Optical Detection of Zero Field Magnetic Resonance in the Triplet State of Chlorophyll b

Sir:

We have observed the zero-field magnetic resonance transitions of the lowest triplet state of chlorophyll b in *n*-octane solution at 2°K by triplet absorption detection of magnetic resonance (TADMR).[1,2] Chlorophyll b exhibits very weak phosphorescence[3] but strong triplet–triplet (T–T) absorption maximizing at about 500 nm,[4] and the TADMR method is particularly well suited for obtaining its triplet state zero field epr spectra.[2] Further, it has been reported that at temperatures below 77°K *n*-octane serves as a Shpolskii-type matrix for chlorophyll, exhibiting sharp line absorption and fluorescence spectra.[5] Using a 4-W argon ion laser as the photoexcitation source, two microwave-induced T–T absorption signals were observed for polycrystalline samples of chlorophyll in *n*-octane with maxima at frequencies of 1000 ± 5 and 870 ± 5 MHz. Both transitions correspond to an increase in T–T absorption intensity (see Figure 1).

The 870-MHz transition consists of several overlapping peaks spread across ~40 MHz. These peaks probably arise from several inequivalent sites in the Shpolskii matrix.[5] The two zero field transitions could also be detected as microwave-induced changes in the fluorescence intensity at 2°K when observing the fluorescence at 647 nm.[6] The third transition was too weak to be detected under present experimental conditions. The observed transitions correspond to ~1% decrease in the fluorescence intensity at 647 nm. The signals disappeared as the sample was warmed above 4°K. The zero field transitions correspond to triplet spin Hamiltonian parameters of $|D| = 0.0312$ cm^{-1} and $|E| = 0.0022$ cm^{-1}.[7]

Both triplet absorption detection and fluorescence detection of magnetic resonance arise from the same effect—a change in the overall steady state population in the triplet state by microwave saturation of the zero field transitions. An increase in the overall triplet state population will cause an increase in the T–T absorption intensity and a decrease in the fluorescence intensity (depletion of the ground state).

From previous TADMR work a microwave-induced increase in T–T absorption will be observed for two of the zero-field transitions when the rates of population and decay for one of the triplet spin sublevels dominates in the intersystem crossing.[2] This dynamical situation would be consistent with both the fluorescence and T–T absorption intensity changes observed for chlorophyll b in the present experiments. It is also consistent with dynamical studies of a similar π-electron system, the Zn porphin triplet state, whose population and decay occurs preferentially through the Z (out-of-plane) spin sublevel.[8] The intersystem crossing rate constants can be measured directly for each of the triplet spin sublevels by observing the changes in either fluorescence intensity or T–T absorption intensity as a function of time after turning on a saturating microwave field;[9] such experiments are in progress to elucidate the triplet state intersystem crossing mechanisms of chlorophyll b.

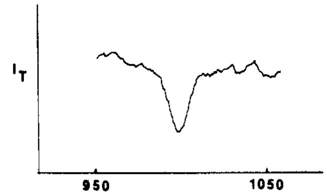

Figure 1. Zero field magnetic resonance signal of the triplet state of chlorophyll b in *n*-octane at 2°K detected by the microwave-induced change in the triplet–triplet absorption intensity. The signal corresponds to an increase in triplet–triplet absorption intensity (decrease in transmitted light, I_T) at 488 nm. The frequency scale is in megahertz.

Acknowledgment. This research has been supported in part by the U. S. Army Research Office (Durham), the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Grant No. IN 97 to Boston University from the American Cancer Society.

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Received December 26, 1973

Solution Behavior of Triphenylphosphine Complexes of Ruthenium(II)

Sir:

$RuCl_2L_3$ and $RuCl_2L_4$ (L = PPh_3) are catalytically active complexes[1,2] which have been widely used for the synthesis of Ru(II) complexes.[3,4] The variable phosphine content is an intriguing feature reminiscent of the PtL_3–PtL_4 system.[5] With the exception of molecular weight measurements, the solution behavior of these two complexes is uncharacterized. This is due in part to the lack of commonly used spectral probes (*e.g.*, CO or hydride ligands.) We report here a variable-temperature ^{31}P nmr study of these complexes which shows their solution behavior to be complex yet readily interpretable.

The proton-decoupled Fourier transform ^{31}P nmr spectrum of $RuCl_2L_4$ in $CHCl_3$ (Figure 1a) consists of two resonances in an intensity ratio of 3:1 at 30°. The less intense resonance falls at the chemical shift of PPh_3. The ^{31}P nmr spectrum of $RuCl_2L_3$ in $CHCl_3$ at 30° (Figure 1b) exhibits a strong signal coincident with the

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