

The Fortrat Diagram : We may rewrite the expressions for the P, R and Q lines, eqⁿ 9(c) and (10) with continuously variable parameters 'p' and 'q':

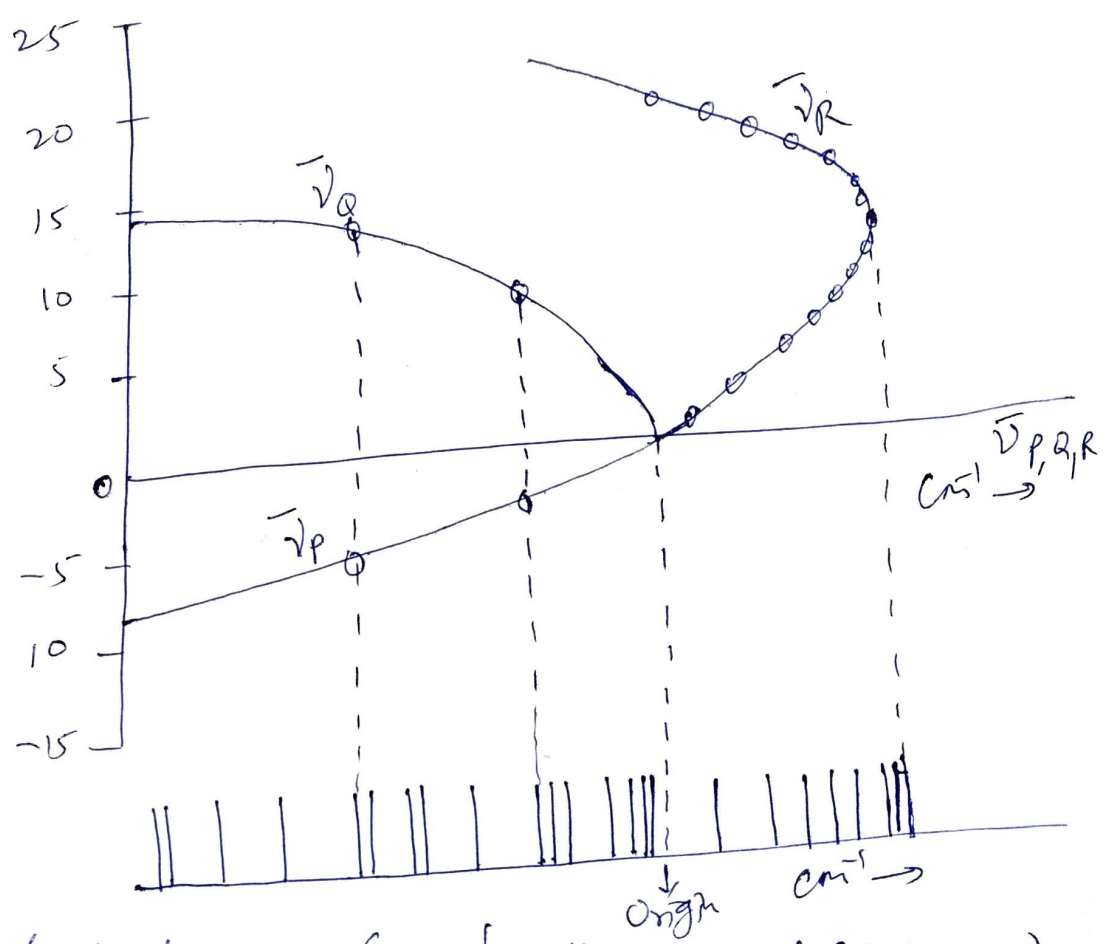
$$\bar{v}_{P,R} = \bar{v}(v', v'') + (B' + B'')p + (B' - B'')p^2 \quad \dots (9)$$

$$\bar{v}_Q = \bar{v}(v', v'') + (B' - B'')q + (B' - B'')q^2 \quad \dots (6)$$

They each represent a parabola, p taking both positive and negative values, while q is positive only.

Choosing, as before $B' < B''$ and a difference δB between them, labelling regions δB positive p with \bar{v}_R and negative p with \bar{v}_P .

These parabolas are usually referred to as the Fortrat parabolas.



Fortrat diagram for $B' < B''$ (not difference)

p and q may in fact take only integral values (but not zero) \rightarrow this fact may be illustrated by drawing circles round the allowed points on the parabolas. We can then read off the $\bar{\nu}$ values of the spectral lines directly from the graph. We show at the foot of the figure the first few lines of each branch with dotted leader lines connecting spectrum and Fortrat diagram at intervals.

Useful properties of the Fortrat diagram \rightarrow the band head is plainly at the vertex of the P, R parabola. We may calculate the position of the vertex by differentiating eqn (9)

$$\frac{d\bar{\nu}_{P,R}}{dp} = A' + A'' + 2(B' - B'')p = 0$$

$$\text{or } p = -\frac{B' + B''}{2(B' - B'')} \text{ for band head} \quad \text{--- (12)}$$

Thus if $B' < B''$ (upper state has longer equilibrium bond length) the band head occurs at positive p values (i.e. in the R branch), the line of maximum wavenumber being given by the nearest positive number to p . For $B' > B''$, the band head occurs in the region of p negative, i.e. in the P branch. From a simple calculation \rightarrow for a 10-1. difference between B' and B'' the band head occurs at $P \approx 10$.

Electronic Spectra of Polyatomic Molecules (17)

We know that the vibrational frequencies of a particular atomic grouping within a molecule, for example, CH_3 , $\text{C}=\text{O}$, $\text{C}=\text{C}$ etc. are usually insensitive to the nature of the rest of the molecule. Other bond properties, such as length or dissociation energy, are also largely of the surrounding atoms in a molecule.

All these properties depend, in the final analysis, on the electronic structure of the bond. As an approximation, we may discuss the structure and hence the spectrum, of each bond in isolation.

Bonds for which this approximation is adequate are usually said to have 'localized' molecular orbitals, i.e. orbitals embracing a pair of nuclei only; other molecules \rightarrow for which this approximation is invalid \rightarrow have non-localized orbitals and are often called 'conjugated'.

When each bond may be considered in isolation, the electronic spectrum of a molecule is the sum of the spectra from each bond.

Result is complex \rightarrow but contains great deal of information about the molecule.

Thus, if some bond series can be recognized for a particular bond we immediately know the

vibrational frequency of that bond and probably a good estimate of its dissociation energy also.

If the rotational structure is resolved, then we have the moment of inertia (from the line spacing) and hence information about the shape and size of the molecule.

Such detailed information is usually obtainable only for molecules studied in the gas phase.

In pure liquids or in solution, molecular rotation is hindered and no rotational structure will be observed.

The blurring of the rotational structure often masks the vibrational line series also ~~and~~ and the electronic spectrum of a liquid is usually rather broad and characterless.

We confine ourselves to gas-phase spectra.

One of the important advantages of electronic spectroscopy — the vibrational, rotational dissociation energies and structures of molecules may be ~~be~~ investigated in their excited states — even a particular molecule may exist in such a state for not much longer than the time it takes to complete few rotations.

Interesting fact → The electronic excitation often leads to change in shape of molecule.