



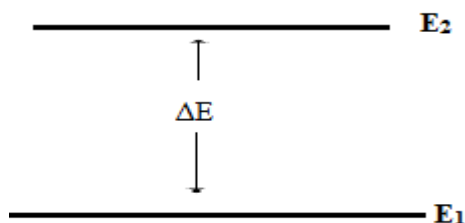
Spectroscopy

The Quantization of Energy:

Towards the end of last century experimental data were observed which were incompatible with the previously accepted view that matter could take up energy continuously. In 1900 Max Planck published the revolutionary idea that the energy of an oscillator is discontinuous and that any change in its energy content can occur only by means of jump between two distinct energy states. The idea was later extended to cover many other forms of the energy of matter.

A molecule in space can have many sorts of energy; it may possess rotational energy by virtue of bodily rotation about its centre of gravity; it will have vibrational energy due to the periodic displacement of its atoms from their equilibrium positions; it will have electronic energy since the electrons associated with each atom or bond are in unceasing motion, etc. The chemist or physicist is early familiar with the electronic energy states of an atom or molecule and accepts the idea that an electron can exist in one of several discrete energy levels – called the energy is quantized. In the similar way the rotational, vibrational, and other energies of a molecule are also quantized- a particular molecule can exist in variety of rotational, vibrational, etc; energy level and can move from one level to another only by a sudden jump involving a finite amount of energy.

Consider two possible energy states of a system- two rotational energy levels of a molecule, for example- labeled E_1 and E_2 in the following diagram:



The suffixes 1 and 2 used to distinguish these levels are, in fact, quantum numbers. The actual significance of quantum numbers goes far deeper than their use as a convenient label- in particular. Transitions can take place between the levels E_1 and E_2 provided the appropriate amount of energy, $\Delta E = E_2 - E_1$, can be either absorbed or emitted by the system. Planck suggested that such absorbed or emitted energy can take the form of electromagnetic radiation and that the frequency of the radiation has the simple form:

$$\nu = \Delta E / h \text{ Hz}$$

$$\Delta E = h\nu \text{ joules}$$

Where E is expressed in term of joule and h is a universal constant-Planck's constant.

The significance of this is that if we take a molecule in state 1 and direct on to it a beam of radiation of single frequency ν (monochromatic radiation), where $\nu = \Delta E / h$, energy will be absorbed from the beam and the molecule will jump to state 2. A detector placed to collect the radiation after its interaction with the molecule will show that its intensity has decreased. Also, if we use a beam containing a wide range of frequencies (white radiation), the detector will show



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that energy has absorbed only from that frequency $\nu = \Delta E/h$, all other frequency being undiminished in intensity. In this way **absorption** spectrum is produced.

Alternatively, the molecule may already be in state 2 and may revert to state 1 with the consequent emission of radiation. A detector would show this radiation to have frequency $\nu = \Delta E/h$ only, and the **emission spectrum** so found is plainly complementary to the absorption spectrum of the previous paragraph.

The Born-Oppenheimer Approximation

For typical diatomic molecule has rotational energy separations of $1-10 \text{ cm}^{-1}$, while in the study of vibrational spectroscopy, it found that the vibrational energy separation of HCl is near 3000 cm^{-1} . Since the energies of the two motions are so different, as a first approximation it may be considered that a diatomic molecule can execute rotations and vibrations quite independently.

This, which can be called Born-Oppenheimer approximation, is tantamount to assuming that the combined rotational -vibrational is simply the sum of the separate energies:

$$E_{\text{total}} = E_{\text{rot.}} + E_{\text{vib.}} \quad (\text{joule})$$

$$\epsilon_{\text{total}} = \epsilon_{\text{rot.}} + \epsilon_{\text{vib.}} \quad (\text{cm}^{-1})$$

Even as a first approach to electronic spectra of diatomic molecules it may be use the Born-Oppenheimer approximation. For the discussion of electronic spectra, it can be written

$$E_{\text{total}} = E_{\text{rot.}} + E_{\text{vib.}} + E_{\text{el.}} \quad (\text{joule})$$

$$\epsilon_{\text{total}} = \epsilon_{\text{rot.}} + \epsilon_{\text{vib.}} + \epsilon_{\text{el.}} \quad (\text{cm}^{-1})$$

which implies that the electronic, vibrational and rotational energies of a molecule are completely independent of each other.

But it can be shown that this approximation is invalid. A change in the total energy of a molecule may then be written:

$$\Delta E_{\text{total}} = \Delta E_{\text{rot.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{el.}} \quad (\text{joule})$$

$$\Delta \epsilon_{\text{total}} = \Delta \epsilon_{\text{rot.}} + \Delta \epsilon_{\text{vib.}} + \Delta \epsilon_{\text{el.}} \quad (\text{cm}^{-1})$$

The approximation order of magnitude of these changes are:

$$\Delta \epsilon_{\text{total}} \approx \Delta \epsilon_{\text{vib}} \times 10^3 \approx \Delta \epsilon_{\text{rot}} \times 10^6$$

and so it can be seen from the above data that vibrational changes will produce a 'coarse structure' and rotational changes a 'fine structure' on the spectra of electronic transitions. It should be noted that whereas pure rotational spectra are shown only by molecule possessing a permanent electric dipole moment and vibrational spectra require a change of dipole during the motion, electronic spectra are given by all molecules since changes in the electronic distribution in a molecule are always accompanied by a dipole change. This means that homonuclear molecules (for example H_2 or N_2), which show no rotation or vibration-rotation spectra, do give an electronic spectrum and show vibrational and rotational structure in their spectra from which rotational constants and bond vibration frequency may be derived.



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