



Small hydrocarbon adsorbates on SnO₂(1 1 0) surfaces: Density functional theory study

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ABSTRACT

Adsorption of three small hydrocarbons molecules (acetylene, ethylene and ethane) on two SnO₂(1 1 0) surfaces is studied by employing density functional theory calculations, slab model and linear combination of atomic orbitals (LCAO) approach. Acetylene and ethylene adsorb preferentially on top of a 5-fold tin atom, while ethane aligns itself with the rows of bridging oxygens and settles between two surface tin atoms. Adsorption energies and changes occurring in the structural characteristics and electronic structure of both the hydrocarbons and SnO₂ surface indicate chemisorption of unsaturated hydrocarbons and physisorption of ethane on reduced surfaces. In all cases of chemisorption there are two contributing mechanisms: charge transfer creating ionic bonding (down-shift of levels) and covalent bonding (broadening of levels).

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1. Introduction

Design of hybrid, organic and inorganic, materials has made new multifunctional materials accessible and large opportunities appear for applications in optoelectronics [1], chemical sensing and catalysis [2], biology and biomedicine [3]. Self-assembly of active organic layers on the inorganic substrate can be used for tuning the activation barriers for the charge transfer across the organic–inorganic interface and chemical reactions at the surface, thus providing opportunities to control chemical reactivity as well as physical processes. Furthermore, interaction of adsorbate molecules with the inorganic substrate can be used to control the growth mode and orientation of the molecules in the organic film.

ITO and TiO₂ are the most common inorganic materials for this purpose. Tin dioxide, SnO₂, also possesses the special property of being a good electric conductor and transparent to the visible light [4]. Consequently, tin dioxide has drawn in recent years a great deal of attention as a functional material for application as solid state gas sensor material, oxidation catalyst, and transparent conductor. In addition, recent studies have shown that tin oxide is a promising material for spintronic applications [5]. Several experimental and theoretical studies, comprehensively reviewed by Batzill and Diebold [6], have been carried out. The influence of the surface composition and structure on the surface reactivity of tin dioxide, the role of atomic scale defects such as oxygen vacan-

cies and the interaction with several smaller molecules such as O₂, CO, CO₂, NH₃, H₂O, BF₃, HCOOH and C₆H₆ have been investigated. These studies concentrate mainly on the (1 1 0) surface, which is the most stable one. The SnO₂(1 1 0) surface makes an ideal model system for theoretical studies [7–9] of interface properties because in practical applications its surface composition can be varied in a controlled way [10], thus allowing a clear comparison between experiment and theory.

The aromatic and organometallic macrocyclic molecules bound to SnO₂ surface are of particular interest for creation of dye-sensitized solar cell systems [11]. Anchoring of the organic molecules can be done either covalently via ester or amide bonding or via hydrogen bonding, electrostatic or van der Waals interactions. Utilization of weak interaction has recently merited increasing attention as a sophisticated methodology to assemble supramolecular photosynthetic architectures [11]. Even if most parts of the systems are fairly well understood separately, the electronic interactions at the interface and the basic mechanisms of adhesion on an atomistic scale are still largely unknown. Charge transfer and electronic properties depend strongly on the orientation and type of linkage between the organic molecules and the surface due to the highly anisotropic nature of the electronic interactions at the interface. The band alignment of tin oxide material with respect to the HOMO/LUMO of the organic molecules determines the barriers for charge carrier transport across the interface.

The aim of the present study is theoretical modelling of organic molecular adsorption on reduced and stoichiometric SnO₂(1 1 0) surfaces. Stoichiometric surface forms in oxygen rich conditions. Reduced surfaces are complex and form many different surfaces

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with varying amounts of oxygen and defects. For our study we have chosen a simple surface that has all of its bridging oxygens removed. This model surface has high surface energy and it is unlikely to form in any usual conditions. However, it gives us a limiting case that allows us to separate the effect of bridging oxygens. It is worth pointing out that systems with more isolated oxygen vacancies may be more reactive as is shown in recent study by Köppen and Langel for TiO_2 [12].

As model organic adsorbates for simulating a molecular π -conjugation on SnO_2 (110) surfaces two small hydrocarbons molecules, ethylene (ethene, C_2H_4) and acetylene (ethyne, C_2H_2), are chosen. In addition, adsorption of a saturated hydrocarbon molecule, ethane (C_2H_6) is studied for comparison. In search of the most likely adsorption modes for different molecular geometries we employ periodic first-principles density functional theory calculations. The changes occurring in the structural characteristics and electronic properties of both the hydrocarbons and SnO_2 surface are investigated, as they reflect both the nature and strength of the electronic interaction. In addition, the calculated adsorption energies, together with the Adsorbate– SnO_2 interaction distance offer a good basis for differentiating between chemisorption and physisorption.

2. Methods and models

All calculations are made using DFT in the periodic linear combination of atomic orbitals (LCAO) approach. There are some advantages in employing LCAO compared to plane-wave (PW) basis. The main advantages lie in the relatively small number of basis functions and unlimited choice of vacuum thickness in between slabs. The LCAO gives a comprehensible description of the molecule–surface interaction in terms of molecular orbitals and substrate bands. Additionally, the LCAO basis also gives the possibility to easily project atomic charges onto atomic or molecular orbitals which gives good chemical intuition when considering bonding [13]. Our calculations are performed using the Dmol³ software [14–16].

The basis functions are one-electron orbitals of free atoms and ions computed in a numerical form prior to the crystal calculations. All electron basis sets are used for all the elements. The specific basis set used in the calculations is a double numerical basis with polarization functions (DNP) [16]. It contains a polarization d function on heavy atoms and a polarization p function on hydrogen. It is comparable in size to the 6-31G** basis set however, as numerical basis sets of a given size are suggested to be much more accurate than Gaussian basis sets of the same size [16]. Exchange and correlation effects are described through the generalized gradient approximation (GGA) with parametrization by Perdew, Burke and

Ernzerhof (PBE) [17]. Charge distribution analysis is performed with Hirshfeld method [18] that gives basis set independent information about the atomic contributions.

The SnO_2 (110) surfaces are built by cleaving from the optimized bulk crystal. The lattice constants of $a = 4.82 \text{ \AA}$, $c = 3.29 \text{ \AA}$ obtained by total energy minimization performed with a $5 \times 5 \times 8$ Monkhorst-Pack k -point sampling agree well with the experimental values of $a = 4.74 \text{ \AA}$, $c = 3.19 \text{ \AA}$. GGA band gap is underestimated by 2.0 eV as compared to the experimental value of 3.6 eV. This is expected as GGA tends to overestimate binding and underestimate the band gap. Calculations with three-, five-, seven- and nine-layer slabs are performed for the relaxation of both stoichiometric (terminated by bridging oxygens) and reduced (no bridging oxygens) surfaces. The same computational parameters as in the bulk calculation are employed except for the k -point sampling where $8 \times 4 \times 1$ k -points are used. The center layer is fixed to bulk configuration during the relaxation of the slab and the vacuum space of 10 Å is placed between slabs to ensure sufficient separation between periodic images in the vertical direction. Fig. 1a illustrates the tin dioxide crystal and its (110) surface. The slab structure of minimum 1×1 unit cell is shown in Fig. 1b in which the top face is stoichiometric and the bottom face is reduced having oxygens removed.

Calculations for surfaces with adsorbates are performed with 2×2 supercell ($13.6 \times 6.6 \text{ \AA}$) to ensure that molecules in neighboring supercells do not interact. Test calculations with three- and five-layer slabs and 10 and 40 Å vacuum were performed. Thermal smearing of 0.136 eV was used to speed convergence but due to the large band gap the effect of occupation is negligible. During the geometry optimization the middle layer of the slab is fixed while allowing all the other layers and the adsorbed molecules to relax.

The adsorption energy is calculated as

$$E_{\text{ads}} = (E_{\text{molecule}} + E_{\text{slab}}) - E_{(\text{molecule+slab})},$$

where $E_{(\text{molecule+slab})}$ and $E_{\text{molecule}} + E_{\text{slab}}$ are the optimized total energies of the adsorbate/ SnO_2 and molecule + substrate systems respectively. Latter terms are calculated with the molecule far in the supercell vacuum.

3. Results

3.1. Bare surfaces and free hydrocarbon molecules

The geometric details of the relaxed clean surfaces, both stoichiometric and reduced, are given in Table 1. Significant change in the geometrical parameters is seen when comparing the three- and five-layers slabs. However, the differences decrease significantly

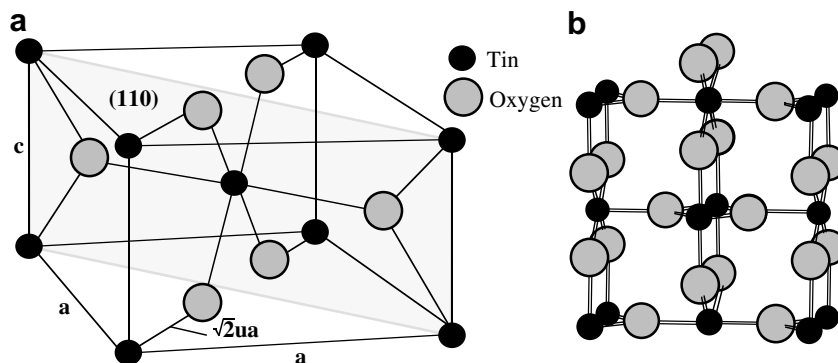


Fig. 1. (a) Tin dioxide crystal unit cell and its (110) surface. (b) Slab 1×1 supercell of (110) surface with the top face stoichiometric and the bottom face reduced. Tin atoms in the corners of the supercell are 5-fold, the centermost surface tin atom is 4-fold on reduced and 6-fold coordinated on stoichiometric surface.

Table 1
Convergence in relaxation of topmost surface atoms

	Sn _{ip}	O _{ip}	O _b
<i>Reduced</i>			
3 layers	0.19	0.30	–
5 layers	0.28	0.34	–
7 layers	0.31	0.35	–
9 layers	0.33	0.36	–
<i>Stoichiometric</i>			
3 layers	0.22	0.24	1.42
5 layers	0.30	0.27	1.49
7 layers	0.32	0.27	1.51
9 layers	0.33	0.27	1.53

Distances are measured from the plane of 5-fold tin atoms. Sn_{ip} is the four/sixfold tin in the center of the surface layer, O_{ip} are the oxygens that are in-plane with tin atoms in bulk configuration. O_b are the bridging oxygens.

Table 2
Free hydrocarbon molecules from PBE/DNP calculations: bond lengths in Å and frontier orbital energies and HOMO–LUMO gap in eV

	Exp. [20–21]		DFT		ϵ_{HOMO}	ϵ_{LUMO}	$\Delta\epsilon$
	C–C	C–H	C–C	C–H			
Acetylene	1.203	1.062	1.214	1.074	–6.91	0.09	7.00
Ethylene	1.334	1.081	1.334	1.092	–6.55	–0.72	5.83
Ethane	1.522	1.083	1.527	1.100	–8.08	1.92	10.00

when comparing five-layers slabs with the seven- and nine-layers slabs. Thus, sufficient geometry convergence for our purpose is achieved with the five-layer slabs which are then further used for adsorption studies.

In order to assess the differences induced into the geometry and electronic structure of the hydrocarbons upon their interaction with the SnO₂ surfaces we give the structural details and molecular orbital (MO) energies of the free molecules at PBE and DNP level in Table 2. As expected from the general performance of DFT [19], the calculated bond lengths given in Table 2 are very close to the experimental values, the differences being negligible.

3.2. Adsorption geometry and energetics

Several possible adsorption sites were selected as starting configurations for the relaxation of the hydrocarbon–SnO₂ systems. Sites were selected around points of high symmetry on the surface. Top and side views of the optimized SnO₂/hydrocarbons slabs are given in Fig. 2. Independent on the starting configuration all three hydrocarbon molecules on the reduced surface find a site that produces minimum energy on top of the 5-fold tin atom. This is not unexpected if realizing that in this orientation the partial positive charge of the tin atom is placed relatively symmetric with respect to the partially negative charged carbons, while the closest negative oxygens of the surface are also symmetric with respect to the positive charged hydrogens (see Fig. 2).

We first consider the reduced surface. While ethylene and acetylene lie symmetrically on top of the tin atom they rotate slightly in the plane of the surface. Ethane however, is not lying flat on the SnO₂ surface but it is tilted considerably bringing the hydrogens closer to the tin atoms. The distances of the molecules from the plane of 5-fold tin atoms range between 3 and 4 Å, with ethane exhibiting not only the longest distance but also lowest adsorption energy (Table 3). This suggests that ethane is physisorbed on the surface, while unsaturated molecules are probably adsorbed with combined mechanism of physisorption and chemisorption.

The adsorption sites on the stoichiometric surface are similar to the ones on the reduced surface, i.e. on top of 5-fold tin atom and

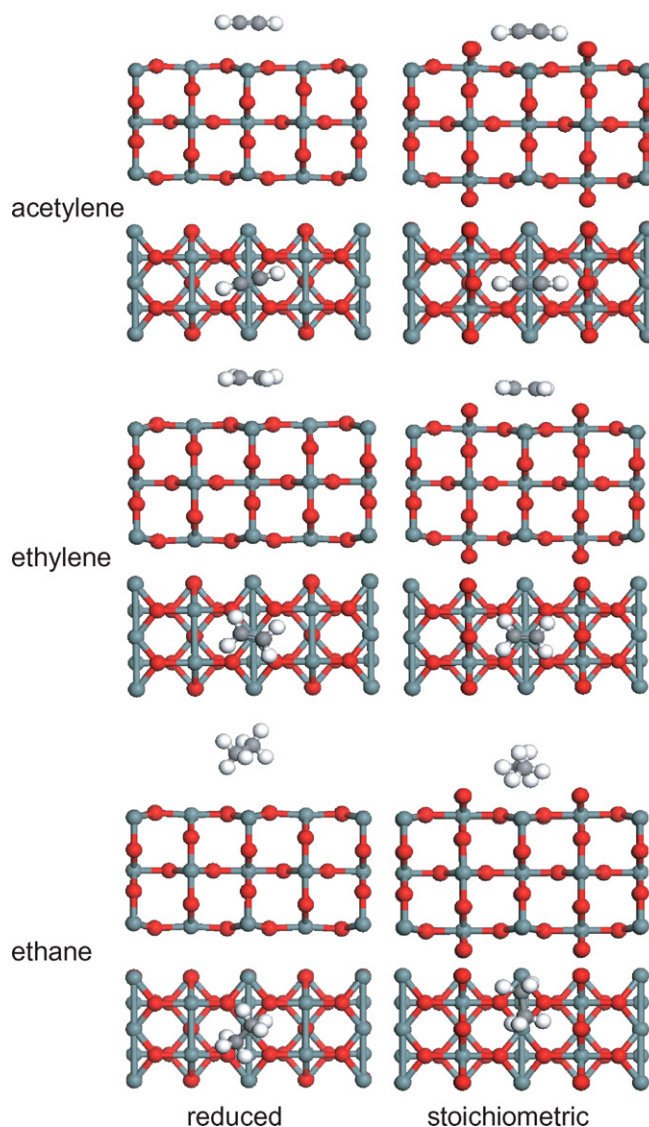


Fig. 2. Side and top view of ethane, ethylene, acetylene adsorbed on the reduced (left) and stoichiometric (right) surfaces of SnO₂.

between the bridging oxygens, as can be seen from Fig. 3. However, the interaction between the molecules and the surface is much stronger, which is evidenced by the shorter molecule–surface distances and by larger adsorption energies. In particular, in case of acetylene the adsorption energy describes clear chemisorption. Moreover, the interaction of acetylene with the surface partially breaks one of the π bonds and disrupts the sp hybridization of the C atoms.

As a result, the molecule loses its linearity and the hydrogen atoms come closer to the bridging oxygens of the surface (see

Table 3
Adsorption energies (eV) and SnO₂ surface – hydrocarbon distances measured as distance of the molecular center-of-mass from the plane of surface 5-fold tin atoms

	Reduced				Stoichiometric			
	eV	Å	$\Delta(\text{C–C})$	$\Delta(\text{C–H})$	eV	Å	$\Delta(\text{C–C})$	$\Delta(\text{C–H})$
Acetylene	0.23	3.09	0.01	0.01	1.02	2.68	0.02	0.03
Ethylene	0.21	3.25	0.01	0.01	0.68	2.91	0.02	0.01
Ethane	0.07	4.42	0.01	0.04	0.32	3.39	0	0.04

The C–C and C–H bonds are given in Å as differences from the ones in the free molecules.

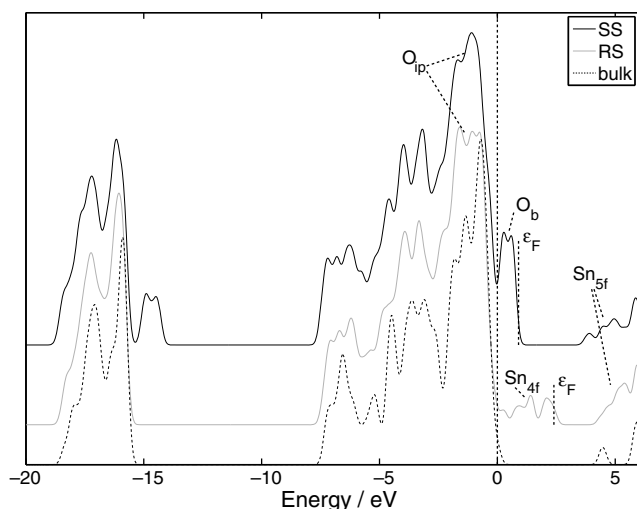


Fig. 3. Density of states of bulk, reduced surface and stoichiometric surface. Bulk DOS is arbitrarily scaled for visualization, whereas surface DOS are directly from 5-layer slabs. The surface DOS are shifted in energy by adjusting the band edges at lower energy to those of the bulk and highest occupation of slab calculation ϵ_F and contributions of atoms in top layer of slabs are indicated.

Fig. 2. At the same time both C–C and C–H bonds become slightly elongated as compared to the ones in the free acetylene molecule, as can be seen in Table 3. A similar elongation of the bonds is observed also for ethylene, which however remains planar, not showing any evidence of a change in the C hybridization state. The saturated ethane however, is exhibiting the weakest interaction among the studied hydrocarbons as can be seen from the adsorption energy and geometry changes. Also its adsorption site is different from that of unsaturated hydrocarbons as it aligns itself with the rows of bridging oxygens and settles between two surface tin atoms.

3.3. Electronic structure

Hirshfeld population analysis of the adsorbed systems reveals that some charge is transferred across the organic–inorganic interface. The changes in charge distribution are presented in Table 4. The charge is transferred from the carbon atoms of the hydrocarbon molecules to the surface atoms nearest to the adsorption site. Most of the charge goes to 5-fold tin atom directly below the adsorbed molecule. Some charge is also transferred to the oxygen atoms and 5-fold tin atoms farther from the adsorbate. The charge transfer is larger in case of adsorption onto the stoichiometric surface as compared to the adsorption on the reduced surface. The unsaturated adsorbates transfer notable amount of charge to tin on surface and some charge to bridging oxygens nearest to the molecule. However, in the case of ethane the participation of the oxygens is negligible and the charge transfers only to the surface

atoms in close proximity. On the reduced surface the charge transfer is significantly weaker. This is due to the increased negative charge (decrease in Lewis acidity) on the reduced surface. Formation of reduced surface involves strong transfer of negative charge to 4-fold tin atoms (0.24 e) and some transfer to 5-fold tins (0.10 e). Therefore, negative charge on tin sites is more saturated and only acetylene experiences a notable transfer of charge from carbon to tin.

The variations in charge distribution are consistent with the conclusions drawn in section 3.2 on the basis of the geometrical changes induced by the interaction of the hydrocarbon molecules with the SnO_2 surface. Positively charged hydrogen atoms tend to turn towards negatively charged oxygens. Also largest charge transfers lead to most notable elongation in C–C bonds.

Density of states (DOS) for the bulk and slabs are presented in Fig. 3. A scissor operator of 2.0 eV is used, which is needed to match the bulk calculated and experimental band gaps. Much of the shape of surface DOS originates from bulk, with additional contributions of surface atoms around the band gap. These are evidenced for the stoichiometric surface by high peaks on top of the valence band originating from p-orbitals of bridging oxygens. For the reduced surface, the contributions on top of the valence band are due to s- and p-orbitals of 4-fold tin atoms. Contributions to conduction band are on both surfaces mostly due to 5-fold tin atoms.

The orbital energies of free molecules (in the middle of slab vacuum) are presented in Fig. 4 together with the total DOS of the adsorbate/ SnO_2 systems. Also, in cases where the molecules and surfaces (reduced and stoichiometric) do not interact chemically the orbital energy levels of the free molecules appear shifted, indicating presence of surface dipole layers at both surfaces, stronger at the stoichiometric one. When acetylene is adsorbed on the stoichiometric surface, its orbital energy levels are shifted down and the HOMO level broadens noticeably. Acetylene on the reduced surface also experiences shift and broadening, but not pronounced. The same behavior is seen also for the other hydrocarbon molecules, which interact less with the reduced surface and more with the stoichiometric one. This is evidenced by smaller shifts and reduced broadening. Additionally, the interaction decreases with the degree of unsaturation of the adsorbed hydrocarbons, indicating the active role of π -orbitals in the adsorbate–substrate interaction. If taking into account also the charge variation described above (see Table 4), we can conclude that the interaction involves charge donated by the π -system into the unoccupied levels of the tin atom. These findings support chemisorption of unsaturated hydrocarbons and physisorption of ethane on reduced surfaces. In all cases of chemisorption there are two contributing mechanisms: charge transfer creating ionic bonding (down-shift of levels) and covalent bonding (broadening of levels). Stronger interaction of unsaturated hydrocarbons on stoichiometric surface compared to reduced one is supposedly connected with the role of bridging oxygens which facilitate the charge transfer between adsorbate and surface.

Table 4

Hirshfeld charges of adsorbed molecules and changes in atom charges in adsorbate system compared to free molecules and surfaces

	Molec.	C	H	Sn_{5f}	$\text{Sn}_{5f}^{\text{nn}}$	O_{ip}	O_{b1}	O_{b2}
<i>Reduced</i>								
Acetylene	0.038	0.028	−0.009	−0.005	0.014	0.000	–	–
Ethylene	0.011	0.007	0.000	0.000	−0.009	0.001	–	–
Ethane	−0.040	−0.016	−0.001	0.009	0.004	0.001	–	–
<i>Stoichiometric</i>								
Acetylene	0.104	0.067	−0.014	−0.074	−0.008	−0.008	0.011	−0.012
Ethylene	0.136	0.041	−0.014	−0.062	−0.014	−0.006	0.002	−0.011
Ethane	0.048	0.001	0.004	−0.028	−0.008	−0.002	0.002	−0.006

Units are electron charges. Table presents average change in charges in carbon and hydrogen atoms of molecules. On the slab changes in fivefold tin directly below molecule (Sn_{5f}), next nearest fivefold tins ($\text{Sn}_{5f}^{\text{nn}}$), in-plane oxygens near the molecule (O_{ip}), bridging oxygens nearest (O_{b1}) and next nearest (O_{b2}) to adsorbate.

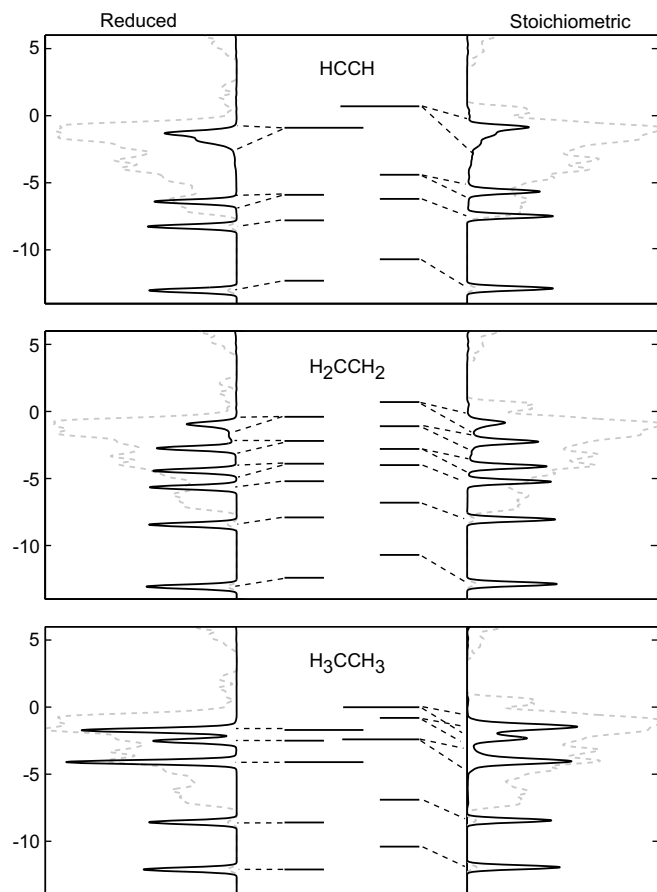


Fig. 4. Density of states of adsorbed molecules. Center column shows free molecule orbitals. Reduced slab is on left and stoichiometric on right. Leftmost column presents DOS of adsorbed molecules (black line) and slabs with adsorbates (grey line), rightmost column gives same for the stoichiometric systems. DOS of the molecules is scaled up for visibility. Acetylene is on top row, ethylene on center and ethane on bottom.

4. Conclusions

Based on DFT-calculations the adsorption sites of three small hydrocarbon molecules were determined. Acetylene and ethylene adsorb preferentially on top of a 5-fold tin atom, while ethane aligns itself with the rows of bridging oxygens and settles between two surface tin atoms. Based on adsorption energies and charge

transfer, unsaturated hydrocarbon molecules on stoichiometric surface experience clear chemisorption and on the reduced surface adsorption is more like physisorption. Ethane appears to be clearly physisorbed on reduced surfaces. The adsorbate–substrate interaction involves mainly the π -orbitals of the molecules, thus being strongest for the acetylene. Presumably, charge is donated by the π -system into the unoccupied levels of the tin atom. This is accompanied also by a partial rehybridisation of the C atom orbitals towards sp^2 and sp^3 for acetylene and ethylene, respectively. In the case of acetylene the rehybridisation is clearly evidenced by the elongation of the C–C bond and the loss of molecular linearity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.susc.2008.08.001](https://doi.org/10.1016/j.susc.2008.08.001).

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