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Abstract

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Photoionization of Vapors of Certain Organic Compounds

In connection with investigations being carried out in our laboratory and in a neighboring laboratory on the electronic properties of aromatic compounds ([1]), especially on the surface of active adsorbents ([2]), it was necessary to obtain values of the energy required to detach electrons from the molecules of these compounds in the gaseous state. The present work was carried out in 1956; preliminary results were obtained in 1955.

For measuring the ionization potentials of organic vapors, the following photoelectric methods were used: 1) the capacitor method, 2) the method of an ionization chamber with gas amplification, 3) the Geiger-counter method.

The capacitor method, thanks to the work of Watanabe and his collaborators ([3]), has in recent years come into wide use. In this method the ionization cuvette is a vessel with two plane electrodes, to which a small voltage is applied (10–20 V). Light, passing between the electrodes, causes photoionization of the vapors under investigation. The ionization current has a magnitude of the order of 10^{-12}–10^{-4} A and is measured with an electrometric amplifier.

In the second method, which we were the first to apply for measuring the ionization potentials of vapors of organic compounds, the cuvette is an ionization chamber with a gas filling. Hydrogen or argon was used as the working gas. With a voltage between the electrodes of 300–500 V and a working-gas pressure up to 100 mm Hg, the ionization chamber gave an amplification of the order of 100–500. Thus, the sensitivity of this method is two orders of magnitude greater than that of the capacitor method.

The cuvette was designed so that it was possible simultaneously to measure the transmission spectra of the vapors under investigation by means of a photomultiplier irradiated by a fluorescent screen made of sodium salicylate.

The Geiger-counter method for studying photoionization was first applied in 1951 ([4]), but subsequently did not come into use, since the results of these studies agreed poorly with the results obtained by the capacitor method, in which secondary processes are reduced to a minimum. We constructed a cylindrical counter with an end window, whose cathode was a glass cylinder 6 cm in diameter coated with a semiconducting layer. As the working gas, in the self-quenching regime a mixture of argon with benzene or methane was used, and in the non-self-quenching regime—hydrogen or argon. This method is the most sensitive, since it makes it possible to record each act of ionization.

The source was a high-voltage hydrogen lamp, the light from which entered the ionization chamber through a vacuum monochromator with a concave—

···diffraction grating of 600 lines/mm, focal length 1 m, operating at normal incidence. The photoionization and transmission spectra were recorded with an ÉPP-09 self-recording instrument.

For benzene, toluene, and *p*-xylene, photoionization was measured by all the methods indicated above. It was established that all three methods give values of the ionization potentials, within the limits of experimental error, that agree with the data of other investigators from series in absorption spectra, which at present are the most reliable.

In measuring the photoionization potentials of low-volatility substances (quinone, phenylhydrazine, phenol, etc.), whose vapor pressure at a temperature of 18° is of the order of 10^{-2}–10^{-3} mm Hg, the Geiger-counter method was used, making it possible to record photoionization currents down to 10^{-19} A.

Fig. 1. Photoionization curves: *1*—toluene; *2*—tetramethylbenzene; *3*—aniline; *4*—dimethylaniline

Figure 1 shows several curves of the dependence of the photoionization current on the wavelength of the incident radiation. Along the ordinate are plotted the natural logarithms of the ratios of the photoionization currents to the number of absorbed quanta, in relative units. The ionization potentials were determined from the break in these curves, which corresponds to the 0—0 transition from the normal state of the molecule to the normal state of the singly charged ion. Ionization by smaller light quanta is caused by transitions from vibrational levels of the normal state of the molecule.

It is seen from Fig. 1 that the quantum yield of photoionization for aromatic amines at wavelengths near the ionization threshold is considerably smaller than for other compounds. According to the Franck-Condon principle, this should indicate that the internuclear distances in the molecules and in the corresponding ions differ appreciably in magnitude.

Fig. 2. Change in the photoionization potentials with the number of substituted hydrogen atoms in benzene (*1*) and in aniline (*2*)

Below is given a table of the first photoionization potentials obtained by us, Table 1.

Table 1

Photoionization of Vapors of Certain Organic Compounds

Compound	Photoionization potentials, Å	Photoionization potentials, eV	Error	Compound	Photoionization potentials, Å	Photoionization potentials, eV	Error
C_6H_6	1340	9.24	$±$0.02	$C_6H_5{-}CH_2{-}NH_2$	1434	8.64	$±$0.02
$C_6H_5CH_3$	1407	8.81	$±$0.02	$C_6H_5{-}OH$	1457	8.52	$±$0.02
o-$C_6H_4(CH_3)_2$	1447	8.56	$±$0.02	Naphthalene	1523	8.14	$±$0.02
m-$C_6H_4(CH_3)_2$	1444	8.59	$±$0.02	$C_6H_5{-}HCO$	1292	9.60	$±$0.02
n-$C_6H_4(CH_3)_2$	1469	8.44	$±$0.02	Quinone	1281	9.67	$±$0.02
$C_6H_3(CH_3)_3$	1474	8.41	$±$0.02	$NH_2{-}NH_2$	1297	9.56	$±$0.02
$C_6H_2(CH_3)_4$	1540	8.05	$±$0.02	(H_2CO) monomer	1137	10.90	$±$0.03
$C_6H(CH_3)_5$	1565	7.92	$±$0.02	$(H_2CO)_2$ dimer	1179	10.51	$±$0.03
$C_6H_5{-}NH_2$	1612	7.69	$±$0.02	$(CH_3)_2C{=}O$	1280	9.71	$±$0.03
$C_8H_5{-}NH{-}NH_2$	1623	7.64	$±$0.02	$CH_3HC{=}O$	1215	10.20	$±$0.03
m-Toluidine	1652	7.50	$±$0.02	$CH_3C_2H_5C{=}O$	1300	9.55	$±$0.03
$C_6H_5{-}NH{-}CH_3$	1689	7.34	$±$0.02	$CH_3C_3H_7C{=}O$	1308	9.47	$±$0.03
$C_6H_5{-}N(CH_3)_2$	1734	7.14	$±$0.03	$(C_2H_5)_2O$	1287	9.65	$±$0.03
				$CH_3C_4H_9OC{=}O$	1296	9.56	$±$0.03

Figure 2 presents the dependence of the ionization potential of benzene derivatives (curve 1) and aniline derivatives (curve 2) on the number of hydrogen atoms replaced by the $-CH_3$ group. The smooth decrease in the ionization potentials with increasing number of replaced hydrogen atoms is associated with an increase in the density of the electron cloud in the benzene ring.

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named after A. A. Zhdanov

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