Standard Terminology Relating to Molecular Spectroscopy[1, 2]

1. Scope

1.1 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E168 Practices for General Techniques of Infrared Quantitative Analysis (Withdrawn 2015)[4]

E204 Practices for Identification of Material by Infrared Absorption Spectroscopy, Using the ASTM Coded Band and Chemical Classification Index (Withdrawn 2014)[4]

E284 Terminology of Appearance

E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy

E456 Terminology Relating to Quality and Statistics

2.2 *Other Documents:*[5]

ISO Guide 30–1981 (E) Terms and definitions used in connections with reference materials

3. Terminology

absorbance, ***A*****—**the logarithm to the base 10 of the reciprocal of the transmittance, (*T*).

$$A = \log_{10}(1/T) = -\log_{10}T \qquad (1)$$

Discussion—In practice the observed transmittance must be substituted for *T*. Absorbance expresses the excess absorption over that of a specified reference or standard. It is implied that compensation has been effected for reflectance losses, solvent absorption losses, and refractive effects, if present, and that attenuation by scattering is small compared with attenuation by absorption. Apparent deviations from the absorption laws (see **absorptivity**) are due to inability to measure exactly the true transmittance or to know the exact concentration of an absorbing substance.

absorption band—a region of the absorption spectrum in which the absorbance passes through a maximum.

absorption coefficient, α**—**a measure of absorption of radiant energy from an incident beam as it traverses an absorbing medium according to Bouguer's law, $P/P_o = e^{-\alpha b}$.

Discussion—In IRS, α is a measure of the rate of absorption of energy from the evanescent wave.

absorption parameter, ***a*****—**the relative reflection loss per reflection that results from the absorption of radiant energy at a reflecting surface: $a = 1 - R$, and R = the reflected fraction of incident radiant power.

absorption spectrum—a plot, or other representation, of absorbance, or any function of absorbance, against wavelength, or any function of wavelength.

absorptivity, ***a*****—** the absorbance divided by the product of the concentration of the substance and the sample pathlength, $a = A/bc$. The units of b and c shall be specified.

Discussion—1—The recommended unit for *b* is the centimetre. The recommended unit for *c* is kilogram per cubic metre. Equivalent units are g/dm^3, g/L, or mg/cm^3.

Discussion—2—The equivalent IUPAC term is "specific absorption coefficient."

absorptivity, molar, ε**—**the product of the absorptivity, *a*, and the molecular weight of the substance.

Discussion—The equivalent IUPAC term is "molar absorption coefficient."

acceptance angle, ***n*****—***for an optical fiber*, the maximum angle, measured from the longitudinal axis or centerline of the fiber to an incident ray, within which the ray will be accepted for transmission along the fiber by total internal reflection.

Discussion—If the incidence angle exceeds the acceptance angle, optical power in the incident ray will be coupled into leaky modes or rays, or lost by scattering, diffusion, or absorption in the cladding. For a cladded step-index fiber in the air, the sine of the acceptance angle is given by the square root of the difference of the squares of the refractive indexes of the fiber core and the cladding, that is, by the relation as follows:

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[1] This terminology is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.94 on Terminology.

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[2] For other definitions relating to nuclear magnetic resonance, see Practice E386.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

$$\sin A = \sqrt{n_1^2 - n_2^2} \quad (2)$$

where A is the acceptance angle and n_1 and n_2 are the refractive indexes of the core and cladding, respectively. If the refractive index is a function of distance from the center of the core, as in the case of graded index fibers, then the acceptance angle depends on the distance from the core center. The acceptance angle is maximum at the center, and zero at the core-cladding boundary. At any radius, r, the sine of the acceptance angle of a graded index fiber is defined in compliance with that of a step-index fiber as follows:

$$\sin A_r = \sqrt{n_1^{\,2} - n_2^2} \quad (3)$$

where A_r is the acceptance angle at a point on the entrance face at a distance, r, from the center, n_r is the refractive index of the core at a radius, r, and n_2 is the refractive index of the cladding. In air, sin A and sin A_r are the numerical apertures. Unless otherwise stated, acceptance angles and numerical apertures for fiber optics are those for the center of the endface of the fiber, that is, where the refractive index, and hence the numerical aperture, is the highest.

accuracy—the closeness of agreement between an observed value and an accepted reference value (see Terminology E456).

Discussion—The term accuracy, when applied to a set of observed values, will be a combination of a random component and a common systematic error or bias component. Since in routine use, random components and bias components cannot be completely separated, the reported "accuracy" must be interpreted as a combination of these two components.

active fiber optic chemical sensor, *n*—a fiber optic chemical sensor in which a transduction mechanism other than the intrinsic spectroscopic properties of the analyte is used to modulate the optical signal.

Discussion—Examples include a pH sensor composed of a chemical indicator substance whose color changes with pH, and an oxygen sensor coupled to an optical fiber bearing a chemical indicator whose fluorescence intensity depends on oxygen concentration.

aliasing—the appearance of features at wavenumbers other than their true value caused by using a sampling frequency less than twice the highest modulation frequency in the interferogram; also known as "folding."

analytical curve—the graphical representation of a relation between some function of radiant power and the concentration or mass of the substance emitting or absorbing it.

analytical wavelength—any wavelength at which an absorbance measurement is made for the purpose of the determination of a constituent of a sample.

angle of incidence, θ**—**the angle between an incident radiant beam and a perpendicular to the interface between two media.

anti-Stokes line (band)**—**a Raman line (band) that has a frequency higher than that of the incident monochromatic beam.

aperture of an IRE, A'**—**that portion of the IRE surface that can be utilized to conduct light into the IRE at the desired angle of incidence.

apodization—modification of the ILS function by multiplying the interferogram by a weighting function the magnitude of which varies with retardation.

Discussion—This term should strictly be used with reference to a weighting function whose magnitude is greatest at the centerburst and decreases with retardation.

attenuated total reflection (ATR)—reflection that occurs when an absorbing coupling mechanism acts in the process of total internal reflection to make the reflectance less than unity.

Discussion—In this process, if an absorbing sample is placed in contact with the reflecting surface, the reflectance for total internal reflection will be attenuated to some value between zero and unity ($O < R < 1$) in regions of the spectrum where absorption of the radiant power can take place.

attenuation index, κ**—**a measure of the absorption of radiant energy by an absorbing material. κ is related to the absorption coefficient by: $n\kappa = \alpha c_o/4\pi\nu$, where c_o = the speed of light in vacuo, ν = the frequency of radiant energy, and n = the refractive index of the absorbing medium.

background—apparent absorption caused by anything other than the substance for which the analysis is being made.

baseline—any line drawn on an absorption spectrum to establish a reference point representing a function of the radiant power incident on a sample at a given wavelength.

basic NMR frequency, ν_0**—**the frequency, measured in hertz (Hz), of the oscillating magnetic field applied to induce transitions between nuclear magnetic energy levels.

bathochromic shift, *n*—change of a spectral band to longer wavelength (lower frequency) because of structural modifications or environmental influence; also known as "red shift."

beamsplitter—a semireflecting device used to create, and often to recombine, spatially separate beams.

Discussion—Beamsplitters are often made by depositing a film of a high refractive index material onto a flat transmitting substrate with an identical compensator plate being held on the other side of the film.

beamsplitter efficiency—the product $4RT$, where R is the reflectance and T is the transmittance of the beamsplitter.

Beer's law—the absorbance of a homogeneous sample containing an absorbing substance is directly proportional to the concentration of the absorbing substance (see also **absorptivity**)

bias—a systematic error that contributes to the difference between a population mean of the measurements or test results and an accepted or reference value (see Terminology E456).

Discussion—Bias is determined by the following equation:

$$\text{bias} = \bar{e} = \frac{1}{n}\sum_{i=1}^{n} e_i \quad (4)$$

where:

n = the number of observations for which the accuracy is determined,
e_i = the difference between a measured value of a property and its accepted reference value, and
$\bar{e}$ = the mean value of all the e_I.

Bouguer's law—the absorbance of a homogeneous sample is directly proportional to the thickness of the sample in the optical path.

Discussion—Bouguer's law is sometimes also known as Lambert's law.

boxcar truncation—identical effective weighting of all points in the measured interferogram prior to the Fourier transform; all points outside of the range of the measured interferogram take a value of zero.

buffer—*in fiber optics*, see **fiber optic buffer**.

bulk reflection—reflection in which radiant energy is returned exclusively from within the specimen.

Discussion—Bulk reflection may be diffuse or specular.

centerburst—the region of greatest amplitude in an interferogram.

Discussion—For unchirped or only slightly chirped interferograms, this region includes the "zero path difference point" and the "zero retardation point."

certified reference material, *n*—a reference material, the composition or properties of which are certified by a recognized standardizing agency or group.

Discussion—A certified reference material produced by the National Institute of Standards and Technology (NIST) is designated a Standard Reference Material (SRM).

chemical shift (NMR), δ**—**the defining equation for δ is the following:

$$\delta = \frac{\Delta\nu}{\nu_R} \times 10^6 \qquad (5)$$

where ν_R is the frequency with which the reference substance is in resonance at the magnetic field used in the experiment and $\Delta\nu$ is the frequency difference between the reference substance and the substance whose chemical shift is being determined, at constant field. The sign of $\Delta\nu$ is to be chosen such that shifts to the high frequency side of the reference shall be positive.

Discussion—If the experiment is done at constant frequency (field sweep) the defining equation becomes

$$\delta = \frac{\Delta\nu}{\nu_R} \times \left(1 - \frac{\Delta\nu}{\nu_R}\right) \times 10^6 \qquad (6)$$

chirping—the process of dispersing the zero phase difference points for different wavelengths across the interferogram, so that the magnitude of the signal is reduced in the short region of the interferogram where all wavelengths would otherwise constructively interfere.

clad—see **cladding**.

cladding, *n—of an optical fiber*, a layer of a optically transparent lower refractive index material in intimate contact with a core of higher refractive index material used to achieve total internal reflection.

Discussion—The cladding confines electromagnetic waves to the core, provides some protection to the core, and also transmits evanescent waves that usually are bound to waves in the core.

concentration, *c***—**the quantity of the substance contained in a unit quantity of sample.

Discussion—For solution work, the recommended unit of concentration is grams of solute per litre of solution.

core, *n—of an optical fiber*, the center region of an optical waveguide through which radiant energy is transmitted.

Discussion—In a dielectric waveguide such as an optical fiber, the refractive index of the core must be higher than that of the cladding. Most of the radiant energy is confined to the core.

correlation coefficient (*r*)**—**a measure of the strength of the linear relationship between *X* and *Y*, calculated by the equation:

$$r_{xy} = \frac{\left(\sum_{i=1}^{n} X_i Y_i\right)}{\left(\sum_{i=1}^{n} X_i^2\right)^{1/2}\left(\sum_{i=1}^{n} Y_i^2\right)^{1/2}} \qquad (7)$$

where:

n = the number of observations in *X* and *Y*.

Discussion—X_i and Y_i are any two mean corrected variables. For the simple linear regression only,

$$r_{xy} = R = (\text{sign of } b_1)(R^2)^{1/2} \qquad (8)$$

where:

R^2 = the coefficient of multiple determination.

critical angle, θ_c**—**the angle whose sine is equal to the relative refractive index for light striking an interface from the greater to the lesser refractive medium: $\theta_c = \sin^{-1} n_{21}$, where n_{21} = the ratio of the refractive indices of the two media.

Discussion—Total reflection occurs when light is reflected in the more refractive of two media from the interface between them at any angle of incidence exceeding the critical angle.

depth of penetration, d_p**—**in internal reflection spectroscopy, the distance into the less refractive medium at which the amplitude of the evanescent wave is e^{-1} (that is, 36.8 %) of its value at the surface:

$$d_p = \frac{\lambda_1}{2\pi\left(sin^2\theta - \eta_{21}{}^2\right)^{1/2}} \qquad (9)$$

where: $n_{21} = n_2/n_1$ = refractive index of sample divided by that of the IRE; $\lambda_1 = \lambda/n_1$ = wavelength of radiant energy in the sample; and θ = angle of incidence.

derivative absorption spectrum—a plot of rate of change of absorbance or of any function of absorbance with respect to wavelength or any function of wavelength, against wavelength or any function of wavelength.

difference absorption spectrum—a plot of the difference between two absorbances or between any function of two absorbances, against wavelength or any function of wavelength.

diffuse reflection—reflection in which the flux is scattered in many directions by diffusion at or below the surface (see Terminology E284).

digitization—the conversion of an analog signal to digital values using an analog-to-digital converter "sampling" or "digital sampling."

digitization noise—the noise generated in an interferogram through the use of an analog-to-digital converter whose least significant bit represents a value comparable to, or greater than, the peak-to-peak noise level in the analog data.

dilution factor—the ratio of the volume of a diluted solution to the volume of original solution containing the same quantity of solute as the diluted solution.

double modulation, *n*—a technique in which a modulated signal is further varied by a second means.

Discussion—As an example, a spectrometer could generate a modulated signal while at the same time that signal is further varied by an external higher frequency modulator; on detection, the conventional spectrometric signal is filtered out so that only the high frequency signal is recorded.

double-pass internal reflection element—an internal reflection element in which the radiant power transverses the length of the optical element twice, entering and leaving via the same end.

effective pathlength (or effective thickness), d_e**—***in internal reflection spectroscopy,* the analog of the sample thickness in transmission spectroscopy that represents the distance of propagation of the evanescent wave within an absorbing sample in IRS. It is defined from the relationship: $R = 1 - \alpha d_e$, and is related to the absorption parameter by: $a = \alpha\ d_e$.

evanescent wave—the standing wave that exists in the less refractive medium, normal to the reflecting surface of the IRE during internal reflection.

extrinsic fiber optic chemical sensor, *n*—a fiber optic chemical sensor in which modulation of the optical signal is not effected through a change in the properties of the fiber itself.

Discussion—Examples include a pH sensor composed of a chemical indicator immobilized at the end of the optical fiber, and a sensor based on Raman, fluorescence, infrared, visible, or other spectral information gathered in the acceptance cone of the fiber.

far-infrared—pertaining to the infrared region of the electromagnetic spectrum with wavelength range from approximately 25 to 1000 µm (wavenumber range 400 to 10 cm^{-1}).

fast Fourier transform (FFT)—a method for speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeroes.

fiber optic buffer, *n*—material placed on or around a cladded optical fiber to protect it from mechanical damage.

Discussion—Mechanical damage can be caused by such things as microbends and macrobends formed during manufacture, spooling, subsequent handling, and pressure applied during use. Buffers may be bonded to the cladding and may also serve the purpose of preventing ambient energy from entering the core.

fiber optic chemical sensor, *n*—a fiber optic sensor that responds to a chemical stimulus.

fiber optic sensor, *n*—a device that responds to an external stimulus and transmits through an optical fiber a modulated optical signal, indicating one or more characteristics of the stimulus.

Discussion—Examples include sensors which provide a suitable signal or impulse to a meter. Such sensors might be found as the active elements in pH meters, strain gages, or pressure gages.

fiber optics, *n*—the branch of science and technology devoted to the transmission of radiant energy through fibers made of transparent materials.

Discussion—Transparent materials include glass, fused silica, and plastic. Optical fibers in fiber optic cables may be used for data transmission, and for sensing, illumination, endoscopic, control, and display purposes, depending on their use in various geometric configurations, modes of excitation, and environmental conditions. The fibers may be wound and bound in various shapes and distributions singly or in bundles. Bundles may be aligned or unaligned. Aligned bundles are often used to transmit and display images.

filter—a substance that attenuates the radiant power reaching the detector in a definite manner with respect to spectral distribution.

filter, neutral—a filter that attenuates the radiant power reaching the detector by the same factor at all wavelengths within a prescribed wavelength region.

fixed-angle internal reflection element—an internal reflection element which is designed to be operated at a fixed angle of incidence.

fluorescence—the emission of radiant energy from an atom, molecule, or ion resulting from absorption of a photon and a subsequent transition to the ground state without a change in total spin quantum number.

Discussion—The initial and final states of the transition are usually both singlet states. The average time interval between absorption and fluorescence is usually less than 10^{-6} s.

*folding***—**see **aliasing.**

Fourier transform (FT)—the mathematical process used to convert an amplitude-time spectrum to an amplitude-frequency spectrum, or *vice versa.*

Discussion—In FT-IR spectrometry, retardation is directly proportional to time; therefore the FT is commonly used to convert an amplitude-retardation spectrum to an amplitude-wavenumber spectrum, and *vice versa.*

Fourier transform infrared (FT-IR) spectrometry—a form of infrared spectrometry in which an interferogram is obtained; this interferogram is then subjected to a Fourier transform to obtain an amplitude-wavenumber (or wavelength) spectrum.

Discussion—1—The abbreviation FTIR is not recommended.

Discussion—2—When FT-IR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; for example, GC/FT-IR; HPLC/FT-IR, and the use of FT-IR should be explicit; that is, FT-IR not IR.

frequency, ν**—** the number of cycles per unit time.

Discussion—The recommended unit is the hertz (Hz) (one cycle per second).

frustrated total reflection (FTR)—the reflection which occurs when a nonabsorbing coupling mechanism acts in the process of total internal reflection to make the reflectance less than unity.

Discussion—In the process the reflectance can vary continuously between zero and unity if: (*1*) An optically transparent medium is within a fraction of a wavelength of the reflecting surface and its distance from the reflecting surface is changed, or (*2*) Both the angle of incidence and the refractive index of one of the media vary in an appropriate manner.

In these cases part of the radiant power may be transmitted through the interface into the second medium without loss at the reflecting surface such that transmittance plus reflectance equals unity. It is possible, therefore to have this process taking place in some spectral regions even when a sample having absorption bands is placed in contact with the reflecting surface.

high-resolution NMR spectrometer—an NMR apparatus that is capable of producing, for a given isotope, line widths that are less than the majority of the chemical shifts and coupling constants for that isotope.

DISCUSSION—By this definition, a given spectrometer may be classed as a high-resolution instrument for isotopes with large chemical shifts, but may not be classed as a high-resolution instrument for isotopes with smaller chemical shifts.

hole-burning, *n*—in luminescence, the photo-induced disappearance of a narrow segment within a broader absorption or emission band.

DISCUSSION—Holes are produced by the disappearance of resonantly excited molecules because of photochemical or photophysical processes.

infrared—pertaining to the region of the electromagnetic spectrum with wavelength range from approximately 0.78 to 1000 µm (wavenumber range 12 800 to 10 cm^{-1}).

infrared spectroscopy—pertaining to spectroscopy in the infrared region of the electromagnetic spectrum.

DISCUSSION—1—Spectroscopy and other related terms are defined in Terminology E135.

DISCUSSION—2—Common applications of infrared spectroscopy are the identification of materials and the quantitative analysis of materials (see, for example, Practices E204 and Practices E168).

instrument line shape (ILS) function—the FT of the function by which an interferogram is weighted.

DISCUSSION—This weighting may be performed optically, due to the finite optical throughput, or digitally, through multiplication by an apodization function, or both. The ILS function is the profile of the spectrum of a monochromatic source producing a beam with the same throughput as the beam in the actual measurement being performed.

instrument response time—the time required for an indicating or detecting device to undergo a defined displacement following an abrupt change in the quantity being measured.

integration period, π—the time, in seconds, required for the pen or other indicator to move 98.6 % of its maximum travel in response to a step function.

DISCUSSION—For instruments with a first-order response, the integration period will be approximately equal to four times the exponential time constant. It is equal to the period, classically defined, for a second order, critically damped response system.

intercorrelation coefficient, (r_{XX}) **—**a measure of the linear association between values of the same type of variable expressed as a correlation coefficient, (r).

DISCUSSION—The variables X and Y are replaced by X_j and X_k in the equation for the correlation coefficient, r.

interferogram, I (δ)**—**record of the modulated component of the interference signal measured as a function of retardation by the detector.

DISCUSSION—1—An alternate symbol is $I(x)$.

DISCUSSION—2—The recommended symbol for the spectrum computed from $I(\delta)$ is $B(\nu)$. An alternate symbol is $B(\sigma)$.

interferogram, double-sided—interferogram measured with approximately equal retardation on either side of the centerburst.

interferogram, laser reference—sinusoidal interferogram of a laser source measured at the same time as the signal interferogram.

DISCUSSION—The zero crossings of this interferogram are used to control sampling of the signal interferogram. It may also be noted that other effectively monochromatic sources can be used in place of the laser.

interferogram, signal—interferogram of the beam of radiant energy whose spectrum is desired.

interferogram, single-sided—interferogram in which sampling is initiated close to the centerburst and continues through that point to the maximum retardation desired.

interferogram, white light—reference interferogram of a broadband light source measured at the same time as the signal interferogram and used to initiate data acquisition of consecutive scans for signal-averaging.

interferometer—device used to divide a beam of radiant energy into two or more paths, generate an optical path difference between the beams, and recombine them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

interferometer, Genzel—interferometer in which the beam is focused in the plane of the beamsplitter and collimated before the moving mirror(s).

interferometer, lamellar grating—interferometer in which the beam is reflected from two interleaved mirrors, one of which is stationary while the other is movable.

DISCUSSION—This type of interferometer is generally used only for far infrared spectrometry.

interferometer, Michelson—interferometer in which an approximately collimated beam of radiant energy is divided into two paths by a beamsplitter; one beam is reflected from a movable mirror and the other from a stationary mirror, and they are then recombined at the beamsplitter.

interferometer, rapid-scanning—interferometer in which the retardation is varied rapidly enough that the modulation frequencies in the interferogram are sufficiently high that the interferogram signal can be amplified directly without additional modulation by an external chopper.

interferometer, refractively scanned—interferometer in which the retardation between two beams is generated by the movement of a wedged optical element.

interferometer, slow-scanning—interferometer in which the retardation is continuously varied, but so slowly that an external chopper is needed to modulate the beam at a frequency which is high enough for ac signal amplification.

interferometer, stepped-scanning—interferometer in which the movable element is held stationary for the length of time required for signal integration and digitization of each sample point, and then translated to the next sample point.

internal conversion, *n*—a transition between electronic states of the same total spin quantum number (multiplicity).

internal, reflection attachment, IRA—the transfer optical system which supports the IRE, directs the energy of the radiant beam into the IRE, and then redirects the energy into the spectrometer or onto the detector. The IRA may be part of an internal reflection spectrometer or it may be placed into the sampling space of a spectrometer.

internal reflection element (IRE)—the transparent optical element used in internal reflection spectroscopy for establishing the conditions necessary to obtain the internal reflection spectra of materials.

DISCUSSION—Radiant power is propagated through it by means of internal reflection. The sample material is placed in contact with the reflecting surface or it may be the reflecting surface itself. If only a single reflection takes place from the internal reflection element the element is said to be a single reflection element; if more than one reflection takes place, the element is said to be a multiple reflection element. When the element has a recognized shape it is identified according to each shape, for example, internal reflection prism, internal reflection hemicylinder, internal reflection plate, internal reflection rod, internal reflection fiber, etc.

internal reflection spectroscopy (IRS)—the technique of recording optical spectra by placing a sample material in contact with a transparent medium of greater refractive index and measuring the reflectance (single or multiple) from the interface, generally at angles of incidence greater than the critical angle.

intersystem crossing—-a transition between electronic states that differ in total spin quantum number (multiplicity).

DISCUSSION—Current experimental evidence indicates this process is nonradiative.

intrinsic fiber optic chemical sensor, *n*—a fiber optic chemical sensor in which the modulation of the optical signal is effected through a change in the properties of the optical fiber itself, and such modulation occurs while the radiant energy is guided by the optical fiber.

irreversible fiber optic chemical sensor, *n*—a fiber optic chemical sensor that undergoes a permanent depletion or degradation of the transduction element as a result of the transduction process.

DISCUSSION—An example is a sensor based on an indicator that reacts irreversibly with the target analyte and that cannot be replenished after measurement.

isoabsorptive point—a wavelength at which the absorptivities of two or more substances are equal.

isosbestic point—the wavelength at which the absorptivities of two substances, one of which can be converted into the other, are equal.

isostilbic point, *n*—in luminescence, the wavelength at which the intensity of emission of a sample does not change during a physical interaction or chemical reaction.

level one (1) test, *n*—a simple series of measurements designed to provide quantitative data on various aspects of instrument performance and information on which to base the diagnosis of problems.

level zero (0) test, *n*—a routine check of instrument performance, that can be done in a few minutes, designed to virtually detect significant changes in instrument performance and provide a database to determine instrument function over time.

linear dispersion—the derivative, $dx/d\lambda$, where x is the distance along the spectrum, in the plane of the exit slit, and λ is the wavelength.

linearity—the property of paired (X, Y) data such that when an equation for a straight line is calculated for that data using linear least-square regression mathematics, no statistically significant reduction to the sum-squared difference of the data from that line is achieved by the addition of another function to that equation for the straight line.

lock signal (NMR)—the NMR signal used to control the field-frequency ratio of the spectrometer. It may or may not be the same as the reference signal.

luminescence—the emission of radiant energy during a transition from an excited electronic state of an atom, molecule, or ion to a lower electronic state.

DISCUSSION—1—The recommended unit for "sample pathlength" is centimetres. This distance does not include the thickness of the walls of any absorption cell in which the specimen is contained.

DISCUSSION—2—In strict usage, a more appropriate term would be "specimen pathlength." This is currently under advisement by Committee E13.

mid-infrared—pertaining to the infrared region of the electromagnetic spectrum with wavelength range from approximately 2.5 to 25 µm (wavenumber range 4000 to 400 cm^{-1}).

modulate, *v*—to vary a characteristic or parameter of an entity in accordance with a characteristic or parameter of another entity.

modulation frequency, f_v**—**the frequency, in Hz, at which radiant energy of a given wavenumber is modulated by a rapid-scanning interferometer.

DISCUSSION—1—This is given by the product of the wavenumber (cm^{-1}) and the rate of change of retardation ($cm \cdot s^{-1}$).

DISCUSSION—2—An alternate symbol is f_o.

molar absorptivity, ε—see **absorptivity, molar.**

monochromator—a device or instrument that, with an appropriate energy source, may be used to provide a continuous calibrated series of electromagnetic energy bands of determinable wavelength or frequency range.

multiple correlation coefficient, (R)**—**the correlation, $r_{y\hat{y}}$, between the accepted reference values, Y_i, and the values determined using the calibration equation, $\hat{Y}_i$, equal to the square root of the coefficient of multiple determination, R^2.

near-infrared—pertaining to the infrared region of the electromagnetic spectrum with wavelength range from approximately 0.78 to 2.5 µm (wavenumber range 12 800 to 4000 cm^{-1}).

*neutral filter***—**see **filter, neutral.**

NMR absorption band; NMR band—a region of the spectrum in which a detectable signal exists and passes through one or more maxima.

NMR absorption line—a single transition or a set of degenerate transitions is referred to as a line.

NMR apparatus; NMR equipment—an instrument comprising a magnet, radio-frequency oscillator, sample holder, and a detector that is capable of producing an electrical signal suitable for display on a recorder or an oscilloscope, or which is suitable for input to a computer.

nuclear magnetic resonance (NMR) spectroscopy—that form of spectroscopy concerned with radio-frequency-induced transitions between magnetic energy levels of atomic nuclei.

numerical aperture (NA), *n*—the sine of one half of the vertex angle of the largest cone of meridional rays that can enter or leave an optical system or element, multiplied by the refractive index of the medium in which the cone is located.

Discussion—Numerical aperture is generally measured with respect to an image point and will vary as that point is moved. For an optical fiber in which the refractive index decreases abruptly from n_1 on the axis to n_2 in the cladding, the maximum theoretical numerical aperture is given by the relation, as follows:

$$NA = n_0 \sin A = (n_1^{2} - n_2^{2})^{1/2} \qquad (10)$$

where, n_0 is the refractive index of the medium from which radiant energy is being launched into the fiber (for air, $n_0 = 1$), A is the acceptance angle, n_1 is usually taken as the refractive index of the core and [mdit]n_2 is the refractive index of the innermost homogeneous cladding. However, for a graded-index fiber, because the NA varies with the distance from the center of the fiber, the true NA depends on the maximum refractive index found on the fiber end-face, which is at the center and is progressively less as the distance from the center increases. Typical numerical apertures for optical fibers range from 0.25 to 0.45. Loose terms such as "openness," "light-gathering ability," "angular acceptance," and "acceptance cone" have been used to describe the numerical aperture (see **acceptance angle**).

Nyquist frequency—modulation frequency or wavenumber above which aliasing occurs.

Discussion—The Nyquist frequency is one half of the sampling frequency.

observed fluorescence lifetime, τ—the time required for the fluorescence intensity to decay to 1/e of its initial value after the termination of excitation.

optical fiber, *n*—a filament-shaped dielectric material that guides radiant energy.

Discussion—An optical fiber usually consists of a single discrete optically transparent transmission element consisting at least of a cylindrical core with cladding on the outside. Though most optical fiber cross sections are circular, there are other cross sections, such as elliptical, rectangular, planar and slotted, for special purposes. All of them are collectively termed as waveguides. The refractive index of the core must be higher than that of the cladding for electromagnetic waves (photons) to remain within and propagate in the fiber. If the incidence angle of rays at the core-cladding interface exceeds the critical angle, the rays will be totally reflected back into the core. The electromagnetic waves can be modulated with an information-bearing signal.

*optical path difference***—**see **retardation.**

*optical retardation***—**see **retardation.**

passive fiber optic chemical sensor, *n*—a fiber optic sensor that utilizes the intrinsic spectroscopic properties of the analyte to modulate the optical signal.

Discussion—Examples include remote fiber Raman, fluorescence, infrared, and visible spectroscopic sensors.

phase correction—the operation in which the effects of an asymmetrical or chirped interferogram are corrected to eliminate instrumental phase contributions.

phase modulation—modulation produced by rapid oscillation of one mirror of a scanning interferometer through an amplitude which is smaller than the shortest wavelength in the spectrum to produce an interferogram which is, to a good approximation, the first derivative of the conventional interferogram.

phosphorescence—the emission of radiant energy from an atom, molecule, or ion resulting from absorption of a photon and a subsequent transition to the ground state with a change in total spin quantum number (see also **intersystem crossing**).

Discussion—The initial state of the transition is usually a triplet state. The average time interval between absorption and phosphorescence is usually greater than 10^{-6} s.

photometer—a device so designed that it furnishes the ratio, or a function of the ratio, of the radiant power of two electromagnetic beams. These two beams may be separated in time, space, or both.

photometric linearity—the ability of a photometric system to yield a linear relationship between the radiant power incident on its detector and some measurable quantity provided by the system.

Discussion—In the case of a simple detector-amplifier combination, the relationship is a direct proportionality between incident radiant power and the deflection of a meter needle or recorder pen.

precision—the closeness of agreement between randomly selected individual measurements or test results (see Terminology E456).

Discussion—The standard deviation of error of a measurement may be used as a measure of *imprecision*.

principal component analysis—a mathematical procedure for resolving sets of data into orthogonal components whose linear combinations approximate the original data to any desired degree of accuracy.

Discussion—As successive components are calculated, each component accounts for the maximum possible amount of residual variance in the set of data. In spectroscopy, the data are usually spectra, and the number of components is smaller than or equal to the number of variables or number of spectra, whichever is less.

pulse Fourier transform NMR—a form of NMR in which the sample is irradiated with one or more pulse sequences of radio-frequency power spaced at uniform time intervals, and the averaged free induction decay following the pulse sequences is converted to a frequency domain spectrum by a Fourier transformation.

quenching, *n*—the reduction of fluorescence by a competing deactivating process resulting from specific interaction between a fluorophor and another substance present in the system.

radiant energy—energy transmitted as electromagnetic waves.

radiant power, P**—**the rate at which energy is transported in a beam of radiant energy.

Raman line (band)—a line (band) that is part of a Raman spectrum.

Raman shift—the displacement in wavenumber of a Raman line (band) from the wavenumber of the incident monochromatic beam.

Discussion—Raman shifts are usually expressed in units of cm^{-1} . They correspond to differences between molecular vibrational, rotational, or electronic energy levels.

Raman spectrum—the spectrum of the modified frequencies resulting from inelastic scattering when matter is irradiated by a monochromatic beam of radiant energy.

Discussion—Raman spectra normally consist of lines or bands at frequencies higher and lower than that of the incident monochromatic beam.

ratioed spectrum, *n*—the calculated ratio of two single-beam spectra, one of which is a background spectrum.

reference compound (NMR)—a selected material to whose signal the spectrum of a sample may be referred for the measurement of chemical shift (see also **chemical shift**).

reference material—a material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials (ISO Guide 30–1981 (E)).

reference spectrum, *n*—an established sample spectrum.

Discussion—This spectrum is typically stored in retrievable format so that it may be compared against the sample spectrum of an analyte.

Discussion—This term has sometimes been used to refer to a **background spectrum;** such usage is not recommended.

reflectance, R**—**the ratio of the radiant power reflected by the sample to the radiant power incident on the sample.

refractive index, *n*—the phase velocity of radiant power in a vacuum divided by the phase velocity of the same radiant power in a specified medium. When one medium is a vacuum, n is the ratio of the sine of the angle of incidence to the sine of the angle of refraction.

regenerable fiber optic chemical sensor, *n*—an active fiber optic chemical sensor that can be used for repetitive measurements by reviving an otherwise permanently depleted or degraded transduction element by chemical or physical means.

Discussion—An example is a sensor based on an indicator that reacts irreversibly with the target analyte, and which makes provision for the periodic regeneration of the indicator substance.

resolving power, R**,** *n*—the ratio $\lambda/\Delta\lambda$ where λ is the wavelength of radiant energy and $\Delta\lambda$ is the resolution expressed in wavelength units; or, alternatively, the ratio $\bar{\nu}/\Delta\bar{\nu}$ where $\bar{\nu}$ is the wavenumber of radiant energy being examined and $\Delta\bar{\nu}$ is the resolution expressed in wavenumber units.

resolution $\Delta\lambda$, $\Delta\bar{\nu}$ **,** *n—of a dispersive spectrometer, in mole–cular spectroscopy*, the wavelength interval, $\Delta\lambda$, or wavenumber interval, $\Delta\bar{\nu}$, of radiant energy leaving the exit slit of a monochromator measured at half the peak detected radiant power.

Discussion—1—For further clarification, the conditions for measurement of the resolution should be given.

Discussion—2—The term "practical resolution," $(\Delta\lambda)^{\pi}S/N$, is the resolution applicable to an instrument operated at a given integration period, π, and a given signal-to-noise ratio, S/N, measured at or near 100 % on a transmittance scale.

Discussion—3—The term "limiting resolution," $(\Delta\lambda)_L$, is the minimum resolution achievable under optimum experimental conditions.

Discussion—4—The term "theoretical resolution," $(\Delta\lambda)_0$, is the computed resolution. This term should be used sparingly and only when all the factors in the computation of resolution are given.

retardation, δ**—**optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation".

Discussion—1—The recommended unit for retardation is cm.

Discussion—2—An alternate symbol is x.

retardation, maximum, Δ**—**the greatest retardation generated by an interferometer in a given scan.

Discussion—1—The nominal resolution of the spectrum is $1/\Delta\ cm^{-1}$.

Discussion—2—An alternate symbol is X.

reversible fiber optic chemical sensor, *n*—a fiber optic chemical sensor in which the transduction element does not undergo a permanent depletion or degradation as a result of the transduction process.

Discussion—An example is an oxygen sensor based on the reversible quenching of fluorescence in an indicator substance by the presence of oxygen.

root mean square difference, (*RMSD***)—**a measure of accuracy determined by the following equation:

$$RMSD = \left(\frac{1}{n}\sum_{i=1}^{n} e_i^2\right)^{1/2} \tag{11}$$

where:

n = the number of observations for which the accuracy is determined, and

e_i = the difference between a measured value of a property and its accepted value.

Discussion—Let $X_1, X_2, \cdots, X_i, \cdots, X_n$ be determinations of a property of a material in n specimens, and let $Y_1, Y_2, \cdots, Y_i, \cdots, Y_n$ be similar determinations by a reference method. Define $e_i = Y_i - X_i$. The *RMSD* contains both systematic and random components of the differences.

sample pathlength, *b*—*in a spectrophotometer*, the distance, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

sample spectrum, *n*—a spectrum, either single-beam or ratioed, that contains spectral features due to an analyte of interest.

sampling—see **digitization.**

sampling frequency—number of interferogram data points digitized per second in a single scan.

sampling interval—difference in retardation between successive sample points in an interferogram.

scattering, 90° (or 180°)—scattering which is observed at an angle of 90° (or 180°) to the direction of the incident beam.

Discussion—These are the usual scattering angles for Raman spectroscopy.

self-quenching, *n*—in luminescence, the reduction of luminescence through the depletion of an excited atomic or molecular entity by interaction with another entity of the same species in the ground state.

sequential excitation NMR; continuous wave (CW) NMR—a form of high-resolution NMR in which nuclei of different field-frequency ratio at resonance are successively excited by sweeping the magnetic field or the radio frequency.

signal-to-noise ratio, *S/N***—**the ratio of the signal, *S*, to the noise, *N*, as indicated by the instrumental read-out indicator.

Discussion—1—Noise as used here is the random variation of signal with time.

Discussion—2—The recommended measure of noise is the maximum peak-to-peak excursion of the indicator averaged over a series of five successive intervals, each of duration ten times the integration period. In some instruments signal-to-noise ratio varies with the signal.

simple linear regression—a statistical method of estimating the linear relationship between a dependent variable *y* and an independent variable *x* using the linear model

$$y = b_o + b_z X + \varepsilon \tag{12}$$

Discussion—The coefficient b_o is the *intercept* and the coefficient b_z is the slope, which are calculated from the data taken on *y* and *x* and ε is the residual error.

single-beam spectrum, *n*—a spectrum determined through one physical path.

Discussion—This spectrum may be simply the instrument response function as measured by the detector, or it may include spectral features resulting from the presence of a sample or sampling device. In a Fourier transform instrument, the single-beam spectrum is that obtained using Fourier transformation of the detected signal.

single-pass internal reflection element—in internal reflection spectroscopy, an internal reflection element in which the radiant power transverses the length of the element only once; that is, the radiant power enters at one end of the optical element and leaves via the other end.

singlet state—an electronic state with a total spin quantum number of zero.

*specimen pathlength***—**see **sample pathlength**.

*spectral bandwidth***—**see **resolution**.

spectral position—the effective wavelength or wavenumber of an essentially monochromatic beam of radiant energy.

*spectral resolution***—**see **resolving power**.

spectral slit width—the mechanical width of the exit slit, divided by the linear dispersion in the exit slit plane.

spectrograph—an instrument with one slit that uses photography to obtain a record of a spectral range simultaneously. The radiant power passing through the optical system is integrated over time, and the quantity recorded is a function of radiant energy.

spectrometer—an instrument for measuring some function of power, or other physical quantity, with respect to spectral position within a spectral range.

spectrometry, *n*—The branch of physical science treating the theory and practice of the measurement of spectra.

spectrophotometer—a spectrometer with associated equipment, so designed that it furnishes the ratio, or a function of the ratio, of the radiant power of two beams as a function of spectral position. The two beams may be separated in time, space, or both.

spectroscopy, *n*—the branch of physical science treating the theory and interpretation of spectra (see Terminology E135).

spectrum, *n*—an actual or notational arrangement of the component parts of any phenomenon, as electromagnetic waves or particles, ordered in accordance with the magnitude of a common physical property, as wavelength, frequency, or mass.

spectrum, internal reflection—the spectrum obtained by the technique of internal reflection spectroscopy.

Discussion—Depending on the angle of incidence the spectrum recorded may qualitatively resemble that obtained by conventional transmission measurements, may resemble the mirror image of the dispersion in the index of refraction, or may resemble some composite of the two.

specular reflection—reflection without diffusion, in accordance with the laws of optical reflection, as in a mirror, (see Terminology E284).

Discussion—Specular reflection is preferred to the term regular reflection.

spin-spin coupling constant (NMR) *J***—**a measure, expressed in hertz (Hz), of the indirect spin-spin interaction of different magnetic nuclei in a given molecule.

Discussion—The notation ${}^{N}\mathrm{J}_{AB}$ is used to represent a coupling over bonds between nuclei *A* and *B*. When it is necessary to specify a particular isotope, a modified notation may be used, such as ${}^{3}J({}^{1}{}^{5}NH)$.

*SRP***,** *n*—see **stray radiant power**.

*SRPR***,** *n*—see **stray radiant power ratio**.

standard error of calibration, (SEC)**—**a measure of calibration accuracy determined by the following equation:

$$SEC = \left(\frac{1}{n - p - 1} \sum_{i=1}^{n} e_i^2 \right)^{1/2} \tag{13}$$

where:

n = the number of observations in the calibration data set,
p = the number of independent variables in the calibration, and
e_i = the difference between a measured value of a property and its accepted value.

standard error of performance, (SEP)**—**a measure of accuracy determined by the following equation:

$$SEP = \left[\frac{1}{n - 1} \sum_{i=1}^{n} (e_i - \bar{e})^2 \right]^{1/2} \tag{14}$$

where:

n = the number of observations for which the accuracy is determined,
e_i = the difference between a measured value of a property and its accepted reference value, and
$\bar{e}$ = is the mean of all the e_I.

Stokes line (band)—a Raman line (band) that has a frequency lower than that of the incident monochromatic beam.

stray radiant energy—all radiant energy that reaches the detector at wavelengths that do not correspond to the spectral position under consideration.

stray radiant power, P_s**—**the total detected radiant power outside a specified wavelength (wave number) interval each side of the center of the spectral band passed by the monochromator under stated conditions for wavelength (wave number), slit dimensions, light source, and detector.

stray radiant power ratio, P_s/P_t**—**the ratio of stray radiant power to the total detected radiant power.

DISCUSSION—$P_t = P_d + P_s$ where P_d is the power detected within the specified wave length (wavenumber)-interval each side of the center of the spectral band passed by the monochromator.

surface reflection—reflection in which radiant energy is returned exclusively at the surface of the specimen.

throughput—the vector product of the area and solid angle of a beam at its focus and the square of the refractive index of the medium in which the beam is focused.

transflection—an experimental method whereby radiant energy that is transmitted through the specimen is returned through the specimen by means of an external reflector.

DISCUSSION—Transflection is sometimes referred to as transmission/reflection interaction.

transmission/reflection interaction—see **transflection.**

transmittance, *T***—**the ratio of radiant power transmitted by the sample to the radiant power incident on the sample.

DISCUSSION—In practice the sample is often a liquid or a gas contained in an absorption cell. In this case, the observed transmittance is the ratio of the radiant power transmitted by the sample in its cell to the radiant power transmitted by some clearly specified reference material in its cell, when both are measured under the same instrument conditions such as spectral position and slit width. In the case of solids not contained in a cell, the radiant power transmitted by the sample is also measured relative to that transmitted by a clearly specified reference material. The observed transmittance is seldom equal to the true transmittance.

triplet state—an electronic state with a total spin quantum number of one.

ultraviolet—pertaining to the region of the electromagnetic spectrum from approximately 10 to 380 nm. The term ultraviolet without further qualification usually refers to the region from 200 to 380 nm.

variable-angle internal reflection element—an internal reflection element which can be operated over a range of angles of incidence.

visible—pertaining to radiant energy in the electromagnetic spectral range visible to the normal human eye (approximately 380 to 780 nm).

wavelength, λ**—**the distance, measured along the line of propagation, between two points that are in phase on adjacent waves.

DISCUSSION—The recommended unit of wavelength in the infrared region of the electromagnetic spectrum is the micrometre. The recommended unit in the ultraviolet and visible region of the electromagnetic spectrum is the nanometre or the angstrom.

wavenumber, $\bar{\nu}$**—**the number of waves per unit length.

DISCUSSION—The usual unit of wavenumber is the reciprocal centimetre, cm^{-1}. In terms of this unit the wavenumber is the reciprocal of the wavelength, λ, when λ is expressed in centimetres.

zero-filling—addition of zero-valued points to the end of a measured interferogram.

DISCUSSION—The result of performing the FT of a zero-filled interferogram is to produce correctly interpolated points in the computed spectrum.

*zero path difference point***—**see **centerburst.**

*zero retardation point***—**see **centerburst.**

4. Keywords

4.1 chemometrics; definitions; molecular spectroscopy and statistics; terminology