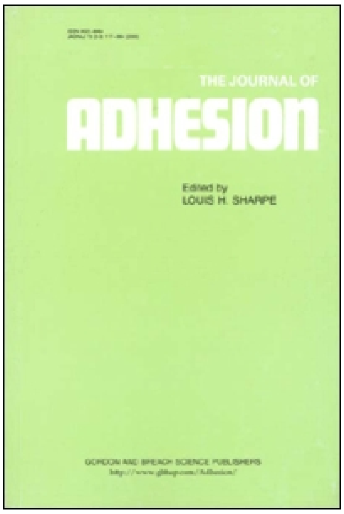
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Electrochemistry as a Tool to Monitor Lewis Acid-Base Reactions between Methacrylonitrile and Metallic Surfaces: A Theoretical and Experimental Proposal

Christophe Bureau[a]; Guy Deniau[a]; Pascal Viel[a]; Gerard Lecayon[a]; Joseph Delhalle[b]
[a] CEA-Saclay, DSM-DRECAM-SRSIM, Gif-sur-Yvette Cedex, France [b] Laboratoire de Chimie Théoretique Appliquée, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

To cite this Article Bureau, Christophe , Deniau, Guy , Viel, Pascal , Lecayon, Gerard and Delhalle, Joseph(1996) 'Electrochemistry as a Tool to Monitor Lewis Acid-Base Reactions between Methacrylonitrile and Metallic Surfaces: A Theoretical and Experimental Proposal', The Journal of Adhesion, 58: 1, 101 — 121

To link to this Article: DOI: 10.1080/00218469608014401

URL: http://dx.doi.org/10.1080/00218469608014401

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1996, Vol. 58, pp. 101–121
Reprints available directly from the publisher
Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

Electrochemistry as a Tool to Monitor Lewis Acid-Base Reactions between Methacrylonitrile and Metallic Surfaces: A Theoretical and Experimental Proposal*

CHRISTOPHE BUREAU, GUY DENIAU, PASCAL VIEL and GERARD LECAYON**

CEA-Saclay, DSM-DRECAM-SRSIM, bât. 462, F-91191 Gif-sur-Yvette Cedex, France

JOSEPH DELHALLE

Laboratoire de Chimie Théoretique Appliquée, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium

Downloaded At: 11:43 22 January 2011

(Received June 27, 1995; in final form December 14, 1995)

This paper presents a tentative extension of the Lewis acid-base concept to the case of an organic molecule interacting with a polarized metallic surface. Towards this aim, we make use of the Density Functional Theory (DFT) viewpoint on Lewis acid-base interactions. This theory has been shown to be relevant to describe adhesion processes at a molecular scale. It allows the introduction of three key parameters, for the molecule as well as for the metallic surface. These are the DFT chemical potential, μ, the absolute hardness, η and the Fukui function, $f(\vec{r})$. In the present paper, we show that the DFT chemical potential, μ, of the metallic surface is linearly related to the electrode potential drop, $\Delta\varepsilon$, imposed between this surface and a reference electrode in an electrochemical cell. Thus, while the chemical potential of the molecule is only determined by its chemical structure, that of the metallic surface can be monitored continuously. This means that the Lewis acidic or basic character of the metallic surface towards the molecule can, in principle, be chosen. We present experimental results arguing in the sense of this model by studying the interaction of 2-methyl 2-propenenitrile (methacrylonitrile) alternatively with a metallic cathode and with a metallic anode. The two different transient molecule/surface interactions are frozen thanks to an anionic electropolymerization of the monomer on the cathode and to a (first reported) cationic electropolymerization of the monomer on the anode. A detailed analysis of the molecular structures of the two resulting polymer/metal interfaces shows results which are in agreement with the theoretical predictions.

This paper is dedicated to Professor Jacques Schultz as an acknowledgement of his constant interest in our work.

KEY WORDS: Lewis acid-base interactions; Density Functional Theory (DFT); DFT chemical potential; electrochemistry; organic molecule/metallic surface interaction; regioselectivity; surface analysis (XPS, UPS); absolute hardness; Fukui function; electropolymerization of methacrylonitrile.

---

* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

** Corresponding author (E-mail address: christophe. bureau@cea. fr)

I. INTRODUCTION

The characterization of molecule/surface interfaces at the molecular scale is of central importance in the understanding of molecule/surface interactions and, hence, adhesion processes.[1] In this field, Fowkes[2] and Bolger[3] have pointed out of the relevance of the Lewis acid-base approach, as developed by Pearson[4] *via* the Hard-and-Soft-Acids-and Bases (HSAB) principle, in the description of molecule/surface interactions ranging from physical forces to chemical bonds. Fairly recently, the Lewis acid-base concept has been expressed on a sound theoretical basis through Density Functional Theory[5–8] (DFT). The indices of reactivity based on this theory have been used successfully to describe molecular Lewis acid-base reactions, *i.e.* reactions of the general type:

$$\mathbf{A} + \mathbf{B} \rightarrow \mathrm{A} \ldots \mathrm{B} \tag{1}$$

where A and B are molecules.[9–11] The results indicate that the DFT formalism provides the HSAB principle of Pearson[4] with a theoretical backing. One should note that reactions of the general type as in Eq. (1) are considered regardless of the *a priori* chemical stability of the A...B adduct. Hence, the DFT model of Lewis acid-base reactions is applicable to thermodynamic[9] as well as kinetic[10,11] studies of molecular reactions. Recently, Lee[12,13] has demonstrated that the HSAB principle can successfully be extended to the case where A or B (or both) are solid surfaces (metals, semi-metals, semi-conductors or insulators). Relating the chemical hardness of solids to their average energy gap, he has discussed the reactivity of solid surfaces and the nature of interactions taking place in adhesion processes.[12]

In the present paper, we shall consider the interaction of an organic molecule–namely, 2-methyl 2-propenenitrile or methacrylonitrile–with a metallic surface. More precisely, we will describe how this interaction is modified when the metal is polarized, *i.e.* serves as the working electrode in a three-electrode electrochemical cell. Our purpose is to examine both interactions when the surface is polarized either as a cathode or as an anode. The molecule/surface interaction is a Lewis acid-base reaction. To describe it, will make use of the DFT formalism mentioned above, of which we will merely recall the main features. Then we will stress how various relevant parameters such as the working electrode potential drop (with respect to a reference electrode) and the molecular chemical potential, μ, play a decisive role in the description of the interaction. Our point will be show that the chemical potential of the metallic surface is linearly related to the working electrode potential drop and, thus, that the Lewis acidic or basic character of the metallic surface with respect to the molecule can be chosen experimently. Finally, we will present the results of two series of recent experiments carried out in our laboratory which address the cathodic and anodic electropolymerization of methacrylonitrile on metalic surfaces. In these experiments, the initial Lewis acid-base reaction between the molecule and the polarized surface leads to an intermediate transient species. Its molecular structure is "frozen" as it thanks to the polymerization reaction it initiates. The molecular structure of the resulting interface is then characterized by means of XPS and UPS (X-ray and Ultraviolet Photoelectron Spectroscopies) techniques. These results are then compared with the structures predicted by the DFT formalism of Lewis acid-base reactions developed in the previous sections. Finally, we examine carefully the approximations used in this interpretation

Downloaded At: 11:43 22 January 2011

of the experimental results and outline the light this work sheds on the understanding of surface interactions.

II. THEORETICAL BACKGROUND: LEWIS ACID-BASE REACTIONS THROUGH REGIONAL DENSITY FUNCTIONAL THEORY

Density Functional Theory (DFT) is a quantum mechanically based theory aimed at the computation of the electronic properties of atoms, molecules or solids.[5] One of the important new concepts brought about by this theory is that it defines, for any atom, molecule or solid, two global properties, namely the chemical potential, μ, and the chemical hardness, η. Their definition is[5]:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad \text{and} \quad \eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} \tag{2}$$

where E is the electronic energy, N the number of electrons and $v(\vec{r})$ is the "external" potential, *i.e.* the potential due to the fixed nuclei. For a given molecule, these μ and η can be computed *via* DFT once the positions of the nuclei are known. The interest of these two (theoretically defined) parameters is that thay can also be connected with experimental data. For a molecule, finite difference approximations to Eqs. (2) lead to[14]:

$$\mu = -\frac{I + A}{2} = -\chi \quad \text{and} \quad \eta = \frac{I - A}{2} \tag{3}$$

where I is the first ionization potential, A the first electron affinity and χ the absolute electronegativity of the system. Lee[12] has shown that the chemical hardness is closely related to the average energy gap in the case of a solid surface. For a metallic surface, finite difference approximations to Eqs. (2) are[7]:

$$\mu = -\Phi \quad \text{and} \quad \eta = \frac{1}{2g(\varepsilon_F)} \tag{4}$$

where Φ is the work function and $g(\varepsilon_F)$ is the density of states at the Fermi level of the given surface. Note that Eqs. (3) and (4) are limiting forms of Eqs. (2), which are derived *via* finite difference approximations in order to exhibit physical parameters relevant to the specified compounds (molecule or surface). In short, atoms, molecules and surfaces are described on the same grounds through this theory.

When two molecules A and B come into interaction, one can compute the electronic structure of the supermolecule A...B through DFT (or any other quantum mechanically based theory). This procedure rapidly becomes too time consuming as the size of A or B increases. To our knowledge, the largest systems so far studied at this level of theory are capable of describing the interaction of methacrylonitrile,[15] formyl[16] or CH_x (x = 1–3) radicals[17] on various sites of Ni(111) and Ni(100) nickel surfaces.

One alternative is to make use of Regional DFT. This approach consists in describing the A...B adduct on the basis of the properties of isolated A and B through first order perturbational DFT. The formalism of this approach has been developed elsewhere,[5,18] and we will merely recall the results which are relevant for our purpose.

Downloaded At: 11:43 22 January 2011

Downloaded At: 11:43 22 January 2011

Suppose A and B bear N_A and N_B electrons, respectively. When A and B come into interaction, a flow of electrons, δN, occurs between A and B, the total number of electrons, $N_{TOT} = N_A + N_B$, remaining constant. Upon integrating this flow of electrons all along the reaction path, Γ, it can be shown that[5,18]:

$$\Delta N = \int_\Gamma \delta N = \frac{\mu_B - \mu_A}{2(\eta_A + \eta_B)} \tag{5}$$

thus , if ΔN is conventionally taken positive, the Lewis base in the $\{A, B\}$ pair is the compound having the highest chemical potential, and the flow of electrons occurs from the region of high chemical potential (the Lewis base) to the region of low chemical potential (the Lewis acid). Moreover, this flow is all the more important as the chemical hardnesses of the two species are low. The corresponding expression for the stabilization energy accompanying the formation of the AB adduct has been derived elsewhere.[5]

Equation (5) evidences the central role played by the electronic chemical potential in establishing the direction of the charge transfer, *i.e.* the nature of the Lewis acid-base reaction.

A higher level of description of the Lewis acid-base interactions may be achieved if one now takes into account the polarisabilities and mutual perturbations of A and B.[5] A first-order perturbation (or linear response) theory has been developed within the DFT framework.[19] It allows the description of the interaction of A and B encompassing: (i) charge transfer between A and B (see above); (ii) electrostatic effects at all orders (ion-ion, ion-dipole, dipole-dipole...etc); (iii) polarisation and polarisability effects.[5,19] Two important features of this theory are that:[5] (i) the overall form of Eq. (5) remains valid, *i.e.* the sign and amount of the charge transfer accompanying a Lewis acid-base reaction is still driven by the relative position of the respective chemical potentials of A and B. Only the μ_i's are replaced by μ_i's, where μ_i' is the *perturbed chemical potential* of species i; (ii) the mutual perturbation is described *via* the introduction (for A and B) of a function, called the Fukui function. For the Lewis acid A for example, the Fukui function is defined by:[5]

$$f_A(\vec{r}) = \left[\frac{\delta \mu}{\delta v_A(\vec{r})}\right]_{N_A} = \left[\frac{\delta \rho_A(\vec{r})}{\delta N_A}\right]_{v_A(\vec{r})} \tag{6}$$

Thus, this function informs on the regions where the electronic density of A, $\rho_A(\vec{r})$, varies when the number of electrons of A changes due to the flow of electrons from B to A. A similar definition holds for the Lewis base. Hence, the regions where the Fukui function of the acid (respectively, the base) is intense are indicative of the sites where A (resp. B) is most reactive. It can be shown that for a molecule, one has the finite-difference approximate relation:[20,21]

$$f_A(\vec{r}) \cong \rho_{\text{LUMO}}^{\text{DFT}}(\vec{r}) = |\psi_{\text{LUMO}}^{\text{DFT}}(\vec{r})|^2 \tag{7}$$

i.e. the Fukui function of an acid is equal to the electronic density of its LUMO in a set of molecular orbitals computed within the DFT formalism (*via* the Kohn-Sham equations, for instance). Identically, it can be shown that the Fukui function of the Lewis base is equal to the electronic density of the HOMO in a set of molecular orbitals computed within the DFT formalism.[20,21] For a metallic surface, the Fukui function is:[7]

$$f(\vec{r}) \cong \frac{g(\varepsilon_F, \vec{r})}{g(\varepsilon_F)} \tag{8}$$

Where $g(\varepsilon_F, \vec{r})$ is the local density of states of the metal at the Fermi level. Even though these orbitals are fundamentally different from Hartree-Fock orbitals,[5] one sees that the DFT formalism approach also encompasses the notions brought about by the frontier orbitals theory.[22] In particular, it is capable of describing the regio- and stereoslectivity of the Lewis acid-base reactions.[23]

Its original contribution stems from the peculiar role played by the chemical potential, μ, which fixes the sign of the charge transfer, and by the absolute hardnesses, η, which reveals the underlying nature of the most effective physical contributions to the interaction (electrostatic or charge transfer). The interest in elucidating such a partition in the case of interfacial reactions and adhesion processes has been stressed by Lee.[12,13] Since our purpose is here to examine the interaction of a given molecule (methacrylonitrile) with two metallic surfaces, we will only focus on the role of the DFT chemical potential. The absolute hardness of methacrylonitrile is $\eta = 5.6\,\text{eV}$ (Eq. (3))[9]. Those of nickel and platinum metallic surfaces are not known precisely but are much smaller, since these metals have a large density of states near the Fermi level (see Eq. (4)). Thus, the denominator of Eq. (5) is almost entirely due to the absolute hardness of the molecule and is, thus, the same in both interactions. Now, the absolute hardness of methacrylonitrile is fairly large,[9,12,13] which means that the electrostatic component may contribute significantly to the overall interaction. As methacrylonitrile has a very large dipole moment ($|\vec{\mu}| \approx 4$ Debyes)[24] this electrostatic component is almost exclusively governed by the interaction between the molecular dipole and the electrostatic field above the metallic surfaces. The effect of this interaction is merely to orientate the molecule in the surface field.[25] The magnitude of the stabilization energy due to this orientation is identical in the anodic and cathodic case at identical surface electrostatic potentials. It corresponds to the following situations: the molecule points its vinylic bond onto the surface when this surface bears a negative charge and points the nitrogen of its cyano group when the surface bears a positive charge.[25]

Hence, we now wish to bring elements to show that besides the HSAB principle, the role of the chemical potential is central in describing surface reactions.

Downloaded At: 11:43 22 January 2011

III. ELECTROCHEMISTRY AS A TOOL TO MONITOR THE ACIDIC OR BASIC CHARACTER OF A METALLIC SURFACE

We now focus on the DFT parameters characterizing a metallic surface being polarized, *i.e.* being used as the working electrode in a three-electrode electrochemical cell. Towards this aim, we will recall some elementary electrochemistry equations concerning the thermodynamic definition of an electrode potential.

It can be shown, on a jellium model of the metallic surface, that the DFT chemical potential of a metallic surface is equal to the electrochemical potential, $\tilde{\mu}_e^{(M)}$, of the metal, defined as the amount of work necessary to bring an electron from infinity in the vacuum to the interior of a (possibly polarized) metal (M):[26]

$$\tilde{\mu}_e^{(M)} = \mu^{\mathrm{DFT}} \tag{9}$$

Let us now consider the electrode potential drop, $\Delta\varepsilon$, which is imposed between the working electrode (superscript (M)) and a reference electrode (superscript (Ref)) in a three-electrode electrochemical cell with solvent S (superscript (S)). This electrode potential drop is defined by:[27]

$$\Delta\varepsilon = V^{(M)} - V^{(\mathrm{Ref.})} = [e\cdot(\phi^{(M)} - \phi^{(\mathrm{S})}) - \mu_e^{(M)}] - [e\cdot(\phi^{(\mathrm{Ref})} - \phi^{(\mathrm{S})}) - \mu_{\mathrm{e}}^{(\mathrm{Ref.})}] \tag{10}$$

where $V^{(X)}$ is the electrode potential of phase X as defined by Trasatti,[28] $\Phi^{(X)}$ is the electrostatic potential inside X (for $X = M$, this is the co-called Galvani potential of the metal), and $\mu_e{}^{(X)}$ is the chemical potential of an electron in X.[27] One can note that this chemical potential is linked, by definition, to the electrochemical potential, $\tilde{\mu}_e^{(X)}$, examined in Eq. (9):

$$\tilde{\mu}_e^{(X)} = \mu_e^{(X)} - e.\phi^{(X)} \tag{11}$$

Hence, Eq. (10) can be rearranged to:

$$\tilde{\mu}_e^{(M)} = -\Delta\varepsilon - (e.\phi^{(S)} + V^{(\mathrm{Ref.})}) \tag{12}$$

Combining Eq. (9) and (12), one has:

$$\mu^{\mathrm{DFT}} = -\Delta\varepsilon + \mathrm{const}(S, \mathrm{Ref.}) \tag{13}$$

i.e. one sees *that there is a linear relationship between the electrode potential, $\Delta\varepsilon$, imposed at the working metallic electrode, and the chemical potential of Density Functional Theory.*[29]

This point is of crucial importance, since it shows that the DFT chemical potential of a metallic surface—an eminently *theoretical* parameter which drives Lewis acid-base reactions, Eq. (5)—can be monitored continuously *via* electrochemistry by imposing the desired electrode potential—an eminently *experimental* parameter. An experimental verification of this result can be found in the linear relationships obtained by Rath and Kolb between the measured work function ($= -\mu^{\mathrm{DFT}}$, cf. Eq. (4)) of a gold electrode dipping into an electrolytic medium and the potential drop imposed with respect to a standard calomel electrode.[30]

Two points need to be stressed concerning Eq. (13):

(i) there is a minus sign in front of $\Delta\varepsilon$, which means that the DFT chemical potential of the surface is raised with respect to the vacuum level as the electrode is polarized cathodically (*i.e.* to more negative values with respect to the reference electrode). Alternatively, it is lowered with respect to the vacuum level when the electrode is polarized anodically. In short, the electrode is likely to become a more and more powerful Lewis base when it is polarized cathodically, and a more and more powerful Lewis acid when it is polarized anodically. A clear distinction must be made between this behavior and the surface charge of the electrode. The global surface charge of the electrode is zero when the applied potential drop is equal to the so-called PZC (Potential of Zero Charge),[27] $\Delta\varepsilon = \Delta\varepsilon^{\mathrm{PZC}}$. The PZC can be measured and is characteristic of the metal and solvent in use.[27] The global surface charge of the metal is negative

Downloaded At: 11:43 22 January 2011

when the applied potential drop is lower than the PZC, and positive when it is higher. Thus, when one tries to impose a molecule/surface interaction with, say, the metal as the Lewis base, one has to check whether the selected potential drop and, hence, the selected DFT chemical potential (Eq. (13)) has the correct position relative to the PZC. Indeed, one can anticipate that it will be difficult to make the surface act as the Lewis base above its PZC, as it bears a global positive charge. This means that the overall density of Lewis basic sites is low;

(ii) the intercept in Eq. (13) does *not* depend on the metal, but only on the solvent and the reference electrode. Since at the PZC (Potential of Zero Charge) the electrochemical potential of the electrode is equal to its work function,[27,30] the constancy of the intercept with respect to the nature of the metal can be tested by plotting the values of $(\Delta\varepsilon^{PZC} - \Phi^{(M)})$ for various metals. The plot is shown for *s*, *p* and *d* metals in water, with PZC's measured with respect to a standard hydrogen electrode as the reference, in Fig. 1 (the corresponding work functions, which are all in quite a narrow range, are also shown for comparison). The intercept is indeed almost constant at fixed {solvent, reference electrode} couple. This shows that the overall position of the range of accessible DFT chemical potentials can be chosen, to a certain extent, through a relevant choice of the solvent and the reference electrode. In addition, this opens the way to making a correspondence of the reactivity scales between various solvents.

Downloaded At: 11:43 22 January 2011

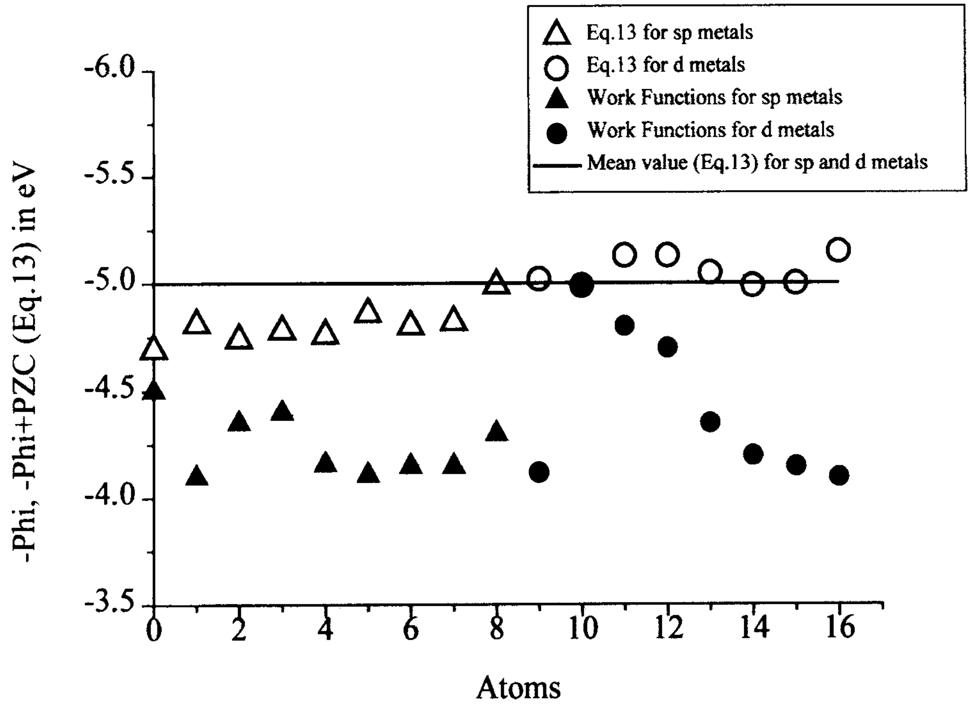


FIGURE 1 Values (in eV) of $(-\Phi^{(M)})$ and $(-\Phi^{(M)} + \Delta E^{PZC})$ for various metals.[30] All PZC's are measured in water with a standard hydrogen electrode as the reference. Metals are in the following order: (sp metals) Hg (liq), Tl (Ga) (liquid alloy), Bi, Sn, Pb, Cd, In, In(Ga) (liquid alloy), Ga(liq); (d metals) Pd, Rh, Ni, Co, Fe, Nb, Ta, Ti.

Downloaded At: 11:43 22 January 2011

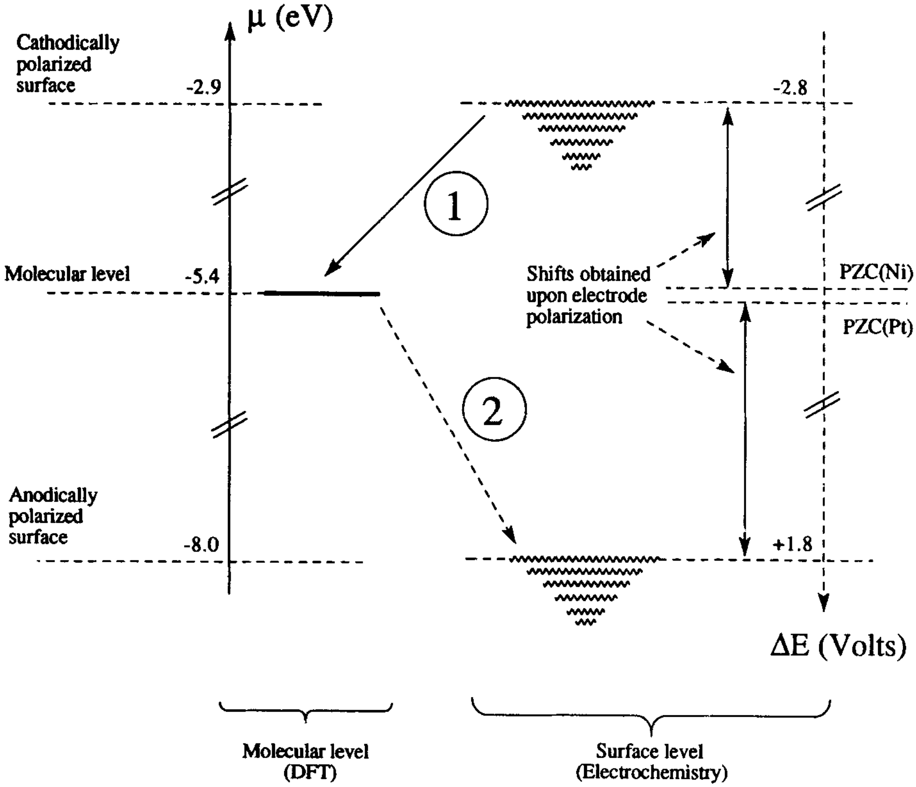


FIGURE 2 Global scheme showing the sign of the charge transfers between methacrylonitrile and a metallic surface cathodically (1 – the surface acts as a base) or anodically (2 – the surface acts as an acid) polarized. the position of the chemical potential of the surface at the PZC is also shown. It is assumed, as a first approximation, that the chemical potential of the molecule is the same in the anodic and cathodic regimes. The correspondance of μ (DFT) and ΔE (electrochemistry) is also shown.

As a conclusion to this paragraph, we see that electrochemistry offers a way to piloting the basic or acidic character of a metallic surface, in the sense of Lewis concepts recalled in Section I. If one considers, as a first approximation, that the position of the chemical potential of a molecule in the solvent, close to the metallic surface, is not modified upon electrode polarization, then one can choose the sign of the charge transfer with the proper electrode potential (Fig. 2).

IV. LEWIS ACID-BASE INTERACTION BETWEEN 2-METHYL 2-PROPENENITRILE AND A CATHODE: EXPERIMENTAL RESULTS AND THEORETICAL INTERPRETATION

Beacuse of the fundamentally "first-order perturbational" nature of the theoretical framework developed in Section I, the overall molecular description provided by the regional DFT model of Lewis acid-base reactions is only valid in the early steps of reaction profiles.[18,29] Thus, the "molecular engineering" view of the molecule/metal

Downloaded At: 11:43 22 January 2011

interaction developed Section in III is only capable of describing the early steps of an interaction leading to (possibly) transient chemisorbed species.

One should note that while this criterion is somewhat restrictive, it nonetheless enables a useful rationalization of important reactions. For instance, it has been tested very recently in the study of initiation reactions of anionic polymerization.[11] It has been shown that ΔN values computed *via* Eq. (5) closely parallel the relative reactivity (μ) of some classical vinylic monomers known to undergo anionic polymerization (acrylonitrile, methacrylonitrile, methyl acrylate, methyl α-cyanoacrylate...), as well as that of anionic initiators (methyl lithium, *n*-butyl lithium, sodium methoxide...). It has also been shown that the regional DFT model covers all the weak points encountered in using earlier reactivity scales. The values of the respective chemical potentials show that the vinylic monomers always constitute the Lewis acid and the organometallic initiator the Lewis base, as expected.

We now wish to make use of this model to describe the initial steps of the interaction between 2-methyl 2-propenenitrile (methacrylonitrile, $H_2C{=}C(CH_3)CN$) and a cathodically-polarized metallic surface. Previous work in our laboratory has shown that the initial interaction of methacrylonitrile with a cathode leads to a grafted film of PolyMethAcryloNitrile (PMAN)[31] through an electropolymerization reaction. In these reactions, the surface of the working electrode in the electrolysis cell is used as the polymerization initiator[31] (Fig. 3): the process is thought to go through an intermedi-

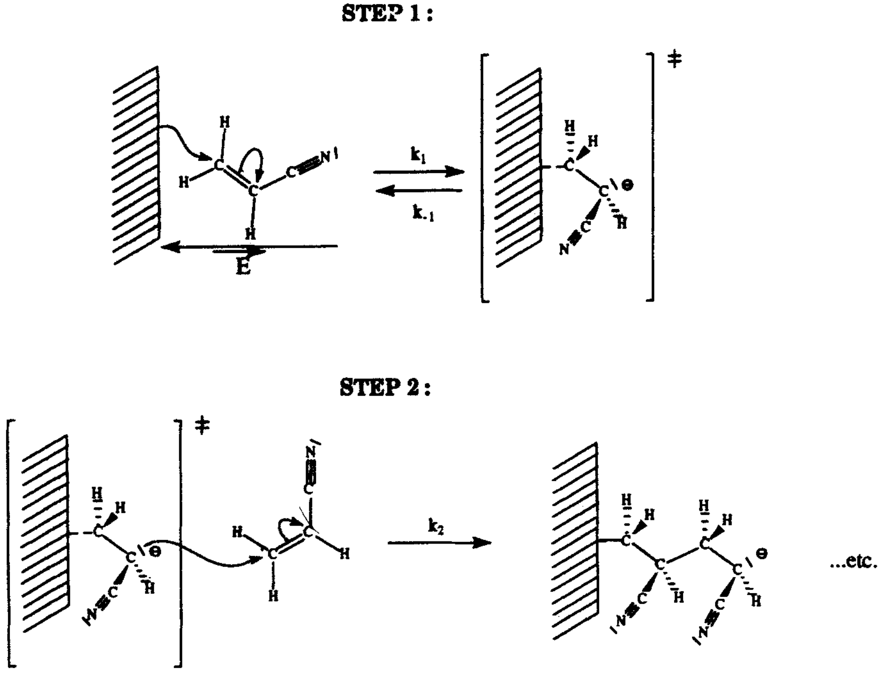


FIGURE 3 Proposed mechanism for the grafting reaction accompanying the electropolymerization of acrylonitrile on a cathodically polarized metallic surface: the cathodically polarized surface acts as a basic initiator for the anodic polymerization.

ate step corresponding to a Lewis acid-base interaction between the polarized surface and the organic molecule (step 1 in Fig. 3). The reaction intermediate thus formed is unstable, as it corresponds to an anion chemisorbed on a negatively-charged surface. Our hypothesis is that this intermediate can itself act as a nucleophile towards a fresh

Downloaded At: 11:43 22 January 2011

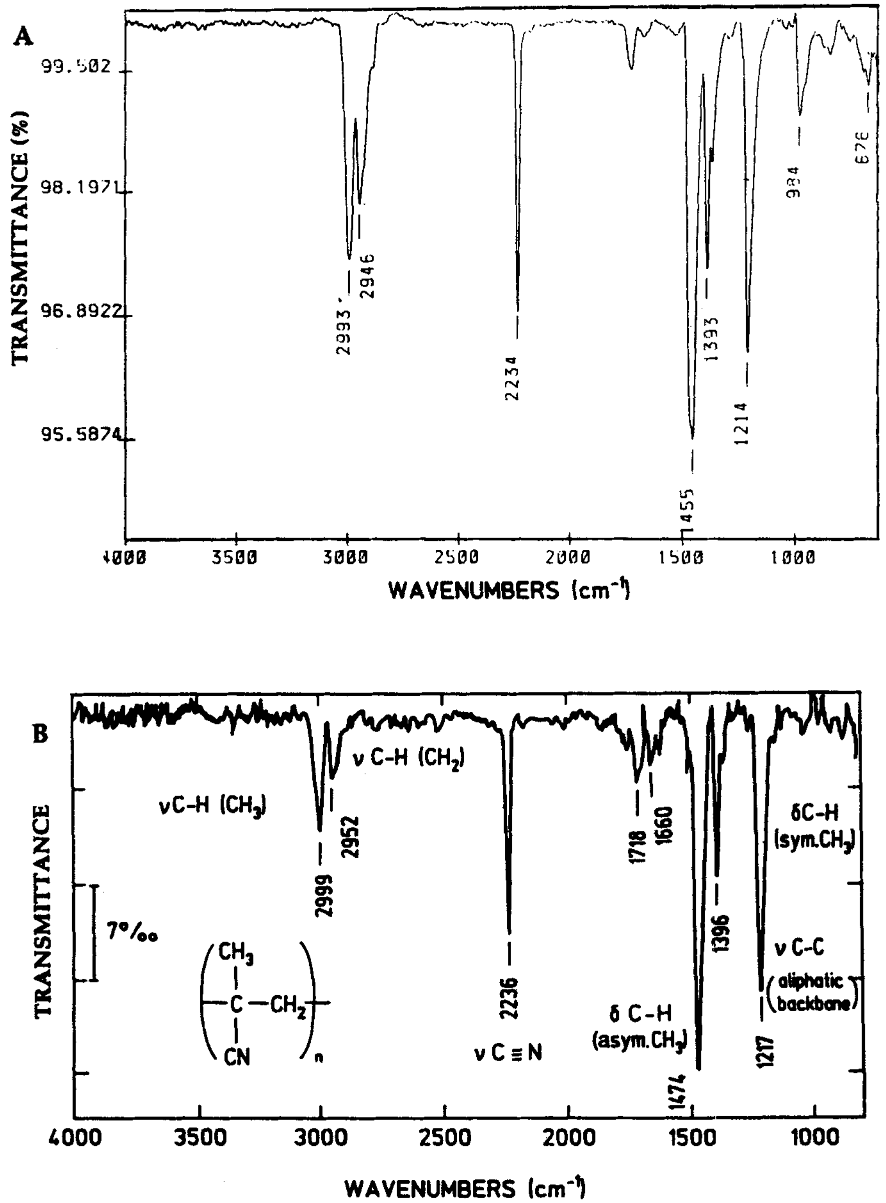


FIGURE 4 IRRAS spectra of a reference commerical PolyMethAcryloNitrile (PMAN) sample (top) and of a thin film obtained by electropolymerization of methacrylonitrile on a nickel cathode (bottom).

methacrylonitrile molecule and start a polymerization reaction (step 2 in Fig. 3).[31] The overall process is thus capable of forcing the formation of chemical bonds between an organic structure (the resulting polymer) and a metallic surface through the initial interface Lewis acid-base reaction.

The assumption for such a mechanism is based on the elucidation of the molecular structure of the reaction products close to the interface. Firstly, homogeneous polymer films having regular molecular structure are formed upon cathodic polymerization on a nickel electrode, as assessed by Infra-Red Reflection Absorption Spectroscopy (IRRAS) (Fig. 4). For these experiments, the nickel surface is set at -2.8 V/(Ag^+/Ag), *i.e.* -2.8 Volts with respect to the reference silver electrode. With PMAN, the film has the same structure as the reference commercial sample, and is not soluble in the traditional solvents for commercial PMAN although it is soluble when the film is mechanically removed from the surface. This results argue towards grafting *vs* reticulation of the polymer on the surface. Secondly, Near Edge X-ray Absorption Fine Structure (NEXAFS) results show that polymer chains indeed have the peculiar orientation depicted in Figure 3, which is the footprint of the local double-layer electric field in which the molecules orientate.[32] Thirdly, impedance spectroscopy measurements show a definite decrease in the interface capacitance upon film formation, even after attempts to dissolve it, a result that points to 10–15% of surface sites being permanently occupied.[33,34] Finally, XPS measurements on very thin (~ 20 Å) PMAN films show a low energy contribution on the Cls line (283.6–283.8 eV) (Fig. 5), which indicates the formation of carbon/nickel bonds.[34,35] A plausible molecular model of the final state of reaction, involving a grafted monomer and nickel clusters to simulate a surface site, has been studied on the basis of Hartree-Fock calculations.[34] It has delivered estimations of the Cls chemical shift of those atoms close to the surface, in good agreement with experiment.[34]

Downloaded At: 11:43 22 January 2011

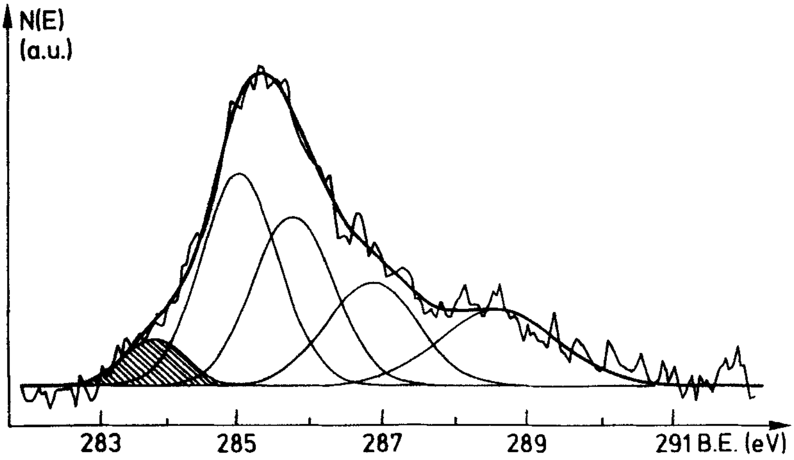


FIGURE 5 Cls lines in the XPS spectra (with tentative decomposition) of an ultra-thin (~ 20Å) PMAN film obtained by electropolymerization of methacrylonitrile on a nickel cathode: besides the levels of the polymer, a low energy contribution (shadowed) evidences the carbon/metal interface bond.

Now let us try to examine the predictions brought about by the regional DFT model of Lewis acid-base reactions. The work function of the nickel surface is 5.15 eV (with respect to the vacuum reference).[27] This means that at the PZC, the DFT chemical potential of the surface is equal to -5.15 eV (vacuum), see Eqs. (4) and (9). The DFT chemical potential of a methacrylonitrile molecule has been computed *via* Eq. (3) and is equal to -5.4 eV.[29] Thus, as $\mu^{\mathrm{DFT}}_{\mathrm{Metal}} > \mu^{\mathrm{DFT}}_{\mathrm{Molecule}}$, the metallic surface acts as a Lewis base towards the molecule at the PZC. Now the PZC of the nickel surface is of the order of -0.5 ± 0.2 V/(Ag^+/Ag) with respect to the reference silver electrode. Thus, when one sets the nickel surface to a -2.8 V/(Ag^+/Ag) potential as in the above experiments, the DFT chemical potential of the metallic surface is raised with respect to the vacuum (Eq. (13)) to reach the value: $\mu^{\mathrm{DFT}}_{-2.8} = -5.15 - (-2.8 + 0.5) \approx -2.9 \pm 0.2$ eV (vacuum). As expected, the metallic surface is even more basic ($\mu^{\mathrm{DFT}}_{\mathrm{Metal}} \gg \mu^{\mathrm{DFT}}_{\mathrm{Molecule}}$) with respect to the molecule. The model, thus, predicts a charge transfer from the surface to the molecule.

Now let us examine the regioselectivity of this charge transfer. As mentioned in Section II, one has to compute the Fukui function of the two reactants. The Fukui functions of a Lewis base metallic Ni_7 cluster mimicking a surface site[15a,17]and that of the Lewis acid methacrylonitrile molecule (cf. Eq. (7)) are shown in Figure 6 and 7a, respectively. Figure 6 shows that the nickel atoms on the edge of the cluster bear the main part of the reactivity of the cluster. This can be interpreted as a result of their unsaturation and connected with the well-known higher reactively of irregular surfaces with respect to regular ones.[36,37] Figure 7a shows that the most reactive site of methacrylonitrile taken as a Lewis acid is the terminal vinylic carbon ($=CH_2$). Assuming that the non-crossing hypothesis holds along the reaction paths, this information leads to the prediction that a carbon/metal interface bond is formed and that the overall resulting structure is that depicted in Figure 3. Thus, it appears that one may look at the final grafted structure (*i.e.* the interface region) as *the "frozen" proof of the initial steps of the metal/molecule interaction.*

Hence, electropolymerization reactions constitute an interesting candidate to test the potentialities of the DFT model of Lewis acid-base interactions between an organic and a metallic surface. Indeed, the polymerization reaction following the grafting step leads to the formation of a sample which can be analyzed *via* traditional "post-mortem" surface techniques (XPS, UPS, Infra-Red Reflection Absorption Spectroscopy (IRRAS), Electrochemical Impedance Spectroscopy (EIS), etc.). There is apparently no need to make use of ultra-fast spectroscopic methods although we seek information on the formation of a reaction intermediate. All the difficulty stems from the sound characterization of the molecular structure of the interface region in the product of reaction.

V. LEWIS ACID-BASE INTERACTION BETWEEN 2-METHYL 2-PROPENENITRILE AND AN ANODE: EXPERIMENTAL RESULTS AND THEORETICAL INTERPRETATION

Let us now examine the alternative procedure in which methacrylonitrile interacts with a platinum anode. The work function of a platinum polycrystalline surface is 5.6 eV (with respect to the vacuum reference).[27] Its DFT chemical potential is thus -5.6 eV (vacuum) and the platinum surface is weakly acid with respect to a methacrylonitrile

Downloaded At: 11:43 22 January 2011

Downloaded At: 11:43 22 January 2011

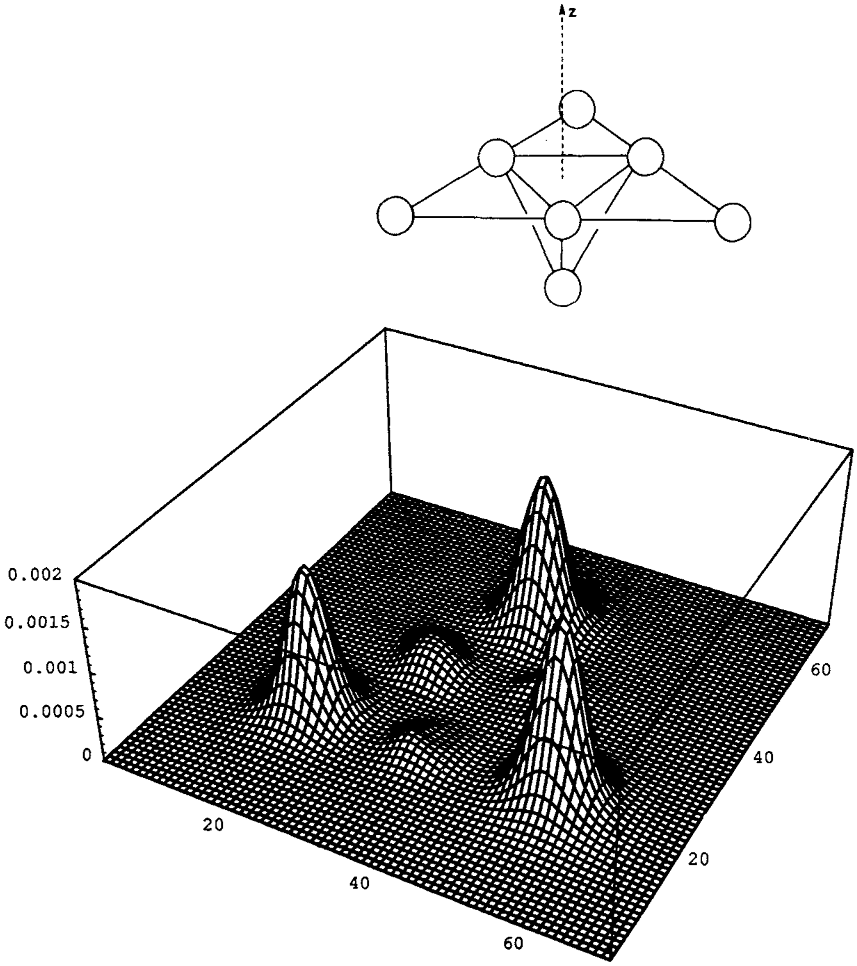


FIGURE 6 3D-plot of the Fukui functions of a Ni_7 cluster taken as a Lewis base, in a plane parallel to the cluster surface (perpendicular to the z axis) and 0.5 Å from the closest nickel atoms. The most intense regions indicate the sites wherefrom charge transfer is likely to occur. The structure of the cluster is shown in the insert.

molecule ($\mu \sim -5.4\,\mathrm{eV}$ (vacuum)). within the selected experimental conditions, the PZC of the platinum surface is $1.0 \pm 0.5\,\mathrm{V/(Ag^+/Ag)}$.[38] In the experiments described below, the platinum electrode is set to a $+1.8\,\mathrm{V/(Ag^+/Ag)}$ potential.[39] Its DFT chemical potential is thus lowered with respect to the vacuum reference (Eq. (13)) to reach the value $\mu^{\mathrm{DFT}}_{+1.8} = -5.6 - (1.8 + 1.0) \approx -8.0 \pm 0.5$ eV (vacuum). Thus, the platinum surface acts as a Lewis acid towards the methacrylonitrile molecules. The model thus predicts a charge transfer from the molecule to the surface.

Now let us examine the regioselectivity of the charge transfer. The Fukui function of the Lewis base methacrylonitrile molecule (cf. Eq. (7)) is shown in Figure 7b. This

Downloaded At: 11:43 22 January 2011

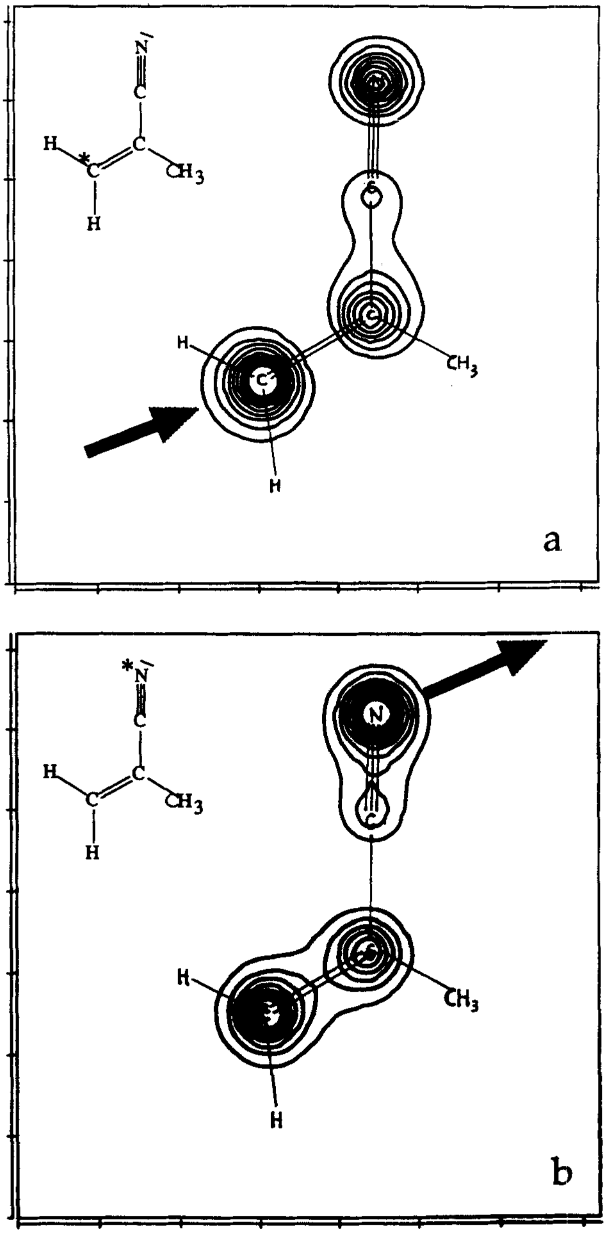


FIGURE 7 Isocontour plots of the Fukui functions of methacrylonitrile as a Lewis acid (a) and as a Lewis base (b). Arrows indicate the molecular sites from which and to which the charge transfer occurs, respectively.

shows that the most reactive site of methacrylonitrile taken as a Lewis base is the nitrogen atom of the nitrile group. Assuming that the non-crossing hypothesis holds along the reaction paths, this information leads to the prediction that a nitrogen/metal interface bond is formed and that the overall resulting structure is that depicted in

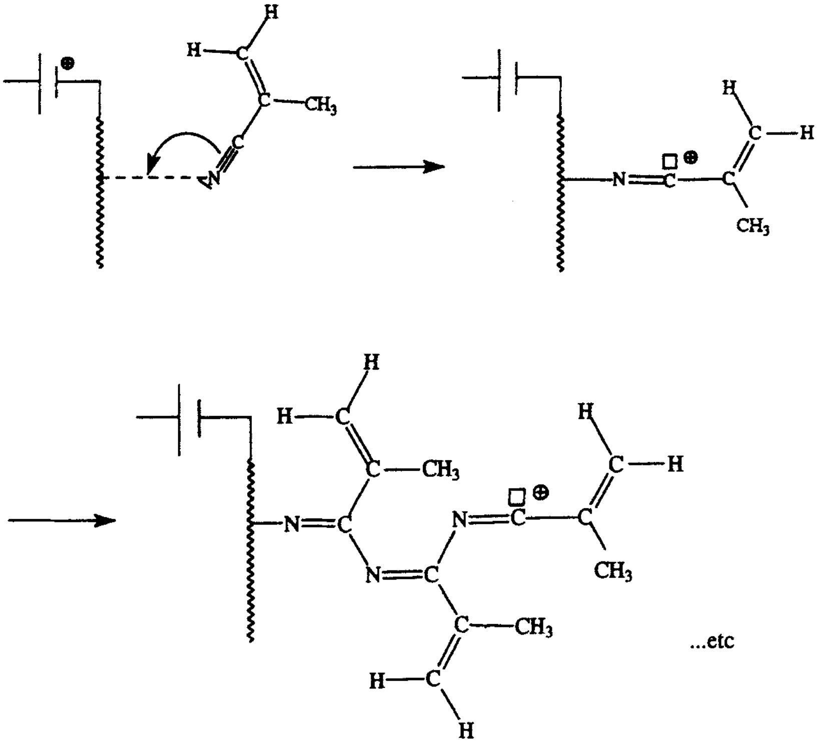


FIGURE 8 Proposed mechanism for the grafting reaction accompanying the electropolymerization of methacrylonitrile on an anodically polarized metallic surface the anodically polarized surface acts as an acid initiator for the cationic polymerization.

Downloaded At: 11:43 22 January 2011

Figure 8. We are now faced with the problem of performing a sound characterization of the molecular structure of the interface region in the product of reaction. This has been the subject of a recent paper and we will only summarize the relevant results.[39]

Some experimental results have been obtained with acrylonitrile on a platinum electrode, and they show: (i) the presence of a broad valence band (UPS), characteristic of an organic semi-conductor, and attributed to conjugate —C=N— bonds, and (ii) untouched pendant $CH=CH_2$ ethylenic groups (IRRAS) from the acrylonitrile molecules.[40] However, IR spectroscopy on the films obtained also shows that $—CH_3$, and $—O—CH_3$ and $—O—CH=CH_2$ groups are present. These features indicate that acetonitrile, CH_3CN, which was used as the solvent, has probably co-polymerized with acrylonitrile ($—CH_3$), and that some of the molecular structures obtained at the end result from an attack of the π bond of the CN groups by an oxidizing radical, formed under classical Faradaic transfer ($—O—CH_3$ and $—O—CH=CH_2$). Should these interpretations be correct, as proposed by Tourillon[41] in the case of acetonitrile, there would be no more relationship between the molecular structure of the final film and the initial steps of the reaction. The possibility of a film being initiated in solution by some oxidized radical and subsequently precipitating on the surface cannot be ruled out, and the results alluded to by Boiziau and Lécayon[40] are, thus, not conclusive in our purpose to examine the actual initial interaction between the vinylic molecule and the anode surface.

New experiments have been caried out recently, in which anodic potentials of $+1.6\mathrm{V/(Ag^+/Ag)}$, $+1.8$ V/$(\mathrm{Ag^+/Ag})$ and $+2.0$ V/$(\mathrm{Ag^+/Ag})$ (with respect to a silver reference electrode) are imposed on a platinum working electrode dipping into pure methacrylonitrile[39] (platinum is used instead of nickel, because nickel would oxidize in the anodic regime). The $i = f(V)$ curves show that methacrylonitrile is not electroactive in the potential range considered.[39] Meanwhile, a film of classical PMAN is obtained upon $+2.0$ V/$\mathrm{Ag^+/Ag)}$ polarization, with no apparent nitrogen/metal bond. Upon $+1.8$ V/$(\mathrm{Ag^+/Ag})$ polarization, a polymer film is obtained, the structure of which is different from PMAN. A low-energy shift of 0.8 eV is observed for nitrogen lone-pair structure in the UPS spectrum as compared with PMAN (Fig. 9e), while the energy gap is reduced, making this sample an organic semi-conductor. The N1s region of the XPS spectrum evidence a low-energy contribution, ~ 1.6 eV below the major polymer peak, *attributed to a nitrogen/platinum interface bond* (Fig. 10c). These results are interpreted as the result of a non-standard cationic polymerization of methacrylonitrile through its nitrile groups, initiated by the metallic anode which acts as a Lewis acid towards the first monomer molecules, leading to a poly-imine type structure (Fig. 8). Upon $+1.6$ V/$(\mathrm{Ag^+/Ag})$ polarization, spectral characteristics show that the structure of the interface is intermediate between no polarization at all, and $+1.8$ V/$(\mathrm{Ag^+/Ag})$ polarization.[38]

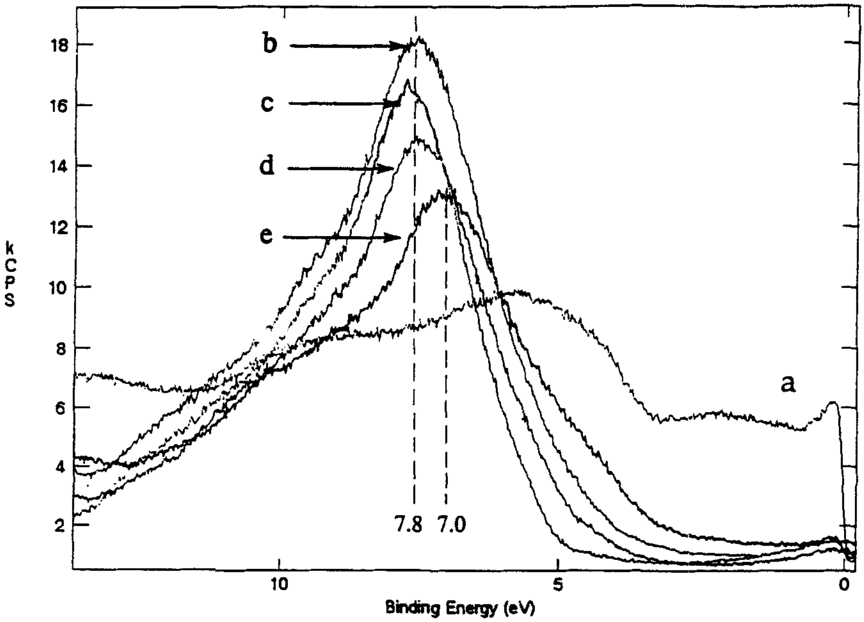


FIGURE 9 UPS spectra of a reference platinum surface (a), of the same surface dipped into pure methacrylonitrile (b), dipped into a solution of PMAN in acetonitrile (c), after $+2.0$ V/$(\mathrm{Ag^+/Ag})$ (d) and after $+1.8$ V/$(\mathrm{Ag^+/Ag})$ (e) polarizations.

Downloaded At: 11:43 22 January 2011

Downloaded At: 11:43 22 January 2011

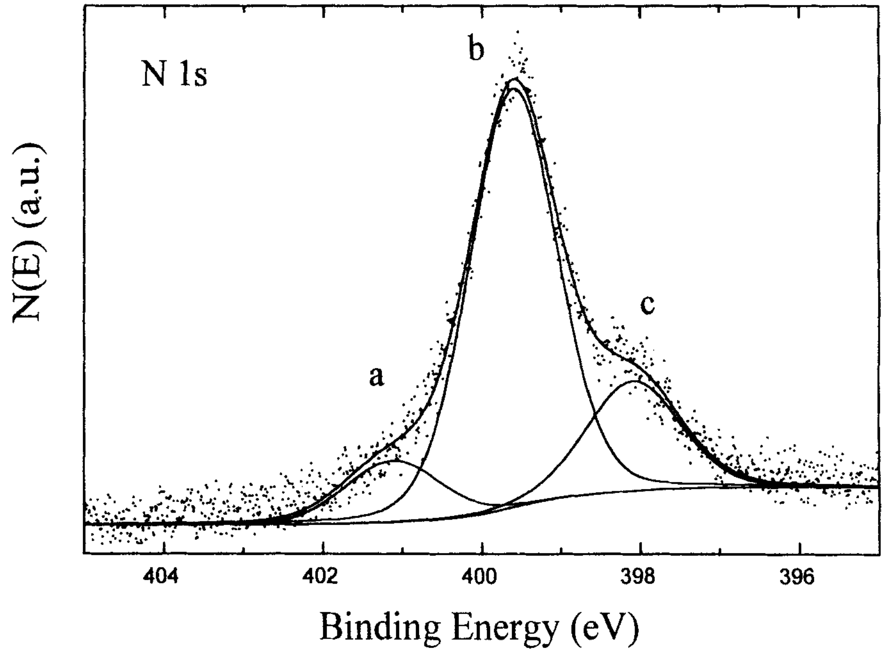


FIGURE 10 N1s line in the XPS spectrum of the interface obtained after + 1.8 V/(Ag$^+$/Ag) polarization of a platinum surface in pure methacrylonitrile. The (b) contribution is related to the bulk polymer nitrogens. The low energy contribution (c) is attributed to a nitrogen/metal bond. The high energy contribution is attributed to oxidation products (a).

A theoretical model has been proposed to help ascertain the results obtained in the + 1.8 V/(Ag$^+$/Ag) polarization case.[29,39] A molecular model is designed which mimics the result of a nucleophilic addition of methacrylonitrile to a metallic site of the surface, rendered by three- and seven-atoms platinum clusters, and leading to a poly-imine structure. This model evidences a bound state when the chemisorption occurs in an interstitial position, as opposed to on-top bonding (Fig. 11). The structure of the organics is considerably distorted in the vicinity of a metallic cluster. Both this distorsion and the proximity of metallic atoms lead to a lowering of the N1s chemical shift of the nitrogen atoms bound to the surface, which is roughly evaluated to be of the order of 2–3 eV with respect to the bulk polymer nitrogens.[39] We estimate that the geometrical perturbation caused by the initial interface bond is still detectable up to about 10Å from the cluster, as a consequence of the peculiar structure of the polymer which presents a partly conjugated (N=C) backbone. A preliminary study of the bulk polymer structure has also been presented, using an all-organic model trimer. A stable conformation is found, in which the (N=C) backbone has a third-order helix structure with pendant ethylenic groups tilted with respect to the plane perpendicular to the helicoïdal axis to overcome steric hindrance (Fig. 12). First attempts at an evaluation of the valence band characteristics show that nitrogen lone-pair type molecular levels are shifted downward by about 0.5 to 1.5 eV with respect to nitrile groups, in good agreement with the 0.8 eV shift measured on the UPS spectra of the + 1.8 V/Ag$^+$/Ag)

Downloaded At: 11:43 22 January 2011

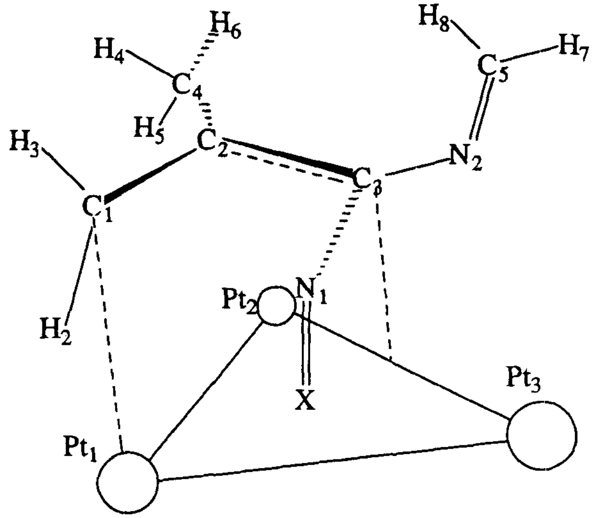


FIGURE 11 Optimized molecular structure of a model mimicking the interface bond formed in the grafting of methacrylonitrile on a platinum metallic site. The calculation is done at the ROHF/MCP level. "X" is a mathematical point indicating the centre of the Pt1-Pt2-Pt3 threefold site.

sample.[39] It is also mentioned that NC group conjugation is still active despite the non-totally-planar geometry, an element which could account for the reduction of the gap observed on the UPS spectra.

These elements lead us to the conclusion that an interface bond has actually been obtained upon + 1.8 V/(Ag$^+$/Ag) polarization, and that the molecular structure of the interface is compatible with a cationic polymerization of methacrylonitrile through its nitrile groups, initiated by a nucleophilic addition of a first monomer molecule to a metallic site (Fig. 8).

However, an examination of the complete set of experimental results obtained at the various potentials show that the above mechanism is apparent only upon + 1.8 V/(Ag$^+$/Ag) polarization, and that it is overcome by some other mechanism at higher anodic potentials. Our interpertation is that the major part of the sample formed upon + 2.0 V/(Ag$^+$/Ag) polarization is made up of a polymer obtained through an indirect radical polymerization consecutive to the oxidation of perchlorate ions which act as radical initiators:[40]

$$ClO_4^- \rightarrow ClO_4^{\cdot} + 1e^- \qquad (14)$$

$$ClO_4^{\cdot} + H_2C{=}C(CH_3)CN \rightarrow ClO_4{-}C(CH_3)(CN){=}CH_2^{\cdot} \text{ ...etc...} \qquad (15)$$

This hypothesis is confirmed by the presence of chlorine (Cl2p levels: traces) in the global spectrum of the + 2.0 V/(Ag$^+$/Ag) polarization sample. Hence, one can infer that the sample obtained upon + 1.8 V/(Ag$^+$/Ag) polarization (no chlorine on the global spectrum) is formed at an oxidation potential which is not anodic enough to provoke

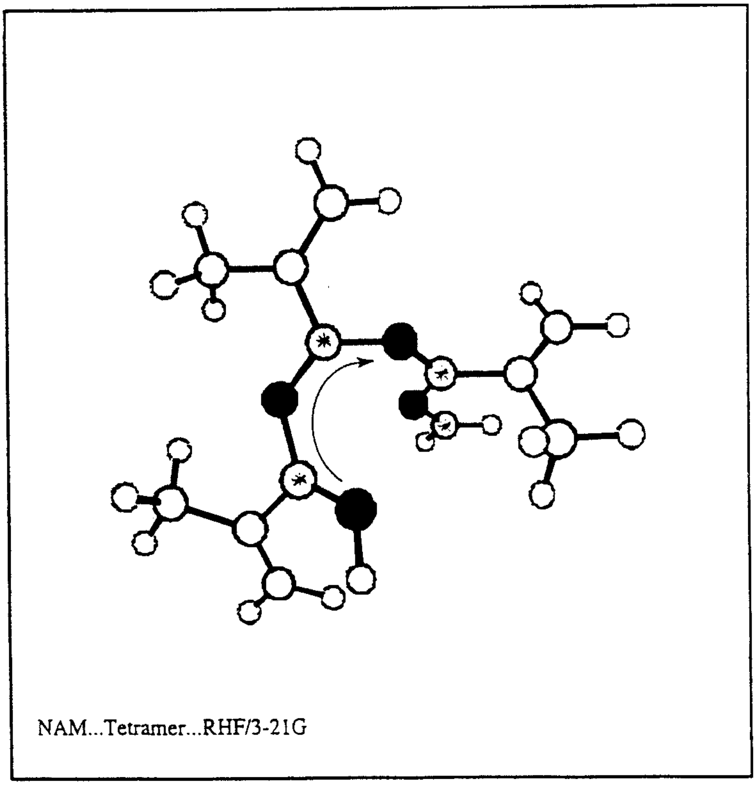


FIGURE 12 Display of the helix-like conformation of a tetramer of poly-methacrylonitrile obtained *via* cationic polymerization through the nitrile groups, which is found after geometry optimization at the RHF/3-21G level. The helicoidal axis is perpendicular to the plane of the figure, and passes within the $-(N{=}C)_n-$ backbone (arrow). Pendant groups have the structure $CH(CH_3){=}CH_2$.

Downloaded At: 11:43 22 January 2011

an oxidation of perchlorate ions, and that the observed polymer film is the result of a direct interaction between the metallic surface and the monomer molecules, since $i = f(V)$ curves show that methacrylonitrile is not electroactive in the anodic range presently examined. Finally, the sample obtained upon + 1.6 V/(Ag^+/Ag) polarization is intermediate between the above + 1.8 V/(Ag^+/Ag) polarization case and the one that is obtained by simple dipping of the platinum surface into the electrolytic medium, *i.e.* methacrylonitrile molecules adsorbed on the platinum surface. The applied potential would, thus, not be sufficient either to oxidize perchlorate ions, or to force metal/molecule bond formation.

These results shed some light on those obtained previously upon cathodic polarization of nickel electrodes, through which a carbon/metal bond and a PMAN grafted film are formed. In this last case, methacrylonitrile is electroactive. Thus, the question as to whether interface bond formation and electroactivity are necessarily connected or not, in the general case of electropolymerization in organic condensed media, is raised. More work is in progress in order to propose a molecular mechanism which would examine the relationship between the two.

VI. CONCLUDING REMARKS

We have shown that the DFT chemical potential, μ, of a metallic surface is linearly related to the electrode potential drop, $\Delta\varepsilon$, which is imposed between the working electrode and the reference electrode of an electrolysis cell (Eq. (13)). Thus, thanks to the DFT model of Lewis acid-base reactions, electrochemistry offers a way to monitor the acidic or basic character of a metallic surface with respect to any given molecule, by choosing the correct electrode potential. We have presented a first tentative experimental test of this hypothesis in the instance of the interaction of 2-methyl 2-propenenitrile (methacrylonitrile). We have monitored the Lewis acidic or basic character of metallic surfaces (an anode and a cathode, respectively) towards a methacrylonitrile molecule. These interactions lead to the formation of a presumed transient chemisorbed species which is frozen as it is, thanks to the polymerization reactions of methacrylonitrile it can initiate . The structures of the grafted polymer films have been analyzed by XPS, UPS and IRRAS. We have mentioned the results of this analysis. They show that the initiating Lewis acid-base reaction leads either to a cationic polymerization (acidic anodic surface) or to an anionic polymerization (basic cathodic surface) of methacrylonitrile, respectively. The resulting molecular structures of the polymer films are seen as frozen proofs of the initial interaction (*i.e.* the initiating Lewis acid-base reaction) as they are in agreement with the regioselectivity predicted by the base and acid Fukui functions of methacrylonitrile, respectively.

Downloaded At: 11:43 22 January 2011

Thus, it appears that the two $(\mu; f(\vec{r}))$ parameters we have put forward are indeed relevant to describe and monitor the course and the extent of electronic charge transfer between a metallic surface and an organic molecule. In the present paper, we only compared the reactivity of a given molecule towards two different metallic surfaces. The latters being very soft, we mentioned that the electrostatic components of the interaction as well as the effects of absolute hardnesses on the amount of charge transfer could be set aside in the comparison of both situations. Comparing our approach with the ones previously proposed in the field of interface reactions, one can notice that this is generally not true.[12,13] Meanwhile, the present work contributes to illustrating the peculiar role of the DFT chemical potential and Fukui functions in describing surface acid-base reactions. More work is in progress to take electrostatic effects into account in order to explain experimental situations involving polarized metallic surfaces. We hope this will contribute to a better understanding to interface reactions.

References

1. See, for example *EURADH '94: Adhesion*, supplement to *Le Vide, Les Couches Minces*, **272** (1994).
2. (a) F. M. Fowkes, *J. Adhesion*, **4**, 155 (1972); (b) F. M. Fowkes, *J. Adhes. Sci. Technol.*, **1**(1), 7(1987)
3. J. C. Bolger and A. S. Michaels, *Interface Conversion* P. Weiss and D. Cheevers, Eds. (Elsevier, New York, 1969), Chap. 1.
4. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
5. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989), p. 224.
6. M. Berkowitz, S. K. Ghosh and R. G. Parr, *J. Am. Chem. Soc.*, **107**, 6811 (1985).
7. W. Yang and R. G. Parr, *Proc. Natl. Acad. Sci. USA*, **82**, 6723 (1985).
8. M. Berkowitz and R. G. Parr, *J. Chem. Phys.*, **88**, 2554 (1988).
9. R. G. Pearson, *Inorg. Chem.*, **27**(4), 734 (1988).

10. R. G. Pearson, *J. Org. Chem.*, **54**, 1423 (1989).
11. A. Tachibana and K. Nakamura, *J. Am. Chem. Soc.*, **117**, 3605 (1995).
12. L. H. Lee, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1990), Chap. 12.
13. L. H. Lee, in *Acid-Base Interactions: Relevance to Adhesion Science and Technology*, K. L. Mittal and H. R. Anderson, Jr. Eds. (VSP, Utrecht, 1991), p. 25.
14. R. G. Parr, R. A. Donnelly, M. Levy and W. E. Palke, *J. Chem. Phys.*, **68**, 3801 (1978).
15. (a) C. Bureau, M. Defranceschi, J. Delhalle, G. Deniau, J. Tanguy and G. Lécayon, *Surf. Sci.*, **311**, 349 (1994); (b) G. Deniau, P. Viel, and G. Lécayon, *Surf. Interf. Anal.*, **18**, 443 (1992).
16. H. Yang and J. L. Whitten, *Langmuir*, **11**, 853 (1995).
17. C. Bureau, M. Defranceschi and J. Delhalle, *Int. J. Quantum Chem.*, **46**, 87 (1993) and references therein.
18. (a) A. Tachibana, *Int. J. Quantum Chem. Symp.*, **21**, 181 (1987); (b) A. Tachibana and R. G. Parr, *Int. J. Quantum Chem.*, **41**, 527 (1992).
19. M. J. Stott and E. Zaremba, *Phys. Rev. A*, **21**(1), 12 (1980).
20. M. Berkowitz and R. G. Parr, *J. Chem. Phys.*, **88**(4), 2554 (1988).
21. W. Yang, R. G. Parr, and R. Pucci, *J. Chem. Phys.*, **81**(6), 2862 (1984).
22. K. Fukui, *Theory of Orientation and Stereoselection* (Springer-Verlag, New York, 1975).
23. (a) C. Lee, W. Yang and R. G. Parr, *J. Mol. Struct.* (*Theochem*), **163**, 305 (1988); (b) W. Langenaeker, M. De Decker and P. Geerlings, *J. Mol. Struct.* (*Theochem*), **207**, 115 (1990).
24. R. D. Nelson, D. R. Lide and A. A. Maryott, Eds., *Handbook of Chemistry and Physics*, 65th ed., Natl. Ref Dat. Ser. NRSDS-NBS 10 (Natl. Bur. Stds., Washington, 1985), p. E-58.
25. (a) C. Bureau, M. Defranceschi, J. Delhalle, G. Lécayon and D. R. Salahub, *J. Mol. Struct.* (*Theochem*), **330**, 279 (1995); (b) C. Boiziau, S. Leroy, C. Reynaud, G. Lécayon, C. Le Gressus and P. Viel, *J. Adhesion*, **23**, 21 (1987).
26. J. Goodisman, *Electrochemistry: Theoretical foundations* (John Wiley and Sons, New York, 1987), p. 160.
27. J. O'M Bockris and S. U. M. Khan, *Surface Electrochemistry: a Molecular Level Approach* (Plenum Press, New York, 1993), p. 90.
28. (a) S. Trasatti, *Electroanal. Chem. Interf. Electrochem.*, **52**, 313 (1974); (b) S. Trasatti, "The Electrode Potential", in *Comprehensive Treatise of Electrochemistry*. vol. I, Eds J. O'M. Bockris, B. E. Conway, E. Yeager, Eds. (Plenum Press, New York, 1980).
29. (a) C. Bureau, Ph.D Thesis, Université Paris VI (1994); (b) C. Bureau, G. Deniau, J. Delhalle, J. Tanguy, G. Lécayon and C. Boiziau, *Le Vide-Les Couches Minces*, **272**, 79 (1994).
30. D. L. Rath and D. M. Kolb, *Surf. Sci.*, **109**, *641 (1981).*
31. (a) G. Lécayon, Y. Bouizem, C. Le. Gressus, C. Reynaud, C. Boiziau and C. Juret, *Chem. Phys. Lett.*, **91**, 506 (1982); (b) J. Deniau, G. Lécayon, P. Viel, G. Zalczer, C. Boiziau, G. Hennico and J. Delhalle, *J. Chem. Phys. Perkin Trans.*, **2**, 1433 (1990); (c) G. Deniau, G. Lécayon, P. Viel, G. Hennico and J. Delhalle, *Langmuir*, **8**, 267 (1992).
32. G. Tourillon, R. Garrett, N. Lazarz, M. Raynaud, C. Reynaud, G. Lécayon and P. Viel, *J. Electrochem. Soc.*, **137**, 2499 (1990).
33. J. Tanguy, G. Deniau, C. Augé, G. Zalczer and G. Lécayon, *J. Electroanal Chem.*, **377**, 115 (1994).
34. C. Bureau, M. Defranceschi, J. Delhalle, G. Deniau, J. Tanguy and G. Lécayon, *Surf. Sci.*, **311**, 349 (1994), and references therein.
35. (a) G. Deniau, P. Viel, G. Lécayon and J. Delhalle, *Surf. Interface Anal.*, **18**, 443 (1992); (b) C. N. R. Rao, P. K. Basu and M. S. Hedge, *Appl. Spectrosc. Rev.*, **15**(1), 1 (1979).
36. C. M. Friend and E. L. Muetterties, *J. Am. Chem. Soc.*, **103**, 773 (1981).
37. S. Mori and M. Yoshida, *STLE Trans.*, **31**, 128 (1988).
38. (a) E. Léonard-Stibbe, G. Lécayon, G. Deniau, P. Viel, M. Defranceschi, G. Légeay and J. Delhalle, *J. Polym. Sci. A*, **32**, 1551 (1994); (b) E. Léonard-Stibbe, Ph.D Thesis, Université Paris VI (1994).
39. C. Bureau, G. Deniau, P. Viel, G. Lécayon and J. Delhalle, accepted in *Surface Science*.
40. (a) C. Boiziau and G. Lécayon, *Surf. Interface Anal.*, **12**, 475 (1988); (b) C. Boiziau, S. Leroy, C. Reynaud, G. Lécayon, C. Le Gressus and P. Viel, *J. Adhesion*, **23**, 21 (1987).
41. G. Tourillon, P. C. Lacaze and J. E. Dubois, *J. Electroanal. Chem.*, **100**, 247 (1979).

Downloaded At: 11:43 22 January 2011