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Experimental Determination of the Dipole Moments of Organic Molecules in Excited Electronic States†

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Modern experimental methods for the determination of dipole moments of organic molecules in excited electronic states are reviewed in detail and their relative merits are discussed.
The principal results obtained with the aid of these methods are presented (compiled in a Table). The bibliography includes 88 references.

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I. INTRODUCTION

The properties of excited‡ molecular states as well as those of the ground state are ultimately determined by the distribution of electron density in the molecule. From this point of view, it is of interest to determine the dipole moments of the molecule in excited states, since the magnitude and orientation of the dipole moment relative to the molecular framework are directly related to the distribution of electron density in the corresponding eigen state. Comparison of the dipole moments in the ground ($\vec{\mu}_g$) and excited ($\vec{\mu}_e$) states makes it possible to infer the nature of the changes in electron density at individual groups of atoms in the molecule following excitation, which is of particular interest for the determination of the reaction centre in the excited state of the molecule undergoing a photochemical reaction and also for the understanding of the relation between the migration of the charge and the redistribution of electron excitation energy. The latter in turn is closely related to various non-radiative deactivation processes and hence to the capacity of the compound for luminescence. Furthermore, the use of the experimental dipole moments of excited states may facilitate a more soundly based choice of parameters in quantum-mechanical calculations of various physicochemical properties of molecules.

Unfortunately $\vec{\mu}_e$ cannot be determined experimentally by the usual methods for the measurement of electrical polarisation, since the lifetime of the excited states is extremely short so that even under intense irradiation this factor makes it difficult to establish an equilibrium concentration of excited molecules sufficiently high for the measurement of electrical polarisation. At the same time, since one is dealing with the optical excitation of the molecule, the method for the determination of the dipole moments of excited states must clearly be spectroscopic. Consequently it is necessary to establish a relation between the principal spectroscopic parameters of the molecule [the energy (frequency) and probability (intensity) of the electronic transition], on the one hand, and the electric dipole moments characteristic of the molecule in the ground and excited states, on the other.

In the last 10–12 years a number of methods for the experimental determination of the moment $\vec{\mu}_e$ have been proposed. It is significant that these methods differ sharply from one another in the nature of the physical phenomena on which they are based and consequently in the spectroscopic parameters which are measured. However, despite the urgency of the problem, so far there has been no adequate review of these methods. The reviews known to the authors[1,2] are extremely short, do not give a complete idea of the available methods and their modifications, and many important results are omitted. The present review probably includes most of the studies (up to 1967) in which the dipole moments of molecules in excited states were measured or estimated experimentally. The principal formulae used to determine the dipole moments are presented in a form convenient for direct practical use—achieved as a result of a number of assumptions which have been justified in practice. At the end of the review there is a Table which presents the principal data on the dipole moments $\vec{\mu}_e$ of a number of molecules and complexes obtained to date.

The methods for the determination of dipole moments which have been fairly widely adopted recently can be usefully combined into the following four groups.

1. The method of spetral shifts, based on the study of the displacements of the frequencies of electronic transitions in the electric field of intermolecular forces and consisting in the analysis of the shifts of the absorption and luminescence bands under the influence of a solvent.

2. The method of electrical polarisation of fluorescence. Here the degree of polarisation of the emission by solutions of the test substances in a powerful electric field is measured, i.e. ultimately the anisotropy of the emission in the direction of the field orienting the molecules is investigated.

3. The method of electrical dichroism. Here the dichroism of the absorption by molecules in a solution placed in a powerful electric field is studied, i.e. the anisotropy of absorption in the direction of the orienting field is considered.

4. The method based on the investigation of the splitting of the fine rotational structure of the absorption bands of

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‡Only excited electronic states are considered here.

certain molecules in the gas phase in a powerful electric field (the Stark effect, which includes not only the excited electronic states but also the ground state).

It must be emphasised yet again that all the methods enumerated above are spectroscopic and require that the test molecule be acted upon by electric fields (external or intermolecular). It should also be noted that all the methods are based on definite model hypotheses concerning the interaction of the molecule with the medium (the Onsager theory, Debye's theory of orientation polarisation, etc.). Each group of methods will be discussed in greater detail.

II. METHOD OF SPECTRAL SHIFTS

The determination of the dipole moments of excited states by the methods of spectral shifts is based on the study of solvatochromism—the displacement of the bands in electronic absorption and emission spectra of the test molecules under the influence of a solvent. The phenomenon of solvatochromism arises from the difference between the energies of the interaction of the molecule with the medium in different electronic states, which is in turn determined by the change in the physicochemical properties (in particular the dipole moment) of the molecule on optical excitation. The fundamental postulates concerning the relation between the parameters characterising the system "test molecule–solvent" and the displacement of the spectra in solution relative to those in the gas phase were described for the first time by Bayliss, McRae, and Ooshika [3-6]. Taking into consideration the equilibrium (eq) and Franck–Condon (F–C) levels in the ground (g) and excited (e) states (Fig. 1), the authors calculated, using second-order perturbation theory, the stabilisation energy of the dissolved molecule (i.e. the energy of its interaction with solvent molecules) in various states. Account was taken of different types of van der Waals interaction (orientation, inductive, and dispersion), while specific interactions of donor–acceptor type were disregarded.

To derive the final expression relating the experimental band shifts to the characteristics of the molecule and the medium, use is made of the Onsager model [7], according to which the molecule is treated as a point dipole in a spherical cavity with radius a (the Onsager radius) within the solvent which is treated as a homogeneous continuous medium with a dielectric constant ϵ and refractive index n. The point dipole interacts with the "reactive" field arising as a result of the orientation-inductive polarisation of the solvent molecules under the influence of the dissolved molecule. The general treatment of the problem [4-6] leads to very complex expressions containing terms each of which describes a particular type of interaction between the molecule and the solvent. These formulae cannot be used directly to determine dipole moments, since they contain a large number of parameters which have not been determined and cannot be determined experimentally. However, with certain assumptions made by McRae (in particular it is assumed that the molecular polarisibility α does not change on excitation, i.e. $\alpha_e = \alpha_g$), it is possible to obtain a fairly simple formula for the frequency shift of a purely electronic absorption transition in polar solvents:

$$\Delta\nu_a = (AL_0 + B)\frac{n_D^2-1}{2n_D^2+1} + C\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n_D^2-1}{n_D^2+2}\right], \qquad (1)$$

where A, L_0, B, and C are constants characterising both the solvent and the solute molecule and $C = (2/hca^3)$: $:(\vec{\mu}_g - \vec{\mu}_e)\vec{\mu}_g$. Here h is the Planck constant, c the velocity of light in a vacuum, n_D the refractive index of the solvent corresponding to the sodium D-line, ϵ the static dielectric constant, a the Onsager radius, and $\vec{\mu}_g$ and $\vec{\mu}_e$ are the dipole moments of the solute molecule in the ground and excited states respectively. It should be noted that, if the shape of the band depends only slightly on the solvent, i.e. the band is displaced virtually as a whole, the shift $\Delta\nu_a$ may be determined from the position of the absorption band maximum.

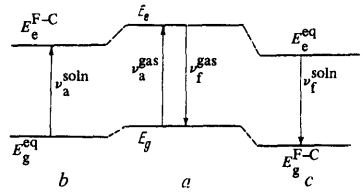


Figure 1. Schematic representation of the electronic levels of a molecule in the gas phase and in solution (ground and first excited states): *a*) absorption and emission (gas); *b*) absorption (solution); *c*) emission (solution).

McRae used Eqn. (1) to estimate $\vec{\mu}_e$ of Phenol Blue having investigated the shifts in the absorption spectra in 21 solvents. The constants A, L_0, and B were determined very approximately from additional experimental data and on the basis of different postulates. Using the known value $\vec{\mu}_g \simeq 5.8$ D and assuming that $\alpha \simeq 4$–5 Å and $\vec{\mu}_g \| \vec{\mu}_e$, McRae estimated $|\mu_e|$ for Phenol Blue to be 7.5–9.1 D and noted that, although this value is of the expected order of magnitude, it does not constitute a significant confirmation of a considerable contribution of the dipolar structure to the excited state of the molecule investigated.

The work of Lippert [8-11], who proposed a method for the determination of μ_e of the first singlet excited state of fluorescing polar molecules, which is significantly higher than μ_g, played an important role in the development of a method for the measurement of the dipole moments of excited molecules. This method is based on the application of the Ooshika formula to determine the difference between the shifts of the absorption ($\Delta\nu_a$) and fluorescence ($\Delta\nu_f$) bands under conditions such that the orientation relaxation time of the solvent molecules (τ_{or}) is much less than the lifetime of the excited fluorescent state (τ_f). The following simple expression is then obtained (neglecting the small terms and the constant):

$$\Delta\nu_{a-f} = \nu_a - \nu_f = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n_D^2-1}{2n_D^2+1}\right)\frac{(\vec{\mu}_e - \vec{\mu}_g)^2}{a^3}, \qquad (2)$$

which relates the Stokes shift of the fluorescence spectrum relative to the absorption spectrum ($\Delta\nu_{a-f}$), to the characteristics of the molecule and the medium. Here ν_a and ν_f are the frequencies of the absorption and fluorescence band maxima respectively and the significance of the remaining quantities is clear from the preceding description. The measurement of ν_a and ν_f in a set of polar and non-polar ($\epsilon = n_D^2$) solvents makes it possible to calculate

μ_e, using specified values of μ_g and a, under the condition $\vec{\mu}_e \| \vec{\mu}_g$ by means of the simple formula

$$\mu_e = \mu_g \pm 0.001\sqrt{ma^3},$$

m being found from a plot of the relation $\Delta\nu_{a-f} = m\Delta f$, where

$$\Delta f = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n_D^2 - 1}{2n_D^2 + 1}\right].$$

The method described was used by Lippert [8-11] to determine the dipole moments μ_e of a number of molecules, in particular stilbene derivatives assuming that $a \sim 0.8\rho$, where ρ is the radius of the smallest sphere enclosing the molecule.

The disadvantages of Lippert's method consist mainly in the failure to take into account the capacity of the molecule to be polarised in an electric (and in particular in a reactive) field and also there is the following important defect: namely, having restricted the treatment to the analysis of the Stokes shift $\Delta\nu_{a-f}$, Lippert [8-11] in fact fails to realise the additional possibilities [compared with formula (1) for example] associated with the independent measurement of both absorption and fluorescence bands. As a result, the experimenter has at his disposal, as in the case of Eqn. (1), only one experimentally measured spectroscopic parameter ($\Delta\nu_{a-f}$) instead of two ($\Delta\nu_a$ and $\Delta\nu_f$), which considerably reduces the effectiveness of the method.

Independently of Lippert, Mataga and coworkers [12-16] also obtained Eqn. (2) on the basis of the Ooshika formula and, having analysed it in detail and compared it with experimental data, concluded, in agreement with Lippert [8-11], that it is possible to determine the difference between the dipole moments of molecules in the ground and excited states from the changes in the Stokes shift $\Delta\nu_{a-f}$ due to orientation interactions. No hypotheses concerning the relative orientation of the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ or the values of μ_g have been put forward by Mataga and coworkers [12-16] and only the values of $|\Delta\vec{\mu}|$ are considered.

Comparison of the experimental and theoretical values makes it possible in some cases to estimate the applicability of a particular method for the calculation of charge distribution in the excited molecule (for example for naphthols, naphthylamines, and carbazole [13,14] and also aniline [17]) and to arrive at certain conclusions concerning the structure of the molecule in the excited state. Molecular excitation is accompanied, according to Mataga's data, by a considerable increase of the dipole moment, which is associated with charge transfer from electron-donor substituents along the conjugated bond chain. It has been established that in α-naphthylamines the increase of the dipole moment on excitation is greater (4.4 D) than in the corresponding β-derivatives (3.5 D), while the values of $|\Delta\vec{\mu}|$ for naphthols are considerably lower (0.5–1 D) than for naphthylamines and the sequence of the changes $|\Delta\vec{\mu}|$ for α- and β-derivatives is reversed.

A rough estimate shows [12-16] that $|\Delta\vec{\mu}|$ for isomeric aminobenzoic acids increases on going from *ortho*- to *meta*-isomers. The quantity $\delta = |\Delta\mu|^2/a^3$, determined from Eqn. (2), is $\delta = 7500$ cm^{-1} for *NN*-dimethyl-α-naphthylamine. This suggests that the $N(CH_3)_2$ group rotates about the C–N bond during the lifetime of the excited state [16]. The authors believe [16] that such rotation becomes possible as a result of charge transfer from the nitrogen to the π-electron system of naphthalene on electronic excitation.

The work of Ito et al. [18], where an attempt was made to measure the change in dipole moments on $n-\pi^*$ excitation of ketone molecules, is of interest. The authors used the McRae formula [5], in which a small term, characterising the so called quadratic Stark effect, was omitted:

$$\Delta\nu_a = \text{dispersion term} + B\frac{n_D^2 - 1}{2n_D^2 + 1} + C\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right], \quad (3)$$

$$B = \frac{1}{hc}\cdot\frac{\mu_g^2 - \mu_e^2}{a^3}, \quad (4)$$

$$C = \frac{2}{hc}\frac{\vec{\mu}_g(\vec{\mu}_g - \vec{\mu}_e)}{a^3} \quad (5)$$

(the notation is the same as above). Since according to Eqns. (4) and (5) it is necessary to determine experimentally either the parameter B or C in order to find μ_e, Ito et al. [18] proposed two versions of the method.

The first version is based on the measurement of the shifts $\Delta\nu_a$ in non-polar solvents with different refractive indices (n_D) (for example hexane, carbon tetrachloride, dioxan§, benzene). For such solvents ($n_D^2 \simeq \epsilon$), the following equation should hold:

$$\Delta\nu_a = \text{dispersion term} + B\frac{n_D^2 - 1}{2n_D^2 + 1} + \text{const.} \quad (6)$$

It has been established experimentally [18] that, for all the compounds investigated, except acetone, the dispersion interaction may be neglected and the following linear relation may be employed:

$$\Delta\nu_a \simeq B\frac{n_D^2 - 1}{2n_D^2 + 1} + \text{const.} \quad (7)$$

The authors confine themselves to the determination of the sign of B only. Since $B > 0$ ("blue" shift of the absorption band), it follows that $\mu_e < \mu_g$, i.e. on $n-\pi^*$ excitation the dipole moment falls.

In the second version of the method the difference between the positions of the absorption band maxima in two polar solvents with approximately the same values of n_D but different ϵ is measured. In such solvents the dispersion terms and the term involving $(n_D^2 - 1)/(2n_D^2 + 1)$ do not change, so that the difference between the frequencies at the band maxima is described by the simple formula

$$\nu_1 - \nu_2 = C\left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2}\right). \quad (8)$$

Ethyl ether and acetonitrile ($n_D = 1.356$ and 1.344 respectively), for example, may be used as solvents. The absorption spectra of these solvents are similar and do not contain intense bands above 2000 Å, which ensures approximate equality of the dispersion terms in Eqn. (3). [5] The dielectric constants ϵ of these solvents differ sharply (4.34 for ether and 37.50 for acetonitrile), which permits the variation of ϵ¶ of their mixtures over a wide range. By measuring ν_a for solutions in each mixture of this kind, it is possible to test the validity of Eqn. (8) and, if it holds, to determine the parameter C and hence μ_e for known values of μ_g and a. The measurements carried out in this way enabled Ito et al. to estimate the dipole moments μ_e of acetophenone on $n-\pi^*$ excitation as 0.5 D ($a \simeq 4.0$ Å). For the remaining ketones investigated by the authors the corresponding values of μ_e do not exceed 0.5 D. Then in all cases μ_e is less than μ_g approximately by 3 D. Using

§However, dioxan behaves in the majority of cases as a polar solvent and does not obey Eqn. (6).

¶The dielectric constant ϵ of the mixture of solvents may be calculated from the formula $\epsilon = \epsilon_0 + bw$, where ϵ_0 is the dielectric constant of ether, b the difference between the dielectric constants of acetonitrile and ether, and w the weight fraction of acetonitrile in solution.

the same method, Semba [19] observed an increase in the dipole moment of nitrobenzene derivatives on excitation in the long-wavelength region and determined the dipole moment of the first singlet state of the *p*-nitroanisole molecule (for $a \simeq 4$ Å and $\mu_g \simeq 5$ D, the dipole moment is $\mu_e \simeq 7$ D).

The version of the McRae method described is very convenient for the estimation of μ_e of sparingly soluble non-fluorescent compounds, but it requires a very cautious approach and tests in each individual case, since the McRae theory, developed for two-component solutions cannot be formally extended to mixtures of two solvents, i.e. to three-component solutions [20].

Gosavi and Rao [21] used Eqn. (8) to determine the dipole moments of the $n-\pi^*$ excited states of thiourea derivatives from the shifts of the $n-\pi^*$ absorption band maximum in ether and acetonitrile without using a mixture of solvents.

Baba et al. [22] applied the McRae formula [Eqn. (3)] and analysed the shifts of the fluorescence spectra. The authors calculated the relative shifts of the absorption ($\delta\nu_{abs}$) and fluorescence ($\delta\nu_{fl}$) bands for various solvents with the same values of n and dispersion terms but different ϵ. Then one obtains for absorption

$$\delta\nu_{abs} = \Delta\nu_{2abs} - \Delta\nu_{1abs} = \frac{2}{hc}\frac{\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)}{a^3}\left(\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right)$$

and for fluorescence

$$\delta\nu_{fl} = \Delta\nu_{2fl} - \Delta\nu_{1fl} = \frac{2}{hc}\frac{\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)}{a^3}\left(\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right),$$

where $\Delta\nu$ are the shifts of the absorption and fluorescence bands in the corresponding solvents (1 and 2) relative to the spectra of the vapour. Hence, under the condition $\vec{\mu}_e \parallel \vec{\mu}_e$, we have

$$\frac{\mu_e}{\mu_g} = \frac{\delta\nu_{fl}}{\delta\nu_{abs}}. \qquad (9)$$

Using acetonitrile and ether and also other solvents [23] with similar n_D, Baba et al. [22] calculated the dipole moment μ_e for $n-\pi^*$-fluorescent states of pyridazine, pyrimidine, and pyrazine [22] and also 9,10-diazaphenanthrene [23]. They found that the dipole moments of pyridazine, 9,10-diazaphenanthrene, and pyrimidine decrease significantly on $n\pi^*$ excitation (by factors of 3.6, 3.4, and 4.2 respectively) and the sign of the dipole moment of pyrimidine is reversed. The authors suggest that these changes are associated with the transition of the sp^2-hybridised n electrons of nitrogen to the π orbital. At the same time for pyrazine $\mu_e \simeq \mu_g \simeq 0$ due to the symmetrical positions of the hetero-atoms.

The method employed by Baba is attractive because in the calculations it is unnecessary to specify the Onsager radius, the value of which usually involves a considerable error. At the same time the exclusive use of solvents with refractive indices n_D which differ only slightly and the assumption that the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ are parallel greatly restricts the scope of the method.

The McRae formula enabled Robertson et al. [24] to estimate the dipole moments of certain excited states (^1L_b, ^1L_a, and ^1B_b) of azulene. The authors demonstrated experimentally the validity of the assumptions underlying the McRae formula [Eqn. (1)] and showed that $AL_0 + B = K$ is constant for the entire series of solvents which they employed. The constant K for the series of solvents (hexane, heptane, pentane, etc.) was determined from the formula $\Delta\nu_a = K(n^2 - 1)/(2n^2 + 1)$ by least squares. In turn, the constant $C = (2/hc)\mu_g(\mu_g - \mu_e)/a^3$ was calculated from the absorption bands shifts in polar solvents so as to obtain best agreement between the calculated and observed shifts $\Delta\nu_a$. The data for alcohols are excluded, since in this case hydrogen bonds may have a significant effect, which is not taken into account by the McRae formula [Eqn. (1)]. The values of $\vec{\mu}_e$ for molecules in the above three excited states were determined for two Onsager radii, $a \simeq 3$ and $a \simeq 4$ Å, and the results obtained were compared with those of the theoretical calculations of Pariser. The authors state that best agreement between the calculated and experimental moment $\vec{\mu}_e$ in the state ^1L_b is achieved with $a > 4$ Å. For the remaining states, the agreement is less satisfactory.

In a study based on the McRae theory and the formula for the shift of the electronic spectra under the influence of the solvent derived by Liptay [26], Beens and Knibbe [25] determined from fluorescence spectroscopic data alone the dipole moments of certain molecular charge-transfer complexes in the excited state. They assumed that $\vec{\mu}_e \parallel \vec{\mu}_g$ and that the Onsager radius $a \simeq 5$ Å. According to these measurement, the dipole moment in the excited state proved to be 10 D, which is consistent with the hypothesis of charge transfer on excitation. Liptay [27] determined the dipole moment of aniline as $\mu_e = 6$ D.

In contrast to these investigations, Kosower [28] attempted to estimate the dipole moment of the excited state without using any previously derived relations. He determined the stabilisation energy ΔE_e of the excited $\pi-\pi^*$ state of the mesityl oxide molecule in water from the shift of the absorption spectra of the aqueous solution relative to the spectrum in iso-octane (it was assumed that in this non-polar solvent the position of the absorption band of the test molecule is the same as in the spectrum of the gaseous compound). The molecular complex of iodine with 1-ethyl-4-methoxycarbonylpyridine ($\mu_g = 13.90$ D; $\Delta E_g = 17.3$ kcal mole^{-1}) was chosen as standard and it was assumed that the stabilisation energy is proportional to the dipole moment; then, according to the authors estimate, $\mu_e \simeq 7.6$ D for mesityl oxide. The lower limit of the dipole moment of Phenyl Blue in the excited state was estimated similarly as 10.2 D, which exceeds the value obtained by McRae [5]. However, this approach to the determination of μ_e cannot be regarded as adequately justified.

The additional possibilities mentioned above, associated with the independent investigation of the shift of the absorption ($\Delta\nu_a$) and fluorescence ($\Delta\nu_f$) spectra of the solutions relative to those in the gas phase, were employed by one of the authors of the present review [29-37]. The method is based on the hypothesis that the effect of solvents on the position of the electronic spectra of molecules is in general determined by intermolecular interactions of the universal van der Waals type. Using these hypotheses, the Onsager model, and general physical considerations without resorting to quantum-mechanical methods of calculation, the author obtained relatively simples expressions for the shifts of the electronic spectra as a function of n and ϵ for the solvent [29]. In the derivation of the formulae, account was taken of the polarisibility of the molecule in the ground and excited states. It is particularly important that the author dealt with the general case where the angle φ between the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ is not 0° or 180°. Such treatment makes it possible to determine this angle together with the moment $\vec{\mu}_e$ from the experimental data and thereby investigate the anisotropy of the distribution of electron density in molecules on optical excitation. Subsequently the author developed a more general theory of the interaction between the solvent and the solute molecule which is valid for any relations between the orientation relaxation time τ_{or} and the lifetime

of the molecule in the excited electronic state τ_{fl}.[38] Furthermore, account was taken of the additional shift of the observed spectrum relative to the true spectrum as a result of the spectral variation of the field strength associated with a light wave acting upon the molecule in the condensed medium. The following expressions were obtained[38] for the case $\tau_{or} \ll \tau_{fl}$, which is most frequently encountered in practise:

$$hc\Delta\nu^s = C_2\left[\frac{2n^2+1}{n^2+2}\frac{\varepsilon-1}{\varepsilon+2} + p^s\frac{n^2-1}{n^2+2}\right] = C_2 f(\varepsilon, n), \quad (10)$$

$$hc\,\Delta\nu^{a-f} = \Delta C^{a-f}\left[\frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right) + p^{a-f}\frac{n^2-1}{n^2+2}\right] = \Delta C^{a-f}\varphi(\varepsilon, n) \quad (11)$$

where $\Delta\nu^S = (\Delta\nu_a + \Delta\nu_f)/2$, $\Delta\nu^{a-f} = \Delta\nu_a - \Delta\nu_f$ (the change in the Stokes shift), and $f(\epsilon, n)$ and $\varphi(\epsilon, n)$ are the so called universal interaction functions.

The dipole moment μ_e and the angle φ between $\vec{\mu}_e$ and $\vec{\mu}_g$ are defined by the following formulae, provided that μ_g and a (the Onsager radius) are known:

$$\mu_e = \sqrt{\mu_g^2 - C_2 hca^3}\ ,$$
$$\cos\varphi = \frac{1}{2\mu_g\mu_e}\left[(\mu_g^2+\mu_e^2) - \frac{\Delta C^{a-f}}{2C_2}(\mu_g^2-\mu_e^2)\right]. \quad (12)$$

The parameters C_2 and ΔC^{a-f} are found from plots based on Eqns. (10) and (11). The auxiliary parameters p^S and p^{a-f} are determined either from the condition that the straight line must pass through the point corresponding to the vapour phase (no shift) or (if no data for the spectra in the gas phase are available) from the condition of optimum linearity of the relation investigated. In the calculation of the parameters C and p good results are obtained by the method of least squares. We may also note that, in the absence of data for the spectra in the vapour phase, one can use the results of measurements of the relative shifts of the band maxima in polar media and the formulae

$$\frac{hc}{\Delta F(n)} = C_2\frac{\Delta f(\varepsilon, n)}{\Delta F(n)} + \text{const.}, \quad (13)$$

$$\frac{hc\delta(\Delta\nu^{a-f})}{\Delta F(n)} = \Delta C^{a-f}\frac{\Delta\varphi(\varepsilon, n)}{\Delta F(n)} + \text{const.}, \quad (14)$$

where

$$\delta\nu^s = \nu_2^s - \nu_1^s;\quad \delta(\Delta\nu^{a-f}) = \Delta\nu_2^{a-f} - \Delta\nu_1^{a-f},$$
$$\Delta F(n) = \frac{n_2^2-1}{n_2^2+2} - \frac{n_1^2-1}{n_1^2+2},$$

in which subscripts 1 and 2 refer to different polar solvents. The values of μ_g and a required for the calculations by Eqn. (12) are determined from electrical measurements (or from tabulated data) and from structural models of the molecules respectively.

Apart from the case discussed above, a widely occurring important special case, corresponding to the condition $\varphi \simeq 0$ or 180°, is also of interest. Then, according to Bakhshiev's investigations[29-32], we have

$$\mu_g = \sqrt{\frac{C_2 hca^3}{1-K^2}};\quad \mu_e = K\mu_g, \quad (15)$$

where

$$K = \pm\frac{1-\frac{\Delta C^{a-f}}{2C_2}}{1+\frac{\Delta C^{a-f}}{2C_2}}$$

(+ for $\varphi = 0$ and − for $\varphi = 180°$).

It is readily seen that, by specifying the value of a, it is possible to determine independently both μ_e and μ_g from spectroscopic data using Eqns. (15). Furthermore, it is significant that μ_e can be found in this case from the known value of μ_g without using the Onsager radius a, because the coefficient K in Eqn. (15) is determined solely by spectroscopic data. Finally, Eqns. (15) may be used for the direct experimental determination of the Onsager radius itself, which is important in studies on new classes of compounds.

The methods described above were employed to investigate the changes in the distribution of electron density on excitation and to determine μ_e and μ_g of a large number of compounds—in particular derivatives of naphthalene, stilbene, diphenyl, aniline, and pyridine[30-32,35,37], for the symmetrical molecules of which $\varphi = 0°$ or 180°. In this case, on excitation to the first singlet state, electron density shifts significantly along the conjugated bond chain from electron-donor to electron-acceptor substituents, this being accompanied by a marked increase of the dipole moment. A similar shift of electron density along the conjugated bond chain occurs also in symmetrically substituted phthalimides[30,37]. However, the greatest interest attaches to the application of these methods to molecules without a symmetry axis, for which $\varphi \neq 0°$ or 180°. Then, as already mentioned, it is possible to determine both the dipole moment μ_e and the angle φ and hence the direction in which electron density is displaced on excitation. The study of asymmetric derivatives of phthalimide[32,34,37] showed that, on excitation of these compounds, electron density is also markedly displaced from donor to acceptor functional groups, approximately along the line joining these groups (Fig. 2). In this connection, it is remarkable that the properties of the long-wavelength electronic transition responsible for the ability of phthalimides to fluoresce depend primarily on the properties of the substituents and the benzene ring appears to play a subsidiary role, behaving, as it were, as a conductor in charge transfer.

A study of $n-\pi^*$ and $n-\sigma$ transitions in molecules with a symmetry axis (acetone, nitromethane, methyl iodide, and bromoform) was undertaken by Bakhshiev[39] using a formula[31] suitable for molecules of this type:

$$\mu_e = \mu_g - \frac{C_1^a hca^3}{2\mu_g}\ , \quad (16)$$

where C_1^a is a constant determined from the shifts of absorption bands only in a series of solvents. The applicability of the method of universal interaction functions and in particular Eqns. (12) and (16) in the study of the physicochemical characteristics of certain molecular charge-transfer complex has been demonstrated[40]. The difference between the dipole moments of the first excited singlet and ground states of a number of benzene derivatives, calculated by the LCAO-MO method in the π-electron approximation and the same quantity determined experimentally by the method of universal interaction functions have been compared[41]. It has been shown that the theoretical and experimental results agree satisfactorily.

In the analysis of the electronic spectra of many organic compounds (in particular derivatives of phthalimide and stilbene), the long-wavelength bands of which correspond to intramolecular charge transfer, it has been found[37,42] that the difference between the dipole moments of the molecule in the ground and first excited electronic state $|\Delta\vec{\mu}|$, determined from the shifts in the spectra, is close in order of magnitude to the dipole moment of the transition $|\vec{D}|$, which is calculated from the intensity of the corresponding band. Since the comparison of $\Delta\vec{\mu}$ and $\vec{D}$ has a definite physical significance, the condition $|\Delta\vec{\mu}| \simeq |\vec{D}|$ can probably serve as one of the quantitative

criteria for the interpretation of the corresponding transition as an "intramolecular charge transfer" band (for further details, see also Saidov et al.[43]). This criterion was successfully employed by Kutsyna and coworkers for the assignment of bands in the spectra of 1,3,4-oxadiazole[44,45] and 1,3,5-triphenyl-2-pyrazoline[45] derivatives. In these and other investigations[45,47,48] Kutsyna and coworkers determined using Bakhshiev's method[29-35] the values of μ_e for the above compounds, the angle φ for 1,3,5-triphenylpyrazoline and its derivatives, and μ_e and μ_g for certain 1,3,4-oxadiazole derivatives, for which $\varphi = 0°$ or 180°. For the latter compounds, values of μ_g and μ_e in fairly good agreement with experimental data were calculated by the LCAO-MO method in the Hückel approximation.

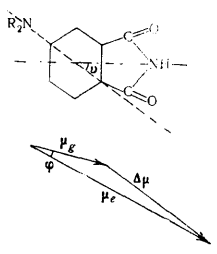


Figure 2. Orientation of the vector $\Delta\vec{\mu}$ relative to the molecular skeleton of 4-aminophthalimide (long-wavelength electronic transition).

The results of the determination of the dipole moments μ_g and μ_e by Bakhshiev's method[29-36] agree well in most cases with the results of other investigators, who employed both similar and completely different methods[31]. At the same time Bakhshiev's method[29-36] makes it possible to obtain relatively simply additional information about the excited state (the orientation of $\vec{\mu}_e$ and the anisotropy of the redistribution of electron density), which cannot be secured by the majority of similar procedures.

The method of determination of μ_e and φ from the shifts of the absorption and fluorescence bands was also proposed independently by Bilot and Kawski[49-56]. Like McRae and Ooshika, they solve[49] the quantum-mechanical problem of the interaction of the molecule with the solvent in second-order perturbation theory and then use the Onsager model. However, in contrast to the earlier investigators[4,5], Bilot and Kawski do not neglect the polarisibility of the molecule but take into account, as in Bakhshiev's work[29,57], the average polarisibility α, which is the same for the ground and excited states. In the special case where it is possible to neglect the polarisibility of the molecules ($\alpha = 0$), Eqn. (2), derived by Lippert and Mataga, follows from the formula of Bilot and Kawski. In the general case Bilot and Kawski[49], following Bakhshiev, assume that $\beta = 2\alpha/a^3 \simeq 1$ (a is the Onsager radius), which simplifies significantly the final relation. Then the formulae of Bilot and Kawski, relating the shifts of the absorption and fluorescence spectra to the parameters of the solvent and the test molecule, assume the following form[53]:

for absorption spectra:

$$\Delta\nu_a = -m_3\left(\frac{2n^2+1}{n^2+2}\right)\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)-m_2\frac{3}{2}\frac{n^4-1}{(n^2+2)^2}, \quad (17)$$

for fluorescence spectra:

$$\Delta\nu_f = -m_4\left(\frac{2n^2+1}{n^2+2}\right)\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)-m_2\frac{3}{2}\frac{n^4-1}{(n^2+2)^2}, \quad (18)$$

and for the Stokes shift:

$$\nu_a-\nu_f = m_1\frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)+\text{const.}, \quad (19)$$

where

$$m_1=\frac{2(\vec{\mu}_e-\vec{\mu}_g)^2}{hca^3}, \quad m_2=\frac{2(\mu_e^2-\mu_g^2)}{hca^3},$$
$$m_3=\frac{2\vec{\mu}_g(\vec{\mu}_e-\vec{\mu}_g)}{hca^3}, \quad m_4=\frac{2\vec{\mu}_e(\vec{\mu}_e-\vec{\mu}_g)}{hca^3}. \quad (20)$$

The following obvious relations obtain between the parameters m:

$$m_3=\frac{m_2-m_1}{1}, \quad m_4=\frac{m_1+m_2}{2}. \quad (21)$$

Using Eqns. (17)–(21), Bilot and Kawski[49-56] determined the dipole moments in the excited state μ_e and the angle φ between $\vec{\mu}_g$ and $\vec{\mu}_e$, with a and μ_g known. In order to calculate μ_e and φ, it is sufficient to find two independent parameters (out of four), for example m_1 and m_2, and then use the following working formulae:

$$\mu_e=\sqrt{\mu_g^2+\frac{1}{2}m_2hca^3}, \quad (22)$$

$$\cos\varphi=\frac{1}{2\mu_g\mu_e}\left[(\mu_e^2+\mu_g^2)-\frac{m_1}{m_2}(\mu_e^2-\mu_g^2)\right], \quad (23)$$

which are virtually the same as Eqns. (12) quoted above. The parameter m_1 is determined as in Bakhshiev's method[29-36] from the slope of the linear plot based on Eqn. (19). The remaining parameters, in particular m_2, can be found most simply from a graphical comparison of the theoretical and experimental shifts of the spectra of the solutions relative to the spectrum of the vapour or a solution in a non-polar solvent [for example on the basis of Eqn. (18)]. When $\varphi = 0°$ or 180°, we obtain from Eqns. (20) and (21)

$$\mu_g=\frac{m_2-m_1}{2}\sqrt{\frac{0.5\,hca^3}{m_1}},$$
$$\mu_e=\frac{m_2+m_1}{2}\sqrt{\frac{0.5\,hca^3}{m_1}}, \quad (24)$$

i.e., by analogy with Eqn. (15), an independent determination of the dipole moments in the ground and excited states is possible. The authors applied this method in the measurement of the dipole moments μ_e of derivatives of stilbene, fluorene, several phthalimides (for the majority of which $\varphi \neq 0$), naphthols, naphthylamines, and a number of other compounds. In particular, Bilot and Kawski[51,53] determined in addition to μ_e the angle φ for phthalimide derivatives, they subsequently measured μ_e for a number of other compounds[54] (including stilbene derivatives) with known values of μ_g and $\varphi \simeq 0$, and finally Kawski[56] determined from Eqns. (24) the values of μ_g and μ_e for naphthols.

On excitation of the molecules of all the compounds investigated to the first singlet state, the dipole moment increases. The experimental values of $|\Delta\vec{\mu}|$ for naphthols and naphthylamines[55] agree satisfactorily with the values calculated theoretically by Mataga and coworkers. The values of μ_e which they obtained agree also with the data of Bakhshiev, Czekalla, Meyer, and Wick (see below) but differ considerably (are lower than) from the analogous data of Lippert. According to these authors, this is

because Lippert fails to take into account the role of the polarisibility of the molecule in the ground and excited states.

In Abe's studies [58-61] a formula whereby it is possible to determine from the shift of the spectra both the dipole moment μ_e and the polarisibility of the molecule α_e in the excited state (using the results of the theoretical study of Margenau [62]) was derived from a direct consideration of the van der Waals interaction between the solvent and solute molecules with a large number of various simplifying assumptions (in particular the assumption that the molecules are spherical and that their polarisibility in combined electronic states is isotropic). To facilitate the calculations, the formula is written in the following simple form [59]:

$$(\mu_e^2 - \mu_g^2) + A\alpha_e = B \ , \qquad (25)$$

where A and B are quantities which depend in a complex manner on a number of the parameters of the test molecule and the medium and have different forms depending on the degree of interaction of the solvent molecules (the significance of the remaining quantities is clear from the foregoing). The method of determination of μ_e and α_e consists in plotting a linear relation between B and A for 7-10 solvents. It is then possible to find α_e from the slope, while the intercept on the ordinate axis yields $B = \mu_e^2 - \mu_g^2$, whence μ_e can be found provided that μ_g is known.

Abe and coworkers used this method to determine the values of μ_e and α_e in $^1B_{1u}$ and $^1B_{2u}$ excited states of the non-polar naphthalene molecule [59] and also in the $n-\pi^*$ excited state of the acetone molecule [60]. In the last case μ_e is much lower than the corresponding values for the ground state. It is also remarkable that the dipole moment μ_e which Abe obtained for acetone proved to be much less than the value which he calculated from the McRae formula (Robertson's method [24]). This last finding the author explains by the fact that McRae did not take into account the polarisibility of the molecule in the excited state, whereas according to Abe's data it increases markedly on excitation of the molecule. Somewhat earlier, while testing the relation which he derived Abe [58] determined, using a less rational method, the polarisibilities and dipole moments of nitrobenzene and acetophenone molecules in the excited state and then, using a simplified formula for the spectral shift, he found the values of μ_e and μ_g also from the spectral shift in non-polar solvents. He established thereby that electronic excitation increases the dipole moments of the molecules. Finally, using his method, Abe determined the dipole moments and polarisibilities in the excited states of four benzene derivatives (nitrobenzene, anisole, acetophenone, and *p*-chloroacetophenone). The high dipole moments of nitrobenzene and acetophenone (μ_e = 6.780 and 4.230 D respectively) were attributed to charge transfer on excitation.

An important feature of Abe's method [58-61] is that he does not employ the model concepts of the physics of dielectrics (in particular the Onsager model), i.e. there is no need to specify or determine independently the Onsager radius of the molecule. Unfortunately, however, the method [58-61] as a whole is based on not altogether correct postulates (the author does not take into account the Franck-Condon principle in the system "test molecule-medium" in the electronic transition and neglects the possibility that the moments $\vec{\mu}_g$ and $\vec{\mu}_e$ are not parallel, etc.), which probably makes this method suitable only for qualitative or semi-quantitative estimates. Furthermore, the applicability of the method is significantly complicated by the fact that it is necessary to know a number of physicochemical parameters of the test substance and the solvent which are difficult to determine.

In a number of studies an attempt was made to use certain of the above relations to determine the dipole moments of the excited state from the measured spectral shifts of the solutions as a function of temperature. The principal advantage of such methods consists in the fact that a smaller number of solvents is required to obtain the necessary data. The physical properties of the solvents and hence also the energy of the interaction of the test molecule with the medium, both in the ground and excited states vary with temperature, which leads to a shift of the electronic spectra. Piterskaya [63] determined μ_e and φ for a number of phthalimide derivatives with the aid of Bakhshiev's formulae (10)-(12). For this purpose, only five solvents (isopentyl alcohol, ethyl acetate, dioxan, anisole, and benzene) were required, instead of the usual 10-15. The dielectric constant ϵ and the refractive indices n of these solvents varied with temperature in the range 20-300°C ($\tau_{or} \ll \tau_{fl}$). The data obtained by this method agree well in most cases with the results obtained in the study of the spectral shifts as a function of the solvent at room temperature [32,34,37].

Pikulik and coworkers [64,65] attempted to extend the limits which restrict the applicability of the McRae formula to liquid solutions and derived a formula suitable for viscous and solid solutions:

$$\nu_{00}^a - \nu_{00}^f = \frac{2(\vec{\mu}_e - \vec{\mu}_g)}{hca^3}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right)\frac{\tau_{fl}}{\tau_{fl}+\tau_{or}} \ . \qquad (26)$$

On the basis of this formula the authors proposed a method for the determination of the dipole moment $\vec{\mu}_e$ by analysing the mirror-image absorption and fluorescence spectra in one solvent (in particular in isobutyl alcohol) at low ($\tau_{or} \gg \tau_{fl}$) and room ($\tau_{or} \ll \tau_{fl}$) temperatures. In Eqn. (26) ν_{00}^a and ν_{00}^f are the frequencies of the purely electronic transitions for absorption and emission respectively. These frequencies may be determined by the method proposed by Pikulik for mirror-image spectra [66]. Eqn. (26) was used to determine $\vec{\mu}_e$ for several phthalimide derivatives with known $\vec{\mu}_g$ and φ (taken from Bakhshiev) and an Onsager radius $a \simeq 4$ Å. The data obtained in this study differ somewhat from Bakhshiev's results but, as pointed out by the authors, when certain additional factors are taken into account, the agreement becomes fairly satisfactory.

For fluorescent but sparingly soluble compounds, it is convenient to employ a method involving the approximate determination of the change in the dipole moments on excitation ($|\Delta\vec{\mu}| = |\vec{\mu}_e - \vec{\mu}_g|$) proposed by Löber [67]. This method involves the measurement of the positions of the fluorescence band maxima only at low ($\tau_{or} \gg \tau_{fl}$) and room ($\tau_{or} \ll \tau_{fl}$) temperatures in one solvent. The method is based on the Lippert-Mataga theory [see Eqn. (2)], and the final relation is of the form

$$(\nu_f)_T - (\nu_f)_t = \frac{2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)|\Delta\vec{\mu}|^2, \qquad (27)$$

where $(\nu_f)_T$ and $(\nu_f)_t$ are the frequencies at the fluorescence band maxima at low and room temperatures respectively. Löber suggests that the measurements may be performed in any solvent because the additional shift of the fluorescence bands due to possible specific interactions over short distances (in particular due to hydrogen bonding) is eliminated in Eqn. (27). Löber determined $|\Delta\vec{\mu}|$ for a series of aminoquinols with a merocyanine group on transition to the first excited singlet state. The solvent

was ethanol because its viscosity (and hence τ_{or}) varies gradually with temperature. In all cases the dipole moment of the molecules was found to increase on excitation and the properties of the substituents proved to be correlated with $|\Delta\bar{\mu}|$ (the Onsager radius a was assumed to be 3 Å). It was also established that, for compounds of the type investigated, non-radiative transitions from excited states with a large dipole moment have a high probability. Unfortunately the data obtained by Löber cannot be compared with the results of other workers.

Summarising, it must be noted that the methods for the experimental determination of μ_e and φ based on the measurements of spectral shifts, are fairly reliable and experimentally simple. It has been shown that these methods do not require the use of any special equipment and reduce solely to the measurement of the contours of the absorption and emission bands for solutions of the test substance in various solvents using standard spectroscopic apparatus. The accuracy of the spectral shift method is almost entirely determined by the accuracy with which μ_g and a are specified. In those cases where the values of a are specified on the basis of chemical structure, the error of the determination may reach 15–20%. However, it should be noted that at present studies are being carried out with the aim of developing methods for the direct experimental determination of a for substances which are not liquid at room temperature. Such methods can evidently significantly increase the precision of the determination of μ_e and φ.

III. METHOD OF ELECTRICAL POLARISATION OF FLUORESCENCE

In 1959 Czekalla[68-70] suggested that the phenomenon of the polarisation of the fluorescence of molecules in liquid solutions placed in an electric field (electrical polarisation of fluorescence) be used to determine the dipole moments of the excited states of the fluorescing molecules. The central feature of this phenomenon consists in the fact that, under the action of a strong electric field of about 150 kV cm^{-1}, the excited polar molecules of the solute are oriented and, on excitation with ultraviolet light, emit partially polarised fluorescence, the degree of polarisation P being low: $P = \dfrac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the fluorescence polarised parallel and perpendicular to the direction of the electric field respectively. According to the classical phenomenological theory developed by Czekalla, the degree of polarisation of the fluorescence P varies linearly with the square of the field strength:

$$P_E - P_0 = 0.1\,\frac{3\cos^2\alpha - 1}{2}\left(\frac{\mu_e}{kT}\right)^2\left(\frac{\epsilon+2}{3}\right)^2 E^2, \qquad (28)$$

where P_E is the degree of polarisation of the fluorescence of the solution in a field E for a solvent with a dielectric constant ϵ, P_0 the degree of polarisation for the same solution without the field, the α the angle between the vector of the electronic transition moment and the dipole moment of the excited state $\vec{\mu}_e$. This angle can be determined either by measuring the electrical dichroism (see below) or on the basis of additional considerations concerning the molecular structure[70]. In the derivation of Eqn. (28) it is assumed, firstly, that the same excited state is responsible for both absorption and fluorescence and, secondly, that the ratio of the average lifetime of the excited state (τ_F) to the dielectric relaxation (principally orientation) time of the molecules in solution (τ_ϵ) is sufficiently large for the attainment of orientation equilibrium in the excited state ($\tau_F/\tau_\epsilon > 3$). The ratio τ_E/τ_ϵ can be determined, for example, from measurements of the degree of polarisation of the fluorescence of the solution P_0 without an electric field using the formula

$$\frac{\tau_F}{\tau_e} = \frac{P_\infty - P_0}{P_0(3 - P_\infty)}, \qquad (29)$$

where P_∞ represents the degree of polarisation of the fluorescence for a solvent with infinite viscosity (usually $P_\infty \simeq 0.45$).

In Czealla's phenomenonological theory only factors associated with the anisotropy of the distribution of the polar molecules oriented by the external electric field are considered but no account is taken of the shift of the fluorescence band occurring because the different dipole moments in the ground and excited states interact in different ways with the external field. Nevertheless, analysis shows that this last factor can have decisive importance in many cases. Therefore Liptay[71] developed a quantum-mechanical theory of the effect of electric fields on the fluorescence of solutions and derived formulae for different experimental conditions giving the relation between the degree of polarisation of fluorescence, on the one hand, and the strength of the external electric field and the form of the fluorescence band, on the other. In these formulae, which were obtained for particular values of the ratio τ_F/τ_ϵ, account is taken of the shift of the fluorescence band on application of the electric field. In its general form this relation is very complex, so that the experimental determination of the dipole moments of excited states using such formulae is possible only in special cases.

In the study of the polarisation of fluorescence by an external field, both linearly polarised and non-polarised ultraviolet radiation can be used for excitation, fluorescence perpendicular to the direction of the distribution of the exciting radiation being observed in both cases. Although the working formula is simpler than in the first case, nevertheless it is desirable to employ non-polarised radiation, because the intensity of the fluorescence and hence the precision of the experiments is thereby considerably increased. With this method of excitation, the following relation, derived with certain simplifying assumptions (in particular assuming the conditions $\vec{\mu}_g \parallel \vec{\mu}_e$), is used to determine μ_e:

$$\frac{P_{E_\nu} - P_{0\nu}}{E^2\left(\frac{\epsilon+2}{3}\right)^2}\left(1 + \frac{0.9}{\tau_F/\tau_\epsilon}\right) = 0.1\,\frac{\mu_e^2}{k^2T^2} + 0.2\,\frac{\mu_e(\mu_e - \mu_g)}{hckT}\,\frac{d\ln I_\nu}{d\nu}, \qquad (30)$$

where I_ν is the intensity of fluorescence with frequency ν and the significance of the remaining quantities is the same as in Eqn. (28). The first term of Eqn. (30) describes orientation effects and the second is due to the displacement of the band under the influence of the field E. The ratio τ_F/τ_ϵ is related by means of Eqn. (31) to the degree of polarisation of fluorescence in the absence of the field when excited by non-polarised radiation:

$$P_0 = \frac{0.3}{0.9 + \tau_F/\tau_\epsilon}. \qquad (31)$$

For liquid solutions, $\tau_F/\tau_\epsilon \gg 1$ and Eqn. (30) becomes simpler:

$$\frac{P_{E_\nu} - P_{0\nu}}{E^2\left(\frac{\epsilon+2}{3}\right)^2} = 0.1\,\frac{\mu_e^2}{k^2T^2} + 0.2\,\frac{\mu_e(\mu_e - \mu_g)}{hckT}\,\frac{d\ln I_\nu}{d\nu}. \qquad (32)$$

This expression can be used for both excitation methods mentioned above [71].

If the conditions $\tau_F/\tau_\epsilon \gg 1$ does not hold, Eqn. (30) is used to estimate μ_e to a first approximation and the estimate is then employed to calculate μ_e to a second approximation by the above general formula containing terms which depend on the form not only of the emission but also of the absorption bands. This procedure greatly complicates the calculation of μ_e but it is necessary in all cases where $\tau_F/\tau_\epsilon \leqslant 1$.

In the determination of the moments μ_e by the method of electrical polarisation of fluorescence, the left-hand side of Eqn. (30) is plotted against $d\ln I/d\nu$. It is significant that the values of μ_e can then be found by two independent methods†: from the intercept which the straight line makes on the ordinate axis and from the slope of the straight line (for known μ_g). Czekalla et al. [72] state that the first method is more accurate and gives rise to an error not exceeding 5%. It is striking that the two methods yield closely similar results in most cases.

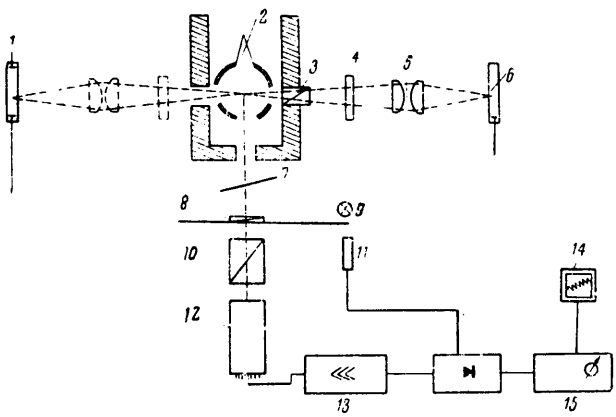


Figure 3. Outline of the apparatus for the determination of $\Delta\bar{\mu}_e$ by electrical polarisation of fluorescence: 1) NVO-200 mercury lamp; 2) cuvette; 3) polariser; 4) filter; 5) condenser; 6) NVO-200 mercury lamp; 7) compensator; 8) $\lambda/2$ plate; 9) reference signal lamp; 10) analyser; 11) photo-cell; 12) photomultiplier; 13) amplifier; 14) pen recorder; 15) valve voltmeter.

The apparatus employed by Czekalla and coworkers for the measurement of the degree of polarisation of fluorescence in an electric field is shown schematically in Fig. 3. The excitation of fluorescence is achieved by radiation from one or two high-pressure mercury lamps. The exciting radiation passes through a light filter which isolates intense lines from the mercury arc spectrum and the light is focussed by means of condensers on the specimen placed between the electrodes of the measuring high-voltage chamber. The radiation from the right-hand side lamp can be linearly polarised by means of a polariser built into a calibrated rotating ring. The measuring high-voltage cuvette is fitted with electrodes of special form (Rogovskii's profile) to exclude edge effects. A constant high potential chosen to give $E \simeq 150$ kV cm^{-1} is applied to the electrodes, the distance between which is 0.465 cm.

The system is thermostatted by passing a special liquid with a high resistivity and a high breakdown voltage through the hollow electrodes. The chamber is fitted with a special device in the form of a bent matt-black tube designed to eliminate the effect of scattered light.

Partially polarised fluorescence is observed in the direction perpendicular to the exciting beam. The beam analysed passes through a half-wave plate rotating at a definite frequency, and then through a rigidly fixed analyser. By means of this device, the polarised part of fluorescence is modulated at a definite frequency and a variable signal is transmitted to a photoelectric multiplier (PEM), is amplified, rectified, and fed to an electronic voltmeter coupled to a pen recorder. The non-polarised part of luminescence remains non-modulated and is therefore not recorded. The signal from the polarised component of the fluorescence can be concentrated by rotating the plane of the compensator through a definite angle. From this angle, read off a dial, it is possible to calculate the degree of polarisation of the fluorescence, using Fresnel's formulae [68]. The auxiliary signal from the incandescent lamp is modulated at the same frequency as the polarised light and controls the operation of the rectifier, locking it to the rotation of the plate.

To determine the degree of polarisation as a function of frequency within the limits of the fluorescence band, it is necessary to place a monochromator or an interference filter between the analyser and the photoelectric multiplier [71,72]. Particular attention is paid to the preparation of the specimen. Apart from the usual methods of purification, it is necessary to degas the solution carefully in order to avoid the electrical breakdown of the specimen in the powerful electric field.

The method of electrical polarisation of fluorescence was used to determine the dipole moments of the excited states of a number of derivatives of a biphenyl, fluorene, and stilbene in benzene and dioxan and also the complex of tetrachlorophthalic anhydride with hexamethylbenzene [70]. Comparison of the results obtained by the method of electrical polarisation of fluorescence with those determined from spectral shifts and by the method of electrical dichroism (see below) shows that the agreement is satisfactory in all the cases investigated.

IV. METHOD OF ELECTRICAL DICHROISM

The phenomenon of electrical dichroism was observed and explained for the first time by Kuhn et al. [73] It consists in the fact that a solution placed in a powerful electric field exhibits anisotropy of absorption in the region of the electronic bands of solute molecules. Hence it follows that, after passage through the solution, natural light becomes partially polarised (degree of polarisation P_E) and the intensity of initially linearly polarised light depends on the angle between the directions of light polarisation and the electric field.

Electrical dichroism is explained by partial orientation of solute molecules in the powerful electric field in consequence of their permanent dipole moment or the anisotropy of their polarisability. It is significant that, under the action of the electric field, the absorption band is also displaced in proportion to the difference $\mu_g - \mu_e$ because of the difference between the dipole moments and polarisibilities of the molecule in the ground and excited states.

†The same also applies to Eqn. (32).

A theory of the phenomenon, taking into account the band shift and therefore making it possible to relate P_E to μ_e, was developed by Liptay and Czekalla [74,75] and also by Labhart [76] (for polarisable molecules). Several versions of this method for the determination of the dipole moments of excited states, differing in the method of measurement of electrical dichroism, were proposed by Liptay, Czekalla, and Wick [69,75,77] and by Labhart [78,79].

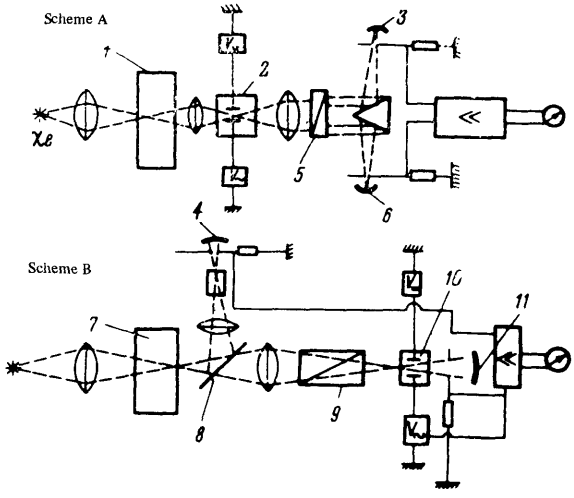


Figure 4. Outline of the apparatus for the determination of $\vec{\mu}_e$ by the method of electrical dichroism: 1) monochromator; 2) cuvette; 3) photomultiplier; 4) photomultiplier; 5) analyser; 6) photomultiplier; 7) monochromator; 8) half-silvered plate; 9) Nicol prism; 10) measuring cell; 11) photomultiplier.

In Czekalla's method‡ (Fig. 4, scheme *A*) the degree of polarisation of natural light at frequency ν is investigated in an electric field of 20–90 kV cm^{-1} (ν is in the region of the absorption band of the solution). Light from a xenon lamp is directed through a monochromator into a measuring cuvette, placed in a steady electric field interrupted at a frequency of 75 Hz. After passing through the analyser, the partially polarised light falls upon the photocathode of the photoelectric multiplier, the signal from which is amplified and recorded.

For the simplest case, in which the dipole moments $\vec{\mu}_g$ and $\vec{\mu}_e$ and also the dipole moment of the electronic transition $\vec{M}$ are parallel, the following relation is valid:

$$P_{E_\nu} = -2.3\,D_\nu\left(0.1\frac{\mu_g^2}{k^2T^2} + 0.46\frac{(\mu_e-\mu_g)\,\mu_g}{hckT}\quad\frac{d\lg\varepsilon_\nu}{d\nu}\right)\left(\frac{\varepsilon+2}{3}\right)^2 E^2, \quad (33)$$

where P_{E_ν} is the degree of polarisation of light at a frequency ν which has passed, in a direction perpendicular to that of the field E, through a solution with an optical density $D\nu$, molar extinction coefficient ϵ_ν, and dielectric constant ϵ. It is readily seen that the number μ_e can be found from the slope of the linear plot of P_E against E^2 knowing the value of μ_g and having determined experimentally D_ν and $d\lg\epsilon_\nu/d\nu$. In the more complex case the method permits the determination also of the angle between the vectors $\vec{\mu}_g$ and $\vec{\mu}_e$ and the dipole moment of the transition $\vec{M}$.

In the method for the investigation of electrical dichroism proposed by Labhart, measurements were made of the intensity of light at frequency ν polarised at a definite angle relative to the direction of the field and transmitted through the absorbing solution at right angles to the direction of the field (Fig. 4 scheme *B*). In this case the light leaving the monochromator falls on a half-silvered mirror which divides the beam into two components: one passes through the comparison cuvette (without an electric field) and the other is polarised and passes through the measuring cuvette to which a constant high potential interrupted at a frequency of 75 Hz has been applied. Both beams are received by the photomultiplier cells and the signals are amplified and transmitted to the apparatus in which the difference between them is recorded.

In Labhart's method the relative change in the intensity of the polarised light I which has passed through the solution without a field (through the comparison cuvette) and in the presence of the field E is also linearly related to E^2 and in the simplest case ($\vec{\mu}_e \parallel \vec{\mu}_g$) the corresponding formula is

$$\frac{\Delta I}{I} \equiv q_E = -\frac{5.29}{3}D_\nu\frac{(\mu_e-\mu_g)\,\mu_g}{hckT}\frac{d\lg\varepsilon_\nu}{d\nu}\left(\frac{\varepsilon+2}{3}\right)^2 E^2. \quad (34)$$

It is readily seen that the dipole moment μ_e can also be obtained from Eqn. (34) given μ_g and having calculated $d\lg\epsilon_\nu/d\nu$ from the absorption spectrum.

Using a method of measurement analogous to that described above [79] and the theory of optical absorption by molecules in solution in an electric field which they developed previously [80,81], Liptay and coworkers determined the dipole moments in the ground and excited states and also the dipole moments of the electronic transitions of a number of symmetrical molecules (nitrobenzene, 4-nitroaniline, 3,5-diamino-1-nitrobenzene, 3,5-dinitroaniline, carbazole, and 3,6-dinitrocarbazole) in dioxan [82]. The results agree well with the determinations of μ_g by the usual electrical methods and also with simple theoretical calculations of μ_g and μ_e. Comparison of the experimental and theoretical data makes it possible to assign to charge transfer two absorption bands of 3,6-dinitrocarbazole. The combination of the methods of measurement proposed by Czekalla and Labhart provides a convenient method for the determination not only of dipole moments but also (in more complex cases) of the mutual orientations of the vectors of the dipole moments and the transition moments. The available methods for the observation of electrical dichroism and also the electrical polarisation of fluorescence have been reviewed in detail [78,79]. The dipole moments μ_e of a number of derivatives of stilbene, fluorene, and biphenyl have also been determined by the method of electrical dichroism. In most cases the results were compared with data obtained by other methods and satisfactory agreement was found.

V. METHOD BASED ON THE STARK EFFECT

The method of determination of the dipole moments of molecules in the ground state from the splitting of the rotational lines in an electric field (Stark effect) measured by microwave spectroscopy is well known [83]. In order to

‡The method of measurement by Czekalla's method described here is due to Labhart [78,79]. For Czekalla's scheme, see, for example, Ref. 69.

use the Stark effect for the determination of the dipole moments of the excited states of molecules, it is necessary to observe the splitting of the fine rotational structure of the vibronic bands in the absorption spectra in an electric field, i.e. optical spectroscopic methods must be used. Such splitting becomes observable in the fairly strong electric fields employed to investigate the electronic spectra of gaseous diatomic or simple monotomic molecules whose rotational structure is well resolved. This of course greatly restricts the choice of the possible objects for investigation.

The dipole moments of $n-\pi^*$-excited states of simple organic molecules (formaldehyde and propynal) were determined for the first time by Freeman and Klemperer [84-86] and the corresponding dipole moment of formyl fluoride was determined by Lombardi et al. [87] Even for these comparatively simple organic molecules, it is not possible to observe complete splitting of the rotational structure. However, when the mutually perpendicular polarised Stark components in the formaldehyde spectrum are observed separately, well resolved doublets are revealed. This makes it possible to determine the dipole moment of the excited state after identifying the bands, provided that the dipole moment of the ground state, the splitting between the components of the doublet, and the electric field strength are known. A different procedure is used for the propynal molecule: after calculating the Stark spectra for postulated dipole moments and comparing them with those observed experimentally, the authors choose the most suitable value of the dipole moment.

It should be noted that only for molecules of the symmetric top type (the formaldehyde molecule may be regarded as such) is it possible to determine by this method the overall dipole moment μ_{ea} of the molecule along the axis of rotation directed along the bond C=O. In other cases it is necessary to determine also the component of the dipole moment μ_{eb} in the plane perpendicular to the direction of μ_{ea}. Despite its restricted applicability, the method based on the Stark effect is important, since it makes it possible, using a simple model, to observe the change in the dipole moment on excitation of the molecule in the gaseous phase, by the most direct method.

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It is useful to compare briefly the characteristics of modern methods used to determine the dipole moments of excited states. As can be seen from the foregoing, the methods most widely used at present are based on the measurement of spectral shifts under the influence of the solvent. These methods are distinguished by simplicity of experimental technique and of the formulae used for the calculations. The preferred methods [29-38,49-56] are those which permit the determination not only of the magnitude but also of the orientation of the moment $\vec{\mu}_e$ relative to $\vec{\mu}_g$, allowing at the same time the role of the polarisability (particularly for molecules with not very large permanent dipole moments). It has been shown [8-16] that failure to take into account the polarisability leads to significantly high values of $\vec{\mu}_e$. However, methods based on the measurements of spectral shifts constitute at the same time also the most approximate procedures for the determination of the permanent dipole moments of free molecules. This is due to the approximations made in the derivation and in the practical application of the formulae required for the calculation. This includes the obligatory use of the simple Onsager model of the interaction between the solute molecule and the solvent and also the necessity to specify or determine independently the Onsager radius which enters into the formulae of the majority of methods based on spectral shifts§. Moreover, another disadvantage of these methods is the need to employ a large number (10-15) of solvents with specially selected values of ϵ and n in order to obtain a sufficiently reliable result; this limits their applicability to sparingly soluble compounds. From this point of view, methods based on the measurements of the temperature variation of the spectral shift, in which the number of solvents required for the investigation is greatly reduced, are very promising.

Unfortunately the most convenient versions of the method of spectral shifts are applicable only to fluorescent molecules and permit the determination of $\vec{\mu}_e$ for the first singlet excited state only. Therefore, despite their approximate nature, the methods based on the analysis of the displacement of absorption spectra alone also merit attention, since they permit the determination of the dipole moments of the higher excited and non-fluorescent (for example $n-\pi^*$) states [18,19,27,39].

The formulae for the determination of $\vec{\mu}_e$ by electrical polarisation of fluorescence were derived on a more rigorous basis. At the same time, for the practical application of these formulae it becomes necessary to make additional simplifying assumptions (for example no account is taken of terms containing polarisibility) which introduce significant systematic errors into the results. Furthermore, there are experimental difficulties associated with the fact that, due to the very weak polarisation of luminescence under the action of an external electric field, a very powerful electric field must be employed, which may lead to the breakdown of the experimental cuvette. This risk leads in turn to the necessity for preliminary careful treatment (degassing) of the solution (usually in benzene). However, even in very powerful fields the effect remains small, which necessitates the employment of very sensitive methods for the recording of the polarised luminescence. This greatly complicates the apparatus and excludes the possibility of the determination of $\vec{\mu}_e$ of weakly luminescent compounds. Because of these considerations, the method of polarised fluorescence is less attractive, although it remains nevertheless the only fairly accurate method for the determination of $\vec{\mu}_e$ in the fluorescent (equilibrium) excited state of the molecule in non-polar solvents.

The method of electrical dichroism permits the determination of the dipole moment of an excited non-equilibrium (Franck-Condon) state with a relatively high precision, although in this case the final formulae are appreciably simplified by various (sometimes very approximate) assumptions. The experimental technique, which remains very complex, is nevertheless simpler than in the previous method because in this case a weaker field is required and the intensity of the partially polarised emission recorded is relatively high. Furthermore, the method is more general, since it permits the determination of μ_e of both fluorescent and non-fluorescent molecules and also of higher excited non-fluorescent singlet and triplet states. Finally, the procedure used to calculate $\vec{\mu}_e$ is much simpler than in the method of polarised fluorescence. All these factors undoubtedly constitute

§Here attention should be drawn to Eqns. (15) and (25) and also the method employed by Baba [22] in which the Onsager radius need not be known for the determination of μ_e.

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definite advantages of the method of electrical dichroism and it is desirable that it be widely employed by the determination of $\vec{\mu}_e$.

The Stark effect has a restricted applicability, as already mentioned. However, this is the most accurate and

Experimental dipole moments of organic compounds in excited electronic states.

№	Compound	μ_g, D	μ_e, D	Method	Refs.
	I. Aromatic compounds				
1	Nitrobenzene	4.0—4.2	6.78	S	61
			9±2	D	82
2	Acetophenone	3.0—3.8	4.23	S	61
			$n\pi^*$0.5	S	18
3	Aniline	1.6	$\Delta\mu$ 2—2.5	S	17
			6.0	S	27
4	4-Nitroaniline	6.2	14	D	77
			15.5	D	82
5	Anisole	1.35	2.37	S	61
6	*p*-Chloroacetophenone	2.23	2.68	S	61
7	3,5-Diamino-1-nitrobenzene	5.8	$1B_2$ 11.8	D	82
			$2A_1$ 15.7	D	82
8	2,5-Dinitroaniline	6.1	11.8	D	82
9	*p*-Dimethylaminobenzonitrile	6.55	23	S	11
			15.7(0°)	S	54
			14.9	F_1	72
			11.1	F_2	72
10	*NN*-Dimethyl-4-nitrosoaniline	6.7—6.9	11.7	S	38
			11.5	D	77
11	*NN*-Dimethyl-4-nitroaniline	6.85	15.0	D	
12	*p*-Nitroanisole	4.8	6.89	S	19
13	4-Dimethylamino-ω-nitrostyrene	7.7	18.0	F_1	72
			17.8	F_2	72
			18.0	D	7
14	Azulene		^1L_b —0.81	S	24
			^1L_a —0.32	S	24
			^1B_b +1.0	S	24
15	Naphthalene	0	0	S	59
16	α-Naphthylamine		$\Delta\mu$ 4.4	S	15
			$\Delta\mu$ 4.1	S	55
17	β-Naphthylamine		$\Delta\mu$ 3.5	S	15
			$\Delta\mu$ 3.4	S	55
18	α-Naphthol	1.5	$\Delta\mu$ 0.5—1.0	S	13
		(1.4)	2.5	S	36
			2.67	S	56
19	β-Naphthol	1.5	$\Delta\mu$ 0.5—1.0	S	13
		(1.8)	3.6	S	36
			3.28	S	56
20	Methyl β-naphthyl ether	1.2	$\Delta\mu$ 0.5	S	12
		(1.2)	2.9	S	36
			2.8	S	56
21	Hexamethylbenzene–tetrachlorophthalic anhydride complex	3.6	14±3	S	70
			7.6(50°)	S	52
			10±1.5	F_1	70
22	4-Amino-4′-nitrobiphenyl	6.0	18	S	10
		(6.7)	16.3(0°)	S	36
			14.5(0°)	S	54
			22.8	F_1	72
			22.2	F_2	72
			23.0	D	77
23	4-Dimethylamino-4′-nitrobiphenyl	6.6	21.2	F_1	72
			23.1	F_2	72
			24.0	D	77
24	4-Amino-4′-cyanobiphenyl	6.0	13.0	F_1	72
			15.3	F_2	72
			16.5	D	72
25	2-Amino-7-nitrofluorene	5.8	25	S	10
		(6.6)	19.7(0°)	S	36
			17.3(0°)	S	54
			18.6	F_1	72
			19.2	F_2	72
			23.0	D	77
26	4-Amino-4′-nitrostilbene	6.5	23.5	F_1	72
			23.4	F_2	72
			22.0	D	77
27	4-Dimethylamino-4′-nitrostilbene	7.1	32	S	10
		(7.3)	24.8(0°)	S	36
			24.7(0°)	S	54
			25.1	F_1	72
			25.2	F_2	72
			26.5	D	77
28	4-Methoxy-4′-nitrostilbene	(5.3)	19.3(0°)	S	36
29	4-Cyano-4′-dimethylaminostilbene	7.1	29	S	10
			$\Delta\mu$ 14	S	36
			21.5(0°)	S	54
			20.2	F_1	72
			21.2	F_2	72
			20.0	D	77
30	4-Dimethylaminobenzylidene-4′-nitroaniline	8.6	38	S	10
		(7.9)	26.2(0°)	S	36
			26.5(0°)	S	49
	II. Heterocyclic compounds				
1	Pyrazine	0	0	S	22
2	Pyridazine	3.94	$n\pi^*$1.10	S	22
3	Pyrimidine	2.2	$n\pi^*$—0.52	S	22
4	Carbazole	1.6—1.9	$\Delta\mu$ 2.2	S	14
			3.1±0.7	D	82
5	Acridine	(9.0)	11.5(0°)	S	31
6	2,5-Diphenyloxadiazole	(3.5)	6.0	S	4
7	2-(4-*N*-Dimethylaminophenyl)-5-phenyl-1-oxa-3,4-diazole	5.13	16.05(0°)	S	44
8	2,5-Diphenyloxazole	1.55	5.1(0°)	S	44
9	2,5-Di-(*p*-anisyl)-1-oxa-3,4-diazole	4.2	8.0(0°)	S	47
10	4-Aminophthalimide	3.5	7.1(15°)	S	36
			7.1(20°)	S	63
			6.8(16°)	S	53
11	3-Aminophthalimide	2.6	5.2(20°)	S	36
			5.1(20°)	S	63
			4.9(19°)	S	51
12	3-Monomethylaminophthalimide	2.7	5.7(25°)	S	36
			5.5(35°)	S	63
13	3-Dimethylaminophthalimide	2.7	5.6(25°)	S	36
14	3-Acetamidophthalimide	2.4	4.1(65°)	S	36
			4.5(90°)	S	51
15	3,6-Diaminophthalimide	2.14	4.7(0°)	S	36
		(2.3)	4.5(0°)	S	63
			5.4(0°)	S	51
16	6-Amino-3-dimethylaminophthalimide	2.14	4.6(40°)	S	32
			4.8(33°)	S	51
17	3,6-Bis(dimethylamino)phthalimide	(2.2)	5.7(0°)	S	36
18	3,6-Diacetamidophthalimide	(5.5)	0(0°)	S	36
19	4-Amino-*N*-methylphthalimide	3.6	9.9	S	64
20	*N*-methyl-4-monomethylaminophthalimide	3.7	10.3	S	64
21	*N*-Methyl-4-dimethylaminophthalimide	3.7	11.15	S	64
22	4-Acetamido-*N*-methylphthalimide	4.6	9.8	S	64
23	3-Amino-*N*-methylphthalimide	2.7	7.2	S	64
24	3-Acetamido-*N*-methylphthalimide	2.4	5.1	S	64
25	γ-[4-5-Hydroxy-3-phenyliso-oxazolyl)-4-butadienyl]-*N*-methylpyridinium betaine	(29)	19	S	36
26	Phenol Blue	5.8	7.5—9.1	S	5
			⩾10.2	S	28
27	Aminoquinols with a merocyanine group		$\Delta\mu$ 3.5—5.5	S	67
28	Dimethylnaphtheurhodine	2.0	12	S	8
29	3,6-Dinitrocarbazole	6.6	19.0	D	82
30	1,3,5-Triphenylpyrazoline	2.58	7.7(40°)	S	46
31	3-(*p*-Chlorophenyl)-1,5-diphenyl-2-pyrazoline	3.39	10.8(23°)	S	46
32	1-(*p*-Chlorophenyl)-3,5-diphenyl-2-pyrazoline	3.87	10.0(40°)	S	46
33	9,10-Diazaphenanthrene	3.93	$n\pi^*$1.15	S	23
	III. Aliphatic compounds				
1	Methyl iodide	1.5	$n\sigma^*$—0.7	S	39
2	Nitromethane	3.2	$n\pi^*$2.9	S	39
3	Bromoform	1.0	$n\sigma^*$—1.7	S	39
4	Formaldehyde	2.34	$n\pi^*$ 1.56	St	85
5	Formyl fluoride	0.595	$n\pi^*$ 1.65	St	87
6	Acetone	2.7—2.8	$n\pi^*$ 1.4	S	39
			$n\pi^*$ 0.86	S	60
7	Propynal	2.39	$n\pi^*$ 0.7	St	86
8	Mesityl oxide		7.6	S	28
9	Thiourea	4.9	$n\pi^*$ 2.5	S	21
10	*N*-Methylthiourea	4.2	$n\pi^*$ 0.1	S	21
11	*NN′*-Diethylthiourea	4.9	$n\pi^*$ 2.8	S	21
12	Tetramethylthiourea	4.7	$n\pi^*$ 0.1	S	21

NOTES TO TABLE

1. In a few cases the limiting values employed by various authors to determine μ_e are indicated in the μ_g column and the figures in brackets represent values obtained by the spectral shift method.

2. In the μ_e column the figures in brackets represent the angles between $\vec{\mu}_g$ and $\vec{\mu}_e$ proposed on the basis of structural considerations when these are 0° or 180°, or obtained by the spectral shift method if they are not 0° or 180°; the values of $|\Delta\vec{\mu}|$ (and not $|\vec{\mu}_e|$) obtained from spectral shifts and also μ_e for the $n-\pi^*$ and $n-\sigma^*$ states and states the symmetry of which is known are indicated on the left-hand side by the appropriate symbols. All the remaining values refer to the lowest singlet excited electronic states.

3. The significance of the symbols in the "method" column is as follows: S—spectral shift method; F_1 and F_2—method of electrical polarisation of fluorescence in which the values of μ_e are determined from the slope or from the intercept on the ordinate axis respectively; D—method of electrical dichroism; St—method based on the Stark effect.

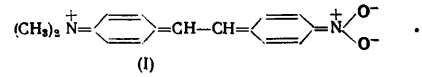
4. All the values of μ_e obtained by the F_1, F_2, and D methods are given for solutions in benzene with the exception of compounds 9 and 29 in Class I whose values are quoted for solutions in dioxan.

direct method for the determination of the dipole moments of excited states of free (i.e. unperturbed by the solvent) molecule. Furthermore, it appears that there is hope that the application of more refined analytical methods and better apparatus will extend somewhat the range of objects susceptible to investigation by this procedure.

It follows from the foregoing that various methods, despite their disadvantages, supplement one another to a considerable degree, which makes it desirable to determine $\vec{\mu}_e$ simultaneously by several of the above methods in important cases.

In conclusion a Table is presented in which the results of the determination of the dipole moments of the excited states of many molecules and complexes by different investigators using the methods described above are compiled. These data lead, in the first place, to the important conclusion that the values of $\vec{\mu}_e$ obtained by different procedures are similar. This finding shows that both the postulates on which the methods employed are based and the results themselves are correct. Furthermore, the data permit certain interesting conclusions to be drawn concerning the electronic structure of the excited states of organic molecules.

Thus comparison of $\vec{\mu}_e$ and $\vec{\mu}_g$ indicates a considerable increase of the polarity of many molecules in the excited state compared with the ground state. For example, in 4-dimethylamino-4′-nitrostilbene this indicates a considerable contribution of the dipolar structure (I) to the electronic state attained when the molecule is excited in the region of the long-wavelength electronic system:

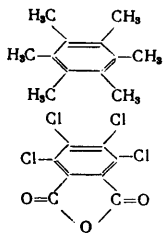


(I)

As already mentioned, the increase of polarity on electronic excitation of the molecule is in general characteristic of many singlet excited states of substances with active functional groups. This behaviour is shown particularly clearly for stilbene, fluorene, and biphenyl derivatives investigated by all the available methods and also oxadiazole and triphenylpyrazoline derivatives. On excitation, not only the magnitude but also the direction of the dipole moment usually changes appreciably. The direction of the vector for the difference between the dipole moment in the excited and ground states indicates the migration of charge from a donor to an acceptor group (transitions with charge transfer). These results, obtained mainly in the study of phthalimides [30,32,34,37,51,53], were described in detail above. Here we shall mention only that they agree well with the conclusions of many theoretical investigations [1,44,45,88].

Interesting data were obtained in the study of the dipole moments of the excited $\pi-\pi^*$ state of alternant and non-alternant hydrocarbons. It was found [59], in particular, that the naphthalene molecule is non-polar in the $^1B_{1u}$ and $^1\Gamma_{2u}$ excited states, as in the ground state, in agreement with the postulates of the molecular orbital theory. The azulene molecule remains polar also in $\pi-\pi^*$ excited states [24], but the direction of $\vec{\mu}_e$ in the first two singlet excited states is the opposite of that of $\vec{\mu}_g$. This indicates electron transfer from the five-membered to the seven-membered ring on excitation. The measurements of $\vec{\mu}_e$ of the first singlet excited state of certain molecular charge-transfer complexes yielded decisive proof of a sharp increase in the polarity of the complex in the excited state. Furthermore, it has been shown, for example [40,57], that in the formation of the iodine complex of 4-methoxycarbonylpyridine there is complete electron transfer from the aromatic molecule to the iodine atom with formation of an ion pair.

The dipole moment $\vec{\mu}_e$ of the sandwich type complex (II), determined by Lippert's spectral shift method and by the method of electrically polarised fluorescence, amounts to 14 ± 3.0 D and 10 ± 1.5 D respectively [70], which indicates an appreciable charge transfer from hexamethylbenzene to tetrachlorophthalic anhydride on excitation (the calculated moment of the structure D^+A^- is about 16 D, while $\vec{\mu}_g$ is only 3.6 D).



(II)

If however, one does not begin with the assumption that the vectors of the difference between the dipole moments of the steady states and the dipole moment of the electronic transition are parallel, as was done by Czekalla and Meyer [70], and the angle between the moments $\vec{\mu}_e$ and $\vec{\mu}_g$ is determined by the spectral shift method, then, as shown by Bilot and Kawski [52], the angle is about 50° and, although the polarisation in the excited state does increase, the increase is much less than found in the preceding investigation ($|\vec{\mu}_e| = 7.6$ D). These results are confirmed by those of Bakhshiev [40].

On transition of molecules to the $n-\pi^*$ excited state, the polarity of the molecule diminishes appreciably compared with the ground state in the majority of cases. Thus the values of $\vec{\mu}_e$ determined by the Stark method for the $n-\pi^*$ states of formaldehyde and propynal are much lower than the corresponding values of $\vec{\mu}_g$. Analogous relations between $\vec{\mu}_e$ and $\vec{\mu}_g$ on $n-\pi^*$ excitation are characteristic also of other carbonyl compounds (various ketones [18] and acetones [39,60]). This is evidence that the transition to the $n-\pi^*$ excited state is localised at the carbonyl group and is associated with its polarisation in the direction opposite to that which obtains in the ground state. The results of recent measurements of $\vec{\mu}_e$ of nitromethane [9,10,39] diazaphenanthrene [23], and derivatives of thiourea [21], pyridazine, and pyrimidine [22] lead to similar conclusions, that is, the decrease of the dipole moment on $n-\pi^*$ excitation, and, for pyrimidine, the reverse direction of the vector $\vec{\mu}_e$ with respect to that of the vector $\vec{\mu}_g$. Similar changes in the direction of the dipole moment on excitation are particularly characteristic of the $n-\sigma^*$ transition [39] (methyl iodide, bromoform), which is evidence of a more important displacement of electron density on $n-\sigma^*$ excitation compared with the $n-\pi^*$ transition. The results of Lombardi et al. [87] do not agree, however, with the concept of the localisation of excitation at a C=O group in the $n-\pi^*$ excitation of the formyl fluoride molecule, since the dipole moment would not then decrease and its sign would remain the same.

The above data for the difference between the changes of dipole moments in charge-transfer $\pi-\pi^*$ and $n-\pi^*$ transitions lead to the conclusion that the difference is one of the principal factors which determine the direction of the shift of the corresponding absorption band when non-polar solvents are replaced by polar solvents (the so called red and blue spectral shifts). The latter, in turn, throws light on the nature of solvatochromism, linking it

mainly to the difference between the electrostatic interactions of the molecules with the solvent in the ground and excited states in consequence of the change in the dipole moment of the molecule in the quantum jump.

Despite the large number of published studies, the investigation of the dipole moments of excited states has essentially only just begun. The main importance of the results obtained consists in the fact that the dipole moment of the excited state is at the present time virtually the only experimental quantity characterising its electronic configuration.

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