other evidence noted above, and because the quantitative understanding of the spectrum of solid HD is of fundamental importance, we suggest that a remeasurement of this spectrum be carried out to ascertain whether a large discrepancy does in reality remain.

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