The probability of direct internal conversion to the ground state is compared with the Stokes shift and the purely electronic transition frequency for solutions at 20°C. The probability has an exponential relation to the shift and frequency. Expressions are derived for the relation of spectral parameters to change in the height of the barrier to radiationless deactivation.

The fluorescence yield from an organic compound is the result of competition between radiative and radiationless transitions. The probability of radiative transition varies comparatively little with the structure of the compound and the conditions (e.g., solvent), provided that these changes are not very large. Nearly all of the variation in the quantum yield in fluorescence (range 0 to 1) is due to change in the probability of radiationless transitions. Until recently, the common view was that this probability is governed directly by the specific structural features of the compound. It has been shown [1-5] that $B^q_j$, the absolute quantum yield in fluorescence (which is obviously dependent on the radiationless internal-conversion transition probability), is closely related to the position of the peak $v_f^{\max}$ in the fluorescence spectrum. This relation of $B^q_j$ to spectral parameters means that the internal-conversion (IC) mechanism is governed only by the mutual disposition of the potential surfaces for the ground and excited states. The solvent and the structure affect this mutual disposition but otherwise have no specific effects.

The general relation of $B^q_j$ to $v_f^{\max}$ is as follows. There is an initial rise in the yield as the fluorescence band moves towards shorter wavelengths (branch A), but this is followed by a fall (branch B). Branch A has been identified as due to direct IC to the ground state [1, 2, 5].

It is simplest to correlate $B^q_j$ with $v_f^{\max}$, but the correlation has several disadvantages. Firstly, the position of the peak is governed by the frequency of the purely electronic (0-0) transition $v_e$ and by the Stokes shift $A\nu_s$. Secondly, the relation is only an indirect reflection of the change in the IC probability; a more quantitative correlation is to be expected if the IC probability is compared directly with $v_e$ or $A\nu_s$.

On the other hand, it is very difficult to choose compounds for which change in solvent or structure produces a change mainly in $v_e$ or $A\nu_s$ alone; the usual situation is that $A\nu_s$ and $v_e$ are affected simultaneously. Fortunately, we have been able to find a fair number of compounds that allow this direct comparison of IC with spectral characteristics in various solvents at 20°C [5, 6].

The probability $q$ of IC to the ground state for a singlet level is given** by

$$q + r = \frac{1 - B^q_j}{\tau},$$

in which $r$ is the probability of transition to the metastable state and $\tau$ is the mean lifetime of the excited state. These $q$ for points on branch A of the relation of $B^q_j$ to $v_f^{\max}$ were compared with the corresponding $A\nu_s$ and $v_e$. The process causing the fall in yield along branch A has been identified as direct IC to the ground state, so only $q$ will be used in what follows to characterize the radiationless deactivation***.

Figure 1 shows $q$ as a function of $A\nu_s$; there are clearly several distinct curves. The chemical structure is not the factor that determines the curve appropriate to a compound, since a given curve may have points corresponding to compounds of different chemical classes (Fig. 1).

---

* Read at the Symposium on Quantum Chemistry, Palanga, June 1965.

** Note: 1) The absolute quantum yields were measured by the relative method previously described [7], in which an FEU-28 photomultiplier is used as detector; 2) $r$ was determined with a phase fluorimeter in Professor Tumerman's laboratory at the Institute of Radiation and Physicochemical Biology; we are indebted to A. N. Surova for performing the measurements, and to Professor Tumerman for providing access to the instrument; 3) It is generally found that $\tau$ is directly proportional to the absolute quantum yield for a given compound in different solvents.

*** It has several times been shown (see [5]) that the transition to the metastable state is the source of branch B in the relation of $B^q_j$ to $v_f^{\max}$.
The other parameters show that the compounds corresponding to a given curve of q against $\Delta \nu_5$ have similar 0-0 transition frequencies 

$$\nu_e = \frac{\nu^\text{max}_f + \nu^\text{max}_a}{2}$$

and similar half-widths for their fluorescence and absorption bands ($\Delta f$ and $\Delta a$). Compounds whose points merely fall near the curve have different $\nu_e$ and also different $\Delta f$ and $\Delta a$. There are regular trends in $\nu_e$ and $\nu_f$ as between curves (rise from curve I to curve IV).

The $\nu_e$, $\Delta f$, and $\Delta a$ are not identical for a given compound in various solvents, nor for different compounds whose points fall on a single curve; this is one reason for the appreciable spread around the curves, e.g., curve II of Fig. 1.

Fig. 1. Relation of q to $\Delta \nu_5$ for solutions (various solvents) for chemical compounds. Curve I: ▲ aminonaphtheurhodine, Δ dimethylaminonaphtheurhodine; curve II: ● 4-dimethylamino-4'-nitrostilbene, ○ 4-amino-4'-nitrostilbene, ◆ 4-dimethylaminobenzal-4'-nitroaniline, ◼ 4-dimethylamino-4'-nitrophenyl, ◈ 4-amino-4'-nitrophenyl, ⊙ m-dinitrodiphenylamine, ◊ 4-diphenylamino-N-methylphthalimide; curve III: □ 4-amino-N-methylphthalimide; curve IV: ■ 4-hydroxy-N-methylphthalimide. The mean $\nu_e$ (cm$^{-1}$) for the curves are: I) 19 000, II) 21 000, III) 22 700, IV) 25 000. The broken line denotes the line of transition between the A and B branches, where the probability of conversion to the metastable state may begin to have an effect. The spectra were processed in accordance with the method described in [11].

Figure 2 shows the relation of q to $\Delta \nu_5$ in semilogarithmic form; the lines are straight, and they coincide or lie very close together (e.g., line II) for compounds with closely similar $\nu_e$, $\Delta f$, and $\Delta a$.

Hence q has an exponential relation to $\Delta \nu_5$ for fixed $\nu_e$, $\Delta f$, and $\Delta a$ of the following form:

$$q = q_0 e^{k \Delta \nu_5}$$

(1)

The relation of q to $\nu_e$ may be derived by reference to compounds in which only $\nu_e$ is affected by change in structure [8] or solvent [9]. $\Delta \nu_5$ remaining constant. Figure 3 shows the relation of q to $\nu_e$ for: curve I, rhodamine dyes in ethanol; curve II, 4-amino-N-phenylphthalimide in various solvents; and curve III, various unrelated compounds. These curves were drawn up by taking points corresponding to a given $\Delta \nu_5$ on the curves relating q to $\Delta \nu_5$ in Fig. 1 (each curve in Fig. 1 corresponds to a particular $\nu_e$). There are only slight variations in $\Delta \nu_5$, $\Delta f$, and $\Delta a$ for the points falling on any given curve relating q to $\nu_e$. These curves show that q is inversely related to $\nu_e$ for a given $\Delta \nu_5$ in all these cases.

This gives us the relation of q to $\nu_e$ for a single compound in different solvents, for related compounds in a single solvent, and for different compounds in various solvents. In each case, the relationship is of the same form, and this result clearly illustrates the relation of q to spectral parameters, with details of the chemical structure having no direct effect.