## This Week's Citation Classic

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Kneubühl F K. Line shapes of electron paramagnetic resonance signals produced by powders, glasses, and viscous liquids. J. Chem. Phys. 33:10748, 1960. [Dept. Chemistry, Johns Hopkins Univ., Baltimore, MD]

Epr represented a new powerful tool in solid state physics, chemistry, and biology. While epr was originally confined to single crystals and solutions of low viscosity, this paper provided an interpretation for epr spectra of powders, glasses, and highly viscous solutions. [The SCI® indicates that this paper has been cited over 335 times since 1961.]

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"This epr paper was written in the Baltimore climate at temperatures and humidities around 99 when I spent a year with W.S. Koski at Johns Hopkins. He provided for everything, a problem, an esr machine, and a lab technician, O. Shafer. The problem was epr of porphyrins¹ prepared by W.S. Caughey at the Johns Hopkins School of Medicine. As most biological and chemical samples, they were either powders or solutions, yet never single crystals. Thus, I had to make the best of it.

"When I arrived in Baltimore I had some ideas on epr since I had just spent a few months with D.J.E. Ingram in England as a Ramsay Memorial Fellow of the University College London, where I was sent by my PhD supervisor H.H. Günthard of the physical chemistry lab at the ETH Institute of Organic Chemistry headed by L Ruzicka and V. Prelog. My stay in England was financed by a Swiss chemist fund. When I described my future work on epr to its chairman, P. Karrer, he passed the remark that every farmer would have an epr machine in his barn.

"At the dawn of the 1950s epr spectra of single crystals and lowviscosity solutions were

well understood. Single crystals allowed the determination of the gtensor and lowviscosity solutions that of its isotropic part. Epr spectra of powders, glasses, and highly viscous solutions required averaging over all orientations of the singlecrystal gtensor. This I could manage without difficulty. The real headache began with solutions of medium viscosities. Here, I tried to solve Fick's diffusion equation in spherical coordinates including Debye's considerations on random rotation. Combination of the resulting angular correlations with the Hamiltonian led to an expression which allowed the description of the variation of the epr line shape with viscosity. However, I felt pretty unsafe. Thus, I asked T.H. Berlin for advice. He not only gave his blessing to my calculations but also invited me to a great crab party at his home. Subsequently I devised an epr experiment on solutions of copper salts in glycerol, where I could vary the viscosity with temperature in a wide range. Theory and experiment agreed. I suppose that this study has found wide interest since it helped at the proper time to extend the gamut of epr from single crystals to powders and solutions, which are undoubtedly dominating in chemistry and

"Towards the end of 1960 I returned to the ETH in Zürich to work at the solid state physics laboratory with C. Busch. First, I continued studies on epr with special emphasis on group theory and the asymmetry of the gtensor. For historic reasons most of this work is published in German.<sup>26</sup> I stopped dealing with epr in the mid1960s and started research on submillimeter waves and infrared: lasers, spectroscopy. stratosphericballoon solar observations, atmospheric and building physics. For this and the papers created in Baltimore I was awarded membership in the Johns Hopkins Society of Scholars in 1976.

Kneubühl F K, Koski W S & Caughey W S. An electron spin resonance study of silver porphyrin. J. Amer. Chem. Soc. 83:160710, 1961.

<sup>2.</sup> Kneubühl F K. Anisotropic spin orbit coupling in paramagnetic resonance. *Phys. Lett.* **2**:1634, 1962; **4**:208, 1963.

<sup>3. ....,</sup> Symmetry and Mikrowellenspektren paramagnettscher Zentren. *Phys. Kondens. Mat.* **1**:41047, 1963.

<sup>4....,</sup>Paramagnetische Zentren mit den Symmetrien n, n und n Phys. Kondens. Mat. 4:5065, 1965.

Bieri A & Kneubühl F K. Vergleichende Betrachtungen zur Gruppentheorie der paramagnetischen Resonanz. Phys. Kondens. Mat. 4:23046, 1965.

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