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# Direct Observation of the Solvent Effects on the Low-Lying nπ* and ππ* Excited Triplet States of Acetophenone Derivatives in Thermal Equilibrium

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S Supporting Information

ABSTRACT: Low-lying excited triplet states of aromatic carbonyl compounds exhibit diverse photophysical and photochemical properties of fundamental importance. Despite tremendous effort in studying those triplet states, the effects of substituents and solvents on the energetics of the triplet manifold and on photoreactivity remain to be fully understood. We have recently studied the ordering of the low-lying nπ* and ππ* excited triplet states and its substituent dependence in acetophenone derivatives using nanosecond time-resolved near-IR (NIR) spectroscopy. Here we address the other important issue, the solvent effects, by directly observing the electronic bands in the NIR that originate from the lowest nπ* and ππ* states of acetophenone derivatives in four solvents of different polarity (n-heptane, benzene, acetonitrile, and methanol). The two transient NIR bands decay synchronously in all the solvents, indicating that the lowest nπ* and ππ* states are in thermal equilibrium irrespective of the solvent polarity studied here. We found that the ππ* band increases in intensity relative to the nπ* band as solvent polarity increases. These results are compared with the photoreduction rate constant for the acetophenone derivatives in the solvents to which 2-propanol was added as a hydrogen-atom donor. Based on the present findings, we present a comprehensive, solvent- and substituent-dependent energy level diagram of the low-lying nπ* and ππ* excited triplet states.
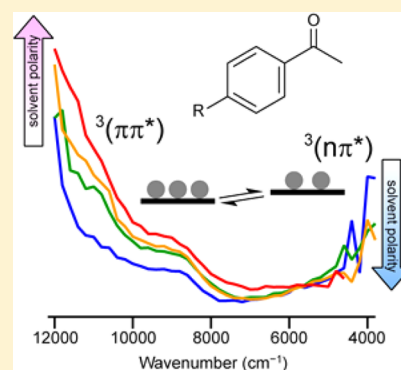
■ INTRODUCTION

Aromatic carbonyl compounds such as acetophenone (AP) and its derivatives have been studied for more than half a century owing to their distinct characteristics in photophysical and photochemical reactions.[1−9] Among the most studied reactions of these compounds is the photoreduction occurring in the presence of a hydrogen-atom donor. Aromatic carbonyl compounds exhibit an intricate triplet manifold in which nπ* and ππ* triplet states lie close in energy to each other, and the photoreduction activity is strongly affected by the nature of the lowest excited triplet (T_1) state within this manifold.[10−16] The triplet energetics is also a subject of recent theoretical investigations.[17−19]

There are two principal factors that can alter the energy level ordering of the low-lying excited triplet states and hence the photoreduction activity: namely, substituent and solvent. Despite their fundamental importance, the effects of substituents and solvents on the proximate excited triplet states have been longstanding questions in the photochemistry of aromatic carbonyl compounds. As an illustrative example of the substituent dependence, 4′-(trifluoromethyl)acetophenone (CF$_3$-AP), AP, and 4′-methylacetophenone (Me-AP) have the T_1 configuration of nπ*, nπ*, and ππ*, respectively, but the rate constant, k_r, for hydrogen abstraction from 2-propanol varies gradually from 6.2×10^6 to 1.2×10^6 to 0.13×10^6 M^{-1} s^{-1}.[11] This substituent-dependent photoreduction activity has been

interpreted in terms of a thermal excitation from the ππ* T_1 state to a close-lying nπ* state.[13,14,20−22] In addition, vibronic coupling between the nπ* and ππ* states, e.g., through an out-of-plane bending vibration, has also been considered responsible for the reactivity of the compounds, which is commonly termed the proximity effect.[23,24] These mechanisms were, however, proposed based primarily on indirect observations with phosphorescence spectroscopy[25−28] and/or on theoretical calculations.[23,24]

Recently we have provided a conclusive picture of the ordering of the low-lying excited triplet states and its substituent dependence in four AP derivatives (AP, CF$_3$-AP, Me-AP, and 4′-methoxyacetophenone (MeO-AP)) using nanosecond time-resolved near-IR (NIR) spectroscopy.[29] We found that the photoreduction activity of the AP derivatives correlates well with the intensity ratio of NIR electronic bands that correspond to nπ* ← nπ* and ππ* ← ππ* transitions, and that the low-lying nπ* and ππ* triplet states of AP, Me-AP, and MeO-AP are in thermal equilibrium. We confirmed the thermal equilibrium by measuring the temperature effect on the band intensity ratio in α,α,α-trifluorotoluene solution. The enthalpy difference $\Delta H = H_{n\pi^*} - H_{\pi\pi^*}$ has been determined to be ~240

cm^{-1} for MeO-AP and ~100 cm^{-1} for Me-AP. The enthalpy difference for AP is even smaller than that for Me-AP.

In this paper, we now address the other crucial factor, solvent effects, which also profoundly affect the excited triplet state energetics in aromatic carbonyl compounds.[11,12,30,31] It is well-known that the $\pi\pi^*$ state is more stabilized than the $n\pi^*$ state with increasing solvent polarity. Because the $\pi\pi^*$ state is much less reactive toward photoreduction than the $n\pi^*$ state,[5,7] stabilization of the $\pi\pi^*$ state in polar solvents is expected to bring about very low reactivity. Lindqvist and co-workers showed that the photoreduction rate constant k_r decreases by about 1 order of magnitude in going from benzene to water.[12] Although k_r does reflect the $\pi\pi^*$ character of the T_1 state, observing triplet–triplet absorption from both of the nearby lowest $n\pi^*$ and $\pi\pi^*$ states in the NIR region is undoubtedly a more direct means to examine the solvent effects on the energy level ordering itself.

In the present study, we measure time-resolved NIR spectra of AP, Me-AP, and MeO-AP in four different solvents, i.e., n-heptane, benzene, acetonitrile, and methanol (in order of ascending $E_T(30)$ value[32]). In all the solvents studied, the transient NIR spectra of the three compounds exhibit two broad electronic bands with various intensities that are assigned to triplet–triplet transitions from the lowest $n\pi^*$ and $\pi\pi^*$ states. As in our previous experiments in benzene,[29] those bands decay in unison. This finding indicates that the thermal equilibrium between the T_1 and T_2 states of the AP derivatives exists irrespective of the solvents used. Furthermore, we observe a significant variation in the intensity ratio of the two bands for Me-AP and MeO-AP with changing solvent polarity from n-heptane (nonpolar) to methanol (polar). In contrast, AP shows little solvent dependence. These results are compared with results of photoreduction kinetic analysis for the $n\pi^*$ state of the AP derivatives in the solvents with 2-propanol added as a hydrogen-atom donor.

■ EXPERIMENTAL SECTION

Materials. Commercially obtained acetophenone (>99%, Fluka) was distilled, and 4′-methylacetophenone (>99%, Fluka) and 4′-methoxyacetophenone (>99%, Aldrich) were recrystallized from ethanol prior to time-resolved measurements. HPLC-grade n-heptane, benzene, acetonitrile, and methanol and UV spectrometry-grade 2-propanol were used as received. The concentration of the AP derivatives was 50 mM in all the solvents.

Nanosecond Time-Resolved NIR Spectroscopy. The apparatus used for nanosecond time-resolved NIR spectroscopy has been described previously.[29,33,34] It employs a dispersive monochromator in combination with alternating current (AC)-coupled detection.[35,36] The AC-coupled technique enables us to detect absorbance difference as small as 1×10^{-6}. The second harmonic of a Q-switched Nd:YAG laser (532 nm; ~7 ns pulse duration; 1.6 mJ energy; 500 Hz repetition rate) was used to pump a dye laser, in which a 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) dye solution was circulated. The second harmonic of the dye laser output was used to photoexcite the sample. The excitation wavelength (325 nm) lies very close to the absorption maximum of the $S_1 \leftarrow S_0$ transition for all the AP derivatives studied. The pulse energy of the excitation light was 30 μJ at the sample position. Changes in absorption spectrum upon photoexcitation were probed with NIR light derived from a tungsten-halogen lamp. The probe light passing through the

sample 1 mm thick was introduced to the dispersive monochromator and detected with a photovoltaic InSb detector that was coupled to a preamplifier. The AC-coupled output of the detector was further amplified and finally processed with a high-speed digitizer mounted on a computer, yielding a time-stream of NIR absorption difference spectra. The spectral resolution was 200 cm^{-1}. The time resolution of the apparatus was approximately 80 ns, which was determined by the temporal response of the InSb detector to a 7 ns pulse. To reduce possible sample degradation and heat accumulation during the measurement, the sample solution was circulated by using a gear pump through a laboratory-built flow cell that comprised two BaF$_2$ windows and a spacer. The sample solution in the reservoir was continuously bubbled with argon gas, which precludes the possibility of quenching of the generated excited triplet states via triplet–triplet energy transfer with molecular oxygen present in the laboratory environment. Furthermore, the sample solution was replenished every 2 h with a fresh solution. For determination of k_r, 2-propanol was added to each solvent at 2.0 M. All measurements were performed at room temperature.

■ RESULTS

Transient Near-IR Spectra. Figure 1 displays representative time-resolved NIR spectra (3800–12000 cm^{-1}) of AP in n-
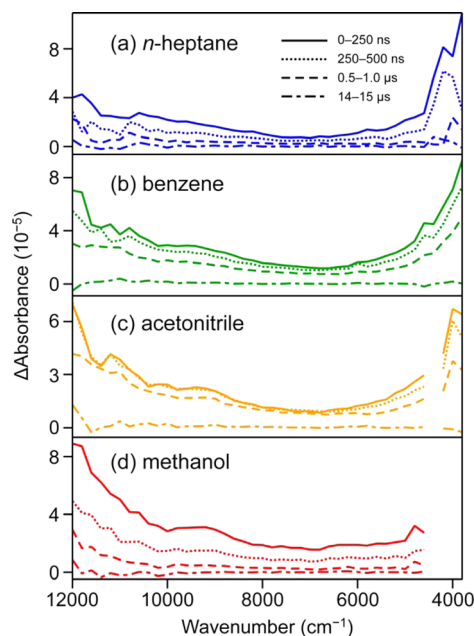

Figure 1. Time-resolved NIR spectra of AP in n-heptane (a), benzene (b), acetonitrile (c), and methanol (d). Solid line, 0–250 ns; dotted line, 250–500 ns; dashed line, 0.5–1.0 μs; dot-dash line, 14–15 μs after photoexcitation of AP.

heptane, benzene, acetonitrile, and methanol. Edges of two very broad bands are seen in this wavenumber region. Note that part of the transient spectra in acetonitrile (Figure 1c) and methanol (Figure 1d) is masked due to the severe interference of solvent's combination bands. The lower wavenumber band ranges from 2000 to 7000 cm^{-1} (with a maximum around 3500 cm^{-1}, as observed previously[29]), and the higher wavenumber band emerges around 7000 cm^{-1} and stretches above 12000 cm^{-1}. The lower wavenumber band is assigned to a triplet–triplet transition from the $n\pi^*$ state ($T_{n\pi^*}$ band) and the higher

wavenumber to that from the $\pi\pi^*$ state ($T_{\pi\pi^*}$ band).[29] As is evident from Figure 1, the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ bands decay synchronously in all the solvents studied. Previously we observed a similar synchronous decay of the two transient electronic bands of AP in benzene and interpreted it as being due to the thermal equilibrium between the $n\pi^*$ and $\pi\pi^*$ states that are the initial states for the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ transitions. The present result indicates that this thermal equilibrium is generally found in other solvents of different polarity, e.g., n-heptane, acetonitrile, and methanol. Synchronous decay dynamics of the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ bands are seen in Me-AP and MeO-AP as well (see Supporting Information, SI, Figures S1 and S2).

In previous work,[29] we showed that the relative intensity of the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ bands correlates well with the reported photoreduction rate constant k_r and reflects the change in the energy level ordering of the lowest $n\pi^*$ and $\pi\pi^*$ states. Therefore, it should also prove useful for studying the solvent effects. Figure 2 shows the transient NIR spectra at 0.5 μs after
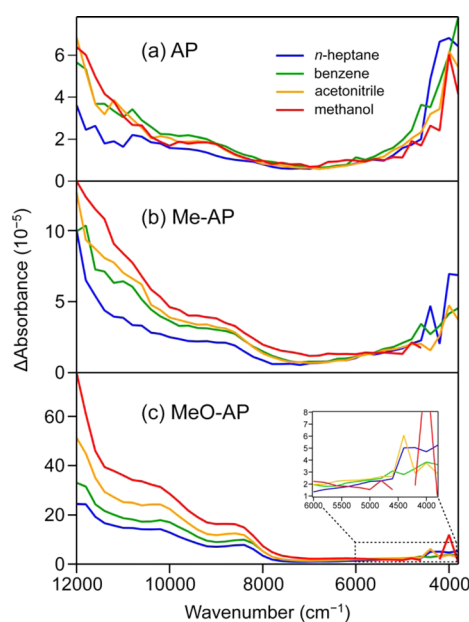

Figure 2. Time-resolved NIR spectra at 0.5 μs after photoexcitation of AP (a), Me-AP (b), and MeO-AP (c) in n-heptane (blue line), benzene (green line), acetonitrile (yellow line), and methanol (red line). The gap around 4000 cm^{-1} in b and c is due to a combination band of the solvent. The inset of c shows an enlarged view of the $T_{n\pi^*}$ band in the 3800−6000 cm^{-1} region.

photoexcitation, of AP, Me-AP, and MeO-AP in n-heptane, benzene, acetonitrile, and methanol. The spectrum at a longer delay time (44−45 μs) has been subtracted as a background. For AP (Figure 2a), the $T_{\pi\pi^*}$ band is almost comparable in intensity to the $T_{n\pi^*}$ band. Although the spectra are somewhat noisy around 4000 and 12000 cm^{-1}, there seems little solvent dependence of these bands. By contrast, for Me-AP (Figure 2b), the $T_{\pi\pi^*}$ band is much more intense than the $T_{n\pi^*}$ band. The intensity of the $T_{\pi\pi^*}$ band increases with increasing solvent polarity from n-heptance (Figure 2b, blue) to methanol (Figure 2b, red), and concurrently the $T_{n\pi^*}$ band decreases. In the case of MeO-AP (Figure 2c), the $T_{n\pi^*}$ band is discernible only in an enlarged scale for all the solvents studied (see the inset of Figure 2c), but the rise of the $T_{\pi\pi^*}$ band with increasing solvent polarity is quite prominent. It is important to note here that the

shape of the two bands remains nearly unaffected by changing the solvent. This observation suggests that both initial and final states involved in the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ transitions, which are actually allowed $n\pi^* \leftarrow n\pi^*$ and $\pi\pi^* \leftarrow \pi\pi^*$ transitions, are affected by the solvent in a similar manner.

To examine the solvent dependence of the relative intensity of the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ bands quantitatively, we calculated the band intensity ratio $I_{\pi\pi^*}/I_{n\pi^*}$ from the spectra shown in Figure 2. The band intensities $I_{n\pi^*}$ and $I_{\pi\pi^*}$ were obtained by integrating the area under the curve of the $T_{n\pi^*}$ and $T_{\pi\pi^*}$ bands between 4400−6400 and 7400−11000 cm^{-1}, respectively. Here we assume that the area calculated for the limited portion of the broad band is proportional to that of the whole band. Although we measured the transient spectra in the 3800−12000 cm^{-1} region, we did not use both edges of this interval (11000−12000 and 3800−4400 cm^{-1}) to minimize the interference of thermal artifacts due to solvent's combination bands in the lower wavenumber region (3800−4200 cm^{-1}) and large peak-to-peak noises in the higher wavenumber region (>11000 cm^{-1}) due to low sensitivity of the InSb detector and low throughput of the monochromator. We chose the same number of data points for both $T_{n\pi^*}$ and $T_{\pi\pi^*}$ bands, but slightly different choices of the integration range turned out to have a negligible effect on the resulting intensity ratio.

The intensity ratios so determined are summarized in Table 1. We have averaged the results from four independent runs,

Table 1. Band Intensity Ratios, $I_{\pi\pi^*}/I_{n\pi^*}$, of the Low-Lying $n\pi^*$ and $\pi\pi^*$ Excited Triplet States of Acetophenone Derivatives in Different Solvents

	n-heptane	benzene	acetonitrile	methanol
AP	1.3 ($\pm$0.1)	1.4 ($\pm$0.1)	1.6 ($\pm$0.1)	1.5 ($\pm$0.1)
Me-AP	2.0 ($\pm$0.1)	2.4 ($\pm$0.2)	2.6 ($\pm$0.1)	2.9 ($\pm$0.1)
MeO-AP	6.5 ($\pm$0.2)	7.1 ($\pm$0.1)	8.6 ($\pm$0.1)	10.6 ($\pm$0.5)

each of which acquired five scans under the same experimental conditions. In all the solvents studied, $I_{\pi\pi^*}/I_{n\pi^*}$ increases as the solute varies from the nonsubstituted compound to the methoxy-substituted compound. This trend agrees with our previous report.[29] The solvent dependence of $I_{\pi\pi^*}/I_{n\pi^*}$ is overall consistent with the qualitative accounts given above. For AP, $I_{\pi\pi^*}/I_{n\pi^*}$ is only slightly larger in polar solvent than in nonpolar solvent. Me-AP shows a moderate variation of $I_{\pi\pi^*}/I_{n\pi^*}$, which increases monotonically by 45% from 2.0 in n-heptane to 2.9 in methanol. The most pronounced increase in $I_{\pi\pi^*}/I_{n\pi^*}$ (63%) with increasing solvent polarity is observed for MeO-AP.

Photoreduction Kinetic Analysis. The apparent photoreduction activity of the AP derivatives is expressed as the product of the intrinsic reaction rate of the $n\pi^*$ state and its population. The stabilization of the $\pi\pi^*$ state in polar solvents should therefore result in decreasing the photoreduction activity. Following the conventional method[11,12,37,38] to see this phenomenon, we also studied the photoreduction of the AP derivatives in n-heptane, benzene, and acetonitrile to which 2-propanol was added as a hydrogen-atom donor. Methanol was not used in this experiment because it could also donate a hydrogen atom (see below). Figure 3 shows the decay kinetics for the $n\pi^*$ state of AP, Me-AP, and MeO-AP, monitored at 5000 cm^{-1} with and without addition of 2-propanol at 2.0 M. Note that the $n\pi^*$ state is the main channel for the reaction, and that the $\pi\pi^*$ state makes only little, if any, contribution due to a small degree of mixing of the $n\pi^*$ state into the lowest $\pi\pi^*$
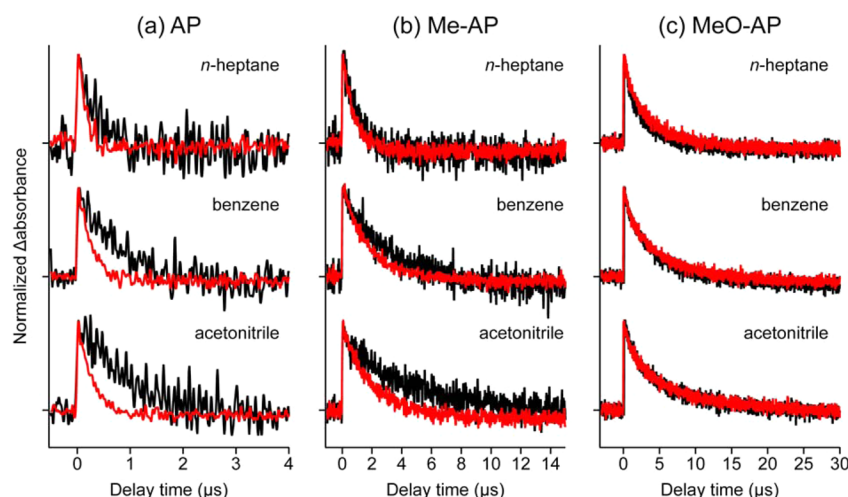
Figure 3. Decay profiles monitored at 5000 cm^{-1} for the nπ* state of AP (a), Me-AP (b), and MeO-AP (c) in *n*-heptane (top trace), benzene (middle trace), and acetonitrile (bottom trace) with (red line) and without (black line) addition of 2.0-M 2-propanol.

state ($\beta^2 < 0.1$).[21,22] The nπ* state of AP (Figure 3a) and Me-AP (Figure 3b) decays faster in the presence of 2-propanol because the excited triplet state reacts with 2-propanol and forms the ketyl radical. These time profiles were obtained with argon bubbling, so the increase in the decay rate constant cannot be attributed to oxygen quenching of the triplet state. Compared to AP and Me-AP, addition of 2-propanol has no appreciable effect on the decay kinetics for MeO-AP (Figure 3c). Similar kinetic profiles are observed for the $\pi\pi$* state, which can be found as Figure S3 in the Supporting Information (SI).

We fit the time profiles in Figure 3 with a single exponential function in order to determine the decay rate constants, k and k_d, measured with and without addition of 2-propanol, respectively. Uncertainties in the derived rate constants are very close to the instrumental response ($\sim$100 ns). The photoreduction rate constant k_r was then calculated by using the relation[11,12]

$$k = k_d + k_r[\text{2-propanol}] \quad (1)$$

We assume that 2-propanol is the sole source of a hydrogen atom and that the solvent molecules are inert with respect to the photoreduction of the AP derivatives. The values of k and k_d obtained from curve fitting and those of k_r then calculated by using eq 1 are shown in Table 2. The k_r values that we obtained for AP (1.3×10^6 M^{-1} s^{-1}) and Me-AP (1.3×10^5 M^{-1} s^{-1}) in

Table 2. Photoreduction Rate Constants and Quantum Yield for Acetophenone Derivatives in *n*-Heptane, Benzene, and Acetonitrile Derived from the Kinetic Analysis

solute	solvent	k (10^5 s^{-1})	k_d (10^5 s^{-1})	k_r (10^5 M^{-1} s^{-1})	Φ
AP	*n*-heptane	69	23	23	0.67
	benzene	38	11	13	0.71
	acetonitrile	35	8.3	13	0.76
Me-AP	*n*-heptane	12	9.4	1.3	0.22
	benzene	5.5	2.7	1.4	0.51
	acetonitrile	4.6	1.8	1.4	0.61
MeO-AP	*n*-heptane	2.7	3.4	0	0
	benzene	2.1	2.2	0	0
	acetonitrile	1.7	1.6	$\approx$0	$\approx$0

benzene are in excellent agreement with the literature values (1.2×10^6 and 1.3×10^5 M^{-1} s^{-1}, respectively).[11,12] AP exhibits a significant decrease in the photoreduction rate constant in benzene ($k_r = 1.3 \times 10^6$ M^{-1} s^{-1}) and acetonitrile (1.3×10^6 M^{-1} s^{-1}) compared with that in *n*-heptane (2.3×10^6 M^{-1} s^{-1}), whereas Me-AP does not show any solvent dependence of k_r. The $\pi\pi$* T$_1$ state of MeO-AP is so low in energy that its photoreduction activity is zero or extremely low.

These kinetic data can also be used to estimate the quantum yield, Φ, for disappearance of the AP derivative in the photoreduction reaction. Based on the generally accepted mechanism of AP photoreduction, the quantum yield Φ is expressed as[38]

$$\Phi = \frac{k_r[\text{2-propanol}]}{k_d + k_r[\text{2-propanol}]} = \frac{k_r[\text{2-propanol}]}{k} \quad (2)$$

The calculated quantum yields are reported in Table 2. The Φ value of 0.71 for AP in benzene is consistent with previous results.[37,38] For AP and Me-AP, Φ increases with increasing solvent polarity. A similar trend has been found for the Norrish type II elimination of butyrophenone in glassy solvents at 77 K.[31]

DISCUSSION

For all the AP derivatives studied, the band intensity ratio $I_{\pi\pi*}/I_{n\pi*}$, which reflects the population ratio of the lowest nπ* and $\pi\pi$* states in thermal equilibrium, has demonstrated clear solvent dependence (see Figure 2 and Table 1). It is determined by the ordering of the two triplet states and the enthalpy difference between them. For AP, which has almost isoenergetic nπ* and $\pi\pi$* states ($\Delta H \approx 0$ cm^{-1}),[39] both states are equally populated and therefore the value of $I_{\pi\pi*}/I_{n\pi*}$ remains nearly constant around unity. Switching of the T$_1$ state could occur depending on the solvent. For Me-AP ($\Delta H \approx$ 100 cm^{-1})[29] and MeO-AP ($\Delta H \approx 240$ cm^{-1}),[29] the T$_1$ state is of $\pi\pi$* character,[11,12,15,16] so the intensity ratio is larger than AP. The $\pi\pi$* T$_1$ state of Me-AP and MeO-AP is further lowered with increasing solvent polarity due to stabilization of the $\pi\pi$* state in polar solvents.[11,30,31] Because the lowest nπ* and $\pi\pi$* states still remain in equilibrium even in acetonitrile and methanol as manifested by the synchronous decay of the T$_{n\pi*}$ and T$_{\pi\pi*}$ bands (see Figure 1c,d), the energy gap between the
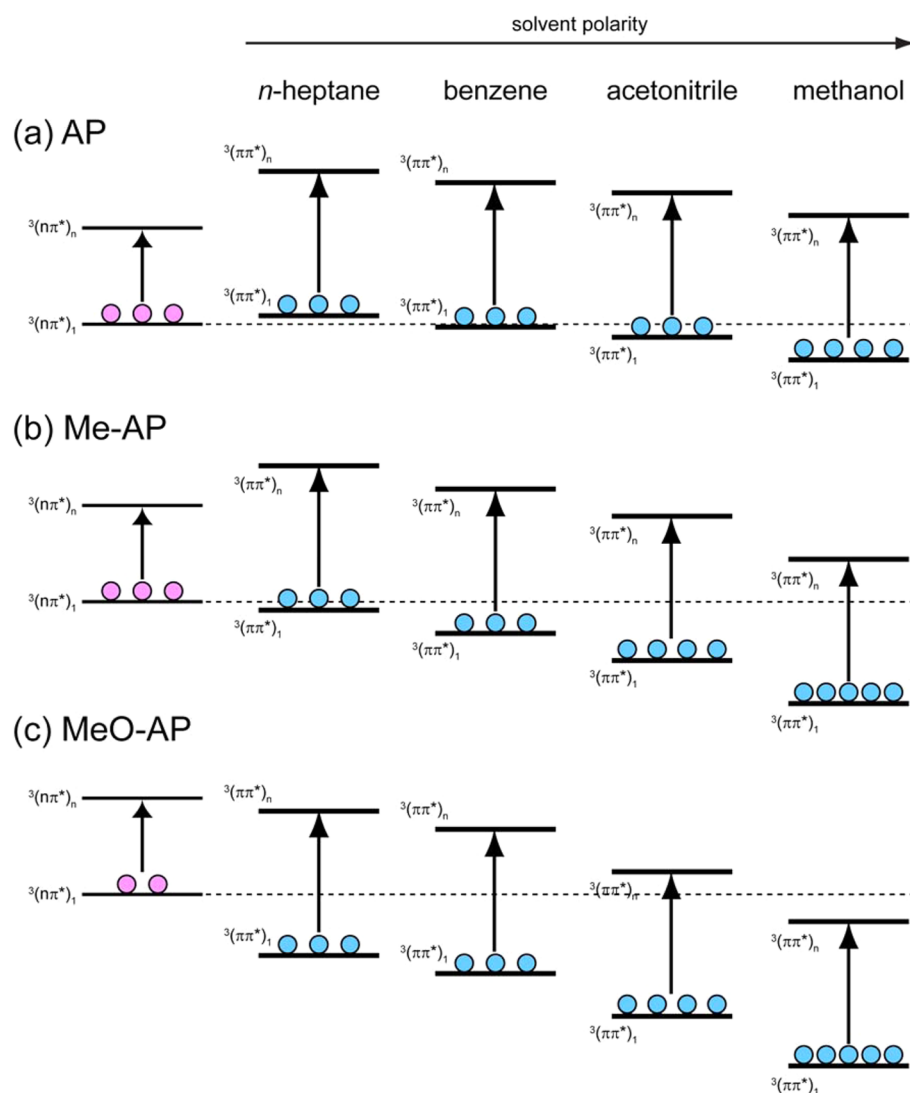
Figure 4. Schematic cartoon showing the solvent- and substituent-dependent change in the relative energy levels of the lowest $n\pi*$ and $\pi\pi*$ excited triplet states of AP (a), Me-AP (b), and MeO-AP (c).

two states in these solvents is most likely of the order of 100 cm^{-1}. Although unfortunately we are unable to obtain the value of ΔH due to a narrow liquid range of the solvents studied, we have gained a better understanding of the solvent- and substituent-dependent variation of the low-lying triplet energy levels, which is schematically illustrated in Figure 4. A similar energy level diagram was proposed by Lamola,[30] but it rests on only the $n\pi*$ phosphorescence at 83 K. In contrast, our diagram (Figure 4) has been derived from the results of direct observation of both $n\pi*$ and $\pi\pi*$ states in ambient solutions (Figure 2 and Table 1).

As opposed to the intensity ratio $I_{\pi\pi*}/I_{n\pi*}$, the photoreduction rate constant k_r of the AP derivatives does not depend considerably on the solvent except for AP (see Table 2). Our interpretation of this seemingly contradictory result is as follows. k_r for Me-AP ($\sim 10^5$ M^{-1} s^{-1}) is 1 order of magnitude smaller than that for AP ($\sim 10^6$ M^{-1} s^{-1}), and it is expected that MeO-AP has an even smaller k_r. Therefore, the solvent effects may not be reflected as evidently in k_r as they are in $I_{\pi\pi*}/I_{n\pi*}$. Another plausible account is that 2.0 M 2-propanol added to the solvent may change, at least to some extent, the properties of the original solvent (e.g., polarity), and how it

does so would depend on the interaction between the two solvent components. Given that, for example, the concentration of neat benzene is 11 M, addition of 2.0 M 2-propanol may be better regarded as forming a binary mixture rather than a small perturbation of benzene. Experiment with much lower concentrations of 2-propanol, which entails further improvement of the signal-to-noise ratio, will help to clarify this issue. The quantum yield Φ appears to show a better correlation with solvent polarity. Nevertheless, it should be mentioned that the assessment of solvent effects on the photoreduction activity just by investigating the overall yield, though conventionally utilized, cannot be free from complicated photochemistry involving side reactions and quenching impurity.[38] This fact makes direct observation of the NIR T$_{n\pi*}$ and T$_{\pi\pi*}$ bands a preferable approach to elucidate the nature of the very energy level ordering of the excited triplet states.

Solute−solvent hydrogen bonding is known to play a role in the energetics and photochemical reactivity of the $n\pi*$ and $\pi\pi*$ triplet states. Rauh and Leermakers showed on the basis of their phosphorescence measurements, that the reactivity of butyrophenone in the type II photoelimination becomes maximum in moderately hydrogen-bonding solvents such as acetonitrile

and acetic acid.[31] Phillips and co-workers studied hydrogen-bonding effects on the dynamics of the MeO-AP $\pi\pi^*$ triplet state in neat acetonitrile and acetonitrile/water (1:1 v/v) mixed solvent, using time-resolved resonance Raman spectroscopy and density functional theory calculations.[40] They found that in the mixed solvent, MeO-AP forms a hydrogen-bond complex with one water molecule, which has distinctly different electronic and structural properties of the triplet state from the free MeO-AP. Of the four solvents studied here, methanol is a typical hydrogen-bonding solvent. However, presumably because the hydrogen-bonding ability of methanol is not as high as that of water, our time-resolved NIR data (Figures 1, 2, S1, and S2) reveal very similar spectral pattern and temporal behavior of the AP derivatives in methanol and other solvents. This result implies that the largest intensity ratio $I_{\pi\pi^*}/I_{n\pi^*}$ observed for methanol is not due to specific hydrogen-bond interaction.

In conclusion, the present study has revealed the solvent effects on the energy level ordering of the low-lying $n\pi^*$ and $\pi\pi^*$ excited triplet states of AP derivatives using the intensity ratio of the triplet–triplet absorption bands in the NIR. In conjunction with our previous work,[29] we have now addressed the two fundamentally important questions in the photochemistry of aromatic carbonyl compounds, i.e., substituent and solvent dependence of the triplet energetics. The ability to observe both electronic transitions between close-lying excited states and vibrational transitions is unique to our method.[29,33,34] It is powerful for studying not only solutions but also photovoltaic materials, which is currently under way in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Representative time-resolved NIR spectra of Me-AP and MeO-AP in *n*-heptane, benzene, acetonitrile, and methanol (Figures S1 and S2) and photoreduction kinetic profiles for the $\pi\pi^*$ state (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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