Theoretical study of the acetonitrile flip-flop with the electric field orientation: adsorption on a Pt(111) electrode surface

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The interaction of acetonitrile on Pt(111) electrode has been studied using density functional theory methods. Periodic calculations for a coverage of 0.25 show that the most stable adsorption mode of acetonitrile in UHV conditions on Pt(111) is the side-on $\eta^2(C,N)$ state. In this state, the short-bridge surface site is energetically preferred to the long-bridge site. The nitrogen end-on on top of a surface platinum atom is also likely to occur. An external uniform electric field introduced in the cluster models perpendicular to the surface serves to mimic the electrode potential. It makes the adsorbed molecule move and orient perpendicular to the surface. Depending on the direction of the electric field, the acetonitrile is oriented with the nitrogen atom or the methyl group toward the surface. Our results are in agreement with recent SFG experiments performed in electrochemical environments.

KEY WORDS: surface electrode; DFT; platinum; acetonitrile.

1. Introduction

The adsorption of acetonitrile on metal surfaces has been a matter of study for more than 25 years [1,2]. Thermal desorption experiments associated with Ranay nickel and isotopic labeling have shown that there is a possible isomerization between acetonitrile (CH_3CN) and isocyanide (CH_3NC) on nickel surfaces containing carbon atoms, Ni(111)-C. In early studies, acetonitrile was assumed to adsorb on nickel surfaces through the nitrogen lone pair with the CN axis perpendicular to the surface, whereas isocyanide was thought to be bonded through both the carbon and nitrogen atoms. Later, a high-resolution electron energy loss spectra at 100 K of these adsorbed species was published [3], which suggested that acetonitrile adsorbs on Ni(111) with both nitrogen and carbon atoms of the cyanide function bonded to the surface metal atoms. This adsorption mode is referred as "η^2-$NCCH_3$ state". The use of this notation originates from the comparison between the ligand of a molecular transition-metal complex and a molecule adsorbed on a metal surface. An approximation made by experimentalists in order to assign frequencies to the adsorbed species relies on analogies with vibrational frequencies of ligands in metal complexes, in particular, that the stretching frequencies of the ligand depends on the coordination mode. This is precisely one of the reasons for the early interest in the adsorption of acetonitrile on metal surfaces: acetonitrile adsorption is weak and it does not dissociate. Transition-metal complexes with undissociated acetonitrile exist [4–6]. However, the analogy is sometimes misleading [7], and the resulting frequency assignment can be false [8]. Sexton *et al*. [9] have used electron energy loss vibrational spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), thermal desorption (TPD) and work function measurements to study the adsorption of acetonitrile on Pt(111). This work suggests a chemisorption at 100 K, with the cyanide group parallel to the surface or slightly inclined. Their results show that one π-bond of CN opens during the adsorption and that there is a rehybridization of the CN triple bond to a double bond. Both carbon and nitrogen atoms of the cyanide group are bonded to the surface. These results are consistent with a "$\eta^2(C,N)$ monolayer state". Sexton *et al*. emphasize that the usual coordination of the acetonitrile ligand in metal complexes is end-bonded via the nitrogen lone pair. They also suggest another minority molecular state, "$\eta^4(C,N)$ state", at a low coverage (less than one monolayer) more strongly bound than the $\eta^2(C,N)$ state, that would occur on a step site. In 1992, Ou *et al*. [10] confirmed the $\eta^2(C,N)$ state with infrared reflection–absorption spectroscopy (IRAS), temperature-programmed desorption (TPD) and work function change. These authors found a red-shift of the C–H stretches of the methyl group for an unannealed submonolayer and interpreted this result as evidence of a β-hydrogen agostic interaction between the acetonitrile and the surface. By warming a multilayer to 213 K, a few kelvin below the monolayer desorption temperature and maintaining this temperature for 1 min, the authors produced annealed submonolayer that, according to IRAS features, contains both terminal and bridge-bonded adsorbate adsorbed via the nitrogen atom.

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There is another motivation for the very early studies of acetonitrile in surface science, namely, its use in electrochemistry as an aprotic solvent for the study of the adsorption on well-defined platinum surface electrodes. Pioneering efforts [11–13] have shown that the electrode potential and the water content are able to control the oxide formation at the platinum surface electrode. The behavior of CH_3CN itself was subsequently studied and found reactive only at extreme potentials [14] for which acetonitrile is reductively adsorbed. However, we will not study this case in the present paper. Examining the relative adsorption of different species, Angerstein-Kozlowska *et al.* [15] have suggested a preference for the end-on adsorption and concluded that an electrochemisorption of acetonitrile occurs through the CN group rather than through the CH_3 group. Infrared reflection-absorption spectroscopy measurements led to the same conclusion for acetonitrile adsorbed on Pt(111) in ultrahigh vacuum (UHV) [16]. Reconciling the two possible orientations of acetonitrile at the surface electrode, Marinkovic *et al.* [17] claimed that both the side-on $\eta^2(C,N)$ and the end-on states can occur, depending on the sign of the applied potential. These authors have been able to follow the transition between the orientations of the adsorbate with *in situ* reflection infrared spectroscopy (subtractively normalized interfacial FTIR spectroscopy, SNIFTIRS) with electrochemical modulation. Recently, Baldelli *et al.* [18] studied the orientation of acetonitrile on a platinum electrode surface using the sum frequency generation (SFG) vibrational spectroscopy. The latter is sensitive only to the interface region between two centrosymmetric media. The interface is that of liquid acetonitrile and the electrode. Their results show that the C–C bond (the C_3 symmetry axis) is perpendicular to the surface. In one range of potential, the molecule is oriented with the nitrogen atom toward the surface, while in a different range it is oriented with the CH_3 toward the surface.

We have undertaken this work in order to evaluate the influence of the potential electrode on the orientation of acetonitrile on Pt(111). The surface is represented by different theoretical models that are presented in Section 2. Section 3 contains the methodological details of calculations. The first step of this work involves the study of the adsorption of acetonitrile on a Pt(111) surface in UHV conditions (Section 4). Results for periodic boundary conditions are also shown and a brief comparison with cluster results is presented. In the last section, cluster models are used to demonstrate that an external uniform field that mimics the electrode potential strongly influences the orientation of the adsorbate. The $\eta^2(C,N)$ mode does not remain when an electric field is applied. However, as the magnitude of the electric field increases, the adsorption modes with the adsorbate perpendicular to the surface become energetically more and more favorable and acetonitrile moves closer to the surface.

This paper is devoted to the modification of the adsorption mode induced by an electric field. This is of primary importance for electrochemistry. As the adsorption modes are also determined for their reactivity, they can also have a strong influence on the catalysis.

2. Surface models

We have used both periodic and cluster approaches to model the Pt(111) surface. In the former, the calculations explicitly take into account the periodicity of the surface. The calculations are periodic in three dimensions (superslab model) and the cell vector perpendicular to the surface is large enough (15 Å) to prevent any interaction between two successive slabs (the vacuum is at least 5.5 Å). We have used a three-layer platinum slab; the three layers are shown in figure 1. We have checked that in the case of the most favorable adsorption mode, namely, the $\eta^2(C,N)$, the adsorption energy and the adsorbate geometries are the same as those for a five-layer slab. The unit cell containing one acetonitrile is a 2×2 cell, corresponding to a coverage of $\theta = 1/4$. This low coverage is enough to minimize the interactions between the adsorbed molecules; this also allows a comparison between the periodic and cluster methods to be made.

The cluster method allows electrochemical processes to be studied. In particular, it is possible, in a cluster approach, to apply a uniform external electric field that mimics the electrode potential. Note that this theoretical model neglects other features of the electrochemical environment such as solvent effect. We used different symmetry-adapted clusters to study chemisorption at different sites. This strategy has already been used for the theoretical study of the adsorption of carbonate on a Pt(111) electrode [8]. A cluster made of 18 platinum atoms, Pt_{18}, is appropriate, for instance, to represent the $\eta^2(C,N)$ short-bridge adsorption mode (figure 2(a)) in which the adsorbate interacts with the surface in a bidentate manner. For the end-on adsorption mode directly on a surface platinum, the interaction is monodentate, and a cluster with Pt_{13} has been selected (figure 2(b)).

3. Computational details

For the periodic approach, we have used the "Vienna *ab initio* Simulation Package code" VASP [19,20]. The calculations have been carried out using the generalized gradient approximation (GGA) with the Perdew-Wang (PW91) exchange-correlation functional [21]. We have chosen the small core ultrasoft pseudopotentials [22,23] and the basis sets supplied with the code. Hence, 10, 1, 4 and 5 electrons are explicitly considered for platinum, hydrogen, carbon and nitrogen respectively. The

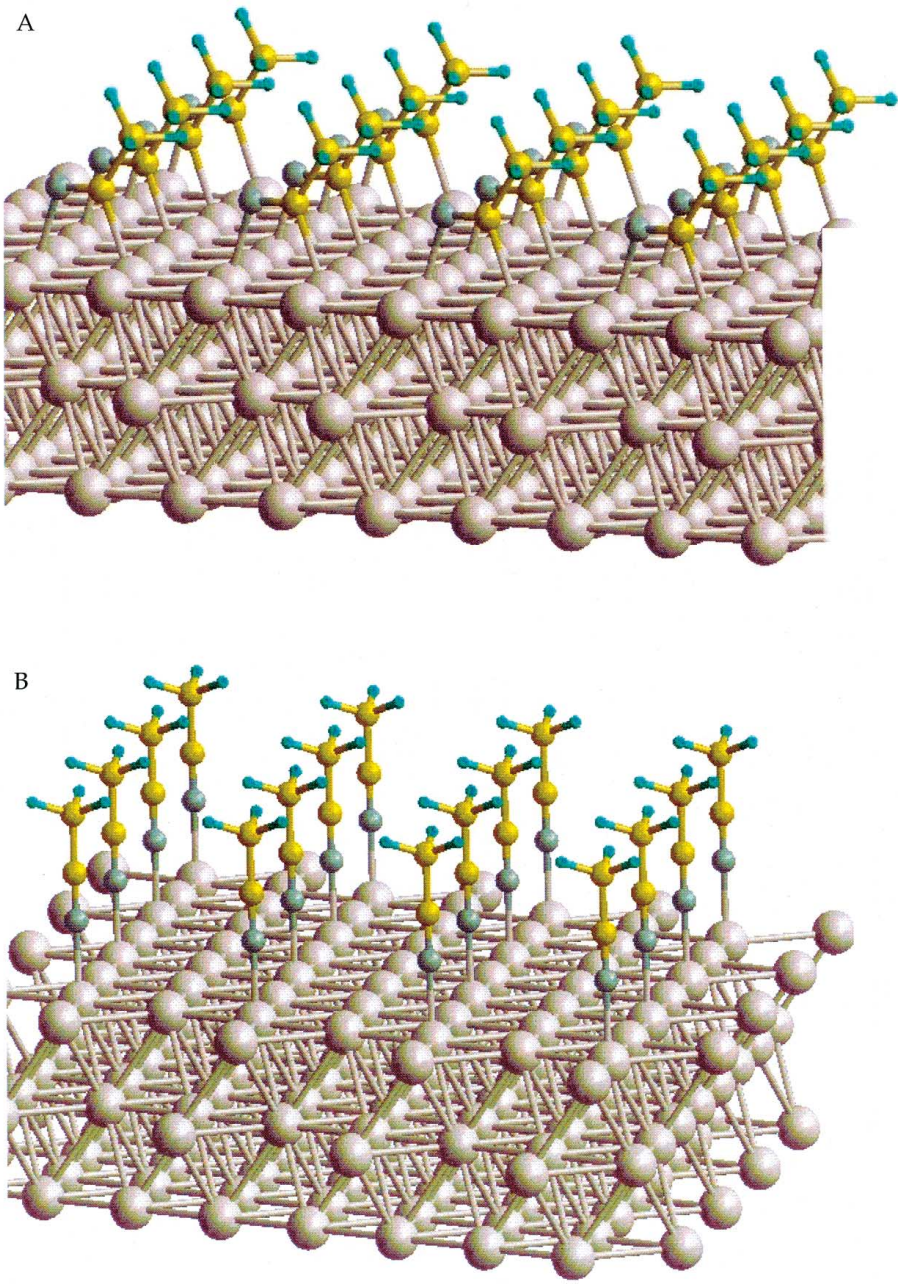

Figure 1. The two most favorable adsorption modes on the three-layer platinum slab at coverage 0.25. (a) The η^2(C, N) bridging mode on the short-bridge site and (b) the nitrogen end-on on top of platinum.

expansion includes all plane waves whose kinetic energy is less than the chosen cutoff energy, 350 eV. In a previous study [24], we checked that this cutoff is sufficiently accurate for the present study. For the periodic slab, *k*-point sampling in the direction normal to the surface is not needed, so that a $5 \times 5 \times 1$ Monkhorst-Pack set could be used. For one of the cases (the nitrogen end-on on top), we have checked that the use of a $10 \times 10 \times 1$ Monkhorst-Pack set led to the same results, both for the energetics and for the geometry.

While the periodic calculations have been carried out with the GGA method, for the cluster calculations we have chosen to use the B3LYP hybrid density functional [25], which is widely used for systems containing transition metals and has been shown to provide better results [26–28]. Hybrid methods are not available using VASP. For the cluster calculations, we have used the Gaussian98 suite of programs [29]. The molecular orbitals are expressed as a linear combination of Gaussian type orbitals. A standard split valence plus polarization basis set, 6-31G*, is used to describe the atoms on the acetonitrile molecule. As in reference [8], we have used a mixed approach to represent the electronic structure of the platinum clusters: the atoms surrounding the adsorption site are described with the relativistic small core effective core potentials (RECP),

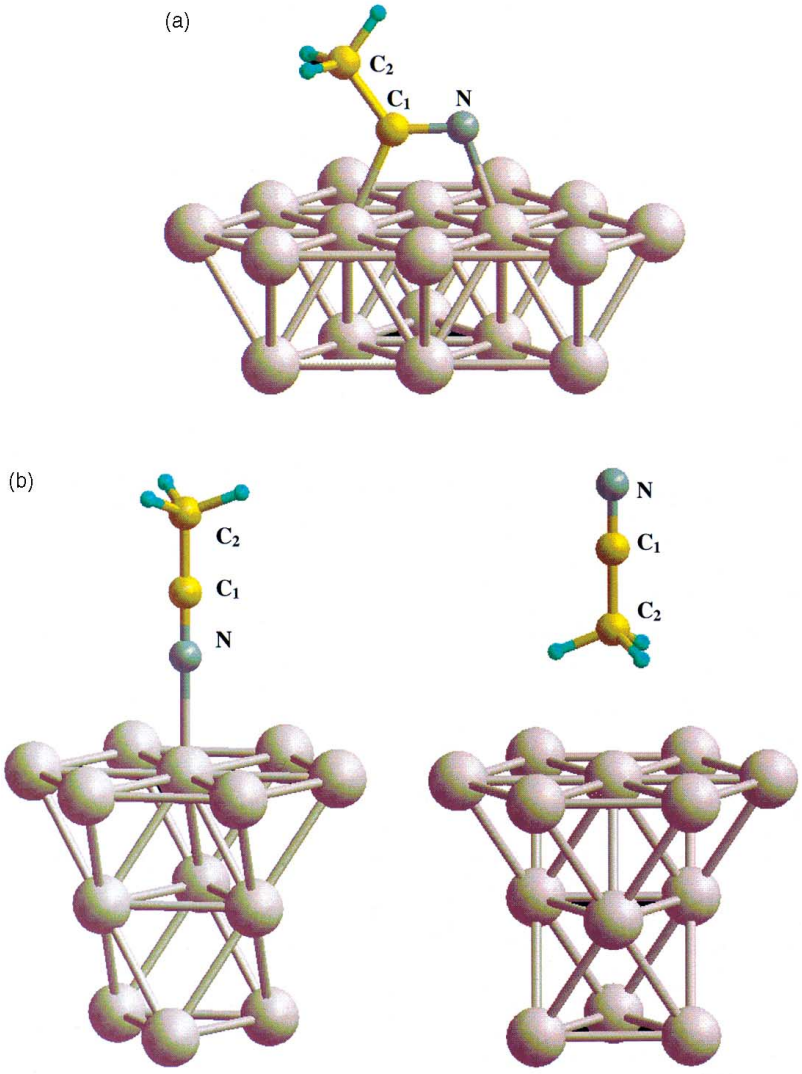

Figure 2. (a) Perspective view of the acetonitrile in the $\eta^2(C,N)$ adsorption mode on Pt_{18}. (b) Perspective views of the perpendicular orientations modes on Pt_{13}. Nitrogen end-on on top of platinum (left-hand side) and CH_3 end-on with carbon on top of a platinum (right-hand side) orientations; in this illustration, the hydrogen atoms point toward the platinum atoms.

which replace the inner core electrons, and by a standard double-ζ basis set, in which the $5s^25p^65d^{10}$ electrons are treated explicitly [30]. The basis set of these atoms is [5s3p/2s1p]. For Pt_{13}, only the seven atoms of the first layer contain 18 electrons, while for Pt_{18}, the four atoms of the short- and long-bridge site contain 18 electron atoms. The atoms belonging to the rest of the cluster are described by one-electron pseudopotentials [31,32] used for embedding purposes.

For all the calculations, the coordinates of the platinum atoms were fixed at their bulk structure values. In all the periodic calculations, the coordinates of all the atoms of acetonitrile were fully optimized. In the case of the cluster calculations, a number of constraints have been introduced. First, because of the limited size and artificial asymmetry of the cluster, it is necessary to avoid transition between two adsorption modes. This point will be developed in a forthcoming work. Next, in order to decrease the computational cost, the total number of parameters to be optimized has been reduced. Thus, for the end-on adsorption modes, the adsorbate was forced to remain perpendicular to the surface, while for the side-on $\eta^2(C,N)$ state, the cyanide group axis was forced to remain on the short-bridge site and the geometrical optimization of the hydrogen atoms was performed so as to keep the C_s symmetry of the acetonitrile molecule (even though the supersystem adsorbate/substrate had lost all of its symmetry elements).

The adsorption energies, E_{ads}, have been calculated by subtracting from the total energy of the optimized system the sum of the energies of the separated acetonitrile and cluster model. With this convention, a negative value of E_{ads} indicates an exothermic adsorption. The reference is the completely separated fragments: on the one hand, the cluster that models the electrode, and, on the other hand, the acetonitrile molecule that is not any more under the influence of

the electric field. Hence, when an external electric field is applied on the supersystem, the energies of the separated fragments are calculated with the same electric field magnitude for the cluster, representing the electrode, and without it for the acetonitrile. Note that there is not an obvious correspondence between the potential at which the experiment is carried out and the magnitude of the field applied on the cluster. The typical value for electrochemical environment is 0.01 au and 1 au of electric field $= 5.2 \times 10^9$ V/cm [33]. In the electrochemical cell, when a potential of 1 V is applied, the electric field is $F \sim 5 \times 10^7$ V/cm ~ 0.01 au [34]. The electric field magnitudes used are kept below values that induce desorption.

4. Adsorption on Pt(111) surface

4.1. Adsorption energies

The adsorption energies are summarized in table 1. We have performed several optimizations with the periodic model, with different starting geometries. The most stable structure is represented in figure 1(a). Acetonitrile is able to adsorb on the surface through the π electrons of the cyanide group. The adsorption mode is a bidentate one, $\eta^2(C, N)$, in which the carbon and nitrogen of the cyanide group interact with platinum atoms. Depending on the distance between the platinum atoms that are involved in the adsorption, there are two adsorption orientations for the $\eta^2(C, N)$ adsorption mode. When the CN axis is parallel to the short bridge, the adsorption energy is -12.8 kcal/mol and it increases to -3.9 kcal/mol for the perpendicular orientation (long-bridge site) showing a decrease in the strength of the interaction. We have tried placing the center of the CN bond on top of a platinum atom; however, the geometry optimization led to desorption of acetonitrile.

Other geometrical optimizations with the periodic model led to less stable structures, in which the molecule axis is perpendicular to the surface, and in which the molecule interacts with the surface through the nitrogen electronic lone pair. Among the nitrogen end-on adsorption modes, with nitrogen toward the surface, the strongest interaction occurs with the nitrogen directly on a platinum surface atom (figure 1(b)). The adsorption energy that we have calculated on the three-layer slab model is -9.4 kcal/mol. When the nitrogen atom is placed above a bridge site or over a hollow site (hcp or fcc), the adsorption energies are less than -2 kcal/mol. We have also tried geometries with the methyl group toward the surface, although this adsorption mode is very unlikely on a surface that is not an electrode. The carbon atom has been put directly on top of a platinum atom, on top of a hollow site and on top of a bridge. In these cases, as expected, we did not find any interaction between the adsorbate and the surface.

We have evaluated the lateral interactions between adjacent adsorbed molecules by subtracting the energy of an isolated molecule with the same geometry as those in the adsorbed acetonitrile monolayer from the energy of an adsorbate. In the case of the $\eta^2(C, N)$ state, there is a small favorable interaction (-2.1 kcal/mol) between the adsorbates, which becomes repulsive by 2.6 kcal/mol for the end-on adsorption mode. These results show that at higher coverage, the adsorption energy difference between the two adsorption modes would increase, thereby favoring the η^2(C,N) state.

Before presenting the results in the presence of an electric field (see next section), we briefly compare the results obtained by the periodic calculations with those of the cluster calculations without any external field. We have chosen two clusters that are suitable to represent the two energetically most favorable adsorption modes. The adsorption energies on Pt_{18} and on Pt_{13} differ from those obtained with the periodic calculations (table 1). However, the η^2(C,N) adsorption is energetically more favored than the adsorption on top. The clusters appear to be less reactive than the slabs. A similar effect had been found previously for the adsorption of propene on Pt(111) [24] and propyne on Cu(111) [35]. For these adsorbates, a CC π bond is broken under adsorption and the adsorption mode is η^2(C,C). First of all, the slab calculations are performed with the GGA density functional that provides an upper bound of the adsorption energies. Next, basis sets are different. Our cluster calculations use a rather limited Gaussian type orbital (GTO) basis set and are not corrected for the basis set superposition error (BSSE). For the η^2(C,N), using counterpoise corrections, we have evaluated the BSSE to be 2.0 kcal/mol. The BSSE correction for the cluster calculations decreases the adsorption energies,

Table 1
Adsorption energies of the acetonitrile on Pt(111) modeled by a three-layer platinum slab and by a Pt_{13} and a Pt_{18} cluster models (in parenthesis). A negative value indicates an exothermic process. The energetically most favorable adsorption mode is η^2(C,N) on the shortbridge

	η^2(C,N)		N end-on	CH_3 end-on
	Short bridge	Longbridge		
E_{ads} (kcal/mol)	-12.8 (-7.9)	-3.9	-9.4 (-0.3)	Desorption

increasing the difference between the cluster and periodic calculations. By contrast, the plane wave basis set used in the periodic calculations have a high cutoff, which achieves better convergence. Finally, the cluster models can suffer from edge effects. In conclusion, the numeric adsorption energies on clusters should be taken with caution.

It should be noted, however, that the limitations of the cluster models are not expected to affect our conclusions on the influence of the external electric field since the focus will be on the trends on a given cluster.

4.2. Adsorption geometries of the adsorbed acetonitrile

The main geometrical parameters of the adsorbed acetonitrile are given in table 2 for the two energetically most favorable adsorption modes. The carbon labeled 1 is that of the cyanide group. For the two modes, the geometry of the adsorbate remains close to that of the gas phase. The largest deviations are the elongation of the N–C_1 bonds and the decrease of the θ, the N–C_1–C_2 angle for the hybdridization in η^2(C,N) mode. This strongly suggests the breaking of one π-bond from the cyanide group (the NC_1 bond is elongated) and the rehybridization of C_1 from sp to sp^2, θ being close to 120.0°. The periodic and cluster optimizations give comparable geometry and distance of the nitrogen atom to the surface. However, there is one remarkable difference for the distance of C_1 to the surface. The periodic result shows that the cynanide group is strictly parallel to the surface, in contrast to the cluster result.

The distances between atoms of the acetonitrile and the surface are rather short, as expected for chemisorption. However, for the nitrogen end-on mode, the distances of the nitrogen atom to the surface calculated with the periodic model and the cluster differ by 0.41 Å. The cluster result gives longer distance between the molecule and the surface, which reflects the smaller adsorption energy obtained with this method. We have already reached similar conclusions with other adsorbates on metal surfaces [24,35].

Ou *et al*. [10] suggested an agostic interaction between the adsorbed η^2(C,N) acetonitrile and the metal surface atoms. In this hypothesis, the orientation of the methyl group is expected to be important. We have carried out an optimization of the η^2(C,N) configuration with two opposite conformations, namely, with one or two CH bonds of the methyl group oriented toward the surface, and found small differences. The energy associated to the former is less stable by 0.8 kcal/mol and 1.4 kcal/mol calculated with the periodic or cluster model respectively. The other geometrical parameters are identical for the two orientations. The C_1–C_2–H angle with the hydrogen atom oriented toward the surface has a value corresponding to the sp^3 hybridization (from 109.1° to 111.7°, depending on the method used for the calculation and on the orientation); this does not indicate a strong agostic interaction. Frequency calculations are presently under investigation.

5. Influence of the electric field on the η^2(C,N) adsorption mode and on the perpendicular approach, orientation of the adsorbate

Starting from the optimized geometry of the η^2(C,N) state obtained on the Pt_{18} cluster model, we have imposed an external uniform field of a larger magnitude (5×10^{-2} au) than has been used in previous studies [8] in the two orientations perpendicular to the surface. The results of the two geometry optimizations are presented in figure 3. The influence of the electric field clearly causes the desorption of the adsorbate. During the first geometry optimization steps, one of the atoms of the cyanide group moves away from the surface, while the other stays almost at the same position. When the electric field is oriented away from the surface, the nitrogen atom moves away from the surface (channel represented in figure 3), while for the opposite orientation it is the carbon atom of the cyanide group that moves away from the surface.

Desorption is likely due to the high electric field strength. By starting from the η^2(C,N) adsorption

Table 2
Principal geometrical parameters of the adsorbed acetonitrile (in Å and °). C_1 is the carbon atom of the cyanide group. h(X) is the height of X above the surface, $d(X_1–X_2)$ is the distance between X_1 and X_2 and θ(N–C_1–C_2) is the angle between the three atoms. The cluster and periodic results are almost identical, except for the nitrogen end-on adsorption mode for which the acetonitrile is obtained farther from the surface with the cluster approaches reflecting a weaker interaction. The left-hand side part of the C_2–H column corresponds to the distance involving the two hydrogen atoms oriented toward the surface

Adsorption mode	Model	h(N)	$h(C_1)$	$h(C_2)$	d(N–C_1)	$d(C_1–C_2)$	$d(C_2–H)$	θ(N–C_1–C_2)
η^2(C,N)	Slab	1.94	1.95	3.14	1.25	1.49	1.10 1.10	127.8
	Cluster	1.93	1.89	3.12	1.26	1.51	1.09 1.10	123.5
N end-on	Slab	2.00	3.16	4.60	1.16	1.44	1.10	180.0
	Cluster	2.41	3.57	5.03	1.16	1.46	1.09	180.0
Free acetonitrile	Slab	–	–	–	1.16	1.45	1.10	180.0
	Cluster	–	–	–	1.16	1.46	1.09	180.0

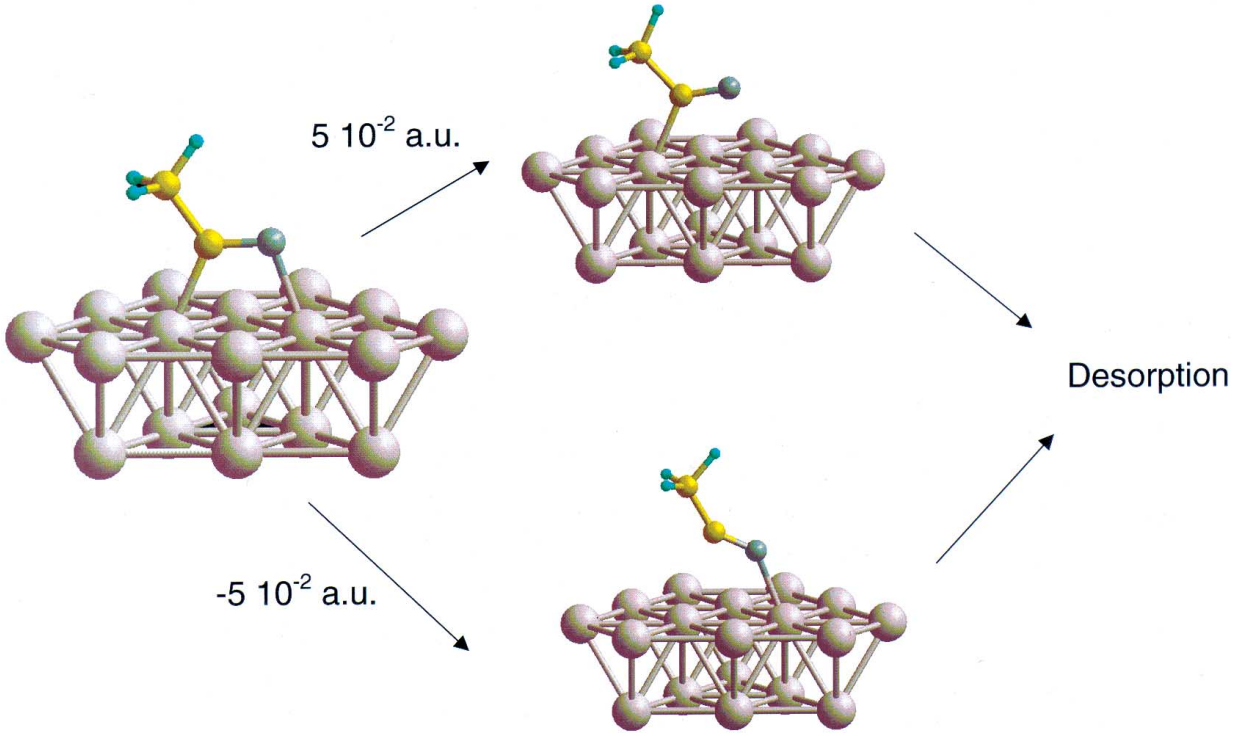

Figure 3. Electric field effect on the η^2(C,N) state. For positive electric field, nitrogen moves away from the surface and acetonitrile desorbs. For negative field, carbon of the cyanide group moves away and the adsorbate desorbs.

geometry optimized without electric field and applying fields with increasing magnitudes, the transition between the η^2(C,N) orientation and the two end-on orientations could be provided. There will be a hysteresis between paths of opposite electric field directions. The full scan study requires numerous calculations and will be carried out soon.

However, the conclusion of the current results are already clear: the external electric field induces a destabilization of the η^2(C,N) state and the adsorbate is oriented perpendicular to the surface, with either the nitrogen or the CH_3 toward the surface. The destabilization for weaker field (10^{-2} and 2×10^{-2} au) is shown in figure 4. The two adsorption modes that should be energetically the most favored ones in electrochemical environment are precisely the study of the next section.

We have introduced an external uniform field to mimic the electrode potential starting from the perpendicular orientation of the adsorbate. Let us first consider the Pt_{13} cluster model (figure 2(b)). The results are presented in figure 4 for two directions of the electric field whose magnitude varies from 0 to 2.50×10^{-2} au The positive values of the electric field correspond to an orientation toward the surface (positive charges move closer to the electrode and negative charges in the opposite sense). We have also reported results for the η^2(C,N) mode, computed on the Pt_{18} cluster because of its symmetry. Despite the use of different clusters, our results show clear tendencies. There are three domains of stability: the nitrogen end-on adsorption mode is the most stable one for a negative orientation of the electric field; the η^2(C,N) mode prevails when the field is weak, and the CH_3 end-on orientation is preferred for the positive electric field. For the latter, we have carried out calculations for the two conformations of the hydrogen atoms, namely, hydrogen pointing toward the hollow sites or hydrogen pointing toward platinum atoms. The second one turns out to be energetically more stable by 5.2 and 4.6 kcal/mol for electric field magnitudes of 1.0×10^{-2} and 2.0×10^{-2} au respectively. Results for this structure are displayed in figure 4. The adsorption energy of acetonitrile in the η^2(C,N) state, which is energetically the most favorable adsorption mode in the absence of any electric field, is indicated and shows a destabilization with increasing electric field. We do not present the results beyond $\pm 0.5 \times 10^{-2}$ since the distortion of the adsorbate becomes too large. It is important to compare the slopes of the curve for two orientations of the electric field. The nitrogen end-on adsorption is more likely to occur than the CH_3 end-on orientation, suggesting that more extreme experimental conditions are needed in order to produce the CH_3 end-on orientation than the nitrogen end-on orientation. This CH_3 end-on is indeed an unusual adsorption mode that does not represent an energy minimum without an applied field.

In figure 4, it is shown that the stabilization increases with the magnitude of the field for the perpendicular orientations. We have also carried out calculations with larger electric field magnitude than those indicated in

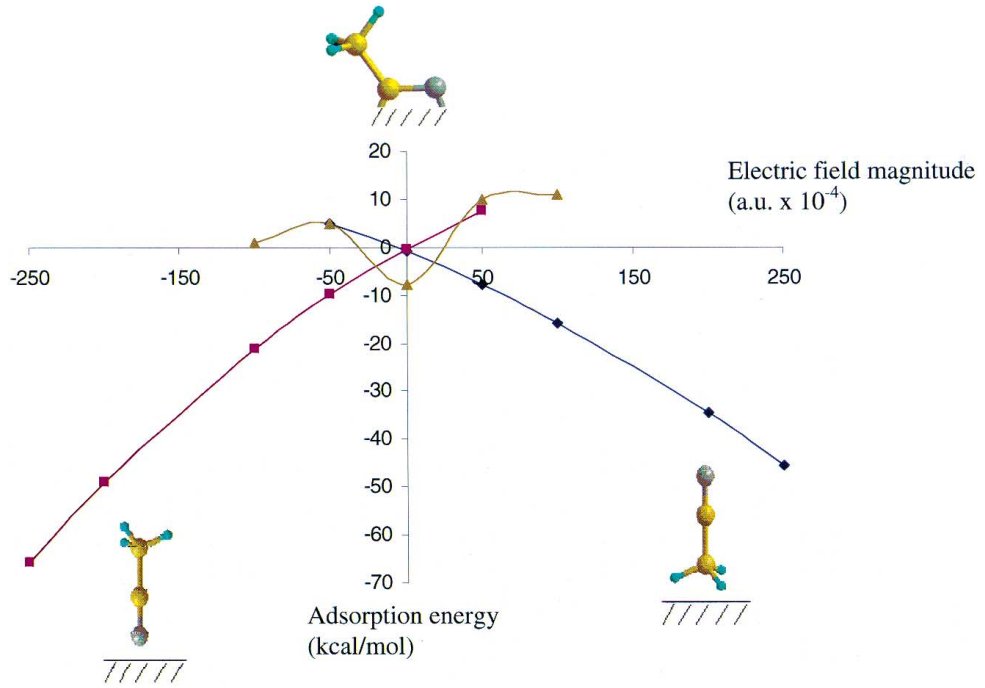

Figure 4. Adsorption energy of acetonitrile on Pt_{13} for the perpendicular adsorption modes and Pt_{18} for the η^2(C,N) adsorption mode versus the electric field magnitude. According to our conventions, the electric field oriented toward the surface is positive. The schemes show the most stable adsorption modes for negative, zero and positive electric field magnitudes. The electric field favors the adsorption with a perpendicular orientation.

figure 4 and failed to find a larger stabilization. Indeed, when the magnitude of the electric field exceeds some values (-3×10^{-2} au or $+4 \times 10^{-2}$ au depending on the orientation), the molecule desorbs.

For the nitrogen end-on adsorption, we have only computed the adsorption on top since it is the most stable mode in the periodic calculations done without electric field. The adsorption at the hollow site was less stable (Section 4.1). We have tested the adsorption with carbon above a hollow site using a Pt_{18} cluster that is symmetry-adapted (see figure 5). We do not have a realistic initial geometry for this adsorption mode since in periodic calculation no adsorption was found. We thus checked the two CH_3 conformations (hydrogen pointing toward the hollow sites or hydrogen pointing toward platinum atoms) and found them energetically equivalent. In figure 6, the result on the hollow site (hydrogen pointing toward the hollow sites) is compared

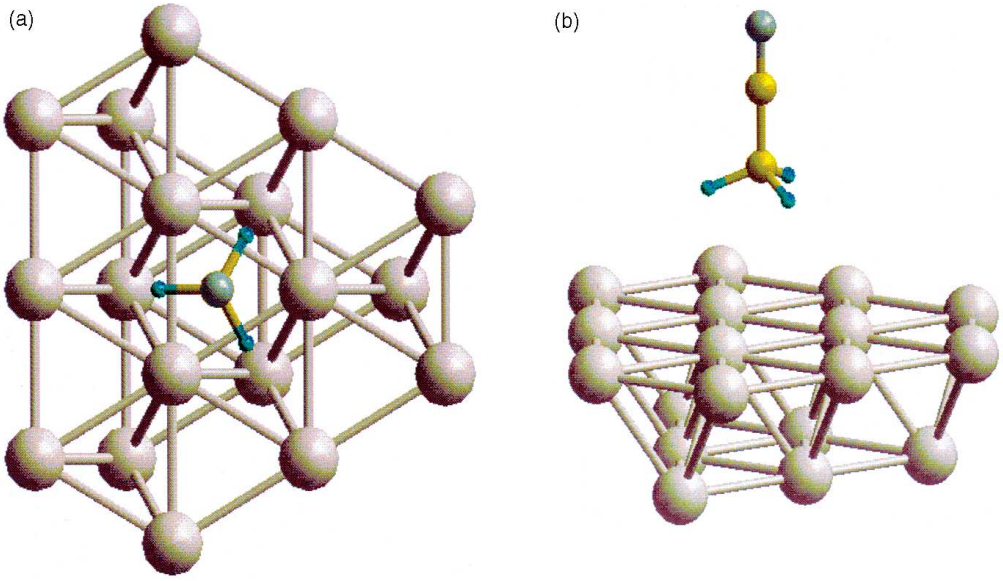

Figure 5. (a) Top view and (b) perspective view of the acetonitrile in the CH_3 end-on adsorption mode with carbon on top of a hollow site adsorption mode on Pt_{18}. In this view, the hydrogen atoms point toward the hollow sites.

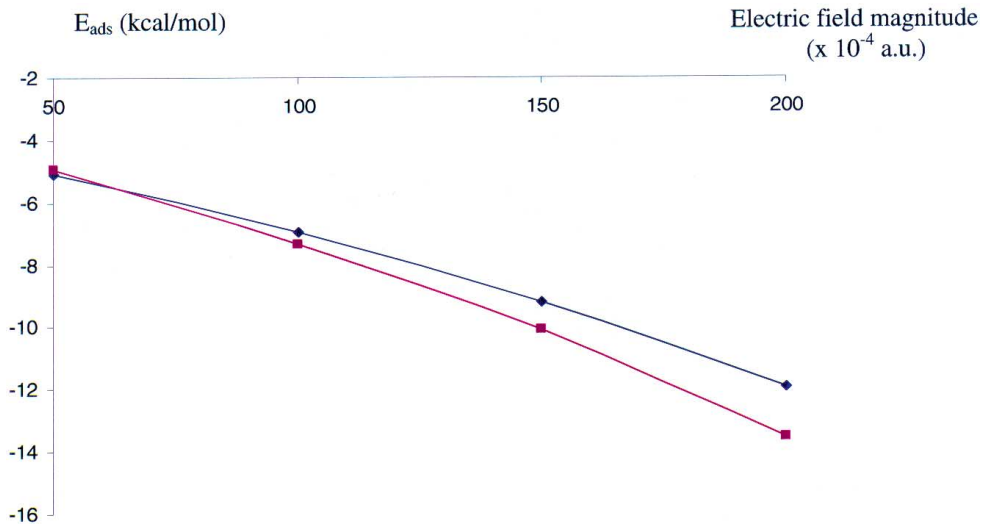

Figure 6. Adsorption energies versus the electric field magnitude of the CH_3 end-on adsorption mode. The values indicated by squares correspond to carbon on top of a platinum (Pt_{13} cluster), while the other points refer to carbon above a hollow site (Pt_{18} cluster). A negative value of E_{ads} stands for an exothermic process. Adsorption energies are larger when the field increases but the difference between the two curves remains small.

with that on the top site. The adsorption energy for the hollow site is slightly larger, although the difference is not very significant; recall that we have simultaneously changed the adsorption site and the cluster model. In figure 4, we chose to depict the latter since the Pt_{13} cluster is also used for the nitrogen end adsorption. However, at this point, we cannot reach a specific conclusion regarding the site of adsorption for the CH_3 end-on adsorption.

Let us now turn our attention to the geometrical parameters. The distances between the closer atom of the adsorbate from the surface and the surface are plotted versus the electric field magnitude for Pt_{13} (figure 7). The larger the electric field, the closer the acetonitrile. This is consistent with an increase of the interaction that sticks more firmly the adsorbate to the surface.

6. Conclusions

We have used two approaches to study the interaction of acetonitrile with Pt(111) electrode. In a first step of our work, periodic calculations performed with the periodic model show that at a 0.25 coverage in the absence of field, acetonitrile adsorbs via the cyanide group parallel to the surface. The CN bridges two surface platinum atoms, the short-bridge adsorption being energetically more stable than the long-bridge adsorption. We have found that the adsorption via the

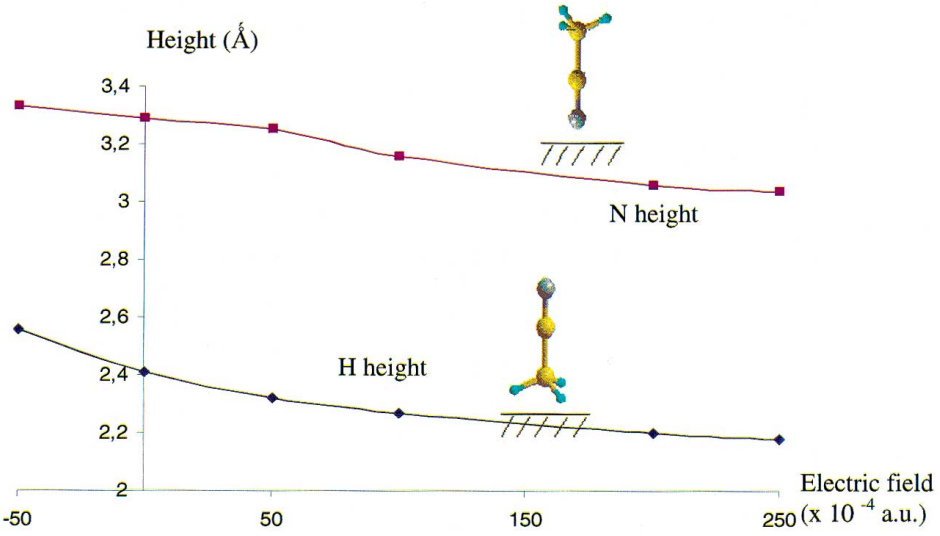

Figure 7. Distances between the Pt(111) surface and the closest atom of the acetonitrile versus the electric field magnitudes. The adsorption modes are perpendicular. The sign of the electric field for the nitrogen approach is reversed. The distance to the surface decreases when the electric field increases.

nitrogen atom with the C_3 axis of the molecule perpendicular to the surface is also a stable configuration with a similar adsorption energy.

We have introduced an external uniform electric field perpendicular to the surface in the cluster model to mimic the electrode potential. Starting from the optimized η^2(C,N) state, acetonitrile desorbs from the surface for large electric field. The molecule tends to have its C_3 axis perpendicular to the surface. Depending on the orientation of the electric field, the molecule desorbs with nitrogen or with CH_3 toward the surface. Finally, we have optimized the interaction of acetonitrile adsorbed perpendicular to the surface with different magnitudes and opposite directions of the electric field. We show that one electric field orientation favors the nitrogen end-on adsorption while the opposite orientation leads to the CH_3 orientation. The different orientations of the adsorbate may change the relative arrangement of the molecules that are activated under adsorption and, hence, the electric field may influence the heteregeneous catalysis.

Future studies will include the calculation of the frequencies of the adsorbed species in order to compare our results with the vibrational frequencies obtained experimentally. We have also started a study on the paths between the different adsorption modes.

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