

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY*

**SPECIFICATION OF COMPONENTS, METHODS AND
PARAMETERS IN FOURIER TRANSFORM
SPECTROSCOPY BY MICHELSON AND RELATED
INTERFEROMETERS**

(Technical Report)

Prepared for publication by
JOHN E. BERTIE

Department of Chemistry, University of Alberta, Edmonton, Canada T6G 2G2

*Membership of the Commission during the preparation of this report (1994–97) was as follows:

Chairman: J. E. Bertie (Canada; 1994–97); *Secretary:* J. F. Sullivan (USA; 1989–95) ; P. Klaeboe (Norway; 1996–97); *Titular Members:* A. M. Heyns (RSA; 1994–97); R. Janoschek (Austria; 1994–97); P. Klaeboe (Norway; 1994–97); S. Tsuchiya (Japan; 1994–97); B. P. Winnewisser (Germany; 1991–97); *Associate Members:* A. M. Bradshaw (FRG; 1991–95); S. M. Cabral de Menezes (Brazil; 1994–97); B. G. Derendjaev (Russia; 1991–95); E. Hirota (Japan; 1994–97) ; J. Kowalewski (Sweden; 1996–97); A. Oskam (Netherlands; 1991–97); C. Zhang (China; 1989–97); *National Representatives:* J. E. Collin (Belgium; 1985–97); M. Chowdhury (India; 1986–95); S. Califano (Italy; 1989–97); J. J. C. Teixeira-Dias (Portugal; 1991–97); Y. S. Lee (Republic of Korea; 1989–97); D. Escolar (Spain; 1991–97); J. Kowalewski (Sweden; 1994–95); S. Suzer (Turkey; 1996–97); S. Içli (Turkey; 1994–95); R. K. Harris (UK; 1994–97).

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference to the source along with use of the copyright symbol ©, the name IUPAC and the year of publication are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Specification of components, methods and parameters in Fourier transform spectroscopy by Michelson and related interferometers (Technical Report)

Abstract: With the goal of ensuring that adequate information is presented in the scientific literature to permit the reproduction of measurements in different laboratories, this paper presents short lists of components, methods and parameters that should be reported in papers that focus on spectra recorded on Fourier transform spectrometers.

INTRODUCTION

The purpose of this project is to provide a short list of components, methods and parameters that should be reported in papers which focus on spectra recorded on Fourier transform spectrometers. The intention is to distribute the list to journal editors with the request that they make it available to authors and referees of such papers, to facilitate their task of ensuring that all relevant information is reported.

It should be noted that most scientists agree that, in addition to adequate specification of the components, methods and parameters used, such papers should include at least one figure that shows a typical spectrum obtained during the work, or a typical portion of a such a spectrum.

Two requirements emerged during the course of the work.

First, it became clear that three separate lists are needed. One list is for spectroscopy at modest resolution, which here means roughly 0.25 cm^{-1} to 8 cm^{-1} resolution, and one list is for spectroscopy at high resolution, which here means a resolution of 0.01 cm^{-1} or better. The uncovered resolution region, 0.01 to 0.25 cm^{-1} is less commonly used, and the list that is most appropriate to the particular instrument and work should be used. The third list is for Raman spectroscopy at modest resolution.

Second, it is desired that the lists should be sufficiently extensive to be scientifically helpful but sufficiently short that authors will actually use them. In principle the instrument manuals supplied by the manufacturer are available and, thus, the description of the instrument, with its default components, methods and parameters, is available for each instrument. In practice this information is rarely in the open literature and usually is not available to people who do not have the particular instrument. Equally, it is rarely available five or ten years after the instrument is introduced. There are, however, enough similarities between different instruments to allow the length of the lists for modest resolution to be reduced slightly by defining a set of assumptions or default components, methods and parameters that apply to the majority of cases at the present time.

Accordingly three lists are presented below. Each list for modest resolution is preceded by the set of assumptions on which it is based. The assumed components, methods and parameters need only be specified when they deviate from those assumption, if the authors who use these lists cite this paper.

The remainder of the paper contains list A for work at modest resolution, list B for high resolution studies, and list C for Raman spectroscopy. Lists A and C are accompanied by brief explanatory notes about some of the entries.

The following people have provided valuable guidance in the preparation of these lists: Brenda P. Winnewisser, John W. C. Johns, Peter R. Griffiths, Peter Klaeboe, Jeanette Grasselli Brown, Ad Oskam, John H. van der Maas, Arlan W. Mantz, Ole Faurskov Nielsen, Guy Guelachvili, Rober W. McKelar and Kirk H. Michaelian.

Notes About List A.

Useful references for the concepts and terms used are:

P. R. Griffiths and J. A. de Haseth. *Fourier Transform Infrared Spectrometry*, Wiley-Interscience, New York, 1986.

J. E. Bertie *Vibrational Spectra and Structure*, Ed. J. R. Durig, Elsevier, Amsterdam, 1985, **14**, 221.

Note that it is not helpful to describe instrument parameters as, e.g., UPF=3. The physical significance of the parameter is required.

If the sampling interval is Δx , wavenumbers from 0 cm^{-1} to $\tilde{\nu}_{\text{max}} = 1/(2\Delta x)$ are sampled correctly. If $\Delta x = 0.6328 \text{ }\mu\text{m}$, $\tilde{\nu}_{\text{max}} = 7899 \text{ cm}^{-1}$ and a spectral bandwidth from 0 to 7899 cm^{-1} is sampled correctly. The spectral intensity may not extend up to 7899 cm^{-1} ; if the signal and associated noise do not extend beyond 3950 cm^{-1} , a larger sampling interval may be used.

The optical retardation velocity, ORV, is the rate at which the optical path difference changes. It is twice the velocity of the moving mirror for a Michelson interferometer, and is 4 or 8 times the mirror velocity for other types of interferometer. Some manufacturers give the ORV indirectly. Thus, Bio-Rad gives the optical retardation velocity as a frequency, e.g., 5 kHz which means that the path difference changes by one He-Ne laser wavelength 5000 times per second. From this, $\text{ORV} = 5000 \times 0.6328 \times 10^{-4} \text{ cm s}^{-1} = 0.32 \text{ cm s}^{-1}$.

Wavenumber calibration is necessary to obtain accurate wavenumbers from FT spectrometers, although they give extremely precise (reproducible) wavenumbers. Calibration is conveniently done with water vapor or indene-camphor-cyclohexane or polystyrene film (A. R. H. Cole, *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*, 2nd edn, IUPAC, Pergamon Oxford, 1977). Most instruments give wavenumbers correct to $\approx \pm 0.1 \text{ cm}^{-1}$ if the laser wavenumber is entered as $15\,798.002 \text{ cm}^{-1}$.

Resolution here means instrumental spectral resolution, which is not uniquely defined. The nominal resolution is conveniently defined as the reciprocal of the maximum optical path difference, X_{max} . (X_{max} equals the maximum mirror displacement multiplied by 2 for a Michelson or by some other factor for certain related interferometers) The actual instrumental resolution is determined by X_{max} and the apodization function, so X_{max} and the apodization function should both be reported. If these can not be determined, the resolution claimed by the manufacturer for the settings used may be substituted, although this is not consistently defined. Note that the spectral resolution actually observed may be determined by the intrinsic width of the spectral line if this is greater than the instrumental resolution.

Two factors that can reduce the instrumental resolution, $\delta\tilde{\nu}$, below that determined by X_{max} and the apodization function are the focal length, F , of the collimating mirror and the diameter, d , of the Jacquinot stop (the limiting aperture of the instrument, frequently the circular aperture at the first focus of the source, but the detector element in some instruments). $\delta\tilde{\nu}/\tilde{\nu} = d^2/(8F^2)$. Typically $F \approx 25 \text{ cm}$ and $d \approx 12 \text{ mm}$, from which $\delta\tilde{\nu} \approx 1 \text{ cm}^{-1}$ between 3000 and 4000 cm^{-1} . These factors should be described if resolution of $\approx 1 \text{ cm}^{-1}$ or better is claimed above 3000 cm^{-1} .

The type of spectrum calculated from the Fourier transform may be either the magnitude spectrum, $I = \sqrt{(C^2 + S^2)}$, or the intensity spectrum, which is also called the phase-corrected amplitude spectrum, $I = C \cos \delta + S \sin \delta$; here all terms change with wavenumber and I , C , S , and δ are the calculated intensity, the cosine transform, the sine transform and the phase angle at the wavenumber in question. Random noise about a zero baseline is always positive in the (uncommon) magnitude spectrum and has random sign in the intensity spectrum

The PNL measure of photometric non-linearity is defined here as: In a single beam spectrum, the ratio of the average baseline position to low wavenumber of the detector cut-off to the maximum signal, times 100%.

LIST A: FOR FOURIER TRANSFORM SPECTROSCOPY AT MODEST RESOLUTION**Default assumptions**

The following components, methods and parameters are defined as the defaults. They are the most commonly used and need not be specified. Deviations from them should be specified.

- A Michelson or related interferometer with rapid continuous mirror scan was used.
- No optical filter was used. If an optical filter was used, specify its temperature and wavenumber range.
- The apodized interferogram was zero-filled before Fourier transformation, so that the Fourier transform gave at least two spectral points in each resolution interval.
- The interferogram was sampled at 0.6328 μm intervals (HeNe laser wavelength), i.e., the spectral bandwidth was in the range 0 to over 3950 cm^{-1} but less than 7899 cm^{-1} .*;
- The source was a continuous incandescent source, e.g., a hot globar or wire, etc..

Group AI Components, methods and parameters that are rarely changed.

These components, methods and parameters should be specified in an accessible journal in the first publication from an instrument. This report should be cited in subsequent papers together with any differences in these specifications.

- The detector. For a cooled detector, its temperature and stated wavenumber range.
- The beamsplitter used and the angle of incidence upon it.
- Whether the interferogram was one-sided or two-sided.
- The optical retardation velocity (for continuous scan).*;
- Any other signal-filters used, e.g. electronic or digital filters.

Group AII Components, methods and parameters that should be given in all papers

- The sample, its temperature, its purity and how this was determined, the method of sampling.
- The instrument manufacturer and model.
- How water and carbon dioxide were removed from the optical path.
- How the wavenumbers were calibrated.*;
- The maximum optical path difference in the interferogram, X_{max} , or the nominal resolution, $1/X_{\text{max}}$, * AND the apodization function.*;
- Other instrumental factors that may reduce the instrumental resolution achieved.*;
- For step scan, the integration time at each point.
- For continuous scan the number of scans signal-averaged in each interferogram.

Group AIII Components, methods and parameters that should be given when quantitative significance is claimed for absolute or relative intensities or lineshapes

- How the phase correction was done, e.g., multiplicative or convolution method.
- The type of spectrum calculated from the Fourier transform.*;
- The PNL measure of photometric non-linearity*;
- Details of any arithmetic processing of the spectra after Fourier transformation and phase correction, with the exception of the use of a stated reference spectrum to calculate the transmittance spectrum, T , or $-\lg T$.

NOTE: * means 'See Notes About List A'

LIST B: FOR FOURIER TRANSFORM SPECTROSCOPY AT HIGH RESOLUTION

The following should be specified in all papers when relevant or should be deducible directly from other information in the paper or in specifically cited references.

- The instrument type, its manufacturer and model number.
- The sample, its purity and how this was determined, the method of sampling.
- Identified line width contributions due to the Doppler effect, pressure-broadening, or other sample properties.
- How water and carbon dioxide were removed from the optical path.
- Wavenumber calibration: Conditions used for calibration spectra and source of calibration reference data.**;
- Signal-to-noise ratio: Value at peak background energy in an absorption measurement, or maximum recorded value in an emission measurement, or equivalent information.
- The radiation source.
- The beamsplitter used and its useful wavenumber range.
- Optical filters used, their range and temperature.
- The detector, and its temperature, D^* value, and wavenumber range.
- Step scan or continuous scan.
- The optical retardation velocity (for continuous scan).
- Whether the interferogram was one-sided or two-sided.
- The total elapsed time for measurement AND the efficiency of the measurement cycle; OR equivalent information including the number of scans or, for step-scan systems, the integration time at each point.
- The digitization (sampling) interval, dx , or the alias bandpass, dx^{-1} , after any digital filtering.
- The maximum optical path difference in the interferogram, X_{\max}
OR the nominal resolution defined as $1/X_{\max}$.
- The apodization function used.
- The diameter, d , of the limiting aperture of the spectrometer.
- The focal length, F , of the collimating mirror.
- The wavenumber interval between original calculated spectral points.
- Characteristics of electronic filters used.
- Characteristics of digital filters used.

The following should also be specified when quantitative significance is claimed for absolute or relative intensities or lineshapes

- The Fourier transform algorithm used, e.g., Cooley–Tukey, variable radix, or other.
- The type of phase correction used, e.g., multiplicative or convolution.
- The type of spectrum calculated from the Fourier transform, e.g., phase-corrected amplitude spectrum or magnitude spectrum (in which zero baseline noise is all positive);
- Information about the linearity of cooled detectors, if used.
- Details of any arithmetic processing of the spectra after Fourier transformation and phase correction, including the use of a reference spectrum to calculate the transmittance or absorbance spectrum.

** e.g., Guy Guelachvili and 23 others, *Pure and Applied Chemistry* 1996, **68**, 193; reprinted in *J. Molecular Spectroscopy* 1996, **177**, 164 and in *Spectrochimica Acta* 1996, **52**, 717.

Notes About List C.

Useful references for the concepts and terms used are:

Recommendations of IUPAC Commission on Molecular Structure and Spectroscopy: E. D. Becker, J. R. Durig, W. C. Harris and G. J. Rosasco. *Presentation of Raman Spectra in Data Collections., Pure and Appl. Chem.* 1981, **53**, 1879.

P. R. Griffiths and J. A. de Haseth. *Fourier Transform Infrared Spectrometry*, Wiley-Interscience, New York, 1986.

Note that it is not helpful to describe instrument parameters as, e.g., UPF = 3. The physical significance of the parameter is required.

The optical retardation velocity, ORV, is the rate at which the optical path difference changes. It is twice the velocity of the moving mirror for a Michelson interferometer, and is 4 or 8 times the mirror velocity for other types of interferometer. Some manufacturers give the ORV indirectly. Thus, Bio-Rad gives the optical retardation velocity as a frequency, e.g., 5 kHz which means that the path difference changes by one He-Ne laser wavelength 5000 times per second. From this, $ORV = 5000 \times 0.6328 \times 10^{-4} \text{ cm s}^{-1} = 0.32 \text{ cm s}^{-1}$.

Wavenumber calibration is necessary to obtain accurate wavenumbers from FT spectrometers, although they give extremely precise (reproducible) wavenumbers. Most instruments give wavenumbers correct to $\approx \pm 0.1 \text{ cm}^{-1}$ if the laser wavenumber is entered as $15\,798.002 \text{ cm}^{-1}$. Recall that in spectroscopic usage 'wavenumber' is short for 'wavenumber of the radiation in vacuum'. The refractive index of air changes little between the visible and the infrared, so use of the vacuum wavenumber of the laser gives the noted accuracy throughout the infrared.

The accurate wavenumber of the exciting laser is required to obtain accurate Raman shifts from accurate absolute wavenumbers, e.g., use of 9394.2 cm^{-1} as the vacuum wavenumber of the Nd YAG laser seems to give Raman shifts accurate to $\approx \pm 0.1 \text{ cm}^{-1}$. The best indicator of accurate calibration is that corresponding Stokes and anti-Stokes lines have the same Raman shift.

Resolution here means instrumental spectral resolution, which is not uniquely defined. It is best measured as the FWHM of a non-lasing emission line from the laser. Otherwise, the nominal resolution is conveniently defined as the reciprocal of the maximum optical path difference, X_{max} . (X_{max} equals the maximum mirror displacement multiplied by 2 for a Michelson or by some other factor for certain related interferometers) The actual instrumental resolution is determined by X_{max} and the apodization function, so X_{max} and the apodization function should both be reported. If these can not be determined, the resolution claimed by the manufacturer for the settings used may be substituted, although this is not consistently defined. Note that the spectral resolution actually observed may be determined by the intrinsic width of the spectral line if this is greater than the instrumental resolution.

Two instrumental factors that can reduce the resolution, $\delta\tilde{\nu}$, below that determined by the X_{max} and apodization function are the focal length, F , of the collimating mirror and the diameter, d , of the Jacquinot stop (the limiting aperture of the instrument). $\delta\tilde{\nu}/\tilde{\nu} = d^2/(8F^2)$. If $F \approx 25 \text{ cm}$ and $d \approx 5 \text{ mm}$, $\delta\tilde{\nu} \approx 0.5 \text{ cm}^{-1}$ at 9000 cm^{-1} . These factors should be specified when significant.

The type of spectrum calculated from the Fourier transform may be either the magnitude spectrum, $I = \sqrt{C^2 + S^2}$, or the intensity spectrum, which is also called the phase-corrected amplitude spectrum, $I = C \cos \delta + S \sin \delta$; here all terms change with wavenumber and I , C , S , and δ are the calculated intensity, the cosine transform, the sine transform and the phase angle at the wavenumber in question. Random noise about a zero baseline is always positive in the (uncommon) magnitude spectrum and has random sign in the intensity spectrum.

The PNL measure of photometric non-linearity is defined here as: In a single beam spectrum, the ratio of the average baseline position to low wavenumber of the detector cut-off to the maximum signal, times 100%.

LIST C: FOR FOURIER TRANSFORM RAMAN SPECTROSCOPY**Default assumptions**

The following components, methods and parameters are defined as the defaults. They are the most commonly used and need not be specified. Deviations from them should be specified.

- A Michelson or related interferometer with rapid continuous mirror scan was used.
- The apodized interferogram was zero-filled before Fourier transformation, so that the Fourier transform gave at least two spectral points in each resolution interval.

Group CI Components, methods and parameters that are rarely changed.

These components, methods and parameters should be specified in an accessible journal in the first publication from an instrument. This report should be cited in all subsequent papers together with any differences in these specifications.

- The detector. For a cooled detector, the temperature and stated wavenumber range.
- The beamsplitter used.
- Whether the interferogram was one-sided or two-sided.
- The optical retardation velocity (for continuous scan).*
- Optical filter used and its useful wavenumber range.
- Any other signal-filters used, e.g. electronic or digital filters.
- The intervals at which the interferogram was sampled.

Group CII Components, methods and parameters that should be given in all papers

- The sample, its temperature and purity and how these were determined, the method of sampling.
- The instrument manufacturer and model.
- How the Raman wavenumber shifts were calibrated.*;
- The excitation wavenumber, and the degree of focusing of the laser beam.*;
- The maximum optical path difference in the interferogram, X_{\max} , or the nominal resolution, $1/X_{\max}$.* AND the apodization function.*;
- Other instrumental factors that may reduce the resolution achieved.*;
- For step scan, the integration time at each point.
- For continuous scan the number of scans signal-averaged in each interferogram.
- The scattering geometry, i.e., the propagation and polarization directions of the incident and scattered light.
- The correction for the throughput of the spectrometer applied to the spectrum.
- Any other corrections applied to the relative intensities.

Group CIII Components, methods and parameters that should be given when significance is claimed for absolute or relative intensities or lineshapes

- How the phase correction was done, e.g., multiplicative or convolution method.
- The type of spectrum calculated from the Fourier transform.*;
- The PNL measure of photometric non-linearity*;
- Details of any arithmetic processing of the spectra after Fourier transformation and phase correction.

NOTE: * means 'See Notes About List C'