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**Recommendations for
EPR/ESR NOMENCLATURE AND
CONVENTIONS FOR PRESENTING
EXPERIMENTAL DATA IN PUBLICATIONS**

(Recommendations 1989)

Prepared for publication by

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Recommendation for EPR/ESR nomenclature and conventions for presenting experimental data in publications (Recommendations 1989)

Abstract - The recommendations presented here contain definitions of basic terms, conventions and practices for data presentation in the area of electron paramagnetic resonance spectroscopy. This part includes those pertaining to spectra of systems with $S = \frac{1}{2}$. Recommended units for microwave frequency (gigahertz), and the static and oscillating magnetic field (tesla) are based on the current usage in the SI system. Definitions and relations for the g -factor, the nuclear hyperfine coupling, and the nuclear electric quadrupole coupling are given, and designations for their anisotropy in crystalline and powder samples are clarified. Required items of experimental conditions to be included in actual EPR data presentation in the text or in graphic presentation of EPR spectra are listed to facilitate accurate transfer of spectral data. This part does not include the areas pertaining to saturation transfer, double resonance and time domain techniques.

COMMENTS

The very first version of the Recommendations on EPR Nomenclature was drafted in 1977 by James R. Bolton, University of Western Ontario, and was the subject of discussion in a group meeting chaired by Dr. Bolton in the VIth ISMAR in Banff, Canada in 1977.

The second version, which was sent out for reviewing by a number of EPR experts in several countries in 1984, was based on the Bolton draft and was revised by Hideo Kon, National Institutes of Health.

The present proposal has been re-written by Kon, taking into account the suggestions and criticisms by twenty-five reviewers during 1984-1985 in consultation with James Vincent of the University of Maryland.

Rationales for the choice in some of the items are inserted in the text (indented and italicized paragraphs).

In view of the extensive use of electron paramagnetic resonance (EPR) spectroscopy (electron spin resonance (ESR) spectroscopy) in chemistry, physics and biology, it is desirable to encourage the use of consistent nomenclature and the presentation of experimental data in a uniform manner. The Commission on Molecular Structure and Spectroscopy recommends the following:

SCOPE

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

NOMENCLATURE AND BASIC DEFINITIONS

2.1 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 part, the magnetic field scanning method is assumed. Other methods, however, are also conceivable. The term electron paramagnetic resonance and the symbol EPR are preferred and should be used for primary indexing.

2.1 Use of the upper case, with no punctuation, "EPR" as opposed to "e.p.r.", is adopted, 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.

2.2 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).

2.3 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) ($1 \text{ T} = 10^4 \text{ gauss}$).

2.3 tesla vs. gauss: both tesla and gauss are units of magnetic induction (magnetic flux density) for which the symbol B has been used. The magnetic field strength H has been recorded in ampere-turn/meter or oersted, and not by gauss. One may argue that "the abscissa of every EPR spectrum is recorded in units of H, namely the field applied to the sample achieved by passing current through coils". However, the calibration of the field strength is inevitably based upon the magnetic induction in matter, whether one uses a standard sample, a proton probe, or the Hall effect. For that reason, it is more appropriate to use B (the magnetic flux density) and specify the method of calibration. The "tesla" rather than "Tesla" is used in SI convention.

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

2.5 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).

2.5 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.

2.6 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.

2.6 "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. IUPAC Manual of Symbols & Terminology for Physicochemical Quantities and Units adopts μ_B (Pure & Appl. Chem. vol. 51, pp. 1-41, 1979) as the Bohr magneton.

2.7 When the paramagnetic species exhibits an anisotropy, the spatial dependency of the g -factor is represented by a 3×3 matrix \underline{g} . The matrix representation is referred to as \underline{g} -matrix. In a general coordinate system, such as (x, y, z) , the components may be designated as g_{xx} , g_{xy} , ..., 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 \underline{g} -matrix will be expressed by g with a single subscript identical to the principal axis designation adopted for the \underline{g} -matrix. A recommended example is: g_X , g_Y , g_Z for the principal axes (X, Y, Z) .

2.7 That \underline{g} is not in general a tensor (neither is the hyperfine coupling constant \underline{A} (ref. 2.8)) was shown by Abragam and Bleaney ("Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford 1970, pp. 166, 170, 651), while the nuclear electric quadrupole coupling \underline{P} (ref. 2.11) is a tensor in the strict sense. Some authors clearly distinguish them by calling \underline{g} and \underline{A} a "matrix" and \underline{P} a "tensor" when all three are involved.

Use of the double subscripts for a general coordinate system and a single subscript for the principal axes has a definite merit of clearly distinguishing the principal components.

The matrices (\underline{g} and \underline{A}) and tensor (\underline{P}) quoted here are defined through the Hamiltonian expression

$$\hat{H} = +\underline{B} \cdot \underline{g} \cdot \underline{S} \underline{U}_B - \sum_a \underline{S} \cdot \underline{A}_a \cdot \underline{I}_a - \sum_a \underline{I}_a \cdot \underline{P}_a \cdot \underline{I}_a$$

where \hat{H} is the Hamiltonian operator, \underline{B} is the magnetic flux density, \underline{S} and \underline{I} are vector spin operators, the summation index a covers all nuclear species (except that $\underline{I} = 0$ nucleus can be omitted and $\underline{I} = \frac{1}{2}$ nuclei have no quadrupole term) and the direct interaction of nuclear spin with the magnetic flux density is omitted.

Use of the double subscripts for a general coordinate system and a single subscript for the principal axes has a definite merit of clearly distinguishing the principal components.

In general, the square roots of the principal values of a symmetric tensor \underline{G} represent the principal values of \underline{g} .

$$G_{ik} = \sum_j g_{ji} g_{jk}$$

A similar condition applies to \underline{A} ; in this case the correct signs of the square roots may be uncertain.

It is too restrictive to choose a specific set of nomenclature for the principal components of \underline{g} , another set for \underline{A} , and another for \underline{P} , in addition to the molecular coordinate axis system which normally is dictated by orbital designations such as $d_{x^2-y^2}$, $2p_z$, etc. The recommendation must allow for the most general case, assuming that all these axis systems occur and do not coincide, and yet, has to make certain that there is no conflict under any circumstances. While this could be done, it would make the convention too complicated and cumbersome for authors to remember. In most writing situations, however, not all of the above mentioned principal axis systems occur and some of them may coincide. Thus authors can choose the principal axis designations for only the necessary matrices.

Considering all these complications, it seems much more practical to leave designation of principal axis systems, to a certain extent, to individual authors. One conceivable drawback in so doing, would be that two authors, describing the same compound, may adopt two different principal axis designations so that one author's g_x , for example, may correspond to g_c of the other. However, this kind of inconsistency can not be completely avoided anyway, even if the two authors adopt the same principal axis designation, unless the convention dictates also the order of g -factors such as, e.g., $g_x > g_y > g_z$. In fact, one might suggest a convention for setting the ordering of the principal values by "taking the average and designating the farthest one from the average as g_z and the next as g_y , etc." However, ordering can not be determined a priori, because it depends on the individual compound. For example, in Cu^{2+} -porphyrin, the g -factor measured with the magnetic field parallel to the four-fold axis is the largest, whereas in low-spin Co^{2+} -porphyrin, the g -factor measured similarly is in the middle, but one would not call the four-fold axis \underline{Z} in one compound and \underline{Y} in another.

Thus, forcing too many details of the principal component designations tends to run into conflict with the orbital designations.

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.

2.7a There are, even in powder spectra, cases in which one can make a specific assignment of principal axes. The recommended convention 2.7(a) is strictly for the cases where no such assignment can be made. Designation of unassigned g-factors in terms of (x,y,z) subscripts should be discouraged, because it may turn out to be in conflict with molecular axis system designation as explained above. Non-committal (1,2,3) is much preferred for unassigned cases.

(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., $g_1(\text{radical 1})$ or $g_1(1)$.

2.8 Hyperfine interactions. 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 3×3 matrix called a hyperfine coupling matrix \underline{A} . \underline{A} is often divided into an anisotropic and an isotropic term as follows:

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

\underline{T} is a traceless 3×3 matrix (sum of the diagonal elements being equal to zero), $\underline{1}$ is a unit matrix of the same dimension. The principal components of \underline{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 \underline{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 \underline{A} and \underline{g} may or may not coincide with each other. In cases where the principal components of \underline{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.

2.9 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

$$A = g\mu_B a$$

2.10 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 .

2.11.a When the nucleus has an electric quadrupole moment (i.e., $I > \frac{1}{2}$), 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. $P_1(^{75}\text{As})$.

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

2.11 Nomenclature for nuclear quadrupole interaction is limited to the minimum necessary for reporting EPR data. Use of notations such as $DQ (= 3P_{zz}/2)$, which appear in some EPR articles, are not included. However, use of these and other parameters derived from \underline{P} should be considered optional, as long as they are clearly defined in terms of the present notation. Numerous different designations are also in use for nuclear quadrupole coupling tensors in other fields of spectroscopy. The relationship of \underline{P} to them should be derived from the definitions given in this recommendation.

PRESENTATION OF EPR DATA AND EXPERIMENTAL CONDITIONS

Reference back to previous publications for experimental method is permitted only if the required specific information is present there.

3.1 At least the following items should be specified in presentation of EPR data to facilitate transfer of spectral information:

- (a) If in solution, name of the solvent (or matrix) and concentration of the solution; for solid materials, methods of sample preparation and mounting
- (b) Temperature of the sample and how it is controlled
- (c) Type of sample cell (e.g. aqueous flat cell)
- (d) Type of resonator used, microwave frequency (GHz or MHz), power level (mW) incident on the resonator and loading information (e.g. dewar insert used); whether the frequency and power level are calibrated or taken from the spectrometer settings; power saturation distorting the spectrum, if any, must be so stated.

3.1(d) The commonly used term "cavity resonator" is replaced by a generic term "resonator", since various types of non-cavity resonators are now in use.

- (e) If Zeeman field modulation is used, frequency (MHz or Hz) and amplitude (mT) of modulation, and whether they are calibrated or from the spectrometer settings

3.1(e) "If Zeeman field modulation is used ..."; in some EPR measurements, Zeeman field modulation and/or analog field scan are not used.

- (f) Type of standard sample, if used for field calibration and/or quantitation of the magnetic species
- (g) Method of g -factor measurement and experimental uncertainties

3.2 When EPR spectra are graphically presented, the following information for abscissa and ordinate should be supplied in addition to the above items:

- (a) If the spectra are obtained by analog field scan, the field scan rate, otherwise, the field step size
- (b) Total field extent and/or field calibration marker and method of field calibration
- (c) Markers indicating the point in a line where the g -factor is measured; use of g -factors in place of field scale is discouraged.
- (d) Ordinate information, if the ordinate is not the direct spectrometer output (e.g. computer processed normalization)
- (e) Presentation mode, e.g. "the first derivative of absorption"
- (f) Filtering information (e.g. analog time constant, digital smoothing specifications, etc.)

3.3 Other conventions in graphical presentation of the spectra:

- (a) The Zeeman field increases to the right.
- (b) The phase should be adjusted so that the start of the first low field line in V_1 mode has a positive excursion.