

# Optical Nuclear Polarization by Selective Population of Nuclear Substates

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The symmetry selection rules for the mixing of states by spin orbit interaction are known to cause unequal population of the three electronic levels of excited triplet states in aromatic molecules. It is shown here that the same selection rules, when combined with the hyperfine interaction, can also produce a selective population and depopulation of the nuclear sublevels. This mechanism is proposed to be responsible for the large optical nuclear polarisation (ONP) in low fields observed experimentally.

## I. Introduction

The optical nuclear polarization (ONP) produced by optically excited triplet states and triplet excitons in molecular crystals was discovered in 1967<sup>1</sup>. More detailed experimental and theoretical investigations<sup>2,3</sup> have shown that this ONP can be produced in high magnetic field by relaxation interactions analogous to the Overhauser effect which transfers the optical electronic polarization caused by the selective population of the electronic triplet substates to the nuclei. However, this mechanism cannot explain the observed large enhancement of the nuclear polarization of the order of  $10^4$  as compared to its static value in low fields ( $H_0 \approx 100$  G) and even less so its marked field and orientation dependence.

In this paper we propose a different mechanism which can explain the experimental results in principle. We intend to show with the simple example of two electrons and two protons that the symmetry selection rules for the mixing of states by spin orbit interaction, which are responsible for the selective population and depopulation of the three electronic triplet levels, can also produce, in combination with the hyperfine interaction, a selective population and depopulation of the nuclear substates.

For a better understanding of the relations between the calculated quantities and the experi-

mental results it is necessary to describe briefly the measuring process.

The protons of a molecular crystal are polarized by optical excitation of triplet states in a polarizing field  $H_0$ . The field strength was varied in a range of  $0.01 \text{ G} < H_0 < 11 \text{ kG}$ , and a preset orientation of the crystal (and molecular) axes with respect to the field  $H_0$  can be chosen.

After termination of the light irradiation the magnetic field  $H_0$  is changed adiabatically to a fixed measuring field  $H_m$ . The nuclear polarization, i.e. the distribution of the nuclear levels in  $H_0$ , is transferred to a distribution over the Zeeman-levels in  $H_m$ , which then can be detected under always constant conditions by a suitable NMR-technique<sup>3</sup>.

If the polarizing field  $H_0$  is large compared to the local dipolar nuclear field  $H_L \approx 1 \text{ G}$ , the generated polarization is given by the expectation value of the total nuclear spin component  $\langle I_z \rangle$  in the field direction  $H_0 \parallel z$ . After an adiabatic change to the field  $H_m$  the measured NMR signal  $S_m$  is proportional to this  $\langle I_z \rangle$ . In an external field  $H_0 \ll H_L$  the expectation value  $\langle I_z \rangle$  becomes zero. Nevertheless, the optical irradiation can result in a non-equilibrium distribution on the nuclear dipolar states. In a time of several  $T_2$ 's the spin system reaches an internal equilibrium, which can be described by a spin temperature  $T_s$ .

It was shown in an early experiment by ABRAGAM and PROCTOR<sup>4</sup> that this spin temperature can be

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<sup>3</sup> K. H. HAUSSER, O. LAUER, H. SCHUCH and D. STEHLIK, Proc. XVI. Coll. Ampere, Bucharest 1970; H. SCHUCH, D. STEHLIK and K. H. HAUSSER, Z. Naturforsch., in print.

<sup>4</sup> A. ABRAGAM and W. G. PROCTOR, Phys. Rev. **109**, 1441 [1968].



measured by adiabatically turning on a large magnetic field  $H_m$ , in which the NMR signal  $S_m$  is given by

$$S_m \propto \frac{1}{T_s} \sqrt{(H_0^2 + H_L^2)}.$$

In the whole field range given above more or less large deviations of  $T_s$  from the thermal equilibrium  $T_L$  (lattice temperature) were observed.

Therefore a mechanism able to explain the observed ONP results has to produce large expectation values  $\langle I_z \rangle \propto H_0/T_s$  in fields  $H_0 \gg H_L$  and a non-thermal equilibrium distribution on the nuclear dipolar levels in "zero" field ( $H_0 \ll H_L$ ).

## II. Nuclear Polarization Caused by Singlet-Triplet Intersystem Crossing

In this section we will show that intersystem crossing from a singlet to a triplet state contributes to the nuclear polarization. We consider a system with two electrons and two protons. We assume that the electronic intersystem crossing is due to first order spin orbit interaction, an interaction which does not affect the nuclear spin states. The hyperfine interaction may in principle also contribute to electronic singlet triplet transitions<sup>5</sup>. The matrix elements of the hyperfine operator, however, are much smaller than the matrix elements of the spin orbit coupling operator  $V_{SL}$  and we assume that the contribution of the hyperfine terms to the intersystem crossing is negligibly small compared with the contribution due to spin orbit coupling. Consequently we neglect the matrix elements of the hyperfine coupling operator between electronic singlets and triplets. We take into account, however, the matrix elements of this operator between the electron nuclear sublevels which belong to the same electronic triplet manifold. The differences in the energies of these magnetic sublevels are so much smaller than all other energy differences between the levels of a molecular or crystalline system that despite the smallness of the matrix elements of the hyperfine operator they give some

important perturbation effects<sup>6</sup> within a given electronic triplet.

We consider a spin Hamiltonian (10), which is the suitable operator within the restrictions mentioned above. Under these conditions the systems with a singlet nuclear spin function form a separate set; they do not contribute to the nuclear polarization and we leave these states out of consideration.

We take as basis functions for the electron triplets the functions  $T_x(e)$ ,  $T_y(e)$ ,  $T_z(e)$ , and for the nuclear triplets  $T_x(n)$ ,  $T_y(n)$ ,  $T_z(n)$  in which  $T_x = 2^{-1/2}(\beta\beta - \alpha\alpha)$ ,  $T_y = 2^{-1/2}(\beta\beta + \alpha\alpha)$ , and  $T_z = 2^{-1/2}(\alpha\beta + \beta\alpha)$ . The products  $T_\mu(e)$ ,  $T_\nu(n)$  form a complete set of spin functions for the system under consideration. We introduce further the function  $\varphi_T$ , the orbital part of the triplet state wave function. The total W.F. for the triplet state is given by the expression

$$\psi_T^i = \left\{ \sum_{\mu\nu} c_{\mu\nu}^i T_\mu(e) T_\nu(n) \right\} \varphi_T. \quad (1)$$

The index  $i$  numbers the various magnetic substates of the triplet; the coefficients  $c_{\mu\nu}^i$  are functions of the magnetic field strength  $H$ .

We consider now the same system in a singlet electronic state. The orbital part of the W.F. is denoted by  $\varphi_S$ , the electron spin function by  $S$ . The total W.F. is of the form

$$\psi_S^j = \varphi_S S \sum_{\nu'} q_{\nu'}^j T_{\nu'}(n). \quad (2)$$

The index  $j$  indicates the three nuclear magnetic substates.

As mentioned before we assume that the crossing from singlet to triplet state is caused by first order spin orbit coupling; we denote the coupling operator by  $V_{SL}$ . From both theoretical and experimental evidence<sup>7,8,9</sup> it is clear that the matrix elements of  $V_{SL}$  between a singlet and a triplet are usually significantly different from each other, and hence that there is a selective crossing to the electron spin states. We assume now that only one of the three components,  $T_x(e)$  say, gives a non-zero matrix element for  $V_{SL}$ . We now obtain the

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<sup>8</sup> a) M. SCHWOERER and H. C. WOLF, Proc. XIV. Coll. Ampère, Ljubljana 1966; b) H. SIXL and M. SCHWOERER Z. Naturforsch. **25a**, 1383 [1970].

<sup>9</sup> M. S. DE GROOT, I. A. M. HESSELMANN, J. SCHMIDT, J. H. VAN DER WAALS, Mol. Phys. **15**, 17 [1968].

following expression for such a matrix element:

$$\begin{aligned}
 & \langle \psi_S^j | V_{SL} | \psi_T^i \rangle \\
 &= \sum_{\nu, \mu} q_\nu^j c_{\mu\nu}^i \langle \varphi_0 S | V_{SL} | \varphi_T T_\mu(e) \rangle \langle T_{\nu'}(n) | T_\nu(n) \rangle \\
 &= \langle \varphi_0 S | V_{SL} | \varphi_T T_x(e) \rangle \sum_\nu q_\nu^j c_{x\nu}^i \\
 &= V_{SL,x} \sum_\nu q_\nu^j c_{x\nu}^i. \quad (3)
 \end{aligned}$$

We introduce the symbol  $V_{SL,\mu}$  for

$$\langle \varphi_0 S | V_{SL} | \varphi_T T_\mu(e) \rangle.$$

The matrix element on the right hand side of (3) is the same for all states  $j$  and  $i$ , hence the probability for crossing from  $\psi_S^j$  to  $\psi_T^i$  is proportional to  $\left\{ \sum_\nu q_\nu^j c_{x\nu}^i \right\}^2$ . Depending on the magnetic field  $H$ , the nuclear W.F. of the singlet may be  $T_x(n)$ ,  $T_y(n)$ ,  $T_z(n)$ , or any linear combination of these functions. The difference in energy of the nuclear spin states even in the presence of a moderately strong magnetic field is usually small compared with  $kT$  unless one measures at very low temperatures. We assume that we are considering our system under such conditions that the initial probability for each of the nuclear spin states of the electronic singlet state is  $1/3$ . This also means that the initial value for  $\langle I_z \rangle$  averaged over the three spin states is zero. When a molecule crosses from a singlet state to a triplet state, we find an average probability that the system crosses to a particular state  $\psi_T^i$  which is proportional to

$$\frac{1}{3} \sum_j \left\{ \sum_\nu q_\nu^j c_{x\nu}^i \right\}^2;$$

because of the orthonormality conditions for the coefficients  $q_\nu^j$ , this expression reduces to  $\frac{1}{3} \sum_\nu c_{x\nu}^i{}^2$ .

The sum of this last expression over all states  $i$  equals one (due to the orthonormality of the coefficients  $c_{x\nu}$  with  $\nu = x, y, z$ ) which means that the proportionality constant equals one. We define

$$P_x^i = \frac{1}{3} \sum_\nu c_{x\nu}^i{}^2. \quad (4a)$$

$P_x^i$  gives the probability that when a singlet molecule from a reservoir with  $\langle I_z \rangle = 0$  crosses to a triplet state  $\psi_T$  and when the spin orbit coupling is only effective between the singlet and the  $T_x$  component of the triplet, it crosses to a particular substate  $\psi_T^i$ . We define similarly

$$P_y^i = \frac{1}{3} \sum_\nu c_{y\nu}^i{}^2 \quad \text{and} \quad P_z^i = \frac{1}{3} \sum_\nu c_{z\nu}^i{}^2 \quad (4b, c)$$

where the effectiveness for the crossing is only due to the  $T_y$  and  $T_z$  component respectively.

Each of the states  $\psi_T^i$  has associated with it a particular expectation value  $\langle I_z \rangle^i$  for the  $z$  component of the nuclear spin. (We assume the magnetic field in the  $z$  direction as defined by the fine structure tensor.)

We finally define the "crossing polarizations"

$$p_x = \sum_i P_x^i \langle I_z \rangle^i, \quad (5a)$$

$$p_y = \sum_i P_y^i \langle I_z \rangle^i, \quad (5b)$$

$$p_z = \sum_i P_z^i \langle I_z \rangle^i. \quad (5c)$$

These functions give the average value for  $\langle I_z \rangle$  in the triplet state and hence for the absolute nuclear polarization, when a molecule crosses from a singlet to a triplet state (with  $T_x(e)$ ,  $T_y(e)$ ,  $T_z(e)$  functions respectively effective for the crossing). This is an initial value for the polarization, unmodified by relaxation and other processes.

It may be, of course, that state  $\psi_T^i$  gets populated because more than one element  $V_{SL,\mu}$  is non-zero. For such a case the formulae we have derived have to be generalized. Instead of (3) we get a matrix element

$$\sum_{\mu\nu} q_\nu^j c_{\mu\nu}^i \langle \varphi_S S | V_{SL} | \varphi_T T_\mu(e) \rangle = \sum_{\mu\nu} q_\nu^j c_{\mu\nu}^i V_{SL,\mu}.$$

The probability for crossing to state  $\psi_T^i$  is now proportional to

$$\left\{ \sum_{\mu\nu} q_\nu^j c_{\mu\nu}^i V_{SL,\mu} \right\}^2. \quad (6)$$

When we carry out the summation over  $j$  and  $\nu$  as we did before and normalize the total probability to 1, we find a probability to cross to a particular state  $\psi_T^i$  which is given by

$$\begin{aligned}
 & \frac{1}{3} \sum_\mu V_{SL,\mu}^2 \sum_\nu c_{\mu\nu}^i{}^2 / \left( \sum_\mu V_{SL,\mu}^2 \sum_{\nu i} c_{\mu\nu}^i{}^2 \right) \\
 &= \sum_\mu V_{SL,\mu}^2 P_\mu^i / \sum_\mu V_{SL,\mu}^2.
 \end{aligned}$$

We define a quantity

$$f_\mu = V_{SL,\mu}^2 / \sum_\mu V_{SL,\mu}^2. \quad (7)$$

This quantity indicates the relative effectiveness of the  $T_\mu$  component for the intersystem crossing. Obviously the relation  $\sum_\mu f_\mu = 1$  holds. The total probability for crossing to a particular substate  $\psi_T^i$  is

now given by  $P^i = \sum_{\mu} f_{\mu} P_{\mu}^i$ . This gives a polarization

$$\sum_{\mu, i} f_{\mu} P_{\mu}^i \langle I_z \rangle^i = \sum_{\mu} f_{\mu} p_{\mu}. \quad (8)$$

When  $f_{\mu} = 1/3$  for  $\mu = x, y$  and  $z$ , the polarization (8) becomes  $1/3 \sum_{\mu} p_{\mu}$ .

Using again the orthogonality relations for the coefficients  $c_{\mu\nu}^i$ , it can be shown that

$$p_x + p_y + p_z = \frac{1}{3} \sum_i \langle I_z \rangle^i = 0 \quad (9)$$

holds for all field strengths. It follows from (8) and (9) that when the crossing is equally effective for the  $T_x(e)$ ,  $T_y(e)$ , and  $T_z(e)$  component, no nuclear polarization occurs. When the three  $f_{\mu}$ 's are different, however, the expression (8) gives usually a non-zero result.

### 1. The "Crossing Polarizations" and their Dependence on Field Strength, Orientation and Hyperfine Parameters

We consider the spin Hamiltonian

$$\mathcal{H} = D S_z^2 + E(S_x^2 - S_y^2) + g_e \mu_e S_z H_z + H_{dd} - g_n \mu_n I_z H_z + \bar{S} \bar{A} \bar{I} \quad (10)$$

in which all quantities have their usual meaning;  $H_{dd}$  is the dipolar coupling operator for the protons. In our calculations we assumed that the principal axes of the fine structure, the hyperfine structure and the dipolar coupling tensor coincide. Furthermore we assume that the two protons are in equivalent positions and have the same hyperfine tensor, so that  $\bar{S} \bar{A}_1 \bar{I}_1 + \bar{S} \bar{A}_2 \bar{I}_2 = \bar{S} \bar{A} \bar{I}$ . The situation is for instance like that for the 9 and 10 proton in anthracene. The term  $H_{dd}$  appears to have little influence on the final results, we neglect this term in most of our calculations. A similar Hamiltonian has been considered by HUTCHISON et al.<sup>6</sup> who considered mainly the energy eigenvalues and not the nuclear polarizations as we want to do. We found, similar to Hutchison, that the diagonalization of (10) is greatly facilitated by the high symmetry of the Hamiltonian.

The Hamiltonian (10) can be diagonalized easily when  $\bar{A} = 0$ . The W.F.'s so obtained are a single product of an electron spin function and a nuclear spin function. When one substitutes the coefficients so obtained in (4) and (5) one finds  $p_x = p_y = p_z = 0$  for all field strengths.

When not all components of  $\bar{A}$  are zero it appears that  $p_x$ ,  $p_y$ , and  $p_z$  are usually non-zero and strongly dependent on field strength and orientation. To show this two approaches are being tried, a perturbation theory approach and exact diagonalization by computer calculations<sup>10</sup>. In the first approach the eigenfunctions of (10) for the case  $\bar{A} = 0$  were chosen as basis functions, the effect of  $A_{xx}$ ,  $A_{yy}$ , and  $A_{zz}$  was calculated by perturbation theory. It appears that  $p_x$ ,  $p_y$ , and  $p_z$  are second or higher order functions of  $A_{xx}$ ,  $A_{yy}$ ,  $A_{zz}$  and their products. It can be shown that a simultaneous change in sign of  $A_{xx}$  and  $A_{yy}$  does not change the polarization, it depends, however, on the sign of  $A_{zz}$ . The perturbation theory expressions are however fairly complex.

For the computer calculations we transformed (10) into a matrix, using basis functions of the type  $T_{\mu}(e) T_{\nu}(n)$  so that diagonalization of the matrix gave us directly the coefficients  $c_{\mu\nu}^i$ . In the Tables 1 and 2 we summarize some of our results for  $p_x$ . For both tables the columns 2, 3 and 4 refer to a C—H fragment with a spin density  $\rho_c$  of about 0.1 at the carbon atom,  $A_{xx} = -3 \cdot 10^6 \text{ sec}^{-1}$ ,  $A_{yy} = -9 \cdot 10^6 \text{ sec}^{-1}$  and  $A_{zz} = -6 \cdot 10^6 \text{ sec}^{-1}$ ; the columns 5, 6 and 7 refer to a C—H fragment with a spin density  $\rho_c$  of about 0.5 at the carbon atom and with hyperfine tensor components  $A_{xx} = -15 \cdot 10^6 \text{ sec}^{-1}$ ,  $A_{yy} = -45 \cdot 10^6 \text{ sec}^{-1}$  and  $A_{zz} = -30 \cdot 10^6 \text{ sec}^{-1}$ . In the columns 1 the field strength is given in gauss. For Table 1 we used the  $D$  and  $E$  values for the fluorene localized triplet  $D = 3 \cdot 10^9 \text{ sec}^{-1}$  and  $E = -9 \cdot 10^7 \text{ sec}^{-1}$  (see <sup>8b</sup>), for Table 2 we used the  $D^*$  and  $E^*$  values one can calculate for fluorene triplet excitons,  $D^* = 1,65 \cdot 10^9 \text{ sec}^{-1}$  and  $E^* = -6 \cdot 10^8 \text{ sec}^{-1}$ . The  $p_x$  values are given in units  $10^{-6}$ . We transformed our formulae so that we could calculate the polarizations for fields in the  $y$  and  $x$  direction. The columns 3 and 6 give strictly speaking  $\sum_i P_x^i \langle I_y \rangle^i$ , the columns 4 and 7 give  $\sum_i P_x^i \langle I_x \rangle^i$ . The columns 2, 3 and 4 and also the columns 5, 6 and 7 refer to the same situation for the molecular system, the only difference being in the orientation of the magnetic field. As will be noticed, the anisotropy of the polarization is remarkable.

<sup>10</sup> E. CALLAGHAN, E. COLBURN and J. P. COLPA, unpublished results.



Table 1

	$\frac{\rho_c}{H_z} = 0.1$	$H_y$	$H_x$	$\frac{\rho_c}{H_z} = 0.5$	$H_y$	$H_x$
5	+ 1.9	+ 251	205	— 73	+ 1507	+ 109
10	+ 0.9	+ 275	288	— 24	+ 2782	+ 220
25	+ 1.0	+ 270	227	+ 21	+ 4600	+ 445
50	+ 0.7	+ 216	16	+ 40	+ 4498	+ 5
75	+ 0.3	+ 179	— 179	+ 38	+ 4070	— 1615
100	— 0.1	+ 158	— 395	+ 30	+ 3820	— 4403
200	— 1.2	+ 110	— 3852	— 4	+ 3138	— 3730
250	—	+ 89	— 38970	—	+ 2594	— 143074
300	—	+ 71	— 329	—	+ 2030	— 142240
500	— 5	+ 28	—	— 117	+ 716	—
750	— 21	+ 11	— 66	— 440	+ 260	— 1627
1000	— 450	+ 4.9	— 25	— 5610	+ 120	— 611
1500	— 5.4	+ 1.6	— 6.8	— 303	+ 38	— 167

$p_x$  in units  $10^{-6}$  for localized fluorene triplets. See the main text for further explanation.

Table 2

	$\frac{\rho_c}{H_z} = 0.1$	$H_y$	$H_x$	$\frac{\rho_c}{H_z} = 0.5$	$H_y$	$H_x$
5	2	5	— 1.6	— 34	+ 69	+ 15
10	1.5	4.1	— 2.3	— 13	+ 64	— 32
25	0.6	3.2	— 5	+ 21	+ 89	— 129
50	0.1	3.9	— 9.8	+ 49	+ 141	— 256
75	— 0.3	5.0	— 15	+ 59	+ 179	— 383
100	— 0.9	6.0	— 20	+ 56	+ 203	— 518
250	— 10	8.4	— 72	— 133	+ 217	— 1802
500	— 618	5	— 1300	— 7890	+ 119	— 29700
550	— 42200	4.3	— 7480	— 53440	+ 103	— 130800
600	— 613	3.7	— 39970	— 16270	+ 89	— 239750
750	— 40	2.4	— 349	— 1052	+ 57	— 8315
1000	— 7.7	1.2	— 52	— 197	+ 30	— 1284
1500	— 1.0	0.4	— 9.3	— 38	+ 10	— 231

$p_x$  in units  $10^{-6}$  for fluorene excitons. See the main text for further explanation.

Other calculations have shown that  $p_x$ ,  $p_y$ , and  $p_z$  are also non-zero when  $A_{xx} = A_{yy} = A_{zz}$ .

In the Tables 1 and 2 the very high values of  $p_x$  at 100 and 550 gauss respectively for a field  $H_z$  and at 250 and 600 gauss respectively for  $H_x$  occur in the regions where one expects a crossing of the energy levels in case one neglects the hyperfine interaction. This interaction gives rise to a non-crossing rule for the magnetic substates, in the "crossing region", however, the W.F.'s behave anomalously and give high nuclear polarizations. Even though the experimental results are still scarce, the ONP in anthracene and fluorene crystals<sup>2,3</sup> shows only smooth curves at relatively low values in the whole field range where crossing could occur. A discussion of this point seems premature, because the theoretical result might be due to the particular choice of the

field direction being parallel to a principal axis of the molecular fine structure tensor. However, this could not be realized in the experiments where the field was oriented with respect to the crystalline axes rather than with respect to the molecular axes.

In crystals one has also to consider the interaction of the triplet electrons with protons of neighbouring molecules (in a singlet state). This gives different values for the hyperfine tensor components, the situation may be less symmetrical also. What we meant to show here is in the first place that  $p_x \neq 0$  etc., and what orders of magnitude are to be expected. For a larger number of protons in a molecule we expect the values of  $p_x$  to be considerably higher than the ones in the tables. Further work along these lines is in progress.

## 2. Nuclear Polarization Caused by Triplet-Singlet Decay

In the previous section we described how the creation of a triplet state may be accompanied by nuclear polarization. We will now briefly discuss the reverse process. We assume again that only the  $T_x$  component of the triplet function gives non-zero matrix elements of  $V_{SL}$ . Matrix elements are then given again by expression (3).

If crossing occurs between  $\psi_T^i$  and  $\psi_S^j$  this happens with a probability proportional to

$$\left\{ \sum_v c_{xv}^i q_v^j \right\}^2.$$

The probability constant is in this case

$$\left[ \sum_j \left\{ \sum_v c_{xv}^i q_v^j \right\}^2 \right]^{-1} = \left\{ \sum_v c_{xv}^i{}^2 \right\}^{-1} = (3 P_x^i)^{-1}$$

in which we have used the orthogonality relations for  $q^j$  and the definition (4a).

Hence if crossing occurs between  $\psi_T^i$  and  $\psi_S^j$  there is a probability

$$\frac{1}{3 P_x^i} \left\{ \sum_v c_{xv}^i q_v^j \right\}^2 \quad (11)$$

that this is a crossing to a particular nuclear substate  $\psi_S^j$ .

We assume now that the nuclei of the singlet state are in a magnetic field strong enough to give nuclear spin states

$$(\alpha\alpha) = 1/\sqrt{2} \{T_y - T_x\}, \quad \beta\beta = 1/\sqrt{2} \{T_y + T_x\}$$

and  $T_z$ , with  $\langle I_z \rangle = +1, -1$ , and  $0$  respectively. For nuclei in a singlet state this is a very good approximation already at fields of a few gauss. This determines the coefficients  $q^j$  in (11). When we take the products of (11) and  $\langle I_z \rangle$  ( $+1, -1$ , or  $0$ ) and sum these products over the substates  $j$  we obtain after some algebraic manipulations

$$-2 c_{xy}^i c_{xx}^i / 3 P_x^i. \quad (12)$$

This quantity gives the average value of  $\langle I_z \rangle$  for molecules in a singlet electronic state to which a triplet  $\psi_T^i$  decayed via spin orbit coupling with the  $T_x$  component of the triplet. Simultaneously the  $\langle I_z \rangle^i$  of the triplet disappears, so that the total polarization created by such a triplet decay is

$$\Delta_x^i = -\langle I_z \rangle^i - 2 c_{xy}^i c_{xx}^i / 3 P_x^i. \quad (13a)$$

When instead of the component  $T_x$  the  $T_y$  or  $T_z$  component is effective, we get similarly

$$\Delta_\mu^i = -\langle I_z \rangle^i - 2 c_{\mu y}^i c_{\mu x}^i / 3 P_x^i. \quad (13b)$$

in which  $\mu$  is  $y$  or  $z$ .

The probability  $P_x^i$  gives the distribution over the levels  $i$  at the moment of crossing. When this distribution does not change before the molecules decay, we get a contribution from the decay which equals

$$\begin{aligned} \sum_i P_x^i \Delta_x^i &= -\sum_i P_x^i \langle I_z \rangle^i - \frac{2}{3} \sum_i c_{xy}^i c_{xx}^i \\ &= -\sum_i P_x^i \langle I_z \rangle^i = -p_x. \end{aligned}$$

This would just cancel the polarization  $p_x$  created by the crossing to the triplet. When the triplet disappears, however, via L. S. coupling with a  $T_y$  or  $T_z$  state, there is certainly a resulting polarization.

In Table 3 we give values for  $\Delta_x^i$  together with  $P_x^i$  and  $\langle I_z \rangle^i$  for the 9 magnetic substates for a field of 50 gauss in the  $z$  direction; the parameter values are  $D = 2.8 \cdot 10^9 \text{ sec}^{-1}$ ,  $E = 2.8 \cdot 10^8 \text{ sec}^{-1}$ ,  $A_{xx} = -3 \cdot 10^6 \text{ sec}^{-1}$ ,  $A_{yy} = -9 \cdot 10^6 \text{ sec}^{-1}$ , and  $A_{zz} = -6 \cdot 10^6 \text{ sec}^{-1}$ . The states in Table 3 are given in the order of decreasing energy.

Table 3.

$\langle I_z \rangle^i$	$P_x^i$	$\Delta_x^i$	
-0.99999830	0.01888527	-0.00000179	$i = 1$
+0.00000135	0.01759668	-0.00000002	2
+0.99999965	0.01632881	+0.00000027	3
	0.05281076		
+0.99996589	0.31700227	+0.00000747	4
-0.00000195	0.31573238	+0.00000195	5
-0.99996786	0.31444605	-0.00000507	6
	0.94718070		
-0.99829305	0.00000208	+0.99829305	7
+0.00000070	0.00000247	+0.02966362	8
+0.99829376	0.00000220	-0.99829376	9
	0.00000855		

See the text for the meaning of the symbols.

## 3. Role of Relaxation

So far we have discussed the ONP due to selective population and depopulation of nuclear substates neglecting relaxation completely, i.e. setting the relaxation rates  $w_{ij}$  between all 9 states equal to zero. We have seen that if population and depopulation are governed by the same spin orbit matrix element the polarizations produced by the two processes cancel each other yielding a net zero polarization, and we have also seen in Section II

under which condition the selection rules yield a finite polarization.

Now, let us consider the influence of relaxation, and for simplicity let us begin with the other extreme of very fast relaxation. In this case we can assume that the distribution of our system over the 9 states follows a Boltzmann equilibrium; hence the selectivity when populating the triplet state is wiped out and we expect a nuclear polarization which results exclusively from the selectivity of the depopulation.

In actual fact, we have to deal with neither of these limiting cases, but with a mixed case where the rate constants of relaxation and of depopulation are of comparable order; if we know all these rate constants the resulting ONP can be calculated. We want to emphasize that in this manner relaxation plays an important role in the mechanism of ONP.

In addition to the effect of relaxation discussed above, any ONP can be destroyed by relaxation processes. If we neglect nuclear spin lattice relaxation in the absence of light which can be done to a very good approximation in most cases<sup>3</sup>, the following contributions must be considered both for intramolecular and intermolecular electron nuclear coupling.

#### 1. Pure electronic relaxation.

The usual selection rules prohibiting a change in the nuclear quantum number is partly lifted by the mixing of states introduced by the hyperfine coupling.

#### 2. Relaxation by time dependent electron nuclear coupling.

#### 3. Cross relaxation.

One process should be mentioned in particular. In a certain range of the magnetic field strength and orientation some electron levels can become close to be degenerate ("crossing region"). Overlap of the energy differences among different pairs of hyperfine levels allows cross relaxation equalizing the populations on the involved levels.

This cross relaxation could also destroy the high polarization which was predicted in Section II for the "crossing region", but which was not observed experimentally.

### III. Conclusion

The main assumptions we made for the singlet triplet crossing are that the operator responsible for the crossing does not contain the nuclear spin operators and that its matrix elements with the electronic triplets  $T_x(e)$ ,  $T_y(e)$  and  $T_z(e)$  are not all equal (which means primarily a selective crossing to electronic spin states). The term  $IAS$  is not responsible for the crossing but gives within the set of magnetic sublevels of an electronic triplet a mixing of the electronic nuclear spin configurations. Under these assumptions one gets a certain probability  $P^i$  for intersystem crossing to a particular substate  $\psi_T^i$ , such that in general  $\sum_i P_i \langle I_z \rangle^i \neq 0$ , so that the combination of selective crossing for the electron spin states and hyperfine coupling leads to a selective nuclear population.

The mechanism we propose here gives according to our calculations a nuclear polarization which depends strongly on both the strength and the direction of the polarizing field  $H_0$ ; positive as well as negative polarizations occur and for the lower field regions an order of magnitude  $10^{-6}$  to  $10^{-4}$  is found. Moreover, the mechanism is able to predict a non-thermal equilibrium distribution on the nuclear dipolar levels at zero external field. All these characteristics are in agreement with the experimental findings. We finally remark that changes in the values for the hyperfine tensor components (not necessarily changes in sign) may give changes in sign and order of magnitude of the polarization.

### Appendix I

We consider in somewhat greater detail the eigenfunctions of (10). Symmetry considerations greatly facilitate the problem of diagonalization of the spin Hamiltonian. In zero field one finds 4 sets of functions, each set belonging to a different irreducible representation of the group  $D_{2h}$ . One of those sets contains only the functions  $T_x(e)$   $T_y(n)$ , and  $T_y(e)$   $T_x(n)$ . In zero field and with neglect of the hyperfine interaction each of the two product functions is a proper solution of the Hamiltonian. When we introduce hyperfine interaction in the zero field case, second order perturbation theory gives the following linear combinations as approximate

solutions:

$$\left\{ 1 - \frac{1}{2} \frac{A_{zz}^2}{(2E)^2} \right\} T_x(e) T_y(n) - \left\{ \frac{A_{zz}}{2E} \right\} T_y(e) T_x(n), \quad (A1)$$

$$\left\{ 1 - \frac{1}{2} \frac{A_{zz}^2}{(2E)^2} \right\} T_y(e) T_x(n) + \left\{ \frac{A_{zz}}{2E} \right\} T_x(e) T_y(n). \quad (A2)$$

[There are no second order terms in the correction terms in (A1) and (A2).] For  $A_{zz} = -6 \cdot 10^6 \text{ sec}^{-1}$  and  $E = -9 \cdot 10^7 \text{ sec}^{-1}$  (see Section II) one finds  $A_{zz}/2E = -0.066$ . In triplet states one may find protons with an  $A_{zz}$  value 4 or 5 times as high as the one used in our example, giving (A2) a coefficient  $\sim 0.33$ . Even if  $V_{SL,y} = \langle \varphi_S S | V_{SL} | \varphi_T T_y \rangle = 0$  the state described by (A2) may have a non-zero probability to get occupied when

$$V_{SL,x} = \langle \varphi_S S | V_{SL} | \varphi_T T_x \rangle \neq 0.$$

When  $A_{zz} \neq 0$  it follows that  $c_{xy} \neq 0$  and hence  $P_x^i \neq 0$  for state (A2) although this state is nearly a  $T_y(e)$  state.

When one sums the  $P^i = \sum_{\mu} f_{\mu} P_{\mu}^i$  over the nuclear substates of a particular electronic level, one gets the relative probabilities for population of this electronic level through intersystem crossing. In zero field we define the relative population probabilities for the three electronic energy levels  $E_x = D - E$ ,  $E_y = D + E$ ,  $E_z = 0$  by summing over all  $i$ 's belonging to the same electronic level  $E_u$

( $u = x, y, z$ )

$$P_u = \sum_{\mu, i(E_u)} f_{\mu} P_{\mu}^i.$$

These are the relative population probabilities, which can be extracted from the experiment designed to determine the optical electronic spin alignment or polarisation (OEP)<sup>8,9</sup>.

It should be emphasized that the actually measured  $P_u$  can be different from the  $f_{\mu}$ , the population probabilities for the  $T_{\mu}(e)$  components by spin orbit intersystem crossing, if hyperfine interaction is present. Even if the proton hyperfine coupling is too small to produce a splitting of the electronic levels (as in all experiments with optically detected ESR), it still mixes the  $T_{\mu}(e) T_{\nu}(n)$  functions. Consequently in a special case, when only  $T_x(e)$  is effective in intersystem crossing, i.e.  $f_{\mu} = 1$  for  $\mu = x$ ,  $f_{\mu} = 0$  for  $\mu \neq x$ , other  $P_u$  besides  $u = x$  can be non-zero.

In the example discussed with the Eqs. (A1, 2)  $P_y$  would amount only to the order of  $10^{-2}$  if only  $T_x$  is assumed to be effective ( $f_x = 1$ ). Nevertheless, the influence of hyperfine coupling cannot be neglected in all cases when interpreting the experimentally determined  $P_u$  in terms of population probabilities for the  $T_{\mu}(e)$  components.

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