Elements of molecular spectroscopy

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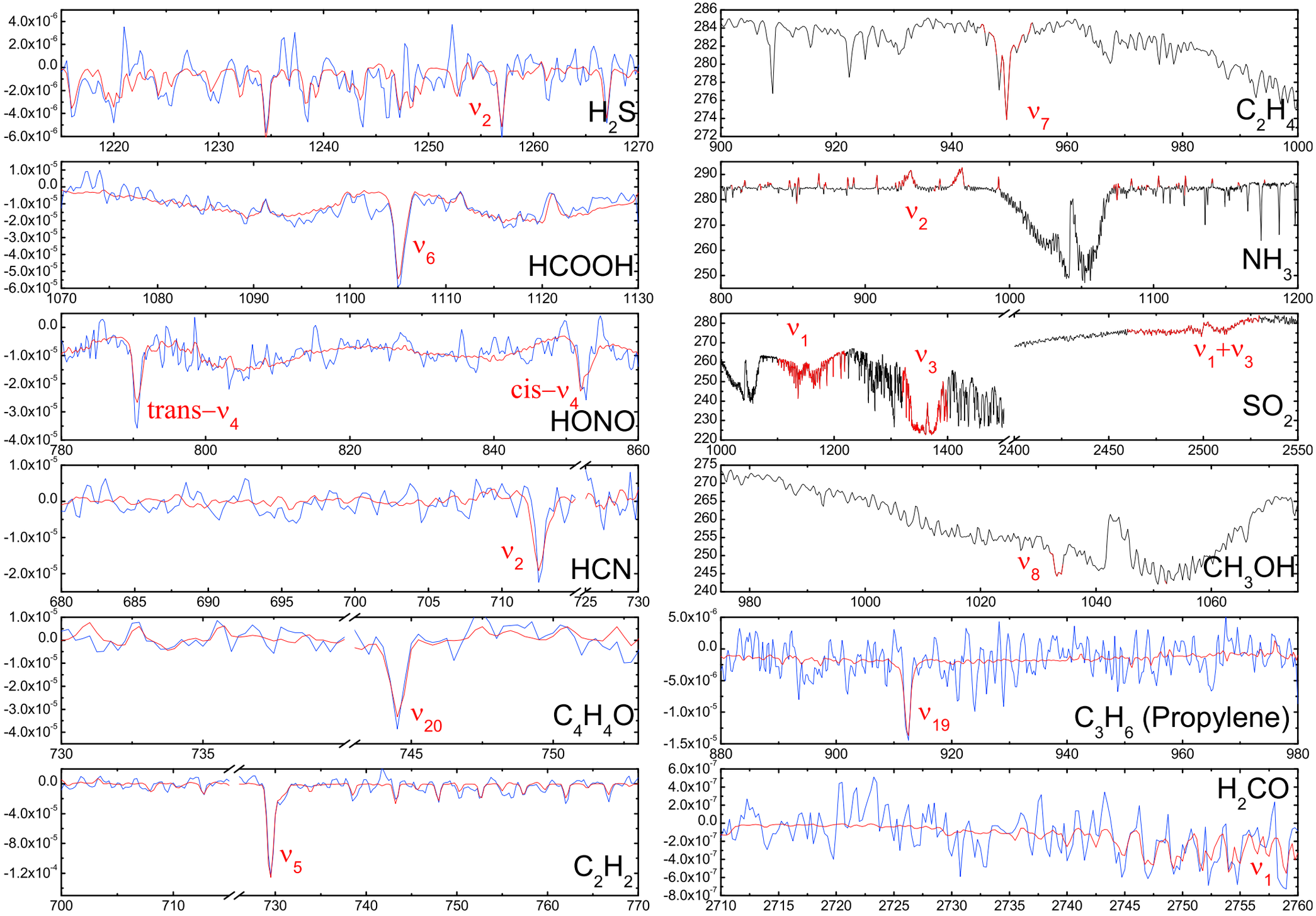
Trace species on the Earth



Clarisse et al., GRL 38 (2011) L10802

Line-by-line data in databases

Mol/Iso	$\nu_{\eta\eta'}$	$S_{\eta\eta'}$	$\Re_{\eta\eta'}$	γ_{air}	γ_{self}	E″	n	δ	iv'	iv''	q'	q''	ierr	iref
21	800.451076	3.197E–26	6.579E–05	0.0676	0.0818	2481.5624	0.78	0.000000	14	6		P 37	465	2 2 1
291	800.454690	9.724E–22	1.896E–02	0.0845	0.1750	369.6303	0.94	0.000000	9	1	341619	331519	000	4 4 1
291	800.454690	3.242E–22	2.107E–03	0.0845	0.1750	369.6303	0.94	0.000000	9	1	341519	331419	000	4 4 1
121	800.455380	1.037E–22	1.657E–03	0.1100	0.0000	530.3300	0.75	0.000000	32	14	46 640	45 540	000	4 4 1
121	800.455380	1.037E–22	1.657E–03	0.1100	0.0000	530.3300	0.75	0.000000	32	14	46 740	45 640	000	4 4 1
101	800.456743	1.680E–23	1.659E–04	0.0670	0.0000	851.0494	0.50	0.000000	2	1	45 244 0–	44 143 0–	301	6 6 1
101	800.457045	1.710E–23	1.689E–04	0.0670	0.0000	851.0469	0.50	0.000000	2	1	45 244 1–	44 143 1–	301	6 6 1
101	800.457310	1.740E–23	1.718E–04	0.0670	0.0000	851.0442	0.50	0.000000	2	1	45 244 2–	44 143 2–	301	6 6 1
121	800.457760	4.726E–23	4.614E–03	0.1100	0.0000	920.0900	0.75	0.000000	32	14	502922	492822	000	4 4 1
121	800.457760	4.726E–23	4.614E–03	0.1100	0.0000	920.0900	0.75	0.000000	32	14	502822	492722	000	4 4 1
24	800.465942	9.792E–27	6.063E–04	0.0754	0.1043	1341.2052	0.69	0.000000	8	3		R 13	425	2 2 1
121	800.466160	1.061E–22	2.720E–03	0.1100	0.0000	632.1200	0.75	0.000000	32	14	471236	461136	000	4 4 1
121	800.466160	1.061E–22	2.720E–03	0.1100	0.0000	632.1200	0.75	0.000000	32	14	471136	461036	000	4 4 1
35	800.472900	3.878E–26	6.919E–04	0.0686	0.0871	629.0354	0.76	0.000000	2	1	1814 4	1713 5	455	5 5 1
101	800.473083	1.270E–23	1.254E–04	0.0670	0.0000	851.0095	0.50	0.000000	2	1	45 244 0 +	44 143 0 +	301	6 6 1
101	800.474860	1.210E–23	1.195E–04	0.0670	0.0000	851.0064	0.50	0.000000	2	1	45 244–1 +	44 143–1 +	301	6 6 1
31	800.475500	1.680E–24	3.617E–05	0.0653	0.0890	1092.4340	0.76	0.000000	2	1	51 547	50 248	002	1 1 2
291	800.476220	9.597E–22	6.010E–03	0.0845	0.1750	361.9747	0.94	0.000000	9	1	341420	331320	000	4 4 1
291	800.476220	3.199E–22	6.010E–03	0.0845	0.1750	361.9747	0.94	0.000000	9	1	341520	331420	000	4 4 1
101	800.476937	1.160E–23	1.145E–04	0.0670	0.0000	851.0037	0.50	0.000000	2	1	45 244–2 +	44 143–2 +	301	6 6 1
101	800.484334	1.740E–23	2.153E–05	0.0670	0.0000	106.0760	0.50	0.000000	2	1	8 4 4–1 +	9 3 7–1 +	301	6 6 1

position

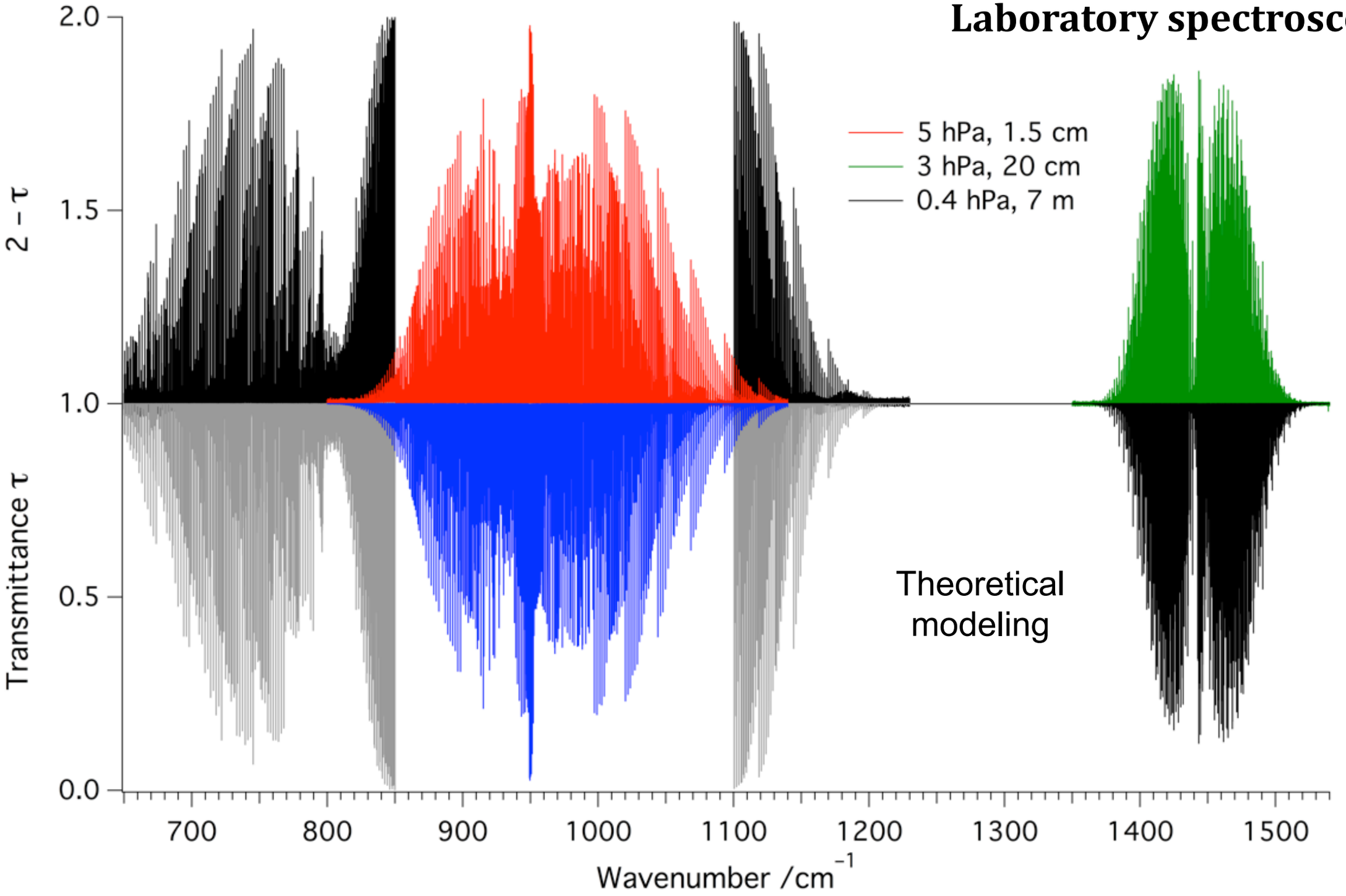
"intensity"

Lower-state energy

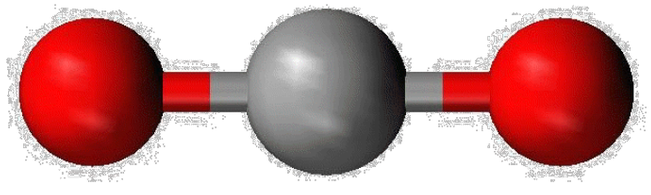
"global" (vibrational) quanta

"local" (rotational) quanta

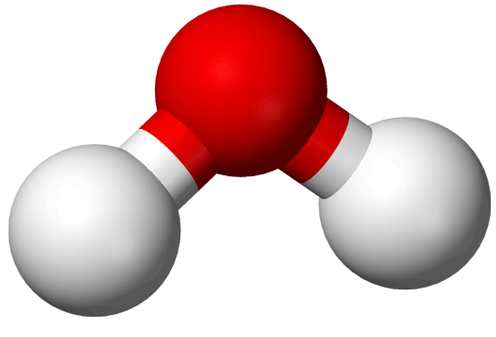
Reference data (10 µm region of C_2H_4)



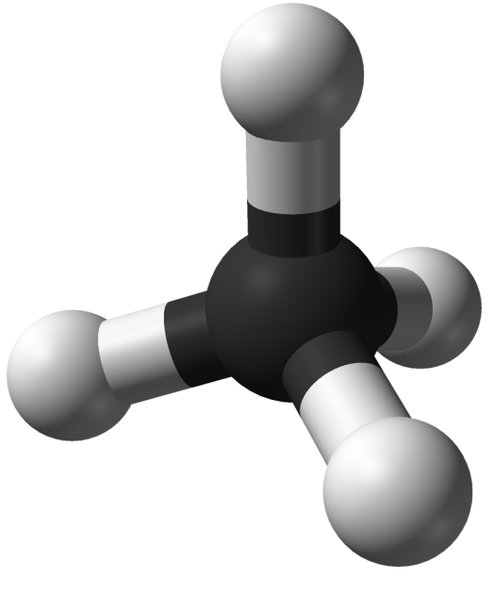
Diversity of molecular structures



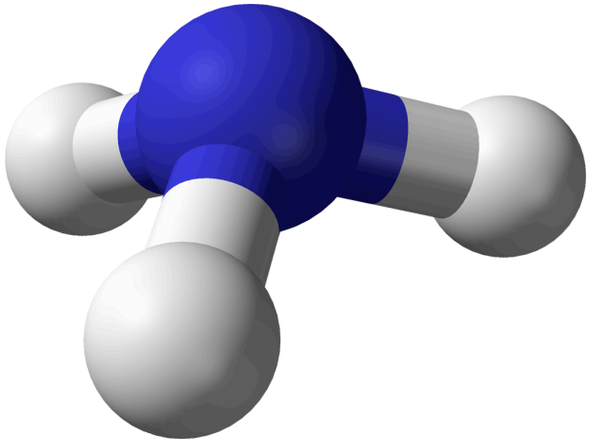
carbon dioxide



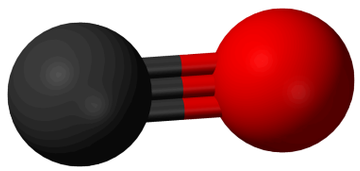
water



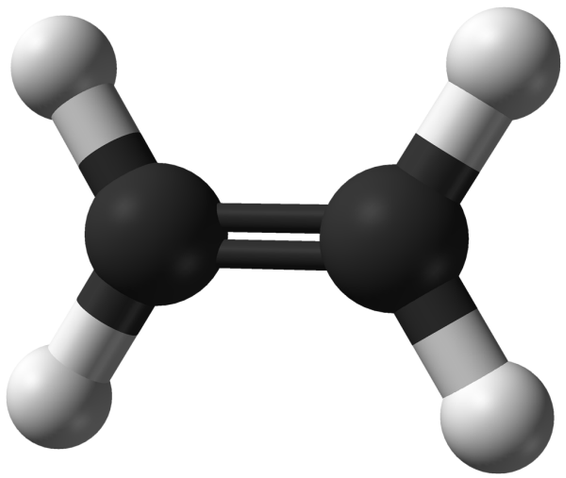
methane



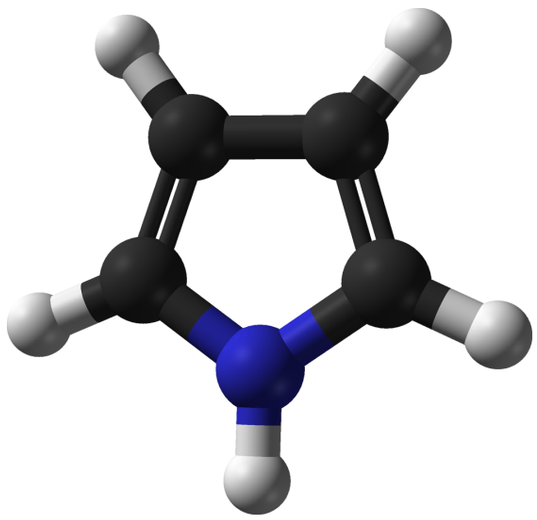
ammonia



carbon monoxide

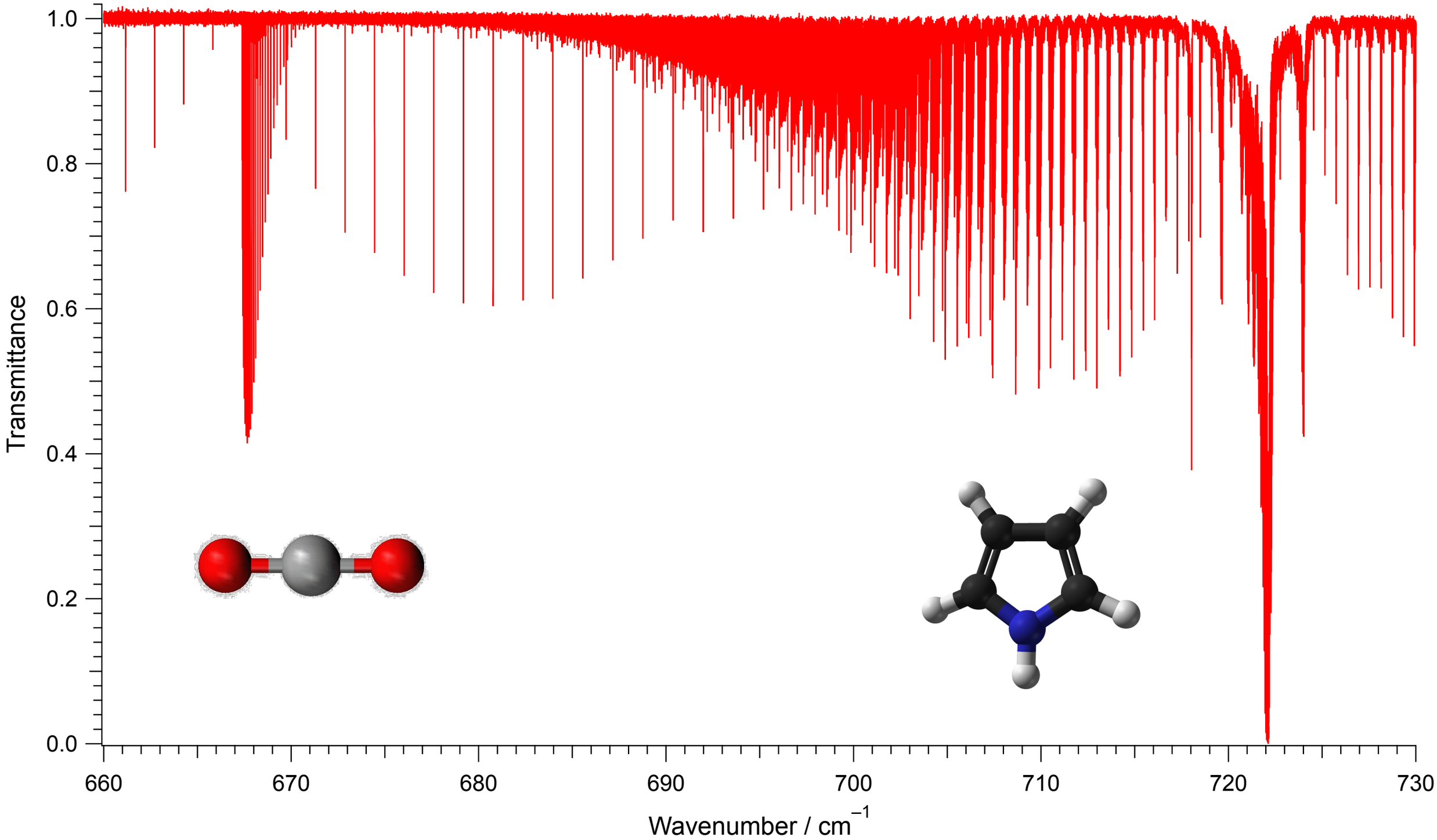


ethylene



pyrrole

Diversity of molecular spectra

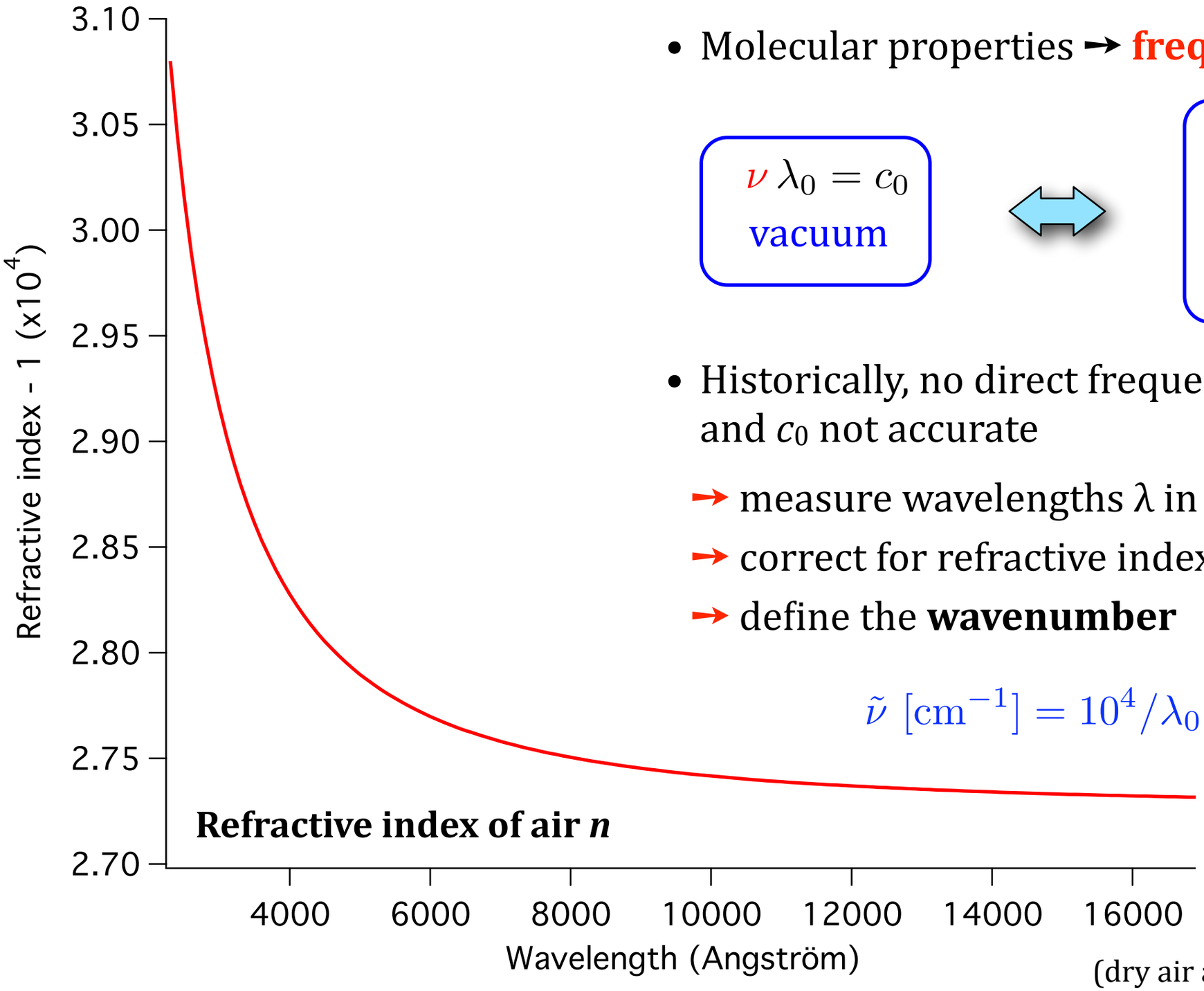


Purpose and outline

- **Lecture** = *Overview of **some** of the building blocks of molecular spectra*

- **Outline**
  - Radiative transfer in a gas
  - Rotation, vibration and electronic motions of molecules (levels and transitions)
  - Line *positions* and *intensities*

Electromagnetic waves: the *wavenumber*



- Molecular properties ➙ **frequencies** (ν)

$$\nu\,\lambda_0 = c_0 \quad \text{vacuum} \qquad \Leftrightarrow \qquad \nu\,\frac{\lambda_0}{n} = \nu\,\lambda = \frac{c_0}{n} \quad \text{medium } (n)$$

- Historically, no direct frequency measurements and c_0 not accurate
  - ➙ measure wavelengths λ in air
  - ➙ correct for refractive index of air ➙ λ_0
  - ➙ define the **wavenumber**

$$\tilde{\nu}\ [\mathrm{cm}^{-1}] = 10^4/\lambda_0\ [\mu\mathrm{m}]$$

(dry air at 15C, 1 atm, 450 ppm CO_2)

Books

- "Spectra of atoms and molecules",
  P.F. Bernath, *Oxford University Press*, 4th edition (2020)

- "Handbook of high-resolution spectroscopy",
  M. Quack and F. Merkt Editors, *Wiley* (2011)

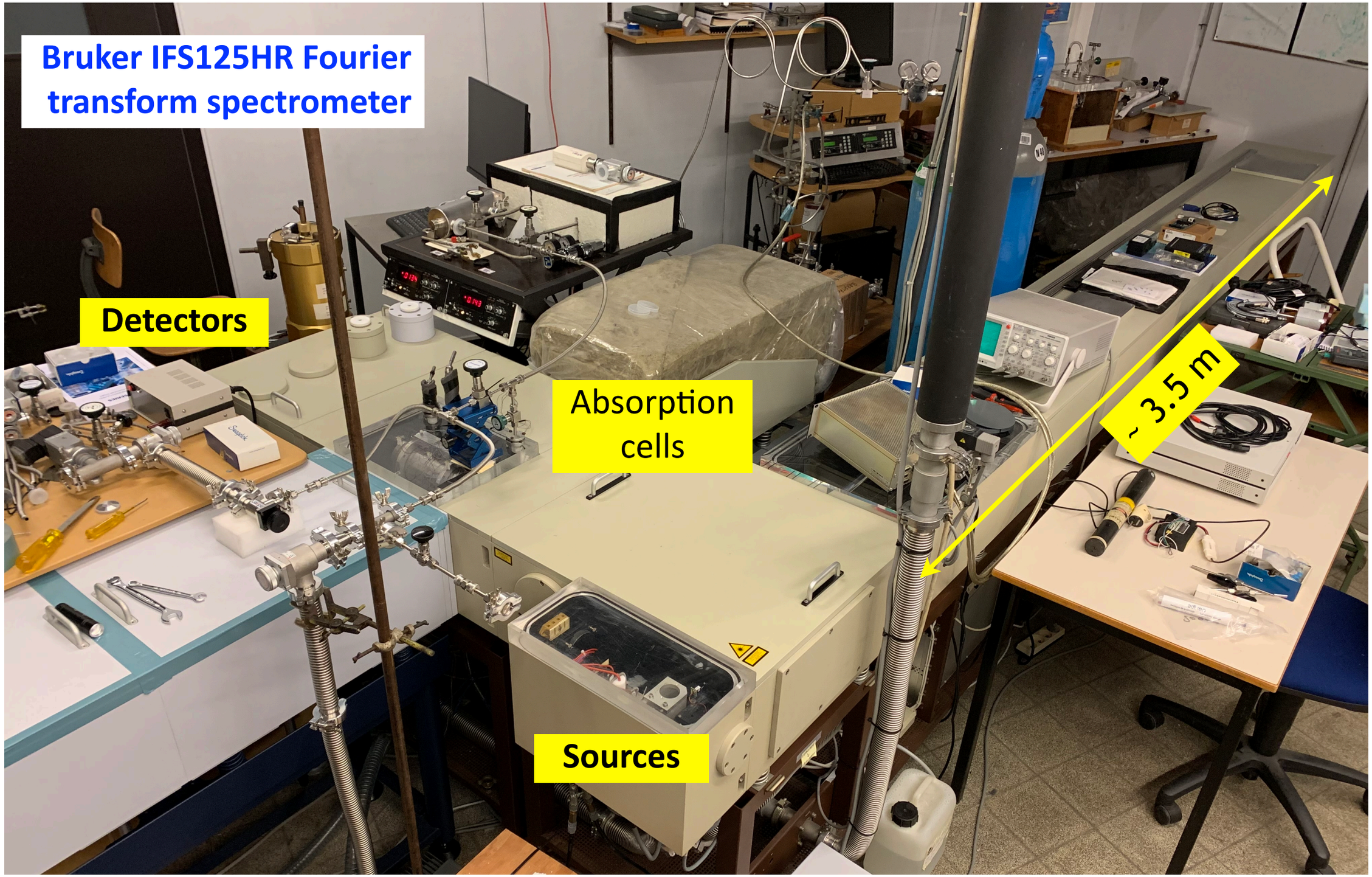
- "Rotational structure in molecular infrared spectra",
  C. di Lauro, *Elsevier*, 2nd edition (2020)

- "Fundamentals of molecular symmetry",
  P.R. Bunker and P. Jensen, *Institute of Physics Publishing* (2005)

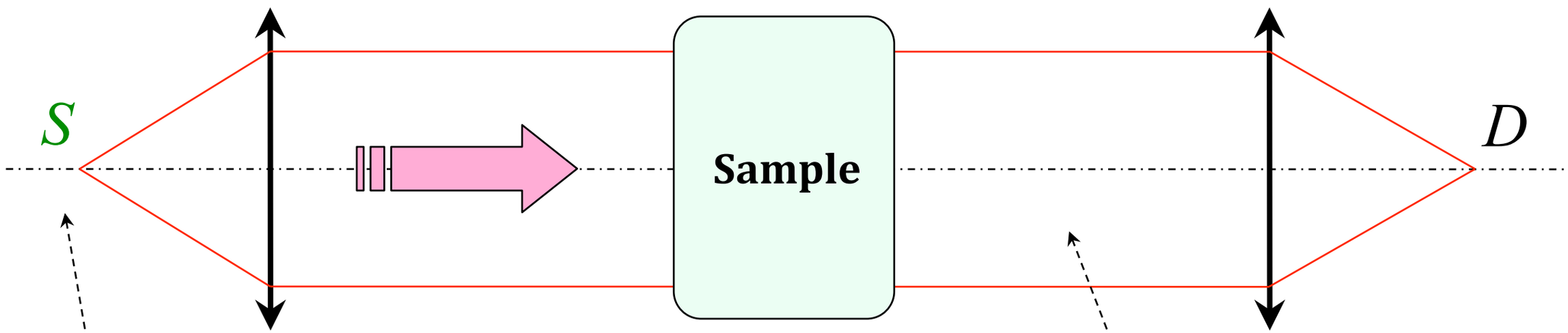
Elements of molecular spectroscopy

Radiative transfer in a gas

“Beer-Lambert spectroscopy”



Collimated beams



$L =$ radiance $(\mathrm{Wsr^{-1}m^{-2}})$

$I =$ irradiance $(\mathrm{Wm^{-2}})$

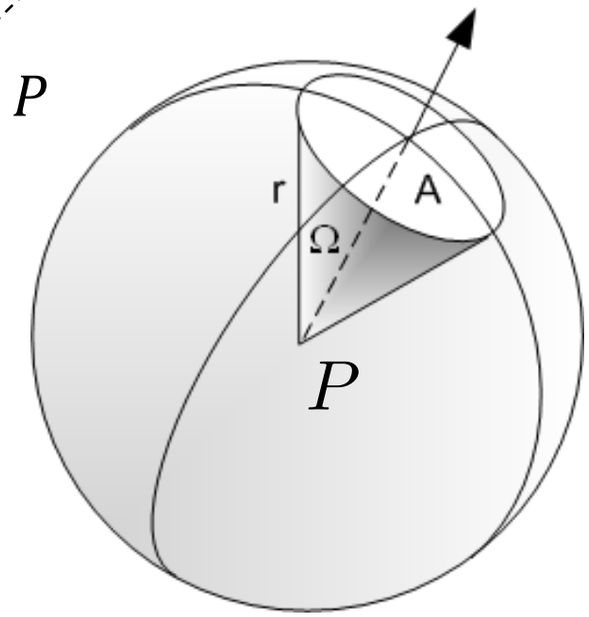
$$= \int I_{\tilde{\nu}}(\tilde{\nu})\, d\tilde{\nu}$$

Spectral irradiance $(\mathrm{Wm^{-1}})$

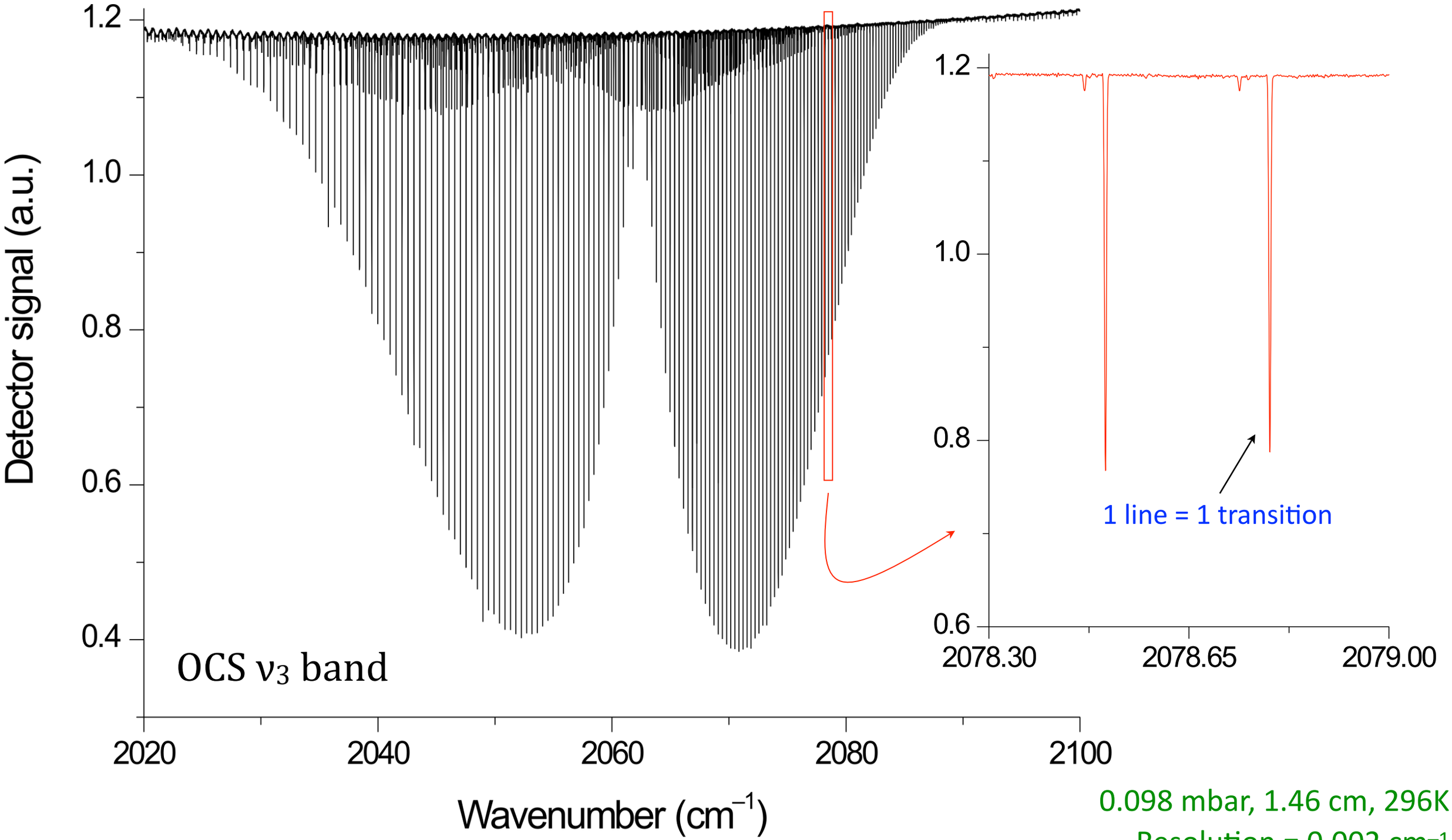
defined in the interval $[\tilde{\nu}, \tilde{\nu} + d\tilde{\nu}]$

Solid angle at P

$$\Omega(\mathrm{sr}) = \frac{A}{r^2}$$



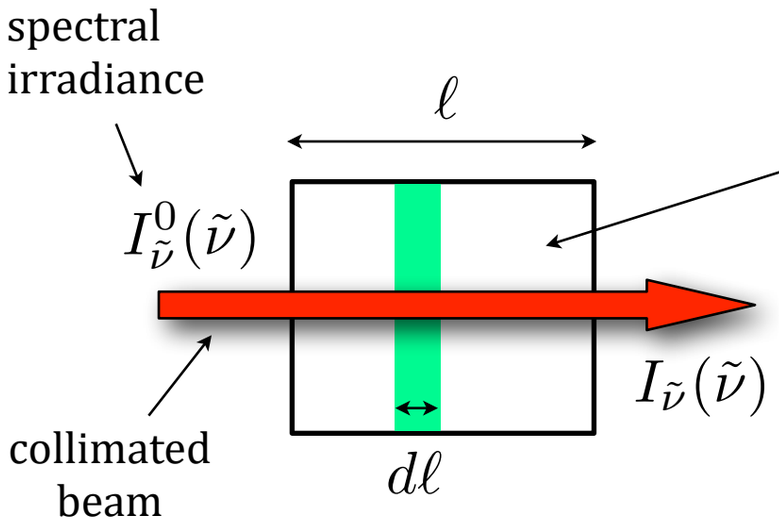
High resolution IR spectroscopy

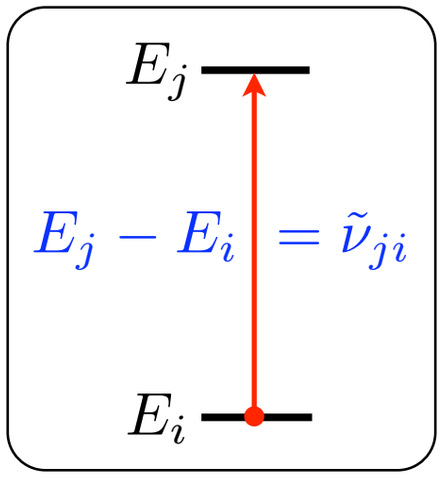


0.098 mbar, 1.46 cm, 296K

Resolution = 0.002 cm^{-1}

Beer-Lambert law





Bohr condition

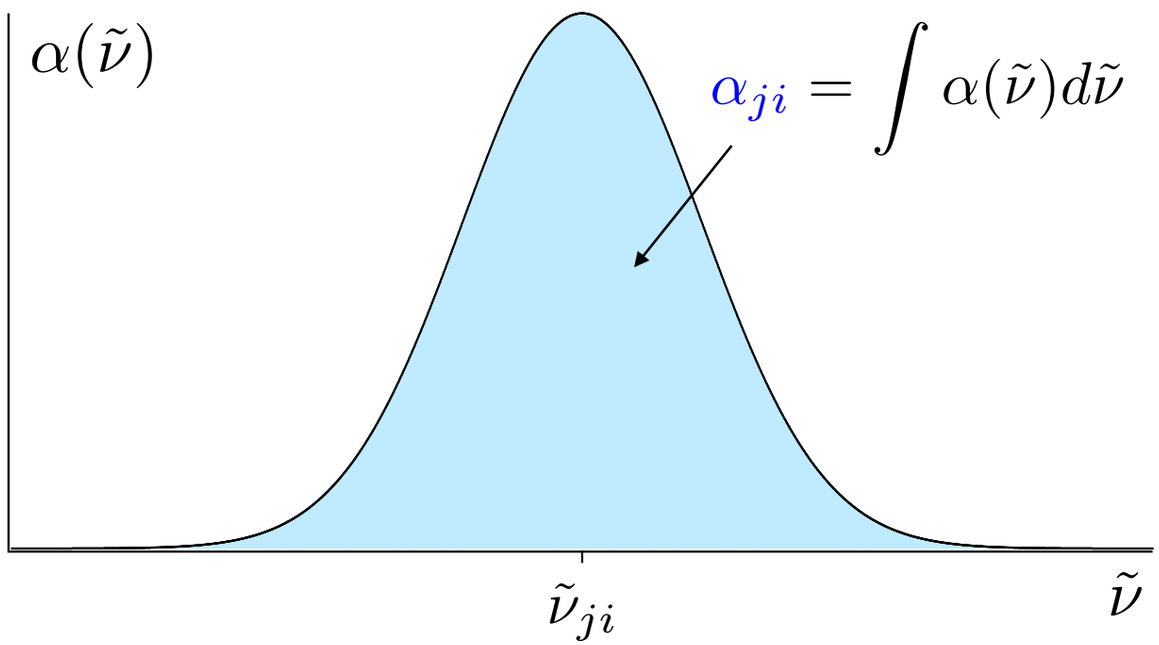
absorption coefficient

$$dI_{\tilde\nu}(\tilde\nu) = -\alpha(\tilde\nu) I_{\tilde\nu}(\tilde\nu)\, d\ell$$

Homogeneous medium

$$I_{\tilde\nu}(\tilde\nu) = I^0_{\tilde\nu}(\tilde\nu)\, e^{-\alpha(\tilde\nu)\,\ell}$$

integrated absorption coefficient (cm^{-2}) :



line shape function

$$\alpha(\tilde\nu) = \alpha_{ji}\, g(\tilde\nu - \tilde\nu_{ij}) = \sigma_{ji}\, N\, g(\tilde\nu - \tilde\nu_{ij})$$

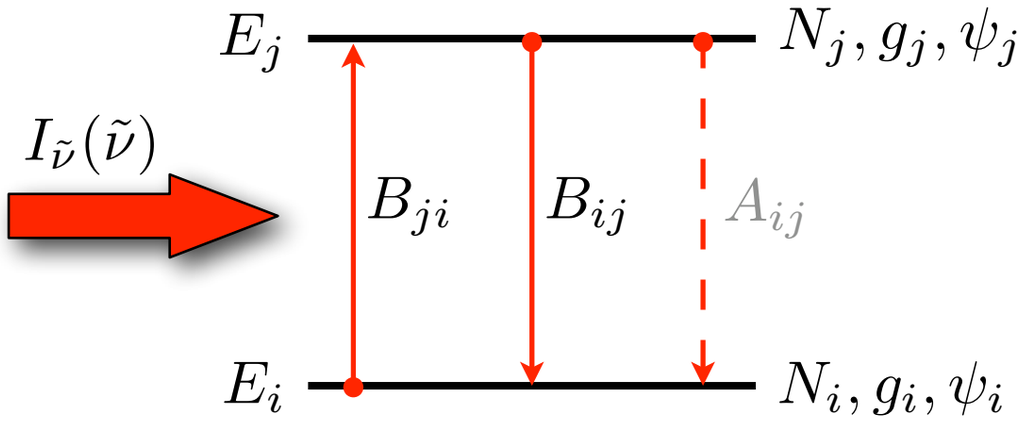
integrated absorption cross section (cm/molecule)

particle density

$$N = \frac{P}{kT}$$

"*line intensity*" in databases

Matter-radiation interaction



absorption "intensity"

$$\alpha_{ji} = h\tilde{\nu}_{ji}\left(\frac{N_i}{g_i} - \frac{N_j}{g_j}\right) g_i\, B_{ji}$$

$$\tilde{\nu}_{ji} = E_j - E_i$$

Semi-classical description (electric dipole interaction)

*Interaction of a quantized two-levels system with a **weak** classically-described electro-magnetic wave*

- **Molecule** = collection of charges q_i at positions $\vec{r}_i$
- **Radiation** = oscillating electric field

Electric dipole moment

$$\vec{\mu} = \sum_i \vec{r}_i\, q_i$$

$$B_{ji}^{(\tilde{\nu})} = \frac{2\pi}{3\hbar^2 c}\frac{1}{4\pi\epsilon_0}\sum_{f=X,Y,Z}\left|\int \psi_j^* \mu_f \psi_i d\tau\right|^2$$

transition moment

Note. First factor for

$$B_{ji}^{(\omega)} \rightarrow \frac{4\pi^2}{3\hbar^2} \text{ and } B_{ji}^{(\nu)} \rightarrow \frac{2\pi}{3\hbar^2}$$

Absorption "intensity"

- Integrated absorption coefficient (cm^{-2}) :

$$\alpha_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\tilde{\nu}_{ji}\left(\frac{N_i}{g_i} - \frac{N_j}{g_j}\right)$$

Dirac notation

$$g_i \sum_{f=X,Y,Z} |\langle\psi_j|\mu_f|\psi_i\rangle|^2$$

S_{ji} ("linestrength")

$$\frac{N_i}{g_i} = \frac{N}{Q}\exp\left\{-\frac{hcE_i}{kT}\right\}$$

- Integrated absorption coefficient per unit pressure [$cm^{-2}atm^{-1}$] at temperature T :

$$\alpha_{ji}^P \equiv \frac{\alpha_{ji}}{P} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{P} I_a \frac{N}{Q(T)}\left(e^{-hcE_i/kT} - e^{-hcE_j/kT}\right) S_{ji}$$

$\approx 3.74\times10^{36}\,\mathrm{C}^{-2}$
$\approx 4.16\times10^{-19}\,\mathrm{D}^{-2}\mathrm{cm}^2$

isotopic abundance

$$\frac{N}{P} = n_L\frac{T_0}{T} \quad (n_L = 2.687\times10^{19}\ \text{molec cm}^{-3}\ \text{atm}^{-1})$$

$T_0 = 273.15\,\mathrm{K}$

- Integrated absorption cross section [cm^{-1}/(molecule cm^{-2})] : (Note. $\sigma_{ji} = \alpha_{ji}/N$)

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) S_{ji}$$

- *Note* – Temperature dependence : "*lower-state energy*" in databases

$$\frac{\sigma_{ji}(T_2)}{\sigma_{ji}(T_1)} = \frac{Q(T_1)}{Q(T_2)}\exp\left\{-\frac{hc}{k}E_i\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\}\frac{1 - e^{-hc\tilde{\nu}_{ji}/kT_2}}{1 - e^{-hc\tilde{\nu}_{ji}/kT_1}}$$

"TIPS": Gamache et al., JQSRT 271 (2021) 107713

Elements of molecular spectroscopy

***Molecular** physics*

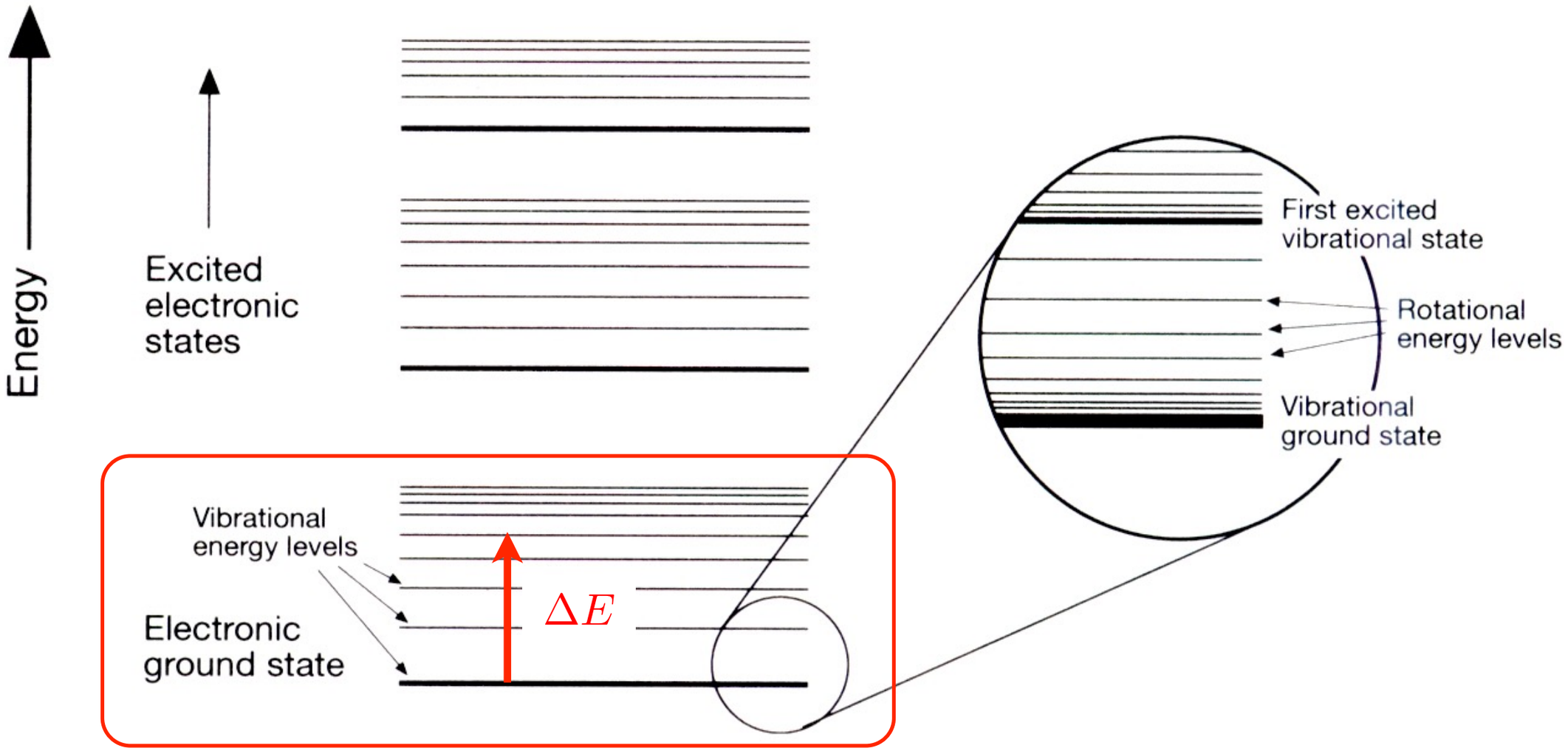
Molecular motions and their energies

Molecule = ensemble of interacting electrons and nuclei

Quantized energies : $E \simeq E_{elec} + E_{vib} + E_{rot}$ $\quad (\psi = \psi_{elec}\,\psi_{vib}\,\psi_{rot})$

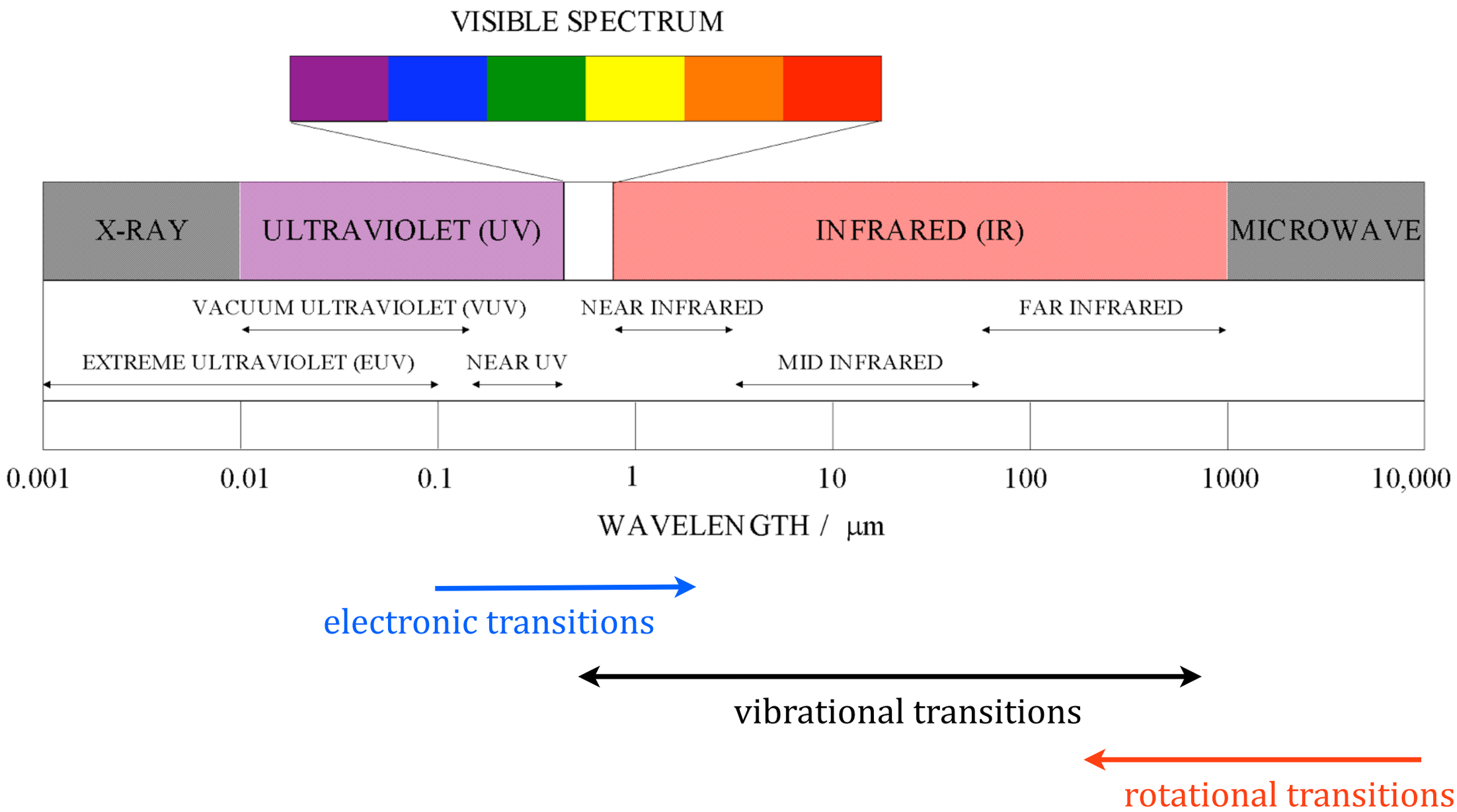
motion of the electrons

motion of the nuclei



Observation of molecular motions

Transitions ➙ Discrete spectrum: $\Delta E \simeq \Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot}$



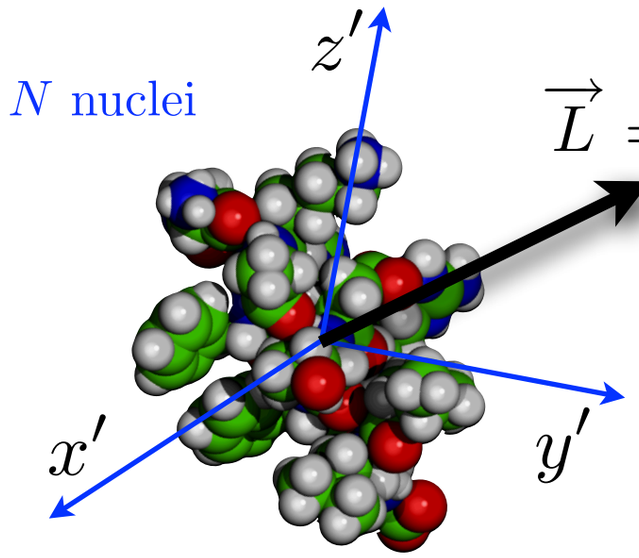
Elements of molecular spectroscopy

Molecular physics – Rotation

Rotational motion of a molecule

(classical mechanics)

- **Angular momentum** in a Cartesian coordinate system



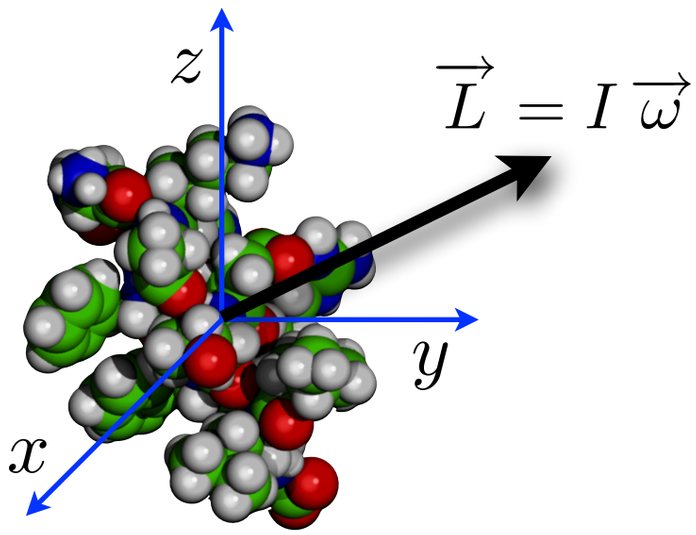
inertia tensor

$$\begin{pmatrix} L_{x'} \\ L_{y'} \\ L_{z'} \end{pmatrix} = \begin{pmatrix} I_{x'x'} & I_{x'y'} & I_{x'z'} \\ I_{y'x'} & I_{y'y'} & I_{y'z'} \\ I_{z'x'} & I_{z'y'} & I_{z'z'} \end{pmatrix} \begin{pmatrix} \omega_{x'} \\ \omega_{y'} \\ \omega_{z'} \end{pmatrix}$$

moments of inertia : $I_{x'x'} = \sum_{i=1}^{N} m_i(y_i'^2 + z_i'^2) \ \ldots$

products of inertia : $I_{x'y'} = I_{y'x'} = -\sum_{i=1}^{N} m_i x_i y_i \ \ldots$

- **Angular momentum** in the *principal axis system*



$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_x & 0 & 0 \\ 0 & I_y & 0 \\ 0 & 0 & I_z \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

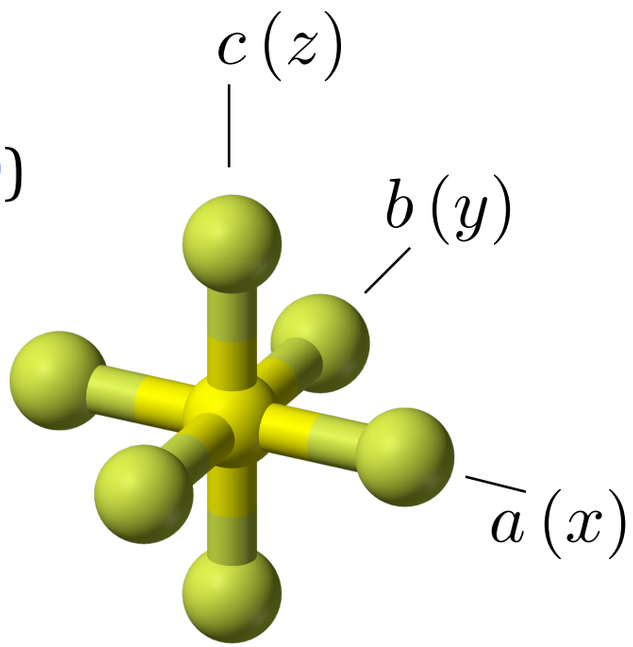
Conventions and classes of molecules

- Principal axis system of a molecule : **Conventions**
  - ***z*** axis = highest order axis of rotational symmetry
  - ***x*** axis = out of the plane of a planar molecule
  - (x, y, z) ➞ (a, b, c) such that $I_a \leq I_b \leq I_c$

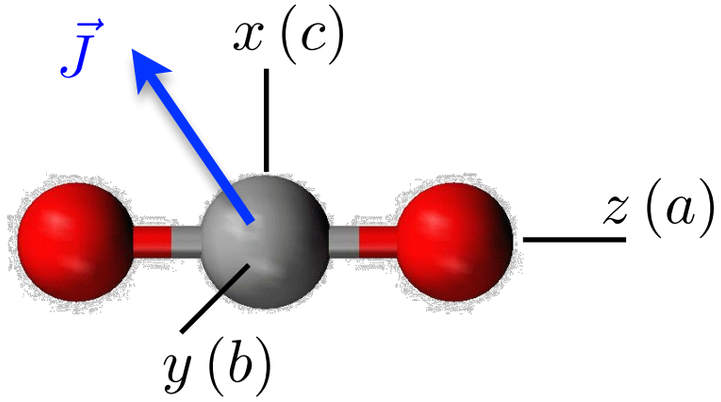
*The moments of inertia are the half-axes of an **ellipsoid** :*

$$\frac{a^2}{I_a^2} + \frac{b^2}{I_b^2} + \frac{c^2}{I_c^2} = 1$$

- **Classification** of the molecules
  - *Linear* or *diatomic* molecules : $I_a = 0$, $I_b = I_c$ (CO_2, HCN, CO)
  - *Spherical* tops : $I_a = I_b = I_c$ (CH_4, **SF_6**)
  - ***Prolate** symmetric* tops : $I_a < I_b = I_c$ (CH_3Cl, C_2H_6)
  - ***Oblate** symmetric* tops : $I_a = I_b < I_c$ (CCl_3H, BF_3)
  - *Asymmetric* tops : $I_a < I_b < I_c$ (H_2O, HNO_3, HCOOH)



Rotation of a linear molecule

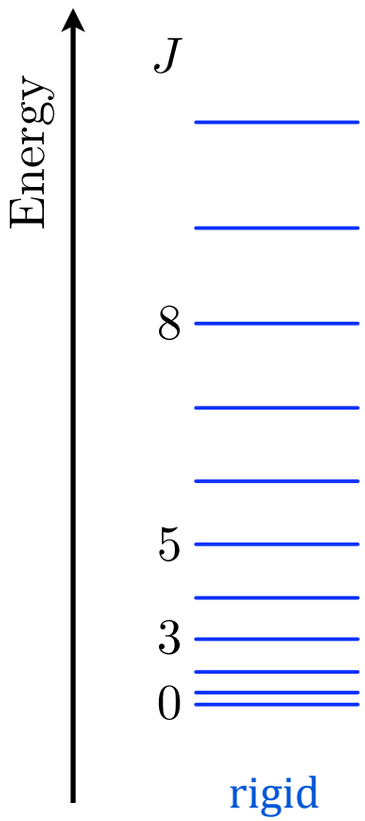


- Rigid rotor

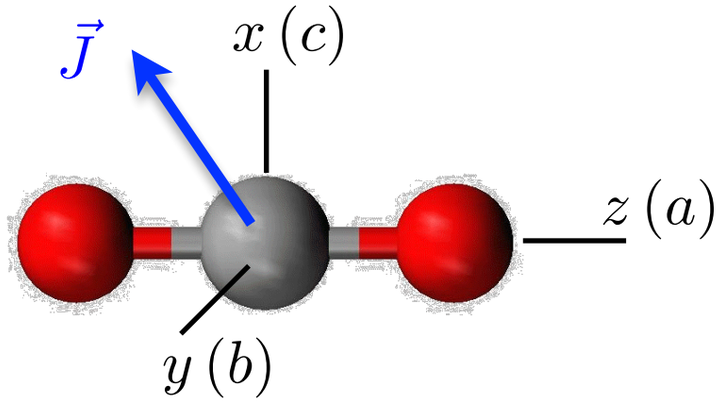
$$E_r(J) = BJ(J+1) \quad \text{with} \quad B = \frac{h}{8\pi^2 c\, I}\,[\mathrm{cm}^{-1}]$$

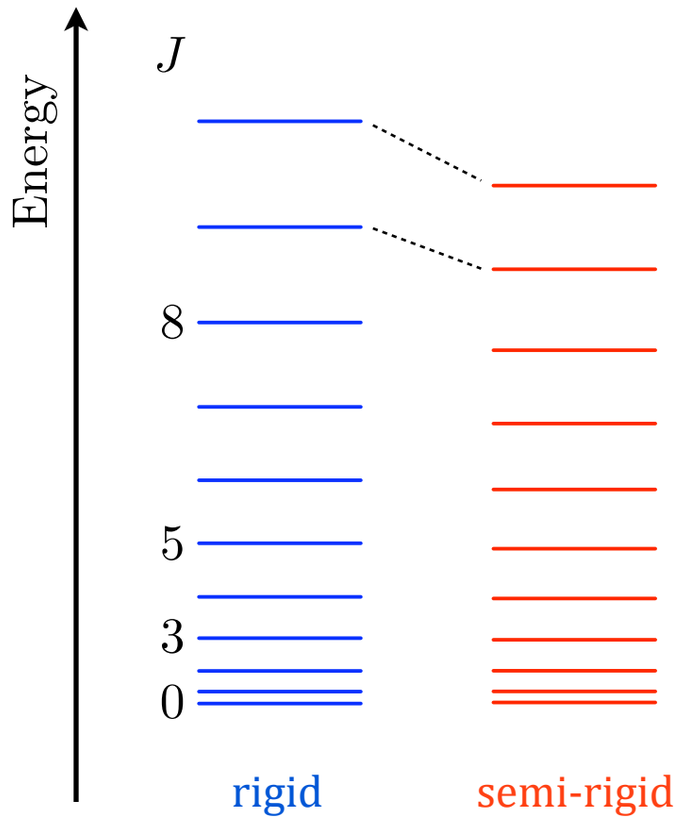
$$(J = 0 \rightarrow \infty)$$

quantum number associated with the molecular angular momentum



Rotation of a linear molecule





- Rigid rotor

$$E_r(J) = BJ(J+1) \quad \text{with} \quad B = \frac{h}{8\pi^2 c\, I}\ [\mathrm{cm}^{-1}]$$

$$(J = 0 \rightarrow \infty)$$

quantum number associated with the molecular angular momentum

- Semi-rigid rotor

$$E_r(J) = BJ(J+1) - DJ^2(J+1)^2 + \ldots$$

- Example : CO_2

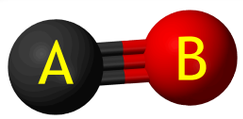
$$B = 0.39022\ \mathrm{cm}^{-1}$$

$$\Rightarrow\ I = 7.1736 \times 10^{-39}\ \mathrm{g\,cm^2/molec},\ r_{\mathrm{CO}} = 1.162\ \text{Å}$$

$$D = 1.334 \times 10^{-7}\ \mathrm{cm}^{-1}$$

- Projection of J on Z laboratory axis : $-J \leq m_J \leq +J$

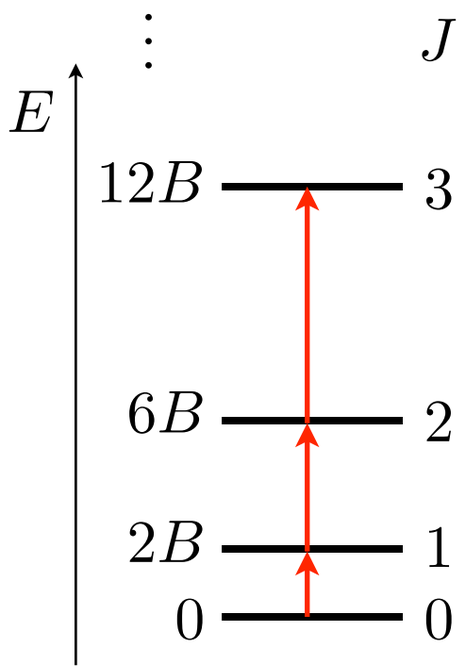
$\Rightarrow$ $2J+1$ levels, degenerate in field-free space



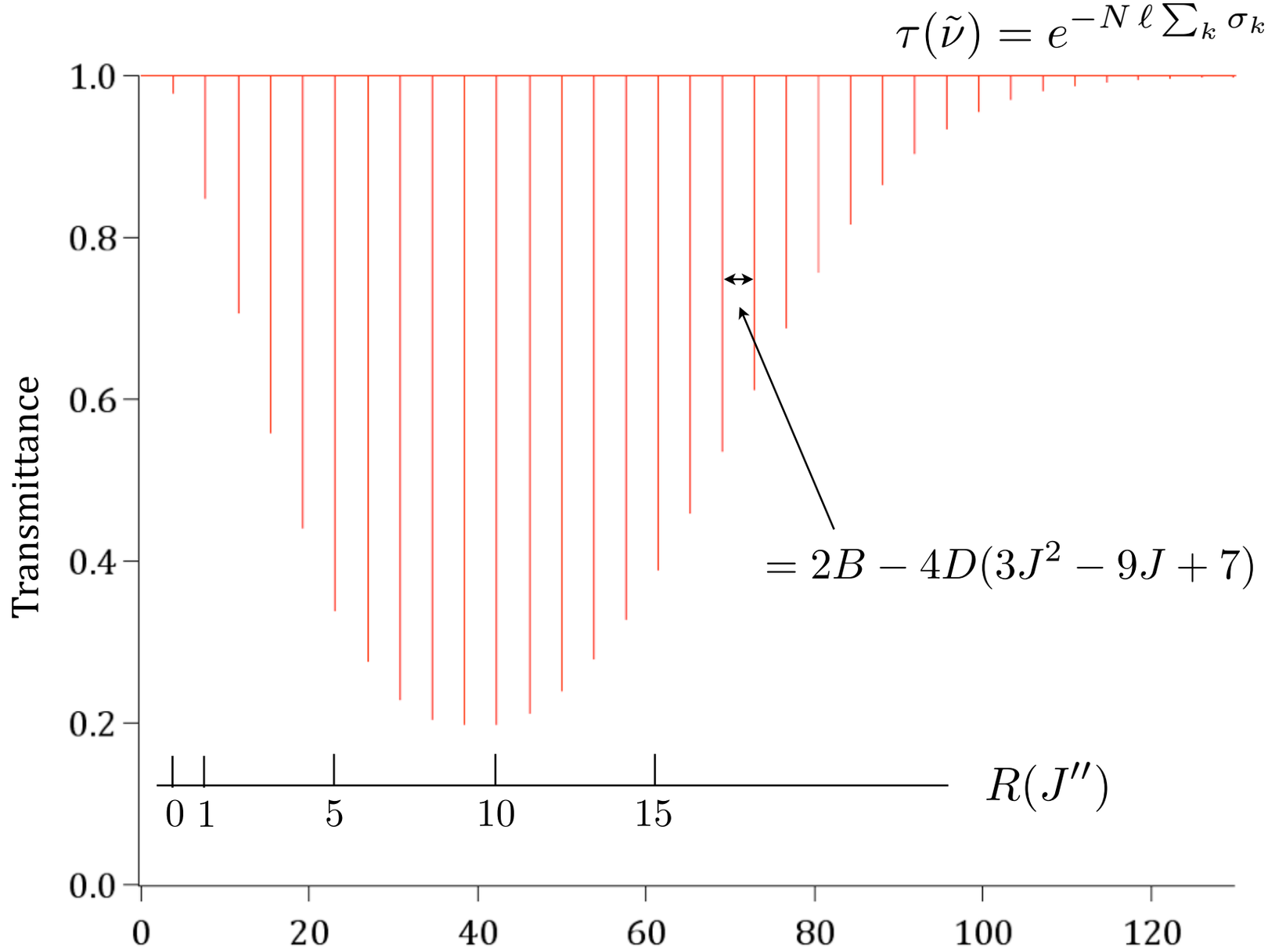
Diatomic molecules : $I = \mu r^2$ with $\mu = m_A m_B/(m_A + m_B)$

Pure rotation spectrum of $^{12}C^{16}O$

Transitions : $\Delta J = +1$



(Rigid rotor)



Line positions :

$$\tilde{\nu}\,(J' \leftarrow J'') = E_r(J+1) - E_r(J) = 2B(J+1) - 4D(J+1)^3$$

$B = 1.923\ \mathrm{cm}^{-1},\ D = 6.12\ 10^{-6}\ \mathrm{cm}^{-1}$

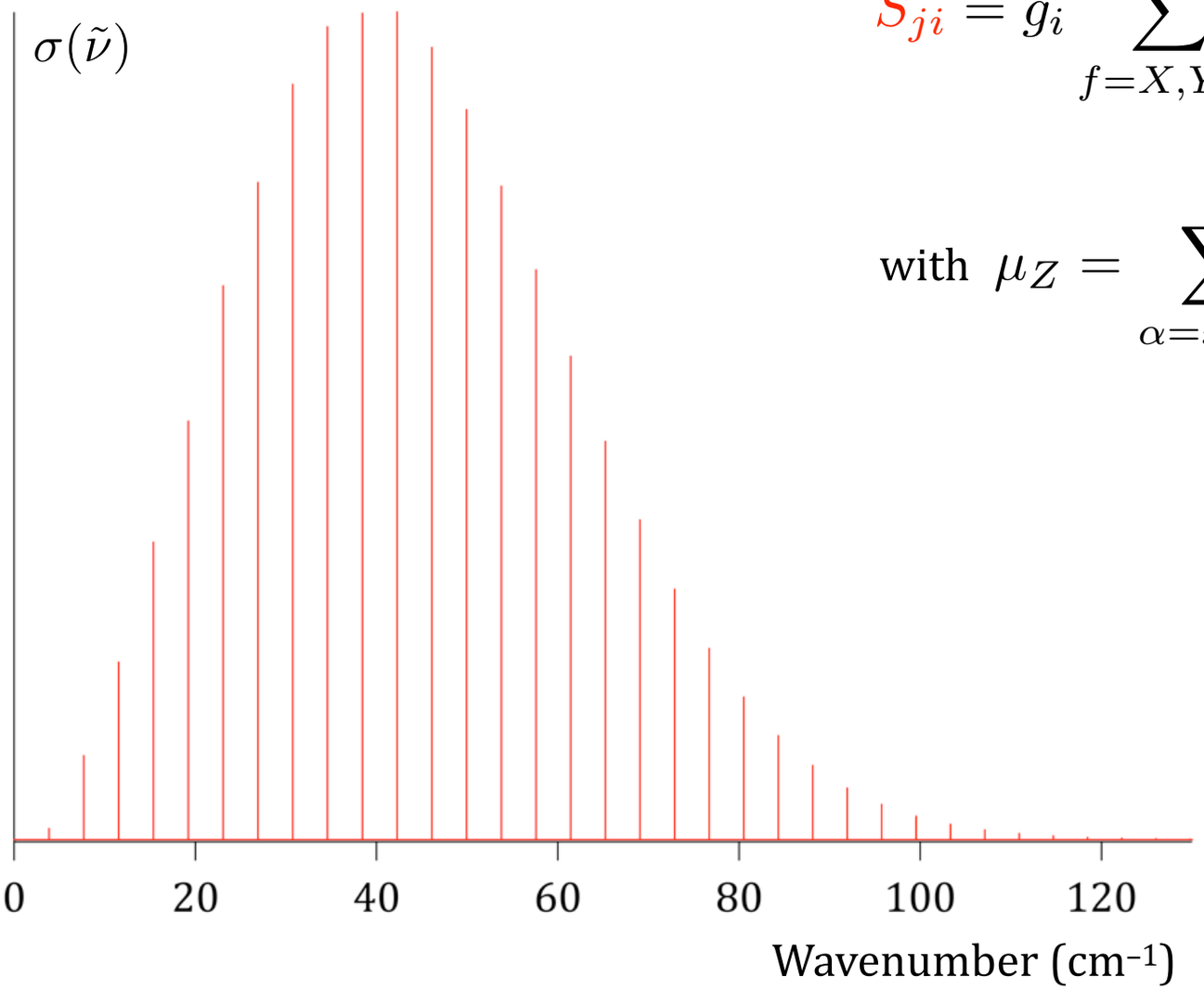
CO pure rotation spectrum : Intensities

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a \, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) S_{ji}$$

$$S_{ji} = g_i \sum_{f=X,Y,Z} |\langle\psi_j|\mu_f|\psi_i\rangle|^2 = 3\, g_i |\langle\psi_j|\mu_Z|\psi_i\rangle|^2$$

(isotropic space)

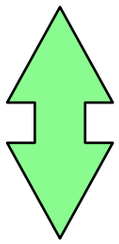
$$\text{with } \mu_Z = \sum_{\alpha=x,y,z} \lambda_{\alpha Z}(\theta,\phi,\chi)\,\mu_\alpha$$



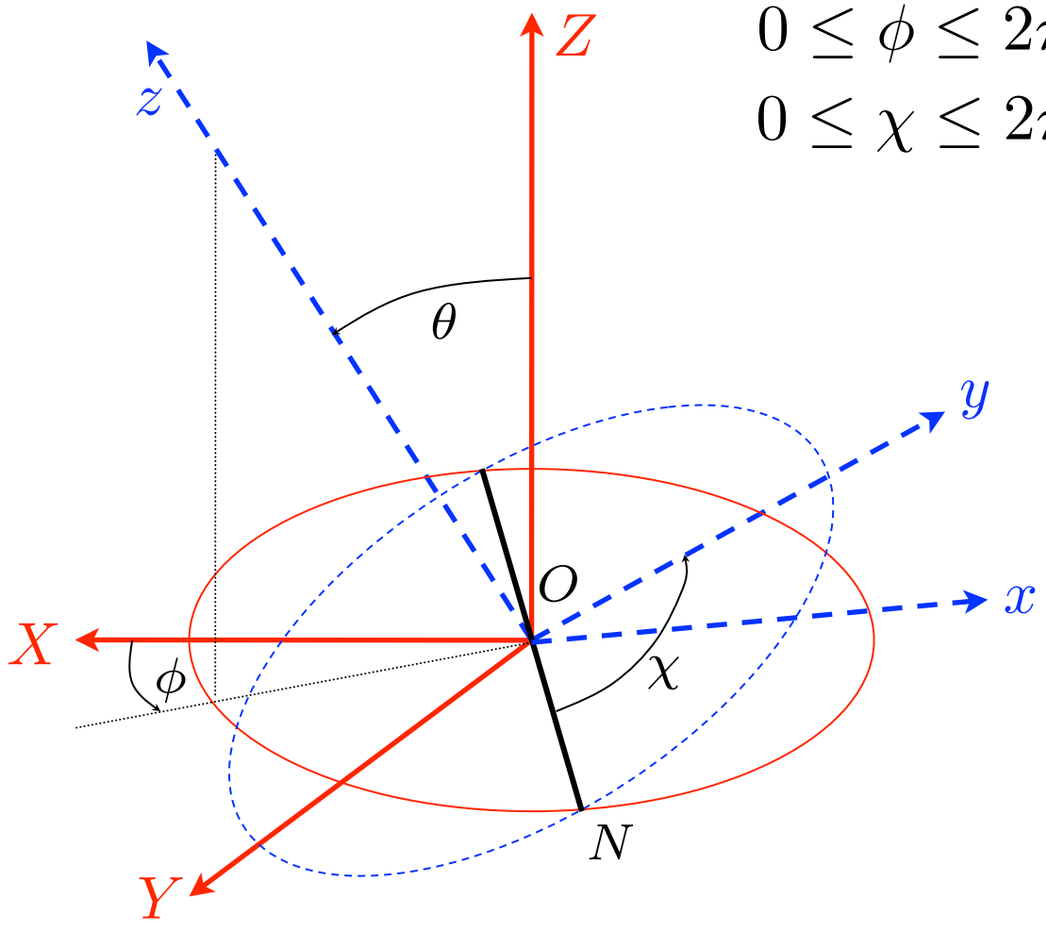
Coordinate systems

$$0 \leq \theta \leq \pi$$
$$0 \leq \phi \leq 2\pi$$
$$0 \leq \chi \leq 2\pi$$

Space-fixed axis system (X, Y, Z)



Euler angles : θ, ϕ, χ



Molecule-fixed frame (*x*, *y*, *z*)

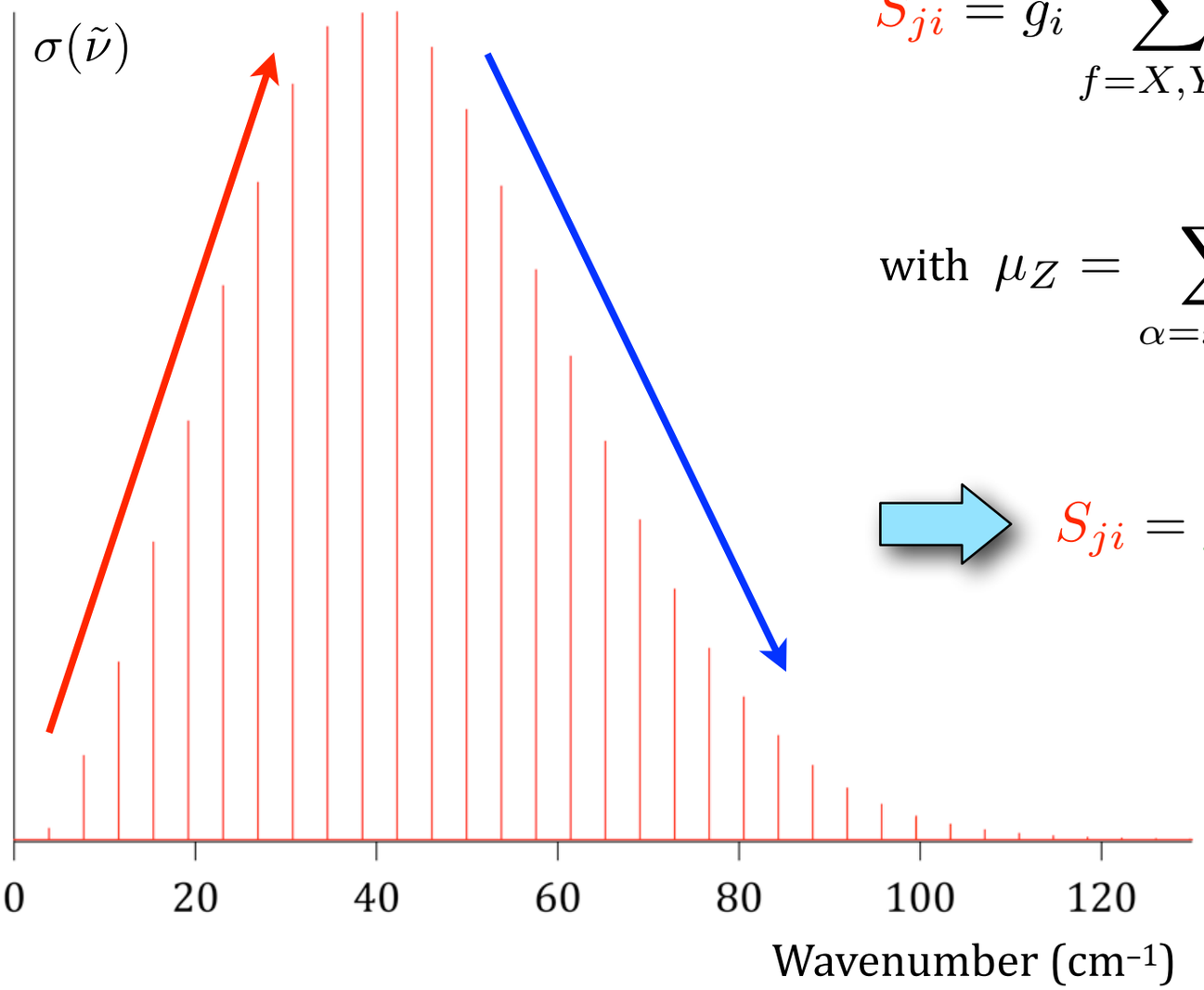
$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \lambda_{xX} & \lambda_{xY} & \lambda_{xZ} \\ \lambda_{yX} & \lambda_{yY} & \lambda_{yZ} \\ \lambda_{zX} & \lambda_{zY} & \lambda_{zZ} \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Transformation matrix ($\lambda^{-1} = \lambda^t$)

$\lambda_{\alpha f}$	X	Y	Z
x	$\cos\theta\cos\phi\cos\chi - \sin\phi\sin\chi$	$\cos\theta\cos\phi\cos\chi + \cos\phi\sin\chi$	$-\sin\theta\cos\chi$
y	$-\cos\theta\cos\phi\sin\chi - \sin\phi\cos\chi$	$-\cos\theta\sin\phi\sin\chi + \cos\phi\cos\chi$	$\sin\theta\sin\chi$
z	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$

CO pure rotation spectrum : Intensities

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a \, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) S_{ji}$$



$$S_{ji} = g_i \sum_{f=X,Y,Z} |\langle\psi_j|\mu_f|\psi_i\rangle|^2 = 3\, g_i |\langle\psi_j|\mu_Z|\psi_i\rangle|^2$$

(isotropic space)

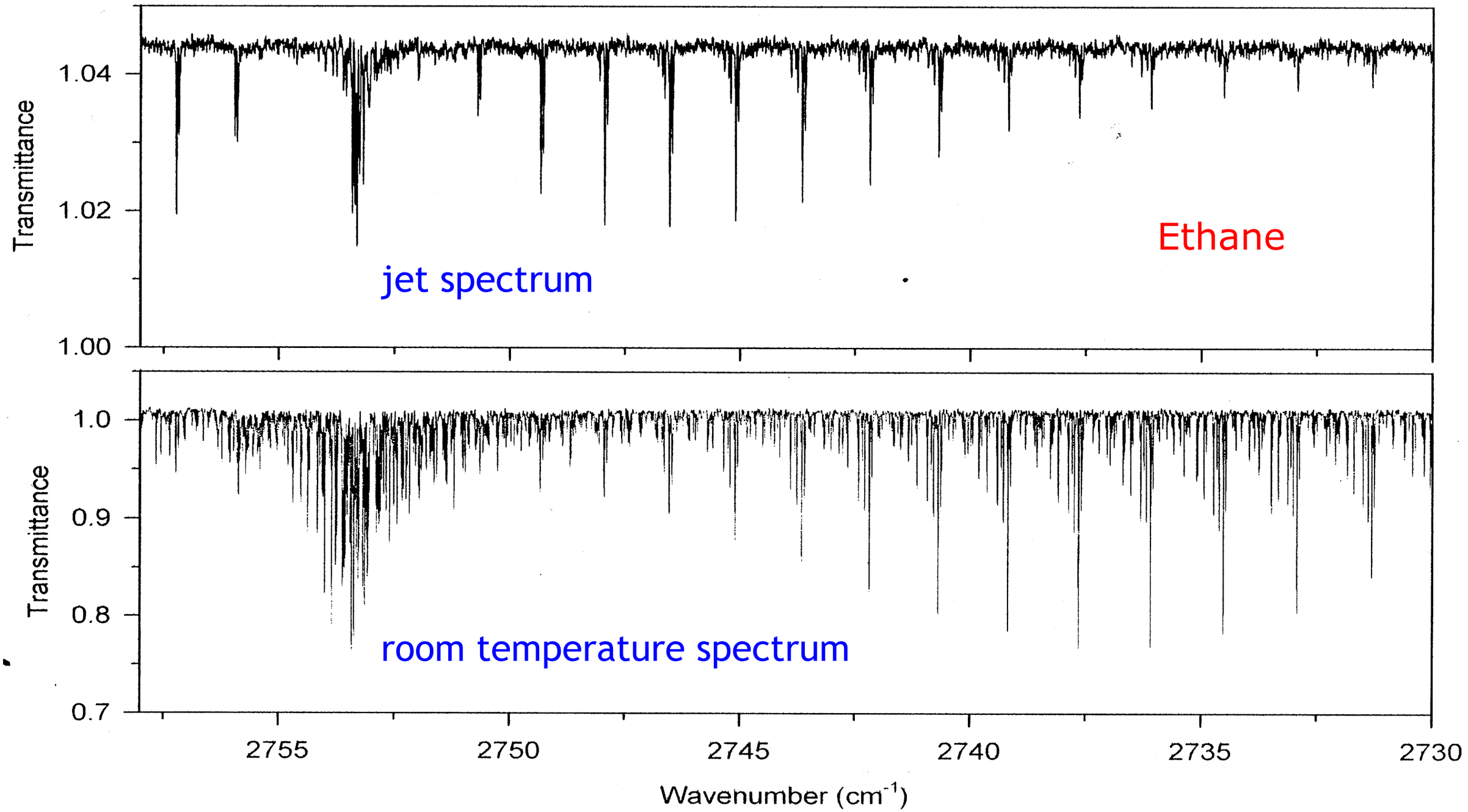
with $\mu_Z = \sum_{\alpha=x,y,z} \lambda_{\alpha Z}(\theta,\phi,\chi)\,\mu_\alpha$ and $\psi_i = \psi_e^i \psi_v^i \psi_r^i$

$$S_{ji} = g_i \underbrace{3\,|\langle\psi_r^j|\lambda_{zZ}|\psi_r^i\rangle|^2}_{= \frac{J+1}{2J+1}} |\mu_z|^2 = (J+1)\,|\mu_z|^2$$

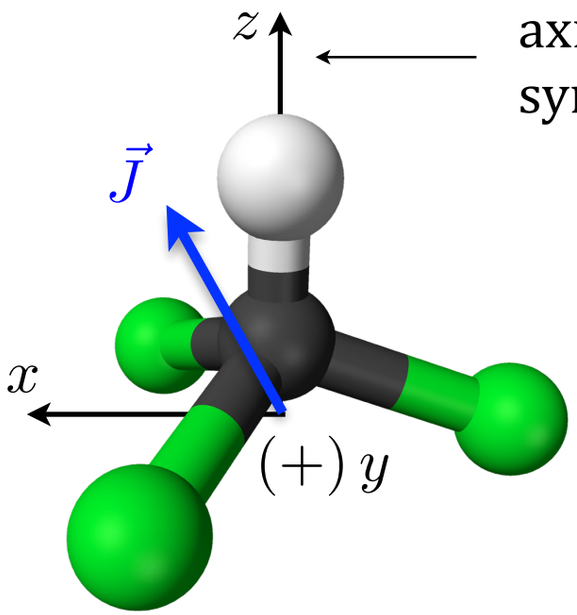
$= 2J+1$

Permanent dipole moment :
$\mu_z = 1.098$ D

Line intensities – Effect of the temperature



Rotation of a symmetric top



- ***Prolate*** *symmetric* tops ($I_z < I_x = I_y$)

➞ $z = a, x = b, y = c$: $I_a < I_b = I_c$ (CH_3Cl)

$$E_r(J,K) = BJ(J+1) + (A-B)K^2$$

Projection of J on the z molecule fixed axis : $-J \leq K \leq +J$

- ***Oblate*** *symmetric* tops ($I_z > I_x = I_y$)

➞ $z = c, x = a, y = b$: $I_a = I_b < I_c$ (CCl_3H)

$$E_r(J,K) = BJ(J+1) + (C-B)K^2$$

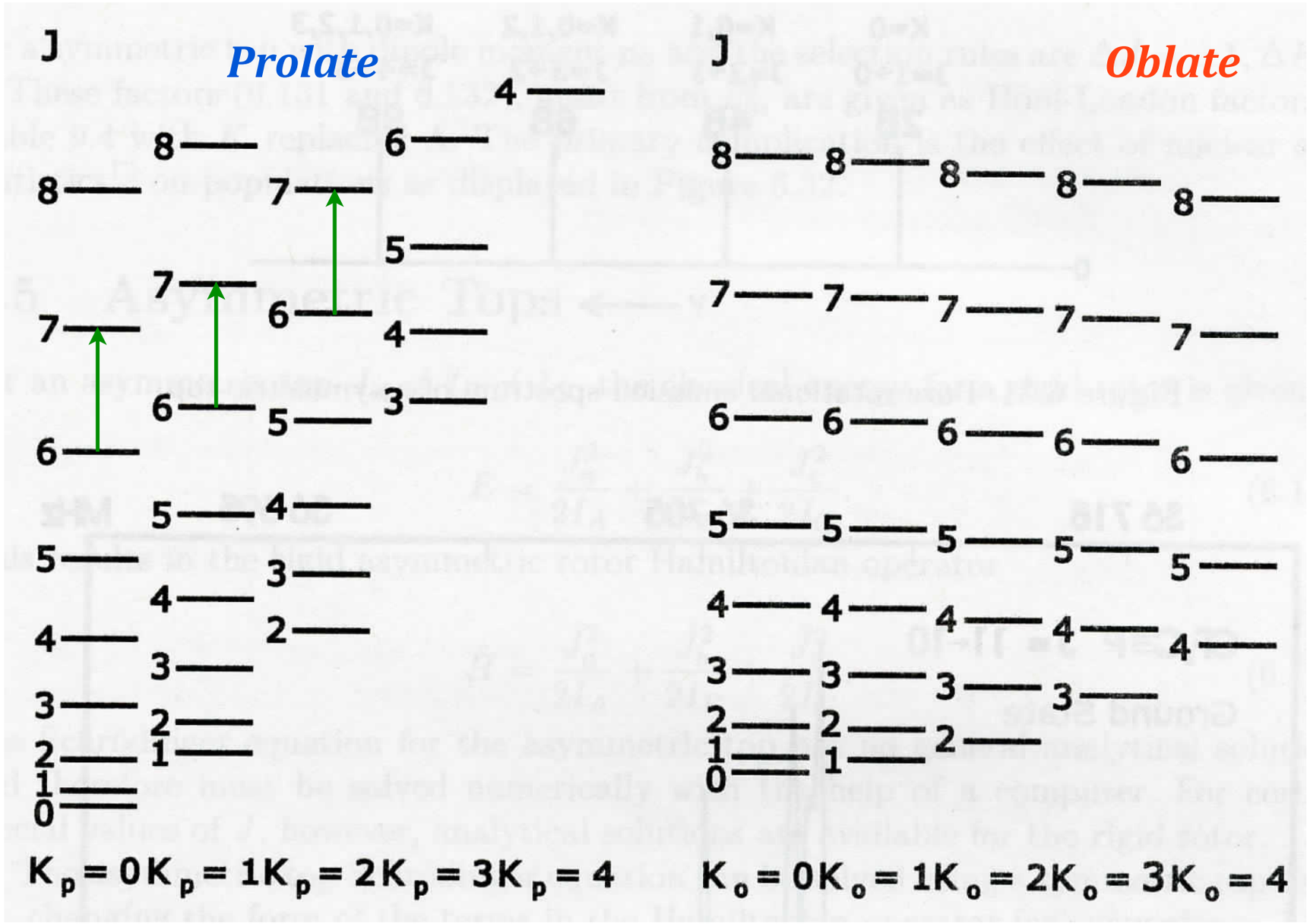
$$A = \frac{h}{8\pi^2 c I_a} \geq B = \frac{h}{8\pi^2 c I_b} \geq C = \frac{h}{8\pi^2 c I_c}$$

Semi-rigid prolate top : $E_r(J,K) = BJ(J+1) - D_J J^2(J+1)^2 + (A-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2$

Rotation of a symmetric top

$\Delta K = 0$

$\Delta J = +1$



$K \neq 0$

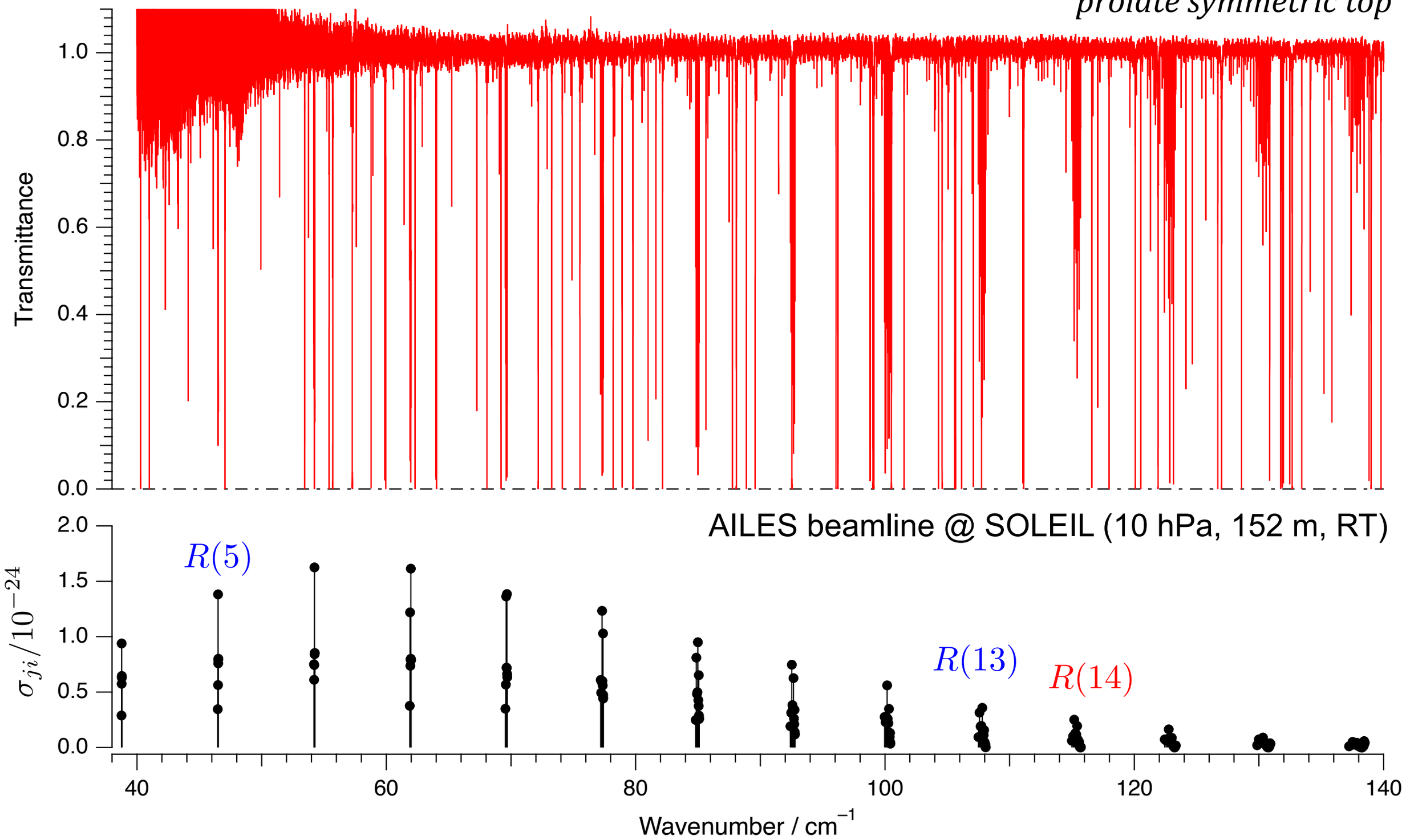
two-fold degeneracy

$$E_r(J,K) = BJ(J+1) + \underbrace{(A-B)}_{>0}K^2$$

$$E_r(J,K) = BJ(J+1) + \underbrace{(C-B)}_{<0}K^2$$

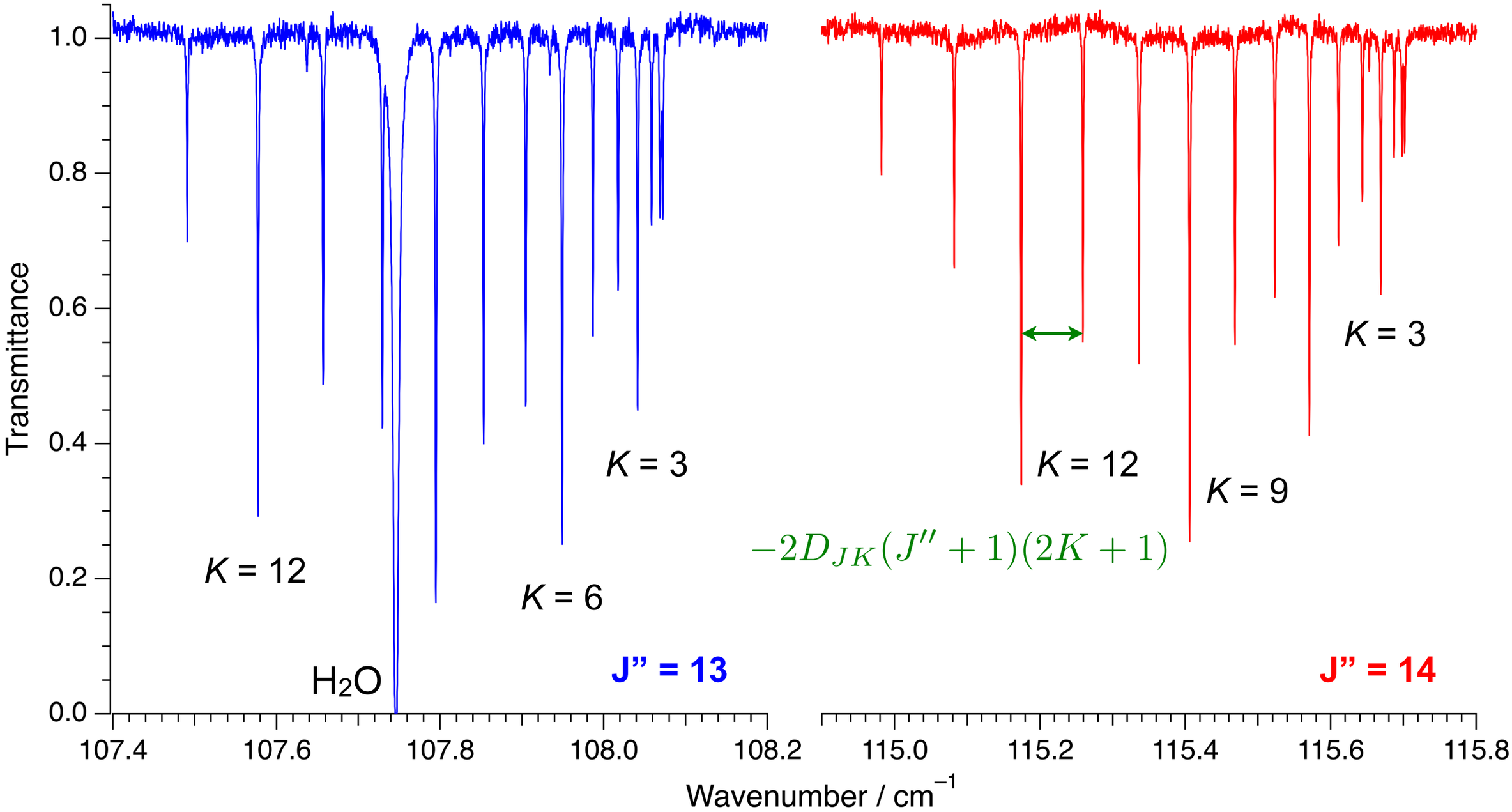
Pure rotation spectrum of $^{12}CH_3D$

prolate symmetric top



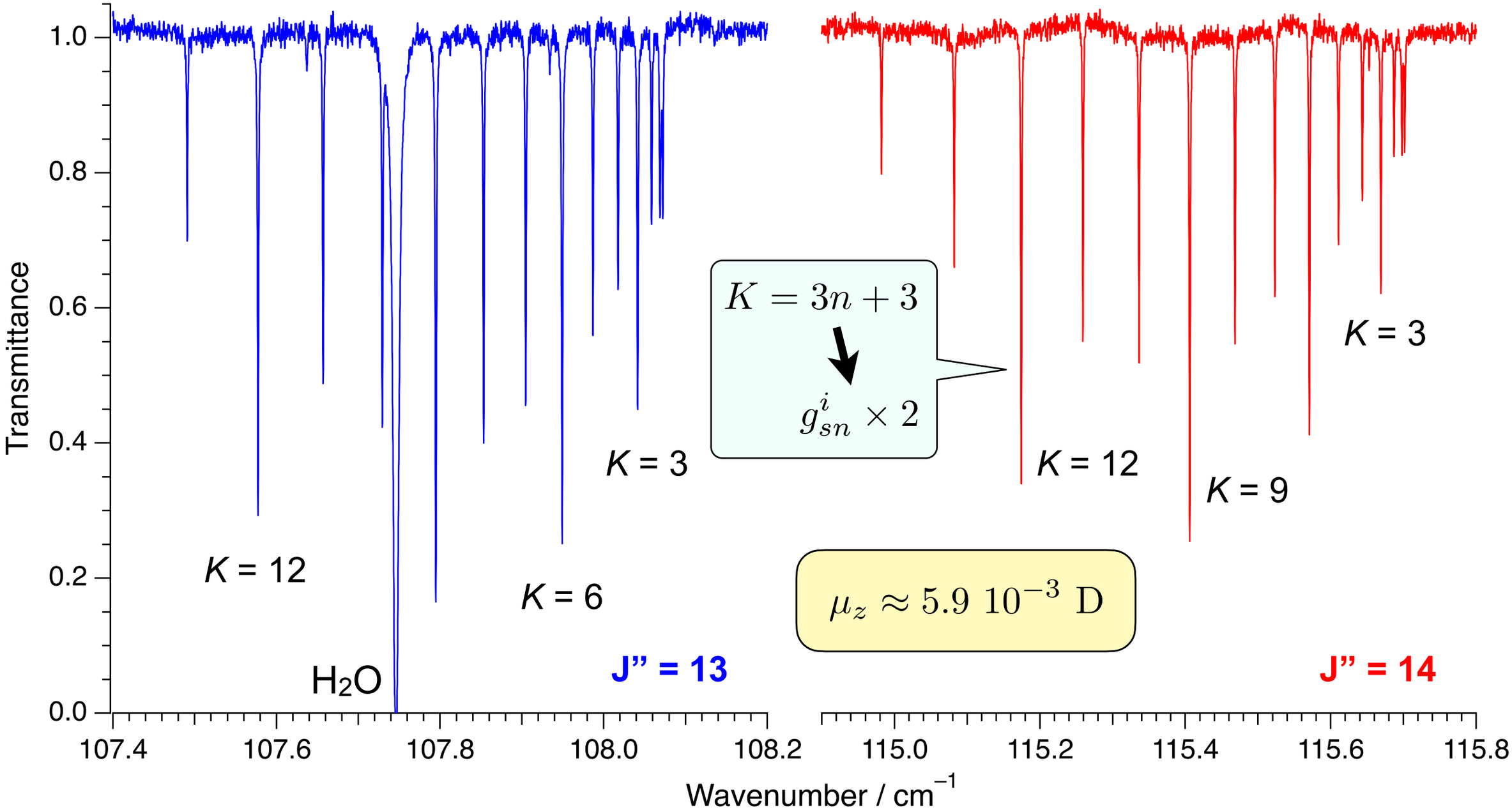
Pure rotation spectrum of $^{12}CH_3D$

AILES beamline @ SOLEIL
10 hPa, 152 m, RT

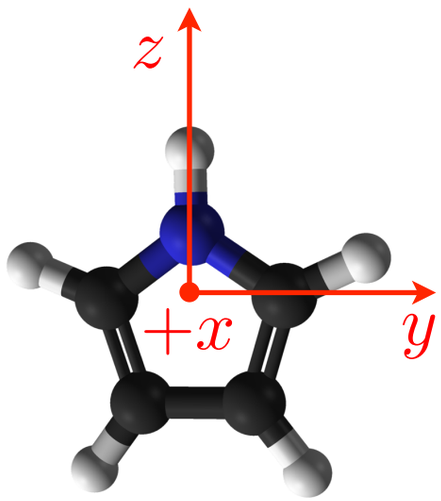


Pure rotation spectrum of $^{12}CH_3D$

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) \underline{S_{ji}} \rightarrow S_{ji} = g^i_{sn}\frac{(J''+1)^2 - K^2}{J+1}|\mu_z|^2$$



Rotation of an asymmetric top

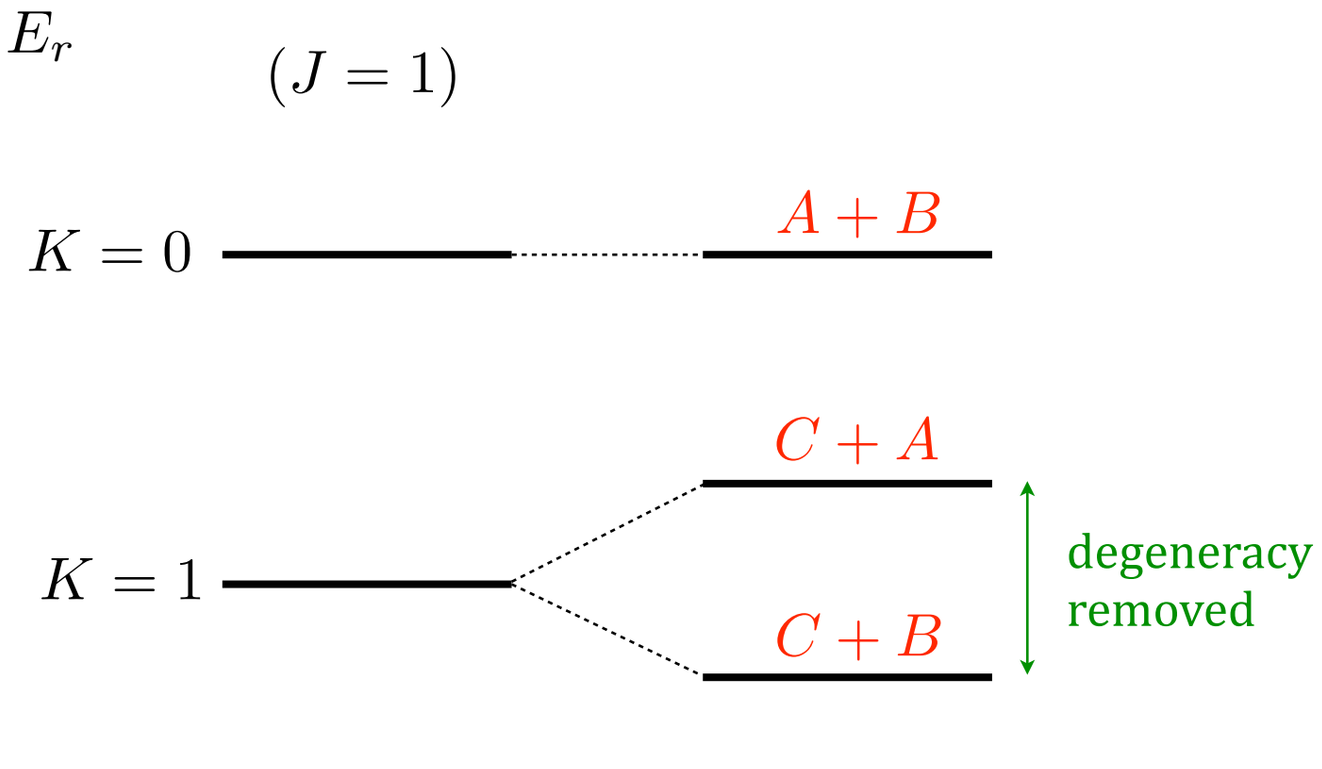


$$x \to c$$
$$y \to a$$
$$z \to b$$

(II^r representation)

near oblate asymmetric top

K splitting ↗ when J ↗ or K ↘



A ≈ 0.305 cm^{-1}
B ≈ 0.300 cm^{-1}
C ≈ 0.151 cm^{-1}

Ray asymmetry parameter

$$\kappa = \frac{2B - A - C}{A - C} \approx 0.94$$

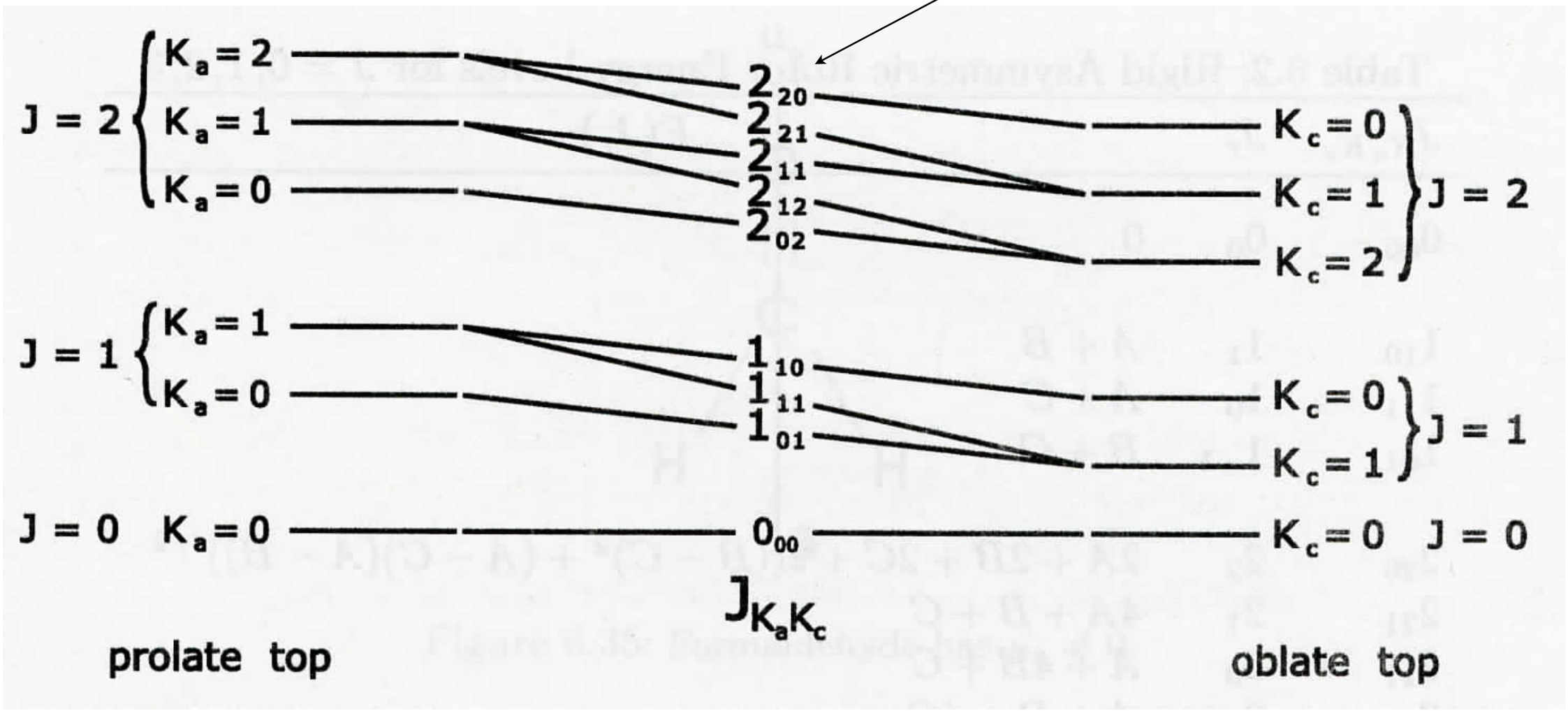
symmetric top

asymmetric top

Rotational levels of asymmetric tops

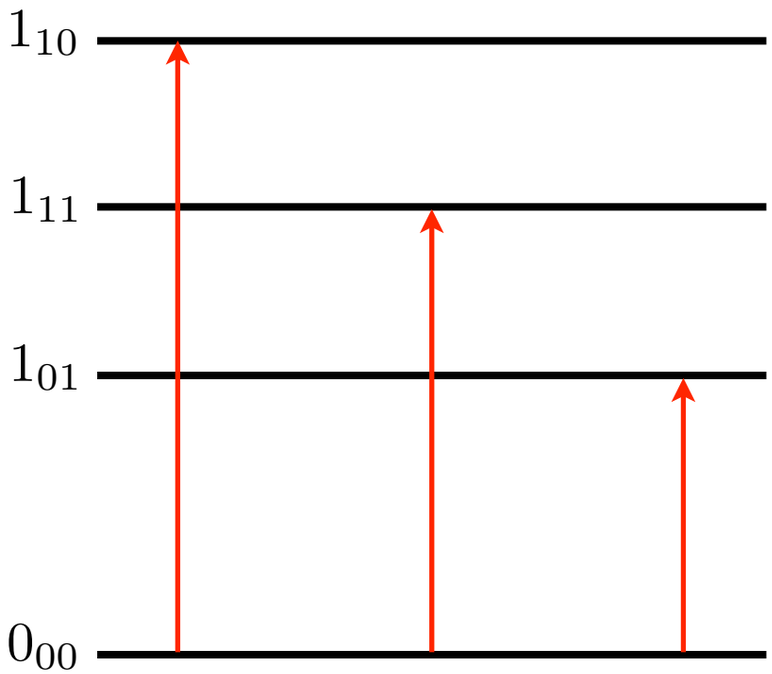
($I_a < I_b < I_c$)

$K_a, K_c =$ pseudo-quantum numbers



$\kappa = -1$ $\qquad$ $\kappa = \dfrac{2B - A - C}{A - C}$ $\qquad$ $\kappa = +1$

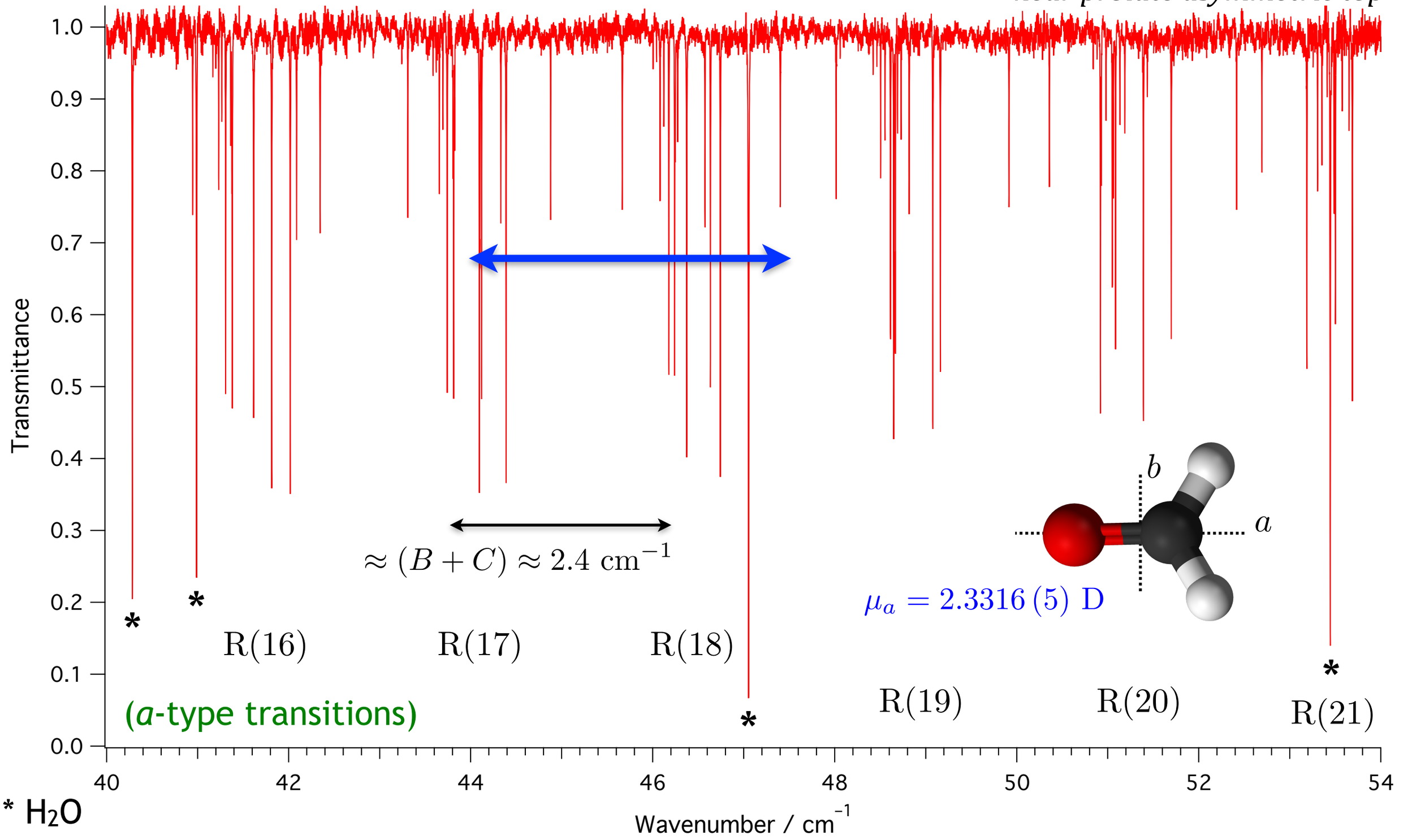
Asymmetric top: rotational transitions



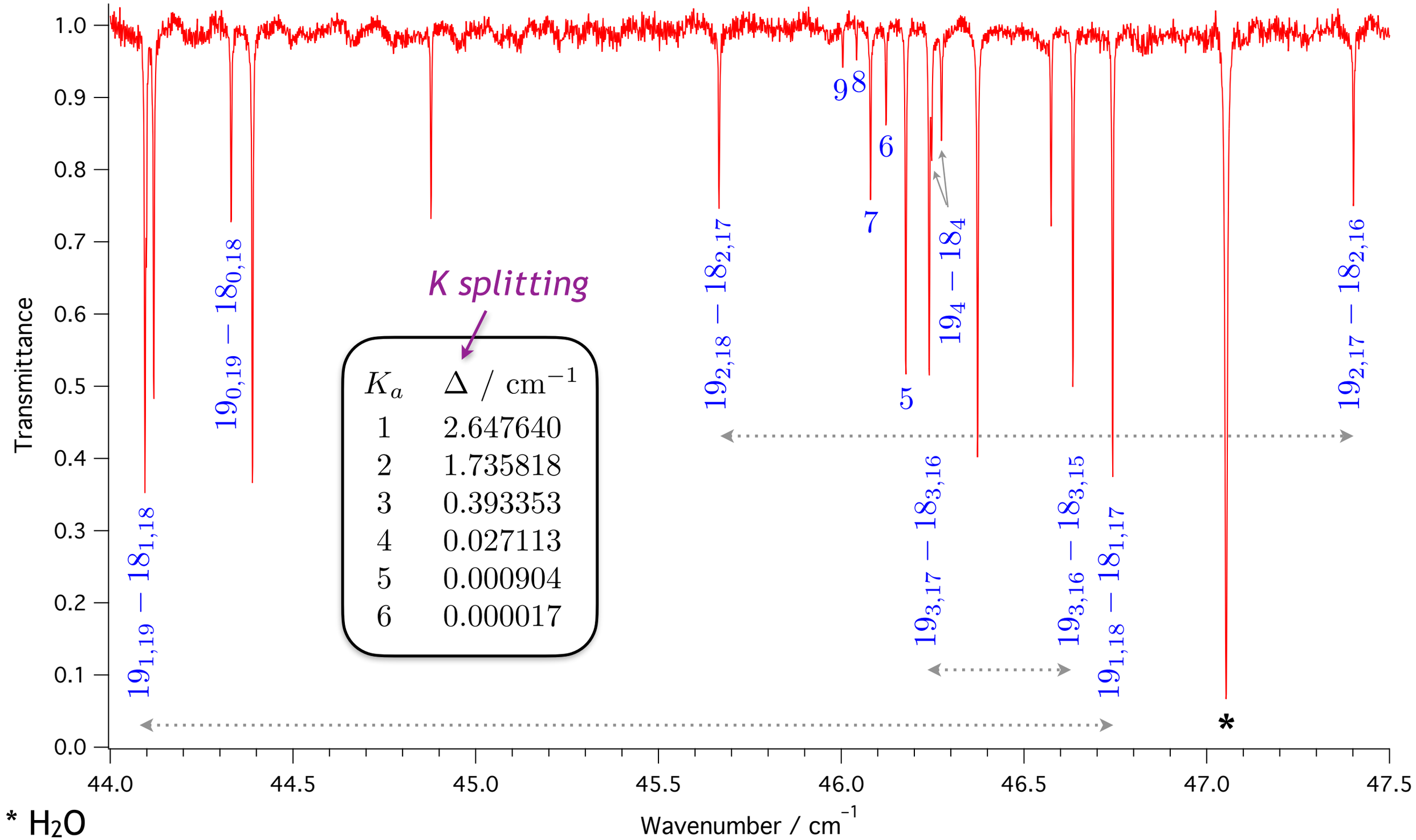
$$\left.\begin{array}{l} c\text{-type } (\mu_c \neq 0): \ \Delta K_a = \text{odd}, \Delta K_c = \text{even} \\ b\text{-type } (\mu_b \neq 0): \ \Delta K_a = \text{odd}, \Delta K_c = \text{odd} \\ a\text{-type } (\mu_a \neq 0): \ \Delta K_a = \text{even}, \Delta K_c = \text{odd} \end{array}\right| \quad \Delta J = 0, \pm 1$$

Pure rotation spectrum of H_2CO

near prolate asymmetric top



Pure rotation of H_2CO – $^{qr}R(18)$



^{qr}R(18) of H_2CO – Levels & transitions

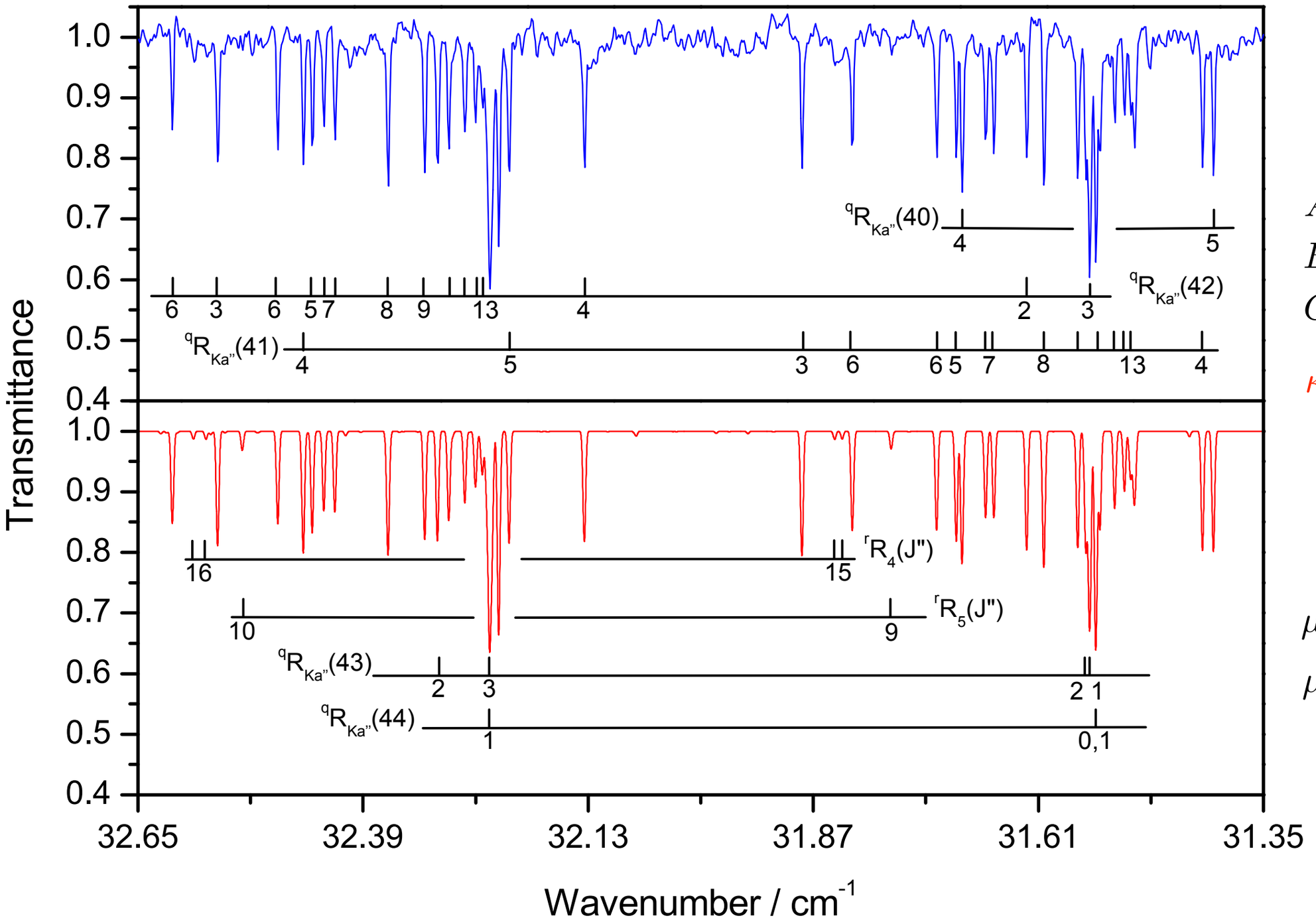
$\Delta J = 1,\ \Delta K_a = 0,\ \Delta K_c = 1$ (*a*-type transitions)

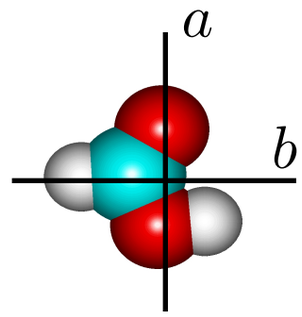
K splitting ↗ when J ↗ or K ↘

J'	Ka'	Kc'	Energy	K splitting	J"	Ka"	Kc"	Energy	K splitting	Transition
19	0	19	450.290804		18	0	18	405.959812		44.330992
19	**1**	**19**	**451.437602**	**29.003850**	**18**	**1**	**18**	**407.342427**	**26.356211**	**44.095175**
19	**1**	**18**	**480.441452**		**18**	**1**	**17**	**433.698638**		**46.742814**
19	2	18	491.755061	10.896075	18	2	17	446.089149	9.160257	45.665912
19	2	17	502.651136		18	2	16	455.249406		47.401730
19	**3**	**17**	**535.936777**	**1.503140**	**18**	**3**	**16**	**489.696030**	**1.109788**	**46.240747**
19	**3**	**16**	**537.439917**		**18**	**3**	**15**	**490.805818**		**46.634099**
19	4	16	592.892958	0.078728	18	4	15	546.645476	0.051615	46.247482
19	4	15	592.971686		18	4	14	546.697091		46.274595
19	**5**	**15**	**665.896911**	**0.002178**	**18**	**5**	**14**	**619.720549**	**0.001274**	**46.176362**
19	**5**	**14**	**665.899089**		**18**	**5**	**13**	**619.721823**		**46.177266**

(values in cm^{-1})

Pure rotation spectrum of HCOOH





$A = 2.586\ \mathrm{cm}^{-1}$

$B = 0.4021\ \mathrm{cm}^{-1}$

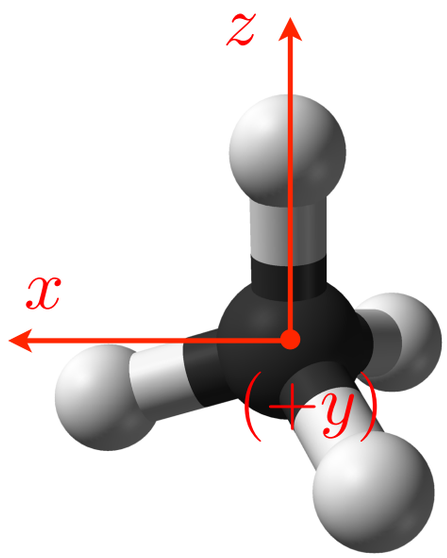
$C = 0.3474\ \mathrm{cm}^{-1}$

$\kappa = -0.951$

$\mu_a = 1.4071\,(8)\ \mathrm{D}$

$\mu_b = 0.227\,(10)\ \mathrm{D}$

Rotation of a spherical top – CH_4



$$I_x = I_y = I_z$$

No preferred direction *(i.e. "K" for symmetric rotors)*

$$E_r(J) = BJ(J+1)$$

(2J+1 degenerate levels for each J)

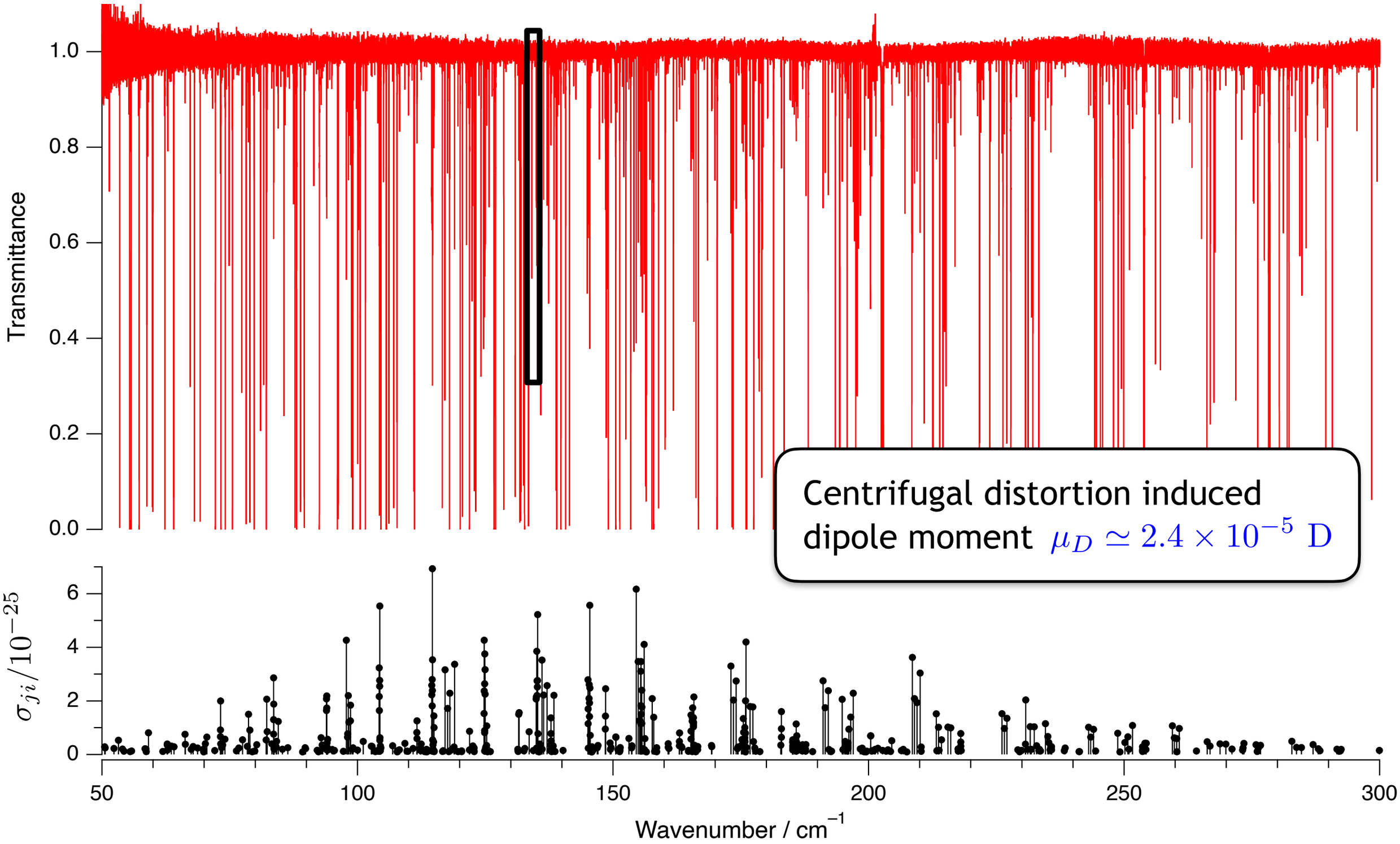
Semi-rigid molecule *: degeneracy partly lifted* → *Identification of the levels?*

$J = 12$

Level	E / cm^{-1}	Level	E / cm^{-1}
A_1 1	814.6460	F_1 1	814.6479
A_1 2	815.1436	F_1 2	814.8843
A_2 1	815.0890	F_1 3	815.1315
E 1	814.6488	F_2 1	814.8665
E 2	814.9931	F_2 2	815.0081
		F_2 3	815.1159

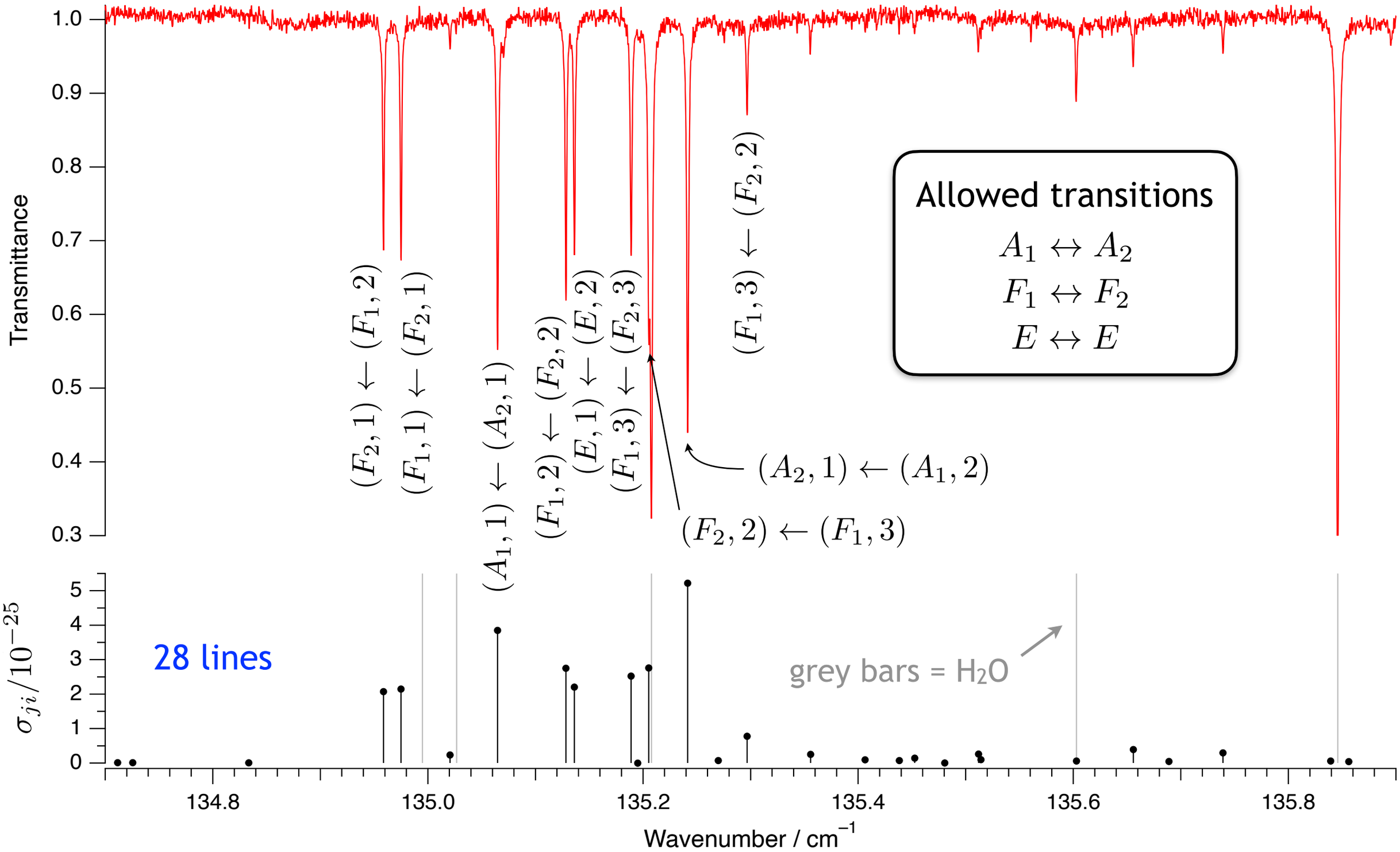
- **symmetry** in $T_d(M)$ group
- **ranking index** (α)

Pure rotation spectrum of CH_4



Centrifugal distortion induced dipole moment $\mu_D \simeq 2.4 \times 10^{-5}$ D

R(12) manifold of CH_4



Elements of molecular spectroscopy

Molecular physics – Vibration

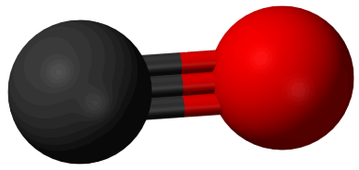
Molecular vibration

Molecule = *N* atoms

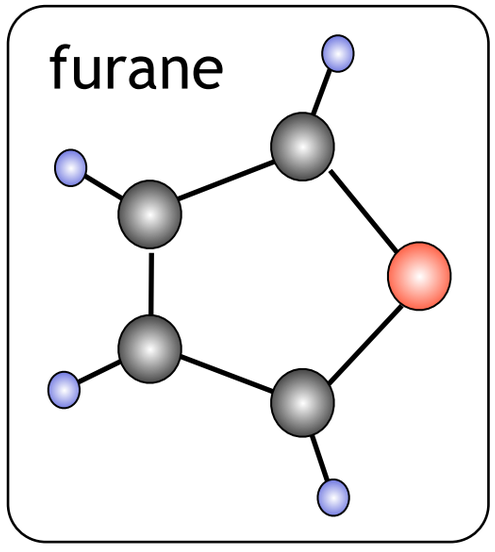
$3N-5$ (linear)

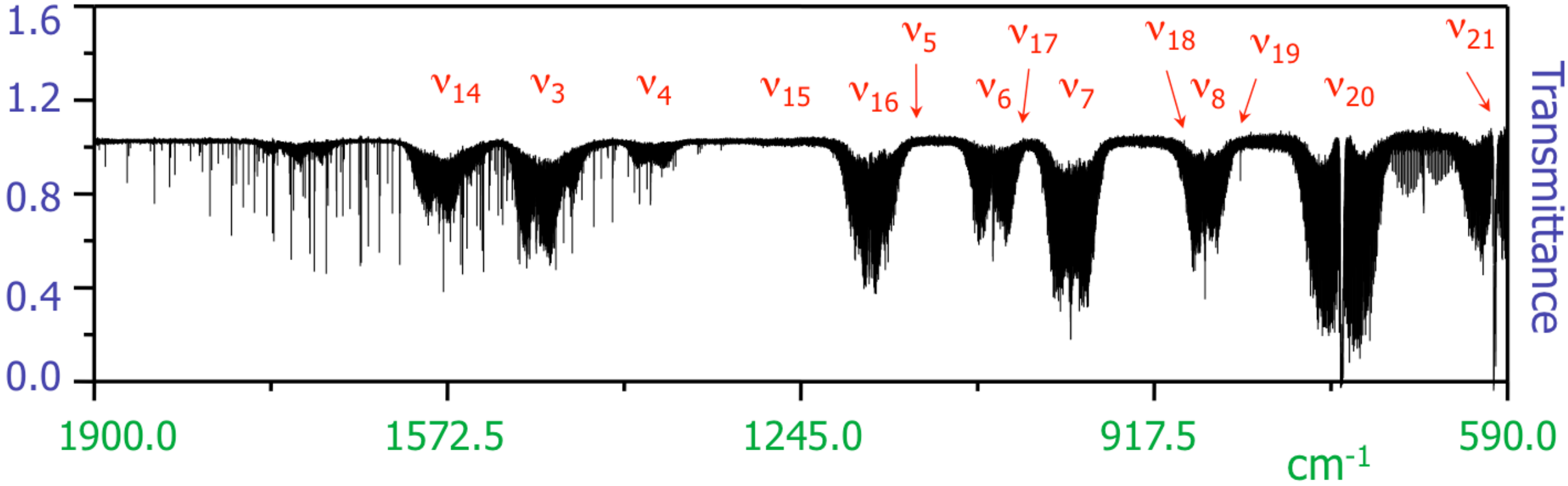
$3N-6$ (non-linear)

modes of vibration

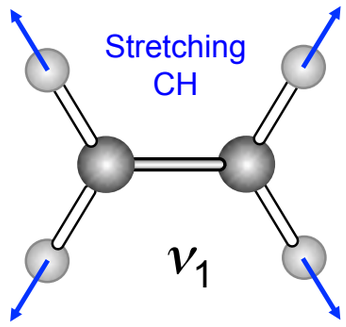


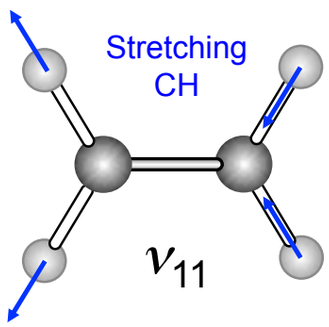
carbon monoxide

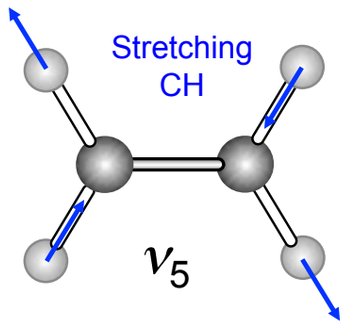




Modes of vibration of ethylene



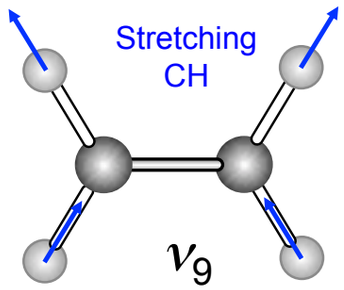


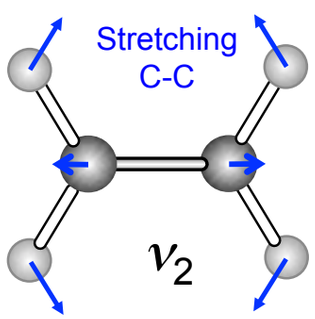


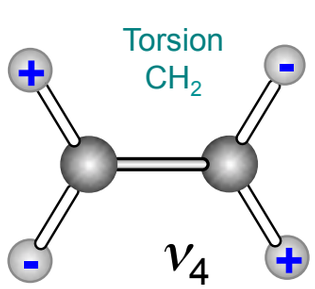
ν_1 a_g 3022 cm^{-1}

ν_{11} b_{1u} 2989 cm^{-1}

ν_5 b_{3g} 3083 cm^{-1}



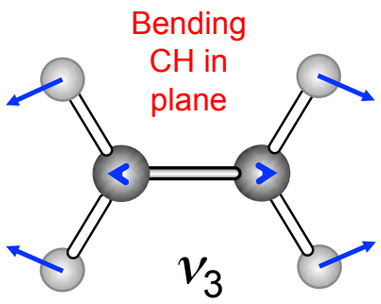


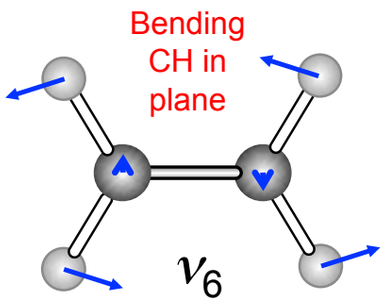


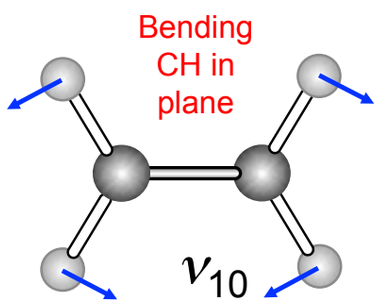
ν_9 b_{2u} 3015 cm^{-1}

ν_2 a_g 1625 cm^{-1}

ν_4 a_u 1026 cm^{-1}



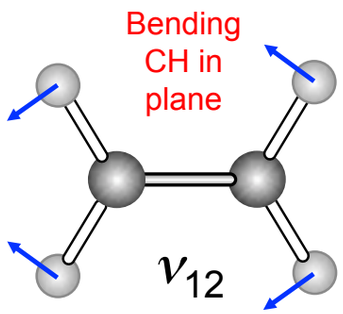


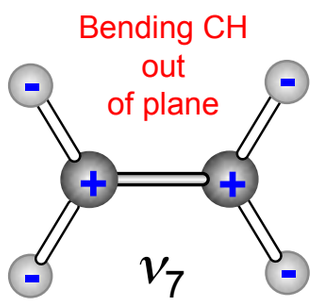


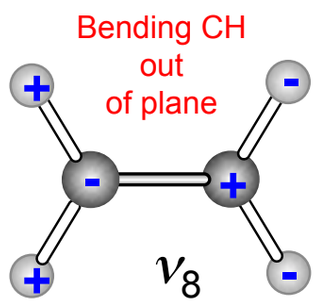
ν_3 a_g 1343 cm^{-1}

ν_6 b_{3g} 1222 cm^{-1}

ν_{10} b_{2u} 826 cm^{-1}







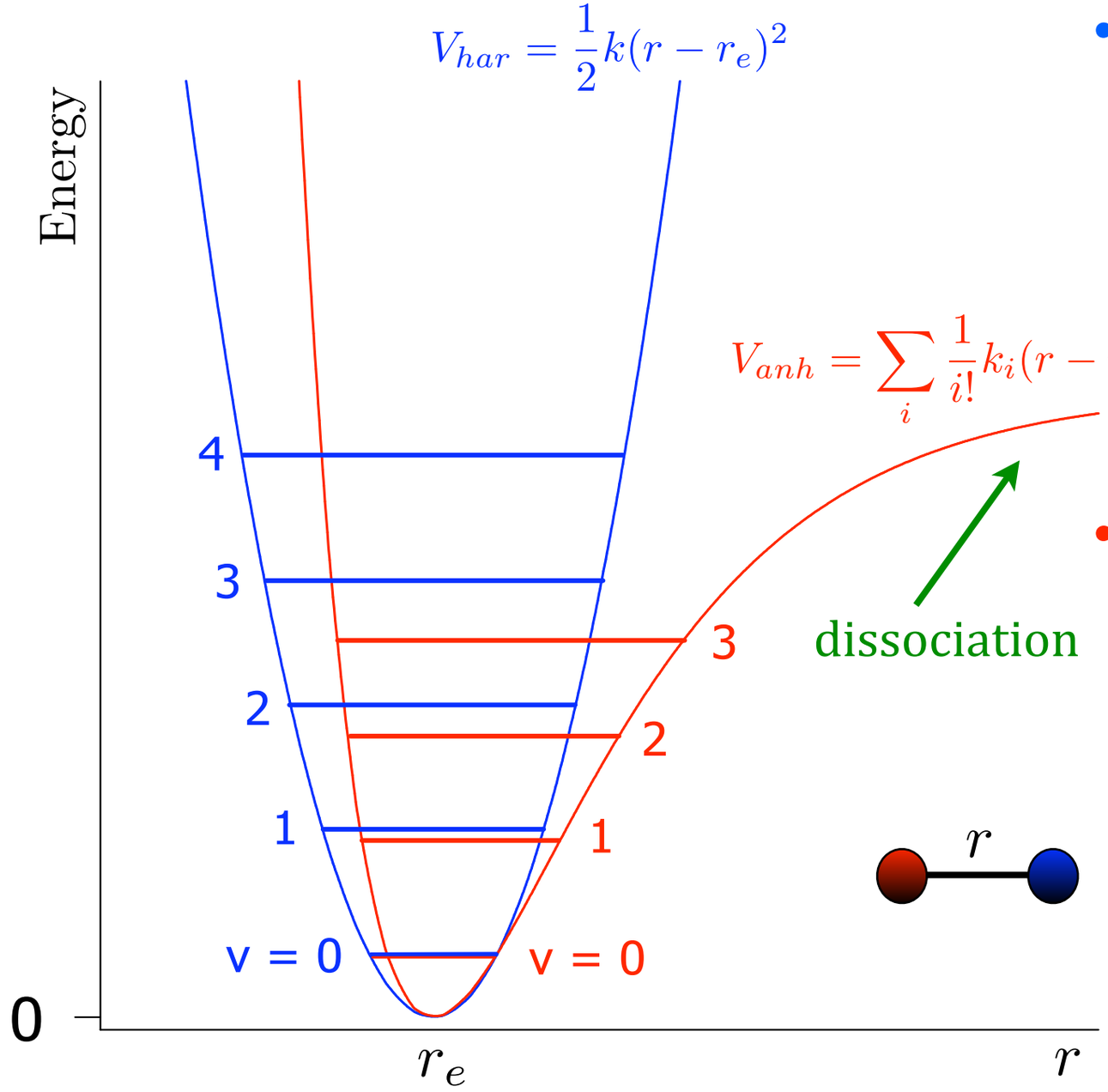
ν_{12} b_{1u} 1442 cm^{-1}

ν_7 b_{3u} 949 cm^{-1}

ν_8 b_{2g} 940 cm^{-1}

Vibration of diatomics

1 degree of freedom of vibration ⇒ **1** mode of vibration



• Harmonic oscillator :

$$E_v = \omega_e(v + 1/2)$$

$$k = \left.\frac{d^2V}{dr^2}\right|_{r=r_e}$$

$$\omega_e = \frac{1}{2\pi c}\sqrt{k/\mu}$$

Reduced mass : $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

• Anharmonic oscillator :

$$E_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \ldots$$

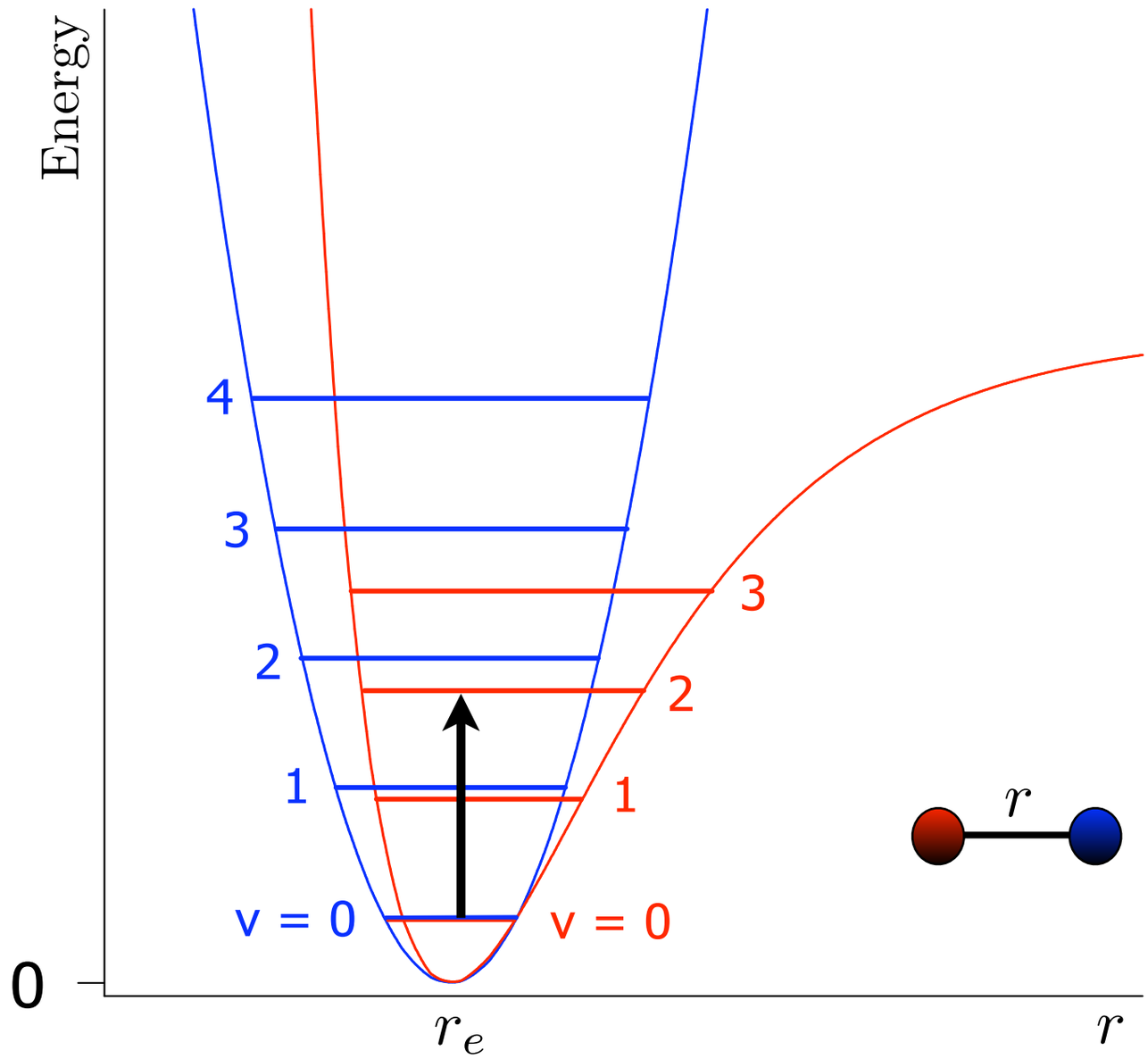
$$\omega_e x_e = -\frac{5\,k_3^2}{48\,\omega_e} + \frac{k_4}{16}$$

Force constants : $k_i = \left.\frac{d^iV}{dr^i}\right|_{r=r_e}$

Diatomics – Vibrational spectrum

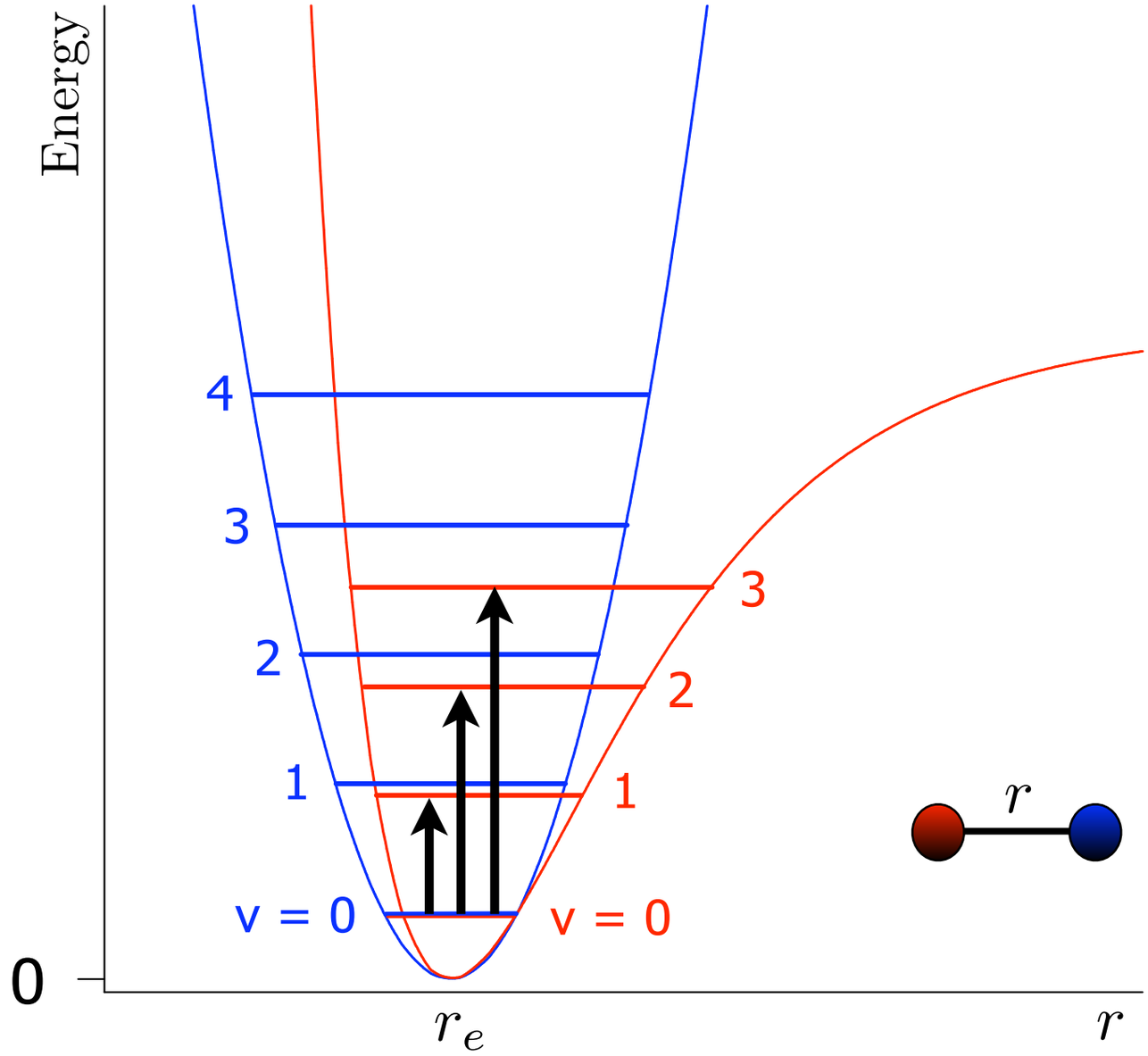
$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) \underline{S_{ji}} \rightarrow S_{ji} = g_i\, 3\, \left|\langle\psi_r^j|\lambda_z z|\psi_r^i\rangle\right|^2 \left|\Delta\mu_z\right|^2$$

dipole moment variation



Diatomics – Vibrational spectrum

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) S_{ji} \rightarrow S_{ji} = g_i\, 3\, \left|\langle\psi_r^j|\lambda_z z|\psi_r^i\rangle\right|^2 \left|\Delta\mu_z\right|^2$$

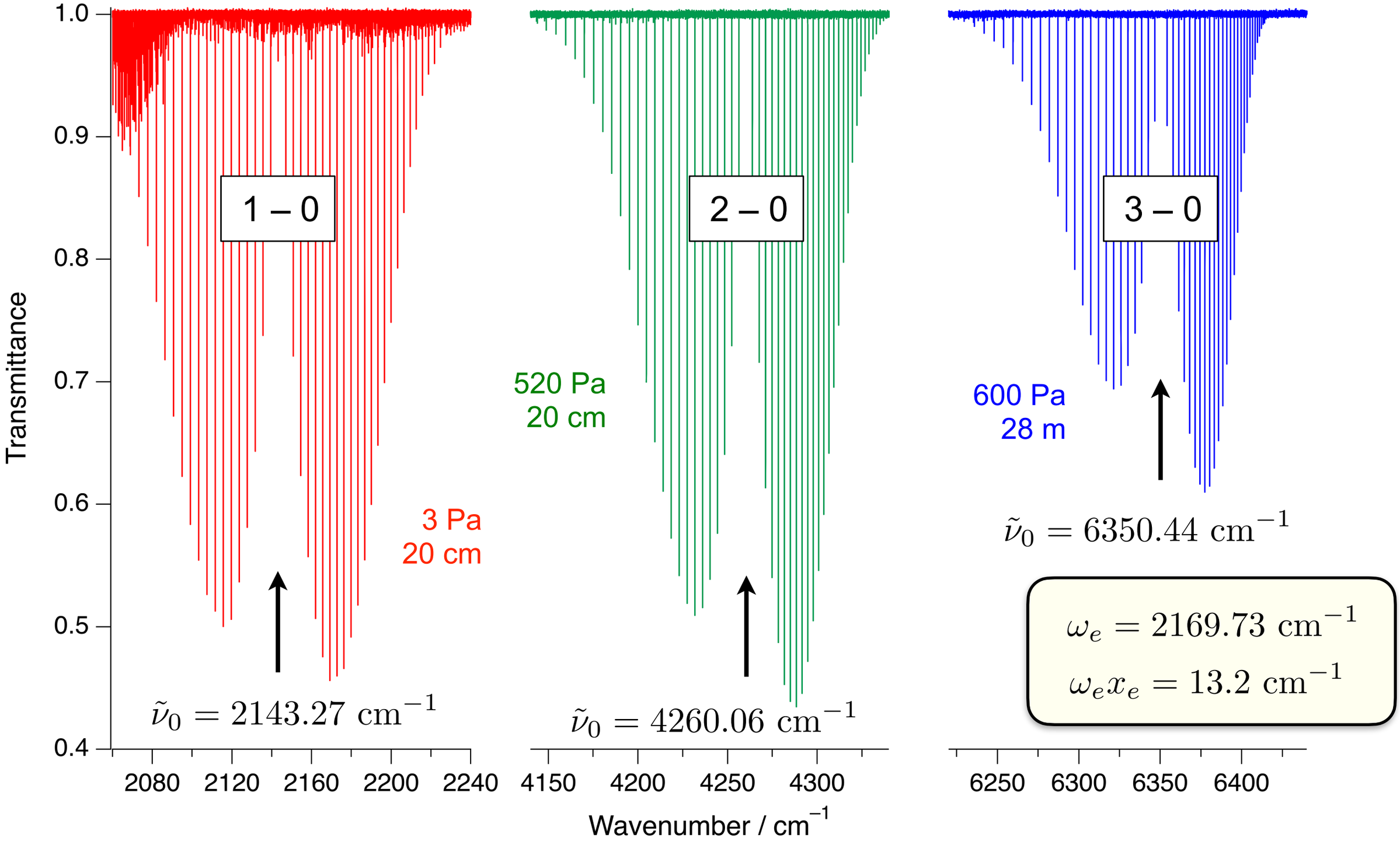


dipole moment variation

heteronuclear diatomics ✓

homonuclear diatomics ✗

Vibrational bands of carbon monoxide

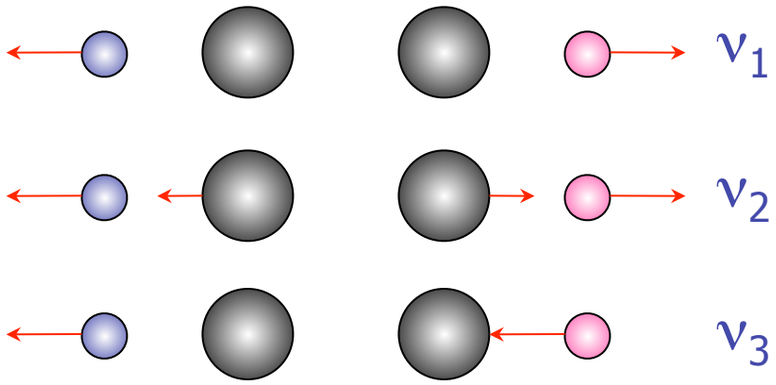


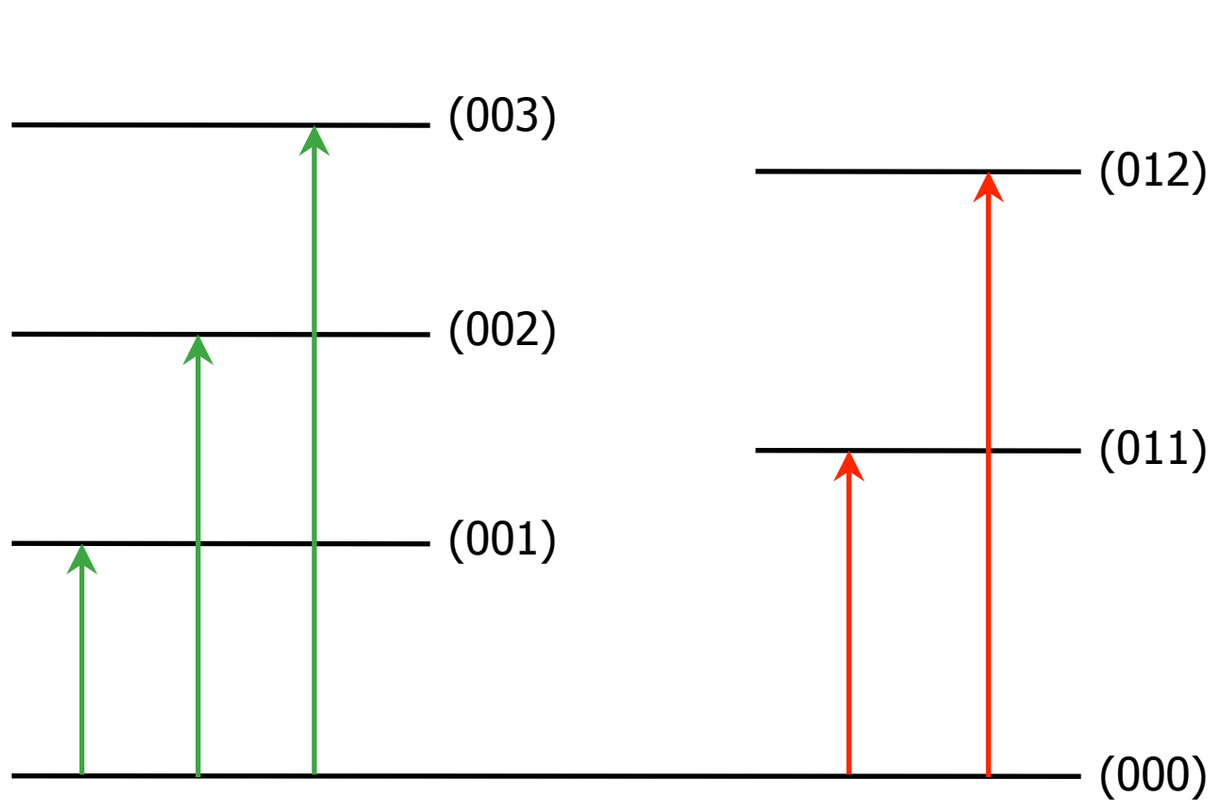
$\omega_e = 2169.73\ \mathrm{cm}^{-1}$

$\omega_e x_e = 13.2\ \mathrm{cm}^{-1}$

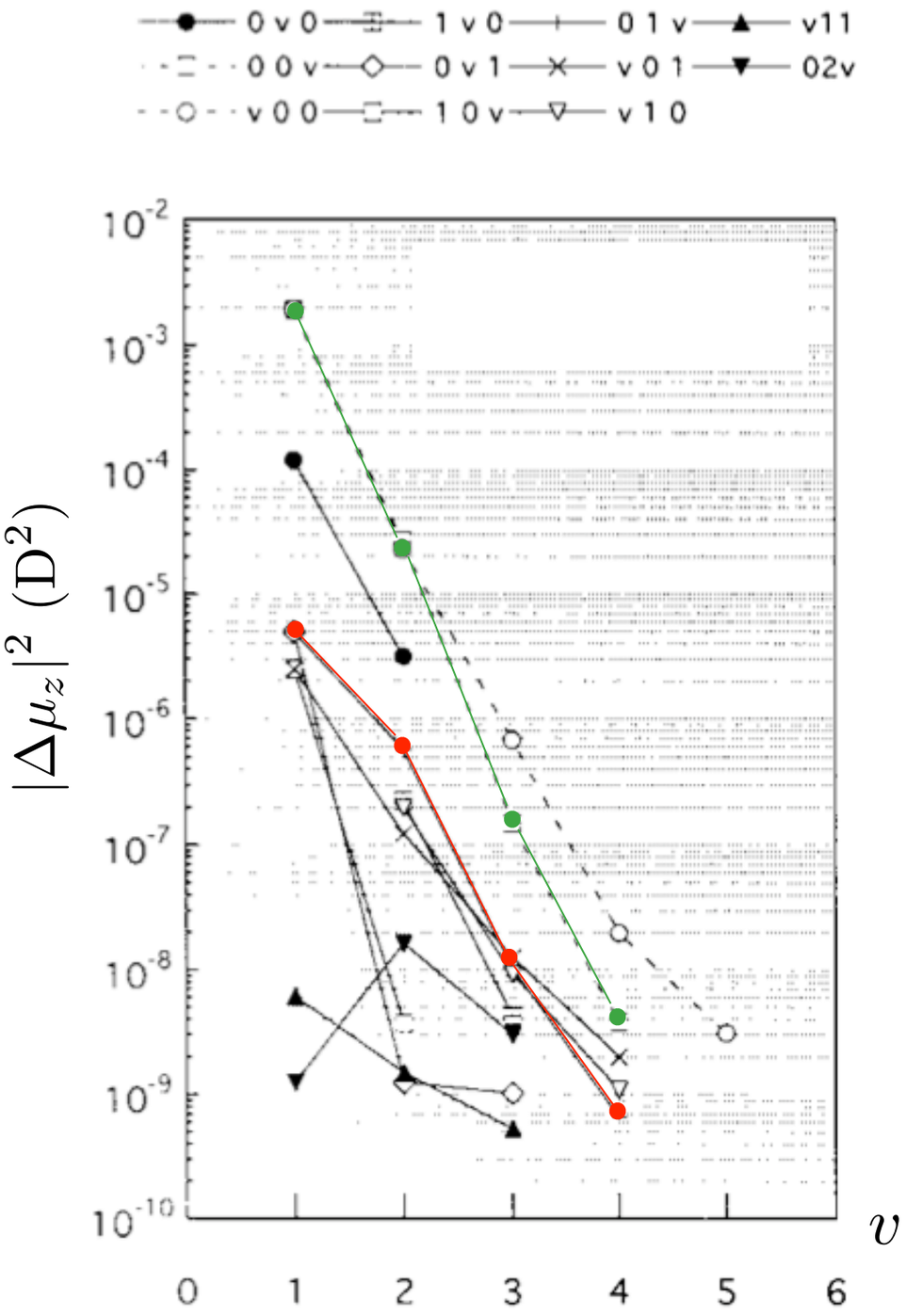
Band intensities

Transitions in **C_2HD** (stretching vibrations)

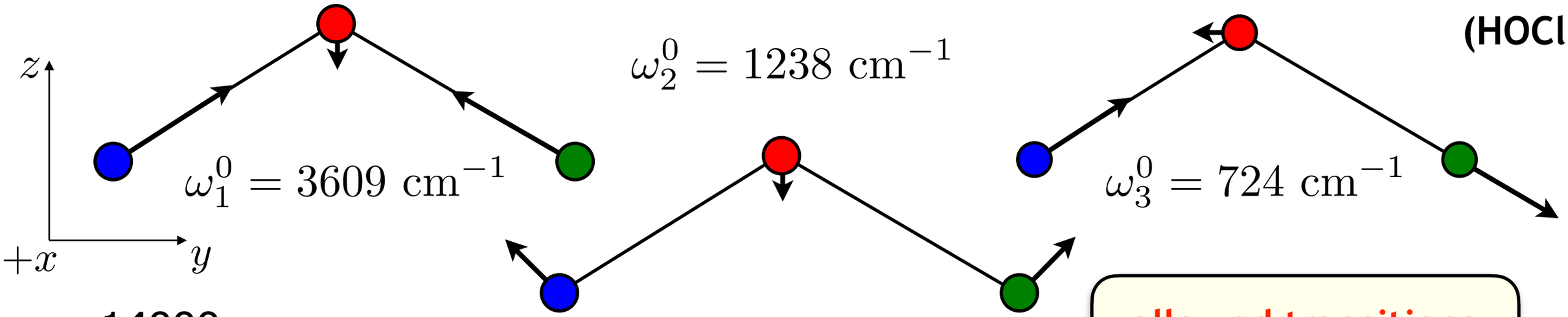




$(v_1 v_2 v_3)$



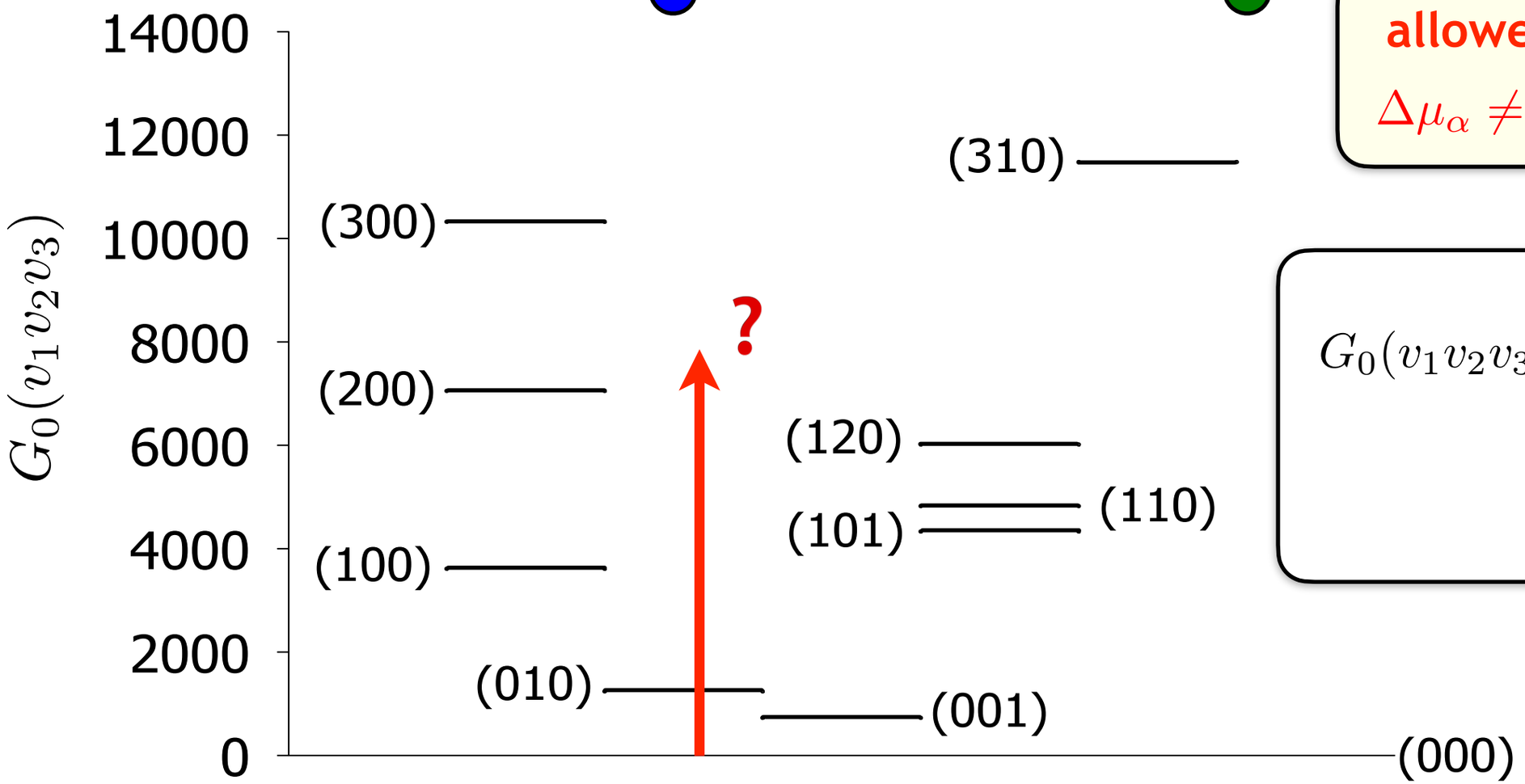
Vibration of non-linear molecules



(HOCl)

allowed transitions

$\Delta\mu_\alpha \neq 0\ (\alpha = x, y, z)$



$$G_0(v_1v_2v_3) = \sum_{i=1}^{3} \omega_i^0 v_i$$

+ anharmonicity

$(v_1v_2v_3)$

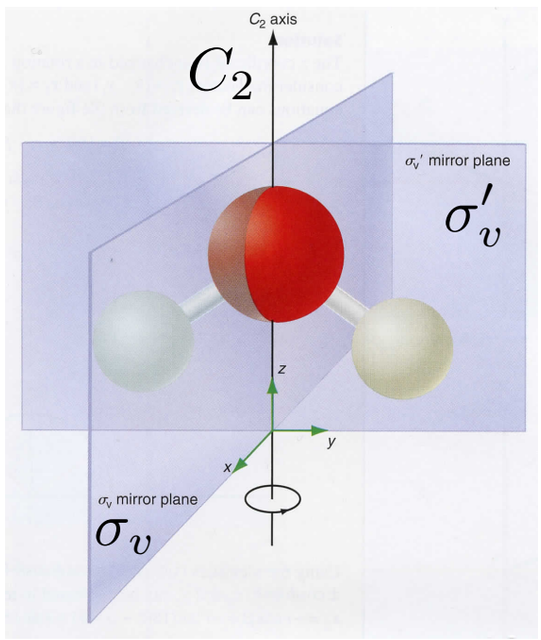
Geometrical symmetry

- Symmetry based on the structure/geometry of the molecule ⇨ **Point groups**

Symmetry Elements and Their Corresponding Operations

Symmetry Elements		Symmetry Operations	
E	Identity	E	leave molecule unchanged
C_n	n-Fold rotation axis	$\hat{C}_n, \hat{C}_n^2, ..., \hat{C}_n^n$	rotate about axis by 360°/n 1, 2, … , n times (indicated by superscript)
σ	Mirror plane	$\hat{\sigma}$	reflect through the mirror plane
i	Inversion center	$\hat{i}$	$(x,y,z) \rightarrow (-x,-y,-z)$
S_n	n-Fold rotation-reflection axis	$\hat{S}_n$	rotate about axis by 360°/n, and reflect through a plane perpendicular to the axis.

- Symmetry of the water molecule



4 symmetry operations:

$E, C_2, \sigma_v, \sigma_v'$

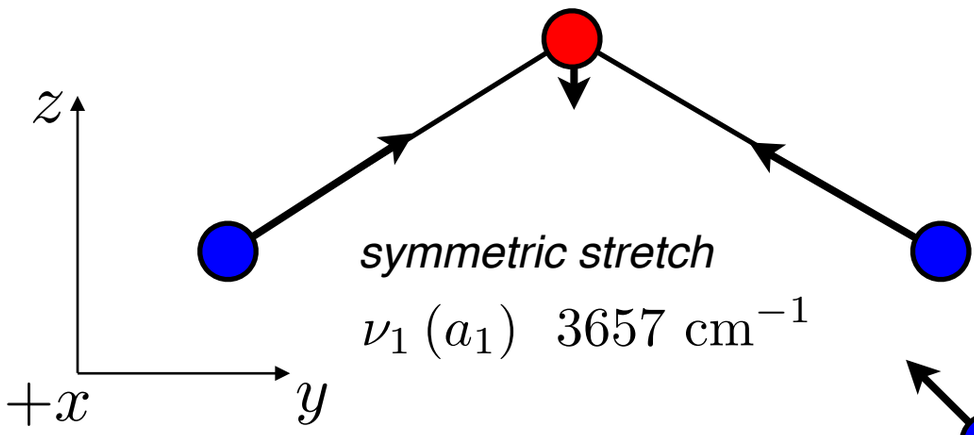
⇨ **Point group C_{2v}**

Character table

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	−1	1
B_2	1	−1	1	−1

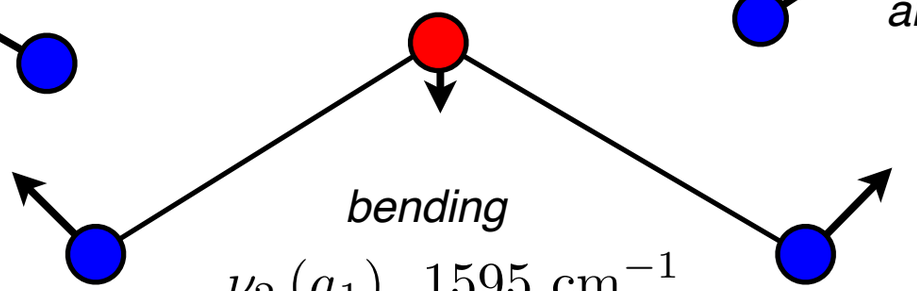
Irreducible representations →

Vibration of polyatomics



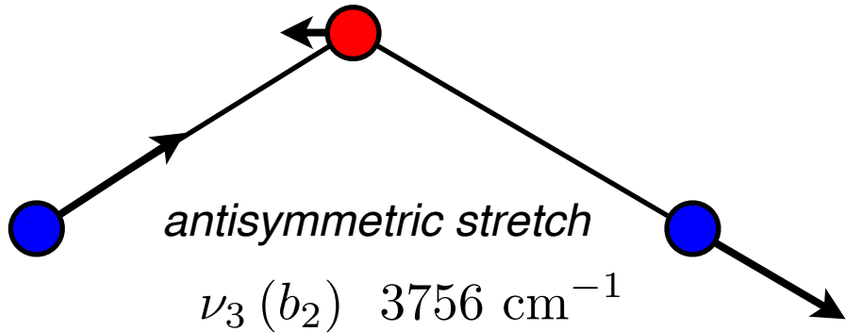
symmetric stretch

$\nu_1\,(a_1)$ 3657 cm^{-1}



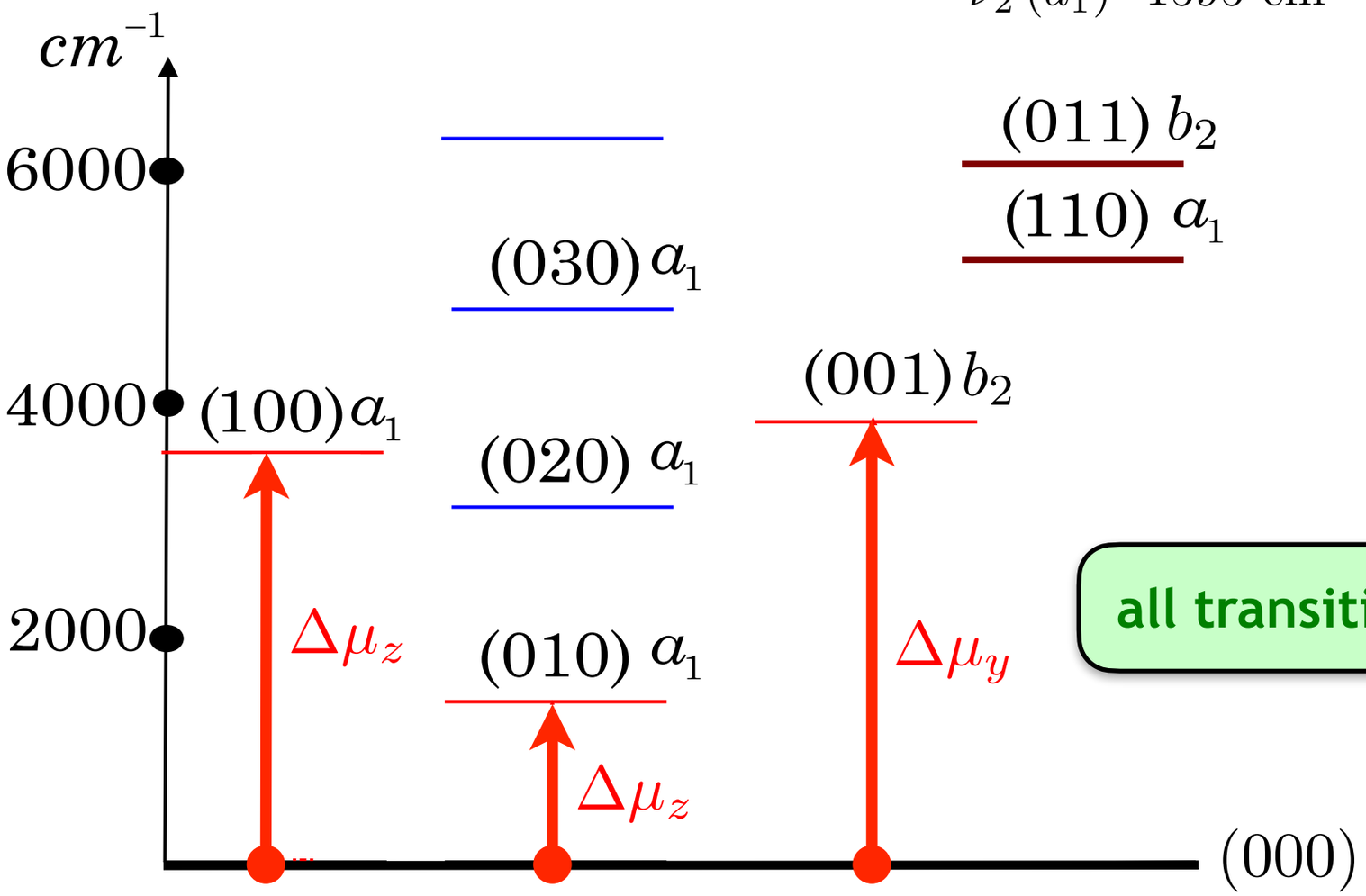
bending

$\nu_2\,(a_1)$ 1595 cm^{-1}



antisymmetric stretch

$\nu_3\,(b_2)$ 3756 cm^{-1}

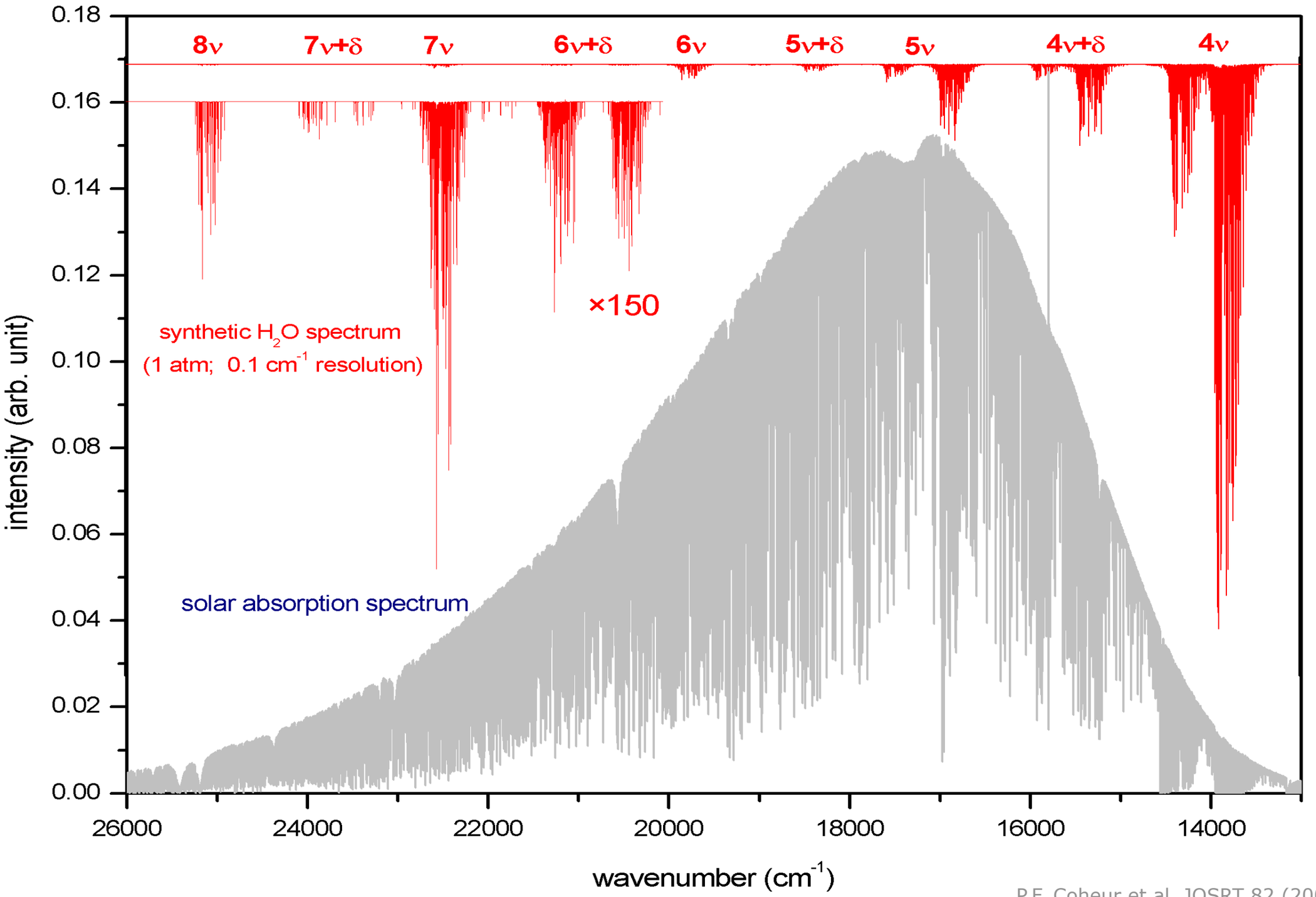


C_{2v}	E	C_2	σ_v	σ'_v	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	
B_1	1	−1	−1	1	y
B_2	1	−1	1	−1	x

all transitions allowed

$\Delta\nu \nearrow$ ⇒ Intensity $\searrow$

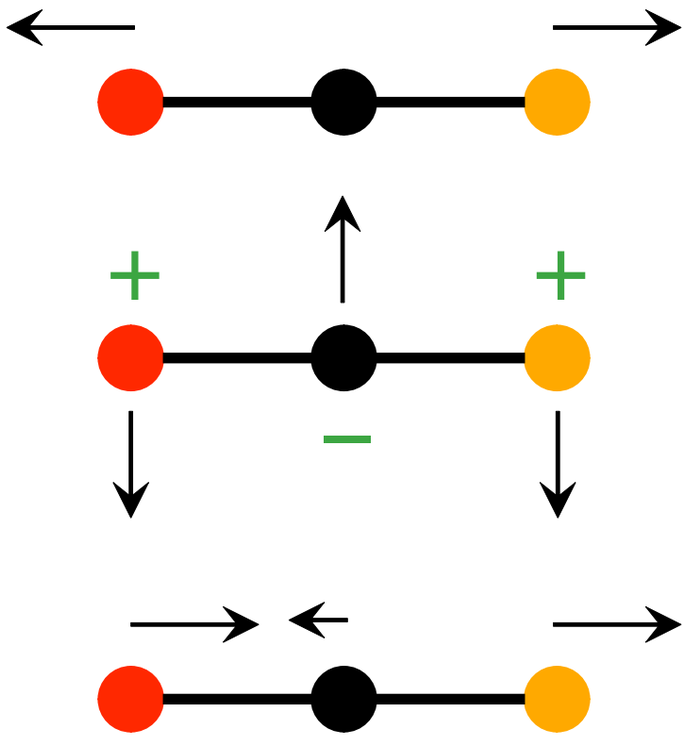
Infrared absorption spectrum of H_2O



P.F. Coheur et al, JQSRT 82 (2003) 133

Vibration of triatomic linear molecules

4 vibrational degrees of freedom



ν_1 (Q_1)

$\omega_1 = 859\ \mathrm{cm}^{-1}$

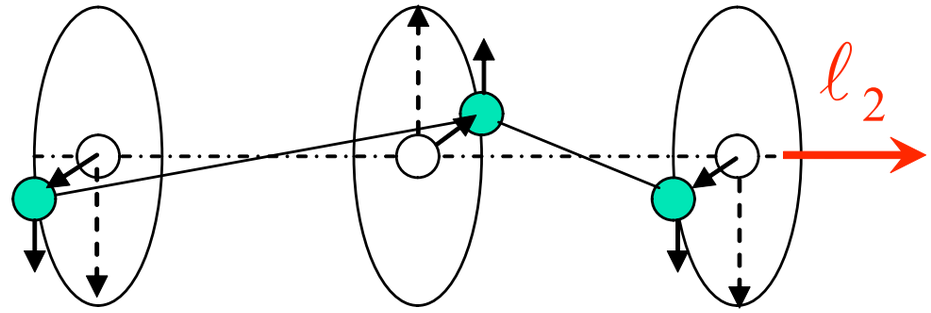
ν_2 (Q_2)

$\omega_2 = 520\ \mathrm{cm}^{-1}$

ν_3 (Q_3)

$\omega_3 = 2062\ \mathrm{cm}^{-1}$

doubly degenerate vibration

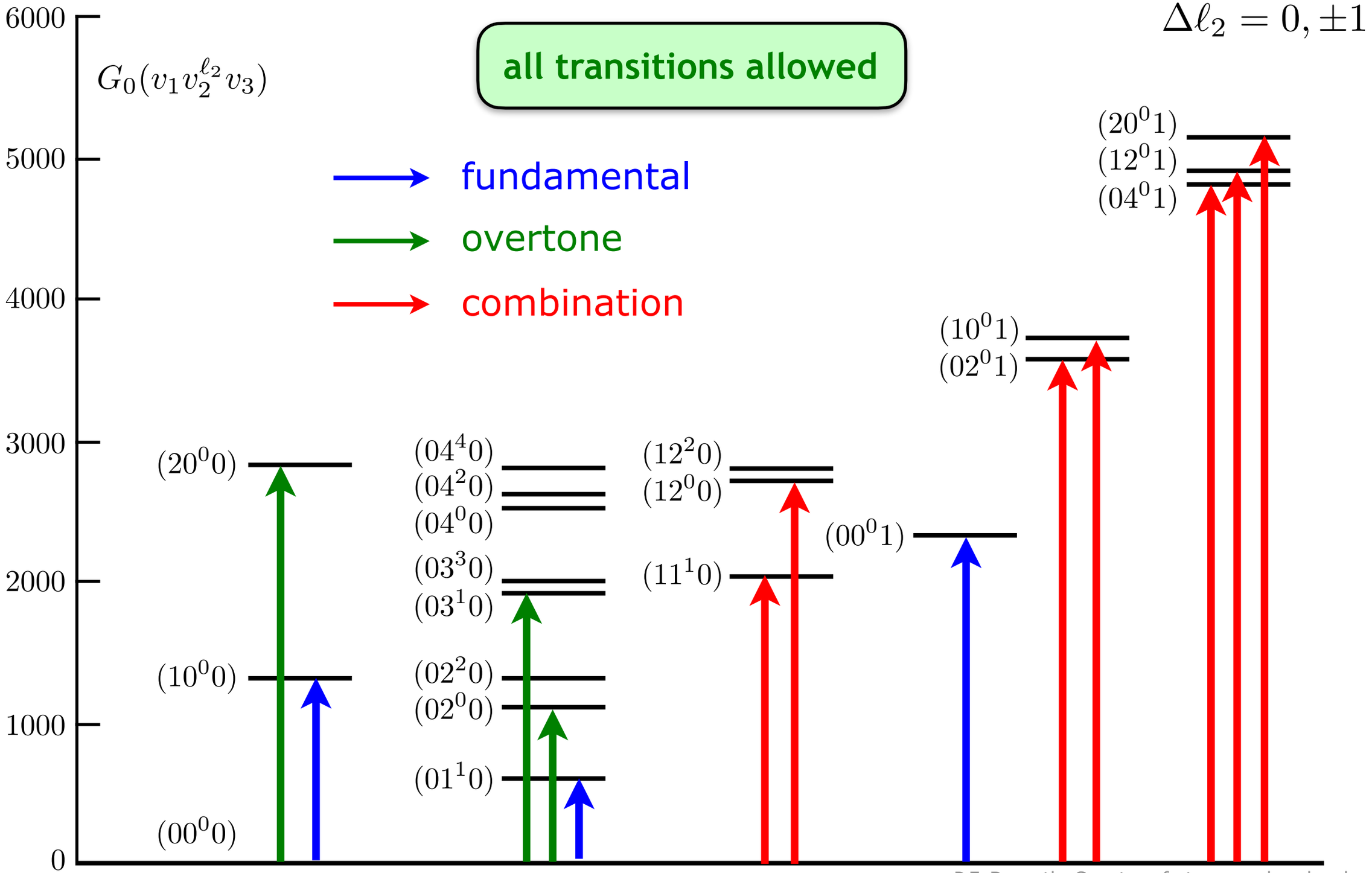


Vib. angular momentum:

$\ell_2 = v_2, v_2–2,\ldots, 1$ or 0

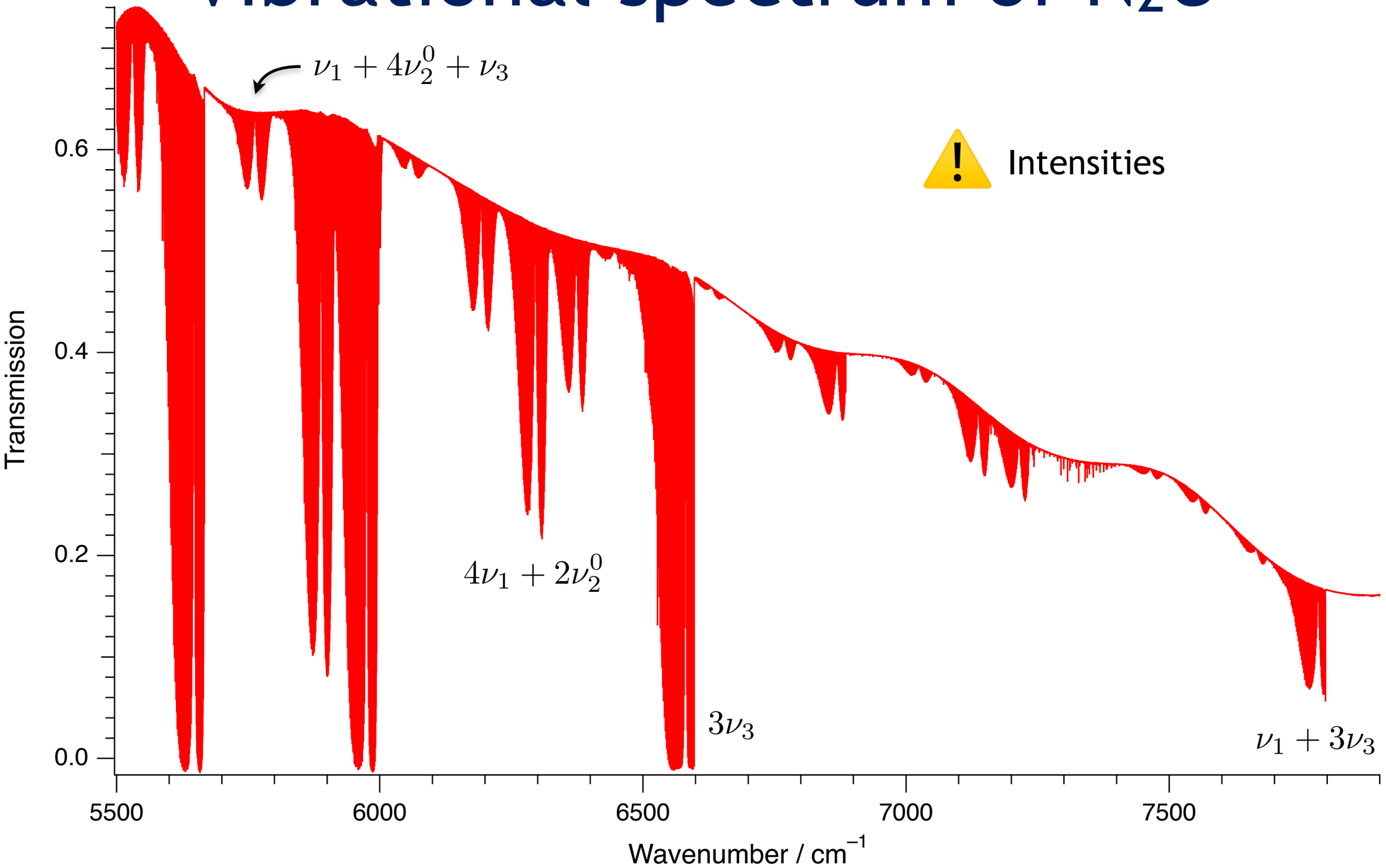
carbonyl sulfide (OCS)

Vibration of "XYZ" triatomics

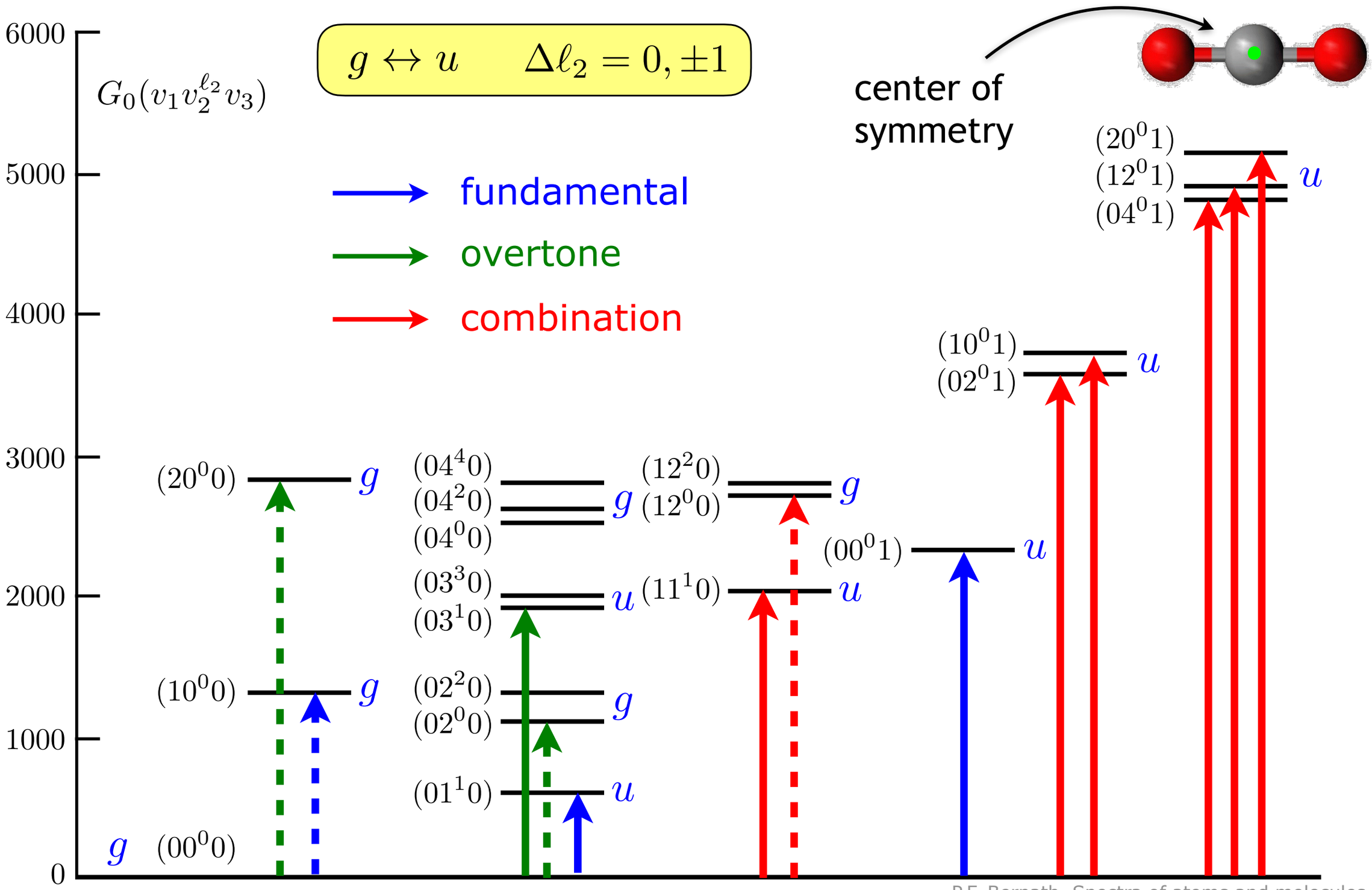


P.F. Bernath, Spectra of atoms and molecules

Vibrational spectrum of N_2O

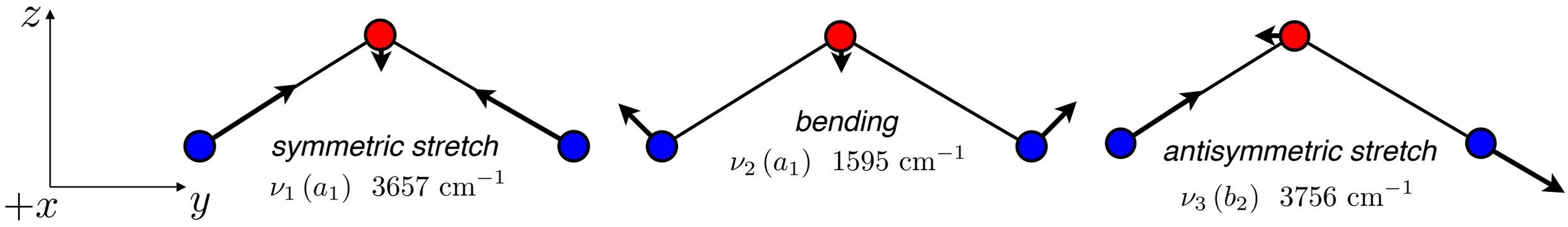


Vibrational of "XYX" triatomics

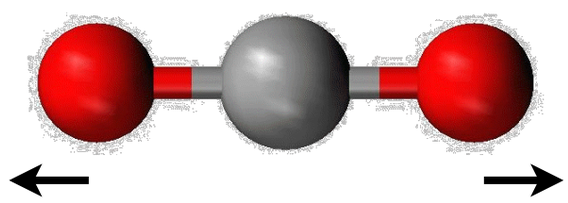


P.F. Bernath, Spectra of atoms and molecules

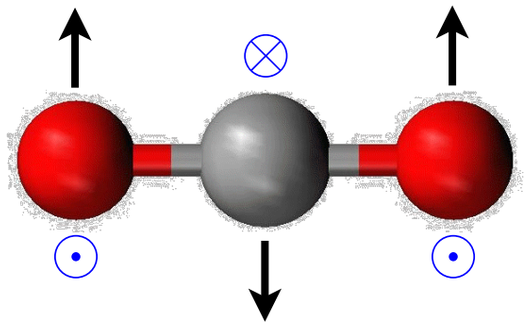
Vibrational selection rules



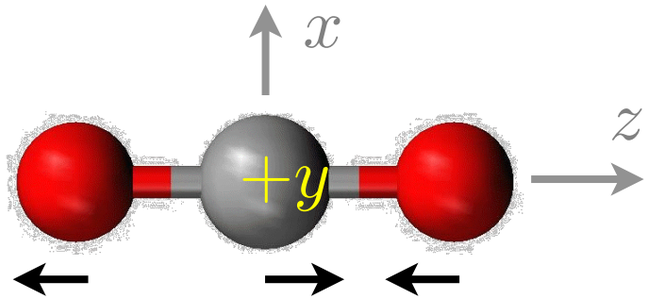
All modes of vibration are infrared **and** Raman active



$\omega_1^0 = 1354\ \mathrm{cm}^{-1}\ (\Sigma_g^+)$



$\omega_2^0 = 673\ \mathrm{cm}^{-1}\ (\Pi_u)$



$\omega_3^0 = 2396\ \mathrm{cm}^{-1}\ (\Sigma_u^+)$

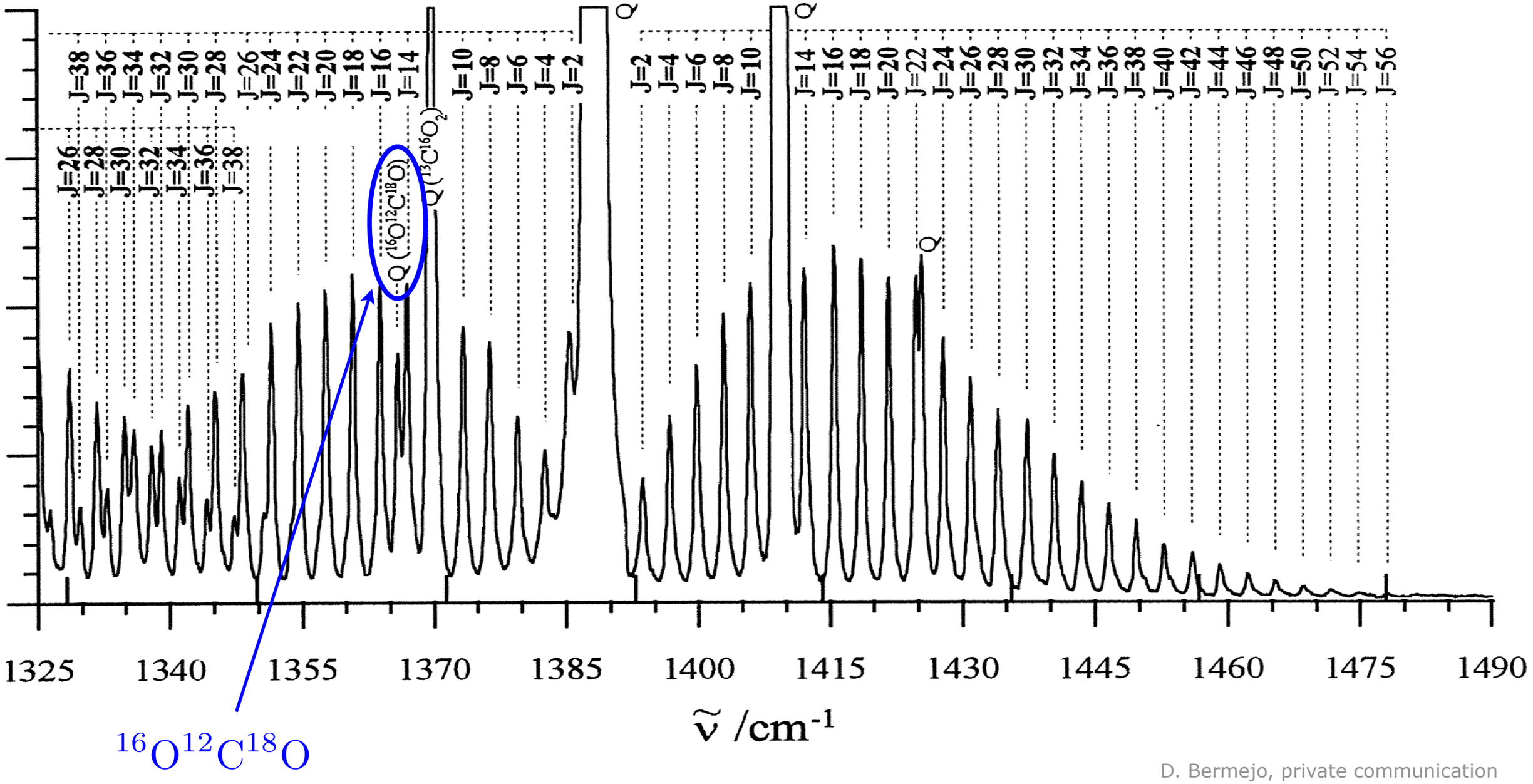
Raman active

Infrared active

centro-symmetrical molecule ➙ ***mutual exclusion rule***

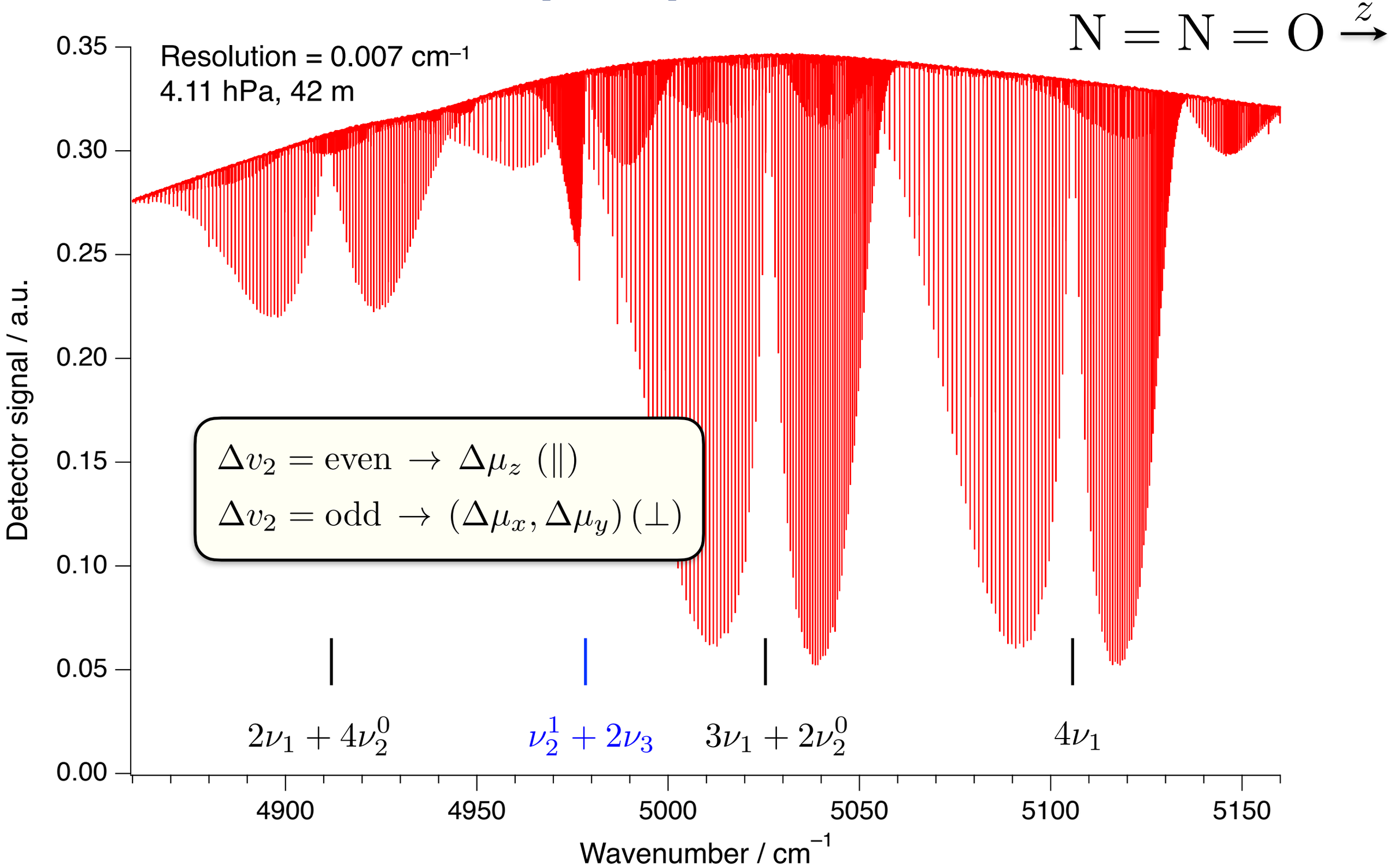
Raman vibrational spectrum

ν_1 band of $^{12}C^{16}O_2$



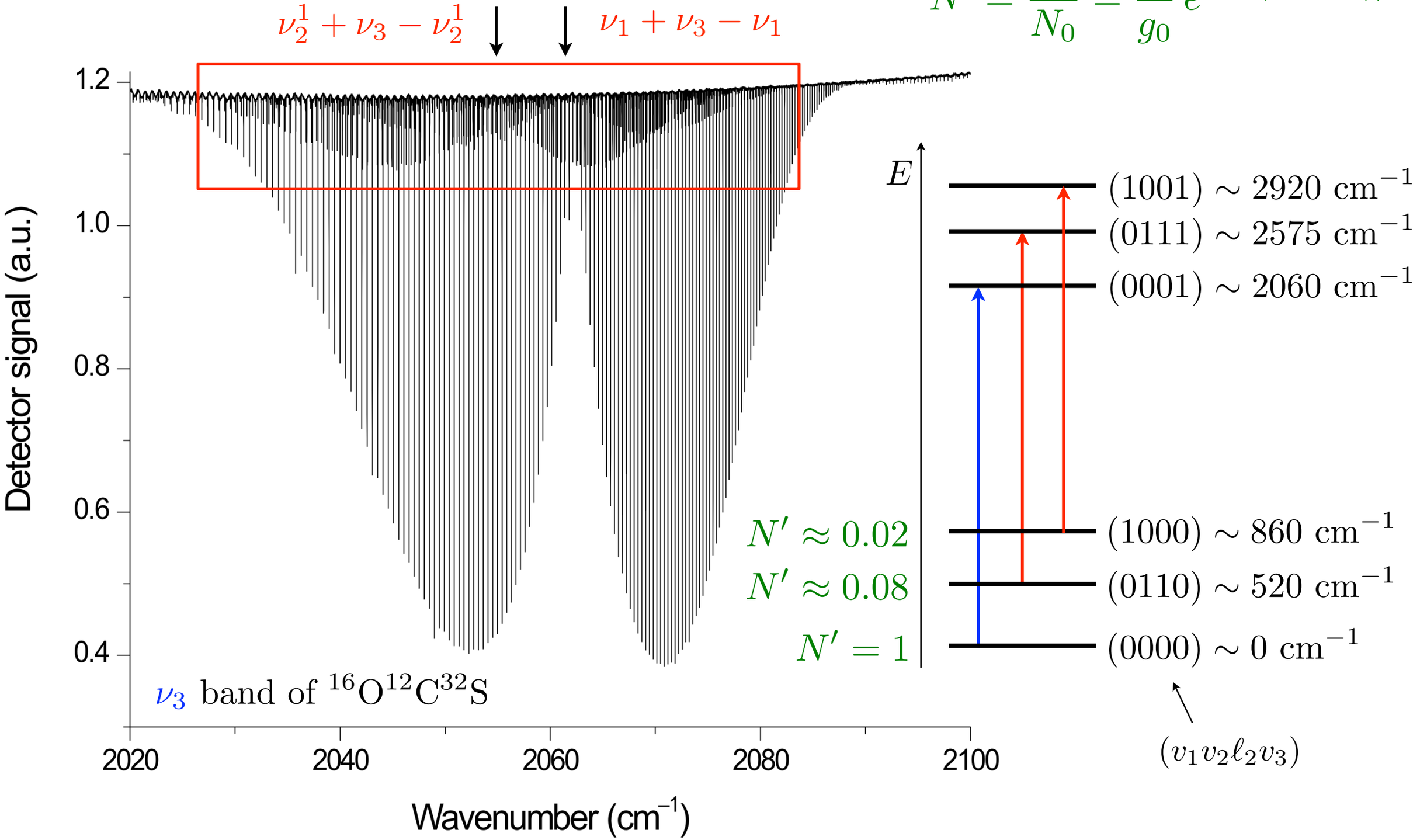
D. Bermejo, private communication

Parallel and perpendicular bands



Hot bands

$$N' = \frac{N_i}{N_0} = \frac{g_i}{g_0}\, e^{-hc(E_i - E_0)/kT}$$

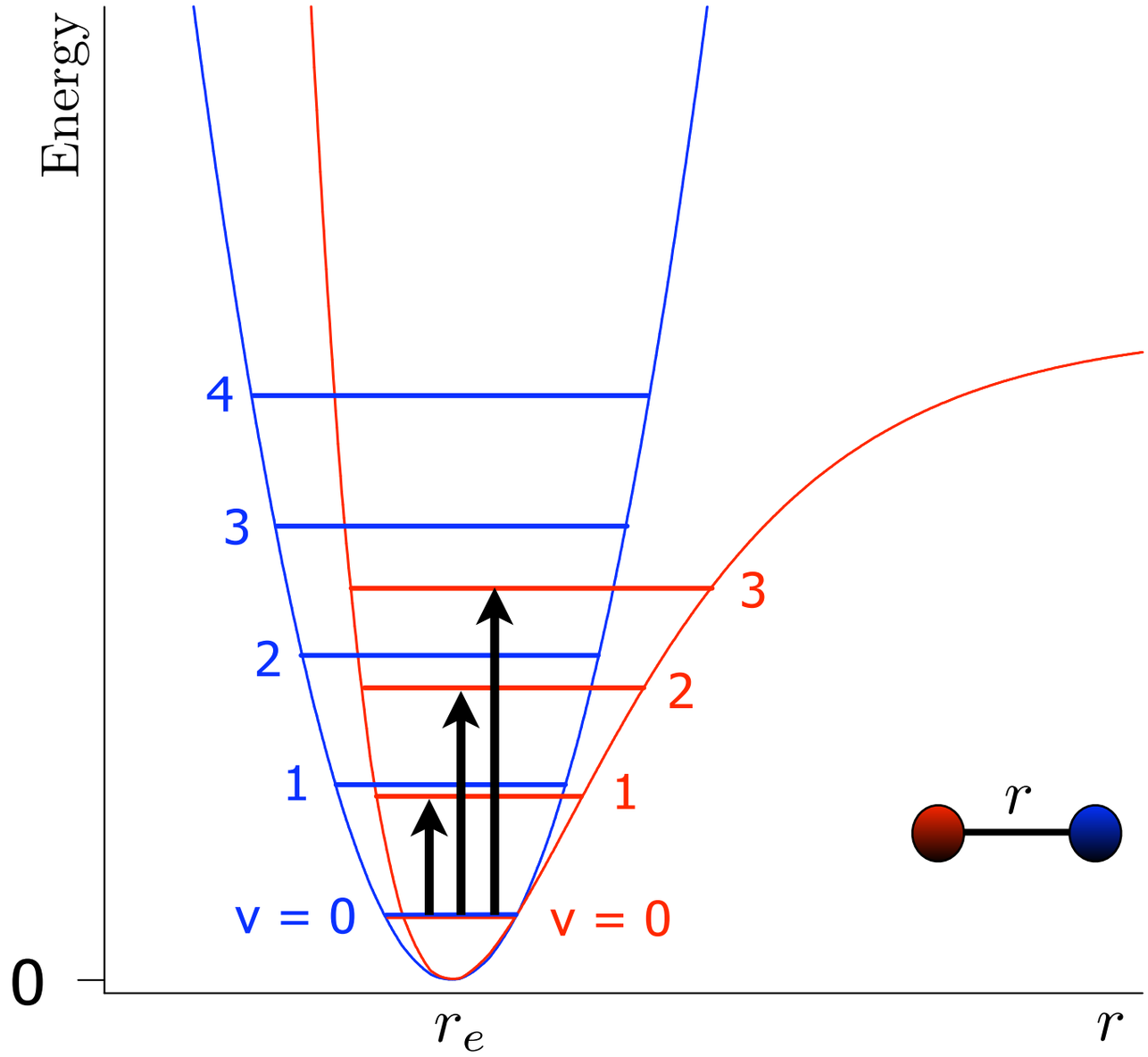


Elements of molecular spectroscopy

Molecular physics – Vibration-rotation transitions

Diatomics – Vibrational spectrum

$$\sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_{ji}}{Q(T)} I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) S_{ji} \rightarrow S_{ji} = g_i\, 3\, \left|\langle\psi_r^j|\lambda_z z|\psi_r^i\rangle\right|^2 \left|\Delta\mu_z\right|^2$$

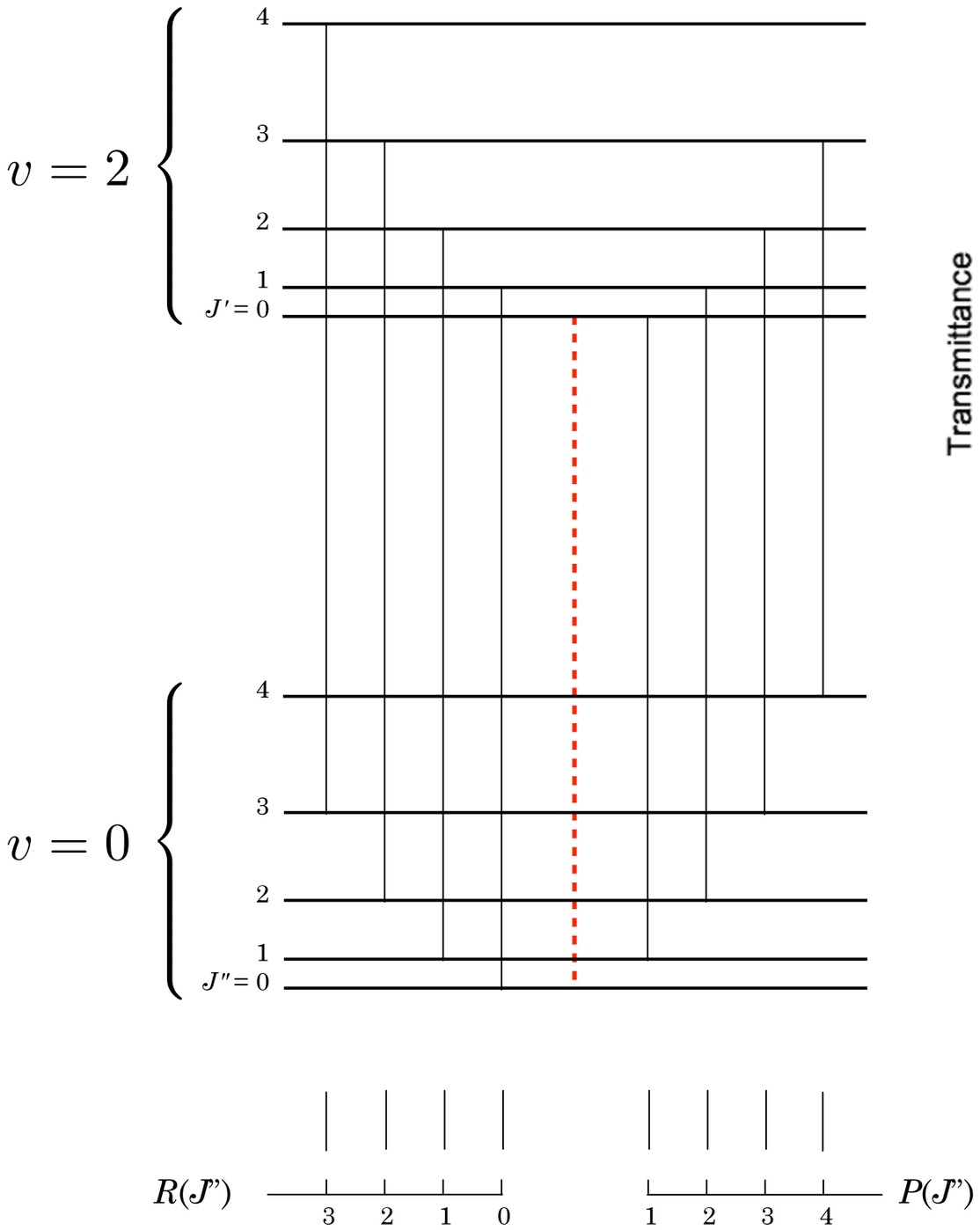


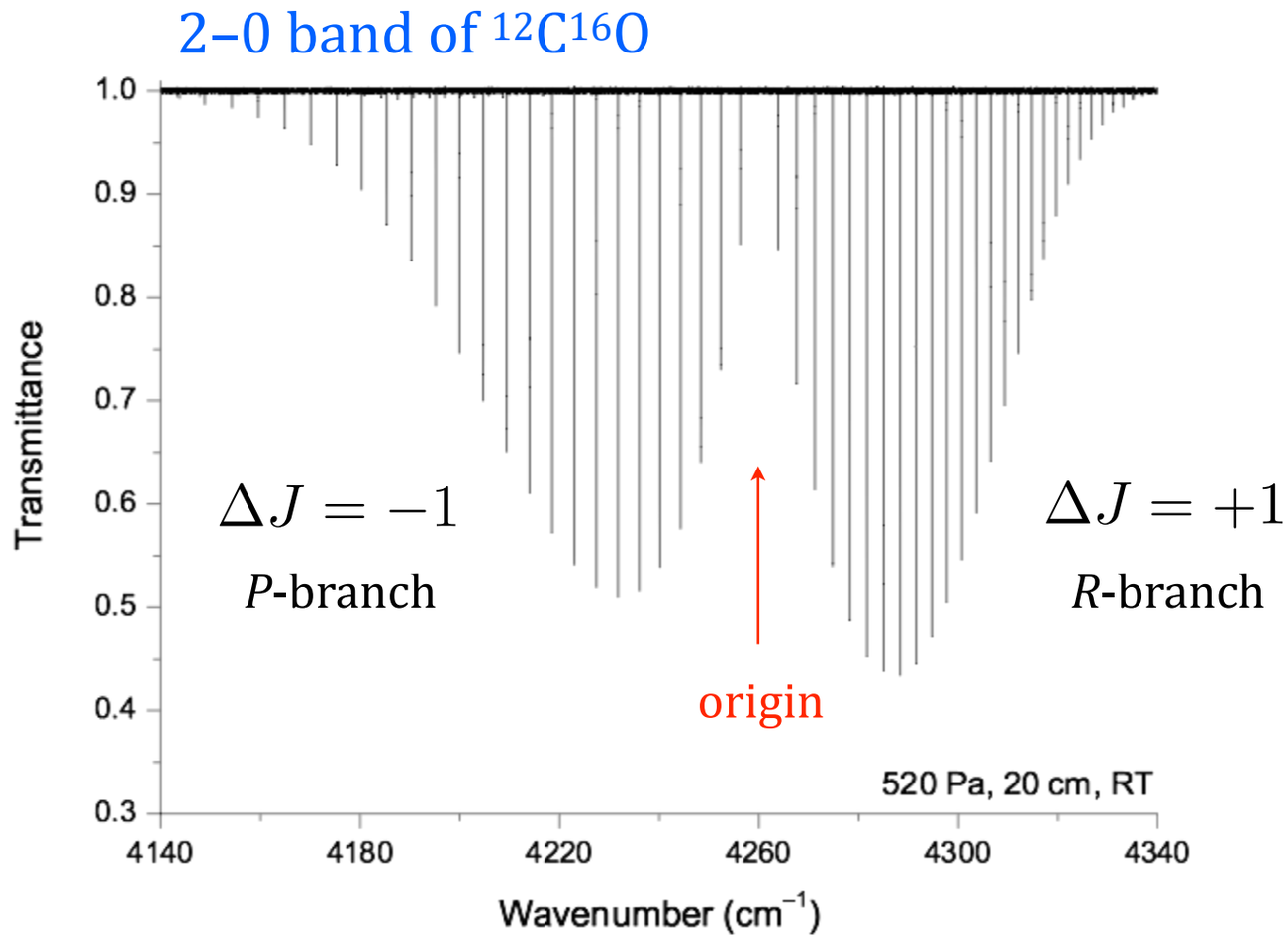
dipole moment variation

heteronuclear diatomics ✓

homonuclear diatomics ✗

Rotational structure of a parallel band

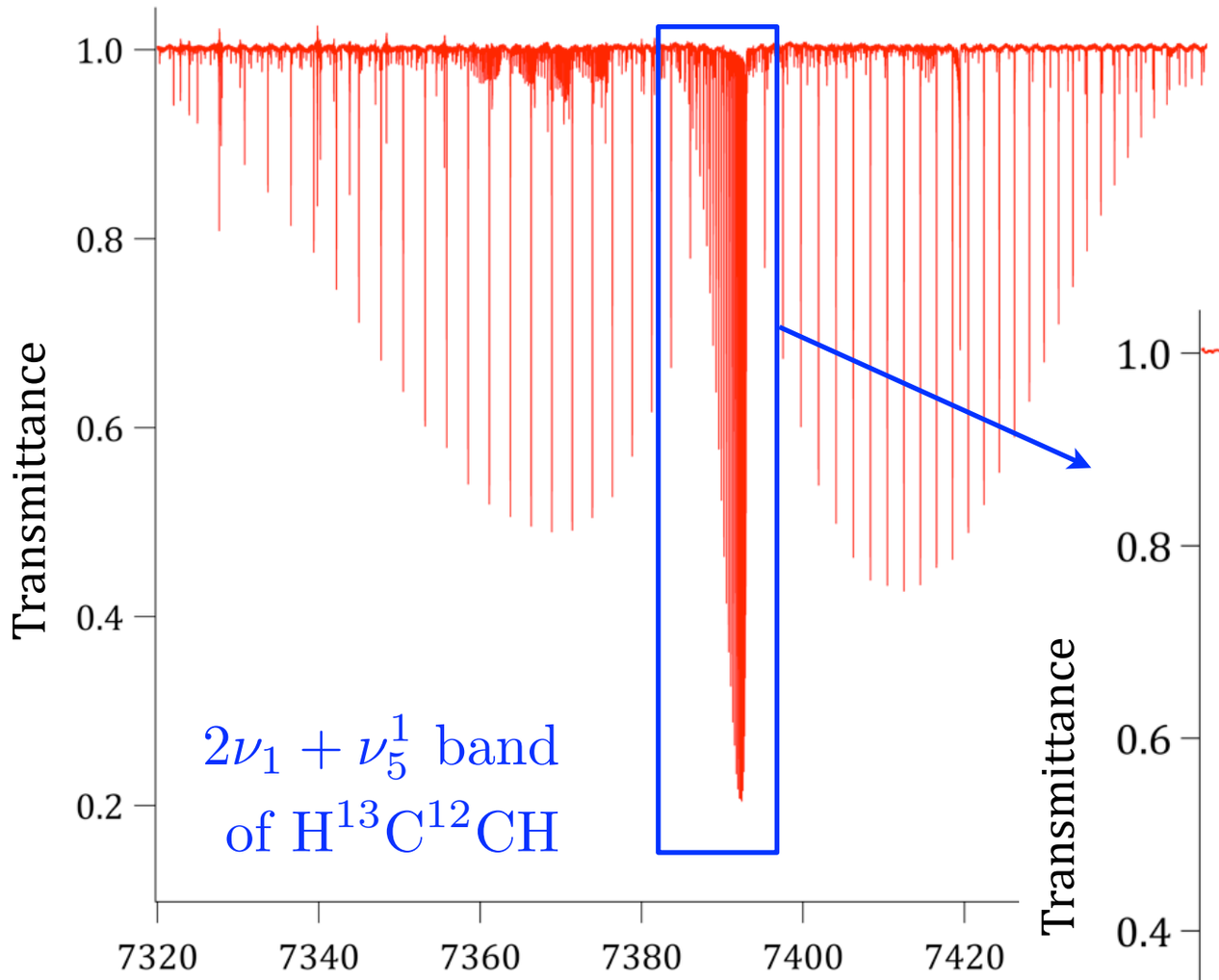




$$R(J) = E'_v - E''_v + E'_r(J+1) - E''_r(J)$$
$$= \tilde{\nu}_0 + B'_v(J+1)(J+2) - B''_v J(J+1)$$
$$= \tilde{\nu}_0 + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2$$

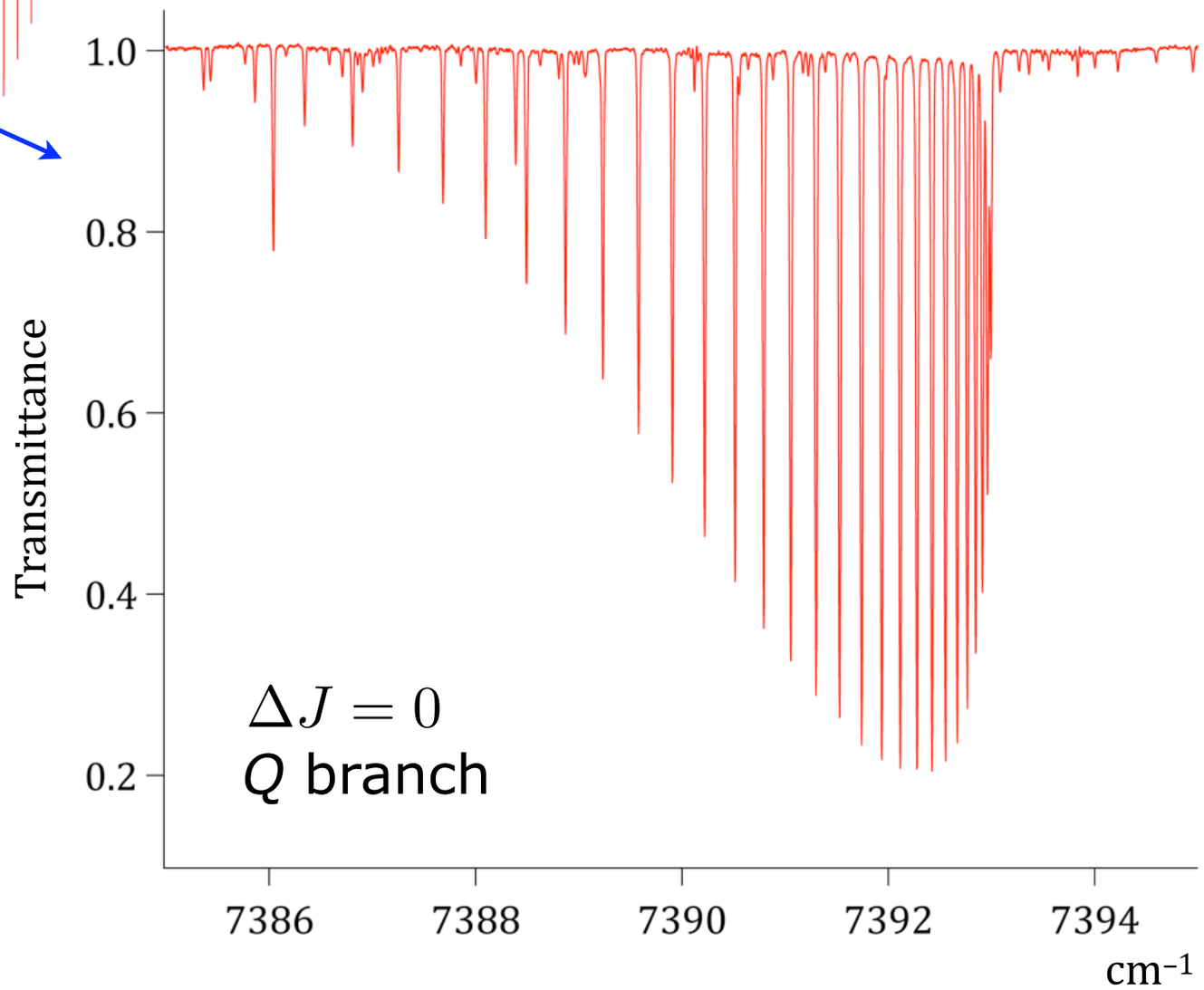
$$P(J) = E'_v - E''_v + E'_r(J-1) - E''_r(J)$$
$$= \tilde{\nu}_0 - (B'_v + B''_v)J + (B'_v - B''_v)J^2$$

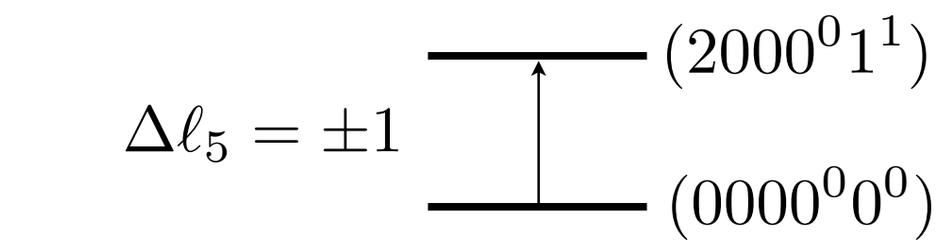
Structure of a perpendicular band



$$Q(J) = \tilde{\nu}_0 + (B'_v - B''_v)J(J+1)$$

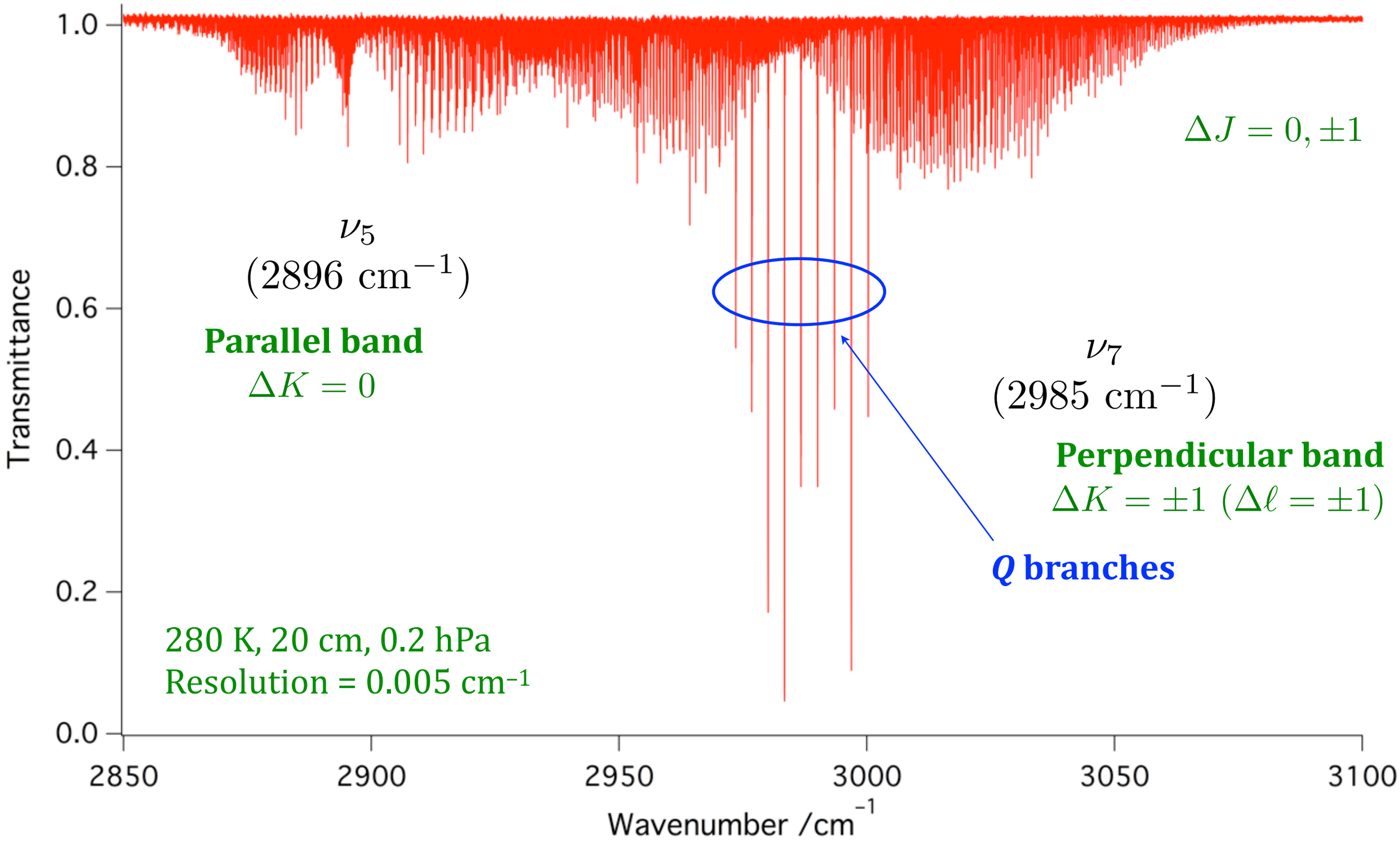
$$J'' = 0 \not\leftrightarrow J' = 0$$



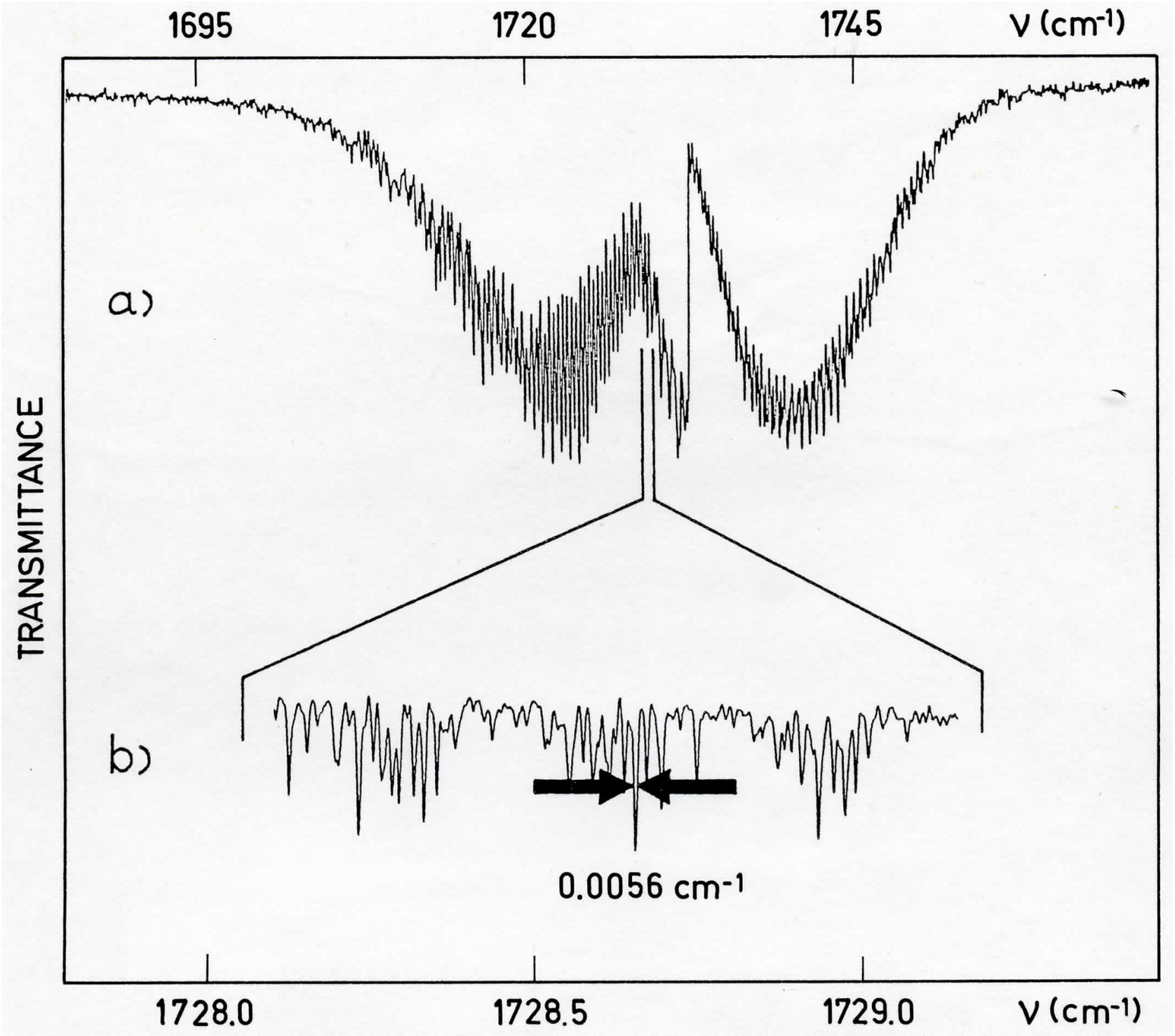


$$(v_1 v_2 v_3 v_4^{\ell_4} v_5^{\ell_5})$$

Symmetric top molecule (C_2H_6)



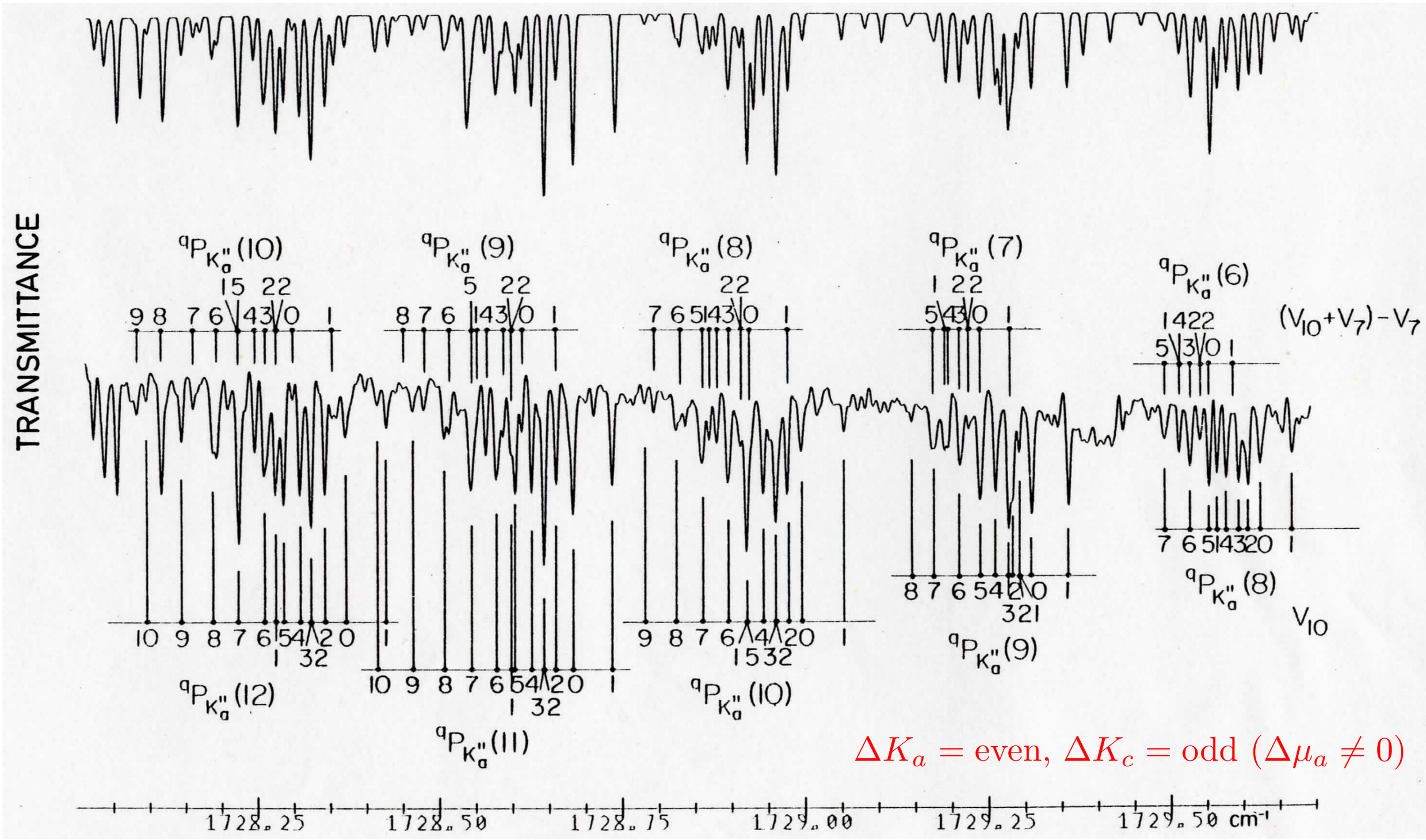
Asym. top – The ν_{10} band of glyoxal



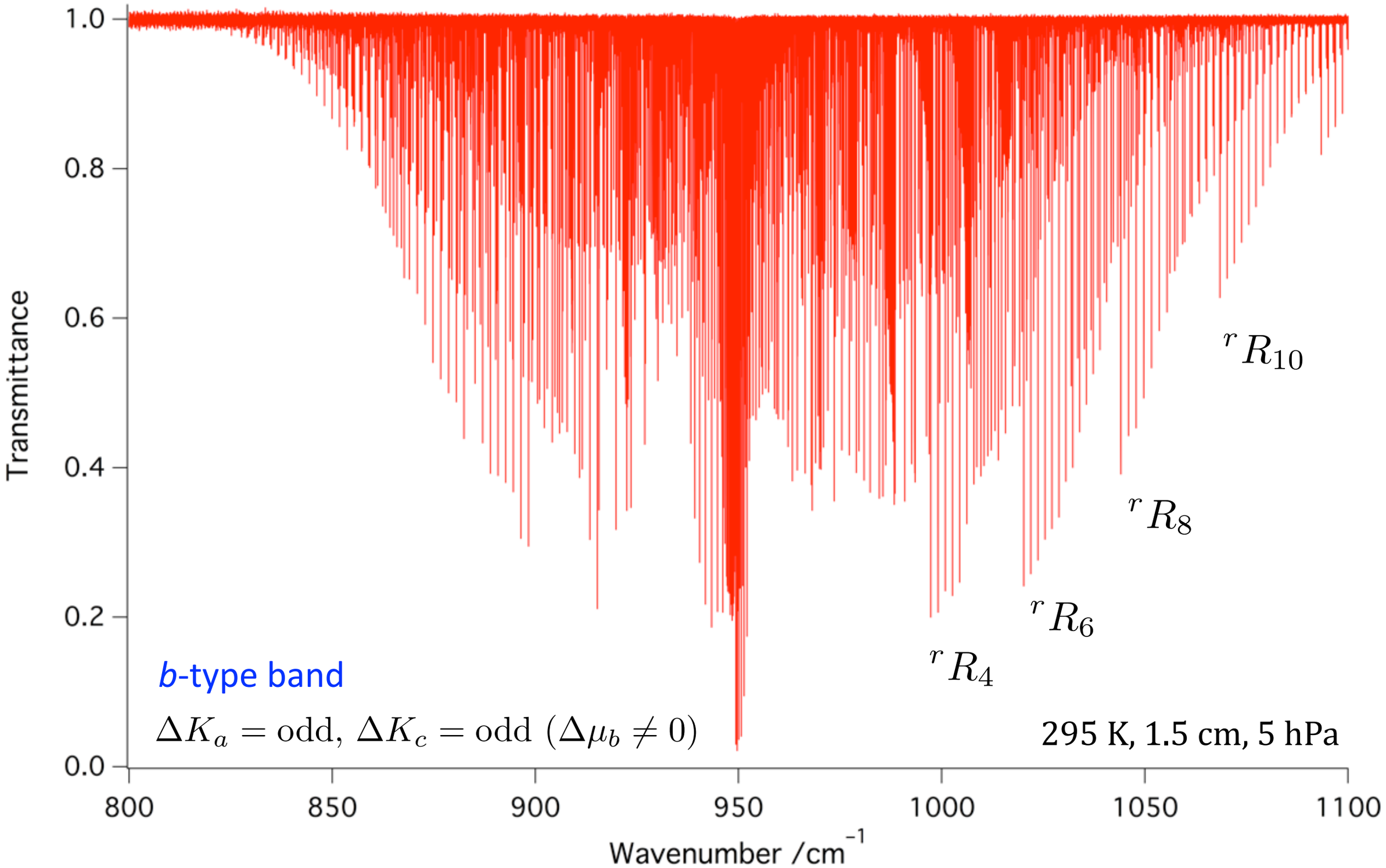
a-type band

Resolution = 0.1 cm^{-1}

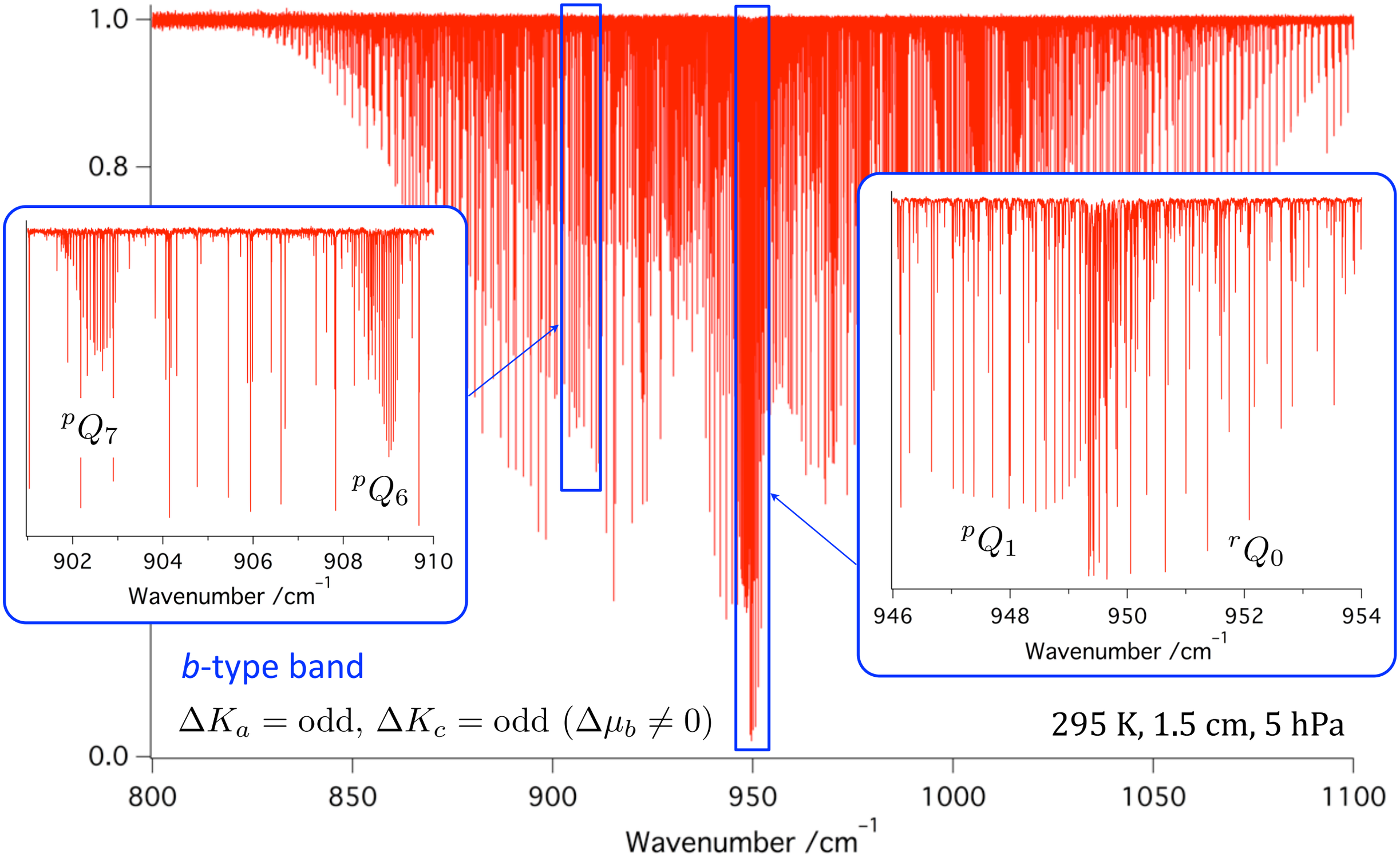
The ν_{10} band of glyoxal - *Cont.*



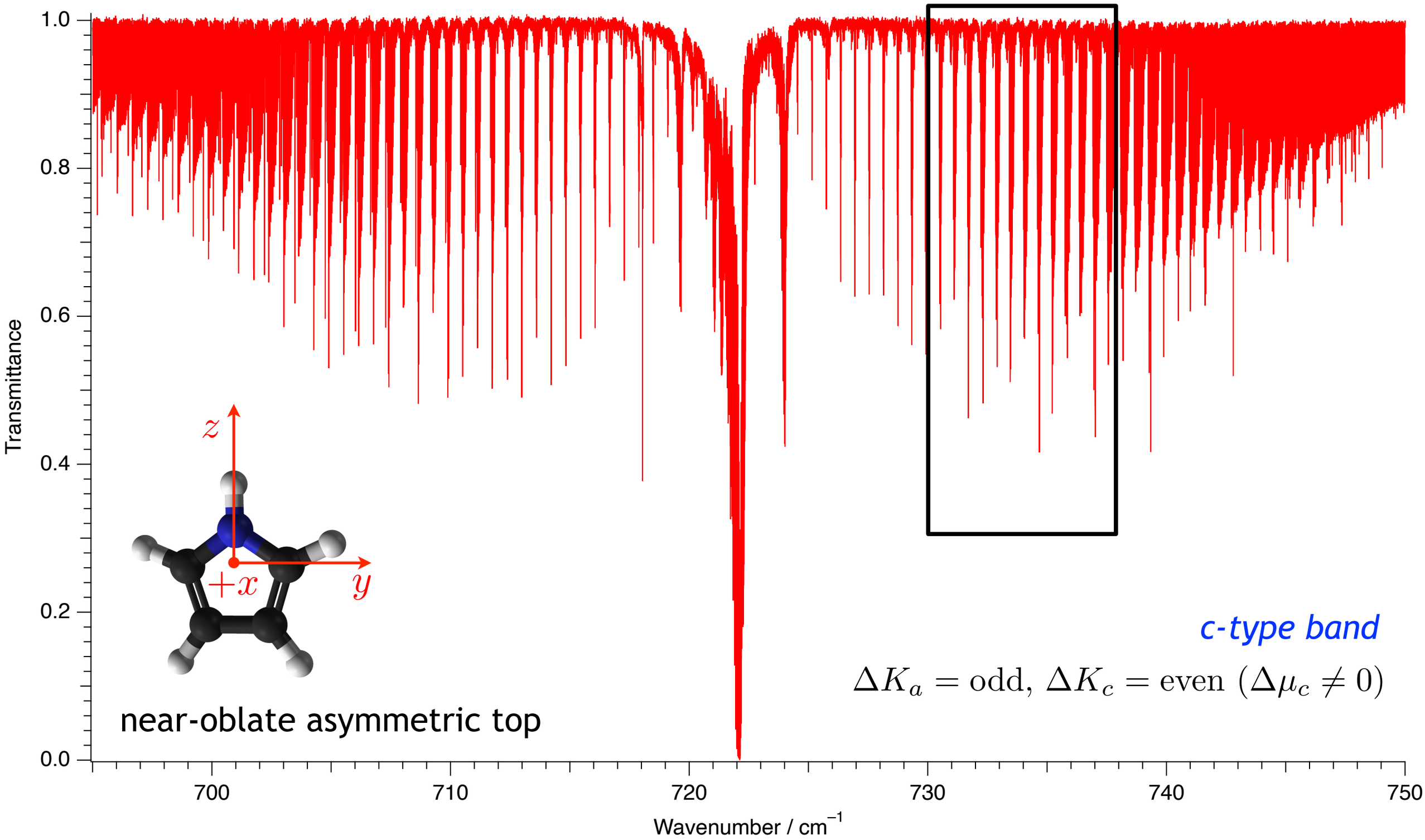
The ν_7 band of ethylene



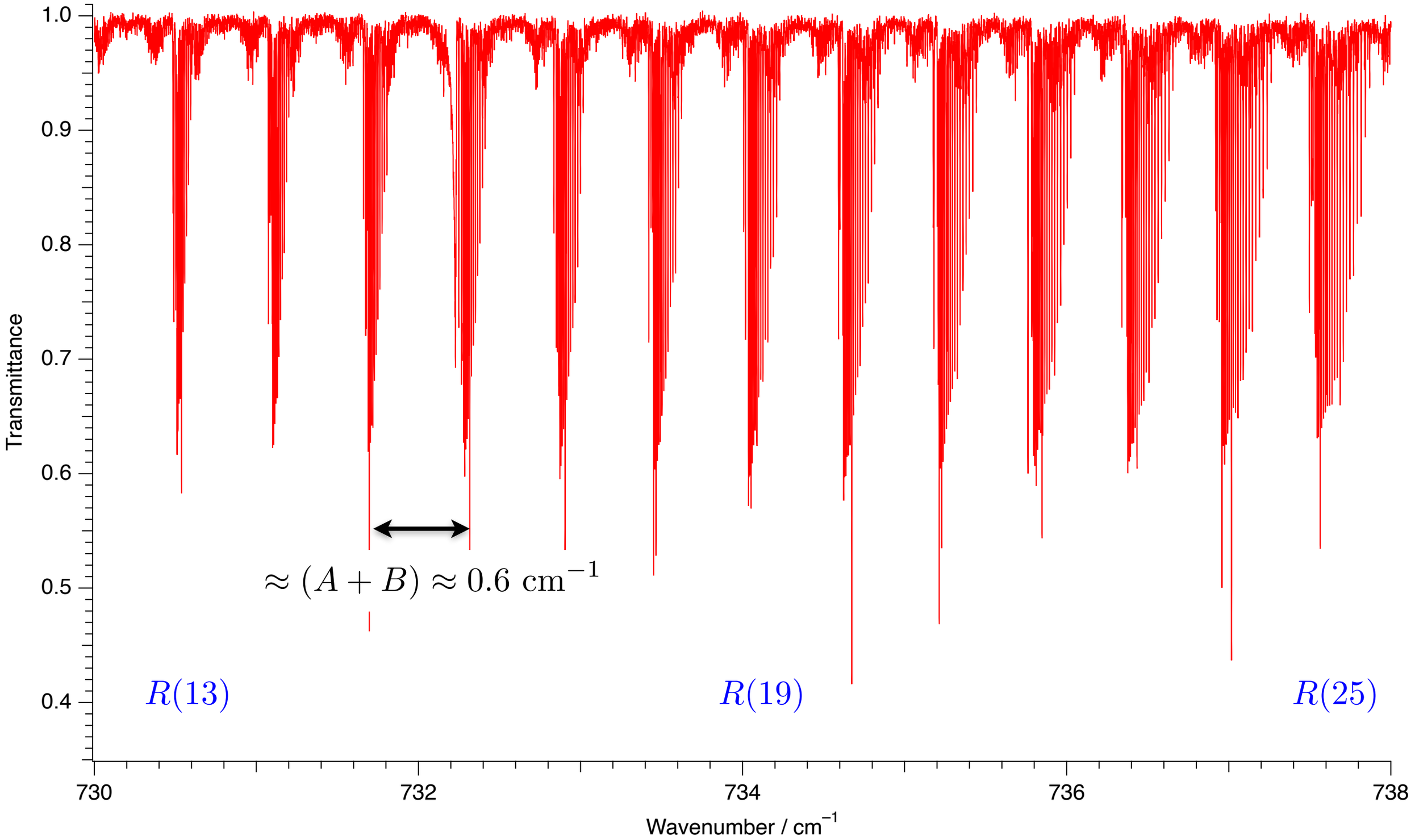
The ν_7 band of ethylene



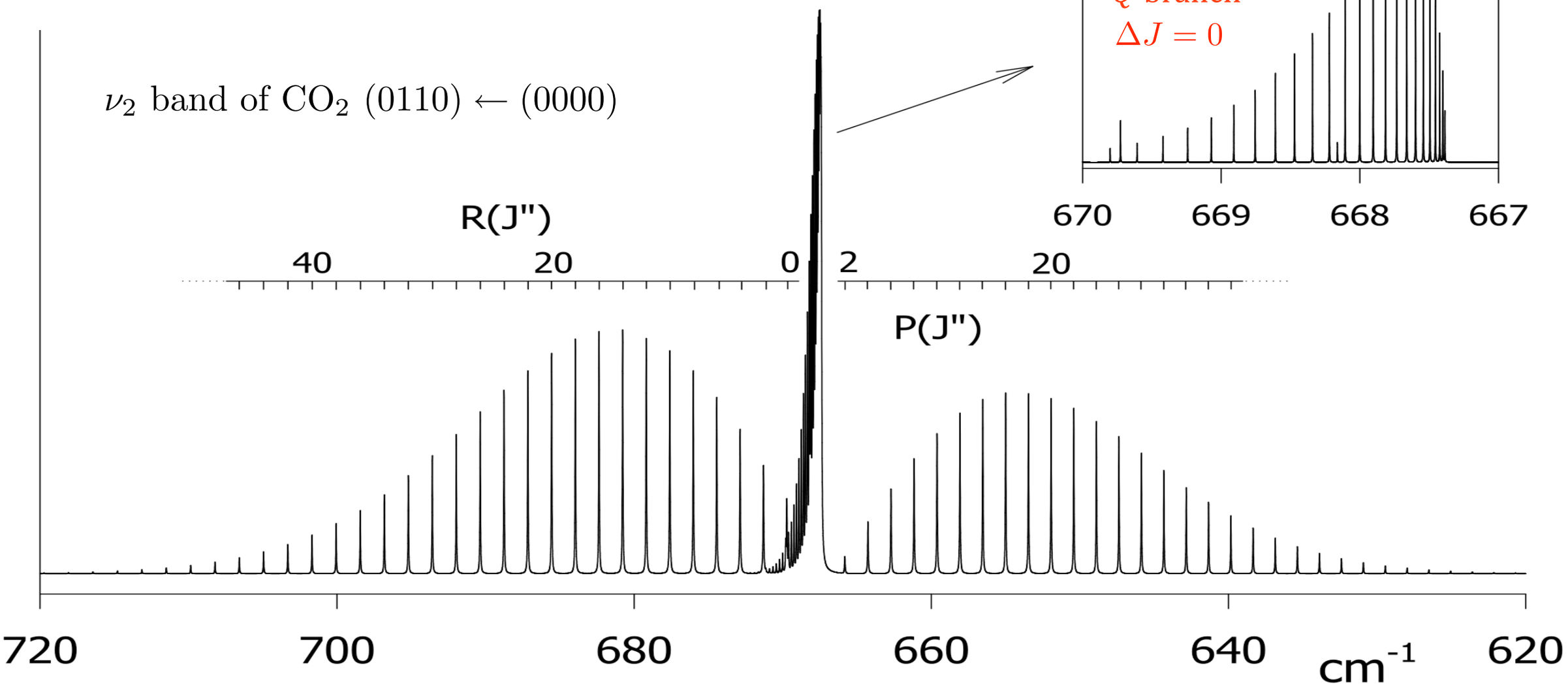
The ν_{22} band of pyrrole



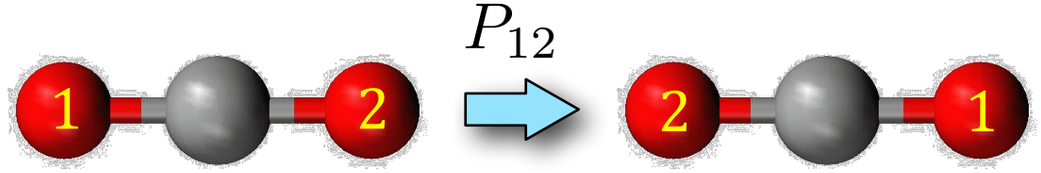
The ν_{22} band of pyrrole – *Cont.*



Missing lines



Pauli exclusion principle



permutation of two ***paired*** particles

$$\hat{P}_{12}\ \psi_i = +\psi_i \ \text{(bosons)}$$
$$\hat{P}_{12}\ \psi_i = -\psi_i \ \text{(fermions)}$$

$$\psi_{tot} = \psi_e \psi_{vib} \psi_{rot} \psi_{espin} \psi_{nspin}$$

Conclusion

- **Lecture** = *Overview of some of the building blocks of molecular spectra*
- Summary
  - Rotation, vibration and electronic energies, transitions and spectra

Line-by-line data in databases

Mol/Iso	$\nu_{\eta\eta'}$	$S_{\eta\eta'}$	$\Re_{\eta\eta'}$	γ_{air}	γ_{self}	E″	n	δ	iv'	iv''	q'	q''	ierr	iref
21	800.451076	3.197E–26	6.579E–05	0.0676	0.0818	2481.5624	0.78	0.000000	14	6		P 37	465	2 2 1
291	800.454690	9.724E–22	1.896E–02	0.0845	0.1750	369.6303	0.94	0.000000	9	1	341619	331519	000	4 4 1
291	800.454690	3.242E–22	2.107E–03	0.0845	0.1750	369.6303	0.94	0.000000	9	1	341519	331419	000	4 4 1
121	800.455380	1.037E–22	1.657E–03	0.1100	0.0000	530.3300	0.75	0.000000	32	14	46 640	45 540	000	4 4 1
121	800.455380	1.037E–22	1.657E–03	0.1100	0.0000	530.3300	0.75	0.000000	32	14	46 740	45 640	000	4 4 1
101	800.456743	1.680E–23	1.659E–04	0.0670	0.0000	851.0494	0.50	0.000000	2	1	45 244 0–	44 143 0–	301	6 6 1
101	800.457045	1.710E–23	1.689E–04	0.0670	0.0000	851.0469	0.50	0.000000	2	1	45 244 1–	44 143 1–	301	6 6 1
101	800.457310	1.740E–23	1.718E–04	0.0670	0.0000	851.0442	0.50	0.000000	2	1	45 244 2–	44 143 2–	301	6 6 1
121	800.457760	4.726E–23	4.614E–03	0.1100	0.0000	920.0900	0.75	0.000000	32	14	502922	492822	000	4 4 1
121	800.457760	4.726E–23	4.614E–03	0.1100	0.0000	920.0900	0.75	0.000000	32	14	502822	492722	000	4 4 1
24	800.465942	9.792E–27	6.063E–04	0.0754	0.1043	1341.2052	0.69	0.000000	8	3		R 13	425	2 2 1
121	800.466160	1.061E–22	2.720E–03	0.1100	0.0000	632.1200	0.75	0.000000	32	14	471236	461136	000	4 4 1
121	800.466160	1.061E–22	2.720E–03	0.1100	0.0000	632.1200	0.75	0.000000	32	14	471136	461036	000	4 4 1
35	800.472900	3.878E–26	6.919E–04	0.0686	0.0871	629.0354	0.76	0.000000	2	1	1814 4	1713 5	455	5 5 1
101	800.473083	1.270E–23	1.254E–04	0.0670	0.0000	851.0095	0.50	0.000000	2	1	45 244 0 +	44 143 0 +	301	6 6 1
101	800.474860	1.210E–23	1.195E–04	0.0670	0.0000	851.0064	0.50	0.000000	2	1	45 244–1 +	44 143–1 +	301	6 6 1
31	800.475500	1.680E–24	3.617E–05	0.0653	0.0890	1092.4340	0.76	0.000000	2	1	51 547	50 248	002	1 1 2
291	800.476220	9.597E–22	6.010E–03	0.0845	0.1750	361.9747	0.94	0.000000	9	1	341420	331320	000	4 4 1
291	800.476220	3.199E–22	6.010E–03	0.0845	0.1750	361.9747	0.94	0.000000	9	1	341520	331420	000	4 4 1
101	800.476937	1.160E–23	1.145E–04	0.0670	0.0000	851.0037	0.50	0.000000	2	1	45 244–2 +	44 143–2 +	301	6 6 1
101	800.484334	1.740E–23	2.153E–05	0.0670	0.0000	106.0760	0.50	0.000000	2	1	8 4 4–1 +	9 3 7–1 +	301	6 6 1

position

"intensity"

Lower-state energy

"global" (vibrational) quanta

"local" (rotational) quanta

Conclusion

- **Lecture** = *Overview of some of the building blocks of molecular spectra*
- Summary
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- Much more
  - Instrumental contributions
  - **Molecular symmetry**, interactions
  - Line profiles
  - …

The end