Photochemistry

Ordering, Interaction, and Reactivity of the Low-Lying nπ* and ππ* Excited Triplet States of Acetophenone Derivatives**
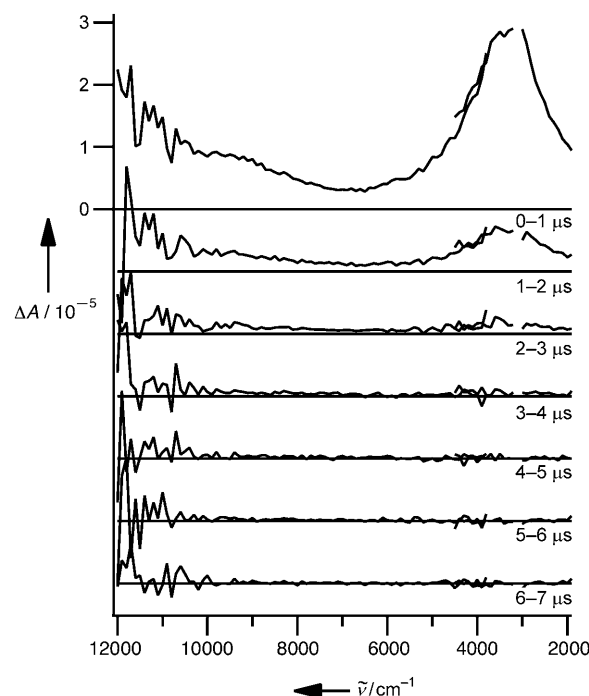
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The diversity of photophysics and photochemistry of the low-lying excited triplet states of aromatic carbonyl compounds has attracted considerable interest in the field of organic photochemistry.[1] For instance, the intersystem crossing rates,[2] phosphorescence lifetimes,[3] and photoreduction activities[4] of these compounds show a marked dependence on both substituents and solvents. Depending on their electronic configurations, the energy of the low-lying triplet states, namely nπ*, ππ*, and charge transfer (CT), can be influenced by substituents and solvents, with possible alterations in the energy-level ordering of the states. The photoreduction proceeds via the T_1 state,[5] which has approximate quantum yields that vary between 1 for the nπ* T_1 state, 0.1 for the ππ* state, and 0 for the CT state.[6] The strong substituent and solvent dependence of the photophysics and photochemistry of aromatic carbonyl compounds has thus been discussed in terms of the energy-level ordering of the nπ*, ππ*, and CT excited triplet states.[7–10]

It is known that the photoreduction activity of aromatic carbonyl compounds varies gradually with substituents or with solvents. In particular, the ππ* T_1 states show varying reactivities that cannot be accounted for solely by energy-level ordering. There have been several arguments about this reactivity variation of the ππ* T_1 state. It is generally considered that the reactivity arises from mixing of the nπ* character into the ππ* state.[1] A mechanism that involves the thermal excitation to a closely lying np* state has also been suggested.[10–12] These arguments are not based on direct experimental evidence on the ordering of the excited triplet states and therefore are not conclusive; conventional spectroscopic techniques have not been effective in observing close-lying excited triplet states of aromatic carbonyl compounds.[13] Thus, it is highly important to experimentally clarify the energy-level ordering and the electronic configurations of the low-lying excited triplet states of aromatic carbonyl compounds. We have constructed a nanosecond time-resolved absorption spectrometer that is suitable for observing the triplet–triplet transitions in the near-infrared region as well as the vibrational transitions in the mid-infrared region.[13] We have focused on the substituent dependence of both the triplet–triplet absorption spectra and the photoreduction activity of a series of acetophenone derivatives.

The time-resolved near-infrared spectra of acetophenone (AP) excited at 325 nm in benzene are shown in Figure 1. Upon photoexcitation, two broad transient absorption bands arise instantaneously within the time resolution of the apparatus, and decay synchronously. One band spans from 2000 to 7000 cm⁻¹, with a peak at 3500 cm⁻¹. The other band starts from 7000 cm⁻¹ and extends to the higher-wavenumber region above 12000 cm⁻¹. The decay of these two bands is completely synchronous with the recovery of the ground-state

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Figure 1. Time-resolved near-infrared spectra of photoexcited acetophenone in benzene. The region around 3000 cm⁻¹ is blocked by the solvent absorption signal.

depletion, as monitored by vibrational bands. By analogy with benzophenone,[14] these bands are unequivocally ascribed to electronic transitions in the triplet manifold.

The near-infrared spectra of 4'-(trifluoromethyl)acetophenone (CF$_3$-AP), AP, 4'-methylacetophenone (Me-AP), 4'-methoxyacetophenone (MeO-AP), and 2-acetonaphthone (AN) in benzene at 0–1 μs (each spectrum is obtained by averaging over 100 spectra between 0 and 1 μs) are shown in Figure 2. For all the compounds studied, transient absorption bands arise instantaneously after photoexcitation and decay synchronously, as in the case of acetophenone. The spectra can be characterized by two distinct components: the lower-wavenumber band centered around 3500 cm^{-1} and the higher-wavenumber band located above 7000 cm^{-1}. As in the case of AP, these transient bands are ascribed to triplet–triplet transitions. The spectrum of CF$_3$-AP shows a strong lower-wavenumber component with a very weak higher-wavenumber component, while the spectrum of AN shows only a higher-wavenumber component. The spectra of the other compounds show both the lower- and higher-wavenumber components, but the intensity ratio between the two components varies markedly. Furthermore, the higher-wavenumber component seems to have a vibrational structure with a spacing of approximately 1500 cm^{-1}. The relative intensity of the lower-wavenumber component to the higher-wavenumber component correlates well with the photoreduction activity, as a higher intensity of the lower-wavenumber component results in a higher photoreduction activity. AN does not show any photoreduction activity in the presence of alcohols.[15] The reported photoreduction rates k_r for CF$_3$-AP, AP, and Me-AP[7,8] are given in Table 1, together with the area intensity ratios $I_r = I_{lower}/I_{higher}$ observed for the four acetophenone derivatives. It is clear that the reactivity of the derivatives increases as the intensity ratio is increased.

Table 1: Photoreduction activity and band intensity ratios of substituted acetophenone derivatives.

	$k_r [\times 10^6 \ s^{-1} \ M^{-1}]$	$I_r = I_{lower}/I_{higher}$ [a]
CF$_3$-AP	6.2[b]	22
AP	1.2[b]	6.7
Me-AP	0.13[b]	1.9
AN	≈0[c]	0

[a] Area intensity ratio of the lower- and higher-wavenumber components. [b] Recorded in 2-propanol/benzene binary mixtures. Values taken from reference [7]. [c] AN does not undergo photoreduction by alcohols; see reference [15].

The relative energies of the lowest nπ* and ππ* states depend on the substituent, therefore the order of the states often alters. We have found that the triplet–triplet absorption spectra of acetophenone derivatives consist of only two components, that is, the lower- and higher-wavenumber components, the intensity ratio I_r of which varies markedly with the substituent. This variation must be related to the alteration of the energy-level ordering of the lowest nπ* and ππ* states, as suggested by the correlation of I_r with the photoreduction activity.

It is already known that the T$_1$ state of CF$_3$-AP has the nπ* configuration and that of Me-AP and MeO-AP has the ππ* configuration.[7,8] The nπ* states are highly reactive toward photoreduction, while the ππ* states are much less reactive.[1,4,7,8] It is clear from Table 1 that CF$_3$-AP, which has the strongest lower-wavenumber component, shows much higher photoreduction activity than Me-AP and MeO-AP, which have weaker lower-wavenumber components. We therefore conclude that the lower-wavenumber component arises from a triplet–triplet transition from an nπ* state, and that the higher-wavenumber component arises from a transition from
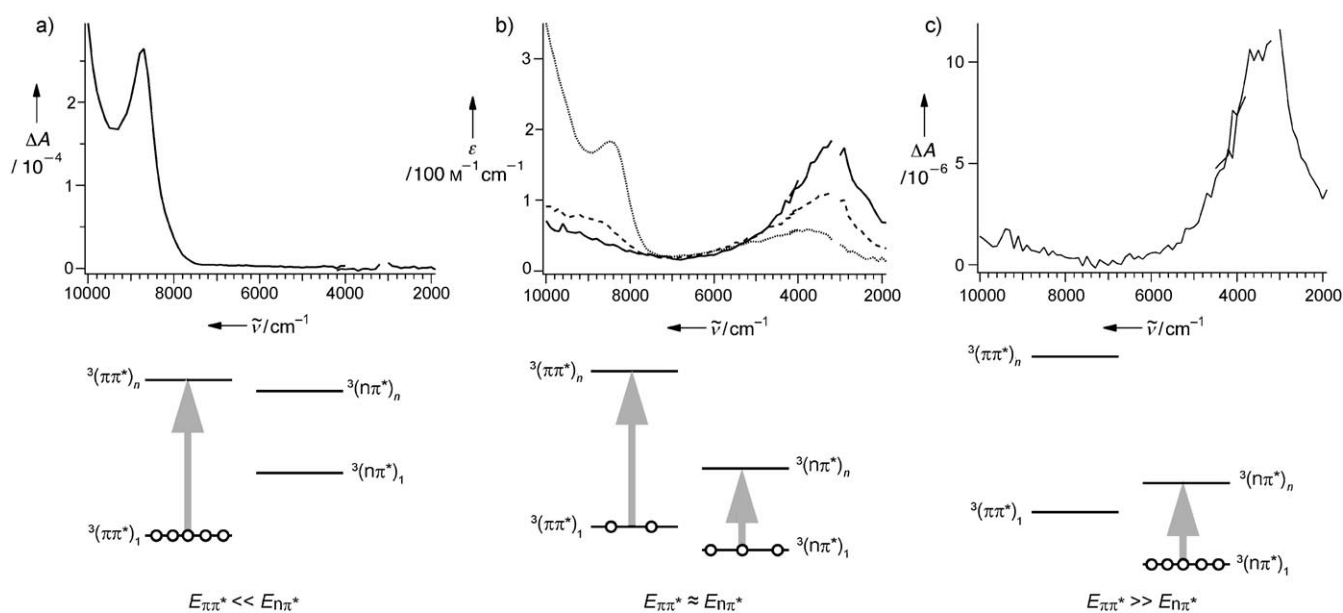

Figure 2. Time-resolved near-infrared spectra at 0–1 μs (upper part) and energy diagrams with transitions corresponding to the bands observed in the spectra (lower) for a) AN, b) AP (——), Me-AP (– – –), and MeO-AP ·····), and c) CF$_3$-AP.

a $\pi\pi^*$ state. Indeed, the spectrum of CF$_3$-AP, for which the $n\pi^*$ T$_1$ state is much lower in energy than the $\pi\pi^*$ state, has only the lower-wavenumber component, while the spectrum of AN, for which the $\pi\pi^*$ T$_1$ state is much lower than the $n\pi^*$ state, has only the higher-wavenumber band. Thus, the initial states of the lower- and the higher-wavenumber components are identified as the $n\pi^*$ and $\pi\pi^*$ states, respectively. The final states of these transitions are likely to have the same electronic configurations as those of the initial states because the $n\pi^* \leftrightarrow n\pi^*$ and $\pi\pi^* \leftrightarrow \pi\pi^*$ transitions are allowed, but the $n\pi^* \leftrightarrow \pi\pi^*$ transition is symmetry-forbidden for planar structures. This assignment is consistent with the fact that the band positions and hence the energy gaps of the initial and final states do not vary much by substitution; the electronic states that have the same electronic configurations are likely to behave in a similar fashion toward substitution. The observed synchronous decay of the two components observed for AP, Me-AP, and MeO-AP indicates that the $n\pi^*$ and $\pi\pi^*$ states are in thermal equilibrium in these three compounds. The thermal equilibration between the low-lying $n\pi^*$ and $\pi\pi^*$ states of the acetophenone derivatives is shown in Figure 2. For AN, the lowest $\pi\pi^*$ state of which is much lower in energy than the lowest $n\pi^*$ state, only the $\pi\pi^*$ state is populated and therefore only the higher-wavenumber component (T$_{\pi\pi^*}$ band) is observed (Figure 2a). For CF$_3$-AP, the lowest $n\pi^*$ state of which is much lower than the lowest $\pi\pi^*$ state, only the $n\pi^*$ state is populated and therefore only the lower-wavenumber component (T$_{n\pi^*}$ band) is observed (Figure 2c). For the molecules where the lowest $n\pi^*$ and $\pi\pi^*$ states are close in energy, as is the case of AP, Me-AP, and MeO-AP, both the $n\pi^*$ and $\pi\pi^*$ states are populated and therefore both the T$_{n\pi^*}$ and $\pi\pi^*$ bands are observed; the intensity ratios of these bands varies with the population ratio of the $n\pi^*$ and $\pi\pi^*$ states (Figure 2b).

We have shown that the low-lying $n\pi^*$ and $\pi\pi^*$ states for AP, Me-AP, and MeO-AP are close in energy and are in thermal equilibrium, which can be directly confirmed by observing the effect of temperature on the spectra. Figure 3 shows the time-resolved infrared spectra at 0–1 µs of photoexcited MeO-AP in α,α,α-trifluorotoluene (TFMT) at 29, 55, and 80 °C. It is clear that the intensity ratio k_r between the lower- and higher-wavenumber components is temperature-dependent; the higher-wavenumber component decreases while the lower component increases in intensity as the temperature increases. This result supports the hypothesis that the two triplet states are in thermal equilibrium and that the population of the lowest $\pi\pi^*$ state decreases, while that of the lowest $n\pi^*$ increases, as the temperature increases. The enthalpy difference between the lowest $n\pi^*$ and $\pi\pi^*$ states can be determined from the temperature dependence of the intensity ratio, assuming a Boltzmann distribution. Figure 4 shows the plot of $\ln(1/I_r)$ versus $1/T$. The enthalpy difference $\Delta H = H_{n\pi^*} - H_{\pi\pi^*}$ between the $n\pi^*$ T$_2$ and $\pi\pi^*$ T$_1$ states is determined from the slope by a least-squares fitting of the observed points to a straight line. ΔH is determined to be (2.9 ± 0.6) kJ mol^{-1} for MeO-AP in TFMT (Figure 4a). The entropy difference $\Delta S = S_{n\pi^*} - S_{\pi\pi^*}$ determined from the intercept is (-1 ± 5) J K^{-1} mol^{-1}; this small value is consistent with the fact that the molecular structures are nearly the same
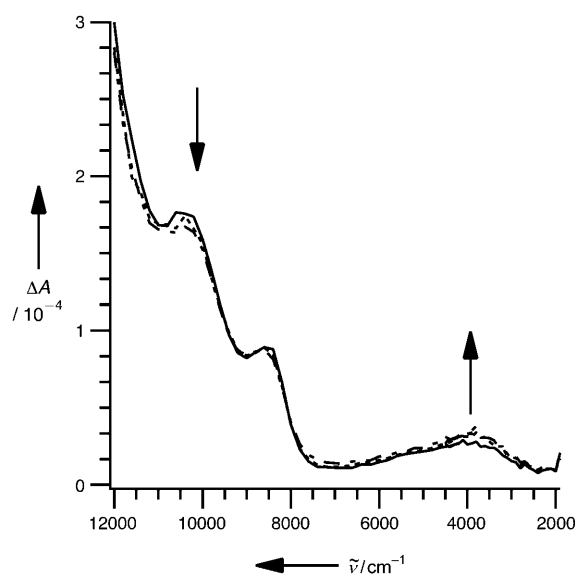
Figure 3. Time-resolved near-infrared spectra at 0–1 µs of photoexcited MeO-AP in α,α,α-trifluorotoluene at 29, 55, and 80 °C (order indicated by the arrows). The spectra are normalized by making the areas of the depletion (negative peak) of the ground-state CO stretching band (not shown) equal.
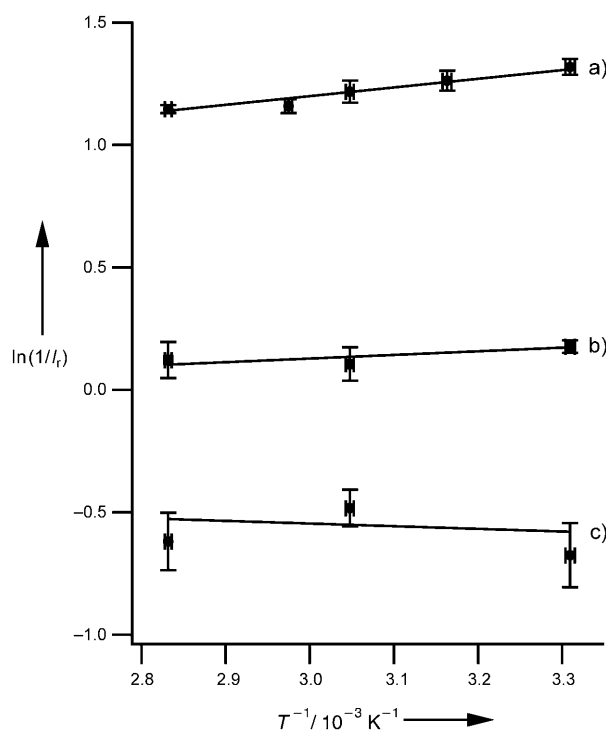

Figure 4. Relative intensities of a) MeO-AP, b) Me-AP, and c) AP plotted against $1/T$.

for the $n\pi^*$ and $\pi\pi^*$ triplet states so that the vibrational, rotational, and translational partition functions and hence the entropy values are nearly the same for the two triplet states.

The temperature dependence of the intensity ratio I_r has also been examined for Me-AP (Figure 4b) and AP (Figure 4c) in TFMT. The enthalpy difference is determined as

$(1.2 \pm 1.2) \, \text{kJ mol}^{-1}$ for Me-AP. Although no reliable value was obtained for AP because of large experimental uncertainties, the enthalpy difference is smaller for AP than for Me-AP. Considering the fact that the entropy differences are likely to be small in AP and Me-AP, as in the case of MeO-AP, the present results are consistent with previous studies, which predict that the energy levels of the lowest $n\pi^*$ and $\pi\pi^*$ states of AP and Me-AP lie closer than those of MeO-AP.[7,9]

Time-resolved mid-infrared spectra at $0–1 \, \mu s$ of photoexcited acetophenone derivatives in carbon tetrachloride are shown for the $900–1900 \, \text{cm}^{-1}$ region in Figure 5. The time-
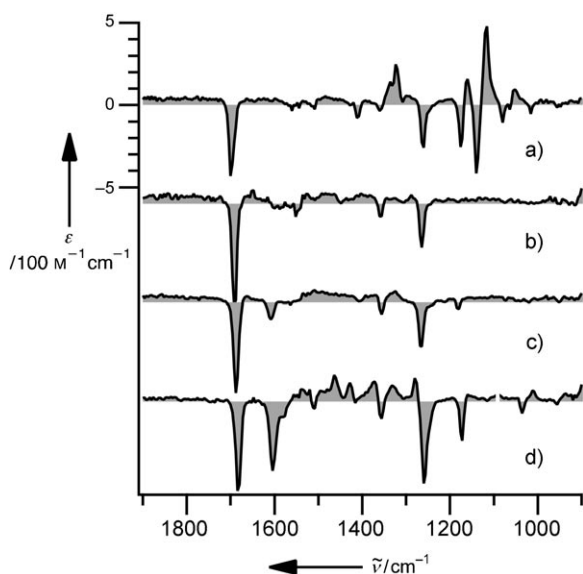
Figure 5. Time-resolved infrared vibrational spectra at 0–1 μs of photoexcited a) CF_3-AP, b) AP, c) Me-AP, and d) MeO-AP.

resolved near-infrared spectra of acetophenone derivatives in carbon tetrachloride (not shown) are very similar to those in benzene, thus showing that the T_1 and T_2 energy gaps in the two solvents do not differ significantly. We used carbon tetrachloride for the mid-infrared measurements because of much wider spectral windows. In these spectra, the negative peaks represent the depletion of the ground state and the positive peaks the generation of the excited triplet state. The spectra of CF_3-AP and CH_3O-AP in the T_1 states have already been reported by Srivastava et al., and the bands at 1326 and $1462 \, \text{cm}^{-1}$ have been assigned to the CO stretching modes.[16] In contrast to the prominent vibrational bands observed for CF_3-AP and MeO-AP, no apparent positive peaks were observed for both AP and Me-AP. Such an absence of sharp vibrational bands in the excited triplet states has previously been reported for benzophenone.[14] Since the CO stretching bands of CF_3-AP and MeO-AP have appreciable intensities, this absence of sharp CO stretching bands in AP, Me-AP, and benzophenone can not be ascribed to their small absorption cross-sections. It is more likely that the vibrational bands of those triplet states are broadened so much for these three molecules that the prominent peaks can not observed. Such broadenings can happen when the exchange between the two triplet states takes place much faster than vibrational

dephasing. The vibrational dephasing time is usually on the order of one picosecond or longer, which corresponds to the vibrational band widths of several wavenumbers. If the exchange between the two triplet states occurs faster than one picosecond, then the effective vibrational dephasing time becomes much shorter than the intrinsic vibrational dephasing time and the resultant vibrational band width is much larger than usual. Although the mechanism of this fast exchange is yet to be elucidated, it is highly likely that the perturbations caused by the surrounding solvent molecules play an essential role and that the rate of exchange becomes larger as the two triplet states come closer together. The fast exchange may well be effective for AP, Me-AP, and benzophenone but not for CF_3-AP and MeO-AP. This supposition of fast exchange is consistent with the idea that the thermal equilibrium is reached between the T_1 and T_2 states of AP, Me-AP, and MeO-AP.

In conclusion, the thermal equilibrium with fast exchange between the T_1 and T_2 states elucidated in the present study very well accounts for the substituent dependence of photoreduction activity of acetophenone derivatives as summarized in the following three points: 1) The population distribution between the T_1 and T_2 states is reflected in the intensity ratio of the lower- and higher-wavenumber components in the triplet–triplet absorption spectra. The population is determined by the free energy difference that is almost equal to the determined enthalpy difference because of very small entropy difference. 2) Only the $n\pi^*$ state has intrinsic photoreduction activity. This conclusion is consistent with the fact that the maximum degree of mixing (β^2) of the $n\pi^*$ state into the lowest $\pi\pi^*$ states is only approximately 5%.[11] 3) The apparent photoreduction activity is expressed by the product of the intrinsic reaction rate of the $n\pi^*$ states and its population. There is no need to consider the intrinsic reactivity of the $\pi\pi^*$ state. Thermal equilibrium between the $n\pi^*$ and $\pi\pi^*$ states plays an important role for acetophenone, 4′-methylacetophenone and 4′-methoxyacetophenone, which all show slightly different photoreduction characteristics.

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