

File-5: Anisotropy The 'g' VALUE

ESR spectroscopy can be introduced by describing the g values for the NO_2 radical trapped in a single crystal of KNO_3 . When the crystal is mounted with the field parallel to the Z-axis of NO_2 (the two fold rotation axis), a 'g' value of 2.006 is obtained when the crystal is mounted with the x or y-axis parallel to the field, a g value of 1.996 is obtained. The molecule is rapidly rotating about the Z-axis in the solid, so the same result is obtained for x or y parallel to the field. The difference in g values with orientation are even more pronounced in transition metal ion complexes and in complexes of the lanthanides and actinides.

The treatment so far has involved so-called isotropic spectra. These are obtained when the radical under consideration has spherical or cubic symmetry. For radicals with lower symmetry, anisotropic effects are manifested in the solid spectra for both the I values and the values. Usually for these lower symmetry systems, the solution spectra qualitatively appear as isotropic spectra because the anisotropic effects are averaged to zero by the rapid rotation of the molecule.

Anisotropy in 'g' arises from coupling of the spin angular momentum with the orbited angular momentum, The spin angular momentum is oriented with the field, but the orbital angular momentum, which is associated with electrons moving in molecular orbitals, is locked to the molecular wave function.