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. It 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.

PACS numbers: 61.72.-y, 66.30.Lw, 72.10.Fk

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

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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\textsuperscript{+}\textsubscript{BC}, H\textsubscript{0}\textsubscript{BC}, H\textsubscript{0}\textsubscript{T}, and H\textsubscript{−}\textsubscript{T}. Hydrogen in Si has negative-\textit{U} properties [9], meaning that the energy of two isolated H\textsubscript{0}\textsubscript{BC} is higher than that of H\textsuperscript{+}\textsubscript{BC} and H\textsubscript{−}\textsubscript{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\textsubscript{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\textsubscript{0}\textsubscript{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\textsubscript{0}\textsubscript{T} calculated dynamically at \textit{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\textsubscript{0}\textsubscript{T} is pushed, the less time the Si atoms have to react.
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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 ($\approx 0.1$ 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, $E_{\text{vib}} = (n + 1/2)\hbar \omega$, are well separated in energy. The measured vibrational mode of the free molecule, 4161 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 $E_{\text{rot}} = j(j + 1)\hbar^2/2MR^2$, 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 \(|1, 1\rangle\), \(|1 + 1\rangle\), and \(|1\rangle\) which implies that \( \text{H}_2 \) can only have odd rotational 
states, that is \( j = 1 \) in our temperature range. This is ortho-hydrogen \((o-\text{H}_2)\), the 
lowest energy state with an even spin combination. The only odd combination of 
spins is \(|1 - 1\rangle\) which implies even rotational states, for us only \( j = 0 \). This is 
para-hydrogen \((p-\text{H}_2)\), 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 \( \text{H}_2 \) 
molecule seen by Raman spectroscopy shows two lines with intensity ratio 3:1, 
separated by 6 cm\(^{-1}\) \((p-\text{H}_2 \text{ at } 4161 \text{ and } o-\text{H}_2 \text{ at } 4155 \text{ cm}^{-1})\). The separation 
between the \( j = 0 \) and \( j = 1 \) states has been measured \([19]\) to be 120 cm\(^{-1}\). The 
case of \( \text{D}_2 \) 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, 
\( o-\text{D}_2 \) is lower than \( p-\text{D}_2 \) (by \( \approx 2 \text{ cm}^{-1} \)), 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 
\( \text{H}_2 \) 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 \( \approx 8 \) 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 
\( M(R/2)^2 \) \((R \text{ is the bond length})\), 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 \( \text{H}_2 \) 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 
(\( \text{NNs} \)), which weakens the H–H bond. At low temperatures, an ortho/para splitting 
of \( \approx 8 \) 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 \( \text{H}_2 \) 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 \( \text{H}_2 \), a single HD, and \( \text{D}_2 \) 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.

![Raman spectrum of \( \text{H}_2 \) in GaAs](image)

**Fig. 3.** The Raman spectrum of \( \text{H}_2 \) in GaAs shows the expected ortho/para splitting (Ref. [20], with permission).

The theoretical predictions [22–25] for \( \text{H}_2 \) in GaAs are fully consistent with the experimental data. The molecule is found to be stable at the \( T_{\text{Ga}} \) 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, \textit{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 \( \text{H}_2 \) moves around in the \( T_{\text{Ga}} \) cage and that the molecule undergoes a weakly hindered rotation.

4. Interstitial \( \text{H}_2 \) in silicon

Isolated interstitial \( \text{H}_2 \) was seen by Raman [31] (in samples exposed to a hydrogen plasma around 250\(^\circ\)C) and, unexpectedly, by FTIR [32, 33] (in thick samples annealed around 1250\(^\circ\)C in a gas, then rapidly quenched). Let us note that the few micrometers probed by Raman must contain of the order of \( 10^{15} \) 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 \( 0.26 \pm 0.02 \) eV and that the activation energy for diffusion of \( H_2 \) is \( 0.78 \pm 0.05 \) 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 \textit{ab initio} Hartree–Fock (with or without Møller–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 (100) 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 $\approx 0.5$ 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.
Repeats 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 $O_1$ 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 $71 \pm 4$ 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 \( \text{H}_2 \) and \( \text{D}_2 \) (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 \( \text{HD} \).

Thus, the \( \text{H}_2 \), \( \text{HD} \), \( \text{D}_2 \) 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- \( \text{H}_2 \) and \( \text{D}_2 \). 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 \( \text{H}_2 \), \( \text{HD} \), and \( \text{D}_2 \) 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 \( \text{H}_2 \) and \( \text{D}_2 \) implies that only ortho- \( \text{H}_2 \) and para- \( \text{D}_2 \) 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 \( \text{H}_2 \) and 33% of \( \text{D}_2 \), 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 $H_2$ line [44]. As the temperature is increased from 4.2 K to 50 K, the two lines disappear and the pairs of HD 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 $H_2$ 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 $\approx 59$ 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.
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 $\alpha$-$H_2$ 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 $\alpha$-$H_2$, 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 $\alpha$-$D_2$). 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 $\alpha$-$D_2$ 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 $\alpha$-$H_2$ [45]. The same is observed for $H_2$ in GaAs. The authors attribute this to a higher diffusivity of $p$-$H_2$ than $\alpha$-$H_2$. Indeed, $\alpha$-$H_2$ 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\textsubscript{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\textsuperscript{+} or only H\textsubscript{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\textsuperscript{+} (or H\textsuperscript{0}) with H\textsubscript{T} (or H\textsuperscript{+}) in the same cell \textit{always} result in the immediate formation of H\textsubscript{2}, never H\textsubscript{2}. Although these simulations are too short to demonstrate that H\textsubscript{2} cannot form, they do demonstrate that H\textsubscript{2} is a possible — if not likely — result. Yet, H\textsubscript{2} has never been observed in the samples in which H\textsubscript{2} is seen (except when associated with platelets). Since the IR intensity of the H\textsubscript{2} lines is at least one order of magnitude stronger than that of H\textsubscript{2}, even small amounts of H\textsubscript{2} would be very visible in the spectra.

But if we rule out both charge states of H\textsubscript{BC} as possible precursors for H\textsubscript{2} formation, and rule out interactions between negatively charged H\textsubscript{T} species (unlikely to be abundant in p-type Si anyway), we are left with the metastable H\textsubscript{T}\textsuperscript{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\textsubscript{2} formation. So far, our simulations succeeded only once in forming interstitial H\textsubscript{2} molecules within a few ps simulation time. This calculation was unrelated to the H\textsubscript{2} issue and the formation of molecules came as a surprise. But the trigger was substitutional Cu: room-temperature simulations of the \{Cu, H\textsubscript{4}\} complex produced Cu + 2H\textsubscript{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\textsubscript{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\textsubscript{2} formation?

What are the lessons to be learned from all this? The abundance of misleading or misinterpreted experimental data for H\textsubscript{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 \textit{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.

**Acknowledgments**

This work is supported in part by a grant from the R.A. Welch Foundation, a contract from the National Renewable Energy Laboratory, and a research award.
from the Humboldt Foundation. Many thanks to Michael Stavola, Joerg Weber, Edward Lavrov, and Knud Bonde Nielsen for inspiring discussions and for permission to reproduce their figures, some of them unpublished. Thanks also to Kirby Wells and Jason McAfee for many MD simulations and to the High Performance Computer Center at Texas Tech for many hours of CPU time.

References

[29] J. McAfee, S.K. Estreicher, unpublished. Note that the discussion for H$_2$ in GaAs in Ref. [30] incorrectly states that the molecule is static in this host. The erroneous statement resulted from a bug in a graduate student who mislabeled a critical file.