Chapter 2

Introduction

Electron paramagnetic resonance (EPR) has traditionally been carried out at microwave frequencies between 9 and 10 GHz (X–band) and magnetic fields around 0.3 T. In the last twenty years, however, a strong trend has evolved to expand the range of microwave frequency and magnetic field to higher values. The origin of this development lies in the fact that high field / high frequency EPR offers several great advantages when compared to conventional X–band EPR. The most important of these advantages are the increased spectral resolution, a gain in sensitivity for samples of limited size or quantity, the accessibility of zero–field fine structure transitions that are 'EPR–silent' at lower frequencies and the sensitivity to different motional frequency regimes.

Despite the associated technical difficulties, the development of spectrometers exploring these field and frequency ranges has steadily evolved. Among other reasons, this development was made possible by the increasing commercial availability of superconducting magnets and advances in microwave source and detector technology.

Following the report of EPR experiments at 150 GHz of the group of Lebedev (Grinberg et al. 1983) around the beginning of the nineties, several other high field EPR spectrometers were built operating at frequencies up to 250 GHz (Weber et al. 1989, Burghaus et al. 1992, Lynch et al. 1988, Prisner et al. 1992); some of them operating in pulsed mode. Since 1996, W–band spectrometers (95 GHz) are commercially available (Schmalbein et al. 1999). However, only very few spectrometers operating at frequencies above 200 GHz and up to 600 GHz have been described so far. (Earle et al. 1996, Reijerse et al. 1998, Moll et al. 1999, Smith et al. 1998, Rohrer et al. 1999, Cardin et al. 1999, M. Knüpling 1999)

In the framework of a research program focused on high–field EPR (Deutsche Forschungsgemeinschaft 1997), a spectrometer operating at a frequency of 360 GHz and at magnetic fields up to 14 T was built up in the course of the work presented here. In conjunction with the existing X–band (9.5 GHz) and W–band (95 GHz) spectrometers this considerably expands the scope of measurement frequencies accessible in our workgroup. As has become obvious already from the experiences gained from the extension to W–band spectroscopy, performing EPR experiments at multiple frequencies provides a better insight into physical and chemical processes than can be achieved by observations at a single frequency only.

Considering the limited number of working spectrometers, it is easily understandable that so far no single best way of dealing with the technical problems encountered when working with frequencies above 200 GHz has evolved. With the strong focus of our workgroup on the elucidation of the structure and functioning principles of bioorganic systems it was of particular interest to see whether the chosen spectrometer configuration would provide a sufficiently high sensitivity and resolution to observe well resolved spectra of paramagnetic biomolecules. One of the goals of this work therefore was to characterize the performance of the spectrometer and to get a better idea about which parts should be optimized.

This thesis is structured in the following way: The next chapter will give a motivation for the extension of EPR to higher microwave frequencies and magnetic fields. In chapter 4, an overview of the theory of Gaussian optics will be given to the extent needed to describe the resonator and transmission line of the spectrometer. The experimental setup of the spectrometer will then be described, followed by the description of the numerical simulation routines developed for the interpretation of the observed spectra. Subsequently, the first experimental results obtained with the spectrometer will be presented. In a final discussion, the main results will be summed up and the most imminent future projects will be plotted out.