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Abstract

The static and dynamic properties of interstitial H_2, HD and D_2 molecules in crystalline silicon are obtained from *ab initio* molecular-dynamics simulations with atomic-like basis sets. The *static* ($T = 0$) calculations agree with those of most other authors: the centre of mass (CM) of H_2 is at the tetrahedral interstitial (T) site, the molecule is a nearly-free rotator, and the activation energy for diffusion is 0.90 eV. However, these results fail to explain a number of experimental observations, such as why H_2 is infrared (IR) active, why the expected ortho/para splitting is not present, why the symmetry is C_1, why the piezospectroscopic tensors of H_2 and D_2 are identical or why the exposure to an H/D mix results in a single HD line which is not only at the wrong place but also much weaker than expected. In the present work, we extend the static calculations to include the constant-temperature *dynamics* for H_2 in Si. At $T > 0$ K, the CM of the molecule no longer remains at the T site. Instead, H_2 'bounces' off the walls of its tetrahedral cage and exchanges energy with the host crystal. The average position of the CM is away from the T site along $\langle 100 \rangle$. Under uniaxial stress, the CM shifts off that axis and the molecule has C_1 symmetry. The H–H stretch frequency calculated from the Fourier transform of the v–v autocorrelation function is close to the measured one. Since the potential energy experienced by H_2 in Si near the T site is very flat, we argue that H_2 should be a nearly free quantum mechanical rotator. Up to room temperature, only the $j = 0$ and $j = 1$ rotational states are occupied, H_2 resembles a sphere rather than a dumbbell, the symmetry is determined by the position of the CM and HD is equivalent to DH in any symmetry. The rapid motion of the CM implies that an ortho-to-para transition will occur if a large magnetic moment is nearby. Several candidates are proposed. Since nuclear quantum effects are not included in our calculations, we cannot address the possibility that the observed vibrational spectrum of H_2 results from a tunnelling excitation as proposed by Stoneham.

1. Introduction

Hydrogen is a common impurity in crystalline silicon. Its interactions are almost always covalent in nature and often result in the formation of Si–H bonds. As a result, H affects the electrical and optical properties of the material. The formation of bonds involving H shifts the energy levels associated with impurities and defects, sometimes resulting in passivation. Further, numerous Raman and infrared (IR) absorption lines appear following the hydrogenation. Most of the stretch modes are in the range 1800–2200 cm^{-1} and correspond to Si–H stretch vibrations [1, 2].

If a sample is grown in or exposed to (at high temperatures) a hydrogen ambient then rapidly quenched, most of the hydrogen which penetrates the crystal ends up in 'hidden' form and shows little or no IR activity [3]. It has long been assumed that the invisible hydrogen is in molecular form [1]. Indeed, early theory predicted [4, 5] that the H$_2$ molecule is stable at the tetrahedral interstitial (T) site where it should be IR inactive. It has also been shown that hidden hydrogen can be rendered very visible by electron irradiation [6] or other damage-inducing treatment. Molecular-dynamics (MD) simulations of interstitial H$_2$ interacting with a vacancy or a self-interstitial show the dissociation of the molecule and the formation of Si–H bonds at the defect [7, 8].

Things became exciting when interstitial H$_2$ molecules were shown to be visible after all. The first Raman observation [9] of H$_2$ in c-Si proved to be caused by molecules associated with H-saturated platelets [10]. However, the Raman signature of isolated interstitial H$_2$ was soon reported [11] in plasma-exposed samples. The same impurity was also seen by IR absorption [12, 13]. The small line associated with H$_2$ is at 3601 cm^{-1} (Raman, room temperature) or 3618 cm^{-1} (IR, 10 K). The linewidth is less than 0.1 cm^{-1} with a 100:1 or better signal-to-noise ratio [14] in thick samples. The interaction between H$_2$ and the host crystal weakens the H–H bond which results in a drop in its stretch frequency by a considerable 550 cm^{-1} relative to that of the free molecule ($\sim$4160 cm^{-1}). Surprisingly, no ortho/para splitting is observed [11].

In oxygen-rich Si samples, three IR lines associated with H$_2$ are seen [15–17] and two of these are associated with H$_2$ trapped near interstitial oxygen (O$_i$). Careful annealing studies show that the binding energy of H$_2$ to O$_i$ is 0.26 $\pm$ 0.02 eV and that the activation energy for diffusion of H$_2$ among interstitial sites is 0.78 $\pm$ 0.05 eV. The diffusion of the molecule is expected to occur along the trigonal axis from T to hexagonal to T sites (T–H–T path). As the temperature is raised, the configurational entropy associated with the number of T sites away from O$_i$ (relative to the number of T sites immediately adjacent to it) results in the free energy becoming a minimum for isolated H$_2$. By 160 °C, all the molecules are at isolated T sites. This is reversible upon cooling below 50 °C. In these samples, isolated molecules are seen [18] up to 350 °C, a temperature at which oxygen-related thermal donors begin to form and complicate the picture.

Deuterium substitutions lead to the observation of D$_2$ and a single HD line [17]. The intensity of the IR line associated with HD is, at most, one-third that of H$_2$ or D$_2$. It should be twice the size of H$_2$ or D$_2$ if we assume equal formation probabilities for H$_2$, HD=DH, and D$_2$. Indeed, the hydrogen solubility as a function of the hydrogen partial pressure P varies [19] as $P^{0.56}$. Thus, in high-temperature hydrogenation, H$_2$ or D$_2$ molecular dissociate at the surface of the crystal, diffuse into the material as atomic species, then form interstitial molecules during the quench. Newman proposed that the HD+HD→H$_2$+D$_2$ should occur with a 135 cm^{-1} gain in zero-point energy, which could account for a reduction in the concentration of HD. Another strange feature of the HD line is that its anharmonic shift is much larger than expected [20].

Uniaxial stress IR experiments [20] for H$_2$ in Si imply that the symmetry of the defect is C$_1$. Stoneham [21] suggested that, by analogy to KCl:Li, the molecule is not at the T

Table 1. Summary of theoretical predictions about interstitial H_2 in Si. The equilibrium orientation of the H–H axis, the H–H bond length, the activation energies for rotation and diffusion, and the stretch vibrational frequencies (when predicted) are given. All the authors find the (CM of the) molecule to be at the T site (LDA and GGA). In [31], the axis of H_2 is off the $\langle 100 \rangle$ direction by 4°. Our results and the experimental data are discussed in the text.

Author	Orientation	H–H (Å)	E_{rot} (eV)	E_{diff} (eV)	Stretch (cm^{-1})
[4]	$\langle 001 \rangle$	0.75	0.093	0.95	—
[5]	$\langle 111 \rangle$	—	—	2.7	—
[23]	$\langle 100 \rangle$	0.86	—	1.1	—
[24]	$\langle 111 \rangle$	—	~ 0	0.56	—
[25]	$\langle 111 \rangle$	0.88	—	—	—
[26]	$\langle 100 \rangle$	0.85	—	—	—
[27]	$\langle 100 \rangle$	0.85	—	>1	3561
[28]	$\langle 111 \rangle$	0.70	~ 0	—	—
[29]	$\langle 111 \rangle$	0.78	0.3	—	—
[30]	$\langle 100 \rangle$	0.83	0.003	0.91	3020
	$\langle 111 \rangle$	0.80	0.002	0.89	3363
[31]	$\langle 100 \rangle$	0.70	0.026	1.22	4470
[32]	$\langle 100 \rangle$	0.82	0.01	0.95	3396
[33]	$\langle 100 \rangle$	0.79	~ 0	0.72	3607
[34]	$\langle 100 \rangle$	0.81	0.012	—	3260
	$\langle 100 \rangle$	0.78	0.011	—	3556

site but off-centre and that a low-frequency tunnelling excitation results in the observed line. In his model, HD might have an energy slightly different from DH, but tunnelling implies that we would see some linear combination of the two. There is no clear experimental evidence in favour or against this model [22].

Even more surprising is that all the theorists who have studied interstitial H_2 in Si predict properties in conflict with most experimental data. The key predictions from [4, 5, 23–34] are summarized in table 1. The majority of authors agree on many points despite the fact that very different theoretical tools are used: semiempirical Hartree–Fock (HF) in saturated [4, 5] or cyclic [24] clusters, *ab initio* HF in saturated clusters [28, 31], first-principles local density-functional (DF) theory in periodic supercells [23, 25, 29] or saturated clusters [26, 27, 33]. A few calculations include the generalized gradient approximation (GGA) [30, 31, 34]. The clusters contain 10 to over 50 host atoms and the periodic cells eight to 64 atoms. When plane-wave basis sets are used, the cutoff energies range from 12 to 48 Ry, while the local basis sets vary from minimal to double-zeta plus polarization. Some authors even performed calculations at numerous levels of theory, including Moller–Plesset corrections to *ab initio* HF and a HF/DF hybrid technique [31, 35]. Thus, the theory so far ranges from approximate and semiempirical to today's state-of-the-art.

Most theorists find a barrier to diffusion comparable to the experimental value and a stretch frequency substantially reduced relative to the free molecule value. They all agree that the centre of mass (CM) of H_2 is at the T site, that the H–H axis lies along either the $\langle 111 \rangle$ or $\langle 100 \rangle$ directions, and that the barrier for rotation of the H–H dumbbell around its CM is exceedingly small, implying a nearly-free rotator at the T site. None of the calculations predicts C_1 symmetry. In contrast, a free rotator at the T site should be IR-inactive. Further, no suggestion is made as to why ortho/para splitting is not seen. The predictions for H_2 in Si are, in fact, quite similar to those for H_2 in GaAs [30, 32, 36, 37] (see later) which suggests that some critical ingredient is missing in all these calculations.

Assuming a classical description for H_2, Jones and co-workers [38] note that the $\langle 100 \rangle$

orientation renders the molecule Raman-active but IR-inactive, that the $\langle 111 \rangle$ orientation implies distinct lines for HD and DH, while a single one is reported. Jones and Hourahine argue [38] that only a $\langle 110 \rangle$ orientation for the molecule at the T site *and* a barrier to rotation of at least 0.17 eV can produce one Raman- and one IR-active mode and a single HD line. However, all the static calculations predict a $\langle 100 \rangle$ or a $\langle 111 \rangle$ orientation and a very flat potential surface for H_2, while uniaxial stress studies [20] imply no symmetry at all (C_1) for the defect.

All these calculations and arguments not only assume a fixed position for the CM of the molecule but also treat it as a classical object: H_2 is thought of as a dumbbell with a well-defined molecular axis and barrier to rotation. The quantum object is different.

The rotational states of *free* H_2 have energies $j(j + 1)\hbar^2/MR^2$. The mass of H (or D) is so small that the j-states are well separated in energy and, at or below room temperature, only the even $j = 0$ and the odd $j = 1$ quantum rotational states are occupied. The latter implies that even combinations of the proton spins of H_2 are realized ($\uparrow\uparrow$ or $\uparrow\downarrow + \downarrow\uparrow$ or $\downarrow\downarrow$), and the former implies the odd combination $\uparrow\downarrow - \downarrow\uparrow$. The result is ortho- and para-H_2, with a 3:1 intensity ratio.

The $j = 0$ state is spherically symmetric. The $j = 1$ state has $m_j = -1, 0$ and $+1$ which are degenerate unless an electric field gradient is present. Thus, $j = 1$ also closely resembles a sphere. Therefore, there is *no* molecular axis or barrier to rotation: H_2 is a tiny sphere. The classical picture of a dumbbell with a well-defined molecular axis is only valid if many j states are involved. This is the case for heavier molecules: for example, N_2 at room temperature includes rotational states up to $j = 8$ and wavefunctions with directionality can be constructed from linear combinations of these states. Many j states can also result from the presence of a hindering potential. In the case of H_2, a weak mixing would not necessarily prevent the observation of the ortho/para splitting but would affect the 3:1 ratio. If too many j states are involved, H_2 would not exhibit an ortho/para splitting.

What is the situation for interstitial H_2 in semiconductors? In GaAs [39, 40], the Raman mode is close to the free molecule value, 3911 cm^{-1} at room temperature, and the ortho/para splitting ($\sim$8 cm^{-1}) with a 3:1 intensity ratio is clearly resolved at low temperatures implying that only the $j = 0$ and $j = 1$ states are involved. Further, no splitting is observed under $\langle 001 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ uniaxial stress [40] implies that H_2 has spherical symmetry, again consistent with $j = 0$ and $j = 1$. When a mixed H/D plasma is used, lines corresponding to H_2, a single HD and D_2 are observed with the anticipated shifts and amplitudes. Since GaAs is partly ionic, we might expect the interactions between H_2 and its host to be rather strong since they involve an electrostatic component. However, H_2 in GaAs behaves like a free rotator and is IR-inactive [40].

As discussed earlier, in c-Si, H_2 is Raman and IR active. Its vibrational mode is over 500 cm^{-1} below the free molecule value, and the ortho/para splitting is not present. This implies either a substantial hindering potential or an efficient mechanism to flip nuclear spins. Uniaxial stress experiments imply C_1 symmetry and the piezospectroscopic tensors of H_2 and D_2 are identical. A single HD line is seen despite the low symmetry. This line is substantially weaker than expected and shows an anomalously large anharmonic shift. Yet, the volume available around the T site is about the same in Si as in GaAs. Further, Si is 100% covalent and all the theorists who calculated the potential energy surface find it to be very flat. Our MD simulations confirm this (see later).

In this paper, we treat H_2 as a nearly free rotator in Si and focus on the dynamics of its CM. Possible reasons for the absence of the ortho/para splitting are discussed under this assumption. The dynamics of the ions are treated *classically*. Thus, no zero-point energies, tunnelling or molecular rotational states are included. Therefore, our calculations cannot address Stoneham's proposal [21] that the observed mode at 3618 cm^{-1} is the result of a

tunnelling excitation. Instead, we explore the possibility that classical MD simulations are valid to describe the dynamics of the CM of H$_2$, HD and D$_2$ in Si. This is supported by the following arguments.

(i) The observed behaviour of D$_2$ is fully consistent with that of H$_2$ at all temperatures. Were quantum mechanical effects dominant for H$_2$, its behaviour would differ from that of the heavier D$_2$. Experimentally, no qualitative difference shows up, even at low temperatures.

(ii) The observed [15–17] trapping and detrapping of H$_2$ at interstitial oxygen shows no hint of quantum behaviour as the molecule moves from an isolated T site to a site near O$_i$ and *vice versa*. The Arrhenius plots are smooth and linear down to low temperatures.

(iii) The tunnelling of H$_2$ among equivalent minimum-energy orientations around a given T site would average the interactions to a high symmetry and render the defect IR-inactive. It is possible that tunnelling occurs in only one plane around the T site, but this implies an unusually asymmetric potential.

(iv) The observed IR lines are very sharp. Some width would be expected to result from tunnelling [22].

2. Theoretical approach

We perform MD simulations for interstitial H$_2$, HD, DH and D$_2$ in Si. The ions are treated as classical particles and the electrons remain at 0 K on the Born–Oppenheimer surface. The electronic energy is obtained using (spin-averaged) density-functional (DF) theory within the local density approximation. The exchange-correlation potential is that of Ceperley–Adler [41] as parametrized by Perdew and Zunger [42]. Norm-conserving pseudopotentials in the Kleinman–Bylander form [43] are used to remove the core electrons from the calculations. Simulated quenching with a time step of 0.2 fs is done to obtain the lowest-energy configurations and potential energy differences. The same time step is used for constant-temperature runs. A Nosé thermostat [44] is used to control the temperature.

The faster but more approximate calculations employ a minimal basis set [45] (one s set for H and one s set and a set of p's for Si) and the energy is obtained from the Harris energy functional [46]. Simulations are also performed with the (approximately) self-consistent version of the minimal-basis code [47]. In these calculations, the host crystal is represented by two periodic supercells: 64 Si atoms with four k points for Brillouin zone sampling and 216 Si atoms with only $k = 0$ (Γ point).

The slower but more accurate *ab initio* method is fully self-consistent and uses the SIESTA code [48, 50]. The valence electron wavefunctions are described with linear combinations of (numerical) atomic orbitals (LCAO) of the Sankey type [45] but generalized to be arbitrarily complete with the inclusion of multiple-zeta orbitals and polarization states. In the present work, basis sets vary from single-zeta (SZ) to double-zeta plus polarization (DZP): two sets of s and p's plus one set of d's on Si, two s's and one set of p's on H. The charge density is projected onto a real-space grid with an equivalent cutoff of 50 Ryd or more to calculate the exchange-correlation and Hartree potentials. The host crystal is represented by a periodic supercells of 64 or 128 Si atoms with the k-point sampling ranging from the Γ point to a $2 \times 2 \times 2$ Monkhorst–Pack grid [51]. We have tested SIESTA in a number of ways including direct comparisons with Van de Walle [49] of energies of various configurations of hydrogen in Si. The agreement is very good (within 0.1 eV).

The major features of all our calculations are remarkably similar and do not depend very much on the cell or basis-set size or k-point sampling. There are two reasons for this. First, our smallest cell contains 64 host atoms, a size which many authors consider large enough to

study localized defects such as H_2. Second, interstitial H_2 induces no substantial relaxation or distortion of its environment. Thus, all the Si atoms in the cell remain nearly perfectly sp^3 coordinated, a situation very well described with minimum basis sets. As for H_2, it is also well represented by s–s overlap only. Note that a system as complex as l-Si is very well described by SIESTA, even with a minimal basis set [52].

3. Results

3.1. Static (T = 0) calculations

When we place H_2 or D_2 anywhere near a T site and quench, its CM coincides almost exactly with the T site. The CMs of HD and DH are of course shifted. The calculated H–H bond length for free H_2 is 0.79 Å, a little longer than the experimental value (0.75 Å). In the 128-Si atoms cell and a DZP basis set, the H–H bond length increases to 0.84 Å indicating a weakened H–H bond. The classical barrier to rotation obtained by calculating the potential energy with the molecular axis aligned along various directions around a fixed CM is very small (a few hundredths of an eV). The H–H stretch frequency was obtained [53] from the dynamical matrix which was computed within the linear response approximation to the density functional perturbation theory. Using a DZ basis set, the frequency was calculated to be 3549 cm^{-1}.

The barrier to diffusion of H_2 along the T–H–T path is obtained dynamically by monitoring the potential energy while exerting a constant force on the molecule in the trigonal direction. This forces the CM of the molecule to move along the T–H–T path while allowing the rest of the crystal to relax freely within the time step imposed on the system (0.2 fs). The calculated barrier to diffusion is 0.90 eV, slightly higher than the measured value 0.78 ± 0.05 eV [15].

It is not surprising that these results are in close agreement with those of most other authors who studied this defect using first-principles techniques. The next step is to include the dynamics.

3.2. Dynamic (T > 0) calculations

Dramatic changes to the static picture result from constant-temperature runs, even at low temperatures. Most of our calculations were done at 10 and 77 K. The central result is that the CM of the molecule moves around a lot. As soon as $T > 0$, this occurs for H_2 and HD as well as D_2. The displacements of the CMs of H_2 and D_2 at 77 K as a function of time are shown in figure 1. Note that the amplitude of the motion exceeds 0.5 Å and that the direction of motion of the CM abruptly changes every few hundred femtoseconds! The molecule bounces off the walls of its tetrahedral cage at a fantastic pace indeed.

Figure 2 illustrates the potential energy variations versus time as H_2 moves around the cage at 77 K. This is the total energy minus the nuclear kinetic energy. At 0 K, it would represent the true potential energy of H_2 at various locations near the T site. As T increases, the host atoms vibrate and also contribute to the total potential energy of the cell. Therefore, the amplitude of the oscillations of the potential energy ($\sim$0.5 eV) overestimates the potential experienced by H_2. However, the figure shows that H_2 moves in a complicated three-dimensional potential.

Figure 3 shows the H–D internuclear distance as a function of time at 77 K for a 12 000 time-step run. Abrupt variations in the amplitude of the oscillation occur as the molecule 'bounces' off the walls of its cage, exchanging energy with the host crystal. The vibrating molecule is not isolated but couples to phonons in a complicated way. Qualitatively identical features are visible in the plots of the amplitudes of H_2 and D_2 versus time.

The H–H stretch frequency can be obtained dynamically from the Fourier transform of the
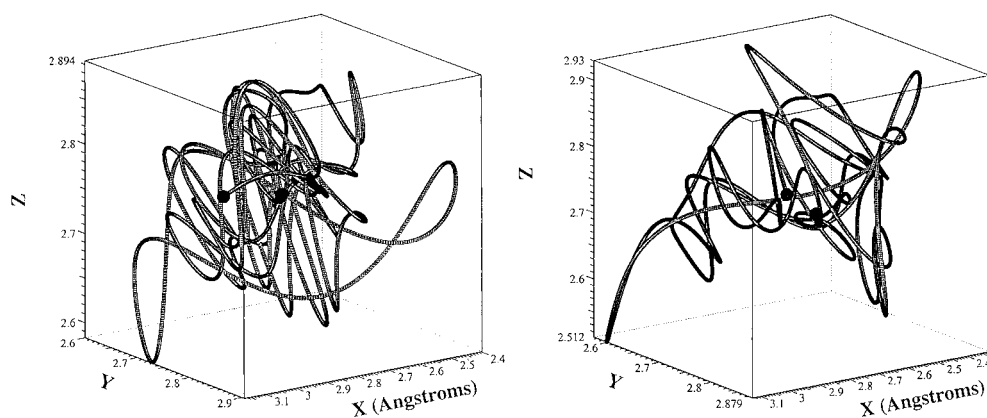
Figure 1. Motion of the centre of mass (CM) of interstitial H$_2$ (left) and D$_2$ (right) molecules as a function of time at 77 K. The T site is at the centre of the cube at (2.75, 2.75, 2.75). The nearest host atoms are far outside this cube, 2.35 Å away from its centre. The sharp changes in direction occur as the molecule bounces off a wall. The typical amplitude of the displacement of the CM is 0.5 Å or so, even for the heavier D$_2$. Five thousand time steps are shown.
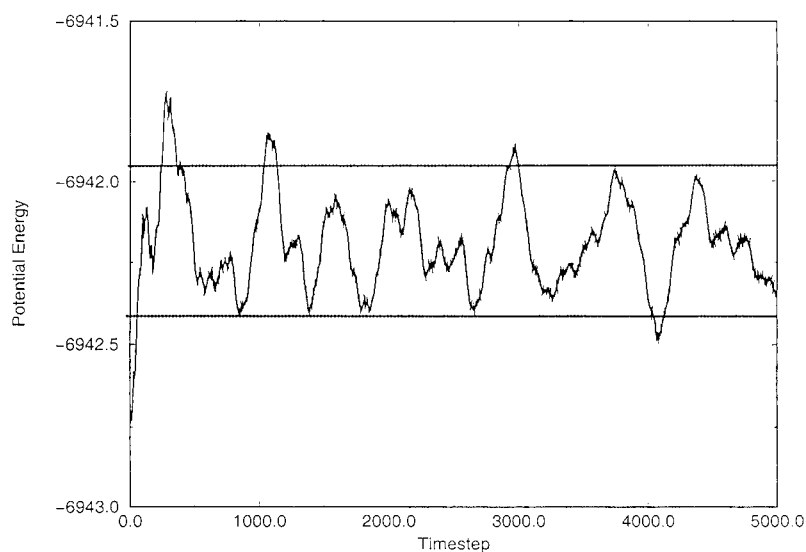
Figure 2. Potential energy (eV) as a function of *time* for interstitial H$_2$ in Si, calculated at 77 K. Very similar curves can be generated for HD and D$_2$. The two horizontal lines correspond to 0.5 eV (see text). Five thousand time steps are shown.

velocity–velocity autocorrelation function [54]. This approach does not require the fitting of a potential to a polynomial or the diagonalization of a dynamic matrix. Instead, the molecule is allowed to move around in its cage at a given temperature and the component of the velocity of each H atom along the H–H bond is saved at every time step and later used to calculate the correlation function. Our simulations involved 12 000 time steps (with $\Delta t = 0.2$ fs) at 30 K with an SZ basis set in the 64 Si-cell. Because the oscillator is perturbed every time H$_2$ bounces off the walls of its cage, very long simulations times are required to obtain an accurate frequency (the H$_2$ mode couples to phonons which involve much longer time scales). For free H$_2$, peaks
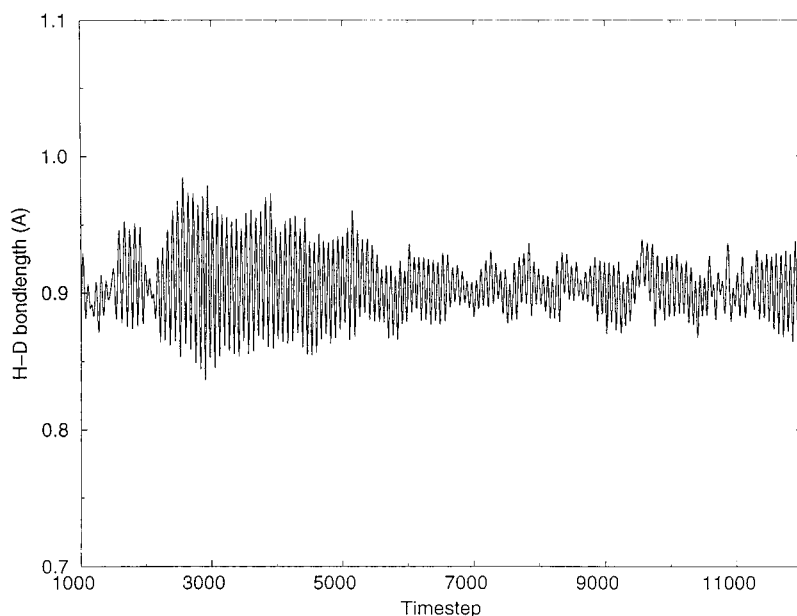
Figure 3. H–D internuclear distance in Å as a function of time step at 77 K. The first 1000 time steps (during which HD thermalizes) are left out. The amplitude of the oscillation varies as HD bounces off the walls, exchanging energy with the host crystal. Similar features are seen for H_2 and D_2.

obtained from various samplings of the calculated data average at 4120 cm^{-1}. For H_2 in Si, the peak is somewhat broader and centred at 3640 cm^{-1}. More on these calculations will be published elsewhere [55].

The random motion of the molecule implies that its *instantaneous* position is (almost) always at a site with no symmetry. However, the *average* position of the CM (calculated over 5000 time steps) changes with the temperature. At 10 K, it is CM is still within 0.01 Å of the T site Then, it begins to shift along the $\langle 100 \rangle$ axis. At 77 and 300 K, it is at (0.08, 0.00, 0.00) and $(-0.04, -0.01, 0.00)$ Å, respectively. At these temperatures, the molecule visits anharmonic regions of the potential further from the T site and the average position of the CM changes.

The Mulliken population analysis provides a qualitative value for the effective charge associated with each atom. Both H atoms in H_2 carry a small positive charge (less than +0.1e). Some electron density is transferred from the H_2 molecule to its Si neighbours. This weakens the H–H bond and lowers the stretch frequency relative to the free molecule value. We monitored the variations of the Mulliken charges as a function of time as H_2 moves around its cage. These variations are very small (typically, in the third digit). This implies that the time dependence of the induced dipole moment is associated with the changing distance between the two nuclei rather than with changes in the effective charges.

We also performed constant-temperature runs with uniaxial stress along the $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions to see if and how the *average* position of the CM is affected. Stress is simulated by compressing the cell along a given direction by 1% or 2% while preserving the volume of the cell. Such a compression corresponds to a stress of the order of the GPa. Table 2 gives the average position of the CM at 77 K relative to the T site for 0%, 1% and 2% stress. The average was obtained from 12 000 time step runs, after thermalization (removing the first 1000 or 5000 time steps does not make much difference). The potential energy of H_2 near the

Table 2. Average Cartesian coordinates of the CM of H$_2$ relative to the T site, $R_{CM}-R_T$ in Å at 77 K under 0%, 1% and 2% uniaxial stress along various directions.

Stress (%)	$\langle 001 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$
0	(0.06, 0.00, 0.00)	(0.06, 0.00, 0.00)	(0.06, 0.00, 0.00)
1	(−0.03, −0.01, 0.02)	(0.01, 0.02, 0.00)	(0.02, 0.01, 0.03)
2	(−0.03, −0.02, 0.04)	(0.05, 0.03, 0.01)	(0.02, 0.03, 0.12)

T site is so flat that applying stress does affect the average position of the CM, which shifts from the $\langle 100 \rangle$ axis, thus lowering the average symmetry from C_{2v} to C_1. These results suggest that the C_1 symmetry observed by IR absorption under uniaxial stress could be stress-induced rather than an intrinsic property of H$_2$ in Si.

However, we want to caution the reader that the actual situation is more complicated. The piezospectroscopic tensors of H$_2$ and D$_2$ are identical [22], a fact which implies a complex relationship between the molecule and its host.

4. Discussion

The properties of interstitial hydrogen molecules in Si are puzzling. The observation of one Raman and one IR line for H$_2$ with no ortho/para splitting, a single HD line at the wrong place and with the wrong intensity, C_1 symmetry under uniaxial stress and other features are impossible to reconcile with the static theoretical predictions published to date. Our own calculations at $T = 0$ K confirm the results obtained by other authors, namely that H$_2$ should be a nearly free rotator, centred at the T site and thus an IR-inactive centre with high symmetry.

Classical MD simulations provide qualitatively new insights into the behaviour of hydrogen molecules in Si. The key result is that the CM of the molecule rapidly moves around the tetrahedral site, with displacements of the order of 0.5 Å within times of the order of 100 fs. In classical terms, the molecule 'bounces' off the walls of its cage. This rapid motion of the CM will have to be included explicitly in any discussion of this problem which includes quantum treatment of the nuclei. The interactions between H$_2$ and the walls of its cage allow the molecule to exchange energy with the host crystal, thus coupling the H–H stretch mode to Si modes.

At $T > 0$ K, the average position of the CM is no longer at the T site but shifts along the $\langle 100 \rangle$ direction as the molecule explores anharmonic regions of the potential. This shift induces a small dipole moment and renders the molecule IR-active.

Thus, both static and dynamic calculations agree that the potential experienced by H$_2$ near the T site is very flat. We consider the possibility that H$_2$ is an almost free rotator in Si. Since the quantum rotational states are well separated in energy, only the spherically symmetric $j = 0$ (para-H$_2$) and the almost spherical $j = 1$ (ortho-H$_2$) states are occupied below room temperature. This implies that the symmetry is not determined by the orientation of the molecular axis of a dumbbell but instead by the position of the CM of the H$_2$ 'sphere' in the crystal. This also implies that HD is identical to DH in any symmetry, which is consistent with a single HD line observed even though the symmetry under uniaxial stress is C_1.

Applying 1% and 2% uniaxial stress along the $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions forces the average position of the CM off the $\langle 100 \rangle$ axis and the symmetry drops to C_1. The effect is small and provides, at best, part of the explanation of the experimental data. In particular, the absence of isotopic shift in the measured piezospectroscopic tensors of H$_2$ and D$_2$ does not come out of our calculations. It could, however, result from the dynamics of the molecules

when simulations long enough to include phonon statistics become computationally tractable (the time step Δt is 0.2 fs because H moves very fast, and an enormous number of time steps is needed to include enough vibrations of the much slower-moving Si atoms).

The very rapid motion of the CM of H_2 suggests possible explanations for the absence of ortho/para splitting [56] in the Raman and IR spectra. A large magnetic field gradient is a most efficient way to flip a nuclear spin and transform ortho-H_2 into para-H_2, the ground rotational state. If a magnetic moment is near the T site where H_2 resides, the rapid motion of the molecule provides the gradient. But what can this magnetic moment be? Three candidates come to mind: ^{29}Si, other ortho-H_2 molecules and neutral interstitial H.

The first candidate can be rejected as ^{29}Si has a natural abundance of less than 5% and a small magnetic moment. The T site is surrounded by ten Si atoms (four nearest and six second-nearest neighbours): on average, there is only one ^{29}Si near every second T site. Therefore, this isotope is not a plausible candidate to induce a full ortho-to-para conversion in less than weeks or months.

The second candidate can also be rejected. Assuming that interstitial H_2 molecules tend to cluster near each other as the sample is quenched, bimolecular (ortho-H_2–ortho-H_2) processes could indeed induce ortho-to-para conversions [57]. However, such bimolecular decays have been observed [57] in a-Si:H and the conversion is described by $dx/dt = -cx^2$, where x is the concentration of ortho-H_2 and c the rate constant. The experiments, done at 4.2 K, gave 0.01/h (as compared to 0.02/h in solid H_2). This does lead to an ortho-to-para conversion but in days or even weeks, much too slowly to explain the experimental data.

The third possibility is intriguing and raises the issue of the formation of H_2 in the bulk. In plasma-exposed samples [11], H penetrates into the crystal in atomic form. In samples hydrogenated at high temperatures from a gas, H_2 molecules dissociate at the surface, diffuse into the crystal as atomic species [19], and H_2 molecules form during the quench. Even though a large fraction of the H ends up as H_2, there always remains some concentration of interstitial hydrogen: bond-centred hydrogen (H_{BC}) or tetrahedral interstitial hydrogen (H_T). The simple reactions

$$H_{BC}^+ + H_T^- \rightarrow H_2 \qquad \text{or} \qquad H_{BC}^+ + H_T^0 + e^- \rightarrow H_2$$
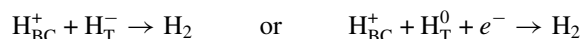
are possible but they should lead to the formation of H_2^* as well. The latter defect is a strong IR centre [58] which has never been seen in the spectra that contain H_2 (other than following electron irradiation [59]). Furthermore, H_{BC}^+ is also very visible by IR absorption [60] and it has never been seen in these samples. This interstitial does exist in the p-type samples [12] but is more likely to be responsible for the formation of the observed {H, B} pairs than of H_2 molecules.

This suggests that the paramagnetic H_{BC}^0 and the metastable H_T^0 species play a role. Indeed, muon spin rotation data [61] show that the paramagnetic fraction of muonium is close to unity above 600 K. Again, the reaction

$$H_{BC}^0 + H_T^0 \rightarrow H_2$$
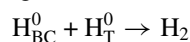
could work, but it should also result in the formation if the very visible H_2^*. Further, the stable charge state of bond-centred hydrogen is +1.

We are left with H_T^0. Our calculations [62] show that its activation energy for diffusion from T-to-T site is extremely low (0.06–0.15 eV, numbers which need to be corrected downward by the zero-point energy of H). Recent studies [63] of the transitions from H_T^- to H_{BC}^+ in c-Si suggest that its diffusivity is 25 orders of magnitude faster than that of H_{BC}. Thus, H_T^0 finds a trap very quickly. In the samples considered here, $H_T^0 + H_T^0 \rightarrow H_2$ reactions would occur very rapidly because of the large energy to be gained by molecule formation. However, some H_T^0 would fail to find a partner and bounce around rapidly from molecule to molecule. We

have performed conjugate gradient calculations [55] to compare the binding energies of H$_2$ and O$_i$ to H$_2$ and H$_T^0$. The latter is about the same as the former, but H$_T$ is very mobile and O$_i$ is not. The rapidly moving H$_T^0$ could come close to H$_2$, either scattering away or generating an exchange H$_2$ + H $\rightarrow$ H + H$_2$. Such an interaction would not involve the formation of stable three-hydrogen complexes (which would result in the observation of at least six lines in samples exposed to an H/D mix) [64].

However, these interactions would convert ortho- into para-H$_2$ in very short times. Indeed, the magnetic moment is due to an electronic, rather than a nuclear, spin which produces a factor gain of $\sim$2000 in the conversion rate. Furthermore, the very large diffusivity of H$_T^0$ suggested by measured transients [63] and calculated activation energies [62] imply that very large gradients near H$_2$ would be realized. As previously mentioned, ortho-to-para transitions occurring as a result of the interactions with nuclear spins lead to conversion rates or 0.01–0.02/h. In the present case, we gain three orders of magnitude by dealing with an electronic spin (with a conversion rate of up to $\sim$1/min) times an unknown factor caused by the very rapid motion of H$_T^0$.

Finally, we performed a few constant-temperature MD simulations for H$_2$ at the T$_{Ga}$ site in GaAs. The CM of the molecule does not move very much at all during simulations identical to those in Si, where H$_2$ is seen to be moving around very rapidly. The partly ionic character of GaAs is the likely culprit. Indeed, displacing the CM of H$_2$ toward a positively charged Ga or a negatively charged As should affect the charge distribution of H$_2$ at a cost in energy. Therefore, even though the molecule in GaAs is surrounded by nuclear magnetic moments, no magnetic field *gradient* is present and the ortho/para splitting remains.

Our calculations shed no light on two issues. First, why is the amplitude of the HD line in Si much lower than one would expect by assuming equal formation probabilities of H$_2$, HD=DH, and D$_2$? Second, why are the piezospectroscopic tensors of H$_2$ and D$_2$ identical, as if hydrogen were not involved? The latter experimental observation argues in favour of Stoneham's tunnelling excitation. However, the present calculations do predict an IR-active molecule with the observed vibrational frequency, C_1 symmetry under uniaxial stress, a single HD line and a mechanism for rapid ortho-to-para conversion. Clearly, the story is not yet finished.

Acknowledgments

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