Hydrogen molecules in silicon located at interstitial sites and trapped in voids

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Abstract

The vibrational modes of H_2 molecules in Si are found using a first-principles method and compared with recent experimental investigations. The isolated molecule is found to lie at a T_d interstitial site, oriented along [011] and is infrared active. The rotational barrier is at least 0.17 eV. The molecular frequency is a sensitive function of cage size and increases to lie close to the gas value for cages about 50% larger than the T_d site. It is suggested that

Raman-active modes around 4158 cm^{-1} are due to molecules within voids.

61.72.Bb, 63.20.Pw

The identification of a molecular form of hydrogen in Si has been a major challenge ever since an interstitial species was, to the best of our knowledge, first proposed by theory.[1,2] Recently, a vibrational band at 1075 cm^{-1} due to an oxygen-hydrogen defect was detected by Fourier transform infrared spectroscopy in Czochralski-grown Si which had been soaked in hydrogen at high temperatures.[3] The presence of hydrogen in the defect was confirmed by an upward shift of 1 cm^{-1} when H was replaced by D. Subsequent work[4] showed that the 1075 cm^{-1} band was composed of a line at 1075.1 cm^{-1} and a shoulder at 1075.8 cm^{-1}. Satellite bands were detected below the main peak, and are analogous with similar satellites seen for interstitial oxygen and attributed to ^{29}Si-^{16}O-^{28}Si and ^{30}Si-^{16}O-^{28}Si defects. This strongly implies that oxygen is also involved in its normal bond centered location. Studies using mixtures of H and D showed that two hydrogen atoms were involved in each of the closely related defects.

The infrared measurements also revealed sharp H-related modes labeled ν_1, ν_2, and ν_3 at 3789, 3731, and 3618 cm^{-1} which shifted downwards by approximately a factor of $\sqrt{2}$ in the D case. In the mixed H-D case, an additional mode lay midway between the H-H and D-D modes for each ν_i, proving that the hydrogen atoms are bonded together. The integrated intensities of ν_1 and ν_2 were correlated with the oxygen related 1075 cm^{-1} band implying that the molecule is located near an oxygen atom in these defects. Recently, studies have been made to find the effect of annealing on the 1075 cm^{-1} and ν_3 bands.[5] On heating between 50 and 130°C the intensities of ν_1, ν_2, and the 1075 cm^{-1} band decreased and there was a correlated increase in the intensity of the ν_3 band. These are reversible changes so that reheating the samples again at a lower temperature results in a decrease in the intensity of ν_3 and a recovery of the other bands. This can be understood if the molecule in the ν_3 site is less stable than those in the ν_1 and ν_2 centers but has a greater entropy, and lower free energy at 130°C arising from a greater number of available sites. The annealing study then showed that the number of sites for ν_3 was equal, to within a factor of about 2, to the number of interstitial T_d sites. This strongly suggests that ν_3 is associated with the isolated molecule and is consistent with the observation of the same mode in float-zone Si which had been soaked in hydrogen.[4]

This assignment, however, causes several problems. First, there is no splitting of the ν_3 band due to ortho- and para-forms of the molecule. Secondly, the infrared activity of the molecule is unexpected, and thirdly the position of the ν_3 band is $\sim$ 540 cm^{-1} below the gas value, and inconsistent with the recent assignment of Raman-active modes around 4158 cm^{-1} to molecules at interstitial sites.[6] It is the aim of this paper to discuss these three issues.

The observation of a single stretch mode of the isolated molecule is in contrast with Raman-scattering studies of H_2 molecules, introduced from a plasma, in GaAs.[7] Here, *two* H-H stretch modes, separated by 8 cm^{-1}, attributed to para- and ortho- H_2 molecules occupying the lowest energy rotational states $J = 0$ and $J = 1$, respectively, were detected in the expected intensity ratio of 1:3. Although the energy difference between these states corresponds to 170 K, they are both occupied, even at cryogenic temperatures, because of the absence of strong nuclear spin-flip processes. It seems likely that this is also true in Si. In this case, if the molecule was freely rotating, then two H-H modes would be expected, whereas only one is detected. This implies, contrary to the case of GaAs, that molecular rotation is prevented by the crystalline field.

The effects of a crystal field on molecular rotation can be understood in terms of a model whereby rotating the molecule by θ from its equilibrium axis is accompanied by an increase in energy equal to $V(1 - cos\ 2\theta)\left(r_0/r\right)^2$ where r_0 is the molecular bond length. The molecular Schrödinger equation is then separable and the solutions in the variables θ and ϕ have definite parity. If $VI/\hbar^2$ is small, then the lowest energy states are the rotational levels $J = 0$ and $J = 1$. Here I is the moment of inertia of the molecule. On the other hand, if $VI/\hbar^2$ is large, then they are symmetric and asymmetric combinations of harmonic oscillator states bound in the potential wells around $\theta = 0$ and $\theta = \pi$. We denote the symmetric and asymmetric states by "+" and "−", respectively. The Pauli exclusion principle tells us that H_2 molecules with parallel nuclear spins must occupy the "−" state and those with antiparallel spins occupy the "+" state. In the case of D_2, those with symmetric spin functions occupy the "+" state while those with asymmetric spin functions occupy the "−" state. For the molecule in Si, we believe $VI/\hbar^2$ is large and the energy difference between the "±" states, $\mu_+ - \mu_-$, is very small. This difference leads to distinct centrifugal potentials,

$$\mu_\pm \left(\frac{r_0}{r}\right)^2,$$

in the two cases. For free rotation, $V = 0$, and $\mu_- - \mu_+ = \frac{1}{2}\hbar^2 J(J+1)/I$. The centrifugal potentials lead to a H-H stretch mode for the $J = 1$ state lying 5.9 cm^{-1} below that of $J = 0$.[8] However, as V increases, the separation between the two stretch modes diminishes. If we assume that the splitting in ν_3 is, in fact, less than 0.1 cm^{-1}, and has not been so far resolved, then $(\mu_- - \mu_+)$ must be less than $0.02\hbar^2/I$ and this imposes a lower limit on the rotation barrier. Using the expressions for μ_+ and μ_- given in Ref. 9, we find the barrier to be at least 0.17 eV. This means that the molecular rotation is frozen below about 70 K.

Thus at low temperatures, the molecules are aligned along one or more axes. The observation of only one mode in the H-D case means that either the hydrogen atoms are equivalent, and the center of the molecule lies on a mirror plane or a C_2 axis, or, if they are inequivalent, then the two H-D modes must be separated by at least 20 cm^{-1} and only one is thermally populated at 10 K.

To investigate the structure and vibrational properties of the isolated molecule, we have carried out density-functional cluster calculations. We have previously used this theory[10] to model the molecule trapped near oxygen. We found there that the stretch frequency of the molecule was 3855.6 cm^{-1} and was infrared active with an effective charge of $0.1e$. We suggested that the upward shift of the 1075 cm^{-1} band was to be understood in terms of a Fermi resonance due to H related modes around 500 cm^{-1}.

The molecule was inserted into a 148 atom H-terminated cluster centered on the tetrahedral interstitial site. The wave-function basis consisted of independent s and p Gaussian orbitals, with eight different exponents, sited at each Si site and three at each H atom of the molecule. A fixed linear combination of two Gaussian orbitals was sited on the terminating H atoms. In addition three Gaussian s and p orbitals were placed at each Si-Si bond center. The charge density was fitted with eight independent Gaussian functions with different widths on each Si atom, and four (three) on the central (terminating) H atoms. Three extra Gaussian functions were placed at each bond center. All atoms, except the terminating H ones, were allowed to relax by a conjugate gradient method. The second derivatives of the energy were found between the two central H atoms. Further details of the method can be found in Ref. 11.

We found that the molecule is stable when oriented along [100], [111], and [110]. These three configurations are essentially degenerate in energy. The rotational barrier is also very small but the uncertainty in the energies can easily exceed 0.1 eV. This is similar to the situation in GaAs.[12] The vibrational modes are given in Table I. These are all close together and lie within 90 cm^{-1} of the ν_3 band. They are slightly lower than that found for the molecule trapped near oxygen (3855.6 cm^{-1}). Stretch modes around 3561 cm^{-1} have also been found by a previous calculation[13] and other first-principles methods,[14,15] although the [110] orientation was not considered. However, they do not agree with Hartree-Fock and density-functional calculations carried out on small clusters which find frequencies close to the gas value.[16] All the calculations predict a low barrier to reorientation of the molecule. We find the H-H length to be 0.785 Å for the [110] and [111] structures and 0.788 Å for the [100] alignment. These are slightly longer than the gas value (0.74 Å). It appears that the energy calculations are not sufficiently accurate to resolve the reorientation energy or the stable alignment. However, the vibrational modes do present us with a method of discriminating between the structures.

Molecules lying along [100], with D_{2d} symmetry, would be infrared inactive while those along [111] possess inequivalent H atoms. The latter defect produces two distinct H-D modes shown in Table I. As these are separated by 0.25 cm^{-1}, they would give two bands with intensities corresponding to the different populations of the defects, contrary to the observations. The ν_3 band could not arise from these defects if the H-D splitting was as large as this. The [110] orientation is infrared active with equivalent H atoms. Only one mode is then expected in the H-D case. We identify the ν_3 band with a molecule lying along [110], although a [111] alignment cannot be completely ruled out. The stretch mode is about 90 cm^{-1} above that of the ν_3 band but considerably lower than that calculated for an isolated molecule. With the present method, this occurs at 4424.8 cm^{-1} (Table 1): about 10% higher than the observed value, although anharmonicity must play a significant role in this overestimate. The harmonic frequency has been estimated to be $\sim$ 4400 cm^{-1}.[17]

The transition dipole moment of the molecule can be calculated directly. This is done by finding the change in the dipole moment of the cluster when the atoms are displaced according to their normal coordinates. The induced dipole lies along [001] (Fig. 1) and arises as there is a slight displacement of the H atoms along this direction. The effective charge of the induced dipole is $0.1e$, comparable with that of the the molecule trapped by oxygen.[10] For the [111] alignment, the effective charge is very similar at $0.08e$.

The molecule is not stable at the center of the puckered hexagon (H site) but this site lies on a diffusion trajectory linking different T_d sites. The energy of a molecule constrained to lie at the H site is 0.72 eV greater than that at a T_d site and this then is an estimate of the migration energy of the molecule. This is appreciably greater than the diffusion energy for H^+ or H^0 of around 0.43 eV.[18]

The low frequency of the molecule is due to to the leaking of charge from the surrounding bonds screening the intramolecular proton-electron attraction. If the cage size was increased, the charge density at the center of the cage would decrease and the molecular frequency would be expected to increase. This is confirmed by a calculation in which the inner shells of Si atoms surrounding the T_d interstitial site are removed and the resulting dangling bonds hydrogenated. Removing just one shell and inserting passivating H atoms leads to a smaller volume for the cage but it is enlarged when ten Si atoms in two shells are removed. Relaxing the cluster in this case gives a H-H bond length of 0.759 Å which is smaller than before. The stretch frequency (Table 1) is then increased to 4324.6 cm^{-1} (H_2) and to 3057.9 cm^{-1} (D_2). These are within 170 cm^{-1} of the modes observed in plasma irradiated material by Raman scattering[6] and about 100 cm^{-1} below the calculated value of the molecule in vacuum. The distance of the center of the cage to a Si (H) atom on the void surface is 4.72 (3.36) Å.

Thus molecules within voids $\sim 50\%$ larger than that surrounding an interstitial site possess frequencies close to the gas value. The void discussed here has a different structure from platelets, where molecules appear to push apart neighboring (111) planes,[19] and these must be considered to be distinct defects. Our results suggest that the 4158 cm^{-1} band is due to molecules within voids and this is consistent with a correlation that has been found between the Raman intensities due to Si-H stretch modes arising from H atoms on the surface of a void, and the 4158 cm^{-1} band.[20] The calculations also suggests that the higher frequencies found by *ab initio* calculations on molecules in small clusters[16] may be due to an underestimate in the charge density at the interstitial site arising from the use of a limited basis set.

In conclusion, we have shown that the crystal-field effects at an interstitial site are sufficiently strong to freeze molecular rotation and the difference between ortho- and para-forms cannot be resolved. The molecule is either aligned along [110], with C_{2v} symmetry, or along [111] if the H-D splitting is smaller than calculated here. The stretch mode is some 540 cm^{-1} redshifted from the gas value and is infrared active. This frequency is very sensitive to the cage size and increases rapidly to the gas value for cages about 50% larger than that at a T_d site. Modes reported around the gas value are due to molecules in voids created by the plasma. The migration energy of the molecule through the solid is found to be 0.72 eV.

Since this work was completed, we have learnt that very recent Raman-scattering measurements on plasma-treated material have detected the ν_3 peak at 3618 cm^{-1} (10 K) with a width of 6 cm^{-1}.[21] No splitting of the peak was detected implying that any difference between ortho- and para-molecular forms is much less than in the gas phase. Furthermore, as [100], [111], and [110] alignments are all Raman-active with presumably equal polarizabilities, and only one peak was detected near 3618 cm^{-1}, it follows that the molecules must be aligned along one direction which is either [111] or [011] in agreement with the conclusions given here.

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TABLES

TABLE I. Calculated and experimental frequencies, cm^{-1}, of free H_2 molecules and molecules trapped in Si with different alignments.

Free molecule	H-H	H-D	D-D
Calculated	4424.8	3831.2	3128.9
Expt. (Ref. 22)	4161	3632	2993
Molecule at T_d site			
alignment	H-H	H-D	D-D
[110]	3708.4	3217.1	2622.2
[111]	3713.0	3221.4, 3221.6	2625.5
[100]	3606.8	3128.6	2559.1
Expt. (Ref. 4)	3618.3	3264.8	2642.5
Molecule in void	H-H	H-D	D-D
Calculated	4324.6	3745.9, 3743.8	3057.9

FIGURES

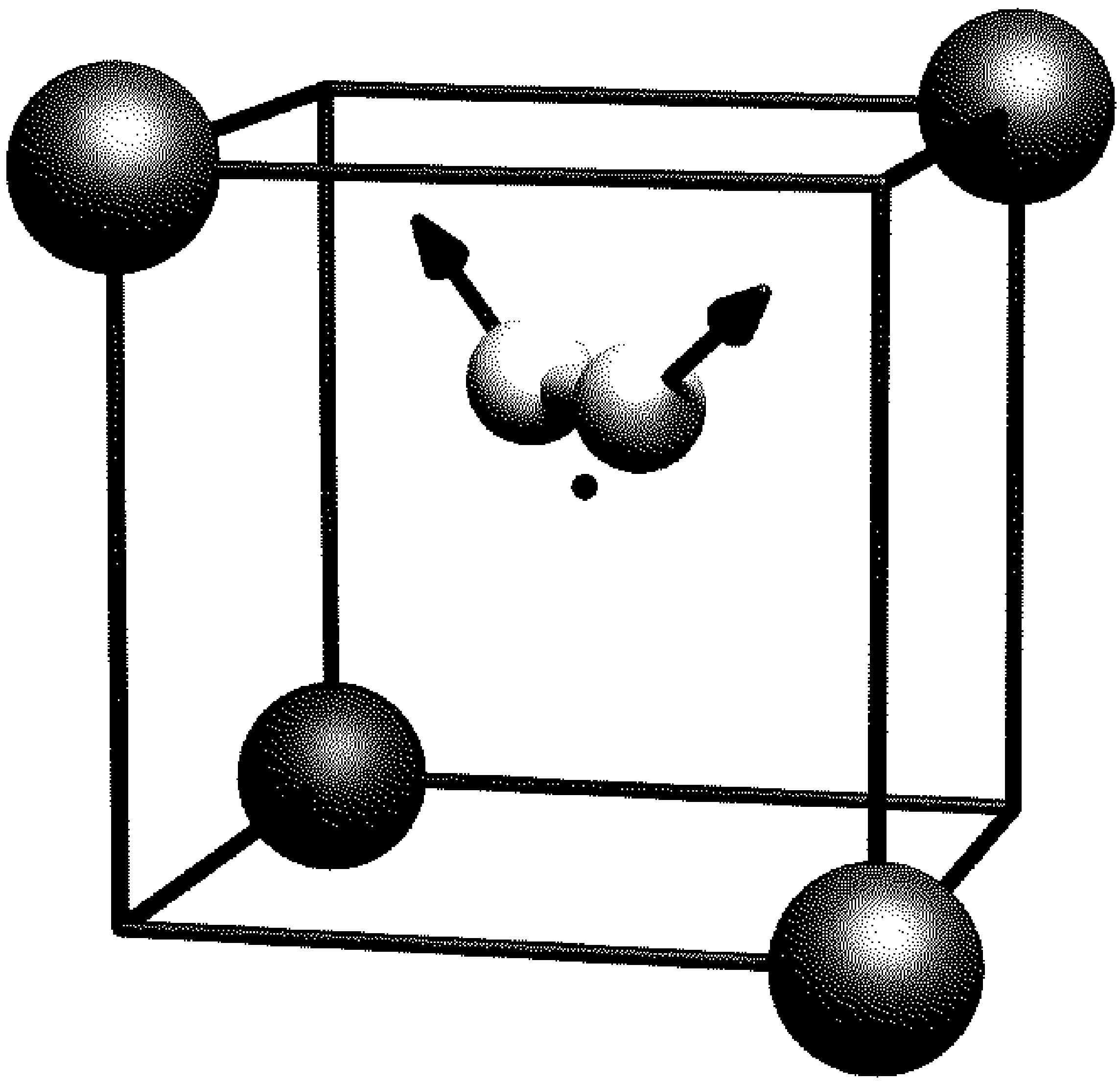

FIG. 1. Schematic figure of the stable form of the molecule at a T_d site aligned along [110]. Arrows show an exaggerated movement of the atoms in the stretch mode leading to a transition dipole along [001]. The dot denotes the center of the cube.