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Abstract

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MASS-SPECTROMETRIC STUDY OF THE SPECTRAL DEPENDENCE OF THE PHOTOIONIZATION EFFICIENCY OF BENZENE DERIVATIVES

In a previous study by our laboratory of the first ionization potentials of a series of molecules by the photoionization method, the ionization-efficiency curves were studied in a small spectral region—several tens of angstroms—near the threshold for the appearance of ions (^1). The study of ionization-efficiency curves over a broader range of excitation energies, as the work (^2) has shown, can provide additional information on the structure of the molecule and of the ions arising upon its ionization.

In the investigation described here of the photoionization processes of gaseous molecules by photons with energies up to 11.7 eV, an apparatus was used that combined a factory-built MI-1305 mass spectrometer and an MV-3 vacuum monochromator (^3). The ion source of the mass spectrometer was modified in such a way that, in addition to ionization by electrons, it also made it possible to carry out ionization by photons. The vacuum monochromator, constructed in the laboratory according to the Seya-Namioka scheme (^4), was designed for the spectral region 2800-500 Å. The monochromator was equipped with a concave diffraction grating of 1200 lines/mm, with a radius of curvature of 0.5 m and concentration of the light in the first order. The size of the ruled surface was 40 × 50 mm.

In the present work, in order to increase the intensity of the ionizing radiation, the entrance and exit slits of the monochromator were widened to 0.40 and 0.35 mm, respectively. Under these conditions the resolving power of the monochromator was no worse than 10 Å, which in the ionization region (7-11 eV) corresponds to a spread of photon energies of 0.05-0.10 eV. The light source was a high-voltage hydrogen lamp (discharge current 1 A, with a voltage drop across the lamp of 500 V). The relative energy distribution in the lamp spectrum was obtained by measuring the fluorescence intensity of a sodium salicylate screen with an FEU-19 photomultiplier, on the assumption that the quantum yield is constant for all wavelengths (^5). In the spectral region 1650-1100 Å, depending on the intensity of the molecular bands of hydrogen, the flux of monochromatic photons crossing the ionization chamber of the mass spectrometer, with the

Fig. 1. Curves of the spectral dependence of the photoionization efficiency of toluene. 1 $-m/e = 92$; 2 $-m/e = 91.0$ $[92^+ \to 91^+]$

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stated monochromator slits, is estimated at 10^{11}-10^{13} photons per second.

The ion current at the output of the mass spectrometer was measured with an SI-01 ion counter having a sensitivity of 10^{-18} A. At a pressure of the vapors under study in the ion source of the order of 10^{-4}-10^{-5} mm Hg, the ion current at the output of the mass spectrometer in the case of molecular ions was 10^{-13}-10^{-15} A. Similar installations have been implemented in the works (ˆ26, ˆ6).

The photoionization of the following compounds was investigated: benzene (C_6H_6), toluene ($C_6H_5CH_3$), *p*-xylene ($C_6H_4(CH_3)_2$), aniline ($C_6H_5NH_2$), methylaniline ($C_6H_5NHCH_3$), dimethylaniline ($C_6H_5N(CH_3)_2$), and benzylamine ($C_6H_5CH_2NH_2$).

The spectral ionization-efficiency curves for toluene, dimethylaniline, and benzylamine are shown in Figs. 1-3. Along the ordinate is plotted the ratio of the photoionization current to the incident radiation flux; along the abscissa, the photon energy. The points on the graphs correspond to the mean values of three successive experiments, with an average deviation of about 10%.

The first ionization potentials, determined from the threshold of ion appearance, agree within the experimental error with those obtained earlier in our laboratory (1). In the case of benzene and its methyl derivatives (see, as an example, Fig. 1 for toluene), a sharp rise of the ionization-efficiency curve is observed near the threshold. The presence of a sharp threshold shows that, in the compounds indicated, the adiabatic ionization potential coincides with the vertical one, which indicates only a small change in internuclear distances upon ionization. The same is true for benzylamine (Fig. 3). In the case of aniline, methylaniline, and dimethylaniline, the rise of the spectral ionization-efficiency curves near the threshold occurs smoothly, so that the adiabatic ionization potential cannot be determined accurately with the monochromaticity of the photons used; the vertical ionization potentials correspond to the points of inflection of the initial portions of the curves and exceed the threshold for the appearance of molecular ions by 0.4-0.6 eV.

Fig. 1. Curves of the spectral dependence of the photoionization efficiency of toluene.
1 $-m/e = 92$; 2 $-m/e = 91.0$ $[92^+ \to 91^+]$.

For all the compounds studied, at photon energies exceeding the threshold for the appearance of molecular ions by 1.3 ± 0.2 eV in the case of methyl derivatives of benzene and by 1.1 ± 0.2 eV in the case of aromatic amines, a new increase in the photoionization yield is observed. It may be assumed that this

Fig. 2. Curves of the spectral dependence of the photoionization efficiency of dimethylaniline. 1 $-m/e = 121$; 2 $-m/e = 119$ $[121^+ \rightarrow 120^+]$

Figure 2: Fig. 2. Curves of the spectral dependence of the photoionization efficiency of dimethylaniline. 1 $-m/e = 121$; 2 $-m/e = 119$ $[121^+ \rightarrow 120^+]$

Figure 3

Figure 3: Figure 3

rise of the ionization-efficiency curves is associated with the removal of one of the π_2-electrons of the benzene ring, which occupy a deeper molecular orbital. In support of this interpretation, the following data may be cited. The first absorption bands of benzene in the region of 2600 and 2000 Å are due to transitions between the levels ${}^1A_{1g}, {}^1B_{2u}$ and ${}^1A_{1g}, {}^1B_{1u}$, respectively, the first transition being associated with excitation of one of the π_3-electrons from the highest occupied molecular orbital to the first vacant level, and the second with excitation of one of the π_2-electrons from a deeper molecular orbital to the same vacant level (7). The difference in the energies of the electrons on the molecular orbitals π_3 and π_2 for benzene is $5.96 - 4.71 = 1.25$ eV (8), which agrees well, within the experimental error, with the value obtained for the second rise both for benzene and for its derivatives. Apparently, for methyl- and even amino-substituted groups of the benzene ring, the energy interval between the molecular–

Fig. 2. Curves of the spectral dependence of the photoionization efficiency of dimethylaniline.
1 $-m/e = 121$; 2 $-m/e = 119$ $[121^+ \rightarrow 120^+]$.

the electron orbitals π_2 and π_3 is preserved, although the first vacant orbital may be noticeably displaced, as follows from the absorption spectra. Recently, the authors of [8], in the case of pyridine, found in the region of the first ionization continuum a Rydberg series with a limit near 10.3 eV. This series was tentatively interpreted by them as the excitation of one of the π_2-electrons from a deep molecular orbital. Since the electronic absorption spectra of benzene and pyridine show great similarity, and their ionization potentials differ little, this also confirms our assumption.

Fig. 3. Curves of the spectral dependence of the photoionization efficiency of benzylamine.
1$-m/e = 107$; 2$-m/e = 106$; 3$-m/e = 105$.

In the case of aromatic amines, with a further increase in the energy of the ionizing photons by 1.1-1.3 eV, a second, stronger rise of the ionization-efficiency curves is observed, corresponding to the formation of an ion in a new excited state. In the series aniline, methylaniline, dimethylaniline, a regular shift of the indicated second increase in photoionization efficiency into the long-wavelength region of the spectrum is observed. This transition is probably connected with the removal of one of the π_1-electrons occupying the deepest molecular orbital

Figure 4

Figure 4: Figure 4

of the benzene ring.

This assumption agrees with the results of [9], where the second ionization potential of benzene (11.49 eV), exceeding the first ionization potential by 2.24 eV, was explained by the removal of one of the most strongly bound π-electrons.

Fig. 4. Mass spectrum of benzylamine vapor at an ionizing-photon energy of 10.15 eV. $I_p = 8.64$ eV.

In the mass spectra of all the compounds studied, broad peaks are observed (occupying a region of 2–3 mass units), with an intensity at the maximum of 0.5–1% of the intensity of the peaks of the principal ions. This fact indicates that processes of decomposition of molecular ions take place in the mass spectrometer. Calculation of the effective mass by the formula

$$M_{\text{eff}} = \frac{m^2}{M},$$

where m is the mass number of the fragment ion and M is the mass number of the molecular ion, shows that dissociation occurs with the removal of one hydrogen atom according to the scheme

$$\mathrm{RH}^{+} \to \mathrm{R}^{+} + \mathrm{H},$$

where RH^{+} is the molecular ion and R^{+} is the same ion without one hydrogen atom. Such decomposition may be induced by collisions with neutral molecules [10], which apparently occurs in most cases. This explanation is confirmed by two facts: 1) the curve of the dependence of the efficiency of induced ionization on photon energy is similar

of the ionization-efficiency curve for the initial ions; 2) with an increase in pressure in the chamber of the mass spectrometer, the ratio of the intensities of induced and molecular ions increases. In the case of methyl- and dimethylanilines (Fig. 2), simultaneously with the formation of molecular ions in the second excited state (2.24 eV), a rather sharp increase in the intensity of broad fragment peaks is observed. At a photon energy of 11.5 eV the intensities of the broad fragment peaks amount to 4 and 7.5% of the intensity of the molecular ions for methylaniline and dimethylaniline, respectively. Thus, within a time of the order of several microseconds (the flight time of the ion from the accelerating plate of the mass-spectrometer ion source to the magnetic mass analyzer), some of the ions have time to dissociate.

In the case of benzylamine (Figs. 3 and 4), along with detachment of an electron from the molecule, dissociative ionization occurs according to the schemes:

$$C_7NH_9 \xrightarrow{h\nu} C_7NH_8^+ + H,$$

$$C_7NH_9 \xrightarrow{h\nu} C_7NH_7^+ + H_2.$$

The appearance potentials of the corresponding ions are 9.21 ± 0.07 eV and 9.35 ± 0.07 eV. Apparently, both fragments are formed from one state of the molecular ion. In addition to the peaks mentioned, in the mass spectrum of benzylamine at an excitation energy of 10.15 eV a number of diffuse peaks are observed: 91 (0.05%), 77 (0.08%), 60 (0.15%), 56 (0.13%), 26 (0.03%), and 16 (0.01%). The relative intensities of the corresponding peaks are given in parentheses, taking the intensity of the parent peak as 100%. The small yield indicates the secondary origin of these peaks. In work from our laboratory ([11]), photodissociation of benzylamine was found with formation of the radicals NH_2, $C_6H_5CH_2$, $C_6H_5CH_2NH$, and $C_6H_5CH_2N$, which were detected upon additional ionization by electron impact. Some of the peaks found in the present work may be attributed to the accompanying secondary process of photoionization of the radicals formed. Such a process requires a quadratic dependence on light intensity. The experimental dependence is intermediate between linear and quadratic, which may indicate the presence of several processes of secondary-ion formation.

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