Electronic Spectroscopy of molecules

Part I: Frank-Condon Principle

B.Sc. (H) Chemistry

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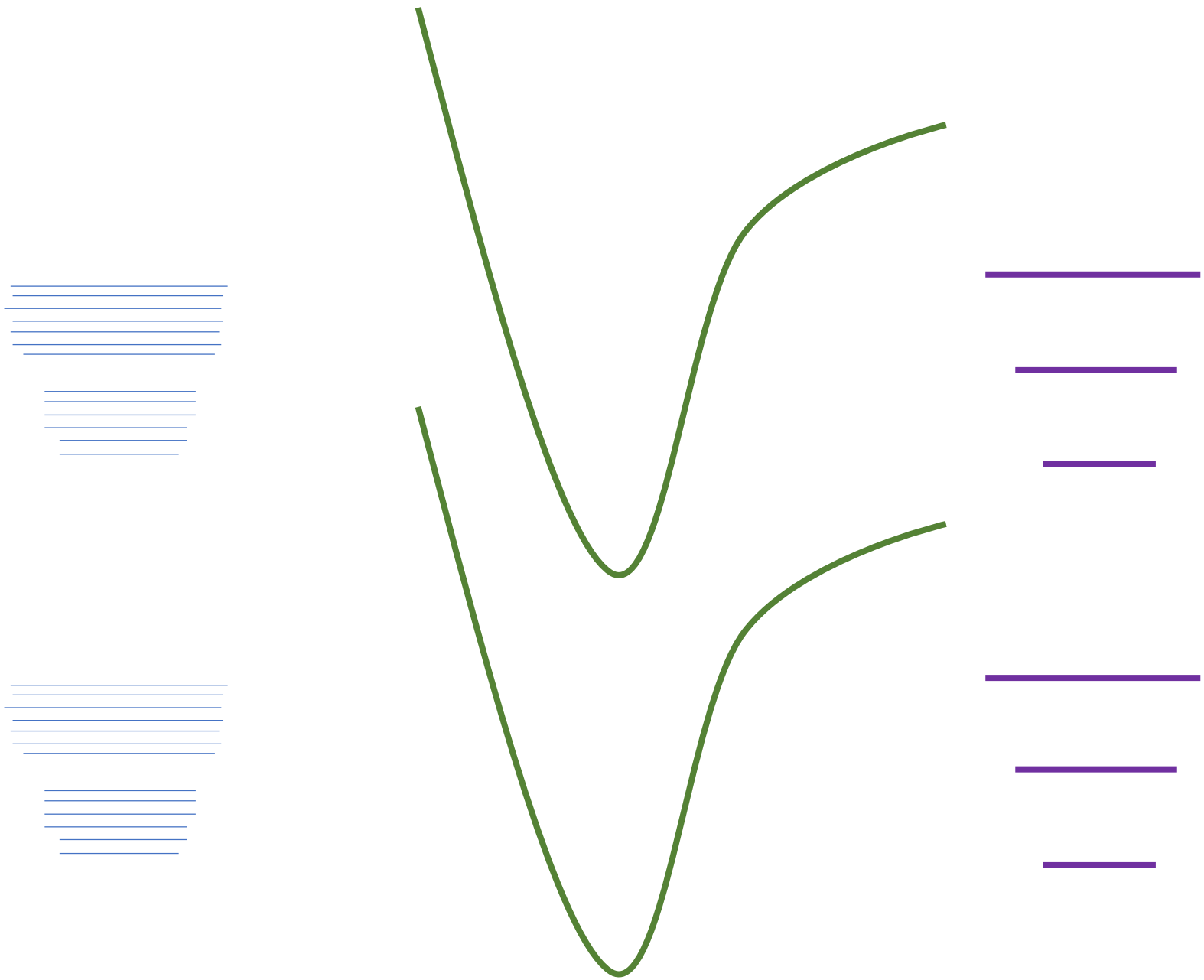
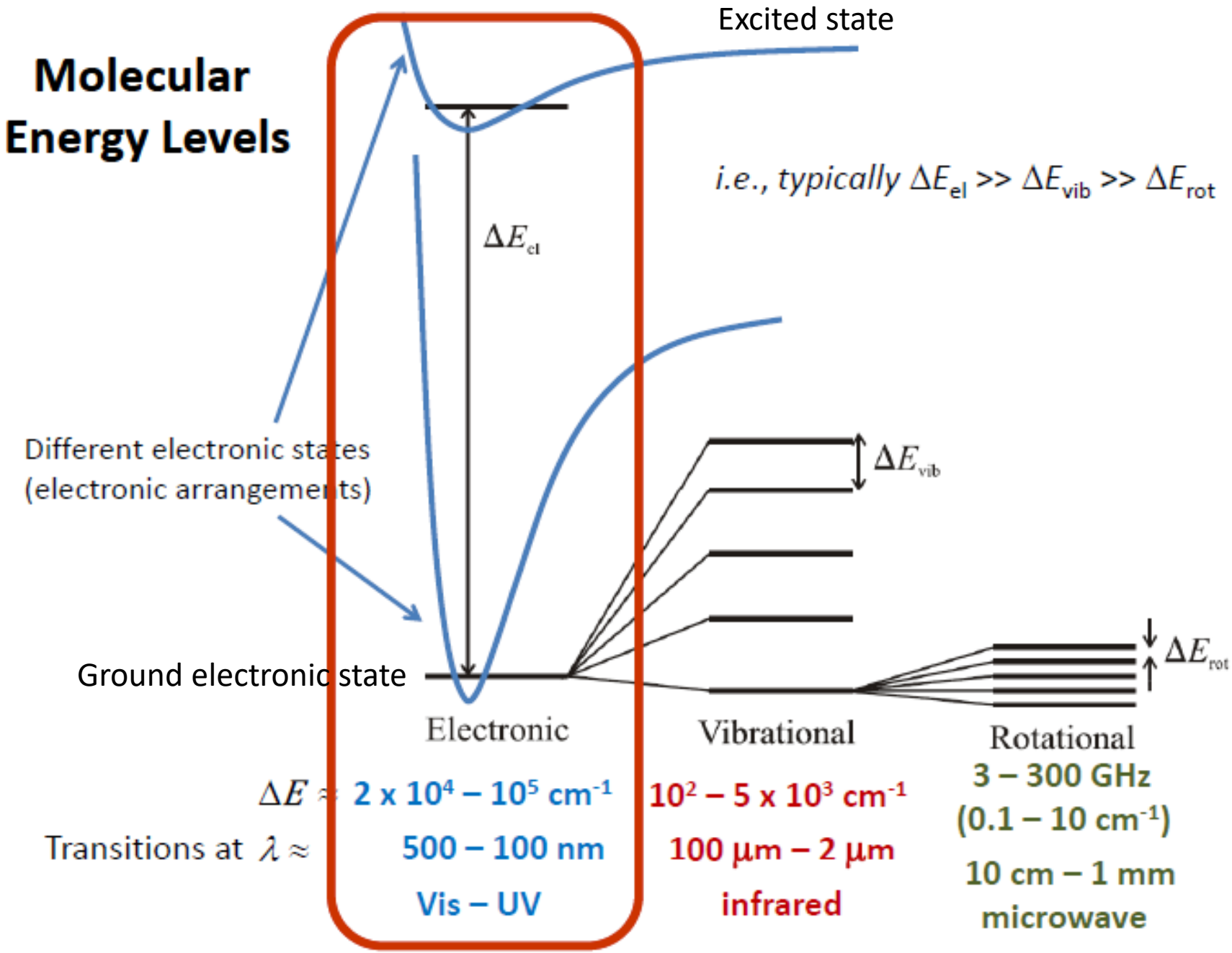
Objective of the Electronic Spectroscopy

- Many of the colours of the objects in the world around us arises from transitions in which an electron is promoted from one orbital of a molecule or ion into another.

- Some cases the relocation of an electron may be so extensive that it results in the breaking of a bond and the initiation of a chemical reaction.

- To understand these physical and chemical phenomena, We need to explore the origins of electronic transitions in molecules.




Molecular Energy Levels
Excited state
i.e., typically $\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$
ΔE_{el}
Different electronic states (electronic arrangements)
ΔE_{vib}
ΔE_{rot}
Ground electronic state
Electronic
Vibrational
Rotational
$\Delta E \approx$ 2 x 10^4 – 10^5 cm^{-1}
10^2 – 5 x 10^3 cm^{-1}
3 – 300 GHz
(0.1 – 10 cm^{-1})
Transitions at $\lambda \approx$
500 – 100 nm
100 µm – 2 µm
10 cm – 1 mm
Vis – UV
infrared
microwave

The Born-Oppenheimer Approximation

The electronic, vibrational, and rotational energies of a molecule are completely independent of each other.

$$E_{total} = E_{electronic} + E_{vibration} + E_{rotation}$$

$$\Delta E_{tot.} = \Delta E_{elec.} + \Delta E_{vib.} + \Delta E_{rot.} \qquad \text{Joule}$$

$$\Delta \varepsilon_{tot.} = \Delta \varepsilon_{elec.} + \Delta \varepsilon_{vib.} + \Delta \varepsilon_{rot.} \; cm^{-1}$$

- *Vibrational changes* will produce a **'coarse structure'** and *rotational changes* a **'fine structure'** on the spectra of electronic transitions.
- Unlike Pure rotational and vibrational spectroscopy where dipole moment and dipole moment change is required, electronic spectra are given by all molecules since changes in the electron distribution in a molecule are always accompanied by a dipole change.

Vibrational Coarse Structure: Progressions

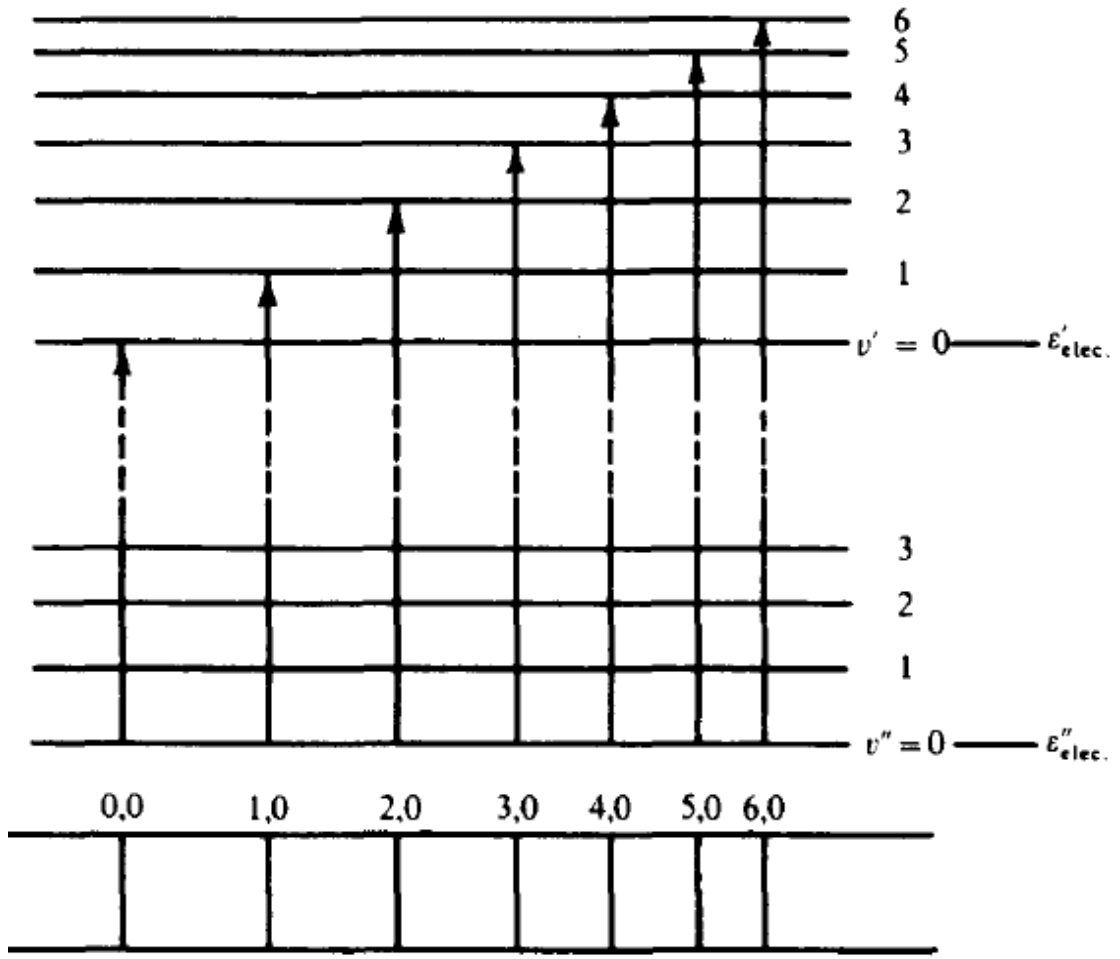
For coarse vibrational spectra, rotational changes could be ignored

$$\varepsilon_{tot.} = \varepsilon_{elec.} + \varepsilon_{vib.} \quad cm^{-1}$$

There is essentially no selection rule for **v** when a molecule undergoes an electronic transition.

Transitions are conventionally labelled according to their (v', v") numbers (note: upper state first), that is (0, 0), (1, 0), (2, 0), etc.

Such a set of transitions is called a band since, under low resolution, each line of the set appears somewhat broad and diffuse, and is more particularly called a v' progression, since the value of v' increases by unity for each line in the set.



Vibrational Coarse Structure: Progressions

$$\Delta E_{tot.} = \Delta E_{elec.} + \Delta E_{vib.} \text{ Joule}$$

$$\Delta \varepsilon_{tot.} = \Delta \varepsilon_{elec.} + \Delta \varepsilon_{vib.}$$

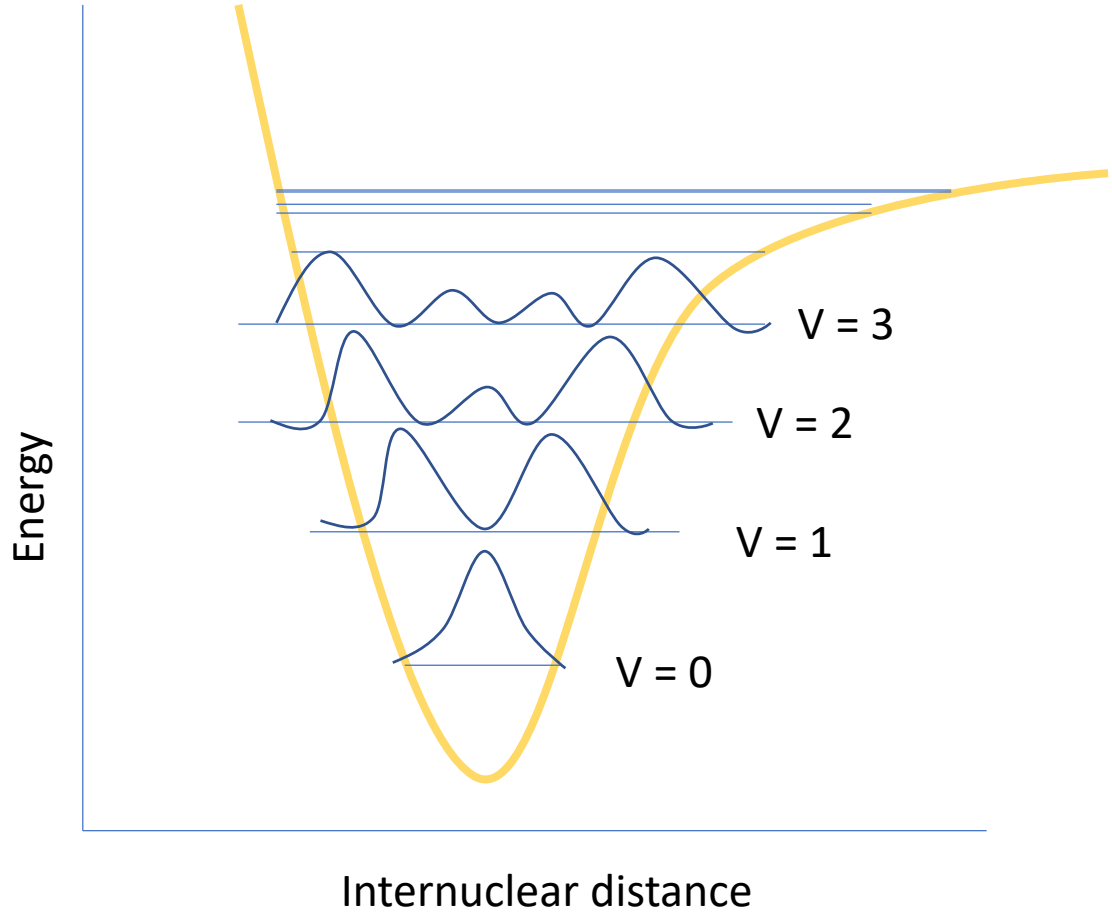
$$\bar{\upsilon}_{\text{spec.}} = (\varepsilon' - \varepsilon'') + \{(\upsilon' + \tfrac{1}{2})\bar{\omega}_e' - x_e'(\upsilon' + \tfrac{1}{2})^2\bar{\omega}_e'\} - \{(\upsilon'' + \tfrac{1}{2})\bar{\omega}_e'' - x_e''(\upsilon'' + \tfrac{1}{2})^2\omega_e''\} \quad \text{cm}^{-1}$$

$\bar{\omega}_e', \bar{\omega}_e'', x_e' \text{and } x_e'' = \text{Can be calculated}$

Morse Potential Curve in electronic transitions

- Classical and quantum theory both suggest that the oscillating atom would spend most of its time *on* the curve at the turning point of its motion, since it is moving most slowly there, i.e, at the extremities.

- Quantum theory, shows that for $v = 0$ the atom is most likely to be found at the *centre* of its motion, i.e. at the equilibrium internuclear distance r_{eq}.



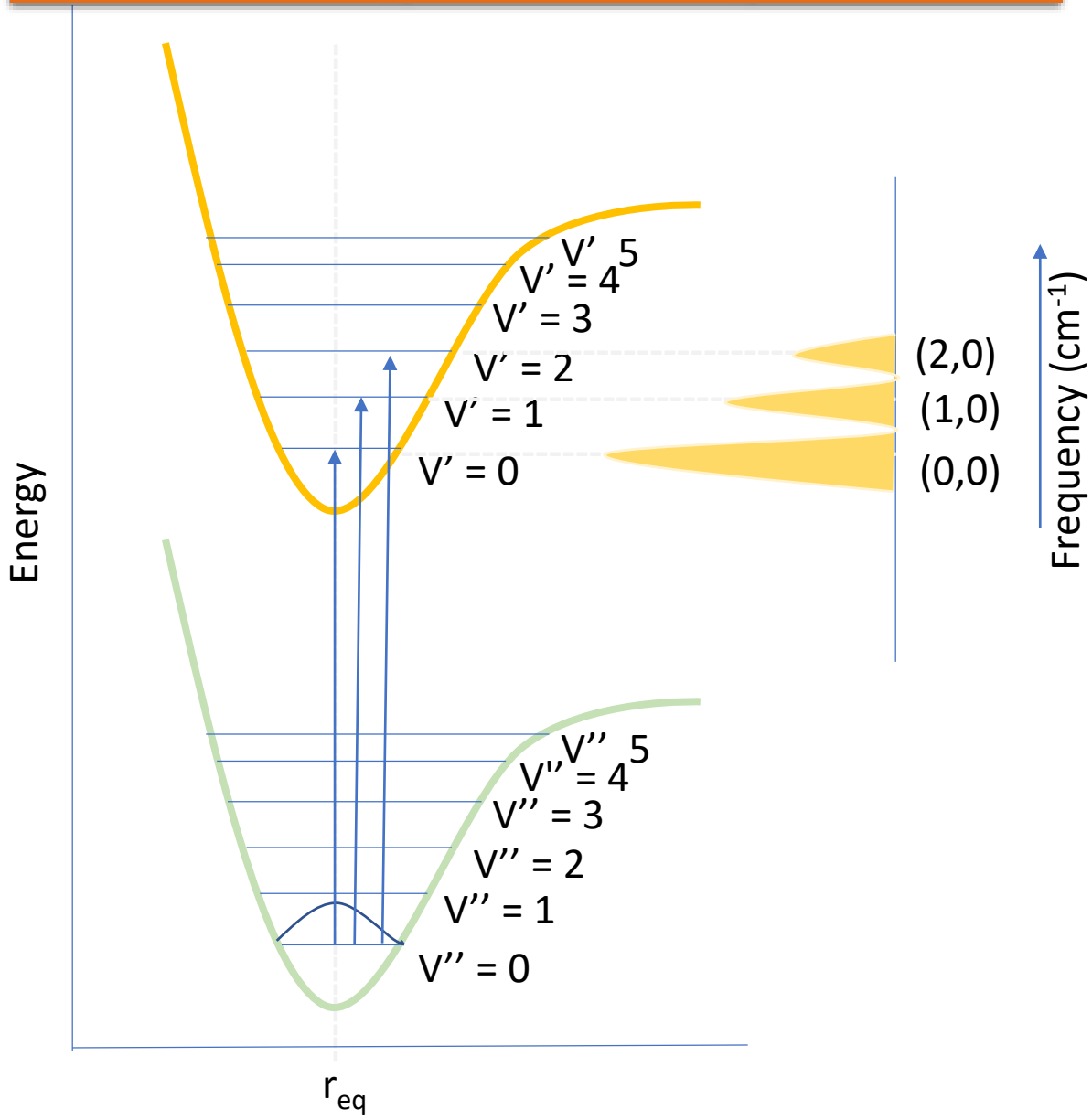
The Franck-Condon Principle

Franck-Condon principle states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

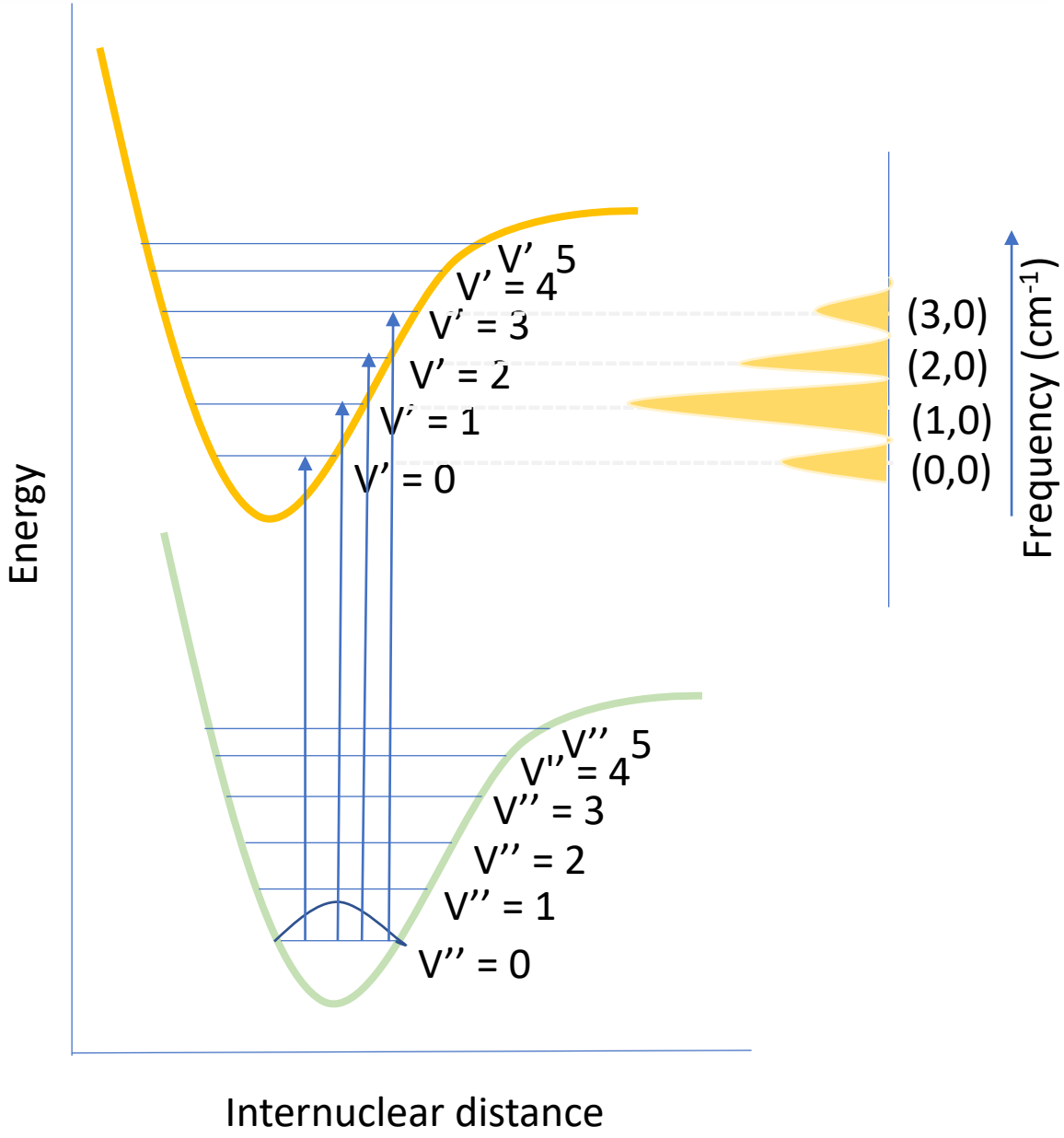
If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground electronic state

We should consider each excited molecule as a new, but rather similar, molecule with a different, but also rather similar, Morse curve because the vibrational frequency, internuclear distance, anharmonicity constants and dissociation energies may differ.

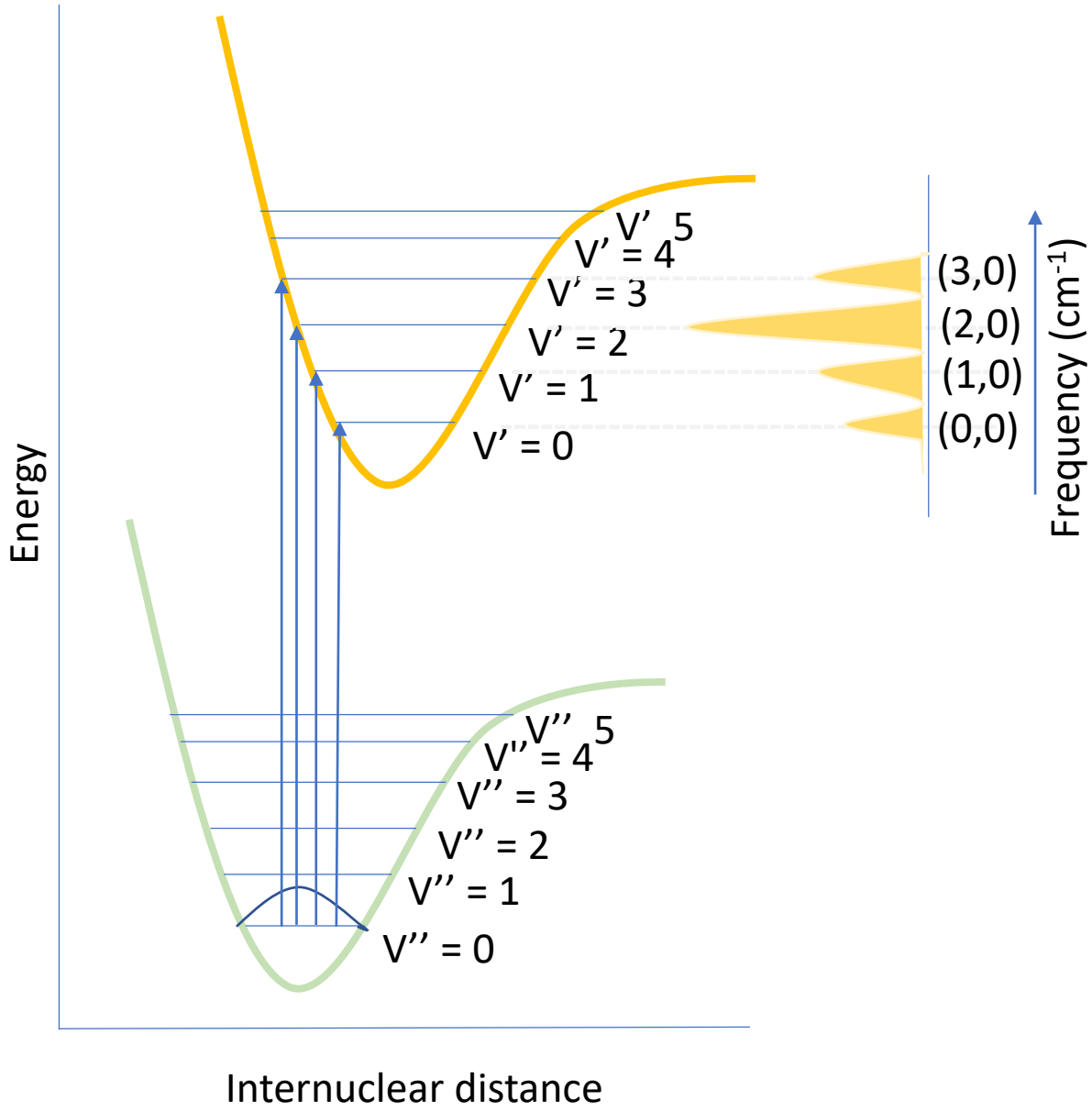
Condition 1: when r_{eq} (ground state) = r_{eq} (excited state)



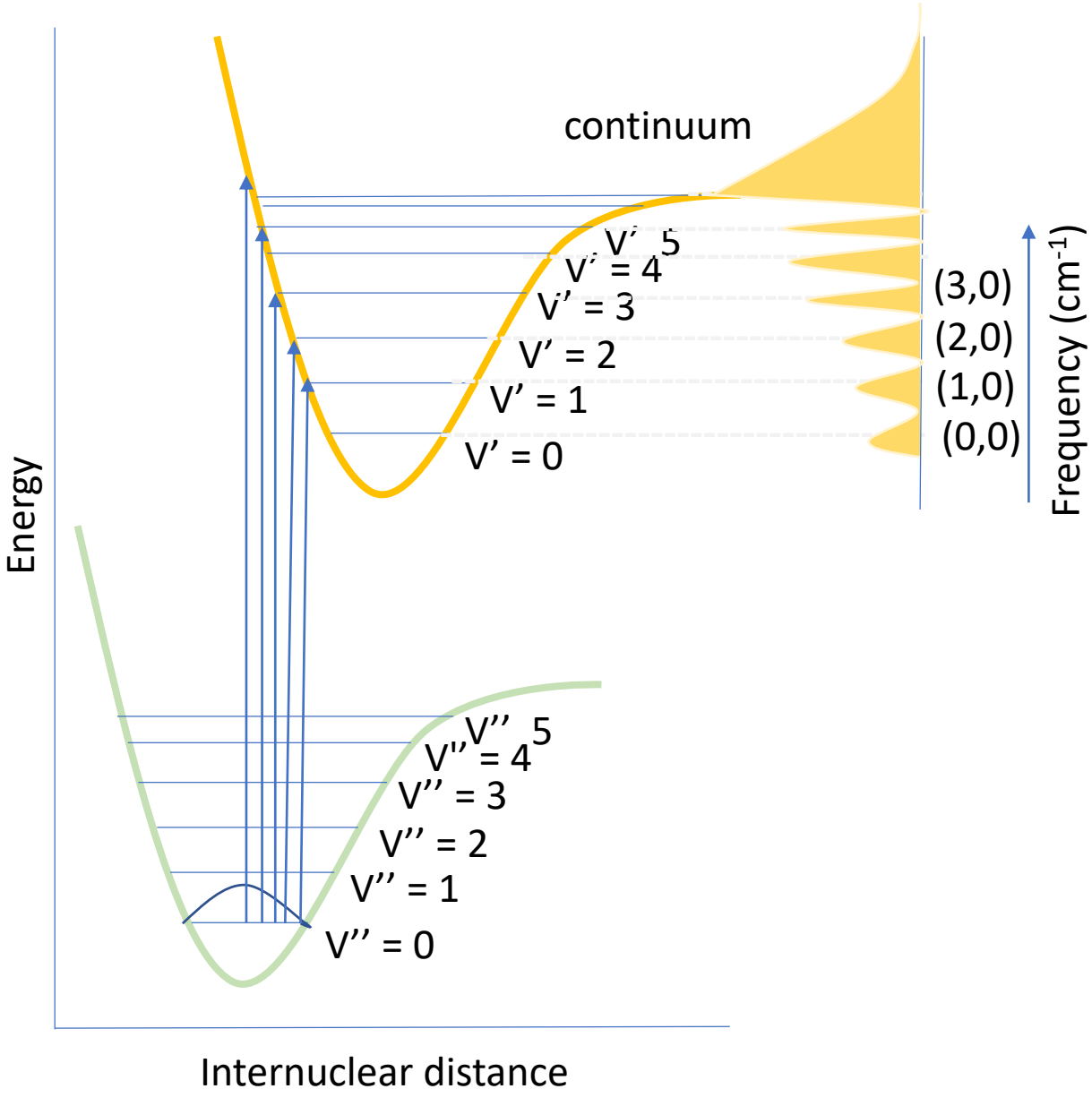
Condition 2: when r_{eq} (ground state) > r_{eq} (excited state)



Condition 3: when r_{eq} (ground state) < r_{eq} (excited state)



Condition 4: when r_{eq} (ground state) << r_{eq} (excited state)



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2. PHYSICAL CHEMISTRY, Thermodynamics, Structure, and Change, 10th Edition By Peter Atkins and Julio de Paula, W. H. Freeman and Company New York.
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Thank You