

## Molecular energy levels and spectroscopy

### 1. Translational energy levels

The translational energy levels of a molecule are usually taken to be those of a particle in a three-dimensional box:

$$E(n_x, n_y, n_z) = \frac{h^2}{2m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)$$

In general, the separation of the translational energy levels is many orders of magnitude smaller than  $kT$ , even for a box with dimensions on the order of molecular sizes. The translational behaviour of molecules therefore appears to be classical.

### 2. Rotational energy levels – diatomic molecules

Diatomic molecules are often approximated as rigid rotors, meaning that the bond length is assumed to be fixed. Solving the Schrodinger equation for a rigid rotor gives the following energy levels:

$$E(J) = B J(J+1)$$

In this equation,  $J$  is the quantum number for total rotational angular momentum, and  $B$  is the rotational constant, which is related to the moment of inertia,  $I = \mu r^2$  ( $\mu$  is the reduced mass and  $r$  the bond length) of the molecule.

$$B = \frac{h}{8\pi^2 c I}$$

$B$  is usually given in units of  $\text{cm}^{-1}$ , and in order to end up with these units, the speed of light in this equation,  $c$ , needs to be in  $\text{cm s}^{-1}$  rather than  $\text{ms}^{-1}$ . Using  $B$  in  $\text{cm}^{-1}$  will yield the energy in the same units.

[Note:  $\text{cm}^{-1}$  are common units in spectroscopy for historical reasons, even though they are non-SI. Units of  $\text{m}^{-1}$  are never used, so don't be tempted to convert, however stupid it might seem...]

The equation above for  $E(J)$  is only approximate. In order to provide a better description of the energy levels of a diatomic molecule, a *centrifugal distortion* term is added to the energy. This takes account of the fact that as a real molecule rotates faster and faster (i.e. with more energy), the bond stretches a little (if you swing a weight attached to a piece of elastic in a circle, you can observe the same effect on a macroscopic scale).

$$E(J) = B J(J+1) - D_J J^2(J+1)^2$$

$D_J$  is called the centrifugal distortion constant, and is several orders of magnitude smaller than  $B$ .

Separations of rotational energy levels correspond to the microwave region of the electromagnetic spectrum. In order for a molecule to absorb microwave radiation, it must have a permanent dipole moment. i.e.  $\mu \neq 0$ . This condition is known as the *gross selection rule* for microwave, or pure rotational, spectroscopy. Specific selection rules arise largely from conservation of angular momentum, and generally involve statements of the allowed changes in quantum number. In general, the selection rule for changes in rotational angular momentum following absorption of a photon is  $\Delta J = 0, \pm 1$ . However, for pure rotational transitions (we will cover mixed rotation-vibration transitions later),  $\Delta J=0$  does not correspond to

a transition since the particle stays in the same state, so the specific selection rule for a pure rotation spectrum is  $\Delta J = \pm 1$ .

The transition energies may be calculated from the energy equation above. For a transition from a level  $J$  to a level  $J+1$ , we have:

$$\begin{aligned}\Delta E(J) &= E(J+1) - E(J) \\ &= B(J+1)(J+2) - D_J(J+1)^2(J+2)^2 - B J(J+1) + D_J J^2(J+1)^2 \\ &= B(J^2 + 3J + 2 - J^2 - J) + D_J(J+1)^2[J^2 - (J+2)^2] \\ &= 2B(J+1) - 4D_J(J+1)^3\end{aligned}$$

Neglecting the centrifugal distortion term, the spacing between lines in a spectrum will be

$$\Delta E(J+1) - \Delta E(J) = 2B(J+2) - 2B(J+1) = 2B$$

i.e. lines in a pure rotational spectrum are (almost) equally spaced by  $2B$  ("almost" because we have neglected the effects of centrifugal distortion). This result is often useful if we are attempting to assign lines in a spectrum in terms of the quantum numbers of the states involved. The separation between a pair of lines allows us to estimate  $B$  (i.e.  $B = \text{separation}/2$ ), and we can use  $\Delta E(J) \approx 2B(J+1)$  to determine the  $J$  values involved in a given transition.

### 3. Rotational energy levels – polyatomic molecules

Polyatomic molecules may rotate about the  $x$ ,  $y$  or  $z$  axes, or some combination of the three. They have moments of inertia  $I_x$ ,  $I_y$ ,  $I_z$  associated with each axis, and also corresponding rotational constants  $A$ ,  $B$  and  $C$  [ $A = h/(8\pi^2 c I_x)$ ,  $B = h/(8\pi^2 c I_y)$ ,  $C = h/(8\pi^2 c I_z)$ ]. The general equation for a moment of inertia is:

$$I = \sum_i m_i r_i^2$$

where the sum is over the atoms in the molecule,  $m_i$  is the mass of atom  $i$  and  $r_i$  is its distance from the rotation axis.

[Note: this explains why only two rotation axes are counted in a diatomic molecule. Rotation about the principal axis would have  $I=0$ , since all the atoms lie along the axis, and since the kinetic energy associated with rotation is  $K = \frac{1}{2} I\omega^2$ , with  $\omega$  the angular frequency of rotation, there would be no energy associated with such a rotation (and therefore no energy levels and no transitions between energy levels).]

In general, the rotational constants  $A$ ,  $B$ , and  $C$  may all be different, and a molecule for which this is true is called an *asymmetric top*. The spectroscopy of such molecules is quite complicated, and beyond the scope of the course. Instead, we will look at *symmetric top* molecules, such as  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CCl}_3\text{H}$  or benzene, for which two of the rotational constants are equal.

Symmetric tops may be divided into *prolate* tops, for which  $B > A, C$  (e.g.  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ) and *oblate* tops, for which  $B < A, C$  (e.g.  $\text{CCl}_3\text{H}$ , benzene). The rotational motion of a symmetric top molecule is described by three quantum numbers:

- $J$  – the total angular momentum
- $K$  – the projection of  $J$  onto the principal axis of the molecule
- $M_J$  – the projection of  $J$  onto some chosen lab-frame  $z$  axis (often just written  $M$ )

Regardless of which category the molecule falls into, the rotational energy is given approximately by:

$$E(J,K) = B J(J+1) + (A-B)K^2$$

When centrifugal distortion is included, this becomes

$$E(J,K) = B J(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

The selection rules for a symmetric top molecule are  $\Delta J = \pm 1$ ,  $\Delta K = 0$ .

Transition energies and line separations may be calculated in a similar way to that worked through above for diatomic molecules, by determining  $E(J+1,K) - E(J,K)$  etc.

#### 4. Vibrational energy levels

To a first approximation, molecular vibrations can be approximated as simple harmonic oscillators, with an associated energy

$$E(v) = (v + \frac{1}{2})h\nu$$

where  $v$  is the vibrational quantum number and  $\nu$  is the vibrational frequency (the symbols look quite similar – don't confuse them!). In the above expression,  $E(v)$  is in units of Joules. Usually, the energies are given in  $\text{cm}^{-1}$ , in which case  $h\nu$  is replaced by  $\omega_e$ , the vibrational wavenumber (i.e. this is simply the harmonic vibrational frequency or energy expressed in units of  $\text{cm}^{-1}$ ).

$$E(v) = (v + \frac{1}{2}) \omega_e$$

This is usually a fairly good approximation near the bottom of the potential well, where the potential closely resembles that of a harmonic oscillator. However, real molecules have anharmonic potentials, and this is taken into account by rewriting the energy as a series expansion, with successively higher order correction terms:

$$E(v) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 x_e\omega_e + (v + \frac{1}{2})^3 y_e\omega_e + \dots$$

Often, only the first correction term, involving  $x_e\omega_e$ , will be used, but note that the source of differences in calculated and measured properties involving vibrational energy levels is frequently neglect of higher order terms. Note that every vibration has a zero point energy found by substituting  $v=0$  into the above equation,  $ZPE = E(0) = \frac{1}{2}\omega_e - \frac{1}{4}x_e\omega_e$

As well as changing the energy of the vibrational levels, anharmonicity has another, less obvious effect: for a molecule with an anharmonic potential, the rotational constant changes slightly with vibrational state. The rotational constant  $B_v$  for a given vibrational state can be described by the expression:

$$B_v = B_e + \alpha_e(v + \frac{1}{2})$$

where  $B_e$  is the rotational constant corresponding to the equilibrium geometry of the molecule,  $\alpha_e$  is a constant determined by the shape of the anharmonic potential, and  $v$  is the vibrational quantum number.

Returning now to considering the vibrational energy levels of a harmonic and an anharmonic oscillator, recall that the energy levels in a harmonic oscillator are equally spaced by an energy  $\omega_e$ . The effect of anharmonicity is that the levels get increasingly closer together as the vibrational quantum number  $v$  increases, until eventually there is no difference in energy between successive quantum states, and the

energy levels form a continuum. The energy at which this occurs (known as the dissociation energy) coincides with the point at which the potential energy function reaches zero and the molecule is no longer bound (this is the reason why the energy levels are no longer quantized). The dissociation energy may be measured either from the bottom of the potential, in which case it is called  $D_e$ , or from the zero point energy, in which case it is called  $D_0$ .

To determine the dissociation energy, we set  $\frac{dE}{dv}$  equal to zero to determine the maximum value of the vibrational quantum number  $v$ .

$$\frac{dE}{dv} = 0 = \omega_e - 2(v_{\max} + \frac{1}{2})x_e\omega_e \Rightarrow (v_{\max} + \frac{1}{2}) = \frac{\omega_e}{2x_e\omega_e}$$

Substituting back into the energy expression above gives

$$D_e = E(v_{\max}) = \frac{\omega_e^2}{4x_e\omega_e}$$

$D_e$  and  $D_0$  are related by

$$D_0 = D_e - E(0)$$

## 5. Rovibrational spectroscopy

Ignoring electronic excitation, the total internal energy of a molecule is the sum of its vibrational and rotational energy.

$$E(v, J) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 x_e \omega_e + B_v J(J+1) - D_v J^2(J+1)^2$$

Transitions between the  $E(v, J)$  levels in which  $v$  changes correspond to absorption of energy in the infrared region of the spectrum. The gross selection rule for a vibrational transition is  $d\mu/dt \neq 0$ . i.e. the molecule must have a dipole moment that changes during the course of the vibration (important note: this requirement may be satisfied *without* the molecule having a permanent dipole). If the vibrations are approximated as simple harmonic oscillators, the specific selection rule is  $\Delta v = \pm 1$ . Since real vibrations are anharmonic, in reality there are contributions from  $\Delta v = \pm 2$ ,  $\Delta v = \pm 3$ , etc, particularly for transitions originating in highly anharmonic regions of the potential. A change in vibrational quantum number  $v$  is often accompanied by a change in rotational quantum number  $J$ , according to the selection rule  $\Delta J = 0, \pm 1$ , so we talk about rovibrational (or vibrotational) transitions, rather than simply vibrational transitions. In a linear molecule,  $\Delta J = 0$  is only allowed if there is an angular momentum perpendicular to the axis. This could arise from a bending vibration or from the electronic angular momentum of an unpaired electron (e.g. OH, NO). A transition between two vibrational states gives rise to a *vibrational band*, made up of P, Q and R branches, corresponding to transitions between rotational states with  $\Delta J = -1, 0$  (if allowed) and 1.

## 5. Populations of energy levels and spectral line intensities – the Boltzmann distribution

The intensities of lines in a spectrum depend upon a linestrength factor related to the overlap between the wavefunctions of the two states, the light intensity, and the population of the lower state. Within a given rotational or vibrational spectrum, the lower state populations are usually the dominant factor. Under thermal conditions, these are given by the Boltzmann distribution.

$$\frac{n_i}{n_0} = g_i \exp(-E_i/kT),$$

where  $g_i$  is the degeneracy and  $E_i$  the energy (relative to the ground state) of state  $i$ . As a consequence, we can predict the most intense peak in a rotational or rovibrational spectrum by maximising the Boltzmann distribution to find the most highly populated rotational state at a given temperature. For rotational lines, the above equation becomes

$$\frac{n_J}{n_0} = (2J+1) \exp[-BJ(J+1)/kT]$$

Setting the first derivative equal to zero and solving for  $J_{\max}$  gives  $J_{\max} = \frac{1}{2} \sqrt{\frac{2kT}{B}} - \frac{1}{2}$ .