

Techniques and Instrumentation

Microwave spectroscopy: - Source, monochromator, beam direction, sample and detector.

* The Source and Monochromator: The usual source in this region is the klystron valve → it emits radiation of only a very narrow frequency range, is called 'monochromator' and acts as its own monochromator.

The actual emission frequency is variable electronically and hence a spectrum may be scanned over a limited range of frequencies using a single klystron.

~~Disadvantage~~ Disadvantage of this source: - Total energy radiation is very small - of the order of mW.

* Beam direction: - Achieved by the use of 'waveguides' - hollow tubes of Copper or Silver, usually of rectangular cross-section - inside which the radiation is confined. Waveguide → may be tapered or bent to allow focusing and directing of radiation.

* Sample and sample space: - In almost all microwave studies so far the sample has been gaseous. Pressure of 0.01 mmHg are sufficient to give a reasonable absorption spectrum.

→ many substances which are usually thought ⁽²⁵⁾ to be as solid or liquid may be examined provided their vapor pressures are above this value. The sample is retained by very thin mica windows in a piece of evacuated waveguide.

* Detector :- Ordinary superheterodyne radio receiver may be used as detector → provided that this may be tuned to the appropriate high frequency. However, a simple crystal detector is found to be more sensitive and easier to use. This detects the radiation focused upon it by the waveguide, and the signal it gives is amplified electronically for display on an oscilloscope, or for permanent record on paper.

Chemical analysis by Microwave Spectroscopy

Microwave spectroscopy → becoming a technique for routine analysis. Even though effectively limited to gaseous samples, it ~~is~~ has much to offer since it is a highly sensitive (0.01 mmHg pressure) and specific analytical tool.

The microwave spectrum of a substance is very rich in lines since many rotational levels are populated at room temperatures.

but the lines are very sharp and their positions can be measured with great accuracy → observation of just a few of them is sufficient to establish the presence of previously examined substance in a sample.

The technique is quantitative → the intensity of the spectrum observed under given conditions is directly proportional to the amount of substance present. Thus mixtures can be analysed.

Whole molecule is examined by microwave spectroscopy → by virtue of its moment (s) of inertia.

This technique can not detect the presence of particular groups in a sample like $-OH$ or $-CH_3$, but it can readily distinguish the presence of isotopes in a sample, and it can even detect different conformational isomers, provided they have different moment of inertia.

One fascinating area of microwave analysis → chemical examination of interstellar space. → detection of simple stable molecules in space. The earliest molecules characterized are water, ammonia and formaldehyde → giving speculation regarding the origins of biological molecules and of life itself.

Such observations concern the emission of microwaves by these molecules and, by comparing the relative intensities of various rotational transitions, particularly in the spectrum of ammonia, accurate estimates can be made of the temperature of interstellar material.

Infra-Red Spectroscopy - Diatomic vibrating rotator

Elasticity of chemical bonds → anomalous results in the rotational spectra of rapidly rotating molecules - the bonds stretched under centrifugal forces.

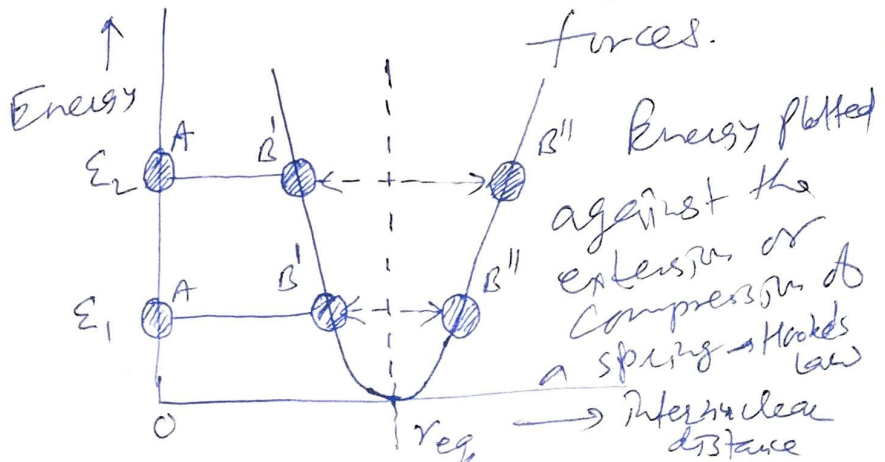
Another consequence of elasticity → atoms in a molecule do not remain in fixed relative positions but vibrate about some mean position.

The Vibrating Diatomic Molecule

The Energy of a diatomic molecule: Two atoms combine to form a stable covalent molecule (e.g. HCl gas) → because of some internal electronic rearrangement.

Chemical bond → phenomenon as balancing of forces.

At the minimum the internuclear distance is referred to as the equilibrium distance r_{eq} , → as the bond length



The bond, like a spring, obey's Hooke's Law

$$f = -k(r - r_{eq}) \quad \text{--- (1)}$$

$f \rightarrow$ restoring force, $k \rightarrow$ force constant

$r \rightarrow$ internuclear distance, The curve is

parabolic and has the form

$$E = \frac{1}{2} k (r - r_{eq})^2 \quad \text{--- (2)}$$

This model of a vibrating diatomic molecule \rightarrow
so-called simple harmonic oscillator model \rightarrow
excellent point for the discussion of vibrational
spectra (an approximation).

The Simple Harmonic Oscillator :- In above

figure, energy plotted according to eqⁿ (2). The
zero of curve and eqⁿ is at $r = r_{eq}$, energy

is excess of this, ϵ_1 , arises because of
extension or compression of the bond. If A
(creator)

is stationary at $r = r_0$, the other atom will
oscillate between B' and B'' . Energy increased

to $\epsilon_2 \rightarrow$ oscillation more vigorous, degree
of compression or extension is greater but

the vibrational frequency will not change.

An elastic bond has a certain vibrational frequency
 \rightarrow dependent upon the mass of the system and
the force constant \rightarrow independent of distortion.