High Resolution Molecular Spectroscopy

University of Cambridge Part II Natural Sciences Tripos

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Contents

1   Interaction of Molecules with Radiation

The essence of spectroscopy is that a photon of frequency ν is absorbed or emitted when there is a transition between two energy levels separated by ΔE, where $\Delta E = h\nu$. In this way, we can probe the energy levels present by measuring the frequencies of the photons which are emitted or absorbed.

1.1   Types of Interactions

There are three types of interactions between matter and radiation. In all three cases, the energy of the photon $h\nu$ matches the energy difference between the two levels ΔE.

stimulated   stimulated   spontaneous
absorption   emission   emission
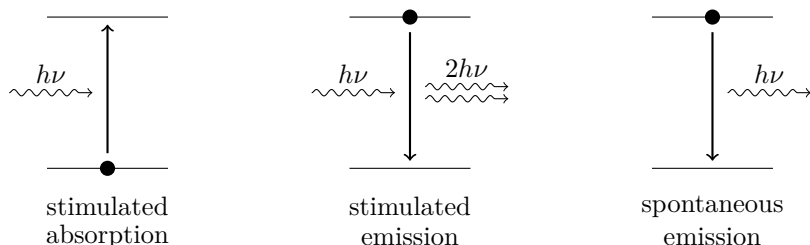
(i) *Stimulated absorption*: a photon is absorbed, and the system moves from a lower to an upper level.

   Examples: IR/UV/Vis spectroscopy.

(ii) *Stimulated emission*: one photon triggers the generation of another, and the system moves from an upper to a lower level.

   Example: LASER.

(iii) *Spontaneous emission*: not triggered by a photon, and the system moves from an upper to a lower level.

   Examples: flame test, emission lamp, LED.

   These three processes all involve the molecule (or atom) moving from one energy level to another, and thus leading to a change in the populations of the levels. Therefore, like other processes, we can sensibly talk about the rate at which these populations change. The rates of these three processes are influences by different factors and so, depending on the circumstances, one may dominate over the other.

1.1.1   The Einstein Coefficients

Consider transitions involving the two levels shown above; let their populations be n_i and n_j, respectively, and let the energy between separation between the levels be $\Delta E = h\nu$. For the momentum we will assume that both levels are non-degenerate, i.e. $g_i = g_j = 1$.

$$n_j \; \underline{\qquad} \; |j\rangle$$

$$n_i \; \underline{\qquad} \; |i\rangle$$

The rate of stimulated absorption can be expressed in terms of the resulting change in the population of the lower level

$$\text{stimulated absorption:} \quad \frac{\mathrm{d}n_i}{\mathrm{d}t} = -B_{ij}\rho(\nu)n_i \,, \tag{1.1}$$

where B_{ij} is the *Einstein B coefficient* for the transition and $\rho(\nu)$ is the energy density of the radiation at frequency ν. The Einstein B coefficient is analogous to the second order rate constant for a chemical reaction, but it has a weird unit of $\mathrm{m\,kg^{-1}}$. $\rho(\nu)\,\mathrm{d}\nu$ is the energy of photon between ν and $\nu + \mathrm{d}\nu$ per unit volume, which can be thought of as the "concentration of photon", having unit of $\mathrm{J\,m^{-3}}$.

Similarly, the rate of stimulated emission can be expressed in terms of the resulting change in the upper level:

$$\text{stimulated emission:} \quad \frac{\mathrm{d}n_j}{\mathrm{d}t} = -B_{ji}\rho(\nu)n_j \,. \tag{1.2}$$

It can be shown that the Einstein coefficients for these two processes are related by $g_i B_{ij} = g_j B_{ji}$, where g_i and g_j are the degeneracies of the levels i and j, respectively. For the present discussion we assumed both levels to be non-degenerate, so $B_{ij} = B_{ji}$. The values of these coefficients are then given by

$$B_{ij} = \frac{8\pi^3}{12\pi\epsilon_0 h^2}R_{ij}^2 \,, \tag{1.3}$$

where ϵ_0 is the permittivity of free space. R_{ij} is the *transition moment* given by

$$R_{ij} = \int \mathrm{d}\tau \, \psi_j^* \hat{\mu}\psi_i \,, \tag{1.4}$$

in which ψ_i and ψ_j are the wavefunctions of the two states, and $\hat{\mu}$ is the *electric dipole moment operator*.

Often we can say whether a transition moment is zero or not just by directly inspecting the symmetry of the integrand — these results in the selection rules which you have already come across. A *forbidden transition* has $R_{ij} = 0$, so there is no absorption or emission of radiation, and an *allowed transition* has $R_{ij} \neq 0$ so transitions can take place.

The rate of spontaneous emission can be written as

$$\text{spontaneous emission:} \quad \frac{\mathrm{d}n_j}{\mathrm{d}t} = -A_{ij}n_j \,, \tag{1.5}$$

where A_{ij} is the Einstein A coefficient. The radiation density is not involved in this expression as no photon is needed for spontaneous emission. Hence, A_{ij} is analogous to a first order rate constant, with unit $\mathrm{s^{-1}}$.

1.1.2 Why Spontaneous Emission

A question is: why do spontaneous emission occur at all? Instead, we can do a thought experiment to imagine what will happen without it.

Consider a body of interest surrounded by a large black body radiator being held at constant temperature T_surr, but they are separated by vacuum.
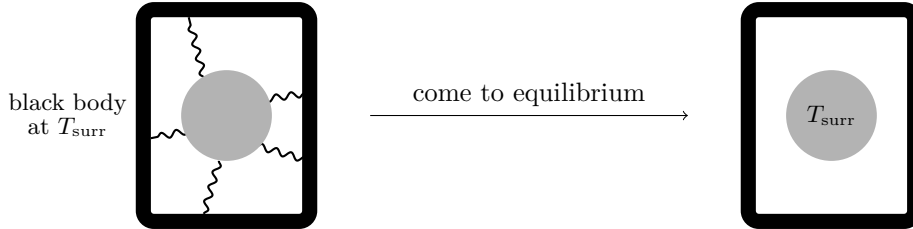
From our experience, we know that the body will eventually come to the same temperature as the black body i.e. the two objects will come to equilibrium. It will do this by gaining or losing energy by absorbing or emitting photons.

The temperature of the object is reflected in the way which particles are distributed amongst the energy levels, as predicted by the Boltzmann distribution. The higher the temperature, the greater the population of the upper levels.

As a simplification, suppose our object has only two energy levels, i and j, and suppose there are only stimulated absorption and stimulated emission. The rate of change of the population of level i is

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \underbrace{-B_{ij}\rho(\nu)n_i}_{\substack{\text{stimulated}\\\text{absorption}}} + \underbrace{B_{ji}\rho(\nu)n_j}_{\substack{\text{stimulated}\\\text{emission}}} . \tag{1.6}$$

At equilibrium, the population will cease to change, so the derivative will be zero. Thus

$$-B_{ij}\rho(\nu)n_{i,\text{eq}} + B_{ji}\rho(\nu)n_{j,\text{eq}} = 0 . \tag{1.7}$$

But we know that $B_{ij} = B_{ji}$, so it follows that, at equilibrium, $n_{i,\text{eq}} = n_{j,\text{eq}}$. This is impossible as it predicts the object to have infinite temperature by Boltzmann distribution.

What this thought experiment shows is that, on its own, stimulated emission and stimulated absorption cannot bring bodies to equilibrium with the surrounding. This is why we need spontaneous emission: this process leads to a reduction in the population of the upper level. We can also see that, as the energy separation between the two levels become greater, the population of the upper level must go down as predicted by Boltzmann distribution. Thus, the rate of spontaneous emission must also increase as the energy separation between levels increase. We will see this in the next section.

1.1.3 Relationship between the Einstein Coefficients

If spontaneous emission is taken into account, the total rate of change of the population of the lower level in our two-level system is

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = -B_{ij}\rho(\nu)n_i + B_{ji}\rho(\nu)n_j + A_{ij}n_j \,. \tag{1.8}$$

We can use this expression to find the relationship between the Einstein A and B coefficients.

For a black body at temperature T, the radiation density is given by the Planck law

$$\rho(\nu)\,\mathrm{d}\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp(h\nu/kT)-1}\mathrm{d}\nu \,. \tag{1.9}$$

A derivation of this is shown in the appendix (section A.1). The Boltzmann distribution predicts that, at equilibrium, the populations of the levels i and j will be

$$n_{i,\mathrm{eq}} = \frac{N}{q}\exp\left(-\frac{\epsilon_i}{k_BT}\right) \text{ and } n_{j,\mathrm{eq}} = \frac{N}{q}\exp\left(-\frac{\epsilon_j}{k_BT}\right) \,, \tag{1.10}$$

where ϵ_i and ϵ_j are the energies of the two levels. The ratio of populations is therefore

$$\frac{n_{j,\mathrm{eq}}}{n_{i,\mathrm{eq}}} = \exp\left(-\frac{\Delta\epsilon}{kT}\right) \,, \tag{1.11}$$

where $\Delta\epsilon = \epsilon_j - \epsilon_i$ is the energy gap.

At equilibrium the derivative of population (1.8) is zero. If we substitute the planck's law and population ratio into the equation and recognize $\Delta\epsilon = h\nu$, we find that

$$A_{ji} = \frac{8\pi h\nu^3}{c^3}B_{ji} \,. \tag{1.12}$$

Two remarks:

(i) the Einstein A and B coefficients are related; and

(ii) the rate of spontaneous emission increases dramatically with frequency $\sim c^3$.

Under typical conditions, spontaneous emissions in microwave is slower than competing processes, whereas in UV/Vis spontaneous emission in dominant.

1.2 Line Widths

Although we refer to peaks as "lines" in spectra, in fact the absorptions we see are not at precisely defined frequencies; rather, there is always a spread of frequencies over which the absorption is seen. If we plot the absorbance against frequency, we typically see a bell-shaped curve. It is usual to specify the width of this line by its *width at half maximum*, $\Delta\nu$.
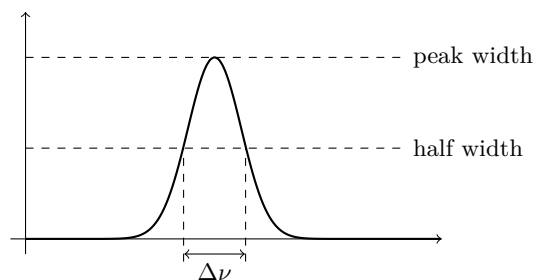
Sometimes the line width is limited by the spectrometer being used, but it is often found that the improvements in the spectrometer eventually lead to no further reduction in the line width. It is then assumed that the line width seen is a fundamental property of the sample itself.

There are a number of different effects which are responsible for the finite width of lines in the spectrum. Understanding these is important as, if the source of the line width is identified, it may be possible to alter the experimental conditions so as to reduce the line width and hence improve the resolution.

The first two types of line broadening we will consider are both associated with the fact that the molecules spend a finite amount of time in any particular energy level. Molecules are constantly moving from one energy level to another, which may occur because of the collisions between molecules, or due to the molecules emitting a photon and so dropping down to a lower level. Whatever mechanism by which the molecule moves from one energy level to another, we can characterise the process by saying that a particular energy level has a certain *lifetime* τ. In quantum mechanics, a finite lifetime implies an uncertainty in the energy of states — this is the generalised principles of uncertainty, which states that

$$\tau \Delta E \approx \hbar. \tag{1.13}$$

We see that a shorter lived state have greater uncertainty in their energies than the longer lived states. This uncertainty in the energy translates to a non-zero line width, as a range of frequencies can now cause the transition. Equation (1.13) can be re-expressed in frequency as

$$\Delta \nu = \frac{1}{2\pi\tau}, \tag{1.14}$$

where $\Delta \nu$ is the uncertainty in the frequency of the line, which we identified as the line width.

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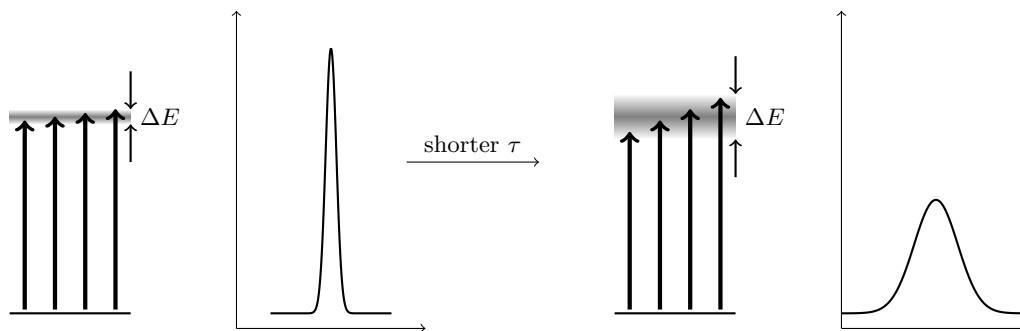
1.2.1 Natural Line Broadening

If a molecule or atom is in anything other than the ground state, it is possible for spontaneous emission to take place, the rate of which is given by (1.5) in terms of the Einstein A coefficient. As a result of this, the excited state has a finite lifetime, leading to line broadening.

We see from equation (1.5) that spontaneous emission is a first-order process so, just as in chemical kinetics, we can use the concept of a half-life to describe its rate. In chemical kinetics the half life is $\ln 2/k_{\text{1st}}$ but it is more usual in spectroscopy to define a natural lifetime, τ_{e}, according to

$$\tau_{\text{e}} = \frac{1}{A_{ij}} \, . \tag{1.15}$$

The linewidth due to this process is hence

$$\Delta\nu = \frac{A_{ij}}{2\pi} \, . \tag{1.16}$$

This kind of line broadening is referred to as *natural line broadening* as it comes about from the fundamental lifetime of the state imposed by the spontaneous emission rate. This is always unavoidable.

Here are some typical values to help you get some sense of it:

(i) Electronic excited state: $\tau_{\text{e}} \approx 10\,\text{nm}$ gives $\Delta\nu = 5 \times 10^4\,\text{cm}^{-1}$ or $16\,\text{MHz}$.

(ii) Rotational excited state: rate is much slower, and typically get $\Delta\nu \sim 10^{-4}\,\text{Hz}$.

1.2.2 Pressure (Collision) Broadening

Collisions between molecules can result in a change of energy level (translational motion well accommodates any deficit or excess of energy) and so the lifetime of a state is determined by the rate of collisions. If we assume that each collision leads to a change in energy level, then the lifetime, τ, is the mean time between collisions. The resulting line broadening can then be estimated using (1.14).

The mean time between collisions can be estimated using gas kinetic theory: the collision rate depends on the size of the molecules (the collision cross-section σ), the temperature and the pressure. As the pressure goes up, the rate of collision increases and so the mean time between collisions (which we identified as the lifetime) decreases. The line width is therefore proportional to the pressure, and hence the name of pressure broadening. With a full treatment of kinetic theory (derivation in appendix (section A.2)), we can obtain the expression

$$\Delta\nu_{\text{press}} = Kp \, , \tag{1.17}$$

where

$$K = \frac{2p\sigma}{\sqrt{k_B T \pi^3 m}} \, . \tag{1.18}$$

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Pressure broadening tends to be the dominant contribution to the line width in microwave spectroscopy and an important contribution for lines in the infra-red.

1.2.3 Doppler Broadening

Our next source of broadening is irrelevant with the lifetime of states. It originates from the Doppler effect.

The Doppler shift is familiar to us as the shift in frequency of a siren as a fire engine passes by. Molecules are moving in random directions relative to the radiation which is passing through the sample and at a range of speeds so the effect is to generate a spread of frequencies which are absorbed or emitted by the molecules: this is the origin of the Doppler induced line width. Of course, the speed with which molecules move is only a tiny fraction of the speed of light, so the frequency shifts are very small compared to the absolute frequency, but nevertheless can be a significant contribution to the line width.
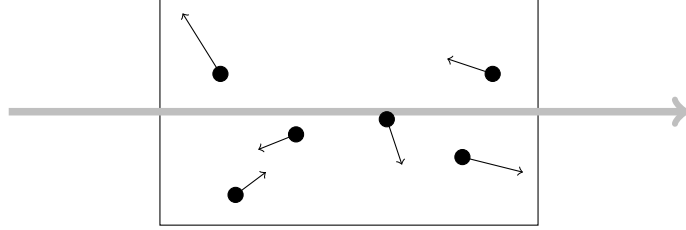
Gas kinetic theory can be used to derive an expression for the Doppler broadening line width. If a molecule is moving at a non-relativistic speed s towards a source of radiation of frequency ν_0, the apparent frequency is shifted to ν_{app}, and if the molecule is moving away from the source of apparent frequency is ν_{rec}, where

$$\nu_{\mathrm{app}} = \left(1 + \frac{s}{c}\right)\nu_0 \, , \; \nu_{\mathrm{rec}} = \left(1 - \frac{s}{c}\right)\nu_0 \, . \tag{1.19}$$

The Maxwell–Boltzmann boltzmann distribution gives the distribution of speeds which in turn leads to a distribution of frequencies received by the molecules. The required distribution is that in one dimension as the Doppler shift depends on the speed along the direction in which the light is passing. This distribution is

$$f(s) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-ms^2/2k_B T} \, , \tag{1.20}$$

where $f(s)\,\mathrm{d}s$ is the fraction of molecules with speeds along the propagation direction if the light between s and $s + \mathrm{d}s$. This expression can be converted into a distribution of frequencies by rewriting (1.19) as

$$s = \pm\frac{c}{\nu_0}(\nu_{\mathrm{obs}} - \nu_0) \, , \tag{1.21}$$

where ν_{obs} includes both the receding and approaching molecules. Hence, we get

$$f(\nu_{\mathrm{obs}}) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left[-\frac{mc^2(\nu_{\mathrm{obs}} - \nu_0)^2}{2k_B T \nu_0^2}\right] \, . \tag{1.22}$$

This distribution is a Gaussian function with its maximum at $\nu_{\mathrm{obs}} = \nu_0$, and drops to a half at

$$\nu_{1/2} = \nu_0 \pm \frac{\nu_0}{c} \left(\frac{2 k_B T \ln 2}{m} \right)^{\frac{1}{2}} . \tag{1.23}$$

Hence we get the expression of Doppler broadening

$$\Delta \nu_{\mathrm{doppler}} = \frac{2\nu_0}{c} \left(\frac{2 k_B T \ln 2}{m} \right)^{\frac{1}{2}} . \tag{1.24}$$

The Doppler broadening is proportional to the frequency: this is in contrast to the pressure broadening which is independent of frequency. Doppler broadening tends to become dominant for transitions in the visible region. At room temperature, Doppler line width in IR is $\sim 10^{-3}\,\mathrm{cm}^{-1}$, while in visible region, this increases to $\sim 0.1\,\mathrm{cm}^{-1}$.

When more that one source of line broadening is present it is not correct simply to add together the different line widths to obtain an overall linewidth. Rather, the line shapes due to the different kinds of line broadening must be convoluted with one another: we will ignore this complication. Where one source of line broadening is dominant then the overall linewidth is, to a good approximation, equal to that of the dominant source.

1.3   Notations and Conventions

Typically in spectroscopy we identify lines as being associated with transitions between energy levels (or states), and we then label the transition according to the quantum numbers which characterise the levels. Selection rules are also expressed in terms of the quantum numbers for the levels involved.

There are conventions about the way in which transitions are labelled and referred to and it is important to adhere to these. Suppose that we are concerned with the transitions between two levels A and B, and that A is the lower energy level.

(i) A transition between these levels can be signified by an arrow connecting them: the lower energy level is always written on the right

- absorption: B ← A
- emission: B → A

(ii) Transitions are labelled with the quantum numbers of the lower level.

(iii) The change in any quantum number is given as

$$\text{(quantum number of upper level)} - \text{(quantum number of lower level)}. \tag{1.25}$$

(iv) Where a distinction is to be made, quantum numbers referring to the lower energy level are denoted with a double prime e.g. J''; quantum numbers referring to the higher energy level are denoted with a single prime e.g. J'.

1.4 How to Think about Spectroscopy

When we record a spectrum, all we end up with is a set of lines whose frequencies and intensities we can measure. What we cannot tell just by looking at the lines is which energy levels are involved in the transition which leads to each line. To find out anything useful from the spectrum, our first step has to be to assign the lines.

By *assign* we usually mean specifying the quantum numbers of the energy levels involved. There may be more than one quantum number needed to specify the level, depending on the complexity of the problem.

The way we go about assigning and interpreting a spectrum is as follows:

(i) We start with a model for the energy levels. Typically, we use the energy levels which are available from solving the Schrödinger equation for simple systems such as the rigid rotor or the harmonic oscillator.

(ii) We then determine the selection rules which apply to these levels and thus predict the form of the spectrum, taking into account that the intensities will be affected by the populations of the energy levels as predicted by the Boltzmann distribution.

(iii) Having done this, we can compare the predicted spectrum with the real spectrum, and see if they can be made to match up. Typically there will be parameters in our model which can be adjusted, such as rotational constants and vibrational frequencies. The process of matching up the experimental and predicted spectra is often aided by looking for patterns, such as repeated spacings of lines.

(iv) If there is reasonable agreement between the two spectra, then the assignment process is complete as we know the assignment for the predicted spectrum. The values of any parameters needed can then be interpreted, for example to obtain bond lengths.

(v) However, the match between the experimental and predicted spectra is rarely perfect. Usually we need to refine our model used for the energy levels in order to obtain a better fit — for example by introducing the effects of anharmonicity or centrifugal distortion.

The process of assigning and understanding a spectrum is thus one of refining the model in order to obtain the best agreement. Recording the spectrum with higher precision or resolution will often reveal further features which require more refinement of the model.

2 Rotational Spectroscopy

As we have already seen before, there are a set of energy levels associated with the overall rotation of molecules; transitions between these levels give rise to spectra which typically appear in the microwave part of the spectrum. Such spectra are called *microwave* or *pure rotation spectra.*

In this section we will extend the discussion to include non-linear molecules and also look at some additional effects, such as centrifugal distortion and the influence of electric fields.

2.1 Classification of Rotating Molecules

For the purposes of this discussion we consider a molecule to be a rigid body in which the atoms occupy fixed positions relative to one another, and in which the nuclei have negligible size.

The *moment of inertia* of a molecule with respect to a particular axis is defined as

$$I = \sum_i m_i r_i^2 \,, \tag{2.1}$$

where m_i is the mass of the atom i and r_i is the perpendicular distance from the atom to the axis.

We can compute the moment of inertia about any axis, but there will be one such axis which has the greatest moment of inertia: this axis is labeled c and has moment of inertia I_c. There is another axis, labeled a, which has the minimum moment of inertia I_a, and it can be shown that this axis is perpendicular to the c-axis. A third axis, labeled b, is perpendicular to the other two; these three axes are called the principal axes. The moments of inertia about these principal axes (the principal moments of inertia) are related according to

$$I_c \geq I_b \geq I_a \,. \tag{2.2}$$

Remark. This is actually because the moment of inertia can be defined as a symmetric 2-tensor, with components

$$I_{ij} = \int \mathrm{d}V \, \rho(\mathbf{x})(x_k x_k \delta_{ij} - x_i x_j) \,. \tag{2.3}$$

Hence it can always be diagonalised, with eigenvalues I_a, I_b and I_c.

Molecules can be classified according to the relationship between the principal moments of inertia.

2.1.1 Spherical Tops

Spherical tops have all three moments of inertia equal; for this to be the case, the molecule must have high symmetry. In terms of group theory, the three rotations (R_x, R_y, R_z) must transform together as a three-dimensional (triply-degenerate) irreducible representation. Those molecules all have no dipole moments, so they do not show rotational spectrum. Examples include CH_4 (T_d) and SF_6 (O_h).

2.1.2 Symmetric Top
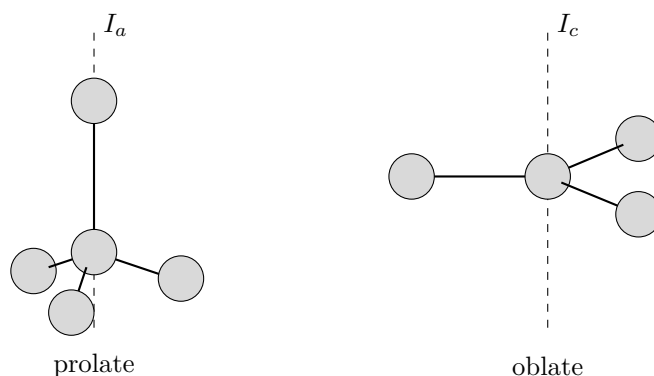
Symmetric tops have two of the moments of inertia equal and the third different from the other two. If the two moments of inertia which are equal are larger than the third moment of inertia, the molecule is termed a *prolate symmetric top*:

$$I_c = I_b > I_a. \tag{2.4}$$

An example is CH_3Cl.

If the two moments of inertia which are equal are smaller than the third moment of inertia, the molecule is termed an *oblate symmetric top*:

$$I_c > I_b = I_c. \tag{2.5}$$

An example is BF_3.

It is evident that symmetric tops must have a certain minimum of symmetry such that two of the rotations e.g. (R_x, R_y) transform together as a two-dimensional irreducible representation. It can be shown that this requirement is satisfied by molecules possessing a single C_n axis, with $n > 2$, or an S_4 axis. This symmetry test is by far the easiest way of deciding whether or not a molecule is a symmetric top.

2.1.3 Asymmetric Tops

In an asymmetric top, all three moments of inertia are different. R_x, R_y, and R_z all transform as one-dimensional irreducible representations.

2.1.4 Linear Molecules
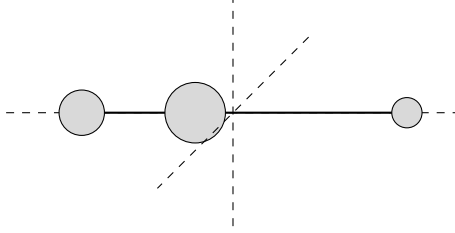
If we consider the atoms to be point masses, then the moment of inertia about the internuclear axis of a linear molecule is zero; the other two moments of inertia, about axes perpendicular to the internuclear axis, are equal. Thus, a linear molecule is a special case of a prolate symmetric top with $I_a = 0$.

2.2 Rotational Energy Levels

The general Hamiltonian for rotation can be written as

$$H = \frac{1}{2}\left(\frac{J_a^2}{I_a} + \frac{J_b^2}{I_b} + \frac{J_c^2}{I_c}\right).$$ (2.6)

The expression of the energy levels vary as the relation between I_a, I_b and I_c changes in different tops.

2.2.1 Symmetry Tops

Prolate Tops

A prolate symmetric top has $I_c = I_b > I_a$, so we can factor the Hamiltonian as

$$H = \frac{1}{2}\left[\frac{\mathbf{J}^2}{I_b} + J_c^2\left(\frac{1}{I_a} - \frac{1}{I_b}\right)\right].$$ (2.7)

Then the evergy levels of a prolate symmetric top can be easily obtained as

$$E_{J,K} = BJ(J+1) + (A - B)K^2,$$ (2.8)

where the quantum number have ranges $J = 0, 1, 2, \ldots$ and $K = -J, -J+1, \ldots, J$. These levels are sometimes denoted J_K. A and B are the rotational constants associated with the moments of inertia about the a- and b-axes, respectively. Their values are given in J by

$$A = \frac{\hbar^2}{2I_a} \qquad B = \frac{\hbar^2}{2I_b}.$$ (2.9)

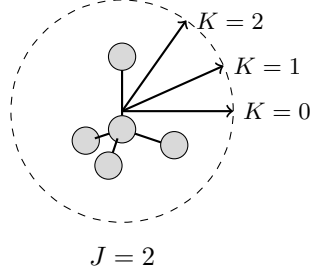Alternatively we can express the energies and rotational constants in wavenumbers:

$$\tilde{E}_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2,$$ (2.10)

where the rotational constants in wavenumbers are

$$\tilde{A} = \frac{h}{8\pi^2\tilde{c}I_a} \qquad \tilde{B} = \frac{h}{8\pi^2\tilde{c}I_b} \,. \tag{2.11}$$

As we see before, the quantum number J gives the magnitude of total angular momentum $\sqrt{J(J+1)}\hbar$. The quantum number K gives the component of the angular momentum along the unique a-axis, which is $K\hbar$.

$$J = 2$$

The diagram below shows the direction of angular momentum (also the rotation axis) of a symmetric top at $J = 2$ and $K = 0, 1, 2$ states.

Oblate Top

For an oblate top, we have $I_c > I_b = I_a$, so we factorise the Hamiltonian as

$$H = \frac{1}{2}\left[\frac{\mathbf{J}^2}{I_b} + J_c^2\left(\frac{1}{I_c} - \frac{1}{I_b}\right)\right] \,. \tag{2.12}$$

The rotational energy levels are therefore

$$E_{J,K} = BJ(J+1) + h(C-B)K^2 \,, \tag{2.13}$$

where as before, $J = 0, 1, \dots$ is the quantum number for the total angular momentum and $K = -J, \dots, J$ is the quantum number for the component of the angular momentum along the unique axis (c-axis). C is the rotational constant associated with the C axis

$$C = \frac{\hbar^2}{2I_c} \,. \tag{2.14}$$

As before, we can also express everything in terms of wavenumbers as well

$$\tilde{E}_{J,K} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2 \,, \tag{2.15}$$

where

$$\tilde{C} = \frac{h}{8\pi^2\tilde{C}I_c} \,. \tag{2.16}$$

The diagram below shows the rotational energy levels of CH_3I with $\tilde{A} = 5.11\,\mathrm{cm}^{-1}$, $\tilde{B} = 0.250\,\mathrm{cm}^{-1}$, and NH_3 with $\tilde{C} = 6.449\,\mathrm{cm}^{-1}$, $\tilde{B} = 10.001\,\mathrm{cm}^{-1}$. Each sequence of energy level with the same value of K is known as a K *stack*.

prolate

oblate

$\tilde{E}\,/\,\mathrm{cm}^{-1}$

$\tilde{E}\,/\,\mathrm{cm}^{-1}$

$K=0 \qquad K=\pm 1 \qquad K=\pm 2$

$K=0 \qquad K=\pm 1 \qquad K=\pm 2$
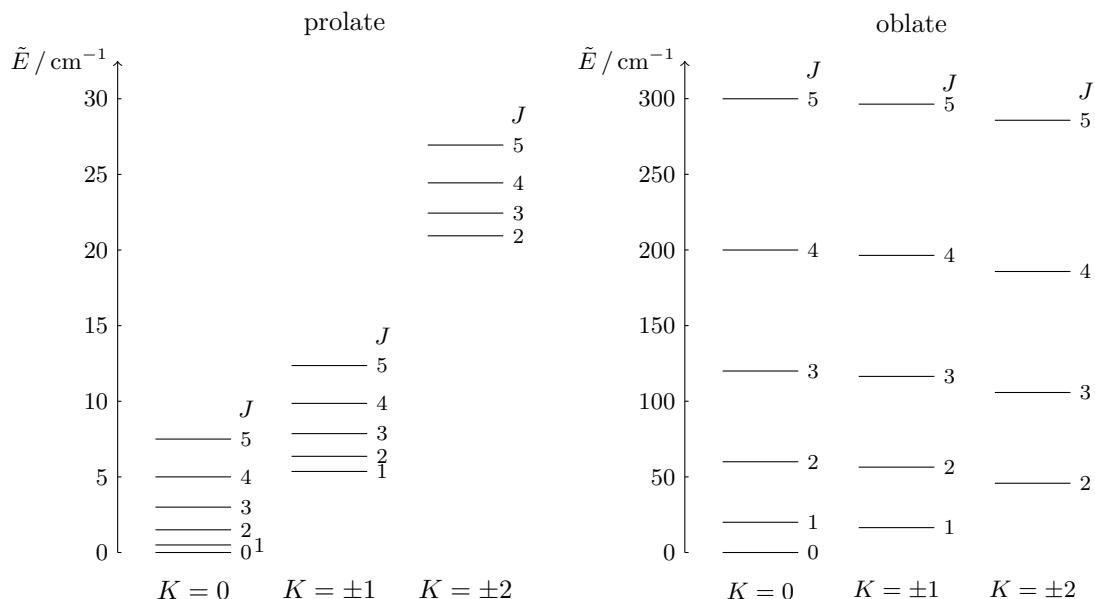
2.2.2 Linear Molecules

As we noted before, linear molecules are a special case of a prolate symmetric top with $I_a \ll I_b, I_c$. The corresponding rotational constant, A, is thus essentially infinite and so we see from the prolate top energy formula (2.10) that only those levels with $K=0$ need be considered as for higher values of K the energy would be too high. Recall that the quantum number K gives the angular momentum about the a-axis, so $K=0$ means that there is no rotation about this axis (which is the internuclear axis).

The energy levels of a linear molecule are thus

$$E_J = BJ(J+1)\,, \tag{2.17}$$

where $J = 0, 1, 2, \ldots$. This is what we are familiar with since IB Introduction to Quantum Mechanics.

2.2.3 Spherical Tops

The spherical top has $I_a = I_b = I_c$, so the Hamiltonian factorises very nicely into

$$H = \frac{\mathbf{J}^2}{2I}\,, \tag{2.18}$$

where I is the moment of inertial about any axis though the center of mass of the molecule. This results in the same form of energy expression as linear molecules.

2.2.4 Asymmetric Tops

The energy levels of asymmetric tops do not conform to any simple analytical expression such as those above for linear molecules or symmetric tops. This does not mean

that their energy levels cannot be calculated, but it is a tedious process involving matrix diagonalisation for each value of J. However, some molecules can be described as "near prolate top" or "near oblate tops" and approximate solutions obtained by expanding the asymmetric wavefunction in a basis formed from symmetric tops functions. However, it is now more common to compute them exactly as required and a range of programs exist for this purpose.

2.3   Selection Rules and Spectra

In order to predict which transitions are allowed, we need to know the selection rules which apply to these energy levels. Determining the form of these rules involves the use of advanced concepts in quantum mechanics; we will therefore simply state the rules.

The gross selection rule is that, for there to be transitions between the rotational levels, the molecule must possess a permanent dipole moment. We can rationalize this by noting that it is the electric vector of the electromagnetic wave which interacts with the molecule. For such an interaction to change the rotational energy, an electric dipole is required as this unsymmetrical charge distribution can interact with the field as the molecule rotates.

Assuming that there is a permanent dipole, the additional selection rules are

$$\Delta J = \pm 1 \quad \Delta K = 0 \,. \tag{2.19}$$

The $\Delta K = 0$ selection rule can be understood by noting that the dipole moment (if there is one) must lie along the unique (symmetry) axis; rotation about this axis does not lead to a change in the orientation of the dipole. $\Delta J = \pm 1$ because a photon carries a unit of angular momentum. For the total angular momentum to conserve, the angular momentum of the molecule must also change by one unit.

2.3.1   Spectra of Symmetric Tops

Knowing the selection rule, all we need to do is to find the separation of two energy levels between which transitions are allowed to predict the spectrum.

For a prolate symmetric top, the energies of the lower and upper states are

$$\tilde{E}_{J'',K} = \tilde{B}J''(J''+1) + (\tilde{A} - \tilde{B})K^2 \tag{2.20}$$

$$\tilde{E}_{J',K} = \tilde{B}J'(J'+1) + (\tilde{A} - \tilde{B})K^2 \,, \tag{2.21}$$

where the K is the same because of the $\Delta K = 0$ selection rule. The energy difference between these levels is

$$\begin{aligned} \tilde{\nu}(J'') &= \tilde{E}'_{J',K} - \tilde{E}''_{J'',K} \\ &= \tilde{B}J'(J'+1) - \tilde{B}J''(J''+1) \,. \end{aligned} \tag{2.22}$$

The allowed transitions have $\Delta J = J' - J'' = \pm 1$. For a transition in absorption, $\Delta J = +1$, giving

$$\tilde{\nu}(J'') = 2\tilde{B}(J'' + 1)\,. \tag{2.23}$$

The transition peas hence occur at $2\tilde{B}$, $4\tilde{B}$, $6\tilde{B}$, so the spacings are constantly $2\tilde{B}$. This is identical to the pattern seen for linear molecules: the similarity comes about because $\Delta K = 0$ for the symmetric top and K is restricted to zero for linear molecules.

However, since $\Delta K = 0$, we can only determine B and I_b from the spectra. No information about A or I_A can be obtained.

2.3.2 Spectra of Linear Molecules

The case of linear molecules has already been covered in Part IB. In fact, as we have already seen, the spectra are of the same form as for a symmetric top.

Shown below is the pure rotational spectrum of $^1\text{H}^{35}\text{Cl}$. The regular spacing of the lines is evident; however, closer inspection reveals that the spacing of the lines are slowly decreasing — this is due to centrifugal distortion, which we will consider in detail in later sections.
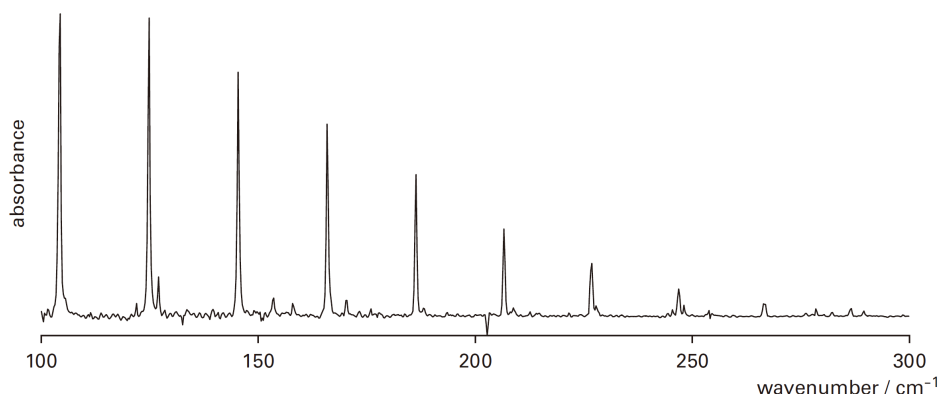

Figure 2.1: Rotational spectroscopy of HCl. Figure adapted from official course notes by Prof. Keeler. Spectrum taken by Prof. Wothers.

2.3.3 Isotopic Substitution

From the spectrum of a symmetric top we can only determine one moment of inertia; for anything more complex than a diatomic, this is insufficient information to determine all the bond lengths. The spectra of isotopic species give additional moments of inertia which, if it is assumed that the (equilibrium) bond lengths do not change on isotopic substitution, may enable us to find bond lengths.

For example, in one of the practical experiments, you will record the spectra of HCN and DCN. The resulting two moments of inertia are sufficient to determine both the $\text{H} - \text{C}$ and $\text{C} - \text{N}$ bond lengths.

2.4 Intensities

The intensity of a transition depends on the details of the three processes by which radiation interacts with the sample. In the IB Molecular Spectroscopy course we assumed that the intensity of an allowed transition was simply proportional to the population of the lower energy level. This is often a good approximation, but in the case of rotational spectroscopy there are further factors which need to be considered in order to understand fully the intensities of the lines.

(i) as the molecule rotates faster at higher J values, the change in the dipole moment increases leading to higher intensity.

(ii) the frequency of the transition affects the net absorption rate (the absorption minus the emission).

A derivation is included in section A.3 for reference. The result is that the intensity of transition from level J vary as

$$I \propto (J+1)\nu_J^2 \exp\left(-\frac{\epsilon_J}{k_B T}\right), \tag{2.24}$$

where ϵ_J is the energy of the Jth level, and ν_J is the frequency of transition arising from this level ($\nu_J = 2B(J+1)$). This result is rather a different dependence than one finds by assuming that the intensity is proportional only to the population of the lower energy level.

2.5 Centrifugal Distortion

So far we have assumed that the rotating molecule is a rigid body, i.e. the bond lengths and angles are unaffected by the rotation of the molecule. Generally, this is a good approximation but in the microwave region measurements can be made with such accuracy that even very small effects due to the lack of rigidity of the molecule can be detected.

Our expectation is that, as the molecule rotates faster and faster (as J increases), the forces on the atoms will cause bonds to stretch and possibly bond angles to change. Such effects are called *centrifugal distortions*. The result of these is that the moments of inertia become dependent on J. In practice, though, it is easier to assume that the moments of inertia remain the same but that the energy levels are slightly deviated from the rigid rotor values. Hence, get an energy expression in a power series expansion.

2.5.1 Symmetry Tops

In the presence of centrifugal distortion, the energy levels of a prolate symmetric top are

$$\tilde{E}_{J,K} = \tilde{B}J(J+1) + (\tilde{A}-\tilde{B})K^2 - \tilde{D}_J J^2(J+1)^2 - \tilde{D}_{JK}J(J+1)K - \tilde{D}_K K^4, \tag{2.25}$$

where $\tilde{D}_J$, $\tilde{D}_{JK}$ and $\tilde{D}_K$ are the (positive) centrifugal distortion constants which have the same dimensions as the rotational constants. This is a two dimensional series expansion in powers of $J(J+1)$ and K^2. Since the effect of centrifugal distortion is usually small, we only considered the first order effect and truncate this series at the second order. The effect of these terms is to bring the levels closer together than they are in the rigid rotor case.

As an example, for CH$_3$I, the measured values are $\tilde{D}_J = 2.09 \times 10^{-7}\,\mathrm{cm}^{-1}$, $\tilde{D}_{JK} = 3.29 \times 10^{-6}\,\mathrm{cm}^{-1}$, $\tilde{D}_K = 8.76 \times 10^{-5}\,\mathrm{cm}^{-1}$, $\tilde{A} = 5.1739\,\mathrm{cm}^{-1}$ and $\tilde{B} = 0.25022\,\mathrm{cm}^{-1}$. As you can see, the centrifugal distortion parameters are orders of magnitudes smaller than the rotational constants, so centrifugal distortions in rotational spectra are really small effects.

The selection rules remain as $\Delta J = \pm 1$ and $\Delta K = 0$, so the term in $\tilde{D}_K$ does not affect the positions of the lines in the spectrum. However, the terms in $\tilde{D}_{JK}$ and $\tilde{D}_J$ do affect the positions of the lines as they depend on J and K. In contrast to the rigid rotor case, transitions with different values of K have different frequencies.

By simple algebra, the transition frequency is

$$\begin{aligned}
\tilde{\nu}(J,K) &= \tilde{E}_{J''+1,K} - \tilde{E}_{J'',K} \\
&= 2(\tilde{B} - \tilde{D}_{JK}K^2)(J+1) - 4\tilde{D}_J(J+1)^3 \, .
\end{aligned} \tag{2.26}$$

Consider, for example, the $J = 1$ to $J = 2$ transition which is in fact two transitions, one with $K = 0$ and one for $K = \pm 1$ (as the energy depends on K^2 we do not need to distinguish between positive and negative values of K). In the absence of centrifugal distortion, these transitions are degenerate, but if centrifugal distortion is taken into account, both transitions move to lower frequencies, with the $K = \pm 1$ transition moving by more than the $K = 0$; the result is that two lines become visible. In general, for a transition from level J to level $J+1$, the presence of centrifugal distortion results in the line splitting into $(J+1)$ closely-spaced components.
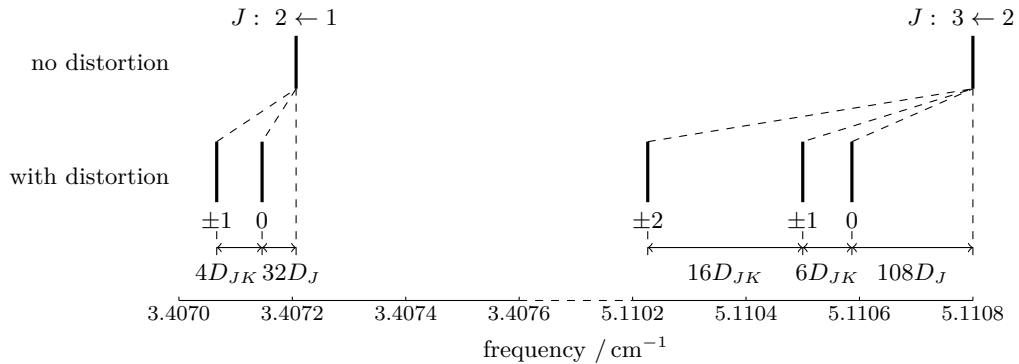
Figure 2.2: The schematic spectrum showing the effect of centrifugal distortion on the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions of CH$_3$F. For this molecule, $\tilde{D}_J = 1.96 \times 10^{-6}\,\mathrm{cm}^{-1}$, $\tilde{D}_{JK} = 1.48 \times 10^{-5}\,\mathrm{cm}^{-1}$, $\tilde{A} = 5.081\,\mathrm{cm}^{-1}$ and $\tilde{B} = 0.5815\,\mathrm{cm}^{-1}$. Note the break in the frequency scale — the change in line positions is very small compared to the separation of the two transitions.

We can also calculate the separation between lines from the same J value, but

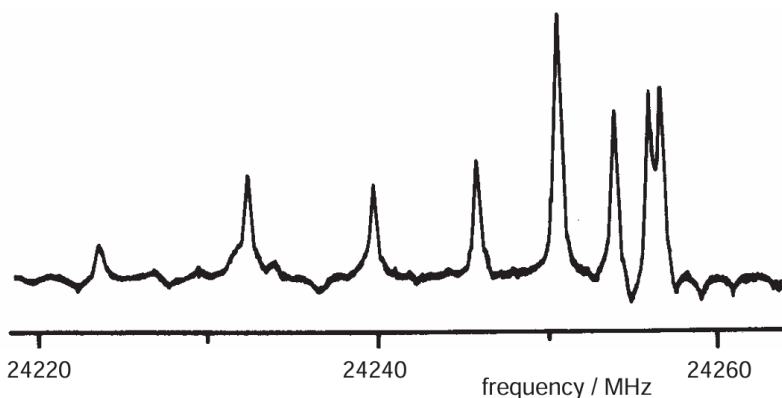Figure 2.3: The $J = 8 \leftarrow 7$ transition of the symmetric top molecule SiH$_3$NCS. The scale runs from 0.8076 to 0.8087 cm^{-1}. Intensity alternation is due to nuclear spin effects. Figure adapted from Hollas.

successive K values (i.e. K and $K + 1$) is

$$\tilde{\nu}(J, K) - \tilde{\nu}(J, K + 1) = 2\tilde{D}_{J,K}(J + 1)(2K + 1) \,. \tag{2.27}$$

It is clear that this separation increases with both K and J, as can be seen in the schematic spectrum above.

2.5.2 Linear Molecules

The effect of centrifugal distortion on the energy levels of a linear molecule is considerably simpler than for a symmetric top (because it is a one dimensional power series)

$$\tilde{E}_J = \tilde{B}_J(J + 1) - \tilde{D}J^2(J + 1)^2 \,, \tag{2.28}$$

where $\tilde{D}$ is the positive centrifugal distortion constant.

Again, the effect of D is to make levels closer together, and the effect increases with J. The frequency of a transition from $J'' = J$ to $J' = J + 1$ is

$$\begin{aligned} \tilde{\nu}_J &= \tilde{E}_{J+1} - \tilde{E}_J \\ &= 2\tilde{B}(J + 1) - 4\tilde{D}(J + 1)^3 \,. \end{aligned} \tag{2.29}$$

Hence, if we plot $\tilde{\nu}(J)/J + 1$ against $(J + 1)^2$, we can obtain a straight line with slope $-4\tilde{D}$ and $2\tilde{B}$.

For a diatomic, it is easy to imagine how the "centrifugal force" due to rotation stretches the bond thus leading to an increase in the moment of inertia. As commented on above, rather than allowing the rotational constant to be a function of J, we simply add an extra term in D. The value of D is clearly related to the ease with which the bond can be stretched, which in turn is related to the force constant of the bond and its harmonic frequency, $\tilde{\omega}$. It can be shown that

$$\tilde{D} = \frac{4\tilde{B}^3}{\tilde{\omega}^2} \,. \tag{2.30}$$

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2.6 The Stark Effect

Molecular and atomic energy levels may be modified when an electric or a magnetic field is applied; as a result the observed spectra will change. These changes may be of help in assigning spectra or may give access to molecular parameters.

In this section we are going to consider the effect of an electric field on the spectrum of a symmetric top molecule possessing a dipole moment. We shall see that the application of the field results in a splitting of the energy levels, called the *Stark effect.* From the splitting it is possible to determine a value for the dipole moment.

2.6.1 Dipole Moment in an Electric Field

In classical physics, an electric dipole $\boldsymbol{\mu}$ interacts with electric field $\mathbf{E}$ with energy
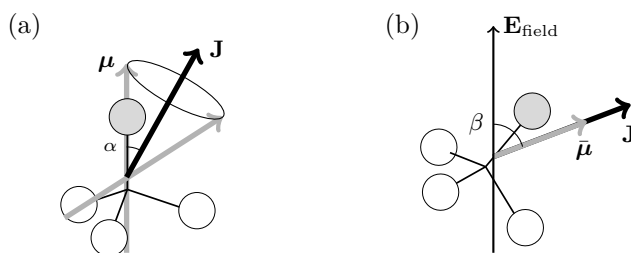
$$-\boldsymbol{\mu} \cdot \mathbf{E}. \tag{2.31}$$

The value of this dot product depends on the angle θ between them, and their magnitudes

$$-\mu E_{\text{field}} \cos\theta. \tag{2.32}$$

We use the subscript to avoid confusion between the electric field and energy.

2.6.2 Energy Levels of Symmetric Top in Electric Field

Consider a prolate symmetric top, such as CH_3F, in which the molecular dipole lies along the unique axis a (the principal C_3 axis).

Recall from that a molecule is rotating about its angular momentum vector $\mathbf{J}$, and that in general, this vector is pointing at some angle to the a-axis. The dipole is thus precessing on a cone at this angle to the direction of $\mathbf{J}$, as shown in figure (a) below. As a result of this precession, the dipole is averaged so that only its projection onto J survives; the components perpendicular to J are averaged to zero. Recall the magnitude of the $\mathbf{J}$ vector is $\hbar\sqrt{J(J+1)}$, and its projection on the J axis is K, so

$$\cos\alpha = \frac{K}{\sqrt{J(J+1)}}. \tag{2.33}$$

Hence, the averaged dipole moment of the rotating molecule is

$$\bar{\boldsymbol{\mu}} = \mu \cos \alpha \hat{\mathbf{J}} = \frac{\|\mu\| K}{\sqrt{J(J+1)}} \hat{\mathbf{J}} \,. \tag{2.34}$$

Now suppose that an electric field is applied and that the molecule is oriented such that $\mathbf{J}$ makes an angle β to the electric field direction, as shown in (b). As we have already discussed, the energy of interaction is $-\bar{\mu} E_{\text{field}} \cos \beta$.

The vector $\mathbf{J}$ cannot point in any direction. Since the applied electric field created a distinct (preferred) direction, the angular momentum must be oriented such that its projection onto the direction of the electric field is M_J where, as usual, M_J takes values in integer steps from $+J$ to $-J$. Hence, we have

$$\cos \beta = \frac{M_J}{\sqrt{J(J+1)}} \,. \tag{2.35}$$

Therefore, the energy of interaction is

$$\begin{aligned} E_{\text{Stark}}(J, K, M_J) &= -\bar{\mu} E_{\text{field}} \cos \beta \\ &= -\frac{\mu E_{\text{field}} K M_J}{J(J+1)} \,. \end{aligned} \tag{2.36}$$

The energy shift caused by the electric field is thus proportional to the field and the dipole moment, and also depends on the three quantum numbers J, K and M_J.

2.6.3 Effect on the Spectrum

From (2.36), we can see immediately that only energy levels with $|K| > 0$ will be affected by an electric field. Let us consider, as an example, the transition between $J = 1$, $K = +1$ and $J = 2$, $K = +1$. In the presence of an electric field the $J = 1$ level will split into three states, with $M_J = -1, 0, 1$. The energy shifts will be

$$E_{\text{Stark}}(1, 1, -1) = \frac{\mu E_{\text{field}}}{2} \quad E_{\text{Stark}}(1, 1, 0) = 0 \quad E_{\text{Stark}}(1, 1, +1) = -\frac{\mu E_{\text{field}}}{2} \,. \tag{2.37}$$

The $J = 2$ level will split into five states with M_J from -2 to $+2$; the energy shifts are

$$E_{\text{Stark}}(1, 1, \pm 2) = \mp \frac{\mu E_{\text{field}}}{3} \quad E_{\text{Stark}}(1, 1, \pm 2) = \mp \frac{\mu E_{\text{field}}}{6} \quad E_{\text{Stark}}(1, 1, 0) = 0 \,. \tag{2.38}$$

The splitting of the energy levels is shown in the diagram below (to avoid clutter, the size of the electric field is given the symbol E).

Assuming that the electric field is parallel to the electric vector of the radiation (experimentally the most convenient arrangement), the selection rule for M_J is $\Delta M_J = 0$, so there are three allowed transitions. The single line, observed in the absence of the field, splits symmetrically into three and, from the shifts in the energy levels, it can be seen that the splitting of the lines in the spectrum is $\mu E_{\text{field}}/3h$ in frequency.
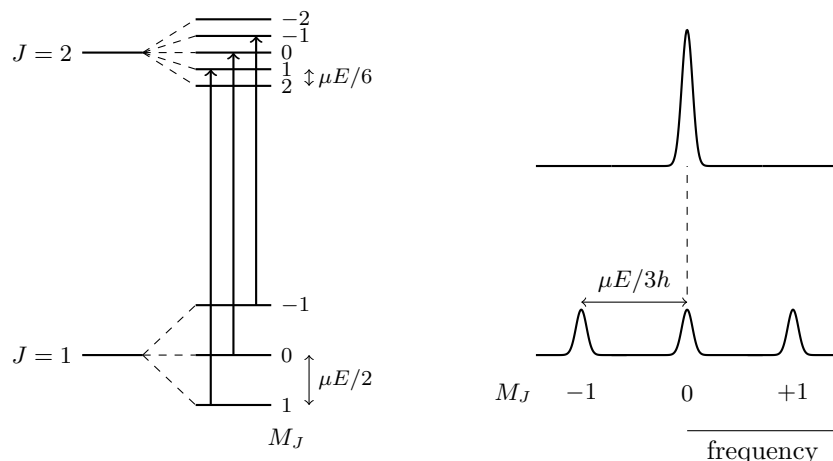
In general, a transition from a level with quantum numbers J and K will split into $(2J + 1)$ lines; the splitting (in frequency units) between adjacent lines is

$$\frac{2\mu E_{\text{field}} K}{h J (J+1)(J+2)} \,. \tag{2.39}$$

There are two main applications of the Stark effect.

(i) Assignment of spectra: assignment means identifying the quantum numbers of the energy levels involved in each transition. By observing the Stark splittings, information on the value of J can be found.

(ii) Measurement of dipole moments: if the magnitude of the electric field is known, then the measured Stark splittings can be used to derive a value for the dipole moment.

2.6.4 Stark Effects for Linear Molecules

As mentioned above, linear molecules have no rotation about the internuclear axis, and so effectively $K = 0$ at all times. Hence the energy levels will not be split by the application of an electric field; there is thus no Stark effect. However, linear molecules do show a *second order Stark effect*, which is where the splitting of the energy levels goes as the square of the electric field strength. The effect described for the symmetric top is first order, as it is linear in the field strength.

3 Vibrational Spectroscopy

Transitions between the set of energy levels associated with molecular vibrations can give rise to absorptions in the infra-red part of spectrum. Changes in vibrational energy are accompanied by simultaneous changes in rotational energy; as rotational energies are much smaller than vibrational energies, these changes in rotational energy lead to fine structure on the vibrational transitions.

An analysis of these these vibrational transitions and their attendant rotational fine structure gives access to molecular parameters such as vibrational frequencies and rotational constants.

3.1 Normal Modes and Symmetry: Revision of Part IB

(i) A normal mode is a motion in which: (1) the centre of mass remains fixed; (2) the atoms all move in phase at the same frequency; (3) the vibrational potential is harmonic.

(ii) A non-linear molecule with N atoms has $3N - 6$ normal modes, and a linear molecule has $3N - 5$ normal modes.

(iii) In the harmonic approximation, each normal mode has a set of energy levels

$$\tilde{E}_{v_i} = \left(v_i + \frac{1}{2} \right) \tilde{\omega}_i \,, \tag{3.1}$$

where $v_i = 0, 1, 2, \ldots$, and $\tilde{\omega}_i$ is the vibrational number of the ith normal mode.

(iv) Each normal mode transforms as a particular irreducible representation.

(v) For a given normal mode i that transforms as $\Gamma^{(i)}$

  (a) The wavefunction of the ground vibrational state $(v_i = 0)$ transforms as the totally symmetric IR, $\Gamma^{\text{tot. sym.}}$.

  (b) The first excited state, $v_i = 1$, has the same IR as the normal mode $\Gamma^{(i)}$.

  (c) For non-degenerate normal modes the even vibrational states $(v_i = 0, 2, 4, \ldots)$ all transform as $\Gamma^{\text{tot. sym.}}$, while the odd vibrational states $(v_i = 1, 3, 5, \ldots)$ all transform as $\Gamma^{(i)}$.

(vi) A transition is allowed in the infra-red if the transition dipole moment between the two states v_i' and v_i is non-zero. This will only be so only if the following direct product contains the totally symmetric IR:

$$\Gamma_{v_i'} \otimes \Gamma_\mu \otimes \Gamma_{v_i} \,, \tag{3.2}$$

where Γ_μ is the IR of the dipole moment operator, $\hat{\mu}$. Γ_μ transforms as the cartesian functions x, y or z.

(vii) A transition will give rise to Raman scattering if, when multiplied out, the following direct product contains the totally symmetric IR:

$$\Gamma_{v_i'} \otimes \Gamma_\alpha \otimes \Gamma_{v_i} \,, \tag{3.3}$$

where Γ_α is the IR of the polarisability operator, $\hat{\alpha}$. Γ_α transforms as the cartesian functions $x_i x_j$.

3.2 Symmetry of the Vibrational Wavefunction

As seen in IB Introduction to Quantum Mechanics, for a diatomic the harmonic oscillator wavefunctions depend only on the displacement from equilibrium position $x = r - r_e$.

In more complex molecules, a normal mode involves several atoms changing their positions in a concerted way. For a given normal mode i this motion can be described by a *normal coordinate Q_i*, which is a combination of the displacements of the individual atoms.

For example, for the symmetric stretch of CO_2 the normal coordinate is

$$Q_{\text{sym.str.}} = \frac{1}{\sqrt{2}}(q_{O1} - q_{O2}). \tag{3.4}$$

The q are mass-weighted coordinates defined as $q_i = m_i^{1/2} z_i$, where z_i is the displacement of atom i from equilibrium position. In this mode, the oxygen atoms move equally and oppositely along the long axis, and the carbon atom does not move.

The normal coordinate for the antisymmetric stretch is more complex

$$Q_{\text{asym.str.}} = \frac{1}{\sqrt{2m_{\text{tot}}}}\left(m_O^{1/2}q_{O1} - 2m_C^{1/2}q_C + m_O^{1/2}q_{O2}\right). \tag{3.5}$$

In this normal coordinate the two oxygen atoms move in the same direction and the carbon moves in the opposite direction. The amount each atom moves depends on its mass. For the bending mode, displacements along x and y would also appear in the normal coordinate.

For a given normal mode the potential energy function, and hence the associated wavefunctions, depends on just this one variable, Q_i. It therefore follows that the harmonic oscillator wavefunctions are also the wavefunctions for any normal mode provided we replace q with the normal coordinate for mode i, Q_i.

In the Part IB course Symmetry and Bonding we used direct products to work out the symmetry of the vibrational wavefunctions for non-degenerate normal modes. Here, we will briefly recap the argument and then go on to extend it to the more complex case of degenerate normal modes.

3.2.1 Non-degenerate Normal Modes

Suppose ground state wavefunction of the non-degenerate i^{th} normal mode, with $v_i = 0$, is $\psi_0 = \exp(-\frac{1}{2}Q_i^2)$. Suppose also normal mode, and hence the normal coordinate Q_i, transforms as the one-dimensional irreducible representation $\Gamma^{(i)}$, then Q_i^2 transforms as

$$\Gamma^{(i)} \otimes \Gamma^{(i)} = \Gamma^{\text{tot.sym.}}. \tag{3.6}$$

Since Q_i^2 is invariant under any symmetry operation, $\exp(Q_i^2)$ is invariant as well, so the ground state wavefunction ψ_0 transforms as the totally symmetric irreducible representation for any non-degenerate mode.

The first excited state wavefunction is

$$\psi_1 = 2Q_1 \exp\left(-\frac{1}{2}Q_i^2\right), \tag{3.7}$$

so it transforms as

$$\Gamma^{(i)} \otimes \Gamma^{\text{tot.sym.}} = \Gamma^{(i)}. \tag{3.8}$$

The next wavefunction is

$$\psi_2 = (4Q_i^2 - 2) \exp\left(-\frac{1}{2}Q_i^2\right). \tag{3.9}$$

We have Q_i^2 and the exponential term both transforming as totally symmetric irreducible representation, and all the scalars are also totally symmetric. Hence, the doubly degenerate wavefunction as $\Gamma^{\text{tot.sym.}}$.

Generally, the kth vibrational wavefunction is

$$\psi_k(Q_i) = H_k(Q_i) \exp\left(-\frac{1}{2}Q_i^2\right), \tag{3.10}$$

where H_k is the kth Hermite polynomial. It is easy to see that the odd orders of Q_i transforms as $\Gamma^{(i)}$, while the even orders of Q_i transforms as $\Gamma^{\text{tot.sym.}}$. Since the odd order Hermite polynomial only contain odd powers, while the even order Hermite polynomials only contain even powers, we arrive at this simple conclusion:

For non-degenerate normal modes the wavefunctions with even v transform as the totally symmetric irreducible representation, and those with odd v have the same symmetry as the normal mode.

3.2.2 Degenerate Normal Modes

The symmetries of the wavefunctions of degenerate normal modes are rather more complex to deal with, and are discussed in section A.4. Here we state the results.

Suppose that a particular degenerate normal mode transforms as $\Gamma^{(i)}$.

 (i) the ground state wavefunction transforms as the totally symmetric irreducible representation $\Gamma^{\text{tot.sym.}}$.

 (ii) the wavefunction of the first excited state, in which there is one quantum of excitation in one of the degenerate normal modes, transforms as $\Gamma^{(i)}$.

Now consider the doubly excited states. Consider the doubly degenerate E node of NH_3, point group C_{3v}. The direct product of E is

$$E \otimes E = (2, -1, 0) \otimes (2, -1, 0) = (4, 1, 0) = E \oplus A_2 \oplus A_1. \tag{3.11}$$

Note the direct product of two two-dimensional irreducible representations necessarily gives a result which is four dimensional.

We can get this result by reading the direct product tables. A selection of those is shown in section 3.5. We can see that, in the table, $E \otimes E = E \oplus [A_2] \oplus A_1$. The IR in the bracket arises from the *antisymmetrized direct product*, and the others are from the *symmetrised direct product*. The details are non-examinable, but it turns out that the symmetries of the vibrational wavefunctions are given only by those IRs arising from the symmetrized direct product. For the present case, these IRs are $A_1 \oplus E$.

Therefore, we have the rules

(iii) the irreducible representation spanned by the wavefunction of the doubly excited state are found by computing the direct product $\Gamma^{(i)} \otimes \Gamma^{(i)}$, and then selecting the ones corresponds to the *symmetrised product.*

(iv) the IR of further excited states are computed by taking more direct products and selecting the symmetrised ones.

As we have seen, the second excited state of the doubly-degenerate E mode in NH_3 transforms as $A_1 \oplus E$. The total dimensionality is 3, which can be rationalised in the following way. This state has two quanta of excitation which can be arranged amongst the two degenerate normal modes in three different ways

$$(1,1) \quad (2,0) \quad (0,2) . \tag{3.12}$$

Because these vibrations form a degenerate pair, these arrangements all have the same energy. There are only three possible arrangements of the quanta because there is only one way of assigning one quantum of excitation to each normal mode.

Note that the direct product of an IR with itself always contains the totally symmetric IR, and that this is part of the symmetrized square.

3.2.3 Overall Symmetry of the Vibration Wavefunction

So far we have described how to find the symmetry of the vibrational wavefunctions associated with a particular normal mode. However, multiple vibrational modes may be excited at the same time in a molecule. The overall symmetry of the vibrational wavefunction of the molecule is easily calculated by taking direct products.

Suppose that for the first normal mode the molecule is in the vibrational energy level with quantum number v_1, and that the irreducible representation of the corresponding wavefunction is Γ_{v_1}; likewise for the second normal mode the quantum number is v_2 and the IR is Γ_{v_2}, and so on for all the modes. We commonly denote such states by

$$(v_1, v_2, v_3, \ldots, v_n) , \tag{3.13}$$

provided that we given an order of the vibrational modes. The irreducible representation of the overall vibrational wavefunction is given by the direct product

$$\Gamma_{\text{overall}} = \Gamma_{v_1} \otimes \Gamma_{v_2} \otimes \ldots \tag{3.14}$$

This works because, by hypothesis, the normal modes are independent of one another.

Since the ground state wavefunction of any normal mode transforms as the totally symmetric irreducible representation, it follows that for a molecule in which none of the vibrational modes are excited — the overall ground state in which all the v_i are zero the overall vibrational wavefunction also transforms as the totally symmetric irreducible representation. Also, if just one normal mode is excited to the $v = 1$ state, and all of the other normal mode shave $v = 0$, it follows that the overall vibrational wavefunction has the same irreducible representation as the normal mode which is excited.

3.3 Determining Allowed Transitions using Symmetry

Again, assuming the molecule is a Harmonic oscillator, the harmonic selection rules apply, which are

(i) The dipole moment must change as the normal coordinate changes about the equilibrium.

(ii) $\Delta v_1 = \pm 1$.

Note the second condition means the quantum number of only one mode is allowed to change by one. In the presence of anharmonicity, transitions with higher values of Δv are weakly allowed, as are transitions in which more than one mode changes quantum number.

The intensity of an infra-red transition between vibrational states i and j depends on the *transition moment*

$$R_{ij} = \int \mathrm{d}\tau \, \psi_i^* \hat{\mu} \psi_j \, . \tag{3.15}$$

This will be non-zero only if the integrand, or some part of it, transforms as the totally symmetric irreducible representation. All we need to do is to compute the direct product

$$\Gamma^{(i)} \otimes \Gamma_\mu \otimes \Gamma^{(j)} \tag{3.16}$$

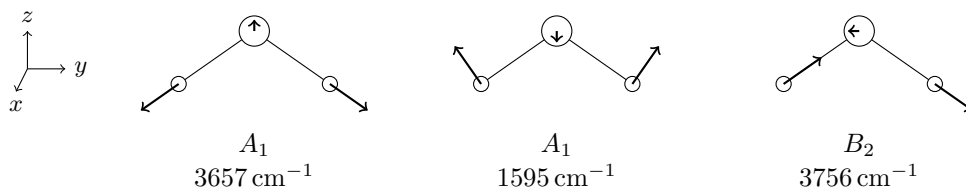to see if it contains $\Gamma^{\text{tot.sym}}$.

3.3.1 Fundamental Transition

A fundamental transition is a process in which the molecules goes from the vibrational ground states of all the normal modes to the first excited state of just one normal mode.

$$(0, 0, \ldots, 0, \ldots, 0) \to (0, 0, \ldots, \underbrace{1}_{v_i}, \ldots, 0) \, . \tag{3.17}$$

Since we know that the ground state transforms as $\Gamma^{\text{tot.sym}}$ and the first excited state of mode i transforms as $\Gamma^{(i)}$, the direct produce we need to evaluate is

$$\Gamma^{(i)} \otimes \Gamma_\mu \otimes \Gamma^{\text{tot.sym.}} \, . \tag{3.18}$$

$$
\begin{array}{ccc}
A_1 & A_1 & B_2 \\
3657\,\mathrm{cm}^{-1} & 1595\,\mathrm{cm}^{-1} & 3756\,\mathrm{cm}^{-1}
\end{array}
$$

This will contain the totally symmetric irreducible representation if and only if $\Gamma^{(i)}$ is the same as (some part of) Γ_μ. Hence the rule:

> A fundamental transition is allowed when the symmetry of the activated normal mode matches that of x, y or z.
> If the fundamental is allowed, the normal mode is said to be *infra-red active*.

As an example, H_2O (C_{2v}) has three normal modes: two of symmetry A_1 and one of symmetry B_2. The fundamentals of A_1 modes are allowed as z transforms like A_1, and the fundamental of B_2 is also allowed as y transforms like B_2.

For the B_2 mode, the triple direct product which gives rise to the totally symmetric irreducible representation is

$$
\underbrace{B_2}_{\Gamma^{(i)}} \otimes \underbrace{B_2}_{\Gamma_y} \otimes \underbrace{A_1}_{\Gamma^{\mathrm{ground}}} \ . \tag{3.19}
$$

The y component of the dipole is involves, and so the *transition dipole* is said to be along y. We can see that in the B_2 mode, the dipole indeed changes along the y direction. We say such a transition is *parallel* since the transition dipole is parallel to the principal axis (z axis).

For the A_1 modes, the z component of the dipole is involves, so the transition dipole is along z and we describe it as *parallel*.

A useful distinction is made between transitions allowed by harmonic selection rule and other transitions which are shown the be allowed by symmetry arguments — these are said to be *symmetry allowed*. Transitions allowed by selections are necessarily symmetry allowed, but there will be transitions not allowed by harmonic selection rules but are nevertheless symmetry allowed.

3.3.2 Overtones

Transitions from the overall ground state to a state with $v_i = 2, 3, \ldots$ for a particular normal mode is called a *overtone*. For example, a *first overtone* is

$$
(0, 0, \ldots, 0, \ldots, 0) \to (0, 0, \ldots, \underbrace{2}_{v_i}, \ldots, 0), \tag{3.20}
$$

and a second overtone is $(0, 0, \ldots, 0, \ldots, 0) \to (0, 0, \ldots, 3, \ldots, 0)$ and so on. These transitions are forbidden by harmonic selection rule but are nevertheless frequently observed as a result of anharmonicity.

Whether or not a particular overtone is allowed is again determined by evaluating the triple direct product

$$\Gamma_{v_i} \otimes \Gamma_\mu \otimes \Gamma^{\text{tot.sym}} \,. \tag{3.21}$$

For non-degenerate modes, simple conclusions can be made. The second excited state transforms as the totally symmetric irreducible representation, so a first overtone will be allowed only if one of the cartesian functions (x, y or z) transforms as the totally symmetric irreducible representation. The third excited state transforms has the same irreducible representation as the first excited state, so it will be allowed if the fundamental is allowed.

3.3.3 Hot Bands

Hot bands are transitions from states other than ground state. They are so-called because their intensity increases as the sample is heated, accounting for the increasing population of the excited vibrational states. We again use the triple direct product to determine whether they are allowed or not.

3.3.4 Combination Lines

A *combination line* is a transition in which the quantum number of more than one normal mode of changes. This is allowed due to anharmonicity.
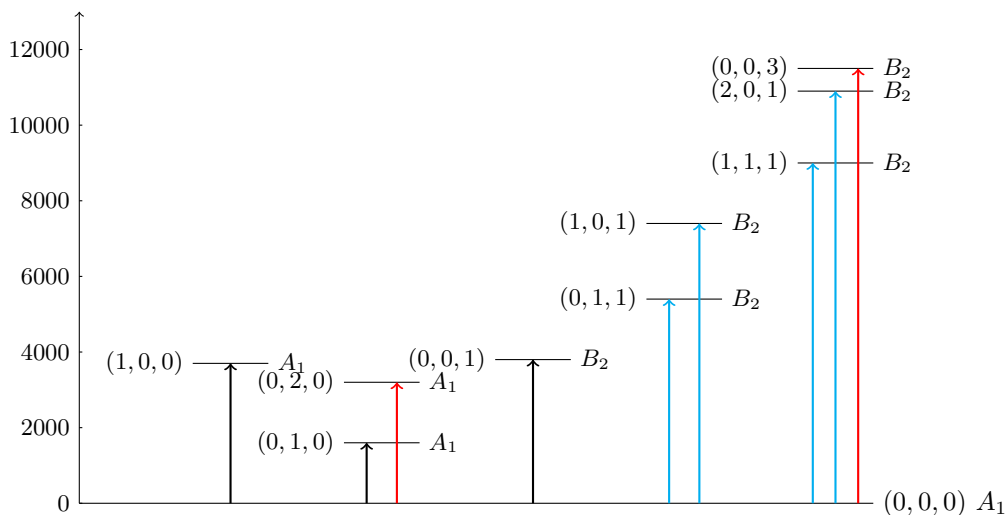

Figure 3.1: Some fundamentals (black), overtones (red), and combination lines (cyan) for H_2O. All of them are symmetry allowed.

A Note of Caution

The symmetry argument is simple and powerful, but it needs some care to applied. It only predicts whether a transition is possible or not, but it does not predict how strong will it be.

For a transition to be strong, the lower level needs to be significantly occupied. In practise, this means that for small molecules, only the transitions from the vibrational ground states are easily observable. Moreover, it is possible for the transition moment integral to vanish even if the transition is symmetry allowed (and here comes the harmonic selection rule $\Delta v = \pm 1$).

The vibrations of real molecules are not strictly harmonic and so the $\Delta v = \pm 1$ rule does not apply rigidly. Under these circumstances a transition which is allowed in principle by symmetry considerations, and also comes from a significantly populated lower level, may be visible. For example, the first overtone is commonly seen although typically with about one tenth of the intensity of the fundamental (on account of the lower transition moment).

3.3.5 Fermi Resonance

In some spectra an overtone or combination line may appear with an unexpectedly high intensity as a result of *Fermi resonance.*

This is best explained with an example. The linear isocyanate anion $[\mathrm{NCO}]^-$ $(C_{\infty v})$ has four normal modes with symmetries Σ^+, Π and Σ^+. The first Σ^+ mode is classified as $\mathrm{C-O}$ stretch and has a frequency of $1240\,\mathrm{cm}^{-1}$. The Π mode is a bending mode with frequency $630\,\mathrm{cm}^{-1}$.

Therefore, the $(1,0,0)$ state has symmetry Σ^+ and the $(0,2,0)$ state has symmetry $\Pi \otimes \Pi = \Sigma^+ \oplus \Delta$. In absence of any special effects, we expect the $(1,0,0)$ state to be $1240\,\mathrm{cm}^{-1}$ above the $(0,0,0)$ ground state, and the $(0,2,0)$ state to be $2 \times 630 = 1260\,\mathrm{cm}^{-1}$ above the ground state. We therefore have two levels with similar energies and the same symmetry Σ^+. We therefore expect the two states to interact and mix. The result is they "push oe another apart", as shown in the diagram below.
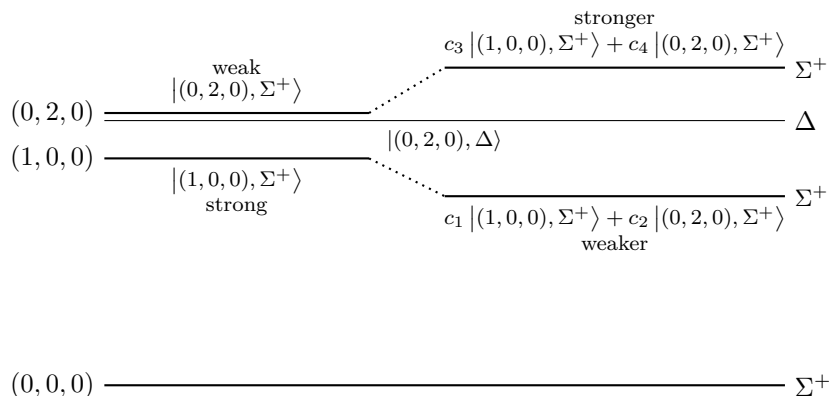
The transition from $(0,0,0)$ to $(1,0,0)$ is an allowed fundamental transition and is expected to be strong. The transition from $(0,0,0)$ to $(0,2,0)$ Σ^+ is symmetry allowed but as this transition is an overtone it is expected to be much weaker. The transition intensity is proportional to the transition moment, so we have

$$\left\langle (1,0,0)\,\Sigma^+ \middle| \hat{\mu} \middle| (0,0,0)\,\Sigma^+ \right\rangle > \left\langle (0,2,0)\,\Sigma^+ \middle| \hat{\mu} \middle| (0,0,0)\,\Sigma^+ \right\rangle \qquad (3.22)$$

Therefore, when the mixing of states happens, the intensities of transitions are also averaged out, and as a result, the transition to the (mainly) $(0, 2, 0)$ state becomes stronger.

$$\underbrace{\left(c_3 \left\langle (1,0,0)\ \Sigma^+ \right| + c_4 \left\langle (0,2,0)\ \Sigma^+ \right|\right) \hat{\mu} \left| (0,0,0)\ \Sigma^+ \right\rangle}_{R_{ij}\text{ after mixing}} > \underbrace{\left\langle (0,2,0)\ \Sigma^+ \left| \hat{\mu} \right| (0,0,0)\ \Sigma^+ \right\rangle}_{R_{ij}\text{ without mixing}}.$$

$$(3.23)$$

Experimentally, we then see two strong lines at $1201\,\text{cm}^{-1}$ and $1282\,\text{cm}^{-1}$.

This borrowing of frequency is known as *Fermi resonance*.

3.4 Rotational Fine Structure

As for diatomics, the vibrational transitions for more complex molecules are accompanied by simultaneous changes in rotational energy which lead to fine structure in the spectrum. Analysis of the fine structure will give structural information in the form of rotational constants. In addition, the form of the fine structure tells us something about the symmetry of the vibrational levels (and hence the symmetry of the normal mode) involved; this information can be useful in assigning the vibrational spectrum.

3.4.1 Linear Molecules

The allowed vibrational transitions in such molecules come in two broad types:

(i) $\Sigma - \Sigma$ transitions, which are classified as parallel transitions. The transition dipole is along z. P and R branches are seen.

(ii) $\Sigma - \Pi$ transitions, which are classified as perpendicular transitions. The transition dipole is along (x, y). P, Q and R branches are seen.

3.4.2 Rotational Fine Structure for $\Sigma - \Sigma$ Transitions

For these transitions the selection rules for the rotational energy levels are

$$\Delta J = +1 : \ R\text{ branch}, \qquad \Delta J = -1 : \ R\text{ branch}. \qquad (3.24)$$

These are identical to those for heteronuclear diatomics and so the resulting P, R branch structure is the same. It can be analysed using the method of combination differences to give values for the rotational constants B_0 and B_1.

Rotational Fine Structure for $\Sigma - \Pi$ Transitions

For these transitions the selection rules for the rotational energy levels are

$$\Delta J = +1 : \ R\text{ branch}, \qquad \Delta J = 0 : \ Q\text{ branch}, \qquad \Delta J = -1 : \ R\text{ branch}. \quad (3.25)$$
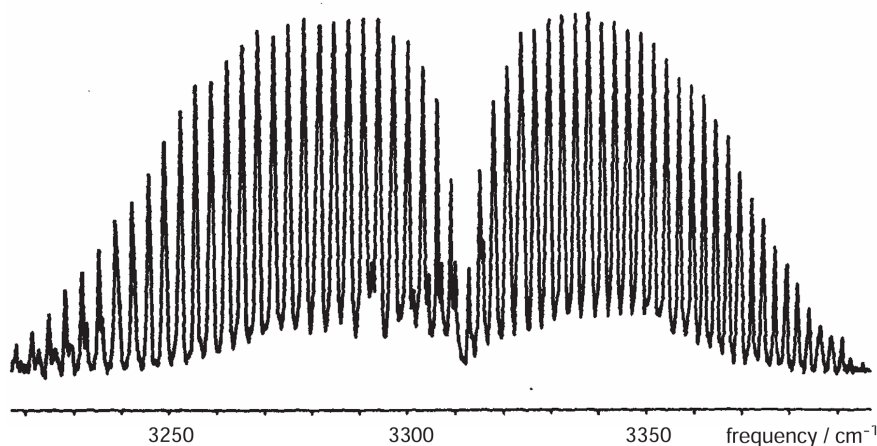
Figure 3.2: An experimental spectrum of the rotational structure associated with the fundamental of a Σ^+ mode of HCN, adapted from Banwell; the P and R branches are clearly visible.
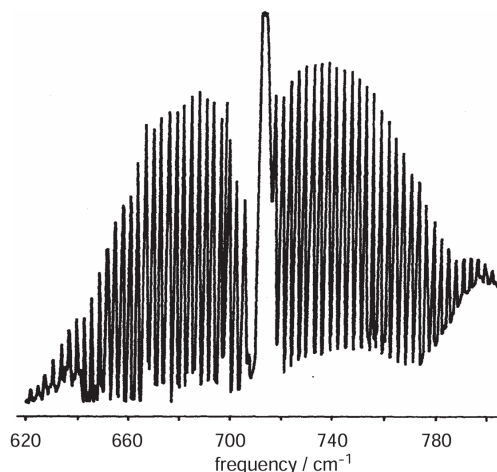

Figure 3.3: An experimental spectrum of the rotational structure associated with the fundamental Π bending mode of HCN, adapted from Banwell; the intense Q branch, made up of many overlapping lines, is clearly visible in the centre of the band.

The frequencies of the lines in the Q branch can easily be shown to be

$$\tilde{\nu}_Q(J) = \tilde{\omega}_0 + J(J+1)(\tilde{B}_1 - \tilde{B}_0). \tag{3.26}$$

Recall that $\tilde{B}_1$ and $\tilde{B}_0$ are not very different, so the separate lines in the Q branch are not as widely separated as those in the P and R branches; indeed, when recorded at moderate resolution it is not uncommon for the Q branch lines not be to resolved from one another but simply to "pile up" and give a strong feature in the centre of the band.

3.4.3 Symmetric Tops

As with linear molecules, the nature of the rotational fine structure depends on the symmetry of the vibrational wavefunctions involved. Broadly, we again need to classify the vibrational transition as perpendicular or parallel.

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Throughout this section, we will use CH_3I as an example. It is a prolate symmetric top with 3 A_1 and 3 E_1 normal modes, all of which are IR active. In C_{3v}, z transforms as A_1, so the A_1 modes are parallel, and (x, y) transforms as E, so the E modes are perpendicular.

Parallel Transitions

For parallel transitions the selections rules for the rotational quantum numbers are

$$\Delta J = 0, \pm 1 \quad \Delta K = 0 \qquad (3.27)$$

with the exception that for $K = 0$, $\Delta J = 0$ is not allowed. For each value of K we thus expect there to be a P, Q, and R branch (with the exception of $K = 0$ for which there is no Q branch).

Recall that the rotational energies for a prolate symmetric top are given by (ignoring centrifugal distortion)

$$\tilde{E}_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2 \,. \qquad (3.28)$$

It is clear that, as $\Delta K = 0$, the term in $(\tilde{A} - \tilde{B})$ does not affect the positions of the lines and so the P, Q, and R branches have exactly the same frequency for any value of K. So, what we will see is a simple PQR-band structure, identical to that for a $\Sigma - \Pi$ transition of a linear molecule.

The presence of centrifugal distortion terms alters this simple picture somewhat. The P, Q and R branches now no longer fall on top of one another, but are very slightly displaced; as a result, the band takes on a more complex appearance. However, at modest resolution the separate P, Q and R branches are often not resolved from one another and so the band appears to have a "simple" PQR structure.

Perpendicular Transition

For perpendicular transitions the selections rules for the rotational quantum numbers are

$$\Delta J = 0, \pm 1 \quad \Delta K = \pm 1 \,. \qquad (3.29)$$

For each value of K we thus expect there to be a P, Q, and R branch corresponding to $\Delta K = +1$ and one for $\Delta K = -1$.

Assuming, for simplicity, that the rotational constants do not change with vibrational state, and ignoring centrifugal distortion, the frequencies of the P, Q, and R branch lines for a prolate top are

$$\tilde{\nu}_P(J, K) = \tilde{\omega}_0 - 2\tilde{B}_J + (\tilde{A} - \tilde{B})(1 \pm 2K) \qquad (3.30)$$

$$\tilde{\nu}_Q(J, K) = \tilde{\omega}_0 + (\tilde{A} - \tilde{B})(1 \pm 2K) \qquad (3.31)$$

$$\tilde{\nu}_R(J, K) = \tilde{\omega}_0 + 2\tilde{B}(J+1) + (\tilde{A} - \tilde{B})(1 \pm 2K) \,. \qquad (3.32)$$
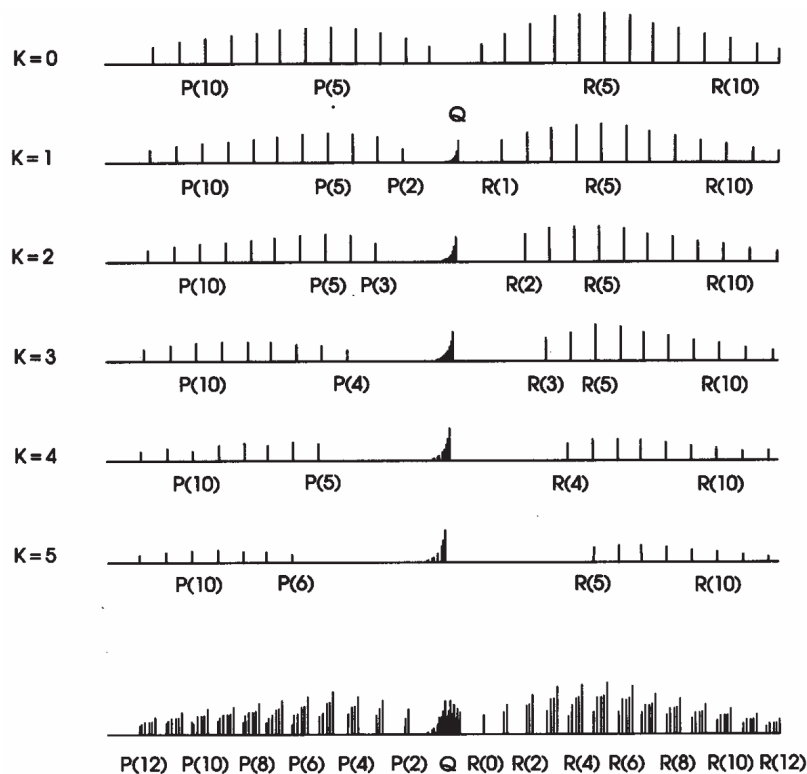
Figure 3.4: A schematic spectrum for a parallel transition of a prolate top, adapted from Bernath. The P, Q and R branches with different K values partly overlaps. Note that since K cannot be larger than J, those lines from levels with $J < K$ are missing from the branches, and that there is no Q branch for $K = 0$.
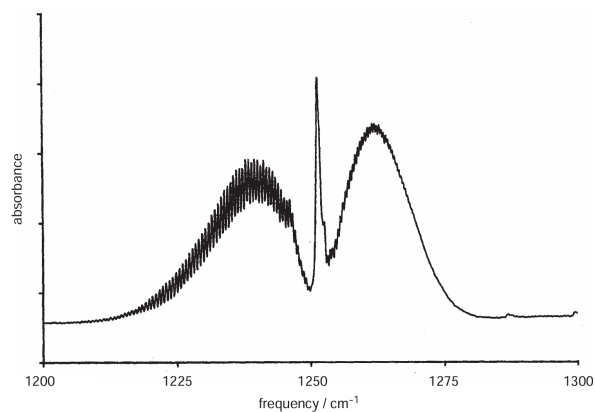

Figure 3.5: The spectrum of a parallel transition for CH_3I, adapted from Banwell. The partly resolved P and R branches are clearly visible, as is the intense Q branch.
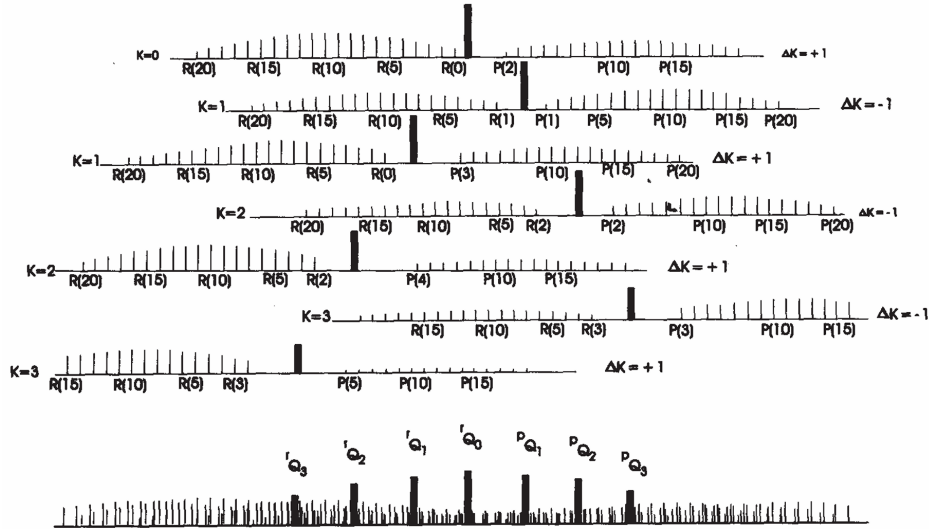
Figure 3.6: A schematic spectrum for a perpendicular transition of a prolate top, adapted from Bernath. A perpendicular band is constructed from overlapping P, Q and R branches from different K values and with $\Delta K = \pm 1$. Note how the lines in the P and R branches form a forest of lines, leaving the narrow Q branches to stand out. (The notation used is that ${}^rQ_K$ is the Q branch corresponding to the transition with $\Delta K = +1$ for a given K, and ${}^pQ_K$ is the Q branch corresponding to the transition with $\Delta K = -1$.)

For each value of K there is a set of PQR branches centred at $\tilde{\omega}_0 + (\tilde{A} - \tilde{B})(1 + 2K)$ (corresponding to $\Delta K = +1$), and another set centred at $\tilde{\omega}_0 + (\tilde{A} - \tilde{B})(1 - 2K)$ (corresponding to $\Delta K = -1$). Since $\tilde{A} - \tilde{B}$ is usually comparable with the rotational constants, the displacement of these sets of PQR branches is easily resolved.

There are so many of these PQR branches that the resulting spectrum is very complex indeed. Typically, in moderate resolution, the only features which are visible are the strong Q branches; the P and R branch lines are so numerous that they merge into one another. It is clear from the above that the separation of the Q branches is $2(\tilde{A} - \tilde{B})$; provided that $\tilde{B}$ is known (e.g. from a parallel transition), it is thus possible to determine $\tilde{A}$. This is in contrast to the pure rotational spectrum from which it is not possible to determine $\tilde{A}$.

3.4.4   Intensities

In the case of pure rotational transitions, it is necessary to take into account both stimulated absorption and stimulated emission in order to explain the observed intensities of the lines. However, in the case of rotational fine structure associated with a vibrational transition, the upper state (which involves a vibrational excitation) is hardly populated, so we usually only need consider stimulated absorption. The dominant factor determining the intensities of these rotational fine structure transitions is thus the populations of the ground states.
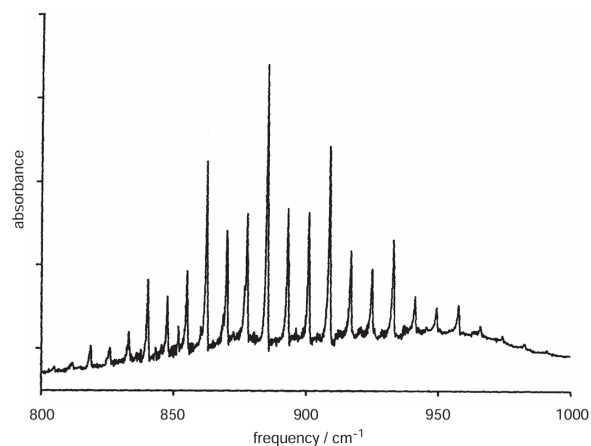
Figure 3.7: The spectrum of a perpendicular transition for CH$_3$I, adapted from Banwell. Only the intense Q branches are visible.

3.4.5 Nuclear Spin Effects

In the IB Molecular Energy Levels and Thermodynamics course we described how, in symmetrical molecules, the intensities of rotational transitions are affected by nuclear spin. For example, we saw that in the fundamental of the asymmetric stretch of ^{12}C^{16}O$_2$, only lines originating from even J levels in the ground state are present.

This discussion was limited to symmetrical linear molecules belonging to point group $D_{\infty h}$. However, similar effects are seen in symmetric top molecules. For example, the Q branches seen in a perpendicular transition of C^{1}H$_3$F show a $2 : 1 : 1 : 2$ intensity alternation on account of the three equivalent hydrogen atoms whose nuclei have spin one half.

3.5 Direct Product

Below are the direct product tables for a selection of some commonly encountered point groups. Direct product is commutative, so only the upper half of the table is shown.

C_{3v}, D_{3h}	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + [A_2] + E$

$C_{\infty v}, D_{\infty h}$	Σ^+	Σ^-	Π	Δ
Σ^+	Σ^+	Σ^-	Π	Δ
Σ^-		Σ^+	Π	Δ
Π			$\Sigma^+ + [\Sigma^-] + \Delta$	$\Pi + \Phi$
Δ				$\Sigma^+ + [\Sigma^-] + \Gamma$

For those with $'$ and $''$, or g and u labels, the products are as follows.

	$'$	$''$
$'$	$'$	$''$
$''$	$''$	$'$

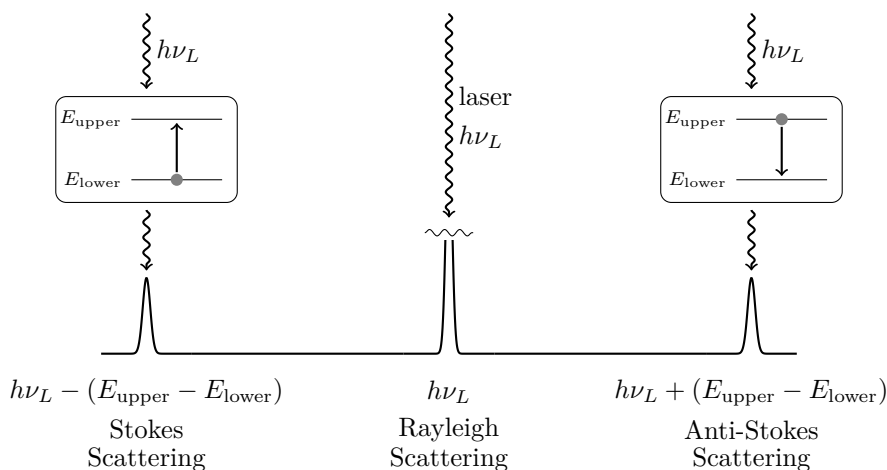|	g	u
g	g	u
u	u	g

4 Raman Spectroscopy

In "normal" spectroscopy we look at the light which is either absorbed or emitted by a molecule. However, there are other processes by which a molecule can interact with radiation, such as *scattering* which is the topic of this section. In a scattering experiment we shine a beam of monochromatic light through the sample and detect photons which emerge from the sample in all directions: these photons are said to be scattered. It is important to realize that these scattered photons do not arise from the original photons being absorbed and then re-emitted (that would be fluorescence/phosphorescence), but from a completely different process.

Typically, only a tiny fraction of the incident photons are scattered so detecting them has in the past represented quite a challenge. However, the ready availability of lasers, which emit intense well-collimated beams of monochromatic light, has made such scattering experiments much easier to perform.

The majority of scattered photons are at exactly the same frequency as the incoming photons from the laser: this type of scattering is called *Rayleigh scattering*. However, it is found that some of the scattered photons have lower energy than the photons from the laser, and some have higher energy than the laser photons. This type of scattering in which there is a change in the photon energy is called *Raman scattering*.

The interpretation of Raman scattering is that in the scattering process the laser photon either loses energy as the scattering molecule moves up from one energy level to another, or gains energy as the molecule moves down from one energy level to another. The energy separation between the scattered photon and the laser photon therefore depends on the separation of the molecular energy levels, and so measurements of the energies of the scattered photons gives information about molecular energy levels, just in the same way as other forms of spectroscopy.

$h\nu_L - (E_{\text{upper}} - E_{\text{lower}})$ Stokes Scattering
$h\nu_L$ Rayleigh Scattering
$h\nu_L + (E_{\text{upper}} - E_{\text{lower}})$ Anti-Stokes Scattering

4.1 Theory of Raman Scattering

An explanation of Raman scattering using quantum mechanics is not possible using the framework we have introduced so far. It is necessary to postulate the existence

of "virtual energy states" which are created by the transient interaction between the molecule and the laser photon: these states are not the same as the normal energy levels of the molecule. The details of this approach are well beyond the level of this course, so we will not pursue it further. We can, however, develop a classical description of scattering which is helpful in interpreting the results of the full quantum mechanical analysis and which will provide us with a framework for understanding the Raman effect.

4.1.1   Classical Description

The key idea in this classical description is that the electric field of the laser light causes a distortion of the electron density of the molecule, resulting in the generation of an induced dipole.[1]

The induced dipole fluctuates in sympathy with the oscillating electric field of the laser light. Classically, a fluctuating dipole generates radiation, and so this induced dipole results in radiation at the same frequency as the laser light: this is the origin of Rayleigh scattering. The size of the induced dipole depends on the *polarisability* of the molecule: the more polarisable the molecule, the greater the distortion caused by a given electric field, the greater the induced dipole and hence the stronger the scattering.

The polarisability is a rank-2 tensor — it may either be *isotropic* or *anisotropic*. For example, in a diatomic molecule it is easier to polarize the electrons parallel to the internuclear axis than it is to polarize them perpendicular to the internuclear axis, so its polarisability is anisotropic.
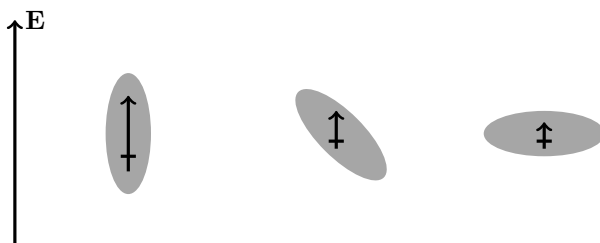
Assume the laser gives an oscillating electric field in the z direction

$$\mathbf{E} = E \sin(\omega_L t)\hat{\mathbf{z}}\,. \tag{4.1}$$

Let the polarisability of the molecule be the simple diagonal form

$$\alpha = \begin{pmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{pmatrix}\,, \tag{4.2}$$

where $\alpha_\perp < \alpha_\parallel$ accounting for the fact that the molecule is more polarisable in along the intermolecular axis.

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[1]The argument we present in this section is somewhat less handwaving than the one presented in the official handout. However, it is still wrong as it is classical.

Now let the molecule rotate in the electric field. We will assume the molecule is rotating in the x, z plane, and the intermolecular axis is making an angle θ with the direction of the electric field. The polarisability tensor is then

$$\alpha(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 0 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix}^{\mathrm{T}} \begin{pmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 0 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix}$$

$$= \begin{pmatrix} \cos^2\theta\,\alpha_\perp + \sin^2\theta\,\alpha_\parallel & 0 & \sin\theta\cos\theta(\alpha_\parallel - \alpha_\perp) \\ 0 & 0 & 0 \\ \sin\theta\cos\theta(\alpha_\parallel - \alpha_\perp) & 0 & \cos^2\theta\,\alpha_\parallel + \sin^2\theta\,\alpha_\perp \end{pmatrix}. \tag{4.3}$$

Therefore, the induced dipole is

$$\boldsymbol{\mu} = \alpha(\theta)\mathbf{E} \tag{4.4}$$

$$= \begin{pmatrix} \cos^2\theta\,\alpha_\perp + \sin^2\theta\,\alpha_\parallel & 0 & \sin\theta\cos\theta(\alpha_\parallel - \alpha_\perp) \\ 0 & 0 & 0 \\ \sin\theta\cos\theta(\alpha_\parallel - \alpha_\perp) & 0 & \cos^2\theta\,\alpha_\parallel + \sin^2\theta\,\alpha_\perp \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ E\sin(\omega_L t) \end{pmatrix} \tag{4.5}$$

$$= E\sin(\omega_L t) \begin{pmatrix} \sin\theta\cos\theta(\alpha_\parallel - \alpha_\perp) \\ 0 \\ \cos^2\theta\,\alpha_\parallel + \sin^2\theta\,\alpha_\perp \end{pmatrix}$$

$$= \frac{1}{2}(\alpha_\parallel + \alpha_\perp)E\sin(\omega_L t) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} + \frac{1}{2}(\alpha_\parallel - \alpha_\perp)E\sin(\omega_L t) \begin{pmatrix} \sin 2\theta \\ 0 \\ \cos 2\theta \end{pmatrix}. \tag{4.6}$$

This induced dipole have two components — one aligned with the electric field of the laser, the other with lower magnitude rotating in the xz plane twice as fast as the molecule.

We now focus on the more interesting direction — the z direction, since it has both components. Define

$$\alpha_{\mathrm{av}} = \frac{1}{2}(\alpha_\parallel + \alpha_\perp) \qquad \Delta\alpha = \frac{1}{2}(\alpha_\parallel - \alpha_\perp), \tag{4.7}$$

and let $\theta = \omega_R t$ i.e. the molecule is rotating at angular frequency ω_R. Then the induced dipole along the z axis is
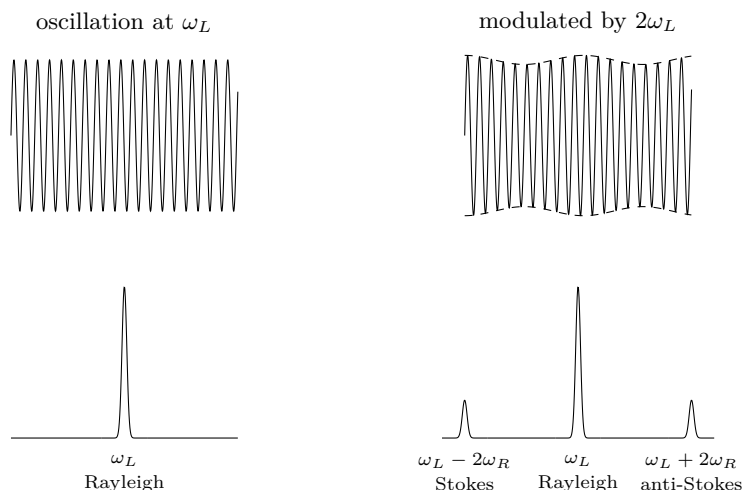
$$\mu_z = \alpha_{\mathrm{av}}E\sin(\omega_L t) + \Delta\alpha E\cos(2\omega_R t)\sin(\omega_L t). \tag{4.8}$$

The first term is has the same frequency as the laser, so it gives rise to the Rayleigh scattering. The second term can be rewritten as

$$\frac{1}{2}\Delta\alpha E\left[\sin((\omega_L + 2\omega_R)t) + \sin((\omega_L - 2\omega_R)t)\right]. \tag{4.9}$$

They are the Stokes and anti-Stokes scattering with frequencies $2\omega_R$ higher and lower than the laser frequency. Note the amplitude of these terms is proportional to $\alpha_\parallel - \alpha_\perp$, the anisotropy of the molecule's polarisability.

In words, what is happening here is that the rotation of an anisotropic molecule leads to a modulation, at the rotational frequency, in the size of the induced dipole, as

oscillation at ω_L modulated by $2\omega_L$

ω_L
Rayleigh

$\omega_L - 2\omega_R$ ω_L $\omega_L + 2\omega_R$
Stokes   Rayleigh   anti-Stokes

is illustrated above. This variation of the dipole results in a corresponding variation in the amplitude of the radiation originating from the dipole. A sine wave which is modulated in amplitude by another sine wave has a Fourier transform in which there are additional components shifted by from the original frequency by $\pm$ the modulation frequency, as is illustrated below.

Within the terms of this explanation, we see that all that is required for Raman scattering due to rotation is that the molecule has an anisotropic polarizability. Therefore, all diatomics (including homonuclear ones) give rise to rotational Raman scattering, as do all linear polyatomic molecules. This is in contrast to microwave spectroscopy where molecules belonging to the point group $D_{\infty h}$ do not give rise to spectra.

The vibration of a molecule leads to a change in the electron density and hence a change in the polarizability of the molecule. As a result, molecular vibrations also give rise to Raman scattering. As we shall see in more detail below, normal modes with are not infra red active may nevertheless give rise to Raman scattering.

The above explanation was great, except it was completely wrong. It predicts the location of shift in the frequency to be twice the frequency that the molecule is vibrating, but in fact, it should be equal to be change in the molecular rotational energy level after the scattering. However, there is no idea of "discrete energy levels" in classical physics — it is a quantum mechanical concept. The classical explanation is doomed to fail.

4.1.2 Quantum Description

As we stated before, the quantum mechanical description of Raman scattering is far beyond the scope of this course. We will only state some results of it.
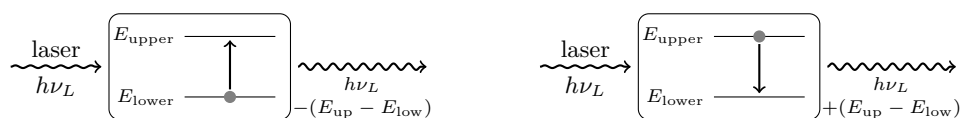
If in the scattering process the molecule moves from a lower energy level, with energy E_{lower}, to a higher energy level E_{upper}, the conservation of energy dictates that

$$h\nu_{\text{Stokes}} = h\nu_L - (E_{\text{upper}} - E_{\text{lower}}) \, . \tag{4.10}$$

Similarly, for a scattering process in which the molecule drops down from E_{upper} to E_{lower} we have

$$h\nu_{\text{anti-Stokes}} = h\nu_L + (E_{\text{upper}} - E_{\text{lower}}) \, . \tag{4.11}$$

The above equations can be easily rewritten in terms of wavenumbers

$$\tilde{\nu} = \tilde{\nu}_L \pm |\Delta\tilde{\epsilon}| \, . \tag{4.12}$$

Whether or not the scattering process is allowed for any particular pair of energy levels will depend on relevant selections rules, which are detailed below. The intensity of the scattering process depends on the polarizability of the molecule and the population of the energy level in which the molecule starts. At equilibrium, these populations will be determined by the Boltzmann distribution.

4.2 Experimental Raman Spectroscopy

The experimental arrangement for Raman spectroscopy is that an intense monochromatic beam of light is directed through the sample, the scattered radiation is then collected and its frequency analysed in the usual way by dispersing it with a prism or a diffraction grating, or analysing it using an interferometer (as in an FTIR experiment). The scattered light comes out in all directions, so it is advantageous to collect it from directions perpendicular to the exciting beam so as to minimize the amount of this intense light which reaches the detector.

Laser light, on account of its high intensity, monochromaticity and high degree of collimation, is ideal for recording Raman spectra. Since the intensity of Raman scattering is very low, but proportional to the intensity of the exciting radiation, it is very advantageous to use an intense source. Any frequency spread in the source translates to a frequency spread in the scattered photons (i.e. a linewidth), so the monochromatic nature of laser light gives the highest resolution spectra. Finally, the collimation of the light means that it can be directed through the sample and, if necessary, passed back and forth many times so as to increase the number of scattered photons.

It is important that the laser light is not absorbed directly by the molecules being studied as this would give rise to fluorescence which would swamp the much weaker signal due to Raman scattering. Photons from the visible region are easy to detect with high sensitivity, so this indicates using a laser in the visible region. However, this increases the chance that the laser light will be absorbed directly.

In the past, it was common to use light at 633 nm (red) from a He-Ne laser or at 515 nm (green) from argon-ion laser. However, recent advances in the efficiency with which infra red photons can be detected, along with the use of Fourier transform instruments for analysing the scattered light, has led to the use of 1064 nm light (which

is in the near infra red) from the Nd-YAG laser. Such near infra red light is far less likely to be absorbed by the molecules.

4.3 Rotational Raman Spectroscopy

Changes in rotational energy lead to Raman scattered light which is separated from the laser line by typical rotational energies i.e. a few cm^{-1}. Detecting such a weak signal close in to the very strong laser line is very challenging experimentally.

4.3.1 Diatomics and Linear Polyatomics

All such molecules have anisotropic polarizability so lead to Raman scattering. The selection rules are

$$\Delta J = 0, \pm 2\,. \tag{4.13}$$

Scattered photons with $\Delta J = 0$ have the same frequency as the laser line, so will not be separable from Rayleigh scattering.

The labelling of the lines requires some care. Recall that:

(i) ΔJ is defined as $(J_{\text{upper}} - J_{\text{lower}})$.

(ii) lines are labelled according to the J value of the lower level.

A Stokes scattering event in which the molecule starts from $J = 0$ and ends in $J = 2$ will appear on the low frequency side of the laser line and will have $\Delta J = J_{\text{upper}} - J_{\text{lower}} = 2 - 0 = +2$. An anti-Stokes scattering event in which the molecule starts from $J = 2$ and ends in $J = 0$ will appear on the high frequency side of the laser line. However, according to the definition above $\Delta J = J_{\text{upper}} - J_{\text{lower}} = 2 - 0 = +2$. The lines are labelled with the J value of the lower level, which in this case 0 for both.

Under typical conditions many rotational levels are occupied so we expect to see several lines corresponding to $J = 0, 1, 2, \ldots$. The situation is therefore reminiscent of the (microwave) rotational spectrum.

Let us first consider the Stokes lines, and assume that the rotational energy levels can be modelled using the rigid rotor, with levels

$$\tilde{E}_J = \tilde{B} J(J + 1)\,. \tag{4.14}$$

The wavenumber of the scattered photon is that of the laser minus the separation of the rotational levels, giving

$$\tilde{\nu}_{\text{Stokes}}(J) = \tilde{\nu}_L - [\tilde{E}_{J+2} - \tilde{E}_J]$$
$$= \tilde{\nu}_L - 2\tilde{B}(2J + 3)\,. \tag{4.15}$$

We therefore see a series of lines at

$$\underbrace{\tilde{\nu}_L - 6\tilde{B}}_{2\leftarrow 0}, \quad \underbrace{\tilde{\nu}_L - 10\tilde{B}}_{3\leftarrow 1}, \quad \underbrace{\tilde{\nu}_L - 14\tilde{B}}_{4\leftarrow 3}\,. \tag{4.16}$$
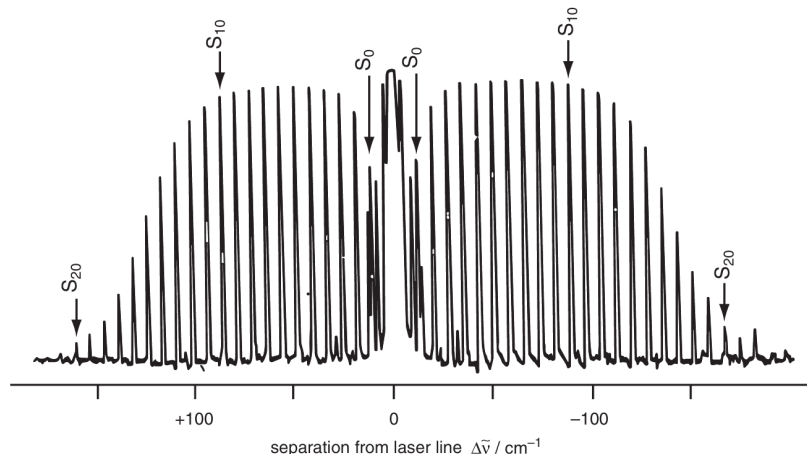
Figure 4.1: The rotational Raman spectrum of $^{15}N^{14}N$, adapted from Hollas. Note that the intensities of the lines with low J values have been somewhat truncated by experimental effects.

Note that the first line is shifted (to lower wavenumber) by $6\tilde{B}$ from the laser line and that subsequent lines are spaced by $4\tilde{B}$.

The anti-Stokes transitions are similar.

$$\tilde{\nu}_{\text{anti-Stokes}}(J) = \tilde{\nu}_L + [\tilde{E}_{J+2} - \tilde{E}_J]$$
$$= \tilde{\nu}_L + 2\tilde{B}(2J+3). \qquad (4.17)$$

The first line is shifted (to higher wavenumber) by $6\tilde{B}$ from the laser line and subsequent lines are spaced by $4\tilde{B}$.

Since both Stokes and anti-Stokes transitions have $\Delta J = +2$, they are all referred to as S branch. The Stokes line closest to the laser is therefore labelled $S(0)$ and subsequent Stokes lines are labelled $S(1), S(2), \ldots$. Similarly, the anti-Stokes line closest to the laser is labelled $S(0)$ and subsequent anti-Stokes lines are labelled $S(1), S(2), \ldots$.

The intensities of these lines follow a contour similar to that for the microwave spectrum.

4.3.2 Symmetric Tops

All such molecules have an anisotropic polarizability so lead to Raman scattering. The selection rules are $\Delta J = 0, \pm 1, \pm 2$, $\Delta K = 0$. Transitions with $\Delta J = \pm 1$ give lines shifted from the laser line by $2\tilde{B}, 4\tilde{B}, 6\tilde{B}, \ldots$, and those with $\Delta J = \pm 2$ give lines shifted from the laser line by $6\tilde{B}, 10\tilde{B}, 14\tilde{B}, \ldots$.

4.3.3 Spherical Tops

Spherical tops have isotropic polarisabilities. They do not give rise to rotational Raman spectra.

4.4 Vibrational Raman Spectra

4.4.1 Diatomics

The gross selection rule is that there must be a change in polarisability during the vibration. This is always the case, so all diatomics give rise to vibrational Raman spectra. The harmonic oscillator selection rule is $\Delta \nu = \pm 1$, as in the infra-red.

If we use the harmonic oscillator energy levels as a simple model, then a transition from $v = 0$ to $v = 1$ leads to a Raman line on the low frequency side of the laser line (Stokes scattering), with frequency

$$\tilde{\nu}_{\text{Stokes}}(1 \leftarrow 0) = \tilde{\nu}_L - \tilde{\omega}\,. \tag{4.18}$$

Similarly, a transition from $v = 1$ to $v = 0$ leads to an anti-Stokes line at

$$\tilde{\nu}_{\text{anti-Stokes}}(1 \to 0) = \tilde{\nu}_L + \tilde{\omega}\,. \tag{4.19}$$

Under typical conditions the $v = 1$ level is barely populated so the anti-Stokes line will be much weaker than the Stokes line.

Rotational Fine Structure

As in the infra-red, a change in vibrational energy can be accompanied by a change in rotational energy. For vibrational Raman spectroscopy the selection rules for rotational levels are:

$$\Delta J = 0, \pm 2\,. \tag{4.20}$$

$\Delta J = -2$ transitions will lead to an O branch and $\Delta J = +2$ will lead to an S branch. Note that this fine structure is spread about the frequency of the vibrationally scattered line (e.g. about $\tilde{\nu}_L - \tilde{\omega}$) and not about the laser line. In addition, the $\Delta J = 0$ transitions form a Q branch, clustered at the centre. If we assume that the rotational levels can be described using a rigid rotor and that the rotational constant is independent of the vibrational state, then the frequencies of the Stokes scattered lines are

$$\tilde{\nu}_O(J) = \tilde{\nu}_L - [\tilde{\omega}_0 - 2\tilde{B}(2J - 1)] \tag{4.21}$$
$$\tilde{\nu}_Q(J) = \tilde{\nu}_L - \tilde{\omega} \tag{4.22}$$
$$\tilde{\nu}_S(J) = \tilde{\nu}_L - [\tilde{\omega}_0 + 2\tilde{B}(2J + 3)] \tag{4.23}$$
$$\tag{4.24}$$

where $\tilde{\omega}_0$ is the frequency of the pure vibrational transition. For the o branch $J = 2, 3, \ldots$ and for the Q and S branches $J = 0, 1, \ldots$. Note that, in this approximation, all of the lines in the Q branch fall on top of one another, and the spacing in the O and S branches is $4\tilde{B}$.

If we make the more realistic assumption that $\tilde{B}$ varies with the vibrational state, then the lines in the Q branch are somewhat spread out, and the spacing in the other branches is no longer constant. The values of the rotational constants can be found by using a modified version of the method of combination differences.
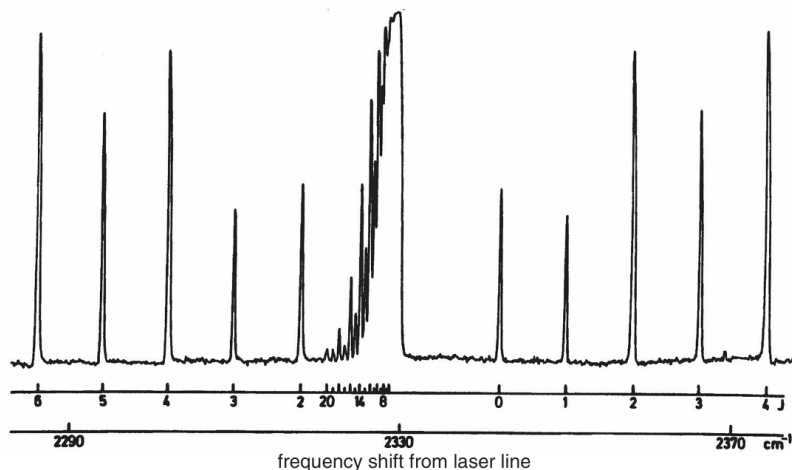
Figure 4.2: The $1 \leftarrow 0$ vibrational transition in the Raman spectrum of $^{14}N_2$ (i.e. the Stokes peaks), adapted from Bernath. the intensity alternation is due to nuclear spin effects. Note that the horizontal scale is the shift in frequency from the laser line, and that all of these peaks are on the low frequency side of the laser. The O branch lines (left) appear at higher absolute frequencies than those in the S branch (right).

4.4.2 Raman Activity of Normal Modes

The intensity of Raman scattering involving a transition between vibrational states i and j depends on the transition moment

$$R_{ij} = \int d\tau\, \psi_i^* \hat{\alpha} \psi_j \,. \tag{4.25}$$

It will be non-zero only if the triple direct product

$$\Gamma^{(i)} \otimes \Gamma_\alpha \otimes \Gamma^{(j)} \tag{4.26}$$

includes the totally symmetric irreducible representation.

Following a similar line of argument as for the infra red, we can easily show that the fundamental of a particular normal mode gives rise to Raman scattering if the IR of the normal mode matches that of $x_i x_j$. Such a mode is said to be *Raman active*. As before, symmetry arguments can be used to examine whether or not overtones or combination lines are Raman active.

Rule of Mutual Exclusion

If a point group contains the centre of inversion i as a symmetry operation, then the character of x, y and z under i must be -1, as by definition, i does the transformation $(x, y, z) \mapsto (-x, -y, -z)$. The character of quadratic functions $x_i x_j$ must be $+1$ because $x_i x_j \mapsto (-x_i)(-x_j) = x_i x_j$. Hence, x_i and $x_i x_j$ must transform as different irreducible representations. Hence we get the rule of mutual exclusion.

> In a centrosymmetric molecule, the fundamental of any normal mode cannot be infra-red active and Raman active at the same time.

4.4.3 Intensities and Polarisations

In non-centrosymmetric molecules it is rare for any of the modes to be Raman inactive. However, it is found that the strength of Raman scattering varies considerably from mode to mode. So-called *breathing modes*, in which all of the bonds around a central atom stretch together, often give rise to particularly strong Raman scattering. In contrast, bending modes give weak scattering.

If the laser light used to excite Raman scattering is plane polarized, then it is found that some of scattered light is polarized in the same direction as the laser light (called the *parallel component*) and some of the scattered light is polarized at right-angles to the laser light (called the *perpendicular component*). The ratio of the intensity of the parallel ($I_\parallel$) to the perpendicular scattering ($I_\perp$) is called the *depolarization ratio ρ*, defined as

$$\rho = \frac{I_\perp}{I_\parallel} \ . \tag{4.27}$$

This ratio is easily measured using polarizing filters.

The detailed theory of Raman scattering shows that $0 \le \rho \le \frac{3}{4}$. Scattering from totally symmetric modes, such as the breathing modes referred to above, tend to have depolarization ratios close to zero i.e. all the scattered light is polarized parallel to the laser light. The Raman bands from such modes are said to be *polarized*.

On the other hand, totally non-symmetric modes often have depolarization ratios close to the theoretical maximum of 3/4 Such bands are said to be *depolarized*. Measurements of ρ can therefore help to distinguish which normal mode is responsible for a particular band.

4.5 Applications of Raman Spectroscopy

Although it is technically more difficult than microwave or infra-red spectra, Raman spectroscopy is useful as it provides complimentary information or, in some cases, information that is simply not obtainable by other forms of spectroscopy.

(i) The vibrational and rotational energy levels of homonuclear diatomics, and the rotational levels of symmetrical linear polyatomics, can only be probed directly using Raman spectroscopy (but electronic spectra may give the same information).

(ii) Vibrational Raman spectroscopy is complementary to infra red when it comes to elucidating the vibrational normal modes: in centrosymmetric molecules, some normal modes may only be detectable using Raman spectroscopy.

(iii) As Raman spectroscopy uses light which is scattered, rather than transmitted, the technique can be used for surface analysis, especially of solid materials.

5 Electronic Spectroscopy of Diatomics

6 Fluorescence and Phosphorescence

A   Appendices

A.1   Black Body Radiation

First consider a photon gas in a three dimensional box model. Analogous to particles in a box, the wavelength of the light must satisfy

$$\lambda = \frac{2L}{n_i}\,, \tag{A.1}$$

and so the total number of states available is

$$\sum_{\mathbf{n}} \approx \int \mathrm{d}^3\mathbf{n} \approx \frac{V}{(2\pi)^3}\int \mathrm{d}^3\mathbf{k} = \frac{4\pi V}{(2\pi)^3}\int_0^\infty \mathrm{d}k\,k^2\,, \tag{A.2}$$

where we assumed $\lambda \ll L$ so we can apply the integral approximation.

For photon, we have

$$E = \hbar k c = \hbar\omega\,, \tag{A.3}$$

and hence

$$\mathrm{d}\omega = c\,\mathrm{d}k\,. \tag{A.4}$$

We may now rewrite our integral as

$$\frac{4\pi V}{(2\pi)^3}\int_0^\infty \mathrm{d}k\,k^2 = \int_0^\infty \mathrm{d}\omega\,\frac{V\omega^2}{2\pi^2 c^3}\,, \tag{A.5}$$

where

$$g(\omega) = \frac{V\omega^2}{2\pi^2 c^3} \tag{A.6}$$

is known as the *density of states* (although it is more common to express it in terms of energy as $g(\omega)\,\mathrm{d}\omega$). It measures the number of states available for a single photon with frequency between ω and $\omega + \mathrm{d}\omega$. There is a further complication for photon — it has two polarisation states (one for each dimension transverse to the direction of propagation). To account for this, we double our density of states to get

$$g(\omega) = \frac{V\omega^2}{\pi^2 c^3} \tag{A.7}$$

The final fact that we need is important: photons are not conserved — you can check this by turning off the light in your room. Therefore, were unable to define a chemical potential for photons. Even in the canonical ensemble we must sum over states with different numbers of photons because these are all accessible states.

We'll start by looking at photons with a definite frequency ω. A state with N such photons has energy $E = N\hbar\omega$. Summing over all N gives us the partition function for photons at fixed frequency,

$$Z_\omega = 1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots = \frac{1}{1 - e^{-\beta\hbar\omega}}\,. \tag{A.8}$$

We now need to sum over all possible frequencies. The independent partition functions multiply, which means that the logs add. We only need to know how many photon states there are with some frequency ω. But this is exactly what the density of states (A.7) tells us. We have

$$
\begin{aligned}
\log Z &= \int_0^\infty \mathrm{d}\omega \, g(\omega) \log Z_\omega \\
&= -\frac{V}{\pi^2 c^2} \int_0^\omega \mathrm{d}\omega \, \omega^2 \log(1 - e^{-\beta\hbar\omega}) \,.
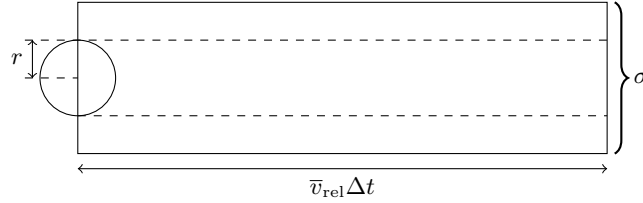\end{aligned}
\tag{A.9}
$$

This seems like a horrible integral to evaluate, but luckily, we don't need to evaluate it! The energy in the photon gas is

$$
E = -\frac{\partial}{\partial\beta} \log Z = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \mathrm{d}\omega \, \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \,.
\tag{A.10}
$$

We obtained our Planck distribution

$$
\rho(\omega)\mathrm{d}\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \mathrm{d}\omega \,.
\tag{A.11}
$$

A.2 Pressure Broadening

By the ideal gas equation, the concentration of gas is given by

$$
c = \frac{N}{V} = \frac{p}{k_B T} \,.
\tag{A.12}
$$

The number of collisions occurred on a specific particle over a time interval Δt is

$$
n_{\mathrm{col}} = \bar{v}_{\mathrm{rel}} \Delta t \sigma c \,,
\tag{A.13}
$$

so the collision rate is

$$
Z = \frac{n_{\mathrm{col}}}{\Delta t} = \bar{v}_{\mathrm{rel}} \sigma c \,.
\tag{A.14}
$$

The Speed distribution of a particle is given by the Maxwell–Boltzmann distribution

$$
\begin{aligned}
f(v)\,\mathrm{d}v &= N v^2 e^{-mv^2/2k_B T}\,\mathrm{d}v \\
&= N' e^{-mv^2/2k_B T} 4\pi\,\mathrm{d}v \,,
\end{aligned}
\tag{A.15}
$$

where we can regard $4\pi v^2\,\mathrm{d}v$ as the integration metric for the whole three dimension space of velocity $\mathrm{d}^3\mathbf{v}$. Hence, the velocity probability distribution is

$$
\phi(\mathbf{v})\,\mathrm{d}^3\mathbf{v} = N' e^{-m\|\mathbf{v}\|^2/2k_B T}\,\mathrm{d}^3\mathbf{v} \,,
\tag{A.16}
$$

which is a Gaussian distribution of variance m/k_BT. In fact this expression can be elegantly derived from a pure symmetry argument, even if we do not know Maxwell–Boltzmann distribution.

The probability distribution of the relative velocity between two particles $\mathbf{v}_{\text{rel}} = \mathbf{v}_1 - \mathbf{v}_2$ is given by the autoconvolution of (A.16), so it is a Gaussian with a doubled variance. Hence, the probability distribution of the relative velocity

$$\psi(\mathbf{v}_{\text{vel}}) \, \mathrm{d}^3 \mathbf{v}_{\text{rel}} = M e^{-m\|\mathbf{v}_{\text{rel}}\|^2/4k_BT} \, \mathrm{d}^3 \mathbf{v}_{\text{rel}} \,, \tag{A.17}$$

and so the relative speed distribution is

$$g(v_{\text{rel}}) = M' v^2 e^{-mv_{\text{rel}}^2/4k_BT} \, \mathrm{d}v_{\text{rel}} \,, \tag{A.18}$$

where we can get the normalisation constant

$$M' = \frac{1}{2\sqrt{\pi}} \left(\frac{m}{k_BT} \right)^{\frac{3}{2}} \tag{A.19}$$

by evaluating the integral. The average relative speed is therefore

$$\overline{v}_{\text{rel}} = \int_0^\infty v g(v_{\text{rel}}) \mathrm{d}v_{\text{rel}}$$

$$= 4\sqrt{\frac{k_BT}{\pi m}} \,. \tag{A.20}$$

Then, we can substitute (A.20) and (A.12) into the collision rate expression (A.14) to get

$$Z = \sigma \left(\frac{p}{k_BT} \right) \left(\frac{16 m k_B T}{\pi m} \right)^{\frac{1}{2}} \tag{A.21}$$

$$= \frac{4p\sigma}{\sqrt{k_BT\pi m}} \,. \tag{A.22}$$

Hence, the pressure broadening is given by

$$\Delta v_{\text{press}} = \frac{1}{2\pi\tau} = \frac{Z}{2\pi}$$

$$= \frac{2\sigma}{\sqrt{k_BT\pi^3 m}} p \,. \tag{A.23}$$

A.3   Microwave Spectra Intensities

Consider the allowed transitions between levels J and $J+1$, with populations n_J and n_{J+1}, respectively. Note that the degeneracy of the lower level is $2J+1$ and of the upper level is $2J+3$. Then the net rate of absorption of photons is given By

$$\frac{\mathrm{d}n_J}{\mathrm{d}t} = -B_{J,J+1}\rho(\nu_J)n_J + B_{J+1,J}\rho(\nu_J)n_{J+1} \,. \tag{A.24}$$

The first term is the stimulated absorption and the second term is the stimulated emission. We ignored the spontaneous absorption because it is insignificant in the microwave regime.

Note that the Einstein B coefficients are not the same for both processes due to degeneracies. As we stated before, the relationship is

$$\frac{B_{ij}}{B_{ji}} = \frac{g_j}{g_i} \, , \tag{A.25}$$

and so we have

$$B_{J+1,J} = \frac{2J+1}{2J+3} B_{J,J+1} \, . \tag{A.26}$$

The populations are given by the Boltzmann distribution

$$n_J = (2J+1)\frac{N}{q} \exp\left(-\frac{\epsilon_J}{k_B T}\right) \tag{A.27}$$

$$n_{J+1} = (2J+3)\frac{N}{q} \exp\left(-\frac{\epsilon_{J+1}}{k_B T}\right) \, . \tag{A.28}$$

The ratio is

$$n_{J+1} = n_J \frac{2J+3}{2J+1} \exp\left(-\frac{h\nu_J}{k_B T}\right) \, , \tag{A.29}$$

where ν_J is the frequency of the corresponding transition.

Substituting everything into the rate expression, we get

$$\frac{\mathrm{d}n_J}{\mathrm{d}t} = -B_{J,J+1}\rho(\nu_J)n_J \left[1 - \exp\left(-\frac{h\nu_J}{k_B T}\right)\right] \, . \tag{A.30}$$

For rotational transitions, $h\nu_J \ll k_B T$, so we may use Taylor expansion to obtain

$$\frac{\mathrm{d}n_J}{\mathrm{d}t} = -B_{J,J+1}\rho(\nu_J)n_J \frac{h\nu_J}{k_B T}$$

$$= -B_{J,J+1}\rho(\nu_J)(2J+1)\frac{N}{q} \exp\left(-\frac{\epsilon_J}{k_B T}\right)\frac{h\nu_J}{k_B T} \, . \tag{A.31}$$

The rate is negative, meaning that overall stimulated absorption is faster than stimulated emission.

Detailed calculations show that the Einstein coefficients depend on rotational levels according to

$$B_{J,J+1} = \frac{J+1}{2J+1} \, . \tag{A.32}$$

Finally, note that spectrometer measures is the rate of absorption (or emission) of energy (that is the power). Each time the population changes by one, a photon of energy $h\nu_J$ is absorbed (or emitted). So, the rate of absorption of energy, I is given by

$$I = \frac{\mathrm{d}n_J}{\mathrm{d}t}h\nu_J \tag{A.33}$$

$$\propto (J+1)\rho(\nu_J)\nu_J^2 \exp\left(-\frac{\epsilon_J}{k_B T}\right) \, . \tag{A.34}$$

If we assume the energy density of photon is constant, then we obtain the final result

$$I \propto (J+1)\nu_J^2 \exp\left(-\frac{\epsilon_J}{k_B T}\right) . \tag{A.35}$$

A.4 Symmetries of the Wavefunctions of Degenerate Normal Modes

Consider a hypothetical centrosymmetric linear molecule $A - A - A$. The bending mode is doubly degenerate: in one mode all molecules move in the x direction, and in the other mode all the molecules are moving in the y direction. They are given normal coordinates $Q_x(x_1, x_2, x_3)$ and $Q_y(y_1, y_2, y_3)$ respectively.

The ground state wavefunction of this degenerate normal mode is

$$\psi_{00} = \exp\left(-\frac{1}{2}Q_x^2\right)\exp\left(-\frac{1}{2}Q_y^2\right) . \tag{A.36}$$

The symmetry operations cause the mixing of the coordinates Q_x and Q_y, so the wavefunctions two parts of the wavefunctions cannot be considered separately.

We want to figure out the irreducible representation of the ground state wavefunction. For example, consider the rotation by ϕ about the z-axis. This results in the mixing of the coordinates

$$\begin{pmatrix} x_i \\ y_i \end{pmatrix} \longmapsto \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix}\begin{pmatrix} x_i \\ y_i \end{pmatrix} . \tag{A.37}$$

Hence we have

$$\begin{pmatrix} Q_x \\ Q_y \end{pmatrix} \longmapsto \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix}\begin{pmatrix} Q_x \\ Q_y \end{pmatrix} . \tag{A.38}$$

Hence the effect of this rotation on ψ_{00} is

$$\exp\left(-\frac{1}{2}Q_x^2\right)\exp\left(-\frac{1}{2}Q_y^2\right)$$

$$\mapsto \exp\left(-\frac{1}{2}[Q_x\cos\phi + Q_y\sin\phi]^2\right)\exp\left(-\frac{1}{2}[-Q_x\sin\phi + Q_y\cos\phi]^2\right)$$

$$= \exp\left(-\frac{1}{2}\left[Q_x^2\cos^2\phi + 2Q_xQ_y\sin\phi\cos\phi + Q_y^2\sin^2\phi\right]\right)$$

$$\times \exp\left(-\frac{1}{2}\left[Q_x^2\sin^2\phi - 2Q_xQ_y\sin\phi\cos\phi + Q_y^2\cos^2\phi\right]\right)$$

$$= \exp\left(-\frac{1}{2}\left[(\sin^2\phi + \cos^2\phi)Q_a^2 + (\sin^2\phi + \cos^2\phi)Q_b^2\right]\right)$$

$$= \exp\left(-\frac{1}{2}Q_x^2\right)\exp\left(-\frac{1}{2}Q_y^2\right) . \tag{A.39}$$

The net result is that ψ_{00} is invariant to the rotation: the same turns out to be true for any symmetry operation of the molecule. It follows that the ground state wavefunction transforms as the totally symmetric IR, Σ^+, which is the same behaviour we have seen for non-degenerate normal modes.

The first excited state has one quanta of excitation which can be in the mode with normal coordinate Q_x, giving the wavefunction

$$\psi_{10} = \underbrace{2Q_x \exp\left(-\frac{1}{2}Q_a^2\right)}_{v_x=1} \times \underbrace{\exp\left(-\frac{1}{2}Q_y^2\right)}_{v_y=0}. \tag{A.40}$$

Alternatively, the quantum of excitation can be in the mode with normal coordinate Q_y, giving the wavefunction

$$\psi_{01} = \underbrace{2Q_x \exp\left(-\frac{1}{2}Q_a^2\right)}_{v_x=0} \times \underbrace{\exp\left(-\frac{1}{2}Q_y^2\right)}_{v_y=1}. \tag{A.41}$$

These two wavefunctions correspond to degenerate states.

As before, let us consider the effect of a rotation by angle ϕ about z on ψ_{10} and ψ_{01}. By simple algebra, we obtain

$$\begin{pmatrix} \psi_{01} \\ \psi_{10} \end{pmatrix} \longmapsto \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} \psi_{01} \\ \psi_{10} \end{pmatrix}. \tag{A.42}$$

Thus ψ_{10} and ψ_{01} transform together in the same way as the normal coordinates Q_x and Q_y. In other words they transform as the same IR as the normal mode, which is identical to the result we found for non-degenerate normal modes. This pair of degenerate normal modes has IR Π, and this is consistent with the mixing going as $\cos\phi$ and $\sin\phi$: for the IR Π the character under the operation $C_z(\alpha)$ is $\cos\alpha$.

For the second excited state there are three possibilities of excitation

$$\psi_{20} = (4Q_x^2 - 2)\exp\left(-\frac{1}{2}Q_x^2\right) \times \qquad \exp\left(-\frac{1}{2}Q_y^2\right), \tag{A.43}$$

$$\psi_{11} = \qquad 2Q_x \exp\left(-\frac{1}{2}Q_x^2\right) \times \qquad 2Q_y \exp\left(-\frac{1}{2}Q_y^2\right), \tag{A.44}$$

$$\psi_{02} = \qquad \exp\left(-\frac{1}{2}Q_x^2\right) \times (4Q_y^2 - 2)\exp\left(-\frac{1}{2}Q_y^2\right). \tag{A.45}$$

We know that the product of the exponential terms is invariant to rotations about z so we can simply ignore these terms in what follows. For reasons that will become apparent it is easier to consider the linear combinations (omitting the exponential terms)

$$\psi_2' = \frac{1}{2}(\psi_{20} + \psi_{02}) = 2(Q_x^2 + Q_y^2) - 2 \tag{A.46}$$

$$\psi_2'' = \frac{1}{2}(\psi_{20} - \psi_{02}) = 2(Q_x^2 - Q_y^2) \tag{A.47}$$

Some straightforward but tedious algebra shows that under a rotation by φ about the z-axis ψ_2' is invariant whereas ψ_2'' and ψ_{11} are mixed, with coefficients going as $\cos 2\phi$ and $\sin 2\phi$.

The invariant wavefunction transforms as one of the Σ IRs, because this invariance under a z rotation is a property of the Σ IR. To work out if the IR is Σ^+ or Σ^- consider the effect of a reflection in xz plane: the coordinate Q_x is unaffected, but Q_y changes sign. However, ψ_2' depends only on the squares of these coordinates, so it is invariant to the reflection. The IR must therefore be $\Sigma^=$.

The two wavefunctions that are mixed must corresponds to a two-dimensional Δ IR because this IR has character $\cos 2\alpha$ under the operation $C_z(\alpha)$. In summary, the second excited state of this doubly-degenerate normal mode has three degenerate wavefunctions which transform as a Σ^+ IR and as a Δ IR.

This is all very well, but it is a rather laborious process. Luckily, it can be sidestepped by using a modified version of the argument we used to find the IR of the second excited-state wavefunction for a non-degenerate mode: we simply compute the direct product $\Gamma^{(i)} \otimes \Gamma^{(i)}$, where $\Gamma^{(i)}$ is the IR of the normal mode. Applying this approach for a Π degenerate mode gives the following direct product

$$\Pi \otimes \Pi = \Sigma^+ \oplus [\Sigma^-] \oplus \Delta \tag{A.48}$$

The difficulty is that the direct product of two two-dimensional IRs necessarily gives a result which has a total dimensionality of four — but we only have three wavefunctions to classify. The resolution of this problem is to understand that the square bracket around Σ^- indicates that this IR corresponds to the antisymmetrized direct product whereas the other IRs correspond to the symmetrized direct product. For vibrational states only the symmetrized direct product is appropriate, so the Σ^- is rejected leaving just $\Sigma^+ \oplus \Delta$. We have already identified these as the IRs spanned by the second excited state. The method by which the IRs resulting from a direct product are classified as being from the symmetrized or antisymmetrized product is described in the course *B8: Symmetry*.