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Hydrogen molecules in 4H-SiC and 2H-GaN

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Abstract
We present the results of theoretical calculations of the structure, diffusion and rotational energies, and the ro-vibrational modes, of the hydrogen molecule in the hexagonal part of 4H-SiC and in 2H-GaN. In both materials, the molecule is stable and aligned along the *c*-axis. Its rotational barrier is sufficiently large that ortho- and para-forms have almost degenerate ro-vibrational modes. The origin of two modes at 4090 and 4110 cm^{-1} attributed to molecules observed in multi-transmission FTIR experiments on Mg doped insulating GaN grown by OMVPE is discussed.

1. Introduction

The hydrogen molecule is a well studied defect in both Si and GaAs where it is almost a free rotator [1–5]. However, little is known about the molecule in wurtzite GaN and even less in SiC. A previous theoretical paper found that in semi-insulating 2H-GaN, the lowest energy configuration of hydrogen is the molecular form with the molecule aligned along the *c*-axis [6]. However, it is not known whether H_2 in SiC and GaN behave as free rotators as in silicon. A recent FTIR experiment on 2H-GaN finds two modes at $\sim$4100 cm^{-1} split by $\sim$20 cm^{-1} and attributed to the ortho- and para-forms of H_2 [7]. This is a surprisingly large splitting in view of the fact that for the free molecule, and those in Si and GaAs, the splitting is between 6 and 10 cm^{-1}. We investigate here the credibility of this proposal by using *ab initio* density functional methods to determine the structure, diffusion and energetics, as well as the ro-vibrational modes and the equilibrium solubility of the molecule in 2H-GaN and 4H-SiC.

2. Method

We use density functional theory (DFT) as implemented in the AIMPRO code [8]. Gaussian orbitals are used as a basis set together with norm-conserving pseudopotentials.

The calculations were carried out in 72 atom unit cells, with a Monkhorst–Pack (MP)-2^3 sampling scheme. For calculations on SiC we used Hartwigsen–Goedecker–Hutter pseudopotentials [9], whereas Troullier–Martins pseudopotentials were used for GaN. The hydrogen atoms were treated with a bare ion potential instead of a pseudopotential. These choices were made simply because the former pseudopotentials are optimal for Gaussian basis sets and incorporate additional information about the atomic configurations. The Troullier–Martins pseudopotentials have been historically generated with plane wave basis sets in mind although it is not expected that the choice of pseudopotential will lead to significantly different vibrational modes. Convergence tests were carried out using MP-4^3 sampling for the ground state structures. Differences in total energy between MP-2^3 and MP-4^3 sampling were generally less than 0.07 eV. For the calculation of the rotational barrier in GaN we used an MP-4^3 sampling. Each Si, C, Ga and N atom has a basis consisting of s, p and d Gaussian orbitals. For Si and C we used 28 and for Ga and N 40 basis functions. Diffusion barriers were determined by displacing the molecule along the *c*-axis and relaxing the supercell while keeping one of the H atoms fixed. For the calculation of the rotational barrier, we kept the centre of the molecule fixed and calculated its energy profile while we rotated the molecule about both the *c*-axis and a vector lying in the basal plane. For these calculations, the host atoms were kept fixed. Finally, for the highest energy configuration corresponding to the rotational barrier, we relaxed the bulk atoms while maintaining fixed H atom positions.

The vibrational modes of the molecule were found by displacing each H atom in turn by about 0.05 Å along each Cartesian axis, then computing the analytic expression for the force acting on both H atoms. The H atom was then displaced −0.05 Å along the same Cartesian axis and the force recomputed. The second derivative of the energy with respect to the movement of each H atom can then be found from the difference between these forces. These second derivatives lead directly to the dynamical matrix of the molecule from which the six molecular frequencies can be found. It is important to note that the calculated frequencies have some anharmonicity included as analytic second derivatives are not used.

3. Results

3.1. Structures and LVMs

In both crystals we find H_2 to lie in the hexagonal channel and aligned along the *c*-axis. In the case of 4H-SiC, the centre of the molecule is shifted 0.20 Å along the *c*-axis from the centre of the chair hexagonal cage towards the nearest Si atoms. In GaN, this displacement is 0.14 Å towards the Ga atoms forming the chair hexagonal configuration. The equilibrium bond lengths are 0.775 Å in SiC and 0.755 Å in GaN. These are 0.009 Å longer in SiC and 0.011 Å shorter in GaN than the calculated bond length of free H_2 (0.766 Å).

The stability of these configurations was tested by trying different starting configurations for H_2 but all relaxed to the ones described above. The stacking of bi-layers in 4H-SiC is given by ABCB. Two of the layers have cubic ABC stacking and two have hexagonal AB stacking. We find the stable site for the molecule in the cubic layers to be 0.7 eV higher than in the hexagonal ones.

The stretch frequency of H_2 is 3800 cm^{-1} in SiC and 4212 cm^{-1} in GaN compared to 4166 cm^{-1} for free H_2. The last value is in good agreement with the room temperature gas value of 4161 cm^{-1} (para-H_2). In GaN and SiC, H_2 has modes at ∼600 and 700 cm^{-1} respectively related to the displacement of the H atoms in the basal plane (see table 1). These modes are however lower in frequency than the highest bulk modes in both SiC and GaN and, although decoupled from the bulk modes, they could not be easily observed.

Table 1. Local vibration modes (LVMs) of H_2 (cm^{-1}) in 2H-GaN, the hexagonal cage of 4H-SiC and for the free molecule. A_1 is the stretch mode of the molecule, A_2 is a translational mode along the *c*-axis; the lower E mode is a purely rotational mode whereas the higher one has a translational component.

Symmetry	4H-SiC	2H-GaN	Free H_2
A_1	3800	4212	4166
E	1300	1162	
A_2	970	836	
E	724	600	

3.2. Calculation of diffusion barriers

The barrier W for diffusion was found as described above. For GaN, we find a barrier of 1.8 eV. The temperature T describing the onset of diffusion can be estimated using $T \sim W(k_B \ln(\nu_0/\nu))^{-1}$, where $\nu_0 \sim 10^{13}$ s^{-1} is a typical atomic jump frequency and $\nu \sim 1$ s^{-1} the number of diffusion steps per second. This gives a value for T around 400 °C. The values of W and T are very much larger than ∼0.8 eV and ∼100 °C found for Si [10].

For 4H-SiC, we calculated the barrier by moving the molecule from its position in the hexagonal channel through a hexagon towards the tetrahedral cage site. However, we found that the molecule dissociates when forced through the hexagon. This implies that the diffusion barrier, >2.5 eV, along the *c*-axis is larger than the binding energy of the two H atoms in the molecule.

3.3. Reorientation barrier and ro-vibrational modes

The molecular reorientation barrier in both materials is well described by the potential

$$U(\theta, \phi) = \sin^2(\theta)(a - b\sin(2\theta)\sin(3\phi))$$

where θ is the angle between the molecular axis and the *c*-axis and ϕ the angle between the projection of the molecular axis onto the basal plane and $[\bar{2}110]$. To simplify the calculations of the rotational levels we ignored the dependence on ϕ and assumed a cylindrical potential $U(\theta) = a\sin^2(\theta)$. This is justified as b is only about 20% of a for both crystals. Moreover, at the maximum of the potential the molecule lies in the basal plane and $U(\theta = 90°, \phi) = a$ is independent of ϕ and b. The barrier height a is taken to be 0.35 eV for SiC and 0.25 eV for GaN, if the bulk atoms of the supercell are kept fixed. Relaxing the bulk atoms reduced these to 0.29 and 0.21 eV for SiC and GaN, respectively.

The potential has a quadratic form near its minima corresponding to $\theta = 0$ and π giving an effective stiffness constant $k' = 2a/r_0^2$ where r_0 is the molecular length. This quadratic potential gives energy levels of a two dimensional harmonic oscillator of the form $(n_1 + n_2 + 1)\hbar\omega$ where $\omega = \sqrt{k'/\mu}$ and μ is the reduced mass of the molecule. Inserting values for a appropriate for GaN we find $\omega = 630$ cm^{-1} in reasonable agreement with the frequency in table 1. We next examine the energy levels due to the full potential having minima at both $\theta = 0$ and π.

Consider now the Schrödinger equation for the molecule whose centre of mass is fixed at a site:

$$\frac{-\hbar^2}{2\mu}\nabla^2\Psi(\boldsymbol{r}) + V(\boldsymbol{r})\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r}).$$

Here $\boldsymbol{r}$ denotes the bond length and alignment in space and μ is the reduced molecular mass. We assume that the potential V includes a vibrational term and is given by $(r_e/r)^2U(\theta)$ +

Table 2. Lowest rotational eigenvalues W_j (cm^{-1}) for H_2, HD and D_2.

j, m	H_2	HD	D_2
SiC			
0, 0	682.70	595.71	497.82
1, 0	682.92	595.74	497.82
1, ±1	1360.3	1187.4	993.4
GaN			
0, 0	570.63	499.64	418.83
1, 0	571.62	499.83	418.84
1, ±1	1139.7	995.6	835.0

$k(r - r_e)^2/2$ with r_e the equilibrium length. With this choice the Schrödinger equation is separable and, writing $\Psi(\boldsymbol{r}) = \chi(r - r_e)e^{im\phi}\Theta(\theta)$, the equation for Θ becomes

$$\frac{1}{\sin\theta\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta} + \frac{1}{B_\nu}(W_j - U(\theta)) = 0 \tag{1}$$

where B_ν is the ro-vibrational constant given by $\frac{\hbar^2}{2\mu r_\nu^2}$. When $U = 0$, the W_j become the familiar rotational energy levels $j(j+1)B_\nu$ with $j \geqslant |m|$.

χ satisfies the oscillator equation [11]

$$\frac{1}{r^2\chi}\frac{\partial}{\partial r}\left(r^2\frac{\partial\chi}{\partial r}\right) - \frac{W_j}{B_\nu r^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{k}{2}(r - r_e)^2\right) = 0.$$

Hence, writing $\chi = S/r$,

$$\frac{1}{S}\frac{d^2S}{dr^2} + \left(-\frac{W_j}{B_\nu r^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{k}{2}(r - r_e)^2\right)\right) = 0.$$

Letting $r = r_\nu$ in the $B_\nu r^2$ term, this equation becomes that of a harmonic oscillator and hence $E = \hbar(\nu + 1/2)\omega + W_j$.

We then need to solve equation (1). Putting $x = \cos\theta$, the equation becomes

$$\frac{1}{\Theta}\frac{d}{dx}\left((1 - x^2)\frac{d\Theta}{dx}\right) - \frac{m^2}{1 - x^2} + \frac{1}{B_\nu}(W_j - U(x)) = 0.$$

This can be written as a Sturm–Liouville equation:

$$\frac{d}{dx}\left(p(x)\frac{d\Theta}{dx}\right) + q(x)\Theta = 0$$

with $p(x) = 1 - x^2$, $q(x) = -\frac{m^2}{1-x^2} + \frac{W_j - U(x)}{B_\nu}$ and is solved numerically.

Because q is an even function of x the solutions are either even under $x \to -x$ or odd. Even solutions obey $\Theta' = 0$ at $x = 0$ and odd solutions obey $\Theta = 0$ at $x = 0$. At $x = 1$, $p(x)\Theta(x)$ must vanish.

The rotational levels for $\nu = 0$ are given in table 2. The two lowest energies of H_2 in GaN at 570 and 1139.7 cm^{-1} are close to those given by the harmonic approximation to U described above. The para-species of H_2 arises from the $j = m = 0$ state while the $j = 1, m = 0$ state yields the ortho-species. The potential has lifted the degeneracy of the $j = 1$ states of the free rotator.

The ro-vibrational transitions observed in IR come from transitions $\Delta\nu = 1$ involving separately ortho- and para-species. Thus the ortho–para splitting of H_2 in GaN is one order of magnitude smaller than in silicon. To obtain an ortho–para splitting of ~20 cm^{-1} the barrier a would have to be as small and around 0.08 eV.

Table 3. The various contributions to the free energy (eV).

T (K)	$-k_B T \ln(Z_{H_2}^{trans})$	$-k_B T \ln(Z_{H_2}^{rovib})$	$-k_B T \ln(Z_{tot}^{GaN})$	$-k_B T \ln(Z_{tot}^{SiC})$
0	0.0	0.26	0.63	0.64
300	−0.3	0.21	0.57	0.58
2000	−2.8	−0.4	−0.7	−0.6

3.4. Solubility

To estimate the molecular equilibrium solubility, we need to calculate the formation energy of H_2 in the crystal given by

$$E^f = E_{tot} - E_{bulk} - \mu_{H_2} \quad (2)$$

where E_{tot} is the energy of the supercell with H_2, E_{bulk} the energy of the supercell without H_2 and μ_{H_2} the chemical potential of free H_2. Ignoring contributions from the vibrational and rotational energies of the molecule in the solid and in vacuum, and using only the calculated energies, we find that in SiC the formation energy $E_{tot} - E_{bulk} - E_{H_2}$ of H_2 is 2.4 eV and in GaN 1.8 eV. The latter is in agreement with the value given in [6].

To take into account the ro-vibrational terms, we found the free energy F with respect to free H_2 using the partition functions Z_{tot} and $Z_{H_2} = Z_{H_2}^{trans} Z_{H_2}^{rovib}$ corresponding to the molecule in the solid and gas states. Thus $F = E^f - k_B T \ln Z_{tot}$ and the chemical potential can be taken as that given by an ideal gas: $\mu_{H_2} = E_{H_2} - k_B T \ln(Z_{H_2})$. Both Z_{tot} and $Z_{H_2}^{rovib}$ include the vibrational and rotational entropy of the molecule with

$$Z_{tot} = \prod_{l=1}^{6} \sum_{n=0}^{\infty} \exp\left(-\frac{\hbar\omega_l (n+1/2)}{k_B T}\right) \sum_{j=0}^{\infty} 4 \exp\left(-\frac{W_j}{k_B T}\right)$$

and

$$Z_{H_2}^{rovib} = \sum_{n=0}^{\infty} \exp\left(-\frac{\hbar\omega (n+1/2)}{k_B T}\right) \sum_{j=0}^{\infty} \alpha_j (2j+1) \exp\left(-\frac{j(j+1)B}{k_B T}\right),$$

where the factor 4 comes from the nuclear degeneracy and $\alpha_j = 1$ for even j (para-H_2) and 3 for odd j (ortho-H_2). The translational entropy of the free molecule is included in

$$Z_{H_2}^{trans} = \frac{k_B T}{p} \left(\frac{m_p k_B T}{\pi \hbar^2}\right)^{3/2}$$

where p is the pressure taken to be 1 atm. The effect of H_2 on the entropy of the crystals is ignored. For $T = 0$, F can be written as $F = E^f + E^{ZP} - E_{H_2}^{ZP}$ where E^{ZP} is the zero point energy of H_2 in the crystal and $E_{H_2}^{ZP}$ that in vacuum.

At $T = 0$, we find that the zero point energy of free H_2 is 0.26 eV. For SiC at this temperature, E^{ZP} is 0.64 eV and this leads to F increasing to 2.8 eV. For GaN, E^{ZP} is 0.63 eV and this leads to F being 2.2 eV.

At $T = 1700\,°C$, F increases, leading to decreased solubilities (see table 3). For SiC, F is now 5.0 eV, leading to an equilibrium concentration of H_2 of $\sim 10^{10}$ cm^{-3}. In GaN, F is now 4.3 eV at 1700 °C and corresponds to an equilibrium concentration of $\sim 10^{12}$ cm^{-3}.

4. Conclusions

In both crystals the molecule lies along the c-axis with a bond length close to that of the free molecule. The equilibrium molecular solubilities are smaller than in Si and the diffusion

energies of the molecule along the *c*-axis are very much higher. In SiC, the migration barrier exceeds the dissociation energy. In both hexagonal materials studied here, H_2 is a static molecule unable to rotate. This contrasts strongly with the molecule in cubic materials such as Si and GaAs. Thus the molecular alignment is fixed by the crystal field and the molecule is not a free rotator. Due to the high rotational barrier the ortho–para splitting is too small to be observed. The confinement in GaN causes the stretch mode to increase with respect to the free molecule. It is clear that the theory finds little support for the assignment of the two lines in GaN given previously which might be caused by molecules bound to different defects [7].

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