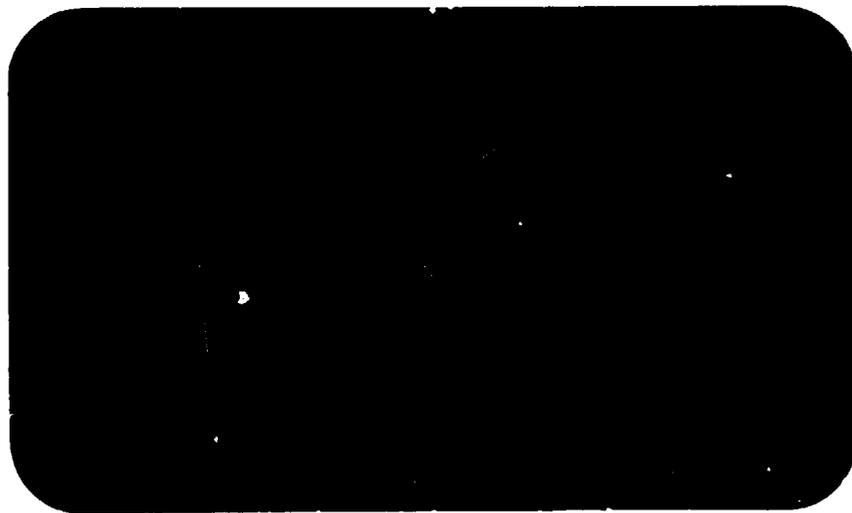


Department of Physics and Measurement Technology



LIU-TEK-LIC--1992-32



**Non-Linear Effects in the Radiolysis-Optically  
Detected ESR of Radical-Ion Pairs in Liquid  
and Glassy Solutions. Reactions and Motion of  
Organic Radicals as Studied by ESR and OD  
ESR Spectroscopy.**

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## **Preface**

This work for the "Teknologie Licenciat" degree has been done during the period July 1989 to September 1992. The first year was in the Institute of Chemical Kinetics and Combustion in Novosibirsk (Russia) and thereafter at the Department of Physics and Measurement Technology, Linköping University. The goals of the visit there were the installation and tuning of the OD ESR spectrometer. In the Chemical Physics laboratory of A. Lund I first got in touch with the halocarbon matrix isolation technique for ESR. This method as well as OD ESR experiments have been employed in the study of reactions and motion of organic radicals and radical cations.

This thesis is divided into two sections. The first part covers an introduction to the Optically Detected Electron Spin Resonance (OD ESR) spectroscopy and a short description of the OD ESR spectrometer built in Linköping University in 1991. In the second section the following original papers are presented:

### Non-Linear effects in OD ESR spectroscopy

- 1) **Multiquantum Resonances in Low-Field Optically Detected ESR of Radical-Ion Pairs.**

V.A. Morozov, O.N. Antzutkin, A.V. Koptug and A.B. Doktorov

*Molecular Physics*, 1991, Vol. 73, No. 3, 517-540.

- 2) **Effects of External Magnetic Fields and Resonance Radiofrequency Radiation on Radical Reactions.**

Yu.N. Molin, O.A. Anisimov, A.V. Koptug, V.O. Saik and O. N. Antzutkin

*Physica B*, 164 (1990) 200-204.

### Reactions and Motion of Organic Radicals Trapped in Freon Matrices

- 3) **Observation of Piperidine Aggregation and of Hydrogen-Proton Transfer between Piperidine Radical Cations and Piperidine Molecules in Freon Matrices. An E.S.R. Study at Cryogenic Temperatures.**

O.N. Antzutkin, M. Lindgren, A. Lund and L. Sjöqvist

*Journal of the Chemical Society, Chem. Comm.*, in press

4) **Dynamics of the Morpholin-1-yl Neutral Radical in  $\text{CF}_2\text{ClCFCl}_2$ . An ESR Investigation and Application of the Anisotropic Exchange Theory for Powder ESR Lineshapes.**

O.N. Antzutkin, N.P. Benetis, M. Lindgren and A. Lund

Accepted for publication in *Chemical Physics*.

The two first papers are results of work performed in the Institute of Chemical Kinetics and Combustion in Novosibirsk. They deal with effects of resonance radiofrequency radiation on radical reactions in the OD ESR experiment. The first paper is the result of a fruitful collaboration with two theoreticians in OD ESR spectroscopy (first and last authors) while the discovery of the phenomenon, interpretations and all experiments have been done by the other two. The second paper is a review of the effects of external magnetic fields and resonance radiofrequency radiation on radical reactions. It has been written on the basis of a few original papers of the first authors and includes unpublished results of the author of this licentiate. The other papers are concerned with the reactions and motion of radicals trapped in freon matrices. They are the results of work performed at the Chemical Physics laboratory in Linköping.

Some results have been presented at AMPERE Congresses:

1) **Multiquantum Transitions. Low-Field OD ESR Studies.**

O.N. Antzutkin, A.V. Koptug, V.O. Saik, O.A. Anisimov,  
A.B. Doctorov, V.N. Morozov

*XXIV International Congress on Magnetic Resonance and Related Phenomena. AMPERE. Poland, Poznan, PD-B114, 1988.*

2) **The Temperature Dependent Optically Detected ESR (OD ESR) Spectra Anomalies in Superviscous Squalane Solutions.**

O.N. Antzutkin, A.V. Koptug, A. Lund and B.M. Tadjikov  
*XXIV International Congress on Magnetic Resonance and Related Phenomena. AMPERE. Greece, Athens, Poster p. 329-330, 1992.*

The latter is the first study adopting the equipment in Linköping. The results are currently under preparation for a larger paper.

**1. The Optically Detected Electron Spin Resonance (OD ESR) Technique.**

**1.1 Development of the method (history).**

The Reaction-Yield Detected Magnetic Resonance (RYDMR) was proposed by E.L. Frankevich (Institute of Chemical Physics, Moscow) in 1966 [1] and developed by his group for photoinduced ion-radical pairs in molecular crystals (OD MR) in 1976 [2]. In 1979 the method was modified for the radiation-induced ion-radical pairs in liquids in the Institute of Chemical Kinetics and Combustion (Novosibirsk, Russia) [3-5]. The time-resolved version of the method - Fluorescence Detected Magnetic Resonance (FDMR) was developed by A. Trifunac *et al.* (Argonne, USA) in 1980 [6,7]. Recently OD ESR instruments for the polymer studies appeared in Japan [8]. Trifunac *et al.* developed also an interesting version of the method to record the FDMR spectra of radical-ions arising under two-quantum laser ionization processes [9]. The absorption versions of RYDMR with photoexcitation were created in the Netherlands (Hoff *et al.* [10]), in USA (Closs *et al.* [11]) and in United Kingdom (McLauchlan *et al.* [12]). A comprehensive review on RYDMR and related phenomena has been written by U. Steiner and T. Ulrich [13].

**1.2 OD ESR. General Description.**

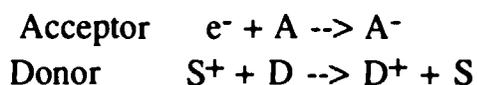
OD ESR is the reaction-yield detected ESR recorded as a change in the recombination fluorescence intensity with the magnetic field under the action of an external microwave field. This is proportional to the yield of

singlet excited molecules formed after radiation-induced radical-ion pair recombination.

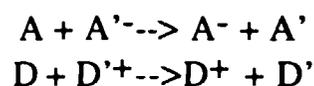
Under X-irradiation the following reactions take place in liquid and glassy solutions (A and D are acceptors and donors of electrons with a sufficient quantum yield of fluorescence):



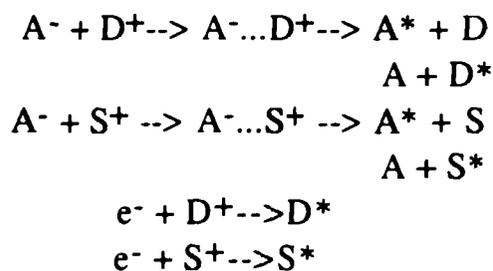
Transfer of the charge and spin to molecules:



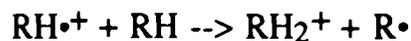
Ion-molecular charge transfer:



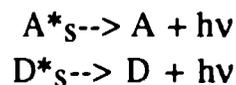
Formation of secondary pairs and excited molecules:



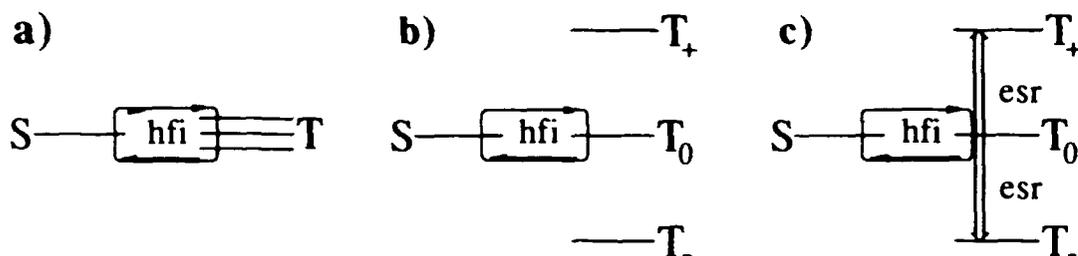
Charge and spin separation, RH is donor or solvent molecule:



Fluorescence ( $A^*_s$ ,  $D^*_s$  are excited molecules in a singlet spin state):



Only spin-correlated geminate ion-radical pairs (GRP) (pairs where both spins are from the same precursor) can be detected using this technique.



**Fig. 1.** Energy-level diagram and singlet-triplet mixing in a radical pair: a) low magnetic field, b) high magnetic field, c) high magnetic field and resonant microwave irradiation;  $hfi$  denotes transitions under hyperfine coupling;  $esr$  denotes resonance transitions in a microwave field.

To describe OD ESR signal formation, let us discuss the spin evolution in the GRP. Under ionizing radiation, the primary radical ion pair of a matrix cation and an electron appears initially in the correlated singlet state since the electron spins were coupled in the original solvent molecule. In the process of recombination the spin correlation in the pair may be violated. The chief causes of this loss of spin correlation are either the hyperfine (hf) coupling of electrons with magnetic nuclei ( $hfi$ -mechanism), a difference in the  $g$ -factors of partners of the GRP ( $\Delta g$ -mechanism), or phase relaxation [14]. The GRP, born mainly in the singlet spin state, can after some time recombine from both singlet and triplet states to yield excited singlet and triplet molecules, respectively. Usually aromatic acceptors are employed for which only singlet excited molecules efficiently emit light. Thus, the intensity of light emitted from a sample is proportional to the probability of GRP to recombine in the singlet spin state,  $W_S$ . It is seen from the RP energy level diagram (Fig. 1) that in the absence of the external magnetic field  $B_0$   $hfi$  (and/or  $\Delta g$ ) mixes efficiently all the sublevels of the GRP and after some time  $W_S$  reaches the value  $1/4$  (according to statistics).

In a high field the Zeeman splitting prevents the singlet from mixing with the  $T_+$  and  $T_-$  triplet levels.  $Hfi$  causes only the  $S \rightarrow T_0$  mixing and the  $W_S$  value increases to  $1/2$ , giving rise to the so-called fluorescence magnetic field effect [15]. In a high magnetic field the sublevels  $T_+$  and  $T_-$  may be populated via the action of a microwave field. The resonant spin transitions of one of the partners in a pair will thus decrease the singlet-level population (the limit of the corresponding probability  $W_S$  is again  $1/4$ ) and the fluorescence intensity forming the

OD ESR signal. According to theoretical predictions, under X- or  $\gamma$ -irradiation of scintillator solutions with magnetic field sweeping, the intensity of the recombination fluorescence decreases when passing each ESR spectrum line of both cation- and anion-radicals of the GRP. It should be noted that the total spin dynamics of ion-radicals in GRP gives rise to the OD ESR signal formation (including dynamics of short-lived  $S^+ \dots A^-$  GRP [3]). As in conventional ESR spectroscopy, OD ESR spectra are often recorded as the first derivative of fluorescence intensity.

### **1.3 Applications and limitations of the OD ESR.**

The optical detection of ESR spectra is characterised by high selectivity. OD ESR spectra are observable for the radical ions that are the partners of spin-correlated pairs, i.e. participate in the geminate recombination. The radicals escaping to the bulk are not optically detected and do not mask the spectra of initial radical ions. This is the main difference between the OD ESR and usual ESR where all paramagnetic particles are detected.

The second distinctive feature of the OD ESR technique is its high sensitivity that is about  $10^9$  times higher than that of the conventional ESR (The minimum stationary concentration of the radical-ions detected is about 10-100 per sample - the result was obtained with the home-made accessory to the "Bruker-ER 200 SCR" commercial X-band ESR spectrometer, MW power was 3.8 W, 3  $\mu$ Ci ionizing radiation source, room temperature, 12.5 minutes accumulation time [16]).

The high sensitivity allows the OD ESR method to be used for recording ESR spectra of short-lived radical-ions participating in geminate recombination in liquid solutions. The minimal lifetime of such radical-ions ranges from tens to hundreds of nanoseconds. However, this method can detect only geminate pairs whose recombination products are represented by the excited molecules capable of fluorescing. Another restriction is that the sample must be light transparent.

The OD ESR usually has relatively low resolution. The width of individual lines in spectra is as a rule more than 0.5 G. Wide lines are due to the MW fields of relatively large amplitudes ( $B_1 = 0.5 - 1$  G) that must be used to induce efficient transitions between the pair sublevels during its lifetime prior to the recombination.

The most important results and applications of the OD ESR technique can be found in Chapters 1.8 and 1.10 of [17] and references given there.

## 2. OD ESR Spectrometer

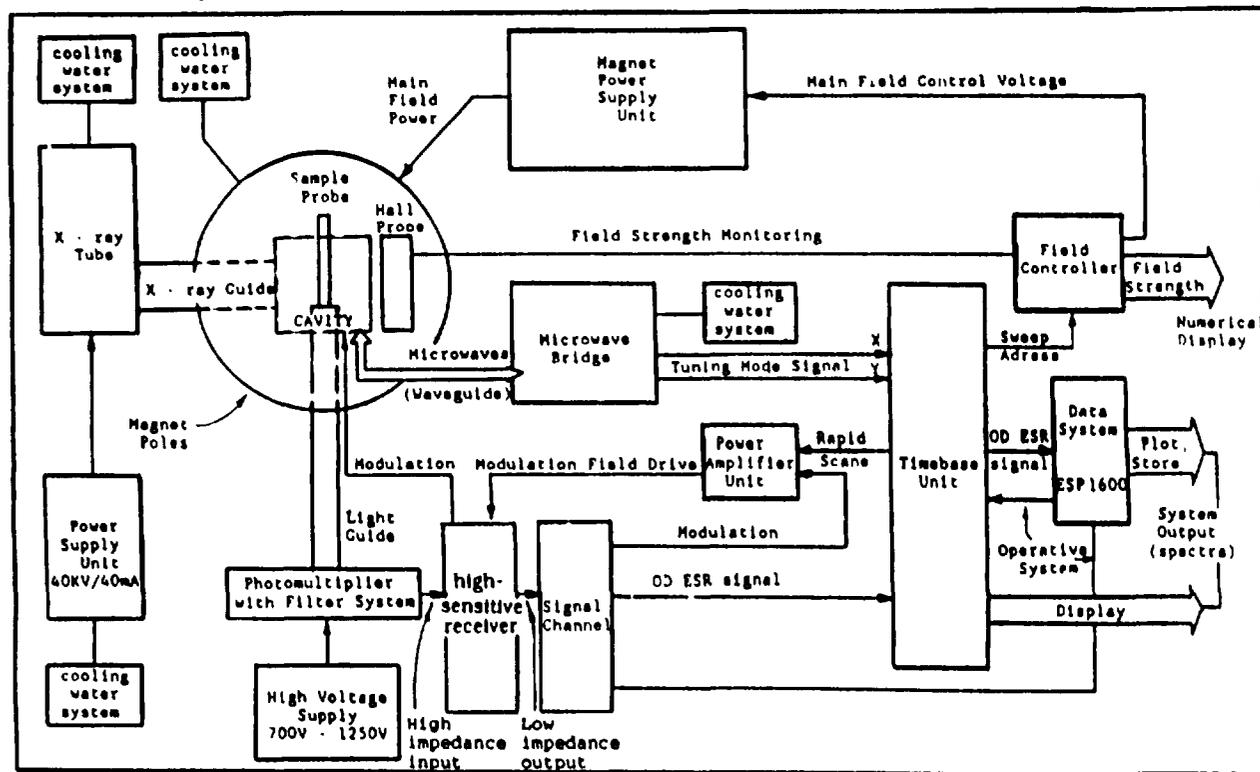
### 2.1 General description.

The OD ESR spectrometer is built on the basis of a Bruker ER 200 SRC spectrometer with ESP 1600 Data System complemented with a source of ionizing radiation and a system of light detection. The set-up is similar to those described in the literature [3,4]. A new high-sensitive receiver was installed. This has a narrow-band digital filtration function, high impedance input and special low impedance output in order to fit the Bruker lock-in device. An improved light collection system was developed. The required bands of the luminescence spectra were selected by filters.

The functional Block Diagram of the X-band OD ESR spectrometer is shown in Fig. 2. A  $0.5 \text{ cm}^3$  sample (in a quartz tube) is inserted into the "Bruker" TE<sub>102</sub> Rectangular Cavity and irradiated continuously by an X-ray diffraction tube (Soviet, type BSV-27 with a *Mo* anode, operating at 35 kV and 35 mA; or "Philips", type PW 2245/20 with a *Mo* or *W* anode, operating at 40 kV and 45 mA) through a window in the cavity. The window is closed by a thin aluminium film that is practically transparent for X-rays and covers a resonant volume of the cavity. Average dose rate of irradiation is *ca.* 80 kRad/h.

The fluorescence light is transmitted from the sample through a quartz lightguide to a photomultiplier tube (Japan type, R-928 (552U), 10 dynodes, UV glass window (185-930 nm),  $10^7$  current amplification, 100  $\mu\text{A}$  anode working current) with the filter-changing system. Operating voltage of the photomultiplier unit was from 700 to 1400 V depending on the intensity of luminescence from the sample (10-100  $\mu\text{A}$ ). A signal from the photomultiplier is directed to the input of the low-noise home-made phase-sensitive receiver.

**Functional Block Diagram - High field OD ESR spectrometer**  
 yellow - Optically Detected accessory to the commercial ER 200 SPC with Data System ESP 1600.



**Fig. 2.** An X-band OD ESR spectrometer (based on a Bruker ER 200D) has been constructed following previous schemes (3). A new high-sensitive receiver having a special narrow-band digital filtration function and an improved light collection system were developed. The fluorescence in the range  $\lambda=240-410$  nm was selected using a band-pass filter to avoid the phosphorescence at longer wavelengths.

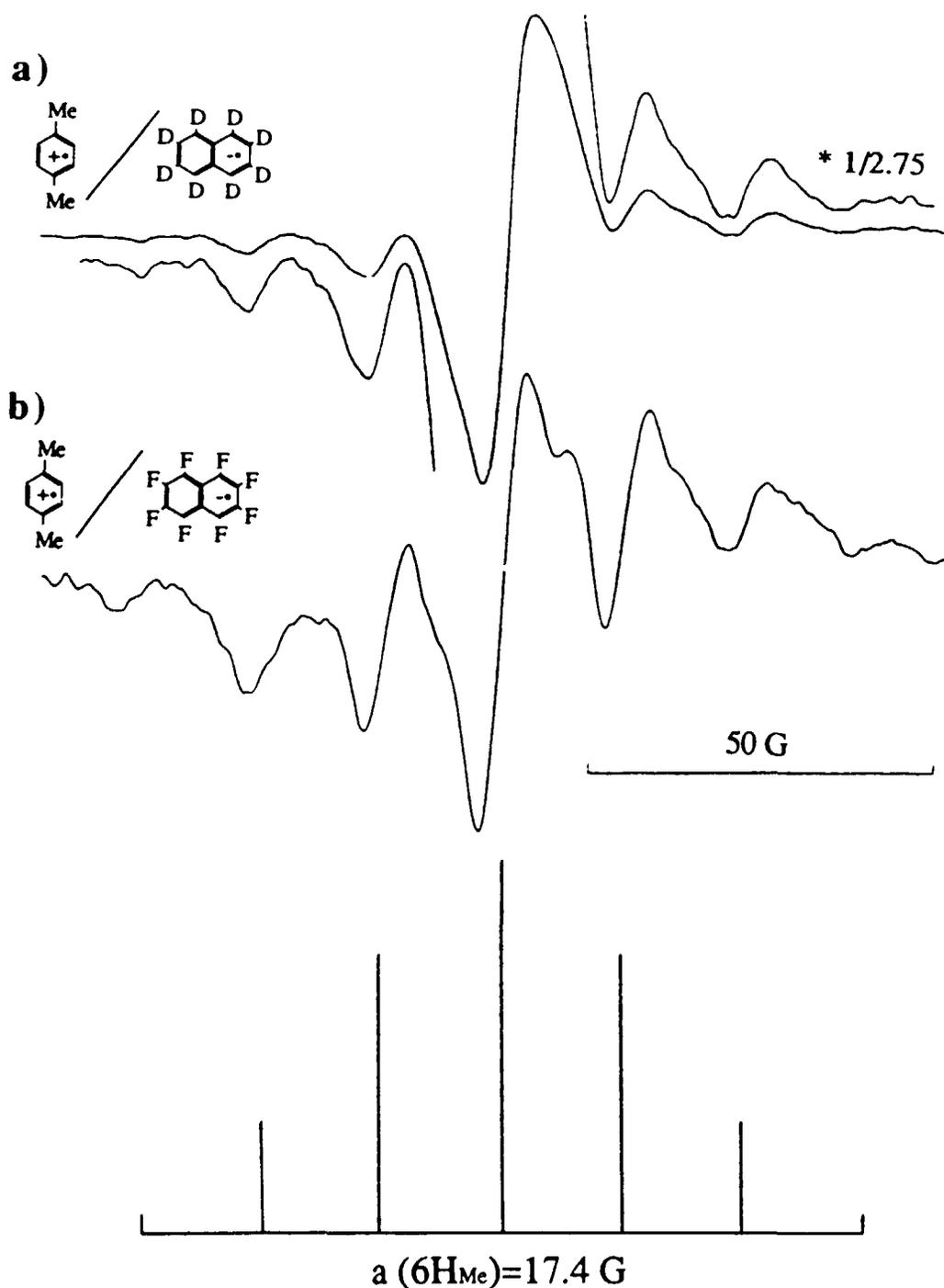
Working modulation frequency can be chosen in the range 62-2048 Hz\*. The DC signal from the phase-sensitive detector is modulated (12.5 KHz) and delivered to the low-impedance lock-in device of the "Bruker" spectrometer. Microwave bridge, magnet, magnetic field controller and all other units of the "Bruker" spectrometer are used without any change. The microwave field is generated by a 500 mW klystron and is directed through a flexible waveguide to the cavity. The operation procedure with the MW bridge and tuning of the cavity are similar to the ordinary ESR experiment. OD ESR spectra are detected using a phase-sensitive detection with the sinusoidal magnetic field modulation (first derivative mode). The accumulation time of an OD ESR spectrum is usually 10-40 minutes. Most of the operations with the ESR spectrometer and manipulations with spectra are carried out with the commercial ESP 1600 Data System which follows the ESR spectrometer.

## 2.2 Sample preparation.

Special quartz flasks with a flat bottom to pass the fluorescence were employed to record the OD ESR spectra of liquid samples. A flask was placed in the cavity on the top polished plate of the quartz lightguide. OD ESR signals are very sensitive even to small amounts of oxygen in the samples since it destroys the spin-correlation in the GRP. Thus, prior to experiments samples were degassed (down to  $10^{-5}$  -  $10^{-6}$  torr) in two steps to remove water and oxygen from them. First, the air over the sample surface was pumped out, second, the sample went through several freeze-pump-thaw cycles. The solvent purity was characterized by the ultraviolet transmission cut-off (wavelength for which the optical density of a 1 cm thick solvent layer equalled unity). Acceptors of holes and electrons of "chemically pure" grade, were obtained commercially and used without further purification.

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\* Due to life-time distribution function of GRP under study, sensitivity of the OD ESR detection increases linearly following a decrease of the modulation frequency down to 50-100 Hz.



**Fig. 3.** OD ESR spectrum of the radical cations of para-xylene in squalane (2,6,10,15,19,23-hexamethyl-tetracosane) solution. The radical-cations were generated by irradiating with a X-ray source a solution containing  $0.03 \text{ mol dm}^{-3}$  para-xylene and the electron acceptors: **a)**  $0.008 \text{ mol dm}^{-3}$  deuteronaphthalene; **b)**  $0.06 \text{ mol dm}^{-3}$  octafluoronaphthalene. Specimen temperature: **a)** 230 K; **b)** 248 K.

The experimental spectrum of the para-xylene radical cation shows a binomial septet with broad intense lines associated with the splitting of six equivalent methyl protons. The splitting between the lines is 17.4 G. Simulated stick spectrum with this splitting is shown below. The large width of the observed lines is related to the unresolved splitting at the protons of the benzene ring.

### **2.3 Acceptors**

It is a real art to find a proper acceptor to the system under study.

Nevertheless, there are some general rules for that choice:

1) At least one of the partners of GRP under study should fluoresce with a sufficient quantum yield, if not, a fluorescent acceptor for holes or electrons should be added to the solution.

2) The ionization potential of hole acceptors should be less than that of the system under investigation (cation radicals) by at least 1 eV. The acceptor concentration in this case must be about 10 times less than that of the system (cation radicals) for sufficient lifetime of the latter as an intermediate cation radical and, thus, its OD ESR signal formation.

3) The electron affinity of acceptors of electrons should be larger than that of the system.

4) Acceptors of holes and electrons must have a sufficient quantum yield of fluorescence (0.2 -1.0).

5) Solubility of acceptors sometimes is a restriction especially for low-temperature experiments.

6) The ESR spectrum of acceptors should be either very narrow (deuteriated aromatic compounds with a linewidth 2 - 3 G) or very broad (perfluorated aromatic compounds) in order to reveal an ESR spectrum of the system under study. Para-terphenyl-d<sub>14</sub>, naphthalene-d<sub>8</sub>, biphenyl-d<sub>10</sub>, perfluorobenzene, perfluronaphthalene are examples of acceptors of electrons (last two) and of both holes and electrons (first three) which are satisfactory in this sense.

Fig. 3 shows a representative OD ESR spectrum of the para-xylene radical-cation in liquid squalane detected at the background of signals from the other partners of radical-ion pairs (radical-anions of naphthalene-d<sub>8</sub> - central narrow singlet, Fig. 3a and naphthalene-f<sub>8</sub> - broad background, Fig. 3b).

### **3. Conventional ESR combined with the matrix isolation technique.**

This method has successfully been employed in the study of reactive species such as radical cations during the last decade. In the gas phase they decompose rapidly. By using the matrix isolation technique the lifetime of the cation-radical can be extended to the required time to

perform an ESR experiment. In this concern both ESR in freons (4-150 K) and OD ESR in liquid and glassy solutions (160-300 K) can be good complementary techniques for the study of structure and dynamics of different organic cation-radicals.

Neutral radicals are often observed as a result of an ion-molecule reaction or deprotonation occurring at higher temperatures (approximately above 100 K) in glassy matrices like  $\text{CF}_2\text{ClCFCl}_2$  and  $\text{CF}_2\text{ClCF}_2\text{Cl}$ . At such temperatures radicals trapped in those matrices start to reorient itself, causing an averaging of the hyperfine and g-anisotropy, due to the softening of the matrices. One can characterize this molecular motion from the ESR lineshape analyses. A similar approach can be employed for the OD ESR spectra of some cation-radicals in superviscous solutions.

In the matrix isolating technique the sample is prepared by mixing a small amount (0.1-1.0 mol %) of the organic compound of interest with a halocarbon solvent like e. g,  $\text{CFCl}_3$ ,  $\text{CF}_3\text{CCl}_3$  and  $\text{CF}_2\text{ClCFCl}_2$  which have high ionization potential and electron affinity. The mixture is cooled down to 77 K and thereafter exposed to X-ray irradiation. Usually the solute has an ionisation potential lower than the solvent one and the positive hole (a primary product of the X-radiolysis) is easily trapped by a solute molecule. The negative ion formed through the reaction of an electron with a matrix molecule exhibits very anisotropic features in the ESR spectrum and contributes only to a broad background signal which does not interfere with the cation spectrum of interest.

#### 4. Comments to the papers

##### Paper 1

In this paper multiquantum resonances (MQR) in low-field OD ESR spectra of radiation-induced radical-ion pairs of aromatic acceptors in liquid and polymeric solutions have been studied experimentally and theoretically. Special experiments have been carried out to prove that such resonances are not caused by the apparatus. The dependencies of resonance shifts and intensities on the radiofrequency field amplitude have been studied.

A general theory for multiquantum OD ESR spectra of radical-ion pairs in liquid solutions has been developed, with spin relaxation processes being neglected. It has been predicted by the theory and

confirmed by experiment that the effective matrix elements of transition are dependent on the  $hfi$  constants for the chief even resonances and are independent for the odd ones.

Fig. 4 shows a representative low-field OD ESR spectrum of 0.001 mol dm<sup>-3</sup> solutions of *p*-terphenyl-d<sub>14</sub> (a) and *p*-terphenyl-h<sub>14</sub> (b) in pentadecane (C<sub>15</sub>H<sub>32</sub>) for different amplitudes of the radiofrequency (RF) field  $H_1$  (pumping frequency 100 MHz, room temperature). When the amplitude of the RF field  $H_1$  exceeds the width of the initial ESR spectrum of pair partners (unresolved singlet), the main resonance (field about 35 G) is inverted due to spin-locking [18]. At a large RF field amplitude, resonances in multiple fields arise along with the main resonance. It has been found that, for the case of the protonated *p*-terphenyl, the double quantum resonance intensity normalized to the main resonance is  $\Delta_h/\Delta_d \approx 3.5$  times larger than that for the case of deuteriated *p*-terphenyl, where  $\Delta_h$  and  $\Delta_d$  are the initial widths of the corresponding main resonances. According to the theory, the effective matrix elements of transitions for double-quantum resonance are proportional to  $aI$  where  $a$  is the largest hyperfine coupling constant and  $I$  is the nuclear spin for this group of magnetoequivalent nuclei. For the deuteriated compound  $a$  is ca. 6.5 times smaller than for the protonated one while  $I$  is twice larger to give a ratio  $a_h I_h / a_d I_d$  of ca. 3.3. The  $hfi$  independence of normalized intensities of triple quantum resonances shows the agreement with theoretical predictions as well.

Another interesting observation was that the plots for the  $k$ th MQR intensities  $I_k$  vs  $(H_1)^k$  have "thresholds" of MQR appearance. The threshold values of RF field amplitudes at which MQR appear are strongly dependent on the solvent/acceptor nature and the acceptor concentration. These peculiarities are of a relaxation nature. OD ESR signals from ion pairs with a diffusional lifetime distribution function appear when  $\omega_e > 1/T_1$ ;  $\omega_e = g\beta H_{1eff}/h$ , where  $H_{1eff}$  is the effective RF field causing the transitions. A shortening of the spin-lattice relaxation time  $T_1$  therefore increases the threshold  $H_1$  values. Thus, one can estimate  $T_1$  from the  $H_1$  threshold values for the double and triple quantum MQR saturation curves.

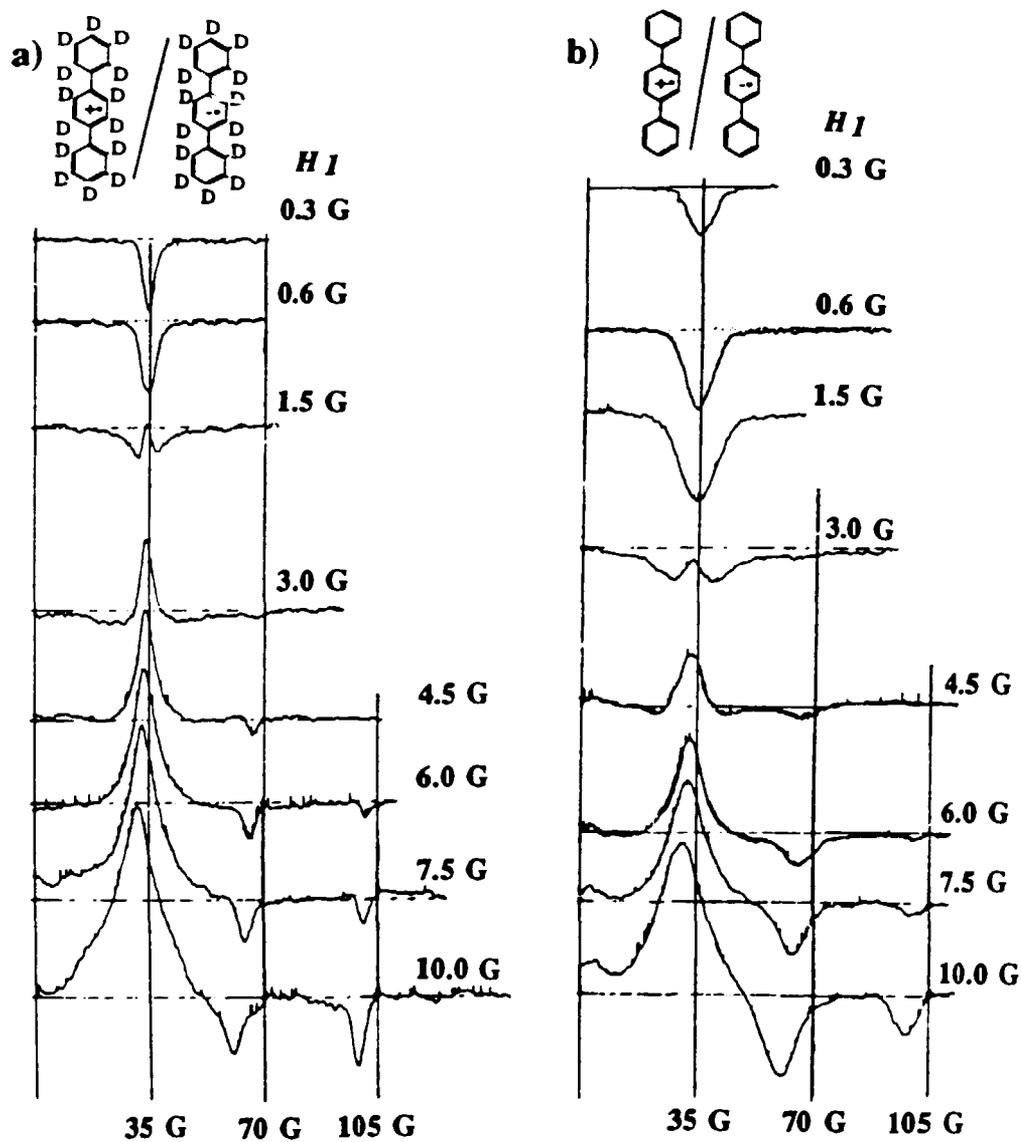


Fig. 4. Low-field OD ESR spectra of  $0.001 \text{ mol dm}^{-3}$  solutions of *p*-terphenyl- $\text{d}_{14}$  (a) and *p*-terphenyl- $\text{h}_{14}$  (b) in pentadecane ( $\text{C}_{15}\text{H}_{32}$ ) for different amplitudes of radiofrequency (RF) field  $H_1$  (pumping frequency 100 MHz, room temperature).

### Paper 2

This paper deals with the effects of the resonance radiofrequency (RF) radiation in the presence of an external magnetic field on the rate of singlet-triplet transitions in a radical pair and hence on its recombination probability in a liquid.

The first effect is the modulation of radical pair recombination kinetics by resonance RF irradiation (RF-induced beats). Application of the resonance RF field results in transitions between the triplet sublevels of the radical pair with a frequency proportional to the amplitude of the RF field. Thus, the population of the  $T_0$  and thereafter the  $S$  sublevel which is coupled with it by hyperfine interaction will oscillate. These oscillations has been observed in the luminescence kinetics of the recombining radical-ion pairs generated by a  $^{90}\text{Sr}$  radioactive source in liquid solutions where the luminescence intensity is proportional to the singlet state population of GRP.

The second phenomenon related to the RF pumping is the spin-locking effect. This effect originates at large amplitudes of the RF field and results in hampering the singlet-triplet transitions in radical pairs. Therefore, the radical pair turns out to be locked in its initial singlet spin state and OD ESR signal appears in the emission mode while it was in the other phase (absorption) at small amplitudes of the RF field.

The inversion of the OD ESR spectrum takes place when the RF field  $H_1$  is higher than the difference of the local fields  $\Delta H$  in the GRP ( $hfi$  or  $\Delta g$ ). This makes the spin-locking effect useful in studies of primary charged species and reactions in radiation chemistry of hydrocarbon solutions since it gives quite different results depending on the width of the ESR spectrum of the hole.

### Paper 3

This paper is an effort to understand why FDMR and OD ESR techniques have failed to detect cation-radicals of some piperidines while they succeeded with tertiary and branched secondary amines [16,19]. An ESR study with the freon isolating technique of piperidine has been done to answer this question. It has been found, that piperidine forms small aggregates in most freon matrices at cryogenic temperatures and upon X-irradiation, hydrogen-proton transfer between piperidine radical cations and piperidine molecules occurs. We suppose that this can happen also in the X-radiolysis of liquid hydrocarbon solutions of piperidine. The

products of the hydrogen atom or proton transfer reactions cannot be detected by the FDMR (or OD ESR) since only ESR signals of ion-radical pairs are in the FDMR spectra.

This is the first publication of the ESR spectra of the piperidine radical cation and neutral piperidin-1-yl radical, trapped in different halocarbon matrices.

#### **Paper 4**

This paper is an extension of the study started in the previous paper on another cyclic amine - morpholine. Direct evidence of the morpholine aggregation and hydrogen-proton transfer reactions has been demonstrated from the isothermal concentration dependence and from temperature variation studies. Moreover, the dynamics of the morpholin-1-yl neutral radical, trapped in  $\text{CF}_2\text{ClCFCl}_2$ , was observed and investigated in detail by using ESR spectroscopy. The major changes of the ESR lineshape were governed by the averaging of the nitrogen hyperfine anisotropy while no exchange of the isotropic hyperfine coupling constants was observed. Geometrical parameters specifying the restricted anisotropic rotation of the whole radical trapped in the matrix were extracted. A barrier of *ca* 3.6 kcal/mol of such a motion was found from the simulation of the experimental spectra using the non-perturbative method. It has been shown that the secular method cannot reproduce the exchange broadened ESR spectra of systems with large hyperfine anisotropy undergoing large internal reorganisation.

The structure of the neutral morpholine-1-yl radical has been also discussed on the basis of (MNDO/INDO) semiempirical quantum chemistry calculation.

#### **Acknowledgements**

I would like to express my deep gratitude to my supervisors Dr. V.O. Saik and Dr. A.V. Koptug in Novosibirsk and to Prof. Anders Lund at Linköping University for encouragement during the course of this work and all valuable discussions.

I would like to thank my colleagues in the BPP lab (Novosibirsk), particularly Prof. Oleg Anisimov, Dr. Valery Melekhov and Dr. Sergei Smirnov, who indeed introduced me to the OD ESR research.

My sincere thanks to all my friends and collaborators in the ESR lab in Sweden, especially Dr. Nikolas Benetis, Dr. Mikael Lindgren, Dr. Lars Sjöqvist and Mr. Roland Ericksson, who have created an inspiring atmosphere to work in and offered a nice collaboration.

I also acknowledge the secretary at the Chemical Physics Laboratory, Mari Löfkvist, for all help during this work.

The financial support from the Swedish Institute ( Sept. 1990 - May 1992) is sincerely acknowledged.

### References

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