Introduction to Molecular Spectroscopy

José Pablo Fonfría
jpablo.fonfria@csic.es

Instituto de Física Fundamental (IFF)
Consejo Superior de Investigaciones Científicas (CSIC)

UAM Master in Astrophysics
Radiative Processes in Astrophysics

Madrid, 9 October 2025

INSTITUTO DE FÍSICA FUNDAMENTAL

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Outline

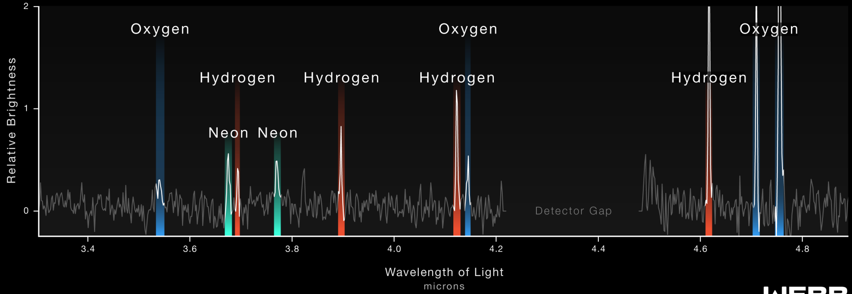
Outline

DISTANT GALAXY BEHIND SMACS 0723

WEBB SPECTRUM SHOWCASES GALAXY'S COMPOSITION

NIRCam Imaging

NIRSpec Microshutter Array Spectroscopy

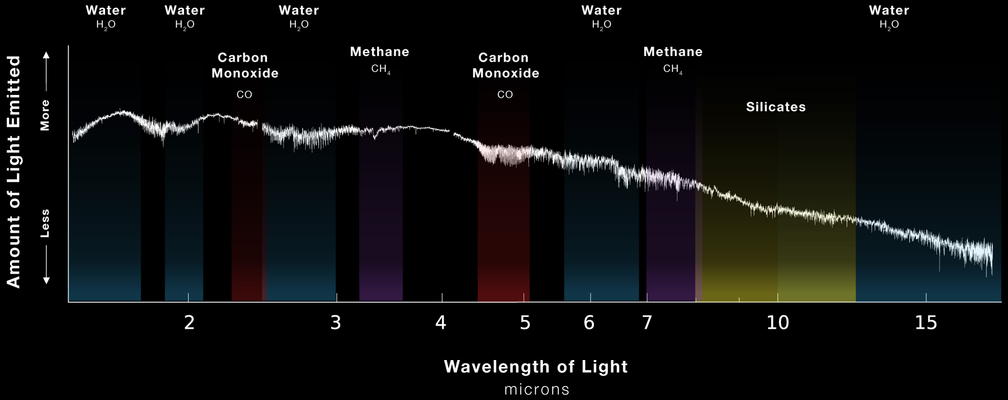


WEBB SPACE TELESCOPE

EXOPLANET VHS 1256 b

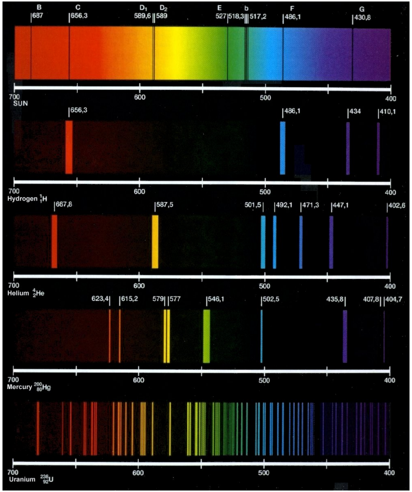
EMISSION SPECTRUM

NIRSpec and MIRI | IFU Medium-Resolution Spectroscopy



WEBB SPACE TELESCOPE

ATOMIC SPECTRA



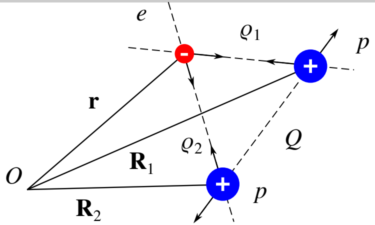
Do we have something similar for molecules?

⬇

YES

Outline

The molecular Hamiltonian: H_2^+, the simplest molecule [3, 4, 5, 6, 8]

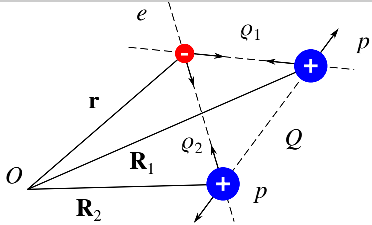


- Schrödinger's equation: $H\Psi = E\Psi$
- H_2^+ is the only molecule for which the Schrödinger's equation can be analytically solved
- The problem for the rest of the molecules is much harder

$$H = T_n + T_e + V_{n-n} + V_{n-e} + V_{e-e}$$

$$H(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}) = -\frac{\hbar^2}{2m_p}\sum_{i=1}^{2}\nabla_{R,i}^2 - \frac{\hbar^2}{2m_e}\nabla_r^2 + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{2}\frac{1}{|\mathbf{R}_i - \mathbf{r}|} + \text{nothing}$$

- Schrödinger's equation: $H\Psi = E\Psi$
- H_2^+ is the only molecule for which the Schrödinger's equation can be analytically solved
- The problem for the rest of the molecules is much harder



$$H = T_n + T_e + V_{n-n} + V_{n-e} + V_{e-e}$$

$$H(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}) = -\frac{\hbar^2}{2m_p}\sum_{i=1}^{2}\nabla^2_{R,i} - \frac{\hbar^2}{2m_e}\nabla^2_r + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{2}\frac{1}{|\mathbf{R}_i - \mathbf{r}|} + \text{nothing}$$

BORN-OPPENHEIMER APPROXIMATION

1. Electrons are about 2000 times lighter than protons and adapts to the nuclei movement ($\mathbf{R}_1$ and $\mathbf{R}_2$ are fixed parameters):

$$H_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \simeq T_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) + V_{n-e}(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$
$$H_e\psi_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \simeq E_e(\mathbf{R}_1, \mathbf{R}_2)\psi_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$

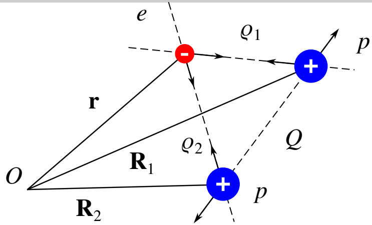
2. Nuclei move in an electronic potential $E_e(\mathbf{R}_1, \mathbf{R}_2)$ ($\mathbf{R}_i$ not fixed anymore):

$$H_n(\mathbf{R}_1, \mathbf{R}_2) \simeq T_n(\mathbf{R}_1, \mathbf{R}_2) + V_{n-n}(\mathbf{R}_1, \mathbf{R}_2) + E_e(\mathbf{R}_1, \mathbf{R}_2)$$
$$H_n\phi_n(\mathbf{R}_1, \mathbf{R}_2) \simeq E_n\phi_n(\mathbf{R}_1, \mathbf{R}_2)$$

Update V_{n-e} and ITERATE!!!

Outline

The molecular Hamiltonian: H_2^+, the simplest molecule [3, 4, 5, 6, 8]



- Schrödinger's equation: $H\Psi = E\Psi$
- H_2^+ is the only molecule for which the Schrödinger's equation can be analytically solved
- The problem for the rest of the molecules is much harder

$$H = T_n + T_e + V_{n-n} + V_{n-e} + V_{e-e}$$

$$H(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}) = -\frac{\hbar^2}{2m_p}\sum_{i=1}^{2}\nabla^2_{R,i} - \frac{\hbar^2}{2m_e}\nabla^2_r + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{2}\frac{1}{|\mathbf{R}_i - \mathbf{r}|} + \text{nothing}$$

BORN-OPPENHEIMER APPROXIMATION

1. Electrons are about 2000 times lighter than protons and adapts to the nuclei movement ($\mathbf{R}_1$ and $\mathbf{R}_2$ are fixed parameters):

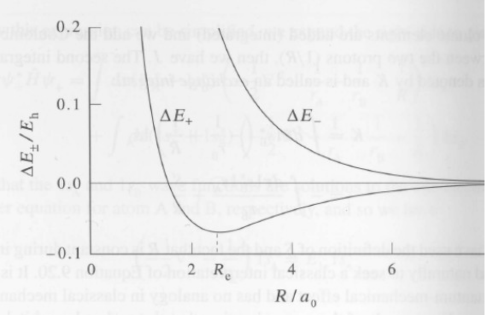
$$H_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \simeq T_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) + V_{n-e}(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$
$$H_e\psi_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \simeq E_e(\mathbf{R}_1, \mathbf{R}_2)\psi_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$

2. Nuclei move in an electronic potential $E_e(\mathbf{R}_1, \mathbf{R}_2)$ ($\mathbf{R}_i$ not fixed anymore):

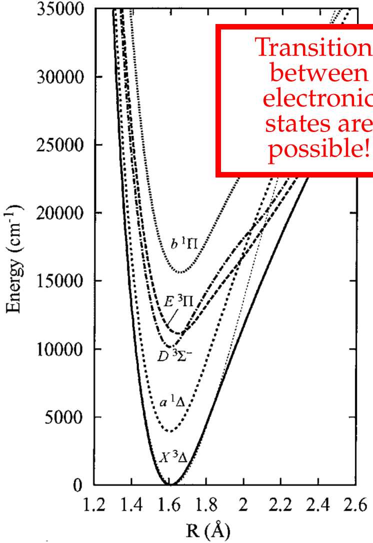
$$H_n(\mathbf{R}_1, \mathbf{R}_2) \simeq T_n(\mathbf{R}_1, \mathbf{R}_2) + V_{n-n}(\mathbf{R}_1, \mathbf{R}_2) + E_e(\mathbf{R}_1, \mathbf{R}_2)$$
$$H_n\phi_n(\mathbf{R}_1, \mathbf{R}_2) \simeq E_n\phi_n(\mathbf{R}_1, \mathbf{R}_2)$$

Electronic potentials (electronic states) [5, 6]

- The lower energy electronic potential for H_2^+ allows for bound states but the higher energy one prevents the molecule to exist
- The electronic potentials for simple molecules with more electrons can be quite complex
- Molecules with more atoms have electronic potential energy surfaces depending on several coordinates



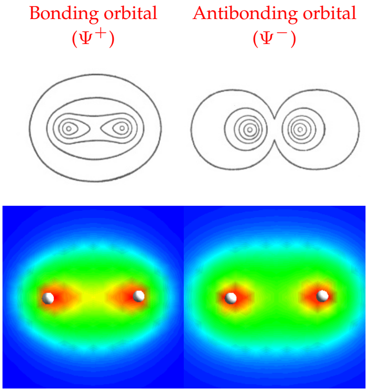
Electronic potentials for H_2^+



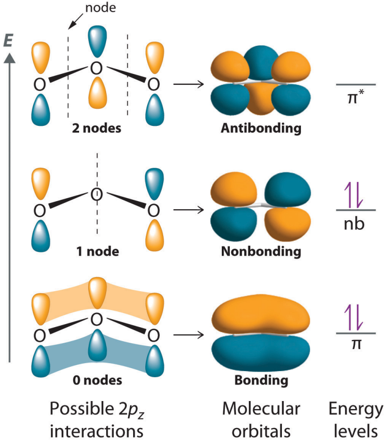
Transitions between electronic states are possible!

Electronic potentials for TiO

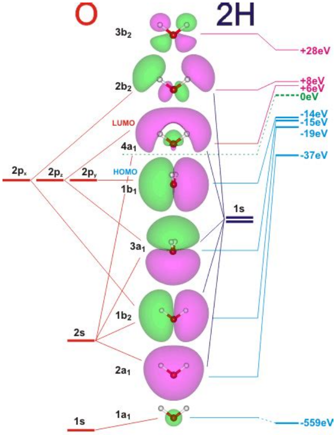
- **Molecular orbitals** are linear combinations of the atomic orbitals
- **Bonding**: Lower energy than the atomic orbitals
- **Anti-bonding**: Higher energy than the atomic orbitals
- **Non-bonding**: Same energy as the atomic orbitals



Orbitals for the H_2^+ molecule



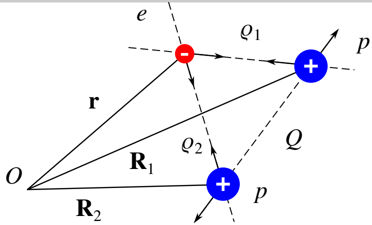
Several orbitals for ozone (O_3)



Several orbitals for water (H_2O)

Outline

The molecular Hamiltonian: H_2^+, the simplest molecule



- Schrödinger's equation: $H\Psi = E\Psi$
- H_2^+ is the only molecule for which the Schrödinger's equation can be analytically solved
- The problem for the rest of the molecules is much harder

$$H = T_n + T_e + V_{n-n} + V_{n-e} + V_{e-e}$$

$$H(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}) = -\frac{\hbar^2}{2m_p}\sum_{i=1}^{2}\nabla^2_{R,i} - \frac{\hbar^2}{2m_e}\nabla^2_r + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{2}\frac{1}{|\mathbf{R}_i - \mathbf{r}|} + \text{nothing}$$

BORN-OPPENHEIMER APPROXIMATION

1. Electrons are about 2000 times lighter than protons and adapts to the nuclei movement ($\mathbf{R}_1$ and $\mathbf{R}_2$ are fixed parameters):

$$H_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \simeq T_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) + V_{n-e}(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$
$$H_e\psi_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2) \simeq E_e(\mathbf{R}_1, \mathbf{R}_2)\psi_e(\mathbf{r}; \mathbf{R}_1, \mathbf{R}_2)$$

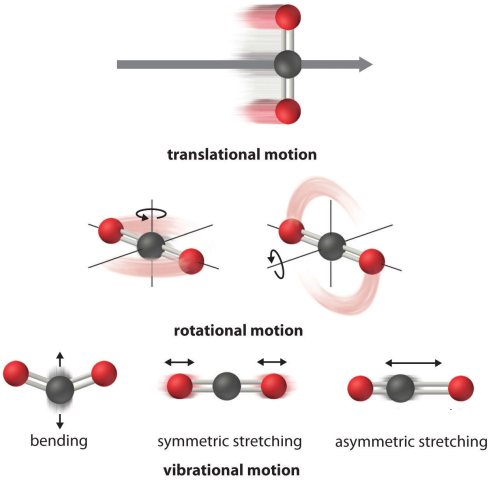
2. Nuclei move in an electronic potential $E_e(\mathbf{R}_1, \mathbf{R}_2)$ ($\mathbf{R}_i$ not fixed anymore):

$$H_n(\mathbf{R}_1, \mathbf{R}_2) \simeq T_n(\mathbf{R}_1, \mathbf{R}_2) + V_{n-n}(\mathbf{R}_1, \mathbf{R}_2) + E_e(\mathbf{R}_1, \mathbf{R}_2)$$
$$H_n\phi_n(\mathbf{R}_1, \mathbf{R}_2) \simeq E_n\phi_n(\mathbf{R}_1, \mathbf{R}_2)$$

- As a bound ensemble of nuclei, a molecule can rotate in space as a rigid rotor and move across space
- They can also vibrate as charged particles in a electrostatic potential
- Rotation and vibration are coupled but at low energies they can be studied separately as rotation is usually much slower than vibration
- As for the Born-Oppenheimer approximation:

$$\begin{aligned} H_n(\mathbf{R}_{\mathrm{CM}}, \alpha, \beta, \gamma, \{\mathbf{P}_i\}_{i=1}^{3N-6}) \simeq\ & H_{\mathrm{trans}}(\mathbf{R}_{\mathrm{CM}}) \\ & + H_{\mathrm{vib}}(\{\mathbf{Q}_i\}_{i=1}^{3N-6}) \\ & + H_{\mathrm{rot}}(\alpha, \beta, \gamma), \end{aligned}$$

  where $\mathbf{R}_{\mathrm{CM}}$ are the coordinates of the mass center, (α, β, γ) are the Euler angles to describe the rotation of a solid, and $\{\mathbf{Q}_i\}_{i=1}^{3N-6}$ are the internal normal coordinates for the nuclei
- For a molecule with N atoms, $3N-6$ is the number of normal modes of vibration ($3N-5$ for a linear molecule; degeneration can exist)

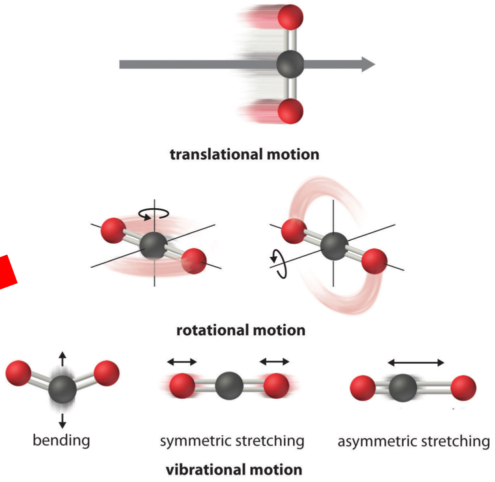


Nuclear motions: Translation, vibration, rotation

- As a bound ensemble of nuclei, a molecule can rotate in space as a rigid rotor and move across space
- They can also vibrate as charged particles in a electrostatic potential
- Rotation and vibration are coupled but at low energies they can be studied separately as rotation is usually much slower than vibration
- As for the Born-Oppenheimer approximation:

$$
\begin{aligned}
H_n(\mathbf{R}_{\mathrm{CM}}, \alpha, \beta, \gamma, \{\mathbf{P}_i\}_{i=1}^{3N-6}) \simeq\ & \cancel{H_{\mathrm{trans}}(\mathbf{R}_{\mathrm{CM}})} \\
& + H_{\mathrm{vib}}(\{\mathbf{Q}_i\}_{i=1}^{3N-6}) \\
& + H_{\mathrm{rot}}(\alpha, \beta, \gamma),
\end{aligned}
$$

  where $\mathbf{R}_{\mathrm{CM}}$ are the coordinates of the mass center, (α, β, γ) are the Euler angles to describe the rotation of a solid, and $\{\mathbf{Q}_i\}_{i=1}^{3N-6}$ are the internal normal coordinates for the nuclei
- For a molecule with N atoms, $3N-6$ is the number of normal modes of vibration ($3N-5$ for a linear molecule; degeneration can exist)

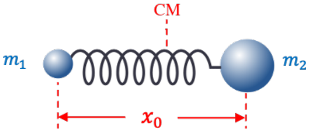


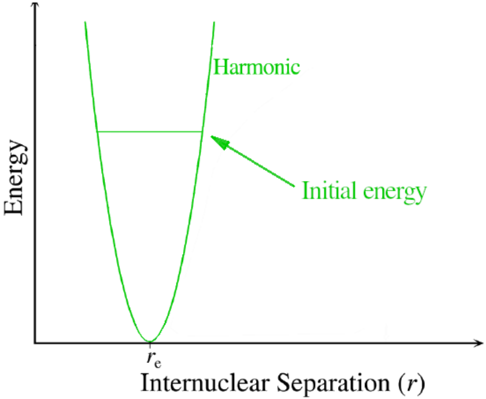
- Classical mechanics:
  - Hooke's law + Newton's laws:

$$F = -k(x - x_0) \quad \Longrightarrow \quad V = \frac{1}{2}k(x - x_0)^2$$

$$\omega_{\text{osc}} = \sqrt{\frac{k}{\mu}} \quad \Longleftrightarrow \quad \nu_{\text{osc}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

  - Continuous energy determined by initial conditions





- Quantum mechanics:
  - Schrödinger's equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right]\psi_{\text{vib}}=E_{\text{vib}}\psi_{\text{vib}},$$

    where x is related to the CM coordinate
  - Quantized energy:

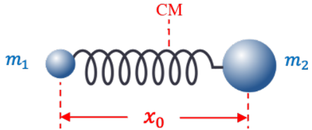
$$E_v=h\nu_e\left(v+\frac{1}{2}\right)=\hbar\omega_e\left(v+\frac{1}{2}\right),\quad v=0,1,2,\ldots$$

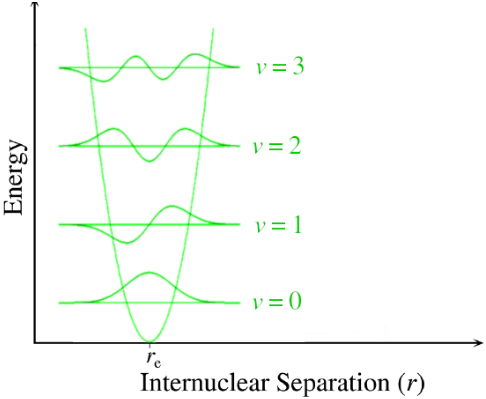
  - $E_0=\frac{1}{2}\hbar\omega_e\neq 0$ (quantum vacuum energy)
  - Transitions between states are possible:

$$E_{v+1}-E_v=h\nu_e=\hbar\omega_e$$

  - Selection rules: $\Delta v=\pm 1$

Reality is more complex!





- Quantum mechanics:
  - Schrödinger's equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V_{\text{Morse}}(x)\right]\psi_{\text{vib}} = E_{\text{vib}}\psi_{\text{vib}},$$

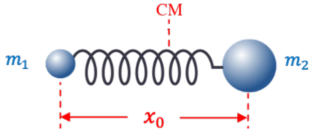
  where x is related to the CM coordinate
  - Morse potential:

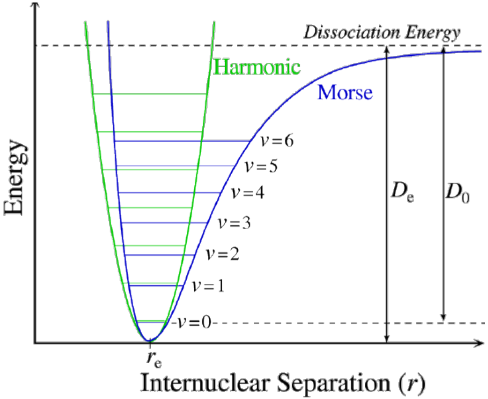
$$V_{\text{Morse}}(x) = D_e\left(1 - e^{-ax}\right)^2$$

  - Quantized energy:

$$E_v = \hbar\omega_e\left(v + \frac{1}{2}\right) - \hbar\omega_e x_e\left(v + \frac{1}{2}\right)^2 + \cdots$$

  - $E_{v+1} - E_v \neq \hbar\omega_e$ (depends on v)
  - Selection rules: $\Delta v = \pm 1, \pm 2, \ldots$
  - The intensity decreases with $|\Delta v|$





Molecule	# atoms	# vib. modes	Type Vib. modes ($\nu_1,\ldots,\nu_n$)	ω_e (cm^{-1})
H_2	2	1	s	4160.9980
CO	2	1	s	2143.2711
SiO	2	1	s	1229.6148
HCN	3	3	s, b, s	3311.4770, 713.461, 2096.8456
H_2O	3	3	s, b, s	3657.0530, 1594.746, 3755.9290
CO_2	3	3	s, b, s	1285.4083, 667.380, 2349.1429
C_2H_2	4	5	3s, 2b	3372.8490, 1974.316, 3294.8390, 612.8710, 730.3320
NH_3	4	4	x, x, x, x	3336.7, 950.4, 3443.8, 1626.7
CH_4	5	4	x, x, x, x	2917.0, 1533.6, 3018.9, 1306.2
HC_3N	5	7	4s, 3b	3327.3708, 2274.000, 2079.0000, 862.0000, 663.2142, 498.8015, 222.4134
CH_3OH	6	12	11x, t	3681, 3000, 2844, 1477, 1455, 1345, 1060, 1033, 2960, 1477
C_2H_6	8	12	2x, s, t, 8x	2953.7, 1388.4, 994.8, 289, 2895.8, 1379.2, 2968.7, 1468.1, ?, 2985.4, 1469, 821.6

Notes.- The unit of wavenumbers ($\tilde{\nu} = \nu/c$) is cm^{-1}. It is a different way of giving frequencies (or energies) very widely used in the IR range. Wavenumbers ($\tilde{\nu}$) are commonly used without the tilde. The vibrational modes can be of stretching (s), bending (b), and torsion (t), in addition to other more complex types, x. Good examples of them are the modes diatomic molecules (stretching), the ν_2 mode of HCN, and the ν_{12} mode of CH_3OH. Not all the vibrational modes are well known, even for not very complex molecules. Energies taken essentially from the NIST (`https://webbook.nist.gov/chemistry/`)

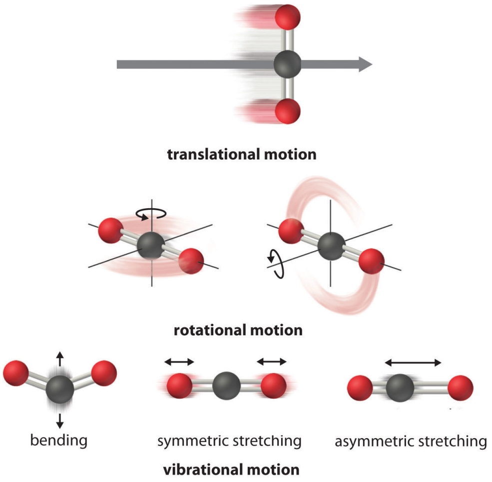
Outline

Nuclear motions: Translation, vibration, rotation

- As a bound ensemble of nuclei, a molecule can rotate in space as a rigid rotor and move across space
- They can also vibrate as charged particles in a electrostatic potential
- Rotation and vibration are coupled but at low energies they can be studied separately as rotation is usually much slower than vibration
- As for the Born-Oppenheimer approximation:

$$\begin{aligned} H_n(\mathbf{R}_{\text{CM}}, \alpha, \beta, \gamma, \{\mathbf{P}_i\}_{i=1}^{3N-6}) &\simeq \cancel{H_{\text{trans}}(\mathbf{R}_{\text{CM}})} \\ &+ H_{\text{vib}}(\{\mathbf{Q}_i\}_{i=1}^{3N-6}) \\ &+ H_{\text{rot}}(\alpha, \beta, \gamma), \end{aligned}$$

  where $\mathbf{R}_{\text{CM}}$ are the coordinates of the mass center, (α, β, γ) are the Euler angles to describe the rotation of a solid, and $\{\mathbf{Q}_i\}_{i=1}^{3N-6}$ are the internal normal coordinates for the nuclei
- For a molecule with N atoms, $3N-6$ is the number of normal modes of vibration ($3N-5$ for a linear molecule; degeneration can exist)



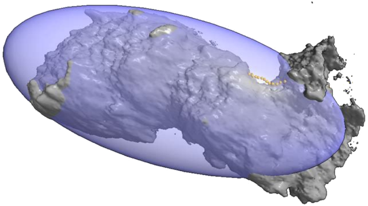
- Classical mechanics:
  - The Hamiltonian for a set of n particles with fixed relative positions (or a solid) is:

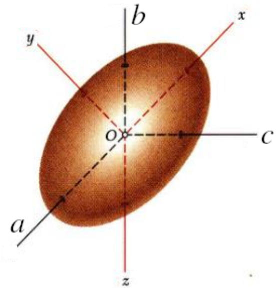
$$H_{\text{rot}} = \frac{1}{2}\mathbf{L}^t \hat{I}^{-1}\mathbf{L},$$

    where $\mathbf{L}$ and $\hat{I}$ are the angular momentum and the inertia tensor
  - For a rigid rotor, the diagonalization of the $\hat{I}$ tensor gives three principal axes a, b, and c and the Hamiltonian in the new basis becomes:

$$H_{\text{rot}} = \frac{L_a^2}{2I_a} + \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c},$$

    where I_a, I_b, and I_c are the eigenvalues of the inertia tensor (defined as $I_a \geq I_b \geq I_c$)





- Quantum mechanics:
  - Schrödinger's equation:

$$H_{\mathrm{rot}}\psi_{\mathrm{rot}} = E_{\mathrm{rot}}\psi_{\mathrm{rot}},$$

where the Hamiltonian for (the nuclei of) a molecule is:

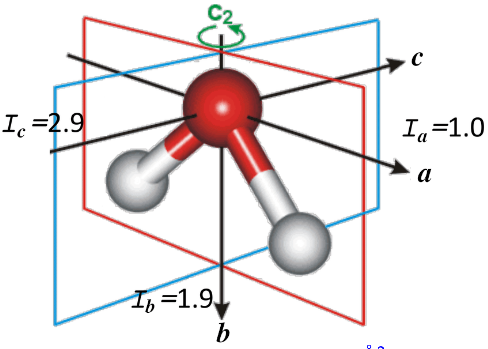
$$H_{\mathrm{rot}} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c},$$

being the rotational angular momentum operator usually dubbed **J** (it can be called **N** sometimes)
  - Important cases:

$$H_{\mathrm{rot}} = \frac{\mathbf{J}^2}{2I_b}, \quad \text{if} \quad I_a = I_c = 0 \quad \text{or} \quad I_a = I_b = I_c$$

$$H_{\mathrm{rot}} = \frac{\mathbf{J}^2}{2I_b} + \left(\frac{1}{2I_z} - \frac{1}{2I_b}\right) J_z^2, \quad \text{where} \quad z = a, c$$

In the last case, if $z = a$, then $I_c = I_b$ and if $z = c$, then $I_a = I_b$



The moments of inertia are $\sim$ 1 amu Å^2 $\simeq 1.66 \times 10^{-40}$ g cm^2

- $\mathbf{J}^2 |nJK\rangle = \hbar^2 J(J+1) |nJK\rangle$
- $J_z |nJK\rangle = \hbar K |nJK\rangle$ in non-asymmetric tops
- Main rotational constants: $A = \frac{\hbar^2}{2I_a}, B = \frac{\hbar^2}{2I_b}, C = \frac{\hbar^2}{2I_c}$
- $A \geq B \geq C$, being B the reference constant
- Symmetric tops: J and K are good quantum numbers
- Asymmetric tops: K_a and K_c are not quantum numbers, just labels related to the closest symmetric tops

Symmetric tops

$[\mathbf{J}^2, H] = [J_z, H] = 0$

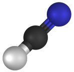
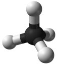
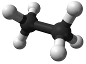
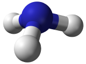
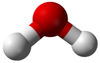
$\mathbf{J}^2$ and J_z are conserved quantities!

Asymmetric tops

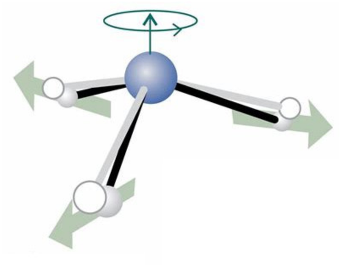
$[\mathbf{J}^2, H] = 0; [J_z, H] \neq 0$

$\mathbf{J}^2$ is conserved but J_z is not!

Top type	Top subtype	Quantum numbers	Condition	E_{rot}
Linear (+diatomic)	—	J	$A = C = 0,\ B \neq 0$	$BJ(J+1)$
Spherical	—	J	$A = B = C$	$BJ(J+1)$
Symmetric	Prolate	$J,\ K$	$A > B = C$	$BJ(J+1) + (A-B)K^2 \quad (K = K_a)$
Symmetric	Oblate	$J,\ K$	$A = B > C$	$BJ(J+1) - (B-C)K^2 \quad (K = K_c)$
Asymmetric	—	$J,\ K_a,\ K_c$	$A > B > C$	$BJ(J+1) + (A-B)K_a^2 - (B-C)K_c^2$

Linear (+diatomic)	Spherical	Symmetric Prolate	Symmetric Oblate	Asymmetric
CO, HCN, CO_2	CH_4, SF_6	CH_3CN, C_2H_6	NH_3, C_6H_6	H_2O, SiC_2, CH_3OH
				

Nuclear motions: Molecular rotation (non-rigid rotor) [3, 1, 10]



- Atoms moves slightly away from rotation axis $\Longrightarrow$ Inertia moment increases $\Longrightarrow$ Effective rotational constant decreases $\Longrightarrow$ Rotational energy decreases
- Centrifugal distortion constant, D:

$$E_{\text{rot}} = BJ(J+1) - DJ^2(J+1)^2$$

- There are many other higher order constants to improve the approximation for different molecular types (e.g., Watson Hamiltonian: $D_J, D_{JK}, D_K, H_J, H_{JK}, H_{JJK}, H_{JKK}, H_K, L_J, \ldots$)

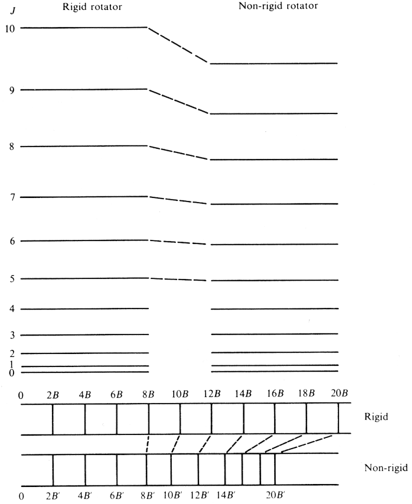


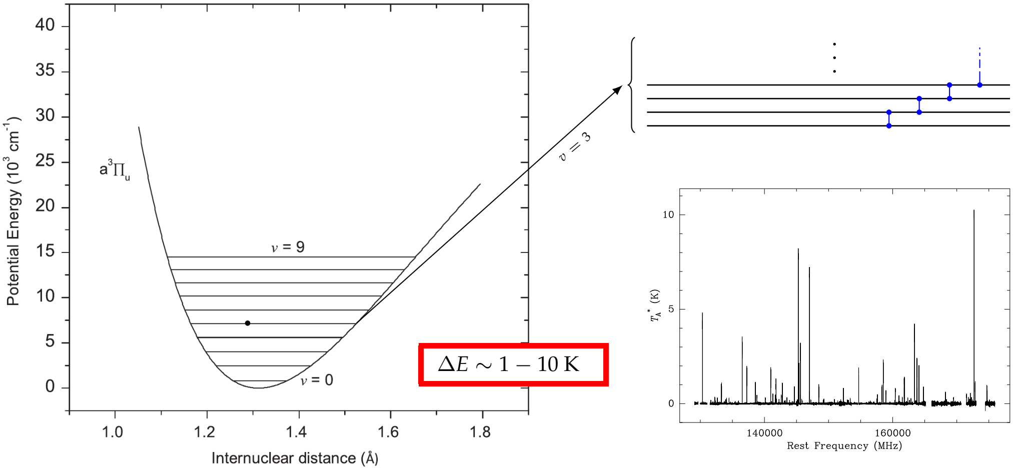
Figure 2.9 The change in rotational energy levels and rotational spectrum when passing from a rigid to a non-rigid diatomic molecule. Levels on the right calculated using $D = 10^{-3}B$.

Nuclear motions: Rotational constants of several molecules

Molecule	# atoms	Top type	A (MHz)	B (MHz)	C (MHz)
H_2	2	Diatomic	—	1823337.730	—
CO	2	Diatomic	—	57635.968	—
SiO	2	Diatomic	—	21787.487	—
HCN	3	Linear	—	44315.976	—
H_2O	3	Asymmetric	835840.3	435351.7	278138.7
H_2S	3	Asymmetric	310667.83	270331.83	141789.63
HCO^+	3	Linear	—	44594.43	—
AlOH	3	Linear	—	15740.3	—
C_2H_2	4	Linear	—	35451.789	—
NH_3	4	Symmetric Oblate	298192.92	298192.92	186695.86
PH_3	4	Symmetric Oblate	133480.128	133480.128	117489.43
H_2CO	4	Asymmetric	281970.56	38833.987	34004.244
H_2CS	4	Asymmetric	291613.3	17698.995	16652.499
CH_4	5	Spherical	157127.223	157127.223	157127.223
HC_3N	5	Linear	—	4549.059	—
CH_3OH	6	Asymmetric	127523.4	24692.5	23760.3
CH_3CN	6	Symmetric	158099.0	9198.8992	9198.8992
C_2H_6	8	Symmetric Prolate	80257.5	19916.530	19916.530
CH_3COOH	8	Asymmetric	11324.236	9494.193	5326.132
C_2H_5OCHO	11	Asymmetric	17746.69	2904.735	2579.146

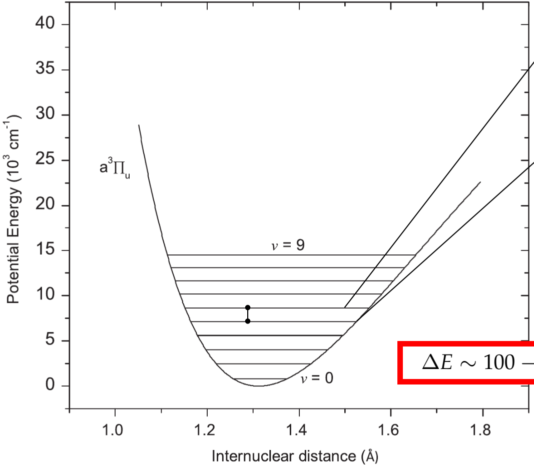
Outline

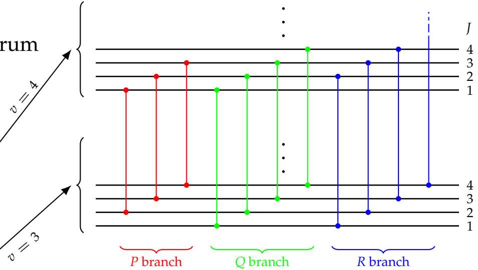
- $\nu = E_{\rm up} - E_{\rm low}$ paying attention to the the selection rules
- Only molecules with a permanent dipole moment has a pure rotational spectrum



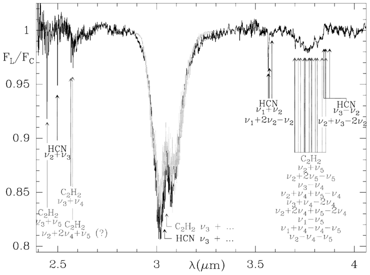
$\boxed{\Delta E \sim 1 - 10\ \mathrm{K}}$

- $\nu = E_{\mathrm{up}} - E_{\mathrm{low}}$ paying attention to the the selection rules
- Homonuclear diatomic molecules have not vibrational spectrum
- Vibrational spectra are similar for families of molecules

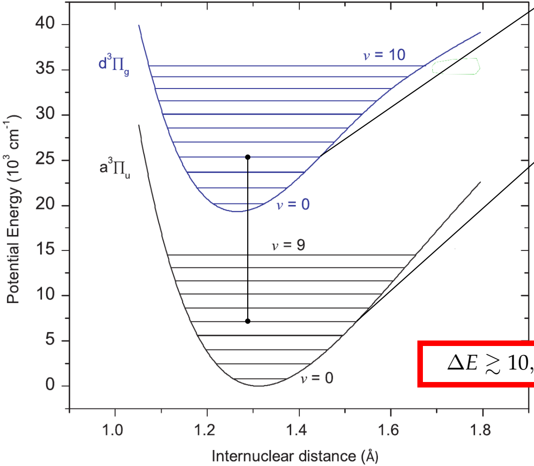




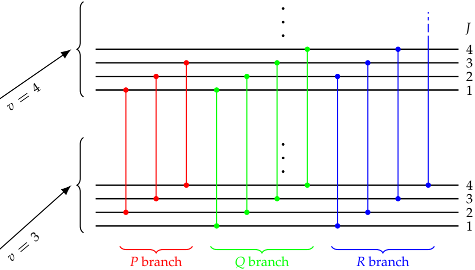
$\Delta E \sim 100 - 1000$ K

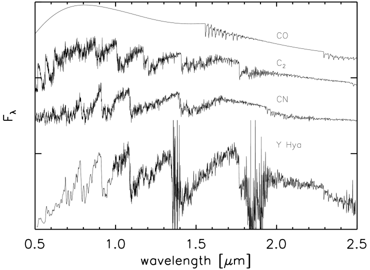


- $\nu = E_{\rm up} - E_{\rm low}$ paying attention to the the selection rules
- All the molecules have electronic spectrum



$\Delta E \gtrsim 10,000$ K





- The frequencies of the transitions are:

$$\begin{aligned}\nu_J &= E_{\mathrm{rot},J+1} - E_{\mathrm{rot},J}\\ &= 2B(J+1) - 4D(J+1)^3 + \cdots\end{aligned}$$

- At a temperature T, the opacity of a line is:

$$k_\nu = \frac{A_{ul}c}{8\pi\nu^2}\frac{g_u}{Z}e^{-E_{\mathrm{low}}/k_BT}\left(1 - e^{-\nu/k_BT}\right),$$

  where Z is the partition function defined as:

$$Z = \sum_{J=0}^{\infty} g_J^s\,(2J+1)\,e^{-E_J/k_BT}$$

  and g_J^s accounts for the statistical weights related to nuclear spins or molecular symmetries

- Only molecules with a permanent dipole moment have a rotational spectrum (e.g., H_2 and C_2H_2 have not this type of spectra)

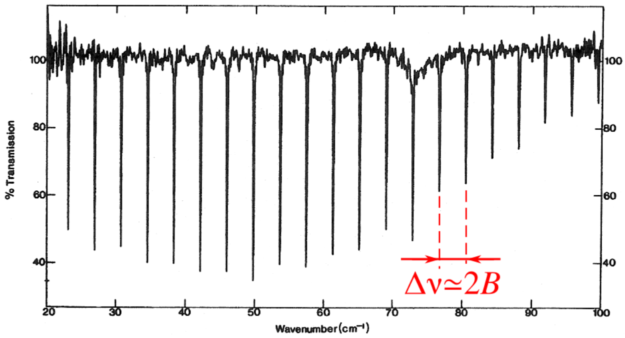


Figure 8.8. Pure rotational spectrum of CO, reproduced with permission from *Modern Aspects of Microwave Spectroscopy*, ed. G. W. Chantry, Academic Press, 1979.

- The frequencies of the transitions are:

$$\begin{aligned}\nu_{v'J',v''J''} &= E_{v'J'} - E_{v''J''}\\ &= \nu_{v',v''} + 2B(J''+1) + \cdots \quad (R)\\ &= \nu_{v',v''} - 2BJ'' + \cdots \quad (P)\\ &= \nu_{v',v''} + 0 + \cdots \quad (Q),\end{aligned}$$

  where the lower and upper rotational levels are usually called J'' and J', respectively
- R branch: $J' = J'' + 1$
- P branch: $J' = J'' - 1$
- Q branch: $J' = J''$, absent in diatomics and certain vibrational transitions
- The intensity decreases with increasing $|\Delta v|$
- The pattern found in the pure rotational spectra appears once per branch in ro-vibrational spectra

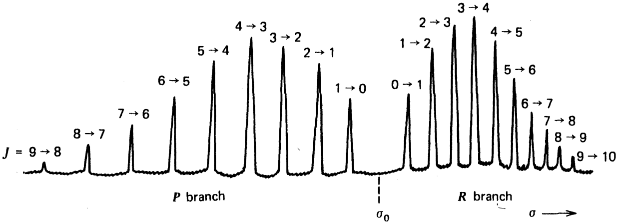


Fig. 4.9 Rotational fine structure of a vibration–rotation band of a diatomic molecule. Note the decreasing spacing with increasing *J* in the *R* branch, and the increasing spacing with increasing *J* in the *P* branch.

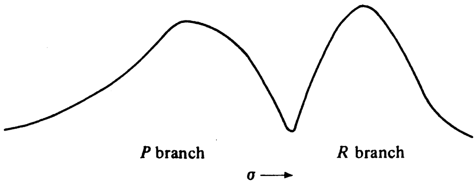


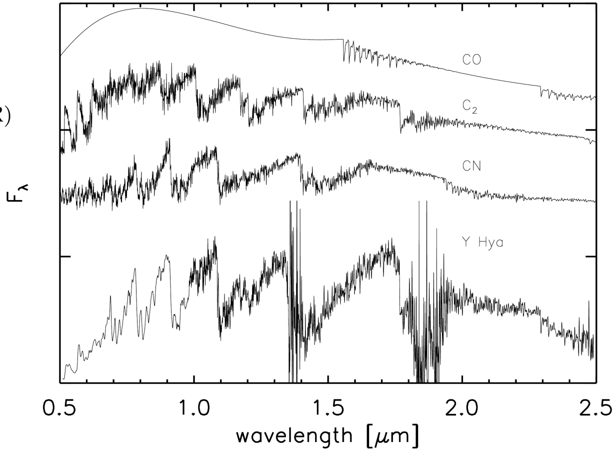
Fig. 4.10 Appearance of a vibration–rotation band of a diatomic molecule under low resolution.

- Ro-vibronic stands for electronic-vibrational-rotational transitions
- The frequencies of the transitions are:

$$
\begin{aligned}
\nu_{e'v'J',e''v''J''} &= E_{e'v'J'} - E_{e''v''J''} \\
&= \nu_{e'v',e''v''} + 2B(J''+1) + \cdots \quad (R) \\
&= \nu_{e'v',e''v''} - 2BJ'' + \cdots \quad (P) \\
&= \nu_{e'v',e''v''} + 0 + \cdots \quad (Q),
\end{aligned}
$$

where e' and e'' are not quantum numbers but labels to order the electronic states

- The vibrational and electronic energy pattern is much less noticeable than the rotational pattern



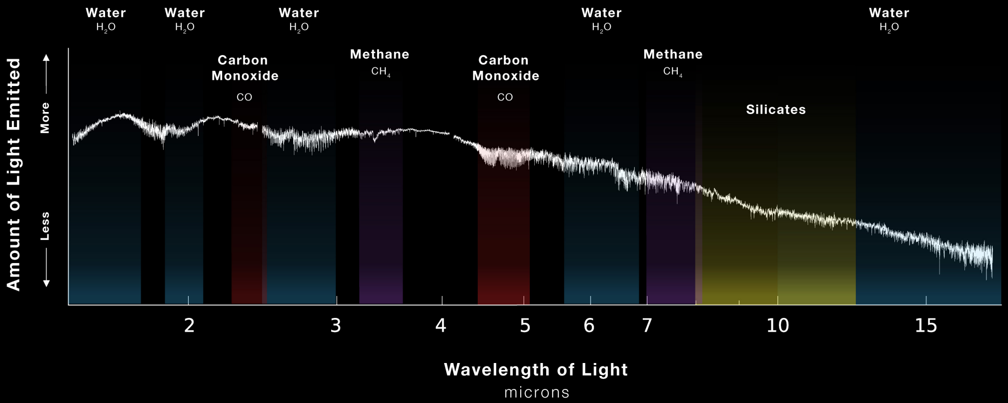
Spectroscopy: Where to find molecular spectra?

- Pure rotational spectra:
  - The Cologne Database for Molecular Spectroscopy (CDMS): `https://cdms.astro.uni-koeln.de/`
  - The database of the JPL Molecular Spectroscopy Team: `https://spec.jpl.nasa.gov/`
  - The Splatalogue: `https://splatalogue.online/#/home`
  - Leiden Atomic and Molecular Database (LAMDA): `https://home.strw.leidenuniv.nl/~moldata/`
- Ro-vibrational spectra:
  - The High-resolution transmission molecular absorption database (HITRAN): `https://hitran.org/`
  - Gestion et Etude des Informations Spectroscopiques Atmosphériques (GEISA): `https://geisa.aeris-data.fr/`
- Ro-vibronic spectra:
  - Exomol: `https://www.exomol.com/`
- Literature:
  - Journal of Molecular Spectroscopy (JMS; `https://www.sciencedirect.com/journal/journal-of-molecular-spectroscopy`)
  - Journal of Chemical Physics (JCP; `https://pubs.aip.org/aip/jcp`)
  - Astronomy & Astrophysics (A&A; `https://www.aanda.org/`)
  - The Astrophysical Journal (ApJ; `https://iopscience.iop.org/journal/0004-637X`)
- Search the web!!!

EXOPLANET VHS 1256 b

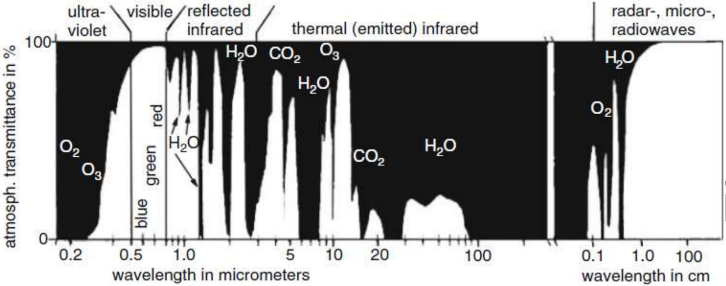
EMISSION SPECTRUM

NIRSpec and MIRI | IFU Medium-Resolution Spectroscopy



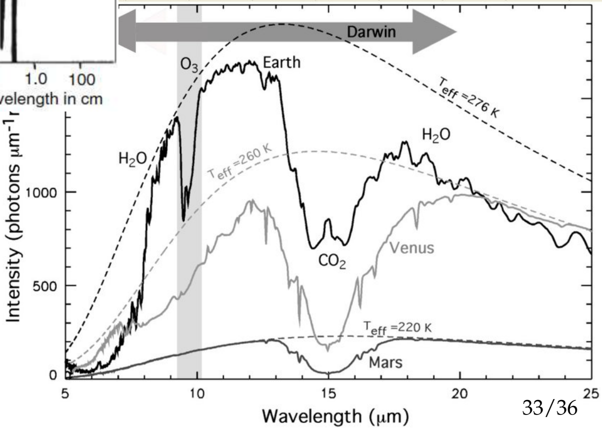
WEBB SPACE TELESCOPE

Spectroscopy: The importance of molecules in our lives



(Atmospheric transmission from the UV to radio wavelength ranges)

(Emission of Earth, Venus, and Mars as seen from space between 5 and 25 μm)



Outline

Summary and final remarks

- Molecules are formed by several nuclei embedded in an electron cloud
- Electrons moves much faster than nuclei
- The energy levels of a molecule can be separated into:
  - electronic, which are related to the electronic configuration,
  - vibrational, which refers how nuclei vibrate in an electronic state,
  - rotational, related to how the molecule rotates around its center of mass
- The energy levels of the vibrational and rotational structure essentially depend on the ω_e and B constants
- The electronic energy pattern is much less predictable
- The spectrum of a molecule is the combination of the energy pattern and the selection rules
- Each molecule has an unique high resolution spectrum. It is its fingerprint
- Pure rotational spectra are observed in the (sub)millimeter range ($\nu \sim 10 - 1000$ GHz; $\lambda \sim 0.1 - 10$ mm)
- Vibrational spectra can be observed in the infrared range ($\nu \sim 100 - 10,000$ cm^{-1}; $\lambda \sim 1 - 100$ μm)
- Electronic spectra are present in the near-infrared and optical ranges ($\nu \gtrsim 10,000$ cm^{-1}; $\lambda \lesssim 1$ μm)

Most of the Universe is cold. Molecules (and their byproducts, as dust) really matter!!!

References

[1] W. Gordy & R. L. Cook, Microwave molecular spectra, John Wiley & Sons, Inc., New York, 1984

[2] L. N. Hand & J. D. Finch, Analytical mechanics, Cambridge University Press, United Kingdom, 1998

[3] G. Herzberg, Molecular spectra and molecular structure. I. Spectra of diatomic molecules, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1963

[4] G. Herzberg, Molecular spectra and molecular structure. II. Infrared and Raman spectra of polyatomic molecules, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1956

[5] G. Herzberg, Molecular spectra and molecular structure. III. Electronic spectra and electronic structure of polyatomic molecules, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1966

[6] J. M. Hollas, Modern spectroscopy, 4th ed., John Wiley & Sons, Ltd., West Sussex, England, 2004

[7] L. D. Landau & E. M. Lifshitz, Course of theoretical physics. I. Mechanics, 3rd ed., Elsevier Ltd., 2007

[8] I. N. Levine, Molecular spectroscopy, John Wiley & Sons, Inc., New York, 1975

[9] S. T. Thornton & J. B. Marion, Classical dynamics of particles and systems, 5th ed., Thomson Learning, Inc., Belmont, California, 2004

[10] C. H. Townes & A. L. Schawlow, Microwave spectroscopy, McGraw-Hill Book Company, Inc., New York, 1955

- Lists of molecules detected in space:
  - The Astrochymist: `https://www.astrochymist.org/`
  - CDMS: `https://cdms.astro.uni-koeln.de/classic/molecules`