

## Molecular Spectroscopy-Some Basic concepts

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**Emission spectroscopy:** a molecule undergoes a transition from a state of high energy  $E_1$  to a state of lower energy  $E_2$  and emits the excess energy as a photon. It consists of some bright lines separated by dark spaces.

**Absorption spectroscopy:** the net absorption of nearly monochromatic (single frequency) incident radiation is monitored as the radiation is swept over a range of frequencies. It consists of dark lines in otherwise continuous spectrum.

### Complementary colour

In UV-visible absorption spectra,  $\text{PbCrO}_4$  shows a peak around 449 nm. What colour would you expect  $\text{PbCrO}_4$  to be?

Answer: 450 nm wavelength corresponds violet light. So it shows complementary colour yellow.



Complementary colour wheel

### Beer-Lambert law

$$A = \epsilon cl$$

Where  $A$  is absorbance ( $A = \log \frac{I_0}{I}$ ),  $\epsilon$  is molar molar absorption coefficient or extinction coefficient (unit  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ),  $c$  is concentration of the sample and  $l$  is path length of the sample.

### Spectral line broadening

Spectral absorptions and emissions are not as infinitely sharp lines but as more or less broad peaks. The reasons for broadening of spectral lines are as discussed below.

#### 1. Narrowness of the slit.

One reason for line broadening is that the mechanical slits in spectrometers are not infinitely narrow and thus allow a range of frequencies, rather than a single frequency, to fall on the detector, hence blurring the pattern.

## 2. Collision broadening

Atoms or molecules in liquid and gaseous phases are in continual motion and collide frequently with each other. These collisions inevitably cause some deformation of the particles and hence perturb, to some extent, the energies of at least the outer electrons in each. This immediately gives a possible explanation for the width of visible and ultra-violet spectral lines, since this deal largely with transitions between outer electronic shells. Equally vibrational and rotational spectra are broadened since collisions interfere with these motions too.

In general, molecular interactions are more severe in liquids than in gases, and gas-phase spectra usually exhibit sharper lines than those of the corresponding liquid.

## 3. Doppler broadening

Again, in liquids and gases the motion of the particles causes their absorption and emission frequencies to show a Doppler shift; since the motion is random in a given sample, shifts to both high and low frequencies occur and hence the spectral line is broadened. In general, for liquids collision broadening is the most important factor, whereas for gases, where collision broadening is less pronounced, the Doppler effect often determines the natural line width.

## 4. Heisenberg uncertainty principle.

Even in an isolated, stationary molecule or atom the energy levels are not infinitely sharp, due to the operation of a fundamental and very important principle, the Uncertainty Principle of Heisenberg. In effect this says that, if a system exists in an energy state for a limited time  $\Delta t$  seconds, then the energy of that state will be uncertain to an extent  $\Delta E$  where

$$\Delta E \times \Delta t = h/2\pi = 10^{-34}$$

## Born–Oppenheimer approximation

It is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move in their field. We can therefore think of the nuclei as being fixed at arbitrary locations, and then solve the Schrödinger equation for the wavefunction of the electrons alone.

An important result of this is that the total wave function,  $\psi_{\text{total}}$  can be factorized into electronic and nuclear contributions,  $\psi_e$  and  $\psi_n$  respectively:

$$\psi_{\text{total}} = \psi_e \psi_n$$

A further approximation involves the factorization of  $\psi_n$  into vibrational and rotational contributions,  $\psi_v$  and  $\psi_r$  respectively, giving:

$$\psi_{\text{total}} = \psi_e \psi_v \psi_r$$

This factorization results in the total energy of a molecule being the sum of the contributions from the electrons, the vibrations and the rotations:

$$E_{\text{total}} = E_e + E_v + E_r$$