

## Excited state dynamics of Michler's ketone: a laser flash photolysis study

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**Abstract**—Steady state absorption and fluorescence as well as the time resolved absorption studies in the pico and subpicosecond time domain have been performed to characterize the excited singlet and triplet states of Michler's ketone (MK). The nature of the lowest excited singlet ( $S_1$ ) and triplet ( $T_1$ ) states depends on the polarity of the solvent — in nonpolar solvents they have either pure  $n\pi^*$  character or mixed character of  $n\pi^*$  and  $\pi\pi^*$  states but in more polar solvents the states have CT character. Concentration dependence of the shapes of the fluorescence as well the excited singlet and triplet absorption spectra provide the evidence for the association of the MK molecules in the ground state.

### INTRODUCTION

One of the widely studied and important photochemical reactions undergone by the aromatic carbonyl compounds is the photoreduction by hydrogen atom abstraction from the suitable hydrogen atom donors, may be the solvent or another solute [1–15]. Effects of the substituent groups as well as the solvents towards these photoreduction reactions have been well studied by different groups in order to elucidate the nature of the excited triplet states. The reactivity of this class of compounds has been shown to depend on the electron distribution in the lowest energy excited triplet ( $T_1$ ) state, i.e. whether it is  $n\pi^*$ ,  $\pi\pi^*$  or charge transfer (CT) state [7, 10, 11, 16]. The relative positions of these three kinds of excited

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states of the aromatic carbonyl compounds, both in the singlet as well as in the triplet manifold, have been seen to depend on the nature of the substituent as well as the solvent [17–20]. A vast number of studies on the reactivity of these compounds have established that the  $n\pi^*$  triplet state is highly reactive towards the photoreduction reaction by hydrogen atom abstraction in comparison with that of the  $\pi\pi^*$  or CT triplet state [10, 11, 17, 21–23].

Benzophenone, the parent of the aromatic carbonyl compounds, has the lowest energy excited singlet and triplet states of  $n\pi^*$  configuration in all kinds of solvents [24, 25]. The triplet state, which is produced with a quantum yield of unity from its precursor singlet state via intersystem crossing process, is highly reactive towards photoreduction reaction [17, 26]. However, on substitution with electron donating groups, such as OH, OCH<sub>3</sub>, NH<sub>2</sub> and N(CH<sub>3</sub>)<sub>2</sub> onto the aromatic rings of benzophenone, the relative positions of the  $n\pi^*$ ,  $\pi\pi^*$  and CT states in either of the singlet or the triplet manifolds are largely affected by the solvent polarity [17–19, 26, 27]. Hence, the reactivity of the substituted benzophenone is largely varied in different kinds of solvents.

Michler's ketone (MK) [4,4'-bis-(dimethylamino)-benzophenone] has been the subject of many investigations for its interesting photophysical and photochemical properties [18, 19, 28–32]. MK exhibits temperature dependent phosphorescence and transient triplet–triplet absorption spectra at low temperature [29]. These results have been interpreted in terms of solvation and conformational changes in the triplet state. The triplet yield for MK is strongly dependent on the solvent characteristics and varies from near unity in hydrocarbon solvents to very small value (<0.2) in alcoholic media [19]. Suppan [31] not only reported a pronounced dependence of the reactivity of the triplet of MK on the nature of the solvents but also on the excitation wavelength. However, systematic work of Schuster *et al.* [19] on this problem proved that this wavelength dependence of the reactivity of the triplet and the photoreduction yield is rather related to the dependence of the triplet lifetime on MK concentration due to self-quenching reaction and product absorption in the excitation wavelength. Schuster *et al.* [19] also presented some arguments in relation to the possible formation of triplet excimers. Liptay *et al.*, however, concluded from their steady state fluorescence anisotropy study in ethanol that molecules of MK form molecular aggregates of large mass by association and the excited state of MK has an unusually short lifetime which is shorter than the relaxation time for orientational redistribution of the solvent molecules [32]. In this work, we have performed the laser flash photolysis study in sub-pico and picosecond time domain in different kinds of solvents to investigate the nature of the excited singlet and triplet states of MK, their lifetimes as well as to provide evidence regarding the association of MK molecules in solution from their transient absorption characteristics.

## EXPERIMENTAL

MK (about 98% pure), obtained from Aldrich (USA), was purified by repeated recrystallization from methanol. All the solvents used were of spectroscopic grade (Spectrochem, India) and used as received without further purification. High purity grade nitrogen gas (Indian Oxygen, purity >99.9%) was used to deaerate the samples. All the experiments were carried out at room temperature ( $296 \pm 1$  K) unless specified otherwise. Steady state absorption spectra were recorded on a Shimadzu model UV-160A spectrophotometer.

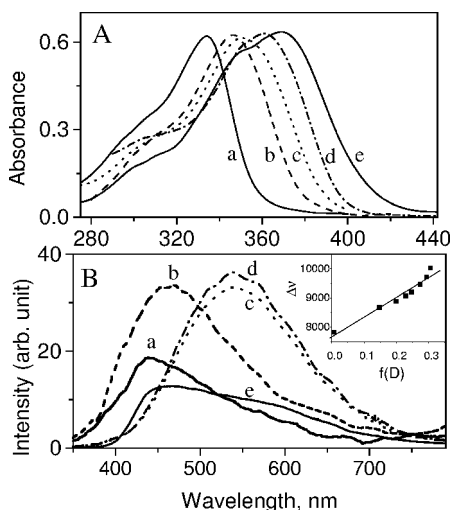
Picosecond transient absorption spectrometer has been described in detail elsewhere [27]. Briefly, the third (355 nm, 3 mJ) harmonic output pulses of 35 ps duration from an active-passive mode locked Nd:YAG laser (Continuum, model 501-C-10) were used for excitation and the continuum (400–900 nm) probe pulses were generated by focusing the residual fundamental in H<sub>2</sub>O/D<sub>2</sub>O mixture. The probe pulses were delayed with respect to the pump pulses using an 1 m long linear translational stage and the transient absorption at different probe delays (upto 6 ns) were recorded by an optical multichannel analyser (Spectroscopic instruments, Germany) interfaced to an IBM-PC. The zero delay position has been assigned to that when the probe light reaches the sample just after the end of the pump pulse. Steady state fluorescence spectra were recorded with this same set up by blocking the probe light.

Relaxation processes taking place in a time domain faster than 50 ps, have been studied using a home-built subpicosecond transient absorption spectrometer. Laser pulses of 100 pico-Joule energy and 70 fs duration at 620 nm, generated from an argon ion pumped colliding pulse mode-locked (CPM) dye laser oscillator, are amplified to about 300  $\mu$ J pulses of 100 fs duration in a five stage dye amplifier pumped by a Nd:YAG laser working at 30 Hz. Pump pulses at 310 nm are generated by doubling the 620 nm output from the amplifier in a 0.5 mm BBO crystal and the residual fundamental was used to generate the white light continuum (400–950 nm) in a flowing water medium of 1 cm path length. The sample solutions were kept flowing through a quartz cell of 2 mm path length. The transient absorption spectra were recorded using the dual diode array optical multichannel analyser and the decay dynamics at a particular wavelength region (10 nm width) were monitored using two photodiodes coupled with the boxcar integrators. The overall time resolution of the absorption spectrometer was determined to be about 500 fs by measuring the growth of the S<sub>1</sub>  $\rightarrow$  S<sub>n</sub> absorption of 1,4-diphenylbutadiene in cyclohexane solution at 650 nm. The transient absorption spectra, being reported here, have been recorded only after a delay of more than one picosecond to avoid any distortion due to group velocity dispersion in the monitoring wavelength region, 400–950 nm.

## RESULTS AND DISCUSSION

Figure 1 shows the ground state absorption and steady state fluorescence spectra of MK in different solvents. Absorption spectra in each solvent is characterized by two main bands. One of them is centered at around 310 nm and it is assigned due to  $n\pi^*$  transition since its maximum is more or less independent of solvent characteristics. The other band is more intense and its shape and maximum position is very sensitive to solvent characteristics. This band has been assigned due to  $\pi\pi^*$  transition [17]. The band maximum shifts to longer wavelength and also the spectral width (FWHM) of the band increases with increase in solvent polarity. The shift of the maximum of the  $\pi\pi^*$  band is as much as 24 nm in dimethylsulfoxide (DMSO) and 32 nm in methanol with respect to that in cyclohexane (CH). The large shift of the maximum of this absorption band in more polar solvents indicates the stabilization of the  $S_1$  state due to its polar character. In addition, the larger shift in methanol than that in acetonitrile (ACN) and DMSO indicates the stabilization of the excited singlet state via formation of intermolecular hydrogen bonds [27, 32]. The extinction coefficient values at the peak of the absorption in different solvents have been reported to be in the range  $3.7\text{--}4.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  [17].

The maximum of the fluorescence band of MK is also sensitive to solvent polarity — the maxima appear at 440 nm in cyclohexane, 465 nm in benzene (BZ) and 545 nm in acetonitrile and DMSO. The fluorescence band in methanol is very broad without having any well-defined maximum, which is, possibly, due to the presence of more than one excited state species present in solution. These species are differently hydrogen bonded with the solvent molecules. According to



**Figure 1.** (A) Absorption and (B) fluorescence spectra of MK in different solvents: cyclohexane (a), benzene (b), acetonitrile (c), DMSO (d) and methanol (e). Inset: the Lippert–Mataga plot for the fluorescence Stokes’ shift with the polarity parameter,  $f(D, n)$ , in benzene-acetonitrile solvent mixtures.

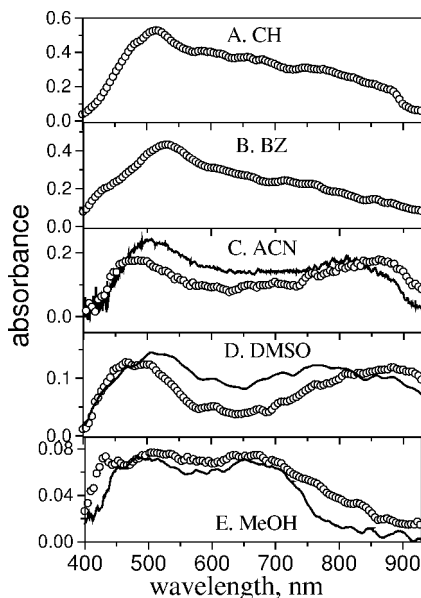
Callis and Wilson [33], there exist at least three kinds of ground state species in a solution of MK in ethanol, most probably two hydrogen-bonded complexes as well as the unassociated molecules. In cyclohexane the fluorescence yield is very low ( $\phi_f = 1.6 \times 10^{-4}$ ). The yield increases gradually with increase in solvent polarity ( $\phi_f$  values are  $1.4, 7.5$  and  $8.0 \times 10^{-3}$  in benzene, acetonitrile and DMSO, respectively). However, in methanol, too, the yield is low ( $\phi_f = 4.0 \times 10^{-3}$ ) due to hydrogen bonding interactions with the solvent. These values agree well with those already reported [24, 32].

The fluorescence maximum shows a continuous shift with increase in solvent polarity of benzene-acetonitrile solvent mixtures of different compositions, in which special kind of solvent interaction, such as intermolecular hydrogen bonding, is absent. The inset of Fig. 1B shows the plot for solvatochromic shift of MK in benzene-acetonitrile solvent mixtures as a function of the reaction field factor  $f(D, n)$ , as defined by the equation (1) ( $D$  and  $n$  are the dielectric constant and refractive index of the solvent, respectively). The change in dipole moment ( $\Delta\mu$ ) due to the  $S_0 \leftrightarrow S_1$  transition, has been calculated to be 6.6 D from the slope of the line representing the least square fit to the plot following the equation (2) [34]. A high  $\Delta\mu$  value indicates that the  $S_1$  state is more polar as compared to that of the ground state. This conclusion is corroborated by the fact

$$f(D, n) = \frac{D - 1}{2D + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad (1)$$

$$\Delta\nu = \frac{2(\mu_e - \mu_g)^2}{hca^3} f(D, n) + \text{constant}, \quad (2)$$

that the width (FWHM) of the absorption band is increased in more polar solvents (e.g. FWHM values of the  $\pi\pi^*$  band are 1772, 2664, 3040  $\text{cm}^{-1}$  in cyclohexane, acetonitrile and DMSO, respectively) and that of the emission band decreases with increase in solvent polarity (e.g. FWHM values of the fluorescence band are 5718, 4773, 4750  $\text{cm}^{-1}$  in cyclohexane, acetonitrile and DMSO, respectively). So it is quite justified to conclude that the  $S_1$  state of MK in cyclohexane and benzene has  $\pi\pi^*$  character with symmetrical charge distribution and less CT character but in more polar solvents the CT character of the  $\pi\pi^*$  state is increased due to the fact that more unsymmetrical charge distribution is favoured by the polar medium. A continuous shift of the fluorescence maximum with increase in solvent polarity indicates that the excited singlet state, to which the molecule is excited, itself is a CT state and excludes the possibility of dual emission due to twisted intramolecular charge transfer (TICT) in the excited singlet state as predicted by Shoute [28]. An important point to observe in Fig. 1 that although the characteristics of cyclohexane and benzene are expected to be similar considering the values of the dielectric constants (2.02 and 2.275, respectively), and the reaction field factors, ( $f(D, n) = 0.004$  and  $0.006$ , respectively), in the case of MK, benzene seems to behave as a more polar solvent than cyclohexane. Shift of the absorption peak in benzene with respect to that in cyclohexane is about 10 nm, whereas that in



**Figure 2.** Transient absorption spectra of MK recorded at zero ps (circle) and 5 ns (line) after the 35 ps laser pulses of 355 nm in cyclohexane (CH), benzene (BZ), acetonitrile (ACN), DMSO and methanol (MeOH).

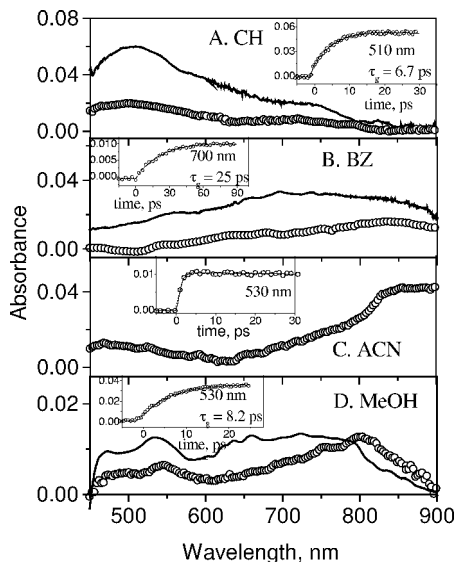
acetonitrile is only about 16 nm. Fluorescence peak is also about 25 nm shifted in benzene as compared to that in cyclohexane. This effect is probably due to non-dipolar character of benzene [27b, 35].

Figure 2 shows the time-resolved transient absorption spectra of MK in different solvents ( $[MK] \sim 2.5 \times 10^{-4} \text{ mol dm}^{-3}$  in cyclohexane and  $5 \times 10^{-5} \text{ mol dm}^{-3}$  in other solvents) due to excitation by 355 nm laser pulses of 35 ps duration. Transient spectra, recorded at zero ps time delay between the pump and probe pulses, i.e. immediately after the laser pulse, in cyclohexane and benzene are very similar. However, the absorption maximum in benzene (530 nm) is red shifted by about 20 nm as compared to that in cyclohexane (510 nm). In both the cases, no evolution of the spectral features is observed upto 6 ns time delay. A comparison between the transient absorption spectrum in benzene as shown in Fig. 2B and that obtained in benzene by our electron pulse radiolysis study [36] and also to that reported by Tahara and Hamaguchi [37], leads us to assign the transient absorption spectra recorded in cyclohexane and benzene obtained in this ps flash photolysis study (Fig. 2A and B) to the triplet state of MK. The life time of the  $T_1$  state in these two solvents have been the subject of many investigations and it has been well established that the lifetime determined experimentally is dependent on the triplet concentration produced and, also, on the concentration of MK used due to T-T annihilation and self quenching reactions, respectively [18–20]. However, the spectral characteristics in pico and subpicosecond time domain are not affected by these intermolecular interactions and hence these aspects will not be discussed here.

In ACN and DMSO, the transient absorption spectra recorded at zero ps and 6 ns time delays show the features different from those observed in benzene and cyclohexane. The spectra recorded at zero ps have two distinct bands with maxima at *ca* 470 and 870 nm and those recorded at 6 ns show the maxima at *ca* 510 and 800 nm. The lifetimes of the  $S_1$  state of MK in these two solvents have been reported to be 640 and 690 ps, respectively, from the fluorescence lifetime measurements [28]. Hence, the transient absorption spectra recorded at zero ps in these solvents can be assigned due to the  $S_1$  state and those recorded at 6 ns to the  $T_1$  state of MK. However, due to very similar nature of the absorption spectra of the  $S_1$  and  $T_1$  states in these solvents, the spectral evolution could not be followed kinetically to determine the lifetime of the  $S_1$  state in the present work. The long lifetimes of the  $S_1$  state in these solvents indicate its CT character and the  $T_1$  state of MK has also been assigned to the CT configuration [17, 19].

In methanol, the transient absorption spectra are very broad but the presence of two bands with maxima at *ca* 515 and 660 nm and 490 and 650 nm in the spectra recorded at zero ps and 5 ns, respectively, after the laser pulse excitation is very evident. The maxima of both the bands show a blue shift as the transient absorption evolves with the delay between the pump and the probe pulses. These kinds of changes in spectral characteristics are very similar to those observed by Hishino and Kogure in their time resolved measurements of the triplet–triplet absorption spectra in soft ethanol glass matrices at different temperatures varying from 77 to 180 K [30]. The blue shifts of the absorption band maxima of the triplet absorption spectra have been assigned due to the reorientation of the intermolecular hydrogen bonded solvent molecules.

Figure 3 shows the time resolved transient absorption spectra of MK in different solvents ( $[MK] \sim 2.5 \times 10^{-4} \text{ mol dm}^{-3}$  in cyclohexane and  $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ , and in other solvents) due to excitation by 310 nm laser pulses of 500 fs duration. In cyclohexane, the spectrum recorded at 1 ps after the laser pulse is seen to have maximum at *ca* 490 nm. With increase in time delay between the pump and the probe pulses the transient absorption increases (as shown in the inset of Fig. 3A) upto about 20 ps and the spectrum recorded at 50 ps time delay shows a maxima at 510 nm. This spectrum is very similar to that obtained due to excitation by 355 nm laser pulses of 35 ps duration (Fig. 2A). The growth lifetime of the transient absorption monitored at 510 nm has been found to be 6.7 ps in this solvent. The short lifetime of the  $S_1$  state of MK in cyclohexane is the characteristic of  $n\pi^*$  state. However, weak fluorescence of MK in cyclohexane also indicates the  $\pi\pi^*$  character of the  $S_1$  state since the  $n\pi^*$  states of the aromatic ketones are non-fluorescent. Therefore, possibly it can be concluded that the  $S_1$  state of MK in this solvent has mixed character of  $n\pi^*$  and  $\pi\pi^*$  states. Several mechanisms have been proposed for this kind of behaviour of the excited electronic states of the aromatic ketones. Wagner and co-workers [21] explained that if the energy gap between these two kinds of states is only a few  $\text{kcal mol}^{-1}$ , there should be a thermal equilibrium between the two during their stay in the excited state [27]. Yang *et al.* [24] explain

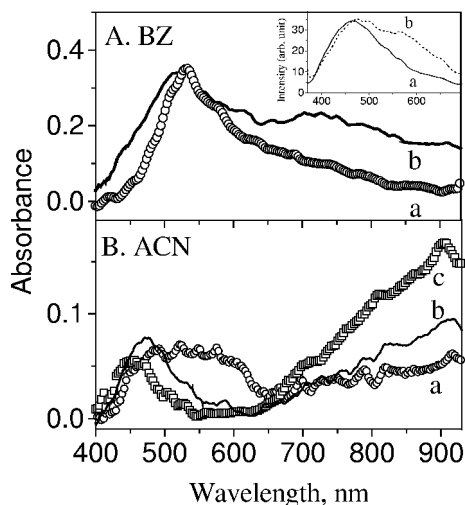


**Figure 3.** Transient absorption spectra of MK recorded at 1 ps (circle) and 100 ps (line) after the 500 fs laser pulses of 310 nm in cyclohexane (CH), benzene (BZ), acetonitrile (ACN) and methanol (MeOH). Insets: the time evolution of the transient absorption monitored at the suitable wavelengths.

the same property by vibronic mixing of  $n\pi^*$  and  $\pi\pi^*$  states — a small amount of  $n\pi^*$  character is mixed into the lowest excited  $\pi\pi^*$  state to show the properties characteristic of a  $n\pi^*$  state. The theoretical analysis of Chandra [38] suggests that the  $n\pi^*$  character can be introduced into the  $\pi\pi^*$  state owing to crossing of the zero order reaction surfaces of the  $n\pi^*$  and  $\pi\pi^*$  states of the ketones. The triplet state of MK both in cyclohexane and benzene has already been characterized and assigned to the  $n\pi^*$  configuration [19, 31].

However, the transient absorption spectrum in benzene recorded at 1 ps time delay due to 310 nm excitation has a very broad absorption band extending throughout the region 400–930 nm with a maximum at *ca* 850 nm. The transient absorption evolves with time and the spectrum recorded at 100 ps is very broad but having a maximum at *ca* 700 nm. The characteristics of the spectra recorded due to 310 nm excitation are very different from those obtained by 355 nm laser excitation. The transient absorption spectrum obtained due to 355 nm excitation has a maximum at 530 nm. This difference in spectral characteristics may, possibly, be due to the difference in concentration of MK used in the pico and subpicosecond experiments (see later). The growth lifetime monitored at this wavelength has been found to be 25 ps (inset of Fig. 3B). In acetonitrile also, a comparison of the spectral features as shown in Figs 2C and 3C reveals that the ratio of the absorbance at 850 nm to that at 470 nm is higher in the absorption spectrum of the  $S_1$  state obtained due to 310 nm excitation (Fig. 3C) than that in the spectrum obtained by 355 nm excitation. However, no evolution of spectral features has been observed with increase in time delay upto a few hundred ps (inset of Fig. 3C). The transient absorption spectrum





**Figure 4.** Transient absorption spectra obtained with different concentrations of MK recorded at zero ps after the 35 ps laser pulses of 355 nm in (A) benzene ([MK] = 1.0 (a) and  $50 \times 10^{-5}$  mol dm $^{-3}$ ) and (B) acetonitrile ([MK] = 1.25 (a), 6.25 (b) and  $50 \times 10^{-5}$  mol dm $^{-3}$ ). Inset of A: the fluorescence spectra of MK in benzene with 1.0 (a) and  $50 \times 10^{-5}$  mol dm $^{-3}$  of MK concentrations.

recorded at 1 ps after the subpicosecond laser pulse in methanol has a major band in the near infra-red region with a maximum at *ca* 800 nm and another minor band in the visible region with a band maximum at *ca* 540 nm. With increase in time-delay the transient absorption evolves to a new absorption spectrum with a broad band in the region 600–800 nm and another in the 450–550 nm region. The growth of the transient absorption has been monitored at 530 nm and the lifetime for the same has been determined to be 8.2 ps.

It has been evident from the Figs 2 and 3 that in each of the solvents, the spectral characteristics of the transients produced due to photolysis by 310 nm and 355 nm light have been different. As mentioned earlier that the ratio of the intensity at maximum of the band in the near-infra-red region to that in the visible region is higher in case of 310 nm than that obtained by 355 nm excitation. The reason for this difference can be considered either due to the difference in excitation wavelengths or due to the effect of concentrations of MK used in the experiment. Since, in our experiments with 310 nm excitation, we need to use very high concentration ( $\sim 1.5 \times 10^{-3}$  mol dm $^{-3}$ ) of MK than that ( $< 5 \times 10^{-5}$  mol dm $^{-3}$ ) used in experiments with 355 nm excitation. Schuster *et al.* [19] also predicted the formation of triplet excimers in this system from their observations on the concentration dependence study on the triplet quantum yield. However, it is well known that formation of excimer via the interaction of an excited molecule with another molecule in the ground state should be diffusion controlled. However, we mentioned earlier that there is no possibility to observe the evolution of the spectral features due to intermolecular interactions in the picosecond and subpicosecond time domain. Hence the possibility that the difference in characteristics of the transient absorption

spectra we observe here due to use of different excitation wavelengths might be either due to association of the molecules in the ground state or creation of different excited states due to excitation by different excitation wavelengths. To distinguish between these two possibilities we conducted the picosecond laser flash photolysis study of MK with varying ground state concentrations ( $1-50 \times 10^{-5} \text{ mol dm}^{-3}$ ) in benzene, acetonitrile and methanol using 355 nm excitation. The transient absorption spectra recorded at zero ps in benzene and acetonitrile have been presented in Fig. 4. It is evident that the characteristics of the triplet absorption spectra of MK in benzene are sensitive to the concentration of MK used. At higher concentrations of the solute, a new band appears at 725 nm and the absorbance increases in the near-infra-red region of the spectrum as compared to that in 530 nm region. However, we could not use concentrations higher than  $5 \times 10^{-4} \text{ mol dm}^{-3}$  due to difficulties in probing the transient absorption with our transverse geometry of detection. In acetonitrile, the effect of the ground state concentration on the characteristics of the excited singlet state absorption is more evident. When the concentration of MK used in flash photolysis experiment is below  $1.25 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $S_1$  state has a broad absorption band in 420–650 nm region and negligible absorption in the 650–930 nm region. However, with increase in concentration of MK, the absorbance in the 650–930 nm region increases, the band in 400–650 nm region becomes narrower and shifts towards blue with no increase in intensity as compared to that obtained with low concentration of MK. The  $S_1$  state spectrum obtained due to ps photolysis by 355 nm excitation with  $3 \times 10^{-4} \text{ mol dm}^{-3}$  of MK is similar to the one obtained due to subpicosecond photolysis by 310 nm light using same concentration of MK (Fig. 3C). Hence it is quite evident that difference in spectral characteristics of the excited singlet and triplet states as shown in Figs 3 and 4 are not due to use of different excitation wavelengths but different concentrations of MK. This leads us to agree with the postulation made by Liptay *et al.* [32] that the molecules of MK undergo some kind of association in the ground state at higher concentrations. However, no indication of this has been obtained in the ground state absorption spectra but the fluorescence spectrum in benzene shows some changes at higher concentration of the solute (inset of Fig. 4A). It is important to note that the association of the molecules in the ground state is less significant in cyclohexane as compared to that in benzene. The non dipolar character of benzene, due to which benzene behaves as a more polar solvent than cyclohexane, as mentioned earlier, probably, can explain this fact. Molecular association is significant in polar solvents.

In methanol, the transient absorption spectra recorded with different concentrations of MK, however, were not significantly different from those in Fig. 2E. Hence the spectrum obtained at 1 ps after 310 nm photolysis is due to the  $S_1$  state and that obtained at 50 ps by 310 nm photolysis (Fig. 3C) as well as those obtained by 355 nm photolysis (Fig. 2E) are due to the triplet state. The differences in characteristics of the triplet spectra, as mentioned earlier, are due to different stages of solvation by intermolecularly hydrogen bonded methanol molecules.

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