# High-Frequency and -Field EPR Study of the $[Fe(H_2O)_6]^{2+}$ Ion

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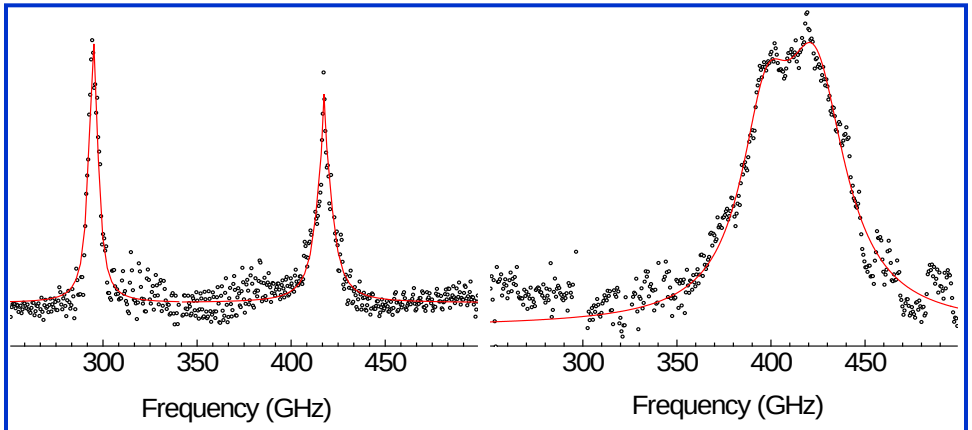
The $Fe^{2+}$ ion in various coordinations is one of the most important species in the living and non-living nature. Owing to its very large zero-field splitting (zfs), it poses great difficulties to an EPR spectroscopist, as no spectra can be observed at the conventional X- or Q-band frequencies. The zfs is described by parameters $D$, $E$ and $B_4^0$ , $B_4^4$ of the spin Hamiltonian

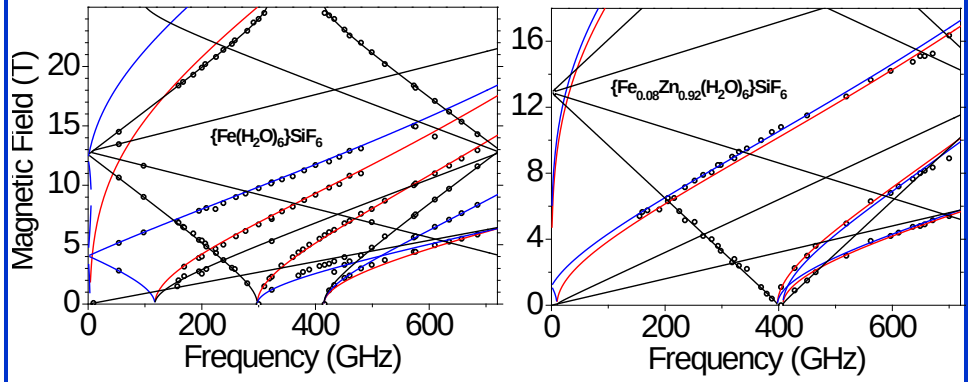
$$H = \beta B \cdot \mathbf{g} \cdot S + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2) + B_4^0 O_4^0 + B_4^4 O_4^4$$

Application of both magnetic field-swept and frequency-swept techniques allowed full characterization of pure $[Fe(H_2O)_6]SiF_6$ (**1**) and Fe-doped $[Zn(H_2O)_6]SiF_6$ (**2**). **1** exhibited $D$ of 11.95 $cm^{-1}$ and $E$ of 0.66 $cm^{-1}$. 4-th order zfs parameters were also determined. $D$ of **2** was larger yet (13.42 $cm^{-1}$) while $E$ was very small (0.05 $cm^{-1}$), which indicates a higher symmetry of **2** compared to **1**, pointing out at a phase change occurring in **1** at low temperatures. The results of quantum-mechanical calculations (Unrestricted Hartree-Fock) were in a semi-quantitative agreement with the experimental zfs parameters.

Theoretical interpretation of the zero-field splitting in transition metal complexes is a topic extensively studied in recent literature and reliable experimental data are needed for continuing progress in that area. Results described above could not be achieved by using conventional instrumentation.




Frequency-swept spectra in zero field of **1** (left) and **2** (right)




Frequency dependencies of high-field EPR resonances for **1** (left) and **2** (right).

**Facilities:** DC Field (25-T resistive "Keck" magnet) and EMR (17-T superconducting magnet).
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