ChemE 2200 – Applied Quantum Chemistry Lecture 6

Today:

The Interaction of Electromagnetic Radiation with Matter:
Vibrational-Rotational Spectroscopy

Defining Question:

Why does an infrared spectrum of a diatomic molecule have *zero* intensity at $\tilde{\nu}$, the vibrational constant?

Reading for Today's Lecture:

McQuarrie & Simon, 13.3, 13.13.

Reading for Quantum Lecture 7:

McQuarrie & Simon, 13.6-13.7.

Recap: Vibrational Transitions and Infrared Spectroscopy

1. Describe the molecule with quantum mechanics.

$$\psi_\mathrm{v} = N_\mathrm{v} H_\mathrm{v}(y) e^{-y^2/2} \quad \mathrm{v} = 0, 1, 2, \ldots \quad H_\mathrm{v}(y) \text{ are the Hermite polynomials.}$$

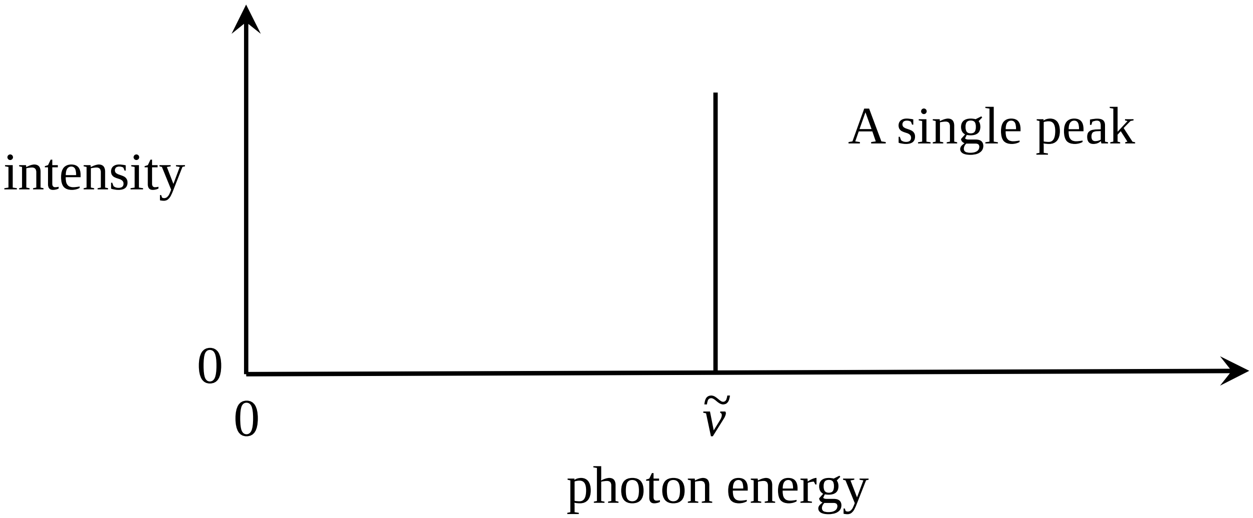
2. Calculate the molecular energy levels E_1, E_2, …

$$\tilde{\nu}_\mathrm{v} = (\mathrm{v} + \tfrac{1}{2})\tilde{\nu} \qquad \tilde{\nu} \equiv \text{vibrational constant} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

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

$$\Delta\mathrm{v} = \pm 1 \qquad \tilde{\nu}_\text{photon} = \tilde{\nu}_{\mathrm{v}+1} - \tilde{\nu}_\mathrm{v} = \tilde{\nu} \quad \text{for } \textbf{\textit{all}} \text{ v}$$

Photon spectrum of a harmonic oscillator:



Vibrational transitions are in the infrared portion of the electromagnetic spectrum.

Actual Rotational Transitions

We assumed constant interatomic separation *R* to obtain the rotational states.

Valid assumption?

Rotation: classical mechanics period of rotation $= \dfrac{1}{\nu_{\text{rotation}}} = 10^{-11}$ sec

Vibration: classical mechanics period of vibration $= \dfrac{1}{\nu_{\text{vibration}}} = 3\times10^{-14}$ sec

$$\frac{\text{rotation period}}{\text{vibration period}} \approx \frac{10^{-11}\ \text{sec}}{3\times10^{-14}\ \text{sec}} \approx 300$$

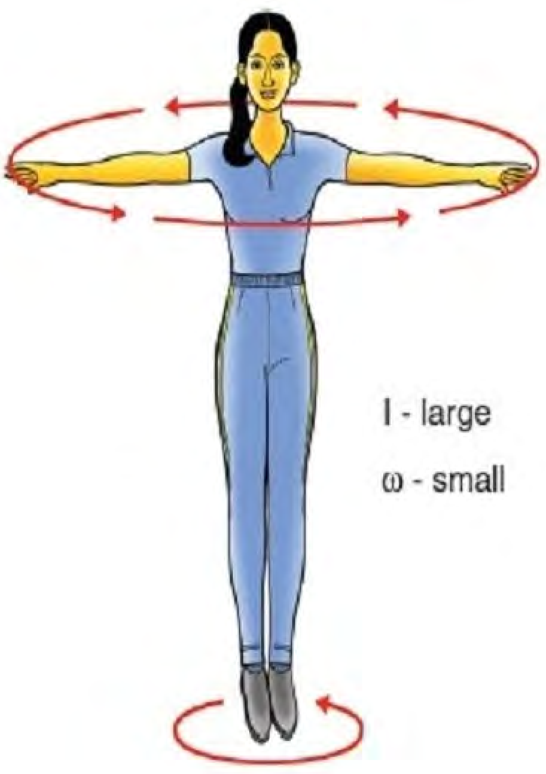
Molecule vibrates ~once for every degree of rotation.

Interatomic separation is essentially constant for a rotation.

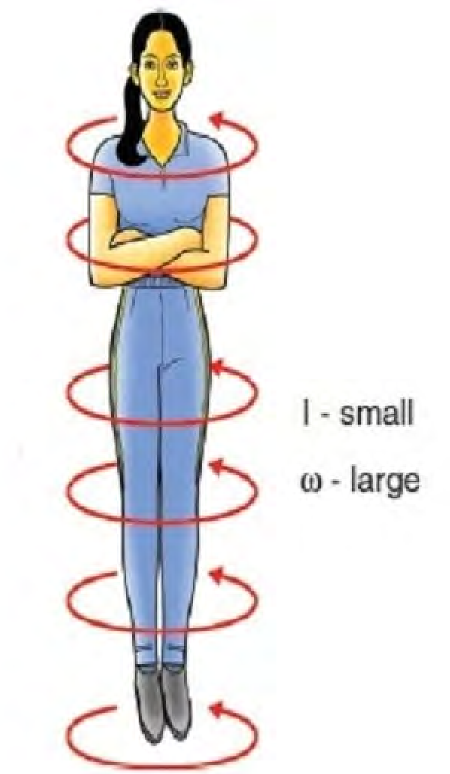
Molecular vibrations do not affect the rotational states.

Rotational-Vibrational Coupling

Classical mechanics analogy – a spinning ice skater



arms extended –
skater spins slowly



arms in –
skater spins rapidly

Imagine the skater’s arms move up and down 300 times for each rotation.

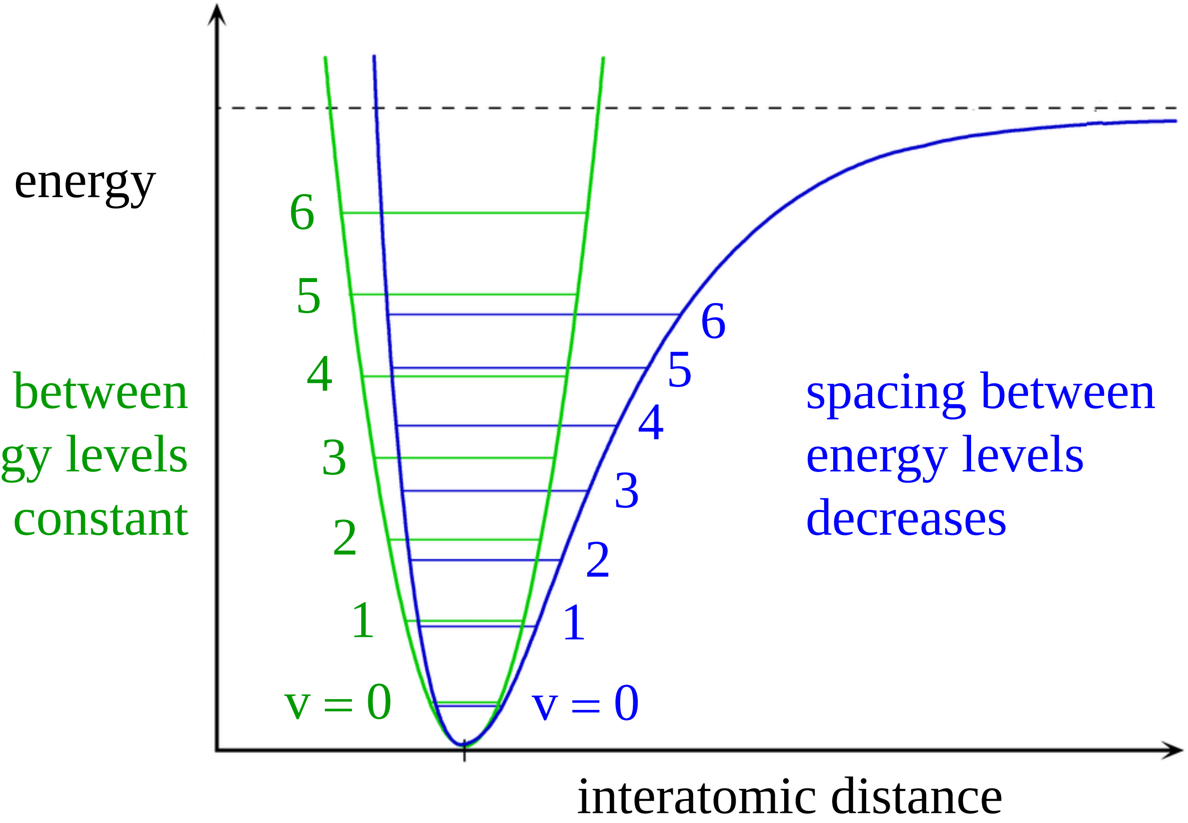
The rotation speed will be approximately constant.

Albiet, it may appear goofy.

Skater images: www.brainkart.com/article/Conservation-of-Angular-Momentum_34618/

Actual Vibrational Transitions

The harmonic potential is an approximation to the actual potential energy curve.



spacing between energy levels is constant

spacing between energy levels decreases

ΔE_{v} is not constant. $\Rightarrow$ multiple peaks in the vibrational photon spectrum.

But excited vibrational energy levels are sparsely populated.

$$\frac{\text{v} = 1 \;\text{ population}}{\text{v} = 0 \;\text{ population}} = e^{-\Delta E / kT} = 3 \times 10^{-5} \text{ for CO at 300K}$$

$\Rightarrow$ Only the peak for v = 0 → 1 is detectable.

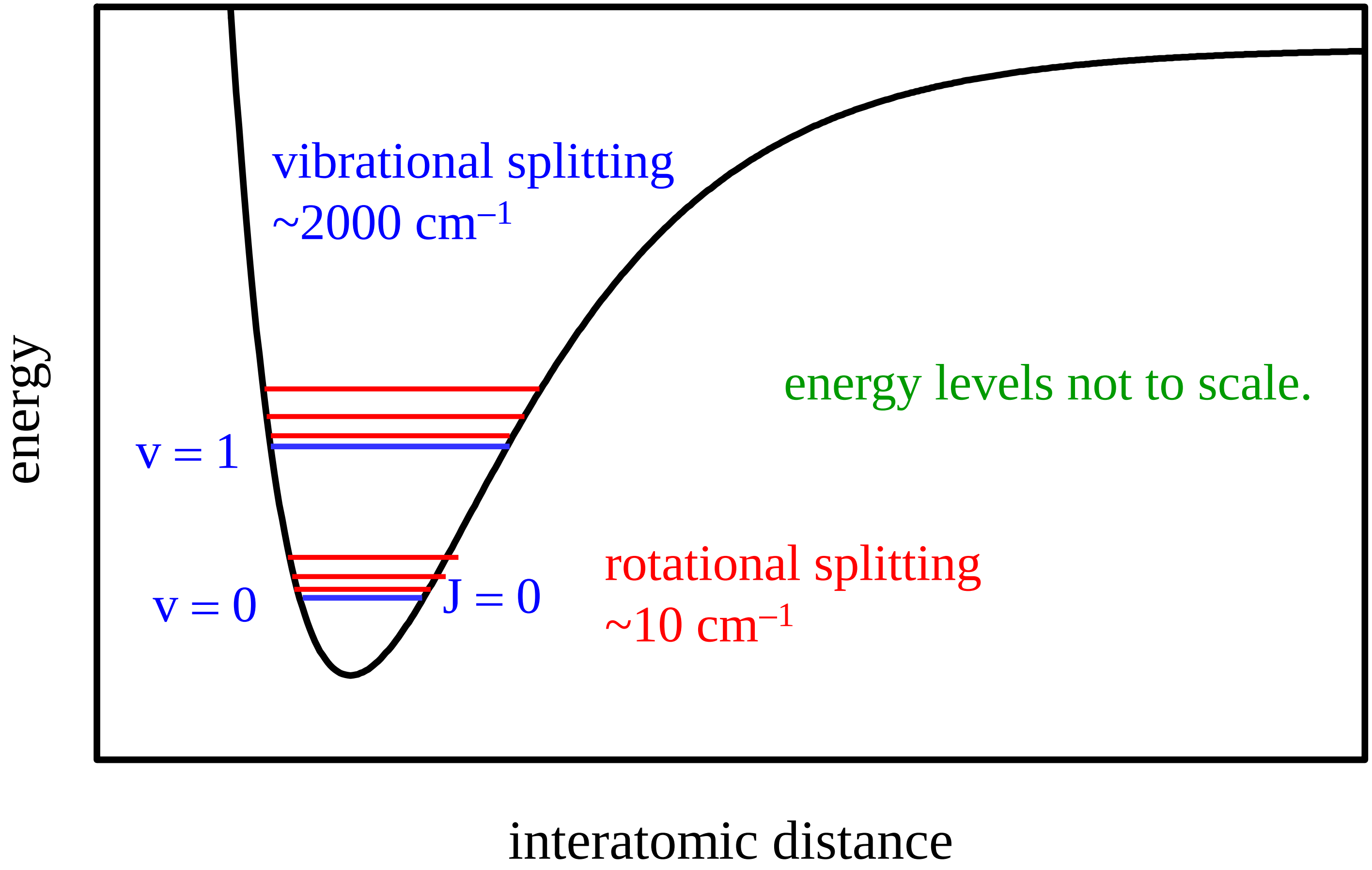
Actual Vibrational Transitions

A vibrational transistion is accompanied by a rotational transition.

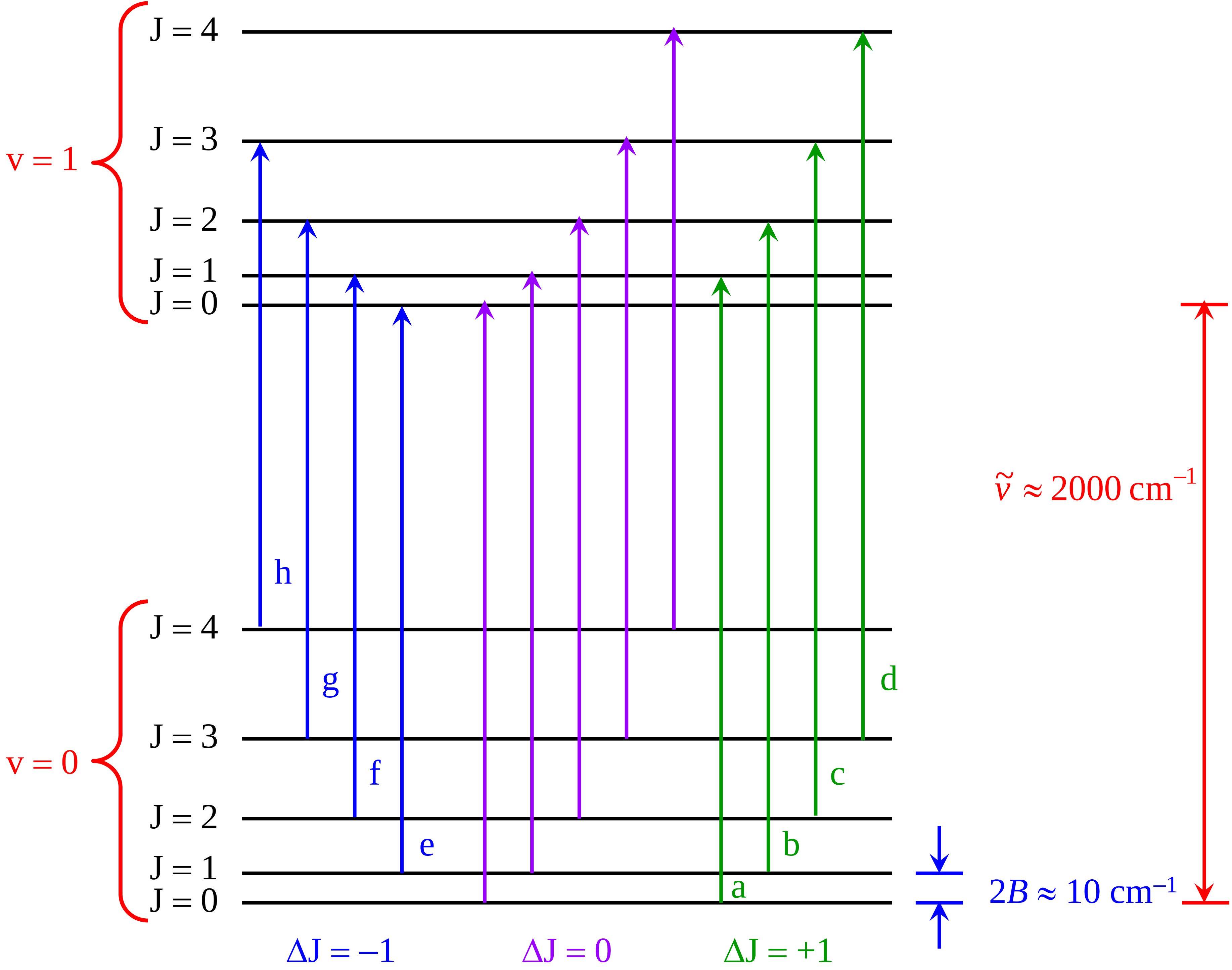
Vibrational selection rules: $\Delta v = \pm 1$ ***and*** $\Delta J = \pm 1$.

In special cases, $\Delta J = 0$ (no rotational transition) is also allowed for diatomic molecules with electronic orbital angular momentum about the bond axis, such as NO.

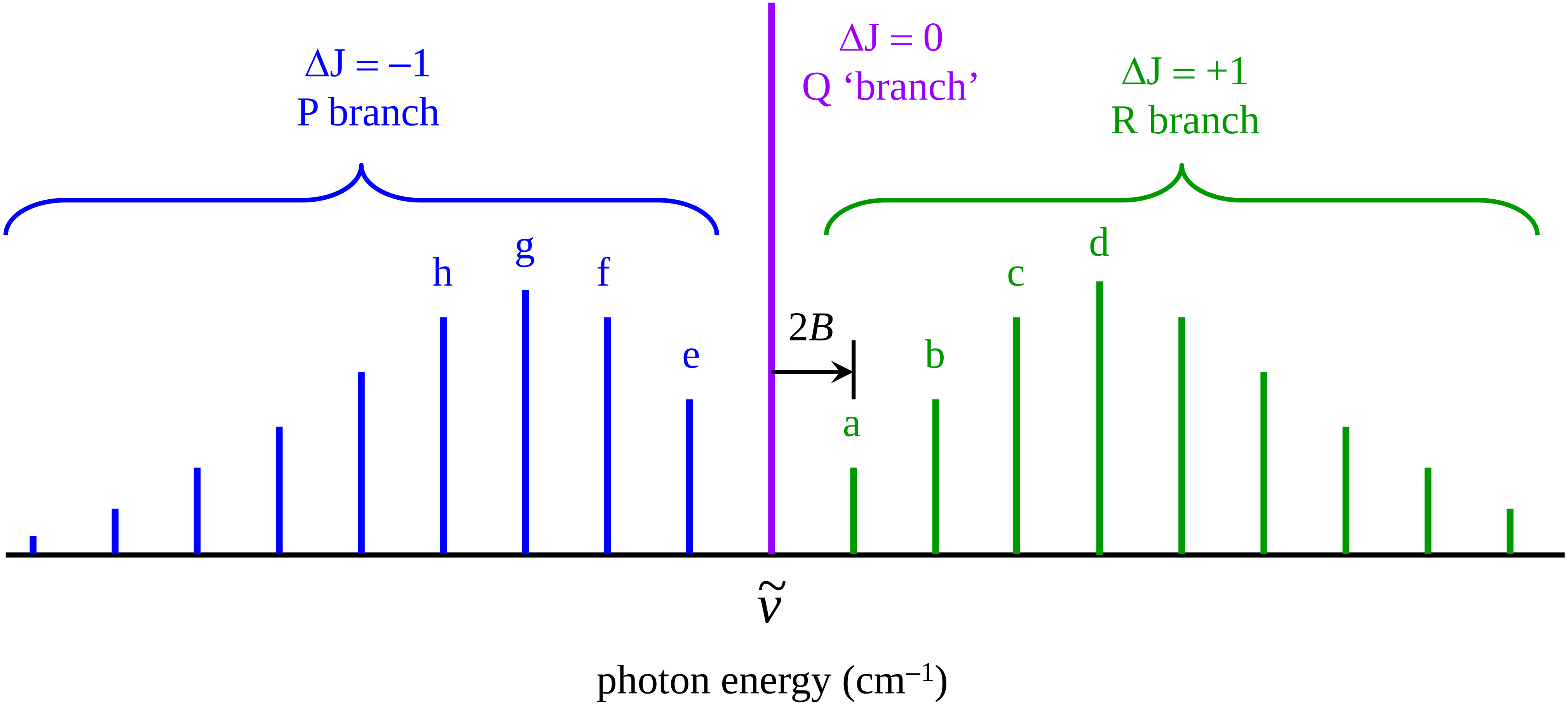
(Draw the molecular orbitals for NO to see this.)



Vibrational-Rotational Transitions



Vibrational-Rotational Photon Absorption Spectrum



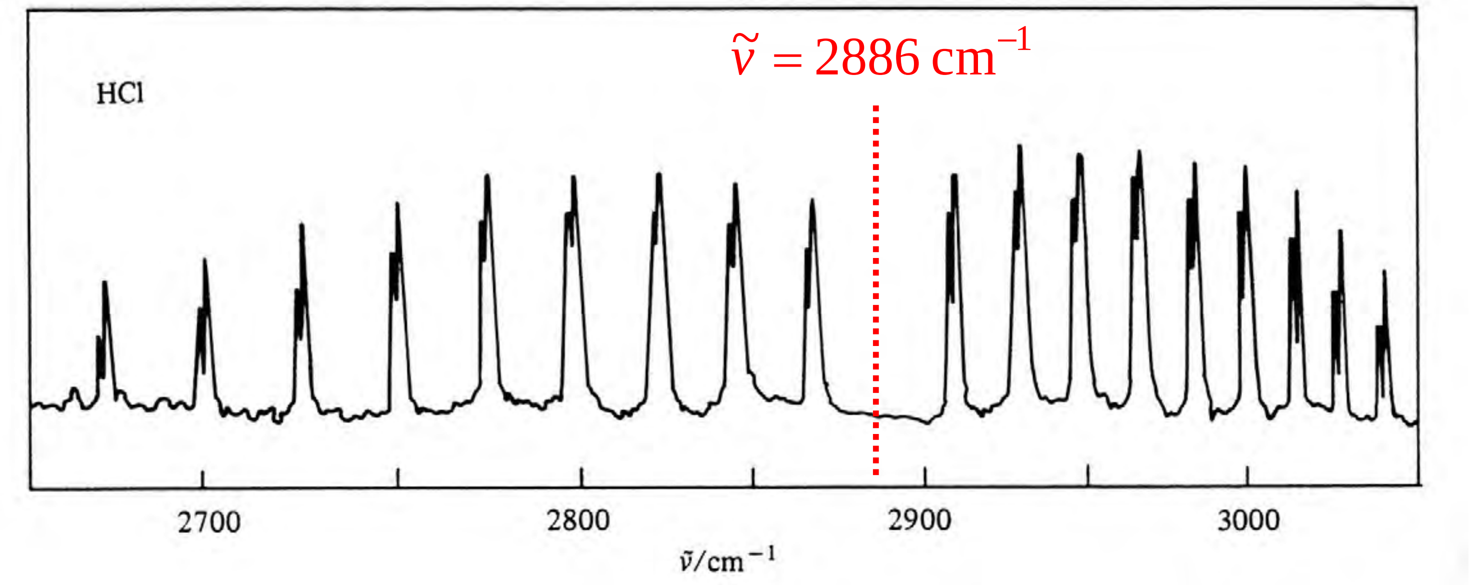
intensity of peak b = intensity of peak e because same initial state

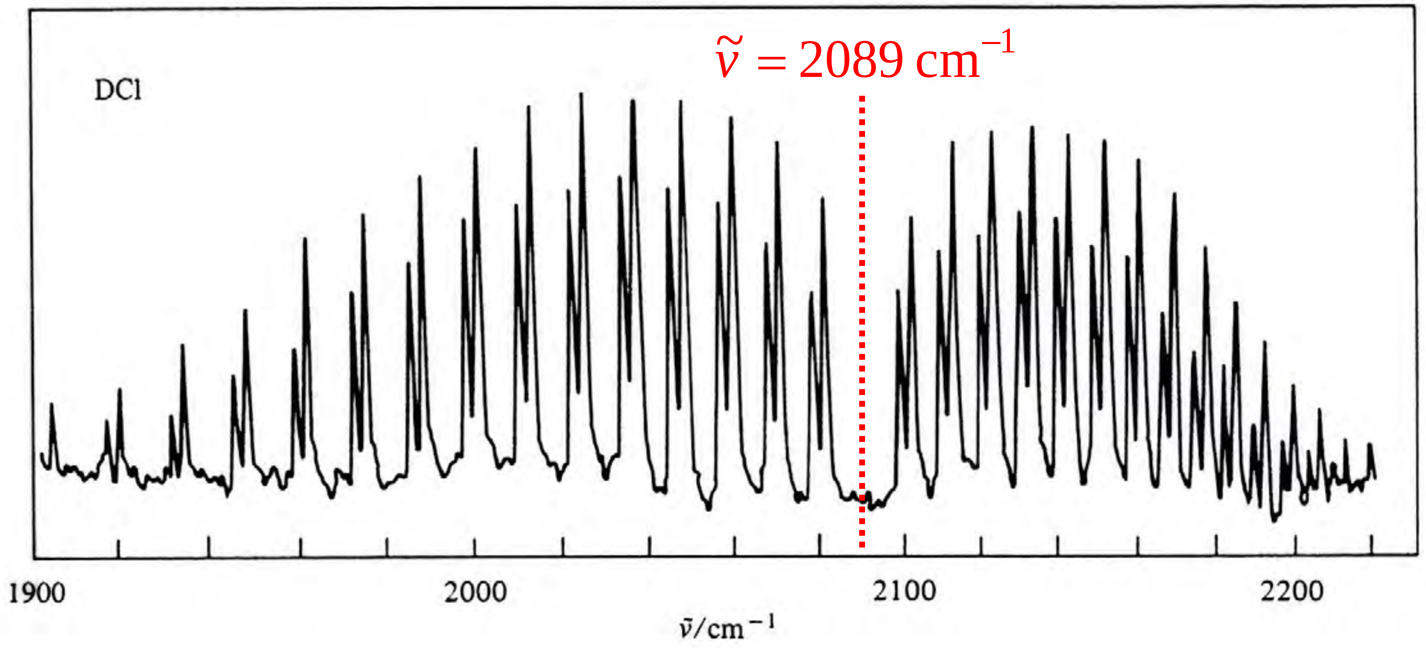
intensity of peak c = intensity of peak f because same initial state

intensity of peak d = intensity of peak g because same initial state

A vibrational-rotational spectrum is in the infrared region of the EM spectrum.

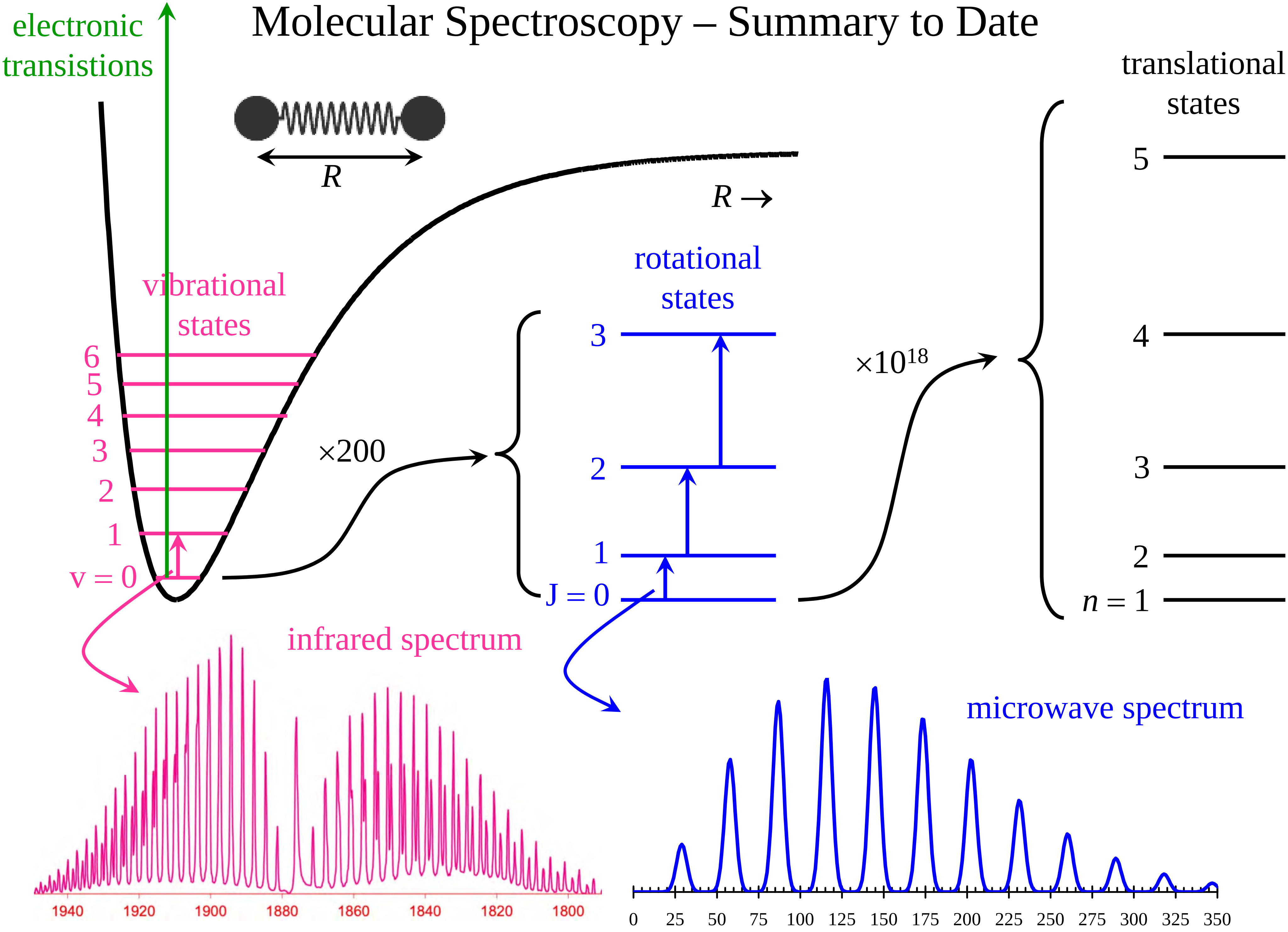
Infrared Spectra of Diatomic Molecules





Spectra from J. H. Noggle, Physical Chemistry, 1996, Figure 13.7, p. 782

Molecular Spectroscopy – Summary to Date



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.

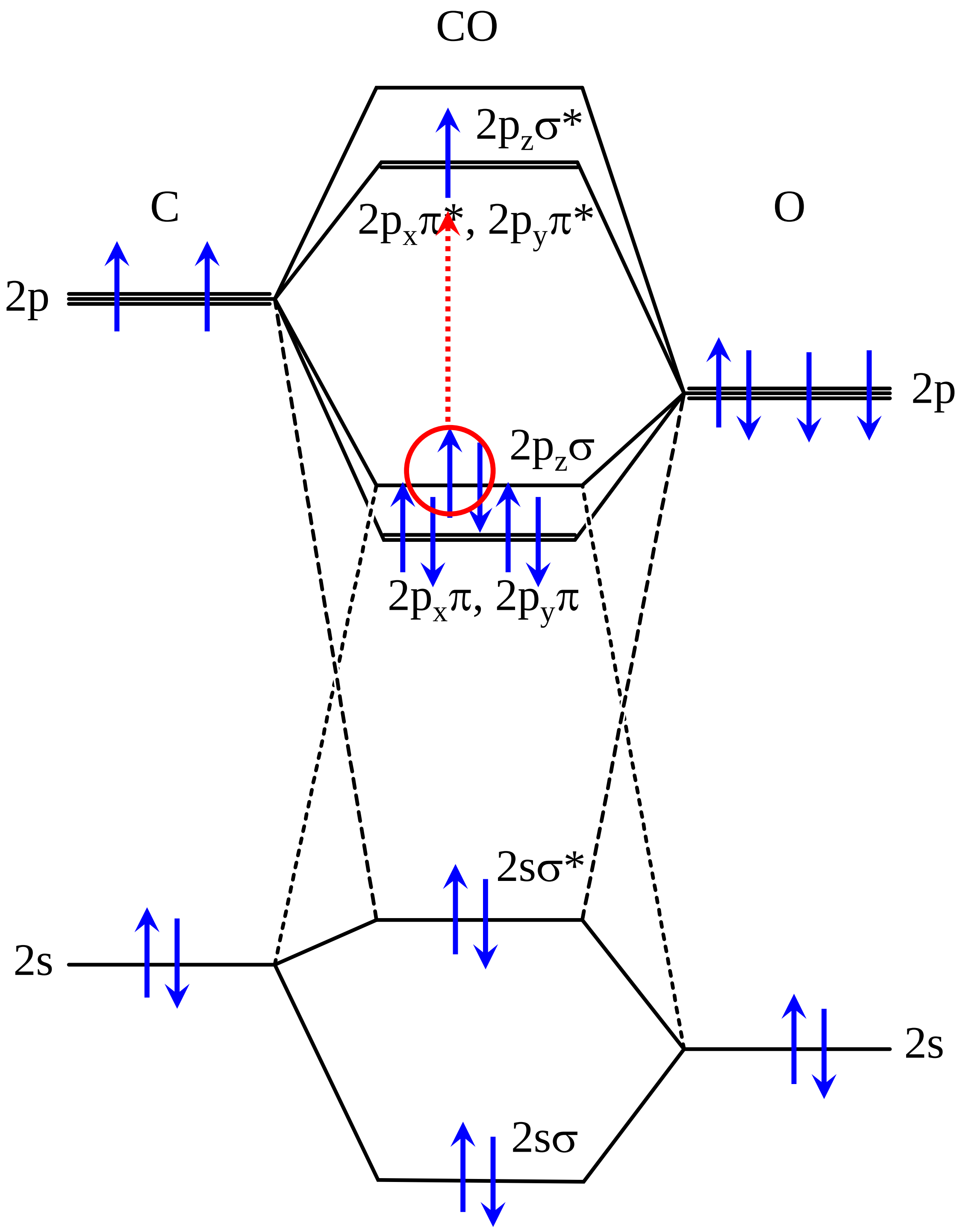
8 electrons in bonding orbitals, 2 electrons in anti-bonding orbitals.

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

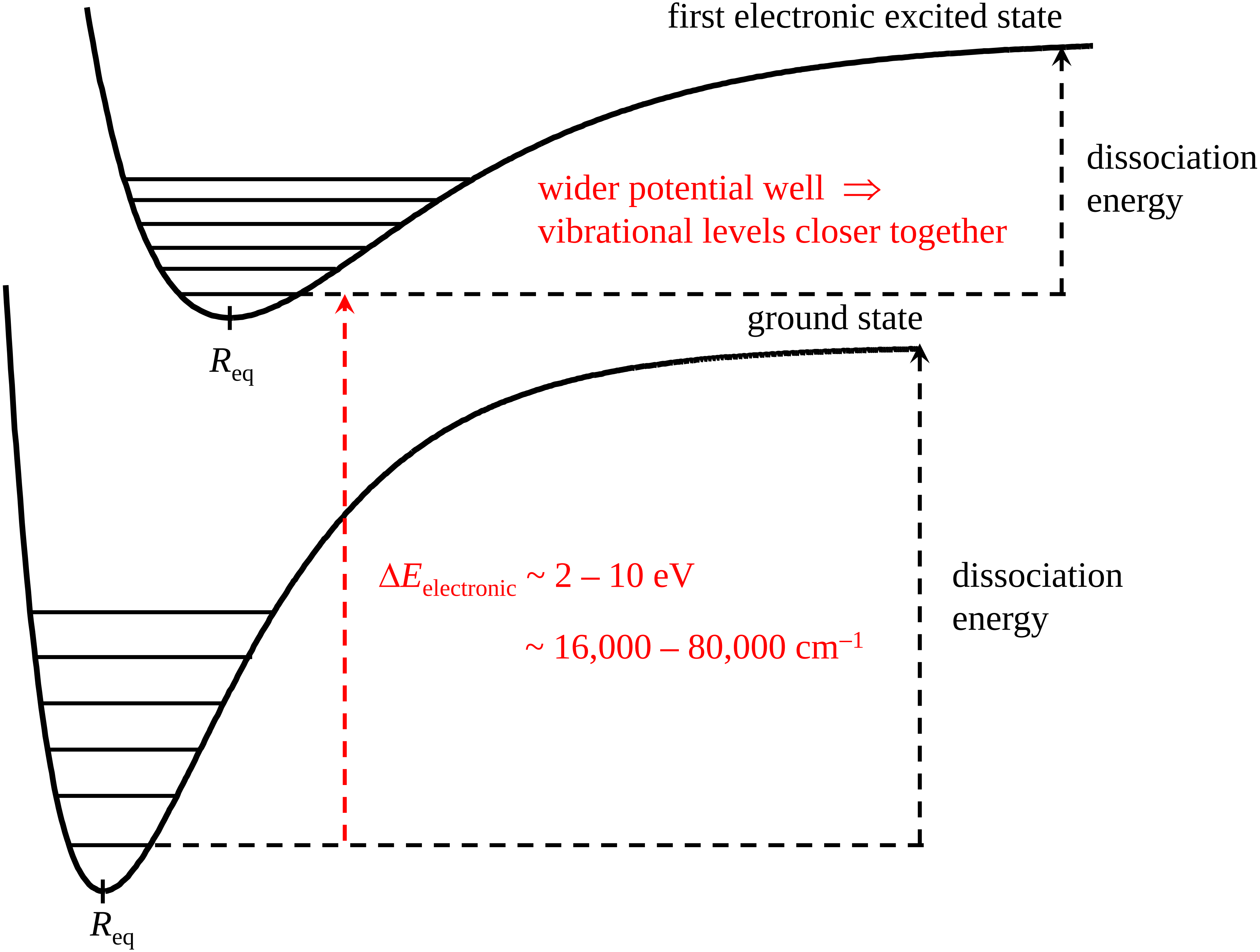
first electronic excited state: $2p_z\sigma \rightarrow 2p_x\pi^*$

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

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



Electronic Ground State and First Excited State

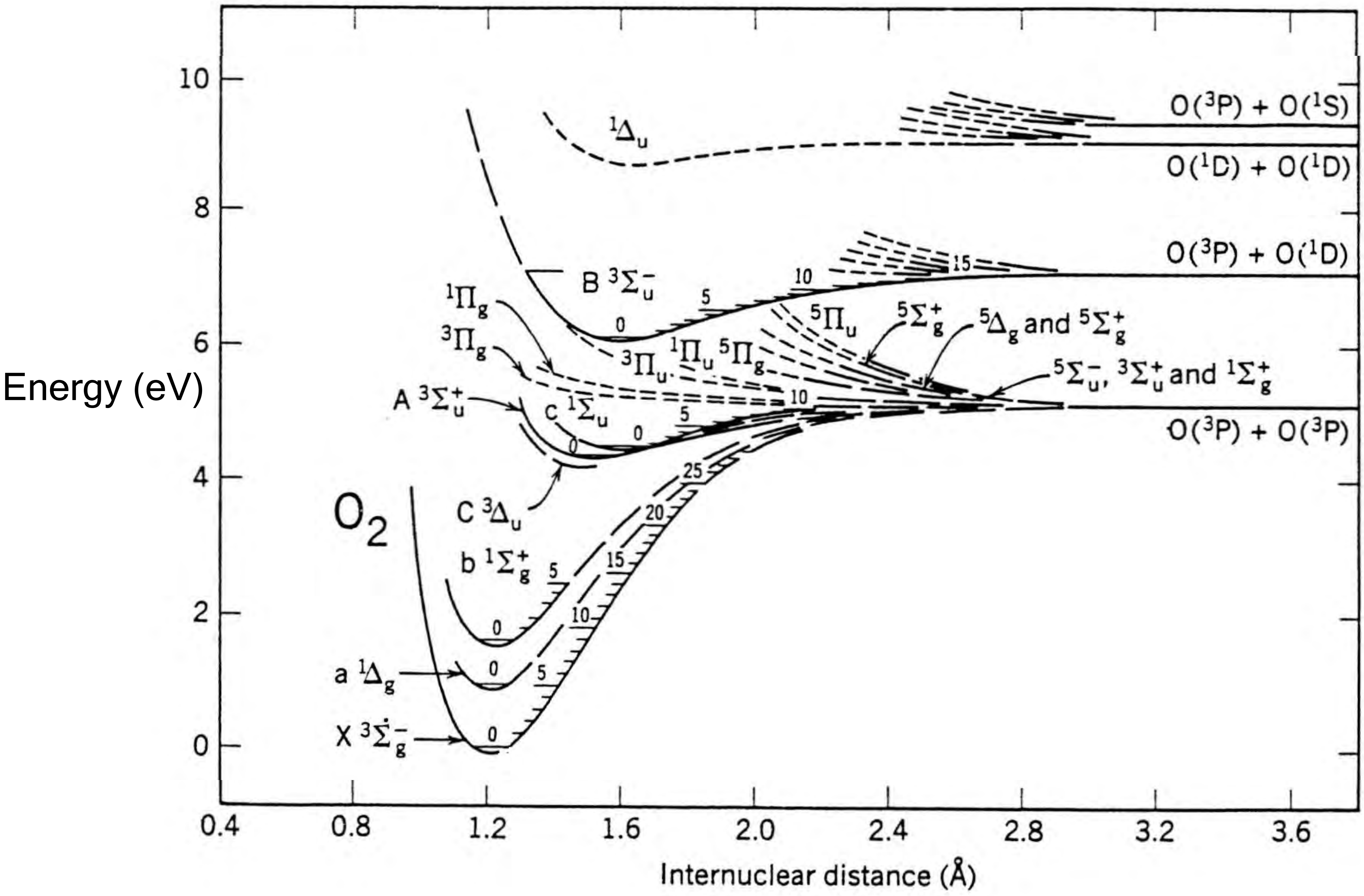


wider potential well $\Rightarrow$
vibrational levels closer together

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

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

Electronic Ground State and Excited States for O_2



F. R. Gilmore, *Potential Energy Curves for N_2, NO, O_2 and Corresponding Ions,*
Rand Corporation Memomrandum RM-4034-1-PR, April 1966