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THRESHOLD PECULIARITIES OF ELECTRON-IMPACT DISSOCIATIVE IONIZATION OF POLYATOMIC MOLECULES: PYRIDINE

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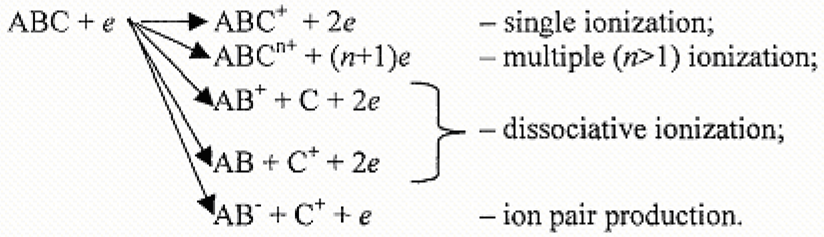
The new data on the electron-impact dissociative ionization cross sections for the deuterated and protonated pyridine molecules are reported. The experiment was carried out in crossed electron and molecular beams using the quadrupole mass-spectrometric technique.

Introduction

Electrons having acquired a certain kinetic energy can be scattered by any molecular target both with changing their energy (i.e. inelastically) and with no change in energy (i.e. elastically). Provided the kinetic energy of electrons exceeds some critical value, a certain part of target molecule can be excited and/or ionized. With further increase of the incident electron energy the qualitative and quantitative pattern of ionization (here we shall restrict ourselves just to that channel of electron-molecule interaction) becomes considerably complicated. In addition, provided it is allowed by the energy balance of scattering reaction, the ionized molecules may dissociate, giving a wide spectrum of interaction products (fragments).

Electron-impact ionization of polyatomic molecules may proceed through various channels each of them being characterized by its own contribution to the production of both neutral and ionized fragments. Thus, for the simplest case of a hypothetic polyatomic target – the triatomic ABC molecule – one may distinguish the following principal mechanisms resulting in the production of at least one ionized fragment [1]:



$$ABC + e \rightarrow ABC^{+} + 2e \quad \text{– single ionization;}$$
$$ABC + e \rightarrow ABC^{n+} + (n+1)e \quad \text{– multiple } (n>1) \text{ ionization;}$$
$$ABC + e \rightarrow AB^{+} + C + 2e, \quad AB + C^{+} + 2e \quad \text{– dissociative ionization;}$$
$$ABC + e \rightarrow AB^{-} + C^{+} + e \quad \text{– ion pair production.}$$

Below we shall deal with the consideration of only the single and dissociative ionization of the "parent" molecule, keeping in mind that in the case of a complex molecule the second reaction is accompanied by a large number of fragmentation channels. It is well known, that the molecular ion AB^{+} may decay with the formation of the ionized fragment both in even:

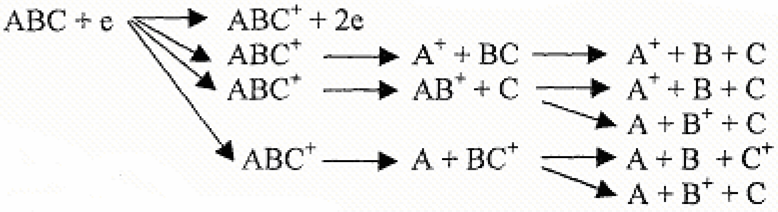
$$AB^{+} \rightarrow A_i^{+e} + B^{\cdot},$$

or odd:

$$AB^{+} \rightarrow A_i^{+o} + B$$

states. As is seen, here we assume that the parent ion is in the odd state and, respectively, the fragment parities are opposite. This situation occurs if the initial molecule is not a free radical [2]. The ion fragments of the A_i^{+o} type are called the initial ones and may be produced both in the ground and excited states, the decay of which, in turn, may produce the further fragments. These products are usually called the secondary (ternary, etc.) ion fragments.

Certainly, the secondary fragments can also fragmentate producing the ions of different parity. The most efficiently such "chain" processes occur during dissociation of complex organic molecules, however, it should be noted that the even fragments are more stable against fragmentation. Therefore, the basic fragmentation channels of the above hypothetic molecule ABC can be "visualized" as follows:



Strictly speaking, the production of other types of ionic fragments (e.g. multiple, associated, etc.) is also possible. In general, the dependence of the ion fragment yield on the scattered electron energy is a characteristic of the parent molecule state and, at the same time, of the probability of the process under study.

According to the Franck-Condon principle, the transition between the molecular states may take place at the internuclear distances corresponding to the ground vibrational level of the initial molecule. The minimal electron energy E_{min}, which is necessary for the dissociative ionization process resulting in the production of an ionic fragment A^+ of a kinetic energy T_{A+} is defined as:

$$E_{min} = E_{DAB} + E_{iA} + T_{A+}(m_{A+} + m_B)/m_B \ ,$$

here: E_{DAB} is the dissociation energy of the AB molecule; E_{iA} is the ionization energy of the A atom; m_A, m_B are the fragment masses, respectively.

The experimental study of the ionization processes induced by the low-energy electron impact is of particular interest in view of the possibility of determination of the appearance energies for different ionic fragments and the elucidation of the threshold regularities and peculiarities of ion production process [3]. The basic experimental requirement is the necessity to provide the ion yield intensity sufficient to detect relatively small amount of ions produced and to achieve the energy resolution sufficient to separate the appearance thresholds for different ions. In the case when the fragments differ in isotope composition [4], another requirement should be imposed – i.e. that of high mass resolution sufficient for product separation.

Experimental

The experiment was carried out using the mass-spectrometric apparatus described in detail elsewhere [4]. Here we should only recall the basic units of the apparatus and its principal parameters. The ions produced were mass separated and detected by means of a quadrupole mass-spectrometer MX 7303 operating with the own ion source providing the production of electron beams of 0.1–1.0 mA current (at the electron current stabilization mode) within the energy range of 0.5–100 eV. The energy resolution was not worse than ±0.5 eV, the mass determination accuracy was about ± 0.5 a.m.u. within the 1–500 a.u.m. mass range. The incident electron energy was varied in a stepwise mode, while the signal from the ion detector (channeltron) proportional to the ion fragment yield (ionization or dissociative ionization cross section) was accumulated in a cyclic mode in a digital form by a multichannel pulse analyzer. The resulting curves (i.e. the energy dependences of ion yield) were computer processed, averaged, smoothed and recorded in a final form.

The electron energy scale was calibrated by measuring the initial areas of ionization curves for Ar atom with subsequent double-differentiation, Marmet filtration and determination of a well known ionization threshold by fitting according to the Breit-Wigner formula [5]. To do this a certain controlled amount of Ar atoms was mixed to the molecular beam source receiver and the Ar^+ ion yield was measured with 0.26 eV energy step. This technique was also used to determine the appearance and threshold energies of the production of the initial molecule ionized fragments. The estimated error of the threshold (appearance) energy determination was not worse than the electron beam energy spread (± 0.5 eV FWHM).

Results and discussion

Figures 1, 2 show the energy dependences of dissociative ionization cross sections for the production of $C_4H_4^+/C_5H_5N$ and $C_4D_4^+/C_5D_5N$ ionized fragments of the initial pyridine molecules differing in the isotope composition, i.e. the protonated C_5H_5N and deuterated C_5D_5N molecules, within the energy range from the threshold up to 100 eV with the 1.3 eV energy step. As is seen, the general behaviours of the both curves are quite similar testifying the similarity of electronic structure of both initial molecules. In the case of the $C_4D_4^+$ ion production (Fig. 1) the dissociative ionization cross section increases at relatively low energies (below 30 eV) with saturation at higher energies. The $C_4H_4^+/C_5H_5N$ ion yield curve (Fig. 2) is characterized by a slight delay in the cross section rise, however the general shape resembles that in the case of deuterated target. Both curves reveal a distinct structure in the flat areas at intermediate electron energies, the origin of which is, certainly, associated with the inclusion of different channels of the production of ionized fragments due to the decay of different repulsive states of both neutral initial molecules and the relevant molecular ions. One should also take into account, that the production of ionized fragments may result not only from the direct dissociative ionization but also from the complicated predissociation and autoionization processes [1–3].

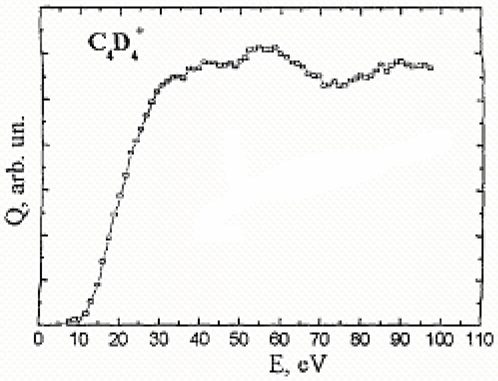


Fig. 1. Energy dependence of dissociative ionization cross section for the $C_4D_4^+/C_5D_5N$ ion fragment production

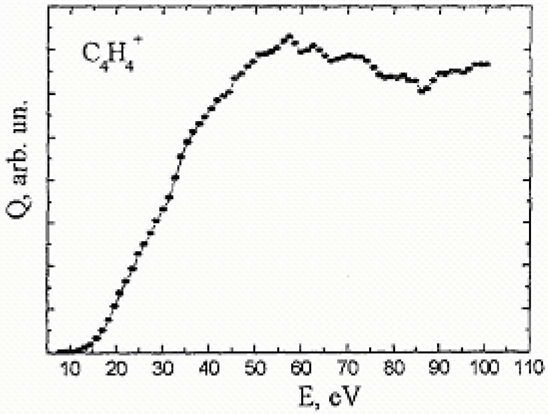


Fig. 2. Energy dependence of dissociative ionization cross section for the $C_4H_4^+/C_5H_5N$ ion fragment production

The near-threshold areas of dissociative ionization curves for both pyridine targets (see Fig. 3) measured with lower electron energy increment (0.26 eV) confirm the statement about the similarity in the dissociative ionization cross section behaviour. The most interesting fact is the clear difference in the appearance energies for both ionized fragments. The quantitative estimation of this effect is given in Table 1 as compared with known data for the protonated target.

Table 1. Appearance energies E_{ap} for ions produced by single and dissociative ionization of protonated and deuterated pyridine molecules

Ion fragment	E_{ap}, eV				
	Our data	[6]	[7]	[8]	[9]
$C_5H_5N^+$	9.84±0.05			9.25±0.50	9.85±0.10
$C_4H_4^+$	12.35±0.05	12.34±0.05	12.34±0.10	11.8±0.5	12.15±0.02
$C_4D_4^+$	11.07±0.05				

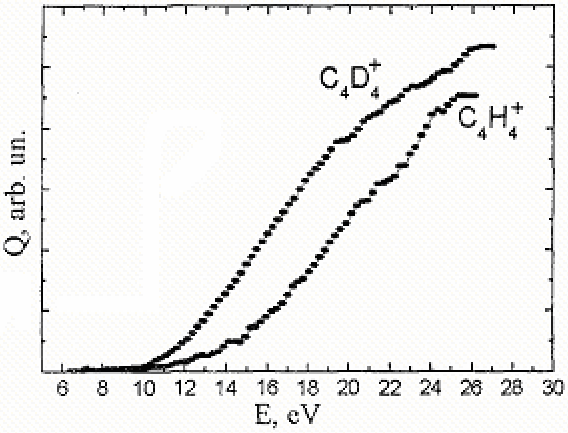


Fig. 3. Threshold areas of dissociative ionization functions for $C_4D_4^+/C_5D_5N$ and $C_4H_4^+/C_5H_5N$ ion production

The analysis of the entries of Table 1 shows an excellent agreement of our $C_4H_4^+/C_5H_5N$ data with those taken from other papers. Our appearance energy value of 12.35 eV almost coincides with that measured in [6,7] by electron-impact technique and slightly differs from photoionization data [8]. Moreover, our threshold energy of the production of the parent ion C_5H_5N (E=9.84 eV) agrees well with that of [9]. A striking difference in the appearance energies for $C_4H_4^+$ and $C_4D_4^+$ fragments (ΔE = 1.28 eV) is three times higher than the energy determination error and, thus, indicates a clear shift of the appearance energy for the deuterated fragment towards the lower energies. This fact confirms our earlier data on other isotope-differing species (see, e.g. [4]) and allows one to state that the introduction of the heavier component into the initial molecule (D instead of H) results in a distinct shift of the appearance energies for ionized fragments produced due to the dissociative ionization reaction.

The main reason for that effect is the perturbation introduced by the presence of the heavier atom(s) in the initial molecules. Most probably, the inclusion of deuterium causes strong vibrational excitation of the parent molecule that may result in the transition of the molecule to the excited repulsive state. The subsequent decay of such repulsive state, provided it is allowed by the energy balance of reaction, results in the appearance of the ionized fragment(s) at lower energy as compared to the protonated target This mechanism confirms our earlier assumption that the above difference in the appearance energies for deuterated and protonated ion fragments depends strongly mainly on the type of the fragment (i.e., secondary, ternary, etc.), not on its molecular mass. High fragmentation efficiency testifies to the fact that the produced ionized fragments have primarily the even parity (see above).

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ПОРОГОВІ ОСОБЛИВОСТІ ДИСОЦІАТИВНОЇ ІОНІЗАЦІЇ БАГАТОАТОМНИХ МОЛЕКУЛ ЕЛЕКТРОННИМ УДАРОМ:

ПІРИДИН

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Повідомляються нові дані про перерізи дисоціативної іонізації електронним ударом для дейтерованих і протонованих молекул піридину. Експеримент проводився у схрещених електронному та молекулярному пучках з використанням квадрупольної мас-спектрометричної методики.