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Abstract

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IONIZATION POTENTIALS OF ORGANIC DYES AND A NUMBER OF COMPLEX MOLECULES IN THE GAS PHASE

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Most complex organic compounds and, in particular, dyes at ordinary temperature have an extremely low vapor pressure. For this reason there are no data on the first ionization potentials of many important classes of compounds in the gaseous state. To obtain the first adiabatic ionization potentials of molecules of a number of volatile compounds, we used the photoionization method (^{1}). To obtain the ionization potentials of sparingly volatile compounds, the same method was used in the present work, with the difference that the ionization cuvette (40 mm in diameter, 50 mm long) was made of metal and was demountable. All seals and insulators for the leads were made of fluoroplastic-4. The design of the cuvette made it possible to heat the substances under investigation up to 250°.

Table 1

Absorption bands and first ionization potentials of some dyes in the gaseous phase

Dye	λ_1	λ_2	I_p	$I_{p-\lambda_1}$	$I_{p-\lambda_2}$
Rhodamine 6Zh	53002.55	–	7.26	4.9	–
Indigo red	53902.3	49752.5	7.32	5.0	4.8
Indigo blue	60482.07	–	7.17	5.1	–
Merocyanine			7.35*		
Quinolinium blue (ethylcyanine)	55262.3	51462.45	7.35*	5.05	4.9
Pinacyanol	61002.05	–	7.25**	5.2	–

* On the red side there is a region with a small ionization yield down to 7.2 eV.
** The region with a small ionization yield continues down to 7.1 eV.

The values of the ionization potentials I_p, obtained earlier, and the new data are collected in Tables 1 and 2*. Since in the present work the amount of absorbed radiation was not measured and, in order to increase the sensitivity, wider slits were used in the monochromator (the resolving power was about 5 Å), for most of the compounds measured no bends were found on the ionization curves, and the (I_p) values in Tables 1 and 2 correspond to the photoionization threshold. As follows from previous work (^{1}), these values should be several hundredths of an electron volt lower than the adiabatic ionization potentials. The error in determining the red limit of photoionization did not exceed 0.03 eV. Tables 1 and 2 also give the positions λ_1, λ_2, λ_3 of the first absorption bands of the compounds in neutral hydrocarbon solvents, expressed in angstroms and electron volts, taken from the literature (see, for example, (^{2})). It is known that the position of the same bands in the gaseous phase differs little from those given here. The last three columns give the differences between the ionization potentials and the positions of the corresponding absorption bands, in eV.

Tables 1 and 2 show that, in the series of compounds presented, there is a regular decrease in the ionization potentials simultaneously with a shift of the first absorption bands into the long-wavelength part of the spectrum. An exception is acetophenone, for which I_p is somewhat higher than in benzaldehyde. Within a single class of compounds, the differences between the ionization potentials and the corresponding absorption bands remain constant to within 0.1-0.2 eV. This empirical regularity, with due caution, may be used to estimate ionization potentials from the positions of the first absorption bands for higher members of a series, if the ionization potentials of the first members of the series have been reliably determined. However, as follows from the data presented, $I_p - \lambda_1$ differs substantially for different classes of compounds, by as much as 2 eV. Thus, for the series of linear polycyclic hydrocarbons from benzene to naphthalene this difference is 4.1-4.3 eV, whereas for quinone and anthraquinone it is 6.1-6.3 eV. Noteworthy is the fact that the ionization potentials of the various dyes listed in Table 2 differ very little from one another and give a red photoionization limit only slightly greater than 7 eV. Similar phenomena were observed earlier in work (^{3}), where it was shown that the sharp increase in photoemission for various classes of dyes lies near 2000 Å, which corresponds to a photon energy of approximately 6 eV.

It is of interest to compare the results obtained with the indirect determination of the ionization potentials of polymethine dyes proposed recently by Scheibe et al. (^{4}). The authors of these works find that the absorption bands in the spectra of polymethine dyes form series that obey the Rydberg formula well. They assume that the first excited level of the dye molecule is hydrogen-like, lying

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* Diploma student V. I. Kleimenov took part in the measurements.

3.4 eV below the ionization limit, as in the hydrogen atom. In their view, only in the ground level is there a conjugated electronic π-system. In the molecule, already at the first excitation level, complete disruption of conjugation occurs, and the excited electron is situated only in the field of the positive molecular skeleton, resembling an electron in the hydrogen atom. Hence, for calculating the ionization potentials I_p of compounds, a very simple formula is proposed: $I_p = E + 3.4$ eV, where E is the energy difference between the ground and first excited levels.

Hydrogen-like character of series of absorption bands has been established for many classes of organic compounds only in the vacuum-ultraviolet region, i.e., at excitation energies greater than 6 eV. This serial regularity has been successfully used to determine the values of the first adiabatic ionization potentials of a number of classes of compounds. The ionization-potential values obtained by the spectroscopic method agree well with the structure of the molecules and with the values of I_p determined by the direct method of photoionization. However, from these same works of Price and Walsh (^{5}) it follows that even in such simple compounds as aliphatic hydrocarbons and alkyl derivatives of benzene, the first members of the Rydberg series are shifted so much that they are difficult to identify; i.e., hydrogen-like character is valid only for the higher members of the series. In other works (^{6}), for these same compounds it was shown that, when the ground state of the molecule is lowered, all terms are lowered; this lowering increases with increasing number and, in the limit, tends toward the magnitude of the lowering of the normal level of the ion, i.e., in higher members of homologous series the convergence of bands to the limit should occur more rapidly than in the first members. We have shown (^{1}) that this regularity can be extended to other benzene derivatives, such as aromatic amines, phenols, etc. Finally, in the work of Price and Walsh (^{7}) it was clearly shown that in the series ethylene, butadiene, and hexatriene the shift

Table 2

Absorption bands and first ionization potentials of complex organic molecules

Compound	λ_1	λ_2	λ_3	I_p	$I_p - \lambda_1$	$I_p - \lambda_2$	$I_p - \lambda_3$
Benzene	25504.9	19806.25	18006.9	9–24	4.3	3.0	2.3
Naphthalene	31404.0	27504.5	22005.65	8.14	4.15	3.65	2.5
Anthracene	38003.26	–	25005.0	7.38	4.1	–	2.4
Naphthacene	4800	–	–	6.88	4.3	–	–
Pyridine	25005.0	19006.4	–	9.40	4.4	3.0	–
Quinoline	31104.0	27504.5	–	8.30	4.3	3.8	–
Acridine	34703.55	25204.9	–	7.78	4.23	2.9	–
Quinone	42003.35	30004.7	25005.65	9.68	6.3	5.0	4.0
Anthraquinone	44003.2	32304.4	–	9.34	6.1	5.0	–
α-Naphthylamine	32003.9	24005.2	–	7.30	3.4	2.1	–

Compound	λ_1	λ_2	λ_3	I_p	$I_p - \lambda_1$	$I_p - \lambda_2$	$I_p - \lambda_3$
β-Naphthylamine	34003.7	28004.4	22005.7	7.25	3.55	2.85	1.55
Benzaldehyde	32803.8	28004.45	24405.1	9.60	5.8	5.15	4.5
Acetophenone	31903.9	27804.45	24405.1	9.65	5.75	5.2	4.55
Benzophenone	33003.75	–	25204.9	9.45	5.7	–	4.55

the band N—V_1 toward the long-wavelength side of the spectrum occurs 1.2 times faster than the decrease in the ionization potentials.

It remains an open question whether the serial regularity established by Scheibe pertains to the gaseous medium or to a molecule located in a medium with a large value of the dielectric constant, which, as is known, reduces the magnitude of the electron detachment energy. From this point of view, taking into account the relationship established above between I_p and E, the ionization-potential values for dyes given by Scheibe cannot be regarded as reliable. Our measurements of the photoemission of electrons from compact dye layers have shown that the value of the work function for these molecular systems, for a wide variety of dyes, is not less than 6 eV.

The ionization potentials of a number of dyes and other complex molecules presented in this work indicate that the ionization potentials calculated by the formula proposed by Scheibe are in most cases greatly underestimated and should be used with caution.

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