Electron Paramagnetic Resonance Spectroscopy

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Abstract: A survey of the activities of the EPR group at ETH is given. The different research areas are discussed briefly and a particular project is highlighted.

Keywords: Electron paramagnetic resonance · ENDOR · EPR methodology · Transition metal complexes

Electron Paramagnetic Resonance (EPR) is a sensitive spectroscopic method for the determination of the geometric and electronic structure, the dynamics and the spatial distribution of paramagnetic species in materials. EPR directly focuses on the unpaired electrons and nuclei in their vicinity and is therefore the method of choice for studying free radicals, triplet states, compounds with transition metal and rare earth ions and defect centers. It is a particularly useful technique for analyzing orientationally disordered systems such as powders or frozen solutions where standard diffraction methods fail.

Traditional continuous wave EPR methods are quite limited in spectral and time resolution, so that the vast potential of EPR spectroscopy cannot be fully utilized. This is in contrast to modern pulse EPR, a new branch of electron paramagnetic resonance, which allows for the design of experiments that can specifically address a given problem and provide utmost resolution by separating interactions from each other. Recently, a multitude of pulse EPR experiments for increasing spectral resolution and sensitivity have been developed [1][2]. Some of the methods that can be used to achieve detailed information about a paramagnetic species are schematically illustrated in Fig. 1.

Field-swept EPR techniques reveal information about the electronic state of the material under study (electron Zeeman interaction), about the coupling between unpaired electrons (fine structure term) and about strong interactions between the unpaired electron and the surrounding nuclei (hyperfine couplings) (Fig. 1a). Interactions with more distant nuclei can be investigated by means of electron nuclear double resonance (ENDOR) (Fig. 1b), and electron spin echo envelope modulation (ESEEM) and hyperfine correlation (HYSCORE) spectroscopy (Fig. 1c). With these techniques the spectral resolution can be improved by orders of magnitude as compared to standard EPR methods. ENDOR, ESEEM and HYSCORE spectra contain information on the type of nuclei in the vicinity of the unpaired electron (nuclear Zeeman interactions), the distances between the nuclei and the electron spin and the spin density distribution (hyperfine interactions), and the electric field gradient caused by the electrostatic charges.

Fig. 1. Illustration of the potential of pulse EPR for structural analysis. The full circle in the schematic molecule indicates the position of the unpaired electron. The shaded regions give a rough estimate of the areas which can be studied with the corresponding techniques. (a) Field-swept EPR, (b) ENDOR, (c) ESEEM and HYSCORE, (d) experiments for measuring distances between unpaired electrons, (e) experiments to study dynamic processes.
(nuclear quadrupole interactions). Furthermore, a number of pulse techniques have been invented to study distances between different paramagnetic centers (Fig. 1d), and to investigate dynamic properties of paramagnetic molecules (Fig. 1e). Pulse EPR methods can thus provide detailed local structure information of ordered and disordered paramagnetic compounds.

The research of the EPR group at ETH, consisting of chemists, physicists and engineers, is targeted to the design of novel pulse EPR and ENDOR methods, the development of computer programs for spectrum simulation, the theoretical computation of the magnetic parameters, the development of EPR instrumentation, as well as the application of EPR spectroscopy in chemistry, biophysics, materials science and environmental science (Fig. 2).

In EPR methodology we concentrate on the design of pulse schemes with the aim of increasing sensitivity and resolution, to reduce measurement time, and to simplify complicated spectra. Examples of recently introduced new pulse experiments are: Electron-Zeeman resolved EPR [3], right-angle wiggling EPR [4], hyperfine decoupling [5][6], radio-frequency driven ESEEM spectroscopy [7], SMART HYSCORE [8], longitudinal detection schemes [9][10], and multiple photon resonances [11].

Traditionally, our research group pays special attention to EPR instrumentation. At present, we focus on the construction of pulse spectrometers [12][13] and rapid pulse programmers, as well as the development of special probeheads operating in the frequency range between 2 and 95 GHz.

Numerical simulations have become an indispensable tool for the interpretation of one- and two-dimensional pulse EPR spectra. Therefore, very versatile software packages are under development to evaluate the magnetic parameters from the experimental data [14]. Quantum-chemical methods, in particular density functional theory, are used to support the assignment and interpretation of the EPR spectra.

In the field of EPR application, we mainly focus on studies of transition metal complexes which are of biological interest or which are relevant in industrial catalysis. Currently, the following areas are pursued: characterization of cytochrome P450, analogues [15], nickel enzyme methyl-coenzyme M reductase and nickel porphinoid F430 model systems, studies of the copper(ii) binding to the murine prion protein [16][17], investigations of cob(ii)alamin, the Co(ii)-form of vitamin B12, and its model compounds [18][19], and of Co(ii) porphyrins [20-22] and Co(iv) corroles [23], analyses of metallophthalocyanines, complexes with low oxidation states such as Rh(0), Co(0) and Ir(0) [24][25], and immobilized Cu(i) Schiff base catalysts on silica.

We now present in more detail one particular group of applications, namely EPR investigations on Co(ii) porphyrin and corrin complexes and corresponding model systems.

For several decades, the dioxygen storage and transport function of the iron-containing heme proteins, hemoglobin and myoglobin, have been the subject of many spectroscopic studies. The analysis of the electronic and geometric structure is difficult because of the fast autoxidation rates of these proteins and the fact that they are EPR-silent. The EPR-active Co(ii) porphyrins have been found to reversibly bind oxygen and have thus become of special interest as models for the natural hemes. The oxygen-carrying Co(ii) porphyrins have also been extensively studied for their use in industrial applications (e.g. in gas separation processes).

Using pulse EPR and ENDOR methods, Co(ii)TPP (cobalt(ii) tetraphenylporphyrin) [20][22], Co(ii)(dimethylglyoximato)-Co(ii) or cob(ii)aloxime) [19], and [Cob(ii)ester] ClO4 (heptamethyl cobyrinate perchlorate) [18], are studied in different matrices. The structures of the compounds are shown in Fig. 3. The influence of axial ligation of a nitrogen base or of oxygenation of the complexes [21] was investigated and compared to the results from cob(ii)alamin, both in its base-on (intramolecular base binding to Co(ii)) and base-off form. Pulse EPR and ENDOR methods provide an excellent tool to gain insight into the spin density distribution in such Co(ii) low-spin complexes. This information is important for the evaluation of the specific bonding characteris-
tatics of the unique corrin ligand versus the more symmetric (and more 'common') Co(II)TPP and Cob(II)aloxime complexes.

In these investigations the g tensor, which contains information about the symmetry and the excited states of the complexes, and the hyperfine interaction of $^{59}$Co have been studied with continuous wave EPR in the microwave frequency range between 9 and 95 GHz. To determine the symmetry of the EPR spectrum in the case of cob(II)alamin in the base-off form, right-angle wiggling EPR [4], where the EPR spectrum is disentangled into a second dimension representing the anisotropy of the spin system, is applied. This method can be used to improve the resolution of EPR spectra of disordered systems and to separate overlapping single-crystal spectra. The two-dimensional right-angle wiggling EPR spectrum with its characteristic ridges is shown in Fig. 4. After a careful interpretation of this data we arrive at the conclusion that the g tensor of cob(II)alamin in the base-off form is axially symmetric.

For the evaluation of the hyperfine interactions of $^1$H, $^2$H, $^{14}$N and $^{15}$N, as well as the nuclear quadrupole couplings of $^3$H, $^{14}$N and $^{59}$Co, a variety of pulse EPR methods have been used. $^2$H nuclei can best be studied with ENDOR spectroscopy at higher microwave frequencies (35–140 GHz), whereas for the determination of the hyperfine and nuclear quadrupole interactions of the nitrogen ligands pulse ENDOR (axial ligands) and the two-dimensional HYSCORE technique (porphyrin and corrin nitrogens and nitrogens of cob(II)aloxime) are the methods of choice. As an example, a HYSCORE spectrum of cob(II)alamin diluted into hydroxocob(III)alamin powder recorded at a microwave frequency of 35 GHz is shown in Fig. 5. The spectrum which is recorded with matched pulses [26] at a temperature of 17 K represents the transition frequencies of the corrin nitrogens and of the remote nitrogen of the dimethylbenzimidazole axial ligand. We found that the interactions of these corrin nitrogens are very sensitive to the ring structure and the $\pi$-acceptor capacity of the surrounding solute molecules.

For an estimate of the magnetic parameters and remove ambiguities, density functional theory has proven to be very well suited. As an example, the computed spin density distribution of cob(II)aloxime is shown in Fig. 6.

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Fig. 5. Matched nitrogen HYSCORE spectrum of cob(I)alamin diluted into hydroxocob(Ill)alamin powder recorded at 35 GHz and a temperature of 17 K.

Fig. 6. Density functional theory calculation of the spin density distribution in cob(I)aloxime (red: positive spin density, blue: negative spin density).

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