small and again the electrostatic interaction seems to be rather small. However, the present approach seems to be least successful in this system.

Concluding Remarks

It is shown that a simple calculation using McLachlan MO's combined with the McClelland treatment based on assumed structure can explain ion pair effects fairly well, although there is much to be improved in order to obtain good quantitative agreement between experimental spin densities and calculated ones. The trends in changes in epr parameters predicted by the calculation agree very well with the observed trends. This implies the basic correctness of the assumed structures. The MO calculations suggest that the relatively small coulombic interaction, $Ze^2/\epsilon r$, is operating in ion pair systems. We think that the reason for this is the effect of strong solvation by solvent molecules (dipole) of cations, which cancels the potential due to the cations. The screening factors which fit the experimental values are closer to the macroscopic dielectric constant rather than to 1.

Even though our calculations are crude, we believe that the results of the present analysis indicate that erroneous results might be obtained in calculation on ion pair systems unless proper consideration is taken of the effects of solvation.

g values of organic radicals have not been used widely for spin density studies. However, the extremely good agreement between ^{13}C splittings and g values seems to indicate that the careful use of g values can provide additional information concerning spin densities on atoms such as oxygen, where the determination of spin density from hfs is not easy.

Acknowledgment. We thank Dr. K. Nakamura for some data on sodium and lithium anthraquinone and helpful discussions concerning assignments of splittings for anthraquinone anions.

Absorption and Emission Spectra of Aromatic Ketones and Their Medium Dependence. Excited States of Xanthone[1]

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Abstract: A detailed examination of the absorption spectra, the polarized phosphorescence spectra, and the polarized excitation spectra of xanthone (C_{2v} symmetry) in polar and nonpolar media has been carried out at 77°K. Five electronic transitions in the absorption region between 27,000 and 44,000 cm^{-1} have been assigned. They are, in order of increasing energy: $^1A_2\ (n,\pi^*) \leftarrow {}^1A_1$, $^1A_1\ (\pi,\pi^*) \leftarrow {}^1A_1$, $^1B_2\ (\pi,\pi^*) \leftarrow {}^1A_1$, $^1A_1$ (CT) $\leftarrow {}^1A_1$ (tentative), and $^1A_1\ (\pi,\pi^*) \leftarrow {}^1A_1$ (tentative). Lifetime and polarization measurements, as well as vibrational features, indicate that the configuration of the lowest triplet state is $n\pi^*$ in the 3-methylpentane (3-MP) solvent but $\pi\pi^*$ in polar solvents. In both EPA and 3-MP the phosphorescence kinetics of xanthone are nonexponential. Time-delayed phosphorescence and excitation spectra show that the mixed kinetics in 3-MP are due to a small amount of the same phosphorescent species ($^3\pi,\pi^*$) which is dominant in EPA. Moreover, polarization spectra indicate that a small amount of the phosphorescent species ($^3n,\pi^*$) which is dominant in 3-MP produces the deviation from the exponential decay in EPA. This phenomenon is suggested to arise mainly from two types of solute–solvent cage configurations.

Owing to their role in photochemical and photobiological reactions, the triplet states of aromatic ketones and aldehydes continue to receive considerable attention from both experimental and theoretical points of view.[2–10] It has been shown that the configuration of the lowest triplet state of these compounds can be correlated with properties such as photochemical reactivity and relaxation behavior. A series of diagnostic criteria has therefore been developed which can guide the assignment of the configuration of the lowest triplet state.[2,3] In some cases, however, these criteria do not allow a clear-cut decision to be made. For instance, it appears that carbonyl compounds with very small energy gaps between $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ configurations have lowest triplet states of a substantially mixed character. This mixing is generally considered to arise by vibrational coupling between the two closely spaced electronic states; experimentally, it is manifested in the polarization characteristics of the phosphorescence.[10–13] A further consequence of the energetic proximity of the triplet states is that a relatively small perturbation of

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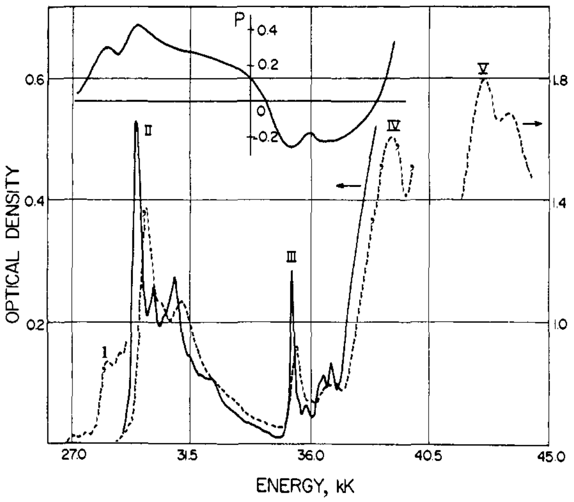


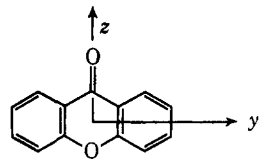
Figure 1. Absorption spectrum and polarized phosphorescence excitation spectrum of xanthone in 3-MP: ---, absorption at 20°C; ——, absorption at 77°K (*ca.* 2 × 10^{-4} *M*, except band I). Insert on the top shows the polarized excitation spectrum at 77°K using the 0–0 band of the phosphorescence. The degree of polarization is defined as $P = (3\cos^2\theta - 1)/(\cos^2\theta + 3) = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$.

one of the states may give rise to a dramatic change of the photochemical behavior of the molecule. Under the influence of polar solvents or substituents, the n,π* and π,π* levels are shifted quite differently, causing them to closely approach *iso*energetic positions or even to interchange position.[2,3]

There appears to be a connection between close-lying triplet-state configurations and the nonexponential phosphorescence decay which has been observed for certain carbonyl compounds.[9,14–16] In some cases this decay could be analyzed in terms of a superposition of two first-order decay processes, and it has been suggested that this anomalous relaxation behavior is due to a simultaneous emission from the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ triplet states.[14] This interpretation implies that vibrational mixing between the two states is not efficient, *i.e.*, that internal conversion is slow enough to allow both states to emit. Clearly, this conclusion is inconsistent with the previously mentioned mixing of near-lying triplet states.

An alternative mechanism for the anomalous emission has recently been offered which involves the production of new species such as an enol or an enolate ion.[17] It is important to note that this explanation requires the carbonyl compound to incorporate a specific structural feature, *i.e.*, α-hydrogen atoms. The experimental data available at this time do not, in our opinion, allow generally applicable conclusions to be drawn regarding the nature of the anomalous emission.

We have found that xanthone (I), a member of the class of flavonoid compounds which includes many brilliant plant pigments,[18] exhibits anomalous emission behavior. In this paper we report the results of a detailed study of this molecule, with particular emphasis on polarization and solvent effects. Xanthone appears to be especially suited for assaying the influence of environment on emission properties, and the results of this study provide further information about the probable origin of the anomalous phosphorescence.



I

Experimental Section

Materials. Xanthone (Matheson Coleman and Bell) was recrystallized from methylcyclohexane and zone refined (*ca.* 100 passes). The material used had mp 174–175° (reported, 173–174°). 3-Methylpentane (Aldrich, Puriss) contained considerable quantities of emitting impurities which were removed by frontal analysis chromatography.[19] EPA (ethanol–isopentane–ether, 5:2:2, American Instrument Co.) was used as received. Water from an ion-exchange column was triply distilled in a nitrogen atmosphere; the second fraction was distilled from a potassium permanganate solution, and the third fraction from a sulfuric acid solution. The remaining solvents were of spectral quality and were used without further purification.

Apparatus and Procedure. The spectrophotofluorimeter employed in this study consists of a 450-W xenon arc excitation source, which is used in conjunction with a Bausch and Lomb 500-mm, *f*/4.4 monochromator and a Spex 750-mm, *f*/6.8 analyzing spectrophotometer, equipped with an EMI 9558 Q photomultiplier tube. The signals are amplified by a picoammeter (Keithly Model 417) and fed into a strip-chart recorder. Both the emission spectra and the excitation spectra are corrected, the former for the response characteristics of the instrument and the latter for the spectral efficiency of the xenon lamp. These corrections, as well as the plotting of the spectra, are performed by computer. For recording polarized spectra, a pair of double Glan-Taylor polarizing prisms (Karl Lambrecht, Crystal Optics, Chicago, Ill.) are introduced into the optical system. To eliminate effects due to the preferential sensitivity of the detector to vertically polarized light, a polarization scrambler (Calcite wedge type; Crystal Optics) is placed in front of the entrance slit of the analyzing monochromator. Time-resolved spectra are obtained by means of a chopper (rotating can). Phosphorescence decay times are measured by blocking the excitation light beam with a simple camera shutter and recording the decay signal on an oscilloscope.

The samples were prepared either in quartz cells or as bare "popsicles."[20] Rectangularly shaped popsicles were used to minimize depolarization effects. The samples in the quartz cells were usually degassed by repeated freeze–pump–thaw cycles. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. To determine the absolute polarization direction in absorption, the stretched-film technique was employed.[21,22] The mechanical orientation of xanthone molecules in a polyethylene sheet was achieved by following a published procedure.[22]

The flash photolysis apparatus used in this study has been described in detail elsewhere. Unit 1[23] has a geometry which permits broadside illumination and is particularly suited for small samples and low-temperature studies. This apparatus was operated with an input energy of about 150 J. The flash duration (1/e time) is *ca.* 10 μsec. The ruby laser[24] flash apparatus was used in conjunction with an ADP crystal; it provides a light output at 347 nm of *ca.* 10^{16} quanta per flash.

Solutions for flash photolysis experiments were prepared and degassed in a reservoir connected to a 7-cm long quartz sample cell with optical quality windows.

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Table I. Absorption Spectrum of Xanthone

Band	ν_{0-0}(77 °K), kK 3-MP	EPA	ν_{max}(298 °K), kK, 3-MP	Oscillator strength, f, 3-MP	Log ϵ_{max} 3-MP	Polarization[a,b]	Assignment
I	27,050		27,150		~0.8	z	$^1A_2 \leftarrow {}^1A_1$ (n,π^*)
II	29,450	29,230	29,780	0.10	4.07	$z^{b,c}$	$^1A_1 \leftarrow {}^1A_1$ (π,π^*)
III	35,280	35,080	35,420	0.02	3.70	y	$^1B_2 \leftarrow {}^1A_1$ (π,π^*)
IV	38,750	38,200	39,050	0.10	4.18	z	$^1A_1 \leftarrow {}^1A_1$ (CT)
V			42,670	0.50	4.73	z	$^1A_1 \leftarrow {}^1A_1$ (π,π^*)
			25,900	~10^{-6}	~0.2	z	$^3A_2 \leftarrow {}^1A_1$

[a] Coordinate orientation as shown for structure I. [b] From phosphorescence excitation. [c] From stretched-film absorption.

Results

Absorption Spectra. The absorption spectrum of xanthone in 3-methylpentane (3-MP) at room temperature and 77 °K is shown in Figure 1. On the basis of polarized absorption and phosphorescence excitation spectra, five electronic transitions can be identified. The pertinent data are collected in Table I.

The second transition (II), which is z polarized (short axis), has an intense 0–0 band at 29,780 cm^{-1}. Transition III, which appears at 35,420 cm^{-1}, is polarized perpendicular to transition II and is substantially less intense. The absolute polarization direction of these transitions was measured in a stretched polyethylene sheet in which the xanthone molecules were predominantly oriented with their long axes (y) parallel to the stretch direction. It is generally accepted that elongated molecules align in this manner, since results obtained in stretched-sheet experiments have been corroborated by an independent method for numerous other systems.[21,22]

The polarized phosphorescence excitation spectra, as monitored in the 0–0 band (25,905 cm^{-1}), showed bands I and IV to be polarized parallel to band II and band III to be polarized perpendicular to band II. The polarization of band V also appears to be parallel to that of band II, but owing to low lamp intensity in this region, this conclusion must be considered tentative.

Band I is extremely weak and can only be observed in a long-path-length absorption cell or in the excitation spectrum of concentrated samples. The four poorly defined peaks correspond to vibrational frequencies of *ca.* 1200 and 600 cm^{-1}. In the presence of even a minute quantity of ethanol, these structural features disappear completely. It is noteworthy that at 25,900 cm^{-1} an additional, but extremely weak absorption band can be observed using the long-path-length cell. This feature, which also appears in the excitation spectrum if concentrated samples are employed, might be mistaken for the 0–0 band of the first transition, but its coincidence with the phosphorescence 0–0 band (*vide infra*) allows it to be assigned to singlet–triplet absorption.

The xanthone spectrum in EPA at 77 °K is very similar to that in 3-MP, except that it is red shifted (*cf.* Table I). Band I cannot be discerned in this solvent. At room temperature in EPA and in water, the various bands are red shifted and substantially broadened relative to the spectrum in 3-MP under the same conditions.

Phosphorescence Spectra. The phosphorescence spectrum of xanthone[25] in carefully purified 3-MP with excitation at 29,600 cm^{-1} (0–0 band of transition II) is shown in Figure 2. The structural features of this spectrum and their interpretation are listed in Table II.

The vibrational bands of this spectrum can be analyzed in terms of the fundamental frequencies 500, 890, and 1665 cm^{-1}, which appear in the Raman and infrared spectra of xanthone. The spectrum is seen to be composed of these three fundamentals and of overtones of the 1665-cm^{-1} band and its combinations with the other two modes.

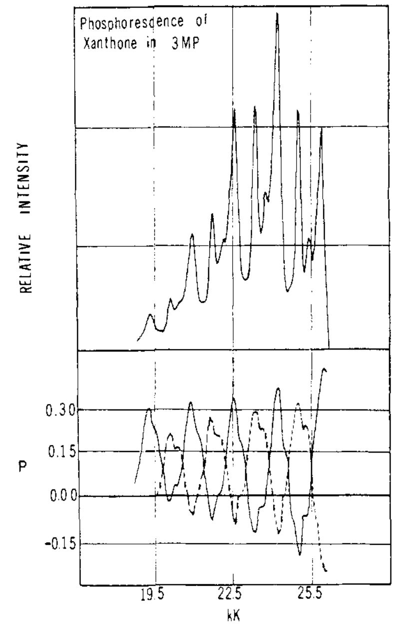

Figure 2. Conventional and polarized phosphorescence spectrum of xanthone in 3-MP at 77 °K: ——, excitation at 29,600 cm^{-1} (band II); - - -, excitation at 35,300 cm^{-1} (band III).

The polarization of this emission is included in Figure 2 (bottom), where the solid line refers to excitation into transition II as explained above, and the broken line represents excitation into the 0–0 band of transition III at 35,300 cm^{-1}. Assuming the first band at 25,905 cm^{-1} to be the 0–0 transition of the phosphorescence, we note that this band and those of the 1665-cm^{-1} progression are positively polarized with respect to band II excitation and negatively polarized with respect to band III excitation. The emission bands associated with the 500- and 890-cm^{-1} vibrations show the opposite behavior.

In 3-MP, the phosphorescence spectrum of xanthone exhibits a small but significant excitation wavelength dependence. With excitation at 29,200 cm^{-1}, the emission spectrum of Figure 3 is obtained, which shows an altered intensity pattern for the vibrational bands

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(25) All the emission spectra were measured with xanthone concentrations in the range 10^{-4}–10^{-7} *M*. In no case was a concentration effect noted.

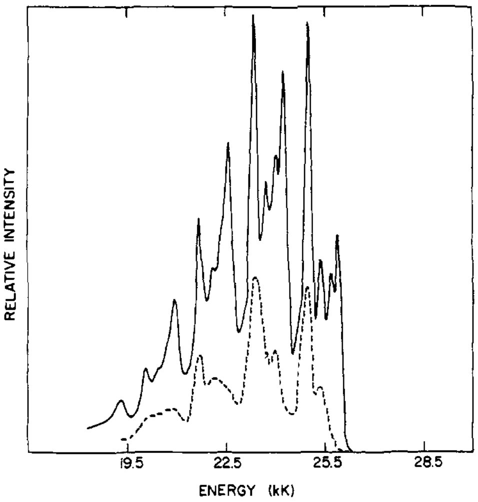

Figure 3. Phosphorescence spectrum of xanthone in 3-MP at 77°K: ——, excitation at 29,200 cm^{-1}; - - -, calculated difference between phosphorescence spectra produced by excitation at 29,200 and at 29,600 cm^{-1} (Figure 2). The intensity scale is arbitrary.

when compared with the emission resulting from 29,600-cm^{-1} excitation (*cf.* Figure 2). The spectrum of Figure 3 shows four fundamental vibrations with frequencies of 260, 530, 930, and 1665 cm^{-1}. Moreover, the total intensity of this spectrum relative to that shown in Figure 2 is substantially lower. These differences in behavior are reflected in the excitation spectra monitored at 25,905 cm^{-1} without time delay, and at 25,000 cm^{-1} with a delay of *ca.* 100 msec (Figure 4). The two excitation spectra coincide with the absorption spectra measured in 3-MP and in ethanol or EPA, respectively.[26a] It is of interest to note that the spectrum generated by plotting the differences between the phosphorescence spectra produced by excitation at 29,200 and at 29,600 cm^{-1} closely resembles the emission spectrum in EPA (*cf.* Figures 3 (dotted spectrum) and 5).[26b]

Table II. Vibrational Structure of the Phosphorescence Spectrum of Xanthone in 3-MP at 77°K

ν, cm^{-1}	$\Delta\nu$, cm^{-1}	Analysis	Ir/Raman spectrum, cm^{-1}
25,906		0–0	
25,409	497	499	/499
25,019	887	886	886/
24,241	1665	1665	1665/1652
23,750	2156	1665 + 499	
23,370	2356	1665 + 886	
22,591	3315	2(1665)	
22,127	3779	2(1665 + 499)	
21,731	4175	2(1665 + 886)	
20,964	4942	3(1665)	
20,493	5413	3(1665 + 499)	
20,011	5895	3(1665 + 886)	
19,359	6547	4(1665)	
18,901	7005	4(1665 + 499)	
18,511	7395	4(1665 + 886)	

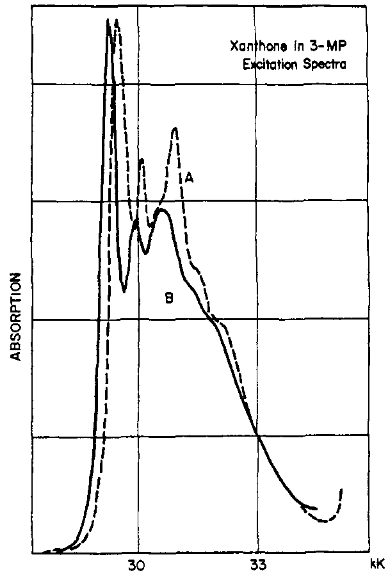

Figure 4. Phosphorescence excitation spectrum of xanthone in 3-MP at 77°K: (A) monitoring the phosphorescence 0–0 band at 25,905 cm^{-1}, (B) monitoring the phosphorescence at 25,000 cm^{-1}.

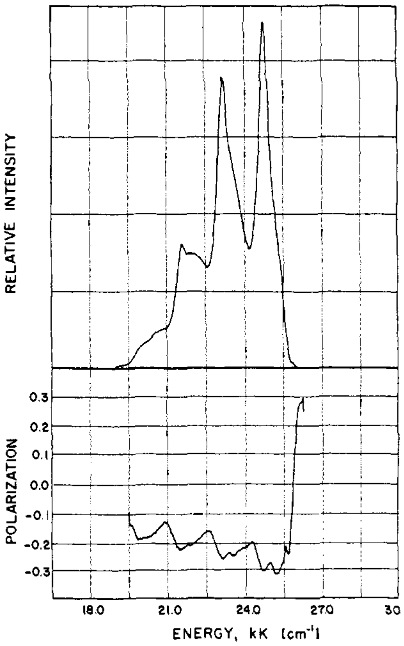

Figure 5. Conventional and polarized phosphorescence spectrum of xanthone in EPA at 77°K; excitation at 29,230 cm^{-1} (band II).

The presence of more than one emitting species is also evident from lifetime measurements, which are described below. An important observation is that the emission properties are independent of the solute concentration in the range 10^{-3}–10^{-7} *M*. The emission behavior in an isopentane–methylcyclohexane mixture and in *n*-octane is analogous to that in 3-MP.

The phosphorescence spectrum of xanthone and its polarization in an EPA glass are shown in Figure 5. Excitation was provided in the 0–0 band of transition II at 29,230 cm^{-1}. The spectrum is less structured than the one in 3-MP (*cf.* Figure 2), and the apparent 0–0 band at 25,905 cm^{-1} is weak and appears only as a tail. The vibrational features lack the characteristic 1665-cm^{-1} mode evident in the 3-MP glass; the prominent

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(26) (a) To exclude effects due to traces of ethanol in the 3-MP, some samples were prepared by distilling the 3-MP over sodium directly into the sample cell. Degassed and aerated samples showed no differences in their emission spectra. (b) Owing to the nature of the solvent, the dotted spectrum in 3-MP (Figure 3) is slightly more resolved than the spectrum in EPA. (Also, compare the former with Figure 7d, which essentially represents the emission in ethanol.)

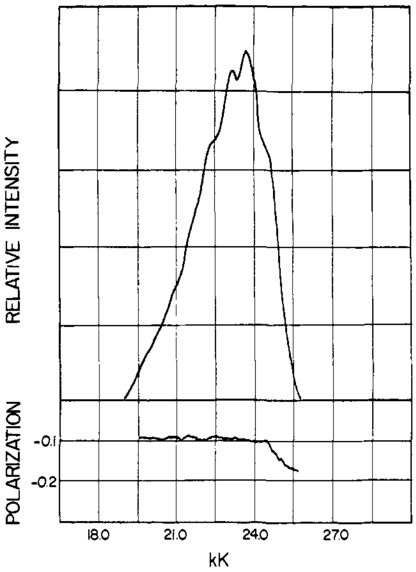

Figure 6. Conventional and polarized phosphorescence spectrum of xanthone in a water-methanol mixture (1:20) at 77°K; excitation at 29,000 cm^{-1} (band II).

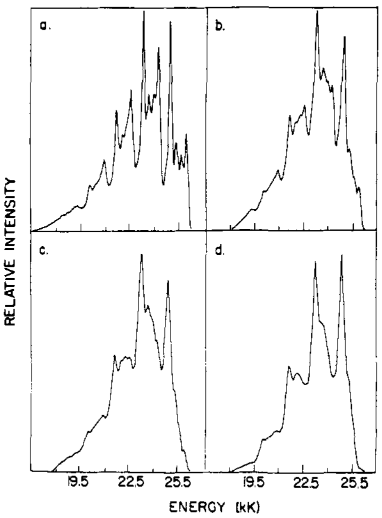

Figure 7. Phosphorescence spectra of xanthone in 3-MP at 77°K at various enthanol concentrations; excitation at 29,250 cm^{-1} (band II): (a) pure 3-MP, (b) 2% (v/v) ethanol, (c) 5% (v/v) ethanol, (d) 10% (v/v) ethanol.

peaks in the EPA emission spectrum are separated by 1620 cm^{-1}. The very weak initial portion of this emission reveals positive polarization with respect to excitation into band II, which is followed by an abrupt drop to negative polarization values at longer wavelengths. Although the 1665-cm^{-1} mode is absent in the EPA emission, it becomes evident in the polarization. Moreover, the detailed structure of the negative polarization closely resembles that of the polarization spectrum in 3-MP (*cf.* Figure 2). With excitation into the 0–0 band of transition III, the polarization behavior is reversed.

In EPA, the excitation spectrum monitored at the first prominent peak (24,760 cm^{-1}) beyond the 0–0 band coincides with the absorption spectrum throughout the accessible region. In both ethanol and ether matrices, the emission spectra are very similar to that in EPA. Only minor differences in the sharpness of structural features distinguish the emission in the three polar matrices (*cf.* Figures 2 and 7d). Thus the ethanol spectrum shows slightly more pronounced structure than the EPA and ether spectra.

The most polar medium examined was a 20:1 methanol–water mixture which forms a good glass. The absorption spectrum in this solvent is slightly red shifted relative to the EPA spectrum, but it retains the same band features. The emission spectrum and its polarization in this matrix with excitation at 29,000 cm^{-1} (band II) are shown in Figure 6. This emission spectrum exhibits little structure, and the polarization is negative throughout the measured region. Moreover, the 0–0 band cannot be unequivocally identified.

Inasmuch as the phosphorescence spectra in 3-MP and in EPA show substantial differences, it was of interest to examine the effect of a small amount of a polar solvent (*e.g.*, ethanol) on the emission in 3-MP. The spectra for solvents containing between 2 and 10% ethanol (by volume) in 3-MP are presented in Figure 7. Even at the lowest ethanol concentration, the effect on the spectrum is dramatic. The spectrum in 10% ethanol coincides with that in pure ethanol. It is noteworthy that there is a striking similarity between the spectra of Figure 7 and the spectrum measured in pure 3-MP with time delays between excitation and detection in the range 20 to about 150 msec.

Although xanthone exhibits no fluorescence in ethanol and in the hydrocarbon solvents, a blue emission can be detected in aqueous solution at room temperature. This spectrum is broad and shows a maximum at 25,200 cm^{-1}. The quantum yield of this emission was measured to be 0.030 ± 0.005. That this emission originates from xanthone follows from the identity of the absorption and excitation spectra. The fluorescence spectrum shows a strong pH dependence. With increasing hydrogen ion concentration, the intensity at the maximum decreases and a new band at 22,400 cm^{-1} appears. The absorption spectrum, on the other hand, is invariant in the range pH 1–10.

Phosphorescence Lifetimes. In 3-MP glass at 77°K, the phosphorescence decay furnishes at least two first-order decay constants corresponding to lifetimes of 25 ± 3 and *ca.* 120 msec, respectively. When the lifetime is measured in the 0–0 band at 25,906 cm^{-1}, essentially only the fast decay is observed. The longer lived component becomes apparent at longer wavelengths, but even here the fast component still predominates ($\geqslant 90\%$). It should be pointed out that the analysis of the phosphorescence decay in terms of two components is quite arbitrary, and there may well be additional species present. By contrast, a long-lived component with a lifetime of 150 ± 10 msec dominates the decay in EPA glass at all wavelengths except in the positively polarized, weak initial portion above 25,800 cm^{-1} (*cf.* Figure 5). In this region the decay is fast as in 3-MP (*ca.* 30 msec). In the methanol-water mixture, only one decay time was evident which is longer (900 ± 100 msec, 77°K) than those observed in the other solvent systems.

Flash Photolysis Experiments. The conventional flash photolysis of xanthone in degassed ethanol and benzene solutions at room temperature shows no transient absorption. Very weak transient absorption which maximizes at *ca.* 390 nm was, however, observed by excitation with frequency-doubled ruby laser radiation (347 nm). The lifetime of this transient is about 50 μsec. Conventional flash excitation of xanthone in EPA at 77°K furnishes a transient with absorption in the same spectral region. The lifetime of this intermediate (160 ± 12 msec) matches that of the dominant phosphorescence component in this medium.

Discussion

The spectral features of xanthone are characteristic of those of aromatic ketones.[2-10] From their position, intensities, vibrational structure, and polarization, the absorption bands of xanthone have been assigned (Table I). These assignments are based on the assumption of a C_{2v} molecular symmetry. The molecular orbital description of simple ketones with C_{2v} symmetry leads to the prediction that the lowest singlet and triplet n,π* states belong to the A_2 representation.[27] Intensive studies of formaldehyde have confirmed these assignments.[28]

The lowest electronic transition (band I) of xanthone in the singlet manifold also meets the criteria established for n,π* transitions.[2,3] First, its intensity is very low ($\epsilon_{0-0} \approx 6$), which is in agreement with the symmetry and spatially forbidden nature of this transition. Secondly, the vibrational features which are spaced about 1200 cm^{-1} match those which have been measured for similar carbonyl compounds[7,9,28] and which have been assigned to the C–O stretching mode. Finally, as anticipated for n,π* transitions, the band appears to be blue shifted in polar solvents.[29]

The intensity of n,π* transitions is usually considered to be due to vibronic coupling (Herzberg–Teller mechanism),[27] or to a breakdown of local symmetry restrictions at the carbonyl group. The rigid structure of the xanthone molecule compared with that of, *e.g.*, benzophenone favors the first path.[30]

Energy and intensity ($f = 0.1$) considerations make the electric-dipole-allowed $^1A_1 \leftarrow {}^1A_1$ transition (Table I) the prime candidate for vibronic coupling with the n,π* ($^1A_2 \leftarrow {}^1A_1$) transition. The former transition carries so much oscillator strength that even slight mixing with the A_2 state *via* the active a_2 vibrational mode can lead to a considerable intensity for the $^1A_2 \leftarrow {}^1A_1$ transition. Since a vibronically induced transition has the polarization of the band serving as source of the borrowed intensity, the $A_2 \leftarrow A_1$ transition is expected to be *z* polarized. This prediction is confirmed by the experimental findings.

The strong band II, whose absolute polarization direction (*z*) has been determined using the stretched-film technique, can be assigned as $^1A_1\ (\pi,\pi^*) \leftarrow {}^1A_1\ (^1L_a)$. This assignment is in agreement with Pariser–Parr–Pople (PPP) and CNDO/2 molecular orbital calculations[31] and fits the molecular orbital description of simple carbonyl compounds. The polarization of the excitation spectrum of the 0–0 transition of this band is close to the theoretical maximum value, which indicates that the transition moment almost coincides with the C=O axis.

A third electronic band (III) appears at *ca.* 35,000 cm^{-1}. Since this transition is reasonably strong and of relatively low energy, we believe it to be of the π,π* type. This transition occurs in the molecular plane and is perpendicular to the ^1L_a band, so it must be long-axis (*y*) polarized and may be identified as $^1B_2\ (\pi,\pi^*) \leftarrow {}^1A_1\ (^1L_b)$. This result is also in accordance with semiempirical calculations.[31] Moreover, the smaller energy gaps between vibrational features of this band compared with those for ^1L_a bands agree with Platt's observations for aromatic hydrocarbons.[32] Band IV is intense ($f = 0.1$) and *z* polarized. At room temperature, it shows a 1200-cm^{-1} red shift when the solvent is changed from 3-MP to water. These observations support a tentative assignment of this band as due to a ring → C=O charge-transfer transition.[2,33] This conclusion is consistent with the absence of the corresponding band in the structurally similar compound methylenexanthene, which lacks the carbonyl group. Band V is the most intense band in the near-ultraviolet region ($f = 0.5$), and it appears to be *z* polarized, although, for experimental reasons, this conclusion is tentative. We are, however, reasonably confident that this band represents a $^1A_1\ (\pi,\pi^*) \leftarrow {}^1A_1$ transition, since CNDO/2 and PPP calculations[31] match the experimental findings with respect to energy, polarization, and intensity.

Having established a reasonable assignment for the main features of the absorption spectrum of xanthone, we can proceed to discuss the emission data and relate them to the absorption results. Since the emission behavior is strongly solvent dependent, we consider first the behavior in 3-MP, a solvent which is relatively inert and which provides a uniform environment. To identify the lowest triplet state, the generally accepted optical criteria will be utilized,[2,3] The average spacing between successive bands of the progression is 1665 cm^{-1}. This frequency can be assigned to the totally symmetric C=O stretching vibration. The singlet–triplet energy gap, *i.e.*, the separation between the longest wavelength band of the $^1A_2\ (n,\pi^*) \leftarrow {}^1A_1$ transition and the 0–0 band of the phosphorescence, is only *ca.* 1150 cm^{-1}, and the measured phosphorescence lifetime is 23 msec.[34] These facts indicate that the lowest triplet state configuration of xanthone is undoubtedly n,π*. The polarization of the phosphorescence of aromatic ketones provides an additional strong criterion for determining the nature of this state.[2-4,7-10] It has been shown that, if the lowest triplet is a $^3(n,\pi^*)$ state, a first-order spin–orbit coupling mechanism between $^1A_1$ and $^3A_2$ is dominant and leads to an in-plane polarization of the 0–0 band of the phosphorescence.[4,27,35] In xanthone this band is directed parallel to the *z*-polarized $^1A_1\ (\pi,\pi^*) \leftarrow {}^1A_1$ transition, consistent with an $^3A_2\ (n,\pi^*)$ assignment. Outside the 0–0 band, only

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[27] J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

[28] W. T. Raynes, *J. Chem. Phys.*, **44**, 2755 (1966), and references therein; G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand-Reinhold, Princeton, N. J., 1966.

[29] M. Kasha, "Light and Life," W. McElroy and B. Glass, Ed., Johns Hopkins University Press, Baltimore, Md., 1955.

[30] This conclusion does not necessarily hold for the closely related compound flavone, where the carbonyl group and the unsaturated moieties are not all coplanar: H. Pownall and J. R. Huber, manuscript in preparation. Here there is the possibility of overlap between orbitals centered on the carbonyl group with nearby π orbitals.

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[32] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963.

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[34] From the oscillator strength of the $^3A_2\ (n,\pi^*) \leftarrow {}^1A_1$ transition, the radiative phosphorescence lifetime can be estimated as about 10 msec.[2]

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the totally symmetric C=O stretching vibrations (1665 cm^{-1}) are also *z* polarized, while the bands associated with the 500- and 890-cm^{-1} vibrations appear to be *y* polarized. The polarization behavior of the two latter bands may be explained on the basis of vibronic interactions which usually derive intensity with the aid of nontotally symmetric vibrations. These vibrations appear in the phosphorescence spectrum when the mixing of electronic states is sensitive to nuclear displacements. Vibrational coupling between the lowest n,π^* triplet state and a closely spaced higher π,π^* triplet state can be excluded as a source for these *y*-polarized bands, since the $^3A_1$ (π,π^*) ← $^1A_1$ transition carries so much less oscillator strength than the $^3A_2$ (n,π^*) ← $^1A_1$ transition that a vibronic mixing in the triplet manifold is not expected to be effective. A reasonable explanation is, however, offered by a *first-order spin–vibronic coupling mechanism*[35] *which introduces vibronic intensity into the singlet–triplet transition.* In the present case, the active mode would be a b_2 vibration.

The emission behavior in 3-MP is complicated by a second emission. The dominant component A ($\geqslant 90\%$), which gives rise to the phosphorescence properties just discussed, is accompanied by a small emission component B, which shows all the characteristics of the xanthone emission in EPA. To discuss this phenomenon in detail we first consider the emission in EPA (*cf.* Figure 5). The shortest wavelength phosphorescence band in this solvent is weak, short lived, and *z* polarized. The remainder of the spectrum is intense, predominantly long lived, *y* polarized, and shows structural details in the polarization spectrum which are identical with those in 3-MP. This behavior can be understood in terms of the superposition of the emission from two different metastable levels. Emission A, which is the same as in 3-MP, is responsible for the short-lived *z*-polarized initial part of the spectrum and the weak, detailed features in the polarization, while the dominant component B is *y* polarized, long lived, and is characterized by a vibrational spacing of 1620 cm^{-1}. Considering emission B on the basis of xanthone with C_{2v} symmetry, one is led to infer that in this medium (EPA) the lowest triplet state is probably $^3A_1$ (π,π^*) and that the 1620-cm^{-1} mode is likely to represent the totally symmetric ring-breathing frequency.[36] Moreover, one may speculate that a first-order spin–orbit coupling scheme provides the dominant route for T ↔ S intensity, so that the observed *y* polarization of this phosphorescence would indicate the perturbing singlet state to belong to a B_2 representation. If this reasoning is correct, this state is most likely the $^1B_2$ (π,π^*) state which appears in the absorption spectrum as band III.

For many carbonyl compounds, it is generally considered that changing the environment from a hydrocarbon solvent to polar media is accompanied by an interchange of the lowest ^{3}(n,π^*) and ^{3}(π,π^*) states.[2,3] The experimental results are consistent with the view that emissions A and B originate from the ^{3}(n,π^*) and ^{3}(π,π^*) states of xanthone, respectively. Depending on the immediate environment, either one state or the other will be lower in energy.[37] These assignments are supported by the results in the highly polar methanol–water mixture. In this matrix (*cf.* Figure 6), the spectral shape, lifetime (τ_p = 0.9 sec), and polarization (*x*) are even more indicative of a π,π^* emitting state than in EPA. Moreover, the observation of fluorescence in water solution might well signifiy that there is also an interchange of the $^1A_2$ (n,π^*) and $^1A_1$ (π,π^*) levels in this very polar solvent.

In both 3-MP and EPA, the dominant emission components A and B, respectively, are accompanied by small amounts of B and A, respectively, which then give rise to the observed nonexponential phosphorescence decay. An explanation of mixed-decay behavior was proposed by Yang and Murov[14] on the basis of investigations of the luminescence of 1-indanone. In both polar and nonpolar glasses, this compound exhibits two groups of emission having different lifetimes but identical excitation spectra. These authors suggested that there is simultaneous emission from the ^{3}(n,π^*) state and a triplet state of mixed n,π^* and π,π^* character. Lim and coworkers[17] have pointed out that this interpretation leads to the conclusion that either internal conversion between the triplet states is slow enough to allow emission from both or there exist different environments which give rise to distinct molecule–solvent cage emission systems even in one component solvents. A reinvestigation of 1-indanone by Lim and coworkers[17] revealed a third component with a slightly different excitation spectrum in addition to the two previously described species. These authors proposed that the three groups of emission arise from the n,π^* triplet state of 1-indanone, the enolate anion of this compound, and the reketonization of this enolate anion in the lowest triplet state. Both the Yang and Lim mechanisms are inapplicable to xanthone. For this compound, the two groups of emission have distinct excitation spectra, which is inconsistent with a mechanism involving two emitting triplet states. The enolization mechanism is clearly not appropriate, since xanthone contains no labile hydrogen atoms.

We proposed that the mixed emission of xanthone is due to different emission systems, *i.e.*, different xanthone–solvent cage systems. Owing to the nonuniformity of EPA, it is not difficult to envision the formation of distinct triplet states by virtue of different molecule–solvent configurations. In other words, xanthone molecules which are surrounded by a solvent cage consisting primarily of isopentane molecules would experience an environment similar to that produced in 3-MP. The emission spectrum of these short-lived states is consequently superimposed on the more persistent phosphorescence of molecules contained in ethanol and/or ether solvent cages. Because 3-MP and octane are one-component systems, the arguments advanced for EPA are no longer strictly applicable in these solvents. If, however, the energies of the $^1A_2$ (n,π^*) and $^1A_1$ (π,π^*) states as well as those of the $^3A_2$ (n,π^*) and $^3A_1$ (π,π^*) states are close and sensitive to slight geometrical distortions of the molecule, even a relatively small variation in the way individual xanthone molecules are constrained in the solvent cage at 77°K

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(37) An inversion of the lowest triplet states of xanthone by going from a nonpolar to a polar solvent was recently suggested by R. N. Nurmukhametov, L. A. Mileshina, and D. N. Shigorin, *Opt. Spectrosc.*, 22, 404 (1967).

may be sufficient to produce, among a whole distribution of structures, two favored solute–solvent cage configurations which can account for the observed differences in lifetime and spectral shape.

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Ultrasonic Absorption in Aqueous Polyelectrolyte Solutions. I

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Abstract: Ultrasonic absorption has been measured in aqueous solutions of salts of polyacrylic acid (HPA) and carboxymethylcellulose (CMC) in the frequency range 1–190 MHz at 25°. The effects of molecular weight, degree of neutralization, concentration, and nature of the cation were studied. The polyelectrolyte solutes produce excess absorption characterized by very wide absorption bands, which greatly hampers a quantitative analysis of the dynamic processes being observed. These processes are shown to be due to counterion interaction with the repetitive segments of the polyion chain rather than to processes due to the chain as a whole. Alkaline earth counterions produce large increases in absorption. This absorption is qualitatively different from that found due to isolated interaction between single $RCOO^-$ groups and the same counterions. Several mechanisms for the polyelectrolyte absorption are suggested and discussed.

The activity coefficients and the mobilities of counterions in polyelectrolyte solutions are much lower than those found at equivalent concentrations of simple electrolytes. These facts are normally explained in terms of counterion binding to the polyion due to the large electric field on the polyion chain. The extent of counterion binding can be explained satisfactorily[1] by models which use a uniformly charged cylinder or sheet as a model for the polyion. The solution is divided into electrically neutral domains and the electrostatic equations are solved for one domain.[1,2] In general, it is observed that the equilibrium and transport properties of polyelectrolytes are predicted semiquantitatively by those models. That is, counterion binding is essentially determined by the overall charge density on the chain. As the concentration of polyelectrolyte increases, the major change predicted by such models is the decrease in extension of the domains so that the counterions are, on the average, closer to the polyion.

In polysulfonate solutions, the counterion binding of the alkali metal ions increases with increasing crystallographic radius of the metal ion,[3,4] suggesting that the counterions are not desolvated when binding to the polyion. Ir and nmr evidence in strong sulfonic acid ion exchange resins supports this view.[5] In solutions of polycarboxylates[6,7] and polyphosphates[8] the trend of increased counterion binding is reversed so that the smallest ions show the highest association. This implies that in addition to overall atmosphere binding, some site binding involving partial desolvation of counterions occurs. Thus the multistep mechanism proposed by Eigen[9] to explain ion association in simple electrolytes can be adapted for counterion binding in polyelectrolytes as depicted in Figure 1. The species B in Figure 1 involves a continuous distribution of counterions interacting with the overall charge density on the polyion. This is the dominant species in polysulfonates. Species C represents some direct contact between conterions and ionogenic groups on the chain and apparently contributes to the counterion binding in polycarboxylate and polyphosphate solutions.

Counterion binding reduces the electrostatic repulsion between neighboring charged sites on the chain. This shielding, which becomes more effective with increased binding, leads to a decrease in the average dimensions of the polymer chain. The change in average extension of the chains is easily seen in the reduced viscosity of the solutions.[3,10] The expansion of the polyion chain is particularly notable when the degree of neutralization of weak polyacids increases.[11] Hence, counterion binding is a complex process which involves the multistep approach of counterions coupled with changes in the average dimensions of the polyion.

Relaxation methods are particularly suitable for studying the dynamics of the complex process of counterion binding. If the various steps in the process are separable on a time scale, the relaxation methods could allow the study of their individual contributions to the overall process. The magnitude of the volume change accompanying the binding of each counterion[4] is large enough[12] to produce a measurable increase in the

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