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Absorption intensity of the $Q_1(0)+Q_1(0)$ and $Q_1(0)+Q_2(0)$ double vibrational transitions in solid parahydrogen

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We present a theoretical calculation of the integrated absorption intensities of the $Q_1(0)+Q_1(0)$ and $Q_1(0)+Q_2(0)$ pure vibrational double transitions in solid parahydrogen which agrees well with recent experimental measurements by Mengel, Winnewisser, and Winnewisser. The infrared activity of these transitions is found to arise from two- and three-body exchange- and dispersion-induced dipole moments.

I. INTRODUCTION

Spectroscopists have long been interested in the infrared (IR) absorption spectrum of solid hydrogen.[1,2] This interest stems largely from the fact that the IR activity of solid hydrogen arises from intermolecular interactions; consequently the IR spectrum of solid hydrogen constitutes an important source of information about these interactions. In addition, solid hydrogen is unique among molecular solids in that its IR spectrum features discrete transitions corresponding to rovibrational transitions of gas phase hydrogen molecules, indicating that the rotational and vibrational quantum numbers of H_2 remain ‘‘good’’ in the condensed phase.

Mengel *et al.*[3,4] have recently identified IR absorption features in solid hydrogen corresponding to the $Q_1(0)+Q_1(0)$ and $Q_1(0)+Q_2(0)$ double transitions, in which a single photon excites the vibrational coordinates of two H_2 molecules simultaneously. They note that these transitions arise from ‘‘induction mechanisms that are not yet understood’’ and the IR activity of these transitions therefore ‘‘remains a fully unsolved question.’’[4]

Previous theoretical treatments[5–7] of the IR activity of solid H_2 explain this activity in terms of the transition dipole moment induced in the H_2 crystal by the permanent electrostatic multipoles of H_2 molecules with $j>0$. What is puzzling about the transitions observed by Mengel *et al.* is that these transitions do not involve rotationally excited states of H_2; hence these electrostatic multipoles are absent. In this paper, we outline an induction mechanism which explains the IR activity of these transitions in terms of isotropic exchange- and dispersion-induced H_2-H_2 dipoles.

II. THEORY OF IR ACTIVITY IN SOLID PARAHYDROGEN

We consider a hexagonal close packed (hcp) crystal of pure parahydrogen (p-H_2) in which the rotational quantum number of each molecule is $j=0$. The transition between crystal states *i* and *f* is IR active only if the transition dipole moment $\mathbf{M}_{if}=\langle i|\mathbf{M}|f\rangle$ is nonzero, where $\mathbf{M}$ is the total dipole moment of the p-H_2 crystal. In the pure vibrational double transitions considered here, no molecule in the crystal changes its rotational state. Consequently, in both the initial state and the final state of the crystal, each H_2 molecule is spherically symmetric, with electrostatic moments that are identically zero. Hence $\mathbf{M}$ contains no contributions from dipoles induced by the quadrupolar electric field (or higher order fields) of individual H_2 molecules. Instead, $\mathbf{M}$ represents the effects of isotropic exchange and dispersion interactions between nearby H_2 molecules. These interactions cause small deformations of the molecules’ electron-density distributions, and ultimately generate the transition dipole moment responsible for the IR activity of the double transitions considered here.

To illustrate these effects, we consider an isolated $(p\text{-H}_2)_2$ dimer in which both molecules have $j=0$. At large H_2-H_2 distances, dispersion forces polarize the molecules and cause a slight buildup of electron density in the region between the molecules. Conversely, when the H_2 molecules are close together, exchange forces shift electron density out of the region between the molecules. Neither of these effects can generate an overall dipole moment if the two p-H_2 molecules have the same vibrational quantum number; however, if the two molecules are in different vibrational states, the $(p\text{-H}_2)_2$ dimer acquires a nonzero dipole moment. This accounts for the absorption features in the gas phase IR spectrum of $(p\text{-H}_2)_2$ which correlate with the $Q_1(0)$ and $Q_2(0)$ vibrational transitions of free H_2.[8]

In the present work, we assume that the total dipole moment of the p-H_2 crystal can be written as the sum of two-body and three-body contributions:

$$\mathbf{M}=\sum_{i<j}\left(\mathbf{M}_{ij}+\sum_{k\neq i,j}\mathbf{M}_{ij,k}\right). \tag{1}$$

The pair dipole $\mathbf{M}_{ij}$ arises from the exchange and dispersion induction mechanisms described above. The irreducible three-body term $\mathbf{M}_{ij,k}$ represents the dipole induced in H_2 molecule *k* by the exchange- and dispersion-induced dipole moment of the nearby pair (i,j) of H_2 molecules, and has the form[9]

$$\mathbf{M}_{ij,k}=\alpha_k[3(\mathbf{M}_{ij}\cdot\mathbf{R}_{ij,k})\mathbf{R}_{ij,k}/R^5_{ij,k}-\mathbf{M}_{ij}/R^3_{ij,k}], \tag{2}$$

where α_k is the isotropic polarizability of molecule *k* and $\mathbf{R}_{ij,k}$ is the vector directed from the midpoint of the (i,j) pair to molecule *k*.

In the double vibrational transitions considered here, the initial and final states of the p-H_2 crystal differ in the vibrational wave functions of two neighboring H_2 molecules, which we will call molecules 1 and 2. We will use the notation $|v_1,v_2\rangle$ to denote the state of the crystal in which these molecules have respective vibrational quantum numbers v_1 and v_2. Terms in $\mathbf{M}$ which do not depend on the bond lengths of molecules 1 and 2 cannot contribute to $\mathbf{M}_{if} = \langle 0,0|\mathbf{M}|v_1,v_2\rangle$; therefore the only portion of Eq. (1) which is relevant for the transitions considered here is

$$\mathbf{M}^{(1,2)} = \mathbf{M}_{12} + \sum_{k\neq 1,2} (\mathbf{M}_{12,k} + \mathbf{M}_{1k,2} + \mathbf{M}_{2k,1}). \tag{3}$$

Because $\mathbf{M}_{ij}$ falls off rapidly with increasing distance,[10] we simplify Eq. (3) further by making the assumption that $\mathbf{M}_{ij} = \mathbf{M}_{ij,k} = 0$ unless molecules i and j are nearest neighbors. Inserting Eq. (2) into Eq. (3) shows that the evaluation of $\mathbf{M}_{if} = \langle 0,0|\mathbf{M}^{(1,2)}|v_1,v_2\rangle$ for a rigid H_2 crystal lattice can be reduced to the computation of various H_2 vibrational matrix elements of $\mathbf{M}_{ij}$ and α_k.

Expressions for $\mathbf{M}_{ij}$ and $\mathbf{M}_{ij,k}$ have been reported for the long-range limit in which only dispersion mechanisms are active and exchange contributions can be neglected.[11,12] However, exchange interactions are not negligible for two H_2 molecules separated by 7.16 a_0 (the equilibrium nearest-neighbor distance in solid H_2). Estimates for the exchange contribution to $\mathbf{M}_{ij}$ and $\mathbf{M}_{ij,k}$ can be obtained from empirical models,[9,13] but these models have not yet been calibrated for transitions involving the $v=2$ level of H_2. We have therefore chosen to evaluate $\mathbf{M}^{(1,2)}$ from *ab initio* quantum chemical calculations[14] which include both dispersion and exchange effects. These calculations are performed using augmented correlation-consistent triple zeta atomic basis sets and a coupled cluster treatment of electron correlation including single and double excitations and a noniterative treatment of triple excitations.

Specifically, we hold two H_2 molecules at a fixed intermolecular distance R and compute the dipole moment μ along the H_2-H_2 bond for several different orientations of the H_2 molecules and at selected H_2 bond lengths (r_i, r_j) between 1.0 a_0 and 2.2 a_0. Angular quadrature over the H_2 orientational degrees of freedom yields the dipole moment of a pair of $j=0$ H_2 molecules separated by the distance R and at our selected (r_i, r_j) values. These results are then fit to polynomials in r_i and r_j to facilitate integration over the vibrational wave functions of the H_2 molecules:

$$\mu(r_i, r_j) = \sum_{n,p} c_{n,p}(r_i + r_j)^n (r_i - r_j)^p. \tag{4}$$

These calculations were performed at $R = 6.5$ a_0, 7 a_0, and 7.16 a_0.

III. RESULTS AND DISCUSSION

Equipped with these *ab initio* results, we evaluate the transition dipole moment $\mathbf{M}_{if}$ by direct summation over the rigid hcp H_2 lattice, using Eqs. (2) and (3) and the H_2-H_2 dipole moments of Eq. (4) calculated at $R = 7.16$ a_0. The integrated absorption coefficients per H_2-H_2 pair for the double vibrational transitions considered here can be computed from $\mathbf{M}_{if}$ as $\tilde{\alpha}_{\text{pair}} = \pi|\mathbf{M}_{if}|^2/3\hbar\epsilon_0$. The values we obtain for in-plane H_2-H_2 pairs, in which both H_2 molecules reside in the same hcp crystal plane, are

$$Q_1(0)+Q_1(0): \quad \tilde{\alpha}_{\text{pair}} = 3.03\times 10^{-21}\ \text{cm}^3/\text{s},$$

$$Q_1(0)+Q_2(0): \quad \tilde{\alpha}_{\text{pair}} = 2.05\times 10^{-21}\ \text{cm}^3/\text{s}.$$

For the $Q_1(0)+Q_2(0)$ transition, the same $\tilde{\alpha}_{\text{pair}}$ value is obtained for out-of-plane pairs in which the two H_2 molecules reside in adjacent hcp crystal planes. For the $Q_1(0)+Q_1(0)$ transition, $\tilde{\alpha}_{\text{pair}} = 0$ for out-of-plane pairs because the hcp lattice has inversion symmetry about the point midway between the two molecules forming such a pair.

Integrated absorption coefficients per H_2 molecule are readily obtained from $\tilde{\alpha}_{\text{pair}}$ as $\tilde{\alpha} = g\tilde{\alpha}_{\text{pair}}$, where g is a factor relating the number of unique nearest-neighbor H_2-H_2 pairs in the crystal to the number of individual H_2 molecules. Because each molecule in the hcp lattice has twelve nearest neighbors, ordinarily $g = 12/2 = 6$; the factor 1/2 prevents ''double counting'' of H_2-H_2 pairs. However, because only in-plane pairs contribute to the absorption coefficient of the $Q_1(0)+Q_1(0)$ transition, $g = 3$ for this transition. Furthermore, the factor 1/2 must be *omitted* from g for the $Q_1(0)+Q_2(0)$ transition because the final vibrational states $|v_1 = 1, v_2 = 2\rangle$ and $|v_1 = 2, v_2 = 1\rangle$ are distinct; therefore $g = 12$ for this transition.

Consequently, the integrated absorption coefficients per H_2 molecule predicted by our model for a rigid hcp H_2 lattice are

$$Q_1(0)+Q_1(0): \quad \tilde{\alpha} = 9.09\times 10^{-21}\ \text{cm}^3/\text{s},$$

$$Q_1(0)+Q_2(0): \quad \tilde{\alpha} = 2.46\times 10^{-20}\ \text{cm}^3/\text{s}.$$

The corresponding experimental integrated absorption coefficients are[3,4]

$$Q_1(0)+Q_1(0): \quad \tilde{\alpha} = 1.8\pm 0.4\times 10^{-19}\ \text{cm}^3/\text{s},$$

$$Q_1(0)+Q_2(0): \quad \tilde{\alpha} = 9.3\pm 0.9\times 10^{-19}\ \text{cm}^3/\text{s}.$$

Our computed absorption coefficients are not in particularly good agreement with the experimental measurements. Although our model does predict (in accord with experiment) that the $Q_1(0)+Q_2(0)$ transition is substantially more intense than the $Q_1(0)+Q_1(0)$ transition, our calculated absorption coefficients are more than an order of magnitude smaller than the observed values.

As we will demonstrate shortly, this discrepancy seems to arise from our assumption that the hcp H_2 crystal lattice is rigid. It is well established that individual molecules in solid H_2 undergo extensive zero-point motion; even in the limit $T\to 0$ K, the root mean-square displacement of a given molecule from its nominal lattice site is about 18% of the nearest-neighbor distance of 7.16 a_0.[15] To properly account for this zero-point motion, we must average the transition dipole moment $\mathbf{M}_{if}$ over the many-body wave function of the solid H_2 crystal.

Such a task is rather daunting. Fortunately, we can recover most of the effects of lattice nonrigidity by examining how the induced H_2-H_2 dipole moments $\mathbf{M}_{ij}$ change due to lattice zero-point motion. Equations (2) and (3) show that the transition dipole moment $\mathbf{M}_{if}$ is a function of $\mathbf{M}_{ij}$ and $\mathbf{M}_{ij}/R^3_{ij,k}$. Because $\mathbf{M}_{ij}$ depends strongly on the distance between molecules i and j,[10] it is reasonable to expect that the average of $\mathbf{M}_{ij}$ over the zero-point motion of the lattice may differ substantially from the value of $\mathbf{M}_{ij}$ evaluated at the nearest-neighbor distance of 7.16 a_0. On the other hand, previous theoretical studies[16,17] of solid H_2 show that the value of $1/R^3_{ij,k}$ averaged over the H_2 lattice zero-point motion is almost identical to its value for a rigid hcp lattice.

We have therefore recomputed the integrated absorption coefficients for the $Q_1(0)+Q_1(0)$ and $Q_1(0)+Q_2(0)$ transitions by simply replacing the induced dipole moments $\mathbf{M}_{ij}$ appearing in Eqs. (2) and (3) with their ''renormalized'' averages over the nearest-neighbor two-particle distribution function of solid H_2 at $T=0$ K. This distribution function was obtained from a variational quantum Monte Carlo simulation of 180 hcp H_2 molecules using periodic boundary conditions and the approximate wave function described in Ref. 18. The H_2-H_2 induced dipole moment matrix elements were assumed to depend on the intermolecular distance R as $\mu(R)=\mu_0 \exp(-\beta R)$, and the parameters μ_0 and β were computed by fitting the *ab initio* dipole moment calculations at $R=6.5$ a_0 and 7 a_0. [Our choice of this functional form was motivated by Ref. 10; adding a long-range inverse power contribution to $\mu(R)$ does not significantly change our results.]

Using the renormalized induced dipole moments in Eqs. (2) and (3), summation over the hcp crystal lattice gives integrated absorption coefficients per H_2 molecule of

$$Q_1(0)+Q_1(0): \quad \tilde{\alpha}=3.4\pm0.1\times10^{-20}\ \text{cm}^3/\text{s},$$

$$Q_1(0)+Q_2(0): \quad \tilde{\alpha}=1.1\pm0.1\times10^{-18}\ \text{cm}^3/\text{s}.$$

The absorption coefficient computed for the $Q_1(0)+Q_2(0)$ transition is in almost quantitative agreement with experiment, while the theoretical absorption coefficient for the $Q_1(0)+Q_1(0)$ transition agrees with experiment to within a factor of five. (The cited uncertainties in $\tilde{\alpha}$ reflect statistical uncertainties in our variational quantum Monte Carlo calculation of the renormalized transition dipole matrix elements.)

The remaining discrepancy between theory and experiment could originate in our omission of induced H_2-H_2 quadrupole moments, which are thought to play a role in the three-body collision-induced IR spectrum of gaseous H_2.[13] Presumably the inclusion of induced quadrupole moments would affect the integrated absorption coefficient of the $Q_1(0)+Q_1(0)$ transition more strongly, as the ''pure two-body'' term $\mathbf{M}_{12}$ for this transition is identically zero and this transition therefore acquires its intensity solely from three-body effects.

In summary, we have presented a model which accounts for the IR activity of the $Q_1(0)+Q_1(0)$ and $Q_1(0)+Q_2(0)$ pure vibrational double transitions observed in solid H_2 by Mengel *et al.*[3,4] The IR activity of these transitions arises from isotropic dipole induction mechanisms. Theoretical analyses of the IR activity of solid H_2 generally ignore these induction mechanisms, because the dipoles induced by the permanent electrostatic multipoles of H_2 are usually much larger than those induced by isotropic exchange and dispersion forces. However, in pure $j=0$ parahydrogen, and in parahydrogen doped with spherical impurities,[19] such multipoles are absent and these weak isotropic induction mechanisms provide the only way to induce IR activity in the solid. As we have seen, the extensive zero-point motion of the H_2 crystal lattice can make these induced moments larger than might otherwise be expected.

Our *ab initio* calculations provide enough data for us to estimate the absorption coefficient of the $Q_2(0)+Q_2(0)$ double transition at $\tilde{\alpha}\approx6\times10^{-25}$ cm^3/s, which is probably too weak to be observed. The $Q_1(0)+Q_3(0)$ double transition may be stronger, although our *ab initio* calculations do not cover the range of H_2 bond lengths needed to give a quantitative estimate of the intensity of this transition. Finally, we note that a polarization study of the $Q_1(0)+Q_1(0)$ transition should prove interesting, as our model predicts that the transition dipole moment for this transition is perpendicular to the c axis of the H_2 hcp crystal.

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