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Furan interaction with the Si(001)-(2 × 2) surface: structural, energetics, and vibrational spectra from first-principles

R Miotto¹ and A C Ferraz²

¹ Centro de Ciências Naturais e Humanas, Universidade Federal do ABC,
Rua Santa Adelia 166, CEP 09210-170, Santo André, SP, Brazil

² Instituto de Física da Universidade de São Paulo, Caixa Postal 66318, CEP 05315-970,
São Paulo, SP, Brazil

E-mail: ronei.miotto@ufabc.edu.br

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Abstract

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 furan on the silicon (001) surface. A direct comparison of different adsorption structures with x-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), high resolution electron energy loss spectroscopy (HREELS), near edge x-ray absorption fine structure (NEXAFS), and high resolution spectroscopy experimental data allows us to identify the [4 + 2] cycloaddition reaction as the most probable adsorbate. In addition, theoretical scanning tunnelling microscopy (STM) images are presented, with a view to contributing to further experimental investigations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the past few years a great deal of effort has been devoted to the study of the adsorption and surface reaction mechanism of organic molecules on silicon surfaces. Indeed, the surface science of silicon single crystals is so diverse that new processes and designs that are parallel with traditional homogeneous organic and organometallic chemistry applied to silicon are continually being discovered and developed [1]. By modifying surfaces with thin films, such as conducting polymers, they can be used in the production of organic transistors [2]. However, the production of such devices requires the development of a well defined organic layer on the substrate surface. As such organic layers are basically formed by exposing the substrate surface to organic compounds, the understanding of the first stages of the surface–organic interaction is crucial in order to improve the quality of the deposited layers. In particular, furan (whose Lewis formula is represented on figure 1) and its polymeric form polyfuran, among other five-membered aromatic heterocyclic molecules, have already been successfully used as building blocks to produce conducting polymers [3, 4].

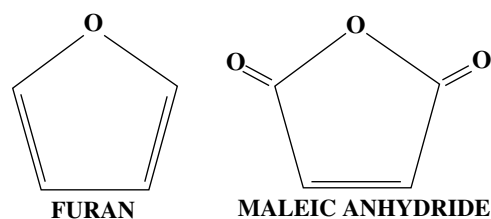


Figure 1. Lewis formula for furan and maleic anhydride.

Despite its importance, the interaction of furan with the silicon (001) surface has not been the subject of many systematic studies. Qiao and co-workers [5], based on a combination of x-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), high resolution electron energy loss spectroscopy (HREELS), and semi-empirical molecular orbital (MO) calculations, suggested that the covalent attachment of furan occurs via a [4 + 2] (as in figure 2) cycloaddition reaction. This picture was very recently confirmed by Lee *et al* [6] via high resolution spectroscopy and near edge x-ray absorption fine structure (NEXAFS). With

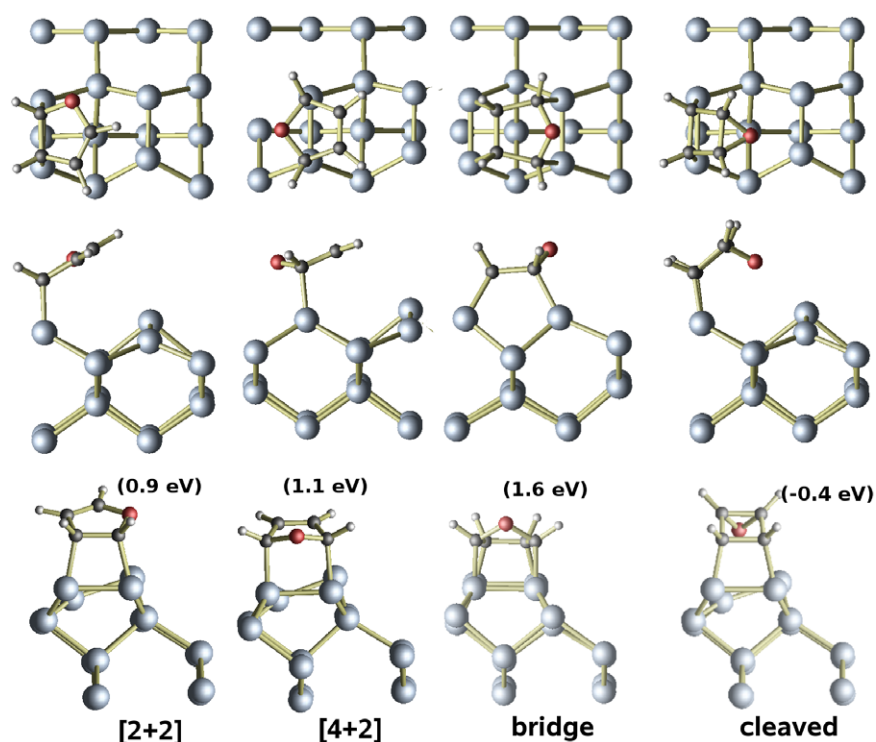


Figure 2. Schematic representation of adsorption models for furan interaction with Si(2 × 2)-(001): the [2 + 2] cycloaddition of the C=C bond ([2 + 2]), [4 + 2] cycloaddition of the carbon atoms on the C–O–C bond ([4 + 2]), bridge like structure with neighbouring Si–Si dimers (bridge), and transformation of both carbon double bonds in single bonds (cleaved). The numbers in parenthesis correspond to the adsorption energies of each considered adsorption model.

a view to contributing to further experimental investigations, and to the understanding and interpretation of more complex systems, including aspects of biochemically active thin films and the role of aromaticity in reactions, 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 furan on the silicon (001) surface.

2. Theoretical considerations

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. The unit cell for the (2 × 2) surface structure is spanned by vectors $\mathbf{a}_1 = a(1, 1, 0)$ and $\mathbf{a}_2 = a(-1, 1, 0)$. The theoretical value of the bulk Si lattice constant a was used in the surface calculations. On the top side of the slab we placed the furan molecule in different configurations, and the back surface was passivated by H atoms arranged in a dihydride structure. Additionally, we made calculations for a single furan molecule placed in a cubic box of 22 Å side. The electron–ion interaction between Si, C, O, and H atoms is described by projector augmented wave (PAW) potentials [7, 8] and the electron–electron exchange–correlation interactions were considered by using a generalized gradient approximation (GGA) [9] to the density functional theory. The single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 340 eV, whereas the cutoff for the augmentation charges is 460 eV. Increasing the energy cutoff to 450 eV did not change the key structural

parameters by more than 0.4%. The difference between total energy values calculated using both plane-wave expansions are smaller than 0.1%. The electronic and ionic degrees of freedom were relaxed by adopting the Vienna *ab initio* simulation package (VASP) implementation [10]. For the Brillouin-zone summation, a single special \mathbf{k} point was used in all free molecule calculations, whereas four special \mathbf{k} points are used for the surface case. 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⁻¹.

The adsorption energy for the furan molecule was calculated as $E_{\text{conf}}^{\text{ads}} = -[E_{\text{conf}} - E_{\text{ref}}]$, where E_{conf} is the total energy for the considered configuration, E_{ref} is the total energy for the free Si(001)-(2 × 2) surface plus the total energy for a free furan molecule in a box of side 22 Å. Following a conjugate-gradient algorithm, a series of initial unrelaxed configurations were submitted to search for a minimum energy state whose final reconstructed structures are discussed in section 3. In order to obtain STM images from the calculated eigensolutions, we employed the Tersoff–Hamann formalism, as described in a previous work [11]. Vibrational loss spectra are calculated as follows: the normal modes and the corresponding frequencies are the solutions of the dynamical problem of the ions driven by the dynamical matrix, or Hessian, that is constructed with the Hellmann–Feynman forces resulting from displacements of the ions from their equilibrium positions. The intensities are derived from the dipole moment of the system calculated for each distorted geometry as proposed by Preuss and co-workers [12, 13]. Core

level shifts are calculated following the theoretical approach suggested by Köhler and Kresse [14]. It is important to note that this theoretical approach is not able to provide absolute core binding energy values but only relative shifts [14].

3. Results

3.1. Preliminary results

For bulk silicon, our first-principles calculations produced 5.47 Å for the equilibrium lattice constant (a_0), 0.90 GPa for the bulk modulus (BM), and 4.39 eV for the cohesive energy, all in good agreement with the experimental values presented in [15]. The calculated theoretical lattice constant obtained for the bulk silicon is used in surface calculations. The clean Si(001)-(2 × 2) surface is characterized by alternating tilted Si–Si dimers, i.e. one dimer component is at a higher position than the other, but neighbouring dimers present opposing tilting directions. 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°. To test the reliability of the carbon, oxygen, and hydrogen PAW potentials, we performed additional calculations. For cubic diamond we obtained 3.60 (3.57) Å, 4.53 (4.42) GPa, and 7.28 (7.37) eV for the cubic lattice constant, bulk modulus, and cohesive energy, respectively, in good agreement with the experimental [15] values given in parenthesis. The water molecule bond length, O–H of 0.97 (0.96) Å, and H–O–H bond angle of 104.4 (104.4)°, are also in very good agreement with the experimental data [15] given in parenthesis. In a similar manner, for bulk ice in its Ih phase, we have found a lattice parameter of 4.43 Å and a cohesion energy of 0.67 eV, in agreement with the experimental findings of 4.50 Å for the lattice constant [16]. Although our calculated cohesion energy exceeds the experimental value of 0.58 eV [17], it is in good agreement with other recent calculations (see [18] and references therein). Furthermore, our calculated bond lengths for the furan molecules C–C, C=C, C–O, and C–H are 1.43 Å, 1.37 Å, 1.37 Å, and 1.09 Å, respectively, in good agreement with the experimental values usually found in organic molecules [15].

3.2. Furan adsorption on Si(2 × 2)-(001) surface

It is now well established that, at low temperatures, the (001) surface of silicon exhibits a c(4 × 2) reconstruction. However, the limited time resolution of the measurements does not allow the proper resolution of the rapid dimer flipping at room temperature, creating the impression of a (2 × 1) surface reconstruction [19]. Although the majority of experiments are performed in such a way that only the (2 × 1) is observed, in order to clearly establish the role of inter-dimer interaction on the adsorption of furan, we have considered a (2 × 2) surface reconstruction. The interaction of furan with the silicon (001) surface was investigated by considering a series of possible adsorption sites, including not only the [2 + 2] and [4 + 2] cycloadditions but also the bridge and inter-dimer structures as these were found to be possible adsorption models for maleic anhydride [20], a similar five-membered aromatic

heterocyclic molecule. As many of the considered structures are found to be highly unstable (from the energetic point of view), in the present work we will focus our attention only to allow selected adsorbed structures obtained via an exothermic process, i.e. when the adsorbed system is lower in energy when compared to the products: the free molecule and the bare silicon (001) surface. We have determined the equilibrium geometries of the furan adsorbed Si(001) surface via a [2 + 2] cycloaddition of the C=C bond (indicated as [2 + 2] on figure 2), via a [4 + 2] cycloaddition of the carbon atoms on the C–O–C bond (indicated as [4 + 2] on figure 2). In addition, we have also considered the possibility of adsorption via a bridge like structure with neighbouring Si–Si dimers (bridge model) and via the transformation of both carbon double bonds in single bonds (cleaved model) as indicated in figure 2.

Our total energy calculations suggest that the most probable adsorption model for the interaction of furan with the silicon (001) surface is the bridge like structure with an adsorption energy of 1.6 eV. The adsorptions via a [4 + 2] and [2 + 2] cycloaddition are also found to be energetically favourable by 1.1 and 0.9 eV, respectively. The cleaved adsorption model, on the other hand, does not correspond to an exothermic process, as its adsorption energy was found to be 0.4 eV higher when compared to the bare silicon surface and the free furan molecule. Qiao and co-workers [5], using the centre of the temperature range for molecular furan desorption observed by XPS, have estimated an adsorption energy of 1.17 eV, in good agreement with our calculated value for the adsorption via a [4 + 2] cycloaddition. Indeed, this adsorption model was pointed out as the most probable adsorbed structure both by Qiao and co-workers [5] and very recently by Lee *et al* [6]. The binding site ordering can be understood by noticing that in the bridge structure there is the formation of two di- σ bonds, while for both the [4 + 2] and the [2 + 2] cycloaddition only one di- σ bond is formed. Although we acknowledge that total energy calculations are a valuable tool in the search for possible structural models, it has turned out that they are not always sufficient to assess the probability of formation [13], as huge energy barriers might prevent their realization. In principle, the height of these barriers could be estimated, for example, following the nudged elastic band (NEB) method [21, 22]. However, for systems where there are a number of possible adsorption sites, as is the case of the adsorption of organic molecules on the silicon surface, energy barriers calculated following this approach should be considered with great care. In this sense, the relative energies reported here are not questionable, but associated with equilibrium structures that may or may not be accessible under experimental conditions. Thus, we believe that total energy calculations alone are not sufficient for complex adsorption systems and must be complemented by consideration of additional fingerprints.

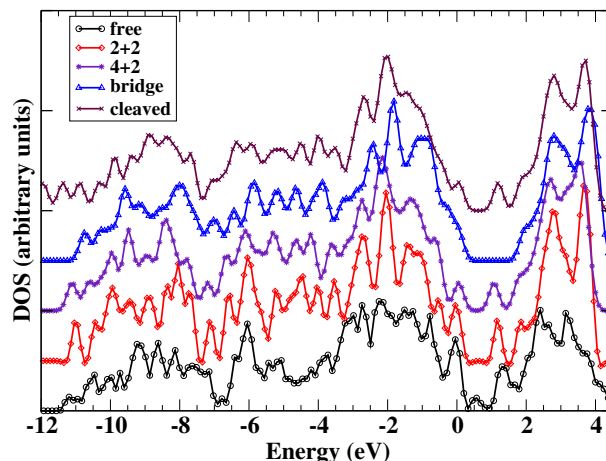
Upon the adsorption of furan in all considered models, with an exception being made for the cleaved structure (not discussed below), all bond lengths and angles of the five-membered aromatic heterocyclic molecule behave in a similar manner, as indicated in table 1. As expected, the main differences are observed for the bonds directly involved in

Table 1. Selected structural parameters for possible adsorption models of furan on Si(001)-(2 × 2). The structures are named following figure 2.

Structure	[2 + 2]	[4 + 2]	[4 + 2] [5]	Bridge
Si-Si (Å)	2.37	2.39	2.41	2.38
Si-C _α	1.95	2.01	1.98	2.00
C _α -C _β	1.59	1.49	1.50	1.56
C _β -C _β	1.53	1.35	1.35	1.58
C _α -O (deg)	1.45	1.45	1.43	1.45
Si-C _α -O (deg)	—	102	106	106
Si-C _α -C _β (deg)	122	109	106	113
Si-Si-C _α (deg)	80	87	88	89

the adsorption process. Single carbon bonds, for example, experience an increase from 1.43 to 1.49 Å, very close to the values found by Qiao and co-workers [5] using a semi-empirical method. In a similar manner C–O bonds changes from 1.37 to 1.45 Å, again in agreement with the 1.43 Å obtained by Qiao and co-workers. The C–H and carbon double bonds for both the [2 + 2] and [4 + 2] cycloaddition reactions, on the other hand, are very close to their original values. These findings are also consistent with the values observed by Qiao and co-workers [5]. For all considered structures, the Si–Si dimer involved in the furan adsorption process gets elongated by approximately 4% with a bond length of 2.37–2.39 Å, comparable with the findings of Qiao and co-workers. For the considered adsorption models, the Si–Si dimer becomes symmetric and the calculated Si–C is around 2.0 Å, which is also in agreement with the findings of Qiao and co-workers [5]. The Si–C–C, and Si–C–O rotation angles are found to be 116°, 108°, and 119°, 102°, and 114°, 106° for the [2 + 2], [4 + 2], and bridge models respectively. All considered rotation angles are consistent with the semi-empirical findings by Qiao and co-workers [5] and with the NEXAFS data obtained by Lee *et al* [6]. It is also important to note that all observed bond lengths and rotation angles are also consistent with the calculated values for the adsorption of other molecules on the silicon surface, such as maleic anhydride [20]. The small expansion of the Si dimer length predicted in our work for all considered models would indicate a softening of the dimer bond, which is also consistent with experimental and theoretical observations for the interaction of other molecules with the silicon surface [23].

In the next step of our study, we have studied changes in the electronic structure of the silicon substrate upon the adsorption of furan. Figure 3 shows the electronic density of states (DOS) for the free Si(001)-(2 × 2) surface and for the silicon surface after its interaction with the furan molecule, considering only the studied adsorption models. In order to make the analysis of the changes in the electronic structure clearer, we have considered the DOS profiles to be shifted by a constant amount. The DOS spectra suggest that the silicon surface is passivated upon the adsorption of furan, as the surface state in the mid-gap (around 0.5 eV) vanishes. The same spectra suggest that the adsorption of furan via the bridge model is responsible for a more complete passivation of the surface with the opening of a band gap of almost 1.7 eV. Apart from this difference, the main profiles of all the

**Figure 3.** Electronic density of states (DOS) for the free Si(001)-(2 × 2) surface (black line with circles) and for [2 + 2] (red line with diamonds), [4 + 2] (violet line with stars), bridge (blue line with triangles), and cleaved (brown lines with x symbols) adsorption models.

considered adsorption models are very similar. Indeed, a direct comparison of our theoretical results and the experimental valence band spectrum obtained by Qiao and co-workers [5] suggests that the analysis of the DOS profiles alone is not enough to disregard any of the considered structures.

Our calculated Si 2p core binding energy shifts are found to be 0.76 eV, 0.74 eV, 0.53 eV, and 0.50 eV for the [2 + 2], [4 + 2], bridge, and cleaved models, respectively. Only the first cycloaddition models are comparable with the experimental findings of 0.78 eV obtained by Lee *et al* [6]. This is the first clear indication that the bridge model, which was found to be the most probable structure from the energetic point of view, might not be the experimentally observed adsorbed structure.

From our structural, electronic and energetic analysis, it is clear that the comparison of theoretical results with other experimental data is essential in order to get an unambiguous determination of the adsorption model of furan on the silicon surface. High resolution electron energy loss spectroscopy (HREELS) is a powerful technique [24] that can be used to identify the adsorbed species by recognition of characteristic vibrational modes. Therefore, a direct comparison between experimental and theoretical loss spectra is capable of providing unambiguous information on possible candidate structures. To set up the dynamical matrix including substrate influence on the vibrations, we include the first five layers of the silicon substrate (and any adatoms if this is the case), corresponding to (at least) a 144-dimensional Hessian matrix. The theoretical energy loss spectra for the [2 + 2], [4 + 2], bridge, and cleaved adsorption models are presented in the inset of figure 4. A close inspection of this inset indicates that the loss spectra of the considered adsorption models are not very different, except for the region between 1000 and 1600 cm⁻¹. This region is amplified in figure 4 and it is clear that only the [4 + 2] adsorption model presents the same loss structures experimentally observed by Qiao and co-workers [5]. Indeed, only for the [4 + 2] model is it possible to clearly identify the losses at 1083 (1094) and 1265

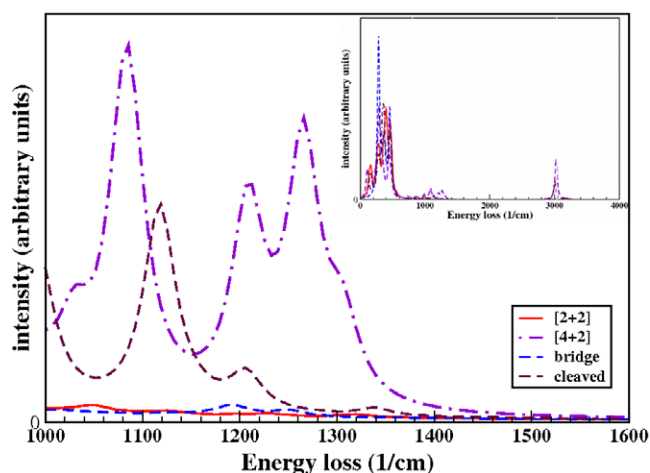


Figure 4. IR spectrum obtained for the [2 + 2] (straight red line), [4 + 2] (dashed and dotted violet line), bridge (dashed blue line), and cleaved (dashed brown lines) adsorption models of furan on the Si(001)-(2 × 2) surface.

(1266) cm^{-1} (experimental values in parenthesis) assigned by Qiao and co-workers to the ring stretch and symmetric $\Delta\text{CC-H}$ bend plus Ring pucker modes, respectively. The 1578 cm^{-1} vibrational loss associated to the C=C str. mode, and considered by Qiao and co-workers [5] as the main indication of the presence of a [4 + 2] cycloadducted species, is not clearly observed in our theoretical loss spectra. Although this mode is correctly identified by us at 1566 cm^{-1} , its intensity is much smaller than the other losses. This is consistent with the fact that this mode was identified by Qiao and co-workers in an oscillating region, i.e. their spectra in this region oscillate with the same amplitude as the mode identified at 1578 cm^{-1} , indicating that its intensity is indeed very small. In this sense, based on the direct comparison of the theoretical and experimental vibrational loss spectra, we conclude that the [4 + 2] adsorption model is probably the structure depicted experimentally.

STM is one of the most widely used surface techniques for the investigation of the adsorption process. Although no theoretical STM images are available for a direct comparison, we believe that these images might be useful for experimentalists in order to support not only our present results but also other available theoretical and experimental findings. Simulated STM images for the [2 + 2], [4 + 2], bridge, and cleaved adsorption models of furan on silicon (001) with a bias voltage of -2.0 eV are presented in figure 5. STM images were obtained from the calculated electronic eigensolutions, following the Tersoff–Hamann formalism, as described in [11]. The (2 × 2) reconstruction is easily identified in all theoretical images with the help of the schematic representation of the adsorbates superimposed on the left side of each figure. It is worth pointing out that the present image is much richer than a constant-current experiment. In contrast to experimental conditions, in our simulation a range of tunnelling currents is considered and represented by different brightnesses. Considering the brighter regions, only the adsorbate and the Si–Si dimer rows can be identified. The

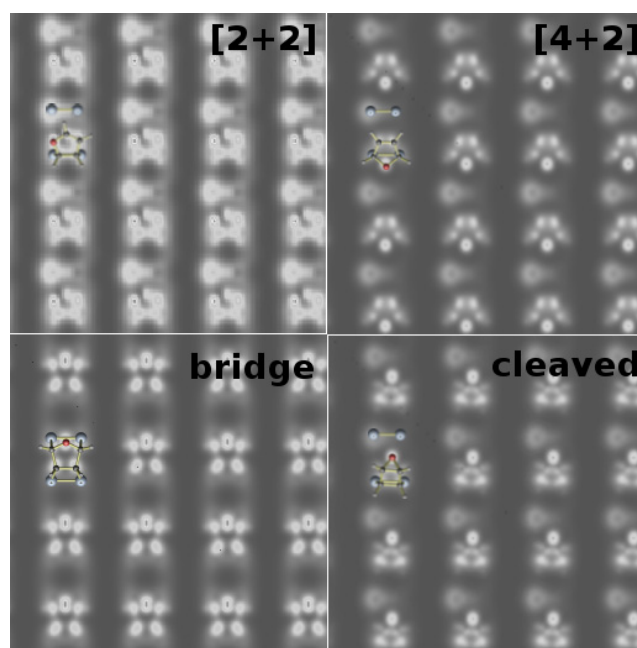


Figure 5. Theoretical STM image obtained for a bias voltage of -2.0 V for the [2 + 2], [4 + 2], bridge, and cleaved adsorption models of furan on the Si(001)-(2 × 2) surface. For clarity, a schematic representation of the adsorbed system is superimposed on the left side of each image.

differences between the simulated STM images for the [4 + 2], bridge and cleaved structures are very small. However, we believe that it is possible to differentiate between the [2 + 2] and [4 + 2] structures. As those structures are found to be the only ones that match the HREELS spectrum, we believe that an STM experiment will clearly confirm our findings.

4. Summary

In this work the interaction of furan with the silicon (001) surface is investigated using the density functional theory. A direct comparison of different adsorption structures with XPS, UPS, HREELS, NEXAFS, and high resolution spectroscopy experimental data allow us to identify the [4 + 2] cycloaddition reaction as the most probable adsorbate. The adsorbate preserves most of the characteristics of the free furan molecule, such as bond lengths and bond angles. Our calculated DOS spectra suggest that the silicon surface is passivated upon the adsorption of furan as no surface states in the mid-gap region are identified. In addition, theoretical STM images are presented, with a view to contributing to further experimental investigations.

Acknowledgments

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