

TripletSinglet Transitions in Organic Molecules. Lifetime Measurements of the Triplet State

Donald S. McClure

Citation: *J. Chem. Phys.* **17**, 905 (1949); doi: 10.1063/1.1747085

View online: <http://dx.doi.org/10.1063/1.1747085>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v17/i10>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Triplet-Singlet Transitions in Organic Molecules. Lifetime Measurements of the Triplet State*

DONALD S. MCCLURE

Department of Chemistry, University of California, Berkeley, California

(Received December 20, 1948)

The emission lifetimes of the metastable triplet states (phosphorescent states) of a large variety of organic molecules have been measured. The lifetimes are in the range from 10^{-4} to about 10 seconds. It is shown that the transition probabilities corresponding to the shorter lifetimes are of the same magnitude as found in the light atoms of which the molecule is composed. The longer lifetimes, on the order of seconds, are found only among the aromatic compounds. A consideration of the perturbing singlet states in aromatic compounds shows that the matrix elements for the intercombination must be very much smaller than those responsible for the intercombination in the free carbon atoms. Direct evidence that the long-lived states of the aromatic compounds are triplet states is obtained by showing that as the atomic number of chemically similar substituents is increased (e.g. substitute Br for Cl), the transition probability increases approximately in proportion to the increase in the square of the spin-orbit interaction energy of the substituent atom. The luminescences are usually observable only when the substance is dissolved in a rigid solvent, and the effect of such a solvent on the lifetimes is discussed. Experimental data relating singlet-triplet absorption strength to triplet state lifetime is presented.

THE work of Lewis and Kasha^{1,2} has brought to the attention of spectroscopists the possibility of studying the triplet states of complex molecules. Before their work, very little was known about such states, and no systematic investigation of them had been attempted. It was known, however, that in rigid media, many organic compounds containing multiple bonds, notably the aromatic compounds, have two emission bands, contrary to the usual opinion that only a fluorescence band should exist. The second band was always found at greater wave-lengths and had a greater lifetime; in some cases many seconds, in contrast to the fluorescence lifetime which are usually between 10^{-6} and 10^{-8} second. Lewis and Kasha interpreted these long-lived, lower energy states as the metastable triplet states of the molecules where they were found. They also interpreted the extremely weak absorption bands of many substances as being due to singlet-triplet absorptions, and found many new examples both of weak absorption bands and of luminescences in rigid media. A considerable amount of indirect evidence supported the contentions of these workers, but it was not until Lewis and Calvin³ measured the paramagnetism of fluorescein in its metastable (2.5-second lifetime) state, that direct evidence of a triplet state was obtained. This, and the later work of Lewis, Calvin and Kasha⁴ on the same molecule, proved that there are two unpaired electrons per excited molecule when fluorescein is in its metastable electronic state.

Both the existence and the method of study of metastable triplet states were established by the work just outlined. The study of the other triplet states of the term manifold could be undertaken if sufficiently

high concentrations of metastable molecules were obtainable. This is possible in many cases. In the present paper, we shall deal only with the lowest triplet state, and shall be primarily concerned with its lifetime.

A low lying metastable triplet state can be present in any molecule having a multiple bond (possibly also in some others, although we shall not deal with them). The type of multiple bond will serve for the purposes of this paper as a broad classification of organic molecules. The experimental results of the lifetime measurements made on several of these classes of molecules are presented in this paper. Direct evidence that the metastable states are triplet states is found on interpreting these results. The lifetimes are qualitatively explained by comparison with intercombination processes in atomic systems, and by approximate calculations. It is also shown that the aromatic compounds have anomalously long-lived states. Selection rules for intercombinations in polyatomic molecules have recently been given.⁵ Further theoretical work on the subject is planned.

I. EXPERIMENTAL

Lifetimes were measured with a mechanical phosphoroscope consisting of a pair of half-sectors mounted on a common shaft in such a way that during half a revolution of the shaft, the sample was exposed to the exciting light, and during the other half-revolution, the exciting light was shut off and a detector observed the after-glow. The detector was a photo-multiplier tube, the anode resistor of which was connected directly across the vertical plates of a cathode-ray tube. For lifetime measurements between 3×10^{-4} sec. and 0.03 sec., a synchronous motor turned the phosphoroscope disks at 30 r.p.s. while the oscilloscope sweep was exactly 60 c.p.s. Thus a decay curve and a zero intensity base line appeared on the screen for each revolution of the phosphoroscope. A disk with 20 narrow equally

* Presented before the Symposium on Molecular Structure and Spectroscopy at the Ohio State University, June 1948.

¹ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944).

² G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

³ G. N. Lewis and M. Calvin, *J. Am. Chem. Soc.* **67**, 1232 (1945).

⁴ G. N. Lewis, M. Calvin, and M. Kasha, *J. Chem. Phys.* (to be published).

⁵ D. S. McClure, *J. Chem. Phys.* **17**, 665 (1949).

TABLE I. Comparison of lifetimes in polar and non-polar rigid solvents.*

	Polar	Non-polar
<i>P</i> -dibromo benzene	0.00030±3 sec.	0.00033±3 sec.
<i>β</i> -iodo naphthalene	0.0025±1 sec.	0.0024±1 sec.
<i>P</i> -dichloro benzene	0.016±1 sec.	0.017±1 sec.
<i>O</i> -dichloro benzene	0.018±1 sec.	0.018±1 sec.
<i>α</i> -fluoro naphthalene	2.13±10 sec.	1.99±10 sec.

* Non-polar solvent: 4 parts methyl cyclohexane, 1 part isopentane. Polar solvent: 5 parts ether, 5 parts isopentane, 2 parts alcohol (E.P.A.). These solvents form clear rigid glasses at 77°K.

spaced notches was mounted on the motor shaft so that the notches on its periphery reduced the flux between the poles of a small electromagnet every 1/20 revolution. This supplied timing markers for the oscilloscope screen. The decay curve and timing marks were photographed and analyzed. An adaptation of this method enabled measurements to be made in the region 0.03–0.3 sec., but few substances fell in this range. For lifetimes of 0.2 sec. or greater a repeated decay pattern was not necessary, and as the resolving time was no problem, the disks were manually turned from the illuminating position to the observation position. The 1 and 5 sec. sweeps for this range were obtained from mechanically operated potentiometers. Calibrating markers were obtained from a pulse generator connected both to the oscilloscope and to a counter. The pulse generator was calibrated by measuring the time for 100 counts. The calibration did not vary more than one percent over periods of several weeks.

The vertical deflections on the oscilloscope screen were proved to be sufficiently linear by calibration with a point light source, using the inverse square law to determine accurately the relative intensities of light falling on the photo-multiplier tube.

The resolving time of the phosphoroscope was 10⁻⁴ sec. at the narrowest slit widths used, so the shortest lifetimes measured were somewhat greater than this. The errors were no greater than 10 percent for all ranges. Probable errors are given with each measurement where the number given is *the error in the last decimal place*. The lifetime values that are given in this paper are mean lifetimes, i.e.,

$$\tau = \frac{t_2 - t_1}{2.31 \times \log I_1 / I_2}$$

The substances studied were in a rigid glassy solution at liquid nitrogen temperature. A small quartz Dewar and a quartz sample tube allowed exciting light of wave-lengths up to the transmission limit of the solvent to enter the sample tube. The use of rigid solutions is discussed by Lewis and Kasha.¹ The light source was a commercial carbon arc having high ultraviolet emission. A water cell and various filters were used to select the radiation desired for a particular sample.

II. THE USE OF RIGID MEDIA

The use of a rigid medium requires some discussion because we want to assume that the measured molecular lifetimes bear some relation to the natural lifetimes of the molecular states.

In the first place, it is necessary to have the substance immersed in a dense phase of some type, as otherwise it would be very difficult to observe the emission from the triplet state. The reasons are as follows. The direct excitation to the triplet state is such a slow process that one cannot in this way build up sufficient emission intensities as to be easily observable. It is therefore necessary to excite the molecule to its upper singlet states and to rely on the process of radiationless internal conversion to carry molecules into the triplet state. By far the greatest fraction of this process takes place when the molecules are in their lowest excited singlet state, before they radiate. Some type of perturbation causes this singlet to become mixed with the metastable triplet, so that for a part of the time, the molecule is in the lowest singlet, and for the other part of the time, it is in an isoenergetic vibrational level of the metastable triplet. If the molecule is isolated, the numbers emitting from the two states will be proportional to the rate of radiation from the two states. Therefore, practically all of the radiation comes from the singlet, because the radiation rate from this state is some 10⁵ times greater than from the triplet (see Section III). On the other hand, if the molecule can lose to its surroundings the vibrational energy it has when in the vibrationally excited triplet, it will go without radiation to the lowest vibrational levels of the metastable triplet. Barring collisional deactivation of the triplet molecules, the relative numbers emitting from the two states will then be proportional to the number in the two states. Since this ratio may be on the order of unity (see, e.g., Table VI), a large amount of triplet radiation may be observed. The excess vibrational energy of the triplet state must therefore be removed by collisions, and therefore the molecule must be in a sufficiently dense phase in order for the phosphorescence of the organic molecule to be observable.

Once a large number of molecules have reached the low lying vibrational levels of the triplet state through the action of the medium, the same medium must be such as not to remove additional energy from the molecule and send it without radiating to the ground state. If an appreciable fraction of the process of going to the ground state is by thermal deactivation, the measured lifetimes will not be the natural ones. In order for thermal deactivation to occur, electronic energy of the excited molecules must be converted into kinetic energy of the surrounding molecules. As is well known, this is a relatively inefficient process compared to the removal of vibrational energy from the same molecule. The momentum transfer from an electron to a molecule is inefficient because of the large mass difference. Never-

theless, the high collision rate in a liquid overcomes this and we usually find that complete thermal deactivation of the triplet state occurs in liquids. If we gradually cool a liquid containing an organic phosphor, the luminescence increases in intensity as the viscosity of the liquid increases. If there is no thermal quenching in the solid state, both the intensity and lifetime of the luminescence should be constant with temperature. No quantum yield measurements have been completed as yet, but there are some data on the temperature independence of the lifetime. Lewis, Lipkin, and Magel⁶ showed that the lifetime of the metastable state of fluorescein is the same at 77°K as it is at 20°K. (All of the lifetimes to be reported in this paper are measured in a rigid glass at 77°K.) It therefore seems likely that the rigid glass may be a medium which can remove vibrational energy from a molecule, but cannot remove electronic energy.

Another fact which indicates that collisional deactivation does not alter triplet state lifetimes is that the decay curves are exponential. This does not prove a complete lack of collisional processes, but if as little as 10 percent of the decay process were a second order thermal deactivation process, this could have been detected as a deviation from the exponential decay law. The deviations from the exponential decay law actually observed were always traced to the presence of impurities, and indeed, the exponential form became one of the criteria of purity. The decay curves were observed over a period of one or two lifetimes.

Collision processes are not the only ones which can affect the lifetimes. Dispersion forces, induced polarization forces and dipole-dipole forces also come into play. Not enough work has been done as yet to estimate accurately the effects of these forces. Table I shows that the lifetimes of a few aromatic halogen compounds are the same in a polar as in a non-polar rigid solvent. This shows that the polarization forces are not very important. Dispersion forces are usually of greater importance in molecules having multiple bonds than are polarization forces. For a molecule in a metastable triplet state, only the higher triplet states of the molecule enter into the calculation of the dispersion force. These are probably closer to the metastable triplet state than the perturbing singlets are to the ground state, so the dispersion forces should be greater in the metastable state than in the ground state. But the mixing in of these higher triplet states should not cause much change in the intercombination probability.

There is one substance, biacetyl, whose triplet state lifetime has been measured in both the vapor phase and in a rigid glass. The emission lifetime of the vapor has been reported⁷ as 1.65×10^{-3} , and 1.40×10^{-3} sec., while the author obtained 1.30×10^{-3} sec. The lifetime is temperature dependent at high temperatures, probably

because of thermal activation to a state from which transitions to the ground state are more rapid than from the triplet state. The lifetime is reported to be about 0.8×10^{-3} sec. at 338°K.⁸ The lifetime measured in a rigid solvent (E.P.A., see note to Table I), at 77°K is 2.25×10^{-3} sec. Probably a large part of the increase over the vapor phase measurement is attributable to the temperature effect, so that any solvent effect would increase the lifetime by only 20 or 30 percent. This example shows that none of the factors mentioned have an important effect on the lifetime of the luminescence of this substance.

For all the reasons just discussed, we may conclude that it is very unlikely that lifetimes of metastable states are changed by as much as a factor of two when the molecule is embedded in a rigid medium. Absolute quantum yield measurements in progress at this laboratory will be the best experimental evidence showing whether or not this conclusion was really justified. Throughout the remainder of this paper, it will be assumed that the measured molecular lifetimes are the same as the true molecular lifetimes.

III. ESTIMATION OF TRANSITION PROBABILITIES

Triplet-singlet transitions occur because the spin-orbit interaction (or other spin and orbital dependent forces) mixes certain singlet states with the triplet state. The square of the amount of singlet character in the triplet state is proportional to the probability of the intercombination transition. The result of a first-order perturbation calculation of the intercombination probability in an atom or molecule is

$$\frac{1}{\tau_{3n}} = P_{3n} = P_{1n} \left(\frac{H_{13}}{\Delta E} \right)^2 \left(\frac{\nu_3}{\nu_1} \right)^3 \quad (1)$$

where the contribution from only one perturbing state is being considered. P_{1n} is the transition probability between the perturbing singlet and the normal state. ν_1 and ν_3 are the frequencies for transitions between the normal state and the perturbing singlet and between the normal state and the triplet. ΔE is the energy difference between the triplet and the perturbing singlet. The quantity H_{13} is the matrix element of the spin-orbit operator between the triplet and the perturbing singlet. In atoms this consists of a radial part, ζ , and an angular part, and is dependent on the configuration of the atom. $\zeta/\Delta E$ is approximately the first-order correction to the wave function in the perturbation calculation applied to the atom when the angular part is considered to be close to unity. The values of ζ are known for most of the atoms, as they are derivable from atomic spectra. It is much more difficult to determine the values of H_{13} for molecules, and this will not be attempted in the present paper. For the approximate

⁶ G. N. Lewis, D. Lipkin, and T. Magel, *J. Am. Chem. Soc.* **63**, 3005 (1941).

⁷ G. M. Almy and S. Anderson, *J. Chem. Phys.* **8**, 805 (1940); R. D. Rawcliff, *Rev. Sci. Instr.* **13**, 414 (1942).

⁸ G. M. Almy and P. R. Gillette, *J. Chem. Phys.* **11**, 188 (1943).

TABLE II. Effects of heavy atom substituents on phosphorescence lifetime and spectra of naphthalene derivatives, and comparison with spectra and strength of ordinary absorption bands.

(a) Triplet-singlet emission band							
Substituent	ζ cm ⁻¹	ν_P cm ⁻¹	α -isomer τ (sec.)	$10^{-5}\tau\zeta^2$	β -isomer τ (sec.)	$10^{-5}\tau\zeta^2$	
F	272	20,970*	1.5±1	1.11	—	—	—
Cl	587	20,700	0.30±4	1.03	21,000	0.47±4	1.62
Br	2460	20,700	0.018±2	1.10	21,100	0.021±1	1.29
I	5060	19,000*	0.0025±1	0.64	21,040	0.0025±1	0.64
OH**	152	—	—	—	21,100	1.30±5	0.30
SH	382	—	—	—	20,800	0.28±1	0.41
H	—	21,300	2.6±2	—	—	—	—
(b) Singlet-singlet absorption bands***							
Substituent	β -halogen naphthalenes only						
	$\bar{\nu}_1$ cm ⁻¹	f_1	$\bar{\nu}_2$ cm ⁻¹	f_2	$\bar{\nu}_3$ cm ⁻¹	f_3	
H	31,200	0.0010	35,000	0.214	45,300	1.1	
Cl	31,080	0.0037	34,620	0.112	44,000	1.4	
Br	31,050	0.0039	34,600	0.127	43,900	1.4	
I	30,900	0.0026	34,300	0.145	41,100	1.4	

* These values from the work of R. V. Nauman, thesis, University of California, 1947. All others from Lewis and Kasha, J. Am. Chem. Soc. 66, 2100 (1944). The highest frequency of the emission band is given.

** The OH compound is to be compared with the SH but not with the halogen compounds.

*** There are three regions of absorption in the near ultraviolet which probably correspond to three electronic transitions. The average frequencies of these regions are designated in the table as $\bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_3$. In the case of the first band, a correction must be made for the overlapping of the second, and in the case of the third, the band is partly beyond the ordinary range of solution spectra work and the integration is somewhat inaccurate.

determination of intercombination transition probabilities in molecules, it is often accurate enough to use the ζ -value of the atoms of which the molecule is composed. The angular part of the atomic matrix element will be sufficiently close to unity for this purpose. Since ζ is approximately a radial integral over $1/r^3$ for the triplet state of the atom, its main contributions come from near the nucleus. We therefore expect that the ζ -value for the heaviest atom in the excited system of the molecule will be a reasonable approximation to the H_{13} value for the molecule.

Without at first going into great detail, one can make some rough estimates, based merely on the types of atoms appearing in the molecule. The values of ζ can be found for most atoms in Condon and Shortley⁹ but because of configuration interactions, the ζ -values for some of the first and second period atoms cannot be given. Reasonable values to use in Eq. (1) were obtained, however, by extrapolating from nearby atoms of the periodic table, using the fact that the ζ -values vary with the fourth power of the effective atomic number. These estimated values are enclosed in parentheses in the tables in which they appear (Tables II and III). Using these values of ζ and taking $\Delta E = 10,000$ cm⁻¹, $P_{1n} = 10^8$ sec.⁻¹, and $(\nu_1/\nu_3)^3 = \frac{1}{2}$, we can give the following estimates of triplet state lifetimes of molecules containing various types of atoms: carbon—0.003 sec.; nitrogen—0.0004 sec.; oxygen—0.0001 sec. In organic

⁹ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

TABLE III. Effects of heavy atom substituents on spectra of benzene derivatives.

(a) Tetraphenyl group IV compounds						
Element	Triplet-singlet emission band				Near ultraviolet absorption band	
	ζ	ν_P cm ⁻¹	τ (sec.)	$10^{-5}\tau\zeta^2$	$\bar{\nu}_a$ cm ⁻¹	f
C*	(28)	28,500	5.4±2	4	38,800	0.015
Si	142	28,200	1.24±5	25	38,100	0.015
Sn	2097	28,400	0.0030±2	14	38,900	0.015
Pb**	7294	23,900	0.010±1	530	>38,500	0.028
(b) Triphenyl group V compounds						
Element	ζ	ν_P cm ⁻¹	τ (sec.)	$10^{-5}\tau\zeta^2$	$\bar{\nu}_a$ cm ⁻¹	f
N	(70)	25,500	0.49±4	2.5	33,300	0.57
P	(231)	25,200	0.014±2	0.8	38,000	0.30
As	1500	25,500	0.0016±3	3.6	40,000	0.33
(c) Halogen derivatives						
Element	ζ	ν_P cm ⁻¹	τ (sec.)	$10^{-5}\tau\zeta^2$	$\bar{\nu}_a$ cm ⁻¹	f
F	272	Too weak to measure			39,120	0.00816
Cl	587	0.004±1			38,540	0.00284
Br	2460	(0.0001)***			38,100	0.00249
I	5060	—			38,580	0.0134
H	28	29,400	7.0±5	—	40,100	0.00147

* Triphenyl methane was used.

** The Pb compound is out of line not only because of the relatively long lifetime but also because of the position of the triplet level and the f of the lowest singlet-singlet transition. There is no adequate explanation as yet.

*** This value was obtained by extrapolating from a number of chloro and bromo compounds whose luminescence lifetimes were measurable. The data of Table IV were used.

molecules containing several different atoms, the heaviest one in the excited system would be expected to have the dominant effect on the lifetime.

One could make more refined estimates for a particular organic compound if enough were known about the perturbing states. Unfortunately, it is not easy to decide which ones they are. This has been done, however, for two classes of compounds. In the following sections on the aliphatic ketones and on the aromatic hydrocarbons, a comparison of estimated and measured lifetimes will be made after it is shown which states of the term manifold of the molecule perturb the metastable triplet. It will be seen that the lifetimes of the aliphatic ketones agree with the estimated ones, and that indeed most lifetimes can be estimated by this simple procedure, but that the lifetimes of the aromatic compounds cannot be estimated in this way. Before further discussing the estimation of lifetimes, we shall bring up an important consequence of Eq. (1).

IV. THE EFFECT OF HEAVY ATOM SUBSTITUENTS ON LIFETIMES

Direct verification that the long lifetime of the metastable state of fluorescein is due to its multiplicity of three came from the measurements of the paramagnetism of the metastable state.^{3,4} Nearly as direct evidence for the triplet state hypothesis has been obtained for a variety of other molecules by simply studying the effect of heavy atom substituents on the lifetimes.

The spin-orbit interaction energy increases very rapidly with atomic number, and in heavy atoms it becomes greater than the electrostatic energy, which stays approximately constant as the atomic number increases. At the same time, the intercombination probabilities increase. The electron coupling gradually changes from $L \cdot S$ to $j \cdot j$. These effects of increasing atomic number should be observable in molecular intercombinations. In fact, if such effects are found in a group of molecules differing only in the atomic number of an atom not directly in the excited system of the molecule, it may be inferred that the transitions so affected are singlet-triplet transitions. The molecules chosen for study were aromatic nuclei with various heavy atoms attached. For example, the halogen naphthalenes, Table II, and the $(\phi)_nX$ compounds, Table III, where ϕ =phenyl, X is some element in main groups IV to VII, and n is the smallest valence of X . In Tables II and III, it is seen that on replacing the heavy atom, X , by the next heavier one, neither the position nor the intensity of the singlet-singlet bands or the position of the triplet level are greatly altered, but the lifetime of the triplet state is markedly decreased. Thus all the factors on the right side of Eq. (1) except ζ remain approximately constant, and one would expect the relation

$$\tau_a/\tau_b = (\zeta_b/\zeta_a)^2 \quad (2)$$

to be approximately obeyed. This is equivalent to saying that $\tau\zeta^2$ is constant throughout a series of similar compounds such as the halogen naphthalenes. The tables show that this relationship is obeyed rather well by the naphthalenes, and not quite as well by the $(\phi)_nX$ compounds. Some further examples which support the validity of (2) are: diphenylene oxide $\tau\zeta^2 = 1.3 \times 10^{-6}$ and the corresponding selenide, $\tau\zeta^2 = 1.7 \times 10^{-6}$; the $\tau\zeta^2 \times 10^4$ values for the p -halogen acetophenones are: chloro, 1.4; bromo, 4.0; iodo, 2.3. The fact that (2) is approximately obeyed is good evidence that spin-dependent forces are responsible for the transitions. We can infer from the similarity to the spectra of the unsubstituted compounds that the corresponding transitions in them are also intercombinations and thus the phosphorescence of benzene and naphthalene are established as intercombination transitions.

Another type of comparison illustrating the atomic number effect is shown in Table IV. The lifetime ratios should be about the same for compounds of differing structure. The actual lifetime ratios are fairly constant, but about twice the ratio to be expected from the simple theory.

One must recognize the limitations of the treatment which has been given. The values of ζ depend on the electron configuration in the atom. We have used the value of ζ corresponding to the lowest lying configuration of the atom, which may or may not be a good approximation to the true matrix element for the molecule. Nevertheless, the extent of the agreement is

TABLE IV. The atomic number effect in the polyhalogen benzenes. Lifetimes are given in seconds.

$X \backslash$	p -di- X	1,3,5 tri- X	1,2,4,5 tetra- X	$\left(\frac{\zeta_{Br}}{\zeta_{Cl}}\right)^2$
Cl	0.016	0.022	0.018	
Br	0.0003	0.00074	0.00055	
Ratio	53	30	33	17.5

remarkable in view of the simplicity of the assumptions. In later more exact work, atomic and molecular orbital calculations may be found to improve the agreement. We are justified at this stage in drawing the important conclusion that the atomic number effect described constitutes good evidence that spin dependent forces are responsible for the electronic transitions we observe as phosphorescence in organic molecules.

V. ALIPHATIC KETONES

It was stated at the end of Section III that the most important perturbing state in the aliphatic ketones could be located with some certainty, and that the measured lifetimes compared favorably with those calculated using Eq. (1) and the atomic ζ -value for oxygen. We have not proved that the emission of long duration (about 0.001 sec.) is due to a triplet-singlet transition, but in view of the long lifetime, no other type of transition seems possible. An attempt to study the atomic number effect in the α - and α - γ -halogen acetones was made, but the bromo- and iodo-compounds had metastable state lifetimes which were too short for the present apparatus to measure. It will be assumed in the remainder of this paper that the metastable state is a triplet state.

The identification of the principal perturbing singlet state is based on a study of the behavior of the ketones toward methyl substitution in the α - and γ -positions. In Table V, the f values for the transitions of interest in the methyl substituted acetones are presented.¹⁰ The f of the 35,000 cm^{-1} transition is practically unaffected by methyl substitution while that of the metastable state is markedly decreased. The f values of the 51,000 cm^{-1} transition¹¹ parallel those of the metastable state very closely. The ratios shown in the last column are roughly constant. The f values of the 60,000 cm^{-1} transition¹¹ increase as methyl substitution proceeds.

The fact that the f -number of the triplet-singlet transition varies with methyl substitution in the same way as the 51,000 cm^{-1} transition, is evidence that the latter is the principal perturbing state. The lifetime of

¹⁰ The f value for the triplet level is determined from the experimental lifetime and from $f = 1.50/\nu^2\tau$, with ν in cm^{-1} and τ in sec. The average frequency of the emission band for all the compounds was nearly the same and equal to 23,000 cm^{-1} . Undoubtedly a modification of this formula should be used here, but the values given are at least proportional to the correct ones. See Section IX.

¹¹ R. S. Holdsworth and A. B. F. Duncan, Chem. Rev. 41, 311 (1947).

TABLE V. Lifetimes of carbonyl luminescences and comparison of f numbers of singlet states with f numbers of triplet states.

Ketone	$\tau \times 10^3$ sec.	$f(ST) \times 10^8$	$f(35,000 \text{ cm}^{-1}) \times 10^4$	$f(51,000 \text{ cm}^{-1}) \times 10^2$	Ratio $f(ST) \times 10^4$
Di-methyl	0.6	4.7	4.54	2.0	2.4
Methyl-ethyl	0.85	3.33	5.82	1.8	1.9
Di-ethyl	1.26	2.25	4.50	0.77	2.9
Methyl isopropyl	1.7	1.6	5.14	0.95	1.7
Di-isopropyl	3.77	0.75	6.86	0.18	4.2
Di- <i>t</i> -butyl	8.6	0.33	6.30	0.16	2.1

TABLE VI. Triplet state lifetimes of polynuclear hydrocarbons.

	Symmetry group	Max ν of fluor. cm^{-1}	Max ν of phos. cm^{-1}	$\frac{\Phi_P}{\Phi_F}$ (approx)*	τ (sec.)
Triphenylene	D _{2h}	29,100	23,800	1.2	15.9 \pm 3
Coronene	D _{6h}	23,600	19,100	1	9.4 \pm 2
Benzene	D _{6h}	38,000	29,400	1	7.0 \pm 5
Fluorene	C _{2v}	33,200	23,750	0.7	4.9 \pm 2
Phenanthrene	C _{2v}	28,700	21,600	0.3	3.3 \pm 2
Naphthalene	D _{2h}	31,750	21,300	0.01	2.6 \pm 2
Chrysene	C _{2h}	27,450	19,800	0.03	2.5 \pm 1
1,2,5,6 dibenz-anthracene	C _{2h}	25,300	18,300	0.01	1.5 \pm 1
1,2 benz-anthracene	C ₂	26,100	16,500	0.001	0.3 \pm 1
Pyrene	D _{2h}	27,000	16,800	0.001	ca. 0.2
Anthracene	D _{2h}	26,600	14,700**	0.0001	—

* Φ_P/Φ_F is the ratio of phosphorescence yield to fluorescence yield. A study of internal conversion between the singlet states and the metastable triplet has been made by Dr. M. Kasha and is soon to be published. He has kindly permitted me to use some of his data to complete this column. The significance of Φ_P/Φ_F in the study of internal conversion was first pointed out by Dr. Kasha.

** Lewis and Kasha, see reference 1. On account of the weakness of the emission and its presence in the infra-red region, the lifetime could not be measured.

the luminescence of acetone can be calculated on this basis using Eq. (1). Taking $\zeta = 152 \text{ cm}^{-1}$, the estimated value for oxygen; $\nu_1 = 51,500 \text{ cm}^{-1}$; $\nu_3 = 30,000 \text{ cm}^{-1}$ and $f_1 = 0.020$, we find $\tau_3 = 0.0029 \text{ sec}$. The actual value, 0.0006 sec., is five times shorter than this. A calculation shows that if the two other nearby states (at 35,000 cm^{-1} and 60,000 cm^{-1}) contribute to the intercombination probability, the lifetime is only slightly decreased, namely to 0.002 sec. Without doubt, the use of the radial atomic integral as an approximation to the matrix element for acetone is rather crude, and the discrepancy could easily disappear if a better value were used. The calculated lifetimes of the other aliphatic ketones are in error by about the same factor, in view of the last column of Table V. The order of magnitude of the result is correct, however, and we expect Eq. (1) using the atomic ζ -value to give approximately the right lifetimes for molecules similar to the aliphatic ketones. The rough estimates of Section III are not very far from what is actually observed. Although a comprehensive study has not been made of many other classes of molecules (classification based on the type of multiple bond), most of the examples encountered support the conclusion that Eq. (1) in the way we have used it leads to nearly the correct triplet state lifetime. Some other examples are to be found in Section VIII.

VI. POLYNUCLEAR HYDROCARBONS

The lifetimes of the polynuclear hydrocarbons are on the order of seconds, which is much longer than in the other types of organic compounds studied, and longer than the estimates of Section III would lead one to expect. The estimates were based on the use of the ζ -value for the lowest lying electron configuration of the carbon atom as an approximation to the matrix element for the singlet-triplet perturbation in the molecule. Apparently in this case, it is a very poor approximation to do this. The lifetimes of some of these compounds are listed in Table VI, along with other data which will be discussed later.

If enough information were available, one could make a better estimate of the discrepancy between observed and calculated lifetimes. The necessary information is a knowledge of the position and symmetry of the excited singlet levels of the molecule, the ground \rightarrow excited-singlet state transition probability, and the selection rules governing the singlet-triplet perturbations in the molecule. The latter have recently been derived,⁵ but only a part of the other necessary information is available. It is possible, however, to estimate the lifetime of the metastable triplet state of benzene, and to estimate the maximum lifetime to be expected for other polynuclear hydrocarbons (under the assumption that ζ is a good approximation to the spin-orbit interaction energy). As was shown by Shull,¹² the metastable triplet state of benzene is perturbed by the $^1B_{1u}$ state. As suggested by Shull and later confirmed by the author,⁵ the metastable triplet state must, as a result, be $^3B_{2u}$. In order to use Eq. (1), we must know the position of the perturbing singlet level, i.e., the $^1B_{1u}$ level.

Shull's assignment of $^1B_{1u}$ as the perturbing singlet was based on the discovery of a β_{2g} vibrational interval

TABLE VII. Comparison of calculated and observed f -numbers for triplet states of polynuclear hydrocarbons.

Compound	$E(^1L_b) \text{ cm}^{-1}$	$E(^3L_a) \text{ cm}^{-1}$	$f(^1L_b) \text{ meas.}$	$\times f(^3L_a) \text{ meas.}$	$\times f(^3L_a) \text{ calc. Eq. (1)}$	Ratio $\frac{\text{calc.}}{\text{meas.}}$
Benzene	38,000	29,400	0.00147	0.0246	1.56	64
Naphthalene	32,000	21,300	0.002	0.123	1.14	9
Phenanthrene	28,300	21,600	0.003	0.081	5.2	64
Chrysene	27,500	19,800	0.005	0.154	6.6	43
Triphenylene	29,200	23,800	0.012	0.0177	31.5	1780
1,2 benz-anthracene	25,800	16,500	0.003	1.85	2.7	1.5

in the triplet-singlet emission spectrum, and is thus the first time that definite experimental evidence has been adduced to distinguish between a B_{1u} and a B_{2u} state. Other assignments¹³ have made use of theoretical calculations of doubtful validity. This fact is mentioned here because it seems to be necessary to reverse the

¹² H. Shull, J. Chem. Phys. 17, 295 (1949).

¹³ See C. C. J. Roothan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948) for references and discussion.

present assignments of the first two excited singlet levels of benzene. The lowest singlet has been assigned the symmetry $^1B_{2u}$, and the second $^1B_{1u}$. Using the spectral similarities of the polynuclear hydrocarbons,¹⁴ the lowest excited singlet, in the nomenclature of Kleven and Platt, is 1L_b and the lowest triplet is 3L_a , and is associated with (belongs to the same electron configuration as) the second excited singlet, 1L_a . The perturbing singlet must not, therefore, be the second excited singlet, but the first, the 1L_b state. The selection rules then require 1L_b to be $^1B_{1u}$, since 3L_a has already been assigned $^3B_{2u}$. This is opposite from the assignment of previous workers cited.

Having located the position of the perturbing singlet state in benzene, we can use the data for this state in Eq. (1) to estimate the lifetime of the triplet state under the assumption that "normal" spin-orbit coupling takes place. Using the analogies between the spectrum of benzene and the other polynuclear hydrocarbons¹⁴ enables us to predict maximum lifetimes for the other hydrocarbons.

In Table VII are presented the f -numbers of the triplet→ground-state transitions computed using Eq. (1) with the data for the 1L_b state of the hydrocarbon, and using the ζ -value for the lowest configuration of atomic carbon. The ratio of this f -number to the true f -number (obtained from the lifetime by the formula of reference 10) is also given. Most of the calculated f -numbers are many times too high. In addition, one must remember that these f 's are minimum values, since only the 1L_b state is considered as a perturbing state. Consideration of only one state is probably a good approximation for benzene, but in the less symmetrical molecules, other states certainly interact with the metastable triplet state, causing the f -number calculated by Eq. (1) to be even larger. There are probably no restrictions on the perturbing states in the

TABLE IX. Triplet state lifetimes of nitro compounds.

	$\nu_P^* \text{ cm}^{-1}$	$\tau \text{ (sec.)}$
α -nitro naphthalene	19,200	0.05
2-nitro fluorene	20,600	0.13
p -nitro biphenyl	20,500	0.080
1,5 dinitro naphthalene	19,900	0.11

* G. N. Lewis and M. Kasha, reference 1.

case of 1,2 benzanthracene, so that the near agreement between calculated and observed f -numbers is fortuitous. One can conclude, therefore, on the basis of Table VII, that the lifetimes of the aromatic hydrocarbons are considerably longer than would at first be expected, and that some prohibition in addition to the change of multiplicity restriction must be operative.

In the case of benzene, one might at first think of the electronic symmetry prohibition, but the use of the experimental $^1A_{1g} \rightarrow ^1B_{1u}$ transition probability (strength of the 2600Å band) has already taken this into account. In most of the other molecules, no such vibrational prohibition exists, yet the lifetimes remain anomalously long. Actual calculation of the matrix elements for spin-orbit interaction, using the method of antisymmetrized products of molecular orbitals fails to show where the difficulty lies, the calculated matrix elements being of the same order of magnitude as those for the free carbon atom.¹⁵

Table VI gives some further data on the polynuclear hydrocarbons. The ratio of phosphorescence to fluorescence (only the order of magnitude is given) varies strikingly throughout the series of compounds, and illustrates one of the difficulties encountered in the study of phosphorescence. In the case of the last three compounds listed, the triplet emission band is extremely weak, and the lifetime measurements were difficult to make. The triplet emission bands of 20-methyl cholanthrene and of fluoro benzene could not be found, probably because of their extreme weakness. This involves the theory of internal conversion, which we have already mentioned in Section II, but it is a large subject and cannot be entered into here.

VII. SUBSTITUTED AROMATIC COMPOUNDS

In Table VIII we give the lifetimes of some substituted benzenes and naphthalenes. The long lifetimes are characteristic of all but the carbonyl and nitro derivatives. It can be seen that the symmetry is not correlated with the lifetime. The somewhat shorter lifetimes of aniline and phenol compared to toluene, can be explained on the basis of the atomic number effect of Section IV.

The carbonyl lifetimes can be explained in the following way. The molecule can be thought of as an aromatic ring perturbed by a carbonyl group if the interaction between these two parts is not too great. It appears

TABLE VIII. Triplet state lifetimes of substituted aromatic compounds (light atom substituents).

(a) Benzene derivatives			(b) Naphthalene derivatives		
Substance	$\tau \text{ (sec.)}$	$\nu_P^* \text{ cm}^{-1}$	Substance	$\tau \text{ (sec.)}$	$\nu_P \text{ cm}^{-1}$
Benzene	7.0 ± 5	29,400	Naphthalene	2.6 ± 2	21,300
Toluene	8.8 ± 2	28,800	α -methyl naphthalene	2.5 ± 2	20,850
Aniline	4.7 ± 3	26,800	α -amino naphthalene	1.5 ± 1	19,000
Phenol	2.9 ± 1	28,600	α -naphthol	1.9 ± 1	20,500**
Fluoro benzene	too weak to measure		β -naphthol	1.3 ± 1	21,100**
Benzoic acid	2.5 ± 2	27,200	α -fluoro naphthalene	1.5 ± 1	20,970
Benzoate ion	0.7 ± 1	27,700	β -naphthoic acid	2.5 ± 2	20,900
Anisole	3.0 ± 1	28,200	Methyl β -naphthyl ketone	0.95 ± 5	20,700†
Aceto-phenone	0.008 ± 2	26,000**	α -nitro naphthalene	0.049 ± 2	19,200**

* The maximum frequency of the long-lived emission band is from the work of R. V. Nauman except where noted. See R. V. Nauman thesis, University of California, 1947.

** G. N. Lewis and M. Kasha, reference 1.

† M. Kasha, private communication.

¹⁴ H. B. Kleven and J. R. Platt, J. Chem. Phys. 17, 470 (1949).

¹⁵ D. S. McClure, unpublished work.

TABLE X. Relation of lifetime to absorption strength.

Compound	Lifetime from absorption band* (sec.)	Measured lifetime (sec.)
Benzene	0.20–1.5**	7.0±5
Bromo benzene	0.0030±5	(0.0001)***
<i>P</i> -dibromo benzene	0.00153±6	0.00033±3
β -bromo naphthalene	0.010±3	0.021±1
β -iodo naphthalene	0.0019±1	0.0025±1

* All these absorption bands had to be corrected for the overlap of the main absorption bands. This overlap is appreciable even though the 0–0 bands of the two transitions are in some cases 10,000 cm⁻¹ apart. An exponential curve fitted to the tail of the main band and extrapolated into the region of the triplet band was assumed to give the right correction. The spectra were taken on the Beckmann spectrophotometer in solution at room temperature, while the lifetimes were measured in rigid E.P.A. (see note to Table I) at 77°K.

** These are the minimum and maximum values. The integration over the bands at room temperature is very inaccurate.

*** See note to Table III(c).

justifiable to make this assumption when considering the lowest triplet states of the aromatic carbonyl compounds because of the results obtained. If the lowest triplet states of the two "parent molecules" are alone considered, the perturbation theory gives fairly simple results for the energy and lifetime of the lowest triplet state of the "compound" molecule. If E is the energy of the triplet state of the "compound" molecule, E_1 and E_2 the energies of the parent molecules, and h_{ij} the matrix element of the perturbation involving the two states, the secular equation is

$$\begin{vmatrix} E_1 + h_{11} - E & h_{12} \\ h_{12} & E_2 + h_{22} - E \end{vmatrix} = 0.$$

The two values of E are thus

$$E_a = E_1 + h_{11} + \frac{h_{12}^2}{\Delta E + \Delta h_{ii}} \quad \text{and} \quad E_b = E_2 + h_{22} - \frac{h_{12}^2}{\Delta E + \Delta h_{ii}}$$

and the corrected wave functions for the perturbed states are

$$\psi_a = \psi_1 \left(1 - \frac{h_{12}^2}{\Delta E^2} \right)^{\frac{1}{2}} + \psi_2 \frac{h_{12}}{\Delta E}, \quad \psi_b = \psi_1 \frac{h_{12}}{\Delta E} + \left(1 - \frac{h_{12}^2}{\Delta E^2} \right)^{\frac{1}{2}} \psi_2.$$

The lifetime of the lowest triplet state of the "compound" molecule (say state b) is then approximately given by

$$\frac{1}{\tau_b} = \frac{1}{\tau_1} \left(1 - \frac{h_{12}^2}{\Delta E^2} \right) + \frac{1}{\tau_2} \left(\frac{h_{12}}{\Delta E} \right)^2.$$

Even if h_{12} could be evaluated accurately, this formula would have only qualitative significance because of the rather severe use of perturbation theory. Nevertheless, it shows that the triplet state lifetimes lie between the lifetimes of the two parent compounds, and we can also deduce that in energy, lifetime and spectrum, the compound molecule will more nearly resemble that parent molecule whose triplet energy level lies the lower. If we suppose that h_{12} is approximately given by the difference

$E_2 - E_b$, we can make rough comparisons with experiment. As an example, we can consider that acetophenone consists of an acetone-like part and a benzene-like part. The triplet level of the benzene molecule is at 29,400 cm⁻¹, that of acetone is at 26,000 cm⁻¹, while that of acetophenone is at 24,000 cm⁻¹. Thus h_{12} is 2000 cm⁻¹ and $(h_{12}/\Delta E)^2$ is 0.35, so that the lifetime of acetophenone should be roughly three times that of acetone. It is actually about ten times that of acetone. In this case, we expect, and find, that the spectrum and lifetime of acetophenone are characteristic of ketones. In the case of methyl β -naphthyl ketone, the triplet level of the hydrocarbon part is below that of the acetone part and the lifetime and spectrum of the combination are more similar to naphthalene than to acetone. In this case the data are: naphthalene, 21,300 cm⁻¹, 2.6 sec.; acetone 26,000 cm⁻¹, 0.0006 sec.; methyl β -naphthyl ketone 20,800 cm⁻¹, 0.95 sec. The calculated value of τ for the combination would be 0.04 sec. These considerations give satisfactory results for a number of other side groups such as the nitrile, carboxyl and nitroso. Thus we can correctly predict the approximate lifetimes of many complex molecules from the information we have about the simple ones.

The lifetimes of the aromatic nitro compounds cannot be explained so simply. Interaction between the nitro group and the ring is too large in this case. The lifetimes are all shorter than in the unsubstituted ring compounds. Nitro benzene has an extremely weak luminescence and nitro methane shows no appreciable long lived luminescence. This constitutes a further barrier to the interpretation. Table IX gives the lifetimes and the maximum frequency of the emission band (position of the triplet level) for a group of aromatic nitro compounds.

An interesting effect of substitution in an aromatic compound is the apparent steric hindrance effect on the lifetimes of the biphenyls. *oo'* difluor biphenyl has its lowest triplet level at 25,700 cm⁻¹ and the lifetime for this state is 0.88±4 sec., while the *pp'* compound has its triplet level at 23,000 cm⁻¹ and a lifetime of 3.2±2 sec. The *pp'* compound is very close to biphenyl in these properties. For biphenyl we have 22,800 cm⁻¹ and 3.6±2 sec.

VIII. OTHER COMPOUNDS

A small amount of data on the triplet state lifetimes of some of the other classes of organic compounds has been obtained. Some of the nitrogen analogs of the polynuclear aromatic hydrocarbons, e.g., pyridine and quinoline, have the long lifetimes characteristic of the corresponding hydrocarbons. One which does not is pyrazine (a benzene ring with two nitrogens para to each other), whose lifetime is 0.020±2 sec. The reason why this should behave differently from the aromatics is not known, but a knowledge of the term scheme of the molecule might give the answer. The straight chain

amidinium dye $\text{NH}_2\text{—CH=CH—CH=NH}_2^+$ can be described by the same metallic model as the aromatic ring compounds¹⁶ and might be expected to behave as they do. Its lifetime, however, is 0.0030 ± 2 sec., approximately what one would expect for a carbon compound according to the estimates of Section III.

The luminescence of the ethylenic compounds has not been studied as yet because of the necessity for exciting them in the far quartz or vacuum region of the ultraviolet. It may well be, in view of Mulliken's theory of the triplet state of ethylene,¹⁷ that no luminescence will be found. If it is assumed that the step-out on the long wave end of the absorption spectrum of cyclohexene¹⁸ (also present in the spectra of other ethylenic compounds) is due to a singlet-triplet transition, the lifetime calculated from this band is 0.002 to 0.005 sec., which is in the range estimated in Section III for carbon-containing compounds. Overlapping by the strong singlet-singlet band prevents a more accurate estimate.

It was assumed by Lewis and Kasha² that the characteristic band of the nitroso compounds at 7500Å is due to a singlet-triplet transition. The absorption strength of the aliphatic nitroso compounds appears to be too great if the entire band in this region is due to the intercombination. Using the published data¹⁹ for the compound 1-chloro-1-nitrosocyclohexane, the calculated lifetime is found to be 4.2×10^{-6} sec. Making proper allowance for the inaccuracy of the relation used to relate absorption strength to emission lifetime (see next section), the value just obtained seems too short for a singlet-triplet transition in this type of molecule. There is also evidence for the lack of any atomic number effect, as examples of bromo and chloro nitroso compounds having the same absorption strength may be found (see reference 19). In view of the similarity of these compounds to the carbonyl compounds, there may

be a triplet band hidden by the singlet band. The luminescences have not been studied as yet because of the difficulties of measuring weak infra-red radiation.

IX. THE CALCULATION OF LIFETIMES FROM THE ABSORPTION STRENGTH

We have done this several times in the previous section, and we calculated f values from lifetimes in Section V. Lewis and Kasha² discussed this problem and were able to give a few examples of the application of the well known equation (their Eq. (1)) for the atomic case to molecules. Since that time, it has been possible to test the accuracy of this equation by comparing measured triplet state lifetimes with the corresponding integrated singlet-triplet absorption bands. The results are given in Table X. In calculating the lifetimes from the absorption band, n^2 has been set equal to 1.0, and $g_u/g_l = 3$. In two of the examples the measured lifetime is considerably shorter than that found from the absorption band, while in the other three it is appreciably greater. Judging from these results therefore, the estimates of lifetimes we have made in Section VIII cannot be considered reliable to within less than a factor of five. The equation which has been derived for isolated atoms is admittedly a poor approximation for molecules embedded in a rigid medium or in a liquid solution. The fact that internal conversion and changes of molecular configuration take place can be allowed for in deriving a similar equation for molecules, but it is difficult to evaluate the parameters which appear in the final equation. We will therefore not go further into this subject, but leave it for some future investigation.

ACKNOWLEDGMENTS

I wish to thank Professor G. E. Gibson for his help in this work. I am also indebted to Dr. David Bohm for suggesting some of the interpretation of the data which has been made and to Dr. M. Kasha for many fruitful discussions of various problems. I also wish to thank the Dow Chemical Company for a fellowship, and the Shell Development Company for a grant-in-aid, both of which assisted in the progress of this work.

¹⁶ W. T. Simpson, J. Chem. Phys. 16, 1124 (1948). I am indebted to Dr. Simpson for letting me have some of this compound.

¹⁷ R. S. Mulliken, Rev. Mod. Phys. 14, 265 (1942).

¹⁸ H. Stuckeln, H. Thayer, and P. Willis, J. Am. Chem. Soc. 62, 1717 (1940). I am indebted to Professor E. P. Carr for some of the original data from this paper.

¹⁹ D. L. Hammick and M. W. Lister, J. Chem. Soc. 1937; 1,489.