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A Mechanism for the Optical Nuclear Spin Alignment in Zero Magnetic Field

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The Optical Nuclear Polarization (ONP) in molecular crystals is a consequence of the selective population and depopulation of the electronic magnetic sublevels of optically excited triplet states due to symmetry selection rules for the mixing of electronic states by spin orbit coupling. Two ONP-mechanisms have been proposed on this basis: The "relaxation"-mechanism, analogous to the Overhauser-effect, treats the optically produced distribution over the electronic magnetic sublevels as a steady state polarization which is transferred partially to the nuclear spin states via suitable hyperfine relaxation. The "crossing polarization"-mechanism takes into account in addition the mixing of states due to the hyperfine interaction in the electronic intersystem crossing processes. In this paper the latter mechanism is extended to a complete description of the dynamics of population and depopulation of the electronic and nuclear spin levels by including also all relaxation processes among the magnetic sublevels. It is shown that only in the extended form the mechanism can account for the experimentally observed optical nuclear spin alignment in zero external field.

I. Introduction

In 1967 it was discovered[1] that nuclei in molecular crystals can be polarized by light irradiation due to the hyperfine coupling of the nuclei to optically excited triplet states. The phenomenon was termed Optical Nuclear Polarization (ONP). In a number of pure and doped crystals the ONP was studied as a function of the applied field, its orientation with respect to the crystalline axes, the intensity and wave-length of the exciting light and the type and concentration of the guest molecules, mostly at room temperature[2, 3], with a few preliminary results at liquid nitrogen[4a] and helium temperature[4b]. The explanation of the ONP starts with the assumption that the nuclear polarization is a consequence of the polarization (alignment) of the triplet electron spins (OEP) which originates from symmetry selection rules for the singlet-triplet intersystem crossing by spin orbit coupling[5, 6].

In a first mechanism[3] proposed for the ONP, the OEP is treated as a steady state polarization which can be transferred partly to the nuclei via hyperfine relaxation analogous to the Overhauser effect[7]. In a second mechanism[8] it was shown that a selective population of nuclear substates results from the selective electronic singlet-triplet crossing (not involving the nuclear spins) due to the mixing of pure electronic and nuclear spin states by the hyperfine coupling. It was demonstrated that these "crossing polarizations" depend strongly on both the strength and the orientation of the applied field (during the polarization) and that the same order of magnitude can be calculated as observed in the experiments.

In this paper we want to present an extension of this "crossing polarization" mechanism by taking into account the relaxation transitions introduced by the hyperfine coupling. It will be shown that only such an extended mechanism is able to account for the nuclear spin alignment in zero field which was observed experimentally[3], while neither the Overhausertype mechanism as a first order perturbation theory nor the simple crossing polarization mechanism as presented in Ref. [8] can produce any nuclear spin alignment.

This is the reason why the presentation in this paper will be made for the case of zero external field, although the mechanism can be extended for all field values. Again as in Ref. [8], the treatment will be restricted to the model of a triplet electronic two proton spin system. As a starting point we describe briefly the experimental findings.

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II. The Optical Nuclear Spin Alignment (ONP in Zero External Field)

If a molecular crystal is irradiated with suitable light in zero field, a non thermal equilibrium distribution is generated on the nuclear substates which persists after the light is turned off provided the nuclear spin relaxation is slow. This zero field alignment is conveniently measured by turning on adiabatically a magnetic field up to a suitable measuring field H_m. The zero field alignment is then transferred to a non thermal distribution over the Zeeman-levels in H_m. The resulting polarization can be observed by a suitable NMR-technique[3].

By this method an inverted nuclear polarization was observed for the protons in doped fluorene crystals and also a negative but weaker one in anthracene crystals doped with phenazine[3]. Furthermore the quantum efficiency of the nuclear polarization was measured. If one compares the number of protons polarized per sec with the number of light quanta absorbed in the singlet state per sec one gets a quantum efficiency for the zero field ONP of the order of 10^{-4}, i.e. 10^4 quanta must be absorbed in the singlet state to polarize one proton per sec[9]. With an intersystem crossing quantum efficiency of 10% one needs about 10^3 generated triplet states to polarize one proton.

The relation between the measured high field polarization and the alignment in zero field can be best explained for a simple spin system. We consider two proton spins coupled by a dipole interaction

$$H_\mathrm{D} = \frac{\gamma^2\hbar^2}{r_{12}^3}\left\{(\boldsymbol{I}_1\cdot\boldsymbol{I}_2) + 3\,\frac{(\boldsymbol{I}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{I}_2\cdot\boldsymbol{r}_{12})}{r_{12}^2}\right\} \qquad (1)$$

where $\boldsymbol{r}_{12}$ is the space vector connecting the two spins I_1 and I_2 having the same gyromagnetic ratio γ. If we choose the coordinate system in such a way that $\boldsymbol{r}_{12}$ is parallel to the z axis and introduce the total spin $I = I_1 + I_2$ we get

$$H_\mathrm{D} = (b/2)(I^2 - 3\,I_z^2) \quad \text{with} \quad b = \gamma^2\hbar^2/r_{12}^3. \qquad (2)$$

This Hamiltonian has the eigenvalues b and the doubly degenerate level with energy $-b/2$ with the eigenfunction $T_z = 2^{-1/2}(\alpha\beta + \beta\alpha)$ and $(\alpha\alpha)$, $(\beta\beta)$ or linear combinations of the latter ones, e.g.

$$T_x = 2^{-1/2}(\beta\beta - \alpha\alpha)$$

and

$$T_y = 2^{-1/2}\,i\,(\beta\beta + \alpha\alpha),$$

which give a complete set of basis functions.

If a magnetic field is turned on adiabatically, then except for exactly $H_0 \parallel z$ there will be no crossing of levels. The z-level will go to the highest Zeeman-level $(\alpha\alpha)$, similarly the x and y level will go to energetically lower Zeeman-levels $(\beta\beta)$ and

$$2^{-1/2}(\alpha\beta + \beta\alpha).$$

An inverted high field polarization then corresponds to an overpopulation of the z-level in zero field with respect to the x and y level.

It is important to notice that the measured polarization does not depend on the orientation of the measuring field with respect to the crystal axis, because generally in multispin systems the anticrossing situation holds. However, it becomes clear, that a straight forward relation between the sign of the measured polarization and the distribution over the zero field levels related to it, requires some knowledge about the energy distribution of the nuclear zero field levels, which gets increasingly more difficult to work out for a many spin system.

III. The Zero Field Electron Spin Proton Spin Wave Functions with Hyperfine Coupling in Second Order

As in our previous paper[8], we consider a model with two electrons in the triplet state and two protons. We take as the spin hamiltonian

$$H = D(S_z^2 - \tfrac{1}{3}S^2) + E(S_x^2 - S_y^2) + \boldsymbol{S}\cdot\hat{A}\cdot\boldsymbol{I}. \qquad (3)$$

We have assumed that the two protons are in equivalent positions and have the same hyperfine tensor, so that

$$\boldsymbol{S}\cdot\hat{A}_1\cdot\boldsymbol{I}_1 + \boldsymbol{S}\cdot\hat{A}_2\cdot\boldsymbol{I}_2 = \boldsymbol{S}\cdot\hat{A}\cdot\boldsymbol{I}.$$

Moreover we assume that the principle axis systems of the fine structure tensor and the hyperfine tensor coincide. Situations like this occur for the 9 and 10 protons of anthracene and for the CH_2 protons in fluorene. We neglect the proton dipolar coupling term when considering protons in a molecule in the triplet state, because the effect of the interaction between the nuclei and the electrons via the hyperfine interaction is orders of magnitude larger than that of the dipolar coupling between the nuclei[10]. We take as the 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 $T_x = 2^{-1/2}(\beta\beta - \alpha\alpha)$; $T_y = 2^{-1/2}i(\beta\beta + \alpha\alpha)$

Table 1

$$
\begin{aligned}
\psi_{\mathrm{T}}^{1} &= \left\{1-\frac{1}{2}\frac{A_{yy}^{2}}{(D-E)^{2}}-\frac{1}{2}\frac{A_{zz}^{2}}{4E^{2}}\right\}|x\,x\rangle+\left\{\frac{-A_{yy}}{D-E}+\frac{A_{xx}A_{zz}}{(D-E)(-2E)}\right\}|z\,z\rangle+\left\{\frac{A_{zz}}{2E}+\frac{A_{xx}A_{yy}}{(-2E)(D-E)}\right\}|y\,y\rangle\\
\psi_{\mathrm{T}}^{2} &= \left\{1-\frac{1}{2}\frac{A_{zz}^{2}}{4E^{2}}\right\}|x\,y\rangle-\left\{\frac{A_{zz}}{2E}\right\}|y\,x\rangle\\
\psi_{\mathrm{T}}^{3} &= \left\{1-\frac{1}{2}\frac{A_{yy}^{2}}{(D-E)^{2}}\right\}|x\,z\rangle+\left\{\frac{A_{yy}}{D-E}\right\}|z\,x\rangle
\end{aligned}
$$

$$
\begin{aligned}
\psi_{\mathrm{T}}^{4} &= \left\{1-\frac{1}{2}\frac{A_{zz}^{2}}{4E^{2}}\right\}|y\,z\rangle+\left\{\frac{A_{zz}}{2E}\right\}|x\,y\rangle\\
\psi_{\mathrm{T}}^{5} &= \left\{1-\frac{1}{2}\frac{A_{xx}^{2}}{(D+E)^{2}}-\frac{1}{2}\frac{A_{zz}^{2}}{4E^{2}}\right\}|y\,y\rangle+\left\{\frac{-A_{xx}}{D+E}+\frac{A_{yy}A_{zz}}{(D+E)(2E)}\right\}|z\,z\rangle+\left\{\frac{-A_{zz}}{2E}+\frac{A_{xx}A_{yy}}{(2E)(D+E)}\right\}|x\,x\rangle\\
\psi_{\mathrm{T}}^{6} &= \left\{1-\frac{1}{2}\frac{A_{xx}^{2}}{(D+E)^{2}}\right\}|y\,z\rangle+\left\{\frac{A_{xx}}{D+E}\right\}|z\,y\rangle
\end{aligned}
$$

$$
\begin{aligned}
\psi_{\mathrm{T}}^{7} &= \left\{1-\frac{1}{2}\frac{A_{yy}^{2}}{(D-E)^{2}}\right\}|z\,x\rangle-\left\{\frac{A_{yy}}{D-E}\right\}|x\,z\rangle\\
\psi_{\mathrm{T}}^{8} &= \left\{1-\frac{1}{2}\frac{A_{xx}^{2}}{(D+E)^{2}}\right\}|z\,y\rangle-\left\{\frac{A_{xx}}{D+E}\right\}|y\,z\rangle\\
\psi_{\mathrm{T}}^{9} &= \left\{1-\frac{1}{2}\frac{A_{xx}^{2}}{(D+E)^{2}}-\frac{1}{2}\frac{A_{yy}^{2}}{(D-E)^{2}}\right\}|z\,z\rangle+\left\{\frac{A_{xx}}{(D+E)}+\frac{A_{yy}A_{zz}}{(D+E)(D-E)}\right\}|y\,y\rangle+\left\{\frac{A_{yy}}{D-E}+\frac{A_{zz}A_{xx}}{(D+E)(D-E)}\right\}|x\,x\rangle
\end{aligned}
$$

and $T_z = 2^{-1/2}(\alpha\beta + \beta\alpha)$. We leave the singlet proton spin wavefunction out of consideration for reasons discussed in a previous paper[8]. The electron spin proton spin part of the wave function for the triplet state i can be expressed as

$$\psi_{\mathrm{T}}^{\mathrm{i}} = \sum_{\mu,\nu} c_{\mu\nu}^{\mathrm{i}}\, T_{\mu}(e)\, T_{\nu}(n)\,. \tag{4}$$

The index i indicates the various magnetic substates of the electronic triplet state. The coefficients $c_{\mu\nu}^{\mathrm{i}}$ have been calculated by second order perturbation theory, the resulting wave functions are summarized in Table 1. As one sees from the table, neither of the states is a "pure" $T_x(e)$, $T_y(e)$ or $T_z(e)$ state. The numbering of the state is chosen such that the first three states are almost pure $T_x(e)$, the next three almost pure $T_y(e)$ and the last three almost pure $T_z(e)$. As a shorthand notation we have introduced $T_{\mu}(e)\,T_{\nu}(n) = |\mu\,\nu\rangle$.

IV. The Probabilities for the Population of the Magnetic Substates

1. *The selectiveness of the intersystem crossing*

Although we neglected the nuclear spin dipolar coupling between the protons in an electronic triplet state, we have to consider this coupling however for protons in an electronic singlet state system. In accordance with the symmetry we have chosen for our model system in Sect. III, we have to assume now that also the principle axis system of the internuclear coupling tensor coincides with the x, y und z axis. This means that the nuclear spin wave functions are simply the functions $T_x(n)$, $T_y(n)$ and $T_z(n)$. (The singlet function may be left out of consideration again.) The total wave function for a system in the electronic singlet state may now be written as $\varphi_{\mathrm{S}} S(e)\, T_{\nu}(n)$, in which φ_{S} and $S(e)$ are the space and spin part respectively of the electron wave function and in which ν may be either x, y or z. Normally one has a Boltzmann distribution over these states, at room temperature however the energy differences between the states are so small compared with kT, that we may assume that in a crystal the three states occur with equal probability before a crystal is subjected to an ONP experiment.

We assume the same mechanism for singlet triplet crossing as outlined in [8], hence we have a spin orbit coupling type of operator V_{SL}, which causes the intersystem crossing. The matrix element of V_{SL} between an electronic singlet and triplet is

$$
\begin{aligned}
&\langle \varphi_{\mathrm{S}}\, S(e)\, T_{\nu}{}'(n)\,|\,V_{\mathrm{SL}}\,|\,\varphi_{\mathrm{T}} \sum_{\mu,\nu} c_{\mu\nu}^{\mathrm{i}}\, T_{\mu}(e)\, T_{\nu}(n)\rangle\\
&\quad= \sum_{\mu} c_{\mu\nu}^{\mathrm{i}} \langle \varphi_{\mathrm{S}}\, S(e)\,|\,V_{\mathrm{SL}}\,|\,\varphi_{\mathrm{T}}\, T_{\mu}(e)\rangle \qquad (5)\\
&\quad= \sum_{\mu} c_{\mu\nu}^{\mathrm{i}} \cdot V_{\mathrm{SL},\,\mu}
\end{aligned}
$$

in which φ_{T} is the space part of the electronic wave function and

$$V_{\mathrm{SL},\mu} = \langle \varphi_{\mathrm{S}}\, S(e) \,|\, V_{\mathrm{SL}} \,|\, \varphi_{\mathrm{T}}\, T_\mu(e) \rangle .$$

As in [8] we consider first the case that only one of the elements $V_{\mathrm{SL},\mu}$, e.g., $V_{\mathrm{SL},x}$, is non zero and hence that only one of the triplet components, $T_x(e)$ in our example, is responsible for the crossing. The matrix element reduces then to $c^{\mathrm{i}}_{x\nu}\, V_{\mathrm{SL},x}$ and the probability of crossing from a singlet electronic state with nuclear spin state $T_\nu(n)$ to a triplet state $\psi^{\mathrm{i}}_{\mathrm{T}}$ is given by $|c^{\mathrm{i}}_{x\nu}|^2 \, |V_{\mathrm{SL},x}|^2$.

We introduce now the coefficient P_x, which gives the number of crossings per second from a singlet state to a triplet state in case the coefficient $|c^{\mathrm{i}}_{x\nu}|^2 = 1$. This coefficient P_x is proportional to $|V_{\mathrm{SL},x}|^2$ and depends among other things on the intensity of the exciting light; P_x does not depend however on the nuclear states involved. The number of crossings per second from a singlet state with nuclear function $T_\nu(n)$ to a triplet substate $\psi^{\mathrm{i}}_{\mathrm{T}}$ becomes now $|c^{\mathrm{i}}_{x\nu}|^2 P_x$ in case the $T_x(e)$ component causes the crossing. We introduce similarly a decay rate k_x which per second and per unit of concentration describes the probability for decay from a triplet state to the singlet ground state in case the $T_x(e)$ component of the triplet causes the transition with the coefficient $c^{\mathrm{i}}_{x\nu} = 1$. The decay rate constant for decay from a state $\psi^{\mathrm{i}}_{\mathrm{T}}$ to a singlet ground state with nuclear function $T_\nu(n)$ is then given by $k_x |c_{x\nu}|^2$.

In case $T_y(e)$ or $T_z(e)$ cause the crossing, one introduces quantities P_y, P_z, k_y and k_z. The generalization for the case that more than one component $T_\mu(e)$ causes the transitions is analogous to a similar generalization treated in full in Ref. [8] and we refer the reader to the relevant part of that paper.

Once the table P_μ or k_μ are known, one easily calculates the rates of population and depopulation for the various sublevels by multiplying with the coefficient $|c^{\mathrm{i}}_{\mu\nu}|^2$. These coefficients can be obtained for our model from the wave functions of Table 1. We summarize the results, correct in second order. in Table 2. In the first column the triplet substate is indicated to which or from which the crossing occurs. In the second column we summarize the coefficients $|c_{x\nu}|^2$ which are relevant when the $T_x(e)$ component causes the crossing. In the third and fourth column the coefficient $|c_{y\nu}|^2$ and $|c_{z\nu}|^2$ are summarized, they refer to the cases in which the $T_y(e)$ and the $T_z(e)$ component respectively is causing the transition. We have indicated also by $T_\nu(n)$ in each column, from which or to which nuclear function, combined with an electronic singlet state, crossing may occur to or from the particular triplet substate, respectively. In Table 2 we introduced the following abbreviations:

$$x = A_{xx}/(D+E)\,; \quad y = A_{yy}/(D-E)\,; \quad z = A_{zz}/2E\,. \tag{6}$$

One conclusion may be drawn immediately from Table 2. The probabilities for crossing from a $T_x(n)$ or $T_y(n)$ or $T_z(n)$ singlet electronic state to a triplet state add up to 1 in each column of Table 2 for each of the three nuclear spin components; hence, the singlet triplet transition does not change the distribution over the nuclear spin levels when we start with equal probabilities for each of the three nuclear states (high temperature approximation). One gets a similar result for the decay when one assumes an infinitely fast relaxation over the

Table 2

	$T_\nu(n)$	$\lvert c_{x\nu}\rvert^2$	$T_\nu(n)$	$\lvert c_{y\nu}\rvert^2$	$T_\nu(n)$	$\lvert c_{z\nu}\rvert^2$
ψ^1_{T}	$T_x(n)$	$1-y^2-z^2$	$T_y(n)$	z^2	$T_z(n)$	y^2
ψ^2_{T}	$T_y(n)$	$1-z^2$	$T_x(n)$	z^2	—	—
ψ^3_{T}	$T_z(n)$	$1-y^2$	—	—	$T_x(n)$	y^2
ψ^4_{T}	$T_y(n)$	z^2	$T_x(n)$	$1-z^2$	—	—
ψ^5_{T}	$T_x(n)$	z^2	$T_y(n)$	$1-x^2-z^2$	$T_z(n)$	x^2
ψ^6_{T}	—	—	$T_z(n)$	$1-x^2$	$T_y(n)$	x^2
ψ^7_{T}	$T_z(n)$	y^2	—	—	$T_x(n)$	$1-y^2$
ψ^8_{T}	—	—	$T_z(n)$	x^2	$T_y(n)$	$1-x^2$
ψ^9_{T}	$T_x(n)$	y^2	$T_y(n)$	x^2	$T_z(n)$	$1-x^2-y^2$

nine triplet substates so that they have permanently an equal occupation. The sum of the relative decay rates to $T_x(n)$, $T_y(n)$ and $T_z(n)$ adds up to 1 in all cases in each column of Table 2 and hence no inequality of the occupation of these levels can be achieved when the relaxation is infinitely fast and the high temperature approximation applies. When one takes into account the Boltzmann distribution over the triplet electronic levels there is no exact can celling any more; the resulting polarization after decay however, would be smaller by the Boltzmann factor corresponding to the electronic energy differences compared to those obtained in the following model (see Sect. V).

It has been shown[8] that a similar addition in case of neglect of relaxation or in case of very fast relaxation does create a polarization when the applied magnetic field is non zero. In the presence of a magnetic field the relevant quantity is not the occupation of the components $T_\nu(n)$ which would again add up to the same number for all nuclear spin states but the occupation multiplied with the $\langle I_z \rangle$ for each state. The sum over these products could lead to a final polarization. In zero field however $\langle I_z \rangle = 0$ for all states and it is only the occupation that counts.

2. *Relaxation by static hyperfine interaction in a solid due to electron relaxation*

In zero external field the electron and nuclear dipole interaction in a 2 electron, 2 proton spin system determines 9 states characterized by the product functions $T_\mu(e)\,T_\nu(n) = |\mu\nu\rangle$.

The pure electron relaxation, due to time modulation of the zero field splitting, of the spin orbit coupling or other mechanisms causes transitions of the kind

$$T_\mu(e)\,T_\nu(n) \leftrightarrow T_\mu{}'(e)\,T_\nu(n)$$

with no change in the nuclear spin orientation and an electron relaxation rate $W^{\mathrm{e}}_{\mu\mu'}$, ($\mu \neq \mu'$; μ, $\mu' = x$, y or z).

Due to the hyperfine coupling, the functions $|\mu\nu\rangle$ do not describe pure states, we have to take linear combinations instead; the new functions, correct in second order, were presented in Table 1. As a consequence of this combining of functions the pure electronic relaxation $W^{\mathrm{e}}_{\mu\mu'}$, can introduce transitions $\psi^{\mathrm{i}}_{\mathrm{T}} \leftrightarrow \psi^{\mathrm{j}}_{\mathrm{T}}$ of such a kind, that the dominating components in these states can have different nuclear spin orientations. We calculated the resulting relaxation rates between the states 1 to 9 with the wave functions of Table 1.

Table 3 collects the induced relaxation rates. Furthermore the mixing reduces the probabilities of the predominantly electronic transitions relative to the pure transition probabilities $W^{\mathrm{e}}_{\mu\mu'}$, the results are collected in Table 4.

Other transitions are possible, if the hyperfine coupling is taken time dependent due to electron spin relaxation. In this case the fluctuating hyperfine field seen by the nuclei produces relaxation transitions with a change in nuclear spin orientation[11]. This mechanism would cause transitions, for instance for the upper states

$$\psi^1_{\mathrm{T}} \leftrightarrow \psi^5_{\mathrm{T}} \quad \text{and} \quad \psi^2_{\mathrm{T}} \leftrightarrow \psi^4_{\mathrm{T}}$$

but not: $\psi^3_{\mathrm{T}} \leftrightarrow \psi^6_{\mathrm{T}}$.

Table 3

transition	rate	transition	rate	transition	rate
$\psi^1_{\mathrm{T}} \leftrightarrow \psi^6_{\mathrm{T}}$	$y^2\,W^{\mathrm{e}}_{yz}$	$\psi^1_{\mathrm{T}} \leftrightarrow \psi^8_{\mathrm{T}}$	$z^2\,W^{\mathrm{e}}_{yz}$	$\psi^4_{\mathrm{T}} \leftrightarrow \psi^8_{\mathrm{T}}$	$z^2\,W^{\mathrm{e}}_{xz}$
$\psi^2_{\mathrm{T}} \leftrightarrow \psi^6_{\mathrm{T}}$	$x^2\,W^{\mathrm{e}}_{xz}$	$\psi^2_{\mathrm{T}} \leftrightarrow \psi^7_{\mathrm{T}}$	$z^2\,W^{\mathrm{e}}_{yz}$	$\psi^4_{\mathrm{T}} \leftrightarrow \psi^9_{\mathrm{T}}$	$y^2\,W^{\mathrm{e}}_{xy}$
$\psi^3_{\mathrm{T}} \leftrightarrow \psi^4_{\mathrm{T}}$	$y^2\,W^{\mathrm{e}}_{yz}$	$\psi^3_{\mathrm{T}} \leftrightarrow \psi^8_{\mathrm{T}}$	$x^2\,W^{\mathrm{e}}_{xy}$	$\psi^5_{\mathrm{T}} \leftrightarrow \psi^7_{\mathrm{T}}$	$z^2\,W^{\mathrm{e}}_{xz}$
$\psi^3_{\mathrm{T}} \leftrightarrow \psi^5_{\mathrm{T}}$	$x^2\,W^{\mathrm{e}}_{xz}$	$\psi^2_{\mathrm{T}} \leftrightarrow \psi^9_{\mathrm{T}}$	$x^2\,W^{\mathrm{e}}_{xy}$	$\psi^6_{\mathrm{T}} \leftrightarrow \psi^7_{\mathrm{T}}$	$y^2\,W^{\mathrm{e}}_{xy}$

Table 4

transition	rate	transition	rate	transition	rate
$\psi^1_{\mathrm{T}} \leftrightarrow \psi^4_{\mathrm{T}}$	$(1-y^2)\,W^{\mathrm{e}}_{xy}$	$\psi^1_{\mathrm{T}} \leftrightarrow \psi^7_{\mathrm{T}}$	$(1-z^2)\,W^{\mathrm{e}}_{xz}$	$\psi^4_{\mathrm{T}} \leftrightarrow \psi^7_{\mathrm{T}}$	$(1-y^2-z^2)\,W^{\mathrm{e}}_{yz}$
$\psi^2_{\mathrm{T}} \leftrightarrow \psi^5_{\mathrm{T}}$	$(1-x^2)\,W^{\mathrm{e}}_{xy}$	$\psi^2_{\mathrm{T}} \leftrightarrow \psi^8_{\mathrm{T}}$	$(1-x^2-z^2)\,W^{\mathrm{e}}_{xz}$	$\psi^5_{\mathrm{T}} \leftrightarrow \psi^8_{\mathrm{T}}$	$(1-z^2)\,W^{\mathrm{e}}_{yz}$
$\psi^3_{\mathrm{T}} \leftrightarrow \psi^6_{\mathrm{T}}$	$(1-x^2-y^2)\,W^{\mathrm{e}}_{xy}$	$\psi^3_{\mathrm{T}} \leftrightarrow \psi^9_{\mathrm{T}}$	$(1-x^2)\,W^{\mathrm{e}}_{xz}$	$\psi^6_{\mathrm{T}} \leftrightarrow \psi^9_{\mathrm{T}}$	$(1-y^2)\,W^{\mathrm{e}}_{yz}$

They are proportional to the hyperfine matrix elements squared and to a spectral density function, whose high frequency cut-off is given by the electron spin relaxation rate. Since the electron zero field splittings correspond to 2×10^8 to 4×10^9 Hz, the relaxation rates are only effective if the electron relaxation time $T_S \lesssim 10^{-9}$—10^{-10} sec; for triplet states in aromatic molecules, however, the relaxation time was found[12] not shorter than 10^{-8} sec, therefore only small contributions by this mechanism are expected.

V. A Model for Optical Nuclear Polarization at Zero Field

We outline first how one has to proceed with our 9 level model in order to find whether the ONP experiments produce an unequal occupation of the nuclear spin states in the ground state molecules.

For each of the nine levels one gets a rate equation of the type

$$\mathrm{d}N_i/\mathrm{d}t = P_i - k_i N_i - \sum_{j \neq i} R_{ij}(N_i - N_j); \quad i, j = 1, \ldots, 9 \tag{7}$$

in which N_i is the number of excited molecules in substate i; P_i gives the rate of population through singlet-triplet crossing; k_i is the decay rate constant; R_{ij} is the relaxation rate constant for relaxation from level i to j. We have assumed here relaxation to equal distribution neglecting the Boltzmann equilibrium for simplicity.

When the crossing to the triplet state is due to the $T_x(e)$ component only, we get according to Sect. IV.1 and Table 2 certain relations between the P_i's such as $P_1 = P_x(1 - y^2 - z^2)$, $P_2 = P_x(1 - z^2)$, $P_3 = P_x(1 - y^2)$, $P_4 = P_5 = P_x z^2$, $P_6 = 0$ etc., where we assume that at the beginning of the ONP experiment all nuclear spin states have equal probability to occur. When the decay is caused by the $T_y(e)$ component of the triplet we get from Table 2 for the k_i's: $k_1 = k_2 = k_y z^2$, $k_3 = 0$, $k_4 = k_y(1 - z^2)$ etc. In the case of doped crystals the molecules to which the singlet triplet crossing takes place and the molecules from which the triplet singlet decay takes place can be of a different kind. If this is the case the coefficient x^2, y^2 and z^2 connected with the coefficient P_x are different from the coefficients x^2, y^2 and z^2 connected with the decay rate k_y, and the former ones will be denoted by x'^2, y'^2 and z'^2. Certain relations between the relaxation rate constants have been mentioned already in Section 4.2: the static hyperfine interaction reduces somewhat the "pure" electronic relaxation between level 1 and 4 or 2 and 5 etc., on the other hand it introduces relaxation between the levels 1 and 6, 2 and 5 etc., as summarized in the Tables 3 and 4. As the experiments are done under steady state conditions, we have to solve the Eq. (7) taking $\mathrm{d}N_i/\mathrm{d}t = 0$ for all i; this gives us the N_i values with which we calculate the quantities $k_i N_i$ which gives us the rate of decay to a ground state molecule with a particular nuclear spin function. In our example in which $T_y(e)$ causes the decay (see Table 2 second column) $k_2 N_2 + k_4 N_4$ gives the rate of production of $T_x(n)$ states; and similarly $k_1 N_1 + k_5 N_5 + k_9 N_9$ for $T_y(n)$ states and $k_6 N_6 + k_8 N_8$ for $T_z(n)$ states where $k_1 = k_2 = k_y z$ etc., as mentioned before. When these rates are different the ONP process produces an unequal distribution over the nuclear levels.

Although this 9 level system is by far too complicated to be solved analytically in a way to give overseeable results we can draw one more general conclusion from this system. We consider a case where all 9 levels have the same occupation in the steady state.

The equations reduce then to

$$0 = P_i - k_i N$$

in which $N = N_1 = N_2 = \cdots = N_9$.

We see that this condition is fulfilled only when P_i/k_i has the same value for all states i. According to Sect. 4.1 and Table 2, this is only the case when the crossing to and from the triplet state is caused by the same component $T_\mu(e)$ and when moreover the coefficients x^2, y^2 and z^2 are the same for the molecule to which the crossing takes place and from which the decay takes place.

The condition given above can be written as $k_i N_i = k_i N = P_i$ for all substates i. As discussed before, the P_i's are proportional to the coefficients in Table 2 and as the coefficients that describe the production of the same nuclear state add up to one for all three nuclear states, we expect that in this particular case the decay to the three nuclear states has the same rate and no polarization is produced.

When the ratio P_i/k_i is not a constant, one will get in general a different decay rate to the three nuclear states, producing in principle an unequal distribution over the nuclear spin levels and hence a zero field ONP. In order to get an estimate of the order of magnitude and the conditions under which a sizeable effect may occur without getting unmanageable formulas we reduce the 9 level model to a four level model, in which we keep, however, the essential features of the nine level model.

We proceed as follows: usually x^2 and y^2 are smaller than z^2 because $|E| < |D|$ and we neglect them compared with z^2 for population and decay. We consider a case where the population takes place via the $T_x(e)$ component of the triplet and the depopulation via the $T_y(e)$ component. When we neglect x^2 and y^2, we see from Table 2 that the levels 7, 8 and 9 are neither active in population nor in decay; moreover, the levels 1 and 2 get the same coefficients; so do the levels 4 and 5. Because of the equality of the coefficients for the levels 1 and 2, we assume that they are equally active in producing $T_y(n)$ and $T_x(n)$ nuclear states after decay; we make the same assumption for the levels 4 and 5. The level 6 however gives in decay only $T_z(n)$ states. What we consider in some detail is whether the rate of decay to the $T_z(n)$ state differs from the rate of decay to the $T_x(n)$ and $T_y(n)$ state (which we assume to be equal).

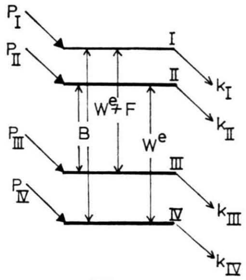

Fig. 1

We introduce a level I which behaves like an average of the levels 1 and 2, level II which is like 3; level III which represents the average of 4 and 5, and level IV which represents level 6. We introduce for the population the coefficients

$$P_{\mathrm{I}} = (1 - z^2)\, P_x; \qquad P_{\mathrm{II}} = P_x;$$
$$P_{\mathrm{III}} = z^2 P_x; \qquad P_{\mathrm{IV}} = 0 \quad \text{(see Table 2)};$$

hence

$$P_{\mathrm{I}} = P_{\mathrm{II}} - P_{\mathrm{III}} = P_x - P_{\mathrm{III}}.$$

We introduce further for the decay rate constants

$$k_{\mathrm{I}} = k_y z'^2; \qquad k_{\mathrm{II}} = 0;$$
$$k_{\mathrm{III}} = k_y (1 - z'^2); \qquad k_{\mathrm{IV}} = k_y$$

(z' is not necessarily equal to z).

In Sect. 4.2 we discussed already the relaxation constants, Table 3 gives together with the definitions of the levels I, II, III and IV the relaxation rate constant

$$B = R_{\mathrm{I\,IV}} = R_{\mathrm{II\,III}} = \tfrac{1}{2}(x^2 W^{\mathrm{e}}_{xz} + y^2 W^{\mathrm{e}}_{yz}).$$

We introduce further a quantity F defined by $F = R_{\mathrm{I\,III}} - R_{\mathrm{II\,IV}}$. From Table 4 we find $F = \tfrac{1}{2}(x^2 + y^2)\, W^{\mathrm{e}}_{xy}$.

For simplicity we assume that

$$W^{\mathrm{e}}_{xy} = W^{\mathrm{e}}_{xz} = W^{\mathrm{e}}_{yz} = W^{\mathrm{e}}.$$

This leads to

$$F = B = \tfrac{1}{2}(x^2 + y^2)\, W^{\mathrm{e}}.$$

From Table 4 we find also that

$$R_{\mathrm{I\,IV}} = (1 - x^2 - y^2)\, W^{\mathrm{e}}.$$

It appears that the magnitude of the ONP effect is sensitive to the difference $R_{\mathrm{I\,III}} - R_{\mathrm{II\,IV}}$, but rather insensitive to a minor change in the values of $R_{\mathrm{I\,III}}$ and $R_{\mathrm{II\,IV}}$ themselves. We therefore take $R_{\mathrm{II\,IV}} = W^{\mathrm{e}}$.

We introduce finally a quantity ΔT_z which gives the rate of production of spins in the $T_z(n)$ state in excess to the rate of average production of $T_x(n)$ and $T_y(n)$ spin states

$$\Delta T_z = k_{\mathrm{II}} N_{\mathrm{II}} + k_{\mathrm{IV}} N_{\mathrm{IV}} - k_{\mathrm{I}} N_{\mathrm{I}} - k_{\mathrm{III}} N_{\mathrm{III}}. \quad (8)$$

We solved the rate equations for levels I, II, III, and IV under steady state conditions and obtained expressions for N_{I}, N_{II}, N_{III} and N_{IV} with which we finally obtained an expression for ΔT_z. The calculation, which is elementary but rather laborious, to say the least, will not be reproduced here; only the result is given.

$$\frac{\Delta T_z}{P_x} = \frac{-B\,[2 B k_{\mathrm{I}} + 2 k_{\mathrm{I}} k_y + 2 F k_y + 6 k_{\mathrm{I}} W^{\mathrm{e}} + (P_{\mathrm{III}}/P_x)\,(2 B k_y + 2 W^{\mathrm{e}} k_y))]}{F[k_y (B + W^{\mathrm{e}}) + 2B\,(B + 2 W^{\mathrm{e}})] + k_y (W^{\mathrm{e}} + B)^2 + 4 B W^{\mathrm{e}} (B + W^{\mathrm{e}}) + k_{\mathrm{I}} k_y (B + W^{\mathrm{e}})}. \quad (9)$$

The quantity $\Delta T_z / P_x$ gives the excess rate of production of spin states in $T_z(n)$ per triplet state which was created and decayed again.

We rewrite this formula in a more convenient way and introduce a few simplifications. The relaxation rates F and B are both due to mixing of simple product states and to hyperfine interaction and are of the same order of magnitude. We assume

$$F = B = L W^{\mathrm{e}} .$$

We noticed already that $k_{\mathrm{I}} = z'^2 k_y$; $P_{\mathrm{III}} = z^2 P_x$; z' and z may but need not to be different. For the sake of simplicity we assume they are equal, for all practical cases they are certainly of the same order of magnitude. We make the following substitutions:

$$F = B = L W^{\mathrm{e}}, \qquad k_{\mathrm{I}} = m\, k_y, \qquad P_{\mathrm{III}} = m\, P_x$$

and $k_y / W^{\mathrm{e}} = q$.

Making the realistic assumption that $m \ll 1$, we find

$$\frac{\varDelta T_z}{P_x} = \frac{-2L(L+4m) - 2qLm}{(1+L)(1+2L) + [4L(1+2L+\frac{1}{2}L^2)]/q + qm(1+L)} , \tag{9A}$$

$$q m > 1 \qquad : \frac{\varDelta T_z}{P_x} = \frac{-2L}{1+L} , \tag{9B}$$

$$L \ll 1; m \ll 1 : \frac{\varDelta T_z}{P_x} = \frac{-2L(L+4m) - 2qLm}{1 + 4L/q + qm} , \tag{9C}$$

$$q \sim 1 \qquad : \frac{\varDelta T_z}{P_x} = \frac{-2L^2 - 10\,Lm}{1 + 7L + 10L^2 + 2L^3 + m(1+L)} , \tag{9D}$$

$$L = 1; m \ll 1 : \frac{\varDelta T_z}{P_x} = \frac{-2 - 2qm}{6 + 14/q + 2qm} , \tag{9E}$$

$$q \sim 10; L < 1 : \frac{\varDelta T_z}{P_x} = \frac{-2L^2 - 28\,Lm}{1 + qm} , \tag{9F}$$

$$q < L < 1 \qquad : \frac{\varDelta T_z}{P_x} = \frac{1}{2} q(L + 4m) . \tag{9G}$$

VI. Discussion

We discuss first the application of our model to the case of localized triplets, which was introduced already in Section 3 and 4. Characteristic here is that usually both $L \ll 1$ and $m \ll 1$. Both are of the order of magnitude of the square of the ratio of a hyperfine tensor element and a fine structure tensor element. In a favorable case like the fluorene triplet state with $2E = 1.8 \times 10^8$ Hz and a hyperfine coupling constant corresponding to a CH-fragment with a spin density of 0.3, i.e. $A_{zz} = 1.8 \times 10^7$ Hz, L and m reach the order of magnitude of 10^{-2}. In this case Eq. (9C) applies and for different values of q the corresponding $\varDelta T_z / P_x$ is given in Table 5.

Table 5

$L = m = 10^{-2}$ q	$\varDelta T_z / P_x$
10	-3×10^{-3}
1	-1.2×10^{-3}
0.1	-0.7×10^{-3}
0.01	-0.2×10^{-3}

For very small values of q, $q < L$, formula (9G) applies which becomes for our case

$$\varDelta T_z / P_x = -q \times 2{,}5 \times 10^{-2}$$

which for $q \ll L$ will lead to $\varDelta T_z / P_x \ll -10^{-4}$. We see from this that for q smaller than L, the polarization becomes proportional to q and gives only very small effects. If $q \gtrsim L$, however, the polarization is less sensitive for a change in the q values, when q changes from 0,1 to 10 the polarization increases approximately by a factor 4. We interpret this as follows: L describes the ratio of hyperfine versus electron relaxation, m that of the population and depopulation rates of the various levels; q gives the ratio between the decay rate and the rate of electronic relaxation. The minor differences in the relaxation rates and population rates are obviously the most important effect when the decay is fairly fast with respect to relaxation. only for $q \lesssim L$ the polarization is decreasing rapidly with decreasing q.

We consider next the case of non linear excitons. We employ here the so called "hopping" model for the excitons which seems appropriate for high temperatures[13], while at low temperature a band structure for the exciton excitation is the more proper description. In the case of the hopping model the triplet state is created and decays at a particular molecule whose hyperfine interaction determines the mixing coefficients in Table 1, hence the m is for hopping excitons of the same order of magnitude as for localized triplets. The electronic spin relaxation for non linear excitons was investigated experimentally for anthracene and naphthalene crystals[12]. It was found to be due to the modulation of the fine structure tensor by the exciton motion and is therefore proportional to the square of the fine structure tensor elements.

On the other hand the hyperfine contribution is proportional to the elements in the hyperfine coupling tensor. Therefore the result is of the same order of magnitude for L as in the case of the localized triplets. Hence we have as previously $L \sim m \sim 10^{-2}$. For q between 0,1 and 10 this leads again to values of $\Delta T_z/P_x$ of the order of magnitude of -10^{-3}. For excitons, however, there is a possibility of very high decay rates for which $q \sim 100$ or $qm \sim 1$ for instance if the exciton diffusion is limited by guest molecules as impurities or by high concentrations of triplet excitons providing fast decay by triplet triplet annihilation. Under these circumstances $\Delta T_z/P_x$ becomes of the order of $-L$ [see formulae (9B) and (9C)] which is -10^{-2}.

We finally mention the case of the linear excitons where the triplet excitation travels along translationally equivalent molecules. Here the fine structure is not time dependent any more due to the exciton motion and therefore no longer responsible for the relaxation, which in this case could be due entirely to the time modulation of the hyperfine tensor components. The W^e, F and B have then the same origin, will be of the same order of magnitude and we have to take $L \sim 1$. For the population by intersystem crossing and for decay the same remarks apply as made in this connection for the hopping exciton in the non linear case, hence we take again $m \sim 10^{-2}$. Our formula (9E) is now valid. For $q \sim 1$, this leads to $\Delta T_z/P_x \sim -10^{-1}$, for $q = 100$ one gets even a polarization $\Delta T_z/P_x \sim -\frac{1}{2}$. For very small values of q however ($q \leqq 10^{-2}$) formula (9E) reduces to $\Delta T_z/P_x \sim -\frac{1}{7}\,q$ so that for $q \sim 10^{-2}$ one finds $\Delta T_z/P_x \sim -10^{-3}$.

VII. Conclusion

The model of polarization by crossing and decay[8] that gives ONP for non zero magnetic field fails to give nuclear spin alignment in zero field. Also a treatment analogous to the Overhauser effect, where first order time dependent perturbation theory is applied to the time dependent part of the hyperfine tensor, gives a zero effect in zero field[3]. This paper shows that by introducing relaxation transitions due to the hyperfine interaction and extending the crossing and decay mechanism in this way, a non zero nuclear spin alignment may be obtained at zero field.

Experimentally it has been found that the quantum efficiency of the nuclear spin alignment process may be up to 10^{-4} spins per absorbed photon; which corresponds to an efficiency per created triplet state which may be as high as 10^{-3}.

As mentioned in the discussion, localized triplets may give an efficiency of 2×10^{-4} to 10^{-3} spins per created triplet state.

Excitons however may be more efficient, depending on the decay rate as compared with the relaxation rate, one finds 10^{-3} to 10^{-1} spins per created triplet state.

Our model is of course a simplified one and one has to be careful in drawing too many conclusions from it, it appears however that it is able to explain how the nuclear spin alignment in zero field can be obtained and it predicts the right order of magnitude for this effect.

Appendix I:
Comparison to the Relaxation-Mechanism

Since the mechanism of the Overhauser-effect is usually presented for a four level system, it seems to be appropriate to compare the treatment presented in this paper with the approximations used in the solution of the rate equations analogous to the Overhauser-mechanism[3].

The basic assumption is, that the hyperfine coupling has no influence on the intersystem crossing probabilities affecting each of the magnetic sublevels, i.e. for the four level model in Fig. 1. levels I and II as well as III and IV would have equal population and decay parameters ($P_{\text{I}} = P_{\text{II}}$ and $P_{\text{III}} = P_{\text{IV}}$ etc.). Such a case can be imagined if the effective hyperfine coupling is reduced due to a fast time modulation; then all static hyperfine admixtures could be averaged to a small value, but the hyperfine relaxation transitions among the four levels would be particularly effective. The final nuclear population difference is then given directly by that in the excited state, because it will not be changed during the decay process. The excess population of interest is given instead of ΔT_z in Eq. (8) by

$$p(n) = \{(N_{\text{II}} + N_{\text{IV}}) - (N_{\text{I}} + N_{\text{III}})\}/\sum_i N_i \quad \text{(A 1)}$$

and a similar quantity can be defined for the electronic spin states

$$p(e) = \{(N_{\text{I}} + N_{\text{II}}) - (N_{\text{III}} + N_{\text{IV}})\}/\sum_i N_i . \quad \text{(A 2)}$$

From the four level rate equations one gets easily the time behavior of $p(n)$

$$\mathrm{d}p(n)/\mathrm{d}t = -(\varrho + w^0)\, p(n) - \sigma\, p(e)\,. \tag{A 3}$$

Relaxation to the Boltzmann equilibrium is left out as before, otherwise the population differences used here have to be replaced by the difference to the Boltzmann equilibrium. Notation of the rates is chosen according to the usual Overhauser-theory[7]. In the notation of Fig. 1 they are

$$\varrho = R_{\mathrm{I\,IV}} + R_{\mathrm{II\,III}} + R_{\mathrm{I\,II}} + R_{\mathrm{III\,IV}}\,,$$
$$\sigma = R_{\mathrm{II\,III}} - R_{\mathrm{I\,IV}}\,.$$

w^0 is resulting from relaxation transitions I ↔ II and III ↔ IV involving other nuclear relaxation processes than the hyperfine coupling to the triplet electronic state.

The simplification of the problem due to the assumption made in the beginning is obvious from (A 3). It is then possible to obtain the electron population difference $p(e)$ from an independent, much simpler treatment of the rate equations of the pure electronic levels only, and the steady state nuclear $p(n)$ will be proportional to it:

$$p(n) = -\frac{\sigma}{\varrho + w^0}\, p(e)\,. \tag{A 4}$$

(A 4) can be extended easily to get the usual expression[7,3] used to describe the Overhauser polarization. In this mechanism no transfer of electronic polarization to the nuclei occurs for $\sigma = 0$, i.e. $R_{\mathrm{II\,III}} = R_{\mathrm{I\,IV}}$ which is predicted from Table 4 for the case of the static hyperfine interaction. Of course, this is the same argument due to which no nuclear polarization by Overhauser-effect is found in non-metalic solids[11]. Even if the hyperfine coupling causes relaxation transitions due to a fast time dependence, $R_{\mathrm{II\,III}}$ and $R_{\mathrm{I\,IV}}$ are expected to be equal for zero field as seen from the mixing coefficients in Table 1 which would occur in time dependent perturbation theory as well. Therefore no spin-alignment is expected in zero field in this case.

The main problem of the "relaxation"-mechanism is the strong initial assumption of an averaged hyperfine coupling which for instance does not apply to the important case of "localized" triplet excitons (hopping model), because the intersystem crossing process then occurs at a particular molecule with its characteristic hyperfine coupling, whose influence cannot be neglected for the intersystem crossing.

Nevertheless this mechanism can still be very valuable, if a magnetic field is applied. It gives an idea of the influence of the relaxation rates at a computationally much easier managable level and gets increasingly more important at higher fields when the mixing coefficients get small for the crossing polarizations but still contribute strongly to the electron polarization[3].

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