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D. N. Shigorin, N. A. Shcheglova, and N. S. Dokunikhin

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structural formulas I-IV

Figure 1: structural formulas I-IV

Abstract

Full Text

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MANIFESTATION OF THE AUTONOMY OF ELECTRONIC GROUPINGS IN THE LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

(Presented by Academician A. N. Terenin on 9 XI 1960)

A quantum-mechanical consideration of the electronic levels of simple molecules with multiple bonds has shown that the excitation process is associated with the participation of the π- and p-electrons of chromophoric groups ($>C=C<$, $C=O$, etc.), whose energy state is influenced by substituents (auxochromes). Thus, in the case of molecules containing $C=C$ bonds (ethylene, etc.), the most probable transition is the $\pi \to \pi^*(N \to V)$ transition: $\sigma^2\pi^2 \to \sigma^2\pi\pi^*$. In compounds containing chromophores with heteroatoms ($C=O$; $C=S$; NO_2; $-N=N-$, $-N=O$, etc.), the most probable transition giving long-wavelength absorption is the $n \to \pi^*(N \to Q)$ transition, when one p-electron from the nonbonding orbital of the heteroatom is transferred to the antibonding π-orbital of the multiple bond: $\sigma^2\pi_x^2Y^2 \to \sigma^2\pi_x^2Y\pi_x^*$.

Consequently, chromophores are defined as groups of atoms permanently linked by mutual interaction with other parts of the molecule and bearing the principal responsibility for the electronic excitation of the entire molecular system.

Does the autonomy of electronic groupings (chromophores) manifest itself both in absorption and in emission (luminescence spectra)? In order to solve this problem, we studied the luminescence spectra of a whole series of complex molecules:

(I) (II) (III) (IV)

(anthraquinone, thioindigo and their derivatives, etc.) in dilute solutions of n-paraffin hydrocarbons ($C = 10^{-4} \div 10^{-5}$ mole $\cdot$ l^{-1}) at $T = 77^\circ$ K. The results of the investigations are given in Fig. 1.

Analysis of the quasilinear luminescence spectra obtained by us for anthraquinone (II), α- and β-monohalogen derivatives of anthraquinone; α-methyl-, α-phenyl-, α-methoxyanthraquinone; phenanthrenequinone (III), anthrone (IV), and others ([2–4]), shows that the intense bands of the spectra, as well as all correspondingly taken weaker bands, are separated from one

Figure 1. Luminescence spectra of anthraquinone derivatives in heptane at 77°K.

Figure 2: Figure 1. Luminescence spectra of anthraquinone derivatives in heptane at 77°K.

chemical structures labeled (V), (VI), (VII), and (VIII)

Figure 3: chemical structures labeled (V), (VI), (VII), and (VIII)

another by a distance averaging 1664 cm^{-1} (for III and IV, 1686 cm^{-1}), which corresponds to the frequency of the valence vibration of the chromophoric group C = O in the ground electronic state. Consequently, in the electronic-vibrational spectra of the indicated group of compounds, the vibrational structure is characterized by the valence vibrations of the chromophoric group C = O, which bears the principal responsibility for the electronic excitation of the system ($n \rightarrow \pi^*$ transition)

Fig. 1. Luminescence spectra of anthraquinone derivatives in heptane at 77°K.
a $-\lambda_{Hg} = 313$ m , *b* $-\lambda_{Hg} = 365$ m : 1 $-\alpha$-chloroanthraquinone; 2 –1,8-dioxyanthraquinone; 3 –1,5-dioxyanthraquinone; 4 –1,4,5,8-tetraoxyanthraquinone (*A* –emission, *B* –absorption), 5 –anthrone (in heptane), the short-wavelength part of the spectrum with $\lambda_{initial} = 4043$ Å is not shown in the photograph; 6 –phenanthrenequinone, 7 –monobrommesobenzanthrone.

not only in absorption spectra, but also in luminescence spectra. For the quasi-line spectra of anthraquinone and a number of its derivatives, the frequencies of totally symmetric vibrations of the condensed aromatic system, analogous to anthracene, are not characteristic. On the contrary, in the line luminescence spectrum of anthracene (I), according to E. V. Shpol'skii and co-workers ([1]), the fine vibrational structure is characterized by the frequencies of totally symmetric vibrations of the condensed aromatic system responsible for the electronic excitation ($\pi \rightarrow \pi^*$ transition). Further, the vibrational structure of the quasi-line luminescence spectra studied by us for the molecules of mesobenzanthrone (V), its bromo derivatives (VI, VII), thioindigo (VIII), and its derivatives ([5]) is not characterized by the frequencies of the valence vibrations of the $C = O$ groups that are constituent parts of the indicated compounds.

The spectra of mesobenzanthrone and its derivatives (V–VII) are characterized by the vibrational frequencies of the aromatic condensed system. Thus, in these compounds the $C = O$ group is not responsible for the electronic excitation and, consequently, is not a chromophore for these molecules. The electronic excitation in these molecules is effected by the π-electron system of the aromatic rings ($\pi \rightarrow \pi^*$ transition). In the quasi-line absorption and luminescence spectra of thioindigo, the fine vibrational structure is distinctly characterized by the frequencies of the valence vibration of the group $> C_1 = C_2 <$ (1540 cm^{-1}), and

not by the frequencies of the $C = O$ group, as was the case in anthraquinone and its derivatives. Consequently, the group $C_1 = C_2$ in thioindigo is a chromophore determining the electronic excitation of the molecule ($\pi \rightarrow \pi$ transition), and therefore its valence-vibration frequency is so characteristically manifested in the quasi-line spectra of absorption and emission. The facts presented indicate that in the absorption and luminescence spectra of complex molecules there appears a certain autonomy of electronic groupings (chromophores) that bear the principal responsibility for electronic excitation; and the valence-vibration frequencies of chromophoric groups constitute the principal characteristic of the vibrational structure of the electronic-vibrational (quasi-line) spectra.

In complex molecules containing several chromophoric groups, upon excitation under given conditions the group that takes direct part is the one that provides the smallest energy difference between the ground and the first excited electronic levels of the system ($h\nu_{\min} = E_{1,e} - E_{0,e}$). It was noted above that quasi-line spectra of complex molecules in which the autonomy of chromophoric groups is manifested can be observed only at low temperatures in weak solutions of paraffin hydrocarbons. Under ordinary conditions, however, the electronic spectra of complex molecules are characterized by strongly broadened bands. The reason is that, in complex molecules, the interaction of electron motion with nuclear vibrations is especially large. As a result of this interaction, electronic energy is converted into the energy of nuclear vibrations; and if at the initial moment of time the vibrational energy is localized on one or several degrees of freedom, then at subsequent moments of time it is redistributed within the entire molecule, which causes the blurring of the vibrational structure of the spectrum ([6]). However, the probability of energy redistribution among vibrational degrees of freedom depends not only on the total reserve of vibrational energy of the system, the properties of the medium, and temperature, but also on the character of the interaction between individual

degrees of freedom, determined by the peculiarities of the chemical structure of the molecules (conjugation, coplanarity, etc.). Under conditions of low temperatures (which cause a decrease in the reserve of vibrational energy and in the interaction of individual degrees of freedom), in the absence of interaction of the luminescing molecules with the solvent and with one another, and also with a relatively weak interaction of the chromophore group (C = O) with the rest of the molecule (II–IV), the excitation energy, initially localized mainly on the electronic and vibrational levels of the chromophore (C = O), will be redistributed much more slowly over the other vibrational degrees of freedom of the system. This also means that the fraction of electronic energy converted during emission into vibrational energy will be distributed mainly over the vibrational levels of the chromophore group responsible for the excitation. As a result, the fine vibrational structure of the spectrum should, to a considerable extent, be characterized by the frequencies of the normal vibrations of the chromophore group, which is in accord with the facts presented above.

Our investigations have shown that in the luminescence spectra of complex

molecules (in dilute solutions of paraffins at low temperatures) containing two different groups, it is possible to excite spectra with electronic transitions (states) corresponding to these groups. Depending on the excitation conditions (λ, T, medium), one or the other, or both electronic states simultaneously, may be obtained, and two spectra (glows) may be observed. Thus, in α-chloroanthraquinone there are two nonequivalent carbonyl (chromophore) groups: upon excitation with $\lambda = 365$ mμ a continuous spectrum is observed ($\lambda_{\text{start}} = 5200$ Å), apparently due to the electronic $n \rightarrow \pi^*$ transition in the C=O group located next to the chlorine atom; whereas upon excitation with $\lambda = 313$ mμ the continuous spectrum is retained and a new spectrum appears with fine vibrational structure, $\lambda_{\text{start}} = 4573$ Å, corresponding to the electronic $n \rightarrow \pi^*$ transition in the free C=O group (Fig. 1).

In the molecule of 1,8-dioxyanthraquinone there are likewise two strongly differing carbonyl groups. Upon excitation with $\lambda = 365$ mμ a continuous spectrum is observed ($\lambda_{\text{start}} = 5516$ Å), while upon excitation with $\lambda = 313$ mμ, in addition to this spectrum, a new spectrum appears with fine vibrational structure ($\lambda_{\text{start}} = 4572$ Å), corresponding to the electronic ($n \rightarrow \pi^*$) transition in the free C=O group. The carbonyl group participating in the formation of a hydrogen bond requires less expenditure of energy for excitation than does the free group. The character of the luminescence spectra of 1,5-dioxyanthraquinone and 1-oxyanthraquinone does not depend on the frequency of the exciting light. The influence of auxochromes (Hal, OH, NH_2, etc.) on the spectra of molecules is manifested in the displacement and broadening of bands, in the redistribution of their intensity (in accordance with the Franck–Condon principle), and sometimes in a complete change in the vibrational structure of the spectrum ([3,4]).

In α-oxy derivatives of anthraquinone, the OH group forms with the chromophore group C = O a hydrogen bond with a predominant value of π-electronic interaction. If, in the formation of the H-bond, the acceptor–donor interaction played the main role, then upon excitation of the molecule (with participation of the $n \rightarrow \pi^*$ transition) a rupture of the hydrogen bond would occur, which would lead to loss of the luminescent properties of the compound. This is confirmed by the sharp weakening of luminescence in α-amino derivatives of anthraquinone in comparison with α-oxy derivatives. It has been established ([7]) that luminescence is absent in orthoaminoazo compounds, whereas orthooxyazo compounds fluoresce brightly. When an intramolecular H-bond is formed with participation of the amino group, the condition of coplanarity is insufficiently fulfilled; therefore in the excited state weakening and even rupture of the hydrogen bond are possible, owing to disruption of the acceptor–donor interaction (as a result of the $n \rightarrow \pi^*$ transition) and to the rather ineffective participation of the NH group in the π-electronic interaction of the system.

A new fact confirming the preservation and strengthening of the H-bond in α-oxy derivatives of anthraquinone in the excited state, as well as its strong influence on the nature of the excited state of the molecule, is the luminescence spectrum

structural formulas IX, X, XI

Figure 4: structural formulas IX, X, XI

of 1,4,5,8-tetraoxyanthraquinone, in which each C=O group participates in the formation of two hydrogen bonds. As a result, four additional quasi-aromatic rings with π-electron interaction are formed in a common system of seven rings, which may be called a kind of quasicoronene (X).

The vibrational analysis of the quasi-linear absorption and emission spectra of this compound showed that electronic excitation in the molecule is effected by a $\pi \rightarrow \pi^*$-transition. The spectra contain frequencies similar to those of coronene, and also show intense bands 1267, 1404, 1564, characteristic of anthracene vibrations [8,9]. The vibrational structure of the spectrum of chinalizarin (XI) is also characterized by frequencies of the aromatic system. In the molecules of 1,4,5,8-tetraoxyanthraquinone (X) and chinalizarin (XI), in the course of excitation, a new chromophoric system arises that includes rings with H-bonds. As a result, the vibrational structure of the quasi-linear spectra is not characterized by the frequencies of the valence vibrations of the C=O group.

Analysis of the luminescence spectra of β-substituted anthraquinone (Br, I, R −O−C=O) permits the conclusion that (under the corresponding excitation conditions) the intensity of the combination-scattering band of the chromophore (C=O) and the intensity of the band corresponding to the $0''$—$0'$-transition in the luminescence spectra vary antibatically.

The facts considered confirm the idea [10] that, in complex molecules, local multicenter electron orbitals may exist with the participation of a certain ensemble of π-electrons moving in the field of directly bonded nuclei, while the more distant environment produces only a certain perturbation. The manifestation of the autonomy of chromophoric groupings in the absorption and emission spectra of complex molecules, depending on their chemical structure and on the excitation conditions, constitutes the subject of further investigations.

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Physicochemical Institute
named after L. Ya. Karpov

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