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Transient Resonance Raman Spectra of Michler's Ketone in the Lowest Excited Triplet State

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Transient resonance Raman spectra of Michler's ketone in the lowest excited triplet state were measured in ethanol and benzene. The spectral features of the T_1 state in these solvents were similar to each other although some frequency shifts were observed. This result suggests that Michler's ketone retains a charge transfer T_1 state in nonpolar solvents as well as in polar solvents.

The photochemical properties of benzophenone and its derivatives in the lowest excited triplet (T_1) state have been extensively studied and it is widely accepted that there is a clear correlation between the electron configuration and the reactivity for hydrogen abstraction: the $n\pi^*$ T_1 state exhibits high reactivity while the $\pi\pi^*$ T_1 state and the intramolecular charge transfer (CT) T_1 state show much less or no reactivity.[1,2] The T_1 state of Michler's ketone (4,4'-bis(dimethylamino)benzophenone, MK) in polar solvents has been regarded as a typical example of the CT T_1 state. Although the character of T_1 MK in polar solvent has been established, there is controversy about T_1 MK in nonpolar solvents. It is known that MK is efficiently photoreduced in nonpolar solvents; in contrast, it shows no reactivity in polar solvents. This significant solvent effect was explained in terms of the inversion of the energy levels in the triplet manifold: the CT triplet state has the lowest energy in polar solvents while the reactive $n\pi^*$ triplet state becomes the lowest in nonpolar solvents owing to the differences in stabilization by the solvent.[2-6] In 1977, Brown and Porter gave another interpretation concerning this phenomenon. They proposed that MK has a CT T_1 state in both polar and nonpolar solvents and the reactivity in nonpolar solvents is due to the thermally populated second lowest $n\pi^*$ triplet state.[7] Therefore the character of the T_1 MK in nonpolar solvents is still uncertain, and gaining insight into this state is essential for understanding the solvent effect on photochemical reactivity of MK. In this paper, we report the first vibrational spectra of T_1 MK in both polar and nonpolar solvents. These data give some new information about the character of T_1 MK from a viewpoint of molecular structure.

The transient Raman and absorption spectra were measured with a nano-second laser system consisting of two sets of pulsed Q-switched Nd:YAG lasers and dye lasers (Spectron SL series). The transient Raman spectra were measured by a pump-probe method. The pumping and the probing beams were focused onto a thin film-like jet stream of sample solution. The scattered light was analyzed by a triple polychromator (Jobin Yvon T6400) and detected with an intensified photodiode array detector (Princeton Instruments IRY-1024G/RB). The transient absorption spectra were measured by using a pulsed Xe lamp (Hamamatsu L2358)

as the monitor light source. The monitoring light that passed through a quartz sample cell was analyzed by a single polychromator (Jobin Yvon HR320) and was detected with an intensified photodiode array detector (Princeton Instruments IRY-700G/B/par). All systems were computer controlled using software developed in our laboratory. The time resolution of this system was determined by the pulse duration of the laser pulse (10-17 ns). In order to acquire the transient Raman and absorption spectra, it was first necessary to purify the MK samples (Wako Chemical Co.) with the following procedure. Purchased MK (colored blue) was dissolved in benzene and washed with water. After the evaporation of benzene, the sample was recrystallized from ethanol. The obtained pure MK (light yellow) was used for the experiment.

Figure 1 shows the transient absorption spectra of T_1 MK measured at 40 ns after the 355 nm excitation. The spectrum in ethanol (Fig. 1A) is essentially the same as that reported by Hoshino and Kogure.[8] The T_1 states of MK in both ethanol and benzene exhibit similar broad absorption over the measured spectral range (400-750 nm). The shifts of the absorption maxima (423, 493 nm in ethanol -> 408, 518 nm in benzene) indicate that the solvent polarity affects the energy of the triplet levels to some extent.

Since T_1 MK shows very broad transient absorption, any wavelength in the visible region can be used for probing the transient resonance Raman scattering. We chose 532 nm so that we could have a direct comparison of the spectra of T_1 MK with T_1 benzophenone (a typical $n\pi^*$ T_1 that was previously measured using 532 nm excitation [9]). The transient resonance Raman spectrum of T_1 MK in ethanol is shown in Fig. 2A. T_1 MK in polar solvents has CT character. It is believed that an electron is transferred from the nitrogen atoms in the dimethylamino groups to the oxygen of the carbonyl group in this T_1 state. As expected, the spectral feature of this typical CT T_1 state is quite different from that of T_1 benzophenone (shown in Fig. 2C). Since Michler's ketone is a 4,4'-substituted benzophenone, it is better to compare Raman spectra of T_1 MK also with that of the T_1 state of a 4,4'-substituted benzophenone having $n\pi^*$ character. We measured Raman spectra of the T_1 state of 4,4'-dichlorobenzophenone and its spectrum is shown in Fig. 2D. The spectral feature of 4, 4'-dichlorobenzophenone in the T_1 state is similar to that of T_1 benzophenone except for the absence of a strong band around 970 cm^{-1}.[10] It is concluded that the difference in the spectral feature between T_1 MK in ethanol and T_1 benzophenone is not ascribable to the change of the vibrational mode induced by 4,4'-substitution but reflect the difference in the character of the T_1 state. The transient resonance Raman spectrum of T_1 MK in benzene is depicted in Fig. 2B. Although some frequency shifts are observed, the

Table 1. The CC stretching frequencies of benzophenone derivatives

	MK in ethanol	MK in benzene	Benzophenone	4-Bromo-benzophenone	4-Chloro-benzophenone	4,4'-Dichloro-benzophenone
S_0	1589		1600	1599 1588	1599 1587	1589
T_1	1583 [a]	1593 [a]	1540 [b]	1545 [c]	1544 [c]	1537 [a]

a) This work. b) Ref.9. c) Ref.12.

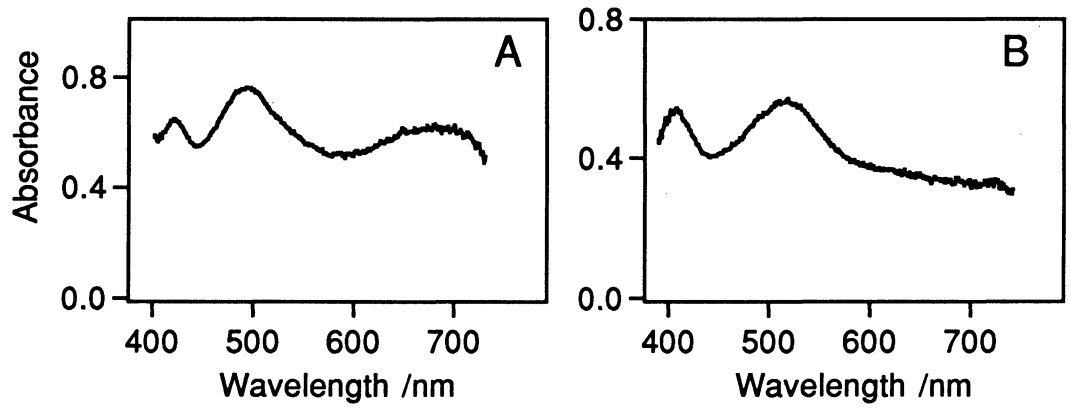

Fig. 1. Transient absorption spectra of Michler's ketone in the lowest excited triplet state obtained from 5×10^{-4} M ethanol (A) and 2.4×10^{-4} M benzene (B) solutions (pump laser 355 nm; delay 40 ns).

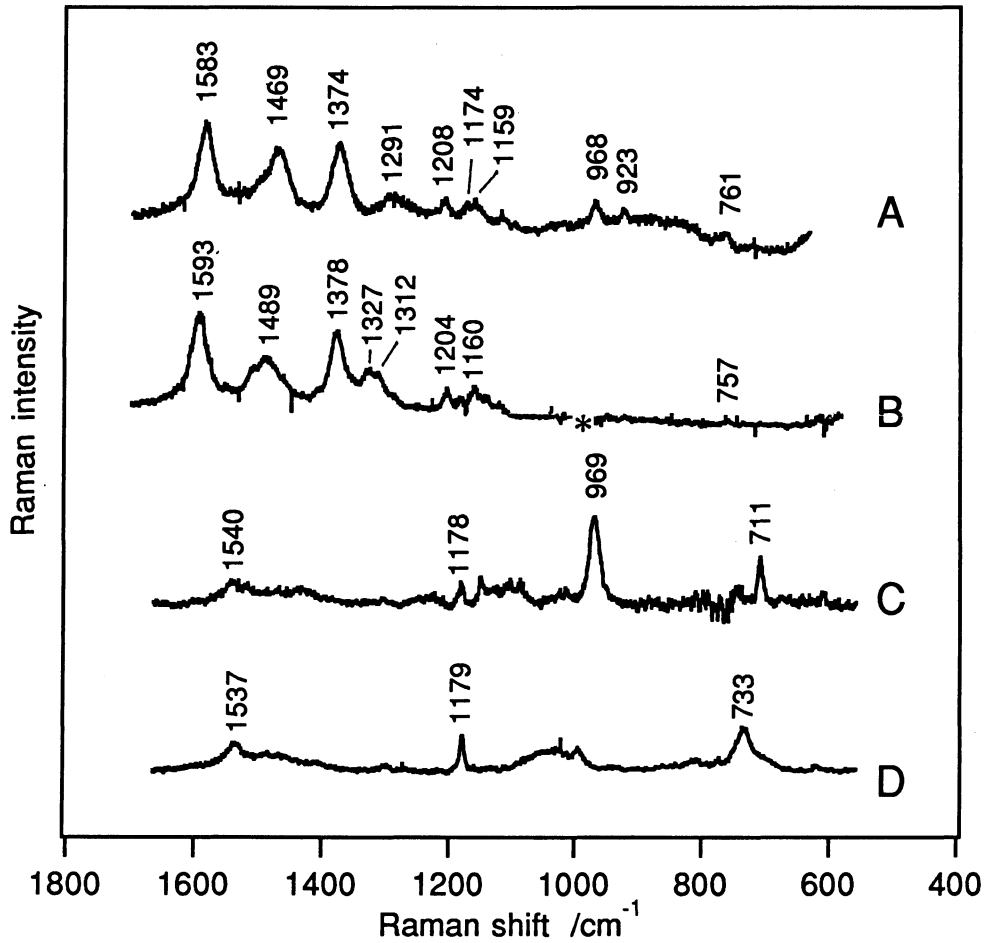

Fig. 2. Transient Raman spectra of Michler's ketone and its related compounds in the lowest excited triplet state measured with 532-nm probing. (A) Michler's ketone in ethanol (2×10^{-3} M; 355-nm pumping; 40 ns), (B) Michler's ketone in benzene (5×10^{-4} M; 355 nm pumping; 40 ns), (C) benzophenone in carbon tetrachloride (3×10^{-3} M; 266-nm pumping; 20 ns), (D) 4,4'-dichlorobenzophenone in carbon tetrachloride (3×10^{-3} M; 266-nm pumping; 20 ns). The solvent bands were subtracted in each spectrum. The asterisk indicates the region overlapped with a strong solvent band.

spectral pattern is very similar to that of T1 MK in ethanol. Full vibrational assignments are not made at the present stage but we can assign the bands at 1583 cm^{-1} (in ethanol) and 1593 cm^{-1} (in benzene) to the CC stretch of the phenyl rings with confidence. The CC stretching frequency is a good indicator of the structure of the rings in the T1 state.[11] The CC stretching frequencies of benzophenone derivatives are compared in Table 1. While the CC stretching frequencies are very similar to one another in the S0 state, they are quite different in the T1 state. The CC stretching frequencies of the $n\pi^*$ T1 states (benzophenone, 4-bromo, 4-chloro, and 4,4'-dichlorobenzophenone) are located around 1540 cm^{-1}. The Raman band of T1 MK in ethanol having CT character is of much higher frequency (1583 cm^{-1}) than those of the $n\pi^*$ T1 states. This means that there is a significant difference in the structure of the phenyl rings between the $n\pi^*$ T1 and the CT T1 states. T1 MK in benzene shows a Raman band due to the CC stretch at 1593 cm^{-1}. This frequency is far from the CC stretching frequencies of the $n\pi^*$ T1 states but is close to that of the CT T1 state. On the basis of (1) the spectral pattern and (2) the CC stretching frequency of the rings, it is concluded that T1 MK retains CT character in nonpolar solvents as well as in polar solvents. Finally, we note that the differences in vibrational frequencies between T1 MK in benzene and in ethanol suggest some structural changes induced by the change in solvent polarity. It is expected that the solvent polarity influences the magnitude of the intramolecular charge transfer occurring in T1 MK. The observed frequency shifts may be ascribed to structural changes reflecting the difference in the magnitude of charge transfer in polar and nonpolar solvents.

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10) The strong band at 969 cm^{-1} of T1 benzophenone was assigned to the "trigonal + breathing" mode of the mono-substituted phenyl ring in Ref 9. It is known that the corresponding band in the ground state disappears upon the para di-substitution. Therefore, the absence of the this band in the Raman spectrum of T1 4,4'-dichlorobenzophenone can be easily explained in terms of the change of the vibrational mode induced by the 4,4'- substitution.
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