

form. Just as for E_{2g} and E_{1g} of benzene so for B_{1g} and B_{2g} of 'acenes it will be essential to include polar structures.

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CHARACTERIZATION OF ELECTRONIC TRANSITIONS IN COMPLEX MOLECULES

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A summary is given of the types of conclusions which may be drawn from a study of the emission properties of complex molecules under optical excitation in suitable systems. The types of radiationless transitions in complex molecules are discussed, and a resultant spectroscopic criterion stated: *The emitting level of a given multiplicity is the lowest excited level of that multiplicity.* Inter-combinations in complex molecules are described, and their importance is shown to arise from the high probability of the excitation of triplet states—a conclusion which runs counter to the trend of spectroscopic thought of a few years ago. An atomic number criterion is stated (after McClure) which permits the *identification of intercombinations by a study of intensity of the transition with heavy atom substitutions in a complex molecule.* Finally, a listing of empirical criteria is made which permits a distinction between pure π -electron transitions ($\pi \rightarrow \pi^*$) and transitions involving excitation of non-bonding N, O, and S atom electrons to anti-bonding π molecular orbitals ($n \rightarrow \pi^*$). The most definitive of these criteria is the *disappearance of $n \rightarrow \pi^*$ transitions in acid media.* An unusual enhancement of the spin-orbit coupling process for $n \rightarrow \pi^*$ transitions is reported and a possible interpretation is given.

Much useful information concerning the electronic states of complex molecules can be gained from a study of the emission properties of such molecules under optical excitation. In particular cases it may be necessary to study the molecule in rigid glass solutions at the temperature of liquid nitrogen in order to observe its light emission properties. However, since there is hardly a case in which light emission can not be observed with a moderate quantum efficiency, the method of emission spectroscopy can be applied almost universally. The information derived from such studies forms an essential supplement to that obtained from absorption spectra in the vacuum ultra-violet, high resolution spectra of vapours, and absorption spectra of solutions. In a series of forthcoming publications by the writer a detailed study of emission spectroscopy of complex molecules is reported.¹ The present paper summarizes the type of information revealed by such investigations.

Radiationless Transitions in Complex Molecules.—Two basic types of radiationless transitions are observed in most complex molecules. These are merely defined here, a full discussion and references being given elsewhere.^{1b, 1c}

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¹ *Emission Spectroscopy of Complex Molecules*, M. Kasha, to be published soon.

(a) Relations between Lifetime and Quantum Yield.

(b) Internal Conversion of Electronic Energy.

(c) Intersystem Crossing of Potential Surfaces.

INTERNAL CONVERSION may be defined as the rapid radiationless combination of excited electronic states of like multiplicity (combination in the spectroscopic sense of undergoing transition between). In general, internal conversion to the ground state does not occur with a high probability, although in certain types of molecules the latter process is significant and diminishes the total intrinsic quantum yield of luminescence.¹⁷ The phenomenon of internal conversion is manifested by the appearance of a unique luminescence, regardless of which state of a given multiplicity is excited. It yields a most useful spectroscopic criterion: *The emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity.*

An important recent application of this criterion is the re-assignment by Shull² of Sklar's lowest calculated triplet level of benzene to the emitting triplet level; Sklar arbitrarily has assigned the observed triplet level to one of the higher calculated levels.

INTERSYSTEM CROSSING is the spin-orbit-coupling-dependent internal conversion. In most cases this is the radiationless transition from the lowest excited singlet level to the lowest triplet level of the molecule. Analogous to *radiative* transitions involving π -electrons (e.g. in aromatic hydrocarbon molecules), a prohibition factor of about 10^6 distinguishes inter-system crossing from internal conversion. Moreover, since spin-orbit coupling forces are involved, the introduction of heavy¹⁸ (i.e. high atomic number) and paramagnetic³ atoms into the molecule will strongly increase the probability of the transition, as will strong external electric and magnetic fields. Despite the large prohibition factor, however, inter-system crossing is a rather probable process in most molecules. In fact, although usually observed only very weakly as a direct absorption from the ground (assumed singlet) state, the lowest triplet state is readily excited to emission (under conditions of low quenching, viz., rigid glass solutions). Thus, the lowest triplet state has been located in several hundred complex molecules through a study of their phosphorescence spectra.^{4, 5}

The facile excitation of the lowest triplet state (by light absorption to the lowest excited singlet state) is really a consequence of the very high rate of internal conversion (e.g. between singlet states). The following analysis of the rates involved may help to make this clear.

A molecule is excited optically to its n th excited singlet state, S^n . Under steady excitation a spectrum is photographed in search for the spontaneous $S^n \rightarrow$ emission (this has not been observed thus far in the cases studied). The ratio of the rate constant (reciprocal "lifetime") for the spontaneous $S^n \rightarrow$ luminescence to the rate constant for the radiationless $S^n \rightarrow S'$ internal conversion is given by the intensity ratio

$$\frac{k_L}{k_{IO}} = \frac{I_{S^n \rightarrow}}{I_{S' \rightarrow S}} < 10^{-4},$$

since the intensity of the fluorescence $S' \rightarrow S$ indicates the number of internal conversions. Numerous observations of this sort have placed the upper limit at the value indicated.

Thus, the internal conversion process takes place at least 10^4 times as fast as the spontaneous $S^n \rightarrow$ emission. The intrinsic lifetime of the latter can be calculated from the integrated absorption of the band corresponding to the $S^n \leftarrow S$ absorption: we shall assume this to be

- (d) m and n -electron Transitions in N -heterocyclics (with C. Reid).
 (e) n -Electron Transitions in Molecules Containing $Y = X$; Groups.
 (f) Internal Conversion to the Ground State.
 (g) Summation of the Quantum Yield.
- ¹ Shull, *J. Chem. Physics*, 1949, **17**, 295.
² Yuster and Weissman, *ibid.*, 1949, **17**, 1182.
³ Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2109.
⁴ Nauman, *Thesis* (University of California, Berkeley, 1947).

10^{-9} sec., a value commonly found for intense u.-v. absorptions.¹⁰ Then the reciprocal rate of the internal conversion process is $1/k_{IC} < 10^{-4}$, $1/k_L < 10^{-12}$ sec.

The natural limit on the rate of internal conversion may well be the time of a vibrational period; shorter estimates are actually obtained from spectroscopic data in some cases. As a consequence of the very high rate it is to be expected that "internally converting levels" will be somewhat broadened in a band width relative to the band width of the "fluorescing level" with a natural lifetime of 10^{-7} to 10^{-9} sec. In other words, the lowest absorption band of a given multiplicity manifold will be better vibrationally resolved than the higher energy bands of the same manifold (e.g. singlet-singlet transitions).

For intersystem crossing we apply an arbitrary prohibition factor of 10^6 , giving an intersystem crossing reciprocal rate

$$1/k_{IS} < 10^6 \cdot 1/k_{IC} < 10^{-7} \text{ sec.}$$

The probability of intersystem crossing in a molecule is measured by the *intersystem crossing ratio* χ , which is defined as the ratio of quantum yields of phosphorescence to fluorescence under steady simultaneous excitation¹⁰

$$\chi = \frac{\Phi_P}{\Phi_F} = \frac{k_{IS}}{k_F} \approx \frac{10^7}{10^9} = 0.1.$$

A fluorescence lifetime of 10^{-8} sec. is arbitrarily assumed here for illustration. The actual observed values of χ are of the order of magnitude of 1 for molecules with π -electron energy levels,¹⁰ indicating that the general assumptions made in the rate analyses are approximately correct.

Intercombinations in Complex Molecules.—Having observed the long-lived luminescence corresponding to the triplet-singlet emission of the molecule, we can locate the converse singlet-triplet absorption band with confidence. (If there are two luminescences, the long-lived one is naturally identifiable as the intercombination process. However, if only a single luminescence is observed, even under conditions of minimum quenching, the criteria to be described below must be applied.)

The intensity (integrated absorption) of the converse absorption band may be calculated from the measured lifetime of the luminescence by the well-known expression^{6, 7}

$$\int \epsilon d\nu = \frac{I}{8\pi c\nu^2 n^2} \cdot \frac{g_u}{g_l} \cdot \frac{I}{\tau_L}$$

From the integrated absorption and an assumed band width for the type of transition in question, the peak molar absorption coefficient can be estimated. Using the latter and the frequency of the o, o-band of the phosphorescence emission spectrum, the singlet-triplet absorption can be found.⁷ Since this is usually about 10^6 times weaker than the normal singlet-singlet transitions, rather long optical paths must be used, or else concentrated solutions or even the pure liquid (or solid) substance must be studied. Under these conditions absorption of light by an impurity easily could be misinterpreted as a forbidden electronic transition, were it not for the double check of correspondence with the o, o-band of the emission spectrum, and with the integrated absorption intensity calculated from the mean lifetime of the emission process.

To identify spectroscopically the long-lived luminescence and converse absorption bands as intercombinations, use is made of the characteristics of the spin-orbit coupling process. As is known from the theory of

⁶ Ladenburg, *Verh. dtsh. physik. Ges.*, 1914, 16, 769; *Z. Physik*, 1921, 4, 451. Tolman, *Physic. Rev.*, 1924, 23, 693. Perrin, *J. Physique Rad.*, 1926, 7, 90; *Ann. physique*, 1929, 12, 169.

⁷ Cf. Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, 67, 994.

atomic spectra, the probability of spin-orbit coupling increases rapidly with increasing atomic number of the atom. This principle has not been applied generally in molecular spectroscopy, although it is well known that, e.g. in the halogen series of molecules, the probability of the singlet-triplet transition in the visible region increases greatly in intensity in the order Cl_2 , Br_2 , I_2 .

McClure⁹ made the valuable extension of this principle to heavy-atom substituted complex molecules, showing that like the (radiationless) intersystem crossing process,¹⁰ the radiative intercombination process likewise increases rapidly in probability with increasing atomic number of the substituent. Thus, the rate constant for phosphorescence $k_p = 1/\tau_p$ as well as the oscillator strength f (or the integrated absorption, $\int \epsilon d\nu$) increase rapidly with increasing atomic number. This is shown clearly in Fig. 1, which is a plot of McClure's data for the monohalo-benzenes

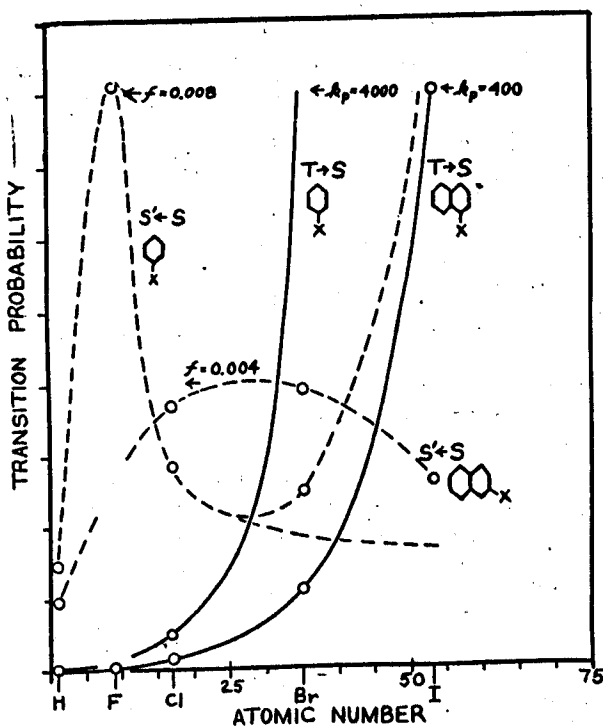


FIG. 1.—The effect of atomic number on intercombinations in the spectra of substituted complex molecules.

and naphthalenes. The solid line indicates the probability of the triplet-singlet emission process measured as the phosphorescence lifetime. The dotted lines show how one of the singlet-singlet transitions behaves for the same series of halo-derivatives. (The increase in f for bromobenzene and especially iodobenzene is probably due to the approach of the non-bonding halogen transition to the benzene 2600 Å absorption; the dotted line is arbitrarily drawn downward to suggest the correction required.) Obviously the atomic number is the wrong parameter against which to plot the probability of singlet-singlet transitions: some other property of the halogen substituent would give a more rational dependence.⁹ The atomic number effect is particularly valuable for the identification of intercombinations because the frequency of the transition changes only

⁹ McClure, *J. Chem. Physics*, 1949, 17, 905.

¹⁰ Matsen (*Symposium on Molecular Structure and Spectroscopy*, Ohio State University, Columbus, Ohio, 13th June, 1950) has presented a molecular orbital treatment of the problem which explains the anomalous f -values of the 2600 Å transition of the halo-benzenes in terms of an inductive effect.

slightly while the intensity changes by a large factor (e.g. the factor is 1000 for the lowest singlet-triplet of the mono-iodonaphthalenes compared with naphthalene).

Armed with this increased knowledge on the nature of intercombinations in complex molecules, great progress in this branch of molecular spectroscopy may be anticipated.

$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ Transitions.—A study of the emission spectral properties of the *N*-heterocyclics, which the writer has carried out together with Dr. C. Reid,¹⁶ has indicated the optical similarities of some of these molecules to such molecules as carbonyl, nitro, and nitroso compounds. In, e.g., the carbonyl compounds, the lowest singlet-singlet transition has been characterized tentatively as a transition corresponding to the excitation of a (nearly) non-bonding (oxygen) electron to an anti-bonding π molecular orbital.¹⁰ We have obtained definite physical evidence for this interpretation and have found analogous transitions (involving the non-bonding nitrogen electrons) in various *N*-heterocyclics (e.g. pyridine, pyrazine, phenazine). For convenience we designate non-bonding electrons as *n*-electrons, and the corresponding transitions as $n \rightarrow \pi^*$ transitions. These transitions are characterized by remarkably different properties in comparison with $\pi \rightarrow \pi^*$ transitions as shown, e.g., by the spectra of the aromatic hydrocarbons. A summary of distinguishing empirical criteria is offered.

VIBRATIONAL BAND WIDTH (VAPOUR SPECTRUM).— $\pi \rightarrow \pi^*$ transitions: moderately broad, owing to unresolved rotational structure. $n \rightarrow \pi^*$ transitions: "atomic" in sharpness, a fact commented upon by numerous observers. This seems to be due to the weakness of the *P* and *R* rotational branches, the strong *Q* branch predominating.

VIBRATIONAL BAND WIDTH (SOLUTIONS).— $\pi \rightarrow \pi^*$ transitions: vibrational fine structure preserved (e.g. the 2600 Å band of benzene). $n \rightarrow \pi^*$ transitions: very blurred, usually only slight vibrational structure remains, even in hydrocarbon solvents. This is all the more striking in view of the sharpness of the vapour absorption lines. Probably it is a characteristic of the non-bonding orbitals which leads to an unusual perturbation in solutions. In hydroxylic and other solvents, vibrational structure is completely blurred. Complex formation, probably involving hydrogen bonding in most cases, occurs and changes the non-bonding character of the orbitals.

ACIDIC SOLVENTS.— $\pi \rightarrow \pi^*$ transitions: the transition is preserved, although some blurring of fine structure occurs; usually there is little change in intensity. $n \rightarrow \pi^*$ transitions: the transition "disappears" (moves to very high energies). Addition of a proton to the non-bonding pair of the hetero-atom greatly increases the binding energy of the "lone pair". This behaviour offers the clearest proof of the excitation of non-bonding electrons in such molecules.

VIBRATIONAL ENVELOPE.— $\pi \rightarrow \pi^*$ transitions: complex vibrational envelope, many normal vibrations excited. $n \rightarrow \pi^*$ transitions: usually a unique ν_{vib} excited; this can probably be explained in terms of the localized character of the non-bonding electron orbital.

RATIO OF TRANSITION PROBABILITIES, P_{11}/P_{31} (singlet-singlet against singlet-triplet).— $\pi \rightarrow \pi^*$ transitions: the oscillator strength ratio $f_{11}/f_{31} \approx 10^6$ for the radiative process. For the radiationless process $\Phi_P/\Phi_F \approx 1$, which implies an equal probability of transition to the lowest triplet (and consequent triplet-singlet emission) and of spontaneous singlet-singlet emission.

For $n \rightarrow \pi^*$ transitions $f_{11}/f_{31} \approx 10^4$, and $\Phi_P/\Phi_F > 1000$. Here is evidence for a striking increase in the probability of the spin-orbit coupling process in such transitions. The increase by a factor 100 to 1000 is much

¹⁰ Mulliken, *J. Chem. Physics*, 1935, 3, 564. McMurry and Mulliken, *Proc. Nat. Acad. Sci.*, 1940, 26, 312. McMurry, *J. Chem. Physics*, 1941, 9, 231 and 241.

more than can be accounted for by an increase in atomic number in going from C to N to O. It is to be noted that the Φ_P/Φ_F property here means that fluorescence is scarcely to be observed in these molecules (some *N*-heterocyclics, all carbonyl, thiocarbonyl, nitro, nitroso, azo compounds): the "forbidden" conversion to the triplet state is essentially complete.

A possible interpretation of the greatly enhanced spin-orbit coupling for $n \rightarrow \pi^*$ transitions is that *sp*-hybridization which is present or can be plausibly introduced into non-bonding orbitals brings the optical electron much closer to the nucleus than in the case of an electron in a π -orbital; the spin-orbit coupling process occurs near the electric field of the nucleus of an atom. There are difficulties in this interpretation,¹² which, however, must be resolved by theoretical computations.

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DISCUSSION OF THE LOWEST SINGLET TRANSITION IN NAPHTHALENE AS A FORBIDDEN TRANSITION $\dot{A}_{1g} - A_{1g}$ AND REMARKS ON THE HIGHER SINGLET LEVELS*

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The absorption system of naphthalene at 3200-2900 Å is interpreted as ${}^1A_{1g} - {}^1A_{1g}$ transition. The infra-red active vibration of 568 cm^{-1} is tentatively suggested as vibration that makes the forbidden transition allowed in second order. In making this analysis, experimental data on absorption and fluorescence in the different states of aggregation of naphthalene and new results obtained for heavy naphthalene were used. The o—o band of the next higher absorption system at 2900-2500 Å is located at 35910 cm^{-1} and of the third absorption system at about 45100 cm^{-1} , both for the vapour. A brief comparison with theoretical results is given.

The near ultra-violet absorption of naphthalene has been studied in the vapour phase,^{1, 2} in liquid,^{3, 4} and in rigid glass solutions,⁴ and in the solid state⁵ (crystal at 20° K). The spectrum consists of two absorption regions lying fairly close together. The long wave part ranging from about 3200-2900 Å shows in the vapour sharp narrow bands, whereas the bands from 2900-2500 Å are broad and diffuse. Moreover, the pattern in which the bands appear is different in the two regions. The measurements in liquid solution give an average extinction coefficient ϵ of 200-300 for the first region and of 5000-6000 for the second region. Furthermore, at 2200 Å a very strong and broad band with little indication of structure was observed^{3, 6} with $\epsilon \sim 100,000$. The absorption spectrum of the solid

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¹ Henri and de Laszlo, *Proc. Roy. Soc. A*, 1924, 105, 662.

² de Laszlo, *Z. Physik. Chem.*, 1925, 118, 369.

³ For example, Morton and de Gouveia, *J. Chem. Soc.*, 1934, 911; Mayneord and Roe, *Proc. Roy. Soc. A*, 1935, 152, 299.

⁴ Kasha and Nauman, *J. Chem. Physics*, 1949, 17, 516.

⁵ Prikhotjko, *J. Physics, U.S.S.R.*, 1944, 8, 257.

⁶ Klevens and Platt, *J. Chem. Physics*, 1949, 17, 479.