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Abstract

Full Text

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DISTRIBUTION OF ELECTRONS BY KINETIC ENERGIES IN THE PHOTOIONIZATION OF METHYL DERIVATIVES OF BENZENE

In work (^{1}), using the photoionization of benzene and aromatic amines as examples, it was shown that measuring the distribution, by kinetic energies, of electrons ejected by light from organic molecules in the free state (in vapors at a pressure of 10^{-3}–$5 \cdot 10^{-3}$ mm Hg) can provide a number of additional data on the mechanism of the photoionization process. The present work gives the results of analogous measurements in the photoionization of methyl derivatives of benzene up to and including durene.

Fig. 1. Distribution of electrons by kinetic energies in the photoionization of toluene

These compounds have rather low ionization potentials (8-9 eV) (^{2}), as a result of which the maximum photon energy, limited by the transmission of the LiF window, exceeded the ionization potentials by 2-3 eV; moreover, the high values of the effective photoionization cross sections near the ionization threshold made it possible to obtain sufficiently large ionization currents at low pressures in the cuvette.

Figure 1 shows the electron energy-distribution curves for the photoionization of toluene (the curves are reduced to unit light intensity). As can be seen from the figure, when the energy of the quanta of the ionizing radiation is increased from values close to the ionization potential, the maximum in the distribution shifts toward higher energies up to a certain definite value, approximately 0.8 eV. With a further increase in the quantum energy, the maximum in the distribution changes its position only very slightly; however, a second maximum appears in the region of higher electron energies, which shifts monotonically toward higher energies as the quantum energy increases. Simultaneously with the appearance of the second maximum in the region of higher energies, the number of electrons having relatively small energies (0.1-0.3 eV) increases noticeably. This means that, beginning with some photon energy, along with the transition from the normal level of the molecule to the normal level of the ion, part of the photon energy is lost within the absorbing system; the magnitude of this loss, E_1^+, is given in Table 1. We associate this loss of part of the photon energy with excitation of the resulting positive molecular ion, which can take place by removal of an electron from a deeper molecular orbital. As a result, a slow electron is formed and an ion, one of whose electrons occupies not the lowest of the free levels.

Table 1

Values of the adiabatic ionization potentials (I_p), the first excited levels of their ions (E_1^+), the maxima of the first and second absorption bands (λ_1, λ_2), and the differences of their energies ($E_{\lambda_2} - E_{\lambda_1}$)

Compound	I_p, eV	E_1^+, eV	λ_1, Å	E_{λ_1}, eV	λ_2, Å	E_{λ_2}, eV	$E_{\lambda_2} - E_{\lambda_1}$, eV
Benzene	9.25	1.5±0.1	2550	4.85	2020	6.15	1.3
Toluene	8.82	1.3±0.2	2620	4.75	2050	6.05	1.3
o-Xylene	8.56	1.3±0.2	2610	4.75			
m-Xylene	8.59	1.3±0.2	2660	4.65			
p-Xylene	8.44	1.3±0.2	2660	4.65			
Mesitylene	8.41	1.3±0.2	2660	4.65			
Durene	8.05	1.3±0.2					
Aniline	7.69	1.2±0.1	2850	4.35	2330	5.35	1.0
Methylaniline	7.34	1.1±0.1	2880	4.30	2380	5.20	0.9
Dimethylaniline	7.14	1.0±0.1	2970	4.17	2500	4.96	0.8

In Table 1, together with the values of the adiabatic ionization potentials, the positions of the maxima of the first and second bands of the molecular absorption spectrum and the corresponding energies are also given. As is seen from the table, the experimentally found energy losses E_1^+ agree rather well with the differences of the quantum energies corresponding to the maxima of the second and first absorption bands. If one assumes ([3],[4]) that the first absorption band of benzene, ${}^1A_{1g} \rightarrow {}^1B_{2u}$, and of its derivatives is due to excitation of an electron from the highest filled molecular orbital to the nearest vacant one, while the second absorption band, ${}^1A_{1g} \rightarrow {}^1B_{1u}$, is due to excitation of an electron from a more deeply lying molecular orbital to the same vacancy, then such agreement speaks in favor of the mechanism of excitation of the positive ion by removal of a more strongly bound π-electron of the benzene ring. The

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

authors of work (5) arrive at a similar conclusion on the basis of an analysis of the vibrational structure of the absorption bands of benzene and deuterated benzene in the region of the first ionization continuum. For benzene, in addition to the previously known Rydberg series converging to the limit 9.247 eV (6), they found new series converging to two limits, 11.48 and 16.84 eV. They associate the second ionization potential, 11.48 eV, with removal of more strongly bound π-electrons; the third ionization potential, 16.84 eV, is explained by them as removal of σ-electrons of the C–C bond. The second ionization potential of benzene, determined spectroscopically, is 0.7 eV higher than the value of the second ionization potential following from our method (10.75 eV).

A characteristic feature of the distribution of electrons over kinetic energies in the photoionization of methyl derivatives of benzene is that, with the appearance of the second group of electrons, the maximum in the distribution—

does not shift sharply into the region of zero electron energies, as was observed in the photoionization of aromatic amines, but remains stationary near one value of the electron energy or else slowly shifts toward smaller values of the electron energy (*o*-xylene, Fig. 2).

Fig. 2. Distribution of electrons by kinetic energies in the photoionization of *o*-xylene

Fig. 3. Distribution of electrons by kinetic energies in the photoionization of durol

or degenerates into a flat top (durol, Fig. 3). This experimental fact can be explained by the phenomenon of pre-ionization, if one assumes the existence of a high excited level of the molecule, lying near the first excited level of the ion and capable of undergoing pre-ionization.

···with a transition to the normal level of the ion. The distribution of electrons emitted as a result of such a transition will not depend on the photon energy, since during its existence in the excited state (10^{-9} s) the molecule has time to reach an equilibrium vibrational state. The indicated phenomenon resembles the independence of the fluorescence spectrum of complex molecules from the wavelength of the exciting radiation; only in the present case, as a result of the transition, what occurs is not the emission of a photon, but the detachment of an electron with a definite kinetic energy. The slow shift of the maximum in the electron energy distribution upon photoionization of *o*-xylene as the photon energy increases after the appearance of the second group of electrons can be explained by an increase in the probability of transition from the excited level of the molecule to the first excited level of the ion. The existence of molecular levels of benzene lying above the normal level of the ion was found in (^{5}). In the case of benzene, even if a pre-ionization process occurs, its probability is small, since a sharp shift of the maximum toward the region of low electron energies is observed at photon energies of 10.7–10.8 eV. However, the heights of the first and second maxima in the case of benzene and its methyl derivatives are approximately the same, whereas for aromatic amines the maximum in the region of low energies is always much higher than all the other maxima. This indicates that, in the present case, the probability of the process leading to the appearance of the group of slow electrons is relatively small. It is likely that this fact, as well as the presence, near the threshold at about 10.7 eV corresponding to the transition to the first excited level of the benzene ion, of discrete absorption bands that may undergo pre-ionization, can explain the fact that it has not been possible spectroscopically to detect Rydberg series converging to this threshold.

Because of the opacity of the LiF window, it was not possible to use photon energies exceeding the ionization potential of benzene by 2.2 eV; however, in the case of *m*-xylene, mesitylene, and durene, at photon energies exceeding the ionization potential by 2.3–2.6 eV, a new sharp maximum appears in the region of zero electron energies. At the same time, the maximum corresponding to the transition to the first excited level of the ion turns into a flat minimum between the two principal maxima. This indicates that at higher photon energies (10.8–11 eV) the transition to the normal and second excited levels of the ions of the indicated compounds is considerably more probable than the transition to the first excited level of the ion. It should be noted that the distance from the normal to the second excited level, determined by us for *m*-xylene, mesitylene, and durene, agrees rather well with the difference, equal to 2.23 eV, between the second and first ionization potentials of benzene given in (^{5}), and coincides, within the errors of measurement, with the calculated value of the excited level of the benzene ion (^{7}), equal to 2.5 eV.

From the experimental results presented it follows that, by the method of measuring the energy distribution of photoelectrons, fine details of the ionization process can be detected.

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Note: Figure translations are in progress. See original paper for figures.