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Structural Differences between $\pi\pi^*$ and $n\pi^*$ Acetophenone Triplet Excited States as Revealed by Time-Resolved IR Spectroscopy

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Ketone triplet excited states are important intermediates in a wide variety of photochemical reactions.[1] Many ketone triplets have been studied previously (e.g., by transient UV−vis absorption[2] or phosphorescence studies[3]), and although those investigations provided valuable data on lifetimes and reactivities of triplet excited states, little direct structural information has been gleaned.[4] Indeed, with the exception of the very recent time-resolved infrared (TRIR) studies of several $\pi\pi^*$ ketone triplets,[5] IR data on organic excited states are extremely scarce.[6]

Acetophenone is a particularly instructive case in point. In nonpolar solvents the lowest triplet state of acetophenone is known to be $n\pi^*$ but the $\pi\pi^*$ state is only slightly higher in energy.[2,3,7] Accordingly, the nature and reactivity of the acetophenone triplet depend strongly on such variables as solvent and phenyl ring substitution.[8] In view of these features, we have begun to examine the TRIR spectra of a variety of substituted acetophenone triplets and now report initial findings from studies of the $^3\pi\pi^*$ state of 4-methoxyacetophenone (**1**) and the $^3n\pi^*$ state of 4-(trifluoromethyl)acetophenone (**2**). These acetophenone derivatives have been shown by previous studies[8] to be prototypical representatives of $^3\pi\pi^*$ and $^3n\pi^*$ reactivities.

We conducted TRIR experiments as described previously[9] and by following the method of Hamaguchi and co-workers.[10] Typical data following 266-nm laser excitation of **1** and various isotopomers of **1** in argon-saturated acetonitrile-d_3 are shown in Figure 1. We attribute the positive bands in Figure 1 to the $\pi\pi^*$ triplet excited state of **1**; the negative bands are due to depletion of ground-state bands. Kinetic traces observed at two of the most prominent bands for unlabeled **1** (the positive band at 1462 cm^{-1} and the negative band at 1676 cm^{-1}) are given in Figure 2. The rate of decay of the triplet 1462 cm^{-1} band equals the rate of recovery of the ground-state 1676 cm^{-1} band. All the other positive and negative bands display the same time dependence as the 1462 and 1676 cm^{-1} signals, respectively. This behavior indicates that all positive bands belong to one species (the triplet excited state) and all negative bands belong to its counterpart (the ground state). That the positive bands represent the triplet excited state is evident from the observation of a dramatic reduction in lifetime ($\tau \leq 50$ ns) in oxygen-saturated solutions.

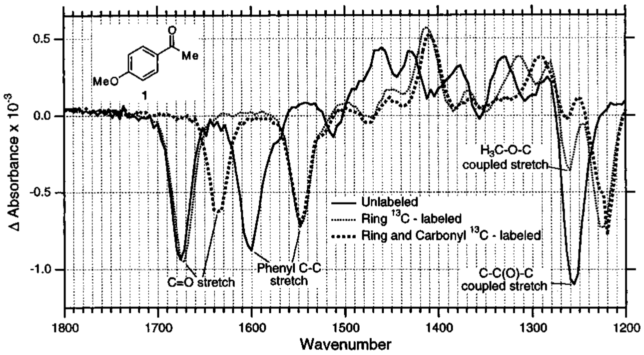

Figure 1. TRIR difference spectra observed over the first 500 ns following 266-nm laser photolysis of **1** (5 mM) and two of its isotopomers in argon-saturated acetonitrile-d_3. Ring ^{13}C-labeled refers to an isotopomer in which all six phenyl ring carbons are ^{13}C-labeled.

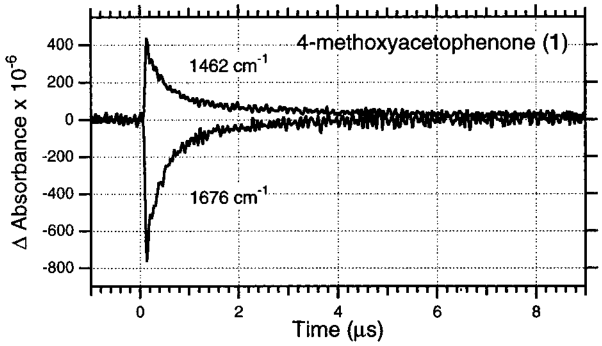

Figure 2. Kinetic traces observed at 1462 and 1676 cm^{-1} following 266-nm photolysis of **1** (5 mM) in argon-saturated acetonitrile-d_3.

A representative TRIR study of the triplet excited state of **2** is presented in Figure 3. Notice the absence of positive IR bands for $n\pi^*$ triplet **2** in the spectral region 1650−1350 cm^{-1} in stark contrast to those observed for $\pi\pi^*$ triplet **1**. To probe the different structural changes that occur upon photoexcitation from ground state → $^3\pi\pi^*$ state vs ground state → $^3n\pi^*$ state, we have examined the isotopically labeled analogues (prepared by conventional literature procedures) of **1** and **2** indicated in Figures 1 and 3.[11] Band assignments, based on all our isotopic studies, are presented in Table 1 and those of prominent ground-state absorptions are included in Figures 1 and 3.[12]

Our TRIR data are qualitatively consistent with classical notions concerning $^3n\pi^*$ and $^3\pi\pi^*$ states as represented by the simple

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(4) A notable exception is formaldehyde whose excited-state structure has been known for some time. See: (a) Brand, J. C. D.; Williamson, D. G. *Adv. Phys. Org. Chem.* **1963**, *1*, 365. (b) Turro, N. J.; Dalton, C. J.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92.

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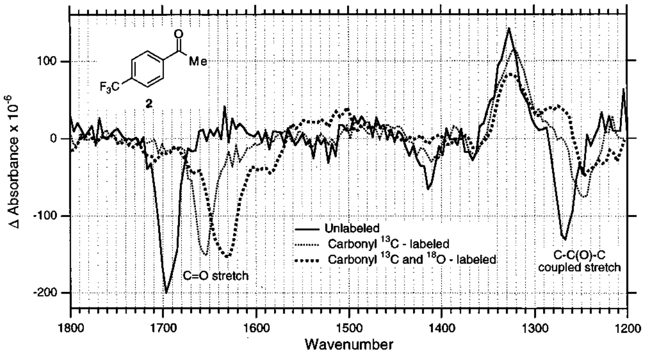

Figure 3. TRIR difference spectra observed over the first 500 ns following 266-nm laser photolysis of **2** (40 mM) and two of its isotopomers in argon-saturated acetonitrile-d_3.

Table 1. IR Band Positions (in cm^{-1}) for $\pi\pi^*$ Triplet **1** and $n\pi^*$ Triplet **2**

	T_1 mode[a]	unlabeled	*C=O	C=*O	*C=*O	*Ph	*Ph−*C=O
1	C−O str (S_0 = 1676)	1462[b]	1426	1460[b]	1424	1450[b]	1410
1	phenyl C−C str (S_0 = 1600)	1462[b]	1462	1460[b]	1462	1450[b]	1450
1	phenyl C−C str (S_0 = 1600)	1430	1426	1430	1424	1412	1410
1	phenyl C−C str (S_0 = 1600)	1378	1376	1378	1374	1368	1366
1	C−C(O)−C str (S_0 = 1256)	1332	1314	1332	1312	1314	1292
1	H_3C−O−C str (S_0 = 1260)	1284[c]	1280	1284	1280	1280	1280[i]
2	C−O str (S_0 = 1696)	1326	1310[d]	1300[d]	1280		
2	phenyl C−C str (S_0 = 1582)	1582[c]					
2	C−C(O)−C str (S_0 = 1270)	1326[c]	1322	1326	1324		

[a] Roughly analogous to the corresponding mode in the ground state. [b] The approximate C−O stretching mode and a phenyl C−C band overlap. [c] Tentative assignment. [d] Approximate band position.

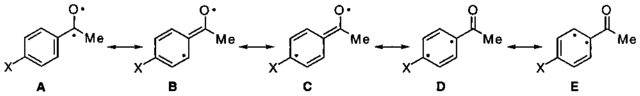

Figure 4. Important resonance contributors for $n\pi^*$ and $\pi\pi^*$ acetophenone triplets.

resonance structures shown in Figure 4.[8] Since the n orbital is located on the carbonyl oxygen, changes in bonding that accompany $n\pi^*$ triplet formation are thought to be localized primarily in the carbonyl portion of the molecule (i.e., resonance form **A**, with minor contributions from **B** and **C**). For $\pi\pi^*$ triplets, on the other hand, changes are expected to be more substantial throughout the entire aromatic system (i.e., resonance forms **B**−**E**).

As indicated in Table 1, we have analyzed our results by correlating triplet IR bands with ground-state vibrational modes. Of course, vibrational modes in the triplet states are not exactly analogous to those of the ground state and, as revealed by our observed isotopic shifts, are also not pure, localized modes. In addition, these isotopic studies indicate that the triplet modes for $\pi\pi^*$ **1** are not identical to those for $n\pi^*$ **2**. Nonetheless, a comparison with ground-state modes is informative.

For example, the C−O stretching vibration in $^3n\pi^*$ **2** appears at a lower frequency relative to that in $^3\pi\pi^*$ **1** (1326 vs 1462 cm^{-1}) and is shifted more substantially from the corresponding ground-state band ($\Delta\nu$ = 370 vs 214 cm^{-1}, respectively). These observations indicate lower double-bond character in the $n\pi^*$ triplet, consistent with the relative importance of resonance contributors for $^3n\pi^*$ and $^3\pi\pi^*$ states and also with recent time-resolved resonance Raman studies of $^3n\pi^*$ benzophenone (ν_{CO} = 1222 cm^{-1} vs 1665 cm^{-1} in S_0) and $^3\pi\pi^*$ 4-phenylbenzophenone (ν_{CO} = 1522 cm^{-1} vs 1665 cm^{-1} in S_0).[13] Recent TRIR studies of $\pi\pi^*$ triplet ketones[5] have revealed C−O stretching frequencies in the range 1524−1617 cm^{-1}. We are presently extending our TRIR investigations to other acetophenone derivatives to refine the correlation of triplet ketone IR stretching frequencies with the nature of the triplet state's electronic configuration.

The C−C(O)−C coupled stretch[14] in both $^3\pi\pi^*$ **1** (1332 cm^{-1}) and $^3n\pi^*$ **2** (1326 cm^{-1})[15] is shifted to higher frequency compared with the corresponding band in the ground state again consistent with expected resonance contributions (Figure 4). Structures **B** and **C** predict greater double-bond character in the C_{Ph}−C(O) bond relative to the ground state, and such a structural change has been predicted by semiempirical calculations of triplet benzophenone.[16] The magnitude of our experimentally observed shift from the corresponding ground-state IR band in $^3\pi\pi^*$ **1** ($\Delta\nu$ = 76 cm^{-1}) and in $^3n\pi^*$ **2** ($\Delta\nu$ = 56 cm^{-1}) may reflect the relative importance of these resonance forms in describing the geometry of each state.

Interestingly, the single phenyl C−C stretch[17] at 1600 cm^{-1} in the ground state of **1** is shifted to lower frequency and appears as three separate bands (1462, 1430, and 1378 cm^{-1}) in the $\pi\pi^*$ triplet. This observation suggests that in $^3\pi\pi^*$ **1** the phenyl ring is severely distorted. In contrast to these results, strong phenyl C−C IR absorptions are not observed for $^3n\pi^*$ **2**. Since the ring C−C mode in the ground state of **2** is much weaker than the corresponding band for **1**,[18] a possible explanation is that this band also has a low extinction coefficient in the triplet. Negative ground-state peaks in our TRIR difference spectra indicate changes in frequency or in the magnitudes of extinction coefficients for the corresponding bands in the triplet. Thus, another possible explanation for the absence of phenyl C−C IR absorption in data for the $^3n\pi^*$ state is that this mode remains unchanged upon excitation of **2** (i.e., resonance form **A**).

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Supporting Information Available: TRIR data for carbonyl ^{13}C-labeled **1**, carbonyl ^{18}O-labeled **1**, carbonyl ^{13}C- and ^{18}O-labeled **1**, and carbonyl ^{18}O-labeled **2** (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[13] (a) Tahara, T.; Hamaguchi, H.; Tasumi, M. *J. Phys. Chem.* **1987**, *91*, 5875. (b) Tahara, T.; Hamaguchi, H.; Tasumi, M. *Chem. Phys. Lett.* **1988**, *152*, 135. (c) Tahara, T.; Hamaguchi, H.; Tasumi, M. *J. Phys. Chem.* **1990**, *94*, 170. 4-Phenylbenzophenone has also been examined by TRIR methods.[6a]

[14] Mode 13 according to Wilson's numbering convention.

[15] The assignment of this band is tentative due to the relatively small shifts observed upon isotopic substitution; however, the negative peak observed at 1270 cm^{-1} in the TRIR difference spectrum (Figure 3) indicates that the ground state coupled C−C(O)−C band is shifted in the triplet.

[16] (a) Hoffmann, R.; Swenson, J. R. *J. Phys. Chem.* **1970**, *74*, 415. (b) Weitzel, K.-M.; Bassler, H. *J. Chem. Phys.* **1986**, *84*, 1590.

[17] Mode 8 according to Wilson's numbering convention.

[18] The ratio of IR intensities for carbonyl to phenyl ring stretching vibrations in the ground state of **1** is approximately 1:1. The corresponding ratio in **2** is approximately 6:1.