

The Rhombic Effect of Zero-Field Splitting
on the Nuclear Relaxation Times. Quenching
of the Electron Spin Angular Momentum

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The effect of the electron-nucleus dipolar interaction on the nuclear relaxation rates can be described by the well known Solomon equation. In the Solomon equation, it is assumed that the S manifold is split by the electron Zeeman energy alone, with an isotropic g factor. When $S > 1/2$, the effect of spin-orbit coupling results in zero-field splitting (ZFS) which alters the spacing of the spin levels. If the ZFS energy is smaller than the electron Zeeman energy, it will only introduce a small perturbation. However, when the ZFS is large compared to both the electron Zeeman energy $h\omega_s$ and the EPR linewidth, its presence may severely alter the nuclear relaxation equations.

Recently the effect of ZFS on the nuclear relaxation rates has attracted attention of a number of authors. In the treatment suggested by the Stockholm group, the electron spin is included in the lattice and the nuclear relaxation times are numerically calculated directly from the spectral densities without invoking the concept of electron spin relaxation times. In the treatment suggested by the Florence group, the electron spin is assumed to be coupled to the lattice through a mechanism whose correlation time is short compared to the electron relaxation time, so that the electron spin system can be described by a single relaxation time τ_s .

In both the treatments of the Stockholm and Florence groups, however, a ZFS tensor is assumed to have an axial symmetry, which is hardly acceptable in actual systems of paramagnetic metal ion complexes. The present paper investigates the effect of the rhombic symmetry of ZFS on the nuclear relaxation rates, T_{1M}^{-1} and T_{2M}^{-1} , in which it is assumed that the rate of molecular rotational motion τ_R^{-1} is much larger than the nuclear Larmor precession rate ω_I . It was shown that the rhombic term E of ZFS drastically reduces the relaxation rates of a paramagnetic molecule with an integer electron spin quantum number. This means a quenching of an electron spin angular momentum, which was predicted by Bloembergen and Morgan (J. Chem. Phys. 34, 842 (1961)). Using the Solomon equation, a very short τ_s , 10^{-13} s, is necessary to account for well resolved NMR spectra of lanthanide shift reagent complexes. However, we suggested that the true value for correlation time of lanthanide ion complexes could be much longer than the accepted value, 10^{-13} s.