Introduction

1

1.1 Role of Quantum Mechanics

This text focuses on the application of spectroscopic diagnostics to gaseous flows. In order to keep the length and scope manageable, we will accept, prima facie, the results of quantum mechanics (explaining quantum mechanics in detail would require another complete text, of which many are already available). That is, we accept that an atom or molecule may exist only in specific quantum states (characterized by quantum "numbers"), with each quantum state having a discrete amount of energy and angular momentum. *Hence, molecular energy is quantized.* Furthermore, we will view the internal energy, which excludes kinetic energy, as the sum of the energy stored in three modes: (1) rotation, (2) vibration, and (3) electronic:

$$E_{\text{tot}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}. \tag{1.1}$$

Note that quantized internal energies lead to discrete differences in energy when molecules change quantum states. These transitions correspond directly with the energy of emitted or absorbed photons (and hence the emission or absorption wavelengths) in discrete spectra. Quantum mechanics also places restrictions on the allowable changes in quantum states during emission and absorption, described by *selection rules*. These selection rules (also simply accepted in this course) dictate which transitions are *allowed* and which are *forbidden*, and greatly simplify the resulting spectra.

1.2 Emission and Absorption Spectra

Emission results when a molecule or atom changes quantum states from higher to lower energy and releases a photon. *Absorption* occurs when a molecule or atom changes quantum states from lower to higher energy by absorbing a photon.

R.K. Hanson et al., *Spectroscopy and Optical Diagnostics for Gases*,
DOI 10.1007/978-3-319-23252-2_1

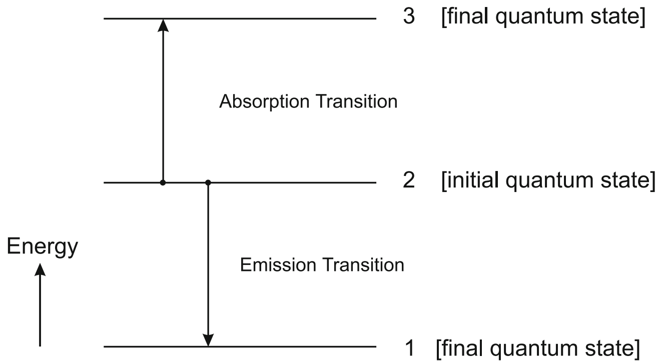

Fig. 1.1 Absorption and emission energy transitions in an atom/molecule

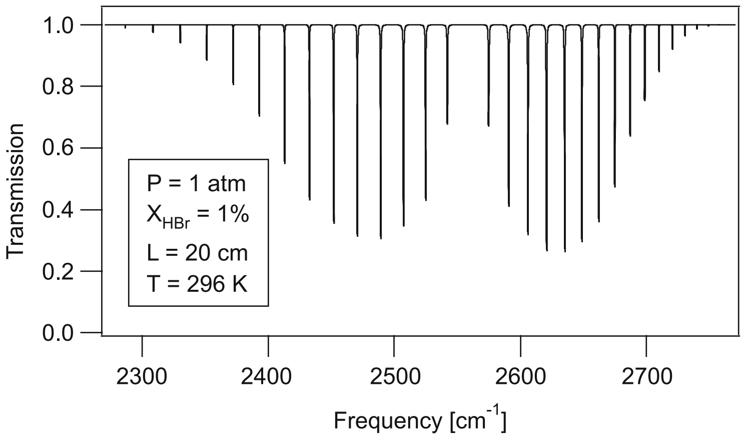

Fig. 1.2 Calculated infrared absorption spectra for HBr. Here frequency (cm^{-1}) is simply 1/wavelength (cm)

The energy of the photon emitted or absorbed is equal to the difference in energy of the two quantum states (by conservation of energy, of course!). Figure 1.1 shows how the energy of a molecule changes during these processes. Example absorption and emission spectra, obtainable by measuring the energies of the photons involved in these processes, are shown in Figs. 1.2 and 1.3.

Our goal: to be able to interpret and predict absorption and emission spectra.

Before being able to interpret spectra, however, we must first know a few basics about light.

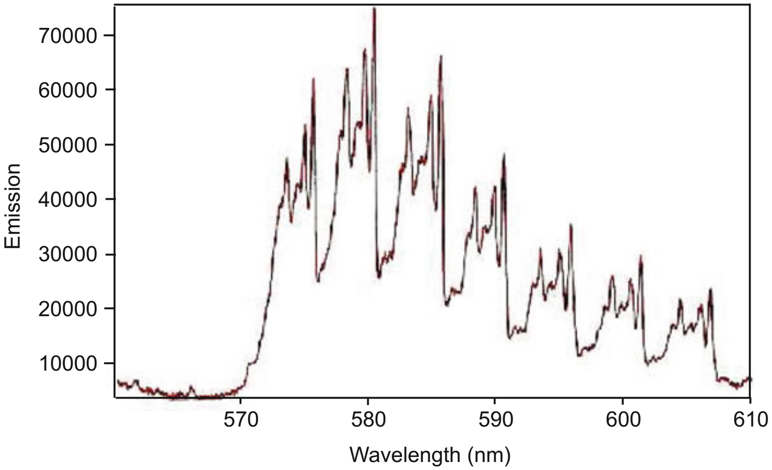

Fig. 1.3 Typical emission spectra of high-temperature air between 560 and 610 nm. The seven large features are part of the $N_2(1^+)$ system of transitions

1.3 Planck's Law

Planck's Law is a fundamental relation that links two ways of thinking about radiation, namely the *particle* and *wave* concepts:

$$\Delta E = E_{\text{upper}} - E_{\text{lower}} = h\nu \tag{1.2}$$

Here ΔE is the energy of the photon (i.e., the *particle*) associated with a molecular transition (emission or absorption) between two quantum states, while ν is the frequency of the corresponding electromagnetic *wave*, and h is Planck's constant:

$$h = 6.63 \times 10^{-34}\,\text{J s} \tag{1.3}$$

Extending Eq. (1.1), we may also express the change in energy of the molecule (i.e., the energy of the photon) as

$$\Delta E = \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E_{\text{elec}}. \tag{1.4}$$

That is, the total change in internal energy of a molecule/atom is the sum of the individual changes in rotational, vibrational, and electronic energy. Energy changes in each of these modes have different magnitudes (as the reader will see in Fig. 1.4, if he/she doesn't already know) and can be classified according to the following:

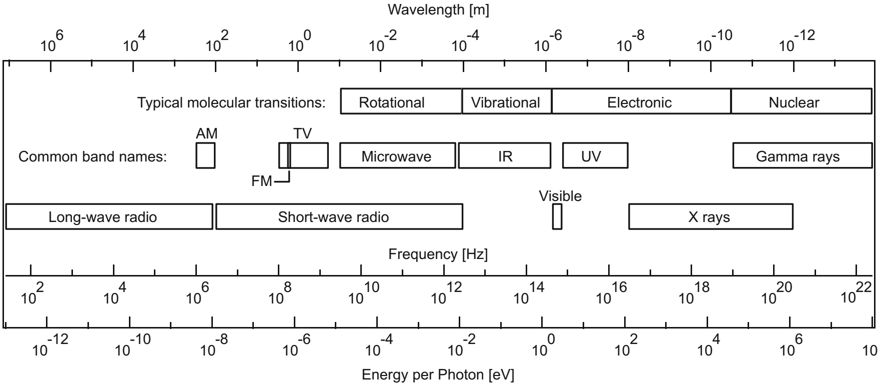

Fig. 1.4 Electromagnetic spectrum

$$\begin{aligned}\Delta E_{\text{rot}} &\rightarrow \text{microwave transitions (rotational)}\\ \Delta E_{\text{rot}} + \Delta E_{\text{vib}} &\rightarrow \text{IR transitions (rovibrational)}\\ \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E_{\text{elec}} &\rightarrow \text{UV/Vis transitions (rovibronic)}\end{aligned}$$

Note that changes in vibrational energy are generally accompanied by changes in rotational energy, and changes in electronic energy are accompanied by changes in vibrational and rotational energy (although ΔE_{rot} and ΔE_{vib} can sometimes be zero).

Thus, absorption or emission spectra generally consist of a number of “lines,” corresponding to the discrete differences in energy between a molecule’s states which are allowed (quantum mechanically) to undergo radiative transitions.

1.4 Wavelength, Frequency, and Other Units and Conversions

Spectroscopy utilizes several different units of length and energy. The most common usage varies with the spectral region in question.

Term	Symbol	Units
Wavelength	λ	Å, nm, μm (microns); 1 Å $= 10^{-8}$ cm $= 0.1$ nm
Frequency	ν	s^{-1}, Hz, MHz, GHz, THz
Wavenumber	$\overline{\nu}, \omega$	cm^{-1}, mK ($10^{-3}\,\text{cm}^{-1} = 1$ milliKayser) (a wavenumber is the number of wavelengths per cm)
Energy	E, ΔE	J, cm^{-1}, ergs, eV (all per photon); kcal/mole

The relationship between wavelength and (temporal) frequency is given by

$$c = \lambda \nu \tag{1.5}$$

where λ is the wavelength of the radiation and c is the speed of light, nominally 3.0×10^8 m/s.

Wavelength and wavenumber (sometimes also called frequency, as in spatial frequency) are related by

$$\overline{\nu} = \omega = 1/\lambda \tag{1.6}$$

From Eqs. (1.5) and 1.6, Planck's Law can be written in several ways:

$$\boxed{\Delta E = h\nu = hc/\lambda = hc\overline{\nu} = hc\omega} \tag{1.7}$$

Hence, a transition is interchangeably expressed in terms of nanometers, angstroms or microns for wavelength and in Hertz or wavenumbers for frequency. In the infrared (IR), use of wavenumber units is quite common; however, in the visible or ultraviolet (UV), nanometer or angstrom units are the norm.

1.5 Spectral Regions

Figure 1.4 shows some of the different regions of the electromagnetic spectrum, along with regions where rotational, vibrational, and electronic transitions tend to occur. The boundaries are somewhat variable in common usage.

As can be seen from Fig. 1.4, units of energy can have many equivalent forms. Knowing the conversion for a few reference points and the scaling may facilitate fluency in every unit. For example,[1]

$$\begin{aligned} \lambda_{1\,\mathrm{eV}} &\approx 12{,}400\,\text{Å} \\ \lambda_{2\,\mathrm{eV}} &\approx 620\,\mathrm{nm} \\ \lambda_{4\,\mathrm{eV}} &\approx 310\,\mathrm{nm} \end{aligned}$$

and

$$\begin{aligned} \lambda\ [\mathrm{nm}] &= 10^7/\overline{\nu}\ [\mathrm{cm}^{-1}] \\ \rightarrow\ 500\,\mathrm{nm} &= 20{,}000\,\mathrm{cm}^{-1} \\ \rightarrow\ 1000\,\mathrm{nm} &= 10{,}000\,\mathrm{cm}^{-1} \end{aligned}$$

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[1] $1\,\mathrm{eV} \approx 1.6 \times 10^{-19}\,\mathrm{J}$.

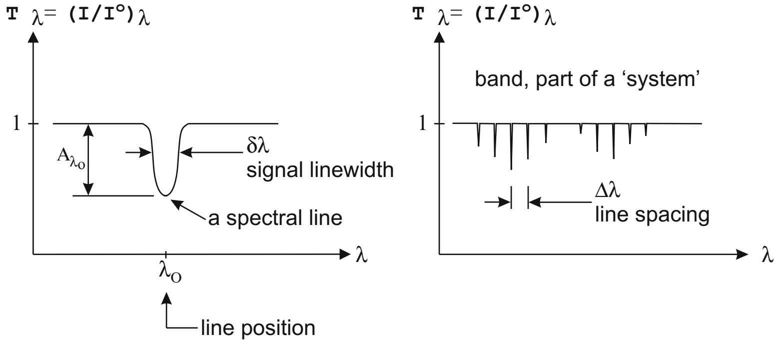

Fig. 1.5 Representative absorption spectra. The *left-hand side* shows a single line, while the *right-hand side* shows a band

1.6 Basic Elements of Spectroscopy

A *line* is the part of a spectrum that corresponds to a transition from one quantum state to another, e.g. a change in a molecule's rotational energy may show a rotational line in a spectrum as shown on the left of Fig. 1.5. Groups of individual lines, with common upper and lower vibrational quantum numbers, may comprise a *vibrational band*, shown on the right of Fig. 1.5. Furthermore, several vibrational bands may comprise an *electronic system*.

1.6.1 Positions, Strengths, and Shapes of Lines

It is convenient to think of spectroscopy as comprised of three primary elements: i.e., the positions, strengths, and shapes of lines. Line positions, which receive emphasis in classical spectroscopy, depend on molecular structure. The strengths and shapes of lines are of particular importance in diagnostics applications. All three elements will be addressed in this reader.

What is the relationship of these spectral features to gaseous properties?

1.	Line positions and spacing (λ_0, $\Delta\lambda$ in Fig. 1.5)	→	molecular parameters (internuclear spacing, bond angles)
2.	Absorbance and linewidth (A_λ, $\delta\lambda$ in Fig. 1.5)	→	composition, temperature, pressure

1.7 Typical Absorption Spectroscopy Setup

Most modern absorption experiments use a laser as the radiation source for several reasons. First, their high intensities allow absorption measurements in very hot gases (with high background emissions levels). Also, because they are

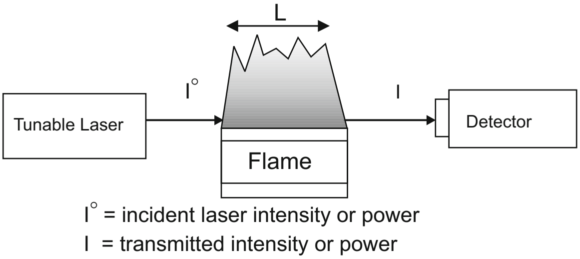

Fig. 1.6 Laser absorption experimental schematic

highly collimated, laser light can travel across substantial distances—up to several kilometers. Furthermore, lasers are often spectrally narrow and tunable in wavelength, allowing high-resolution measurements of absorption spectra. Alternatively, absorption spectra may be recorded with a spectrally broad light source (e.g., globar) and a tunable spectral filter (e.g., grating monochromator), but such spectra are *artificially broadened* owing to the (relatively) large spectral bandwidth of the filters currently available.

1.8 Beer's Law of Absorption

The governing law for absorption spectroscopy describes the relationship between the incident and transmitted laser intensities, shown in Fig. 1.6. By way of introduction, Beer's Law is simply listed below. In Chap. 7 it will be derived.

$$\textbf{Beer's Law} \qquad T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L) \tag{1.8}$$

T_ν is the fractional transmission at frequency ν, k_ν is the spectral absorption coefficient [cm^{-1}], and L is the absorption path length [cm]. The combined quantity $k_\nu L$ is known as the *spectral absorbance*. The spectral absorption coefficient for a single, spectrally isolated transition (typical of atoms and small molecules) is given by

$$k_\nu = S \times \phi(\nu \text{ or } \lambda) \times P_i \tag{1.9}$$

For Eq. (1.9), S is the "strength" of the transition (common units are cm^{-2} atm^{-1}), ϕ is the "lineshape function" (common unit is cm), and P_i is the partial pressure of the absorbing species (unit is atm). Beer's Law can also be expressed in terms of absorption:

$$A_\nu = 1 - T_\nu = \left(\frac{I^0 - I}{I^0}\right)_\nu = 1 - \exp(-k_\nu L) \tag{1.10}$$

1.9 Spectral Absorption Coefficient

Later in the course we will derive relations for the spectral absorption coefficient, k_ν, which appears in Beer's Law of absorption (Eq. (1.8)). We will find that k_ν is proportional to: (1) the population density n_i in the lower level i of an absorption transition, and (2) a parameter (e.g., f_{osc} or B_{12}) that characterizes the strength of the transition. Here f_{osc} is known as the oscillator strength and B_{12} is an Einstein coefficient for absorption between levels 1 and 2.

Thus, absorption from a level i will only occur at frequencies corresponding to quantum-mechanically allowed transitions, and the magnitude of the absorption coefficient depends on the population density in i and the oscillator strength of the transition.

1.10 Boltzmann Distribution

Boltzmann's equation for the fraction of molecules in energy level i is [1]

$$F_i = \frac{n_i}{n} = \frac{g_i \exp\left(-\frac{\epsilon_i}{kT}\right)}{Q}, \tag{1.11}$$

where the partition function, Q, is given by

$$Q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{kT}\right) = Q_{\text{rot}} Q_{\text{vib}} Q_{\text{elec}} \tag{1.12}$$

The Boltzmann distribution function describes the equilibrium distribution of molecules (or atoms) of a single species over its allowed quantum states. Here g_i is the degeneracy of level i (i.e., the number of individual states with a common energy, ϵ_i) and Q is a specific, energy-weighted sum over all levels known as the partition function. There are some subtle differences between "states" and "levels" which will require careful attention later in this course. Note that the overall partition function Q may be written as a product of partition functions for the different types of internal energy, since these energies are taken to be additive. The parameter T is the temperature, and the species may be said to be in local thermodynamic equilibrium (LTE) if the populations in all the quantum levels obey Boltzmann's equation. In essence, this equation *defines temperature*.

Reference

1. W.G. Vincenti, C.H. Kruger, *Physical Gas Dynamics* (Krieger Publishing Company, Malabar, FL, 1965)