SPECTROSCOPY

1. Introduction

Interaction between electromagnetic radiation and matter is studied using spectroscopic methods. The study of this interaction as a function of frequency or wavelength and electromagnetic radiation itself makes spectroscopy a very versatile and powerful tool for the investigation of atomic and molecular structure. It allows identification of samples, of the determined composition of the samples (speciation), and of the amount of different species present (quantification), these being objectives in any analytical procedure. The aspect of quantification in spectroscopic methods is called spectrometry. Within the wide range of electromagnetic radiation, optical spectroscopy conventionally summarizes the ultraviolet (uv), visible, and infrared (ir) spectral regions. However, it is extended to include shorter and longer wavelengths that interact with matter by the same basic mechanism of coupling with the electric vector of the electromagnetic field. Accordingly, mass, acoustic, particle energy, and magnetic resonance spectroscopy are excluded (see MASS SPECTROMETRY; MAGNETIC SPIN RESONANCE).

Spectroscopic techniques can both identify and quantify in a single measurement. Therefore, the identical application of spectroscopy range from bench analysis of chemical samples in the laboratory over process monitoring in chemical plants to detection and monitoring of pollutants in the atmosphere, and as new applications in optical biosensors and chemosensors. All of these will be discussed in this article. A wide range of compounds can be detected with high specificity, even in multicomponent mixtures. Many spectroscopic methods are noninvasive, involving no sample collection, pretreatment, or contamination (see NONDESTRUCTIVE EVALUATION). Because only optical access to the sample is needed, instruments can be remotely situated for environmental and process monitoring using, eg, fiber optics. Spectroscopy provides rapid real-time results, and allows continuous long-term monitoring. In addition, spectra carry information on sample conditions, eg, temperature and pressure.

The many applications of optical spectroscopic methods rely just on a few basic mechanisms of light–matter interaction, eg, scattering, absorption, and emission. In spectroscopic analysis, species are identified by the frequencies and structures of absorption, emission, or scattering features. Since electromagnetic emission exhibits amplitude, frequency, phase, state of polarization, and time dependence, all these features can be used to characterize the interaction between light and matter, and to quantify it by changing the amplitude or intensity.

Absorption (α absorptance, absorption factor), transmision (τ transmittance, transmission factor), and reflection (ρ reflectance, reflection factor) of a nonscattering and nonfluorescent sample add up to 1 (1):

$$\alpha + \tau + \rho = 1 \tag{1}$$

According to International Union of Pure and Applied Chemistry (IUPAC) rules, the terminology for the different quantities in spectroscopy depend on the units of concentration, on whether the absorbance is decadic or a napierian logarithm, and on the conventions employed in the different spectral regions. In case of measuring gases and liquids in cells, multiple reflections on the cell walls can

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influence the absorptance. For this reason, sometimes an internal absorptance α_i is defined. This happens also in the case of solid samples that cannot be compensated by a nonabsorbing reference sample as is done in the case of liquids or gasses, for which the reference cell is filled with all components except the one to be measured. In optical spectroscopy, internal properties are defined to exclude surface effects and effects of the cuvette, eg, reflexion losses. This leads to the customary form of the Lambert-Beer-Bouguer law

$$\frac{\phi_{tr}}{\phi_0} = \frac{I_{tr}}{I_0} = \tau_i = 1 - \alpha_i = \exp(-\kappa c l) \tag{2}$$

The definitions relate to absorbance A_{10} or A_e using the internal absorptance α_i. However, the i in the absorptance α is often omitted. Accordingly, the decadic absorbance is defined as

$$A_{10} = -\lg(1 - \alpha_i) \tag{3}$$

and the napierian absorbance

$$A_e = -\ln(1 - \alpha_i) \tag{4}$$

Both definitions use absorption coefficients as molar napierian κ, as molar (decadic) ε, (linear) decadic a or (linear) napierian α.

$$a = \frac{A_{10}}{l} \qquad \alpha = \frac{A_e}{l} \qquad \varepsilon = \frac{a}{c} = \frac{A_{10}}{cl} \qquad \kappa = \frac{\alpha}{c} = \frac{A_e}{cl} \tag{5}$$

where normally the concentration c is used in mol/dm^3, therefore the molar (decadic) coefficient ε, sometimes called the extinction coefficient, has the unit mol^{-1} dm^3 cm^{-1}. The term "extinction" should properly be reserved for the sum of the effects of absorption, scattering, and luminescence. In principle, all these quantities should be used in spectroscopy in terms of spectral intensity $I(\tilde{\nu})$ as a function of wave number $\tilde{\nu}$, or frequncy ν across the spectrum. However, especially in the visible and uv range wavelength, units of nanometers (nm) [$I(\lambda)$] are used instead of frequency. The principles for absorption, fluorescence, and reflection are shown in Fig. 1.

In practice, deviation from the Bouguer-Lambert-Beer's law can occur especially when high concentrations are examined. This deviation might stem from chemical interactions in the sample, from multiple scattering in the opaque or inhomogeneous media, or from instrumental effects, eg, insufficient resolving power or stray light. In part, these deviations can be overcome by calibration curves that are established if quantified information is desired.

Scattering techniques (2,3) record the change of a usually monochromatic probe signal scattered by a sample. It can involve elastic (energy-conserving) interactions, eg, Rayleigh scattering, where photons undergo only a change in momentum, or the inelastic (energy-changing) Raman effect, in which scattering is accompanied by discrete changes in frequency. Rayleigh scattering occurs for

all species having dimensions much smaller than the wavelength of the probe light, Mie scattering occurs from larger dielectric particles, and Tyndall scattering from discontinuities, eg, interfaces. These elastic processes provide little chemical information, but in atmospheric applications can furnish a return signal for laser ir radar (lidar) sounding. The Raman effect is weaker by factors of $\sim 10^3$, but spectroscopic analysis of scattered Raman light reveals spectral shifts characteristic of different chemical species (4–6) (see INFRARED TECHNOLOGY).

Emission spectroscopy is the analysis, usually for elemental composition, of the spectrum emitted by a sample at high temperature, or that has been excited by an electric spark or laser. The direct detection and spectroscopic analysis of ambient thermal emission, usually in the ir or microwave regions, without active excitation, is often termed radiometry (7). In emission methods, the signal intensity is directly proportional to the amount of analyte present.

Another type of emission is luminescence (8). Fluorescence and phosphorescence are types of luminescence, ie, emission attributed to selective excitation by previously absorbed radiation and chemical reaction rather than to the temperature of the emitter (9–11). Laser-induced and X-ray fluorescence are important analytical techniques.

In case of reflection, Lambert cosine law allows us to determine diffuse reflection as useful in thin-layer chromatography (12) using the Kubelka Munk function (13). Regular reflection (14) gains increasing interest either to measure reflectivities as in ellipsometry (15) or interferometric methods (16) or measuring refractometry based on evanescent field techniques (17). However, total and regular reflection have their main field of application in the areas of biochemical and chemical optical sensing (18).

Many schemes for exploiting processes of absorption, emission, and scattering have been developed around the experimental details of available light sources, detectors, and spectral analyzers. Spectroscopic analysis has been strongly impacted by the development of lasers (19,20), used both as powerful monochromatic excitation sources and as broadly tunable spectroscopic probes (21–25). Lasers are routinely used both in laboratory analysis and for active remote sensing (26,27). Their extremely high spectral intensity (photons per unit bandwidth) and spatial coherence (low divergence, allowing tight focusing) make even weak scattering processes, eg, the Raman effect, useful. Lasers have been exploited for many of the newer nonlinear responses (28–31) and for ultrasensitivity procedures that allow the detection of single atoms and molecules (32) (see TRACE AND RESIDUE ANALYSIS). Herein, optical spectroscopy for laboratory analysis, giving some attention to remote sensing using either active laser-based systems (33–36) or passive (radiometric) techniques (37–40) is emphasized.

2. Background

2.1. The Electromagnetic Spectrum. Electromagnetic radiation is characterized by its wavelength, λ, frequency, ν, or wavenumber, $\tilde{\nu}$, which are related in equation 6:

$$\nu = c/\lambda \qquad \tilde{\nu} = 1/\lambda = \nu/c \tag{6}$$

where c is the speed of light. Energy of radiation is related to frequency ν or wavenumber $\tilde{\nu}$. Units for wavelength are commonly nanometers (nm) or micrometers (μm) ($1\,\text{nm} = 10\,\text{Å} = 10^{-3}\,\mu\text{m} = 10^{-9}\,\text{m}$); for frequency, some multiple of cycles per second (hertz); and for wavenumber, reciprocal centimeters (cm^{-1}) ($1\,\text{cm}^{-1} \approx 30\,\text{GHz}$). The photon energy is

$$E = h\nu = hc/\lambda = hc\tilde{\nu} \tag{7}$$

where h is Planck's constant, and so is proportional to the frequency and wavenumber ($1\,\text{eV} \sim 8066\,\text{cm}^1$).

The electromagnetic spectrum is conventionally divided into several energy regions characterized by the different experimental techniques employed and the various nuclear, atomic, and molecular processes that can be studied; these are summarized in Table 1.

2.2. Atomic and Molecular Energy Levels. Absorption and emission of electromagnetic radiation can occur by any of several mechanisms. Those important in spectroscopy are resonant interactions in which the photon energy matches the energy difference between discrete stationary energy states (eigenstates) of an atomic or molecular system:

$$\Delta E_{\text{system}} = \Delta E_{\text{photon}} = h\nu \tag{8}$$

This condition is known as the Bohr frequency. Transitions between different types of eigenstates have characteristic energies (see Table 1), and so occur in different spectral regions. All of these regions have at least some applications to chemical analysis, but the most useful are rotational, vibrational, and electronic transitions. Molecules and molecular ions exhibit all three types of spectra; atoms and atomic ions undergo only electronic transitions.

Rotational transitions in gaseous molecules occur in the far-ir and microwave regions, generally $\lambda > 100\,\mu\text{m}$. Very light species absorb at shorter wavelengths according to

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \tag{9}$$

where f is the force constant, and μ the reduced mass (41). In fact, the strong, dense rotational spectrum of water vapor for $\lambda > 15\,\mu\text{m}$ makes operation in fir difficult. Microwave spectroscopy is an important discipline oriented more toward molecular structure research than chemical analysis (see MICROWAVE

TECHNOLOGY). The radar region, which includes longer microwaves and shorter radio waves ($\lambda \sim 0.54-133$ cm), is used for the detection and ranging of extended objects, from raindrops to aircraft to large weather systems. Microwave and radio wave spectroscopy is useful for detecting molecules in astronomical sources (radio astronomy).

Molecules vibrate at fundamental frequencies that are usually in the mid-ir. Some overtone and combination transitions occur at shorter wavelengths. Because ir photons have enough energy to excite rotational motions also, the ir spectrum of a gas consists of rovibrational bands in which each vibrational transition is accompanied by numerous simultaneous rotational transitions. In condensed phases, the rotational structure is suppressed, but the vibrational frequencies remain highly specific. Information on the molecular environment can often be deduced from line widths, frequency shifts, and additional spectral structure owing to phonon (thermal acoustic mode) and lattice effects.

Shorter wavelength radiation promotes transitions between electronic orbitals in atoms and molecules. Valence electrons are excited in the near-uv or visible. At higher energies, in the vacuum uv (vuv), inner-shell transitions begin to occur. Both regions are important to laboratory spectroscopy, but strong absorption by O_2 and O_3 make the vuv unsuitable for atmospheric monitoring. Electronic transitions in molecules are accompanied by structure from vibrational and, in gases, rotational transitions (vibronic and rovibronic bands). Deep inner-shell electronic transitions can be induced by X-ray excitation, useful for elemental analysis (see X-RAY TECHNOLOGY). Electronic transitions typically have larger absorption cross-sections than vibrational transitions, and hence greater analytical sensitivity, but spectral overlap and interferences are more likely to be problems.

2.3. Transition Widths and Strengths. The widths and strengths of spectroscopic transitions determine the information that can be extracted from a spectrum, and are functions of the molecular parameters summarized in Table 2. Detectivity is determined by spectral resolution and transition strength. Resolution, the ability to distinguish transitions of nearly equal wavelength, depends on both the widths of the spectral features and characteristics of the instrumentation. Unperturbed transitions have natural, $\Delta\nu_N$, widths owing to the intrinsic lifetimes of the states involved. The full width at half-maximum (fwhm), is defined as $\Delta\nu_N = (2\pi\tau)^{-1}$, where τ is the natural lifetime for a spontaneous transition in the absence of external perturbations. Natural line widths can be resolved by modern laser spectroscopies under laboratory conditions.

Natural line widths are broadened by several mechanisms (42). Those effective in the gas phase include collisional and Doppler broadening. Collisional broadening results when an optically active system experiences perturbations by other species. Collisions effectively reduce the natural lifetime, so the broadening depends on a characteristic impact time, τ_C, that is typically 1 ps at atmospheric pressure:

$$\Delta\nu_C = \frac{1}{2\pi}\left(\frac{1}{\tau} + \frac{1}{\tau_C}\right) \tag{10}$$

Doppler broadening arises from the random thermal agitation of the active systems, each of which, in its own rest frame, sees the applied light field at a different frequency. When averaged over a Maxwellian velocity distribution, ie, assuming noninteracting species in thermal equilibrium, this yields a linewidth (fwhm) in reciprocal centimeters (cm^{-1}).

$$\Delta\tilde{\nu} = 7 \times 16 \times \ 10^{-7}\tilde{\nu}_0(T/M)^{-1/2} \tag{11}$$

where T is the sample temperature in kelvin, M is the molecular weight of the species in amu, and $\tilde{\nu}_0$ is the transition energy in reciprocal centimeters. The Doppler broadening of a transition represents the fundamental lower limit for resolution unless special nonlinear spectroscopies are exploited.

Natural and collisional broadening are homogeneous processes because all radiators experience the same local effects. These produce, for both gases and liquids, a Lorentzian line shape, with $\Delta\nu$ (fwhm) $= (2\pi\tau')^{-1}$, where τ' is the effective lifetime of a radiator's uninterrupted oscillation period. In gases, this shape is distorted by Doppler broadening, an inhomogeneous effect having a Gaussian distribution. The contour of a gas-phase transition is thus the mathematical combination (convolution) of the Lorentzian and Gaussian functions, the Voigt profile.

For condensed species, additional broadening mechanisms from local field inhomogeneities come into play. Short-range intermolecular interactions, including solute–solvent effects in solutions, and matrix, lattice, and phonon effects in solids, can broaden molecular transitions significantly.

Finally, instrumental broadening results from resolution limitations of the equipment. Resolution is often expressed as resolving power, $\nu/\Delta\nu$, where $\Delta\nu$ is the probe line width or instrumental bandpass at frequency ν. Unless $\Delta\nu$ is significantly smaller than the spectral width of the transition, the observed line is broadened, and its shape is the convolution of the instrumental line shape (apparatus function) and the true transition profile.

With inadequate resolution much of the information in a complex spectrum can be lost leading to consequent degradation of specificity and loss of quantitative accuracy. In condensed phases, demands on instrumental resolution are modest. In gases at atmospheric pressure, collisional broadening is the dominant mechanism. There is usually a linear relationship between pressure and line width such that pressure-broadening coefficients are typically $0.0001–0.005(cm{\cdot}kPa)^{-1}$($0.01–0.5(cm{\cdot}atm\ )^{-1}$) for ir rovibrational transitions. Thus ir spectrometers used in remote atmospheric sensing might need $0.1\,cm^{-1}$ resolution for scanning the troposphere (lower atmosphere), but analysis in the stratosphere ($>25\,km$) may require $<0.01\,cm^{-1}$. Somewhat lower resolution may suffice for the uv–vis because of larger collisional and Doppler broadening. For laboratory gas samples, low pressures may be used to obtain the narrowest line widths. Under these conditions, instrumental resolution becomes an important consideration. The most advanced techniques of high resolution interferometry and tunable-laser spectroscopy are required.

The strength of a photon–molecule interaction is determined by the frequency-dependent cross-section $\sigma(\nu)$, expressed in centimeters squared (cm^2)

for absorption and related to $a(\nu)$ in equation 5; or by the differential cross-section $d\sigma(\nu)/d\Omega$ in units of cm^2/sr for scattering (34). The latter specifies the likelihood that active species scatter some portion of the incident laser fluence (photons/cm^2) into a viewing solid angle, $\Delta\Omega$, measured in steradians (Fig. 2). The cross-sections can be expressed as in equation 12:

$$\sigma(\nu) = \sigma_0 \cdot L(\nu - \nu_0, \Delta\nu) \tag{12}$$

where σ_0 (or $d\sigma_0/d\Omega$) is the peak value for absorption (scattering) and $L(\nu - \nu_0,\Delta\nu)$ is a symmetrical line-shape function parameterized by a center frequency, ν_0, and linewidth $\Delta\nu$.

An important semiclassical measure of the frequency-integrated absorption cross-section, known as Ladenburg's formula, is equation 13:

$$\int \sigma(\nu) d\nu = \pi r_c c f \cong S(\text{cm}^2 \cdot \text{frequency}) \tag{13}$$

where r_c is the classical electron radius (2.8×10^{-13} cm) and f is the oscillator strength for the transition (43,44). Similar expressions can be written for the differential scattering or fluorescence cross-sections (34). The f-values or line strengths, S, can in principle be calculated from quantum mechanics, but are generally obtained empirically. The parameter S is related to a matrix element, d_{ij}, connecting the initial and final states of the transition, ie, $S \propto (d_{ij})^2$, where d_{ij} has dimensions typical of an atom ($\sim 10^{-8}$ cm). The maximum value of the line-shape function is inversely proportional to the line width, so the peak absorption (or angle-integrated scattering) cross-sections, σ_0, can be approximated as in equation 14:

$$\sigma_0 \sim S/\Delta\nu \tag{14}$$

The peak absorption (scattering) cross-sections are thus useful comparative measures of detectivity because the latter is a product of the line strength and the practical line resolution.

2.4. General Instrumental Considerations. A spectroscope disperses light for visual observation, using a slit to define the source, a collimating lens, a dispersive prism or grating, and an objective lens or telescope. Spectroscopes fitted with wavelength scales and cameras are termed spectrometers and spectrographs, respectively. A monochromator is a spectrometer having an exit slit in the focal plane to isolate a narrow wavelength region. If the output is focused on a detector for quantitative intensity measurements it becomes a spectrophotometer. The use of such instrumentation constitutes the field of spectroscopy (sometimes called spectrometry), although spectroscopes themselves are, as of the 1990s, of little importance, for the electromagnetic spectrum extends from ~ 10 to $\sim 10^{24}$ Hz, compared to the visible region of only $(3.8–7.5) \times 10^{14}$ Hz.

Selecting suitable materials and components for a very broad frequency range presents special problems. Front-surface reflecting optics are usually required because of the lack of suitable achromatic optical materials. Strong absorption by the atmosphere in many regions requires instrumentation that

operates in a vacuum or an optical path that can be purged using a transparent gas. Table 3 indicates components and materials typically used in the important near-uv, visible, and ir regions.

The principles of the arrangements to measure absorption, transmission, and reflection are combined in Fig. 3 for various frequency regions.

3. Radio Wave and Microwave Spectroscopy

The longer wavelengths of the electromagnetic spectrum in the microwave range are used to probe molecular rotation and hyperfine structure (47). A recent review on the theory and application of microwave spectroscopy to structure determination is given with an overview of the theory and the microwave spectrometers (48). An important application is radio astronomy (49–52), which uses both radio and microwaves for chemical analysis on galactic and extragalactic scales. Herein, the terrestrial uses of microwave spectroscopy are emphasize (53–55). Additional applications can be found in the field of spectrochemical analysis and for the characterization of quantum dots (56,57).

3.1. Instrumentation. Microwaves have dimensions comparable to those of the experimental apparatus, so neither geometrical optics nor electrical circuit theory applies. Analysis by electromagnetic wave theory is required. Microwave sources are electronic rather than thermal. Klystrons, used most frequently, induce radiofrequency (rf) fields in a resonant cavity using a modulated electron beam, providing coherent output tunable over a 10% frequency range. Magnetrons, traveling-wave tubes, and backward-wave oscillators are also useful sources. Klystrons and magnetrons cover $\sim$5–50 GHz, but can be tuned into the submillimeter region using crystal multipliers. No dispersion is required, because these sources are essentially monochromatic. Microwaves are transmitted through metal waveguides that also serve as gas sample cells. Thin mica (qv) windows are used when necessary. Detectors are crystal rectifiers and sometimes bolometers.

3.2. Applications. Molecules couple to an electromagnetic field through their electric dipoles, so only those having a permanent dipole moment exhibit significant rotational spectra. For such species, microwave spectroscopy yields highly precise moments of inertia and details of centrifugal distortion. Applied electric or magnetic fields induce Stark or Zeeman spectra, respectively. The former provide the magnitude of the dipole moment. The latter yield its sign and also the quadrupole moment, a measure of the asymmetry of the molecular charge cloud. Degeneracies of electron and nuclear spin states can be removed using applied magnetic fields, revealing energy differences that typically correspond to microwave frequencies. This is the basis of such important techniques as nuclear magnetic resonance (nmr) and electron paramagnetic resonance (epr) (also called electron spin resonance, esr), which fall outside the definition herein of optical spectroscopy. The comparison between microwave and nmr spectroscopy in order to attest the utility and importance of the connections between these two methods is interesting (58).

Microwave spectroscopy is used for studying free radicals and in gas analysis (59). Much laboratory work has been devoted to molecules of astrophysical

interest (60). The technique is highly sensitive: 10^{-12} mol may suffice for a spectrum. At microwave resolution, frequencies are so specific that a single line can unambiguously identify a component of a gas mixture. Tabulations of microwave transitions are available (61,62). Remote atmospheric sensing (63) is illustrated by the analysis of trace ClO, O_3, HO_2, HCN, and N_2O at the part per trillion level in the stratosphere, using a ground-based millimeter-wave superheterodyne receiver at 260–280 GHz (64). Recent developments in experimental methods for the study of transient molecules not only in the atmosphere, but also in laboratories rely also on high resolution spectroscopy of transient molecules and its application to molecular dynamics (65). These methods compare modern techniques in conventional and Fourier transform (ft) microwave spectroscopy (66) and demonstrating ft microwave spectroscopy as an improved tool for investigation of rotational spectra (67).

4. Infrared Spectroscopy

Infrared spectroscopy has broad applications for sensitive molecular speciation. Infrared frequencies depend on the masses of the atoms involved in the various vibrational motions, and on the force constants and geometry of the bonds connecting them. Band shapes are determined by rotational structure, and hence by the molecular symmetry and moments of inertia. The rovibrational spectrum of a gas thus provides direct molecular structural information, resulting in very high specificity. A larger number of articles and books cover theory, instrumentation, and applications (68–71). The vibrational spectrum of any molecule is unique, except for those of optical isomers. Every molecule, except homonuclear diatomics, eg, O_2, N_2, and the halogens, has at least one vibrational absorption in the ir. Several texts treat ir instrumentation and techniques (37,72–74) and their applications (75–78).

4.1. Instrumentation. The ir region was developed using dispersive techniques adapted as appropriate from uv–vis spectroscopy. Unfortunately, ir sources and detectors tend to be inefficient compared to those for other spectral regions.

In early ir spectrometers (79), mechanically chopped light from a broadband source passed through a sample cell, was dispersed by a monochromator by either refraction in a prism or diffraction from a reflection grating, and converted into an alternating current (ac) electrical signal by a detector. This signal was amplified with a lock-in amplifier, thus distinguishing the modulated source beam from thermal ir radiation naturally emitted by the sample. Rotation of the dispersing element scanned the frequencies across the detector, and proper mechanical and electrical manipulation yielded a plot of signal intensity versus wavelength or wavenumber. Highly sophisticated grating spectrophotometers became available commercially in the 1950s, covering the mid-ir and having resolutions of $\sim 1\ cm^{-1}$. Many of these instruments employed a double-beam configuration, in which a set of rotating mirrors switched the source beam alternately through the sample and through an equivalent reference path many times per second. These signals were compared at the detector, and their ratio

provided a spectrum free from artifacts owing to atmospheric absorption, variations in source output, and absorption and scattering by cell windows.

Greatly improved performance was achieved using the Fourier transform spectrometer (fts) (80–82), essentially a Michelson interferometer in which a collimated light beam divided by a partially reflecting beam splitter is recombined after the optical delay (retardation) of one arm is changed by a scanning mirror. The resulting signal strength as a function of mirror travel is an interferogram, from which the desired spectrum (intensity vs. wavenumber) can be obtained by performing a Fourier transform. The discovery of the Cooley-Tukey fast Fourier transform (fft) algorithm in 1962 and the availability of powerful and inexpensive computers, led to Fourier spectroscopy becoming a practical technique.

There are several reasons for the high performance of Fourier instruments. Whereas a scanning spectrometer records a spectrum sequentially, one spectral resolution element at a time, an interferometer processes information from all frequencies simultaneously giving the multiplex or Fellgett advantage. Interferometers also have a throughput (Jacquinot) advantage, accepting a large solid angle of radiation, and hence passing a much greater light flux than can slit-limited monochromators. These two advantages can be converted into orders-of-magnitude improvements in resolution, scan time, and/or signal-to-noise (S/N) ratio, the three related instrumental parameters that are of the greatest practical interest to the analyst. The resolution of an fts is approximately the reciprocal of the maximum retardation, or twice the mirror travel. A resolution of $0.1\,cm^{-1}$ thus requires a mirror travel of only 5 cm. Many commercial interferometers offer at least this capability, and research instruments are marketed that can resolve better than $0.002\,cm^{-1}$. For kinetics studies and monitoring unstable species, scan rates of 50 Hz are available for short mirror travel (low resolution). Step-scan instruments can achieve nanosecond time resolution (83).

Besides bench and research-grade Fourier transform infrared (ftir) instruments, which have largely replaced dispersive spectrometers, compact and robust ftir analyzers are available specifically for on-line process monitoring. Permanently aligned, industrially hardened instruments are vibration- and shock-resistant and sealed against dust and moisture. Units are available that can monitor many dozens of gases at less than parts per million sensitivities.

The development of nearly monochromatic lasers that can be continuously frequency tuned throughout much of the ir (see Table 3) has revolutionized vibrational spectroscopy (84–86). By far the most used are lead salt semiconductor tunable diode lasers (TDLs), which can be tuned over $50–100\text{-}cm^{-1}$ intervals in continuous scans of $>1\,cm^{-1}$. Commercial TDL systems are modular, consisting of a cryogenic or liquid nitrogen-cooled laser source assembly, collimating optics, a simple mode-selecting monochromator, and a photodetector with lock-in amplifier. Because of the limited tuning ranges, TDLs are not suited for general survey spectroscopy, but do offer the highest resolution ($<0.0003\,cm^{-1}$). In addition to continuous tuning, these can be operated at discrete frequencies, tuning on and off a resonance many times per second for instant quantification. Industrial analytical applications of TDLs include stack-gas monitors for various pollutants. Other tunable sources, eg, color-center lasers (87), optical parametric oscillators (OPOs) (88), and far-ir lasers (89,90), are also useful in high resolution

spectroscopy. Recently, quantum cascade lasers have been introduced as a powerful tool (91,92).

4.2. Sampling. Almost any sample can be prepared for ir analysis (93,94). Cells for gases and liquids, typically 10 cm and 0.1 mm paths, respectively, are available in many configurations. For trace gases, compact small-volume folded-path cells offer adjustable optical paths up to 200 m (95). Gaseous species can be isolated in crystal lattices by dilution in an inert gas that is condensed at cryogenic temperatures (matrix isolation) (96–98). This eliminates Doppler and collisional broadening and suppresses rotational structure, concentrating all the intensity of a band in one sharp absorption line for increased sensitivity. Solutions and gels can be coated directly on ir-transmitting salt plates or microporous plastic films (99). Immersion probes are used for *in situ* analysis in chemical reaction vessels and process streams.

Solids can be observed directly in thin sections, as mulls in mineral or halocarbon oils, as finely ground dispersions in pressed disks of an ir-transparent salt, eg, KBr, as films cast from solutions, or as solutions in solvents having few ir absorptions, eg, CCl_4 or CS_2. Specular reflection from a solid-surface samples the outer $\sim$10 μm of materials, such as coatings (qv) and films. Nonspecularly reflected light is collected by mirrors in diffuse reflectance spectroscopy, useful for powdered samples and rough surface solids. Examples of such techniques are the characterization of monolayers by specular reflectance (100) and of catalysts by diffuse reflectance (101). Infrared light can be polarized by wire-grid or Brewster's angle pile-of-plates polarizers for the study of oriented and crystalline solids (102).

Specialized sampling techniques include ir microscopes that focus down to 10 μm (approximately the ir diffraction limit) for spectra of less than nanogram samples. This is useful in fiber analysis and forensics (103–106). In attenuated total reflection (ATR), an ir beam is transmitted inside a thin, highly refractive crystal (Zn, Se or Ge) by multiple internal reflection; the evanescent wave that penetrates some fraction of a wavelength into the surrounding lower index medium is absorbed by a sample in optical contact with the crystal, providing a useful sampling technique for gels, slurries, strongly absorbing liquids, and coatings (107,108). External reflection methods are also used for solids and films (109). Spectra of small samples under pressures of up to 100 GPa (10^6 atm) can be obtained using diamond anvil cells (110). Many devices have been designed for holding samples at cryogenic or elevated temperatures (111). Time-resolved techniques are available for the study of transient species (112–114).

For process monitoring and analysis in chemical plants, transmission of the ir beam through fiber optics allows safe access to a small sample region in harsh environments far removed from the spectrometer (115–119). Mid-ir transmitting fibers are available (see Table 3), although usefulness is limited by moisture sensitivity, brittleness, and impurity absorptions. Systems employing low power diodes and silica fibers have been demonstrated for monitoring explosive gases and NH_3, using near- and mid-ir absorption.

For open-path atmospheric monitoring, the two basic optical arrangements are point-to-point (bistatic), where the source and detector are separated and the volume to be sampled lies between them and single-ended (monostatic), in which a probe beam is returned from a retroreflecting target (a mirror or topographic

feature) and traverses the sampled volume twice. The optical path length through the sample may be ill-defined, yielding a column density averaged over the total path, so results are usually given in units of concentration × length. Sea-level atmospheric sounding is limited to regions free of H_2O and CO_2 absorption. Significant portions of the ir (~1.4, ~1.9, 2.5–2.9, 4.2–4.4, 5.5–7.5, and >15 μm) are unusable (120). High altitude observatories and balloon-borne spectrometers, however, can conduct useful upper atmospheric and astronomical observations even in the far-ir (89).

4.3. Null-Background Techniques. In conventional absorption spectroscopy, the difference between two large quantities, the incident and transmitted intensities, is measured, thus limiting the minimum detectable absorbance, A_{min} to $\sim 10^{-3}$. This can be greatly improved using null-background techniques, where the detected signal is (within limits) proportional to the source intensity. An example is harmonic or derivative spectroscopy (84), in which a narrow-band light source is frequency-modulated and synchronously amplified at the modulation frequency (or at a *n*th-order harmonic), yielding the first (*n*th-order) derivative of the absorption profile. This eliminates the background, reduces effects of low frequency drifts in the source, and discriminates against spurious signals lacking a sharp wavelength dependence at the modulated frequency. For TDLs, the drive current is modulated using standard rf sources; balloon-borne TDL spectrometers have reached A_{min} to $\sim 10^{-5}$ (121), and laboratory values of 10^{-8} have been reported.

Another such technique is direct calorimetric measurement of the radiant energy absorbed as the latter is converted into kinetic motion (heat) (4). In photoacoustic spectroscopy (pas) (122–125) pressure modulation caused by absorption of a modulated source is synchronously detected by a sensitive microphone transducer (spectrophone). A closed gas cell is required (for maximum sensitivity, an acoustically resonant one), and the microphones used are very small, so pas is suited for the analysis of small samples. Liquids or solids can be placed in direct contact with piezoelectric or pyroelectric transducers that convert pressure waves or temperature changes into an electrical signal. Typical applications of pas are for opaque solids, highly scattering media, eg, biological specimens, and low concentration gases, including pollutants (126). The pas detection has been demonstrated for volatile organics at <ppb levels using line-tunable CO and CO_2 lasers. The parameter A_{min} can theoretically reach 10^{-10}. Achievable sensitivity is illustrated by the analysis of ethylene (qv), C_2H_4, at the 20 parts per trillion level in air at 10 μm (127).

A closely related technique useful for localized gas concentrations and leaks is photoacoustic detection and ranging (padar) (128). A laser pulse tuned to an absorption line generates an acoustic signal that is detected by a parabolic microphone. A range resolution of 1 cm out to 100 m is feasible.

4.4. Applications. Infrared spectroscopy is broadly applicable to analytical problems of molecular speciation and quantification (75,129,130), for most molecules have strong fundamental vibrational transitions in the mid-ir. In the region 3–8 μm, many chemical functional moieties exhibit characteristic group frequencies that are relatively independent of the molecular environment, providing information on the chemical nature of the absorber (131,132). An example is the strong C=O stretching mode in saturated aliphatic ketones at

1705–1725 cm^{-1} (see KETONES). At longer wavelengths, the frequencies are influenced more by the skeletal vibrations of the molecule. This is known as the fingerprint region where even similar species may have sufficiently different spectra to be readily distinguished.

Single-component unknowns can be identified by simply comparing their spectra with reference spectra, of which many catalogs are available (133). Reference spectra are also available in digitized versions, and searches of databases (qv) can be made rapidly by computer. Even if no reference spectrum of the unknown is available, the group frequencies may provide enough information for an experienced spectroscopist to make a full identification. The rovibrational structure in gaseous samples further increases specificity, and also furnishes an estimate of the sample temperature that may be useful in remote sensing.

Mixtures can be identified with the help of computer software that subtracts the spectra of pure compounds from that of the sample. For complex mixtures, fractionation may be needed as part of the analysis. Commercial instruments are available that combine ftir, as a detector, with a separation technique, eg, gas chromatography (gc), high performance liquid chromatography (hplc), or supercritical fluid chromatography (134,135). Instruments, eg, gc/ftir, are often termed hyphenated instruments (136). Pyrolyzer (137) and thermogravimetric analysis (tga) instrumentation can also be combined with ftir for monitoring pyrolysis and oxidation processes (138) (see ANALYTICAL METHODS, HYPHENATED INSTRUMENTS).

Quantitative analysis based on Beer's law (eq. 1) is performed by measuring the absorption at a peak of known strength. In n-component mixtures, n such features are measured and the resulting set of simultaneous linear equations is solved for the n concentrations. Detection limits depend on the intrinsic band strengths, the optical configuration employed (especially the path length), and the spectral resolution. For solutions, these are typically in the range of 0.1–1%, with precisions of a few percent of the quantity measured. For narrow absorptions, sensitivity improves with increasing resolution until the latter becomes somewhat less than the absorption width. Tunable lasers, because of their narrow line widths and easy adaptability to derivative detection, provide excellent sensitivity. Low power TDLs monitoring sharp rovibrational lines in gaseous samples can detect molecules at the ppb level at atmospheric pressures over a single-pass 10-cm path length.

The ir spectral region is particularly useful for organic compounds, which have sufficiently distinctive spectra to be easily identified and quantified. Areas of application include drug analysis (139), biological systems (140–142), surface analysis (143), isotopic analysis (144), polymers (145,146), and electrode processes in solutions (spectroelectrochemistry) (147). Infrared remote sensing can be as varied as monitoring volatile organics in indoor air by ftir (148), ethylene emissions from a petrochemical plant at the ppb level using a monostatic CO_2 laser system (149), general atmospheric monitoring with TDLs (150), and upper atmospheric studies using airborne ftir (151,152) (see AIR POLLUTION; INFRARED TECHNOLOGY). Novel applications are known in biology (153) and clinical medicine (154).

4.5. Near-Infrared Spectroscopy. Many vibrational overtones and combinations, especially of hydrogen-containing functional groups, appear in

the near-infrared (nir). Although these bands are broad and weak, transmission and reflection nir spectroscopies have emerged as important probes for industrial and process analysis (155–159), eg, monitoring moisture, saturation of oils, and protein and fat content in the food and agricultural industries. The nir radiation can probe, with minimal sample preparation, long-path, concentrated, and aqueous samples that would totally absorb longer wavelengths. The potential loss of sensitivity is offset by instrumental advantages, eg, dependable low cost tunable laser sources, sensitive detectors, and fiber optics suitable for industrial environments. Usually, grating or ftir spectrometers are used, but low resolution bandpass filters may suffice. Filters can be either fixed-frequency interference or tunable acoustooptic (160,161). Because nir bands often overlap, chemometric techniques (162–164) are useful in data reduction (see CHEMOMETRICS).

Solid-state multielement detector arrays in the focal planes of simple grating monochromators can simultaneously monitor several absorption features. These devices were first used for uv–vis spectroscopy. Infrared coverage is limited (see Table 3), but research continues to extend the response to longer wavelengths. Less expensive nir array detectors have been applied to on-line process instrumentation (165) (see PHOTODETECTORS).

Examples of nir analysis are polymer identification (166,167), pharmaceutical manufacturing (168), gasoline analysis (169,170), and on-line refinery process chemistry (171). The nir fiber optics have been used as immersion probes for monitoring pollutants in drainage waters by attenuated total internal reflectance (172). The usefulness of nir for aqueous systems has led to important biological and medical applications (173). Interesting applications in spectroelectrochemistry are published (174).

4.6. Far-Infrared Spectroscopy. In this wavelength range of 1000–100 μm and in the frequency range of 10^{11}–10^{12} Hz ("terahertz" range), rotational transitions of polar molecules in the gas phase as well as vibrational modes of crystals and biological macromolecules are examined (175–177). Another application is measurement of hydrogen bonds, especially in matrices. Furthermore, single- and double-strand DNA could be discriminated, therefore terahertz spectroscopy is a potential application for genomics (178). Quantum dots are also characterized (179). It can also be used in environmental pollution control, therefore this method is considered as having high potential for the future.

4.7. Radiometry. Radiometry is the measurement of radiant electromagnetic energy (37,38,180), considered herein to be the direct detection and spectroscopic analysis of ambient thermal emission, as distinguished from techniques in which the sample is actively probed. At any temperature above absolute zero, some molecules are in thermally populated excited levels, and transitions from these to the ground-state radiate energy at characteristic frequencies. From Wien's displacement law, $\lambda_{max}T = 2898\,\mu\text{m}\cdot\text{K}$, the emission maximum at 300 K is near 10 μm in the mid-ir. This radiation occurs at just the energies of molecular rovibrational transitions, so thermal emission carries much the same information as an ir absorption spectrum. Detection of the emissions of remote thermal sources is the ultimate passive and noninvasive technique, requiring not even an optical probe of the sampled volume.

When the spectral characteristics of the source itself are of primary interest, dispersive or ftir spectrometers are readily adapted to emission spectroscopy. Commercial instruments usually have a port that can accept an input beam without disturbing the usual source optics. Infrared emission spectroscopy at ambient or only moderately elevated temperatures has the advantage that no sample preparation is necessary. It is particularly applicable to opaque and highly scattering samples, anodized and painted surfaces, polymer films, and atmospheric species (181). The *Voyager* interferometric spectrometer (IRIS) spectra from the outer planets demonstrated the analytical capabilities of ftir emission spectroscopy. As an example of industrial monitoring, smokestack effluents have been analyzed by ftir at a range of 74 m, using H_2O/CO_2 concentration ratios to distinguish gas and oil combustion (182). Field-deployable commercial instruments achieve sensitivities of the order of ppm·m out to 1 km using retroreflectors.

Direct analysis of weak ambient thermal radiation in the presence of an intense solar background is difficult. A sensitive technique for detecting these signals is laser heterodyne radiometry, in which one measures not the emitted frequency itself, but the beat frequency between this and another, accurately known, frequency. The incident radiation is combined with the output of a coherent local oscillator (LO), usually a fixed-frequency laser, in a high speed photomixer, thus generating a difference frequency called the intermediate frequency (IF), which is synchronously detected and amplified. The IF preserves the spectral characteristics of the source, but shifts this information into the rf region, where sensitive radio detection techniques can be used. The tuning range is limited by the IF bandwidth of the mixer. The HgCdTe photodiodes used in the ir provide a spectrum covering $\pm 0.08\,cm^{-1}$ around the LO frequency. The requirement of finding a molecular transition this close to a gas laser frequency is highly restrictive, so the technique is not suitable for speciation, but rather for monitoring one or a few specific molecular features. Tunable diode lasers have sufficient power to serve as local oscillators, permitting continuous tunability, but any single TDL is limited to a tuning range of some $100\,cm^{-1}$. Heterodyne radiometry provides excellent sensitivity, and has been used with appropriate receiving telescopes for detection of constituents of planetary and stellar atmospheres.

5. Molecular Uv–Vis Absorption Spectroscopy

Spectroscopy in the uv–vis detects electronic transitions, and so is applicable to both atoms and molecules. This is a mature technique having important qualitative and quantitative applications (183–187).

5.1. Instrumentation and Sampling. Quartz spectrographs and photographic plates long served for the near-uv–vis–nir region (188), but modern commercial recording instruments employ holographic gratings and photomultiplier tubes or (in the nir) avalanche photodiode detectors to cover $\sim 190\,nm – 3\,\mu m$ (see HOLOGRAPHY; PHOTODETECTORS). A typical benchtop spectrophotometer has 2-nm resolution in the uv–vis, but dual-grating research instruments can resolve 0.05 nm. In the vacuum ultraviolet (vuv), special techniques are required (189–191). Molecular oxygen absorbs below ~190 nm , and below the transmission

limit of lithium fluoride, LiF (105 nm), no bulk optical materials are suitable, even as window materials. This specialized region is not used for routine chemical analysis.

Simple uv–vis monochromators are widely used with solid-state imaging arrays (192,193), called optoelectronic imaging devices (OIDs) or optical multichannel analyzers (OMAs), placed in the focal plane to record a spectrum nearly instantaneously. These are the modern equivalent of the photographic plate, and have the advantage over an emulsion of rapid response and real-time results. An array detector consists of a set of photodiodes together with an integral electronic readout scheme. Arrays having time-gated windows as short as 5 ns are useful for spectroscopy and kinetics of short-lived and unstable species, for which arrays have obvious advantages over mechanically scanned spectrophotometers, and are often superior to fts. Two-dimensional (2D) arrays designed for image recording can be used for time-resolved spectroscopy by rastering a temporally changing spectrum across the second dimension of the array. Modern routine spectrometers use charge-coupled devices (CCD) (194,195) as detection elements that provide wavelength resolutions even below 1 nm in dependence on the grating used and repetition times of a few milliseconds. Even CMOS technology (196) is coming up as a modern substitute for photoplates, enabling fast recording times and high resolution. Such cameras have made uv–vis spectroscopy a very interesting method and suitable for many applications. A recent review compares photodetectors (197).

Interferometry is difficult in the uv because of much greater demands on optical alignment and mechanical stability imposed by the shorter wavelength of the radiation (198). In principle, any fts interferometer can be operated in the uv when the proper choice of source, beam splitter, and detector is made, but in practice good performance at wavelengths much shorter than the visible has proved difficult to obtain. Some manufacturers have claimed operating limits of 185 nm, and ft laboratory instruments have reached 140 nm (191). More low priced results are obtained using diode array spectrometers that use the above mentioned CCD devices and a so-called polychromator (a monochromator without an exit slit), which allows monitoring of many wavelenghts in parallel on the diode array (199).

Tunable uv–vis lasers are well developed (21). Optically pumped organic dye lasers provide especially useful continuously tunable high power sources, widely used in laboratory research on spectroscopy and photochemistry (see PHOTOCHEMICAL TECHNOLOGY SURVEY). A single output frequency is selected from the broad-band fluorescence by a dispersive optical cavity. Pulsed dye lasers, pumped with fixed-frequency Nd:YAG, excimer, or Cu-vapor lasers, or by flashlamps, can provide high peak powers at repetition rates to 100 Hz and line widths of $0.1–1\,cm^{-1}$, which can be improved to $<0.01\,cm^{-1}$ with an intracavity etalon (a pair of parallel plates acting as an interferometer). A given dye–solvent combination can typically be tuned continuously over a 40–80-nm range. Using Ar^+ or Kr^+ pump lasers, continuous wave (cw) operation is possible having output powers of 0.1–1 W. Multimode cw cavities can achieve line widths of a few gigahertz, and commercial ring-laser geometries improve the resolution to <0.5 MHz over a $1\text{-}cm^{-1}$ continuous scan. Dye lasers have certain drawbacks. These are complex devices requiring a separate pump laser (or at least a flashlamp)

and having demanding optical and alignment requirements, especially the synchronization of the tuning elements. Moreover, dye lasers usually require a flowing dye system (for cw operation, a liquid dye jet) to dissipate heat generated by the pump. Other useful laser sources are available (see Table 3), including conversion of longer wavelength tunable lasers by Raman shifting or by frequency doubling in nonlinear media.

Most of the specialized ir sampling methods described have uv equivalents with appropriate modifications. Sample cells (cuvettes) for solutions, typically of 1-cm path lengths, may be of glass or quartz, and are available for sample volumes as small as a few microliters. There is a wide choice of suitable solvents, including (for $\lambda > 200$ nm) water and most saturated organic compounds. Difference spectroscopy with double-beam instruments is used in the uv–vis not only to eliminate background effects, but to assess the effects of changes in pH, temperature, or solvent on one of two otherwise identical samples. Specialized hardware allows the direct scanning of electrophoresis gels and films. Derivative spectroscopy (200,201) by either numerical differentiation or beam modulation methods is important in determining absorbances of weak features obscured by stronger peaks. Photoacoustic methods are employed for strongly absorbing samples. Glass and polymer fiber optics are available for process monitoring.

5.2. Applications. Ultraviolet–visible absorption results from transitions between outer-electron shells. The specific moiety or structure responsible is termed the chromophore. Compounds having only single C–O bonds generally absorb only in the vuv. Saturated organic compounds containing heteroatoms exhibit uv transitions, and the π electrons of an unsaturated bond or aromatic nucleus are strong chromophores, absorbing more strongly and at longer wavelengths (to the visible) in conjugated and fused-ring systems. Inorganic species having incomplete electron shells, notably transition-metal cations, also absorb in the uv–vis.

The uv–vis spectra do not offer the unique group frequencies and fingerprinting ability of the ir, but different chromophores exhibit absorptions at specific wavelengths, λ, and have characteristic intensities. These are tabulated in handbooks as λ_{max} and ϵ_{max}, where ϵ_{max} is a molar decadic absorption coefficient equivalent to the $a(\nu)$ of equation 1, but in units typically of L/(mol·cm). Thus the ketone C=O has a strong absorption at 195 nm and a much weaker one at 270–285 nm. Spectral atlases and cataloges are available (202–204), as are specialized treatments of laboratory analysis in such fields as pharmaceuticals (qv) (205,206) and biomedical diagnostics (207) . Scanning uv–vis diode-array absorption detectors are used in hplc, and can cover 190–600 nm in 0.1 s using a 10-μL sample. The instrumentation is reviewed in Ref. 208, curve-fitting techniques are discussed (209,210), and various detectors are compared (211). In addition, a comparison with nuclear magnetic resonance (nmr) is possible (212).

Photon energies sufficient to promote electronic transitions can also excite vibrational and rotational transitions, so the electronic spectra of gaseous molecules consist of highly structured rovibronic bands, having very high specificity. In condensed phases, rotational structure is suppressed, but the molecules still vibrate, resulting in vibronic bands with progressions of characteristic vibrational frequencies that accompany each electronic transition. The uv offers high sensitivity and excellent quantitative accuracy. The greater uv absorption

cross-sections (see Table 2) and more efficient uv sources and quantum detectors result in detection limits several orders of magnitude better than in the ir. On the other hand, spectroscopic congestion may be a problem. Many strong transitions occur in a relatively narrow wavelength region. Spectral overlap, and the greater susceptibility of shorter wavelength radiation to Rayleigh and particulate scattering and turbulence, limits the use of uv spectroscopy for identifying complex mixtures in process streams or in the atmosphere.

Atmospheric and remote-sensing applications of uv–vis spectroscopy have been reviewed (213,214). Many volatile organics absorb in the near-uv, and the vapors exhibit rovibronic structure suitable for identification and quantification if interferences can be avoided. Especially suitable for uv monitoring are the strong Huggins (300–370 nm) and Hartley (210–300 nm) bands of O_3; other inorganics, eg, NO_2 and SO_2, have been successfully analyzed at kilometer distances (see OZONE).

The main application of uv–vis spectrometry is to examine liquid or gas samples in routine analysis. The techniques, instrumentation and data handling are described in (186,215–217). Detection of uv–vis is typical in chromatography, either liquid or tlc; furthermore it is a basis of optical sensors being either optrodes (218) or using fluorescence or reflectance. In past years, the optical sensors have been reviewed frequently (219–221).

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Table 1. **Regions of the Electromagnetic Spectrum**

Region	Wavelength limits[a]	Frequency or photon energy[a]	Transitions observed or excited
radio waves	>30 cm	$<1{,}000$ MHz	hyperfine structure from nuclear spins and isotopic shifts
microwaves	1 mm–30 cm	300–1 GHz	rotation and inversion of molecules; cyclotron resonance of electrons in solids
far-infrared (fir) (sub-millimeter waves)	50–1000 μm	200–10 cm^{-1}	molecular rotations and certain low frequency bending, torsional, and skeletal vibrations; lattice modes in solids
mid-infrared	2.5–50 μm	4,000–200 cm^{-1}	fundamental molecular vibrations (rovibrational spectra)
near-infrared (nir)	0.8–2.5 μm	12,500–4,000 cm^{-1}	vibrational overtones and combinations
visible (vis)[b]	400–800 nm (0.4–0.8 μm)		valence electrons
near-ultraviolet (uv)[c]	200–400 nm		valence electrons (atomic and rovibronic molecular spectra)
vacuum ultraviolet (vuv)	10–200 nm	125–6 eV	inner-shell electrons; ionization
X-rays	0.01–10 nm (0.1–100)	125–0.125 keV	inner-shell electrons; nuclear
γ-rays	<0.01 nm	>0.125 MeV	nuclear

[a]Values are approximate.
[b]Also defined as 380–780 nm by DIN-NORM 5031.
[c]Also defined as 200–380 nm by DIN-NORM 5031.

Table 2. **Line-Shape Parameters**

Parameter	Transitions		
	Rotational	Vibrational	Valence electronic
line frequency, $\tilde{\nu}$, cm^{-1}	1–100	100–4,000	<50,000(>200 nm)
natural linewidth, $\Delta\tilde{\nu}_N$, cm^{-1}	$<10^{-11}$	$<10^{-7}$	$<3\times10^{-3}$
Doppler width at 300 K, $\Delta\tilde{\nu}_D$, cm^{-1}	<0.0005	<0.01	0.01–0.2 (∼0.0005 nm)
natural radiative lifetime, t_N, s	$>10^{-1}$	$>2\times10^{-4}$	$>2\times10^{-9}$
peak Doppler-broadened absorption cross-section, s_A, cm^2	$<10^{-20}$	$\leq10^{-18}$	10^{-11}–10^{-16a} $<10^{-17b}$
peak differential scattering cross section, $d\,s/d\,W$, $cm^{2/sr}$			
Rayleigh	negligible	negligible	$<2\times10^{-13a,c}$ $<10^{-26b,d}$
Raman	$<10^{-27}$	$<10^{-28}$	$\sim10^{-24a}$ $<5\times10^{-16a,e}$
fluorescence	negligible	negligible	10^{-20}–10^{-25b}

[a]Values are for atoms.
[b]Values are for molecules.
[c]Values are for resonant scattering by atomic vapors.
[d]Values are for nonresonant scattering of visible and near-uv radiation by atmospheric gases; resonant Raman scattering approaches 10^{-24} cm^2/sr.
[e]Values are for STP atmospheric conditions.

Table 3. **Components and Materials Used in uv–vis–ir Spectroscopy**[a]

Instrumental parameter	Far-infrared[b]	Mid-infrared[c]	Near-uv, visible, and near-ir[d]
broad-band thermal sources	plasma emission from high pressure mercury arc lamp	blackbodies: Nernst glower (zirconia), globar (silicon carbide), nichrome wire cole	deuterium lamp (160–370 nm) Xe arc lamp (300 nm–1.3 μm) quartz-envelope tungsten–halogen lamp (350 nm–2.5 μm)
continuously tunable laser sources	CO_2 laser frequency difference generation (65–1000 μm) microwave sideband mixing (> 70 μm)	OPO (16 μm) color-center lasers (1.5–4 μm) nonlinear optical mixing (2–9 μm) semiconductor diodes (3–28 μm) spinflip Raman (5–6 μm) waveguide CO_2 (9–11 μm)	organic dye lasers (320 nm–1.3 μm) OPO (>410 nm) Ti:sapphire laser (700–1000 nm) frequency conversion of other lasers (>190 nm) diode lasers (>670 nm)
detectors	pyroelectric (DTGS, LT) doped-germanium and InSb bolometers Golay pneumatic cell	photoconductors (<40 μm) (InSb; doped germanium; MCT) thermal (thermocouples, bolometers) pyroelectric (DTGS, LT)	photomultipliers (120 nm–1.1 μm) photodiodes (InAs, InGaA, Si, Ge) photoconductors (Si, Ge)
array detectors	none	PtSi (<5 μm) InSb (<5 μm) MCT (<12 μm) doped Si (10–30 μm)	silicon arrays (175 nm–1.1 μm) photographic emulsions (<1.2 μm) Ge arrays (700 nm–1.5 μm) InSb, PbSe, PtSi
general optical materials	polyethylene, Mylar quartz diamond (>6 μm)	alkali halide crystals fluorite, CaF_2 (<9 μm) ZnSe (800 nm–20 μm) AgCl (420 nm–25 μm) KRS-5 (550 nm–40 μm)	alkali halide crystals glass (300 nm–2.2 μm) quartz (170 nm–3.5 μm) diamond (220 nm–4 μm) sapphire (150 nm–6 μm) fluorite (120 nm–9 μm)
fiber optics	none	fluoride glasses (900 nm–5 μm) chalcogenide glasses (2.2–12 μm) hollow metal fibers (~10 μm)	silica glasses quartz (250 nm–1.3 μm)

[a]DTGS = deuterated triglycine sulfate; KRS-5 = mixed thallium bromide–iodide; LT = lithium tantalate; MCT = mercury cadmium telluride; and OPO = optical parametric oscillator.
[b]50–1000 μm.
[c]2.5–50 μm.
[d]200 nm–2.5 μm.

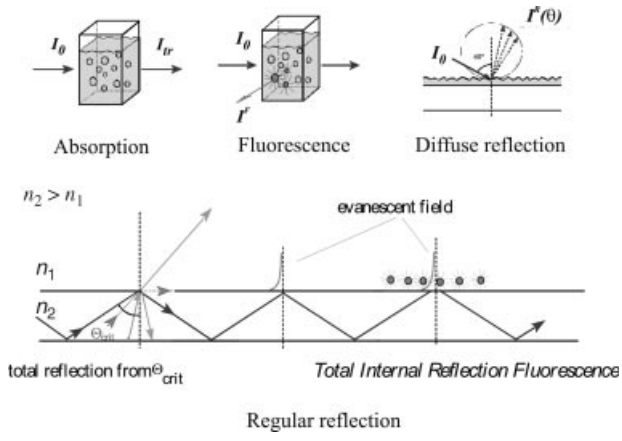

Fig. 1. Arrangements for absorption, fluorescence, and reflection measurements.

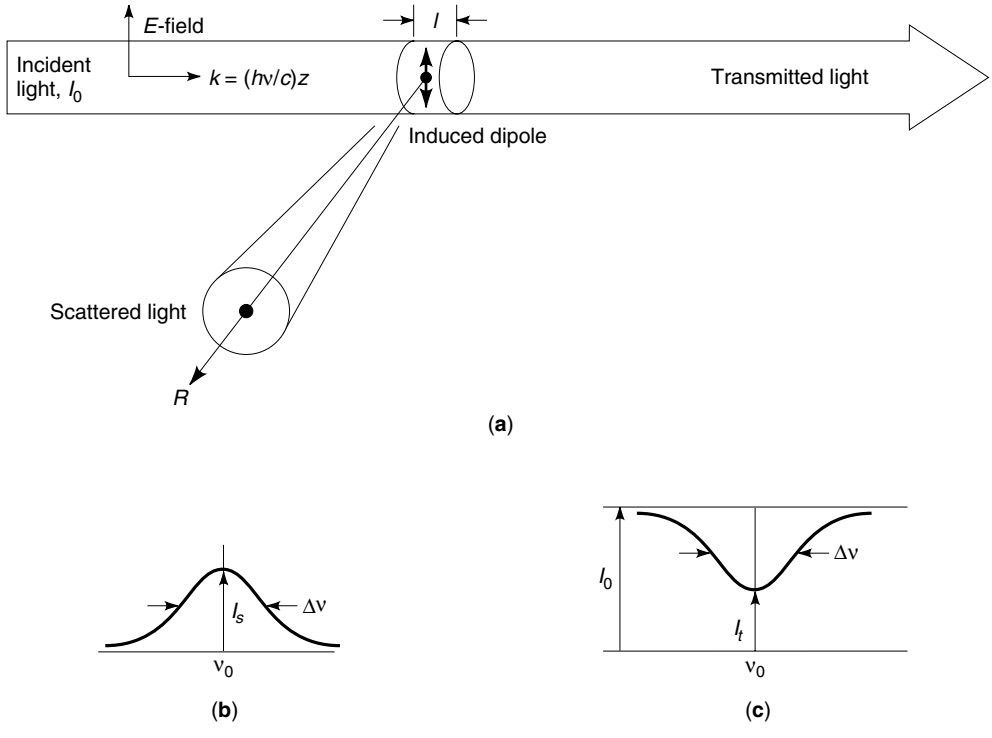

Fig. 2. An incident electromagnetic field of intensity, I_0, having an associated electric field, E, induces dipole oscillation in the absorbers. The transmitted intensity, I_t, is reduced by absorption; of the radiated (scattered) light, a portion, I_s, is shown here detected in a conventional right-angle configuration with collection solid angle $\Delta\Omega_0$. (**a**) Schematic of the absorption/scattering, where $I_0 = (\frac{1}{2})ce_0 \mid E \mid^2$ in W/m^2; (**b**) plot of scattered light, I_s, versus frequency, where $I_s = I_0 Nl(d\sigma/d\Omega) \cdot \Delta\Omega_c$, and $\Delta\Omega_c$ is proportional to (detector area)/R^2; and (**c**) plot of transmitted light, I_t, versus frequency, where $I_t = I_0 \exp(-N\sigma 1) \approx I_0(1 - N\sigma l)$ for $N\sigma l \ll 1$.

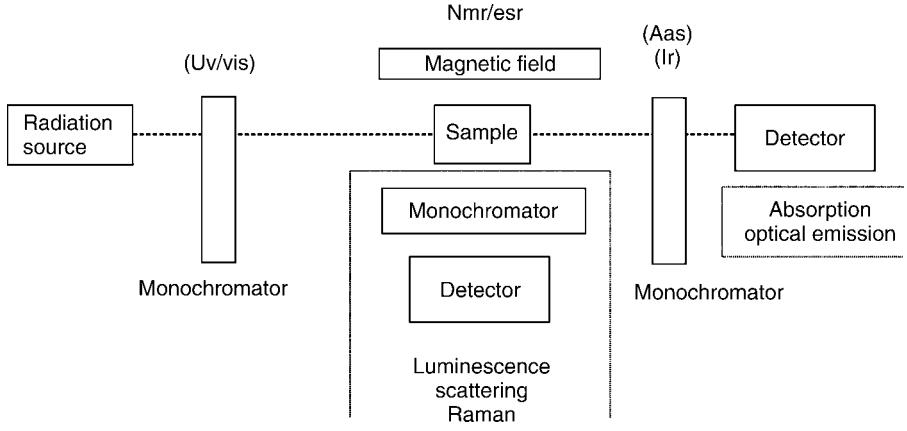

Fig. 3. Principle set-ups for absorbance, scattering, and emission measurements is dependant on the wavenumber region. Independent of the wavenumber in optical spectroscopy instrumentation contains source, frequency selection (element of dispersion: monochromator), sample compartment and detection unit. Absorbance is measured along the optical axis, scattering and luminescence in the perpendicular axis. In uv–vis spectroscopy, the monochromator is placed in front of the sample (photodegradation) and in ir behind the sample (self-radiation of sample) (see also Refs. 45,46.)