

Energetics and Vibrational Frequencies of Interstitial H₂ Molecules in Semiconductors

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The incorporation of H₂ molecules on interstitial sites in various semiconductors is investigated using a density-functional-pseudopotential approach. The vibrational frequency of the interstitial molecules is shifted down compared to the free molecule. The results confirm a recent assignment of Raman lines to interstitial H₂ in GaAs [Vetterhöffer *et al.*, Phys. Rev. Lett. **77**, 5409 (1996)], but contradict the conclusion of Murakami *et al.* [Phys. Rev. Lett. **77**, 3161 (1996)] that the frequency for H₂ in Si is close to the free-molecule value. The interaction between interstitial molecules and the host is elucidated, and the significant weakening of the H-H bond is correlated with the semiconductor host charge density near the interstitial site. [S0031-9007(98)05497-0]

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Hydrogen can be incorporated in semiconductors in a number of different configurations: as an isolated interstitial, bound to impurities, bound to native defects, etc. [1]. There have been many indications that hydrogen also forms interstitial H₂ molecules. A number of computational studies have shown that interstitial H₂ molecules have positive binding energies, though the binding energy is smaller than in vacuum [2]. Experimental observations of H₂ molecules were lacking until recently, due to the challenging nature of the measurement. H₂ has no dipole moment, rendering it invisible to infrared spectroscopy. In addition, low concentrations of H₂ pose a sensitivity problem.

Two studies have recently appeared in the literature in which Raman spectroscopy is used to study interstitial H₂ in Si [3] and in GaAs [4]. The results from these studies are hard to reconcile: in GaAs [4], the vibrational frequency of the stretch mode is found to be significantly lower, by 227 cm⁻¹, than the value in H₂ gas. The results for Si [3], on the other hand, show virtually no lowering of the vibrational frequency. It is difficult to understand how immersion of the molecule in the semiconductor could significantly affect the vibrational modes in GaAs, but not in Si. In order to resolve this apparent conflict and to further our understanding of the physics of H₂ incorporation we have performed a first-principles computational study of interstitial H₂ in five different semiconductors: Si, GaAs, InAs, GaP, and GaN (in the zinc blende structure). Combined with calculations for H₂ in vacuum, our results enable us to examine trends and develop an understanding of the physics of incorporation of a strongly bound molecule in the semiconducting environment.

Our investigations show that incorporation of H₂ in an interstitial position results in a lowering of the binding energy, an increase in the bond length, and a lowering of the vibrational frequency. These features will be explained on the basis of the interaction between H₂ and the host charge density. Our calculated lowering of the frequency for H₂ in GaAs agrees with the experimental

value obtained in Ref. [4]. For silicon, we obtain an even larger shift, a result that is also consistent with the physics of the interaction between H₂ and the semiconductor. Our result conflicts with the experiments of Ref. [3], and potential explanations for this discrepancy will be suggested.

The calculations are based on density-functional theory in the local-density approximation (LDA) [5] and *ab initio* pseudopotentials [6] to describe the semiconductor host atoms. For hydrogen we use the Coulomb potential. Interstitial H₂ is calculated in 32-atom supercells, a size which was found to suffice to extract properties of isolated interstitials [7]. A plane-wave basis set with an energy cutoff of 48 Ry is sufficient to reach convergence of the physical quantities of interest, including differences in bond lengths, vibrational frequencies, and energy differences between various configurations. *Absolute* values for the bond length are converged to within 0.006 Å at this cutoff, and absolute energies to within 0.15 eV per H atom. The calculations for the molecule in vacuum were performed in a simple cubic supercell with a lattice parameter of 8.46 Å and plane-wave cutoffs up to 96 Ry.

We have not used a generalized gradient approximation (GGA). While use of the GGA brings certain calculated quantities closer to experiment, the improvement is not universal. In addition, a variety of choices for the GGA algorithm is currently available, with no consensus about an optimum. We therefore considered it prudent to adhere to the LDA formalism at this time. Vibrational frequencies tend to be underestimated in the LDA [8], but these deviations are systematic and should not interfere with the trends that will emerge.

The calculations were performed at the experimental lattice constant of each of the semiconductors; in the case of silicon we verified that this choice of lattice constant (which differs slightly from the theoretical value) has no effect on the energetics or vibrational frequencies. The H₂ molecule was placed at various interstitial positions in the lattice, in various orientations. In agreement with our earlier work [7,9] on Si we found that the lowest-energy

state occurs for the molecule placed at a tetrahedral interstitial (T_d) site, oriented along a $\langle 100 \rangle$ direction. The $\langle 111 \rangle$ orientation is only 0.01 eV higher in energy; the barrier to reorientation of the molecule is therefore negligible. The vibrational frequencies for these two orientations are also very similar. In compound semiconductors, two distinct T_d sites exist, one surrounded by cations, the other by anions; we label these, for the example of GaAs, T_d^{Ga} and T_d^{As} . Results will be given for both sites. The $\langle 100 \rangle$ orientation was found to yield the lowest energy in all the cases studied here; however, the $\langle 111 \rangle$ orientation is only slightly higher in energy (by a few 0.01 eV).

Full energy optimizations were performed, in which the H atoms as well as two shells of host atoms were allowed to relax. In Si, GaP, GaAs, and InAs we found that the host-atom relaxations were small (atoms moved by less than 0.03 Å for $\langle 100 \rangle$ orientation of H_2), lowering the total energy by less than 0.2 eV, and raising the vibrational frequencies by less than 50 cm^{-1} . In contrast, host-atom relaxations turned out to be very important in GaN: Because of its smaller lattice constant, the interstitial space available to the molecule is much smaller than in the other materials, and stronger interactions with the host atoms are indeed expected.

Once the equilibrium position, orientation, and bond length of the molecule were established, a series of calculations was carried out for different bond lengths in order to obtain a potential energy curve for determination of the vibrational frequencies. The host atoms were kept fixed at the positions appropriate for the equilibrium bond length. The light mass of the hydrogen justifies this approach; indeed, the hydrogen vibrations occur at much higher frequencies than those of the host atoms.

Anharmonic effects are important in H_2 : for the free molecule, the harmonic frequency is 4400 cm^{-1} [10], and anharmonic terms lower this value by 239 cm^{-1} to

4161 cm^{-1} [11]. We evaluated both harmonic and anharmonic terms by fitting the calculated potential energy curve to a sixth order polynomial. Around the minimum bond length, $d = d_0$, the potential energy can then be expressed as (keeping terms up to fourth order)

$$E(d) = E(d_0) + \frac{k}{2}(d - d_0)^2 + \alpha(d - d_0)^3 + \beta(d - d_0)^4. \quad (1)$$

The coefficient of the quadratic term yields the harmonic frequency, $\omega_0 = \sqrt{k/M}$, where M is the reduced mass. To express the frequency in units of cm^{-1} , ω should be divided by $2\pi c$. The coefficients α and β describe the anharmonic contributions. The transition between the ground state and the first excited state is given by [12]:

$$\omega = \omega_0 + \Delta\omega = \omega_0 + 3\frac{\hbar}{M} \left[-\frac{5}{2} \left(\frac{\alpha}{k} \right)^2 + \frac{\beta}{k} \right]. \quad (2)$$

For H_2 in vacuum we obtain $k = 31.7 \text{ eV}/\text{\AA}^2$, $\alpha = -30.9 \text{ eV}/\text{\AA}^3$, and $\beta = 44.9 \text{ eV}/\text{\AA}^4$, which yield $\omega_0 = 4135 \text{ cm}^{-1}$, $\Delta\omega = -190 \text{ cm}^{-1}$, and $\omega = 3945 \text{ cm}^{-1}$. The experimental value for the vibrational frequency of H_2 in the gas is 4161 cm^{-1} [11]; our computational approach thus underestimates this frequency by 216 cm^{-1} , consistent with previous LDA studies [8].

Table I lists values for the various quantities discussed above, as well as for the energy difference ΔE , which reflects the amount by which the energy of interstitial H_2 exceeds that of H_2 in vacuum. This quantity is obtained by taking the calculated total energy of the semiconductor supercell containing H_2 , and subtracting the energies of a supercell without H_2 as well as the energy of H_2 in vacuum.

TABLE I. First-principles results for structural, energetic, and vibrational properties of H_2 molecules oriented along $\langle 100 \rangle$ at tetrahedral interstitial sites in various semiconductors. For comparison, values for H_2 in vacuum are also listed. a is the lattice constant, $\rho(T_d)$ is the charge density at the interstitial site, ΔE is the energy difference between interstitial H_2 and H_2 in vacuum, d_0 is the equilibrium bond length, k is the force constant, ω_0 is the harmonic frequency, and $\Delta\omega$ is the difference in frequency between the interstitial and the free molecule.

Material	a (Å)	site	$\rho(T_d)$ ($e^-/\text{\AA}^3$)	ΔE (eV)	d_0 (Å)	k ($\text{eV}/\text{\AA}^2$)	ω_0 (cm^{-1})	$\Delta\omega$ (cm^{-1})
Vacuum	0	0	0.771	31.7	4135	0
InAs	6.08	T_d^{In}	0.012	0.45	0.785	28.4	3917	-218
		T_d^{As}	0.013	1.12	0.789	27.6	3856	-279
GaAs	5.65	T_d^{Ga}	0.015	0.85	0.791	27.1	3824	-311
		T_d^{As}	0.019	1.27	0.802	24.9	3750	-385
GaP	5.43	T_d^{Ga}	0.019	0.96	0.798	25.5	3709	-426
		T_d^{P}	0.021	1.18	0.792	26.6	3789	-346
Si	5.43	T_d	0.023	0.80	0.817	21.4	3396	-739
GaN	4.50	T_d^{Ga}	0.046	2.90	0.789	27.4	3847	-288
		T_d^{N}	0.038	4.35	0.760	33.8	4271	-136

No zero-point energies are included. We note that our results for energies and structure of H_2 in Si and GaAs are in general agreement with those of previous first-principles calculations (quoted in Ref. [2]); small quantitative differences can be attributed to the higher degree of convergence employed in the present work [13]. To our knowledge, only one calculation of vibrational frequencies has previously been reported. Nakamura *et al.* [14] performed Hartree-Fock calculations on a small Si cluster and derived a value of the vibrational frequency of 4470 cm^{-1} . No results were given for the free molecule, and the convergence of the calculational parameters was not discussed, making it difficult to assess the reliability of the results.

Accurate calculation of the anharmonic terms requires evaluation of the potential energy curve for a large number of displacements. Such a determination is beyond the scope of the present work, in which we want to examine general trends in the effect of the environment (type of semiconductor and location in the lattice) on the vibrational properties. We therefore focus on the harmonic frequency obtained from the fit [Eq. (1)]. The last column in Table I lists the frequency difference between the interstitial molecule and free H_2 .

In order to enable a comparison between our calculated values and experiment, we make two assumptions: (i) The anharmonicity in the case of interstitial H_2 is comparable to that of H_2 in vacuum. Our estimates of the anharmonic terms indicate that this is true to within 100 cm^{-1} . (ii) The correction term (216 cm^{-1}) that brings the frequency for free H_2 in agreement with experiment also applies to interstitial H_2 . Since the vibrational properties are still dominated by the H-H interaction, the LDA error can indeed be expected to be systematic. These two reasonable assumptions allow us to compare the frequency shift $\Delta\omega$ directly with experiment.

The first conclusion we draw from Table I is that there is a clear correlation between the bond length d_0 and the force constant k (and hence the vibrational frequency), as shown in Fig. 1. To a very good approximation, k can be expressed as

$$k = k_f - 219.0\Delta d, \quad (3)$$

where k_f is the force constant for free H_2 in vacuum (in $\text{eV}/\text{\AA}^2$) and $\Delta d = d_0 - d_{0f}$, with d_{0f} the calculated equilibrium bond length of H_2 in vacuum (in \AA). The slope is close to the prediction based on the anharmonic term; indeed, starting from Eq. (1) for free H_2 (i.e., $k = k_f$ and $d_0 = d_{0f}$) and taking the second derivative yields

$$E''(d) = k_f + 6\alpha(d - d_{0f}), \quad (4)$$

to first order in $(d - d_{0f})$.

Table I also shows that the vibrational frequency decreases along with the lattice constant a of the semiconductor—up to a point. For large a there is little direct interaction between the H_2 molecule and the host atoms;

the relaxation of the host atoms is small and its effect on the vibrational frequency is negligible. The interaction increases as the lattice constant goes down, resulting in lower values of ω , and higher values of ΔE . Repulsion between H atoms and host atoms (which would lead to a stiffening of the force constant and an increase in frequency) does not seem to play any significant role, except for T_d^P in GaP, and in GaN. In fact, immersion of the molecule in the semiconductor charge density leads to a weakening of the bond. This trend obviously breaks down for semiconductors with a very small lattice constant, such as GaN. In this case strong repulsion occurs between the molecule and the host atoms; in essence, there is not enough room in the interstitial cage to accommodate the molecule, resulting in a large value of ΔE and an increased value of ω .

We noted above that the vibrational frequency is insensitive to the orientation of the molecule as well as to relaxation of the host atoms (with the exception of GaN). These observations indicate that the interaction between H_2 and the host does *not* involve atomic repulsion or hybridization of wave functions. Instead, we picture the molecule being immersed in the low-density electron gas near the interstitial site. This description is supported by Nørskov's calculations for H_2 molecules in jellium [15], in which a decrease of the binding energy was found, along with a reduction in the vibrational frequency. Nørskov attributed these effects to a filling of the antibonding resonance.

We actually find a direct monotonic relationship between the magnitude of the host charge density at the interstitial site and the bond length (or force constant) of the molecule (excluding the case of GaN): the higher the

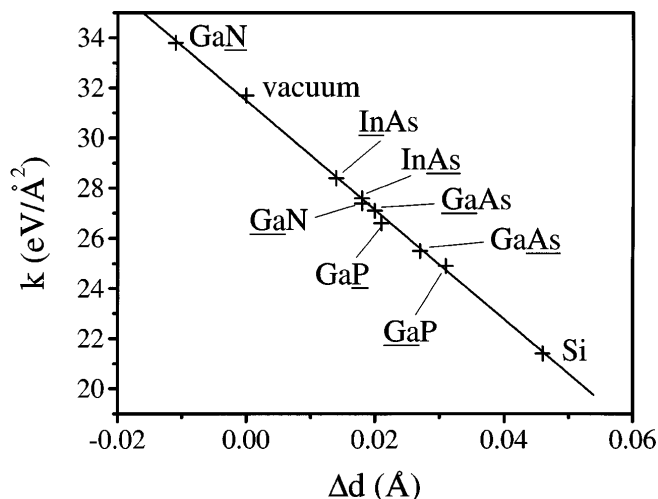


FIG. 1. Calculated force constant for interstitial H_2 molecules as a function of calculated bond length deviation (referenced to the bond length of free H_2), as listed in Table I. Data points are labeled according to the semiconductor host and the type of T_d site (surrounded by cations or anions, depending on which element is underlined). The solid line is a linear fit.

charge density, the longer the bond length (and the lower the vibrational frequency). The relationship is linear for H_2 in semiconductors with lattice constant $a \geq 5.65 \text{ \AA}$; deviations from linearity indicate that the interaction becomes more complex for Si and GaP. The shift in vibrational frequency is clearly larger for H_2 in semiconductors than in noble gas solids, or in solid N_2 or O_2 ; the difference can be attributed to the larger value of the charge density at the interstitial sites in the semiconducting hosts.

Finally, we discuss comparisons with experiment. Two values have recently been reported for vibrational frequencies of H_2 in semiconductors observed by Raman spectroscopy. Vetterhöffer *et al.* [4] reported a shift of -227 cm^{-1} for H_2 in GaAs, compared to the free molecule. Our calculated value for the most stable position of H_2 in GaAs yields $\Delta\omega = -311 \text{ cm}^{-1}$, i.e., within 84 cm^{-1} of the experimental value, which can be considered reasonable agreement. The small calculated energy difference between different orientations of the molecule also agrees with the conclusions of Ref. [4] about the ease of rotational motion of H_2 .

Murakami *et al.* [3] reported a value of 4158 cm^{-1} for H_2 in Si, i.e., within a few wave numbers of the frequency in H_2 gas. Our calculated value for H_2 in Si, on the other hand, shows a downward shift of over 700 cm^{-1} . In addition, given the physical trends discussed above, one definitely expects the value for Si to be lower than the value for GaAs [4]. In light of this analysis, we conclude that the frequency measured by Murakami *et al.* is not representative of interstitial H_2 . The similarity of this value to the free-molecule value points towards H_2 molecules incorporated in some other form—maybe at or near the surface of the sample, or in voids.

In summary, we have presented a first-principles theoretical study of H_2 incorporation in a variety of semiconductors. The H_2 interstitial molecules prefer to be located at the tetrahedral interstitial site, in the $\langle 100 \rangle$ orientation; rotational barriers are very small, however. In compound semiconductors the T_d site surrounded by cations is always lower in energy. The vibrational frequency is shifted down from the free- H_2 value by a significant amount; the size of the shift can be correlated with the magnitude of the charge density at the T_d site. The relation between the force constant and the bond length

was derived (Fig. 1) and is given in Eq. (3); this simple expression allows predictions of the force constant and the frequency based on a calculation of the bond length alone. Our calculations are in good agreement with recent experiments for H_2 in GaAs [4], but show significant discrepancies with experimental results for H_2 in Si [3], suggesting that the frequencies observed in that work are *not* related to interstitial H_2 .

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