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Discrimination of Rotational Isomers of Jet-Cooled Acetophenone Derivatives as Studied by Sensitized Phosphorescence Excitation Spectroscopy

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The $S_1(n,\pi^*)\leftarrow S_0$ and $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectra of jet-cooled *o*- and *m*-substituted (fluoro- and methyl-) acetophenones have been measured. The two rotational isomers (*O-cis* and *O-trans* isomers) of each molecule arising from the orientation of the acetyl group with respect to *o*- or *m*-substituent have been discriminated. The energy difference in the 0–0 transition between the two isomers is less than 100 $\mathrm{cm^{-1}}$ for *m*-substituted acetophenone but more than 300 $\mathrm{cm^{-1}}$ for *o*-substituted acetophenone. The characteristic energy difference can be explained from the fact that the electronic excitation is localized on the C=O group.

In a series of papers, we have reported the studies on discrimination of the rotational isomers of *o*- and *m*-substituted phenols, anisoles, and benzaldehydes using the electronic transition in a supersonic free jet.[1—6] In molecules such as phenols and anisoles, the $S_1(\pi,\pi^*)\leftarrow S_0$ excitation energy difference between the rotational isomers amounts to 100—300 $\mathrm{cm^{-1}}$ for both *m*- and *o*-substituted compounds. On the other hand, it was found that the $S_1(n,\pi^*)\leftarrow S_0$ and $T(n,\pi^*)\leftarrow S_0$ transition energy differences between the rotational isomers are quite different for *m*- and *o*-substituted benzaldehydes (several tens $\mathrm{cm^{-1}}$ for the former and 400—500 $\mathrm{cm^{-1}}$ for the latter). The characteristic difference in the transition energy between phenol derivatives and benzaldehyde derivatives is caused by their difference in the nature of the electronic excited state.

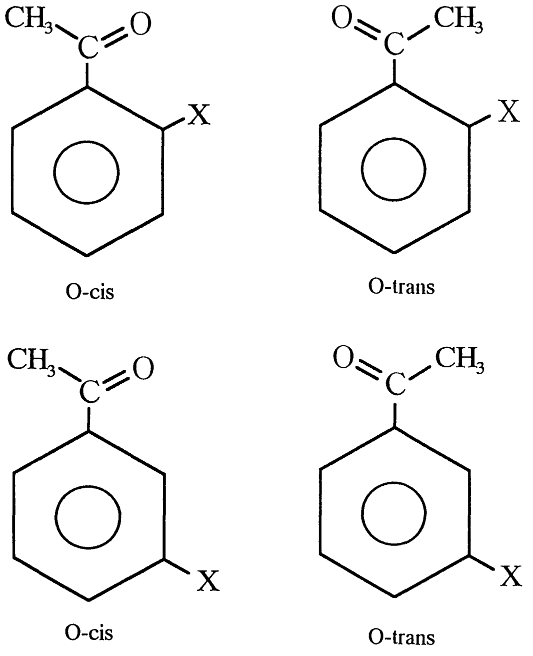

Fig. 1. The molecular structures of *O-cis* (*sp*) and *O-trans* (*ap*) rotational isomers of *o*- and *m*-substituted acetophenones. X indicates substituent.

In the present work, we extended the study to the rotational isomers of *o*- and *m*-substituted acetophenones. There exist two rotational isomers for each molecule. They are *O-cis(sp)* and *O-trans (ap)* isomers arising from orientation of the oxygen atom of the acetyl group with respect to the *o*- or *m*-substituent (Fig. 1). Similar to the case of substituted benzaldehydes, it is expected that the rotational isomers of subsitituted acetophenone are easily discriminated by the electronic spectrum of the jet-cooled molecule. In general, acetophenone derivatives are nonfluorescent and have a low efficiency of ionization. It is difficult therefore to apply the technique such as laser induced fluorescence (LIF) and multiphoton ionization (MPI) to these molecules. However, they are usually highly phosphorescent, and we can measure the electronic spectrum by phosphorescence excitation spectroscopy. However, the application of this technique to jet-cooled molecules is not easy because of a very weak phosphorescence signal gained by a space fixed photomultiplier from the molecules having a long phosphorescence lifetime and moving with a high speed in the jet. The difficulty had been solved by the development of a new spectroscopy called sensitized phosphorescence excitation spectroscopy, which uses sensitized phosphorescence emitted by a solid phosphor to which the triplet-state molecules in the jet collide.[7,8] We used this spectroscopy for the measurements of the electronic spectra of the substituted acetophenones.

By using this spectroscopy, we observed the $S_1(n,\pi^*)\leftarrow S_0$ transitions of *o*-, *m*-, and *p*-fluoroacetophenones, and *o*-, *m*-, and *p*-methylacetophenones. For each molecule except for *p*-derivatives, the existence of the two rotational isomers was confirmed. The difference in the electronic excitation energy between the two isomers is large for *o*-substituted acetophenone, but very small for *m*-substituted acetophenone, indicating the electronic excitation localized on the C=O group in the $S_1(n,\pi^*)$ state. Similar results were also obtained for the $T_1(n,\pi^*)\leftarrow S_0$ transitions. These results are consistent with those of benzaldehyde derivatives.

In our recent work, a remarkable difference was found for photochemical behaviors of the rotational isomers of *o*-methylbenzaldehyde in their $S_1(n,\pi^*)$ and $T(n,\pi^*)$ states.[6] The *O-cis* isomer was found to undergo a photochemical reaction involving intramolecular hydrogen abstraction (photoenolization). A similar reaction was also suggested for *o*-methylacetophenone.

Experimental

The sensitized phosphorescence excitation spectra of jet-cooled molecules were measured with the same apparatus as that reported elsewhere.[7] The sample was heated up to about 320 K to obtain sufficient vapor pressure and was seeded in 3 atm He gas. The gas mixture was expanded into a vacuum chamber through a pulsed nozzle with an orifice of 800 μm diameter. The UV output of a dye laser (Lambda Physik FL 3002) pumped by a XeCl excimer laser (Lambda Physik LPX100) was used as an exciting light source. The laser light crossed the jet 15 mm down stream of the nozzle. The triplet state molecules produced by the intersystem crossing from the S_1 state or by the direct laser excitation travel for about 40 μs further down stream from the excitation position and collides with a liquid-nitrogen-cooled copper surface which is covered with the solid sample serving as a sensitized phosphor. When the triplet state molecules collide with the phosphor surface, the energy transfer occurs and the sensitized phosphorescence is emitted. The sensitized phosphorescence was detected by a photomultiplier (HTV R585) and the signal was processed by a gated photon counting system (Ortec 9302, 9315, 9325 and a home made gate generator).

The samples, *o*-, *m*-, and *p*-fluoroacetophenones and *o*-, *m*-, and *p*-methylacetophenones (Tokyo Kasei) were used without further purification.

Results

A. *p*-Substituted Acetophenones. First of all, the results of *p*-substituted acetophenones having no rotational isomer are shown. Figure 2(a) shows the $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *p*-fluoroacetophenone. The longest wavelength, prominent band at 27591 cm^{-1} is assigned to the band origin. On the higher frequency side of the 0–0 band, several low frequency bands appear with displacements of 34, 64, and 88 cm^{-1} from the origin. These bands can be assigned to the levels of the internal rotation of the methyl group in the S_1 state similar to the case of acetophenone.[8] The frequencies of 34, 64, and 88 cm^{-1} represent the 2e, 3a$_1$, and 4e levels in the conventional notation of the internal rotation levels. It is suggested from the observed intensity pattern that the most stable conformation of the methyl group with respect to the molecular framework is quite different between the S_0 and S_1 states.

Figure 2(b) shows the $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *p*-methylacetophenone. The 0–0 band is located at 27445 cm^{-1}. The spectral feature is almost the same as that of *p*-fluoroacetophenone. The frequencies of 43, 75, and 96 cm^{-1} represent the internal rotation levels.

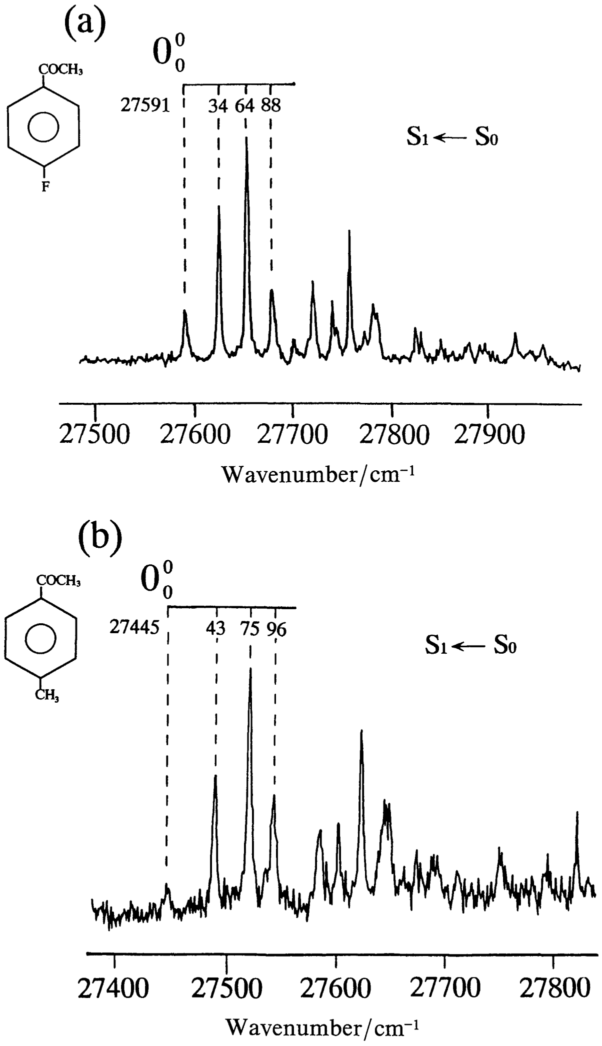

Fig. 2. (a) The $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *p*-fluoroacetophenone. (b) The $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *p*-methylacetophenone.

The $T(n,\pi^*)\leftarrow S_0$ transition was also observed. The energy of the 0–0 transition of *p*-fluoroacetophenone is 26104 cm^{-1}. The 0–0 band is exclusively strong in the spectrum but its absolute intensity is about 1/20 of that of the $S_1\leftarrow S_0$ transition. For *p*-methylacetophenone, the transition could not be observed because of the very low signal intensity.

From these results, the $S_1(n,\pi^*)$—$T(n,\pi^*)$ energy gap is 1341 cm^{-1} for *p*-fluoroacetophenone.

B. *m*-Substituted Acetophenones. Figure 3(a) shows the $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *m*-fluoroacetophenone. As seen from the figure, it has a complex structure. The structure can be decomposed to two progressions due to methyl torsion. The two band origins are located at 27047 and 27111 cm^{-1}, the energy difference being 64 cm^{-1}. The frequencies of 31, 60, and 85 cm^{-1} for the former, and 31, 60, and 82 cm^{-1} for the latter represent 2e,

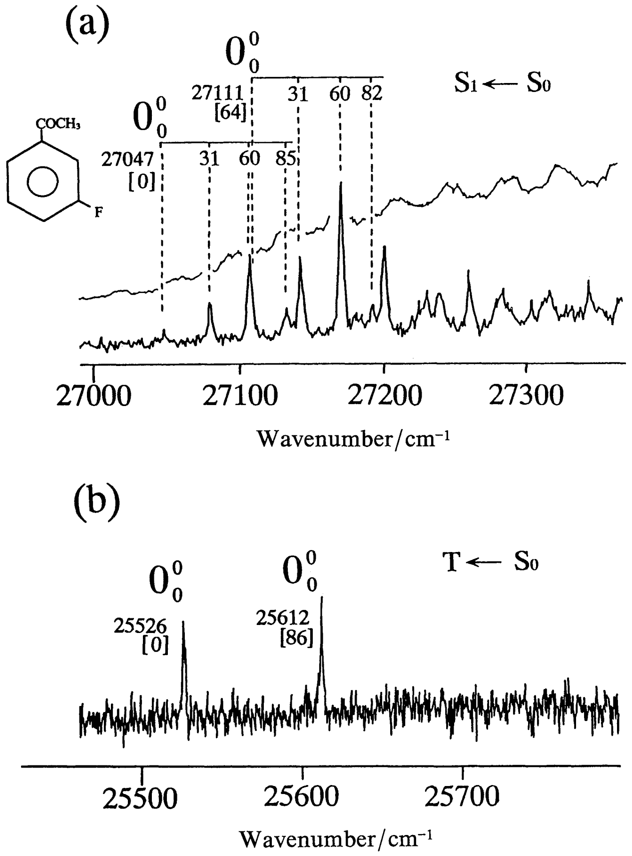

Fig. 3. (a) The $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *m*-fluoroacetophenone. (b) The $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *m*-fluoroacetophenone. The upper trace in (a) represents the laser power.

3a₁, and 4e levels, respectively. The 3a₁ band of the former accidentally overlaps with the 0–0 band of the latter. The two band origins are ascribed to the two rotational isomers, namely *O-cis* and *O-trans* isomers of *m*-fluoroacetophenone. If this assignment is right, we also expect the appearance of two origin bands in the spectrum due to $T(n,\pi^*)\leftarrow S_0$ transition.

Figure 3(b) shows the $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *m*-fluoroacetophenone. As expected, two 0–0 bands are observed at 25526 cm⁻¹ and 25612 cm⁻¹, which are assigned to the two rotational isomers. The energy difference between the two rotational isomers is 86 cm⁻¹. The intensities of the two bands are comparable, indicating that the two isomers have almost equal stabilities.

Figures 4(a) and 4(b) show the $S_1(n,\pi^*)\leftarrow S_0$ and $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectra of jet-cooled *m*-methylacetophenone. All the bands appear in pair of a small frequency separation. The pair bands can be ascribed to two rotational isomers. For the $S_1(n,\pi^*)\leftarrow S_0$ transition, the band origins of the two isomers are located at 27284 and 27288 cm⁻¹, the energy difference being 4 cm⁻¹. The situation is similar for the $T(n,\pi^*)\leftarrow S_0$ transition. The 0–0 bands are located at 25771 and 25774 cm⁻¹, the energy difference being only 3 cm⁻¹. Such a small energy difference was seen also in the case of *m*-methylbenzaldehyde.[6]

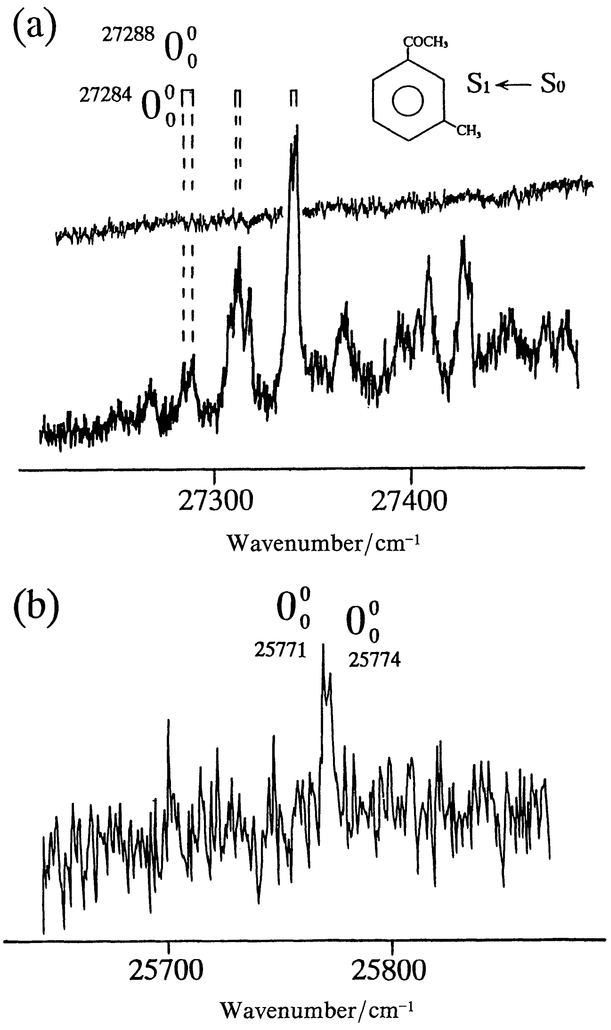

Fig. 4. (a) The $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *m*-methylacetophenone. (b) The $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *m*-methylacetophenone. The upper trace in (a) represents the laser power.

C. *o*-Substituted Acetophenones. Figures 5(a) and 5(b) show the $S_1(n,\pi^*)\leftarrow S_0$ and $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectra of jet-cooled *o*-fluoroacetophenone, respectively. It is seen in Fig. 5(b) that two 0–0 bands appear at 25746 and 26074 cm⁻¹, the frequency difference being 328 cm⁻¹. These bands are attributed to the 0–0 bands of the $T(n,\pi^*)\leftarrow S_0$ transitions of the two rotational isomers. The $S_1\leftarrow S_0$ spectrum also consists of two components. One origin is located at 27188 cm⁻¹ and the other origin at 27522 cm⁻¹. The energy difference amounts to 334 cm⁻¹, which is nearly equal to the difference in the $T\leftarrow S_0$ transition energy. The progression developing from the origin is assigned to the internal rotation of the methyl group. The frequencies of the internal rotation shown in the figure are slightly different from those of *m*- and *p*-substituted acetophenones. This suggests that the internal rotation of the methyl group is considerably affected by the *o*-substituent. In the case of *o*-methylacetophenone, the signal of sensitized phosphorescence could not be detected. But a spectrum having a complicated structure could be observed by multiphoton ionization spectroscopy. The complicated MPI spectrum and the absence of the sensitized phosphorescence suggest the existence of a fast nonradiative relaxation process (probably, intramolecular reaction) in the triplet state.

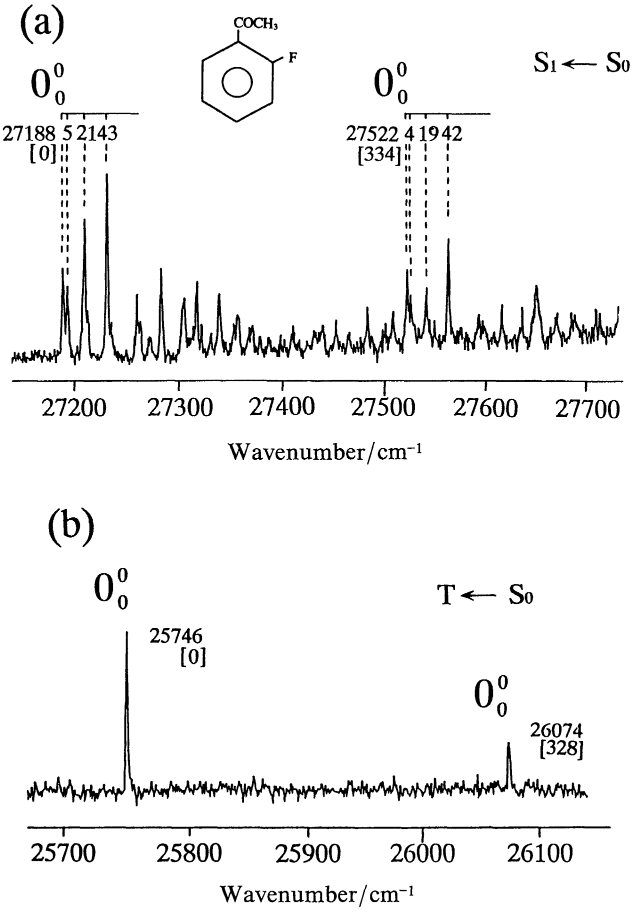

Fig. 5. (a) The $S_1(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *o*-fluoroacetophenone. (b) The $T(n,\pi^*)\leftarrow S_0$ sensitized phosphorescence excitation spectrum of jet-cooled *o*-fluoroacetophenone.

Discussion

The spectroscopic data obtained in the present work are summarized in Tables 1 and 2. It is seen from the tables that both the $S_1(n,\pi^*)\leftarrow S_0$ and $T(n,\pi^*)\leftarrow S_0$ transitions are shifted to blue in *p*-substituted acetophenone relative to those of acetophenone. On the other hand, red shift is seen for all the isomers of *m*-substituted acetophenones except for the $S_1\leftarrow S_0$ transition of the isomers of *m*-methylacetophenone. In *o*-fluoroacetophenone, the band origin of one isomer is red-shifted but the other blue-shifted. It is interesting to compare the direction of the shift with that of the $S_1(n,\pi^*)\rightarrow S_0$ transition of substituted benzaldehyde. For example, in *p*-fluorobenzaldehyde, the $S_1(n,\pi^*)\leftarrow S_0$ transition exhibits a large blue shift relative to benzaldehyde, and all the rotational isomers of *o*- and *m*-fluorobenzaldehydes except for the $T_1\leftarrow S_0$ transition of the isomers of *m*-fluorobenzaldehyde show red shift.[6] So the direction of shift is parallel between substituted benzaldehyde and substituted acetophenone. It is noted that the direction of the shift is entirely different between substituted phenol and substituted benzaldehyde or acetophenone. In phenols, *o*- and *p*-substituted phenol exhibits red shift while *m*-substituted phenol shows blue shift. The difference reflects the difference in the nature of the S_1 state, that is, the (π,π^*) states for substituted phenol and the (n,π^*) state for substituted benzaldehyde or acetophenone.

The characteristic nature of the $S_1(n,\pi^*)$ or $T(n,\pi^*)$ state of substituted acetophenone is also reflected in the difference in the excitation energy between the two rotational isomers, that is, the difference is very small for *m*-substituted acetophenone but very large for *o*-substituted acetophenone. This can be explained from the fact that the electronic excitation is essentially localized on C=O of the acetyl group in the $S_1(n,\pi^*)$ or $T(n,\pi^*)$ state. In *m*-substituted acetophenone, the

Table 1. Spectroscopic Data of the $S_1(n,\pi^*)$ and $T(n,\pi^*)$ States of Fluoroacetophenones. The Data of Acetophenone is Also Listed for Comparison.[8] All Frequencies are in cm⁻¹

Molecule	*o*-Fluoro			*m*-Fluoro			*p*-Fluoro	Acetophenone
$S_1\leftarrow S_0$ 0_0^0	27188		27522	27047		27111	27591	27279
Δ[a]		334			64			
Shift[b]	−91		+243	−232		−168	+312	0
$T\leftarrow S_0$ 0_0^0	25746		26074	25526		25612	26104	25791
Δ[a]		328			86			
Shift[b]	−45		+283	−265		−179	+313	0
S_1-T gap	1442		1448	1521		1499	1487	1488

a) Δ indicates the frequency difference of the 0–0 transition between the two rotational isomers. b) The frequency difference of the 0–0 band from that of acetophenone. The − and + signs indicate red and blue shifts, respectively.

Table 2. Spectroscopic Data of the $S_1(n,\pi^*)$ and $T(n,\pi^*)$ States of Methylacetophenones. The Data of Acetophenone is Also Listed for Comparison.[8] All Frequencies are in cm^{-1}

Molecule	*o*-Methyl	*m*-Methyl			*p*-Methyl	Acetophenone
$S_1 \leftarrow S_0$ 0_0^0		27284		27288	27445	27279
Δ[a)]			4			
Shift[b)]		+5		+9	+166	0
$T \leftarrow S_0$ 0_0^0		25771		25774		25791
Δ[a)]			3			
Shift[b)]		−20		−17		0
$S_1 - T$ gap		1513		1514		1488

a) Δ indicates the frequency difference of the 0–0 transition between the two rotational isomers. b) The frequency difference of the 0–0 band from that of acetophenone. The − and + signs indicate red and blue shifts, respectively.

distance between the C=O group and the substituent at *m*-position is far for both rotational isomers. Therefore, the electronic excitation energy is not greatly affected by the orientation of the C=O group. Contrary, in *o*-substituted acetophenone, the excitation energy changes greatly by the orientation because of a close distance between the C=O group and the substituent. In the case of the $S_1(\pi,\pi^*)$ of substituted phenol, the difference in the excitation energy between the rotational isomers is comparable between the *o*- and *m*-substituted phenols, showing the spread of the π-electronic excitation over the whole molecule.

The $S_1(n,\pi^*)-T(n,\pi^*)$ energy gap is almost constant at ca. 1490 cm^{-1} for all the molecules and isomers, although a slightly smaller value is found for *m*-fluoroacetophenone. The constant energy gap implies that the electronic structures of the $S_1(n,\pi^*)$ and $T(n,\pi^*)$ states of each molecule are very similar except for spin, and the energies of the both states are perturbed by almost equal amounts irrespective of the nature of the perturbation.

The remaining problem is the assignment of the two 0–0 bands to individual rotational isomers. In the case of *o*-fluoroacetophenone, the intensity ratio of the two origin bands is about 3:1, the lower energy 0–0 band being more intense. The reported population ratio is 1:9 for *O-cis* isomer to *O-trans* isomer.[9] Therefore, we tentatively assigned the 0–0 band of 27188 cm^{-1} to *O-trans* isomer and that of 27522 cm^{-1} to *O-cis*. In the case of *m*-substituted acetophenone, the intensities of two 0–0 bands are almost the same, suggesting nearly equal population. Therefore, the assignment is difficult only from the intensity ratio.

Finally, we have to mention the case of *o*-methylacetophenone for which the measurement of the phosphorescence excitation spectrum failed. *o*-Methylacetophenone is known to be a typical molecule undergoing the intramolecular photoenolization reaction like *o*-methylbenzadehyde or *o*-methylbenzophenone.[10–16] The oxygen atom of the acetyl group abstracts the hydrogen atom of the methyl group at *o*-position after photoexcitation. The reaction will selectively occur in the *O-cis* isomer. This explains the nonphosphorescence of the *O-cis* isomer. It was reported that the ratio of *O-cis* to *O-trans* is 7:3[17] or 84:16[18] in the solution and 93:7[19] from calculation. The intramolecular enolization reaction for the abundant *O-cis* isomer and a small amount of the *O-trans* isomer explain the failure of the measurement of the phosphorescence excitation spectrum for this molecule.

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