N. G. BAKHSHIEV

1963

SovietRxiv

Abstract

Full Text

N. G. BAKHSHIEV

A NEW SPECTROSCOPIC METHOD FOR STUDYING THE ANISOTROPY OF ELECTRONIC TRANSITIONS IN POLAR MOLECULES

(Presented by Academician A. N. Terenin, 11 IV 1963)

It is known that electronic transitions in molecules are characterized by a certain anisotropy. The direction of the vector **D** of the dipole moment of the corresponding transition coincides with the direction along which the displacement of electron density occurs when the molecule absorbs or emits a quantum of light. Knowledge of the absolute orientation of the vector **D** relative to the molecular skeleton is important for understanding its electronic structure and is of considerable interest.

At present a number of methods are known that make it possible to study the polarization of electronic transitions in molecules. All of them (with the exception of the case of crystals) are based on creating, by one means or another, and studying an artificial optical anisotropy of the sample, which is a consequence of the intrinsic anisotropy of the molecules composing the substance and which manifests itself when the randomness of their orientation in space is disturbed. The latter is achieved as a result of the action on the system under study of fields of mechanical (1–6) or electrical (7–8) forces, and in particular cases also of intense polarized light (9–11). Information on the absolute orientation of the moments of electronic transitions is then obtained as a result of analyzing data from polarization measurements (absorption dichroism or the degree of polarization of fluorescence). We note that the usual methods of polarized fluorescence of optically isotropic objects (solutions, amorphous solids, etc.) make it possible to determine only the relative orientation of the absorption and emission oscillators in a molecule (12–14).

In the present work the idea is set forth of a new spectroscopic method for studying the anisotropy of electronic transitions in polar molecules, which does not require the creation of artificial optical anisotropy of the sample or the carrying out of any polarization measurements. In this method, the determination of the absolute orientation of the vector **D** of the moment of an electronic transition relative to the molecular skeleton is based on studying the influence of intermolecular interactions on the absorption and fluorescence spectra of the molecule under consideration (15–19).

In works (18,19), on the basis of a theory (16) describing the influence of universal (20) intermolecular interactions (orientational, induction, dispersion, etc.)

Fig. 1

Figure 1: Fig. 1

on the position of the electronic spectra of molecules in liquid two-component solutions, a general spectroscopic method was proposed for determining the permanent dipole moments of molecules in the ground ($\vec{\mu}_g$) and first excited ($\vec{\mu}_e$) electronic states, as well as the angle α between the moments $\vec{\mu}_g$ and $\vec{\mu}_e$. It is not difficult to show that the vector $\Delta\vec{\mu}$, which is the vector difference of the moments $\vec{\mu}_e$ and $\vec{\mu}_g$, coincides in direction with the vector $\mathbf{D}$ of the moment of the corresponding electronic transition and thereby directly indicates in which direction the electron density is displaced when the molecule absorbs or emits a quantum of light (we assume here that the absorption and emission oscillators either coincide in direction or form a small angle with one another).

It is known that the vector of the electric moment of any overall neutral system of electric charges (in particular, a molecule) is determined by the equality (21)

$$\vec{\mu} = \sum_i e_i \mathbf{R}_i, \tag{1}$$

where the summation extends over all elementary charges (electrons and nuclei) entering into the system, and $\mathbf{R}_i$ is the radius vector drawn to the charge e_i from some arbitrary initial point O. If $\mathbf{R}_1$ and $\mathbf{R}_2$ denote the radius vectors of the centers of gravity of, respectively, the positive and negative charges of a molecule in the ground state (Fig. 1a), then

Fig. 1

$$\vec{\mu}_g = -Q(\mathbf{R}_2 - \mathbf{R}_1) = -Q\mathbf{l}_Q, \tag{2}$$

where Q is the total charge.

Let, as a result of excitation, a redistribution of the electron density occur in the molecule, accompanied by transfer of part of the negative charge $-q$ in the direction $I - I$ (Fig. 1b). Naturally, in this case the center of gravity of the negative charges will shift, whereas the center of gravity of the positive charges (nuclei) will remain practically unchanged. Then

$$\vec{\mu}_e = Q\mathbf{R}_1 - (Q - q)\mathbf{R}_2 - q\mathbf{R}_3 = -Q\mathbf{l}_Q - q\mathbf{l}_q = \vec{\mu}_g + \Delta\vec{\mu}. \tag{3}$$

It is easy to see that the direction of the vector $\Delta\vec{\mu}$ coincides with the direction $I - I$, along which charge transfer occurs upon excitation, i.e., ultimately, with the direction of the transition moment vector $\mathbf{D}$. Thus, if the magnitude and absolute orientation of the moment $\vec{\mu}_g$ relative to the molecular skeleton are known (which, generally speaking, in most cases presents no special difficulty), then, by determining from spectroscopic data by the method (18,19) the values of $\vec{\mu}_e$ and α, one can directly obtain information on the polarization of the electronic transition under study by finding the direction of the vector

$$\Delta\vec{\mu} = \vec{\mu}_e - \vec{\mu}_g. \tag{4}$$

Let us turn to specific examples. Earlier, in work (19), the values of μ_g, μ_e, and α were determined for a number of phthalimide derivatives, and considerations were presented concerning the electronic structure of the indicated molecules in the ground and first excited electronic states. In this case the moments $\vec{\mu}_g$ were calculated on the basis of the vector-additivity scheme by means of the expression

$$\mu_g^2 = \mu_{0g}^2 + \mu_{xg}^2 + 2\mu_{0g}\mu_{xg}\cos[\widehat{\mu_{0g}, \mu_{xg}}], \tag{5}$$

where $\vec{\mu}_{0g}$ and $\vec{\mu}_{xg}$ are, respectively, the dipole moments of the phthalimide molecule and of the substituent, while the quantities $\vec{\mu}_e$ and α were found from spectroscopic data (18,19). Let us try to determine the absolute polarization of the long-wavelength electronic transition in the molecules of 3-aminophthalimide and 4-aminophthalimide in two ways—from the electronic structure of these molecules and with the aid of the spectroscopic method developed here.

According to (19), the processes occurring in these molecules upon absorption or emission of a light quantum in the region of the long-wavelength transition can be expressed by the following scheme

[chemical reaction scheme]

i.e., as a result of excitation, there is an enhancement of the conjugation of the amino group with the ring, accompanied by charge transfer from the nitrogen atom to the oxygen of one of the carbonyl groups along the chain of conjugated bonds. Obviously, in this case the transition-moment vector **D** must coincide with the straight line I—I, passing through the corresponding N and O atoms (Fig. 2 b, g).

[Figure with vector constructions and molecular structures, panels a, b, v, g]

Fig. 2

Taking as the principal direction from which the angles are measured the direction of the dipole moment $\vec{\mu}_{0g}$ of unsubstituted phthalimide (clockwise positive, counterclockwise negative), it is not difficult, from the structural model of the molecule, to determine the values of the desired angles ϑ. The corresponding values are given in the next-to-last column of Table 1.

On the other hand, the direction of the vector **D** can be determined, as shown above, from the vector relation (4). In Fig. 2 a, v the corresponding constructions are shown for both molecules studied. As in (19), the values of μ_g

were calculated by formula (5) from the condition $\mu_{0g} = 2.14$ D ([22,23]) and $\mu_{xg} = 1.50$ D ([24,25]), the angles between the moments μ_{0g} and μ_{xg} being taken equal to 90° and 30°, respectively, for 3-amino- and 4-aminophthalimide. The values of the angles γ were determined from the construction, while the angles α and the moments μ_e were taken from work (19) (see Table 1). The final results, i.e., the values of the angles ϑ between the direction of the vector $\Delta\vec{\mu}$ and the vector $\vec{\mu}_{0g}$, are given in the last column of Table 1. Comparison of the values of ϑ, determined

···obtained by different methods attest to their good agreement (the deviation in both cases lies within ±10°).

Thus, the proposed method can apparently be used to study anisotropy and to determine the absolute polarization of electronic transitions in polar molecules. As already indicated, when it is used there is no need to create an artificial optical anisotropy of the sample or to carry out polarization measurements. It is only necessary to know the positions of the absorption and fluorescence spectra of the molecule under study in a series of solvents, as well as the absolute orientation of the moment $\vec{\mu}_g$ in the ground state relative to the molecular skeleton.

Table 1

Substance	μ_g, D according to ([18])	μ_e, D according to ([19])	γ, deg	α, deg, according to ([19])	ϑ, deg, by electric dichroism	ϑ, deg, by spectr. method
3-aminophthalimide	2.6	4.9	35	20°	4	−3
4-aminophthalimide	3.5	6.7	13	15°	37	42

In conclusion it should be noted that, as was already mentioned, we have not dealt here with more complex cases: noncoincidence in the direction of the oscillators of absorption and emission, the role of various relaxation (intra- and intermolecular) processes, etc. All these phenomena, which may affect the applicability of the method, deserve special consideration.

Received
2 IV 1963

CITED LITERATURE

[1] A. Jablonski, Nature, **131**, 839 (1933); Acta Phys. Polon., **3**, 421 (1934); **4**, 311, 371 (1935).

[2] P. P. Feofilov, ZhETF, **12**, 328 (1942); J. Phys. USSR, **7**, 68 (1943).
[3] S. Anderson, J. Opt. Soc. Am., **39**, 49 (1949).
[4] L. V. Smirnov, DAN, **82**, 237 (1952); Izv. AN SSSR, ser. fiz., **17**, 695 (1953).
[5] T. Bettelheim, R. Stein, J. Polym. Sci., **27**, 367 (1958).
[6] J. Tanizaku, Bull. Chem. Soc. Japan, **32**, 75 (1959).
[7] W. Kuhn, H. Dührkop, H. Martin, Zs. Phys. Chem. (B), **45**, 121 (1939).
[8] J. Czekalla, Zs. Elektrochem., **64**, 1221 (1960); Chimia, **15**, 26 (1961).
[9] A. Teitel, Naturwiss., **13**, 370 (1957).
[10] A. Albrecht, J. Chem. Phys., **27**, 1413 (1957); J. Molec. Spectr., **6**, 84 (1961).
[11] B. S. Neporent, O. V. Stolbova, Optics and Spectroscopy, **10**, 294 (1961).
[12] S. I. Vavilov, V. L. Levin, Zs. Phys., **16**, 136 (1923).
[13] S. I. Vavilov, Collected Works, **1**, Publishing House of the USSR Academy of Sciences, 1952, p. 129.
[14] P. P. Feofilov, Polarized Luminescence of Atoms, Molecules, and Crystals, Publishing House of the USSR Academy of Sciences, 1959.
[15] N. G. Bakhshiev, Izv. AN SSSR, ser. fiz., **22**, 1387 (1958); Optics and Spectroscopy, **7**, 52 (1959); Candidate Dissertation, GOI, 1959.
[16] N. G. Bakhshiev, Optics and Spectroscopy, **10**, 717 (1961).
[17] N. G. Bakhshiev, Optics and Spectroscopy, **12**, 350, 473, 557 (1962).
[18] N. G. Bakhshiev, Optics and Spectroscopy, **13**, 43 (1962).
[19] N. G. Bakhshiev, Optics and Spectroscopy, **13**, 192 (1962).
[20] B. S. Neporent, N. G. Bakhshiev, Optics and Spectroscopy, **8**, 777 (1960).
[21] I. E. Tamm, *Foundations of the Theory of Electricity*, Moscow, 1956.
[22] Landoldt-Börnstein, Tabellen. Atom- u. Molekularphys., Vol. 2, Molekeln, 2, Berlin, 1951.
[23] N. Lumbroso, R. Dabard, Bull. Soc. Chim. France, No. 5, 749 (1959).
[24] A. Few, J. Smith, J. Chem. Soc., **1949**, 733.
[25] M. Aroney, R. LeFevre, J. Chem. Soc., **1960**, 3600.

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