TIME-RESOLVED OPTICAL NUCLEAR POLARIZATION BY RAPID FIELD SWITCHING

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A novel time-resolved ONP technique is presented using pulsed UV excitation and rapid magnetic field switching. The potential of the new technique for studying excited triplet state dynamics on the microsecond time scale is demonstrated on a fluorene/acridine crystal. The technique also yields a significant enhancement of the ONP effect compared to constant-field experiments

1. Introduction

Optical nuclear polarization (ONP) in pure and doped aromatic molecular crystals has been shown to result from the coupling of nuclear spins to spin polarized electronic triplet states populated in an optically driven excitation cycle [1,2]. The coupling may be provided by a static hyperfine interaction in an electron triplet level crossing (LC) region [3], by electron spin—nuclear spin relaxation resulting from a time dependent hyperfine interaction [4], or by externally applied radio frequency fields tuned to "forbidden" electron spin—nuclear spin transitions [5,6]. A common feature of previous ONP experiments is that the crystal under investigation is irradiated continuously with UV light in a constant magnetic field until sufficient nuclear polarization develops to be detected by standard NMR techniques. Here we present a new class of ONP experiments, using pulsed UV irradiation together with rapid field switching designed to yield a dynamic picture of the ONP effect and the associated optical excitation cycle as well as to optimize the ONP.

To understand the strategy behind our experiments, consider the principle points of the mechanism for ONP induced by static hyperfine coupling [2,3,7]. First, UV excitation populates an electronic triplet state selectively, in the sense that the three electron spin sublevels are populated with different efficiencies. Second, electron spin relaxation occurs in the excited triplet state. There are in principle three different relaxation rates, one for each pairing of electron spin sublevels. Third, decay from the excited triplet state to the ground singlet state may again be selective, in the sense that the three electron spin sublevels may decay at different rates. Selective population, relaxation and decay processes govern the creation and evolution of electron spin polarization. Being of purely electronic origin, these processes do not normally affect nuclear spins, since the energy splittings between electron spin sublevels are typically much larger than the hyperfine coupling. However, in a narrow magnetic field region around an electron spin level crossing, the hyperfine coupling mixes electron spin and nuclear spin states so that the same processes may create nuclear polarization. If ONP is generated with continuous UV irradiation, only the combined effects of population, relaxation, and decay can be observed. On the other hand, if a pulsed UV source is used to initiate all optical excitation cycles simultaneously, it should be possible to couple and decouple nuclear spins from particular processes within the cycle simply by switching the magnetic field into and out of the LC region. The contributions of the various processes to the net ONP effect should then be observable. In addition, we should be able to extract kinetic parameters for relaxation and decay processes.

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2. Methods and materials

Our experiments make use of the two-phase technique employed in standard ONP experiments [2,7] In the polarization phase, the sample is held in the fringe field of a 43.5 kG superconducting magnet. An auxiliary coil is used to adjust the base polarization field B_p An externally triggered N_2 laser provides 10 ns UV pulses at 337 nm. An additional field ΔB, collinear with B_p, can be switched on and off with rise and fall times of 2 μs by pulsing current through a second auxiliary coil. A master pulse programmer controls the timing sequence of UV and field pulses. The general timing sequence during the polarization phase for the experiments reported here is shown in fig 1. The 50 ms delay between consecutive UV pulses is long compared to excited triplet lifetimes at room temperature, where all of our experiments were performed. After accumulating nuclear polarization for 15–60 s, the sample is transferred into an NMR probe in the superconducting magnet for the detection phase ONP is then measured as the magnitude of the proton FID signal following a single 185 MHz rf pulse.

Experiments were performed on single crystals of fluorene-d_8h_2 doped with 1000 ppm acridine. The crystal preparation has been described earlier [7] We have used fully as well as partly deuterated acridine guest molecules. In agreement with earlier results [2,7,8], acridine protons have no significant effect on the overall ONP. Since the fluorene crystals show clean cleavage planes perpendicular to the crystalline c-axis, they are readily oriented with the c-axis along

the direction of B_p The c-axis coincides with the long, in-plane x-axis of all molecules in the crystalline unit cell.

3. Results and discussion

Earlier ONP experiments on the fluorene/acridine system have shown a characteristic, dispersion-shaped ONP field dependence around 400 G when B_p is oriented along the molecular x-axis [2,8] Studies with the rf ONP technique [5] have established that this ONP effect is associated with the room temperature LC field B_{LC}^λ = 398 G of the acridine triplet state [8]. In agreement with the earlier results, a negative ONP extremum is observed for B_p = 410 G
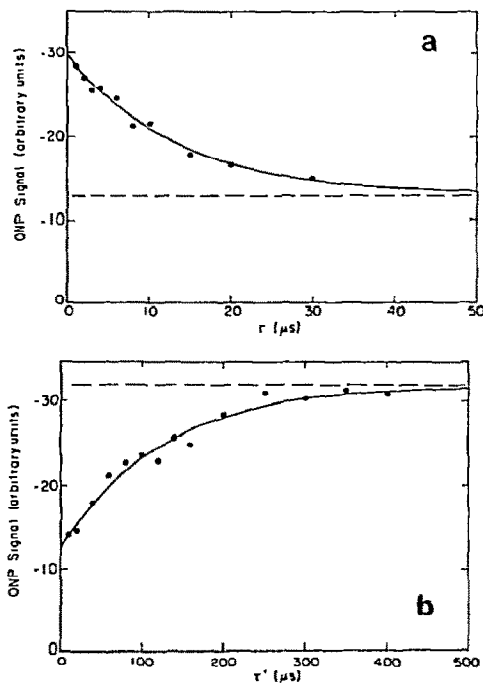
I ig. 2 ONP signals $S(\tau, \tau')$, proportional to initial polarization rate from fluorene-d_8h_2 doped with 1000 ppm acridine B_p = 410 G, ΔB = 100 G (see fig. 1); T = 300 K Solid curves are least-squares exponentials Dashed lines are asymptotic limits (a) $S(\tau, \tau'$ = 5 ms), fit to exponential with 14 μs time constant Asymptotic limit equals constant-field (ΔB = 0) ONP level (b) $S(\tau$ = 1 $\mu s, \tau')$, fit to exponential with 125 μs time constant.

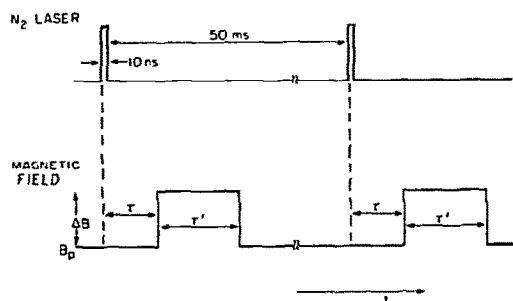I ig 1 General timing sequence for polarization phase of time-resolved ONP experiments. B_p = base polarization field; ΔB = switched auxiliary field.

Using this as a base field, and with B = 100 G, we measured the ONP effect $S(\tau, \tau')$ based on the timing sequence in fig. 1. We report the results of the following two experiments:

(a) Variable τ, fixed τ' = 5 ms $S(\tau, \tau'$ = 5 ms) is shown in fig. 2a.

(b) Fixed τ = 1 μs, variable τ'. $S(\tau$ = 1 μs, $\tau')$ is shown in fig. 2b.

The significant features of the results in fig. 2 are summarized below.

(1) The ONP effect is significantly enhanced by field switching when τ is short and τ' is long.

(2) Two distinct time constants are measured in experiments (a) and (b). The time development in both cases is exponential. Least-squares fits yield a time constant of 14 ± 2 μs in fig 2a and a time constant of 125 ± 5 μs in fig 2b.

(3) Fig. 2a shows that a field switch applied with $\tau \geqslant 40$ μs, but well within the lifetime of the acridine triplet state, does not appreciably alter the observed ONP.

Independent of any other measurements on the fluorene/acridine system, we can most simply interpret the results in fig. 2 by assigning the 14 μs time constant to a hyperfine-mediated nuclear spin relaxation time in the excited triplet state and the 125 μs time constant to the lifetime of the excited state. The picture that emerges is that large additional nuclear polarization is generated in the selective population of the triplet state at B_p. Relaxation at B_p then reduces that polarization to the level normally observed in a constant-field ONP experiment. This interpretation assumes that nuclear spins are coupled to electron spin processes at B_p and completely decoupled at $B_p + \Delta B$.

Now let us compare our interpretation with known properties of the fluorene/acridine system. Pure electron spin relaxation in the acridine triplet state has been studied as a function of temperature [9] It can be explained by a mechanism depending on the modulation of the zero field splitting tensor by thermal population of low-energy vibrational levels, a mechanism well studied at low temperatures both experimentally [10] and theoretically [10,11]. The electron spin relaxation time at room temperature in high field is found to be ≈5 μs [9]. Nuclear spin relaxation in the excited state is expected to be due to the mixing of electronic and nuclear spin

states by the static hyperfine coupling. Thus, the nuclear spin relaxation rate W_n should be related to the pure electron spin relaxation rate W_e by $W_n \approx C_{hf}^2 W_e$, where C_{hf} is a hyperfine mixing coefficient which varies between $2^{-1/2}$ at B_{LC} and 0 at $B_p \gg B_{LC}$. The acridine triplet lifetime has been measured by triplet absorption studies to be T_L = 300 μs at room temperature [12]. The fact that our long time constant is only 125 μs may be explained by involving a residual nuclear spin relaxation time $T_{1n} \approx 200$ μs at $B_p + \Delta B$ The apparent lifetime T_{LA} is then related to the true lifetime by $T_{LA}^{-1} = T_L^{-1} + T_{1n}^{-1}$ The mixing coefficients at B_p should then be ≈4 times larger than those at $B_p + \Delta B$. Model calculations of the mixing coefficients [3] support this as a possible explanation.

So far, we have presented field switching solely as a means of coupling and decoupling nuclear spins from electron spins. However, field switching itself may actually alter the nuclear polarization in the excited state. The spin eigenstates at B_p are mixed states of nuclear and electron spin, while those at $B_p + \Delta B$ are nearly direct products of nuclear spin states and electron spin states. Selective population at B_p produces nuclear polarization. If we assume that the field switch transfers state populations adiabatically, we expect that the corresponding nuclear polarization at $B_p + \Delta B$ may be different. Using a perturbation theory approach to find the spin eigenstates as a function of field [3], we estimate the maximum relative change in nuclear polarization induced by adiabatic field switching to be 50%. The fact that the ONP in fig. 2a approaches the constant-field level when τ is only 40 μs is evidence that the effect is even less than our estimate.

4. Conclusions

We have demonstrated the utility of pulsed ONP experiments as a means of extracting dynamic, excited state parameters in ONP-active triplet states. The data presented here provide support for the assignment of the ONP observed in fluorene/acridine systems at $B_p \approx 400$ G and $B_p \| x$ to the excited acridine monomer triplet state.

In addition to our rapid magnetic field switching experiments, other time-resolved ONP experiments

are possible. In particular, pulsed rf ONP studies are being pursued elsewhere [13].

As it becomes possible to monitor the contributions of individual electronic processes to the net ONP effect using pulsed ONP techniques, experiments may be designed to maximize the ONP effect ONP may be achieved in systems where it would otherwise not be observed, notably in systems with rapid relaxation and non-selective decay or in systems at low temperature, where relaxation is negligible and where the ONP contributions of selective population and selective decay may cancel one another.

Acknowledgement

References

[1] K H Hausser and H C. Wolf Advan Magn Reson 8 (1976) 85

[2] D Stehlik, in. Excited states, Vol 3, ed. EC Lim (Academic Press, New York, 1978) p 203

[3] J P. Colpa and D Stehlik, Chem Phys 21 (1977) 273 289

[4] J Allgeier, V Macho, D Stehlik, H M Vieth, W Auch and J U. von Schutz Chem Phys Letters 86 (1982) 522

[5] H M. Vieth V Macho and D Stehlik, J Phys Chem 83 (1979) 3435

[6] M Deimling, H Brunner, K P Dinse, K H Hausser and J P Colpa, J Magn Reson. 39 (1980) 185

[7] V Macho J P Colpa and D Stehlik, Chem Phys 44 (1979) 113

[8] V Macho, thesis, University of Berlin (1981)

[9] I Tujara, R Morehouse, C J Winscom and W Vollmann Proceedings of the Congress Ampere, Delft (1980)

[10] P J.F Verbeck, C.A. van 't Hoff and J Schmidt, Chem Phys Letters 51 (1977) 292, P.J F Verbeck, A L.M Dicker and J Schmidt Chem Phys Letters 56 (1979) 585

[11] P.J F Verbeck and J Schmidt, Chem Phys Letters 63 (1979) 384

[12] B Prass, F Tujara F Seill and D Stehlik, J Luminescence 24/25 (1981) 4

[13] H M. Vieth, to be published