CH$_3$CN on Si(001): Adsorption Geometries and Electronic Structure

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In this work we employ the state of the art pseudopotential method, within a generalized gradient approximation to the density functional theory, to investigate the adsorption process of acetonitrile on the silicon surface. Our first-principles calculations indicate that CH$_3$CN adsorbs via a [2+2] cycloaddition reaction through the C$\equiv$N group with an adsorption energy around 35 kcal/mol, close to the 30 kcal/mol estimated by Tao and co-workers. The electronic structure and the surface states calculated for the adsorbed system are also discussed.

1   Introduction

In the last few years, the great number of technological applications for the use of organic films has motivated several investigations of the semiconductor-organic interface formation, with a view to control the interface bonding sites for linking other organic substituents. One of such organic compounds is acetonitrile. Recent experimental works [1, 2] suggest that this molecule is molecularly adsorbed on Si(001) through the C$\equiv$N group in a di-σ configuration, leaving a C=N functionality on the surface for further reaction and modification. In this work, we employed the state of art pseudopotential technique within a generalized gradient approximation framework in order to investigate the adsorption of CH$_3$CN on the silicon (001) surface.

The surface was modelled in a super-cell geometry, with an atomic slab of six Si layers and a vacuum region equivalent to eight atomic layers. On the top side of the slab we placed the CH$_3$CN molecule in different configurations. The pseudopotentials for Si, C, and H were derived by using the scheme of Troullier and Martins [3] and the electron-electron exchange-correlation interactions were considered by using a generalized gradient approximation (GGA) [4] of the density functional theory. As for the surface calculations, the single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 35 Ry. For the Brillouin-zone summation, four special **k** points were used. The atoms were assumed to be in their fully relaxed positions when the forces acting on the ions were smaller than 0.005 eV/Å.

2   Results

For bulk silicon our first-principles calculations produced 5.50 Å for the equilibrium lattice constant (a_o), 0.86 GPa for the bulk modulus (BM), and 4.39 eV for the cohesive energy, all in good agreement with the experimental values presented in Ref. [5]. The calculated theoretical lattice constant obtained for the bulk silicon is used in surface calculations. The clean Si(001)–(2×1) surface is characterized by a tilted Si–Si dimer, i.e. one dimer component is at a higher position than the other. Our calculations support this model: the Si–Si dimer is found to have a bond length of 2.30 Å and a vertical buckling of 0.73 Å, indicating a tilt angle of 17.8°. The bond lengths for the CH$_3$–CN molecule are found to be C–C=1.44 Å, C–N=1.59 Å, and C–H=1.11 Å, in good agreement with available experimental data [5].

Our results indicate that CH$_3$CN adsorbs via a [2+2] cycloaddition reaction through the C$\equiv$N group [Fig. 1] with an adsorption energy around 35 kcal/mol, close to the 30 kcal/mol estimated by Tao and co-workers [1]. Upon the adsorption of CH$_3$–CN, the Si–Si dimer gets elongated by approximately 2% and becomes symmetric. This is in agreement with experimental [6] as well as theoretical [7] findings for other small hydrocarbon molecules, like acetylene and ethylene. Structural data for the Si–Si dimers that do not correspond to an adsorption site are not discussed, as they are very similar to the values found for the free surface. For the adsorbed structure, the calculated C–H bond length of ~1.11 Å is in good agreement with early theoretical estimates for other small hydrocarbon molecules [7] and is close to that observed for the free CH$_3$–CN molecule. Our calculations also indicate that the C–Si bond length is approximately 1.90 Å, which is again comparable to the C–Si bond length observed for other hydrocarbons (see, for example, Ref. [7]).

The surface band structure resulting from our calculation for the adsorbed system is shown in Fig. 2. We have identified four surface states within the fundamental band gap of silicon: these are labelled σ, p$_1$, p$_2$, and p$_3$. As seen in Fig. 2, the p$_1$ state with binding energy of approximately 0.1 eV and the unoccupied p$_3$ state are mainly localized on the nitrogen atom. The p$_2$ and σ states, on the other hand,
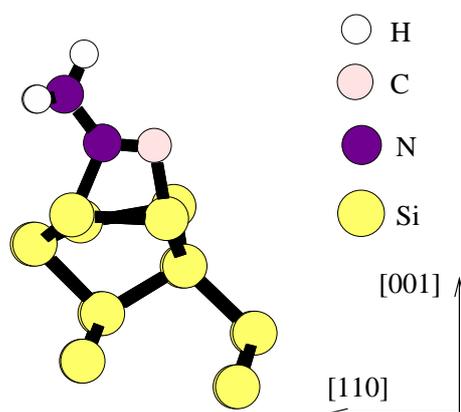
Figure 1. Schematic view of the [2+2] cycloaddition adsorption of CH$_3$CN on the Si(001)–(2×2) surface through the C≡N group.

are distributed among the adsorbate and the Si–Si dimer underneath it, and represent the interaction between Si–Si ppσ and different CN orbital components of the CH$_3$CN molecule.

3   Summary

We have performed first-principles calculations for the atomic and electronic structure of the adsorption of acetonitrile on the silicon surface. Our first-principles calculations indicate that CH$_3$CN adsorbs via a [2+2] cycloaddition reaction through the C≡N group with an adsorption energy around 35 kcal/mol, close to the 30 kcal/mol estimated by Tao and co-workers. The electronic structure and the surface states of the adsorbed system are also discussed.

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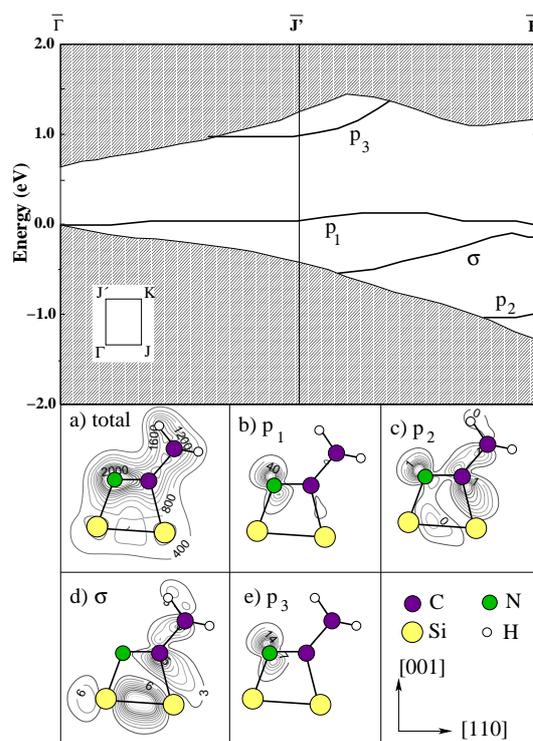
Figure 2. The electronic band structure and electronic charge density contour plots for selected surface states of the CH$_3$CN:Si(001) surface. The projected bulk spectrum is shown by hatched regions. The charge density plots are on the [110]-[001] plane.

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