Example 1. $w=z^{\alpha}$ gives the preceding duality law $(a+3)(A+3)=4$, $\alpha=(a+3)/2$.

Example 2. $w=e^{z}$ provides $U=e^{2Rez}$, $V=-1/|w|^{2}$. Hence the force field with $a=-3$ is dual to the force field with potential $e^{2x}\approx|z|^{\infty}$.

Remark. A similar duality law holds in quantum mechanics (R. Fauv, CRAc Sci Paris, 1958).

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Current trends in EPR spectroscopy

*Hans van Willigen**

During the past decade the field of EPR spectroscopy has seen a surge of activity reminiscent of the developments in NMR in the sixties and seventies. One sign of the vitality of this branch of spectroscopy is the recent publication of a number of texts dealing with modern instrumentation and novel applications[1–3]. (The reader is referred to these texts for further information on the developments sketched in the following paragraphs.) Another is the formation of an International EPR Society a few years ago. In the United States the importance attached to this field of research, especially its biochemical and biomedical applications, is evident from the existence of three EPR research centres[4].

Following the example set by NMR spectroscopists, a major focus of research is the application of pulsed (or time-domain) EPR methods. For many years pulsed EPR was the domain of a small number of investigators with the expertise to build their own spectrometers[5]. Developments in the field of microwave components and digital data acquisition instrumentation have considerably simplified the task of constructing sophisticated pulsed EPR machines. At the same time improvements in instrumentation have led to the development of new applications. It is a sign of the maturation of this field of research that a commercial instrument has recently become available. This should lead to a significant increase in the application of time-domain EPR in the study of paramagnetic systems.

Probably the main area of application of pulsed EPR is in electron spin echo (ESE) measurements of hyperfine couplings between unpaired electrons and nuclear spins. This has proven to be a powerful technique to get information on electronic and geometric structure of paramagnetic species in amorphous materials. Particularly noteworthy are applications in the study of the structure of metalloproteins. Time-domain EPR measurements also give information on electron spin relaxation times (T_1, T_2). Pulsed EPR measurements of relaxation times have been used in detailed studies of molecular motion of free radicals in solution. In the last few years a number of research groups have reported on the construction and applications of Fourier transform EPR spectrometers. Among other things FT EPR can be used to study transient-free radicals (*vide infra*). 2D FT EPR has been used to study motional dynamics and the kinetics of electron exchange.

Another area of interest is the construction and application of high-frequency continuous-wave (cw) and

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pulsed EPR instruments using superconducting magnets. As in the case of NMR, the main advantages of increasing the frequency (and thus magnetic field) employed in EPR measurements are the increase in sensitivity and spectral resolution. Instruments employing microwave frequencies as high as 250 GHz (compared with the 9-10 GHz used in standard X-band EPR spectrometers) have been reported. The increase in sensitivity can be exploited in studies of small samples such as single crystals of biological interest. The increase in spectral resolution stems from the (sometimes very small) differences in g values of free radicals. A mixture of free radicals may give resolved resonance peaks when using a high-frequency spectrometer, whereas an X-band instrument may give only a single peak. The g value also can be affected by interaction of the paramagnetic molecule with the environment. Thus high-frequency EPR can find use in studies of heterogeneous systems. The increased spectral resolution is of special interest in studies of paramagnetic molecules in amorphous solids. The effect of g-value anisotropy will be more readily observable and can be exploited in angle-selective electron nuclear double resonance (ENDOR) measurements to obtain information on electron-spin–nuclear-spin hyperfine interactions that cannot be resolved by EPR. The g-value anisotropy also can be exploited to get information on anisotropic molecular motion.

The work of a number of groups is concerned with the development of instrumentation for EPR imaging. With an EPR imaging spectrometer the spatial distribution of electron spins in inhomogeneous samples can be probed. Possible applications include the study of the distribution of paramagnetic centres created by ionizing radiation and the study of diffusion of free radicals.

Early on in the development of EPR it was recognized that it could be an ideal spectroscopic tool to study transient-free radicals generated in chemical reactions. The high spectral resolution offered by EPR facilitates identification of such species which can be of help in establishing reaction mechanisms. In addition information can be obtained on the kinetics of radical formation and decay. Conventional EPR instruments are not very well suited to monitor chemical kinetics because of their relatively slow response time. However, fast chemical reactions initiated by pulsed-laser excitation or pulse radiolysis can be monitored with a number of novel EPR techniques. The first, which has found broad application in recent years, makes use of a cw EPR spectrometer that has been modified to enable direct detection of the evolution of the EPR signal following a laser or radiolysis pulse. The method offers nanosecond time resolution and provides important information on reaction mechanisms through the phenomenon of chemically induced electron spin polarization (CIDEP). A complete analysis of the spectral data not only yields information on chemical kinetics, but also gives information on the spin selectivity of the reaction steps and on spin relaxation times. Among other things the method is being used to study photosynthetic reaction centres.

Time-domain EPR methods constitute an alternative way to monitor free radicals formed in chemical reactions. ESE has been used to measure free radicals formed with a laser pulse or with pulse radiolysis. It has

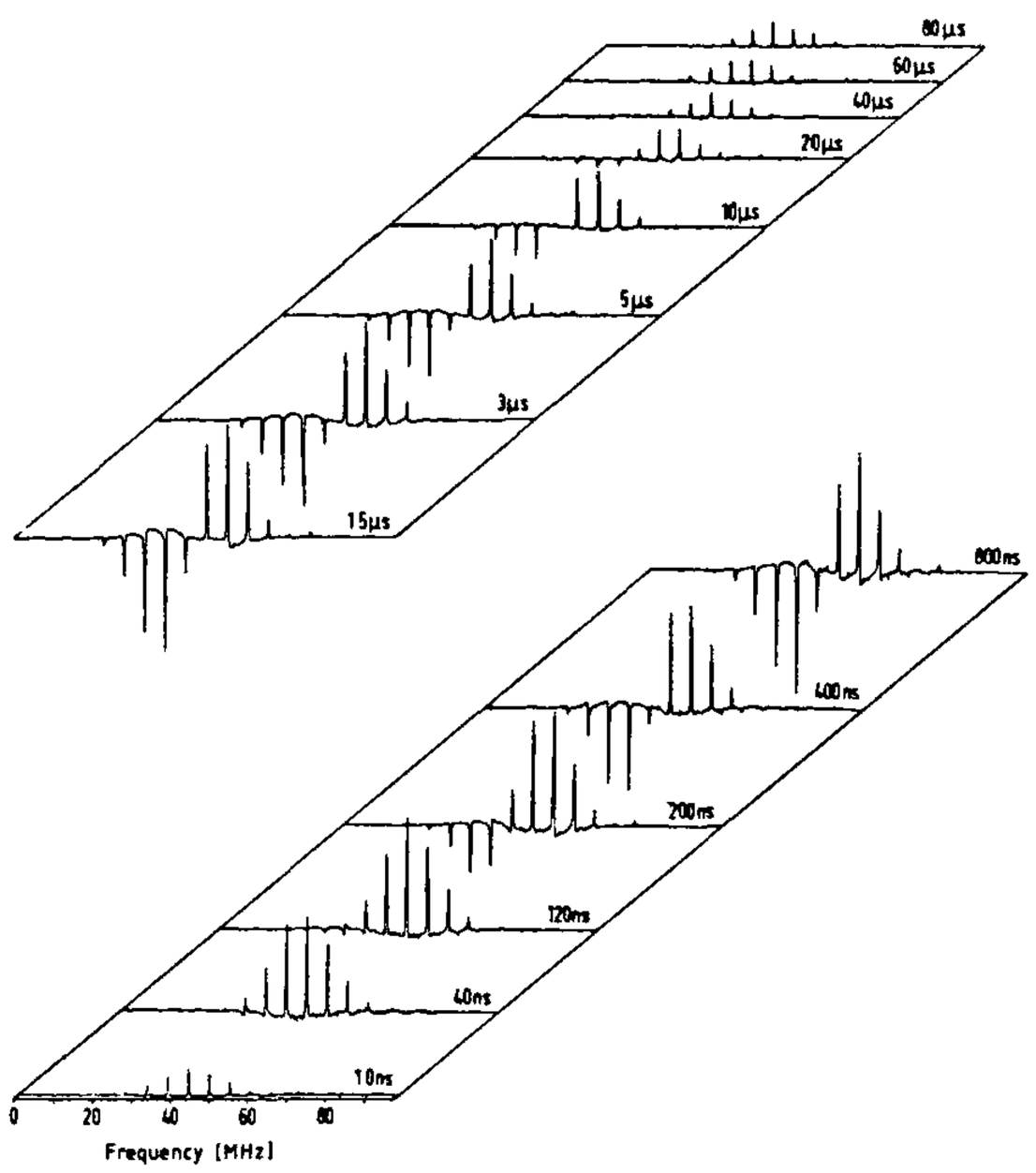

Figure 1. Time development of the FT-EPR spectrum of the duroquinone anion radical formed by pulsed laser induced electron transfer from ZnTPP to duroquinone[6] Solvent ethanol.

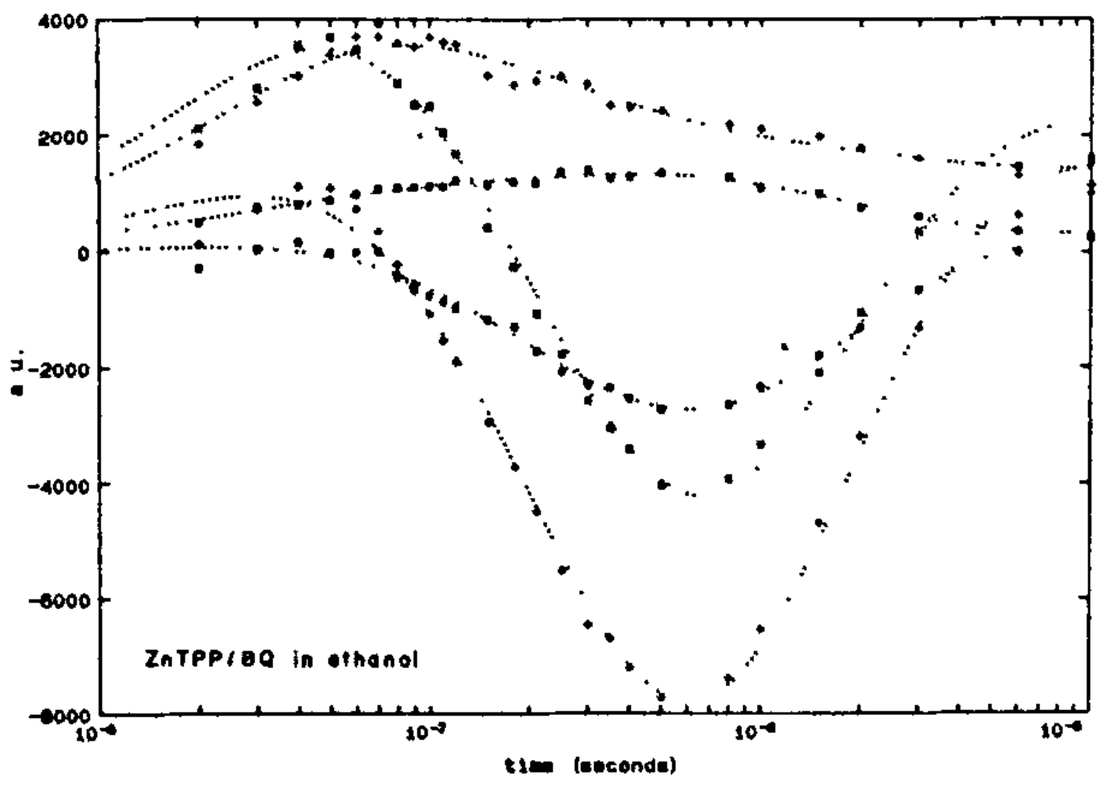

Figure 2. Time development of the amplitudes of the hyperfine components in the spectrum of the benzoquinone anion formed by pulsed laser induced electron transfer from ZnTPP to benzoquinone[7].

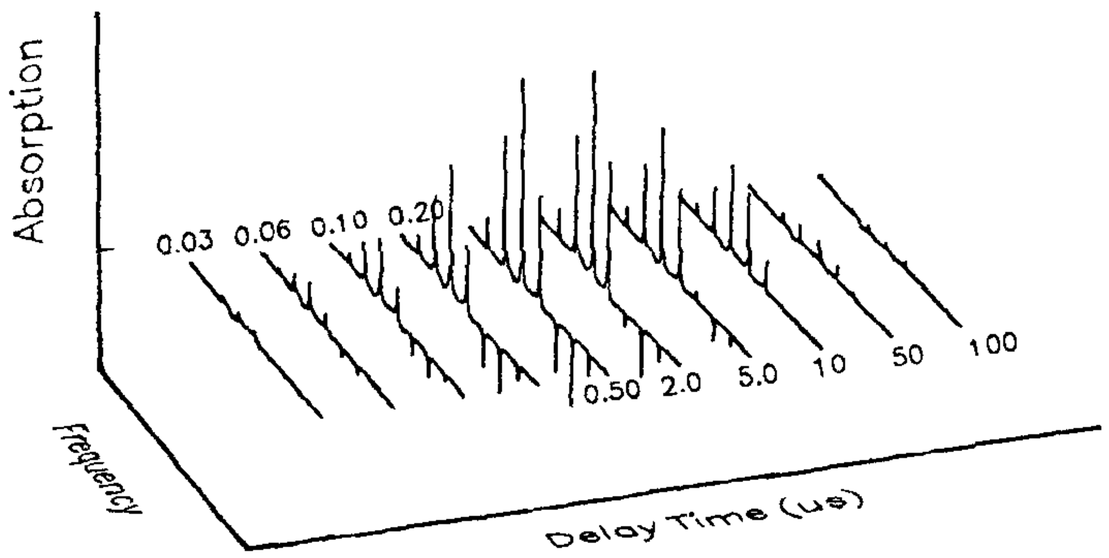

Figure 3. Time development of the FT-EPR spectra from the (perdeuterated) acetone ketyl radical formed by a pulsed laser induced hydrogen abstraction reaction in a solution of acetone (perdeuterated) in 2-propanol (perdeuterated)[8].

been shown that FT EPR is particularly suited for the study of the formation and decay of free radicals produced photochemically. The method provides the ultimate in sensitivity, spectral resolution, and time resolution. Examples of the application of FT EPR in studies of photochemical reactions are given in Figures 1–3. Figure 1 gives the spectra of the duroquinone anion radical formed by photoinduced electron transfer from zinc tetra-phenylporphyrin (ZnTPP) at various times after the excitation of ZnTTP[6]. Noteworthy is the appearance of emission as well as absorption peaks due to CIDEP. The time evolution of the amplitudes of the hyperfine lines in the spectrum of the benzoquinone anion generated by electron transfer from ZnTPP is given in Figure 2. A complete analysis gives detailed information on chemical rate constants as well as rate constants governing electron spin dynamics[7]. Finally, Figure 3 shows spectra from the acetone ketyl radical formed in a photochemical reaction of acetone with 2-propanol[8].

In conclusion it can be stated that the range of applications of EPR has been considerably broadened in recent years as a result of the increase in sophistication of instrumentation, measurement techniques, and data analysis. Particularly in the areas of biology and biochemistry these developments have led to a rapid growth in the number of research groups utilizing EPR.

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Collisions with Earth over geologic times and their consequences to the terrestrial environment

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Collision of comets and asteroids appears to be a forceful mechanism as an alternative to volcanism for creating stress on life on the earth but a general theory of mass extinctions over geologic ages is difficult to formulate from the meagre observations available so far. Geochemical results in the Indian subcontinent at Cretaceous–Tertiary boundary are presented and the relative importance of Deccan volcanism and asteroidal impact hypothesis is discussed.

To kill the evil doers, wielding a sword
Like ferocious comet Keshava appears in the form of Kalki.
Victory to Thee! Oh Lord Hari

Jayadev in *Gita Govinda*
– circa 12th century AD

Examination of lunar craters, photographs of planetary and satellite surfaces taken by space missions and laboratory studies of lunar samples and meteorites have revealed the importance of interplanetary collisions as a prime process in the formation of planets and in carving out their surfaces as we see them today. In the early stages of the formation of the solar system, once

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