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Temperature Dependence of Fluorescence Spectra and Fluorescence Polarization of Some Organic Compounds in Polar Solvents. The Franck-Condon Excited States

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Fluorescence and absorption spectra and fluorescence polarization were measured at different temperatures, ranging from room temperature to 77°K, for 9,10-diazaphenanthrene, 2-naphthol and 2,3-naphthalenediol in polar solvents. At about 120°K, the fluorescence spectra shifted rapidly to the blue as the temperature was lowered. This observation is quantitatively interpreted on the basis of a kinetic scheme involving competitive rate processes, *viz.*, radiative transition from the Franck-Condon excited state, as defined for the dipole orientation of the solvent, and relaxation of the Franck-Condon state into the equilibrium excited state. The Franck-Condon destabilization energies are evaluated from the observed blue shifts. Along with the fluorescence blues hifts, the degrees of polarization increased rapidly, but at a somewhat higher temperature of about 140°K. This phenomenon is related to the rotational relaxation of the solute molecule, and is discussed in comparison with the fluorescence blue shift.

It is generally accepted that, in organic compounds in solution, absorption and emission transitions occur according to the Franck-Condon principle.[1-4] The effect of this principle on the electronic spectra is of especial importance when both solute and solvent molecules are polar, and there is a difference in the dipole moment between the ground and excited states of the solute. At the instant of the formation of its excited state, the solute molecule is considered to be surrounded by the solvent molecules whose orientation is appropriate to the ground state of the solute. Such a situation is referred to as the Franck-Condon excited state. This state may pass into the equilibrium excited state, where the solvent orientation is appropriate to the excited state, through a process of relaxation. Thus the fluorescence transition originates usually from the equilibrium excited state.

A few attempts have been made to obtain experimental evidence for the participation of the Franck-Condon principle in the solvent effect on the electronic spectra of aromatic compounds.[2-4] These investigations are based on the idea that the relaxation process mentioned above should be inhibited if the solvent has such a high viscosity that the relaxation time is longer than the fluorescence lifetime.

In addition to the relaxation of the solvent orientation from the Franck-Condon into the equilibrium excited state, rotational relaxation of the solute molecule may occur during the fluorescence lifetime, which leads to the depolarization of the fluorescence.[5-7] The two relaxation processes would be correlated with each other through the viscosity and hence the temperature of the solvent.

The purpose of the present study is to obtain detailed and definite information as to the Franck-Condon excited state by dealing quantitatively with these relaxation phenomena. Thus, absorption and fluorescence spectra along with degrees of fluorescence polarization were measured in a wide range of temperature with 9,10-diazaphenanthrene, 2-naphthol and 2,3-naphthalenediol as polar solutes. It has been reported[8] that for the diazaphenanthrene the dipole momet is smaller in the fluorescent

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1) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

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excited state, which is of an (n,π^*) type,[9] than in the ground state.

Experimental

Materials. 9,10-Diazaphenanthrene (Aldrich Chemical Co., U.S.A.) was purified either by the method described in a previous paper[8] or by zone melting. 2-Naphthol and 2,3-naphthalenediol were recrystallized from ligroin and from water, and were further purified by vacuum sublimation.

Mixtures of isopentane and *n*-butyl chloride (volume ratio, 6.5 : 3.5) and of ethyl ether, isopentane and ethanol (volume ratio, 8 : 3 : 5) were used as polar solvents; these mixtures, abbreviated to PB and EPA respectively, give good rigid glasses at 77°K. Isopentane was passed through a freshly activated silica-gel column, and the other solvents were purified by methods described in "Organic Solvents."[10]

Apparatus and Procedure. Absorption spectra were obtained with a Hitachi EPS-3 spectrophotometer, and fluorescence spectra and their polarizations were measured with an apparatus constructed in our laboratory.[11] All these measurements were made on sample solutions in a 1-cm square quartz cell which was placed in a glass Dewar with quartz windows. For cooling the sample cell, nitrogen gas was passed through liquid nitrogen, and then led to the Dewar. The cell could be maintained at any desired temperature between 280 and 77°K by controlling the flow velocity of the nitrogen gas. The errors in the temperature were estimated to be ±1°K. The degrees of polarization, *P*,[11] were measured by the method of photoselection, and were corrected for instrumental factors in the usual manner.[11]

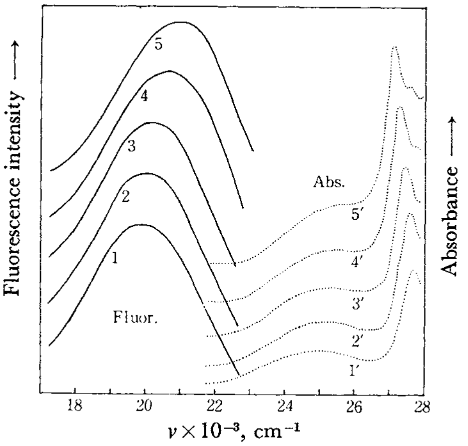

Fig. 1. Fluorescence and absorption spectra at different temperatures for 9,10-diazaphenanthrene in PB.
1, 24°; 2, −78°; 3, −150°; 4, −168°; 5, −196°; 1′, 23°; 2′, −53°; 3′, −118°; 4′, −156°; 5′, −196°C

Results

The fluorescence and absorption spectra of 9,10-diazaphenanthrene, 2-naphthol and 2,3-naphthalenediol observed at different temperatures are shown in Figs. 1—3. To avoid confusion the spectral curves are moved upward successively. The position of the fluorescence maximum or peak is plotted against temperature in Figs. 4—6.

The *P* values for the fluorescence with respect to excitation into the lowest singlet excited state were determined at different temperatures. The results are shown in Figs. 4—6.

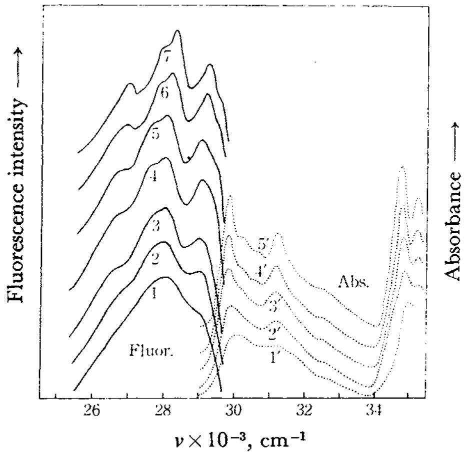

Fig. 2. Fluorescence and absorption spectra at different temperatures for 2-naphthol in EPA.
1, 24°; 2, −53°; 3, −117°; 4, −134°; 5, −152°; 6, −171°; 7, −196°; 1′, 24°; 2′, −69°; 3′, −135°; 4′, −161°; 5′, −196°C

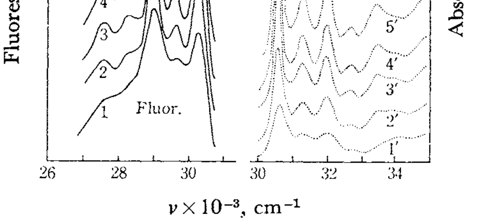

Fig. 3. Fluorescence and absorption spectra at different temperatures for 2,3-naphthalenediol in EPA.
1, 22°; 2, −57°; 3, −109°; 4, −136°; 5, −167°; 6, −196°; 1′, 23°; 2′, −59°; 3′, −109°; 4′, −148°; 5′, −196°C.

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[9] E. Lippert and W. Voss, *Z. Physik. Chem., N. F.*, **31**, 321 (1962).

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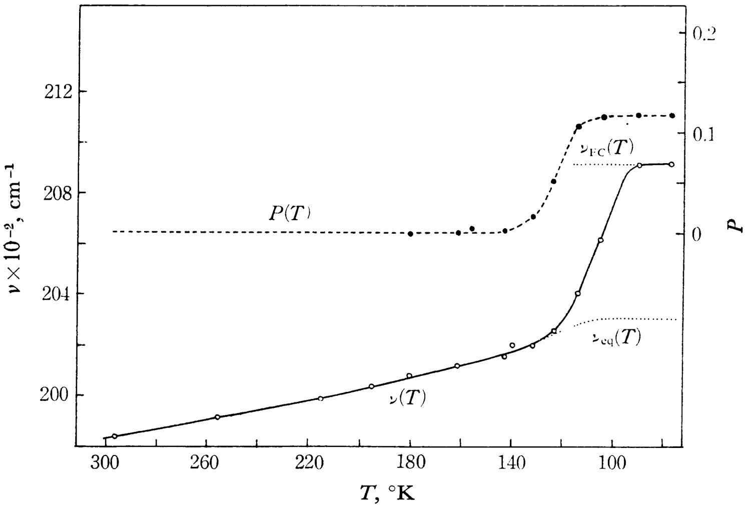

Fig. 4. Plots of ν and P *vs.* T for 9,10-diazaphenanthrene in PB. ν represents the frequency of the fluorescence maximum.

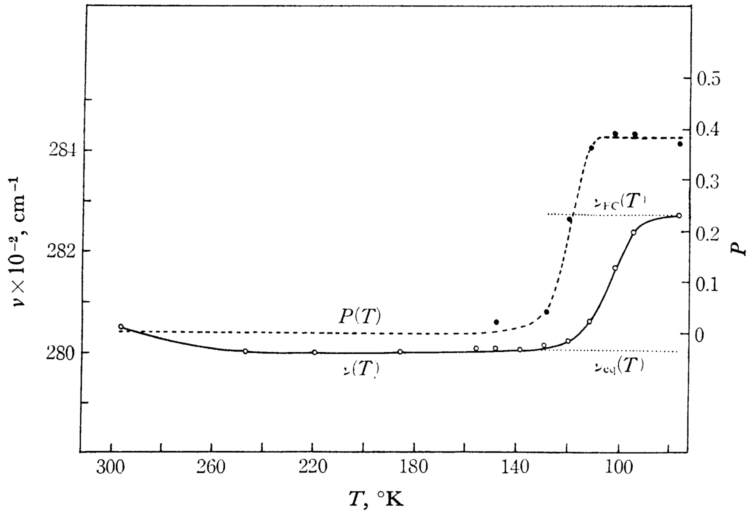

Fig. 5. Plots of ν and P *vs.* T for 2-naphthol in EPA. ν represents the frequency of the fluorescence peak at about 28000 cm^{-1}.

Discussion

Since polar substances were employed as solutes and solvents in this study, the solute dipole-solvent dipole interaction is expected to play a major role in understanding the behavior of the observed electronic spectra. The ground state of a solute molecule will hereafter be denoted by *g*, and the lowest singlet excited state in which we are interested will be denoted by *e*. Thus, the dipole moments in the *g* and *e* states are expressed as μ_g and μ_e, respectively.

For 9,10-diazaphenanthrene, $\mu_g = 3.9$D;[12] the *e* state is known to be of an (n,π^*) type,[9] and the value of μ_e was determined to be 1.15D from the solvent effect on the absorption and fluorescence spectra.[8] Thus the electronic transition $g \rightarrow e$ is accompanied by a marked decrease in the dipole moment. For 2-naphthol, $\mu_g = 1.4$D;[12] the *e* state is the $L_b(\pi,\pi^*)$, and the dipole moment increases by 0.5—1D on going from the *g* to the *e* state.[13] As regards 2,3-naphthalenediol no pertinent data are available for μ_g and μ_e values, but the situation is probably similar to that in 2-naphthol.

Franck-Condon Blue Shift. An absorption transition occurs in general from the equilibrium ground state to the Franck-Condon excited state.

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[12] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, San Francisco (1963).

[13] N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 465 (1956).

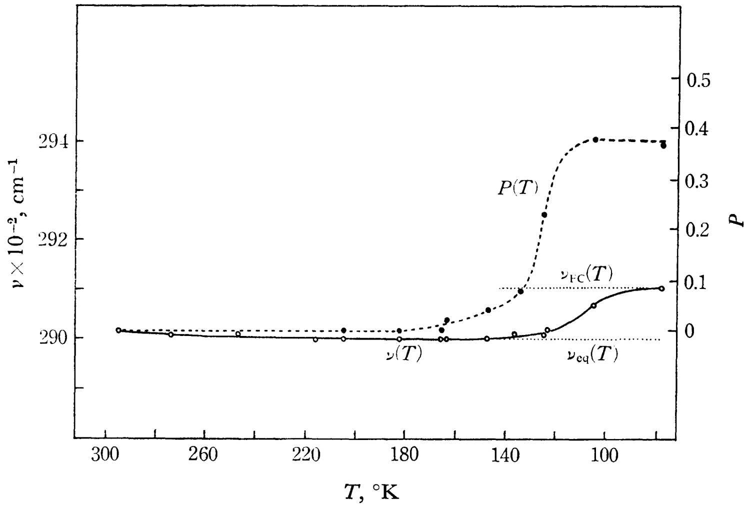

Fig. 6. Plots of ν and P *vs.* T for 2,3-naphthalenediol in EPA. ν represents the frequency of the fluorescence peak at about 29000 cm^{-1}.

If it is assumed that there is complete reorientation of the solvent dipoles in the excited state, the fluorescence transition will start from the equilibrium excited state for the Franck-Condon ground state where the solvent orientation is appropriate to the excited state.

Dielectric constants (D) and refractive indices (n) of solvents will increase with a decrease of the temperature. On the above assumption, we expect from the theory of the solvent effect[13,14] that as the temperature decreases both the absorption (corresponding to $g\rightarrow e$) and fluorescence (corresponding to $e\rightarrow g$) spectra are gradually displaced to the blue for 9,10-diazaphenanthrene in which $\mu_e<\mu_g$, and to the red for 2-naphthol and 2,3-naphthalenediol in which $\mu_e>\mu_g$. This expectation is fulfilled in the case of the absorption spectra (*cf.* Figs. 1—3). The fluorescence spectra show similar behaviors at temperatures higher than 120°K.

With all the solute compounds studied, the fluorescence spectrum shifts rapidly to the blue as the temperature is lowered below 120°K. At such low temperatures the solvent becomes rigid, and the reorientation of the solvent dipoles will be inhibited partly or completely, depending on the viscosity of the solvent. The blue shift is therefore attributable to the fact that the fluorescence transition occurs also from the Franck-Condon excited state. The blue shift of this kind will be called a "Franck-Condon blue shift." In the light of the foregoing discussions, it can readily be understood that such a blue shift does not take place in the case of the absorption transition.

In Figs. 4—6, $\nu(T)$ represents the frequency in wavenumbers of the fluorescence maximum or peak which was actually observed as a function of temperature. Let $\nu_{eq}(T)$ and $\nu_{FC}(T)$ represent the corresponding frequencies which would be observed if the fluorescence were to originate exclusively in the equilibrium excitated state and the Franck-Condon excited state, respectively. At high temperatures $\nu_{eq}(T)$ will agree with $\nu(T)$, whereas in the low-temperature region where the Franck-Condon blue shift takes place, $\nu_{eq}(T)$ must deviate from $\nu(T)$. For the latter region, $\nu_{eq}(T)$ curve was obtained by extrapolation from the $\nu(T)$ curve at higher temperatures. (See the dotted lines in Figs. 4—6.)

On the other hand, $\nu_{FC}(T)$ is considered to agree with the observed $\nu(T)$ at temperatures near 77°K. The $\nu_{FC}(T)$ curve for the higher temperatures was obtained again by extrapolation.

Now, let $\nu_{eq}(T)$ and $\nu_{FC}(T)$ at 77°K be written as ν^0_{eq} and ν^0_{FC}. Then, the difference

$$\delta\nu^0_{FC}=\nu^0_{FC}-\nu^0_{eq}\ (=E^0_{FC}/hc) \qquad (1)$$

corresponds to the sum of the Franck-Condon destabilization energies, denoted by E^0_{FC}, for the

TABLE 1. CONSTANTS RELATED TO TEMPERATURE DEPENDENCE OF FLUORESCENCE SPECTRA AND FLUORESCENCE POLARIZATION

	9,10-Diazaphenanthrene in PB	2-Naphthol in EPA	2,3-Naphthalenediol in EPA
$\delta\nu^0_{FC}$ (cm^{-1})	610	265	100
E^0_{FC} (kcal/mol)	1.75	0.76	0.29
c_1	1.20×10^8	5.89×10^7	4.78×10^7
c_2 (deg)	1.96×10^3	1.87×10^3	1.95×10^3
$E_{a,r}$ (kcal/mol)	3.9	3.7	3.9
$E_{a,r'}$ (kcal/mol)	6.5	8.3	7.0

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14) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

excited and ground states at 77°K. In Eq. (1), $\boldsymbol{h}$ is the Planck constant, and $\boldsymbol{c}$ is the volocity of light. The values of $\delta\nu^0_{\mathrm{FC}}$ and E^0_{FC} are given in Table 1.

In general, absorption and fluorescence bands of a polar solute molecule will undergo frequency shifts on changing the solvent from a nonpolar to a polar substance. Their respective frequency shifts will be designated as $\Delta\nu_a$ and $\Delta\nu_f$. If, at a given temperature, the viscosity of the solvent is so low that the fluorescence is observed only from the equilibrium excited state, $\Delta\nu_a-\Delta\nu_f$ corresponds to the sum of the Franck-Condon destabilization energies, denoted by E_{FC}, at that temperature. According to McRae,[14] $\Delta\nu_a-\Delta\nu_f$ $(=E_{\mathrm{FC}}/\boldsymbol{hc})$ is approximately given as[*2]

$$\Delta\nu_a - \Delta\nu_f = \frac{E_{\mathrm{FC}}}{\boldsymbol{hc}} \simeq \frac{2}{\boldsymbol{hc}}\frac{(\mu_g-\mu_e)^2}{a^3}\left[\frac{D-1}{D+2}-\frac{n_{\mathrm{D}}^2-1}{n_{\mathrm{D}}^2+2}\right] \tag{2}$$

where a is the cavity radius, and n_{D} and D are the refractive index for the sodium D line and dielectric constant of the polar solvent. Equation (2) shows that E_{FC} should be large when dipole moments differ greatly between the ground and excited states and the solvent has a large orientation polarization.

For 9,10-diazaphenanthrene in PB, $\delta\nu^0_{\mathrm{FC}}$ amounted to 610 cm^{-1}, while $\Delta\nu_a-\Delta\nu_f$ at 23°C was found to be 250 cm^{-1} with n-pentane as the nonpolar reference solvent; that is, the E_{FC} value is much larger at 77°K than at room temperature. This observation is in agreement with the expectation that when the temperature is lowered the D value of the solvent will increase to a far greater extent than its n_{D} value.

It is seen in Table 1 that E^0_{FC} for 9,10-diazaphenanthrene is considerably large as compared with E^0_{FC} for the naphthalene derivatives. This might be interpreted as due to the fact that $(\mu_g-\mu_e)^2$ is of much higher value for the diazaphenanthrene.

Relaxation from the Franck-Condon Excited State into the Equilibrium Excited State. Let $\delta\nu(T)$ denote the difference between $\nu(T)$ and $\nu_{\mathrm{eq}}(T)$:

$$\delta\nu(T) = \nu(T) - \nu_{\mathrm{eq}}(T) \tag{3}$$

The experimental results shown in Figs. 4—6 were found to be reproduced very well by empirical relations of the following type:

$$\delta\nu^0_{\mathrm{FC}}/\delta\nu(T) = 1 + c_1 \exp(-c_2/T) \tag{4}$$

where c_1 and c_2 are constants inherent to each of the solute-solvent systems. In Fig. 7 are shown the $\delta\nu(T)$ curves as obtained from Eq. (4) with the constants c_1 and c_2 given in Table 1. In the same figure are also given the experimental points, which are seen to fall on the $\delta\nu(T)$ curves.

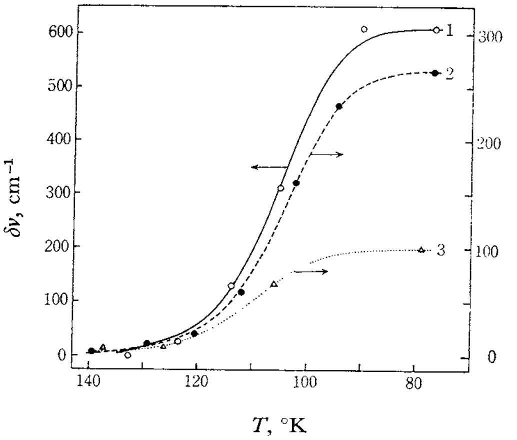

Fig. 7. Calculated $\delta\nu(T)$ curves and experimental points.
1, 9,10-diazaphenanthrene; 2, 2-naphthol; 3, 2,3-naphthalenediol.
The ordinate to be used is indicated by an arrow.

The relaxation process in which the solvent molecules surrounding the excited solute molecule reorient themselves from the Franck-Condon to the equilibrium state is assumed to be of the first order with respect to the solute. The deactivation processes of the solute molecule can then be represented by a kinetic scheme shown in Fig. 8, with the rate constants denoted by k's. Here the asterisk refers to the excited state, f and q mean fluorescent and nonfluorescent transitions, respectively, and the subscript r indicates the relaxation process mentioned above. Among the various rate constants, k_r is considered to be particularly sensitive to temperature; hence it is written as $k_r(T)$, the other constants being regarded as independent of temperature.

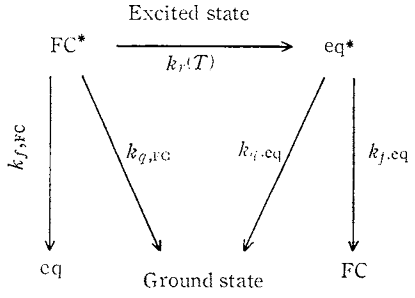

Fig. 8. Kinetic scheme of deactivation processes.

Let $\phi_{\mathrm{FC}}(T)$ and $\phi_{\mathrm{eq}}(T)$ denote the quantum yields of the fluorescence emissions from the Franck-Condon and equilibrium excited states, respectively. Then it follows from the scheme of Fig. 8 that

$$\phi_{\mathrm{FC}}(T) = \frac{k_{f,\mathrm{FC}}}{k_r(T) + k_{f,\mathrm{FC}} + k_{q,\mathrm{FC}}} \tag{5}$$

[*2] The meaning of the symbol $\Delta\nu$ used in this paper is different from that of the same symbol in McRae's paper. It can be shown, however, that in either case $\Delta\nu_a-\Delta\nu_f$ is expressed in the same form.

$$\phi_{\mathrm{eq}}(T) = \frac{k_r(T)}{k_r(T) + k_{f,\mathrm{FC}} + k_{q,\mathrm{FC}}} \times \frac{k_{f,\mathrm{eq}}}{k_{f,\mathrm{eq}} + k_{q,\mathrm{eq}}} \tag{6}$$

It is to be expected that, if both $\phi_{\mathrm{FC}}(T)$ and $\phi_{\mathrm{eq}}(T)$ are of finite values, there appear simultaneously two kinds of fluorescence spectra associated with FC*→eq and eq*→FC transitions. Actually this is not the case, as is seen from Figs. 1—3, so that the two spectra in question are assumed to coalesce into a single spectrum. It is further assumed that the frequency of the fluorescence maximum or peak is expressed as

$$\nu(T) = \frac{\phi_{\mathrm{FC}}(T)}{\phi_{\mathrm{FC}}(T) + \phi_{\mathrm{eq}}(T)}\nu_{\mathrm{FC}}(T) + \frac{\phi_{\mathrm{eq}}(T)}{\phi_{\mathrm{FC}}(T) + \phi_{\mathrm{eq}}(T)}\nu_{\mathrm{eq}}(T) \tag{7}$$

A combination of Eqs. (3) and (5)—(7) leads to the following equation:

$$\delta\nu^0_{\mathrm{FC}}/\delta\nu(T) = 1 + \tau_f k_r(T) \tag{8}$$

where τ_f is the lifetime of the fluorescence from the equilibrium excited state, *i. e.*,

$$\tau_f = 1/(k_{f,\mathrm{eq}} + k_{q,\mathrm{eq}})$$

In the derivation of Eq. (8), assumptions have been made that

$$k_{f,\mathrm{FC}} \simeq k_{f,\mathrm{eq}}$$

and

$$\nu_{\mathrm{FC}}(T) - \nu_{\mathrm{eq}}(T) = \delta\nu_{\mathrm{FC}}(T) \simeq \delta\nu^0_{\mathrm{FC}}$$

The latter relation is to be reasonable in the limited range of T under consideration.

Let us express $k_r(T)$ by an equation of the Arrhenius type, that is

$$k_r(T) = A\exp(-E_{a,r}/\boldsymbol{R}T) \tag{9}$$

and put

$$\tau_f A = c_1 \tag{10}$$

$$E_{a,r}/\boldsymbol{R} = c_2 \tag{11}$$

Then Eq. (8) becomes identical in form with Eq. (4). In other words, in the empirical relation of Eq. (4), c_1 is related to the fluorescence lifetime τ_f, and c_2 to the activation energy $E_{a,r}$ of the relaxation process. It may be noted in this connection that the natural lifetimes, τ°_f, of 9,10-diazaphenanthrene, 2-naphthol and 2,3-naphthalenediol as obtained from the absorption intensities are 5.0×10^{-7}, 5.7×10^{-8} and 4.5×10^{-8} sec, respectively. From these τ°_f values and a knowledge of the fiuorescence quantum yields, the actual lifetime, τ_f, was estimated to be about 5×10^{-8} sec for 9,10-diazaphenanthrene and about 1×10^{-8} sec for the two naphthalene derivatives. The values of $E_{a,f}$ obtained from the c_2 values are given in Table 1.

The relaxation time for the process FC*→eq* (Fig. 8) will be denoted by $\tau_r(T)$. Since $\tau_r(T) = 1/k_r(T)$, it follows from Eq. (8) that

$$\frac{\delta\nu^0_{\mathrm{FC}}}{\delta\nu(T)} = 1 + \frac{\tau_f}{\tau_r(T)} \tag{12}$$

It is seen that, at the temperature where $\delta\nu(T) = (1/2)\,\delta\nu^0_{\mathrm{FC}}$, $\tau_r(T)$ is equal to τ_f; that is, the relaxation time is of the order of 10^{-8} sec.

In the foregoing argument the fluorescence lifetime τ_f was defined with respect to the equilibrium excited state. It would not be unreasonable to presume that

$$k_{q,\mathrm{FC}} \simeq k_{q,\mathrm{eq}}$$

Then, if $k_r(T)\to0$, the lifetime of the Franck-Condon excited state becomes equal to τ_f. With finite values of $k_r(T)$, the former lifetime will be shorter than τ_f. Even in such cases, however, the mean lifetime of the excited solute molecules as a whole, which include the molecules belonging to the Franck-Condon excited state and to the equilibrium excited state, is found to be given by τ_f.[*3] Thus, in the following discussion, τ_f will be used as the fluorescence lifetime regardless of the vlaues of $k_r(T)$.

Temperature Dependence of Fluorescence Polarization and Rotational Relaxation. As is seen in Figs. 4—6, the fluorescence P values increase rapidly as the temperature is lowered below 140°K; this temperature is somewhat higher than the temperature where the fluorescence blue shifts begin.

The temperature dependecnce of the fluorescence polarization is obviously related to the rotational relaxation of the solute molecule. At 77°K, the viscosity of the solvent must be too high for the solute molecule to rotate within the fluorescence lifetime τ_f. The value of P at this temperature, denoted by P_0, will therefore be regarded as its value in the absence of rotational relaxation. At higher temperatures the rotational depolarization of fluorescence may take place, and the P value will be given by [6,7]

$$\frac{1/P(T) - 1/3}{1/P_0 - 1/3} = 1 + \frac{\tau_f}{\tau_{r'}(T)} \tag{13}$$

where $\tau_{r'}(T)$ stands for the relaxation time for rotation of the solute molecule. It should be noted that Eq. (13) is analogous to Eq. (12).

Since $k_r(T) = 1/\tau_r(T)$, it follows from Eq. (9) that

$$1/\tau_r(T) = A\exp\left(-E_{a,r}/\boldsymbol{R}T\right) \tag{14}$$

Similarly, $1/\tau_{r'}(T)$ is expressed as

[*3] This statement is based on the following considerations. According to the kinetic scheme of Fig. 8

$$\mathrm{d}N^*_{\mathrm{eq}}/\mathrm{d}t = -[k_r(T) + k_{f,\mathrm{FC}} + k_{q,\mathrm{FC}}]N^*_{\mathrm{FC}}$$

$$\mathrm{d}N^*_{\mathrm{eq}}/\mathrm{d}t = k_r(T)N^*_{\mathrm{FC}} - (k_{f,\mathrm{eq}} + k_{q,\mathrm{eq}})N^*_{\mathrm{eq}}$$

where N^*_{FC} and N^*_{eq} are the numbers of molecules belonging to the FC* and eq* states, respectively. Combining these equations on the assumption that $k_{f,\mathrm{FC}} \simeq k_{f,\mathrm{eq}}$ and $k_{q,\mathrm{FC}} \simeq k_{q,\mathrm{eq}}$, we obtain

$$\mathrm{d}(N^*_{\mathrm{FC}} + N^*_{\mathrm{eq}})/\mathrm{d}t = -(k_{f,\mathrm{eq}} + k_{q,\mathrm{eq}})(N^*_{\mathrm{FC}} + N^*_{\mathrm{eq}})$$

$$1/\tau_{r'}(T) = A' \exp(-E_{a,r'}/RT) \qquad (15)$$

The $P(T)$ curves shown in Figs. 4—6 were found to be satisfactorily represented by Eq. (13) with $\tau_{r'}(T)$ in the form of Eq. (15). Thus, the activation energies $E_{a,r'}$ were determined from the analysis of the $P(T)$ curves, with the results listed in Table 1.

Comparison of the Two Relaxation Processes. We are concerned with two relaxation processes; one is associated with the passage from the Franck-Condon to the equilibrium excited state, and the other is the rotational relaxation of the solute. These relaxation processes will hereafter be represented by R and R′, respectively.

The relation between the relaxation R′ and fluorescence depolarization is generally established, and is represented by Eq. (13). The temperature dependence of ν, on the whole, is similar to that of P, and the observed $\nu(T)$ curve at low temperatures can be explained by the kinetic scheme of Fig. 8, which leads to Eq. (8) or (12). As has been pointed out, Eq. (12) is analogous to Eq. (13). Both equations are of the same form, and involve one and the same fluorescence lifetime, τ_f. Furthermore, τ_r and $\tau_{r'}$ are dependent on a common factor, *i. e.*, the viscosity of the solvent. Thus, we might conclude that the rapid blue shift of the fluorescence spectra at low temperatures is due to prohibition of the relaxation process R.

Let us turn to discussion of the difference between the two relaxation phenomena. It was experimentally found that, in every case, the ratio of the left-hand side of Eq. (12) to that of Eq. (13) was larger than unity in the temperature region of interest (*cf.* Figs. 4—6). This along with the expressions of Eqs. (12) and (13) means that $\tau_r(T) < \tau_{r'}(T)$; further, it is seen in Table 1 that $E_{a,r} < E_{a,r'}$

The above observations may be rationalized by considering the difference between the detailed mechanisms of the two relaxation processes. In the relaxation R, the solvent dipoles in the vicinity of the solute molecule reorient themselves to a configuration which is energetically favorable in relation to the charge distribution of the excited state of the solute. On the other hand, in the relaxation R′ the excited solute molecule must rotate with reference to laboratory-fixed coordinate axes, and such a rotational motion is presumably hindered by attraction between solute and solvent molecules, produced by dipole-dipole interaction or hydrogen bonding. Therfore, one may expect that the relaxation R occurs more easily than the relaxation R′, and that $\tau_r(T) < \tau_{r'}(T)$ and $E_{a,r} < E_{a,r'}$.

Other Related Problems. For 2-naphthol and 2,3-naphthalenediol, EPA was used as the solvent; accordingly, a hydrogen-bonded complex was probably formed between the solutes and the solvent. In general, the Franck-Condon principle should be taken into account also with respect to hydrogen bonding.[15] It is inferred, however, that in the case of the hydrogen-bonded complex in question the relaxation from the Franck-Condon to the equilibrium excited state of the complex is completed within the fluorescence lifetime, even at 77°K.[16] For this reason, in the discussion of the fluorescence blue shift, no consideration has been given to the relaxation process involving hydrogen bonding.

It has been recognized that often the Arrhenius equation is not applicable to the temperature dependence of dielectric and other relaxation processes in liquids at low temperatures where the liquid substances show glassy behavior.[17] As has been stated, however, the present experimental results were satisfactorily analyzed with the relaxation times $\tau_r(T)$ and $\tau_{r'}(T)$ expressed in the forms of Eqs. (14) and (15) which are based on the Arrhenius equation.

In Figs. 1—3 are shown in part the second electronic absorption bands. In 9,10-diazaphenanthrene the second absorption band corresponds to the $g \rightarrow L_b$ transition, and in the naphthalene derivatives it corresponds to the $g \rightarrow L_a$. On lowering the temperature, each of these absorption bands is gradually displaced to the red as may be expected.

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