Franck-Condon Principle.

The simplest way to state this principle is that in an electronic transition, during the transition ro-vibrational degrees are treated frozen. The transition that occurs according to the F-C principle is termed as Franck-Condon Transition or vertical transition.

consider such transition probability

$$P = \int \Psi_f \, f \, \Psi_i \, d\tau \quad \text{where}$$

$$\Psi_f = \Psi_{fe} \, \Psi_{v_e} \, \Psi_{Rotf} \quad : \quad \text{final state}$$
$$\& \quad \Psi_i = \Psi_{ie} \, \Psi_{v_e} \, \Psi_{Rote} \quad : \quad \text{initial state.}$$

f : transition which can be dipole, quadrupole

Obviously in expression for P (neglecting rotational part)

$$\int \Psi_{fe} \, f \, \Psi_{ie} \, d\tau_e \quad \text{would be the contrib-}$$

from electronic part and comprise a transit^n dipole (for example) as f depends on e^- co-ord.

The factor $\int \Psi_{v_f} \, \Psi_{v_i} \, d\tau_v$ desides the strength of the transition over spectrum of final vibrational states of a given electronic states.

This is termed as 'Franck-Condon factor'

In the potential energy diagram of molecule if vertical lines are drawn from the turning points of initial state, therey define a region

called 'Franck-Condon region'. Part of
the vibrational wave function belonging to
this region plays vital role in determining
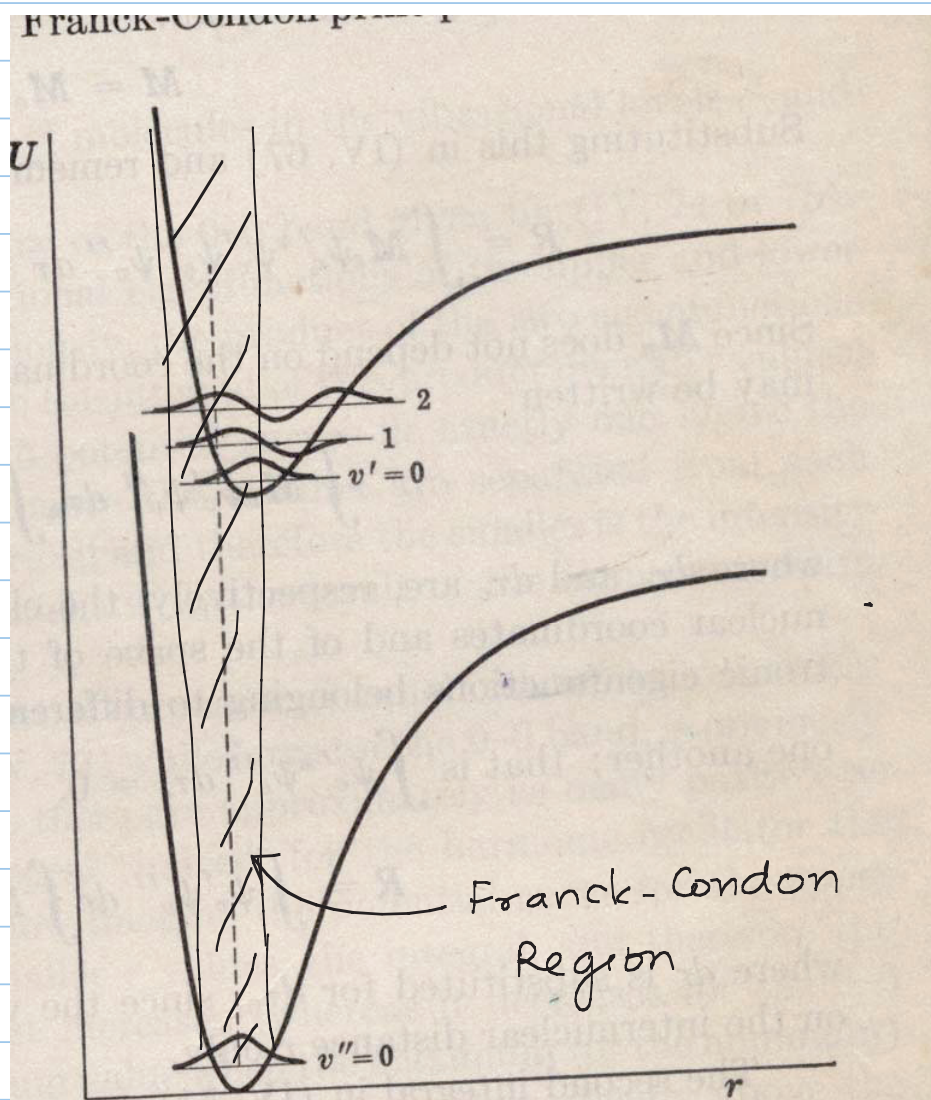'F-C factor'.
Following picture explains this idea-

FIG. 91. **Franck-Condon Principle According to Wave Mechanics.** The potential curves are so drawn that the "best" overlapping of the eigenfunctions occurs for $v' = 2, v'' = 0$ (see the broken vertical line).
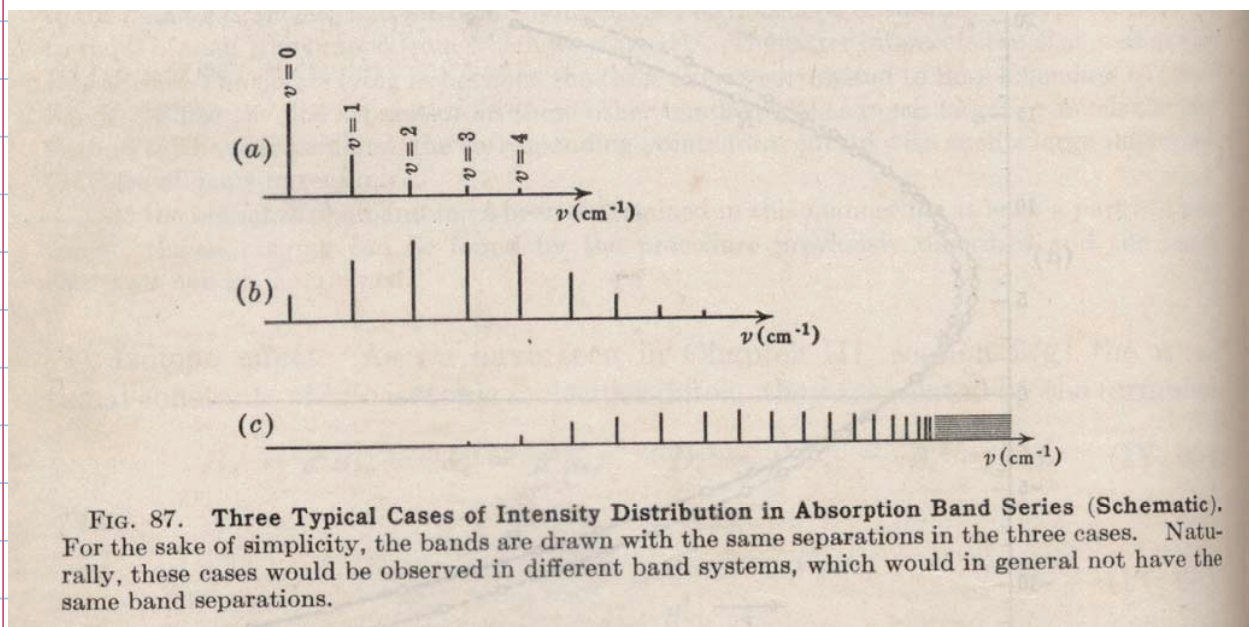
ibution in other progressions is qualitatively

...iled proof and a quantitative refinement of

The dotted line indicate the best overlapping point.
Obviously if the initial vibrational level is not $v''=0$ then the corresponding vib. wave function peaks near the classical turning points. In that case the max. overlap point is near the inner turning point due to anharmonic nature of the curve.

However, the overall spread of transition over various v' states is determined by the relative position of equilibrium bond length for bound–bound transition. For various relative positions the spectrum will look different as shown below.

FIG. 87. **Three Typical Cases of Intensity Distribution in Absorption Band Series (Schematic).** For the sake of simplicity, the bands are drawn with the same separations in the three cases. Naturally, these cases would be observed in different band systems, which would in general not have the same band separations.
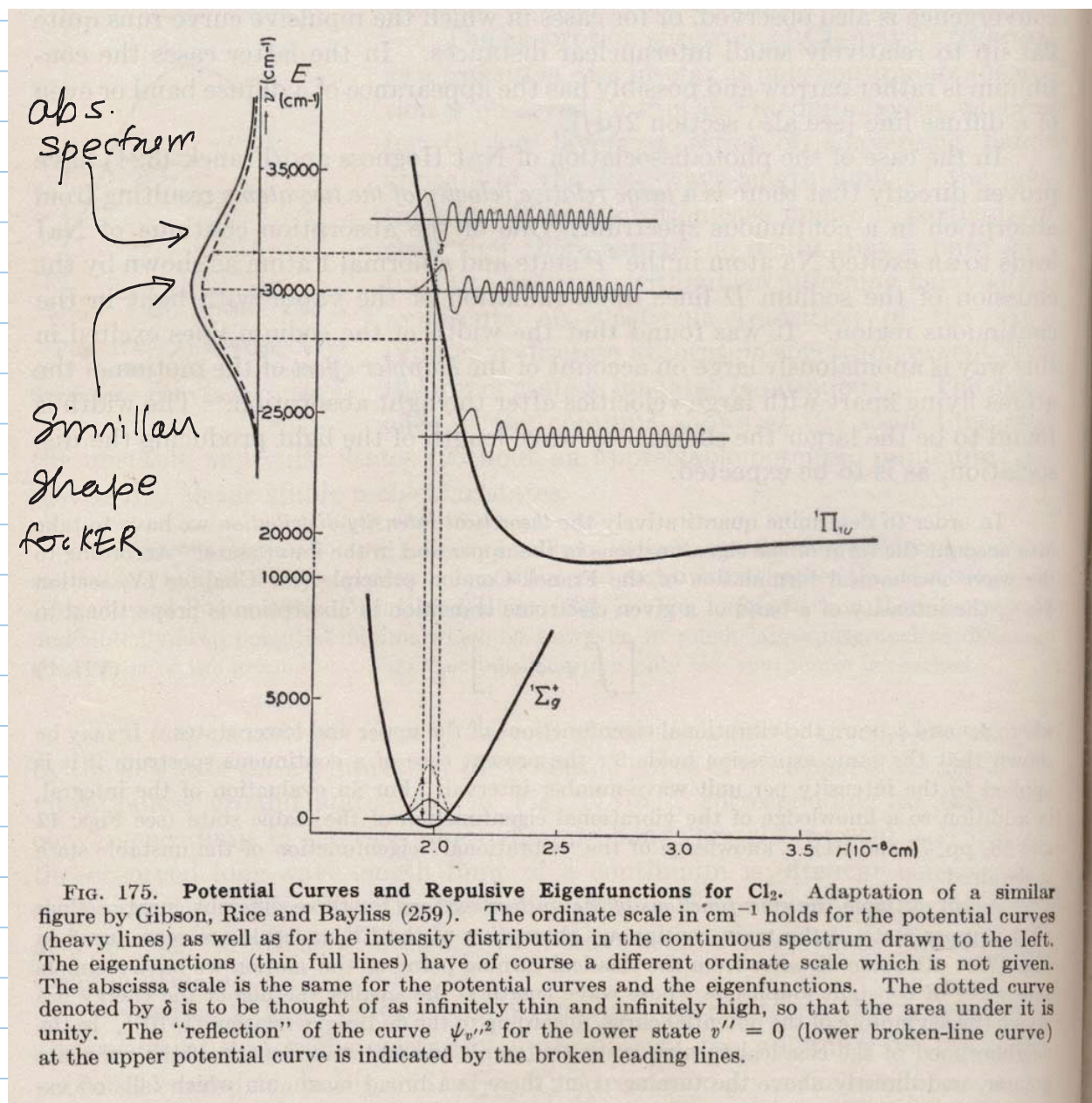
In the bound–repulsive transition, the situation is reflected in the kinetic energy released in the fragments.

For example if the initial bound state curve is known and if the transition happens

to the pure repulsive part of the excited state with initial vib. state being $v=0$, looking at the KER spectrum of the fragments one can estimate the slope of the rep. curve
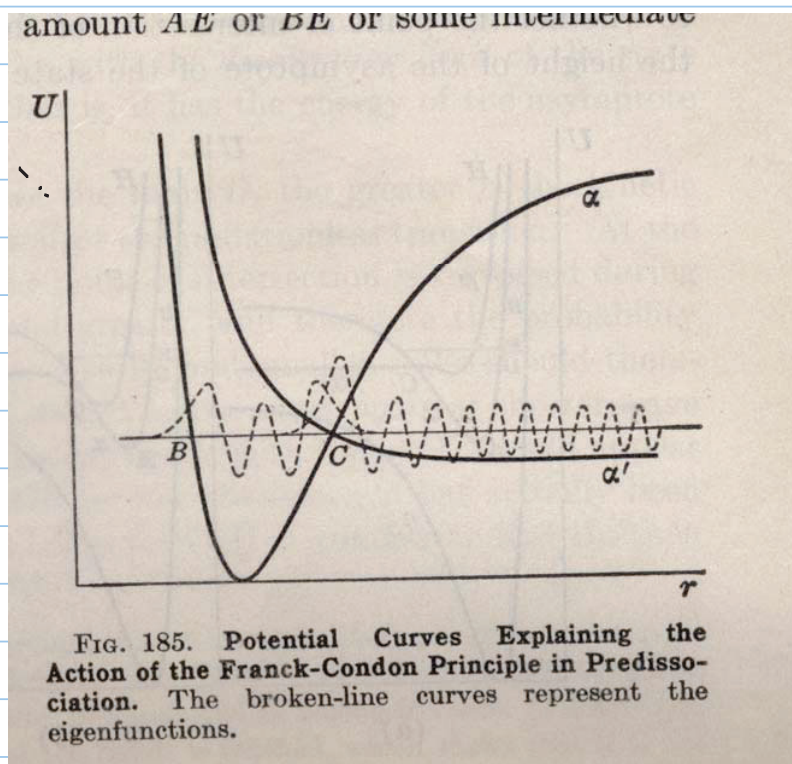
This 'Reflection Principle'.

abs. spectrum

Similar shape for KER

FIG. 175. **Potential Curves and Repulsive Eigenfunctions for Cl_2.** Adaptation of a similar figure by Gibson, Rice and Bayliss (259). The ordinate scale in cm^{-1} holds for the potential curves (heavy lines) as well as for the intensity distribution in the continuous spectrum drawn to the left. The eigenfunctions (thin full lines) have of course a different ordinate scale which is not given. The abscissa scale is the same for the potential curves and the eigenfunctions. The dotted curve denoted by δ is to be thought of as infinitely thin and infinitely high, so that the area under it is unity. The "reflection" of the curve $\psi_{v''}^2$ for the lower state $v'' = 0$ (lower broken-line curve) at the upper potential curve is indicated by the broken leading lines.

This also shows why transition to repulsive part of the pot. energy curve are continuous
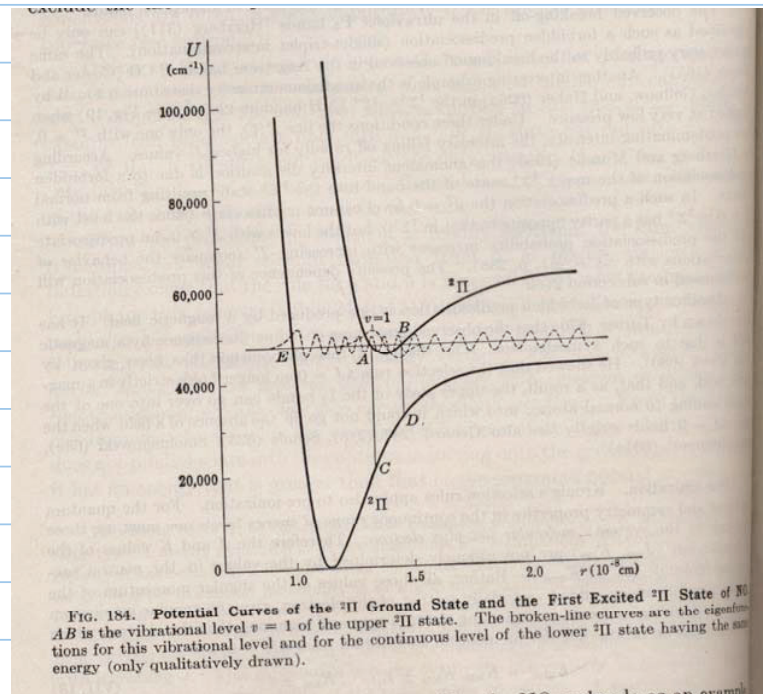
Predissociation

1. Just like autoionization of atom, if there is overlap between the repulsive part of a potential energy curve with a bound part of another pot. energy curve with same symmetry, the two states can interact leaking population from bound state to repulsive states. This is one case of predissociation. Due to the presence of repulsive state the bound state becomes pseudo bound and this reflects in the increased width or continuous nature of the spectral lines. (Bound vibrational life time decrease)

amount AE or BE or some intermediate

FIG. 185. Potential Curves Explaining the Action of the Franck-Condon Principle in Predissociation. The broken-line curves represent the eigenfunctions.
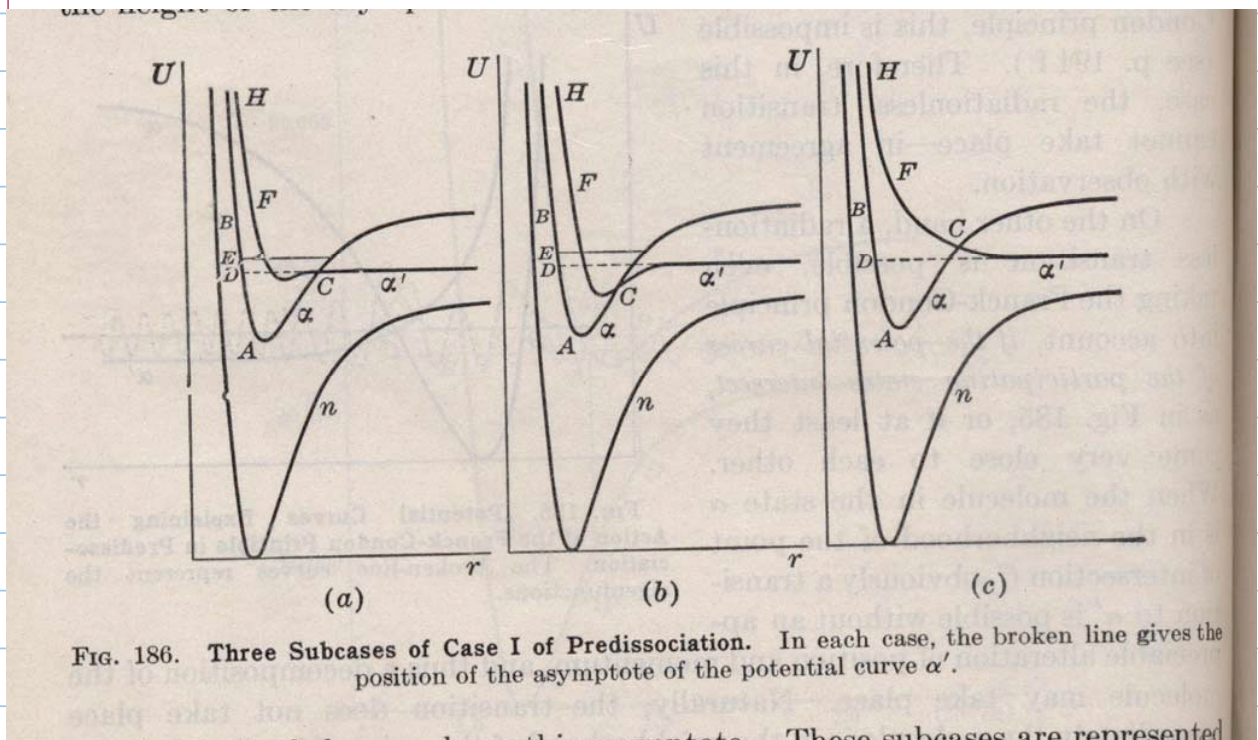
Franck-Condon principle plays vital role in determining the strength of predissociation. For example any bound excited state lies in vibrational cont. of ground state. However, the predissociation of these states

is almost ineffective due to poor Franck-Condon factor.

FIG. 184. Potential Curves of the $^2\Pi$ Ground State and the First Excited $^2\Pi$ State of NO. AB is the vibrational level $v = 1$ of the upper $^2\Pi$ state. The broken-line curves are the eigenfunctions for this vibrational level and for the continuous level of the lower $^2\Pi$ state having the same energy (only qualitatively drawn).

Various possibilities of predissociation through mixing of electronic states.

FIG. 186. Three Subcases of Case I of Predissociation. In each case, the broken line gives the position of the asymptote of the potential curve α'.

2. Another possibility of predissociation is via mixing of high rotational levels with those of vibrational continuum of the same electronic state. This can be pictured as the fast rotations cause huge centrifugal stretching which can no more be sustained by the vibrational coupling.

FIG. 187. Observed (Stable) Rotational Levels of HgH for the Different Vibrational Levels of the $^2\Sigma$ Ground State [after Hulthén (342)]. The doublet splitting is not shown. The broken line gives the position of the dissociation limit.
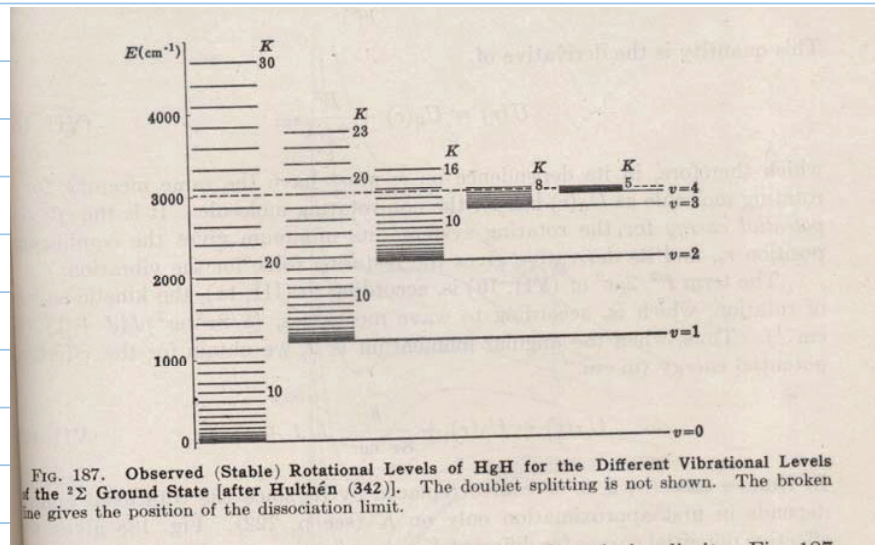
Correspondingly the pot energy curves for each vib. level would look diff.

FIG. 188. Effective Potential Curves of HgH in the Ground State [after Villars and Condon (686)]. The vibrational levels indicated refer to the lowest curve with $K = 0$. For the remaining curves they are displaced upward by an amount equal to the energy difference of the minima.

ly to the observations made on HgH (see Fig.