INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON MOLECULAR STRUCTURE
AND SPECTROSCOPY

NOMENCLATURE AND CONVENTIONS
FOR REPORTING MÖSSBAUER
SPECTROSCOPIC DATA

(RECOMMENDATIONS 1975)

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INTRODUCTION

These Recommendations are in considerable measure based on a report of the ad hoc Panel on Mössbauer Data of the Numerical Data Advisory Board of the Division of Chemistry and Chemical Technology of the National Research Council, U.S.A. (Chairman, Professor J. J. Zuckerman), which took into account several earlier documents, especially the National Bureau of Standards (U.S.A.) Special Publication 260-13 and the report of the Mössbauer Spectroscopy Task Group of Committee E-4 (Metallography) of the American Society for Testing and Materials (Chairman, Professor R. H. Herber).

The Recommendations incorporate modifications suggested by the present and immediate past Chairman of Commission Li (Professor D. H. Whiffen and Dr. M. A. Paul), the Chairman of Commission 1.5 (Professor N. Sheppard), Professor N. N. Greenwood (consulted by Commission 1.5) and a number of other scientists who wrote to make specific suggestions.

A. PROPOSED CONVENTIONS FOR THE REPORTING OF MOSSBAUER DATA

I. Text

(a) the method of sample mounting, sample thickness, sample confinement, and appropriate composition data for alloys, solid solutions or frozen solution samples;
(b) the form of the absorber (single crystal, polycrystalline powder, inert matrix if used, evaporated film, rolled foil, isotopic enrichment, etc.);
(c) the apparatus and detector used and comments about the associated electronics (e.g. single channel window, escape peak measurements, solid-state detector characteristics, etc.) if unusual; data acquisition time if unusual;
(d) the geometry of the experiment (transmission, scattering, in-beam, angular dependence, etc.);
(e) the critical absorbers or filters, if used;
(f) the method of data reduction (e.g. visual, by computer, etc.) and curve-fitting procedure: (See Notes A-1 and A-2);
(g) the isomer shift convention used or the isomer shift of a standard (reference) absorber. Positive velocities are defined as source approaching absorber. Sufficient details concerning the isomer shift standard should be included to facilitate interlaboratory comparison of data (See Note A-3 and Table); and
(h) an estimate of systematic and statistical errors of the quoted parameters.

II. Numerical or tabulated data

Information collected and summarized in tabular form should include:
(a) the chemical state of source matrix and absorber;
(b) the temperature of source and absorber and the constancy of these parameters over the length of the data acquisition period;
(c) values of the parameters required to characterize the features in the Mössbauer spectrum (given in mm/s, cm/s or other appropriate units (See IIIB)) with estimated errors;
(d) the isomer shift reference point with respect to which the position parameters are reported;
(e) the observed line-widths defined as the full-width at half maximum peak-height;
(f) the line intensities or (relative) areas of each component of the hyperfine interaction spectrum observed, when pertinent.

III. Figures illustrating spectra

Scientific communications in which Mössbauer effect measurements constitute a primary or significant source of experimental information should include an illustration of at least one spectrum (i.e. % transmission or absorption or counting rate vs an energy parameter) to indicate the quality of the data. Such figures should include the following information features:
(a) a horizontal axis normally scaled in velocity or frequency units (e.g. mm/s or MHz. Channel number or analyzer address-values should not be used for this purpose); (see Note A-4)
(b) a vertical axis normally scaled in counts per channel or related units; (See Note A-5)
(c) an indication, for at least one data point, of the statistical counting error limits; (See Note A-6)
(d) individual data points (rather than a smoothed curve alone) should be shown. Computed fits should be indicated in such a way that they are clearly distinguishable from the experimental points.

B. MANUAL OF TERMINOLOGY, SYMBOLS, AND UNITS FOR MOSSBAUER SPECTROSCOPY

The symbols for physical quantities are in italics. If the units selected by the experimenter are not SI units, they should be defined in the text.

Isomer shift \( \delta \) m/s mm/s (=10\(^{-5}\) m/s) Measure of the energy difference between the source (\( E_1 \)) and the absorber (\( E_5 \)) transition. The measured Doppler velocity shift, \( \delta \), is related to the energy difference by \( E_1 - E_5 = \delta E c \) (where \( E \) is the Mössbauer gamma energy and \( c \) is the speed of light in vacuum) (See Note B-1a, B-1b).

Nuclear quadrupole moment (spectroscopic) \( eQ \) C\(^m\(^2\)\) C cm\(^2\) (=10\(^{-4}\) C m\(^2\)) A parameter which describes the effective shape of the equivalent ellipsoid of the nuclear charge distribution. \( Q > 0 \) for prolate (e.g. \(^{57}\)Fe, \(^{197}\)Au); \( Q < 0 \) for oblate (e.g. \(^{99}\)Sn, \(^{125}\)I) nuclei.

Electric Field Gradient (EFG) tensor \( V/\text{m}^2 \) V/cm\(^2\) (=10\(^{7}\) V/cm\(^2\)) A second rank tensor describing the electric field gradient specified by \( \eta \) and \( V_{ij} \); in addition the Euler angles may be required specifying the orientation of the tensor principal axes. (See below) (See Note B-3)

Principal component of EFG \(-V_{xx}\) \( V/\text{m}^2 \) V/cm\(^2\) (=10\(^{7}\) V/cm\(^2\)) \( (3\hbar\eta/\mathcal{C}) = eQ \) (where \( e \) is the proton charge, \( V_{xx} \) is the largest component of the diagonalized EFG). \( eQ \) M/s \( mm/s \) (=10 m/s)

Quadrupole coupling constant \( e^2qQ/\hbar \) Hz MHz (=10\(^{6}\) Hz) Product of \( V_{xx}/\hbar \) and the nuclear quadrupole moment, \( eQ \). (See Note B-1b)

Quadrupole splitting \( \Delta \) m/s mm/s (=10\(^{-7}\) m/s) The measured Doppler velocity difference between the two peaks seen in quadrupole split spectra from nuclides such as \(^{57}\)Fe and \(^{99}\)Sn. \( \Delta \) is related to the quadrupole coupling constant as \( \Delta = 1/2\hbar(\delta E_1/\delta E_5)\hbar^2qQ(1 + \eta^2/3) \) (See Note B-2)

Asymmetry parameter \( \eta \) \( V_{xx}/V_{yy} \) or \( V_{yy}/V_{xx} \) \( V_{zz}/V_{xx} \) The ratio of the difference in the transmitted or scattered intensity at resonance maximum and off-resonance, relative to the intensity off-resonance. (See Note B-4)

Line width \( \Gamma_{\text{exp}} \) m/s mm/s (=10\(^{-3}\) m/s) Full width at half maximum of the observed resonance line(s)

Natural line width \( \Gamma_{\text{nat}} \) m/s mm/s (=10\(^{-3}\) m/s) Theoretical value of the full width at half maximum of the nuclear transition, usually calculated from lifetime data

Resonance effect magnitude \( \epsilon \) The fraction of all Mössbauer gamma rays of the transition which are emitted (\( \epsilon \)) or absorbed (\( \overline{\epsilon} \)) without significant recoil energy loss. (See Note B-5)

Mossbauer thickness \( t \) barn (=10\(^{-28}\) m\(^2\)) The effective thickness of a source (\( t_1 \)) or absorber (\( t_5 \)) in the optical path. (See Note B-6)

Resonance cross-section \( \sigma_0 \) m\(^2\) barn (=10\(^{-28}\) m\(^2\)) The cross-section for resonant absorption of the Mössbauer transition gamma ray (See Note B-7)

Magnetic flux density \( B \) T = Wb/m\(^2\) Magnetic flux density at the nucleus (from experiment) in those cases in which the magnetic hyperfine interaction can be described by an effective field. In other cases the vector components of the magnetic hyperfine interaction should be reported if possible. (See Note B-8)

Vibrational anisotropy \( \varepsilon_\omega \) When the vibrational anisotropy tensor \( (\varepsilon_\omega) \) is axially symmetric

\[ \varepsilon_\omega = (1/\mathcal{C})((x_\parallel^2) - (x_\perp^2)) \]

where \( (x_\parallel) \) and \( (x_\perp) \) are the mean square vibrational amplitudes of the Mössbauer nucleus parallel and perpendicular to the cylindrical symmetry axis through the Mössbauer atom, and \( \mathcal{C} \) is the wavelength of the Mössbauer radiation divided by 2\( \pi \)

Intensity asymmetry \( \Delta \) For a randomly oriented sample with \( \eta = 0 \) and for \( 1/2 \equiv \tau = 3/2 \) magnetic dipole transitions, this is the ratio of the area under the \( \tau \) transition peak to the area under the \( \sigma \) transition peak

\[ A = \int_0^{\pi/2} e^{-\alpha(\cos^2 \theta)} \sin \theta \ d\theta \]

and is independent of sample orientation. (See Note B-9)
(A-1). If data are analyzed by computer, a brief description of the program should be given to identify the algorithm used. The number of constraints should be specified, (e.g. equal line-widths or intensities, etc.) and a measure of the goodness of fit should be indicated.

(A-2). If measurements of very high accuracy are reported and the discussion of the reality of small effects is an important part of the work, then the following items should be included:

1. the functional form and all parameters used in fitting (i.e. the constraints should be clearly stated);
2. the treatment of the background (e.g. assumed energy independent, experimentally subtracted, etc.);
3. the relative weighting of abscissa and ordinate (e.g. equal weighting);
4. a measure of the statistical reliability;
5. the number of replications and the agreement between these if applicable;
6. an estimate of systematic errors as primary results.

(A-3). The table in the adjacent column contains a list of materials which have been proposed and are being used for isomer shift standards. The proposals are partly based on the tabulation by R. L. Cohen and G. M. Kalvius [Nuc1. Instr. Methods 86, 209 (1970)]. That article also discusses some criteria in the choice of materials for isomer shift standards, and provides an extensive list of references.

(A-4). Constant acceleration spectrometers to be used for work in the mm/s range can be calibrated with respect to velocity using either metallic iron foil of at least 99.99% purity (e.g. N.B.S. Standard Reference Material SRM 1541 or equivalent) or an optical method based on interferometric or Moiré pattern techniques. The ground state (g₀) and excited state (g₁) splitting in metallic iron have been reported. [See, for example, the values quoted in J. G. Stevens and R. S. Preston, Mössbauer Effect Data Index, Covering the 1970 Literature, (edited by J. G. Stevens and V. E. Stevens), p. 16. IFI/Plenum, New York (1972), and in other references cited therein. (See also J. J. Spijkerman, J. R. DeVoe and J. C. Travis, N.B.S. Spec. Pub. 260-20, Washington, D.C. 1972 and C. E. Violet and D. N. Pipkorn, J. Appl. Phys. 42, 4339 (1971)). The temperature dependence of g₀ can be estimated from data quoted in the J. J. Budnick, L. J. Bruner, P. J. Blume and B. L. Boyd, J. Appl. Phys. 32, 1205 (1961), and R. S. Preston, S. S. Hanna and J. Heberle, Phys. Rev. 128, 2207 (1962). [See R. H. Herber in Mössbauer Effect Methodology, Vol. 6, (Edited by I. Gruverman) Plenum Press, New York (1971)]. In the absence of independent linearity measurements, a quadrupole split doublet should not be used to effect velocity calibration of spectrometers.

(A-5). It has become customary to display data obtained in transmission geometry with the resonance maximum 'down' and scattering data with the resonance maximum 'up'. In either case sufficient data should be shown far enough from the resonance peaks to establish the non-resonant base line.

(A-6). In most instances (where the data are uncorrected counting results), the standard deviation (i.e.: the square root of the second moment of the distribution) is given by \( \sqrt{N} \), where \( N \) is the number of counts scaled per velocity point. For corrected data (i.e. when background or other non-resonant effects are subtracted from the raw data), the error propagated should be computed by normal statistical methods which are briefly described in the text or figure legend. Fiducial marks bracketing the data point to show the magnitude of the standard deviation are often useful in indicating the spread of the data.

(B-1a). The centre of a Mössbauer spectrum is defined as the Doppler-velocity at which the resonance maximum is (or would be) observed when all magnetic dipole, electric quadrupole, etc. hyperfine interactions are (or would be) absent. The contribution of the second order Doppler shift \( (\delta_{D}) \) should be indicated, if possible. The isomer shift \( (\delta) \) is the sum of this term and the chemical isomer shift \( (\delta_{C}) \).

(B-1b). The SI unit of energy for both isomer shift and quadrupole coupling constant should be J, as also for \( \Delta \). The measured quantity is the velocity (m/s) which can be converted to energy as appropriate.
(B-2). Quadrupole splittings are frequently reported in megahertz, especially when direct comparison with NMR or NQR data can be effected (e.g. in the case of $^{129}$I). If such units are used in conjunction with data derived from Doppler shift measurements, the conversion factors should be stated.

(B-3). The sum $(V_{xx} + V_{yy} + V_{zz}) = 0$ regardless of the choice of axes. In the absence of magnetic hyperfine interaction, principal axes are chosen so that the off-diagonal matrix elements vanish, $V_q = 0$ ($i,j = x,y,z$; $i \neq j$) and are defined such that

$$|V_{xx}| \gg |V_{yy}| \gg |V_{zz}|,$$

so that $0 \leq \eta \leq 1$.

$$(EFG)_{ij} = -(\partial^2 V/\partial x_i \partial x_j) \quad x_i, x_j = x, y, z.$$

(B-4). This parameter is calculated from the relationship

$$\varepsilon = (I(\infty) - I(0))/I(\infty),$$

where $I(0)$ is the counting rate (or transmission or scattering intensity) at the resonance maximum, and $I(\infty)$ is the corresponding rate at a velocity at which the resonance effect is negligible. If corrections for non-resonant gamma- or X-rays, or other base-line corrections, have been made in evaluating $I$, these should be stated.

(B-5). The recoil-free fraction can be related to the expectation value of the mean square displacement of the Mössbauer atom by the relationship

$$f = \exp (-k^2(x^2))$$

where $k$ is the wave number of the Mössbauer gamma ray and $x$ is the displacement taken along the optical axis.

(B-6). The $t$ parameter is usually calculated for a thin absorber from the relationship $t = n \sigma_0 a f$, in which $n$ is the number of Mössbauer element atoms per unit area in the optical path, $\sigma_0$ is the cross-section for recoilless scatter-

(B-7). This parameter is usually calculated from the relationship

$$\sigma_\tau = (h^2 c^2/2\pi)E^2(1 + \alpha_T)^{-1}(1 + 2\ell)(1 + 2\ell)^{-1}.$$

Where $E_\tau$ is the transition energy; $I$ and $I_e$ are the excited and ground state spins, respectively; and $\alpha_T$ is the total internal conversion coefficient of the Mössbauer transition.

(B-8). 1 Tesla (10 kG) equals 1 Wb/m$^2$.

(B-9). For $^{57}$Fe and $^{199}$Sn the following table summarizes the conventions which relate the shape of the equivalent ellipsoid of electronic charge surrounding the nucleus, the sign of $V_{zz}$, the sign of the excited state nuclear quadrupole moment, $Q_{32}$, the sign of the quadrupole coupling constant $e^2qQ/h$, the doublet intensity ratio $R$ (defined as the area ratio of the more positive velocity peak divided by that of the more negative velocity peak in the absence of a magnetic hyperfine interaction), and the angular dependence ratio $A$ for the $\sigma$ ($\Delta m = 0, \pm 1$) and $\pi$ ($\Delta m = \pm 1$) transitions for the axially symmetric case:

$$\begin{array}{cccc}
\text{shape} & \text{prolate} & \text{oblate} & \text{prolate} & \text{oblate} \\
\text{V}_{zz} & - & + & - & + \\
\text{Q}_{32} & + & + & - & - \\
e^{2}qQ & - & + & + & - \\
R & E_{3/2} < E_{1/2} & E_{3/2} > E_{1/2} & E_{3/2} > E_{1/2} & E_{3/2} < E_{1/2} \\
\sigma/\pi (= A^{-1}) & \pi/\sigma (= A) & \pi/\sigma (= A) & \sigma/\pi (= A^{-1})
\end{array}$$

37Fe 199Sn