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Abstract

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DEPENDENCE OF THE ABSORPTION SPECTRA OF VAPORS OF ORGANIC COMPOUNDS ON CONCENTRATION

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In studies (^{1,2}) of the fluorescence of β-naphthylamine vapors, one of us established a dependence of the absorption coefficient of the vapors on their vapor pressure. Subsequently, in studying the absorption and fluorescence spectra of the family of substituted phthalimides ($^{3-5}$), we found no substantial changes in the absorption spectra of the vapors as a function of their pressure, which varied within comparatively narrow limits near 0.1 mm Hg. At the same time, together with A. A. Solodovnikov (^{6}), we established that the addition of helium to vapors of 3-dimethylamino-6-aminophthalimide causes a decrease in their absorption coefficient, with peculiar dependences on the vapor pressure of the phthalimide, analogous to those that had been found in (^{2}) for β-naphthylamine vapors. This result shows that an interaction exists between molecules of 3-dimethylamino-6-aminophthalimide, manifested at considerably lower vapor pressures than those used in the absorption measurements in (^{4,5}). In this connection, it was of interest to investigate the dependence of the absorption spectra of vapors of a series of aromatic compounds on their concentration, varied over wide limits.

As the objects of study, compounds were selected which, according to the classification proposed in (^{3,7}), belong to different categories, namely: anthracene (I), 3-acetylaminophthalimide (II), 3-aminophthalimide (III), and 3-dimethylamino-6-aminophthalimide (IV). The molecules of substance I, which has spectra with a partially allowed structure, belong to simple polyatomic molecules. Substances II, III, and IV were found (^{4,5}) to have continuous spectra. They belong to complex polyatomic molecules; moreover, from II to III and IV there is a transition from modulation spectra to quenching spectra.

The measurements were made with the apparatus described in (^{5}); for high concentrations (vapor pressure $\sim$ 5—0.1 mm Hg), quartz cuvettes of length 2 and 40 cm were used, while for measurements at lower concentrations (vapor pressure 10^{-1}—10^{-3} mm Hg) a multiple-pass cuvette was constructed according to White' s scheme (^{7}), improved by Bernstein and Herzberg (^{8}), allowing measurements to be carried out with an optical path length up to 40 m. The radius of curvature of the cuvette mirrors was 1 m. The vapor pressures of the phthalimide derivatives as a function of temperature were determined by one of us (^{9}).

The main results of the investigations are presented in Fig. 1, in which the relative values of the absorption coefficient, $\varepsilon_{\text{rel}} = \varepsilon/\varepsilon_{\text{max}}$, are plotted along the ordinate axis. The concentration values to which the curves in Fig. 1 refer, as well as the values of the intensities of the bands, are given in Table 1.

It follows from the figure that, when the concentration is varied within a certain interval, changes occur in the form of the absorption spectra; moreover, the character of the changes and, chiefly, the region of concentrations in which these changes occur depend on the nature of the molecules being studied.

Let us consider the character of these changes using as an example the vapors of 3-aminophthalimide, investigated over the widest concentration interval ($60 \cdot 10^{15}$—$0.038 \cdot 10^{15}$ molecules/cm^3, or 3.6—$1.9 \cdot 10^{-3}$ mm Hg). A decrease in concentration from $60 \cdot 10^{15}$ to $2.5 \cdot 10^{15}$ molecules/cm^3 does not cause any changes

Table 1

Substance	Vapor T, °K	Pressure, mm Hg	Concentration $C \cdot 10^{-15}$, molecules/cm^3	Optical path length, cm	Designations in Fig. 1
I. Anthracene	493	$1.85 \cdot 10^{-1}$	3.6	42	a
I. Anthracene	493	$1.74 \cdot 10^{-1}$	3.4	42	
I. Anthracene	493	$9.3 \cdot 10^{-2}$*	1.8	42	
I. Anthracene	493	$4.8 \cdot 10^{-2}$	0.95	42	
II. 3-acetylaminophthalimide	498	$3.25 \cdot 10^{-1}$	6.3	42	a
II. 3-acetylaminophthalimide	498	$8.6 \cdot 10^{-2}$	1.6	42	
II. 3-acetylaminophthalimide	498	$3.6 \cdot 10^{-2}$	0.7	42	
II. 3-acetylaminophthalimide	498	$2.6 \cdot 10^{-2}$*	0.5	42	
II. 3-acetylaminophthalimide	498	$2 \cdot 10^{-2}$	0.39	42	
III. 3-aminophthalimide	518	3.58	60	2	a
III. 3-aminophthalimide	493	$1.25 \cdot 10^{-1}$*	2.55	42	a
III. 3-aminophthalimide	493	$6.2 \cdot 10^{-2}$	1.26	42	

Substance	Vapor T, °K	Pressure, mm Hg	Concentration $C \cdot 10^{-15}$, molecules/cm^3	Optical path length, cm	Designations in Fig. 1
III. 3-aminophthalimide	463	$2.6 \cdot 10^{-2}$	0.47	400	
III. 3-aminophthalimide	463	$1.2 \cdot 10^{-2}$	0.25	400	
III. 3-aminophthalimide	463	$5.2 \cdot 10^{-3}$	0.105	1600	
III. 3-aminophthalimide	463	$3.15 \cdot 10^{-3}$*	0.065	2000	
III. 3-aminophthalimide	463	$1.9 \cdot 10^{-3}$	0.038	3200	
IV. 3-dimethylamino-6-aminophthalimide	503	$1.17 \cdot 10^{-1}$	2.26	42	
IV. 3-dimethylamino-6-aminophthalimide	450	$5.2 \cdot 10^{-3}$	0.11	1600	
IV. 3-dimethylamino-6-aminophthalimide	450	$3.2 \cdot 10^{-3}$	0.07	1600	

* Pressures at which changes in the spectra cease.

in the shape of the spectrum. Further lowering of the concentration to $0.1 \cdot 10^{15}$ molecules/cm^3 is accompanied by a slight narrowing of the band and its gradual shift toward higher frequencies, and then by the appearance of traces of the vibrational structure of the spectrum (a break in the curve), which, upon further lowering of the concentration from $0.065 \cdot 10^{15}$ to $0.038 \cdot 10^{15}$ molecules/cm^3, does not become sharper—the appearance of the spectrum ceases to depend on concentration. Thus, the range of concentrations of 3-aminophthalimide vapor in which the change in the shape of the spectrum takes place lies approximately in the interval $0.1 \cdot 10^{15}$—$1 \cdot 10^{15}$ molecules/cm^3.

The other substances were investigated over a narrower range of concentrations; nevertheless, from the data given it follows that, in the case of 3-acetylaminophthalimide, the cessation of changes in the shape of the spectrum upon lowering the pressure occurs at a concentration of $0.5 \cdot 10^{15}$ molecules/cm^3, and in the case of anthracene, at a concentration of $1.8 \cdot 10^{15}$ molecules/cm^3.

Thus, on passing from anthracene to 3-aminophthalimide, a lowering is observed

Fig. 1

Figure 1: Fig. 1

in the lower limiting concentration at which changes in the shape of the spectra begin, i.e., intermolecular interactions become stronger with an increase in the degree of intramolecular interactions (4,5).

The shape of the spectra of the 3-dimethylamino-6-aminophthalimide investigated by us does not change even when the concentration is lowered to $0.07 \cdot 10^{15}$ molecules/cm^3. It follows from this that either changes in the spectrum occur at still lower concentrations than in the case of 3-aminophthalimide, or, in the case under consideration, these interactions cannot influence the shap-

of the spectral band, representing an attenuation spectrum, whose mechanism of formation is apparently different from that for substances I, II, III (10). The second assumption seems more probable, since the effect of helium on the spectra of 3-dimethylamino-6-aminophthalimide shows (6) that the interactions considered here do occur in this case.

Fig. 1

In our studies (4,5) of the spectra of substituted phthalimides, which were carried out at vapor pressures from 0.1 to 0.4 mm Hg, it was concluded, on the basis of the independence of the vapor absorption spectra from pressure, that the continuous character of the spectra obtained was due in its origin exclusively to intramolecular interactions. The results of the present study show that, in reality, the form of the spectra of the first members of the series investigated is determined not only by intra-, but also by intermolecular interactions. As the degree of intramolecular interactions increases, according to the degree by which the substances were arranged in a series in (4), the influence of intermolecular forces on the spectra weakens.

Several preliminary remarks should be made concerning the nature of the intermolecular interactions under consideration.

It follows from the data presented that the intermolecular interactions causing a change in the form of the spectra occur either at large distances of the order of hundreds of angstroms, or else—if the corresponding perturbations of the molecular systems occur upon close collision—the perturbed state of the molecule is preserved for 10^{-7}–10^{-5} sec.

after collision. We do not have data that would allow us to choose between these two extreme points of view.

It should be noted that the assumption of collisions between the molecules under study leads to changes in their structure that persist for a relatively long time interval, of the order of 10^5 sec., equivalent to the supposition that the transition of a molecule from the perturbed state to the normal state is associated with overcoming some potential barrier.

The assumption of interaction at large distances is equivalent to the supposition that relatively weak intermolecular interactions can cause such changes in the nuclear structure of the molecule, or in the state of its electron shell, as lead to a noticeable change in the character of the electronic spectra. Calculations carried out by Coulson and Davies [11], and also by Haugh and Hirschfelder [12], using the "monopole" method proposed by London [13], show that, in the case of extended molecules with conjugated bonds, the interactions between π-electron shells constitute the predominant part of the dispersion forces. One may therefore expect that, in our case, intermolecular interactions cause certain displacements of the mobile π-electron shells. These displacements may be the cause of the broadening of the spectra.

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