

2

Electromagnetic Radiation and its Interaction with Atoms and Molecules

2.1 Electromagnetic radiation

Electromagnetic radiation includes, in addition to what we commonly refer to as 'light', radiation of longer and shorter wavelengths (see Section 3.1). As the name implies it contains both an electric and a magnetic component, which are best illustrated by considering plane-polarized (also known as linearly polarized) radiation. Figure 2.1 illustrates one photon of such radiation travelling along the x axis. The electric component of the radiation is in the form of an oscillating electric field of strength E and the magnetic component is in the form of an oscillating magnetic field of strength H . These oscillating fields are at right angles to each other, as shown, and, if the directions of the vectors E and H are y and z respectively, then

$$\left. \begin{aligned} E_y &= A \sin(2\pi\nu t - kx) \\ H_z &= A \sin(2\pi\nu t - kx) \end{aligned} \right\} \quad (2.1)$$

where A is the amplitude. Therefore, the fields oscillate sinusoidally with a frequency of $2\pi\nu$ and, because k is the same for each component, they are in-phase.

The plane of polarization is conventionally taken to be the plane containing the direction of E and that of propagation; in Figure 2.1 this is the xy plane. The reason for this choice is that interaction of electromagnetic radiation with matter is more commonly through the electric component.

2.2 Absorption and emission of radiation

In Figure 2.2(a) states m and n of an atom or molecule are stationary states, so-called because they are time-independent. This pair of states may be, for example, electronic, vibrational or rotational. We consider the three processes that may occur when such a

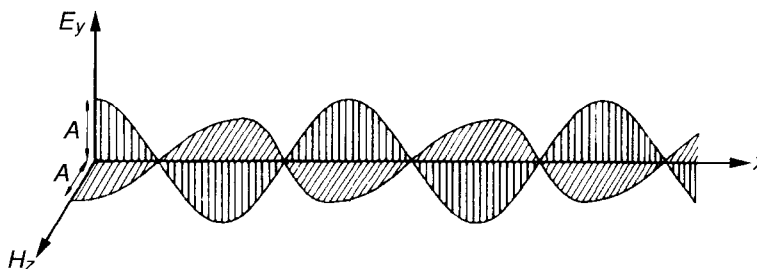


Figure 2.1 Plane-polarized electromagnetic radiation travelling along the x axis; E_y is the electric component; H_z is the magnetic component

two-state system is subjected to radiation of frequency ν , or wavenumber $\tilde{\nu}$, corresponding to the energy separation ΔE where

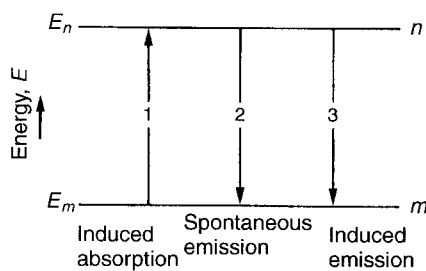
$$\Delta E = E_n - E_m = h\nu = hc\tilde{\nu} \quad (2.2)$$

These processes are:

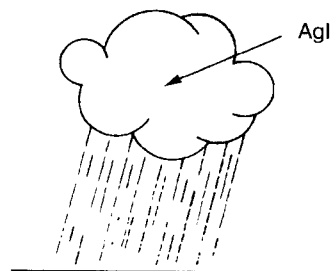
1. *Induced absorption*, in which the molecular (or atom) M absorbs a quantum of radiation and is excited from m to n :



This is the familiar absorption process illustrated by the appearance of an aqueous solution of copper sulphate as blue due to the absorption of the complementary colour, red, by the solution.



(a)



(b)

Figure 2.2 (a) Absorption and emission processes between states m and n . (b) Seeding of a rain cloud with silver iodide (AgI) to induce a shower of rain

2. *Spontaneous emission*, in which M^* (in state n) spontaneously emits a quantum of radiation:



Almost all emission that we usually encounter, such as that from a sodium vapour or tungsten filament lamp, is of the spontaneous type.

3. *Induced, or stimulated, emission*. This is a different type of emission process from that of type 2 in that a quantum of radiation of wavenumber $\tilde{\nu}$ given by Equation (2.2) is required to induce, or stimulate, M^* to go from n to m . The process is represented by



and may seem rather unusual to anyone used only to the spontaneous emission process. There is a useful analogy between induced emission, requiring the presence of radiation of the correct wavenumber for it to occur, and the seeding of a cloud with silver iodide crystals in order to induce it to shed a shower of rain which it would not otherwise do, as shown in Figure 2.2(b). The silver iodide plays the part of the quantum of radiation necessary to induce the process. The reason why the absorption process is strictly referred to as induced absorption may now be appreciated since, of course, it requires the presence of radiation of wavenumber $\tilde{\nu}$ in order to occur.

The rate of change of population N_n of state n due to induced absorption is given by

$$\frac{dN_n}{dt} = N_m B_{mn} \rho(\tilde{\nu}) \quad (2.6)$$

where B_{mn} is a so-called Einstein coefficient and $\rho(\tilde{\nu})$, the spectral radiation density, is given by

$$\rho(\tilde{\nu}) = \frac{8\pi hc\tilde{\nu}^3}{\exp(hc\tilde{\nu}/kT) - 1} \quad (2.7)$$

Similarly, induced emission changes the population N_n by

$$\frac{dN_n}{dt} = -N_n B_{nm} \rho(\tilde{\nu}) \quad (2.8)$$

where B_{nm} is the Einstein coefficient for this process and is equal to B_{mn} . For spontaneous emission, we have

$$\frac{dN_n}{dt} = -N_n A_{nm} \quad (2.9)$$

where A_{nm} is another Einstein coefficient and the absence of $\rho(\tilde{\nu})$ indicates a spontaneous process. In the presence of radiation of wavenumber $\tilde{\nu}$ all three processes are going on at once and, when the populations have reached their equilibrium values, we have

$$\frac{dN_n}{dt} = (N_m - N_n)B_{nm}\rho(\tilde{\nu}) - N_n A_{nm} = 0 \quad (2.10)$$

At equilibrium N_n and N_m are related, through the Boltzmann distribution law, by

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{\Delta E}{kT}\right) \quad (2.11)$$

if the degrees of degeneracy g_n and g_m of states n and m are the same. Putting this relationship and the expression for $\rho(\tilde{\nu})$, given in Equation (2.7), into Equation (2.10) gives the result

$$A_{nm} = 8\pi hc\tilde{\nu}^3 B_{nm} \quad (2.12)$$

This equation illustrates the important point that spontaneous emission increases rapidly relative to induced emission as $\tilde{\nu}$ increases. Since lasers (Section 9.1) operate entirely by induced emission the equation is particularly relevant to laser design.

Worked example 2.1

Question. For temperatures of 25 °C and 1000 °C, calculate the ratio of molecules in a typical excited rotational, vibrational and electronic energy level to that in the lowest energy level, assuming that the levels are 30 cm⁻¹, 1000 cm⁻¹ and 40 000 cm⁻¹, respectively, above the lowest energy level. [Three significant figures are sufficient. Assume that, for the excited rotational level, the rotational quantum number J is 4, and remember that each level is $(2J + 1)$ -fold degenerate. Assume that the vibrational and electronic energy levels are non-degenerate.]

Answer. Using Equation (2.11) for the rotational energy level with $J=4$, and the Planck relation between energy and wavenumber of Equation (2.2), we have

$$\begin{aligned} \frac{N_n}{N_m} &= \frac{N_J}{N_0} = \frac{2J+1}{1} \exp\left(-\frac{hc\tilde{\nu}}{kT}\right) \\ &= 9 \exp\left(-\frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 30 \text{ cm}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}}\right) \\ &= 7.79 \text{ at } 25 \text{ }^\circ\text{C} \text{ (298 K)} \\ &\text{and } 8.70 \text{ at } 1000 \text{ }^\circ\text{C} \text{ (1273 K)} \end{aligned}$$

(Remember that exponentials and logarithms have no units so that the units of this exponential must cancel.)

For the vibrational energy level:

$$\begin{aligned}\frac{N_v}{N_0} &= \exp\left(-\frac{6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 1000}{1.381 \times 10^{-23} \times 298}\right) \\ &= 8.01 \times 10^{-3} \text{ at } 25^\circ\text{C} \\ &= 0.323 \text{ at } 1000^\circ\text{C}\end{aligned}$$

For the electronic energy level:

$$\begin{aligned}\frac{N_e}{N_0} &= \exp\left(-\frac{6.626 \times 10^{-34} \times 2.998 \times 10^{10} \times 40\,000}{1.381 \times 10^{-23} \times 298}\right) \\ &= 1.40 \times 10^{-84} \text{ at } 25^\circ\text{C} \\ &= 2.35 \times 10^{-20} \text{ at } 1000^\circ\text{C}\end{aligned}$$

These calculations show how rotational energy levels are much more heavily populated than are vibrational energy levels which, in turn, are much more heavily populated than electronic energy levels – indeed, at room temperature, there is zero population of a typical electronic energy level. The calculations also show how the populations increase with increasing temperature so that, at very high temperatures, populations of electronic states can become important. For example, the temperature of hydrogen atoms in the exterior (the photosphere) of a star can be of the order of 6000 K. The interior of the star acts as continuum source of radiation and the huge path length of absorbing atoms, together with their high temperature, results in the Balmer series being observed *in absorption* due to the appreciable population of the $n = 2$ level.

The Einstein coefficients are related to the wave functions ψ_m and ψ_n of the combining states through the transition moment R^{nm} , a vector quantity given by

$$R^{nm} = \int \psi_n^* \boldsymbol{\mu} \psi_m \, d\tau \quad (2.13)$$

for interaction with the electric component of the radiation. The quantity $\boldsymbol{\mu}$ is the electric dipole moment operator, and

$$\boldsymbol{\mu} = \sum_i q_i \mathbf{r}_i \quad (2.14)$$

where q_i and \mathbf{r}_i are the charge and position vector of the i th particle (electron or nucleus). The transition moment can be thought of as the oscillating electric dipole moment due to the transition. Figure 2.3 shows the π and π^* molecular orbitals of ethylene and, if an electron is promoted from π to π^* in an electronic transition, there is a corresponding non-zero transition moment. This example illustrates the important point that a transition moment

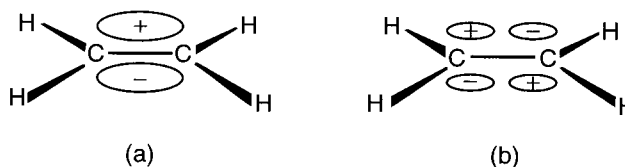


Figure 2.3 (a) A π and (b) a π^* molecular orbital of ethylene

may be non-zero even though the permanent electric dipole moment is zero in both the states m and n .

The square of the magnitude of \mathbf{R}^{nm} is the transition probability and is related to B_{nm} by

$$B_{nm} = \frac{8\pi^3}{(4\pi\epsilon_0)3h^2} |\mathbf{R}^{nm}|^2 \quad (2.15)$$

where $|\mathbf{R}^{nm}|$ is the magnitude of vector \mathbf{R}^{nm} . The following illustrates how B_{nm} may be found experimentally in the case of an absorption experiment.

The experiment is illustrated in Figure 2.4(a), where radiation of intensity I_0 falls on the absorption cell of length ℓ containing absorbing material of concentration c in the liquid phase. The radiation emerges with intensity I , and scanning the radiation through an appropriate wavenumber range of the absorption, say $\tilde{\nu}_1$ to $\tilde{\nu}_2$, and measuring I_0/I produces

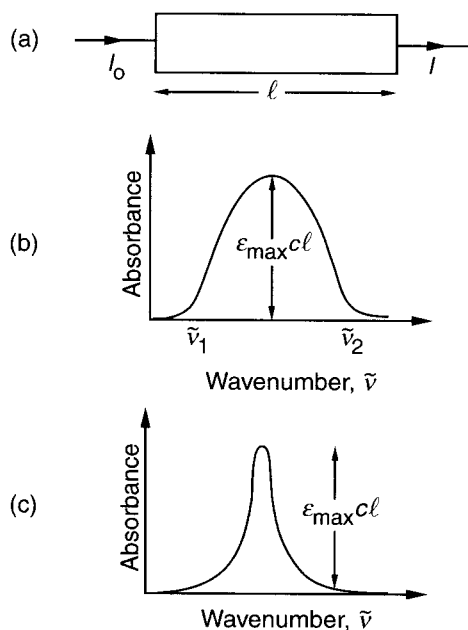


Figure 2.4 (a) An absorption experiment. (b) A broad and (c) a narrow absorption band with the same ϵ_{\max} ; c is the concentration of the absorbing material in the liquid phase

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the absorption spectrum typically measured as absorbance, defined as $\log_{10}(I_0/I)$. According to the Beer–Lambert law the absorbance A is proportional to c and ℓ , so that

$$A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon(\tilde{\nu})c\ell \quad (2.16)$$

where ε is a function of $\tilde{\nu}$ and is the molar absorption coefficient or molar absorptivity (it used to be known as the molar extinction coefficient, which will be encountered in older texts). Since A is dimensionless, ε has dimensions of $(\text{concentration} \times \text{length})^{-1}$ and the units are very often $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$. The spectrum is shown in Figure 2.4(b). The quantity ε_{max} corresponds to the maximum value of A and is sometimes used as a measure of the total absorption intensity. However, the spectrum in Figure 2.4(c), which has the same ε_{max} but a much lower integrated intensity, illustrates the dangers of using ε_{max} . What we should do is to integrate the area under the curve; then, provided $N_n \ll N_m$ so that decay of state n by induced emission is negligible,

$$\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon(\tilde{\nu})d\tilde{\nu} = \frac{N_A h \tilde{\nu}_{nm} B_{nm}}{\ln 10} \quad (2.17)$$

where $\tilde{\nu}_{nm}$ is the average wavenumber of the absorption and N_A is the Avogadro constant.

If the absorption is due to an electronic transition then f_{nm} , the oscillator strength, is often used to quantify the intensity and is related to the area under the curve by

$$f_{nm} = \frac{4\varepsilon_0 m_e c^2 \ln 10}{N_A e^2} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon(\tilde{\nu})d\tilde{\nu} \quad (2.18)$$

The quantity f_{nm} is dimensionless and is the ratio of the strength of the transition to that of an electric dipole transition between two states of an electron oscillating in three dimensions in a simple harmonic way, and its maximum value is usually 1.

The transition probability $|R^{nm}|^2$ is related to selection rules in spectroscopy: it is zero for a forbidden transition and non-zero for an allowed transition. By ‘forbidden’ or ‘allowed’ we shall mostly be referring to electric dipole selection rules (i.e. to transitions occurring through interaction with the electric vector of the radiation).

The electric dipole moment operator $\boldsymbol{\mu}$ has components along the cartesian axes:

$$\mu_x = \sum_i q_i x_i; \quad \mu_y = \sum_i q_i y_i; \quad \mu_z = \sum_i q_i z_i \quad (2.19)$$

where q_i and x_i are, respectively, the charge and x coordinate of the i th particle, and so on. Similarly, the transition moment can be resolved into three components such that

$$R_x^{nm} = \int \psi_n^* \mu_x \psi_m dx; \quad R_y^{nm} = \int \psi_n^* \mu_y \psi_m dy; \quad R_z^{nm} = \int \psi_n^* \mu_z \psi_m dz \quad (2.20)$$

and the transition probability is related to these by

$$|\mathbf{R}^{nm}|^2 = (R_x^{nm})^2 + (R_y^{nm})^2 + (R_z^{nm})^2 \quad (2.21)$$

2.3 Line width

The ubiquitous use of the word ‘line’ to describe an experimentally observed transition goes back to the early days of observations of visible spectra with spectroscopes in which the lines observed in, say, the spectrum of a sodium flame are images, formed at various wavelengths, of the entrance slit. Although, nowadays, observations tend to be in the form of a plot of some measure of the intensity of the transition against wavelength, frequency or wavenumber, we still refer to peaks in such a spectrum as lines.

Figure 2.5 shows, for a sample in the gas phase, a typical absorption line with a HWHM (half-width at half-maximum) of $\Delta\nu$ and a characteristic line shape. The line is not infinitely narrow even if we assume that the instrument used for observation has not imposed any broadening of its own. We shall consider three important factors that may contribute to the line width and shape.

2.3.1 Natural line broadening

If state n in Figure 2.2(a) is populated in excess of its Boltzmann population by absorption, the species M^* in this state will decay to the lower state until the Boltzmann population is regained. The decay is a first-order process, so that

$$-\frac{dN_n}{dt} = kN_n \quad (2.22)$$

where k is the first-order rate constant and

$$\frac{1}{k} = \tau \quad (2.23)$$

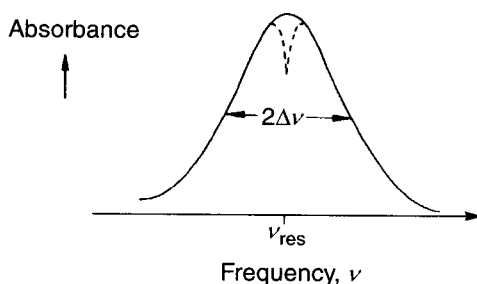


Figure 2.5 Typical (gaussian) absorption line showing a HWHM (half width at half maximum) of $\Delta\nu$ and a Lamb dip (dashed curve)

Here, τ is the time taken for N_n to fall to $1/e$ of its initial value (where e is the base of natural logarithms) and is referred to as the lifetime of state n . If spontaneous emission is the *only* process by which M^* decays, comparison with Equation (2.9) shows that

$$k = A_{nm} \quad (2.24)$$

The Heisenberg uncertainty principle in the form

$$\tau \Delta E \geq \hbar \quad (2.25)$$

(see Equation 1.16) relates the lifetime to the smearing out, in terms of energy, of the state n . This equation illustrates the point that state n has an exactly defined energy only if τ is infinite, but, since this is never the case, all energy levels are smeared out to some extent, with resulting line broadening.

Combining Equations (2.12) and (2.15) relates A_{nm} to the transition probability

$$A_{nm} = \frac{64\pi^4 \nu^3}{(4\pi\epsilon_0)3hc^3} |\mathbf{R}^{nm}|^2 \quad (2.26)$$

so that, from Equation (2.25),

$$\Delta \nu \geq \frac{32\pi^3 \nu^3}{(4\pi\epsilon_0)3hc^3} |\mathbf{R}^{nm}|^2 \quad (2.27)$$

The dependence of $\Delta \nu$, the frequency spread, on ν^3 results in a much larger value for an excited electronic state, typically 30 MHz, than for an excited rotational state, typically 10^{-4} – 10^{-5} Hz, because of the much greater ν for an excited electronic state.

Equation (2.27) illustrates what is called the natural line broadening. Since each atom or molecule behaves identically in this respect it is an example of homogeneous line broadening, which results in a characteristic lorentzian line shape.

Natural line broadening is usually very small compared with other causes of broadening. However, not only is it of considerable theoretical importance but also, in the ingenious technique of Lamb dip spectroscopy (see Section 2.3.5.2), observations may be made of spectra in which all other sources of broadening are removed.

2.3.2 Doppler broadening

Whether radiation is being absorbed or emitted the frequency at which it takes place depends on the velocity of the atom or molecule relative to the detector. This is for the same reason that an observer hears the whistle of a train travelling towards him or her as having a frequency apparently higher than it really is, and lower when it is travelling away from him or her. The effect is known as the Doppler effect.

If an atom or molecule is travelling towards the detector with a velocity v_a , then the frequency ν_a at which a transition is observed to occur is related to the actual transition frequency ν in a stationary atom or molecule by

$$\nu_a = \nu \left(1 - \frac{v_a}{c}\right)^{-1} \quad (2.28)$$

where c is the speed of light. Because of the usual Maxwell velocity distribution there is a spread of values of v_a and a characteristic line broadening given by

$$\Delta\nu = \frac{\nu}{c} \left(\frac{2kT \ln 2}{m}\right)^{1/2} \quad (2.29)$$

where m is the mass of the atom or molecule; this $\Delta\nu$ is normally far greater than the natural line width. The broadening is inhomogeneous, since not all atoms or molecules in a particular sample behave in the same way, and results in a line shape known as gaussian.

2.3.3 Pressure broadening

When collisions occur between gas phase atoms or molecules there is an exchange of energy, which leads effectively to a broadening of energy levels. If τ is the mean time between collisions and each collision results in a transition between two states there is a line broadening $\Delta\nu$ of the transition, where

$$\Delta\nu = (2\pi\tau)^{-1} \quad (2.30)$$

derived from the uncertainty principle of Equation (1.16). This broadening is, like natural line broadening, homogeneous and usually produces a lorentzian line shape except for transitions at low frequencies, when an unsymmetrical line shape results.

2.3.4 Power, or saturation, broadening

The equilibrium populations of energy levels, given by the Boltzmann distribution law of Equation 2.11, are maintained through exchange of energy by collisions. However, when the ground and excited energy levels m and n , respectively, are close together the population ratio N_n/N_m at equilibrium is close to 1. As a result, the equilibrium may be seriously disturbed when, in obtaining an absorption spectrum, the molecular sample is subjected to radiation of intensity I . As I is increased the limit of $N_n/N_m = 1$ is approached, the Beer–Lambert law (Equation 2.16) breaks down, ϵ becomes dependent on I , and saturation is said to occur. Clearly, this occurs more readily the closer the energy levels n and m . Consequently, saturation is more common in microwave and millimetre wave spectroscopy,

although, as we shall see in Chapter 9, the extremely high power of a laser source may result in saturation effects in higher energy regions of the spectrum.

One effect of saturation, and the dependence of ε on I , is to decrease the maximum absorption intensity of a spectral line. The central part of the line is flattened and the intensity of the wings is increased. The result is that the line is broadened, and the effect is known as power, or saturation, broadening. Typically, microwave power of the order of 1 mW cm^{-2} may produce such broadening. Minimizing the power of the source and reducing the absorption path length ℓ can limit the effects of power broadening.

2.3.5 Removal of line broadening

Of the four types of broadening that have been discussed, that due to the natural line width is, under normal conditions, much the smallest and it is the removal, or the decrease, of the effects of only Doppler, pressure and power broadening that can be achieved.

Except at very low frequencies, pressure broadening may be removed simply by working at a sufficiently low pressure. Doppler broadening may be reduced or removed by two general methods, which will be discussed briefly below.

2.3.5.1 Effusive atomic or molecular beams

An effusive beam of atoms or molecules (see Ramsey, 1956 in the bibliography) is produced by pumping them through a narrow slit, typically $20 \mu\text{m}$ wide and 1 cm long, with a pressure of a few torr on the source side of the slit. The beam may be further collimated by suitable apertures along it.

Such beams have many uses, including some important applications in spectroscopy. In particular, pressure broadening of spectral lines is removed in an effusive beam and, if observations are made perpendicular to the direction of the beam, Doppler broadening is considerably reduced because the velocity component in the direction of observation is very small.

2.3.5.2 Lamb dip spectroscopy

In 1969 Costain devised a very elegant method of eliminating Doppler broadening without using an effusive beam. Figure 2.5 shows a Doppler-broadened line, and Figure 2.6 illustrates an absorption experiment in which the source radiation is reflected back through the cell, by a reflector R, to the detector. We assume that the source radiation is narrow compared with the line width, a condition that may be satisfied with, for example, microwave or laser radiation. Tuning the source to a frequency ν_a , higher than the resonance frequency ν_{res} at the line centre, results in only molecules such as molecules 1 and 2 in Figure 2.6, which have a velocity component v_a away from the source (see Equation 2.28), absorbing radiation. On the return journey of the radiation back to the detector a new group

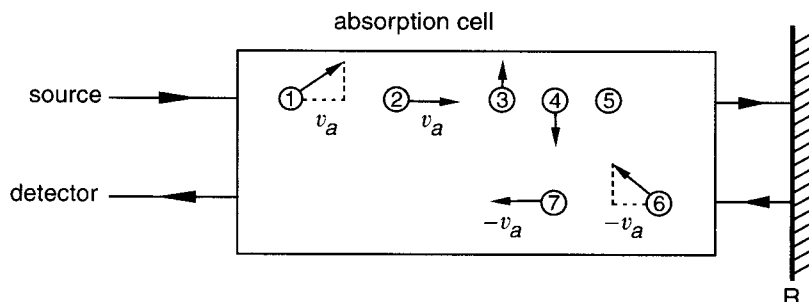


Figure 2.6 Three typical groups of molecules, with velocities v_a (molecules 1 and 2), 0 (molecules 3–5), and $-v_a$ (molecules 6 and 7) towards the source in a Lamb dip experiment

of molecules, such as 6 and 7, which have a velocity component $-v_a$ away from the source, absorb at, say, ν_a^- . Because of this, when the radiation is tuned to ν_a , for example, the number of molecules in the lower state m of the transition and having a velocity component v_a away from the source is depleted. This is referred to as hole burning in the usual Maxwell velocity distribution of molecules in state m .

Molecules such as 3, 4 and 5 in Figure 2.6, which have a zero velocity component away from the source, behave uniquely in that they absorb radiation of the same frequency ν_{res} whether the radiation is travelling towards or away from R, and this may result in saturation (see Section 2.3.4). If saturation occurs for the set of molecules 3, 4 and 5 while the radiation is travelling towards R, no further absorption takes place as it travels back from R. The result is that a dip in the absorbance curve is observed at ν_{res} , as indicated in Figure 2.5. This is known as a Lamb dip, an effect which was predicted by Lamb in 1964. The width of the dip is the natural line width, and observation of the dip results in much greater accuracy of measurement of ν_{res} .

Saturation is clearly achieved more readily if states m and n are close together, as is the case for microwave or millimetre wave transitions, but, even if they are far apart, a laser source may be sufficiently powerful to cause saturation.

Exercises

2.1 The number of collisions z that a molecule in the gas phase makes per unit time, when only one species is present, is given by

$$z = \pi d^2 \left(\frac{8kT}{\pi m} \right)^{1/2} \frac{p}{kT}$$

where d is the collision diameter, m the molecular mass, T the temperature, and p the pressure. For benzene at 1 Torr and 293 K, and assuming $d = 5 \text{ \AA}$, calculate z and hence the pressure broadening $\Delta\nu$, in hertz, of observed transitions.

2.2 Calculate in hertz the broadening $\Delta\nu$ of transitions in HCN at 25 °C due to the Doppler effect in regions of the spectrum typical of rotational transitions (10 cm^{-1}), vibrational transitions (1500 cm^{-1}) and electronic transitions ($60\,000\text{ cm}^{-1}$).

2.3 As a function of frequency, the spectral radiation density is given by

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp(h\nu/kT) - 1}$$

Calculate typical values in the microwave ($\nu = 50\text{ GHz}$) and near-ultraviolet ($\tilde{\nu} = 30\,000\text{ cm}^{-1}$) regions.

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