10

Molecular spectroscopy

10.1 Introduction to molecular spectroscopy

- Spectroscopy involves the interaction and exchange of electromagnetic radiation with matter.
- Molecular spectroscopy can be used to identify compounds, to measure how much of a compound is present, and to determine molecular properties.
- Absorption of energy can only take place when the energy of the radiation exactly matches the difference between molecular energy levels.
- The electromagnetic spectrum includes radiation with a large range of energies that can interact with various processes within molecules.

10.2 Molecular energies and spectroscopy

- Motion in molecules results in translational, rotational, and vibrational energies, all of which are quantized.
- The Schrödinger equation can be applied to molecules as well as to atoms.
- The Born–Oppenheimer approximation allows the different types of molecular energy to be treated independently

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} + E_{\text{translation}}$$

- Molecules can be treated as both waves and particles. Applying the de Broglie equation to a molecule moving in a box is a simple model that demonstrates the quantization of energy.
- Transitions between energy levels involve discrete quantities of energy and give rise to spectra.
- Translational energy levels are too close together for transitions between them to be observed spectroscopically, but rotational and vibrational energy levels are spaced far enough apart to be the basis of important spectroscopic techniques.
- Because of the different spacings between the energy levels for different types of molecular energy, the spectra appear in different parts of the electromagnetic spectrum.

For practice questions on these topics, see questions 1–5 at the end of this chapter (p.510).

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10.3 General principles of spectroscopy

- In absorption spectroscopy, molecules absorb photons with energies that correspond to the difference between energy levels in the molecule. Absorption of radiation promotes the molecule from its ground state to an excited state.
- In emission spectroscopy, radiation is emitted when an excited molecule falls back to the ground state.
- In absorption spectroscopy, a spectrum may be presented as an absorption spectrum or a transmission spectrum.
- An absorption spectrum is recorded by varying the energy of radiation incident on a sample and monitoring how much radiation is absorbed at each energy.
- Radiation can be absorbed when its energy corresponds to the *difference* in energy between energy levels in a molecule.
- The *position* of a peak in a spectrum is related to the *difference* in energy between energy levels, ΔE.
- The *intensity* of the peaks is related to the *number* of transitions that occur when radiation is absorbed. This depends on:
  - the concentration of the solution, c, and the path length, l, according to the Beer–Lambert law: $A = \varepsilon c l$, where A is the absorbance and ε is the molar absorption coefficient;
  - the population of energy levels, according to the Boltzmann distribution;
  - the selection rules for the particular form of spectroscopy, which determine whether a particular transition is allowed.

For practice questions on these topics, see questions 6–12 at the end of this chapter (pp.510–511).

10.4 Rotational spectroscopy

- Rotational spectra are recorded in the gas phase. The transitions correspond to microwave and far infrared radiation.
- Quantized rotational energy is described by $E_J = hBJ(J+1)$ for a diatomic molecule, where B is the rotational constant and J is the rotational quantum number.
- Selection rules:
  - gross (general): the molecules must have a permanent electric dipole to show a spectrum;
  - specific: the rotational quantum number can only change by 1: $\Delta J = \pm 1$.
- At 298 K, the population of molecules is spread through many rotational levels.
- The rotational spectrum of a diatomic molecule consists of a series of evenly spaced lines. The energy difference between successive lines is always $2hB$. (The spacing in frequency units is $2B$ and in wavenumber units is $2B/c$.)
- The rotational constant, $B = \dfrac{h}{8\pi^2 I}$, can be found from the spacing of the lines in the spectrum. (I is the moment of inertia.)
- The bond length, r_0, is found using $I = \mu r_0^2$, where μ is the reduced mass.

For practice questions on these topics, see questions 13–17 at the end of this chapter (p.511).

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10.5 Vibrational spectroscopy

- Infrared radiation is absorbed during transitions between vibrational energy levels.
- The chemical bond in a diatomic molecule can be represented by a spring undergoing simple harmonic motion with a frequency given by

$$\nu = \frac{h}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

  where k is the force constant of the bond and μ is the reduced mass of the two atoms forming the bond.
- Vibrational energy is quantized according to

$$E_v = (v + \tfrac{1}{2})h\nu$$

  where v is the vibrational quantum number (v = 0, 1, 2, . . . , ∞).
- Infrared spectroscopy is governed by selection rules:
  - the molecule must undergo a change in electric dipole moment during vibration;
  - $\Delta v = \pm 1$.
- For a harmonic oscillator, vibrational transitions between different levels all have the same energy. At room temperature, the predominant transition is from the vibrational ground state ($v = 0 \rightarrow v = 1$).
- Vibrational spectra can be used to measure the force constant, k, of a bond.
- Similar models can be applied to polyatomic molecules that have several vibrational modes.
- A molecule containing N atoms has:
  - $(3N - 5)$ vibrational modes if it is a linear molecule;
  - $(3N - 6)$ vibrational modes if it is a non-linear molecule.
- Transitions occur simultaneously between vibrational and rotational states. This results in vibration–rotation spectra.
- Raman spectroscopy uses the Raman effect, in which light scattered by the sample has its frequency shifted to a higher or lower frequency. The energy difference between the incident and scattered radiation corresponds to the difference in energy between vibrational and rotational levels in the molecules.

For practice questions on these topics, see questions 18–24 at the end of this chapter (p.511).

10.6 Electronic spectroscopy

- Electronic spectroscopy involves the excitation of electrons by absorption of UV or visible radiation.
- The colour of substances is due to the absorption of some wavelengths of visible light by the molecules. The colour observed is due to the light *not* absorbed.
- Each electronic state has several vibrational (and rotational) states associated with it.
- Absorption of photons by electronic states obeys the Frank–Condon principle: the excitation of an electron by the absorption of a photon occurs on a much shorter timescale than that of nuclear motions.
- Electronic excitation may lead to breaking of bonds (photodissociation), causing photochemical reactions.
- A chromophore is the part of a molecule that is responsible for absorption of a photon of UV/VIS radiation.

For a practice question on these topics, see question 26 at the end of this chapter (p.511).

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10.7 Spin resonance spectroscopy

- Electrons have spin, which is characterized by a *spin quantum number*, s, where $s = \frac{1}{2}$.
- Neutrons and protons also have spin. Atomic nuclei have a *nuclear spin quantum number*, I. $I = \frac{1}{2}$ for ^{1}H, ^{13}C, ^{19}F, and ^{31}P. ($I = 0$ for nuclei where nuclear spins are paired.)
- When placed in an *external magnetic field*, the electron spin states, or the nuclear spin states, have different energies depending on their alignment with or against the magnetic field.
- In spin resonance spectroscopy, the sample is placed in a strong external magnetic field and irradiated with the appropriate energy, ΔE, to promote the electron or nucleus from the lower energy spin state to the higher energy spin state. For electron spin, ΔE corresponds to energy in the microwave region; for nuclear spin, ΔE corresponds to the energy of radio waves.
- *ESR spectroscopy* is used to study species with unpaired electrons.
- *NMR spectra* can be recorded for nuclei with unpaired spins. The most commonly used NMR nuclei have $I = \frac{1}{2}$ but spectra can also be recorded when $I = 1, 1\frac{1}{2}$, etc.
- The nuclear spin comes into resonance when irradiated with electromagnetic radiation with the *Larmor frequency* and the nucleus is promoted into the higher energy spin state.
- *Chemical shift* is characteristic of nuclei (e.g. ^{1}H) in a particular environment within a molecule. It occurs due to shielding effects by electrons around the nucleus and is measured by the difference, δ, of the resonance frequency from that of a standard (e.g. tetramethylsilane for ^{1}H nuclei).
- The relative intensities of the resonance signals in a ^{1}H spectrum depend on the number of ^{1}H nuclei in the molecule giving rise to the signal.
- NMR signals show fine structure due to splitting by adjacent nuclei through *spin–spin* coupling.

For practice questions on these topics, see questions 26–29 at the end of this chapter (p.511).

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Concept review

By the end of this chapter, you should be able to do the following.

- Understand the basic principles of molecular spectroscopy in terms of the quantization of molecular energy and transitions between molecular energy levels when matter interacts with radiation.
- Use the 'particle in a box' model to account for quantization in a one-dimensional system.
- Calculate the energy of radiation from its wavelength, frequency, or wavenumber and interconvert between these quantities.
- Use the Beer–Lambert law to find the absorbance, *A*, of the solution and hence the ratio of the intensities of the transmitted and incident radiation, or to find the molar absorption coefficient, depending on what data are available.
- Assign the type of molecular transition associated with radiation of a particular energy in the electromagnetic spectrum.
- Describe in general terms how molecular spectra can be measured.
- Differentiate between absorption and transmission spectra and between absorption and emission spectra.
- Account for the relative populations of energy levels by using the Boltzmann distribution.
- Describe the origin and appearance of rotational spectra.
  - Describe and use the rigid rotor model for a diatomic molecule.
  - State and use the selection rules for rotational spectra.
  - Use spectral data to calculate moments of inertia and bond lengths in diatomic molecules.
- Describe the origin and appearance of infrared spectra.
  - Describe and use the simple harmonic oscillator model for a diatomic molecule.
  - State and use the selection rules for vibrational spectra.
  - Use spectral data to calculate force constants of chemical bonds.
- Describe the types of vibrations that can occur in diatomic and triatomic molecules.
  - Calculate the number of modes of vibration in a molecule.
- Understand what is meant by a vibration–rotation spectrum.
- Understand what is meant by a Raman spectrum.
- Describe the origin and appearance of electronic spectra for molecules.
  - Account for the colours of compounds in terms of the wavelength of radiation absorbed.
  - Explain what is meant by a chromophore.
- Describe the origin and appearance of NMR spectra.
- Determine which nuclei will show NMR spectra.
- Explain what is meant by *chemical shift* and *integration curve* and how these are used to interpret NMR spectra in terms of molecular structure.
- Predict the fine structure in an NMR spectrum of an $I = \frac{1}{2}$ nucleus from the molecular structure.

Table 10.4 Summary of the types of spectra in the chapter

Type of transition	Region of electromagnetic spectrum	Typical units on *x*-axis of spectrum	Description of spectrum
Electronic	Ultraviolet and visible	Wavelength: λ/nm	Broad absorption bands rising from the baseline
Vibrational	Infrared	Wavenumber: $\tilde{\nu}$/cm^{-1}	Peaks point downwards in a transmission spectrum
Rotational	Far infrared and microwave	Wavenumber: $\tilde{\nu}$/cm^{-1}	Series of evenly spaced lines (pointing downwards in a transmission spectrum or upward in an absorption spectrum)
Nuclear spin	Radiofrequency	Chemical shift: δ/ppm	Resonance signals rising from the baseline. Signals often show fine structure due to spin–spin coupling. Integration curve of ^{1}H spectrum shows area of each signal, which is proportional to the number of ^{1}H nuclei responsible for the signal

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Key equations

Born–Oppenheimer approximation	$E_{total} = E_{electronic} + E_{vibration} + E_{rotation} + E_{translation}$	(10.1)
Beer–Lambert law	$A = \varepsilon \times c \times l$	(10.8)
	where $A = \log_{10}\left(\frac{I_0}{I_t}\right)$	(10.7)
Boltzmann distribution of molecules between energy levels	$\frac{n_{upper}}{n_{lower}} = \frac{g_{upper}}{g_{lower}} e^{\left(\frac{-\Delta E}{k_B T}\right)}$	(10.9)
Moment of inertia of a diatomic molecule	$I = \mu r_0^2$	(10.12)
Reduced mass of a diatomic molecule	$\mu = \frac{m_1 m_2}{m_1 + m_2}$	(10.13)
Rotational energy levels of a diatomic molecule	$E_{rotation} = E_J = \frac{h^2}{8\pi^2 I} J(J+1)$	(10.14)
Frequency of vibration of a diatomic molecule acting as a harmonic oscillator	$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$	(10.18)
Vibrational energy levels of a diatomic molecule	$E_{vibration} = E_v = \left(v + \frac{1}{2}\right)h\nu$	(10.20)
Energy difference between the two spin states for an	$I = \frac{1}{2}$ nucleus $\Delta E = \frac{\gamma B h}{2\pi}$	(10.23)

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