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Mechanism of metal cationization in organic SIMS

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Abstract

A scenario of metal cationization in which the organic molecule combines with a neutral excited metal atom is proposed. Ionization of the nascent complex occurs via ejection of an electron during the association process. Electron structure calculations for the model systems $C_6H_6 + Me$ ($Me = Ag, Cu, Au$) using the density functional theory give a strong argument in favor of the proposed mechanism.

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1. Introduction

In order to achieve high yields of large molecular ions in SIMS of organic materials, cationization of sputtered neutral molecules (M) by complexation with substrate metal atoms (Me) to form ions $(M + Me)^+$ is often used [1,2]. However, the underlying mechanism(s) of this complex *metal-cationization* process are far from being understood in detail. The conventional scenario of the process is the association above the surface of a *neutral sputtered molecule* (M) and *metal cation* (Me)⁺. The association process can occur in the surface region (preformed complex), in the surface vicinity still under action of the force field of the surface, or out of influence of the surface. In any case, the organometallic ion yield *must be* sensitive to the work function of the surface and *correlate* to the metal cation yield. However, recent experimental studies of possible cationization mechanisms [3,4] show that the commonly accepted scenario for metal cationization is not adequate [4].

In the present report, the recombination of excited molecules and metal atoms above the surface and decay via electron emission, locking the system in the ionic state, is proposed to contribute to the yield of cationized molecules. This process, known as associative ionization, can happen if the total energy of the reactants at a certain separation distance exceeds the total energy of the $(M + Me)$ system. The energy excess is transferred to ionization and carried away by an electron liberated in the autoionization process. To demonstrate the possibility of such a kind of process we calculated the potential energy curves for $C_6H_6 + Me$ ($Me = Ag, Cu, Au$) as model systems, using the ABINIT code [5], an implementation of the density functional theory.

2. Theoretical framework

Associative ionization (Hornbeck–Molnar process [6]) is a unique ionization process that occurs when an electronically excited atom A^* or a ground state one collides with a species B , resulting in the formation of a charged association complex:



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When A approaches B, the energy difference between the potential energy curve of the molecular ion AB^+ and some of the curves describing the A^*-B interaction may decrease. At certain distances R_c between A^* and B the latter curves can cross the former one. At distances $R \leq R_c$ the state of the system becomes an autoionizing one and may decay with the escape of an electron, locking the system in the ion state. The emission of an electron constitutes a way to dissipate the energy released by the reaction. Conditions favoring the curve crossing are a strong AB^+ bond and a repulsive state with a high excitation energy of the A^*-B system. Some transition metal-benzene compounds, being appropriate model systems for organometallics containing phenyl groups, may have the mentioned properties. Cations of these complexes are relatively strongly bonded due to the specific interaction between the π -orbitals of the hydrocarbon and the d-orbitals of the transition metal.

As it has been recently revealed, metastable Ag^* ($4d^9 5s^2$, $^2D_{5/2}$) atoms constitute the next most important fraction (up to 6%, being as large as three orders of magnitude higher than the yield of Ag^*) of the total flux sputtered from the clean Ag surface [7], after the neutral Ag atoms. The excitation energy for this state is high enough, 3.75 eV. The state of the $C_6H_6-Ag^*$ ($4d^9 5s^2$) complex is repulsive. On these grounds, we propose the associative ionization can work for transition metal-benzene association.

To perform the calculations, we used both the generalized gradient approximation (GGA) (for $C_6H_6 + Ag$ system) and the local spin density approximation (LSDA) (for $C_6H_6 + Cu$ and $C_6H_6 + Au$ systems), which are implemented in the ABINIT code [5]. The calculations of the potential energy curves were performed in C_{6v} symmetry for all the systems in question. The computational details, including calculations of binding energies, bond lengths and ionization potentials for the considering organometallics and their constituents, are published elsewhere [8].

3. Results and discussion

The results of the calculations are shown in Fig. 1(a)–(c). The isoenergetic d orbitals of a $Me[(n-1)d^9 ns^2]$ are split into different potential energy curves when it approaches a benzene molecule.

The upper potential energy curve of the $C_6H_6 + Me^*[(n-1)d^9 ns^2]$ system corresponds to the transition from the lowest energy $d-x^2-y^2$ and d_{xy} orbitals. The lower one corresponds to the transition from the degenerate d_{xz} and d_{yz} orbitals. It is seen that, for $C_6H_6 + Ag^+$ and $C_6H_6 + Cu^+$, the upper curve crosses the ionic one on the attractive side of the potential well. In this case, the cross-section of associative ionization has maximal values. For $C_6H_6 + Au^+$, this crossing occurs on the repulsive side of the well, resulting in lower values of the cross-section [9]. The curve originating from the $d_{xz}(d_{yz})$ orbital does not cross the ionic one in this case. In the case of silver, that curve crosses the ionic one practically in continuum, but for copper, it does within the potential well. It is seen that, even if the real ionic potential well is shallower at identical equilibrium distances (the binding energies are overestimated by the LSDA), that does not change the qualitative picture.

The potential energy diagrams allow the energy threshold for the reaction (1) E_{th} to be estimated. It is seen that for the $C_6H_6 + Ag^*$, the reaction can proceed if the relative energy of the benzene approaching metal is a few eV, the precise value being different for the different excited states.

According to our calculations, associative ionization should proceed most effectively between Cu^* and C_6H_6 , and least effectively for the gold-benzene pair. Obtaining quantitative estimates for relative yields of cationized molecules is difficult, mainly because it must significantly depend on the yield of excited atoms, which might be different for the metals in question. Only the data for Ag^* emission are available at the moment. Nevertheless, a strong argument in favor of the proposed mechanism of cationization can be derived from the analysis of velocity distributions of cationized molecules.

Because transition metals bind to a hydrocarbon molecule containing phenyl rings by interaction of the metal d-orbitals with π -orbitals of phenyl side groups, one should expect the similar features in potential energy curves for any organic molecules containing phenyl groups. Taking that into account, we calculated the velocity distribution $N(v)$ of cationized polystyrene oligomers lifted up from the silver surface. The experimental distribution $f_{Me^*}(v_2)$ of sputtered metastable Ag^* atoms [7] was convoluted with the distribution of neutral polystyrene oligomer tetramers

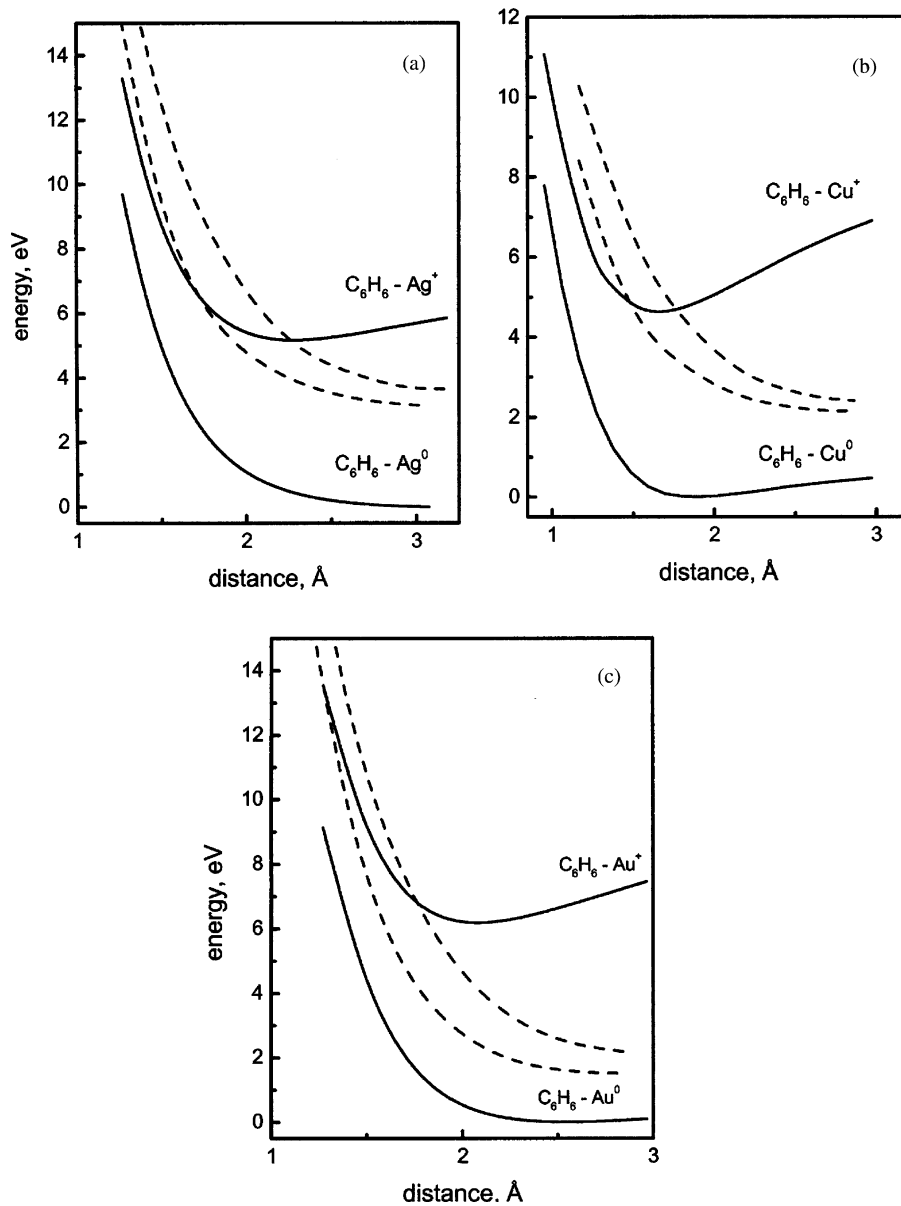


Fig. 1. Potential energy curves for the model systems $C_6H_6 + Me$ ($Me = Ag, Cu, Au$). The solid curves correspond to the ground state (lower one) and the ionic state (upper). The energies of the excited states are shown with dashed curves (see text).

$f_M(v_1)$ obtained by MD simulation in [10]. Since the angular distributions of the emitted particles are unknown, in first approximation, we assume them to be isotropic. In the calculation of $N(v)$, we added up the product $\sigma_{ai}(v_{rel}; v_{th}) \times f_M(v_1) \times f_{Me^*}(v_2)$ over different orientations of v_1 and v_2 (different relative

velocities of reactants v_{rel}) leading to the same value of v provided the condition $v_{th} \leq v_{rel} \leq v_{max}$ is fulfilled, where v_{th} and v_{max} are the threshold and maximal values of the relative velocity, respectively. σ_{ai} is the cross-section of associative ionization, which depends on the relative velocity (energy E_{rel})

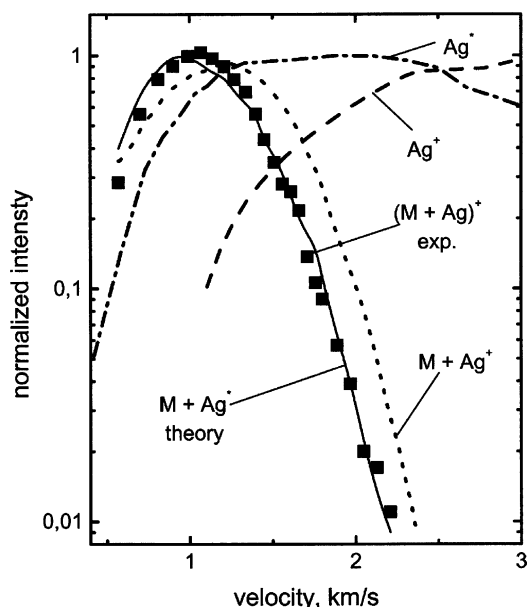


Fig. 2. Velocity distribution of sputtered polystyrene tetramers: squares are the experimental data [3], solid line is the theory taking into account the associative ionization process, dotted line is the convolution of the distributions of neutral tetramers [10] and Ag^+ ions. The experimental velocity distributions of Ag^+ and Ag^* are shown by dashed and dash-dot line correspondingly.

as $\sigma_{\text{ai}} \sim (E_{\text{rel}} - E_{\text{th}})^{3/2} / E_{\text{rel}}$ [9]. We used $v_{\text{th}} = 1.55$ km/s and $v_{\text{max}} = 1.95$ km/s, which seem to be reasonable. The results of the calculations are shown in Fig. 2 in comparison with the experimental data. The velocity distributions of sputtered metastable Ag^* atoms and Ag^+ ($f_{\text{Me}^+}(v_2)$ and $f_{\text{Me}^+}(v_2)$, respectively) obtained in [7], as well as the convolution of just $f_{\text{M}}(v_1)$ and $f_{\text{Me}^+}(v_2)$ at the same velocity constraints are also shown for a comparison. It is seen that the theoretical distribution of cationized molecules formed via associative

ionization reproduces the experiment fairly well. In contrast, just the convolution of the spectra of sputtered metal ions and neutral molecules (not taking into account any specific velocity-dependent mechanism of their association) shifts the $(\text{M} + \text{Me})^+$ spectrum towards higher energies as compared to the experimental one.

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