

MULTIPLE PHOSPHORESCENCE EMISSION AND EXCITED STATE SWITCHING OF ARYLKETONES IN ACETIC ACID AT 77 K

G. FAVARO

Istituto di Chimica Fisica, Università di Perugia, 06100 Perugia (Italy)

(Received January 18, 1982; in revised form February 26, 1982)

Summary

A study of the phosphorescence emission of benzophenone and some electron-withdrawing substituted derivatives (ketones I) and electron-releasing substituted derivatives (ketones II) in acetic acid solution at 77 K has shown the presence of three types of bands. On the basis of their vibronic structure and lifetime and of the effects of concentration and exciting wavelength on the intensity and spectral distribution, they were assigned to an n,π^* transition of the solvent-free molecule, a π,π^* transition of the solvent-bonded molecule and some kind of aggregate. Triplet excitation energies for the n,π^* and π,π^* transitions were found to invert their positions on going from ketones I (n,π^* lowest triplet) to ketones II (π,π^* lowest triplet).

Results obtained previously for the different photophysical behaviour of ketones I and ketones II at room temperature are discussed in the light of the information obtained from the phosphorescence study at 77 K.

1. Introduction

Interest in the characterization of the lowest excited states of carbonyl compounds has always been high. In fact the nature of the excited states plays an important role in determining the efficiencies of ketone photoreactions [1 - 7] as well as of the monomolecular and bimolecular processes [8, 9] leading to deactivation of the excited molecule and the absence of photochemical activity. Variations in the substituent or the solvent can lead to a reversal of the energetic disposition of the lowest states; thus both the photochemical reactivity and the spectral characteristics change. Absorption and luminescence spectroscopy, including pulse techniques for lifetime measurements, are considered to be the most versatile tools for investigating the nature of the excited states.

In connection with our interest in the bimolecular interactions of excited aryl ketones, such as energy transfer and quenching, and in their dependence on structural and environmental effects [8 - 11], we have investigated the phosphorescence emission of a series of aromatic ketones in acetic acid solu-

tion at liquid nitrogen temperature. The molecules under study were benzophenone (B) and some derivatives with electron-withdrawing groups (4,4'-dichlorobenzophenone (4,4'-ClB), 4-carboxybenzophenone (4-COOHB) and 3-benzoylpyridine (3-BP) and with electron-releasing groups (4,4'-dimethoxybenzophenone (4,4'-CH₃OB), 4-hydroxybenzophenone (4-OHB), 4-aminobenzophenone (4-NH₂B), 4,4'-(bis)-dimethylaminobenzophenone (MK), 2-hydroxybenzophenone (2-OHB) and 2-aminobenzophenone (2-NH₂B)). Previous studies of their efficiency as sensitizers [8] and their possible roles as energy donors or quenchers in acetic acid solution [9] have shown that there is a clear-cut difference between electron-withdrawing and electron-releasing substituted ketones. For convenience, we shall divide the substituted aryl ketones into two general groups, classified as ketones I (B and the electron-withdrawing substituted compounds) and ketones II (the electron-releasing substituted compounds).

Ketones I have previously been found to be efficient triplet sensitizers and to show fairly intense phosphorescence in acetic acid solution at room temperature [8]. Ketones II neither are sensitizers nor phosphoresce at room temperature, but they behave as quenchers of ketones I [8, 9]. This behaviour has been considered to be caused by a state switching of the lowest n, π^* and π, π^* triplet states in going from electron-withdrawing substituted molecules (n, π^* lowest triplet state) to electron-releasing substituted molecules (π, π^* or charge transfer (CT) lowest triplet state). Since both classes of compounds show phosphorescence emission in acetic acid solution at liquid nitrogen temperature, our objective was to characterize the emitting states by their energies and lifetimes at 77 K and finally to gain more insight into the causes of the different behaviour of ketones I and ketones II in acetic acid solution at room temperature.

2. Experimental details

The ketones under study were all commercial products and were purified before use as described previously [9]. The glacial acetic acid (Carlo Erba RPE) used as the solvent was purified following the literature method [12] and showed negligible emission at low temperature.

The emission spectra at 77 K were measured using a Hitachi-Perkin-Elmer MPF-3 spectrofluorometer which was equipped with an accessory for phosphorescence measurements.

Sample concentrations were varied in the range 10^{-2} - 10^{-5} M to explore the effect of concentration on the spectral behaviour. No absorption or phosphorescence excitation measurements were carried out at low temperature because of the opacity of the matrix. In order to obtain the triplet lifetimes and their dependence on both exciting and emission wavelengths, intensity measurements were performed at various speeds of the phosphoroscope chopper with all other experimental conditions kept constant. The triplet lifetimes were evaluated from the slopes of semilogarithmic plots of the inten-

sity ratios I°/I versus the reciprocal of the rotation frequency of the chopper. This frequency was calibrated using the phosphorescence decay of acetophenone in methylcyclohexane (3 ms [4]). The calibration plot was found to be linear up to a reduction in the intensity to approximately 15% of its initial value, corresponding to a rotation frequency of 30 Hz. The deviation observed below this value was assumed to be due to the experimental uncertainty at low rotation speeds rather than to non-exponential decay kinetics [4]. Therefore no quantitative measurements were performed with chopper frequencies lower than 30 Hz. Thus lifetime values in the range 1 - 80 ms could be measured with reasonable accuracy ($\pm 5\%$). Only a rough estimate was feasible for longer lifetimes, whilst differences in lifetimes longer than 300 ms could not be discriminated. Phosphorescence lifetime measurements by the pulse technique previously described [8] led to less meaningful results because the exciting and emission wavelengths could not be selected by filters with the same accuracy as that attained by the monochromators of the fluorometer.

3. Results

All the compounds studied exhibited multiple phosphorescence emission in acetic acid solution at liquid nitrogen temperature. There was appreciable overlap of the components but in most cases they could be partially or completely resolved by varying the exciting wavelength, the concentration or the speed of the phosphoroscope chopper. Although the quantum yield measurements were not reliable at 77 K because of the opacity of the matrix, the total emission intensities were assumed to be approximately comparable with each other, with the exception of 2-OHB for which the emission was barely detectable. For this reason the data referring to this compound are very uncertain.

Three different types of bands were detected in the phosphorescence spectra. We shall refer to them as α , β and γ phosphorescence. They were differently characterized by the emission and exciting wavelengths and lifetimes, were differently affected by the substituent and the concentration and exhibited a different vibronic structure. Examples of α , β and γ phosphorescence are shown in Fig. 1.

The lifetime and triplet energy values for the multiple components are reported in Tables 1 and 2 for ketones I and ketones II respectively. Generally, the lifetime values can be considered to be reasonably accurate for the short-lived emissions, but only limiting values are indicated for the long-lived emissions. Approximate values are also reported for those cases where the measurement conditions could not be chosen in such a way as to obtain linear plots of $\log(I^{\circ}/I)$ versus time. Examples of the experimental decay curves are shown in Figs. 1 and 2. The E_T values reported in Tables 1 and 2 refer to the highest energy band or shoulder in each spectrum and are less accurate in those cases where the spectra were so broad that no sharp 0-0 bands were observed (generally, for γ phosphorescence).

The three types of emission are characterized as follows.

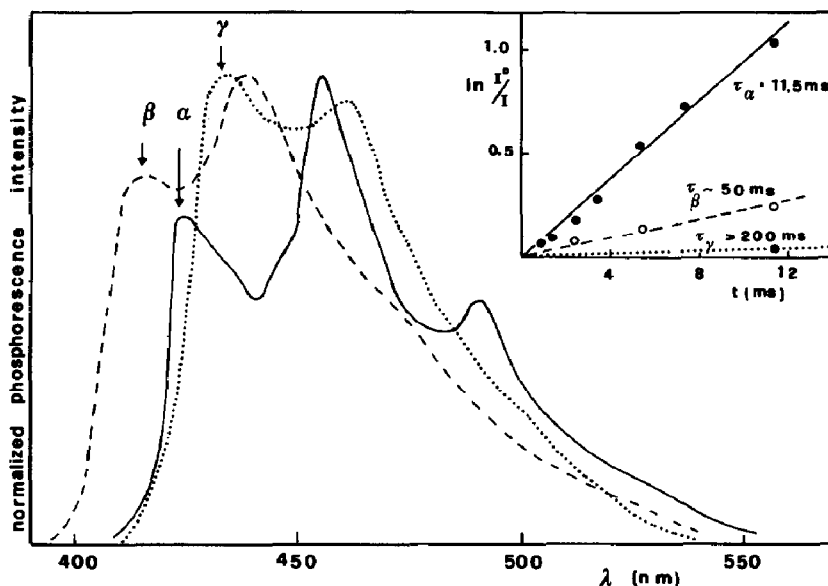


Fig. 1. Phosphorescence emissions of 4,4'-CH₃OB in acetic acid solution at 77 K: —, α phosphorescence ($c = 9 \times 10^{-3}$ M; $\lambda_{\text{exc}} = 380$ nm); ---, β phosphorescence ($c = 10^{-4}$ M; $\lambda_{\text{exc}} = 310$ nm); ···, γ phosphorescence ($c = 8 \times 10^{-4}$ M; $\lambda_{\text{exc}} = 370$ nm). Decay plots for the three emissions are shown in the inset.

TABLE 1

Triplet energies E_T and lifetimes τ_T of ketones I at room temperature and liquid nitrogen temperature

Ketones I	293 K		77 K			
	E_T ($\times 10^3 \text{ cm}^{-1}$)	τ_T^a ($\times 10^{-3}$ s)	α phosphorescence		β phosphorescence	
			E_T ($\times 10^3 \text{ cm}^{-1}$)	τ_T ($\times 10^{-3}$ s)	E_T ($\times 10^3 \text{ cm}^{-1}$)	τ_T ($\times 10^{-3}$ s)
4-COOHB	22.9	0.041	23.2	6.2	23.9	65
4,4'-ClB	23.5	0.026	23.1	4.2	24.1	20
3-BP	23.3	0.007	23.5	4.0	24.3	32
B	23.9	0.035	23.4	4.0	24.8	40

^aData taken from ref. 9.

α phosphorescence is a short-lived emission ($\tau_\alpha \approx 4 - 15$ ms) which exhibits a sharply structured progression ($\Delta\bar{\nu} = 1600 \text{ cm}^{-1}$). This emission was observed for both classes of compounds and was the lowest energy transition for all ketones I and for 4-OHB and 4,4'-CH₃OB. Electron-withdrawing substituents have little effect on the energy and lifetime, whereas electron-releasing substituents produce an appreciable increase in the emission and excitation energies. A decrease in the contribution of α phosphorescence to the total emission was observed when both the concentration and the exciting wavelength were decreased as shown in Figs. 3 and 4 for B. Therefore this

TABLE 2

Triplet energies E_T and lifetimes τ_T for ketones II at liquid nitrogen temperature

Ketones II	α phosphorescence		β phosphorescence		γ phosphorescence	
	E_T ($\times 10^3$ cm $^{-1}$)	τ_T ($\times 10^3$ s)	E_T ($\times 10^3$ cm $^{-1}$)	τ_T ($\times 10^3$ s)	E_T ($\times 10^3$ cm $^{-1}$)	τ_T ($\times 10^3$ s)
4,4'-CH ₃ OB	23.7	11.5	23.9	≈ 50	≈ 23	> 200
4-OHB	23.5	13	23.6	> 200		
4-NH ₂ B	23.8	17	22.5	30	≈ 20	> 300
2-OHB	24.4	< 20		> 100		
2-NH ₂ B	24.6	13	≈ 22	≈ 30	≈ 21	> 50
MK	23.8	11	21.5	> 300	≈ 20	> 300

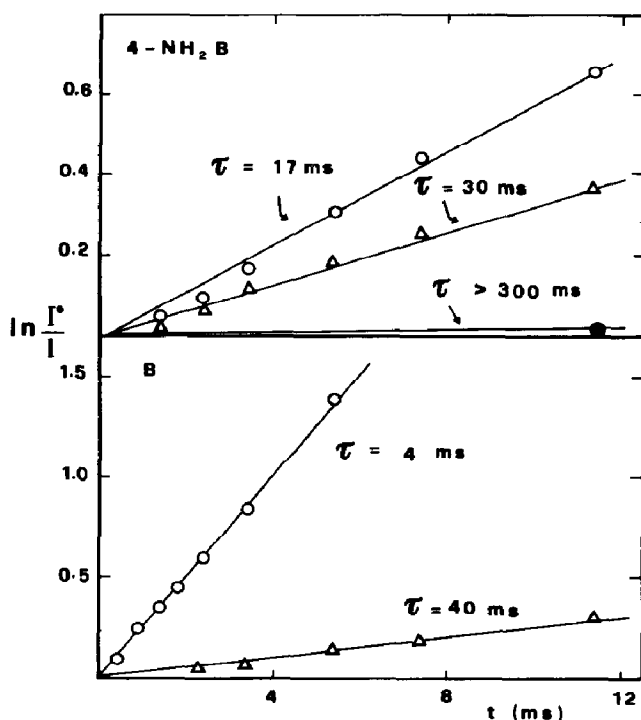


Fig. 2. Decay plots for the multiple emissions of B (○, α phosphorescence ($c = 1.7 \times 10^{-2}$ M; $\lambda_{exc} = 360$ nm; $\lambda_{em} = 460$ nm); Δ , β phosphorescence ($c = 3.5 \times 10^{-4}$ M; $\lambda_{exc} = 280$ nm; $\lambda_{em} = 400$ nm)) and 4-NH₂B (○, α phosphorescence ($c = 10^{-2}$ M; $\lambda_{exc} = 270$ nm; $\lambda_{em} = 420$ nm); Δ , β phosphorescence ($c = 7 \times 10^{-4}$ M; $\lambda_{exc} = 280$ nm; $\lambda_{em} = 445$ nm); ●, γ phosphorescence ($c = 7 \times 10^{-4}$ M; $\lambda_{exc} = 330$ nm; $\lambda_{em} = 505$ nm)) in acetic acid solution at 77 K.

transition could be isolated for all ketones I by the excitation of relatively concentrated solutions ($c > 5 \times 10^{-3}$ M) at low energy ($\lambda_{exc} \approx 380$ nm). In the case of ketones II, it could be isolated only for 2-NH₂B ($\lambda_{exc} = 270$ nm; $c = 6 \times 10^{-3}$ M) and for 4-OHB and 4,4'-CH₃OB, which exhibited an intermediate behaviour. However, measurements of the triplet lifetime were generally

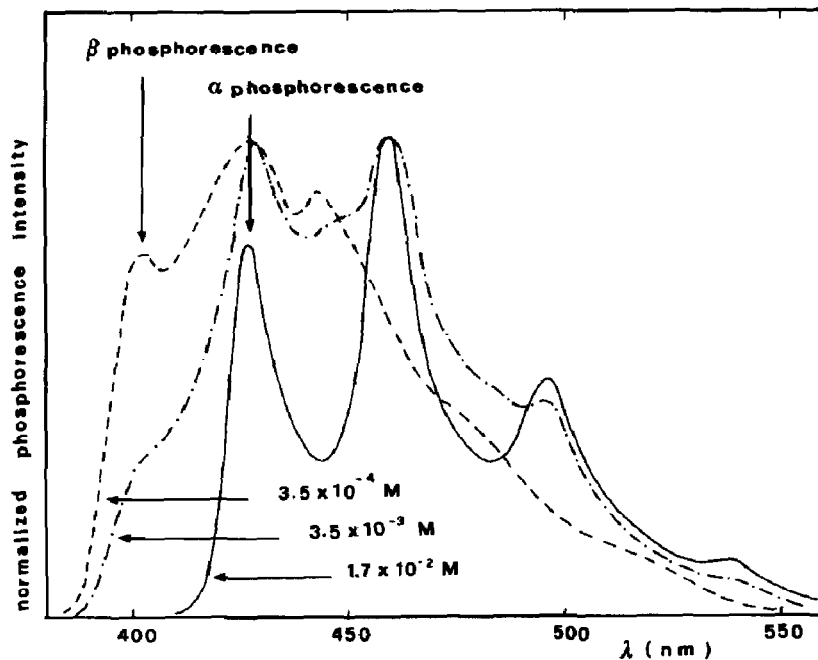


Fig. 3. Effect of concentration on the phosphorescence emission of B in acetic acid solution at 77 K.

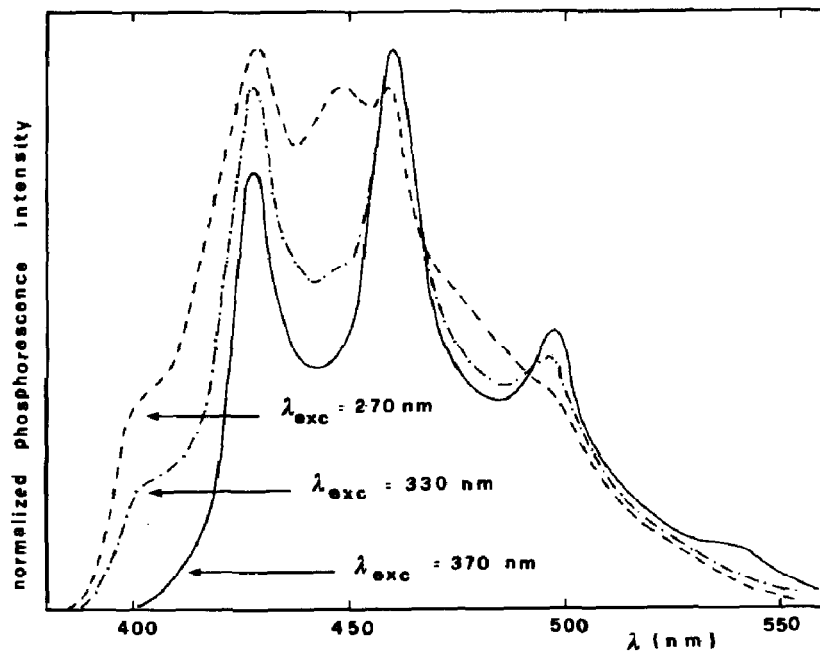


Fig. 4. Effect of the exciting wavelength on the phosphorescence of B in acetic acid solution at 77 K ($c = 1.7 \times 10^{-3}$ M).

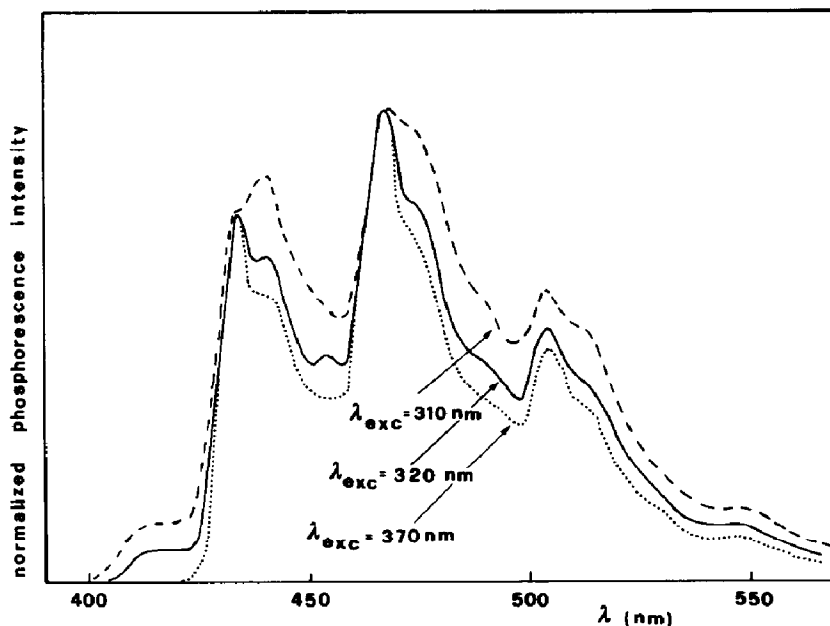


Fig. 5. Effect of the exciting wavelength on the components of the α phosphorescence of 4,4'-ClB ($c = 9 \times 10^{-3}$ M).

feasible at an emission wavelength where the overlap with the other phosphorescence components was negligible. The intensity of the α phosphorescence decreased under prolonged irradiation.

An interesting feature which resulted from the contribution of three nearby transitions ($\bar{\nu}_{0-0}$ values of 23 100, 22 700 and 22 000 cm^{-1}) with the same vibrational spacing ($\Delta\bar{\nu} = 1600 \text{ cm}^{-1}$) and similar lifetimes was observed for the α phosphorescence of 4,4'-ClB. The relative intensities of these bands changed when the exciting wavelength was changed as shown in Fig. 5. This behaviour is likely to occur for all the compounds but could only be resolved for 4,4'-ClB.

β phosphorescence is a relatively long-lived emission ($\tau_{\beta} > 20 \text{ ms}$) which is generally rather broad. A vibrational progression is still detectable ($\Delta\bar{\nu} \approx 1300 - 1600 \text{ cm}^{-1}$). Both electron-withdrawing and electron-releasing substituents lower the energy of this transition. Contrary to what was observed for α phosphorescence, this emission appears at higher excitation and emission energies for ketones I than for ketones II except for 4-OHB and 4,4'-CH₃OB. Also, the effect of concentration is opposite to what was observed for α phosphorescence, since a decrease in concentration increases the intensity. Therefore this emission could be isolated for ketones I and for 4-OHB and 4,4'-CH₃OB by the excitation of low concentration ($c < 10^{-3}$ M) solutions at high energy ($\lambda_{\text{exc}} \approx 280 \text{ nm}$) and low chopper rotation speed (about 50 Hz). Complete resolution was impossible for the other ketones; the best result that could be obtained is illustrated in Fig. 6 for 4-NH₂B. The β phosphorescence of 2-OHB was detected only by the decrease in the slope of the decay plot

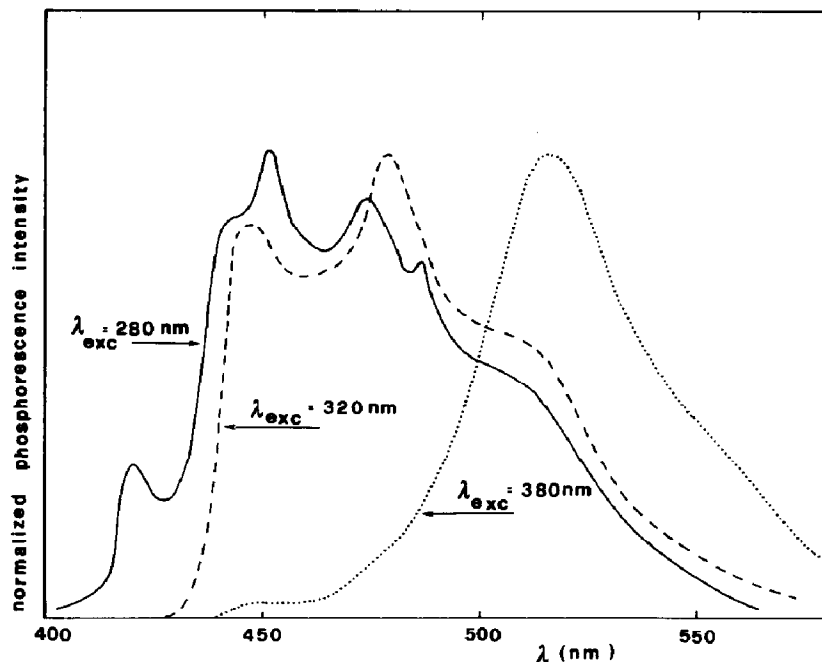


Fig. 6. Phosphorescence emissions of 4-NH₂B ($c = 7.6 \times 10^{-3}$ M) in acetic acid solution at 77 K; —, prevalent α phosphorescence; - - -, prevalent β phosphorescence; · · ·, prevalent γ phosphorescence.

with decreasing concentration. In contrast with α phosphorescence, this emission was stable under irradiation.

The γ phosphorescence is a more long-lived emission ($\tau_\gamma > 100$ ms) which is very broad. This emission was observed for some ketones II (4,4'-CH₃OB, 2-NH₂B, 4-NH₂B and MK) at low excitation energies ($\lambda_{exc} > 330$ nm). An increase in concentration produces an increase in the intensity and a shift of the maximum to a lower energy. No effect was produced by irradiation.

4. Discussion

4.1. General remarks

The occurrence of multiple phosphorescence spectra is not unusual for carbonyl compounds. A single explanation for their origin has not been given and the question is still open. The alternative explanations which have been proposed can be summarized as follows.

(i) The double emission arises from two nearby triplet states of different orbital origin, presumably the n, π^* and π, π^* lowest triplet levels or some mixture of them [13 - 17].

(ii) The carbonyl compound interacts with the solvent or is constrained by the solvent cage in a polar environment, giving rise to different excited species and/or states [18 - 25].

(iii) The carbonyl compound can exist in various molecular geometries, each of them being characterized by different excitation and emission spectra [26, 27].

(iv) The multiple emission results from the reversible [28] or irreversible [29] formation of photoproducts.

The results obtained for the molecules under study allowed us to gain some insight into the origin of the multiple phosphorescence in acetic acid solution at 77 K. The vibronic structure and lifetime give information regarding the orbital character of the excited state involved. The effects of concentration, irradiation and exciting wavelength provide evidence that the multiple phosphorescence originates from different molecular species. In fact the wavelength dependence of the emissions can be explained by assuming that distinct ground state spectroscopic species are excited. This hypothesis is also supported by the irradiation effect because only the species which is responsible for the α phosphorescence is photosensitive. The concentration effect provides information on the nature of the different species which can originate from either intramolecular distortions (different geometrical conformations) or intermolecular processes (solute-solvent or solute-solute interactions).

4.2. Assignment of the emissions

The very short lifetime and the regular 1600 cm^{-1} spacing between vibronic bands enables the α phosphorescence to be assigned to the emission from an n,π^* excited state. The close similarity in structure and the wavelength dependence of the multiple α components observed for 4,4'-ClB (Fig. 5) suggest that they belong to molecular species with only slightly different electronic structures. They are probably three conformational isomers which differ in the mutual orientation of the benzene rings.

The longer lifetime and the broadness and slightly lower vibrational frequency of the β phosphorescence suggest that it originates from a π,π^* excited state or from a mixed $n,\pi^*-\pi,\pi^*$ state.

A comparison of the effects of concentration on α and β phosphorescence shows that their contributions to the total emission can be inverted by varying the concentration when the excitation is performed at appropriate wavelengths (Fig. 3). Since β phosphorescence, which possesses the most marked π,π^* character, increases in intensity on dilution, it should come from a specific solute-solvent interaction leading to either a hydrogen-bonded species or a molecule constrained in a more polar solvent environment. In contrast, the triplet responsible for the α phosphorescence, which possesses a sharp n,π^* character, should belong to either solvent-free excited molecules or molecules in a less polar solvent cage.

The effect of concentration on both the intensity and the energy of γ phosphorescence suggests that this emission may originate from microcrystallites in different states of aggregation. An emission of this type has been observed for MK in an alkane solution [26].

4.3. Effect of the substituents

The effect of electron-releasing substituents on α and β phosphorescence is as expected since they increase the n,π^* energy and lower the π,π^* energy. In contrast, the effect of the electron-withdrawing substituents on the π,π^* β phosphorescence is opposite to that expected. The inductive effect of the chlorine substituent, which would increase the π,π^* energy, is exceeded by conjugative effects [5] so that the $^3\pi,\pi^*$ state for 4,4'-ClB may lie at a lower energy than that of the unsubstituted compound. The inductive effect of the heterocyclic nitrogen atom (3-BP) and both the inductive and conjugative effects of the carboxylic group (4-COOHB) should increase the π,π^* energy. There is no obvious explanation for the opposite behaviour observed. Tentatively, we propose that the stabilization of the π,π^* states when electron-attracting groups are introduced is due to a decrease in the repulsion between the two aromatic rings and hence to a greater planarity and overlap between the orbitals of the rings and those of the carbonyl group.

4.4. Comparison of low temperature and room temperature results

The classification of the compounds being investigated as ketones I and ketones II is mainly based on their room temperature behaviour.

The absorption spectra of ketones I show the lowest n,π^* transition which is characterized by low extinction coefficients ($\log \epsilon = 2.1 - 2.6$) in the 300 nm region. Solvent and substituent effects are in agreement with this assignment [8]. There is no sign of an n,π^* transition in the absorption spectra of ketones II which exhibit a fairly intense band ($\log \epsilon = 3 - 4$), probably a π,π^* transition with some CT character, even in those cases (4-OHB and 4,4'-CH₃OB) where the n,π^* transition was evident in less polar solvents [8].

Ketones I show phosphorescence emission in acetic acid solution at room temperature, whereas no phosphorescence emission is detectable for ketones II under the same conditions. The triplet energies E_T and lifetimes τ_T for ketones I are reported in Table 1. Exponential decay curves indicate a single emitting state at room temperature [9]. The vibrational structure ($\Delta\bar{\nu} \approx 1600 \text{ cm}^{-1}$), the regular substituent effect (energy lowering by electron-withdrawing groups) and the singlet-triplet energy difference ($\Delta\bar{\nu}_{T_1-S_1} < 3000 \text{ cm}^{-1}$) indicate an n,π^* transition [1, 6]. The good linear relationship ($\rho = 0.83, r = 0.990$) between the edges of the phosphorescence emission and the maxima of the lowest n,π^* absorption, which is shown in Fig. 7, substantiates the hypothesis that the same type of excited state might well be responsible for the room temperature emission of all ketones I [30, 31].

Finally, ketones I and II exhibit different behaviour towards a suitable energy acceptor ($\text{Ru}(\text{bpy})_3^{2+}$) since ketones I act as sensitizers whilst ketones II do not [8]. However, ketones II are quenchers of the room temperature phosphorescence of ketones I. The kinetic parameter k_q for this process approaches the diffusional value, except for 4,4'-CH₃OB and 4-OHB for which k_q has a noticeably lower value. This behaviour has been attributed to the occurrence of reversible energy transfer [9].

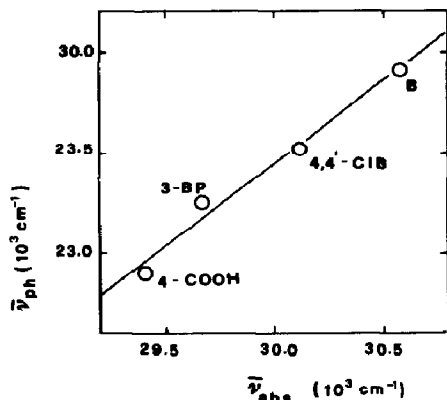


Fig. 7. Correlation diagram of the phosphorescence edges of ketones I against the n, π^* absorption maxima at room temperature.

The low temperature results provide further support for the hypothesis of reversible energy transfer, even though some other details of the mechanism proposed for the interaction between ketones I and ketones II should be reviewed.

We have determined that the solute-solvent interaction gives rise to at least two different species which are characterized by α and β phosphorescence at 77 K and differ from each other with respect to hydrogen bonding and/or environmental polarity. The local environment should also be important in determining the room temperature properties. Frozen solutions obtained by sudden cooling should provide data on the equilibrium ratio of solvent-free to solvent-bonded species which exists at room temperature. However, we have no quantitative information regarding excitation spectra and emission quantum yields, and consequently it has not been possible to determine just how important a role each species plays in determining the room temperature behaviour. All that we can say is that α phosphorescence can be more easily isolated from ketones I than β phosphorescence can (except in the case of 4-COOHB), whereas more evidence for β phosphorescence is obtained for ketones II. When the electronic properties of the substituents are taken into account, it is clear that hydrogen-bonded species should be stabilized by electron-releasing substituents and that the stabilization should increase on CT excitation. Therefore, also considering that the room temperature absorption spectra should correspond to the prevailing form, we propose that ketones I are almost exclusively in the solvent-free form whilst ketones II are present in solution essentially as solvent-bonded species.

In the light of this hypothesis only the triplet belonging to the solvent-free species (ketones I) is able to emit phosphorescence and to sensitize the phosphorescence of an acceptor at room temperature because of its relatively long lifetime in solution, whereas the triplet formed by the solvent-bonded species (ketones II) should undergo very fast radiationless decay at room temperature. Therefore it neither emits phosphorescence nor sensitizes.

The intermediate behaviour of 4,4'-CH₃OB and 4-OHB fits this hypothesis well since these poor electron-releasing substituents should give rise to π,π^* excited states with a slight CT character. Therefore no stabilization occurs on excitation of the hydrogen-bonded molecules and the π,π^* emitting triplet level lies above that of the solvent-free molecule. A sizable number of solvent-free molecules should also be present at room temperature even though their absorption will be obscured by the more intense π,π^* absorption of the solvent-bonded species. Their concentration is not sufficient for the room temperature phosphorescence to be observed, but their triplet energy is high enough to make the back transfer exothermic, especially to 4-COOHB and 4,4'-ClB for which in fact the lowest k_q values were found [9].

Generally, the donor concentrations used in the quenching experiments were so high ($c > 6 \times 10^{-3}$ M) that the effect of the solvent-bonded species could not be detected at room temperature. However, the quencher concentrations were low enough ($c \approx 10^{-5} - 10^{-6}$ M) to have practically only the solvent-bonded species in solution. Only in the case of 4,4'-CH₃OB and 4-OHB were concentrations of the order of magnitude of 10^{-4} M necessary for quenching to be observed. In these cases the concentration, as well as the nature of the substituent, contribute to make the participation of the solvent-free molecules in the interaction mechanism efficient.

4.5. Concluding remarks

The results described show that multiple emission must be considered to be a general phenomenon for aryl ketones in acetic acid solution at 77 K. This does not disagree with the report by Groenen and Koelman [26] that the phosphorescence emissions from 4,4'-ClB and 4,4'-CH₃OB in a different solvent do not depend on the wavelength of excitation as the emissions from 4,4'-NH₂B and MK do. In fact the acetic acid solvent, because of its moderately high polarity and/or hydrogen bonding ability, contributes to the gradual switching of the excited states as do the substituents, thus allowing the nature of the lowest emitting state to be varied progressively from a predominantly n,π^* configuration (α phosphorescence) to a predominantly π,π^* or CT configuration (β phosphorescence) by changing the substituent as is illustrated in the correlation scheme of Fig. 8. This state switching does not occur within a specific molecular configuration but is the consequence of a solute-solvent interaction favoured by electron-releasing substituents and much more by CT excitation. The difference in the 0-0 frequency between α and β phosphorescence gives the stabilization energy on excitation of the solvent-bonded molecule relative to the solvent-free molecule which is of the order of 5 kcal mol⁻¹ for the amino- and dimethylamino-substituted compounds. The value of the stabilization energy on excitation should be of importance in determining the solvent reorientation following excitation which should occur at room temperature. This implies that, compared with the ground state, more solvent-free molecules will exist in the excited state for ketones I and more solvent-bonded molecules will exist in the excited state for ketones II. Owing to the proximity of the triplet levels for 4,4'-CH₃OB

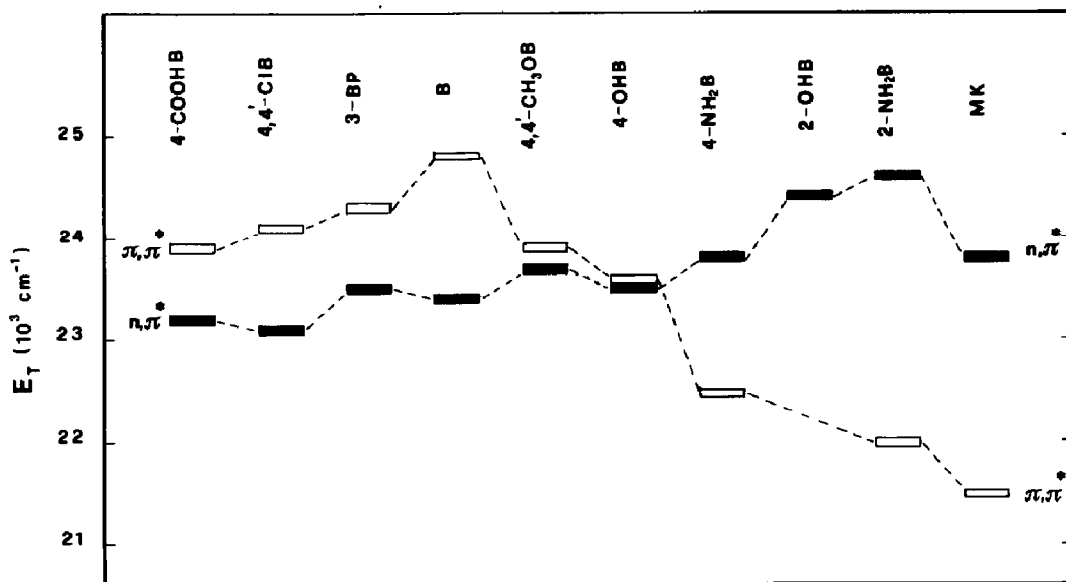


Fig. 8. Correlation diagram showing the dispositions of the emitting triplet states of aryl ketones in acetic acid solution at 77 K.

($\Delta\bar{\nu} \approx 200 \text{ cm}^{-1}$) and 4-OHB ($\Delta\bar{\nu} \approx 100 \text{ cm}^{-1}$), such reorientation should be less important for these molecules.

Finally, we must recall that B [20, 32] and 3-BP [33] also exhibit similar behaviour in aqueous solution. In these cases the hydrogen-bonded form has been found to prevail in acidic solution where the sensitizing power and the emission intensity at room temperature decrease. Substituted benzophenones could not be examined in water because of their insolubility. However, in a mixed solvent (water-ethanol) the amino and hydroxy derivatives showed multiple emissions at 77 K and a lack of sensitizing power and phosphorescence emission at room temperature as they were in hydrogen-bonded form.

We can generalize these results and state that aryl ketones are always present in hydrogen bonding solvents as solvent-bonded and solvent-free molecules. The nature of the substituent and the local environment govern which form plays the most important role in determining the photophysical behaviour.

Acknowledgment

A grant from the Italian Consiglio Nazionale delle Ricerche is acknowledged.

References

- 1 G. Porter and P. Suppan, *Trans. Faraday Soc.*, 61 (1955) 1664.
- 2 J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, 66 (1962) 2456.

- 3 N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser and R. Dusenbery, *J. Am. Chem. Soc.*, **89** (1967) 5466.
- 4 N. C. Yang and R. Dusenbery, *J. Am. Chem. Soc.*, **90** (1968) 5899.
- 5 P. J. Wagner, A. E. Kemppainen and H. N. Schott, *J. Am. Chem. Soc.*, **95** (1973) 5604.
- 6 R. G. Brown and G. Porter, *J. Chem. Soc., Faraday Trans. I*, **73** (1977) 1569.
- 7 P. J. Wagner, *Pure Appl. Chem.*, **49** (1977) 259.
- 8 G. Favaro and F. Masetti, *J. Phys. Chem.*, **83** (1979) 2129.
- 9 G. Favaro and F. Masetti, *J. Photochem.*, **15** (1981) 241.
- 10 G. Favaro, *Chem. Phys. Lett.*, **21** (1973) 401.
- 11 G. Favaro, *Chem. Phys. Lett.*, **23** (1973) 592.
- 12 M. A. Winnick and C. K. Lee, *Mol. Photochem.*, **6** (1974) 477.
- 13 W. Klöpffer, *Chem. Phys. Lett.*, **11** (1971) 482.
- 14 N. C. Yang and S. Murov, *J. Chem. Phys.*, **45** (1966) 4358.
- 15 M. E. Long and E. C. Lim, *Chem. Phys. Lett.*, **20** (1970) 413.
- 16 E. Migirdicyan, *Chem. Phys. Lett.*, **12** (1972) 473.
- 17 N. Kanamaru, M. E. Long and E. C. Lim, *Chem. Phys. Lett.*, **26** (1974) 1.
- 18 R. Rusakowicz, G. W. Byers and P. A. Leermakers, *J. Am. Chem. Soc.*, **93** (1971) 3263.
- 19 R. D. Rauth and P. A. Leermakers, *J. Am. Chem. Soc.*, **90** (1966) 2246.
- 20 G. Favaro, *Chem. Phys. Lett.*, **31** (1975) 87.
- 21 E. Malawer and C. Marzacco, *J. Mol. Spectrosc.*, **46** (1973) 341.
- 22 P. R. Callis and R. W. Wilson, *Chem. Phys. Lett.*, **13** (1972) 417.
- 23 D. M. Rayner, P. K. Tolg and A. G. Szabo, *J. Phys. Chem.*, **82** (1978) 86.
- 24 H. J. Pownall and J. R. Huber, *J. Am. Chem. Soc.*, **93** (1971) 6429.
- 25 P. J. Wagner, M. May and A. Haug, *Chem. Phys. Lett.*, **13** (1972) 545.
- 26 E. J. J. Groenen and W. N. Koelman, *J. Chem. Soc., Faraday Trans. II*, **74** (1978) 58, 69.
- 27 H. J. Pownall, R. E. Connors and J. R. Huber, *Chem. Phys. Lett.*, **22** (1973) 403.
- 28 Y. Kanda, J. Stanislaus and E. C. Lim, *J. Am. Chem. Soc.*, **91** (1969) 5085.
- 29 N. Y. C. Chu and D. R. Kearns, *J. Am. Chem. Soc.*, **94** (1972) 2619.
- 30 A. A. Lamola, *J. Chem. Phys.*, **47** (1967) 4810.
- 31 G. Favaro, *J. Photochem.*, **15** (1981) 89.
- 32 G. Favaro and G. Bufalini, *J. Phys. Chem.*, **80** (1976) 800.
- 33 G. Favaro and F. Masetti, *J. Phys. Chem.*, **82** (1978) 1213.