Optical Nuclear Polarization by Selective Population of Nuclear Substates

J. P. Colpa

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

and K. H. Hausser and D. Stehlik

Max-Planck-Institut, Abt. Molekulare Physik, Heidelberg, Germany

(Z. Naturforsch. **26 a**, 1792—1799 [1971]; received 31 July 1971)

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[1]. More detailed experimental and theoretical investigations[2,3] 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 experimental 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 $0.01\ \mathrm{G} < H_0 < 11$ 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[3].

If the polarizing field H_0 is large compared to the local dipolar nuclear field $H_\mathrm{L} \approx 1$ G, the generated polarization is given by the expectation value of the total nuclear spin component $\langle I_z \rangle$ in the field direction $H_0 \| z$. 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 $H_0 \ll H_\mathrm{L}$ 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[4] that this spin temperature can be

---

Reprints request to Prof. Dr. K. H. Hausser, Max-Planck-Institut Abt. Molekulare Physik, *D-6900 Heidelberg*, Jahnstraße 29.

[1] G. Maier, U. Haeberlen, H. C. Wolf, and K. H. Hausser, Phys. Lett. **25 A**, 384 [1968].

[2] G. Maier a. H. C. Wolf, Z. Naturforsch. **23 a**, 1068 [1968].

[3] 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.

[4] 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

$$S_{\mathrm{m}} \propto \frac{1}{T_{\mathrm{S}}} \sqrt{(H_0^2 + H_{\mathrm{L}}^2)}\,.$$

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 $\langle I_z \rangle \propto H_0/T_{\mathrm{S}}$ in fields $H_0 \gg H_{\mathrm{L}}$ and a non-thermal equilibrium distribution on the nuclear dipolar levels in "zero" field ($H_0 \ll H_{\mathrm{L}}$).

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[5]. 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[6] 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 $T_x(\mathrm{e})$, $T_y(\mathrm{e})$, $T_z(\mathrm{e})$, and for the nuclear triplets $T_x(\mathrm{n})$, $T_y(\mathrm{n})$, $T_z(\mathrm{n})$ 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 $T_\mu(\mathrm{e})$, $T_\nu(\mathrm{n})$ form a complete set of spin functions for the system under consideration. We introduce further the function φ_{T}, the orbital part of the triplet state wave function. The total W.F. for the triplet state is given by the expression

$$\psi_{\mathrm{T}}^i = \Big\{ \sum_{\mu\nu} c_{\mu\nu}^i \, T_\mu(\mathrm{e}) \, T_\nu(\mathrm{n}) \Big\} \varphi_{\mathrm{T}}\,. \tag{1}$$

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 φ_{S}, the electron spin function by S. The total W.F. is of the form

$$\psi_{\mathrm{S}}^j = \varphi_{\mathrm{S}} \, S \sum_{\nu'} q_{\nu'}^j \, T_{\nu'}(\mathrm{n})\,. \tag{2}$$

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[7,8,9] 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, $T_x(\mathrm{e})$ say, gives a non-zero matrix element for V_{SL}. We now obtain the

---

[5] R. Kaptein and L. J. Oosterhoff, Chem. Phys. Lett. **4**, 195 and 214 [1969]; G. L. Closs and A. D. Trifunac, J. Amer. Chem. Soc. **92**, 2183 [1970].

[6] C. A. Hutchison, J. V. Nicholas and G. W. Scott, J. Chem. Phys. **53**, 1906 [1970].

[7] J. H. van der Waals and M. S. de Groot, The Triplet State, Int. Symp. Beirut, 1967, ed.: A. B. Zahlan.

[8] a) M. Schwoerer and H. C. Wolf, Proc. XIV. Coll. Ampère, Ljubljana 1966; b) H. Sixl and M. Schwoerer Z. Naturforsch. **25a**, 1383 [1970].

[9] 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:

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

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

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

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 ψ_S^j to ψ_T^i is proportional to $\left\{\sum_\nu q^j_\nu\,c^i_{x\nu}\right\}^2$. Depending on the magnetic field H, the nuclear W.F. of the singlet may be $T_x(\mathrm{n})$, $T_y(\mathrm{n})$, $T_z(\mathrm{n})$, 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 ψ_T^i which is proportional to

$$\tfrac{1}{3}\sum_j\left\{\sum_\nu q^j_\nu\,c^i_{x\nu}\right\}^2;$$

because of the orthonormality conditions for the coefficients q^j_ν, this expression reduces to $\frac{1}{3}\sum_\nu c^{i\;2}_{x\nu}$. 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

$$P^i_x=\tfrac{1}{3}\sum_\nu c^{i\;2}_{x\nu}.\tag{4a}$$

P^i_x gives the probability that when a singlet molecule from a reservoir with $\overline{\langle I_z\rangle}=0$ crosses to a triplet state ψ_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 ψ_T^i. We define similarly

$$P^i_y=\tfrac{1}{3}\sum_\nu c^{i\;2}_{y\nu}\quad\text{and}\quad P_z=\tfrac{1}{3}\sum_\nu c^{i\;2}_{z\nu}\tag{4b, c}$$

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

Each of the states ψ_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"

$$p_x=\sum_i P^i_x\langle I_z\rangle^i\,,\tag{5a}$$

$$p_y=\sum_i P^i_y\langle I_z\rangle^i\,,\tag{5b}$$

$$p_z=\sum_i P^i_z\langle I_z\rangle^i\,.\tag{5c}$$

These functions give the average value for $\overline{\langle I_z\rangle}$ in the triplet state and hence for the absolute nuclear polarization, when a molecule crosses from a singlet to a triplet state (with $T_x(\mathrm{e})$, $T_y(\mathrm{e})$, $T_z(\mathrm{e})$ 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 ψ_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

$$\sum_{\mu\nu} q^j_\nu\,c^i_{\mu\nu}\langle\varphi_S S\,|\,V_{SL}\,|\,\varphi_T\,T_\mu(\mathrm{e})\rangle=\sum_{\mu\nu} q^j_\nu\,c^i_{\mu\nu}\,V_{SL,\mu}\,.$$

The probability for crossing to state ψ_T^i is now proportional to

$$\left\{\sum_{\mu\nu} q^j_\nu\,c^i_{\mu\nu}\,V_{SL,\mu}\right\}^2.\tag{6}$$

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

$$\tfrac{1}{3}\sum_\mu V^2_{SL,\mu}\sum_\nu c^{i\;2}_{\mu\nu}\Big/\Big(\sum_\mu V^2_{SL,\mu}\sum_{\nu i} c^{i\;2}_{\mu\nu}\Big) = \sum_\mu V^2_{SL,\mu}\,P^i_\mu\Big/\sum_\mu V^2_{SL,\mu}\,.$$

We define a quantity

$$f_\mu=V^2_{SL,\mu}\Big/\sum_\mu V^2_{SL,\mu}\,.\tag{7}$$

This quantity indicates the relative effectiveness of the T_μ component for the intersystem crossing. Obviously the relation $\sum_\mu f_\mu=1$ holds. The total propability for crossing to a particular substate ψ_T^i is now given by $P^i = \sum_{\mu} f_\mu P^i_\mu$. This gives a polarization

$$\sum_{\mu,i} f_\mu P^i_\mu \langle I_z \rangle^i = \sum_{\mu} f_\mu p_\mu . \qquad (8)$$

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 $c^i_{\mu\nu}$, it can be shown that

$$p_x + p_y + p_z = \tfrac{1}{3} \sum_{i} \langle I_z \rangle^i = 0 \qquad (9)$$

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_μ'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

$$\mathcal{H} = D S_z^2 + E(S_x^2 - S_y^2) + g_\mathrm{e} \mu_\mathrm{e} S_z H_z + H_\mathrm{dd} - g_\mathrm{n} \mu_\mathrm{n} I_z H_z + \bar{S} \bar{\bar{A}} \bar{I} \qquad (10)$$

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 $\bar{S} \bar{\bar{A}}_1 \bar{I}_1 + \bar{S} \bar{\bar{A}}_2 \bar{I}_2 = \bar{S} \bar{\bar{A}} \bar{I}$. 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.[6] 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 $\bar{\bar{A}} = 0$. 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 $\bar{\bar{A}}$ 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[10]. In the first approach the eigenfunctions of (10) for the case $\bar{\bar{A}} = 0$ 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 $T_\mu(\mathrm{e})\ T_\nu(\mathrm{n})$ so that diagonalization of the matrix gave us directly the coefficients $c^i_{\mu\nu}$. 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 ϱ_c of about 0.1 at the carbon atom, $A_{xx} = -3 \cdot 10^6\ \mathrm{sec}^{-1}$, $A_{yy} = -9 \cdot 10^6\ \mathrm{sec}^{-1}$ and $A_{zz} = -6 \cdot 10^6\ \mathrm{sec}^{-1}$; the columns 5, 6 and 7 refer to a C—H fragment with a spin density ϱ_c of about 0.5 at the carbon atom and with hyperfine tensor components $A_{xx} = -15 \cdot 10^6\ \mathrm{sec}^{-1}$, $A_{yy} = -45 \cdot 10^6\ \mathrm{sec}^{-1}$ and $A_{zz} = -30 \cdot 10^6\ \mathrm{sec}^{-1}$. 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 $D = 3 \cdot 10^9\ \mathrm{sec}^{-1}$ and $E = -9 \cdot 10^7\ \mathrm{sec}^{-1}$ (see [8b]), for Table 2 we used the D^* and E^* values one can calculate for fluorene triplet excitons, $D^* = 1{,}65 \cdot 10^9\ \mathrm{sec}^{-1}$ and $E^* = -6 \cdot 10^8\ \mathrm{sec}^{-1}$. 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 $\sum_i P^i_x \langle I_y \rangle^i$, the columns 4 and 7 give $\sum_i P^i_x \langle I_x \rangle^i$. The columns 2, 3 and 4 and also the 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.

---

[10] E. CALLAGHAN, E. COLBOURN and J. P. COLPA, unpublished results.

Table 1

	$\varrho_c = 0.1$			$\varrho_c = 0.5$		
	H_z	H_y	H_x	H_z	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

	$\varrho_c = 0.1$			$\varrho_c = 0.5$		
	H_z	H_y	H_x	H_z	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[2,3] 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 ψ_{T}^i and ψ_{S}^j this happens with a probability proportional to

$$\Big\{\sum_\nu c_{x\nu}^i \, q_\nu^j\Big\}^2 .$$

The probability constant is in this case

$$\Big[\sum_j \Big\{\sum_\nu c_{x\nu}^i \, q_\nu^j\Big\}^2\Big]^{-1} = \Big\{\sum_\nu c_{x\nu}^{i\;2}\Big\}^{-1} = (3\,P_x^i)^{-1}$$

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

Hence if crossing occurs between ψ_{T}^i and ψ_{S} there is a probability

$$\frac{1}{3\,P_x^i}\Big\{\sum_\nu c_{x\nu}^i \, q_\nu^j\Big\}^2 \tag{11}$$

that this is a crossing to a particular nuclear substate ψ_{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

$$-\,2\,c_{xy}^i\,c_{xx}^i/3\,P_x^i . \tag{12}$$

This quantity gives the average value of $\langle I_z\rangle$ for molecules in a singlet electronic state to which a triplet ψ_{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

$$\varDelta_x^i = -\,\langle I_z\rangle^i - 2\,c_{xy}^i\,c_{xx}^i/3\,P_x^i . \tag{13a}$$

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

$$\varDelta_\mu^i = -\,\langle I_z\rangle^i - 2\,c_{\mu y}^i\,c_{\mu x}^i/3\,P_x^i . \tag{13b}$$

in which μ 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

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

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 $\varDelta_x^i$ 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 $D = 2.8\cdot 10^9\ \mathrm{sec}^{-1}$, $E = 2.8\cdot 10^8\ \mathrm{sec}^{-1}$, $A_{xx} = -3\cdot 10^6\ \mathrm{sec}^{-1}$, $A_{yy} = -9\cdot 10^6\ \mathrm{sec}^{-1}$, and $A_{zz} = -6\cdot 10^6\ \mathrm{sec}^{-1}$. The states in Table 3 are given in the order of decreasing energy.

Table 3.

$\langle I_z\rangle^i$	p_x^i	$\varDelta_x^i$	
− 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[3], 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 $\bar{I}\bar{\bar{A}}\bar{S}$ 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 ψ_{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 magntide 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 $D_{2\mathrm{h}}$. 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:

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

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

[There are no second order terms in the correction terms in (A1) and (A2).] For $A_{zz} = -6 \cdot 10^6$ sec^{-1} and $E = -9 \cdot 10^7$ 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 ~ 0.33. Even if $V_{\mathrm{SL},y} = \langle \varphi_{\mathrm{S}} S | V_{\mathrm{SL}} | \varphi_{\mathrm{T}} T_y \rangle = 0$ the state described by (A2) may have a non-zero probability to get occupied when

$$V_{\mathrm{SL},x} = \langle \varphi_{\mathrm{S}} S | V_{\mathrm{SL}} | \varphi_{\mathrm{T}} T_x \rangle \neq 0 .$$

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) [8, 9].

It should be emphasized that the actually measured P_u can be different from the f_μ, the population probabilities for the T_μ(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_μ(e) T_ν(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_μ(e) components.

One of us (J.P.C.) wants to thank the Max Planck Institut in Heidelberg for its hospitality during the summer months of 1971 and the National Research Council of Canada for a research grant. We also want to thank ELIZABETH COLBOURN for her very valuable assistance with the computer calculations.