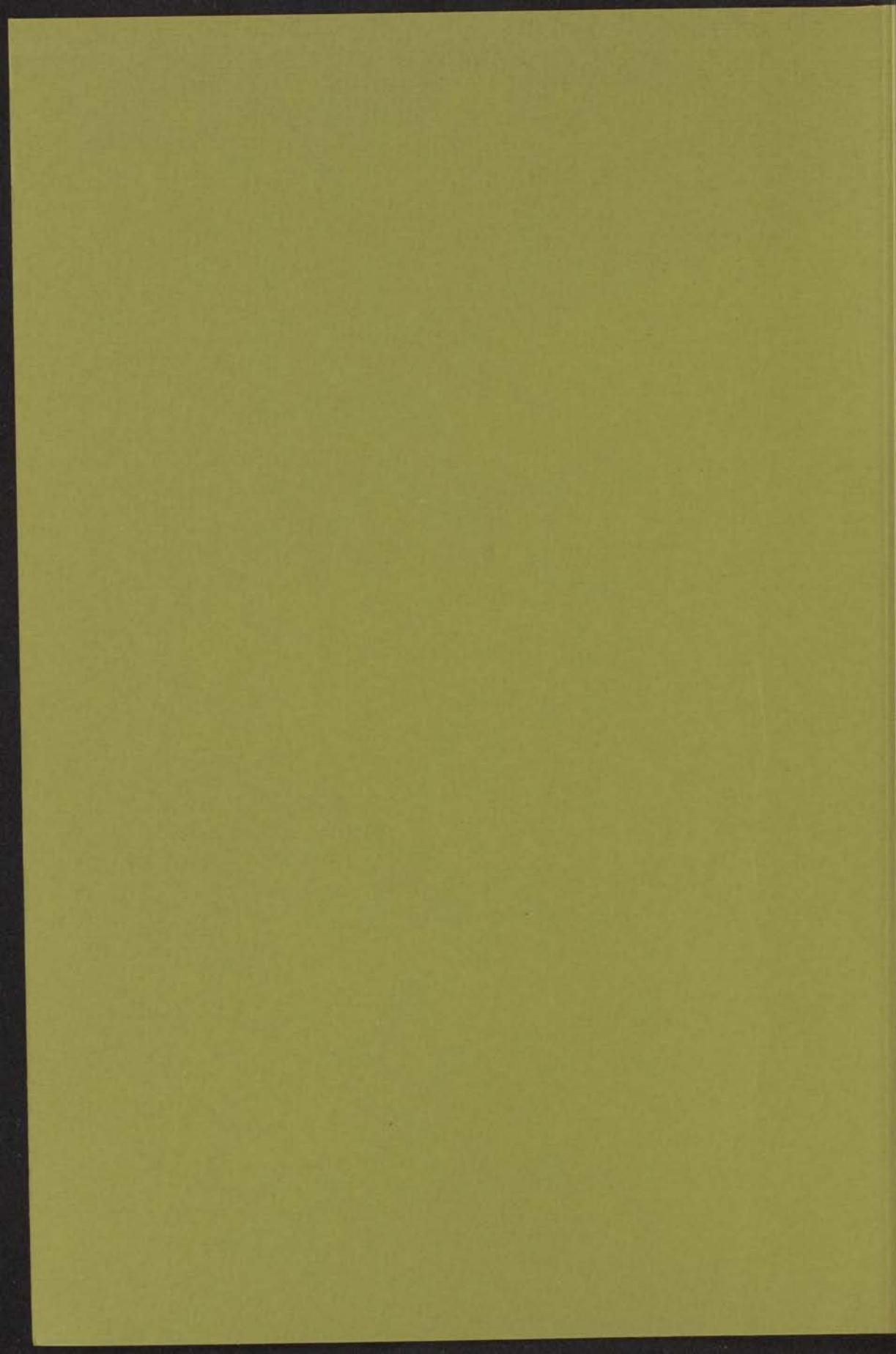


21 NOV. 1972

LEVEL ANTICROSSING AND CROSS-RELAXATION
IN PHOSPHORESCENT ORGANIC CRYSTALS

BERNOUT LORENTZ
voor theoretische natuurkunde
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W. S. VEEMAN



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PROEFSCHRIFT

ter verkrijging van de graad van Doctor in de Wetenschap en
Natuurwetenschappen aan de Rijksuniversiteit te Leiden,
op gezag van de Rector Magnificus Dr. A. E. Cohen,
Hoofdman in de Faculteit der Letteren, volgens besluit van
het college van Delen van de Universiteit op voordracht
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IN THE HISTORY OF THE UNITED STATES

1875

**LEVEL ANTICROSSING AND CROSS-RELAXATION
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het college van Dekanen te verdedigen op woensdag
29 november 1972 te klokke 16.15 uur

door

WIEBREN SJOERD VEEMAN
geboren te Marssum in 1942

*aan mijn ouders
van het Instituut voor Fysica*

PROMOTOR: PROF. DR. J. H. VAN DER WAALS

DE PHOSPHORESCENT ORGANIC CRYSTALS

PHOSPHORESCENT

de verhandeling van de hand van Doctor in de Wetenschappen
in de Faculteit der Letteren, en de Rijksuniversiteit te Leiden.
op verzoek van de Faculteit der Letteren, volgens besluit van
de Rector van de Universiteit der Letteren, volgens besluit van
de Rector van de Universiteit der Letteren, te Leiden, op
20 November 1913 te Leiden 1613

door

WILHELM SIEGHE VERMAN
geboren te Bremen in 1881

STREKINGEN

1. De invloed van verschillende factoren op de experimenteel beschreven in dit verslag en op andere belangrijke experimenten in het gebied van de fysica wordt beschreven door de auteur.

J. de Groot, Phys. Rev. 102 (1954) 331.

2. Misschien is het bekend dat de kwantumtheorie in de natuur van twee punten afhangt, namelijk van de constante van de gravitatie en van de constante van de elektrische lading. Het is algemeen bekend dat de waarde van de constante van de gravitatie niet kan worden gemeten, maar dat de waarde van de constante van de elektrische lading kan worden gemeten. Het is algemeen bekend dat de waarde van de constante van de elektrische lading kan worden gemeten.

R. G. L. Groot en J. de Groot, Nat. Phys. 11 (1954) 105.

3. De bepaling van het aantal deeltjes, die in een bepaalde tijd een bepaalde afstand afleggen, kan worden gedaan door de bepaling van de verandering van de elektrische lading van de deeltjes. Het is algemeen bekend dat de waarde van de constante van de elektrische lading kan worden gemeten.

J. de Groot, J. de Groot en J. de Groot, Phys. Lett. 10 (1954) 340.

4. In dit verslag wordt op een eenvoudige wijze de invloed van de constante van de elektrische lading op de waarde van de constante van de elektrische lading besproken. Het is algemeen bekend dat de waarde van de constante van de elektrische lading kan worden gemeten.

J. de Groot, Phys. Lett. 1 (1954) 370.

5. Het is algemeen bekend dat de waarde van de constante van de elektrische lading kan worden gemeten.

J. de Groot, Phys. Lett. 1 (1954) 370.

aan Iet, Sieward en Anke

J. de Groot, Phys. Lett. 1 (1954) 370.

FRONTIER PROF. DR. J. H. VAN DER WAALE

van der Waaie, J. H.

S T E L L I N G E N

1. Er bestaat een overeenkomst tussen de experimenten beschreven in dit proefschrift en spin-exchange experimenten in gassen zoals bijvoorbeeld beschreven door Dehmelt.

H.G. Dehmelt, Phys. Rev. 109 (1958) 381.

2. Bixon, Jortner en Dothan stellen dat quantumbeats in de emissie van twee coherent geëxciteerde, aangeslagen toestanden van gelijke symmetrie ook kunnen optreden in de emissie-intensiteit die geïntegreerd is over een bol rondom het aangeslagen molecuul. Dit is alleen juist in het geval dat de emissie van een foton niet de enige mogelijkheid tot deactivatie van deze aangeslagen toestanden is.

M. Bixon, J. Jortner en Y. Dothan, Mol. Phys. 17 (1969) 109.

3. In tegenstelling tot wat Nishimura, Tinti en Vincent beweren, zijn de relatieve stralingsloze vervalsnelheden van de drie componenten van de laagste triplettoestand van fosforescerende moleculen niet te meten met de "microwave induced delayed phosphorescence"-methode.

A.M. Nishimura, D.S. Tinti en J.S. Vincent,
Chem. Phys. Lett. 12 (1971) 360.

4. In artikelen over optisch gedetecteerde electronspin resonantie houdt men er te weinig rekening mee, dat het aantal aangeslagen moleculen drastisch kan veranderen, wanneer de veld sweep (of frequentie sweep) door een ESR lijn zich voltrekt in een tijd die niet veel korter is dan de levensduur van de twee betrokken niveaus.

A.L. Kwiram, Chem. Phys. Lett. 1 (1967) 272,

J. Schmidt, I.A.M. Hesselmann, M.S. de Groot en J.H. van der
J.H. van der Waals, Chem. Phys. Lett. 1 (1967) 434,

L.T. Cheng en A.L. Kwiram, Chem. Phys. Lett. 4 (1969) 457,

M. Sharnoff, Symp. Faraday Soc. 1969,

M.A. El-Sayed, D.V. Owens en D.S. Tinti,

Chem. Phys. Lett. 6 (1970) 395.

5. Uit de ESR experimenten van Sharnoff aan triplet-excitonen in benzenophenon volgt, dat de Davydov-splitsing voor de triplet-excitonband groter moet zijn dan de Davydov-splitsing die bepaald is door Hochstrasser en Lin met Zeeman- en Stark-experimenten.

M. Sharnoff, J. Chem. Phys. 51 (1969) 451,

R.M. Hochstrasser en T.S. Lin, J. Chem. Phys. 49 (1969) 4929.

6. De zeer precieze bepaling van de nulveld-splitsingsparameters van de laagste triplettoestand van organische moleculen, zoals deze o.a. door Hutchison en zijn groep in Chicago wordt uitgevoerd, heeft alleen zin, wanneer de concentratie van foto-chemisch gecreëerde paramagnetische producten en hun interactie met de bestudeerde moleculen bekend zijn.

C.A. Hutchison, The Triplet State, Cambridge University Press, 1967, 63.

7. De definitie van links en rechts circulair gepolariseerd licht zoals oorspronkelijk in de optica gegeven, is niet aan te bevelen.

M. Born en E. Wolf, Principles of Optics, Pergamon Press, London, New York, Paris, Los Angeles, 1959.

8. Provotorov stelt, dat in een magnetisch resonantie-experiment bij toenemende amplitude H_1 van het magnetisch wisselveld de lijnbreedte van een absorptielijn kan toenemen, maar dat deze bij een verder stijgende H_1 weer afneemt. Dit is niet in overeenstemming met zijn vergelijking voor de geabsorbeerde energie.

B.N. Provotorov, Sov. Phys: JETP 14 (1962) 1126.

9. Degenen die hun winterse trimoefeningen afstemmen op een eventuele Elfstedentocht, zouden kunnen bedenken, dat volgens de 11^e graads machtreeks aangepast aan alle voorgaande (twaalf) Elfstedentochten, de volgende tocht pas in het jaar 3693 verwacht kan worden.

C O N T E N T S

	page
Chapter 1 INTRODUCTION	9
Chapter 2 PHOSPHORESCENCE AND RELATED MAGNETIC PROPERTIES OF AROMATIC CARBONYL CRYSTALS	13
A Introduction	13
B The triplet state in the absence of a magnetic field	14
C The effect of an external magnetic field	22
Chapter 3 EXPERIMENTAL PROCEDURE	27
A The apparatus	27
B A typical experiment	28
Chapter 4 PRINCIPLES OF LEVEL CROSSING, LEVEL ANTICROSSING AND CROSS-RELAXATION	31
A Introduction	31
B Level crossing in atomic systems - the Breit equation	31
C The possibility of level crossing in systems of low symmetry	41
D Level anticrossing	42
E The effect of hyperfine interaction on level anticrossing	46
F Interacting spins - cross-relaxation	51

EXPERIMENTAL RESULTS

	page
Chapter 5	
A Benzophenone	59
1 Preparation and structure of the crystal	59
2 Level anticrossing	60
3 Cross-relaxation between two triplet spins	73
4 Cross-relaxation between a triplet spin and an impurity spin	77
B Perdeuterated benzophenone (benzophenone-d ₁₀)	78
C 4,4'-dibromobenzophenone	81
1 Preparation and structure of the crystal	81
2 Level anticrossing and cross-relaxation	81
D 4,4'-dichlorobenzophenone	97
1 Preparation and structure of the crystal	97
2 Level anticrossing and cross-relaxation	97
E Other systems studied	99
 Chapter 6	
A The slow-recovery lines	103
B Free hydrogen atoms as the cause of the S-lines	110
C Electron spin polarization and photochemistry	116
D Transitions in a two-spin system induced by an r.f. magnetic field - experimental distinction between LAC and CR	118
 REFERENCES	 126
 SUMMARY	 130
 SAMENVATTING	 132

CHAPTER 1

INTRODUCTION

When two energy levels of an atomic or molecular system cross as a function of an external parameter physical properties of the system may change in the crossing region. In this thesis we study the change of radiative properties of a photo-excited organic crystal when two states corresponding to different orientations of the spin angular momentum are made to cross by varying the strength of an external magnetic field. Then, depending on the intrinsic properties of the system, three different effects may possibly be observed in the light emission from the excited crystal: level crossing (LC), level anti-crossing (LAC) and cross-relaxation (CR).

Level crossing has been studied in atomic gases since the experiments of Wood and Ellet (1923) and Hanle (1924). They studied the resonance fluorescence of mercury vapour excited with linearly polarized light at 2537 \AA and observed that the polarization and intensity of the emission changed sharply when a magnetic field of 2 Gauss was applied. This was explained to be a consequence of the splitting by Zeeman interaction of the three components of the mercury 3P_1 state, which are degenerate in zero magnetic field. This Hanle effect is an example of LC at zero magnetic field. Later LC effects at non-zero fields have been found and LC has since become a widely used technique to study the energies and lifetimes of the states of

complicated atoms and two- and three-atomic molecules in the gas phase.

If two states that in a first approximation are expected to cross are coupled by an additional perturbation we may have instead of a "crossing" an "anticrossing". Such LAC also may lead to changes in the radiative properties of the system as first demonstrated on Li atoms by Eck, Foldy and Wieder (1963).

The investigations which led to this thesis were started to see if these crossing effects might also be found in the phosphorescence emitted by organic crystals when excited with u.v. light. Soon it became clear that for reasons to be given later no LC effect is to be expected in the phosphorescence from a solid. However LAC effects were observed in the phosphorescence from organic crystals: by Sixl and Schwoerer (1970 a) in naphthalene and by Veeman and Van der Waals (1970 a) in benzophenone. In these experiments the phosphorescence intensity is measured as a function of magnetic field strength. For certain special orientations of the magnetic field a sharp but small increase of phosphorescence intensity is found in the crossing region of two spin components of the lowest triplet state of the phosphorescent molecules.

In such a "spectrum", in which the derivative of the intensity of the phosphorescence emitted by the benzophenone crystal is recorded as a function of the applied field, we found to our surprise besides the main LAC line many other even smaller lines, see fig. 1.1. These we have all been able to assign to other LAC effects and to CR processes. Later Sixl (1971) observed similar lines in the naphthalene crystal.

A CR process may occur when at a certain magnetic field the transition frequencies of two spin systems become equal or almost equal. Then, because of the interaction between the spins so-called flip-flop transitions, where two or more spins simultaneously make a transition with conservation of total energy, try to bring the two spin systems in equilibrium. Until 1970 CR was studied by means of susceptibility measurements and magnetic resonance experiments on solid

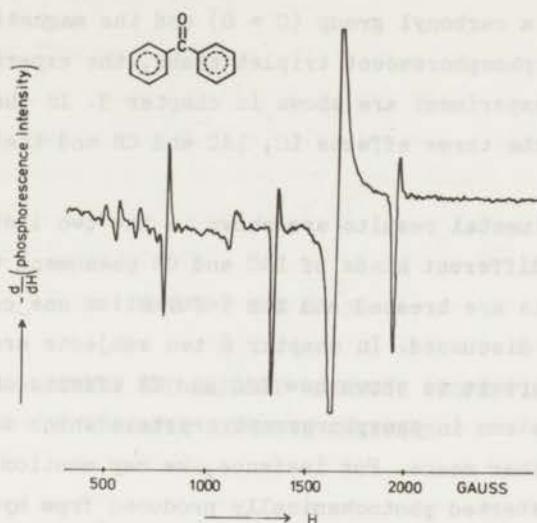


Fig. 1.1 The derivative of the phosphorescence intensity as a function of magnetic field strength for benzophenone with \vec{H} parallel to the C = O bond at $T = 1.3$ K. The strong line at about 1700 Gauss is the LAC line. Every line corresponds to a light increase.

paramagnetic systems. The possibility of CR in photo-excited triplet states has been mentioned by Gorter (1969).

Since LAC and CR have previously been studied as separate effects in different systems and under completely different circumstances, one would expect these two effects to be easily distinguishable from each other. However it will become clear that it is rather difficult and often even impossible to decide whether the intensity changes found in the phosphorescence from an excited organic crystal are caused by LAC or CR. Experimental evidence will be presented that in a very dilute paramagnetic system such as an excited organic crystal, effects which at first sight seem due to CR in reality have to be ascribed to LAC and vice versa. The close relationship between LAC and CR has already been pointed out by Caspers (1964).

After a discussion in chapter 2 of the phosphorescence of molecules with a carbonyl group ($C = O$) and the magnetic properties related to the phosphorescent triplet state, the experimental set up and a typical experiment are shown in chapter 3. In chapter 4 the principles of the three effects LC, LAC and CR and their relation is considered.

The experimental results are shown in the two last chapters. In chapter 5 the different kinds of LAC and CR phenomena that occur in organic crystals are treated and the information one can get from these experiments is discussed. In chapter 6 two subjects are treated: in the first part it is shown how LAC and CR effects can be used to detect spin systems in phosphorescent crystals which so far escaped detection by other means. For instance, we may mention here that we seem to have detected photochemically produced free hydrogen atoms in the benzophenone crystal which live $10^{-4} - 10^{-6}$ sec only and show strong electronic spin polarization.

In the second part of the last chapter it is demonstrated how in a particular case one can distinguish between a LAC and a CR effect by means of an experiment in which a radio frequency magnetic field is applied.

CHAPTER 2

PHOSPHORESCENCE AND RELATED MAGNETIC PROPERTIES OF AROMATIC CARBONYL CRYSTALS

A Introduction

This thesis deals with the phosphorescence of aromatic molecules containing a carbonyl group. The radiative and magnetic properties of these molecules when excited with UV light in many cases are largely determined by the C = O group and benzophenone will be used as a characteristic example.

Benzophenone in its ground state is a diamagnetic ($S = 0$), approximately planar molecule (fig. 2.1). The molecules form an orthorhombic crystal, the structure of which we shall discuss later.

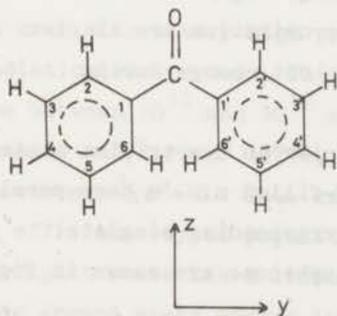


Fig. 2.1 Benzophenone and its axis system; because of the steric hindrance of the two neighbouring ortho hydrogens the molecule is only approximately planar.

B. The triplet state in the absence of a magnetic field

When a benzophenone molecule is irradiated with UV light an electron may be promoted from a filled molecular orbital (m.o.) to an empty m.o., bringing the molecule in an excited state. As is well-known (see for instance Kasha 1960) the m.o.'s of a planar molecule like benzophenone can be classified into three types: σ -, π - and n-orbitals.

The σ -orbitals are more or less located between every two atoms connected by a bond in fig. 2.1. The highest electron density in these orbitals is found between the two atoms.

The π -orbitals are delocalized over the molecule with the maximum density under and above the molecular plane. The π -orbitals very often are represented as linear combinations of $2p_x$ -orbitals of the carbon and oxygen atoms.

The σ - and π -orbitals are divided into bonding (σ , π) and antibonding (σ' , π') orbitals. In the ground state of the molecule all bonding orbitals are filled with two electrons with antiparallel spins, the antibonding orbitals are empty.

The n-orbitals or "non-bonding" orbitals are found only in molecules with atoms having more than four valence-electrons (N, O, S, etc.). In benzophenone there are two n-orbitals, in the ground state both filled with two electrons. The two n-orbitals in good approximation are oxygen $2s$ and $2p_y$ atomic orbitals (Kasha 1960).

By irradiation with near UV light ($\sim 3000 \text{ \AA}$) an electron from the highest bonding orbital π or from the $2p_y$ n-orbital can be excited into the lowest antibonding orbital π' , thus giving a $\pi\pi'$ or $n\pi'$ excited state. These excited states in very good approximation are singlet states ($S = 0$) because the electron spins do not change during excitation (see fig. 2.2).

The same electron configurations also give rise to two triplet states ($S = 1$) where the two electrons in the half-filled m.o.'s have parallel spins; they have a lower energy than the corresponding singlets.

The four lowest excited states in benzophenone are shown in fig.2.2

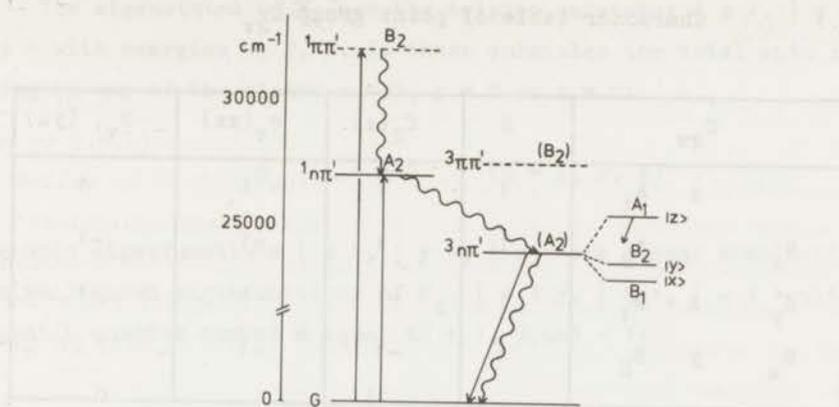


Fig. 2.2 The four lowest excited states of benzophenone; the $\pi\pi'$ states have a higher energy than the $n\pi'$ states but their position is not known accurately. The states are labelled with the irreducible representations of point group C_{2v} (see table 2.1) which is only the approximate symmetry of benzophenone because of the non-planarity. The symmetry labels in parentheses denote the symmetry of the orbital part of the electron wave function. The solid arrows in the figure represent radiative, the wavy lines radiationless transitions.

where it is indicated that the $n\pi'$ states have a lower energy than the $\pi\pi'$ states (Dym and Hochstrasser 1969). All molecules we studied have an $n\pi'$ state as lowest triplet state.

After excitation of benzophenone into the singlet state $^1n\pi'$ it goes over with a very high probability to the lowest triplet state via a radiationless process. This "intersystem crossing" has a rate found to be between 10^{11} and 10^{12} sec^{-1} (Dym and Hochstrasser 1969 and Busch, Rentzepis and Jortner 1971), which is much higher than that of the fluorescence $^1n\pi' \rightarrow G$. Thus excitation in the singlet manifold is a very efficient way of populating the lowest triplet state. The triplet state has a lifetime of a few milliseconds and its decay to the ground state occurs largely via the emission of light (phosphorescence).

Table 2.1

Character table of point group C_{2v}

C_{2v}		E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
z	A_1	1	1	1	1
R_z	A_2	1	1	-1	-1
R_y	x B_1	1	-1	1	-1
R_x	y B_2	1	-1	-1	1

Because the molecules we consider have no axes of symmetry higher than two-fold, a triplet state even in zero magnetic field has three non-degenerate substates. In a first approximation the hamiltonian for our problem is (see Van der Waals and De Groot 1967)

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{SS} + \mathcal{H}_{SO}$$

where \mathcal{H}_0 represents the spin-independent part, \mathcal{H}_{SS} the dipolar interaction between the electron spins and \mathcal{H}_{SO} the spin-orbit coupling. \mathcal{H}_{SS} is mainly responsible for the zero-field splitting and \mathcal{H}_{SO} for the mixing of singlets and triplets that leads to phosphorescence. When considering \mathcal{H}_{SS} and \mathcal{H}_{SO} as perturbations to the eigenstates of \mathcal{H}_0 the zero-field splitting of the triplet state can be represented by a spin hamiltonian of the form (Stevens 1952).

$$\mathcal{H}_S = -XS_x^2 - YS_y^2 - ZS_z^2 \quad (2.1)$$

S_x, S_y, S_z are the components of the total spin angular momentum operator \vec{S} ; x, y, z are the principal axes of the dipolar interaction tensor. Unless stated otherwise we shall assume these axes to coincide with the molecular axes.

The eigenstates of \mathcal{H}_S are the triplet substates $|x\rangle$, $|y\rangle$, $|z\rangle$ with energies X, Y, Z. In these substates the total spin is lying in one of the planes $x = 0$, $y = 0$ or $z = 0$:

$$S_u |u\rangle = 0 \quad (u = x, y, z) \quad (2.2)$$

The spin eigenfunctions $|x\rangle$, $|y\rangle$, $|z\rangle$ are linear combinations of the well-known eigenfunctions of S_z $|+1\rangle$, $|0\rangle$, $|-1\rangle$ with magnetic quantum number m equal to $+1$, 0 and -1 :

$$\begin{aligned} |x\rangle &= 2^{-\frac{1}{2}} \{ |-1\rangle - |+1\rangle \} \\ |y\rangle &= 2^{-\frac{1}{2}} i \{ |-1\rangle + |+1\rangle \} \\ |z\rangle &= |0\rangle \end{aligned} \quad (2.3)$$

An electric dipole transition between a triplet and a singlet state is forbidden and phosphorescence occurs because of the mixing by spin-orbit coupling between singlet and triplet states. Hence the triplet spin components no longer are pure triplet states; a small amount of singlet character is mixed in. Again because of the relatively low symmetry of the molecule the three triplet substates in general have different amounts of singlet character. The radiative and as we shall see also the radiationless decay probability in benzophenone are therefore different for the three substates.

McClure (1952) has shown by symmetry arguments that the mixing between two $\pi\pi'$ states, one a singlet the other a triplet, is very small. The mixing between two $n\pi'$ states likewise is very small. Relatively strong mixing however may occur between the $n\pi'$ and $\pi\pi'$ states of fig. 2.2 (Hameka 1956; Hameka and Oosterhoff 1958; Goodman and Krishna 1963; Veeman and Van der Waals 1970 b).

Even with a very simple model one can predict which triplet substate has the largest singlet contamination. In this model the spin-orbit coupling hamiltonian is approximated by the sum of atomic

contributions and the two-electron part is neglected.

$$\mathcal{H}_{SO} = \sum_i \mathcal{H}_{SO}(i) = \sum_K \sum_i \gamma_K \vec{l}_{iK} \cdot \vec{s}_i \quad (2.4)$$

Here \vec{s}_i is the spin angular momentum operator for electron i , \vec{l}_{iK} the orbital angular momentum for electron i about the nucleus of atom K and γ_K is a constant determined from spectral data on atom K .

The matrix element of \mathcal{H}_{SO} between a $\pi\pi'$ singlet state and the u ($u = x, y, z$) substate of the lowest $n\pi'$ triplet is a sum of products of an integral over positional coordinates and an integral over spin coordinates; the first integral is a matrix element of \vec{l}_{iK} between two m.o.'s and the second a matrix element of \vec{s}_i between the singlet spinfunction and triplet spinfunction $|u\rangle$ (see for instance Veeman and Van der Waals 1970 b equation (6)).

By expanding the integrals over m.o.'s in integrals over atomic orbitals one finds the result to be dominated by a single one-center integral (Goodman and Krishna 1963; Veeman and Van der Waals 1970 b):

$$\langle 2p_{x,0}(i) | \vec{l}_{i0}^{(u)} | 2p_{y,0}(i) \rangle ; \quad (2.5)$$

this involves the oxygen $2p_x$ orbital which enters via the expansion of the π m.o. into atomic orbitals and the oxygen $2p_y$ orbital as the n -orbital participating in the excitation process.

From symmetry considerations it follows that (2.5) vanishes unless $u = z$. Thus $s_i^{(z)}$ is the only component of \vec{s}_i which has to be considered in the integral over spin coordinates between the singlet spinfunction and one of the triplet spinfunctions. Consequently this integral is unequal to zero only for the substate $|z\rangle$, (see for instance Van der Waals and De Groot 1967, eq. (4)). Accordingly, in this simple model the substate $|z\rangle$ is the only one to become contaminated with singlet character and therefore able to emit phosphorescence.

Apparently, which of the substates carries the radiation is determined

Table 2.2

	$ x \rangle$	$ y \rangle$	$ z \rangle$
k^r	0.07 (0.02)	0.10 (0.02)	1
$k \text{ sec}^{-1}$	36 (1)	54 (1)	625 (10)
$\tau \text{ msec}$	28 (1)	18 (1)	1.60 (0.02)
N	1	0.69 (0.15)	0.03 (0.02)
P	0.97 (0.22)	1	0.56 (0.35)

Radiative decay rates (k^r), total decay rates (k), lifetimes ($\tau = k^{-1}$), steady-state populations (N) and populating rates (P) of the three triplet states of benzophenone; the quantities k^r , N and P are in relative units only. The values are averages of three measurements, the numbers in parentheses are the standard deviations of the mean. The populating rates have not been determined directly, but derived from the expressions

$$P_u = N_u k_u$$

Because N_z is very small the error in the values for N_z and thus for P_z is relatively large.

by the direction of the n-orbital on the oxygen atom involved in the excitation. (A physical manifestation of the importance of this spin-orbit coupling on the oxygen atom is the reduction of phosphorescence

lifetimes by a factor of the order of 10^{-3} when a carbonyl group is inserted into an aromatic molecule).

How very well this model predicts which triplet substate is the radiative one is shown in table 2.2, where the experimental relative radiative decay rates $k_u^{(r)}$ and total decay rates k_u (radiative plus radiationless) are given in the two top lines. These values were determined (Van der Poel and Veeman 1971) with the microwave induced delayed phosphorescence method (Schmidt, Veeman and Van der Waals 1969; Antheunis, Schmidt and Van der Waals 1970; Schmidt 1971). Similar measurements have been performed by Chan and Schmidt (1969) in this laboratory and more recently by Winscom and Maki (1971). Their results are in good agreement with the values of table 2.2.

From the numbers in table 2.2 one can see that $|z\rangle$ not only has the largest radiative decay rate but also the largest total decay rate and therefore the shortest lifetime.

The experiments to be described in this thesis, including the decay rate measurements of table 2.2, are always made at such a low temperature ($T = 1.3$ K) that spin lattice relaxation transitions between the triplet substates can be neglected during the lifetimes of the states. Then with continuous irradiation of the molecules the steady-state populations of the substates are determined by the populating and depopulating rates and not by the Boltzmann factor at 1.3 K! These steady-state populations also were determined for benzophenone in the microwave induced phosphorescence experiments; see fourth line in table 2.2. Very surprisingly only 1-3% of the excited benzophenone molecules are found in the substate $|z\rangle$, almost all excited molecules being in $|x\rangle$ or $|y\rangle$. The primary reason for these extreme steady-state populations found in all our "pure" single crystals is, that in contrast to the depopulating rates, the populating rates $P_u = N_u k_u$ are roughly equal for the three substates.

The following explanation for these comparable populating rates has been suggested by Chan and Schmidt (1969)). So far we have pretended that the lowest triplet state of benzophenone is populated

via intersystem crossing from $^1n\pi'$. However, in an ideal molecular crystal not the separate molecules are excited, but because of a weak interaction between the molecules the crystal is excited collectively in an exciton state (Davydov 1971). In these exciton states a single excitation can be thought to be transferred at a very high rate between identical molecules. Immediately after excitation the crystal is in a singlet exciton state and as in a single molecule it crosses over into the lower lying triplet exciton state in a time of the order 10^{-11} - 10^{-12} sec.

In a real crystal not all the molecules are identical, some are close to a physical distortion or chemical impurity and may therefore have a triplet state a little lower in energy than the bottom of the exciton band. Most of the triplet excitons therefore are caught in these "traps" before decaying to the ground state. Because of strong phonon-exciton coupling the spin-lattice relaxation between the three triplet exciton spin components is very fast (Sharnoff 1969) and the explanation of the comparable populating rates P_u of the trapped molecules that suggests itself then is that the populations of the triplet exciton states have reached Boltzmann equilibrium before they get trapped. This mechanism also explains the equal populating rates of the substates of the lowest triplet state of anthracene present as a guest molecule in a fluorene host (Sixl and Schwoerer 1970 b; Gromer, Sixl and Wolf 1972). In this mixed crystal the excitation of the anthracene triplet state is thought to go via the fluorene triplet exciton band.

From now on we shall only consider the phosphorescence from molecular traps and treat it as a property of single molecules. The triplet excitons, which live very short and hardly give a contribution to the phosphorescence of our crystals, enter only as intermediate states in the populating of the triplet state of molecular traps.

Most important for what follows is that in benzophenone and the other molecules here considered one has an almost empty radiative triplet substate and two filled, far less radiative substates.

C. The effect of an external magnetic field

When a magnetic field is applied the spin-hamiltonian (2.1) changes into:

$$\mathcal{H}_S = -X S_x^2 - Y S_y^2 - Z S_z^2 + g\beta \vec{H} \cdot \vec{S} \quad (2.6)$$

where, as usual for organic triplets, the assumption has been made that the g -tensor is isotropic (see for instance Hutchison 1967).

The eigenfunctions and eigenenergies of (2.6) can be calculated by diagonalizing a 3×3 matrix and when \vec{H} is parallel to one of the three principal axes x , y or z these can be written in analytical form (Van der Waals and De Groot 1967). In strong magnetic fields the eigenstates tend to the well-known eigenstates of the component of spin angular momentum along \vec{H} with eigenvalues $+1, 0, -1$.

The two orientations $\vec{H} // z$ (z orientation) and $\vec{H} // x$ (x orientation) are very important for our experiments, because only for these two orientations two of the three triplet substates of benzophenone (where $Z > Y > X$) cross at a certain magnetic field, see figs. 2.3 a and 2.3 b. In these two orientations the eigenfunctions and eigenenergies of the triplet substates are:

$$\begin{aligned} \vec{H} // z \quad | + \rangle &= 2^{-\frac{1}{2}} \left\{ \left(1 - \frac{Y-X}{2\alpha_z} \right)^{\frac{1}{2}} | x \rangle + i \left(1 + \frac{Y-X}{2\alpha_z} \right)^{\frac{1}{2}} | y \rangle \right\} \\ | 0 \rangle &= | z \rangle \\ | - \rangle &= 2^{-\frac{1}{2}} \left\{ \left(1 + \frac{Y-X}{2\alpha_z} \right)^{\frac{1}{2}} | x \rangle - i \left(1 - \frac{Y-X}{2\alpha_z} \right)^{\frac{1}{2}} | y \rangle \right\} \end{aligned} \quad (2.7)$$

$$\epsilon_+ = -\frac{1}{2} Z + \alpha_z$$

$$\epsilon_0 = Z$$

$$\epsilon_- = -\frac{1}{2} Z - \alpha_z$$

where $\alpha_z = \left\{ \frac{1}{4}(Y-X)^2 + (g\beta H)^2 \right\}^{\frac{1}{2}}$.

$$\begin{aligned} \vec{H} // x \quad | + \rangle &= 2^{-\frac{1}{2}} \left\{ \left(1 - \frac{Z - Y}{2\alpha_x} \right)^{\frac{1}{2}} | y \rangle + i \left(1 + \frac{Z - Y}{2\alpha_x} \right)^{\frac{1}{2}} | z \rangle \right\} \\ | 0 \rangle &= | x \rangle \end{aligned} \quad (2.8)$$

$$| - \rangle = 2^{-\frac{1}{2}} \left\{ \left(1 + \frac{Z - Y}{2\alpha_x} \right)^{\frac{1}{2}} | y \rangle - i \left(1 - \frac{Z - Y}{2\alpha_x} \right)^{\frac{1}{2}} | z \rangle \right\}$$

$$\epsilon_+ = -\frac{1}{2} X + \alpha_x$$

$$\epsilon_0 = X$$

$$\epsilon_- = -\frac{1}{2} X - \alpha_x$$

where $\alpha_z = \left\{ \frac{1}{4}(Z - Y)^2 + (g\beta H)^2 \right\}^{\frac{1}{2}}$.

From the properties of the zero-field states and the above formulae one arrives at the following predictions about the situation in a magnetic field:

z orientation: the two heavily populated, almost non-radiative zero-field substates $| y \rangle$ and $| x \rangle$ are mixed together giving two new eigenstates $| + \rangle$ and $| - \rangle$. State $| 0 \rangle$ is still underpopulated but has the largest radiative probability.

x orientation: the radiative and non-radiative transition probabilities of $| z \rangle$ are now divided over the new eigenstates $| + \rangle$ and $| - \rangle$ which are therefore radiative but underpopulated. The state $| 0 \rangle$ in this orientation is almost non-radiative but has a large population.

These statements are substantiated by electron spin resonance (ESR). In an ESR experiment a microwave magnetic field is applied with a frequency ν . When $h\nu$ is equal to the splitting between two of the three triplet substates transitions between this pair of states may be induced. When the upper state of the two states involved is less populated than the lower one, microwave power is absorbed by the spin system. Emission of microwaves is induced when the upper state is more populated than the lower one.

In a system of identical triplet spins in general three ESR lines are

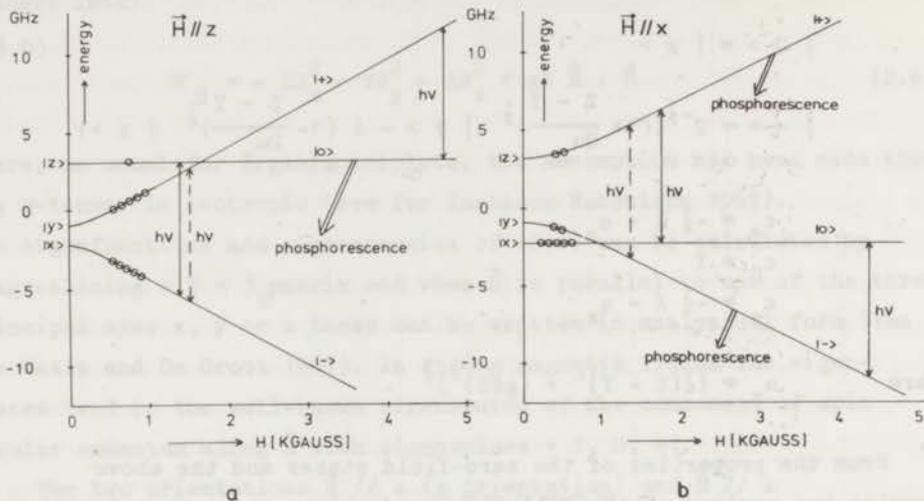


Fig. 2.3 The Zeeman splitting of the benzophenone triplet state with a magnetic field $\vec{H} // z$ (a) and with $\vec{H} // x$ (b). The " $\Delta m = 1$ " ESR transitions are indicated by full lines, the " $\Delta m = 2$ " transitions by broken lines for a microwave frequency of ~ 9 Ghz. The number of open circles gives an impression of the steady-state populations of the substates in a magnetic field at liquid helium temperature.

found, two " $|\Delta m| = 1$ " transitions and one " $|\Delta m| = 2$ " transition (see fig. 2.3). However, in a benzophenone crystal not all triplet spins are identical, because the crystal unit cell has four differently oriented molecules in it.

In fig. 2.4 we show the result of an ESR experiment on a benzophenone crystal in which the field \vec{H} is parallel to the z axis of one of the four molecules in the unit cell. In this figure the derivative of the microwave power as a function of magnetic field is recorded and the

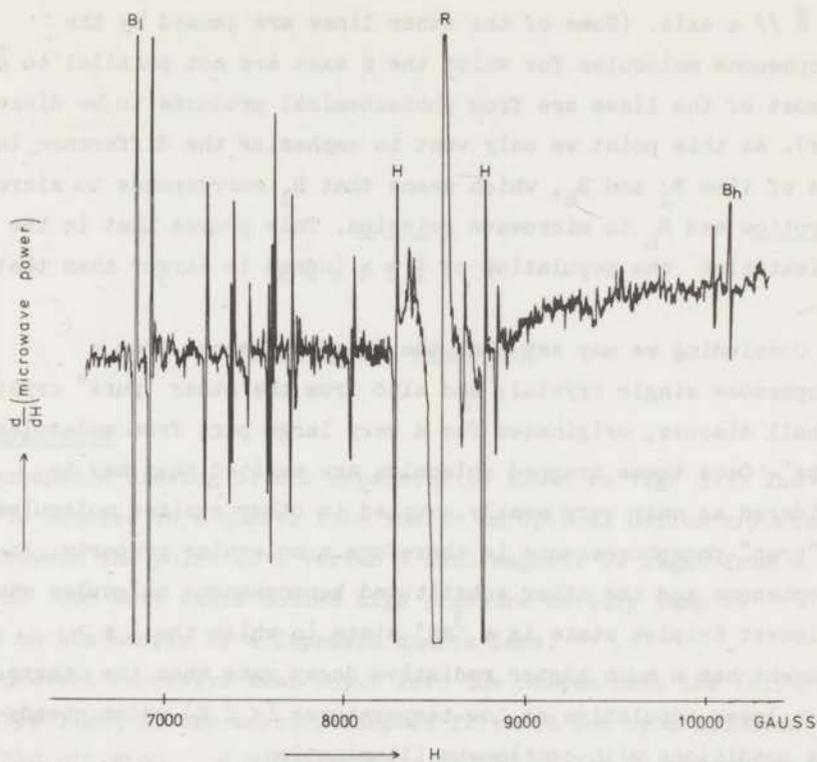


Fig. 2.4 The ESR spectrum of benzophenone with $\vec{H} // z$ axis of one of the sites at 1.3 K. The superheterodyne K-band spectrometer used for this experiment has been built in this laboratory by Blok and Kooter (1972). The microwave power incident on the sample is 100 n Watt, the modulation frequency 300 Hz.

lines at the lowest and highest magnetic fields, labelled B_1 and B_n are those of the " $|\Delta m| = 1$ " transitions of the benzophenone molecules with $\vec{H} // z$ axis. (Some of the other lines are caused by the benzophenone molecules for which the z axes are not parallel to \vec{H} , but most of the lines are from photochemical products to be discussed later). At this point we only want to emphasize the difference in phase of line B_1 and B_n , which means that B_1 corresponds to microwave absorption and B_n to microwave emission. This proves that in the z orientation the population of $| + \rangle$ indeed is larger than that of $| 0 \rangle$.

Concluding we may say that the phosphorescence from a benzophenone single crystal, and also from the other "pure" crystals we shall discuss, originates for a very large part from molecular "traps". Once these trapped molecules are excited they may be considered as only very weakly coupled to other excited molecules. The "trap" phosphorescence is therefore a molecular property. In benzophenone and the other substituted benzophenone molecules studied the lowest triplet state is a $^3_{nm'}$ state in which the $| z \rangle$ component has a much higher radiative decay rate than the others, but a much lower population at low temperatures (< 2 K) under steady-state conditions with continuous illumination.



CHAPTER 3

EXPERIMENTAL PROCEDURE

A. The apparatus

A schematic drawing of our apparatus is shown in fig. 3.1. The crystal is mounted in a quartz tube inside an optical helium cryostat, placed between the poles of a Varian 9 inch magnet. UV light from a Philips SP 1000 Watt water cooled high pressure mercury lamp is focussed on the sample by a Suprasil quartz lens.

To prevent excessive heat input into the helium bath the infrared and visible light of the mercury lamp is filtered out by a solution filter (240 g/l $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ plus 45 g/l $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$) and a Chance Pilkington OX 7 glass filter. The spectrum of the radiation used to excite the sample is shown in fig. 3.2.

The phosphorescence is detected via a quartz lightpipe (Schott) by an EMI 9524 B photomultiplier. An 0.25 m Ebert monochromator or a Balzers interference filter is used between the lightpipe and the PM to measure the phosphorescence with a bandwidth of 3-100 Å centered at the 0-0 band of the phosphorescence.

The sample tube can be rotated from the top of the cryostat about a horizontal axis, the magnet about a vertical axis. With this arrangement every orientation of the magnetic field relative to the molecular axes can be attained.

In order to observe the small changes in phosphorescence

lines at the lowest and highest magnetic fields, labelled 1, and 2, are those of the $|m| = 1$ transitions of the hyperfine structure with $I // z$ axis. Lower magnetic fields are associated with the $|m| = 0$ transitions. At this point we can see that the population of the $|m| = 0$ state of line 2, is much larger than that of line 1, and the intensity of line 2 is much larger than that of line 1.

Concluding we say that the phosphorescence signal is a function of the magnetic field with an acceptable signal-to-noise ratio phase sensitive detection was used. This was done by a low frequency (20-40 Hz), small amplitude modulation of the magnetic field with two extra coils on the poles of the magnet, while the output of the PM was fed into a PAR selective amplifier and lock-in detector that supplied the modulation signal.

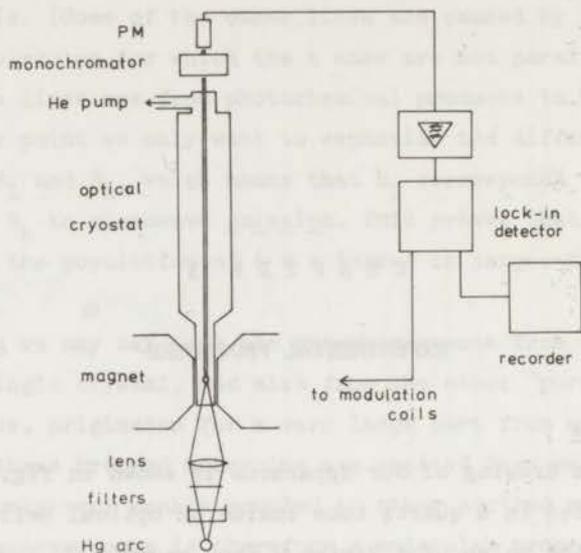
Fig. 3.1 Schematic drawing of the apparatus.

The magnetic field strength is measured by an AEG proton NMR Gaussmeter combined with a Hewlett-Packard electronic counter.

B. A typical experiment

Before we start with a discussion of the theoretical aspects of LC, LAC and CR it is useful to consider the procedure of a typical experiment.

The direct goal of the experiments is to measure the phosphorescence



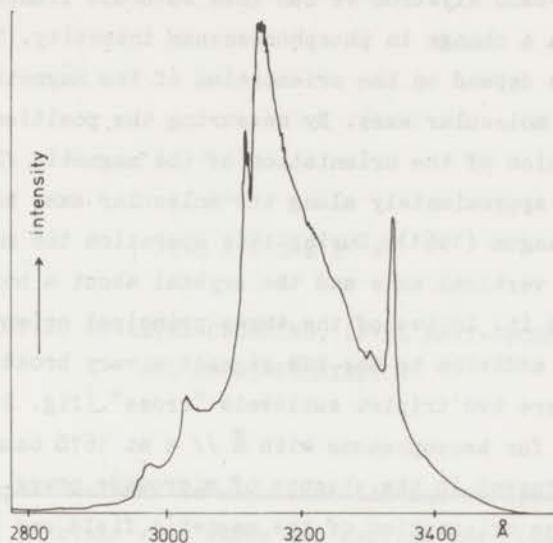


Fig. 3.2 The spectrum of the mercury lamp SP 1000 plus filters used to excite the crystals.

intensity as a function of magnetic field. Because the position and line form of the lines in the resulting spectrum (see for instance fig. 1.1) are strongly dependent on the orientation of the magnetic field relative to the molecular axes, we have to orient the crystal into a known position relative to the magnetic field. In fact, the three strongest lines of fig. 1.1 can be found only when the magnetic field is very closely parallel to the z axis of the benzophenone molecule. That is probably the reason why a spectrum like that of fig. 1.1 has not been found before.

The precise orientation of the crystal is done in two steps. After the crystal is mounted in the cryostat the magnetic field is roughly oriented along a molecular axis by using ESR with optical

detection. This is done as described by Schmidt (1971) with a microwave helix mounted around the crystal and connected to a microwave coaxial line. With an X-band klystron we can then saturate transitions, which are observed via a change in phosphorescence intensity. The positions of the ESR lines depend on the orientation of the magnetic field relative to the molecular axes. By measuring the positions of these lines as a function of the orientation of the magnetic field the field can be oriented approximately along the molecular axes as described by Hutchison and Mangum (1961). During this operation the magnet is rotated about a vertical axis and the crystal about a horizontal axis perpendicular to it. In two of the three principal orientations we then observe in addition to the ESR signals a very broad line close to the field where two triplet sublevels "cross" (fig. 2.3). This is the LAC signal, for benzophenone with $\vec{H} // z$ at 1678 Gauss (fig. 1.1), which is also present in the absence of microwave power. A final adjustment of the orientation of the magnetic field can now be made by making this line as narrow as possible.

As shown in fig. 1.1 more lines are found (also independent of the microwaves!) when the phosphorescence intensity is recorded as a function of magnetic field strength. The widths of these lines are independent of the orientation of the magnetic field and they can also be found when the magnetic field is not along a principal axis. These lines are caused by other LAC effects and CR processes involving more than one spin. To get information about these effects the field strengths at which these lines occur, are determined for several orientations of the magnetic field.

CHAPTER 4

PRINCIPLES OF LEVEL CROSSING, LEVEL ANTI-CROSSING AND CROSS-RELAXATION

A. Introduction

In this chapter we want to show that LAC and CR effects may be found in organic crystals when these are excited into the lowest triplet state, but that LC is not to be expected in such systems. More in particular we shall see that LAC and CR may cause a change in the intensity of the phosphorescence emission from the excited crystals, and in fact, this is the way we observe these effects.

In essence LC and LAC are phenomena that may occur in systems of non-interacting atoms or molecules, whereas CR processes arise because of the interactions in an ensemble. So let us first look at a system of isolated atoms or molecules and see what is meant by LC and LAC. Later we shall consider what may happen when we allow for interaction between the sub-systems in the ensemble and then it will become clear that in our systems it is rather difficult and sometimes even impossible to distinguish between LAC and CR.

B. Level crossing in atomic systems - the Breit equation

In atomic spectroscopy it has been known for a long time that when an atom with two or more closely spaced excited levels is excited, interference effects may be found. These interference effects manifest

themselves as a variation in the intensity of the radiation emitted. The first experiments which showed such interference were performed by Wood and Ellet (1923) and Hanle (1924) on mercury atoms which at zero magnetic field have three degenerate spin components of the excited 3P_1 state. The quantum mechanical explanation of this Hanle or zero-field LC effect has been given by Breit (1933).

Colegrove, Franken, Lewis and Sands (1959) found the first example of LC at a non-zero magnetic field in helium atoms. In these atoms crossings occur between Zeeman levels of two excited states 3P_2 and 3P_1 at certain values of an external magnetic field (see end of this chapter). Since then LC has become a very important technique for studying the energies and lifetimes of complicated atoms. Quite recently LC effects in two-atomic molecules have been found by German, Zare and Crosley (1971). All these experiments have been performed in gases.

The purpose of our early experiments was to investigate whether crossing effects can be found in the phosphorescence from organic molecules in a crystal. It turned out that LC, in the strict sense, cannot be observed in our kind of systems, but that anti-crossing situations arise. In order to show why, let us first look at a general expression, the Breit equation, which can be used to explain both LC and LAC and from which we can derive the experimental conditions necessary to observe these effects.

Consider an atom or molecule with two excited states ϕ_a and ϕ_b and energies E_a and E_b (fig. 4.1)

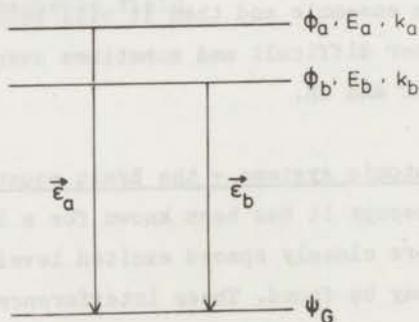


Fig. 4.1

For instance ϕ_a and ϕ_b may be two spin components of an excited triplet state, say $| + \rangle$ and $| 0 \rangle$ of fig. 2.3 a. Both excited states can be populated from the ground state, let us assume by absorption of a photon, although this assumption is not a necessary one. Decay to the ground state occurs via spontaneous emission but may also partly go via radiationless processes; the total decay rates are k_a and k_b sec^{-1} . The emission from ϕ_a and ϕ_b corresponds to the transition moments

$$\vec{M}_{Ga} = \langle \psi_G | e\vec{r} | \phi_a \rangle = \vec{\epsilon}_a | M_{Ga} | \quad (4.1)$$

$$\vec{M}_{Gb} = \langle \psi_G | e\vec{r} | \phi_b \rangle = \vec{\epsilon}_b | M_{Gb} |$$

where $\vec{\epsilon}_a, \vec{\epsilon}_b$ are unit vectors with Cartesian components that may be complex, for instance in the case of circularly polarized light.

Now suppose the molecule is excited at time $t = 0$ with an incoherent light pulse of duration τ which is so short that according to the Heisenberg principle

$$\tau \cdot \Delta E \gtrsim \hbar, \quad (4.2)$$

the uncertainty in energy ΔE of the photons in the pulse exceeds the difference in energy between ϕ_a and ϕ_b

$$\Delta E > |E_a - E_b|. \quad (4.3)$$

Both conditions (4.2) and (4.3) are fulfilled when

$$\tau < \hbar |E_a - E_b|^{-1}. \quad (4.4)$$

If the exciting pulse, which we assume to be propagating along the z axis (fig. 4.2), has a linear polarization $\vec{\epsilon}$ so directed that both ϕ_a and ϕ_b can be excited, then the wave function of the system after excitation will be a time-dependent linear combination of ϕ_a and ϕ_b :

$$\Psi(t) = a(t) \phi_a + b(t) \phi_b \quad (4.5)$$

Here

$$a(0) = \langle \phi_a | \vec{\epsilon} \cdot e\vec{r} | \Psi_G \rangle = \lambda |M_{Ga}| \quad (4.6)$$

$$b(0) = \langle \phi_b | \vec{\epsilon} \cdot e\vec{r} | \Psi_G \rangle = \mu |M_{Gb}|$$

with

$$\lambda = (\vec{\epsilon} \cdot \vec{\epsilon}_a^*) \quad \mu = (\vec{\epsilon} \cdot \vec{\epsilon}_b^*) \quad (4.7)$$

The time-development of $\Psi(t)$ is determined by the Schrödinger equation:

$$a(t) = a(0) \exp(-i \frac{E_a t}{\hbar}) \quad (4.8)$$

$$b(t) = b(0) \exp(-i \frac{E_b t}{\hbar})$$

Also we know that the states ϕ_a and ϕ_b are decaying to the ground state with decay rates k_a and k_b :

$$|a(t)|^2 = |a(0)|^2 \exp(-k_a t) \quad (4.9)$$

$$|b(t)|^2 = |b(0)|^2 \exp(-k_b t),$$

and following Weisskopf (1931) and Breit (1933) we write:

$$\begin{aligned}
 a(t) &= a(0) \exp \left[\left(-iE_a - \frac{1}{2}k_a \right) t \right] \\
 b(t) &= b(0) \exp \left[\left(-iE_b - \frac{1}{2}k_b \right) t \right]
 \end{aligned}
 \tag{4.10}$$

This combination of a quantum mechanical expression (4.8) and a phenomenological relation (4.9) can only be approximately correct. Later we shall discuss its limitations and see that the result should be valid in the situation of present interest.

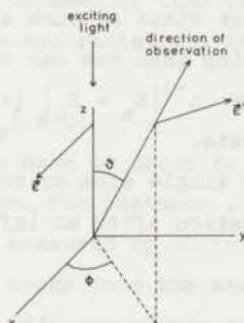


Fig. 4.2 The geometry of excitation and observation.

Now assume that the photons emitted by the system in the direction (θ, ϕ) (fig. 4.2) are detected by a detector which is capable of detecting photons with energies in the range from E_a to E_b and with linear polarization $\vec{\epsilon}'$. Then the probability $W(t)$ that this detector detects a photon at time t is:

$$\begin{aligned}
 W(t) &\propto \left| \langle \Psi_G | \vec{\epsilon}' \cdot \vec{e} | \Psi(t) \rangle \right|^2 = \\
 &= |\lambda\lambda'|^2 |M_{Ga}|^4 \exp(-k_a t) + |\mu\mu'|^2 |M_{Gb}|^4 \exp(-k_b t) \\
 &\quad + 2\text{Re} \left[\lambda\lambda' \mu^* \mu'^* |M_{Ga}|^2 |M_{Gb}|^2 \exp \left\{ -i \left(\frac{E_a - E_b}{\hbar} \right) t - \frac{1}{2}(k_a + k_b)t \right\} \right]
 \end{aligned}
 \tag{4.11}$$

where the numbers λ' and μ' are the components of the transition moments along the direction of polarization $\vec{\epsilon}'$

$$\lambda' = (\vec{\epsilon}' \cdot \vec{\epsilon}_a) \quad \mu' = (\vec{\epsilon}' \cdot \vec{\epsilon}_b) \quad (4.12)$$

The proportionality constant of (4.11) is determined by the experimental conditions. Besides the two terms in (4.11) showing the normal exponential decay of the states ϕ_a and ϕ_b , a third term occurs which oscillates in time. This phenomenon is called a quantum beat (see for instance Podgoretskii and Khrustalev 1964) and it can be observed only when the system is excited in a time $\tau < \hbar |E_a - E_b|^{-1}$. Quantum beats have not yet been found in the phosphorescence from organic molecules. If the triplet state of such a molecule is populated via intersystem crossing then one can only hope to observe quantum beats if their frequency $\hbar^{-1} |E_a - E_b|$ is appreciably lower than the intersystem crossing rate.

The probability W that our single atom or molecule has emitted a photon of the specified polarization after an infinitive time is:

$$W = \int_0^{\infty} W(t) dt$$

$$\propto \frac{|\lambda\lambda'|^2 |M_{Ga}|^4}{k_a} + \frac{|\mu\mu'|^2 |M_{Gb}|^4}{k_b} \quad \begin{array}{l} \text{incoherent} \\ \text{terms} \end{array} \quad (4.13)$$

$$+ 2 |M_{Ga}|^2 |M_{Gb}|^2 \operatorname{Re} \left[\frac{\lambda\lambda' \mu^* \mu'^*}{\frac{1}{2}(k_a + k_b) + i \frac{(E_a - E_b)}{\hbar}} \right] \quad \begin{array}{l} \text{coherent} \\ \text{term} \end{array}$$

This expression, the Breit equation, describes the intensity of the emission observed from an atom or molecule when it has been excited in a non-stationary state which is a linear superposition of two "stationary" excited states ϕ_a and ϕ_b . It consists of an incoherent part and a coherent or interference term which gives a non-negligible contribution only when $(E_a - E_b) / \hbar$ is of the order of $\frac{1}{2} (k_a + k_b)$ or less.

If instead of a single atom or molecule we have an ensemble of non-interacting identical atoms or molecules then W of (4.13) is proportional to the emission intensity from the ensemble with a fixed number of molecules raised to the excited state. Thus even with continuous irradiation one may measure a change in emission when the two excited states ϕ_a and ϕ_b can be tuned by a magnetic field so that $|E_a - E_b| \lesssim \frac{1}{2}\hbar(k_a + k_b)$. This is called level crossing.

A LC effect can only occur when the coherent term in (4.13) is not negligibly small and therefore three conditions have to be fulfilled:

$$1^\circ. E_a - E_b \lesssim \frac{1}{2}\hbar(k_a + k_b); \quad (4.14)$$

the difference in energy of the two states has to be of the same order of magnitude or smaller than the average width of the states caused by radiative and radiationless decay.

$$2^\circ. \text{Both } |M_{Ga}| \text{ and } |M_{Gb}| \neq 0; \quad (4.15)$$

both excited states have to decay to the same final state by the same decay mechanism. For instance, the Lamb shift in atomic hydrogen cannot be measured by LC in the absence of electric fields because the decay from the state 2S is a two-photon process and the decay from 2P a one-photon process (Rose and Carovillano 1961).

$$3^\circ. \text{The numbers } \lambda, \mu, \lambda', \mu' \text{ all } \neq 0; \quad (4.16)$$

λ and $\mu \neq 0$ means that whatever the excitation mechanism, there must be a probability to find the system after excitation in ϕ_a and ϕ_b . From λ' and $\mu' \neq 0$ it follows that if we have a detector which selectively measures light from one of the states only, e.g. light with polarization $\vec{\epsilon}_a$, then no LC effect will arise.

Because λ' and μ' depend on the relative position of the detector, the contribution of the coherent term in (4.13) to the total emission intensity also depends on the direction of observation and polarization.

In particular one can show (Bixon, Jortner and Dothan 1969) that in the case where the two transitions involved have orthogonal transition moments, i.e.

$$(\vec{\epsilon}_a \cdot \vec{\epsilon}_b^*) = 0, \quad (4.17)$$

the contribution of the coherent term when integrated over a spherical surface vanishes, because

$$\int_0 \lambda' \mu'^* d\Omega = 0. \quad (4.18)$$

Thus in order to observe quantum beats or LC effects in a system obeying (4.17) the detector has to collect light over a limited angle only. This is true for every direction of $\vec{\epsilon}$ and $\vec{\epsilon}'$ and implied by the conservation of the number of photons. The only result of the LC effect is a change in the angular distribution of the emission.

For instance, if in our example the transitions to ϕ_a and ϕ_b were circularly polarized in opposite directions in the xy plane, then the vectors $\vec{\epsilon}_a$ and $\vec{\epsilon}_b$ would have as components

$$\begin{aligned} \vec{\epsilon}_a &= (2^{-\frac{1}{2}}, 2^{-\frac{1}{2}}i, 0) \\ \vec{\epsilon}_b &= (2^{-\frac{1}{2}}, -2^{-\frac{1}{2}}i, 0) \end{aligned} \quad (4.19)$$

If now the directions of polarization of the exciting and detecting polarizers are

$$\begin{aligned} \vec{\epsilon} &= (1, 0, 0) \\ \vec{\epsilon}' &= (-\sin \phi, \cos \phi, 0) \end{aligned} \quad (4.20)$$

(see fig. 4.2; $\vec{\epsilon}'$ is assumed parallel to the xy plane and perpendicular to the observation direction) then

$$\begin{aligned}
 \lambda &= 2^{-\frac{1}{2}} \\
 \mu &= 2^{-\frac{1}{2}} \\
 \lambda' &= 2^{-\frac{1}{2}} i e^{i\phi} \\
 \mu' &= -2^{-\frac{1}{2}} i e^{-i\phi} .
 \end{aligned}
 \tag{4.21}$$

The coefficient $\lambda\lambda' \mu^* \mu'^*$ appearing in the coherent term is proportional to $e^{2i\phi}$. Therefore, in agreement with (4.18) a detector that gathers light in an entire cone $d\theta$ about the z axis would not see intensity changes when the distance $E_a - E_b$ is changed by some external parameter.

The situation can be compared to the famous double slit experiment of Young where two slits are irradiated by a lamp and an interference pattern is found on a shield behind the slits. The light intensity integrated over the shield does not depend on the distance between the slits, only the angular distribution of the light that has passed the slits.

In the case that $\vec{\epsilon}_a$ is not orthogonal to $\vec{\epsilon}_b$ the integral (4.18) is different from zero and the number of photons would not seem to be conserved. The reason for this inconsistency is that the combination of (4.8) and (4.9) to give (4.10) is incorrect when simultaneously $(\vec{\epsilon}_a \cdot \vec{\epsilon}_b^*) \neq 0$ and $E_a - E_b$ of the order of $\frac{1}{2}\hbar(k_a + k_b)$, as noticed by Bixon et. al. (1969). Because in our experimental situations we never have $(\vec{\epsilon}_a \cdot \vec{\epsilon}_b^*) \neq 0$ together with $E_a - E_b \sim \frac{1}{2}\hbar(k_a + k_b)$, (4.10) may be used to describe our experiments; the number of photons is conserved in all our cases.

Successful LC experiments have been performed in systems with a high symmetry like atoms and small molecules. A classical case is the experiment of Colegrove et. al. (1959) on helium atoms. Here several crossings are found between Zeeman states of the 2^3P_1 and 2^3P_2 excited states with different magnetic quantum number (fig. 4.3).

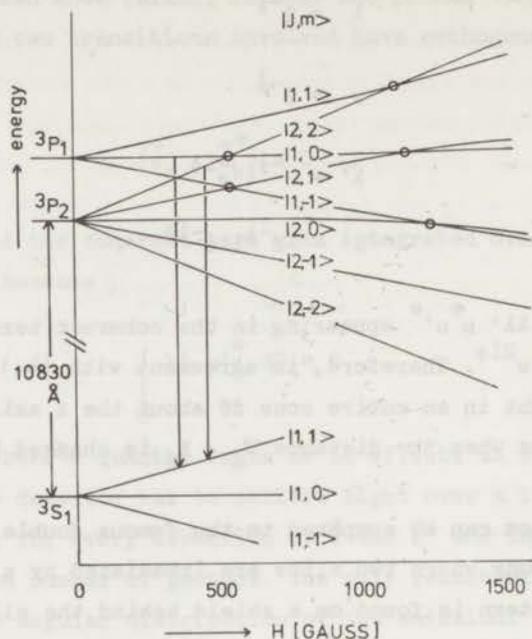


Fig. 4.3 Zeeman components of the excited 2^3P_1 , 2^3P_2 and 2^3S_1 states of helium. Crossings of states that give rise to LC effects are indicated by a circle. Arrows, indicating emission to the lower state, are shown only for one pair of crossing states, i.e. for the transitions $|2,2\rangle \rightarrow |1,1\rangle$ and $|1,0\rangle \rightarrow |1,1\rangle$.

The helium atom in the external field is invariant under the operations of the point group $C_{\infty v}$ and the two crossing states belong to different irreducible representations as is required for two atomic states to cross.

The crossings of states in fig. 4.3 are indicated by a circle and all give rise to a LC effect when a proper choice of the polarization of the excitation and detected light is made. For instance the crossing between $|2,2\rangle$ of state 2^3P_2 and $|1,0\rangle$ of 2^3P_1 is of the

type mentioned in our example: $|2,2\rangle$ decays via circularly polarized light σ_+ , $|1,0\rangle$ via circularly polarized light σ_- , both to $|1,1\rangle$ of 3S_1 . When the polarization of the exciting light and of the polarizer in front of the detector is chosen as in our example a change in emission intensity is found when the magnetic field is swept through the crossing.

C. The possibility of level crossing in systems of low symmetry

When speculating about the possibility of level crossing in molecular crystals one encounters two interrelated complications that make it improbable that such effects can be observed. First one has the non-crossing rule (von Neumann and Wigner 1929) which states that two levels with the same symmetry are not allowed to cross as a function of a single external parameter, because in general always a perturbation exists which splits the two states apart. Secondly, there is the practical problem of small imperfections in the orientation of the molecules in the crystal relative to the applied field. Let us consider what to expect in the case of benzophenone.

In the triplet state of benzophenone one might hope to find LC with the magnetic field parallel to the z axis or parallel to the x axis (fig. 2.3). If the symmetry of the benzophenone molecule were accurately C_{2v} then in both orientations the two crossing states belong to different irreducible representations of the symmetry group of the molecule plus field. (In the z orientation the $|+\rangle$ and $|0\rangle$ states are antisymmetric and symmetric, respectively for the operation C_2 ; in the x orientation the $|0\rangle$ and $|-\rangle$ states are antisymmetric and symmetric, respectively for reflection in the yz plane).

However, in the solid the symmetry of the molecules is lower than C_{2v} (Dym and Hochstrasser, 1969) and the combined system molecule + crystal field + applied magnetic field has no elements of symmetry anymore. Hence by the non-crossing rule one would expect the actual crossings to disappear for both the z and x orientations.

But even if the molecule in the crystal site had C_{2v} symmetry, no crossing of triplet substates would occur in an actual experiment

because therefore it is necessary to orient the magnetic field precisely parallel to the z or x axis. A small deviation destroys the symmetry, and then the non-crossing rule comes in again.

For instance, consider the crossing between $| + \rangle$ and $| 0 \rangle$ in the z orientation. If the magnetic field is not exactly parallel to z, but has a small component H_x along x, then the term $g\beta H_x S_x$ of the Zeeman operator has a matrix element between $| + \rangle$ and $| 0 \rangle$:

$$\langle + | g\beta H_x S_x | 0 \rangle = \delta \quad (4.22)$$

The two states do not cross anymore but are split by an energy $2|\delta|$ and by criterion (4.14) of the previous paragraph there will be no LC effect if $2|\delta|$ exceeds the average width of the states. For our triplet state molecules the lifetime is never shorter than 10^{-3} sec and the corresponding width thus is of the order of 1 KHz. To find a LC effect in the phosphorescence of these molecules it would therefore be necessary that $2|\delta|/\hbar \ll 10^{-3} \text{ sec}^{-1}$. This situation would be reached when the angle between the magnetic field and the z axis is smaller than 10^{-5} degree!

We conclude that it seems impossible to find a LC effect in the phosphorescence from an organic crystal. In benzophenone the deviation from C_{2v} of the molecule + magnetic field are too large to make a LC effect possible. Further, the molecules in a real crystal are not expected to be parallel to within the excessively narrow limits quoted.

D. Level anticrossing

When, because of the non-crossing rule, two states do not cross we may have an "anticrossing" situation. Although no actual crossing occurs one still may observe a change in the emission intensity from the two states. To show what is happening let us again consider a system of isolated molecules with two states ϕ_a , and ϕ_b , which would cross each other as a function of a magnetic field if the perturbation V that mixes them were absent.

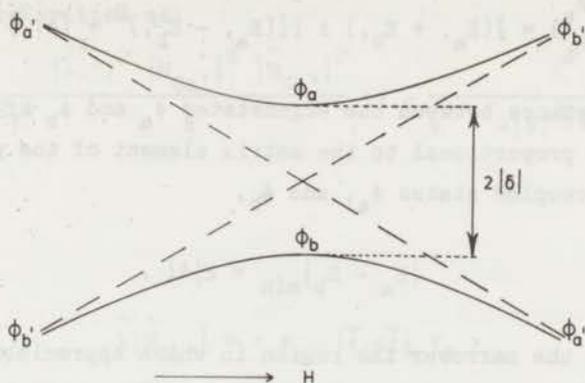


Fig. 4.4 LAC of two states $\phi_{a'}$ and $\phi_{b'}$.

Suppose

$$\delta = \langle \phi_{a'} | V | \phi_{b'} \rangle \quad (4.23)$$

then the new eigenfunctions ϕ_a , ϕ_b and eigenenergies E_a , E_b are (see fig. 4.4):

$$\begin{aligned} \phi_a &= (1 + |R|^2)^{-\frac{1}{2}} (R^* \phi_{a'} + \phi_{b'}) \\ \phi_b &= (1 + |R|^2)^{-\frac{1}{2}} (\phi_{a'} - R \phi_{b'}) \end{aligned} \quad (4.24)$$

with

$$R = \frac{\delta}{\frac{1}{2}|E_{a'} - E_{b'}| + \{ \frac{1}{4}(E_{a'} - E_{b'})^2 + |\delta|^2 \}^{\frac{1}{2}}} \quad (4.25)$$

and

$$\frac{E_a}{E_b} = \frac{1}{2}(E_a + E_b) \pm \left\{ \frac{1}{4}(E_a - E_b)^2 + |\delta|^2 \right\}^{\frac{1}{2}} \quad (4.26)$$

The minimum distance between the eigenstates ϕ_a and ϕ_b of the total hamiltonian is proportional to the matrix element of the perturbation V between the uncoupled states ϕ_a and ϕ_b ,

$$|E_a - E_b|_{\min} = 2|\delta| \quad (4.27)$$

The smaller δ , the narrower the region in which appreciable mixing between ϕ_a and ϕ_b occurs. At the magnetic field where $E_a - E_b$ is minimal (or $E_a = E_b$), $|R| = 1$ and with a proper choice of phases the wave functions ϕ_a and ϕ_b are the symmetrical and antisymmetrical combination of ϕ_a and ϕ_b , independent of the particular value of δ ($\delta \neq 0$).

Now we want to know what happens to the light emission of a molecule in such a LAC situation. The Breit equation (4.13) also describes LAC if one takes for ϕ_a and ϕ_b of (4.5) the eigenstates ϕ_a and ϕ_b of fig. 4.4.

In (4.13) the quantities λ , λ' , μ , μ' , M_{Ga} , M_{Gb} , k_a , k_b , E_a and E_b now refer to the states ϕ_a and ϕ_b and in the LAC region these are varying rapidly with the strength of the magnetic field. To see what happens it is convenient to write the Breit equation in terms of properties of the uncoupled states ϕ_a and ϕ_b , for a specific case that comes close to the situation encountered in our experiments:

- 1^o. one of the states, say ϕ_a , is being populated, either by using a polarizer in the exciting light or via selective intersystem crossing in the case where ϕ_a and ϕ_b are two triplet substates (see chapter 2),
- 2^o. only the light from the other state ϕ_b , is detected, again by using a polarizer or owing to selection rules for the radiative decay in the triplet state.

With the expressions (4.24) the Breit equation (4.13) for this case then can be written as:

$$W \propto \frac{2|R|^2}{(1 + |R|^2)^2} \frac{|\hat{\lambda}'|^2 |\hat{M}_{Ga'}|^2 |\hat{M}_{Gb'}|^2}{k} \left\{ 1 - \frac{k^2}{k^2 + 4|\delta|^2 + (E_{a'} - E_{b'})^2} \right\} \quad (4.28)$$

where

$$\hat{\lambda} |\hat{M}_{Ga'}| = \langle \phi_{a'} | \vec{\epsilon} \cdot e\vec{r} | \Psi_G \rangle \quad (4.29)$$

$$\hat{\mu}' |\hat{M}_{Gb'}| = \langle \Psi_G | \vec{\epsilon}' \cdot e\vec{r} | \phi_{b'} \rangle$$

$$\hat{\lambda} = (\vec{\epsilon} \cdot \vec{\epsilon}_{a'}^*) \quad (4.30)$$

$$\hat{\mu}' = (\vec{\epsilon}' \cdot \vec{\epsilon}_{b'}) ;$$

the $\hat{}$ denotes that the symbols are properties of the uncoupled states and we have assumed $k_{a'} = k_{b'} = k$.

The first term in (4.28) comes from the incoherent terms in (4.13), the second part from the coherent term.

We have seen that in our type of experiment we may always expect the coupling between $\phi_{a'}$ and $\phi_{b'}$ to be strong compared to the line width so we consider what happens when $|\delta| \gg \hbar\omega$ which causes the second (i.e. coherent) term in (4.28) to disappear. Then, as a function of magnetic field two regions can be distinguished:

- 1^o. region of negligible coupling; if $(E_{a'} - E_{b'}) \gg |\delta|$ it follows from (4.25) that $R \sim 0$ and therefore $W \sim 0$, which means that no light can be detected. This result is obvious for the present situation: the states $\phi_{a'}$ and $\phi_{b'}$ in very good approximation are the eigenstates and because we have assumed that only $\phi_{a'}$ is being excited we cannot expect to detect light from $\phi_{b'}$.

2°. The crossing region; here $|E_a - E_b| \lesssim |\delta|$ and W of (4.28) varies via R with the external parameter. For $E_a = E_b$, we find in particular

$$W = \frac{\frac{1}{2} |\hat{\lambda}_{\mu'}|^2 |\hat{M}_{Ga'}|^2 |\hat{M}_{Gb'}|^2}{k} \quad (4.31)$$

Apparently, the intensity of the light detected at the field where $E_a = E_b$, is independent of $|\delta|$ and completely determined by the incoherent part of (4.13) and (4.28).

In contrast to the LC case, for LAC the intensity of the emission received by the detector when integrated over a sphere does depend on the distance between the anticrossing states and thus varies with the external parameter. Of course energy is conserved, and the apparent contradiction resides in the following. In our example ϕ_a is exclusively populated, but only emission from ϕ_b is being detected. Since the Breit equation holds for a fixed number of excited molecules saturation effects may not occur and for a strict validity of the simple equation (4.31) we have to assume that a constant population in the excited state is maintained by the deactivation of ϕ_a , via radiationless processes or the emission of light for which the detector is insensitive. We shall return to this problem in connection with our experiments.

The situation of a negligible line width compared to the coupling $k \ll |\delta|/\hbar$ is thought to obtain for almost all our experiments. A possible exception is the "crossing" of the hyperfine components of 4,4'-dibromobenzophenone to be discussed later.

E. The effect of hyperfine interaction on level anticrossing

In order to get insight into the LAC effects to be expected for a phosphorescent triplet state we cannot simply identify the two excited states of our previous example with two of the $S = 1$ electron spin states, but in addition we have to consider interaction with the nuclei.

The triplet state.

Suppose we have a molecule where the electron spin $S = 1$ is coupled to a nuclear spin $I = \frac{1}{2}$. Owing to hyperfine and nuclear Zeeman interaction every electron spin state then is split into two hyperfine states (fig. 4.5).

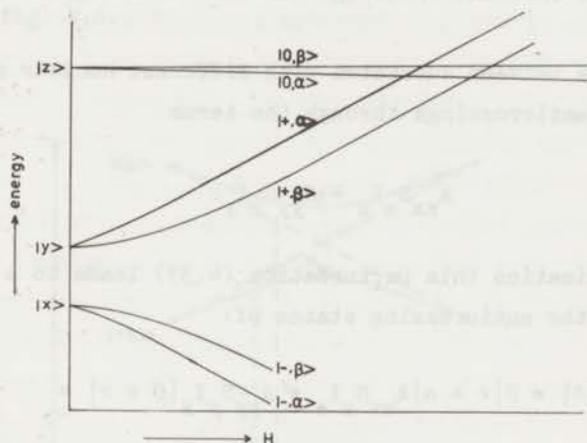


Fig. 4.5 Crossing between hyperfine components of two triplet substates with $\vec{H} // z$.

The spin hamiltonian of the system with $\vec{H} // z$ is

$$\mathcal{H} = \mathcal{H}_S + g\beta H_z S_z - g_N \beta_N H_z I_z + A_{xx} S_x I_x + A_{yy} S_y I_y + A_{zz} S_z I_z, \quad (4.32)$$

where it has been assumed that the principal axes of the hyperfine tensor coincide with those of the electronic dipolar tensor. In first order the hyperfine splitting of the electronic levels is determined by the terms

$$- g_N \beta_N H_z I_z + A_{zz} S_z I_z$$

and the eigenstates which result when neglecting the other terms

$$A_{xx} S_x I_x + A_{yy} S_y I_y,$$

are shown in fig. 4.5. The splitting of the state $|0\rangle$ is caused by the nuclear Zeeman interaction only, because for this state $S_z |0\rangle = 0$. Instead of one crossing of $|+\rangle$ and $|0\rangle$ in the purely electronic case, we see in fig. 4.5 four crossings. Two of these are crossings between states with the same nuclear spin wave functions and they should change into anticrossings for the reasons given in section 4 C.

The crossings between substates with different nuclear spin functions become anticrossings through the terms

$$A_{xx} S_x I_x + A_{yy} S_y I_y. \quad (4.33)$$

In a first approximation this perturbation (4.33) leads to a minimum distance between the anticrossing states of:

$$\begin{aligned} 2|\delta| &= 2|\langle + | \alpha [A_{xx} S_x I_x + A_{yy} S_y I_y] | 0 \beta \rangle| = \\ &= |\zeta_x^* A_{yy} - i \zeta_y^* A_{xx}|. \end{aligned} \quad (4.34)$$

Here we have abbreviated

$$|+\rangle = \zeta_x |x\rangle + \zeta_y |y\rangle,$$

where the coefficients ζ_x and ζ_y are given by (2.7). The distance $2|\delta|$ expressed as a frequency is of the order of several MHz, i.e. much higher than k . Further it is only very slightly dependent on the precise orientation of the magnetic field.

In fact, in many instances the principal axes of the hyperfine tensor will not coincide with those of the dipolar tensor, as supposed thus far. For the orientation in which two of the electron spin levels "cross", the component of nuclear angular momentum along this direction then no longer is a good quantum number and the hyperfine interaction will cause all crossings to change into anticrossings. This is the

situation met in most of our experiments and is another argument against the occurrence of LC effects in phosphorescent crystals.

It is interesting to consider the extreme situation where A_{xx} and A_{yy} both are zero and the magnetic field is perfectly oriented along the principal axis z . Even then one would not find an increase in light intensity due to LC. The reason for this becomes clear when looking at fig. 4.6.

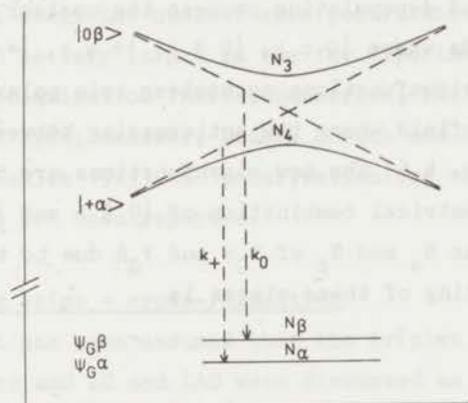


Fig. 4.6 One crossing of fig. 4.5 considered in more detail;

$\Psi_{G\alpha}$ and $\Psi_{G\beta}$ are the two ground state components.

Although the states $|0\beta\rangle$ and $|+\alpha\rangle$ (dashed lines) cross each other when $A_{xx} = A_{yy} = 0$, a LC effect is not observed because the states $|0\beta\rangle$ and $|+\alpha\rangle$ decay to different final states; see condition (4.15). This result is in agreement with the well-known fact (see for instance Podgoretskii et al. 1964) that no interference effects can be observed if, after a photon has been emitted, one can determine the channel by which the system has decayed. In the situation of fig. 4.6 the decay channel may be determined, for instance by measuring the state of the nuclear spin after the decay to the ground state.

When A_{xx} and A_{yy} are not both equal to zero, the situation of

fig. 4.6 might be very effective in creating high nuclear spin polarizations. For instance, assume that by some selection rule the electronic state $|0\rangle$ decays much faster to the ground state than the $|+\rangle$ and $|-\rangle$ states. As seen in Ch. 2 this is the case in benzophenone for instance. Then at the field where LAC occurs between $|0\beta\rangle$ and $|+\alpha\rangle$, the ground state component Ψ_G^β (see fig. 4.6) becomes more populated than Ψ_G^α . To see this consider an ensemble of molecules for which the rates for populating the triplet components $|0\rangle$ and $|+\rangle$ are P_0 and P_+ , their depopulating rates k_0 and k_+ . Let us assume that during the populating and depopulating process the nuclear spin remains unchanged. Then at fields where $|0\alpha\rangle$, $|0\beta\rangle$, $|+\alpha\rangle$, $|+\beta\rangle$, $|-\alpha\rangle$, $|-\beta\rangle$ are the correct eigenfunctions no nuclear spin polarization can appear. However, at the field where the anticrossing between $|0\beta\rangle$ and $|+\alpha\rangle$ is found (fig. 4.6) the new eigenfunctions are the symmetrical and antisymmetrical combination of $|0\beta\rangle$ and $|+\alpha\rangle$ and the change in populations N_α and N_β of Ψ_G^α and Ψ_G^β due to the populating and depopulating of these states is

$$\frac{dN_\alpha}{dt} = -N_\alpha \left(\frac{1}{2}P_0 + \frac{1}{2}P_+ \right) + \frac{1}{2}k_+ (N_3 + N_4) \quad (4.35)$$

$$\frac{dN_\beta}{dt} = -N_\beta \left(\frac{1}{2}P_0 + \frac{1}{2}P_+ \right) + \frac{1}{2}k_0 (N_3 + N_4)$$

Here N_3 and N_4 are the equal populations of the excited states. In steady state

$$\frac{dN_\alpha}{dt} = \frac{dN_\beta}{dt} = 0$$

and together with (4.35) this yields:

$$\frac{N_{\alpha}}{N_{\beta}} = \frac{k_{+}}{k_{0}} \quad (4.36)$$

From table 2.2 it follows that for benzophenone for instance $k_{+} \approx 0.1 k_{0}$. The actual nuclear spin polarization would be a few times smaller than given by (4.36) because molecules which are excited into triplet components not considered in fig. 4.6 do not contribute to the spin polarization and further nuclear spin-lattice relaxation has been neglected. But still the nuclear spin polarization that might be achieved could be very large. In the few experiments on optical nuclear spin polarization (Maier, Haeberlen, Wolf and Hausser 1968; Maier and Wolf 1968; Hausser, Lauer, Schuch and Stehlik 1970; Colpa, Hausser and Stehlik 1971) the polarization due to LAC between hyperfine states has not yet been reported.

F. Interacting spins - cross-relaxation

So far it has been assumed that the triplet spins are isolated from each other and LC and LAC were discussed as properties of individual molecules. To each triplet we could assign specific spin eigenstates having an energy width $\hbar k$ that was solely determined by the lifetime of the excited state concerned,

$$\hbar k_u = \hbar \tau_u^{-1} ;$$

since τ_u is of the order of a msec, this width when expressed as a frequency is less than 1 KHz.

In actual systems, however, the magnetic interactions between the spins play an important role. The theory of spin-spin interaction is a complicated subject which we will not consider here. From our point of view the most important result of this interaction is a broadening of the energy levels.

Because of the interaction between the spins each spin feels a

local field, varying with time and dependent on the site of the spin, which has to be added to the external magnetic field \vec{H} . If the local field is small compared to \vec{H} then the component parallel to \vec{H} gives a certain spread in the energies of the eigenstates of the individual spins, but these remain sharp; this effect is usually referred to as inhomogeneous broadening.

In case the spins are identical the precession of one spin around \vec{H} causes an oscillating field perpendicular to \vec{H} which may reorient another spin. This shortens the lifetime of the spins in a given state and therefore, owing to the uncertainty principle, broadens the individual states; this effect is often called homogeneous broadening (see for instance Abragam and Bleaney 1970, p. 54). The width hk' of a spin state that results from homogeneous broadening by spin-spin interaction is related to the spin-spin relaxation time T_2 :

$$hk' \propto \hbar T_2^{-1} \quad (4.37)$$

Spin-lattice relaxation in principle can also cause lifetime shortening of the spin states and thereby contribute to the homogeneous width. But, because in a solid the spin-lattice relaxation time T_1 is very much longer than T_2 and in our case was seen to be even longer than the lifetime of the excited state, we may neglect it.

From the rare data on spin-spin relaxation times in excited organic solids we may conclude that T_2 is of the order of a few microseconds (Schmidt 1972), which is very much shorter than the triplet lifetimes τ_u . So the width hk' due to spin-spin interaction dominates that due to radiative and radiationless decay or spin-lattice relaxation by a factor of the order of $10^2 - 10^3$.

The question now is what happens when two spin components a and b of a triplet spin cross. Already far from the level crossing situation, which required $E_a - E_b \lesssim \frac{1}{2}\hbar(k_a + k_b)$, the two homogeneously broadened states with widths $(k'_a + k_a)$ and $(k'_b + k_b)$ overlap. Then the interaction between the spins is of the same order of magnitude as the difference

in energy of the two states a and b. In that case the states of the individual spins lose their meaning: the crystal should be considered as one large system instead of an ensemble of weakly interacting individual spins (Abragam 1967, Ch. 5). Any effect resulting from the overlapping of spin states broadened by spin-spin interaction is a collective effect. Level crossing in the strict sense - as a phenomenon that arises in an individual molecule - can only occur when $k \gg k'$ which certainly does not apply to the triplet states of phosphorescent organic crystals. These stochastic processes, like spin diffusion through flip-flop transitions, destroy the phase coherence between the two states necessary for a LC effect, long before the triplet state decays. The observation of LC in emission from a solid might be possible in the case of a very short-living excited state where $k > k'$.

For the occurrence of a LAC effect in a system of coupled spins, on the other hand, it is necessary that the minimum splitting between the two anticrossing states $2|\delta|$ (see fig. 4.4) exceeds the width k' due to spin-spin interaction. This condition can easily be fulfilled because $|\delta|$ is determined by the perturbation which couples the two crossing states and may be much larger than k' .

The distinction between effects occurring in individual molecules and the collective cross-relaxation effects discussed below is not impaired by any inhomogeneous broadening that may arise from spin-spin interaction, inhomogeneous external magnetic fields, imperfect crystals, etc. Because, the spin system can always be thought divided into smaller subsystems in which only homogeneous broadening occurs, just like the partition of an inhomogeneously broadened magnetic resonance line into homogeneously broadened spin packets.

Instead of describing the interaction in an ensemble of spins in terms of homogeneously broadened quantum states the problem is often approached in a thermodynamic way. Because of their interaction two identical spins A and B (for the moment thought to be $S = \frac{1}{2}$) can exchange Zeeman energy. When spin A at a certain time is in a spin state $| + \rangle$ and spin B in $| - \rangle$, then a so-called flip-flop process can

occur where A goes from $| + \rangle$ to $| - \rangle$ and simultaneously B from $| - \rangle$ to $| + \rangle$ so that energy is conserved. In a system of identical spins these flip-flop processes, which are the cause of the homogeneous broadening, tend to bring the spin system in internal equilibrium in a time T_2 . As soon as this equilibrium has been reached a spin temperature T_S can be defined by the relation (Abragam 1967):

$$\frac{N_+}{N_-} = \exp\left(\frac{E_- - E_+}{kT_S}\right), \quad (4.38)$$

where N_+ and N_- are the populations, E_+ and E_- the energies of the states $| + \rangle$ and $| - \rangle$. When for some reason the spin temperature differs from the lattice temperature T_L , it will tend to become equal to T_L in a time T_1 , the spin-lattice relaxation time. A spin temperature thus can be defined only when $T_2 \ll T_1$ (Abragam 1967) as is the case in a solid. When spins $S > \frac{1}{2}$ having more than two states are involved, a spin temperature may be assigned to every pair of states.

Now imagine we have an ensemble consisting of two different types of spins, S_1 and S_2 which at a certain external magnetic field have different transition frequencies. No energy conserving flip-flop processes between one spin S_1 and another spin S_2 can then occur and so there is no direct contact between the spin systems S_1 and S_2 . These two spin systems then can each be in internal equilibrium with two different spin temperatures T_{S_1} and T_{S_2} .

When now in a certain magnetic field the two transition frequencies are made equal to within the width of the states, then via flip-flop processes the two spin systems may come into equilibrium with a common spin temperature. This process is called cross-relaxation (De Vrijer and Gorter 1952; Bloembergen, Shapiro, Pershan and Artman 1959).

As an example let us consider an ensemble of triplet spins in a magnetic field parallel to the z axis (fig. 4.7).

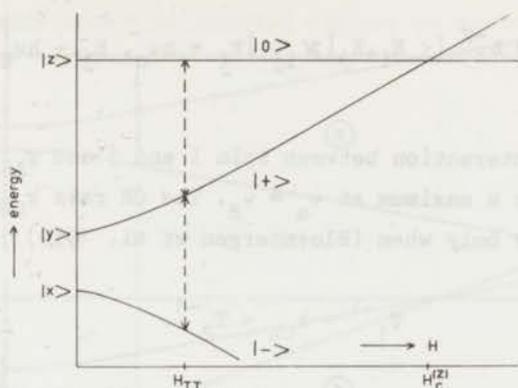


Fig. 4.7 The three spin components of a triplet state with $\vec{H} // z$.

The transition frequencies $\nu_{0 \leftrightarrow +}$ and $\nu_{+ \leftrightarrow -}$ between the states $|0\rangle$ and $|+\rangle$, $|+\rangle$ and $|-\rangle$ respectively, are different except at the field H_{TT} . Consequently, the spin temperatures corresponding to these transitions will in general be different when the temperature of the crystal is so low that spin-lattice relaxation may be neglected compared to the triplet state lifetimes. However, at the field H_{TT} flip-flop processes can occur which tend to equalize both spin temperatures and therefore change the steady state populations of the three spin components. Because the phosphorescence intensity depends on the steady state populations one understands that CR may lead to a change in phosphorescence intensity. Most of the lines in fig. 1.1 can be explained by this kind of process as shown in the next chapter.

In the simple description of CR as a heat contact between two heat reservoirs (the two spin systems S_1 and S_2) a CR rate k_{CR} can be defined as the rate at which the two spin systems come to equilibrium. This rate is proportional to the probability w_{ij} of a flip-flop process where spin i increases its energy by an amount $h\nu_\alpha$ and spin j decreases its energy by $h\nu_\beta$ while the balance of energy $h(\nu_\alpha - \nu_\beta)$ is taken up or provided by the interaction between all spins (Bloembergen et al. 1959, eq. 6a)

$$k_{CR} \propto w_{ij} = \hbar^{-2} \left| \langle E_i, E_j | \mathcal{H}_{ij} | E_i + \hbar\nu_\alpha, E_j - \hbar\nu_\beta \rangle \right|^2 g_{\alpha\beta} \quad (4.39)$$

where \mathcal{H}_{ij} is the interaction between spin i and j and $g_{\alpha\beta}$ is a line shape function with a maximum at $\nu_\alpha = \nu_\beta$. The CR rate k_{CR} is a meaningful quantity only when (Bloembergen et al. 1959)

$$T_1^{-1} < k_{CR} < T_2^{-1}. \quad (4.40)$$

Finally we want to show that a close relation exists between LAC and CR which makes it difficult to distinguish between these two effects. Consider two coupled identical triplet spins in a magnetic field, again parallel to the z axis. In fig. 4.8 a the three levels of one triplet state are given, in fig. 4.8 b the level scheme of a triplet pair. In these figures the interaction between the spins has not been taken into account. By comparing fig. 4.8 a and b we see that at the field H_{TT} where we expect a CR effect in a, a crossing between two states of the triplet pair is found in b. Because of the interaction between the two spins this crossing should change into an anticrossing. So CR at a field where two transition frequencies become equal corresponds to an anticrossing of two states in the scheme of the spin pair. Whether effects occurring at this field should be described as LAC or more properly as CR depends, as discussed above, on the width and the mutual distance $2|\delta|$ of the anticrossing states in fig. 4.8 b. If $2|\delta|$ is of the same order of magnitude or smaller than the homogeneously broadened states of fig. 4.8 b, then the effect is CR. This is often the case but in the last chapter we shall see that there are situations where the ensemble of spins can be divided into spin pairs (or small groups) with the interaction within a pair being much stronger than between spins of different pairs. In that case the distance between the anticrossing states in the level scheme for the spin pair is greater than their widths and the resulting effect on

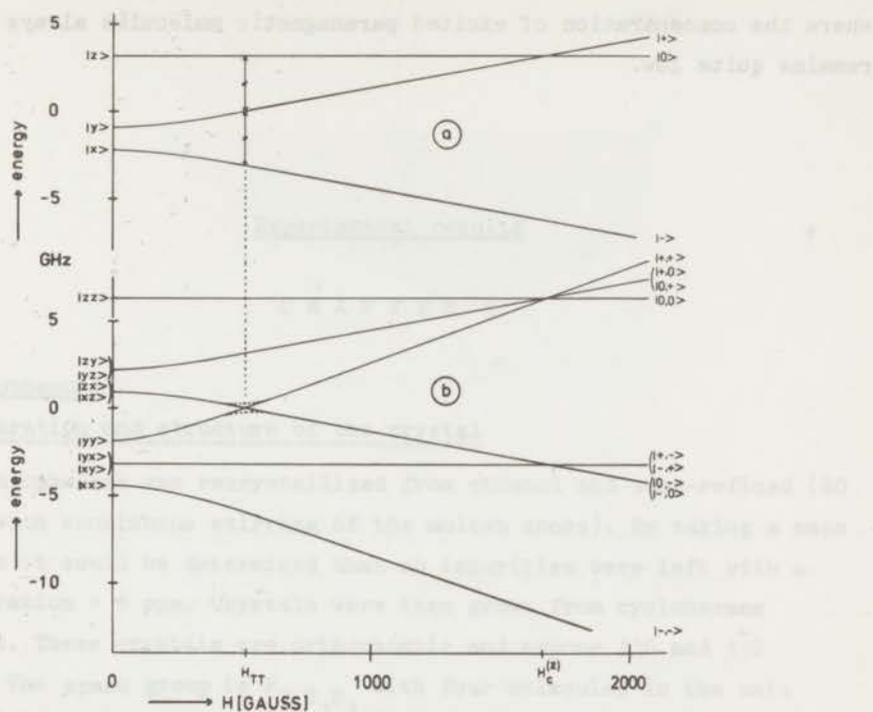


Fig. 4.8 a. The energies of a triplet state with $\vec{H} // z$.
 b. The energies of the spin components of a triplet pair found by summing the energies of individual states, e.g. $\epsilon_{+,0} = \epsilon_+ + \epsilon_0$.

the phosphorescence intensity should be called LAC. That this is not merely a question of description but has a physical meaning will be shown by an experiment discussed in chapter 6.

In fig. 4.8 CR or LAC also occurs at the field $H_c^{(z)}$, where the states $|+,->$ and $|-,+>$ cross $|0,->$ and $|-,0>$.

In the CR processes so far considered two spins in first instance are involved and therefore they are called two-spin CR processes. Three- or more - spin CR processes are also possible (see for instance Van Duyneveldt, Tromp and Gorter 1968) but, with one exception to be

Experimental results

C H A P T E R 5

A. Benzophenone

1. Preparation and structure of the crystal

Benzophenone was recrystallized from ethanol and zone-refined (40 passes with continuous stirring of the molten zones). By taking a mass spectrum it could be determined that no impurities were left with a concentration > 1 ppm. Crystals were then grown from cyclohexane solution. These crystals are orthorhombic and expose 110 and $\bar{1}\bar{1}0$ planes. The space group is $P_{2_1}^2 2_1 2_1$ with four molecules in the unit cell which are transformed into each other by the operation of the three two-fold screw axes $C_2(a)$, $C_2(b)$, $C_2(c)$ parallel to the crystal axes a, b and c. We number the four molecules in the unit cell according to the convention:

$$\begin{aligned} C_2(a) & 1 \rightarrow 2 \\ C_2(b) & 1 \rightarrow 3 \\ C_2(c) & 1 \rightarrow 4 \end{aligned} \quad (5.1)$$

The orientation of the molecular z axes relative to the crystal axes is shown in fig. 5.1. The z axes make an angle of $\sim 17^\circ$ with the crystal b axis and $\sim 4^\circ$ with the ab-plane. The direction cosines of all three axes of one molecule relative to the crystal axes are given by Dym, Hochstrasser and Schafer (1968).

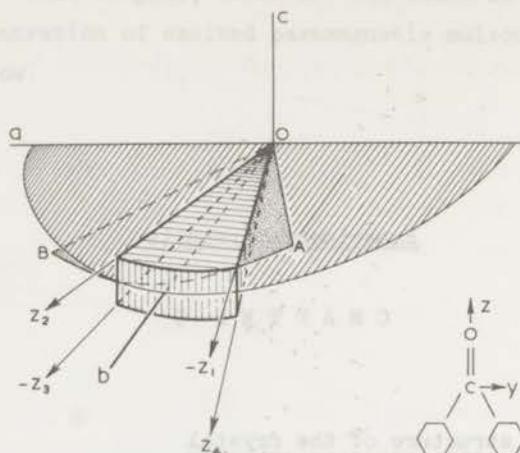


Fig. 5.1 The direction of the z axes of the four benzophenone molecules in the unit cell of the crystal.

2. Level anticrossing

The phosphorescence intensity of a benzophenone crystal as a function of magnetic field at $T = 1.3$ K is shown in fig. 5.2 a for \vec{H} parallel to the molecular z axis, in fig. 5.3 for $\vec{H} // x$ and in fig. 5.4 for $\vec{H} // y$. (The spectrum of 5.2 a is similar to that of fig. 1.1). Sharp changes in the phosphorescence intensity are found for $\vec{H} // z$ and $\vec{H} // x$. All lines are the result of LAC and CR processes as discussed in this and the following chapter.

We start with the strongest lines of fig. 5.2 a and fig. 5.3, denoted by L_1 . These relatively great changes in phosphorescence intensity are found at the field where two substates of the triplet state "cross" (see fig. 5.2 b and 2.3). Crossing does not occur with $\vec{H} // y$ and therefore no such line appears in fig. 5.4. These lines L_1 are due to the LAC effect discussed in chapter 4 and they show a characteristic property: when the magnetic field is turned away from the z or x axis, the line broadens very rapidly. The more accurately

the magnetic field is parallel to the z or x axis, the narrower the line, see fig. 5.5.

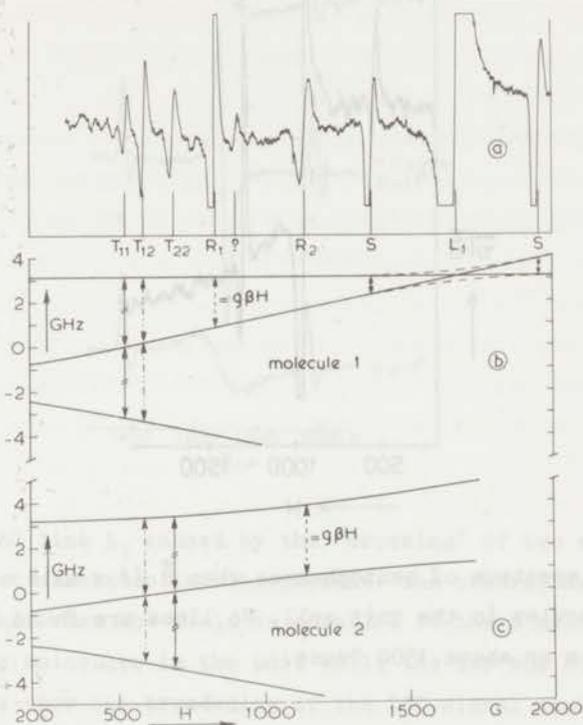


Fig. 5.2 The spectrum of benzophenone found with \vec{H} parallel to the z axis of molecule 1, together with the triplet energy levels of molecules 1 and 2 in this orientation. The vertical axis in the spectrum corresponds to minus the derivative of the phosphorescence intensity I with respect to the field.

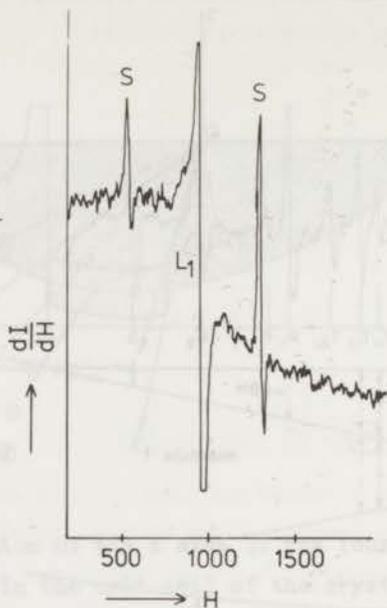


Fig. 5.3 The spectrum of benzophenone when $\vec{H} // x$ axis of one of the molecules in the unit cell. No lines are found below 500 Gauss or above 1500 Gauss.

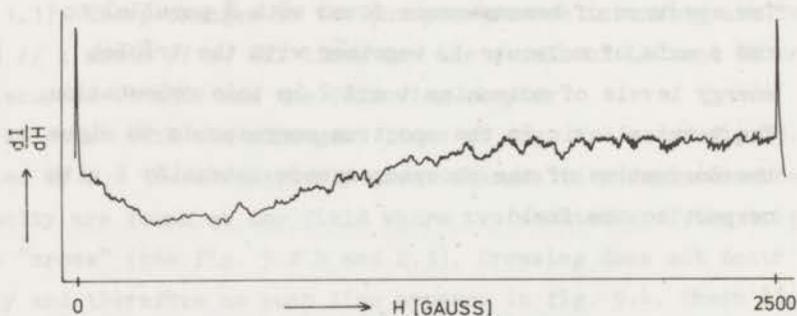


Fig. 5.4 The spectrum of benzophenone when $\vec{H} // y$ axis of one of the molecules in the unit cell. No lines are present, the peaks are markers.

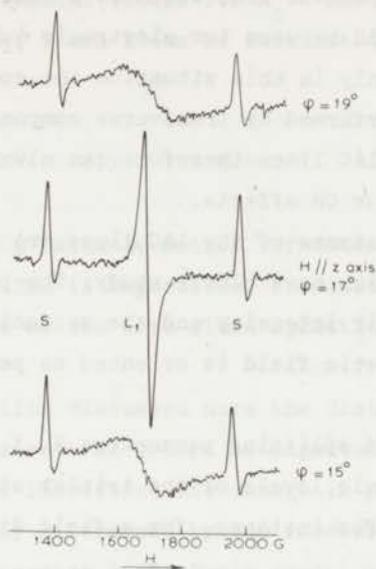


Fig. 5.5 The LAC line L_1 , caused by the "crossing" of two electronic triplet substates in benzophenone. The central trace is obtained when the field is parallel to the z axis of one of the molecules in the unit cell; the top and bottom traces show the broadening of the LAC signal caused by rotating the magnetic field two degrees away from the z axis. By contrast the lines denoted by S, which arise from cross relaxation with hydrogen atoms (see next chapter), show no orientation dependent broadening. The vertical axis in the figure corresponds to the derivative of the phosphorescence intensity with respect to the field.

The orientation dependent line width can be easily understood when we remember (section 4C) that the component of the magnetic field perpendicular to the z (or x) axis couples the two crossing states. The larger this component the larger the region over which the states are coupled and the broader the resulting LAC line.

The orientation dependent line width is a characteristic property of the line caused by LAC between two electronic substates of the triplet state because only in this situation the coupling between the "crossing" states is performed by transverse components of the Zeeman operator. This type of LAC lines therefore can always be distinguished from other LAC effects or CR effects.

Now the general features of the LAC lines are understood there remain three aspects which need closer study: The positions of the lines in the field, their intensity and the mechanism responsible for the width when the magnetic field is oriented as perfectly as possible. The positions.

From the zero-field splitting parameters X, Y and Z the magnetic field where two electronic levels of the triplet state cross can be calculated from (2.8). For instance, for a field directed along the x axis

$$H_c^{(x)} = \frac{hc}{g\beta} \{(X-Y)(X-Z)\}^{\frac{1}{2}} \quad (5.2)$$

where X, Y, Z are in cm^{-1} and H_c in Gauss. The crossing fields for other orientations follow from (5.2) by cyclic permutation of X, Y, Z; of course only in two orientations a real solution is obtained. The agreement between the crossing fields H_c , calculated from the zero-field splitting parameters determined by Chan and Schmidt (1969) and the positions of the LAC lines L_1 is quite good; see table 5.1.

Table 5.1

	calculated from z.f.s. parameters	measured values
$H_c^{(x)}$	931 Gauss	930 Gauss
$H_c^{(z)}$	1678 Gauss	1670 Gauss

Inversely, from experimental values for $H_c^{(x)}$ and $H_c^{(z)}$ the zero-field splitting parameters X , Y and Z can be calculated with the aid of (5.2) and the relation

$$X + Y + Z = 0 \quad . \quad (5.3)$$

This is thought to be a valuable method for determining these parameters in cases where ESR is impossible, for instance when the triplet lifetime is very short or the zero-field splitting very large.

The intensity.

In the LAC situation discussed here the distance between the two anticrossing states is several orders of magnitude greater than the width of these states. Therefore, the change in phosphorescence intensity is completely determined by the incoherent part of the Breit equation. However in chapter 4 the Breit equation was derived under the condition that the number of molecules in the excited state remains constant as a function of \vec{H} and the effect of radiationless deactivation was not explicitly considered. This does not hold in our situation and we shall first derive an expression in which one allows for radiationless decay.

Suppose that in fig. 4.4 the uncoupled states ϕ_a , and ϕ_b , have populating rates P_a , and P_b , depopulating rates k_a , and k_b , and radiative depopulating rates k_a^r , and k_b^r . These rates are magnetic field dependent linear combinations of the corresponding zero-field rates and can be calculated if the magnitude and direction relative to the molecular axes of the magnetic field are known.

When there is no coupling between ϕ_a , and ϕ_b , (far from the anti-crossing) then in steady-state with continuous irradiation the populations of ϕ_a and ϕ_b are:

$$N_a \approx N_{a'} = \frac{P_{a'}}{k_{a'}} \quad N_b \approx N_{b'} = \frac{P_{b'}}{k_{b'}} \quad . \quad (5.4)$$

The intensity of the phosphorescence emitted by these molecules then is:

$$I' = N_a k_a^r + N_b k_b^r = \frac{P_{a'}}{k_{a'}} k_a^r + \frac{P_{b'}}{k_{b'}} k_b^r \quad (5.5)$$

At the magnetic field where owing to LAC the stationary states are an equal mixture of ϕ_a and ϕ_b , the steady-state populations N_a and N_b of the new eigenstates ϕ_a and ϕ_b are

$$N_a = N_b = \frac{P_{a'} + P_{b'}}{k_{a'} + k_{b'}} \quad (5.6)$$

The phosphorescence intensity from these molecules in ϕ_a and ϕ_b now becomes

$$I = \frac{P_{a'} + P_{b'}}{k_{a'} + k_{b'}} (k_a^r + k_b^r) \quad (5.7)$$

If $I \neq I'$ then LAC causes a change in phosphorescence intensity. From (5.5) and (5.7) it follows that, at least when steady-state conditions are maintained, a change in phosphorescence intensity due to LAC can only occur because of the presence of radiationless decay. If there is no radiationless decay no LAC effect can be found by simply measuring the total emission intensity without using a polarizer.

For all LAC lines in benzophenone and the other molecules studied in the next sections, we found $I > I'$, the lines correspond to an increase of phosphorescence intensity. From the values for the populating and depopulating rates of benzophenone determined experimentally (table 2.2) one predicts I and I' to be in arbitrary units

$$I' = 1.0 \pm 0.4 \quad (5.8)$$

$$I = 0.9 \pm 0.2$$

The errors are the standard deviations. The experiment shows $I > I'$ but this is well within the error limits of (5.8).

The LAC effect in benzophenone is relatively weak because, in contrast to naphthalene, the ratios k_a^r/k_a , and k_b^r/k_b , are nearly equal. If these ratios would be equal it follows from (5.5) and (5.7) that no LAC effect could be found under conditions of slow passage where at every magnetic field the system is in a steady-state. However, if the magnetic field sweep could be made fast relative to the decay rates of the individual levels while still remaining adiabatic in the quantummechanical sense (i.e. in a time appreciably longer than $\frac{1}{4\pi|\delta|}$) then a change in phosphorescence intensity can be observed even if $k_a^r/k_a = k_b^r/k_b$. The phosphorescence intensity immediately after such a sweep is

$$I_{\text{fast passage}} = N_a k_b^r + N_b k_a^r \quad (5.9)$$

For benzophenone $I_{\text{fast passage}}$ is about eight times larger than I and I' of (5.8). Unfortunately, such a fast passage with a sweep time much shorter than the triplet lifetimes could not be made with the standard equipment in the case of benzophenone, but for longer living systems this method is very advantageous and it has been used by Sixl et al. (1970) with naphthalene.

The line width.

An important question, difficult to answer is: what determines the width of the LAC line when the magnetic field has been so oriented that this width is minimal. The residual width in benzophenone for both the z and x orientations is 30 Gauss, which is somewhat larger than that of the optically detected ESR lines.

We believe that the following interactions, in the order of their importance, may be responsible for the width of the LAC lines in benzophenone:

1°. Hyperfine interaction; the electronic triplet spin in benzophenone is coupled to several nuclear spins of the hydrogen atoms and therefore the electron spin components of the triplet states are split into many hyperfine states. Instead of one "crossing" at the field H_c we get many crossings at fields around H_c ; see for instance fig. 4.5 in the case of hyperfine interaction with one proton only. As shown in the previous chapter crossings between hyperfine states in general become anticrossings because of certain terms in the hyperfine interaction. So L_1 in figs. 5.2 a and 5.3 must be built up from several LAC lines shifted in magnetic field, corresponding to anticrossings between the hyperfine states of two electronic manifolds.

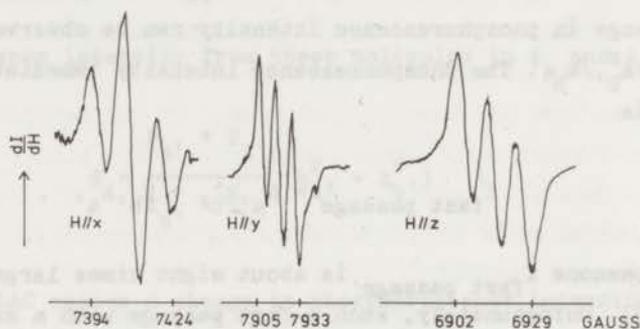


Fig. 5.6 The hyperfine splitting of the low-field $|\Delta m| = 1$ ESR line in benzophenone in the three principal orientations. These lines were detected optically by measuring the phosphorescence intensity I . In a benzophenone molecule only nuclear spins $I = \frac{1}{2}$ are present and therefore the three hyperfine components have to be explained by hyperfine interaction with two equivalent protons. Then it is surprising that in the z and y orientation the three components have equal intensities. A simple explanation may be that in these orientations the two nuclear spins involved are polarized.

In fig. 5.6 the hyperfine splitting of the ESR lines of benzophenone is shown for the three principal orientations. From this we conclude (see however the remarks about the anomalous intensities in the figure caption) that relatively strong hyperfine coupling exists between the triplet spin and two equivalent protons. It is reasonable to assume that these two protons are the two ortho hydrogens bonded to carbon atoms 2 and 2' (see fig. 2.1), especially because one of the unpaired electrons which form the triplet state is localized more or less in the oxygen $2p_y$ orbital pointing straight to these hydrogen atoms. The components of the hyperfine tensor for these hydrogens can be determined from the ESR spectra of fig. 5.6:

$$|A_{xx}| \approx 12, |A_{yy}| \approx 12 \text{ and } |A_{zz}| \approx 10 \text{ Gauss.}$$

Here it has been assumed that the principal axes of the hyperfine tensor coincide with the molecular axes, which must be (nearly) true for the two ortho protons concerned.

From the hamiltonian (4.32), where now $\vec{I} = \vec{I}_1 + \vec{I}_2$ represents the spin angular momentum of two protons, and the values of A_{xx} , A_{yy} and A_{zz} just given we have calculated the splitting of the spin states in the crossing region as shown in fig. 5.7. Because the states $|01\rangle$, $|02\rangle$, $|+3\rangle$ and $|+4\rangle$ in this figure are curved noticeably over a region of more than 30 Gauss we believe that in benzophenone hyperfine interaction is the main cause of the width of the LAC lines. Or, in terms of the terminology introduced at the end of the last chapter, one may say that the observed signal width is mainly due to inhomogeneous broadening caused by unresolved hyperfine structure.

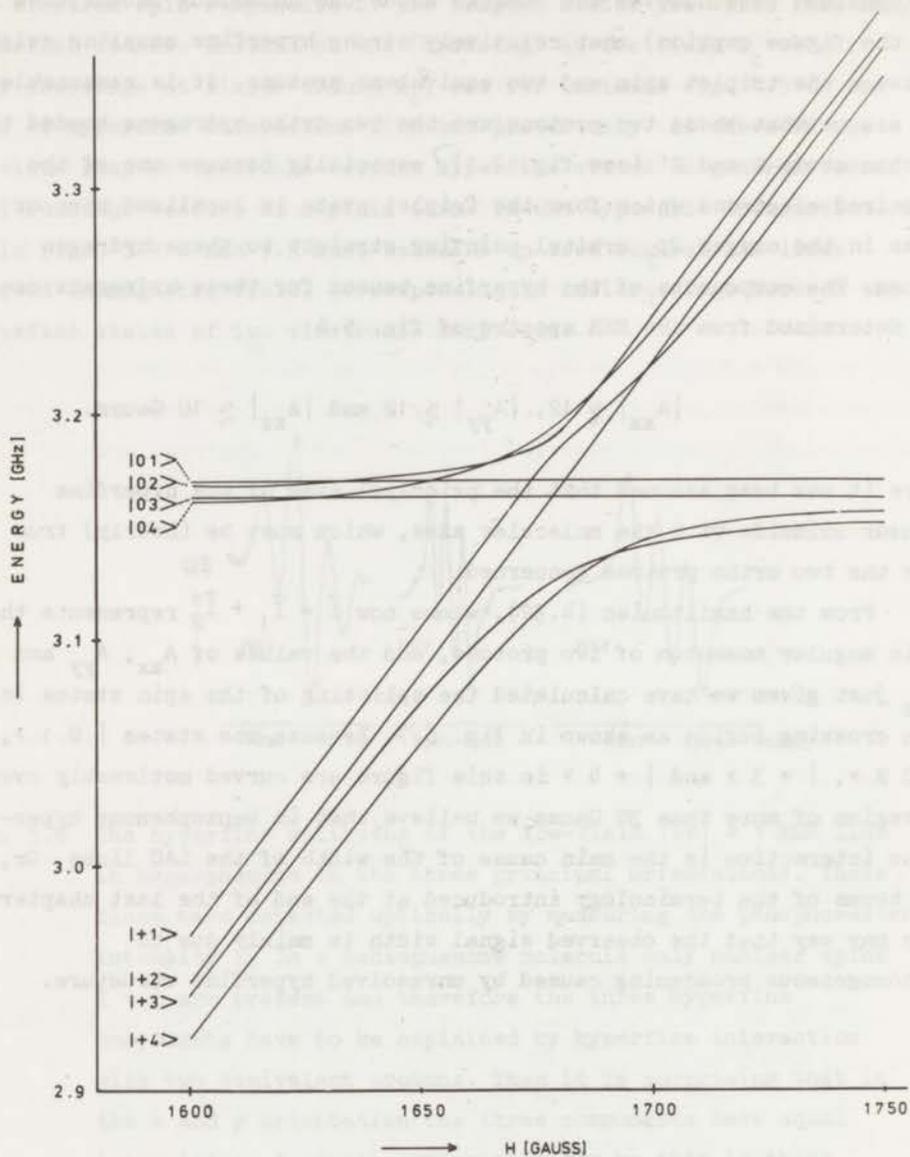


Fig. 5.7 The hyperfine states of the triplet levels $|0\rangle$ and $|+\rangle$ in the crossing region, calculated from the hamiltonian (4.32) with the values of the hyperfine tensor quoted above. To get an idea where the labels in this figure stand for we give for one value of H below the crossing field $H_c^{(z)}$ the approximate wave functions. Of course these wave functions change rapidly with increasing magnetic field.

At H = 1600 Gauss, from top to bottom

$$\begin{aligned}
 |01\rangle &\approx 0.99 |z;1,-1\rangle \\
 |02\rangle &\approx 0.10 |y;1,-1\rangle + 0.99 i |z;1,0\rangle \\
 |03\rangle &= 1.00 i |z;0,0\rangle \\
 |04\rangle &\approx 0.12 |y;1,0\rangle - 0.10 i |x;1,0\rangle + 0.99 |z;1,+1\rangle \\
 |+1\rangle &\approx 0.66 |x;1,+1\rangle + 0.75 i |y;1,+1\rangle \\
 |+2\rangle &= 0.76 |y;0,0\rangle + 0.66 i |x;0,0\rangle \\
 |+3\rangle &\approx 0.65 |x;1,0\rangle + 0.15 |z;1,+1\rangle + 0.75 i |y;1,0\rangle \\
 |+4\rangle &\approx 0.65 |x;1,-1\rangle + 0.14 |z;1,0\rangle + 0.75 i |y;1,-1\rangle ;
 \end{aligned}$$

where x,y,z label the zero-field electron spin states and the other two quantum numbers the nuclear states

$$\begin{aligned}
 |;1,+1\rangle &= \alpha\alpha \\
 |;1,0\rangle &= 2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha) \\
 |;1,-1\rangle &= \beta\beta \\
 |;0,0\rangle &= 2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha) .
 \end{aligned}$$

In the linear combinations given above wave functions with a coefficient < 0.10 have been left out.

In fig. 5.7 crossings of states still occur, partly because in the calculation we took $A_{xx} = A_{yy}$, but even without this assumption crossings will remain as long as we assume that the axes of the hyperfine tensors for the two protons coincide with the principal axes of the zero-field splitting tensor. However, in the benzophenone crystal there is a deviation from C_2 symmetry and it is improbable that the principal axes of the zero-field tensor exactly coincide with those of the hyperfine interaction with the 2,2' hydrogens. Further, weaker hyperfine interaction with the other eight hydrogens will change crossings into anticrossings.

2°. A spread in the orientation of the phosphorescent molecules.

In fig. 5.7 it has been assumed that the magnetic field is parallel to the z axis of all phosphorescent molecules of one site. However, when the phosphorescent molecules are not perfectly parallel the magnetic field is misoriented for some of the molecules and it is clear that this broadens the line. To give the LAC line a width of 30 Gauss, a spread in orientation of about 1 degree is enough! Such a spread does not seem unreasonable because the phosphorescence originates from traps, molecules found in distorted regions of the crystal. However from the observation that the width of the LAC lines proves independent of the way the crystals are grown, from the melt or from solution, we believe that the spread in orientation is less than 1°.

3°. Cross-relaxation; at the magnetic field where two triplet substates cross two transition frequencies are equal, for instance in the z orientation at $H_c^{(z)}$ $\epsilon_0 - \epsilon_+ = \epsilon_+ - \epsilon_-$ (see also the crossing between $|+,-\rangle$, $|-,+\rangle$ and $|0,-\rangle$, $|-,0\rangle$ in fig. 4.8 b). Therefore at $H_c^{(z)}$ a two-spin CR process may occur. This, however, is not thought to give a sizable contribution to the LAC, because as shown in the next paragraph the change in phosphorescence intensity expected for this particular process is small compared to the intensity of the LAC line.

4°. Spin-lattice relaxation; we have assumed throughout this thesis that spin-lattice relaxation between the triplet substates can be

neglected during the lifetimes of the substates. This assumption is based on the result of microwave experiments in zero-field and ESR at 1.3 K. However, at the magnetic field where two triplet substates cross this might not be true. For instance, in the experiments of Pound (1951) and Purcell and Pound (1951) it was found that in LiF crystals the spin-lattice relaxation times for the Li and F nuclear spins are much shorter in magnetic fields weaker than the local field than in high fields. In our crystals at the field where two triplet substates cross a similar effect might contribute to the line broadening of the LAC line. However it is not thought to be important, because our LAC show no temperature dependent width.

As a conclusion about the LAC lines we can say that these lines may be very useful for determining the zero-field splitting parameters of phosphorescent molecules, particularly in situations where ESR experiments are difficult to perform. Furthermore, the width of these lines gives an indication how well the molecular axes of the phosphorescent molecules are parallel to each other in the crystal. By making the LAC line as narrow as possible we have an easy criterion for orienting the magnetic field parallel to one of the principal axes of the zero-field splitting tensor.

3. Cross-relaxation between two triplet spins

To explain that in fig. 5.2 a the lines denoted by T_{11} , T_{12} and T_{22} are caused by CR between two excited triplet state molecules, we remember that the benzophenone crystal has four molecules per unit cell. When the magnetic field is parallel to a crystal axis all molecules are equivalent and the energies of the triplet substates of all four molecules have the same dependence on magnetic field. When the magnetic field is parallel to a plane formed by two crystal axes, then there are two pairs of molecules, the molecules within a pair being equivalent. For instance when $\vec{H} // ab$ plane then molecules 1 and 4 are equivalent and also 2 and 3.

When the magnetic field is parallel to the z axis of one of the molecules, say molecule 1 then in good approximation molecules 1 and 4

are still equivalent and also 2 and 3, because the z axes make a very small angle only with the ab plane. Thus with $\vec{H} // z$ of molecule 1 only two different sites have to be considered in a first approximation, for instance sites 1 and 2. The level schemes of these two molecules are given in fig. 5.2 b and c.

The line denoted in fig. 5.2 a by T_{11} is caused by CR between two excited molecules 1 and is found at the field where $\epsilon_0 - \epsilon_+ = \epsilon_+ - \epsilon_-$; $\epsilon_0, \epsilon_+, \epsilon_-$ are the energies given by (2.7). At this field flip-flop transitions may occur if the CR rate k_{CR} is of the same order of magnitude as the decay rates, or higher. These flip-flop transitions change the populations of the triplet substates and it is therefore easy to see that in general the phosphorescence intensity will change. But to predict that the phosphorescence intensity increases for such a process under steady-state conditions in benzophenone as the experiments learn, is much more difficult because the rate equations are non-linear:

$$\frac{dN_0}{dt} = P_0 - k_0 N_0 + k_{CR} (N_+^2 - N_- N_0)$$

$$\frac{dN_+}{dt} = P_+ - k_+ N_+ - 2k_{CR} (N_+^2 - N_- N_0) \quad (5.10)$$

$$\frac{dN_-}{dt} = P_- - k_- N_- + k_{CR} (N_+^2 - N_- N_0)$$

These equations express that cross-relaxation tries to equalize both spin temperatures involved or $N_0/N_+ = N_+/N_-$.

From the discussion about the intensity of the LAC line in the preceding paragraph it followed that the error in the populating and depopulating rates was too large to predict that the LAC line

corresponds to a light increase. For that reason and because k_{CR} is not known, it has not been tried to solve (5.10). However, just as for LAC it is easy to see what happens when the field sweep is very fast compared to the depopulating rates. In that case, if the CR rate k_{CR} is not much lower than the characteristic sweep rate, two neighbouring molecules 1 both in state $| + \rangle$ can make a flip-flop transition. Then one of the molecules considered goes from state $| + \rangle$ to $| 0 \rangle$ and simultaneously the other from $| + \rangle$ to $| - \rangle$. The result of this process is an increase of the population of the radiative state $| 0 \rangle$. The reverse flip-flop transition $| 0 \rangle \rightarrow | + \rangle$ and $| - \rangle \rightarrow | + \rangle$, which decreases the population of $| 0 \rangle$, is much less probable because the population of $| 0 \rangle$ is so much smaller. Also this last process would increase instead of decrease the difference of the spin temperatures of the two transitions. Hence the net result of such a fast passage experiment would be an increase of the population of $| 0 \rangle$ and therefore an increase of phosphorescence intensity. In a slow passage experiment the effect is much weaker, because just as discussed in the LAC case the ratio k^r/k now enters and this is about equal for the three triplet substates in benzophenone.

In the same way line T_{12} of fig. 5.2 a can be explained as the result of a CR process between excited molecules 1 and 2 and T_{22} as CR between two excited molecules 2 (see also fig. 5.2 b and c).

The correctness of these assignments was further substantiated by rotating the magnetic field in the plane OAB of fig. 5.1 which contains the z axis of molecule 1. When the magnetic field is rotated in this plane the T-lines shift as indicated in fig. 5.8 by small open circles. The solid lines in this figure represent the field strength at which the cross-relaxation lines are expected as calculated from the zero-field splitting parameters, the direction cosines of the molecular axes relative to the crystal axes and the transformation properties (5.1). In order to keep things simple it has been assumed in this calculation that the magnetic field is rotated in the ab plane instead of plane OAB of fig. 5.1. Because the experimental points refer to the case

where \vec{H} is in the plane OAB the deviation of the experimental points from the calculated curve becomes noticeable at the right of fig. 5.8. But otherwise the agreement between the experiments and the calculated curves is good.

When ϕ falls outside the region covered by the curves in fig. 5.8 $\epsilon_0 - \epsilon_+$ cannot be made equal to $\epsilon_+ - \epsilon_-$ in any magnetic field and then no triplet-triplet CR lines are found anymore. Also when \vec{H} is parallel to the x or y axis of the molecule calculation shows that the condition for triplet-triplet CR cannot be fulfilled and indeed no T-lines are found in figs. 5.3 and 5.4.

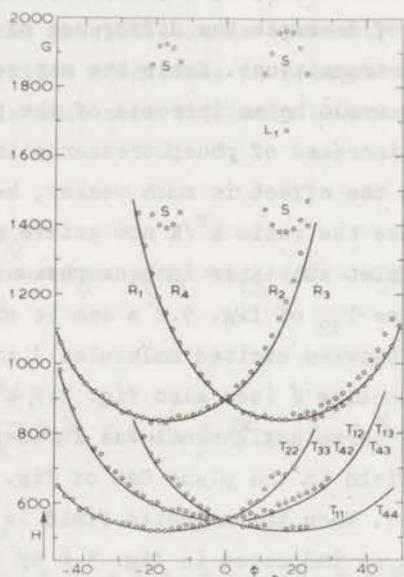


Fig. 5.8 The shift of the lines of fig. 5.2 a when the magnetic field is rotated in the plane OAB of fig. 5.1. The angle ϕ is the angle the field makes with the crystal b axis. The open circles are experimental points, the solid lines are calculated from the zero-field splitting parameters with the approximation that \vec{H} is in the ab plane instead of in OAB. When a line stops the possibility of the particular kind of CR disappears.

In none of the crystals studied three- or more-spin CR processes between the electron spins were found. Apparently the concentration of excited molecules is so low that the CR rate of these processes is much smaller than the rates of decay of the triplet substates.

Because the T-lines are caused by two excited molecules one might expect that the intensity of these lines depends in a quadratic way on the intensity of the exciting light. Although this does not seem to be the case the absolute line intensities have not been investigated further. A deviation from the quadratic relation can well be caused by the complicated trapping mechanism and the possibility of mutual annihilation of the excitons.

4. Cross-relaxation between a triplet spin and an impurity spin

In benzophenone crystals with \vec{H} parallel to a molecular z axis at least four lines are found (fig. 5.2 a) which cannot be explained by CR or LAC between triplet spins only. These lines are denoted by R_1 , R_2 and S. The S-lines, which are also found when $\vec{H} // x$ axis of benzophenone and likewise in substituted benzophenone crystals, are the subject of the first part of the last chapter. The lines denoted by R_1 and R_2 (fig. 5.2 a) are found at magnetic fields H where the splitting between two triplet substates of molecule 1 respectively molecule 2 is equal to $g\beta H$ (fig. 5.2 b and c) where g is the free electron g -value. Again, when the magnetic field is rotated these lines R_1 and R_2 are always found at the fields where the distance between two triplet substates equals $g\beta H$ as shown in fig. 5.8. The splitting of R_1 at large positive values of ϕ into two lines is again ascribed to the fact that molecules 1 and 4 then become noticeably inequivalent, because \vec{H} is not parallel to the ab plane as assumed in the calculation.

From this we conclude that the lines are caused by a two-spin CR process between benzophenone molecules excited into the triplet state and free radicals. The radical lines are not immediately present when an experiment is started with a crystal not previously irradiated, but appear after 10-15 minutes of irradiation. So we believe that these

radicals are the result of a photochemical process. In irradiated benzophenone radical signals can also be observed by ESR. For instance the strong line at about 8400 Gauss in fig. 2.4 is an ESR signal from a free radical. The radical has not been identified.

Before concluding this section we like to mention very similar experiments on ruby recently reported by Muramoto, Fukuda and Hashi (1971). They find, also by optical detection, LAC and CR signals on excitation of the ruby. In contrast to our experiments the CR signals result from CR processes between one excited and one ground state chromium atom while the LAC occurs between two levels of the 4A_2 ground state.

B. Perdeuterated benzophenone (benzophenone-d10)

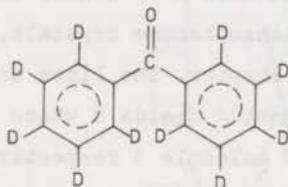


Fig. 5.9 Benzophenone-d10.

The spectra of benzophenone-d10 are shown in figs. 5.10 for $\vec{H} // z$ and in fig. 5.11 for $\vec{H} // x$. The general features of these spectra are very much the same as in benzophenone-h10, but two differences are found:

- 1^o. all LAC and CR signals are weaker in benzophenone-d10 compared to benzophenone-h10,
- 2^o. the lines denoted by S in the spectra of benzophenone-h10 (figs. 5.2 a and 5.3) are missing here; this will be discussed in the next chapter.

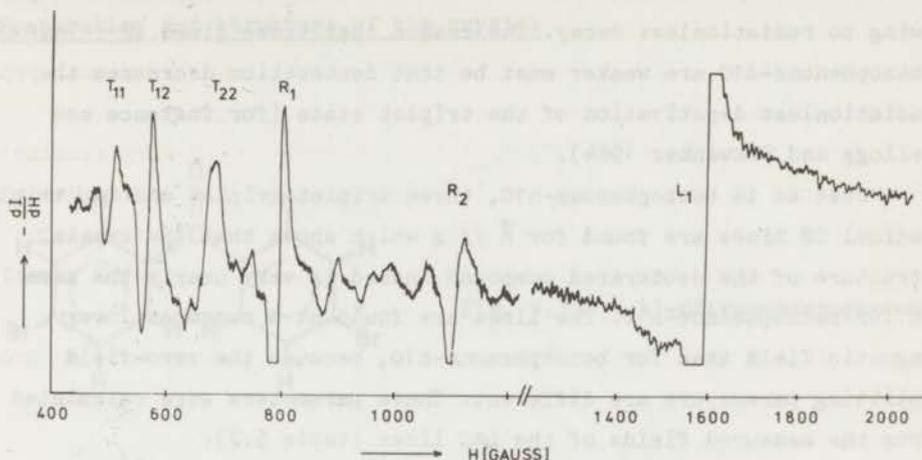


Fig. 5.10 The spectrum of benzophenone-d₁₀ with $\vec{H} // z$ axis of one molecule in the unit cell. The spectrum at the left of the break is taken with an RC time of 3 sec, the spectrum at the right with RC = 0.3 sec and a five times smaller gain. The triplet-triplet and triplet-radical CR lines are again denoted by T and R. Compared to benzophenone (fig. 5.2 a) the two S-lines are missing. The LAC line is 34 Gauss broad.

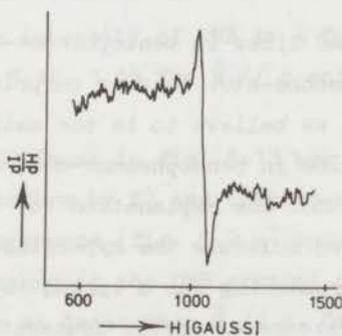


Fig. 5.11 The LAC line of benzophenone with $\vec{H} // x$. In this orientation no other lines are found.

We already mentioned that the LAC line and CR lines exist only owing to radiationless decay. The reason that these lines in benzophenone-d10 are weaker must be that deuteration decreases the radiationless deactivation of the triplet state (for instance see Kellogg and Schwenker 1964).

Just as in benzophenone-h10, three triplet-triplet and two triplet-radical CR lines are found for $\vec{H} // z$ which shows that the crystal structure of the deuterated compound indeed is very nearly the same as for benzophenone-h10. The lines are found at a somewhat lower magnetic field than for benzophenone-h10, because the zero-field splitting parameters are different. These parameters were calculated from the measured fields of the LAC lines (table 5.2).

Table 5.2

	X	Y	Z (cm^{-1})
benzophenone-h10	-0.0738	-0.0316	0.1054
benzophenone-d10	-0.0777	-0.0236	0.1013

The width of the LAC lines in benzophenone-d10 is of the same magnitude as in benzophenone-h10. This is surprising because the hyperfine interaction, which we believe to be the main cause of the broadening of the LAC line in benzophenone-h10, is ~ 6 times smaller in the deuterated compound. The explanation for this inconsistency may be that in the deuterated molecule the hyperfine interaction is not the main cause of the broadening but a spread in the zero-field splitting due to the presence of partly deuterated molecules. Further irregularities in the orientation may be more important in benzophenone-d10 than in benzophenone-h10, because of these impurities.

C. 4,4'-dibromobenzophenone

1. Preparation and structure of the crystal

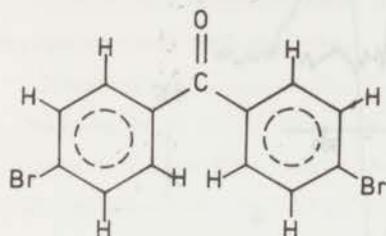


Fig. 5.12 4,4'-dibromobenzophenone

4,4'-dibromobenzophenone (DBB) was recrystallized from ethanol and zone-refined (40 passes with continuous stirring of the molten zones). The crystals were grown from ether solution and are orthorhombic. The space group is assumed to be $Ccc2$ (Structure Reports 1952) with four molecules in the unit cell. The molecular z axes are all parallel to the crystal c axis. The orientation of the x axes relative to the crystal axes is not known, but by ESR experiments we have established that the x axes also are parallel to within a few degrees.

2. Level anticrossing and cross-relaxation

The phosphorescence intensity of DBB as a function of magnetic field is shown in figs. 5.13, 5.14 for $\vec{H} // z$ and in fig. 5.15 for $\vec{H} // x$.

The lines below 1000 Gauss in fig. 5.13 are caused by triplet-triplet CR (denoted as before by T) and triplet-radical CR (denoted by R). In contrast to benzophenone (fig. 5.2 a) only one T-line and one R-line are observed, because in the DBB crystal all molecules are magnetically equivalent; at least when $\vec{H} // z$. Otherwise these lines are analogous to the T and R lines in benzophenone.

A more striking difference with the spectrum of benzophenone, however,

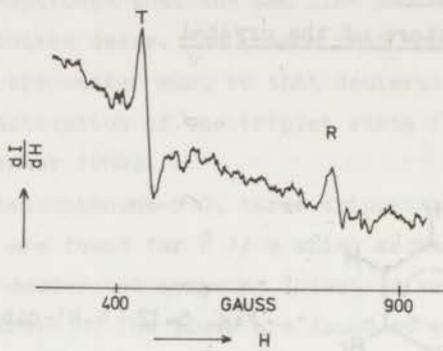


Fig. 5.13 The spectrum of DBB at 1.3 K with $\vec{H} // z$ for H below 1000 Gauss. T and R denote the triplet-triplet and triplet-radical CR lines.

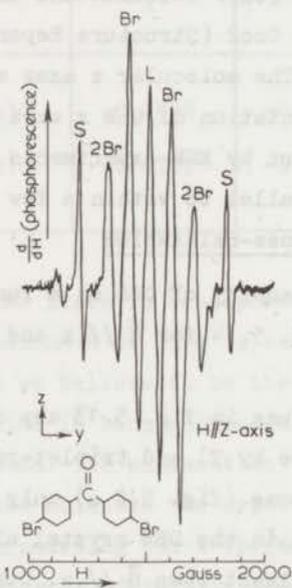


Fig. 5.14 The spectrum of DBB at 1.3 K with $\vec{H} // z$ for H between 1000 and 2000 Gauss. No lines are found above 2000 Gauss.

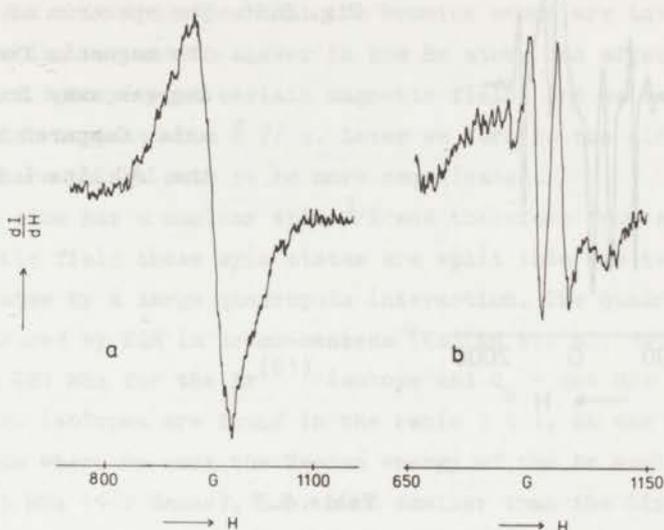


Fig. 5.15 The spectrum of DBB when, using ESR, the magnetic field is oriented as perfectly as possible parallel to the x axis (fig. a).

When the magnetic field is rotated a few degrees away from the x axis the spectrum shown in b is observed.

is observed in the z orientation for fields above 1000 Gauss (fig. 5.14). In this figure the S-lines are closely related to the S-lines in benzophenone and they will be discussed in the next chapter; here we concentrate on the lines denoted by 2Br, Br and L. When the magnetic field is turned away a few degrees from the z axis then the line L broadens in contrast to the lines 2Br and Br which only shift a little, see fig. 5.16. The line L is found at the magnetic field where the triplet substates $| + \rangle$ and $| 0 \rangle$ of DBB cross each other and we conclude that it results from the anticrossing of these two electron spin states. In table 5.3 the zero-field splitting parameters are given calculated from ESR experiments and the positions of the LAC lines L.

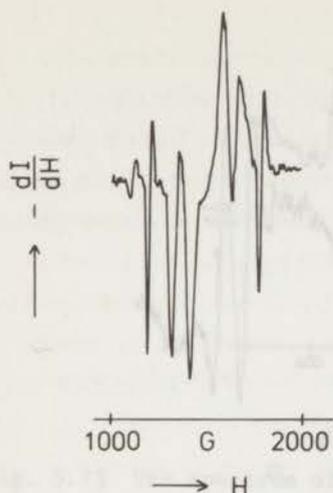


Fig. 5.16 The spectrum of DBB when the magnetic field is a few degrees away from the z axis. Compared to fig. 5.14 the LAC line L is broadened.

Table 5.3

	ESR	LAC
X	-0.0715 cm^{-1}	-0.0717 cm^{-1}
Y	-0.0251	-0.0256
Z	0.0966	0.0974

The z.f.s. parameters of 4,4'-dibromobenzophenone determined by ESR and LAC experiments. The signs have been chosen as in benzophenone.

The lines denoted by 2Br and Br in fig. 5.14 are not found in benzophenone and this indicates that the bromine atoms are involved. The first question we want to answer is how Br atoms can affect the phosphorescence intensity at certain magnetic fields and we begin by considering what happens when $\vec{H} // z$. Later we turn to the situation with $\vec{H} // x$ where things seem to be more complicated.

Every Br atom has a nuclear spin $3/2$ and therefore four spin states. In zero magnetic field these spin states are split into two two-fold degenerate states by a large quadrupole interaction. The quadrupole splitting measured by NQR in bromo-benzene (Kojima et. al. 1953) is equal to $Q_1 = 221$ MHz for the Br⁽⁸¹⁾ isotope and $Q_2 = 264$ MHz for Br⁽⁷⁹⁾. The two isotopes are found in the ratio 1 : 1. At the low magnetic fields where we work the Zeeman energy of the Br nuclear spins is less than 5 MHz (~ 2 Gauss), i.e. much smaller than the linewidths of our signals. Hence in discussing the energy levels we shall further neglect the Zeeman splitting and only consider the large quadrupole splittings. Then we have in good approximation for all values of the magnetic field for each Br spin two two-fold degenerate states $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ split by an energy Q_1 for Br⁽⁸¹⁾ and Q_2 for Br⁽⁷⁹⁾.

The coupling between the triplet electron spin and the Br nuclear spins in the same molecule arises from the hyperfine interaction

$$\mathcal{H}_{\text{HF}} = \vec{S} \cdot \vec{A}_1 \cdot \vec{I}(1) + \vec{S} \cdot \vec{A}_2 \cdot \vec{I}(2) \quad (5.11)$$

where $\vec{I}(1)$ and $\vec{I}(2)$ are the nuclear spin operators of the two Br atoms and \vec{A}_1, \vec{A}_2 the hyperfine tensors. In our optically detected ESR experiments we could not find any "forbidden" ESR lines corresponding to the simultaneous transition of an electron spin and one or two Br nuclear spins. This implies that the hyperfine interaction is not large. In fact, a small hyperfine interaction is expected because the spin density of the triplet electrons on the C atoms bonded to Br is small in an $n\pi'$ triplet state of aromatic carbonyl compounds (Kasha 1960) and also because the gyromagnetic ratio of the Br nuclear spin

is low ($\gamma_{\text{Br}} \approx \frac{1}{4}\gamma_{\text{H}}$).

With this information about the Br nuclear spins we can answer our first question. It turns out that the lines denoted by Br and 2Br in fig. 5.14 are found at those magnetic fields where the splitting between the triplet substates $| + \rangle$ and $| 0 \rangle$ is equal to 240, respectively 480 MHz. The energy 240 MHz is close to the mean of the quadrupole splittings of the two Br isotopes and 480 MHz is twice this average splitting.

These lines can equally well be explained as the result of a CR process between the triplet electron spin system and the Br nuclear spin system or as LAC in the combined spin system. Because it offers a nice illustration of the relation between CR and LAC we shall first explain the lines Br and 2Br as a CR process and then as a LAC effect and see if the conclusions we reach agree for the two interpretations.

The cross-relaxation picture.

In this picture the triplet electron spin system and the Br nuclear spin system are considered to be two weakly coupled systems. At the magnetic field where the lines Br and 2Br are found the splitting between the triplet substates $| 0 \rangle$ and $| + \rangle$ is equal to the splitting between two spin states of a single Br spin, or of a Br pair (fig. 5.17). The lines labelled Br then are due to a two-spin CR process, the lines labelled 2Br to a three-spin CR process.

Just as in benzophenone, the $| z \rangle$ substate in zero field or $| 0 \rangle$ in non-zero magnetic field is the state with the largest radiative decay rate and with the smallest steady-state population. To see whether the CR processes mentioned above lead to an increase or decrease of the phosphorescence intensity, we encounter the same difficulty as discussed in the paragraph about the triplet-triplet CR in benzophenone. It is easy to see what happens when the CR rate is much higher than the decay rates and the magnetic field is swept through the line in a time much shorter than the inverse of these decay rates. Then, at a field below $H_c^{(z)}$ molecules go from the populated weakly radiative state $| + \rangle$ to the empty strongly radiative state

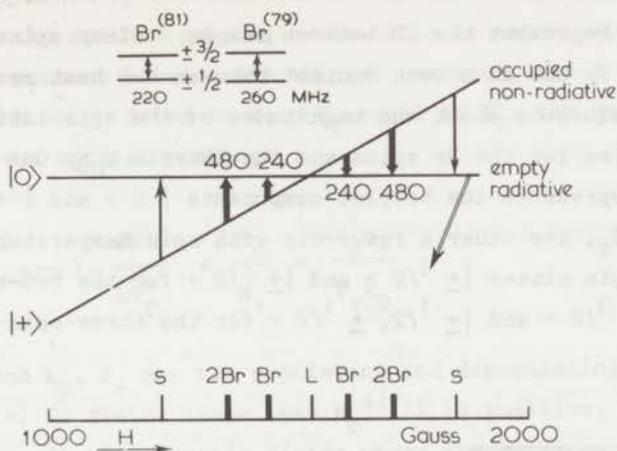


Fig. 5.17 The two triplet substates $|0\rangle$ and $|+\rangle$ of DBB as a function of magnetic field for $\vec{H} // z$. The fields are indicated where CR with one and two Br nuclear spins occurs.

$|0\rangle$ and at the same time one or two Br nuclear spins make a transition from their upper state $|+\frac{3}{2}\rangle$ to the lower state $|+\frac{1}{2}\rangle$. The total energy is then conserved but the population of the radiative state $|0\rangle$ is increased and thus the phosphorescence intensity rises. A similar process would happen during CR at the fields higher than $H_c^{(z)}$. However, in our experiments the magnetic field sweep is always so slow that the system remains in a steady-state all the time. Then, only by solving the rate equations analogous to (5.10) we might hope to predict whether the CR processes discussed here lead to an increase or decrease of the phosphorescence intensity. This has not been done because the CR rate is unknown and the error in the populating and depopulating rates of the phosphorescent state too large to predict the sign of such a subtle effect. Experimentally we find all lines in fig. 5.14 correspond to an increase in light intensity, so qualitatively the picture of what happens during a fast sweep is

not so bad.

When we represent the CR between the Br nuclear spins and the triplet spin in DBB as a heat contact between two heat reservoirs we can draw conclusions about the magnitudes of the spin-lattice relaxation time for the Br spins and the CR rate k_{CR} . One of the reservoirs represents the triplet components $|0\rangle$ and $|+\rangle$ with spin temperature T_T , the other a reservoir with spin temperature T_{Br} of the Br nuclear spin states $|\pm^{3/2}\rangle$ and $|\pm^{1/2}\rangle$ for the two-spin CR case or $|\pm^{3/2}, \pm^{3/2}\rangle$ and $|\pm^{1/2}, \pm^{1/2}\rangle$ for the three-spin CR process (fig. 5.18).

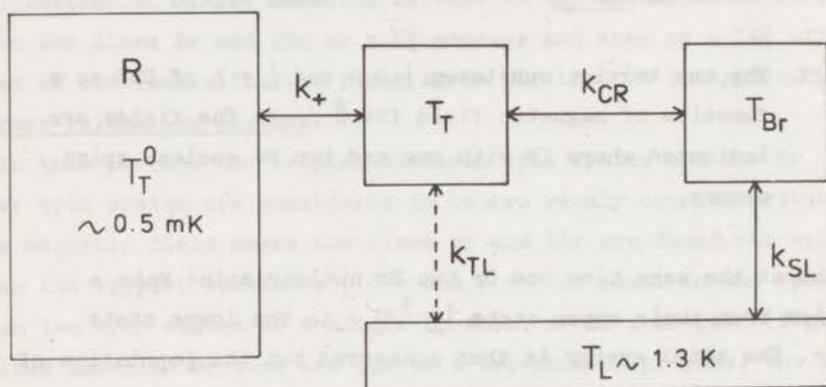


Fig. 5.18 Cross-relaxation between the triplet spin system with spin temperature T_T and the bromine nuclear spin system with temperature T_{Br} . The temperature of the "refrigerator" R is calculated from the zero-field steady-state populations in a magnetic field where $|\epsilon_+ - \epsilon_0| = 240 \text{ MHz}$. The lattice temperature T_L is the crystal temperature.

Because in our experiments the temperature is so low that spin-lattice relaxation of the triplet spins can be neglected during the lifetime of the substates, the spin temperature T_T (in the absence of CR) is

completely determined by the relative steady-state populations established in the optical pumping cycle. This is represented in fig. 5.18 by a heat contact between the triplet reservoir and a "refrigerator" R which tries to keep T_T equal to T_T^0 , the value determined by the optical pumping:

$$\exp\left(-\frac{\Delta E}{kT_T^0}\right) = \frac{N_0}{N_+} = \frac{P_0 k_+}{P_+ k_0} \quad (5.12)$$

where P_0 , P_+ and k_0 , k_+ are the populating and depopulating rates of $|0\rangle$ and $|+\rangle$. In fields lower than $H_c^{(z)}$ ΔE is positive, in higher fields negative. At the magnetic fields where the Br lines occur, $|T_T^0|$ is about 0.5 mK. The heat reservoir of the Br nuclear spins is in contact via spin-lattice relaxation with the lattice with a temperature $T_L \approx 1.3$ K. The spin temperature of the Br nuclear spins in the absence of CR, T_{Br}^0 , is equal to T_L .

If $T_T^0 \neq T_{Br}^0$ then owing to CR both spin temperatures change in such a way that the difference between them decreases, thus T_T shifts towards T_L . In a fast passage sweep the number of excited molecules remains equal and then a shift of T_T towards T_L results in a larger population of $|0\rangle$ and therefore in an increase of phosphorescence intensity. As discussed before, this effect is weakened in a slow passage sweep.

The triplet spin temperature T_T during CR is determined by the competition between three rates:

the rate of heat exchange between R and the triplet system, which is of the order of the depopulating rate k_+ of substate $|+\rangle$ (because $k_0 \gg k_+$);

the CR rate k_{CR} between the triplet system and the Br nuclear spins;

the spin-lattice relaxation rate k_{SL} of the Br nuclear spins. The changes of T_T and T_{Br} during CR depend on the relative magnitude of these three rates and we can distinguish the following cases

according to which of the rates is lowest

1°. slow cross-relaxation $k_{CR} \ll k_+, k_{SL}$

2°. slow spin-lattice relaxation $k_{SL} \ll k_{CR}, k_+$

3°. slow "cooling" of the triplet spins $k_+ \ll k_{CR}, k_{SL}$

4°. an intermediate case $k_+ \sim k_{CR} \sim k_{SL}$.

In the first case T_T and T_{Br} hardly change during the CR process from their values T_T^0 and T_{Br}^0 and CR has a negligible influence.

In the second case T_T in steady-state is almost equal to T_T^0 , but a substantial change in T_T may occur initially when the CR contact is established. Because the Br system in this case is almost isolated from the lattice T_{Br} and T_T tend to become equal in a short time and then both temperatures are pulled towards T_T^0 . The Br spins are polarized by the contact with the triplet spins. If in our experiments situation 2° would occur, then a change in phosphorescence intensity would be found only during the first moments of CR contact. In steady-state with CR the change in phosphorescence intensity would be very small, or not even measurable. This does not hold for the lines labelled Br and 2Br in fig. 5.14, but the situation 2° will arise in the next chapter.

In the third case the triplet system via the Br nuclear spin system is in strong contact with the lattice. The contact with the lattice is stronger than with the "refrigerator" R and therefore the populations of triplet substates $| + \rangle$ and $| 0 \rangle$ in the presence of CR are determined by the Boltzmann factor corresponding to the lattice temperature. We think this situation applies to the Br lines in DBB because of the following considerations. First we established that the LAC line of fig. 5.14 when integrated is about equal to the change in phosphorescence intensity observed when equalizing the populations of

the triplet substates $| + \rangle$ and $| 0 \rangle$ via saturation of the ESR transition that connects them. This finding is in agreement with (5.7). Further, Boltzmann equilibrium between $| 0 \rangle$ and $| + \rangle$ at the field where $\epsilon_+ - \epsilon_0 = 240$ MHz corresponds in good approximation to equality of the populations of $| + \rangle$ and $| 0 \rangle$ at 1.3 K. Therefore, in case 3^o we expect a change in phosphorescence intensity equal to that observed due to LAC between $| + \rangle$ and $| 0 \rangle$. This clearly holds for the Br lines in fig. 5.14 because their widths happen to be equal to the width of the LAC line. Thus we conclude that for this CR process $k_{CR} \gg k_+$ and further that the spin-lattice relaxation rate k_{SL} of the Br nuclear spins is much higher than k_+ , which does not seem unreasonable because it is known that spins with a large quadrupole coupling have short spin-lattice relaxation times (Abragam 1967).

The lines denoted by 2Br in fig. 5.14 correspond to case 4^o of (5.13). When k_{CR} and/or k_{SL} become of the order of k_+ the contact via the Br nuclear spins with the lattice is no longer strong enough to bring the two triplet components $| + \rangle$ and $| 0 \rangle$ in complete equilibrium with the lattice and this results in a relatively weaker line 2Br. That the CR rate for the three-spin CR process is smaller than for the two-spin process is not surprising because it is a higher order process.

The level anticrossing picture.

In the LAC picture the triplet electron spin and two Br nuclear spins are considered as one molecular spin system. The states of this spin system as a function of magnetic field for $\vec{H} // z$ are shown in fig. 5.19. The states are denoted by three labels: the first refers to the electronic spin state, the two others to the states of the Br nuclear spin pair. Each state in this figure is four-fold degenerate because each Br spin has two spin states which both are degenerate on the scale of fig. 5.19. At the magnetic field $H_c^{(z)}$ anticrossings occur between electron spin states with the same nuclear wave function. The other crossings in fig. 5.19 are between spin states with different nuclear wave functions. Therefore, the lines denoted by Br and 2Br in

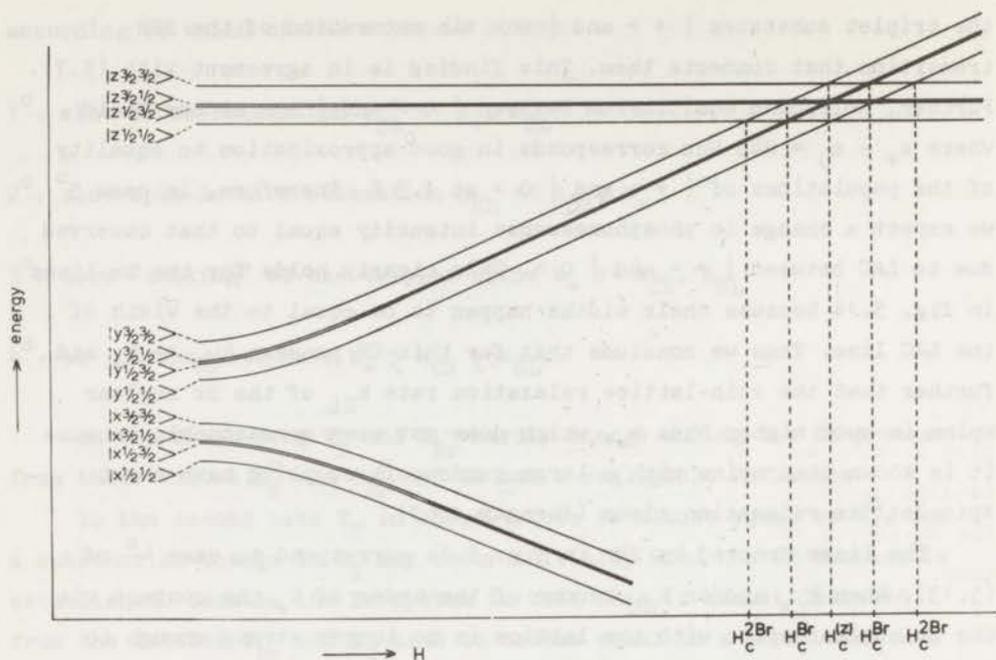


Fig. 5.19 The possible crossings when the triplet spin and two Br nuclear spins are considered as one system. The nuclear spin quantum numbers $3/2$ and $1/2$ stand for $\pm 3/2$ and $\pm 1/2$.

fig. 5.14 may also be interpreted as crossings between electronic spin states with different nuclear wave functions, which change into anti-crossings by the effect of hyperfine interaction. The same hyperfine interaction arises in the formula for the CR rate (4.39) and therefore it seems worthwhile to consider this interaction in more detail. The hyperfine interaction (5.11) can be represented as

$$\begin{aligned}
 \mathcal{H}_{\text{HF}} &= A_{xx} S_x I_x(1) + A_{y'y'} S_{y'} I_{y'}(1) + A_{z'z'} S_{z'} I_{z'}(1) + \\
 &A_{xx} S_x I_x(2) + A_{y''y''} S_{y''} I_{y''}(2) + A_{z''z''} S_{z''} I_{z''}(2) = \\
 &= S_x A \{I_x(1) + I_x(2)\} + \qquad (5.14) \\
 &S_y \{B \cos \phi (I_{y'}(1) + I_{y''}(2)) + C \sin \phi (I_{z'}(1) - I_{z''}(2))\} + \\
 &S_z \{-B \sin \phi (I_{y'}(1) - I_{y''}(2)) + C \cos \phi (I_{z'}(1) + I_{z''}(2))\}
 \end{aligned}$$

Here it has been assumed that the tensor of the hyperfine interaction is diagonal in the axes system x, y', z' for Br atom 1 and x, y'', z'' for Br atom 2 (fig. 5.20), with principal values A, B, C along these axes.

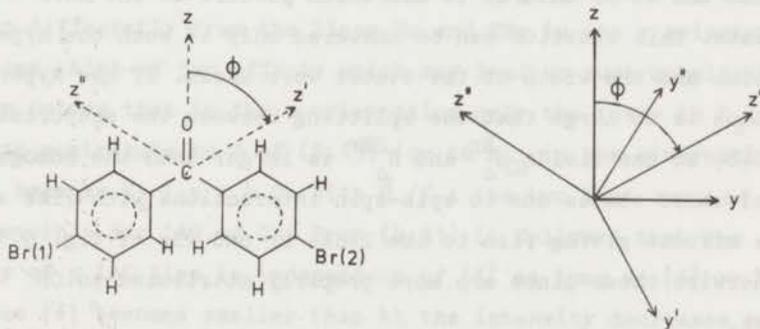


Fig. 5.20 The principal axes systems in 4,4'-dibromobenzophenone. The x axis is the same for all three systems.

When two states of fig. 5.19 $|+\chi_1\rangle$ and $|0\chi_2\rangle$ cross, where $|\chi_1\rangle$ and $|\chi_2\rangle$ are nuclear spin wave functions, then this becomes an anticrossing if

$$\langle +\chi_1 | \mathcal{H}_{\text{HF}} | 0\chi_2 \rangle = \delta > \hbar k_{\text{eff}} ; \qquad (5.15)$$

k_{eff} is the width of the states of fig. 5.19. In the picture we are considering, interaction with other triplet systems is assumed to be negligible and k_{eff} is determined by the decay properties of the electronic spin components and the spin-lattice relaxation between the nuclear spin states which we have seen to be fast.

At first sight we would expect the anticrossing lines at H_c^{Br} to be smaller than the LAC line at $H_c^{(z)}$ because at H_c^{Br} fewer molecules are involved.

However, if the spin-lattice relaxation between the nuclear states of the electronic manifolds is faster than their lifetimes, all molecules in $| + \rangle$ and $| 0 \rangle$ contribute to the LAC signals at H_c^{Br} and therefore these lines are as strong as the LAC line at $H_c^{(z)}$. That the lines 2Br are smaller points to the case where $|\delta|$ becomes of the order of $\hbar k_{\text{eff}}$. As we have seen this weakens the LAC effect.

We have presented two completely different pictures for the same phenomenon and it is natural to ask which picture is the more appropriate. This question can be answered only if both the hyperfine interaction and the width of the states were known. If the hyperfine interaction is so large that the splitting between the anticrossing states $2|\delta|$ at the fields H_c^{Br} and $H_c^{2\text{Br}}$ is larger than the homogeneous widths of these states due to spin-spin interactions with like spins, then the effects giving rise to the lines Br and 2Br of fig. 5.14 are LAC, otherwise these lines are more properly attributed to CR processes.

For the lines Br we cannot say which effect is the cause but for the lines 2Br we concluded in the LAC picture that $|\delta|$ must be of the order of $\hbar k_{\text{eff}}$. The homogeneous width of the states involved is not smaller than k_{eff} which means that for the line 2Br we have the case that $2|\delta|$ is of the order of the homogeneous width. According to the definition of chapter 4 section F these lines are then caused by a CR process.

Whatever picture is used, we arrive in both cases at the conclusion that the spin-lattice relaxation time of the Br nuclear

spins at a magnetic field of the order of 1500 Gauss and temperature between 1.3 and 4.2 K is shorter than $k_+^{-1} \sim 20$ msec. Apart from this conclusion specific for the experiments in DBB we can draw a more general conclusion:

If there is no information about the magnitude of the interaction between two spin systems or if one is not interested in the precise mechanism of the process, then phenomena caused by CR between two systems can equally well be described as arising from a LAC effect in the combined system and vice versa.

In the x orientation the results are more complicated and not really understood. When the magnetic field is oriented parallel to the x axis by making the ESR lines stationary, a broad LAC line (width 72 Gauss) is found without any further lines (fig. 5.15 a). By turning the magnet away from this orientation sharper lines appear on the (broadened) LAC line (fig. 5.15 b). It seems without doubt that these lines are caused by the Br nuclear spins but the question is why they behave so differently from the lines Br and 2Br in the z orientation.

We can think of two effects which may lead to such complications. First, we notice that in the z orientation only the terms in S_x, S_y of (5.14) can contribute to δ of (5.15) (or to k_{CR} in the alternative CR picture) because $S_z | z \rangle = 0$. With $\vec{H} // x$ the two last rows of (5.14) are responsible for LAC or CR. From (4.31) it followed that the intensity of a LAC line is independent of $|\delta|$ as long as $|\delta| \gg \hbar k$ but as soon as $|\delta|$ becomes smaller than $\hbar k$ the intensity decreases roughly with a factor $|\delta|^2 / \hbar^2 k^2$ as can be derived from (4.28). Hence, if B and C of (5.14) were substantially smaller than k_{eff} but A larger, then in the z orientation $|\delta|$ may be large enough to cause changes in phosphorescence intensity but with $\vec{H} // x$ $|\delta|$ might be too small to effect a change in the emission intensity. The ratio of the hyperfine components of Br substituted on a ring are not known, but for chlorine A indeed is larger than B and C, probably at least by a factor of 10 (see for instance Buckley and Harris 1970). In our DBB crystal k_{eff} is not thought to exceed 10^6 sec^{-1} and the explanation given above thus

requires that both B and C are well below 1 MHz!

Another possibility, to which one is led by the considerable width of the LAC line, is that in contrast to the z axes the molecular x axes are not exactly parallel but show a spread in orientation. In order to arrive at a more definite explanation it would be necessary to make a careful study of the behaviour of these lines as a function of the orientation of the magnetic field. Unfortunately, our procedure for growing the crystals and mounting them in the sample tube proved to be such that the DBB x axes lie roughly perpendicular to the axis of the tube. That is they fall in a region which, because of the geometry of our present experimental set up, is inaccessible for experiments with a high degree of orientational precision.

D. 4,4'-dichlorobenzophenone

1. Preparation and structure of the crystal.

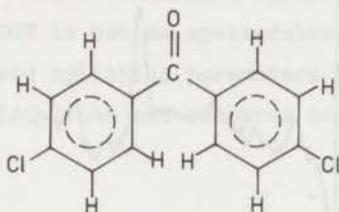


Fig. 5.21 4,4'-dichlorobenzophenone

4,4'-dichlorobenzophenone (DCB) was recrystallized from ethanol and zone-refined (40 passes). The crystals were grown from ether solution and are monoclinic with four molecules in the unit cell. The molecular axes of all four sites are parallel; the direction cosines of the molecular axes relative to the crystal axes are given by Dym and Hochstrasser (1969).

2. Level anticrossing and cross-relaxation.

The spectra of DCB are given in figs. 5.22 and 5.23. The low-field spectrum of fig. 5.22 shows the triplet-triplet and triplet-radical CR line which proves that indeed all DCB molecules in the crystal are magnetically equivalent when $\vec{H} // z$.

The spectra in fig. 5.23 show the LAC lines and the S-lines around them. We may point to two differences compared to benzophenone and DBB. First, the S-lines are split and second, they are found at magnetic fields much closer to the LAC lines.

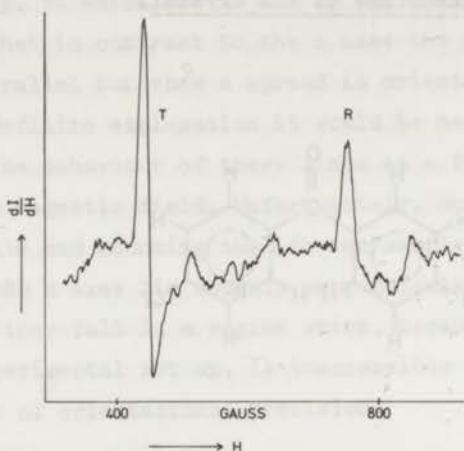


Fig. 5.22 The triplet-triplet and triplet-radical CR line in DCB for $\vec{H} // z$.

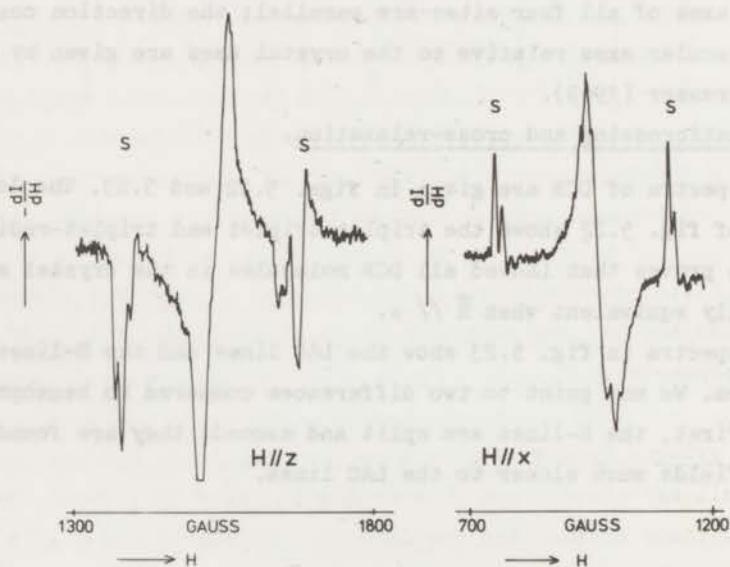


Fig. 5.23 The LAC lines and S-lines in DCB.

The LAC lines, especially in the x orientation, have a structure which is thought to be caused by the chlorine nuclear spin. Just as in DBB the nuclear spin states are split by a quadrupole interaction which, however, is much smaller than for the bromine nuclei (for Cl⁽³⁵⁾ in ClC₆H₅ Q ~ 35 MHz, Das and Hahn 1958). Therefore the splitting of the LAC line in DCB is not as spectacular as in DBB.

The zero-field splitting parameters have been determined from the position of the LAC lines and compared to the values calculated from ESR (table 5.4).

Table 5.4

	ESR	LAC
X	-0.0719 cm ⁻¹	-0.0720 cm ⁻¹
Y	-0.0237	-0.0245
Z	0.0956	0.0966

The z.f.s. parameters of 4,4'-dichlorobenzophenone determined by ESR and LAC experiments. The signs have been chosen as in benzophenone.

E. Other systems studied

In all systems we have looked at LAC and/or CR signals were observed. These systems are, besides the crystals already mentioned, single crystals of anthraquinone, pyrimidine as a guest molecule in a benzene crystal, durene aldehyde in a durene crystal, single

crystals of 4-bromobenzaldehyde and of 4,4'-difluorobenzophenone.

The spectra of most of these components are complicated and only partly understood. In all these substances photochemical products (triplets and doublets) are detected via CR. Here we only give the results of two of these crystals; pyrimidine in benzene and 4,4'-difluorobenzophenone.

Pyrimidine in benzene.

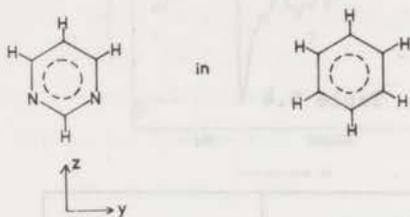


Fig. 5.24 Pyrimidine in benzene.

The crystal preparation and the populating and depopulating of the lowest triplet state are given by Burland and Schmidt (1971).

The LAC lines are shown in fig. 5.25; these are broader than in benzophenone (74 Gauss for $\vec{H} // x$ and 53 Gauss for $\vec{H} // z$).

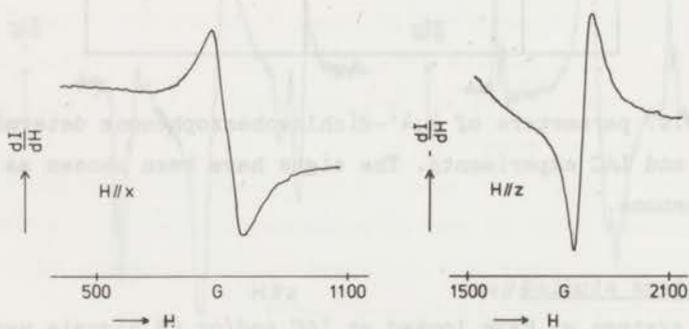


Fig. 5.25 The LAC lines in a pyrimidine/benzene crystal. Both lines correspond to an increase in light intensity. The line in the z orientation is 8 times weaker than in the x orientation.

Also in this crystal a free radical is detected via CR (see fig. 5.26).

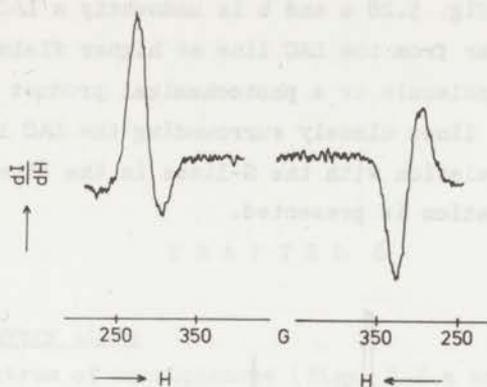


Fig. 5.26 The line found at 293 Gauss with $\vec{H} // x$ which is the result from CR between pyrimidine and a free radical.

The line shape of this line depends on the direction of the field sweep. In the next chapter we shall see that this is characteristic for a line resulting from CR between a triplet spin and a spin species with a relatively slow spin-lattice relaxation.

4,4'-difluorobenzophenone.

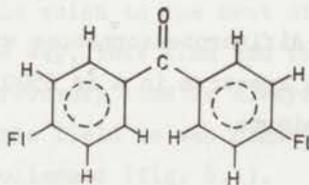


Fig. 5.27 4,4'-difluorobenzophenone.

The spectrum of 4,4'-difluorobenzophenone with $\vec{H} // z$ is given in fig.

5.28. This spectrum is quite different from the corresponding spectra of benzophenone, 4,4'-dibromobenzophenone and 4,4'-dichlorobenzophenone. The strongest line of fig. 5.28 a and b is undoubtedly a LAC line. The two lines relatively far from the LAC line at higher fields seem to be caused by an impurity molecule or a photochemical product excited into the triplet state. The lines closely surrounding the LAC line in fig. 5.28 seem to have no relation with the S-lines in the other crystals and no explanation is presented.

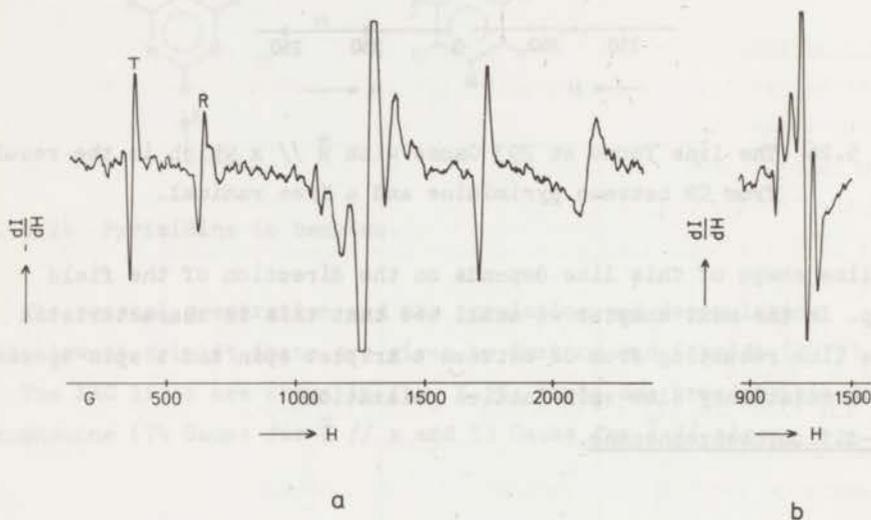


Fig. 5.28 The spectrum of 4,4'-difluorobenzophenone with $\vec{H} // z$; the sweep rate of the spectrum in a is 2500 Gauss/5 minutes, in b 1000 Gauss/0.5 minute.

CHAPTER 6

A. The slow-recovery lines

In the spectrum of benzophenone (figs. 5.2 a and 5.3), 4,4'-dibromobenzophenone (fig. 5.14) and 4,4'-dichlorobenzophenone (figs. 5.23) a pair of lines is found almost symmetrically located around the LAC line. These lines we call slow-recovery or S-lines, because of their peculiar "slow" behaviour. When the magnetic field is swept through one of these lines and then swept back again, the line involved is either completely absent or weak in the reverse sweep. If we wait a certain time before sweeping back, we may find the S-line again. The time one has to wait before the line has recovered its original intensity is strongly dependent on the crystal. In our first experiments on benzophenone (Veeman and Van der Waals 1970 a) the recovery time was about 30 seconds. Later, in experiments with new benzophenone crystals which to the best of our knowledge had been prepared in the same way, this time had increased to more than 10 hours! In DBB and DCB the recovery time is always longer than 10 hours.

When the magnetic field is set right on top of one of these S-lines, the line collapses (fig. 6.1).

When the recovery time is very long the only way to find a collapsed line again is by sweeping through its partner on the opposite side of the LAC line. An example of this is given in fig. 6.2 where three subsequent sweeps through the spectrum of benzophenone are shown together with an explanation of what happens.

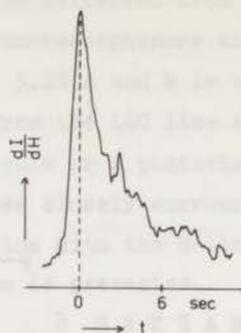


Fig. 6.1 The collapse of an S-line of benzophenone when the magnetic field is set on top of the line at time $t = 0$.

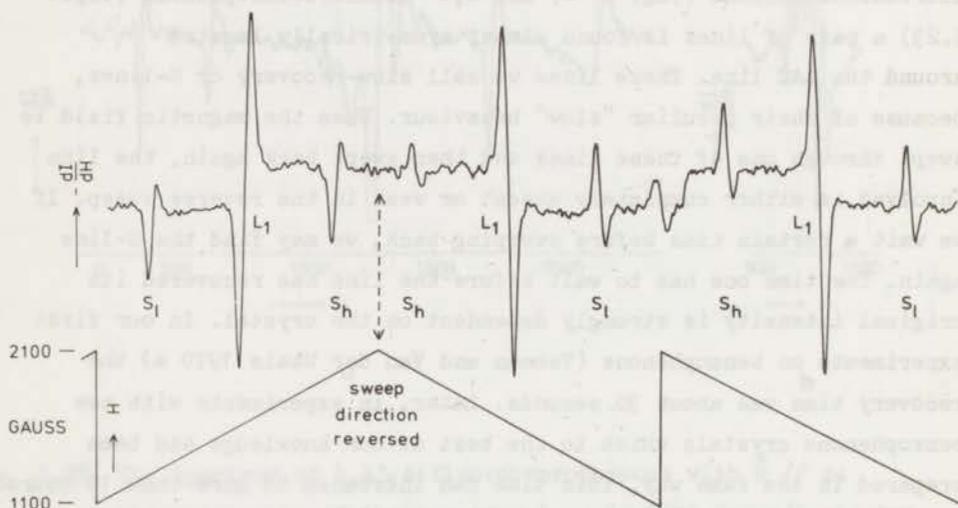


Fig. 6.2 Three subsequent sweeps through the S-lines of benzophenone with $\vec{H} // z$. In the first sweep the magnetic field is increased from 1100 to 2100 Gauss and two lines around the LAC are observed, S_1 and S_h . At the end of this sweep the sweep direction is reversed and in the second sweep the high-field S-line S_h is found to be much weaker than in the first sweep. If the sweep time is made longer than used in

this spectrum (1000 Gauss in 2.5 minutes) the high-field S-line S_h in the second sweep is completely gone. The original line intensity can only be recovered by sweeping through the low-field S-line S_l , as shown at the right.

A similar behaviour of the S-lines in DCB is shown in fig. 6.3.

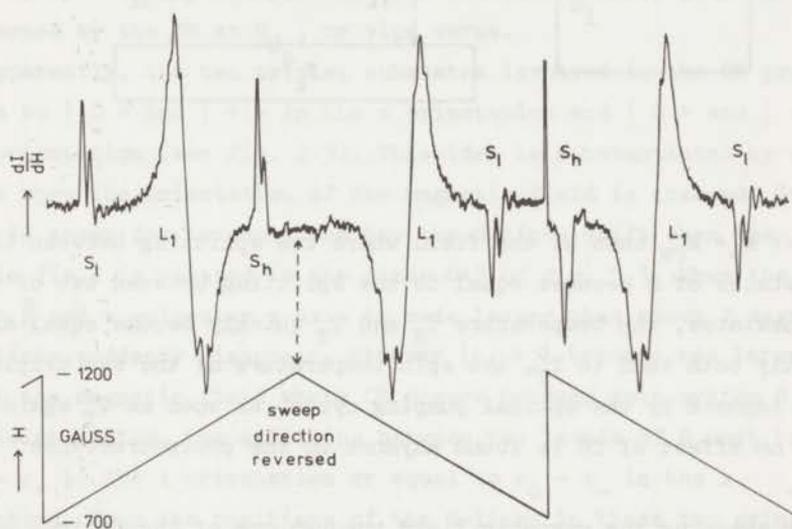


Fig. 6.3 Three subsequent sweeps through the S-lines of 4,4'-dichlorobenzophenone with $\vec{H} // x$. The sweep time is 500 Gauss in 10 minutes.

The slow behaviour is what one would expect for these lines resulting from CR between a triplet state system and another spin system with a slow spin-lattice relaxation (case 2^o of section 5C), $k_{SL} \ll k_{CR}, k_+$. This case is once more represented in fig. 6.4; T_S here represents the spin temperature of the unknown system S, which we shall later identify with "free" hydrogen atoms.

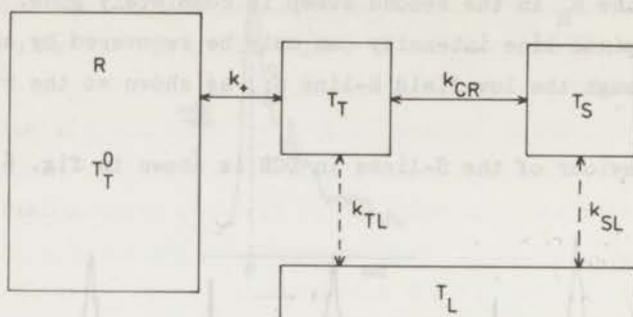


Fig. 6.4.

When $k_{SL} \ll k_+ < k_{CR}$ then at the field where the splitting between the two spin states of S becomes equal to the splitting between two of the triplet substates, the temperature T_S and T_T quickly become equal and subsequently both tend to T_T^0 , the spin temperature of the two triplet substates imposed by the optical pumping cycle. As soon as T_T again equals T_T^0 no effect of CR is found anymore on the phosphorescence intensity.

After sweeping the magnetic field through one of the S-lines say S_1 at field H_{S_1} , the spins S are polarized and have the same spin temperature as the two triplet substates. When the field is then swept once more through the field H_{S_1} no effect in the light intensity can be observed as long as the polarization of the spins S is unchanged. A recovery time of the S-line of more than 10 hours found for $T \leq 4.2$ K in some of the benzophenone crystals, in DCB and in DBB implies that the spin-lattice relaxation time of spins S is longer than 10 hours.

When the magnetic field is swept slowly through an S-line, the spins S become polarized already before the magnetic field has reached the point where the cross-relaxation rate is maximal and instead of a dispersion-shaped line we find approximately the first half of it (see e.g. first signal in fig. 6.2). When the field sweep is made faster, the line shape approaches the normal derivative form.

In fig. 6.2 and 6.3 we have seen that an S-line which has been collapsed can be made to reappear by sweeping through the other S-line. This is easy to understand: when the two triplet substates involved are the two states which are anticrossing at the field H_c the electron spin temperature T_T^0 at the left of the crossing is roughly opposite to that at the right of the crossing. Thus when the spins S have been polarized by the triplet spins at the CR field H_{S_1} this polarization is reversed by the CR at H_{S_2} , or vice versa.

Apparently, the two triplet substates involved in the CR process have to be $|0\rangle$ and $|+\rangle$ in the z orientation and $|0\rangle$ and $|-\rangle$ in the x orientation (see fig. 2.3). This idea is substantiated by what happens when the orientation of the magnetic field is changed. In fig. 5.8 it is shown for benzophenone how the S-lines shift when the magnetic field is rotated in the plane OAB of fig. 5.1. When the angle between \vec{H} and a molecular z axis is made larger than about 7 degrees the S-lines suddenly disappear, because $|\epsilon_0 - \epsilon_+|$ becomes too large.

At the magnetic field where CR occurs between spin system S and the triplet system, the splitting between two levels of S must be equal to $\epsilon_0 - \epsilon_+$ in the z orientation or equal to $\epsilon_0 - \epsilon_-$ in the x orientation. From the positions of the S-lines in these two principal orientations the splitting between the two states of the system S can be calculated. The results are summarized in table 6.1.

	H_{S_1}	H_{S_2}	H_{S_3}	H_{S_4}	H_{S_5}	Triplet substates
z orientation						$ 0\rangle, +\rangle$
x orientation						$ 0\rangle, -\rangle$

Table 6.1

molecule	orientation	measured magnetic fields of S-lines	calculated splitting of system S	$E_3 - E_4$ of free hydrogen atoms (see fig. 6.5)
benzophenone	$\vec{H} // z$	1380 (2) Gauss 1970 (2)	830 (6) MHz 806 (6)	837 MHz 801
	$\vec{H} // x$	505 (5) 1300 (2)	1013 (3) 859 (6)	1005 845
4,4'-dibromobenzophenone	$\vec{H} // z$	1234 (2) 1843 (2)	850 (6) 834 (6)	850 808
4,4'-dichlorobenzophenone	$\vec{H} // z$	1371 (2)	480 (6)	838
		1381 (2)	455 (6)	837
		1398 (2)	410 (6)	835
		1656 (2)	425 (6)	817
		1675 (2)	475 (6)	816
		1684 (2)	495 (6)	815
	$\vec{H} // x$	759 (2)	440 (6)	926
	774 (2)	408 (6)	923	
	1122 (2)	410 (6)	868	
	1135 (2)	438 (6)	862	

Table 6.1 The splittings of the spin system S responsible for the slow lines. The energies in the fourth column are calculated with the aid of (2.7) and (2.8) from the magnetic fields given in the third column. The fields in this column are the mean of five experiments for benzophenone and three experiments for the other molecules.

The numbers in parentheses are the standard deviations of the mean. For benzophenone when $\vec{H} // x$ axis of molecule 1 the splitting between $|0\rangle$ and $|- \rangle$ of molecule 1 at 505 Gauss is 845 MHz, the corresponding splitting in molecule 2 whose x axis makes an angle of 22° with \vec{H} , is 1013 MHz. It is assumed that molecule 2 is responsible for the S-line, but this is not proven.

For 4,4'-dichlorobenzophenone it is indicated that the S-lines are split into three components when $\vec{H} // z$ and into two components for $\vec{H} // x$ (see fig. 5.23).

The results of the experiments on 4,4'-difluorobenzophenone have not been included because the assignment of the lines in fig. 5.28 is not clear.

The energies in the last column are the splitting between the two lower spin states of a free hydrogen atom (fig. 6.5) calculated with the Breit-Rabi formula.

B. Free hydrogen atoms as the cause of the S-lines

The idea occurred to us that the unknown spin system might consist of the two lowest states of photochemically produced free hydrogen atoms. A free hydrogen atom has an electron spin $\frac{1}{2}$ and a nuclear spin $\frac{1}{2}$, coupled by a very large isotropic hyperfine interaction (coupling constant $a = 1421$ MHz) which leads to the energy level scheme of fig. 6.5.

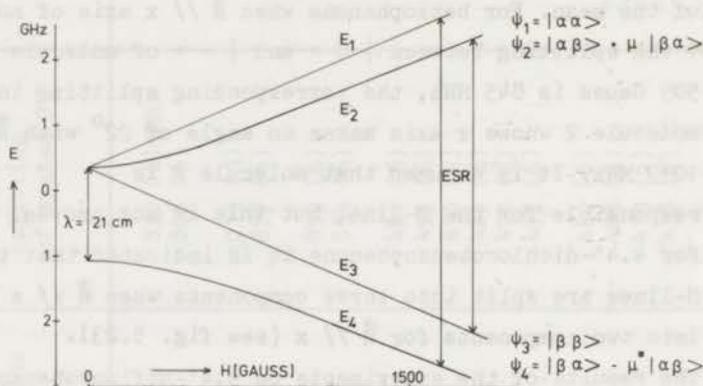


Fig. 6.5 The spin states of a free hydrogen atom according to Breit and Rabi (1931).

For comparison the splitting $E_3 - E_4$ between the two lowest spin states ψ_3 and ψ_4 at the magnetic fields where the S-lines are found, is given in the last column of table 6.1. For benzophenone and DBB the agreement of these energies with the calculated splittings of system S is surprising. The splittings in DCB are roughly half of the energies $E_3 - E_4$ and also much smaller than the difference $E_1 - E_2$ of the hydrogen atoms.

Because of the close agreement between the energies of the two last columns of table 6.1 for benzophenone and DBB it seems that indeed in these crystals free hydrogen atoms are causing the S-lines. However experiments which we shall discuss next do not prove this unambiguously and therefore it is no more than a reasonable assumption that the free

hydrogen atoms cause the S-lines.

The most remarkable thing about the S-lines, assuming free hydrogen atoms to be responsible, is the missing of CR lines with the two upper states of fig. 6.5. At the magnetic fields of interest the splitting between ψ_1 and ψ_2 is much smaller than between ψ_3 and ψ_4 e.g. at 1500 Gauss $E_1 - E_2 = 593$ MHz and $E_3 - E_4 = 828$ MHz. Therefore one might expect to find a further pair of S-lines closer around the LAC lines; such lines however are not found.

Independent of the precise form of the interaction between the benzophenone triplet system and the hydrogen atoms, one can show that the same interaction that causes the CR transition $| + \rangle \rightarrow | 0 \rangle$ and simultaneously $\psi_3 \rightarrow \psi_4$ (low field S-line S_1) should also be effective for the CR process $| + \rangle \rightarrow | 0 \rangle$ and $\psi_2 \rightarrow \psi_1$. The same is true for the processes $| + \rangle \rightarrow | 0 \rangle$, $\psi_4 \rightarrow \psi_3$ and $| + \rangle \rightarrow | 0 \rangle$, $\psi_1 \rightarrow \psi_2$. Here $| 0 \rangle$ and $| + \rangle$ are the triplet substates with $\vec{H} // z$ and $\psi_1, \psi_2, \psi_3, \psi_4$ the four spin states of the hydrogen atom. The missing of two S-lines can therefore not be the consequence of some selection rule but must be attributed to a much smaller population (at least ten times smaller) of ψ_1 and ψ_2 relative to ψ_3 and ψ_4 . Because at 1500 Gauss the coefficient $|\mu|$ of fig. 6.5 is smaller than 0.16 this means that in these hydrogen atoms the electron spin is strongly polarized in the state $m_S = -\frac{1}{2}$. The mechanism causing this spin polarization is not clear, but we believe the polarization to be established during the photochemical creation or subsequent recombination of the hydrogen atoms. In the next section this will be discussed further.

ESR experiments on irradiated benzophenone crystals at helium temperatures show two lines (denoted by H in fig. 2.4) which are

- 1°. split by 530 Gauss and symmetrical around the field where free radical signals are found,
- 2°. existing longer than 30 minutes after the exciting light is cut off,

3°. independent of the orientation of the magnetic field.

We conclude that the ESR signals of fig. 2.4 denoted by H are caused by "free" hydrogen atoms, although the hyperfine splitting constant of these atoms calculated from the ESR line (1484 MHz) is somewhat larger than the free atomic value 1421 MHz. But according to experiments of Hall and Schumacher (1962) on hydrogen atoms doped in CaF_2 such a deviation seems possible. So we conclude that hydrogen atoms are present in benzophenone crystals irradiated at helium temperatures. Furthermore these ESR experiments show that already with a very weak microwave field ESR transitions can be induced in the hydrogen atoms. Therefore in a number of experiments it has been tried to saturate the ESR transitions in the H atoms causing the S-lines (see fig. 6.5) with a microwave oscillator and a broad band helix. By saturation or near saturation the population of the two upper states would be increased to such an extent that two extra S-lines would appear. In spite of several attempts this has been without success. Still assuming H atoms to cause the S-lines, the only explanation can be that the lifetime of the hydrogen atom as a free atom is very short. The microwave power of the tunable microwave oscillator is limited (~ 100 mW) and it is conceivable that the microwave induced transition probability in the hydrogen is much smaller than the inverse of the free atom lifetime t . In that case there is hardly any change in population of ψ_1 and ψ_2 . With the same microwave equipment however we could saturate transitions between benzophenone triplet substates and thus the lifetime of the free hydrogen atoms has to be shorter than $\sim 10^{-4}$ sec.

The hydrogen atoms which we detected by ESR, however, lived longer than 30 minutes so the hydrogen atoms responsible for the S-lines cannot be the same as the atoms causing the ESR signals. Also with another experiment we can prove that the H atoms causing the ESR spectrum are not responsible for the S-lines. We have shown before that by sweeping slowly through an S-line the spins S become polarized for a long time. Thus via the contact with the "cold" triplet state the

populations of ψ_3 and ψ_4 change, so that approximately only one of these states is populated. Which one depends on which S-line is collapsed. Then this should have an effect on the relative intensity of the two ESR lines denoted by H in fig. 2.4 but this is not observed.

The following experiment also strongly suggests that the lifetime of the hydrogen atoms causing the S-lines is very short. After sweeping through one of the S-lines it has been tried to induce by microwave irradiation transitions between the hydrogen states ψ_3 and ψ_4 in order to re-establish an equal population of ψ_3 and ψ_4 so that by sweeping again through this S-line it has its original intensity. However irradiation with the proper frequency during half an hour did not have any effect.

There seem to be two kinds of hydrogen atoms: one transient kind living 10^{-4} sec or shorter, which cannot be detected by ESR because of their short lifetime, but is responsible for the S-lines. Another, metastable kind lives 30 minutes or longer and that causes the ESR signals. Anticipating the next section it seems that the difference in lifetime depends on whether the hydrogen atoms are in a situation where they can recombine with triplet state benzophenone or not.

In a crystal of perdeuterated benzophenone we could not find any S-lines (figs. 5.10 and 5.11). This, at first sight, supports our idea that free H atoms are responsible for the S-lines in benzophenone. Then, however, the question arises why we do not see CR with free deuterium atoms. Although the hyperfine interaction in a free deuterium atom is much smaller than in a free hydrogen atom, it is large enough to resolve any S-lines from the strong LAC line, if the former were to appear. Two explanations are possible: first it has been noticed (Heller 1969; Yip and Siebrand 1972) that deuteration decreases the rate of certain photochemical reactions which as we shall see in the next section, may be responsible for the formation of free hydrogen or deuterium atoms. The second possible explanation is the following. In order to effect a change in the phosphorescence intensity the lifetime of the "free" H atoms may not be much shorter than the inverse of the rate for CR between the phosphorescent molecules and the H atoms. The

CR rate for D atoms $k_{CR}^{(D)}$ however must be lower than for H atoms, $k_{CR}^{(H)}$, because the gyromagnetic ratio γ_D of a deuterium nuclear spin is about 6.5 times smaller than that of a proton, γ_H . Whether the interaction between the phosphorescent molecules and the nuclear spins of the free atoms is via exchange interaction with the electrons, or via direct dipole-dipole coupling, in any case one would expect (see 4.39)

$$\frac{k_{CR}^{(D)}}{k_{CR}^{(H)}} = \left(\frac{\gamma_D}{\gamma_H}\right)^2 \approx \frac{1}{40}$$

It thus may be that the lifetime of the free deuterium atoms is too short compared to $k_{CR}^{(D)}$ to cause a change in phosphorescence intensity of benzophenone-d₁₀. To a certain extent this supports the idea of the existence of very short-living H atoms in benzophenone.

It is surprising that the S-lines in 4,4'-dichlorobenzophenone are caused by a spin system with a much smaller energy splitting (table 6.1) further the S-lines in this crystal are split (fig. 5.23).

Apparently, the substituting of two Cl atoms for two H atoms in the benzophenone molecule completely changes the S-lines and this also holds for fluorine substitution (see fig. 5.28). The recovery time > 10 hours again points to a spin system with a very long spin-lattice relaxation. This, together with the energy splittings of table 6.1, is the only knowledge we have about the unknown spin system which may be weakly bonded hydrogen atoms, photochemically produced "free" chlorine atoms, or colour centers.

Besides the above arguments which are more or less in favour of the existence of free hydrogen atoms in benzophenone and 4,4'-dibromobenzophenone, we have to mention an experiment which seems to disagree with this conclusion. This experiment has been inspired by the following reasoning. As said before, it is very likely that the lifetime of the free H atoms responsible for the S-lines is so short because they can recombine with benzophenone molecules. Further, we have seen that when

the S-line is collapsed the proton spin of the free atom stays polarized for a long time, which must mean that the polarization of the proton spin has to be transferred to the recombination product because the H atom itself lives only 10^{-4} sec or shorter. But then it should be possible to destroy the nuclear spin polarization (and rekindle the corresponding S-line) by applying an r.f. field which saturates the transitions between the two proton states in the recombination product. Unfortunately, attempts to do this have failed. A difficulty in this experiment is that we do not know the splitting of the two spin states that have to be "tickled" in the recombination product, because it is quite possible that the product is a radical (a ketyl radical, see next section) and then the splitting and thus the r.f. frequency to be used depends on the hyperfine interaction. Moreover, the lines may be very narrow.

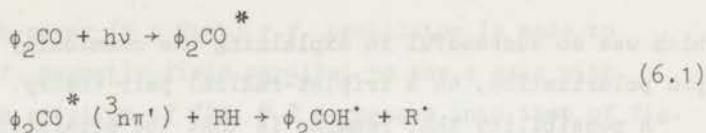
In spite of this negative experiment we believe that there are many arguments in favour of short-living H atoms being responsible for the S-lines. Then the conclusion from the S-lines is that these H atoms show a very strong electronic spin polarization.

C. Electron spin polarization and photochemistry.

In the previous section we arrived at the conclusion that when irradiating benzophenone (and 4,4'-dibromobenzophenone) crystals with UV light transient "free" hydrogen atoms occur which show a strong spin polarization: only the two lower spin states ψ_3 and ψ_4 of fig. 6.5 are populated. At the magnetic fields involved these two states correspond in reasonable approximation to the two hyperfine components with $m_I = \pm \frac{1}{2}$ of the electron spin state with $m_S = -\frac{1}{2}$. In the model we proposed the lifetime of the hydrogens as free atoms is short (10^{-4} - 10^{-6} sec) and therefore, to reach a steady-state, free atoms must be formed continuously with their electron spin parallel to the field by some photochemical process.

Spin polarization in photochemical products is not unusual. Many examples of photochemically induced nuclear spin polarization have been found (see for instance Kaptein 1971 and references in there), but only a few experimental results on photochemically induced electron spin polarization have been reported (Smaller, Remko and Avery 1968; Atkins, Buchanan, Gurd, McLauchlan and Simpson 1970). Smaller et. al. found photochemical products with one half of the hyperfine ESR lines in emission and the other half in enhanced absorption. Atkins et. al. observed products with all hyperfine lines in emission, which points to a pure electron spin polarization without nuclear spin polarization.

At first sight there is a remarkable resemblance between our results and those of Atkins et. al.. They observed emission ESR spectra from free radicals obtained by the exposure at room temperature of carbonyl compounds such as benzophenone in liquid paraffin solution to a pulse of 3371 Å light from a laser. The free radicals are thought to be produced through abstraction of hydrogen atoms from solvent molecules by excited carbonyl molecules. It is well-known that on irradiating benzophenone in solution ketyl radicals are formed through transfer of hydrogen atoms (Porter and Wilkinson 1961):



where $\phi_2\text{CO}$ = benzophenone

RH = hydrogen containing solvent molecule

$\phi_2\text{COH}^{\cdot}$ = ketyl radical.

The lowest $n\pi'$ triplet state is the reactive state of benzophenone in this process (Beckett and Porter 1963).

Suppose the radicals giving the emission ESR spectra observed by Atkins et. al. were the solvent radicals R^{\cdot} and if the electron spins forming the bond R-H are in a singlet state at the moment the bond is broken then the hydrogen atoms would come off in a state $m_s = -\frac{1}{2}$, just what we observe!

Apart from this general, very speculative consideration, the photochemistry of benzophenone in liquid solution does not seem to provide a clue to the mechanism that yields the S-lines in our spectra of solid benzophenone at liquid helium temperatures. The short lifetimes of the free hydrogen atoms and the long memory time of the nuclear spin polarization imposed by the CR may indicate that the H atoms recombine to a recombination product and become free again after a while, maintaining their state of nuclear polarization. A continuous process of recombination and separation between certain hydrogens and another system then must exist and during this (photochemical) process the electron spin polarization is thought to be created. It is reasonable to assume that the system which recombines with the hydrogen atoms is a triplet state benzophenone molecule, giving a ketyl radical. But it is not clear to us how pure electron spin polarization can be created in the process of the formation of the ketyl radical through recombination of a triplet state molecule and a free hydrogen atom. In particular we do not see how to explain our results by extending the radical pair theory of Closs (1969), Kaptein and Oosterhoff (1969),

which was so successful in explaining the chemically induced nuclear spin polarization, to a triplet-radical pair theory.

A possibility that remains is that the separation of an H atom from the ketyl radical is responsible for the spin polarization. But, since nothing is known about such a photochemical process this is just a speculation.

D. Transitions in a two-spin system induced by an r.f. magnetic field - experimental distinction between LAC and CR.

Several times we have mentioned that it is often difficult or even impossible to decide whether a change in phosphorescence intensity is caused by LAC or CR. This is illustrated in section 5C for 4,4'-dibromobenzophenone where the lines Br and 2Br of fig. 5.14 could be explained equally well as the result of a LAC effect or of a CR process. This distinction is so difficult because, as shown in section 4F and 5C, at the magnetic field where a two-spin CR process can occur between spins S_1 and S_2 , an anticrossing is found in the energy scheme of the combined system $F = S_1 + S_2$. A change in phosphorescence intensity at this magnetic field is attributed to a CR or LAC effect depending on the magnitude of the interaction between S_1 and S_2 relative to the width of the spin states near the crossing.

In this section we want to show that in some cases one can experimentally prove which of the two effects is involved. Therefore let us consider the following experiment. An r.f. coil is mounted in the cryostat close to a benzophenone crystal. The coil is mounted in such a way that when the magnetic field is parallel to the z axis of one of the benzophenone molecules the r.f. magnetic field is also parallel to this z axis. In this orientation the dependence of the phosphorescence intensity on magnetic field is shown in fig. 6.7 a; on either side of the LAC line two S-lines are present. Further, remember that the derivative of the phosphorescence intensity is shown because of magnetic field modulation and phase-sensitive detection of the P.M. output.

When now a high-power (~ 5 Watt) r.f. oscillator is made to produce a strong r.f. magnetic field parallel to the z axis with frequency 65 MHz the spectrum of fig. 6.7 a changes into that of fig. 6.7 b. Apart from a number of strong lines in the LAC region it is surprising that the S-lines have got two satellites around them. The strong lines in the LAC region are easily explained as changes in phosphorescence intensity caused by r.f. induced transitions between the two triplet substates $|0\rangle$ and $|+\rangle$ which have, close to the anticrossing, somewhere a splitting of 65 MHz. The r.f. power is so large that even with the r.f. field as perfectly parallel to the z axis as possible the first and second harmonics of 65 MHz give strong changes in phosphorescence intensity at the magnetic fields where $|\epsilon_0 - \epsilon_+| = 130$ MHz and 195 MHz. It could be checked however, that the satellites of the S-lines are caused by the 65 MHz r.f. field.

Neither in the free hydrogen atom, nor in the benzophenone molecule spin states exist which have a splitting of 65 MHz at the fields where the satellites of the S-lines occur. However, we can find this splitting in the combined system $F = S_1 + S_2$ where S_1 is the triplet system (substates $|0\rangle$ and $|+\rangle$) and S_2 corresponds to the hydrogen states ψ_3 and ψ_4 of fig. 6.5. The states $|0\psi_4\rangle$ and $|+\psi_3\rangle$ of spin F are crossing each other in the absence of an interaction between S_1 and S_2 at the magnetic field H_{S_1} where the low-field S-line is observed. A crossing between $|0\psi_3\rangle$ and $|+\psi_4\rangle$ is found at a higher field H_{S_2} . As a result of the interaction \mathcal{H}' between S_1 and S_2 these crossings become anticrossings and in the case of fig. 6.6 the new eigenfunctions are

$$\begin{aligned}\phi_1 &= \{1 + |R|^2\}^{-\frac{1}{2}} (R |0\psi_4\rangle + |+\psi_3\rangle) \\ \phi_2 &= \{1 + |R|^2\}^{-\frac{1}{2}} (|0\psi_4\rangle - R |+\psi_3\rangle)\end{aligned}\tag{6.2}$$

where R is given by (4.25)

$$R = \frac{\delta}{\frac{1}{2}|\Delta E| + \{\frac{1}{4}(\Delta E)^2 + |\delta|^2\}^{\frac{1}{2}}}\tag{6.3}$$

and

$$\delta = \langle 0\psi_4 | \mathcal{H}' | +\psi_3 \rangle .$$

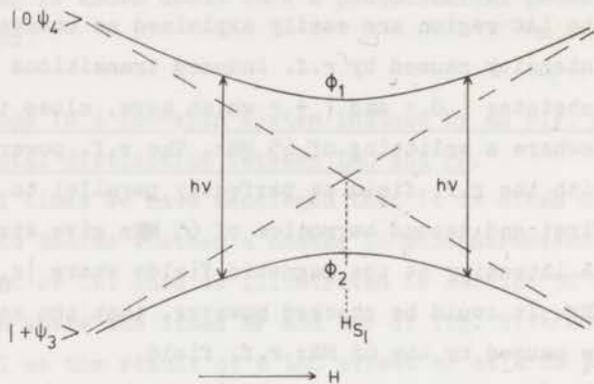


Fig. 6.6. The anticrossing of two states of spin F at the field where the low-field S -line S_1 is found.

Owing to the mixing between $|0\psi_4\rangle$ and $|+\psi_3\rangle$ an r.f. field with amplitude H_1 parallel to z can induce transitions between ϕ_1 and ϕ_2 with a transition moment:

$$\begin{aligned} & \langle \phi_1 | g\beta H_1 \{S_z(T) + S_z(H)\} - g_N \beta_N H_1 I_z | \phi_2 \rangle = \\ & = \frac{-RH_1}{1+|R|^2} \{g\beta \operatorname{Re}(i\zeta_x \zeta_y^*) - (g\beta - g_N \beta_N) \frac{|\mu|^2}{1+|\mu|^2}\} \end{aligned} \quad (6.4)$$

where $S_z(T)$ and $S_z(H)$ operate on the triplet spin and hydrogen electron spin, respectively, and I_z on the hydrogen nuclear spin; ζ_x and ζ_y are given by (2.7)

$$|+\rangle = \zeta_x |x\rangle + \zeta_y |y\rangle ;$$

μ is the coefficient shown in fig. 6.5.

Close to the crossing, where $R \neq 0$, the transition moment (6.4) is non-zero. Because at magnetic fields unequal to H_{S_1} ϕ_1 and ϕ_2 have different steady-state populations and different radiative decay rates, inducing a transition between ϕ_1 and ϕ_2 will change the phosphorescence intensity. So the satellites of the S-lines in fig. 6.7 b are ESR lines resulting from transitions between two states of spin F. Of course, the condition for observing these optically detected ESR lines is that the transition moment (6.4) squared is not much smaller than the decay rates of ϕ_1 and ϕ_2 , thought to be mainly determined by the lifetime of the hydrogen atoms as free atoms. We return to this point later.

Experimentally it was found that the satellites shift away from the S-lines and become weaker when the r.f. frequency is increased. Above 75 MHz no satellites are observed anymore. This is explained by looking at fig. 6.6 and the transition moment (6.4). By increasing the r.f. frequency the ESR transitions in fig. 6.7 b move to fields where R and thus the transition moment (6.4) are smaller, and more r.f. power is needed to induce transitions between ϕ_1 and ϕ_2 . So the disappearance of the satellites when using frequencies above 75 MHz is caused by lack of r.f. power. By lowering the frequency each S-line and its two satellites collapse into one.

If, instead of magnetic field modulation, the r.f. power is modulated in amplitude only the ESR satellites of each S-line are observed when the photomultiplier output is detected by phase-sensitive detection locked to the phase of the frequency with which the r.f. power is modulated. The detection system now no longer is sensitive to the central, r.f. independent S-line (or LAC line) and the observed spectrum is shown in fig. 6.7 c.

Important in the present context is that two resolved ESR signals are observed in this way for each of the S-lines, with r.f. frequencies as low as 25 MHz. Below 25 MHz one broad line is observed. From the frequency dependence of these satellites the interaction between the

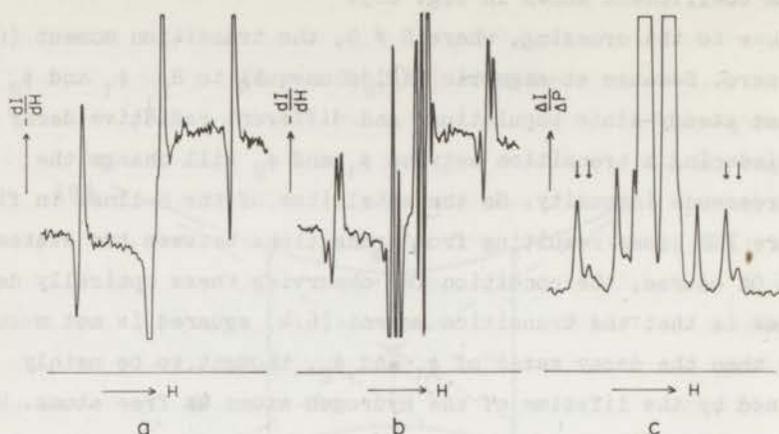


Fig. 6.7 a The LAC line and two S-lines in benzophenone with $\vec{H} // z$ axis.

b The same spectrum when irradiated with a high-power r.f. magnetic field // z axis with frequency 65 MHz. In fig. a and b the magnetic field is modulated with 40 MHz and phase-sensitive detection of the P.M. output is used; therefore the derivative of the phosphorescence intensity with respect to the magnetic field is recorded. The field sweep rate is 1000 Gauss/1 minute.

c The same spectrum as in b but now the r.f. power P is modulated between zero and maximum. Therefore the quantity along the vertical axis is proportional to the change in phosphorescence intensity. By modulating the r.f. power only the r.f. power dependent lines show up. The satellites of the S-lines are indicated by arrows. The magnetic field sweep rate is 1000 Gauss/5 minutes.

hydrogen atom and the triplet state benzophenone is estimated at between 10 and 20 MHz. The existence of these ESR lines very strongly suggests that the S-lines are not caused by CR but are the result of a LAC effect between well-defined energy levels.

That the assignment of the satellites is correct, is supported by what happens when the r.f. magnetic field is applied perpendicular to the static magnetic field. Then the transition moment for transitions between ϕ_1 and ϕ_2 of fig. 6.6 vanishes. This is in agreement with the experimental observation: the satellites become very weak.

In the first part of this chapter we explained the S-lines as the result of a CR process. The slow behaviour could be explained because via CR the hydrogen nuclear spin is polarized and this persists for a long time because the spin-lattice relaxation for the hydrogens is so slow. In chapter 5 section C it has been shown that the two pictures, CR and LAC, lead to the same conclusions so that it is not necessary to "translate" the explanation of the S-lines based on CR as given in the beginning of this chapter into LAC language. We only want to mention that the slow character of these lines again stems from the fact that the hydrogen nuclei are polarized. The mechanism causing this polarization is exactly as described in chapter 4 section E.

The satellites around the S-lines show exactly the same slow behaviour as the S-lines, which is apparent in fig. 6.7 c. Here the magnetic field is swept more slowly than in fig. 6.7 a and b and one sees that the satellites at the higher field are smaller than their partners at lower fields. Also, the satellites steal intensity from the S-lines, compare fig. 6.7 a and b. This is because the hydrogen spins already become polarized when ϕ_1 and ϕ_2 are coupled by the r.f. field since the governing rate equations are almost exactly like (4.35).

For the other CR lines in benzophenone (signals T_{11} , T_{12} , T_{22} , R_1 and R_2 of fig. 5.2 a) no satellites of the kind shown in fig. 6.7 b for the S-lines are found when irradiating with a strong r.f. magnetic field at a frequency between 25 and 100 MHz and still using magnetic field modulation. However, when modulating the power of a 50 MHz field

we observe one unresolved ESR signal at every field where a T- or R-type line occurs. We have not made an extensive study of the r.f. induced signals associated with the T and R lines. In a CR picture they are difficult to explain. In LAC language their observation with a frequency of 50 MHz implies that the interaction δ between the two crossing states is weak, because apparently $50 \text{ MHz} \geq 2|\delta|/\hbar$ (see 4.23) and fig. 4.4). Hence we are led to the conclusion that the magnetic interaction within pairs of molecules responsible for the T and R lines is of the order of 10 MHz, or less. This is very small, for instance compared to the exchange interaction between two excited nearest neighbours in the benzophenone crystal which is of the order of 9000 MHz (the Davydov splitting in the triplet exciton band of benzophenone, Hochstrasser and Lin 1968). Thus, for a signal due to nearest neighbour interaction the LAC region in fig. 4.8 around H_{TP} would extend over more than 1000 Gauss and therefore we would not see its effect on the intensity of the phosphorescence. But it is remarkable that no pairs seem to exist which have an interaction of the order of hundreds of MHz. The fact that we always see narrow T and R lines corroborates our conclusion that the interaction responsible for these lines is quite weak and it therefore must relate to non-nearest neighbours.

The r.f. experiments, besides providing an illustration of the difference between LAC and CR also tell us two things about the hydrogen atoms. First, the interaction between the hydrogen atom and the triplet benzophenone involved in the LAC seems to be the same for all pairs, otherwise one would not find two separate satellites around the S-lines. This means that the hydrogen atoms are found in a fixed position at a fixed distance relative to the excited benzophenone molecules!

The second conclusion we can draw concerns the lifetime of the hydrogens as "free" atoms. Apparently, with an r.f. amplitude $H_1 \sim 3$ Gauss we can induce transitions between states of the combined spin system: benzophenone triplet-hydrogen free atom. The field H_1 present in the helix when optically detecting ESR in benzophenone is estimated

to be 20 mGauss. Thus, with an r.f. amplitude of 3 Gauss we can induce ESR transitions in a system which lives $\sim (3/0.02)^2 = 2250$ times shorter than the 20 msec lifetime of states $| + \rangle$ and $| - \rangle$ in benzophenone. In this way we can limit the lifetime of the "free" hydrogen atoms between about 10^{-6} and 10^{-4} sec.

REFERENCES

- Abragam, A., 1967, The principles of nuclear magnetism, Oxford, Clarendon Press.
- Abragam, A. and Bleaney, B., 1970, Electron paramagnetic resonance of transition ions, Oxford, Clarendon Press.
- Antheunis, D.A., Schmidt, J. and van der Waals, J.H., 1970, Chem. Phys. Letters 6, 255.
- Atkins, P.W., Buchanan, I.C., Gurd, R.C., McLauchlan, K.A. and Simpson, F., 1970, Chem. Comm. 513.
- Beckett, A. and Porter, G., 1963, Trans. Faraday Soc. 59, 2038.
- Bixon, M., Jortner, J. and Dothan, Y., 1969, Mol. Phys. 17, 109.
- Bloembergen, N., Shapiro, S., Pershan, P.S. and Artman, J.O., 1959, Phys. Rev. 114, 445.
- Blok, H. and Kooter, H., 1972, unpublished results.
- Breit, G., 1933, Rev. Mod. Phys. 5, 91.
- Breit, G. and Rabi, I.I., 1931, Phys. Rev. 38, 2082.
- Buckley, M.J. and Harris, C.B., 1970, Chem. Phys. Letters 5, 205.
- Burland, D.M. and Schmidt, J., 1971, Mol. Phys. 22, 19.
- Busch, G.E., Rentzepis, P.M. and Jortner, J., 1971, Chem. Phys. Letters 11, 437.
- Caspers, W.J., 1964, Theory of spin relaxation, New York, London, Sydney, Interscience Publishers.
- Chan, I.Y. and Schmidt, J., 1969, Symp. on Magneto Optical Effects, Faraday Soc.

- Closs, G.L., 1969, J. Am. Chem. Soc. 91, 4553.
- Colegrove, F.D., Franken, P.A., Lewis, R.R. and Sands, R.H., 1959, Phys. Rev. Letters 3, 420.
- Colpa, J.P., Hausser, K.H. and Stehlik, D., 1971, Z. Naturforsch. 26A, 1792.
- Das, T.P. and Hahn, E.L., 1958, Solid State Physics, Suppl. 1, eds. Seitz and Turnbull, New York, Academic Press.
- Davydov, A.S., 1971, Theory of molecular excitons, New York, London, Plenum Press.
- de Vrijer, F.W. and Gorter, C.J., 1952, Physica 18, 549.
- Dym, S., Hochstrasser, R.M. and Schafer, M., 1968, J. Chem. Phys. 48, 646.
- Dym, S. and Hochstrasser, R.M., 1969, J. Chem. Phys. 51, 2458.
- Eck, T.G., Foldy, L.L. and Wieder, H., 1963, Phys. Rev. Letters 10, 239.
- German, K.R., Zare, R.N. and Crosley, D.R., 1971, J. Chem. Phys. 54, 4039.
- Goodman, L. and Krishna, V.G., 1963, Rev. Mod. Phys. 35, 541.
- Gorter, C.J., 1969, in: Polarisation, matière et rayonnement (Société Française de Physique, Paris).
- Gromer, J., Sixl, H. and Wolf, H.C., 1972, Chem. Phys. Letters 12, 574.
- Hall, J.L. and Schumacher, R.T., 1962, Phys. Rev. 127, 1892.
- Hameka, H.F., 1956, Thesis, Leiden.
- Hameka, H.F. and Oosterhoff, L.J., 1958, Mol. Phys. 1, 358.
- Hanle, W., 1924, Z. Physik 30, 93.
- Hausser, K.H., Lauer, O., Schuch, H. and Stehlik, D., 1970, Coll. Ampere, Bucharest.
- Heller, A., 1969, Mol. Photochem. 1, 257.
- Hochstrasser, R.M. and Lin, T., 1968, J. Chem. Phys. 49, 4929.
- Hutchison, C.A. and Mangum, B.W., 1961, J. Chem. Phys. 34, 908.
- Hutchison, C.A., 1967, The Triplet State, ed. Zahlan, Cambridge University Press, p. 63.
- Kaptein, R., 1971, Thesis, Leiden.
- Kaptein, R. and Oosterhoff, L.J., 1969, Chem. Phys. Letters 4, 195, 214.

- Kasha, M., 1960, Radiat. Res. Suppl. 2, 243.
- Kellogg, R.E. and Schwenker, R.P., 1964, J. Chem. Phys. 41, 2860.
- Kojima, S., Tsukada, K., Ogawa, S. and Shimauchi, A., 1953, J. Chem. Phys. 21, 1415.
- Maier, G., Haeberlen, U., Wolf, H.C. and Hausser, K.H., 1968, Phys. Letters 25A, 384.
- Maier, G. and Wolf, H.C., 1968, Z. Naturforsch. 23A, 1068.
- McClure, D.S., 1952, J. Chem. Phys. 20, 682.
- Muramoto, T., Fukuda, Y. and Hashi, T., 1971, Phys. Letters 34A, 175.
- Podgoretskii, M.I. and Khrustalev, O.A., 1964, Sov. Phys. Uspekhi 6, 682.
- Porter, G. and Wilkinson, F., 1961, Trans. Faraday Soc. 57, 1686.
- Pound, R.V., 1951, Phys. Rev. 81, 156.
- Purcell, E.M. and Pound, R.V., 1951, Phys. Rev. 81, 279.
- Rose, M.E. and Carovillano, R.L., 1961, Phys. Rev. 122, 1185.
- Schmidt, J., Veeman, W.S. and van der Waals, J.H., 1969, Chem. Phys. Letters 4, 341.
- Schmidt, J., 1971, Thesis, Leiden.
- Schmidt, J., 1972, Chem. Phys. Letters 14, 411.
- Sharnoff, M., 1969, Symp. on Magneto Optical Effects, Faraday Soc.
- Sixl, H. and Schwoerer, M., 1970, a. Chem. Phys. Letters 6, 21
b. Z. Naturforsch. 25A, 1383.
- Sixl, H., 1971, Thesis, Stuttgart.
- Smaller, B., Remko, J.R. and Avery, E.C., 1968, J. Chem. Phys. 48, 5174.
- Stevens, K.W.H., 1952, Proc. Roy. Soc. 214, 237.
- Structure Reports, 1952, 16, 515 ed. A.J.C. Wilson, et. al., Oosthoek's Uitgeverij Utrecht, 1959.
- van der Poel, A.L.J. and Veeman, W.S., 1971, unpublished results.
- van der Waals, J.H. and de Groot, M.S., 1967, The Triplet State, ed. Zehlan, Cambridge University Press, p. 101.
- van Duyneveldt, A.J., Tromp, H.R.C. and Gorter, C.J., 1968, Physica 38, 205.
- Veeman, W.S. and van der Waals, J.H., 1970, a. Chem. Phys. Letters 7, 65
b. Mol. Phys. 18, 63.

von Neumann, J. and Wigner, E., 1929, Z. Phys. 30, 467.

Weisskopf, V., 1931, Ann. d. Physik 9, 23.

Winscom, C.J. and Maki, A.H., 1971, Chem. Phys. Letters 12, 264.

Wood, R.W. and Ellet, A., 1923, Proc. Roy. Soc. 103, 396.

Yip, R.W. and Siebrand, W., 1972, Chem. Phys. Letters 13, 209.

SUMMARY

In the experiments discussed in this thesis the phosphorescence intensity is measured as a function of the strength and orientation of an applied magnetic field for UV irradiated organic molecular crystals at low temperature (≤ 4.2 K). For certain orientations of the magnetic field a recording of the intensity of the phosphorescence as a function of the field yields a "spectrum" with rather narrow lines corresponding to an increase or decrease of the emission intensity.

All these lines in the systems investigated - single crystals of benzophenone, 4,4'-dibromobenzophenone, 4,4'-dichlorobenzophenone, 4,4'-difluorobenzophenone and the mixed crystal pyrimidine in benzene - are ascribed to level anticrossing and cross-relaxation effects.

Sofar these two effects were studied in different areas of physics: level anticrossing in spectroscopic research on atomic gases at room temperature and cross-relaxation in magnetic resonance experiments and susceptibility measurements on solids at low temperatures. However, level anticrossing and cross-relaxation appear to be so closely related that in our experiments it is very hard or even impossible to distinguish between them.

It is shown that another related effect, level crossing, can not show up in the phosphorescence of our organic crystals.

The primary goal of this research was to investigate if these "crossing" effects occur in the phosphorescence from organic crystals. But these "spectra" also yield information.

First, they give information about the phosphorescent molecules, like the zero-field splitting parameters and (qualitatively) about the orientation and the spread in the orientation of the phosphorescent molecules in the crystal, the interaction between the phosphorescent molecules and about hyperfine interaction in the phosphorescent molecules.

Secondly, other paramagnetic systems present in the phosphorescent crystals may be detected optically owing to the influence they have via level anticrossing and cross-relaxation on the phosphorescence intensity. In some cases this means an improvement in detection sensitivity compared to magnetic resonance. In this way many photochemical products are detected (but in most cases not identified). In particular we want to mention the detection of "free" hydrogen atoms which live very short and show a strong electron spin polarization.

In the last part of chapter 6 experiments using a r.f. magnetic field are discussed which show that many lines in our "spectra" which at first sight seem to be caused by a cross-relaxation process, should be explained as resulting from level anticrossing.

SAMENVATTING

In de experimenten welke in dit proefschrift zijn beschreven, wordt de intensiteit van de fosforescentie van met ultraviolet licht bij $T \leq 4,2$ K bestraalde organische moleculaire kristallen gemeten als functie van de sterkte en richting van een aangelegd magnetisch veld. Wanneer men de gemeten fosforescentie intensiteit als functie van de veldsterkte registreert, blijkt dat men voor bepaalde oriëntaties van het magneetveld een "spectrum" krijgt dat tamelijk smalle lijnen vertoont die corresponderen met een toe- of afname van de emissie intensiteit.

Al deze lijnen in de onderzochte systemen - éénkristallen van benzophenon, 4,4'-dibroombenzophenon, 4,4'-dichloorbenzophenon en 4,4'-difluorbenzophenon en het verdunde mengkristal pyrimidine in benzeen - worden toegeschreven aan level anticrossing en cross-relaxatie effecten.

Tot dusver werden deze beide effecten bestudeerd in verschillende gebieden van de natuurkunde: level anticrossing in spectroscopisch onderzoek van atomaire gassen bij kamertemperatuur en cross-relaxatie in magnetische resonantie experimenten en susceptibiliteits metingen aan vaste stoffen bij lage temperatuur. Level anticrossing en cross-relaxatie blijken echter zo verwant te zijn dat ze in onze experimenten niet of slechts met grote moeite te onderscheiden zijn.

Van een ander effect uit de atoomspectroscopie, level crossing,

wordt aangetoond dat het niet kan worden gevonden in de fosforescentie van de door ons bestudeerde organische kristallen.

Het directe doel van dit onderzoek was na te gaan of deze "crossing" effecten in fosforescerende kristallen optreden. Daarnaast blijkt dat men ook informatie uit dergelijke spectra kan halen.

In de eerste plaats gegevens over de fosforescerende moleculen zelf, zoals de nulveld splitsingsparameters en kwalitatieve gegevens over de ligging en spreiding in de ligging van de fosforescerende moleculen in het kristal, interactie tussen de fosforescerende moleculen onderling en hyperfijn interactie in de fosforescerende moleculen.

In de tweede plaats kunnen andere paramagnetische systemen die in het fosforescerende kristal aanwezig zijn, dankzij de invloed die zij hebben via level anticrossing of cross-relaxatie op de fosforescentie intensiteit, optisch gedetecteerd worden. In sommige gevallen betekent dit, vergeleken met magnetische resonantie, een verbetering van de detectie gevoeligheid. Op deze manier zijn in benzophenon en gesubstitueerde benzophenon kristallen veel photochemische producten aangetoond (maar in de meeste gevallen niet geïdentificeerd). Hiervan willen wij in het bijzonder noemen zeer kort levende, photochemisch gecreëerde "vrije" waterstof atomen die een sterke electron spin polarisatie vertonen.

In het laatste gedeelte van hoofdstuk 6 komen experimenten ter sprake waar met behulp van een magnetisch r.f. veld aangetoond wordt dat vele lijnen in onze "spectra" die op het eerste gezicht lijken te zijn veroorzaakt door cross-relaxatie processen in werkelijkheid beter met level anticrossing kunnen worden verklaard.

Na het behalen van het diploma H.B.S.-B aan de toenmalige Rijks H.B.S. te Leeuwarden begon ik in 1960 met de studie voor electro-technisch ingenieur aan de Technische Hogeschool te Delft. In 1963, na het propadeutisch examen electrotechniek, veranderde ik mijn studierichting in die voor natuurkundig ingenieur. Hiervoor werd in 1964 het propadeutisch examen, in 1966 het kandidaatsexamen en in april 1967 het doctoraal examen afgelegd.

Het experimentele onderzoek voor het kandidaats- en doctoraal examen is verricht in de Werkgroep "Magnetische Resonantie" onder leiding van Prof.Dr.Ir. J. Smidt.

De tijd tussen doctoraal examen en de inlijving bij de Koninklijke Luchtmacht, eind 1967, was ik als ingenieur-assistent werkzaam in bovengenoemde Werkgroep.

Na de opleiding tot vaandrig bij de Koninklijke Luchtmacht werd mij, op verzoek van de Rijksuniversiteit te Leiden, vrijstelling van militaire dienst verleend en werd ik wetenschappelijk medewerker in de toen pas opgerichte Werkgroep "Moleculen in Aangeslagen Toestand" onder leiding van Prof.Dr. J.H. van der Waals.

Het onderzoek wat tot dit proefschrift heeft geleid, is gestart in 1969.

Zowel in Delft als in Leiden heb ik bij het Natuurkundig Prakticum geassisteerd. Van 1964 tot 1967 in Delft bij het derdejaars practicum en vanaf 1970 in Leiden bij het eerstejaars practicum.

Van lang voordat de experimenten werden uitgevoerd tot op het ogenblik dat de titelpagina werd getypt, hebben vele mensen met hun energie en inventiviteit bijgedragen aan de totstandkoming van dit proefschrift.

In het bijzonder wil ik noemen de heer S. Verdegaal, die de roestvrijstalen optische helium cryostaat heeft ontworpen en vervaardigd, en de heren J.F. Benning, J. van den Berg en T. Nieboer die voor het mechanische deel van de meetopstelling hebben gezorgd. Enkele glas en kwarts onderdelen zijn vervaardigd door de heren L. van As en H. van Zanten.

Voor het zuiveren van chemicaliën heb ik nooit tevergeefs een beroep gedaan op de heer M. Noort, terwijl de cryogene afdeling van het Kamerlingh Onnes Laboratorium mij steeds heeft voorzien van vloeibare stikstof en vloeibaar helium.

De discussie met de andere leden van de Werkgroep MAT heeft veel bijgedragen aan het uiteindelijke resultaat. De heer A.L.J. van der Poel assisteerde mij bij vele metingen.

De heer W.F. Tegelaar heeft mij terzijde gestaan bij het tekenen van de figuren welke door de heer W.J. Brokaar zijn gefotografeerd.

Marja Muns heeft op zeer energieke wijze het manuscript getypt.

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