

IUPAC Recommendations

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Glossary of methods and terms used in analytical spectroscopy (IUPAC Recommendations 2019)

<https://doi.org/10.1515/pac-2019-0203>

Received February 3, 2019; accepted October 2, 2019

Abstract: Recommendations are given concerning the terminology of concepts and methods used in spectroscopy in analytical chemistry, covering nuclear magnetic resonance spectroscopy, atomic spectroscopy, and vibrational spectroscopy.

Keywords: Analytical spectroscopy; atomic spectroscopy; infrared; nuclear magnetic resonance; Raman; vibrational spectroscopy.

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Article note: Sponsoring body: IUPAC Analytical Chemistry Division (Division V): see more details on page 774.

This work was prepared under the project 2017-027-1-500: Spectroscopic methods of analysis (chapter 5 of the IUPAC Orange Book) under task group Chair Derek Craston and membership John Chalmers, Joanna Collingwood, Geoffrey Dent, Heidi Goenaga-Infante, Adam LeGresley, Andreas Limbeck, Martin Resano, Torsten Schoenberger, Jose Luis Todoli, Neil Telling and John Warren,

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1 Introduction

Spectroscopy is a study of the interaction between matter and *electromagnetic radiation*.

The origins of spectroscopy began with the study of visible light, most notably the fundamental studies of crude *spectra* of sunlight by Isaac Newton in 1672, but the definition of the term has expanded to include the analysis of spectra covering the entire range of the electromagnetic spectrum. This vast frequency range correlates to an equally wide range of energy *transitions* required to allow the absorption and emission of electromagnetic radiation. The term spectroscopy therefore encompasses a range of disparate techniques, covering phenomena including nuclear disintegration, excitation of electrons, and molecular vibrations and rotations. These can all give valuable qualitative and quantitative information about the physical and chemical properties of materials, as summarized in Table 1.

Spectroscopy, *spectrometry*, spectrophotometry, and spectrography are terms used to refer to the measurement of radiation *intensity* as a function of *frequency* or *wavelength* and are often used to describe experimental spectroscopic methods. Spectral *measuring instruments* [VIM 3.1] are referred to as *spectrometers*, spectrophotometers, spectrographs, or spectral analysers.

Spectroscopic methods in Analytical Chemistry involve measurements of the frequency and intensity of electromagnetic radiation emitted, absorbed, or reflected as a consequence of transitions between different energy states within the nucleus, atom, or molecule. The output of a spectrometer is referred to as a *spectrum* and can be used for both qualitative and quantitative purposes.

Following VIM [1] and present IUPAC format, the concept entries of these Recommendations provide the term(s), the definition, and explanations by examples and notes. Additionally, the document the information is taken from is stated as “Source” using the respective reference number (*e.g.*, [2] for the third edition of the Orange Book). Within a given entry, terms referring to other concepts defined in these Recommendations appear in italics on first use. The same holds for VIM terms, although these are marked with the VIM entry number, *e.g.*, *measurement principle* [VIM 2.4], because the definition is not reproduced here.

Fundamental terms are taken from the Green Book [3] and other IUPAC Recommendations with no change or with minor changes in formatting.

Table 1: Regions of the electromagnetic spectrum.

Spectral region	Approximate wavelength (wavenumber) range	Energy transitions studied in matter	Analytical techniques (spectroscopy)
Gamma	1–100 pm	Nuclear transitions and disintegrations	Gamma-ray
X-ray	6 pm–100 nm	Ionization by inner electron removal	X-ray; X-ray fluorescence
Vacuum ultraviolet	10–200 nm	Ionization by outer electron removal	
Ultraviolet	200–400 nm	Excitation of valence electrons	UV-VIS
Visible	400–780 nm	Excitation of valence electrons	UV-VIS
Near-infrared	780 nm–2.5 μm (12 800–4000 cm^{-1})	Excitation of valence electrons; molecular vibrational overtones	Near-IR
Mid-Infrared	2.5–25 μm (4000–400 cm^{-1})	Molecular vibrations: stretching and deformations	Infrared (IR) spectroscopy, Raman spectroscopy
Far-infrared	25–1000 μm (400–10 cm^{-1})	Molecular rotations	Far-IR, Terahertz spectroscopy
Microwave	0.1–30 cm	Molecular rotations and electron spin	electron spin resonance, microwave spectroscopy
Radio-frequency	10^{-1} – 10^3 m	Molecular rotations and nuclear spin	nuclear magnetic resonance

These Recommendations are limited to three basic forms of spectroscopy used in analytical chemistry, namely, nuclear magnetic resonance, vibrational spectroscopy, and atomic spectroscopy. Other techniques are either discussed elsewhere (e.g., UV in Chromatography) or fall outside the scope of this edition of the Orange Book.

1 atomic spectroscopy

Measurement principle [VIM 2.4] of *spectroscopy* for the study of *electromagnetic radiation* absorbed and emitted by atoms.

Note: Atomic spectra may be emission or absorption spectra.

2 molecular spectroscopy

Measurement principle [VIM 2.4] of *spectroscopy* for the study of rotational, vibrational, and *electronic transitions* of molecules.

Note: Molecular spectra may be emission or absorption spectra.

3 nuclear magnetic resonance spectroscopy (NMR)

Measurement principle [VIM 2.4] of *spectroscopy* to measure the precession of magnetic moments placed in a magnetic induction based on absorption of *electromagnetic radiation* of a specific *frequency* by an atomic nucleus.

Note 1: Nuclei having a suitable magnetic moment include ^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P .

Note 2: The technique is used as a method of determining structure of organic molecules, or as a mechanism for quantification.

Source: [4].

4 spectrometry

Measurement of quantities related to *electromagnetic radiation* or charged particles as a means of obtaining information about a system and its components.

Examples: *electron emission spectrometry*, mass spectrometry.

Source: [5] p 1738. See also: *spectroscopy*.

5 spectroscopy

Study of chemical systems by the *electromagnetic radiation* with which they interact or that they produce.

Examples: *atomic absorption spectroscopy*, *nuclear magnetic resonance spectroscopy*.

Source: [5] p 1738. See also: *spectrometry*.

2 General terms

Fundamental terms defined here are from the IUPAC Green Book (3rd edition) [3] and “Handbook of vibrational spectroscopy” [6].

6 absorbance, A

deprecated: extinction

obsolete: attenuation

Logarithm of the division of incident *radiant power* (P_0) by transmitted radiant power (P_{tr}).

$$A = \log_a(P_0/P_{tr}) = -\log_a(T) = -\log_a(1 - \alpha_i), \text{ where } T \text{ is the } \textit{transmittance} \text{ and } \alpha_i \text{ is the } \textit{absorptance}.$$

Note 1: The base a of the logarithm should be specified. See *decadic absorbance* (\log_{10} , lg), and *Napierian absorbance* (ln).

Note 2: Although the term absorbance used by chemists often means the decadic absorbance as measured (see *experimental absorbance*), the data must be corrected for reflection, scattering, and luminescence if absorbance is to have absolute numerical significance.

Note 3: Confusingly, the term absorbance is also widely used for the negative logarithm of the ratio of the final to the incident intensities of processes other than transmission, such as *attenuated total reflection* and *diffuse reflection*.

Source: [3] p 36. See also: *internal absorbance*.

7 absorptance, α

absorption factor

Absorbed *radiant power* (P_{abs}) divided by incident radiant power (P_0). $\alpha = P_{abs}/P_0$

Source: [3] p 36.

8 absorption coefficient

See: *linear decadic absorption coefficient*, *linear Napierian absorption coefficient*, *molar decadic absorption coefficient*, *molar Napierian absorption coefficient*.

9 absorption index, k

imaginary refractive index

Imaginary part of the complex *refractive index* describing absorption of *electromagnetic radiation*.

Source: [3] p 37.

10 absorption spectrum

General term for the *spectrum* of *electromagnetic radiation* absorbed by a sample.

Note 1: The ordinate quantity may be absorption cross-section, *absorption coefficient*, or *absorbance*.

Note 2: If the ordinate quantity is the absorbance, but not otherwise, the spectrum may be called an absorbance spectrum.

Source: [6].

11 accidental degeneracy

Condition that occurs when two or more normal transitions have the same energy as a matter of coincidence, as opposed to because of symmetry conditions.

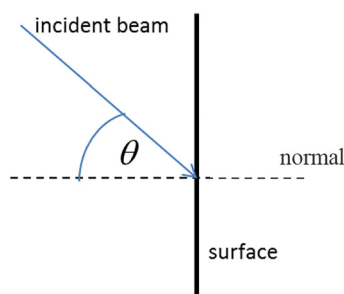
Source: [6].

12 aliasing

See: *folding (in spectroscopy)*.

13 angle of incidence, θ

Angle between a beam of *electromagnetic radiation* and a line normal to a surface.



14 anisotropic

nonisotropic

Having properties that depend on direction.

Source: [7] p 2198. See also: *isotropic*.

15 apodization

Technical term for changing the shape of a mathematical function, electrical signal, or optical transmission to remove or smooth a discontinuity at the edges, literally meaning 'removing the foot'.

Note 1: Originally, 'apodization' described the procedure by which *Fourier-transform infrared* spectra are corrected for the side lobes that appear in the wings of *spectral bands* when the interferogram is not zero at its limits, by multiplying the interferogram prior to Fourier transformation by a weighting function that is zero at its limits (see *Fourier transform spectroscopy*). Its use has broadened in recent years to include weighting functions that are not zero at their limits.

Note 2: Apodization is also used for manipulating FIDs (*free induction decay*) to enhance specific components of the signal, for example to improve *signal-to-noise* or resolution, and is achieved by application of specific shapes to the FID, *e.g.*, in *nuclear magnetic resonance spectroscopy*: exponential, Gaussian or sine-bell; in *infrared spectroscopy*: Boxcar, Happ-Genzel, Norton-Beer, cosine.

Source: [6].

16 apodization function

window function

Mathematical function that effects *apodization*.

17 array detector

Photoelectric detector in which a large number of pixels are distributed, usually in regularly spaced lines and usually over a rectangular area.

Source: [6].

18 asymmetric Fourier-transform spectroscopy

See: *dispersive Fourier-transform spectroscopy*.

19 attenuated total reflection (ATR)

frustrated total internal reflection

Internal reflection from an absorbing material at angles of incidence at or above the critical angle.

See also: *attenuated total reflection spectroscopy*, *multiple attenuated total reflection*.

20 attenuation index

See: *complex refractive index*.

21 band-pass filter

bandpass filter

1. Optical filter that passes a *spectral band* of *wavelengths* within a certain range and centred at a certain wavelength and that rejects *radiation* of a wavelength outside of the range.

2. Electrical filter that passes a band of electrical signals with a certain *frequency* range, centred at a certain frequency, that rejects signals at frequencies outside of the range.

Source: [6]. See also: *high-pass filter*, *low-pass filter*.

22 bandwidth

See: *spectral bandwidth*.

23 beam splitter

Device to split a beam of *electromagnetic radiation* into two parts.

Note: In an ideal 2-beam *Fourier-transform spectrometer*, the beam splitter would transmit half of the radiation and reflect half of it to create the two beams.

Source: [6].

24 Beer-Lambert law

Beer-Lambert-Bouguer law

Absorbance of a beam of collimated monochromatic *radiation* in a homogeneous isotropic medium is proportional to the absorption path-length, l , and to the concentration, c , or (in the gas phase) to the pressure of the absorbing species.

Note 1: This law holds only under the limitations of the Lambert law [8] p 361, and for absorbing species exhibiting no concentration or pressure-dependent aggregation.

Note 2: The law can be expressed as $A(\lambda) = \lg(P_\lambda^0/P_\lambda) = \varepsilon(\lambda)cl$, where the proportionality constant $\varepsilon(\lambda)$ is the *molar decadic absorption coefficient* and P_λ^0, P_λ are, respectively, the incident and transmitted *spectral radiant power*.

Note 3: Spectral radiant power must be used because the Beer–Lambert law holds only if the *spectral bandwidth* of the ultraviolet, visible, or *infrared radiation* is narrow compared to *line widths* in the *spectrum*.

Source: [8] p 307.

25 Cauchy function

Function $y = a/(b^2+x^2)$ where a and b are constants. If x is replaced by $\tilde{\nu} - \tilde{\nu}_0$ this function yields a *Lorentzian band* centred at $\tilde{\nu}_0$.

Source: [6].

26 charge coupled device (CCD)

Device that stores information in the form of charge packets in an array of closely spaced capacitors.

Note 1: The packets can be transferred from one capacitor to the next sequentially by electronic manipulation, so that the information contained in the array can be sequentially read electronically.

Note 2: In *spectroscopy*, the charge packets are created by interaction with *radiation* and the devices are extremely sensitive detectors for *near IR* and visible radiation.

Source: [6].

27 circular birefringence

Difference between the refractive indices of an optically active medium for left, n^L , and right, n^R , circularly polarized *radiation* ($n^L - n^R$).

Note 1: “Circular birefringence” is also used to describe the phenomenon of having different refractive indices for left and right circularly polarized radiation.

Note 2: Like the *refractive indices* (n^L, n^R), circular birefringence changes with *wavenumber*.

Source: [6].

28 complex refractive index, \hat{n}

refractive index

Speed of light in a given medium divided by speed of light in vacuum.

Note 1: $\hat{n} = n + i\kappa$. The real part, n , is usually called the ‘refractive index’, and is the entire refractive index when no radiation is absorbed. The imaginary part, κ , describes absorption (see *absorption index*).

Note 2: The older literature, and some physics literature today, uses $\hat{n} = n(1 + i\kappa)$ where κ is called the attenuation index. For simplicity, this usage is discouraged.

Source: [3] p 37.

29 decadic absorbance, A_{10} , A

Absorbance calculated with logarithm base 10.

Note: Confusion with *Napierian absorbance* must be avoided.

Source: [3] p 36.

30 degeneracy, g

Number of states that have the same *energy level*.

Source: [6]. See also: *accidental degeneracy*.

31 dephasing

phase relaxation

Loss of coherence between the upper and lower states of a *transition*.

Note 1: The term ‘dephasing’ arises from the density matrix formalism that is used in a phenomenological approach to simplify the description of the relaxation dynamics of a molecule coupled to its surroundings.

Note 2: Dephasing leads to either *homogeneous broadening* or *inhomogeneous broadening* depending on the system. The continually changing intermolecular interactions cause a shift of the *frequency* of the intramolecular vibration. If these interactions change much more slowly than the amplitude of this shift, heterogeneous broadening results and causes a *Gaussian band*. If these interactions change much faster than the amplitude of this shift, homogeneous broadening occurs and the observed *spectral band* is a notionally narrowed *Lorentzian band*. In the general case, the broadening due to dephasing is neither homogeneous nor heterogeneous and the line shape is neither Gaussian nor Lorentzian.

Source: [6].

32 derivative spectroscopy

Measurement method [VIM 2.5] of *spectroscopy* in which the absorbance, or other spectral ordinate, is differentiated n times with respect to *wavenumber* or *frequency* to give the n^{th} derivative *spectrum*, *i.e.*, the spectrum of the n^{th} derivative of the original spectrum.

Note: The technique is used to transform changes of slope in the original spectrum into more prominent features in the derivative spectra and is extensively used in the near-infrared to flatten spectral baselines to improve subsequent chemometric study.

Source: [6].

33 detector gate width

detector integration time

Time for signal integration after start of detection.

Note: Optimization of gate width allows detection of species with different decay rates.

Reference [51].

34 difference spectroscopy

Measurement method [VIM 2.5] of *spectroscopy* in which *spectral subtraction* is used to help the study and identification of individual species in a mixture.

Source: [6].

35 diffuse reflectance, R

remittance

remission fraction

Diffuse reflected (remitted) *radiant power* (P_{rem}) divided by incident radiant power (P_0). $R = P_{\text{rem}}/P_0$.

Note 1: The sum of remittance, *transmittance*, and *absorptance* equals one.

Note 2: Some authors distinguish between remittance and diffuse reflectance by excluding *specular reflection* in the latter.

Source: [6].

36 diffuse reflection

remission

Reflection in which *electromagnetic radiation* incident on a scattering surface at a certain angle is reflected (remitted) over all angles.

Note: Diffuse reflection is a complicated process and involves *transmission*, *reflection*, and *scattering*.

Source: [6]. See also: *remittance*.

37 diffuse transmission

Process in which radiation is transmitted by a scattering sample and leaves the sample in directions other than that required by *Snell's law of refraction*. The process is complicated and involves transmission, reflection, and scattering.

Source: [6]. See also: *transmission*.

38 dipole coupling

transition-dipole transition dipole coupling

Coupling of different motions through dipole-dipole forces.

Note: In *vibrational spectroscopy* of crystals, intermolecular vibrational coupling through interaction of resonant transition dipoles throughout the whole crystal.

Source: [6].

39 dispersive Fourier-transform spectroscopy

asymmetric Fourier-transform spectroscopy

Fourier-transform spectroscopy using a Michelson or other two-beam *interferometer* with the sample placed in one arm of the interferometer.

Note: This method provides information about the phase change as well as the amplitude change caused by the sample.

Source: [6].

40 dispersive spectrometer

Spectrometer in which *electromagnetic radiation* is separated spatially into its component *wavenumbers* by a dispersive element, such as a prism or a diffraction grating.

Source: [6].

41 double-beam spectrometer

Spectrometer in which beams of *electromagnetic radiation* from the source reach the detector *via* two paths, one through the sample and the other through a reference.

Note 1: The *radiant power* in each beam is measured at each *wavenumber*.

Note 2: The output of a double-beam spectrometer is termed a double-beam *spectrum*. The ordinate of a double-beam spectrum is related to the radiant power that reaches the detector in the sample beam divided by that in the reference beam. The spectrum has a flat baseline where the sample does not absorb.

Note 3: The reference is usually a material having the same composition as the sample but lacking the analyte.

Source: [6].

42 electric dipole moment, p , μ

dipole moment

Vector quantity of a dipole that in an electric field (\mathbf{E}) has a potential energy $E_p = -\mathbf{p} \cdot \mathbf{E}$

Note 1: The direction of the dipole moment is from the negative to the positive charge.

Note 2: Electric dipole moment has also the magnitude of equal separated charges of opposite sign times the distance between them. It is usually expanded as: $\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \sum_k (\partial\boldsymbol{\mu}/\partial Q_k) Q_k + \sum_k (\partial^2\boldsymbol{\mu}/\partial Q_k^2) Q_k^2 + \sum_{i < j} (\partial\boldsymbol{\mu}/\partial Q_i) (\partial\boldsymbol{\mu}/\partial Q_j) Q_i Q_j +$ higher order terms, where the Q_k , *etc.* are the normal coordinates and $\boldsymbol{\mu}_0$ is the equilibrium dipole moment of the molecule.

Note 3: SI unit: C m. Common unit: Debye, $D \approx 3.335\,64 \times 10^{-30}$ C m. See Green Book (3rd edition) p26 note 9 for alternative ways of expressing dipole moment [3].

Source: [3] p 26.

43 electromagnetic radiation (EM)

Flow of energy through space propagated as synchronized sinusoidal waves of the electric field, E , and the magnetic field H .

Note 1: Electromagnetic radiation is characterized by *frequency* ν , *wavelength* λ , and speed c , where $\nu\lambda = c$.

Note 2: The wavelength and velocity change when radiation enters a medium. In its interaction with atoms and molecules, radiation behaves like particles, called photons, with zero mass, energy $h\nu$, and momentum h/λ , where h is the Planck constant $h = 6.626\,070\,15 \times 10^{-34}$ J s. [9]

Source: [6].

44 electromagnetic transition

Transition accompanied by the emission or absorption of a photon.

Note 1: The *frequency* of the photon (ν) is related to the energy difference of the transition by $h\nu = \Delta E = |E_2 - E_1|$, where h is the Planck constant.

Note 2: In general, an electromagnetic transition obeys certain rules called “electromagnetic selection rules”.

Source: [10].

45 electron emission spectrometry

Measurement principle [VIM 2.4] of *spectrometry* for the study of electrons emitted by atoms.

46 electronic transition

Transition in an atom, ion, or molecule from an electronic energy level E_1 to another energy level E_2 .

Source: [10].

47 emittance, ε

emissivity

Radiant excitance (M) emitted by the sample divided by radiant excitance emitted by a black body (M_{bb}) at the same temperature. $\varepsilon = M/M_{\text{bb}}$

Note: The term “excitance” can be replaced by “power” or “flux” if the sample and the black body have the same area and by *intensity* if, in addition, the emission is measured as a collimated radiation beam.

Source: [3] p 35.

48 energy level of a free atom, ion or molecule

energy level
energy state

Set of one or more *stationary quantum states* of a free atom, ion, or molecule having a particular internal energy.

Note: SI unit: J. Common unit: electron volt, symbol eV, where $1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}$. Energy levels are also expressed as kJ mol^{-1} .

Source: [10].

49 excimer laser

Pulsed gas *laser* that typically emits *radiation* in the ultraviolet range.

Note: The lasing medium is made up of a gas mixture containing a halogen and a noble gas such as Ar and F_2 or Xe and Cl_2 .

Source [51].

50 excitation energy

Minimum energy required to bring a system to a specified higher *energy level*.

Note: Usually excitation energy refers to the energy of *transition* from the *ground state* to a higher energy level (excited state).

Source: [2] p 223.

51 excited state of a free atom, ion, or molecule

excited state

Stationary quantum state of a free atom, ion, or molecule of energy greater than that of the *ground state*.

Source: [11] p 205.

52 experimental absorbance, A_{10}

Decadic absorbance as measured with no corrections for other processes.

Note 1: The term emphasizes that radiation might be lost from the beam by reflection, luminescence, scattering, and possibly vignetting (e.g., spectral shifts introduced from changing a radiation beam diameter or shape), and not solely by absorption.

Note 2: *Internal absorbance* is used to term absorbance corrected for other processes.

Source: [6].

53 folding (in spectroscopy)

aliasing

The appearance of peaks at incorrect frequencies in a mathematically-processed spectrum due to insufficient density of datapoints in the time-domain spectrum or from peaks outside of the sampled frequency range.

Note 1: Folding is a consequence of *undersampling* in *spectroscopy*.

Note 2: In *vibrational spectroscopy*, when a *spectrum* is sampled correctly only up to a *wavenumber* $\tilde{\nu}_M$, radiation of wavenumber $\tilde{\nu} > \tilde{\nu}_M$ appears to have a wavenumber between 0 and $\tilde{\nu}_M$, as follows:

Range of wavenumber $\tilde{\nu}$	$\tilde{\nu}_{app}$
$[\tilde{\nu}_M, 2\tilde{\nu}_M]$	$2\tilde{\nu}_M - \tilde{\nu}$
$[2\tilde{\nu}_M, 3\tilde{\nu}_M]$	$\tilde{\nu} - 2\tilde{\nu}_M$
$[3\tilde{\nu}_M, 4\tilde{\nu}_M]$	$4\tilde{\nu}_M - \tilde{\nu}$
$[4\tilde{\nu}_M, 5\tilde{\nu}_M]$	$\tilde{\nu} - 4\tilde{\nu}_M$

This process can be simulated by folding a spectrum that shows the correct wavenumbers back onto itself at $\tilde{\nu}_M$ and its multiples.

Source: [6]. See also: *Nyquist criterion*.

54 Fourier-transform spectroscopy

Fourier-transform spectrometry

Measurement method [VIM 2.5] whereby *spectra* are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of *electromagnetic radiation* or other type of radiation.

Note 1: This procedure can be applied to a variety of spectroscopies, including optical spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy, and electron spin-resonance spectroscopy.

Note 2: There are several methods for measuring the temporal coherence of the radiation, including the CW (continuous wave) Michelson or Fourier-transform spectrometer and the pulsed Fourier-transform spectrograph (which is more sensitive and has a much shorter sampling time than conventional spectroscopic techniques).

Source: [8] p 344.

55 free induction decay (FID)

Indication [VIM 4.1] from a pulsed *spectroscopy* experiment that takes the form of damped sine waves arising from the excited system returning to equilibrium.

Note: In *nuclear magnetic resonance spectroscopy*, the FID consists of sine waves oscillating at the *Larmor frequency* (ω) and dampened by *net dephasing time* relaxation (T_2^*), $\sin(\omega t)\exp(-t/T_2^*)$.

Source: [6].

56 frequency, ν , f

Number of cycles of periodic motion in unit time.

Note 1: In *spectroscopy*, the periodic motion is of the electric and magnetic vectors of *electromagnetic radiation*.

Note 2: Frequency is related to the energy change of an *electromagnetic transition*, ΔE , induced when electromagnetic radiation is absorbed through $\Delta E = h\nu$, where h is the Planck constant.

Note 3: SI unit: Hz, where $1 \text{ Hz} = 1 \text{ s}^{-1}$.

57 Fresnel reflection

Reflection of radiation from a surface that is smooth and large with respect to the *wavelength* of the radiation. A reflected beam, of *intensity* governed by the Fresnel equations, is produced at an angle of reflection equal to the angle of incidence.

Note: May be termed *specular reflection* for non-scattering samples.

Source: [6].

58 frustrated multiple internal reflection (FMIR)

See: *multiple attenuated total reflection*.

59 frustrated total internal reflection

See: *attenuated total reflection*.

60 full width at half maximum (FWHM), W , Γ

full width at half height (FWHH)

Interval between the two points across a section of a *spectrum* where the ordinate is equal to half the maximum ordinate of the section.

Note 1: W is a measure of *line or band width*.

Note 2: FWHM has units of *wavelength, wavenumber, frequency, or energy*.

Note 3: For *infrared absorption spectra*, the FWHM must be measured from a spectrum that is plotted linear in absorbance.

Note 4: In *Raman spectra*, the FWHM can be measured directly from the spectrum of scattered light *intensity* unless the instrument response function varies significantly across the band.

Note 5: Inclusion of “full” distinguishes FWHM from *half-width at half maximum*.

Source: [6, 8].

61 Gaussian band

Spectral band with the shape $H_G \exp[-4\ln 2(\tilde{\nu} - \tilde{\nu}_0)^2/W^2]$, where H_G is the band maximum (peak height), W is the *full width at half maximum*, and $\tilde{\nu}_0$ is the peak *wavenumber*.

Source: [6].

62 ground state of a free atom, ion or molecule

ground state

Ground energy level of minimum internal energy of a free atom, ion, or molecule.

Note: It is conventional to assign the relative energy value of zero to this level.

Source: [6].

63 Hadamard transform spectrometer

Multiplexing *spectrometer* that uses the optical components of a *dispersive spectrometer* with a Hadamard encoding mask.

Source: [6].

64 half width at half maximum (HWHM)

half width at half height (HWHH)

One half of the *full width at half maximum*.

Source: [6].

65 high-pass filter

1. Optical filter that excludes radiation of wavenumber lower (wavelength higher) than a certain value and passes radiation of wavenumber above (wavelength lower) than this value.

2. Electrical filter that blocks signal with a modulation frequency lower than a certain cut-on value and passes signals of frequency above this value.

Source: [6]. See also: *band-pass filter*, *low-pass filter*.

66 Hilbert transforms of a spectrum

Functions that interrelate the real part, f' , and imaginary part, f'' , of the *refractive index*, $\hat{n} = n + ik$, or *relative permittivity*, $\hat{\epsilon} = \epsilon' + i\epsilon''$, through

$$f'(\tilde{\nu}_a) - f'_\infty = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{f''(\tilde{\nu})}{\tilde{\nu} - \tilde{\nu}_a} d\tilde{\nu}$$

$$f''(\tilde{\nu}_a) - f''_\infty = \frac{-1}{\pi} P \int_{-\infty}^{\infty} \frac{f'(\tilde{\nu}_a) - f'_\infty}{\tilde{\nu} - \tilde{\nu}_a} d\tilde{\nu}$$

where P means that the principal part of the integral is taken at the singularity.

Source: [6].

67 imaginary refractive index

See: *absorption index*.

68 instrument line shape (ILS)

Idealized form of a feature in a spectrometer corresponding to a *transition*.

Note 1: Ideal line shapes include *Lorentzian*, *Gaussian*, and *Voigt* functions, whose parameters are the line position, maximum height, and *half-width*.

Note 2: For *Fourier-transform* spectra, ILS varies with the *apodization function* used.

Source: [6].

69 integrated intensity

Area under a *spectral band* in an *absorption spectrum* where the *absorption* is linearly proportional to the amount of absorber in unit area.

Note 1: The area under a band in a *transmittance* spectrum is not linearly proportional to the amount of absorber.

Note 2: The absorption quantity is usually a Beer-Lambert *absorption coefficient*, but recently $\tilde{\nu}\alpha_m''(\tilde{\nu})$, the *wavenumber* times the imaginary part of *local molar polarizability*, has been used for neat liquids to correct for dielectric effects.

Source: [6]. See also: *infrared intensity* and associated entries within the Green Book [3] p 37.

70 integration range of a spectrum

integration range

Frequency or *wavenumber* range over which the *integrated intensity* of an *absorption band* is measured by numerical integration of the area under the band.

Note 1: For *Gaussian bands*, integration over one *full width half maximum* to each side of the band centre yields 98 % of the area under the band.

Note 2: *Lorentzian bands* integration over 3.1 or 15.9 full width half maximum to each side yields 90 % and 98 % of the band area.

Source: [6].

71 intensified charge coupled device detector (ICCD)

Charge coupled device with a prior amplification system to improve sensitivity.

Note 1: The intensifier used is based on a microchannel plate (MCP), which converts the incoming photons to electrons by means of a photocathode. Generated electrons are multiplied in a second step by the MCP and then reconverted to photons using a phosphorous screen. Finally, derived photons are detected with a CCD device.

Source: [51].

72 intensity of radiation, I , E

intensity

irradiance

deprecated: radiant flux

Radiant power (P) per unit area (A) that is received at a surface. $I = dP/dA$.

Note 1: Intensity and irradiance are formally the same quantity, but the term intensity is usually used for collimated beams of radiation. (See [3] p 35 Note 5).

Note 2: SI unit: W m^{-2} .

Source: [3] p 35. See also: *spectral intensity*, *radiant intensity*.

73 intensity spectrum

See: *single beam spectrum*.

74 interference (in analytical spectroscopy)

Effect that causes a change in the measured *absorbance*, or of the *intensity* for a given concentration, due to the presence of one or more components accompanying the analyte in the material submitted for, or the reagents used in, the analysis.

Note: Interference in analytical spectroscopy should not be confused with interference of beams in an *interferometer*.

Source: [10].

75 interferometer

Device in which beams of *electromagnetic radiation* are superimposed causing interference in order to extract information.

See also: *continuous scan interferometer*, *step-scan interferometer*, *Fourier-transform spectroscopy*.

76 internal absorbance, A_i

Absorbance in the absence of reflection, scattering or luminescence.

Note 1: Internal absorbance is a rarely used term in quantitative absolute *intensity* studies to emphasize that the necessary corrections of the transmittance for reflection and other cell effects have been made. Instrument manufacturers usually use the raw, uncorrected transmittance when calculating the absorbance. See *experimental absorbance*.

Note 2: Formally, $A_i = -\log_{10}(1 - \alpha_i)$, $A_i = -\log_{10}(T_i)$ for a sample that does not scatter or luminesce, where α_i is the *internal absorptance* and T_i is the *internal transmittance*.

Source: [6].

77 internal absorptance, α_i

Absorptance fully corrected for surface effects and effects of the cell, such as reflection, scattering, luminescence, and vignetting losses.

Note: If scattering and luminescence in the sample are negligible, $\alpha_i + T_i = 1$, where T_i is *internal transmittance*.

Source: [3] p 36.

78 internal transmittance, T_i , τ_i

internal transmission

Transmittance fully corrected for surface effects and effects of the cell, such as reflection, scattering, luminescence, and vignetting losses.

Note: If scattering and luminescence in the sample are negligible, $\alpha_i + T_i = 1$, where α_i is *internal absorptance*.

Source: [6].

79 irradiance

See: *intensity of radiation*.

80 isotropic

Having properties that are independent of direction.

Source: [7] p 2198. See also: *anisotropic*.

81 Kramers–Kronig transforms of a spectrum

Functions based on the physical principle of causality that interconvert the real and imaginary parts of complex optical quantities when they are known over a sufficiently wide (strictly infinite) *wavenumber* range. They are frequently used to interconvert the real part, f' , and imaginary part, f'' , of the *refractive index*, $\hat{n} = n + ik$, the dielectric constant (*relative permittivity*), $\hat{\epsilon}_r = \epsilon'_r + i\epsilon''_r$, or the logarithm of the complex reflection coefficient $re^{i\varphi}$ through

$$f'(\tilde{\nu}_a) - f'_\infty = \frac{2}{\pi} P \int_0^\infty \frac{\tilde{\nu} f''(\tilde{\nu})}{\tilde{\nu}^2 - \tilde{\nu}_a^2} d\tilde{\nu}$$

$$f''(\tilde{\nu}_a) = \frac{-2\tilde{\nu}_a}{\pi} P \int_0^\infty \frac{f'(\tilde{\nu}) - f'_\infty}{\tilde{\nu}^2 - \tilde{\nu}_a^2} d\tilde{\nu}$$

where P means that the principal part of the integral is taken at the singularity.

Note: All functions used to model *vibrational spectra* obey the Kramers–Kronig transforms as long as the real parts are even functions of wavenumber and the imaginary parts are odd functions of wavenumber, so that the Kramers–Kronig transforms are equivalent to the *Hilbert transforms*.

Source: [6].

82 laser

Source of ultraviolet, visible, or *infrared radiation* that produces light amplification by stimulated emission of radiation, from which the acronym is derived.

Note 1: The radiation emitted is coherent except for superradiance emission.

Note 2: All lasers contain an energized substance that can increase the *intensity of radiation* passing through it.

Source: [8] p 362.

83 light

Electromagnetic radiation visible to the human eye.

Note: In general, spectroscopic usage, 'light' is synonymous with 'radiation' when the specific wavelength is not relevant.

Source: [6].

84 line width

linewidth

Extent of a spectral line, usually measured as the *full width at half maximum*.

Note: Line width may be expressed in terms of *wavelength*, *wavenumber*, or *frequency*.

See also: *natural line width*.

85 linear decadic absorption coefficient, a , K

decadic absorption coefficient

Decadic absorbance (A_{10}) divided by path-length (l). $a = A_{10}/l$.

See also: *linear Napierian absorption coefficient*, *molar decadic absorption coefficient*, *molar Napierian absorption coefficient*.

Source: [3] p 36.

86 linear Napierian absorption coefficient, α

Napierian absorption coefficient

Napierian absorbance (A_e) divided by path-length (l). $\alpha = A_e/l$.

Note: α is the reciprocal of the *optical absorption depth*

See also: *linear decadic absorption coefficient*, *molar decadic absorption coefficient*, *molar Napierian absorption coefficient*.

Source: [3] p 36.

87 liquid crystal tunable filter (LCTF)

Optical device based on polarization interference caused by *transmission* through a series of birefringent liquid crystal layers of different thicknesses that allow a narrow *wavelength* region to be selected and tuned over a broad spectral range.

Source: [6].

88 lock-in amplifier

Amplifier that amplifies only those signals that have, within a specified *spectral bandwidth*, the same *frequency* as, and a specified phase relation with, the selected reference signal.

Source: [6].

89 Lorentzian band

Band with the shape $H_L W^2 / [W^2 + 4(\tilde{\nu} - \tilde{\nu}_0)^2]$, where H_L is the peak height, W is the full width at half maximum, and $\tilde{\nu}_0$ is the peak wavenumber.

Source: [6].

90 low-pass filter

1. Optical filter that excludes *radiation* of *wavenumber* greater (wavelength lower) than a certain value and passes radiation of wavenumber below (wavelength greater than) this value.
2. Electrical filter that blocks signal with a modulation frequency above a certain cut-on value and passes signals of frequency below this value.

Source: [6]. See also: *high-pass filter*, *band-pass filter*.

91 magic angle

54.74°, the angle at which the Legendre polynomial $P_2(\cos \theta) = 1/2(3\cos^2 \theta - 1)$ equals zero.

Note 1: The name arises from solid state NMR, in which rapidly spinning a sample about an axis at 54.74° to the magnetic field ‘magically’ converts into sharp lines the very broad bands that are due to coupling of the magnetic dipoles in the solid.

Note 2: This angle is important in the estimation of the molecular orientation in polymer fibres by *vibrational spectroscopy*. In particular, if for a particular vibrational band, the dichroic ratio measured parallel and perpendicular to the fibre axis is unity for many degrees of orientation of the fibre, then the oscillating dipole must lie very close to 54.74° to the axis of the polymer chain.

Source: [6].

92 molar decadic absorption coefficient, ε

molar absorption coefficient
deprecated: extinction coefficient
deprecated: molar absorptivity

Decadic absorbance (A_{10}) divided by path-length (l) and amount concentration (c). $\varepsilon = A_{10}/(cl)$.

Note: ‘Extinction coefficient’ or ‘molar absorptivity’ have been widely used for the molar absorption coefficient, unfortunately often with values given in ill-defined units. Use of these terms has been discouraged since the 1960s, when international agreement with non-chemical societies reserved the word where the *absorption* is linearly proportional to the amount of absorber in unit area ‘extinction’ for diffusion of radiation, *i.e.*, the sum of the effects of *absorption*, scattering and luminescence.

See also: *linear decadic absorption coefficient*, *linear Napierian absorption coefficient*, *molar Napierian absorption coefficient*.

Source: [3] p 36.

93 molar Napierian absorption coefficient, κ

Napierian absorbance (A_e) divided by path-length (l) and amount concentration (c). $\kappa = A_e/(cl)$.

See also: *linear decadic absorption coefficient*, *linear Napierian absorption coefficient*, *molar decadic absorption coefficient*.

Source: [3] p 36.

94 multiple attenuated total reflection (MATR)

multiple internal reflection (MIR)
frustrated multiple internal reflection (FMIR)

Process in which *attenuated total reflection* occurs sequentially several times with the same sample.

Source: [6].

95 Napierian absorbance, A_e , B

Absorbance calculated with logarithm base e (natural or Napierian logarithm).

Note 1: Confusion with the *decadic absorbance* must be avoided.

Source: [3] p 36.

96 net absorption cross-section, σ_{net}

absorption cross-section, σ

Molar Napierian absorption coefficient divided by the Avogadro constant. $\sigma_{\text{net}} = \kappa/N_A$.

Source: [3] p 37.

97 noise

Random fluctuations occurring in a signal that are inherent in the combination of instrument and method.

Note: Noise can be defined as peak-to-peak noise, which is the difference between the largest and smallest values of these fluctuations in a given region, or as root-mean-square noise, which is the standard deviation of the noise in that region. For digital data with approximately 100 independent data points, the peak-to-peak noise is about five times greater than the root-mean-square.

Source: [13] p 1663.

Different kinds of noise are defined in Table 97.1 (Source [6]).

Table 97.1: Definitions of types of noise associated with *spectroscopy*.

Kind of noise	Definition	Notes
1/f noise	Noise for which the amplitude increases as the modulation frequency decreases.	
amplifier-readout noise	Noise that is observed, due to the processes of reading an amplifier, in the absence of analytical, background and dark current signals.	
excess dark current noise	Noise in the dark current of a photomultiplier tube or focal plane array that is due to non-thermal sources.	
flicker noise, multiplicative noise	Noise in excess of the <i>quantum noise</i> or <i>shot noise</i> that is proportional to the magnitude of the photon signal.	[1]
Johnson noise	Noise generated by the thermal motion of electrons.	
noise equivalent power, ϕ_N	<i>Incident radiation power</i> that yields a signal-to-noise ratio of 1 within a <i>bandwidth</i> of 1 Hz at the <i>wavelength</i> or <i>wavenumber</i> of interest	
Photomultiplier (PMT) multiplication noise	Noise caused by random fluctuations in the gain within a photomultiplier tube due to the random nature of the secondary emission of electrons at the dynodes.	
quantization noise	Noise due to the finite resolution of any readout device.	
digitization noise		
quantum noise	Fundamental noise due to the random emission of photons from a source.	
Schottky noise	Noise that is observed when a current passes through or is generated at an interface	
Shot noise	Noise in the current or measured voltage that is due to both <i>quantum noise</i> and <i>PMT multiplication noise</i> .	
white noise	Noise that has approximately the same amplitude at all frequencies	

Notes: [1] Flicker noise is usually caused by variations in the experimental variables that control the *radiance* of the source (source flicker noise) or by fluctuations in the sample (analyte flicker noise).

98 nominal spectral resolution

nominal resolution
resolution

Spectral resolution setting on an instrument that a user sets to record a *spectrum*.

Note: The actual resolution achieved is related to this, to the width of the bands studied and to the alignment of the instrument.

Source: [6].

99 nonisotropic

See: *anisotropic*.

100 Nyquist criterion

Result of information theory that a sine wave can be completely reconstructed if its ordinate is known at two or more points in a cycle.

Source: [6].

101 Nyquist frequency, f_{Nyquist}

Highest *frequency* or *wavenumber* that can be characterized by sampling at a given rate in order to be able to fully reconstruct the signal without artefacts.

Note: The *Nyquist sampling theorem* states that an FID or interferogram must be sampled at a rate at least twice the highest frequency in the FID or interferogram in order to reproduce the correct frequencies in an NMR or *Fourier-transform infrared* spectrum, respectively, without folding (*folding in spectroscopy*) artefacts. $f_{\text{Nyquist}} = 1/2 \nu$.

Source: [14].

102 optical throughput of a spectrometer, G

optical throughput
étendue

Volume in phase space, a function of the area of the emitting source (S) and the solid angle into which it propagates (Ω). $d^2G = dS d\Omega$.

103 path-length, l , s

path length

Length of the optical path through the sample.

Note 1: In a transmission cell the path-length is usually taken as the distance between the windows.

Note 2: SI unit: m. Commonly used units: μm , mm.

Source: [6]. See also: *optical path difference*.

104 phase relaxation

See: *dephasing*.

105 radiance, L

Radiant power emitted or passing through a small transparent element of surface in a given direction from the source about the solid angle Ω , divided by the solid angle and by the orthogonally projected area of the element in a plane normal to the given beam direction θ , $dS_{\perp} = dS \cos \theta$, $L = d^2P/d\Omega dS_{\perp}$.

Note: SI unit: $\text{W sr}^{-1} \text{m}^{-2}$.

Source: [8], [3] p 34.

106 radiant energy density, ρ , w

Radiant energy (Q) per unit volume (V). $\rho = dQ/dV$.

Note: SI unit: J m^{-3} .

Source: [6], [3] p 34.

107 radiant excitance, M

emitted intensity

deprecated: emitted radiant flux

Radiant power emitted per unit area of the source. $M = dP/dA_{\text{source}}$

Note: SI unit: W m^{-2} .

Source: [3] p 34.

108 radiant intensity, I_e

Radiant power per solid angle in the direction of the point from which the source is being viewed. $I_e = dP/d\Omega$.

Note 1: Radiant intensity should not be confused with *intensity of radiation* (irradiance).

Note 2: SI unit: W sr^{-1} .

Source: [3] p 34, 35.

109 radiant power, P , Φ

radiant flux

Radiant energy (Q) in unit time (t). $P = dQ/dt$.

Note 1: IUPAC notes the previous use of ‘flux’ for ‘flux density’ in the third edition of the Green Book ([3] p 81), but now recommends that ‘flux’ is simply a rate of flow (of energy, mass, heat, radiation).

Note 2: SI unit: W.

Source: [3] p 34.

110 radiofrequency (RF)

Frequency or band of frequencies in the range 10^4 to 10^{12} Hz.

111 received radiant flux density, I , E , ϕ_0

incident flux density

irradiance

Radiant power incident on unit area.

Note 1: SI unit: W m^{-2} .

Note 2: In *atomic absorption spectroscopy* incident flux density at a given *wavelength* is given the symbol $\phi_0(\lambda)$.

Source: [6]. See also: *intensity of radiation*.

112 reflectance, ρ , R

Spectral intensity reflected by the sample divided by spectral intensity incident on the sample.

Note: For non-scattering and non-luminescent samples the sum of *absorptance* (α), *transmittance* (τ), and *reflectance* (ρ) equals one.

Source: [6].

113 reflection

Process by which *electromagnetic radiation* is reflected by a sample. For non-scattering samples the term means *Fresnel reflection*; for scattering samples the term includes *regular reflection* and *volume reflection* or *diffuse reflection*.

Source: [6].

114 refractive index

See: *complex refractive index*.

115 regular reflection

See: *specular reflection*.

116 relative permittivity, ϵ_r

3×3 tensor that gives, to first order, the electric displacement, \mathbf{D} , in a material in terms of the applied electric field, \mathbf{E} , through $\mathbf{D} = \epsilon_r \epsilon_0 \mathbf{E}$, where ϵ_0 is the permittivity of vacuum.

Note 1: For isotropic materials the tensor is diagonal with the 3 diagonal elements equal, so a single quantity ϵ_r suffices.

Note 2: The equation $\mathbf{D} = \epsilon_r \epsilon_0 \mathbf{E}$ is valid at all frequencies, and ϵ_r is a complex quantity, $\hat{\epsilon}_r = \epsilon_r' + i\epsilon_r''$, where ϵ_r'' describes absorption. ϵ_r' is termed 'real dielectric constant', and ϵ_r'' is termed 'imaginary dielectric constant'.

Note 3: Relative permittivity is the square of the *refractive index*, thus $\hat{\epsilon}_r = \hat{n}^2$ or, for a non-absorbing isotropic material, $\epsilon = n^2$.

Source: [3] p 16, [6].

117 remission

See: *diffuse reflection*.

118 remission fraction

See: *diffuse reflectance*.

119 remittance

See: *diffuse reflectance*.

120 resolving power, R

Wavelength (or *wavenumber* or *frequency*) divided by the *spectral resolution* at that wavelength (or wavenumber or frequency); $R = \lambda/\delta\lambda$ ($=\tilde{\nu}/\delta\tilde{\nu} = \nu/\delta\nu$).

Note: Resolving power characterizes the performance of a spectrometer, or the degree to which a *spectral line* (or laser beam) is monochromatic.

Source: [3] p 36.

121 scattering coefficient, s , μ_s

Negative Napierian logarithm of the ratio of the *intensity of radiation* scattered (I_s) by a non-absorbing sample to the incident intensity (I_0), divided by the *path-length*, l .

$$s = -\ln(I_s/I_0)/l$$

Note: SI unit: m^{-1} .

Source: [6].

122 signal-to-noise ratio (SNR, S/N, SNR_{dB}), $R_{\text{S/N}}$

Power of signal divided by power of *noise*.

Note 1: When signal and noise are measured across the same impedance, SNR is often calculated as the root-mean-squared amplitude of the signal divided by the root-mean-squared amplitude of the noise.

Note 2: The value of signal-to-noise ratio may be expressed in decibel (SNR_{dB}) as ten times the logarithm to base 10 of signal-to-noise ratio.

Note 3: Initialisms should not be used to denote a quantity in expressions and formulae. $R_{\text{S/N}}$ is recommended.

Source: [6].

123 single beam spectrum

intensity spectrum

Output of a single beam spectrometer as a function of wavenumber or wavelength.

Note: A single-beam *spectrum* is often termed an ‘intensity spectrum’ (the measured radiant power is the *intensity* times the area of the detector) and does not have a flat baseline.

Source: [6].

124 single-beam spectrometer

Spectrometer that measures *radiant power* that reaches the detector at each *wavelength* without reference to another *spectrum* in real time.

Note: Most *Fourier-transform spectrometers* are single-beam spectrometers.

Source: [6].

125 slit width of a dispersive spectrometer

slit width

Distance between the blades of the entrance or exit slits in a monochromator.

Note: Spectral slit width is the range of *wavenumbers/wavelengths or frequencies* that the physical slit widths allow to be passed by the monochromator and is often determined as the *full width at half maximum* measured by the instrument for a line that is known to be extremely sharp.

Source: [6].

126 spectral band

Region of the *absorption/transmission spectrum* in which the *absorbance/transmission* passes through a maximum/minimum.

Note: The use of the term “spectral band” implies a wider region of the spectrum than “spectral line” (see *spectral line of an atom*).

127 spectral bandwidth

bandwidth

Upper *frequency* minus lower frequency in a continuous band of frequencies.

Note: SI unit: hertz, Hz.

Source: [6].

128 spectral intensity, $I_{\tilde{\nu}}(\tilde{\nu})$, $E_{\tilde{\nu}}(\tilde{\nu})$

spectral irradiance

Intensity of radiation per unit *wavenumber* at wavenumber $\tilde{\nu}$. $I_{\tilde{\nu}}(\tilde{\nu}) = dI/d\tilde{\nu}$.

Note 1: Spectral intensity and spectral irradiance are formally the same quantity, although the term spectral intensity is usually used for collimated beams of radiation.

Note 2: SI unit: W m^{-1} . Common unit: $\text{W m}^{-2}/\text{cm}^{-1}$.

Source: [6], [3] p 34.

129 spectral radiance, $L_{\tilde{\nu}}(\tilde{\nu})$, $L_{\lambda}(\lambda)$

spectral brightness

Radiance in unit wavenumber (wavelength) interval at wavenumber $\tilde{\nu}$ (wavelength λ).Note: SI unit: $\text{W m}^{-3} \text{sr}^{-1}$. Common unit: $\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$.

Source: [6], [8] p 2276.

130 spectral radiant energy density, $\rho_{\tilde{\nu}}(\tilde{\nu})$, $\rho_{\lambda}(\lambda)$ *Radiant energy density* in unit wavenumber (wavelength) interval at wavenumber $\tilde{\nu}$ (wavelength λ).Note: SI unit: J m^{-2} .

Source: [6].

131 spectral range of a spectrometer*Wavelength range* for which a *spectrometer* can be used.

Note: Spectral range depends essentially on the radiation source, the optical components of the wavelength selector, and the detector.

Source: [10].

132 spectral resolution of an instrument, $\delta\tilde{\nu}$, $\delta\nu$, $\delta\lambda$ spectral resolution
resolutionSmallest difference between *wavenumbers* (or *wavelengths* or *frequencies*) at which different spectral properties may be distinguished, measured as the *full width at half maximum*.Note 1: An equivalent definition is the minimum separation of two infinitely sharp lines of equal *intensity of radiation* that allows the presence of two lines to be seen in the measured *spectrum*.Note 2: Resolution depends strongly on the *instrument line shape* “function” of the *spectrometer* and on the *natural line width*.Source: [3] p 36. See also: *nominal spectral resolution*.**133 spectral slit width**See: *slit width of a dispersive spectrometer*.**134 spectral subtraction**Ordinate of one *spectrum* minus ordinate of another spectrum.

Note 1: Spectral subtraction may be used to improve the ability to detect of minor components in the spectrum of a mixture.

Note 2: Successful use of the technique requires spectra, such as *absorbance* and *Raman spectra*, in which the ordinate is linear in concentration; a precisely agreeing *wavenumber* scale; and a very high *signal-to-noise ratio*.

Source: [6].

135 spectrometer

Measuring instrument [VIM 3.1] that separates *electromagnetic radiation* into its component *frequencies* and transforms the *radiant power* at each frequency into an electrical signal.

Source: [6].

136 spectrum (vibrational)

Graph of a quantity derived from the *radiant power* at each *wavelength* (*frequency* or *wavenumber*) as ordinate plotted against the *wavelength* (*frequency* or *wavenumber*) of *electromagnetic radiation* as abscissa.

Note 1: In *mid-infrared* and *Raman spectroscopy*, *wavenumber* is mostly used today, while it is more commonly replaced by *wavelength* in *near infrared spectroscopy*.

Note 2: Quantities plotted include *absorbance*, *absorption coefficient*, *transmittance*, *reflectance*, *luminescence*.

Source: [6].

137 specular reflection

regular reflection

Reflection of electromagnetic radiation from a surface such that each incident ray is reflected at the same angle to the surface normal as the incident ray, but on the opposing side of the surface normal in the plane formed by incident and reflected rays.

Note 1: An image reflected by the surface in this way is reproduced in mirror-like (specular) fashion.

138 stray light

Electromagnetic radiation that does not follow the usual path through a *spectrometer* and consequently appears in a *spectrum* at a *frequency* or *wavenumber* different from its initial value. The term is also used to refer to radiation that passes around the sample instead of through it, and consequently is not modified by the sample and seriously affects absolute and relative *intensities*.

Source: [6].

139 superradiance emission

See: *laser*.

140 transition

Change of *energy level* of a system.

Note: In *spectroscopy*, a transition is caused by interaction of an atom, ion, or molecule with *electromagnetic radiation*.

Source: [6]. See also: *electronic transition* and *electromagnetic transition*.

141 transition-dipole transition dipole coupling

See: *dipole coupling*.

142 transmission

Process in which *electromagnetic radiation* passes through a material, entering it on one side and leaving it on another.

Note 1: For non-scattering, non-luminescent samples, the transmitted beam obeys Snell's law of refraction, and the term internal transmission (see above) is used when surface reflection effects are not included in transmission within the sample.

Note 2: For scattering, non-luminescent materials, transmission consists of two processes, direct transmission and diffuse transmission, and is sometimes called total transmission.

Source: [6].

143 transmission factor

See: *transmittance*.

144 transmission fraction

See: *transmittance*.

145 transmission spectrum

transmittance spectrum

General term for the *spectrum* of transmitted *electromagnetic radiation*.

Note: The ordinate quantity is usually the percentage of the incident radiation that is transmitted, usually called the percent transmission, with range 0 to 100 %. If the ordinate quantity is the fraction transmitted, *i.e.*, the *transmittance*, the ordinate range is 0 to 1 and the spectrum may be called a transmittance spectrum.

Source: [6].

146 transmittance, T , τ

transmission factor
transmission fraction

Transmitted *radiant power* at wavenumber $\tilde{\nu}$ divided by incident radiant power.

Note 1: For non-scattering, non-luminescent samples, the sum of *absorptance* (a), transmittance (T), and *reflectance* (ρ) equals one.

Note 2: For scattering, non-luminescent samples, the term ‘transmission fraction’ is usually used instead of transmittance.

Source: [3] p 36. See also: *percent transmission*.

147 two-dimensional (2-D) correlation spectroscopy

Measurement principle [VIM 2.4] of *spectroscopy* in which spectra are recorded at different magnitudes of an applied external perturbation of the sample and are processed to yield a *2-D correlation spectrum*.

Note 1: The external perturbation may be time dependent (chemical reactions, physical relaxation processes), or static (temperature change, concentration change).

Note 2: Correlation spectroscopy is used in *infrared spectroscopy*, *nuclear magnetic resonance spectroscopy* (*COSY*, *TOCSY*), *fluorescence spectroscopy* and others.

Source: [6]. See also: [15, 16].

148 two-dimensional (2-D) correlation spectrum

Three-dimensional surface in which two of the dimensions show *frequency axes* (ν_1, ν_2) and the third axis shows a correlation function of the spectral intensities observed at ν_1 and ν_2 .

Note 1: The shape of the surface shows whether the bands at the two wavenumbers are or are not correlated, and hence allows deductions to be made about the extent to which the different parts of the molecule are linked in their response to the applied external perturbation.

Source: [6]. See: *dynamic spectrum*.

149 undersampling

Sampling less frequently than is required by the *Nyquist criterion*.

Note: Undersampling occurs when an analogue signal is digitized with less than two data points per *wavelength* of the shortest wavelength (highest *wavenumber*) *radiation* that reaches the detector.

Source: [6]. See: *folding in vibrational spectroscopy*.

150 vacuum wavelength

See: *wavelength in vacuum*.

151 Voigt function

Convolution of *Gaussian* and *Lorentzian* (Cauchy) *functions*.

Source: [6].

152 wavelength in medium, λ

wavelength

Distance travelled by a wave of *electromagnetic radiation* in one cycle in a non-absorbing medium of real *refractive index* n . $\lambda = \lambda_0/n$.

Note 1: In spectroscopy, the unqualified term ‘wavelength’ frequently means the *vacuum wavelength*, and symbol λ frequently means λ_0 .

Note 2: SI unit: m. Common unit: nm or μm .

Source: [6].

153 wavelength in vacuum, λ_0

vacuum wavelength

Distance travelled by a wave of *electromagnetic radiation* in one cycle in vacuum.

Note: SI unit: m. Common unit: nm or μm .

Source: [6].

154 wavenumber in medium, σ

wavenumber

Reciprocal of *wavelength* of *electromagnetic radiation*. $\sigma = 1/\lambda$.

Note 1: In spectroscopy, the unqualified term ‘wavenumber’ (sometimes referred to as “reciprocal centimetre” cm^{-1}) often means *vacuum wavenumber*, and symbol σ often means $\tilde{\nu}$.

Note 2: SI unit: m^{-1} . Common unit: cm^{-1} .

Source: [6].

155 wavenumber in vacuum, $\tilde{\nu}$

vacuum wavenumber

Reciprocal of the *vacuum wavelength* of *electromagnetic radiation*. $\tilde{\nu} = 1/\lambda_0$.

Note 1: Wavenumber is related to the energy change, ΔE , induced when the radiation is absorbed by $\Delta E = hc_0\tilde{\nu}$, where h is the Planck constant and c_0 the speed of the radiation.

Note 2: Wavenumber should only be used when no confusion with frequency is possible.

Note 3: The symbol ν is often used instead of $\tilde{\nu}$; this usage should be discouraged.

Note 4: SI unit: m^{-1} . Common unit: cm^{-1} .

Source: [6].

156 window function

See: *apodization function*.

157 working range of a spectrometer

working range

Range of *absorbance* or *intensity* which a *spectrometer* can measure with *accuracy* [VIM 2.13] and *precision* [VIM 2.15].

Note: Working range varies in different parts of the *spectral range*.

Source: [10].

158 zero filling

Addition of zeros to a *free induction decay* or *interferogram* to decrease the frequency or wavenumber spacing between points in the *Fourier-transformed spectrum*.

Source: [6].

159 zero path difference

In a Michelson *interferometer* or other two-beam interferometer, the position of the moving mirror at which the optical paths are equal.

Source: [6].

3 NMR spectroscopy

Nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency that depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms. Differentiation in NMR signals between similar nuclei within a molecule is seen primarily due to differences in the electron density at each nucleus. This variation in electron density is a consequence of the geometric arrangement of atoms and the specific interaction with the electrons surrounding them.

The propensity of a nucleus to undergo this phenomenon is dependent on its nuclear spin, a net combination of the spins from the protons and neutrons within the nucleus. All nuclei with a non-zero spin exhibit some NMR activity, but those with a value of $1/2$ are most amenable, as they provide the simplest and best resolved spectra, with ^1H , ^{13}C , ^{15}N , ^{19}F and ^{31}P being some of the most frequently studied nuclei.

NMR provides a rich source of information on the magnetic environment of nuclei through their chemical shifts, the connectivity of nuclei within a molecule through their multiplicities and *spin-spin couplings*, and the ratio of nuclei through their integrals. NMR is used extensively for structural characterization, quantitation of analytes, biological imaging, inter-molecular interactions, reaction kinetics, and assessment of physical properties.

The experimental manifestation of NMR, *nuclear magnetic resonance spectroscopy*, usually involves three basic, sequential steps:

- The alignment (polarization) of the magnetic nuclear spins in an applied, static magnetic induction B_0 .

- The perturbation of this alignment of the nuclear spins by employing *radiofrequency* (RF) pulses.
- The detection of the RF as the nuclear spins return to equilibrium.

160 ^{13}C -HMQC-NOESY

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with 1 carbon and 2 hydrogen dimensions.

Note 1: In the initial HMQC step, magnetization is transferred from ^1H to ^{13}C and back again. This is then followed by a *NOESY* step in which the magnetization is transferred to any other hydrogen nucleus close by before detection.

Note 2: The technique requires ^{13}C labelling.

Note 3: The *spectrum* is used to obtain restraints for structure calculations.

Source: [17]. See also: [18].

161 ^{13}C -NOESY-HSQC

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with one carbon and two hydrogen dimensions.

Note 1: Magnetization is exchanged between all hydrogens using the *nuclear Overhauser effect* before being transferred to neighbouring ^{13}C nuclei and then back to ^1H for detection.

Note 2: The *spectrum* is used to obtain restraints for structure calculations.

Source: [19]. See also: [6, 18].

162 ^{15}N -NOESY-HSQC

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with 1 nitrogen and 2 hydrogen dimensions.

Note: Magnetization is exchanged between all hydrogens using the *nuclear Overhauser effect* before being transferred to neighbouring ^{15}N nuclei and then back to ^1H for detection. This *spectrum* can be used to obtain restraints for structure calculations.

Source: [19]. See also: [18].

163 ^{15}N -TOCSY-HSQC

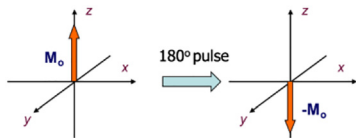
Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with 1 nitrogen and 2 hydrogen dimensions.

Note An isotropic mixing step transfers magnetization between ^1H spins. Then the magnetization is transferred to neighbouring ^{15}N nuclei and back to ^1H for detection. This can help identify amino acid types.

Source: [19]. See also: [18], *total correlation spectroscopy*.

164 180° pulse

Pulsed *radiofrequency* signal in *NMR* that rotates the bulk magnetization vector (M_0) of a nuclear spin to its opposing direction, effectively inverting the signal, (e.g., from the $+z$ to $-z$ axis).

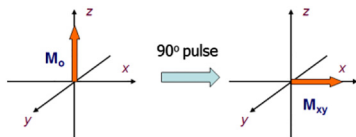


Source: [20].

165 90° pulse

Pulsed *radiofrequency* signal that rotates the bulk magnetization vector (M) of a nuclear spin to its orthogonal plane.

Note: In a simple 1D *NMR* experiment, this is from the z axis to the xy plane.



Source: [20].

166 acquisition time (AT), t_a

Duration of the digitization of a *free induction decay*.

Note: $t_a = 1/2 N/f_{SW}$ with number of data points N and *NMR spectral width* f_{SW}

Source: [14]. See also: *dwell time*.

167 adiabatic pulse

Radiofrequency pulse that inverts spins by using a frequency sweep during the pulse.

Note 1: Adiabatic pulse allows very high *spectral bandwidth* and accurate *flip angles* to be achieved with high tolerance to spatial variations in *RF* field intensity and is thus of value in excitation of nuclei with frequency ranges.

Note 2: the sweep must be slow enough to satisfy the adiabatic condition $d\theta/dt \ll \gamma B_{eff}$ where B_{eff} is the effective radiofrequency magnetic flux density and θ is the angle between B_{eff} and abscissa.

Source: [21].

168 Bloch equations

Set of coupled differential equations which can be used to describe the behaviour of a magnetization vector under any conditions.

Note: When properly integrated, Bloch equations yield X' , Y' , and Z' components of magnetization within the rotating frame of reference as a function of time

Source: [22].

169 Bloch Siegert shift

Frequency difference seen for a nuclear magnetic resonance signal when a radiofrequency field is applied during the acquisition time.

Note: The shift arises from the effective magnetic field generated by the applied RF field. The resonances are always moved away from the frequency of the irradiating field and are inversely proportional to the difference in frequency between the irradiation and the resonance.

Source: [21].

170 Boltzmann distribution of nuclear spins

Distribution of nuclear spins among their possible *energy levels* at thermal equilibrium.

Note: For a positive *gyromagnetic ratio*, produces population excess (polarization) in the direction of B_0 . The population difference between the spin state can be expressed as

$$\frac{N_i}{N} = \frac{e^{-\frac{\epsilon_i}{kT}}}{\sum_{j=1}^M e^{-\frac{\epsilon_j}{kT}}}$$

where T is the thermodynamic temperature, k is the Boltzmann constant, N_i is the number of spins in excited state i , N is the total number of spins and ϵ_i and ϵ_j are the energies of states i and j respectively.

171 CBCA(CO)NH/HN(CO)CACB

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note: Magnetization is transferred from $^1\text{H}\alpha$ and $^1\text{H}\beta$ to $^{13}\text{C}\alpha$ and $^{13}\text{C}\beta$, respectively, and then from $^{13}\text{C}\beta$ to $^{13}\text{C}\alpha$. From here it is transferred first to ^{13}CO , then to ^{15}NH and then to ^1HN for detection. Along with *CBCANNH* and *HSQC* this forms the standard set of experiments needed for backbone assignment.

Source: [23]. See also: [18].

172 CBCANH/HNCACB

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note 1: Magnetization is transferred from $^1\text{H}\alpha$ and $^1\text{H}\beta$ to $^{13}\text{C}\alpha$ and $^{13}\text{C}\beta$, respectively, and then from $^{13}\text{C}\beta$ to $^{13}\text{C}\alpha$. From here it is transferred first to ^{15}NH and then to ^1HN for detection. For each NH group there are two $\text{C}\alpha$ and $\text{C}\beta$ peaks visible. Along with the *CBCA(CO)NNH* and *HSQC* this forms the standard set of experiments needed for backbone assignment.

Source: [17]. See also: [18].

173 CC(CO)NH

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note 1: Magnetization is transferred from the side-chain hydrogen nuclei to their attached ^{13}C nuclei. Then isotropic ^{13}C mixing is used to transfer magnetization between the carbon nuclei. From here, magnetization is transferred to the carbonyl carbon, on to the amide nitrogen and finally the amide hydrogen for detection. The chemical shift is evolved simultaneously on all side-chain carbon nuclei, as well as on the amide nitrogen and hydrogen nuclei, resulting in a three-dimensional *spectrum*.

Note 2: This method is a useful spectrum for obtaining carbon side-chain assignment.

Source: [24]. See also: [18].

174 chemical shift anisotropy in NMR (CSA)

Chemical shift difference between *isotropic* and *anisotropic* states in *nuclear magnetic resonance spectroscopy*.

Note 1: Nuclei which are part of a specific functional group resonate at different frequencies depending on shielding by the local electronic environment and thus can give information on their relative orientation.

Note 2: Chemical shift anisotropy also contributes to nuclear spin relaxation.

Source: [25].

175 chemical shift in NMR, δ

The fractional variation of the resonance frequency of a nucleus in *nuclear magnetic resonance spectroscopy* relative to the resonance frequency of the nucleus in a given reference in consequence of its magnetic environment.

Note 1: The chemical shift for nucleus X in sample s, $\delta_{X,s}$ is $\delta_{X,s} = \frac{(v_{X,s} - v_{X,r})}{v_{X,r}}$ where $v_{X,s}$ is the resonance frequency of X in the sample and $v_{X,r}$ is the resonance frequency in the reference.

Note 2: Chemical shift is usually reported in 'parts per million' or ppm, where the difference of frequencies in the numerator have unit Hz, and the frequency of the reference in the denominator has unit MHz.

Note 3: The alternative use of Hz/MHz is recommended as best practice in the Green Book to remove ambiguity regarding the symbol ppm.

Source: [4] p 1807.

176 combined rotation and multiple pulse spectroscopy (CRAMPS)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* for obtaining high-resolution *solid-state nuclear magnetic resonance* spectra on nuclei with high gyromagnetic ratio such as ^1H and ^{19}F .

Note: CRAMPS is based on coherent-averaging theory, which attempts to describe the time evolution of a system in terms of an average Hamiltonian derived from the density matrix formalism of quantum mechanics.

Source: [26].

177 constant time evolution

Segment of a *pulse sequence* in *nuclear magnetic resonance spectroscopy* that allows evolution of *chemical shift* during a fixed time period rather than through the traditional symmetrical incremented delays.

Source: [21].

178 correlation spectroscopy in NMR (COSY)

Homonuclear *two-dimensional nuclear magnetic resonance spectroscopy* correlation experiment showing cross peaks representing *spin-spin coupling* between pairs of nuclei.

Note 1: COSY is the simplest and original 2D experiment, but still one of the most common along with its many variations including those with multiple quantum filters, solvent suppression and optimization for long range couplings.

Note 2: COSY is often used to show the *spin-spin coupling* between hydrogen nuclei 2 or 3 bonds apart (H,H-COSY).

Source: [27]. See also: *correlation spectroscopy*.

179 correlation spectroscopy through long-range coupling (COLOC)

Heteronuclear (typically ^{13}C) detected long range 2D correlation experiment in *nuclear magnetic resonance spectroscopy* that has mostly been superseded by *heteronuclear multiple bond correlation* (HMBC) experiments and its variants.

Note 1: COLOC is often used to show *spin-spin coupling* between hydrogen and carbon nuclei 2 and 3 bonds apart.

Source: [27]. See also: [18].

180 correlation time, τ , τ_c

Parameter related to the mean time during which a molecule maintains its spatial geometry.

Note: For an internuclear vector, correlation time is approximately equal to the average time for it to rotate through an angle of one radian.

Source: [22].

181 coupling constant

See: *spin-spin coupling constant*.

182 cross polarization with magic angle spinning NMR (CP/MAS)

Combined use of *cross polarization* with magic-angle spinning for *solid-state nuclear magnetic resonance spectroscopy*.

Source: [27].

183 cross polarization

Technique in *solid-state nuclear magnetic resonance spectroscopy* that enables polarization from abundant spins such as ^1H or ^{19}F to be transferred to dilute spins such as ^{13}C or ^{15}N to enhance *signal-to-noise ratio*.

Note: Cross polarization requires that nuclei are dipolar coupled to one another.

184 cross-relaxation appropriate for minimolecules emulated by locked spins (CAMELSPIN)

See: *rotating-frame NOE spectroscopy*.

185 decoupling

See: *heteronuclear decoupling, homonuclear decoupling*.

186 decoupling in the presence of scalar interactions (DIPSI)

Pulse sequence in *nuclear magnetic resonance spectroscopy* often used for *isotropic* mixing in *total correlation spectroscopy* (TOCSY) experiments due to its efficiency over large *spectral bandwidths*.

Source: [21].

187 diffusion ordered spectroscopy (DOSY)

Pseudo-two-dimensional nuclear magnetic resonance spectroscopy experiment that resolves NMR signals of a one-dimensional *nuclear magnetic resonance spectrum* in a second dimension through the diffusion times of their corresponding molecules.

Note 1: DOSY is used to differentiate signals from different molecules based on their effective sizes.

Note 2: DOSY relies on spatially encoding the analyte by use of *pulsed-field gradients*.

Source: [21].

188 dipolar coupling in nuclear magnetic resonance spectroscopy

magnetic dipole–dipole interaction in NMR

Direct through-space interactions of nuclear magnetic moment vectors proportional to the inverse cube of internuclear distance.

Note: In *isotropic* solution, dipolar couplings average to zero as a result of diffusion but are present in *solid-state nuclear magnetic resonance spectroscopy* and their effect on nuclear spin relaxation are measurable through *nuclear Overhauser effects* (NOEs).

Source: [22].

189 distortionless enhancement by polarization transfer (DEPT)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* used for determining the presence of primary, secondary and tertiary heteronuclei.

Note 1: DEPT is a 1D technique which is used typically for ^{13}C .

Note 2: The DEPT experiment for ^{13}C differentiates between CH, CH₂ and CH₃ groups by variation of the selection angle parameter (the *flip angle* of the final ^1H pulse): 135° angle gives all CH and CH₃ in a phase opposite to CH₂; 90° angle gives only CH groups, the others being suppressed; 45° angle gives all carbons with attached protons with the same phase.

Source: [27].

190 double pulsed-field gradient spin-echo excitation (DPFGSE)

Pulse sequence in *nuclear magnetic resonance spectroscopy* in which *pulsed-field gradients* are applied to a doubled *spin echo* sequence to cleanly and precisely excite particular resonances.

Source: [28].

191 double resonance

Nuclear magnetic resonance spectroscopy experiment where excitation is applied independently to two distinct frequency ranges.

Note: Double resonance is most commonly applied for *spin decoupling*.

Source: [20].

192 double-labelled protein

Shorthand for a protein which has been uniformly ^{15}N - and ^{13}C -labelled.

193 double-quantum filtered correlation spectroscopy (DQF-COSY)

Variant of the *COSY* experiment with a double quantum filter to remove, or at least reduce, impact of large singlet peaks on dynamic range and artefacts.

Source: [27].

194 dwell time (DW), τ_d

Time interval between sampled data points.

Note: $\tau_d = 1/f_{\text{SW}}$, where f_{SW} is the *NMR spectral width*

Source: [21]. See also: *acquisition time*.

195 echo time (TE), T_E

In *nuclear magnetic resonance spectroscopy*, time interval between the middle of the first *radiofrequency* pulse and the peak of the spin echo.

Source: [21].

196 electronic reference to access *in vivo* concentrations (ERETIC)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* that generates an electronic signal in a *nuclear magnetic resonance spectrometer* which is detected simultaneously to the sample *free induction decay* during the acquisition.

Note: This approach is used to simplify the quantification of signals in the resulting NMR spectra by avoiding the need for the use of internal or external reference materials.

Source: [29].

197 Ernst angle, θ_E

When signal averaging in a single-pulse *nuclear magnetic resonance spectroscopy* experiment, *flip angle* giving the best *signal-to-noise ratio* for a given combination of *spin-lattice relaxation time* and repetition rate.

Note: Named after Richard Ernst. It is employed to allow the maximum signal to noise to be generated in a fixed amount of time. $\cos(\theta_E) = e^{-(t_d+t_a)/T_1}$, where t_d is the interpulse delay, t_a is the acquisition time, and T_1 is *longitudinal relaxation time*.

Source: [21].

198 exchange spectroscopy (EXSY)

Nuclear magnetic resonance spectroscopy experiment, which is the same as a *NOESY*, but for the purposes of observing nuclei exchanging chemical environments during the course of the experiment through conformational or chemical exchange.

Source: [27].

199 excitation sculpting

Robust method of generating selective excitation through combination of shaped pulses and *pulsed-field gradients* in *nuclear magnetic resonance spectroscopy*.

Source: [21].

200 fast field cycling NMR relaxometry (FFC-NMR)

Relaxometry to measure the nuclear *spin-lattice relaxation* rate constant as a function of the applied magnetic field strength in *nuclear magnetic resonance spectroscopy*.

Note: FFC-NMR is used to study molecular dynamics of molecules across a range of applications including molecular motion in solids and ligand-metal binding.

Source: [30].

201 flip angle, α

tip angle

Rotation that the net magnetization experiences during the application of a *radiofrequency* pulse in *nuclear magnetic resonance spectroscopy*.

Note: For a strong and rectangular RF-pulse of constant amplitude (B_1) and duration (t_p), the resultant flip angle is approximately proportional to the *frequency* (f_1) of the B_1 field: $\alpha = \gamma B_1 t_p$, where γ is the *gyromagnetic ratio*.

202 gated decoupling

Application of *spin decoupling* only during selected time periods in a pulse experiment in *nuclear magnetic resonance spectroscopy*.

Note 1: Gated decoupling is used to eliminate either $^1\text{H} - ^{13}\text{C}$ *spin-spin coupling* or the *nuclear Overhauser effect* from a 1D ^{13}C *spectrum*.

Note 2: If the decoupler is turned off during acquisition this is usually referred to as ‘gated decoupling’ while decoupling turned on during acquisition is usually referred to as ‘inverse gated decoupling’.

Source: [20].

203 globally optimized alternating-phase rectangular pulses (GARP)

Spin decoupling pulse sequence in *nuclear magnetic resonance spectroscopy* used to provide *decoupling* over a large frequency range.

Note: GARP is typically used to remove ^{13}C sidebands in ^1H *nuclear magnetic resonance spectra*.

Source: [27].

204 gradient pulse

See: *pulsed-field gradient*.

205 gradient-selected experiment

Nuclear magnetic resonance spectroscopy experiment where *pulsed-field gradients* are employed to filter out unwanted resonances from a *spectrum* rather than the classic phase-cycling approach.

Source: [27].

206 gyromagnetic ratio, γ

see *magnetogyric ratio*

207 H(CCO)NH

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with one nitrogen, and two hydrogen dimensions.

Note 1: Magnetization is transferred from the side-chain hydrogen nuclei to their attached ^{13}C nuclei. Then isotropic ^{13}C mixing is used to transfer magnetization between the carbon nuclei. From here, magnetization is transferred to the carbonyl carbon, on to the amide nitrogen and finally the amide hydrogen for detection.

Note 2: Requires ^{15}N and ^{13}C labelling

Note 3: Useful *spectrum* for obtaining hydrogen side-chain assignments.

Source: [31]. See also: [18].

208 HBHA(CO)NH

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with one nitrogen and two hydrogen dimensions.

Note 1: Magnetization is transferred from $^1\text{H}\alpha$ and $^1\text{H}\beta$ to $^{13}\text{C}\alpha$ and $^{13}\text{C}\beta$, respectively, and then from $^{13}\text{C}\beta$ to $^{13}\text{C}\alpha$. From here it is transferred first to ^{13}CO , then to ^{15}NH and then to ^1HN for detection.

Note 2: Requires ^{15}N and ^{13}C labelling

Note 3: Useful *spectrum* for obtaining $\text{H}\alpha$ and $\text{H}\beta$ assignments.

Source: [32]. See also: [18].

209 HCCH-COSY

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with one carbon and two hydrogen dimensions.

Note 1: Magnetization is transferred from the side-chain hydrogen nuclei to their attached ^{13}C nuclei. Magnetization is then exchanged between neighbouring ^{13}C nuclei *via* the J-coupling and finally transferred back to the side-chain hydrogen atoms for detection.

Note 2: The *nuclear magnetic resonance spectrum* can be useful in aiding side-chain assignment.

Source: [33]. See also: [18].

210 HCCH-TOCSY

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with one carbon and two hydrogen dimensions.

Note 1: Magnetization is transferred from the side-chain hydrogen nuclei to their attached ^{13}C nuclei. This is followed by isotropic ^{13}C mixing and finally the transfer back to the side-chain hydrogen atoms for detection.

Note 2: *The nuclear magnetic resonance spectrum* is used for side-chain assignment.

Source: [34]. See also: [18], *total correlation spectroscopy*.

211 Hahn echo

See: *spin echo*.

212 heteronuclear decoupling

decoupling

Spin decoupling in nuclear magnetic resonance spectroscopy between two different nuclei (e.g., ^{13}C and ^1H) by appropriate excitation of the decoupled nucleus.

Note 1: Heteronuclear decoupling is normally performed to simplify spectra or to enhance *signal-to-noise ratio* by combining individual components of the NMR signal.

Note 2: Notation: $^{13}\text{C}\{^1\text{H}\}$ denotes observation of ^{13}C nucleus with simultaneous decoupling of ^1H nuclei.

Source: [20]. See also: *homonuclear decoupling*.

213 heteronuclear multiple bond correlation NMR (HMBC)

Two-dimensional nuclear magnetic resonance spectroscopy that gives correlations between carbons and protons that are separated by two, three, and, sometimes in conjugated systems, four bonds.

Note 1: Direct one-bond correlations are suppressed.

Note 2: HMBC gives connectivity information much like a proton-proton *COSY*.

Note 3: The *intensity* of cross peaks depends on the *spin-spin coupling constant*, which for three-bond couplings follows the Karplus relationship. For dihedral angles near 90° , the coupling is near zero. Thus, the absence of a cross peak does not confirm that carbon-proton pairs are many bonds apart.

Note 4: Because of the wide range (0 to 14 Hz) of possible carbon-proton couplings, two experiments are often performed. One optimized for 5 Hz couplings and the second optimized for 10 Hz. This gives the optimum *signal-to-noise ratio*. Alternatively, a compromise value of 7 to 8 Hz can be used. There are also “accordion” versions that attempt to sample the full range of couplings.

Source: [35].

214 heteronuclear multiple-bond correlation over two bonds (H2BC)

Variant of the *heteronuclear single quantum correlation* (HSQC) and *heteronuclear multiple bond correlation* (HMBC) experiment in nuclear magnetic resonance spectroscopy that almost exclusively correlates ^1H nuclei with heteronuclei separated by two covalent bonds.

Source: [19]. See also: [18].

215 heteronuclear multiple-quantum correlation NMR (HMQC)

Simplest implementation of an inverse detected ^1H heteronuclear correlation *nuclear magnetic resonance spectroscopy* experiment.

Source: [27].

216 heteronuclear multiple-quantum correlation with additional TOCSY transfer (HMQC-TOCSY)

Variant of *heteronuclear multiple bond correlation* (HMBC) spectroscopy that shows correlations from a heteronucleus (e.g., ^{13}C) to not only its directly bound ^1H but also to all other ^1H nuclei within the *spin system*.

Source: [27]. See also: *total correlation spectroscopy*.

217 heteronuclear Overhauser effect spectroscopy (HOESY)

Heteronuclear variant of *nuclear Overhauser effect spectroscopy* (NOSEY) showing through space interaction between ^1H and a heteronucleus, typically ^{13}C .

Source: [27].

218 heteronuclear shift correlation NMR (HETCOR)

Directly-observed one-bond heteronuclear correlation experiment in *nuclear magnetic resonance spectroscopy*.

Note: HETCOR has largely been replaced by the indirectly observed *heteronuclear single quantum correlation* experiment due to its greater sensitivity. It does however have the advantage of greater resolution in the heteronuclear dimension.

Source: [27].

219 heteronuclear single quantum correlation (HSQC)

heteronuclear single quantum coherence

^1H (inverse) detected *two-dimensional nuclear magnetic resonance spectroscopy* heteronuclear experiment that correlates ^1H nuclei with their directly coupled nucleus through a single bond.

Source: [27].

220 heteronuclear single quantum correlation with additional TOCSY transfer (HSQC-TOCSY)

Variant of the *heteronuclear single quantum correlation* (HSQC) experiment that shows correlations from a heteronucleus (e.g., ^{13}C) to not only its directly bound ^1H but also to all other ^1H nuclei within the *spin system*.

Source: [27]. See also: *total correlation spectroscopy*.

221 heteronuclear single quantum multiple-bond correlation (HSQMBC)

Variant of the *heteronuclear single quantum correlation* (HSQC) experiment that provides pure absorption, antiphase line shapes for precise, direct measurement of $^nJ(\text{C,H})$ spin-spin coupling constants.

Source: [19]. See also: [18].

222 HN(CA)CO

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note 1: the magnetization is transferred from ^1H to ^{15}N and then *via* the N-C α J-coupling to the $^{13}\text{C}\alpha$. From there it is transferred to the ^{13}CO *via* the $^{13}\text{C}\alpha$ - ^{13}CO J-coupling. For detection the magnetization is transferred back the same way: from ^{13}CO to $^{13}\text{C}\alpha$, ^{15}N and finally ^1H .

Note 2: each NH group will show correlations to both their own and adjacent carbonyls group.

Source: [36]. See also: [18].

223 HN(CO)CA

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note: The magnetization is passed from ^1H to ^{15}N and then to ^{13}CO . From here it is transferred to $^{13}\text{C}\alpha$ and the chemical shift is evolved. The magnetization is then transferred back *via* ^{13}CO to ^{15}N and ^1H for detection. This is similar to the HNCA, but is selective for the C α of the preceding residue.

Source: [37]. See also: [18].

224 HNCA

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note: The magnetization is passed from ^1H to ^{15}N and then *via* the N-C α J-coupling to the $^{13}\text{C}\alpha$ and then back again to ^{15}N and ^1H hydrogen for detection. Each NH group will show correlations to both their own and the previous residue's $^{13}\text{C}\alpha$.

Source: [38]. See also: [18].

225 HNCO

Three-dimensional nuclear magnetic resonance spectroscopy for the assignment of protein structure with nitrogen, carbon and hydrogen dimensions.

Note: Magnetization is passed from ^1H to ^{15}N and then selectively to the carbonyl ^{13}C *via* the ^{15}NH - ^{13}CO J-coupling. Magnetization is then passed back *via* ^{15}N to ^1H for detection.

Source: [38]. See also: [18].

226 homonuclear decoupling

decoupling

Spin decoupling in *nuclear magnetic resonance spectroscopy* between two signals of the same nuclear isotope.

Note: Homonuclear decoupling is normally performed through selective excitation of specific NMR signals within a *spectrum* or through pure shift experiments such as *PSYCHE*.

Source: [20]. See also: *heteronuclear decoupling*.

227 homonuclear Hartmann-Hahn spectroscopy (HOHAHA)

See: *total correlation spectroscopy*.

228 imaginary NMR spectrum

imaginary spectrum

In *nuclear magnetic resonance spectroscopy*, one of two equally sized blocks of frequency data 90° out of phase to each other produced by Fourier transformation of the time domain signal.

Note 1: Usually the imaginary frequency data is not displayed and is used for phase correction of the real *spectrum*.

Note 2: In simple 1D spectra this equates to the NMR signals being in dispersion mode.

Source: [21].

229 incredible natural-abundance double-quantum transfer experiment (INADEQUATE)

Nuclear magnetic resonance spectroscopy experiment designed to show homonuclear *spin-spin coupling* correlations between low natural abundance nuclei such as ¹³C.

Note: 2D variant shows each coupled pair of nuclei gives a pair of peaks on the INADEQUATE *spectrum* which both have the same vertical coordinate, which is the sum of the chemical shifts of the nuclei; the horizontal coordinate of each peak is the chemical shift for each of the nuclei separately.

Source: [27].

230 insensitive nuclei enhanced by polarization transfer (INEPT)

Pulse sequence in *nuclear magnetic resonance spectroscopy* that involves the transfer of nuclear spin polarization from spins with large Boltzmann population differences to nuclear spins of interest with low Boltzmann population differences.

Note 1: INEPT uses *spin-spin* coupling for the polarization transfer in contrast to *nuclear Overhauser effect* (NOE) which arises from dipolar cross-relaxation.

Note 2: INEPT is a building block for many heteronuclear NMR experiments.

Source: [27].

231 inverse gated decoupling

See: *gated decoupling*.

232 inversion pulse

Pulse in *nuclear magnetic resonance spectroscopy* that completely inverts the magnetization of a spin, e.g., $+z$ to $-z$.

Note: The inversion pulse can be a simple 180° or composite pulse.

233 inversion recovery sequence

inversion recovery

Spin echo sequence preceded by a 180° inversion pulse used to determine spin-lattice relaxation times in *nuclear magnetic resonance spectroscopy*.

Note: The sequence is typically denoted as $180^\circ - \tau - 90^\circ$.

Source: [20]. See also: *inversion time*.

234 inversion time (TI), T_1

Time between the inversion pulse and the sampling pulse(s) in an *inversion recovery sequence*.

Note: $T_{1, \text{null}}$ is the value of T_1 when longitudinal magnetization (M_z) is close to zero at the end of the TI interval.

235 J-modulated spin-echo (J-MOD)

Nuclear magnetic resonance pulse sequence that refocuses spin vectors that have fanned out due to field inhomogeneity or *chemical shift* differences.

Note: J-MOD is typically denoted as $90^\circ - \tau - 180^\circ - \tau$ (echo).

Source: [20]. See also: *spin echo*.

236 J-resolved spectroscopy (J-RES)

Two-dimensional nuclear magnetic resonance spectroscopy resolving chemical shift information in one dimension and *spin-spin coupling* in the second.

Note 1: J-RES exists as both homonuclear and heteronuclear variants.

Note 2: The homonuclear variant can generate homonuclear decoupled projection when processed with a tilt function.

Source: [27].

237 Knight shift, K

Frequency shift in the *nuclear magnetic resonance spectrum* of a paramagnetic species that refers to the relative shift K in NMR frequency for atoms in a metal (e.g., sodium) compared with the same atoms in a nonmetallic environment (e.g., as a salt).

Note: The observed shift reflects the local magnetic field produced at the metal nucleus by the magnetization of the conduction electrons.

Source: [39].

238 Larmor angular frequency, ω , ω_L

Larmor frequency

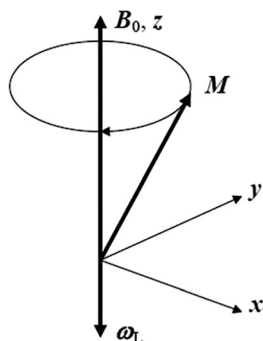
Frequency at which nuclei with a *nuclear spin* precess (*Larmor precession*) around the direction of an external magnetic induction B_0 . $\omega_L = -\gamma B_0$, where γ is the *gyromagnetic ratio* of the nucleus.

Source: [3, 20].

239 Larmor precession

Precession of the magnetic moment (M) of an object at an angular frequency, ω_L , about a static magnetic induction (B_0), named after Joseph Larmor.

Note: Larmor precession can be visually compared to the precession of a tilted gyroscope in an external torque-exerting gravitational field.



Source: [20].

240 longitudinal relaxation

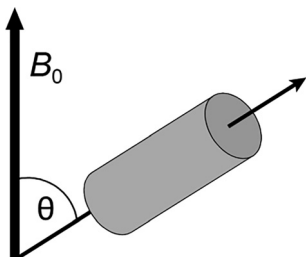
See: *spin-lattice relaxation*.

241 magic angle spinning (MAS)

Technique in *solid-state nuclear magnetic resonance spectroscopy* to remove or reduce the influence of *anisotropic* interactions by rapid sample rotation about the *magic angle*.

Note 1: Much like in the case of solutions, MAS effectively averages orientation-dependent interactions and allow high resolution spectra.

Note 2: The rate of spinning must be greater than or equal to the magnitude of the anisotropic interaction to average it to zero.



where B_0 is external magnetic induction and θ is the axis of rotation of the sample at an angle of approx. 54.74° to the external magnetic induction.

Source: [21].

242 magnetic dipole–dipole interaction in NMR

See: *dipolar coupling in nuclear magnetic resonance spectroscopy*.

243 magnetic flux density

See: *static magnetic flux density*.

244 magnetogyric ratio, γ

gyromagnetic ratio

Magnetic moment μ of a nuclide divided by its spin angular momentum J .

$\mu = \gamma J = \gamma (h/2\pi) \sqrt{I(I+1)}$, where I is the spin quantum number of the nuclide and h is the Planck constant.

Note 1: γ can be either positive (e.g., ^1H , ^{13}C) or negative (^{15}N , ^{29}Si). For particular values of the magnetic induction B_0 and the magnetic quantum number m , γ determines the *energy level* of the nucleus.

$$E = -m\gamma (h/2\pi)B_0.$$

Note 2: SI unit: $\text{rad s}^{-1} \text{T}^{-1} \equiv \text{C kg}^{-1}$.

Source: [40].

245 multiple-quantum magic angle spinning NMR (MQMAS)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* used to obtain high-resolution NMR spectra of quadrupolar nuclei by removal of the anisotropy of the quadrupole interaction, involving creating a triple-quantum (or 5Q) coherence.

Source: [41].

246 multiplet

Feature in a *nuclear magnetic resonance spectrum* that is split but is too complex to easily interpret.

Note: A multiplet is distinguished from *multiplicity of NMR peaks* that give well-resolved doublet, triplet, quartet, quintet *etc.*

247 multiplicity of NMR peaks

multiplicity

Splitting into more than one peak of an NMR signal due to interaction with other magnetic vectors, normally adjacent nuclei.

Note 1: Multiplicity can arise from spin, spin (J) coupling and, in solids and restrained media, *dipolar coupling*.

Note 2: In its simplest form multiplicity results in patterns associated with the $2nI+1$ rule (singlet, doublet, triplet, quartet, pentet *etc.*) although complex *multiplets* arise through variation in *spin-spin coupling constants* and second order multiplets exist where peak overlap occurs.

Source: [14].

248 net dephasing time, T_2^*

T2-star

Measured time constant associated with *spin-spin relaxation* for loss of magnetization in the xy plane.

Note: T_2^* includes losses due to B_0 inhomogeneity as well as spin-spin relaxation and is always less than or equal to the *spin-lattice relaxation time* (T_2).

Source: [20], [42] p 2493.

249 non-uniform sampling (NUS)

Technique employed within a high dimensionality *nuclear magnetic resonance spectroscopy* experiment that acquires only a subset of the data points traditionally acquired linearly thus enabling a reduction in experiment time or an increased resolution in the resultant spectra.

Note: NUS uses reconstruction methods to allow the extraction of complete sets of *chemical shift* information.

250 nuclear electric quadrupole moment, eQ

quadrupole moment of a nucleus

Parameter that describes the effective shape of the ellipsoid of nuclear charge distribution.

Note 1: Non-zero quadrupole moment indicates that the charge distribution is not spherically symmetric.

Note 2: By convention, the value of eQ is taken to be positive if the ellipsoid is prolate and negative if it is oblate.

Source: [43].

251 nuclear magnetic resonance relaxometry (NMRR)

relaxometry

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* to measure nuclear relaxation variables.

Note: NMRR generally involves analysis of time domain NMR signals to generate simplified NMR data rather than conventional full frequency resolved NMR spectra.

252 nuclear magnetic resonance spectrum

NMR spectrum

Representation of *nuclear magnetic resonance spectroscopy* data with at least one dimension a frequency domain.

Note: An NMR *spectrum* typically involves the Fourier transform of a *free induction decay*. See *Fourier-transform spectroscopy*.

253 nuclear Overhauser effect (nOe, NOE), η

nuclear Overhauser enhancement

Change of *intensity* of one resonance when the spin transitions of another are somehow perturbed from their equilibrium populations.

Note 1: The nuclear Overhauser effect at nucleus *i* for perturbation of spin *S* is expressed as a relative intensity change between the equilibrium intensity (*I*) and that in the presence of the nOe (*I*₀). $\eta_i(S) = (I - I_0)/I_0$. The effect may be given as a percentage $\eta \times 100\%$.

Note 2: nOe allows a measure of through space rather than through bond interactions between nuclei and is proportional to the inverse 6th power of the internuclear distance.

Note 3: η can be positive or negative depending on the motional properties of the molecule and the signs of the *gyromagnetic ratios*.

Source: [21], [42].

254 nuclear Overhauser effect difference spectroscopy

nOe difference spectroscopy

One dimensional nuclear magnetic resonance spectroscopy that yields, through subtraction of spectra generated with and without selective excitation of a specific resonance, the *nuclear Overhauser enhancement* of nuclei spatially close to a selectively excited nucleus.

Source: [27].

255 nuclear Overhauser effect spectroscopy (NOESY)

nuclear Overhauser enhancement spectroscopy

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* based on the *nuclear Overhauser effect* to observe nuclei that are close to each other in space.

Note 1: NOESY is typically run as a homonuclear ¹H experiment.

Note 2: A NOESY *spectrum* yields through space correlations *via* dipolar cross-relaxation.

Note 3: For small molecules, NOE may be observed between protons that are up to 0.4 nm apart, while the upper limit for large molecules is about 0.5 nm.

Note 4: NOESY also detects chemical and conformational exchange, when it is termed *exchange spectroscopy* (EXSY).

Source: [27].

256 nuclear quadrupole resonance spectroscopy (NQR)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* where splitting of the nuclear spin states is determined by the electrostatic interaction of the nuclear charge density with the external electric potential of the surrounding electron cloud.

Note: Unlike NMR, NQR transitions of nuclei can be detected in the absence of a magnetic field.

Source: [43].

257 nuclear spin

See: *spin of a nucleus*.

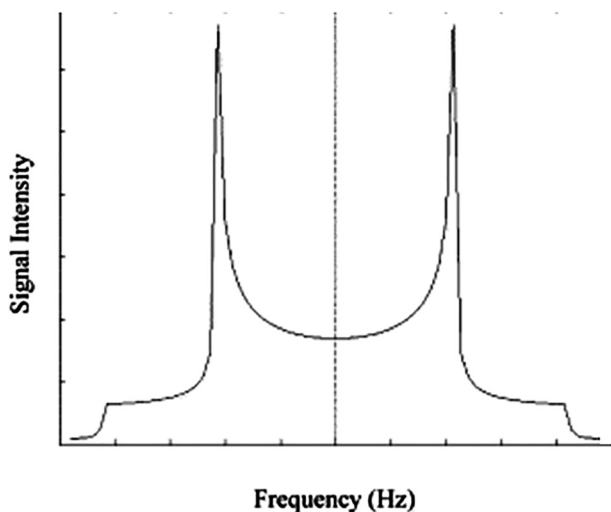
258 observation frequency

Frequency corresponding to the centre of the *spectrum* window for a given nucleus under observation and the nominal frequency used to generate the hard, full spectrum pulses.

Source: [14].

259 Pake doublet

Characteristic line shape seen in *solid-state nuclear magnetic resonance spectroscopy* arising from dipolar coupling between two nuclei.



260 phase correction

Linear combination of the real and imaginary parts of a 1-D *nuclear magnetic resonance spectrum* to produce peaks with pure absorption mode line shape.

Note: The phase correction is normally described by the automatic or manual setting of a fixed zero order and a frequency dependent first order phase constant.

Source: [21].

261 phase cycling

Component of *nuclear magnetic resonance spectroscopy* experiment that repeats a *pulse sequence* changing only the phases of the pulse(s) and the phase-sensitive detector reference.

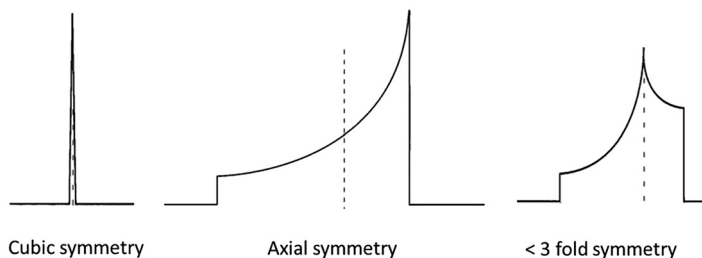
Note: the resultant *FID*'s are then added to suppress undesirable signal components and/or to produce the desired effect of a pulse sequence (*e.g.*, multiple quantum filter)

Source: [20].

262 powder pattern

Very broad and distinctive line shape seen in a static *solid-state nuclear magnetic resonance spectroscopy* experiment with a typical magnitude of 10^2 to 10^5 Hz.

Note: A powder pattern is a summation of the multitude of signals arising from crystals with different orientations within the magnetic induction.



263 precession

Classical description of the behaviour of nuclear magnetic moments, in which the vectors rotate about the B_0 axis at their *Larmor angular frequencies*.

Source: [21].

264 presaturation

Technique to suppress a particular *nuclear magnetic resonance spectroscopy* signal where a long low-power pulse is applied to that specific resonance prior to the main *pulse sequence*.

Note: Presaturation is typically used as a method for *solvent suppression*.

Source: [27].

265 pulse sequence

Timed series of radiofrequency pulses and magnetic field gradients that define a part or whole of a *nuclear magnetic resonance spectroscopy* experiment.

266 pulsed-field gradient (PFG)

gradient pulse

Short, timed pulse in *nuclear magnetic resonance spectroscopy* that momentarily destroys the magnetic field homogeneity within the sample through a spatial-dependent field intensity.

Note 1: The net result of the pulse is that spins are dispersed in the transverse plane (defocussed) and produce zero net magnetization.

Note 2: A PFG is characterized by its power, shape, duration and axis.

Note 3: PFG techniques are used in magnetic resonance imaging, spatially-selective NMR, and *diffusion ordered NMR spectroscopy* (DOSY).

Source: [21].

267 pure shift yielded by chirp excitation (PSYCHE)

Nuclear magnetic resonance spectroscopy experiment generating homonuclear spin-spin decoupled spectra.

Note: The effect is achieved through the concatenation of partial *free induction decays* generated with a series of swept adiabatic pulses.

Example: ^1H spectrum with no ^1H , ^1H coupling.

Source: [44].

268 quadrature detection in nuclear magnetic resonance spectroscopy

Collection of time domain *nuclear magnetic resonance spectroscopy* data on both the x and y axes of the rotating frame of reference to allow discrimination of positive and negative frequencies.

Source: [21].

269 quadrupole moment of a nucleus

See: *nuclear electric quadrupole moment*.

270 quadrupolar nuclide

Nuclide with spin quantum number $I > 1/2$ and a non-spherical distribution of charge in the nucleus giving rise to a *nuclear electric quadrupole moment* (eQ).

271 quadrupolar relaxation

Relaxation mechanism in *nuclear magnetic resonance spectroscopy* arising from intramolecular quadrupolar interactions with electric field gradients.

Source: [20]. See also: *quadrupolar nuclide*.

272 radiation damping

Line-broadening effect on intense signals in high field *nuclear magnetic resonance spectroscopy*.

Note 1: Radiation damping occurs when the rotating transverse magnetization of the sample is intense enough to induce large enough electromotive force in the *radiofrequency* coil strong enough that it feeds back to the sample. This causes a rotation of magnetization back to the +z axis and results in line-broadening of the intense peak.

Note 2: Radiation damping can also produce other effects including changes to amplitude and phase of adjacent peaks.

Source: [27].

273 radiofrequency (RF) coil

In *nuclear magnetic resonance spectroscopy*, an inductor-capacitor resonant circuit used to set up B_1 magnetic inductions in a sample and to detect the signal from the sample.

274 real spectrum

In *nuclear magnetic resonance spectroscopy*, one of two equally sized blocks of frequency data 90° out of phase to each other produced by Fourier transformation of the time domain signal.

Note: Usually only the real frequency data is displayed and in simple 1D spectra equates to the NMR signals being absorption mode (in-phase).

Source: [21]. See also: *imaginary spectrum*, *Fourier-transform spectroscopy*.

275 relaxation reagent

Paramagnetic species added to a sample in a *nuclear magnetic resonance spectroscopy* experiment to promote more rapid *spin-lattice relaxation* and allow a faster pulse repetition rate.

Example: Tris(acetylacetonato)chromium(III) (chromium(III) acetyl acetate, $\text{Cr}(\text{acac})_3$) is typically used.

Source: [14].

276 relaxometry

See: *nuclear magnetic resonance relaxometry*.

277 repetition time (TR), T_r

Time duration between repetitions of a *nuclear magnetic resonance pulse sequence* including the pulse sequence, *acquisition time* and *relaxation delay*.

Source: [21].

278 residual dipolar coupling (RDC)

Dipolar coupling, but of a reduced magnitude to that seen in solids, observed in a liquid sample between spins in a molecule where there is incomplete averaging of spatially *anisotropic* dipolar couplings.

Note 1: RDC is typically achieved through partial alignment of molecules in the liquid state through spatially aligned gels or liquids.

Note 2: RDC is used to provide 3D structural information on molecules.

279 rotating-frame NOE spectroscopy (ROESY)

cross-relaxation appropriate for minimolecules emulated by locked spins (CAMELPSIN)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* yielding through-space correlations via *spin-spin relaxation*.

Note 1: ROESY is similar to the NOESY experiment (see *nuclear Overhauser effect spectroscopy*) and is useful for determining which signals arise from protons that are close to each other in space even if they are not bonded.

Note 2: ROESY has the advantage over the NOESY experiment that its response does not go through a null at specific correlation times and is thus preferred for molecules having molecular masses of a few thousand Da.

Source: [27].

280 rotational echo double resonance (REDOR)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* allowing recoupling of heteronuclear dipolar coupling under *magic angle* spinning.

Source: [45].

281 saturation transfer difference spectroscopy (STD)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* that allows detection of transient binding of small molecule ligands to macromolecular receptors.

Note: Range of applicable dissociation constants is approximately 10^{-3} M to 10^{-8} M. The experiment relies on ligand-signal attenuation through spin diffusion saturation propagating from the macromolecule.

Source: [46].

282 selective decoupling

Spin decoupling of a specific resonance by selective irradiation.

283 selective excitation

selective irradiation

Application of a frequency selective *radiofrequency* pulse(s) to a single resonance or a discrete band of frequencies.

Note: Selective excitation is usually achieved through the application of long, low power (soft) pulses.

Source: [21].

284 selective pulse

Radiofrequency pulse with a narrow frequency *spectral bandwidth* (long, low-power pulse) to excite nuclei in a limited chemical shift range (see *selective excitation*).

Source: [14].

285 single crystal nuclear magnetic resonance spectroscopy

Solid-state nuclear magnetic resonance spectroscopy on a single crystal in a similar manner to that used in X-ray diffraction.

Note: A large crystal is mounted on a ‘tenon’, which is in turn mounted on a goniometer head. If the orientation of the unit cell is known with respect to the tenon, then it is possible to determine the orientation of the NMR interaction tensors with respect to the molecular frame.

Source: [47].

286 solid-state nuclear magnetic resonance spectroscopy (SSNMR)

Application of *nuclear magnetic resonance spectroscopy* to solids.

Note: SSNMR is characterized by the presence of *anisotropic* (directionally dependent) interactions. *Chemical shift anisotropy* (CSA) and internuclear dipolar coupling result in severe line-broadening of the corresponding NMR signals and specific hardware and methods are required to perform SSNMR to mitigate some of these issues including *magic angle spinning* (MAS).

Source: [22].

287 solvent suppression

In *nuclear magnetic resonance spectroscopy* reduction or removal of large, unwanted resonances from solvents to improve *spectrum* quality and dynamic range through selective excitation and exploiting differences in relaxation times between solvent and analyte signals.

Source: [20].

288 spectral width in NMR, f_{SW}

spectral width

Frequency range that describes the width of the *spectrum* window of a specific nucleus in *nuclear magnetic resonance spectroscopy*.

289 spin of a nucleus

nuclear spin

spin

Intrinsic angular momentum of a nucleus (or other sub-atomic particle).

Note 1: The magnitude of nuclear spin is $(h/2\pi)\sqrt{I(I+1)}$ where I is the spin quantum number and h is the Planck constant.

Note 2: In *nuclear magnetic resonance spectroscopy*, only nuclei with spin $I > 0$ are observable.

Note 3: The spin of a nucleus is dependent on the numbers and alignments of the spins of its individual protons and neutrons.

Note 4: Nuclei with a spin of $1/2$ generate the simplest *nuclear magnetic resonance spectra* and are thus the most commonly studied.

Source: [40].

290 spin decoupling

Irradiation of a nucleus in *nuclear magnetic resonance spectroscopy* to prevent spin-spin coupling.

See also: *homonuclear decoupling*, *heteronuclear decoupling*.

291 spin echo (SE)

Hahn echo

Refocusing of spin magnetization usually by 2 consecutive *radiofrequency* pulses.

Note 1: The simplest form of the spin-echo *pulse sequence* consists of 90° -pulse, a 180° -pulse, and then an echo. The time between the middle of the first RF pulse and the peak of the spin echo is called the *echo time* (T_E).

Note 2: SE is typically used within a pulse sequence to refocus chemical shift by pulses 90° , $T_E/2$, 180° , $T_E/2$. (See also: *flip angle*.)

Source: [21].

292 spin system

Group of magnetic nuclei that interact amongst themselves through *spin-spin coupling* but do not interact with any nuclei outside the spin system.

Source: [48].

293 spin-lattice relaxation

longitudinal relaxation

T_1 relaxation

T_1 relaxation

Mechanism in *nuclear magnetic resonance spectroscopy* by which the component of the magnetization vector along the direction of the static magnetic induction reaches thermodynamic equilibrium with its surroundings through loss of energy of the excited nuclear spins to the surrounding molecular lattice. The resultant exponential decay of signal is characterized by the spin-lattice relaxation time T_1 (reciprocal of the rate constant of this mechanism).

Note: T_1 dictates the time required between individual NMR scans to ensure the system has returned to equilibrium.

Source: [14]. See also: *spin-lattice relaxation time*.

294 spin-lattice relaxation time, T_1

spin-lattice time constant

Reciprocal of the rate constant of *longitudinal relaxation*.

See also: *spin-spin relaxation time, net dephasing time*.

295 spinning sidebands

Satellite peaks in a *nuclear magnetic resonance spectrum* symmetrically spaced either side of a main peak at a frequency offset related to the rate of spinning of the sample.

Note: In *solid state nuclear magnetic resonance spectroscopy* this occurs if the sample is spun at a rate less than the magnitude of the *anisotropic* interaction,

Source: [48].

296 spin-spin coupling

spin coupling

Effect of the relative orientation of the magnetic fields of adjacent nuclei on each other and the resultant splitting of their signals in *nuclear magnetic resonance spectroscopy* (*multiplicity*).

Note 1: For two proximal nuclei A and B, magnetic field at nucleus A is the sum of the nuclear shielding and the magnetic field at nucleus B. If nucleus B has two possible orientations in field due to spin $\frac{1}{2}$ then nucleus A will experience two possible magnetic fields and therefore give two distinct frequencies. The frequency difference between these two lines is called the *spin-spin coupling constant* J_{AB} .

Note 2: Spin-spin coupling is transmitted through intervening bonding electrons, in contrast to the through space dipolar mechanism.

Note 3: SI unit: Hz.

Source: [14].

297 spin-spin coupling constant, J

coupling constant

Frequency difference between two nuclear magnetic resonance lines arising from *spin-spin coupling*.

Note: Parentheses may be used (for example) to indicate the species of nuclei coupled, *e.g.*, $J(^{13}\text{C}, ^1\text{H})$ or, additionally, the coupling path, *e.g.*, $J(\text{POCF})$. Where no ambiguity arises, the elements involved can be, alternatively, given as subscripts, *e.g.*, J_{CH} . The nucleus of higher mass should be given first. nJ indicates coupling through n bonds.

Source: [42] p 2592.

298 spin-spin relaxation

transverse relaxation

T2 relaxation

Loss of magnetization in the xy plane (in the absence of B_0 inhomogeneities) through the interchange of energy between nuclear spins resulting in some precessing faster than the *Larmor frequency* and some slower.

Note: The resultant exponential decay of signal is characterized by the *spin-spin relaxation time* T_2 (reciprocal of the rate constant of this mechanism).

Source: [14]. See also: *net dephasing time*.

299 spin-spin relaxation time, T_2

transverse relaxation time

Reciprocal of the rate constant of *spin-spin relaxation*.

Source: [42] p 2493. See also: *spin-lattice relaxation time*, *net dephasing time*.

300 static magnetic flux density, B_0

magnetic flux density

static magnetic field

Flux density of the magnetic field of a *nuclear magnetic resonance spectrometer* about whose direction the nuclear magnetic moment precesses.

Note 1: The value of B_0 is expressed in Tesla or as the nominal proton *precession* frequency (*e.g.*, 14 T or 600 MHz).

Note 2: Static magnetic induction is related to the magnetic field H through the equation $B = \mu H$ where μ is the permeability of the material.

Source: [20], [42] p 2492, [3] p 17.

301 symmetrization

Method of removing artefacts from a *two-dimensional nuclear magnetic resonance spectrum* that are symmetrical about the diagonal (*e.g.*, *HH COSY*) or the f_1 axis (*e.g.*, *tilted J-resolved spectra*). Values equidistant from midline are compared and replaced the lower (or average) value of the two.

Source: [21].

302 t_1 in two-dimensional nuclear magnetic resonance spectroscopy

t_1 in 2-D NMR

Time domain arising from the regular increments of the delay period in *two-dimensional nuclear magnetic resonance spectroscopy*.

303 t_2 in two-dimensional nuclear magnetic resonance spectroscopy

t_2 in 2-D NMR

Time domain in *two-dimensional nuclear magnetic resonance spectroscopy* arising from direct *free induction decay* detection.

304 t_1 noise in two-dimensional nuclear magnetic resonance spectroscopy

t_1 noise in 2-D NMR

Streaks of spurious artefact signals in a *two-dimensional nuclear magnetic resonance spectrum* parallel to the f_1 axis at the f_2 of a strong resonance.

Source: [21].

305 T1 relaxation

See: *spin-lattice relaxation*.

306 T2 relaxation

See: *spin-spin relaxation*.

307 three-dimensional nuclear magnetic resonance spectroscopy

3-D NMR

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* in which data are collected in three time domains.

Note: A 3-D NMR experiment may be constructed from a 2-D NMR experiment by inserting an additional indirect evolution time and a second mixing period between the first mixing period and the direct data acquisition.

See also: *triple-resonance nuclear magnetic resonance spectroscopy*.

308 time domain

Condition in *nuclear magnetic resonance spectroscopy* where the independent variable of all functions is time.

Example: The display of an *FID*.

Source: [14].

309 time domain nuclear magnetic resonance spectroscopy (TD-NMR)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* run at low magnetic field strengths where data analysis is performed directly on the *free induction decay*, often through the extraction of relaxation time constants

See also: *relaxometry*.

310 tip angle

See: *flip angle*.

311 total correlation spectroscopy (TOCSY)

homonuclear Hartmann-Hahn spectroscopy (HOHAHA)

Two-dimensional nuclear magnetic resonance homonuclear correlation experiment, which creates correlations between all protons within a given *spin system*, not just between geminal or vicinal protons as in *COSY*.

Note: TOCSY uses a spin lock to allow propagation of magnetization through scalar couplings.

Source: [27].

312 total suppression of spinning sidebands (TOSS)

Technique to suppress spinning sidebands in *solid-state nuclear magnetic resonance spectroscopy* with *cross polarization* in *magic angle spinning* experiments.

Source: [27].

313 transverse relaxation

See: *spin-spin relaxation*.

314 transverse relaxation optimized spectroscopy (TROSY)

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy*, usually in protein NMR, that improves peak sharpness for molecules having a molecular mass of greater than 100 kDa.

Note: TROSY relies on the cancellation of the dipolar coupling and *chemical shift anisotropy* (CSA) components of the transverse relaxation (see *spin-spin relaxation*).

Source: [25].

315 transverse relaxation time

See: *spin-spin relaxation time*.

316 triple-resonance nuclear magnetic resonance spectroscopy

triple-resonance NMR

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* using three NMR-active nuclei.

Note: For proteins the three nuclei are usually ^1H hydrogen, ^{13}C carbon, and ^{15}N nitrogen, which requires suitable labelling of the sample.

317 two-dimensional nuclear magnetic resonance spectroscopy

2-D NMR

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* in which data are collected in two *time domains*: acquisition of the *free induction decay* (t_2) and a successively incremented delay (t_1).

Note: The resulting data matrix is subjected to two successive Fourier transforms to produce a *spectrum* with two frequency axes, usually either *chemical shift*/chemical shift (*correlation spectroscopy*) or chemical shift/J-coupling (see *J-resolved spectroscopy*).

Source: [20].

318 WALTZ decoupling

See: *wideband, alternating-phase, low-power technique for residual splitting*.

319 wideband, alternating-phase, low-power technique for residual splitting

WALTZ decoupling

Cluster of pulses applied repeatedly for *heteronuclear decoupling*.

Note: WALTZ is commonly used for proton decoupling during the acquisition of ^{13}C spectra.

Source: [21].

320 Zeeman levels

Energy levels of a nucleus arising from the interaction of its magnetic dipole with an external magnetic field.

Source: [20].

321 zero-field nuclear magnetic resonance spectroscopy

zero-field NMR

Measurement method [VIM 2.5] of *nuclear magnetic resonance spectroscopy* in which *nuclear magnetic resonance spectra* are acquired in an environment carefully screened from magnetic fields, including from the Earth's field allowing the direct detection of J-spectra in the absence of Zeeman interactions (see *Zeeman levels*).

Source: [49].

4 Atomic spectroscopy

In optical spectroscopy, energy absorbed to move an electron to a higher energy level and/or the energy emitted as the electron moves to a lower energy level is absorbed or emitted in the form of photons. Because each element has a unique number of electrons, an atom will absorb/release energy in a pattern unique to its elemental identity (*e.g.*, Ca, Na, *etc.*) and thus will absorb/emit photons in a correspondingly unique pattern. The type of atoms present in a sample, or the amount of atoms present in a sample, can be deduced from measuring these changes in light wavelength and light *intensity*. In this section, optical spectroscopy terms are provided for *atomic emission*, *atomic absorption* and *atomic fluorescence* spectroscopies

An encyclopedia of spectroscopy and spectrometry was published in 2016 that has inspired many definitions here [40].

322 ablation by sputtering

Bombardment of a sample surface with ions resulting in the removal of atoms from their lattice sites, and thus an ongoing discharge process that causes continuous ablation of the sample.

Source: [50].

323 ablation efficiency in LIBS

Mass of sample removed in *laser-induced breakdown spectroscopy* divided by the energy delivered by the laser beam.

Source: [51].

324 ablation rate

Depth of sample layer removed in the glow discharge process per unit time.

Note: Ablation rate is usually expressed in nm s^{-1} .

Source: [50].

325 ablation threshold fluence in LIBS

Minimum *fluence* required to achieve ablation of the sample.

Source: [51].

326 absorption path-length

Path-length of a beam of radiation in an absorbing medium.

Source: [10].

327 acid transient effects in ICP spectrometry

Increase in signal equilibration time or in *wash out time* caused by a modification in inorganic acid concentration.

Source: [52].

328 additional gases in flame atomic spectroscopy

Gases added to a combustion mixture.

Note: An inert diluent is non-reactive, an auxiliary gas is reactive.

Source: [10].

329 aerosol

Sol in which the dispersed phase is a solid, a liquid or a mixture of both and the continuous phase is a gas (usually air).

Note 1: Owing to their size, the particles of the dispersed phase have a comparatively small settling velocity and hence exhibit some degree of stability in the Earth's gravitational field.

Note 2: An aerosol can be characterized by its chemical composition, its radioactivity (if any), the particle size distribution, the electrical charge and the optical properties.

Note 3: In *inductively-coupled plasma spectrometry* the sample is delivered to the *plasma* as an aerosol, where the continuous gas phase is argon.

Source: [53] p 1805.

330 aerosol transport phenomena in ICP spectrometry

Processes occurring inside the *spray chamber* or desolvation system responsible for the modification of the *primary aerosol* to finally yield the *tertiary aerosol*.

Note: These phenomena include solvent evaporation, droplet coalescence or coagulation, inertial droplet losses, gravitational settling and turbulence losses.

Source: [52].

331 analyte transport rate in ICP spectrometry

Mass of analyte reaching the *plasma* per unit time.

Source: [52].

332 atomic absorption spectroscopy (AAS)

Measurement method [VIM 2.5] of *atomic spectroscopy* for measuring the amount of a chemical element based on the measurement of the *absorption* of characteristic *electromagnetic radiation* by atoms in the vapour phase.

Source: [40].

333 atomic emission spectroscopy (AES)

Measurement method [VIM 2.5] of *atomic spectroscopy* for measuring the amount of a chemical element based on the measurement of the *intensity* of characteristic *electromagnetic radiation* emitted by atoms or molecules.

Source: [40].

334 atomic excitation source

excitation source

Atomizer intended to convert free atoms to an *excited state*.

Source: [10].

335 atomic fluorescence spectroscopy (AFS)

Measurement method [VIM 2.5] of *atomic spectroscopy* for measuring the amount of a chemical element based on the measurement of the re-emission of characteristic *electromagnetic radiation* by atoms, following the absorption of radiation in the vapour phase.

Note: The *wavelengths* of the absorbed and re-emitted radiation may be identical (*atomic resonance fluorescence spectroscopy*) or different.

Source: [40].

336 atomic vapour

Vapour containing free atoms of analyte.

Source: [10].

337 atomization

Conversion to an *atomic vapour*.

Source: [10].

338 atomization curve in electrothermal AAS

Graph of *absorption* against *atomization* temperature.

Source: [54].

339 atomizer

Device used in *atomic spectroscopy* to achieve atomization.

Note: Examples are a flame or *electrothermal atomizer*.

Source: [10].

340 axial viewing mode

Inductively-coupled plasma optical emission spectrometer configuration in which the entrance slit is aligned with the main *plasma* axis.

Note 1: The large amount of light captured in this method, includes information from the sample of interest plus background, which can be considerable.

Note 2: Matrix interferences, which originate in the cooler plasma tail, can degrade precision and accuracy.

Source: [52].

341 background continuum emission in LIBS

Intense continuous background usually observed in *laser-induced breakdown spectra*

Note: The continuum emission originates from *Bremsstrahlung* radiation, which predominates the first part of the *plasma* life time and decreases with further plasma evolution.

Source: [51].

342 background equivalent concentration, c_{BE}

Concentration of a given element measured at a given *wavelength* providing the same *intensity* as the background.

Source: [52].

343 breakdown threshold fluence in LIBS

Minimum *fluence* required to achieve measurable emission signals

Note: Usually the breakdown-threshold fluence is orders of magnitude higher than the *ablation-threshold fluence*.

Source: [51].

344 Bremsstrahlung emission

Portion of the continuum *spectrum* originating from the energy lost by high velocity electrons as they interact with positively charged ions without combining with them.

Source: [52].

345 Bremsstrahlung radiation

Photons with a broad energy distribution produced by losses in kinetic energy due to the deceleration of charged particles connected with the emission of *electromagnetic radiation*.

Source: [51].

346 capacitive microwave plasma

Plasma generated by a capacitor in presence of a microwave field.

Source: [52].

347 characteristic line

Spectral line of an atom used for the measurement of analyte concentration by *atomic spectroscopy*.

Note: Characteristic lines include resonance and non-resonance lines.

Source: [10].

348 chemical modifier for electrothermal atomic absorption spectroscopy

Substance added to an *electrothermal atomizer* to obtain a better analyte *atomization*, or to alter the vaporization and/or atomization of interferences, thus mitigating interferences.

Source: [54].

349 continuum source in atomic spectroscopy

Source that emits *electromagnetic radiation* with relatively constant *intensity* over a broad spectral region.

Note: The use of such a source allows for correction of spectral interferences.

Source: [54, 55].

350 depth resolution

Capability to distinguish between two consecutive layers in a layered material.

Note 1: With GD-OES nanometre or even atomic-layer depth resolution can be obtained.

Note 2: Usually the parameters used in the sputtering process (discharge parameters, selected gas and pressure) restrict the achievable depth resolution.

Source: [50].

351 depth-profiling

Process by which the sample is sputtered ‘atomic layer by layer’ using suitable conditions.

Note 1: Depth profile analysis can be accomplished by time resolved measurement of the generated emission signals.

Note 2: Depth profiling using signal versus time measurement requires knowledge of the *ablation rate*, which must be known, or has to be calculated, from measurements of suitable materials.

Source: [50].

352 desolvation in atomic spectroscopy

desolvation

Removal of the solvent in *atomic spectroscopy*, giving rise to particles of the solute either in the solid or gas phase.

Source: [10].

353 detection efficiency in inductively-coupled plasma spectrometry

Probability that a given atom in the *plasma*-probed volume generates a detectable signal.

Source: [52].

354 direct current glow discharge optical emission spectroscopy (DC GD-OES)

Measurement method [VIM 2.5] using *optical emission spectroscopy* in which *atomization* and excitation occur in a *glow electrical discharge* sustained by a direct current electric field.

Note 1: Generated argon ions impact with high energy on to the surface of the cathode, which can thus be ablated in a purely mechanical way (cathodic sputtering) or the cathode can be heated to assist evaporation (thermal volatilization).

Note 2: DC GD-OES is only applicable for electrically conducting samples.

Source: [50].

355 direct-injection burner

Burner in a *flame atomic spectrometer* in which the fuel, the oxidant and the sample solution are injected into the flame. (See *flame in flame atomic spectroscopy*).

Note: This burner generally produces a turbulent flame.

Source: [10].

356 discharge

See: *electric discharge*.

357 dispersion of a sample in atomic spectroscopy

Conversion of the whole or part of a liquid or solid sample into a physical form sufficiently finely divided to allow it to be atomized (see *atomization*) upon introduction into the *atomizer*.

Source: [10].

358 double-pulse laser-induced breakdown spectroscopy

Measurement method [VIM 2.5] of *laser-induced breakdown spectroscopy* in which reactions are induced by the interaction of the evolved *plasma* and the remaining part of the laser pulse, or with a following laser pulse provided from a second laser system.

Source: [51].

359 dual viewing mode

Inductively coupled plasma spectrometer that allows axial viewing mode or radial viewing mode.

Source: [52].

360 Echelle spectrometer

See: *GD-OES spectrometers with simultaneous detection*.

361 electric discharge

discharge

Transmission of electrical current by a *plasma* in an applied electric field through a normally non-conducting medium.

Note: An *inductively-coupled plasma* is a kind of electric discharge.

362 electron number density

Number of free electrons in vapour phase per volume unit.

Note: SI unit: m^{-3} .

Source: [56].

363 electrothermal atomic absorption spectroscopy (ETAAS)

Measurement method [VIM 2.5] of *atomic absorption spectroscopy* in which the sample is atomized by an *electrothermal atomizer*.

Source: [54].

364 electrothermal atomizer

Atomizer that is heated by the passage of electrical current through its body to the temperature required for analyte atomization.

Note 1: An electrothermal atomizer typically consists of tube, rod, strip and filament made of refractory material that is heated by a low voltage, high current device, providing a means of obtaining variable temperatures according to the nature of the analyte.

Note 2: Electrothermal atomizers are often made of graphite (polycrystalline electrographite), and glassy carbon, termed 'graphite furnace'.

Source: [54]. See also: *electrothermal atomic absorption spectroscopy*.

365 electrothermal vaporization

Technique for sample introduction based on the use of a solid furnace heated at a controlled temperature to vaporize the sample prior to its introduction into an *inductively-coupled plasma*.

Source: [54, 55].

366 E_{sum}

Energy that must be supplied to an atom to transfer it from the ground atomic state to a given ionic *excited state*.

Source: [10].

367 excitation source

See: *atomic excitation source*.

368 flame atomic spectrometer

Spectrometer to make measurements by *flame atomic spectroscopy*.

369 flame atomic spectroscopy

flame atomic spectrometry

Measurement method [VIM 2.5] of *atomic spectroscopy* that uses a *flame* to excite atoms.

370 flame background in flame atomic spectroscopy

See: *spectral background of an atomizer or excitation source*.

371 flame in flame atomic spectroscopy

Continuously flowing mixture of hot gases with a stationary position that derives its heat content from a strongly exothermic, irreversible chemical reaction between a *fuel* and an oxidant.

Note 1: The flame in general consists of a primary-combustion zone, a secondary-combustion zone and an interconal zone.

Table 371.1: Terms relating to flames in *flame atomic spectroscopy*. Source: [10].

Term	Definition	Note
fuel	Reducing agent that reacts with oxidant to provide the energy necessary for <i>atomization</i> and excitation.	
laminar flame	<i>Flame</i> for which the gas flow rate is sufficiently low such that the incoming gaseous flow of fuel and air is laminar, as is the flame.	The cross-section of the flame can have any shape.
oxidant	Oxidizing agent that reacts with the <i>fuel</i> providing the energy necessary for <i>atomization</i> and excitation.	
oxidizing flame	<i>Flame</i> obtained using an excess of <i>oxidant</i> .	
reducing flame	<i>Flame</i> obtained using an excess of <i>fuel</i> .	
separated flame	<i>Flame</i> in which the secondary-combustion zone is separated from the primary-combustion zone.	
turbulent flame	<i>Flame</i> in which the burnt-gas flows in an irregular pattern	

372 flow spoiler

Component of a *flame atomic spectrometer* for creating turbulence in the stream of mist in the spray chamber and removing the largest droplets from this mist by deposition.

Source: [10].

373 fluence, F , H

Energy of a beam of *electromagnetic radiation* delivered per unit area. $F = \int I dt = \int (dP/dA)dt$ where I is *intensity* and P *radiant power*.

Note: SI unit: $J m^{-2}$. Common unit $J cm^{-2}$.

Source: [51], [3] p 35.

374 fraction atomized

See: *local fraction atomized*.

375 gate delay in laser induced breakdown spectroscopy

time delay in laser induced breakdown spectroscopy

Time between the application of a laser pulse and the start of detection in *laser-induced breakdown spectroscopy*.

Note 1: The gate delay varies from some hundreds of nanoseconds to several microseconds.

Note 2: Use of a suitable gate delay allows the high *intensity* background continuum emission present in the early stages of *plasma* formation to be removed.

Source: [51].

376 GD-OES spectrometers with simultaneous detection

Spectrometers for *glow discharge optical emission spectroscopy* that allow simultaneous monitoring of selected spectral ranges or the whole emission spectra.

Note 1: GD-OES spectrometers mostly use the so called Paschen–Runge mounting, where the entrance slit, the curved grating and different detectors are aligned along the Rowland circle. Alternatively, Echelle spectrometers (see *GD-OES spectrometers with simultaneous detection*) are used, which use an Echelle grating in combination with a prism for *wavelength* separation.

Source: [50].

377 generator coupling efficiency in inductively-coupled plasma spectrometry

Fraction of the energy generated being used for creating and maintaining the *plasma* in an *inductively-coupled plasma spectrometer*.

Source: [52].

378 glow discharge source

Component of an *atomic emission spectrometer* employing a *glow electric discharge* used in *atomic emission spectroscopy* for qualitative and quantitative analysis of solid materials.

Note: Glow discharge allows volatilization as well as excitation of analytes and sample matrices.

Source: [50].

379 glow electric discharge

glow discharge

Electric discharge in gas at low pressure (100 to 1000 Pa).

Note 1: In *atomic emission spectroscopy* argon is used as the inert working gas that generates the *plasma*.

Note 2: In the prevailing electrical field the produced ions are accelerated towards the cathode, resulting in a continuous bombardment of the sample surface.

Source: [50].

380 glow-discharge optical emission spectroscopy (GD-OES)

Optical emission spectroscopy in which a *glow electric discharge* excites atoms at the surface of a sample, which is made the cathode of the discharge.

381 Grimm-type cathode

Cathode for a *glow electric discharge* consisting of a flat sample, which is cooled during the discharge process so that *thermal volatilization* is suppressed and the sample material is removed by sputtering only.

Source: [50].

382 hollow-cathode discharge source

Glow discharge source with a graphite cathode, into which the sample is inserted in the form of drillings, a pressed pellet or a dry solution residue.

Note: For this source, sample volatilization takes place mainly by thermal effects.

Source: [50].

383 hollow-cathode lamp

line source

Glow discharge source of spectral lines of an atom in which the cathode is made of the desired element.

Note: It is often referred to as line source, as opposed to a *continuum source*.

Source: [55].

384 incident power

Power supplied by a generator to the *plasma*.

Source: [56].

385 inductively-coupled plasma (ICP)

Plasma produced by induction by means of a high-frequency (about 2500 Hz) electromagnetic field. The region of gas at high temperature and free from the field is taken as the region of observation.

Source: [52]. See also: *inductively-coupled plasma optical emission spectroscopy*, *inductively-coupled plasma mass spectrometry*.

386 inductively-coupled plasma spectrometry

inductively-coupled plasma spectroscopy

ICP

Measurement method [VIM 2.5] of *atomic spectroscopy* that uses an *inductively-coupled plasma* to excite and ionize atoms.

Note: ICP methods are described by their method of detection of ions in the plasma and include *inductively-coupled plasma optical emission spectroscopy*, and *inductively-coupled plasma mass spectrometry*.

387 inductively-coupled plasma mass spectrometry (ICP-MS)

Measurement method [VIM 2.5] of *atomic spectrometry* that uses an *inductively-coupled plasma* to excite and ionize atoms with measurement of the number and kind of ions in the plasma using mass spectrometry.

388 inductively-coupled plasma optical emission spectroscopy (ICP-OES)

Measurement method [VIM 2.5] of *atomic spectroscopy* that uses an *inductively-coupled plasma* to excite and ionize atoms with measurement of the number and kind of ions in the plasma from their emission of *electromagnetic radiation* (see *optical emission spectroscopy*).

389 inductively-coupled plasma robustness

plasma robustness

Ability of an *inductively-coupled plasma* to withstand slight modification in the operating conditions and/or matrix composition with no significant changes in its fundamental characteristics (*i.e.*, temperatures, electron number density) or the analytical figures of merit (*i.e.*, sensitivity, detection limits or *signal-to-noise ratio*)

Source: [52].

390 inductively-coupled plasma thermal pinch

Decrease in the *inductively-coupled plasma* volume normally caused when an organic volatile solution is delivered to it. Organic vapours diffuse towards the outermost area of the plasma and its volume decreases.

Source: [52].

391 inductively-coupled plasma torch

Quartz component of an *inductively coupled plasma spectrometer* where the *plasma* is generated and stabilized.

Note: In ICP the torch is an open three concentric tubes assembly allowing the introduction of the three gas streams constituting the plasma. The inner tube of the torch can be made of a different material such as alumina and is usually called the injector.

Source: [52].

392 initial plasma radiation zone in inductively-coupled plasma optical emission spectroscopy

Inductively-coupled plasma volume in *inductively-coupled plasma optical emission spectroscopy* where the analytically relevant light emission begins to be observed.

Source: [52].

393 injector in an inductively-coupled plasma torch

See: *inductively-coupled plasma torch*.

394 interference curve in atomic spectroscopy

Graph of *absorbance* or *intensity* plotted as a function of the concentration of an interfering element in an *atomic spectroscopy* experiment.

395 inverse Bremsstrahlung

Absorption of photon energy by free electrons.

Note: Inverse Bremsstrahlung increases the kinetic energy of the electrons, which is important for heating the *plasma*.

Source: [51]. See also: *Bremsstrahlung emission*, *Bremsstrahlung radiation*.

396 ionic cloud in atomic spectroscopy

Gas phase containing free ions of analyte.

Source: [10].

397 ionization buffer in atomic spectroscopy

Buffer that decreases and stabilizes the ionization of free atoms of analyte by increasing the concentration of free electrons in the *atomizer*.

Source: [10].

398 ionization energy

Minimum energy that must be supplied to remove an electron from an atom in the *ground state*.

Source: [10].

399 laser ablation

Removal of material as an *aerosol* from a surface on irradiation by a *laser* beam.

Source: [51].

400 laser induced breakdown spectroscopy (LIBS)

Measurement method [VIM 2.5] of *atomic spectroscopy* that uses a focused *laser* beam to ablate, atomize and excite atoms from a sample surface with subsequent measurement of the generated *electromagnetic radiation*.

Source: [51].

401 laser-induced breakdown spectrum

Emission spectrum generated as a consequence of the decay of the excited states generated in a *laser-induced plasma* that consists of a continuous background and element-specific atomic or ionic lines and molecular bands.

Note: LIBS spectra cover a wide *wavelength* range: commonly LIBS measurements are taken between the wavelengths of 200 nm and 1000 nm.

Source: [51].

402 laser-induced plasma

Local *plasma* formed by the interaction between a *laser* beam and a solid sample and initiated by the production of primary electrons by *multiphoton ionization* and thermionic photoemission mechanisms.

Note: As well as electrons, laser-induced plasma contains ions, and neutral atoms as well as excited species of the ablated matter. Decay of these excited species generates the light emission analysed in *laser-induced breakdown spectroscopy*.

Source: [51].

403 line

See: *spectral line of an atom*.

404 line-broadening in atomic spectroscopy

Increase in the theoretical width of a *spectral line* owing to thermal motion of emitting atoms (Doppler effect), to electric field (*Stark effect*), to *self-absorption* and to pressure (Lorentz effect).

Note: Line-broadening increases the *measurement uncertainty* [VIM 2.26] of a measurement.

Source: [10].

405 line profile

Graph of the variation of emitted radiation *intensity* as a function of *wavelength* (emission line) or the variation of the *absorption factor* as a function of *wavelength* (absorption line).

Source: [10].

406 line source

See: *hollow-cathode lamp*.

407 local fraction atomized

fraction atomized

Number of free atoms divided by the total number of atoms of the analyte present in the gaseous phase in the observation volume in *atomic spectroscopy*, the latter being the volume confined by the atomizer or immediately adjacent to it.

Source: [10].

408 low sample consumption system in inductively-coupled plasma spectrometry

Liquid-sample introduction system to an *inductively-coupled plasma spectrometer* adapted to work at sample flow rates below $100 \mu\text{L min}^{-1}$.

Note: The system is normally composed of a micro-*nebulizer* and a low inner volume spray chamber.

Source: [52].

409 L'vov platform

See: *platform atomization in electrothermal atomic absorption spectroscopy*.

410 measurement efficiency in inductively-coupled plasma spectrometry

Number of detector events per atom in the sample.

Source: [52].

411 microwave cavity

Resonant cavity that permits focusing a microwave field inside a discharge tube thus giving rise to a standing wave.

Source: [52].

412 microwave-induced plasma

microwave plasma

Plasma generated in a *microwave cavity*.

Note: The plasma results as a consequence of ionization of a given gas in presence of electrons and a microwave field.

Source: [52].

413 multiphoton ionization

Absorption of multiple photons by an atom such that the accumulated energy of the absorbed photons is greater than the ionization potential of the atom.

Source: [51].

414 nebulization

Conversion of a liquid into an *aerosol* consisting of droplets suspended in a gas stream.

Source: [10].

415 nebulizer

Device for producing *nebulization*.

Source: [10].

416 non-specific emission or attenuation

Electromagnetic radiation, within the *bandpass filter* used, emitted by, or absorption caused by, atoms, molecules and radicals that are subject to the *atomizer* by all components, apart from the analyte, that are present there during measurement.

Note: These effects include scattering or absorption effects by solid particles.

Source: [10].

417 normal plasma analytical zone in inductively-coupled plasma optical emission spectroscopy

Inductively-coupled plasma volume mainly responsible for emission of analytically-useful *light* because processes leading to excited species, such as droplet desolvation, element vaporization, *atomization* (or ionization) and excitation have been completed.

Source: [52].

418 observation height

Vertical distance between the optical axis of observation in a *flame atomic* or *inductively coupled plasma optical spectrometer* and the horizontal plane of the top of the burner or the *ICP* load coil, respectively.

Source: [10].

419 optical emission spectroscopy (OES)

Measurement principle [VIM 2.4] of *atomic emission spectroscopy* in which the emitted *electromagnetic radiation* is in the range of *frequencies* from the infrared, through visible, to the ultra-violet region.

Note: OES is used as the detector in *inductively-coupled plasma optical emission spectroscopy*, and *glow-discharge optical emission spectroscopy*.

420 overall efficiency of atomization

In *atomic spectroscopy*, mass of analyte converted into free atoms in the *atomizer* divided by mass of analyte entering the dispersion device.

Source: [10].

421 Paschen-Runge mounting

See: *GD-OES spectrometers with simultaneous detection*.

422 Penning excitation/ionization in inductively-coupled plasma spectrometry

Collisional excitation and ionization mechanism of *inductively-coupled plasma spectrometry* involving analyte atoms and metastable argon atoms.

Source: [52].

423 percentage transmission of sample

In *atomic spectroscopy*, flux of mass of sample divided by the flux of mass of solvent blank, measured under the same conditions, expressed as a percentage.

Source: [10].

424 permanent modifier in electrothermal atomic absorption spectroscopy

Substance added together with the sample or standards in *electrothermal atomic absorption spectroscopy* that is refractory, or forms a refractory species (*e.g.*, a carbide), and thus does not need to be renewed for several *atomization* cycles.

Note: This is a particular type of *chemical modifier for electrothermal AAS*.

Source: [57].

425 plasma

Matter brought into the gaseous state, largely ionized, and emitting and absorbing *electromagnetic radiation*.

Note 1: In practice, the term 'plasma' is restricted to cases where the temperature is greater than 7000 K.

Note 2: A plasma may be generated by an *electric discharge*.

Source: [56].

426 plasma arc

Plasma formed by an *arc-discharge*.

Note: The discharge is blown through a suitable orifice to form a plasma jet. The high-temperature, electric field-free gaseous region is designed as the region of observation.

Source: [10].

427 plasma excitation temperature

Temperature governing the number density of atomic species in their *ground state* and *excited states* following a Boltzmann distribution.

Source: [56].

428 plasma gases in inductively-coupled plasma

Gas streams used to maintain and stabilize the *inductively-coupled plasma*. The external stream is the main constituent of the plasma and confines the plasma avoiding melting of the torch walls; the intermediate gas stream keeps the plasma at a given height above the top of the torch and, the central stream carries the *aerosol* and promotes its injection in the plasma central channel.

Source: [52].

429 plasma induction zone

Inductively-coupled plasma volume where there is a maximum interaction between the electromagnetic field and the plasma gas (mostly argon). This is the plasma's hottest area and has a toroidal configuration.

Source: [52].

430 plasma ionization temperature

Temperature associated with the *energy level* of *plasma* ions.

Source: [56].

431 plasma local thermodynamic equilibrium (LTE)

Condition for which the temperatures estimated from different particles (atoms, molecules, ions, electrons) constituting a *plasma* are locally coincident.

Source: [56].

432 plasma robustness

See: *inductively-coupled plasma robustness*.

433 plasma shielding in laser induced breakdown spectroscopy

Prevention of *laser* pulse energy from reaching a sample surface as a result of the presence of a *laser-induced plasma*.

Note: The main process leading to plasma shielding is the absorption of the laser energy by electrons (*inverse Bremsstrahlung*) and *multiphoton ionization* (mainly relevant for shorter laser wavelengths).

Source: [51].

434 plasma termination in laser induced breakdown spectroscopy

Extinction of the *plasma* after a *laser* pulse as a consequence of *self-absorption* (quenching) and recombination of electrons and ions.

Note: The time elapsed between initiation and extinction of the plasma ranges from tenths of microseconds to a few milliseconds.

Source: [51].

435 platform atomization in electrothermal atomic absorption spectroscopy

L'vov platform

Sample support made of graphite that is inserted into the *atomizer* tube in *electrothermal atomic absorption spectroscopy*. The sample, a liquid or a solid, is deposited onto this platform, from which it undergoes all the transformations leading to *atomization*. The use of a platform delays atomization, until a more stabilized temperature in the gas phase is reached.

Source: [54].

436 pneumatic nebulizers

Nebulizers for which the *aerosol* generation principle is based on the exposure of the liquid sample to a high velocity gas stream.

Note: Most common designs include cross flow, concentric, parallel path, entrained and Babington and V Groove.

Source: [52].

437 preheating inductively-coupled plasma zone

preheating plasma zone

Inductively-coupled plasma volume where tertiary *aerosols* suffer from complete solvent evaporation, element salt vaporization and dissociation into atoms.

Source: [52].

438 premix burner

Burner in a *flame atomic spectrometer* in which the fuel, the oxidant and the *aerosol* are mixed before reaching the flame. (See *flame in flame atomic spectroscopy*).

Note: A premix burner generally produces a laminar flame (see *flame in flame atomic spectroscopy*).

Source: [10].

439 primary aerosol

Aerosol generated by a *nebulizer*.

Note: Usually, primary aerosols contain coarse droplets, they are polydisperse in terms of drop diameters and they are turbulent.

Source: [52].

440 pulse duration of a laser

pulse width
pulse length

Time duration of *laser* pulses.

Note: Pulse duration depends on the laser system used and can vary between hundreds of femtoseconds to a few nanoseconds.

Source: [51].

441 pulse energy of a laser

Total optical energy content of a *laser* pulse. Integral of optical power over *pulse duration*.

Note: Pulse energies range from microjoules to millijoules for Q-switched lasers, whereas mode-locked lasers achieve much lower pulse energies (picojoules, nanojoules or sometimes several microjoules).

Source: [51].

442 pulse frequency

See: *repetition rate of a pulsed laser*.

443 pulsed laser

Laser system that emits *electromagnetic radiation* in the form of pulses of a defined and constant duration.

Note: A pulsed laser produces no continuous optical wave.

Source: [51].

444 pyrolysis curve in electrothermal atomic absorption spectroscopy

Graph of *absorption* against pyrolysis temperature in *electrothermal atomic absorption spectroscopy*.

Source: [54].

445 quartz atomizer

Atomizer that is used to atomize those elements that form volatile species (*e.g.*, hydrides) at relatively low temperatures (*e.g.*, 1000 °C or below).

Note: These can be heated externally or positioned in a flame (see *flame in flame atomic spectroscopy*).

Source: [55].

446 radial viewing mode

Inductively coupled plasma optical emission spectrometer configuration in which the *plasma* and the entrance slit are perpendicular and from which the signal is taken perpendicularly to the main plasma axis.

Note: This configuration yields lower sensitivities than the *axial viewing mode*.

Source: [52].

447 radiofrequency (RF) generator in an inductively-coupled plasma spectrometer

Component of an *inductively-coupled plasma spectrometer* responsible for the generation of alternating current in the radiofrequency portion of the electromagnetic spectrum (see Table 1).

Source: [52].

448 radiofrequency glow discharge optical emission spectroscopy (RF-GD-OES)

Optical emission spectroscopy in which a radiofrequency-powered *glow discharge* is operated with frequencies in the low megahertz range.

Note: The use of these frequencies establishes a negative direct current (DC)-bias voltage on the sample surface. The DC-bias is the result of an alternating current waveform that is centered about negative potential; as such it more or less represents the average potential residing on the sample surface. Radio-frequency has ability to appear to flow through insulators (non-conductive materials).

Source: [50].

449 reference flux density, $\phi_r(\lambda)$

Intensity transmitted by the reference medium in a *double-beam spectrometer*.

Source: [10]. See also: *sample flux density*.

450 reflected power

Incident power that is not absorbed by the *plasma*.

Source: [56].

451 repetition rate of a pulsed laser

pulse frequency

Number of *laser* pulses emitted by a *pulsed laser* system per unit time.

Note 1: For laser systems with *pulse duration* in the nanosecond regime repetition rates range from 1 to 20 Hz, whereas for femtosecond laser systems increased repetition rates up to 1000 Hz are possible.

Note 2: SI unit: Hz.

Source: [51].

452 residence time in electrothermal atomic absorption spectroscopy

Time in which the analyte is confined within the observation volume in *electrothermal atomic absorption spectroscopy*.

Source: [54].

453 resonant inelastic X-ray scattering (RIXS)

resonant X-ray emission
resonant X-ray Raman

Measurement method [VIM 2.5] of inelastic X-ray spectroscopy that uses a hard or soft X-ray beam to excite transitions of core-level electrons into empty energy levels. The subsequent transition of an electron into the core state is accompanied by X-ray emission with characteristic momentum and energy.

Note: The incident photon energy is selected for resonance with an X-ray absorption edge of the system, such that the observed shifts in momentum and energy provide element-specific chemical sensitivity, with the capacity to distinguish the same element located at inequivalent sites.

Source: [58].

454 Rowland circle

See: *GD-OES spectrometers with simultaneous detection*.

455 Saha's ionization equation

Saha–Langmuir equation

Equation that relates the ionization state of an element present in a gas in thermal equilibrium to the temperature and the pressure of the medium.

Note 1: For a gas composed of a single atomic species, the Saha equation is written:

$$(n_{i+1}/n_i)n_e = 2\lambda^{-3}(g_{i+1}/g_i)\exp[-(\epsilon_{i+1} - \epsilon_i)/kT]$$

where n_i is the number density of atoms with i electrons removed, g_i is the degeneracy of the i th state, ϵ_i is the ionization energy of the i th state, n_e is the number density of electrons, λ is the thermal de Broglie wavelength of an electron, k is the Boltzmann constant, and T is the thermodynamic temperature of the gas.

Note 2: The thermal de Broglie wavelength is given by:

$$\lambda = \sqrt{\frac{h^2}{2\pi m_e kT}}$$

where h is the Planck constant, k the Boltzmann constant, T temperature, and m_e the mass of an electron.

Source: [56].

456 sample flux density, $\phi_s(\lambda)$

Intensity transmitted by the atomizer when the latter is supplied with the sample solution or a reference solution.

Source: [10]. See also: *reference flux density*.

457 saturator

Buffer containing interfering element(s) in sufficient quantity to reach the limit of enhancement or dispersion (*i.e.*, saturation) of the *interference curve*.

Source: [10].

458 self-absorption

Partial absorption of *electromagnetic radiation* emitted by excited atoms in an atomic emission source by atoms of the same kind present in the source.

Note 1: As a result of self-absorption, the observed *intensity* of a *spectral line* may be less, and its width greater, than would be the case for a source having a very small optical path and the same concentration of emitting atoms per unit volume.

Note 2: Self-absorption may occur in all emitting sources, whether they are homogeneous or not, thermal or non-thermal.

Source: [10].

459 self-reversal in atomic emission

Absorption of *electromagnetic radiation* emitted from the centre of an *ionic cloud* by outer layers of the emitting vapour, which are cooler than the centre.

Note 1: The *intensity* measured at the centre of a line is less than the intensity measured on either side of the centre.

Note 2: In extreme cases, the intensity at the centre of the line is so weak that only the wings remain, giving the appearance of two fuzzy lines.

Source: [10].

460 sequential detection in glow discharge optical emission spectrometry

Sequential spectrometers use a dispersive element (grating) in combination with entrance and exit slits for selection of specific wavelengths. Geometric arrangements include the Czerny-Turner and the Ebert-geometry, both offering high resolution measurements. However, they do not permit simultaneous recording of different spectral lines, even for single emission line *intensity*, and adjacent spectral background has also to be measured sequentially.

Source: [50].

461 solvent blank flux density, $\phi_{\tau}(\lambda)$

Intensity transmitted by the *atomizer* when the latter is supplied with the solvent blank.

Source: [10].

462 solvent nucleation

Solvent condensation on solid particles or droplets contained in an *aerosol*.

Source: [52].

463 solvent transport rate in an inductively-coupled plasma spectrometer

Mass of solvent, both in liquid and vapour forms, reaching an *inductively-coupled plasma* per unit of time.

Source: [52].

464 spectral background of an atomizer or excitation source

Electromagnetic radiation, within the *bandpass* used, emitted by, and/or in the case of *atomic absorption spectroscopy*, absorbed in, the *atomizer* when nothing is supplied to the atomizer but the gases involved in its operation.

Note: In the case of *flame atomic spectroscopy*, the term “flame background” is used.

Source: [10].

465 spectral line of an atom

spectral line
line

In *atomic spectroscopy*, a very narrow band of *frequencies of electromagnetic radiation* emitted or absorbed by atoms, which undergo a single *electronic transition*.

Note 1: The radiation is centred on a peak whose *wavelength* characterizes the line and which corresponds to the emission or absorption maximum.

Note 2: A distinction is made between lines corresponding to transition of neutral atoms (*e.g.*, Ba I 553.548 nm and 577.762 nm) and ions (*e.g.*, Ba II 455.403 nm).

Source: [10].

466 spray chamber

Chamber of a *nebulizer* in which the sprayed liquid is converted to mist. Some of the droplets of this mist may evaporate, coalesce, or deposit in the chamber and subsequently drain away as waste.

Source: [10].

467 sputter rate

Mass of material removed from a sample surface in unit time

Note: Usually the sputter rate is given in unit $\mu\text{g s}^{-1}$.

Source: [50].

468 stop-flow conditions in electrothermal atomic absorption spectroscopy

Stoppage to the otherwise constant flow of argon gas to the *atomizer* in *electrothermal atomic absorption spectroscopy*, that can be programmed to occur during atomization, for the purpose of increasing the residence time of the analyte atoms and thus the associated signal.

Source: [54].

469 synchrotron X-ray spectroscopy

X-ray spectroscopy performed using a high *intensity*, continuous polychromatic synchrotron X-ray source.

Source: [59].

470 tertiary aerosol in an inductively-coupled plasma spectrometer

Aerosol that reaches an *inductively-coupled plasma*.

Note: Such aerosols are finer, less polydispersed and less turbulent than *primary aerosols*.

Source: [52].

471 thermal dispersion

Procedures whereby an *aerosol* is produced at a high temperature, for example by sparks, arcs, furnaces, lasers, cathodic sputtering or electron-beam.

Source: [10].

472 thermal volatilization

Process in *glow-discharge atomic emission spectroscopy* in which sample volatilization occurs by heating due to sample bombardment with argon ions.

Note 1: The process causes evaporation of the sample constituents in accordance to their boiling-points.

Note 2: Although this technique offers highest detection power for most volatile elements its use in routine applications is still limited by the analytical challenges posed by the transient nature of the analyte signal.

Source: [50].

473 time delay in laser induced breakdown spectroscopy

See: *gate delay in laser induced breakdown spectroscopy*.

474 time-resolved laser-induced breakdown spectroscopy

Measurement method [VIM 2.5] of *laser-induced breakdown spectroscopy* in which the emitted radiation is monitored with time resolution sufficiently high to resolve different stages in the *lifetime* of the *laser-induced plasma*.

Source: [51].

475 total sample consumption system

Liquid-sample introduction system able to achieve 100 % *transport efficiency*.

Source: [52].

476 transport efficiency of a sample

Mass of analyte entering the *atomizer* of a *flame atomic spectrometer* or the *plasma of an inductively-coupled plasma spectrometer* divided by the mass of analyte entering the dispersion device.

Source: [10].

477 ultrasonic nebulizers

Nebulizers whose *aerosol* generation principle is based on the transfer of the energy from a vibrating transducer to the liquid sample.

Source: [52].

478 volatilization

Conversion of the solute particles containing the analyte from the solid and/or liquid phase to the vapour phase.

Source: [10].

479 wall atomization in electrothermal atomic absorption spectroscopy

Electrothermal atomic absorption spectroscopy in which the sample is deposited directly onto the wall of the *electrothermal atomizer* tube, from which it undergoes all the transformations leading to *atomization*.

Source: [54].

480 wash out time

Time required for the output signal of an *inductively-coupled plasma spectrometer* for a given analyte to fall back to baseline levels from the end of sampling time and/or after introducing a blank solution.

Source: [52].

481 X-ray emission spectrum

Spectrum comprising the continuum *Bremsstrahlung* and the most energetic characteristic *spectral lines* defined by differences in binding energy between electron *energy levels*.

Source: [59].

482 X-ray spectroscopy

Measurement of X-rays emitted by a solid that has been bombarded with electrons. *Spectrum* consists of continuous (*Bremsstrahlung*) and discrete (characteristic) parts.

Source: [59].

5 Vibrational spectroscopy

This section on *vibrational spectroscopy* covers *infrared* (IR) and *Raman spectroscopy*. Both have an extensive range of molecular structure, environmental, identification and quantitative analysis of material applications (both bulk and surface), which, *inter alia*, include academic and industrial research, product quality assurance and process control, remote-sensing, forensics (crime scene, art and archaeology), agricultural product quality assessment, clinical and bio-medical research and diagnoses. Today, a wide range of instruments to suit a wide range of applications and to suit specific purposes are available from laboratory-based research tools to industrial process-analysers to hand-held spectrometers, to at point-of-care medical devices.

Infrared spectroscopy involves the absorption (or interaction) of *infrared radiation* with matter. The IR region of the electromagnetic *spectrum* is typically divided into three sub regions, the near-IR (NIR) region extends from *wavenumbers* about $12\,800\text{ cm}^{-1}$ to 4000 cm^{-1} (*wavelengths* 780 nm to $2.5\text{ }\mu\text{m}$), the mid-IR region from 4000 cm^{-1} to 400 cm^{-1} ($2.5\text{ }\mu\text{m}$ to $25\text{ }\mu\text{m}$), and the far-IR region from 400 cm^{-1} to about 10 cm^{-1} ($25\text{ }\mu\text{m}$ to approximately $1000\text{ }\mu\text{m}$). A mid-IR spectrum is that typically used for “fingerprinting” a material and can also be utilised for physical form and/or chemical group identification. The astronomer Sir William Herschel discovered the first non-visible (near-infrared, NIR) region of the electromagnetic spectrum in 1800. Early developments in observations and instrumentation for both NIR and mid-IR came to the fore in the early 1900s, with major studies on molecular group-characteristic structures using mid-IR spectroscopy being continually developed in the 1900s.

The observation of inelastic scattering of photons of light was demonstrated and reported in 1928 by Sir C.V. Raman and K.S. Krishan. Like infrared spectroscopy, it can be used to study the vibrational, rotational and low-frequency *modes of vibration* of a substance. Today, the inelastic scattering of light by monochromatic radiation (a *laser*) is known as *Raman scattering*, with the shift in energy of the observed photons yielding similar but complementary information to that observed within an infrared spectrum.

For a molecular vibration to be infrared active, *i.e.*, produce an absorption band, then the vibration must be accompanied by a change in dipole moment; for a molecular vibration to be Raman-active, then during the vibration there must be a change in *polarizability*.

483 amorphous material transmitting infrared radiation (AMTIR)

Amorphous glasses made from elements of groups 4, 5 and 6 of the Periodic Table that transmit *infrared radiation*.

Note: AMTIRs are hard but can be brittle.

Examples: AMTIR-1, which is $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$, and AMTIR-3, which is $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$.

Source: [6].

484 amplitude modulation

Modulation of the amplitude of a beam of *electromagnetic radiation*; by the movement of a moving mirror in a rapid scan *Fourier-transform spectrometer* or by a mechanical chopper in other *spectrometers*.

Source: [6].

485 anharmonicity

See: *electrical anharmonicity, mechanical anharmonicity*.

486 anisotropic Raman scattering

Raman scattering by the anisotropic part of the derived *polarizability tensor*.

Source: [6].

487 anomalous dispersion of the refractive index

Changes in real *refractive index* of a material in the vicinity of an absorption band in which real *refractive index* decreases markedly with decreasing *wavenumber* on the high wavenumber side of an absorption band, then increases rapidly through the band centre and decreases markedly on the low wavenumber side of the band, before resuming *normal dispersion* at wavenumbers far from the band.

Source: [6].

488 anomalously polarized Raman band

Raman band with a *depolarization ratio* greater than 0.75, as is frequently observed in *surface-enhanced resonance Raman spectroscopy*.

Source: [6].

489 anti-Stokes Raman scattering

Raman scattering of *electromagnetic radiation* in which the scattered radiation has greater energy (greater *wavenumber*) than the exciting radiation.

Source: [6]. See also: *Stokes Raman scattering*.

490 asymmetric top

Rotor whose three principal moments of inertia are all different.

Source: [6] See also: *symmetric top*.

491 atomic polar tensor (APT)

3×3 tensor that gives the change in the components of the molecular dipole moment when the atom is displaced in three-dimensional space.

Note 1: The rows correspond to different components of the dipole moment and the columns to x , y and z displacements.

Note 2: APTs have been widely used in the analysis of *infrared absorption intensities*.

Note 3: SI unit: C. Common unit: $\text{D \AA}^{-1} \approx 3.335\,64 \times 10^{-20} \text{ C}$.

Source: [6].

492 attenuated total reflection spectroscopy

internal reflection spectroscopy (IRS)

frustrated total internal reflection spectroscopy

Measurement method [VIM 2.5] of *vibrational spectroscopy* based on *internal reflection* from an absorbing material at angles of incidence at or above the critical angle (*attenuated total reflection*).

Note: Attenuated total reflection occurs where the material absorbs. The resulting *spectrum* resembles an *absorption spectrum* of the sample.

Source: [6].

493 band shape

Description of the profile of a *spectral band*.

Note: For a given band, the band shape is independent of the band height in *Raman spectra*, infrared absorption spectra and *pATR spectra*. The band shape changes if the band height changes in infrared transmission spectra or *attenuated total reflection spectra*.

Source: [6].

494 Bragg filter

Optical filter used, for example, to attenuate *Rayleigh scattering* while transmitting *light* subject to *Raman shift*.

Note: Historically, a Bragg filter was a colloidal dispersion of spheres in a regular close packed array, which selectively diffracts/reflects *wavelengths* that satisfy the Bragg diffraction criterion for the lattice but transmits all other wavelengths. Now largely superseded by Volume Bragg Gratings, where photo-induced modulation of the *refractive index* of the filter medium is used to form a volume phase hologram with reflecting planes separated by a well-defined spacing. In each case, angle tuning is used to match the laser wavelength to the Bragg diffraction condition. The filter can be manufactured either as a notch filter, which transmits wavelengths either side of the laser line, or as an edge filter, which only transmits wavelengths longer than the laser line (*i.e.*, Raman light subject to *Stokes scattering*).

Source: [6].

495 centre burst

center burst

Spectral region of an *interferogram* around zero-path-difference where *intensity* is greatest.

Source: [6].

496 channel fringes

See: *interference fringes*.

497 Christiansen effect

Collections of solid particles that are transparent to *radiation* of a particular *wavelength* and are slightly larger than the wavelength of the radiation transmit poorly due to reflection and scattering from the interfaces. The *transmission* increases markedly at wavenumbers at which the *refractive index* of the particles is close to that of the surrounding medium.

Note: The Christiansen effect frequently causes strong absorption bands from coarsely ground particles to be distorted due to the change in refractive index associated with the anomalous dispersion of the refractive index through the absorption region.

Source: [6].

498 Christiansen filter

Optical filter based on the *Christiansen effect*.

Note: Such filters have been made from quartz particles in air, immersed in CCl_4 , or immersed in mixtures of CCl_4 and CS_2 .

Source: [6].

499 circular dichroism (CD)

Measurement principle [VIM 2.4] of *vibrational spectroscopy* based on the difference in absorbance of left- and right-handed circularly polarized *light* by a material as a function of *wavelength*.

Note 1: Circular dichroism is measured as $k^L - k^R$ where k^L and k^R are the *absorption indices* of the sample for left and right circularly polarized radiation, respectively. Some authors use the *linear decadic absorption coefficient* or *molar decadic absorption coefficient* to calculate circular dichroism instead of the absorption index.

Note 2: Like the *absorption indices* (k^L , k^R), circular dichroism changes with *wavenumber*.

Note 3: Most biological molecules, including proteins and nucleic acids, are chiral and show circular dichroism in their ultraviolet absorption bands, which may be used as an indication of secondary structure. Metal centres that are bound to such molecules, even if they have no inherent chirality, usually exhibit CD in absorption bands associated with ligand-based or ligand-metal charge-transfer transitions. CD is frequently used in combination with absorption and magnetic circular dichroism studies to assign *electronic transitions*.

Source: [6], [60] p 1265.

500 coherent anti-Stokes Raman spectroscopy (CARS)

Measurement method [VIM 2.5] of *Raman spectroscopy* that uses third-order susceptibility and is one of several four-wave mixing spectroscopies. The excitation is through lasers of wavenumber $\tilde{\nu}_1$ and $\tilde{\nu}_2$, which coincide spatially and temporally in the sample and produce an output laser of wavenumber $\tilde{\nu}_3 = 2\tilde{\nu}_1 - \tilde{\nu}_2$.

Note 1: Experimentally, $\tilde{\nu}_1$ is kept constant and $\tilde{\nu}_2$ is scanned. A laser beam output is observed at the wavenumber for *anti-Stokes Raman scattering* $\tilde{\nu}_1 + \tilde{\nu}_M$ when $\tilde{\nu}_1 - \tilde{\nu}_2 = \tilde{\nu}_M$, where $\tilde{\nu}_M$ is the wavenumber of an active vibration in the sample.

Note 2: The Raman scattered radiation emerges as a laser beam instead of being scattered into three dimensions, thus greatly enhancing the sensitivity over that in *normal Raman scattering*.

Source: [6].

501 collision broadening

See: *pressure broadening*.

502 combination transition

Transition in which more than one vibration changes its degree of excitation; *i.e.*, in which more than one vibrational quantum number changes.

Note 1: Combination band results from a combination transition.

Note 2: Combination transitions are either sum or difference transitions, although some authors restrict them to sum transitions.

Source: [6].

503 constant resolution tunnelling intensity

See: *normalized tunnelling intensity*.

504 continuous scan interferometer

Interferometer in which the *optical path difference* is continually changed.

Note 1: Continuous scan interferometer is typically used for *Fourier-transform infrared spectroscopy*.

Note 2: In slow scan interferometers, the rate of change of *optical path difference* is less than 0.05 cm s^{-1} and a mechanical chopper or some other ancillary modulation is frequently used to provide an adequate modulation frequency.

Note 3: In rapid-scan interferometers, the rate of change of *optical path difference* is above 0.05 cm s^{-1} , high enough that no additional modulation is needed.

Source: [6]. See also: *step-scan interferometer*.

505 Coriolis coupling

Coupling between rotational and vibrational molecular motion caused by *Coriolis forces*.

Source: [6].

506 Coriolis force

In vibrational theory, the motion of a polyatomic molecule is usually initially regarded as the independent superposition of a rotation and a vibration, with the vibration considered in a coordinate system that rotates with the molecule. This initial treatment must be corrected for centrifugal forces and for Coriolis forces. The Coriolis force on an atom is given by $F_{\text{Coriolis}} = 2m v_a \omega \sin\varphi$, where m is the mass of the atom, v_a is its apparent velocity in the rotating coordinate system, ω is the angular velocity of the coordinate system, and φ is the angle between the velocity vector and the axis of rotation.

Note: SI unit: N.

Source: [6].

507 correlation splitting

See: *Davydov splitting*.

508 critical angle, θ_c

Smallest angle of incidence at which total internal reflection occurs.

Note: If n_2 and n_1 are the refractive indices, and $n_2 > n_1$, at the boundary, $\sin\theta_c = n_1/n_2$.

Source: [6].

509 crystal field splitting

The removal of a *degeneracy* of the *energy levels* of molecules or ions due to the lower site symmetry created by a crystalline environment.

Note 1: The term site splitting may be used more generally to refer to any effect due to differences in energies of locations on a crystal.

Note 2: 'Crystal field splitting' is sometimes incorrectly used synonymously with the term 'ligand field splitting'.

Source: [61] p 2234. [6]. See also: *site splitting*.

510 Davydov splitting

correlation splitting
exciton splitting

Appearance of more than one *spectral band* in the *spectrum* of a crystal when only one is seen in that of the gas due to intermolecular vibrational coupling.

Note: Davydov splitting arises from the dynamic intermolecular forces in the crystal.

Source: [6].

511 deformation vibration

Vibration in which the dominant change from equilibrium is in one or more valence angles.

Source: [6].

512 depolarization ratio, ρ

Raman *intensity* with the electric vector of the scattered *radiation* perpendicular to that of the incident radiation divided by the Raman intensity with electric vectors parallel.

Note: In *normal Raman scattering* with linearly polarized exciting radiation, $\rho \leq 0.75$ for totally symmetric vibrations and $\rho = 0.75$ for all other vibrations.

Source: [6].

513 depolarized Raman band

Raman band with *depolarization ratio* $\rho = 0.75$ for linear polarized incident radiation in *normal Raman spectroscopy*.

Source: [6]. See: *polarized Raman band*.

514 depth of penetration in attenuated total reflection, d_p

Distance from the boundary with the internal reflection element at which the mean square electric field *intensity* of the evanescent wave, *i.e.*, the intensity of a collimated radiation beam, is reduced to $1/e$ of its value at the boundary.

Note 1: In *photoacoustic spectroscopy* (PAS), an analogous definition may be cited for strongly absorbing samples. For weakly absorbing photoacoustic samples, the depth of penetration is given by the *thermal diffusion depth*. In practice, the depth below the surface that gives rise to most of the measured photoacoustic *spectrum* is the lesser of the thermal diffusion depth and the optical *absorption depth*.

Note 2: SI unit: m. Common unit: μm .

Source: [6]. See: *attenuated total reflection*.

515 dichroism

Dependence of *absorbance* on the type of polarization of the measuring beam.

Source: [8] p 324. See: *circular dichroism*.

516 difference transition

Combination transition that does not start at the *ground state* and in which at least one vibration decreases and at least one vibration increases its degree of excitation; *i.e.*, a transition in which more than one vibrational quantum number changes and at least one becomes smaller.

Note: A difference band or difference tone results from a difference transition.

Source: [6].

517 divided spinning cell

Measuring instrument [VIM 3.1] for *Raman spectroscopy* incorporating a dish-shaped cell that is divided by a vertical partition through its middle to allow different liquids in its two halves. It is rotated about a vertical axis through its centre and the Raman scattered radiation from each half is measured alternately. With a standard liquid in one half and a sample in the other it is used to determine Raman scattering intensities relative to the standard.

Source: [6].

518 dynamic spectrum

Spectrum of a material under the influence of an applied external perturbation represented by a variable τ , relative to a reference spectrum.

Note: The reference spectrum may be chosen in many ways; *e.g.*, it may be the average over τ , of the observed spectrum, or it may be zero. See also: *two-dimensional correlation spectroscopy* and *two-dimensional correlation spectrum*

Source: [6].

519 electrical anharmonicity

anharmonicity

Influence of terms that are of 2nd and higher order in the normal coordinate Q in the expansion of the *electric dipole moment*.

Note: Electrical anharmonicity should not be confused with *mechanical anharmonicity*.

Source: [6]. See: Note in *electric dipole moment*. See also: *electrical harmonicity*.

520 electrical harmonicity

harmonicity

Influence of the linear term, $\sum_k (\partial\mu/\partial Q_k) Q_k$, in the expansion of the *electric dipole moment*. Q is the *normal coordinate*.

Note: Electrical harmonicity should not be confused with *mechanical harmonicity*.

Source: [6]. See: Note in *electric dipole moment*.

521 electron energy loss spectroscopy (EELS)

Measurement method [VIM 2.5] of *vibrational spectroscopy* in which a constant-energy beam of electrons passes through or is reflected from a sample and the energy distribution in the transmitted or reflected beam is analysed to give a *spectrum* of number of electrons against electron energy loss.

Note: EELS is used for the study of electronic states and has an energy resolution of 0.25 eV or better (corresponding to an approximate wavenumber of 2000 cm⁻¹).

Source: [6].

522 electro-optic parameter (EOP)

equilibrium charge, charge flux (ECCF)

Characteristic quantity used in the analysis of absolute infrared *intensity* data chosen on the assumption that the *electric dipole moment* of the molecule can be described as the vector sum of bond dipole moments.

Note 1: The original EOPs were μ_k^0 , the equilibrium bond moment, and $\partial\mu_k/\partial R_t$, the change in the electric dipole moment of bond k with change in internal displacement coordinate t . A later and completely equivalent formulation uses equilibrium atomic charges, q_α^0 , and charge fluxes, $\partial q_\alpha/\partial R_t$, which are also called EOPs as well as ECCF for equilibrium charge, charge flux.

Note 2: In Note 1, R , are vibrational coordinates such as bond stretching, angle deformation, or torsion about a bond.

Source: [6].

523 ellipticity, ψ

Degree to which linearly polarized incident *electromagnetic radiation* becomes elliptically polarized in an absorbing optically active medium.

$$\tan \psi = (E_R - E_L) / (E_R + E_L) = \tanh(k^L - k^R)\pi l / \lambda$$

where E_R and E_L are the electric vectors of right and left circularly polarized radiation, k^L and k^R are the *absorption indices* of the sample for left and right circularly polarized radiation, λ is the *wavelength* of the radiation and l is the *path-length* through the medium.

Note: SI unit: rad = 1.

Source: [6].

524 equilibrium charge, charge flux (ECCF)

See: *electro-optic parameter*.

525 étendue

See: *optical throughput of a spectrometer*.

526 evanescent wave

Part of a standing-wave normal to a reflecting surface that extends beyond the reflecting surface when an electromagnetic wave undergoes *total internal reflection*.

Source: [6].

527 Evans Hole

Unexpected minimum or hole in a broad absorption band due to a gap being created in a broad distribution of states by *Fermi resonance*.

Source: [6].

528 excitation profile

Graph of Raman *intensity* at the desired *Raman shift* against *wavenumber* of the excitation.

Source: [6].

529 exciton splitting

See: *Davydov splitting*.

530 external reflection spectroscopy

Measurement method [VIM 2.5] of *spectroscopy* in which radiation is reflected from a sample of higher *refractive index* than that of the incident medium.

Source: [6].

531 extraordinary wave

extraordinary ray

In a uniaxial crystal *electromagnetic radiation* with electric vector oblique to the optic axis and which does not obey the normal laws of refraction.

Note: In uniaxial crystals the optic axis coincides with the symmetry axis. The *refractive index* of the crystal is the same in all directions perpendicular to the optic axis but is different along the optic axis. Consequently, electromagnetic rays or waves that do not travel along the optic axis experience different refractive indices in different directions perpendicular to their direction of propagation. Two waves result, one has its electric vector perpendicular to the optic axis and forms the *ordinary wave*. The other is the extraordinary wave.

Source: [6].

532 far-infrared radiation

See: *infrared radiation*.

533 Fermi resonance

Cubic anharmonic resonance (see *anharmonicity*), *i.e.*, any interaction caused by cubic terms in the *vibrational potential energy*.

Note 1: Traditionally, Fermi resonance was defined as the anharmonic interaction between a fundamental state and one or more overtone or *combination transitions*.

Note 2: Fermi resonance is usually identified by the presence of more than one band of comparable *intensity* when only one fundamental is expected. Also seen as an *Evans hole*.

Source: [6].

534 finesse of a spectrometer

Free spectral range divided by *resolution*.

Source: [6].

535 fingerprint bands

Infrared and *Raman bands* that are characteristic of a particular molecule rather than a functional group.

Source: [6].

536 fingerprint region

Region of a *spectrum* that contains *fingerprint bands* as well as bands with characteristic group frequencies.

Note: The fingerprint region is often associated with the region of the mid-infrared or *Raman spectrum* of *wavenumbers* between 1500 cm^{-1} and 400 cm^{-1} . (See *infrared radiation*.)

Source: [6].

537 Fourier-transform infrared (FT-IR) spectroscopy

Fourier-transform infrared spectrometry

Infrared spectroscopy in which a *Fourier-transform spectrometer* is used to separate the transmitted radiation into its component *wavenumbers*.

538 Fourier-transform Raman spectroscopy

Fourier-transform Raman spectrometry

Raman spectroscopy in which a *Fourier-transform spectrometer* is used to separate the scattered radiation into its component *wavenumbers*.

Note: This technique usually uses *near-infrared* excitation.

Source: [6].

539 Fourier-transform spectrometer

Spectrometer in which radiation is separated into its component *wavenumbers* by Fourier transformation of the *interferogram* produced by an *interferometer*.

Source: [6]. See also: *Fourier-transform spectroscopy*.

540 free spectral range, $\Delta\tilde{\nu}$

For a Fabry-Perot or *laser* cavity, *wavenumber* interval between successive longitudinal cavity *modes of vibration*; $\Delta\tilde{\nu} = 1/(2nl)$, where l is the cavity spacing and n is the *refractive index* of the material in the cavity.

Note: SI unit: m^{-1} .

Source: [6].

541 frustrated total internal reflection spectroscopy

See: *attenuated total reflection spectroscopy*.

542 grazing incidence

Angle of incidence of a beam of *electromagnetic radiation* greater than 70°.

Note: Ideally the angle of incidence should be greater than 80°

Source: [6].

543 group frequency

Frequency in *vibrational spectroscopy* that is characteristic of a particular chemical functional group.

Note: The frequency is usually given as a *wavenumber*.

Source: [6].

544 harmonic constant, ω_e , ω_k

harmonic wavenumber

Coefficient of $(v + 1/2)$ in the *vibrational term value*, determined by the harmonic terms in the *vibrational potential energy*.

Note: SI unit: m^{-1} . Common unit: cm^{-1} .

Source: [6].

545 harmonicity

See: *electrical harmonicity*, *mechanical harmonicity*.

546 high resolution electron energy loss spectroscopy (HREELS)

vibrational electron energy loss spectroscopy (VEELS)

Electron energy loss spectroscopy in which the energy resolution is between 1 and 5 meV (*wavenumber* 8 cm^{-1} and 40 cm^{-1}).

Note: HREELS is used to detect vibrational motion.

Source: [6].

547 homogeneous line-broadening

homogeneous broadening

Line-broadening by mechanisms that affect every molecule of the same species in the sample in the same way.

Note: Such mechanisms do not require an ensemble of spectroscopically non-equivalent molecules of the same species. Such mechanisms are the *natural line width*, which is usually negligible in *vibrational spectroscopy*, and intra- or inter- molecular interactions, including anharmonic vibrational interactions (see *anharmonicity*), that reduce the *lifetime* of the *excited state*.

Source: [6].

548 hot transition

Electronic transition between an *excited state* and a state in which all vibrational quantum numbers are the same or greater.

Note 1: A hot band arises from a hot transition.

Note 2: A hot transition has the same changes in vibrational quantum numbers as a fundamental, *overtone transition*, or *sum transition* but it originates in an excited vibrational state not the *ground state*.

Source: [6].

549 hyperpolarizability, β

Coefficient of the second order term in the relation between the *electric dipole moment* μ of a molecule and the electric field E , which acts on the molecule, $\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3$.

Note 1: Hyperpolarizability is a scalar for isotropic entities and a 3×3 tensor for others.

Note 2: SI unit: $C^3 m^3 J^{-2}$.

See: *polarizability*.

550 hyper-Raman spectroscopy (HRS)

Raman spectroscopy in which scattering occurs through *hyperpolarizabilities*. A two-photon technique in which an intense pulsed beam of *electromagnetic radiation* is focused onto the sample. When sufficient power is present in the pulse, two photons may interact with the one molecule to create a virtual state at double the frequency of the laser excitation. Raman scattering from this virtual state to an excited vibrational state of the *ground state* then occurs.

Note: Intense scattering is obtained from less symmetric vibrations and from some vibrations not intense in Raman scattering.

Source: [6].

551 hyperspectral imaging

Measurement method [VIM 2.5] to obtain information about the spatial composition of a sample by obtaining a *spectrum* at each spatially resolved point of the sample.

Source: [6].

552 improper rotation axis, S_n

In *spectroscopy*, a rotation-reflection axis, which is a symmetry element such that rotation by $2\pi/n$ about the axis followed by reflection through a plane perpendicular to the axis transforms an object into itself.

Note: In crystallography, a rotation-inversion axis, which is a symmetry element such that rotation by $2\pi/n$ about the axis followed by inversion through the centre of symmetry transforms an object into itself.

Source: [6].

553 inelastic electron tunnelling spectroscopy (IETS)

Measurement method [VIM 2.5] of *vibrational spectroscopy* to obtain *spectra* of molecules on metal oxide surfaces.

Note: IETS yields vibrational spectra of adsorbates with high resolution (better than 0.5 meV) and low limit of detection (below 10^{13} molecules are required to provide a spectrum).

Source: [62, 63].

554 infrared radiation (IR)

infrared

Electromagnetic radiation of wavelength between approximately 780 nm and 1000 μm or of *wavenumber* between approximately $13\,000\text{ cm}^{-1}$ and 10 cm^{-1} .

Note 1: The infrared range is sub-divided into three regions: *near-infrared*: 780 nm to 2.5 μm ($12\,800$ to 4000 cm^{-1}); *mid-infrared*: 2.5 to 25 μm (4000 to 400 cm^{-1}) and *far infrared*: 25 to 1000 μm (400 to 10 cm^{-1}). See Table 1.

Note 2: The wavelength regions given are commonly used in chemistry and relate to working ranges of infrared *spectrometers*. Note that in other disciplines (e.g., astronomy) the terms are defined for different ranges.

Note 3: If there is no ambiguity the term 'infrared' is used for the mid-infrared region.

See: *infrared spectroscopy*, *Raman spectroscopy*.

555 infrared spectroscopy

Measurement principle [VIM 2.4] of *vibrational spectroscopy* using *infrared radiation*.

Note: Without qualification, 'infrared spectroscopy' usually refers to use of the mid-infrared (*wavelength* range 2.5 to 25 μm , *wavenumber* range (4000 to 400 cm^{-1}) region of the electromagnetic spectrum (see Table 1).

556 inhomogeneous broadening

Line-broadening by mechanisms that arise from an ensemble of spectroscopically non-equivalent molecules of the same species. Such molecules exist, for example, when molecules occupy non-equivalent sites in a condensed phase, and when gaseous molecules have different velocities and, thus, shift the observed *wavenumber* differently through the *Doppler effect*.

Source: [6].

557 interference fringes

channel fringes

Sinusoidal *intensity* variation due to interference of *electromagnetic radiation* that undergoes multiple reflection between two flat and parallel surfaces.

Note 1: Interference fringes are frequently observed in the *transmission spectrum* of a cell with flat windows and in non-scattering polymer films.

Note 2: A *spectrum* of interference fringes is termed a channel spectrum.

Source: [6].

558 interference record

interference function

Record of the signal from the detector of a two-beam *interferometer* as the *optical path difference* between the two beams is varied.

Note: The interference record contains a part that is constant and a part that varies with the path difference.

Source: [6].

559 interferogram

Pattern formed by wave interference produced by an *interferometer*, especially one represented on a screen or chart recorder.

560 internal reflection

Reflection of *electromagnetic radiation* from a material of lesser *refractive index* than that of the incident medium.

Source: [6].

561 internal reflection element

Transparent or semi-transparent material of high *refractive index* that carries *infrared radiation* to a sample in *internal reflection* and *attenuated total reflection* measurements.

Note: The sample is mounted in optical contact with the element.

Source: [6].

562 internal reflection spectroscopy (IRS)

See: *attenuated total reflection spectroscopy*.

563 inverse Raman Scattering

Raman scattering showing *absorption* when *Stokes Raman scattering* exceeds *anti-Stokes Raman scattering*, in an experiment in which a sample is simultaneously illuminated by coincident beams from a continuum source and a pulse laser at $\tilde{\nu}_0$. Energy is absorbed from the continuum at $\tilde{\nu}_0 + \tilde{\nu}_s$ where $\tilde{\nu}_s$ is the *wavenumber* of a Raman-active vibration in the sample that is excited by this process, and this energy is emitted at $\tilde{\nu}_0$.

Source: [6].

564 inverse spatially offset Raman spectroscopy

Variant of *spatially offset Raman spectroscopy* in which a sample is illuminated with a ring of laser light and the *Raman scattering* is collected from the centre of the ring.

565 IRTRAN™

Kinds of crystal transparent to *infrared radiation* used as windows and filters in *infrared spectroscopy*.

Note 1: IRTRAN 1 to IRTRAN 5 are hot-pressed forms of MgF_2 , CdF_2 , MgO , ZnSe and ZnS , respectively.

Note 2: IRTRAN is a registered trade mark of Eastman Kodak Co.

Source: [6].

566 Jacquiot stop

J-stop

Aperture in the optics of a *Fourier-transform spectrometer*, typically between the source and the *interferometer*, designed to be the limiting aperture when no other optical element such as the detector serves this purpose.

Source: [6].

567 kinetic coupling

Coupling of vibrational displacements through terms in the *vibrational kinetic energy*.

Note: Two displacement coordinates must share a common atom if they are to undergo kinetic coupling.

Source: [6].

568 KRS-5

Eutectic (42 % TlBr , 58 % TlI) mixture of thallium bromide and thallium iodide transparent to *infrared radiation* used as window in *infrared spectroscopy*.

Note: KRS-5 transmits well down to 200 cm^{-1} . It is practically insoluble in water but its *refractive index* is rather high (approximately 2.35). It is rather plastic and deforms with time, and it is poisonous.

Source: [6].

569 Kubelka Munk function

remission function

$f(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the *diffuse reflectance* from a sample of infinite depth.

Note: Theoretically $f(R_\infty)$ equals the ratio of the *linear decadic absorption coefficient* to the scattering coefficient. Under the assumptions of the Kubelka Munk theory, if the scattering coefficient at a given *wavenumber* is a constant for a given set of samples, $f(R_\infty)$ is directly proportional to the product of the absorption coefficient and concentration of each component of a mixture, analogous to the behaviour of *absorbance* under Beer's law.

Source: [6]. See also: *volume reflection*.

570 Kubelka Munk reflection

See: *volume reflection*.

571 lifetime broadening

Homogeneous line-broadening due to the limited lifetime of energy states involved in a *transition*.

Note: The lifetime may be limited by the natural lifetime, by collisions, as in *pressure broadening*, or by anharmonic vibrational interactions as in phonon-phonon collisions in solids.

Source: [6].

572 lifetime of an excited state

lifetime

Duration of existence of a molecule in an *excited state* before returning to a lower *energy level* (usually the *ground state*).

573 local mode of vibration

local mode

Mode of vibration localized in one type of bond.

Note: For highly excited CH stretching vibrations anharmonic interactions mix the *normal modes of vibration* to the point that each observed mode of vibration behaves as a local mode

Source: [6].

574 local molar polarizability, $\hat{\alpha}_m(\tilde{\nu})$

molar polarizability

Defined under the assumption of the Lorentz local field by the Lorentz-Lorenz formula:

$$\hat{\alpha}_m(\tilde{\nu}) = 3V_m\epsilon_0 \frac{\hat{\epsilon}(\tilde{\nu}) - 1}{\hat{\epsilon}(\tilde{\nu}) + 2} = 3V_m\epsilon_0 \frac{\hat{n}^2(\tilde{\nu}) - 1}{\hat{n}^2(\tilde{\nu}) + 2}$$

where V_m is the molar volume and $\hat{\epsilon}$ and \hat{n} are the complex *dielectric constant* and *refractive index*, respectively. To allow description of absorption, $\hat{\alpha}_m(\tilde{\nu})$ is complex: $\hat{\alpha}_m(\tilde{\nu}) = \alpha'_m(\tilde{\nu}) + i\alpha''_m(\tilde{\nu})$.

Note 1: The imaginary molar polarizability shows the absorption band free from long range dielectric effects that distort the *band shapes* of very strong absorptions.

Note 2: SI unit: $\text{J}^{-1} \text{C}^2 \text{m}^2 \text{mol}^{-1}$.

Source: [6]. See also: *polarizability*.

575 mechanical anharmonicity

anharmonicity

Influence of cubic and higher-order terms in *vibrational potential energy*.

Note: Mechanical anharmonicity should not be confused with *electrical anharmonicity*.

Source: [6].

576 mechanical harmonicity

harmonicity

Influence of quadratic terms in *vibrational potential energy*.

Note: Mechanical harmonicity should not be confused with *electrical harmonicity*.

Source: [6].

577 mid-infrared radiation

See: *infrared radiation*.

578 Mie scattering

Scattering of *electromagnetic radiation* by particles with diameters that are greater than or similar to the *wavelength* of the radiation but are too small to yield *specular reflection* or *diffuse reflection*.

Source: [6].

579 mode of vibration

vibration mode

mode

vibration

Independent vibrational motion of a molecule.

Note: In *vibrational spectroscopy* ‘mode’ or ‘vibration’ is used for *normal mode of vibration*.

Source: [6].

580 molar ellipticity, $\Theta(t, \lambda)$

Ellipticity divided by the amount concentration of the optically active absorbing material and by the path-length at temperature (t) and *wavelength* (λ).

Note: SI unit: $\text{rad m}^2 \text{mol}^{-1}$.

Source: [6].

581 multiplex advantage

Decrease in *measurement uncertainty* [VIM 2.26] obtained by measuring *intensity* at many different *wavelengths* simultaneously, as is done, for example, in *Fourier-transform spectroscopy*.

Source: [6].

582 natural lifetime of an excited state, Δt

Lifetime of an *excited state* of a molecule that is isolated from radiation fields and other molecules or entities.

Note: The lifetime is limited by the probability of spontaneous emission to a lower state. If an *excited state*, n can only emit spontaneously to a single lower state m , the natural lifetime of state n equals the reciprocal of A_{mn} , the Einstein transition probability of spontaneous emission.

Source: [6].

583 natural linewidth

Line width of a molecular *spectral band* that arises from the probability of spontaneous emission in the absence of radiation fields and interaction with other molecules or entities.

Note 1: The natural linewidth, measured as the *full width half maximum* equals $1/(2\pi c_0 \Delta t)$, where Δt is the *natural lifetime* of the *excited state*.

Note 2: If the excited state n can only emit spontaneously to a single lower state m the natural linewidth is $1.86 \times 10^{-38} \tilde{\nu}_{mn}^3 \langle m|\mu|n \rangle^2$, when the transition wavenumber $\tilde{\nu}_{mn}$ is in cm^{-1} and the *dipole moment* μ is in Debye ($1 \text{ D} \approx 3.335 64 \times 10^{-30} \text{ C m}$). In the infrared, typical natural linewidths are approximately 10^{-7} cm^{-1} .

Source: [6].

584 near-infrared radiation

near-IR

Infrared radiation of which *vacuum wavenumbers* range from approximately $12\,800 \text{ cm}^{-1}$ to 4000 cm^{-1} and *wavelengths* range from approximately 780 nm to 2500 nm .

Note: The region is often divided into the silicon region between $12\,800 \text{ cm}^{-1}$ and 9000 cm^{-1} (800 nm and 1100 nm) and the lead sulfide region between 9000 cm^{-1} and 4000 cm^{-1} (1100 nm and 2500 nm), where the names reflect the common detector for the region.

Source: [6].

585 non-dispersive infrared spectroscopies

Kinds of *infrared spectroscopy* in which the effect of the sample on the radiation from the source is measured as a whole without exploring the dependence on *wavenumber*.

Note: These methods are mainly used to obtain adequate *optical throughput* for process measurement and monitoring

Example: *Two-dimensional infrared correlation spectroscopy*.

Source: [6].

586 normal coordinate, Q_k

Formal mathematical description of a normal vibration. When the potential energy, V , is harmonic and the kinetic energy, T , is calculated in the limit of infinitesimally small displacements, the normal coordinates are defined as independent entities such that “(for non-linear molecules)”

$$V = \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 \text{ and } T = \frac{1}{2} \sum_{k=1}^{3N-6} \dot{Q}_k^2$$

where λ_k is the k^{th} eigenvalue and \dot{Q} is $\partial Q/\partial t$. Normal coordinate Q_k is related to the internal displacement coordinates, R_i , through the elements, $L_{ik} = \partial R_i/\partial Q_k$ of the k^{th} column of the eigenvector matrix \mathbf{L} . Normal coordinates are not independent when the potential energy is anharmonic, or the displacements are not infinitesimal. See also: *normal coordinate analysis* and *vibrational eigenvector*.

Note: SI unit: $\text{kg}^{1/2} \text{ m}$. Common unit: $\text{u}^{1/2} \text{ \AA} \approx 4.07497 \times 10^{-24} \text{ kg}^{1/2} \text{ m}$.

Source: [6].

587 normal coordinate analysis

Calculation of the *normal modes of vibrations* of a molecule or crystal under the assumptions that the potential energy is harmonic and the displacements from equilibrium are infinitesimal. See also: *normal coordinate* and *vibrational eigenvector*.

Source: [6].

588 normal dispersion of the refractive index

normal dispersion

Slow decrease of real *refractive index* of a material in a non-absorbing *spectral region* far from regions of strong absorption as the *wavenumber* decreases.

Source: [6].

589 normal incidence

Incidence of a beam of *electromagnetic radiation* when the *angle of incidence* $\theta = 0^\circ$, *i.e.*, the incident radiation beam is normal to the surface.

Source: [6].

590 normal mode of vibration

normal vibration mode
normal mode
normal vibration

One of the $3N - 6$ ($3N - 5$ for a linear molecule) *modes of vibration* that would add to give the total vibrational motion in a molecule if the interatomic potential were strictly quadratic in the displacements from equilibrium.

Note: Normal modes of vibration is an idealized concept that has proved extremely useful in analysing *spectra* in *vibrational spectroscopy*.

Source: [6].

591 normal Raman scattering

See: *Raman scattering*.

592 normalized tunnelling intensity (NTI)

constant resolution tunnelling intensity

Second differential of intensity with respect to bias voltage divided by first differential of intensity with respect to bias voltage.

Note: Normalized tunnelling intensity is plotted against the bias voltage to report *inelastic electron tunnelling spectroscopy* data.

Source: [6].

593 null-balance double beam spectrometer

See: *optical null double beam spectrometer*.

594 numerical aperture (NA)

For an optical fibre, $n_o \sin \theta_a$, where n_o is the *refractive index* of the exterior medium and θ_a is the maximum input half angle that can support propagation.

Source: [6].

595 optical absorption depth, μ_β

Depth in a sample at which the *intensity* of an incident beam is reduced to $1/e$ of its value at the surface of the sample.

Note 1: μ_β is the reciprocal of the *linear Napierian absorption coefficient*.

Note 2: SI unit: m. Common unit: μm .

Source: [6].

596 optical constants

Collective name for the real *refractive index*, n and the *absorption index* (imaginary refractive index), k .

597 optical null double beam spectrometer

null-balance (NTI) double beam spectrometer

Spectrometer in which the ratio of the *radiant power* in the two beams at each *wavenumber* is measured opto-mechanically by inserting a linear optical attenuator into the reference beam until the two signals measured by the detector are equal, then measuring the displacement of the optical attenuator.

Source: [6].

598 optical path difference (OPD)

optical retardation

Path-length difference between the arms of a two-beam *interferometer*.

Note 1: The term optical retardation is derived from ‘phase retardation’, which refers to the change in the phase of the electromagnetic radiation in the interferometer.

Note 2: SI unit: m. Common unit: cm.

Source: [6].

599 optical rotatory dispersion (ORD)

Wavelength dependence of the angle of rotation of the plane of linearly-polarized radiation when transmitted through optically active materials.

Source: [6].

600 ordinary wave

ordinary ray

In a uniaxial crystal *electromagnetic radiation* with electric vector perpendicular to the optic axis and which obeys the normal laws of refraction.

Note: In uniaxial crystals the optic axis coincides with the symmetry axis. The *refractive index* of the crystal is the same in all directions perpendicular to the optic axis but is different along the optic axis. Consequently, electromagnetic rays or waves that do not travel along the optic axis experience different refractive indices in different directions perpendicular to their direction of propagation. Two waves result, one has its electric vector perpendicular to the optic axis and forms the ordinary wave. The other is the *extraordinary wave*.

Source: [6].

601 overtone transition

Transition between the *ground state* and a state in which a single *mode of vibration* is multiply excited.

Note: An overtone band results from an overtone transition.

Example: Transition from the ground state to the state in which $v_i \geq 2$, $v_{j \neq i} = 0$.

Source: [6].

602 pATR spectrum

deprecated: absorbance spectrum

$-\log_{10}$ of the *spectrum* obtained in *attenuated total reflection spectroscopy*.

Note: The term is used to avoid the confusing, but common and incorrect, practice of calling it the *absorbance spectrum*.

Source: [6].

603 photoacoustic saturation

Condition in *photoacoustic spectroscopy* in which all bands with greater than a certain absorption *intensity* appear to have the same intensity.

Note: Photoacoustic saturation arises when the sample is optically opaque and thermally thin, *i.e.*, when the *thermal diffusion depth*, L , is greater than the *optical absorption depth*, μ_β , and less than the sample thickness. The condition may be relieved by increasing the modulation frequency sufficiently that L becomes less than μ_β , *i.e.*, that the sample becomes thermally thick.

Source: [6].

604 photoacoustic spectroscopy (PAS)

Measurement method [VIM 2.5] of *spectroscopy* in which the absorption of *electromagnetic radiation* by the sample is detected by the emission of sound generated by a thermal pressure wave in the sample.

Source: [6].

605 photothermal spectroscopy

Measurement method [VIM 2.5] of *spectroscopy* in which the absorption of *electromagnetic radiation* by a sample is detected as a result of the heat generated by the absorption.

Source: [6].

606 polarizability, α

polarizability volume

Coefficient of the first order term in the relation between the *electric dipole moment* μ of a molecule and the electric field E , which acts on the molecule, $\mu = \mu_o + \alpha E + \beta E^2 + \gamma E^3$.

Note 1: Polarizability is a scalar for isotropic entities and a 3×3 tensor for others.

Note 2: SI unit: $\text{J}^{-1} \text{C}^2 \text{m}^2$.

Note 3: The term ‘polarizability volume’ results when polarizability is defined in equations under the esu or Gaussian system. To obtain the SI unit $\text{J}^{-1} \text{C}^2 \text{m}^2$, the polarizability volume must be multiplied by $4\pi\epsilon_0$ before converting the volume unit to m^3 . ϵ_0 is the *permittivity of vacuum*.

Source: [6]. See also: *hyperpolarizability*, *local molar polarizability*.

607 polarized Raman band

Raman band with *depolarization ratio* $\rho \leq 0.75$ for linear polarized incident radiation in normal *Raman spectroscopy*.

Source: [6]. See also: *depolarized Raman band*.

608 potential coupling

Coupling of vibrational displacements through terms in the *vibrational potential energy*. The second-order (quadratic) terms cause harmonic potential coupling while the cubic and higher terms cause anharmonic potential coupling.

Source: [6]. See also: *harmonicity*, *anharmonicity*.

609 p-polarization

transverse magnetic (TM) polarization

Polarization when *electromagnetic radiation* is incident upon a surface with its electric vector in the plane of incidence and, therefore, inclined to the reflecting surface unless the incidence is normal.

Source: [6].

610 pressure broadening

collision broadening

Increase in the *line width* of a *spectral line* of a gas due to molecular collisions and other intermolecular interactions that reduce the *lifetime* of an *excited state*.

Note: At pressures sufficiently low that the line width is far smaller than the line *wavelength*, the line width increases linearly with pressure, the broadening is homogeneous and the line shape is *Lorentzian*.

Source: [6].

611 quantum cascade laser (QCL)

Laser that emits *mid-infrared radiation*.

Note: A QCL can be used as a source for *infrared spectroscopy*.

612 Raman band

Spectral band in Raman spectroscopy.

613 Raman optical activity (ROA)

Phenomenon that vibrations in chiral molecules and materials Raman-scatter right circularly polarized incident radiation to a different extent than left circularly polarized incident radiation.

Note: In practice, the circular polarization of the exciting beam, or of the scattered beam, or of both beams simultaneously, may be selected. Raman optical activity is usually specified as ‘right minus left’ circular polarizations, in unfortunate contrast to the ‘left minus right’ specification that is universal in vibrational circular polarization and other forms of optical activity.

Source: [6].

614 Raman scattering

normal Raman scattering

Inelastic scattering of *electromagnetic radiation* by molecules that are excited to higher *energy levels*.

Note 1: Normal Raman scattering occurs through changes in polarizability of a molecule during a vibration, not the hyper-polarizabilities, and is excited by radiation that is not in resonance with *electronic transitions* in the sample.

Note 2: The energy of the scattered photon can be lesser (*Stokes Raman scattering*) or greater (*anti-Stokes Raman scattering*) than that of the incident photon.

615 Raman shift

Raman wavenumber shift

Difference in *wavenumber* between the incident and scattered *electromagnetic radiation* in *Raman spectroscopy*.

Note: SI unit: m^{-1} . Common unit: cm^{-1} .

Source: [6].

616 Raman spectroscopy

Measurement principle [VIM 2.4] of *vibrational spectroscopy* based on *Raman scattering*.

Note: Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations.

617 Raman spectrum

Graph of the *intensity* of scattered electromagnetic radiation in *Raman spectroscopy* against *Raman shift*.

Note: Commonly a Raman spectrum is obtained between approximately 100 cm^{-1} and 3500 cm^{-1} and is a complement to its counterpart mid-infrared *spectrum*.

618 Raman wavenumber shift, $\Delta\tilde{\nu}$

Raman shift

Wavenumber of exciting *electromagnetic radiation* minus wavenumber of the scattered radiation.

Note 1: SI unit: m^{-1} . Common unit: cm^{-1} .

Note 2: $\Delta\tilde{\nu}$ is positive for *Stokes Raman scattering* and negative for *anti-Stokes Raman scattering*.

Source: [6].

619 rapid-scan Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy in which the optical path difference is continually changed at a rate of 0.05 cm s^{-1} or greater.

Source: [6]. See also: *continuous scan interferometer*.

620 Rayleigh scattering

Light scattering in which the incident and scattered *electromagnetic radiation* has the same frequency.

621 reflection-absorption at grazing incidence

Reflection-absorption with very thin layers of an absorbing material on a metallic substrate and the *angle of incidence* between 70° and 90° .

Note: As the incident radiation beam travels nearly parallel to the sample surface, the electric vector of the radiation is then either parallel or nearly perpendicular to the surface.

Source: [6]. See *reflection-absorption infrared spectroscopy*.

622 remission function

See: *Kubelka Munk function*.

623 resonance Raman scattering (RR)

Raman scattering that occurs through the polarizability of a molecule, (not the hyperpolarizabilities) and is excited by electromagnetic radiation that is in resonance with electronic transitions or vibronic transitions in the sample.

Source: [6].

624 rotational branch

Spectral lines in the *rotation-vibration spectrum* of a gas that derive from the same change in rotation quantum number, J .

Note 1: $\Delta J = J_{\text{upper}} - J_{\text{lower}} = -2, -1, 0, +1$ and $+2$ for the O, P, Q, R and S branches, respectively.

Note 2: The most commonly observed branches for simple molecules are the P, Q and R branches in *infrared spectroscopy* and the O, Q and S branches in *Raman spectroscopy*.

Source: [6].

625 rotation-vibration spectrum

Spectrum that shows absorption or emission of radiation during *transitions* between rotational-vibrational states of a molecule.

Source: [6].

626 scattering geometry

Relation between the propagation directions, k_i, k_s , and the polarization directions, p_i, p_s , of the incident and scattered radiation, usually expressed in terms of laboratory-fixed or crystal-fixed Cartesian axes.

Note: A common notation, due to Porto, is $k_i(p_i p_s)k_s$.

Source: [6].

627 site splitting

Appearance of more than one *band* in the *spectrum* of a crystal when only one is seen in that of the gas, when this splitting is attributed to either the molecule lying on a crystal site of lower symmetry than that of the gaseous molecule or to molecules occupying more than one type of crystal site. See *crystal field splitting*.

Note: Site splitting arises from the static intermolecular forces in the crystal.

Source: [6].

628 spatially offset Raman spectroscopy (SORS)

Measurement method [VIM 2.5] of *Raman spectroscopy* in which the sample is illuminated at one location, and the Raman signal is collected from a different location on the sample surface.

Note: SORS allows chemical analysis of objects beneath diffusely scattering surfaces, such as tissue, powders and translucent plastics.

629 spherical top

Molecule whose three principal moments of inertia are all the same. An isotropic molecule.

Source: [6].

630 Stark effect

Effect of an electric field on molecular *energy levels* and, hence, on a *spectrum*.

Note: The spectral changes may be single lines splitting into *multiplets*, frequencies shifts, inactive vibrations becoming active, or changed intensities of active vibrations.

Source: [6].

631 step-scan interferometer

Interferometer (typically used for *Fourier-transform infrared spectroscopy*) in which the *optical path difference* is changed by a certain amount, held constant, or modulated if *phase modulation* is desired, while the signal at the current path difference is recorded, then the process is repeated.

Source: [6].

632 stimulated Raman scattering (SRS)

Two-photon *Raman scattering* occurs when a picosecond pump beam is used to create a virtual state and a probe beam of a frequency to match the frequency of *Stokes Raman scattering* from the virtual state to a specific vibrational level. The Stokes emission is stimulated thus depopulating the virtual state very quickly and increasing the scattering efficiency for the chosen vibration by orders of magnitude. SRS is a non-linear process, so sufficient photons from both the pump and probe beams must be present on the molecule at the one time.

633 Stokes Raman scattering

Stokes scattering

Raman scattering of *electromagnetic radiation* in which the scattered radiation has lesser energy (lesser *wavenumber*) than the exciting radiation.

Source: [6]. See also: *anti-Stokes Raman scattering*.

634 sum band

Band resulting from a *sum transition*.

Source: [6].

635 sum transition

Combination transition between the *ground state* and a state in which more than one vibration is excited; *i.e.*, a *transition* from the ground state in which more than one quantum number increases.

Source: [6].

636 sum-frequency spectroscopy

Nonlinear optical technique in which *pulsed lasers* at frequencies ω_1 and ω_2 are overlapped at a surface and light emitted at the sum of the two frequencies, $\omega_1 + \omega_2$, is detected. One laser is normally in the mid-*infrared* and the other in the visible or near-*infrared*.

Source: [6].

637 surface-enhanced hyper-Raman spectroscopy (SEHRS)

Measurement method [VIM 2.5] of *Raman spectroscopy* by which the *Raman spectrum* is significantly enhanced simultaneously by both the hyper-Raman (see *hyper-Raman spectroscopy*) and surface-enhanced Raman (see *surface-enhanced Raman spectroscopy*) effects.

Note: Very high enhancement factors of 10^{20} have been claimed.

638 surface-enhanced infrared absorption (SEIRA)

Measurement method [VIM 2.5] of *infrared spectroscopy* by which the intensity of absorption bands of molecules within a few nanometers of the surface of metal particles is increased by interactions with surface plasmons (the collective resonance of electrons near the surface of metal islands).

Note: The metals that give the largest enhancement are silver and gold, but this phenomenon has been reported to occur with at least eight other metals.

Source: [6].

639 surface-enhanced Raman spectroscopy (SERS)

Measurement method [VIM 2.5] of *Raman spectroscopy* by which the intensity of vibrational bands in the *Raman spectra* of molecules within a few nanometers of the surface of microscopically rough metals, metal colloids and metal nanoparticles is increased by several orders of magnitude.

Note 1: The metals that give the largest enhancement are silver, gold and copper, but this phenomenon has been reported to occur with a range of other metals.

Note 2: Other mechanisms of enhancement are known but the common usage of SERS is with a metal or with related systems and implies enhancement through interaction with a surface plasmon.

Source: [6].

640 surface-enhanced resonance Raman spectroscopy (SERRS)

Measurement method [VIM 2.5] of *surface-enhanced Raman spectroscopy* (SERS) by which the *Raman spectrum* is significantly enhanced when the conditions occur that whilst undergoing SERS the molecules are excited by radiation that is in resonance with *electronic transitions* in the sample.

Note: Enhancements of 10^{14} to 10^{15} have been measured.

641 surface-enhanced, spatially offset Raman spectroscopy (SESORS)

Measurement method [VIM 2.5] of *Raman spectroscopy* that combines *spatially offset Raman spectroscopy* and *surface-enhanced Raman spectroscopy* (SERS) enabling the detection of a SERS signal deep within diffusely scattering samples.

642 symmetric (in vibrational spectroscopy)

Term used in at least two senses in *vibrational spectroscopy*. In general usage, a symmetric molecule is a molecule with high symmetry. In more specific usage, a property is symmetric with respect to a symmetry element if it remains unchanged by the action of the corresponding symmetry operation.

Source: [6].

643 symmetric top

Molecule that has two equal principal moments of inertia with the third one different.

Source: [6] See also: *asymmetric top*.

644 symmetry coordinate, S , S_i

Each S_i is a linear combination of general coordinates, usually internal coordinates, constructed to take advantage of the molecular symmetry. The S_i are elements of the vector S . They have the same units as the general coordinates from which they were constructed.

Source: [6].

645 symmorphic space group

Space group that does not contain screw-axes and glide planes.

Source: [6].

646 thermal diffusion depth, L , μ_s

thermal wave decay length

In *photoacoustic spectroscopy*, $L = \sqrt{D/\pi f}$, where D is *thermal diffusivity* and f is *modulation frequency* of the *electromagnetic radiation*.

Note 1: SI unit: m. Common unit: μm .

Note 2: 63 % of the PAS signal originates within the thermal diffusion depth.

Source: [6].

647 thermal diffusivity, D , a

Thermal conductivity divided by the product of the specific heat and the density.

Note: SI unit: $\text{m}^2 \text{s}^{-1}$.

Source: [6].

648 thermal wave decay coefficient, a_s

Reciprocal of the thermal diffusion depth (L). $a_s = 1 / L$.

Note: SI unit: m^{-1} .

649 thermal wave decay length

See: *thermal diffusion depth*.

650 tip-enhanced Raman spectroscopy (TERS)

Measurement method [VIM 2.5] of *Raman spectroscopy* combining *surface-enhanced Raman spectroscopy* and scanning using an atomic force microscope or scanning tunnelling microscope to give complementary maps of a surface.

See: [64].

651 total internal reflection

Internal reflection from a non-absorbing material at angles of incidence at or above the critical angle.

Source: [6].

652 transfectance

Spectral intensity of a transflected beam divided by spectral intensity of the incident beam in a *transflection* experiment.

Note: ‘Transflectance’ has also been used to mean transflection, and this usage is strongly discouraged.

Source: [6].

653 transflection

Reflection absorption at *near-normal incidence* when the thickness of the absorbing medium is large enough to yield an interpretable *spectrum*. The substrate is usually a mirror for mid-infrared measurements and a ceramic disk for near-infrared measurements. The *angle of incidence* is typically between 0° and 45° .

Note: Transflection is widely used in IR microscopy and is particularly convenient for measuring transmission-like spectra in a near-infrared instrument configured for *diffuse reflection* measurements by mounting the sample on a non-absorbing diffusely reflecting substrate.

Source: [6].

654 transmission Raman spectroscopy (TRS)

Measurement method [VIM 2.5] of *Raman spectroscopy* in which the sample is illuminated on one side and the Raman signal is collected from the opposite side.

Note: TRS allows chemical analysis of objects beneath diffusely scattering surfaces, e.g., within tissue, powders and pharmaceutical tablets or capsules.

655 vibration mode

vibration

See: *mode of vibration*.

656 vibrational circular dichroism (VCD)

Circular dichroism, $k^L - k^R$, for vibrational transitions.

Note: Vibrations in chiral molecules and materials absorb left circularly polarized radiation to a different extent than right circularly polarized radiation.

Source: [6].

657 vibrational eigenvector, L , L_{ik}

Part of the solution of the matrix equation of *normal coordinate analysis*, $\mathbf{GFL} = \mathbf{LA}$. Each element L_{ik} of L is a vibrational eigenvector, and gives the change in internal coordinate R_i during unit change in the *normal coordinate* Q_k , as shown in matrix form by

$$\mathbf{R} = \mathbf{LQ}, \text{ i.e., } L_{ik} = \partial R_i / \partial Q_k.$$

Eigenvectors are sometimes expressed in terms of symmetry coordinates or Cartesian coordinates.

Note: SI unit: $\text{kg}^{-1/2}$. Common unit: $u^{-1/2} = 2.45400 \times 10^{13} \text{ kg}^{-1/2}$.

Source: [6].

658 vibrational kinetic energy, T

Kinetic energy of the molecule as a function of the displacements of the atoms from equilibrium positions. For Cartesian displacement coordinates (x, y, z) , $T = \sum_{\alpha} 1/2 m_{\alpha} (\dot{x}_{\alpha}^2 + \dot{y}_{\alpha}^2 + \dot{z}_{\alpha}^2)$, where the sum is over all atoms and \dot{x}_{α} , etc., are the displacement velocities. For internal coordinates $T = 1/2 \mathbf{P}^t \mathbf{G} \mathbf{P} = 1/2 \dot{\mathbf{R}}^t \mathbf{G}^{-1} \dot{\mathbf{R}} = 1/2 \sum_{ij} G_{ij}^{-1} \dot{R}_i \dot{R}_j$ where $\dot{\mathbf{R}}^t$ and $\dot{\mathbf{R}}$ are the row and column vector, respectively, of the $\partial R_i / \partial t$, \mathbf{P}^t and \mathbf{P} are the row and column vector, respectively, of the momenta conjugate to the R_i , \mathbf{G}^{-1} is the inverse of the \mathbf{G} matrix and G_{ij}^{-1} is the ij^{th} element of \mathbf{G}^{-1} . The elements of the \mathbf{G} matrix are defined by $G_{ij} = \sum_{\alpha} \frac{1}{m_{\alpha}} B_{i\alpha} B_{j\alpha}$ where $B_{i\alpha}$ and $B_{j\alpha}$ relate the i^{th} and j^{th} internal coordinate to the α^{th} Cartesian coordinate through the equation $\mathbf{R} = \mathbf{BX}$ in which \mathbf{X} is the column vector of the Cartesian coordinates.

Note: SI unit: J.

Source: [6].

659 vibrational potential energy, V

Potential energy of the molecule as a function of the displacements of the atoms from equilibrium positions. The harmonic terms are quadratic in the displacements and the anharmonic terms are of cubic, quartic and higher orders in the displacements.

Q are normal coordinates

$$2V = \sum_k \lambda_k Q_k^2 + \sum_{ijk} k_{ijk} Q_i Q_j Q_k + \text{higher order terms}$$

In terms of internal coordinates,

$$2V = \sum_i F_{ii} R_i^2 + \sum_{i,j \neq i} F_{ij} R_i R_j + \sum_{i,j,k} F_{ijk} R_i R_j R_k + \text{higher order terms}$$

Note: SI unit: J.

Source: [6].

660 vibrational spectroscopy

Measurement principle [VIM 2.4] of *spectroscopy* to analyse molecular properties based on vibrations (bond stretching or deformation modes) in chemical species.

Note: Typically, vibrational spectroscopy uses electromagnetic radiation lower in energy than the visible *spectrum* *i.e.*, infrared or *near infrared* (see Table 1).

661 vibrational term value, G

Vibrational energy, E , expressed in *wavenumber* units. $G = E/(hc)$, where h is the Planck constant and c is the speed of light in vacuum.

Note 1: G is usually written with zero-energy at the minimum of the potential energy curve for a diatomic molecule as: $G = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \text{higher order terms}$, and for a polyatomic molecule $G = \sum_k \omega_k (v_k + g_k/2) + \sum_{i \neq j} X_{ij} (v_i + g_i/2) (v_j + g_j/2) + \text{higher order terms}$, where $v, v_k, \text{etc.} = 0, 1, 2, 3, \dots$, and g is the degeneracy of a vibration. X_{ij} are the anharmonic constants.

Note 2: SI unit: m^{-1} . Common unit: cm^{-1} .

Source: [6].

662 vibronic transition

Transition that changes the electronic and vibrational state of the molecule.

663 volume reflection

Kubelka Munk reflection

deprecated: diffuse reflection

Re-emergence of *electromagnetic radiation* from the surface of incidence after penetrating into a powdered sample.

Source: [6].

664 wavenumber shift, $\Delta\tilde{\nu}$

See: *Raman wavenumber shift*.

Index of symbols and abbreviations

α	absorptance
α	polarizability
α_i	internal absorptance
$\tilde{\alpha}_m(\tilde{\nu})$	local molar polarizability
β	hyperpolarizability
γ	gyromagnetic ratio
Γ	full width at half height
δ	chemical shift in NMR
$\delta\nu$	<i>spectral resolution</i> at frequency ν
$\delta\tilde{\nu}$	<i>spectral resolution</i> at wavenumber $\tilde{\nu}$
$\delta\lambda$	<i>spectral resolution</i> at wavelength λ
ΔE	energy change of an <i>electromagnetic transition</i>
$\Delta\tilde{\nu}$	Raman wavenumber shift
$\Delta\tilde{\nu}$	free spectral range
Δt	natural lifetime of an excited state
ε	emittance
ε_i	<i>energy level</i> of i^{th} state (see: <i>Boltzmann distribution of nuclear spins</i>)
$\hat{\varepsilon}_r$	relative permittivity
η	nuclear Overhauser effect
θ	angle of incidence
θ_c	critical angle
θ_E	Ernst angle
Θ	molar ellipticity
κ	attenuation index (see: <i>complex refractive index</i>)
λ	wavelength in medium
λ_0	wavelength in vacuum
μ	electric dipole moment
μ_β	optical absorption depth
μ_s	thermal diffusion depth
μ_s	thermal diffusion depth
ν	frequency
$\tilde{\nu}$	wavenumber
$\tilde{\nu}_0$	peak <i>wavenumber</i>
ρ	depolarization ratio
ρ	radiant energy density
ρ_ν, ρ_λ	spectral radiant energy density
σ	wavenumber in medium
τ	transmittance
τ, τ_c	correlation time
τ_d	dwell time
τ_i	internal transmittance
ϕ_0	received radiant flux density
$\phi_r(\lambda)$	reference flux density
$\phi_s(\lambda)$	sample flux density
ϕ_N	noise equivalent power (see: <i>noise</i>)

$\phi_T(\lambda)$	solvent blank flux density
Φ	radiant power
ψ	ellipticity
ω, ω_L	Larmor frequency
ω_e, ω_k	harmonic constant
a	thermal diffusivity
a_s	thermal wave decay coefficient
A	absorbance
A_{10}	experimental absorbance
A_{10}, A	decadic absorbance
A_i	internal absorbance
B	radiofrequency magnetic flux density (see: <i>adiabatic pulse</i>)
B_0	static magnetic flux density
c	speed of <i>electromagnetic radiation</i>
c	speed of <i>electromagnetic radiation</i>
c_{BE}	background equivalent concentration
d_p	depth of penetration in attenuated total reflection
D	thermal diffusivity
E	received radiant flux density
$E_{\bar{\nu}}$	intensity of radiation
eQ	nuclear electric quadrupole moment
f	frequency
f_{Nyquist}	Nyquist frequency
f_{SW}	NMR spectral width
F	fluence
g	degeneracy
G	optical throughput of a spectrometer
G	vibrational term value
h	Planck constant (see: <i>electromagnetic radiation</i>)
H	fluence
H_G	peak height (band maximum) (see: <i>Gaussian band, Lorentzian band</i>)
I	intensity of radiation
I	received radiant flux density
I_0	incident <i>intensity of radiation</i>
$I_{\bar{\nu}}$	spectral intensity
I_e	<i>radiant intensity</i>
I_s	<i>intensity of radiation scattered</i> (see: <i>scattering coefficient</i>)
J	rotation quantum number (see: <i>rotational branch</i>)
J	spin-spin coupling constant
k	absorption index
K	Knight shift
l	path-length
L	radiance
L	thermal diffusion depth
L, L_{ik}	vibrational eigenvector
$L_{\bar{\nu}}, L_{\lambda}$	spectral radiance
M	radiant excitance
\hat{n}	complex refractive index
p	electric dipole moment
P	radiant power
P_0	incident radiant power (see: <i>absorptance, diffuse reflectance</i>)
P_{abs}	absorbed radiant power (see: <i>absorptance</i>)
P_{rem}	remitted radiant power (see: <i>diffuse reflectance</i>)
Q_k	normal coordinate
R	remittance (see: <i>diffuse reflectance</i>)
R	resolving power
$R_{S/N}$	signal-to-noise ratio
s	scattering coefficient

S, S_i	symmetry coordinate
S_n	improper rotation axis
t_{aq}	acquisition time
T_2	spin-lattice relaxation time
T_2^*	net dephasing time
T	transmittance
T	vibrational kinetic energy
T_E	echo time
T_i	internal transmittance
T_I	inversion timeinversion time
T_r	repetition time
V	vibrational potential energy
V_m	molar volume (see: <i>local molar polarizability</i>)
w	radiant energy density
W	full width at half height
AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
AFS	atomic fluorescence spectroscopy
AMTIR	amorphous material transmitting infrared radiation
APT	atomic polar tensor
AT	acquisition time
ATR	attenuated total reflection
CAMELPSIN	cross-relaxation appropriate for minimolecules emulated by locked spins (see: <i>rotating-frame NOE spectroscopy</i>)
CARS	coherent anti-Stokes Raman spectroscopy
CCD	charge coupled device
CD	circular dichroism
COLOC	correlation spectroscopy through long-range coupling
COSY	correlation spectroscopy
CP/MAS	cross polarization with magic angle spinning NMR
CRAMPS	combined rotation and multiple pulse spectroscopy
CSA	chemical shift anisotropy
CW	continuous wave (see: <i>Fourier-transform spectroscopy</i>)
DC	direct current. (See: <i>radiofrequency glow discharge optical emission spectroscopy, direct current glow discharge optical emission spectroscopy</i>)
DC GD-OES	direct current glow discharge optical emission spectroscopy
DEPT	distortionless enhancement by polarization transfer
DIPSI	decoupling in the presence of scalar interactions
DOSY	diffusion ordered spectroscopy
DPMGSE	double pulsed-field gradient spin-echo excitation
DQF-COSY	double-quantum filtered correlation spectroscopy
ECCF	equilibrium charge, charge flux (see: <i>electro-optic parameter</i>)
EELS	electron energy loss spectroscopy
EM	electromagnetic radiation
EOP	electro-optic parameter
ERETIC	electronic reference to access in vivo concentrations
ETAAS	electrothermal atomic absorption spectroscopy
EXSY	exchange spectroscopy
FFC-NMR	fast field cycling NMR relaxometry
FID	free induction decay
FMIR	frustrated internal reflection spectroscopy (see: <i>multiple attenuated total reflection</i>)
FT-IR	Fourier transform infrared (see: <i>Fourier-transform infrared spectroscopy</i>)
FWHH	full width at half height (see: <i>full width at half maximum</i>)
FWHM	full width at half maximum
GARP	globally optimized alternating-phase rectangular pulses
GD-OES	glow discharge optical emission spectroscopy
H2BC	heteronuclear multiple-bond correlation over two bonds

HETCOR	heteronuclear shift correlation NMR
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple-quantum correlation NMR
HMQC-TOCSY	heteronuclear multiple-quantum correlation with additional TOCSY transfer
HOESY	heteronuclear Overhauser effect spectroscopy
HOHAHA	homonuclear Hartmann-Hahn spectroscopy (see: <i>total correlation spectroscopy</i>)
HREELS	high resolution electron energy loss spectroscopy
HRS	hyper-Raman spectroscopy
HSQC	heteronuclear single quantum correlation
HSQMBC	heteronuclear single quantum multiple-bond correlation
HSQC-TOCSY	heteronuclear single quantum correlation with additional TOCSY transfer
HWHH	half width at half height (see: <i>half width at half maximum</i>)
HWHM	half width at half maximum
ICCD	intensified charge coupled device detector
ICP	inductively-coupled plasma
ICP-MS	inductively-coupled plasma mass spectrometry
ICP-OES	inductively-coupled plasma optical emission spectroscopy
IETS	inelastic electron tunnelling spectroscopy
INADEQUATE	incredible natural-abundance double-quantum transfer experiment
INEPT	insensitive nuclei enhanced by polarization transfer
ILS	instrument line shape
IR	infrared (see: <i>infrared radiation</i>)
IRS	internal reflection spectroscopy (see: <i>attenuated total reflection spectroscopy</i>)
J-MOD	J-modulated spin-echo
J-RES	J-resolved spin-echo
LIBS	laser-induced breakdown spectroscopy
LTE	local thermal equilibrium (see: <i>plasma local thermodynamic equilibrium</i>)
MATR	multiple attenuated total reflection
MCP	microchannel plate (see: <i>intensified charge coupled device detector</i>)
MIR	multiple internal reflection (see: <i>multiple attenuated total reflection</i>)
MQMAS	multiple-quantum magic angle spinning NMR
NA	numerical aperture
NMR	nuclear magnetic resonance (see: <i>nuclear magnetic resonance spectroscopy</i>)
NMRR	nuclear magnetic resonance relaxometry
nOe, NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
NQR	nuclear quadrupole resonance (see: <i>nuclear quadrupole resonance spectroscopy</i>)
NUS	non-uniform sampling
OES	optical emission spectroscopy
OPD	optical path difference
ORD	optical rotatory dispersion
PAS	photoacoustic spectroscopy
PFG	pulsed-field gradient
PSYCHE	pure shift yielded by chirp excitation
QCL	quantum cascade laser
RAIRS	reflection-absorption infrared spectroscopy
RDC	residual dipolar coupling
REDOR	rotational echo double resonance
RF	radiofrequency
RF-GD-OES	radiofrequency glow discharge optical emission spectroscopy
RIXS	resonant inelastic X-ray scattering
ROA	Raman optical activity
ROESY	rotating-frame NOE spectroscopy
RR	resonance Raman (see: <i>resonance Raman scattering</i>)
SE	spin echo
SEHRS	surface-enhanced hyper-Raman spectroscopy
SERRS	surface-enhanced resonance Raman spectroscopy
SERS	surface-enhanced Raman spectroscopy
SESORS	surface-enhanced, spatially offset Raman spectroscopy

SIERA	surface-enhanced infrared absorption
S/N	signal-to-noise ratio
SNR	signal-to-noise ratio
SNR _{dB}	signal-to-noise ratio measured in decibel
SORS	spatially offset Raman spectroscopy
SRS	stimulated Raman spectroscopy
SSNMR	solid-state nuclear magnetic resonance spectroscopy
STD	saturation transfer difference spectroscopy
T2-star	net dephasing time
TD-NMR	time domain nuclear magnetic resonance spectroscopy
TE	echo time/echo time
TERS	tip-enhanced Raman spectroscopy
TI	inversion time/inversion time
TM	transverse magnetic (see: <i>p-polarization</i>).
TOCSY	total correlation spectroscopy
TOSS	total suppression of spinning sidebands
TR	repetition time
TROSY	transverse relaxation optimized spectroscopy
TRS	transmission Raman spectroscopy
VCD	vibrational circular dichroism
VEELS	vibrational electron energy loss spectroscopy (see: <i>high resolution electron energy loss spectroscopy</i>)

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Acknowledgments: Many of the terms listed within the General Section and the section on vibrational spectroscopy are based on a Glossary of Terms compiled by John Bertie.¹ Additional input and up-dates have been compiled by John Chalmers and Geoffrey Dent, on behalf the UK Infrared and Raman Discussion Group (IRDG).²

¹ John Bertie, with the help of John Chalmers and Peter Griffiths for the Glossary of Terms used in Vibrational Spectroscopy for the *Handbook of Vibrational Spectroscopy*, Vol. 5., pp.3745-3793, edited by J.M Chalmers and P.R. Griffiths, published by John Wiley & Sons Ltd., Chichester ©2002. Help and advice on specific topics for this were given by: Colin Bain, Don Dahm, Bonner Denton, Neil Everall, Kerry Hipps, Richard Jackson, Glen Loppnow, Howard Mark, Robin McDowell, Jeanne McHale, Kirk Michaelian, Larry Nafie, Isao Noda, Andre Sommer, and Gwyn Williams.

² IRDG members, in particular Karen Faulds, Duncan Graham, Neil Everall, Pavel Matousek, and Ewen Smith, contributed in these inputs and additions.

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