CHEMISTRY LETTERS, pp. 873-876, 1993.

The Infrared Spectra of Triplet 4-Phenylbenzophenone

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Microsecond time-resolved IR (TRIR) spectroscopy has been used to record the infrared spectra of the ππ* triplet states of 4-phenylbenzophenone and its ^{18}O and ^{13}C analogues.There is a definite shift in the frequency to lower wavenumber of the ν(CO) vibration. The intensity of the C-O vibration is similar in the ground and excited state. This is the first report of the infrared spectra of the excited triplet state of aromatic carbonyl compounds in room temperature solution.

Photochemical hydrogen abstraction by aromatic carbonyls has been studied extensively as an organic photochemical reaction of fundamental importance.1) The reactions are known to proceed through the lowest excited triplet (T_1) state. The nature of the triplet state is known to determine the reactivity; an nπ* triplet is known to be much more reactive than a ππ* triplet.2) The direct observation of excited states is an important step in the unravelling of the photochemical mechanisms of hydrogen abstraction. The vast majority of excited state species have been detected and studied by either UV/VIS absorption or luminescence.3) Such studies provide information on the lifetimes of excited states but are not suitable for extracting structural information. Vibrational data of excited states is particularly valuable in this respect. The matrix isolation technique has allowed the study of a limited number of long lived triplets by infrared spectroscopy.4) At room temperature time-resolved resonance Raman spectroscopy has been used to elucidate the difference in structure between the T_1 state of benzophenone which is nπ* in nature and the ππ* triplet of 4-phenylbenzophenone.5)

The CO stretching vibration, ν(CO), of the triplet should be very diagnostic in the determination of the nature of the C-O bond in the excited state. Time-resolved resonance Raman spectra showed that for the nπ* benzophenone the ν(CO) shifted approximately 450 cm^{-1} in the triplet state while for the ππ* 4-phenylbenzophenone the shift was much smaller. The combination of the Raman with infrared data should provide a more complete insight into the structure of these excited states. In addition to the frequency information, the infrared intensity may give a measure of the degree of double bond character of the ν(CO) vibration (ν(C=O) being much more intense than ν(C-O) in the infrared spectra). Band intensity is not so simply related to the bonding in the Raman spectra.

Time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis with fast infrared detection, has been widely applied to the study of metal carbonyl photochemistry.6) TRIR has also provided valuable structural information on the excited states of a limited number of coordination compounds.7) The extremely high extinction coefficients of metal carbonyl vibration makes them particularly suitable to study by

TRIR. The TRIR technique has been limited by the infrared detectors which are much less sensitive than photomultipliers or other such detectors for the UV and visible region. This has meant that there are few applications of TRIR to organic photochemistry where the infrared absorptions are much less intense.[8)] The TRIR apparatus at KAST has been described in detail previously.[9)] Briefly it consists of a modified Hitachi dispersive spectrometer (I-3000) and a Spectra-Physics cw Q-switched Nd:YLF laser (TFR) as an excitation source. The apparatus is completely computer controlled making a scanning TRIR spectrometer. Low noise amplification of the signal from the liquid nitrogen cooled MCT detector allows the detection of very weak transient signals (ΔAbsorbance < 10^{-6}). The preparation of 4-phenylbenzophenone and its isotopically substituted analogues has been described previously.[5b)]

Figure 1(a) shows the FTIR spectrum of 4-phenylbenzophenone in the ground electronic state. Figure 1(b) shows the TRIR spectrum (8 cm^{-1} resolution) of 4-phenylbenzophenone obtained over the first microsecond after 262 nm excitation by the fourth harmonic of the Nd:YLF laser. It is clear that the flash depletes the parent compound and generates a species with many intense infrared absorptions. We are confident in the assignment of these bands to the triplet 4-phenylbenzophenone because the lifetime of the absorptions assigned to the triplet were found to be O_2 dependent.

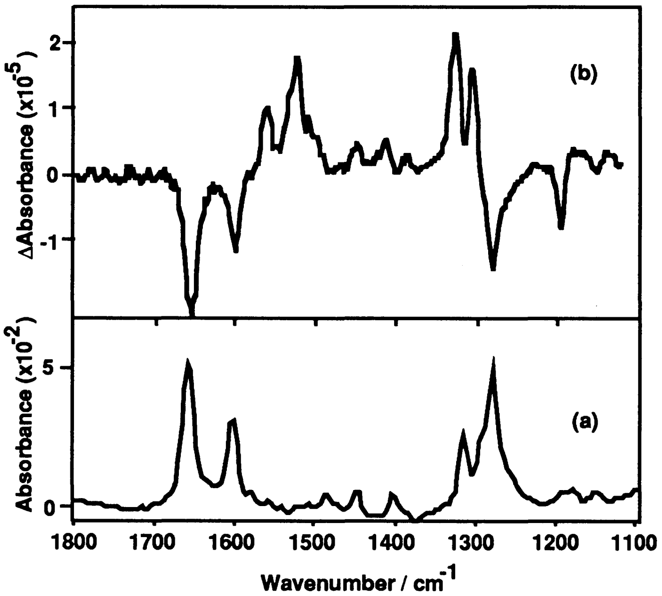

Fig.1. (a) The FTIR spectrum (8 cm^{-1} resolution) of the ground state; and (b) the TRIR spectrum (8 cm^{-1} resolution), obtained 1μs after the UV pulse, of 4-phenylbenzophenone.

The band at 1524 cm^{-1} is assigned to a vibration containing ν(CO) of the triplet state based on comparison with the previously published Raman spectra (a band at 1522 cm^{-1} in the Raman spectra of triplet 4-phenylbenzophenone was assigned to contain a contribution of ν(CO).[5b)] Confidence in this assignment is given by examining the TRIR spectra of ^{18}O and ^{13}C substituted 4-phenylbenzophenone. Figure 2 shows the TRIR spectra of ^{18}O and ^{13}C substituted together with unsubstituted 4-phenylbenzophenone. The substitution of ^{18}O causes the ground state ν(CO) vibration to shift from 1654 to 1628 cm^{-1}. Similarly, the ν(CO) vibration of the ^{13}C substituted compound shifts from 1654 to 1620 cm^{-1}. There is a second intense absorption band, at 1280 cm^{-1}, which shifts upon ^{13}C substitution to 1264 cm^{-1} and this vibration is assigned to the C-Phenyl stretch. No shift in the 1280 cm^{-1} absorption is observed in the ^{18}O spectrum. The only band of the triplet to show any significant shift upon ^{18}O substitution is that at 1524 cm^{-1} which is shifted to 1512 cm^{-1}. The 1524 cm^{-1} band is also shifted in the TRIR spectrum of ^{13}C substituted 4-phenylbenzophenone. The frequency shifts we have observed are consistent with the previously reported Raman spectra and we are confident in the assignment of this band to a normal mode having carbonyl stretching character. The intensity of this carbonyl band in the triplet state has comparable intensity to that of the ground state. This gives an indication that there is mainly double bond character in this vibration in the excited state. Such an intense ν(CO) vibration is not seen in the TRIR spectrum of the nπ* triplet of benzophenone (not shown)10) and the spectrum showed only depletion of the ground state. This observation is consistent with the nπ* triplet having single bond character.

There appears to be two bands at 1328 and 1306 cm^{-1} in the triplet spectrum of 4-phenylbenzophenone. They are most likely to arise from one single band overlapped with a negative band of the ground state. Although the precise wavenumbers are not known it can be seen that there is no change in the intensity and position of these bands in the ^{18}O substituted spectrum. Whereas, the ^{13}C substituted spectrum shows a shift in the most intense band from 1328 to 1296 cm^{-1}. The shift in these triplet bands, upon only ^{13}C substitution and not ^{18}O substitution, allows tentative assignment of these bands to a C-Phenyl stretching vibration in the excited state. They probably correspond to the Raman band at 1297 cm^{-1}, which shifts down to 1283 cm^{-1} upon ^{13}C substitution with virtually no shift upon ^{18}O substitution. There are also three weak vibrations that are observed in all three triplet spectra. A complete list of the observed triplet bands is given in Table 1.

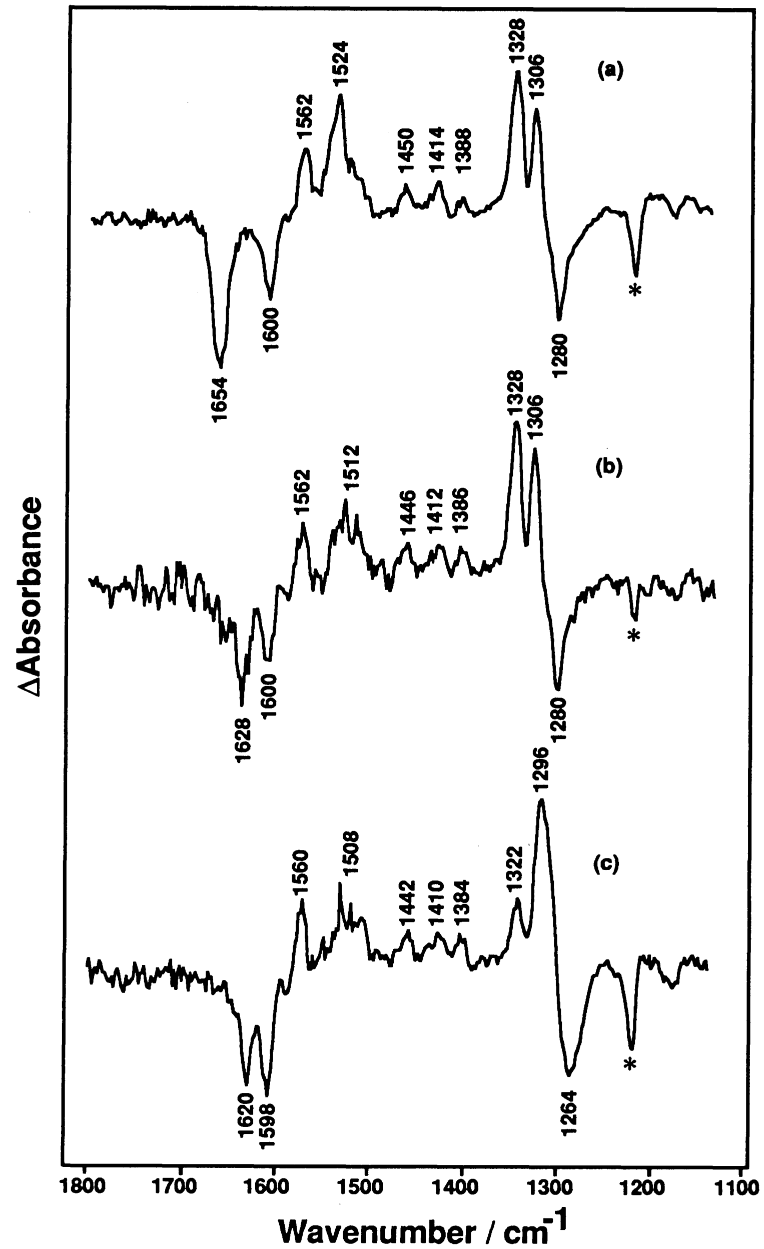

Fig.2. TRIR spectra, obtained 1 μs after UV excitation of (a) unsubtituted; (b) ^{18}O substituted and (c) ^{13}C substituted 4-phenylbenzophenone (the band labelled with a * is due to a thermal artifact which occurs at infrared frequencies corresponding to solvent absorptions.10)11)

Table 1. The observed infrared frequencies of triplet 4-phenylbenzophenone by TRIR spectroscopy

	$Ph_2{}^{12}C^{16}O$	$Ph_2{}^{12}C^{18}O$	$Ph_2{}^{13}C^{16}O$
S_0	1654	1628	1620
	1600	1600	1598
	1280	1280	1264
T_1	1562	1562	1560
	1524	1512	1508
	1450	1446	1442
	1414	1412	1410
	1388	1386	1384
	1328 /1306[a)]	1328 / 1306[a)]	1322 / 1296[a)]

a)The precise wavenumber is masked by overlap with parent absorptions.

We have shown that TRIR spectroscopy can be used to observe the triplet infrared spectra of organic carbonyl triplets and the $\pi\pi^*$ triplet spectra are consistent with the excited state having mainly CO double bond character. Further work is being carried out to establish a more complete infrared assignment of the excited state spectra.

We thank the Science and Technology Agency of Japan for support. We are especially indebted to Dr. Tahei Tahara for preparation of the ^{18}O and ^{13}C samples and many fruitful discussions. We also thank Professor Martyn Poliakoff and Professor John M. Kelly for helpful discussions.

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(Received February 17, 1993)