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TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF THE LOWEST EXCITED TRIPLET STATE OF BENZIL

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Abstract : The time-resolved resonance Raman spectrum of the first excited triplet state of benzil is reported in the range 400-1700 cm^{-1} . A comparative vibrational analysis of the ground state and the triplet state is given, and structural implications are discussed.

Benzil is a representative molecule of the α -dicarbonyls class which is extensively studied in reason of its interesting and diversified photophysical and photochemical properties (1,2). It is also a typical photoinitiator of radical polymerization (3,4). Skewed (dihedral angle between the planes of the two carbonyl groups $\approx 111^\circ$ in crystal) (5) and near-trans planar (6,7) forms were found for the ground (S_0) and lowest triplet (T_1) states, respectively.

Resonance Raman spectroscopy with pulsed Laser excitation and multichannel optical detection is a very sensitive tool to detect transient species in solution and the analysis of vibrational spectra gives unique information about their molecular structure. We have used the pump-then-probe technique to analyse by resonance Raman spectroscopy the first triplet state (T_1) of benzil.

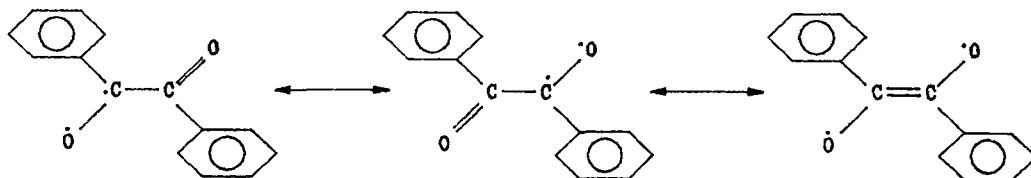
The T_1 state of benzil was populated by pump excitation into the $S_1 \leftarrow S_0$ absorption band at 248 nm and 308 nm in conjunction with $T_1 \leftarrow S_1$ intersystem crossing, and was probed at 483 nm, i.e. in resonance with the visible $T_n \leftarrow T_1$ absorption (8,9). Excitations at 248 and 308 nm (20 ns, 2 mJ) were obtained with an excimer Laser (questek 2040) : KrF and XeCl respectively. Probe excitation at 483 nm (8 ns, 1.5 mJ) was achieved by pumping Coumarine 480 in a dye laser (Quantel TDL 50) with the third harmonic of a 10 Hz Q-switched Nd : Yag Laser (Quantel model YG 581 C).

Analysis of the transient Raman spectrum has been made by comparison with the ground state one. The same transient triplet spectrum was observed in methanol, acetonitrile, 2 propanol, cyclohexane and carbon tetrachloride. The assignments corresponding to the S_0 and T_1 states are given in table 1. These assignments have been confirmed by the analysis of the isotopic frequency shifts observed for two isotopic derivatives (benzil -D₁₀, benzil -¹⁸O₂) (10).

The main vibrational change observed on going from S_0 to T_1 (table 1) is a considerable decrease of the CO stretching frequency ($\Delta\nu \text{ CO} = -213 \text{ cm}^{-1}$) in accord with the $n\pi^*$ nature of T_1 . Moreover one remarks an important increase of the stretching frequency of the intercarbonyl C-C bond ($\Delta\nu \text{ CO-CO} = +110 \text{ cm}^{-1}$)

but, contrary to what was observed for benzophenone (11), the main ring modes (8a-19a-12-1) remain only weakly disturbed.

This means that the electronic perturbation in triplet benzil is localized essentially on the dicarbonyl fragment. This perturbation can be summarized as resulting from a notable weakening of the π -character of the CO bonds and a strengthening of the π -character of the intercarbonyl CO-CO bond. The dominant intensity of the Raman band due to the intercarbonyl C-C bond stretching underlines the highly symmetric character of this vibration. This point is strongly in favor of a trans conformation of this triplet species. The structure can thus be described by a delocalized form intermediate between the following configurations :



This conclusion is in agreement with the structural results reported by Chan and Heath (6) from electron nuclear double resonance experiments and by Fessenden and Col. (7) from transient microwave dielectric absorption measurements.

Note that, on the other hand, weakly enhanced transient Raman spectra ascribed to the ketyl radical and to the anion radical have been found (10) with probe excitation at 370 nm (9, 12) for solutions containing hydrogen atom donors (alcohols : methanol, ethanol, 2-propanol) and electron donors (TEA) respectively.

Finally, another transient Raman spectrum has been detected (10) in acetonitrile solutions for high pump excitation energy (248 nm) and power, which is probably due to the radical product of cleavage : $C_6H_5\cdot CO$, first observed from flash photolysis experiments (1,13).

Table 1 : Raman frequencies (cm^{-1}) and assignments of the ground state (S_0) and triplet state (T_1) spectra of benzil.

Mode assignments	S_0	T_1
C=O stretching	1676/1668	1430
8a (ring CC stretching)	1595	1580
19a (ring CC stretching)		
+ CH in plane bending	1492	1480
19b ?	1453	1457
9a (CH in plane bending)	1176	1195
CO-CO stretching	1048	1160
18a (CH in plane bending)	1020	1030
12 (trigonal)	1000	997
		984 (sh)
1 (ring breathing)	700	701
mixed CC + CO def	616	592

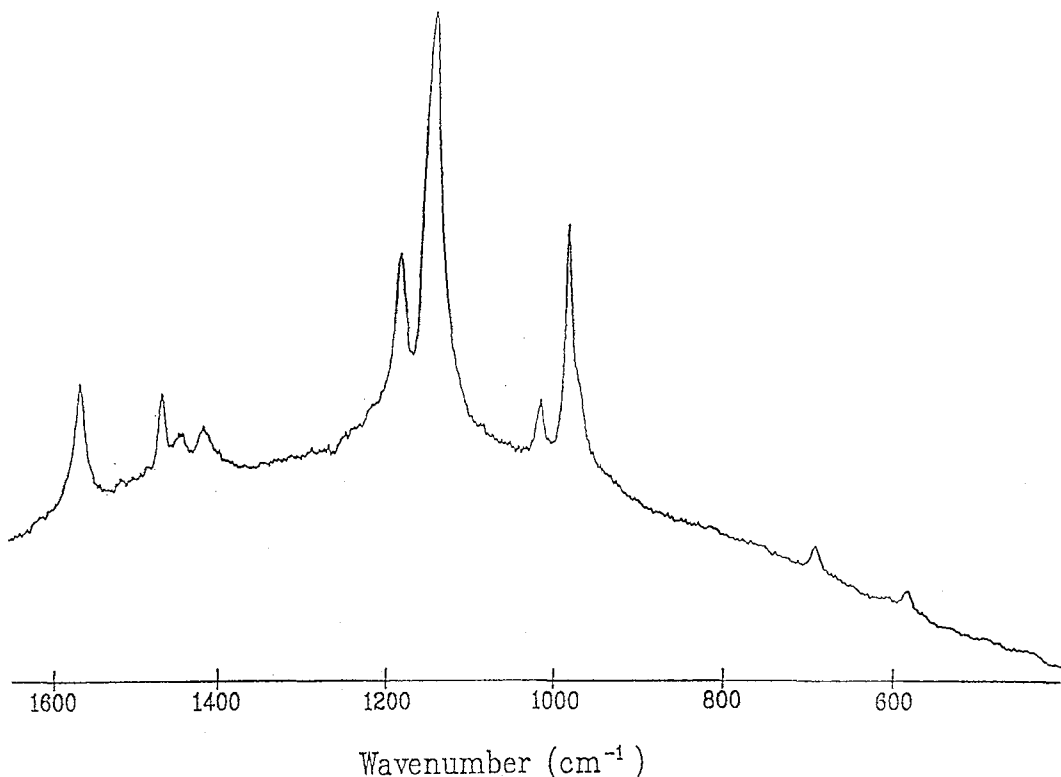


Fig.1 - Time-resolved resonance Raman spectrum (1700-400 cm^{-1}) excited at 483 nm (pump at 248 nm) of the T₁ transient of benzil in deaerated CCl₄ (solvent bands have been subtracted).

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