

Intensity of Vibrational-Electronic Spectra :

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~~Quantum Mechanics~~ Franck-Condon Principle

Although quantum mechanics imposes no restrictions on the change in the vibrational quantum number during an electronic transition — The vibrational lines in a progression are not all observed to be of the same intensity.

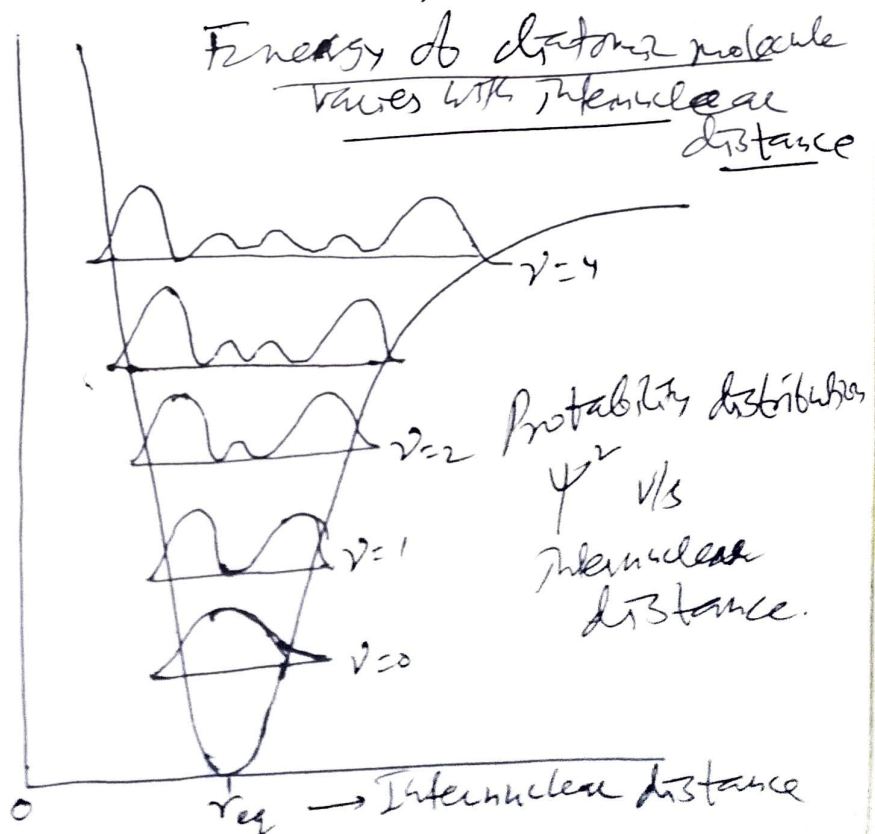
In some spectra the (0,0) transition is the strongest. In some cases the intensity increases to maximum at some value of v' , while in others only a few vibrational lines ~~are~~ with high v' are seen, followed by a continuum.

All these types of spectrum \rightarrow explicable in terms of the Franck-Condon Principle.

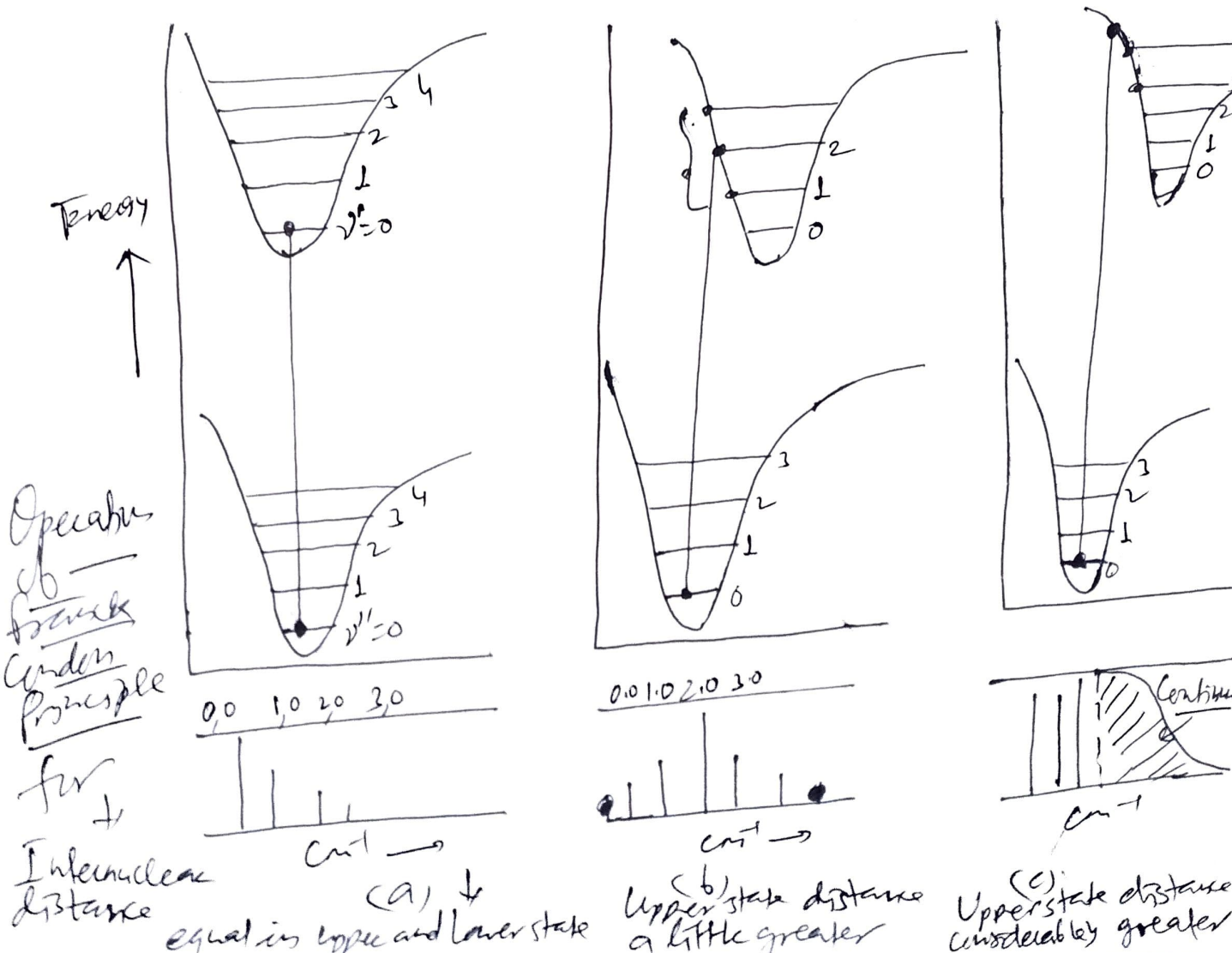
"An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition".

Morse Curve

One atom is \uparrow considered fixed in the $x=0$ a.p.f. and the other is allowed to oscillate between the limits of curve.



If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable w.r.t. dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground electronic state. There will probably be differences in such parameters as vibrational frequency, equilibrium internuclear distance, or dissociation energy between the two states \rightarrow This means that we should consider each excited molecule as a new molecule with a different Morse curve but also rather similar but rather similar



(a) The upper electronic state having the same equilibrium internuclear distance as the lower. The Franck-Condon principle suggests that a transition occurs 'vertically' on this diagram. Since the internuclear distance does not change so if we consider the molecule to be initially in the ground state electronically ($v''=0$) and vibrationally ($v''=0$) the most probable transition is that indicated by the vertical line in fig (a). The strongest spectral line of the $v''=0$ progression is (0,0).

Quantum mechanically some chance of the atoms being near the extremities steering from the ends of the $v''=0$ and finishing in the $v'=1, 2, \dots$ etc. states. The (1,0) (2,0) etc. lines diminish rapidly in intensity.

In fig (b) the excited electronic state has a slightly greater internuclear separation than the ground state. Now a vertical transition from the $v''=0$ level will most likely occur into the upper vibrational state $v'=2$. In general the upper state most probably reached will ~~most likely~~ most probably reached will depend on the difference between the equilibrium separations between the lower and upper states.

In B_g(c) the upper state separation is considerably ⁽⁹⁾ greater than that in the lower state, the vibrational level to which a transition takes place has a high v' value. Transitions can now occur to a state where the excited molecule has energy in excess of its own dissociation energy.

From such states the molecule will dissociate without any vibrators and the atoms which are formed may take up any value of kinetic energy, the transitions are not quantised and a continuum results.

The situation is rather more complex for emission spectra \rightarrow now transitions take place from both ends of the vibrational limits with equal probability \rightarrow each progression will show two maxima which will coincide only if the equilibrium separations are the same in both states.

Rotational Fine Structure of Electronic-Vibrational Transitions

So far \rightarrow electronic spectrum of a diatomic molecule consists of one or more series of convergent lines constituting the vibrational coarse structure on each electronic transition. Normally, each of these 'lines' is observed to be broad and diffuse \rightarrow in good resolution

each appears as a cluster of many very close lines. \rightarrow This is rotational fine structure (10)

To a very good approximation we can ignore centrifugal distortion and we have the energy levels of a rotating diatomic molecule

$$\epsilon_{\text{rot.}} = \frac{h}{8\pi^2 I c} J(J+1) = B J(J+1)$$

$I \rightarrow$ moment of inertia

$B \rightarrow$ rotational constant ($J = 0, 1, 2, \dots$)

$J \Rightarrow$ rotational quantum number

$$\text{cm}^{-1} \quad (1)$$

By Born-Oppenheimer approximation total energy of diatomic molecule is

$$\epsilon_{\text{total}} = \epsilon_{\text{elec.}} + \epsilon_{\text{vib.}} + B J(J+1) \text{ cm}^{-1} \quad (2)$$

Changes in the total energy

$$\Delta \epsilon_{\text{total}} = \Delta \{ \epsilon_{\text{elec.}} + \epsilon_{\text{vib.}} \} + \Delta \{ B J(J+1) \} \text{ cm}^{-1} \quad (3)$$

Wave number of a spectroscopic line for such a change

$$\bar{\nu}_{\text{spectr.}} = \bar{\nu}(\nu', \nu'') + \Delta \{ B J(J+1) \} \text{ cm}^{-1} \quad (4)$$

~~Ques~~ $\bar{\nu}(\nu', \nu'') \rightarrow$ wave number of an electronic vibrational transition. \rightarrow corresponds to any of the transitions (0,0) or (1,0) etc. We are mainly concerned with $\Delta \{ B J(J+1) \}$.