PHOSPHORESCENCE IN HETEROSUBSTITUTED ORGANIC COMPOUNDS

by

FRANK CUTHBERT ADAM

A Thesis submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Science
in the
Department of Chemistry

We accept this thesis as conforming to the
standard required from candidates for the
degree of Master of Science.

Members of the Department of Chemistry.

The University of British Columbia

April, 1953.
ABSTRACT

A review of recent literature pertaining to phosphorescent studies was made and, on this basis, a mechanism was developed to explain the short-lived afterglow found in some organic compounds where $n \rightarrow \pi^*$ transitions occur.

An apparatus for measuring phosphorescent lifetimes was described with some of the results obtained thereon. The principal difficulties met with were also described.
ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Dr. C. Reid for the assistance and encouragement received from him during the course of this investigation.

I also wish to express my thanks to the Shell Oil Company of Canada for financial assistance given to me in the form of a Research Fellowship.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. General</td>
<td>1</td>
</tr>
<tr>
<td>II. Assignment of Long-Lived Emission to Triplet-Singlet Transitions</td>
<td>4</td>
</tr>
<tr>
<td>III. Spin-Orbit Coupling and the Triplet-Singlet Selection Rule</td>
<td>7</td>
</tr>
<tr>
<td>IV. Symmetry Selection Rules</td>
<td>9</td>
</tr>
<tr>
<td>V. $n - \pi$ Transitions</td>
<td>10</td>
</tr>
<tr>
<td>VI. Discussion</td>
<td>13</td>
</tr>
<tr>
<td>VII. Phosphorescence of Aliphatic Ketones</td>
<td>19</td>
</tr>
<tr>
<td>VIII. Nitrogen Containing Compounds</td>
<td>26</td>
</tr>
<tr>
<td>IX. Halo Substituted Compounds</td>
<td>28</td>
</tr>
<tr>
<td>Experimental Section:</td>
<td></td>
</tr>
<tr>
<td>X. General</td>
<td>29</td>
</tr>
<tr>
<td>XI. Oscilloscope and Detector Units</td>
<td>30</td>
</tr>
<tr>
<td>XII. Ultra-Violet Sources</td>
<td>31</td>
</tr>
<tr>
<td>XIII. Light Beam Interrupters</td>
<td>32</td>
</tr>
<tr>
<td>XIV. Sample Suspension</td>
<td>36</td>
</tr>
<tr>
<td>XV. Experimental Results</td>
<td>39</td>
</tr>
<tr>
<td>A. Calibration</td>
<td>39</td>
</tr>
<tr>
<td>B. Lifetime Measurements</td>
<td>40</td>
</tr>
<tr>
<td>C. Trinitrobenzene &quot;complexes&quot; with KCN</td>
<td>45</td>
</tr>
<tr>
<td>D. Solvent Studies</td>
<td>46</td>
</tr>
<tr>
<td>XVI. Discussion</td>
<td>48</td>
</tr>
<tr>
<td>XVII. Future Studies</td>
<td>50</td>
</tr>
<tr>
<td>Bibliography</td>
<td>52</td>
</tr>
</tbody>
</table>
I. GENERAL

The near ultra-violet spectra of conjugated organic molecules arise from the excitation of non-localized \( \pi \)-electrons from the higher bonding molecular orbitals (MO) to the lowest antibonding MO. Each transition involving different orbitals gives rise to a new absorption peak. The band at the longest wavelength corresponds to excitation of an electron from the highest filled bonding orbital to the lowest unfilled antibonding orbital. Each of the bands observed is allowed by selection rules, and involves large changes in charge distribution, for otherwise they are of low intensity. These strong bands may be observed in any phase, although they may show variation in vibrational structure, intensity and spectral distribution.

When the extent of unsaturation is increased, the potential field in which the \( \pi \)-electrons travel also becomes greater, so that the innermost molecular orbitals are lowered in energy, and their electrons more tightly bound. This results in large screening effects, so that electrons in the higher bonding orbitals are more loosely bound and therefore more labile. The opposite effect is observed for the antibonding orbitals. The net result is that the long wavelength band is displaced to the red end of the spectrum. This may be compared to the differences found between the members of the alkali or the halogen family in atomic spectra. Since the variation is not rapid for small changes in the conjugated system, the spectra of similar types of compounds vary but little, so that assignments of the bands appearing in hydrocarbons may be compared (1), or variconjugate sequences may be built up (2).
practice will be used extensively in this paper.

The result of the absorption act will usually leave the molecule in a state of high vibrational excitation, from which thermal energy will be dissipated before any other process occurs. The time lapse for this operation is very short compared with an emission process, where the electron drops back to the ground state. This being the case emission occurs at longer wavelengths than the corresponding absorption. In fact, so rapid is the thermal dissipation process, emission usually takes place from the lowest excited orbital, regardless of the part of the ultraviolet spectrum in which the original absorption act took place. The upper states are therefore more intimately connected than one would suppose from looking at an ultra-violet spectrogram. Thus, where as many bands may occur in absorption, only one, or possibly two, will appear in emission. The observation of these bands will depend largely upon the experimental conditions involved, since emission is a relatively slow process and is only one of several competing processes leading to deactivation of the molecule.

When only one band is observed in emission there appears a very strong resemblance between it and the lowest energy absorption band. The vibrational structure and intensity distribution will be very much the same, if one is reflected, as with a mirror, into the other. In other words, these two bands are "mirror-images" (3). Should two bands appear in emission, the lower band will usually (but not necessarily) be of mild intensity, and will have a distinctive after-glow. This may be interpreted to mean that the transition involved is "quasi-forbidden" and therefore of low probability. This emission band is very sensitive to
the experimental environment, as may be seen from a consideration of the rate constant for the process involved. This value may be calculated from the absorption spectrum by means of the formula:

\[ \int \varepsilon d\bar{\nu} = 3.47 \times 10^8 \times \frac{g_u}{g_e} \times \frac{12 \times 1}{n^2} \times \frac{1}{2} \times k_e \]  

where the left hand side is the integrated area of absorption, \( g_u \) and \( g_e \) represent the multiplicities of the states involved, \( n \) is the index of refraction of the solvent, \( \bar{\nu} \) is the absorption frequency (in cm\(^{-1} \)).

while \( k_e \) is the rate constant for the emission process. For most allowed \( \pi-\pi \) transitions the value of \( k_e \) is about \( 10^8 \) sec\(^{-1} \), while for multiplicity \( (g_u = 3, g_e = 1) \) forbidden transitions, it is less than one in the case of hydrocarbons. This \( \pi-\pi \) transition corresponds to the phosphorescent band and has an upper state with electron spins all paired but two, and a lower state where all electrons are paired. Such a transition is forbidden by multiplicity considerations. Since emission will be observed only when \( k_e \) is as large as the sum of the rate constants for all other non-radiative deactivating processes, the sensitivity of phosphorescence to external conditions may be easily appreciated. The rate constants for collisional deactivations are large so that observation of fluorescence, and in particular phosphorescence, is generally restricted to low pressure gas phase experiments, or to rigid glasses at reduced temperature.

To measure the lifetime, \( \tau \), of the phosphorescent after-glow one can find the rate constant for the absorption process by using formula (1) and setting:

\[ k_e = \frac{1}{\tau} \]

The value so obtained will be the "true" lifetime, and represents the
time required for the intensity of emission to fall to \( \frac{1}{\text{e}} \) of its original value. For molecules with mean lifetimes of greater than \( 10^{-4} \) sec., however, such a procedure is very inaccurate since the absorption bands are very small. Another method is to measure directly the variation in intensity as a function of time and to substitute the values so obtained into the equation:

\[
ke \leq 2.303 \frac{(\log I_0 - \log I)}{t_1 - t_0} = \frac{1}{\tau} \quad (2)
\]

where \( I \) is the intensity at time \( t_1 \). The inequality obtains in the presence of competing processes which tend to depopulate the upper state and hence produce smaller values for \( \tau \).

II. ASSIGNMENT OF LONG-LIVED EMISSION TO TRIPLET-SINGLET TRANSITIONS

The five basic papers on phosphorescence published in the last twelve years (3,4,5,6) have firmly established the fact that the triplet-singlet (T-S) transition is the principal cause of afterglow in non-crystalline super-cooled solutions of complex molecules. In these works the authors conducted their experimentation in such a manner that any postulated mechanism, other than that which they propose, cannot be considered without reservation. They have demonstrated that such hypotheses as ionization, crystal defects (4), distorted or tautomeric molecules, solvent effects, or bond redistribution mechanisms (5) could not be in accordance with the generality of the phenomenon.

In order to explain the high emission intensity of the phosphorescent band compared to the low probability of absorption Kasha (17) has suggested the use of a modified Franck-Condon potential energy diagram
(Fig. 1) in which each potential energy line is to be considered as a section of an energy hypersurface extending through an "n" dimensional space where n is the number of conjugated atoms. The initial absorption of light (A) raises an electron from the ground state (S) to the coordinate $S_1$ or $S_2$, presumably with high vibrational energy. This $S - S$ ($\pi - \pi$) transition is highly allowed and corresponds to the principal absorption band. Following the absorption (A) will occur the rapid vibrational cascade to the point where the triplet hypersurface (T) crosses that of the singlet ($S_1$). Since this intersection represents a condition of similar energy and interatomic distance for the two states, the electron may proceed to the zero-points of either the $S_1$ or T curves. If the former course is taken, then emission occurs out of the "fluorescent" band. On the other hand, emission from the T zero-point gives rise to the "phosphorescent" band, since this transition is T - S, and is forbidden by multiplicity.

The most important consideration of the above is the fact that the $S - T$ crossover takes place in a non-radiative manner and, as a consequence, is not appreciably affected by the multiplicity selection rule which applies only to optical (radiative) intercombinations. In actual practice there is a small effect because usually the fluorescence yield is much greater than the phosphorescence yield. This process will allow relatively high concentration of triplet state molecules to be built up as long as the $S_1 - T$ crossover is not too high on the $S_1$ hypersurface. On the other hand, if the $S - T$ crossover is very close to the triplet state zero point, then electrons which had originally entered T could be raised by thermal (vibrational) energy back over the $S_1 - T$
FIGURE I.

Energy Distribution of the Potential Energy Hypersurfaces.
crossover into the $S_1$ state, from which emission could occur spontaneously in the fluorescent band. Conceivably this could occur some time after the initial absorption act, and would endow the fluorescent band with the property of afterglow. This was called $\alpha$-phosphorescence by Jablonski (8) who discovered the phenomenon while studying the emission characteristics of dyes. Since $\alpha$-phosphorescence arises from thermal excitation it should have a strong temperature dependence, while the "true" or $\beta$-phosphorescence should not.

III. SPIN-ORBIT COUPLING AND THE TRIPLET-SINGLET SELECTION RULE

The selection rule which does not permit optical intercombination between states of dissimilar multiplicity is a fundamental rule of atomic spectroscopy (9) but is based upon rather idealized concepts regarding the total angular momentum of the atom. If there is assumed to be no interaction between the components of orbital angular momentum (1) and the components of spin momentum (s), then the $l$ values are coupled vectorially to give the total angular momentum $L$. Similarly the $s$ values are coupled to give the resultant spin momentum $S$. The total angular momentum results from combining vectorially the $L$ and $S$ components, to give the resultant $J$ value. The procedure is called Russell-Saunders or $(L - S)$ coupling. Within the confines of the assumptions made this principle must obey the "Law of Conservation of Spin Momentum", and accordingly all spins must remain paired through any electronic transition, or $\Delta S$ must equal zero. If, however, complete interaction between spin and orbital components is allowed, then the $l$-value is coupled directly to the $s$ value of each electron to give the resultant contribution $j$ to the total angular momentum. This is known as spin-orbit $\{j - j\}$ coupling, for
which term values and spin quantum numbers have no meaning. Clearly the situation which exists in reality lies between pure L - S and pure j - j coupling, since singlet-triplet transitions occur with measurable probability.

The result of a first order perturbation on the inter-combination probability for atoms and molecules is, according to McClure (10)

\[ \frac{1}{T_{3n}} = P_{3n} = P_{n} \left( \frac{h \omega}{\Delta E} \right) \left( \frac{\nu_{3}}{\nu_{1}} \right)^{3} \]  

(3)

where \( \nu_{3} \) and \( \nu_{1} \) are respectively the frequencies of ground to triplet and ground to singlet transitions, with probabilities \( P_{3n} \) and \( P_{1n} \). \( H_{13} \) is the matrix element of the spin-orbit operator, and \( \Delta E \) is the singlet-triplet spacing. Since the spin-orbit operator is not calculable for molecules, McClure uses the atomic \( \tilde{\gamma} \) values, where \( \tilde{\gamma} \) corresponds to the radial part of the atomic spin-orbit operator. The use of it presupposes radial symmetry, and its value depends rather strongly upon the atomic number of the particular atom being considered. McClure utilizes this condition of radial symmetry, and with extrapolated \( \tilde{\gamma} \) values, obtains crude estimates of lifetime (\( \tilde{T} \)) for carbon (0.003 sec.), nitrogen (0.004 sec.), and oxygen (0.0001 sec.). He further assumes that the heaviest atom in the system has the dominant effect on the lifetime.

McClure has suggested in a later paper (11) that the spin-orbit matrix elements may possibly cancel each other when aromatic hydrocarbons are considered. This could possibly account for the long lifetimes (ca 20 sec.) of these compounds. A more recent paper by Mizushima and Kiode (12) indicates that possibly the long lived benzene phosphorescence may be explained by assuming that a two step mechanism takes place.
This involves a transition from the lowest triplet to an intermediate singlet to ground. In this particular approach Dirac's relativistic quantum mechanics are used but yield McClure's results if spherical potential symmetry is assumed. The principal contribution to the lifetime comes from the transition between the triplet to intermediate singlet.

While the foregoing may serve to explain the case of aromatic hydrocarbons, nothing has appeared in print to show why heterocyclics should also have long lifetimes. Both of the hypotheses put forth for hydrocarbons assume that each atom is similar. In fact, the simplification of the relativistic terms which appear in the second paper depend upon this assumption.

IV. SYMMETRY SELECTION RULES

The second selection rule commonly met in molecular spectroscopy is one which varies from compound to compound and is determined only by their respective symmetry groups. Group theoretical considerations (13) show that for a dipole transition between states $A$ and $B$ the matrix element

$$
\int \psi_A \times \psi_B \, dx
$$

will be different from zero (allowed) only if $\Gamma A \times \Gamma B = \Gamma x$ where $\Gamma x$ is the irreducible representation of the polarization axis (x, y or z) and $\Gamma \psi_A \times \Gamma \psi_B$ is the direct product of the representations of the lower and upper orbitals respectively. If the above integral is zero then the transition is not allowed by symmetry. Vibrational perturbations may, however, disturb the symmetry of the molecule in such a manner that $\Gamma A \times \Gamma B \times \Gamma \text{vib} = \Gamma x$ and the transition becomes
allowed. The direct product \( \Gamma_\sigma \times \Gamma_\pi \) represents the vibronic (1\( \pi \)) (vibrational x electronic) upper state, since excitation usually occurs from the zero point of vibrational energy. Bands which gain intensity in this manner are not usually strong. The long-wave absorption of benzene at \( \lambda 2900 \) has been attributed to a symmetry forbidden transition \( (15) \). Similarly, Mulliken (1\( \pi \)) has assigned the long wavelength aliphatic carbonyl band to be of this type.

Since symmetries are based upon idealized structures (e.g., valence bond) where all hybridization is assumed perfect, then if in reality these bonds are distorted in the ground state for some reason or other, any higher symmetry ascribed to such a molecule must be regarded as a first order approximation. In this way some \( \sigma \) bonds may be considered to have \( \pi \) characteristics and vice versa, and dipole transitions which may be forbidden for the "pure" \( \pi \) structures may become slightly allowed for the real structure with \( \sigma \) character.

V. \( n - \pi \) TRANSITIONS

When atoms of hydrocarbons are substituted by heteroatoms very often new absorption bands appear which can only be ascribed to the presence of heteroatoms. Thus aliphatic aldehydes and ketones have absorption peaks at about \( \lambda 2900, \lambda 1900, \) and \( \lambda 1700 \), while the corresponding ethylenes only have a band in the \( \lambda 1900 \) region. Mulliken (1\( \pi \)) has suggested that the \( \lambda 2900 \) and \( \lambda 1900 \) bands might be caused by excitation of the non-bonding (n) electrons in the oxygen atomic orbitals into the excited state molecular orbitals. This possibility arises due to the large electron affinity of the oxygen atom which gives rise to highly polar bands, with resultant shift of the electronic centre of gravity.
towards the heterocatom. This results in looser binding of all the oxygen valence electrons. Electron impact experiments of Jowitt (16) and vacuum spectrograms of Walsh (17) indicate that the ionization potential of the "n" electrons has been lowered from 17 ev. in oxygen to 11 ev. in acetone. This compares to about 14.4 ev. for the ionization potential of the \( \pi \) electrons.

The assignments given by Mulliken for acetone are as follows:

- \( \lambda 2900, n - \pi \), symmetry forbidden;
- \( \lambda 1900, n - \sigma \), allowed by symmetry,

and representing excitation to an antibonding \( \sigma \) orbital lying along the CO bond. The \( \lambda 1700 \) band is the allowed \( \pi - \pi \), corresponding to the \( \lambda 1900 \) band of ethylene. This band is, in the case of acetone, displaced to shorter wavelength due to the higher potential field in which the \( \pi \) electrons travel.

McMurry (18) has shown that the same situation exists for higher aldehydes and ketones. According to Platt (1) the \( n - \pi \) band shifts to the red only about half as fast as the lowest \( \pi - \pi \) transition with increase in extent of conjugation, so that in larger systems the \( n - \pi \) transition is hidden beneath the lowest \( \pi - \pi \) band.

The same situation exists for other systems containing thioketo, nitroso and similar groups. According to Platt atoms containing "n" electrons when affixed to a \( \pi \) system of a given size, give rise to bands which appear at progressively smaller frequencies in the order -COOH, -C=N-, -NC2, -C=N, -C=O, -N=N-, COCO, -N=O, where the -COOH and -NO2 bands are about 15,000 cm\(^{-1}\) higher than the corresponding -C=O and -N=O bands, respectively. The triplet states associated with these (singlet) bands should show roughly the same correspondence. However, the most
important consideration is the fact that these heteroconjugates, because they are different from carbon, introduce spin-orbit factors which may appreciably affect the triplet-singlet transition processes for the molecule.

McGonnell (19) has shown that one possible criterion for distinguishing between $n \rightarrow \pi$ and $\pi \rightarrow \pi$ transitions is by the use of solvation effects, as first suggested by Kasha (20). Solvent molecules aggregate about a polar heterosubstituted molecule in the ground state in a manner most likely to lower the energy of the system. Upon excitation, where a localized $n$ electron is shifted to a non-localized MO with the consequent decrease in dipole, the solvent-solute system no longer has a minimum energy distribution. Thus the interaction may be considered to be repulsive with respect to the excited molecule. Furthermore, this effect should be more pronounced with more polar solvents, so that a blue shift of $n \rightarrow \pi$ bands may be observed while changing solvents from, for instance, hexane to water. On the other hand, $\pi \rightarrow \pi$ transitions exhibit a red shift, or a very weak blue shift when the same progression of solvents is used.

Another possible explanation in the view of the author of the present paper, could be a protonation effect of the heteroatom, which would lower the ground state relative to the upper state. In the case of $\pi \rightarrow \pi$, the reverse would hold since, in general, the upper state is the polar structure while the ground state is the covalent structure. $n \rightarrow \pi$ transitions usually give rise to rather weak bands even when allowed by selection rules, so that when intensity relationships are considered along with solvation effects, then very reasonable band
VI. DISCUSSION

There have appeared recently a number of papers which are relevant to the problems involved in the study of phosphorescence. Some of these have already been referred to under the subject of $n \rightarrow \pi$ transitions. However, perhaps the most important of these recent papers was that of McClure (21) who showed the importance of quantum yield determinations in the estimation of the true lifetimes of organic compounds. This may be seen from the formula:

$$T = T_0 \frac{(1 - \phi_f)}{\phi_p}$$

where $T$ is the true lifetime and $T_0$ is that lifetime found by intensity vs. time relationships. The factor $(1 - \phi_f)$ represents the number of electrons in the triplet state. This is the difference between the number of photons absorbed minus the number which have fluoresced. The ratio of this value to the number of photons emitted in the phosphorescent band gives the probability of deactivation by non-radiative channels. The determination of these fluorescent-phosphorescent yields is usually very difficult and relatively few absolute yields have yet been published. Although qualitative estimates may be made in some cases, usually recourse must be made to experiment. In any case, some of the arguments in McClure's earlier spin-orbit paper are somewhat weakened when existing values of quantum yields are used to correct the experimental lifetimes found there. Consideration of these factors has led the author of the present paper to review and reorganize some of the existing data and try to explain a few
Perhaps the most striking feature of many compounds with short lifetimes is the fact that the phosphorescent bands are intimately associated with the \( n - \pi \) transitions which appear in absorption. In many cases the absorption and phosphorescent bands bear mirror-image similarities to each other, as for instance in biacetyl, benzophenone and nitrosoethane. In each of these cases, and for most of the other examples studied from this point of view, the \( n - \pi \) transition appeared as a separate band in absorption, and was never concealed under the main \( \pi - \pi \) system. On the other hand, whenever the \( n - \pi \) band is concealed by the principal \( \pi - \pi \) band, then usually long life-times were observed. Two compounds showing this characteristic long afterglow and hidden \( n - \pi \) bands are \( \beta \)-methyl naphthyl ketone and benzoic acid.

Such a correlation could be interpreted to mean that the lifetime is dominated by the lowest forbidden transition of a molecule. Thus if the hydrocarbon triplet-singlet emission band lies below that of the \( n - \pi \) triplet-singlet, then long life-times might be expected. This state of affairs is shown \(^{10}\) both by biphenyl compounds and by methyl phenyl and, as mentioned, methyl naphthyl ketones. In the first case, \( o, o' \)-difluoro diphenyl has a lifetime of \( 0.88 \pm 0.4 \) sec. While the corresponding para isomer has a lifetime of \( 3.2 \pm 2 \) sec. This value is similar to that of the parent hydrocarbon, \( 3.6 \pm 2 \) secs. In the ortho compounds the rings are not coplanar so that there is a blue shift in the \( \pi \)-spectrum compared to biphenyl. This presumably exposes the \( n - \pi \) band of the fluoro compound. For the case of the ketones the measured lifetimes run 2.6 seconds for naphthalene, 0.95 seconds for methyl naphthyl ketone and
0.006 seconds for acetophenone.

Recent work in this laboratory (22) has indicated that the use of the high atomic number salts of fluorescein produces no change in the transition probabilities due to spin-orbit forces. This implies that spin-orbit effects are somewhat dependent upon the extent to which the heteroatom enters into the mesomeric system, and therefore should not be too pronounced in compounds such as halo-substituted benzenes. The lack of atomic number effect reported by McClure for 1-halo,1-nitroso cyclohexanes, therefore, seems to be reasonable, since there is little overlap between the halo atom and the nitroso \( \pi \)-system, since the valency structure of the carbon atom is tetrahedral. Apart from this, McClure has ascribed the entire nitroso \( n \rightarrow \pi \) band to be due to a triplet-singlet transition. This is not likely. The same objection may be raised against the assignment made by Lewis and Kasha (4) for nitrosobenzene. These compounds behave essentially the same as carbonyl compounds in that usually only one emission band is observed and this band has, in principal, measurable phosphorescent afterglow characteristics. In fact, the same usually applies to any emission process which may be associated with the \( n \rightarrow \pi \) process in absorption. One exceptional group of compounds are the nitrogen heterocyclics which will be dealt with in a little more detail in a later section.

The energy levels predicted by simple molecular orbital theory occur in degenerate singlet-triplet pairs. When inter-electronic forces are considered, the levels are split, so that the singlet level rises and the triplet level falls in energy, so that the calculated energies predict the centre of gravity of the two levels. Configurational interaction
further splits the pair (23). The net spreading of the two levels generally amounts to about 10,000 cm.\textsuperscript{−1} in the case of aromatic hydrocarbons (7). Clearly, for these compounds the splitting between the first excited singlet and the first triplet state is primarily a function of the electronic spins involved, and not so much a function of the electronic charge, since in each case this value is constant. Both the singlet ground state and the excited states have electron distributions which are spread over a large number of the atoms in the system, consistent with the LCAO (linear combination of atomic orbitals) approximation.

When excitation of localized electrons takes place, as in an n → π transition, the situation must be somewhat different. If a heteroconjugated compound loses one non-bonding electron by ionization, say, then the effective positive charge is localized upon the heteroatom, whereas excitation of a non-localized electron leaves a positive "hole" distributed over a wider range. The former process would involve quite drastic rearrangement of the nuclear coordinates of the atoms adjacent to the heteroatom, while the second case the effect is felt by each atom, and accordingly, the shift in interatomic distances should be slight. Thus the two processes might conceivably have marked differences in effect. Should excitation take place to intermediate orbitals, with no ionization, the same arguments should hold, but to a lesser extent. Since electronic transitions which occur with large changes in nuclear coordinates are unlikely, from Franck-Condon arguments, we are forced to the conclusion that the electrons involved in an n → π transition must remain largely localized on the heteroatom to which they were affixed in the ground state. In other words, the process is essentially atomic and may be considered as
a modified Rydberg transition with an upper state determined by the molecular orbital rather than one of the respective atomic orbitals. The two electrons in such transitions are therefore held quite closely together by virtue of the nuclear charge of the heteroatom, regardless of their relative spin characteristics.

The spin orbit coupling operator will mix triplet and singlet states strongly (consistent with the atomic number) when only atoms are considered. This will lead to convergence of the two states, since the spin properties which caused the initial separation are no longer discrete quantities. Clearly the application of these atomic characteristics to molecules will depend upon how much the molecular process departs from that found in atoms. Therefore the extent of splitting will depend upon the extent to which the electron in the upper molecular orbital (i.e. "intermediate atomic orbital") is retained in the vicinity of the heteroatom. Obviously this will be a function of the electronegativity of the atom. This leads to the supposition that the amount of spin-orbit coupling, as well as the triplet-singlet splitting, is strongly dependent upon the electronegativity of the heteroatom as well as the atomic number.

The situation may be represented in a diagramatic way as in Fig. 2. These illustrations show the electronic levels of the ground states and first excited state, with potential energy as the ordinate and interatomic distance as the abcissa. They are crude approximations to a free electron model.

The appearance of short lifetimes therefore depends upon three factors; whether or not an \( n \rightarrow \) transition is involved in the lowest excited state of a molecule, whether or not the \( n \)-atom has a high atomic
Energy levels involved in excitation of electrons in different systems.

FIGURE 2.
number and, lastly, what the effective electron affinity of the n-atom is with respect to the rest of the molecule. To show the trend of these postulates it is possible to compare the effects caused by elements of the first row, where the electronegativity increases rapidly, and the atomic number increases slowly. Similarly one can compare members of a single periodic family with slowly varying electron affinity and rapidly changing atomic number. The latter plan is difficult in view of the fact that the halide family is the only one that is reasonably complete but suffers from the limitation that the halo atoms can never become formal members of a mesomeric system due to their unitary valency state.

VII. PHOSPHORESCENCE OF ALIPHATIC KETONES

As was mentioned in the previous section, some of the results of McClure's original spin-orbit paper (10) are somewhat in doubt. One such argument that is weakened is the assignment of the 51,000 cm$^{-1}$ transition as the principal perturbing singlet to the phosphorescent band of the lower ketones. This interpretation was based upon a correlation between oscillator strengths ($f$) of the emission bands and those appearing in absorption at 1900 Å. Since the $f$-values are found by the formula $f = 1.5/\nu^2\tau$, in which uncorrected lifetimes were used, the correlation may be in part fortuitous, since corrected ketone lifetimes show little variance (20). The transitions involved in emission probably are $n - \pi$, and the associated $n - \pi^*$ transitions. Previous considerations of spin-orbit coupling would cause considerable "mixing" of these two bands, so that the principal perturbing singlet might therefore be the $n - \pi^*$ 35,000 cm$^{-1}$ band, and not, as previously supposed, the $n - \sigma$ band at 51,000 cm$^{-1}$. Unfortunately a calculation by equation (3) is difficult since the evaluation of $\Delta E$ is
critical and cannot be ascribed with certainty.

Any explanation offered to account for the peculiarities in emission spectra of the carbonyl compounds must also be consistent with the concepts of spectroscopy as well as with the many results obtained by Noyes, Kaskan and coworkers (24-29) from their studies on vapor phase fluorescence of acetone and of biacetyl. The salient points found in these papers and which must be explained are:

1. Acetone has a short lived (10^{-6} sec.) and long lived component (10^{14} sec.)

2. Phosphorescent lifetime (\tau) varies with temperature and pressure. Increase in 25° decreases \tau by a factor of two.

3. Predissociation or other photochemical processes are involved, producing biacetyl, among other products.

4. Temperatures from 120°C. to 150°C. result in loss of fluorescence structure. The wavelength maximum also shifts from about 4525 Å to about 4300 Å.

5. Oxygen at pressures of 20 to 100 mm. at room temperature caused the same effects as (4).

6. Nitrogen has no effect upon structure or frequency maximum.

7. Stern-Volmer plot of reciprocal fluorescence efficiency (1/Q) versus pressure of acetone yields straight line only over 300°C., but over a certain pressure (ca 40 mm.) between 200°C. and 300°C. a straight line is obtained.

8. Q is independent of intensity.

9. As oxygen is added, 1/Q rises sharply to constant value; as temperature is raised the variation in 1/Q becomes smaller, until 200°C.,
when no further change is noted. This constant value is roughly independent of temperature and tends to be higher with increased acetone pressures.

(10) Nitric oxide has the same effect. It quenches wavelengths longer than 4500 Å most efficiently.

(11) Neither H₂ nor N₂ cause any change at all.

(12) A mixture of biacetyl at 80 mm. and acetone at 200 mm. show no structure at room temperature.

(13) Iodine reduces quantum yield for decomposition. In addition the absorption spectrum should be noted to have very little structure (30) and that photodecomposition can only be observed on the high frequency side of the n → π band.

The primary supposition is that a symmetry forbidden n → π transition is involved. If such is the case the (o - o) vibrational bands will not be present, and the lowest frequency in absorption will be due to a (o - ω) transition, where ω is the quantum number of the vibrational perturbation which makes the transition allowed. Analogously, the highest frequency in emission will also be (o - ω), except that now the vibration belongs to the ground electronic state. In this manner there will be a spacing between the emission and absorption bands of approximately 2ω cm.⁻¹ where ω is the lowest normal vibration leading to the perturbation. Formaldehyde, which has the same symmetry as acetone, has γ-polarized absorption bands (32). Other considerations indicate that acetone has the same polarization characteristics. Such being the case, the perturbation must be a carbonyl bending vibration which, for acetones, has the value 528 cm.⁻¹ (33). This leads to an absorption-fluorescence spacing
of roughly 1000 cm$^{-1}$ and corresponds closely to the minimal value obtained experimentally.

Assuming, therefore, that the transition involved is indeed $n \rightarrow \pi$ then the effect of spin-orbit coupling must be expected. As previously mentioned, the most likely of the possible states to be "mixed" are the $n \rightarrow 1 \pi$ and $n \rightarrow 3 \pi$. A consequence of this is that the two states should be quite close together in a Franck-Condon hyperspace. One possible model is shown in Fig. 3.

Excitation takes place by (A) in the normal manner, to the hypersurface, from which point vibrational energy may be dissipated so that the electron reaches the $1 \pi$ or $3 \pi$ zero points ($1 \pi_0$ and $3 \pi_0$) without radiation. Fluorescence will occur from $\pi_0$ when the correct vibrational perturbation occurs, and with a mean lifetime of about $10^{-6}$ second.

Phosphorescence may occur from the $3 \pi_0$ level with a longer mean lifetime since such a transition is doubly forbidden. The lack of structure in absorption is principally due to the fact that the vibrational levels are not discretely spaced, because of mixing of the two states in the area indicated within the circle. This mixing results in removal of the classical turning points of a harmonic oscillator, such that the resultant oscillator is now anharmonic in a most unpredictable way. Most of the structure in fluorescence should come from the $3 \pi \rightarrow n$ transition, since surely the $3 \pi_0$ is the lowest lying state and therefore least affected by mixing.

The dashed curve ($3 \pi^*$) in Fig. 2 represents the $3 \pi$ state along a different choice of interatomic coordinates. In this particular section of hyperspace, the triplet state molecule is unstable to certain undetermined modes of vibration, and dissociates spontaneously into two molecular
Figure 3.

Distribution of Energy Levels in Acetone
fragments, presumably free radicals (31). Thus bond rupture may result from the initial absorption act (predissociation) or by subsequent thermal excitation of the triplet state molecules. The quantum yield of photodecomposition is probably quite high, even at room temperature. Since the emission from the discrete band is also reasonably intense, then thermal decomposition must account for a large percentage of the product formed, in absence of chain reactions. Continuum begins at 3000 Å (31) so the asymptote to the \( ^3\text{K}^* \) state is known relative to the ground state. Below this level a rearrangement mechanism is reported to take place (34) but the end products appear to be the same, so that distinction between this and the thermal process mentioned above cannot be considered as a serious objection.

At elevated temperatures, the thermal dissociation, collisional deactivation and repopulation of the \( ^1\text{K}^- \) level all serve as competing processes to the \( ^3\text{K}^- - n \) transition, which is, as mentioned, chiefly responsible for the structure observed in emission. The last process named will shift the emission maximum to the blue, although the same effect would be observed if the remaining two processes completely deactivated the triplet state. However, since oxygen produces the same effect at room temperature, such a proposition may be discarded. The action of oxygen and nitric oxide is indeed interesting. Both these substances are known to be paramagnetic and, as such, are liable to upset the singlet-triplet transition probability to a marked extent (35). Conceivably this would have a much more profound effect upon the singlet-triplet crossover probability than it would upon the triplet-singlet radiative process, since the former case is only partly affected by selection rules (36). If this is the case,
then the observed results follow.

The effect of biacetyl in removing the fine structure is probably due to an energy transfer process involving intermolecular collision. The energy of the acetone triplet state molecule is of the correct order of magnitude for such an occurrence, since the emission bands of acetone overlap the absorption bands of biacetyl.

The fluorescent yield data are all consistent with the proposed mechanism. The values are expected to drop with increase in pressure, (concentration quenching), temperature (thermal decomposition) and oxygen content (predissociation). A recent paper (29) apparently overlooked this last possibility, so that the conclusions drawn up there are left in some doubt.

The reason for the effect caused by iodine is rather more difficult to ascertain. Since methyl iodide is formed, at least part of the free methyl radical produced is lost to this source, but does not necessarily account for lower quantum yields. In view of the solubility and color of acetone-iodine systems, complex formation seems a likelihood (37). Whether or not such a complex would have a different predissociational threshold from that of pure acetone is not known. A recent paper by Reid (38) indicates that sizeable concentrations of triplet state molecules may be built up when complex formation takes place, and that these complexes cause abnormal break-down of selection rules upon photodissociation. This is due to the strongly asymmetrical electric fields set up by the complexing molecule. Such could easily be the case here, although relevant lifetime measurements would have to be made. The absorption process is primarily a property of the complex, while emission
takes place from the lowest excited orbital of one of the components which originally formed the complex. Whether or not this would minimize the amount of predissociation is not known.

VIII. NITROGEN CONTAINING COMPOUNDS

Pyridine has an \( n-\pi \) transition which appears as a sidehill on the \( 39000 \text{ cm}^{-1} \pi-\pi \) transition. Absorption spectrograms done in the gas phase (39) place the \( \pi-\pi \) transition between 3000 and 3300 A, while the \( n-\pi \) transition which appears only in the liquid phase lies between 3600 and 4000 A. There are three diffuse maxima at 25500, 26490 and 27500 cm.\(^{-1}\) which disappear in acid solution. These three peaks appear as the strongest lines of the phosphorescent spectrum and therefore correspond to the lowest excited state of the pyridine molecule. An upward limit of the integrated absorption strength of these three bands may be placed at unity, although in all likelihood the value is much smaller. This leads to a mean lifetime of at least one second. By equation (1) and (3) the integrated \( n-\pi \) absorption may be calculated to have an area of about \( 3 \times 10^4 \), which is too low by at least a factor of two, consistent with the minimal lifetime chosen. The \( n-\pi \) may therefore be considered to be the principal perturbing singlet to the \( n-\pi \) transition. The spectral separation of these two bands (\( \Delta \lambda \)) is 8,500 cm.\(^{-1}\).

The three diazines have more distinct \( n-\pi \) bands, being fairly well resolved from the main \( \pi-\pi \) system (40). Pyrazine has an emission band with maxima about 26300, 25800, 25100 and 24400 cm.\(^{-1}\) as determined in this laboratory. The assignment of these bands is difficult in the absence of long path length absorption spectrograms, but since the band system shifts but little from that of pyridine, the \( \pi-\pi \) band must be
expected to be approximately in the same spectral region (3000 to 3300 Å). Whether or not the phosphorescent band corresponds to this emission in part or in entirety cannot be ascertained without knowledge of the \( n - {^3\pi} \) band in absorption. If the emission should be due principally to the \( n - {^3\pi} \) transition, we are led to a separation of \( n - {^1\pi} \) and \( n - {^3\pi} \) of not more than 4,000 cm\(^{-1}\) with a consequent increase in spin-orbit effect due to the nitrogen. The splitting may be lower in this case due to the fact that two nitrogens in the ring are "pulling" electrons toward them, whereas in pyridine there is only one. Coupled with the fact that the \( n - {^1\pi} \) band has about a tenfold increase in integrated area for the diazines over that in pyridine, we are led to the shortened lifetimes observed by McClure, with which qualitative agreement is found in this laboratory.

The case of nitro and nitroso compounds should be considered here. Nitroso aromatic compounds compare to the carbonyl molecule previously discussed, but the \( n - \pi \) transitions of these compounds appear quite close to the limit of photographic plates (11,000 cm\(^{-1}\)) and well beyond the limit of most photomultiplier tubes. Accordingly, no lifetimes for these compounds have been noted. One substituted nitroso methane, however, has a slightly lower absorption region (14,500 cm\(^{-1}\)) and emission (13,600 cm\(^{-1}\)) according to Lewis and Kasha (4). This leads to a triplet-singlet separation of some 1,000 cm\(^{-1}\), less than that of heterocyclics, but greater than that of a ketone.

The nitro group is extremely deficient in electrons. Spin-orbit effects should be large, and \( T - S \) splitting small. The \( n - \pi \) should be fairly far toward the blue. S-trinitro benzene, according to McConnell (19) has an \( n - \pi \) transition at 4,000 Å well to the blue of the longest
transition. Presumably the same holds true for nitrobenzene, since the lifetime is estimated to be between 0.01 and 1 second (3), but this compound has a very poor quantum yield so that the lifetime must indeed be much longer. Since the $n \rightarrow \pi$ transitions in these compounds are not the lowest electronic process, and since not much splitting of $T - S$ levels is expected by previous assumptions, then as a consequence long lifetimes for these compounds are expected when quantum yield corrections are made. These corrected lifetimes should therefore correspond to that of a hydrocarbon with approximately the same degree of unsaturation, and conversely.

IX. HALO SUBSTITUTED COMPOUNDS

These compounds are difficult to deal with, since the precise nature of interaction with the conjugated system is not fully understood. That hyperconjugation effects are present cannot be denied. Presumably these effects are a balance between the electronegativity and the atomic polarizability of the halogen atom. Only one thing is certain, fluorobenzene has no detectable afterglow, while the other halogens have afterglow but no fluorescence. With the exception of fluorobenzene all have poor phosphorescence yields. Fluorobenzene also has a higher oscillator strength than the parent hydrocarbon or of any of the other halogen compounds. Estimations of the corrected bromobenzene lifetime lead to a result which is about six times that obtained from the well resolved (supposed) $T - S$ band. Although this admits to other explanations, it seems to indicate, by the arguments used for carbonyl compounds, that an $n \rightarrow \pi$ band of little splitting has occurred, so that the emission is again a combination of $\alpha$- and $\beta$-phosphorescence. Whether or not an $n \rightarrow \pi$ transition should occur at such long wavelengths and with such
little splitting is indeed a moot question. If interaction with the ring is small, then the effective electronegativity might be quite large, but quite reasonable objection could be raised against such a proposition. However, this effect should be more pronounced in the other higher members of the series, namely, chlorine and fluorine. Indeed the fluorine compound has no detectable lifetime, while chlorine analog has a mean life of 0.1 sec. (corrected). Thus the arguments seem to hold in a most qualitative sense. The low oscillator strengths for these proposed \( n - \pi \) transitions (which are formally allowed by symmetry) may be explained by using modified Franck-Condon arguments.

EXPERIMENTAL SECTION

X. GENERAL

Most of the methods that have been developed to measure phosphorescent lifetimes by the direct method of determining the intensity vs. time relationships utilize four basic components to produce, detect and display the phenomenon. Broadly speaking these are as follows; first is the ultra-violet light source, followed in turn by a light beam interrupter, detector and finally a cathode ray oscilloscope (CRO) which takes the interrupted signal from the detector tube (usually a photomultiplier tube) and displays the intensity vs. time curve directly upon the screen. Sometimes the order of the first two components is reversed so that the power input of the light source is intermittent. Inherent in the generation of square-wave illuminating sources is the main problem associated with lifetime measurements, regardless of which of the two
variations is used.

One type of apparatus is that described by McClure (10). The output of a commercial carbon arc was collimated and focussed upon one of two half sector discs which were mounted upon a common shaft. The sample was situated between these two discs and the phototube placed behind the last sector. These discs were set in such a manner that the light beam, after passing through the first slot, illuminated the sample. As the shaft turned just as soon as the incident beam was "chopped" by the first sector, the slot in the second disc allowed any phosphorescent afterglow arising in the sample to reach the phototube. The shaft was driven by a 30 cps. synchronous motor, and the sweep frequency of the CRO set at 60 cps. Around the periphery of one disc were twenty equally spaced notches, which ran between the poles of a small electromagnet. This changed the flux and thereby gave rise to a signal every 1/600 of a second. In this manner three signals were observed on the CRO screen simultaneously, the decay curve of the phosphorescent sample, a zero intensity base time and the time calibration "pips". Such an apparatus appeared to be relatively easy to set up with readily available materials and to be just as applicable and effective as other more expensive and elaborate methods mentioned in the literature. Accordingly, work was begun to construct such an apparatus.

XI. OSCILLOSCOPE AND DETECTOR UNITS

A Du Mont type 303 high-gain, wide band, cathode ray oscilloscope was used in these experiments. This instrument has rapid following characteristics with a vertical amplifier which will degrade a 0.01 µsec.
rising time not more than 0.03 $\mu$sec. The sweep circuit contains a delay line of 0.25 $\mu$sec to obviate difficulties in sweep starting times. Time calibration circuits are built in so that signal time characteristics may be estimated from damped oscillations of 100, 10, 1, and 0.1 $\mu$sec. peak to peak, within $\pm$ 3%. This CRO is also equipped with a 35 mm. fixed focus recording camera. The photographs taken were enlarged 35 times by an enlarger built in this laboratory.

The calibration dials were checked against a Hewlett-Packard Oscillator, model 2020. This device is reputed to be accurate to within a 1% error.

The phototubes used were RCA Radiotron 931A, with an S-4 response. These are eleven stage photomultiplier tubes using a 1000 volt activating potential. The output of the phototube was connected to the $Y$-input terminal of the CRO by coaxial cable to reduce extraneous pickup to a minimum.

XII. ULTRA-VIOLET SOURCES

A number of different irradiation lights were used. It became quite apparent early in the research that selection of possible sources was limited to those using direct current. This is in itself very unfortunate, since in the absence of expensive equipment such sources are of extremely low wattage output. This restriction is necessitated by the fact that if AC sources are used and the light beam interrupter is not synchronized with the exact 60 cps. or some multiple thereof, there occurs an interference phenomenon which causes fluctuation of the incident intensity. This results in vertical wandering of the trace which is being displayed upon the screen of the CRO.
Carbon arcs have a rather limited ultra-violet output, but a very constant intensity. Iron arcs give a reasonable amount of ultra-violet radiation, but tend to sputter, yielding a trace which "jitters" considerably. Aluminum, copper and magnesium have the same limitations. A compromise can be reached to some extent by using a carbon (upper) cathode and iron anode. This couple may be used to advantage in some situations. A low pressure DC mercury arc was also constructed, but it gave an irregular output which was incapable of being properly focussed.

The use of spark discharges was also investigated. These were obtained by shorting a 20 μF condenser, charged to 1000 v., between two magnesium terminals. The illumination was fairly intense but, as will be seen later, was of no great consequence with respect to resolution of the problem.

The use of such low intensity sources immediately present difficulties with respect to the optics of the system, since light losses by scattering and reflection must be cut to an absolute minimum in order to obtain a signal of reasonable intensity and stability. This particular phase of the work occasioned considerable difficulty, and required a large percentage of the time spent in doing this present research. However, a certain amount of success was attained in reducing light losses to a minimum.

XIII. LIGHT BEAM INTERRUPTERS

Two different methods of generating squarewave illuminating sources. The first of these was patterned essentially after the previously described apparatus of McClure, except that the CRO time calibrating circuits were used rather than the magnetic impulse method.
The straight drive coupling upon the original apparatus as received from the workshop was replaced by a step-pulley V-belt linkage. This gave a unit with variable speeds and appreciably less vibration. The original light gauge copper sectors were replaced by \( \frac{1}{8}'' \) copper discs, with a slot of \( 90^\circ \) of arc cut beyond the \( 4'' \) radius. The discs were then carefully balanced on level knife edges. A light-tight box was also constructed in such a manner as to divide the unit into three parts. One contained the arm, the second the sample and discs, and the last contained the phototube housing. After a little use, however, the brass journals showed signs of excessive wear, and gave rise to an anharmonicity of revolution, such that synchronization with the sweep frequency of the CRO could no longer be obtained.

Accordingly, two ball bearing mandrels were ordered. One was mounted a \( 3/8'' \times 19'' \) aluminum disc with 60 radial teeth cut into the periphery. With this disc it was hoped to reduce the lower limits of lifetimes detectable by the present method. While the teeth were cut with the absolute minimal tolerance of professional gear-cutting machinery, they were still not absolutely true, so that the recurrent traces displayed upon the CRO were not exactly repetitive. Upon the second mandrel was mounted an aluminum base \( 10'' \) phonograph recording, slotted through \( 90^\circ \) of arc at the \( 8'' \) radius. The traces obtained from this generator were very clear and, in general, the operation was very smooth. The range of lifetimes which could be measured using this machine were those between about 0.1 and \( 10^{-3} \) seconds. Very few compounds had lifetimes within this range. The arrangement of the apparatus may be seen in Fig. 4.

The lower limit of lifetimes which could be measured is set by
**Table of Components**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Arc Source</td>
</tr>
<tr>
<td>2</td>
<td>Screen</td>
</tr>
<tr>
<td>3</td>
<td>Water Filter</td>
</tr>
<tr>
<td>4</td>
<td>Quartz Lens</td>
</tr>
<tr>
<td>5</td>
<td>Iris Diaphragm &amp; Filter</td>
</tr>
<tr>
<td>6</td>
<td>Interrupter Disc</td>
</tr>
<tr>
<td>7</td>
<td>Ball Bearing Mandrel</td>
</tr>
<tr>
<td>8</td>
<td>1/4 H.P. Motor</td>
</tr>
<tr>
<td>9</td>
<td>Quartz Dewar</td>
</tr>
<tr>
<td>10</td>
<td>Phototube Housing</td>
</tr>
<tr>
<td>11</td>
<td>High Tension Lead</td>
</tr>
<tr>
<td>12</td>
<td>Signal Lead</td>
</tr>
<tr>
<td>13</td>
<td>1000 V. Power Pack</td>
</tr>
<tr>
<td>14</td>
<td>Oscilloscope</td>
</tr>
</tbody>
</table>

**Figure 4.**

Arrangement of Apparatus
the speed of the disc. To increase this speed above 3600 rpm. involves some personal hazard, as well as introducing an excessive flutter on the displayed signal. Since it was desired to reduce the lower limit of the lifetime range by another factor of a hundred or so, methods other than those described have been investigated quite recently.

Instead of attempting to synchronize the sweep frequency of the CRO with the frequency of revolution of the disc, it proved possible to use the output of the phototube to trigger the sweep of the CRO as well as to provide a signal for the Y-input. This may be done by keeping the grid bias of the gating multivibrator tube V-205-A such that it cannot conduct until triggered by a potential in the opposite sense. This potential can be provided by the signal from the phototube. Accordingly, the signal lead is passed first to the Y-input of the CRO and then to the external triggering circuit with a 1 megohm resistor in series. Using this variation it should be possible to measure lifetimes to the order of 100 µsecs. quite accurately. The principal advantages of such a method are that the duration of afterglow may be measured almost independently of the speed and harmonicity of the interrupter. Furthermore, the sweep-writing controls admit to complete variation so that the signal may be expanded to any desired size. The lower limit is therefore determined by the rate of cut-off of the light beam. Herein lies the principal difficulty. Rapid cut-off is very difficult to obtain. While horizontal jitter is eliminated, varying intensity of illumination triggers the sweep at different parts of the cycle, so that vertical jitter is obtained. The use of a carbon arc eliminates this last fault, but, as previously mentioned, has a lower output of ultr-violet light than some of the other
arcs mentioned.

A number of flash sources were investigated for possible application to the self-triggering sweep technique. Camera shutters have extremely slow cut-off speeds. The spark discharge mentioned earlier also suffers from the same limitation. Air jets were aimed across the terminals to dissipate the heat and the ions formed during the discharge. While this showed some improvement, the results were still far from satisfactory. Rapidly rotating sectors appear to yield the best cut-off characteristics for any purely mechanical method.

XIV. SAMPLE SUSPENSION

As was previously mentioned, the use of low intensity arcs necessitates precise optics with a minimum number of interfaces. The first investigation carried out concerned the use of Pyrex test-tubes to hold the frozen glass. The usual procedure in the laboratory is to dissolve the sample in a test tube full of EPA (5 parts ether, 5 parts isopentane to 2 parts alcohol) and freeze the whole in liquid nitrogen. Since Pyrex absorbs below 3000 Å quartz must be used for determinations below this point. However, if the walls of the test-tube can be made thin enough, Pyrex may be used much farther down in the ultra-violet. Accordingly, attempts were made to produce thin walled flat faced Pyrex "bubbles". The first trials were made by blowing bubbles of glass and compressing two sides together with tweezers fitted with large flat ends. The vials produced in this manner varied considerably in their dimensions. Highly polished carbon moulds were therefore prepared and glass blown into them. These vials were much more consistent in size and thickness and were, in fact, quite good in the optical sense, but would not stand the thermal
shock of sudden cooling in liquid nitrogen. This was thought to be due to
strains introduced into the glass by rapid cooling while in the mould.
Heating the mould to a red heat helped a little, but the product was still
unreliable with respect to fracture on cooling or rough handling.

Another interesting method of sample suspension is that of using
a square metal rod with a slot milled into one end to a depth of about
3/16 of an inch, and fluted at the other end. This slot forms three sides
of a wall, of which the fourth consists of a film of cellophane stretched
across the side of the bar and restrained in this position by masking
tape. The sample is introduced into the top of the well with an eye-
dropper as soon as the bar has reached thermal equilibrium with liquid
nitrogen. The cellophane cannot be removed after the sample has frozen.
This method admits to possible use when it is desired that the light beam
should not pass through the walls of a dewar, for the metal bar may be
placed so that the sample protrudes above the top of the flask, while the
lower end is immersed in the liquid nitrogen. Aluminum was found to be
better than brass in the construction of the bar since the polished
surfaces are highly resistant to tarnish. Aluminum also has better thermal
conductivity and ultra-violet reflection characteristics than does brass.

Perhaps the most generally applicable method of sample prepara-
tion developed recently is the "popsicle" technique. This consists of
freezing the desired solution in a mould made from square brass tubing.
When the sample has almost solidified, which takes about ten minutes, a
"stick" is pushed just below the surface of the glass and the mould with
the contained popsicle completely immersed in the liquid nitrogen for
another two or three minutes. The excess nitrogen is then poured off,
and the mould plunged into water at room temperature and of depth only slightly less than the height of the mould. At the same time the stick is pulled until the glass slides free from the sides of the mould, whereupon the popsicle is reimmersed in liquid nitrogen to prevent further melting. The popsicle so produced has flat sides and will transmit light to the limit of the solvent itself. Three moulds were prepared, with highly polished inside walls, the last abrasive used being buffing powder in oil applied with a leather strop. The ends of the moulds were machined to fit snugly and pinned in position. Two of these three moulds have 18 mm. inside dimensions while the other measures 8 mm. from face to face. The best "sticks" to use are wooden dowels with a brass screw partly driven into one end of each. It is impossible to immerse such a stick too far into the glass in the manufacture of a popsicle and, further, the sample is not as likely to fall off upon subsequent handling as is the case with the more thermal conducting metal sticks first used. The solution and mould should be frozen simultaneously, for when the liquid is poured into the cold mould, a clouded glass often occurs. Much higher concentrations of solute are obtained by cooling the sample slowly.

The study of the polarization properties of emission was also attempted. Thin films of cellophane may be prepared containing small amounts of solute. If this film is stretched, a turning moment is given to the solute molecules so that they become oriented along one axis. The light emission from a sample prepared in this manner should be partially polarized. An ether solution of collodion and benzophenone was poured onto a plane glass surface were not very pliable and crystallized out pure benzophenone readily. Sheet "Parafilm" was investigated for use as
a base. This material is very pliable and retains the distorted form once stretched. No easy way could be found to affix a sample to it, however. This material also has a very long-lived phosphorescence at liquid nitrogen temperatures. This emission has no visually detectable polarization (using "polaroid" plates).

XV. EXPERIMENTAL RESULTS

A. A calibration of the Du Mont Oscilloscope dial settings against the Hewlett-Packard oscillator are as follows:

1. Time Calibration

<table>
<thead>
<tr>
<th>Dial Setting (CRO)</th>
<th>H.P. Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 sec.</td>
<td>97.5 sec</td>
</tr>
<tr>
<td>10</td>
<td>9.3</td>
</tr>
<tr>
<td>1</td>
<td>0.78</td>
</tr>
<tr>
<td>0.1</td>
<td>0.067</td>
</tr>
</tbody>
</table>

2. Multiplier B

<table>
<thead>
<tr>
<th>Dial Setting (CRO)</th>
<th>Read</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>4076</td>
</tr>
<tr>
<td>1000</td>
<td>1019</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>40</td>
<td>37.1</td>
</tr>
<tr>
<td>10</td>
<td>11.23</td>
</tr>
<tr>
<td>2</td>
<td>2.16</td>
</tr>
<tr>
<td>0.3</td>
<td>(ca)0.32</td>
</tr>
</tbody>
</table>
3. Multiplier C

<table>
<thead>
<tr>
<th>Dial Setting</th>
<th>Read</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>5.0</td>
<td>2.78</td>
</tr>
</tbody>
</table>

These values are corrected as nearly as possible for parallax arising from the fact that the trace appeared upon the curved cathode ray tube and were measured from a planar grid. The maximum deviation from these average values is ± 3%. The largest error produced in the present method arises in the enlargement procedure. This error is detectable but not extremely large, and was minimized by projecting a picture of a 60 cycle sine wave and adjusting the enlarger until the peak to peak measurements were equally balanced on either side of the optical axis of the enlarging system. The variation in the peak to peak measurements so determined was no more than 5% between those at the centre of the negative compared to those at either side. The errors in the present method are therefore small.

B. Lifetime Measurements

The most accurate lifetimes determined were determined by the following procedure. Using the same solvents a blank was prepared in each case for comparison against the sample. In this way compensations for any extraneous time constants in the electrical circuits were made. The glasses from these two runs were placed in the apparatus and the recurrent signal adjusted until the desired trace was obtained. A picture was taken of the sample and exposure of the time calibration curve superposed
at the bottom of the same frame. The following frame contained a picture of the blank. Subsequent to developing the negative pairs were placed upon each other in the correct positions and fixed there with masking tape. Each pair was projected, the intensity being taken as the vertical displacement of the sample curve from the "zero-intensity" line. The time ratio was calculated from the peak to peak distance of the time calibration damped oscillation. These results were plotted on semi-log paper and the best slope taken. Two representative prints are shown in Fig. 5a.

Experiments designed to ascertain solvation, concentration, temperature and complex formation effects were conducted. A series of runs were done using a methyl cyclohexane (5 parts) and isopentane (1 part) glass containing various amounts of benzophenone. A comparison set was also run with benzophenone using an alcohol glass (8 parts ethanol, 1 part methanol and 1 part isopropyl alcohol). Both series were determined at -190°C. For the non polar hydrocarbon glasses the effective concentrations of benzophenone were \( 3 \times 10^{-3} \text{M} \), \( 3 \times 10^{-4} \text{M} \) and \( 3 \times 10^{-5} \text{M} \). At concentrations above this range benzophenone separated out, while concentrations below the lowest quoted above gave rise to emission of too low intensity to measure. Comparison of the results found within this range compared very favorably with the corresponding range of concentrations of the lifetimes determined for the alcohol solvents. Within the range of concentrations studied for both solvents no variation in lifetimes could be detected.

Concentrated alcoholic solutions of anthracene, \( \beta \) naphthylamine, \( \beta \) naphthylamine hydrochloride, \( \beta \) naphthol, trinitrobenzene (TNB) and trinitrofluorenone (TNF) were mixed with the correct volume of stock
Figure 5a.
Superposition of the traces obtained for Benzophenone and EPA blank - 180°C.
Figure 5b.

Trace of Benzophenone at \(-180^\circ C\).

Upper curve showing non-exponential character,
while lower one is logarithmic.
Figure 5c.
Trace obtained from Original Apparatus.
(65.8 mg/cc.) benzophenone in alcohol to give approximately 1:1 molecular ratios. The resulting solutions were then made up into E.P.A. solutions, and their lifetimes determined at -190°C, to ascertain whether or not any complex formation took place and, if so, what effect there would be upon the transition probability. In each case the blank contained the correct concentration of complexing agent. No effect could be detected. All lifetimes so determined were found to be within the range 0.001 ± 1, the value of the lifetime of benzophenone in E.P.A.

Attempts to measure the temperature effect upon the lifetime of benzophenone were not successful. The first attempt was made by allowing the liquid nitrogen to boil away from a dewar containing the sample. Unfortunately, as the temperature rose slightly above -190°C, the isopentane of the E.P.A. began to liquify and evaporate. This caused a sharp decrease in the phosphorescent emission to a level which could not be determined. Certain polar glasses are available for use at alcohol-dry ice temperatures, but apparently give rather large solvation effects. This may be seen from the comparison spectrograms in Fig. 6.

A large number of other compounds were investigated in order to ascertain lifetimes. Acetophenone has a lifetime of 0.006 ± 2 seconds and benzil a lifetime of 0.003 ± 1 second, both from E.P.A. Both of these compounds have rather high quantum yields, but most of the others studied showed very little luminescence. Benzalacetone was distilled in vacuo and crystallized out of the melt. This compound gives rise to a faint royal blue luminescence. A number of derivatives of ketones and aldehydes were prepared in the hopes of finding a lifetime of the imine (-C=N-) structure to give a direct comparison to the corresponding carbonyl compound.
Figure 6.

Emission Spectra of Benzophenone.

(a) EPA - 180°C.

(b) Diethylene glycol - 90°C.
Representative oximes, semi-carbazones, phenyl hydrazones and azines of benzaldehyde, acetophenone, benzophenone, bezalacetone and acetone, were prepared. None of the compounds gave rise to emission which was of sufficient intensity to be studied with the present apparatus. Even the powerful (1000 watt) G.E. AH-6 high pressure A.C. mercury arc was not sufficient to give quantitative results. Benzaldehyde, however, has a short lifetime, estimated to be about 0.002 seconds. This result is not too accurate, however, because full amplification of the CRO was used in combination with the AH-6 AC arc, and the resulting signal was not very steady.

Using methylcyclohexane-isopentane glasses swept for two hours with "Premium Grade" nitrogen gas to rid these solvents of dissolved oxygen produced no variation in the lifetime of benzophenone. This attempt was made to see whether or not the same effect could be obtained for a solid phase determination as is for the case of acetone in the vapor phase (Section VII). It may well be the case here that more rigorous out-gassing is required before the threshold concentration for the oxygen effect is reached. In complete absence of oxygen the lifetime of the benzophenone might well be longer. However, the complete removal of oxygen is an extremely difficult task, and the result here quoted must not be taken as conclusive evidence.

C. Trinitrobenzene "Complexes" with KCN

A short study was made upon the effect KCN has upon s-trinitrobenzene (TNB) and colorless 2,4,6-trinitrobenzoic acid (TNBA). When the almost colorless aqueous solutions of either of these compounds are prepared, addition of KCN resulted in a red luminescent red solution.
Under the influence of ultra-violet light an orange-colored emission was observed. It was found later that the same effect could be observed by the addition of any base, but not with metallic sodium in dry xylene solution. By the addition of various sodium salts of weak acids, the strength of the acid TNB was found to be between that of carbonic and hydrocyanic acids ($K_a^{-1} = 10^{-7}$ and $10^{-10}$). Concentrated caustic produced no further change in color. When a solution of TNBA is made basic a time lag of some five seconds may elapse before a color change occurs.

D. Solvent Studies

Attempts were made to find non-polar glasses suitable for making glasses at dry ice-alcohol temperatures. Cyclohexane and mixtures of n-heptane and isoctane were tried but were found unsuccessful, as cyclohexane preferentially crystallized out of the lower melting substituents. The recently reported glasses made from pure cyclohexane required rigorous outgassing and elimination of all liquid-vapor interfaces. Such procedures are extremely inconvenient for facile laboratory procedure (12). Both diethylene glycol and glycol have been found to be much superior to glycerol at this temperature, since neither of these compounds fluoresce, and may be readily distilled in vacuo. Neither suffer from the extremely high viscosity found with glycerol at room temperature and both are excellent solvents, particularly the diethylene glycol. The last traces of water cannot be removed from the technical grades by distillation and may begin to crystallize out after a short time at the lower temperatures. These glasses are therefore satisfactory if used immediately, but the use of analytical reagents is suggested for more stable glasses. Alcohol and ether were added to these glycols to see whether or not a glass could be
produced at both dry ice-alcohol (-90°C) and liquid nitrogen (-180°C) temperatures. This was not successful.

Mineral oil makes beautiful glasses at -90°C, but fluoresces quite strongly in the blue, probably due to the presence of ketone groups. The use of this solvent is suggested for fluorescent studies in spectral regions well removed from the above blue band. The glass so formed is actually the only non polar glass found to solidify at dry ice-alcohol temperatures.

Several attempts were made to get room temperature glasses. Boric acid glasses were tried with small amounts of acetophenone, but the mutual solubilities were such that no emission from acetophenone was obtained. Boric acid itself gives rise to a pink emission. Sucrose-water glasses were prepared but most compounds studied had limited solubilities in water. An optimum concentration for the glass is 300% by weight of sucrose added to trailing water and allowed to cool. Alcohol-sucrose glasses were not obtained. Gelatine and Difco "Bacto-Agar" fluoresce with a blue color at room temperature.

The addition of a small amount of isopentane (5 - 10% by volume) has been found to stabilize many glasses which normally crack at liquid nitrogen temperatures. In view of the work done with EPA at the different temperatures previously mentioned, it is felt that addition of this compound results in a glass remaining very nearly fluid until a temperature which is not more than 20°C above that of liquid nitrogen. Evaporation of isopentane is probably the principal reason why glasses may not be frozen a second or third time, once they have been warmed to room temperature.
XVI. DISCUSSION

It has been shown that it is possible to measure the phosphorescent lifetimes of certain organic compounds by the methods described. Two limitations to the method still remain. First of all each of the sources of ultra-violet light which was available was entirely too weak to measure the afterglow for most compounds. While several methods were devised to minimize light losses, the incident beam was still of too low an intensity to make the method generally applicable. The absence of absolute quantum yields further invalidates any results that were obtained. Accordingly the results of the experiments designed to determine the effect of concentration and of the polarity of the solvent are left in some doubt. Assuming therefore that the quantum yields are constant in each of these cases, it may be stated that the lifetime of benzophenone does not depend upon the concentration (within the limits studied) nor upon the polarity of the particular solvent within which it is dissolved.

The negative results obtained from the experiments designed to study the effect of complex formation are also somewhat dubious in the absence of quantum yield determinations. The formation of weak complexes may be assumed to be an equilibrium reaction. If the equilibrium constant is small, however, then the unassociated benzophenone would give rise to a signal of the correct form. Therefore, on the basis of the lifetime results alone, the formation of complexes of benzophenone with aromatic amines and phenols and hydrocarbons (electron donor molecules) is not indicated. Nor is complex formation indicated with trinitrobenzenes and trinitrofluorenone (electron acceptor molecules).
The dependence of the lifetime of benzophenone upon temperature could not be decided. Any results obtained with the diethylene glycol glass were somewhat invalidated by the fact that the spectra are not similar. If the effect was purely that of temperature, a slight red shift would be expected, with a possible reduction or intensification of some of the vibrational bands. The result obtained was totally unexpected, and was attributed to solvent-solute interaction of an undetermined nature. If the effect was purely one of temperature, rather drastic rearrangement of the present concepts of spectroscopy would be indicated.

As mentioned before, the lack of determination of an oxygen effect upon lifetimes of organic phosphors was attributed to the fact that oxygen concentrations much beyond the optimum required to produce an effect were still present and the result must therefore be taken as inconclusive.

While observing the trace obtained in a lifetime determination, often a non-exponential component was obtained as in Fig. 5(b). The effect was not reproducible. A disc with a very narrow slot in the periphery was made up, and a sample of benzophenone irradiated in the \( \kappa - \kappa \) region. Since the effect did not obtain, it was assumed that the phenomenon did not arise from the emission band being "fed" from a different, shorter-lived upper state. The explanation is still unknown. The lower part of the curve yields the same measured lifetime as that obtained when the phenomenon does not occur.

The results obtained from basic solutions of trinitrobenzene and trinitrobenzoic acid indicate in the first case that an acid-base reaction has occurred, resulting in the formation of a TNB anion. In the case of TNBA, evidently spontaneous decarboxylation occurs before
formation of the same anion. This view is supported by Hickinbottom (41) and by the fact that often a time lag was observed before the change in color was obtained. The exact formulation of the colored anion is difficult to ascertain. Presumably the molecule, on dissociation, loses a proton, leaving an unshared pair on one carbon atom. These electrons will be in an $\text{sp}^2$ orbital and are localized in the plane of the molecule. The consequent fate of these electrons cannot be decided. If the pair remain localized then the red coloration may be due to an $n \rightarrow \pi$ transition.

Such an explanation seems unlikely, since it is probably non-localization which gives rise to ionization in the first place. What appears to be more likely explanation appears when a free radical electron distribution is assumed. In this case, the distribution of the electrons is non-localized, and they may appear with zero energy upon any of the ortho carbon atoms and any of the nitrogen atoms of the nitro groups. This would lower the electron deficiency of present in the latter groups, so that, in effect, they behave more as nitroso groups. This results in an $n \rightarrow \pi$ transition of a different sort. There are difficulties with this, or with any other explanation that can be proposed. Since TNB gives no colored complex with metallic sodium, as benzophenone does, a stable free radical-ion process may be eliminated. The true explanation at the present moment remains obscure.

XVII. FUTURE STUDIES

If plans are made to carry on the work of the measurement of the lifetimes of organic phosphors, two factors should be immediately considered. The method as it now stands is applicable to only a very few
compounds with sensitive emission bands. The only solution to such a difficulty is the purchase of a very steady, high wattage D.C. source, or the construction of a discharge tube which may be activated by a square-wave electrical supply (28). The second consideration is with regard to accurate fluorescence yield determinations. Any effective change in lifetime must be checked against a change in luminescent efficiency, as was previously indicated. Should these problems be met with successfully, then perhaps the best piece of experimental work that could be done would be to prove the temperature dependence of the various $n \rightarrow \pi$ transitions in which little triplet-singlet splitting occurs.

The problem would be difficult, since quantum yield determinations conducted in the normal way do not differentiate between fluorescence and $\alpha$- and $\beta$-phosphorescence, but do, in fact, measure the total fluorescence efficiency. No suggestions can be made as to the method of differentiation, but vigorous elimination of dissolved oxygen is a necessity. The problems involved are complex and interdependent, so that final resolution of them seems at the moment far away. Such being the case, perhaps future research time should be directed along more productive channels until some different methods are discovered which will finally lead to solution of the problems involved.
BIBLIOGRAPHY

35. Galanin, M.D. C.A., 66, 8971 (1952)
38. Reid, C. J. Chem. Phys., 20, 1214 (1952)
42. Phibbs, M.K. and Schiff, H.I. J.C.P. 17, 843 (1949)