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The H_2 Molecule in Semiconductors: An Angel in GaAs, a Devil in Si

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The electrical and optical properties of semiconductors are largely determined by the defects and impurities they contain. Without a doubt, hydrogen is the impurity which exhibits the most varied and exotic properties. In most semiconductors, it is found in three charge states and four configurations. It forms (at least) two types of dimers as well as small and large precipitates such as platelets. H also interacts with impurities and defects. It removes or changes the electrical activity of many shallow and deep centers, and catalyzes the diffusion of interstitial oxygen (in Si). Sometimes, it exhibits quantum tunneling and is associated with unusual effects such as Fermi resonances. But one of the most exotic forms of hydrogen in GaAs and Si is the interstitial H_2 molecule, which appears to play a critical role in processes such as the "smart cut". It is the only interstitial molecule observed (so far) in semiconductors. In GaAs, it behaves like a nearly-free rotator, with properties very much as one would expect them to be. But in Si, the early experiments were puzzling. No *ortho/para* splitting was observed, the symmetry appeared to be C_1, the single HD line was at the wrong place and had the wrong amplitude, and other features seemed strange as well. Recent experimental studies have now resolved many issues. However, the behavior of the simplest molecule in the Universe proved to be a tough nut to crack, which goes to show that devils can be a lot more fun than angels after all.

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1. Hydrogen in crystalline semiconductors

Hydrogen is an unavoidable impurity in most semiconductors. It penetrates into the material during the growth (from the source material or the ambient) and during many processing steps such as wet etching, the deposition of surface layers (wet oxides, nitrides, organic masks), or even metallic contacts. Hydrogen can also be introduced by exposure to plasma at a few hundred degrees Celsius or proton implantation. It is virtually always present somewhere during a process and

removing it normally requires high-temperature treatments. A number of reviews on hydrogen in semiconductors have been published in the past few years [1–3].

Once hydrogen finds its way into a crystalline semiconductor, it diffuses readily and seeks distorted or strained regions of the crystal where it forms a covalent bond, usually with a host atom. Such distorted or strained regions of the crystal always exist near defects (impurities as well as native defects). The trapping of H results in some relief of the strain around the defect, a change in its geometrical configuration, and a shift of the associated energy eigenvalues. Thus, hydrogenation shifts energy levels. The levels can shift from the gap into a band ("passivation"), from a band into the gap ("activation"), or within the gap. Hydrogen passivates shallow acceptors and donors as well as many deep levels associated with native (point or extended) defects. It is well-known for tying up dangling bonds at vacancies. It activates substitutional C in Si, and shifts the deep levels associated with many transition metal impurities [4]. In addition to changing the electrical properties of the material, hydrogen also changes its optical properties by creating centers visible by photoluminescence (PL) or Fourier-transform infrared absorption (FTIR) and Raman spectroscopies.

Hydrogen also catalyzes the diffusion of interstitial oxygen in Si [5]. Even small amounts of H dramatically enhance the formation rate and concentration of O-related thermal donors, without H becoming itself a part of these complexes. Two types of models have been proposed to explain this process (for a review, see [6]). In one, H saturates a Si dangling bond while O is at its saddle point for diffusion. This stabilizes the saddle point, thus lowering the activation energy. In the other, H attaches directly to interstitial O thus transforming the Si–O–Si structure with two "fixed" points (the two Si atoms) into a Si...H–O–Si configuration (H is at an angle) in which the {H,O} pair can rotate about its only remaining fixed point, the Si atom. This issue is far from resolved but illustrates how diverse the interactions of H in semiconductors are.

In a defect- and impurity-free semiconductor, interstitial H is found at a distorted bond-centered (BC) site [7, 8] or a tetrahedral interstitial (T) site. In Si, it exists as H^+_{BC}, H^0_{BC}, H^0_T, and H^-_T. Hydrogen in Si has negative-U properties [9], meaning that the energy of two isolated H^0_{BC} is higher than that of H^+_{BC} and H^-_T. Figure 1 shows a schematic potential energy diagram for interstitial hydrogen in Si [10]. However, there is a barrier for the transition of H^0 from the T to the BC sites. The BC site becomes a minimum of the potential energy only when an Si–Si bond distorts. In the perfect crystal, the time needed for this distortion to occur is of the order of 100 fs as it is governed by the gamma phonon. Molecular-dynamics (MD) simulations show that this timescale is much longer than the time spent by H^0_T at a given T site: the barrier for T-to-T diffusion is incredibly low. Figure 2 shows the barrier for diffusion of H^0_T calculated dynamically at $T = 0$ K. In these calculations, H is pushed with a fixed force from T to T site and the crystal is allowed to relax. The faster H^0_T is pushed, the less time the Si atoms have to react.

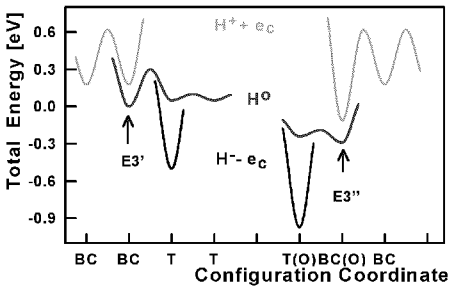

Fig. 1. Potential energy diagram (Ref. [10], with permission) for the various charge states of isolated H in Si. H^+ (top curves) exists only at the BC site and H^- (bottom curves) only at the T site. H^0 (E3' center) is stable at the BC site and metastable at the T site. It diffuses much too fast from T to T site to overcome the T to BC barrier. This conversion occurs when H^0_T arrives in the vicinity of a defect or impurity (E3" center) and self-traps at a nearby BC site.

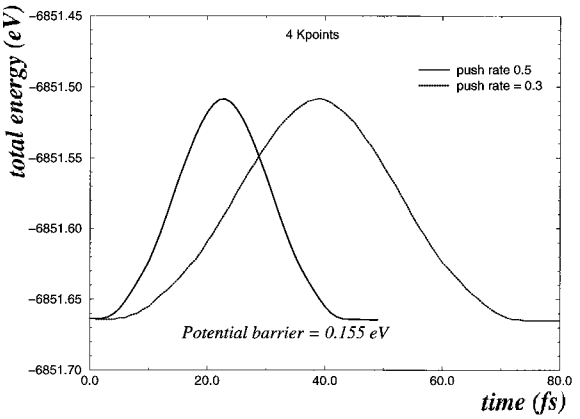

Fig. 2. Neutral H is pushed at 0.3 eV/Å or 0.5 eV/Å from T site to T site in Si at 0 K. The host atoms are allowed to relax (conjugate gradients) using first-principles, density-functional based MD simulations in 64 host atom supercells with a $2 \times 2 \times 2$ Monkhost–Pack k-point sampling. The time step is 0.2 fs. The calculated barrier for diffusion (0.155 eV) must be reduced by the zero-point energy of hydrogen (≈ 0.1 eV).

The T to BC transition occurs only when the fast H^0_T self-traps at a BC site in the vicinity of a defect or impurity [10], most commonly interstitial O in Czochralski Si or substitutional C in floating-zone material. Theory shows [6] that H^0_T is indeed attracted to such regions of the crystal.

H–H interactions lead to the formation of dimers and larger precipitates. The two best-known dimers are H_2 and H^*_2, but at least two other dimers (with the H's farther apart) have been reported [11, 12]. The interstitial H_2 molecule has been predicted to be stable over 20 years ago [13, 14] but has only recently been

observed. To date, seven distinct Raman lines associated with H_2 molecules in different surroundings in Si have been reported. The H_2^* complex [15, 16] consists of one host-host bond replaced by two host-H bonds, with one H near a BC site and the other in an antibonding position along the same trigonal axis.

When large concentrations of H are present, for example in the first few microns of a sample exposed to a hydrogen plasma, H tends to precipitate into extended structures called platelets, most often in {100} and sometimes in {111} planes. The growth of these platelets most probably involves H_2 molecules [17] and is critical to the "smart cut" [18] process.

The story of hydrogen in semiconductors is rich and fascinating. It involves a wide range of phenomena, allows the close collaboration between *ab initio* theorists and experimentalists, especially those using microscopic tools such as FTIR, Raman, or PL. This paper is a review of the properties of the isolated interstitial H_2 molecule in the two crystalline semiconductors in which it has been observed: GaAs and Si.

2. The free H_2 molecule

The energy spectrum of the free, neutral H_2 molecule includes electronic, vibrational, rotational, and (nuclear) spin states. We are interested in the states of the molecule in the temperature range in which experiments in semiconductors have been performed, that is 4 K up to room temperature. Light excitations involved in the FTIR and Raman experiments result in vibrational transitions.

The *electronic* states are separated by several eV. Under the conditions of interest, only the ground electronic state is involved.

The *vibrational* states, $E_{\rm vibr} = (n + 1/2)\hbar\omega$, are well separated in energy. The measured vibrational mode of the free molecule, 4161 $\rm cm^{-1}$, means that the separation between adjacent vibrational levels is about 0.5 eV, which is of the order of 6,000 K.

The *rotational* states have energies $E_{\rm rot} = j(j+1)\hbar^2/MR^2$, where R is the bond length. These states are separated by an amount inversely proportional to the reduced mass of the molecule. The heavier the molecule, the closer to each other the rotational states are. For something as heavy as N_2, this is $j(j+1)0.47$ meV, which means that the states $j = 0, 1, \ldots, 7$ or so are occupied at room temperature. For H_2 on the other hand, the rotational energies are $j(j+1)7.3$ meV and only $j = 0$ and $j = 1$ are occupied at room temperature. Occupying $j = 2$ requires some 800 K! Since $j = 0$ has only $m_j = 0$, it is spherically symmetric, while $j = 1$ has $m_j = -1$, 0, +1. Unless an electric field gradient is present, these m_j states are energetically degenerate and H_2 in the $j = 1$ state is a linear combination of these three states with equal coefficients. Thus, the $j = 1$ state also resembles a sphere. In order to get directionality, a molecule that looks like a dumbbell, one needs linear combinations of many j-states, that is a more massive molecule, with

closely-spaced rotational energy levels or a hindering potential which mixes the j-states.

Finally, the (nuclear) *spin* states must be considered. The two protons are two fermions and this implies that the total wave function must be antisymmetric. There are four combinations of the two spins. The three symmetric combinations are $\uparrow\uparrow$, $\uparrow\downarrow + \downarrow\uparrow$, and $\downarrow\downarrow$ which implies that H_2 can only have odd rotational states, that is $j = 1$ in our temperature range. This is *ortho*-hydrogen (o-H_2), the lowest energy state with an even spin combination. The only odd combination of spins is $\uparrow\downarrow - \downarrow\uparrow$ which implies even rotational states, for us only $j = 0$. This is *para*-hydrogen (p-H_2), the ground state. Transitions from odd to even rotational states (or vice versa) are forbidden unless there is a mechanism for flipping nuclear spins. This requires for example large magnetic field gradients. Thus, the free H_2 molecule seen by Raman spectroscopy shows two lines with intensity ratio 3:1, separated by 6 cm^{-1} (p-H_2 at 4161 and o-H_2 at 4155 cm^{-1}). The separation between the $j = 0$ and $j = 1$ states has been measured [19] to be 120 cm^{-1}. The case of D_2 is opposite because the nuclei are bosons and the wave function must be symmetric. Since "ortho" refers to the species with the largest statistical weight, o-D_2 is lower than p-D_2 (by ≈ 2 cm^{-1}), the two lines have intensity ratio 1:2, and the separation between $j = 0$ and $j = 1$ is 60 cm^{-1}.

It is useful to get a feel for *timescales*. The vibrational frequency of the free H_2 molecule is 4161 cm^{-1}. Using $\lambda\nu = c$ and $\tau(\text{vib.}) = 1/\nu$, one finds that the time involved in one complete oscillation is ≈ 8 fs. But how long does it take for the molecule to rotate? The proton wave functions are not delocalized over the entire molecule and the protons are limited by the speed of light: a 360° rotation takes a finite amount of time. An estimate is obtained semiclassically from $L = I\omega$. If we set $L^2 = l(l+1)\hbar^2$ and $l = 1$, write the moment of inertia of each proton as $M(R/2)^2$ (R is the bond length), and use $\tau(\text{rot.}) = 2\pi/\omega$, the amount of time required for rotation is of the order of 250 fs. That is long enough for about 30 vibrations! Let us note that the same order of magnitude results from the measured energy separation [19] between $j = 0$ and $j = 1$, 121 $cm^{-1} = h/\tau(\text{rot.})$, which gives 280 fs.

3. Interstitial H_2 in GaAs

The hydrogen molecule has been detected in plasma-exposed GaAs by Raman spectroscopy [20, 21]. Its observed properties are very much like one would expect them to be. At room temperature, the Raman mode is at 3911 cm^{-1}, about 250 cm^{-1} lower than the free-molecule value. Such a drop is expected because the wave function of the molecule in GaAs tends to overlap with its nearest neighbors (NNs), which weakens the H–H bond. At low temperatures, an *ortho/para* splitting of ≈ 8 cm^{-1} is clearly resolved (Fig. 3) with the expected 3:1 intensity ratio. This implies that only the $j = 0$ and $j = 1$ states are involved. No line splitting

is observed under ⟨001⟩, ⟨110⟩ or ⟨111⟩ uniaxial stress [21], implying that H_2 has spherical symmetry, an observation consistent with a nearly-free rotator in the $j = 0$ or $j = 1$ states. When a mixed H/D plasma is used, lines corresponding to H_2, a single HD, and D_2 are observed. These lines show the anticipated amplitudes and anharmonic shifts, except that the intensity of HD is rather low. None of these lines has yet been seen by FTIR.

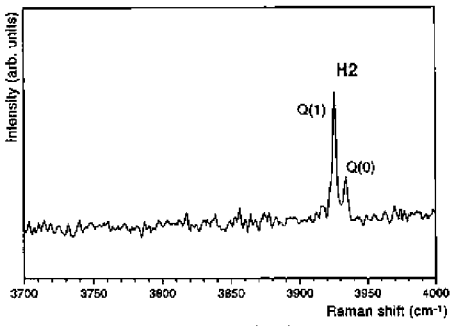

Fig. 3. The Raman spectrum of H_2 in GaAs shows the expected *ortho/para* splitting (Ref. [20], with permission).

The theoretical predictions [22–25] for H_2 in GaAs are fully consistent with the experimental data. The molecule is found to be stable at the T_{Ga} site (the center of mass is at the T site with four Ga NNs) with a very small barrier for rotation, implying a nearly free rotator. The H–H stretch frequency calculated by various authors is within 5% or so of the measured one. We have performed first-principles (classical as far as the atomic nuclei are concerned) MD simulations in 64 host atom periodic supercells, *ab initio* pseudopotentials, and atomic-like basis sets using the SIESTA [26, 27] method. A time step of 0.2 fs was used. As expected, the $T = 0$ K results fit nicely with the static calculations of other authors. The vibrational frequency of H–H calculated from linear response theory [28] is 3824 cm^{-1}, in close agreement with the observed Raman mode. MD runs at room temperature [29, 30] show that the center of mass of H_2 moves around in the T_{Ga} cage and that the molecule undergoes a weakly hindered rotation.

4. Interstitial H_2 in silicon

Isolated interstitial H_2 was seen by Raman [31] (in samples exposed to a hydrogen plasma around 250°C) and, unexpectedly, by FTIR [32, 33] (in thick samples annealed around 1250°C in a gas, then rapidly quenched). Let us note that the few micrometers probed by Raman must contain of the order of 10^{19} molecules per cm^3, while the high-temperature treatments results in some 10^{16} molecules per cm^3 throughout the volume.

The H_2 line is at 3601 cm^{-1} (Raman, room temperature) and 3618 cm^{-1} (FTIR, 10 K). The IR line width is less than 0.1 cm^{-1} with about 100 to 1 signal-to-noise ratio. The frequency drop by over 550 cm^{-1} relative to free H_2 is much larger than anticipated. It indicates that the NNs Si atoms around H_2 "steal" some electron density from the H–H bond, weakening it, which lengthens the bond and reduces the stretch frequency. But a single H_2 line was observed instead of the expected two lines with 3:1 ratio, corresponding to *o*- and *p*-H_2.

Another surprise came from FTIR experiments involving a mix of hydrogen and deuterium. The D_2 line is observed as well as a single HD line [34]. But the intensity of the IR line associated with HD is less than one-third that of H_2 or D_2, while it should be twice their size if one assumes 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 [35] as $P^{0.56}$. Thus, in the high-temperature hydrogenation, H_2 or D_2 dissociate at the surface of the crystal, diffuse into the material as atomic species, then form interstitial molecules during the quench. Yet another strange feature of the HD line is that its anharmonic shift is much larger than expected [36]. The line is higher by 85 cm^{-1} than estimated (including anharmonic corrections).

Uniaxial stress IR experiments [36] for H_2 in Si show that the line splits for all stress directions, and the splitting pattern implies C_1 symmetry! Further, the same experiments with D_2 show quantitatively identical splittings [37]. But the rate at which the lines split (i.e. the elements of the piezospectroscopic tensor) should be proportional to the frequency, i.e. inversely proportional to square root of the mass, and rate of splitting should differ by $\sqrt{2}$ for H_2 and D_2. But the observed splittings are identical (within 1%).

In oxygen-rich Si samples, three H_2-related IR lines are present [34, 38, 39]. None shows an *ortho/para* splitting. Two lines are associated with H_2 trapped near interstitial oxygen (O_i) and the third is isolated interstitial H_2. Annealing studies show that the binding energy of H_2 to O_i is 0.26 ± 0.02 eV and that the activation energy for diffusion of H_2 is 0.78 ± 0.05 eV. However (Fig. 4), the O_i line shifts and splits into two lines with intensity ratios 3:1 (for $\{O_i, H_2\}$) and 1:2 (for $\{O_i, D_2\}$).

Yet, the (static) theoretical predictions for interstitial H_2 in Si are that its center of mass is at the T site, with the H–H axis along a $\langle 100 \rangle$ or $\langle 110 \rangle$ direction and a barrier for rotation very close to zero (typically 0.1 eV or less, excluding the zero-point energy). Various authors almost invariably find a stretch frequency substantially reduced relative to the free molecule value, typically within 5% of the measured value. Similar conclusions were reached by more than a dozen authors, some using molecular clusters, others periodic supercells; some using semiempirical Hartree–Fock, others *ab initio* Hartree–Fock (with or without Moller–Plesset corrections for electron correlation), others yet with density-functional theory (within local density approximation (LDA) or generalized gradient correction (GGA));

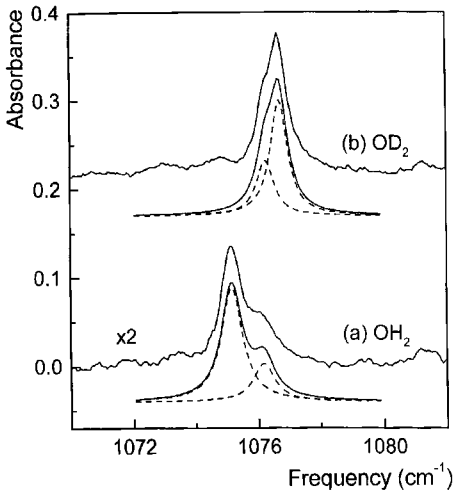

Fig. 4. FTIR spectra for D_2 (b) and H_2 (a) trapped near interstitial O in Si. The oxygen line splits into two components with 1:2 and 3:1 intensity ratios (Ref. [37], with permission).

some with local basis sets, others with plane wave (for details references, see the discussion in Ref. [30]).

While the various predictions differ in the finer details, the general picture painted by all of them is that of a nearly-free rotator centered at the T site: a high-symmetry, IR-inactive, molecule, with no hint as to why the *ortho/para* splitting should be missing, why the HD line should be far off-center and about 8 times weaker than expected, or why the stress-splittings of H_2 and D_2 should be identical. The splitting of the O_i line is usually not discussed.

First-principles MD simulations [30] done at 0 K confirm the static predictions. The center of mass is at the T site, the H–H axis points along $\langle 100 \rangle$ with other orientations very close in energy. The vibrational modes of H_2, HD, D_2 obtained from linear response theory are 3549, 3081, 2511 cm^{-1}, respectively: within 69, 184, 132 cm^{-1}, respectively from the measured ones. Let us note that the HD mode is at the wrong place.

MD simulations are constant temperatures (30 K, 77 K, and 300 K) show that the molecule rapidly bounces around in its cage. The center of mass is nearly free to move within a volume of radius ≈ 0.5 Å around the T site (Fig. 5). The typical time needed to abruptly change direction is of the order of 120 fs. No complete rotation of the molecule is observed. However, since a free H_2 molecule in the $j = 1$ state needs some 250 fs to make one turn, a hindered rotator should need longer times — possibly beyond the reach of MD simulations with a 0.2 fs time step. Under uniaxial stress, the calculated average position of the center of mass appears to move off the high-symmetry axis, but again, the simulation times are too short for such predictions to be solid.

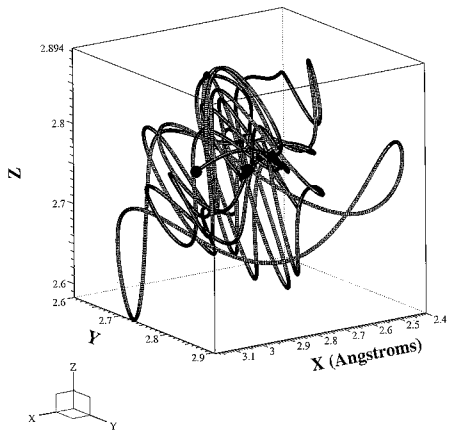

Fig. 5. MD simulations for H_2 at the T site in Si at 77 K show that its center of mass moves very rapidly as the molecule bounces within its cage [30]. Let us note the very abrupt changes of direction. The maximum displacement of the center of mass is about 0.5 Å away from the T site.

Repeated attempts to induce the formation of H_2 molecules in the cell starting from two H interstitials have been unsuccessful, maybe because of insufficient simulation (real) times. However, whenever one of the two hydrogen interstitials in the cell is H_{BC}, the H_2^* complex invariably results: we have never observed $H_{BC}^+ + H_T^-$ to give H_2: it always gives H_2^* instead.

Thus, the various experimental data for hydrogen molecules in Si agree only on the presence of interstitial H_2 and D_2 in Si and its low vibrational frequency. But the molecule is IR-active, the *ortho/para* splitting is not observed (except in the splitting of O_i line), the symmetry appears to be ridiculously low, the piezospectroscopic tensors of H_2 and D_2 are identical, the single HD line is much too weak and at the wrong place, and all the theorists make predictions which are at odds with the data.

5. The solution

Thanks to the persistence and cleverness of Michael Stavola and his collaborators at Lehigh University, everything has recently been shown to be perfectly simple and logical. The key was the observation [40] of a second HD line in Si, a new line that is not present at 4 K but is dominant at 77 K (Fig. 6). The experiments were done in samples exposed to a mixed H_2/D_2 gas at 1250°C then quenched. The "new" HD line is at 3191 cm^{-1}, very close to its expected position relative to the H_2 and D_2 lines, and 74 cm^{-1} lower than the "old" HD line at 3265 cm^{-1}. A plot of the log of the relative intensities of the 3191 and 3265 lines vs. inverse temperature [40] gives a straight line and yields the activation energy 71 ± 4 cm^{-1}, very close to the 74 cm^{-1} separation between the two HD lines. This

value is also very close to the separation between $j = 0$ and $j = 1$ rotational states of the free molecule (Sec. 2). In contrast to H_2 and D_2 (for which only rotational states with even or with odd parity are allowed, depending on the nuclear spin state), even and odd rotational states are allowed for HD.

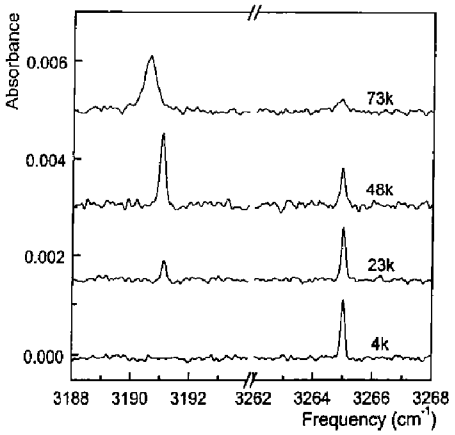

Fig. 6. FTIR spectra of HD in Si vs. temperature (Ref. [40], with permission).

Thus, the H_2, HD, D_2 lines at 3618, 3191, and 2643 cm^{-1} are all purely vibrational transitions with $j = 1$ in both the ground and first excited vibrational states. The "old" HD line (at 3265 cm^{-1}) is a ro-vibrational transition from $j = 0$ in the ground vibrational state to $j = 1$ in the first excited state. This transition includes one quantum of rotational energy, the 74 cm^{-1}. The corresponding transition is forbidden for *ortho-* and *para-* H_2 and D_2. The $j = 0$ to $j = 0$ transition of HD is not seen, suggesting that it is electric-dipole forbidden.

These experimental data imply that the selection rules for the electric-dipole allowed transitions of H_2, HD, and D_2 in Si are $\Delta j = 0$ but the $j = 0$ to $j = 0$ transition is not IR active. Thus, the usual selection rule $\Delta j = \pm 1$ for the rotational states of a free rotator is broken in tetrahedral symmetry for the $j = 1$ state but not for the $j = 0$ state. Applying these rules to H_2 and D_2 implies that only o-H_2 and p-D_2 are visible by FTIR (both involve $j = 1$ to $j = 1$ transitions). Therefore, no *ortho/para* splitting should be expected in the FTIR spectra. Further, only 75% of H_2 and 33% of D_2, but 100% of HD are visible. An estimate [40] of the effective dipole moments of the three molecules combined with the visible fraction of each species and the intensity of the new 3191 cm^{-1} line suggests that the relative concentrations of all three species are close to the expected ones.

Further evidence that these selection rules hold and the explanation of the strange uniaxial stress data were soon obtained by the same group [41]. In tetrahedral symmetry, the $j = 0$ state becomes A_1 while the $j = 1$ state becomes T_2 and is threefold degenerate. Therefore, the $j = 1$ to $j = 1$ transition between degenerate

states involves a rotronic coupling [42] leading to a dynamic breaking of the usual selection rules. The positions and strengths of the lines under uniaxial stress fit perfectly the ones calculated by Kaplyanskii [43] for T_2 to T_2 transitions under uniaxial stress. Further, as noted by Chen et al. [41], the splitting arises from a perturbing potential energy whose effect is calculated from the matrix elements of rotational wave functions, all of which are independent of the mass. Thus, the splittings should be identical for H_2 and D_2, as observed.

The next question is that of the molecule trapped near interstitial oxygen. The story is inherently more complicated because there are many more lines to discuss. The low-temperature FTIR data show that O_i lines split into two components with intensity ratio 3:1 for $\{O_i, H_2\}$ and 1:2 for $\{O_i, D_2\}$. At 4.2 K, (i) the $\{O_i, H_2\}$ complex has two lines associated with H_2 at 3731 and 3789 cm^{-1} (note: they are separated by 58 cm^{-1}) as well as a weak satellite at 3737 (6 cm^{-1} from the 3731 line); (ii) the $\{O_i, D_2\}$ complex has two lines associated with D_2 at 2715 and 2775 cm^{-1} (note: they are separated by 60 cm^{-1}) as well as a weak satellite at 2716 (1 cm^{-1} from the 2715 line); (iii) the $\{O_i$,HD$\}$ complex has two lines at 3285 and 3304 cm^{-1} (separated by 19 cm^{-1}) and no satellite. The initial explanation proposed [34, 38, 39] was that there are two inequivalent configurations for each of these complexes, but this failed to explain the strange splitting of the O_i line.

Again, the key was to look at the temperature dependence of the HD line [44]. As the temperature is increased from 4.2 K to 50 K, the two HD lines disappear together and two new lines appear together, 3282 and 3341 cm^{-1} (note: these are separated by 59 cm^{-1}). A plot of the log of the intensity ratio of the 3282 and 3285 lines vs. $1/T$ reveals an activation energy of 19 cm^{-1}, precisely the splitting of the two low-temperature HD lines.

Several points are critical here. *First*, increasing the temperature populates a rotational level of HD located 19 cm^{-1} above $j = 0$. Thus, 19 cm^{-1} is the separation between $j = 0$ and $j = 1$. Let us note that the $j = 0$ to $j = 0$ transition is no longer forbidden (the symmetry is lower because of the presence of O_i). *Second*, the pairs of HD lines appear and disappear together, indicating that one deals with two transitions of a single complex, not with two metastable configurations. This must be true for $\{O_i, H_2\}$ and $\{O_i, D_2\}$ as well. *Third*, the two transitions observed for H_2, HD, and D_2 are all separated by ≈ 59 cm^{-1}, independent of the mass. This suggests that the same transitions are responsible and reminds us of the mass-independent splitting of the lines observed under uniaxial stress. Then, the $j = 1$ level splits because of the applied stress. Here, the $j = 1$ level splits because of the presence of oxygen, more precisely, because O has a large electron affinity, resulting in a large dipole moment, hence an electric field gradient. This is summarized in Fig. 7, which shows the ro-vibrational energy diagram and the observed transitions for (a) isolated HD and (b) the $\{O_i, HD\}$ complex at (i) 4.2 K and (ii) $T > 10$ K. Let us note that the $j = 1$ state has $m_j = -1, 0, +1$ and should split into three components even though only two are seen in the experiments.

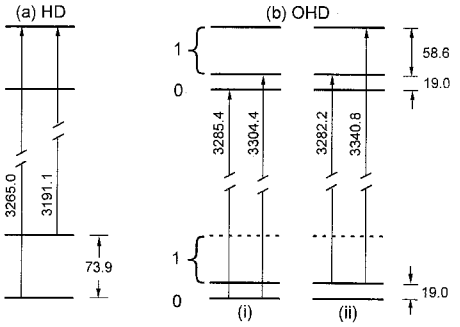

Fig. 7. Observed IR transitions for (a) isolated interstitial HD in Si and (b) for the $\{O_i, HD\}$ complex at (i) 4.2 K and (ii) $T > 10$ K (see text). From Ref. [44], with permission.

The consequences are the following. There is a single configuration of the interstitial molecule trapped near O_i. The O_i line splits because the interactions between *o*-H_2 and O_i and between *p*-H_2 and O_i are not quite identical. The electric field associated with oxygen splits the $j = 1$ level. The two strongest H_2 lines are transitions involving *o*-H_2, from the lower branch of $j = 1$ in the ground vibrational state to the lower and upper branches of $j = 1$ in the first excited vibrational state. The same holds for *p*-D_2. Finally, the weak satellites observed at 3737 (or 2716) cm^{-1} for H_2 (or D_2) are the $j = 0$ to $j = 0$ transitions, dipole allowed when O_i is nearby, that is *p*-H_2 (or *o*-D_2). For a detailed discussion of the relative intensities of these lines, see Ref. [44].

6. Open questions and discussion

Thus, the behavior of interstitial H_2 molecules in semiconductors, so easy to understand in GaAs and so tricky in Si, is now fully explained. Or is it? Even though *p*-H_2 and *o*-D_2 are not IR-active in Si, they should be visible by Raman spectroscopy. The first experiments failed to detect both species even at low temperatures. But recent work has shown that the local temperature at the laser spot (now measured from the Stokes/anti-Stokes ratio) is substantially higher than that measured elsewhere on the sample because of the low thermal conductivity of the plasma-exposed layer. This resulted in broader lines and unresolved splittings. This technical problem is now solved and the most recent Raman spectra [45] do show the *ortho* and *para* species (Fig. 8).

However (Fig. 9), the two lines have a very different annealing behavior: *p*-H_2 disappears at much lower temperatures than *o*-H_2 [45]. The same is observed for H_2 in GaAs. The authors attribute this to a higher diffusivity of *p*-H_2 than *o*-H_2. Indeed, *o*-H_2 and *p*-H_2 are sufficiently different to induce measurably distinct shifts in the O_i line. The authors propose that this could be the case for HD as

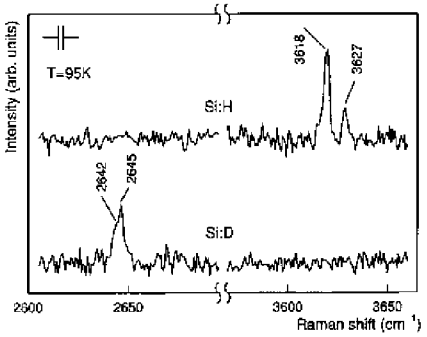

Fig. 8. Most recent Raman spectra showing *ortho-* and *para-* H_2 and D_2 species in Si (Ref. [45], with permission).

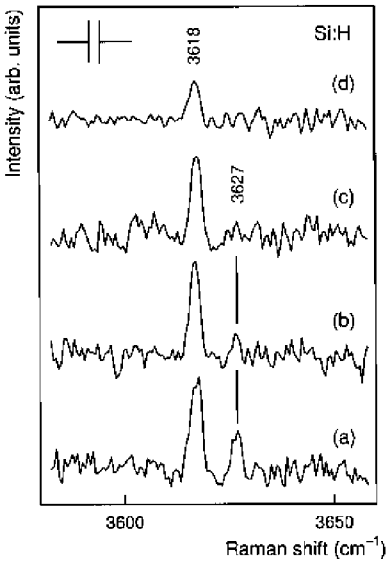

Fig. 9. The p-H_2 line anneals out much faster than the o-H_2 line, leading to speculation that the activation energy for diffusion of H_2 depends on its rotational state (Ref. [42], with permission).

well, most of which being in the $j = 0$, $m_j = 0$ state. This suggests an alternative explanation for the low intensity of the HD line in both Si and GaAs. While it is possible that the details of the shape of the wave function affect activation energies, quantifying this effect remains to be done.

Another open question is the comparison of Si and GaAs. Since o-H_2 and p-D_2 are IR-active T_2 to T_2 transitions in Si, should not they be IR-active in GaAs as well? But the uniaxial stress Raman data [21] failed to show a splitting of the lines in GaAs while the splitting is very visible in the IR data in Si [36]. This

could be associated with the width of the Raman lines and their broadening under uniaxial stress, and the insufficient resolution of the Raman setup used.

Finally, there is the issue of the formation of H_2 starting with interstitial H. Large concentrations of interstitial molecules are present following both plasma exposure and high-temperature anneals in a hydrogen gas. If only H_{BC}^{+} or only H_{T}^{-} interstitials are present (as suggested by the negative-U argument [9]), long-range repulsion should prevent the formation of molecules. Further, MD simulations of H_{BC}^{+} (or H_{BC}^{0}) with H_{T}^{-} (or H_{T}^{0}) in the same cell *always* result in the immediate formation of H_2^*, never H_2. Although these simulations are too short to demonstrate that H_2 cannot form, they do demonstrate that H_2^* is a possible — if not likely — result. Yet, H_2^* has never been observed in the samples in which H_2 is seen (except when associated with platelets). Since the IR intensity of the H_2^* lines is at least one order of magnitude stronger than that of H_2, even small amounts of H_2^* would be very visible in the spectra.

But if we rule out both charge states of H_{BC} as possible precursors for H_2 formation, and rule out interactions between negatively charged H_{T}^{-} species (unlikely to be abundant in p-type Si anyway), we are left with the metastable H_{T}^{0}. Why would there be such an abundance of this metastable (albeit fast-diffusing) species in the bulk?

An alternative is that there exists a mechanism other than the simple H–H interactions which triggers H_2 formation. So far, our simulations succeeded only once in forming interstitial H_2 molecules within a few ps simulation time. This calculation was unrelated to the H_2 issue and the formation of molecules came as a surprise. But the trigger was substitutional Cu: room-temperature simulations of the {Cu, H_4} complex produced Cu + $2H_2$, leaving Cu in place as a trap for more hydrogen. Of course, we do not suggest that Cu is the culprit. But could the formation of H_2 be triggered by the multiple trapping [46] of H at some defect or impurity (maybe O or C), which would act as a catalyst for H_2 formation?

What are the lessons to be learned from all this? The abundance of misleading or misinterpreted experimental data for H_2 in Si reminds us that any measured spectrum, regardless how sharp and clean, may only be a part of the story. The interpretation of raw data is rarely unique, and *ab initio* theory often plays an important role in this interpretation. Careful measurements of microscopic nature (FTIR, Raman, PL, EPR, or other), obtained under controlled conditions, always provide pieces of a puzzle. How these pieces fit together, and even to which puzzle they belong, are questions rarely answered when a single technique is used. Nature works in sometimes mysterious, but always clever, ways.

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