

Acrylonitrile on Cu(100): A density functional theoretical study of adsorption and electrochemical grafting

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We present a density functional theoretical study of neutral and negatively charged complexes of acrylonitrile (AN) with several clusters representing the Cu(100) surface. An external electric field is used to induce electron transfer onto the adsorbed molecule, in order to model the initial stage of electrochemical polymerization of AN on a copper electrode. We compare different possibilities of AN interaction with the metal and determine the most favorable configurations of the adsorbates in the absence and in the presence of the electric field. We discuss the influence of the electrochemical polarization on the type of AN adsorption, in relation with the experimental data on the adsorption of AN and electrochemical grafting of polyacrylonitrile. © 1996 American Institute of Physics. [S0021-9606(96)00332-7]

I. INTRODUCTION

Coating of metal surfaces with organic films is attracting attention in view of metal surface modification and corrosion protection. A promising approach consists in the electrochemically initiated polymerization of acrylonitrile (AN) and similar vinyl monomers. It has been shown that, in stringent conditions, highly uniform and adherent thin polyacrylonitrile (PAN) films can be deposited in a cathodic process on certain commodity metals (Ni, Cu), whereas on others (Al, Zn) the polymer film can easily peel off.¹⁻⁴ Moreover, in the former case, the film is insoluble in the usual solvents of chemically synthesized PAN, even though the chemical structures are essentially the same. From an ellipsometric study,⁵ it appears that the reduction of the oxide initially present at the metal surface is a prerequisite for PAN film deposition on nickel. Electrochemical impedance data⁶ show that a somewhat higher portion of the nickel surface is blocked by electrodeposited PAN than when the polymer is simply cast on top of nickel. X-ray photoelectronic spectroscopy (XPS) experiments performed on a very thin polymethylacrylonitrile film⁷ indicate the presence of a low binding energy C1s line, which is attributed to the species bound to the metal. All those data point to the existence of a specific interaction between the metal and the polymer leading to high adhesion between the substrate and the coating.

Lécayon *et al.*^{1,2} have put forward the hypothesis of chemical grafting of electrodeposited PAN to the metal due

to the formation of a metal-carbon covalent bond. A tentative mechanism proposed for the initial stages of the formation of the metal-polymer bond includes:

- (i) The dipole orientation and activation of the monomer molecule in the strong electric field present in the vicinity of the polarized electrode.
- (ii) Vinyl-end-on chemisorption and electron transfer from the cathode to the organic molecule, yielding a σ -bound intermediate.
- (iii) The latter then drives the chemical polymerization.

Lécayon *et al.* assume an anionic polymerization process.^{1,2} Mertens *et al.*^{3,8} obtained evidence in favor of a radical polymerization mechanism and they argue that the reduction of chemisorbed AN is partial, i.e., yielding a radical species instead of an anion. Furthermore, they observed that at higher anodic potentials the polymer cannot be grafted and readily peels off; that behavior was attributed to a complete charge transfer process that would break the metallo-organic bond. Both variants of the mechanism are sketched in Fig. 1.

The possibility of chemically grafting an electrodeposited polymer to the electrode surface is very interesting from both fundamental and applied viewpoints. The mechanism presented above implies that the adsorption of AN on the metal cathode under electrochemical conditions is fairly different from adsorption on a non-polarized metal from the gas phase, since it is well established that in the latter case it is the nitrile group that essentially interacts with the metal.⁹⁻¹¹

In order to improve on the understanding of those processes, several theoretical studies using quantum-chemical methods have been recently performed. Calculations of the

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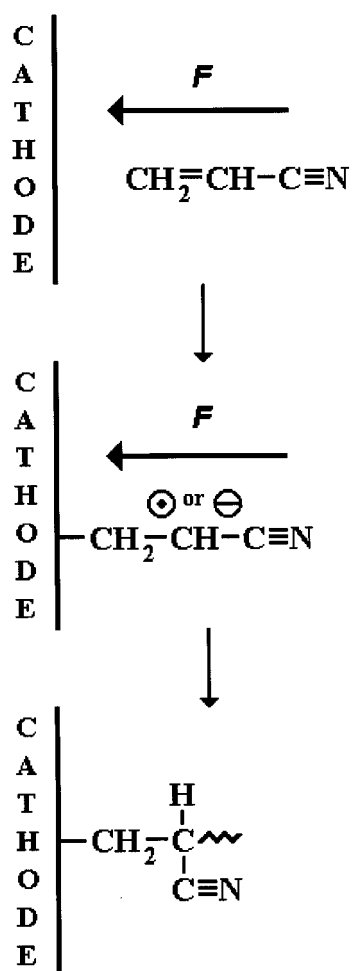


FIG. 1. Scheme of cathodic grafting of acrylonitrile onto metal.

molecular geometry and electronic properties of several isolated vinyl monomers containing the nitrile group and their anionic derivatives (with H^- added to model adsorption at a reactive surface site of the cathode) were performed at the Hartree–Fock level, with various basis sets.^{12–14} In particular, the effect of a strong electric field (up to 2.1×10^8 V/cm) applied along the CN or C=C bond of the neutral molecules was investigated in order to simulate the polarization induced in the monomers approaching the cathode. It was shown that the field polarizes strongly the lowest unoccupied molecular orbital (LUMO) of AN, which corresponds to a π -orbital delocalized over the entire molecule. While in zero field, the probability density of the LUMO is high on both vinyl carbons and the nitrogen, the field shifts it towards the terminal vinyl carbon atom thus activating it for bonding with the negatively charged metal electrode. The participation of the π -orbitals of the nitrile group is significant as well.

Bureau *et al.*⁷ carried out Hartree–Fock calculations on a neutral complex of the saturated methacrylonitrile monomer, $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CN}$, with a Ni cluster representing the Ni(111) surface, thus considering the final state of polymerization, i.e., the grafted polymer. Having imposed that

the terminal carbon atom be in the interstitial position above the triangle of the nearest nickel atoms, the authors found a bound state for this system, thus indicating the possibility of the polymer end-on chemisorption. Based on those results, they were also able to interpret the XPS spectrum of electrodeposited polymethacrylonitrile on Ni.

Fredriksson *et al.*⁴ addressed the nature of the specific interaction between the monomer and the metal. They carried out a density functional study of the complexes between the AN molecule or its radical-anion and single atoms of different transition metals, namely, Ni, Cu, and Zn. They found bound states for the former two metals, but not for the latter; this is consistent with their experimental data, which indicate that adherent polymer coatings cannot be obtained on Zn.⁴

We also note that a very recent density functional study¹⁵ has provided a successful interpretation of near-edge x-ray absorption fine structure spectroscopy (NEXAFS) data for the adsorption of an AN multilayer on a metal substrate. That investigation has, however, not dealt with the nature of the interaction between AN and the metal.

In this work, we address the adsorption of AN and the initial stages of the electrodeposition of PAN on copper, i.e., (i) the adsorption of the AN monomer on the metal and (ii) the subsequent negative charge transfer driven by the cathodic polarization of the metal electrode. We present a theoretical study of the interaction of acrylonitrile with copper clusters when the systems are neutral or negatively charged, embedded or not in an external electric field (EF). We choose copper as the metal, since its clusters are, in terms of computational efforts, the simplest among the metals known to support strongly adherent PAN films. The immediate purpose of our work is to evaluate the subtle interplay of EF, charge transfer due to electrochemical polarization, and complexation with the metal, that determines the mechanism of grafting an organic molecule to an electrode. From a more general standpoint, this theoretical work deals with the possible types of adsorption of an organic molecule possessing multiple active sites, on various clusters of a metal.

II. METHODOLOGY

The calculations are performed in the framework of the density functional theory (DFT), see, e.g., Ref. 16. This method is a nonempirical approach, alternative to Hartree–Fock-based theories, that presently finds wider applications to chemical problems, due to the possibility to include a significant part of the electron correlation energy; correlation is essential for a correct description of transition metal compounds. Based on a number of case studies, guidelines for the choice of the DFT calculation schemes providing reliable values for the desired molecular properties, are well established up to now.

A. The electrode

Since it was shown that the oxide layer (always present at the surface of a commodity metal in air) is reduced prior to electrodeposition on nickel,⁵ the electrode surface can be

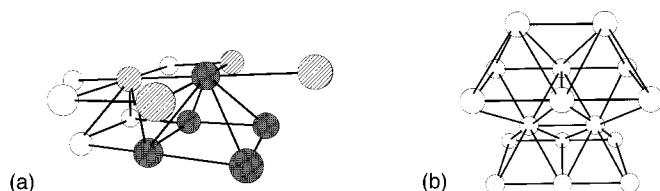


FIG. 2. Patterns for the copper clusters; (a) $\text{Cu}_{14}(8,6)$; note that this cluster contains $\text{Cu}_5(4,1)$ —atoms in dark shading, and $\text{Cu}_9(5,4)$ —atoms in dark and light shading; (b) $\text{Cu}_{16}(2,6,2,6)$, out of which one forms $\text{Cu}_{10}(2,6,2)$, $\text{Cu}_8(2,6)$, and Cu_2 clusters by successively removing the bottom layer; note that $\text{Cu}_8(2,6)$ and Cu_2 can be reached from pattern (a) as well.

represented by clusters of metal atoms, without considering oxygen. We are confident that this holds for copper as well, since the electrochemical characteristics of the AN polymerization on Cu is essentially the same as on Ni.^{3,4} The interaction between the metal and the organic molecule being likely of a local character, a cluster approach to the problem appears reasonable. Based on the above considerations, we thus model the electrode surface by copper clusters.

We choose the clusters (Fig. 2) as fragments of the fcc crystal (100) face, with interatomic distances fixed at the bulk crystal values. In the $\text{Cu}_9(5,4)$ cluster (where the subscript indicates the total number of copper atoms in the cluster and the numbers in parentheses denote the composition of its layers; here, 5 atoms in the upper layer and 4 in the bottom layer), the upper layer is large enough to study various types of AN adsorption; furthermore, the central atom has the same number of nearest neighbors as on the actual (100) surface. Therefore, this cluster will be our system of choice. However, since it will be shown that the AN molecule can be bound to two metal atoms, we also consider the $\text{Cu}_{14}(8,6)$ cluster, in which both central copper atoms have the right coordination number.

For a preliminary discussion and in order to test the cluster-size dependence of our results, we also study complexes with several other clusters as well. A truncated analog of the above cluster, $\text{Cu}_5(1,4)$, permits to compare the adsorption on-face (i.e., on a square (100) crystal face) and on-top (on a single copper atom). For the latter type of adsorption, the results from Ref. 4 will be invoked as well, in order to evaluate the role of the coordination number of the adsorption site. To study the adsorption on-edge (i.e., on two crystal edge atoms), we use the $\text{Cu}_8(2,6)$ cluster; comparison with its truncated version $\text{Cu}_2(2,0)$, and its extended versions, $\text{Cu}_{10}(2,6,2)$ and $\text{Cu}_{16}(2,6,2,6)$, will be made to justify the choice of two-layer clusters.

B. The electric field

The nonpolarized electrode is simply modelled by not considering any external EF (we also neglect the effect of the electrolytic medium). On the contrary, an EF is taken into account to mimic the electrochemical polarization; the direction of EF is set normal to the (100) cluster plane and defined as the z direction with the metal taken as the negative pole (cathode). The aim of introducing EF is to cause a reasonable

charge transfer from the cluster to an AN monomer; the criterion chosen for the value of EF is that the charge on AN be about -1 . We note that our preliminary tests have shown that for a given complex: (i) the charge on the AN molecule is virtually independent of the geometry of the complex (in particular, it does not change during geometry optimization from a reasonable starting geometry); (ii) the charge transfer evolves approximately linearly with EF (which facilitates the setting of its value); and (iii) the charge transfer in a given EF does slightly depend on the cluster size, a one-electron transfer requiring a field in the range $0.8\text{--}1.0 \times 10^8$ V/cm (these are very reasonable values when comparing to those estimated in nonlinear optics^{17,18}).

It is important to recall that the total energy of a charged molecule in an EF depends on the choice of the origin of coordinates, which is arbitrary; in other words, the total energy is no longer unambiguously defined. The same holds for the molecular orbital levels. In the context of this work, this has the following implications for anionic species:

(i) It is meaningless to calculate the electron affinity in an electric field as the energy difference between the neutral and charged species since there is an arbitrariness in determining the energy of the latter.

(ii) The binding energy of a charged complex, which is defined as the energy difference between the complex and the isolated components, cannot be determined unambiguously, for the same reason. Nevertheless, we calculate the binding energies of the complexes by always placing the upper layer of copper at the same z coordinate ($z=0$). In this way, we maintain the electrode surface at the same electrostatic potential in various systems, as is the actual case in a potentiostatically polarized electrode surface, irrespective of transformations on it. Note that, by doing so we do not try to equalize the electrostatic energy of different complexes since their centers of charge would occupy different positions.

C. The computational approach

The calculations were performed in the framework of the density functional method implemented in the DMol program.¹⁹ The basis set was double zeta numeric with polarization (DNP); this choice is based on the evaluation of the electron affinity of AN, as will be discussed below in greater detail, since in this work, we deal much with negative ions. The core orbitals were frozen during the self-consistent field (SCF) iterations, and we chose a medium mesh size for the calculations.

Geometry optimizations are carried out within the local spin density approximation (LSD) with the Vosko–Wilk–Nusair functional²⁰ (denoted VWN), which usually gives reasonable geometrical parameters. The geometry optimizations were unconstrained except for the distances between copper atoms that were kept at the bulk crystal values (nearest-neighbor distance of 2.551 \AA).

Although the overall description of binding within LSD calculations is good, this approach shows a strong tendency to overestimate binding energies; therefore, the inclusion of nonlocal corrections is strongly recommended. Among the

TABLE I. Geometrical parameters of acrylonitrile neutral molecule and radical anion. The labels are those defined in Fig. 3. The bond lengths are in Å and the bond angles in degrees. We also provide the calculated total energies in eV.

	Acrylonitrile				Radical anion VWN/DNP ^b
	Expt. ^a	HF/3-21G ^a	HF/6-31G* ^a	VWN/DNP ^b	
C ² C ³	1.426	1.427	1.443	1.410	1.381
C ¹ C ²	1.339	1.319	1.320	1.336	1.412
C ¹ H ¹	1.086	1.072	1.074	1.097	1.097
C ¹ H ²	1.086	1.071	1.074	1.097	1.096
C ² H ³	1.086	1.072	1.074	1.099	1.102
C ³ N	1.164	1.140	1.136	1.169	1.195
C ¹ C ² C ³	122.6	122.7	122.1	123.2	126.6
H ¹ C ¹ C ²	121.7	121.7	121.9	120.7	121.8
H ² C ¹ C ²	121.7	121.9	120.7	121.6	120.7
H ³ C ² C ¹	121.7	121.0	122.0	120.8	118.4
C ² C ³ N		180.2	180.0 ^c	180.0 ^c	180.4
E_{tot}		-4593.60	-4619.39	-4608.32 (VWN) -4672.03 (BVWN)	-4608.50 (VWN) -4672.35 (BVWN)

^aReference 12.^bThis work.^cNot optimized.

options available in DMol, the implementation of Becke's 1988 version of a gradient-corrected exchange potential²¹ was shown to provide a most successful improvement for transition metal carbonyls.²² It is often considered sufficient to introduce nonlocal corrections in a final nonself-consistent evaluation of the energy at a negligible additional computational cost, while only the VWN potential is used throughout the SCF iterations.¹⁹ If not stated otherwise, the binding energies discussed in this work are calculated in this way (denoted BVWN). Although we find that the electron affinities calculated at VWN and BVWN levels do not differ substantially, we only present the BVWN values for the sake of uniformity. In addition, the binding energies of several key structures are calculated in the most precise and computationally demanding way provided by DMol, namely, using throughout the SCF iterations both the gradient-corrected exchange potential by Becke²¹ and the gradient-corrected correlation by Perdew and Wang;²³ this approach is hereafter noted BP. When discussing binding energies, basis-set superposition errors (BSSE) should be estimated; an advantage of the DMol numeric basis sets are low BSSE values associated with them, i.e., significantly less than 5 kcal/mol.²²

III. RESULTS AND DISCUSSION

The discussion consists of three sections. First, we briefly describe the individual components. In the second section, we discuss the results obtained for the complexes of AN with copper clusters in the absence of an external electric field, in order to evaluate the adsorption on a nonpolarized electrode. In the third section, we address the results obtained when the system is embedded into an external electric field, which model the interaction with the copper cathode and the electrochemically induced charge transfer.

A. Acrylonitrile and copper clusters

1. Acrylonitrile neutral molecule and radical anion

In Table I, we compare the DFT-VWN optimized bond lengths in AN with, on the one hand, the experimental values and, on the other hand, those obtained using the Hartree-Fock (HF) method. We observe that the DFT results are satisfactory. DFT provides excellent C=C and C≡N bond lengths, while the HF values are somewhat underestimated. The C-C bond length is slightly underestimated by DFT, while the HF value with a poorer basis is closer to experiment than that obtained with a more extended basis set. Both HF and DFT bond angles are within 1° from the experimental values. A major point, already noted by Fredriksson *et al.*,⁴ is that the single, double, and triple characters of the bonds in the DFT geometry are easily identified.

In the AN radical anion, we observe that C-C and C=C bond characters are reversed and the nitrile bond is elongated. This is readily accounted for by the occupation of the former LUMO, which is a π -orbital antibonding over the double and triple bonds but bonding over the single bond of the neutral molecule.

The calculated electron affinity (EA) of AN was used as a key control parameter for the choice of the basis set, among those implemented in DMol. Prediction of electron affinities is a complex problem. Specifically, for AN, even high-level Hartree-Fock and MP2 calculations with augmented Gaussian basis sets²⁴ fail to obtain a bound state for the radical anion (which we take as a positive sign for EA), contrary to a small but positive experimental estimate of 0.01–0.02 eV, as well as to a general theorem^{25,26} predicting the existence of stable anions for molecules having dipole moments larger than a certain critical value of 1.625 D; we note that experimentally the dipole moment of AN is 3.69 D.²⁷ The DNP

basis which we use is not Gaussian but numeric and has approximately 6-31G** quality.¹⁹ It yields positive, though overestimated, EA values of 7.4 kcal/mol (0.32 eV) at the B88+VWN level and 4.2 kcal/mol (0.18 eV) at VWN level, calculated as the difference between the energies of the radical anion and the neutral molecule with the geometries optimized with the same basis set. Larger basis sets do not change these values significantly, while with a smaller basis set, not including polarization functions, the EA of AN becomes negative.

2. Copper clusters

We begin this discussion with the simplest cluster, Cu₂. Even though we are using the crystal geometry for all the clusters in this work, it is interesting to note that the standard VWN bond-length optimization for the Cu₂ molecule exactly reproduces the experimental value, 2.219 Å.²⁸ While bearing in mind that, in principle, such an agreement could not be obtained without relativistic corrections²⁹ and not excluding the possibility that the agreement could be fortuitous, we nevertheless regard this result as indicating the quality in the description of the metal–metal bonds within DFT. We obtain that the copper atoms essentially conserve their original 3d¹⁰4s¹ electronic configuration and the bond is built from their 4s electrons.

When adding the second layer of 6 copper atoms to build up the Cu₈(2,6) cluster and thus raising the coordination number of the two upper atoms to 5, the spin of the cluster remains zero in the ground state (though the number of electrons is even, spin-unrestricted calculations are able to provide a state of higher spin multiplicity). However, there is considerable promotion from *d* and *s* to 4*p* orbitals. The charge polarization in this cluster is negligible.

When examining clusters with an odd number of electrons, a criterion of their adequacy to represent the metal emerges. Irrespective of the spin multiplicity of a single metal atom (copper in the ground state is a doublet), in a nonmagnetic bulk metal, the system (at 0 K) and, *intuitively*, each atom within it, have zero spin due to band formation. The spin on surface atoms can be expected to be higher, since these have fewer neighbors to share the electrons with. Nevertheless, we expect that even the surface atoms in a nonmagnetic metal present the lowest possible spin. Therefore, we consider the spin density on the copper atoms in the clusters as such a criterion to evaluate how close they are to actual metallic copper atoms.

In the Cu₅(1,4) cluster with C_{4v} symmetry, the highest occupied orbital is doubly degenerate and occupied by three electrons; these mainly belong to the Cu₄ plane. Consequently, there is virtually no spin on the upper Cu atom, but only a small positive charge. The largest part of the unpaired spin density is partitioned among the four lower Cu atoms.

Extending the upper layer to 5 Cu atoms as in Cu₉(5,4) and thus obtaining for the central Cu atom the coordination number it has on the real (100) surface, we observe only negligible nonzero spin and charge on the central Cu atom, while the promotion from the 3*d* and 4*s* orbitals to 4*p* or-

TABLE II. Electron affinity of copper clusters.

	VWN kcal/mol / eV	BVWN kcal/mol / eV	Expt., eV ^a
Cu ₂	23/0.99	24/1.05	0.842±0.10
Cu ₅	51/2.21	50/2.16	1.92 ±0.05
Cu ₈	48/2.07	46/1.99	1.53 ±0.05
Cu ₉	49/2.14	48/2.09	2.45 ±0.15
Cu ₁₄	56/2.43	49/2.13	-

^aReference 27.

bitals is more pronounced. The spin density is mostly concentrated on the peripheral Cu atoms of the upper layer, whose coordination number is the lowest in this cluster.

In all the clusters, because of their low coordination number, the peripheral atoms are not expected to represent the copper surface atoms as accurately as the central atoms of a layer. In the open-shell clusters, the unsaturation of the peripheral copper atoms manifests by their significant spin density. We therefore believe that modelling the AN complexation on these sites is somewhat less reliable.

As a matter of fact, the central atom of Cu₅(1,4) and Cu₉(5,4), the upper atoms in Cu₈(2,6), and both atoms in Cu₂ are very similar to each other; moreover, according to the “spin criterion” mentioned above, they resemble actual copper surface atoms, which is important for the comparison of AN bonding with various clusters. However, since the AN molecule is likely to be bound to the metal surface via two copper atoms, we also consider the more extended Cu₁₄(8,6) cluster, in which both central atoms in the upper layer have the correct number of nearest neighbors.

However, one should bear in mind that the dependence of the characteristics of adsorption on the cluster size is complex and nonmonotonous, as was demonstrated for CO on Cu(100) clusters by Bagus and co-workers,³⁰ due to changes in the nature and energy of the highest occupied electronic levels. A larger cluster is not necessarily a better cluster for a given problem.

Since we are interested in the transfer of a negative charge from copper, it is important to test also how the electron affinities of the clusters are described within the DFT approach. Table II shows that the EAs calculated as the energy difference between the negatively charged and neutral clusters, at both VWN and BVWN levels, are on the order of 1–2 eV and in qualitative agreement with experiment. (Recall that our clusters, both neutral and negatively charged, have frozen geometries of crystal fragments, while the geometry of real clusters can be different.) Note that these values are much lower than that of the real Cu(100), which has EA (and ionization potential) equal to the work function, 4.59 eV (106 kcal/mol).²⁷

B. AN/copper complexes in the absence of an electric field

The results for different types of adsorption are collected in Table III.

TABLE III. Major characteristics of acrylonitrile–copper complexes in the absence of electric field. The bond lengths are in Å, the angles in degrees, the Hirshfeld charge on the AN moiety (q) in $|e|$ units, and the complex binding energy (E_b) in kcal/mol. For negatively charged complexes, the binding energy is evaluated relative to the energies of the negative cluster and neutral AN (which is the most favorable combination of the isolated components).

	Bond lengths							Dihedral angles				q	E_b	
	C ¹ C ²	C ² C ³	C ³ N	C ¹ Cu	C ² Cu	C ³ Cu	NCu	C ² C ³ N	H ¹ H ²	H ² H ³	H ³ C ³		C ³ H ¹	BVWN
AN–Cu ₅ on top	1.402	1.414	1.172	1.978	2.022	-	-	178	160	3	194	3	-0.17	-12.8
[AN–Cu ₅] ⁻ on top	1.416	1.411	1.175	1.962	1.984	-	-	176	159	0	196	5	-0.38	-19.8
AN–Cu ₅ on face	1.494	1.411	1.203	2.096	2.074	2.006	2.042	175	119	-1	220	22	-0.39	22.7
[AN–Cu ₅] ⁻ on face	1.490	1.416	1.198	2.075	2.064	2.016	2.353	174	118	3	220	19	-0.62	25.7
AN–Cu ₈ on edge	1.402	1.405	1.203	2.015	2.015	2.009	2.018	157	157	9	185	10	-0.22	-4.4
[AN–Cu ₈] ⁻ on edge	1.409	1.404	1.208	2.022	2.011	1.982	2.044	171	156	9	183	13	-0.39	2.0
AN–Cu ₂ on edge	1.413	1.362	1.198	2.002	2.607	2.503	1.877	160	142	24	158	36	-0.21	6.4
AN–Cu ₉ on edge	1.427	1.362	1.201	2.075	2.847	2.375	1.893	167	138	23	169	30	-0.34	29.2
[AN–Cu ₉] ⁻ on edge	1.432	1.361	1.208	2.074	2.490	2.377	1.898	167	138	23	169	30	-0.49	28.1
[AN–Cu ₁₄] ⁻ on edge	1.437	1.362	1.202	2.116	2.619	2.473	1.937	167	133	22	165	40	-0.34	36.9
[AN–Cu ₁₄] ⁻ on edge	1.444	1.363	1.204	2.006	2.631	2.507	1.946	165	135	24	157	44	-0.47	35.4

1. AN on Cu₉(5,4), Cu₁₄(8,6), AN–Cu₈(2,6), and AN–Cu₂: Adsorption on-edge

On Cu₉(5,4), we have found a single type of AN coordination [see Fig. 4(a)]. We choose that the carbon be bound to the central copper and nitrogen to a peripheral one, and not vice versa, for the sake of comparison; in Sec. III 3, it will be shown that, in EF, the carbon atom can be the only AN atom bound to copper, and we wished this copper atom to be the most representative, i.e., possessing the correct coordination number. However, we also studied the corresponding complex of AN with Cu₁₄(8,6), in which the coordination number of both metal atoms bound to AN is correct, and obtained essentially the same type of bonding and charge distribution.

The optimized structure of AN–Cu₉(5,4) is a complex with the C=C and C≡N groups asymmetrically coordinated each at one copper atom. Only two copper atoms, out of five available, show distances with AN atoms indicating the formation of chemical bonds; the shortest contacts are with the two terminal backbone atoms (1.89 Å with N, 2.08 Å with C¹). This complex is rather a di- σ -complex than a di- π -complex of Dewar's type. The changes in bond lengths in AN, relative to the isolated molecule, are similar to those observed in the AN radical anion: C¹C² and C³N strongly elongate, while C²C³ assumes a double-bond character. However, the negative charge on AN (-0.34) is far lower

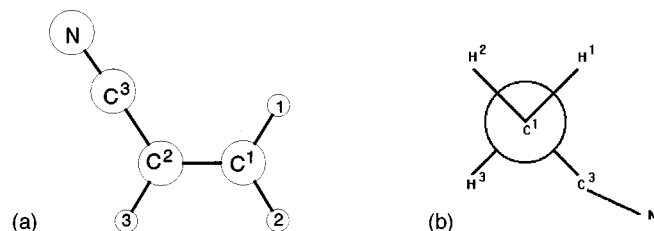


FIG. 3. Acrylonitrile: (a) atom labeling; (b) scheme of the conformation adopted upon adsorption.

than -1. The reason for the geometric rearrangement is related to the lower availability of two $2p$ electrons (on the terminal carbon and nitrogen atoms) for the π system because of their involvement in bonding with copper. In fact, the molecule in the complex becomes nonplanar; the C²C³N bond angle slightly deviates from 180°, which can be interpreted as the change in apparent hybridization of all backbone atoms, primarily C¹. Consequently, a new π bond is formed between the two central carbon atoms. Even though the complex described here corresponds to a local minimum, its total energy turns out to be *higher* than that of isolated AN and Cu₉; by a value as high as 29 kcal/mol at the BVWN level, but only by less than 2 kcal/mol at the BP level of theory. It is interesting to note here that at the local density VWN level, the energy of the complex is *lower* by 29 kcal/mol, which is a good illustration of the well-known tendency of LDA to overestimate binding energies. Comparing the effect of nonlocal potentials, we see that the post-SCF BVWN gradient exchange correction rather tends to underestimate the binding energy in this system, while the BP gradient exchange and correlation corrections, which are applied self-consistently, yield a more reasonable binding energy value.

Since only two copper atoms directly interact with AN, we leave only Cu₂ in the upper layer of the cluster, in a symmetric environment; that leads to the Cu₈(2,6) cluster. We find that AN is adsorbed on this cluster with all four backbone atoms [Fig. 4(b)]; all four bond lengths with copper are practically equal and the deviation of AN from planarity is relatively minor: this system appears to be a di- π -complex. Both carbon–carbon bonds are equal as well. This complex is slightly more stable by 4 kcal/mol than the isolated components.

Now consider the simplest cluster permitting the adsorption on-edge, Cu₂. The equilibrium geometry of AN–Cu₂ is closer to that obtained for Cu₉ than Cu₈, i.e., a very distorted di- σ -complex. This is an interesting result, since it indicates that the qualitative difference between the adsorption geom-

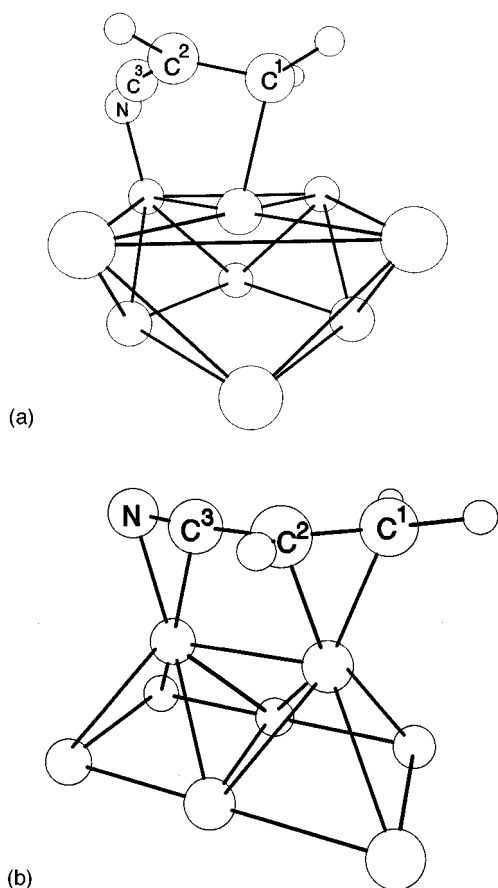


FIG. 4. Neutral acrylonitrile-copper cluster complexes on-edge: (a) with $\text{Cu}_9(5,4)$; (b) with $\text{Cu}_8(2,6)$.

eries of AN on Cu_9 and on Cu_8 is not a simple consequence of the inequivalence between the central and peripheric Cu atoms in Cu_9 . The complex AN-Cu_2 is less stable than its components (as well as AN-Cu_9), by 6 kcal/mol.

Note that in the series of AN complexes with Cu_2 , Cu_9 , and Cu_{14} clusters having the same type of bonding, adsorption becomes less favorable as the cluster size and the coordination number of the metal atoms directly bound to the organic molecule increase: the more saturated the copper atoms in the cluster, the lower their tendency to form new chemical bonds.

2. $\text{AN-Cu}_5(1,4)$ vs AN-Cu and $\text{AN-Cu}_5(4,1)$: Adsorption on-top and on-face

We now turn to Cu_5 . Though less appropriate than Cu_{14} , Cu_9 , and Cu_8 in the sense of approximating a real $\text{Cu}(100)$ surface, it is convenient to study the possibilities of on-top and on-face adsorption.

The $\text{Cu}_5(1,4)$ cluster is chosen primarily in order to establish connection, on the one hand, with the calculations by Fredriksson *et al.*⁴ treating AN complexation with a single copper atom and, on the other hand, with our further results for a larger $\text{Cu}_9(5,4)$ cluster, with on-atom adsorption in the presence of EF. Since it has been established for Ni-AN that the complex with C=C is more stable than that with CN

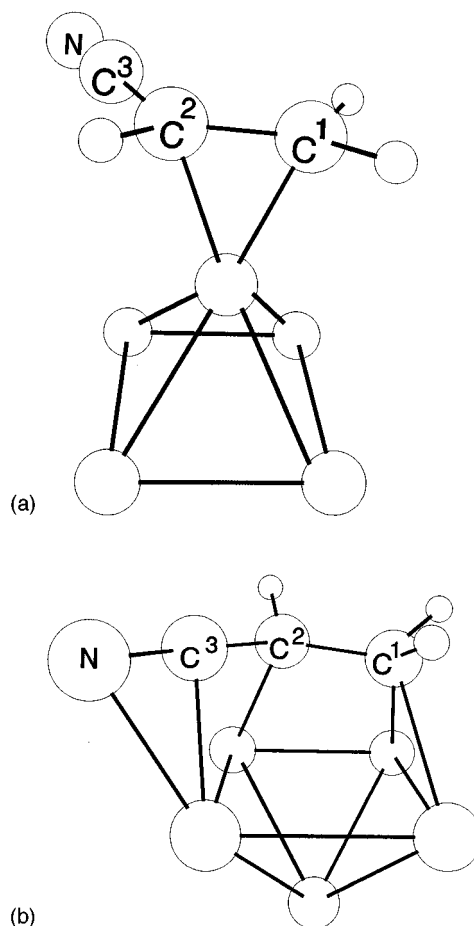


FIG. 5. Neutral acrylonitrile- Cu_5 complexes: (a) with $\text{Cu}_5(1,4)$, on-top; (b) with $\text{Cu}_5(4,1)$, on-face.

(Ref. 4) and since this possibility is more relevant in view of molecule orientation in EF, we considered only this possibility with $\text{Cu}_5(1,4)$. In the optimized geometry [Fig. 5(a)], we find that the bond lengths between the vinyl carbon atoms and the copper atom are almost equal (1.98 Å and 2.02 Å) and that both C^1C^2 and C^2C^3 bonds show an intermediate length (1.402 Å and 1.414 Å). This complex is 13 kcal/mol more stable than its isolated components.

In a complex with a single Cu atom, at the same level of theory, Fredriksson *et al.* have found a much greater difference between the two Cu-C bond lengths (1.91 and 2.53 Å). Such a significant distortion was reasonably attributed to the antibonding interaction between two occupied orbitals, $4s$ or Cu and p_z of C^2 . In the $\text{Cu}_5(1,4)$ cluster (and to even a greater extent in the bulk metal), this copper orbital is involved into the bonding with other metal atoms; therefore, this repulsion is reduced and C^2 gets closer to the copper atom. The bond lengths in the $\text{C}^2\text{C}^3\text{N}$ fragment remain practically unaffected upon interaction with $\text{Cu}_5(1,4)$. However, in the complex with a single copper, a marked shortening of C-C bond is calculated (1.409 to 1.389 Å); this shortening can be viewed as compensating the bond deficiency of C^2 (as the double bond with C^1 is almost broken) since the Cu atom

turns out to be rather far from C^2 . The bonding energy of this AN–Cu complex is -2 kcal/mol.

We conclude that the distortion of the complex towards a σ -bonded geometry is overestimated when the copper surface is modeled with a single atom. Adding the second copper layer, to form $Cu_5(1,4)$, we clearly see that *if* AN were adsorbed with its double bond at a single copper atom on a cluster, it would yield an almost symmetric π complex. However, our study with the $Cu_9(5,4)$ cluster has shown that in the presence of another copper atom in the vicinity, there is no potential minimum at all corresponding to a complex of AN with a single copper atom. The geometry optimization shows that the nitrile group turns toward the metal. This suggests that, in the absence of EF, an on-top complex could emerge only if all the sites around one copper atom were unavailable for some reason.

We now consider the possibility to coordinate AN on $Cu_5(4,1)$. We find a potential minimum for a complex in which all four AN backbone atoms are bonded to all four copper atoms of the upper layer [Fig. 5(b)]; this complex is 23 kcal/mol higher in energy than the separated AN and Cu_5 moieties. Therefore, on-face adsorption, within this crude model of the surface, appears to be less favorable than on-top; however, we have to bear in mind that on an extended cluster, the latter leads to an on-edge type of AN adsorption.

3. AN/Cu: Discussion

The results of our calculations indicate that neutral AN is preferentially adsorbed on Cu(100) on-edge, with both vinyl and nitrile groups coordinated at metal atoms. We now compare this conclusion with relevant experimental and theoretical data; we first invoke data on molecules containing either a C=C bond or a nitrile group, and then turn to AN, which contains both.

Studies treating the interaction of ethylene with transition metals are numerous. In a most recent density functional study,³¹ the bonding of ethylene to a single copper atom, a dimer, and a trimer (D_{3h}) was considered by Fournier. The author found that the most stable structure was in all cases with the ligand bonded to a single atom, on-top; with Cu_3 , the complex on-edge lies only a few kcal/mol higher, and there is no minimum corresponding to the molecule coordinated at all three copper atoms, which can be regarded as on-face geometry for Cu(111).

From combined electron energy loss spectroscopy (EELS) and x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) studies, it appears that acetonitrile, CH_3CN , is weakly chemisorbed on Cu(100) via a π or σ nitrogen orbital; however, the nature of its adsorption strongly depends on the metal; on Pt(111) the interaction is strong and a rehybridization to an $\eta^2(C,N)$ complex takes place.³²

We now consider the data on the adsorption of AN on metals. Surface-enhanced Raman scattering (SERS) data¹⁰ indicate that on polycrystalline Ag, AN lies flat on the surface, with both C=C and CN groups interacting with the metal. According to UPS and metastable de-excitation spectroscopy (MDS) data,⁹ on polycrystalline Ni, AN is adsorbed

with its nitrile group end-on. A NEXAFS study on polycrystalline Ni (Ref. 33) shows that (i) when there is a layer of adsorbed AN molecules, there occurs a strong interaction between the nickel surface and the nitrogen atoms of the AN molecules, the C=N bonds are normal to the surface, also indicating the end-on coordination of a nitrile group; (ii) however, when a thin electrodeposited polymer layer is present, the polymer backbone is normal to the surface with the C≡N groups noninteracting and parallel to it. According to combined NEXAFS, UPS, and Fourier transform infrared (FTIR) experiments at 95 K,¹¹ AN is only physisorbed with a flat orientation on Au(111), while on Pt(111) it is chemisorbed mainly due to an interaction of the nitrogen lone pair orbital with the surface. Therefore, the geometries found for AN adsorbates are reversed with respect to those observed with acetonitrile: a strong interaction with a group VIII metal, e.g., Ni or Pt, brings about nitrogen end-on chemisorption, while a weak adsorption on a group I transition metal, such as Au, takes place in a flat orientation. Parent *et al.*¹¹ infer from their experiments that the HOMO and LUMO levels of AN *do not interact* with Pt; they suppose intuitively that the strong delocalization of the frontier orbitals prevents or weakens an attractive interaction with the metal, due to a small overlap with the metal bands compared to a localized state.

In conclusion, the experimental data show that on a group I transition metal, AN is most likely adsorbed in a flat orientation on the surface, with both vinyl and nitrile groups coordinated at metal atoms, and the adsorption is rather weak. We are not aware of experimental data for AN adsorbed on Cu, but the type of geometry we arrive at on the basis of our calculations is consistent with the general notions for AN adsorption on transition metals inferred from experiments. Furthermore, the experimental data suggest that the di- π -complex obtained with $Cu_8(2,6)$ would be a more plausible structure for AN on Cu than the di- σ -complexes predicted with $Cu_{14}(8,6)$, $Cu_9(5,4)$, and Cu_2 . A challenging perspective for the future would be to study the interaction of AN with Ni clusters, which may be expected to have a different nature.

4. Negative ions

In order to model the cathodic charge transfer, we now turn to the negatively charged systems, by adding one electron to the complexes described above. In all cases, the changes in the optimized geometries and binding energies are relatively minor in comparison to the corresponding neutral complexes. We relate this fact to the observation that the major part of the negative charge, according both to Hirshfeld and Mulliken population analyses, remains on the copper cluster. At first glance, this distribution seems to be contradicting the chemical intuition based on the electronegativities of the elements. However, we have already shown that both the calculated and experimental electron affinities of the copper clusters are larger than that of the AN molecule. The extra negative charge is, therefore, preferentially located on the copper cluster.

TABLE IV. Major characteristics of negatively charged acrylonitrile–copper complexes in the presence of electric field. The bond lengths are in Å, the angles in degrees, the Hirshfeld charge on the AN moiety (q) in $|e|$ units, and the complex binding energy (E_b) in kcal/mol. The binding energy is evaluated relative to the energies of the negative cluster and neutral AN (which is the most favorable combination of isolated components) for the $z=0$ position of the upper copper layer.

	Bond lengths							Dihedral angles					E_b		
	C ¹ C ²	C ² C ³	C ³ N	C ¹ Cu	C ² Cu	C ³ Cu	NCu	C ² C ³ N	H ¹ H ²	H ² H ³	H ³ C ³	C ³ H ¹	q	BVWN	BP
[AN–Cu ₉] [−] on top $F_z=0.77\times 10^8$ V/cm	1.429	1.375	1.200	2.179	3.165	178	135	36	176	13	−0.89	−2.4	−31.6
[AN–Cu ₉] [−] on edge $F_z=0.77\times 10^8$ V/cm	1.473	1.358	1.210	2.051	2.626	2.432	1.961	171	130	43	145	42	−0.85	27.9	−15.1
[AN–Cu ₉] [−] on edge $F_z=1.03\times 10^8$ V/cm	1.488	1.360	1.212	2.086	2.738	2.485	1.939	169	129	51	133	47	−1.01	23.9	
[AN–Cu ₅] [−] on top $F_z=1.03\times 10^8$ V/cm	1.469	1.386	1.206	1.957	2.297	174	144	50	193	−27	−1.03	−61.2	
[AN–Cu ₅] [−] vinyl on face $F_z=1.03\times 10^8$ V/cm	1.502	1.399	1.200	2.233 2.253	2.321 2.480	178	120	53	232	−45	−1.13	−2.2	
[AN–Cu ₅] [−] flat on face $F_z=1.03\times 10^8$ V/cm	1.471	1.399	1.213	2.058 2.384	2.218	2.019	2.316	168	125	14	203	18	−1.04	32.8	

While bearing in mind a certain arbitrariness of any atomic charge partitioning scheme, let us follow in greater detail the charge distribution within the cluster taking [AN–Cu₈(2,6)][−] as an example. In spite of the total negative charge of the cluster, the two upper copper atoms directly bound to AN, bear a small positive charge, while the lower copper layer is heavily negatively charged. If we add third and fourth copper layers (freezing the geometry of AN adsorption), as in [AN–Cu₁₀(2,6,2)][−] and [AN–Cu₁₆(2,6,2,6)][−], the charges on AN and the upper two copper atoms to which the organic molecule is bound, virtually do not change (the same negative charge being redistributed between the lower copper layers). We also note that if copper in the calculation is deliberately made less prone to accept the negative charge by modifying its basis set [namely, eliminating all atomic orbitals (AOs) above 4s and freezing all AOs below 4s], no significant effect is observed. On the basis of these results, the charge distribution appears to be quite “robust,” since it is model independent; this, therefore, suggests that it can correspond to a certain reality. We conclude that a second copper layer of sufficient size is essential for the reasonable description of the charge distribution in the copper cluster of the negative complexes, while further lower layers are probably unnecessary. Therefore, in our opinion, the choice of two-layer clusters is justified.

C. AN/copper complexes embedded in an electric field

In order to model the electrochemically induced charge transfer from copper to AN, we apply to the complexes an electric field normal to the metal surface. The results are reported in Table IV.

Raynaud *et al.*¹² on the basis of Hartree–Fock calculations and recently Fredriksson *et al.*⁴ using DFT have found

only slight changes in the geometry of the neutral AN molecule and its radical anion in a strong EF of 2×10^8 V/cm. We also observe that when an EF of ca. 10^8 V/cm is applied along the CN bond, the geometry does not change significantly; the nitrile bond elongates by less than 0.01 Å, despite the strong concentration of negative charge observed on the nitrogen (which is mainly due to the polarization of the σ and not the π system). Certainly, the field strength is insufficient to open the carbon–carbon double bond, as was proposed in an early work by Lécayon *et al.*¹ Therefore, the differences in geometries of the AN moiety in the complexes with respect to those of isolated AN and AN[−] compounds that we observe in the complexes discussed below, should be attributed to a specific interaction with the metal and not merely to the effect of EF.

Qualitatively, in EF, two opposite factors determine the orientation and the geometry of the organic molecule in the complex with the metal cluster. The metal tends to bind to several backbone atoms, as we have seen in the absence of EF, and thus to align the molecule along the cluster surface. At the same time, the field tends at first to align the dipole of the molecule along the field, i.e., normally to the cluster surface, which requires breaking some of the bonds with the metal, and, finally, to pull the AN anion away since its total energy decreases in the direction opposite to the field, thus dissociating the complex. The items relevant for the evaluation of the grafting mechanism are, therefore, to estimate whether (i) there is a bound state for AN and AN[−] on copper clusters in a given EF; (ii) there is a (local) minimum corresponding to a σ complex postulated by Lécayon *et al.*; (iii) multiply coordinated complexes survive in EFs; (iv) if there are multiple minima (with evaluation of their relative stabilities and barriers between them).

We shall discuss the negatively charged complexes lead-

ing to the $[\text{AN}]^-\text{[Cu}_n]^\circ$ type of charge separation in EF, which seems realistic. However, it should be noted that, in addition, we also studied neutral complexes (leading to $[\text{AN}]^-\text{[Cu}_n]^+$) since the precise charge state of the electrode transferring electrons under polarization is not clear. It is interesting that the results are very similar in both cases; therefore, the differences in the total charge of the copper cluster appear to be of marginal importance. We focus our attention first on the complexes with Cu_9 ; the complexes with Cu_5 will be discussed later for the sake of comparison, in order to evaluate the influence of the cluster size on the results.

With $\text{Cu}_9(5,4)$ in the field of 7.7×10^7 V/cm, we find that the charge carried by the AN moiety in negatively charged complexes is on the order of $-0.9|e|$, i.e., the charge transfer is almost complete. Two representative complexes are found.

The first complex ‘‘on-edge’’ corresponds to that found in the absence of EF [shown in Fig. 4(a)], with C^1 bound to one copper atom and N to another. In comparison to the zero-field complex, the bond to N is slightly longer (1.96 vs 1.90 Å), C^3 and C^2 are also slightly further away from copper (2.43 vs 2.38 Å, 2.63 vs 2.49 Å) reflecting the tendency of the nitrile group to be aligned with the field. Within the AN moiety, the $\text{C}^1\text{--C}^2$ bond elongates (1.47 vs 1.43 Å), while the $\text{C}^2\text{--C}^3$ bond length does not change (1.36 Å). C^2 is not bonded to copper and remains rather unsaturated; it could therefore be the active site for the initiation of the AN polymerization. We propose that this complex, though different from the one postulated by Lécayon *et al.*,² could be an intermediate for further polymerization of AN.

The second complex (Fig. 6) has no counterpart in the absence of EF. It has only one bond with the cluster, namely, C^1 is bound to one copper atom, while the rest of the molecule tends to align along EF; it can be referred to as a σ complex. All the bond lengths within the AN moiety are close to their values in isolated AN^- , except for $\text{C}^1\text{--C}^2$ that is slightly longer (1.43 vs 1.41 Å), which is likely due to the bonding of C^1 with Cu. Therefore, the reactivity of C^2 in this complex can be at least the same or slightly higher than in noncoordinated AN^- . The bonds around C^2 are practically coplanar, thus indicating sp^2 hybridization, while C^1 shows considerable deviation towards sp^3 hybridization. A certain π bonding along $\text{C}^1\text{--C}^2$ still persists, which can be inferred not only from the bond length. In fact, the angle between $\text{C}\equiv\text{N}$ and the field is 46° , while simple modeling shows that by means of rotation along the $\text{C}^1\text{--C}^2$ bond, the CN group could be aligned exactly parallel to EF. What prevents CN against aligning is not the steric interaction between H^3 and copper since the nearest $\text{H}\text{--Cu}$ distance is about 3.4 Å in the minimum geometry and 2.8 Å if aligned. We are therefore led to the conclusion that the rotation around $\text{C}^1\text{--C}^2$ is still significantly hindered, and this effect is still larger than the aligning action of EF.

The binding energy of the σ complex is -2 kcal/mol, while the planar complex is 28 kcal/mol less stable than its isolated components, i.e., a value close to that for the similar configuration in the absence of EF. The BP calculation, though changing the binding energy absolute values of the

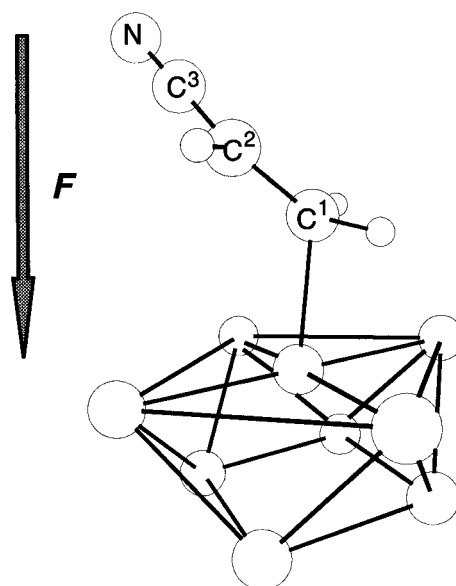


FIG. 6. Negatively charged acrylonitrile- $\text{Cu}_9(5,4)$ complex on-top, in the presence of an electric field of 0.77×10^7 V/cm.

complexes (-32 kcal/mol for the σ complex vs -15 kcal/mol for the planar one) does not change the relative stability order. Therefore, the gain in energy due to dipole orientation and shift in effective charge center in EF are energetically more important than the dissociation of the $\text{Cu}\text{--N}$ bond. Furthermore, for the complexes with the $\text{Cu}_{14}(8,6)$ cluster, the on-edge complex is expected to be more weakly bound, as was the case in the absence of EF, while for the σ complex significant changes in the binding energy are not likely since the extension of the cluster in the latter case does not concern the active site directly. Thus, we believe that *the preference for the σ complex in these conditions should persist for any cluster extensions.*

When increasing the EF value to 10^8 V/cm, the charge on AN becomes slightly higher than $-1|e|$, i.e., the charge transfer is full. In such field, the doubly coordinated complex does survive; its geometry changes further along the same direction as discussed above for the on-edge complex. However, there is no longer any bound state for the σ complex; the AN radical ion rather tends to leave the cluster. The fact that it would have only one loose bond with the cluster, together with the alignment of its dipole, appears to facilitate the dissociation. We believe this result is important and can be directly related to the actual experimental situation. First, as we have shown, this type of complex is the most favorable at low EF; therefore, it is likely to be the initial state when the field is increased. Second, this way of decomposition is intuitively realistic. Finally, it coincides well with the experimental observation of the absence of polymer grafting when the reaction is carried out at a very high cathodic potential, corresponding to a higher relative EF.

With the $\text{Cu}_5(100)$ cluster orientation in the field of 10^8 V/cm, we find three potential minima for the complexes, two of them with AN on-face and one with AN on-top. The first complex corresponds to the zero-field complex on the upper

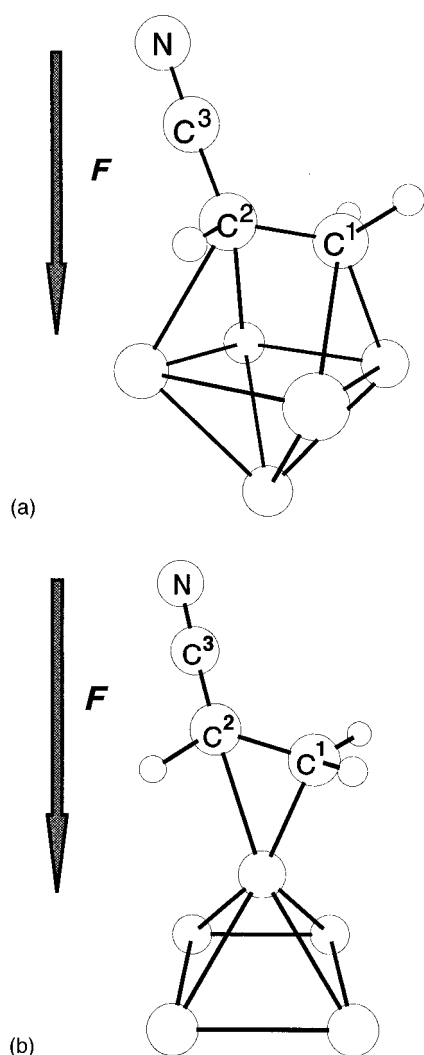


FIG. 7. Negatively charged acrylonitrile- Cu_5 complexes, in the presence of an electric field of 1.03×10^8 V/cm: (a) with $\text{Cu}_5(4,1)$, vinyl on-face; (b) with $\text{Cu}_5(1,4)$, on-top.

Cu_4 plane, with all four backbone atoms bound to copper [see Fig. 5(b)]; qualitatively, the geometries do not differ. The second complex has no zero-field counterpart: the two vinyl carbons remain bound to the Cu_4 plane, while the nitrile group tends to orient its dipole along the field [Fig. 7(a)]. The geometry of this complex is most distorted: the C^1 - C^2 bond retains no double-bond character, as indicated by its length (1.50 Å), as well as by dihedral angles between the bonds at both its carbons; moreover, the rotation around this bond is such that π overlap would be negligible. The third complex [Fig. 7(b)] originates from AN bound to $\text{Cu}_5(1,4)$ in the absence of the field. The key difference from the zero-field complex is that the distances from the copper atom to the vinyl carbons are strongly unequal (1.96 Å for $\text{Cu}-\text{C}^1$ vs 2.30 Å for $\text{Cu}-\text{C}^2$). This geometry resembles that of a σ complex. Here also, we observe the same tendency to distortion towards a singly bonded structure, although less pronounced than in the previous complex. We note that there is no potential minimum for this type of complex on the Cu_4

face with the terminal carbon bound interstitially; the optimization from such an initial geometry yields the second complex, with both carbon atoms bound. The complex with AN on-top has a binding energy of -61 kcal/mol, that of the vinyl-on-face complex is -2 kcal/mol, while the flat complex is 33 kcal/mol less stable than its components.

We now compare the Cu_5 results to those obtained with the Cu_9 cluster. In spite of the low coordination number of all Cu atoms in the Cu_5 cluster, which would favor multiple coordination with an organic molecule, we find in both cases that AN coordinated to one copper atom yields the most stable complex in EF. Even though we globally reach the same conclusion, some important features of the two most favorable, on-top, complexes do however differ. This is the case for the geometry: the upper Cu atom in $\text{Cu}_5(1,4)$ being less saturated, the bonds with both C^1 and C^2 are stronger; in the complex with Cu_5 , in spite of a higher EF value, the difference between the two C-Cu bond lengths is attenuated, both are shorter; hence, the C^1 - C^2 length is closer to a single bond, rotation around C^1 - C^2 bond is easier, and the angle between $\text{C}\equiv\text{N}$ and the field is lower, 35° . A more important difference is that, even in the case of full charge transfer, the Cu_5 -AN complex when binding occurs to one copper atom is bound; had we limited our modeling to this system, we would not have been able to observe the dissociation of the σ -complex in a reasonably strong EF.

Our calculations on the systems embedded in EF show that, as long as the EF does not pull the species apart, the most energetically favorable configuration is a σ complex with the nitrile end pointing away from the copper surface. Nevertheless, complexes with multiple coordination and planar orientation survive in EF as well; since only these exist without EF, there is a question if their rearrangement into the σ complex is feasible, i.e., the question of the barrier between the AN orientations along and away from the cluster surface in the presence of EF. The search for a transition state in these systems would require an enormous computational effort as well as the consideration of other effects, e.g., due to the solvent. We can only speculate that in a nonrigid system like this one, the barrier separating various types of adsorption should not be excessively high.

IV. CONCLUSIONS

In the absence of an electric field, our calculations indicate that acrylonitrile, when adsorbed on $\text{Cu}(100)$, is coordinated to two copper atoms with both vinyl and nitrile ends to the metal surface. This is in accordance with experimental data for adsorption on the group I transition metals. The details of the geometry depend on the choice of the copper cluster; however, even the minimum two-atom cluster describes the adsorption reasonably well, confirming the local character of the interaction.

Full charge transfer from the cluster to the organic moiety is found for electric fields on the order of 10^8 V/cm. This value represents a reasonable order of magnitude for a field in the electrode vicinity. Therefore, the electrochemically induced charge transfer has been modeled by embedding a

negatively charged complex in an EF directed according to the electrode polarity. For the complexes with a strong charge polarization, two-layer copper clusters are necessary and sufficient for a reasonable description of the charge distribution. In such electric fields, a minimum corresponding to the adsorption on-edge persists.

However, if the field is not too large and causes only partial charge transfer, a more stable configuration is constituted by a σ complex with AN attached via one bond between the terminal carbon atom and one copper atom, while the nitrile group tends to align along the field. This rearrangement corresponds to the field-induced reorientation and grafting postulated previously by Lécayon *et al.*^{1,2}

In a stronger electric field, causing full charge transfer, there is no bound state for the σ complex; the AN radical anion rather tends to leave the metal surface. Even though our calculations do not provide a direct proof of the radical mechanism proposed by Mertens *et al.*,^{3,8} this result suggests that the AN anion species does not remain adsorbed on the electrode; therefore, anionic polymerization should not lead to a chain grafted to the metal surface. Furthermore, this observation may be related to the absence of grafting at higher cathodic potentials, a feature which is observed experimentally.⁸

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