Fluorescence of Solutions and Dielectrical Properties of Solvents

S. Sambursky and G. Wolfsohn

Department of Physics, Hebrew University, Jerusalem

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Because of different red shifts of the absorption and fluorescence spectrum of anthracene in solution, the longest wave absorption band is separated from the shortest wave fluorescence band. This "(0-0) separation" and the red shift are explained as effects of interaction between molecules in the liquid state and are discussed in the light of Onsager's theory of liquids.

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IT has been shown in a previous paper[1] that there is a disparity between the red shift of the absorption and fluorescence spectra of substances in solutions as compared with these spectra in the vapor state. It was found that the shift of the fluorescence spectrum is larger than that of the absorption spectrum. Consequently the longest wave absorption band no longer coincides with the shortest wave fluorescence band, as is the case when these bands are measured in the vapor state. The discrepancy which will be referred to below as the (0-0) separation increases with the general red shift and can reach values up to several hundred cm^{-1}. The red shift is accompanied by a broadening of the bands both in absorption and emission. The broadening and red shift of bands in solutions are analogous to effects produced in spectral lines by the pressure of foreign gases. No analogy to the (0-0) separation has, however, been observed in line spectra.

Several attempts have been made to explain the red shift but these have usually been restricted to primary correlation with the dielectric properties of solvents. An effort by Henri[2] to connect the dielectric constant of the solvent with the red shift was not very satisfactory. Seshan[3] attempted to set up a relationship between the red shift and the refractive index. Discussion has also been directed to the influence of the dipole moment on the shift.[4] All these explanations have been qualitative. It appears likely that a quantitative explanation of the shift as well as of the correlated (0-0) separation can be developed only on the basis of recent theories of the liquid state. Such an explanation when found would also provide an optical method for the study of the liquid state through measurements of the fluorescence and absorption spectra in solutions.

If we assume that the observed effects are caused by the interaction of the fluorescing molecule with the molecules of the solvent, we shall have three distinct types of interaction to consider: the orientation effect, the induction effect, and the dispersion effect. The total energy arising between two molecules f and s with the dipole moments μ_f and μ_s and the polarizabilities α_f and α_s is given by[5]

$$U = -\frac{1}{R^6}\left[\frac{2}{3}\frac{\mu_f^2\mu_s^2}{kT} + \mu_f^2\alpha_s + \mu_s^2\alpha_f + \frac{2}{3h}\sum_{\chi,\tau}\frac{a_{\varphi\chi}^2 \cdot a_{\sigma\tau}^2}{\nu_{\varphi\chi} + \nu_{\sigma\tau}}\right]. \quad (1)$$

In our case index f will represent the fluorescent molecule and the index s the molecule of the solvent. The sum in the last term has to be extended over all transition frequencies $\nu_{\varphi\chi}$ and $\nu_{\sigma\tau}$ of both molecules and their corresponding moments of transition $a_{\varphi\chi}$ and $a_{\sigma\tau}$. The ground states of the molecules f and s are φ and σ and

$$\nu_{\varphi\chi} = (E_\chi - E_\varphi)/h = -\nu_{\chi\varphi}. \quad (1a)$$

The orientation effect given by the first term presupposes that both molecules have permanent dipole moments. The second and third term represent the induction effect, i.e., the interaction by polarization of the dipole molecule

[1] S. Sambursky and G. Wolfsohn, Trans. Faraday Soc. 36, 427 (1940).

[2] V. Henri, J. de Physique 3, 181 (1922).

[3] P. K. Seshan, Trans. Faraday Soc. 32, 689 (1936).

[4] G. Scheibe and W. Frömel, Hand- u. Jahrb. Chem. Phys. 9, 174 (1936).

[5] F. London, Trans. Faraday Soc. 33, 8 (1937).

with its neighboring molecules, while the dispersion effect (last term) describes the synchronized vibrations induced in one molecule by the rotating charges of another. This interaction occurs in both polar and non-polar molecules and can reach considerable values in cases of resonance.

In considering the (0-0) separation between the fluorescence and absorption spectrum and the total red shift of both, it will be found convenient to choose solvents whose molecules possess no dipole moment so that μ_s is zero and there is no orientation effect. If we also choose as fluorescent substance a dipole-free molecule such as anthracene, then the interaction with the surrounding molecules will be restricted to the dispersion effect, as long as the fluorescent molecule is in its ground state, and consequently the energy of the ground state will be lowered by a certain amount L_1 compared with its value in the gaseous state. When, however, this molecule has been excited by absorption, two effects occur, as follows:

First a dipole is generally created, polarizing the solvent by induction. It should be emphasized that the two accompanying phenomena of absorption and induction in solution should be viewed as a single process. Therefore the energy of the excited anthracene molecule in solution will be larger than that of the same molecule in the vapor state by the amount of energy involved in the induction process. This induction energy is distributed over the excited molecule and the polarized molecules of the surrounding solvent and all or part of it is dissipated as thermal energy and therefore does not return, when the excited molecule returns to its ground state. The difference in energy between the absorption and emission processes can thus at least partially be identified with the dissipated energy.

There is a second effect which will operate in the same direction: the dispersion energy will also change by excitation. It will further be shown that the binding of the fluorescent molecule with its surroundings will generally increase by excitation, causing an increased lowering of the excited state as compared with its value in the gaseous state. It can be assumed that a part of this increase of energy too will be dissipated as thermal energy before fluorescence occurs.

Let E_1 and E_2 be the energies of the ground level and the excited level in the gaseous state, L_1 the dispersion energy in the ground state, L_2 the dispersion energy in the excited state, and D the induction energy accompanying the creation of the dipole μ by excitation. Then the energy of the ground state of anthracene in the surrounding solvent will be given by $E' = E_1 + L_1$. After absorption the molecule reaches an excitation energy

$$E''_a = E_2 + L_2 + D(1-\gamma) - (L_2 - L_1)\delta,$$

where γ and δ are the fractions of D and of $L_2 - L_1$ dissipated before fluorescence occurs. Hence the excited state before fluorescence has the value

$$E''_f = E_2 + L_2 + D.$$

The (0-0) separation is given by

$$E''_a - E''_f = -[\gamma D + \delta(L_2 - L_1)], \qquad (2a)$$

while the total red shift of the fluorescence spectrum is

$$(E_2 - E''_f) - (E_1 - E') = -(D + L_2 - L_1). \qquad (2b)$$

Quantitative results may be obtained with the aid of Onsager's theory of polar liquids which is in good agreement with experiment despite the simplicity of his assumptions. According to Onsager[6] we may picture the anthracene molecule in the center of a spherical cavity with a dielectric constant 1 and a radius a. In a sufficiently dilute solution the sphere will be surrounded only by molecules of the solvent whose dielectric constant is ϵ. Let us suppose that the excited anthracene molecule in the vapor state has a dipole moment μ. In solution it will induce a reaction field in the cavity whose field strength is given by

$$R = \frac{2(\epsilon-1)}{2\epsilon+1} \cdot \frac{\mu'}{a^3},$$

where

$$\mu' = \frac{(n^2+2)(2\epsilon+1)}{3(2\epsilon+n^2)}\mu$$

is the dipole moment of anthracene in the reaction field. μ' is of course larger than μ owing to the fact that both n, the refractive index of anthracene, and ϵ are larger than unity. The interaction energy D between the excited mole-

[6] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

TABLE I. Summary of data. The frequencies are given in cm^{-1}.

Solvent	ϵ^1	A	ν_{abs}	ν_{fl}	(0-0)-separation	Red shift (fluor.)
CO_2	1.54[2]	0.325	26990	26900	90	415
pentane	1.83	0.470	26716	26600	116	715
hexane	1.87$_5$	0.490	26652	26524	128	791
cyclohexane	2.01	0.555	26602	26458	144	857
decalin	2.16$_5$	0.620	26512	26349	163	966
CCl_4	2.22	0.642	26378	26136	242	1179
p-xylene	2.27	0.660	26410	26155	255	1160
dioxane	2.28	0.665	26468	26294	174	1021
benzene	2.28	0.665	26378	26136	242	1179
mesitylene	2.36	0.695	26419	26143	276	1172
diphenyl	2.53[3]	0.757	26273	25933	340	1382
naphthalene	2.54[4]	0.760	26239	25875	364	1440
phenanthrene	2.72[5]	0.823	26000	25580	420	1735

[1] Except when otherwise is indicated, the figures given refer to ϵ at 20°C.
[2] ϵ at 10°. Calculated from the data given by Uhlig, Kirkwood, and Keyes, J. Chem. Phys. 1, 155 (1933) and the density measurements of Lowry and Erickson, J. Am. Chem. Soc. 49, 2729 (1937). The result is in agreement with the former measurements of Linde, Wied. Ann. 56, 546 (1895).
[3] At 85°C.
[4] At 90°C.
[5] At 110°C. We are indebted to Mr. S. Meiboom for carrying out the measurements of ϵ for naphthalene and phenanthrene in this institute.

cule and the solvent is then given by $D = -R\mu'$ or

$$D = -\frac{2(n^2+2)^2(2\epsilon+1)(\epsilon-1)}{9(2\epsilon+n^2)^2} \cdot \frac{\mu^2}{a^3} = -A \cdot \frac{\mu^2}{a^3}. \quad (3)$$

It is above assumed that all or a part of this energy is dissipated and that the energy of the emitted radiation will be smaller by this amount than the energy absorbed. If this assumption is correct, the (0-0) separation, as far as it is caused by the dissipation of induction energy, will be proportional to the factor A.

Since the dispersion effect also has to be considered as an interaction of periodic dipole moments, this proportionality will also hold for the dispersion energies L_1 and L_2, except in case of resonance, which will be dealt with later. It is to be expected that the (0-0) separation as a whole will be proportional to the factor A. As D, L_1, L_2 are proportional to A, the total red shift Eq. (2b) should likewise be proportional to this factor.

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Owing to the smallness of the (0-0) separation as compared with the width of the bands it can be measured accurately only if absorption of fluorescence light in the solution is prevented. An arrangement similar to that described in the

previous paper was therefore used, giving a fluorescent layer not more than 1 mm in depth, with an anthracene concentration of 10^{-4} mole/liter. Wave-lengths were measured for both fluorescence and absorption against a superimposed iron spectrum. Photograms were taken with a large Moll microphotometer. The solvents used and the corresponding values of ϵ and A are given in the first columns of Table I. For the calculation of A, a value of the refractive index n of anthracene equal to $\epsilon^{\frac{1}{2}}$ for this substance was used ($\epsilon = 2.7$). The range of the factor A is limited by the comparative small variation of ϵ in dipole free solvents. In no suitable solvent does the dielectric constant exceed 2.8. Substances which are liquid at room temperature were investigated at 20°C, whereas diphenyl, naphthalene, and phenanthrene were observed at temperatures lying roughly 10° above their melting point. The absorption and fluorescent cell was maintained at the required temperature in an electric furnace. A special cell was constructed for the observation of anthracene in liquid CO_2, a cross section of which is given in Fig. 1. The quartz plates Q were cemented with piceine to two covers C screwed on a cylindrical iron ring R. Absorption was observed in the direction AB, while for the observation of fluorescence a beam of light was directed into the aperture F and the fluorescence emitted through B measured. A piece of copper T in which a thermocouple could be introduced for temperature control was attached to one of the covers. For the filling of the cell one cover was unscrewed and the necessary quantity of anthracene deposited by evaporation from a solution in acetone. A weighed quantity of solid CO_2 was then placed on the plate and the cover screwed back. The anthracene is quickly dissolved in liquid CO_2.

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Quantitative results are given in Table I and Figs. 2 and 3. The key to the numerical symbols in Fig. 2 and 3 is given in the first column of Table I. In columns ν_{abs} and ν_{fl} the frequencies of the longest wave absorption band and the shortest wave fluorescence band are given. The difference between these figures is the (0-0) separation. The last column gives the total red
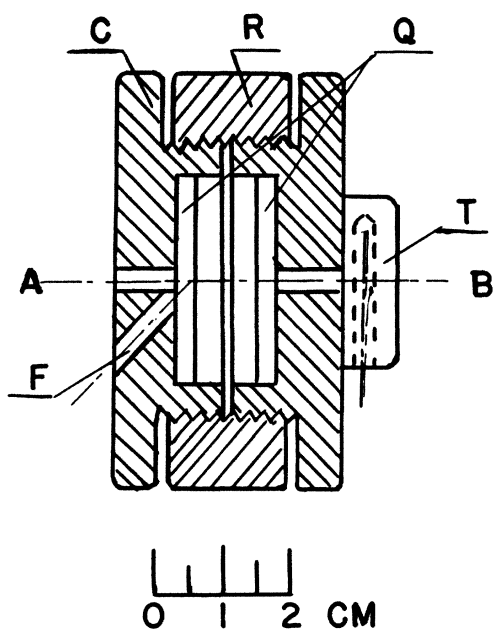
FIG. 1. Cross section of cell for observation of anthracene in liquid CO_2.

shift, based on the value $\lambda = 3660A$; $\nu = 27315$ cm^{-1} both for ν_{abs} and ν_{fl} in the vapor state.[7]

As can be seen from Figs. 2 and 3, in which the (0-0) separation and the total red shift of the fluorescence spectrum are plotted against A, the expected proportionality holds for a number of dipole free liquids. A number of the solvents display a larger separation and red shift than would be allowed for by a linear relation. In all of these cases the main region of absorption lies in the neighborhood of the absorption bands of anthracene itself, i.e., between 2500A and 2000A. The solvents obeying the linear law are those which absorb only in the far ultraviolet, e.g., hexane near 1500A and CO_2 near 1600A and 1000A. These circumstances suggest that the additional effects may be explained as a result of resonance. It cannot be expected that Onsager's theory dealing with static dipoles should give a full account of the dispersion effect as far as it

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[7] This value was adopted on the basis of absorption measurements of anthracene vapor by Göpfert, Zeits. wiss. Phot. **34**, 156 (1935) and measurements by Pringsheim, Ann. Acad. Sci. Techn. Varsovie **5**, 29 (1938) in the fluorescence spectrum. The two maxima given by Pringsheim—3640A and 3690A—are probably imaginary and due to reabsorption, the real maximum apparently being situated in the gap between them. With $\lambda = 3660A$ as maximum the distance to the next maximum becomes about 1400 cm^{-1} as was to be expected.

is dependent on frequency. This must be found by making a direct use of Eq. (1).

Since the fluorescing molecule is found in the upper state φ' before fluorescence occurs, the difference between the dispersion energy in the ground state φ and in the excited state φ' is due to the transition $\varphi \to \varphi'$. Owing to this transition the last term in Eq. (1) will be changed mainly by $\nu_{\varphi\varphi'}$ changing in $\nu_{\varphi'\varphi}$. Hence the difference $L_2 - L_1$ for the dispersion energy is in the first place given by

$$L_2 - L_1 = -\frac{1}{R^6}\frac{4}{3h}a_{\varphi\varphi'}^2 \cdot \nu_{\varphi\varphi'} \cdot \sum_{\tau} \frac{a_{\sigma\tau}^2}{\nu_{\sigma\tau}^2 - \nu_{\varphi\varphi'}^2}. \quad (4)$$

Since $\nu_{\sigma\tau}$ is greater than $\nu_{\varphi\varphi'}$ in all observed cases, there results an increase of the dispersion energy in the excited state of anthracene and consequently an additional separation and red shift.

Since $a_{\sigma\tau}^2 \cdot \nu_{\sigma\tau}$ is proportional to the molar absorption coefficient for the frequencies $\nu_{\sigma\tau}$, one can estimate the value of the sum in Eq. (4) from the absorption coefficients of the solvents used. Both for the (0-0) separation and the red shift a proportionality is to be expected between

$$\sum_{\tau} \frac{a_{\sigma\tau}^2}{\nu_{\sigma\tau}^2 - \nu_{\varphi\varphi'}^2}$$

and the deviations of the actual measurements from the straight lines in Figs. 2 and 3. The agreement is fairly good in all cases where data for the absorption coefficients are obtainable up to at least 2000A.
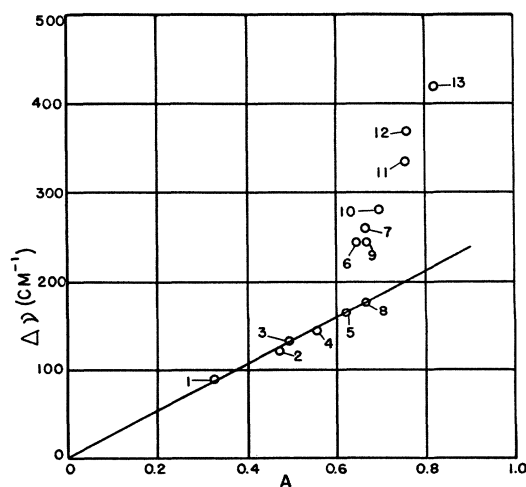

FIG. 2. $\nu_{abs} - \nu_{fl}$ plotted against the factor A.

It should be possible to explain the non-linear effects directly from Onsager's theory, if one assumes that ϵ varies with the frequency and calculates its value from that of the refractive index of the solvent at the maximum absorption wave-length of anthracene. Unfortunately such a calculation is possible only for benzene and even here only approximately, while data on the refractive indices in the ultraviolet are not available for the other solvents absorbing in the nearer ultraviolet. Values of n for benzene[8] have been measured up to 2700A, where $n = 1.65$. By extrapolation into the main absorption region near 2500A, a value for n may be assumed lying between 1.7 and 1.8 which would give $\epsilon = n^2$ as roughly equal to 3. This makes the factor A in Eq. (3) a little greater than 0.9. This is the value actually obtained if the point for benzene in Fig. 2 is móved horizontally to cut the straight line. The same procedure carried out in Fig. 3 gives a correction somewhat too large.

It may also be pointed out that the broadening of the bands depends on ϵ and that this broadening becomes more pronounced in the cases of resonance. With CO_2 the bands are still narrow enough for the secondary maxima to be resolved, on the violet side in absorption and on the red side in emission, whereas for example with naphthalene the maxima are very shallow and blurred. The values of the half-breadth for the first bands in fluorescence are approximately 400 cm^{-1} for CO_2, 500 cm^{-1} for dioxane, and 900 cm^{-1} for naphthalene.

It is not to be expected that the interpretation of red shift and (0-0) separation which has been

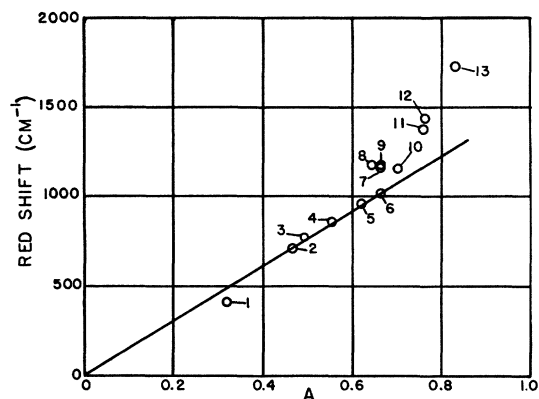8 T. M. Lowry and C. B. Allsopp, Proc. Roy. Soc. A133, 26 (1931).

FIG. 3. Red shift plotted against the factor A in Eq. (3).

advanced above will provide a satisfactory quantitative fit for all cases observed. Both Onsager's model which replaces the molecules of the solvent by a continuum and the simplifications involved in Eq. (4) for the dispersion effect are approximations which necessarily introduce a certain discrepancy between experiment and theory. Thus in the case of CO_2 the red shift found is smaller and the (0-0) separation greater than was expected from theory. In the case of benzene, carbon tetrachloride, p-xylene, and in particular mesitylene, again, the values found for the (0-0) separation were somewhat greater than as calculated from Eq. (4).

It is planned to extend these investigations to the case of polar liquids and polar fluorescent substances, whereby it is hoped to shed further light on the mechanism of interaction between fluorescent solutes and their solvents.