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Infrared activity of hydrogen molecules trapped in Si

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The rovibrational-translational states of a hydrogen molecule moving in a cage site in Si, when subjected to an electrical field arising from its surroundings, are investigated. The wave functions are expressed in terms of basis functions consisting of the eigenfunctions of the molecule confined to move in the cavity and rovibrational states of the free molecule. The energy levels, intensities of infrared and Raman transitions, effects of uniaxial stress, and a neighboring oxygen defect are found and compared with existing experimental data.

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Hydrogen molecules have long been expected to be low-energy defects in Si, but the observation by infrared (IR) absorption of what appeared to be isolated hydrogen molecules trapped at cage sites was quite unexpected. While there is no difficulty in understanding that molecules trapped at low-symmetry sites in a range of materials would be IR active, the same is not true with molecules at tetrahedral cage sites in Si. The usual argument to explain their activity is that the lattice electric field $F_i$ induces a dipole moment $\alpha_i F_i$ on the molecule in direction $i$. Here, $\alpha_i$ is the molecular polarizability. However, the electric field at the $T_2$ cage site is actually zero, and a zero-point movement of the center of mass of the molecule has been invoked to provide an interaction. Now, if the molecule can freely rotate, Condon noted that this dipole moment couples with the electric field of the IR radiation and leads to the same selection rules as for Raman scattering: namely, $\Delta j = 0$ or 2. In addition, transitions involving both ortho-$H_2$ with $j=1$, and para-$H_2$ with $j=0$, should occur and hence four IR transitions are expected at low temperatures. However, experiments indicate that only one mode at 3618.4 cm$^{-1}$ is detected. This has led to suggestions that the molecule is static but recent studies demonstrate that this is not correct and the mode arises from a $\Delta j = 0$ transition from a degenerate $j = 1$ state. Thus it appears that the para-$H_2$ species is not IR active – possibly because of symmetry reasons. A further difficulty then emerges when considering the transitions for HD. Two transitions are detected corresponding to $\Delta j = 1$ and $\Delta j = 0$. The first disagrees with Condon’s analysis and implies that something new is needed.

We show here, using a simple model, that the infrared intensity does not arise from the polarization induced in the molecule undergoing zero-point motion, but from a polarization of the Si lattice by the electric field arising from the quadrupole moment of a rotating molecule. Further, we show that the ground state of the para-$H_2$ species transforms as $A_1$ and the only dipole allowed transition involves a so far undetected $\Delta j = 2$ transition. Transitions between $T_2$ states accounts for the observed $\Delta j = 0$ transition. The effect of a nonuniform electric field due to the lattice on the molecule is crucially important in understanding the activity of HD. We show that two transitions with $\Delta j = 0$ and 1 then arise. Moreover, the model accounts for the effect of stress and a nearby oxygen impurity on the molecular spectrum.

The Hamiltonian of the molecule moving in the cage surrounding a tetrahedral site contains kinetic and potential terms dependent on the center-of-mass coordinates, defined by spherical polar coordinates $(R, \Theta, \Phi)$, as well as internal coordinates defined by the molecular length and orientation in space $(r, \theta, \phi)$ with the axes assumed parallel to the cube edges. For a spherical cavity, the translational motion leads to a center-of-mass wave function described by $f_i(R) Y_{LM}(\Theta, \Phi)$, and the internal motion to rovibrational wave functions $\chi_j(r-r_c) Y_{jm}(\theta, \phi)$. For illustrative purposes, we take $f_i(R)$ to be a $\delta$ function so that the center of mass is at a fixed distance, $R \approx 0.13$ Å, from the $T_2$ site: a value consistent with the zero-point displacement found by molecular dynamics. Our results are, however, insensitive to $R$. The electric field $F_i$ arising from the lattice is modeled by placing charges of $4e$ on each Si atom and $-2e$ at each bond center and, where relevant, an additional $-e/9$ on a bond centered oxygen interstitial. Such a field is at the upper limit of what is to be expected. We have assumed that there is no charge density at the $T_2$ site. In fact, this leads to a reduction in the vibration frequency of the molecule which we can take into account by reducing the molecular stretch force constant. The potential energy of the molecule depends on the electric field $F_i$ and its gradient $F_{ij}$ at the center of the molecule and is given by:

$$-\frac{1}{2} \alpha_{ij} F_i F_j - \frac{i}{2} \Theta_{ij} F_{ij},$$

where the polarizability and quadrupole moment are expressed in terms of the molecule alignment $r$ by:

$$\alpha_{ij} = \alpha(r) \delta_{ij} + \frac{\gamma(r)}{3r^2}(3r_i r_j - r^2 \delta_{ij}),$$

$$\Theta_{ij} = \frac{1}{2r^2} \Theta(r)(3r_i r_j - r^2 \delta_{ij}).$$

This energy depends on both the position of the center of mass and the molecular alignment. Figure 1 shows this molecular potential energy, which is dominated by the quadrupole term, of the $H_2$ molecule when the center of mass is located at $(R, \Theta, \Phi)$, with $R = 0.13$ Å, while aligned along $\Theta=\Phi=\Phi$ with $r$ equal to the equilibrium bond length $r_e$.

We note that variations in the potential are $\sim \pm 200$ cm$^{-1}$ and directions where the molecule is aligned away from the four Si neighbors are favored. The weak potential is consistent with ab initio calculations and would not prevent molecular rotation. This justifies our use of basis states made from those of a freely rotating molecule. The Hamiltonian...
matrix elements for each vibrational state \( \nu \), in the absence of \( F_j \), are \( \hbar \omega_0(\nu + 1/2) + B_{ij}(j+1)/\mu + 2L\Delta/M \). Here, \( \omega_0, B_{ij}, \mu \), and \( M \) are the fundamental stretch frequency, rovibrational constant, reduced mass, and total molecular mass. \( 2\Delta/M \) is the energy separation between \( L=0 \) and 1 cavity states that we take for \( H_2 \) to be \( \sim 1000 \text{ cm}^{-1} \) which again can be related to the energy profile of the molecule around the \( T_d \) site.\(^1\) A Taylor series expansion of \( \alpha(r), \gamma(r), \) and \( \Theta(r) \) about \( r_e \) with the molecular constants taken from Refs. 7 and 17 enabled the potential-energy matrix elements to be found numerically using Lebedev’s method. Matrix elements of this Hamiltonian between different rotational, \( j < 6 \), and cavity states, \( L<2 \), were found for each \( \nu \) and the energy levels and wave functions determined.

The intensity of an infrared transition between states \( |\nu = 0,n \rangle \) and \( |\nu = 1,m \rangle \) is related to the transition dipole moment \( P_i(n,m) \) in direction \( i \). This has two contributions: the first comes from the induced dipole, as given by Condon, and the second comes from the dipole induced in the Si lattice by the molecule. The second term is from the field \( F_j(a) \) arising from the quadrupole moment of the molecule at the site of an atom \( a \) with atomic polarizability \( \alpha_a \):\(^2\)

\[
P_i(n,m) = \begin{cases} 
\nu=0,n & |\alpha_j F_j + \sum_a \alpha_a F_j(a) | \nu=1,m \\
\sim \sqrt{\frac{\hbar}{2\mu \omega_0}} \left| \alpha_j \right|^2 F_j(a) \sum_a \alpha_a F_j(a) \right| m 
\end{cases}
\]

where the prime denotes the derivative with \( r \). The effective charge for the oscillator is \( \sqrt{2\mu \omega_0 \sum_a |P(n,m)|^2/(3\hbar)} \),\(^1\) where the sum is over degenerate \( n \) and \( m \) states. The first term in \( P_i \) is zero when \( R=0 \) as then \( F_j \) vanishes and is of order \( 10^{-3} e \) for \( R \sim 0.13 \text{ Å} \). The second term dominates and

FIG. 2. \( z \) component of effective charge vector \( \alpha_j(\theta,\phi)F_j + \sum_a \alpha_a F_j(a) \), in units of \( e \), of a \( H_2 \) molecule at the \( T_d \) site vs \( \theta, \phi \) describing its alignment. Note that the effective charge varies by \( \pm 0.15 e \).

Fig. 2 shows that its \( z \) component has a magnitude compatible with the experimental effective charge of \( \sim 0.08 e \).\(^4\) The strength of a Raman transition is proportional to \( \sum |\alpha_j(\theta,\phi)|^2 \). Condon’s result is easily derived from Eqs. (1) and (2) when \( F_j \) is a fixed uniform field.

Rotating \( H_2 \) by \( 180^\circ \) about its center of mass leaves the Hamiltonian and dipole moment unchanged. This symmetry allows us to classify each state as “even,” \( + \), or “odd,” \( - \), corresponding to para- and ortho-hydrogen, respectively.

For \( H_2 \), the ground state has \( A_1^+ \) symmetry and is derived from orbitals with even \( j \), while the first excited state has \( T_2^+ \) symmetry and arises from orbitals with odd \( j \). Both states have contributions from the \( L=0 \) and \( L=1 \) cavity orbitals. Figure 3 shows the ground-state wave function that is peaked in the troughs of the potential, i.e., in the direction away from the Si atoms.

FIG. 3. \( A_1^+ \) wave function for center of mass of \( H_2 \) molecule at \( (R,\Theta,\Phi) \), with \( R=0.13 \text{ Å} \), and aligned along \( (\Theta,\Phi) \). Note that the peaks correspond with directions away from the four Si neighbors. The wave function is normalized over the surface of a sphere.
are now possible as shown in Fig. 4. Good agreement with the experimental value of 71 cm−1 was found in Ref. 9, transitions between 

transition and parity must be conserved. Thus, as noted in

weaker transitions is 2.6:1 compared with 2:1 found here. The

dipole moment transforms as $T_2^+$ and hence an orbitally

degenerate state must comprise the initial or final IR transition and parity must be conserved. Thus, as noted in Ref. 9, transitions between $A_1^+$ states are IR inactive, in contrast with transitions between $T_2^-$ states of ortho-hydrogen. Figure 4 shows the lowest-energy states and their symmetries for $\nu=0$ and 1 along with the intensities of the IR and Raman-active transitions between them. An IR-active transition [not shown in Fig 4(a)] involving para-H₂ between $A_1^+$ and $T_2^-$, derived primarily from a $j=2$ orbital, occurs at 340 cm$^{-1}$ above the ortho-transition with an effective charge of $-0.1e$, but this has not been detected. The only detected transition, labeled $a$ in Fig 4(a), has a strength in good agreement with the calculation. Very recently, Raman scattering has detected the transition between $A_1^+$ states in both H₂ and D₂.19

For HD on the other hand, rotating the molecule by 180° about its center of mass displaces the center of the molecule to a new location. Its interaction with the surrounding lattice is then changed, as the field $F_i$ is nonuniform, and the Hamiltonian and dipole moment are now different. Parity is then not conserved and transitions between $A_1$ and $T_2$ states are now possible as shown in Fig. 4(b). At low temperatures, only the $A_1\rightarrow T_2$ $b$ transition is seen but the stronger transition between $T_2$ states, labeled $a$, is detected at 23 K after molecules have been thermally excited from $A_1$ to $T_2$. The experimental ratio of the effective charges for the $a$ and $b$ transitions is 2.6:1 compared with 2:1 found here. The weaker $T_2\rightarrow A_1$ transition $c$ has not been reported to date. The calculated $\nu=0,A_1-T_2$ separation of 74 cm$^{-1}$ is in very good agreement with the experimental value of 71 cm$^{-1}$.

Application of a general stress results in a displacement of the lattice and a change to the field $F_i$. The symmetry is now lowered leading to a splitting of the $T_2^-$ levels. We take the atomic displacements to be given by elasticity theory and Fig. 5 shows the calculated splittings in the $T_2^-$ manifolds for H₂. We find the piezospectroscopic parameters $B_g$, $C_g$, $B_e$, and $C_e$ (Fig. 5), respectively, to be 4.3, 5.4, 4.6, and 5.5 cm$^{-1}$ GPa$^{-1}$. These are in excellent agreement with experimental values of 4.5, 5.4, 4.5, and 5.4 cm$^{-1}$ GPa$^{-1}$ found by assuming identical shifts for $\nu=0$ and $\nu=1$. For D₂, we get 4.1, 5.3, 4.2, and 5.9 cm$^{-1}$ GPa$^{-1}$ demonstrating that the splittings are almost independent of isotopic mass in agreement with earlier theoretical and experimental findings.12 As has been noted previously, this result arises from the mass independence of the interaction given in Eq. (1).

The presence of oxygen at a neighboring bond center site leads to an additional electric field and a change in symmetry to $C_{1h}$, or to $C_{sb}$ if the lattice field is negligible. This also results in a splitting of the $T_2$ states and to a greater number of IR transitions. We assume that the perturbation by oxygen can be modeled by a single point charge, and neglect the strain due to the impurity, and show in Fig. 6 the spectra for H₂, HD, and D₂. Experimentally for H₂, transitions $a$, $b$, and $c$ are detected in agreement with the calculations with the energy separations $c-b$ and $a-b$ being 6.1 and 57.9 cm$^{-1}$, respectively, compared with 10 and 68 cm$^{-1}$ found here.

For HD, four transitions, $h$, $b$, $a$, and $d$ are observed—two weak ones from the ground and two from the first excited...
state. We find that transitions \( a \rightarrow h \) are all active with transitions \( b \rightarrow e \) all being of similar activity. The energy separations and transition strengths found here for all the defects are not especially sensitive to the parameters \( R \) and \( \Delta \), but in the case of oxygen, they are sensitive to the assumed charge on oxygen and clearly the model will only obtain the correct transitions if this is modeled correctly. If the lattice polarization is reduced with respect to the charge on oxygen, then agreement is found with experiment in that only two dominant transitions \( b \) from the ground, and \( a \) from the first excited state, occur. The separation of \( b \) and \( a \) according to our theory is 40 cm\(^{-1}\) and about twice the observed value of 19 cm\(^{-1}\) but the separation between \( a \) and \( d \) is 48 cm\(^{-1}\) in fair agreement with experiment at 58.6 cm\(^{-1}\). Much better agreement with the experimental ortho-para splitting has been found by a similar method but using a quite different perturbing potential.\(^1\)

In conclusion, we have found that the IR activity of the molecule does not require a movement of the molecule away from the tetrahedral site, as has been thought previously, but a polarization of the surrounding lattice. The effective charges relating to the strengths of the IR transition are then the same for \( \text{H}_2 \) as \( \text{D}_2 \) and in agreement with the data, unlike a model where the activity arises from a displacement of the molecule from the lattice site.\(^2\) The splitting of the lines observed under stress, or by the presence of a neighboring oxygen impurity, can be modeled in a simple way and the results are in reasonable agreement with experiment. The analysis shows that there are other as yet undetected IR transitions at low temperatures albeit with low intensities. The method we have introduced is clearly applicable to molecules in a wide range of materials, e.g., GaN.

Finally, we note an interesting consequence of the splitting of the \( T_2^\text{v} \) state of \( \text{H}_2 \) in the presence of oxygen. The energy separation between the energetically lowest ortho-\( A^\prime^\text{v} \) state and para-\( A^\prime^\text{v} \) states is only 82 cm\(^{-1}\) for \( \text{H}_2 \) near O, compared with 118 cm\(^{-1}\) for \( \text{H}_2 \) at a \( T_d \) site. This implies that ortho molecules would favor the former sites. It is known that \( \text{H}_2 \) is weakly bound to oxygen with a binding energy about 0.28 eV.\(^2\) Upon warming to around 30°C, molecules move reversibly between the two sites. Thus ortho-\( \text{H}_2 \) near oxygen sites is in equilibrium with the same nuclear species at \( T_d \) sites. This is also true for the para species. However, the binding energy of ortho-\( \text{H}_2 \) at O sites is lower by 118 – 82 or 36 cm\(^{-1}\) than for para-\( \text{H}_2 \). Thus, the equilibrium fraction of ortho- to para-\( \text{H}_2 \) species at oxygen sites should be about 20% larger than at \( T_d \) sites. Such an effect has not yet been reported.

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7. This ignores splitting of the \( j = 2 \) state into \( T_2 + E \).
19. We take \( \alpha \) to be 20 au and related to the bulk Si dielectric constant by the Clausius-Mossotti relation \( \alpha = (3/\varepsilon_0) \times ((\varepsilon_1 - 1)/(\varepsilon_1 + 2)) \) (see Ref. 24).