

# I General introduction

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## A Definition and substances

In the context of these tables the term free radical means a chemically stable or transient paramagnetic atomic or molecular species which derives its paramagnetism from a single, unpaired valence shell electron. Following this definition the tables cover

- a) atoms and atomic ions in ground and excited  $^2S$  and  $^2P$  states,
- b) diatomic and linear polyatomic molecules in  $^2\Sigma$  and  $^2\Pi$  states,
- c) polyatomic molecules and molecular ions which arise or may be thought to arise from the break of a single bond of a diamagnetic molecule or molecular ion,
- d) mono-(tri-, penta-, etc.) – negative or – positive ions of neutral organic or inorganic compounds.

Not classified as free radicals are atoms or molecules in ground or excited electronic states with multiplicities larger than two (e.g. O,  $^3P$ ; O<sub>2</sub>,  $^3\Sigma$ ; N,  $^4S$ ; molecules in excited triplet states), transition metal ions and their complexes deriving their paramagnetism exclusively or mainly from d- and f-electrons and charge transfer complexes. However, a number of polyatomic molecular species which do not fulfill the above definition are included because their properties closely resemble those of structurally closely related free radicals. These are

- e) metal(0) complexes and clusters,
- f) high spin polyradicals with electron exchange or dipolar couplings not greatly exceeding the Zeeman or hyperfine interactions, triplet carbenes and poly-carbenes,
- g) selected transition metal complexes deriving their paramagnetism from free radical ligands and the electrons of the center atom.

The volumes cover only compounds with unambiguously verified or at least very plausibly assumed structures. Papers which only state the presence of free radicals in a sample and do not give detailed structures nor magnetic properties are not reviewed. Also not covered are publications which deal exclusively with other topics than experimental determinations of magnetic properties of free radicals. Such work may however be mentioned in footnotes or as further references at the appropriate places.

The ordering of the substances into subclasses is given in the general table of contents. The ordering within the subclasses is explained, where not self explanatory, in the introductions to the individual chapters.

The literature was considered mainly for the period of 1985 to 2001. The earlier literature was covered in: Magnetic Properties of Free Radicals, Landolt-Börnstein, New Series, Group II, Vol. 1, Berlin: Springer, 1965; Landolt-Börnstein, New Series, Group II, Vols. 9a–9d2, Berlin: Springer, 1977–80; Landolt-Börnstein, New Series, Group II, Vols. 17a–17h, Berlin: Springer, 1986–90. Further information on free radicals is also found in: Radical Reaction Rates in Liquids, Landolt-Börnstein, New Series, Group II, Vols. 13a–13e, Berlin: Springer, 1984–85; Landolt-Börnstein, New Series, Group II, Vols. 18a–18e2, Berlin: Springer, 1994–97.

## B Magnetic properties

The magnetic properties of most free radicals can conveniently be represented by parameters describing their interaction with an external magnetic field and the intra-molecular hyperfine interactions, i.e. the parameters  $g$  and  $a_\lambda$  of the Spin-Hamiltonian

$$H = \mu_B B_0 g S - \sum_{\lambda} \mu_N g_{N\lambda} B_0 I_{\lambda} + \sum_{\lambda} S a_{\lambda} I_{\lambda}$$

where  $\mu_B$ ,  $\mu_N$ ,  $B_0$ ,  $\mathbf{g}$ ,  $\mathbf{S}$ ,  $g_{N\lambda}$ ,  $\mathbf{a}_\lambda$ ,  $\mathbf{I}_\lambda$  are the Bohr magneton, the nuclear magneton, the magnetic induction, the  $g$ -tensor of the radical, the electron spin operator, the nuclear  $g$ -factor of nucleus  $\lambda$ , the hyperfine coupling tensor of nucleus  $\lambda$ , and the spin operator of nucleus  $\lambda$ , respectively.

$\mathbf{g}$  is symmetric and the mean value of its diagonal elements

$$g = 1/3 \sum_{i=1}^3 g_{ii}$$

is called the isotropic  $g$ -factor. For many radicals  $g$  deviates only slightly from the  $g$ -factor of the free electron

$$g_e = 2.002319304386(20) .$$

$\mathbf{a}_\lambda$ , the hyperfine coupling tensor, describes the dipolar and contact interaction between the electron spin momentum and the nuclear spin momentum of nucleus  $\lambda$  of the radical.  $\mathbf{a}_\lambda$  is most often also symmetric and the mean value

$$a_\lambda = 1/3 \sum_{i=1}^3 a_{ii, \lambda}$$

is called the isotropic hyperfine coupling constant or splitting parameter. If a radical contains several nuclei which interact there are several tensors  $\mathbf{a}_\lambda$ . In general their principal axes do not coincide, nor do they with the principal axes of  $\mathbf{g}$ .

For polyatomic radicals in the gas phase the above Spin-Hamiltonian does not apply and four magnetic hyperfine coupling constants  $a$ ,  $b$ ,  $c$ ,  $d$  are needed to describe the interaction between a nuclear and the electron spin. These are defined and explained in the introduction to the tables on inorganic radicals.

Polyradicals and certain radicals on transition metal complexes have  $N$  unpaired electrons located on different molecular segments  $k$ . Their Spin-Hamiltonian is

$$H = \mu_B \sum_k B_0 \mathbf{g}^k \mathbf{S}^k + J \sum_{l>k=1}^N \mathbf{S}^k \mathbf{S}^l + \mathbf{S} \mathbf{D} \mathbf{S} + \sum_{k=1}^N \sum_{\lambda} \mathbf{S}^k \mathbf{a}_\lambda^k \mathbf{I}_\lambda^k$$

where the nuclear Zeeman terms are omitted and

$$\mathbf{S} = \sum_k \mathbf{S}^k .$$

$J$  is the electron exchange parameter and  $\mathbf{D}$  the zero-field splitting tensor.  $\mathbf{D}$  is symmetric and traceless, i.e.

$$\sum_{i=1}^3 D_{ii} = 0$$

and consequently the two zero-field splitting parameters

$$D = 3/2 D_{33}$$

$$E = 1/2 (D_{11} - D_{22})$$

completely determine the tensor.  $J$  determines the energy separation of different spin states of the  $N$ -Spin System. For  $N = 2$

$$J = E_{\text{triplet}} - E_{\text{singlet}}$$

and for  $N = 3$

$$3/2 J = E_{\text{quartet}} - E_{\text{doublet}} .$$

Further information on the description of  $N$ -electron spin systems are found in the introductions to the appropriate chapters.

There are many experimental techniques in both continuous wave or pulse forms for the determination of the Spin-Hamiltonian parameters  $g$ ,  $a_\lambda$ ,  $J$ ,  $D$ ,  $E$ . Often applied are Electron Paramagnetic or Spin Resonance (EPR, ESR), Electron Nuclear Double Resonance (ENDOR) or Triple Resonance, Electron-Electron Double Resonance (ELDOR), Nuclear Magnetic Resonance (NMR), occasionally utilizing effects of Chemically Induced Dynamic Nuclear or Electron Polarization (CIDNP, CIDEPE), Optical Detection of Magnetic Resonance (ODMR) or Microwave Optical Double Resonance (MODR), Laser Magnetic Resonance (LMR), Atomic Beam Spectroscopy, and Muon Spin Rotation ( $\mu$ SR). The extraction of data from the spectra varies with the methods, the systems studied and the physical state of the sample (gas, liquid, unordered or ordered solid). For the detailed procedures the reader is referred to the original literature and the monographs (D) listed below. Further, effective magnetic moments  $\mu_{\text{eff}}$  of free radicals are often known from static susceptibilities. In recent years such determinations are rare, but they may be mentioned in the tables. A list of references covering the abundant earlier literature is found in: Magnetic Properties of Free Radicals, Landolt-Börnstein, New Series, Group II, Vol. 1, Berlin: Springer, 1965, Vols. 9a–9d2, Berlin: Springer, 1977–80 and Vols. 17a–h, Berlin: Springer, 1986–90.

## C Arrangements of the tables

For the display of the data the volumes are divided into chapters on specific classes of compounds. These are prepared by authors who are experts in these fields. Each chapter is headed by an introduction which specifies the coverage, the ordering of substances, details of the data arrangement, the special general literature and special abbreviations, if necessary. The tables are followed by the references belonging to the individual entries. A small overlap between chapters has been allowed for reasons of comprehensiveness and consistency. An index of all substances appears at the end of the last subvolume of the series.

Within the individual chapters the data are arranged in columns in a manner, which, as far as possible, holds for all chapters:

The *first* column (Substance) describes the structure of the species. It contains the gross formula including charge and, where appropriate, information on the electronic state. Whenever possible a structural formula is also given or a reference to a structural formula displayed elsewhere.

The *second* column (Generation/Matrix or Solvent/Method/ $T$  [K]) briefly describes the method of generation of the species, the matrix or solvent in which it was studied, the experimental technique applied to obtain the magnetic properties and the temperature for which the data are valid in Kelvin. 300 normally means an unspecified room temperature.

The *third* column contains the magnetic properties. For radicals it is headed  $g$ -Factor,  $a$ -Value [mT], and the information on  $g$  is given first where available. If only one value is listed it is the isotropic  $g$ -factor. If four values are listed the first three are the principal elements of  $g$ , the fourth denoted by “is:” is the mean value. For axially symmetric  $g$  occasionally only the two principal elements and the isotropic  $g$  are listed. These entries are followed by the information on the hyperfine interactions. It states the nuclei by their chemical symbols, a left upper index denoting the isotope, if necessary. Numbers preceding the chemical symbols note the number of equivalent nuclei, i.e. 3H means three equivalent  $^1\text{H}$  nuclei. Right hand indices of the symbols or information given in parentheses point to positions of the nuclei in the structural formulae. The  $a$ -values are displayed following the symbols. If only one value is given it is the

isotropic part of the coupling tensor. If four values are listed the first three are the principal values of  $\mathbf{a}$ , the fourth denoted by “is:” is the isotropic part. Signs are given if they are known. Errors are quoted in parentheses after the values in units of the last digit quoted for the value.

In the tables on high spin systems the *third* column also gives the available information on the exchange and zero-field parameters  $J$ ,  $D$  and  $E$ , and the heading is changed accordingly. Further, in some tables where liquid-crystal data are reported column five may give besides the isotropic coupling constant  $a$  the shift  $\Delta a$  caused by the partial alignment. It is related to the elements of  $\mathbf{a}$  by

$$\Delta a = 2/3 \sum_{i,j} \mathbf{O}_{ij} a_{ji}$$

where  $\mathbf{O}_{ij}$  are the elements of the traceless ordering matrix. For the extraction of the parameters from the spectra the original literature and the introduction to the individual chapters should be consulted. Finally, for radicals observed in the gas phase the *third* column lists the hyperfine coupling constants  $a$ ,  $b$ ,  $c$ ,  $d$ . The general unit of  $a$ -values in column three is milli-Tesla (mT) with the occasional and well founded exception of Mc/s (MHz) for a few cases. The original literature often quotes coupling constants in Gauss and the conversion is

$$1 \text{ mT} = 10 \text{ Gauss} = 28.0247 (g/g_e) \text{ Mc/s} .$$

For the interaction energy terms  $J$ ,  $D$  and  $E$  the unit  $\text{cm}^{-1}$  is used with  $1 \text{ cm}^{-1} = c_0^{-1} \cdot 1 \text{ c/s}$  where  $c_0$  is the vacuum light velocity.

The *fourth* column (Ref./Add. Ref.) lists the reference from which the data of the former columns are taken. This reference may be followed by additional but secondary references to the same subject. All references belonging to one chapter are collected in a bibliography at the end of this chapter, and the respective pages are referred to at the top of each page.

Throughout the chapters footnotes give additional information or explanations. A list of general symbols and abbreviations are found at the end of each subvolume and the last subvolume contains an index.

## D Monographs, reviews and important conference proceedings

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