

14.2 Electron paramagnetic resonance (EPR) spectroscopy

The recommendations contain definitions of basic terms, conventions and practices for data presentation in the area of EPR spectroscopy. This includes those pertaining to spectra of systems with $S = 1/2$. A version for systems with $S > 1/2$ may follow. This does not include the areas pertaining to saturation transfer, double resonance and time domain techniques.

14.2.1 Nomenclature and basic definitions

Electron paramagnetic resonance (EPR) spectroscopy (ESR-spectroscopy)

Electron paramagnetic resonance (EPR) and/or electron spin resonance (ESR) is defined as the form of spectroscopy concerned with microwave-induced transitions between magnetic energy levels of electrons having a net spin and orbital angular momentum. In the present context, the magnetic field scanning method is assumed. Other methods, however, are conceivable. The term electron paramagnetic resonance and the symbol EPR are preferred and should be used for primary indexing.

Note: Use of the upper case, with no punctuation, "EPR" as opposed to "e.p.r.", is adopted here, since it is consistent with the existing IUPAC NMR nomenclature. Also "paramagnetic" should be used, since it comprises other than 'spin only' systems. On the other hand, "ESR" has been so widely used that it is not practical to exclude it completely.

Oscillating magnetic field (frequency and amplitude)

The *frequency* (ν) of the oscillating magnetic field applied to induce transitions between the magnetic energy levels of electrons is measured in gigahertz (GHz) or megahertz (MHz).

The *amplitude* of the oscillating magnetic field is designated by B_1 . The recommended unit is the millitesla (Mt).

Static magnetic field

The static magnetic field at which the EPR spectrometer operates is measured by the magnetic flux density B and the recommended unit is the tesla (T) ($1 \text{ T} = 10^4$ gauss).

EPR absorption and dispersion

A single transition and a set of degenerate or unresolved transitions are referred to as a line. The line shape is often described to be Lorentzian, Gaussian, or a mixture of the two. Absorption or dispersion lines are commonly presented in the first or the second derivative mode.

Symbols for the modes are U_1 and U_2 for dispersion first and second derivatives, respectively, and V_1 and V_2 for absorption. Spectra recorded out-of-phase with respect to the Zeeman field modulation are indicated by adding primes to the previous symbols (e.g. V_2' for second derivative out-of-phase absorption).

Note: Although this version of the recommendation does not include the saturation transfer technique (ST-EPR), it seems appropriate to standardize the mode designations here for future extension.

***g*-factor**

In the absence of nuclear hyperfine interactions (*vide infra*), B and ν are related by

$$h\nu = g\mu_B B$$

where h is the Planck constant, μ_B is the Bohr magneton $eh/(4\pi m_e)$, and the dimensionless scalar g is called g -factor. Use of the term g -value is discouraged.

Note: In the absence of nuclear hyperfine interaction the nuclei involved have no nuclear spin, and therefore, there will be no nuclear Zeeman term or nuclear electric quadrupole term. Thus the relation is rigorously correct for $S = \frac{1}{2}$ systems.

***g*-matrix**

When the paramagnetic species exhibits an anisotropy, the spatial dependency of the g -factor is represented by a 3x3 matrix g . The matrix representation is referred to as g -matrix. In a general coordinate system, such as (x, y, z) , the components may be designated as g_{xx}, g_{xy}, \dots , etc. In cases where a principal axis system can be assigned, in which the off-diagonal terms are zero, the three principal values of the g -matrix will be expressed by g with a single subscript identical to the principal axis designation adopted for the g -matrix. A recommended example is: g_x, g_y, g_z for the principal axes (X, Y, Z) .

For a powder spectrum, if a specific assignment is not made, the following conventions are recommended:

- (a) In a spectrum having the characteristics of lower than axial symmetry with three distinct lines, g_1 , g_2 , and g_3 are used for the low, middle and high field line in that order.
- (b) In a spectrum having the characteristics of apparently uniaxial symmetry, exhibiting a parallel and a perpendicular feature, the lines are designated as g_{\parallel} and g_{\perp} , respectively.
- (c) In a spectrum representing more than one paramagnetic species, designations of g -factors must include some species identification in parenthesis, e.g., g_1 (radical 1) or $g_1(1)$.

Hyperfine coupling constant

The interaction energy between the electron spin and a magnetic nucleus is characterized by the hyperfine coupling constant A with units in joules. A/h and $A/(hc)$ may be reported in Mhz and cm^{-1} , respectively. Expressing A in units of tesla, millitesla, or gauss is rejected. When the paramagnetic species has magnetic anisotropy the hyperfine coupling is expressed by a 3x3 matrix called a hyperfine coupling matrix \mathbf{A} . \mathbf{A} is often divided into an anisotropic and an isotropic term as follows:

$$\mathbf{A} = \mathbf{T} + [\text{Tr}(\mathbf{A})/3] \mathbf{1}$$

\mathbf{T} is a traceless 3x3 matrix (sum of the diagonal elements being equal to zero), $\mathbf{1}$ is a unit matrix of the same dimension. The principal components of \mathbf{A} , when resolved, are denoted by A with the principal axis designation added as the subscript (e.g., A_a , A_b , A_c , if (a,b,c) is chosen as the principal axes for \mathbf{A}). If the absolute sign of a principal component is deduced theoretically, it should be given in parentheses as e.g. $A_a/h = (+) 70$ Mhz. The principal axis systems for matrix \mathbf{A} and \mathbf{g} may or may not coincide with each other. In cases where the principal components of \mathbf{A} are not resolved, the hyperfine interaction in a line is described in terms of A' with the same subscript adopted for the g -factor of the line in which the hyperfine interaction is observed.

Splitting of lines

Hyperfine interaction usually results in splitting of lines in an EPR spectrum. The splitting (a) is measured in units of millitesla (Mt). The relation between the hyperfine splitting and hyperfine coupling constant must be derived for each system, e.g. by computer simulation, depending upon the accuracy desired. For cases where higher-order terms can be neglected and the effects of the nuclear Zeeman term need not be taken into account, the splitting a is related to the absolute value of the hyperfine coupling constant A by

$$A = g\mu_B a$$

Note: The nuclear species giving rise to the hyperfine interaction should be explicitly stated, e.g. "the hyperfine splitting due to ^{65}Cu ". When additional hyperfine splittings due to other nuclear species are resolved, the nomenclature should include the designation of the nucleus, and the isotopic number, e.g. $a(^{14}\text{N})$. If the splittings are assigned to more than one nucleus of the same nuclear species, they may be distinguished by adding subscripts such as $a(^{15}\text{N}_1)$ and $a(^{15}\text{N}_2)$. The same conventions apply to the nuclear hyperfine coupling constant A .

Nuclear electric quadrupole coupling tensor

When the nucleus has an electric quadrupole moment (i.e., $I > 1/2$), its interaction with the surrounding molecular electric field-gradient is expressed by a second rank tensor \underline{P} called the nuclear electric quadrupole coupling tensor. The principal components of \underline{P} , if resolved by analysis of a hyperfine spectrum, are denoted by P with the principal axis designation as the subscript (e.g. P_1, P_2, P_3 , for the principal axes (1,2,3)).

In the presence of axial symmetry, the axial component of \underline{P} tensor, e.g. P_3 is defined by

$$P_3 = eQq/[2I(2I-1)]$$

where eQ is the nuclear quadrupole moment, q is the axial electric field gradient at the nucleus and I is the nuclear spin. Deviation from axial symmetry is expressed by the asymmetry factor $\eta = (P_1 - P_2)/P_3$. The nuclear species involved must be specified following the conventions for hyperfine interactions, e.g. $P_1(^{75}\text{As})$.

Values of P are expressed in joules; P/h and $P/(hc)$ may be reported in MHz and cm^{-1} , respectively.