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The Use of Coherent Spectroscopy
in the Study of Intramolecular Tunneling Processes
in Excited Triplet States

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Abstract

Intramolecular tunneling in the lowest triplet state of cyclopentanone is investigated using optically detected electron spin coherence techniques. The results, when analyzed with exchange theory, show that the tunneling occurs on a time scale longer than the triplet lifetime of cyclopentanone in contrast to what has been reported earlier (A. L. Shain and M. Sharnoff, Chem. Phys. Lett. 22, 56 (1973).)

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I INTRODUCTION

Tunneling is an example of an energy exchange process which can occur in photo-excited triplet states of organic molecules. It has recently been shown that optically detected coherence experiments¹⁻³ are very useful in measuring the time development of excited states whose lifetimes are limited by processes other than decay to the ground state and, as such, tunneling is amenable to study. Triplet state tunneling between localized states of isotopically mixed crystals has already been studied⁴ using these techniques and in this communication, we wish to discuss how optically detected spin coherence can be applied to an intra-molecular configurational tunneling process. In particular, we will discuss the techniques with regard to the interconversion between excited electronic states of cyclopentanone.

Optically Detected Magnetic Resonance (ODMR) in cyclopentanone at liquid He temperatures was first reported by Sharnoff and coworkers⁵. Three zero-field transitions were initially found; however, Shain and Sharnoff⁶ subsequently detected six additional resonances (two "satellite" triads) of much lower intensity separated from the "normal" triad by 9 to 214 MHz. A double resonance experiment using two microwave fields to excite transitions in different triads simultaneously seemed to indicate an interaction between cyclopentanone molecules having resonance frequencies associated with the different triads. An exchange

mechanism was postulated by Shain and Sharnoff as a quantum mechanical tunneling between electronic configurations of the same cyclopentanone molecule, which can be generally classified as an intramolecular process. The exchange rate was placed between $5 \times 10^2 \text{ sec}^{-1}$ and $5 \times 10^7 \text{ sec}^{-1}$, which represents limits placed by the triplet sublevel lifetimes and the resolution of the EPR lines respectively.

Using both CW and pulsed ODMR experiments, we would like to show that the exchange process, if indeed there is one, does not display a temperature dependence and occurs on a time scale longer than the excited state lifetimes of the cyclopentanone triplet state.

II EXPERIMENTAL

Cyclopentanone (MC & B reagent grade) was washed with H_2SO_4 , rinsed with H_2O and dried over Na_2SO_4 . After several vacuum distillations, a small amount was sealed under vacuum in a quartz ampoule which could be placed inside a slow-wave helix. Phosphorescence spectra showed a very broad emission extending from roughly $3600\text{\AA}$ to well into the visible region ($5500\text{\AA}$) and peaked at approximately $4300\text{\AA}$. All experiments were conducted with the spectrometer set at $4300\text{\AA}$ and with the slits open wide enough to get maximum phosphorescence intensity without saturating the photomultiplier.

All microwave experiments were done using the experimental arrangement for ODMR described elsewhere⁷. For EPR spectra, the

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microwaves (15-30mW) were amplitude modulated either by the sweeper or by PIN diodes and phase detected; to ensure sweep linearity, a digitally stepped voltage ramp was used to externally drive the sweeper. The experimental procedure for spinlocking has also been described previously⁷; the only difference in these experiments was that due to the short triplet lifetimes of cyclopentanone, higher duty cycles were used (12 Hz). The frequency used for all experiments was 3394.4 MHz, corresponding to the |D-E| transition.

III DISCUSSION

Since most EPR absorption lines in organic solids are inhomogeneously broadened, one generally cannot apply the elegant theories of the effect of exchange on lineshapes developed by Anderson, Kubo, and others⁸. Conventional time-resolved spectroscopy is not capable of detecting the decrease in lifetime expected if exchange is taking place, since a steady-state system (with respect to exchange) is being sampled in time and yields instead the lifetimes of the triplet sublevels due to decay to the ground singlet state. On the other hand, a coherence technique such as optically detected spinlocking¹, can effectively isolate an ensemble of cyclopentanone molecules at a time t_0 and monitor their evolution so that processes which remove molecules from the ensemble after t_0 are manifested in a reduced lifetime.

The theoretical approach to exchange problems in triplet states is best handled by the modified Bloch equation method⁹,

in which additional terms are included in the equations of motion for the individual r-vector components¹⁰. For two exchanging systems A and B, six first-order differential equations result and can be solved¹¹ to give effective values for the decay rate and resonance frequency of the system one is actually observing ("A"). If the H_1 field frequency ω is the same as the Larmor frequency of system A in the absence of exchange, the results using the Swift and Connick¹¹ equations adapted for triplet state exchange by van't Hof and Schmidt¹² are

$$(\Delta\omega)_{\text{eff}} = \frac{W_+(\delta\omega\tau)}{1+(\delta\omega\tau)^2} \quad (1)$$

$$(k)_{\text{eff}} = k_{\text{ave}} + \frac{W_+(\delta\omega\tau)^2}{1+(\delta\omega\tau)^2} \quad (2)$$

where W_+ is the promotion rate for exchange from system A to system B; τ is the lifetime of the excitation in system B; $\delta\omega$ is the difference in Larmor frequencies of the two systems, and k_{ave} is the average lifetime of the two sublevels coupled in system A and is given by $\left(\frac{k_z + k_y}{2}\right)$.

Physically, $(\Delta\omega)_{\text{eff}}$ is a frequency shift term in which the time the excitation spends in system B is reflected in the Larmor frequency measured for system A. $(k)_{\text{eff}}$ is the decay rate one observes in a spinlocking experiment on system A while k_{ave} is the decay rate in the absence of exchange.

To understand the applications to tunneling, it is useful to examine limiting cases for $(\Delta\omega)_{\text{eff}}$ and $(k)_{\text{eff}}$:

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IV. SUMMARY

We have shown that optically detected spinlocking can be a useful probe for investigating intramolecular exchange in organic triplet states. By combining the results of spinlocking with CW spectra, one can determine the time scale that exchange is taking place on; quantitative values for the lifetime of the species in its exchanged environment can be obtained if the system is known to be in thermal equilibrium. In the case of cyclopentanone, the exchange process does not increase the spinlocking decay rate over the triplet limit nor does it change with temperature. Therefore, either exchange is not occurring or it takes place on a time scale longer than the triplet lifetime of cyclopentanone.

V. ACKNOWLEDGEMENT

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Captions

Figure 1: Temperature dependence of $T_{1\rho}$ for the $|D-E|$ transition of cyclopentanone. The shaded region represents the upper limit for the lifetime of the spinlocked state, based on previously determined sublevel phosphorescence lifetimes. The average $T_{1\rho}$ was found to be 3.02 ± 0.28 msec.

Figure 2: (a) Decay of the spinlocked $|Z\rangle \leftrightarrow |Y\rangle$ transition of cyclopentanone. The vertical axis is in arbitrary units, normalized to the initial change in phosphorescence due to the first $\pi/2$ pulse, ΔI_0 . (cf. Reference 7). ΔI is the change in phosphorescence after the final $\pi/2$ probe pulse.

(b) Narrowing of the $|D-E|$ EPR line by coherent averaging. The lineshape is Lorentzian with a FWHM of 660 Hz and represents a narrowing of four orders of magnitude from the CW line.

Figure 3: Temperature dependence of the $|D-E|$ transition frequency of cyclopentanone. The average frequency is 3394.44 ± 0.36 MHz.

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Fig. 1

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Fig. 2

Fig. 3

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