

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY*

**PRESENTATION OF RAMAN SPECTRA IN
DATA COLLECTIONS**

(Recommendations 1981)

Prepared for publication by
E. D. BECKER, J. R. DURIG, W. C. HARRIS
and G. J. ROSASCO

*Membership of the Commission during the preparation of these recommendations (1977-1979) was as follows:

Chairman: E. D. BECKER (USA); *Secretary:* G. ZERBI (Italy); *Titular Members:* J. H. BEYNON (UK); V. A. KOPTYUG (USSR); C. N. R. RAO (India); C. SANDORFY (Canada); T. SHIMANOUCI (Japan); D. W. TURNER (UK); *Associate Members:* P. DIEHL (Switzerland); F. DÖRR (FRG); J. R. DURIG (USA); J. G. GRASELLI (USA); B. JEŻOWSKA-TRZEBIATOWSKA (Poland); S. LEACH (France); P. M. RENTZEPIS (USA); H. A. WILLIS (UK); *National Representatives:* G. HERZBERG (Canada); H. W. THOMPSON (UK).

PRESENTATION OF RAMAN SPECTRA IN DATA COLLECTIONS

(RECOMMENDATIONS 1981)

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY
Subcommittee on Infrared and Raman Spectroscopy

INTRODUCTION

These recommendations relate to the Raman spectra of isotropic materials that are intended for permanent retention in data collections. They are a more comprehensive version of the "Recommendations for the Presentation of Raman Spectra for Cataloging and Documentation in Permanent Data Collections" which were published in *Pure and Applied Chemistry* **36**, 277 (1973). The current recommendations are based on a report published by the Ad Hoc Panel on Raman Spectral Data, convened by the Numerical Data Advisory Board of the National Academy of Sciences-National Research Council of the United States (1). A provisional version of these Recommendations was published (2) and has been modified slightly as a result of comments received.

There is a recognized need to establish a set of guidelines for the presentation of Raman spectral data that deal with the format for data presentation and the experimental parameters required to define the spectrum properly. Although these recommendations are directed toward Raman spectra prepared for permanent collections, many of them are also pertinent to spectra presented in journals.

There are a number of different types of phenomena which come under the general category of Raman scattering. These include "normal" Raman scattering, resonance Raman scattering, coherent anti-Stokes Raman scattering, hyper-Raman effect, etc. The present recommendations are not intended to encompass all these aspects of the field of Raman scattering, but rather will deal with the presentation of data primarily representing "normal" Raman scattering from isotropic materials. The guidelines define a minimum set of parameters which should be specified. These parameters, or analogous parameters adapted to the particular field of interest, will be necessary for adequate data presentation in many fields of Raman spectroscopy. For example, the parameters presented below should be regarded as a minimal subset of those necessary for the specification of resonance Raman spectra in isotropic materials.

It seems useful to define different classes for spectral data which allow variation in data quality. These classes are defined in analogy to similar infrared data classifications which have been proposed by the Coblenz Society (3,4) and adapted by IUPAC (5).

Critically defined physical data. Spectra in this category are of such high quality that they are acceptable as physical constants of the substances under precisely defined conditions. Specifications for this class are not discussed in this document.

Research quality analytical spectra. Data in this category are those in which the sample and spectrum conform to the best current and commonly practiced Raman spectrometry procedures.

Approved analytical spectra. Data in this category are those for which the sample and spectrum are of sufficient quality for use in the identification of materials.

There are, of course, many other spectra of high quality that cannot be classified into the above categories because certain information is lacking. These may be referred to as Unevaluated Spectra.

This report was prepared for publication by J. R. Durig, W. C. Harris, G. J. Rosasco and E. D. Becker. It has the approval of the Commission on Molecular Structure and Spectroscopy, with the following membership (1977-79): E. D. Becker (chairman), USA; G. Zerbi (secretary), Italy; J. H. Beynon, UK; V. A. Koptug, USSR; C. N. R. Rao, India; C. Sandorfy, Canada; T. Shimanouchi, Japan; D. W. Turner, UK; P. Diehl, Switzerland; F. Dörr, Germany; J. R. Durig, USA; J. G. Grasselli, USA; B. Jezowska-Trzebiatowska, Poland; S. Leach, France; P. M. Rentzepis, USA; H. A. Willis, UK.

SPECIFICATIONS

The recommendations for parameter specifications are listed in Table I under four categories: (A) Sample, (B) Excitation Source, (C) Raman Spectrometer and (D) Experimental Configuration. The guideline used in the selection and specification of parameters is that all information which is significant to the intended physical or chemical interpretation of the data should be presented. In addition, for research quality analytical data, it is suggested that the information presented should be sufficient to allow some evaluation of the data.

The list of parameters under each category in Table I is generally self-explanatory, but additional discussion of the categories is presented below.

DISCUSSION

A. Sample

The information presented in this category should include sample characteristics which either affect the observed spectrum or make the data more useful. It is extremely important that the structure and purity of the sample be established by accepted independent techniques. In the case of a sample in which there is resonance Raman scattering the spectrum can be very different in appearance from that observed in a normal Raman experiment; an acknowledgement of this resonance and possibly the presentation of the electronic absorption spectrum for the material would be very useful.

It is important to recognize that sample heating caused by the exciting laser beam may be significant. Thus, when a temperature is quoted for the spectrum, a description of the method of measurement should be given (i.e., the temperature of a surrounding heat sink, an internal probe temperature, or a spectroscopically determined temperature), and an estimate of the temperature uncertainty would be useful.

B. Excitation source

It is not normally necessary to present details of the measurement of laser power or the transmission function of the filters. The intent of specifications B3 and B4 is to allow a reliable judgement of the power and/or irradiance levels used to perform the experiment.

C. Raman spectrometer

Selection of the optimum value of spectral slit width in terms of signal level and resolution is left to the discretion of the scientist. As a general rule the scan rate (cm^{-1}/s) should not exceed the value of the ratio of the spectral slit width (cm^{-1}) to 4 times the value of the time constant (sec), i.e.,

$$\text{Scan rate } \left(\frac{\text{cm}^{-1}}{\text{s}} \right) \leq \frac{\text{Spectral slit width } (\text{cm}^{-1})}{4 \times \text{time constant } (\text{s})}$$

In this context, the time constant is defined as the $1/e$ -time of the electronics, i.e., the time for the recording system to reach a value of $(1 - 1/e)$ for a unit step function input. The spectral slit width is operationally defined as the full width (in cm^{-1}) at half height of the peak observed as the spectrum of a "narrow line source" (e.g., a laser plasma line).

For Research Quality Analytical spectra, the spectral slit width should be determined by actual measurement. For Approved Analytical spectra, this information may be obtained from a calculation utilizing the linear dispersion and mechanical slit width of the instrument or from the manufacturer's specifications. Any significant variations of the spectral slit width over the range of the Raman spectrum should also be specified.

The parameters describing response presented in C6 are important in determining the relative "intensity" of a series of bands covering a fairly broad frequency range in the Raman spectrum of a material. The term "system" is meant to include the effects of both the spectrometer and the detector. "Relative response function" can be defined in the context of a calibration utilizing a broad band, continuous standard light source. It is quite feasible to extract useful information on the response of the system by recording the Raman spectrum of a defined standard material.

D. Experimental configuration

It is recommended (D1) that the scattering geometry and the sample cell orientation be described by reference to some conveniently defined orthogonal axis system. This axis system in many cases might be defined by axes parallel to the optical axis of the fore-optics and/or spectrometer, the long direction of the entrance slit, and a third direction perpendicular to these two. This form of specification (D1) is preferred to traditional descriptions (i.e., back scattering, transverse illumination, etc.)

TABLE I. Parameters recommended for the specification of Raman spectral data.

Type of parameter	Research Quality Analytical Spectra	Approved Analytical Spectra
A. Sample		
1. Name and structural formula	Specify	Specify
2. a. State, e.g., gas, liquid, solid (powder, etc.), solution (solvent and concentration)	Specify	Specify
b. Color (if any), reference to an absorption spectrum	Specify absorption spectrum	Specify color
3. Impurities	No impurity bands evident	Impurity bands acceptable if identified
4. Temperature (kelvin, K)	Specify	Specify
5. Pressure, if other than ambient	Specify	Specify
B. Excitation source		
1. Type of laser	Specify	Specify
2. Wavelength (nanometers, nm)	Specify	Specify
3. Laser power (watts, W)		
a. at laser	Specify	Specify
b. at sample	Specify	...
4. Optical elements in beam		
a. Narrow band filter, attenuators, etc.	Specify	Specify
b. Effective aperture and focal length of laser focusing lens	Specify	...
C. Raman spectrometer		
1. Spectrometer manufacturer and model (or equivalent description)	Specify	Specify
2. Detector characteristics, e.g., response type or manufacturer and model	Specify	Specify
3. Spectral slit width at the exciting wavelength (cm^{-1})	Specify	Specify
4. Scan rate (cm^{-1}/s)	Specify	Specify
5. Time constant of recording electronics (s)	Specify	Specify
6. System response as a function of Raman shift		
a. Relative response function		...
b. Demonstrate by reference to a "standard" compound	Specify either a or b	Specify
D. Experimental configuration		
1. Scattering geometry specified with respect to a set of orthogonal axes	Specify	Specify
2. Sample cell	Specify	Specify
3. Special arrangements; e.g., spinning sample, multipass irradiation (approximate enhancement)	Specify	Specify
4. Polarization measurements		
a. Specify X(Y,Y)Z for experiments used to determine mode symmetry or measure depolarization ratio (see Fig. 1)	Specify	Specify
b. Optical elements; e.g., polarizer, scrambler	Specify	Specify
c. Solid angle of collection lens	Specify	...

Item 4a recommends that the experimental geometry [X(Y,Y)Z] employed to determine mode symmetry by the measured depolarization ratios can be more generally specified by a symbol $k_i(e_i, e_s)k_s$ (6). The vector $k_i(k_s)$ refers to the direction of propagation of the incident (scattered) light, and the vector $e_i(e_s)$ refers to the direction of electric field polarization of the incident (scattered) light. These vectors should be referred to a convenient orthogonal axis system. This system will generally be identical to the system defined in D1, but in any case should be easily relatable to the system defined in D1. This form of specification (D4a) is preferred to traditional names such as parallel and perpendicular or horizontal and vertical, etc.

For the purposes of this document the depolarization ratio will be defined in a restricted, operational sense. Two separate spectra are measured, corresponding to the following geometries (see Fig. 1):

$$k_i(e_i, e_s)k_s \hat{=} X(Y, Y)Z$$

$$k_i(e_i, e_s)k_s \hat{=} X(Y, X)Z$$

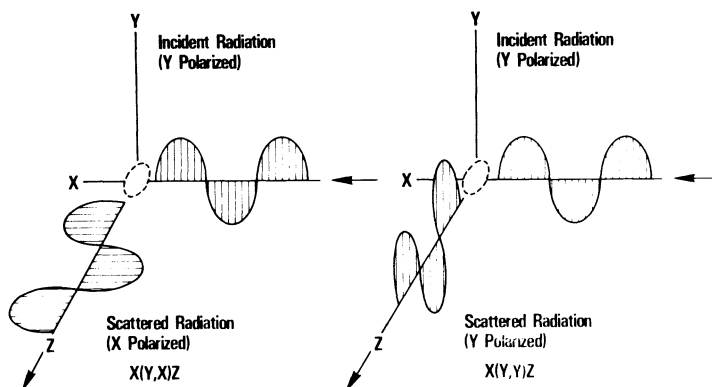


Figure 1. Geometry involved in the measurement of depolarization ratios. (A left-handed coordinate system is used here for ease of visualization but is not recommended for general use.)

This experiment implies that the incident light is linearly polarized and that the scattered light is polarization-analyzed to select the necessary components. Further, the polarization dependence of the system response (C6) must be eliminated by a suitable optical technique (e.g., use of a scrambler plate) or a correction applied to the recorded spectra. The ratio of the suitably corrected peak height or the integrated area of a band observed in experiment X(Y,X)Z to that observed in experiment X(Y,Y)Z is defined as the depolarization ratio, i.e.,

$$\rho = \frac{I[X(Y, X)Z]}{I[X(Y, Y)Z]}$$

Depolarization ratios may be measured from peak heights or integrated areas, and both may be useful in different applications. It should be realized that these measurements may be different, since the depolarization ratio varies significantly across the band. The basis of the measurement (peak height or area) should always be stated.

This quantity is useful for assigning mode symmetries and for verification of structural formula and chemical identification. The technique is recommended for routine measurement of depolarization ratios for analytical purposes.

SPECTRAL FORMAT

Within the context of these recommendations the most important spectral information involves the frequency shifts, relative "intensity," and depolarization ratio (related to the vibrational symmetry type) or the Raman bands of the material.

A. Graphical presentation

It is necessary that a graphical presentation of the spectrum be made for both Research Quality and Approved Analytical Spectra. The format for this presentation is as follows:

Abcissa - This should be linear in wavenumber shift, zero at the right, with the wavenumber shift increasing from right to left. The accuracy of the wavenumber scale should be not less than $\pm 5 \text{ cm}^{-1}$ for Approved Analytical data and $\pm 2 \text{ cm}^{-1}$ for Research Quality Analytical data. Note that the wavenumber shifts should refer to free space values; however, the accuracy required is not so stringent, in general, as to require a differentiation between reciprocal wavelength in vacuo and in air.

Ordinate - This should be linear and proportional to the intensity (power) or the Raman signal, increasing upwards. The units of the intensity scale should be actually observed photocurrent or count rate or an equivalent measurement. This intensity scale will be more significant when a "standard" spectrum is defined. The amount of any suppression of the "zero" light level should be stated.

B. Depolarization ratio

Research Quality Analytical data should present the two spectra utilized in the determination of the depolarization ratio such that the two spectra may be easily compared and the approximate values of the ratio are graphically evident. It is suggested that the two spectra be superimposed on a single chart if this does not detract from the clarity of the presentation. This presentation is also urged for Approved Analytical data.

C. Tables of Raman data

It is required for Research Quality Analytical data and urged for Approved Analytical data that the information on wavenumber shift, intensity relative to a specified feature of the spectrum or to some other reference signal, and depolarization ratio be presented for the principal bands of the spectrum in a table accompanying the spectral chart. For Approved Analytical Data the numerical values of the depolarization ratio of the principal bands should be presented on the spectral chart if not included in a table. The method of calculation of the depolarization ratio, i.e., peak height or band area ratios, and any dependence on exciting wavelength should be specified.

D. Spectral data catalogs

It is urged that the format for the presentation of spectral data catalogs be in reasonable and practical agreement with the format previously summarized in part A. There are additional specific recommendations applying to such catalogs as follows:

1. It is desirable that the spectrum should show the date of measurement and, if the spectrum is a part of a compilation, the name of the contributing laboratory.
2. The Raman format should agree with the infrared format; i.e., a 2:1 scale compression in the abscissa above 2000 cm^{-1} .
3. A minimum ratio of the maximum of the strongest band in the spectrum to the peak-to-peak noise at the "baseline" should be 100:1 or better.
4. The intensity unit of the ordinate may be selected such that the strongest bands are off scale by a factor not exceeding 1000 if this is necessary to obtain a satisfactory record of the weaker significant bands. The strongest bands should then be rescanned at an appropriately reduced intensity unit with the specific reduction ratio indicated in the chart.

REFERENCES

- (1) *Applied Spectroscopy* 30, 20 (1976).
- (2) *IUPAC Inf. Bull.*, No. 2 (1978).
- (3) *Anal. Chem.* 38, No. 9, 27A (1966).
- (4) *Anal. Chem.* 47, No. 11, 945A (1975).
- (5) *IUPAC Inf. Bull.*, No. 50 (1976).
- (6) T. C. Damen, S. P. S. Porto and B. Tell, *Phys. Rev.* 142, 570 (1966).