The Energetics of Formation of Doubly Charged Benzene Ions by Field Ionization

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Using a retarding potential energy analyzer the appearance potential of doubly charged benzene ions formed by field ionization was found to be 14.0 ± 0.3 eV. This appearance potential supplies evidence for the desorption of $C_6H_6^{++}$ ions in a chainlike structure from the surface of the field anode.

The energy distributions and appearance potentials of some singly charged ions generated by field ionization at Pt-tips have been discussed previously[1]. A retarding potential energy analyzer was used to obtain this information. The present communication reports on the energy analysis of doubly charged benzene ions, which is of particular interest for elucidating the energetics of formation of doubly charged ions by field ionization.

The result of the energy analysis of the M^+ and M^{++} benzene ions by a retarding potential energy analyzer is shown in Figure 1. The retardation curves display the dependence of the ion current transmitted through the retarding electrode on the voltage difference $(U_E - U_R)$ between the emitter and this electrode. The curves were recorded using a Pt-tip with a surface contaminated by prolonged FI of hydrocarbons. The M^{++} ion intensities obtained with clean Pt-tips were found to be extremely low. The dependence of the formation of the M^{++} ions on the surface condition of the emitter has already been pointed out[2].

For singly charged ions the AP is experimentally determined from the equation $AP = U_E - U_R + \Phi_R$, where Φ_R is the work function of the retarding electrode and $(U_E - U_R)$ is that voltage difference where the ion current through the retarding grid just vanishes. The AP of singly charged molecular ions is equal to the ionization potential of the molecule[1]. With $\Phi_R = 4.9$ eV an $AP(M^+)$ of 9.2 ± 0.1 eV is found for the M^+ benzene ions from Figure 1. This value agrees with the first ionization potential (I_1) of benzene within the experimental accuracy.

In analogy to the AP of singly charged ions the AP of doubly charged species may also be defined by the equation $AP(M^{++}) \equiv U_E - U_R + \Phi_R$. From several measurements at different Pt tips the AP of $C_6H_6^{++}$ benzene ions was found to be 14.0 ± 0.3 eV. This value is in agreement with that of Goldenfeld et al.[3], who employed a somewhat different method for the AP determination.

Goldenfeld et al.[4] suggested that the doubly charged ions are generated by post ionization of desorbing singly charged ions. Applying the definition of AP as stated above this model assumption leads to the equation $AP(M^{++}) = (I_1 + I_2)/2$ where I_2 is the second ionization potential of the molecule. From the measured $AP(M^{++})$ a value of 28 eV is derived for $I_1 + I_2$ of benzene. This value exceeds that of 26 eV[5] obtained by electron impact ionization, by 2 eV and is thus clearly outside the limits of accuracy of the measuring technique employed.

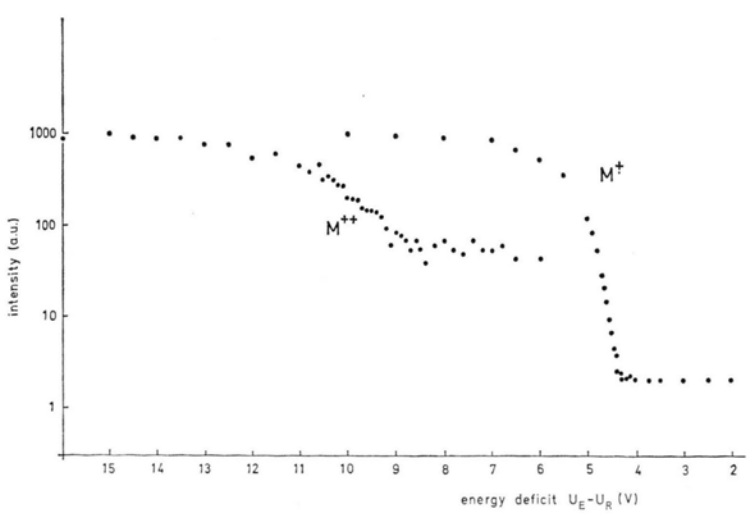

Fig. 1. Retardation curves of singly and doubly charged benzene ions.

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It has been demonstrated repeatedly [6, 7] that M^{++} ions are formed from singly charged ions field adsorbed on the emitter surface. The desorption is induced by the tunneling of a second electron into the emitter:

$$\text{a) } M \xrightarrow{-e} *M^{+} \qquad \text{b) } *M^{+} \xrightarrow{-e} M^{++} \qquad (1)$$

where $*$ represents a chemical bond between the molecular ion and the surface. It has already been pointed out [7] that step (1 b) is only possible when the $M^{+\cdot}$ ion is not adsorbed below the critical ionization distance for the transfer of the second charge. Therefore in the case of metal emitters it must be assumed that the surface is covered with an organic deposit. Due to the high field strength required for small ionization distances the generation of M^{++} ions on clean metal surfaces is not likely and it is questionable whether neutral molecules can reach the emitter surface under these conditions. In order to interprete the $AP(M^{++})$ value on the basis of the proposed model a potential energy diagram for the desorption of M^{++} ions is shown in Figure 2. Curves (a) and (b) represent the interaction energies of the $M^{+\cdot}$ and M^{++} ions with the emitter surface as a function of the distance x, assuming that no external field is applied and that the emitter surface is covered with organic deposit up to x_0. Due to the fact that the radicalic $M^{+\cdot}$ ions bind to radical sites of the surface their interaction is stronger than that of the M^{++} ions. Curves (a_F) and (b_F) arise from the original curves (a) and (b) on applying an external field. The diagram is shown for the limiting case that an adiabatic transition leads to the desorption of M^{++} ions at x_2 without thermal activation. Therefore the potential curve (b_F) of the M^{++} ion cross that of the $M^{+\cdot}$ ion at the minimum of (a_F). For the sake of simplicity the potential drop across the surface layer from $x=0$ to $x=x_0$ has been drawn linearly. The following equation can be derived from Figure 2:

$$e\,x_2\,F = I_2 - \Phi_E + \Delta E - e^2/x_2 \qquad (2)$$

where ΔE represents the binding energy of the $M^{+\cdot}$ ion to the surface at x_2 and e^2/x_2 stands for the image force potential of the M^{++} ion. For the critical retardation of singly charged ions formed at x_2 the following equation holds [8]:

$$AP(M^{+}) = U_E - U_R + \Phi_R = e\,x_2\,F + e^2/4\,x_2 + \Phi_E .$$

Replacing e by $2e$ the equation for the critical retardation of M^{++} ions is obtained:

$$\begin{aligned} 2\,AP(M^{++}) &= 2\,(U_E - U_R + \Phi_R) \\ &= 2\,e\,x_2\,F + 2\,\Phi_E + e^2/x_2 . \end{aligned} \qquad (3)$$

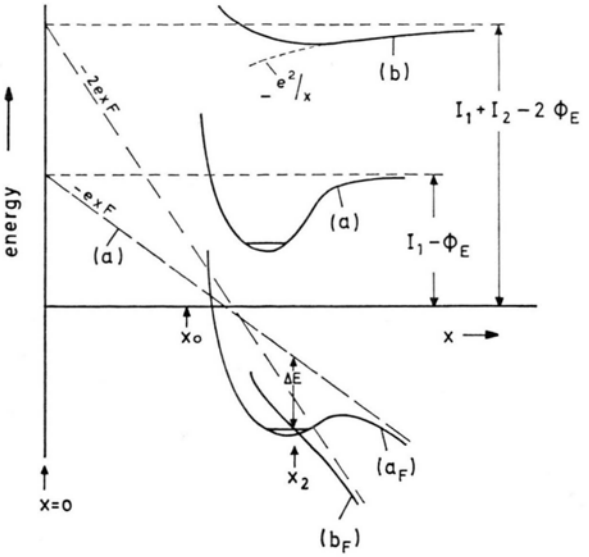

Fig. 2. Potential energy diagram of the interaction energies of $M^{+\cdot}$ and M^{++} ions with a metal emitter surface which is covered with an organic deposit up to the distance x_0. Curves (a) and (b) represent the interaction energies of $M^{+\cdot}$ and M^{++} respectively without an external field applied to the field anode whereas curves (a_F) and (b_F) show the influence of an external field an (a) and (b). I_1 and I_2 are the first and second ionization potential of M, and Φ_E is the work function of the emitter.

Combination of (2) and (3) yields

$$AP(M^{++}) = I_2 + \Delta E - e^2/2\,x_2 . \qquad (4)$$

This means that the AP of the doubly charged molecular ions is independent of the first ionization potential I_1. It is further remarkable that the $AP(M^{++})$ is dependent on the image force, which is in contrast to the case of singly charged ions whose AP is independent of any image force term. The same holds for the AP of M^{++} ions on the basis of the post ionization model mentioned. The term ΔE is assumed to be the sum of the purely chemical bond energy ΔE_B and the image force potential of the singly charged ion at x_2: $\Delta E = \Delta E_B + e^2/4\,x_2$. Thus Eq. (4) can be written in the form

$$AP(M^{++}) = I_2 + \Delta E_B - e^2/4\,x_2 . \qquad (5)$$

For benzene the second ionization potential $I_2 = 16.8$ eV was obtained using electron impact ionization and applies to the ring structure of $C_6H_6^{++}$ [5]. The low value for the $AP(C_6H_6^{++}) = 14.0$ eV can thus only be explained by assuming an open structure for $*C_6H_6^{+}$ and consequently also for $C_6H_6^{++}$ in the reaction step (1 b). Decomposition reactions of the $C_6H_6^{++}$ ions observed in the time range of 10^{-10} sec and at temperatures of about 600 °C [9] also confirm this conclusion. The rupture of the

benzene ring is probably induced by the reaction step (1 a).

The second ionization potential I_2 of the chain structure of $C_6H_6^{++}$ cannot be determined directly because of the additional two terms in Equation (5). However, the image force term should be small as the metal surface is covered with a dielectric layer. ΔE_B is also small (1 – 2 eV) if the desorption of the ion is accompanied by bond rearrangement in the organic surface layer [7]. Due to the fact that in general the AP is correlated with the minimum energy of formation of ions by FI the contribution of the last two terms in Eq. (5) should be in the order of 1 eV.

The mechanism of desorption of M^{++} ions shown in Fig. 2 refers to ions formed at the minimum ionization distance. There is a certain probability, however, that M^{++} ions are formed at larger distances $x > x_2$ leading to higher energy deficit with respect to the emitter potential. This effect together with variations of ΔE_B may be the main reason for the flatter retardation curves of M^{++} ions as compared to those of the M^+ ions shown in Figure 1.

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