

# Observation of the $S_3(0)$ Transition in Solid Parahydrogen and a Theory of Solid-State Rovibrational Line Widths

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The  $S_3(0)$  transition ( $\nu = 3 \leftarrow 0$ ,  $J = 2 \leftarrow 0$ ) in solid parahydrogen has been observed at  $12\,058.98\text{ cm}^{-1}$  with a width of  $0.25\text{ cm}^{-1}$  (fwhm). The line width of this transition is broader than that of the pure rotational  $S_0(0)$  transition. Although line widths usually narrow with vibrational excitation due to diminished coupling among molecules and a larger mismatch between the energies of the excitons and phonons, all observed  $S_\nu(0)$  ( $\nu = \nu \leftarrow 0$ ,  $J = 2 \leftarrow 0$ , for  $\nu = 1, 2, 3$ ) transitions exhibit line widths which are larger than that of the pure rotational transition. This has led us to develop a new theory of solid-state line widths. The  $S_\nu(0)$  line widths are herein shown to be a result of the mixing of the simultaneous state  $Q_\nu(0) + S_0(0)$  manifold ( $\nu = \nu \leftarrow 0$ ,  $J = 0 \leftarrow 0$  and  $\nu = 0 \leftarrow 0$ ,  $J = 2 \leftarrow 0$ , respectively, for two neighboring molecules) into the zeroth-order  $S_\nu(0)$  manifold. The derived transition moment illustrates that only states with a total exciton momentum,  $\mathbf{k}$ , of zero are accessed. The line widths of all  $S_\nu(0)$  transitions are reproduced theoretically by considering the consequences of simultaneously placing two excitons,  $Q_\nu(0)$  and  $S_0(0)$ , in the lattice. Although both can propagate independently, the interactions allowing the propagation of rotational energy among lattice sites is much stronger than that for vibrational energy. As a result, the rotational excitation hops much more quickly than that of vibration. By considering the roton's dephasing due to the presence of the simultaneously-created  $Q_\nu(0)$  excitation, one can calculate the contribution of this coherence relaxation (i.e.,  $T_2$  relaxation) process to the overall frequency uncertainty of each  $S_\nu(0)$  transition. Due to this scattering, the crystal state irreversibly decays from  $|Q_\nu(0) + S_0(0)\rangle_{\mathbf{k}=0}$  to  $|Q_\nu(0) + S_0(0)\rangle_{\mathbf{k}\neq 0}$ , thus rendering the state unmeasurable by changing the phase relationship between the initial and final states. All  $\Delta J = 2$  rovibrational line widths have been calculated using this method; our theoretical line widths closely reproduce those observed experimentally.

## I. Introduction

Probing intermolecular interactions in condensed media is difficult due to the close proximity of the molecules and their strong interactions. These interactions broaden absorptions, thus obscuring intermolecular dynamics and rendering high-resolution spectroscopy useless. With its weakly interacting molecules and dearth of permanent multipole fields, solid parahydrogen offers a relatively unobscured view of solid-state intermolecular interactions. Additionally, because of its relative simplicity, hydrogen readily lends itself to theoretical study; interactions can be calculated from first principles. Due to the antisymmetry constraint on the total wave function, the hydrogen molecule can only be in the spherically symmetric ground rotational state ( $J = 0$ ) if the nuclear spins are antiparallel (parahydrogen,  $p\text{-H}_2$ ). The lowest rotational state possible for molecular hydrogen with parallel nuclear spins (orthohydrogen,  $o\text{-H}_2$ ) is then  $J = 1$ , even at absolute zero. Due to the large rotational constant of hydrogen, only these two rotational levels have any population at liquid helium temperatures. The simplicity and beauty of the hydrogenic spectrum makes solid  $p\text{-H}_2$  an ideal system to study in order to gain insight into solid-state interactions.

Although isolated molecular hydrogen has no electric dipole-allowed transitions, instantaneous multipole moments of nearby molecules can induce dipoles in surrounding molecules. These multipole fields have strong distance dependences; hence, their effects are more readily observable in the solid than in the gas. The strong fundamental  $S_1(0)$  transition ( $\nu = 1 \leftarrow 0$ ,  $J = 2 \leftarrow 0$ ) was observed in the first infrared investigation of solid

hydrogen.<sup>1</sup> VanKranendonk has developed a theory describing the intensity and band width of this transition due to the hopping of the entire  $S_1(0)$  rovibron throughout the lattice.<sup>2</sup> Since this initial investigation many new hydrogenic transitions have been observed in nearly pure  $p\text{-H}_2$ , nearly pure  $o\text{-H}_2$ , and many concentrations in between. VanKranendonk has pioneered the theoretical investigations into many of these hydrogenic transitions and the nature of solid-state interactions.

Many of the observed transitions are unique to the solid state, in which observations of impurity  $J = 1$   $\text{H}_2$  molecules, pairs, and higher order clusters interact with each other or with  $J = 0$  molecules upon absorbing radiation. The microwave work by Hardy et al. illustrating the  $J = 1$  pair splittings is a beautiful example of these interactions.<sup>3</sup> Recently the high resolution and sensitivity which laser spectroscopic techniques afford have been applied to this problem. Very intricate patterns with line widths an order of magnitude narrower than those in the gas phase have been observed.<sup>4</sup> The  $Q_1(0)$  transitions ( $\nu = 1 \leftarrow 0$ ,  $J = 0 \leftarrow 0$ ) of impurity  $\text{D}_2$  and  $\text{HD}$  in  $p\text{-H}_2$  crystals observed by Weliky et al. are also an excellent example of a static interaction of the excitation on an impurity molecule with the surrounding hydrogen molecules.<sup>5,6</sup> Other transitions such as the tetrahexacontapole ( $2^6$ -pole)-induced  $W_0(0)$  and  $W_1(0)$  transitions ( $\nu = 0 \leftarrow 0$ ,  $J = 6 \leftarrow 0$  and  $\nu = 1 \leftarrow 0$ ,  $J = 6 \leftarrow 0$ , respectively) are narrow enough to show the crystal field splitting of the M levels within the  $J = 6$  rotational manifold.<sup>7,8</sup> All of these spectral patterns illustrate relatively static solid-state interactions since the excitations are to a very good approximation localized on the absorber due to either energy mismatches between the impurity absorber and the surrounding molecules or, in the cases of  $W_1$ -

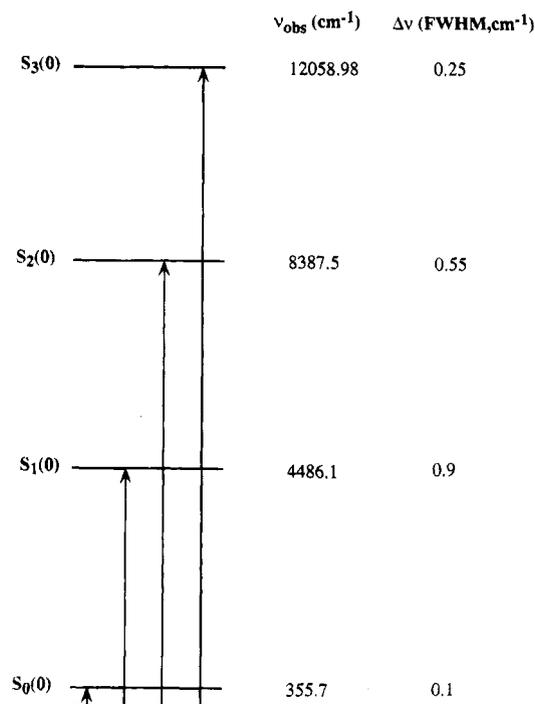
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(0) and  $W_0(0)$ , very stringent distance dependences of the tetrahexacontapole–tetrahexacontapole ( $2^6$ -pole– $2^6$ -pole) interactions. In each situation, hopping of the excitation among molecules is severely limited.

Nonlocalized hydrogen excitations such as  $Q_1(0)$  and  $S_0(0)$  ( $J = 2 \leftarrow 0$ ) in  $p$ - $H_2$  crystals provide qualitatively different information about the solid. In these situations, the intermolecular interactions are strong enough to facilitate the hopping of excitons (one quantum of vibrational, rotational, or rovibrational energy, called here vibrons, rotons, or rovibrons, respectively, which can move among lattice sites and, hence, have a wave vector associated with their motion) throughout the lattice. The simplest case is that of  $S_0(0)$ , a resonant roton which hops via the electric quadrupole–quadrupole (EQQ) interaction of any two molecules. As illustrated by the line width of the  $S_0(0)$  transition, observed to be dependent on  $o$ - $H_2$  concentration, two types of broadening are present in this system: natural population relaxation ( $T_1$ ) and coherence relaxation or dephasing ( $T_2$ ). In nearly pure  $p$ - $H_2$ , the line widths of both the infrared and Raman transitions are approximately  $0.1 \text{ cm}^{-1}$  (fwhm), but the line width increases linearly with increasing  $J = 1$  concentration.<sup>9,10</sup> The impurity broadening of the  $p$ - $H_2$  transitions results from a purely  $T_2$ -phase relaxation process in which the parahydrogen excitons scatter off  $o$ - $H_2$  molecules.<sup>9–12</sup>

Each exciton has a wave vector,  $\mathbf{k}$ , associated with its motion through the lattice. In a pure  $p$ - $H_2$  lattice, the roton moves resonantly between molecules; hence, no disruption of the molecular energy or phase occurs as the EQQ interaction facilitates its propagation. This means that as long as a resonant exciton can move freely throughout the lattice, the transition is not inhomogeneously broadened in any manner. The fact that the EQQ interaction inherently causes no broadening is borne out in Igarashi's calculations of the  $S_0(0)$  Raman-active line widths.<sup>13</sup> When the exciton encounters an impurity, it can no longer freely hop. The impurity destroys the symmetry of the lattice and, therefore, the periodic potential in which the exciton moves; the exciton must either avoid the impurity, thus affecting the exciton's phase, or hop to the impurity, thereby paying costs both in energy and phase.<sup>12,13</sup> In this manner, impurities (e.g.,  $o$ - $H_2$ ) increase the energy uncertainty by giving rise to inhomogeneous broadening.<sup>12,13</sup> Several authors have examined this problem by treating the impurity as a lattice imperfection through perturbation theory.<sup>14,15</sup> Their theoretical  $S_0(0)$  line widths for impurity concentrations of 1–5% seem to match experiments very well.<sup>16</sup> This indicates that as the roton hops its phase is altered simply by the destruction of the symmetry of the lattice due to the presence of an impurity, not by any particular characteristics of the impurity. The same result was observed for the hopping of a vibron in solid parahydrogen.<sup>14</sup> This destruction of phase can be viewed in two different ways, that of the destruction of the  $\Delta\mathbf{k} = 0$  selection rule upon hopping of the roton through the lattice; or equivalently that the Bloch wave which was the eigenfunction of the pure crystal containing an  $S_0(0)$  excitation is no longer an accurate wave function to describe an impure crystal.

Igarashi's result yielding an infinitely narrow  $S_0(0)$  line width in pure  $p$ - $H_2$  does not agree with the experimental evidence.<sup>9,10,13</sup> This indicates that the experimentally obtained  $0.1 \text{ cm}^{-1}$  linewidth of the  $S_0(0)$  transition in nearly pure  $p$ - $H_2$  is the natural line width due to the relaxation of the  $S_0(0)$  roton into the bath of crystal phonons (i.e., this line width is completely a result of  $T_1$  population relaxation). This conclusion is supported by the observed line widths for the  $S_1(0)$  and  $S_1(1)$  transitions of  $D_2$  impurities, which are also approximately  $0.1 \text{ cm}^{-1}$ .<sup>5,17</sup> Since these  $D_2$  rovibrational transitions are completely localized on



**Figure 1.** Previous work illustrating the frequencies and line widths of all observed  $\Delta J = 2$  rovibrational transitions in solid parahydrogen at low impurity concentrations.

the impurity due to the large energy mismatch with the surrounding hydrogen molecules, little inhomogeneous broadening of these lines occurs. Since the vibrational lifetimes are so much longer than those of rotation due to a larger energy mismatch with the phonon spectrum, the  $D_2$   $\Delta J = 2$  line widths must be solely a result of population relaxation of the rotational excitation.<sup>18,19</sup> The facts that the localized impurity  $S$  transitions give similar linewidths to that of the host's  $S_0(0)$  transition in nearly pure solid  $p$ - $H_2$  and that the rotational lifetime is much shorter than that of vibration confirm that the residual line width observed in nearly pure  $p$ - $H_2$  crystals is due to the natural decay of the  $J = 2$  rotational state. Figure 1 summarizes the observed  $S_0(0)$  frequencies and line widths in approximately 99.8% parahydrogen.

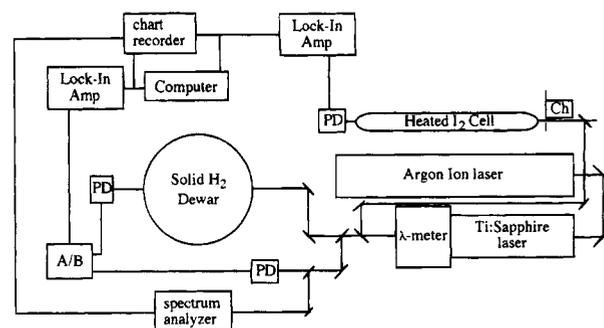
For the hopping of a  $J = 2$  roton to occur, the instantaneous quadrupole moments of two neighboring molecules must interact, thus having a  $R^{-5}$  dependence (EQQ or electric quadrupole–quadrupole interaction). Any sort of  $T_2$  broadening depends on the magnitudes of the intermolecular interactions which couple nearby molecules, thus facilitating the hopping of the exciton through the lattice. As the distance dependences of these interactions become more stringent or as energy discrepancies between the absorbing molecule and the surrounding molecules increase, excitations become more and more localized yielding line widths largely due to  $T_1$  relaxation. These situations can lead to very sharp transitions.<sup>3,4,6–8,17–19</sup> Sharp lines in solid hydrogen are not limited to cases of impurities and localized transitions, however. The  $\Delta\mathbf{k} = 0$  selection rule is satisfied for every absorption in a pure  $p$ - $H_2$  crystal and only breaks down in the presence of impurities or in impurity-induced transitions. This condition alone can lead to very narrow lines as well.<sup>7,8,18,19</sup> The narrowest lines yet observed, however, have been those of the localized impurity  $D_2$   $Q_1(0)$  transitions which have been on the order of a few megahertz hwhm.<sup>5,6,20</sup> These observations give great incentive to develop solid  $p$ - $H_2$  both as a probe of solid-state interactions and as a host matrix for high-resolution spectroscopy.

In addition to the observation of the pure rotational  $S_0(0)$  transition, the rovibrational transitions  $S_1(0)$  and  $S_2(0)$  ( $\nu = 1 \leftarrow 0$ ,  $J = 2 \leftarrow 0$ , and  $\nu = 2 \leftarrow 0$ ,  $J = 2 \leftarrow 0$ , respectively) have both been observed by Fourier transform infrared spectroscopy (FTIR) with line widths that are broader than that of the  $S_0(0)$  at low  $o$ - $H_2$  concentrations.<sup>21,22</sup> Although five sublevels of the  $J = 2$  state exist, only transitions to  $M = \pm 2$  are infrared allowed due to the crystal symmetry. The  $S_1(0)$  transition is very strong; therefore, an exact line-width measurement is difficult due to saturation, but the most reliable measurement gives it as  $0.9 \text{ cm}^{-1}$ .<sup>21</sup> The  $S_2(0)$  line width has been measured in our laboratory to have a line width of  $0.6 \text{ cm}^{-1}$  at a slightly higher impurity concentration,  $0.3\% J = 1$ .<sup>22</sup> For purposes of comparison with other  $\Delta J = 2$  line widths, the  $S_2(0)$  transition is estimated to have a line width of approximately  $0.55 \text{ cm}^{-1}$  (fwhm) at  $0.2\%$  orthohydrogen impurity concentration. All host molecule  $S_\nu(0)$  transitions satisfy the  $\Delta k = 0$  selection rule which results from a sum over all the lattice sites in the crystal. If all the molecules at the lattice sites are identical (e.g., a pure  $p$ - $H_2$  crystal), this condition is rigorously satisfied. Even if some impurities exist, this selection rule is often very nearly satisfied.<sup>18,23,24</sup> This selection rule only breaks down significantly at relatively high impurity concentrations ( $\geq 2\%$ ) or when the transition is caused by an impurity in the surrounding molecules (e.g., the  $Q_1(0)$  transition of hydrogen<sup>25</sup>). Since the  $S(0)$  transitions do not require the presence of a  $J = 1$  molecule, for sufficiently low impurity concentrations the  $\Delta k = 0$  selection rule is satisfied, giving rise to a line width contribution on the order of  $10 \text{ MHz}$  as a result of this approximate condition.<sup>26</sup>

In determining line widths of rotational transitions, impurity-induced dephasing of the exciton as it hops throughout the lattice has been considered, as have the natural lifetimes of the states as they decay into phonon modes. Although these mechanisms have proven very useful for the description of the pure rotational  $S_0(0)$  line widths and the line widths of impurity transitions, both of these pictures predict that an excitation with one or more quanta of vibrational energy (e.g.,  $S_1(0)$  or  $S_2(0)$ ) should be narrower than the pure rotational transition. The rovibron cannot hop as quickly as a pure roton due to the weaker vibrational coupling among molecules.<sup>11,27</sup> Since this rovibrational excitation would then hop more slowly, it would encounter fewer impurities off of which its phase could be scattered. This  $T_2$  mechanism then predicts that the  $S_\nu(0)$  line widths should follow the progression  $S_0(0)$ ,  $S_1(0)$ ,  $S_2(0)$ ,  $S_3(0)$ , etc., in order of decreasing line width. In terms of a  $T_1$  line width, as the discrepancy between the phonon energy and that of the excitation in the lattice increases, the excited states are longer-lived; the line widths consequently narrow. The rotational energy of all these rovibrational transitions, however, is approximately the same, thus any decay via phonon interactions should be similar for all the observed transitions, giving very similar line widths for all the rovibrational states. The observed line-width progression from broadest to narrowest is  $S_1(0)$ ,  $S_2(0)$ ,  $S_3(0)$ ,  $S_0(0)$  for  $99.8\%$  solid parahydrogen. Seemingly, no rovibrational excitation will be narrower than the pure rotational excitation. This problem has led us to develop a theory which accounts for these observations.

## II. Experimental Section

The solid parahydrogen sample preparation is described in detail in previous papers.<sup>5,8,17</sup> Hydrogen gas (Midwest Welding Supply Co.) is first purified by passing it through a palladium film (Johnson-Mathey hydrogen purifier) to remove any non-hydrogenic impurities; it is then converted to  $99.8\%$   $p$ - $H_2$  by passing the gas over a paramagnetic nickel silicate catalyst<sup>28</sup> at



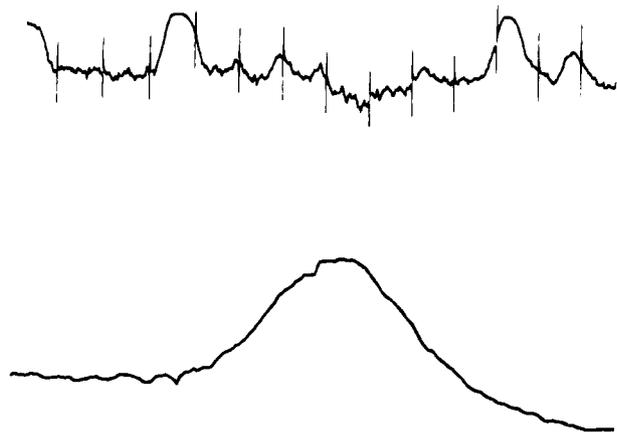
**Figure 2.** Experimental setup for observation of the  $S_3(0)$  transition. The laser was passed through the sample, and the photodiode-detected signals ratioed to normalize the laser power. The frequency was measured by an external wavelength meter while iodine reference lines were recorded simultaneously.

liquid hydrogen temperatures. The converted gas is flowed into a  $10 \text{ cm}$  copper cell with wedged sapphire windows and frozen onto the cell walls. The dewar housing the cell was constructed by Infrared Laboratories, Inc. The hydrogen gas is flowed into the cell at a rate such that the liquid helium cooled cell is at a temperature of approximately  $7 \text{ K}$ . The newly formed crystal is cooled to  $4.2 \text{ K}$ . Crystals formed in this manner are optically transparent and largely free of cracks, but the center of the cell usually remains empty.

Pumped by a Coherent Innova 100 argon ion laser, a Coherent Model 899-29 titanium sapphire ring laser provided tunable near-infrared radiation which was passed through a  $99.8\%$  solid parahydrogen crystal ( $0.2\%$  orthohydrogen). Absorptions were detected by the change in intensity of the chopper-modulated laser after one pass through the sample. One beam passing through the crystal and one beam before the crystal were ratioed to normalize the signal, thus accounting for any laser power fluctuations. The titanium sapphire laser ( $\text{Ti:Al}_2\text{O}_3$ ) is frequency stabilized to  $500 \text{ kHz}$  (rms) by an external  $1 \text{ GHz}$  Fabry-Perot cavity. The scanning can be performed manually over a  $1 \text{ cm}^{-1}$  ( $30 \text{ GHz}$ ) range, or the laser can be controlled by the computer and Coherent's AUTOSCAN program. The system scans by piecing together  $10 \text{ GHz}$  segments for any frequency range desired. The computer reads the wave meter, thus giving an absolute frequency measurement good to seven digits. For a finer frequency measurement, iodine reference lines are collected simultaneously and compared to those already published.<sup>29</sup> A  $2 \text{ GHz}$  spectrum analyzer is then used as an etalon to give reference marks, thus dividing up the  $30 \text{ GHz}$  scan into 15 smaller  $2 \text{ GHz}$  sections. These reference ticks, with the iodine lines, then allow for absolute frequency measurements with accuracy to eight significant digits. Since all the iodine transitions in this frequency range are hot bands, the cell is heated to  $600 \text{ }^\circ\text{C}$ . The published data between  $11\,000$  and  $13\,000 \text{ cm}^{-1}$  were recorded at  $700 \text{ }^\circ\text{C}$ ; therefore, the intensities of these reference lines should not be relied upon when comparing with the literature. The data were collected simultaneously by the computer and a chart recorder. The experimental setup is illustrated in Figure 2. The sensitivity of the lock-in amplifier was  $100 \text{ mV}$ , and the time constant was varied from  $0.3$  to  $10 \text{ s}$ . The polarization dependence of this transition was also checked by inserting a half-wave plate followed by a polarizer to insure that the radiation was plane-polarized. Both polarizations, parallel and perpendicular to the crystal axis, were checked.

## III. Observations and Analysis

Depending on the impurity concentration, the  $S_0(0)$  line width varies from  $0.1 \text{ cm}^{-1}$  in pure  $p$ - $H_2$  up to  $1.5 \text{ cm}^{-1}$  in a very



**Figure 3.** The lower trace shows the observed  $S_3(0)$  transition of solid parahydrogen (0.2% orthohydrogen impurity). The absorption in the upper trace are iodine reference lines at 12 058.751 3  $\text{cm}^{-1}$  and 12 059.261 5  $\text{cm}^{-1}$ . The sharp features in the reference trace are transmission peaks from a Fabry–Perot spectrum analyzer and are separated by 2 GHz. Frequency increases from left to right.

impure crystal.<sup>3–5,11</sup> Since the EQQ interaction is much stronger than is the vibrational coupling interaction, the  $S_0(0)$  roton should hop much more quickly than any of the  $S_v(0)$  rovibrons. If the only broadening mechanism were that of the  $T_2$  scattering of the exciton as it propagates through the lattice, one would expect that the  $S_0(0)$  transition would exhibit a much broader line width than those of any rovibrational transitions for a given impurity concentration; this, however, is not the observed result.

The observed  $S_3(0)$  spectrum and the iodine reference are given in Figure 3. At the peak, the  $S_3(0)$  transition approximately corresponds to a 3.5% absorption for one pass through the crystal. The chopper modulated sensitivity is  $7 \times 10^{-3}(\Delta I/I)$ . The polarization dependence of this transition was also examined. Although only the  $M = \pm 2$  level of the  $S_v(0)$  band should be infrared active due to the crystalline symmetry, no difference in intensity was observed as the polarization was changed.

If one views the  $S_3(0)$  state as being composed of a  $Q_3(0)$  excitation and a  $S_0(0)$  excitation on the same molecule, one can readily consider the mixing in of the simultaneous transition in which these two excitations,  $Q$  and  $S$ , are on two different molecules. Barocchi et al. used the complimentary mixing process (that of  $S_1(0)$  mixing into the  $Q_1(0) + S_0(0)$  state) to explain the observed Raman-active simultaneous transition. This transition should be Raman forbidden but has intensity due to mixing with the Raman-allowed  $S_1(0)$  transition.<sup>30</sup> The interaction which allows the hopping of a roton and thus mixes these two manifolds is the EQQ interaction. Due to rotation–vibration coupling, these two manifolds are of different energy. The degree of mixing of the  $S_3(0)$  and the  $Q_3(0) + S_0(0)$  manifolds, where in the latter case one molecule is vibrationally excited and a different one is rotationally excited, depends not only on the form and magnitude of the EQQ potential but also on the inverse of the energy separating these two manifolds. Using perturbation theory, we can obtain an expression for the excited-state wave function. It is seen to be largely composed of the  $S_v(0)$  state, with small contributions from the simultaneous states formed with all the surrounding molecules. Suppose that the  $S_i(0)$  rovibron is on molecule  $i$  and it is mixed with states consisting of separate excitons,  $Q_v(0)$  and  $S_0(0)$ ; the corrected wave function is given in eq 1. The value  $A$  is a normalization factor, while  $M$  and  $M'$  represent the projections of the angular momenta of the  $S_v(0)$  and  $S_0(0)$  on the crystal axis, respectively. The sum over nearest neighbors,  $j$ , includes all the pairs of

$$|\Psi_i^M\rangle = A|S_v(0)_i^M\rangle + \sum_j \sum_{M'} \frac{\langle Q_v(0)_i + S_0(0)_j^{M'} | \hat{V}_{ij}^{\text{EQQ}} | S_v(0)_i^M \rangle}{E^{S_v(0)} - E^{Q_v(0)+S_0(0)}} |Q_v(0)_i + S_0(0)_j^{M'}\rangle \equiv A|S_v(0)_i^M\rangle + \sum_j \sum_{M'} T(\mathbf{R}_{ij})^{M,M'} |Q_v(0)_i + S_0(0)_j^{M'}\rangle \quad (1)$$

molecules able to absorb one photon of radiation simultaneously with the central molecule. The prime on the summation indicates the exclusion of the term  $j = i$ . The wave function  $|S_v(0)_i\rangle$  represents the state in which molecule  $i$  is in the excited  $S_v(0)$  state (i.e.,  $v = v, J = 2$ ) and all other molecules are in the lowest rovibrational state ( $v = 0, J = 0$ ). This is to say

$$|S_v(0)_i^M\rangle \equiv |v, 2^M\rangle \prod_{k \neq i} |0_k\rangle$$

Likewise

$$|Q_v(0)_i + S_0(0)_j^{M'}\rangle \equiv |v, 0_i\rangle |0, 2^{M'}\rangle \prod_{k \neq i, j} |0_k\rangle$$

Due to lattice symmetry constraints on the infrared selection rules<sup>18</sup>,  $M = \pm 2$  for  $S_v(0)$  but all  $S_0(0)_j$   $M'$  values are accessed with varying probabilities as is shown later. The Hamiltonian mixing the manifolds is the EQQ interaction;

$$\hat{V}_{ij}^{\text{EQQ}} = \epsilon_{22} \left( \frac{R}{R_{ij}} \right)^5 \sum_{m,n} C(224; mn) C_{2,m}(\Omega_i) C_{2,n}(\Omega_j) C_{4,m+n}^*(\Omega_{ij}) \quad (2)$$

where

$$\epsilon_{22} = (70)^{1/2} Q_i Q_j / R^5$$

$Q_i$  and  $Q_j$  represent the quadrupole moments of molecules  $i$  and  $j$ , respectively, and  $C(224; mn)$  are Clebsch–Gordan coefficients.  $C_{2m}(\Omega_i)$ , etc., are Racah spherical harmonics in which  $\Omega_i$  and  $\Omega_j$  represent angular orientations of molecules  $i$  and  $j$ , respectively, while  $\mathbf{R}_{ij}$  (with magnitude  $R_{ij}$  and angular orientation  $\Omega_{ij}$ ) is the position vector from molecule  $i$  to molecule  $j$ . The EQQ parameter,  $\epsilon_{22}$ , in (2) has a  $R^{-5}$  distance dependence due to the interaction of two quadrupole moments. The average energy mismatch between the  $S_v(0)$  and  $Q_v(0) + S_0(0)$  manifolds is given by

$$W_v = E_{S_v(0)} - E_{Q_v(0)+S_0(0)} \approx (E_{S_v(0)} - E_{Q_v(0)}) - E_{S_0(0)} \quad (3)$$

where  $E_{S_v(0)}$ ,  $E_{S_0(0)}$ , and  $E_{Q_v(0)}$ , are the experimentally observed frequencies of the  $S_0(0)$ ,  $S_v(0)$ , and  $Q_v(0)$  transitions, respectively. The value of  $W_v$  increases approximately linearly with  $v$ :

$$W_1 = 21.9 \text{ cm}^{-1}$$

$$W_2 = 38.8 \text{ cm}^{-1}$$

$$W_3 = 55.44 \text{ cm}^{-1}$$

To obtain the probability of accessing the simultaneous state, one sums the square of the mixing over all lattice sites. The contribution of the simultaneous state to the overall wave

function at the central molecule from each surrounding molecule is given by eq 4:

$$P_{Q_v(0)_i+S_0(0)_j}^{MM'} = |T(\mathbf{R}_{ij})^{M,M'}|^2 = \frac{|\langle Q_v(0)_i + S_0(0)_j | \hat{V}_{ij}^{EQQ} | S_v(0)_i \rangle|^2}{W_v} \quad (j \neq i) \quad (4)$$

where

$$\langle Q_v(0)_i + S_0(0)_j | \hat{V}_{ij}^{EQQ} | S_v(0)_i \rangle = \langle v_i = v, J_i = 0; v_j = 0, J_j = 2, M_j = M' | \hat{V}_{ij}^{EQQ} | v_i = v, J_i = 2, M_i = M; v_j = 0, J_j = 0 \rangle_{i \neq j}$$

For the case of primary interest here (i.e.,  $M = \pm 2$ ), the matrix elements are given by

$$\sqrt{\frac{14}{5}} \frac{Q_v Q_0}{R_{ij}^5} [(-1)^M C(224; \pm 2, \pm M, M \pm 2) C_{4, \pm 2 + M}(\Omega_{ij})]$$

where the bar over a number indicates its negative (e.g.,  $\bar{M} = -M$ ). The quantity  $T(\mathbf{R}_{ij})^{M,M'}$  describes the delocalization of the rovibrational excitation between two molecules and is hence the relevant quantity describing the mixing of the two manifolds,  $S_v(0)$  with  $Q_v(0) + S_0(0)$ . This probability, or square of mixing is then summed over all neighbors to obtain the total contribution of simultaneous state density to the central molecule. We have, after a straightforward calculation

$$\sum_j \sum_{M'} P_{Q_v(0)_i+S_0(0)_j}^{\pm 2, M'} = \sum_j \sum_{M'} |T(\mathbf{R}_{ij})^{\pm 2, M'}|^2 = \frac{Q_v^2 Q_0^2}{20 W_v^2 R^{10}} \sum_j \left[ \left( \frac{9}{2} \cos^4 \theta_{ij} - 21 \cos^2 \theta_{ij} + \frac{173}{10} \right) \left( \frac{R}{R_{ij}} \right)^{10} \right] \quad (5)$$

where  $\theta_{ij}$  is the azimuth of the vector  $\mathbf{R}_{ij}$  with respect to the crystal axis. The summation over  $j$  in eq 5 converges quickly and yields the normalization factor

$$A = [1 - \sum_j \sum_{M'} |T(\mathbf{R}_{ij})^{\pm 2, M'}|^2]^{1/2} = \begin{array}{ll} 0.985 & \text{for } v = 3 \\ 0.975 & \text{for } v = 2 \\ 0.932 & \text{for } v = 1 \end{array}$$

For all cases the mixing is small, but it is this mixing which introduces extra broadening in addition to the natural line width of the  $S_v(0)$  excitation. The variation of mixing with  $v$  explains the experimentally observed variation of the  $S_v(0)$  line widths as is shown below.

Different symmetry constraints apply to the single and double transitions. For the single molecule transition, the dipole moment,  $EQQ$  interaction, and final states are all most conveniently represented in the crystal frame, the axis of highest symmetry being the crystalline  $C_3$  axis of the  $D_{3h}$  point group. The most symmetric axis when considering the simultaneous state, however, is that connecting the pair of excited molecules. The simultaneous state is then best represented in the pair frame. These two transitions occur by different mechanisms and therefore have different dipole moment expressions. In the  $S_v(0)$  single molecule transition, a transient quadrupole moment on the absorbing molecule polarizes the surrounding molecules,  $j$ , which then reinteract with the central molecule. Due to the space anisotropy of the hcp lattice, a net dipole is induced in the absorbing molecule:

$$\mu_k^i \equiv \mu_k^{S_v(0),i} = (15)^{1/2} \sum_j \sum_M (-1)^k \frac{Q_i \alpha_j}{R_{ij}^4} C(123; kM) C_{2,M}(\Omega_i) C_{3,M-k}^*(\Omega_{ij}) \quad (6)$$

Since the lattice belongs to the  $D_{3h}$  point group, only values of  $k - M = \pm 3$  (where  $k = 0, \pm 1$  represent the spherical components of the dipole relative to the crystal axis and  $M$  is the projection of the  $J = 2$  angular momentum onto the crystalline axis) are possible to yield a nonzero lattice sum over sites  $j$ , and, therefore, a nonzero dipole moment.<sup>11</sup> Since  $|M| \leq J = 2$ , only the  $|J = 2, |M| = 2$  states of the  $S_v(0)$  transition have a perpendicular dipole moment  $|k| = 1$ .

For the simultaneous transition,  $Q_v(0) + S_0(0)$ , the transition dipole is different. The mechanism is one of a transient quadrupole on molecule  $j$  inducing a dipole moment in its neighbors,  $i$ . The inducing molecule and its neighboring molecules (at sites  $R_i$ ) then simultaneously absorb one photon. The excited state consists of the vibrational excitation on molecule  $i$  and the rotational energy on molecule  $j$ . This transition involves these two molecules only; no lattice sum is contained in the microscopic transition moment  $\mu_k^{ij}$ . This transition moment and the resulting simultaneous state are then best represented in the pair frame which gives identical expressions for in and out of plane pairs:

$$\mu_k^{ij} = (15)^{1/2} \frac{Q_i \alpha_j}{R_{ij}^4} (-1)^k C(123; k\bar{k}) C_{2,k}(\omega_j)$$

where now  $\omega_j$  represents the angular orientation of molecule  $j$  with respect to the pair axis. Therefore, the transition moment is

$$\langle Q_v(0)_i + S_0(0)_j | \mu_k^{ij} | 0 \rangle = (-1)^k (3)^{1/2} C(123; k\bar{k}) \frac{Q_j \langle v | \alpha | 0 \rangle}{R_{ij}^4} \delta_{m,k}$$

Where  $m$  is the projection of the angular momentum onto the axis connecting the pair of molecules. To conserve angular momentum only simultaneous transitions to the  $m = k = 0, \pm 1$  pair frame states are allowed. Comparison of the simultaneous and single-molecule transitions requires that they be described in the same frame of reference. Transformation of the  $m = 0, \pm 1$  pair frame states into linear combinations of crystal states  $M = \pm 2, \pm 1, 0$  provides an equivalent description of the simultaneous state in the crystal frame. In contrast to the single-molecule transition, the symmetry changes in transition between the ground and excited states in the simultaneous excitation. Because of this change in symmetry from  $D_{3h}$  to  $C_3$  and the corresponding change in the orientation of the quantization axis upon transition to the simultaneous state, all crystal frame  $M'$  levels contribute to the description of the optically active double molecule excitation ( $Q_v(0) + S_0(0)$ ). Once both transitions are in the same reference frame, one can explicitly calculate the angularly dependent interactions connecting the  $M = \pm 2$  levels of the  $S_v(0)$  manifold and all  $M$  levels of the  $S_0(0)$  roton in the  $Q_v(0) + S_0(0)$  manifold. These matrix elements have been calculated for both in and out of plane pairs using the expression for the  $EQQ$  interaction given in eq 2 to mix contributions from all possible  $M$  levels of the  $S_0(0)$  excitation into the  $S_v(0)$  wave function.

The microscopic transition moment at any lattice site is then given by the matrix element between the initial and final states where one considers the final state to be a combination of single ( $S_v(0)$ ) and double ( $Q_v(0) + S_0(0)$ ) molecule probability amplitudes. Defining the vibrational excitations as being placed

on molecule  $i$ , the  $EQQ$  interaction only allows for the delocalization of the roton onto sites  $R_j$  since it only mixes rotational levels. Since all lattice sites are equivalent and the lattice provides a periodic potential, the Bloch waves describe the possible excited states,  $U(\mathbf{R}_i)$  which are of the form<sup>11,31</sup>

$$U(\mathbf{R}_i) = (1/N)^{1/2} e^{-i\mathbf{k}\mathbf{R}_i} |\Psi_i^M\rangle \quad (7)$$

where  $|\Psi_i^M\rangle$  is given by eq 1. This wave vector, or the total exciton momentum, gives the phase of the probability amplitude  $|\Psi_i^M\rangle$  at site  $\mathbf{R}_i$ . Using  $U(\mathbf{R}_i)$  from eq 7 as the wave function, the microscopic transition moment can be obtained at each lattice site,  $\mathbf{R}_i$  (eq 8).

$$\begin{aligned} \sum_M \langle S_v(0)_i^M + \sum_j \sum_{M'} T(\mathbf{R}_{ij})^{M,M'} [Q_v(0)_i + S_0(0)_j^M] \rangle |\mu_k^i + \mu_k^{ij}|0\rangle e^{-i\mathbf{k}\mathbf{R}_i} = \sum_M \{ \langle S_v(0)_i^M | \mu_k^i |0\rangle + \sum_j \sum_{M'} T(\mathbf{R}_{ij})^{M,M'} \langle Q_v(0)_i + S_0(0)_j^M | \mu_k^{ij} |0\rangle \} e^{-i\mathbf{k}\mathbf{R}_i} \quad (8) \end{aligned}$$

These microscopic moments are then summed over all lattice sites to obtain the total macroscopic transition moment:<sup>11</sup>

$$\mu_k^{\text{total}} = \sum_{R_i} [\mu_k^i + \mu_k^{ij}] \quad (9)$$

Assuming an infinite lattice and no impurities, all molecules in the lattice are identical before excitation; therefore, a molecule's transition moment is independent of the lattice site at which the excitation will eventually be located. As a result, the transition moment factors out of the sum over lattice sites  $\mathbf{R}_i$  from eq 9 due to the translational symmetry of the lattice, yielding

$$(1/N)^{1/2} \left\{ \sum_M \langle S_v(0)^M | \mu_k^{(1)} |0\rangle + \sum_j \sum_{M'} T(\mathbf{R}_{ij})^{M,M'} \langle Q_v(0) + S_0(0)_j^{M'} | \mu_k^{(2)} |0\rangle \right\} \sum_{\mathbf{R}_i} e^{-i\mathbf{k}\mathbf{R}_i}$$

where  $\mu_k^{(1)}$  and  $\mu_k^{(2)}$  are the single- and double-molecule transition moment operators, respectively, which are independent of the lattice site  $\mathbf{R}_i$ . Utilizing the fact that eq 10 is a discrete  $\delta$  function for  $\mathbf{k} = 0$ :

$$(1/N) \sum_{\mathbf{R}_i} e^{-i\mathbf{k}\mathbf{R}_i} = \delta_{\mathbf{k}=0} \quad (10)$$

one obtains eq 11 which illustrates the  $\Delta\mathbf{k} = 0$  overall momentum selection rule allowing transitions to only one state of the entire band; this selection rule characterizes transitions in pure solids and is especially clean and obvious in the case of solid  $p\text{-H}_2$  due to the weak intermolecular interactions.<sup>11</sup> Here the selection rule, shown in eq 11 below, governs only the total exciton momentum  $\mathbf{k} = \mathbf{k}_{Q_v(0)} + \mathbf{k}_{S_0(0)} = \mathbf{k}_{S_v(0)} = 0$ , characterizing the final state:

$$N^{1/2} \left\{ \sum_M \langle S_v(0)^M | \mu_k^{(1)} |0\rangle + \sum_j \sum_{M'} T(\mathbf{R}_{ij})^{M,M'} \langle Q_v(0) + S_0(0)_j^{M'} | \mu_k^{(2)} |0\rangle \right\} \delta_{\mathbf{k}_Q + \mathbf{k}_S = 0} \quad (11)$$

This  $\delta$  function governing the total exciton momentum of the simultaneous transition, not those of the roton and vibron separately, is indicative of double transitions in that there is no interference between the two excitations due to the fact that

two molecules simultaneously absorb one photon.<sup>11,12</sup> This  $\delta$  function also governs the total exciton momentum of the  $S_v(0)$  rovibron. As a result of this  $\Delta\mathbf{k} = 0$  selection rule, the intensity of the  $\mathbf{k} = 0$  level is  $N$  times stronger than would be observed in the absence of this momentum selection rule. The only active state of the entire band is that characterized by  $\mathbf{k} = 0$ .

In the case of the single transition, the  $S_v(0)$  exciton is generated with wave vector  $\mathbf{k} = 0$ . In a pure crystal, the  $EQQ$  interaction gives rise to no additional broadening;<sup>13</sup> thus, since the  $\mathbf{k} = 0$  level is very narrow, broadening can arise only from the natural lifetime of the rotational excitation which, from the experimental data on the  $S_0(0)$  transition, has been determined to correspond to a line width of approximately  $0.1 \text{ cm}^{-1}$ .<sup>32</sup> Due to the mixing of the double transition into the  $S_v(0)$ , however, another situation arises. The simultaneous state  $Q_v(0) + S_0(0)$  is initially excited with the total wave vector  $\mathbf{k} = \mathbf{k}_Q + \mathbf{k}_S = 0$ .<sup>11</sup> The  $Q_v(0)$  and  $S_0(0)$  excitations can, however, hop separately throughout the lattice. The Bloch state (eq 7) and  $\Delta\mathbf{k} = 0$  selection rule only hold due to the periodicity of the potential for the entire exciton  $\mathbf{k} = \mathbf{k}_Q + \mathbf{k}_S = 0$ . The presence of the vibrationally excited ( $Q_v(0)$ ) molecule next to the rapidly hopping  $S_0(0)$  roton destroys the lattice periodic potential in which the roton hops. In other words, since all molecules are involved in the hopping process, the phase relation between the two isolated excitons is changed upon hopping of either exciton, and our initially excited state of  $\mathbf{k}_{\text{total}} = 0$  can no longer be measured due to this phase decay. A similar mechanism is successfully employed by Morishita and Igarashi in describing the absorption profile of the  $Q_v(0) + S_0(0)$  simultaneous state. In their situation, however, many different overall  $\mathbf{k} = 0$  states are accessed, each having different energy; they merely need to satisfy the relation,  $\mathbf{k}_Q = -\mathbf{k}_S$ . As a consequence of this momentum selection rule for the double transition, many different values of the wave vectors for the  $Q$  and  $S$  transitions are allowed, as long as they add up to zero. They explicitly calculate the multiple scattering effect of the vibron on the phase of the roton.<sup>12</sup> The state which we are concerned with, however, is infinitely narrow (in the absence of relaxation) due to the fact that by starting from the degenerate  $M = \pm 2$ ,  $\mathbf{k} = 0$  state in the  $S_v(0)$  manifold, the mixing in of the double transitions does not lift the  $M$  degeneracy, nor does the interaction broaden the original perturbed state. From the familiar expression for the second-order energy due to perturbation, if only one energy level mixes with any number of others at different energies, still only one level with a perturbed energy is obtained.<sup>33</sup> Each of the contributing  $\mathbf{k} = 0$  simultaneous states in the overall perturbed  $S_v(0)$  wave function (eq 11) can decay into the many  $\mathbf{k} \neq 0$  simultaneous states upon  $EQQ$ -mediated roton hopping, resulting in the observed, previously unexplained  $S_v(0)$  line-widths.

To calculate the  $S_v(0)$  line width, we first need to use eq 3 to calculate the strength of the  $EQQ$  interaction which connects the two manifolds ( $S_v(0)$  and  $Q_v(0) + S_0(0)$ ). Using values of the quadrupole matrix elements calculated by Karl and Poll<sup>34</sup> and using  $R_0 = 3.794 \text{ \AA}$  as the intermolecular separation between nearest neighbors, one can readily calculate  $\epsilon_{22}$ . The angular dependence is more complicated. Contributions from both in plane (ip) and out of plane (op) lattice sites are mixed into the wave function, yielding a  $J = 2$  roton on a surrounding molecule ending up in any of the possible values of  $M'$ . Keeping the infrared selection rule,  $\Delta m^{\text{pair}} = 0, \pm 1$ , in mind, the actual populations of the  $M^{\text{crystal}}$   $S_0(0)$  levels are readily determined by rotating the coordinate system from the pair frame to that of the crystal. So the  $EQQ$  interaction (eq 4) mixes the  $S_v(0)$   $M = \pm 2$  manifold with the entire  $M$  manifold of the roton

within the simultaneous state. Due to the angular dependence of the  $EQQ$  interaction potential, each lattice site yields a different contribution to the probability of forming a simultaneous state.

Rotational excitations hop much more readily among molecules due to the greater strength of the  $EQQ$  interaction than that of the vibrational coupling interaction. As a result one can regard the vibron as localized relative to the roton due to its slower motion. As an excitation hops throughout the lattice, it encounters lattice imperfections and impurities which destroy the lattice symmetry, thus destroying the  $\Delta\mathbf{k} = 0$  exciton momentum selection rule. As used previously in deriving the transition moment, all molecules must be identical for one to factor the transition matrix element out of the lattice sum which then gives rise to the  $\Delta\mathbf{k} = 0$  selection rule according to eq 11. As a result of the asymmetric potential it creates, an impurity alters the initially prepared phase of the roton as the roton hops, thus rendering it unable to be measured.<sup>12</sup> This change in phase manifests itself as a  $T_2$  phase relaxation leading to uncertainty in the measured frequency of the transition. Due to small admixtures of the  $Q_v(0) + S_0(0)$  simultaneous states in the overall " $S_v(0)$ " transition, the roton and vibron are created simultaneously on nearby molecules. The then independently hopping roton experiences the vibron as an impurity which scatters its phase, thus involving all the molecules in the lattice. The mere fact that the double transition has been made and the roton can hop independently of the vibron creates uncertainty in the frequency of the transition. The act of hopping destroys the phase relationship between  $\mathbf{k}_Q$  and  $\mathbf{k}_S$  which was established upon initial excitation in the pure parahydrogen lattice, thus rendering the initially excited state unmeasurable. Consequently, this mixing in of the double transition presents a new situation which gives rise to a broadening of "single" rovibrational transitions.

If we treat this destruction of phase as the system relaxes from the  $|S_v(0)\rangle_{\mathbf{k}=0} + \sum T(\mathbf{R})|Q_v(0) + S_0(0)^M\rangle_{\mathbf{k}=0}$  state to the  $|S_v(0)\rangle_{\mathbf{k}=0} + \sum T(\mathbf{R})|Q_v(0) + S_0(0)^M\rangle_{\mathbf{k}=0}$  manifold, the overall line width of the observed transition will be given by the square of the mixing in of  $|Q_v(0) + S_0(0)\rangle_{\mathbf{k}=0}$  multiplied by the rate of decay.<sup>35,36</sup> Since the hopping of the roton destroys the phase relations between the ground and excited states (much like collisional broadening) and, as previously established, rotors hop much more quickly than do rovibrons, the rate of  $S_0(0)$  exciton hopping gives the decay rate of the infrared active transition. The  $S_v(0)$  line width is then given by

$$\Delta\nu_{S_v(0)} = [A_v^2 \Gamma_{S_v(0)} + \sum_M \{ (\sum_j |T(\mathbf{R}_{ij})|^{\pm 2M}|^2) (\Gamma_{S_0(0)} + \sum_n \sum_{M'} \langle 2M'_n | V_{jn}^{EQQ} | 2M_j \rangle \rangle) \}] \quad (12)$$

Since the mixing due to the  $EQQ$  interaction falls off as  $R^{-5}$ , only nearest neighbors are considered to undergo a simultaneous transition. By summing over all 12 nearest neighbors, we obtain the square of the total mixing (i.e., the total probability) for the simultaneous states' contributions to the observed transition. The angular portions of the  $EQQ$  matrix elements (calculated both manually and with a program provided by Teresa J. Byers) giving the mixing of each  $M'$  level of the  $S_0(0)$  roton in the  $Q_v(0) + S_0(0)$  simultaneous state with the  $M = \pm 2$  levels of  $S_v(0)$  were calculated at each lattice site using eq 4, where  $\epsilon_{22}$  and  $W_v$  depend on the transition being studied. Note that in the above equation the mixing of wave functions and the ensuing dynamics are separate. Every molecule has a wavefunction given by eq 7 with a nonzero density of simultaneous states at each lattice site. The total line width is given by the sum of

**TABLE 1: Comparisons of  $S_v(0)$  Line Widths: Experiment vs Theory Using Eq 12**

observed transition	measured line width (fwhm, $\text{cm}^{-1}$ )	total calculated line width (fwhm, $\text{cm}^{-1}$ )
$S_1(0)$	$0.9 \pm 0.2$	$1.10 \pm 0.06$
$S_2(0)$	$0.55 \pm 0.10$	$0.484 \pm 0.02$
$S_3(0)$	$0.25 \pm 0.05$	$0.321 \pm 0.02$

(a) the population of the pure  $S_v(0)$  state multiplied by its natural decay rate and (b) the probability of forming the  $\mathbf{k} = 0$  simultaneous state multiplied by the sum of the  $S_0(0)$  natural decay rate and the rate of  $S_0(0)$  dephasing to the bath of  $\mathbf{k} \neq 0$  states as a result of the  $EQQ$  interaction. The central molecule,  $i$ , has 12 nearest neighbors,  $j$ , on which the  $S_0(0)$  roton can be initially located. After a time given by the inverse of the  $EQQ$  hopping rate for a  $J = 2$  roton, the  $S_0(0)$  excitation can hop to any of its nearest neighbors,  $n$ , with any orientation,  $M'$ , relative to the crystal axis. The dephasing upon hopping of the  $S_0(0)$  roton which was created next to a vibrational impurity in the double molecule transition gives the decay of the initially prepared  $\mathbf{k}_{\text{total}} = 0$  state, and thus the major source for the line width of the transition.

Although a  $T_2$  process, this relaxation mechanism, analogous to collisional broadening, is a homogeneous effect; a Lorentzian line shape should be obtained. The fact that three different relaxation mechanisms are inherently present in a pure  $p\text{-H}_2$  sample (see the last equation) and the fact that any impurities such as  $o\text{-H}_2$  will lead to inhomogeneous broadening, due to the destruction of the initial  $\Delta\mathbf{k} = 0$  selection rule, complicate the observed line shape. Additionally, due to mixing with the simultaneous state, the  $|M| \neq 2$   $S_v(0)$  levels also become weakly allowed. These will appear slightly shifted in energy from the main  $|M| = 2$  transition. The line width due to the convolution of three Lorentzians is given by the addition of their line widths; therefore, the total calculated line widths (see Table 1) are the sum of the individual contributions from the  $S_v(0)$  and  $S_0(0)$  natural linewidths (both approximately  $0.1 \text{ cm}^{-1}$  as determined from Schoemaker's Raman-active  $S_0(0)$  line width) and the herein calculated line-width contribution from roton dephasing. The natural line widths of the zeroth order  $S_v(0)$  states should be similar to that of the  $S_0(0)$  since they are all  $\Delta\mathbf{k} = 0$  rotational transitions with comparable rotational energies which are all well above the Debye frequency. The signal-to-noise ratio of approximately 10, however, limits the line-shape analysis.

Several approximations have been made in these line-width calculations. The calculated quadrupole moments for the second overtones were not part of those presented by Karl and Poll.<sup>34</sup> A linearly extrapolated value of the quadrupole moment (0.63 atomic units) was used to calculate  $\epsilon_{22}$  for  $S_3(0)$  mixing with the  $Q_3(0) + S_0(0)$  manifold. This quantity itself introduces some error. Also, as previously mentioned, only nearest neighbors were considered to be able to undergo a double transition. Rough calculations indicate that next nearest neighbors have a much smaller probability of simultaneously absorbing one photon. The total contribution to the line width from this process should be approximately 2% of the nearest-neighbor contribution. A bit of uncertainty in the value of  $W_v$  comes from the frequencies of the  $S_0(0)$ ,  $S_v(0)$ , and  $Q_v(0)$  transitions used in its calculation. The Raman transitions were used for  $Q_2(0)$  and  $Q_3(0)$ , while an approximation to the center of the band was used for  $Q_1(0)$ . The  $S_0(0)$  transition, meanwhile, has three Raman active transitions, that used here was  $355.7 \text{ cm}^{-1}$  corresponding to the IR-active  $|M| = 2$  transition. Additionally, the decay rate of the transitions  $S_v(0)$  should all be approximately the same. They were all assumed to be  $0.1 \text{ cm}^{-1}$ , but these should be more accurately measured.

The observed lack of polarization dependence strongly supports this proposed mechanism. All  $M$  levels of the  $S_0(0)$  roton mix in with the  $S_v(0)$  state. Since the density of states in the simultaneous transition is so large and the intensity is enhanced by the  $\Delta k = 0$  selection rule, the mixing gives comparable intensity to that of the zeroth-order  $S_v(0)$  state itself. As a rough experimental test, by using Lee's  $S_2(0)$  and  $Q_2(0) + S_0(0)$  integrated intensities, upon squaring eq 11 to get the intensity, the contribution to the intensity from the simultaneous state multiplied by the square of the mixing is 2.2 times as large as that from the zeroth-order  $S_2(0)$  state. This indicates that as a result of the strong contribution to the overall intensity of the simultaneous state, no obvious polarization dependence should be observed since both parallel and perpendicular polarizations give rise to  $\mathbf{k} = 0$   $Q_v(0) + S_0(0)$  simultaneous transitions. By calculating the parallel and perpendicular simultaneous state transition moments in the pair frame and transforming them into the crystal frame for in and out of plane cases, the intensities should be in a ratio of 1:1.145; parallel:perpendicular relative to the crystal axis. If the simultaneous state were not contributing significantly to both the intensity and the line width, a strong polarization dependence should be observed since only the perpendicular  $S_v(0)$  transition is allowed due to symmetry considerations. The signal-to-noise ratio with chopper modulation was not large enough to detect any subtle difference in intensity in the  $S_3(0)$  transition, but no drastic intensity change was observed. If no mixing of states were occurring, the line widths would also be much narrower than those which are observed.

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