Spectroscopy 1: rotational and vibrational spectra

The origin of spectral lines in molecular spectroscopy is the absorption, emission, or scattering of a photon when the energy of a molecule changes. The difference from atomic spectroscopy—the energy of a molecule can change not only as a result of electronic transitions but also because it can undergo changes of rotational and vibrational state. Therefore, molecular spectra are more complex than atomic spectra. However, they contain information about more properties, and their analysis leads to values of bond strengths, lengths, angles, and a variety of molecular properties. Molecular spectroscopy is also useful to astrophysicists and environmental scientists because the chemical composition of interstellar space and of planetary atmospheres can be inferred from their rotational vibrational and electronic spectra.

General features of spectroscopy

The relations between the frequency, \( \nu \), wavelength, \( \lambda \), and wavenumber, \( \tilde{\nu} \):

\[
\tilde{\nu} : \lambda = \frac{c}{\nu} \quad \tilde{\nu} = \frac{\nu}{c}
\]
Experimental techniques

**Emission spectroscopy:** a molecule undergoes a transition from a state of high energy $E_1$ to a state of lower energy $E_2$ and emits the excess energy as a photon.

**Absorption spectroscopy:** the net absorption of nearly monochromatic (single-frequency) incident radiation is monitored as the radiation is swept over a range of frequencies. The energy of the photon emitted or absorbed: $h \nu = E_1 - E_2$

**Spectrometers** – instruments that detect the frequency composition of electromagnetic radiation scattered, emitted, or absorbed by atoms and molecules.

The general layout of an absorption spectrometer: radiation from an appropriate source is directed toward a sample. Light transmitted, emitted, or scattered by the sample is collected by mirrors or lenses and strikes a **dispersing element** that separates radiation into different frequencies. The intensity of light at each frequency is then analyzed by a suitable detector.

*Polychromatic* sources – span a wide range of frequencies; *monochromatic* sources – span a very narrow range of frequencies around a central value. Many commercial spectrometers use light sources from black-body radiation from hot materials, which can provide radiation spanning a wide range of frequencies.
Far-infrared radiation ($35 \text{ cm}^{-1} < \tilde{\nu} < 200 \text{ cm}^{-1}$): a typical source is a mercury arc inside a quartz envelope, most of the radiation is generated by the hot quartz. Mid-infrared radiation ($200 \text{ cm}^{-1} < \tilde{\nu} < 4000 \text{ cm}^{-1}$): *Nernst filament* (a ceramic filament containing oxides of zirconium, yttrium, thallium, and cerium heated to 1200-2000 K) or *globar* (a rod of silicon carbide electrically heated to $\sim 1500$ K). A *tungsten filament* gives out intense light in the range $320 \text{ nm} < \lambda < 2500 \text{ nm}$ when heated to $\sim 3000$ K. Used in household light fixtures and in commercial spectrometers. A *quartz-tungsten-halogen lamp* – iodine gas is used to extend the lifetime of the filament. A *gas discharge lamp* – a common source of ultraviolet and visible radiation. In a *xenon discharge lamp*, an electrical discharge excites xenon atoms to excited states, which then emit ultraviolet radiation. At $p < 1\text{kPa}$, the output of a xenon lamp consists of sharp lines superimposed on a broad intense background due to emission from a *plasma*, a complex mixture of ions, formed from neutral atoms by the electrical discharge. High-pressure xenon lamps have emission profiles similar to that of a black body heated to 6000 K. In a *deuterium lamp*, excited D$_2$ molecules dissociate into electronically excited D atoms, which then emit intense radiation between 200-400 nm.

The measurement of absorption spectra with a polychromatic source requires a dispersing element, but it is not necessary when the source is monochromatic and can be tuned over a range of values. *Kryston* and the *Gunn diode* – electronic devices used to generate tunable microwave radiation. *Lasers* – generate tunable monochromatic electromagnetic radiation; different types of laser are used to cover different regions of the electromagnetic spectrum.
Synchrotron radiation from a *synchrotron storage ring* – consists of an electron beam (a series of closely spaced packets of electrons) traveling in a circular path of several meters in diameter. Electrons traveling in a circle are constantly accelerated by the forces that constrain them to their path, so they generate radiation. Synchrotron radiation spans a wide range of frequencies including the infrared and X-rays. Except in the microwave region, synchrotron radiation is much more intense than can be obtained by most commercial sources. The disadvantage – the source is large and costly; it is usually a national facility, not a laboratory commonplace.

**The dispersing element**

A *diffraction grating* – consists of a glass or ceramic plate into which fine grooves have been cut and covered with reflective aluminum coating. The grating causes interference between waves reflected from its surface, and constructive interference occurs when

\[ n\lambda = d(\sin \theta - \sin \phi) \]

\( n = 1, 2, \ldots \) - the *diffraction order*,
\( \lambda \) - the wavelength of the diffracted radiation, \( d \) – the distance between grooves, \( \theta \) - the angle of incidence of the beam, and \( \phi \) - the angle of emergence of the beam. For a given \( n \) and \( \theta \), larger differences in \( \phi \) are observed for different wavelength when \( d \) is similar to \( \lambda \).
For example, compare dispersion of $\lambda = 500$ and 400 nm light ($n = 1$, and $\theta = 30^\circ$) by grating with $d = 1000$ nm and 10000 nm. With 10000 nm grating, $\phi = 26.7^\circ$ and 27.4° and with $d = 1000$ nm $\phi = 0^\circ$ and 5.7°. So, a grating with a smaller $d$ (closer to $\lambda$) disperses 400-500 nm radiation over a wider range. Wide angular separation results in wide spatial separation between wavelengths away from the grating, where a detector is placed.

In a **monochromator**, a narrow exit slit allows only a narrow range of wavelengths to reach the detector. Turning the grating around an axis perpendicular to the incident and diffracted beams allows different wavelengths to be analyzed – the absorption spectrum is built up one narrow wavelength range at a time. Typically, the grating is swept through an angle that investigates only the first order of diffraction ($n = 1$). In a **polychromator**, there is no slit and a broad range of wavelengths can be analyzed simultaneously by array detectors.

**Raman spectroscopy**

In **Raman spectroscopy**, molecular energy levels are explored by examining the frequencies present in the radiation scattered by molecules. A monochromatic incident laser beam is passed through the sample and the radiation scattered from the front face of the sample is monitored. About 1 in $10^7$ of the incident photons collide with the molecules, give up some of their energy and emerge with a lower energy (lower-frequency Stokes radiation). Other incident photons may collect energy from the molecules (if they are already excited) and emerge as high-frequency anti-Stokes radiation.
component of radiation scattered into the forward direction without change of frequency – **Rayleigh radiation**. Raman spectroscopy is complementary to infrared spectroscopy because different selection rules are obeyed.

**Detectors**
A detector – a device that converts radiation into an electric current or voltage for appropriate signal processing and display, may consist of a single radiation-sensing element or of several small elements arranged in one- or two-dimensional arrays. The *photomultiplier tube* (PMT) – a sensing element in which the photoelectric effect is used to generate an electrical signal proportional to the intensity of light that strikes the detector. In a PMT, photons first strike the *photocathode* – a metallic surface to which a large negative potential is applied. Each ejected electron is accelerated by a potential difference to another metallic surface (*dynode*), from which more electrons are ejected. The function of the dynode is to amplify the current produced at the photocathode. After traveling through the chain of dynodes, all the ejected electrons are collected at the final metallic surface (*anode*). A PMT can produce up to $10^8$ electrons per photon that strikes the photocathode. A problem – *dark current* – at room temperature, a small number of electrons on the photocathode have sufficient energy to be ejected even in the dark, which, interferes with measurements on the sample. Solution – lower the temperature: for applications that require detection of very low levels of radiation, a PMT can be cooled to 77 K immersion into an insulated container filled with liquid nitrogen.
An alternative to the PMT – photodiode, a solid-state device that conducts electricity when struck by photons. Photodiodes are easy to manufacture, but not very sensitive. Their performance can be improved by accelerating the photo-generated electrons with a very large electrical potential difference. The high-energy electrons then collide with other atoms and ionize them creating an avalanche of secondary charge carriers – avalanche photodiodes. With appropriate choice of material, photodiodes can be used to detect light of a wide range of wavelength: silicon – for visible region, germanium – for the near-infrared region of spectrum.

The charge-coupled device (CCD) – a two-dimensional array of up two six million small photodiode detectors. A wide range of wavelengths from a polychromator are detected simultaneously.

**Resolution**
A spectrometer’s resolution – the smallest observable separation between two closely spaced spectral bands. Depends on instrumental factors (the distance between grating grooves, the distance between the grating and the slit placed in front of the detector, etc.) and on the wavelength of incident radiation.
The intensities of spectral lines

**Transmittance**, $T$ – the ratio of the transmitted intensity, $I$, to the incident intensity:

$$ T = \frac{I}{I_0} $$

The transmitted intensity varies with the length $l$ of the sample and the molar concentration [J] of the absorbing species:

$$ I = I_0 10^{-\varepsilon[J]l} \textbf{Beer-Lambert law} $$

$\varepsilon$ - the **molar absorption coefficient** (extinction coefficient). The molar absorption coefficient depends on the frequency of the incident radiation and is greatest where the absorption is most intense. The dimensions of $\varepsilon$ are $1/(\text{concentration} \times \text{length})$: L mol$^{-1}$ cm$^{-1}$ or alternatively cm$^2$ mol$^{-1}$. The latter units (area per mole) demonstrate that $\varepsilon$ may be regarded as a molar cross-section for absorption: the greater the cross-sectional area of the molecule for absorption, the greater its ability to block the passage of the incident radiation.

The **absorbance**, $A$: $A = \log \frac{I_0}{I}$ or $A = -\log T$

The Beer-Lambert law then becomes $A = \varepsilon[J]l$

The Beer-Lambert law implies that the intensity of electro-magnetic radiation transmitted through a sample at a given wave-number decreases exponentially with the sample thickness and the molar concentration.
The maximum value of the molar absorption coefficient, $\varepsilon_{\text{max}}$ – an indication of the intensity of a transition. Absorption bands generally spread over a range of wavenumber. The integrated absorption coefficient, $A$ – the sum of the absorption coefficients over the entire band; corresponds to the area under the plot of the molar absorption coefficient against wavenumber:

$$A = \int_{\text{band}} \varepsilon(\tilde{\nu}) d\tilde{\nu}$$

For lines of similar widths, the integrated absorption coefficients are proportional to the heights of the lines.

**Selection rules and transition moments**

A ‘selection rule’ – a statement about whether a transition is allowed or forbidden. Selection rules apply to molecular spectra and depend on the type of transition. The underlying classical idea – for the molecule to be able to interact with the electromagnetic field and absorb or create a photon of frequency $\nu$, it must possess a dipole oscillating at that frequency. This transient dipole is expressed quantum mechanically in terms of the transition dipole moment, $\mu_{fi}$, between states $|i\rangle$ and $|f\rangle$:

$$\mu_{fi} = \langle f | \mu | i \rangle = \int \psi_f^* \mu \psi_i$$

$\mu$ - the electric dipole moment operator. The size of the transition dipole – a measure of the charge redistribution that accompanies a transition: a transition will be active (and generate or absorb photons) only if the accompanying charge redistribution is dipolar. Only if the transition moment is nonzero, the transition can contribute to the spectrum. Thus, to identify the selection rules, we must establish the conditions for which $\mu_{fi} \neq 0$. 
A gross selection rule – specifies the general features a molecule must have if it is to have a spectrum of a given kind. For instance, we shall see that a molecule gives a rotational spectrum only if it has a permanent dipole moment. A detailed study of transition moment leads to the specific selection rules that express the allowed transitions in terms of changes of quantum numbers: the rule $\Delta l = \pm 1$ for the angular momentum quantum number.

**Linewidths**

A number of effects contribute to the widths of spectroscopic lines. Some contributions can be modified by changing the conditions but other cannot be changed and represent an inherent limitation on resolution.

**Doppler broadening**

The Doppler effect in gaseous samples – radiation is shifted in frequency when the source is moving towards or away from the observer. When a source emitting electromagnetic radiation of frequency $\nu$ moves with a speed $s$ relative to an observer, the observer detects radiation of frequency

$$
\nu_{\text{receding}} = \frac{\nu}{\left(\frac{1-s/c}{1+s/c}\right)^{1/2}}
$$

$$
\nu_{\text{approaching}} = \frac{\nu}{\left(\frac{1+s/c}{1-s/c}\right)^{1/2}}
$$

For non-relativistic speeds ($s \ll c$):

$$
\nu_{\text{receding}} = \frac{\nu}{1+s/c}
$$

$$
\nu_{\text{approaching}} = \frac{\nu}{1-s/c}
$$

Molecules reach high speeds in all directions in a gas, and a stationary observer detects the corresponding Doppler-shifted range of frequencies. Some molecules approach the observer, some move away; some move quickly, others slowly. The detected spectral line is the profile from all the resulting Doppler shifts. The profile reflects the distribution of velocities parallel to the line of sight.
This profile is a bell-shaped Gaussian curve. The Doppler line shape is therefore also a Gaussian. When the temperature is $T$ and the mass of the molecules is $m$, then the observed width of the line at half-height is

\[
\delta \nu_{\text{obs}} = \frac{2 \nu}{c} \left( \frac{2kT \ln 2}{m} \right)^{1/2} \quad \delta \lambda_{\text{obs}} = \frac{2 \lambda}{c} \left( \frac{2kT \ln 2}{m} \right)^{1/2}
\]

For example, for a molecule like N$_2$ at room temperature, $\delta \nu/ \nu \approx 2.3 \times 10^{-6}$. For a typical rotational transition wavenumber of 1 cm$^{-1}$ ($\nu \approx 30$ GHz), the linewidth is about 70 kHz. Doppler broadening increases with $T$ because the molecules acquire a wider range of speeds. To obtain spectra with maximum sharpness - work with cold samples.

**Lifetime broadening**

Spectroscopic lines from gas-phase sample are not infinitely sharp even when Doppler broadening has been largely eliminated at low $T$. The residual broadening is due quantum mechanical effects. When the Shrödinger equation is solved for a system changing with time, it is found that it is impossible to specify energy levels exactly. If on average system survives in a state for a time $\tau$, the *lifetime* of the state, its energy levels are blurred by $\delta E$:

\[
\delta E = \frac{\hbar}{\tau}
\]

This lifetime broadening is called ‘uncertainty broadening’.

\[
\delta E = \hbar c \delta \tilde{\nu} \quad \text{therefore} \quad \delta \tilde{\nu} = \frac{5.3 \text{cm}^{-1}}{\tau/ \text{ps}}
\]
No excited state has an infinite lifetime – all states are subject to some lifetime broadening. The shorter the lifetimes of the states involved in a transition, the broader the corresponding spectral lines. Two processes are responsible for the finite lifetimes: **collisional deactivation** (dominant for low frequency transitions) – arises from collisions between molecules or with the walls of the container. The collisional linewidth can be minimized by working at low pressures. The second process – spontaneous emission of photons by excited states. The rate of spontaneous emission cannot be changed. Hence it is a natural limit to the lifetime of an excited state. The resulting lifetime broadening – the **natural linewidth** of the transition. The natural linewidth – an intrinsic property of the transition and cannot be changed by modifying the conditions. Natural line width depend strongly on the transition frequency (they increase with $\nu^3$), so low-frequency transitions (such as the microwave transitions of rotational spectroscopy) have very small natural linewidths, and collisional and Doppler line-broadening processes are dominant. The natural lifetimes of electronic transitions are very much shorter than for vibrational and rotational transitions, so the natural linewidths of electronic transitions are much greater than those of vibrational and rotational transitions. For example, a typical electronic excited state natural lifetime is about 10 ns – a natural width is about $5 \times 10^{-4} \text{ cm}^{-1}$ (15 Mhz). A typical rotational state natural lifetime is about $10^3$ s – a natural linewidth is only $5 \times 10^{-15} \text{ cm}^{-1}$ (~$10^{-4}$ Hz).