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Referee report on the Ph. D. thesis entitled "^{1}H Relaxation Processes in Solutions of Nitroxide Radicals – ^{14}N/^{15}Isotope Effect", submitted by Mrs. Mgr. Agnieszka Korpala"

The thesis of Mrs. Korpala deals with the analysis of nuclear ^{1}H spin-lattice relaxation dispersion data of several organic molecular solvents in the presence of paramagnetic solute molecules containing a nitroxide group. Whereas the role of bare paramagnetic centers on the relaxation behavior has been dealt with in numerous previous studies, Mrs. Korpala is faced with such centers in the presence of hyperfine interactions with neighboring nitrogen nuclei, ^{14}N and ^{15}N. Since, as said, the two isotopes have different spins (1 and ½, respectively) the electronic level scheme is modified in different ways. This leads, in each case, to significant terms in the expression of the ^{1}H spin-lattice relaxation rate. It has been attempted in this thesis to apply this approach to the experimental results. Quite successfully, as I will point out below.

The work combines experimental and theoretical parts in a quite balanced way. As far as the experiments are concerned, Mrs. Korpala gives an account of the sample preparation and the FC experiments themselves, which have essentially been performed on a FC relaxometer at the University of Bayreuth during her stay in the group of Prof. E. Rössler (University of Bayreuth, Germany). The focus of the thesis is put, however, on the analysis of those data within the frame of a theoretical approach developed by Prof. Kruk whom I consider the leading scientist in relaxation theory in. Mrs. Korpala makes clear statements on which part of the work was due to herself and how sharing of her part and that of Prof. Kruk is to be considered.

Starting my more detailed comments on the manuscript itself I first like to say that Mrs. Korpala develops it in a quite careful way, starting off, apart from the Introduction, with some basics of nuclear spin relaxation (section 1). In section 2 she presents, by turning from

more general statements about the dominating interactions towards very specific informations about available motional models, a quite nice account of what kind of spectral densities can be expected in the actual model system. I learn about the tradeoff between the physical relevance of processes and the complexity of describing these processes. So, I understand eq. 39 as being a pragmatic "compromise", but I also learn that it is difficult to get model free information when considering such kinds of correlation functions. Also section 3, where Mrs. Korpala presents the relaxation equation starting off from a density matrix formulation, is well formulated in a concise manner. She carefully discusses several possible cases of diamagnetic and paramagnetic systems. Section 4, which discusses the "history" of theoretical approaches describing nuclear spin relaxation in the presence of paramagnetic centers, points out that there has been a close interplay between instrumental possibilities and theory. The development and today´s availability of powerful FC relaxometers provides new possibilities which motivated theory to go beyond early approaches. With this section Mrs. Korpala prepares her turning over to the more specific parts of her thesis, starting in section 5 with the general discussion of ^{1}H relaxation in nitroxide radical solutions. This section, which I consider as a quite central one, contains in a dense but appropriate way all relevant informations on the hyperfine parameters, the energy level schemes of both cases, ^{14}N (eqs. 67-69) and ^{15}N (eqs. 65-66), the corresponding graphical schemes (Fig. 5.1) and the ^{1}H spin-lattice relaxation rates of both cases (eqs. 73-74). The significance of the various terms is illustrated in Figs. 5.2-5.4. One notes that there is, at certain combination of hyperfine interaction and solvent mobility parameters, the possibility of relaxation enhancement at intermediate Larmor frequencies. In sections 5.3 Mrs. Korpala rationalizes the appearance of such enhancements within the frame of this approach. And she points out the sensitivity of these features as motional parameters are varied (Figs. 5.7-5.13). Then, from section 6 on, Mrs. Korpala turns to the experiments and the data analysis. In section 6, though in a quite short way, she describes the FC relaxometry method and provides the necessary informations about the sample preparation. Section 7 presents the enormous set of experimental data covering the relaxation dispersion curves of three solvent molecules (decalin, glycerol and propylene glycol) in the absence (Figs. 7.1, 7.12 and 7.26) and in the presence of the nitroxide radicals. In the latter case the experiments were carried out at various solute concentrations (e. g. Fig. 7.5) and at various temperatures in order to "separate" the paramagnetic contribution and to modify the motional behavior of the solvents (Figs. 7.3, 7.16, 7.28). I also like to

stress again that in all cases the experiments were carried out using both, ^{14}N and ^{15}N isotopically labelled nitroxides. The analysis of the data turns out to be a successful application of the theoretical approach presented in section 5. Keeping some structural (distances) and spectroscopic (hyperfine coupling strength) parameters fixed the excellent fits (Figs. 7.6, 7.18 and 7.30) yield dynamical parameters such as translational and rotational correlation times and diffusivities which are compared with data gained from experiments on the pure solvents. The comparison demonstrates the appropriateness of the approach quite well. For each of the three solvents Mrs. Korpala also illustrates the weight of the diverse contributions of the relaxation rate expressions. Whereas her kind of presentation of the results occasionally appears somewhat dense and difficult to read such that it does not always become clear what kind of easy-to-understand-arguments are hidden behind the formal description, the concluding summary (section 8) emphasizes the essential points in a well written way. Here, Mrs. Korpala includes statements about the competing factors eventually leading to the observed relaxation enhancement as well as about limitations of the appropriateness of the motional model. In a short concluding section some perspectives, thereby extending this type of study to paramagnetic molecules which contain two dipolarly coupled electrons, are discussed on the basis of a preliminary experiment (section 9).

When I now come to judge on the thesis I like to mention again that this work combines in a unique way experiments and theory. Well, Mrs. Korpala has been able to successfully apply a theoretical approach stemming from her supervisor (Prof. Kruk) to a couple of model systems. To do this requires deep knowledge of the theory, experimental skills and the ability to carry out an involved data analysis. Mrs. Korpala was able to fulfill all those tasks in the best possible way. The written manuscript is complete, correct and interesting to read. Needless to say that the work is of high scientific value; this is proven by eight high rank publications at which Mrs. Korpala signs as coauthor. In addition she attended several times the Ampere summer schools in Zakopane. Having been myself member of the poster evaluation committee in Zakopane I remember quite well that at least once she presented a poster which was considered as being one of the best ones. Concluding, I am persuaded that the thesis of Mrs. Korpala earns the grade "**very good" (5.0)**.

Franz Fujara