The University of Manitoba

THE TRIPLET-TRIPLET ABSORPTION SPECTRA OF SEVERAL AROMATIC HETEROCYCLIC MOLECULES

by

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ABSTRACT

A triplet-triplet (T-T) absorption study in the region 11,000 cm^{-1} to 27,000 cm^{-1} has been carried out for several aromatic heterocyclic molecules. A continuous cross illumination technique was used in EPA glass at 77°K. The lifetime of decay of the absorption was obtained using a flash technique and a comparison was made with phosphorescence lifetime data to verify the T-T nature of the transitions.

The T-T absorption spectrum obtained for phthalazine in EPA has been compared with that obtained in a previous study using an isopentane-n-butyl alcohol glass. By comparison the T-T absorption maxima of phthalazine have been found to be blue shifted by about 400 cm^{-1} in an EPA glass over an isopentane-n-butyl alcohol glass. An explanation of this effect has been given which is based on the amount of $n\pi^*$ character in the T_1 state of phthalazine in the two different solvents.

A new low energy T-T band has been found at 12,040 cm^{-1} in 5, 6-benzoquinoline. The new transition has been assigned as $^3L_b \leftarrow {}^3L_a$ in nature on the basis of its similarity to a T-T band which has been found in the iso-π-electronic hydrocarbon phenanthrene.

Two previously unreported T-T bands starting at 14,910 cm^{-1} and 24,180 cm^{-1} have been found in dibenzothiophene and are tentatively assigned as being $\pi\pi^* \leftarrow \pi\pi^*$ in nature. A comparison of the T-T spectrum of dibenzothiophene with that of phenanthrene, biphenyl, and fluorene has also been made in order to assess the effect of the sulfur atom on triplet state π electronic structure of the two neighboring aromatic rings.

A previous study on the T-T absorption spectra of coumarin and two of its 4-hydroxy derivatives has been extended to four additional substituted coumarin derivatives in order to investigate the effects of substituents on the T-T absorption of these molecules. The observed T-T spectra and triplet state lifetimes show a marked dependence on the presence and position of the hydroxy substitution. An explanation of the results has been developed which is based on the mixing of $n\pi^*$ char- into the lowest $\pi\pi^*$ triplet state. The effect of methyl substitution has also been investigated, but was found to lead to relatively small changes in the T-T spectra of these molecules.

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INTRODUCTION

I. General Discussion

Information on the upper triplet states of many heterocyclic molecules is still lacking despite the photobiological importance of some of these molecules (1). In the present study a triplet-triplet (T-T) absorption technique is employed to investigate the triplet states of several heterocyclic molecules, some of which are known to possess photobiological properties.

A knowledge of the characteristics of the upper triplet states of aromatic molecules is important in the study of the role played by the triplet state in certain photochemical and photophysical processes. For instance, the absorption spectrum of the lowest triplet state, T_1, is necessary for the understanding of biphotonic reactions (2, 3, 4), and the occurence of energy transfer from high triplet states (5, 6). In addition to yielding information on the upper triplet states of molecules, the monitoring of T-T absorption following flash excitation has proven to be a useful method of studying the properties of the lowest triplet state. This technique is especially useful for investigations of the decay of the T_1 state in systems where radiative decay is not the rate determing process (7, 8). The initial triplet state absorption following flash excitation has also been used by some workers to determine the quantum yield of triplet state production, Φ_T, in various systems (9).

Absorption bands of the type $T_n \leftarrow T_1$ were first observed by Lewis et al (10, 11) for solutions of fluorescein and diphenylamine

in rigid glass solution, prior to the identification of the lowest triplet state with the phosphorescent state by Lewis and Kasha (12). In their experiments Lewis et al used a continuous cross excitation to produce a steady-state triplet population, with normal procedures being used to observe the absorption spectrum of the T_1 state. The steady-state technique has not been employed to a large extent in the detection of T-T absorption spectra, primarily due to the low triplet populations which are achieved by this method, but also because of the requirement that the spectra be observed at low temperature or in some other rigid medium. McClure (13) used this method for the study of T-T absorption in a number of aromatic molecules in rigid glass solution in the 14,300 cm^{-1} to 27,800 cm^{-1} range. The spectral range studied by McClure was extended by Craig and Ross (14) to 13,300 cm^{-1} to 38,900 cm^{-1} for a series of aromatic molecules, including two nitrogen heterocyclic molecules. In recent years, the use of the steady-state technique has been extended by Henry and Kasha (15) in an attempt to observe T-T absorption at energies down to 10,000 cm^{-1} for several aromatic hydrocarbons and a number of nitrogen and oxygen heterocyclics.

The recent development of continuous-wave (CW) lasers as an excitation source has greatly increased the sensitivity of the steady-state method of measuring T-T absorption spectra (24, 25). The highly directional nature of the laser radiation allows it to be focused into a small area of the sample to produce high concentrations of triplet state molecules. Therefore, it is possible to detect T-T absorption

in molecules with a shorter triplet state lifetime than would be possible if conventional excitation sources were employed.

The majority of T-T absorption studies in recent years have employed the synchronized flash technique developed by Porter and coworkers (16-21). In this technique a high intensity flash tube is used to populate the T_1 state of the sample with a secondary flash tube being used to record the transient spectrum on a photographic film. The synchronized flash techique has allowed the detection of T-T absorption under conditions where the T_1 state has a lifetime as short as 10^{-5} sec., such as in fluid solutions and in the gas phase. In addition, the large depletion of the ground state, which is obtained by the flash method, has permitted the direct determination of extinction coefficients for T-T transitions from the decrease in the intensity of the singlet-singlet (S-S) absorption bands (22, 23).

The development of the flash technique has resulted in several investigations of the triplet states of photobiologically important molecules. The T-T absorption spectra of several porphyrin and chlorophyl dervatives have been studied by Livingston and Fujimori (26). A number of conjugated polyenes, which are thought to play an important role in photosynthesis and vision, have been studied by several workers (27-31). In most of the studies on conjugated polyenes T-T absorption spectra were only observed if a photosensitizer was present. However, Land et al have recently obtained T-T spectra for conjugated polyenes using a pulse radiolysis excitation technique in the absence of a photosensitizer (32, 33). The pulse radiolysis tech-

nique has also been used by Hayon to observe the T-T absorption spectra of uracil (34).

II. Factors Affecting the Observation of T-T Absorption Spectra

The upper triplet states of aromatic molecules can really only be studied by T-T absorption methods because of the low extinction coefficients of the spin-forbidden $T_n \leftarrow S_o$ transitions and interference due to overlapping S-S transitions. While $T_n \leftarrow T_1$ transitions are spin allowed, the possibility of detecting them will depend to a great extent on the degree to which the metastable triplet state, T_1, can be populated. The radiative and radiationless processes which contribute to the population and deactivation of the T_1 state are shown in figure (1). The definition of the terms fluorescence, phosphorescence, internal conversion, and intersystem crossing can be found in any standard text dealing with molecular luminescence such as reference (35). In addition, it should be noted that in a frozen glass or other rigid media the radiative and radiationless processes, $T_1 \rightarrow S_o$, are usually intramolecular in nature. In the liquid phase or gas phase, on the other hand, there are radiationless intermolecular processes which are usually the rate determining processes for deactivation of the T_1 state.

As mentioned previously, in the steady-state technique for observing T-T absorption a stable triplet state population is achieved by a continuous illumination of the sample, whereas in the flash technique a relatively large instantaneous triplet state population is achieved by means of a high intensity flash source. The large difference in the triplet state population, which is achieved by the two methods, will impose different restrictions on the systems which can

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.

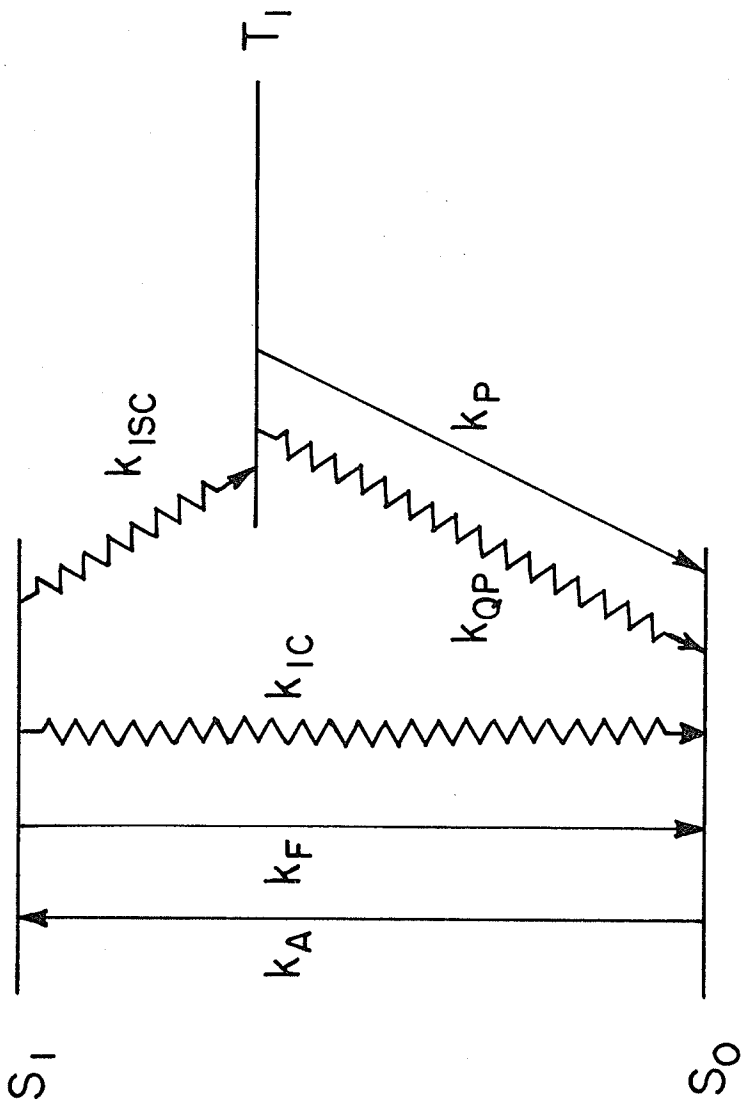
k_F = the rate constant of fluorescence (sec^{-1}).

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 $T_1 \rightarrow S_o$ (sec^{-1}).


T_1
k_{ISC}
k_P
k_{QP}
k_{IC}
k_F
k_A
S_1
S_0

be studied by each method. In the following discussion a brief account of the factors affecting the observation of T-T absorption by the two techniques will be presented.

(a) Steady-State Technique

The factors which influence the observation of T-T absorption using a continuous illumination excitation source for the population of the T_1 state have been noted by several authors. Craig and Ross (14) noted that the steady-state triplet concentration must be sufficiently high to give measureable $T_n \leftarrow T_1$ absorption, and that there must be an absence of strong $S_n \leftarrow S_o$ bands in the $T_n \leftarrow T_1$ region of interest. In a more detailed presentation of T-T absorption criteria Henry and Kasha (36) noted important characteristics of the $S_n \leftarrow S_o$ primary excitation band, and they discussed several properties of the triplet state which will affect the steady-state triplet population.

The $S_n \leftarrow S_o$ primary excitation band should possess certain characteristics in order to facilitate the observation of T-T absorption. In order to produce as large a steady-state triplet population as possible it is necessary that the $S_n \leftarrow S_o$ excitation band have a high extinction coefficient at an energy that is accessible with the excitation source being used. In addition, there is the requirement that there be an absence of strong $S_n \leftarrow S_o$ bands in the $T_n \leftarrow T_1$ region being investigated. This is especially important for the use of the steady-state technique since the low triplet state population that is achieved with continuous illumination excitation sources will mean a much higher concentration of molecules in the ground singlet

state. The $S_n \leftarrow S_o$ absorption band would then mask the $T_n \leftarrow T_1$ absorption band of interest if it occurred in the same spectral region. For T-T absorption studies using the flash excitation technique this requirement may not be important due to a large depopulation of the ground state.

The photochemical decomposition of the sample has been mentioned as a factor in T-T absorption studies (36). Since the steady-state method, using conventional excitation sources, is always carried out in rigid media, decomposition may occur by biphotonic processes in which one quanta of radiation is absorbed to reach the T_1 state, and another quanta to reach a highly excited state in which ionization may occur. The photoproducts which are formed in this way will not only cause a decrease in the steady-state triplet population, but can also produce interference in the T-T absorption spectrum.

Several characteristics of the T_1 state will affect the magnitude of the steady-state triplet population which can be achieved by a continuous illumination source. These include the radiative triplet state lifetime τ_p^o, the observed triplet state lifetime τ_p, and the ratio of the rate constants for intersystem crossing and fluorescence k_{ISC}/k_F. The effect on these properties of using rigid solution, deuteration of the molecule, and spin-orbital perturbations has been noted (36), and a brief account of these effects is presented in the following discussion.

In order to build up a sufficient concentration of triplet state molecules to give a measurable absorption it is necessary that

the observed triplet state lifetime τ_p be greater than about 0.1 sec. By making use of rigid solutions the deactivation of the T_1 state by intermolecular processes may be minimized. The rate of deactivation of the triplet state will then depend solely on intramolecular radiationless and radiative processes as shown in equation (1):

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

where k_p and k_{QP} are the rate constants for phosphorescence and intersystem crossing, respectively. The observed triplet state lifetime τ_p will then be given by equation (2):

$$\tau_p = \frac{1}{k_p + k_{QP}} \qquad (2)$$

Since the radiative triplet state lifetime τ_p^o is given by equation (3):

$$\tau_p^o = \frac{1}{k_p} \qquad (3)$$

the observation of T-T absorption bands may be further facilitated if τ_p can be made to approach τ_p^o by reducing k_{QP}, the rate constant for the intramolecular radiationless process $T_1 \rightarrow S_o$.

The deuteration of the molecule being studied has been shown to increase the observed triplet state lifetime. Robinson and Frosch (37, 38) suggested that the effect of deuteration was to decrease the Franck-Condon factor of the radiationless transition. An expression for the Franck-Condon factor, F, is given in equation (4):

$$F = \sum_{P} P\left[\prod_{n=1}^{N} |\langle \chi_n^o(v_n) | \chi_n(0) \rangle|^2\right] \qquad (4)$$

where χ_n and χ_n^o are vibrational wavefunctions of normal mode n in the initial and final states, respectively (39). Since the Robinson-Frosch theory predicts that $k_{QP} \propto F$, a decrease in the Franck-Condon factor will decrease the rate constant for the radiationless decay $T_1 \rightarrow S_o$. The work of Siebrand (39) on the relative magnitude of Franck-Condon factors in molecules differing only in isotopic substitution has substantiated the suggestion of Robinson and Frosch as to the cause of the decrease in k_{QP} upon deuteration of a particular molecule.

An increase in the strength of the spin-orbital perturbation by introducing a heavy atom substituent on the molecule, or by using a heavy atom solvent, may increase the ratio of the rate constant for intersystem crossing to that for fluorescence, k_{ISC}/k_F. The increase in the spin-orbital perturbation arises because of the dependence of the spin-orbit coupling hamiltonian H_{SO} on atomic number Z, as shown in equation (5):

$$H_{SO} = \frac{e^2}{2m^2c^2} \sum_{K=1}^{N} \sum_{i=1}^{n} \frac{Z_K(\text{eff})}{r_{iK}^3} \vec{l}_i \cdot \vec{s}_i \qquad (5)$$

where $\vec{l}_i$ and $\vec{s}_i$ are the one-electron orbital angular momentum and spin angular momentum operators, respectively, and $Z_K(\text{eff})$ is an effective electrical field of nucleus K at electron i (35). The radiative and radiationless transition probabilities, k_P and k_{QP}, are also enhanced

by an increase in the spin-orbital perturbation. It is therefore difficult to predict the overall effect of a change in the spin-orbital perturbation on the steady-state triplet population. However, there are indications that under most conditions in rigid media it will serve to decrease the T_1 population (36).

(b) Synchronized Flash Technique

Several of the factors mentioned in connection with the observation of T-T absorption using the steady-state technique are also important in the use of the synchronized flash technique. These include the observed triplet state lifetime τ_p, the ratio of the rate constant for intersystem crossing to that for fluorescence, k_{ISC}/k_F, and the problem of the photochemical decay of the sample. The extinction coefficient of the $S_n \leftarrow S_o$ primary excitation band is not as important in the use of the flash technique because of the high intensity of the flash.

The photochemical decomposition of the sample is a greater problem when a flash excitation source, rather than a continuous illumination excitation source, is used to populate the triplet state. This is partly because the exposure of the sample to a very high intensity of light in a short period of time is an ideal situation for the occurence of photochemical decomposition via biphotonic reactions. In addition, it is more difficult to filter the intense light from a flash source, resulting in a higher probability that other photochemical reactions will occur.

The largest application of the flash technique in the obser-

vation of T-T absorption bands has been on systems in the liquid or gas phase (17-20, 26-31). In the liquid or gas phase the deactivation of the triplet state will be governed by several intermolecular processes in addition to the intramolecular processes given in equation (1). The generalized expression for the rate of triplet state decay in solution is given by equation (6):

$$-\frac{d[T]}{dt} = k_P[T] + k_{QP}[T] + k_{TT}[T]^2 + k_{TS_o}[T][S_o] + \sum_i k_{QM_i}[M_i][T] \qquad (6)$$

where the third and fourth terms on the right side of equation (6) are self-quenching terms, and the fifth term represents quenching by impurity molecules M_i (8). Normally in fluid solutions the radiationless processes, given by terms 2-5 in equation (6), will govern the rate of decay of the T_1 state and phosphorescence will not be observable. The presence of unsuspected quenching species was responsible for the fact that the earlier studies on the rate of triplet decay in fluid solutions indicated that the intramolecular radiationless process $T_1 \rightarrow S_o$ was dependent on the viscosity of the solvent (7, 18, 20). The apparent viscosity dependence of k_{QP} arose because experiments designed to measure the first-order rate constant given by $k_P + k_{QP}$ were actually measuring a pseudo first-order rate constant k' given by equation (7):

$$k' = k_P + k_{QP} + \sum_i k_{QM_i}[M_i] \qquad (7)$$

where the third term on the right of equation (7) arises from unsuspected quenching species M_i (8). Dissolved oxygen is thought to be primarily responsible for the bimolecular quenching of the triplet state in fluid solution (35). Consequently, if the rate of decay of the triplet state is a factor in the observation of T-T absorption, the rate constant k' in equation (7) may be made to approach the intrinsic first-order rate $k_P + k_{QP}$ by reducing the dissolved oxygen content of the solution. Methods of deoxygenating solutions have been given by Parker (42) and by Linschitz, Steel, and Bell (8).

The effect of a change in the strength of spin-orbital perturbations on the observation of T-T absorption will depend to a large extent on the processes which deactivate the triplet state. In rigid solution the deactivation of the T_1 state will be dependent only on the first two terms on the right side of equation (6). An increase in the spin-orbit perturbation will serve to increase both k_P and k_{QP}, as well as the ratio of the rate constant for intersystem crossing to that for fluorescence. The overall effect will therefore be difficult to predict, as was the case for steady-state studies in rigid media. In fluid solutions, however, the deactivation of the triplet state will probably be rate determined by the quenching term $\sum_i k_{QM_i}[M_i][T]$ in equation (6). Since the rate constants k_{QM_i} are generally independent of spin-orbit perturbations, an increase in the perturbation will only serve to increase the ratio k_{ISC}/k_F. The initial triplet state population following flash excitation will therefore be increased by increasing the spin-orbit perturbation in this particular case.

This effect has been experimentally verified by Wilkinson et al (9), who observed an increase in the quantum yield of triplet state formation with an increase in the external spin-orbital perturbation.

III. The Scope of the Present Work

The present work was undertaken in an attempt to provide a greater body of knowledge on the upper triplet states of heterocyclic molecules. In this regard the T-T spectrum, in the region 11,000 cm^{-1} to 27,000 cm^{-1}, was investigated for a number of heterocyclic molecules, and an attempt was made to correlate the results with known luminescence properties of the molecules.

The molecular systems studied in this work include a series of oxygen heterocyclics, several nitrogen heterocyclics, and a sulfur heterocyclic. The oxygen heterocyclics consist of a series of substituted coumarin derivatives for which an attempt is made to rationalize the effects of the various substituents on the observed T-T spectra of the molecules. In the case of the nitrogen heterocyclics a search was made for new $T_n \leftarrow T_1$ bands, and for phthalazine the effect on the T-T spectrum of two adjacent nitrogen atoms is disscussed. For the sulfur heterocyclic, dibenzothiophene, a search was made for $T_n \leftarrow T_1$ bands, and the results are compared with possible hydrocarbon model molecules in an attempt to assess the degree of conjugation of the heteroatom with the two neighboring aromatic rings.

EXPERIMENTAL METHODS

A steady-state cross illumination technique employing a Cary 14 spectrometer was used to obtain the T-T absorption spectra. The procedure was originally described by Henry and Kasha (15), and involved modifying the Cary 14 by cutting an opening in the sample compartment in order to permit cross excitation of the sample as shown in figure (2). The samples were prepared as 10^{-4} to 10^{-5} molar solutions in EPA (5:5:2 by volume mixture of ether, isopentane, and ethanol), and were cooled to a clear glass at $77^{o}K$ in a sample cell contained in a dewar made entirely of quartz (No. 203908 quartz cell dewar flask, H. S. Martin Co., Evanston, Ill.). The cross excitation of the sample was provided by a 1000-W BH_6 Hg arc filtered by a 1 cm. path of $NiSO_4 \cdot 6H_2O$(500 g./litre H_2O) and a Corning glass filter (Cs 7-54). In some instances the Corning glass filter was dispensed with in order to allow a higher intensity of light to reach the sample. The Cary IR tungsten source was used as the analyzing light for the spectral region studied which had a maximum range of from 3500 Å to 9000 Å. A 1 cm. water filter was placed in front of this source in order to eliminate cracking of the rigid glass solution due to heating.

The absorption spectrum of the sample was first scanned in the desired spectral region with the analyzing light alone (designated curve I). The spectrum was then rescanned during simultaneous cross excitation (designated curve II). Finally, the excitation source was shut off and the spectrum was again rescanned with the analyzing light alone (designated curve III). By comparison of curves I and

FIGURE 2

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

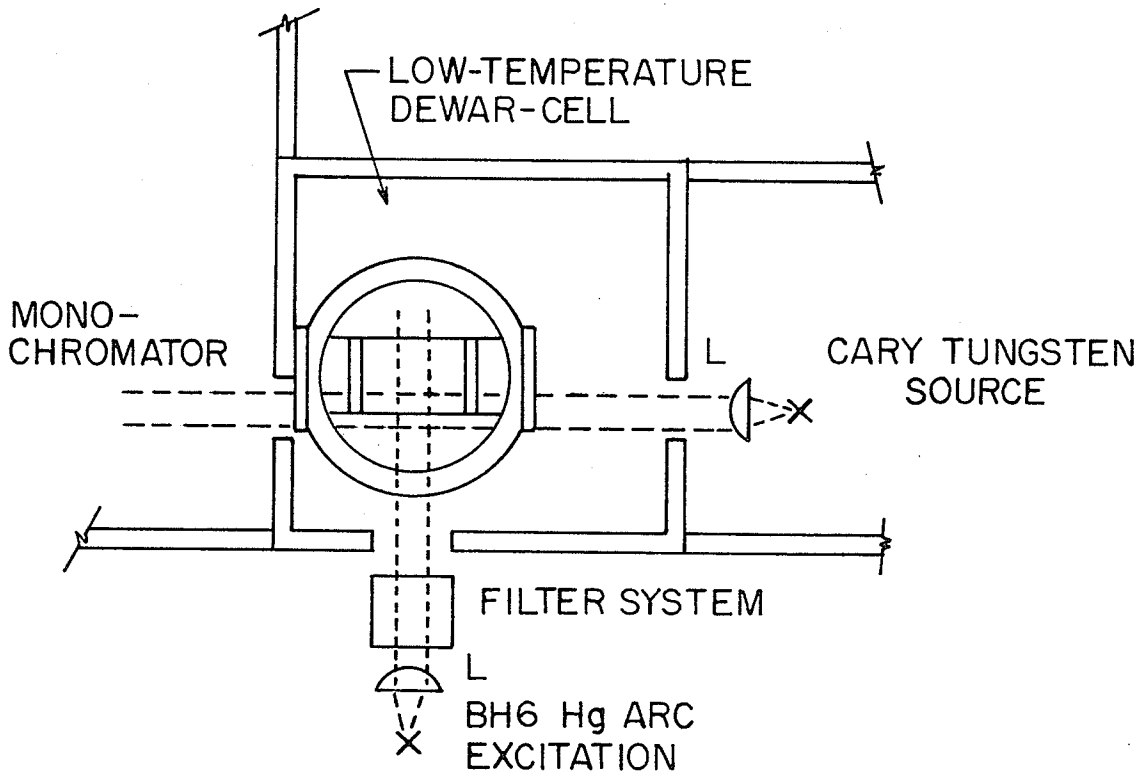
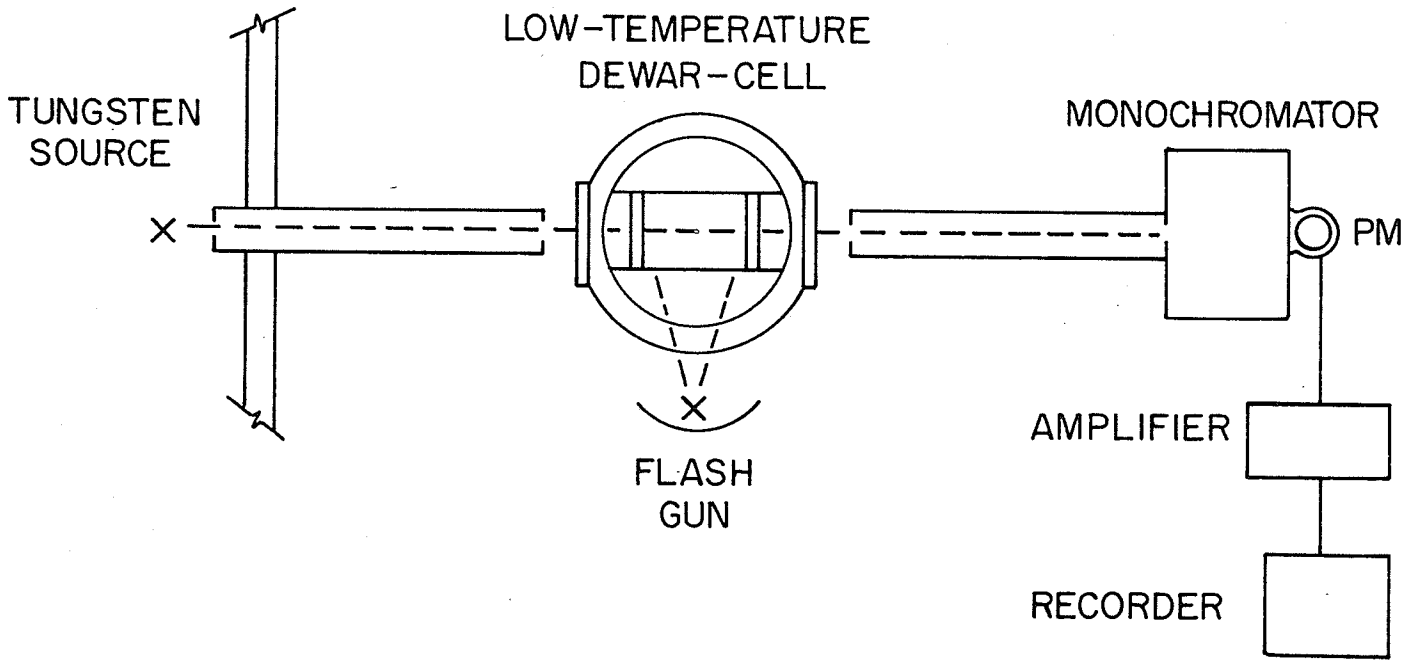

LOW-TEMPERATURE
DEWAR-CELL
MONO-
CHROMATOR
L
CARY TUNGSTEN
SOURCE
FILTER SYSTEM
L
BH6 Hg ARC
EXCITATION

FIGURE 3

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


LOW-TEMPERATURE
DEWAR-CELL
TUNGSTEN
SOURCE
MONOCHROMATOR
PM
AMPLIFIER
FLASH
GUN
RECORDER

II it is possible to determine the spectral interference from any relatively long lived photoproducts. If spectral interference from photoproducts was present, the subtraction of III from II gave the T-T absorption spectrum.

The triplet lifetimes were measured by monitoring the decay of T-T absorption following flash excitation. The experimental arrangement as shown in figure (3) was a modification of one which was originally described by Porter (41). The analyzing light source consisted of a lamp (General Electric CPR 18A, 6V) powered by a six volt storage battery. The collimated beam from the light source was passed through the sample, which had been prepared as described previously, and then entered a 0.25 m. Jarrell-Ash grating monochromator set at the T-T absorption maximum of the sample. The transmitted beam was detected by a phototube (Hamamatsu R106), and the amplified signal was monitored on a recorder (American Instrument Co. X-Y recorder). The flash excitation of the sample was provided by an electronic flash gun (Honeywell Model 65C) with the polystyrene filter removed.

The triplet state decay was recorded as the intensity of the light transmitted by the sample versus time. The relative concentrations of triplet molecules will then be given by log (X_o/X_t) where X_o is the transmittance prior to flash excitation and X_t is the transmittance at time t after excitation. Since the decay should be first-order, a plot of ln log (X_o/X_t) vs. t was fitted to a straight line using a least mean squares analysis. The negative reciprocal of the slope of the line yielded the lifetime. From five to ten measurements

were made on each sample with no significant variation in lifetime being found as the number of exposures of the sample to the flash was increased. All the lifetimes obtained for a particular sample were averaged and the standard deviation was determined. A measure of the fit of the data to a first-order decay is given by the correlation coefficient r:

$$r = \frac{\sum_{i=1}^{n} (X_i-\bar{X})(Y_i-\bar{Y})}{\left[\sum_{i=1}^{n} (X_i-\bar{X})^2 \sum_{i=1}^{n} (Y_i-\bar{Y})^2\right]^{\frac{1}{2}}} \qquad (8)$$

where the X_i correspond to values of t and the Y_i to values of the function ln log (X_o/X_t). A perfect correlation will be indicated if r = -1 and no correlation if r = 0. The average value of r for each of the molecules studied is included in Tables I and II.

In the measurement of the T-T absorption spectra and the triplet state lifetimes it was often found advantageous to off-centre the dewar in the analyzing light beam as shown in figure (2). By off-centering the dewar the number of triplet molecules in the path of the analyzing beam could be increased because of the existence of a concentration gradient of excited molecules across the absorption cell. In this way the intensity of weak T-T bands could be increased to the point where they were observable in the spectrum.

The specially prepared, high purity EPA was obtained from the American Instrument Co. The molecules studied were obtained as relatively high purity chemicals from the following sources: Aldrich Chemical Co. (3-methylcoumarin, 7-hydroxy 4, 8-dimethylcoumarin); K & K

Laboratories (phthalazine, dibenzothiophene, 7-hydroxycoumarin, 5, 6-benzoquinoline, 7, 8-benzoquinoline); Eastman Kodak Co. (7-hydroxy-4-methylcoumarin). The purity of the compounds being studied was not expected to be a problem because of the low steady-state concentration of triplet state molecules which is achieved with the excitation source used in this study. The T-T nature of the observed absorption peaks was also checked by a comparison of the lifetime of decay of the peak with phosphorescence lifetime data available in the literature.

RESULTS

In the present study T-T absorption was observed in four coumarin derivatives and in four other heterocyclic molecules. In the four coumarin derivatives and dibenzothiophene no observation of T-T absorption has been previously reported, although T-T absorption has been observed in coumarin, 4-hydroxycoumarin, and dicumarol in a previous study (44). When the present study had been completed, it was reported in the literature that a T-T band had been found in phthalazine that was similar to the band observed in this study (42). In the case of 5, 6-benzoquinoline and 7, 8-benzoquinoline T-T absorption maxima have been previously reported (14, 43). However, no T-T spectra for these molecules were found in the literature. The technique used in this study also allowed an intensive investigation to be made in the low energy region (15,000 cm^{-1} to 11,000 cm^{-1}) for weak T-T transitions. As a result an additional T-T transition has been found for 5, 6-benzoquinoline which was previously unreported. The triplet state lifetimes, obtained from the decay of T-T absorption peaks, provide an independent means of checking on the values obtained from phosphorescence studies. In several cases no triplet state lifetime data have been previously reported in the literature and the values obtained from this study represent new information on the triplet states of these molecules.

The observed T-T absorption spectra are presented in figures (4-11). In addition, the spectra for the three previously investigated coumarin derivatives are presented in figures (12-14) for purposes of

comparison. The ordinates represent arbitrary intensity units and are not comparable from spectrum to spectrum. The peak ratios within a given spectrum cannot be quantitatively compared from molecule to molecule because varying amounts of stray light may enter the detector, depending on the extent to which the dewar containing the sample was offset with respect to the analyzing light beam. However, the peak ratios are expected to be roughly comparable from molecule to molecule since most of the light from the analyzing beam which does not pass through the absorption cell will be scattered by the walls of the dewar, and will therefore not enter the detector.

The position of the observed maxima, the vibrational spacing, and the T-T lifetime data are summarized in Table II for the coumarin derivatives and Table I for the other heterocyclic molecules for which T-T absorption was observed. The quoted errors in the T-T lifetime data of Tables I and II represent a range obtained in five to ten measurements on the same sample. The lifetimes measured from the decay of the T-T spectra were all determined in EPA. The solvents used in the phosphorescence studies are given in the footnotes to Tables I and II. The general agreement between the observed T-T lifetimes and the phosphorescence lifetimes found in the literature confirms the T-T nature of the absorption bands.

As mentioned previously, the technique used in this study allowed the observation of spectral interference from relatively long lived photoproducts. For the 7-hydroxycoumarin derivative a fair amount of absorption due to a photoproduct was present from about

25,000 cm^{-1} to the high energy limit of the study. However, this did not interfere with the T-T spectrum which occured at a lower energy. The benzoquinoline derivatives showed only a relatively small amount of photodecomposition from about 24,000 cm^{-1} to 27,000 cm^{-1}. In the case of phthalazine there was a relatively large amount of photodecomposition in the region 25,500 cm^{-1} to 28,000 cm^{-1}. In order to indicate that the T-T spectrum is less accurate in this region the high energy portion of the spectrum in figure (4) is drawn with a dashed line. A similar indication is made in figure (7) for dibenzothiophene in the region 26,500 cm^{-1} to 28,000 cm^{-1} in which a relatively large amount of absorption due to photoproduct was detected.

FIGURE 4

T-T absorption spectrum of phthalazine in EPA rigid glass solution at $77^{o}K$ in the range 19,000 cm^{-1} to 28,000 cm^{-1}: (ordinate) arbitrary linear absorption units; (-----) region where the spectrum is known less accurately.

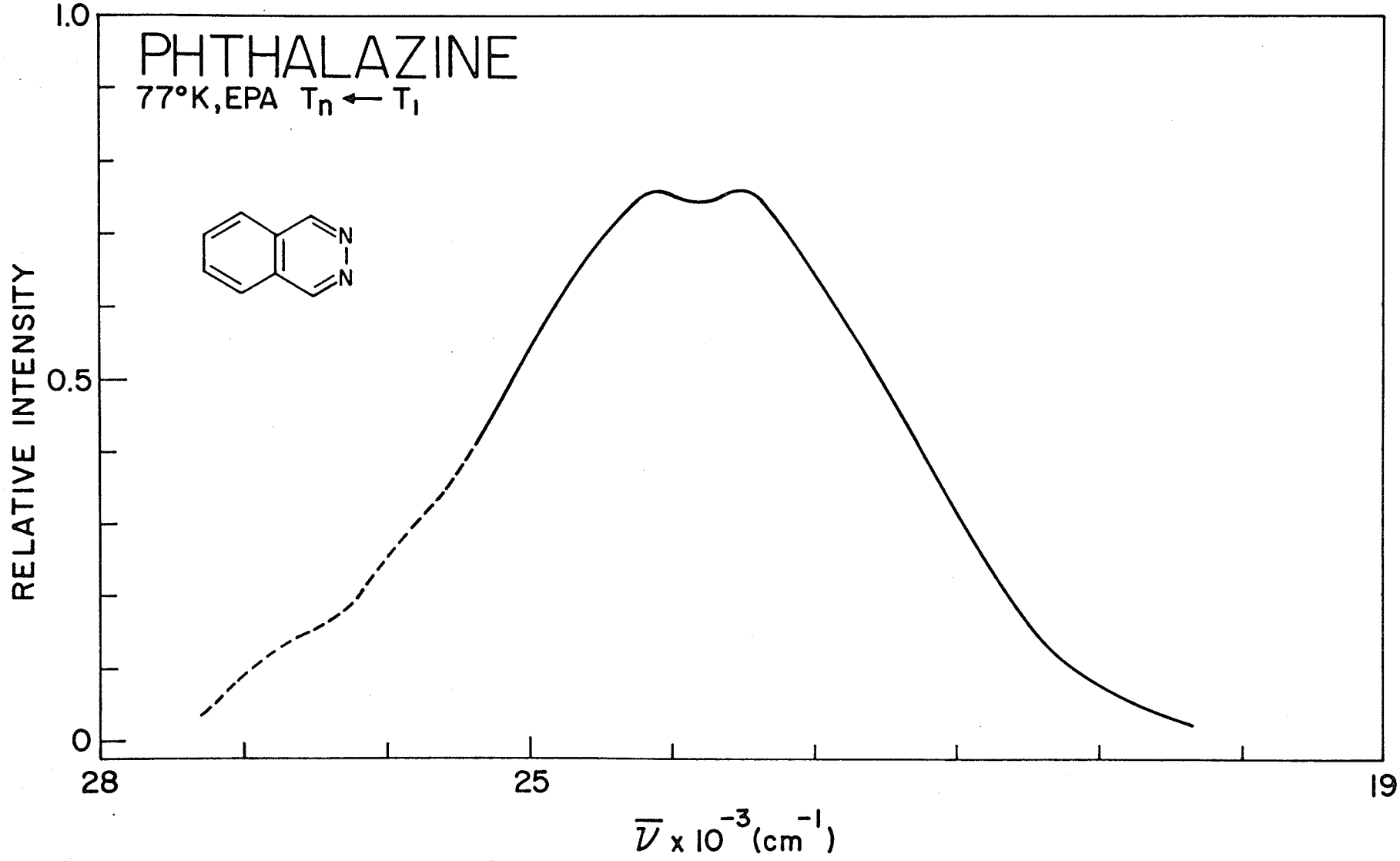

PHTHALAZINE
77°K, EPA $T_n \leftarrow T_1$
RELATIVE INTENSITY
1.0
0.5
0
28
25
19
$\overline{\nu} \times 10^{-3} (cm^{-1})$

FIGURE 5

T-T absorption spectrum of 5, 6-benzoquinoline in EPA rigid glass solution at 77^{o}K in the range 11,000 cm^{-1} to 25,000 cm^{-1}: (ordinate) arbitrary linear absorption units.

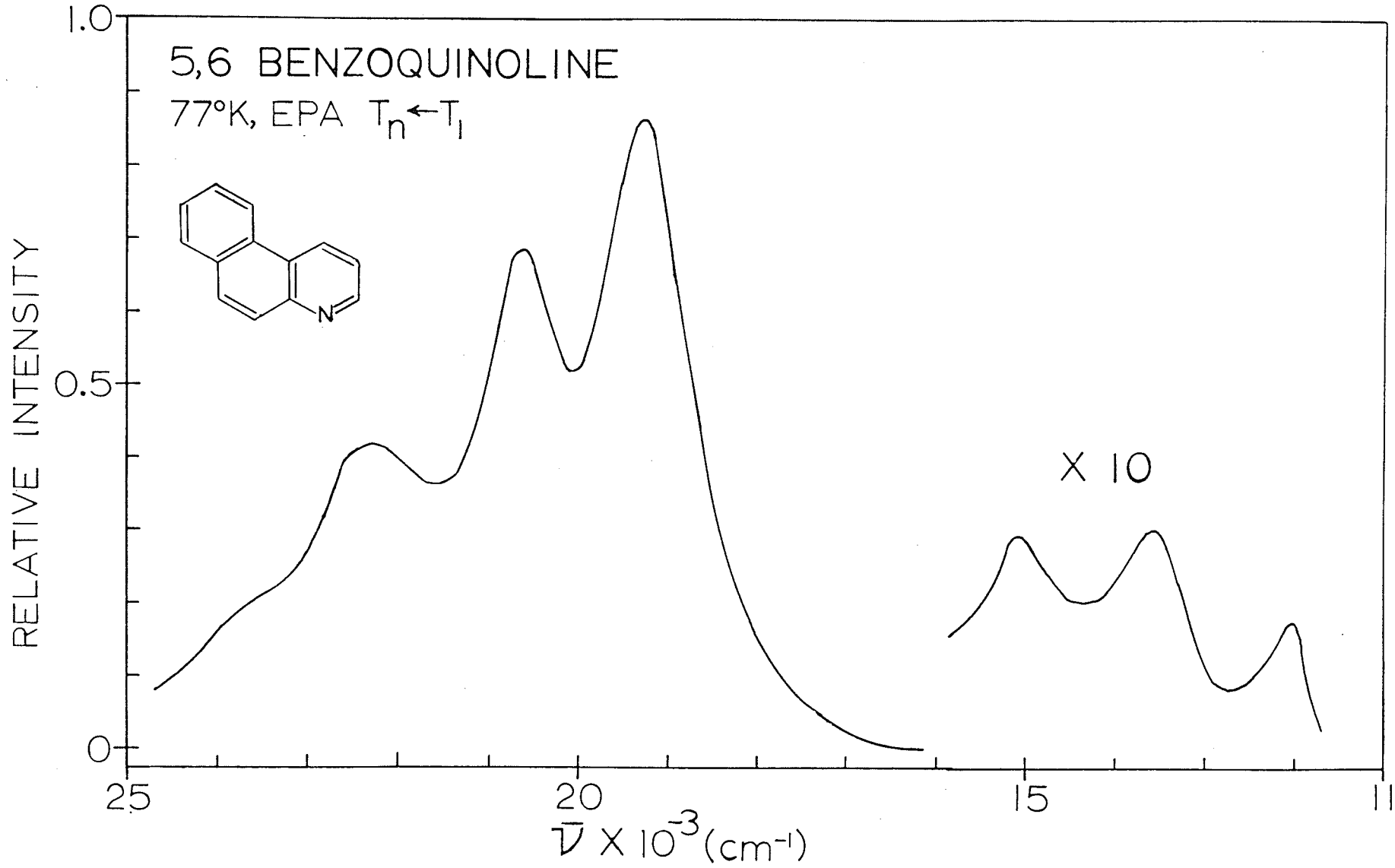

5,6 BENZOQUINOLINE
77°K, EPA $T_n \leftarrow T_1$
N
X 10
RELATIVE INTENSITY
1.0
0.5
0
25
20
15
11
$\bar{\nu} \times 10^{-3}$ (cm^{-1})

FIGURE 6

T-T absorption spectrum of 7, 8-benzoquinoline in EPA rigid glass solution at 77°K in the range 16,000 cm^{-1} to 25,000 cm^{-1}: (ordinate) arbitrary linear absorption units.

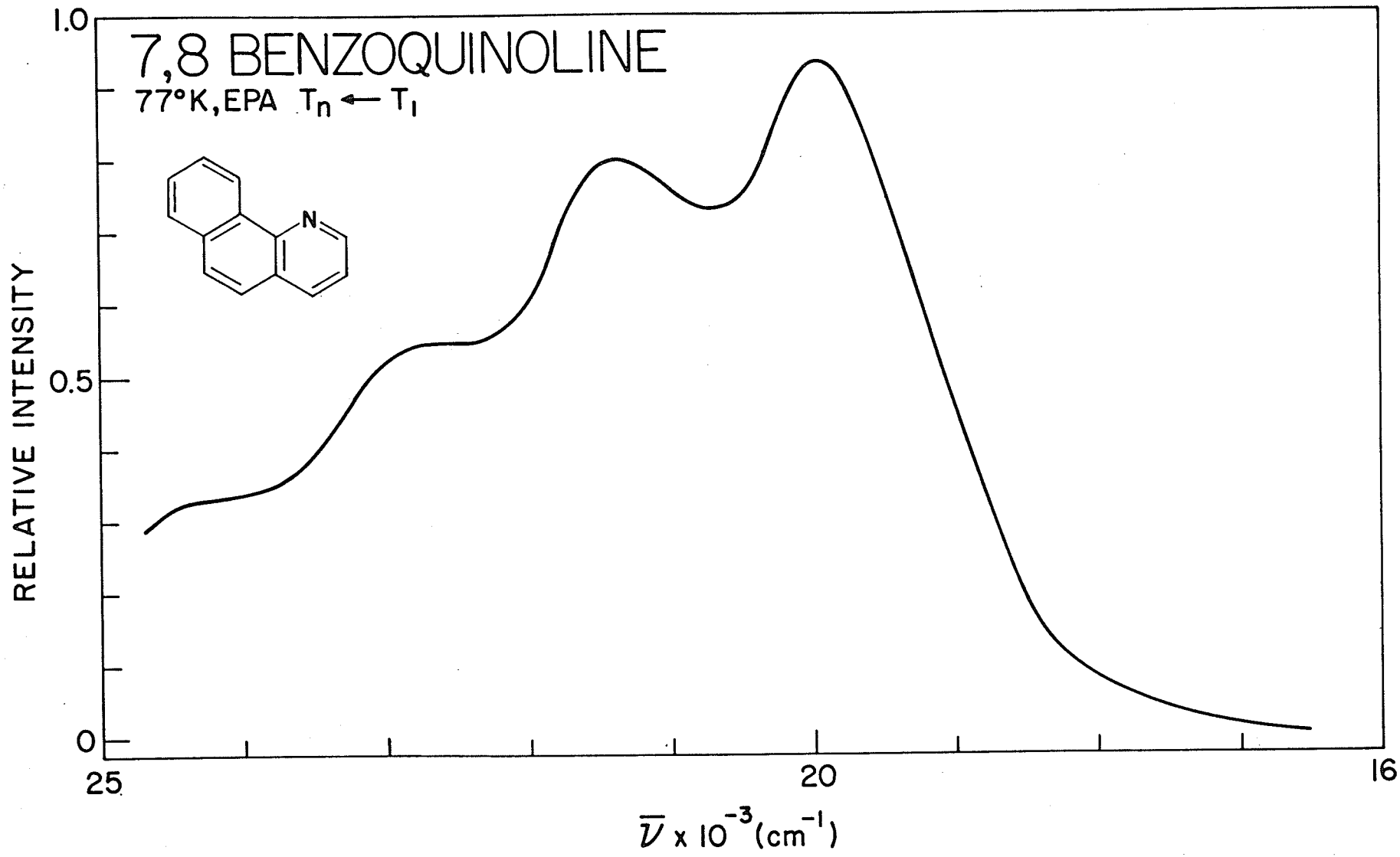

7,8 BENZOQUINOLINE
77°K, EPA $T_n \leftarrow T_1$
N
RELATIVE INTENSITY
1.0
0.5
0
25
20
16
$\overline{\nu} \times 10^{-3} (cm^{-1})$

FIGURE 7

T-T absorption spectrum of dibenzothiophene in EPA rigid glass solution at 77°K in the range 14,000 cm^{-1} to 29,000 cm^{-1}: (ordinate) arbitrary linear absorption units; (-----) region where the spectrum is known less accurately.

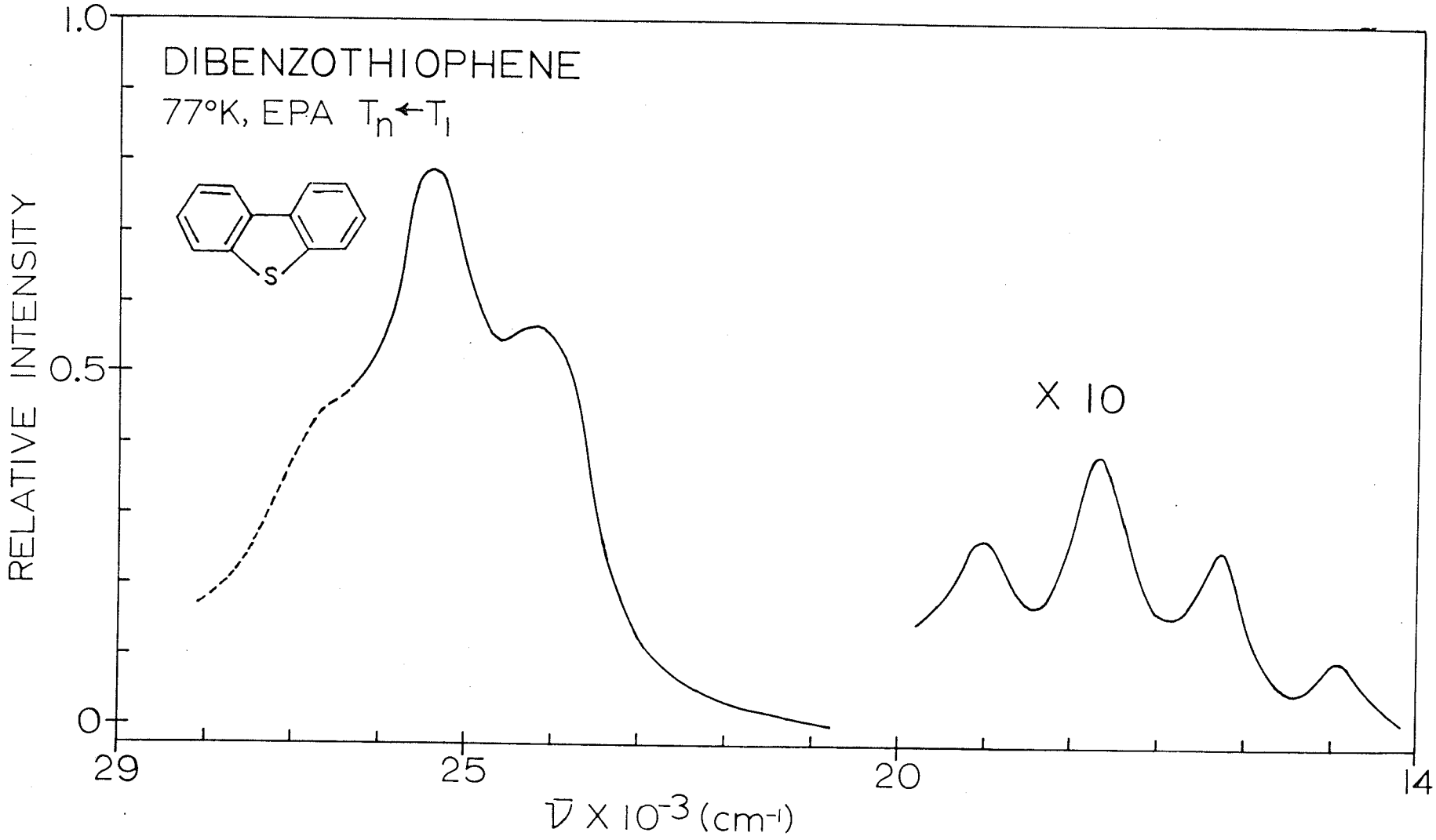

DIBENZOTHIOPHENE
77°K, EPA $T_n \leftarrow T_1$
S
X 10
RELATIVE INTENSITY
1.0
0.5
0
29
25
20
14
$\bar{\nu} \times 10^{-3}$ (cm^{-1})

FIGURE 8

T-T absorption spectrum of 3-methylcoumarin in EPA rigid glass solution at 77°K in the range 20,000 cm^{-1} to 29,000 cm^{-1}: (ordinate) arbitrary linear absorption units.

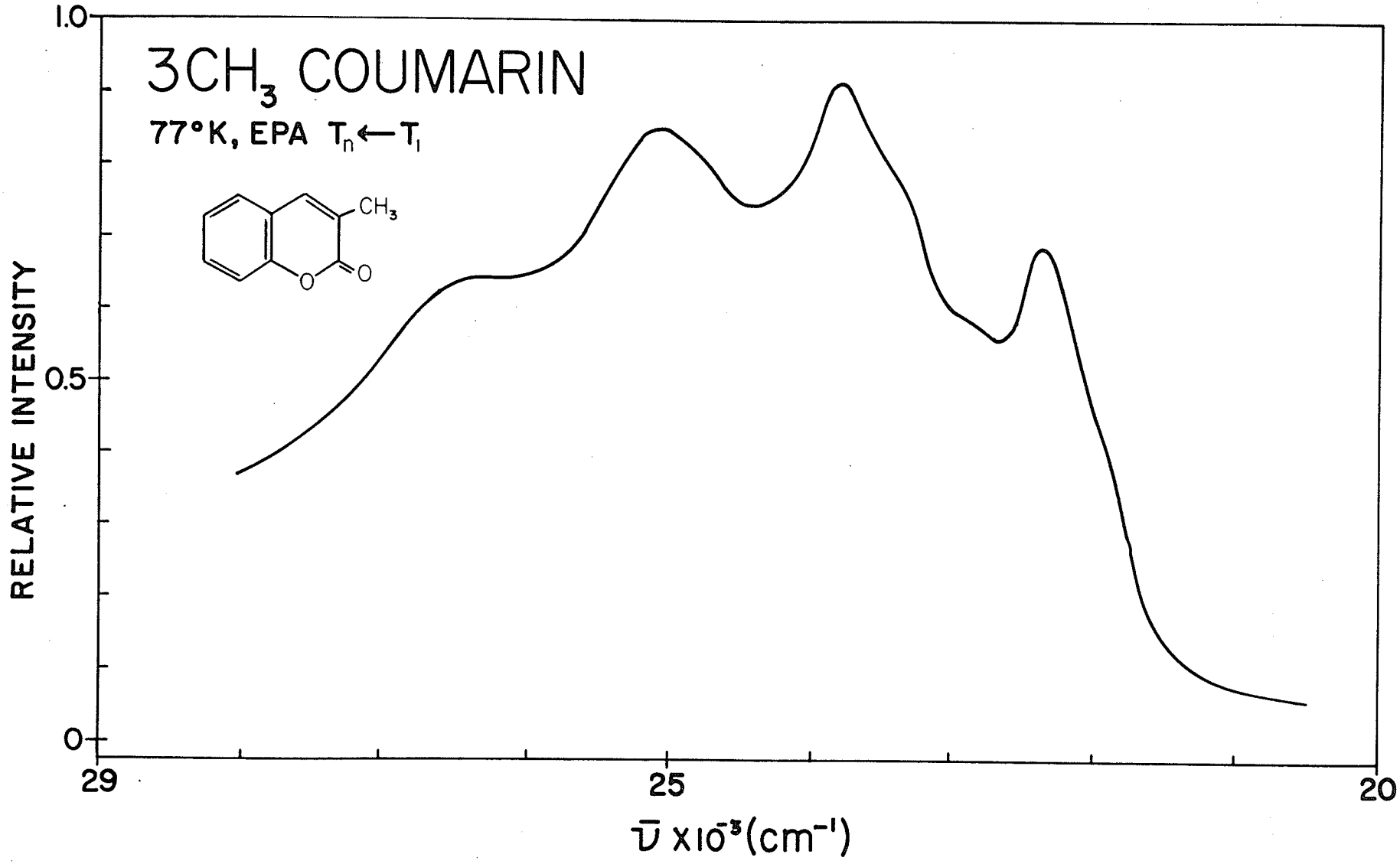
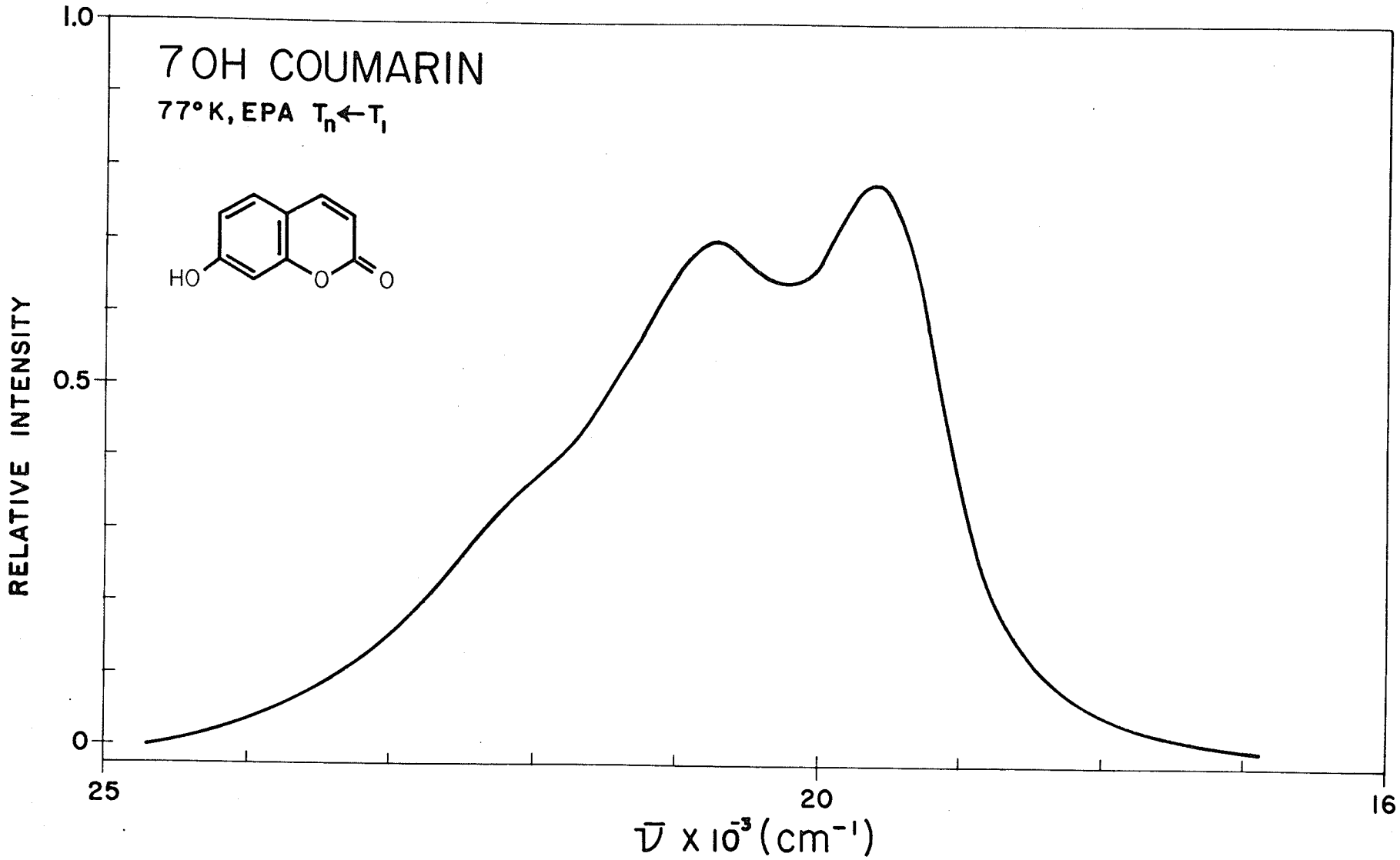

3CH3 COUMARIN
77°K, EPA Tn←T1
CH3
O
O
1.0
0.5
0
RELATIVE INTENSITY
29
25
20
ν̄ x10⁻³(cm⁻¹)

FIGURE 9

T-T absorption spectrum of 7-hydroxycoumarin in EPA rigid glass solution at 77°K in the range 16,000 cm^{-1} to 25,000 cm^{-1}: (ordinate) arbitrary linear absorption units.


7 OH COUMARIN
77° K, EPA $T_n \leftarrow T_1$
HO
O
O
1.0
0.5
0
RELATIVE INTENSITY
25
20
16
$\bar{\nu} \times 10^{-3}$ (cm^{-1})

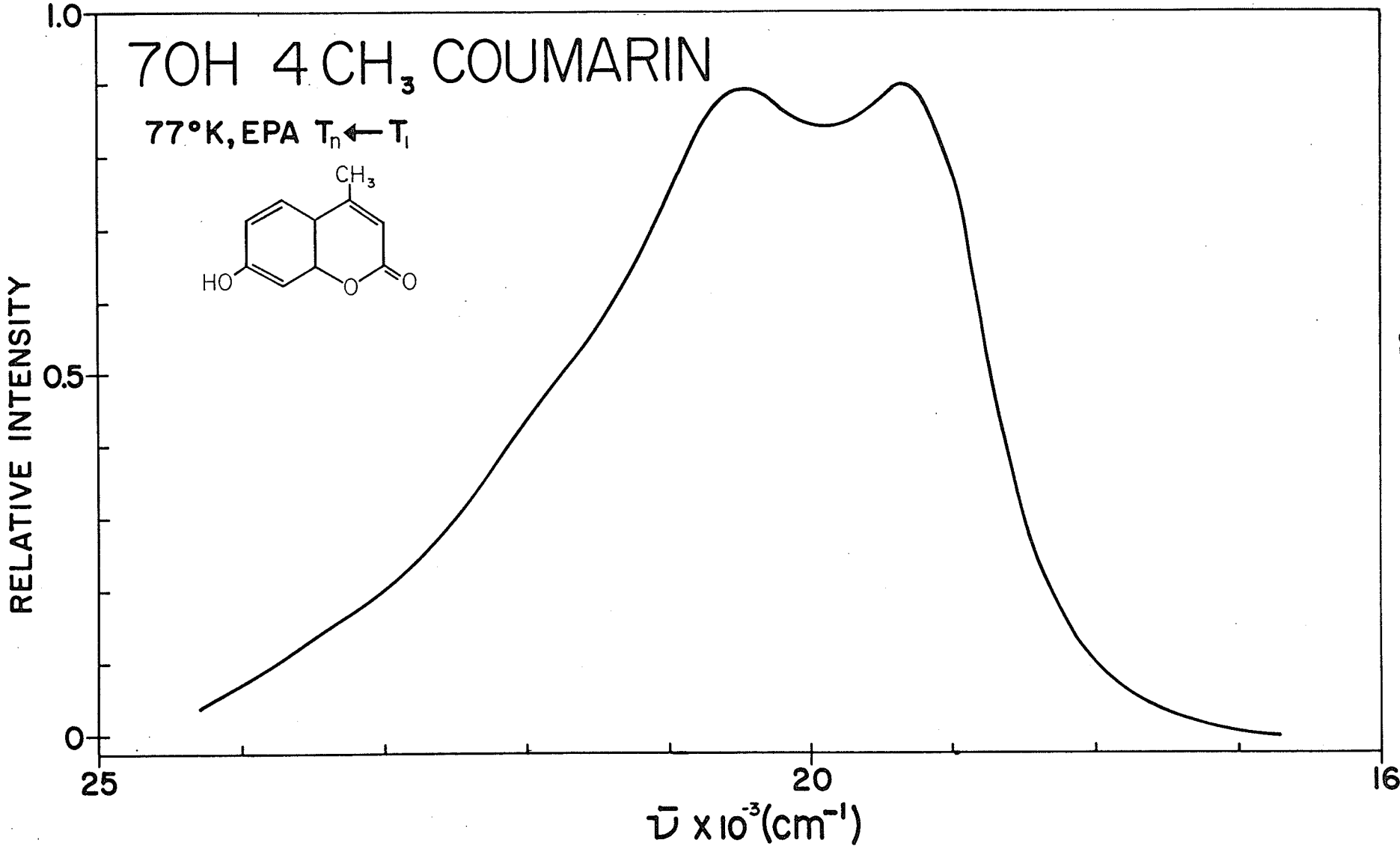

7OH 4 CH3 COUMARIN
77°K, EPA Tn ← T1
CH3
HO
O
O
1.0
0.5
0
RELATIVE INTENSITY
25
20
16
ν̄ x 10-3(cm-1)

FIGURE 11

T-T absorption spectrum of 7-hydroxy-4,8-dimethyl-coumarin in EPA rigid glass solution at 77°K in the range 16,000 cm^{-1} to 25,000 cm^{-1}: (ordinate) arbitrary linear absorption units.

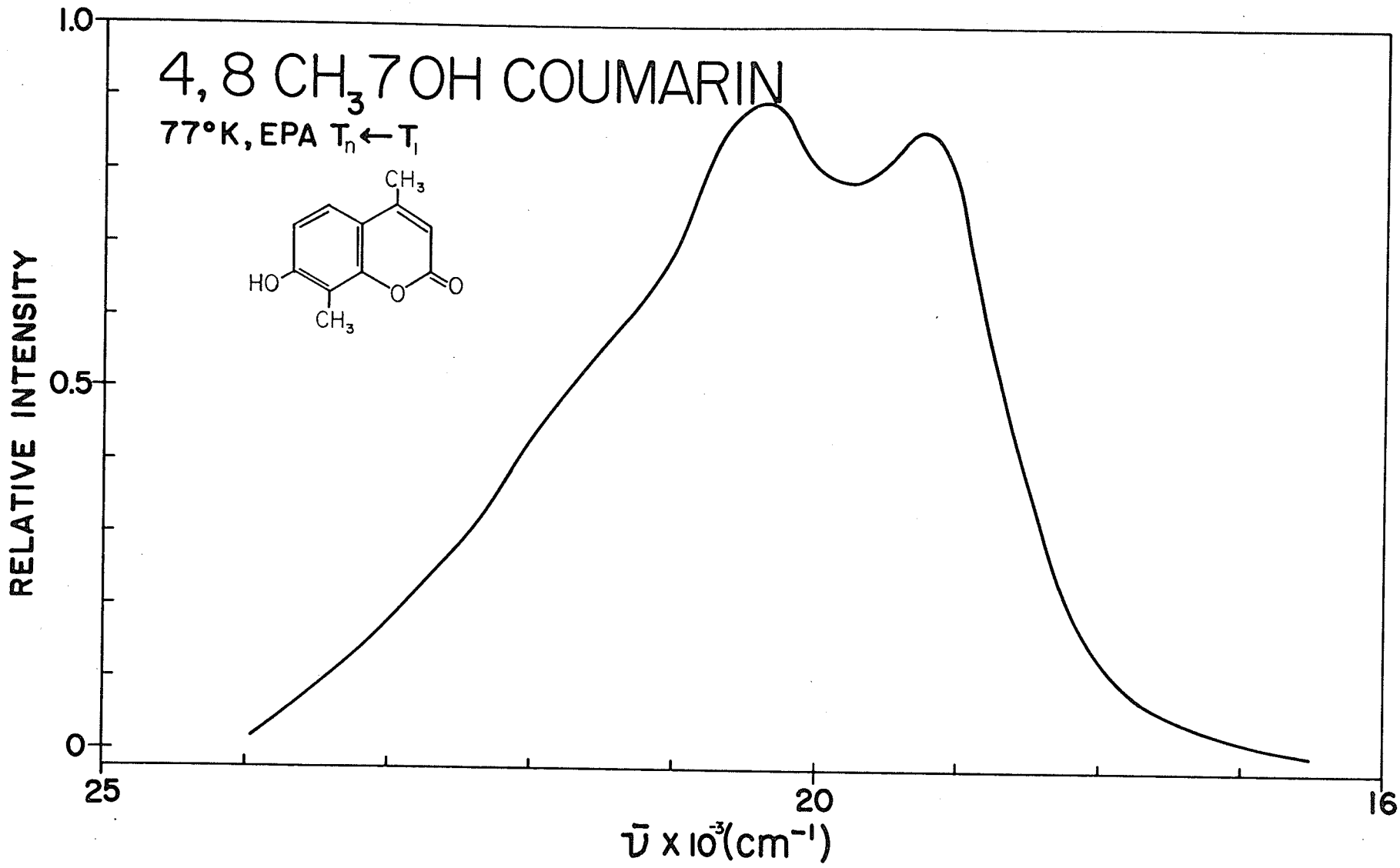

4, 8 CH3 7 OH COUMARIN
77°K, EPA Tn ← T1
CH3
HO
O
O
CH3
1.0
0.5
0
RELATIVE INTENSITY
25
20
16
ν̄ x 10⁻³(cm⁻¹)

FIGURE 12

T-T absorption spectrum of coumarin in EPA rigid glass solution at 77°K in the range 20,000 cm^{-1} to 27,000 cm^{-1}. (ordinate) arbitrary linear absorption units.

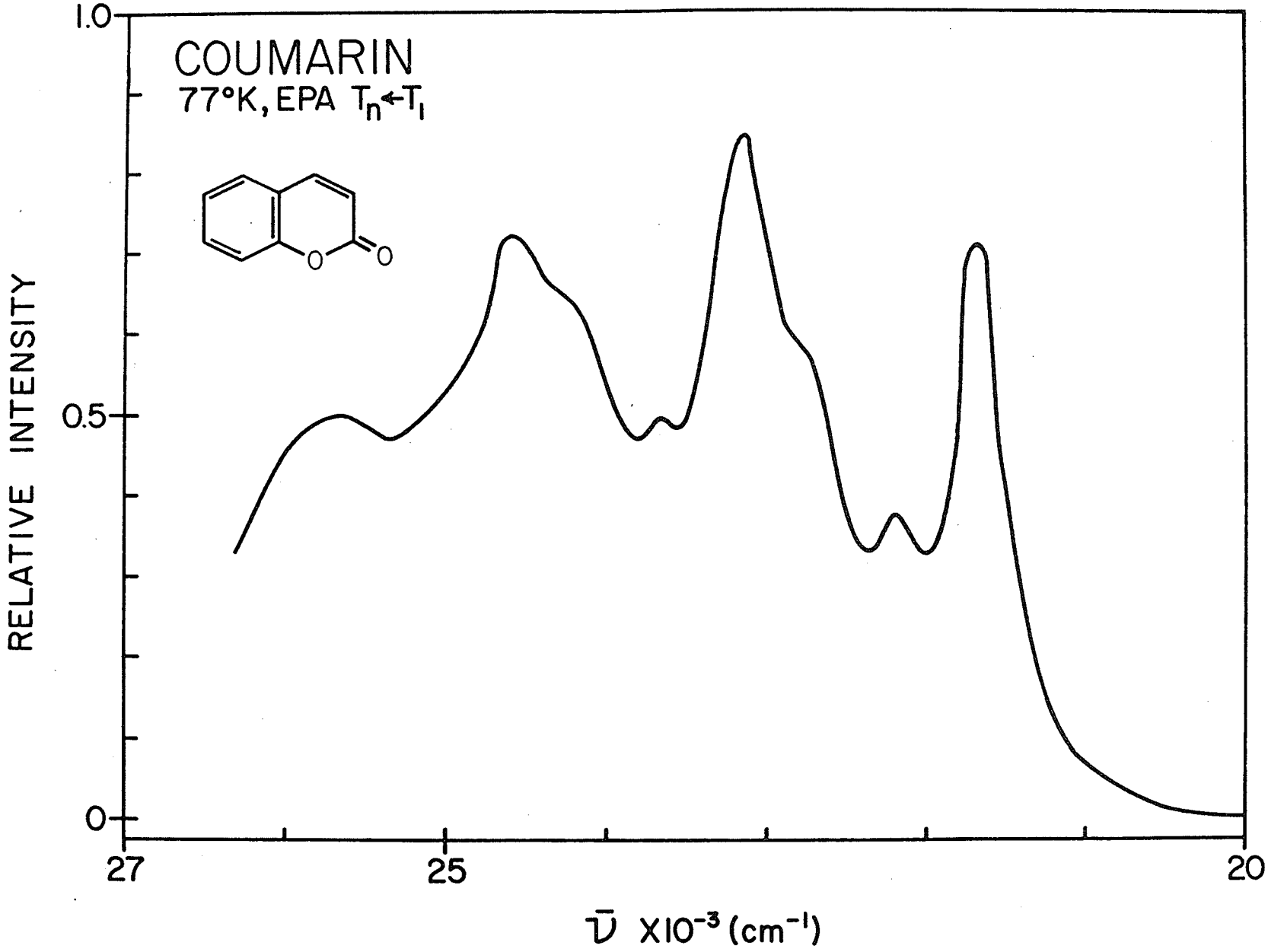

COUMARIN
77°K, EPA $T_n \leftarrow T_1$
RELATIVE INTENSITY
1.0
0.5
0
27
25
20
$\bar{\nu}$ X10^{-3} (cm^{-1})
O
O

FIGURE 13

T-T absorption spectrum of 4-hydroxycoumarin in EPA rigid glass solution at 77°K in the range 18,000 cm^{-1} to 27,000 cm^{-1}: (ordiate) arbitrary linear absorption units; (-----) region where the spectrum is known less accurately.

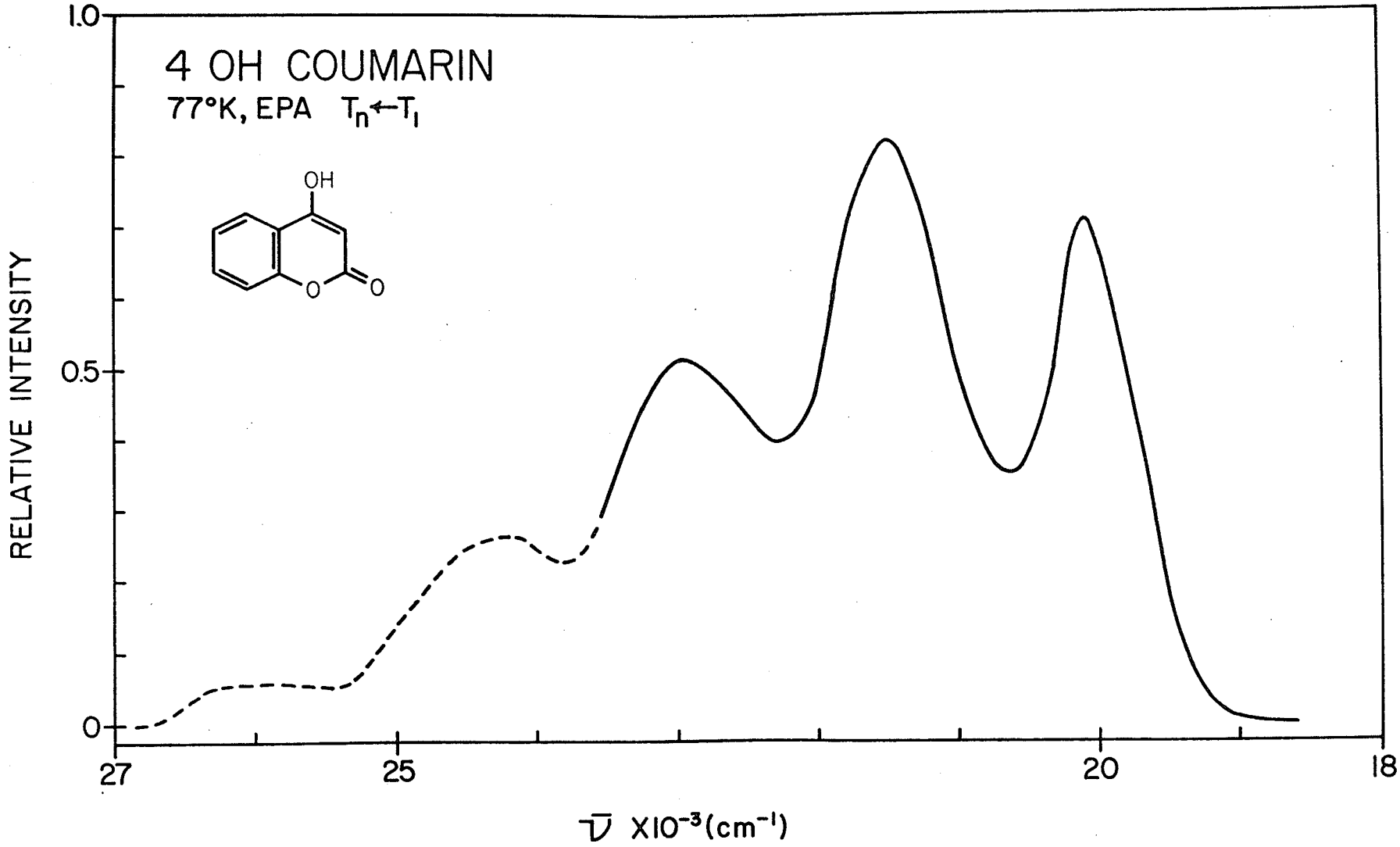

4 OH COUMARIN
77°K, EPA $T_n \leftarrow T_1$
OH
O
O
1.0
0.5
0
RELATIVE INTENSITY
27
25
20
18
$\bar{\nu}$ X10^{-3}(cm^{-1})

FIGURE 14

T-T absorption spectrum of dicumarol in EPA rigid glass solution at 77°K in the range 18,000 cm^{-1} to 27,000 cm^{-1}: (ordinate) arbitrary linear absorption units.

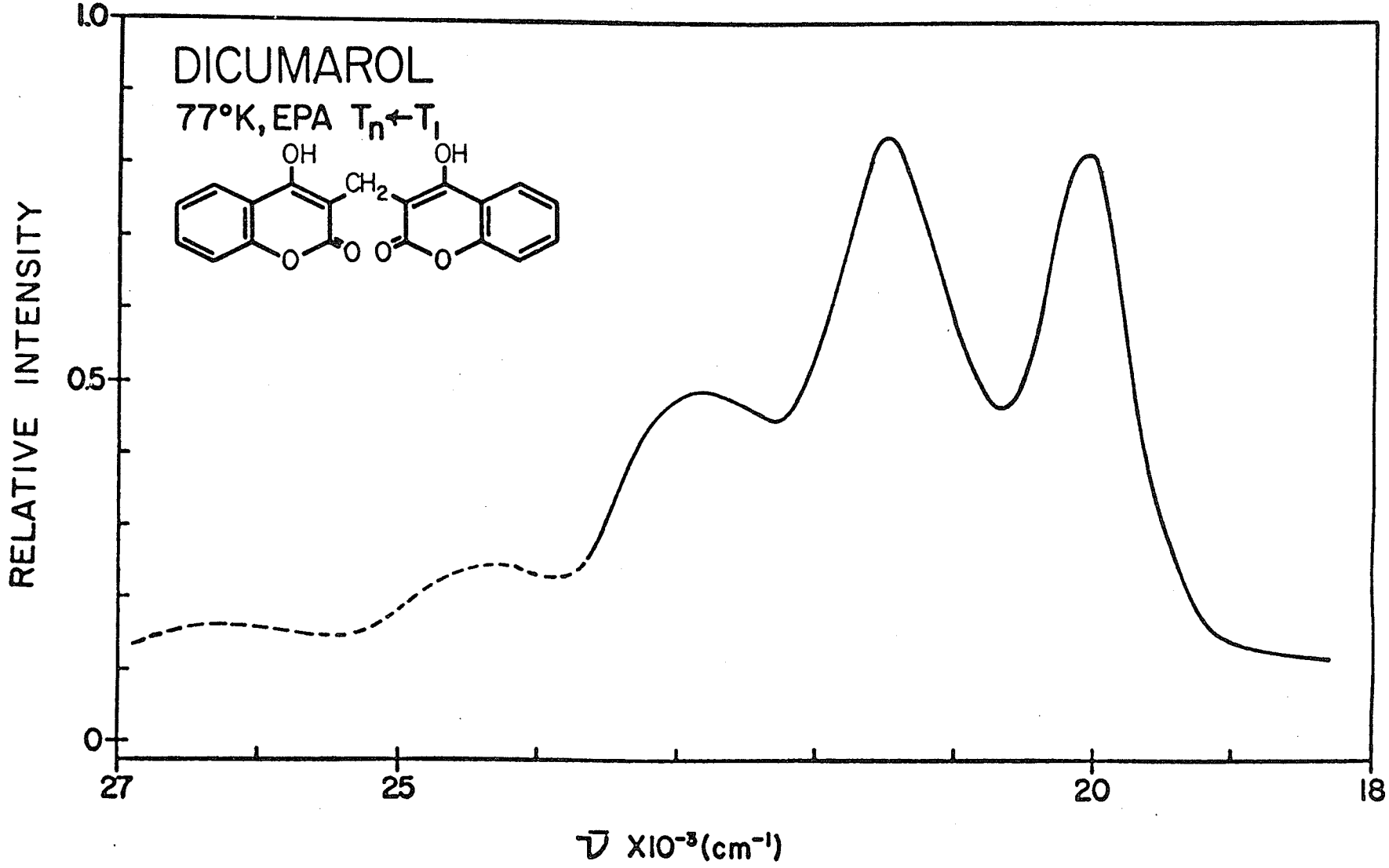

DICUMAROL
77°K, EPA $T_n \leftarrow T_1$
OH
OH
CH_2
O
O
O
O
1.0
0.5
0
RELATIVE INTENSITY
27
25
20
18
$\bar{\nu}$ X10^{-3}(cm^{-1})

TABLE I

TRIPLET-TRIPLET ABSORPTION MAXIMA
OF OTHER HETEROCYCLIC MOLECULES

Molecule	Observed Maxima (cm^{-1})	Spacing (cm^{-1})	Lifetime (sec)	Average r§	Phosphorescence Lifetime (sec)
Phthalazine	23 490 ± 100		0.35 ± 0.01	-0.9970	0.42 ± 0.04† (42)
	24 125 ± 100	635			
Dibenzothiophene	14 910 ± 100		1.45 ± 0.01	-0.9998	1.3‡ (54)
	16 270 ± 100	1 360			
	17 690 ± 100	1 420			
	19 040 ± 100	1 350			
	24 180 ± 75				
	25 400 ± 50	1 220			
5, 6-Benzoquinoline	12 040 ± 100		3.44 ± 0.02	-0.9999	3.1 (50)
	13 580 ± 100	1 540			
	15 060 ± 100	1 480			
	19 280 ± 50				
	20 620 ± 50	1 340			
7, 8-Benzoquinoline	19 940 ± 50		2.30 ± 0.02	-0.9999	2.2 (50)
	21 375 ± 50	1 435			

§ See text
† In a n-butyl alcohol-isopentane (7:3 by volume mixture) rigid glass at 77°K
‡ In a diethyl ether rigid glass at 77°K

TABLE II

TRIPLET-TRIPLET ABSORPTION MAXIMA
OF COUMARIN DERIVATIVES

Molecule	Observed Maxima (cm^{-1})	Spacing (cm^{-1})	Lifetime (sec)	Average r§	Phosphorescence Lifetime (sec)
Coumarin	21 700 ± 50		0.47 ± 0.01	-0.9994	0.54† (58)
	23 140 ± 50	1 440			
	24 600 ± 50	1 460			
3-CH_3-Coumarin	22 375 ± 50		0.38 ± 0.01	-0.9988	
	23 800 ± 50	1 425			
	25 075 ± 75	1 275			
4-OH-Coumarin	20 100 ± 50		1.4 ± 0.2		1.5† (58)
	21 500 ± 50	1 400			
	22 980 ± 75	1 480			
Dicumarol	20 020 ± 50		1.3 ± 0.2		1.3 ± 0.2‡ (63)
	21 520 ± 75	1 500			
	22 890 ± 75	1 370			
7-OH-Coumarin	19 600 ± 50		0.90 ± 0.01	-0.9994	1.1† (58)
	20 725 ± 75	1 125			0.6 (59, 60)
7-OH-4-CH_3-Coumarin	19 350 ± 50		1.51 ± 0.02	-0.9998	
	20 475 ± 75	1 125			
7-OH-4,8-CH_3-Coumarin	19 250 ± 50		1.70 ± 0.01	-0.9999	
	20 375 ± 75	1 125			

§ See text
† In an ethanol rigid glass at 77°K
‡ In an ethanol-dimethylformamide (3:1 by volume mixture) rigid glass at 77°K

DISCUSSION

I. Phthalazine

The T-T absorption spectrum which was obtained for phthalazine in EPA is shown in figure (4). The spectrum shows a fairly weak band with two poorly resolved maxima at about 23,490 cm^{-1} and 24,125 cm^{-1}. In comparison, the results of Alvarez and Hadley for phthalazine in an isopentane-n-butyl alcohol glass (7:3 by volume mixture) would indicate that the two lowest energy maxima of this T-T absorption band occur at 23,040 cm^{-1} and 23,780 cm^{-1} (42). In the latter case the phosphorescence lifetime was found to be 0.42 ± 0.04 sec., whereas the triplet state lifetime in EPA was found to be 0.35 ± 0.01 sec.

The lowest triplet state of phthalazine has been assigned as predominantly $\pi\pi^*$ on the basis of the zero-field splitting parameters (45) and the phosphorescence lifetime data (46). However, the T_1 state of phthalazine may acquire a significant amount of $n\pi^*$ character in the following way. In aza-aromatics containing two or more adjacent nitrogen atoms, the nonbonding orbitals can form molecular orbitals which are linear combinations of the individual nonbonding orbitals on the different nitrogen atoms. In the case of a diaza-aromatic the two nonbonding molecular orbitals are $n_+ = 1/\sqrt{2}(n_a + n_b)$ and $n_- = 1/\sqrt{2}(n_a - n_b)$ (35). For the particular case of phthalazine, the existence of two adjacent nitrogen atoms should give rise to a strong interaction between the nonbonding electron pairs. This will cause the lowest triplet state of $n\pi^*$ configuration, resulting from $^*\pi \leftarrow n_-$ excitation, to lie at a lower energy than would be expected for a mol-

ecule such as quinoxaline, wherein the two nitrogen atoms are much further apart. The decrease in energy of the lowest $^3(n\pi^*)$ state of phthalazine will result in a decrease in the energy gap with the lowest triplet state of $\pi\pi^*$ configuration, and will therefore facilitate the vibronic mixing of these states (45, 46). The energy dependence of the vibronic mixing of the T_1 state of phthalazine with higher triplet states, T_n, can be seen using first-order perturbation theory as shown in equation (9):

$$T_1' = T_1^o + \sum_{n \neq 1} \frac{\langle T_n^o | H_{vib} | T_1^o \rangle}{\Delta E_{1n}} \cdot T_n^o \qquad (9)$$

where the perturbing hamiltonian, H_{vib}, in equation (9) is the first-order term in the Herzberg-Teller expansion of the electronic hamiltonian in the normal vibrational coordinates of the T_1 state (35, 48). If the vibronic mixing of the lowest $^3(n\pi^*)$ and $^3(\pi\pi^*)$ states of phthalazine is strong enough the T_1 state should therefore have a significant amount of $n\pi^*$ character.

Several of the features of the phosphorescence spectrum of phthalazine have been explained by Lim and Stanislaus (45) and Baba et al (46) on the basis of a strong vibronic perturbation of the emitting $^3(\pi\pi^*)$ state by a nearby $^3(n\pi^*)$ state. In hydroxyl solvents the 0-0 band of phosphorescence was found to be shifted to higher energy by about 150 cm^{-1} (45) which would indicate a significant amount of $n\pi^*$ character in the lowest triplet state. The appearance of out-of-plane vibrations in the $\pi^* \rightarrow \pi$ phosphorescence (45, 46) can be explained

by a strong vibronic coupling of the lowest energy $^3(\pi\pi^*)$ and $^3(n\pi^*)$ states. In addition, the phosphorescence of phthalazine was found to be predominantly polarized in the molecular plane (45, 46), while phosphorescence from a $^3(\pi\pi^*)$ state is expected to be polarized out of the molecular plane due to spin-orbit coupling with allowed $\pi^* \leftarrow n$ transitions (35, 47). A spin-orbit coupling mechanism which will lead to in-plane polarized phosphorescence is the second-order effect involving vibronic mixing of the lowest energy $^3(\pi\pi^*)$ and $^3(n\pi^*)$ states, and spin-orbit coupling of the $^3(n\pi^*)$ state with $^1(\pi\pi^*)$ states (35, 48). Since the lowest energy $\pi^* \leftarrow n$ transition in phthalazine is symmetry forbidden (49), the direct spin-orbit coupling between the T_1 state of $\pi\pi^*$ character and singlet states of $n\pi^*$ character might be expected to be less important than the second-order effect in conferring singlet character to the to the lowest $^3(\pi\pi^*)$ state.

The vibronic perturbation of the T_1 state of phthalazine by nearby $^3(n\pi^*)$ states may also be invoked to explain the difference in the T-T results which were obtained in this study and that by Alvarez and Hadley (42). The shift in the T-T absorption maxima by about 400 cm^{-1} to higher energy in an EPA glass over an isopentane-n-butyl alcohol glass could be explained as arising from a significant amount of $n\pi^*$ character in the lowest triplet state. In the isopentane-alcohol glass, hydrogen bonding of solvent molecules to the nonbonding electrons may occur thereby raising the energy of the T_1 state relative to that in EPA where the alcohol is more likely to be hydrogen bonded to the large amount of ether which is present (45). Consequently, if the upper tri-

plet state, T_n, is unaffected by the solvent, the $T_n \leftarrow T_1$ transition should occur at a higher energy in an EPA glass than in an isopentane-n-butyl alcohol glass.

The increase in the triplet state lifetime in the isopentane-alcohol glass as compared to an EPA glass can be explained as being due to an increase in the energy of the $^3(n\pi^*)$ states relative to the lowest energy $^3(\pi\pi^*)$ state. Since it has been proposed that the phosphorescence of phthalazine gains its intensity via vibronic coupling between the lowest $^3(n\pi^*)$ and $^3(\pi\pi^*)$ states and spin-orbit coupling between the $^3(n\pi^*)$ state and $^1(\pi\pi^*)$ states (46), the increased energy separation of the two triplet states will result in less singlet character in the T_1 state. This can be seen by reference to the expression for the perturbed triplet T_1' resulting from second order perturbation theory as shown in equation (10):

$$T_1' = T_1^o + \sum_k \sum_{n \neq 1} \frac{\langle S_k^o | H_{SO} | T_n^o \rangle \langle T_n^o | H_{vib} | T_1^o \rangle}{\Delta E_{1k} \cdot \Delta E_{1n}} \cdot S_k^o \qquad (10)$$

where H_{vib} is the same as was described for equation (9)(39, 48). In phthalazine the T_n states will be of $n\pi^*$ character and the S_k states will be of $\pi\pi^*$ character. If hydrogen bonding of solvent molecules to the nonbonding electrons of the nitrogen atoms occurs then the ΔE_{1n} in equation (10) should increase, and the ΔE_{1k} should stay about the same. As a result, the singlet character of the T_1 state of phthalazine should decrease in an isopentane-alcohol glass as compared

with an EPA glass. The radiative and radiationless rates will therefore decrease for the transition $T_1 \rightarrow S_o$, resulting in a longer triplet state lifetime for phthalazine in a solvent which can hydrogen bond to the nonbonding electrons of the nitrogen atoms.

II. 5, 6-Benzoquinoline and 7, 8-Benzoquinoline

The T-T absorption spectra of 5, 6-benzoquinoline (1-azaphenanthrene) and 7, 8-benzoquinoline (4-azaphenanthrene) are shown in figures (5) and (6) respectively. Both spectra show a fairly intense transition originating at about 19,500 cm^{-1}. In addition, a very weak transition was detected for 5, 6-benzoquinoline which originated at 12,040 cm^{-1} and consisted of two additional peaks with a vibrational spacing of approximately 1500 cm^{-1}.

The $T_n \leftarrow T_1$ absorption band at about 19,500 cm^{-1} has been observed by other workers, although no actual spectrum of this band has appeared in the literature. Craig and Ross (14) reported the vibrational maxima of this band as preliminary results, but spectral interference due to photoproducts was thought to be a factor in their results. More recently, West et al (43) have reported the features of this band with polymethylmethacrylate (PMMA) as the solvent. The observed vibrational spacing of the 19,500 cm^{-1} band is about 1400 cm^{-1}, and therefore corresponds to the energy of a carbon-carbon ring stretching mode. Since the lowest triplet state of azaphenanthrenes has been assigned as $\pi\pi^*$ on the basis of triplet lifetime data and luminescence spectra (50), the higher energy $T_n \leftarrow T_1$ transition is probably $\pi\pi^* \leftarrow \pi\pi^*$ in nature.

The very weak T-T transition originating at 12,040 cm^{-1} in 5, 6-benzoquinoline has not previously been reported in the literature. The relative intensity of the two T-T bands which were observed for 5, 6-benzoquinoline would indicate that the high energy transition

is approximately fifty times as probable as the low energy transition. The vibrational spacing of the new T-T band is about 1500 cm^{-1} which would indicate that it probably involves a $\pi\pi^* \leftarrow \pi\pi^*$ transition as was predicted for the 19,500 cm^{-1} band.

The azaphenanthrenes differ from the parent conjugated hydrocarbon phenanthrene only in the replacement of one of the carbon atoms by a nitrogen atom. The introduction of a heteroatom is not expected to produce any significant changes in the π energy levels. It may therefore be useful to compare the T-T spectrum of the heteroconjugated molecule with that of the corresponding isoelectronic hydrocarbon as has previously been done by Platt (51) for the S-S transitions of a number of heterocyclic molecules. In fact, the T-T spectra of 5, 6-benzoquinoline and phenanthrene in the region 11,000 cm^{-1} to 25,000 cm^{-1} do show a very close similarity. In comparison with the T-T spectrum of 5, 6-benzoquinoline that of phenanthrene shows a very weak band progressing from 12,075 cm^{-1} and a much more intense band progressing from about 20,300 cm^{-1} (15). The slight blue shift of the phenanthrene spectrum over that of 5, 6-benzoquinoline would be partially explained by the observation that the T_1 state of phenanthrene lies about 100 cm^{-1} lower in energy than does that of 5, 6-benzoquinoline (35). The weak T-T band of phenanthrene has been assigned as $^3L_b \leftarrow {}^3L_a$ in Platt notation by Henry and Kasha (15) on the basis of the forbidden nature of the transition and the triplet state energy calculations of Kearns (52). By analogy with the iso-π-electronic hydrocarbon phenanthrene it would therefore seem possible to assign

the T-T transition originating at 12,040 cm^{-1} in 5, 6-benzoquinoline as also being $^3L_b \leftarrow {}^3L_a$ in nature.

III. Dibenzothiophene

The T-T absorption spectrum of dibenzothiophene is shown in figure (7). The spectrum shows two absorption bands in the energy region 11,000 cm^{-1} to 27,000 cm^{-1}. The lowest energy band originates at 14,910 cm^{-1} and has a vibrational progression of three additional maxima with a spacing of about 1400 cm^{-1}. A much more intense band consisting of two fairly well resolved maxima with a vibrational spacing of about 1220 cm^{-1} was found starting at 24,180 cm^{-1}. From the relative intensity of the two T-T absorption bands it can be estimated that the transition probability of the 24,180 cm^{-1} band is about forty times as great as that of the band originating at 14,910 cm^{-1}.

The lowest triplet state of dibenzothiophene has been assigned as $\pi\pi^*$ in character on the basis of the work on solvent shifts of phosphorescence by Nurmukhametov and Gobov (53). This assignment is in agreement with the work of Siegel and Judeikis (54) on the zero-field splitting parameters of dibenzothiophene. In addition, the long triplet state lifetime as shown in Table I is consistent with the $\pi\pi^*$ assignment of the triplet state of dibenzothiophene. The $T_n \leftarrow T_1$ transition at 14,910 cm^{-1} can therefore be assigned as $\pi\pi^* \leftarrow \pi\pi^*$ as the vibrational spacing of this band corresponds to that of a carbon-carbon ring stretching mode. A similar assignment can be made for the $T_n \leftarrow T_1$ transition at 24,180 cm^{-1} as the vibrational spacing suggests that it also primarily involves the excitation of a π electron.

It is of interest to compare the T-T spectrum of dibenzothiophene with that of phenanthrene and biphenyl. Phenanthrene is iso-

π-electronic with the structurally related heterocyclic molecules carbazole, dibenzofuran, and dibenzothiophene. The suggestion has therefore been made that phenanthrene should provide a better hydrocarbon model than biphenyl or fluorene in correlating the ππ* states of these heterocyclic molecules (51). The similarities between the S-S absorption spectra of the heterocyclic molecules and that of phenanthrene have tended to confirm this suggestion (55, 56). For the particular case of dibenzothiophene, where the sulfur atom has d orbitals available for forming π bonds, a relatively high degree of conjugation with the two aromatic rings might be expected (57). However, the values of the zero-field splitting parameters for the T_1 state of the heterocyclic molecules have not supported the preceding viewpoint (54). In particular, the value of the zero-field parameter D was found to be significantly larger for the heterocyclic molecules than for phenanthrene, but about the same as for biphenyl and fluorene. The implications of a relatively larger value of D can be seen by reference to the expression for D obtained from the antisymmetric spatial part of the triplet wavefunction, $|\Psi(i,j)\rangle$, as shown in equation (11):

$$D = \frac{3g^2\beta^2}{4} \langle\Psi(i,j)\left|\frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5}\right|\Psi(i,j)\rangle \qquad (11)$$

where r_{ij} and its components refer to the separation of the two unpaired electrons i and j (35). The larger value of D for the heterocyclic molecules will then reflect a smaller average separation of the two unpaired electrons over that in the T_1 state of phenanthrene.

If this is the case, the conjugation of the heteroatom with the aromatic rings must be smaller in the T_1 state of these molecules than that of the -C=C- group of phenanthrene. This would indicate that biphenyl or fluorene may be better hydrocarbon model molecules than phenanthrene for the $\pi\pi^*$ states of carbazole, dibenzofuran, and dibenzothiophene.

With the results obtained in the present work it is possible to compare the T-T spectrum of dibenzothiophene with previous T-T results obtained for phenanthrene, biphenyl, and fluorene. Since there has been no observation of a $T_n \leftarrow T_1$ band in the 11,000 cm^{-1} to 15,000 cm^{-1} region in biphenyl or fluorene, a comparison with such bands in dibenzothiophene and phenanthrene is not possible. However, a $T_n \leftarrow T_1$ band has been found in the 15,000 cm^{-1} to 30,000 cm^{-1} region in all these molecules, and it is possible to compare the energies of the T_n levels which are reached in the transitions. Using the experimental data found in reference (35), the energies of the T_n levels are 42,410 cm^{-1}, 50,140 cm^{-1}, and 47,500 cm^{-1} for phenanthrene, biphenyl, and fluorene respectively. In comparison, if a value of 24,600 cm^{-1} is used for the energy of the T_1 state (35), the energy of the corresponding T_n level in dibenzothiophene is 48,780 cm^{-1}. The T_n energy of dibenzothiophene is therefore more than 6000 cm^{-1} higher than that of phenanthrene, but between that of biphenyl and fluorene. Since the energy of the T_1 level of phenanthrene has been found to be 21,730 cm^{-1}, the large difference in the energy of the T_n levels of phenanthrene and dibenzothiophene is not solely reflected in the energies of the low-

est triplet states of these molecules. The T-T absorption data would therefore seem to provide some evidence that biphenyl and fluorene are better hydrocarbon model molecules than phenanthrene for the triplet state π electronic structure of dibenzothiophene.

IV. Coumarin Derivatives

The T-T spectra of the four coumarin derivatives studied in this work along with the results for coumarin, 4-hydroxycoumarin, and dicumarol obtained in a previous study are presented in figures (8-14). The observed vibrational maxima and triplet state lifetime data are presented in Table II. A comparison of the spectra would indicate that methyl substitution provides a minor spectral perturbation in comparison to hydroxy substitution. The T-T spectra of the 4-hydroxy derivatives show a simple vibronic progression of four peaks with a vibrational spacing of about 1400 cm^{-1}, typical of the carbon-carbon ring stretching mode observed in the singlet and triplet spectra of aromatic molecules. The coumarin and 3-methylcoumarin spectra, on the other hand, are much more complicated. The position of the hydroxy group also has an effect on the T-T results as can be seen by a comparison of the spectra for the 4-hydroxy and 7-hydroxy derivatives. The vibrational structure of the 7-hydroxycoumarin T-T band is relatively unresolved and slightly blue shifted in comparison to that of 4-hydroxycoumarin.

The general orbital character of the lowest triplet state has been established as $\pi\pi^*$ in coumarin, 4-hydroxycoumarin, and 7-hydroxycoumarin on the basis of phosphorescence lifetime data and the zero-field splitting parameters (58-60). The same assignment of the T_1 state of coumarin and 4-hydroxycoumarin has been made on the basis of phosphorescence polarization measurements (61, 62). Similarly on the basis of the zero-field splitting parameters and phosphorescence

lifetime data, the T_1 state of dicumarol has also been assigned as $\pi\pi^*$ in character (63). A possible interpretation of the T-T spectral differences in coumarin and its hydroxy derivatives is in terms of an alteration of the degree of $n\pi^*$ character in the lowest triplet state upon hydroxy substitution.

The electron donating nature of the hydroxy group is expected to raise the energy of the $n\pi^*$ states of the hydroxy substituted derivatives relative to those of coumarin. Since phosphorescence gains its intensity via spin-orbit coupling of $T_1(\pi\pi^*)$ and the ground state to $n\pi^*$ states of opposite multiplicity, the increased energy separation between these states will lead to less $n\pi^*$ character in the states of the hydroxy substituted coumarin derivatives. This can be seen clearly by examining the expression for the transition dipole moment for the $T_1 \rightarrow S_o$ transition as shown in equation (12):

$$\vec{M}(T_1 \rightarrow S_o) = \sum_n \frac{\langle S_o|H_{SO}|T_n\rangle\langle T_n|\vec{P}|T_1\rangle}{\Delta E_{on}} + \sum_n \frac{\langle S_o|\vec{P}|S_n\rangle\langle S_n|H_{SO}|T_1\rangle}{\Delta E_{1n}} \qquad (12)$$

In coumarin and its derivatives the intermediate states T_n and S_n will be of $n\pi^*$ character. The substitution of a hydroxy group on the coumarin molecule will increase their energies and thus increase the energy denominators ΔE_{on} and ΔE_{1n}. Evidence for this effect shows up in the phosphorescence spectra as the 0-0 band of phosphorescence is weaker in 4-hydroxycoumarin than in coumarin (62). Moreover the

phosphorescence lifetimes of the hydroxy substituted derivatives are two to three times longer than for coumarin (62).

More important for the present argument is that the increased energy of the $n\pi^*$ states in the hydroxy derivatives will also cause the energy separation of the T_1 state and the higher energy $^3(n\pi^*)$ states to be increased relative to coumarin. Thus the vibronic mixing of these states, which is dependent on a similar energy denominator as seen in equation (9), will not be as great in hydroxy substituted derivatives of coumarin. On the basis of both vibronic and spin-orbit coupling the T_1 state of coumarin is therefore expected to have more $n\pi^*$ character than the T_1 state of its hydroxy derivatives.

In order to interpret the increased spectral complexity of the $T_n \leftarrow T_1$ spectrum of coumarin relative to 4-hydroxycoumarin in terms of more $n\pi^*$ character in the T_1 state of coumarin, it must be assumed that the upper state T_n is essentially similar in the two molecules. This assumption is not unreasonable in light of the substantial intensity and similar vibrational spacing of about 1400 cm^{-1} in the two spectra, both of which indicate that the transition is primarily $\pi\pi^* \leftarrow \pi\pi^*$ in nature. Moreover the energies of the T_n states in the two molecules obtained from the sum of phosphorescence and T-T energies are very similar (43,550 cm^{-1} for coumarin and 43,900 cm^{-1} for 4-hydroxycoumarin) (58). If this interpretation is correct, the extra complexity in the T-T spectra of coumarin could be attributed to the appearance of out-of-plane bending modes due to the coupling of the T_1 state with $n\pi^*$ states.

It is possible to interpret the T-T spectrum of 7-hydroxycou-

marin in the same way. As mentioned previously, the lowest triplet state of 7-hydroxycoumarin has been assigned as predominantly $\pi\pi^*$ in character (58-60). The phosphorescence lifetime of this molecule is intermediate between that for coumarin and 4-hydroxycoumarin. Thus it could be argued that the $n\pi^*$ character of the T_1 state of 7-hydroxycoumarin is intermediate between that of the 4-hydroxy derivative and the parent compound. The lack of resolved vibrational structure in this particular band as compared with that of 4-hydroxycoumarin could be attributed to underlying and unresolved out-of-plane vibrational components which serve to broaden the resultant spectrum. However the evidence for this interpretation is not as strong in this case. The observed vibrational spacing of 1125 cm^{-1} is less than is normally observed for the carbon-carbon ring stretching mode. The decreased spacing could be a result of the underlying structure of the band, but it could also be due to a terminal state of different character in the T-T transition. The energy of the excited triplet state is also substantially lower than in the other two cases (41,000 cm^{-1} for 7-hydroxycoumarin). The latter interpretation must therefore be mentioned as a possible cause for the T-T spectral differences in this molecule. Indeed it cannot be completely eliminated as a cause for the differences in the T-T spectra of 4-hydroxycoumarin and coumarin.

The effect of methyl substitution seems to provide only a minor perturbation on the π electron structure of the molecule as evidenced by the similarity in the T-T spectra of the different methyl substitu-

ted derivatives. Although the overall T-T spectra are unaltered, the substitution of a methyl group does lead to small energy shifts. In the series of 7-hydroxy derivatives methyl substitution also leads to a progressive change in the relative intensities of the two vibrational maxima with increasing substitution. With regards to the energy shifts, it is of interest that methyl substitution gives rise to a blue shift in the T-T band of coumarin but an increasing red shift with increasing methyl substitution of the 7-hydroxy derivatives. This effect could be interpreted as evidence that either the T_1 or T_n states involved in the transition is of different character in the two types of molecules.

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