

A STUDY OF THE PHOSPHORESCENT TRIPLET STATE OF CYCLOALKANONES BY PULSE OPTICALLY DETECTED MAGNETIC RESONANCE

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Summary

Previous studies of saturated cycloalkanones have characterized the phosphorescent triplet state as n,π^* . To elucidate further the characteristics of the excited state of these compounds of photochemical importance, we report the dephasing studies on the spin coherence in the phosphorescent triplet state. For these molecules where the excitation is localized on the carbonyl moiety, spin relaxation is a direct function of the perturbing atoms in the vicinity of the chromophore.

1. Introduction

The photochemistry of carbonyl-containing compounds is an area of study which is still not well understood because of the complexity of the primary process. However, these carbonyl compounds constitute an important class of molecules in photochemistry because of the high quantum yields associated with the phosphorescent triplet state from which many photochemical reactions occur. The study of the primary process of complex systems should be initiated by the study of very simple molecules which should then be used as models for the more complex molecules. The cyclic aliphatic ketones are one of the simplest types of such carbonyl compounds.

The triplet state of cyclopentanone and other cycloalkanones has been observed and characterized as an n,π^* state [1 - 3]. Use of the zero-field techniques of phosphorescence microwave double resonance has yielded the dynamic parameters such as the feeding and depopulating rates of the phosphorescence triplet state in cyclopentanone [4 - 6]. Several years ago, we reported some preliminary results on the nature of the triplet state of cyclopentanone, cyclohexanone and 1,4-cyclohexanedione in neat crystals

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and in single crystals of *p*-xylene, *p*-dichlorobenzene and *p*-dibromobenzene [7]. In this paper we report the use of optically detected magnetic resonance (ODMR) spectroscopy in the study of the phosphorescent triplet state of several cycloalkanones.

2. Materials and method

The spin hamiltonian used in this study is given by the dipolar interaction of the two triplet electrons:

$$\mathcal{H}_{ss} = DS_z^2 + E(S_x^2 - S_y^2)$$

where D and E are the spatial integrals involving spin-spin dipolar interaction and are termed the zero-field splitting parameters and S_x , S_y and S_z are the triplet state spin operators. The dipolar interaction is anisotropic and is a function of spatial delocalization and anisotropic interaction along the three principal axes of the molecule.

While optically pumping the phosphorescent triplet state, the simultaneous application of microwave energy corresponding to any one of the three resonances will cause a redistribution of populations within the two coupled levels. The effect is a change in the phosphorescence intensity. The optically detected signals will then be made to yield the zero-field splitting energies directly.

The block diagram of the experimental arrangement is shown in Fig. 1 and is briefly described below. Optical excitation is accomplished by focusing a 100 W superhigh pressure mercury lamp through appropriate filters before using it to pump the triplet state of samples within the liquid helium Dewar. The samples are placed in a helical microwave antenna made of a flattened wire. An externally adjustable reflector placed at a distance of $\lambda/4$ from the helix allows better coupling at the mismatch created at the junction between the helix and the semirigid stainless steel cable. A 3/4 m monochromator equipped with a thermoelectrically cooled photomultiplier is used to detect the phosphorescence emission from the sample. A microprocessor-controlled photon counter allows the study of molecules with very low quantum yields. The computer also controls the programmable pulse sequence generator which switches the appropriately phase-shifted microwave power into the sample. The details of the computer interfaces are given elsewhere [8]. Additional experimental details are also given elsewhere [9, 10].

At the very low temperatures of boiling liquid helium and below the occupied density of photon states available for the thermal spin relaxation process is very low and the triplet state sublevels are effectively isolated. It has been shown by several workers that the theories of coherence in two-level systems are applicable to triplet states in which three two-level systems exist [11, 12]. Hence measurements of coherence times could be accessible for study within the triplet state of phosphorescent molecules. The results of these pulse studies in the cyclic ketones are presented here.

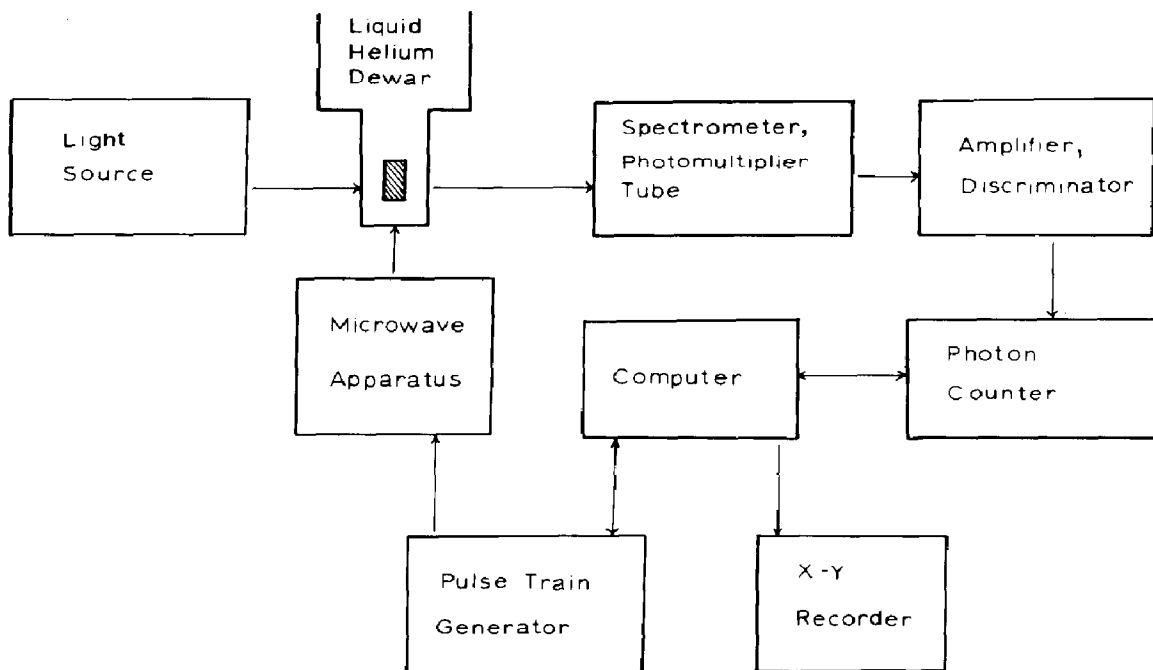


Fig. 1. Block diagram of the microprocessor-controlled electron spin echo apparatus used in the study (see text).

3. Results and discussion

The zero-field splitting energies for the three magnetic sublevels of the triplet state are shown in Table 1 together with a summary of the total phosphorescence decay constants. A more detailed table of these parameters is given in ref. 7. The zero-field splittings vary relatively little and fall within 10% of each other regardless of solvent, except for 1,4-cyclohexanedione. In the neat dione, the two carbonyl groups are not coplanar and are non-equivalent. In addition, the possible intramolecular coupling between the two chromophores may lead to slightly anomalous zero-field splittings. The interpretation that the two observed resonances belong to the two non-equivalent carbonyl groups arose from the electron spin double-resonance experiments in which the continuous saturation of the transition of one carbonyl group while adiabatically sweeping through the resonance of the other carbonyl group did not affect the intensity of the rapid passage signal.

The phosphorescence decay rates of the ketones in neat crystals and in *p*-xylene are very different from those of the ketones in *p*-dichlorobenzene or *p*-dibromobenzene. The small rate constants in the halogenated solvents could be due either to the enhanced efficiency of the radiative mechanism and the concomitant lowering of the non-radiative relaxation rate and/or to a pseudo Jahn-Teller-type interaction which is absent in *p*-xylene and the pure crystals.

TABLE 1

Zero-field transitions (± 2 MHz) and total phosphorescence rate constants ($\pm 10\%$) for several alkanones observed at 1.4 K [7]

	Pure	In <i>p</i> -xylene	In <i>p</i> -dichlorobenzene	In <i>p</i> -dibromobenzene
<i>Cyclopentanone</i>				
Transitions (MHz)	5022 ^a	5022	5070	5290
	3397	3398	3396	3580
	1625	1624	1674	1710
k_z (s ⁻¹)	775	820	83	110
k_y (s ⁻¹)	80	100	160	67
k_x (s ⁻¹)	725	810	3.5	12
<i>Cyclohexanone</i>				
Transitions (MHz)	5076	5400	5026	5303
	3367	3611	3381	3584
	1752	1792	1645	1718
k_z (s ⁻¹)	400	260	180	88
k_y (s ⁻¹)	30	20	39	63
k_x (s ⁻¹)	700	330	1.9	13
<i>Cyclohexanedione</i>				
Transitions (MHz)	— ^b	— ^b	4534	5306
	2953 (2214)	2184	3072	3586
	—	1474	1460	—
k_z (s ⁻¹)	— (—)	180	330	88
k_y (s ⁻¹)	36 (30)	28	44	54
k_x (s ⁻¹)	370 (500)	540	2.0	16
<i>Tetrahydrothiopyran-4-one</i>				
Transitions (MHz)			4713	
			3049	
			1660	
k_z (s ⁻¹)			160	
k_y (s ⁻¹)			29	
k_x (s ⁻¹)			4.4	

^aFrom ref. 6.

^bThe assignment in energy ordering is not unique.

The coupling of the electronic relaxation mechanisms to vibrational modes of aliphatic ketones has been well established [2, 3, 13]. Whether or not the ketones are disturbed in the halogenated benzene hosts such that the non-totally symmetric vibrations are not coupled as effectively is a question open to further study. To obtain further information regarding the role of vibronic activity of the α hydrogens in the electronic relaxation mechanism we are investigating the effects of their isotopic substitution in cyclic ketones. The extreme variation in the rate constants along any given

spin direction attests to the importance of intermolecular solvent perturbation in the conformation of the ketones.

The spin relaxation times of the ketones in selected single-crystal hosts are shown in Table 2. The method is analogous to the pulse techniques used in nuclear magnetic resonance. The pulse sequence and its effects on the magnetization vector are shown in Fig. 2. The usual $\pi/2$ pulse is applied along the x' axis in the rotating frame. After a delay τ , during which the magnetization vector "fans out" in the x - y plane, a π pulse will cause a refocusing along the $-y'$ axis. The final probe pulse is required because the detection method observes population differences in the two sublevels. Hence the vector has to be tilted along the z direction in order to observe the

TABLE 2

Coherence dephasing times of several cyclohexanones by pulse optically detected magnetic resonance at 1.4 K

Guest	Host	Transition (MHz)	T_2^* (μ s)	T_2 (μ s)	$T_2\rho^a$ (μ s)
Cyclopentanone	<i>p</i> -dichlorobenzene	—	—	—	
		3396	0.13	2.5	
Cyclohexanone- <i>h</i> ₁₀	<i>p</i> -dichlorobenzene	5026	0.34	1.6	280
		3381	0.35	1.5	
		1645	0.30	—	
Cyclohexanone- <i>d</i> ₁₀	<i>p</i> -dichlorobenzene	5033	0.10	2.1	1400
		3384	0.12	2.4	720
Cyclohexanone	<i>p</i> -dibromobenzene	5303	0.47	1.5	430
		3584	0.47	1.3	800
		1718	0.42	—	
1,4-cyclohexanedione	Neat polycrystals ^b	2953 (2214)	0.16 (0.13)	2.3 (2.0)	85
1,4-cyclohexanedione	Neat plates ^b	2953 (2213.5)	0.18 (0.17)	2.4 (2.3)	
1,4-cyclohexanedione	<i>p</i> -dichlorobenzene	4534	0.50	6.6	890
		3072	0.42	4.5	770
Tetrahydrothiopyran-4-one	Neat crystal	—	—	—	
		3609 1887	0.23 0.25	3.8 3.2	
Tetrahydrothiopyran-4-one	<i>p</i> -dichlorobenzene	4713	0.24	5.4	
		3049	0.21	5.6	
		1660	0.20	5.0	
δ -valerolactone	<i>p</i> -dichlorobenzene	4834	0.23	0.65	510
		3337	0.30	0.71	800
		1493			

^aCarr-Purcell pulse sequence with $2\tau = 1 \mu$ s ($\pm 30\%$).

^bValues in parentheses are for the second carbonyl group (see text).

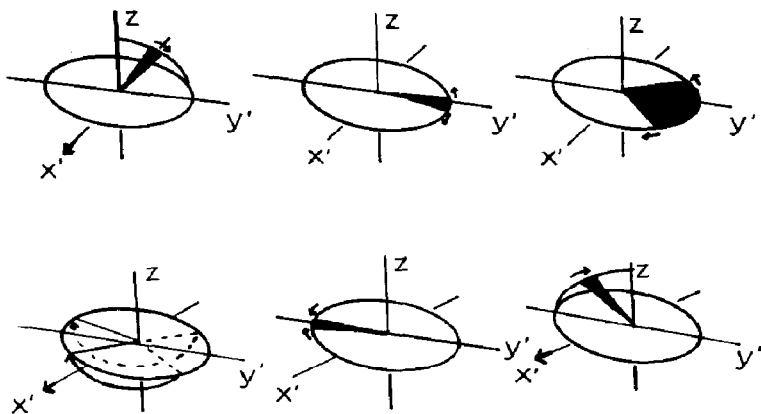


Fig. 2. Pulse sequence used to measure spin echo decay times. The initial $\pi/2$ pulse lays the magnetization vector in the x - y plane. After a delay, a π pulse refocuses the vector in the $-y'$ direction. A probe pulse $\pi/2$ is finally applied along the x' axis and the echo decay is observed by varying the delay times.

effects of the pulse sequence upon the coherence within the triplet state. T_2 measurements can be made by varying the two delays and observing the intensity of the phosphorescence.

In addition, echo shapes can be obtained by fixing one of the delay periods while varying the other. The echo shape traced out by this pulse sequence can be analyzed and the inhomogeneous T_2^* obtained as shown in Table 2. A detailed explanation of the echo shape analysis is described elsewhere [14].

The effects of spin diffusional processes can be suppressed by a pulse sequence originally developed by Carr and Purcell [15]. Some representative times from the Carr-Purcell experiment are shown in Table 2. The dramatic increase in the relaxation times as measured by the Carr-Purcell pulse sequence compared with the decay times of the spin echo is an indication that nuclear spin diffusion is an important contributor to the T_2 process. In fact, the decay times obtained from the Carr-Purcell experiment deviated by only about an order of magnitude from the average of the phosphorescence decay times of the two sublevels which were coupled by the microwave field. These results are consistent with the limiting case of the Carr-Purcell experiment in which as the delay τ approaches zero the experiment becomes equivalent to a spin-locking experiment. In none of the systems did $T_{1\rho}$ times from the spin-locking experiment deviate more than 20% from the average of the lifetimes for the phosphorescence process.

Recently, the differential saturation method has become an important technique in ODMR in differentiating the relative contributions of homogeneous and inhomogeneous linewidths to the total ODMR linewidth. The details of the technique have been reported elsewhere, but briefly the technique is to detect the phase of the phosphorescence intensity while amplitude modulating the microwave power and sweeping through the

transition [16]. Simultaneously, a very soft (several microwatts) broad band decoupling power is applied, the frequency of which spans the entire ODMR linewidth. The effect is to saturate and hence to suppress the entire homogeneous linewidth while retaining the intensity of the inhomogeneous component of the linewidth. Thus, if a dip in the ODMR line is observed, then it represents the homogeneous linewidth. Only the neat dione, the dione in the *p*-dichlorobenzene host and the thiopyranone neat crystals showed dips in the total ODMR linewidth. These homogeneous linewidths were consistent with the lifetimes calculated from the echo decay measurements.

The spin relaxation results for the deuterated cyclohexane show an effective narrowing of the homogeneous linewidth compared with the protonated ketones as measured by the echo decay. The large increase in the lifetime obtained from the Carr-Purcell experiment for the deuterated molecule is consistent with the longer lifetimes for this molecule.

Interestingly, δ -valerolactone showed a large deviation in the homogeneous relaxation time, the cause of which may be the highly interactive oxygen in the vicinity of the triplet electrons. However, the zero-field splittings and the inhomogeneous relaxation times paralleled those for the ketones in the same host.

In summary, the pulse ODMR technique does allow subtle differences in the excited states of these molecules to be observed. Unless perturbing atoms are adjacent to the carbonyl group, the effects are very small. One exception is the 1,4-cyclohexanedione for which the unusual conformation allows for a large degree of interaction to occur between the two carbonyl groups. Finally, results of the isotopic studies appear to indicate that the α hydrogens play a large role in the spin relaxation of the phosphorescent triplet state of these aliphatic cyclic ketones.

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