

THE ELECTRON SPIN ECHO TECHNIQUE AS A SPECTROSCOPIC TOOL

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INTRODUCTION

After the first initial few pioneering experiments on electron spin echoes (ESE) in the years 1958-1961 [1-3], little development in this field occurred for a period of more than ten years. This situation has changed considerably thanks to the availability of new technology in microwave sources, amplifiers and other components. Consequently it is now relatively easy to build an ESE spectrometer. Initially these instruments were mainly used to study systems that are paramagnetic in the ground state. The techniques were utilized for a variety of purposes: to measure the spin-spin relaxation times, T_2 , (or more generally the phase memory times T_M), the spin-lattice relaxation times, T_1 , saturation transfer correlation times, to disentangle overlapping EPR lines by taking advantage of differences in T_M and T_1 , and to measure the perturbation of molecular symmetry as affected by the application of small electric fields.

A very important discovery was that the echo decay envelope often shows an oscillatory behavior with a spectrum that is comprised of the evolution frequencies of coherences, induced by the intense microwave pulses, among the hyperfine levels. Thus this nuclear modulation provides a new means, ESEEM (Electron Spin Echo Envelope Modulation) for measuring ENDOR frequencies occurring at low frequencies, e.g. those of nuclei with a small gyromagnetic ratio. One great advantage of this method is that no resonant rf field is required for creating the nuclear spin coherence and therefore the lack of an appreciable nuclear spin transition moment is not a limiting factor as in conventional cw or

pulsed ENDOR experiments.

The development of high power, pulsed tunable dye lasers has made the ESE technique a particularly powerful tool for studying photochemically and photo-physically induced transient radicals and triplet states. With this experimental combination it is possible to capture the ESE signal just after the laser pulse, before the transient paramagnetic state decays. In currently available spectrometers, systems can be probed for response within 200 ns or less. Apart from the fact that the short-lived paramagnetic species are often too scarce for detection by cw EPR methods, the ESE technique also exploits the strong spin polarization that accompanies laser flash excitation to enhance further the sensitivity of the experiment. Moreover one can follow kinetic processes in a simple and direct manner.

The two capabilities of ESE, namely to detect the EPR spectrum of transient paramagnetic species, and to measure the resonance spectrum of nuclei coupled to the electron spin, combine to make ESE an extremely attractive method for the study of hyperfine interactions in short-lived radicals and photo-excited triplet states. This power is clearly demonstrated by the progress that has been made in the last few years in the study of the elusive metastable triplet state of pyridine. The main aim of this paper is to review the recent achievements in the spectroscopy of this particular molecule that have been made possible through the application of ESE techniques. In addition we will report recent achievements in the development of ESE techniques at high microwave frequencies that promise to be of great interest for a number of future applications.

SPECTROSCOPY OF THE TRIPLET STATE OF PYRIDINE

The properties of the lowest triplet state of pyridine have remained a mystery for spectroscopists for more than 25 years. The puzzling items were the apparent absence of fluorescence and phosphorescence and the failure to detect any magnetic resonance signal that could be related to the triplet state. Spectroscopy in which electron spin echoes were involved solved this riddle [4]. It proved possible to obtain a field-swept, ESE-detected EPR spectrum by exciting the sample (pyridine as a 0.1 % guest in a benzene host single crystal) with a pulsed laser (pulse duration 10 ns) in the 0-0 absorption at 286 nm. From an orientational study the directions of the spin axes together with the zero-field splittings could be established. The results indicated that the lowest triplet state T_0 includes considerable $n\pi^*$ character. In support of this result is the observation that the EPR lines are split into three components, owing to the large hyperfine interactions with ^{14}N characteristic of an appreciable $^3n\pi^*$ admixture.

A remarkable finding is the presence of two sites A and B for all four magnetically inequivalent molecules in the unit cell of the benzene host. The observed splitting of the EPR lines is a manifestation of the distorted character of pyridine in its T_0 state, which results from vibronic coupling between two close-lying $^3n\pi^*$ and $^3\pi\pi^*$ states with 3B_1 and 3A_1 symmetry. This vibronic coupling creates a double minimum in the potential surface of the lowest triplet state along an out-of-plane bending coordinate of b_1 symmetry. The two possible nonplanar configurations are frozen by the crystal field. A study of the angular dependence of the ^{14}N -hyperfine splitting confirms this model [5] and shows that the N-atom has moved out of the plane of the molecule.

When scanning the wavelength of the exciting laser and detecting the ESE signal of the A- or B-site it is possible to obtain the $S_1 \leftarrow S_0$ excitation spectrum of pyridine in benzene. When detecting on the A-site, weak additional bands appear at the low energy side of

the "0-0" transition of B. A further ESE study revealed that this weak part derives from a minor portion of the pyridine molecules that have their two-fold axis rotated by $\pi/3$ in the plane of the molecule. This finding confirms a suggestion by Brownrigg [6] but moreover enabled us to identify this type of trap.

The kinetic properties of the triplet sublevels have been obtained from the evolution of the ESE signals upon variation of the delay time t_d between the laser flash and the microwave pulses. The results for the relative populating and depopulating rates of the triplet sublevels can be understood by considering the theory for spin-orbit coupling in aza-aromatic molecules and the resulting selectivity in the routes for intersystem crossing [7].

The aim of the most recent study of pyridine was to obtain a precise insight in the distortion of this molecule in its lowest triplet state. The necessary information was provided by an investigation of the hyperfine and quadrupole tensors of the deuterium atoms in pyridine- d_5 via Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy. The results of this study in combination with those on the hyperfine interaction with the N-atom enabled us to determine the spin density distribution and molecular geometry of pyridine in its lowest triplet state in remarkable detail. It is found that the molecule, planar in the ground state, obtains upon excitation in the triplet state a boat-like structure in which the nitrogen atom is tilted by no less than 40° with respect to the plane of the ortho- and meta-carbon atoms. Like the structure the spin density distribution should not be regarded as a state of $n\pi^*$ or $\pi\pi^*$ character: the π orbital on the nitrogen atom carries about 40 % of the spin density, the n-orbital about 10 % [8].

HIGH FREQUENCY PULSED ELECTRON SPIN RESONANCE

The obvious advantage of working at high microwave frequencies is that it allows the study of paramagnetic systems with large zero-field splittings. In addition the absolute sensitivity will increase dramatically. Another attrac-

tion is that one can separate overlapping EPR lines of free radicals with small differences in g -value. An interesting possibility is to select molecules with specific orientations with respect to the external magnetic field via the line broadening induced by the anisotropy of the g -factor [9].

It looks natural to combine the advantages of high frequency cw EPR with ESE techniques. To this end an ESE spectrometer has been constructed in our laboratory at the University of Leiden operating at 94.9 GHz (W-band). This spectrometer has been designed especially for orientational studies on single crystals at liquid helium temperatures allowing optical access. The details of this instrument have been presented elsewhere [10-12] and here we will only review its main characteristics.

The microwave bridge has been designed in such a way that two microwave pulses are generated with a duration of 350 ns and 700 ns respectively at a frequency of 94.9 GHz. The cavity is a Fabry-Pérot resonator which is located in the tail of a liquid helium cryostat. Here the microwave B_1 field is in the vertical direction perpendicular to the static magnetic field B_0 of a split-coil superconducting magnet. The sample is located in a tube that can be rotated about a horizontal axis. Since the whole cryostat containing the superconducting magnet can be rotated about a vertical axis we can bring the static magnetic field B_0 parallel to any desired axis of the sample.

An important consideration in the construction was the separation of the cryogenic cooling of the superconducting magnet and that of the sample. For this purpose a superconducting magnet cryostat with a room temperature bore was chosen. The cooling of the sample is provided by the bath cryostat which contains the insert with the Fabry-Pérot resonator and the sample, and which is placed inside the room-temperature bore. A great advantage is that samples can be changed without affecting the operation of the superconducting magnet. In addition it is possible to irradiate the sample either with a lamp or a laser via a quartz window in the bottom of the

cryostat. The light emitted by the sample is collected by a small quartz prism at the end of a light pipe which directs the emission to a photomultiplier located at the top of the cryostat.

The test experiments performed with this spectrometer [10,11] demonstrate two attractive features of electron spin echo spectroscopy at 95 GHz. The first aspect regards the sensitivity. We find that the minimum detectable number of spins at 95 GHz is about $10^{2.5}$ times smaller than at 9.5 GHz. Here we see the advantage of the high microwave frequency for samples that are limited in size. The second aspect is the possibility to take advantage of the small anisotropy of the g -tensor to select molecules with specific orientations with respect to the external magnetic field in a randomly oriented sample.

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