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FUNDAMENTAL ASPECTS OF PHOTOSENSITIZATION. INTERCOMBINATIONS IN MOLECULES

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DEPARTMENT OF CHEMISTRY
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TALLAHASSEE, FLORIDA

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FUNDAMENTAL ASPECTS OF PHOTOSENSITIZATION.
INTERCOMBINATIONS IN MOLECULES

Department of Chemistry, Florida State University

Tallahassee, Florida

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Project Supervisor:
M. Kasha

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Department of Chemistry, Florida State University, Tallahassee

Table of Contents

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MOLECULAR ELECTRONIC SPECTROSCOPY.
SPIN INTERCOMBINATIONS IN MOLECULES(1,2)

By M. Kasha and S. P. McGlynn
Department of Chemistry, Florida State University
Tallahassee, Florida

This review covers selected topics of research published in molecular electronic spectroscopy in 1955. The topics in this general category which are undergoing rapid development at present are (a) spectra of molecular complexes, (b) spectroscopy of molecules in crystals, including polarizations and assignments, (c) study of spin-intercombinations in molecules, (d) study of transitions of n,π type, (e) intermolecular energy transfer; and, extending the general category, (f) spectra of transition metal ions in various environments.

From this broad range of topics this review will abstract but one: we shall review the topic Spin-Intercombinations in Molecules.

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(1) The survey of the literature pertaining to this review was concluded in December 1955.

(2) The writing of this review was done as part of the work related to a research program supported by the Office of Scientific Research, U. S. AIR FORCE, under a contract with the Florida State University.

Our method will be the setting of a perspective by a coverage of key papers on this topic from past literature. Integrated with this treatment will be all pertinent papers published in 1955. This presentation should have the advantage of a certain unity, although at the same time failing to catalog the many papers published in unrelated fields. The yearly service performed by the Annual Reports of the Chemical Society (London) cannot be overlooked, however, and makes up for the latter deficiency. As the present method of review is extended, most important papers will have been surveyed in a brief cycle of years.

The topic we have selected is greatly in need of review. In the literature of about ten years ago, very little if any mention was made of the subject of spin-orbital interaction in molecules. The number of papers on this and related topics has increased rapidly in recent years, to the point where they now number well over one hundred. It thus appears worthwhile to organize and examine what has been done thus far in these subjects, and to cast the research of the past year against this background.

GENERAL BACKGROUND

The full development of this field of research came late in the history of molecular spectroscopy, and in some respects in an unexpected way. The theory of spin-orbital coupling and its application to the electronic spectra of atoms and diatomic molecules had been known since the early years of the development of quantum mechanics. It seemed natural to suppose with Sponer and Teller (1):

> 'As in the case of atoms we have, in first approximation, the selection rule that only states of the same multiplicity combine with each other. Intercombinations occur with appreciable intensity only if the molecule contains some heavier atoms.'

Developments since 1944 have shown that, although high-Z atoms have their expected effect, frequently spin-intercombinations occur with great intensity even in molecules composed of atoms of atomic number 8 or less. Thus, a type of transition which usually is neglected in atomic spectroscopy except in heavy atom cases, assumes great importance in molecular spectroscopy, and dominating importance in the light emission properties of most molecules. As we shall see, this extraordinary result is due entirely to the important role played by <u>radiationless transitions</u> in complex molecule spectroscopy. As a consequence of these, the lowest triplet states of most molecules are readily populated upon light absorption which excites the allowed singlet states (ground singlet states assumed thruout). On the other hand, the radiative intercombinational transition probabilities are extremely small in (light atom) complex molecules, just as in atomic and diatomic cases. The transition probability for emission of light is measured by the decay constant (reciprocal mean lifetime), so that a high intensity (quantum efficiency) of emission need not be incompatible with a highly forbidden transition.

The fact that complex molecules emit phosphorescence at low temperatures was known since the <u>pre-twentieth-century</u> observations of Wiedemann (2) on solid solutions and Dewar (3) on crystals. The apparent general requirement of a solid state medium was puzzling, if not distasteful to the spectroscopist nurtured on unperturbed gaseous molecule spectra. There were numerous attempts to interpret the spectra on the basis of complicated solid state interactions. Although Lewis, Lipkin, and Magel (4) and Terenin (5) speculated on the possibility that the phosphorescence emission might be triplet → singlet in nature, alternative hypotheses were considered equally suitable. Finally, the general identification of the phosphorescence emission of polyatomic or complex molecules as a triplet → singlet emission was made in 1944 by Lewis and Kasha (6). At the time of publication of this paper the theoretical justification for the identification was not very secure, nor was the apparent incompatibility with the behavior of atomic and diatomic systems fully recognized. Nevertheless, the paper catalyzed almost feverish research activity in this field, and it is appropriate to acknowledge a debt of gratitude owed by spectroscopists to G. N. Lewis for his contribution to this general advance in spectral accessibility. Before 1944 the interest in intercombinational transitions in molecules was severely limited by the lack of experimental information.

Subsequently, much work has been published relating to spin-intercombinations: on the triplet → singlet emissions of numerous molecules, the very weak singlet → triplet absorption spectra, the transient triplet → triplet absorption spectra, the study of spin-orbital perturbations -- intramolecular and intermolecular -- introduced by high-Z and paramagnetic atoms. These researches have enhanced considerably the understanding of the nature of radiationless transitions in complex molecules, and of the application of spin-orbital coupling theory to molecular cases. Applications are following close on the heels of this spectroscopic work. These include the interpretation of fluorescence quenching, photochemical reactions, photochromism and thermochromism, and perhaps most important of all, the theory of chemical reactivity.

Previous reviews touching on this general topic have been rather fragmentary, but are useful sources: Kasha (7), Förster (8), Kasha (9), and Craig (10).

THEORETICAL COMMENTARY

Electric dipole and magnetic dipole transitions between pure singlet and pure triplet states are forbidden rigorously on account of the orthogonality of the spin wave-functions. The intervention of spin-orbital coupling brings about a mixing of singlet and triplet states, destroying their purity, and permitting intercombinations between nominal singlet and triplet states to be observed. Great interest attaches, therefore, to the form of the spin-orbital Hamiltonian, since only by a thorough knowledge of its form and action can the spectroscopist realize fully his opportunities for observation of intercombinations.

The spin-orbital interaction operator in its generalized form is given by Dirac (11): cf. Mott and Sneddon (12). The spin-orbital interaction part of the total Hamiltonian is introduced as a relativistic correction. The strongest contribution to spin-orbital interaction occurs when the electron comes closest the nucleus, and is travelling with relativistic velocities. Consequently, insofar as spin-orbital interaction influences chemical behavior (cf. below), it may be said that in those cases there is evidenced a <u>relativistic chemical effect</u>.

How the symmetry of the spin-orbital interaction operator may be deduced for any symmetry of the nuclear potential, V, has been shown by Weissman (13) and Mizushima and Koide (14). However, the simplest discussion is obtained by allowing V to have spherical symmetry, whereupon the properties of the operator become evident immediately. This case is applicable strictly only to atoms (see Kramers (15)), but it has been applied to molecules as an approximation by McClure (16) (vide infra). It is found that the spin-orbital interaction operator may be separated into sums containing orbital and spin factors which are separately symmetric or antisymmetric under electron interchange. The antisymmetric spin factors lead to mixing of singlet and triplet states, and the symmetric spin factors lead to multiplet splitting. The orbital factors determine the orbital types of the states which may mix (16)(17). The validity of the separation of the orbital and spin parts of the Hamiltonian has been discussed by Weissman (13) and Ross (18).

The spin-orbital interaction operator involves the gradient of the potential. This will be largest in the proximity of the nuclei of the atoms on which the (molecular) orbitals are centered, and particularly large close to the nucleus of highest atomic number (Z) in the molecule. In the special case of one high-Z atom in a molecule otherwise composed of low-Z atoms, e.g., thiophene, bromobenzene, etc., where most of the contribution to spin-orbital coupling in a molecular electronic orbital is derived from a single atom, the assumption of a spherical potential as made by McClure (16) is not an unreasonable one. Furthermore, since most of the contribution to the spin-orbital interaction derives from the electron's orbital motion nearest the nucleus, the form of the orbital wavefunction in this vicinity will be of unusual importance. In ordinary valence and spectroscopic calculations the form of the orbital wavefunction near the nucleus is comparatively less important. Consequently, the use of Slater-type orbital wavefunctions in calculations of spin-orbital interaction may be open to question. Both of the published calculations (14)(17) use Slater orbitals.

For a hydrogenic atom, the transition probability for spin-intercombinations has an 8th power dependence (the matrix elements of the spin-orbital interaction depending on the 4th power) on Z, the atomic number (see Condon and Shortley (19)). A strong Z dependence is found also in molecular spin-intercombinations, as shown in numerous experimental results to be cited below.

In the application of the theory of spin-orbital interaction to the case of benzene, the result is obtained that the observed mean lifetimes for the triplet → singlet emission are up to 1000 times greater than those calculated from the atomic spin-orbital coupling factors (McClure (20)).

McClure (17) has shown that this may arise from a fortuitous cancellation, on symmetry grounds, of the matrix elements for spin-orbital interaction in the planar molecule. On the other hand, Mizushima and Koide (14) have shown that $\sigma-\pi$ interaction would be sufficient to account for the observed long intercombinational lifetime in benzene. In order to decide which of the theories is applicable to benzene, polarization studies of the phosphorescence emission would be necessary. Thus far, such a study has not been made.

PHOTOMAGNETISM STUDIES

Before proceeding to spectroscopic observations, it is worthwhile to review the experimental work on the paramagnetic susceptibility of the phosphorescent, or lowest triplet, state of complex molecules. At the time that the phosphorescence emission was interpreted as a triplet → singlet emission, such measurements seemed an important and necessary proof of the interpretation. Moreover, here was a delicious opportunity, since near-saturation of the excited state could be obtained under certain conditions (see (4) for example). Subsequent spectroscopic studies, based on the nature of spin-orbital interactions, have made direct measurements of paramagnetic susceptibility unnecessary for assignment of state multiplicity. Nevertheless, it is an interesting chapter in the development of the field, and new work on this phase has appeared very recently.

Lewis and Calvin (21) carried out exploratory experiments on the paramagnetism of a dyestuff excited to its phosphorescent state. This work was followed by a thorough quantitative study by Lewis, Calvin, and Kasha (22). For acid fluorescein dye a satisfactory measurement of the paramagnetic susceptibility was obtained, confirming the triplet assignment for the phosphorescent state.

It is interesting to note that empirical photomagnetic experiments were carried out earlier by Fröhlich, Szalay, and Ször (23). These authors investigated the behavior of dyestuffs in solid solutions, in the form of plates, suspended in a magnetic field. A photomagnetic effect was noted. Yamamoto (24) also carried out a series of magnetic dichroism researches on solid solutions of dyestuffs, upon illumination. His results confirm the photomagnetism results of Lewis, Calvin, and Kasha (22).

Porter (25) has commented on the need for further paramagnetism studies of the phosphorescent state; he was unaware of the researches described immediately above.

Direct measurements of paramagnetic susceptibility have been extended by Evans (26) recently to include fluorescein dye, 1-hydroxy-2-naphthoic acid, and triphenylene. Using an apparatus different from the Theorell balance used by Lewis, Calvin, and Kasha (22), Evans not only observed positive results in each case, but also was able to follow the decay of paramagnetic susceptibility with time upon extinction of the exciting light. The time constants for this decay, which was observed to be exponential, coincided with the decay constants for the phosphorescence emission. This provides proof that the paramagnetism arises from excited triplet states which decay spontaneously, and not, e.g., from radicals disappearing by a bimolecular recombination process.

RADIATIONLESS TRANSITIONS: INTERSYSTEM CROSSING

In molecular electronic spectroscopy internal conversion may be defined as the rapid radiationless combination of electronic states of like multiplicity. Experience indicates that, in general, internal conversion takes place between excited levels, but not between the lowest excited level and the ground level. This evidence is summarized in the rule (9): The emitting level of a given multiplicity is the lowest excited level of that multiplicity. This behavior depends on the relative spacing of the electronic levels, and on the necessity for removal of the excess vibrational energy by intermolecular collisions. In solid solution experiments at 77°K only the behavior of naphthacene (27) and azulene (28) have provided anomalies, both of these also having exceptional energy spacings. Theoretical studies relating to the general problem of radiationless transitions in molecules have been carried out by Teller (29), Duschinsky (30), and Davydov (31).

Recently, crystal spectroscopic studies at 20° and 4°K have provided many further examples of the breakdown of normal internal conversion. These examples are particularly interesting since they involve molecules which behave normally at 77°K in solid solution emission studies. Evidently, at very low temperatures, the intermolecular collision process is inhibited to the point where vibrational energy cannot be carried off effectively. Hence, essentially "resonance" emission may occur. This technique is rich in possibilities for resolution of superposed electronic transitions in molecules. Such observations have been reported recently in a series of exploratory researches on molecular crystals by Pesteil _et al_ (32,33,34,35,36,37,38,39). Of particular interest is their report of two triplet → singlet emissions in benzene: one at 30574 cm^{-1}, which they assign as ${}^3B_{1u} \rightarrow {}^1A_{1g}$; and one at 38724 cm^{-1}, which they assign as ${}^3E_u^- \rightarrow {}^1A_{1g}$. The lowest triplet of benzene is well known from earlier work (6,40,41,54,55). The second triplet has been predicted by theory (see Roothaan and Mulliken (42)) and it has been reported by Pesteil to be evident in absorption in the spectrum of crystalline benzene at 83°K (43,44)(see footnote on p. 230, rev. (10), however). The observations of Ham (45), which were described as evidence for the second triplet in benzene, have been criticized by Bayliss and Hulme (46). Further examples of the apparent breakdown of internal conversion have been found recently by Sidman and McClure (47) in their very thorough study of the absorption and emission spectra of solid crystal solutions biacetyl and biacetyl-d-6 at 20°K and 4°K.

A further anomaly of low temperature crystal spectroscopy was noted by Pesteil et al (see above), in which apparently at the lowest temperatures, the electronic transition is displaced to lower frequencies by a vibrational quantum, compared with higher temperature spectra. We shall not elaborate on this since it has no direct bearing on internal conversion.

Intersystem crossing has been defined as the spin-orbital coupling dependent internal conversion in molecules (9). The intensity of the phosphorescence emission (in terms of quantum efficiency, i.e., number of $T \rightarrow S$ quanta emitted per number of $S' \leftarrow S$ quanta absorbed) does not measure the probability of $T \rightarrow S$ emission, but is determined by the ratio of the transition probabilities for the (radiationless) intersystem crossing ($S' \rightarrow T$) and the spontaneous fluorescence ($S' \rightarrow S$). (It is assumed here that S' is an excited singlet state lying above the lowest triplet state T, and that most of the triplet excitation occurs by intersystem crossing from this singlet). The intersystem crossing ratio $\chi = \Phi_P/\Phi_F$ therefore measures this transition probability ratio (Kasha (9); see McClure (20), especially Table VI), and states the relative quantum efficiency for phosphorescence and fluorescence. If the transition probability for fluorescence becomes too small, the lowest triplet state may become the only emitting state in the molecule. This situation is especially common where the lowest singlet-singlet transition is of n,π type (9).

Since intersystem crossing is spin-orbital coupling dependent, perturbation effects involving the electric field of high-Z nuclei or the magnetic field of paramagnetic atoms should be observable. Kasha (9) has observed a strong Z dependence of the Φ_P/Φ_F ratio in halogenated aromatic molecules (cf. Yuster and Weissman (48)). In certain organometallic chelates involving rare earth ions, Yuster and Weissman (48) have found the same effect, and in a case where the ion was paramagnetic, an especially strong perturbation was noted. In all such studies the main effect observed is a great increase in the Φ_P/Φ_F ratio, while the total quantum efficiency remains essentially constant.

Recently Becker and Kasha (49, 50) have made use of spin-orbital perturbation effects to establish the lowest triplet state of the chlorophyll molecule. A porphyrin molecule, phthallocyanine, and several chlorophyll species were studied each without a metallic atom, and containing both heavy and paramagnetic atoms. The effects observed were exactly parallel to the predictions of spin-orbital coupling theory. The lowest triplet levels of the chlorophylls and the porphyrin studied were thus established with certainty.

Porter and Windsor (51) (see also Porter (25)) have applied the synchronized flash (flash photolysis) spectroscopic method to the study of triplet states in fluid solutions. Their kinetic analysis has given important new information concerning the intersystem crossings involved. However, at the same time, further problems of interpretation have arisen, causing these authors to emphasize the need for a critical examination of the triplet state interpretation of the phosphorescent state. At this juncture, there seems to be no doubt concerning the validity of the triplet state interpretation. However, the flash technique undoubtedly offers a valuable method of study of triplet state excitations, depopulations, and reactions.

TRIPLET STATES: TRIPLET → SINGLET EMISSION STUDIES

Lewis and Kasha (6) gave spectroscopic data on the phosphorescence emission spectra of 89 molecules. We have already discussed their interpretation of these as lowest triplet → singlet emissions (see General Background section, above). Of the molecules studied, only the results given for stilbene and ethylene and its halogen derivatives are now known to be wrong (see Potts, in section on Singlet → Triplet Absorption Spectra); for the remaining cases the emissions are authentic. Kasha (7) presented a discussion of the function of the rigid glass solution, and elaborated on the mechanism of excitation of the lowest triplet state; further triplet → singlet emission data were reported (e.g., hexachlorobenzene and phenanthrene). One general conclusion drawn from this earlier work is that the viscous or rigid medium used as a solvent serves mainly to inhibit diffusion controlled quenching of the triplet state. On the other hand, Lewis and Kasha (52) stressed the fact that if the lowest triplet state intrinsic mean lifetime were short enough, triplet → singlet emission would be observable even in the liquid and gaseous state. Porter and Windsor (51) in the papers already referred to have made studies recently on the lowest triplet state in liquid solutions (see Radiationless Transition section above, and section on Triplet → Triplet Absorption Spectra, below), although under their conditions triplet → singlet emissions could not be observed directly. The studies of luminescence spectra of vapors, by Robinson (53), involve triplet → singlet emissions. The case of biacetyl vapor luminescence is another well known example (52; see also 47) of a strong triplet → singlet emission of a complex molecule in the vapor state. In such cases, the inherent short lifetime allows emission to occur without complete quenching. In other cases, where the triplet → singlet lifetime is relatively long (see below), only singlet → singlet emission is observed in the vapor luminescence spectrum.

More detailed studies of triplet → singlet emission spectra have been made subsequent to the research of Lewis and Kasha. Thus, the triplet → singlet emission spectrum of <u>benzene</u> was carefully re-studied and a vibrational analysis carried out by Shull (40); parallel studies on benzene have been made by Dikun and Sveshnikov (41, 54, 55). Pesteil <u>et al</u> (33, 39) have recently studied the triplet → singlet emission in crystalline benzene, and also crystalline hexachlorobenzene (37, 38), at very low temperatures. Some of their results already have been mentioned in the section on Radiationless Transitions. The <u>naphthalene</u> triplet → singlet emission was restudied by Ferguson, Iredale, and Taylor (56), who gave vibrational analyses for naphthalene, and monosubstituted and disubstituted naphthalenes. In the case of <u>anthracene</u>, Reid (57) presented indirect evidence against the lowest triplet level reported by Lewis and

Kasha (6). Padhye, McGlynn, and Kasha (58) have restudied the lowest triplet level in anthracene and have confirmed the level reported by Lewis and Kasha. Triplet → singlet emission spectra of anthracene and several substituted anthracenes, singlet → triplet absorption spectra, and solvent-perturbation experiments (see below) were used to confirm the assignment. McGlynn, Padhye, and Kasha (59) presented a correlation diagram for the lowest triplet levels for the first four linear polyacenes. Craig (10) has discussed the symmetry assignment of electronic levels in this series.

Besides the polyacene hydrocarbons described above, phosphorescence spectra were reported for various pyrene hydrocarbons by Ilina and Shpolskii (60) and for coronene and 1,2-benzoperylene by Bowen and Brocklehurst (61). McClure (20) had previously reported frequency data on triplet → singlet transitions of pyrene, coronene, and other hydrocarbons not studied by Lewis and Kasha. Neporent and Inyushin (62) reported phosphorescence and fluorescence spectra of phthallimide and eleven derivatives.

Becker and Kasha (50) published spectroscopic data on the lowest triplet → singlet transitions in several chlorophylls and porphyrins. Their observations are complemented by the studies of Livingston (63), who has used the synchronized flash technique to study the lowest triplet state of the chlorophylls. The observations using this technique yield triplet → triplet absorption spectra, and also lifetimes of the triplet state under the experimental conditions used. The research of Witt (64) parallels that of Livingston.

The transition probability for triplet → singlet emission is measured by the decay constant, or the reciprocal of the intrinsic mean lifetime. Numerous studies of the mean lifetime of the lowest triplet state of molecules are now published. Some discretion must be exercised in using the published data directly, since only the intrinsic mean lifetime in the absence of quenching is a true measure of the transition probability. Probably, lifetimes determined for dilute solutions of a molecule in rigid glass solvents approach the intrinsic lifetimes, according to quantum efficiency measurements (see below). McClure (20) published the first detailed study of triplet → singlet lifetimes in complex molecules. His measurements provided proof of the intercombinational character of the emission, thru his demonstration of the Z-effect on the emission lifetime in halogenated hydrocarbons. His correlation of the mean lifetimes with spin-orbital coupling factors for the substituting atoms gave semi-quantitative agreement. Similar observations were made by Yuster and Weissman (48) on the dibenzoylmethane derivatives of trivalent metal ions, including some rare earth ions. Kaskan and Duncan (65) made a study of the triplet → singlet emission lifetimes of ketones in the gaseous state. An empirical study of phosphorescence lifetimes was made by Sveshnikov and Petrov (66), who studied the influence of the medium on the lifetimes. A comprehensive empirical study of phosphorescence lifetimes was published by Dikun, Petrov, and Sveshnikov (67), with data on numerous mono, di, and tri-substituted hydrocarbons. Similar empirical phosphorescence lifetime studies were made by Pyatnitskii (68). The study of triplet → triplet absorption spectra (see pertinent section, below) affords independent information on lowest triplet state lifetimes, although in fluid solvents the quenching effect markedly shortens the observed lifetime. Thus, Craig and Ross (69), Porter and Windsor (51), Livingston (63) and Porter and Wright (70) have determined lifetimes by following the decay of triplet → triplet absorption. Apparatus for phosphorescence lifetime determination has been described recently by Skarsvåg (71) and van Roggen and Vroom (72).

Studies of quenching of phosphorescence of organic molecules have been published recently by Kato and Koizumi (73) and Kato, Kimura, and Koizumi (74). Measurements of absolute yield of phosphorescence were reported earlier by Gilmore, Gibson, and McClure (75).

In this paragraph we shall itemize theoretical papers having special reference to intercombinations and triplet states in molecules; papers on calculation of electronic levels in which triplet states are incidental will not be covered. In the section Theoretical Commentary, reference has already been made to the paper on selection rules for intercombinations by McClure (16) and the paper on the vector model for spin-orbital interaction by Weissman (13). The papers on calculation of matrix elements for spin-orbital coupling in benzene by McClure (17) and Mizushima and Koide (14) also were alluded to briefly. Transition probability calculations for spin-orbital interaction in atoms had been published by King and Van Vleck (76). Barnes, Bray, and Harrick (77) reported briefly on spin-orbital and spin-spin interaction parameters for molecular hydrogen, as derived from radiofrequency spectroscopic measurements. Herman (78) considered symmetry selection rules involved in molecular intercombinations. This paper seems to suffer from inaccurate translation and is otherwise difficult to evaluate. Kovner and Sverdlov (79) have described a simple method for calculation of triplet states by the Valence Bond method (Rumer diagrams). Longuet-Higgins and Pople (80) have studied excited states of odd alternant hydrocarbon radicals and ions, and relate the singlet-triplet separation of the ion to the separation of the two low-lying doublets of the radical (cf. Longuet-Higgins and Murrell (81)). Merrifield (82) has compared matrix elements for excitons of singlet and triplet multiplicity.

SINGLET → TRIPLET ABSORPTION SPECTRA

Radiative spin-intercombinations are highly forbidden in complex molecules just as in the case of atoms. Consequently, singlet → triplet absorption intensities are extremely low, and triplet → singlet emission lifetimes correspondingly long. A factor of about 10^6 relates the corresponding singlet → singlet transition probabilities.

Because of the very low transition probabilities for the spin-intercombination absorption case, considerable difficulty is experienced in observing singlet → triplet electronic absorption bands, and distinguishing them from bands due to vibrational harmonics and impurities. This will be evident in the examples which follow.

Lewis and Kasha (52) carried out the first systematic search for singlet → triplet absorption bands in molecules. They made use of the classical relation between absorption and emission probabilities (cf. reference in Kasha (9)) as a guide to amenable cases. Their work suffered from their failure to realize the importance of the Z-effect on intercombinational transition probabilities. Consequently, only the singlet → triplet absorption band reported for benzene is authentic; the absorption bands for the remaining molecules investigated by them have been shown subsequently to be singlet → singlet in nature. McClure, Blake, and Hanst (83) made use of the Z-effect in intercombinations in their study of singlet → triplet absorption bands of halogenated benzenes and naphthalenes.

The case of benzene deserves special mention as the singlet → triplet absorption band has been investigated by numerous researchers. Sklar (84) first reported observing this band, although the absorption curve was not published. Lewis and Kasha (52) reported a detailed spectrum observed for 10 cm. of liquid benzene. The correspondence with the previously observed triplet → singlet emission was used as a criterion of authenticity. Also they demonstrated that the vibrational overtones, although observable even in the visible region, could not account for the observed ultraviolet bands owing to the rapid diminution of the intensity of overtones with frequency. Pitts (85) reinvestigated the same band. McClure, Blake, and Hanst (83) gave additional proof of its intercombinational character by demonstrating its intensification with increasing Z of substituent atoms. Shibata, Kushida, and Mori (86), on the other hand, reported weak absorption bands for benzene in the visible region. They designated these as singlet → triplet, whereas they were identified previously by Lewis and Kasha (52) as merely vibrational harmonics (See reference (10), footnote on p. 230; and reference (59), footnote 12). Cheshko (87) believed the bands reported for benzene by Lewis and Kasha (52) to be due to impurities; however, the data he published on his research merely indicates that his benzene was never pure enough to observe the bands.

In the case of <u>pyridine</u>, Reid (88) reported in detail on two weak transitions in the ultraviolet region. Recently Brealey (89) has shown that both of these bands are due to a very small impurity of pyrazine in pyridine.

In the <u>ethylene</u> molecule Snow and Allsopp (90) made an early report on a weak absorption band near 2100 A, which they assigned as singlet → triplet. Moffitt (91) supported their assignment with theoretical calculations. Thus, this assignment of Snow and Allsopp is evidently the first authenticated singlet → triplet observation in complex molecules. These bands were studied further by Carr and Stücklen (92), Picket, Muntz, and McPherson (93), and recently by Potts (94). Lewis and Kasha (6) had reported phosphorescence emission in halogenated ethylenes near 4000 A. Potts searched for phosphorescence in tetramethylethylene and found none.

From the energy and the lifetime point of view, the phosphorescences reported by Lewis and Kasha for ethylenes do not appear to be authentic.

Sidman and McClure (47) have recently observed weak absorption bands in biacetyl at low temperature, which they assign as the lowest singlet → triplet absorption. Padhye and Desai (104) have reported on the lowest singlet → triplet absorption band in thiophene.

The difficulties which occur in the discrimination of very weak absorption bands due to impurities and vibrational harmonics, from those due to authentic spin-intercombinations can be overcome in applicable cases by the use of the solvent-perturbation technique (Kasha (95); see section on Intermolecular Spin-Orbital Perturbations).

TRIPLET → TRIPLET ABSORPTION SPECTRA

Triplet → triplet absorption bands are of course not intercombinational in nature, but are discussed here because of their dependence on triplet excitation. The bands are inherently medium strong to intense, since the only selection rule would involve orbital symmetry. Where favorable population of the lowest triplet is attainable, the transient absorption originating in this metastable state is readily observed.

Early in the research conducted by Lewis on the phosphorescence state of molecules, observations on transient absorption spectra were recorded and identified as "absorption spectra of the phosphorescent state." Today these are recognized as triplet → triplet absorption spectra, and are essential for the location of upper triplet levels in molecules.

Lewis, Lipkin, and Magel (4) published data on a triplet → triplet absorption band of the acid fluorescein dye, and Lewis and Lipkin (96) observed a triplet → triplet absorption band in diphenylamine. Clar (97) reported observations on a triplet → triplet absorption band in triphenylene. Sveshnikov and Dikun (98) reported difficulty in reproducing Lewis, Lipkin, and Magel's result on acid fluorescein.

McClure (99) made a general study of triplet → triplet absorption spectra in complex molecules. Spectra and frequencies were reported for ten molecules, mainly aromatic hydrocarbons and simple derivatives. Craig and Ross (69) extended triplet → triplet absorption studies still farther, giving data on various aromatic hydrocarbons and multiple ring nitrogen heterocyclics. Their determination of lowest triplet state lifetimes have been referred to previously. Craig and Ross also noted photodecomposition effects, which constitute an interference in the physical absorption work.

All of the above observations have been made in rigid glass solutions at low temperature. The development of the synchronized flash spectroscopic method has made it possible to study triplet → triplet absorption spectra in fluid solutions at room temperature. Thus Porter and Windsor (51), Porter and Wright (70), Livingston (63), and Witt (64) have carried out such studies in papers already referred to. McClure and Hanst (100) have recently used the synchronized flash technique to study triplet → triplet absorption in aromatic ketones.

Ross (101) has made a theoretical study of the optimal optical conditions for triplet → triplet absorption studies.

There are two difficulties which exist in this field at present. First, photodecomposition may constitute a serious interference especially in the flash method, owing to the high light intensities used. Second, there is a gap at present, due to experimental inaccessibility, between the lowest triplet observed in phosphorescence, and upper triplets observed in triplet → triplet absorption. Thus, in benzene, no triplet → triplet absorptions have been observed as yet, possibly because they exist in the near infra-red region.

The observations of thermochromism are related to the subject of triplet → triplet absorption spectroscopy. These are discussed in the last section of this review.

INTERMOLECULAR SPIN-ORBITAL PERTURBATIONS

Even if only intramolecular spin-orbital effects could be observed, intercombinations in molecules would have an important bearing on chemical problems. The discovery of intermolecular spin-orbital perturbations serves to make ideas on intercombinations in molecules of direct applicability to the development of chemical reaction mechanisms. Such a possibility is just becoming apparent to chemists and has been almost entirely neglected up until now. In this section we shall be concerned with physical intermolecular effects. Chemical effects will be listed in the next section.

Kasha (95) made use of the Z-effect on intercombination absorption intensity, extending previous work in an intermolecular spin-orbital perturbation experiment. Ethyl iodide was used as a solvent to bring about an enhancement of the singlet → triplet absorption intensity in a naphthalene derivative. Ham (45) made similar observations on benzene, in which he observed enhancement of absorption bands in between the individual singlet → singlet near-ultraviolet absorption bands of benzene. Bayliss and Hulme (46) have questioned Ham's assignment of the observed bands as singlet → triplet; admittedly his observed intensities are very high for intercombinations, and the possibility of confusion with the singlet → singlet absorptions in this case is rather great.

McGlynn and Kasha (102) have made a comprehensive extension of the earlier observations of Kasha (95). Many new examples were found of singlet → triplet band enhancement, and the dependence on Z was fully delineated. Up to 100-fold enhancements were observed with alkyl iodide solvents. Of particular interest is their demonstration that vibrational harmonics and impurity absorption bands (which are necessarily singlet → singlet) are unaffected by solvents containing high-Z atoms. This, as mentioned earlier, offers a criterion of authenticity for singlet → triplet absorption work, in those cases where the solvent-perturbation method can be used. In some cases, a reaction of the solute with the high-Z atom solvent makes the method inapplicable. Dyck and McClure (103) have recently used the solvent-perturbation method to induce the singlet → triplet absorption band in trans-stilbene. This band could not be detected in the absence of an external perturbation, and the converse emission also was not observable.

The solvent-perturbation experiments of Kasha (95) were undertaken because of the known Z-dependence of intermolecular fluorescence quenching. Since the spin-orbital Hamiltonian has a high Z-dependence, it was expected that the mechanism of "heavy atom" fluorescence quenching could be due to an intermolecular spin-orbital perturbation. The demonstration of singlet → triplet absorption band enhancement offered direct proof of this interpretation of fluorescence quenching. This paved the way to other intermolecular or chemical applications.

The Russian researchers have thought along rather different lines from those described in this review. The work of Terenin, Karyakin et al indicate that they have not recognized the mode of excitation of triplet states, and the dependence of spin-orbital interaction on atomic number. Thus, Ermolaev and Terenin (105) do not believe that triplet states can be excited directly by light absorption and dispute the Lewis and Kasha (6) interpretation of phosphorescence. They believe that intermolecular energy transfer may be required for excitation of triplet → singlet emission. Terenin (5) in his first writings on the subject acknowledged Lewis, Lipkin, and Magel's (4) tentative discussion on the possibility of the triplet → singlet interpretation of phosphorescence. On the other hand, in this and later papers he and his co-workers laid emphasis on the need for "paramagnetic quenching" as a mechanism of excitation of the lowest triplet state. In a long series of researches Terenin and Karyakin studied the intermolecular paramagnetic quenching by O_2 molecules (106, 107, 108, 109, 110) and NO molecules (111). Mainly anthraquinone derivatives were studied, both in the gaseous and in the adsorbed state. Karyakin and Kalenichenko (112) continued their efforts to induce triplet → singlet emission by intermolecular magnetic perturbation effects by adsorption of aminoanthraquinones on silica gel surfaces impregnated with paramagnetic ions, Cu^{++}. They observed an infrared luminescence which they believed to represent the triplet → singlet emission of the adsorbed molecule. Probably they had observed an intramolecular energy transfer between the π-electron levels of the aminoanthraquinones and the d-levels of the Cu^{++} ion; the reported emission was at 8800 A, which corresponds to the wavelength of the cupric absorption band. Such intramolecular energy transfers are known since the work of Weissman (113) on rare earth chelates; in the experiments of Karyakin and Kalenichenko adsorption probably is accompanied by chelations of the metal by the organic molecule adsorbed.

Bowen and co-workers also have carried out intermolecular quenching experiments, investigating fluorescence quenching in the gaseous state by both high-Z atom containing molecules, and paramagnetic molecules. Bowen and Metcalf (114) and Metcalf (115) reported preliminary studies of this sort, following earlier work by Bowen *et al*. Recently Stevens (116) has adduced a spin-orbital perturbation mechanism to explain high-Z and paramagnetic atom quenching. Bowen et al (117, 118) have reported further work on fluorescence quenching, with intercombinational interpretation.

Reid et al (57, 119,120) have investigated the light emission properties of both trinitrobenzene-aromatic hydrocarbon molecular complexes, as well as hydrocarbon-hydrocarbon complexes. The trinitrobenzene-aromatic hydrocarbon complexes yielded emission spectra closely resembling the triplet → singlet emission spectra of the parent aromatic hydrocarbon. Reid has proposed a mechanism to account for this behavior based on the idea that in the molecular complex the plane of symmetry of the hydrocarbons is destroyed, resulting in non-vanishing matrix elements for spin-orbital interaction as compared with the parent hydrocarbon. Orgel (121) and Sponer (122) have discussed some aspects of this work. The results of Reid et al are especially interesting since they illustrate that in aromatic hydrocarbons the intercombinational transition probability is sensitive to other effects than those due to field of high-Z and paramagnetic atoms.

INTERCOMBINATIONS IN PHOTOCHEMICAL AND CHEMICAL REACTION MECHANISMS

As an empirical science, photochemistry has been a field of active investigation paralleling the earliest investigations of spectroscopy. The application of spectroscopic theory to photochemistry has been fragmentary. Probably, the neglect of <u>intersystem crossing</u> information in photochemical researches has resulted in a delay in spectroscopic interpretation. Typifying some of the more recent photochemical investigations has been an emphasis on the rôle of triplet states and intercombinations in photochemical processes. In an earlier paper Calvin and Dorough (123) discussed a photoöxidation reaction with a possible triplet state intermediate. Recently, Seely and Calvin (124) have studied in detail a photoreduction reaction involving a triplet state intermediate. These researches deal with porphyrin-like molecules. Ashkinazi and Karpitskaya (125) have described photochemical investigations on Zn and Cu analogs of chlorophyll. Becker and Kasha (49, 50) have discussed the role of triplet states in the photosynthetic system. Beacom (126) has investigated photochemical reactions of transition metal complexes.

Bowen and Tanner (127) have published recent results om the photochemistry of anthracene. Livingston (128) has reviewed the primary act in photochemical reactions sensitized by polyatomic molecules. Fujimori (129) has described a comprehensive photochemical investigation which reviews general interpretations in various systems of biological importance, including photosynthesis. Norrish and Porter (130) discussed the production of triplet state molecules by photolytic techniques. Callear and Robb (131) described work on the mercury photosensitized decomposition of ethylene, in which the lowest triplet state of ethylene is described as an intermediate in its decomposition to acetylene and hydrogen. A valuable discussion of this process was conducted by Bauer, Kistiakowsky, Callear, Robb, Patrick, Ogg, Walsh, and Porter (132).

In chemical reaction theory, triplet states usually are not involved directly in thermally induced reactions, although there are some cases in which a particularly low energy barrier makes this possible. A situation of this sort prevails in the recent researches on <u>relative methyl affinity</u> (relative rate of addition of methyl radicals) by Szwarc <u>et al</u> (133,134,135,136,137). This work indicates that there is a linear relationship between the log of the methyl affinity and the energy of the lowest triplet state of the aromatic molecule, for some 14 aromatic hydrocarbons investigated. The transition state is taken to lie at the position of crossing of the two energy curves which apply to the interaction of the radical with the singlet ground state and the lowest triplet state. The experimental methyl affinity values of Szwarc et al have been corroborated by Hey and Williams (138), and Coulson (139) shows how theoretical values may be deduced. Levy, Newman, and Szwarc (137) have referred to unpublished work of Coulson and of Matsen which indicates that the correlation proposed by Szwarc et al may not be unique.

Isomerization reactions involving triplet state mechanisms have been studied quite extensively in the past, e.g., in the work of Magee, Shand, and Eyring (140). Recently Davies and Evans (141) have extended this field of research.

Magnetic catalysis of chemical reactions have been considered in many early researches, and we include a brief review here for its relation to the present problem. A theoretical study of the mode of interaction involved has been published by Wigner (142). An early research in this topic was published by Harman and Eyring (148), who considered the effect of paramagnetic substances on chemical reactions. Gelles and Pitzer (144, 145, 146) have studied the effect, of diamagnetic and paramagnetic ions of the same size and charge, on decarboxylation rates of malonic type acids. The paramagnetic ion Dy^{+++} yielded a 10% increase in rate of the reaction at the conditions used. A cis-trans isomerization is involved in the proposed reaction mechanism. McConnell (147) has proposed an alternative interpretation to the magnetic interaction ideas favored by earlier workers.

THERMOCHROMISM AND PHOTOCHROMISM

Recent researches on thermochromic and photochromic phenomena, i.e., the reversible production of colored substances upon heating and light excitation, have indicated some interesting relationships to the spectroscopic work reviewed above. On the other hand, the additional complexity of these topics has left their interpretation in a rather uncongealed state for the present.

Schönberg and Schutz (148) in an early paper reported on the thermochromism of bixanthylene. Recent researches by Schönberg et al (149, 150) and Mustafa and Sobhy (151) have resulted in the conclusion that substituents which hinder coplanarity of the two main parts of the molecule lead to an interference with thermochromic behavior. Grubb and Kistiakowsky (152) studied the thermochromism of bianthrones. Their interpretation indicates that the origin of color is due essentially to a triplet → triplet absorption, in which the lowest triplet is populated by thermal excitation from the ground singlet. Matlow (153) carried out an LCAO-MO calculation on bixanthylene and bianthrone, giving values of the energy differences between the singlet planar ground state molecule and the lowest triplet state perpendicular molecule; these results are in accord with the experimentally observed values. Nilsen and Fraenkel (154) carried out paramagnetic resonance absorption experiments on bianthrone, which serve to confirm the existence of paramagnetic molecules in solution, whose concentration is temperature dependent. At room temperatures it was found that the paramagnetic molecules were absent. In the solution experiments, the paramagnetic resonance absorption was reversible with temperature. In the crystalline state, an irreversible high temperature paramagnetic resonance absorption was noted.

Photochromic behavior has been reported by Hirshberg (155) in compounds related to bianthrone. The color is induced by ultraviolet illumination at low temperatures, and is spontaneously reversible in the dark at a rate depending on the temperature. Presumably, the colored species is not a product of photofragmentation, but is some electronic state or geometrical modification of the original molecule. The relation of this modification to that produced in thermochromism studies has become a topic of some controversy. Careful spectroscopic investigation should eventually decide the issue. In this section we omit all discussion of photochromism in which definite evidence of photofragmentation has been found, as in the work of Lewis and Lipkin (96) and other well known papers by Lewis. Bergmann and Fischer (156) and Hirshberg and Fischer (157) reported on thermochromism and photochromism of bianthrone compounds, and Hirshberg and Fischer (158) reported similar results in spiran compounds. Kortüm, Theilacker et al (159, 160) have taken issue with the interpretation made by Hirshberg and Fischer regarding the relation between the photochromic and thermochromic phenomena. Unfortunately, a somewhat mediaeval polemic has marred the discussion of this subject (161, 162).

The study of photochromism and thermochromism should be of exceptional interest to the spectroscopist because of the possibilities it offers for the study of low-lying electronic states of complex molecules. Extrapolating the paramagnetic resonance absorption results of Nilsen and Fraenkel (154) indicates these could be exceptionally low-lying triplet states. The results reported also indicate a pronounced effect of the solid medium on the potential function of rather cumbersome molecules, apparently hindering the free excitation of electronic states of contrasting geometry. It is quite possible that the full understanding of thermochromic and photochromic phenomena in appropriate complex molecules could serve as the shortest bridge between molecular spectroscopy and molecular chemistry.

LITERATURE CITED(3)

(1) Sponer, H. and Teller, E., Revs. Modern Phys., 13, 75 (1941).

(2) Wiedemann, E., Ann. Physik, 34, 446 (1888),

(3) Dewar, J., Roy. Inst. Proc. 12, 557 (1888); 14, 665 (1895). Proc. Roy. Soc. (London), 68, 360 (1901).

(4) Lewis, G. N., Lipkin, D., and Magel, T. T., J. Am. Chem. Soc., 63, 3005 (1941).

(5) Terenin, A., Acta Physicochimica U.R.S.S., 18, 210 (1943) (In English).

(6) Lewis, G. N., and Kasha, M., J. Am. Chem. Soc., 66, 2100 (1944).

(7) Kasha, M., Chem. Revs., 41, 401 (1947).

(8) Förster, Th., Naturwissenschaften, 36, 240 (1949).

(9) Kasha, M., Faraday Soc. Discussion No. 9, 14 (1950).

(10) Craig, D. P., Revs. Pure and Applied Chem. (Roy. Australian Chem. Inst.) 3, 207 (1953).

(11) Dirac, P. A. M., "Quantum Mechanics," Clarendon Press, Oxford, England, 1947, 3rd ed., p. 252-274.

(12) Mott, N. F., and Sneddon, I. N., "Wave Mechanics and Its Applications", Clarendon Press, Oxford, England, 1948, p. 296-350.

(13) Weissman, S. I., J. Chem. Phys., 18, 232 (1950).

(14) Mizushima, M., and Koide, S., J. Chem. Phys., 20, 765 (1952).

(15) Kramers, H. A., "Die Grundlagen der Quantentheorie," Akademische Verlagsgesellschaft M. B. H., Lepizig, 1938, p. 239 ff.

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(3) In a few cases the original paper was not available, and only Chemical Abstracts was consulted. In these cases, the Chemical Abstracts reference is added.

(16) McClure, D. S., J. Chem. Phys., 17, 665 (1949).

(17) McClure, D. S., J. Chem. Phys., 20, 682 (1952).

(18) Ross, I. G., "Spin-Orbital Coupling in Atoms and Molecules," Department of Chemistry, Florida State University, Tallahassee, 1956.

(19) Condon, E. U., and Shortley, G. H., "The Theory of Atomic Spectra," The University Press, Cambridge, England, 1951, p. 122 ff.

(20) McClure, D. S., J. Chem. Phys., 17, 905 (1949).

(21) Lewis, G. N., and Calvin, M., J. Am. Chem. Soc., 67, 1232 (1945).

(22) Lewis, G. N., Calvin, M., and Kasha, M., J. Chem. Phys. 17, 804 (1949).

(23) Fröhlich, P., Szalay, L., and Ször, P., Acta Chem. Phys. Univ. Szeged (Hungary), 2, 96 (1948).

(24) Yamamoto, D., J. Chem. Soc. Japan, 72, 693, 782 (1951). Bull. Chem. Soc. Japan, 24, 211, 214 (1951).

(25) Porter, G., Comment in Faraday Soc. Discussion No. 17, 229 (1954).

(26) Evans, D. F., Nature, 176, 777 (1955).

(27) McGlynn, S. P., Padhye, M. R., and Kasha, M., J. Chem. Phys., 23, 593 (1955).

(28) Beer, M., and Longuet-Higgins, H. C., J. Chem. Phys., 23, 1390 (1955).

(29) Teller, E., J. Phys. Chem., 41, 109 (1937).

(30) Duschinsky, F., Acta Physicochim. U.R.S.S., 7, 551 (1937) (In German).

(31) Davydov, A. S., Zhur. Eksptl. Teoret. Fiz. 24, 397 (1953). (Phys. Abstracts, 57, 1316 (No. 10377)(1954)).

(32) Pesteil, P., Ann. phys., 10, 128 (1955).

(33) Pesteil, P., and Pesteil, L., Compt. rend., 238, 75 (1954); 240, 1987 (1955).

(34) Pesteil, P., and Barbaron, M., Compt. rend., 238, 226, 1789 (1954); J. phys. radium, 15, 92 (1954).

(35) Barbaron, M., and Pesteil, P., Compt. rend., 238, 1400 (1954).

(36) Pesteil, P., Zmerli, A., and Barbaron, M., Compt. rend., 239, 255 (1954).

(37) Pesteil, P., Pesteil, L., and Kara, R., Compt. rend., 240, 960 (1955).

(38) Zmerli, A., and Pesteil, P., Compt. rend., 240, 2217 (1955).

(39) Pesteil, P., Zmerli, A., and Pesteil, L., Compt. rend., 241, 29 (1955).

(40) Shull, H., J. Chem. Phys., 17, 295 (1949).

(41) Dikun, P. P., and Sveshnikov, B. Ya., Doklady Akad. Nauk S.S.S.R. 65, 827 (1949) (Chem. Abstracts 44, 7659i (1950)).

(42) Roothaan, C. C. J., and Mulliken, R. S., J. Chem. Phys. 16, 118 (1948).

(43) Broude, V. L., Medvedev, V. S., and Prikhotko, A. F., Zhur. Eksptl. Teoret. Fiz., 21, 665 (1951). (Chem. Abstracts, 46, 8958e (1952)).

(44) Davydov, A. S., Zhur. Eksptl. Teoret. Fiz., 21, 673 (1951). (Chem. Abstracts, 46, 8959d (1952)).

(45) Ham. J. S., J. Chem. Phys., 21, 756 (1953).

(46) Bayliss, N. S., and Hulme, L., Australian J. Chem., 6, 257 (1953).

(47) Sidman, J. W., and McClure, D. S., J. Am. Chem. Soc., 77, 6461, 6471 (1955).

(43) Yuster, P., and Weissman, S. I., J. Chem. Phys., 17, 1182 (1949).

(49) Becker, R. S., and Kasha, M., "Luminescence Spectroscopy of Molecules and the Phytosynthetic System," in *The Luminescence of Biological Systems*, Frank H. Johnson, Editor, American Association for the Advancement of Science, Washington, D. C., 1955, p. 25.

(50) Becker, R. S., and Kasha, M., J. Am. Chem. Soc., 77, 3669 (1955).

(51) Porter, G., and Windsor, M. W., J. Chem. Phys., 21, 2088 (1953); Faraday Soc. Discussion No. 17, 178 (1954).

(52) Lewis, G. N., and Kasha, M., J. Am. Chem. Soc., 67, 994 (1945).

(53) Robinson, G. W., J. Chem. Phys., 22, 1147, 1384 (1954).

(54) Dikun, P. P., and Sveshnikov, B. Ya., Zhur. Eksptl. Teoret. Fiz., 19, 1000 (1949). (Chem. Abstracts, 44, 6727d (1950)).

(55) Dikun, P. P. and Sveshnikov, B. Ya., Doklady Akad. Nauk. S.S.S.R., 65, 637 (1949). (Chem. Abstracts, 44, 10517c (1950)).

(56) Ferguson, J., Iredale, T., and Taylor, J. A., J. Chem. Soc. (London), 1954, 3160.

(57) Reid, C., J. Chem. Phys., 20, 1212, 1214 (1952); J. Am. Chem. Soc., 76, 3264 (1954).

(58) Padhye, M. R., McGlynn, S. P., and Kasha, M., Symposium on Molecular Structure and Spectra, Ohio State University, June 1954. J. Chem. Phys., ~~(in press).~~ 24, 588 (1956).

(59) McGlynn, S. P., Padhye, M. R., and Kasha, M., J. Chem. Phys., 23, 593 (1955).

(60) Ilina, A. A., and Shpolskii, E. V., Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz., 15, 585 (1951). (Chem. Abstracts, 46, 8973d (1952).

(61) Bowen, E. J., and Brocklehurst, B., J. Chem. Soc. (London), 1954, 3875.

(62) Neporent, B. S., and Inyushin, A. I., Doklady Akad. Nauk. S.S.S.R., 98, 197 (1954). (Chem. Abstracts, 49, 12970d (1955)).

(63) Livingston, R., J. Am. Chem. Soc., 77, 2179 (1955).

(64) Witt, H. T., Z. physik. Chem. (Frankfurt, N.F.), 4, 120 (1955).

(65) Kaskan, W. E., and Duncan, A.B.F., J. Chem. Phys., 18, 427 (1950).

(66) Sveshnikov, B. Ya., and Petrov, A. A., Doklady Akad. Nauk S.S.S.R., 71, 461 (1950). (Chem. Abstracts, 44, 5217g (1950)).

(67) Dikun, P. P., Petrov, A. A., and Sveshnikov, B. Ya., Zhur. Eksptl. Teoret. Fiz., 21, 150 (1951). (Chem. Abstracts, 45, 8357i (1951)).

(68) Pyatnitskii, B. A., Izvest. Akad. Nauk S.S.S.R., Ser. Fiz., 15, 597 (1951). (Chem. Abstracts 46, 8972i (1952)).

(69) Craig, D. P., and Ross, I. G., J. Chem. Soc. (London), 1954, 1589.

(70) Porter, G., and Wright, F. J., Trans. Faraday Soc., 51, 1205 (1955).

(71) Skarsvåg, K., Rev. Sci. Inst., 26, 397 (1955).

(72) van Roggen, A., and Vroom, R. A., J. Sci. Instruments, 32, 180 (1955).

(73) Kato, S., and Koizumi, M., Bull. Chem. Soc. Japan, 27, 189 (1954).

(74) Kato, S., Kimura, K., and Koizumi, M., J. Chem. Soc. Japan, (Pure Chemistry Section), 76, 262 (1955).

(75) Gilmore, E. H., Gibson, G. E., and McClure, D. S., J. Chem. Phys., 20, 829 (1952); 23, 399 (1955).

(76) King, G. W., and Van Vleck, J. H., Phys. Rev., 56, 464 (1939).

(77) Barnes, R. G., Bray, P. J., and Harrick, N. J., Phys. Rev., 91, 475 (A) (1953).

(78) Herman, V. L. (German, V. L.), Compt. rend. acad. Sci. U.R.S.S., 48, 243 (1945). (In English).

(79) Kovner, M. A. and Sverdlov, L. M., Doklady Akad. Nauk S.S.S.R., 59, 1129 (1948). (Translated by H. Shull, Dept. Chemistry, Indiana University, Bloomington, Indiana).

(80) Longuet-Higgins, H. C., and Pople, J. A., Proc. Phys. Soc. (London), A68, 591 (1955).

(81) Longuet-Higgins, H. C., and Murrell, J. N., Proc. Phys. Soc. (London), 68, 601 (1955).

(82) Merrifield, R. E., J. Chem. Phys., 23, 402 (1955).

(83) McClure, D. S., Blake, N. W., and Hanst, P. L., J. Chem. Phys., 22, 255 (1954).

(84) Sklar, A. L., J. Chem. Phys., 5, 669 (1937).

(85) Pitts, A. C., J. Chem. Phys., 18, 1416 (1950).

(86) Shibata, K., Kushida, H., and Mori, S., Proc. Phys. Soc. Japan 6, 156 (1951); Bull. Chem. Soc. Japan, 24, 188 (1951).

(87) Cheshko, F. F., J. Phys. Chem. (U.S.S.R.), 27, 157 (1953). English translation available from Spectroscopy Laboratory, Dept. of Chemistry, Florida State University, Tallahassee, Florida.

(88) Reid, C., J. Chem. Phys., 18, 1673 (1950).

(89) Brealey, G. J., J. Chem. Phys., ~~(in press)~~, 24, 571 (1956).

(90) Snow, C. P., and Allsopp, C. B., Trans. Faraday Soc., 30, 93 (1934).

(91) Moffitt, W. E., Proc. Phys. Soc. (London), 63, 1292 (1950).

(92) Carr, E. P., and Stücklen, H., J. Chem. Phys., 4, 760 (1936).

(93) Pickett, L. W., Muntz, M., and McPherson, E. M., J. Am. Chem. Soc., 73, 4862 (1951).

(94) Potts, W. J., Jr., J. Chem. Phys., 23, 65 (1955).

(95) Kasha, M.,J. Chem. Phys., 20, 71 (1952).

(96) Lewis, G. N., and Lipkin, D., J. Am. Chem. Soc., 64, 2801 (1942).

(97) Clar, E., J. Chem. Soc. (London), 1950, 1823.

(98) Sveshnikov, B. Ya., and Dikun, P. P., Doklady Akad. Nauk S.S.S.R., 59, 37 (1948). (Chem. Abstracts, 42, 5776f (1948)).

(99) McClure, D. S., J. Chem. Phys., 19, 670 (1951).

(100) McClure, D. S., and Hanst, P. L., J. Chem. Phys., 23, 1772 (1955).

(101) Ross, I. G., J. Optical Soc. Am., 44, 40 (1954).

(102) McGlynn, S. P., and Kasha, M., Symposium on Molecular Structure and Spectra, Ohio State University, June 1954. (In preparation for publication. Cf. McGlynn, S. P., Dissertation, Florida State University, Tallahassee, Florida, January 1956).

(103) Dyck, R. H., and McClure, D. S., Unpublished work (Department of Chemistry, University of California, Berkeley, California), August 1955.

(104) Padhye, M. R., and Desai, S. R., Proc. Phys. Soc. (London), 65A, 298 (1952).

(105) Ermolaev, V. L., and Terenin, A. N., Akad. Nauk S.S.S.R., Pamyati S. I. Vavilova (S. I. Vavilov Memorial Volume, Academy of Sciences U.S.S.R.), 1952, 137. (Chem. Abstracts, 47, 7901h (1953)).

(106) Karyakin, A. V., and Terenin, A. N., Izvest. Akad. Nauk S.S.S.R., Ser. Fiz., 13, 9 (1949) (Chem. Abstracts 43, 7829h (1949)).

(107) Karyakin, A. V., and Galanin, M. D., Doklady Akad. Nauk S.S.S.R., 66, 37 (1949). (Chem. Abstracts, 43, 6085d (1949)).

(108) Karyakin, A. V., Izvest. Akad. Nauk S.S.S.R., Ser. Fiz., 15, 556 (1951). (Chem. Abstracts, 46, 8971h (1952).

(109) Karyakin, A. V., and Kalenichenko, Ya. I., Zhur. Fiz. Khim., 26, 103 (1952). (Chem. Abstracts, 47, 4747h (1953)).

(110) Karyakin, A. V., and Terenin, A. N., Doklady Akad. Nauk S.S.S.R., 97, 479 (1954). (Chem. Abstracts, 49, 12970i (1955)).

(111) Karyakin, A. V., Terenin, A. N., and Kalenichenko, Ya. I., Doklady Akad. Nauk S.S.S.R., 67, 305 (1949). (Chem. Abstracts, 43, 7828d (1949)).

(112) Karyakin, A. V., and Kalenichenko, Ya. I., Doklady Akad. Nauk S.S.S.R., 66, 191 (1949). (Chem. Abstracts, 43, 6085h (1949).

(113) Weissman, S. I., J. Chem. Phys., 10, 214 (1942).

(114) Bowen, E. J., and Metcalf, W. S., Proc. Roy. Soc., A 206, 437 (1951).

(115) Metcalf, W. S., J. Chem. Soc. (London), 1954, 2485.

(116) Stevens, B., Trans. Faraday Soc., 51, 610 (1955).

(117) Bowen, E. J., Trans. Faraday Soc., 50, 97 (1954).

(118) Bowen, E. J., and West, K., J. Chem. Soc. (London), 1955, 4394.

(119) Reid, C., J. Chem. Phys., 22, 252 (1954).

(120) Moodie, M. M., and Reid, C., J. Chem. Phys., 20, 1510 (1952); 22, 1126 (1954).

(121) Orgel, L., Quart. Revs. Chem. Soc. (London), 8, 422 (1954).

(122) Sponer, H., Electronic Spectroscopy, Ann. Rev. Phys. Chem., 6, 193 (1955).

(123) Calvin, M., and Dorough, G. D., J. Am. Chem. Soc., 70, 699 (1948).

(124) Seeley, G. R., and Calvin, M., J. Chem. Phys., 23, 1068 (1955).

(125) Ashkinazi, M. S., and Karpitskaya, V. E., Ukrain. Khim. Zhur., 20, 20 (1954) (In Russian). (Chem. Abstracts, 49, 1436d (1955)).

(126) Beacom, S. E. (Univ. Connecticut, Storrs), Dissert. Abstr. 15, 31 (1955). (Chem. Abstracts, 49, 5132d (1955)).

(127) Bowen, E. J., and Tanner, D. W., Trans. Faraday Soc., 51, 575 (1955).

(128) Livingston, R., Record Chem. Progr. (Kresge-Hooker Sci. Lib.), 16, (No. 1), 13 (1955). (Chem. Abstracts 49, 15443b (1955)).

(129) Fujimori, E., Report Inst. Ind. Sci. (Univ. Tokyo), 4, 93-151 (1955).

(130) Norrish, R. G. W., and Porter, G., Faraday Soc. Discussion, No. 17, 40 (1954).

(131) Callear, A. B., and Robb, J. C., Faraday Soc. Discussion, No. 17, 21 (1954).

(132) Bauer, S. H., Kistiakowsky, G. B., Callear, A. B., Robb, J. C., Patrick, C. R., Ogg, R. A., Walsh, A. D., and Porter, G., Faraday Soc. Discussion, No. 17, pp. 91-95 (1954).

(133) Levy, M., and Szwarc, M., J. Chem. Phys., 22, 1621 (1954); J. Am. Chem. Soc., 77, 1949 (1955).

(134) Szwarc, M., J. Chem. Phys., 23, 204 (1955).

(135) Rembaum, A., and Szwarc, M., J. Am. Chem. Soc., 77, 3486, 4468 (1955).

(136) Leavitt, F., Levy, M., Szwarc, M., and Stannett, V., J. Am. Chem. Soc., 77, 5493 (1955).

(137) Levy, M., Newman, M. S., and Szwarc, M., J. Am. Chem. Soc., 77, 4225 (1955).

(138) Hey, D. H., and Williams, G. H., J. Chem. Phys., 23, 757 (1955).

(139) Coulson, C. A., J. Chem. Soc. (London), 1955, 1435.

(140) Magee, J. L., Shand, W., Jr., and Eyring, H., J. Am. Chem. Soc., 63, 677 (1941).

(141) Davies, M., and Evans, F. P., Trans. Faraday Soc., 51, 1506 (1955).

(142) Wigner, E., Z. physik. Chem., B23, 28 (1933).

(143) Harman, R. A., and Eyring, H., J. Chem. Phys., 10, 557 (1942).

(144) Gelles, E., and Pitzer, K. S., J. Am. Chem. Soc., 75, 5132 (1953).

(145) Gelles, E., J. Am. Chem. Soc., 75, 6199 (1953).

(146) Gelles, E., and Pitzer, K. S., J. Am. Chem. Soc., 77, 1974 (1955).

(147) McConnell, H., J. Chem. Phys., 20, 1043 (1952).

(148) Schönberg, A., and Schutz, O., Ber. deutsch. chem. Ges. 61, 478 (1928).

(149) Schönberg, A., Mustafa, A., and Sobhy, M. E. E., J. Am. Chem. Soc., 75, 3377 (1953).

(150) Schönberg, A., Mustafa, A., and Asker, W., J. Am. Chem. Soc., 76, 4134 (1954).

(151) Mustafa, A., and Sobhy, M. E. E., J. Am. Chem. Soc., 77, 5124 (1955).

(152) Grubb, W. T., and Kistiakowsky, G. B., J. Am. Chem. Soc., 72, 419 (1950).

(153) Matlow, S. L., J. Chem. Phys., 23, 152 (1955).

(154) Nilsen, W. G., and Fraenkel, G. K. (published as Nielsen and Fraenkel. Cf. Errata: J. Chem. Phys., 21, 2232 (1953)) J. Chem. Phys., 21, 1619 (1953).

(155) Hirshberg, Y., Compt. rend., 231, 903 (1950).

(156) Bergmann, E. D., and Fischer, E., Bull. soc. chim. France, 17, 1084 (1950).

(157) Hirshberg, Y., and Fischer, E., J. Chem. Soc. (London), 1953, 629.

(158) Hirshberg, Y., and Fischer, E., J. Chem. Soc. (London), 1952, 4522; Hirshberg, Y., Frei, E. H., and Fischer, E., J. Chem. Soc. (London), 1953, 2184; 1954, 297, 3129; J. Chem. Phys., 21, 1619 (1953).

(159) Kortüm, G., Theilacker, W., Zeininger, H., and Elliehausen, H., Chem. Ber., 86, 294 (1953).

(160) Theilacker, W., Kortüm, G., and Friedheim, G., Chem. Ber., 83, 508 (1950).

(161) Hirshberg, Y., and Fischer, E., J. Chem. Phys., 23, 1723 (1955).

(162) Kortüm, G., Theilacker, W., and Braun, V., J. Chem. Phys., 23, 1723 (1955).

Interpretation of the Lowest Frequency Electronic Absorption Bands of Inorganic Molecules of Type $XO_y^{z(-)}$ as $n \rightarrow \pi^*$ Transitions[1]

Sean P. McGlynn and Michael Kasha
Department of Chemistry, Florida State University
Tallahassee, Florida

The lowest electronic transitions of simple molecules of type $XO_y^{z(-)}$ were studied theoretically. In the formula, O is an oxygen, or a sulfur atom; X is generally a non-metallic, or a transition metal atom; $y = 1, 2, 3, 4$; $z = 0, 1, 2, 3$.

The procedure was: (a) Group-orbitals for the O-atoms were formulated as LCAO's appropriate to the molecular point group. (b) The total MO's were constructed from the O group-orbitals and the central atom AO's. In doing this, use was made of the criterion of maximum overlapping of wavefunctions[2,3], and the non-crossing rule,[4] and by consideration of the "energies" of the isolated group-orbitals.[5,6] Simultaneously, the total MO's were graded in energy. (c) Finally, the single configuration approximation to the state functions was used. From this, symmetries and relative energies of the various molecular states were derived.

The following table summarizes the results. Column five gives the selection rule (A, allowed; F, forbidden) for the lowest frequency transition. The last column gives the experimental absorption intensity (S, strong, molar absorption coefficient > 1000; W, weak, molar absorption coefficient < 50).

There is agreement between the predicted selection rules and the observed intensities, in spite of the approximations used. In most cases the transition is of n $\rightarrow \pi^*$ type (this nomenclature here refers to the AO origins of the MO's, and is merely a convenient codification, having its usual significance only in planar molecules). This result is physically reasonable. Those MO's which are mainly non-bonding (n) are relatively unaffected in energy during the process of formation from the AO's. Consequently, the highest filled orbitals in the molecule are more likely to be of (n) type than bonding (π, σ) type. The lowest energy transition will be expected to be from a "non-bonding" orbital to a pi-antibonding orbital. In all the cases labelled n $\rightarrow \pi^*$ in Table I, the n-orbitals are the non-bonding MO's which are appropriate linear combinations of $2p\pi$ oxygen (or sometimes, sulfur) AO's.

To a first approximation, the n-orbital energy should be independent of the central atom. Conversely, the energy of the antibonding (π) MO will be a function of the electronegativity of the central atom. Thus, the order of the electronegativities (Mulliken scale[7]) of the central atom should be the reverse order of the frequencies for the lowest n $\rightarrow \pi^*$ transitions. The theoretical basis for this simple correlation is found in the semi-empirical treatment of n $\rightarrow \pi^*$ transitions by Goodman and Shull.[8] The predicted order of transition frequency (D_{3h} group) is, e.g., $NO_3 < NO_3^- \approx SO_3 < SO_3^= < SiO_3$, which is the same as the experimental order.

Our study is being extended to the $C_{\infty v}$ and $D_{\infty h}$ group, including VO^{++}, UO_2^{++}, and related molecules. Preliminary considerations for UO_2^{++} indicate that the lowest frequency molecular transition is $n \rightarrow \pi^*$ (${}^1\Sigma_g^+ \rightarrow {}^1\Delta_u$) and is symmetry forbidden (weak absorption band observed). The participation of f-electrons in this case is being investigated.

In our full report to follow shortly, we shall present the details of our study and a correlation with the voluminous and largely uninterpreted literature which exists on the spectra of these molecules. Although our treatment is a fundamentally primitive one, we believe it offers some systematization of a field which is at present largely neglected. It is our hope that this preliminary study will draw additional attention of theoretical and experimental spectroscopists to this group of simple molecules.

(1) This research was done under a contract between the Office of Scientific Research, ARDC, and the Florida State University.

(2) L. Pauling, J. Am. Chem. Soc., 53, 1365, 3225 (1931).

(3) J. C. Slater, Phys. Rev., 38, 1109 (1931).

(4) Cf., e.g., C. A. Coulson, "Valence", Clarendon Press, Oxford, 1951, pp. 61-65.

(5) R. S. Mulliken, Rev. Modern Phys., 14, 204 (1942).

(6) A. D. Walsh, J. Chem. Soc. (London), 1953, 2260-2329.

(7) R. S. Mulliken, J. Chem. Phys., 2, 782 (1934); *ibid.*, 3, 573 (1935).

(8) L. Goodman and H. Shull, J. Chem. Phys., 22, 1138 (1954).

Table 1

Summary of Results on Lowest Frequency Electronic Transitions in Simple Inorganic Molecules

Symmetry Group	Molecules	Number of Valence Electrons	Transition	Selection Rule	Observed Intensity[a]
T_d	$AsO_4^{\equiv}$, $CrO_4^{=}$, MnO_4^{-}, ($MoO_4^{=}$), OsO_4, ReO_4^{-}, RuO_4, $UO_4^{=}$, $VO_4^{\equiv}$, $WO_4^{=}$	24[b]	$n \rightarrow \pi^*$ $\left\{ \begin{array}{l} ^1A_1 \nrightarrow {}^1A_2 \\ ^1A_1 \nrightarrow {}^1E \\ ^1A_1 \nrightarrow {}^1T_1 \\ ^1A_1 \rightarrow {}^1T_2 \end{array} \right\}$ b	A[c]	S
T_d	$CS_4^{=}$	22	$\pi \rightarrow n, n \rightarrow \pi^*$ $\{ ^3A_1 \rightarrow {}^3T_2 \}$ c,d	A	S
T_d	RuO_4^{-}	25	$n \rightarrow \pi^*$, $\pi^* - \pi^*$. $\{ ^2T_2 \rightarrow {}^2A_1 \}$ c,d	A	S
T_d	$RuO_4^{=}$	26	$n \rightarrow \pi^*$, $\pi^* \rightarrow \pi^*$ $\{ ^3A_1 \rightarrow {}^3T_2 \}$ c,d	A	S
D_{3h}	NO_3^{-}, ($CO_3^{=}$), $CS_3^{=}$, ($SiO_3^{=}$), SO_3	24[e,f]	$n \rightarrow \pi^*$ $\{ ^1A_1' \nrightarrow {}^1A_1'' \}$	F	W
D_{3h}	NO_3	23[g]	$n \rightarrow \pi^*$ $\{ ^2A_2' \rightarrow {}^2A_2'' \}$	A	S
C_{3v}	BrO_3^{-}, IO_3^{-}, $SeO_3^{=}$, $SO_3^{=}$	26	$n \rightarrow \pi^*$ $\{ ^1A_1 \nrightarrow {}^1A_2 \}$	F	W

Symmetry Group	Molecules	Number of Valence Electrons	Transition	Selection Rule	Observed Intensity[a]
C_{2v}	NO_2^-	18[h,i]	$n \longrightarrow \pi^*$ $\left\{ {}^1A_1 \not\longrightarrow {}^1A_2 \right\}$	F	W
C_{2v}	ClO_2	19[j,k,l]	$n \longrightarrow \pi^*$ $\left\{ {}^2A_1 \longrightarrow {}^2B_2 \right\}$	A	S
C_{2v}	ClO_2^-	20	$n \longrightarrow \pi^*$ $\left\{ {}^1A_1 \longrightarrow {}^1B_1 \right\}$	A	S

(a) In the case of uncertain data, e.g., where the absorption band appears as a shoulder on a stronger band, the molecular species is enclosed in parentheses.

(b) M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20, 837 (1952), gave a semi-empirical calculation of the MO energies for MnO_4^- and $CrO_4^=$ (also ClO_4^-). Our assignment coincides with theirs. See footnote (c).

(c) In the single configuration approximation (also assumed by Wolfsberg and Helmholtz) all states arising from the same configuration are, of course, energy degenerate. In the 24 valence electron T_d case, the allowed component of the configurational transition is taken to determine the selection rule.

(d) This is one of the allowed components of the configurational transition.

(e) H. McConnell, J. Chem. Phys., 20, 700 (1952) suggested that the lowest frequency absorption bands in NO_3^-, $CO_3^=$, $CS_3^=$ might be $n \rightarrow \pi^*$ transitions.

(f) Walsh (cf. Reference 6) has treated $NO_3^=$, CO_3^-, and SO_3 with results which coincide with ours.

(g) Walsh (cf. Reference 6) has treated NO_3 giving the (multiplicity mis-labelled) transition ${}^1A_2' \longrightarrow {}^1E'$ (allowed).

(h) Walsh (cf. Reference 6) has treated the 18 valence electron C_{2v} molecule SO_2 giving ${}^1A_1 \rightarrow {}^1B_1$ (allowed) as the lowest frequency transition.

(i) W. G. Trawick and W. H. Eberhardt, J. Chem. Phys., 22, 1462 (1954) concluded from polarization studies of single crystals of sodium nitrite that the lowest frequency transition was of $n \rightarrow \pi^*$ type, with the n-orbital identified as a nitrogen atom AO.

(j) Walsh (cf. Reference 6) has treated ClO_2 giving the lowest frequency transition as $^2B_1 \rightarrow {}^2A_2$ (allowed).

(k) Our assignment agrees with the requirements set by the detailed spectroscopic studies on the 21,016 cm^{-1} band of ClO_2 made by J. B. Coon, J. Chem. Phys., 14, 665 (1946).

(l) R. S. Mulliken (cf. Reference 5) has treated the triatomic molecules in detail; however, although his results apply to the ionic species, he did not consider them explicitly.

ON THE APPLICATION OF THE MOLECULAR ORBITAL METHOD TO THE SPECTRA OF SUBSTITUTED AROMATIC HYDROCARBONS[‡]

Lionel Goodman*

Department of Chemistry, Florida State University,
Tallahassee, Florida

Ian G. Ross

Department of Physical Chemistry, University of Sydney,
New South Wales, Australia

and

Harrison Shull*

Department of Chemistry and Institute for Atomic Research,
Iowa State College, Ames, Iowa

[‡] Supported in part by the Ames Laboratory of the Atomic Energy Commission and by a contract between the Office of Scientific Research, Air Research and Development Command and the Florida State University.

*Present addresses: L. G., The Pennsylvania State University, State College, Pennsylvania; H. S., The University of Indiana, Bloomington, Indiana.

(Abstract) The MO theory of the spectra of substituted hydrocarbons is presented in rather general terms, with careful emphasis on the precautions to be observed in introducing the inevitable approximations. Previous treatments of the problem, notably by Sklar, Herzfeld, and Matsen, are then examined. Satisfactory calculations of energy-level shifts are considered to require closer attention to the definition and dissection of the perturbed Hamiltonian. The most interesting intensity effects concern the enhancement of weak transitions: here earlier treatments do not satisfy the requirements of orthonormality of the perturbed MOs, and unjustifiably neglect interactions with intense transitions. The consequences of neglecting overlap in these calculations are discussed in an appendix.

INTRODUCTION

In the course of independent work[1,2], the present authors have had occasion to examine in detail the papers of Sklar[3,4] on the intensities of substituted benzenes and of Herzfeld[5] on the corresponding energy shifts. The results of these interesting papers have been widely quoted and used (see e.g., the recent papers of Nagakura and Baba[6] and of Ramamurty[7]). In this paper we propose to examine the same problem from more straightforward procedures and to compare critically the results thus obtained with those of the previous authors.

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(1) L. Goodman and H. Shull, J. Chem. Phys. 23, 33 (1955).
(2) I. G. Ross, Thesis, London (1952).

(3) A. L. Sklar, J. Chem. Phys. 7, 986 (1939).
(4) A. L. Sklar, J. Chem. Phys. 10, 135 (1942).

(5) K. F. Herzfeld, Chem. Rev. 41, 233 (1947).

(6) S. Nagakura and H. Baba, J. Am. Chem. Soc. 74, 5693 (1952).

(7) S. Ramamurty, Indian J. Phys. 28, 325 (1954).

Hydrocarbon π-electron Energies

Consider a parent hydrocarbon of N carbon atoms, with each of which is associated a π-type atomic orbital (AO), substituted by a single substituent, -X, which has a π AO interacting with the π-electron system of the hydrocarbon. If H represents the effective π one-electron Hamiltonian of the substituted compound, Φ_x the substituent π AO and Φ_j the unperturbed MO eigenfunctions of the parent hydrocarbon, then the orbital energies ϵ appropriate to the substituted compound can be derived by generalized perturbation theory; in the approximation analogous to second-order perturbation theory[8] these are:

$$\epsilon_j = H_{jj} + \sum_{i=1}^{N}{}' \frac{(H_{ji})^2}{(H_{jj}-H_{ii}} - \frac{(H_{jx}-S_{jx}H_{jj})^2}{(H_{xx}-H_{jj})} \qquad (1a)$$

$$\epsilon_x = H_{xx} + \sum_{i=1}^{N} \frac{(H_{xi}-S_{xi}H_{xx})^2}{(H_{xx}-H_{ii})} \qquad (1b)$$

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(8) See, for example, Pauling and Wilson, 'Introduction to Quantum Mechanics', McGraw-Hill, P. 195.

in which $H_{xx} = \int \bar{\phi}_x H \phi_x dv$; $H_{ji} = \int \bar{\phi}_j H \phi_i dv$; $S_{jx} = \int \bar{\phi}_j \bar{\phi}_x dv$; $H_{jx} = \int \bar{\phi}_j H \bar{\phi}_x dv$ and the prime on the summation indicates omission of the term with zero denominator. It is convenient to introduce the Sklar-Herzfeld migration coefficient, λ_i, defined by

$$\lambda_i = (H_{xi} - S_{xi} H_{xx})/(H_{xx} - H_{ii}), \tag{2}$$

which is a measure of the extent of interaction between the ring and substituent. We shall also approximate by neglecting the matrix elements H_{ji}, which implies neglect of the inductive effect of the substituent upon the parent hydrocarbon[9].

Eqs. (1a) and (1b) are then written very simply:

$$\epsilon_j = H_{jj} - (\lambda_j + S_{jx})^2 (H_{xx} - H_{jj}) \tag{3a}$$

$$\epsilon_x = H_{xx} + \sum_{i=1}^{N} \lambda_i^2 (H_{xx} - H_{ii}). \tag{3b}$$

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(9) Expansion of the integral H_{ij} in terms of AO's yields:

$$H_{ij} = \sum_{u=1}^{N} c_{ju} c_{iu} \int \phi_u H' \phi_u dv + \sum_{u} \sum_{w} c_{ju} \, c_{iw} \int \phi_u H' \phi_w dv.$$

The first type of integral represents the increment in the Coulomb integral of the uth carbon atom, whereas the second is the analogous increment in the bond exchange integral between atoms u and w due to the field of the substituent. These are just the terms that are conventionally attributed to the 'inductive effect' of the substituent. We have shown elsewhere (ref. 1) that Sklar's argument for neglect of the inductive effect (ref. 3) based on the similarity of the observed spectrum for anilinium ion with that of benzene is fallacious and leads to considerable errors when applied to substituents which both resonate with and exert an inductive effect upon the ring simultaneously. In this paper, we are not concerned with quantitative details and consequently ignore the inductive effect for brevity and convenience.

We obtain the energy of the ground state in which ψ_x and each of the occupied ψ_j contain two electrons by simple summation over the orbital energies:

$$E = 2 \sum_j^{o} \epsilon_j^{o} + 2 \epsilon_x = 2 \sum_j^{o} H_{jj} + 2H_{xx} - 2 \sum_j^{o} (\lambda_j + S_{jx})^2 (H_{xx} - H_{jj}) + 2 \sum_{i=1}^{N} \lambda_i^2 (H_{xx} - H_{ii}) \qquad (4)$$

In these and subsequent equations, a superscript ^{o} on the summation indicates summation only over occupied orbitals, ^{v} summation over vacant orbitals.

Eqs. (3) are generalizations of Matsen's[10] eqs. (4) and (5), and eq. (4) is a generalization of the expression for the energy obtainable by Herzfeld's[5] approach and assumptions, namely:

$$E = 2 \sum_j^{o} H_{jj} + 2H_{xx} + \sum_{i=1}^{N_v} \lambda_i^2 (H_{xx} - H_{ii}). \qquad (5)$$

Eq. (4) reduces to eq. (5) if one omits S_{jx}. If one can bring oneself to accept (!) the validity of all these assumptions, then evaluation of the migration coefficients, λ_i, and the unperturbed energy differences, $H_{xx} - H_{ii}$ determines the energy shift of the spectrum of any hydrocarbon as a result of charge migration from the substituent. The Sklar-Herzfeld procedure now divides the total Hamiltonian, H, of the substituted compound into a sum of two terms, $H^o + H^x$, so chosen that H^o has

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[10] F. A. Matsen, J. Am. Chem. Soc. 72, 5243 (1950).

as its eigenfunctions the Φ_j of the unperturbed parent hydrocarbon. H^x is then interpreted as a perturbation due to the substituent and is replaced by the potential of the neutral substituent atom less that of a missing π-electron. By utilizing this operator, it is then possible to calculate H_{ii} and H_{ix} in a straightforward manner. H_{xx} is evaluated experimentally as the negative of the ionization potential of CH_3X.

We have shown elsewhere[1], however, that a very important part of the perturbation of the parent hydrocarbon by the substituent arises from the change in the electron repulsion integrals over the parent hydrocarbon orbitals as a result of the change in the latter. It is a consequence of the sensitivity of these integrals to the perturbed charge distribution that this effect must be included either in H^o or in H^x if the Hamiltonian is to be divided in this fashion. Thus, if H^o is chosen as above, then H^x bears no necessary direct relationship to the ionization potential of -X. One could equally well have chosen H^x to agree with the ionization potential of -X, but then the integrals over H^o would, in general, bear no simple relation to corresponding integrals over the unperturbed hydrocarbon wave-functions and the unperturbed Hamiltonian. A further criticism of the procedure of <u>theoretically</u> calculating transition energy shifts by formulas which just involve simple differences of orbital energies is that a tacit assumption is made about the Hamiltonian. Namely, that such a procedure corresponds to a median Hamiltonian[1,11], $\frac{1}{2}(\bar{H} + F)$, where F is the Hartree-Foch one electron Hamiltonian operator and $\bar{H}$ is a core part, containing the kinetic energy and nuclear framework operators. For certain excited states a major error can be incurred by theoretical calculation with the incorrect operator[12]. This is especially true for calculation and comparison of energies of excited states with different nodal properties. It is possible to evaluate H_{ix} and $H_{xx} - H_{ii}$ with more validity either by an empirical procedure, or by one involving a self-consistent-field approach. For further work along more rigorous lines, the reader is referred to ref. 1.

Intensities in the π-electron Spectra of Substituted Benzenes

In turning now to a consideration of spectral intensities, we particularize the treatment to the specific case of benzene, leaving a discussion of some aspects of the wider problem to the appendix. Moreover, we shall concentrate especially on

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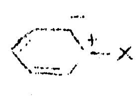
(11) R. G. Parr, J. Chem. Phys. 19, 799 (1951).

(12) L. Goodman and H. Shull, paper presented at The Symposium for Molecular Structure and Spectroscopy, at The Ohio State University, Columbus, Ohio, June 1954.

transitions stemming from the forbidden B_{2u}-A_{1g} band (occurring at 2600 Å) of the parent molecule.

This transition in a monosubstituted benzene, C_6H_5X, acquires the symmetry designation B_1-A_1 of group C_{2v}, and is now formally allowed. The forbiddenness of the parent transition, and the direction of polarization, namely, at right angles to the C-X bond, are special features of this particular problem, for they conspire to make the final intensity especially weak, which in turn should favor the validity of a straightforward perturbation treatment. Experimental support for the latter expectation is afforded by the fact[13] that in polysubstituted compounds the transition moment is very closely the vector sum of the transition moments of the appropriate monosubstituted benzenes, for a large class of substituents.

The special features of this particular problem are most easily understood in terms of the valence bond theory, to which we turn for a moment. In the VB theory, only polar bond-structures can give rise to contributions to a transition moment. Hence we need consider only the following types of structure here: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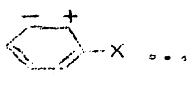
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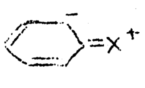
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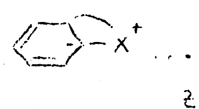
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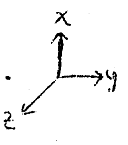

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(13) J. R. Platt, J. Chem. Phys. 19, 263 (1951).

State wave-functions will each contain contributions from structures of these and kindred higher-energy kinds, and the weights of structures like P,Q, ... in which the substituent does not formally participate, will differ from the weights of the corresponding structures in benzene itself. This last of course is simply the formal expression of that part of the inductive effect due to the π-electron system. If overlap is neglected, the transition moment integral emerges as a weighted sum of the dipole moments of structures P,Q,...,U,V,... individually. It is at once seen that the *y* components of these dipole moments are predominantly larger than the corresponding *x*-components, and indeed that the latter vanish in a number of important structures, such as Q and V.

Now in benzene the intensity of a forbidden transition can be regarded as having been stolen from allowed transitions, and for transitions whose lower level is the ground state, the major source of intensity will be the known $E_{1u}-A_{1g}$ transition (1850 Å). Consequently, in the expanded expression for the transition moment of the 2600 Å absorption in C_6H_5X, those terms involving structures P,Q,... can be attributed directly to stealing from the intensities of allowed transitions in benzene itself, especially the transition noted above.

Terms involving structures U,V,... are peculiar to a perturbation by an interacting substituent. Now, when the transition is polarized in the x-direction, only structures like U contribute to the intensity, whereas both U and V have to be reckoned with for y-polarized transitions. Having regard to the general pattern of the magnitudes of the dipole moment components, noted above, it is seen that the intensity of a transition which becomes y-polarized (such as B_{1u}-A_{1g}) will be more enhanced by substitution than the intensity of one which becomes x-polarized.

The algebra of the MO method does not allow the same clean dissection of the final transition moment into two parts with such clear physical meanings. However, there is a formal similarity. Namely, the transition moment comes out as a sum of (a) terms allowing for the interaction of the individual benzene MOs with the appropriate AO of the substituent ("migration moment"), and (b) a term which takes account of the mixture of the perturbed B_{2u} state with the proper component of the perturbed E_{1u} state, the degeneracy of which has of course already been removed. An intuitive understanding of the terms (a) is not aided by the fact that they only creep in via the normalizing coefficients of certain perturbed MO wave-functions, in the B_{2u}-A_{1g} case.

Since a significant part of the total intensity can be ascribed to stealing from the 1850 Å transition in benzene, it is next noted that the results of a numerical calculation of the perturbed intensity are likely to be high as far as this term is concerned, since a calculation based on single-configuration wave-functions of the intensity of the allowed band predicts an oscillator strength ($\underline{f}$ = 2.64) over two times too large (observed $\underline{f}$ = 0.6 - 1.2[14,15]). That is, this part of the transition moment is likely to be nearly twice as large as it should be. The inclusion of configuration interaction, which with benzene cuts the intensity down to a reasonable figure ($\underline{f}$ = 0.8[16]) is quite impracticable here.

We now develop the required theory, on the basis of single-configuration MO wavefunctions in general terms. We do not start immediately with the wave-functions previously used in discussing transition energies since these are not necessarily the most suitable for calculating the corresponding intensities.

Perturbed MO wave-functions are written down as before, taking for the $\bar{\phi}_i$ the benzene MOs, in their real form, as defined by Sklar's Eq. (7)[3]. The substituent is attached to position I, along the $\underline{y}$ axis (axes as in figure above). To simplify the notation, we adopt henceforth the following convention.

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(14) L. W. Pickett, M. Muntz and E. M. McPherson, J. Am. Chem. Soc. 73, 4862 (1951).
(15) W. J. Potts, J. Chem. Phys. 23, 73 (1955).

(16) C.W.L. Bevan and D. P. Craig, Trans. Faraday Soc., 47, 564 (1951).

Subscripts i, j *run over* 0, 1, 2, 3; p, q *run over* -1, -2; *and* k, l *are unrestricted*.

We then have the following (Eq. (6b) has such a simple form because the orbitals Φ_p are antisymmetric under reflection in the *yz*-plane, the remaining orbitals being symmetric with respect to this operation):

$$\Psi_i = \sum_j{}' a_{ij}\,\Phi_j + a_{ix}\,\Phi_x \qquad (6a)$$

$$\Psi_p = \sum_q{}' a_{pq}\,\Phi_q \qquad (6b)$$

$$\Psi_x = \sum_j{}' a_{xj}\,\Phi_j + a_{xx}\,\Phi_x \qquad (6c)$$

The $\underline{a_{kl}}$ are coefficients, the best possible values for which would be obtained by solving the secular equations derived from the seven primitive wavefunctions Φ. In the approximation in which Eqs. (1a) and (1b) give the perturbed energies, we would have

$$\begin{aligned} a_{ix}/a_{ii} &= -(\lambda_i + S_{ix}), \quad a_{xi}/a_{xx} = \lambda_i \\ a_{kl}/a_{kk} &= H_{kl}/(H_{kk}-H_{ll}) \ . \end{aligned} \qquad (7)$$

However, we can separate out the question of how refined the calculation of these coefficients must be by supposing for the time being that they are 'exact'.

Having in mind Eqs. (7), we shall assume that the perturbation is weak enough for the following to apply:

$$\begin{aligned} &a_{ii},\ a_{pp},\ a_{xx} && \text{are approximately unity} \\ &a_{ix},\ a_{xi},\ S_{ix} && \text{are of order } \lambda \\ &a_{ij},\ a_{pq} && \text{are of order } \lambda^2 \end{aligned} \qquad (8)$$

The final expression for the transition moment will be obtained as a sum of terms of order λ^2. Consequently, we may only omit from the algebra terms smaller than these. The MOs (6) must be orthonormal. Normalization leads to the following relations between the coefficients:

$$\begin{aligned} a_{ii} &= 1 - \tfrac{1}{2}a_{ix}^2 - S_{ix}a_{ix} \\ a_{pp} &= 1 \\ a_{xx} &= 1 - \tfrac{1}{2}\sum_i a_{xi}^2 - \sum_i a_{ix}S_{ix}\ , \end{aligned} \qquad (9)$$

plus terms of order λ^3,... To the same approximation, the orthogonality relations are:

$$\begin{aligned} a_{ij} + a_{ji} + a_{ix}a_{jx} + a_{ix}S_{jx} + a_{jx}S_{ix} &= 0 \\ a_{pq} + a_{qp} &= 0 \\ a_{xi} + a_{ix} + S_{ix} &= 0 \end{aligned} \qquad (10)$$

While Eqs. (10) are not used specifically in what follows, compliance with them is mandatory: for if, with a particular set of coefficients $\underline{a_{kl}}$, the residue after evaluating the left-hand side of any of the Eqs. (10) is of order λ^k, there will be spurious contributions to the transition moment of the same order of magnitude.

Wave-functions Ψ_g and Ψ_e are now written down for the ground and excited states. For the present purpose we can omit the spin wave-functions, and antisymmetrization also, since all the orbitals are orthogonal and the transition moment is a sum of one-electron operators. For convenience, we also leave out the serial numbers of the eight electrons. Then[17]

$$\Psi_g = \psi_0 \psi_0 \psi_1 \psi_1 \psi_{-1} \psi_{-1} \psi_x \psi_x \qquad (11a)$$

$$\begin{aligned} {}_e = \cos\left(\frac{\pi}{4} - \Lambda\right)&\{\psi_0 \psi_0 \psi_1 \psi_1 \psi_{-1} \psi_2 \psi_x \psi_x\} \\ + \sin\left(\frac{\pi}{4} - \Lambda\right)&\{\psi_0 \psi_0 \psi_1 \psi_{-2} \psi_{-1} \psi_{-1} \psi_x \psi_x\} \end{aligned} \qquad (11b)$$

The quantity Λ in Eq. (11b) is a parameter concerning which we may say either: that the degeneracy which in benzene obtains between the orbitals $\Phi_{\pm 1}$ and between $\Phi_{\pm 2}$ no longer holds -- the $\psi_{\pm k}$ belong to different representations, A_2 and B_2 of group C_{2v} -- so that the two configurations in (11b) are of unequal energy and therefore do not mix equally any more; or: that Λ measures the mixing of wave-functions analogous[18] to the lowest energy B_{2u} and E_{1u} wave-functions of

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[17] There is a misprinted sign in Eq. (9') of Sklar[3], which is the appropriate equation in that paper with which to compare the present Eq. (11b).

[18] By 'analogous' is meant that benzene wave-functions are obtained from (11) by writing Φ for ψ, and omitting the two ψ_x factors.

unsubstituted benzene. The latter interpretation can be confirmed by setting $\Lambda = 0$ in (11b); then (11b) is the analogue of the B_{2u} wave-function of benzene itself, while if the sign of the second term is changed, there results the appropriate component (i.e. of B_1 symmetry) of the pair of E_{1u}-like wave-functions.

The moment $\vec{M}$ of the transition between the two states is then readily evaluated in terms of one-electron moments

$$\vec{M}_{kl} = \int \Psi_k \, (e \, \vec{x}) \, \Psi_l \, dv:$$

$$\vec{M} = \int \Psi_f \Sigma_i \, e \, \vec{x}_i \, \Psi_e \, dv = \cos\left(\frac{\pi}{4} - \Lambda\right) \vec{M}_{-12} + \sin\left(\frac{\pi}{4} - \Lambda\right) \vec{M}_{1-2} \qquad (13)$$

and this in turn can be expanded solely in terms of benzene transition moments $M^o_{kl} = \int \Phi_k \, (e \, \vec{x}) \, \Phi_l \, dv$, the direction of the transition precluding the direct participation of terms in Φ_x. If overlap is neglected, the non-zero moments are

$$\vec{M}^o_{0-1} = \tfrac{1}{2}\sqrt{2}\, R \, \vec{x}_o = -\vec{M}^o_{-23} \; ; \; \vec{M}^o_{1-2} = \tfrac{1}{2} R \, \vec{x}_o = - M^o_{1-2} \qquad (14)$$

where R is the C-C bond distance in benzene, and $\vec{x}_o$ is a unit vector in the $\underline{x}$ direction. Then, using Eqs. (8) and (9)[19]

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(19) Sin Λ is normally positive, and $\underline{a}_{13}$, $\underline{a}_{20}$ will normally have opposite signs; nevertheless, there is still extensive cancellation among the terms of (14) which leads one to recall with misgivings the host of neglected terms of order λ^3.

$$M = \tfrac{1}{2} R \left\{ (a_{2x}S_{2x} - a_{1x}S_{1x} + \tfrac{1}{2} a_{2x}{}^2 - \tfrac{1}{2} a_{1x}{}^2) + \sqrt{2}\,(a_{13} - a_{20}) + 2 \sin\Lambda \right\} \vec{x} \qquad (15)$$

In the B_{2u}-A_{1g} transition of benzene, the moments $\vec{M}^{o}_{1-2}$ and $\vec{M}^{o}_{-12}$ are equal and opposite, and in the total transition moment have equal coefficients, thus cancelling each other precisely. In a monosubstituted molecule, both equalities, of magnitude and weight, are destroyed, giving, as Eqs. (13) and (15) show, two distinguishable sources of intensity.

Comment on previous treatments of this problem centers on two aspects of our derivation of Eq. (15): conformity of the perturbed wave-functions with the requirements of orthonormality to the accuracy prescribed by (8), and inclusion or omission of the mixing coefficient Λ of Eq. (11b). We must also consider the adequacy of the methods used to calculate the coefficients $\underline{a}_{kl}$.

Sklar commenced by approximating ψ_i of Eq. (6a) by Φ_i, and ψ_x of (6c) by $\Phi_x + \Sigma_i^v \lambda_i \Phi_i$ -- that is, the interaction was supposed to take the form of leakage of electrons from the substituent into orbitals unoccupied by an electron of like spin. There appears to be no justification for dropping the terms in ψ_x involving occupied orbitals -- in fact, these seem to be just the most important ones. These wave-functions are now no longer orthogonal, and, more seriously, were not properly normalized. Antisymmetrized product wave-functions based on these non-orthogonal orbitals were then set up, and the moment integral was calculated taking due account of the non-orthogonality. This calculation can fairly be described as arduous. Inspection of Eq. (15), however, the first terms of which are simply the difference between the normalizing coefficients $\underline{a}_{11}$ and $\underline{a}_{22}$, reveals that neglect of such coefficients is quite inadmissible. Sklar's final formula (Eq. (13) of ref. 3) is thus quite incorrect; and indeed, if due account is taken of the requirements of normalization, a new expression for the transition moment results the terms of which roughly cancel each other out, and which thus hardly predicts any significant increase in intensity at all! These criticisms, to which others are added below, suggest that the formulae of Sklar's papers on intensities[3,4] be used only with the utmost caution.

We next examine the validity of a transition moment calculation based on the wave-functions of second-order perturbation theory. The terms in Eq. (14) are all of order λ^2, and in particular explicitly include coefficients of the type $\underline{a}_{ij}$. According to second-order perturbation theory, these are, quoting from Eqs. (7),

$$\underline{a}_{ij} = \underline{H}_{ij} / (H_{ii}-H_{jj})$$

(omitting the normalizing factor $\underline{a}_{ii}$ which is close to unity). Neglect of the inductive effect by setting $\underline{H}_{ij}$ equal to zero means that these terms are simply omitted, which is the procedure adopted by Sklar[3] and Matsen[10]. This is seen to be an arbitrary approximation, but one which could conceivably be reasonable were the matrix elements $\underline{H}_{ij}$ especially small.

However, if the perturbation expansion is carried one step further still, $\underline{a}_{ij}$ acquires some extra terms, one of which is not negligible under any conditions; i.e., we now have (omitting overlap for simplicity):

$$\underline{a}_{ij} = \frac{H_{ij}}{H_{ii}-H_{jj}} + \frac{H_{ix}H_{xj}}{(H_{ii}-H_{xx})(H_{ii}-H_{jj})} \qquad (16)$$

Comparison with Eqs. (2) shows that the new term is of order λ^2, and the necessity of including it follows at once.

We must also point out that certain pairs of these perturbation-theory wave-functions are insufficiently orthogonal: thus, when Eqs. (7) and (16) are substituted into the first of the Eqs. (10), there is a residue of order λ^2. In the light of the comments made regarding Eqs. (10), it is necessary to take heed of this non-orthogonality -- most conveniently by orthogonalizing[20] the perturbed wave-functions before proceeding further.

We come finally to the mixing coefficient first introduced in Eq. (11). We note that Matsen[10], in an appendix, drew attention to the possible importance of this quantity, but did not consider it in his calculations. To calculate sin Λ it is necessary to evaluate the matrix element of the total hamiltonian between the E_{1u}-like and B_{2u}-like wave-functions

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(20) P. O. Lowdin, J. Chem. Phys. 18, 365 (1950).

of C_6H_5X. Attempts to do this by the regular ASMO method break down because sin Λ emerges as a small difference between sums of very many large terms. Semi-empirical procedures, however, can be used to estimate the likely importance of this mixing coefficient. The result of calculations of intensities using a more definitive calculational scheme, shortly to be published[21], show that for small interactions, whether of an inductive or resonance kind, the change in the mixing coefficient Λ is the dominant influence on the intensity. The relative importance of Λ decreases as the substituent-ring resonance interaction becomes larger, but it is clear that any treatment which wholly ignores the mixing coefficient is grossly inadequate.

Nor can it be assumed that the occurrence of a term like our Λ is a peculiarity of the benzene problem alone, where it arises particularly imperatively because the MOs happen to be degenerate in the parent hydrocarbon. It is too early in our present state of understanding of molecular spectra to say whether intrinsically weak bands frequently steal large amounts of intensity from stronger bands, by vibrational

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(21) L. Goodman and H. Shull, to be published in J. Chem. Phys. Independent calculations relating to purely inductive substituents will be published by D. P. Craig and I. G. Ross in J. Chem. Soc. (London).

perturbations, but this begins to look likely (as, for example, in the weak 3200 A transition of naphthalene[22], the interpretation of which is hindered by just this phenomenon). Attachment of a substituent would seem to be no less drastic a perturbation than the excitation of a particular active vibration, and one can foresee, with some regret, the necessity of exploring the interaction of other molecular levels with the levels of direct interest if the intensity effects of substitution are to be accounted for in hydrocarbons generally[23].

The change in the mixing coefficient Λ also affects the transition energy shifts. Thus, besides the substituent perturbation on the orbital energies, the variation of the mixing coefficient between the configurational wave functions and the change in the electron repulsion integrals over the orbitals involved in the excitation process (J_{1-2}, J_{-12}, K_{1-2}, K_{-12} in usual notation), must be taken into account. Success in attributing changes in transition energies to

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(22) See e.g., D. S. McClure, J. Chem. Phys. 22, 1668 (1954), and references therein.

(23) Indeed, we might well have included in the present treatment of benzene a further parameter to take into account interaction of the ground state with the excited E_{2g}-like states; this was omitted because the term thus introduced into the final expression for the transition moment, Eq. (15), is likely to be distinctly smaller than $2s\Lambda$.

orbital energy perturbation alone hinges on the magnitude of the second factor and the variation of the [illegible] electron repulsion integrals with the perturbation. Expansion of these integrals over the perturbed orbitals shows that for small perturbations they vary as λ^{2},[21], which is indeed identical to the variation of the orbital energies in Eq. (3). By correct choice of empirical parameters, then, these integrals need not be evaluated explicitly; however, calculations which neglect such effects are likely to give only qualitatively useful results.

Appendix

We wish to investigate the magnitudes of the effects introduced by the neglect of overlap integrals in the framework of the simplest molecular orbital approach to substitution problems. In particular, the calculation of , transition probability integrals will be discussed, with benzene providing a specific example.

In alternant hydrocarbons, the overlap effects are especially simple and will be reviewed briefly. The lowest energy transition for a 2n π-electron alternant hydrocarbon takes place between corresponding bonding and antibonding levels, $\underline{a}$ and $\underline{\bar{a}}$. The MO's corresponding to these levels may be written[24]

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(24) H. C. Longuet-Higgins, J. Chem. Phys., 18, 265 (1950); C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. 36, 193 (1940); and B. H. Chirgwin and C. A. Coulson, Proc. Royal Soc. (London) 201A, 96 (1950).

$$\bar{\Phi}_a = \frac{1}{\sqrt{N_a}} \sum_{u=1}^{2n} C_{au}\,\phi_u = \left[M(1+\gamma_a S)\right]^{-\frac{1}{2}}\left[\sum_u^{*} C_{au}\,\phi_u + \sum_w^{o} C_{aw}\,\phi_w\right]$$

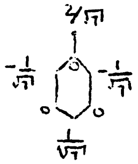
$$\bar{\Phi}_{\bar{a}} = \frac{1}{\sqrt{N_{\bar{a}}}} \sum_{u=1}^{2n} C_{\bar{a}u}\,\phi_u = \left[M(1-\gamma_a S)\right]^{-\frac{1}{2}}\left[\sum_u^{*} C_{au}\,\phi_u - \sum_w^{o} C_{aw}\,\phi_w\right] \qquad (17)$$

where M, the normalization constant with overlap neglected, is of the order of 2n; and S, the nearest neighbor overlap integral, $\sim \frac{1}{4}$. γ_a defines the energy of the orbitals a and $\bar{a}$, which, relative to the π-electron coulomb integral of sp^2 carbon, are $\pm \gamma_a \beta$. The starred terms refer to one alternating set of atomic orbitals, the "o" terms referring to the other set, w. The transition moment formulae may then be written

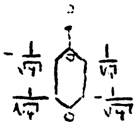
$$\vec{M}_{a\bar{a}} = \frac{(1-\gamma_a^2 S^2)^{-\frac{1}{2}}}{M}\left[\sum_u^{*} C_{au}^2\,\vec{r}_u - \sum_w^{o} C_{aw}^2\,\vec{r}_w\right] \qquad (18)$$

provided that the cross terms between non-adjacent atomic centers can be regarded as negligible, since those involving adjacent centers, $\int \phi_u \vec{r}\,\phi_{u+1}\,dv$, just cancel out. It is clear then that for transitions between corresponding bonding and antibonding levels, the effect of overlap is mainly felt through the normalization factor. Since $S \sim \frac{1}{4}$ and, for the lowest energy transition, $|\gamma_a| \sim 1$, its neglect introduces an error of perhaps 5% in the transition moment integral. However, if the transition does not take place between corresponding levels, the nearest neighbor cross terms no longer cancel out and the normalization factor becomes considerably more overlap dependent -- specifically, $\left[1 + \gamma_a \gamma_{\bar{b}} S^2 + (\gamma_a + \gamma_{\bar{b}}) S\right]^{-\frac{1}{2}}$. Since the nearest neighbor cross terms are of the order S, a considerable error is possible, especially for weak transitions whose total moment integral may be small due to cancellation of many large overlap dependent atomic moments.

In general, as far as we need to consider, for the calculation of transition moments upon purely conjugative substitution, two effects are important: (1) Corresponding alternant levels in the hydrocarbon are no longer so; (2) New atomic moment integrals appear involving ϕ_x. The relative influence of these effects will of course depend upon the hydrocarbon and the orientation of the substituent, The second effect plays no role in the benzene long wavelength transition, upon monosubstitution. We need only to consider the degree of "nonalternantness" of the substituted levels. It is convenient to consider at first the benzyl radical, which may be considered the limiting case of a substituent, having the same electronegativity and thus the same coulomb integral as the sp^2 carbons about the ring. Although the levels are still alternant, the transition no longer takes place between corresponding bonding and antibonding levels, as was the case in benzene. Consider the transition moment $\vec{M}_{1-2}$. The MO's are[24]



Φ_1



Φ_{-2}

The overlap dependence of the product of the normalization factors is $(1 - S)^{-\frac{1}{2}}$ by virtue of the fact that Φ_1 is a zero energy MO and is overlap independent. The transition moment is $(N_1 N_{-2})^{-\frac{1}{2}}(3)^{\frac{1}{2}}(S/2-1)R$. Even though both the cross terms and the normalization factor are overlap sensitive, the moment is virtually independent. Thus, in this limiting case where the substituent has electronegativity equal to that of the hydrocarbon carbon atoms, inclusion of overlap has little effect (a similar result holds for $\vec{M}_{-12}$) on the transition moments.

Turning to the situation where the substituent has arbitrary electronegativity, greater than sp^2 carbon, examination of Eq. (1) shows that the orbital energies depend on overlap in two ways: (1) through the difference $(H_{ii} - H_{xx})$; (2) through the substituent - hydrocarbon overlap term, $H_{ii}S_{ix}$. The first factor is dependent only upon the hydrocarbon overlap integrals through the relation $H_{ii} = H'_{ii}\ (1 + \gamma_a S)$ (primed quantities indicating neglect of overlap), showing that the calculated perturbation is increased for bonding orbitals through neglect of overlap. The converse is true for antibonding orbitals. But it is clear that as long as the difference ($H_{ii} - H_{xx}$) is large, i.e., the perturbations are small, this factor will not be important. The second factor involves H_{ii}. This quantity governs the dependence of the orbital, on the substituent-hydrocarbon overlap integral, which is strong when E_i is large; it clearly vanishes for a zero energy MO. Because of this term, bonding orbitals will be more overlap-sensitive when the substituent perturbation is weak (electronegativity high). The antibonding orbitals generally are little perturbed, so as to remain nearly constantly sensitive to overlap for all values of H_{xx}. The conclusion is that the hydrocarbon overlap integrals are more important in the case of large perturbations; the substituent - hydrocarbon overlap, with small ones, -- as is illustrated for the bonding ethylene orbital in Fig. 1.[25]

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(25) Exact solutions of the 3 x 3 secular equation were obtained as a function of H_{xx}, assuming the substituent - nearest - carbon exchange integral constant for all H_{xx}, and equal to β_{c-c}. Also assumed was neglect of non-nearest-neighbor exchange and overlap integrals. All carbon atoms were assigned the coulomb integral α.

The solutions all converge when $H_{xx} = \alpha$, since E_1 is then a zero energy MO; but the perturbations ($E_i - H_{ii}$) diverge as H_{xx} is lowered in accord with the first factor.

It is clear then that through neglect of overlap the greatest percentage discrepancy in the orbitals will be incurred at high substituent electronegativities, and in general this will be the case for the transition moment integrals. This same general conclusion applies to the calculation of transition energy and ionization potential shifts by the simplest MO procedure.

Finally, a remark may be made on the empirical evaluation of H_{xx}. This parameter is frequently estimated from shifts in the transition energy or ionization potential[10]. Inversion of Eq. (1) for H_{xx}, in terms of the first ionization potential shift $-\Delta I = (E_a - H_{aa})$ gives

$$H_{xx} = \left[H_{aa} + \frac{(H_{xa} - S_{ax} H_{aa})^2}{(\Delta I)_{obs}} \right] \frac{1}{1 + \gamma_a S} , \qquad (19)$$

which shows that the value of H_{xx} will depend upon both hydrocarbon and substituent - hydrocarbon overlap integrals. Here too, inspection of Fig. 1 reveals that neglect of overlap causes the most discrepancy for highly electronegative substituents.

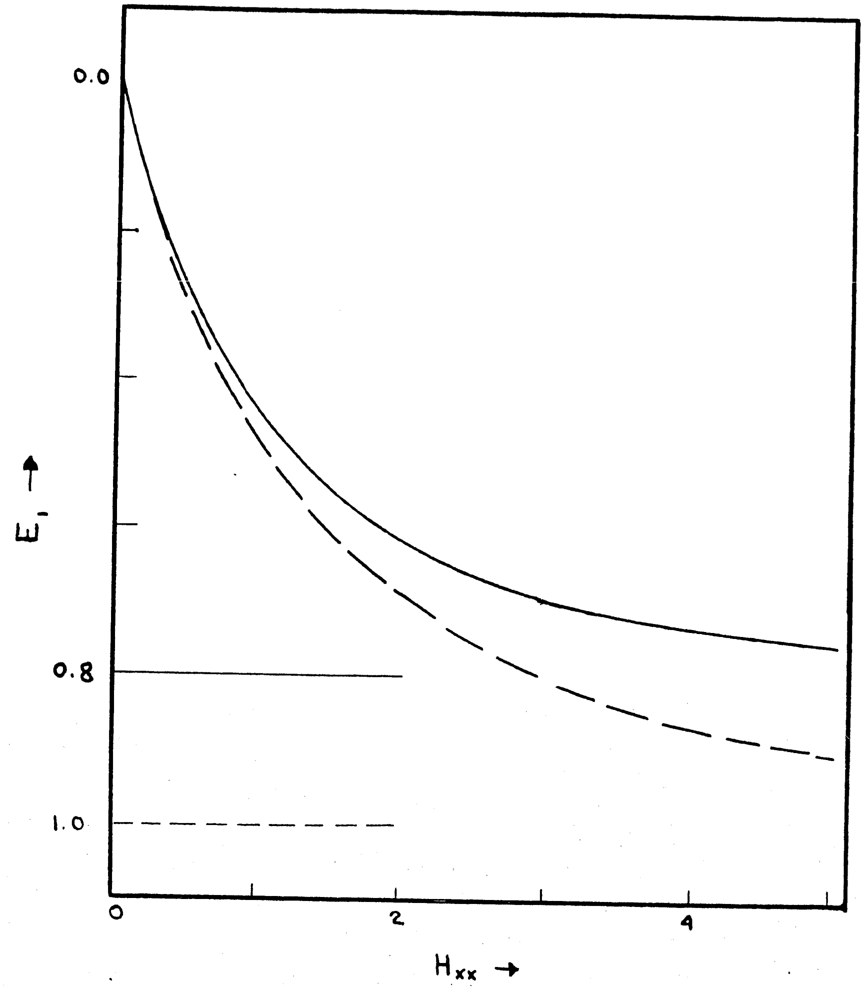

Fig. 1.—Variation of lowest π electron orbital energy as a function of electronegativity of a conjugating substituent. Broken lines: all overlaps neglected; full lines: $S = 0.25$. The coulomb integral H_{xx} and orbital energy E_1 are in units of γ. The horizontal lines show the limiting values of E_1 at vanishing perturbation.

THEORY OF SOLVENT EFFECTS ON MOLECULAR ELECTRONIC SPECTRA. FREQUENCY SHIFTS[1]

by E. G. McRae

Department of Chemistry, Florida State University

Tallahassee, Florida

(Abstract)

The effects of electric dipole interactions on electronic band frequencies in solution spectra are analyzed theoretically. A general expression for the frequency shift is derived by perturbation theory. The frequency shift is the sum of contributions from dispersive and static dipole interactions. The dispersive contribution represents the <u>general red shift</u>, which is present in all solution spectra; it depends in part on the <u>weighted mean wavelength</u> characteristic of the solvent. In the electrostatic contribution the role of the quadratic Stark effect is emphasized. The introduction of a simple electrostatic model permits the derivation of formulae relating frequency shifts in both emission and absorption spectra to the refractive index and static dielectric constant of the solvent. Illustrative numerical applications are described.

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(1) This work was carried out under a contract between the U. S. Air Force, Office of Scientific Research, ARDC, and the Florida State University.

I. INTRODUCTION

In several recent discussions of solvent effects in electronic spectra, solvent-induced frequency shifts have been interpreted in terms of electric dipole interactions. The well-known red shift[2] in the spectra of non-polar solutes has been related by Bayliss[3] to the solvation energy of the transition dipole, while the work of Ooshika[4] indicates that the red shift is caused by dispersive interactions. Several authors[3,4,5,6] have discussed frequency shifts in the spectra of polar solutes in terms of the relative solvation energies of the permanent dipoles appropriate either to the combining states of the solute, or to the resonance structures contributing to those states. As has been stressed by Bayliss and

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(2) Shifts to lower frequencies relative to the vapor frequency are called red shifts, and shifts to higher frequency, blue shifts. In algebraic expressions, red shifts will be designated by a negative sign, blue shifts by a positive sign.

(3) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(4) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

(5) L. G. S. Brooker, *Experientia Supplementum II*, (*XIVth International Congress of Pure and Applied Chemistry*), 229 (1955).

(6) N. S. Bayliss and E. G. McRae, THIS JOURNAL, **58**, 1002 (1954).

McRae[6], it is necessary in general to consider the frequency shifts arising from interactions involving the solute permanent dipoles as superposed on a <u>general red shift</u>[7], which is present in all solution spectra.

In this paper we present a further discussion of frequency shifts caused by dipole interactions. The most important contribution of this study is the derivation, by perturbation theory, of a general expression for the frequency shift. It is hoped that this formulation will serve to correlate previous interpretations, and provide the basis for a more precise and complete qualitative interpretation. A second contribution of the present work is the derivation, from the general expression, of formulas linking the frequency shift to the solvent refractive index and static dielectric constant. The formulas presented here are more widely applicable than those previously put forward[3,4].

II. THEORETICAL

The method of treatment consists of the application of second order perturbation theory to the calculation of the electronic state energies of a solution containing N identical solvent molecules and one solute molecule. We suppose in the beginning that the molecules have fixed positions and

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(7) Bayliss and McRae[6] used the term <u>polarization red shift</u>.

orientations. In view of the comparative rapidity of electronic transitions, the same positions and orientations are appropriate to the ground and excited states of the solute.

In the zeroth order of approximation, we consider the molecules not to interact. The zeroth-order electronic state functions of the solution are then made up of products of state functions for the unperturbed component molecules. Neglecting the non-orthogonality of the latter, we shall employ simple product functions, for which we introduce notations such as

$$\Phi^0_{a(p)b(q)j} = \phi_0^{v(1)} \ldots \phi_a^{v(p)} \ldots \phi_b^{v(q)} \ldots \phi_0^{v(N)} \phi_j^{u} ,$$

$$\Phi^0_{a(p)j} = \phi_0^{v(1)} \ldots \phi_a^{v(p)} \ldots \phi_0^{v(q)} \ldots \phi_0^{v(N)} \phi_j^{u} \quad \text{and}$$

$$\Phi^0_{a(p)0} = \phi_0^{v(1)} \ldots \phi_a^{v(p)} \ldots \phi_0^{v(q)} \ldots \phi_0^{v(N)} \phi_0^{u} ,$$

where for example $\Phi_{a(p)b(q)j}$ denotes the zeroth-order function representing the state of the solution in which the solute molecule is in its jth excited electronic state ϕ_j^u, and the pth and qth solvent molecules are in their ath and bth excited states $\phi_a^{v(p)}$, $\phi_b^{v(q)}$ respectively[8].

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(8)(a) It should be noticed that the subscripts for unexcited solvent molecules are omitted, but the subscript for the unexcited solute molecule is retained.
(b) The above notations embrace all of the required zeroth-order functions, for in the approximations of the present treatment, matrix elements involving zeroth-order functions corresponding to the simultaneous excitation of more than two solvent molecules are zero.

Throughout this paper the notations u and $v(p)$ will refer to the solute and the pth solvent molecules, and the subscript zero will indicate the ground electronic state of a single molecule.

The zeroth-order electronic state energies are sums of the electronic state energies of the unperturbed component molecules; e.g. the energy corresponding to $\Phi^{o}_{a(p)j}$ is given by $W^{o}_{aj} = (N-1)w^{v}_{o} + w^{v}_{a} + w^{u}_{j}$, where w denotes the electronic state energy of an unperturbed molecule. Energy differences will be expressed in cm^{-1}, and denoted by ν ; thus, for example, the energy difference between the ith and jth states of the solute will be expressed by $\nu^{u}_{ji} = (w^{u}_{j} - w^{u}_{i})/hc$, where h and c have the usual meanings.

We represent the energy of interaction of the molecules in solution by the classical energy of dipole interaction, which is given in the point-dipole approximation by

$$\mathcal{H}' = -\sum_{p=1}^{N} \Theta^{u\,v(p)}\mathcal{M}^{u}\mathcal{M}^{v(p)} - (1/2)\sum_{p=1}^{N}\sum_{q=1}^{N} \Theta^{v(p)v(q)}\mathcal{M}^{v(p)}\mathcal{M}^{v(q)}, \quad (1)$$

where $\mathcal{M}$ denotes the instantaneous magnitude of the dipole moment of a molecule and Θ is a geometrical factor dependent on the mutual orientation and separation of two dipoles.

The energy of the state Φ_i, corresponding in the zeroth order of approximation to Φ_i^o, is governed principally by the matrix elements $H_{j,i} = W^o\delta_{ji} + \int \Phi_j^o \mathcal{H}' \Phi_i^o \, d\tau$ (δ_{ji} is the Kronecker delta), $H_{a(p)j,i} = \int \Phi_{a(p)j}^o \mathcal{H}' \Phi_i^o \, d\tau$ and $H_{a(p)b(q)i,i} = \int \Phi_{a(p)b(q)i}^o \mathcal{H}' \Phi_i^o \, d\tau$. Here and in what follows, the state functions are for simplicity taken to be real. In view of (1), the matrix elements may be written

$$H_{j,i} = W_i^o \delta_{ji} - \sum_{p=1}^{N} \Theta_{ji,oo}^{u\,v(p)} M_{ji}^u M_{oo}^v - (1/2) \sum_{p=1}^{N} \sum_{q=1}^{N} \Theta_{oo,oo}^{v(p)\,v(q)} (M_{oo}^v)^2 \delta_{ji}, \tag{2}$$

$$H_{a(p)j,i} = - \Theta_{ji,ao}^{u\,v(p)} M_{ji}^u M_{ao}^v - (1/2) \sum_{\substack{q=1,\\ \neq p}}^{N} \Theta_{ao,oo}^{v(p)\,v(q)} M_{ao}^v M_{oo}^v$$

and

$$H_{a(p)b(q)i,i} = - (1/2) \sum_{\substack{q=1,\\ \neq p}}^{N} \Theta_{ao,bo}^{v(p)\,v(q)} M_{ao}^v M_{bo}^v \, . \tag{3}$$

Here M denotes a matrix element of the dipole moment (e.g. $M_{ji}^u = \int \phi_j^u \mathcal{M} \phi_i^u \, d\tau$), and Θ denotes a geometrical factor of proportionality between the product of the moments of two rigid point dipoles and their energy of interaction (e.g. the energy of interaction of two rigid point dipoles whose moments are respectively M_{ji}^u and M_{ao}^v, and which belong respectively to the solute and pth solvent molecules, is given by $-\Theta_{ji,ao}^{u\,v(p)} M_{ji}^u M_{ao}^v$).

Confining our attention to non-degenerate states of the solute, the energy of the state Φ_i is given according to second order perturbation theory[9] by

$$W_i = H_{i,i} + \sum_{j \neq i} \frac{(H_{j,i})^2}{W_i^0 - W_j^0} + \sum_{p=1}^{N} \sum_{a \neq 0} \frac{(H_{a(p)i,i})^2}{W_i^0 - W_{ai}^0}$$

$$+ \sum_{p=1}^{N} \sum_{a \neq 0} \sum_{j \neq i} \frac{(H_{a(p)i,i})^2}{W_i^0 - W_{aj}^0} + (1/2) \sum_{p=1}^{N} \sum_{\substack{q=1,\\ \neq p}}^{N} \sum_{a \neq 0} \sum_{b \neq 0} \frac{(H_{a(p)b(q)i,i})^2}{W_i^0 - W_{abi}^0} . \quad (4)$$

A similar expression for W_0 is obtained by replacing i by o. The frequency shift, $\Delta\nu$, is given by

$$hc\Delta\nu = \overline{(W_i - W_o)} - (W_i^0 - W_o^0) \quad (5)$$

where the bar indicates a time-average value.

General Formula.-- In order to obtain a simple expression for the frequency shift, it will be assumed that all the (point) dipoles associated with any one molecule (i.e. transition dipoles as well as permanent dipoles) may be considered to lie at the same point in the molecule. Eq. (4) can then be reduced to a form in which the energy is related explicitly to environmental contributions to the electric field at the solute dipoles. The time-average of this expression yields, through (5), a general formula for the frequency shift.

In the explicit reduction of (4), it will be assumed that the molecules can be considered as optically isotropic. However, as will be shown later, the formulas given below

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(9) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", Wiley, New York, 1944, p. 95.

require only minor modification, if either the solute or the solvent molecules or both can be considered <u>rod-like</u>, in the sense of having all dipole moments parallel.

The term by term reduction of (4) can be accomplished without further gross approximations. Let $\underset{\sim}{E}^u$ denote the field at the solute dipoles, due to the permanent dipoles of the surrounding solvent molecules. In view of (2), the first term in (4) reduces to

$$W_i^0 - \underset{\sim}{M}_{ii}^u \cdot \underset{\sim}{E}^u - (1/2) \sum_{p=1}^{N} \sum_{\substack{q=1 \\ \neq p}}^{N} \oplus_{00,00}^{v(p)\,v(q)} \left(M_{00}^{v}\right)^2 \qquad (6)$$

The terms under summation in (6) represent the energy of interaction of solvent permanent dipoles, and make no contribution to the frequency shift.

The second term in (4) can be written

$$-\frac{1}{hc} \sum_{j \neq i} \frac{\left(\underset{\sim}{M}_{ji}^u \cdot \underset{\sim}{E}^u\right)^2}{\nu_{ji}^u}$$

For an isotropic molecule, the value of $\left(\underset{\sim}{M}_{ji}^u \cdot \underset{\sim}{E}^u / M_{ji}^u E^u\right)^2$ averaged over all states $j \neq i$ is 1/3. Consequently the second term in (4) becomes approximately

$$-\frac{(E^u)^2}{3hc} \sum_{j \neq i} \frac{\left(M_{ji}^u\right)^2}{\nu_{ji}^u}$$

Making use of the usual expression for the isotropic polarizability of a molecule[10], this becomes

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(10) Reference 9, p. 121.

$$-(1/2)\,(E^{u})^{2}\,\alpha_{i}^{u} \qquad , \qquad (7)$$

where α_{i}^{u} denotes the static isotropic polarizability of the solute molecule in its ith excited electronic state.

With the aid of (2), the third term in (4) can be written

$$-\frac{1}{hc}\sum_{p=1}^{N}\sum_{a\neq 0}\frac{(\Theta_{ii,ao}^{u\,v(p)}M_{ii}^{u}M_{ao}^{v})(\Theta_{ii,ao}^{u\,v(p)}M_{ii}^{u}M_{ao}^{v}+\sum_{q=1,\neq p}^{N}\Theta_{ao,oo}^{v(p)v(q)}M_{ao}^{v}M_{oo}^{v}}{\nu_{ao}^{v}}$$

$$-\frac{1}{4hc}\sum_{p=1}^{N}\sum_{a\neq 0}\frac{(\sum_{q=1,\neq p}^{N}\Theta_{ao,oo}^{v(p)v(q)}M_{ao}^{v}M_{oo}^{v})^{2}}{\nu_{ao}^{v}}$$

The second sum represents the energy of interaction of permanent and induced solvent dipoles, and makes no contribution to the frequency shift. The first sum can be written

$$-\frac{1}{hc}\sum_{p=1}^{N}\sum_{a\neq 0}\frac{(\underset{\sim}{E}_{i}^{v(p)u}\cdot\underset{\sim}{M}_{ao}^{v(p)})(\underset{\sim}{E}_{i}^{v(p)u}+\sum_{q=1,\neq p}^{N}\underset{\sim}{E}^{v(p)v(q)})\cdot\underset{\sim}{M}_{ao}^{v(p)}}{\nu_{ao}^{v}}$$

where $\underset{\sim}{E}_{i}^{v(p)u}$ denotes the field at the dipoles belonging to the pth solvent molecule, due to the permanent dipole of the solute molecule in its ith excited state, and $\underset{\sim}{E}^{v(p)v(q)}$ denotes the field at the same point, due to the permanent dipole of the qth solvent molecule. The second factor in parenthesis in the above expression represents the field at the pth solvent molecule, due to the permanent dipoles of the surrounding molecules. We shall neglect the contribution of solvent dipoles to this field, on the ground that the percentage error thereby incurred in the above sum will be large only when the solvent is highly polar, and in that case terms of the type we are discussing at present make a relatively small contribution to the frequency shift. Making use of the properties of isotropic molecules, we obtain

$$-(1/2)\sum_{p=1}^{N}\left(E_i^{v(p)u}\right)^2\alpha_0^v \quad ,$$

where α_0^v denotes the static isotropic polarizability of a solvent molecule in its ground state. Let $\mathbf{m}_i^{v(p)}$ denote the moment of the dipole induced in a solvent molecule by the field $\mathbf{E}_i^{v(p)u}$. The above expression then becomes $-(1/2)\sum_{p=1}^{N} E_i^{v(p)u} m_i^{v(p)}$, which can be written alternatively

$$-(1/2)\, M_{ii}^{u}\, e_i^{u} \quad , \qquad (8)$$

where $\mathbf{e}_i^u$ denotes the field at the solute dipoles, due to solvent induced dipoles such as that with moment $\mathbf{m}_i^{v(p)}$.

Utilizing (2), the fourth term in (4) can be written

$$\sum_{p=1}^{N}\sum_{a\neq 0}\sum_{j\neq i}\left(1-\frac{\nu_{ji}^u}{\nu_{ao}^v}\right)\left(\Theta_{ji,ao}^{uv(p)}M_{ji}^{u}\right)^2\frac{1}{hc}\,\frac{\nu_{ao}^v\left(M_{ao}^v\right)^2}{\left(\nu_{ao}^v\right)^2-\left(\nu_{ji}^u\right)^2} \quad .$$

From the above expression, we obtain

$$\sum_{p=1}^{N}\sum_{a\neq 0}\sum_{j\neq i}\left(1-\frac{\nu_{ji}^u}{\nu_{ao}^v}\right)\frac{1}{hc}\,\frac{\nu_{ao}^v\left(\mathbf{E}_{ji}^{v(p)u}\cdot\mathbf{M}_{ao}^{v(p)}\right)^2}{\left(\nu_{ao}^v\right)^2-\left(\nu_{ji}^u\right)^2}$$

which for isotropic molecules may be written approximately

$$\sum_{p=1}^{N}\sum_{a\neq 0}\sum_{j\neq i}\left(1-\frac{\nu_{ji}^u}{\nu_{ao}^v}\right)\left(E_{ji}^{v(p)u}\right)^2\frac{1}{3hc}\,\frac{\nu_{ao}^v\left(M_{ao}^v\right)^2}{\left(\nu_{ao}^v\right)^2-\left(\nu_{ji}^u\right)^2} \quad .$$

It is convenient to introduce a weighted mean wavelength, defined by

$$L_{ji} = \sum_{a\neq 0} \frac{(M_{ao}^{v})^2}{(\nu_{ao}^{v})^2 - (\nu_{ji}^{u})^2} \Big/ \sum_{a\neq 0} \frac{\nu_{ao}^{v}(M_{ao}^{v})^2}{(\nu_{ao}^{v})^2 - (\nu_{ji}^{v})^2}$$

We then obtain, for the fourth term in (4),

$$-(1/2)\sum_{p=1}^{N}\sum_{j\neq i}(1-\nu_{ji}^{u}L_{ji})(E_{ji}^{v(p)u})^2\,\alpha_{0}^{v}(\nu_{ji}^{u}) .$$

Here $\alpha_{0}^{v}(\nu_{ji}^{u})$ denotes the isotropic polarizability of a solvent molecule, appropriate to an oscillating field of frequency ν_{ji}^{u}. Let $m_{ji}^{v(p)}$ denote the amplitude of the dipole moment induced in a solvent molecule by an oscillating field of amplitude $E_{ji}^{v(p)u}$ and frequency ν_{ji}^{u}. We then obtain

$$-(1/2)\sum_{p=1}^{N}\sum_{j\neq i}(1-\nu_{ji}^{u}L_{ji})\,E_{ji}^{v(p)u}\,m_{ji}^{v(p)} ,$$

which can be written alternatively:

$$-(1/2)\sum_{j\neq i}(1-\nu_{ji}^{u}L_{ji})\,M_{ji}^{u}\,e_{ji}^{u} . \qquad (9)$$

Here $\underset{\sim}{e}_{ji}^{u}$, for example, denotes the field at the solute dipoles, due to solvent induced dipole with moment $\underset{\sim}{m}_{ji}^{v(p)}$.

As is made clear by (3), the fifth term in (4) represents the energy of an interaction between solvent molecules only. Consequently, this term makes no contribution to the frequency shift.

From (6), (7), (8) and (9) we find an expression for the energy W_i , and a similar expression for W_0 results on replacing i by o. The frequency shift in the transition between the ground state and the ith excited state is given, according to (5), by

$$\begin{aligned}\Delta\nu_{io} = (1/2hc)\Big[&\sum_{j\neq o}(1-\nu_{jo}^{u}L_{jo})M_{jo}^{u}\,\overline{e_{jo}^{u}} - \sum_{j\neq i}(1-\nu_{ji}^{u}L_{ji})M_{ji}^{u}\,\overline{e_{ji}^{u}} \\ &+(1/2hc)(M_{oo}^{u}\,\overline{e_{o}^{u}} - M_{ii}^{u}\,\overline{e_{i}^{u}}) \\ &+(1/hc)\,\overline{(\boldsymbol{M}_{oo}^{u} - \boldsymbol{M}_{ii}^{u})\cdot\boldsymbol{E}^{u}} \\ &+(1/2hc)(\alpha_{o}^{u}-\alpha_{i}^{u})\,\overline{(E^{u})^{2}}\end{aligned} \qquad (10)$$

where the bars indicate time-average values.

If either the solute or solvent molecules or both can be considered rod-like instead of isotropic, (4) can be reduced in a manner similar to that described above. If the solute molecule is rod-like, the final formula differs from (10) only in the fourth term, which becomes

$$(3/2hc)(\alpha_{o}^{u}-\alpha_{i}^{u})\;\overline{(\boldsymbol{M}_{oo}^{u}\cdot\boldsymbol{E}^{u}/M_{oo}^{u})^{2}}$$

where α_{o}^{u} and α_{i}^{u} again denote isotropic polarizabilities. If the solute molecule is not rod-like, the final formula is the same as (10).

Relationship to Macroscopic Properties.-- Eq. (10) may be written in a form involving the reaction fields of the solute dipoles. These may in turn be related to macroscopic properties of the solvent. We may identify $\overline{e_{ji}^{u}}$, for example, with the reaction field r_{ji} of the dipole whose moment is M^{u}_{ji}. The reaction field r_{ji} arises formally from the polarization of the solvent by an oscillating field whose frequency is ν^{u}_{ji}; therefore it should be related to the square of the solvent refractive index at this frequency. A slightly different interpretation should be placed on the reaction fields r_i and r_0, which are to be identified respectively with $\overline{e^{u}_{i}}$ and $\overline{e^{u}_{0}}$. These reaction fields arise from the contribution of induced dipoles to the static polarization of the solvent, and should therefore be related to the square of the solvent refractive index, extrapolated to zero frequency. The third term in (10) may be written $(1/hc)(\mathbf{M}^{u}_{00} - \mathbf{M}^{u}_{ii}) \cdot \mathbf{R}$, where $\mathbf{R}$ denotes the reaction field corresponding to $\mathbf{E}^{u}$. (Obviously, R should not be identified with $\overline{E^{u}}$). $\mathbf{R}$ arises from the contribution of the solvent permanent dipoles to the static polarization of the solvent, and should therefore be related to that part of the static dielectric constant attributable to orientation polarization.

A difficulty arises in the treatment of the fourth term in (10), since $\overline{(E^{u})^{2}}$ cannot be related to macroscopic solvent properties through identifications such as those indicated above. However we may be sure that when R is comparatively large, $\overline{(E^{u})^{2}}$ will be of the same order of magnitude as R^{2}. Somewhat arbitrarily we adopt

$\overline{(E^u)^2} = 3\mathcal{R}^2$ ($\mathcal{R}$ large) . For a rod-like solute molecule, we choose $\overline{(\underset{\sim}{M}{}^u_{oo}\cdot\underset{\sim}{E}{}^u/M^u_{oo})^2} = \mathcal{R}^2$ ($\mathcal{R}$ large). The advantage of these assumptions is that the last term in (10) and the corresponding expression for a rod-like solute molecule become the same, viz. $(3/2hc)\,(\alpha^u_o - \alpha^u_i)\,\mathcal{R}^2$.

We shall utilize the well known expression for the reaction field, derived on the basis of a point dipole at the center of a spherical cavity in a homogeneous dielectric[11].

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[11] C. J. F. Bottcher, "Theory of Electric Polarization", Elsevier, Amsterdam, 1952, p. 64.

For an absorption transition starting from the ground state, we have for an isotropic solute molecule

$$\mathcal{R} = \frac{2\,(M^u_{oo} + \alpha^u_o \mathcal{R})}{a^3}\;\frac{D' - 1}{2D' + 1}$$

where D' denotes the contribution of the permanent dipoles to the static dielectric constant of the solvent, and a denotes the cavity radius. The expression in parenthesis represents the dipole moment of the solute molecule in solution. For most molecules, the ground-state isotropic polarizability is about one-half the cube of the most suitable cavity radius[12], so that we derive approximately:

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[12] Reference 11, p. 206.

$$\mathcal{R} = \frac{2\,M^u_{oo}}{a^3}\left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+2}\right] \qquad (11)$$

where we have substituted for $D'-1/D'+2$ by the factor in brackets, involving D, the static dielectric constant of the solvent, and n_o, the solvent refractive index extrapolated to zero frequency.

The value of R appropriate to emission bands depends on the degree of dipole reorientation occurring in the interval between population of the excited state, and emission. We consider two limiting cases: if there is negligible dipole reorientation, the value of R is the same as that for the corresponding absorption band. On the other hand, if there is complete dipole reorientation, we have for a transition starting from the ith excited state:

$$R = \frac{2(M_{ii}^{u} + \alpha_i^{u} R)}{a^3} \frac{D'-1}{2D'+1}$$

Neglecting terms involving powers of $D'-1/D'+2$ higher than the second, we obtain after a short calculation similar to the derivation of (11):

$$R = \frac{2M_{ii}^{u}}{a^3}\left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+2}\right]\left\{1 - \frac{2(\alpha_o^{u}-\alpha_i^{u})}{a^3}\left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+2}\right]\right\} \quad (11')$$

For the remaining reaction fields, we have in both absorption and emission bands:

$$r_{ji} = \frac{2M_{ji}^{u}}{a^3}\frac{n_{ji}^2-1}{2n_{ji}^2+1} \qquad r_{jo} = \frac{2M_{jo}^{u}}{a^3}\frac{n_{jo}^2-1}{2n_{jo}^2+1} \quad (12)$$

$$r_i = \frac{2M_{ii}^{u}}{a^3}\frac{n_o^2-1}{2n_o^2+1} \qquad r_o = \frac{2M_{oo}^{u}}{a^3}\frac{n_o^2-1}{2n_o^2+1} \quad (13)$$

where n_{ji}, for example, denotes the solvent refractive index for light of frequency ν_{ji}^{u}. In (13) it would have been more accurate to write $M_{ii}^{u} + \alpha_{i}^{u} R$ in place of M_{ii}^{u}, and a similar expression in place of M_{oo}^{u}. However this refinement would not greatly improve the accuracy of the final expression for the frequency shift, because whenever R is large, the term involving the reaction fields r_i and r_o makes a relatively small contribution to the shift.

In view of the above discussion, including (11), (12) and (13), we obtain for the frequency shift in an absorption transition from the ground state to the ith excited state of an isotropic molecule:

$$\begin{aligned}\Delta\nu = 2.13 \times 10^{-30} & \left[\sum_{j \neq o} \left(\frac{1}{\nu_{jo}^{u}} - L_{jo} \right) \frac{f_{jo}^{u}}{a^3} \frac{n_{jo}^2 - 1}{2n_{jo}^2 + 1} \right. \\ & \left. - \sum_{j \neq i} \left(\frac{1}{\nu_{ji}^{u}} - L_{ji} \right) \frac{f_{ji}^{u}}{a^3} \frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \right] + \frac{1}{hc} \frac{(M_{oo}^{u})^2 - (M_{ii}^{u})^2}{a^3} \frac{n_o^2 - 1}{2n_o^2 + 1} \qquad (14) \\ & + \frac{2}{hc} \frac{\underset{\sim}{M}_{oo}^{u} \cdot (\underset{\sim}{M}_{oo}^{u} - \underset{\sim}{M}_{ii}^{u})}{a^3} \left[\frac{D-1}{D+2} - \frac{n_o^2 - 1}{n_o^2 + 2} \right] + \frac{6}{hc} \frac{(\underset{\sim}{M}_{oo}^{u})^2 (\alpha_o^{u} - \alpha_i^{u})}{a^3} \left[\frac{D-1}{D+2} - \frac{n_o^2 - 1}{n_o^2 + 2} \right]^2\end{aligned}$$

where in the first term we have introduced the oscillator strength, which, for a transition between the ith and jth states of the solute, for example, is given by[13]

$$f_{ji}^{u} = 4.704 \times 10^{29} \nu_{ji}^{u} (M_{ji}^{u})^2 = -f_{ij}^{u} \qquad (\ M_{ji}^{u} \text{ in e.s.u.})$$

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[13] R. S. Mulliken and C. A. Rieke, <u>Rep. Prog. Physics</u>, **8**, 231 (1941).

Eq. (14) is applicable to emission transitions only in the cases in which there is no appreciable dipole reorientation in the excited state. If there is complete dipole reorientation, (11'), (12) and (13) are applicable, and give for the frequency shift in the emission transition from the ith excited state to the ground state of an isotropic solute molecule:

$$\begin{aligned}\Delta\nu &= 2.13 \times 10^{-30} \left[\sum_{j \neq o} \left(\frac{1}{\nu^u_{jo}} - L_{jo} \right) \frac{f^u_{jo}}{a^3} \frac{n^2_{jo}-1}{2n^2_{jo}+1} \right. \\ &\left. - \sum_{j \neq i} \left(\frac{1}{\nu^u_{ji}} - L_{ji} \right) \frac{f^u_{ji}}{a^3} \frac{n^2_{ji}-1}{2n^2_{ji}+1} \right] + \frac{1}{hc} \frac{(\underset{\sim}{M}^u_{oo})^2 - (\underset{\sim}{M}^u_{ii})^2}{a^3} \frac{n_o^2-1}{2n_o^2+1} \\ &+ \frac{2}{hc} \frac{\underset{\sim}{M}^u_{ii} \cdot (\underset{\sim}{M}^u_{oo} - \underset{\sim}{M}^u_{ii})}{a^3} \left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+2} \right] \\ &+ \frac{2}{hc} \frac{\underset{\sim}{M}^u_{ii} \cdot (5\underset{\sim}{M}^u_{ii} - 2\underset{\sim}{M}^u_{oo})(\alpha^u_o - \alpha^u_i)}{a^6} \left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+2} \right]^2 \end{aligned} \tag{14'}$$

where we have neglected terms involving powers of $[D-1/D+2 - n_o^2-1/n_o^2+2]$ higher than the second.

From (14) and (14'), the frequency difference between the 0-0 bands in the absorption and emission transitions between the ground and the excited states of an isotropic solute molecule is predicted to be:

$$\begin{aligned}\Delta\nu\,(\text{absorption}) - \Delta\nu\,(\text{emission}) &= \frac{2}{hc} \frac{(\underset{\sim}{M}^u_{oo} - \underset{\sim}{M}^u_{ii})^2}{a^3} \left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+1} \right] \\ \frac{2}{hc} \frac{(\alpha^u_o - \alpha^u_i)[3(M^u_{oo})^2 - 5(M^u_{ii})^2 + 2\,\underset{\sim}{M}^u_{oo} \cdot \underset{\sim}{M}^u_{ii}]}{a^6} &\left[\frac{D-1}{D+2} - \frac{n_o^2-1}{n_o^2+2} \right]^2 \end{aligned} \tag{15}$$

III. DISCUSSION

The result of the treatment given in Sec. II is embodied in Eqs. (10), (14) and (14')[14].

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(14) These equations represent the solvent effect on the frequency of the 0-0 band. As the 0-0 band cannot always be identified in solution spectra, the equations must be compared with observed frequency shifts in band maxima, relative to the corresponding band maxima in the vapor spectrum. The latter should be determined by drawing the envelope of the vibrational structure. Unless the frequency shifts are comparable with or larger than the band width, the above procedure for applying the equations cited is valid only insofar as there is no significant solvent effect on band shape. Similar remarks apply to Eq. (15).

Eq. (10) is limited to transitions between non-degenerate states of the solute, but is otherwise generally applicable. It is fundamentally correct even though it is approximate, and therefore provides the basis for a sound qualitative interpretation of frequency shifts caused by dipole interactions. Because of the simplifications invoked in its derivation, especially the point-dipole approximation and the approximations inherent in second-order perturbation theory, the environmental fields appearing in (10) should not always be taken literally. For example, if the solute permanent charge distribution consists of positive and negative charges separated by several Ångstroms, it does not make sense to speak literally of the field at the solute dipole. Instead, the environmental fields should be considered simply as parameters whose qualitative variation from solvent to solvent can often be inferred, either from the macroscopic properties of the solvent or through consideration of hydrogen bonding. Again, if either the solute or solvent molecule is non-polar, but contains highly polar groups whose moments cancel, it is not realistic to put the time-average of the field $\underset{\sim}{E}^{u}$ equal to zero, even though this is implied formally in the derivation of Eq. (10).

Eq. (14) represents the frequency shift in absorption bands. Unless the solvent and solute are both polar, frequency shifts in corresponding absorption and emission bands are predicted to be equal. When the solvent and solute are both polar, frequency shifts in emission bands are represented by (14) if there is negligible dipole reorientation in the excited state, or by (14') if there is complete dipole reorientation. For example, frequency shifts induced in fluorescence spectra by rigid-glass solvents are represented by (14), since in such solvents the dielectric relaxation times are some orders of magnitude greater than the lifetime of the excited state ($\sim 10^{-8}$ seconds). On the other hand the relaxation times of most liquid solvents at room temperature are about 10^{-10} seconds[15], so that shifts induced by them in fluorescence

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(15) D. H. Whiffen, *Quart. Rev. Chem. Soc.*, $\underset{\sim}{4}$, 131 (1950).

spectra are represented by (14'). In the application of (14) to frequency shifts induced by solid polar solvents, the adopted dielectric constant should be the value extrapolated from that of the liquid solvent.

Eqs. (14) and (14') are of course subject to the same limitations as (10), and an additional limitation is imposed by the use of the simple model for the solute in solution. In particular, (14) and (14') do not apply to frequency shifts caused in part by hydrogen bonding.

Because of the assumption of identical solvent molecules in the derivation of (10), this formula and the formulas derived from it apply to frequency shifts induced by pure solvents only. The generalization to mixed solvents can be achieved in cases in which the solvent composition near the solute molecule can be assumed equal to the bulk composition. In that case, the weighted mean wavelength of a mixed solvent is a linear combination of weighted mean wavelengths of the solvent components, the coefficients being the appropriate mole fractions.

Dispersive Interactions.-- The first term in (10) represents a contribution from dispersive interactions. It will ordinarily be negative, because $\nu_{jo}^{u} > \nu_{ji}^{u}$ for $j > i$ (the states being numbered in order of increasing energy). In practice we observe frequency shifts in only the first few electronic bands of the solute, and these lie at lower frequencies than that of the onset of solvent absorption. The first term represents the general red shift.

The expression for the general red shift consists of a sum of terms, each of which corresponds to a virtual transition starting from one of the combining states of the solute. Each term contains the reaction field of a dipole whose moment oscillates with a frequency equal to the appropriate transition frequency and with amplitude equal to the appropriate transition dipole moment. According to the present formulation, the general red shift depends in part on the weighted mean wavelength, which is a function of the frequency, characteristic of the solvent.

If none of the transitions which make an important contribution to the general red shift lie close in frequency to a solvent absorption band, the weighted mean wavelength may be considered approximately as a constant. Whenever this is the case, we shall for definiteness adopt the value at zero frequency, denoting it by L_0.

The weighted mean wavelength may be taken as a constant in all applications to strong transitions ($f \sim 1$), because any frequency shifts are governed mainly by the term corresponding to the transition in question. In applications to weak transitions, the frequency-dependence of the weighted mean wavelength may be important if the solvent begins to absorb at a frequency close to that of the transition in question.

Limits are set on L_0, the weighted mean wavelength at zero frequency, by the inequalities

$$\sum_{a\neq 0}{}' \frac{(M_{a0}^{v})^2}{(\nu_{a0}^{v})^2} \Big/ \sum_{a\neq 0}{}' \frac{(M_{a0}^{v})^2}{\nu_{a0}^{v}} > L_0 > \frac{2}{3hc} \sum_{a\neq 0}{}' \frac{(M_{a0}^{v})^2}{(\nu_{a0}^{v})^2} \Big/ \alpha_0^{v},$$

where the primes indicate summation over terms corresponding to known transitions in the absorption spectrum of the solvent in question.

As long as the frequency and intensity of at least one strong transition is known, the limits are sufficiently close that their arithmetic mean is a good estimate of L_0. For example, we have for the solvent benzene, utilizing the known polarizability, the formula relating the oscillator strength to the transition dipole moment and the information in Table I:

$1850 > L_0 > 650$ (Ångstrom units) yielding $L_0 \approx 1250$ Å. This value is quite insensitive to refinements such as taking into account some Rydberg transitions. It is appropriate to many benzene derivatives as well as to benzene itself.

Unfortunately the ultraviolet absorption spectra of most other common solvents are not sufficiently well known for the above method to be useful. However we discuss a few typical solvents as follows:

Cyclohexane: from the absorption spectrum[16] we have $L_o < 1450$ Å, and guess $L_o \approx 1000$ Å. This value should be equally applicable to most saturated hydrocarbon solvents .

Dioxane: from the absorption spectrum[17] we have $L_o < 1800$ Å. Since the oscillator strength of the first band (0.11) is less than that of the λ 1800 Å band of benzene, the value of L_o for dioxane probably lies between those for benzene and cyclohexane.

Water: from the absorption spectrum[18] we have $L_o < 1350$ Å, suggesting a value of L_o approximately equal to or less than that for cyclohexane.

It should be noticed that the values of L_o tend to increase in the same order as the solvent refractive index.

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(16) L. W. Pickett, M. Muntz and E. M. McPherson, *J. Am. Chem. Soc.*, **73**, 4862 (1951).

(17) L. W. Pickett, N. J. Hoeflich and Tien-Chuan Liu, *J. Am. Chem. Soc.*, **73**, 4865 (1951).

(18) K. Watanabe and M. Zelikoff, *J. Opt. Soc. Amer.*, **43**, 753 (1953).

Comparison with Previous Work.-- In the first term in (14), the general red shift is related to the solvent refractive index. This expression may be compared in an interesting way with that previously derived by Bayliss[3]. To facilitate the comparison, we write the result of the present treatment in the form

$$\begin{aligned} 1.07 \times 10^{-14} \biggl\{ & -\frac{2L_{io} f_{io}^{u}}{a^3} \frac{n_{io}^2 - 1}{2n_{io}^2 + 1} \\ & + \sum_{\substack{j \neq o, \\ \neq i}} \biggl[\left(\frac{1}{\nu_{jo}^{u}} - L_{jo} \right) \frac{f_{jo}^{u}}{a^3} \frac{n_{jo}^2 - 1}{2n_{jo}^2 + 1} - \left(\frac{1}{\nu_{ji}^{u}} - L_{ji} \right) \frac{f_{ji}^{u}}{a^3} \frac{n_{ji}^2 - 1}{2n_{ji}^2 + 1} \biggr\} \biggr] \end{aligned} \quad (16)$$

whereas the Bayliss expression is $-1.07 \times 10^{-14} \frac{1}{\nu_{io}^{u}} \frac{f_{io}^{u}}{a^3} \frac{n_{io}^2 - 1}{2n_{io}^2 + 1}$. The first term in (16) differs from the Bayliss expression in that it contains $2L_{io}$ in place of $1/\nu_{io}^{u}$. Terms such as those under summation in (16) appear also in the treatment due to Ooshika[4]. However, the result of the present treatment is not identical with that obtained by Ooshika. In particular, the weighted mean wavelength appears, in the present work, in place of the wavelength of onset of solvent absorption in Ooshika's expression. This modification is considered to be quite important, because the two wavelengths do not in general vary in the same way from solvent to solvent.

Application to Benzene.-- The terms under summation in (16) make a dominant contribution to the red shift in weak transitions, since f_{io}^{u} is then small. This point may be illustrated by a numerical application of (16) to the shifts induced by the solvent cyclohexane in the λ 2500 Å and λ 2000 Å absorption bands of benzene. We assume that the shifts are caused by the transitions indicated in the first column of Table 1[19], the notations and assignments being those of Pariser[20]. Since the intensities of the transitions between excited states are unknown, we prefer to apply (16) in an indirect way, by calculating the intensities that these transitions must have in order to account for the observed shifts. Possible contributions from forbidden transitions between excited states will be neglected. For the radius of the benzene molecule, we adopt $a = 3.0$ Å. Since the first absorption band of cyclohexane lies at a considerably higher frequency than any of the benzene transitions indicated in the Table, the weighted mean wavelength may be considered approximately as a constant. We adopt the value indicated above, viz. $L_0 = 1000$ Å. With the transition intensities, transition frequencies and solvent refractive indices, n , indicated in the Table, we require in order to fit the observed shift of

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(19) Transitions to still higher energy states must unfortunately be omitted, for practical reasons. However, the contributions of such transitions probably tend strongly to cancel.

(20) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

TABLE 1

FREQUENCY SHIFTS IN THE BENZENE SPECTRUM

Transition[a]	f	ν(cm^{-1})	n	Contribution to $\Delta\nu$ (cm^{-1})	
				λ 2500Å band	λ2000Å band
$A_{1g}^{-} \rightarrow B_{2u}^{+}$	0.002[b]	40,000	1.49[f]	-3	2
$A_{1g}^{-} \rightarrow B_{1u}^{+}$	0.12[c]	50,000	1.56[g]	112	-238
$A_{1g}^{-} \rightarrow E_{1u}^{+}$	1.2[c]	55,000	1.58[g]	951	951
$B_{2u}^{-} \rightarrow E_{2g}^{+}$	(0.72)[d]	30,000[e]	1.45[f]	(-1368)[d]	0
$B_{1u}^{+} \rightarrow E_{2g}^{-}$	(0.50)[d]	19,000[e]	1.43[f]	0	(-1785)[d]
		Observed shift		-308[b]	-1070[b]

(a) Notations and assignments of Pariser[20].
(b) Reference 21.
(c) Reference 16.
(d) Values required to fit observed shifts.
(e) Differences of energies calculated by Pariser[20].
(f) Landolt-Bornstein, "Physikalisch-chemisch Tabellen", Springer, Berlin, 1935, Part 3 (II), p. 1683.
(g) Extrapolated from literature values.

308 cm^{-1} in the λ 2500 Å band[21] that the oscillator strength of the $B_{2u}^{-} \rightarrow E_{2g}^{+}$ transition be 0.7. This value is in accord with the fact that the transition is allowed. The fifth column in the Table shows the contribution of each transition to the shift. The $A_{1g}^{-} \rightarrow B_{2u}^{-}$ transition itself is seen to contribute only one per cent of the total. A similar calculation shows that in order to fit the observed shift of 1070 cm^{-1} in the λ 2000 Å band[21], the oscillator strength of the $B_{1u}^{+} \rightarrow E_{2g}^{-}$ transition must be 0.5, again an appropriate value for an allowed transition. The last column of the Table shows that the $A_{1g}^{-} \rightarrow B_{1u}^{+}$ transition itself contributes about one-quarter of the total shift.

The above example indicates that the frequency shifts are caused predominantly by strong transitions. The intensities of these transitions are probably not greatly altered upon the introduction of substituents into the benzene ring. Consequently, we are able to explain Ferguson's[22] observation that in the λ 2500 Å bands of weakly polar substituted benzenes, the frequency shifts are all about the same, and in particular are independent of the λ 2500 Å band intensities.

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(21) N. S. Bayliss and L. Hulme, *Australian J. Chem.*, **6**, 257 (1953).

(22) J. Ferguson, *J. Chem. Phys.*, **24**, 1263 (1956).

Effect of the Weighted Mean Wavelength.-- The influence of the weighted mean wavelength is manifest in the relative magnitudes of the general red shift induced by different solvents. The general red shift is observed directly only when both the solvent and solute are non-polar. In such cases, it is known that the frequency shift is approximately proportional to $n^2-1\ /\ 2n^2+1$, where n denotes the solvent refractive index at some particular visible or near-ultraviolet frequency[3,21,23]. (The linearity is also observed in certain other cases, which will be discussed later). From the relatively few studies in which frequency shifts have been referred to the vapor frequency[3,21,24,25], it appears that the plots of $\Delta\nu$ *vs.* $n^2-1/2n^2+1$ do not in general extrapolate to the origin, as they should according to Bayliss' theory, but tend to cut the frequency axis beyond the origin. This behavior

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(23)(a) N. D. Coggeshall and A. Pozefsky, *J. Chem. Phys.*, **19**, 980, (1951);
(b) G. M. Badger and R. S. Pearce, *Spectrochim. Acta*, **4**, 280 (1951);
(c) J. Ham, *J. Am. Chem. Soc.*, **76**, 3875 (1954).

(24)(a) S. Sambursky and G. Wolfsohn, *Trans. Faraday Soc.*, **36**, 427 (1940);
(b) G. Kortüm and B. Finckh, *Z. physikal. Chem.*, **B52**, 263 (1942).

This work has been summarized and discussed by Förster[25].

(25) Th. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Gottingen, 1951, p. 135.

led Bayliss[3] to suggest that the frequency shift is caused in part by interactions other than those accounted for by his theory. Actually, the discrepancy may arise from the slightly incorrect form of the Bayliss expression. According to the present theory, the frequency shift is approximately proportional to $(AL_0+B)(n^2-1/2n^2+1)$, which is a form of (16) obtained by replacing refractive indices and weighted mean wavelengths at all frequencies by n and L_0 respectively. A and B denote constants characteristic of the solute. Since the weighted mean wavelength tends to be shorter for solvents of lower refractive index, the plot of $\Delta\nu$ vs. $(AL_0+B)(n^2-1/2n^2+1)$ should pass nearer the origin than that of $\Delta\nu$ vs. $(n^2-1/2n^2+1)$, while still retaining the linearity of the latter plot. Because of the difficulty of estimating L_0, A and B , the possibility of the former plot cutting the frequency axis far on the red-shift side of the origin cannot definitely be excluded, although this appears unlikely if AL_0 and B are of comparable magnitude. Inspection of (16) suggests that this is actually the case; AL_0 probably predominates slightly in strong transitions, B in weak transitions.

Electrostatic Interactions.-- The remaining terms in (10) represent the contribution of electrostatic interactions. The second term represents the contribution of interactions between the solute permanent dipoles and the solvent dipoles thereby induced, and the third term represents the contribution of interactions between the permanent dipoles of the solute and solvent molecules. The fourth term represents the contribution of the interactions between the permanent dipoles of the solvent molecules and the solute dipoles thereby induced. Since it is proportional to the square of the field intensity produced by the solvent permanent dipoles, the fourth term may be said to represent the quadratic Stark effect.

The representation of the electrostatic contribution as a sum of terms is somewhat artificial, being a consequence of second-order perturbation theory. The same expressions could have been derived by the conventional methods of electrostatics, with due cognizance of the non-equilibrium polarization of the solvent immediately after the transition. The treatment by perturbation theory is preferable, because it is consistent with the treatment of the dispersive interactions.

In the last three terms in (14) and in (14'), the contributions of electrostatic interactions are expressed in terms of the static dielectric constant of the solvent and the solvent refractive index extrapolated to zero frequency. It will be recalled that the third terms were derived on the assumption of an isotropic solute molecule, and the fourth terms were derived on an assumption which is likely to be valid only when both the solvent and the solute are highly polar.

The dependence on the solvent of the frequency difference between the 0-0 bands of corresponding absorption and fluorescence bands should be interpretable in terms of electrostatic interactions only. Since the interpretation is complicated neither by the general red shift nor by solute dipole-induced solvent dipole interactions, concurrent studies of absorption and fluorescence spectra should provide more definite information about the dipole moment of the solute in its lowest excited singlet state than can be inferred from data on absorption spectra alone. Eq. (15) represents the frequency difference mentioned above.

Comparison with Previous Work.-- Eq. (14) may be compared with the formula derived by Ooshika[4]. As far as the electrostatic contributions are concerned the two expressions appear to be quite different, but the difference is probably superficial. However, the present result has the substantial advantage that the electrostatic contribution is expressed in closed form.

The present theory leads naturally to a classification of solutions previously adopted by Bayliss and McRae[6]. In their case I (both solute and solvent non-polar) the first term in (10) alone contributes to the frequency shift. In case II (solute non-polar, solvent polar) the first and fourth terms contribute, while in case III (solute polar, solvent non-polar) the first and second terms contribute. In case IV (both solute and solvent polar), all four terms make a contribution. Case I has already been discussed above. In the following discussion of cases II - IV, we shall avoid unnecessary duplication of that given in the previous paper[6], with which we are substantially in agreement, confining our attention to certain modifications or extensions suggested by the present work.

Cases II and III of Bayliss and McRae.-- In the discussion of case I, it was mentioned that the frequency shifts vary approximately linearly with $n^2-1/2n^2+1$. The same behavior is ordinarily observed in cases II and III, although in case II, apparently anomalous shifts are produced by highly polar solvents such as water[21], methanol[24,25] and ethanol[21,26]. The phenomena in case II do not necessarily conflict with the theory, since we may say that the first term in (10) is ordinarily much larger than the fourth (i.e. the general red shift is dominant) but that if the solvent is highly polar the fourth term (i.e. the quadratic Stark effect) may make an important contribution. In case III, the dependence of the frequency shift on the solvent refractive index is represented by the first two terms in (14) or (14'). Since n_0 ordinarily differs little from n [27], the theory readily explains the observed behavior.

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(26) R. Schnurmann and W. F. Maddams, J. Chem. Phys., **19**, 1430 (1951).

(27) The solvent water is exceptional in this respect. [28]The value of n_0^2 is about 5, while n^2 for visible light is 1.77[28].

(28) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth, London, 1955, p. 10.

Case IV of Bayliss and McRae.-- To simplify this discussion, we write the last two terms of (10) in the form involving the reaction field, viz. $(1/hc)(\underset{\sim}{M}^{u}_{00} - \underset{\sim}{M}^{u}_{ii}) \cdot \underset{\sim}{R}$ and $(3/2hc)(\alpha^{u}_{0} - \alpha^{u}_{i}) R^{2}$ respectively. Here, the significance of the reaction field is analagous to that of $\underset{\sim}{E}^{u}$, as discussed at the beginning of this Section. The nature of the phenomena in case IV depends critically on the relative magnitude of the above terms. In all cases of practical interest, the first of the two terms contributes a significant proportion of their sum. Whether or not the contribution of the second term is important can only be judged from the experimental results, because the difference between ground and excited state polarizabilities (indeed, even the sign of the difference) is in general difficult to predict.

If the contribution of the quadratic Stark effect is indeed negligible[29], the qualitative interpretation is the same as that previously proposed[6]. However we are able to give semi-quantitative expression to the qualitative theory, with the aid of (14) or (14'). We illustrate this by the application of an approximate form of (14) to the λ 5500 Å absorption band of phenol blue.

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(29) "Negligible" has a different meaning in the discussion of case IV than in that of the preceding cases, the discussion of case IV being carried on at a lower level of approximation.

Application to Phenol Blue.-- Solvent effects in the phenol blue spectrum have been studied by Brooker and Sprague[30], whose results imply that the frequency shifts increase in the order of solvent dielectric constant. The more extensive study by LeRosen and Reid[31] shows that there is no correlation with the dielectric constant, but that the shifts induced by hydrocarbon and aryl halide solvents vary regularly with the solvent refractive index. LeRosen and Reid found no correlation of the shifts induced by other solvents with any solvent macroscopic property or combination of such properties. They did, however, present a qualitative interpretation of the results in terms of various types of intermolecular interactions, including hydrogen bonding.

Eq. (14) may be written in the approximate form

$$\Delta\nu = (A L_0 + B')\frac{n_D^2-1}{2n_D^2+1} + C\left[\frac{D-1}{D+2} - \frac{n_D^2-1}{n_D^2+1}\right] \qquad (17)$$

where refractive indices at all frequencies have been replaced by the value appropriate to the sodium D line, and the quadratic Stark effect has been neglected. A , B' and C are constants characteristic of the solute. Fig. 1 illustrates the fit of the

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(30) L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.*, **63**, 3214 (1941).

(31) A. L. LeRosen and C. E. Reid, *J. Chem. Phys.*, **20**, 233 (1952).

above equation to the experimental results for phenol blue.

In Fig. 1, points are shown for all solvents whose effects have been measured[30,31], except water. In the case of water, (17) is inapplicable because of the considerable difference between n_o and n_D[27].

For saturated hydrocarbon solvents, bromocyclohexane, aliphatic alcohols and water, the value of L_o was taken to be 1000 Å; for other solvents, 1250 Å was adopted. The fit of predicted and observed shifts was insensitive to B'/A ; the assumed ratio, which is arbitrary, places equal weight on AL_o and B for saturated hydrocarbon solvents. The best value of C/A was determined by the method of least squares, omitting the points represented in the figure by open circles. The value of A was adjusted to make the theoretical straight line pass through the points for n-heptane and pyridine (the vapor spectrum is not available). The neglect of the quadratic Stark effect is justified by the fit of the points to a straight line, as shown in the Figure.

A glance at Fig. 1 shows that the solvents are separated into two distinct series according to their ability to form a hydrogen bond with the solute. Although (14) is not applicable to the total frequency shifts caused in part by hydrogen bonding, it may be capable of predicting that part of the shift exclusive of the contribution of hydrogen bonding. The points representing non-hydrogen bonding solvents are fitted to the full straight line with a root mean square deviation of about 100 cm^{-1}, which is of the same order of magnitude as the experimental error in the determination of band frequencies in solution spectra ($\sim 50\ cm^{-1}$). The points representing non-polar solvents illustrate the behavior mentioned above as typical of class III. The remaining points (non-hydrogen bonding polar solvents) show that frequency shifts in class IV may be correlated with a particular function of both the dielectric constant and refractive index of the solvent, even though there is no general correlation with either quantity separately.

The theory is evidently capable of reproducing the gross features of the phenomena, but not all of the finer details. For example, all of the points representing the aliphatic ethers lie near the full straight line, but the relative shifts induced by different members of this group of solvents do not support the theory. No doubt the discrepancies are due in part to the simplifying assumptions about the refractive index and the weighted mean wavelength, the crudity of the model, and the anisotropy of phenol blue. At least one of the discrepancies, in the case of the solvent dioxane, may reflect a more fundamental failure of the approach based on (14). The dioxane molecule has two non-adjacent dipolar groups whose moments cancel, so that the effective reaction field $\underset{\sim}{R}$ is probably greater than is indicated by the macroscopic properties (cf. the discussion of (10) at the beginning of this Section).

LeRosen and Reid[31] tried to explain the results which they obtained with non-hydrogen bonding solvents in terms of solute dipole-induced solvent dipole interactions only. The present work indicates that permanent dipole interactions make an important contribution to the frequency shifts induced by polar solvents.

The constant C, which appears in the approximate form of (14), corresponds to $(2/hca^3)(\underset{\sim}{M}{}^u_{oo}-\underset{\sim}{M}{}^u_{ii})\cdot\underset{\sim}{M}{}^u_{oo}$ in (14), so that from the best value of C found as indicated above (-1530 cm^{-1}) we may calculate the excited state permanent dipole moment of phenol blue. The ground state dipole moment is 5.80 Debye[32]. The most appropriate cavity radius probably lies between 4 Å and 5 Å. If we assume that the ground and excited state dipole moments are parallel, we calculate the excited state dipole moment to be between 7.5 Debyes ($a = 4$ Å) and 9.1 Debyes ($a = 5$ Å). Both are of the expected order of magnitude, but they do not offer strong support for the suggestion[30] that a Zwitterion structure contributes heavily to the excited state.

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(32) C. P. Smyth, "Dielectric Behavior and Structure," McGraw Hill, New York, 1955, p. 348.

Application to Merocyanines.-- We now discuss the remarkable solvent-induced frequency shifts observed in the lowest-frequency singlet-singlet absorption bands of merocyanine dyes. The results of extensive studies, mainly by Brooker and co-workers[33,34], are typified by those illustrated in Fig. 2a. The three dyes IV, V and IX (notations of Brooker, Keyes and Heseltine[34]) have a common acidic (electron-attracting) nucleus, and basic (electron-repelling) nuclei whose basicity decreases in the order IV > V > IX[34]. Almost certainly, this is the order of decreasing ground state permanent dipole moment. The outstanding feature of the frequency shifts, as revealed by Fig. 2a, is that the band of the most highly polar dye (IV) shifts to higher frequencies as the water content of the solvent is increased, while the band of the least polar dye (IX) shifts initially to lower, and then to higher frequencies. Intermediate behavior is exhibited by the dye of intermediate dipole moment.

The phenomena have been interpreted by Brooker[5] in terms of the relative solvent stabilization of polar and non-polar resonance structures, and this approach has been elaborated by

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(33) L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman and S. G. Dent, *J. Am. Chem. Soc.*, **73**, 5332 (1951).
(34) L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, *J. Am. Chem. Soc.*, **73**, 5350 (1951).

Brooker and co-workers have studied solvent effects on maximum extinction coefficients as well as band frequencies.

Simpson[35] and by Platt[36]. As a particular application of the present theory, we advance an alternative (but not fundamentally different) explanation in terms of the quadratic Stark effect.

The merocyanine dyes have just the right combination of properties to favor the quadratic Stark effect. First, they are highly polar, implying that in moderately or highly polar solvents R (and hence R^2) is particularly large; second, the first singlet transition is strong ($f \sim 1$). The second property makes it reasonable to assume, as is necessary in the following interpretation, that the polarizability of any given dye in its lowest singlet excited state is considerably less than in its ground state. This can be understood upon inspection of the usual formula for the polarizability[10]. The lowest singlet transition, being strong, makes a sizeable contribution to the ground state polarizability, and a negative contribution of the same magnitude to the lowest excited singlet state polarizability.

A particularly simple discussion is made possible by writing (10) in a form appropriate to the limiting case of large R , viz.

$$\Delta\nu - \Delta\nu_{Ref} = (1/hc)(\mathbf{M}^{u}_{00} - \mathbf{M}^{u}_{ii}) \cdot \mathbf{R} + (3/2hc)(\alpha^{u}_{0} - \alpha^{u}_{i}) R^{2} \quad (18)$$

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(35) W. T. Simpson, *J. Am. Chem. Soc.*, **73**, 5359 (1951).
(36) J. R. Platt, *J. Chem. Phys.*, **25**, 80 (1956).

where $\Delta\nu_{Ref}$ represents the frequency shift induced by a non-polar reference solvent, and the frequency shift as again expressed in terms of $\underset{\sim}{R}$ instead of $\underset{\sim}{E}^{u}$. We assume that in order to preserve the orthogonality of ground and excited electronic state functions in a series of merocyanines of decreasing ground state dipole moment, the excited state dipole moments either stay nearly constant or tend to increase in the same order as the ground state dipole moments decrease. In Fig. 2b, the frequency shift $\Delta\nu - \Delta\nu_{Ref}$ is plotted against R in the three possible cases: $M^{u}_{oo} - M^{u}_{ii}$ greater than, less than and equal to zero. (In the discussion of visible merocyanine spectra, the ground and excited state permanent dipole moments may be considered parallel). The comparison of Figs. 2a and 2b shows that (18) is capable of reproducing the gross features of the phenomena, for R may be assumed to increase monotomically with water content in an aqueous pyridine solvent. The comparison must remain purely qualitative, because there is in this case no reliable way of relating R to the solvent composition. Indeed, the reaction field has only formal significance in the present application. The reason for this has been explained, with explicit reference to $\underset{\sim}{E}^{u}$, at the beginning of this Section. Eq. (18) itself is far from realistic, because the first two terms in (10) may well suffer significant changes on passing from solvent to solvent. However it is unlikely that the consideration of the general red shift, for example, would alter the qualitative conclusions drawn here.

In spite of the drastic simplifications which have been introduced, the present discussion is readily shown to involve quantities of the correct order of magnitude. For this purpose the ordinate in Fig. 2b was chosen to run to 2 x 10^5 e.s.u., which is the order of magnitude of the reaction field indicated by the simple model, for a solvent of high dielectric constant and $M_{00}^{u} =$ 10 Debyes. The difference between the ground and excited state permanent dipole moments is almost certainly of the order of a few Debyes, and 1.5 Debyes was chosen for the sake of illustration. In order to reproduce the gross features of the phenomena within the chosen range of R, the difference between the ground and excited state isotropic polarizabilities must be 0.5 - 1.0 x 10^{-23} cm^3, i.e., about one-third of the contribution of a strong visible transition to the ground state polarizability.

In his discussions of the phenomena, Brooker[5] has focused attention on the plot of the peak extinction coefficient ϵ_m against the corresponding wavelength λ_m, and he has associated the maxima in such curves with the <u>iso-energetic point</u>, at which the principal polar and non-polar resonance structures have equal energies. At the isoenergetic point the ground and excited state dipole moments of the solute in solution should be equal. From (18) we find that the condition for a minimum value of $\Delta\nu - \Delta\nu_{Ref}$ $(M_{ii}^{u} > M_{oo}^{u})$ is $M_{oo}^{u} + 3\alpha_{o}^{u}R = M_{ii}^{u} + 3\alpha_{i}^{u}R$. For a rod-like solute molecule, $3\alpha_{o}^{u}$ and $3\alpha_{i}^{u}$ are polarizabilities appropriate to a field directed parallel to the dipole moments, so that $M_{oo}^{u} + 3\alpha_{o}^{u}R$ and $M_{ii}^{u} + 3\alpha_{i}^{u}R$ represent dipole moments of a rod-like solute molecule in solution. Since the merocyanines may be considered nearly rod-like, the present theory suggests that in the approximation of neglecting the first two terms in (10), the minimum in $\Delta\nu - \Delta\nu_{Ref}$ should be associated with the isoenergetic point. The minimum in $\Delta\nu - \Delta\nu_{Ref}$ and the maximum in the plot of ϵ_m vs. λ_m ordinarily occur at nearly the same solvent composition[37]. The present discussion thus tends to support the views previously expressed by Brooker[5], and in fact indicates that Brooker's conclusions remain valid even if there are more than two resonance structures making important contributions to the combining states.

Other Interactions.-- Finally we point out that not all frequency shifts are caused entirely by dipole interactions, but

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(37) This is not the case in the curves for Brooker, Keyes and Heseltine's dyes IX and X[34]. However, since these dyes are relatively weakly polar, the first two terms in (10) may make an important contribution.

that other types of interaction may make important or even dominant contributions in certain cases. For example, charge-transfer complex formation is generally accompanied by shifts in band frequencies; this topic has been reviewed recently[38]. Again, a large frequency shift may arise from intermolecular repulsive forces, in the event that the solute molecule suffers a marked change of equilibrium size[39] or shape[40,41] upon excitation.

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(38)(a) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954);
(b) L. E. Orgel, *Quart. Rev. Chem. Soc.*, **8**, 422 (1954).

(39)(a) N. S. Bayliss and A. L. G. Rees, *J. Chem. Phys.*, **8**, 377 (1940);
(b) N. S. Bayliss, A. R. H. Cole and B. G. Green, *Australian J. Sci. Res.*, **A1**, 472 (1948);
(c) A. L. G. Rees, *J. Chem. Phys.*, **8**, 429 (1940).

(40) K. W. Hausser, R. Kuhn and E. Kuhn, *Z. physikal Chem.*, **B29**, 417 (1935).
This work has been summarized and discussed by Förster[41].

(41) Reference 25, p. 136.

(Caption to Fig. 1)

Fig. 1. Calculated vs. observed frequency shifts in the λ 5500 Å band of phenol blue. The frequency shifts are calculated from Eq. (17) ($\mathcal{A} = -5.5 \times 10^{8}\ \mathrm{cm}^{-2}$, $\mathcal{B}' = -5500\ \mathrm{cm}^{-1}$, $\mathcal{C} = -1530\ \mathrm{cm}^{-1}$). Hydrogen bonding solvents (open circles) are indicated by name. The remaining solvents (full circles) are indicated as shown below. In the following list of solvents, the refractive index and static dielectric constant of each solvent are quoted in that order. In a few cases, static dielectric constants are not available; values estimated from those for related compounds were used in the calculation, and the estimated values are given below in parentheses. The solvents are listed in the order in which they induce increasing red shifts.

H	Heptane	1.390	1.9	Ac	Acetone	1.360	21.0
Oc	Octane	1.391	1.9	ClB	Chlorobenzene	1.519	5.5
Ch	Cyclohexane	1.419	2.0	CD	Carbon disulfide	1.618	2.6
Dd	Dodecane	1.417	2.0	BrCh	Bromocyclohexane	1.491	7.9
EtE	Ethyl ether	1.345	4.4	ClT	p-Chlorotoluene	1.516	5.6
BuE	Butyl ether	1.393	(3.4)	An	Anisole	1.509	4.3
IpE	Isopropyl ether	1.363	(3.9)	PhE	Phenyl ether	1.574	3.7
AmE	Amyl ether	1.409	2.8	BrB	Bromobenzene	1.553	5.2
D	Dioxane	1.417	2.2	IT	o-Iodotoluene	1.603	(5)
B	Benzene	1.493	2.3	P	Pyridine	1.502	12.4
				IN	1-Iodonapthalene	1.695	(4)

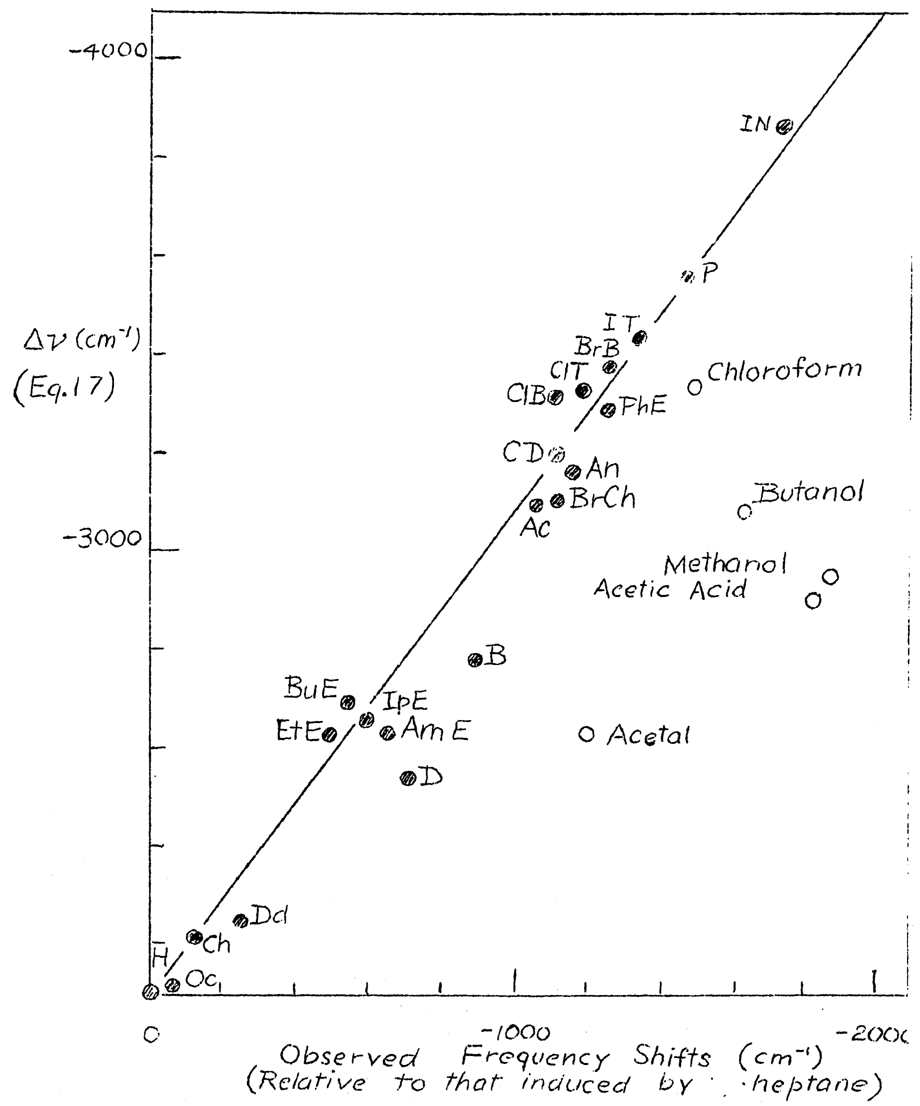
-4000
-3000
Δν (cm⁻¹)
(Eq. 17)
0
-1000
-2000
Observed Frequency Shifts (cm⁻¹)
(Relative to that induced by heptane)
IN
P
IT
BrB
ClT
ClB
PhE
Chloroform
CD
An
BrCh
Ac
Butanol
Methanol
Acetic Acid
B
BuE
IpE
EtE
Am E
Acetal
D
Dd
Ch
H
Oc

Fig 1

(Caption to Figs. 2a and 2b).

Fig. 2a (top). Variation of merocyanine band frequency with percentage of water in aqueous pyridine solvent. The abscissa is the frequency shift relative to the shift induced by pure pyridine. Curves are drawn for three merocyanine dyes, whose ground state dipole moments are considered to decrease in the order: IV $>$ V $>$ IX (see text). The optical data and dye notations are those of Brooker, Keyes and Heseltine[34].

Fig. 2b (bottom). Variation of band frequency with the reaction field, according to Eq. (18) ($\alpha_o^u - \alpha_i^u = 0.67 \times 10^{-23}$ cm^3, $M_{oo}^u - M_{ii}^u = 1.5, 0, -1.5$ Debyes). These curves are meant to illustrate the general behavior predicted by the theory. The numbers are considered to be of the correct order of magnitude (see text), but are otherwise arbitrary. The curves do not refer specifically to the dyes of Fig. 2a.

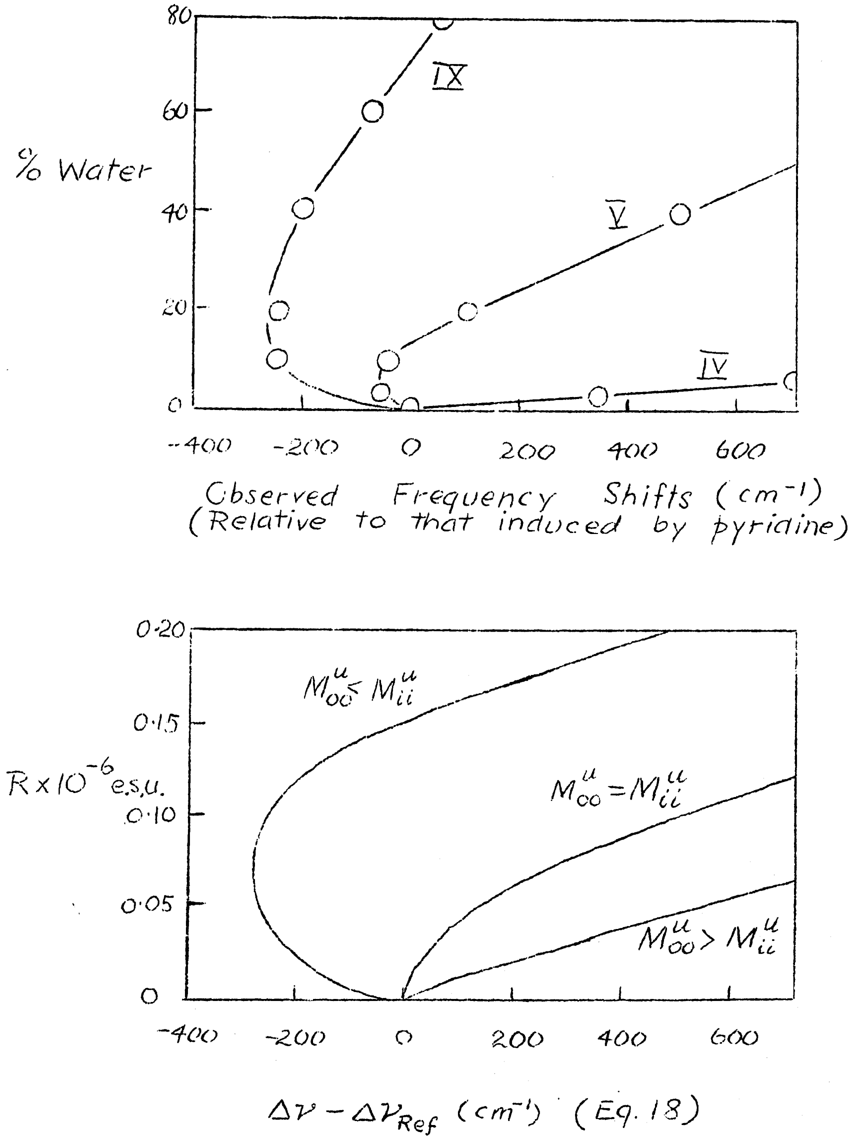
80
60
40
20
0
% Water
IX
V
IV
-400
-200
0
200
400
600
Observed Frequency Shifts (cm-1)
(Relative to that induced by pyridine)
0·20
0·15
0·10
0·05
0
R x 10-6 e.s.u.
$M^u_{oo} < M^u_{ii}$
$M^u_{oo} = M^u_{ii}$
$M^u_{oo} > M^u_{ii}$
-400
-200
0
200
400
600
$\Delta\nu - \Delta\nu_{Ref}$ (cm-1) (Eq. 18)

Fig. 2

25X1