ChemE 2200 – Applied Quantum Chemistry Lecture 7

Today:

The Interaction of Electromagnetic Radiation with Matter

Electronic Transitions

Defining Question:

What is a vertical transition?

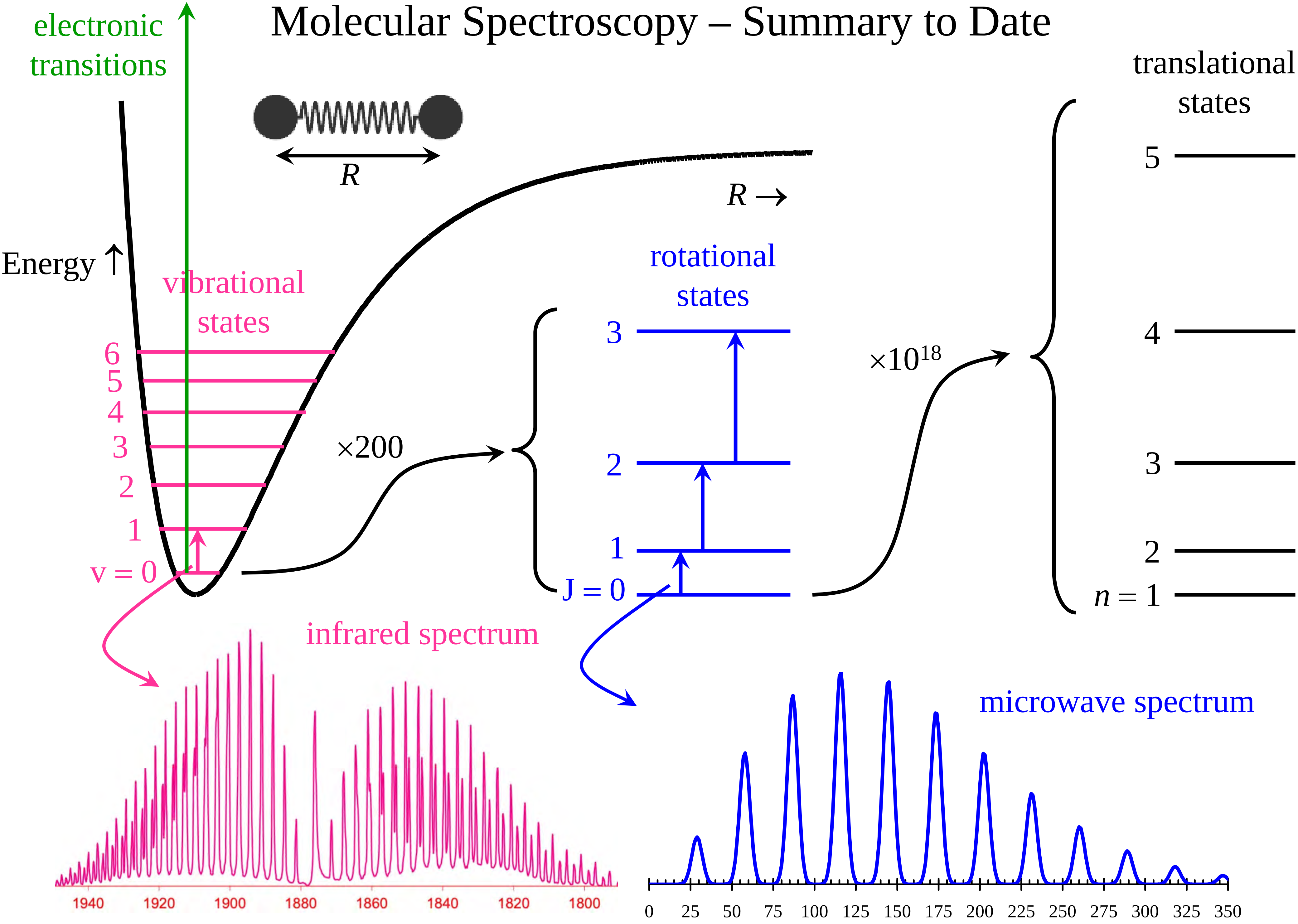
Reading for Today's Lecture:

McQuarrie & Simon, 13.3, 13.13.

Reading for Quantum Lecture 8:

McQuarrie & Simon, 15.1 – 15.2.

Molecular Spectroscopy – Summary to Date



electronic transitions

vibrational states

rotational states

translational states

infrared spectrum

microwave spectrum

Recap: Electronic Transitions: 1. Determine Wavefunctions

Molecular Orbitals (MOs)
from Linear Combinations
of Atomic Orbitals (LCAOs)

Example: Combine
atomic orbitals of
C and O to form CO.

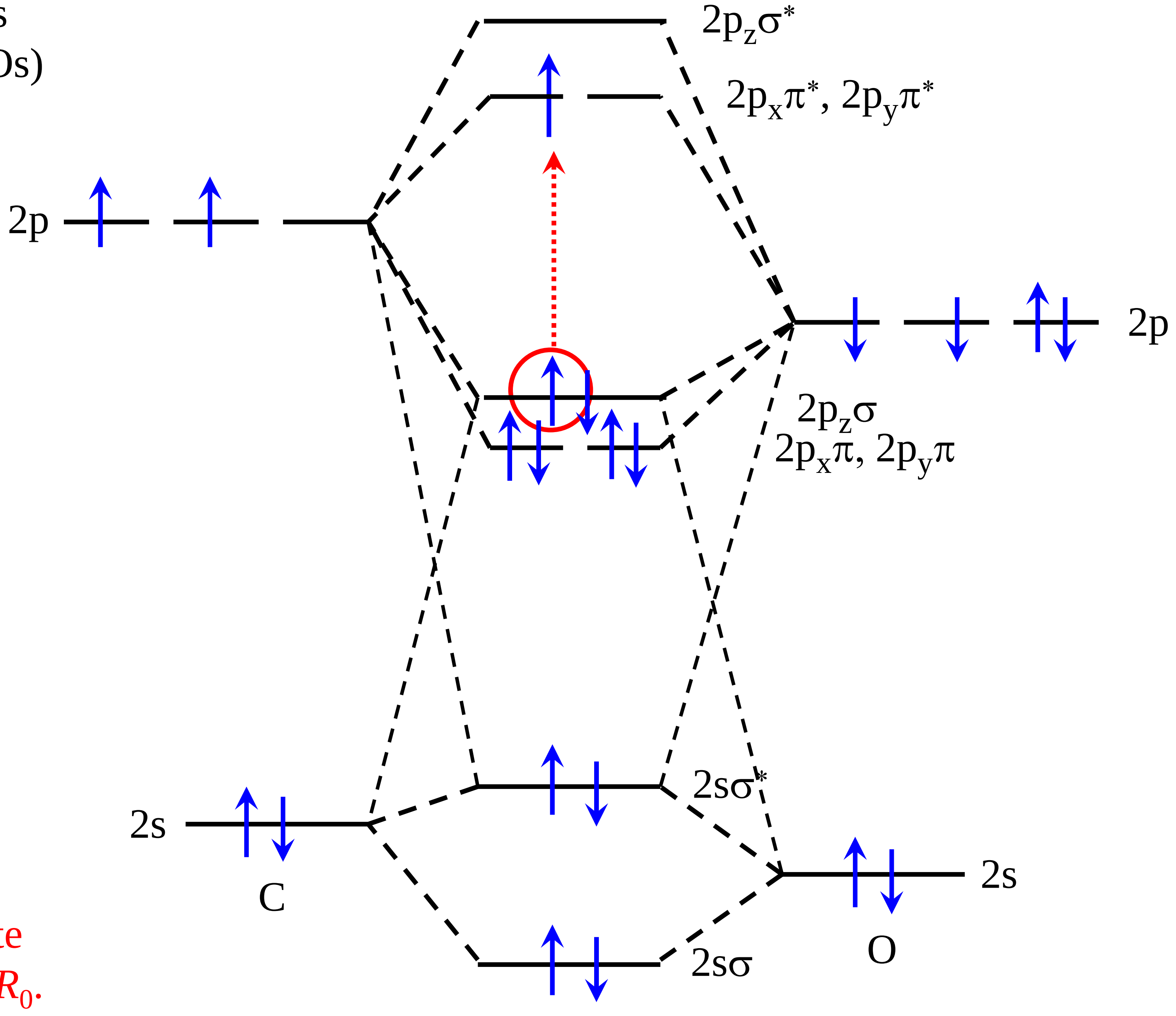
8 electrons in bonding orbitals, 2 electrons in anti-bonding orbitals.

$$\text{bond order} = \frac{8-2}{2} = 3$$

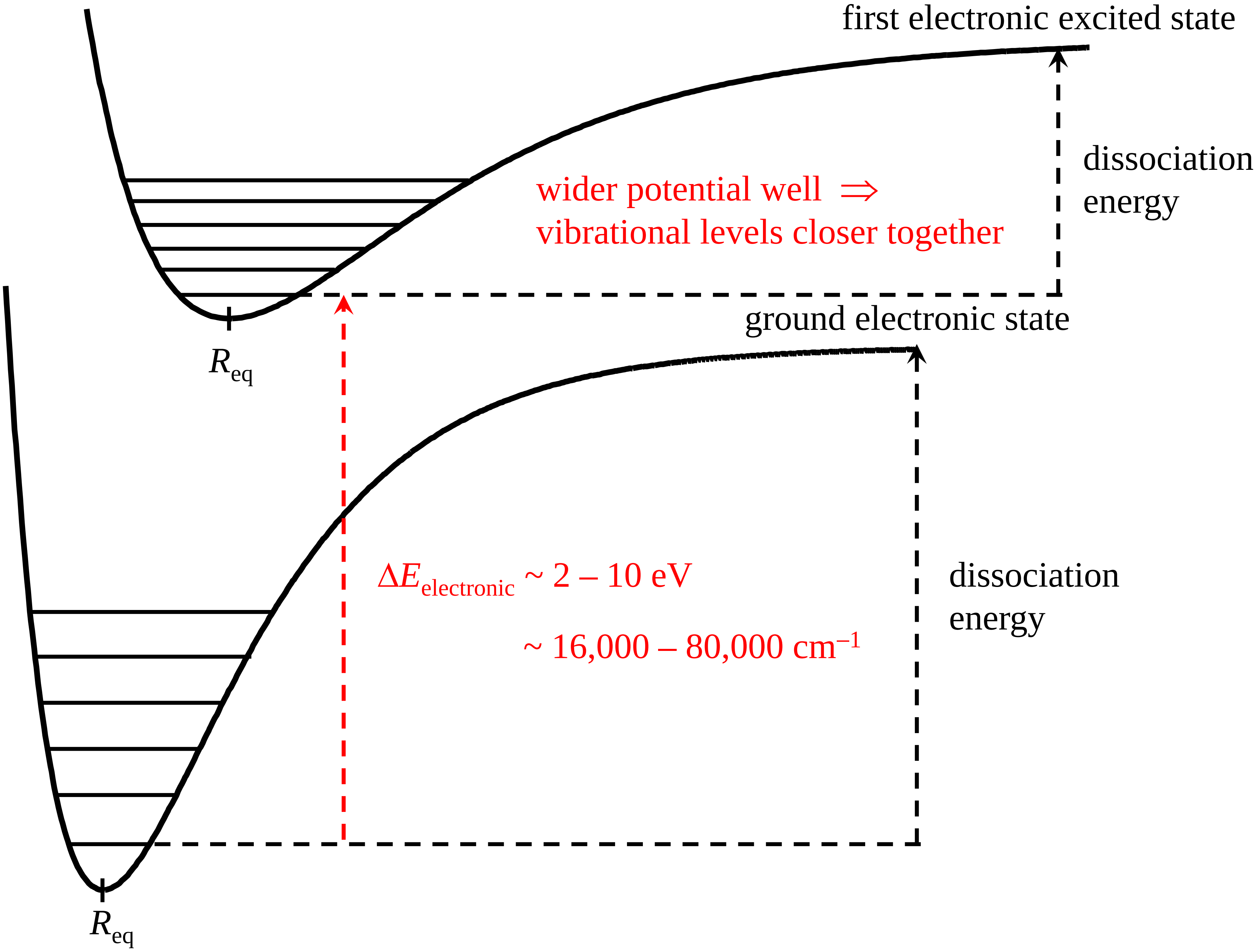
first electronic excited state: $2p_z\sigma \rightarrow 2p_x\pi^*$

$$\text{bond order} = \frac{7-3}{2} = 2$$

Potential energy curve of first electronic excited state is less deep with a longer R_0.



Recap: Electronic Ground State and First Excited State



first electronic excited state

dissociation energy

wider potential well $\Rightarrow$
vibrational levels closer together

R_{eq}

ground electronic state

$\Delta E_{\text{electronic}} \sim 2 - 10$ eV

$\sim 16{,}000 - 80{,}000$ cm^{-1}

dissociation energy

R_{eq}

Electronic Transitions

1. Describe the molecule with quantum mechanics. ✓

Molecular Orbitals (MOs) from Linear Combinations of Atomic Orbitals (LCAOs).

2. Calculate the molecular energy levels E_1, E_2, … ✓

Molecular-Orbital Energy-Level Diagrams

3. Determine the selection rules for photon-induced transitions.

peak intensity $\propto \int \psi^*_{\text{final}} \hat{T} \psi_{\text{initial}} \, d\tau$ $\quad \hat{T} \equiv$ transition operator $\quad$ see McQ & S 13.11

$\psi_{\text{molecule}} = \psi_{\text{rotational}}(R)\psi_{\text{vibrational}}(R)\psi_{\text{electronic}}(r_1, r_2, r_3, \ldots, r_n)$ $\quad$ for n electrons.

A photon with $v = 10^{15}$/sec interacts only with the electronic portion of ψ_{molecule}.

The integral thus separates into two terms:

$$\text{peak intensity} \propto \underbrace{\left[\int \psi^*_{\text{electr,final}} \hat{T} \psi_{\text{electr,initial}} \, d\tau\right]}_{\substack{\text{A constant for a particular} \\ \text{electronic transition,} \\ \text{such as } 2p_z\sigma \rightarrow 2p_x\pi^*}} \times \underbrace{\left[\int \psi^*_{\text{J'}}(R')\psi^*_{\text{v'}}(R')\psi_{\text{J}}(R)\psi_{\text{v}}(R) \, d\tau\right]}_{\substack{\text{This effectively reduces to} \\ \int \psi^*_{\text{v'}}(R')\psi_{\text{v}}(R) \, d\tau}}$$

Electronic Transitions – Selection Rules

$$\text{peak intensity} \propto \int \psi^{*}_{v'}(R')\psi_{v}(R)d\tau$$

Peak intensity is proportional to the overlap between
the initial vibrational state and the final vibrational state.

To evaluate this overlap integral, we make a key assumption:

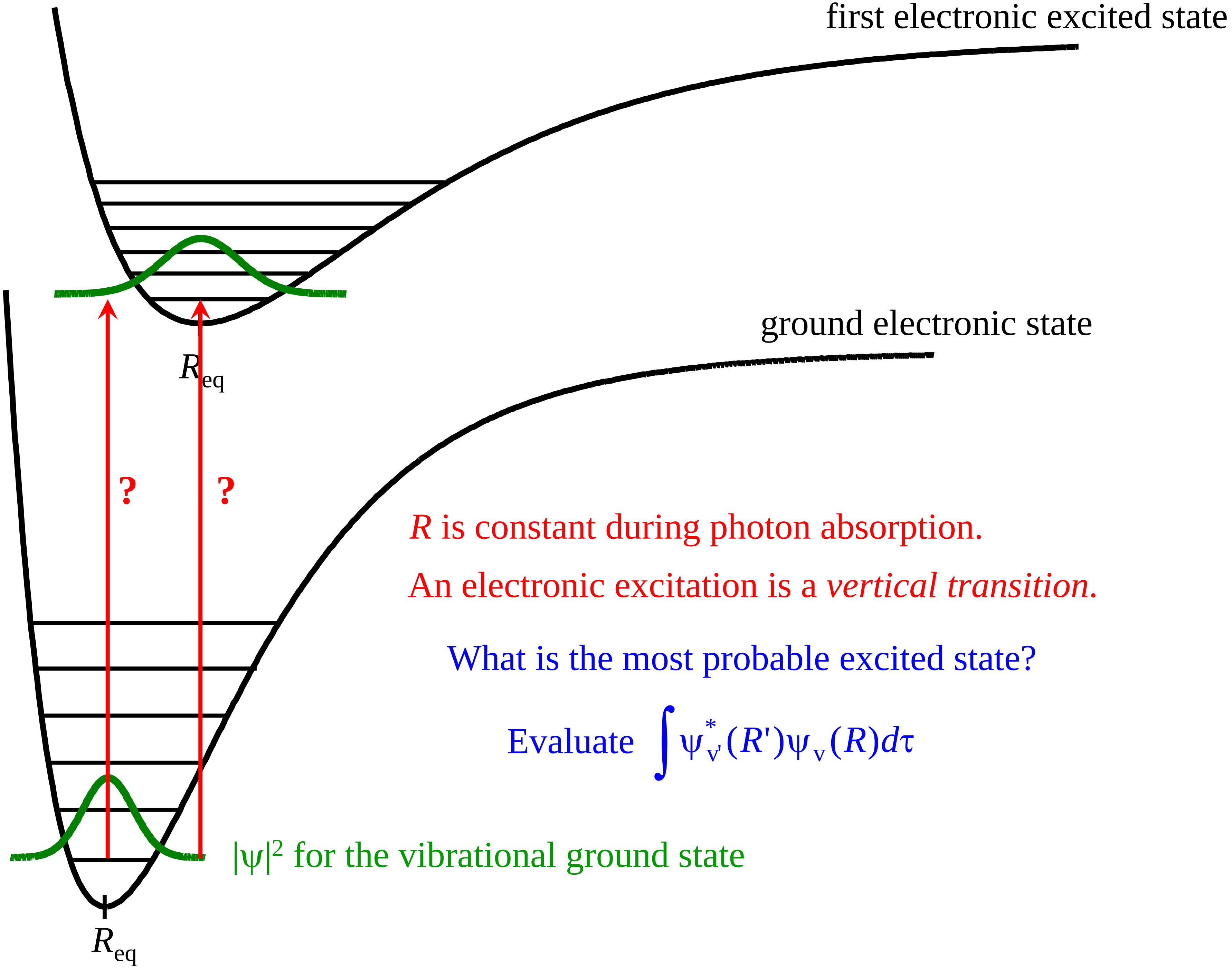
The nuclei are stationary during an electronic transition.

The Franck-Condon Principle (1926).

Analogous to the Born-Oppenheimer Approximation (1927).

Electrons in molecular orbitals respond instantly to movement of the nuclei.

Electronic Transitions



R is constant during photon absorption.

An electronic excitation is a *vertical transition*.

What is the most probable excited state?

Evaluate $\int \psi^*_{v'}(R')\psi_{v}(R)\,d\tau$

Vertical Transition Probabilities

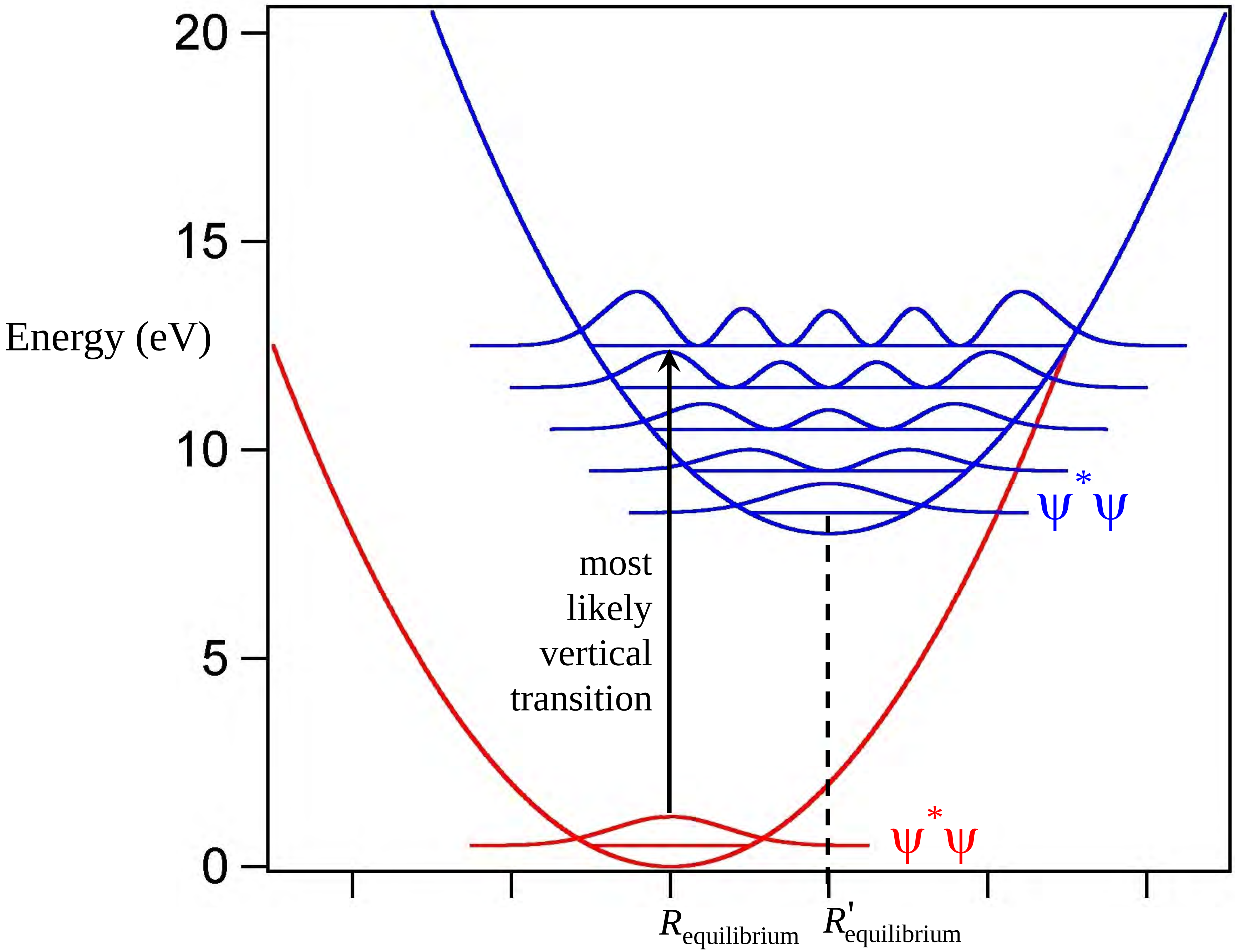
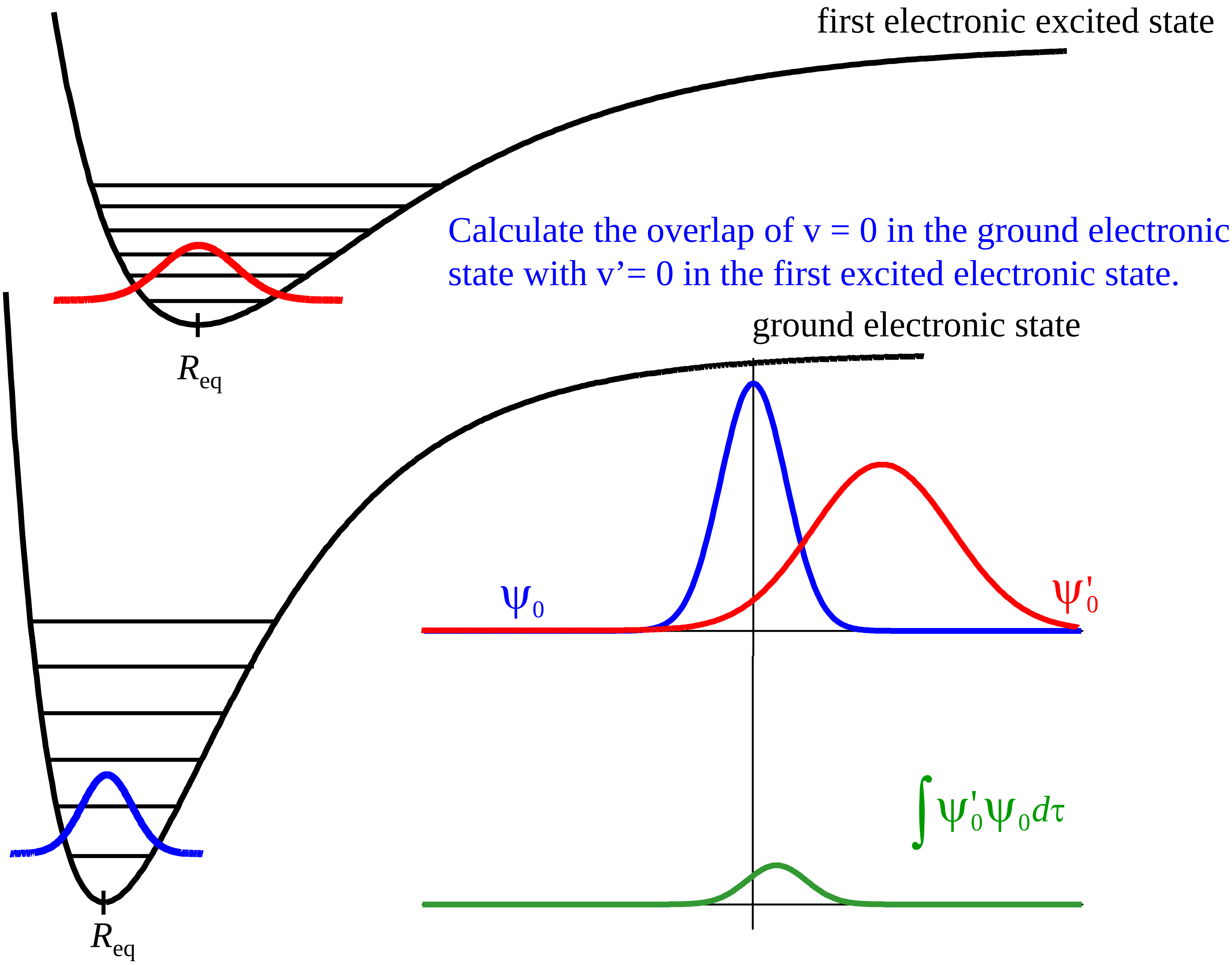


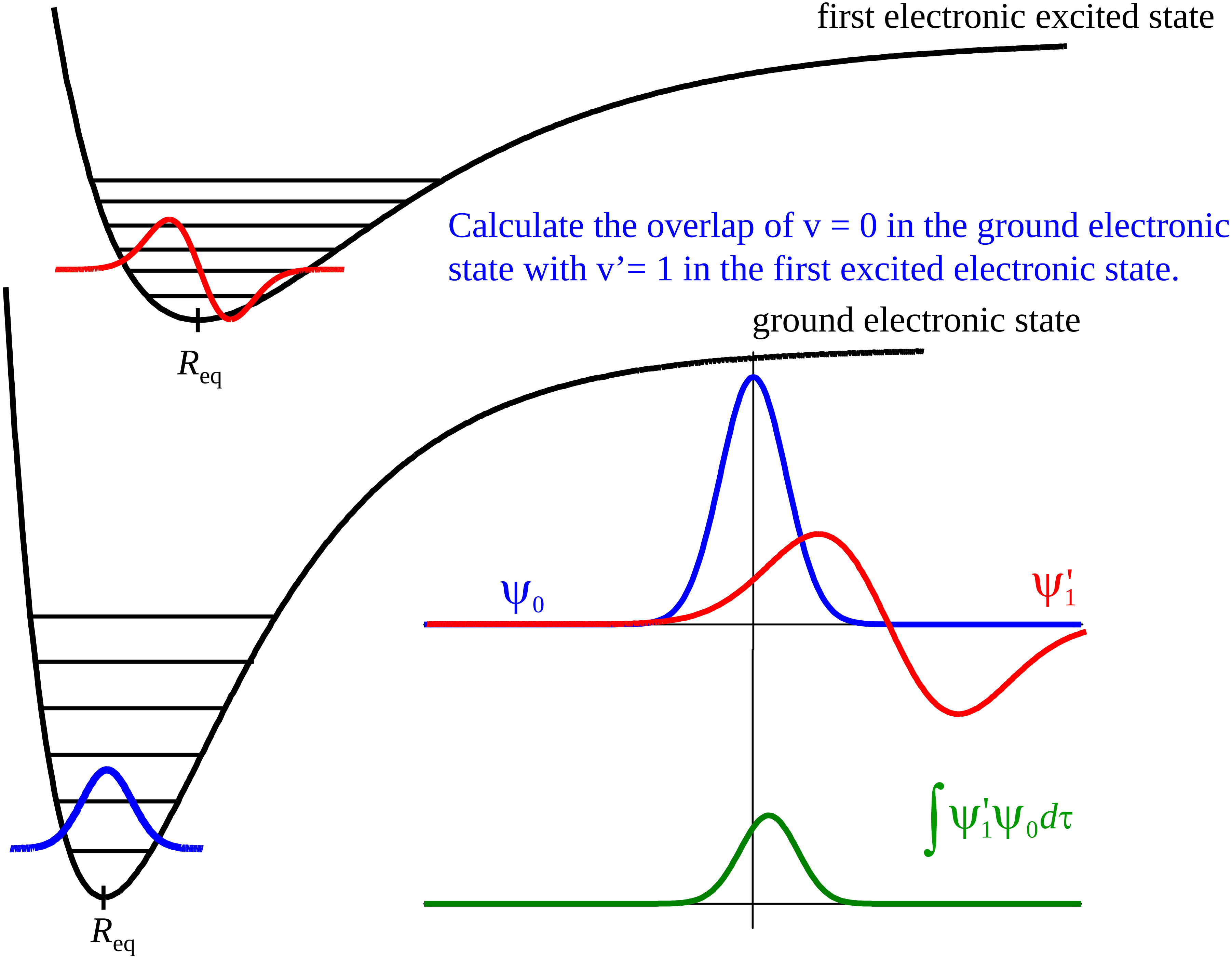
Image from Chem.libretexts.org/Courses/Pacific_Union_College/Quantum_Chemistry/Molecular_spectroscopy/

Calculating the Vibrational Overlap Integral



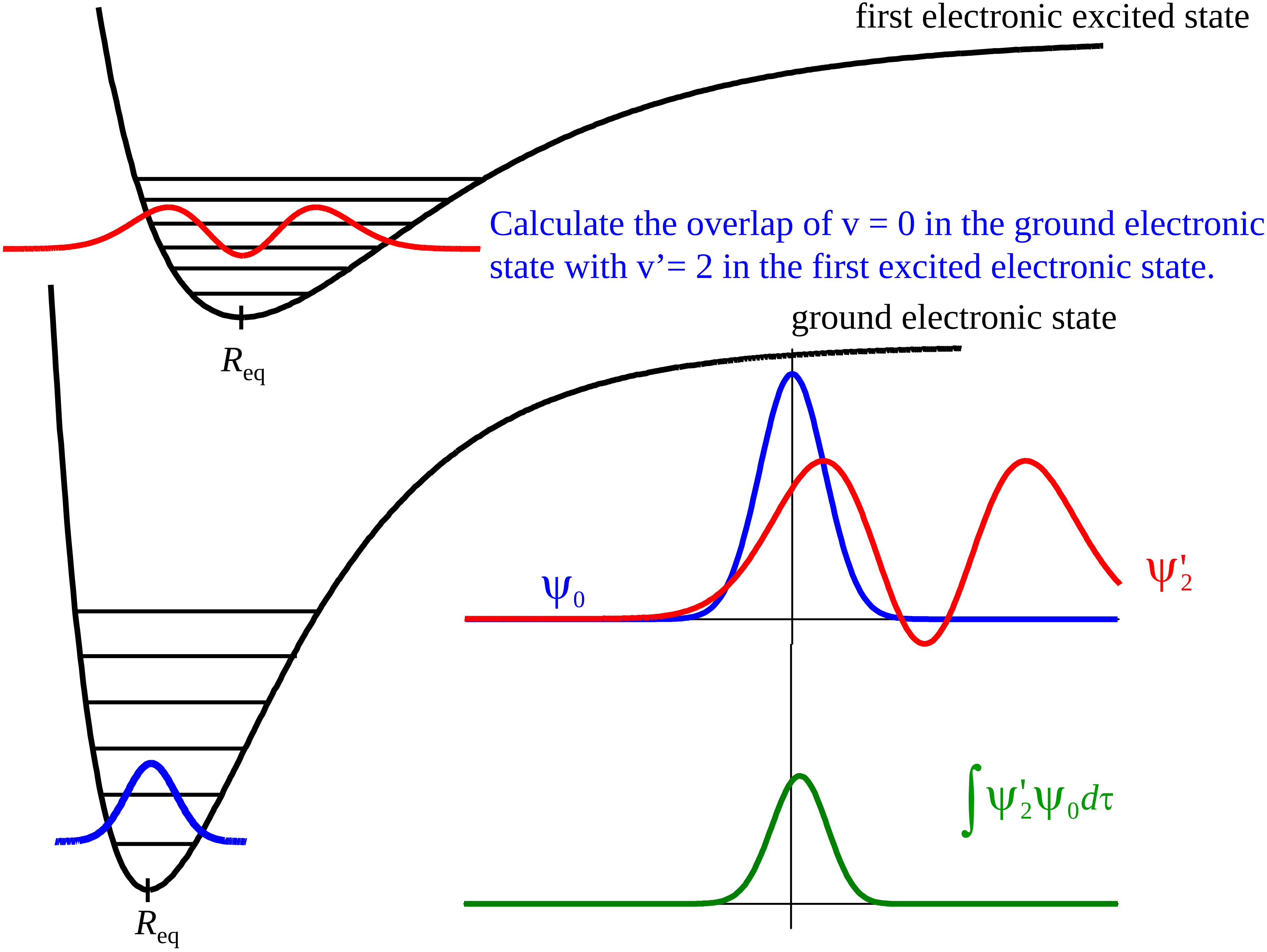
Calculate the overlap of v = 0 in the ground electronic state with v’= 0 in the first excited electronic state.

Calculating the Vibrational Overlap Integral



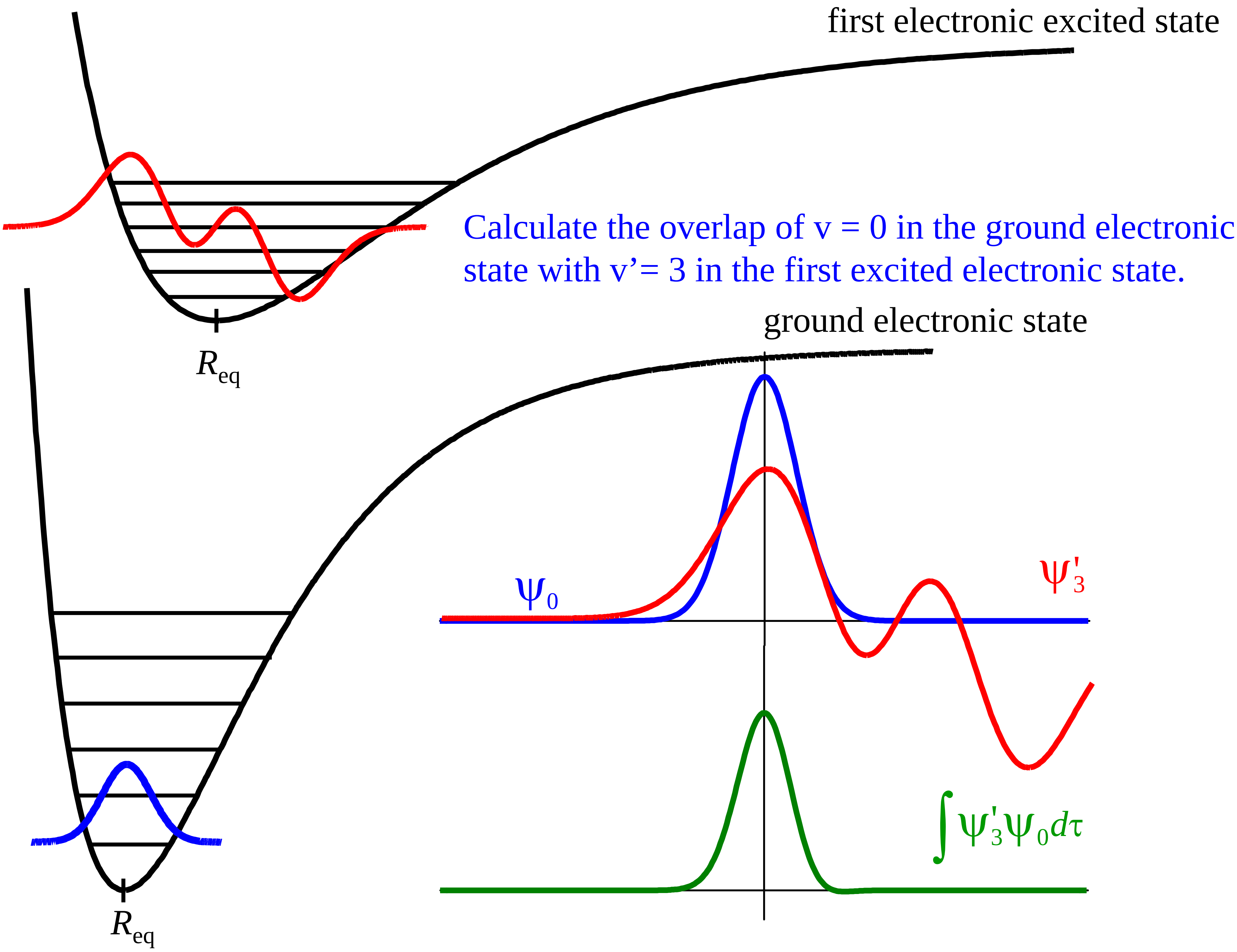
Calculate the overlap of v = 0 in the ground electronic state with v’= 1 in the first excited electronic state.

Calculating the Vibrational Overlap Integral



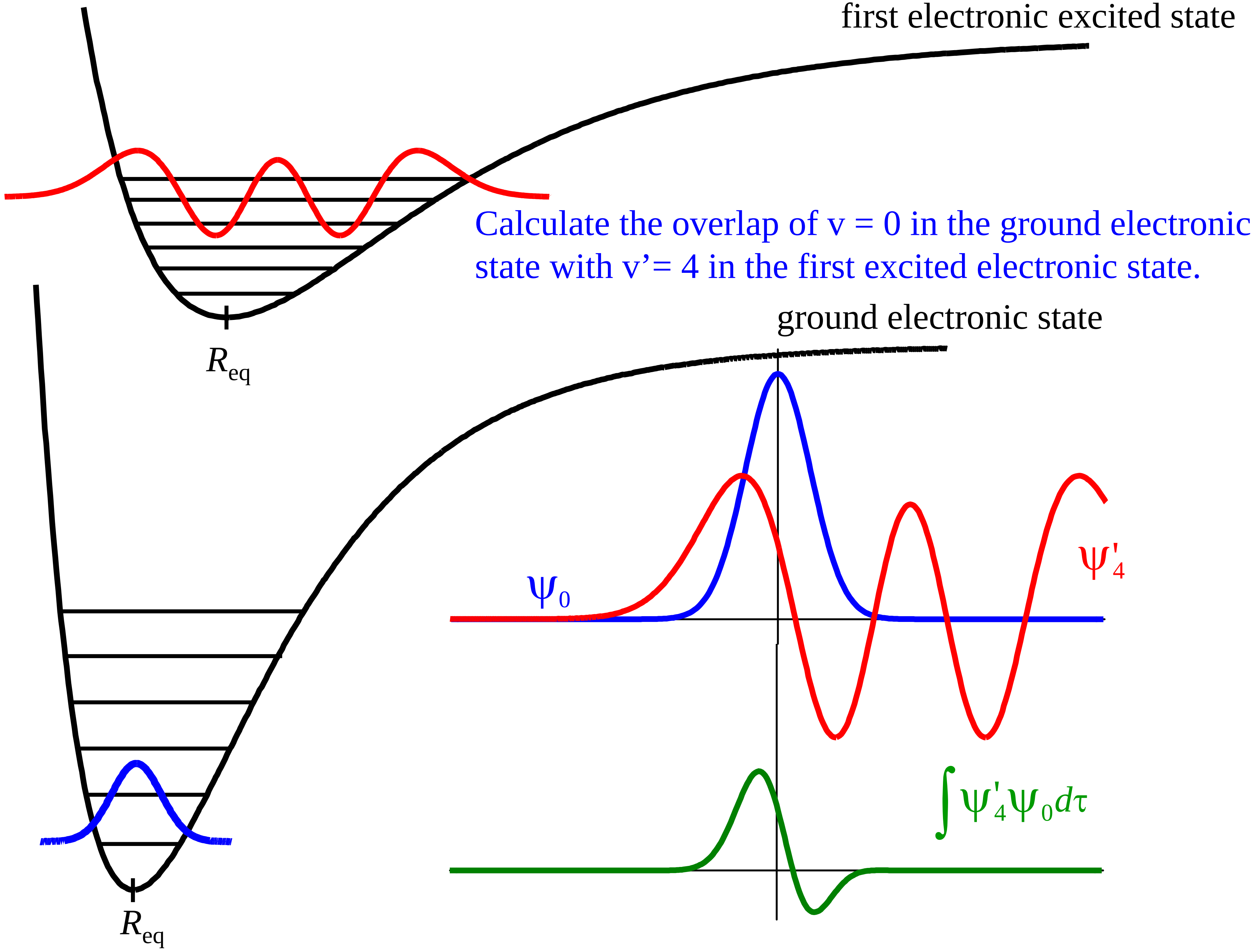
Calculate the overlap of v = 0 in the ground electronic state with v’= 2 in the first excited electronic state.

Calculating the Vibrational Overlap Integral



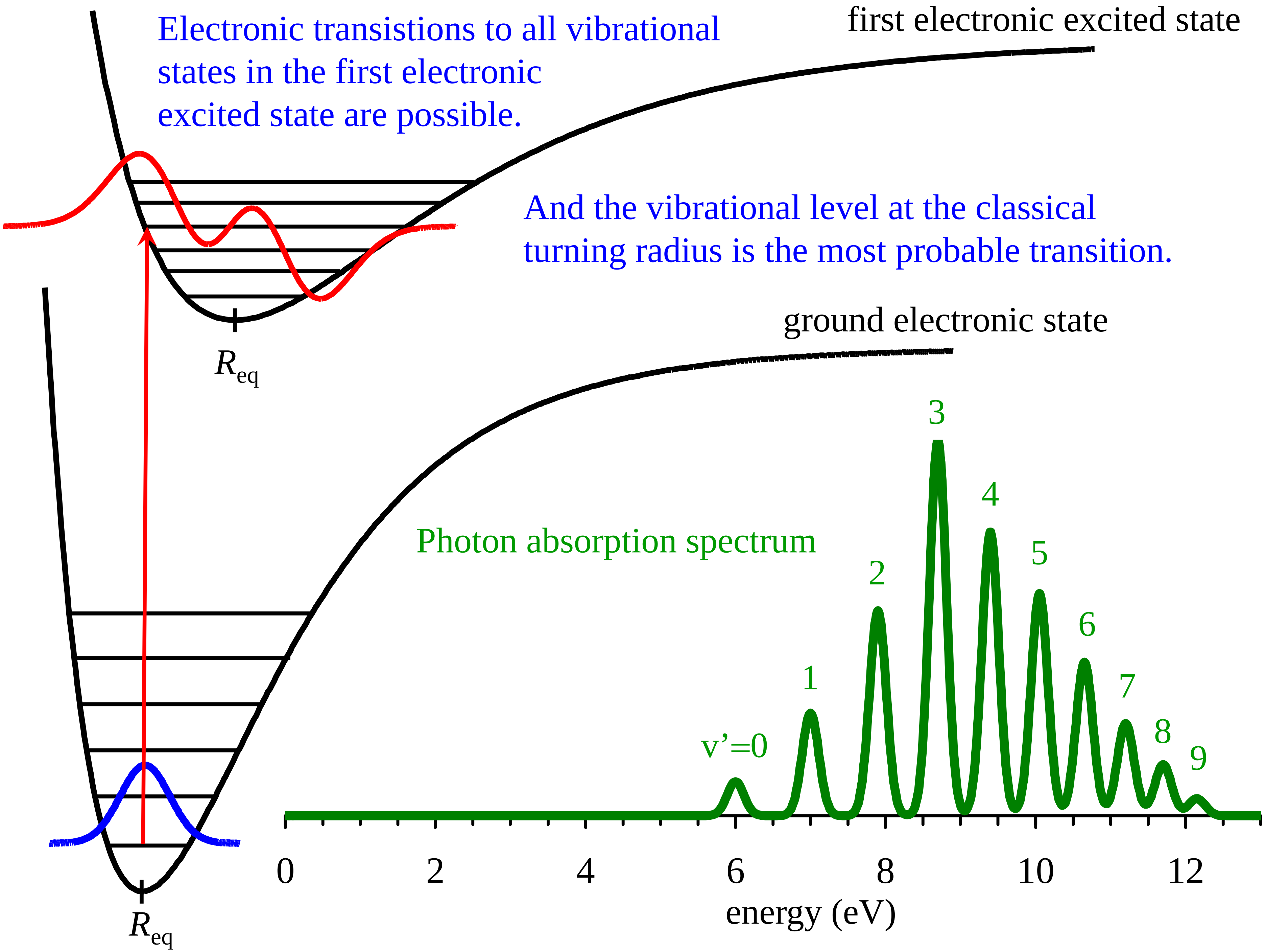
Calculate the overlap of v = 0 in the ground electronic state with v’= 3 in the first excited electronic state.

Calculating the Vibrational Overlap Integral



Calculate the overlap of v = 0 in the ground electronic state with v’= 4 in the first excited electronic state.

Electronic Transitions – Photon Absorption Spectrum



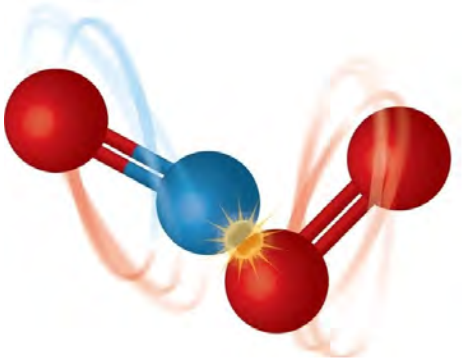
Electronic transistions to all vibrational states in the first electronic excited state are possible.

And the vibrational level at the classical turning radius is the most probable transition.

Photon absorption spectrum

Fates of Electronic-Vibrational Excited States

1. Chemical Reaction – molecule dissociates
2. Radiative Decay – molecule emits a photon
3. Non-Radiative Decay – molecule transfers energy to other gas molecules by collisions



Which fate is more likely?

transition	EM band	ΔE	ν_{photon}	collision rate[*]	spontaneous emission rate[**]
electronic	UV/visible	10-30 eV	$\sim 10^{15}$/sec	$\sim 10^{10}$/sec	$\sim 10^{8}$/sec
vibrational	infrared	~0.3 eV	$\sim 10^{13}$/sec	$\sim 10^{10}$/sec	$\sim 10^{2}$/sec
rotational	microwave	~0.001 eV	$\sim 10^{11}$/sec	$\sim 10^{10}$/sec	$\sim 10^{-4}$/sec

collision rate > spontaneous emission rate

All excited states decay by collisions?

No – collision energy << electronic energy.

Typical K.E. at 300 K = 0.025 eV. $(\langle v \rangle = 475$ m/sec for CO)

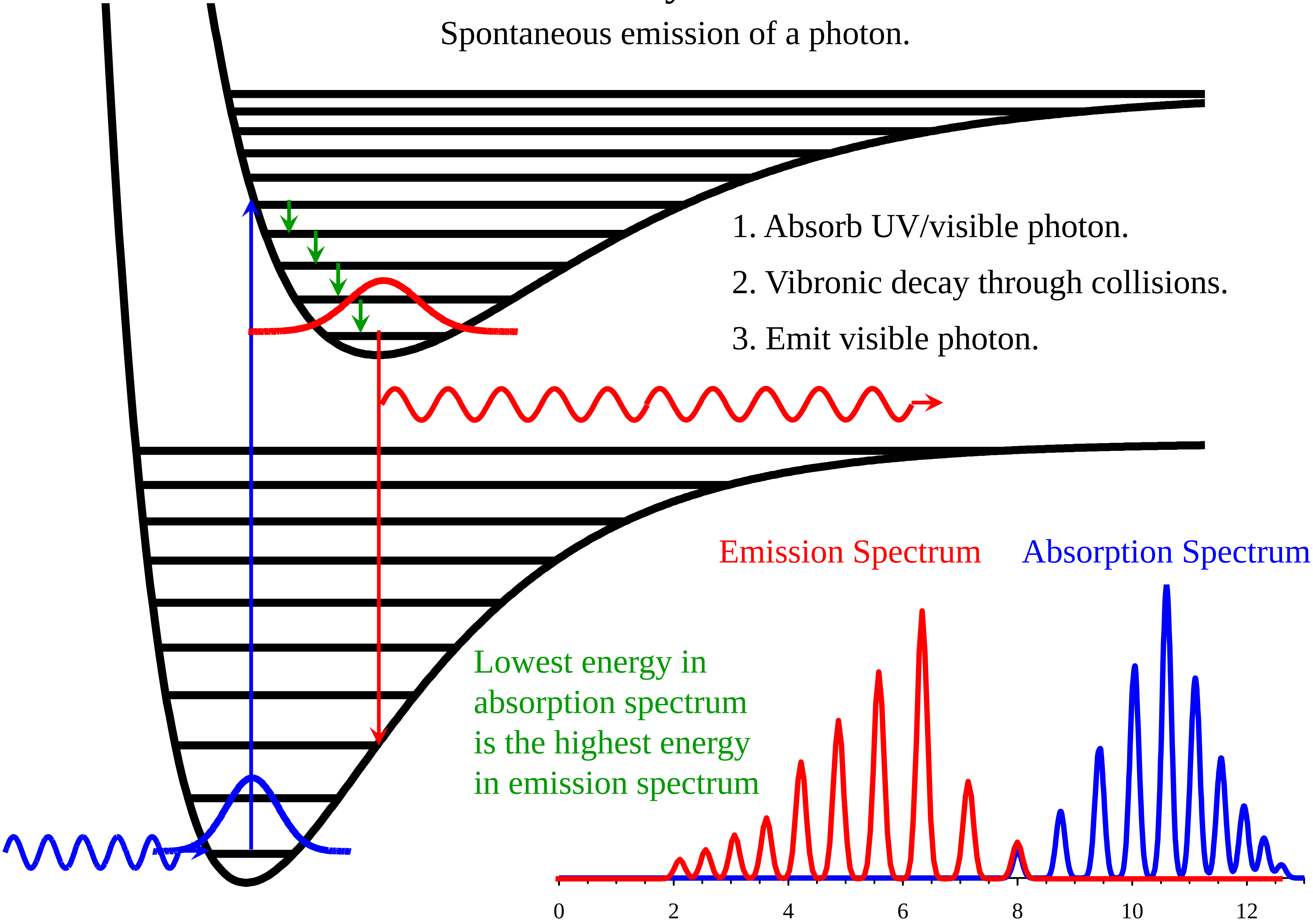
[*] CO at 300K and 1 atm

[**] spontaneous emission rate $\propto \nu^3$

Image from G. Graziano, *Molecular collisions: A crash course in energy transfer*. Nature Review Chemistry 2, 0127 (2018)

Radiative Decay - Fluorescence

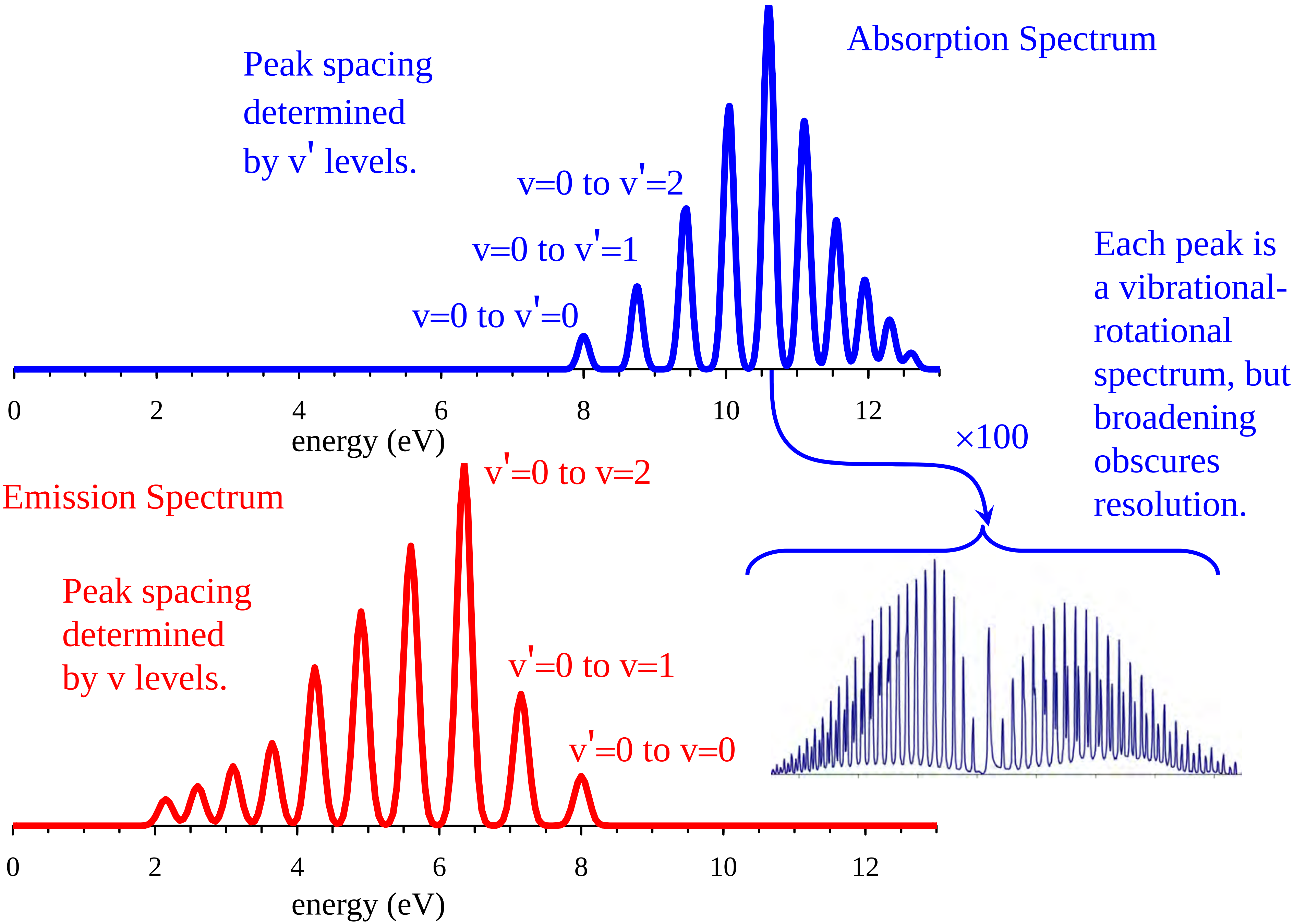
Spontaneous emission of a photon.



1. Absorb UV/visible photon.
2. Vibronic decay through collisions.
3. Emit visible photon.

Lowest energy in absorption spectrum is the highest energy in emission spectrum

Radiative Decay - Fluorescence



Absorption Spectrum

Peak spacing determined by v' levels.

v=0 to v'=2

v=0 to v'=1

v=0 to v'=0

Each peak is a vibrational-rotational spectrum, but broadening obscures resolution.

×100

Emission Spectrum

Peak spacing determined by v levels.

v'=0 to v=2

v'=0 to v=1

v'=0 to v=0

Fluorescence: absorb UV photon, emit visible photon. Fast process: 1 ps to 1 ms.