Introduction to molecular spectroscopy

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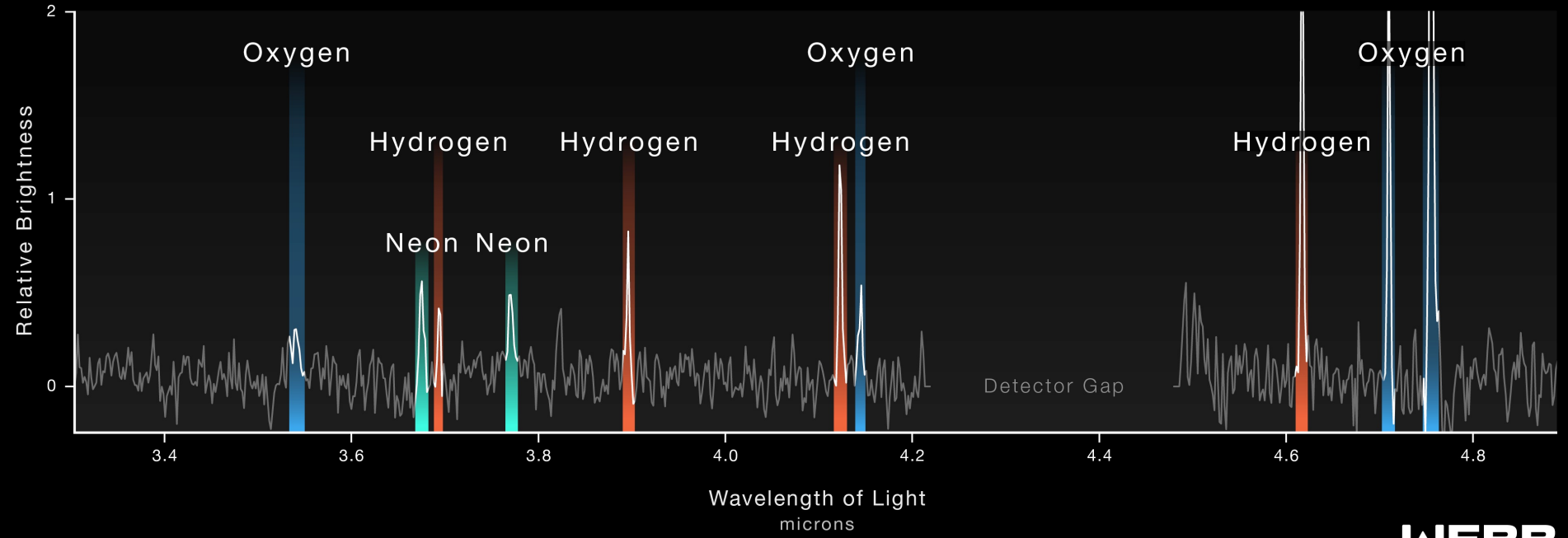
UAM Master in Astrophysics – Radiative Processes in Astrophysics

DISTANT GALAXY BEHIND SMACS 0723

WEBB SPECTRUM SHOWCASES GALAXY'S COMPOSITION

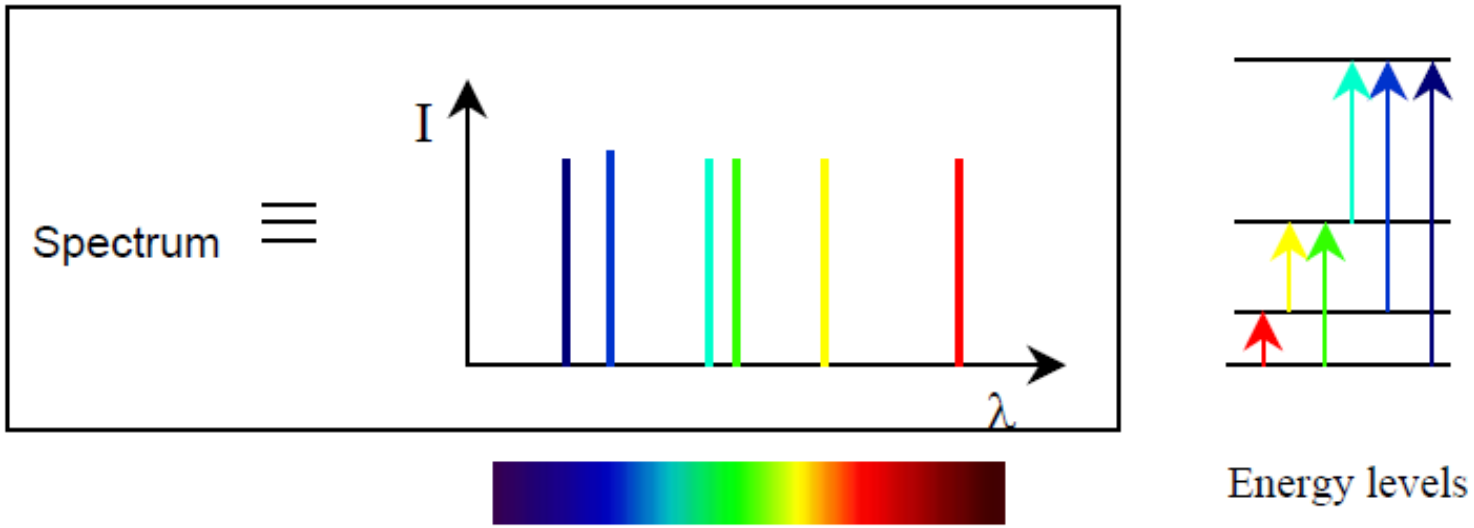
NIRCam Imaging

NIRSpec Microshutter Array Spectroscopy



WEBB
SPACE TELESCOPE

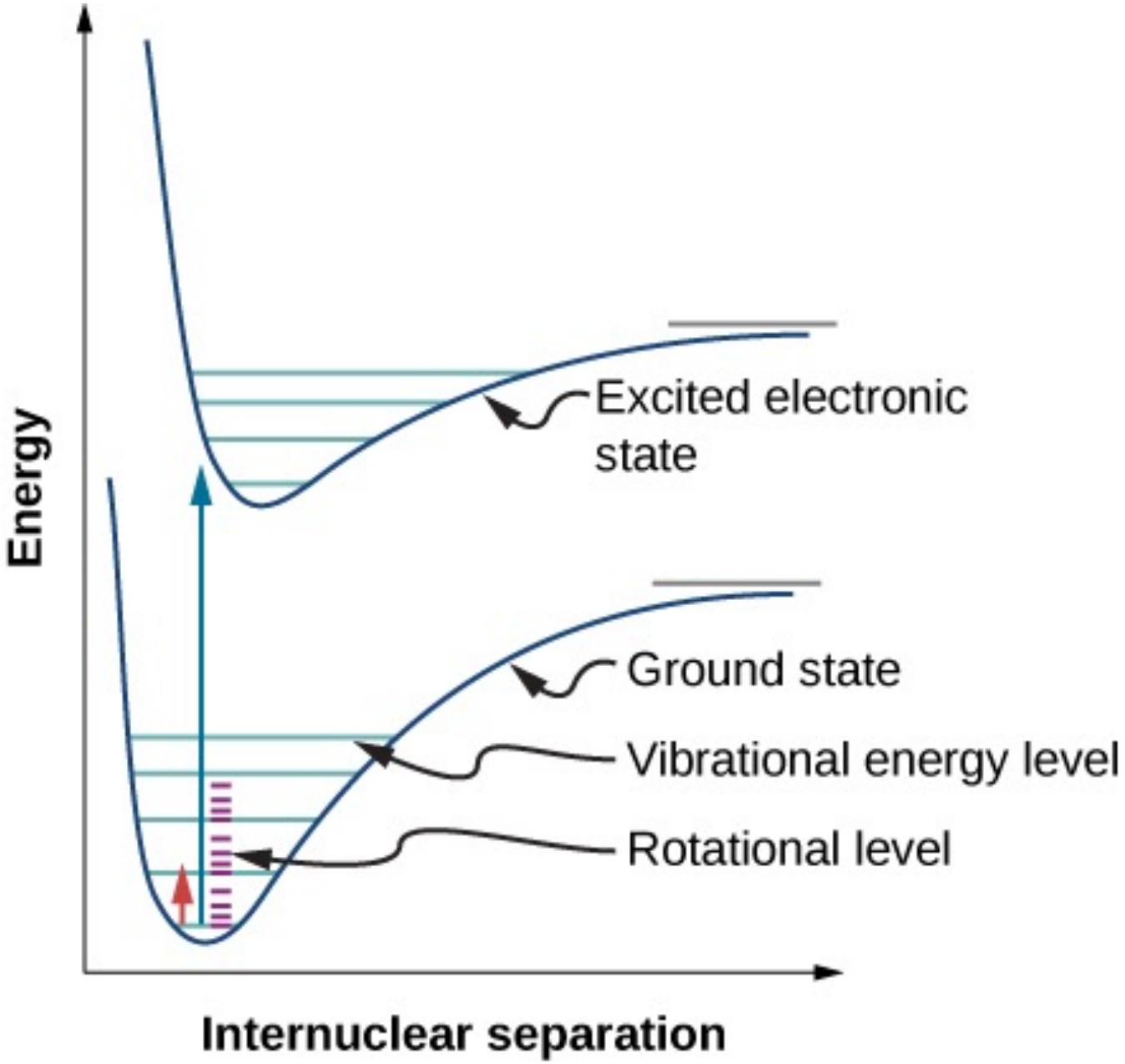
Molecular spectroscopy: Energy levels and transitions



Quantum Mechanics: Molecules have discrete energy levels

Radiative transitions between them create the spectrum of the molecule

Molecular spectroscopy: Energy levels and transitions



Organization of this lesson

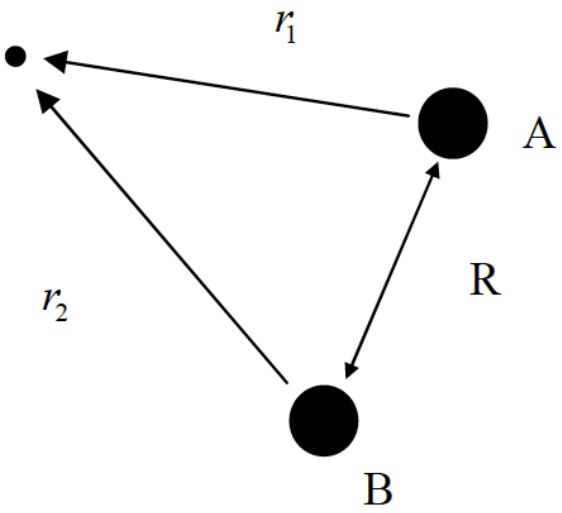
Electronic
Vibrational Levels
Rotational

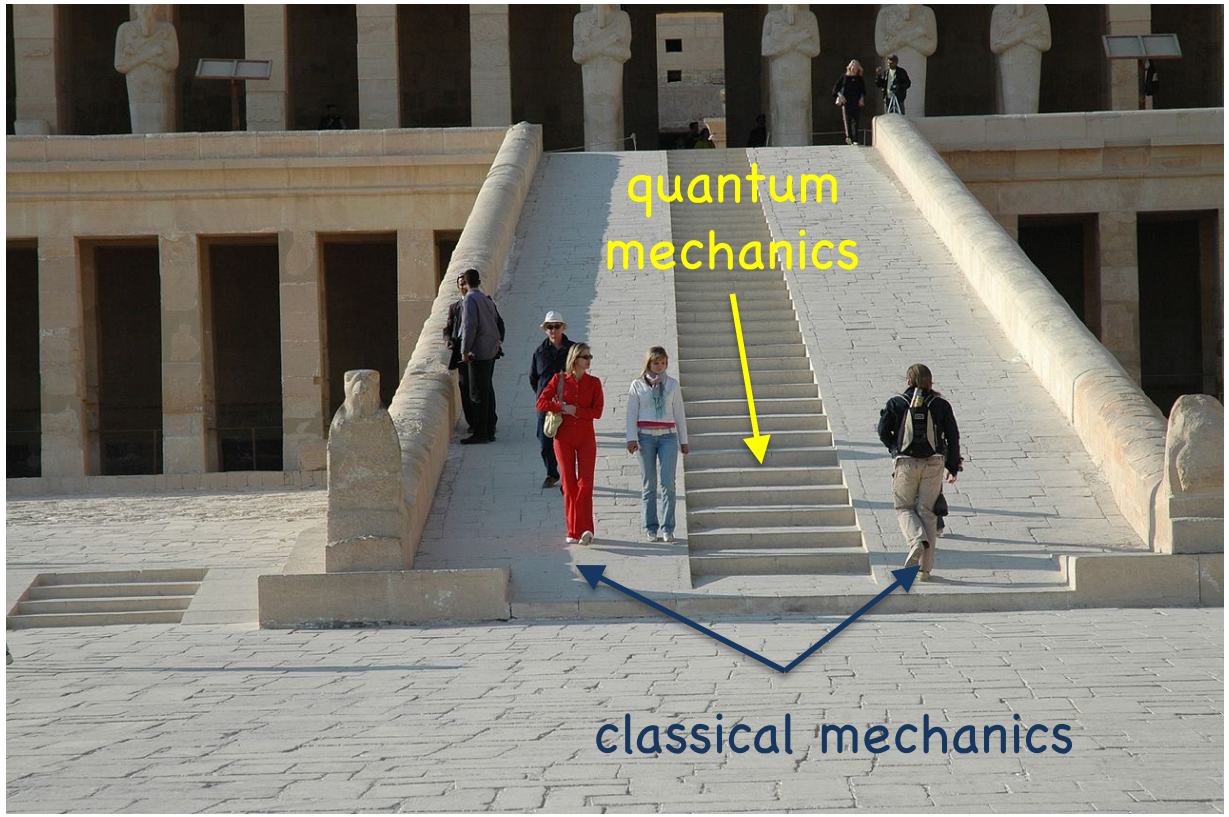
Electronic
Vibrational Spectrum
Rotational

Electronic levels of molecules

Let’s consider a system of 2 nuclei and 1 electron (the simplest molecule: H_2^+)

We aim to solve the quantum mechanics to get the energies of the quantum levels





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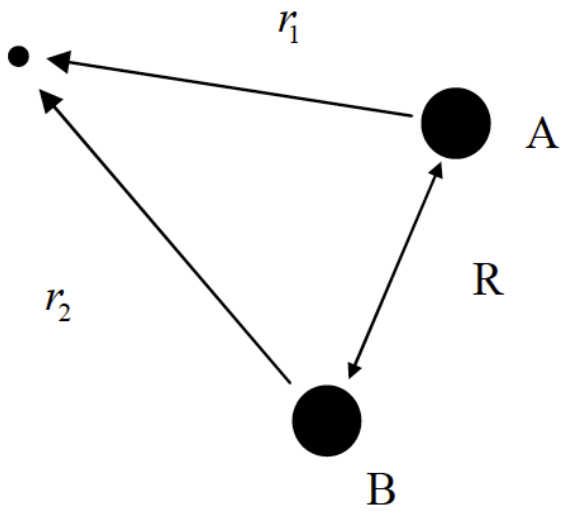


Our friend: *the Schrödinger equation*

$$H\Psi = E\Psi$$

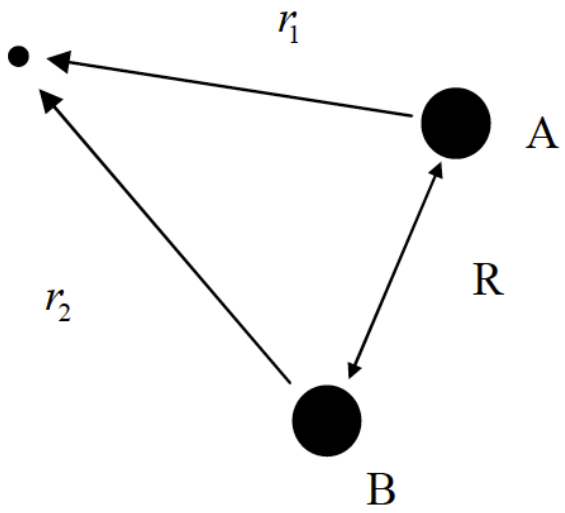
kinetic energies of A, B, and e — *interactions between particles potential energies*

$$\hat{H}\left(R_A, R_B, r, P_A, P_B, p\right) = \underbrace{-\frac{\hbar^2}{2m_e}\vec{\nabla}_r^{\,2}}_{KE \text{ of electron}} - \cancel{\frac{\hbar^2}{2m_p}\vec{\nabla}_A^{\,2}} - \cancel{\frac{\hbar^2}{2m_p}\vec{\nabla}_B^{\,2}} + \left(\underbrace{-\frac{e^2}{r_1} - \frac{e^2}{r_2}}_{\text{electron-nucleus attraction}} + \underbrace{\frac{e^2}{R}}_{\text{nuclear repulsion energy}} \right)$$

Born-Oppenheimer approximation

protons are 1836 times heavier than electrons
nuclei are slow and electrons are fast
nuclei can be assumed to be static compared with the motion of electrons

Let's consider a system of 2 nuclei and 1 electron (the simplest molecule: H_2^+)
We aim to solve the quantum mechanics to get the energies of the quantum levels



kinetic energies of A, B, and e

interactions between particles
potential energies

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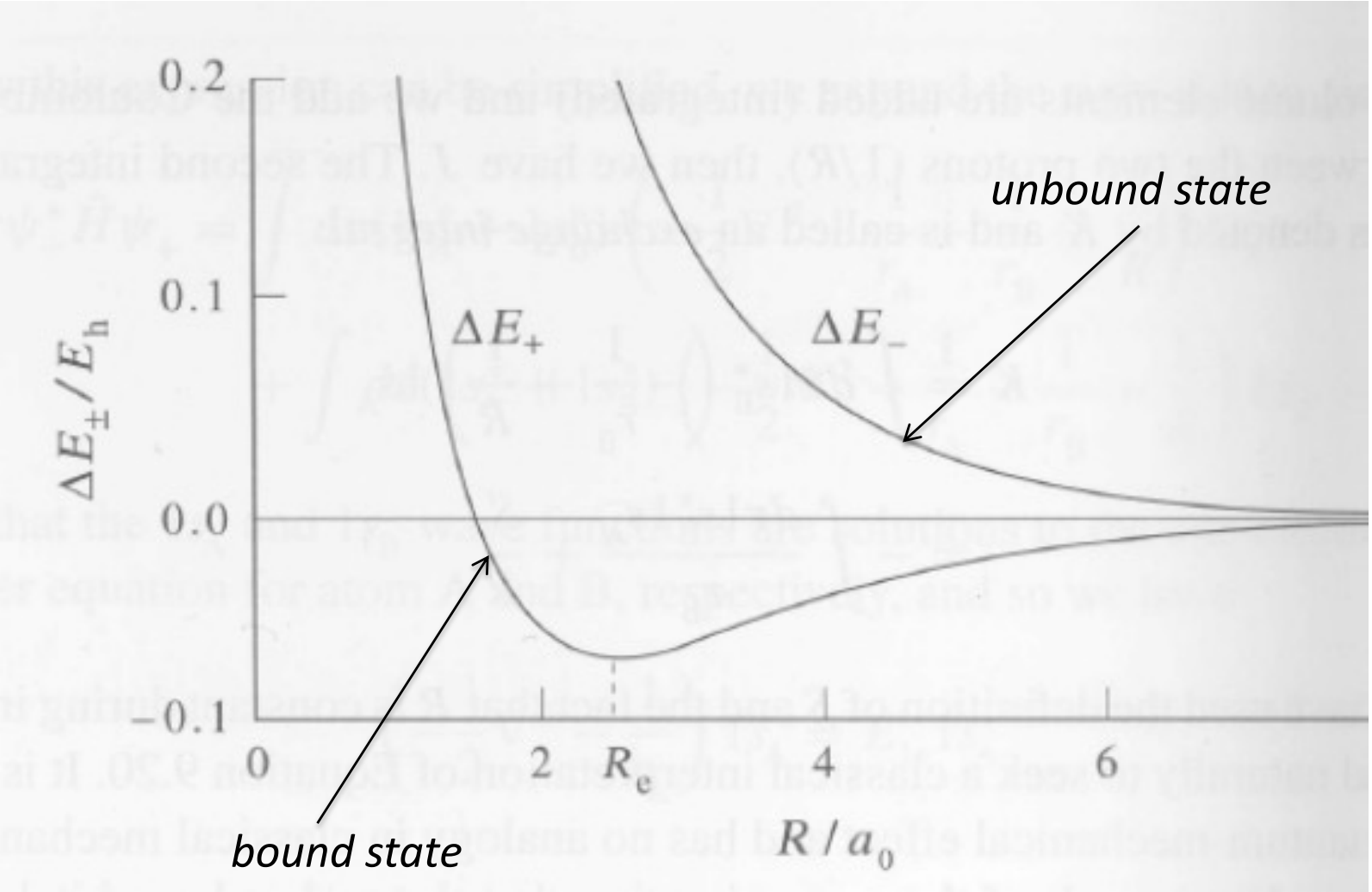
$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\vec{\nabla}_r^{\,2} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \quad \Rightarrow \quad H_{el}\Psi = E_{el}\Psi$$

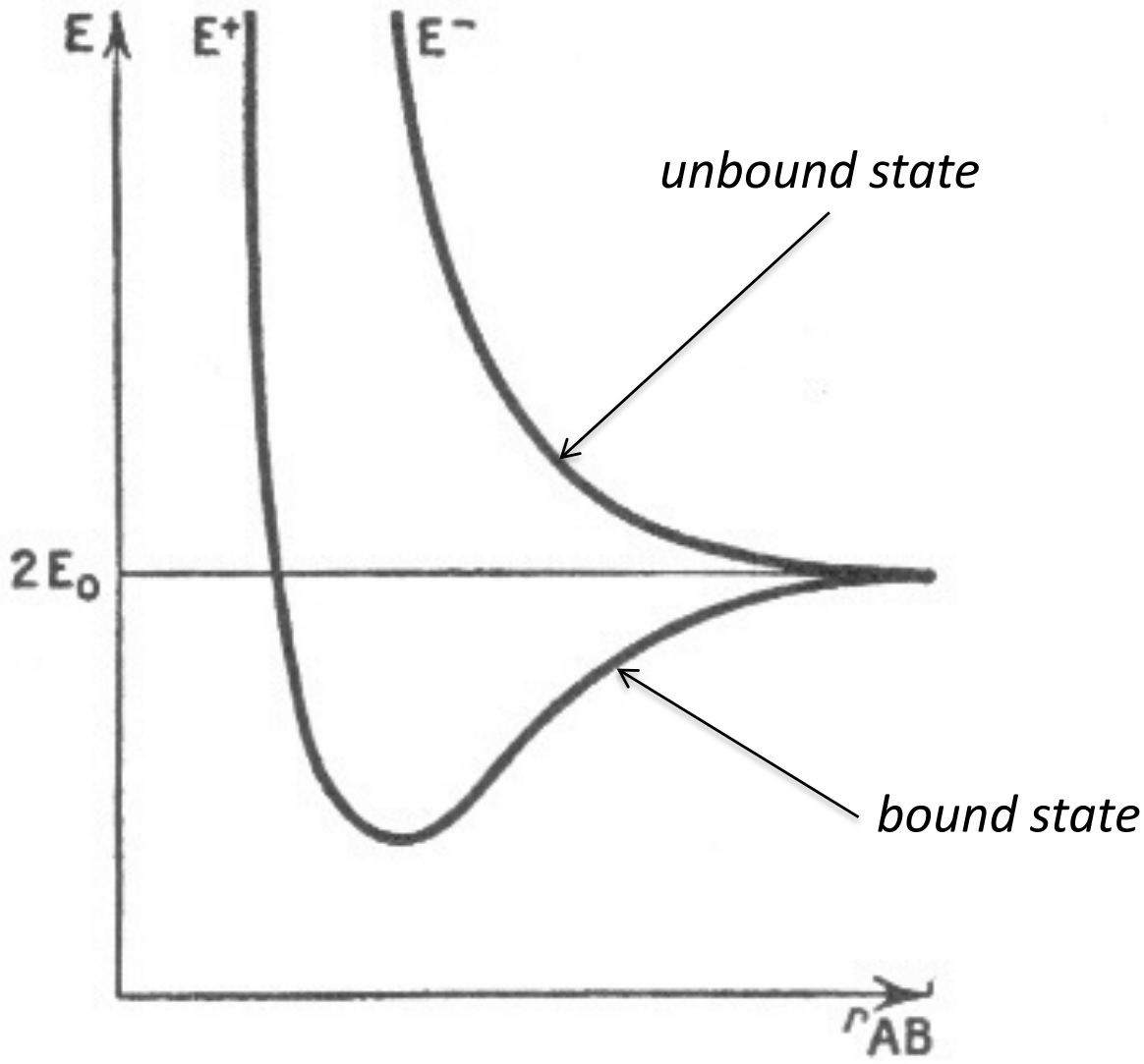
Potential energy curves for H_2^+

Electronic energy of the system as a function of the separation between the 2 nuclei



These are the electronic states of the molecule

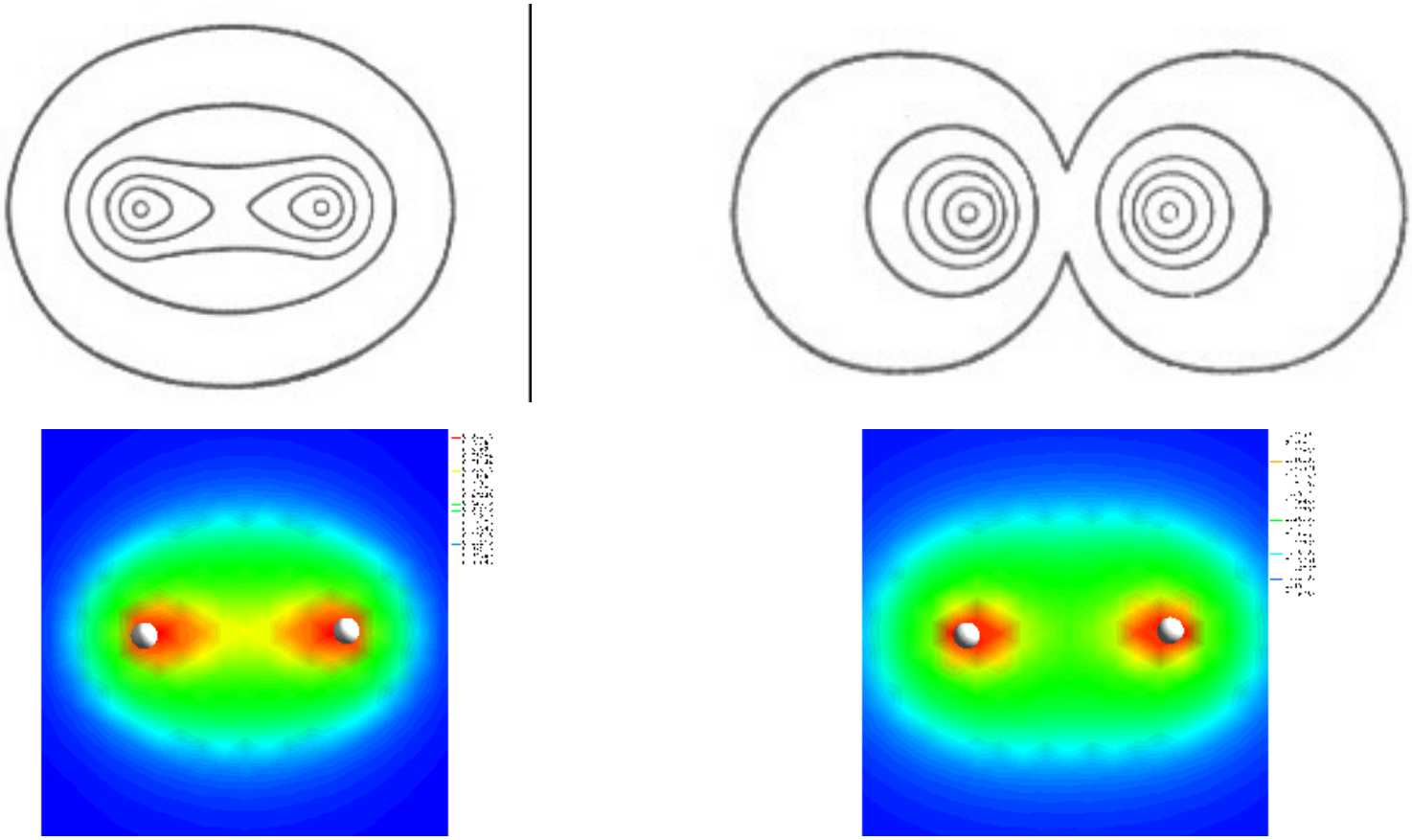
Potential energy curves for H_2



Molecular orbitals for H_2

(shown as probability density functions of electrons)

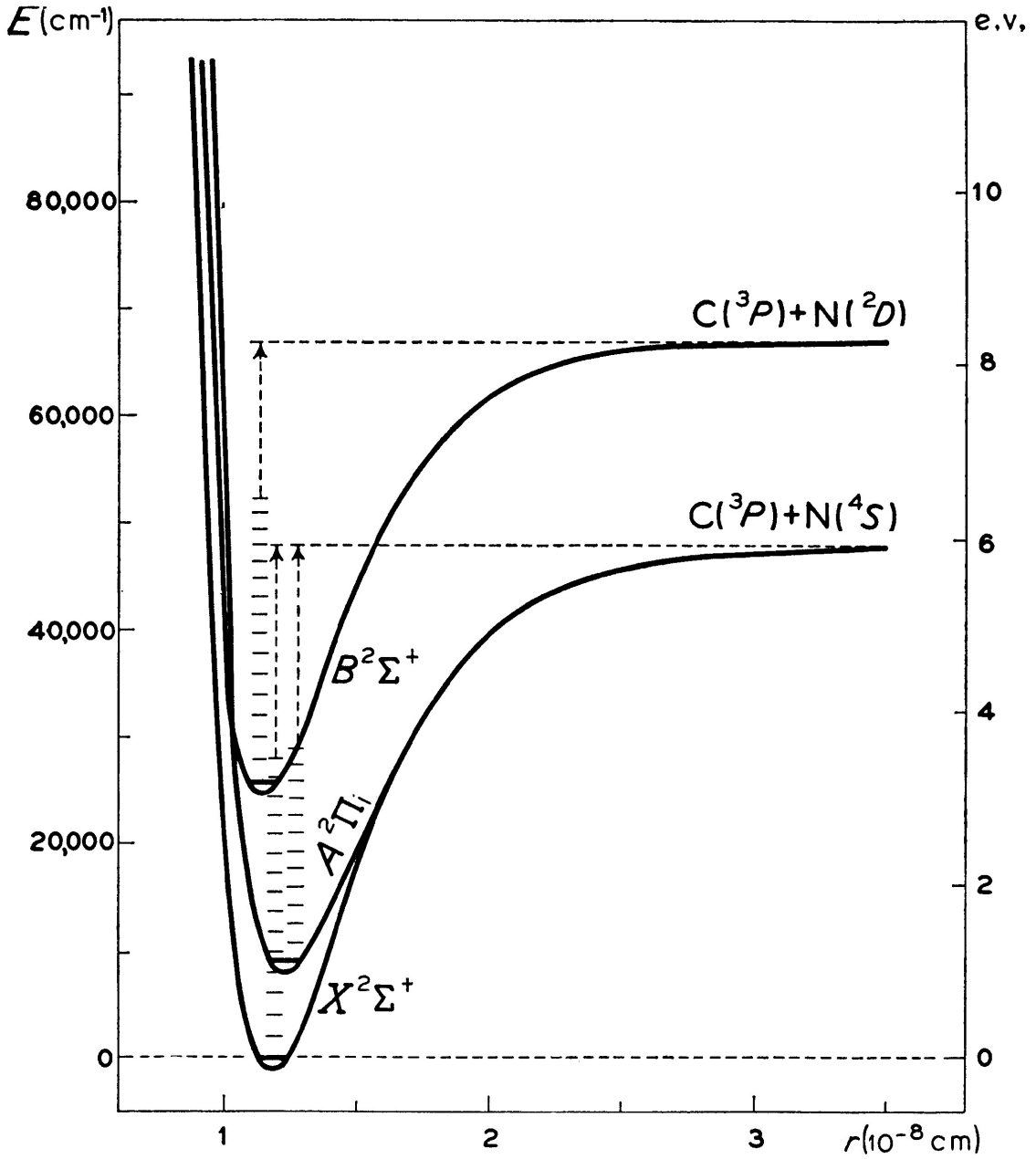
ψ^+ ψ^-



In Ψ^+ the electron density has a maximum between the two nuclei → chemical bond

In Ψ^- the electron density is concentrated around each nuclei

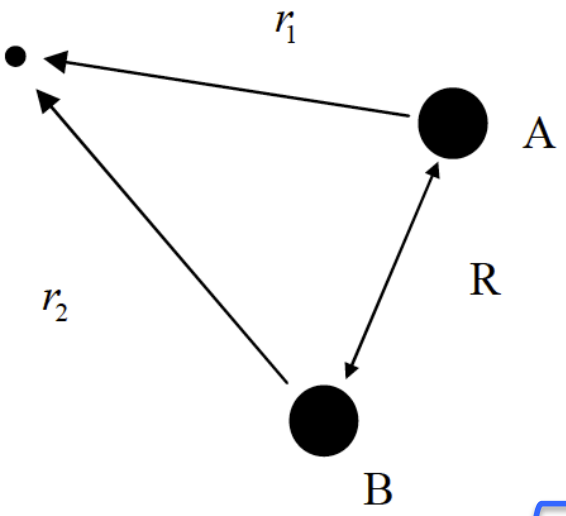
Potential energy curves of CN



from Herzberg "Molecular spectra and Molecular Structure"

Motion of nuclei

We come back to our system of 2 protons and 1 electron (H_2^+)
We now focus on the motion of nuclei



kinetic energies of A, B, and e

interactions between particles
potential energies

$$\hat{H}\left(R_A, R_B, r, P_A, P_B, p\right) = \underbrace{-\frac{\hbar^2}{2m_e}\vec{\nabla}_r^{\,2}}_{KE \text{ of electron}} - \frac{\hbar^2}{2m_p}\vec{\nabla}_A^{\,2} - \frac{\hbar^2}{2m_p}\vec{\nabla}_B^{\,2} + \left(\underbrace{-\frac{e^2}{r_1} - \frac{e^2}{r_2}}_{\text{electron-nucleus attraction}} + \underbrace{\frac{e^2}{R}}_{\text{nuclear repulsion energy}} \right)$$

In an electronic bound state, the motion of nuclei are not completely independent:
There are 3 types of degrees of freedom that describe the motion of nuclei:

* translation (not quantized)
* vibration
* rotation

vibrational and rotational energies, as electronic energy, are quantized (only discrete energies are possible)

Born-Oppenheimer approximation: separation of electronic and nuclear motions (justified due to the very different time scales at which electrons and nuclei move)

$$\hat{H}\left(R_A, R_B, r, P_A, P_B, p\right) = \underbrace{-\frac{\hbar^2}{2m_e}\vec{\nabla}_r^{\,2}}_{\text{KE of electron}} - \frac{\hbar^2}{2m_p}\vec{\nabla}_A^{\,2} - \frac{\hbar^2}{2m_p}\vec{\nabla}_B^{\,2} + \left(\underbrace{-\frac{e^2}{r_1} - \frac{e^2}{r_2}}_{\text{electron-nucleus attraction}} + \underbrace{\frac{e^2}{R}}_{\text{nuclear repulsion energy}} \right)$$

$$\hat{H}_T = \hat{H}_e + \hat{H}_n$$

The same approximation can be done for vibrational and rotational motions because vibrations are much faster than rotations

$$\hat{H}_n = \hat{H}_{vib} + \hat{H}_{rot}$$

The energy of a molecule can be presented as sum of electronic energy, vibrational energy, and rotational energy. This allows to treat each phenomenon (electronic, vibrational, and rotational) independently

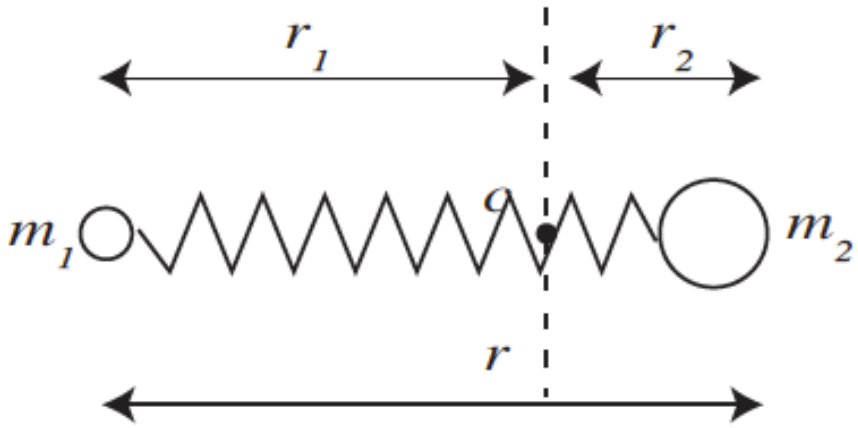
$$\hat{H}_T = \hat{H}_e + \hat{H}_{vib} + \hat{H}_{rot}$$

Vibrational levels of molecules

Vibration in a diatomic molecule: the simple harmonic oscillator

Scheme from Franck Houwing Lectures

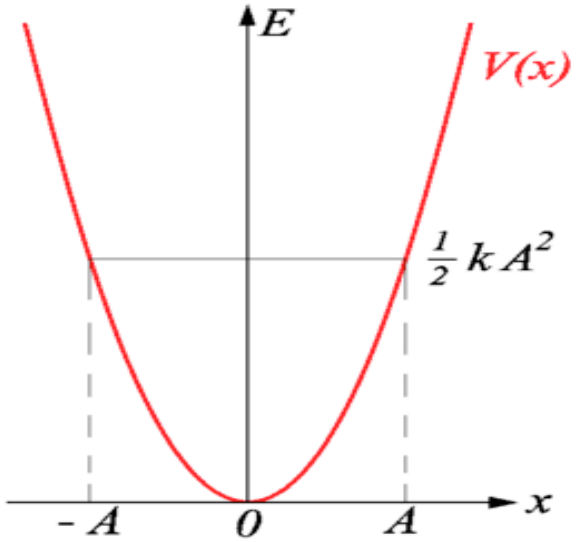
Let's consider a diatomic molecule as two masses connected by a massless spring obeying Hook's law



According to classical mechanics, there is only one discrete oscillation frequency, but the energy, related to the amplitude of the vibration, can take any value

$$\nu'_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$E_{clas} = \frac{1}{2}kA^2$$



where $x = r - r_e$

Vibration in a diatomic molecule: the simple harmonic oscillator

Scheme from Franck Houwing Lectures

In quantum mechanics, one must write the Schrödinger equation

Hamiltonian $\left\{\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right\}\Psi = E\Psi$

Kinetic energy operator__ $\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2}$

Potential operator _____ $+\frac{1}{2}kx^2$

Eigenvalue _____ E

Eigenfunction _____ Ψ

The vibrational energy is discretized according to the quantum number v

$$E_v = \left(v+\frac{1}{2}\right)h\nu_{osc}$$

v = 0, 1, 2, 3, …

Vibration in a diatomic molecule: the simple harmonic oscillator

FACTS:

Vibrational energy is discretized according to quantum number v: $E_v = (v + ½)\, h\nu'_{osc}$

$v = 0, 1, 2, 3, \ldots$

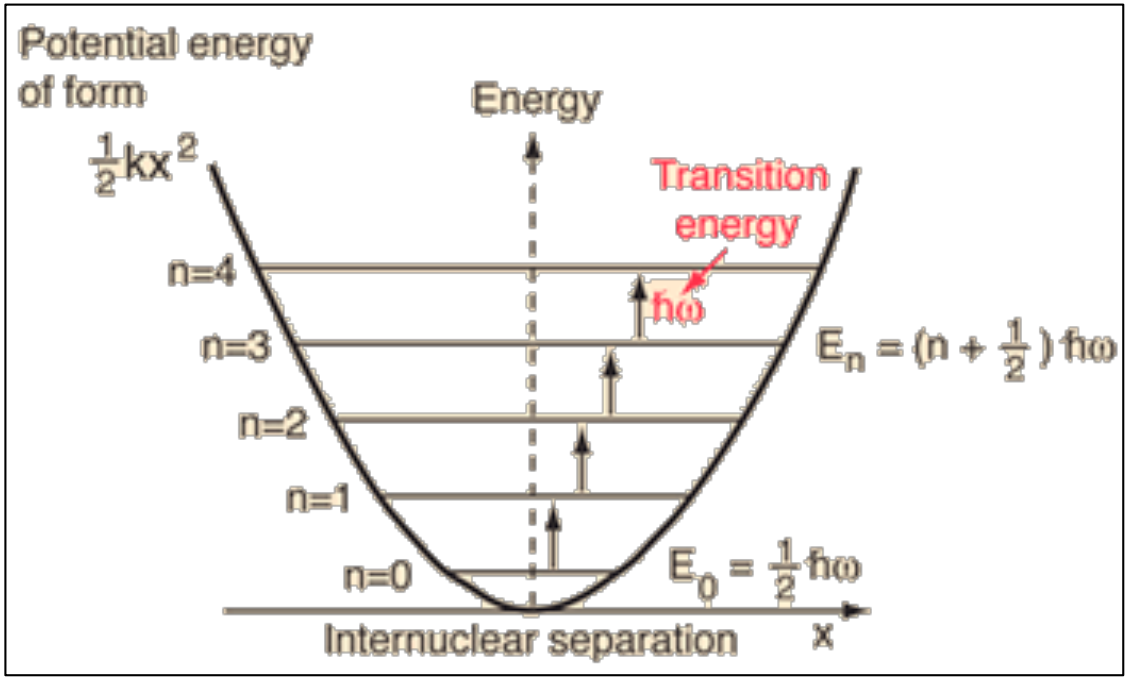
In the ground vibrational state (v=0) the energy is not zero

Energy separation between adjacent levels is constant: $E_{v+1} - E_v = h\nu'_{osc}$

Selection rule: $\Delta v = \pm 1$

All lines are coincident. Pure vibrational spectrum consists of one single line.

…but reality is not like that



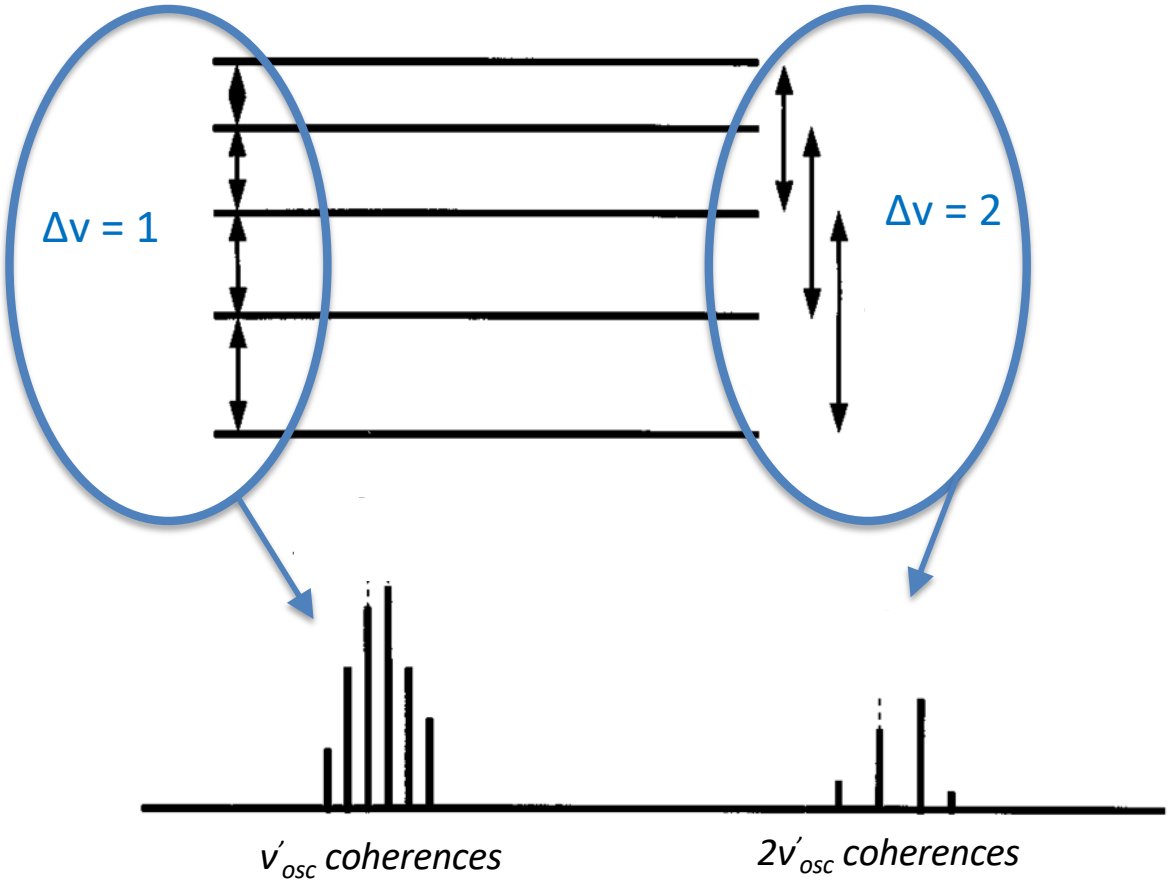
Reality of vibration in a diatomic molecule: anharmonicity

harmonic term *anharmonic terms*

Level energies, still quantum number v: $E_v = h\nu'_{osc}(v+½) - h\nu'_{osc}x_e(v+½)^2 + h\nu'_{osc}y_e(v+½)^3 + \ldots$

Energy separation between adjacent levels decreases with increasing v

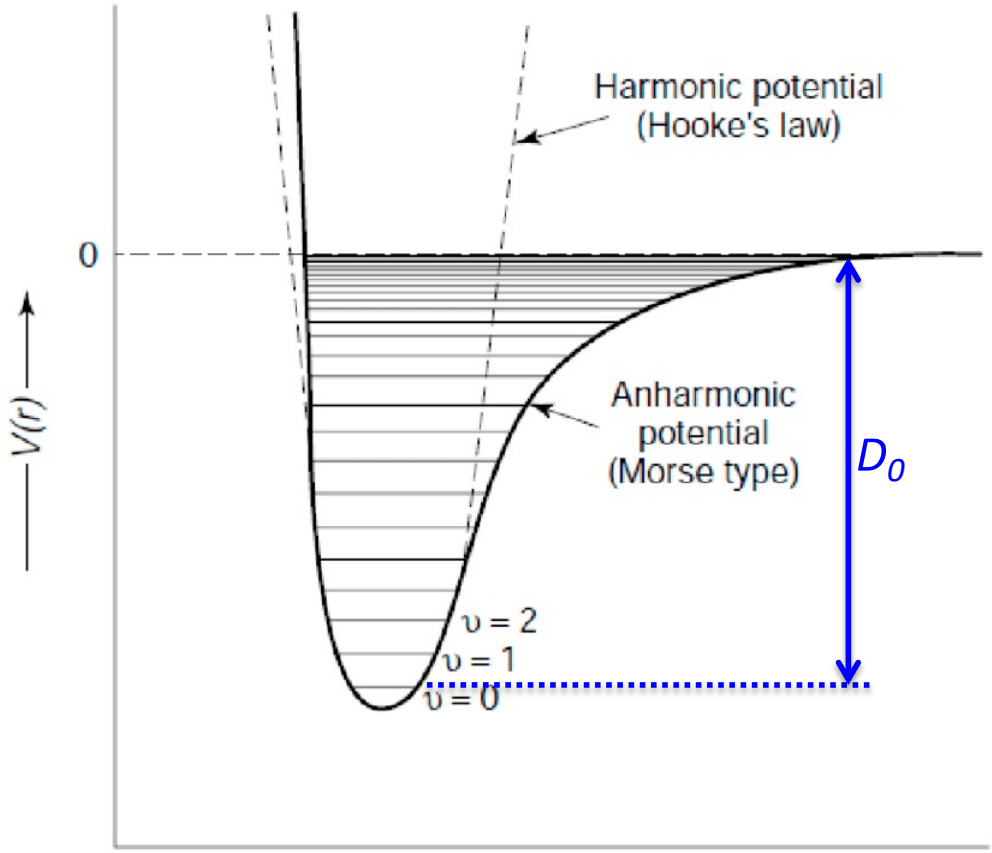
Selection rule: $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$ but $\Delta v = \pm 1$ is the most intense



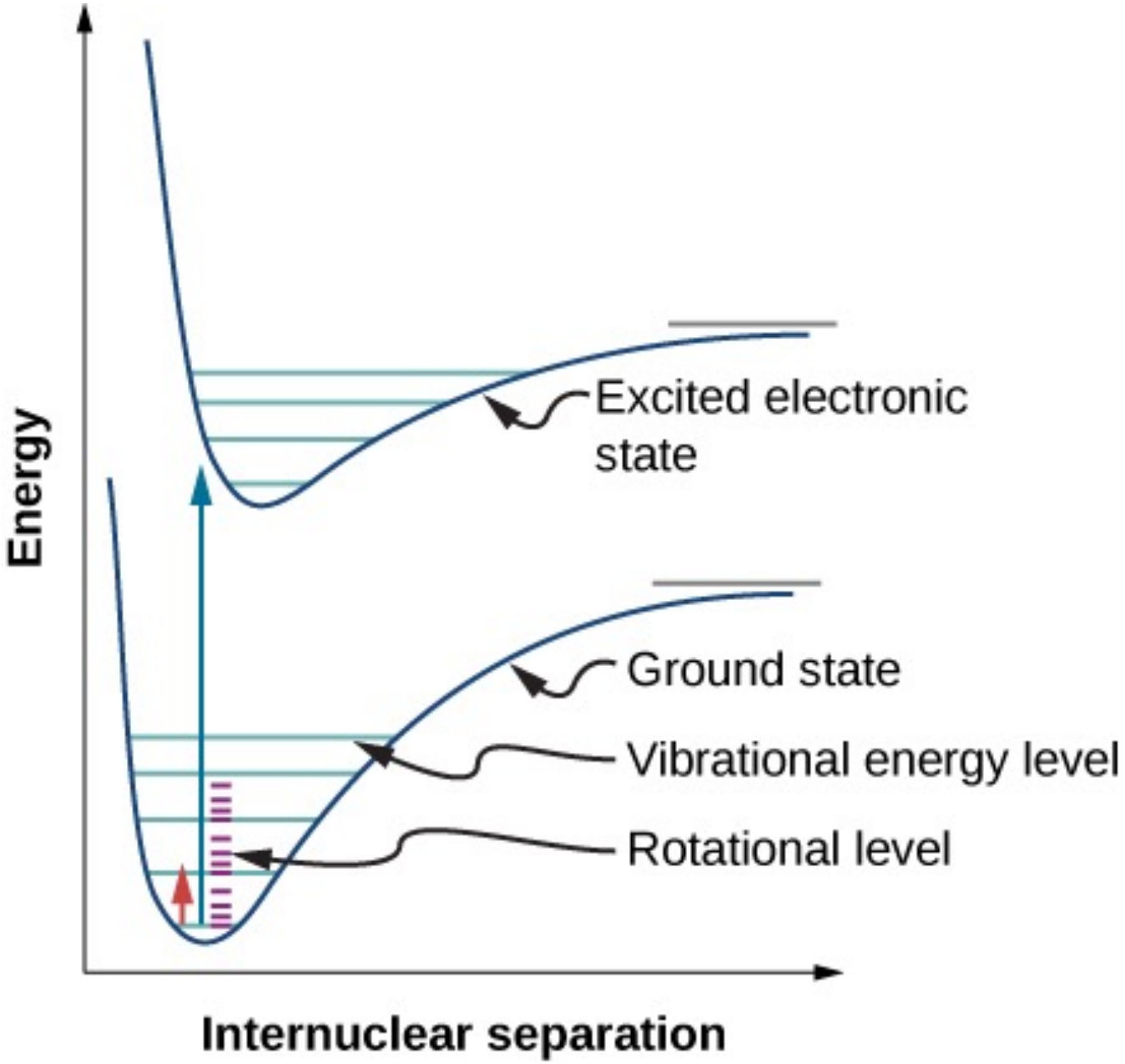
Reality of vibration in a diatomic molecule: anharmonicity

Vibrational levels lie in the potential energy curve of a bound electronic state

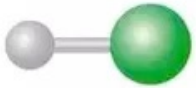
The distance from v=0 to the continuum is the dissociation energy D_0

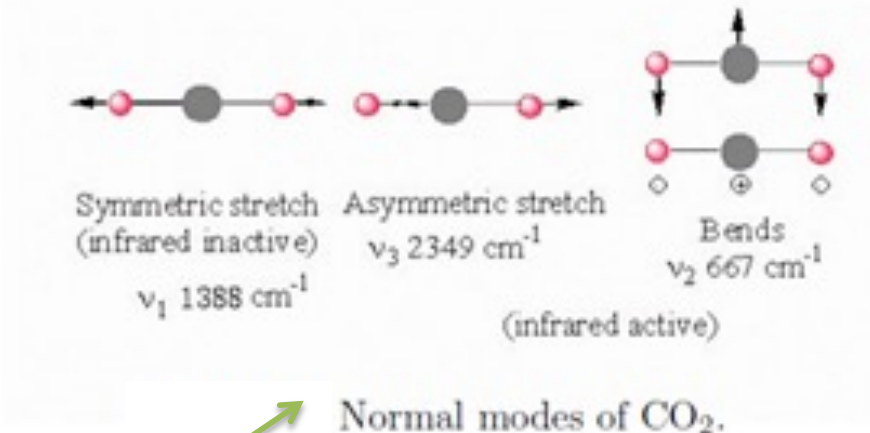


Molecular spectroscopy: Energy levels and transitions

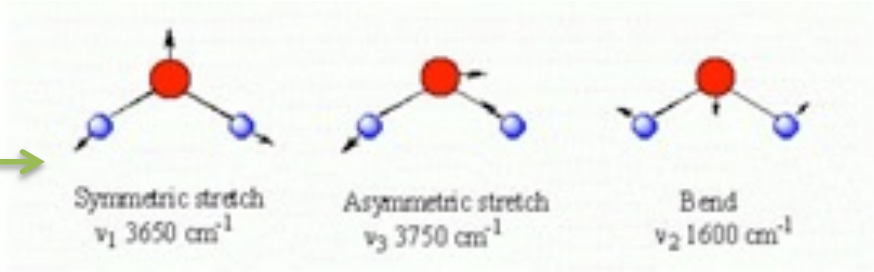


Vibration in a polyatomic molecule

Type of molecule	*N*	Degrees of freedom	Modes
Monatomic, e.g. Ne	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl 	2	6	3 translational 2 rotational 1 vibrational
Triatomic linear, e.g. CO_2	3	9	3 translational 2 rotational 4 vibrational
Triatomic non-linear, e.g. H_2O	3	9	3 translational 3 rotational 3 vibrational



Normal modes of CO_2.



Normal modes of H_2O.

Each vibration mode has its own set of vibrational levels

Rotational levels of molecules

Born-Oppenheimer approximation: separation of electronic and nuclear motions (justified due to the very different time scales at which electrons and nuclei move)

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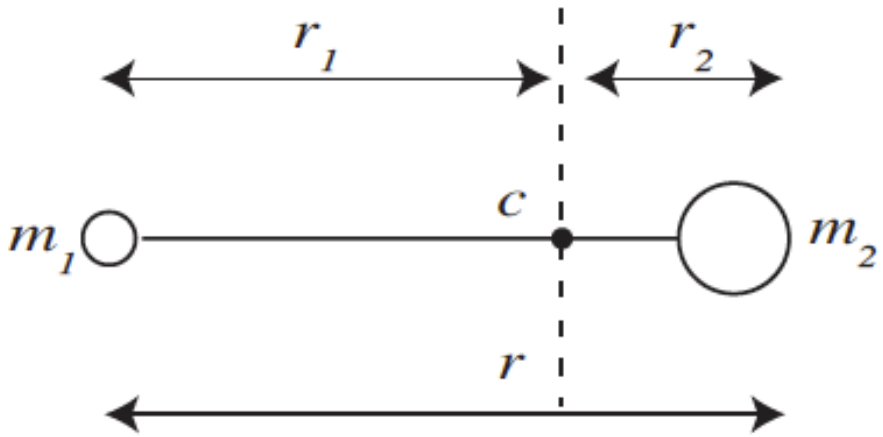
$$\hat{H}_T = \hat{H}_e + \hat{H}_{vib} + \hat{H}_{rot}$$

Rotation in a diatomic molecule: the rigid rotator

Scheme from Franck Houwing Lectures

Let's consider a diatomic molecule as two masses connected by a rigid massless rod of length *r*



According to classical mechanics, the energy of rotation is given by

$$E = \frac{1}{2} I\omega^2 \qquad \omega = 2\pi \nu'_{rot}$$

where ν'_{rot} is the frequency of rotation, which can have any value, and *I* is the moment of inertia

$$I = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

Rotation in a diatomic molecule: the rigid rotator

Scheme from Franck Houwing Lectures

In quantum mechanics, one must write the Schrödinger equation

$$H\Psi = E\Psi$$

where H = Hamiltonian, Ψ = wavefunction, E = eigenvalue.

Since there is no potential energy to be considered in this problem, the Hamiltonian is simply the kinetic energy operator given by

$$H = \frac{p^2}{2\mu}$$

The rotational energy *F* is discretized according to the quantum number *J*

$$F(J) = \frac{E}{hc} = \frac{h}{8\pi^2 cI} J(J+1) = BJ(J+1)$$

J = 0, 1, 2, 3, …

where *B* is the rotational constant for that molecule

$$B = \frac{h}{8\pi^2 cI}$$

Rotation in a diatomic molecule: the rigid rotator

Rotational energy levels and spectrum

Rotational energy scales with *J(J+1)*

Ground rotational state (*J* = 0) has $E_{rot} = 0$

Selection rule: $\Delta J = \pm 1$

$$E_{rot} = B\,J\,(J+1)$$

$$\nu = 2B\,(J+1)$$

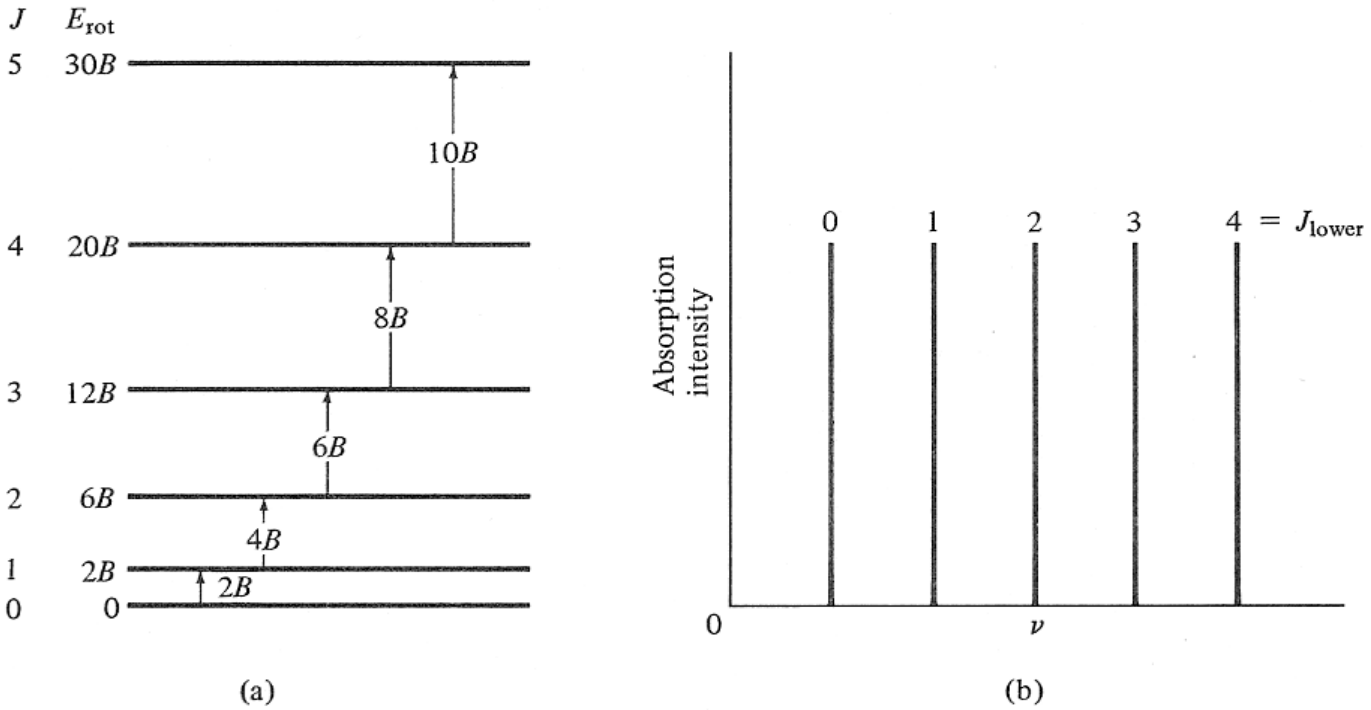


Figure 4.2 (a) Energy levels of a rigid diatomic rotor, showing dipole-allowed transitions. (b) Absorption spectrum of such a rotor.

Pure rotational spectrum of CO

Rotational lines regularly spaced by *2B*

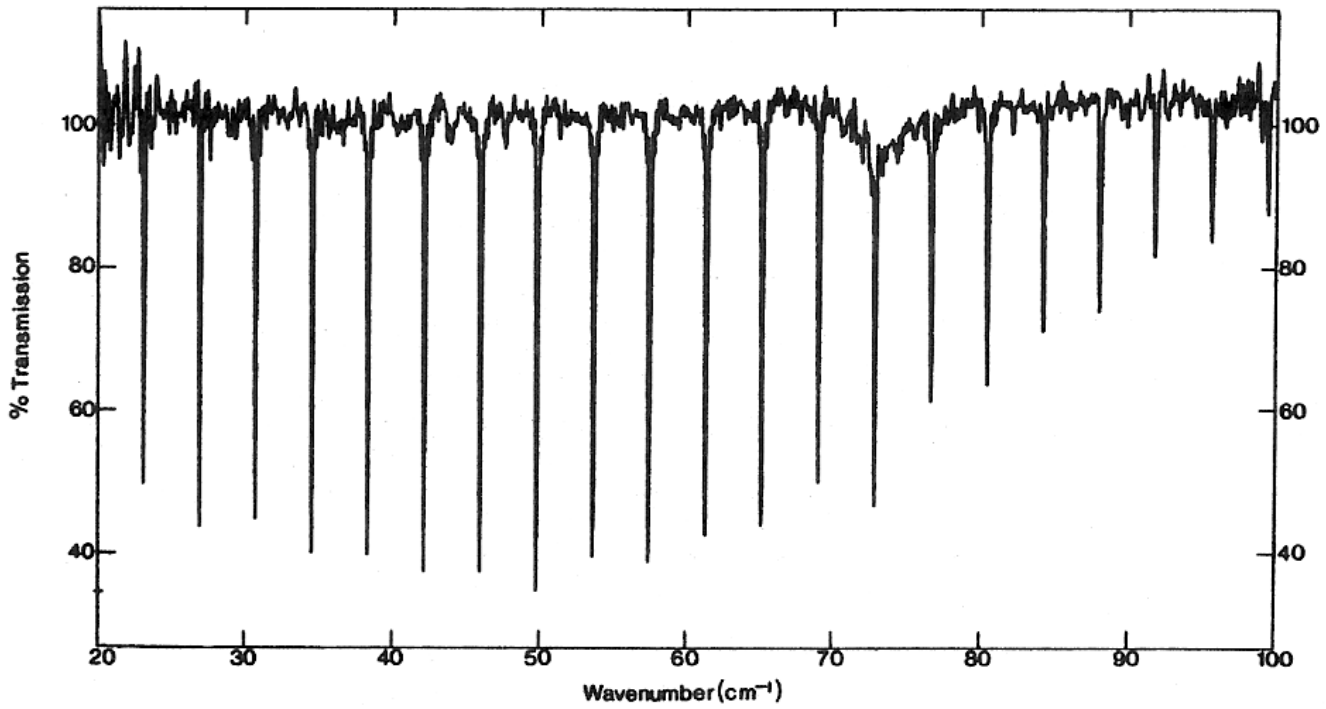
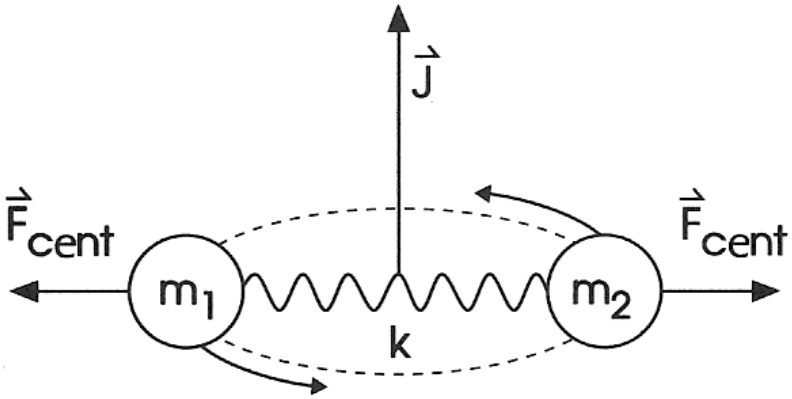


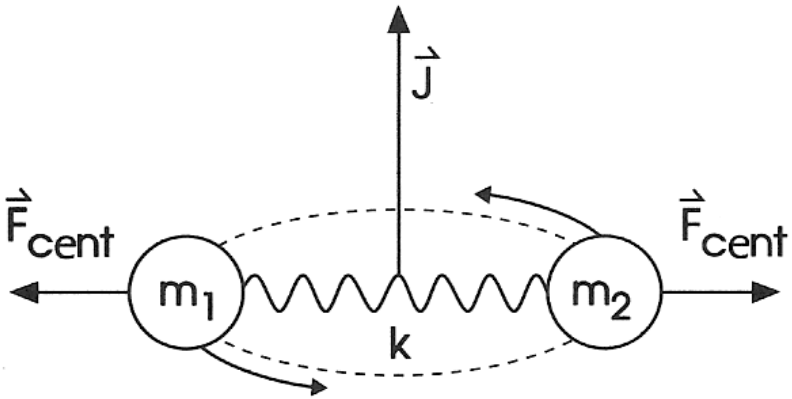
Figure 8.8. Pure rotational spectrum of CO, reproduced with permission from *Modern Aspects of Microwave Spectroscopy*, ed. G. W. Chantry, Academic Press, 1979.

Rotation in a diatomic molecule: the non-rigid rotator

When molecules rotate, the nuclei are submitted to centrifugal forces which increase the distance between them, and increase the moment of inertia and thus decrease the rotational constant *B*



Rotation in a diatomic molecule: the non-rigid rotator



The rotational energy is given by

$$E_{rot} = B\,J\,(J+1) - D\,J^2\,(J+1)^2$$

centrifugal distortion constant

Now frequencies are given by

$$\nu = 2B\,(J+1) - 4D\,(J+1)^3$$

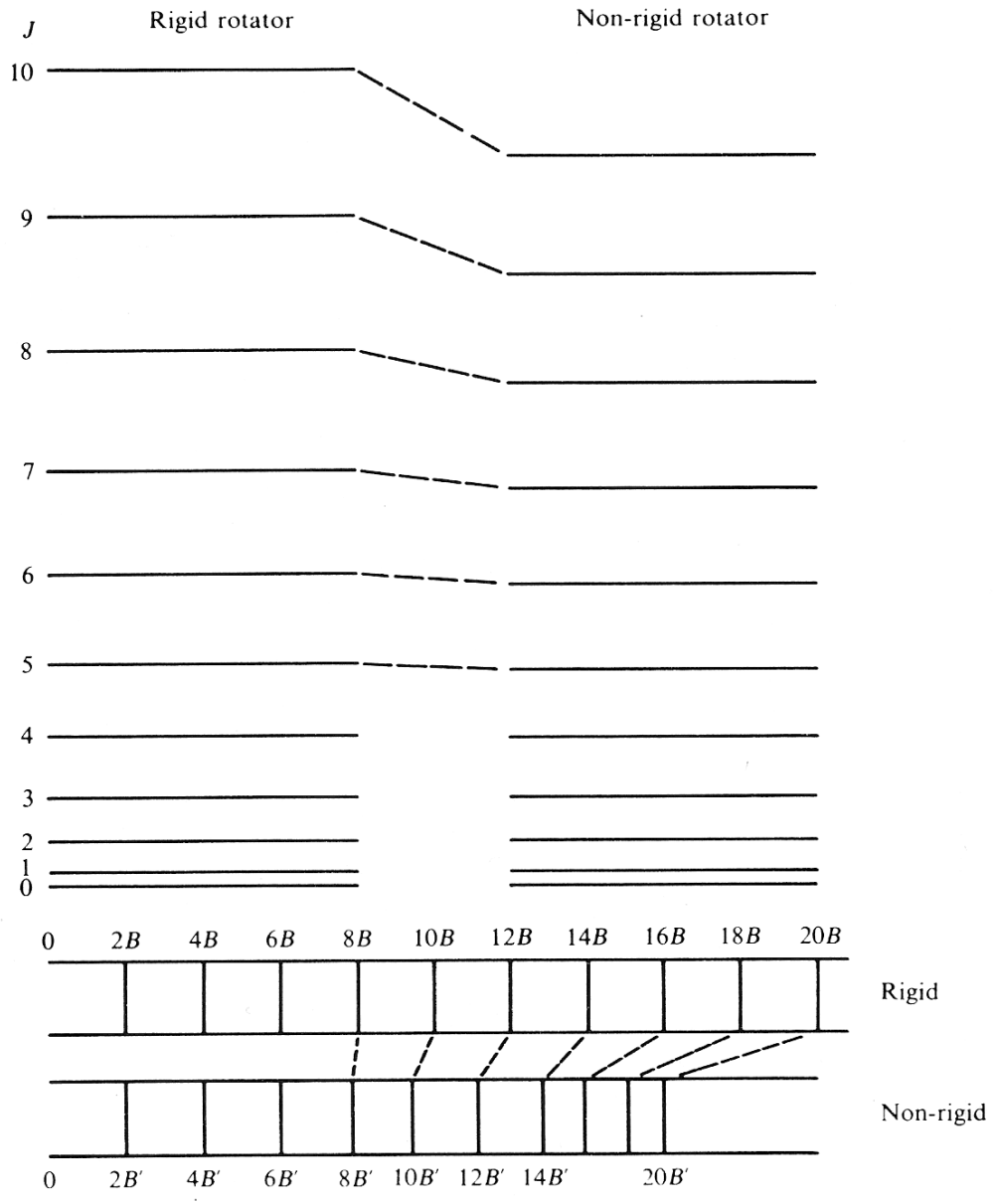
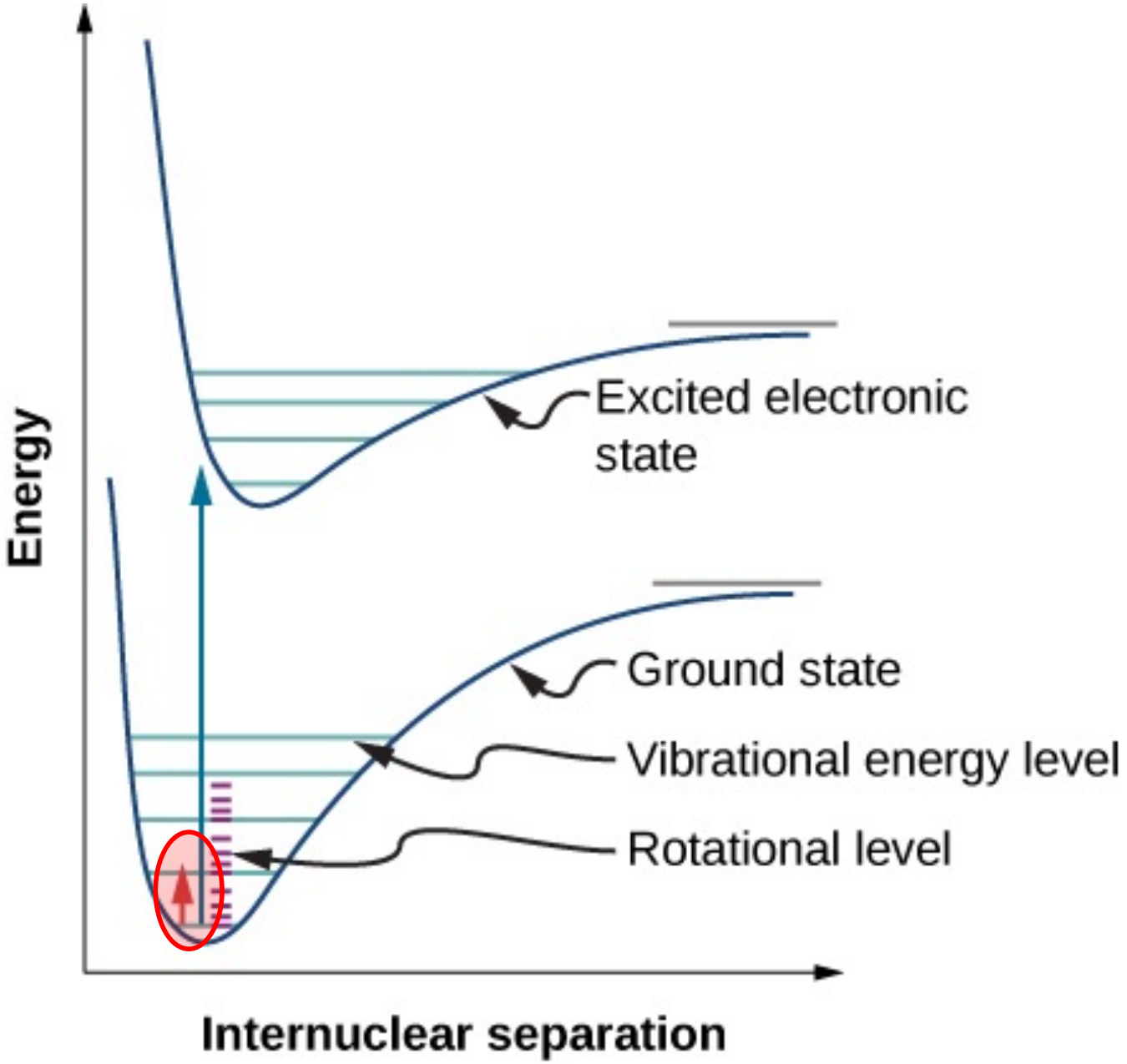


Figure 2.9 The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D = 10^{-3}B$.

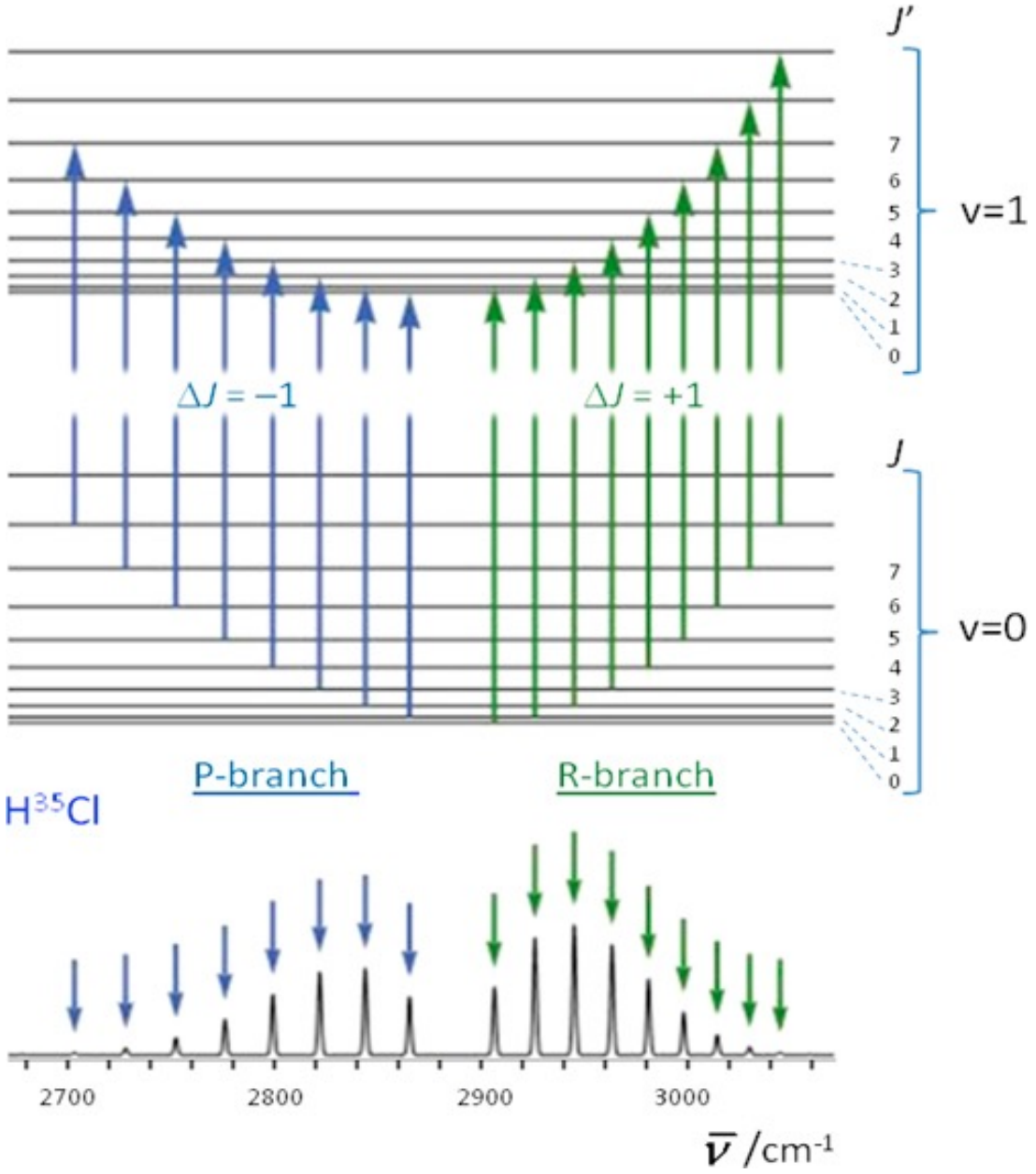
Concluding remarks

Molecular spectroscopy: Energy levels and transitions



Rovibrational spectrum

A vibrational transition (band) consists of multiple rotational transitions



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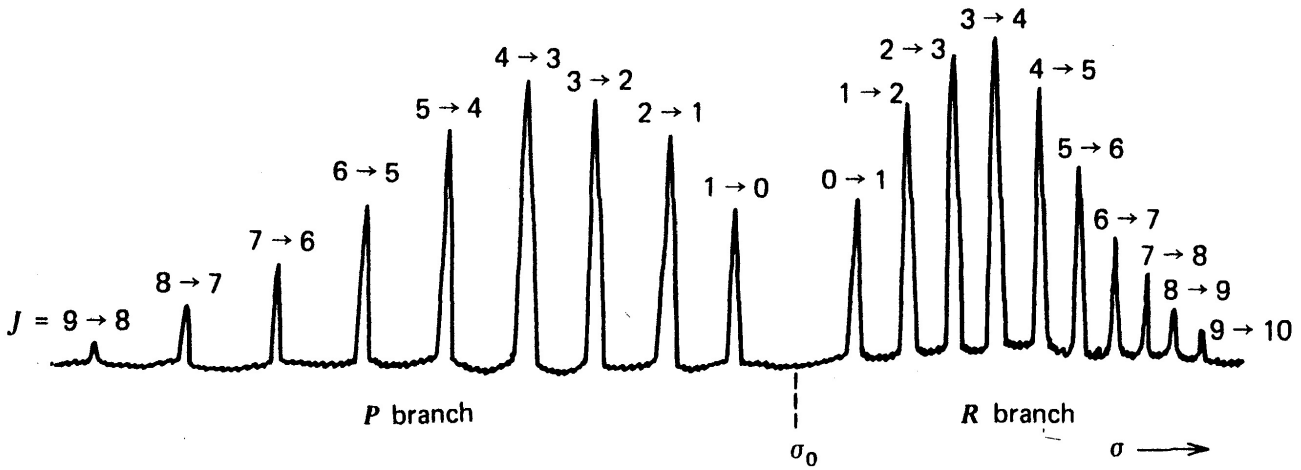


Fig. 4.9 Rotational fine structure of a vibration–rotation band of a diatomic molecule. Note the decreasing spacing with increasing J in the R branch, and the increasing spacing with increasing J in the P branch.

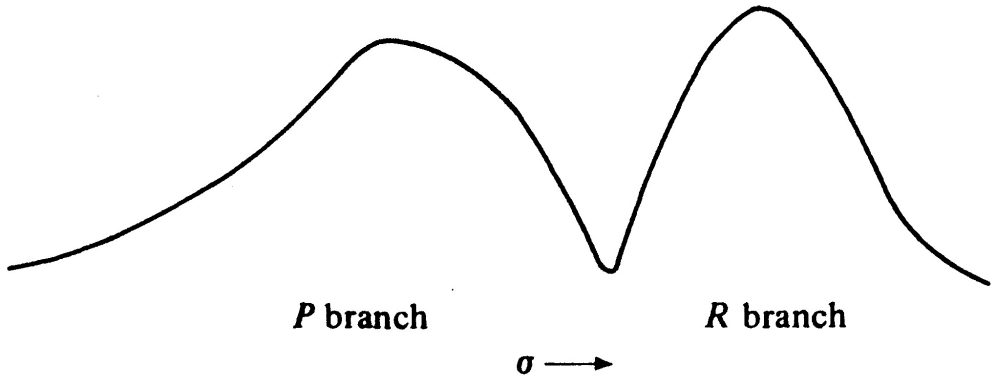
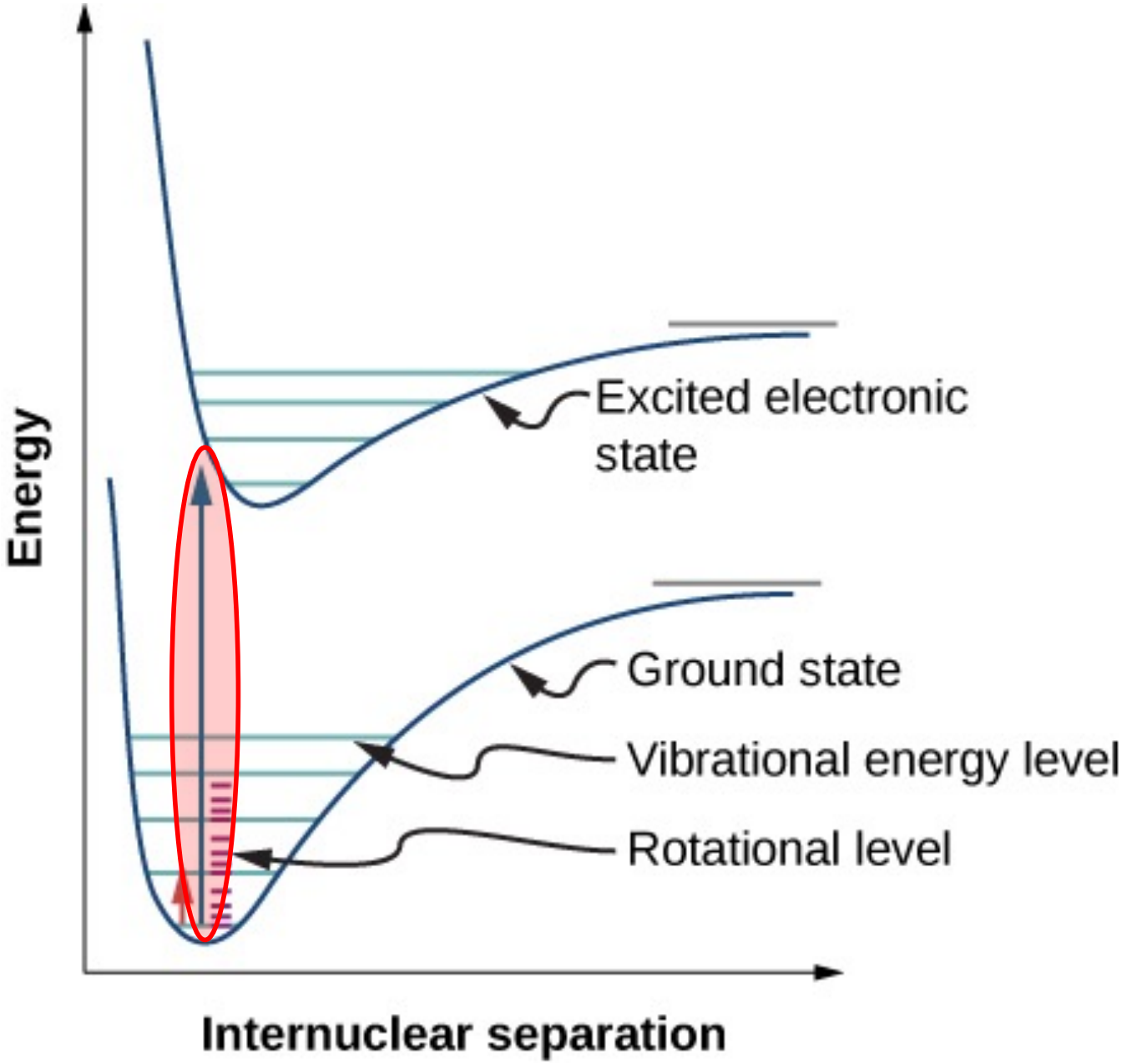


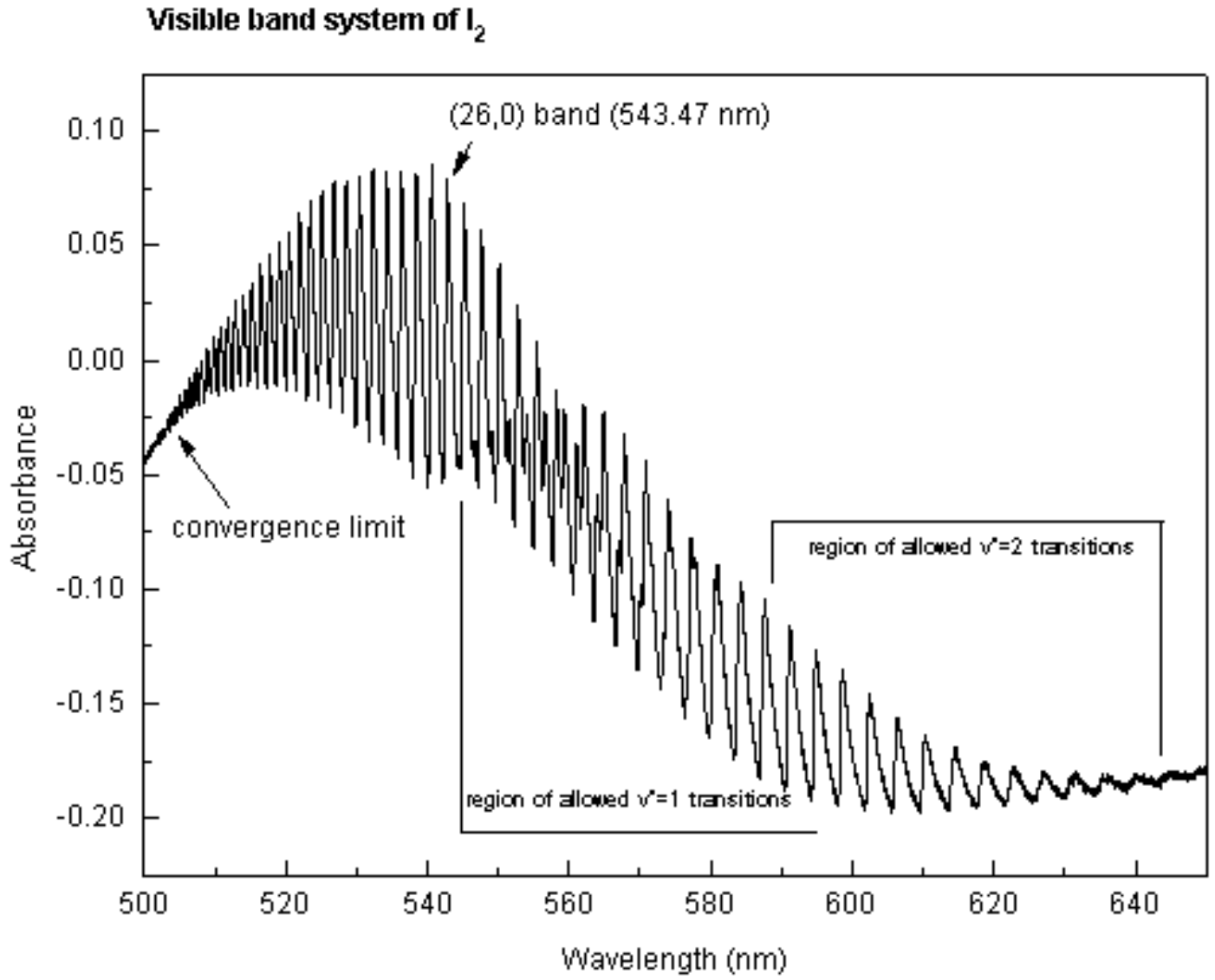
Fig. 4.10 Appearance of a vibration–rotation band of a diatomic molecule under low resolution.

Molecular spectroscopy: Energy levels and transitions



Electronic spectrum

An electronic transition do also have vibration and rotation structure

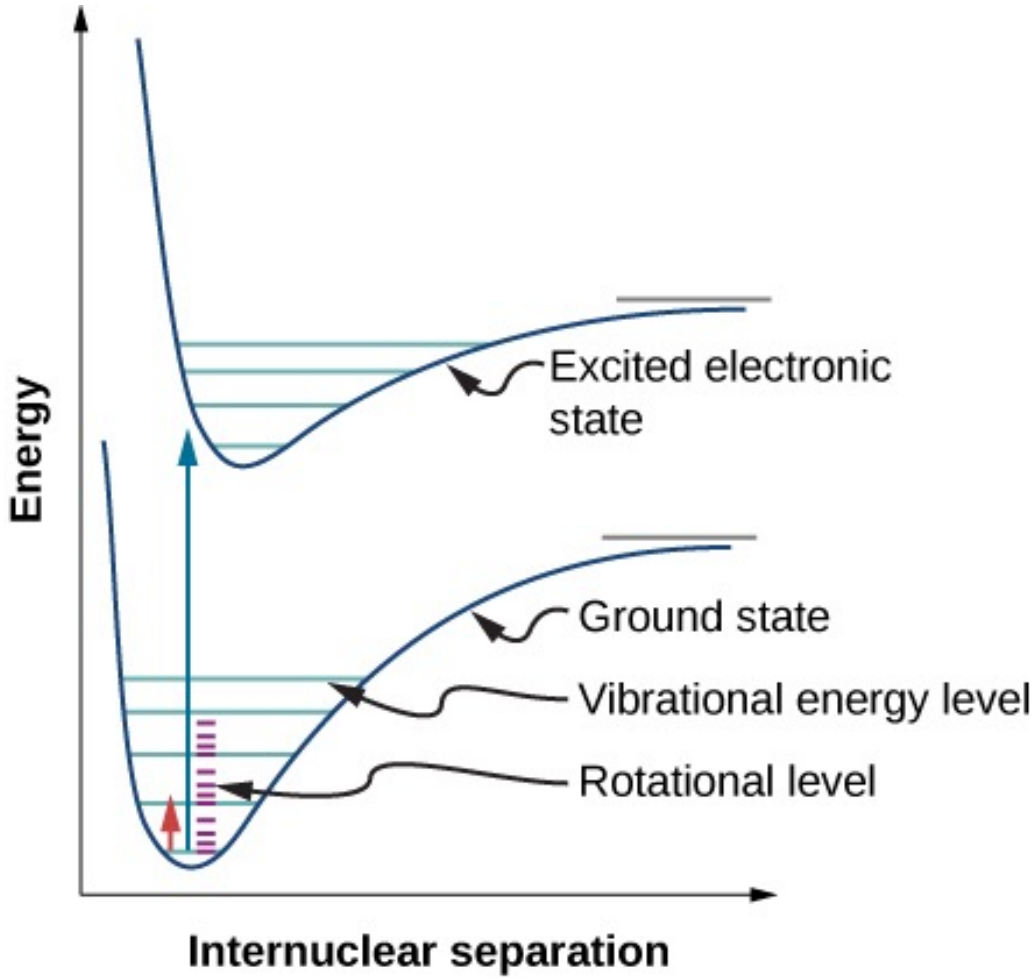


Molecular spectroscopy: Times involved

Electrons:
attosec scales
10^{18} /sec

Vibration:
CO v=0
10^{14} /sec

Rotation:
CO J=1
10^{11} /sec



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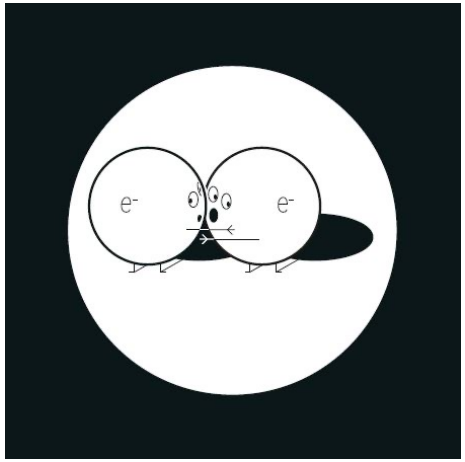


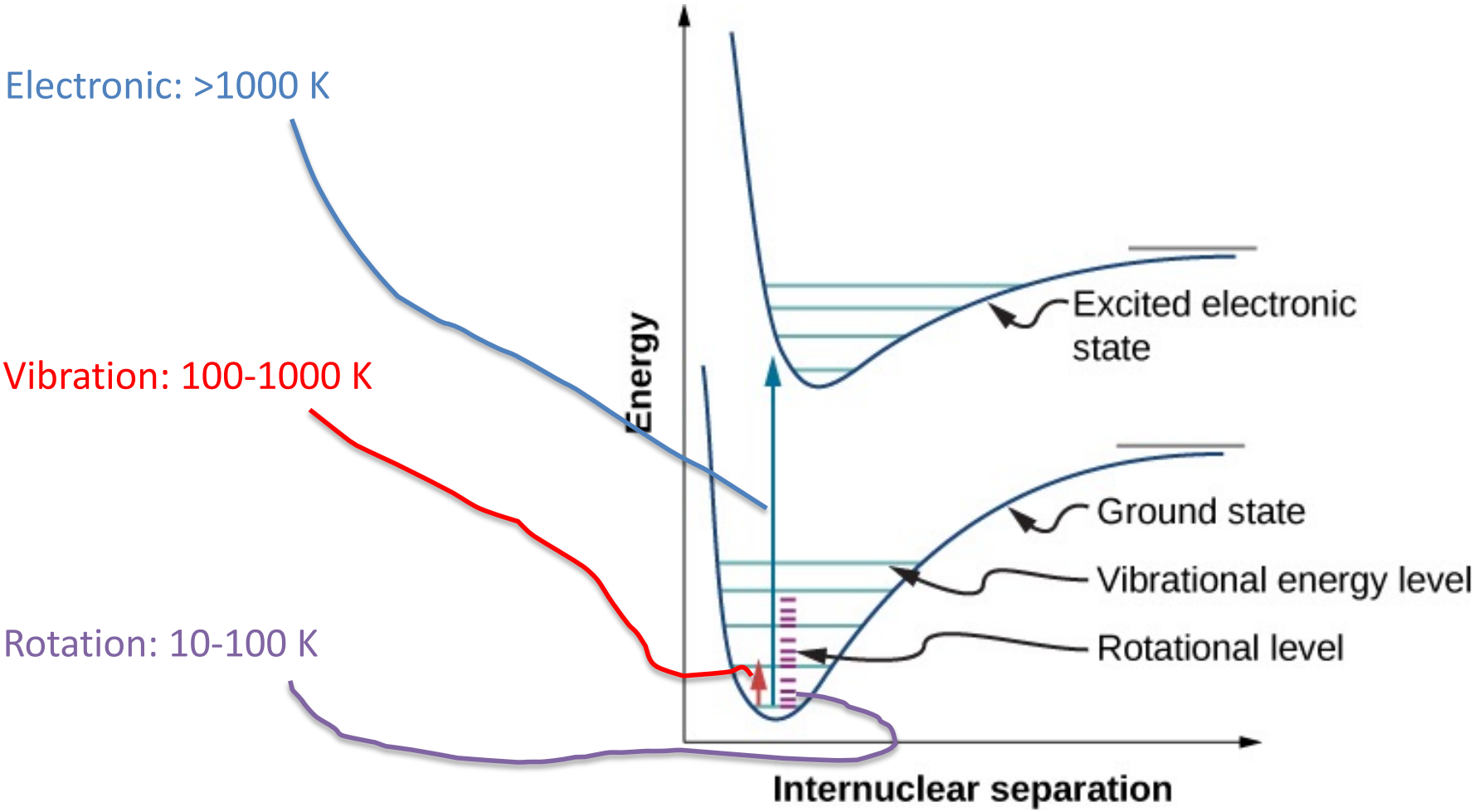
The Nobel Prize in Physics 2023

Ill. Niklas Elmehed © Nobel Prize Outreach
Pierre Agostini

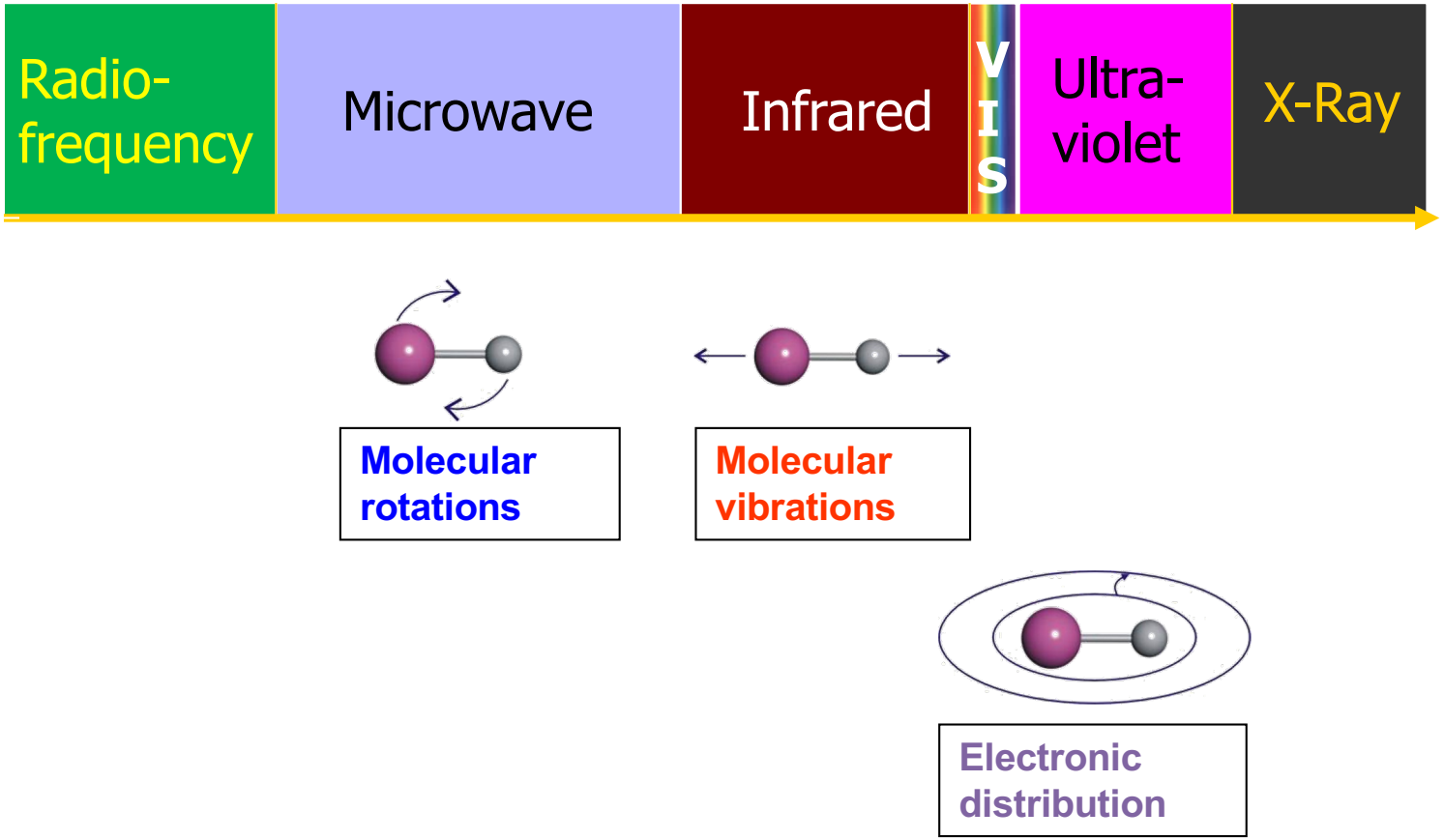
Ill. Niklas Elmehed © Nobel Prize Outreach
Ferenc Krausz

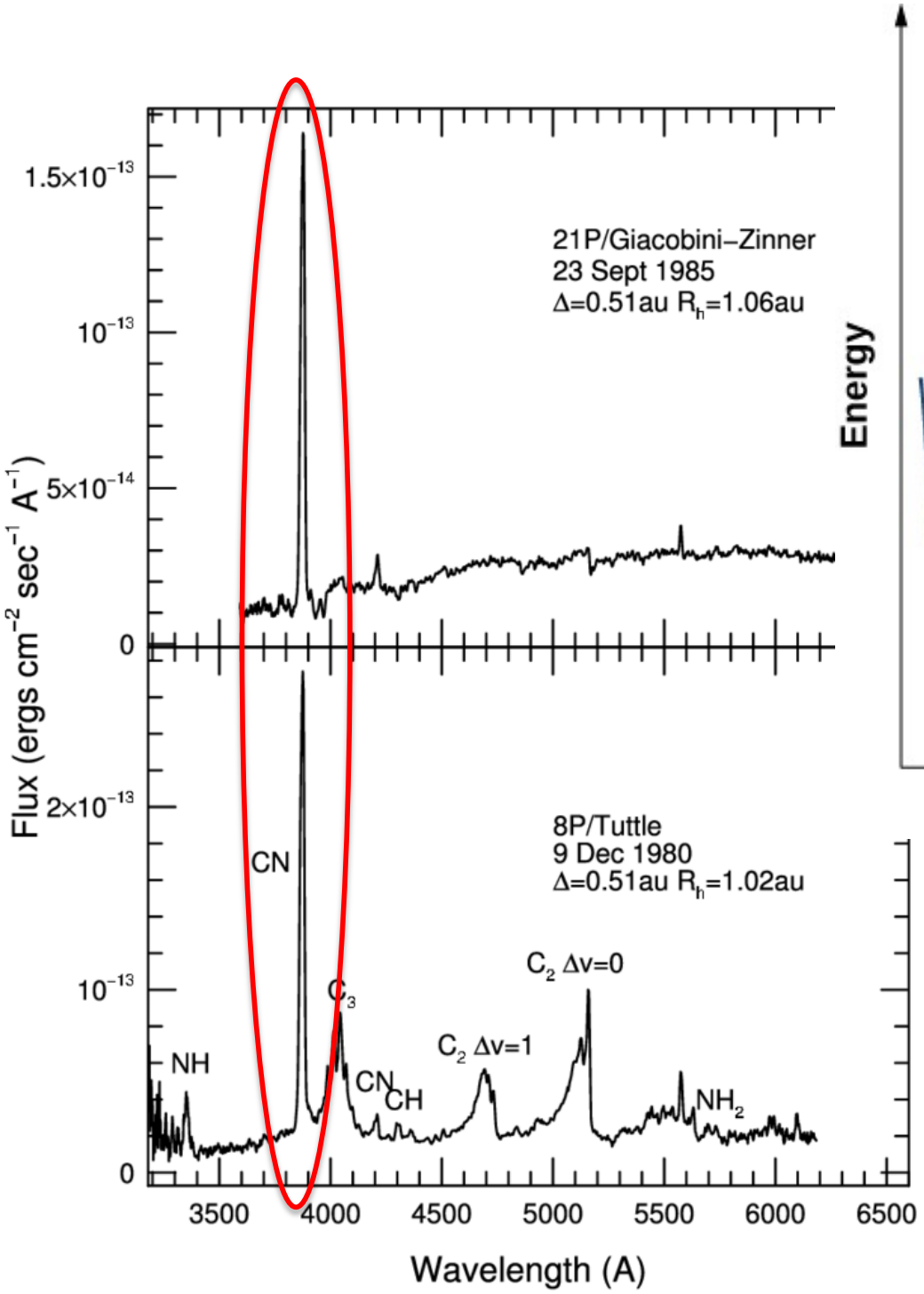
Ill. Niklas Elmehed © Nobel Prize Outreach
Anne L'Huillier

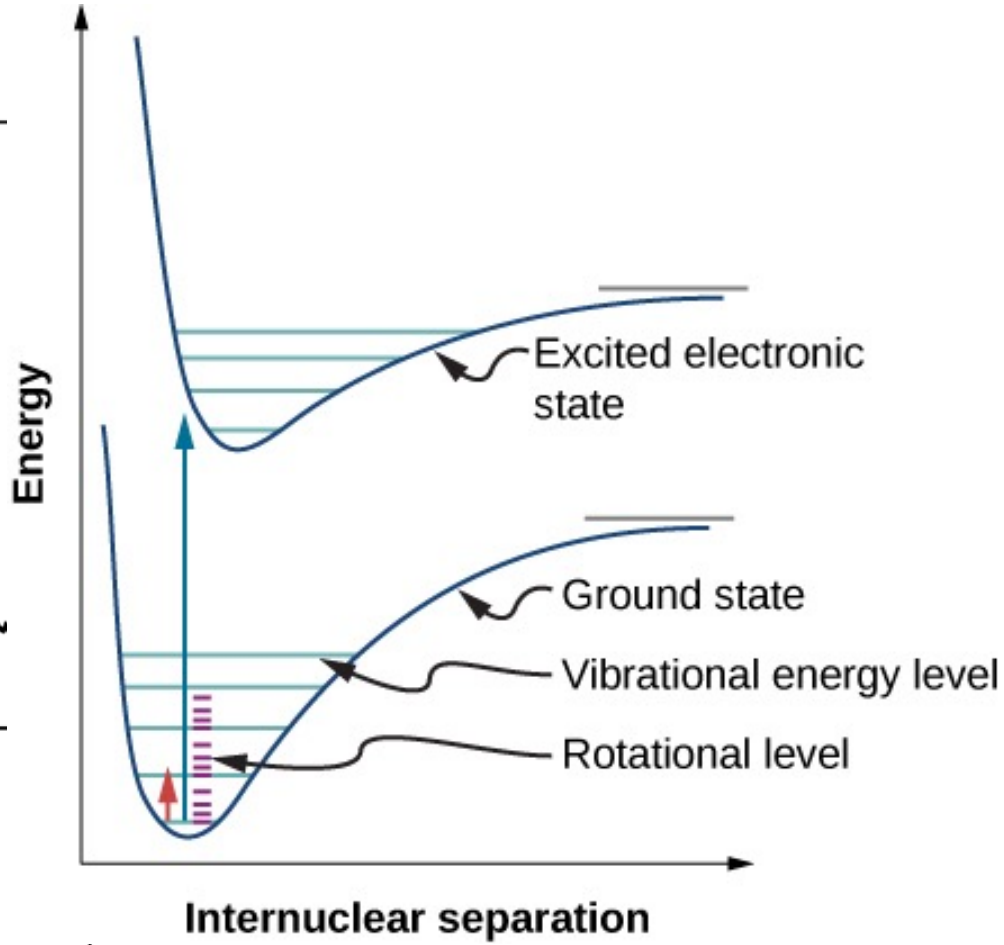
Molecular spectroscopy: Energies involved

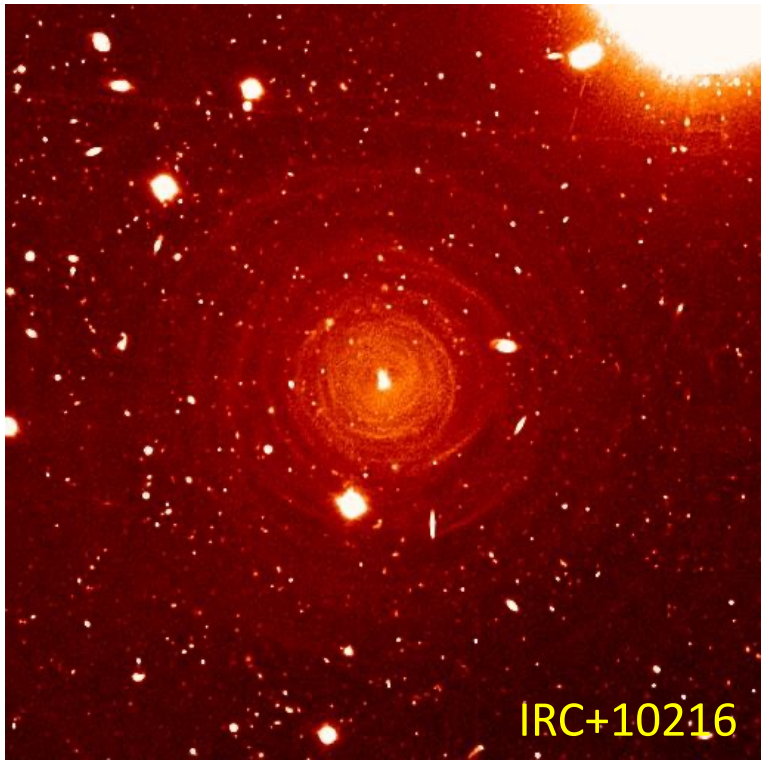


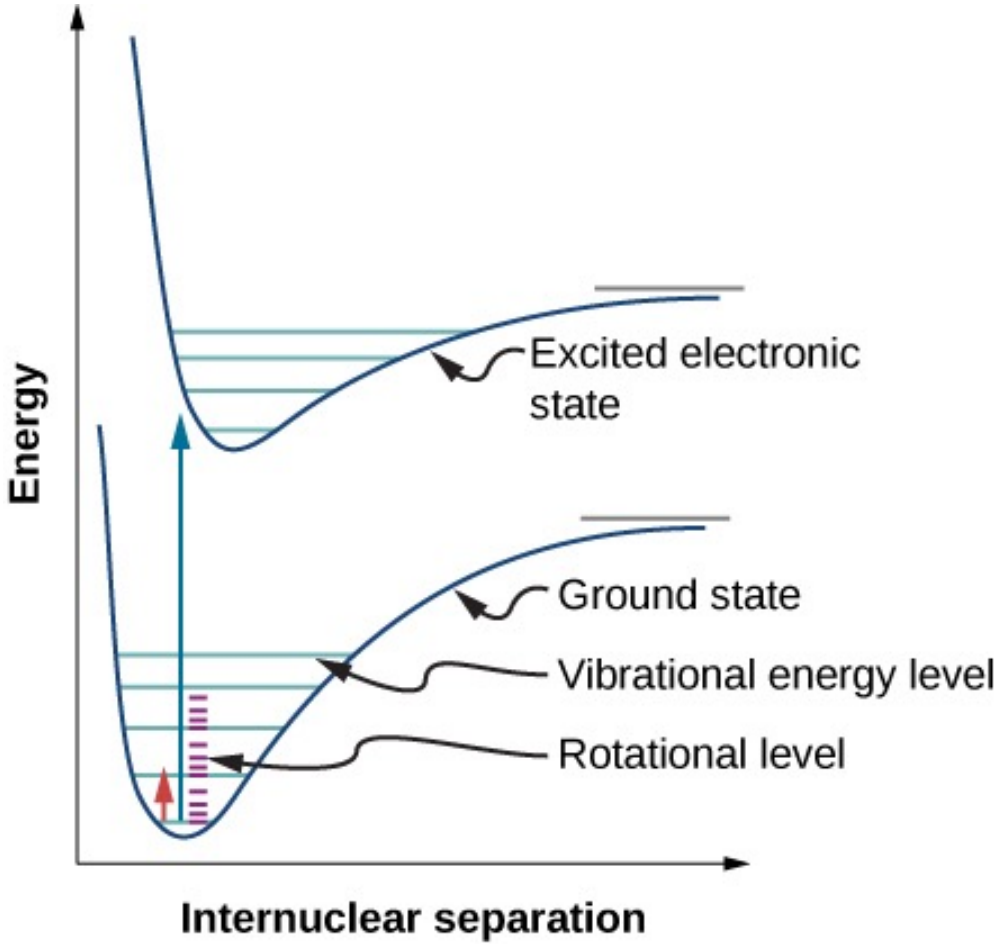
Types of molecular transitions across the electromagnetic spectrum

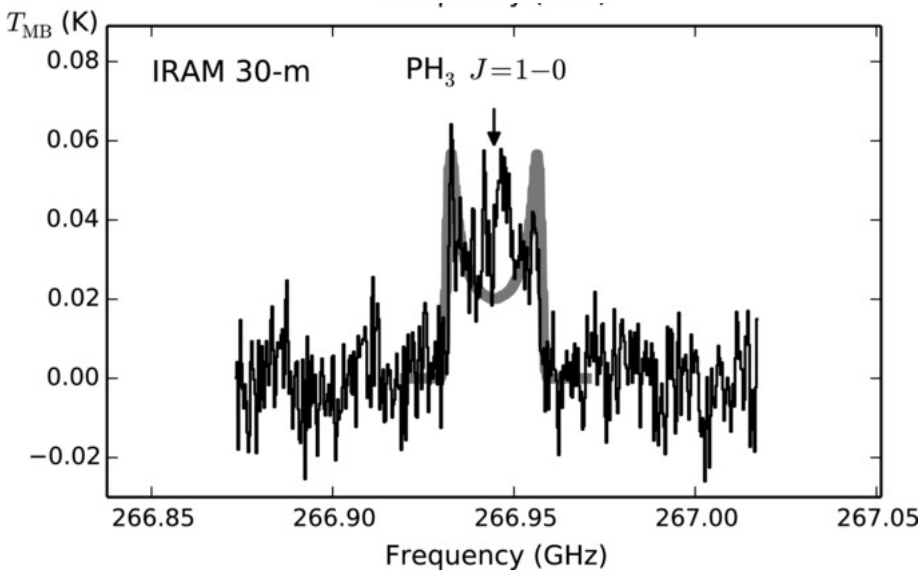



21P/Giacobini–Zinner
23 Sept 1985
Δ=0.51au R_h=1.06au
8P/Tuttle
9 Dec 1980
Δ=0.51au R_h=1.02au
Flux (ergs cm^-2 sec^-1 A^-1)
1.5×10^-13
10^-13
5×10^-14
0
2×10^-13
10^-13
0
CN
C3
NH
CN
CH
C2 Δv=1
C2 Δv=0
NH2
3500
4000
4500
5000
5500
6000
6500
Wavelength (A)

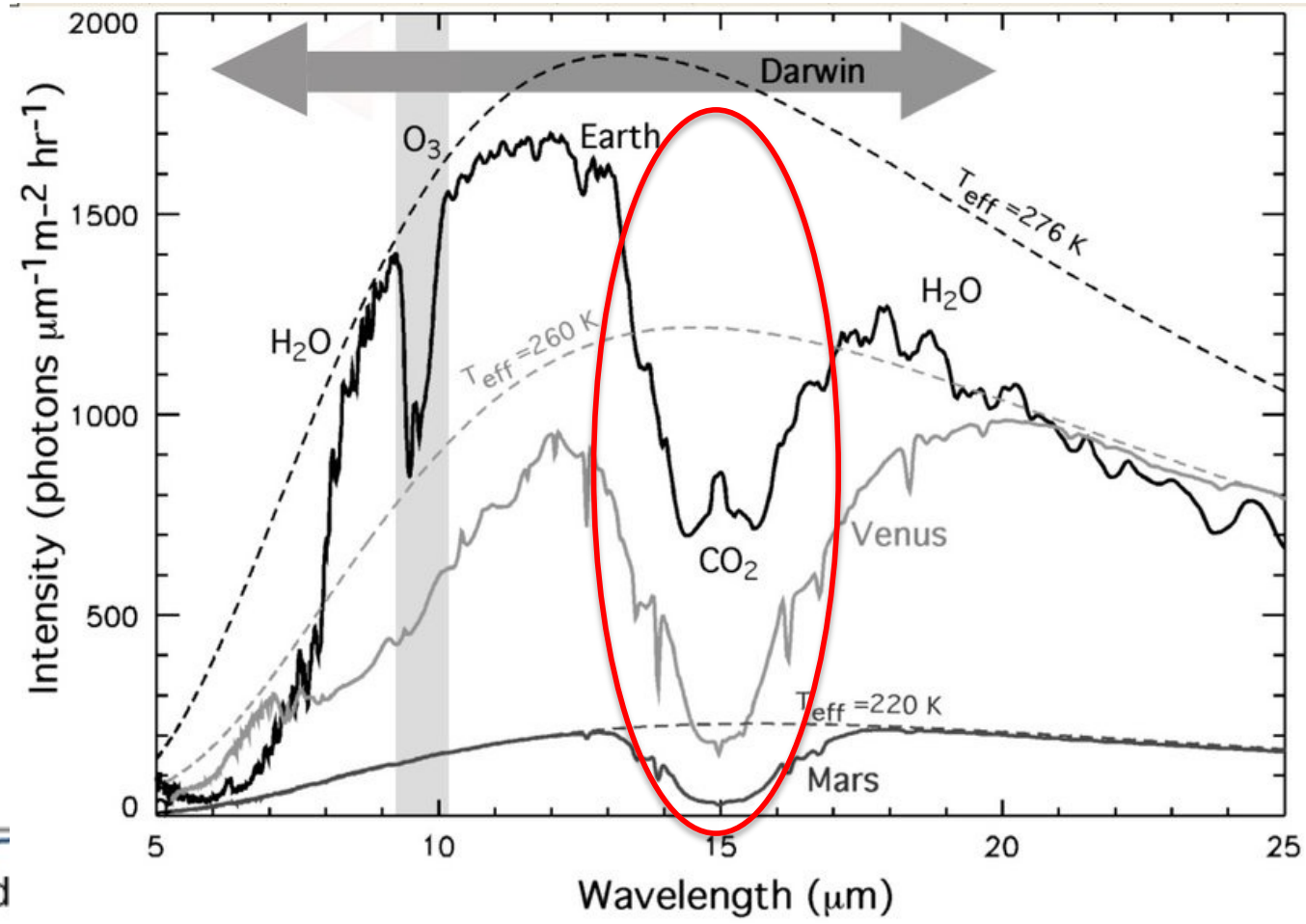

Energy
Excited electronic state
Ground state
Vibrational energy level
Rotational level
Internuclear separation

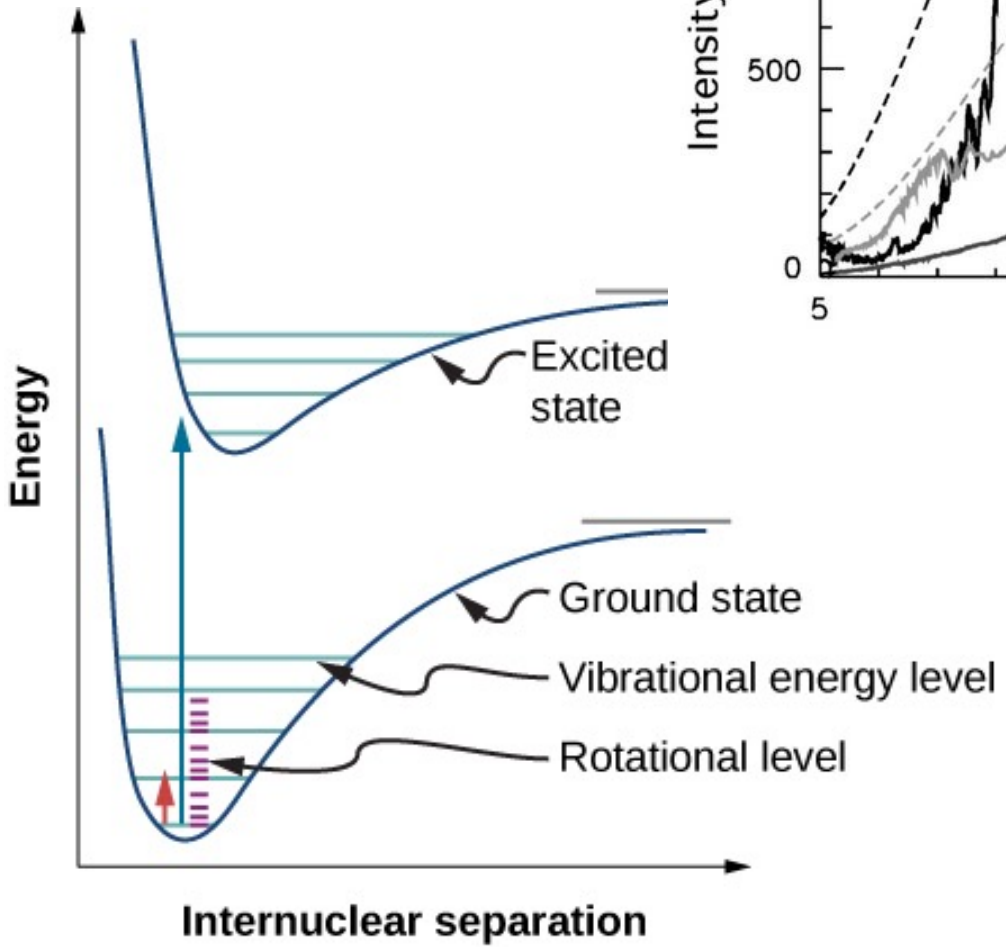


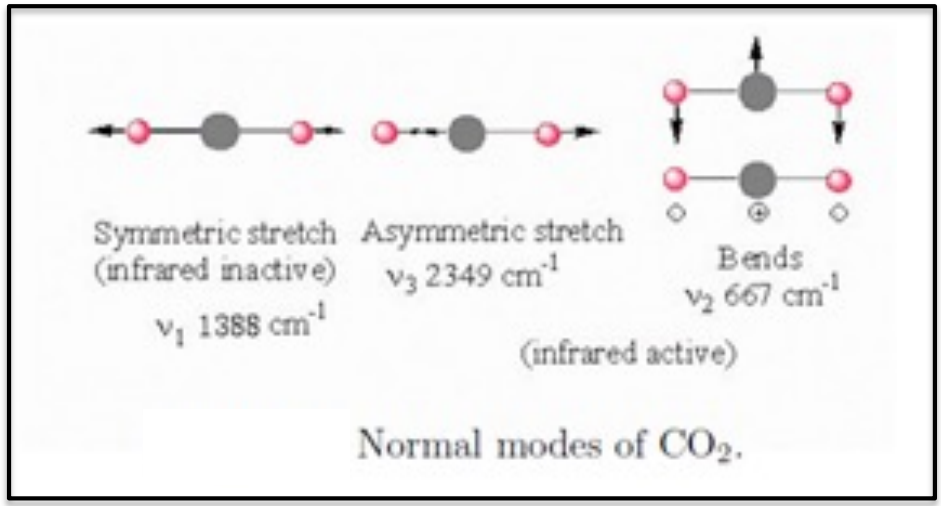




1.112 1.123 $wavelength\ (mm)$


Darwin
O_3
Earth
T_{eff} =276 K
H_2O
H_2O
T_{eff} =260 K
CO_2
Venus
T_{eff} =220 K
Mars
Intensity (photons μm^{-1}m^{-2} hr^{-1})
Wavelength (μm)
0
500
1000
1500
2000
5
10
15
20
25


Energy
Excited state
Ground state
Vibrational energy level
Rotational level
Internuclear separation


Symmetric stretch
(infrared inactive)
ν_1 1388 cm^{-1}
Asymmetric stretch
ν_3 2349 cm^{-1}
(infrared active)
Bends
ν_2 667 cm^{-1}
Normal modes of CO_2.