

THE TRIPLET STATE PROPERTIES OF FLAVONES:  
A STUDY OF TRIPLET-TRIPLET ABSORPTION  
AND LUMINESCENCE SPECTRA,  
AND A MOLECULAR ORBITAL INVESTIGATION  
OF THE TRIPLET STATE ENERGIES

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FRANCIS J. GREGORY

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FRANCIS J. GREGORY

A dissertation submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
of the degree of

MASTER OF SCIENCE

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### ACKNOWLEDGEMENTS

This work is dedicated to my wife Claudette, whose support was instrumental in its completion, and to my parents. I would also like to thank Dr. Bryan Henry for his unselfish cooperation, and the Chemistry Department for their financial aid. The warmest appreciation is extended to all my instructors and fellow students who at one time or another helped me along my way.

ABSTRACT

Triplet-triplet absorption spectra of flavone, 7-hydroxy-flavone and 5-methyl-7-hydroxy flavone in the region  $12,000 \text{ cm}^{-1}$  to  $29,000 \text{ cm}^{-1}$  were obtained in EPA glass at  $77^\circ\text{K}$  using a continuous cross illumination technique. The T-T decay lifetime was recorded using a flash technique, and a comparison was made with measured phosphorescence lifetime data in order to verify the T-T nature of the transitions. The presence of interference due to photoproducts was noted in the attempt made to measure the T-T absorption spectra of 5-hydroxy flavone and 5-hydroxy-7-methyl flavone. The photoproduct absorption spectra of these molecules between  $14,000 \text{ cm}^{-1}$  and  $25,000 \text{ cm}^{-1}$  has been recorded.

The total emission spectra of flavone, 7-hydroxy flavone, 5-methyl-7-hydroxy flavone, 5-hydroxy flavone and 5-hydroxy-7-methyl flavone were obtained in EPA glass at  $77^\circ\text{K}$ . The range investigated was between 300 and 700 nanometers. An attempt to explain the lack of fluorescence in the emission spectrum of flavone and its appearance in the emission spectra of the hydroxy derivatives has been made. It is proposed that because of the reduced efficiency of intersystem crossing caused by the shifting of the  $n\pi^*$  states in the hydroxy derivatives, fluorescence is able to compete effectively with phosphorescence in these compounds.

Theoretical calculations have been carried out utilizing a combination of CNDO methods based on the CNDO/S formalism of

Jaffe, et al. Calculations of the energy of the lowest triplet state, as well as the calculation of T-T transition energies and oscillator strengths have been performed on flavone, 7-hydroxy flavone and 5-methyl-7-hydroxy flavone. The cartesian coordinates for all atoms in each molecule were determined by systematic construction of each molecule using standard bond lengths and bond angles and the assumption of a planar geometry in flavone. The calculations were able to account accurately for both the energies of the T-T transitions and their relative intensities. The agreement between experimental and calculated results was excellent in the case of flavone.

Although the correlation was slightly poorer for the two 7-hydroxy derivatives, the agreement in these latter two compounds is still very good. The sensitivity of this computational method to the geometry of the molecule examined was mentioned, and has been used to discuss the validity of the assumption of planar geometry in flavone.

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## INTRODUCTION

Despite the lack of information on the triplet states of many heterocyclic molecules, the role of such states both in photochemical and photobiological processes cannot be underestimated. Because of their abundance in nature and their increasing use in pharmacy, heterocyclic molecules are being studied more thoroughly today than in the past. Investigations however tend toward the biological and biochemical aspects of the compounds, and many of the physical properties of the molecules, notably those related to their triplet states, are neglected. The present study was undertaken in an attempt to extend the knowledge of triplet states to a family of heterocyclic molecules commonly found in plants.

Flavones, whose formation in plants requires the presence of light, are found to be naturally occurring in the leaves and petals of many plants. When found in high concentrations, flavones and hydroxy substituted flavones are known to contribute markedly to the colouration of the plant (1). Besides their occurrence in plant material, hydroxy flavones are known to be important antioxidants and are useful in the protection of Vitamin C from oxidation (2).

## I. General Description of Triplet-Triplet Studies.

The first recognition of a spectroscopic phenomenon having to do with the triplet state was made by Sklar in 1937 (3). The weak intensity of the absorption that Sklar observed in benzene was at that time tentatively assigned as a singlet-triplet intercombination transition. Efforts to further understand the "metastable" state known as the triplet state increased. It was Lewis and Kasha who in 1944 identified phosphorescence as being the result of radiative combination between the lowest triplet state and the ground singlet state (4). Seven years later McClure published a comprehensive survey of triplet-triplet (T-T) absorption (5). This was the first well organized survey since the initial observation of T-T absorption carried out by Lewis, Lipkin and Magel on a solution of fluorescein in boric acid glass (6). Since the time of these studies, much research has been carried out on the triplet states of organic molecules and it is now felt that triplet states are fairly well understood. That the triplet states of organic molecules are extremely important owing to their involvement in photochemical and photobiological reactions is also recognized (7,8). The lowest triplet state is of particular interest since it is from this level that both T-T absorption and phosphorescence occur.

In order to observe T-T absorption or phosphorescence it is necessary that a certain percentage of the ground state molecules in the sample being studied are excited to the lowest

FIGURE 1

Radiative and radiationless processes contributing to the population and deactivation of the  $T_1$  state. The rate constants  $k$  have the following meanings:

$k_A$  = number of quanta absorbed per second per molecule.

$k_F$  = the rate constant of fluorescence ( $\text{sec}^{-1}$ ).

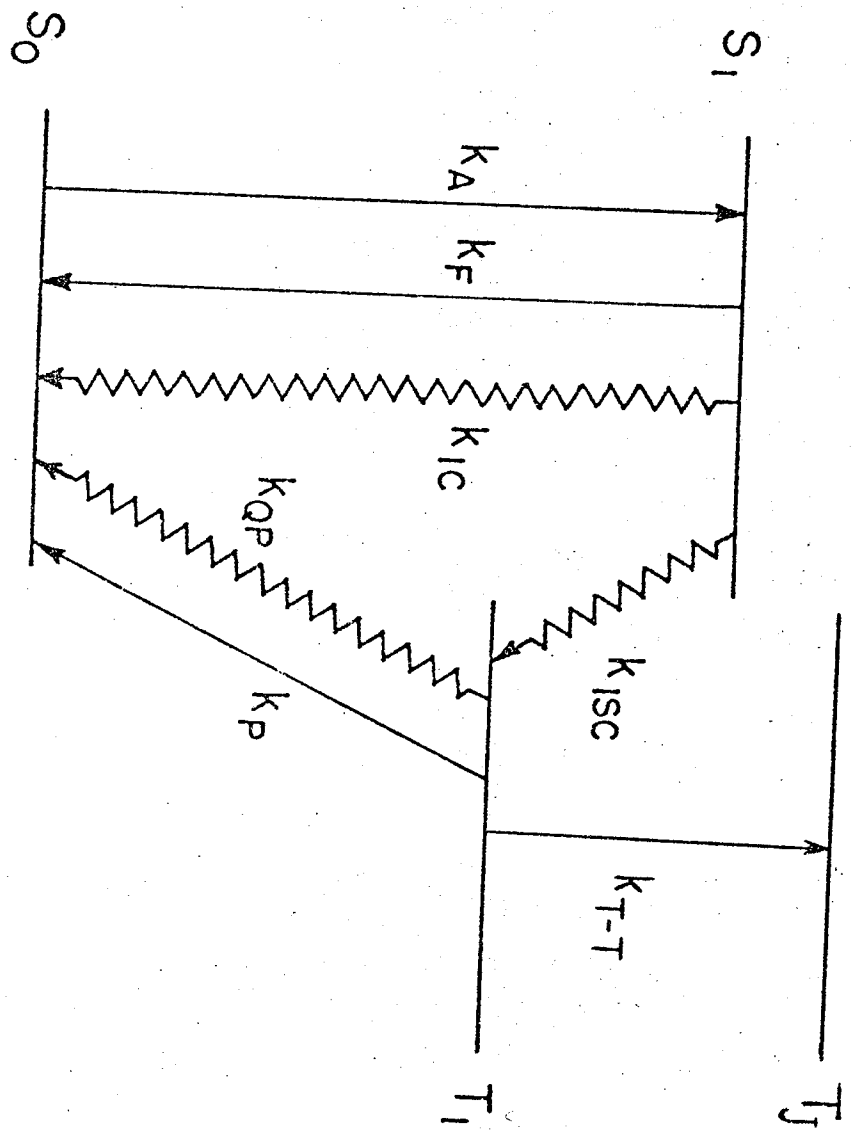
$k_{IC}$  = the rate constant of internal conversion ( $\text{sec}^{-1}$ ).

$k_{ISC}$  = the rate constant of intersystem crossing ( $\text{sec}^{-1}$ ).

$k_P$  = the rate constant of phosphorescence ( $\text{sec}^{-1}$ ).

$k_{QP}$  = the rate constant of the intramolecular radiationless process  $T_1 \rightarrow S_0$  ( $\text{sec}^{-1}$ ).

$k_{T-T}$  = the rate constant of triplet-triplet absorption ( $\text{sec}^{-1}$ ).



triplet state. The primary photophysical processes leading to the population of  $T_1$  and the pathways of triplet-triplet excitation and decay are best visualized by the use of a Jablonski diagram as shown in figure (1). From the relative position of the molecular energy levels in the Jablonski diagram it would seem that the most simple method of populating  $T_1$  would be by direct excitation. This however is found to be a most inefficient process under ordinary conditions due to the low absorption coefficients associated with  $T_1 \leftarrow S_0$  transitions. Population of  $T_1$  is best achieved via excitation of the ground state molecule to an excited singlet state, with subsequent vibrational deactivation to  $S_1$ . The triplet manifold is then populated via intersystem crossing from the lowest excited singlet state  $S_1$ . Both absorption and emission processes are included in figure (1), with the radiative and radiationless processes being represented by solid and wavy lines respectively. Further explanation of the terminology and processes involved is available in any book dealing with molecular luminescence (9). This section deals primarily with T-T absorption. A more thorough discussion of phosphorescence will be given in the following section.

Two methods are customarily used in the investigation of T-T absorption. They are the steady state and the synchronized flash techniques developed by Lewis et al (6,10) and Porter (11) respectively. The former method is useful when the triplet state lifetime  $\tau_p$  is greater than 0.1 second. In rigid solution,

in which intermolecular processes are minimized, deactivation of  $T_1$  is determined solely by intramolecular radiationless and radiative processes. This is shown in equation (1):

$$\frac{-d [T]}{dt} = k_p [T] + k_{QP} [T] \quad (1)$$

where  $k_p$  and  $k_{QP}$  are the rate constants for phosphorescence and radiationless deactivation from  $T_1$  to  $S_0$  respectively. The observed triplet state lifetime  $\tau_p$  is given by equation (2):

$$\tau_p = 1/(k_p + k_{QP}) \quad (2)$$

Only when  $\tau_p$  is greater than 0.1 second will there be a sufficient buildup of triplets such that T-T absorption may be observed. The source of illumination required to obtain this necessary steady state population of triplets must understandably be of high intensity. High intensity mercury arcs are most often used, but recently, lasers are being frequently used. Other than being susceptible to the triplet state lifetime, the steady state technique is affected by such factors as the efficiency of intersystem crossing as compared to fluorescence, photo-instability of the excited states, and the presence of strong  $S_i \leftarrow S_0$  bands in the  $T_i \leftarrow T_1$  region. A summary of the important criteria for maximizing the steady state population of the lowest triplet state has been given by Henry and Kasha (12).

The synchronized flash technique has the advantage that compounds which possess a triplet state lifetime of the order of  $10^{-4}$  seconds can be studied (9), and as a result the technique



is not restricted to rigid media. In this technique, a high energy flash lasting only several microseconds is produced by the discharge of a high voltage capacitor. A continuous light source passes through the sample perpendicular to the direction of the light from the flash, through a monochromator set at a fixed wavelength, and into a photomultiplier. The flash populates the lowest triplet state and energy is absorbed from the continuous source to produce the triplet-triplet transitions. The absorption of the sample at any wavelength is recorded on an oscilloscope. By varying the wavelength on the monochromator leading to the photomultiplier tube, the total T-T absorption spectrum may be obtained. Although the flash technique is subject to most of the criteria to which the steady state method is, the former method is much more sensitive to problems arising from photoproduct interference. This is because of the higher intensity of the flash, and the inherently greater difficulty of filtering a flash as opposed to a continuous source of excitation. Both methods however have yielded excellent results.

As indicated, triplet-triplet studies can be undertaken in the gas, liquid or solid phase. The majority of work has however been carried out in rigid solution due to the negligible contribution of intermolecular deactivation processes under such conditions. Equation (3) is the generalized expression for the total rate of deactivation of the triplet state, including both

intramolecular and intermolecular processes.

$$\frac{-d[T]}{dt} = k_p [T] + k_{QP} [T] + k_T [T]^2 + k_{TS_0} [T] [S_0] + \sum_i k_{QM_i} [M_i] [T] \quad (3)$$

The third and fourth terms are radiationless self-quenching terms and the fifth represents quenching due to impurity or foreign molecules  $M_i$ . The contribution from the last term is extremely significant in the gas and liquid phases due to the high probability of intermolecular interaction. In fact, it is because of quenching species such as molecular oxygen that phosphorescence in fluid solutions is often not observed. The purpose of using rigid solutions is obviously to prevent the interaction between impurities and the solute molecules, and thus enable phosphorescence to be observable.

No change in multiplicity is required in singlet-singlet transitions, and such transitions are allowed at least with respect to multiplicity. Triplet-triplet transitions are by the same token also multiplicity allowed. Data are not available on all the triplet levels of a molecule studied, but rather are restricted to the lowest and a few of the higher triplet states. The investigation by emission of the triplet states immediately above the lowest ones is difficult due to extremely rapid internal conversion processes occurring between the triplet levels.

The electrons in an organic molecule can be differentiated by the type of molecular orbital to which they belong. Aromatic molecules utilize both the highly localized sigma ( $\sigma$ ) and

delocalized pi ( $\pi$ ) bonding molecular orbitals. Heterocyclic molecules also use  $\sigma$  and  $\pi$  bonding, but also contain highly localized non-bonding (n) molecular orbitals. Excitation of an electron from a  $\sigma$ ,  $\pi$  or n molecular orbital to an excited antibonding  $\sigma^*$  or  $\pi^*$  molecular orbital is possible in heterocyclic molecules, whereas excitations from  $\sigma$  and  $\pi$  orbitals are the only possible transitions in aromatic molecules. Because of the high energy required to excite a bonding  $\sigma$  electron to an antibonding  $\sigma^*$  or  $\pi^*$  molecular orbital,  $\sigma\sigma^*$  and  $\sigma\pi^*$  states are of little interest in conventional excitation studies. The promotion of a  $\pi$  or n electron to a  $\sigma^*$  antibonding molecular orbital also requires large energies. The energy required in such excitations is equivalent to that found in the vacuum ultraviolet region of the spectrum, and therefore  $\pi\sigma^*$  and  $n\sigma^*$  states are also not common to conventional excitation studies. Only  $n\pi^*$  and  $\pi\pi^*$  states significantly contribute to the excitation spectra of heterocyclics, while  $\pi^*\leftarrow\pi$  transitions are the main type of excitation in aromatics.

The orbital character of the lowest triplet state in a heterocyclic molecule may be pure  $n\pi^*$  or  $\pi\pi^*$  whereas aromatic molecules generally have  $\pi\pi^*$  triplet states. As indicated, the presence of non-bonding electrons in nitrogen and oxygen heterocyclics and in aromatic ketones generates the possibility of  $n\pi^*$  states. Aromatic ketones and aldehydes often have pure  $n\pi^*$  orbital character in  $T_1$ , but when both  $n\pi^*$  and  $\pi\pi^*$  states are possible, the lowest triplet may be found to be a hybrid

of the two. (Equation (4)).

$${}^3\psi = a{}^3\phi(\pi\pi^*) + b{}^3\phi(n\pi^*) \quad (4)$$

In the above relation,  ${}^3\psi$  is the resultant orbitally mixed state resulting from the mixing of the orbitally pure  ${}^3\phi(\pi\pi^*)$  and  ${}^3\phi(n\pi^*)$  states, and the factors a and b are the mixing coefficients. The criteria used to discriminate between  ${}^3(n\pi^*)$  and  ${}^3(\pi\pi^*)$  states can lead to confusing results when the triplet state under consideration is of the mixed type. This point will be further discussed in the following section.

## II. Emission Studies.

With the increase in the number of molecules found to exhibit T-T absorption, most scientists have become aware of the importance of the involvement of triplet states in most fields of chemistry. However, the phenomenon of phosphorescence remains even today the more familiar manifestation of the triplet state. This familiarity is likely a direct result of studies carried out subsequent to the monumental work by Lewis and Kasha in which the luminescence of eighty-nine compounds was examined (4). Early studies were mainly restricted to aromatic molecules, undoubtedly due to the relatively long phosphorescence lifetimes they exhibit. More recently however, the improvement of our understanding of the mechanism of phosphorescence, as well as our increased technological efficiency have enabled the study of phosphorescence to be extended to molecules exhibiting very weak emission.

Phosphorescence is not the only type of emission produced by organic molecules. Kasha's rule (13) states that the emitting level of a given multiplicity is the lowest excited level of that multiplicity. Accordingly, we expect two types of emission: one from  $T_1$ , called phosphorescence; and one from  $S_1$  which is labelled fluorescence. Experimentally it is found that some molecules fluoresce while others only phosphoresce. In other cases, both fluorescence and phosphorescence are observed. The absence of both types of emission is also common. The pre-

sence or absence of fluorescence and/or phosphorescence has been found to depend on the relative rates of both the radiative and radiationless processes taking place. Solvent and temperature effects on luminescence have also been noted, and are the result of a change in the relative rates of the radiative and radiationless processes.

The rates of the radiative and radiationless processes shown in figure (1) are found to be quite dependent on the orbital character of the states between which the transition is taking place. The efficiency of the radiationless transitions will be discussed here. A discussion of the radiative transitions is forthcoming.

Population of  $T_1$  is generally from the lowest excited singlet state  $S_1$ , although upper triplet states may be significant in the population of  $T_1$ . Internal conversion from higher excited singlet states to  $S_1$  and from the higher excited triplet states to  $T_1$  is generally quite rapid, and therefore the rate determining step in the population of  $T_1$  is the intersystem crossing process. In a molecule whose lowest triplet state is  $\pi\pi^*$ , the singlet state from which intersystem crossing to  $T_1$  is occurring may be a  $\pi\pi^*$  or an  $n\pi^*$  state. Using the theory of radiationless transitions given by Robinson (14), El-Sayed has shown that the  $S_{n\pi}^* \rightarrow T_{\pi\pi}^*$  and  $S_{\pi\pi}^* \rightarrow T_{n\pi}^*$  radiationless transitions are far more efficient than the  $S_{\pi\pi}^* \rightarrow T_{\pi\pi}^*$  and  $S_{n\pi}^* \rightarrow T_{n\pi}^*$  transitions (15). Whether intersystem crossing may possibly occur between any two states is obviously dependent

on the relative positions of those two states, since such deactivation will occur from a state of high energy to a state of lower energy. Therefore the relative positions of the lowest  $S_{n\pi}^*$ ,  $S_{\pi\pi}^*$ ,  $T_{n\pi}^*$ ,  $T_{\pi\pi}^*$  states will be of interest in the examination of the intersystem crossing rate of a molecule.

The increased efficiency of intersystem crossing between states of different orbital character as noted by El-Sayed enables it to compete effectively with radiative fluorescence from  $S_1$ . As a result  $T_1$  becomes populated to some extent, and phosphorescence may be observable. This contrasts with the situation in which the arrangement of the lowest singlet and triplet  $n\pi^*$  and  $\pi\pi^*$  states is such that only transitions between states of similar orbital character is possible. In this case the less efficient  $S_{n\pi}^* \rightarrow T_{n\pi}^*$  or  $S_{\pi\pi}^* \rightarrow T_{\pi\pi}^*$  transitions do not enable intersystem crossing to effectively compete with fluorescence. Here fluorescence is the only luminescence likely to be seen. A series of papers containing a more detailed description of the competitive nature of the radiationless and radiative processes as a function of the relative positions of the lowest  $S_{n\pi}^*$ ,  $S_{\pi\pi}^*$ ,  $T_{n\pi}^*$ ,  $T_{\pi\pi}^*$  states is available in the literature (16,17,18). The reader is referred to these papers for a more thorough description of the processes which affect relative fluorescence and phosphorescence intensities.

In any discussion of the lowest triplet state of a molecule, an important piece of information is its orbital character. As indicated earlier, in aromatic hydrocarbons, the lowest triplet