

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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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°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°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 (sec^{-1}).

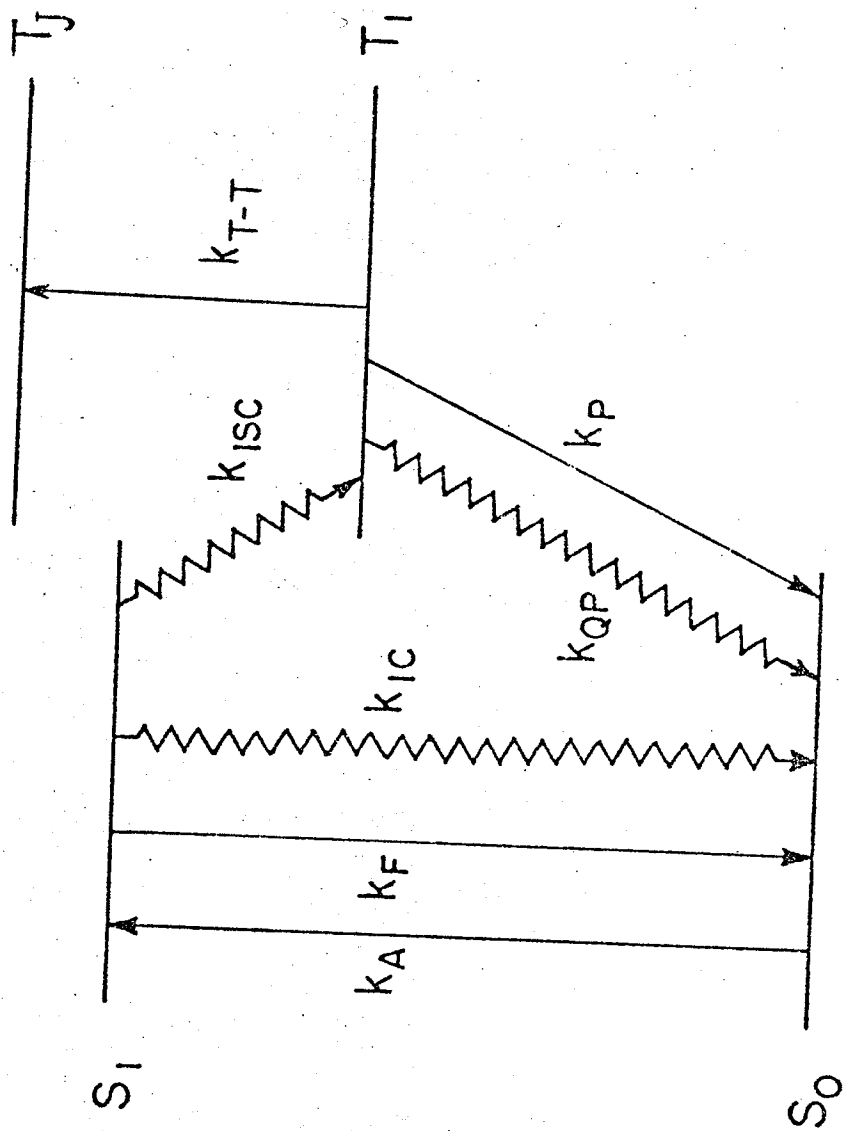
k_{IC} = the rate constant of internal conversion (sec^{-1}).

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

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

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

k_{T-T} = the rate constant of triplet-triplet absorption (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 τ_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 τ_p is given by equation (2):

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

Only when τ_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 $S_1 \leftarrow S_0$ bands in the $T_1 \leftarrow T_1$ 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.

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

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 (σ) and

delocalized pi (π) bonding molecular orbitals. Heterocyclic molecules also use σ and π bonding, but also contain highly localized non-bonding (n) molecular orbitals. Excitation of an electron from a σ , π or n molecular orbital to an excited antibonding σ^* or π^* molecular orbital is possible in heterocyclic molecules, whereas excitations from σ and π orbitals are the only possible transitions in aromatic molecules. Because of the high energy required to excite a bonding σ electron to an antibonding σ^* or π^* molecular orbital, $\sigma\sigma^*$ and $\sigma\pi^*$ states are of little interest in conventional excitation studies. The promotion of a π or n electron to a σ^* 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

state is reached by the excitation of a single π electron to an excited antibonding π^* orbital. This results in a triplet state whose configuration is said to be $\pi\pi^*$. The formation of $n\pi^*$ triplets in heterocyclic molecules and aromatic aldehydes and ketones has also been noted. In the situation in which both types of triplet states, that is $n\pi^*$ and $\pi\pi^*$ are possible, the properties of the triplet state observed are dependent on which of the two states is lower in energy. Properties such as the phosphorescence lifetime, the energy gap between T_1 and S_1 , the polarization of the phosphorescence 0,0 band and the presence of particular vibrational frequencies are all diagnostic of the orbital character of T_1 . These criteria are not unique, since other perhaps less reliable factors are also available in the identification of the orbital character of T_1 (9).

In equation (3), presented in the previous section, the implication is that, in order for phosphorescence to be observable, the total radiationless decay rate must not significantly exceed the phosphorescence decay rate. Phosphorescence is rarely apparent in the fluid phase because of the extremely efficient radiationless processes which take place under such conditions. The quenching of phosphorescence by impurities such as molecular oxygen is one such process. Therefore, as in T-T absorption studies, supercooled rigid glass solutions have played an increasing role in the elucidation of phosphorescence spectra. Solvents commonly used include ethanol, 3-methyl pentane,

hexane, mixtures of ethyl ether and ethanol (E:E), and mixtures of ethyl ether, isopentane and ethanol (EPA). Extreme purity of both the solvent and solute is critical because of the possibility of efficient emission from an impurity. EPA mixed solvent is used in the present study, and is sufficiently pure to permit accurate phosphorescence studies. No phosphorescence of the EPA solvent system is apparent from freshly opened bottles, but a slight blue-green emission is noted in aged samples. This interfering emission is probably caused by the peroxides formed by the air oxidation of the ether molecules.

Based on experimental results, it is well documented that phosphorescence originating from $n\pi^*$ triplet states has a distinctly shorter decay time than do decay times resulting from emission from $\pi\pi^*$ triplet states. In regard to the actual magnitudes of $^3(n\pi^*)$ and $^3(\pi\pi^*)$ phosphorescence emissions, a decay half-life greater than one second is considered to be from a $^3(\pi\pi^*)$ states, whereas a lifetime less than 10^{-1} seconds is from a $^3(n\pi^*)$ state. The difference in radiative lifetimes between $^3(\pi\pi^*)$ and $^3(n\pi^*)$ states results from differences in the spin-orbit coupling involved. The transition from T_1 to S_0 is multiplicity forbidden. In order for phosphorescence to occur, there must be spin-orbit coupling of T_1 to some singlet state which has a non-zero transition dipole moment to the ground state. Since states of different orbital parentage mix most efficiently, a $T_1^3(\pi\pi^*)$ state will be coupled to $^1(n\pi^*)$

states. However, the allowed transition moment of an $S_1^1(n\pi^*) \rightarrow S_0$ transition is low, and the coupling of such transitions to $T_1^3(\pi\pi^*) \rightarrow S_0$ transitions does not give much "allowed" transition dipole moment to the $T_1^3(\pi\pi^*) \rightarrow S_0$ transition. Thus a $T_1^3(\pi\pi^*)$ state is expected to exhibit a long phosphorescence lifetime. On the other hand, a $T_1^3(n\pi^*)$ state will be coupled to $^1(\pi\pi^*)$ states which have highly allowed transition moments. Thus the phosphorescent $T_1^3(n\pi^*) \rightarrow S_0$ transition contains a strong "stolen" transition dipole moment, and accordingly the phosphorescence lifetime of a $T_1^3(n\pi^*)$ state is quite short.

Another factor which may permit differentiation between $\pi\pi^*$ and $n\pi^*$ T_1 triplet states is the energy gap between the emitting T_1 state and the lowest excited singlet state S_1 . The singlet-triplet interval is given by equation (5), where E_s and E_t are the energies of the lowest singlet and triplet states respectively; and K_{nk} is the electrostatic exchange integral for an nk electron configuration.

$$E_s - E_t = 2K_{nk} \quad (5)$$

K_{nk} is given by

$$K_{nk} = \iint \psi_n(x_1) \psi_k(x_1) \psi_n(x_2) \psi_k(x_2) \{e^2 / |x_1 - x_2|\} dx_1 dx_2 \quad (6)$$

where $\int \psi_n(i) \psi_k(i) dx_i$ ($i = 1$ or 2) are the overlap integrals. It is obvious from equation (6) that the singlet-triplet energy gap is directly related to the overlap between the orbitals n and k . In $\pi\pi^*$ states the overlap is between an

out-of-plane π orbital and an out-of-plane π^* orbital. This overlap is strong and therefore the exchange integral is large, yielding a large singlet triplet energy gap. This gap is smaller however in $n\pi^*$ states since here the overlap between an in-plane n orbital and an out-of-plane π^* orbital is much weaker. Experimentally it is found that the energy separation between $n\pi^*$ and $^3(n\pi^*)$ states is approximately $2000-4000\text{ cm}^{-1}$, whereas the energy gap is from $3000-20,000\text{ cm}^{-1}$ between $^1(\pi\pi^*)$ and $^3(\pi\pi^*)$ states.

Polarization data can be obtained only when the phosphorescing molecule exhibits a well defined 0,0 band. Generally, emitting $^3(n\pi^*)$ states are in-plane polarized and $^3(\pi\pi^*)$ states are out-of-plane polarized. In the polarization of the phosphorescence 0,0 band, the important consideration is the orbital character of the perturbing state. That is, phosphorescence from a $^3(n\pi^*)$ state is in-plane polarized because the perturbing state is $\pi\pi^*$. Similarly the perturbing $n\pi^*$ state in $^3(\pi\pi^*)$ phosphorescence yields out-of-plane polarization. The difficulty in obtaining polarization data lies in our ability to obtain a well resolved phosphorescence spectrum, something which is not always possible.

In well resolved phosphorescence spectra, vibrational modes are often quite pronounced. The analysis of the vibrational structure is often indicative of the orbital character of the state from which emission is occurring. Aromatic molecules, which contain σ and π electrons exhibit charac-

teristic ring stretching frequencies which indicate a triplet $\pi\pi^*$ state. In aromatic ketones, the C-O stretching vibrations are often quite pronounced in the phosphorescence spectrum, which is evidence that the emission is from an $n\pi^*$ state. Should the lowest triplet state lie in close proximity to another triplet state, it becomes difficult to determine the orbital character of T_1 since the vibrational envelope is often less well defined (19). This loss of resolution is likely due to the vibronic interaction between the two closely spaced triplet states.

The four criteria just discussed aid tremendously in the assignment of the orbital character of the lowest triplet state. This is strictly true only when T_1 is configurationally pure. When an orbitally mixed configuration is involved, results from phosphorescence lifetimes and the singlet-triplet energy gap are often ambiguous. Under such circumstances the vibrational structure of the phosphorescence spectrum is either very complex or poorly resolved. Thus polarization data cannot be obtained or are confusing. In cases where the results indicate a mixed triplet state, assignment of the orbital character of T_1 should be undertaken with caution, and by considering as many criteria as can be obtained.

III. Development of Theoretical Methods of Electronic Absorption Studies.

(a) Early Methods.

Since the birth of quantum mechanics, chemists have been interested in its application to the calculation of the electronic structure of molecules. The molecular orbital (MO) approach has proved to be the most flexible of all methods, and the present discussion includes the development of the techniques from the earlier ab initio calculations to the more recent CNDO formulations. During the development of many of the methods of calculation, particularly in the earlier studies, correlation was sought between experimental and calculated singlet-singlet spectra. The present interest is however primarily in the correlation of triplet-triplet spectra, and where possible, an effort has been made to limit the discussion accordingly.

The earliest methods involved ab initio calculations in which only fundamental constants such as the speed of light, the charge and mass of the electron and Planck's constant were used as input in the calculations. Although such methods were relatively straightforward, they were hindered by severe computational difficulties. It became obvious that such methods were not feasible for large molecules in a practical sense, and work was directed to methods which combined experimental results with theoretical calculations, that is, the semi-empirical methods. These methods often required very crude

approximations, whose effects were minimized by the choice of numerical values for some of the terms in the calculations such that the results obtained agreed with the known experimental findings. Results obtained in this fashion were then further tested in similar calculation on other molecules.

The development of semi-empirical methods led to the recognition that the electronic properties of planar unsaturated or aromatic molecules could be determined by considering only the π electron system of the molecule. The possibility of separating the σ and π electron systems by treating the σ electrons as a rigid nonpolarizable core led to the well known Huckel Molecular Orbital (HMO) method (20). (A review of the HMO method is available in reference (21)). Although it has the merit of simplicity, the Huckel method utilizes the approximation that the many electron function of a molecule, $\psi(1,2,3,..)$ may be factored into a series of one electron functions, $\psi(1), \psi(2), \dots$, where each $\psi(j)$ is a one electron function, dependent only on the space and spin coordinates of the j^{th} electron. This implies that we can tell which electron occupies which spin orbital, an obvious impossibility. Also, difficulty arises in giving a precise definition of the one-electron Hamiltonian. Another serious approximation is that all electron-electron repulsions are either neglected or averaged out through the use of empirical parameters. The failure of the method in predicting electronic absorption transitions as well as its weaknesses in several other areas

has resulted in the method being replaced by the more elaborate Extended Huckel Method (EHMO) (22). This method will be discussed later.

(b) The Pariser, Parr and Pople Self-Consistent Field Molecular Orbital Method.

With the formulation of the self-consistent field (SCF) method of Roothaan (23) and its application by Pariser and Parr (24) and Pople (25) the difficulty of neglect or averaging out of the electron-electron repulsions inherent in HMO theory has been corrected. The Pariser, Parr and Pople (PPP) method incorporates the purely theoretical method of antisymmetrized products of molecular orbitals, and includes configuration interaction. Configuration interaction, which is a method of generating spectroscopic states by allowing states which arise from different electronic configurations to interact, is included since it has been shown (25) that different configurations cannot always be treated independently. Moreover the interaction of various configurations often leads to important changes in molecular properties, particularly excited levels. The method also includes semi-empirical quantities for the atomic orbital integrals involving the core Hamiltonian. In the π electron approximation, significant simplification is achieved in the evaluation of the electronic repulsion integrals by representing the π orbital by a uniformly charged sphere. Differential overlap is considered in this treatment, and

further simplification of the calculations is achieved by setting the overlap integral $S_{\mu\nu}$ equal to zero if $\mu \neq \nu$, and assigning a value of unity if $\mu = \nu$. A more thorough mathematical treatment is available in the original papers of Pariser, Parr and Pople.

The PPP theory was primarily designed to predict both wavelength and intensity of the main visible and near ultraviolet electronic absorption bands of unsaturated organic molecules. The first triplet-triplet calculations using this method were carried out by Pariser (26) on benzene, naphthalene, anthracene, tetracene and pentacene. In this study, the author took advantage of several generalizations applicable to even alternant hydrocarbons. These included the neglect of differential overlap, as well as limited configuration interaction (CI). CI was restricted to ground state and singly excited configurations whose energy lay within three electron volts of the lowest energy configuration of the particular symmetry representation. This restriction in the author's opinion was due to the fact that further CI would increase the work tremendously, while not significantly improving the final result. In the treatment of the core, Pariser considered only nearest neighbour resonance interaction, while penetration integrals were either neglected or taken to be constant. The results obtained by Pariser yielded energies for the lowest triplet which were too low; some as much as twenty percent. The oscillator strengths for the T-T transitions were, on the other hand, too high.

The author also noted an inversion of the intensities of the two first T-T transitions in the naphthalene molecule as compared to experiment. Pariser made no effort to account for this important discrepancy, although he did stress that the calculations were based on an isolated molecule. He stated that small discrepancies are possible since the experimental results were determined on molecules which were not isolated, but rather in an environment where the solvent matrix may have played a part.

Pariser's pioneering work in the study of T-T transitions inspired many others. Further study using the PEP-SCF-MO method was undertaken on naphthalene by DeGroot and Hoytink (27) in order to remedy the problem of the inverted triplet-triplet transition oscillator strengths found by Pariser. They felt that the error in his calculations was due to fact that although all singly excited configurations with respect to the ground singlet state were included, singly excited configurations with respect to the lowest triplet state were neglected. DeGroot and Hoytink therefore repeated Pariser's calculations using however a more extended treatment of configuration interaction. They considered all configurations whose energies lay below 7.5 electron volts, both singly and doubly excited with respect to the lowest triplet configuration. All other parameters remained the same as those used by Pariser. In this case however, the erroneous intensities were found to be in the correct order, in agreement with experiment (28).

About the same time as the work of DeGroot and Hoytink, Orloff extended the theoretical study of T-T transitions to a series of twelve alternant hydrocarbons (29). By utilizing the Coulomb integrals and resonance integrals given by Pariser (26) and restricting CI to first order, Orloff was able to predict the energy of the most intense T-T transition for each molecule to within 0.1 electron volt of the experimental value. Agreement for the weaker transitions was however only good to about 0.5 electron volts. In a subsequent paper (30) it was shown that agreement between the calculated and experimental oscillator strengths for the molecules studied by Orloff was good when the former results were scaled by a factor of one-sixth. The successful application of the SCF-MO method of Pariser, Parr and Pople by Orloff led to an equally successful calculation of the T-T absorption spectra of phenylnaphthalenes (31).

Theoretical treatment of the T-T transitions of aromatic hydrocarbons based on the PPP method seemed to have developed to the point where calculated results agreed well with experiment. Meyer et al (32) did not approve however, of the methods used up to that date to limit the extent of configuration interaction. Accordingly they proposed a less restricted method using very large CI. The application of their methods to T-T studies of naphthalene, anthracene and tetracene gave excited state energies for the higher triplet states which agreed within one electron volt of the observed values.

Useful as the PPP method is, chemists were not satisfied with the restriction to purely π electron systems and planar molecules. The PPP-SCF-CI method had been designed mainly for π electron systems, and its extension to molecules containing non-bonding electrons met with little success. In order to remove these restrictions, such that $n \rightarrow \pi^*$ transitions could be examined, methods were sought in which all the valence electrons could be incorporated into the calculations. Such methods comprise the subject of the following section.

(c) All-Valence Electron Semi-Empirical Self-Consistent Field Methods.

One of the earliest all-valence electron methods was that of Wolfsberg and Helmholz (33) in which the spectra and electronic structure of three tetrahedral inorganic ions were investigated. In this study, diagonal matrix elements H_{ii} were taken from valence state ionization potentials, and the off diagonal elements H_{ij} determined from the approximation proposed by Mulliken (34), that is $H_{ij} = kS_{ij} (H_{ii} + H_{jj})/2$. Although the results obtained did not agree quantitatively with experimental results, qualitative agreement was found both in the energies and intensities of the transitions.

Yet another treatment of all valence electrons is the Extended Huckel method developed by Hoffmann (22). Unlike the basic Huckel method described earlier, the extended method is not restricted to π electrons. The method has essentially

replaced the original Huckel method, but like its predecessor, performs miserably in the prediction of spectral properties.

Of all the all-valence-electron, self consistent field, molecular orbital methods, the calculations using the complete neglect of differential overlap (CNDO), developed by Pople et al (35) are probably the most widely used. The method is an approximation to a full LCAO-SCF calculation, using a minimal basis set, that is a basis set consisting only of inner shell and valence shell atomic orbitals. In the CNDO treatment, the SCF approximation is that all integrals of the form $(\mu\nu|\rho\sigma)$ shown in equation (7) are neglected unless $\mu=\nu$ and $\rho=\sigma$. Since the number of remaining parameters is relatively small, application of the method to large molecules is possible.

$$(\mu\nu|\rho\sigma) = \iint \phi_{\mu}(1)\phi_{\nu}(1) \{ e^2/r_{12} \} \phi_{\rho}(2)\phi_{\sigma}(2) d\tau_1 d\tau_2 \quad (7)$$

In the application of the CNDO method to some diatomic and small polyatomic molecules (36), Pople and Segal noted that although the method appeared to yield good molecular orbitals and electron populations, a few weaknesses were apparent. Energy changes involved with changing bond lengths were found to be in error. Bond lengths were found to be too short and binding energies too large. In order to correct for these discrepancies, two modifications in the method were made. The modified version has been labelled the CNDO/2 version, whereas the unmodified method is labelled CNDO/1. The first change

made was that certain penetration type terms were omitted, since it was their contribution which led to excess bonding resulting in shorter bonds and higher binding energies. Secondly, the atomic matrix elements concerning the core, that is, the $U_{\mu\mu}$, were obtained with both the electron affinity and ionization potential of the atom, rather than with just the latter. In addition to these modifications, an extension of the theory was made to include open shell configurations in the CNDO/2 formalism. The authors applied the new method to symmetrical AB_2 and AB_3 type systems and found that good agreement was achieved between calculated equilibrium angles, dipole moments and bending force constants, and experimental results (37). Bond lengths, which in the CNDO/1 method came out too short, were found to be for the most part very good using the modified version. However, as with the CNDO/1 method, the stretching force constants determined by CNDO/2 were found to be consistently too large.

Several attempts to use the CNDO/2 method in the calculation of singlet-singlet spectra did not prove too successful (38,39,40). The difficulty was with the intermingling of σ and π orbitals, and only after slight modifications, were Del Bene and Jaffe (41) able to successfully calculate both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ singlet-singlet transitions in aromatic and heterocyclic molecules. The changes involved the substitution of semiempirical Coulomb integrals similar to those used in the PPP method; and second, the introduction of a new parameter

κ to differentiate resonance integrals between σ orbitals from those between π orbitals. Results obtained with these modifications were further refined by a limited CI calculation. The modified CNDO/2 method of Jaffe et al was labelled the CNDO/S method.

Jaffe and co-workers successfully extended the theoretical study of singlet-singlet spectra from benzene, pyridine and diazines (41) to five membered rings (42), monosubstituted benzenes and pyridines (43) and several small molecules (44). In an extended study of $n \rightarrow \pi^*$ transitions (45), Jaffe et al found that replacement of the Pariser approximation for the two center Coulomb repulsion integrals by the Nishimoto-Mataga approximation (46), significantly improved the calculated position of the ${}^1B_{1u} \leftarrow {}^1A_{1g}$ electronic transition in benzenoid compounds.

The calculation of triplet state energies for a number of carbonyl, aromatic and heterocyclic molecules has been carried out by Chang, Jaffe and Masmanidis (47) using the CNDO/S formalism. Based on the results obtained in their study, the authors concluded that the application of the method to the prediction of T-T transitions is possible.

The authors have produced a computer program which is a general purpose combination of the CNDO/2 and CNDO/S methods. The combined methods are applicable to the calculation of spectral properties of both open and closed shell systems.

Prior to the release of this program, only one earlier study of calculated T-T spectra using the CNDO/S method has been published. In an effort to reproduce the T-T spectra of coumarin and 7-hydroxy coumarin using Jaffe's original CNDO/S method (41), Crozet (48) was unable to correlate his calculated findings with his experimental results. He concluded that the CNDO/S method was yet not reliable in the calculation of higher excited triplet states. Whether the same conclusion is applicable with the combined CNDO/2 - CNDO/S methods will be discussed later.

IV. Scope of the Present Work.

The present study was undertaken in order to extend the knowledge of upper triplet states to a series of heterocyclic molecules known collectively as flavones. The emission spectra of flavone and four of its derivatives were obtained in EPA mixed solvent at 77°K in order to see whether the use of this solvent produced any significant changes in their emission spectra previously obtained in other systems.

Triplet state energies and T-T transition energies and oscillator strengths have been calculated for flavone, 7-hydroxy flavone and 5-methyl-7-hydroxy flavone in order to examine the applicability of the CNDO/2 - CNDO/S method to molecules of this size. The calculations are also applied to coumarin and 4-hydroxy coumarin in an attempt to examine the similarity of the upper triplet states of the two molecules.

EXPERIMENTAL METHODS

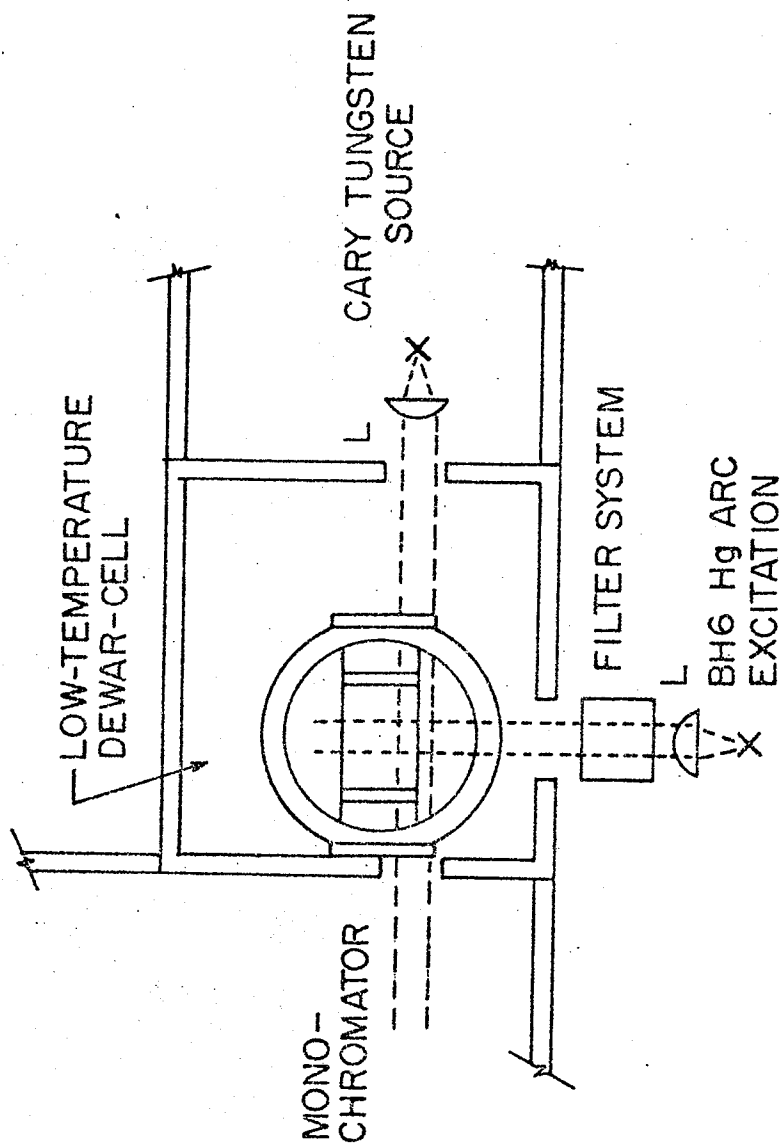
The T-T absorption spectra were obtained on a Cary 14 spectrophotometer, using the steady state cross illumination technique previously described by Henry and Kasha (49). The procedure involves cross excitation of the sample by an intense light source through an opening cut into the side of the sample compartment, while the analyzing light passes through the sample perpendicular to the exciting light.

In obtaining the T-T absorption spectra, the position of the sample in the spectrophotometer is very critical. The geometry of the system results in a concentration gradient of triplets throughout the sample container, with more triplets being formed on the side closer to the exciting light. Therefore rather than having the analyzing beam pass through the centre of the sample, having the beam off centred, that is closer to the exciting light results in the enhancement of weak transitions (Figure 2).

The absorption spectra as well as emissions and lifetime studies were carried out in EPA glass at 77°K. The molecules studied: flavone, 7-hydroxy flavone (Aldrich Chemical Company), 5-hydroxy flavone, 5- hydroxy - 7-methyl flavone and 5-methyl-7-hydroxy flavone (ICN Pharmaceuticals) were of relatively high purity and were used as received. Each compound was dissolved in EPA mixed solvent (ethyl ether, isopentane, ethyl alcohol 5:5:2) (American Instrument Company) and frozen to a clear glass at 77°K in a dewar containing an all quartz cell

FIGURE 2

T-T absorption optical arrangement showing the low temperature dewar cell in the Cary 14 spectrophotometer sample compartment, with auxiliary excitation source.



approximately eight centimeters long (No. 203908 quartz cell dewar flask, H.S. Martin Co., Evanston, ILL.). The EPA was passed through an activated silica gel column in order to remove traces of water which caused clouding of the otherwise clear glass. Impurity absorption in the T-T spectra of the flavones is not expected to be a problem because of the low concentration of excited state molecules. Moreover the T-T character of the spectra was verified by lifetime studies (see results section).

With a 1000-watt BH_6 mercury arc as the exciting light and the I.R. tungsten source of the Cary as the analyzing beam, three scans were obtained in the spectral region from 3500\AA° to 9000\AA° . The first scan (I) was carried out with the analyzing beam alone. The second (II) was carried out during simultaneous cross excitation from the mercury arc, while the third scan (III) was again carried out with the analyzing light alone. This method enable us to identify interference due to photoproducts (III-I) and also obtain the triplet-triplet absorption spectrum (II-III).

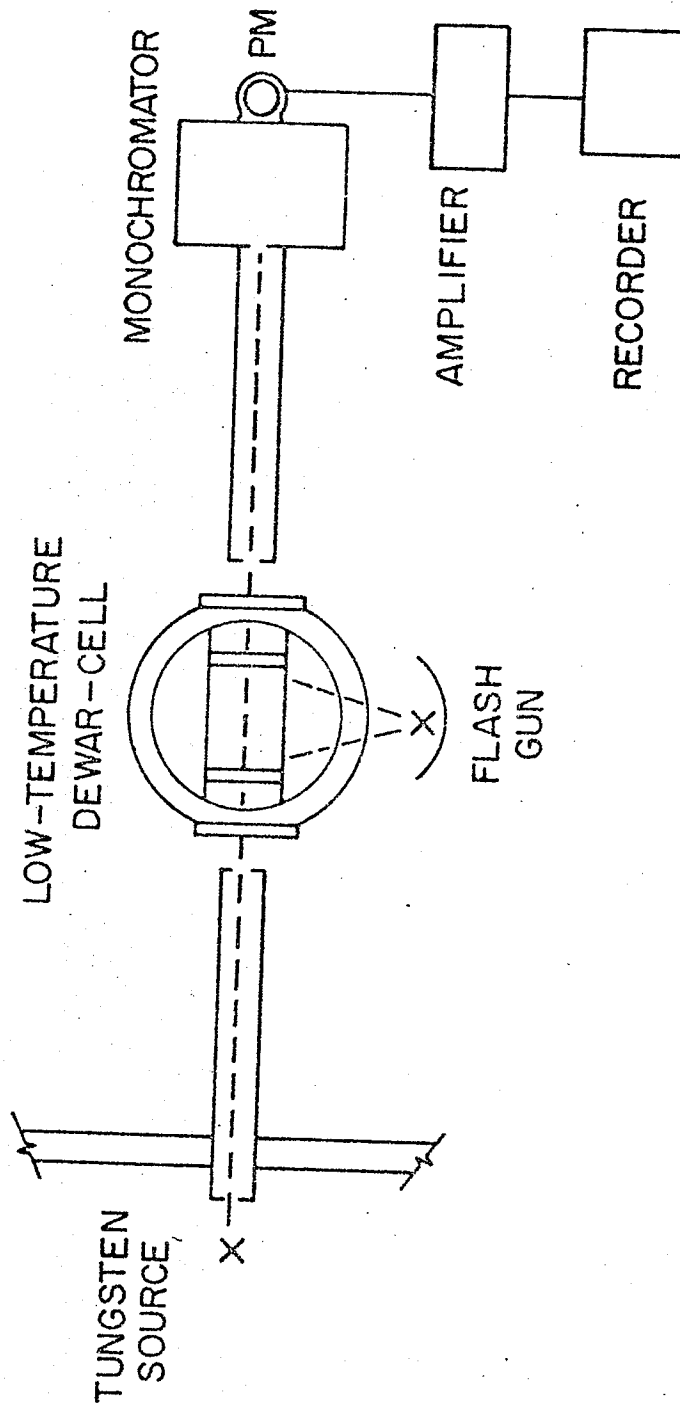
In obtaining the spectra, heating of the sample was reduced by placing a one centimeter cell filled with distilled water in front of the analyzing source. The light from the mercury arc was filtered by means of a one cm. path of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (500g/l of H_2O) and a Corning glass filter (Cs 7-54), but in some cases the glass filter or both were dispensed with in order to increase the intensity of light striking the sample.

A modification of the experimental arrangement of Porter (50) was used to measure the decay of T-T absorption following flash excitation (Fig. 3). Light from a Thorn Halogen 12v/55w bulb was collimated and passed through the sample prepared as described previously, and then admitted into a 0.25 m. Jarrell-Ash grating monochromator, which was set at the T-T absorption maximum of the sample. The intensity of the transmitted light was measured by means of a phototube (Hamamatsu R106), the signal amplified (Gencom Nanometer Model 911), and recorded on an X-Y recorder (Omnigraphic 2000, Houston Instruments). The excitation was provided by an electronic flash gun (Honeywell Strobosnar 780) with its protective polystyrene cover removed.

The decay of the triplet state was recorded as intensity of light transmitted versus time. A plot of $\ln \log (X_0/X_t)$ versus time, where X_0 is the transmittance of the sample before flashing and X_t the transmittance at time t following the flash, was fitted to a straight line with a least mean squares analysis. The triplet lifetime was obtained as the negative reciprocal of the slope. From ten to twenty trials were done for each sample, with very little variation being noticed. The average values were obtained, as well as the standard deviation from the mean. The correlation coefficient r , which is a measure of the fit of the data in this case to a first order decay, was calculated from the equation:

FIGURE 3

Flash apparatus used to obtain triplet state lifetimes
from the decay of T-T absorption.



$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (8)$$

In this case x_i corresponds to values of t and y_i to values of $\ln \log (x_o/x_t)$. Perfect correlation is indicated if $r=-1$, whereas a value of 0 indicates no correlation.

In the measurement of the phosphorescence spectra, the molecules were once again dissolved in EPA and the solution cooled to 77°K. Here the initial concentrations of solutions were slightly larger than for the T-T experiments, and were of the order of 10^{-3} to 10^{-4} molar. Each solution was placed in a sample tube consisting of a 5mm. quartz tube with a 2mm. finger and then frozen in a quartz dewar. A modified Aminco spectrophotofluorimeter (4-8401 A° motor driven monochromator with an All-61041 grating, 3150 A° blaze at the excitation position, and a 4-8401 A° motor driven type monochromator with an A248-61041 grating at the analyzing position) was used to obtain all phosphorescence spectra in the spectral range from 3000 A° to 9000 A°. Excitation of the sample was achieved by a Mercury-Xenon lamp (200 watt Hanovia 901-B), and emission was detected by a photomultiplier tube (Hamamatsu R446S). A photomultiplier microphotometer (Aminco 10-280) served both as a high voltage power supply and amplifier for the phototube, with the signal recorded on an Aminco X-Y recorder (model 1620-827). Phosphorescence was isolated from scattered light and fluorescence by placing a Corning glass

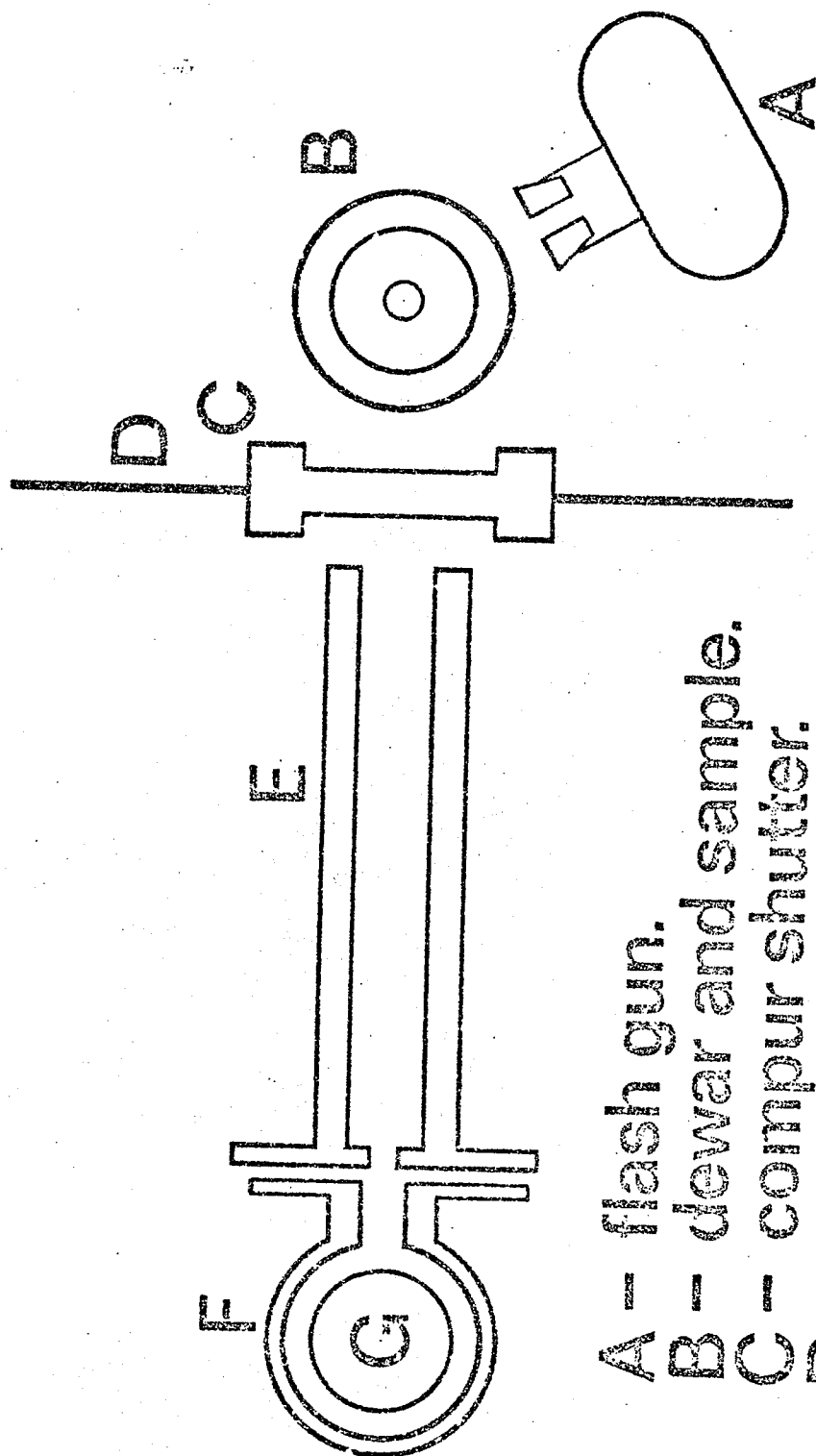
cut-off filter (Cs O-52) immediately in front of the photomultiplier tube. The filter cut off approximately 90% of light below 4000 Å°. All spectra were calibrated with a mercury arc. No correction was made for the variation in spectral sensitivity of the analyzing monochromator and photomultiplier tube.

Phosphorescence lifetimes were determined on an apparatus described by Charlton and Henry (51) (Figure 4). Sample preparation was as described for the phosphorescence spectra. The apparatus consisted of a Honeywell Strobosonar 780 electronic flash gun (polystyrene protective cover removed) which connected to a synchro compur shutter so that triggering of the shutter mechanism caused the flash to fire, and after approximately ten milliseconds, the shutter to open. The time delay shielded the phototube from both exciting light and fluorescence, but allowed the transmittance of the longer lived phosphorescence. The phosphorescence passed through the shutter, down a brass collimating tube (id. 5 mm.) to a housed Hamamatsu IP21 photomultiplier tube. The signal was fed into a photomultiplier microphotometer (Aminco 10-280) and reproduced as a plot of intensity versus time on an Aminco X-Y recorder (model 1620-827), whose X-axis was used as a calibrated time base. As in the triplet-triplet decay lifetimes, the average phosphorescence lifetime for a molecule was determined along with the standard deviation of at least ten trials. The correlation coefficients were again calculated. Determination

of lifetimes for the phosphorescence studies was accomplished by fitting a \ln (intensity) versus time plot to a straight line by means of the least squares analysis.

FIGURE 4

Flash apparatus used to obtain triplet state lifetimes
from the decay of phosphorescence emission.



- A - flash gun.
- B - dewar and sample.
- C - counting shutter.
- D - mounting plate and baffle.
- E - collimating tube.
- F - photomultiplier housing.
- G - photomultiplier.

RESULTS

I. Absorption and Emission Spectra.

T-T absorption spectra in EPA glass at 77°K have been determined for flavone, 7-hydroxy flavone and 5-methyl - 7-hydroxy flavone, and are presented in figures (5-7) respectively. The spectra generally represent the best spectrum for each molecule, taken from ten or more trials. Small changes in intensity of exciting light, and particularly the offsetting of the dewar with respect to the analyzing beam, resulted in very significant changes in the intensity of the T-T absorption. Quantitative comparison of peak ratios within a given spectrum is only approximately possible because of the varying amounts of light entering the detector. The ordinates represent arbitrary intensity units and are not comparable from spectrum to spectrum.

The positions of the observed maxima and their associated errors are summarized in Table I. The positions of the principal maxima as well as the associated errors are average results taken from a series of five or more T-T absorption spectra run for each molecule. The uncertainties in the positions of the shoulders are estimates based partly on their relative intensities. The T-T lifetimes and phosphorescence lifetimes are also included in Table I, as are the correlation coefficients for each series of lifetime measurements. As mentioned previously, the values of the lifetimes are based on at least

ten trials. Where available, results of lifetime studies from the literature are given. Relatively good agreement between the T-T and phosphorescence lifetimes confirms the T-T nature of the absorption bands.

In an attempt to observe T-T absorption in 5-hydroxy flavone and 5-hydroxy - 7-methyl flavone, a very broad and intense absorption due to photoproducts was observed. The transient species was present as long as the glass remained frozen but disappeared after the glass melted. The photoproduct absorption spectra of the two flavone derivatives are shown in Figures 8 and 9. Once again the peak intensities cannot be compared from spectrum to spectrum because the units along the ordinate are of arbitrary intensity. The positions of the absorption bands along with their estimated uncertainties are given in Table II.

The total emission spectra of flavone, 7-hydroxy flavone, 5-methyl - 7-hydroxy flavone, 5-hydroxy flavone and 5-hydroxy - 7-methyl flavone in EPA glass at 77°K were obtained and are presented in Figures (10-14) respectively. The fluorescence maxima and phosphorescence maxima are summarized in Table III. As in the absorption spectra the ordinates in the emission spectra represent arbitrary intensity units.

FIGURE 5

T-T absorption spectrum of flavone in EPA rigid glass solution at 77°K in the range 13,000 cm^{-1} to 28,000 cm^{-1} : (ordinate) arbitrary linear absorption units.

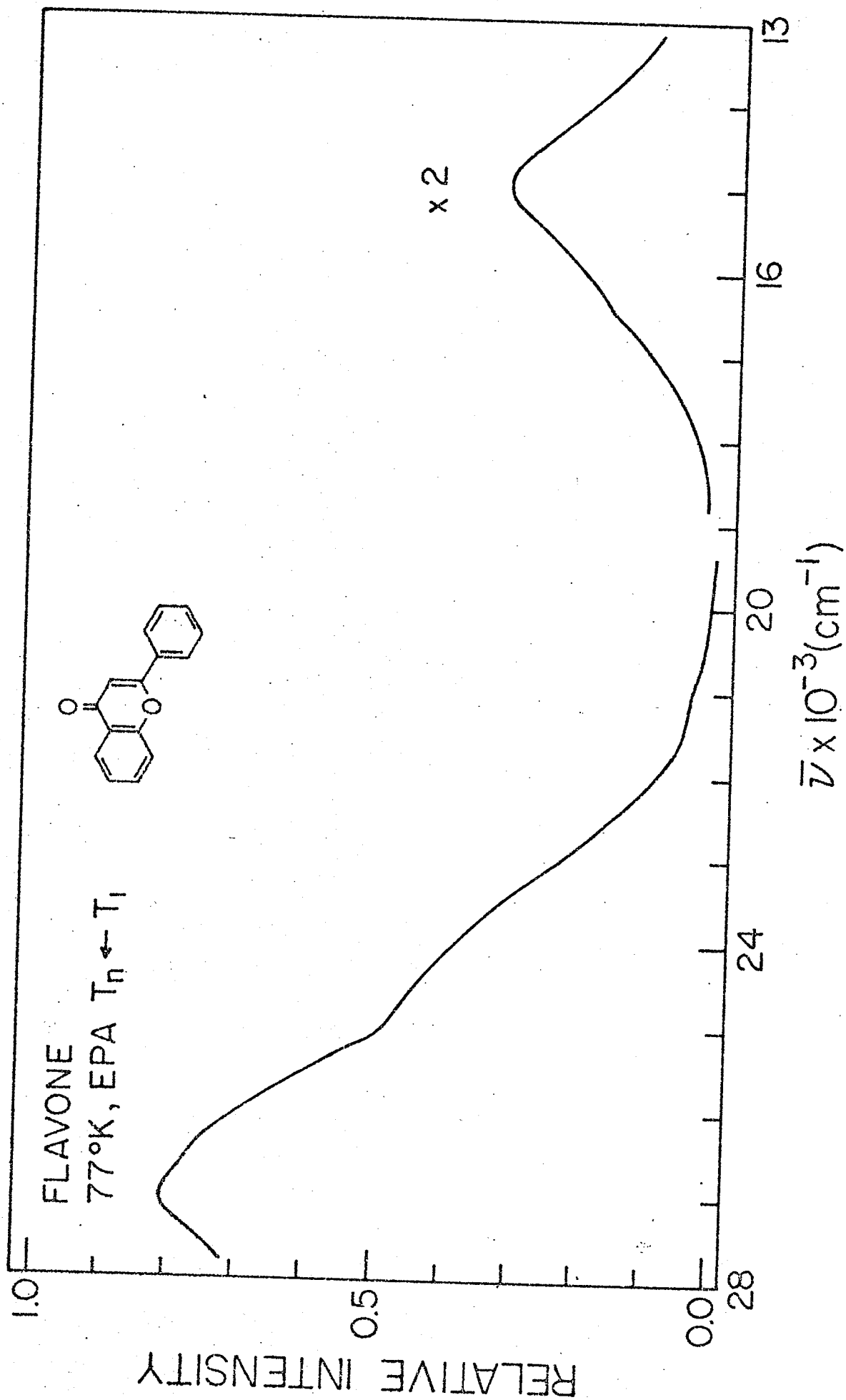


FIGURE 6

T-T absorption spectrum of 7-hydroxy flavone in EP̄A rigid glass solution at 77°K in the range 12,000 cm^{-1} to 29,000 cm^{-1} : (ordinate) arbitrary linear absorption units.

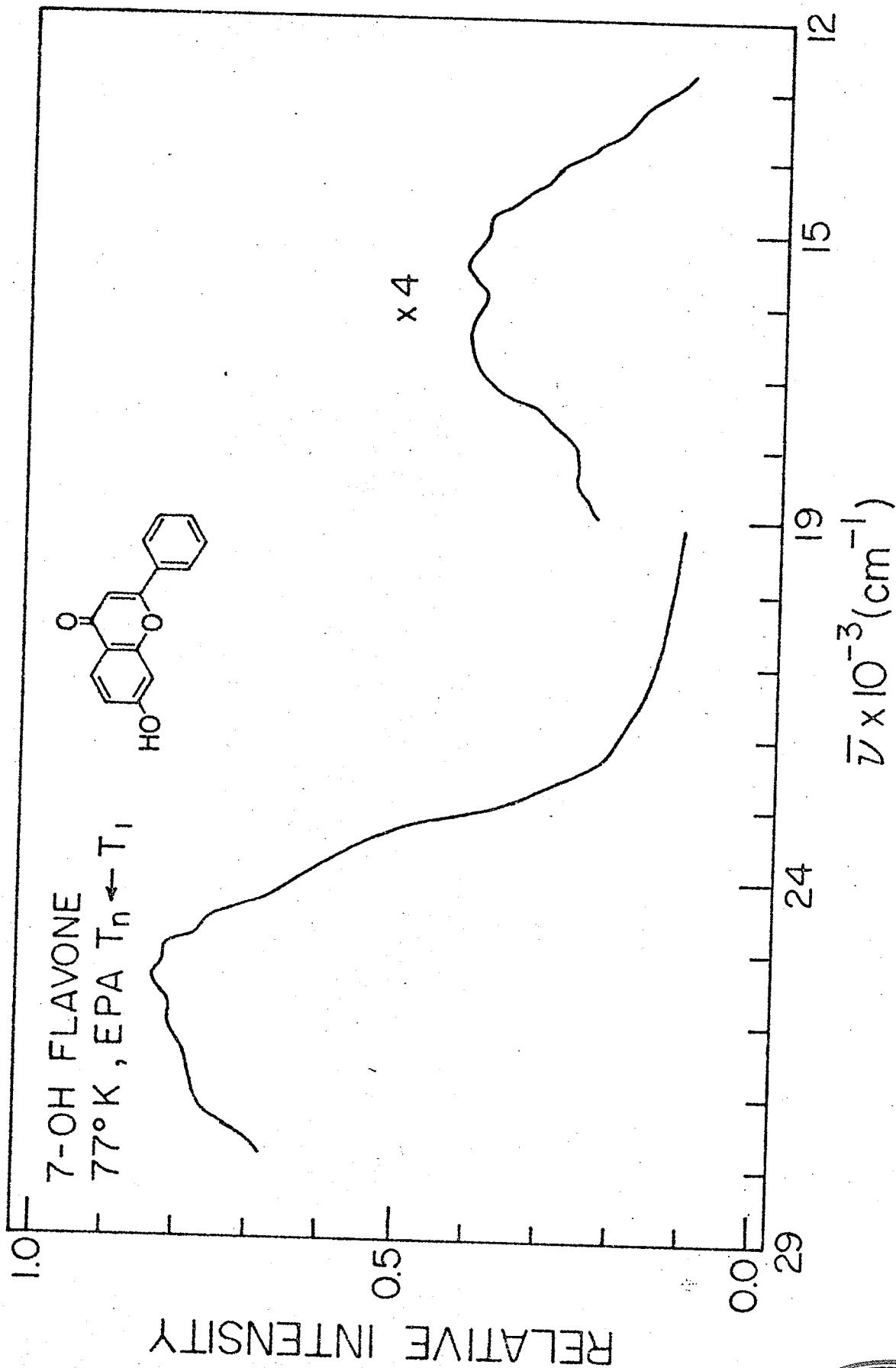


FIGURE 7

T-T absorption spectrum of 5-methyl-7-hydroxy flavone in EPA rigid glass solution at 77°K in the range 12,000 cm^{-1} to 29,000 cm^{-1} : (ordinate) arbitrary linear absorption units.

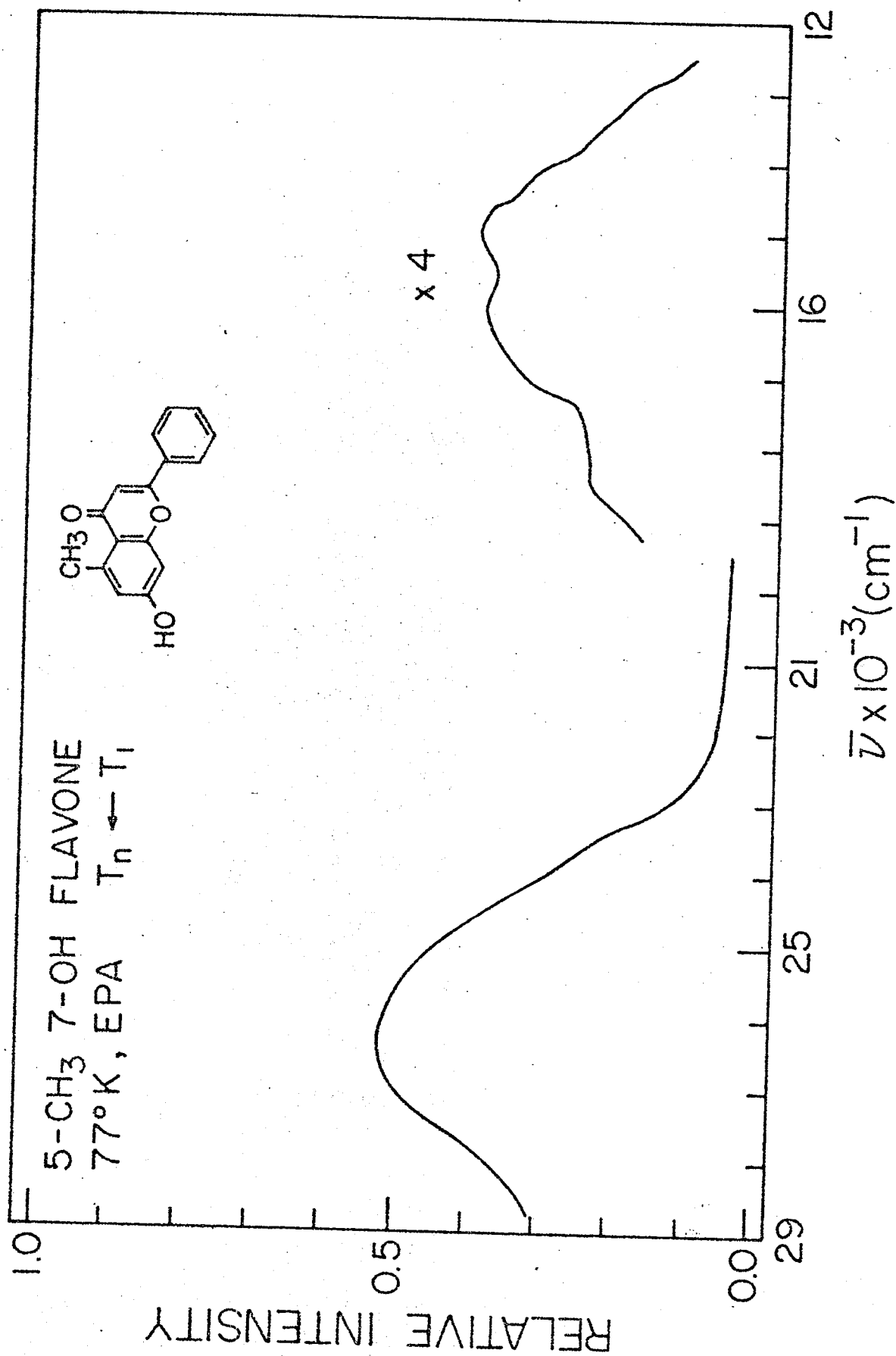


FIGURE 8

Photoproduct absorption spectrum of 5-hydroxy flavone in EPA rigid glass solution at 77°K in the range 14,000 cm^{-1} to 25,000 cm^{-1} : (ordinate) arbitrary linear absorption units.

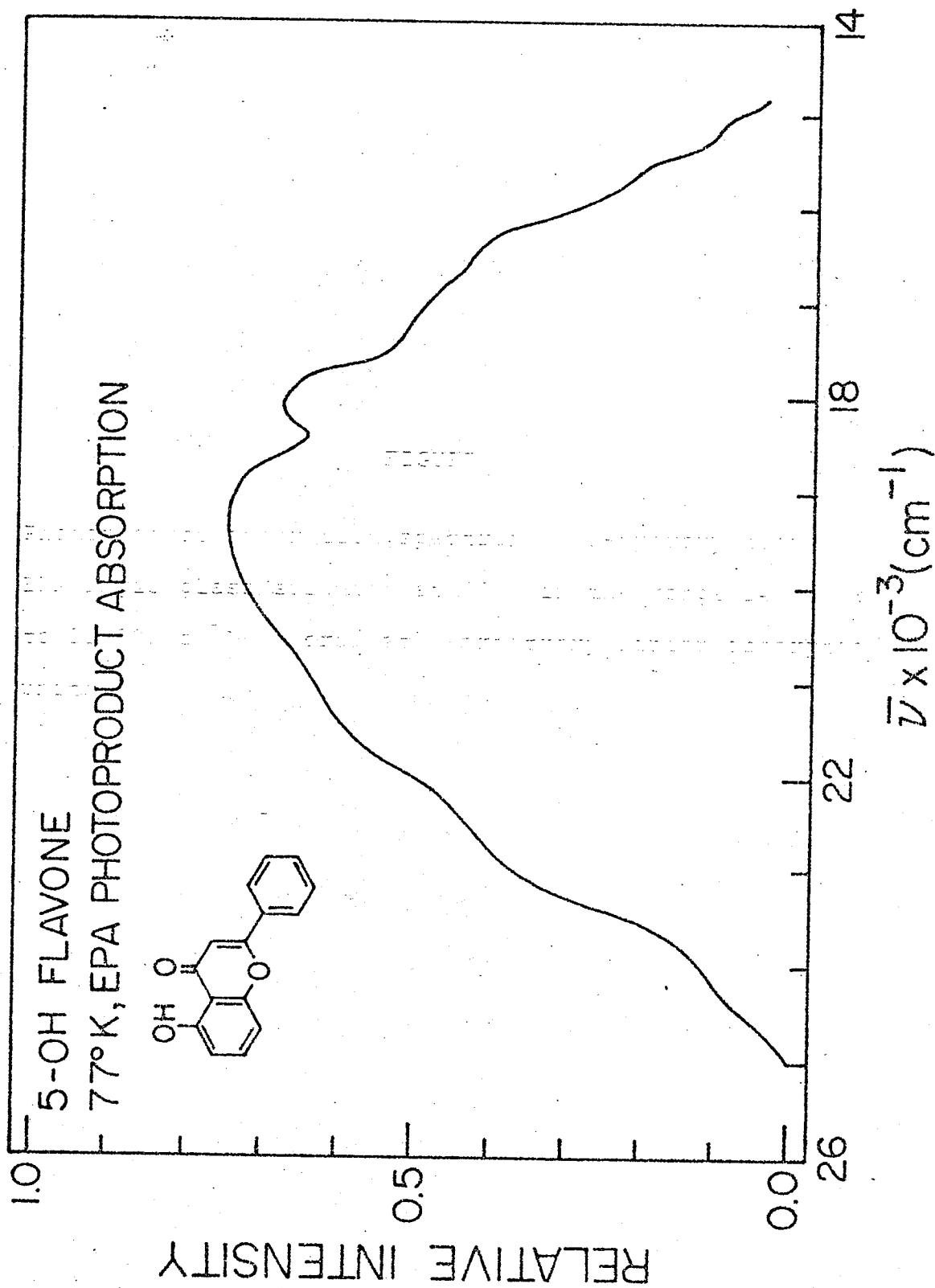


FIGURE 9

Photoproduct absorption spectrum of 5-hydroxy-7-methyl flavone in EPA rigid glass solution at 77°K in the range 14,000 cm^{-1} to 25,000 cm^{-1} : (ordinate) arbitrary linear absorption units.

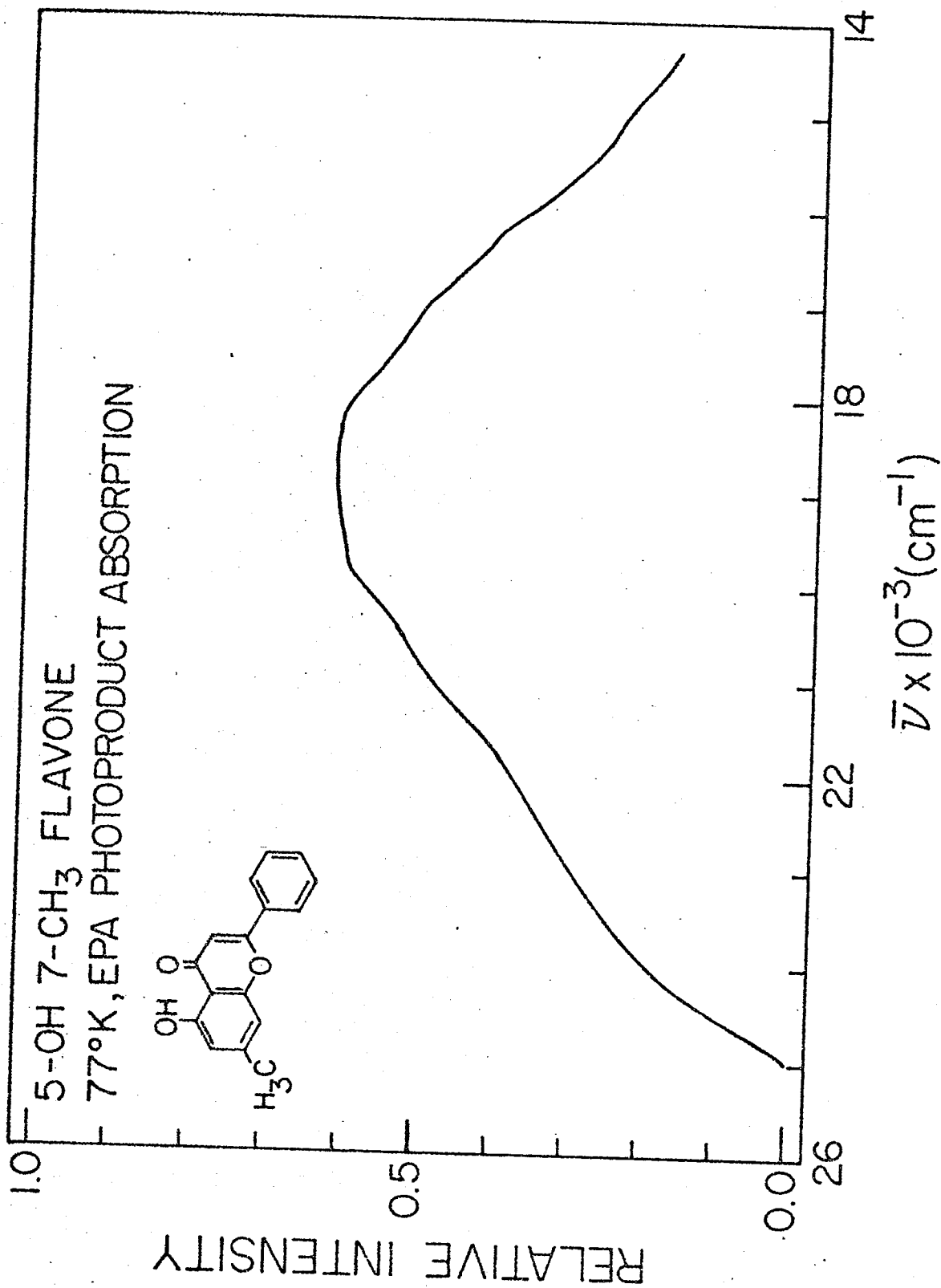


FIGURE 10

Total emission spectrum of flavone in EPA rigid glass
solution at 77°K in the range 300 nm to 700 nm: (ordinate)
arbitrary linear absorption units.

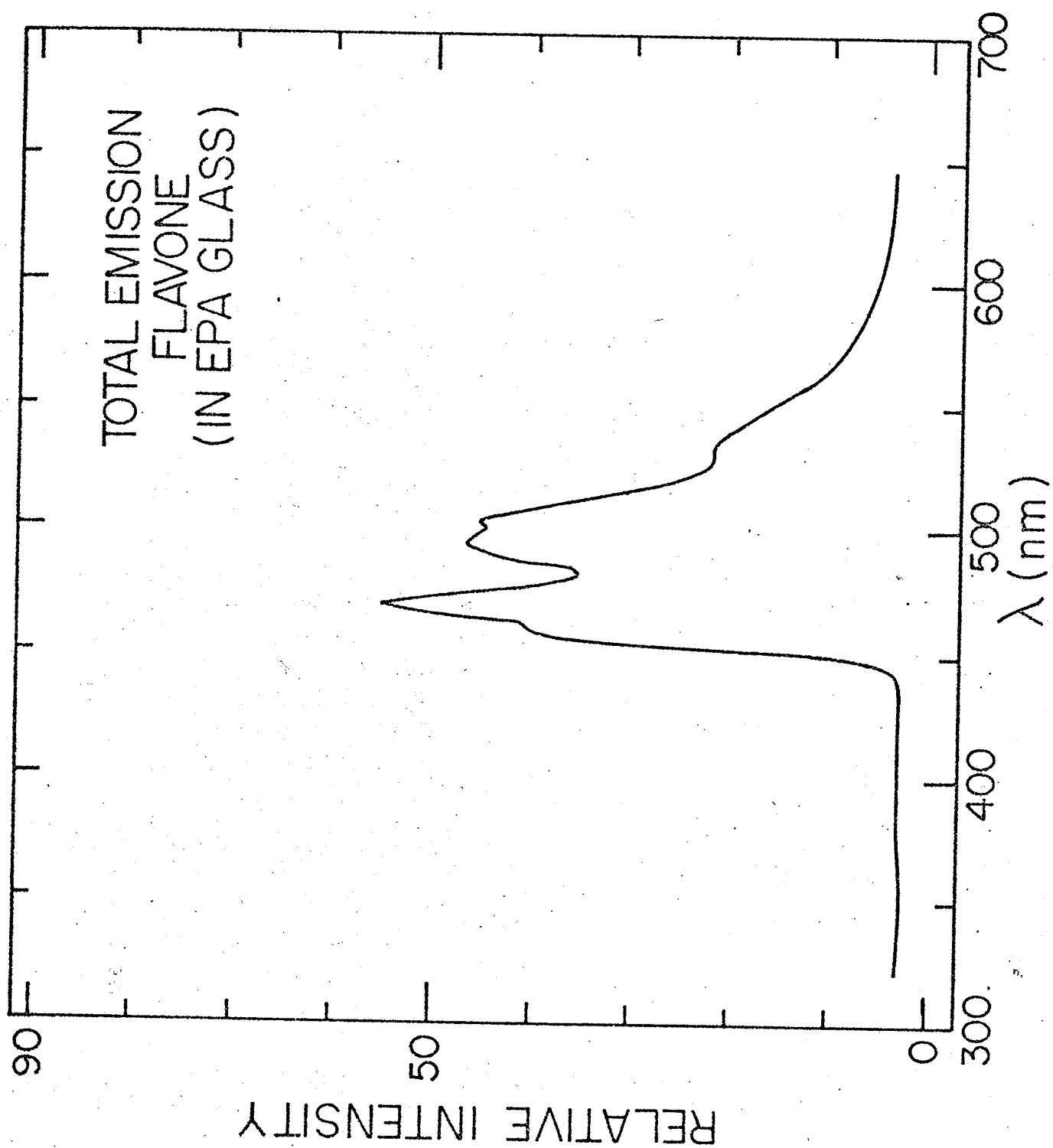


FIGURE 11

Total emission spectrum of 7-hydroxy flavone in EPA rigid glass solution at 77°K in the range 300 nm to 700 nm: (ordinate) arbitrary linear absorption units.

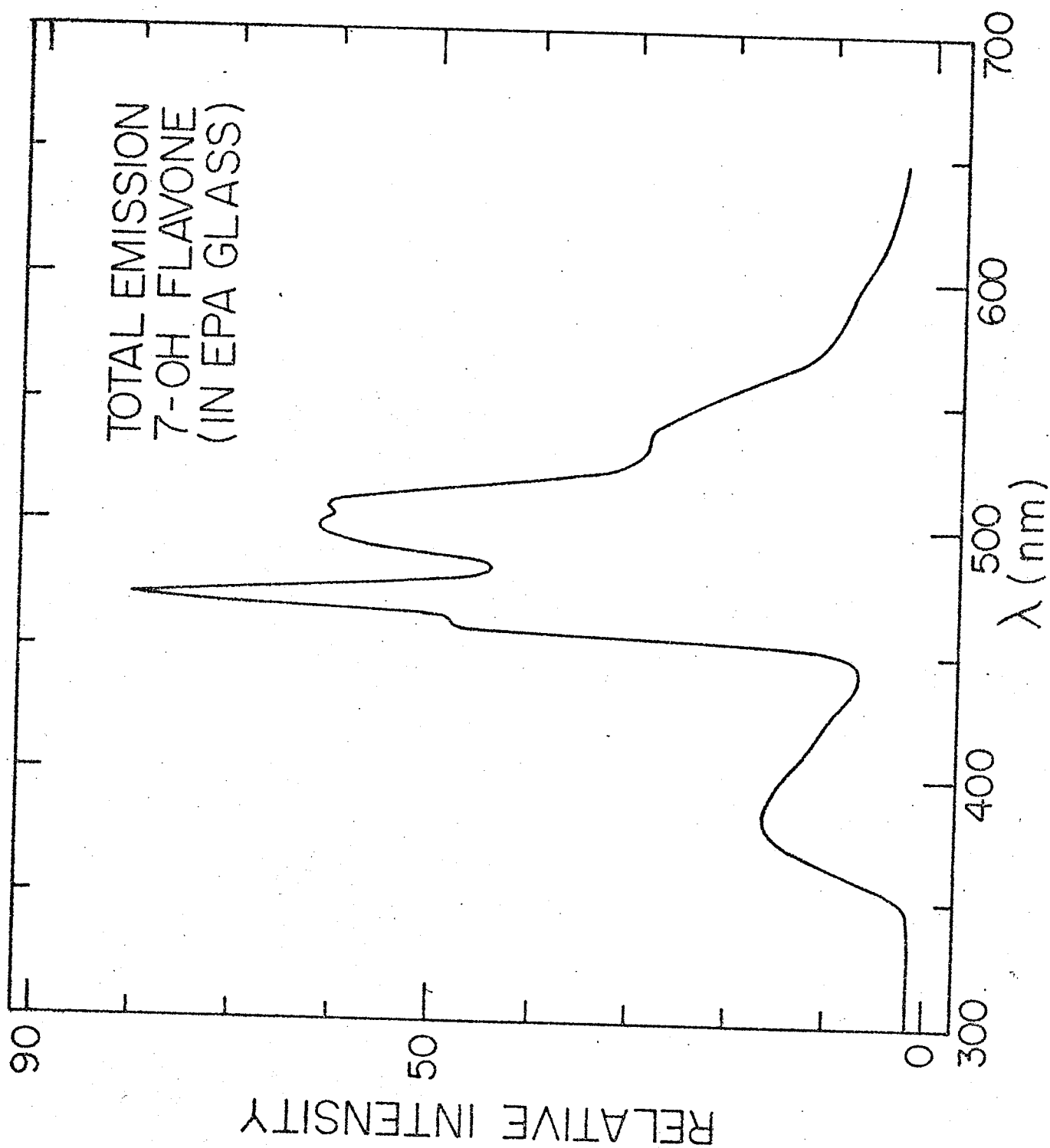


FIGURE 12

Total emission spectrum of 5-methyl-7-hydroxy flavone
in EPA rigid glass solution at 77°K in the range 300 nm
to 700 nm: (ordinate) arbitrary linear absorption units.

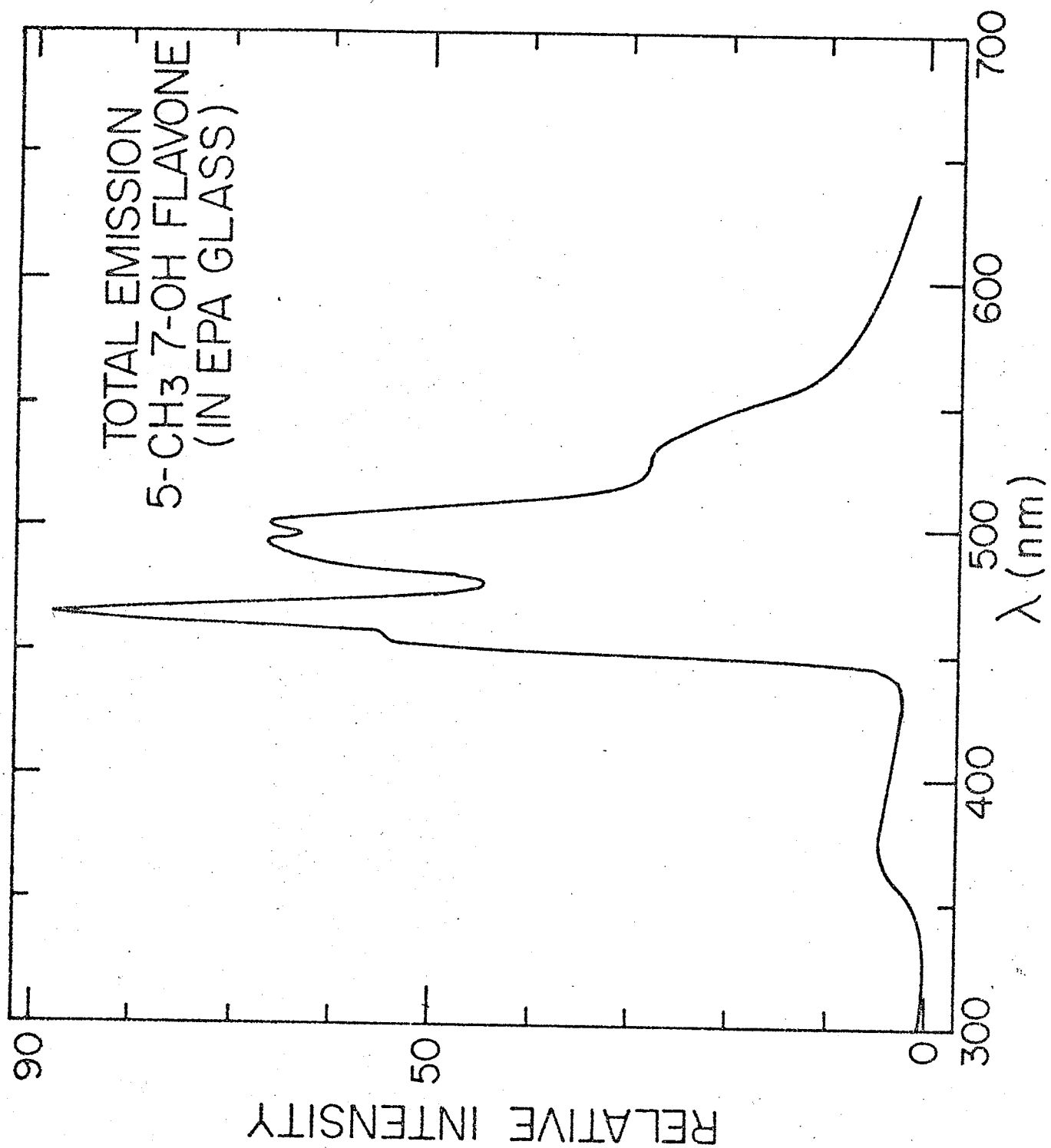


FIGURE 13

Total emission spectrum of 5-hydroxy flavone in EPA rigid
glass solution at 77°K in the range 300 nm to 700 nm:
(ordinate) arbitrary linear absorption units.

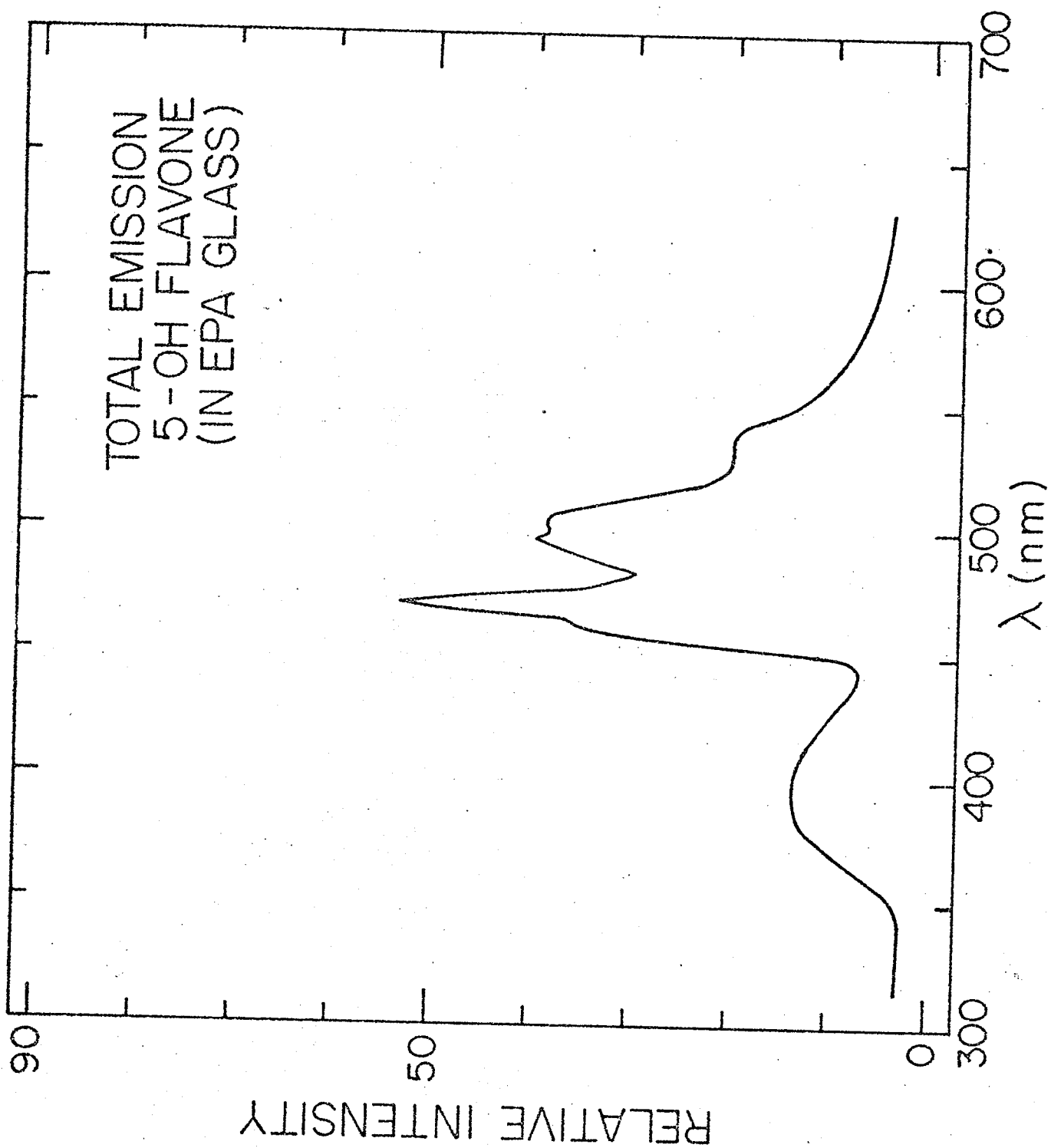


FIGURE 14

Total emission spectrum of 5-hydroxy-7-methyl flavone in
EPA rigid glass solution at 77°K in the range 300 nm to
700 nm: (ordinate) arbitrary linear absorption units.

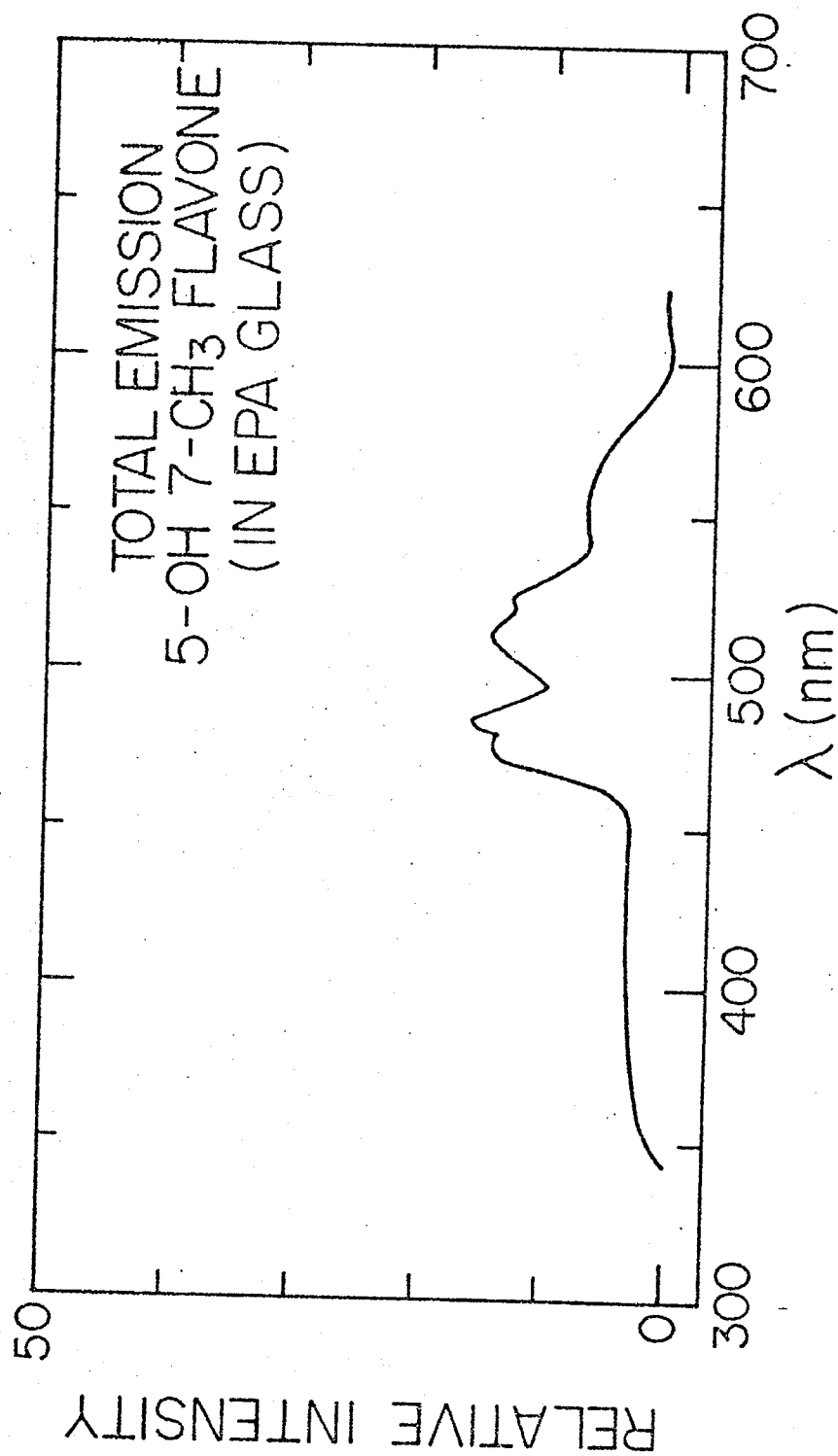


TABLE I

TRIPLET-TRIPLET ABSORPTION MAXIMA
OF FLAVONE DERIVATIVES

Molecule	Observed Maxima (cm ⁻¹)	Lifetime (sec)	Average r	Phosphorescence Lifetime (sec)	Average r
Flavone	27 100 ± 100	0.70 ± 0.01	-0.9998	0.65 ± 0.01	-0.9997
	24 150 ± 400(s)			0.60 ξ (61)	
	14 950 ± 100			0.675 § (60)	
7-OH Flavone	25 375 ± 100	0.65 ± 0.02	-0.9999	0.62 ± 0.01	-0.9997
	23 400 ± 400(s)				
	18 500 ± 100				
	16 600 ± 200				
	15 500 ± 100				
5-CH ₃ -7-OH Flavone	26 400 ± 200	0.61 ± 0.01	-0.9995	0.51 ± 0.01	-0.9997
	23 500 ± 400(s)				
	18 500 ± 100				
	16 200 ± 200				
	15 000 ± 200				

(s) = Shoulder

ξ In absolute ethyl alcohol rigid glass at 77°K

§ In a diethyl ether, ethyl alcohol (1:1 by volume mixture) rigid glass at 77°K

TABLE II
PHOTOPRODUCT ABSORPTION MAXIMA
OF
FLAVONE DERIVATIVES

Molecule	Photoproduct Absorption Maximum (cm ⁻¹)
5-OH Flavone	19 400 \pm 200
5-OH-7-CH ₃ Flavone	18 800 \pm 300

TABLE III

EMISSION CHARACTERISTICS OF FLAVONE DERIVATIVES

Molecule	Fluorescence (nm)	Phosphorescence (nm)
Flavone	none	459 (s) 468 494 502 532 (s)
7-OH Flavone	382	462 (s) 472 497 507 538 (s)
5-CH ₃ -7-OH Flavone	375	456 (s) 466 493 502 531 (s)
5-OH Flavone	393	462 (s) 471 497 504 538 (s)
5-OH-7-CH ₃ Flavone	none	477 (s) 484 512 524 555 (s)

(s) = Shoulder

II. Molecular Orbital Calculations.

In order to evaluate the T-T absorption energies using the modified CNDO/S method of Jaffe, et al., described in the introduction, it is first necessary to obtain the atomic coordinates of the molecule. Generally, the coordinates are determined from the known crystal structure of the molecule, but in the case of flavone and its derivatives, such information is not presently available. In fact, information from crystallographic data is not always accurate, as the atomic coordinates of a molecule in its crystalline form need not be identical to the coordinates in another environment. This is more likely to be important in molecules containing substituent groups, where different orientations of the substituent could result in different molecular packing in the crystalline form. The phenyl ring in flavone could result in such differences.

The assumptions made by Orlov, et al., (52) for the geometry of the chromone molecule formed the basis for our description of the geometry of flavone. The authors assumed the chromone molecule to be flat with $r_{\text{benz}} = r_{2.3} = 1.40\text{\AA}$; $r_{9.1} = r_{1.2} = r_{4.10} = r_{3.4} = 1.45\text{\AA}$ and $r_{\text{C=O}} = 1.20\text{\AA}$. All bond angles were taken to be 120° . For numbering in flavone see Table IV.

Chromone differs from flavone only in that it lacks a phenyl group at carbon 2. In the determination of the coordinates of the flavone molecule, the bond joining the phenyl group to chromone was taken to be the same as the ring-ring bond in the biphenyl

molecule, that is 1.51 \AA (53,54). In a theoretical study of the steric effects in hydrocarbon molecules containing phenyl groups (55), the bond joining the phenyl group to naphthalene in 2-phenyl naphthalene was assumed to be 1.5 \AA . Our assumption of a 1.51 \AA bond length thus seems reasonable, as 2-phenyl naphthalene and flavone are structurally very similar. All carbon-carbon bond lengths in the phenyl group were taken to be 1.40 \AA , and all angles 120° . All carbon-hydrogen bonds in flavone were taken as 1.07 \AA .

A study of the zero field splitting in the phosphorescent triplet state of 2-phenyl naphthalene (31) resulted in the conclusion that the molecule was planar in its lowest triplet state. The structural similarity of 2-phenyl naphthalene and flavone having previously been made apparent, the assumption that the structure of flavone in its lowest triplet state be planar does not seem unreasonable. This however need not be the case, but is reasonable since this geometry would result in the greatest overlap of the π electron orbitals, and therefore the greatest stability of the molecule (55).

The actual atomic coordinates for flavone were obtained by assigning the coordinates $(0,0,0)$ to one atom, with subsequent calculation of the coordinates of the other atoms from a knowledge of all bond lengths and angles. The coordinates so determined for flavone are shown in Table IV.

For 7-hydroxy flavone the basic flavone coordinates were not altered. The carbon-oxygen bond length at carbon 7

was taken as 1.35 \AA , the oxygen-hydrogen bond as 0.94 \AA and the carbon-oxygen-hydrogen bond angle as 112° . These parameters were taken from an average of values given for the hydroxy group on the phenol molecule (56,57). Although the two planar configurations in phenol are identical, this is not the case in 7-hydroxy flavone. It has been noted that the CNDO/S calculations may be quite sensitive to geometry, and so two trials were run in the calculation of the triplet energies of 7-hydroxy flavone. In one the hydroxyl hydrogen pointed down, away from the chromone nucleus, and in the second it pointed toward the chromone nucleus. The results showed very small differences and therefore the choice of geometry of the hydroxyl group in 7-hydroxy flavone did not present a problem.

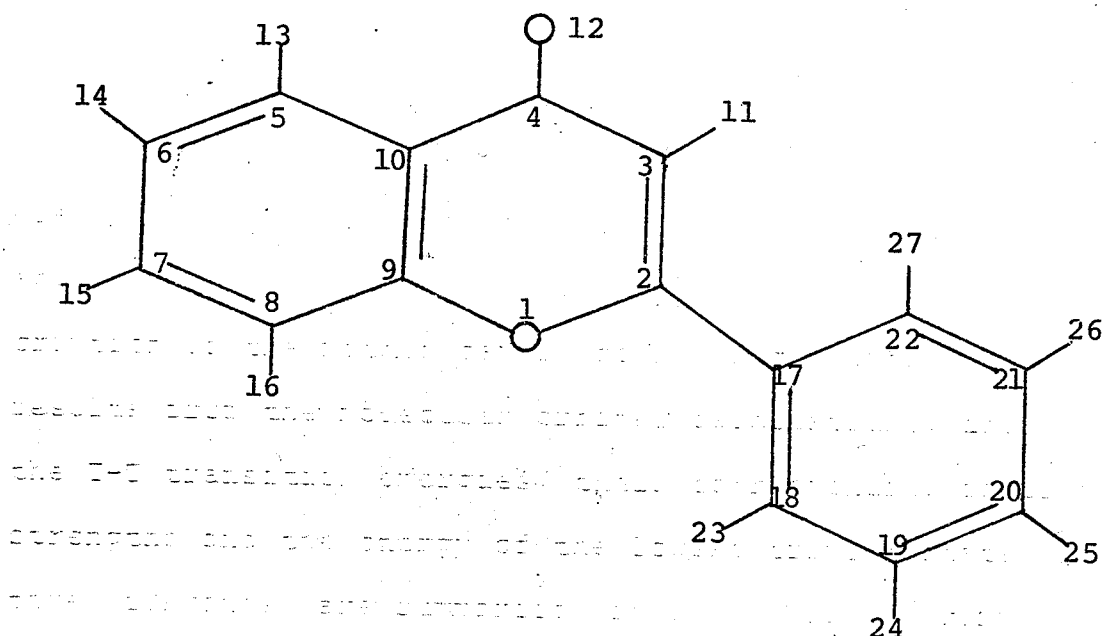
In 5-methyl - 7-hydroxy flavone the carbon-carbon bond length at carbon 5 was taken as 1.50 \AA , the carbon-hydrogen bonds as 1.09 \AA , and the carbon-carbon-hydrogen bond angles as 110° . The orientation of substituent groups again was not a problem in the determination of the atomic coordinates. The coordinates used for 7-hydroxy flavone and 5-methyl - 7-hydroxy flavone are summarized in Tables V and VI respectively.

The program used for the calculation of the triplet states of the flavones was a general purpose combination of the CNDO/S and CNDO/2 programs, with a refinement consisting of combining SCF and CI calculations to obtain extrapolated triplet energies. The program was able to handle both open

and closed shell systems. Computations were carried out by a straightforward application of the Roothaan restricted Hartree-Fock open shell method (41,42,43,45). The matrix elements were evaluated according to the rules of the ZDO approximation in the CNDO/S form (58). A more detailed description of the method can be found in the introduction. The results from the molecular orbital calculations, including the T-T transition energies, their corresponding oscillator strengths and the energy of the lowest triplet state of the three flavones, are summarized in Table VII. A comparison between theoretical and experimental T-T transitions is given in Table VIII.

TABLE IV

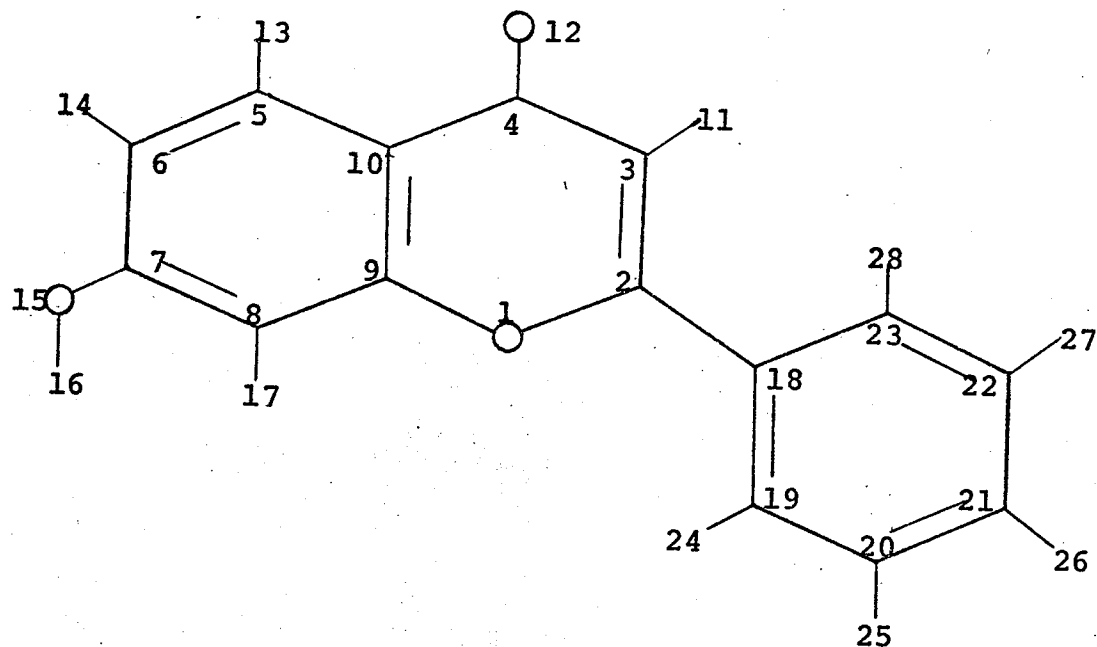
ATOMIC COORDINATES USED FOR MOLECULAR
ORBITAL CALCULATIONS FOR FLAVONE



ATOM	AT. NO.	COORDINATES		
		X	Y	Z
1	8	3.68	-0.73	0.00
2	6	4.94	0.00	0.00
3	6	4.94	1.40	0.00
4	6	3.68	2.13	0.00
5	6	1.21	2.10	0.00
6	6	0.00	1.40	0.00
7	6	0.00	0.00	0.00
8	6	1.21	-0.70	0.00
9	6	2.42	0.00	0.00
10	6	2.42	1.40	0.00
11	1	5.86	1.94	0.00
12	8	3.68	3.33	0.00
13	1	1.21	3.17	0.00
14	1	-0.93	1.94	0.00
15	1	-0.93	-0.54	0.00
16	1	1.21	-1.77	0.00
17	6	6.24	-0.76	0.00
18	6	6.24	-2.16	0.00
19	6	7.46	-2.86	0.00
20	6	8.67	-2.16	0.00
21	6	8.67	-0.76	0.00
22	6	7.46	-0.06	0.00
23	1	5.32	-2.69	0.00
24	1	7.46	-3.93	0.00
25	1	9.60	-2.69	0.00
26	1	9.60	-0.22	0.00
27	1	7.46	1.02	0.00

TABLE V

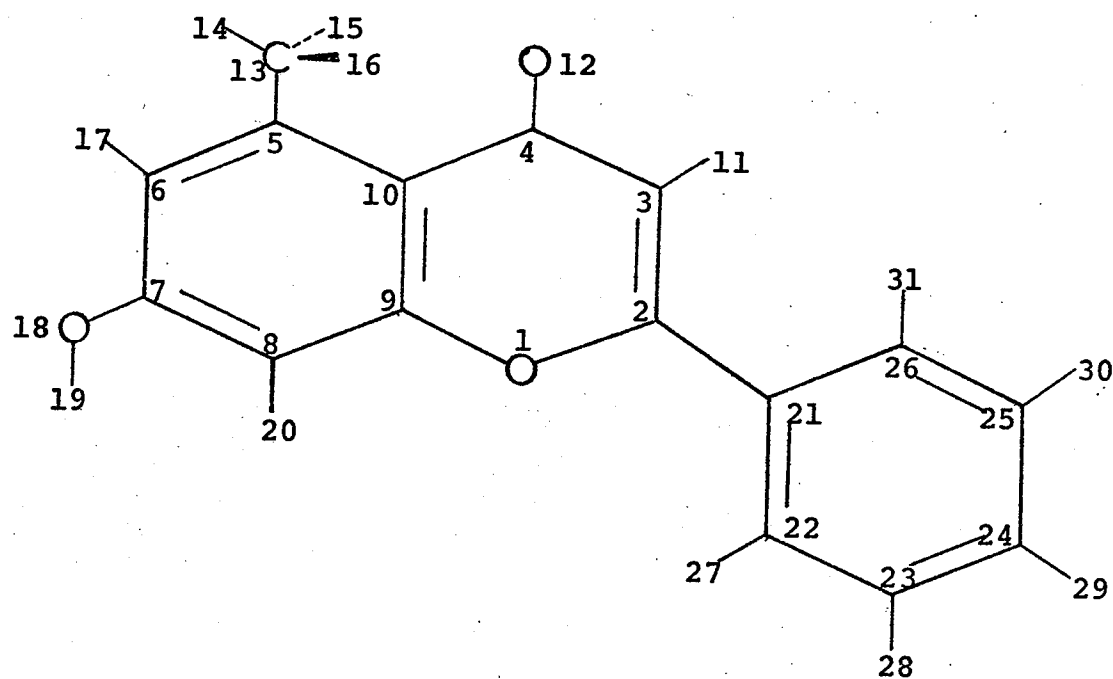
ATOMIC COORDINATES USED FOR MOLECULAR
ORBITAL CALCULATIONS FOR 7-OH FLAVONE.



ATOM	At. No.	COORDINATES		
		X	Y	Z
1	8	3.68	-0.73	0.00
2	6	4.94	0.00	0.00
3	6	4.94	1.40	0.00
4	6	3.68	2.13	0.00
5	6	1.21	2.10	0.00
6	6	0.00	1.40	0.00
7	6	0.00	0.00	0.00
8	6	1.21	-0.70	0.00
9	6	2.42	0.00	0.00
10	6	2.42	1.40	0.00
11	1	5.86	1.94	0.00
12	8	3.68	3.33	0.00
13	1	1.21	3.17	0.00
14	1	-0.93	1.94	0.00
15	8	-1.17	-0.68	0.00
16	1	-1.04	-1.61	0.00
17	1	1.21	-1.77	0.00
18	6	6.24	-0.76	0.00
19	6	6.24	-2.16	0.00
20	6	7.46	-2.86	0.00
21	6	8.67	-2.16	0.00
22	6	8.67	-0.76	0.00
23	6	7.46	-0.06	0.00
24	1	5.32	-2.69	0.00
25	1	7.46	-3.93	0.00
26	1	9.60	-2.69	0.00
27	1	9.60	-0.22	0.00
28	1	7.46	1.02	0.00

TABLE VI

ATOMIC COORDINATES USED FOR MOLECULAR
ORBITAL CALCULATIONS FOR 5-CH₃-7-OH FLAVONE.



ATOM	At. No.	COORDINATES		
		X	Y	Z
1	8	3.68	-0.73	0.00
2	6	4.94	0.00	0.00
3	6	4.94	1.40	0.00
4	6	3.68	2.13	0.00
5	6	1.21	2.10	0.00
6	6	0.00	1.40	0.00
7	6	0.00	0.00	0.00
8	6	1.21	-0.70	0.00
9	6	2.42	0.00	0.00
10	6	2.42	1.40	0.00
11	1	5.86	1.94	0.00
12	8	3.68	3.33	0.00
13	6	1.21	3.60	0.00
14	1	0.19	3.97	0.00
15	1	1.61	3.97	-0.94
16	1	1.61	3.97	0.94
17	1	-0.93	1.94	0.00
18	8	-1.17	-0.68	0.00
19	1	-1.04	-1.61	0.00
20	1	1.21	-1.77	0.00
21	6	6.24	-0.76	0.00
22	6	6.24	-2.16	0.00
23	6	7.46	-2.86	0.00
24	6	8.67	-2.16	0.00
25	6	8.67	-0.76	0.00
26	6	7.46	-0.06	0.00
27	1	5.32	-2.69	0.00
28	1	7.46	-3.93	0.00
29	1	9.60	-2.69	0.00
30	1	9.60	-0.22	0.00
31	1	7.46	1.02	0.00

TABLE VII

SUMMARY OF T-T TRANSITION ENERGIES, OSCILLATOR STRENGTHS AND THE ENERGY OF THE LOWEST TRIPLET STATE AS DETERMINED FROM MOLECULAR ORBITAL CALCULATIONS FOR SEVERAL FLAVONE DERIVATIVES.

FLAVONE		7-OH FLAVONE		5-CH ₃ -7-OH FLAVONE	
22343 cm ⁻¹		22389 cm ⁻¹		22444 cm ⁻¹	
Frequency (cm ⁻¹)	Oscillator Strength	Frequency (cm ⁻¹)	Oscillator Strength	Frequency (cm ⁻¹)	Oscillator Strength
7622	0.0000	7293	0.0002	6993	0.0000
7880	0.0001	7785	0.0000	7568	0.0001
8921	0.0003	8905	0.0003	8910	0.0002
10440	0.0001	10209	0.0000	10417	0.0000
11065	0.0000	11042	0.0000	11006	0.0000
11670	0.0001	11342	0.0000	11160	0.0001
12074	0.0001	11995	0.0001	11959	0.0001
14894	0.0034	14716	0.0001	13706	0.0000
16819	0.0001	14859	0.0035	14817	0.0036
24133	0.0047	23645	0.0024	23527	0.0058
24924	0.0001	25181	0.0001	24120	0.0001
27066	0.1205	26756	0.0779	26585	0.0335
30760	0.0365	29101	0.0035	27991	0.0711
31136	0.0000	29883	0.0303	28783	0.0000

TABLE VIII

COMPARISON OF EXPERIMENTALLY AND THEORETICALLY DETERMINED
VALUES OF THE T-T TRANSITION ENERGIES FOR THE FLAVONE DERIVATIVES.

	THEORY			EXPERIMENT
	$T_j - T_1$	E_{T-T} ($\times 10^{-3} \text{cm}^{-1}$)	Oscillator Strength	E_{T-T} ($\times 10^{-3} \text{cm}^{-1}$)
Flavone	9	14,894	0.0034	14,950 \pm 100
	11	24,133	0.0047	24,150 \pm 400
	13	27,066	0.1205	27,100 \pm 100
7-OH Flavone	10	14,859	0.0035	15,500 \pm 200
				16,600 \pm 200
				18,500 \pm 100
	11	23,645	0.0024	23,400 \pm 400
	13	26,756	0.0779	25,375 \pm 100
5-CH ₃ -7-OH Flavone	10	14,817	0.0036	15,000 \pm 200
				16,200 \pm 200
				18,500 \pm 100
	11	23,527	0.0058	23,500 \pm 400
	13	26,585	0.0335	26,400 \pm 200

DISCUSSION

I. Absorption Spectra.

The T-T absorption spectra of flavone and two of its derivatives are presented in figures (4-6). A summary is given in Table I of the observed maxima and the triplet state lifetime data. The agreement between the triplet-triplet decay and phosphorescence decay times unequivocally establishes the T-T nature of the absorption. The T-T spectra of the three flavones are broad and unresolved, and lack the vibrational structure typical of carbon-carbon ring stretching modes in aromatic molecules. The carbonyl stretching frequency is likewise not present, despite the presence of the carbon-oxygen group in flavone. Flavone exhibits three maxima: at $27,100\text{ cm}^{-1}$, $14,950\text{ cm}^{-1}$ and an unresolved shoulder at $24,150\text{ cm}^{-1}$. The large energy differences between the absorption maxima suggest three distinct T-T transitions rather than the vibrational band of a single electronic transition. In comparison the T-T spectra of 7-hydroxy flavone and 5-methyl-7-hydroxy flavone are similar in overall envelope, but are red shifted. Further, the low energy transitions in the two 7-hydroxy derivatives are much more structured than in flavone, which may be indicative of vibrational sub-structure or perhaps yet another electronic transition. A slight blue shift of 5-methyl-7-hydroxy flavone over 7-hydroxy flavone is noted. The magnitude

of the shift suggests that the effect of the methyl group on the π electron system is negligible. Previous studies attest to the minor contribution of methyl substituents in T-T absorption spectra (59).

Assignment of the orbital character of the lowest triplet state in flavone is not a straightforward application of the rules used to discriminate between $^3(n\pi^*)$ and $^3(\pi\pi^*)$ states. A summary of the rules is available in the literature (9). Difficulty arises due to the rather ambiguous results acquired through lifetime data, polarization studies, the singlet-triplet energy gap and phosphorescence spectra (60). The triplet state lifetime for flavone (0.65 seconds) lies between the values expected for lifetime studies of pure $^3(n\pi^*)$ and pure $^3(\pi\pi^*)$ states. Flavone has a relatively low symmetry, C_s , and as a result each of the cartesian coordinates does not transform as an irreducible representation different from the irreducible representations of the remaining coordinates. Thus polarization studies are of little help. Equally perplexing is the fact that the singlet-triplet energy gap in flavone lies between that of a pure $^3(n\pi^*)$ state and a pure $^3(\pi\pi^*)$ state (60). Finally, the presence of carbonyl stretch frequencies or ring stretching modes often yields information on the character of T_1 , but in the case of flavone and its derivatives studied here, the phosphorescence spectra show no indication of a vibrational progression, but rather display broad peaks.

In spite of these difficulties, the lowest triplet state in flavone has been assigned as $^3(\pi\pi^*)$, based primarily on triplet state lifetime data (60,61,62) and on internal "heavy atom" effects (60,63). Due to the similarities of triplet state lifetimes and T-T absorption spectra in flavone, 7-hydroxy flavone and 5-methyl-7-hydroxy flavone, the orbital assignment of T_1 in the latter two is tentatively set at $^3(\pi\pi^*)$.

Although Pownall (60) does identify the lowest triplet state of flavone as being of $\pi\pi^*$ character, he further indicates that some $n\pi^*$ character is present. This statement is consistent with the observation by Dym and Hochstrasser (64) that aromatic ketones with molecular symmetry lower than C_{2v} are likely to have configurationally mixed states rather than configurationally pure $n\pi^*$ or $\pi\pi^*$ states.

The presence of the hydroxy group in 7-hydroxy flavone and 5-methyl-7-hydroxy flavone is expected to raise the energy of their $n\pi^*$ states relative to those in flavone. Consequently, in the hydroxy substituted molecules the separation between T_1 , which is of $^3(\pi\pi^*)$ character, and the upper $^3(n\pi^*)$ states will be larger than in flavone. Under such circumstances, it is interesting to speculate as to why the T-T absorption spectra of the three molecules are so similar.

Since T_1 in all three compounds is thought to be mainly of $\pi\pi^*$ character, it is reasonable that the energies of the lowest triplet states in the three compounds be approximately the same. This is borne out, as is described in the following

section, by the similarity in energy of the 0,0 bands in the phosphorescence spectra of the three flavones. It is not inappropriate to hypothesize from the correspondence of both the lowest triplet state energies and the T-T absorption spectra of the three flavones that the terminal triplet states in all three compounds are similar. An extension of this hypothesis is that the T-T transitions involved are $\pi\pi^* \leftarrow \pi\pi^*$ in nature. This follows logically since, if the transitions were $n\pi^* \leftarrow \pi\pi^*$ in nature, the transition energies would be higher in the two hydroxy derivatives than they would in flavone. This is a direct result of the effect of the hydroxy substituent as described previously.

The above explanation seems reasonable. But what reasoning can be used to explain the increased structure present in 7-hydroxy flavone and 5-methyl-7-hydroxy flavone? With the raising of the $n\pi^*$ states upon hydroxy substitution, the interaction between $^3(n\pi^*)$ and $^3(\pi\pi^*)$ states is likely to be reduced. This reduced interaction in the two hydroxy derivatives may be the factor resulting in the increased substructure in their T-T absorption spectra. This may be the case since, as stated previously, when two triplet states are energetically very close, the resulting vibronic interaction often obliterates the fine structure. This was mentioned with reference to phosphorescence spectra, but may have some bearing in T-T absorption spectra.

An interesting correspondence may be noted regarding both the broadness of the T-T absorption spectrum of flavone and the geometries of the states to which transition from T_1 occur.

An aromatic molecule structurally very similar to flavone, that is 2-phenylnaphthalene, is found to have a vibronically well defined T-T absorption spectrum (31). The authors express the view that this is the result of transitions taking place between states with similar potential energy surfaces. A previous study by the same authors (65) indicated that the lowest triplet state in mono-phenylnaphthalenes was planar. Since the T-T absorption spectra in their more recent study are so well defined, it is proposed that the upper triplet states involved in the transitions are also planar.

In contrast with the mono-phenylnaphthalene results, the T-T absorption spectra of two diphenylnaphthalenes are rather broad and structureless. This suggests that although T_1 is, as indicated earlier, planar, the upper triplet states may indeed be non-planar. As has been discussed earlier, flavone is assigned a planar T_1 state on the basis of its similarity to 2-phenylnaphthalene. Although the similarities between the two molecules is quite obvious, by no means does this correspondence provide conclusive evidence as to the geometry of the lowest triplet state in flavone. The assumption seems valid however, since it is not expected that the presence of the two oxygen atoms in flavone will prevent the formation of a planar structure. Based on the discussion of geometry in the mono and diphenylnaphthalenes, it seems reasonable to propose from the broad structureless T-T spectrum of flavone, that the upper triplet states involved in the observed T-T transitions

are not planar. The same argument may be applied to the 7-hydroxy derivatives, as the hydroxy and methyl substituents are not likely to affect the geometry to any great extent. Obviously, the fact that the T-T spectra of the three compounds are broad and not well defined may be due to factors other than the one described. The proposal described here may in fact be applicable here, but by no means should it be assumed that this is the only possibility.

The steady state technique employed in the study of T-T absorption at 77°K offers excellent conditions for the occurrence of a process such as biphotonic absorption. In this process, the absorption of a single photon, leading to excitation to the lowest triplet state T_1 , is followed by the absorption of a second photon resulting in further excitation. The absorption of the second photon may simply excite the electron in T_1 to a higher triplet state. However, if the photon is of sufficient energy, the process may result in ionization. The possibility of interference from the products of such an ionization process is a factor which must be considered in the study of T-T absorption.

In an attempt to observe T-T absorption in 5-hydroxy flavone and 5-hydroxy - 7-methyl flavone, a very intense absorption due to photoproducts was observed. The presence of the photoproducts was in both cases sufficient to impede assessment as to the presence of T-T absorption. The photoproduct absorption spectra of 5-hydroxy flavone and 5-hydroxy - 7-methyl

flavone are displayed in figures (8) and (9) respectively. Table II lists the absorption maxima for the two compounds. A variation in colour from violet to purple was evident in the samples containing the photoproducts, undoubtedly due to the length of time the samples were exposed to the arc. The coloured species did not fade upon sitting at 77°K, but did disappear when the sample melted. Upon refreezing, the glass again appeared uncoloured.

A possible reason for the formation of photoproducts could be associated with the solvent, EPA. During the examination of T-T absorption in diphenylamine, Craig and Ross (66) remarked that the excitation induced absorption of diphenylamine was not likely to be due to diphenylamine itself, but rather to a photoproduct present in the EPA glass. Irradiation of diphenylamine yielded a green colour, which was found to remain as long as the solution remained frozen. Further investigation pointed to the diphenylamine cation as being responsible for the T-T absorption. The authors noted that the green colouration and the T-T absorption, which were both due to the cation, were present only in EPA solution. Diphenylamine, dissolved in a mixture of isopentane and methyl-cyclohexane (PMh) (5:1 by volume), did not exhibit either phenomenon when irradiated. It was felt that only in a solvent containing an electron acceptor, such as EPA, could photoionization of diphenylamine occur. PMh contains no such acceptor and therefore the cation is not formed. Although the situation described for

EPA is not inconceivable, it is perhaps unlikely since it might be expected that the hydroxyl hydrogen in the ethyl alcohol would be hydrogen bonded to the large amount of ethyl ether present, thereby diminishing its availability to the much less concentrated solute (67).

According to the preceeding discussion, it appears unlikely that intermolecular hydrogen bonding is present between the solvent EPA and either of the two 5-hydroxy flavone derivatives. On the other hand, both 5-hydroxy and 5-hydroxy - 7-methyl flavone are unlike the other flavones studied here in that intramolecular hydrogen bonding of the 5-hydroxy group to the carbonyl oxygen is possible. Such bonding is observed in ethanol solution both at 77°K (68,61) and at room temperature (69). Infrared studies support the presence of such an interaction (69). With respect to the photoproduct absorption in 5-hydroxy flavone and 5-hydroxy - 7-methyl flavone, perhaps the hydroxyl hydrogen acts as an electron acceptor in the same way that Craig and Ross assumed the alcohol present in EPA to act in the case of diphenylamine. This statement requires further substantiation.

II. Emission Spectra

The total emission spectrum of flavone presented in figure (10) consists of phosphorescence only, and is in excellent agreement with previously published results (60,68,62). Although the three earlier studies are carried out at liquid nitrogen temperature, slight differences in the various emission spectra of flavone are apparent. These differences are likely due to varying solvent effects present in the different solvent systems. Ethanol is the most popular solvent (68,62), but mixtures of ether and ethanol (60) have also been used. The present study is the first carried out in which flavone is dissolved in EPA. The absence of fluorescence in EPA is in accordance with the studies carried out in other solvent systems.

The phosphorescence spectrum of flavone is composed of five poorly resolved maxima with the highest energy maximum occurring at approximately 459 nanometers. The broadband nature of the phosphorescence emission does not permit assignment of the orbital configuration of T_1 based upon carbonyl or ring stretching frequencies. The broadness of the peaks and the absence of a well-defined 0,0 band may be examined using Franck-Condon considerations. Several authors have indicated that the resolution of the maxima in absorption and emission spectra may be affected by the geometries of the states between which transitions occur (70). Specifically, it has been stated that transitions arising between states of dissimilar geometry tend

to result in broader maxima than do transitions between geometrically similar states. The lack of high resolution in the emission spectrum of flavone could be attributed to transitions arising between geometrically different ground triplet and singlet states. It has been indicated in this study that the lowest triplet state of flavone is planar, although the assignment has not been confirmed. A Russian team has expressed the opinion that due to steric hindrances flavone cannot be planar in its singlet ground state (71). Since the geometries of the lowest triplet state and the ground singlet state have not yet been established, any assessment of the contribution to the broadness of the emission spectrum of flavone made by transitions between geometrically different states would not be significant. Even if the geometries were known it seems unlikely that the above factor is the sole phenomenon responsible for the broadband appearance of the emission spectrum of flavone.

The total emission spectra of 7-hydroxy flavone, 5-methyl-7-hydroxy flavone, 5-hydroxy flavone and 5-hydroxy-7-methyl flavone are presented in Figures (11 - 14) respectively. Table III includes the emission characteristics, that is the fluorescence and phosphorescence maxima of flavone and its derivatives. The emission spectrum of 7-hydroxy flavone has previously been determined in ethanol at 77°K, (68) and the results agree well with those of the present study. Similarly, the phosphorescence wavelength maximum of 5-hydroxy flavone in ethanol at 77°K

has been reported (61). The results presented for 5-hydroxy, 7-methyl flavone and 7-hydroxy - 5-methyl flavone are new.

All four derivatives of flavone exhibit phosphorescence, and all but 5-hydroxy - 7-methyl flavone appear to fluoresce. Phosphorescence emission of the derivatives appears similar to that of the parent molecule flavone; the only differences being slight variations in the intensities and resolution of the maxima. Substitution by the hydroxy group, both in the 5 and 7 positions results in a three nanometer shift of the highest energy maximum to lower energy. The effect of methyl substitution on the other hand appears slightly more complex. Methyl substitution at the 5 position of 7-hydroxy flavone shifts the phosphorescence spectrum to higher energy, whereas substitution at the 7 position of 5-hydroxy flavone results in a shift to lower energy. These differences are probably not significant as methyl substitution produces only minor effects.

One of the most striking features of the emission spectra is the appearance of fluorescence upon hydroxy substitution. The fluorescence is quite intense in 7-hydroxy flavone and 5-hydroxy flavone, much weaker in 5-methyl - 7-hydroxy flavone and completely missing in 5-hydroxy - 7-methyl flavone. The lack of fluorescence in 5-hydroxy - 7-methyl flavone may in fact be accurate, but may on the other hand be the result of the overall weak intensity of the emission of the molecule. A relatively high sensitivity was required in order to resolve the emission

of 5-hydroxy - 7-methyl flavone, and even then, the emission recorded was quite weak. If the ratio of fluorescence to phosphorescence is as small in 5-hydroxy - 7-methyl flavone as it is in the other flavone derivatives; then it is possible that the fluorescence may be hidden beneath the noise.

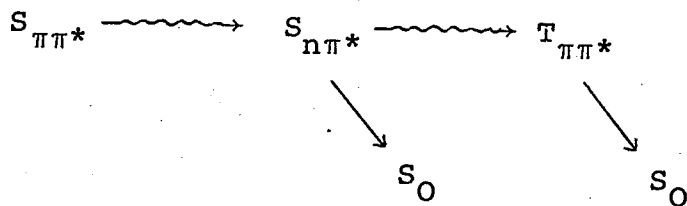
The absence of fluorescence in flavone noted in this study agrees well with the literature. In an earlier study of the emission spectrum of flavonoids, fluorescence of 7-hydroxy flavone in ethanol solution at 77°K was not observed (68). Although the phosphorescence and fluorescence of 5-hydroxy - 7-methyl flavone have not yet been reported outside the present study, the fluorescence of 5-hydroxy flavone has been examined before. These earlier studies have indicated that fluorescence of 5-hydroxy flavone both in ethanol and in neutral solvents is absent at room temperature (69) and at liquid nitrogen temperature (68,61).

The absence of fluorescence in flavone and its appearance in 5-hydroxy flavone and the 7-hydroxy flavones is an interesting phenomenon which warrants further discussion. The possibility that the fluorescence of the flavone derivatives is solvent dependent may explain why it is observed in EPA but not in ethanol or neutral solvents. The possibility that the fluorescence is due to impurities present in the sample is unlikely considering the intensity of the luminescence in each compound. Moreover, the purity of the compounds as received was high.

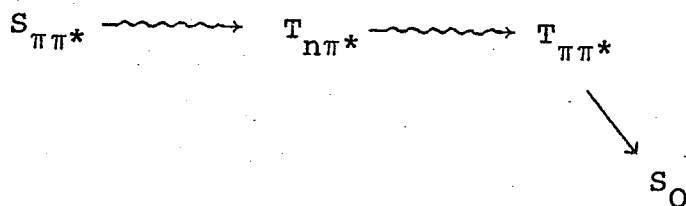
Both fluorescence and phosphorescence depend on the relative positions of the lowest excited singlet and triplet $n\pi^*$ and $\pi\pi^*$ states, as well as on the relative radiationless intercombination transition efficiencies. These efficiencies may be at least qualitatively determined using the El-Sayed selection rules (15). Based on these selection rules, a series of papers has been published by V.G. Plotnikov on the relative positions of $n\pi^*$ and $\pi\pi^*$ states in molecules in relation to their optical properties (16,17,18). In the third paper in the series, the author proposes five classes of molecules in which only one heteroatom is present in each molecule. Each class is defined on the basis of the relative positions of their excited states; that is the lowest $S_{n\pi^*}$, $S_{\pi\pi^*}$, $T_{n\pi^*}$, and $T_{\pi\pi^*}$ configurations are arranged in order of decreasing energy. Higher excited states are not directly involved in the luminescence properties of the molecules and are therefore not considered.

In order to utilize such a system, it is first necessary to obtain the relative positions of the lower triplet and singlet states in flavone. On the basis of spectral data, Efimov, et al., (62) determined the energies and relative positions of the lower singlet and triplet $n\pi^*$ and $\pi\pi^*$ states in flavone. As anticipated the lowest triplet state in flavone is of $\pi\pi^*$ character. The order of the lower singlet and triplet $n\pi^*$ and $\pi\pi^*$ states from high to lower energies is $S_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{n\pi^*}$

and $T_{\pi\pi^*}$. In the format presented by Plotnikov, flavone is placed in class III, in which the most probably deactivation processes following excitation would be:



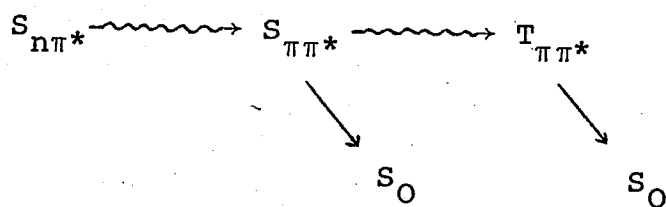
and



In the above processes, a wavy arrow denotes a non-radiative process, and a solid arrow indicates a radiative process. Plotnikov indicates that the rates of non-radiative deactivation, that is, the $S_{n\pi^*} \xrightarrow{\text{wavy}} T_{\pi\pi^*}$ and $S_{\pi\pi^*} \xrightarrow{\text{wavy}} T_{n\pi^*}$ transitions are about three or four orders of magnitude more rapid than fluorescence from either the $S_{n\pi^*}$ state or the $S_{\pi\pi^*}$ state. Accordingly, such a system would exhibit only phosphorescence.

The emission spectrum of flavone is quite easily explained by the application of the El-Sayed selection rules. That of 7-hydroxy flavone is less readily explained, as knowledge of the relative positions of the excited states in this molecule is not available. However, 7-hydroxy flavone and 5-methyl -

7-hydroxy flavone can be analyzed by treating the hydroxy and methyl groups as perturbations on the basic flavone system. Hydroxy substitution is expected to raise the energy of the $n\pi^*$ states relative to the $\pi\pi^*$ states; that is both the $S_{n\pi^*}$ state and the $T_{n\pi^*}$ state will be shifted to higher energy. Three possibilities are presented with regard to this shift. Firstly, if the $n\pi^*$ states in being raised, do not exceed the $S_{\pi\pi^*}$ state in energy, then the emission spectrum will still be composed of phosphorescence only, with perhaps only a change in intensity being apparent. Secondly the $S_{\pi\pi^*}$ and $S_{n\pi^*}$ states may exchange positions due to the shift, such that the order from high to low energy is $S_{n\pi^*}$, $S_{\pi\pi^*}$, $T_{n\pi^*}$, and $T_{\pi\pi^*}$. This arrangement corresponds to class IV in the Plotnikov scheme (18), and such a system would exhibit only phosphorescence from the $T_{\pi\pi^*}$ state. Finally if both the singlet and triplet $n\pi^*$ states are shifted sufficiently that they exceed the $S_{\pi\pi^*}$ state in energy, then the most probable deactivation following excitation of this class V molecule would be:



Since emission from $S_{\pi\pi^*}$ is about as efficient as the non-radiative process $S_{\pi\pi^*} \xrightarrow{\text{wavy}} T_{\pi\pi^*}$, both phosphorescence and fluorescence will be observed. It is possible that the last explanation is the situation in the case of the 7-hydroxy

flavone molecule. With methyl substitution in the 5 position, the relative positions of the excited states are not significantly affected. Therefore 5-methyl-7-hydroxy flavone displays both phosphorescence and fluorescence as does 7-hydroxy flavone. In fact, Efimov, et al., (62) explained that the quenching of fluorescence in flavone was due to the intercombination transition $S_{n\pi^*} \xrightarrow{\text{wavy line}} T_{\pi\pi^*}$. They also noted that the shifting of the $n\pi^*$ states could be responsible for the appearance of fluorescence in some flavone derivatives (72). The same explanation could be invoked in the explanation of the emission spectrum of 7-hydroxy flavone and the other fluorescing hydroxy derivatives. Just as the presence of $n\pi^*$ states between the lowest singlet and triplet $\pi\pi^*$ states causes the fluorescence to disappear in flavone, several nitrogen heterocycles with intermediate $n\pi^*$ states fail to exhibit fluorescence (15).

Results from the present study indicate that 5-hydroxy flavone fluoresces. In the previous studies mentioned which disagree with this result, the authors of one particular paper (61) credit the lack of fluorescence to the intramolecular hydrogen bond in the 5-hydroxy flavone molecule. This hydrogen bond is thought to neutralize the electron donor properties of the hydroxy group, and therefore inhibit its effect on the emission. In other words 5-hydroxy flavone is essentially the same as flavone. The discrepancy between the two studies may be due to the differences between the solvent systems used, which may affect the ability of 5-hydroxy flavone to form an

intramolecular hydrogen bond.

III. Comparison of Experimental Results to Calculated Values.

The results of the theoretical study of the T-T absorption spectra of flavone, 7-hydroxy flavone, and 5-methyl-7-hydroxy flavone as determined using the combined CNDO/2 and CNDO/S methods discussed earlier are listed in Table VII. The table is restricted to those transitions whose energies lie below the maximum energy studied experimentally. In no case did the energy investigated experimentally exceed $29,000 \text{ cm}^{-1}$, and thus the relatively intense T-T transitions predicted to lie above this energy cannot be compared. For the sake of clarity, only calculated transitions whose oscillator strengths exceed 0.001 are included in the comparison of the two sets of results. The weaker transitions have been omitted in order to highlight those transitions which should most readily be observed experimentally. This omission should simplify the comparison of the experimental to the theoretical results. The comparative results are listed in Table VIII.

The energy of the lowest triplet state for each molecule is included in Table VII. It is interesting to note that flavone has the lowest triplet energy of the three compounds. The calculated value for the energy of T_1 in flavone is $22,343 \text{ cm}^{-1}$, and is in good agreement with the experimentally determined value of $22,000 \text{ cm}^{-1}$ given by Efimov, et al., (62). However, the latter value has been obtained in a study carried out in hexane solution. In our studies EPA is used as the solvent. Efimov, et al., note a blue shift in the phosphorescence spectrum of

flavone in ethanol as compared to hexane solution. This shift signifies that the energy of T_1 of flavone in ethanol is likely to be slightly higher than the energy determined in hexane. The energy of T_1 both in 7-hydroxy flavone and 5-methyl-7-hydroxy flavone appears to be slightly higher compared to flavone itself. Hydroxy substitution, which is expected to produce the larger effect on the electronic distribution in flavone, results only in a 46 cm^{-1} increase in energy in the 7-hydroxy flavone molecule. Although the increase with methyl substitution is about the same as hydroxy substitution, both changes are rather insignificant in comparison to the large energy of the lowest triplet state of flavone.

In comparing the experimental results and the semi-empirical calculations of the T-T absorption spectra, two factors will be considered. These are both the positions and intensities of the maxima. Experimental oscillator strengths were not determined due to difficulties inherent in obtaining molar extinction coefficients of T-T transitions. The numerical values of the oscillator strengths calculated for the flavones will therefore not be taken as absolute. Rather, they will be used for relative comparison in checking the intensities of the experimental maxima.

Molecular orbital calculations indicate that three T-T transitions in flavone should be observed below $30,000 \text{ cm}^{-1}$. These transitions, which correspond to transitions to the excited triplet states nine, eleven and thirteen are predicted to

be seen experimentally at $14,894\text{ cm}^{-1}$, $24,133\text{ cm}^{-1}$, $27,066\text{ cm}^{-1}$ respectively. The agreement of these results with the actual observed T-T absorption spectrum of flavone is startling. The coincidence between calculated and observed peak maxima is excellent, the former lying well within the experimental error of the latter. Moreover, the calculated oscillator strengths predict the relative intensities of the maxima quite well. The prediction of a transition slightly above $24,000\text{ cm}^{-1}$ reinforces the previous belief that the unresolved peak in flavone is indeed a separate transition and not a vibrational peak related to the more intense absorption at $27,000\text{ cm}^{-1}$. Good agreement such as is presented here has previously been reported by Orloff in a study of triplet states in alternant hydrocarbons (29) using the semiempirical PPP-SCF-MO theoretical treatment. Orloff interprets this conformity as resulting from the improved correlation between states of similar multiplicity. The author notes that transitions between states of different multiplicities are expected to result in poorer correlation. For example, the decoupling of a pair of electrons in a $T_1 \leftarrow S_0$ transition would result in large intrashell energy changes. However, only smaller intershell changes are present in T-T transitions since there is no decoupling of electrons involved.

Three transitions are also prominent in the calculations carried out for 7-hydroxy flavone. In this case however, the agreement is not as good as in the case of flavone. The most intense peak is predicted almost 1400 cm^{-1} too high, while the

transition seen experimentally as a shoulder on the most intense maximum is computed to be blue shifted by 245 cm^{-1} . Oscillator strengths are comparatively reasonable. The two lower energy transitions are calculated to be of equal intensity, but both significantly weaker than the high energy transition. Two curious features are evident in the low energy transitions of 7-hydroxy flavone. Firstly, it appears that the $14,894 \text{ cm}^{-1}$ transition which in flavone terminated in the T_9 state, is in 7-hydroxy flavone essentially isoenergetic, but terminating in the tenth excited triplet state. This phenomenon is probably the result of the relative interchange of the T_9 and T_{10} states in 7-hydroxy flavone due to the presence of the hydroxy substituent. The second anomaly in regard to the low energy transition in 7-hydroxy flavone, is that its comparison to the calculated energy for the transition is more difficult since experimentally the low energy transition is composed of three maxima rather than just one. The three peaks are most likely vibrational peaks of a single T-T transition. Consequently the calculated value for the energy of that particular T-T absorption should be compared to the 0,0 band, which we will take to be the lowest energy transition of the vibrational band. Although this comparison does not place the calculated result within the error limits of the experimental transition, the agreement is still quite good.

Theoretical calculations for 5-methyl-7-hydroxy flavone show a red shift of all maxima relative to those determined for

7-hydroxy flavone. Again three transitions are predicted. The calculated upper triplet states in this derivative correspond to those in 7-hydroxy flavone, although the agreement between theory and experiment with regard to both peak position and intensity is slightly better in 5-methyl-7-hydroxy flavone. The three low energy vibrational peaks present in 7-hydroxy flavone are also present in 5-methyl-7-hydroxy flavone. As in the former case, the calculated energy should be compared to the lowest energy maximum of the vibrational band. The fact that the methyl group induced little change in the results obtained from the calculations supports the experimental finding that the alkyl group does not affect the π electron system to any significant extent.

Difficulties and slight discrepancies in the comparison of experimental and theoretically calculated T-T transition energies are unavoidable since the calculated values are usually based on an ideally isolated molecule. On the other hand, the experimental results are determined in rigid or fluid solution. The geometry of any molecule under investigation may be different under different environmental conditions; just as the geometry may vary between ground and excited states of the molecule. In the case of flavone, calculations were carried out under the assumption that the molecule is planar. Although several papers mentioned earlier indicate that flavone has a non-planar ground singlet state, the important geometry in the study of T-T transitions is logically the lowest triplet state.

The excellent results obtained from the present calculations are probably due to our accurate description of the geometry of T_1 in flavone.

SUMMARY AND CONCLUSION

In this study, knowledge of the triplet states of flavone and several of its derivatives has been extended through the examination of their T-T absorption spectra and emission spectra. The T-T absorption spectra of flavone, 7-hydroxy flavone, and 5-methyl-7-hydroxy flavone obtained in EPA mixed solvent at 77°K have been obtained for the first time. No triplet state lifetimes have previously been reported for either 7-hydroxy flavone or 5-methyl-7-hydroxy flavone. The previously reported triplet state lifetimes for flavone agree well with the present study. Although the earlier studies made use of ethanol solutions, the agreement of the lifetimes attests to the similarity of the EPA system to ethanol as a solvent. Due to the absorption by photoproducts produced during excitation, the T-T absorption spectra and triplet state lifetimes of 5-hydroxy flavone and 5-hydroxy-7-methyl flavone were not obtained. However, the photoproduct absorption spectra of these two compounds were measured in rigid EPA glass, and also represent new data.

The total emission spectra of flavone and its four derivatives listed above have been obtained. The emission spectra presented here are new, since no study of flavone or any of its derivatives has been reported using EPA. While the emission spectra of flavone, 7-hydroxy flavone and 5-hydroxy flavone in solvents other than EPA have been reported, the emission spectra of 5-hydroxy-7-methyl flavone and 7-hydroxy-5-methyl flavone

reported in this study are the sole emission spectra presently available for these two molecules. Notable is the agreement of the various emission spectra of flavone as determined in different solvents. Also noteworthy is the unanimous agreement that flavone does not fluoresce. Discordance is noted however in the emission spectra of 5-hydroxy flavone and 7-hydroxy flavone as determined in EPA and ethanol. In ethanol solution, no fluorescence is apparent from either 5-hydroxy flavone or 7-hydroxy flavone, whereas it is quite intense in the emission spectra of the two flavone derivatives in EPA. An explanation as to the absence of fluorescence in flavone and its appearance in the hydroxy derivatives has been proposed based on the relative rates of the radiationless transitions occurring after excitation.

Calculations have been carried out using a combination of the all-valence electron, semi-empirical, self consistent field CNDO/2 and CNDO/S methods. This was done in order to examine the feasibility of applying such a method to a molecule as large as flavone. The energies and oscillator strengths of the T-T transitions in flavone, 7-hydroxy flavone and 5-methyl-7-hydroxy flavone have been calculated, and a comparison made with the experimental T-T absorption spectra. The agreement was found to be very good; the calculated energies of the T-T transitions generally lying well within the error limits of the experimental maxima. Calculated oscillator strengths agreed qualitatively with the intensities of the experimentally

determined maxima for each molecule.

The method used to calculate the T-T absorption energies appears to yield very good results. It must be stressed however, that the method is very sensitive to the coordinates of the atoms that are used as input in the calculations. Consequently the accuracy of the final results depends largely on the accuracy with which the geometry of the molecule can be determined.

APPENDIX I

List of Failures.

Other than the five flavones discussed previously, several other compounds were examined for the presence of T-T absorption. The list of molecules studied which did not exhibit T-T absorption is given in Table IX. 5-hydroxy flavone and 5-hydroxy - 7-methyl flavone have been included in this table because they failed to display T-T absorption, but since they have been thoroughly discussed with respect to their photoproduct absorption, they will not be mentioned again. The presence or absence of photoproduct absorption is also indicated in this table.

Experimental conditions used in studying 3-hydroxy flavone, 5-hydroxy flavone, 5-hydroxy - 7-methyl flavone, 8-methoxy flavone, 2,6-di-hydroxy-para-benzoquinone, 2,3,5,6-tetrahydroxy-para-benzoquinone, 2,6-dimethoxy-para-benzoquinone and salicylaldehyde were identical to those used for the determination of T-T absorption spectrum of flavone. The equipment and techniques involved were also identical. At least ten trials were carried out for each compound with varying concentrations, and the dewar offset in order to enhance T-T absorption. Painstaking effort failed to reveal even the slightest indication of T-T absorption in 3-hydroxy flavone, salicylaldehyde and the three benzoquinones. In the molecules yielding negative T-T absorption results, further study into the phosphorescence spectra and lifetimes, as

well as the triplet state lifetime was discontinued. The exceptions to this rule were 5-hydroxy flavone and 5-hydroxy - 7-methyl flavone, whose phosphorescence spectra were measured and discussed, and 8-methoxy flavone.

A very weak T-T absorption appeared to be present in 8-methoxy flavone, but was so weak as to not be readily differentiable from the background noise. In an effort to see if such an absorption process was indeed occurring, an attempt at measuring the triplet state lifetime of 8-methoxy flavone was undertaken. The lifetime appeared to be very short lived, approximately forty milliseconds, but was further complicated by an unusual non exponential decay, apparently due to the presence of more than one decay process. The non exponential decay was readily visible when recorded on an oscilloscope. One possible explanation for this unusual decay is the presence of an impurity in the frozen solution. For an impurity to interfere in a triplet-triplet process, the concentration would have to be significant, a situation unlikely with the high purity of chemicals used.

TABLE IX

COMPOUNDS WHICH DID NOT EXHIBIT T-T OR PHOTOPRODUCT ABSORPTION

Molecule	T-T Absorption	Photoproduct Absorption	Energy (cm^{-1})
1) 3-OH Flavone	No	No	-
2) 5-OH Flavone	No	Yes	19,400
3) 5-OH-7-CH ₃ Flavone	No	Yes	18,800
4) 8-OCH ₃ Flavone	No	No	-
5) 2,5-(OH) ₂ -p-Benzoquinone	No	No	-
6) 2,3,5,6-(OH) ₄ -p-Benzoquinone	No	No	-
7) 2,6-(OCH ₃) ₂ -p-Benzoquinone	No	No	-
8) Salicylaldehyde	No	No	-

Source: 1) Biochemical Laboratories, Inc.

2) ICN-K&K Laboratories, Inc.

3,4) ICN Pharmaceuticals, Inc.

5) Eastman Kodak Company

6,7) Aldrich Chemical Company

8) Fisher Scientific Company

APPENDIX II

Coumarin Studies.

Molecular orbital calculations for the T-T transitions in coumarin and 4-hydroxy coumarin were undertaken in an attempt to provide additional evidence to support a previously proposed explanation for the difference between the T-T absorption spectra of the two molecules. It was expressed by Henry and Lawler (59) in their study of the T-T absorption of coumarin and several of its derivatives that the differences in the T-T absorption spectra of coumarin and 4-hydroxy coumarin were due to decreased $n\pi^*$ character in the lowest triplet state of 4-hydroxy coumarin as compared to coumarin itself. Based on the similar appearances of the T-T absorption spectra of the two molecules, the authors assumed that the upper triplet states involved in the transitions were essentially the same both in coumarin and 4-hydroxy coumarin. The increased complexity found in the T-T spectrum of coumarin was therefore explained on the basis of increased $n\pi^*$ character in T_1 .

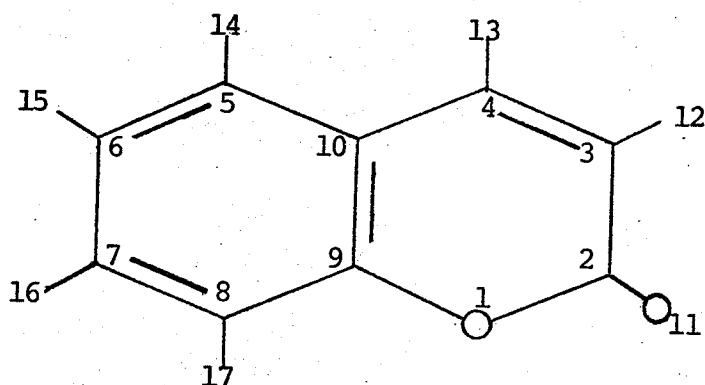
The appearance of a vibrational spacing of 1400 cm^{-1} in coumarin and 4-hydroxy coumarin indicates that the T-T transition is primarily $\pi\pi^* \leftrightarrow \pi\pi^*$ in nature (59). Also, the T_j energies in the two molecules obtained from the sum of phosphorescence and T-T energies are very similar. It is of interest here to see if molecular orbital calculations corroborate the assumption of similar upper triplet states T_j .

Calculations were carried out for coumarin and 4-hydroxy coumarin with the identical program used for triplet-triplet transition energies in the flavone molecules. As with the flavones, the only input required was the atomic coordinates of the molecule of interest. Determination of the cartesian coordinates was also carried out in the manner described for the flavones. Bond angles and bond lengths used to calculate the atomic coordinates were obtained from the following references: coumarin (73) and 4-hydroxy coumarin (74). All calculations were carried out assuming a planar configuration. Because of the mobility of the hydroxy group in 4-hydroxy coumarin, two planar configurations are possible, and for the sake of comparison, calculations have been executed for both configurations. The numbering used and the final cartesian coordinates obtained for coumarin, 4-hydroxy coumarin (L), and 4-hydroxy coumarin (R) are presented in Tables X and XII respectively. The letters (L) and (R) refer to the direction, that is left or right, in which the hydroxy group is pointing in each of the two possible configurations of 4-hydroxy coumarin.

Table XIII consists of a catalogue of the energy of the lowest triplet state T_1 , the frequency and oscillator strength of each T-T transition located below $27,000 \text{ cm}^{-1}$. The table lists only those transitions whose energy lies below $27,000 \text{ cm}^{-1}$ because no experimentally determined T-T transition exceeds this energy. Comparison between the calculated and experimentally determined T-T transitions is summarized in Table XIV.

TABLE X

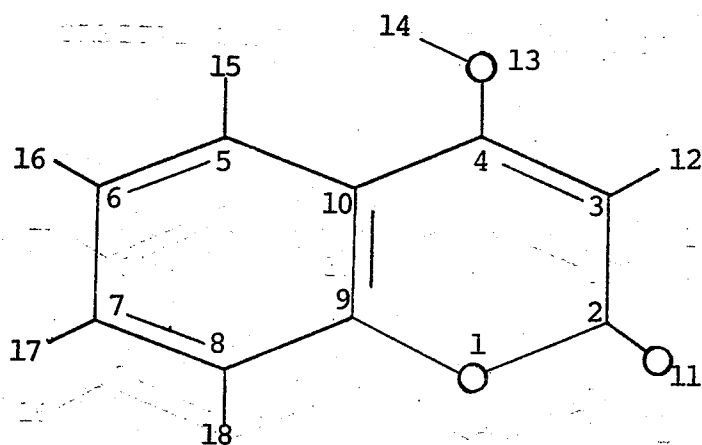
ATOMIC COORDINATES USED FOR MOLECULAR
ORBITAL CALCULATIONS FOR COUMARIN.



ATOM	At. No.	COORDINATES		
		X	Y	Z
1	8	3.54	-0.71	0.00
2	6	4.76	-0.11	0.00
3	6	4.81	1.32	0.00
4	6	3.70	2.05	0.00
5	6	1.19	2.09	0.00
6	6	0.00	1.40	0.00
7	6	0.00	0.00	0.00
8	6	1.19	-0.69	0.00
9	6	2.38	0.03	0.00
10	6	2.40	1.41	0.00
11	8	5.72	-0.85	0.00
12	1	5.75	1.84	0.00
13	1	3.70	3.13	0.00
14	1	1.19	3.17	0.00
15	1	-0.94	1.94	0.00
16	1	-0.94	-0.54	0.00
17	1	1.19	-1.77	0.00

TABLE XI

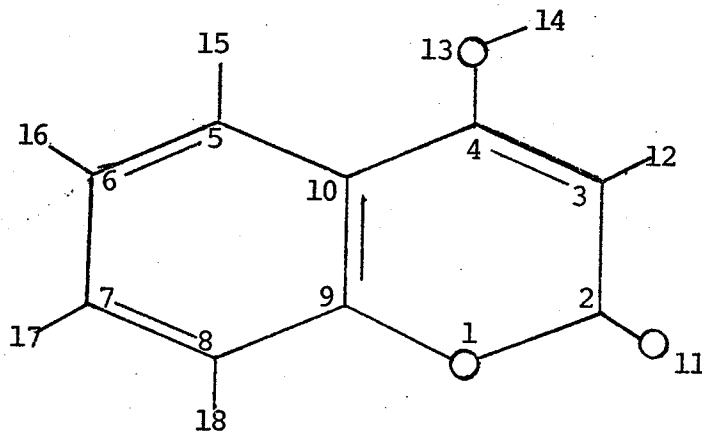
ATOMIC COORDINATES USED FOR MOLECULAR
ORBITAL CALCULATIONS FOR 4-OH COUMARIN(L)



ATOM	At. No.	COORDINATES		
		X	Y	Z
1	8	3.54	-0.82	0.00
2	6	4.78	-0.25	0.00
3	6	4.87	1.07	0.00
4	6	3.78	1.86	0.00
5	6	1.23	2.04	0.00
6	6	0.00	1.36	0.00
7	6	0.00	0.00	0.00
8	6	-1.16	-0.81	0.00
9	6	2.39	-0.08	0.00
10	6	2.41	1.28	0.00
11	8	5.73	-0.98	0.00
12	1	5.81	1.60	0.00
13	8	3.80	3.21	0.00
14	1	2.93	3.57	0.00
15	1	1.27	3.12	0.00
16	1	-0.93	1.91	0.00
17	1	-0.96	-0.50	0.00
18	1	1.13	-1.89	0.00

TABLE XII

ATOMIC COORDINATES USED FOR MOLECULAR
ORBITAL CALCULATIONS FOR 4-OH COUMARIN(R)



ATOM	At. No.	COORDINATES		
		X	Y	Z
1	8	3.54	-0.82	0.00
2	6	4.78	-0.25	0.00
3	6	4.87	1.07	0.00
4	6	3.78	1.86	0.00
5	6	1.23	2.04	0.00
6	6	0.00	1.36	0.00
7	6	0.00	0.00	0.00
8	6	1.16	-0.81	0.00
9	6	2.39	-0.08	0.00
10	6	2.41	1.28	0.00
11	8	5.73	-0.98	0.00
12	1	5.81	1.60	0.00
13	8	3.80	3.21	0.00
14	1	4.68	3.57	0.00
15	1	1.27	3.12	0.00
16	1	-0.93	1.91	0.00
17	1	-0.96	-0.50	0.00
18	1	1.13	-1.89	0.00

TABLE XIII

SUMMARY OF T-T TRANSITION ENERGIES, OSCILLATOR STRENGTHS AND THE ENERGY OF THE LOWEST TRIPLET STATE AS DETERMINED FROM MOLECULAR ORBITAL CALCULATIONS FOR COUMARIN AND 4-OH COUMARIN.

E_{T_1}	COUMARIN		4-OH COUMARIN(L)		4-OH COUMARIN(R)	
	24816 cm^{-1}		24689 cm^{-1}		24977 cm^{-1}	
	Frequency (cm^{-1})	Oscillator Strength	Frequency (cm^{-1})	Oscillator Strength	Frequency (cm^{-1})	Oscillator Strength
T_j						
2	6477	0.0020	3492	0.0007	3379	0.0008
3	7700	0.0002	8389	0.0000	7974	0.0001
4	10337	0.0031	9365	0.0002	9497	0.0000
5	13008	0.0000	12304	0.0000	12328	0.0000
6	13760	0.0049	13772	0.0039	13495	0.0032
7	22398	0.0477	22054	0.0180	21589	0.0130
8	24416	0.0143	24126	0.0214	23918	0.0264
9	25297	0.0000	25497	0.0000	25683	0.0180
10	26705	0.0015	26867	0.0390	25928	0.0000

TABLE XIV

COMPARISON OF EXPERIMENTALLY AND THEORETICALLY DETERMINED VALUES
OF THE T-T TRANSITON ENERGIES FOR COUMARIN AND 4-OH COUMARIN.

	THEORY			EXPERIMENT
	$T_j - T_1$	E_{T-T} ($\times 10^{-3} \text{cm}^{-1}$)	Oscillator Strength	E_{T-T} ($\times 10^{-3} \text{cm}^{-1}$)
Coumarin	6	13,760	0.0049	
	7	22,398	0.0477	$21,700 \pm 50$
	8	24,416	0.0143	$23,140 \pm 50$
	10	26,705	0.0015	$24,600 \pm 50$
4-OH Coumarin(L)	6	13,772	0.0039	
	7	22,054	0.0180	
	8	24,126	0.0214	
	10	26,867	0.0390	$20,100 \pm 50$
				$21,500 \pm 50$
4-OH Coumarin (R)	6	13,495	0.0032	$22,980 \pm 75$
	7	21,589	0.0130	
	8	23,918	0.0264	
	9	25,683	0.0180	

Transition energies are readily comparable, but since experimental oscillator strengths have not been determined by the authors, only relative intensity correlations are discussed.

At first glance the correlation between theoretical and experimental results does not appear too bad. The three experimentally determined maxima are lower in energy than the predicted values, but still in relatively good agreement. The transition predicted to be observed between $13,000\text{ cm}^{-1}$ and $14,000\text{ cm}^{-1}$ in coumarin and 4-hydroxy coumarin cannot be discussed in terms of its accuracy, since in the study carried out by Henry and Lawler, energies below $18,000\text{ cm}^{-1}$ were not examined. The major flaw apparent upon more careful scrutiny of the theoretical calculations is that three separate T-T transitions are predicted between $20,000\text{ cm}^{-1}$ and $27,000\text{ cm}^{-1}$ for both coumarin and 4-hydroxy coumarin, whereas only one electronic transition is seen experimentally in each case. The three maxima observed correspond in both compounds to a vibrational band resulting from a single electronic transition. Consequently a comparison of positions and intensities is out of order, since the two methods cannot even agree on the number of T-T transitions present.

In order to verify the theory that the difference between the T-T spectra of coumarin and 4-hydroxy coumarin are due to a different amount of $n\pi^*$ character in the lowest triplet states of the two molecules, what we had hoped to see was that in each

molecule, only one transition be predicted, and that that transition occur to the same upper triplet state in both molecules. The difficulty with the values calculated here is that in each case one cannot unambiguously associate either of the three theoretical values with the one experimental result. Thus, any argument as to whether or not the upper triplet state involved in the T-T transition in coumarin is the same as that involved in 4-hydroxy coumarin is purely guesswork and on the basis of the present study cannot be substantiated.

In the previous study of the flavones, it is noted that the agreement between experimental and theoretical values for the energy of T_1 is excellent, as is the accuracy with which the positions and intensities of the maxima are predicted. This however is not the situation with coumarin and 4-hydroxy coumarin. Phosphorescence studies indicate that the lowest triplet state energies in coumarin and 4-hydroxy coumarin are $21,834 \text{ cm}^{-1}$ and $23,810 \text{ cm}^{-1}$ respectively (75). These energies, particularly that of coumarin, are significantly lower than the calculated energies listed in Table XIII. Comparison of the positions of the T-T transition maxima is meaningless since it cannot be ascertained which of the three transitions corresponds with the one experimental electronic transition. Shifts due to hydroxy substitution are equally confusing. The substitution appears to shift the experimental vibrational band to lower energy,

and although theory predicts the same shift between coumarin and 4-hydroxy coumarin (R), comparison of coumarin and 4-hydroxy coumarin (L) appears more complex. In the latter pair, all but the high energy transition are red shifted.

It therefore appears that molecular orbital calculations are not of much use in predicting correctly the T-T transitions in coumarin and 4-hydroxy coumarin. Accordingly such calculations shed no new light on whether or not the upper terminal triplet states in coumarin and 4-hydroxy coumarin are in reality similar, as proposed by Henry and Lawler. The inapplicability of the calculations to the coumarin molecules may be due to poor agreement between the geometry used to carry out the calculations and the actual geometry of coumarin and 4-hydroxy coumarin in their lowest triplet state. Calculations on the coumarins were performed utilizing a planar geometry, and although the two molecules may indeed be planar in their respective ground singlet states, it is possible that this is not the geometry of T_1 in coumarin and 4-hydroxy coumarin. It is also reasonable that in order to obtain good correlation between experimental and calculated T-T absorption maxima, it is the geometry of T_1 , not S_0 that need be accurately described. In fact, previous studies indicate that the excellent agreement achieved in the case of flavone is attributable to the geometry of T_1 having been properly assigned as planar. For coumarin and 4-hydroxy coumarin, the planar structures apparent when

the molecules are in their crystalline form, were used for the calculations, and these planar assignments may not coincide with the true geometry of T_1 ; hence one obtains a poor correlation between experimental and theoretical and T-T transitions.

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