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Mechanism of metal cationization in organic SIMS

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Abstract

A mechanism for metal cationization of phenyl group containing hydrocarbons is discussed. Intact molecules and their fragments are emitted from a thin organic layer covering a metal surface bombarded by fast ions. It is shown that the process of associative ionization of a neutral hydrocarbon molecule and a neutral excited metal atom, occurring above the surface, may contribute to the yield of cationized molecules. To demonstrate this we have calculated the potential energy curves for the model system $C_6H_6 + Me$ (Me = Ag, Cu, Au) making use of the density functional theory. The initial states of the metal atoms approaching the benzene ring along the C_6 symmetry axis were set as the ground, ionic, and excited in $(n-1)d^9ns^2$ electronic configuration.

1. Introduction

A solid under bombardment by a keV energy ion beam emits secondary particles (including polyatomic ones) in different charge states. The analysis of ion fractions of the total flux of sputtered particles is the basis of the secondary ion mass spectrometry (SIMS) technique, widely used as an analytical tool to obtain chemical information on the uppermost monolayer of various solid surfaces [1]. For metal substrates covered by organic material, large intact molecules and molecular fragments are emitted, providing valuable analytical information. However, the qualitative and quantitative analyses of surface chemical species by means of SIMS still suffer from an insufficient knowledge of the mechanisms of secondary ion emission.

In order to achieve high yields of large molecular ions in SIMS of organic materials, cationization of sputtered particles by complexation with substrate atoms is often used [2,3]. In these experiments, an organic analyte is deposited onto a clean metal surface. The measurements show that the yield of analyte molecule cations is very low. In a number of cases, such as low weight oligomers of polystyrene cast on silver, no intact charged molecules were detected [4]. This is due to high ionization potentials of organic molecules (~9 eV) as compared to the work function of metals. In addition, any collisional ionization has to be accompanied by an essential transfer of energy into ro-vibrational degrees of freedom, leading the molecule to decay. In this respect, metal cation adduction to a neutral molecule is not an energy consuming process. Therefore, sputtered metal species can serve as an external source for analyte molecule ionization.

The process of organometallic complex $(M + Me)^+$ formation is thought to be due to the association above the surface, of the independently

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sputtered organic molecule (M) and metal ion $(Me)^+$. 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 all the cases organometallic ion yield *must be* sensitive to the work function of the surface and *correlate* to the metal cation yield.

The molecular dynamics simulations of particle induced emission of polystyrene tetramers $[C_4H_9(C_8H_8)_4H]$ deposited on the silver substrate [5] show emission of intact polystyrene molecules, which are in favor of the association hypothesis. However, the recent experimental studies of possible cationization mechanisms [4,6] show that the commonly accepted scenario for metal cationization is not adequate. In these experiments, analyte molecules include unsaturated fatty acids and low molecular weight styrene-based oligomers cast on a number of metal substrates (Al, Cr, Cu, Pd, Ag, In, Au and Pb). The cationized molecule yields are detected for all the supports except Al. Although varying with the considered molecule and substrate the yields do not correlate with the yields of metal atom cations. For example, silver cationized molecules are emitted from metallic and oxidized silver surfaces with similar intensities [4]. The metal ion yield is by orders of magnitude higher for the oxidized surface than for the clean one, being as low as 10^{-4} for the latter. In some cases, the measured yields of cationized molecules are as high as 50 times that of metal ions, assuming recombination probability close to unity [4]. This seems to be scarcely probable. In addition, double cationization events with two metal particles are detected for Cu, Pd, Ag, and Pd supports and styrene-based polymers [6]. If single cationization by a metal ion is a low probability event (due to the low yields of the constituents), double cationization of a given organic molecule by two independent metal ions seems to be unrealistic [6]. All the facts given above point to the possible existence of other mechanism(s) of cationization.

In the present work, the process of associative ionization of a neutral hydrocarbon molecule and a neutral *excited* metal atom occurring above the surface is proposed to contribute to the yield of cationized molecules. This process resulting in the formation of $(M + Me)^+$ ion from the neutral reactants M and Me 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, stabilizing the molecular ion.

To demonstrate the possibility of such a kind of process we used $C_6H_6 + Me$ (Me = Ag, Cu, Au) as model systems. For these systems, the potential energy curves for the case when the metal atom approaches the benzene ring along C_6 symmetry axis were calculated. The calculations were performed, in the supercell geometry, using the ABINIT code [7], an implementation of the density functional theory.

Our simulations show that the crossing of the potential energy curves of neutral and ionized C_6H_6–Me system is only possible if the metal atom is in one of the metastable states of the electronic configuration $(n-1)d^9ns^2$. An estimation of the velocity distribution of sputtered polystyrene tetramers cationized by Ag^+, agreeing with the experimental data, gives a strong argument in favor of the associative ionization mechanism.

2. Theoretical framework

2.1. Associative ionization

Associative ionization (Hornbeck–Molnar process [8]) 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

$$A^* + B \rightarrow AB^+ + e^- \tag{1}$$

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 $R \leqslant R_c$ 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 (Fig. 1).

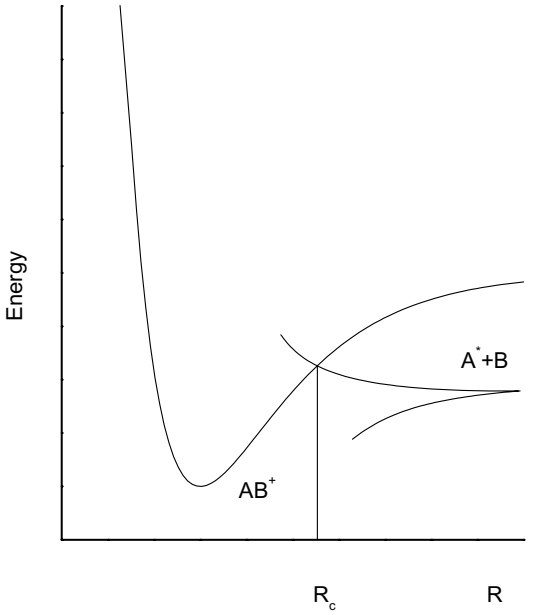

Fig. 1. Scheme of associative ionization process.

In the semiclassical approach, the cross-section of the process can be calculated with the formula [9]

$$\sigma_{\mathrm{ai}}(v_{\mathrm{rel}}) = \frac{4\pi}{v_{\mathrm{rel}}} f \int_{R_0}^{R_c} R^2 \Gamma(R) \sqrt{1 - \frac{U(R)}{E}}\,\mathrm{d}R, \qquad (2)$$

where E is the relative energy of the colliding particles, v_{rel} is their relative velocity, $U(R)$ is the interaction potential in the initial channel, R_0 is the distance of the closest approach, $\Gamma(R)$ is the width of the autoionizing state, and f is the probability for the system to be in the initial channel.

Assuming the main contribution to the cross-section to come from the distance R close to the cross point, Eq. (2) can be essentially simplified as

$$\sigma_{\mathrm{ai}}(E) = A \frac{(E - E_{\mathrm{th}})^{3/2}}{E}, \qquad (3)$$

where $A = 4\pi\sqrt{2\mu}R_c^2\Gamma(R_c)/3|\mathrm{d}U/\mathrm{d}R|_{R_c}$, E_{th} is the threshold energy for reaction (1), and μ is the reduced mass of the colliding particles.

2.2. Model system

As it can be seen in Fig. 1, 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 [10].

As it has been recently revealed, metastable $Ag^*(4d^95s^2,\ ^2D_{5/2})$ atoms constitute the next most important fraction (up to 6%, being as large as three orders of magnitude higher than the yield of Ag^+ ions) of the total flux sputtered from the clean Ag surface [11], after the neutral Ag atoms. The excitation energy for this state is high enough, 3.75. The state of the C_6H_6–$Ag^*(4d^95s^2)$ complex is repulsive. Indeed, neutral benzene–transition metal complexes in the ground state are weakly bonded compounds. Excitation of an electron from the $(n-1)$d shell into the ns shell weakens the bond, resulting in an antibonding state, due to the strengthening of the Pauli repulsion between metal s electrons and valent benzene ones. Based on these facts we propose that the associative ionization can work for transition metal–benzene association. To test this possibility we performed first principles calculations of the potential energy curves for the model system $C_6H_6 + Me$ (Me = Ag, Cu, Au). It should be noted that associative ionization is a more energetically favorable channel for the formation of organometallic complexes than just association of a metal ion with a molecule. Indeed, the latter process demands an additional process of either radiative or thermolecular relaxation to occur in order to stabilize the complex $(M + Me)^+$. Otherwise, it will undergo rapid unimolecular decay.

2.3. Computational details

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 [7]. Real ion–electron interaction potentials were replaced by GGA-based

pseudopotentials (generated by the code of Fritz Haber Institute [12]), and by LSDA-based Troullier–Martins pseudopotentials [13]. The GGA is a priori considered as more accurate in binding energy calculations than the LSDA. However, the latter is essentially less computer time consuming. We will show below that the LSDA provides results with a sufficient level of accuracy for the purpose of the qualitative discussion.

In order to reduce the effect of the positive potential of atoms in adjacent supercells on the total energy in the case of the charged systems, a large cubic supercell of 18.55 Å (35 Bohr) was used in the calculation. The kinetic energy cutoff parameter for the plane waves was set at 25 hartree (1 hartree = 27.211 eV). The change of the cutoff energy from 25 to 40 hartree for a neutral silver atom in the cubic supercell of 13.25 Å (25 Bohr) results in changing the total energy by less than 1 mhartree. The excitation energies were obtained via Δself-consistent-field (ΔSCF) approach involving energy differences between DFT SCF calculations of ground and excited state configurations, which have different symmetries [14].

Before calculating the potential energy surfaces, we made some preliminary calculations for the metal atoms, a benzene molecule, and metal–benzene cations. The ionization potential of Ag was calculated to be 6.98 eV (7.59 eV is the experimental value [15]). The excitation energy for a $Ag(4d^9 5s^2)$ state is 3.96 eV, close to the experimental excitation energies for the multiplet states $^2D_{5/2}$ and $^2D_{3/2}$ and 4.3 eV, respectively).

We also performed the geometry optimization for C_6H_6 using the Broyden–Fletcher–Goldfarb–Shanno algorithm [16]. The computed C–C and C–H bond lengths (1.39 and 1.09 Å, respectively) are in good agreement with the experimental values (1.40 and 1.08 Å, respectively [17]). The geometry optimization for $(C_6H_6 + Ag)^+$ yields C_s symmetry with η^2 Ag^+ coordination. The binding energy in this coordination was calculated to be 1.93 eV, being by ~0.3 eV greater than the value obtained in [18]. Bauschlicher et al. [18] have found the same η^2 coordination at the minimal energy of the system. According to other works [19–21], minimal energy of $(C_6H_6 + Ag)^+$ corresponds to C_{6v} symmetry (η^6 coordination). Difference in the binding energies between η^2 and η^6 coordinations is rather small, being about 0.01 eV in [18]. This value in our calculations is 0.17 eV. Taking into account that equilibrium distances for the two coordinations are nearly the same, 2.27 Å (η^2) and 2.31 Å (η^6), we performed all further calculations in C_{6v} symmetry. It allowed the computer efforts to be reduced.

The geometry optimization of C_6H_6 in the LSDA gives practically no difference as compared to the GGA calculations. The LSDA produces same C_s symmetry for $(C_6H_6 + Ag)^+$, and, as it could be expected, overestimates the binding energy (2.57 eV). However, the ionization potential of Ag (7.17 eV) is closer to the experimental value (7.59 eV) [15], than that obtained in the GGA. The equilibrium distance in the LSDA is less by ~0.1 Å than the GGA's one. We assumed that the discrepancy in the binding energies cannot have an effect on our rather qualitative discussion. Therefore, as the first approach economizing computer time, we used the LSDA for benzene–gold and benzene–copper cations. The ionization potentials of Cu and Au obtained in LSDA are 7.65 and 8.83 eV, respectively, being within the range of usual accuracies (±0.5 eV) of such calculation methods. The experimental values are 7.74 and 9.24 eV, respectively [15].

2.4. Velocity distribution

Assuming that molecule and the metal atom sputter independently, the velocity distribution of the cationized molecules forming via associative ionization can be estimated from the formula

$$N(v) \propto \int \sigma_{ai}(v_{rel}; v_{th}) f_M(\boldsymbol{v}_1) f_{Me}(\boldsymbol{v}_2) \times \delta\left(v - \left|\frac{v}{v+1}\boldsymbol{v}_1 + \frac{1}{v+1}\boldsymbol{v}_2\right|\right) d\boldsymbol{v}_1\, d\boldsymbol{v}_2, \quad (4)$$

where $f_M(\boldsymbol{v}_1)$ and $f_{Me}(\boldsymbol{v}_1)$ are the velocity distribution functions for emitted molecules and metal atoms, respectively, $\delta(x)$ is the delta function, $v_{rel} = |\boldsymbol{v}_1 - \boldsymbol{v}_2|$ is still the relative velocity, v is the mass ratio of the molecule and the metal atom.

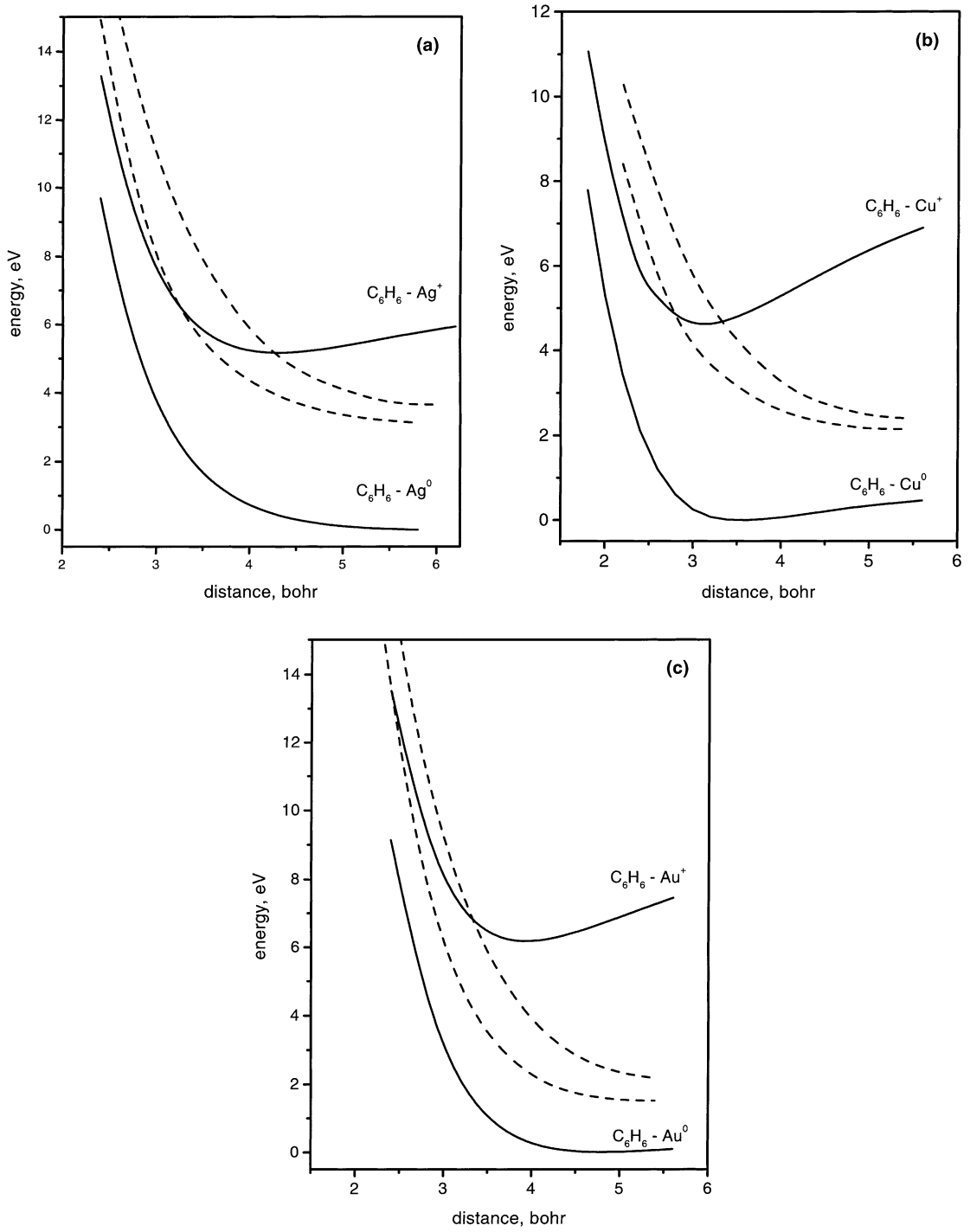

Fig. 2. The potential energy curves for the model systems C_6H_6 + Me (Me = Ag, Cu, Au). Solid curves correspond to the ground state (lower one) and the ionic state (upper). The energies of the excited states are shown with dashed curves (see text).

The summation should be made over all $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$, provided the condition $v_{\text{th}} \leqslant v_{\text{rel}} \leqslant v_{\max}$ is fulfilled, where v_{th} and $v_{\max}$ are the threshold and maximal values of the relative velocity, respectively.

3. Results and discussion

We calculated the potential energy curves for the neutral, charged, and excited $[(n-1)\text{d}^9 n\text{s}^2]$ system of $C_6H_6 + Me^{0,+,*}$, when the metal atom (Ag, Cu, Au) approaches the benzene ring along the C_6 symmetry axis.

The results of the calculations are shown in Figs. 2a,b, and c. The isoenergetic d orbitals of a Me $[(n-1)\text{d}^9 n\text{s}^2]$ are split into different potential energy curves when it approaches a benzene molecule. The upper potential energy curve of the $C_6H_6 + Me^*[(n-1)\text{d}^9 n\text{s}^2]$ 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. Adding a second electron to the s orbital of the metal atom increases the Pauli repulsion between the s metal electrons and the benzene valence electrons. As a result, these excited states are antibonding. Therefore, the energy gap between the excited states and the vacuum level (the ionic state) is getting narrower while the separation distance between the metal atom and the benzene molecule is decreasing. 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 due to the minimal derivative in the denominator of A factor (Eq. (3)). For $C_6H_6 + Au^+$, this crossing occurs on the repulsive side of the well, resulting in lower values of the cross-section. The curve originating from the $d_{xz}(d_{yz})$ orbital does not cross the ionic one in this case. In the case of silver, this 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), this does not change the qualitative picture.

The potential energy diagrams allow the energy threshold for reaction (1) to be estimated. It is seen that for the $C_6H_6 + Ag^*$ system, reaction (1) 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 benzene rings by interaction of the metal d orbitals with π orbitals of phenyl side groups [10], one should expect similar features in potential energy curves for any organic molecules containing phenyl groups. Taking this into account, we calculated the velocity distribution $N(v)$ of cationized polystyrene oligomers lifted up from the silver surface, using Eq. (4). The experimental distribution $f_{\text{Me}^*}(v_2)$ of sputtered metastable Ag^* atoms [11] was convoluted with the distribution of neutral polystyrene oligomer tetramers obtained by the MD simulation in [5]. 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 $\sigma_{\text{ai}}(v_{\text{rel}}; v_{\text{th}}) \times f_{\text{M}}(v_1) \times f_{\text{Me}^*}(v_2)$ over different orientations of v_1 and v_2 (different v_{rel}) leading to the same value of v. We used $v_{\text{th}} = 1.55$ km/s and $v_{\max} = 1.95$ km/s, which seem to be reasonable. The results of the calculations are shown in Fig. 3 in comparison with the experimental data. The velocity distributions of sputtered metastable Ag^* atoms and Ag^+ ions ($f_{\text{Me}^*}(v_2)$ and $f_{\text{Me}^+}(v_2)$, respectively) obtained in [11], 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

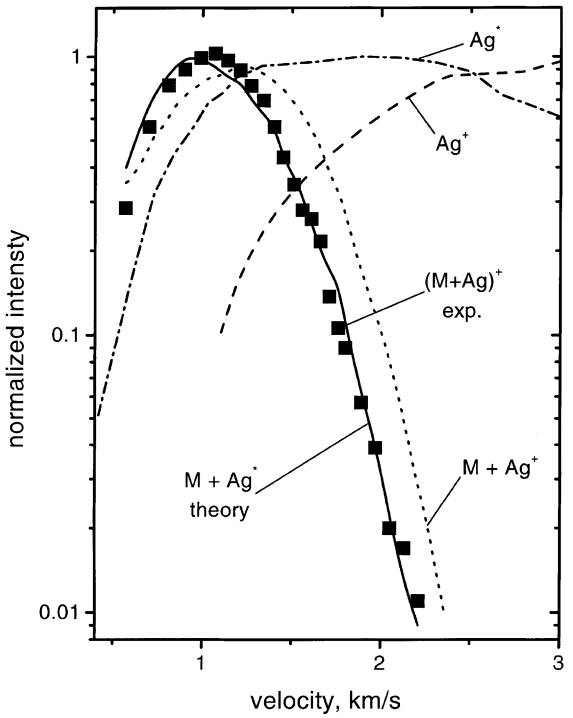

Fig. 3. The velocity distribution of sputtered polystyrene tetramers: squares are the experimental data [4], solid line is the theory taking into account the associative ionization process, dot line is the convolution of the distributions of neutral tetramers and Ag^+ ions. The experimental velocity distributions of Ag^+ and Ag^* are shown by dash and dash–dot lines correspondingly.

formed via associative ionization reproduces the experiment fairly well. At the same time, 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) gives the $(M + Me)^+$ spectrum shifted to higher energies as compared to the experimental one.

The relatively high yield of excited silver atoms, making it possible for them to associate with independently sputtered neutral polystyrene oligomers, is a consequence of the specific mechanism of atomic excitation in sputtering [22]. According to Wucher and Scroubek [22], excited Ag^* atoms are formed by fast resonant neutralization of ions containing a d-hole. d-Hole ions are the result of the collective electronic excitations induced by the interaction between projectile and recoil target atoms with conduction band electrons. Because d-band metal electrons are more localized than s electrons, the overlapping between s orbitals of an emitted d-hole ion and s orbitals of the metal will be larger than between d orbitals, favoring the electron capture into 4s orbital of the silver atom. Therefore, the mechanism resulting in high yield emission of electronically excited atoms, and, as a consequence, the proposed mechanism of phenyl group containing hydrocarbons cationization, should be specific for transition metal substrates.

Recent experiments [23] have demonstrated that using cluster ions instead of atomic ones as projectiles increases the degree of electronic subsystem excitation in the collision cascade region. As a consequence, the number of excited atoms should rise, resulting in increasing the yield of cationized molecules.

To conclude, it should be noted that determining relative contributions of the different processes to metal cationization requires additional experiments with the aim to find out an influence of the surface conditions on the probability of cationization. The associative ionization process occurring out of influence of the surface should be insensitive to variations of the substrate work function. At the same time, increasing the work function can create the conditions when the position of an 'active' energy level (ground or excited one) of the forming organometallic complex comes above the Fermi level. Electron transfer from the departing molecule (if it is close enough to the surface) into empty levels of the conduction band should essentially increase the yield of cationized molecules.

4. Conclusions

Making use of the density functional theory, the potential energy curves for the $C_6H_6 + Me$ system (Me = Ag, Cu, Au) being in the ground, ionic, and excited states of $(n-1)d^9ns^2$ electronic configuration were calculated. It is shown that when the constituents approach closely enough at some critical distance the potential energy curve of the excited state can cross the ionic curve. The ionic state of the system becomes thermodynamically

favored. As a result, the system undergoes autoionizing transition, thereby releasing the reaction energy. This process known as associative ionization is assumed to occur above the surface, taking place for any organic molecules containing phenyl rings.

The convolution of the experimental velocity distribution of sputtered excited silver atoms with the MD calculated velocity distribution of emitted polystyrene tetramers, taking into account the associative ionization cross-section, gives the $(M + Me)^+$ distribution close to the experimental one.

Additional experiments on finding out an influence of the surface conditions on the yield of cationized molecules are required to obtain a deeper insight into metal cationization in sputtering.

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