

tion of solutions should be of major importance. Moreover, ion-selective electrodes are most effective for the measurement of exactly those ionic species (*e.g.*, Na⁺, K⁺, Ca²⁺, F⁻, SO₄²⁻, S²⁻, NO₃⁻, ClO₄⁻, etc.) which are most difficult to measure by other techniques.

Ion-selective electrodes measure the activities of ions in solution and do so with considerable sensitivity and selectivity. Such measurements are rapid and non-destructive and can be carried out on a continuous, automated basis. Because of these desirable characteristics ion-selective electrodes are being used widely for chemical studies, biomedical measurements, pollution and oceanographic monitoring, and industrial

control. About two dozen types of ion-selective electrodes are already available, but more are being developed as the fundamentals of electrode operation and selectivity are elucidated.

At the present time, we find ourselves in the pleasant position of having suitable electrodes selective for many important ions. Table II illustrates some of the recent analytical applications of these electrodes. The state of the art has now progressed to the point where accurate analytical measurements using these electrodes are readily carried out and where ion-selective electrodes are being used increasingly for fundamental chemical and biochemical studies.

Photophysical Primary Steps in Solutions of Aromatic Compounds

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The electrons of molecules in nonexcited states reside in the lowest molecular orbitals. The energies of these orbitals, *i.e.*, the energies of these electrons, can be determined experimentally by photoelectron spectroscopy.^{2a} For theoretical methods see, *e.g.*, Jungen.^{2b}

The electrons of a ground-state molecule are often classified, for simplicity, as to the electronic systems to which they belong. For most organic molecules the electrons can be classified as follows: σ electrons which form localized σ bonds; π electrons which form π bonds, not necessarily localized; nonbonding n electrons which are localized in valence shells of atoms, and do not participate in complex formation such as hydrogen bonding, charge-transfer complexes, etc.; and δ electrons which are situated in the inner shells of atoms. In certain types of molecules, especially in molecules containing π electrons, one or more electrons can be promoted to higher orbitals without decomposing the molecule. The molecule is then said to be in an excited state and the promotion energy is called excitation energy.

In this paper we shall concern ourselves with two questions: what are the physical mechanisms by which a molecule can leave the excited state and how do these mechanisms compete with each other? All processes following absorption and leading to the first reaction product are called primary steps. The first reaction

product could for instance be an intermediate if the photochemical reaction is a multistep reaction, or it could be the original molecule in its ground state.

Theoretical approaches to the kinetics of radiationless transitions have been obtained by using time-dependent perturbation theory to obtain probabilities for Born-Oppenheimer zeroth-order excited-state transitions. However the excited states are not pure in view of configuration interaction between nearly degenerate zeroth-order states. The optically excited state can be described in terms of a superposition of molecular eigenstates and it can be shown that the resulting wave function exhibits an exponential nonradiative decay. The line width and the radiationless lifetime can be expressed in terms of a single molecular parameter, the square of interaction energy between the zeroth-order state and the manifold of all vibronic states located within one energy unit around that state.^{2c-e} "Internal conversion" and "radiationless intersystem crossing" are then better termed "internal mixing" and "intersystem mixing," respectively.

Luminescence spectroscopy is a useful tool to investigate the mechanisms of transformation of electronic excitation energy and the primary steps in photochemistry if the latter compete with the luminescence but do not quench it beyond an experimental limit in intensity. The following quantities are measured in luminescence spectroscopy.

(1) Quantum efficiency, $Q_f \equiv n_e/n_a \leq 1$, where n_a = number of quanta absorbed, n_e = number of quanta emitted. The sum of the quantum yields of all competing processes, fluorescence included, is unity, by definition.

(2) Spectral quantum distribution $q(\bar{\nu})$, which should preferably be plotted—by international recommendation—as the relative number of quanta emitted within

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wave number intervals of equal size.³ From this one can obtain the absolute luminescence spectrum by the normalizing condition

$$\int q(\bar{\nu})d\bar{\nu} = Q_t$$

(3) Decay time

$$\tau \equiv \int_0^{\infty} tI(t)dt / \int_0^{\infty} I(t) dt \leq \tau_0 \leq \tau_e$$

The radiative lifetime τ_e can be obtained from the area

$$\int_0^{\infty} \epsilon c d \ln \nu$$

of the corresponding absorption band. Its order of magnitude is given roughly by the relation $\tau_e \approx 10^{-4}/\epsilon_{\max}$, where ϵ , the molar extinction coefficient, is given in liters/mole centimeter and τ_e is in seconds. The natural lifetime, τ_0 , is determined by all spontaneous deactivation mechanisms together.

(4) Degree of polarization, $P \equiv (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} are the intensities of the luminescence light polarized parallel and perpendicular, respectively, to the exciting light. In liquids, due to random orientation, the limiting values are $-1/3 \leq P \leq +1/2$. The more rigid the medium and the shorter the decay time, the nearer is P either to $-1/3$ or to $+1/2$, depending on whether the transition moments for absorption and emission are perpendicular or parallel^{4,5} to each other.

A schematic diagram of a spectrofluorimeter with polarization attachment and with devices for variable-pressure and variable-temperature investigations is given in ref 6. For measurements of relative quantum efficiencies see Parker,⁷ and of decay times see Kramer.⁸ Decay functions have been measured using the mode-locking laser technique.⁹

Relaxation Phenomena and Solvent Effects

During an electronic transition the position and the velocity of all atomic nuclei of a molecule remain almost unchanged (Franck-Condon principle). With each transition the physical properties of a molecule are changed since the electronic charge distribution is changed. In different excited states, therefore, such properties as electric dipole moment or electric quadrupole moment or nuclear configuration, as well as dissociation constants, pH values, and the ability for complex formation, are different. For example, in substituted aromatic compounds basic sites often are

more basic and acidic sites more acidic in the $^1(\pi^*, \pi)_1$ state than in the ground state.¹⁰ If both such functional groups are present it might be that the molecule in its fluorescing state exists either as a cation or as an anion, but at no pH value of the solution in its neutral form (Figure 1¹¹).

Besides the normal Stokes red shift which is essentially due to the fact that absorption and fluorescence transitions in most cases occur from lower to higher vibrational terms, there is an anomalous Stokes red shift of the fluorescence band maximum, as compared with the spectral position of the absorption band maximum, which is due to intermolecular interaction effects. With each electronic transition a relaxation process will start before all other processes. With increasing Stokes red shift an increasing percentage of absorption energy finally would be transformed into heat. Even if the quantum efficiency of fluorescence equals 1, the energy efficiency does not, unlike the resonance fluorescence effect of atoms.

If the electric dipole moment changes with an electronic transition the mean orientation of surrounding polar solvent molecules will change (Figure 2¹²). These solvent effects give rise to photophysical relaxation cycles. Each electronic transition brings the thermodynamical system solute-solvent to a so-called Franck-Condon state. Then reorientation processes will start which are due to changes in intermolecular interaction energy, and the system tends to achieve the thermodynamical equilibrium state. By second-order perturbation theory it is possible to calculate the difference $\mu_e - \mu_g$ between the dipole moments of the two electronic states from the dependency of the anomalous Stokes red shift on the polarity of the solvent.¹³⁻¹⁷

$$\bar{\nu}_a - \bar{\nu}_f \sim (\mu_e - \mu_g)^2 \Delta f$$

$$\Delta f = \frac{D - 1}{D + 1/2} - \frac{n^2 - 1}{n^2 + 1/2}$$

where D = dielectric constant and n = refractive index.

A second possibility for the determination of molecular excited-state dipole moments comes from the effect of polar solvent molecule concentration on the anomalous Stokes red shift of solute fluorescence in mixtures of polar and inert solvents.^{18,19} Let us assume the solute molecule possesses a certain number of sites on its surface which could be occupied by polar solvent molecules; these then have two possibilities, either to occupy such a site or to remain free in the solution. Langmuir's adsorption isotherm equation can then be applied to

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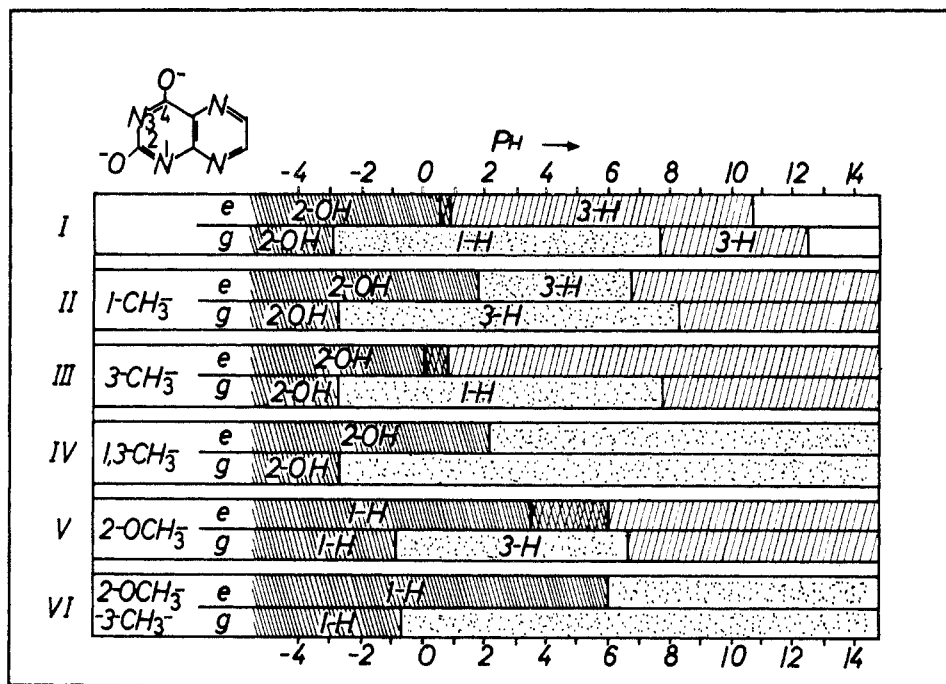


Figure 1. pK values of lumazine compounds:¹¹ e, excited state; g, ground state.

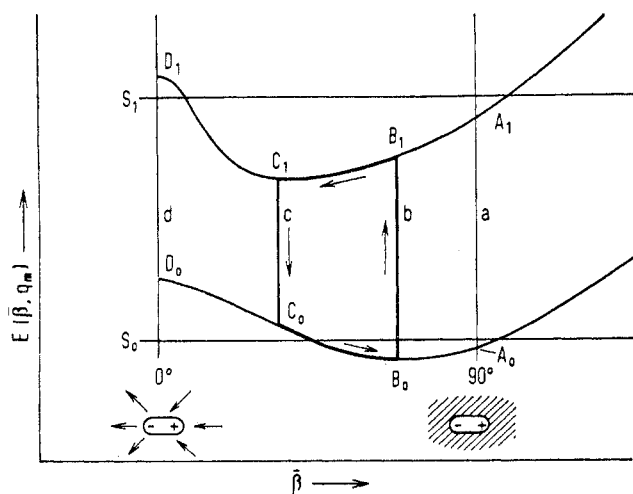


Figure 2. A photophysical relaxation cycle.¹² $\bar{\beta}$ is the mean angular deviation of a nearest-neighbor polar solvent molecule dipole moment from the electric field produced by a solute molecule, the dipole moment of which is higher in the first excited singlet state, S_1 , than in the electronic ground state, S_0 . Straight lines refer to the free molecule.

ternary mixtures at different temperatures and the adsorption enthalpy determined. At higher concentrations of polar solvent molecules the higher density outside of the cage (formed by nearest neighbors) increases the red shift. On the other hand, the Coulomb repulsion forces between adsorbed molecules decrease the adsorption energy and hence the number of adsorbed molecules and the observed red shift. The two effects therefore cancel each other to a large extent.

The values for dipole moments of $^1(\pi^*, \pi)_1$ states of substituted aromatic compounds obtained by these two methods are in fairly good agreement with each other and with the results obtained by some other

methods developed in the meantime utilizing effects of external electric fields on the absorption and fluorescence spectra of solutions.^{13,14,20,21} The anomalous Stokes red shift, however, is small at high temperatures because thermal motion acts against better orientation, and it is also small at low temperatures when the viscosity of the solvent becomes so high and the relaxation time so large that the solution cannot achieve thermal equilibrium during the lifetime of the fluorescence excited state. For most aromatic compounds the fluorescence decay time is of the order of magnitude of 1 nsec and the anomalous Stokes red shift achieves its maximum at a temperature where the first relaxation time of the solvent also has a value of about 1 nsec.^{12,22}

Radiationless Transitions

Radiationless processes can be divided into those which have activation energies and those which do not. A transition to an unstable state leading to photolysis can be achieved either by direct absorption to that state, in which case the dissociation is called "photodissociation," or by acquisition of activation energy from a stable excited state, in which case the effect is called "predissociation" (Figure 3²³). Fluorescence quenching of aromatic nitro compounds, for instance, occurs by predissociation.²⁴ Luminescence concentration quenching in many cases is due to excimer predissociation.

Radicals formed by photolysis in a randomly oriented solution will show randomly oriented spin directions

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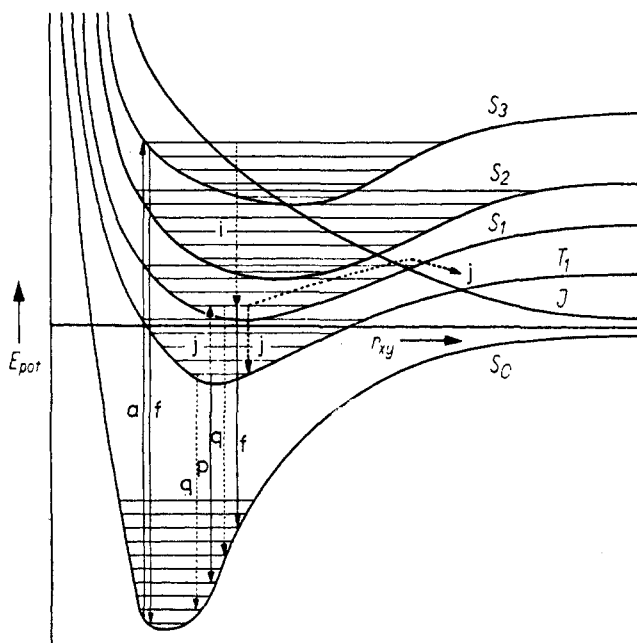


Figure 3. Potential energy surface diagram showing electronic states of a diatomic molecule X-Y (or a separated chemical bond) and transitions.²⁵ r_{xy} is the nuclear distance: a, absorption of photons; b, bimolecular addition reactions, dimerization; c, complex formation; d, dissociation; e, predissociation; f, fluorescence: spontaneous emission; g, fluorescence: induced emission; h, annihilation, P-type delayed fluorescence; i, internal conversion of excitation energy within a given spin system; j, interconversion (energy dissipation by collisions etc., and vice versa); k, radiationless intersystem crossing (intercombination); l, delocalization of energy: exciton formation; m, energy migration; n, ring closure; o, oxidation (by atomic or molecular oxygen); p, phosphorescence; q, quenching; r, relaxation processes, intermolecular; s, sensitized reactions; t, tautomerism; u, rearrangements (umlagerungen); v, isomerization (*cis-trans*, etc.); w, hydrogen atom abstraction (wasserstoffatomabspaltung); x, redox reactions, univalent; y, protolytic reactions; z, ionization: solvated electron formation and capture.

even if the decomposition is performed in the presence of an external magnetic field. As a consequence relaxation processes will start to approach Boltzmann distributions of the electron spin orientations which should be either parallel or antiparallel to the applied magnetic field. This relaxation process is accompanied by optical polarization effects in electron spin resonance spectra^{25,26} and is followed by dynamic nuclear spin polarization due to the angular momentum conservation rule.^{27,28} We are starting such investigations using the rare gas matrix isolation method as described by Weltner.²⁹

If the excited states of a free molecule are not too far apart from each other energetically, the rate for radiationless internal conversion is much higher than that for radiative deactivation, and the lowest excited S_1 will be reached so fast that fluorescence can be observed

only due to the radiative conversion $S_1 \rightarrow S_0$. The lowest excited states, S_1 , of indole,³⁰ tryptophan,³¹ and *p*-dimethylaminobenzonitrile³² are slightly polar states of the 1L_b type, but the highly polar 1L_a state is not far from it. With increasing polarity of the solvent the intermolecular interaction energy between the solvent and the 1L_a state of the solute is much larger than the $L_b - L_a$ difference. In its thermodynamic equilibrium the system will then be in its 1L_a state and, therefore, only fluorescence from the 1L_a state will be observed. In inert solvents, however, only the fluorescence from the 1L_b state will occur. Solvents of intermediate polarity and intermediate viscosity might show both fluorescence bands which could be easily distinguished by the sign of the fluorescence polarization degree since the transition moment for transitions from the ground state to the 1L_a state is much higher than that to the 1L_b state.^{33,34}

If the highest filled molecular orbital of a heteroaromatic compound is a nonbonding n orbital, the rate of the $\pi^* \rightarrow \pi$ fluorescence from the lowest lying singlet state of the π -electronic system to the ground state might be smaller than the rate of the radiationless $n \rightarrow \pi$ transition which brings the molecule into an ${}^1(\pi^*,n)_1$ excited state. The intramolecular univalent redox reactions $\pi^* \rightarrow n$ between the different n and π electronic systems in most cases are radiationless because they are passing through ${}^3(\pi^*,\pi)$ and ${}^3(\pi^*,n)$ triplet states. The radiative lifetimes of the ${}^1(\pi^*,n)$ state of symmetric tetrazine³⁵ and of 9,10-diazaphenanthrene^{36,37} are so small that their $\pi^* \rightarrow n$ fluorescence has been observed (Figure 4³⁸). The $\pi^* \rightarrow n$ transition moment does not vanish because of the partial s character of the n orbital and is, therefore, directed perpendicular to the molecular plane of the n -electron system so that the absorption polarization degree is negative if the fluorescence is excited by $\pi^* \leftarrow \pi$ absorption processes.³⁹

Isotopic effects have been observed showing that deuteration of either component of the system increases the luminescence quantum efficiency as well as the lifetime of the emitting state but decreases the amount of polarization of luminescence in solutions.^{30,39-44} Förster⁴⁰ suggests a direct relation between the mech-

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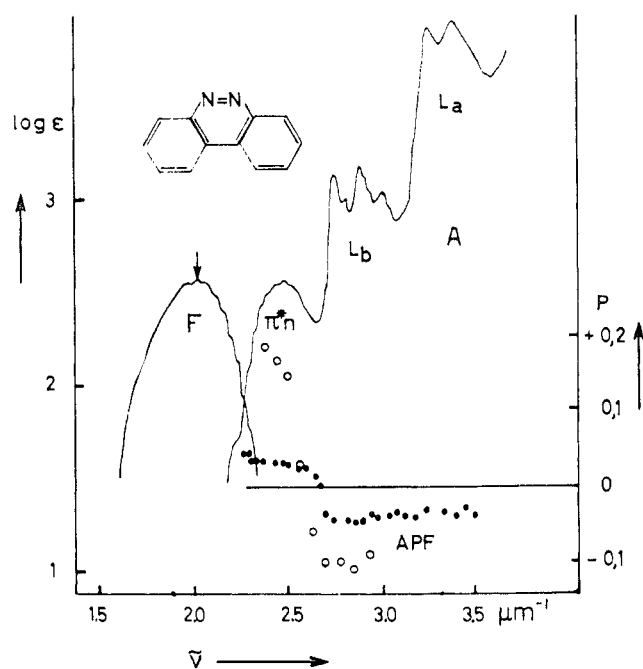


Figure 4. Fluorescence and absorption spectra⁴⁸ (F and A, respectively) and the absorption polarization spectrum APF: (O) 10^{-3} M in Nujol; (●) 10^{-5} M methylcyclohexane-isopentane (3:1).

anism of the anomalous Stokes red shift and interconversion processes by direct and very strong coupling between the excited solute and the surrounding polar solvent molecules.

The different types of coupling and the different kinetic behavior observed by Förster for both water and heavy water solvents might depend on the different maximum vibrational amplitudes. The coupling mechanism might either be a mechanical one due to the vibrational modes present in the above-mentioned cage (which the inner shell solvent molecules form around the solute) or it might be an electronic coupling. When discussing the latter case one should consider that there is no electronic excited state of the water molecule available and, therefore, an exciton formation allowing for delocalization of electronic excitation energy is not possible. However, it might be possible that the solute excitation energy proceeds to the solvent cage *via* nonstationary states as they are known from Raman scattering theory.⁴⁵ For a discussion of long-range and short-range energy coupling see Förster⁴⁶ and Merrifield,⁴⁷ respectively.

Isomerization Reactions and Shapes of Potential Surfaces

Potential surfaces are different for different electronic states and they are changed, therefore, by each transition. Azobenzene does not fluoresce at all. Compared with 9,10-diazaphenanthrene, the two phenyl

groups of the azobenzene molecule are not linked together by a second bond so that torsional modes around the N=N double bond and the C—N single bonds become possible. The torsional modes allow for transformation of the excitation energy into heat by interacting with the surrounding solvent molecules. Presumably the lifetimes of the lowest lying excited states of azobenzene are shortened drastically by torsional modes.^{48,49}

The first absorption band and the corresponding fluorescence band of 9-methoxy-10-phenanthrenecarboxanil have almost the same vibrational structure as phenanthrene itself. These transitions to and from the 1L_b state of the phenanthrene system are shifted to the red and intensified by the substitutions in 9,10 position. Even the twisting vibrations do not quench the fluorescence totally since the excitation energy is essentially localized in the phenanthrene π -electronic system. The aniline group, therefore, is not necessarily coplanar with the phenanthrene aromatic system but might be oriented perpendicular to it. The n electrons located at its nitrogen atom may then interact with an excited aromatic π -electron system (just as that of the 1L_b state of phenanthrene) and, therefore, an excimer with a T-bone type structure might be formed (Figure 5⁵⁰). Di-alkylanilines are well known for being strong electron donors for charge-transfer complex formation and especially for the formation of heteroexcimers.⁵¹

In the aromatic *o*-hydroxyazomethine compounds there is a double minimum potential for the position of the proton along the intramolecular hydrogen bond.^{52,53} Under these conditions *cis-trans*-isomerization reactions, therefore, proceed along a pathway of potential minima, each step of which needs an activation energy of less than 7 kcal/mol, as compared with an activation energy of about 20 kcal/mol for corresponding hydrocarbons having no such intramolecular hydrogen bond.

Planar *cis-trans* isomers have almost the same π -electronic structure and almost identical absorption spectra. *p*-Dimethylaminocinnamionitrile is an example.⁵⁴ Stilbene, however, has a nonplanar *cis* form due to steric hindrance. An energy diagram for the lowest lying states is given in Figure 6.⁵⁵ Due to torsional quenching, fluorescence is observable only at temperatures sufficiently low that viscosity is large enough. Insofar as the *cis-trans* photoisomerization proceeds *via* triplet states,⁵⁶ one should assume that the

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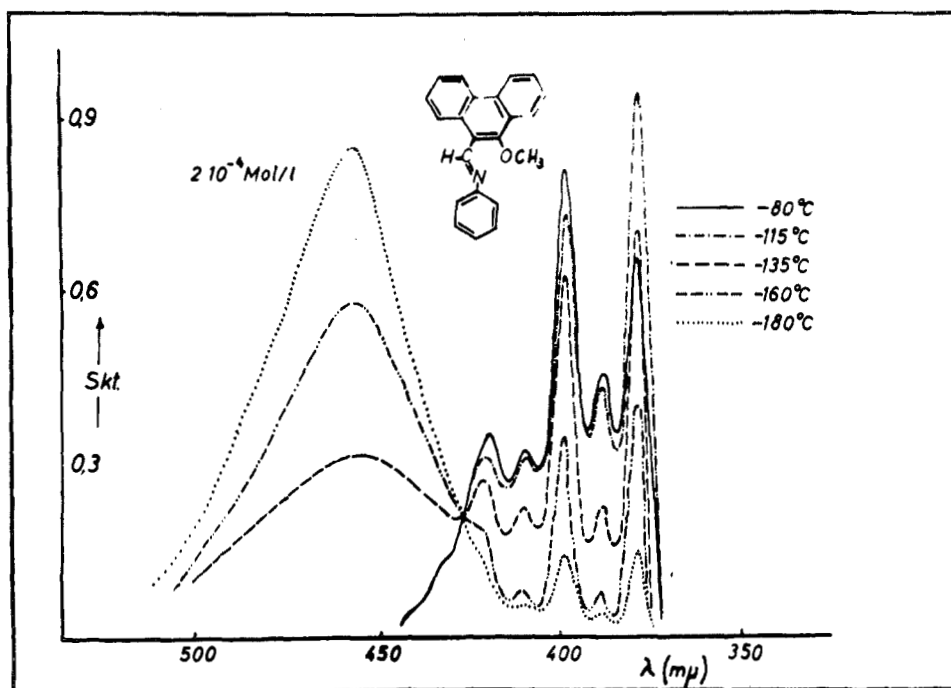


Figure 5. Temperature dependence of fluorescence in methylenecyclohexane-isopentane (3:1).⁵⁰

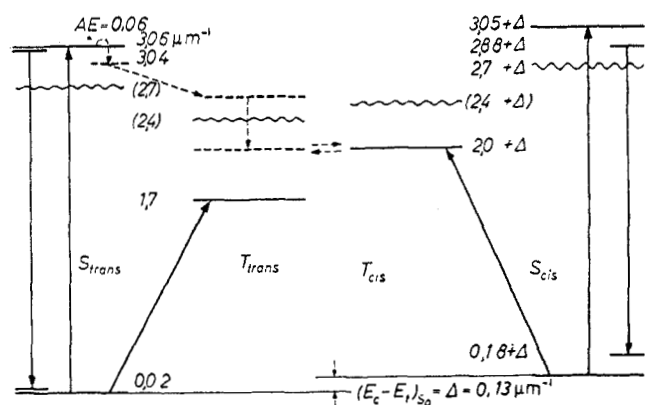


Figure 6. Energies of electronic states of stilbene isomers; waves: benzophenone S_1 and T_1 energies.⁵⁵

reaction proceeds to a certain extent between the states $T_2(trans)$ and $T_1(cis)$.⁵⁵ This is possible since the rate for conversion has the order of magnitude of a reciprocal vibrational frequency, as has the torsional mode. Internal conversion $T_2(trans) \rightarrow T_1(trans)$ competes with the *trans-cis* isomerization $T_2(trans) \rightarrow T_1(cis)$. Intersystem crossing, $T_1(cis) \rightarrow S_0(cis)$, competes with *cis-trans* isomerization $T_1(cis) \rightarrow T_2(trans)$. Intersystem crossing is allowed by spin-orbit coupling which could be increased by heavy-atom effects. In the photo-stationary state of 3,3'-dibromostilbene only the *cis* form is present, but no *trans* isomer could be found.⁵⁷

Bianthryl has the high symmetry of point groups D_2 or D_{2d} . At low temperatures in inert solvents and rigid media its fluorescence spectrum shows a well-resolved vibrational structure, just the mirror image of the corresponding first absorption band. However at higher

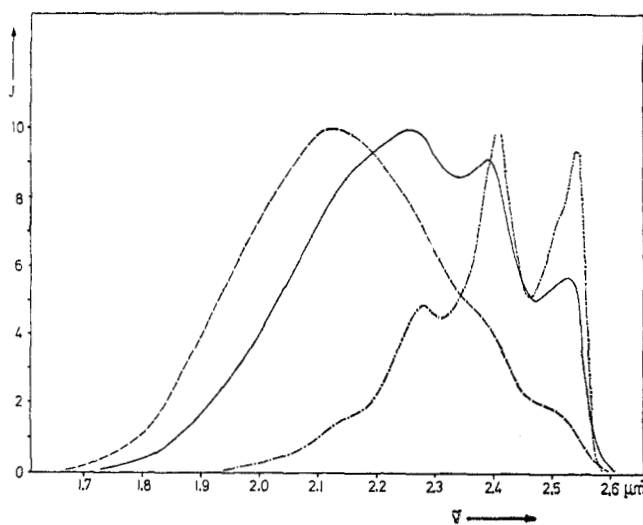


Figure 7. Fluorescence spectra of bianthryl, $7 \times 10^{-5} M$ in glycerine at⁵⁸ (---) 344°K, (—) 238°K, (— · —) 182°K.

temperature, in lower viscosity media, or in polar solvents the fluorescence shows the anomalous Stokes red shift of a structureless broad band (Figure 7⁵⁸) as has been discussed above for polar compounds which possess a higher electric dipole moment in the fluorescing state. This is in contradiction to the assumption that a molecule of such a high symmetry should have a vanishing molecular dipole moment in every electronic state. The Stokes red shift of bianthryl increases with increasing solvent polarity factor, Δf , and the slope asymptotically approaches the value to be expected for the biradical formed by the transfer of one electron from one anthryl group to the other. The resulting nonequivalency of the two anthryl groups is then as-

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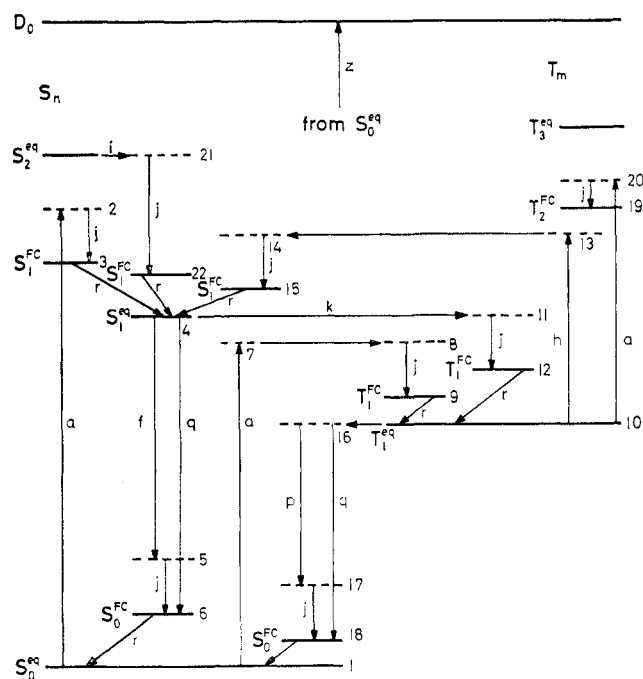


Figure 8. Primary steps diagram (see caption to Figure 3).

sumed to be induced by polar solvent molecules. Stabilization occurs by the twisting vibration which at times passes through an angle of 90° because of a rather large amplitude of the twisting mode in the first excited singlet state. Along the twisting angular vibrational coordinate the potential function presumably possesses two minima at angles $90^\circ \pm \delta$ which are symmetrical to the minimum at 90° of the ground state. Further investigations are in progress.⁵⁸

The primary steps discussed so far are summarized in Figures 3 and 8. For further information about photo-physical primary steps *via* triplet states the attention of the reader is drawn to preceding papers in this journal^{47,59,60} and by Bennett.⁶¹

Induced Emission. The Organic Dye Solution Laser

Lasers as light sources have the advantages that the light is intense, rather monochromatic, and polarized. However, if the excitation energy is too high in intensity, in addition to high-temperature effects, an additional source of error may occur: stimulated emission. This effect reduces the decay time, increases the quantum efficiency, and sharpens the fluorescence band.

In 1962 Morontz, et al.,⁶² pointed out that the triplet-singlet $T_1 \rightarrow S_0$ organic dye laser would not be possible because of the very small transition moment. In 1964 several coworkers and I⁶³ gave a first report on $S_1 \rightarrow S_0$ organic dye solution laser theory. In 1966 first experimental results were obtained by Sorokin,⁶⁴ Schäfer,⁶⁵ and Spaeth.⁶⁶

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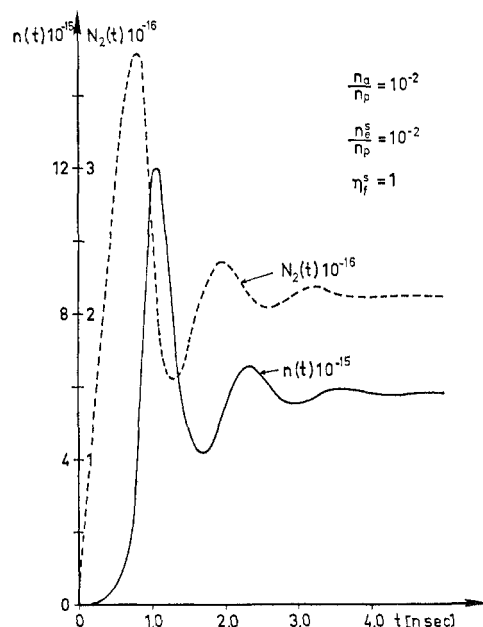


Figure 9. Calculated densities⁶⁸ of fluorescence photons (n) and excited molecules (N_2), respectively, if fluorescence quantum yield for spontaneous emission, Q_f^s , is 1.

By application of Statz-de Mars type equations developed by Rapp,⁶⁷ it became evident that Lorentzian band shapes will be maintained by the organic dye solution laser even if high-intensity laser impulses are used for excitation. However, the fluorescence intensity will show an oscillating behavior if the pulse intensity exceeds 10 MW. Just after such a pulse has started the solute molecules will absorb light and the excited-state density increases, followed by an increase of fluorescence photon density which initially is only due to spontaneous fluorescence. However, if fluorescence photon density is high enough, induced emission starts and the excited-state population density decreases, followed by a decrease of photon density, etc. (Figure 9⁶⁸). This result will greatly help the investigation of primary processes in photochemical reactions if both the absorbing species and the reaction product fluoresce.

Even in biochemical dark reactions, not only in photobiology, excited states may play an essential role. The lowest excited electronic states of pigments, aromatic amino acids, etc., could be reached by accumulation of vibrational energy since large molecules have a large number of normal vibrations. Triplet-triplet annihilation may then lead to the formation of singlet states, thus providing the system with still higher amounts of energy available for further reactions. For further literature see Edelman,⁶⁹ Foote,⁷⁰ and Konev.³¹

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