PULSED ELECTRON-ELECTRON DOUBLE RESONANCE IN AN $S=\frac{1}{2}$, $I=\frac{1}{2}$ SYSTEM

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Pulsed electron-electron double resonance techniques have been applied to the $\dot{C}H$ fragment in an irradiated single crystal of malonic acid. Damped Torrey oscillations about the pumping field and also about the observing field have been observed, and the spin-lattice and cross-relaxation times have been measured directly. Display of the transient signal intensity at a constant delay as a function of the pump frequency (i.e., relaxation spectroscopy) yielded very narrow EPR hyperfine lines.

A pulsed electron-electron double resonance (ELDOR) experiment consists in irradiating one part of an EPR spectrum with a pulsed microwave source and observing the resulting transient response at another portion of the spectrum. Three such experiments were reported 10 years ago,[1] but to our knowledge none since then.

The first portion of this Letter is devoted to the use of pulsed ELDOR for the direct observation of relaxation processes. One can also display the magnitude of some transient ELDOR effect as the pulsed (pumping) microwave source is swept in frequency, which we call relaxation spectroscopy. We have performed one such experiment, which is described near the end of the Letter, observing unusually narrow lines. It may well be the most significant new result presented here.

In the present work pulsed ELDOR has been applied to the radical $\dot{C}H(COOH)_2$ formed in an irradiated single crystal of malonic acid.[2] To a very close approximation this center consists of one free electron with spin $S=\frac{1}{2}$ coupled to one nuclear spin $I=\frac{1}{2}$. The nuclear Zeeman and hyperfine interactions are of the same order of magnitude, resulting in relatively intense "forbidden" lines in many orientations.[2,3] Each of the four EPR lines is inhomogeneously broadened by weak interactions with other protons.

All of the experiments described here involve pumping a forbidden line and observing an allowed line, or vice versa. They were performed at X band, at room temperature, and at a single orientation of the crystal selected to give maximum intensity of the forbidden lines (see Fig. 1). The EPR intensity of the forbidden lines was 1/7 that of the allowed lines. The pump klystron delivered up to 1 W of microwave power to one mode of a bimodal cavity,[4] and this power could be pulsed using a microwave diode switch. The second resonant cavity mode was coupled to the spectrometer which included a wide-band receiver sensitive to the transient change of the absorption. The signal was stored in a boxcar integrator, the gate of which was opened in synchronism with the pumping pulse sequence. An isolation greater than 80 dB between the pumping and observing modes permitted the signal to be observed during the pulses. The magnetic field was modulated at 20 Hz, which was low enough that no rapid-passage effects could occur, and the boxcar was followed by a phase detector. Some preliminary experiments were performed without field modulation, but its use improved the base-line stability.

The energy levels and relaxation paths are represented in Fig. 1. Here the W's refer to relaxation probabilities which couple the indicated levels. Anticipating the results of the present

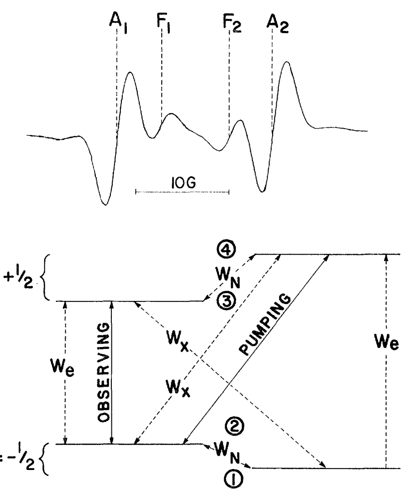

FIG. 1. The EPR spectrum of $\dot{C}H(COOH)_2$ observed under the conditions of the present experiment, and the energy levels and transition probabilities for this system.

work, the six relaxation paths (dashed lines in Fig. 1) are adequately described by the three indicated relaxation probabilities, and $W_e \gg W_x \gg W_N$. The experimentally accessible quantities are the apparent relaxation times T_{1e} and T_x which describe the return to thermal equilibrium of the population differences N_2-N_3 (or N_1-N_4) and $(N_2+N_3)-(N_1+N_4)$, respectively. In the present case $T_x^{-1}=2W_x+2W_N$.

As an example of the type of phenomena under consideration here, let us suppose that the observing frequency corresponds to the allowed transition $2 \rightarrow 3$ and that we irradiate the forbidden interval $2 \rightarrow 4$ with a pulse of pump power. Any change in the population of the level which is in common, i.e., N_2, will give rise to a signal. For instance, if one equalizes the populations $N_2 = N_4$, the initial signal should correspond to about 50% of the EPR line intensity.

This experiment was performed by looking at the time dependence of the signal during and after the pumping pulse [see Fig. 2(a)]. Immediately after the onset of the pulse a damped oscillating signal was observed about a level well above the base line. The frequency of the oscillations was $\propto H_2$ where H_2 is the pumping field. We interpret these oscillations to be a precession about H_2 of the fictitious spin which can be defined for the forbidden transition.[5] As the fictitious magnetic moment precesses, N_1 is modulated and gives rise to the observed oscillations. Since the spin-lattice relaxation time is much longer than T_2, the oscillations vanish with a time constant T_2.[6] One finds T_2 for the fictitious spin to be about 8 μsec. Since the forbidden line is 1/7 as intense as the allowed line, the fictitious spin can be treated as though it had a gyromagnetic ratio of $7^{-1/2}$ that of the electron. We have performed the inverse experiment of observing the forbidden line while pumping on the allowed line. For a given H_2, these oscillations are indeed $7^{1/2}$ times faster. The value for T_2 for the normal spin also is about 8 μsec.

Whether one observes an allowed line and pumps a forbidden line, or vice versa, the initial oscillations are quickly damped and the signal decays, with the pumping pulse still on, in an exponential manner with a time constant $T_{1e}=40 \pm 5$ μsec [see Fig. 2(a)]. If the observing power is very low, there is an abrupt change of the decay time constant to 20 μsec when the pumping power is turned off. A simple rate calculation on a four-level system shows that this change from T_{1e} to $T_{1e}/2$ is to be expected.

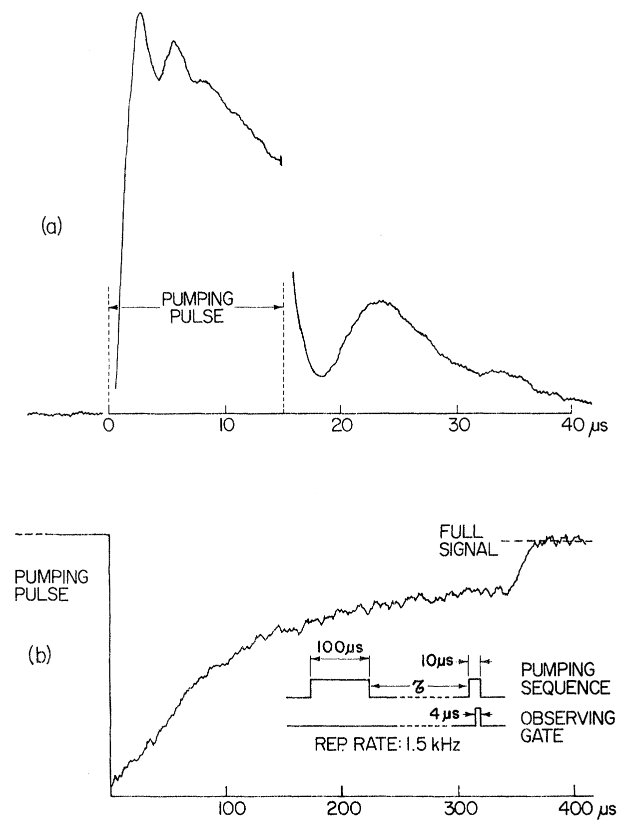

FIG. 2. (a) The transient change of an allowed line during and following the application of pump power to a forbidden transition. (b) The transient measurement of the cross-relaxation time. The pumping pulse sequence and gate timing are indicated.

When the observing power approaches saturation, we have found damped oscillations which commence when the pump power is turned off, of frequency proportional to the observing field H_1. When H_2 is turned off, there are sudden shifts of some spin packets of the inhomogeneously broadened line into resonance. There are two reasons for these shifts. The first is the so-called Bloch-Siegert[7] shift as modified by Ramsey[8] of amount $\frac{1}{2}(\gamma H_2)^2/\Delta\omega = 0.1$ MHz, where $\Delta\omega$ is the separation of the two microwave sources and there is no necessity that H_2 correspond to magnetic resonance. The second is the coherence splitting of the common level[9] by an amount $\gamma H_2/7^{1/2} \simeq 1$ MHz. Suddenly satisfying the resonance condition will give rise to Torrey oscillations.[6] Freeman[10] has described a similar effect in a double NMR experiment.

If after an initial pulse one tries again to get a transient signal by sending a second pulse, one must wait until the system has recovered to its initial state. The recovery time is $T_x/2$. These considerations lead to a way of determining T_x. The pulse sequence used for the T_x measurement consisted of a 100-μsec pulse, at the end of which the transient signal was almost zero, followed by a short pulse after a variable delay τ. The observing gate was opened during the short pulse. The delay τ was swept and the signal was recorded as a function of τ [see Fig. 2(b)]. We have found that $T_x = 300 \pm 30$ μsec. The ratio of the measured values T_{1e}/T_x is in good agreement with the intensity ratio of the forbidden/allowed EPR lines, and it is for this reason that we believe W_N processes are not playing a significant role in the present experiment. That is, this experiment measures the relaxation time connecting the manifold of two levels labeled 1 and 4 (Fig. 1) with the manifold of two levels labeled 2 and 3, where this time is much longer than the spin-lattice relaxation time. If W_N were of the same order as W_x, a substantially shorter value of T_x would have been found.

Finally we consider the spectroscopic application of these ideas. The technique of cw ELDOR has been used in the past in order to improve the resolution of EPR spectra.[11] These workers monitored the steady-state signal intensity at the observed portion of the spectrum as a function of the frequency difference of the observing and pumping microwave sources. In the present work experiments were performed in which the transient signal intensity at a constant delay was recorded as a function of the difference frequency. The observing resonant condition was set on one of the allowed lines (A_2) and the pump frequency slowly swept through the transition corresponding to the forbidden line F_1. The resulting line (Fig. 3) appears to be a superposition of a very narrow line (width at half-height $\simeq 100$ kHz) and a wider one. The width of the broad line depends on H_2 and is approximately $\gamma H_2/7^{1/2}$. It arises, we suggest, from a coherence splitting of the common level. (Freeman and Anderson[9] show that the type of sweep employed in the present experiment should result in a broadened line rather than a doublet.) The discovery of the narrow line is very interesting although we do not have a model to account for it. Its width is affected by H_1, but not by H_2. If we assume that the width in the limit of small H_1 is the spin-packet linewidth, then we can extract a value of T_2 which agrees within a factor between 2 and 3 with our transient T_2 measurement.

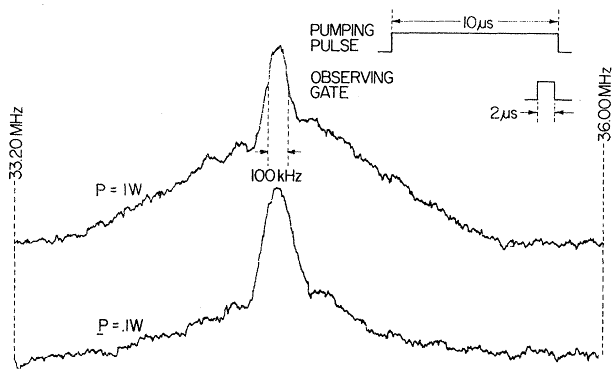

FIG. 3. The frequency-swept experiment (see text). The timing of the pumping pulse and observing gate is indicated. The abscissa is the difference of the observing and pumping microwave frequencies.

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