Principes de la spectroscopie

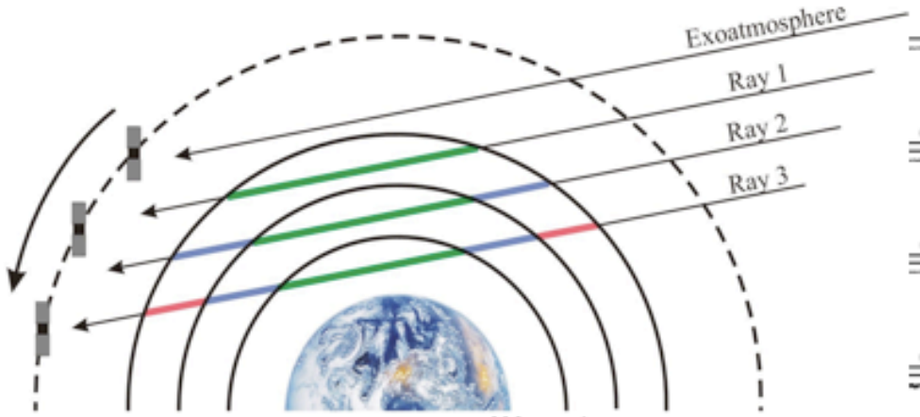
Jean Vander Auwera

Service de Chimie Quantique et Photophysique
Université Libre de Bruxelles, Belgique

Principes de la spectroscopie

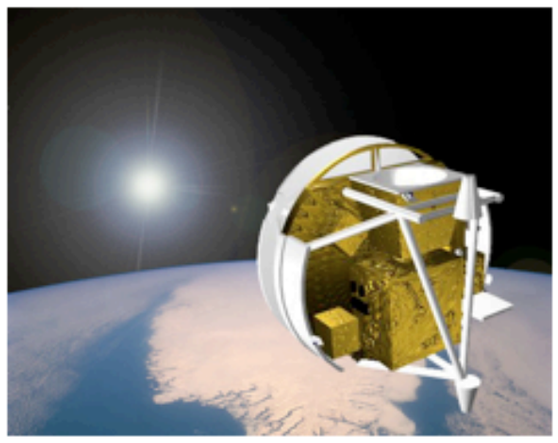
Introduction

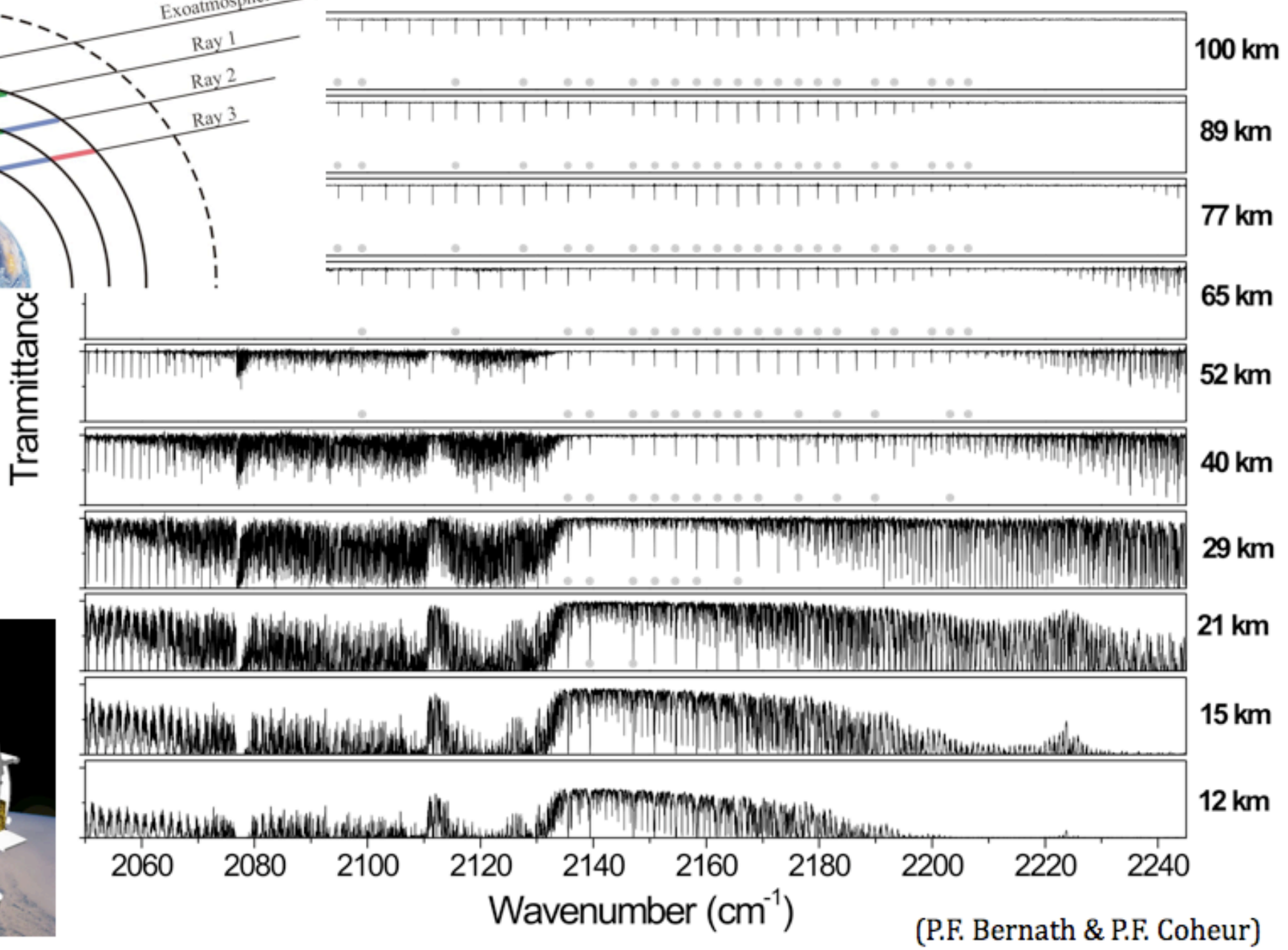
Remote sensing from space (occultation)



ACE

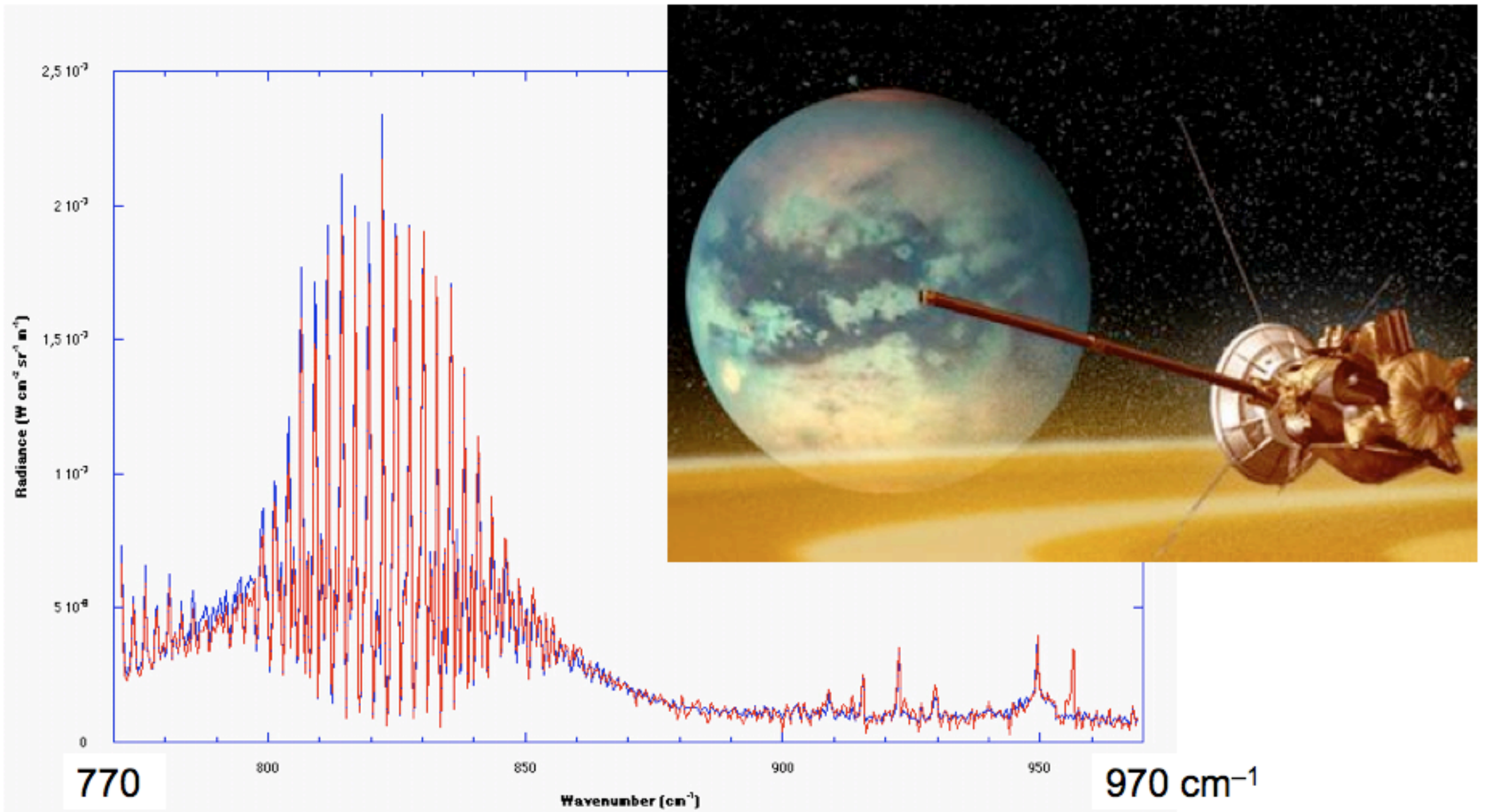
Absorption FTIR
(750 – 4400 cm^{-1})





(P.F. Bernath & P.F. Coheur)

Extra-terrestrial atmospheres (Titan)



CIRS spectrum of the ν_9 band of ethane (A. Coustenis, Meudon)

Databases: Line-by-line data in Hitran

Table 3. Example of HITRAN line-transition format.

Mol/Iso	ν_{ij}	S_{ij}	$\Re_{ij}$	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

Note: FORTRAN Format (I2,I1,F12.6,1P2E10.3,0P2F5.4,F10.4,F4.2,F8.6,2I3,2A9,3I1,3I2) corresponding to the following:

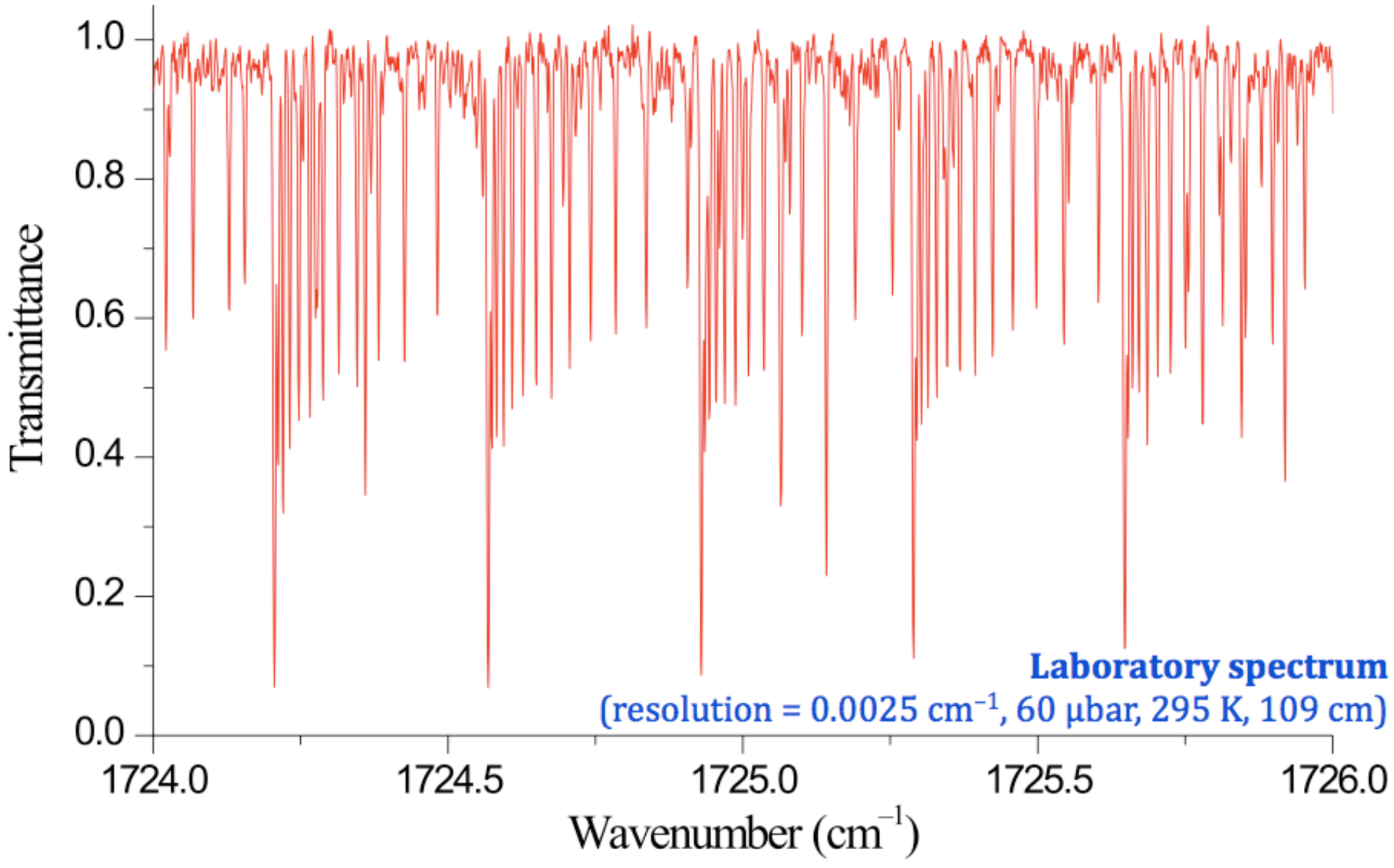
Mol	I2	molecule number
Iso	I1	isotope number (1 = most abundant, 2 = second most abundant, etc.)
ν_{ij}	F12.6	frequency in cm^{-1}
S_{ij}	E10.3	intensity in $cm^{-1}/(molecule \cdot cm^{-2})$ @ 296 K
$\Re_{ij}$	E10.3	weighted transition moment-squared in $Debye^2$
γ_{air}	F5.4	air-broadened halfwidth (HWHM) in cm^{-1}/atm @ 296 K
γ_{self}	F5.4	self-broadened halfwidth (HWHM) in cm^{-1}/atm @ 296 K
E''	F10.4	lower state energy in cm^{-1}
n	F4.2	coefficient of temperature dependence of air-broadened halfwidth
δ	F8.6	airbroadened pressure shift of line transition in cm^{-1}/atm @ 296 K
iv', iv''	2I3	upper state global quanta index, lower state global quanta index
q', q''	2A9	upper state local quanta, lower state local quanta
ierr	3I1	accuracy indices for frequency, intensity, and air-broadened halfwidth
iref	3I2	indices for table of references corresponding to frequency, intensity, and halfwidth

more than 2×10^6 lines

H_2O, CO_2, O_3, N_2O, HNO_3, HOBr, HCOOH … (42 species)

Correctness, completness, accuracy, origin… ?

Reference data (ν_2 band of HNO_3)



Purpose and outline

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

- Outline
  - Electromagnetic radiation
  - Radiative transfer in a gas
  - Molecular physics : Rotation, vibration, vib.-rot. transitions
  - Line profiles

  - **NO** instrumental contributions

Books

- "Spectra of atoms and molecules", P.F. Bernath, *Oxford University Press* (2005)

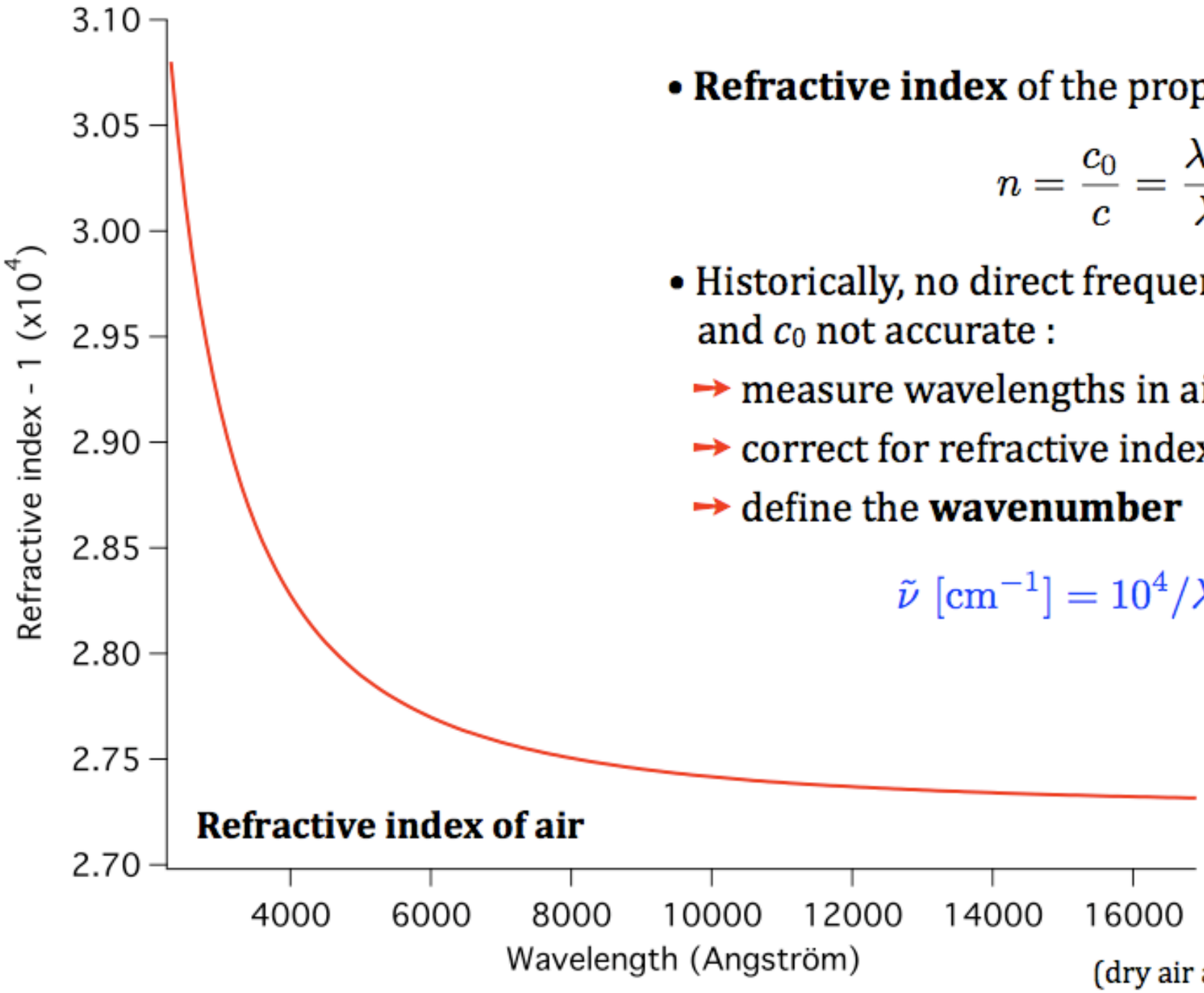
- "Atoms, molecules and photons", W. Demtröder, *Springer* (2006)
- "Fundamentals of molecular symmetry", P.R. Bunker and P. Jensen, *Institute of Physics Publishing* (2005)

- "Physical chemistry. A molecular approach", D.A. McQuarrie and J.D. Simon, *University Science Books* (1997)
- "Physical chemistry", P. Atkins and J. De Paula, *Oxford University Press* (2006)

Principes de la spectroscopie

Electromagnetic radiation

Electromagnetic waves: the *wavenumber*



- **Refractive index** of the propagation medium :

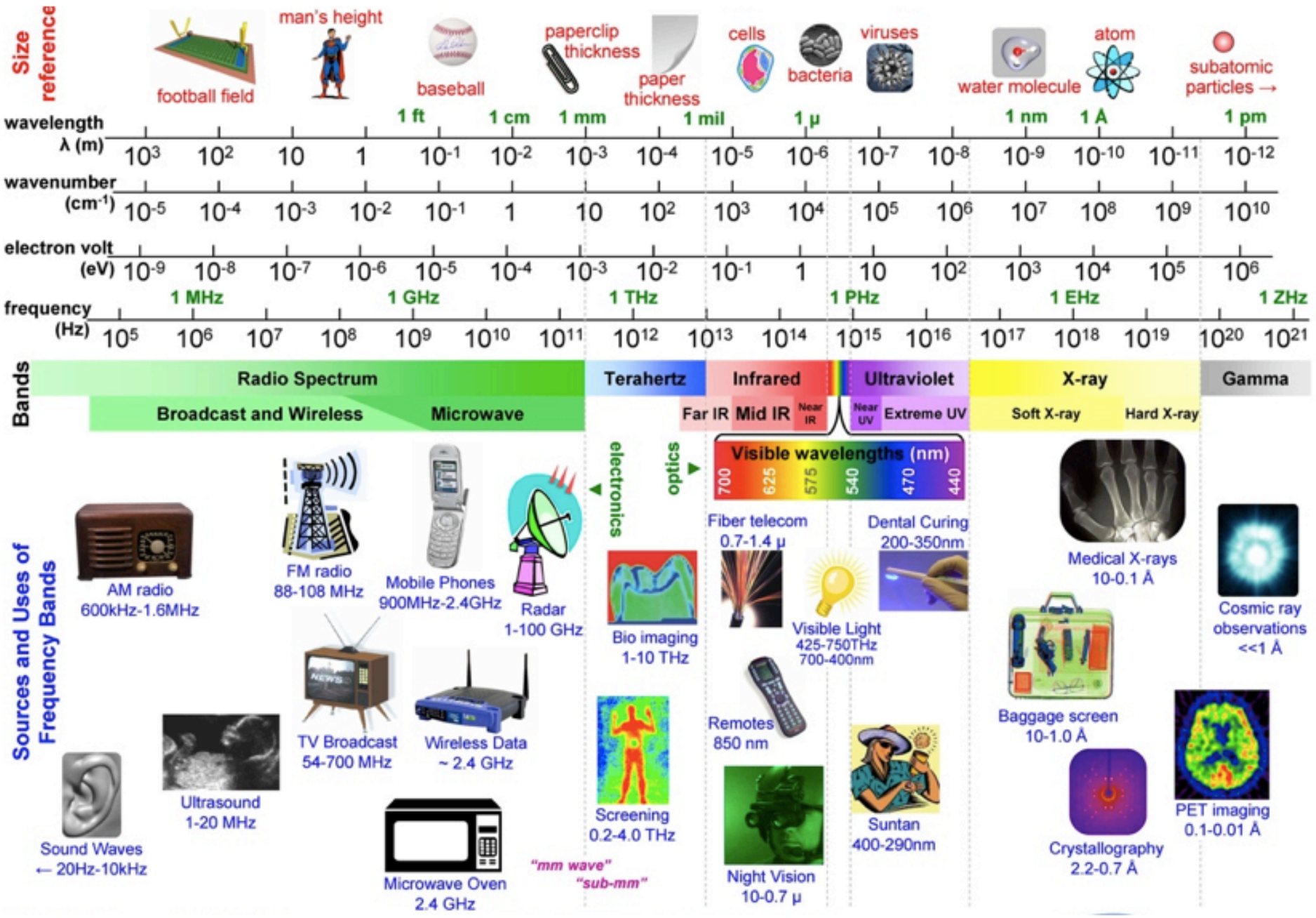
$$n = \frac{c_0}{c} = \frac{\lambda_0}{\lambda}$$

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

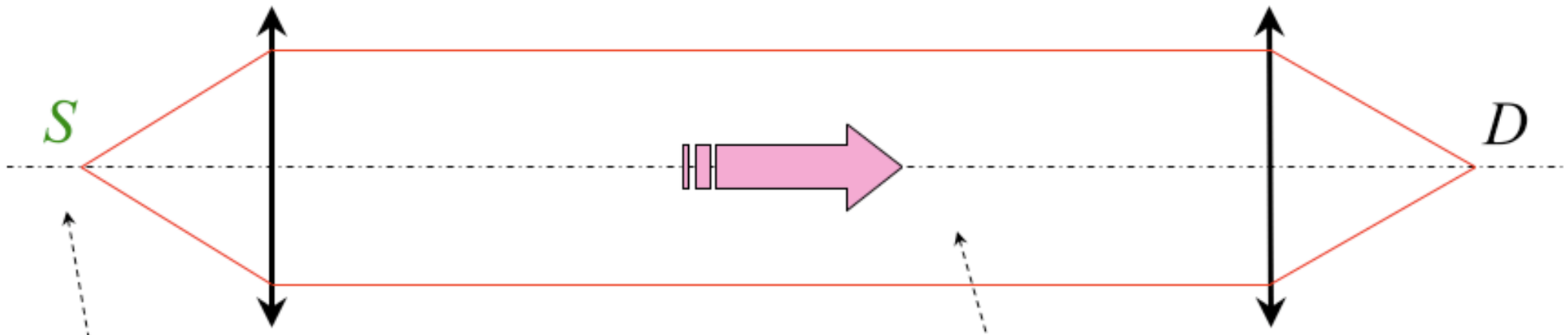
$$\tilde{\nu}\ [\mathrm{cm}^{-1}] = 10^4/\lambda_0\ [\mu\mathrm{m}]$$

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

The electromagnetic spectrum



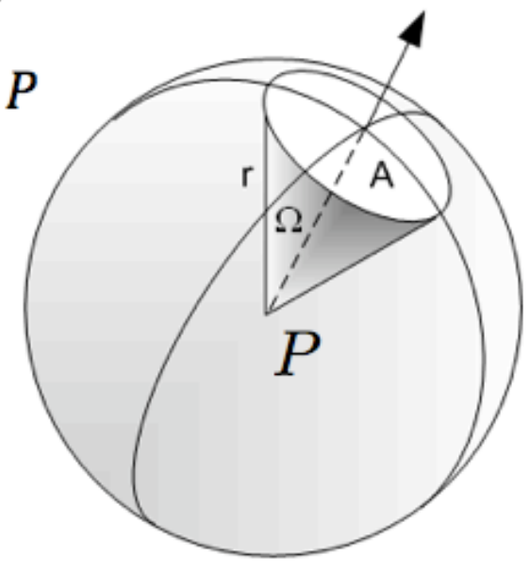
Collimated beams



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

Solid angle at P

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



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

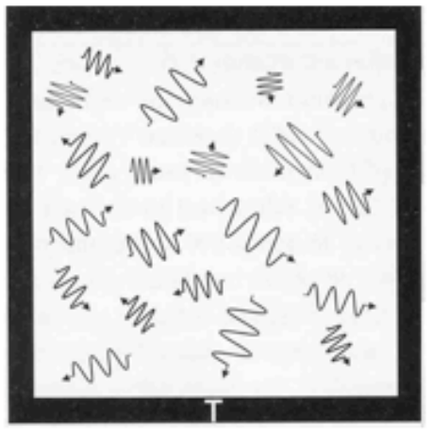
$$= \int I_{\tilde{\nu}}(\tilde{\nu})\, d\tilde{\nu}$$

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

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

Radiation in equilibrium with matter

(Blackbody radiation)



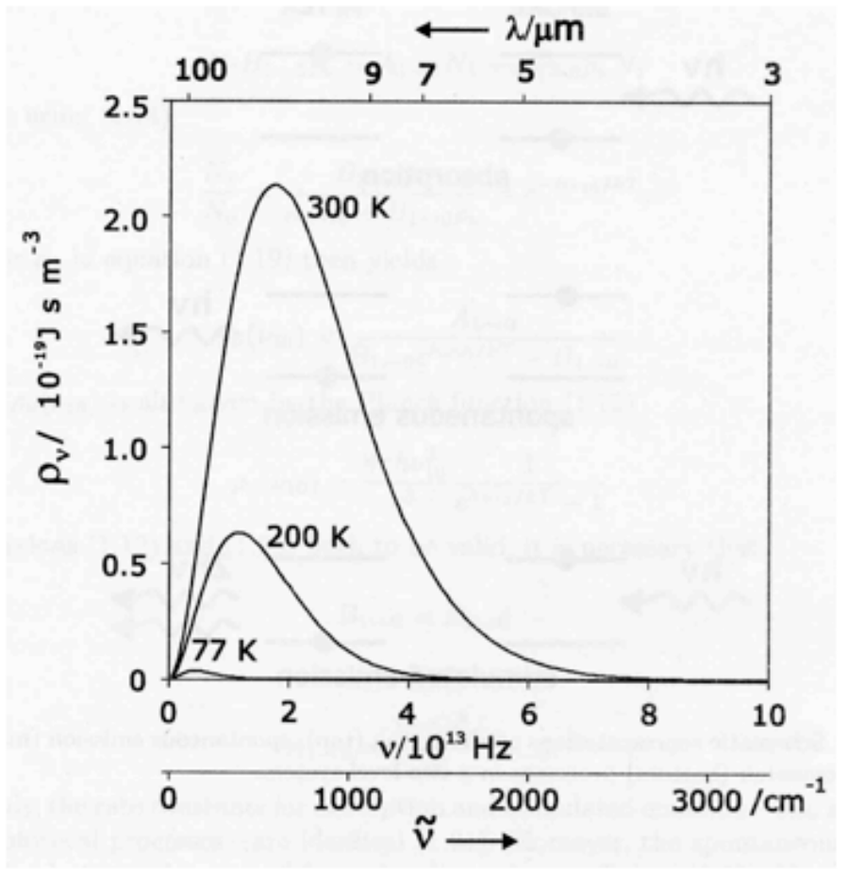
• An opaque container at temperature T encloses a gas of photons emitted by its walls. At equilibrium, the distribution of photon energies is determined solely by this temperature.

• Radiant energy density (J m^{-3}) in the cavity at temperature T :

$$\rho(T) = \int_0^\infty \rho_{\tilde{\nu}}(\tilde{\nu}, T)\, d\tilde{\nu}$$

Note : $I(\tilde{\nu}) = c\,\rho(\tilde{\nu})$

spectral radiant energy density (J m^{-2})
= radiant energy density in the interval $[\tilde{\nu}, \tilde{\nu} + d\tilde{\nu}]$



Planck's radiation law :

$$\rho_{\tilde{\nu}}(T) = 8\pi h c \tilde{\nu}^3 \frac{1}{\exp\{hc\tilde{\nu}/(kT)\} - 1}$$

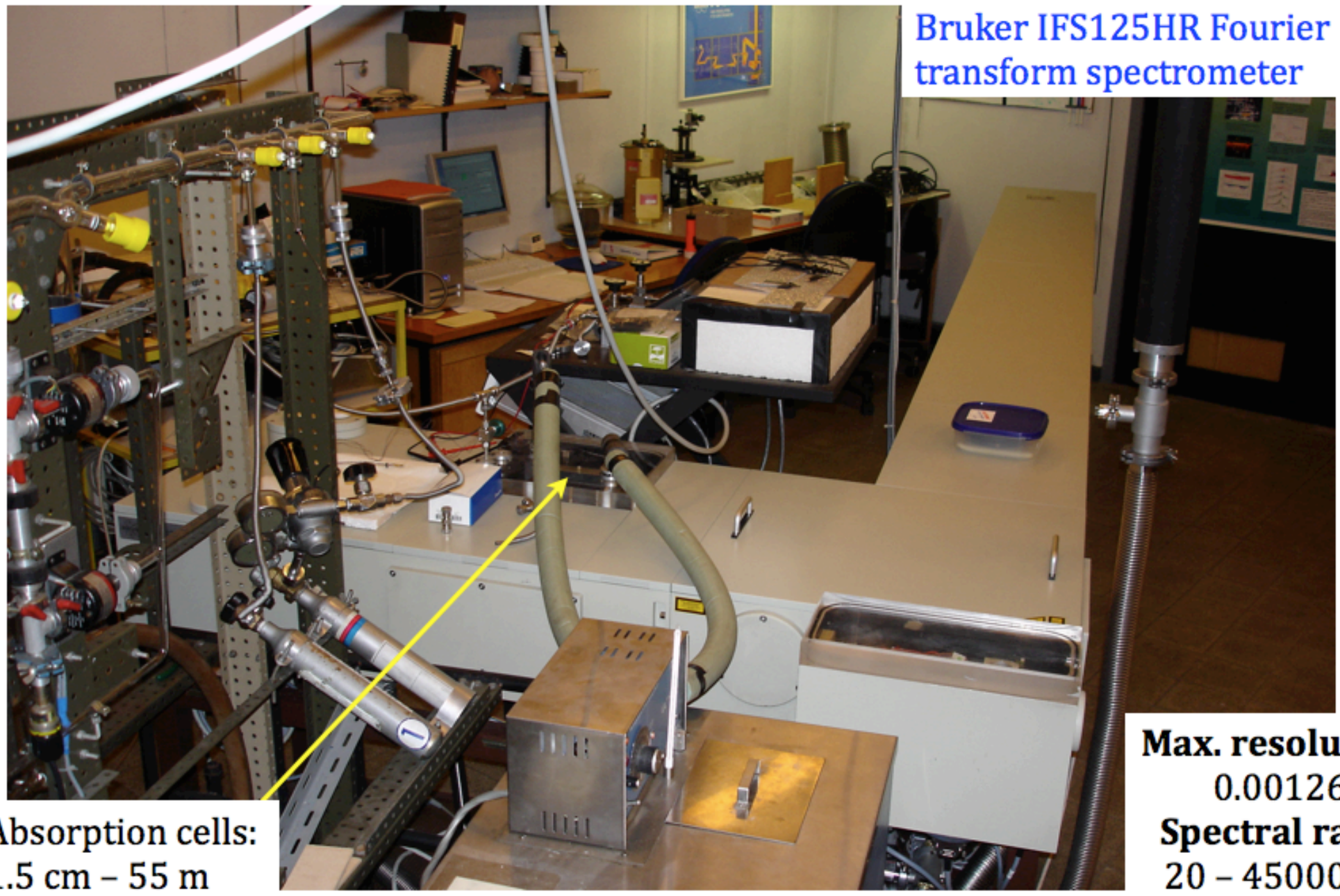
Note. Change of variables not straightforward

$$\rho_\lambda(T) = \rho_{\tilde{\nu}\to\lambda}(T) \left|\frac{d\tilde{\nu}}{d\lambda}\right| = \rho_{\tilde{\nu}\to\lambda}(T)\, \frac{1}{\lambda^2}$$

Principes de la spectroscopie

Radiative transfer in a gas

“Beer-Lambert spectroscopy”

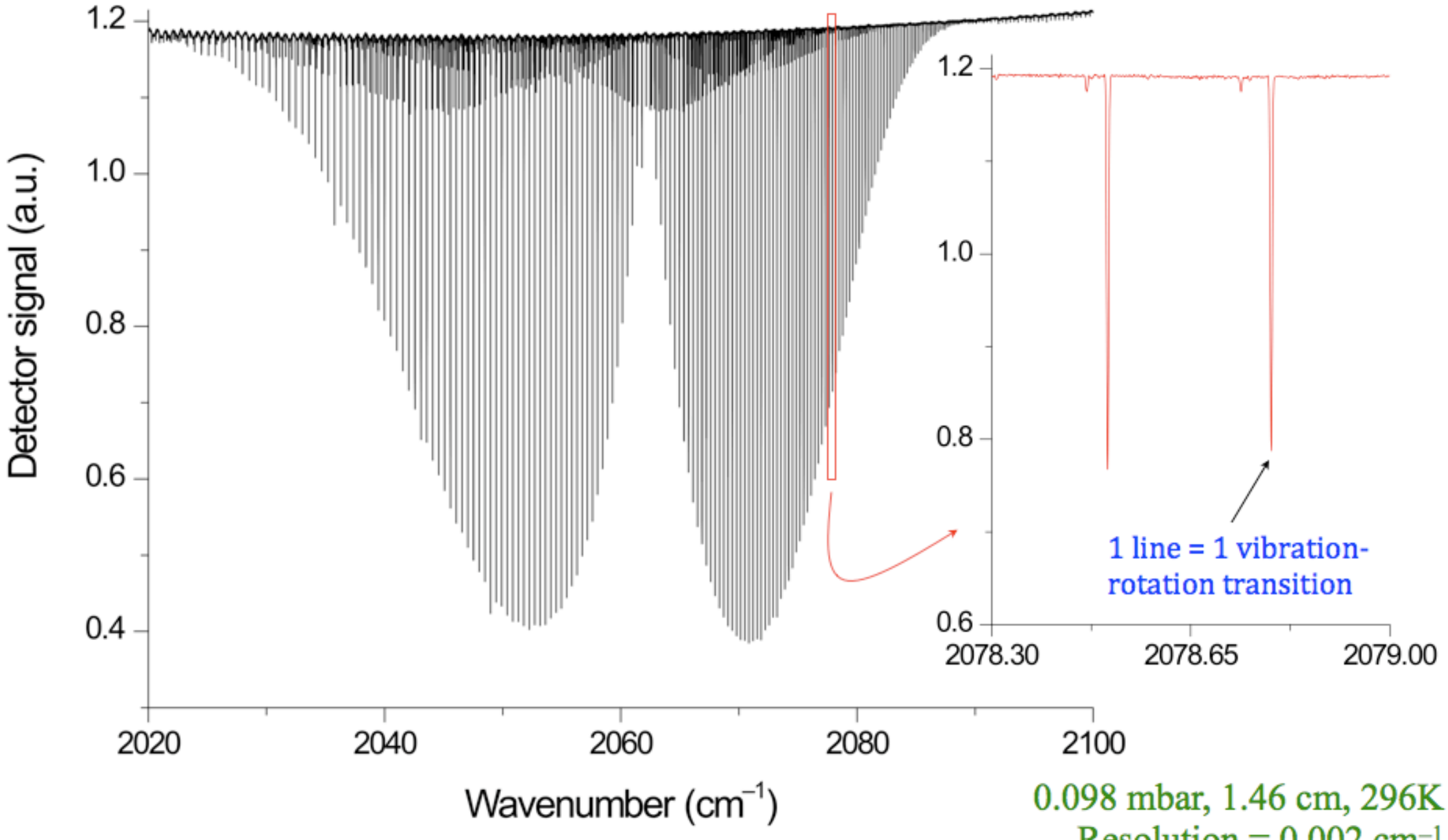


Bruker IFS125HR Fourier transform spectrometer

Absorption cells:
1.5 cm – 55 m

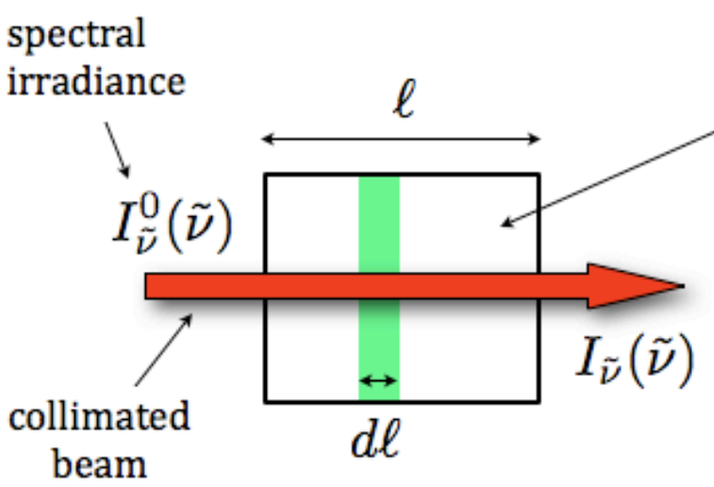
Max. resolution :
0.00126 cm^{-1}
Spectral range :
20 – 45000 cm^{-1}

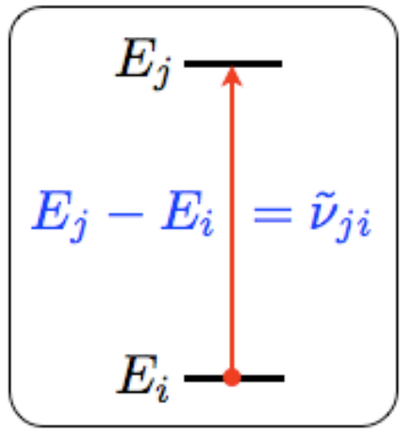
High resolution IR spectroscopy



0.098 mbar, 1.46 cm, 296K
Resolution = 0.002 cm^{-1}

Beer-Lambert law





Bohr condition

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

Homogeneous medium

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

- Transmittance τ :

$$\tau(\tilde\nu) = I_{\tilde\nu}(\tilde\nu)/I^0_{\tilde\nu}(\tilde\nu) = e^{-A(\tilde\nu)}$$

- Absorption A_b :

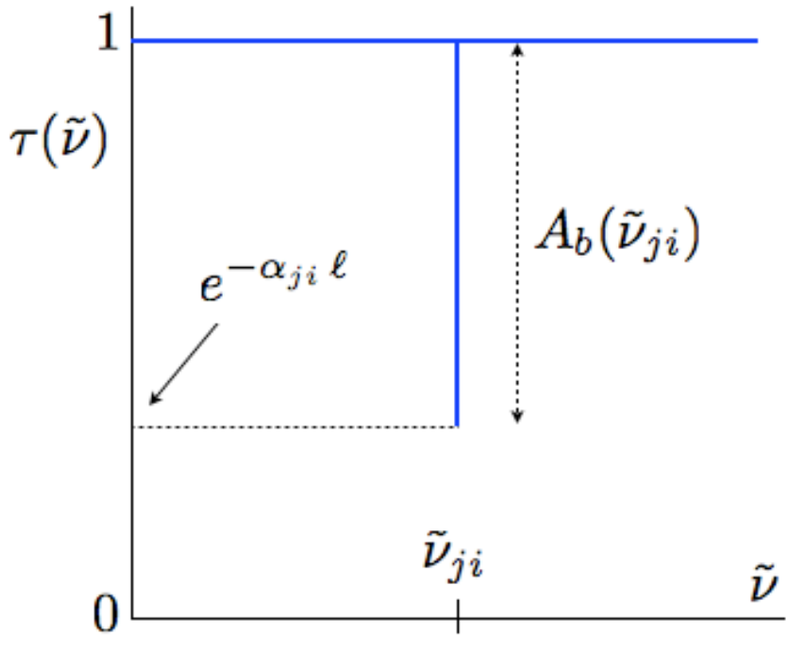
$$A_b(\tilde\nu) = 1 - \tau(\tilde\nu)$$

- Absorbance A :

$$A(\tilde\nu) = \alpha(\tilde\nu)\,\ell = \sigma(\tilde\nu) N \ell$$

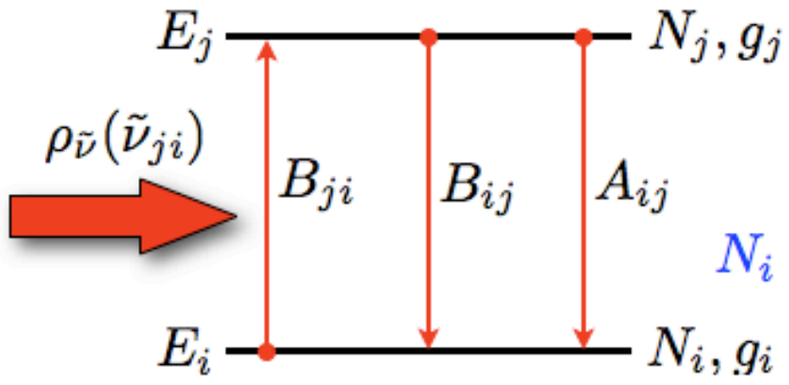
integrated absorption coefficient

$$= \alpha_{ji}\,\delta(\tilde\nu - \tilde\nu_{ji}) \qquad = P/kT$$



Absorption and emission of radiation

$N = N_i + N_j$ two-levels systems per unit volume at temperature T in equilibrium with radiation :



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

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

$B\,\rho_{\tilde{\nu}}$, A_{ij} } transition probabilities per second

Absorption	Stimulated emission	Spontaneous emission
$dN_j/dt = B_{ji}\,\rho_{\tilde{\nu}}(\tilde{\nu}_{ji})\,N_i$	$dN_j/dt = -B_{ij}\,\rho_{\tilde{\nu}}(\tilde{\nu}_{ji})\,N_j$	$dN_j/dt = -A_{ij}\,N_j$

Relations between the Einstein coefficients

from the Boltzmann distribution

- Thermal equilibrium → Rate of population of j = its rate of depopulation

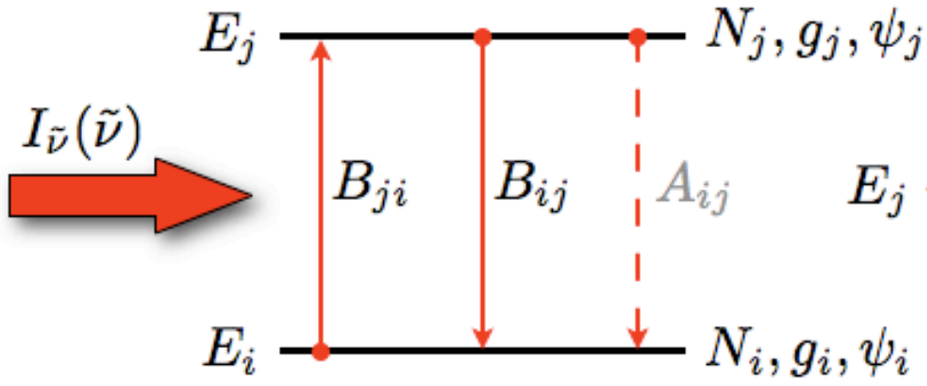
$$B_{ji}\,\rho_{\tilde{\nu}}(\tilde{\nu}_{ji})\,N_i = B_{ij}\,\rho_{\tilde{\nu}}(\tilde{\nu}_{ji})\,N_j + A_{ij}N_j \Rightarrow \frac{N_j}{N_i} = \frac{B_{ji}\,\rho_{\tilde{\nu}}(\tilde{\nu}_{ji})}{B_{ij}\,\rho_{\tilde{\nu}}(\tilde{\nu}_{ji}) + A_{ij}} = \frac{g_j}{g_i}\exp\left(\frac{-hc\,\tilde{\nu}_{ji}}{kT}\right)$$

- Solving for $\rho_{\tilde{\nu}}$ and equating to Planck's law yields

$$g_i\,B_{ji} = g_j\,B_{ij} \qquad A_{ij} = 8\pi hc\,\tilde{\nu}_{ji}^3\,B_{ij}$$

Note. $A_{ij} = \frac{8\pi h\,\nu_{ji}^3}{c^3}B_{ji}$ *or* $A_{ij} = \frac{8\pi\hbar\,\omega_{ji}^3}{\pi^2 c^3}B_{ji}$

Matter-radiation interaction



Radiative transfer in $N = N_i + N_j$ two-levels sytems per unit volume at temperature T

Total radiant energy density absorbed per unit time :

$$\frac{d\rho}{dt} = -\int_0^\infty \frac{dI_{\tilde{\nu}}(\tilde{\nu})}{d\ell}\, d\tilde{\nu} = \int_0^\infty \alpha(\tilde{\nu}) I_{\tilde{\nu}}(\tilde{\nu}) d\tilde{\nu} = \frac{dN_j}{dt} hc\,\tilde{\nu}_{ji} = B_{ji}\rho_{\tilde{\nu}}(\tilde{\nu}_{ji})\, g_i \left(\frac{N_i}{g_i} - \frac{N_j}{g_j}\right) hc\,\tilde{\nu}_{ji}$$

$$\Rightarrow \quad \boxed{\alpha_{ji} = \int_0^\infty \alpha(\tilde{\nu})\, d\tilde{\nu} = h\tilde{\nu}_{ji} \left(\frac{N_i}{g_i} - \frac{N_j}{g_j}\right) g_i\, B_{ji}}$$

Matter-radiation interaction = **electric dipole** interaction

- **Molecule** = collection of charges q_i at positions $\vec{r_i}$ ⇒ Electric dipole moment $\vec{\mu} = \sum_i \vec{r_i}\, q_i$
- **Radiation** = oscillating electric field

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

transition moment

Note. First factor for $B_{ji}^{(\omega)} \to \frac{4\pi^2}{3\hbar^2}$ and $B_{ji}^{(\nu)} \to \frac{2\pi}{3\hbar^2}$

Absorption "intensity"

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

Dirac notation

$$\alpha_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\tilde{\nu}_{ji}\left(\frac{N_i}{g_i} - \frac{N_j}{g_j}\right) g_i \sum_{f=X,Y,Z} |\langle\psi_j|\mu_f|\psi_i\rangle|^2$$

S_{ji} ("line strength")

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

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

$\approx 3.74 \times 10^{36}\,\mathrm{C}^{-2}$
$\approx 4.16 \times 10^{-19}\,\mathrm{D}^{-2}\mathrm{cm}^2$

I_a: isotopic abundance

273.15 K

$$\frac{N}{P} = n_L \frac{T_0}{T} \quad (n_L = 2.687 \times 10^{19}\ \text{molec cm}^{-3})$$

$$\alpha_{ji}^P = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\tilde{\nu}_{ji}\frac{n_L T_0}{Q(T)T} I_a\, e^{-hcE_i/kT}\left(1 - e^{-hc\tilde{\nu}_{ji}/kT}\right) S_{ji}$$

- Integrated absorption cross section [cm^{-1}/(molecule cm^{-2})] :

(Note. $\sigma = \alpha/N$)

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

Total internal partition function

- By definition :

$$Q(T) = \sum_{\text{all states}} g\, e^{-hcE/kT}$$

internal motions

- Calculation = approximations (Herzberg, IR & Raman [ch. 2, 8]; Gamache *et al*, JQSRT) :

$$E = E_{elec} + E_{vib} + E_{rot} + \cdots = E_e + E_v + E_r + \ldots$$

$$Q(T) = \sum_{\text{electronic}} g_e\, e^{-hcE_e/kT} \sum_{\text{vibrational}} g_v\, e^{-hcE_v/kT} \sum_{\text{rotational}} g_r\, e^{-hcE_r/kT} \ldots$$

$Q_{elec} = 1$ (often)

Harmonic approximation :

$$Q_{vib} = \Pi_i \left(1 - e^{-hc\omega_i/kT}\right)^{-d_i}$$

degeneracy of mode *i*

$$E_r = f(B_0, D_0 \ldots)$$

- Further difficulties : torsion, resonances ...

Principes de la spectroscopie

***Molecular** physics*

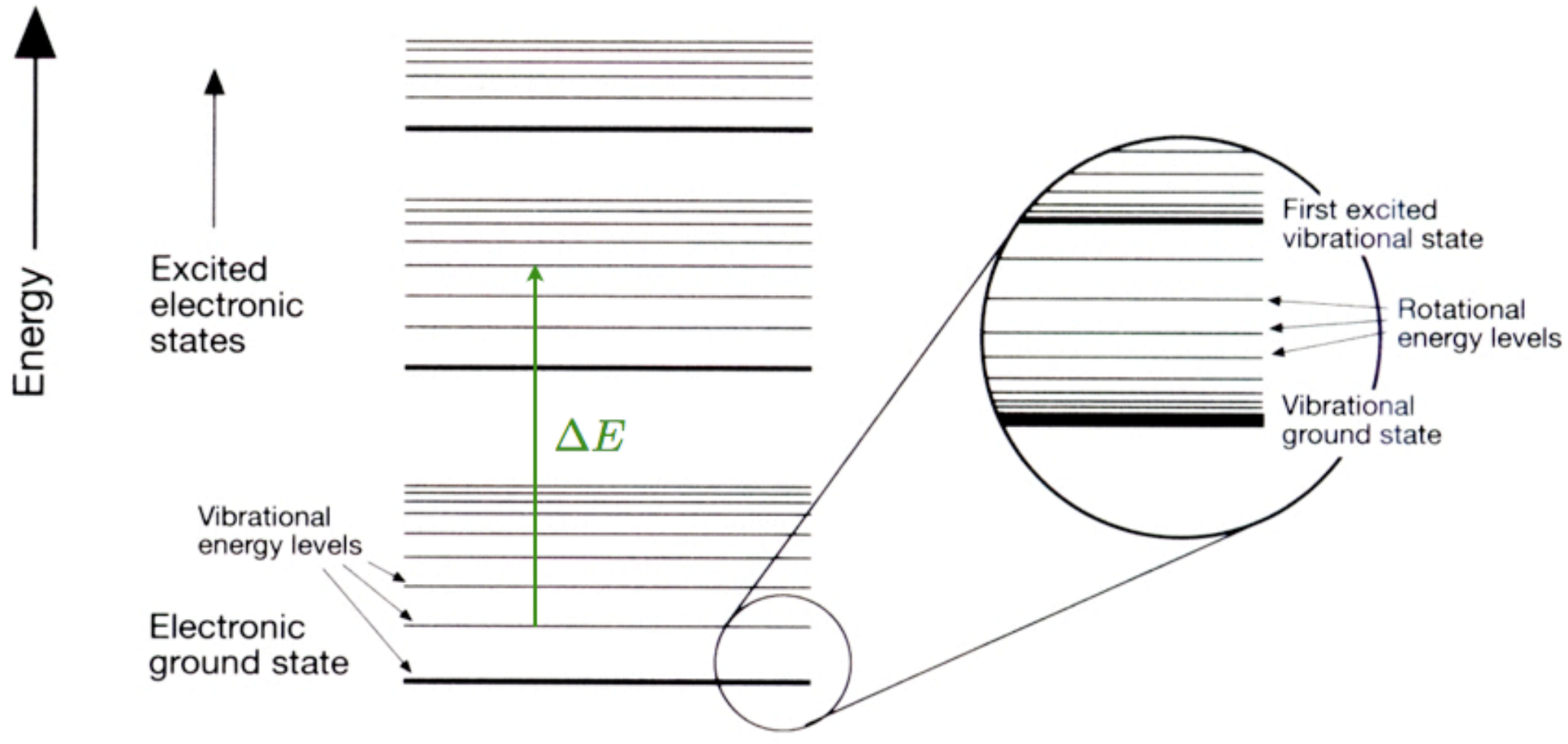
Molecular motions and their energies

Molecule = ensemble of interacting electrons and nuclei

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

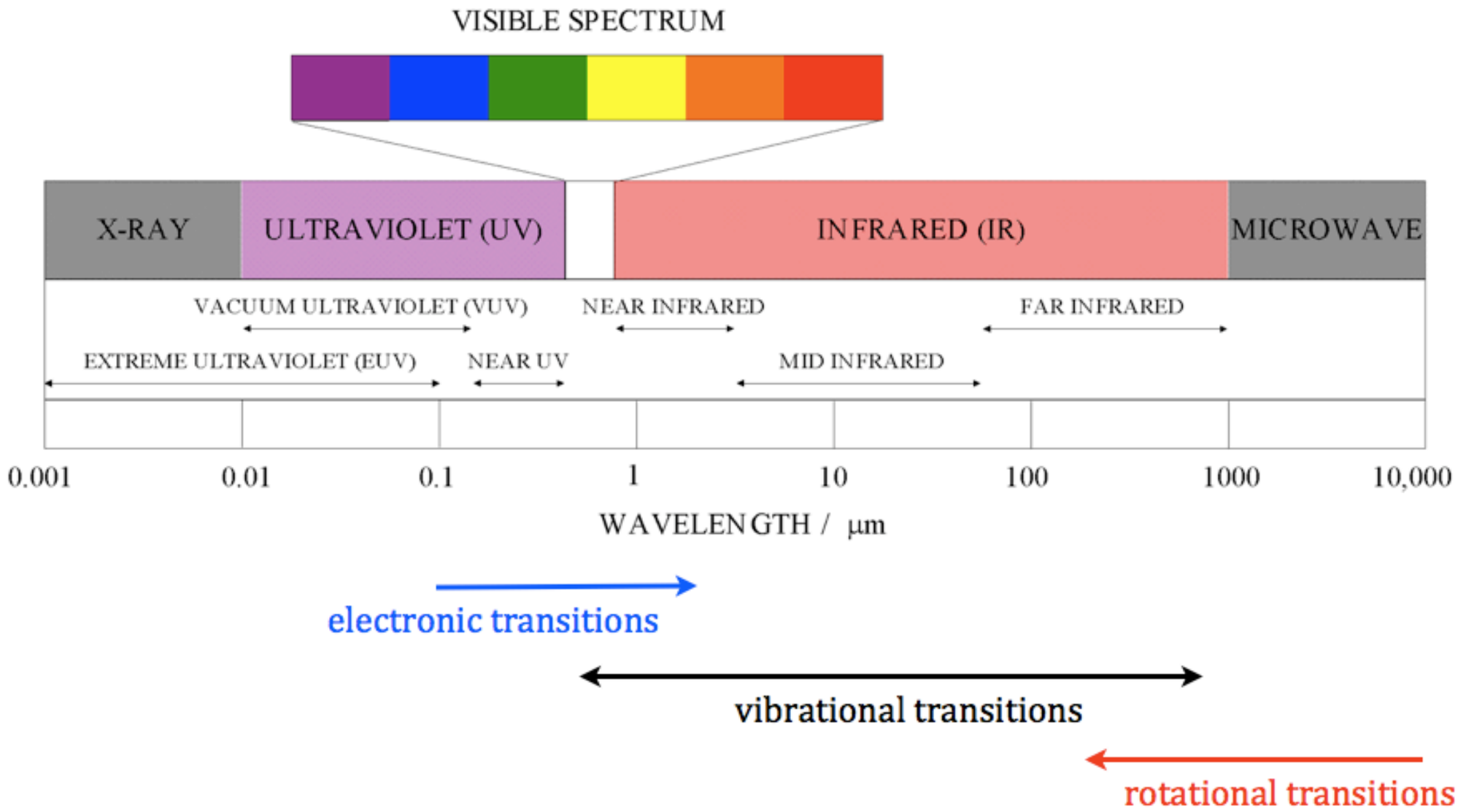
motion of the electrons

motion of the nuclei



Observation of molecular motions

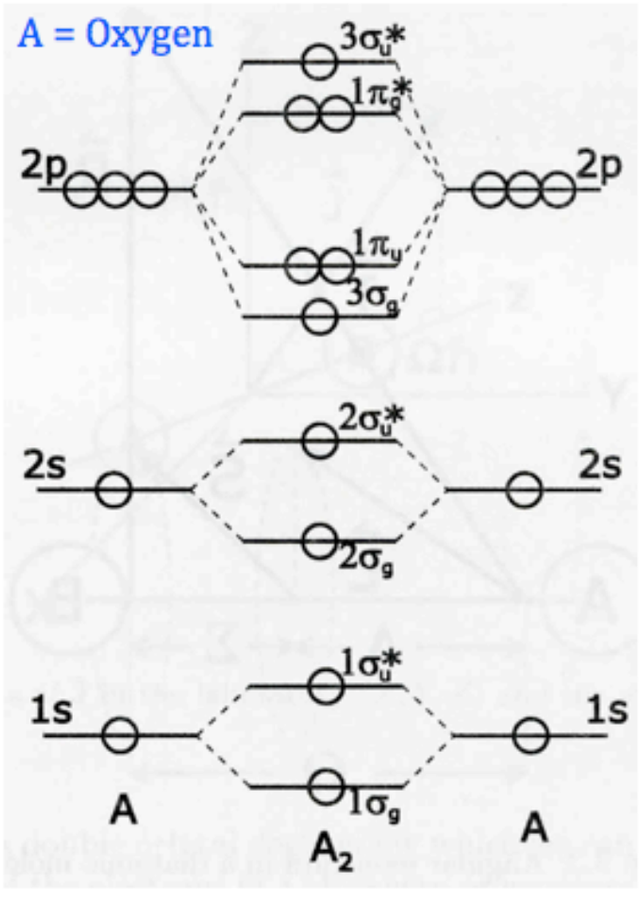
Transitions → Discrete spectrum: $\Delta E \simeq \Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot}$



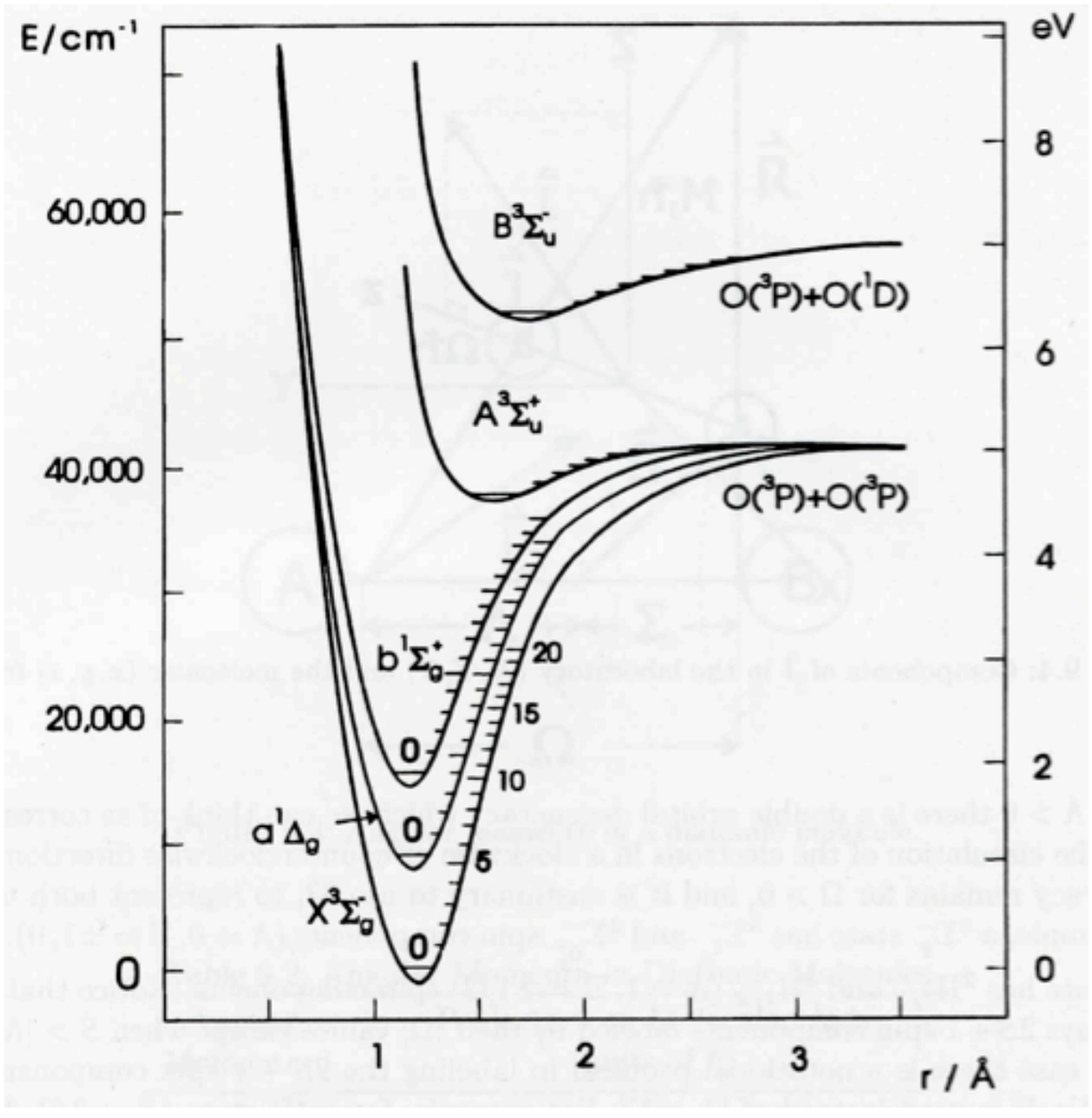
Electronic states of O_2

Electronic configuration of

- **O** : $1s^2\,2s^2\,2p^4$
- **O_2** : $1\sigma_g^2\,1\sigma_u^2\,2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,1\pi_u^4\,1\pi_g^2$



Electronic states of O_2



Electronic states of O_2 (2)

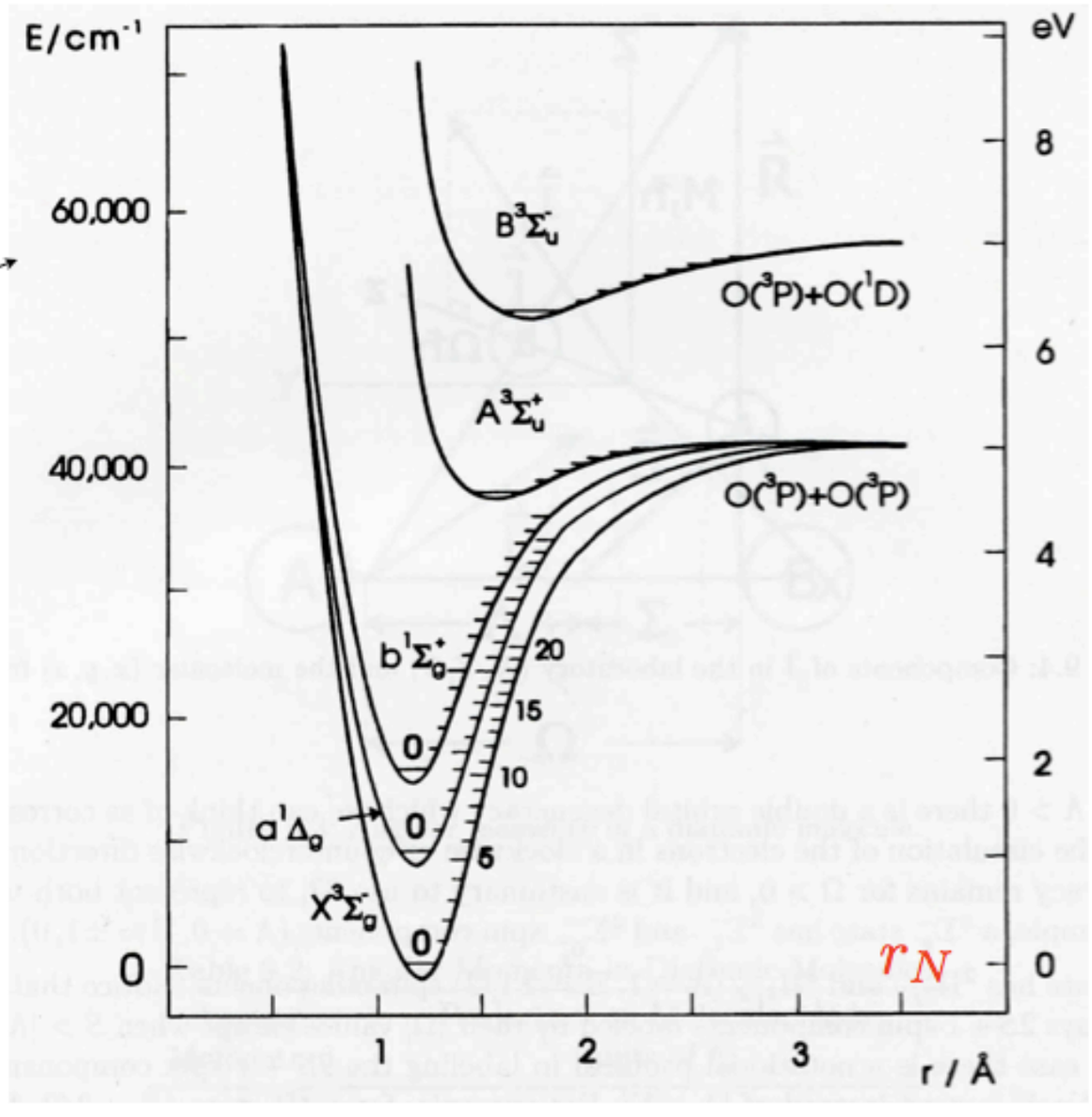
Electronic configuration of

- **O** : $1s^2\,2s^2\,2p^4$
- **O_2** : $1\sigma_g^2\,1\sigma_u^2\,2\sigma_g^2\,2\sigma_u^2\,3\sigma_g^2\,1\pi_u^4\,1\pi_g^2$

$$\hat{H}_{elec}\,\psi_{elec} = E_{elec}(r_N)\,\psi_{elec}$$

$$\begin{aligned}\hat{H}_{elec} &= \hat{T}_e(r_e) \\ &+ \hat{V}_{ee}(r_e) + \hat{V}_{NN}(r_N) \\ &+ \hat{V}_{eN}(r_e, r_N)\end{aligned}$$

Electronic states of O_2



This lecture : **Ground electronic state**

Principes de la spectroscopie

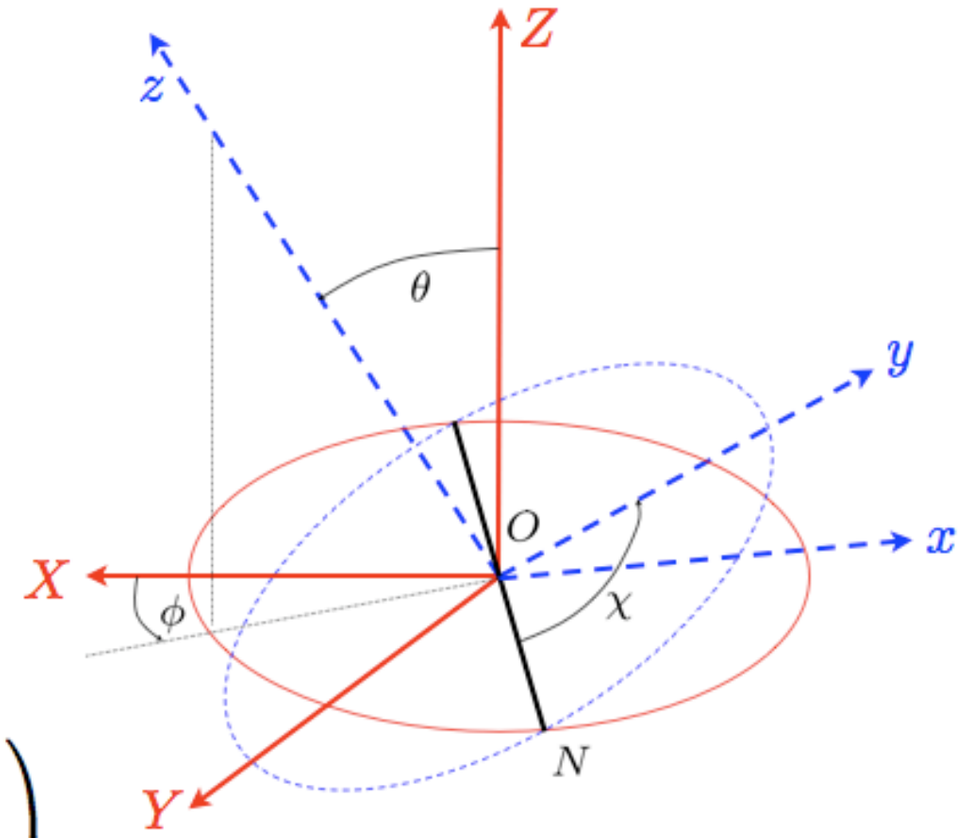
Molecular *physics – Rotation*

Coordinate systems

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

Euler angles : θ, ϕ, χ

Molecule-fixed frame (x, y, z)



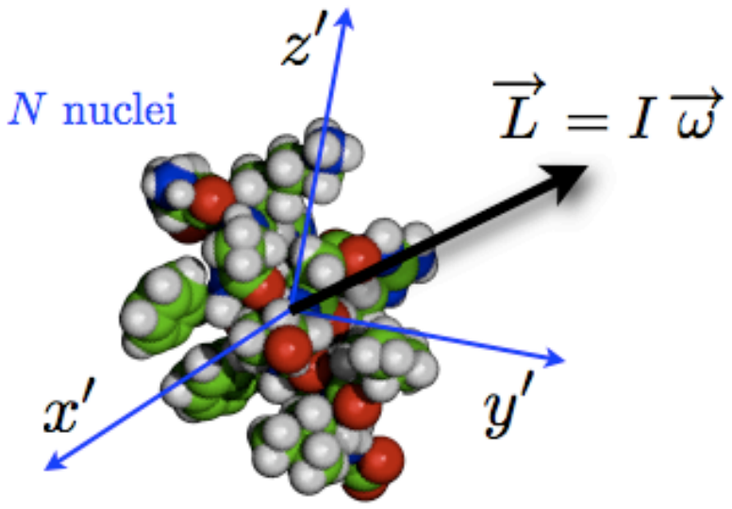
$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \lambda_{xX} & \lambda_{xY} & \lambda_{xZ} \\ \lambda_{yX} & \lambda_{yY} & \lambda_{zY} \\ \lambda_{zX} & \lambda_{zY} & \lambda_{zZ} \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Transformation matrix

$\lambda_{\alpha f}$	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	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$

Rotational motion of a molecule (classical mechanics)

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



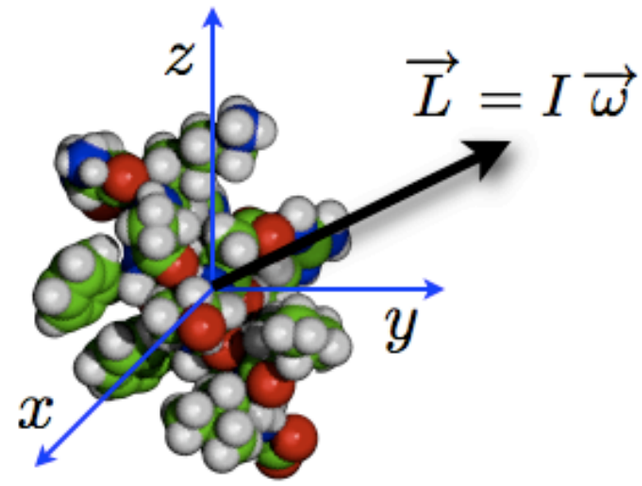
inertia tensor

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

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

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

- **Classical kinetic energy** in the *principal axis system*



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

$$\Rightarrow E_c = \frac{1}{2}\vec{\omega}\, I\, \vec{\omega} = \sum_{\alpha=x,y,z} \frac{1}{2} I_\alpha \omega_\alpha^2 = \sum_{\alpha=x,y,z} \frac{L_\alpha^2}{2I_\alpha}$$

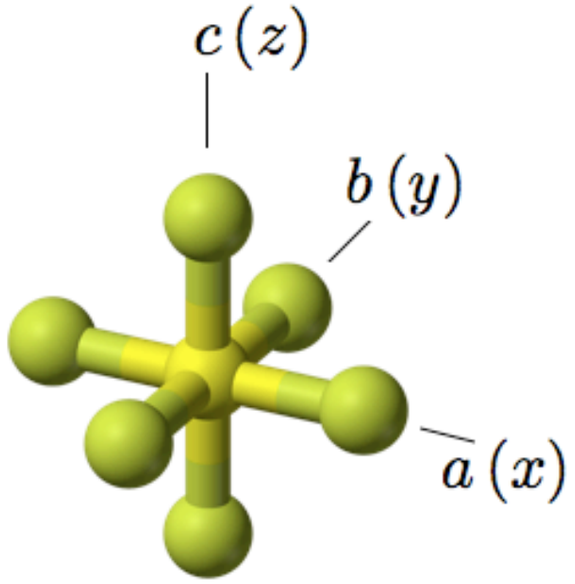
Conventions and classes of molecules

- 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 $I_a \leq I_b \leq I_c$

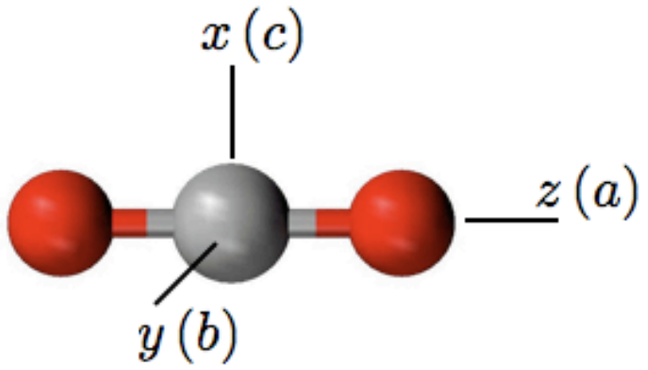
The moments of inertia are the half-axes of an ellipsoid :

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

- **Classification** of the molecules
  - *Linear* molecules : $I_a = 0$, $I_b = I_c$ (CO_2, HCN)
  - *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



- Classical kinetic energy of a rigid rotor :

$$E_c = \frac{J_x^2}{2I} + \frac{J_y^2}{2I} = \frac{J^2}{2I}$$

J = customary symbol for angular momentum

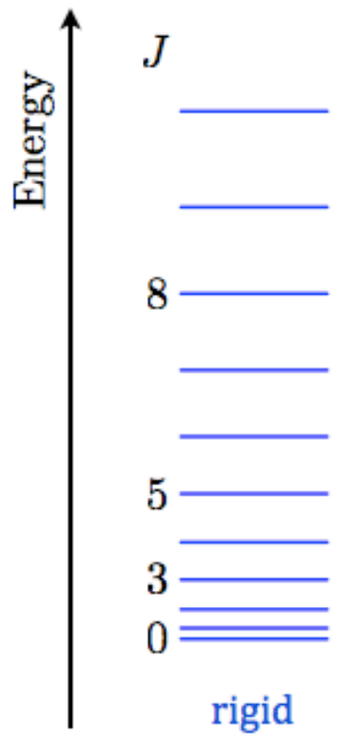
- Schrödinger equation of a rigid rotor

$$\hat{H} = \frac{\hat{J}^2}{2I} \quad \Rightarrow \quad \hat{H}\psi_r = E_r\psi_r$$

spherical harmonics

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

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



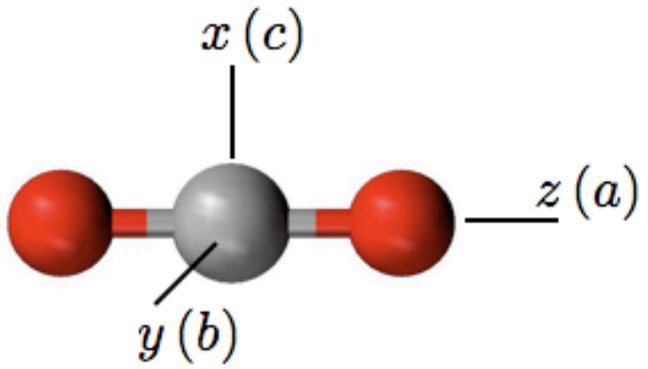
- Degeneracy of the rotational levels :

$$\hat{J}_Z\psi_r = m\hbar\psi_r \text{ with } -J \le m \le J$$

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

$\mathrm{CO_2}$: $B = 0.39022\ \mathrm{cm}^{-1}$, $I = 7.1736 \times 10^{-39}\ \mathrm{g\ cm^2/molec}$, $r_{\mathrm{CO}} = 1.162$ Å

Rotation of a linear molecule (2)



- Classical kinetic energy of a rigid rotor :

$$E_c = \frac{J_x^2}{2I} + \frac{J_y^2}{2I} = \frac{J^2}{2I}$$

J = customary symbol for angular momentum

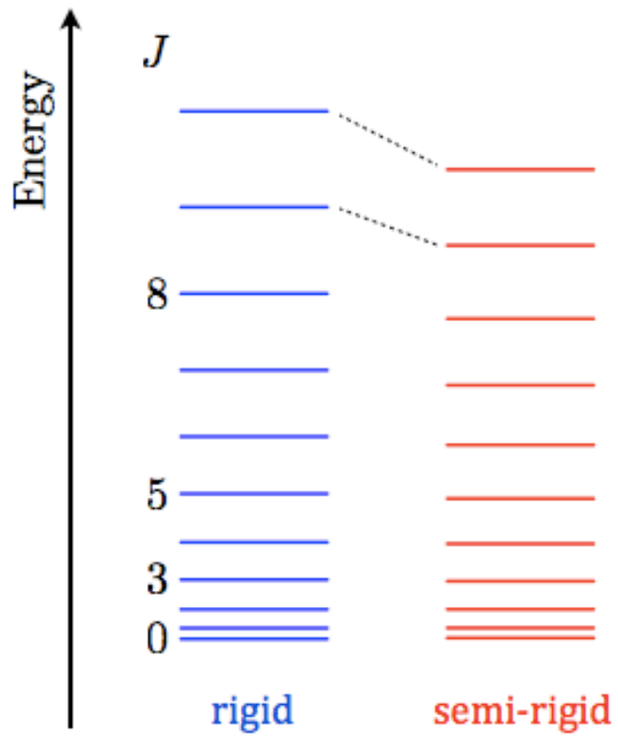
- Schrödinger equation of a rigid rotor

$$\hat{H} = \frac{\hat{J}^2}{2I} \quad \Rightarrow \quad \hat{H}\psi_r = E_r\psi_r$$

spherical harmonics

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

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



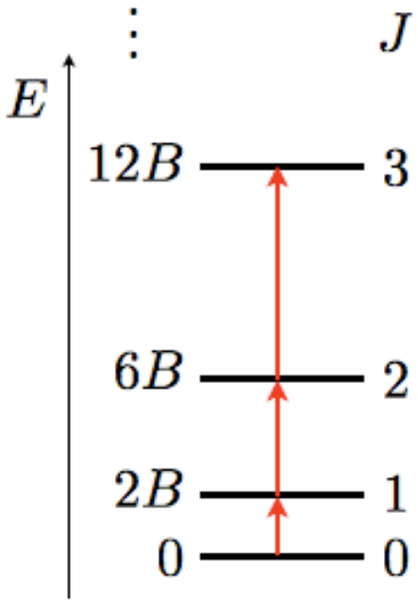
- Semi-rigid rotor

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

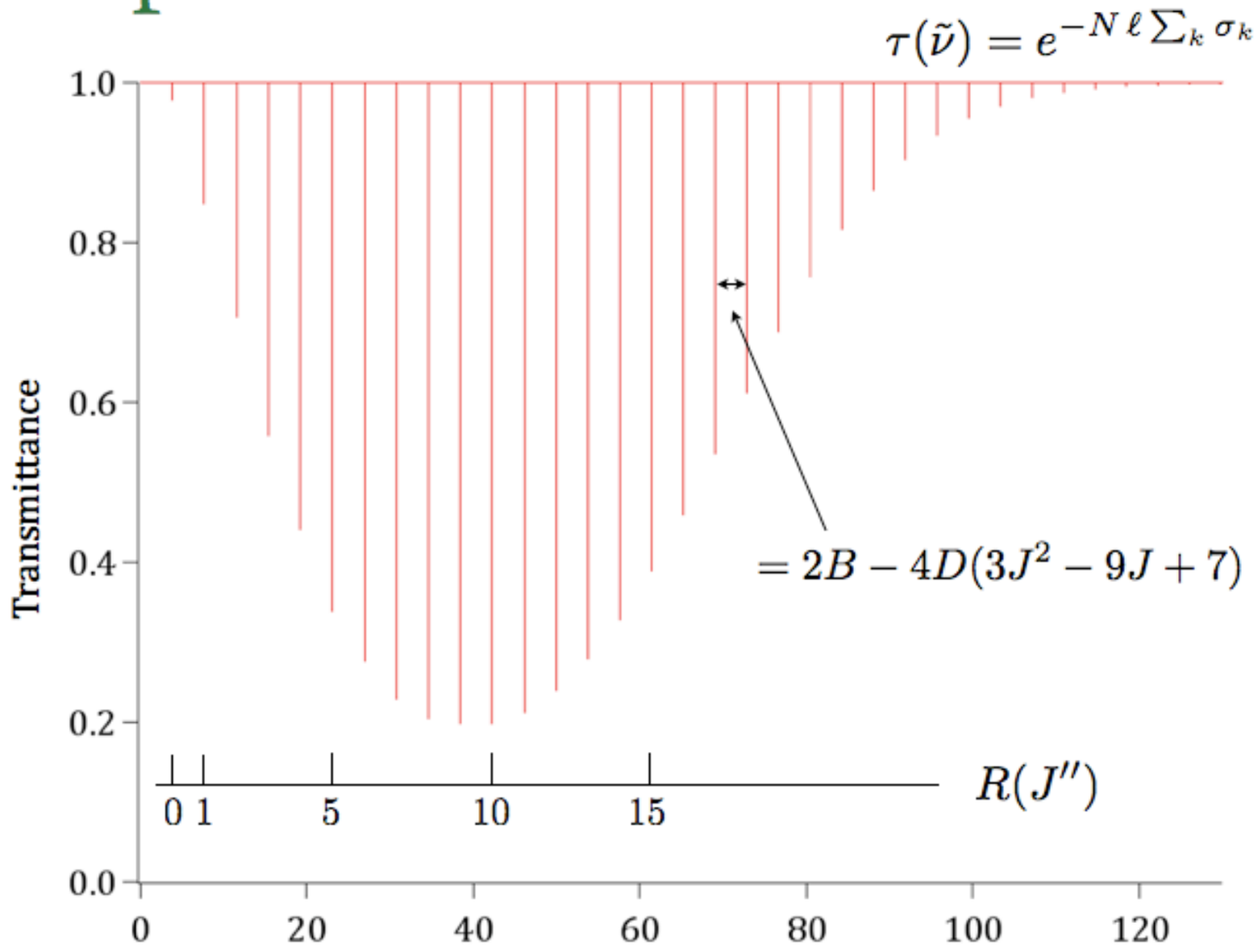
$$\mathrm{CO_2}: \; D = 1.334 \times 10^{-7}\ \mathrm{cm}^{-1}$$

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

Transitions : $\Delta J = \pm 1$



(Rigid rotor)



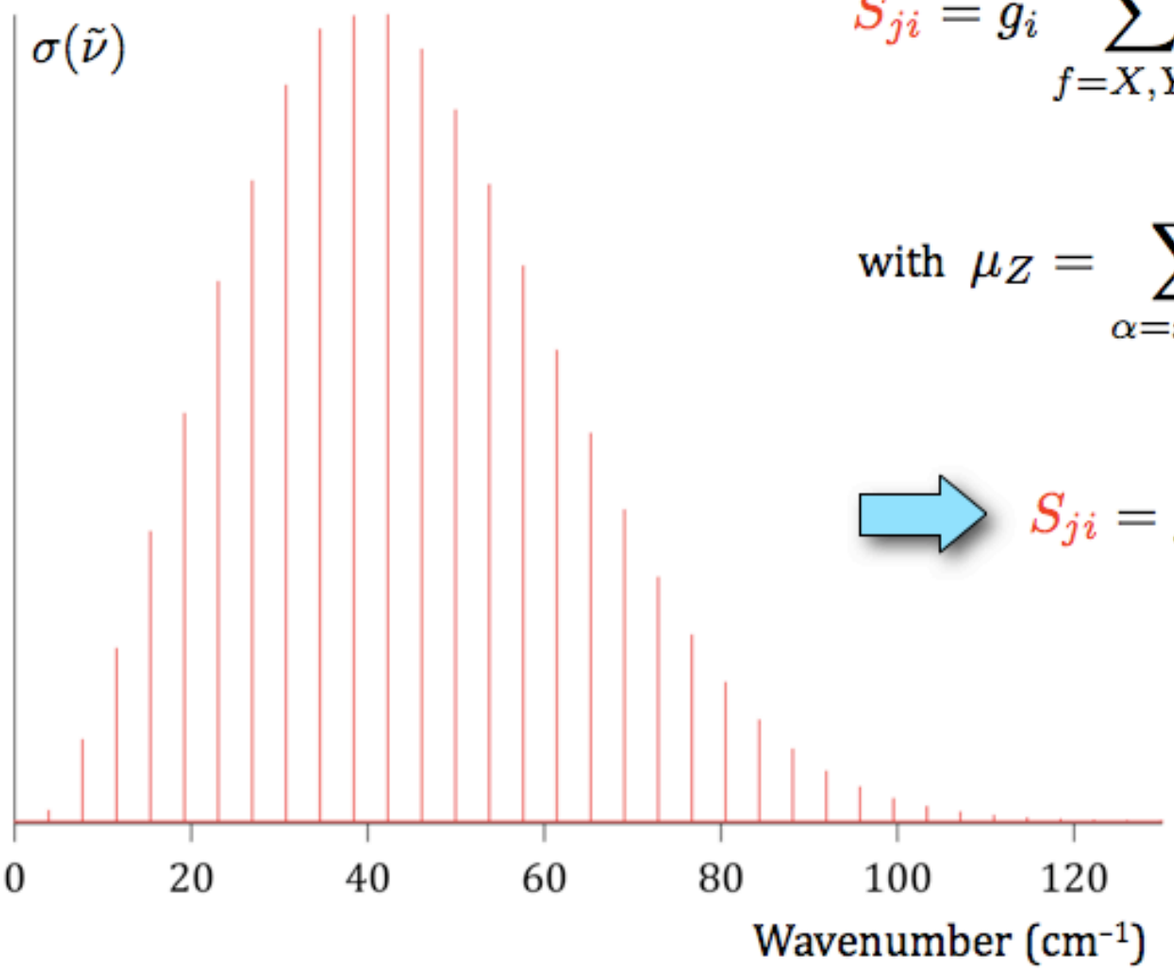
Line positions :

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

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

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)

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

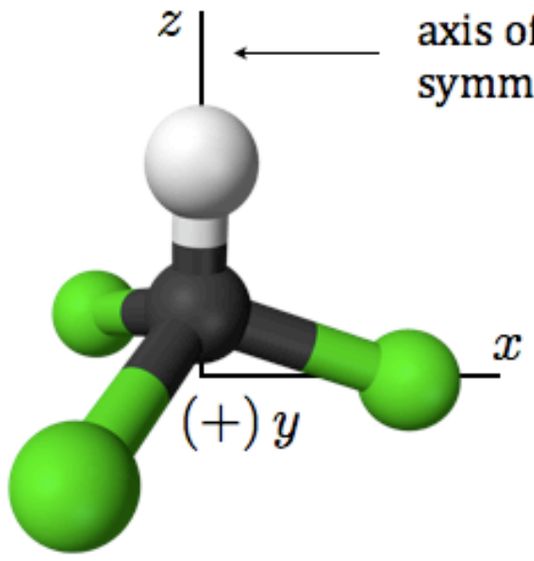
$$\Rightarrow S_{ji} = g_i \underbrace{3\,|\langle\psi_r^j|\lambda_{zZ}|\psi_r^i\rangle|^2}_{= \frac{J+1}{2J+1}} |\mu_z|^2 = (J+1)\,|\mu_z|^2$$

$= 2J+1$

Permanent dipole moment :

$\mu_z = 1.098$ D

Rotation of a rigid symmetric top



- Hamiltonian operator ($I_x = I_y$) :

$$\hat{H} = \frac{\hat{J}_z^2}{2I_z} + \frac{1}{2I_x}(\hat{J}_x^2 + \hat{J}_y^2) = \frac{\hat{J}^2}{2I_x} + \left(\frac{1}{2I_z} - \frac{1}{2I_x}\right)\hat{J}_z^2$$

- ***Prolate*** *symmetric* tops ($I_z < I_x = I_y$)
- ➞ $z = a, x = b, y = c$: $I_a < I_b = I_c$ (CH_3Cl)

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

- ***Oblate*** *symmetric* tops ($I_z > I_x = I_y$)
- ➞ $z = c, x = a, y = b$: $I_a = I_b < I_c$ (CCl_3H)

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

$-J \leq K \leq +J$

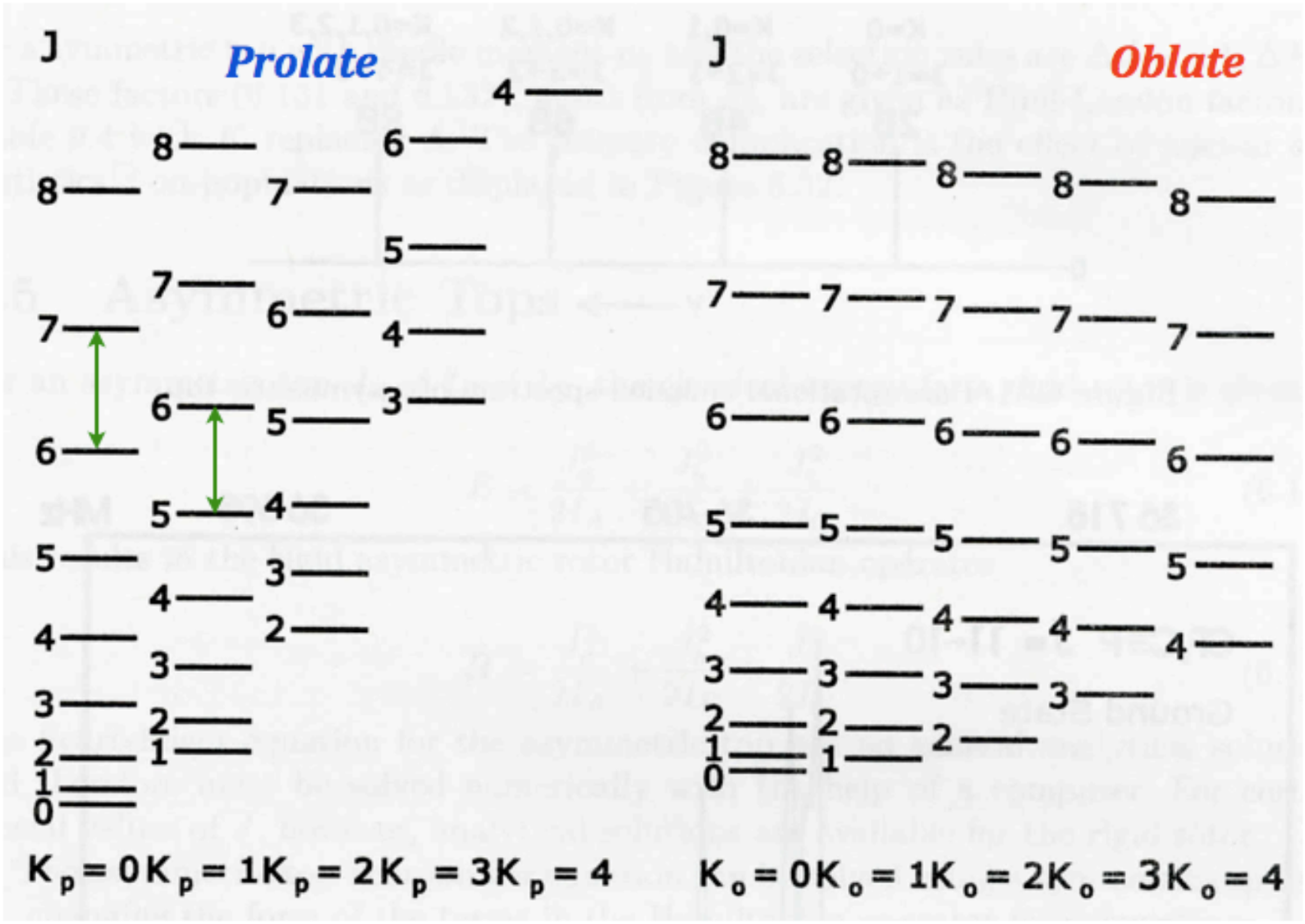
$$A = \frac{h}{8\pi^2 c I_a} \geq B = \frac{h}{8\pi^2 c I_b} \geq C = \frac{h}{8\pi^2 c I_c}$$

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 rigid symmetric top

$\Delta K = 0$

$\Delta J = \pm 1$



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

Hamiltonian matrix of a symmetric top

- Schrödinger equation for a rigid symmetric top :

$$\hat{H}\,|\psi_r\rangle = E_r\,|\psi_r\rangle \quad \Leftrightarrow \quad \hat{H}\,|JK\rangle = E_r\,|JK\rangle$$

$$\hat{H} = \frac{\hat{J}^2}{2I_x} + \left(\frac{1}{2I_z} - \frac{1}{2I_x}\right)\hat{J}_z^2 \quad \Rightarrow \quad \text{Eigenfunctions :} \quad \hat{J}^2|JK\rangle = \hbar^2 J(J+1)|JK\rangle$$

$$\hat{J}_z|JK\rangle = \hbar\, K|JK\rangle$$

- In a set of (*basis*) functions $|\,J\,K\,\rangle$, the Hamiltonian is represented by a matrix. Its elements are $\langle JK|\hat{H}|J'K'\rangle$
- For $J = 1$:

$$\hat{H} = \begin{array}{c} \\ \langle 1,1| \\ \langle 1,0| \\ \langle 1,-1| \end{array} \begin{array}{c} \begin{array}{ccc} |1,1\rangle & |1,0\rangle & |1,-1\rangle \end{array} \\ \begin{pmatrix} E_r(1,1) & 0 & 0 \\ 0 & E_r(1,0) & 0 \\ 0 & 0 & E_r(1,-1) \end{pmatrix} \end{array}$$

$= \langle 1,-1|\hat{H}|1,-1\rangle$

The Hamiltonian matrix of a rigid symmetric top is *diagonal*

Rigid asymmetric tops ($I_a < I_b < I_c$)

- Hamiltonian :

$$\hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c} = \frac{1}{\hbar^2}\left(A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2\right)$$

A, B, C = rotational constants

$$= \frac{A+B}{2}\left(\hat{J}_a^2 + \hat{J}_b^2\right) + C\hat{J}_c^2 + \frac{A-B}{2}\left(\hat{J}_a^2 - \hat{J}_b^2\right)$$

$$= \left(\frac{A+B}{2}\right)\hat{J}^2 + \left(C - \frac{A+B}{2}\right)\hat{J}_c^2 + \left(\frac{A-B}{4}\right)\left[(\hat{J}^+)^2 + (\hat{J}^-)^2\right]$$

Oblate symmetric top

$$\hat{J}^\pm = \hat{J}_a \pm i\hat{J}_b$$

$$\hat{J}^\pm|JK\rangle = \hbar\sqrt{J(J+1) - K(K\mp 1)}\,|JK\mp 1\rangle$$

$$\Rightarrow \langle JK\mp 2|(\hat{J}^\pm)^2|JK\rangle = \hbar^2\sqrt{(J\pm K)(J\mp K+1)(J\pm K-1)(J\mp K+2)}$$

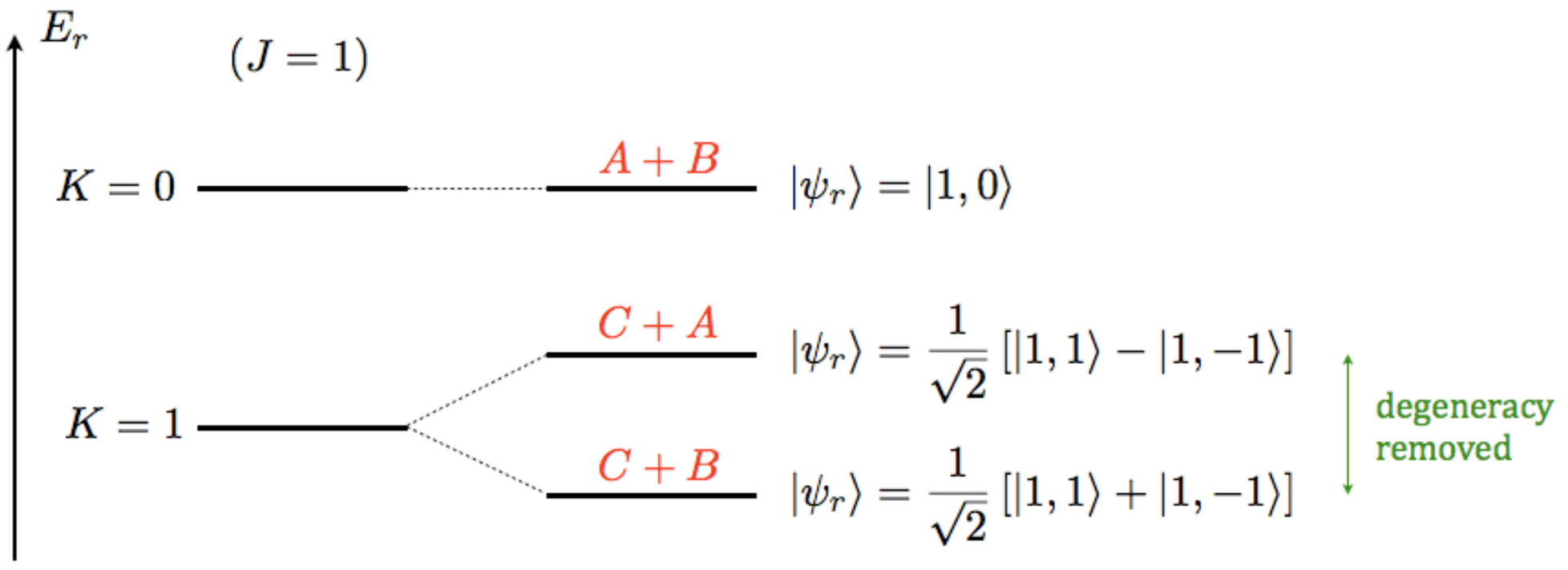
- Hamiltonian matrix ($J = 1$) :

$$\hat{H} = \begin{array}{c} \\ \langle 1,1| \\ \langle 1,0| \\ \langle 1,-1| \end{array} \begin{array}{c} \begin{array}{ccc} |1,1\rangle & |1,0\rangle & |1,-1\rangle \end{array} \\ \begin{pmatrix} C + (A+B)/2 & 0 & (A-B)/2 \\ 0 & A+B & 0 \\ (A-B)/2 & 0 & C + (A+B)/2 \end{pmatrix} \end{array}$$

Diagonalisation of Hamiltonian matrix

- **Schrödinger equation** = system of *n* linear equations (*n* = 3 for *J* = 1)
  - → Energies and wavefunctions = solutions of the secular equation : $|\hat{H} - E\,I| = 0$
  - → Coordinate transformation (diagonalisation) :

Identity matrix

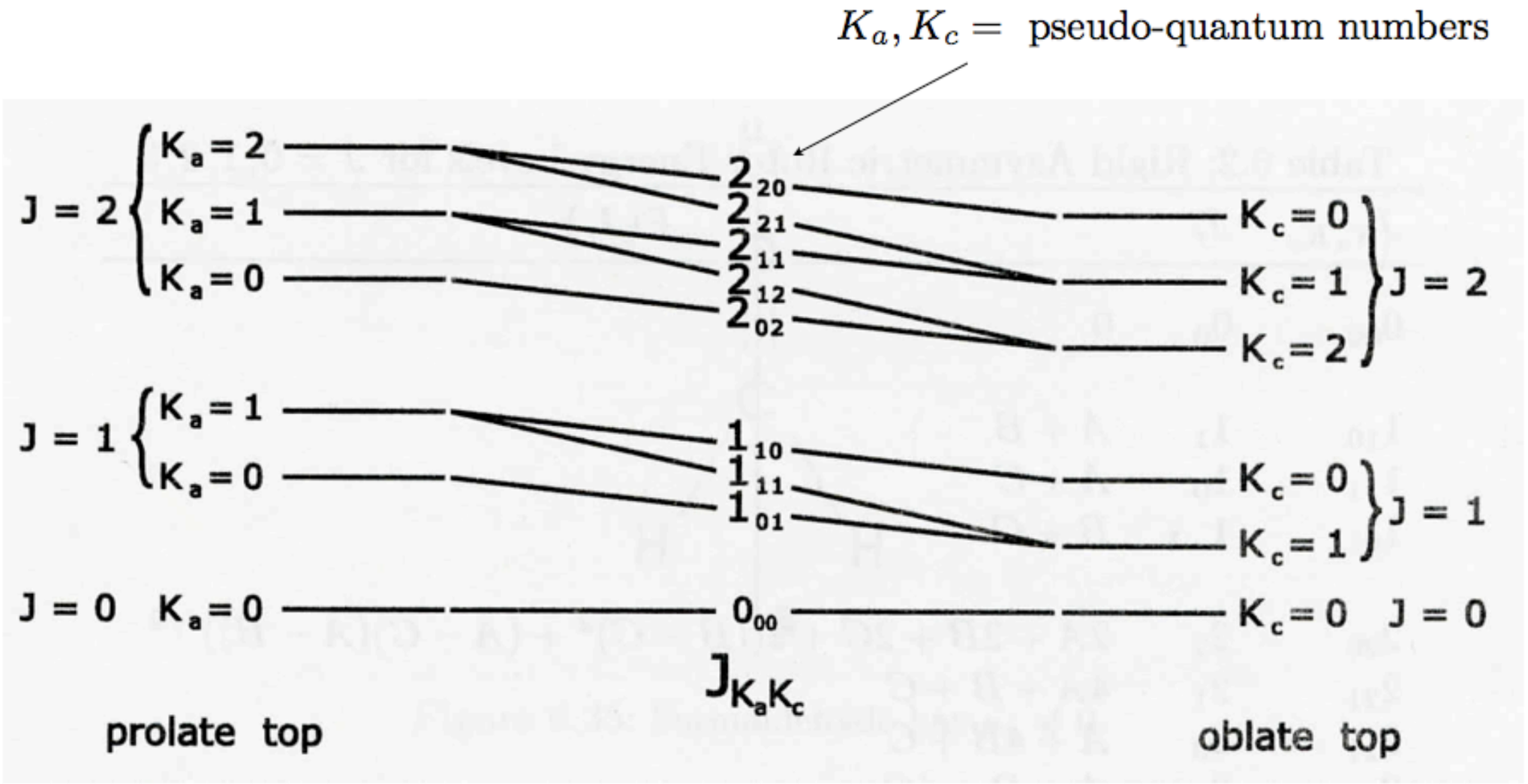


Before — *Oblate symmetric top*

After diagonalisation — *Asymmetric top*

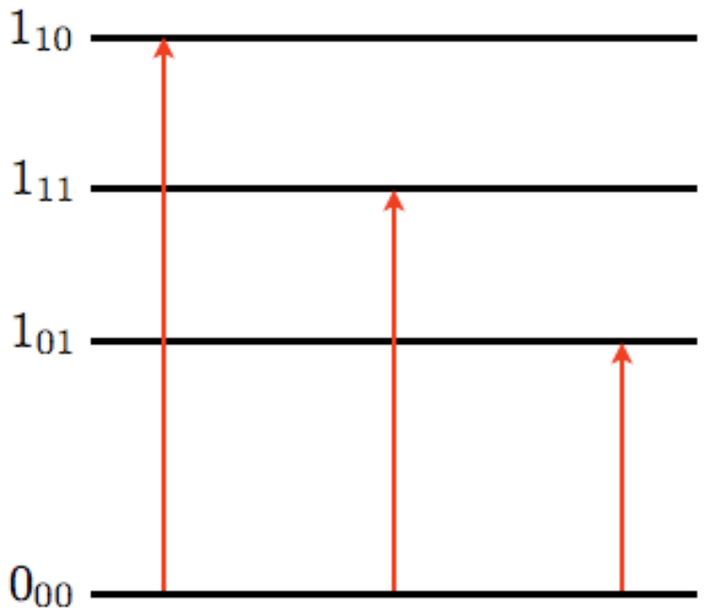
Splitting ↗ when J ↗ or K ↘

Levels of asymmetric tops



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

Asymmetric top: rotational transitions



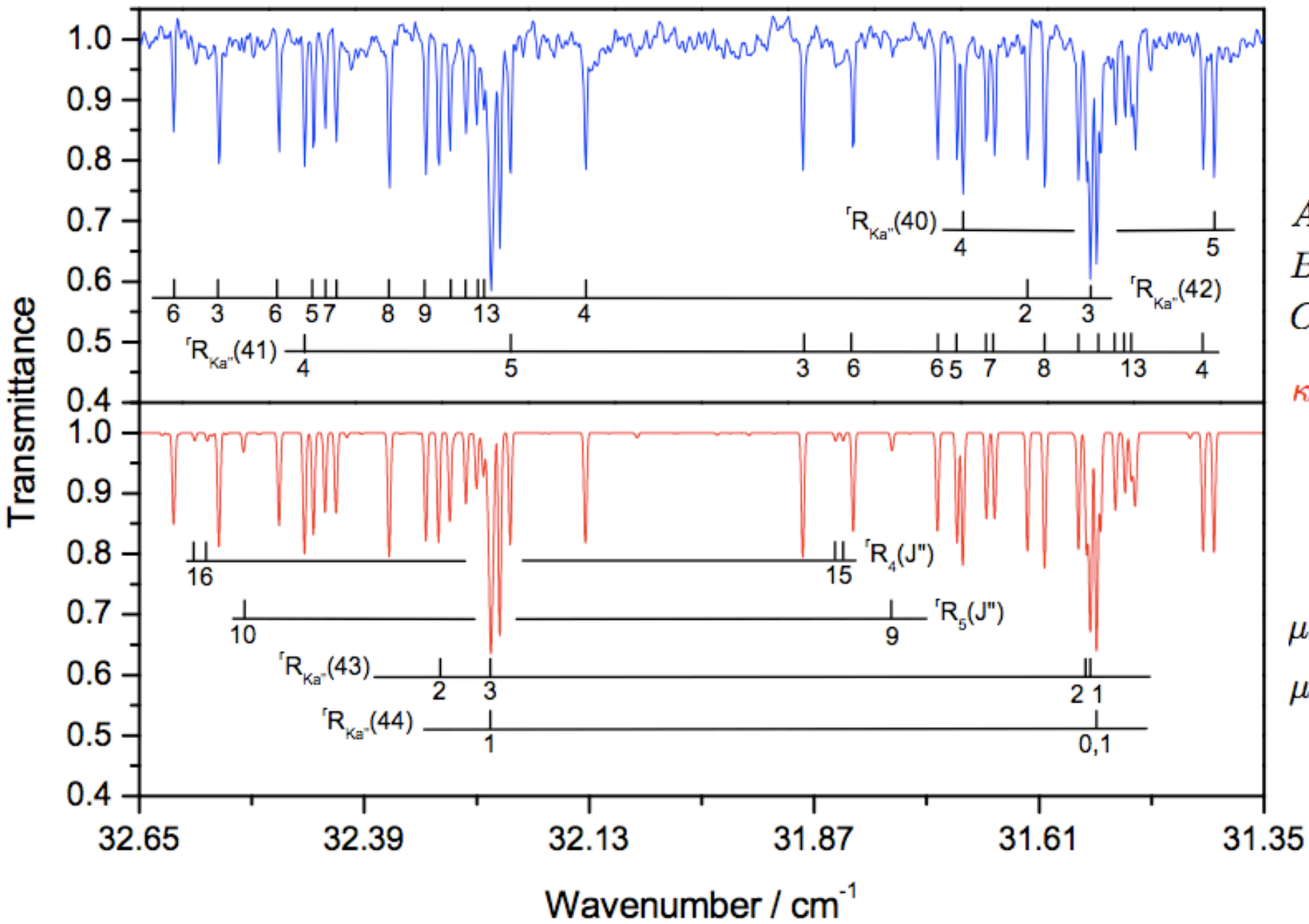
c-type ($\mu_c \neq 0$) : $\Delta K_a = \text{odd}, \Delta K_c = \text{even}$

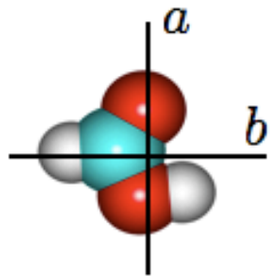
b-type ($\mu_b \neq 0$) : $\Delta K_a = \text{odd}, \Delta K_c = \text{odd}$

a-type ($\mu_a \neq 0$) : $\Delta K_a = \text{even}, \Delta K_c = \text{odd}$

$\Delta J = 0, \pm 1$

Pure rotation spectrum of HCOOH





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

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

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

$\kappa = -0.951$

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

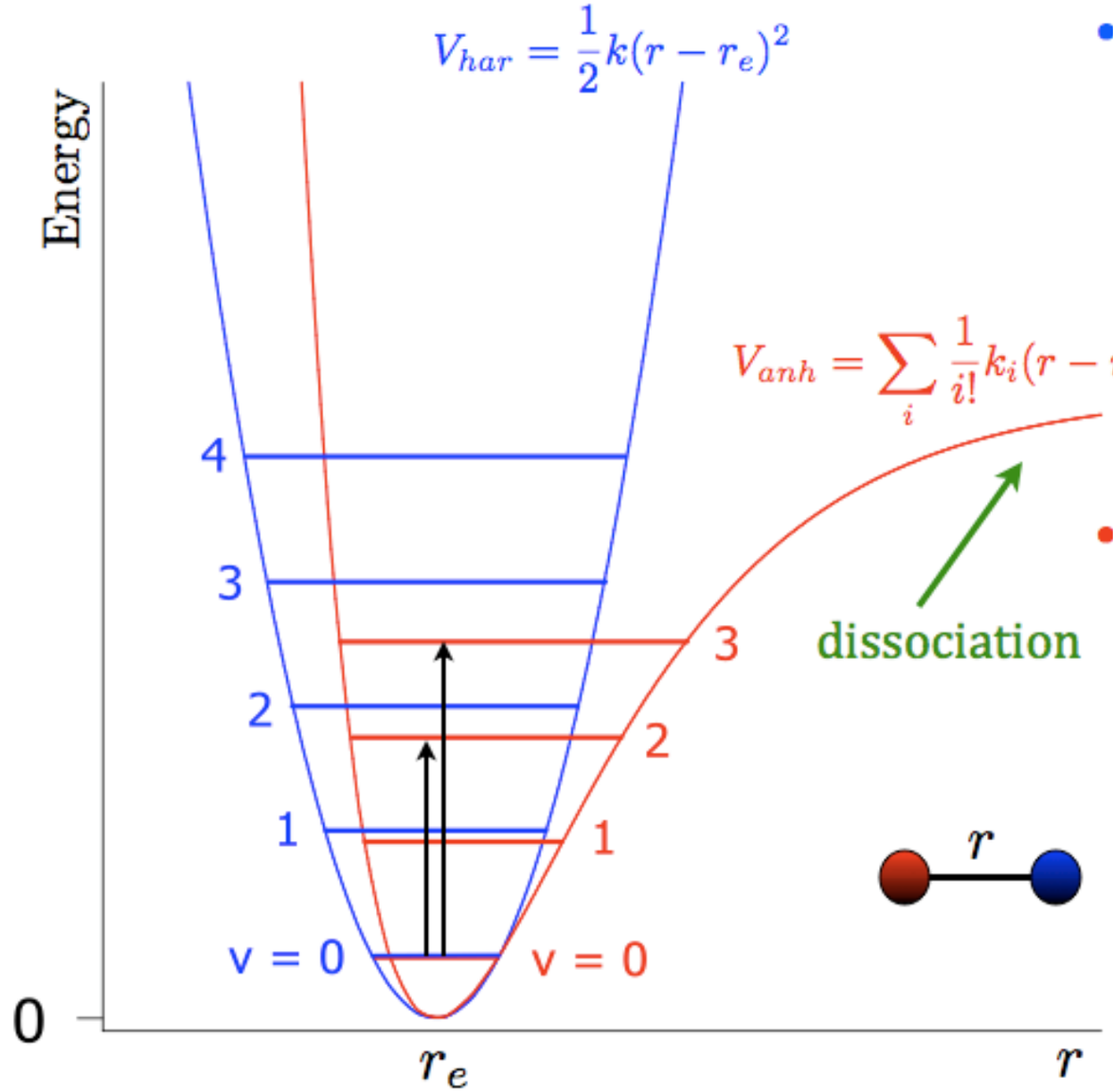
$\mu_b = 0.227\,(10)\ \mathrm{D}$

Principes de la spectroscopie

Molecular *physics – Vibration*

Molecular vibration : diatomic molecule

Linear molecule : 3N–5 degrees of freedom



- **Harmonic oscillator :**

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

$$k = \frac{d^2V}{dr^2}$$

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

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

- **Anharmonic oscillator :**

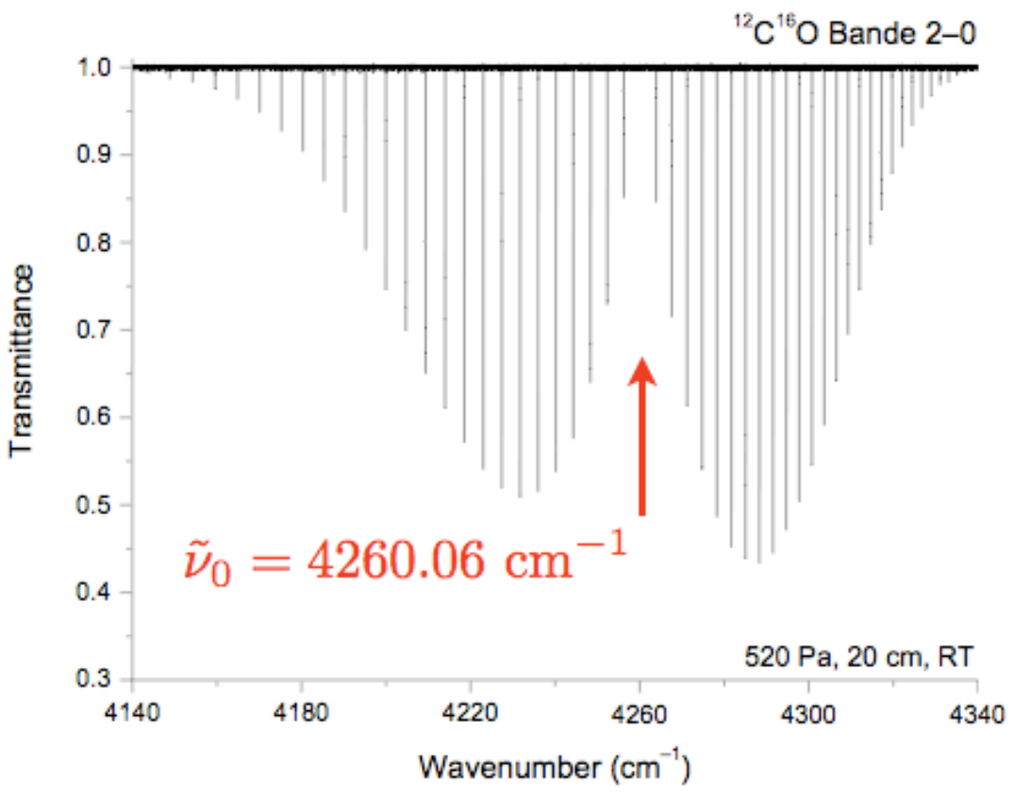
$$E_v = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \ldots$$

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

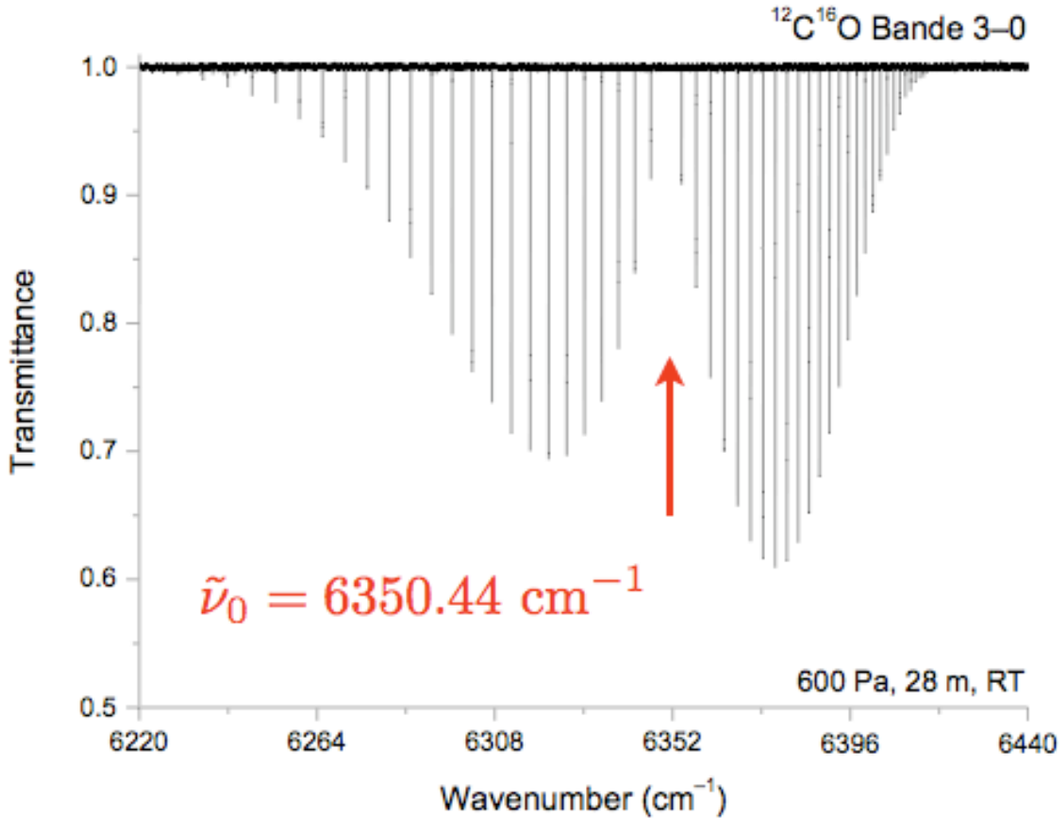
Force constants : $k_n = \frac{d^nV}{dr^n}$

Vibrational bands of carbon monoxide

First overtone ($v = 0 \rightarrow v = 2$)



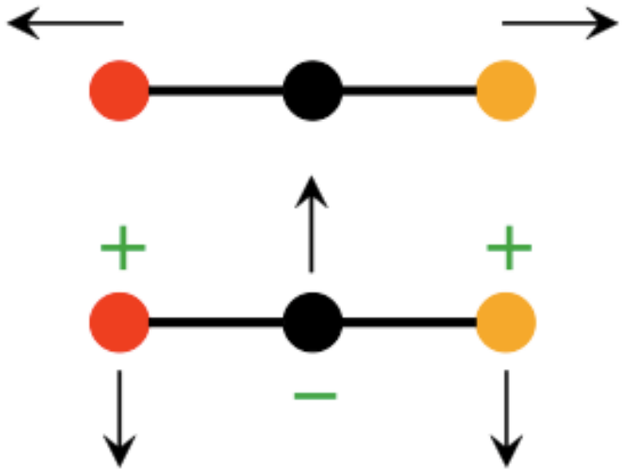
Second overtone ($v = 0 \rightarrow v = 3$)



$$\tilde{\nu}_0 = \omega_e\, v' - \omega_e x_e\, v'(v'+1) \quad \Rightarrow \quad \omega_e = 2169.73\ \mathrm{cm}^{-1}, \quad \omega_e x_e = 13.2\ \mathrm{cm}^{-1}$$

Vibration of triatomic linear molecules

Carbonyl sulfide OCS (4 vibrational degrees of freedom)

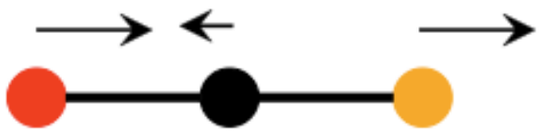


ν_1 (Q_1)

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

ν_2 (Q_2)

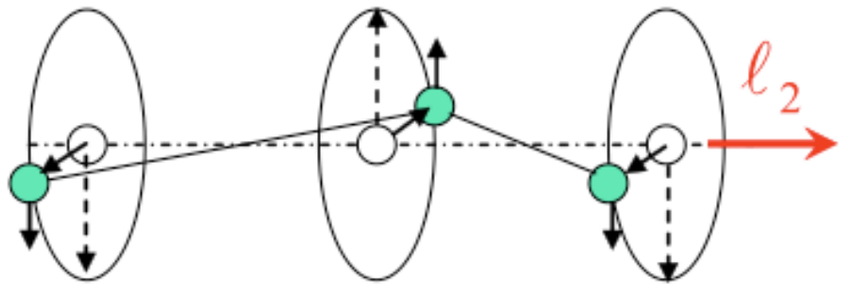
$\omega_2 = 520\ \mathrm{cm}^{-1}$



ν_3 (Q_3)

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

doubly degenerate vibration



Vib. angular momentum:

$\ell_2 = v_2, v_2-2, \ldots, 1 \text{ or } 0$

Energy :

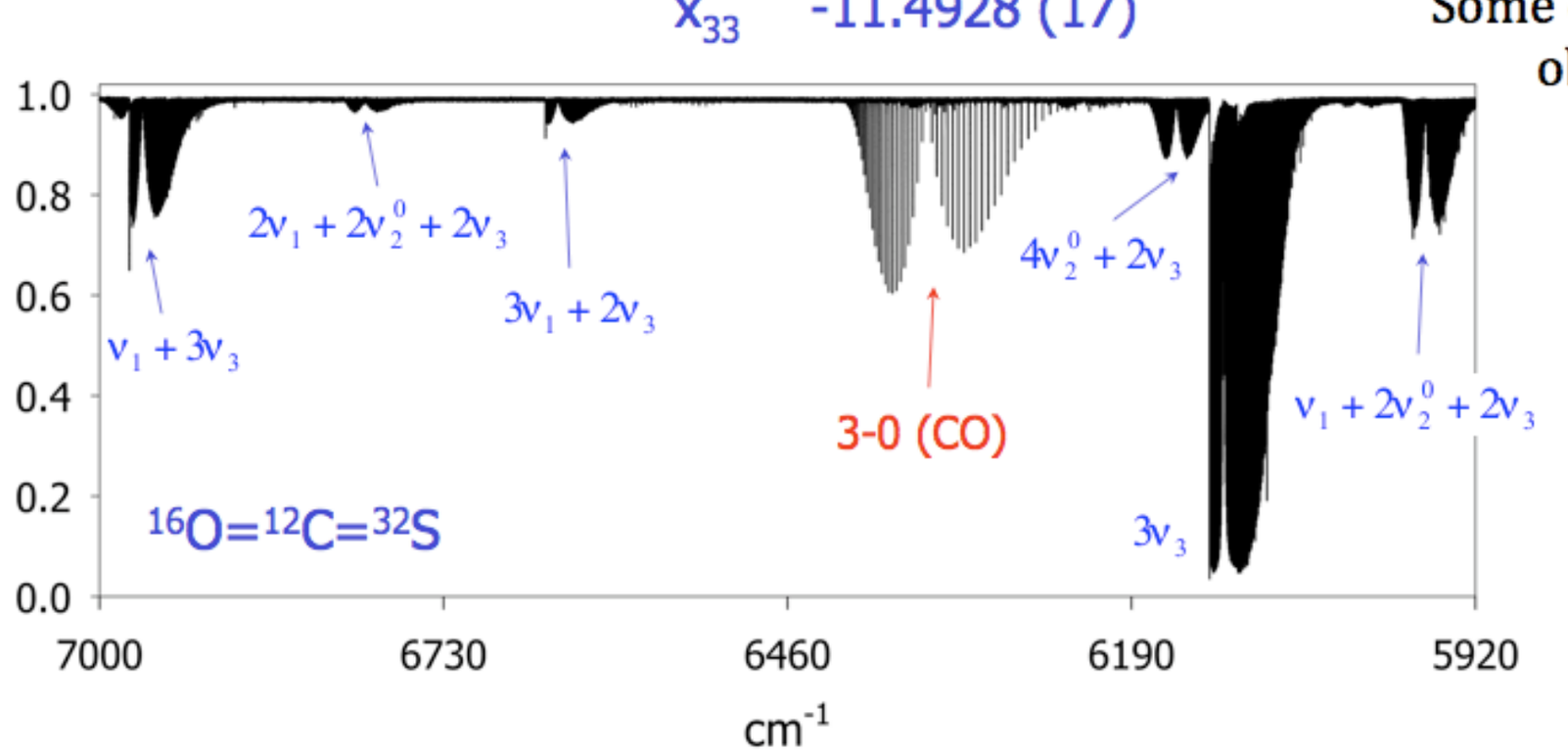
$$G_0(v_1 v_2 \ell_2 v_3) = E_v(v_1 v_2 \ell_2 v_3) - E_v(0) = \sum_{i=1}^{2N-3} \omega_i^0 v_i + \sum_{i \le j=1}^{2N-3} x_{ij}^0 v_i v_j + g_{22}^0 \ell_2^2 + \ldots - B_v \ell_2^2$$

Included in the rotational part of the energy

Vibrational spectroscopy of OCS

ω_1	866.7001	(24)	x_{11}	-3.4060	(19)
ω_2	520.197058	(11)	x_{12}	-3.2672	(30)
ω_3	2072.8173	(31)	x_{22}	0.60713	(55)
			x_{13}	-3.1944	(53)
g_{22}	-0.17884	(55)	x_{23}	-7.5074	(20)
			x_{33}	-11.4928	(17)

(all values are in cm^{-1}, superscript "0" omitted)



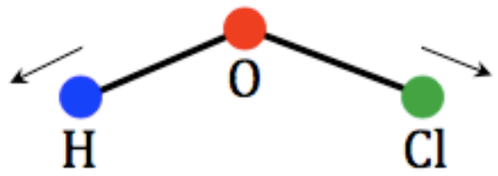
Some combination bands observed in the near infrared

$$\Delta\ell_2 = 0, \pm 1$$

Vibration of non-linear molecules

- Normal modes of vibration of **HOCl** (C_s) :
  (**3** vibrational degrees of freedom)

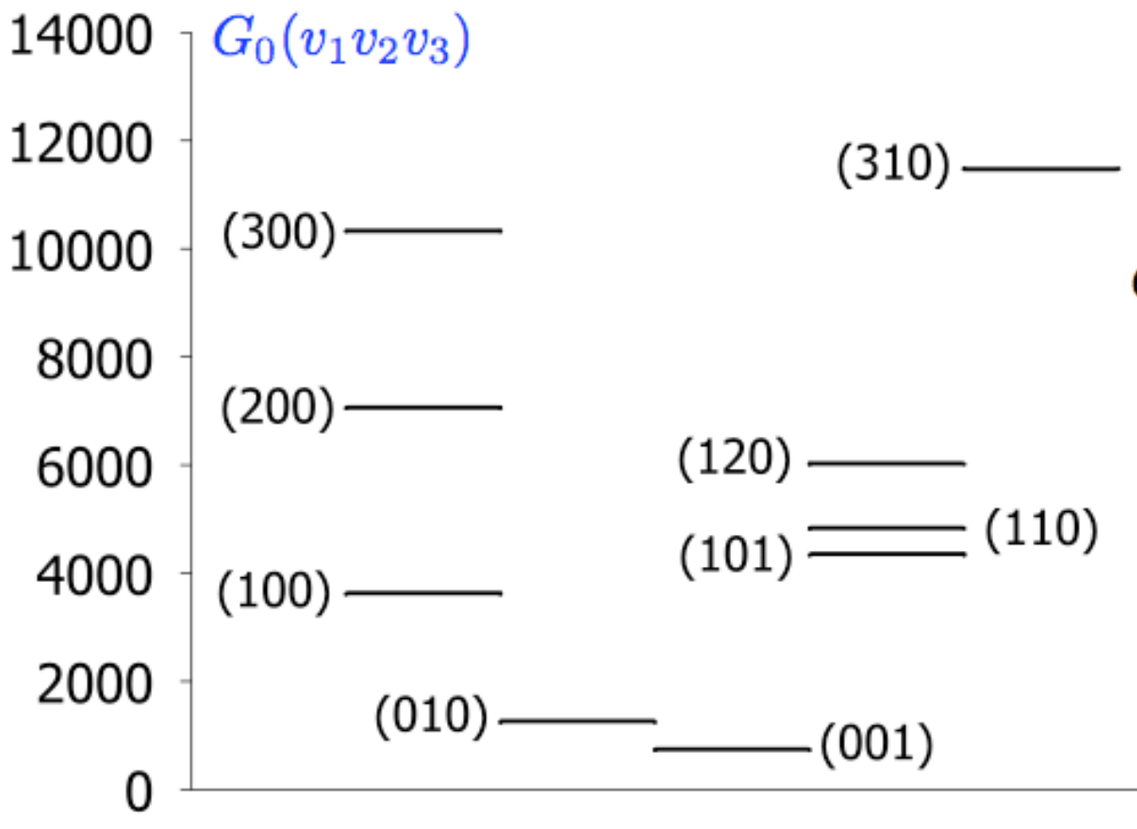
ω_1 = 3609 cm^{-1}



ω_2 = 1238 cm^{-1}

ω_3 = 724 cm^{-1}

- Vibrational energy levels of **HO^{35}Cl** :

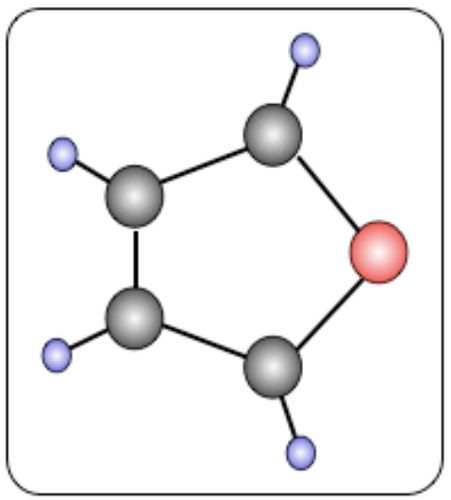


$$G_0(v_1v_2v_3) = E_v(v_1v_2v_3) - E_v(000)$$

$$= \sum_{i=1}^{3} \omega_i^0 v_i + \sum_{i \le j} x_{ij}^0 v_i v_j + \ldots$$

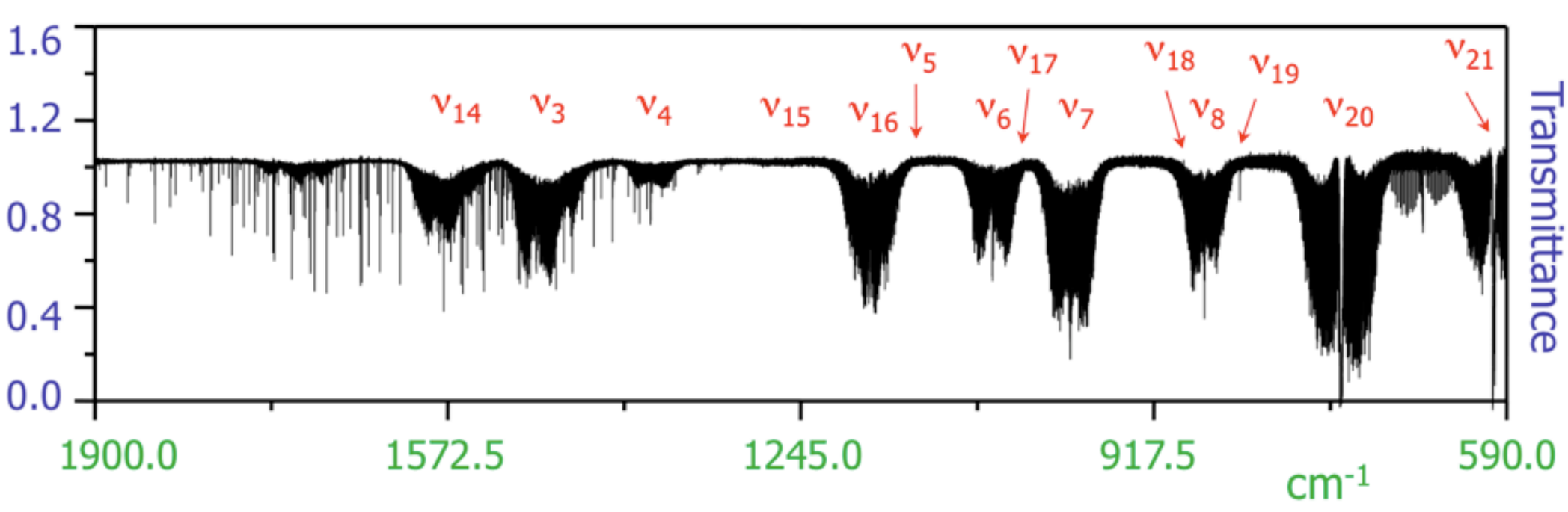
$G_0(000) = 0$

Fundamental bands of furane



C_4H_4O

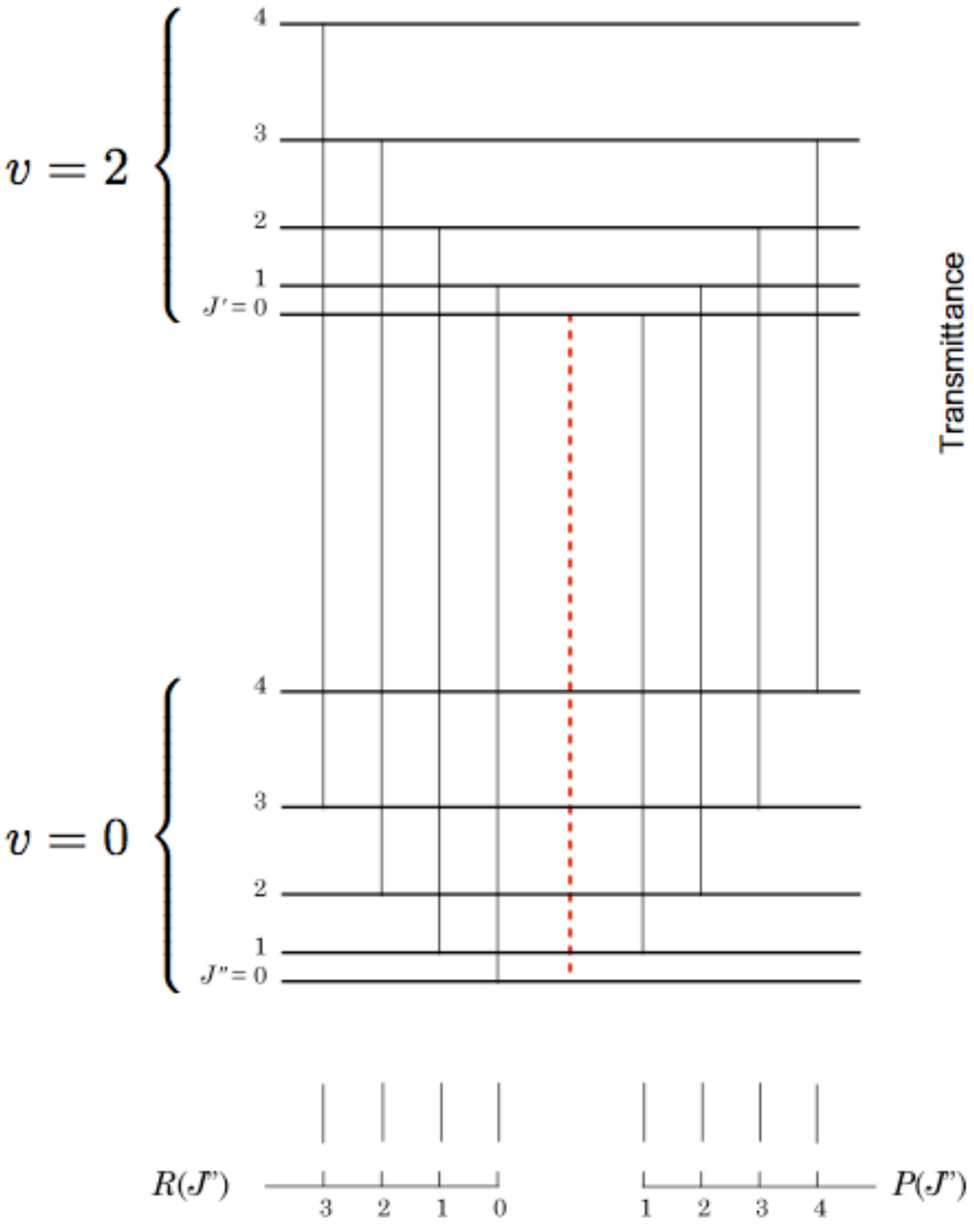
21 modes of vibration

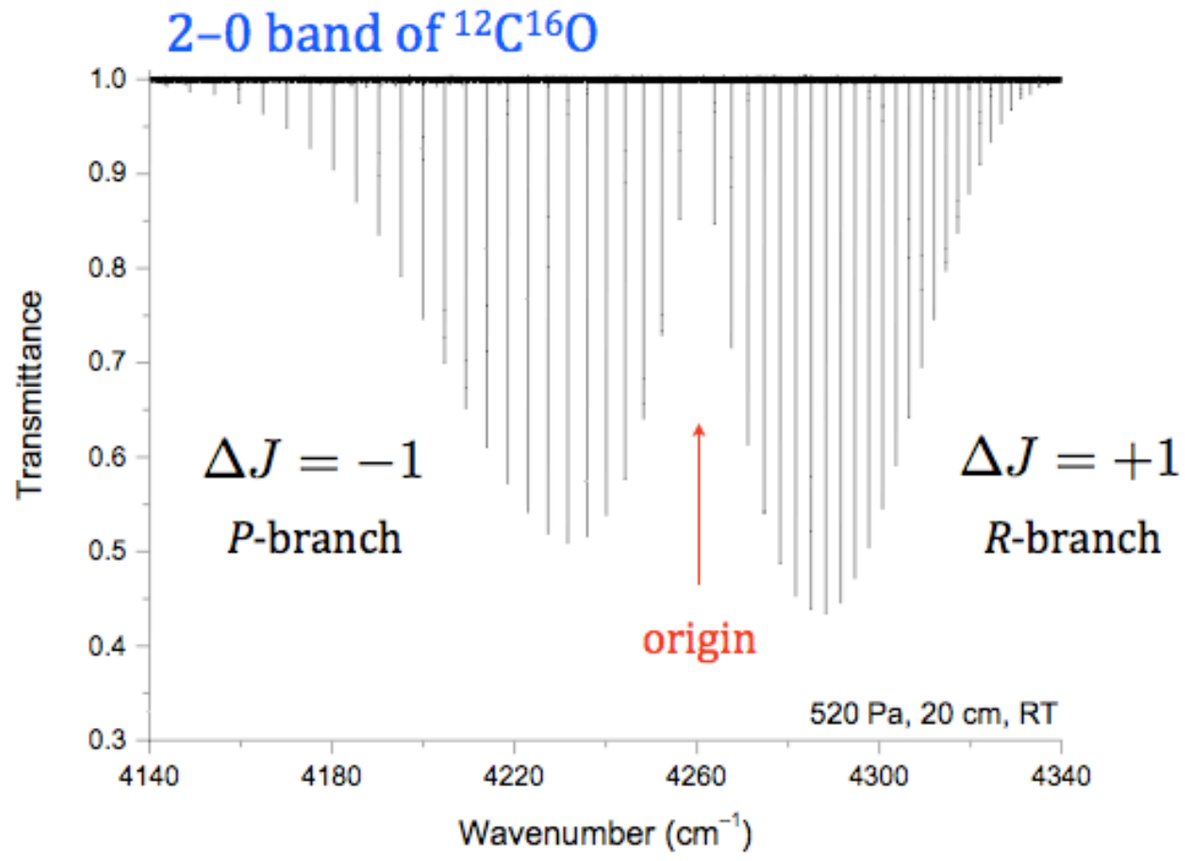


Principes de la spectroscopie

***Molecular** physics – Vibration-rotation transitions*

Rotational structure of a parallel band

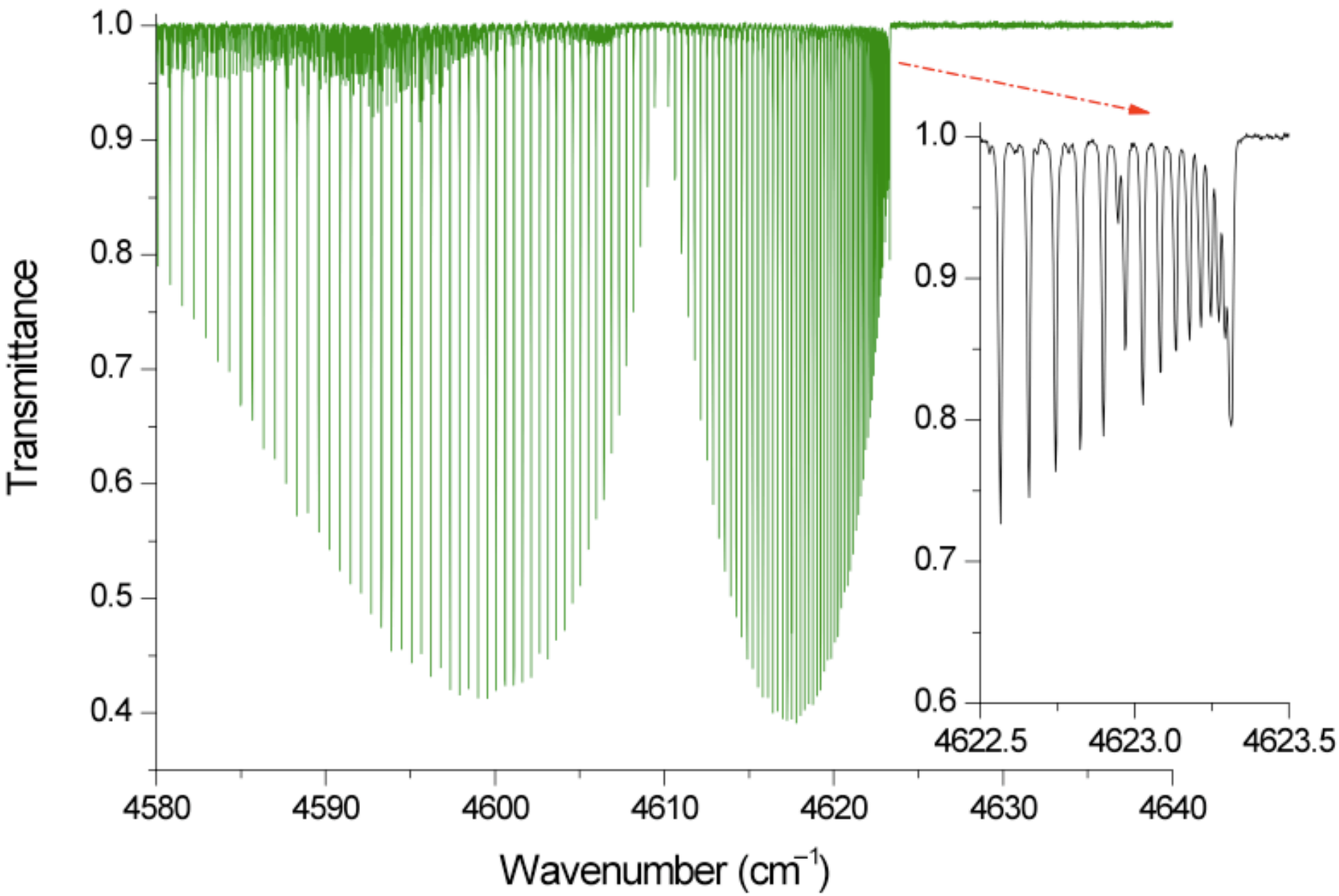




$$R(J) = E'_v - E''_v + E'_r(J+1) - E''_r(J)$$
$$= \tilde{\nu}_0 + B'_v(J+1)(J+2) - B''_v J(J+1)$$
$$= \tilde{\nu}_0 + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2$$

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

Band head

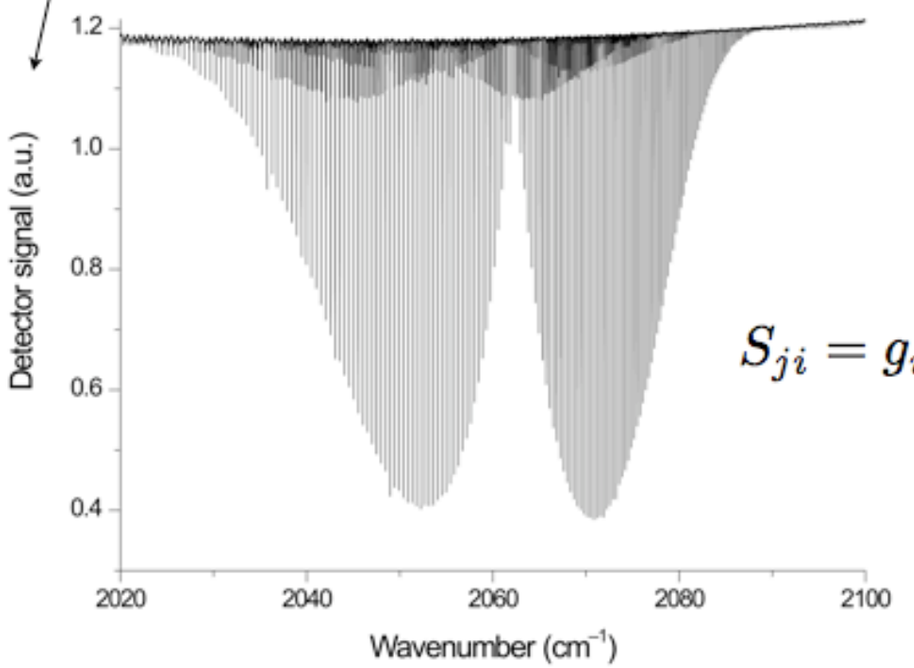


$$R(J) = \tilde{\nu}_0 + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2$$

Vibration-rotation intensities

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

$$I(\tilde{\nu}) = I_0(\tilde{\nu})\, e^{-N\,\ell\sum_k \sigma_k}$$



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

(isotropic space)

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

$$S_{ji} = g_i\, 3 \sum_\alpha \underline{|\langle\psi_r^j|\lambda_{\alpha Z}|\psi_r^i\rangle|^2} \left|\underline{\langle\psi_v^j|\sum_r Q_r\left(\frac{\partial\mu_\alpha}{\partial Q_r}\right)_{eq} + \ldots|\psi_v^i\rangle}\right|^2$$

$\equiv \mu_\alpha^{(v)}$

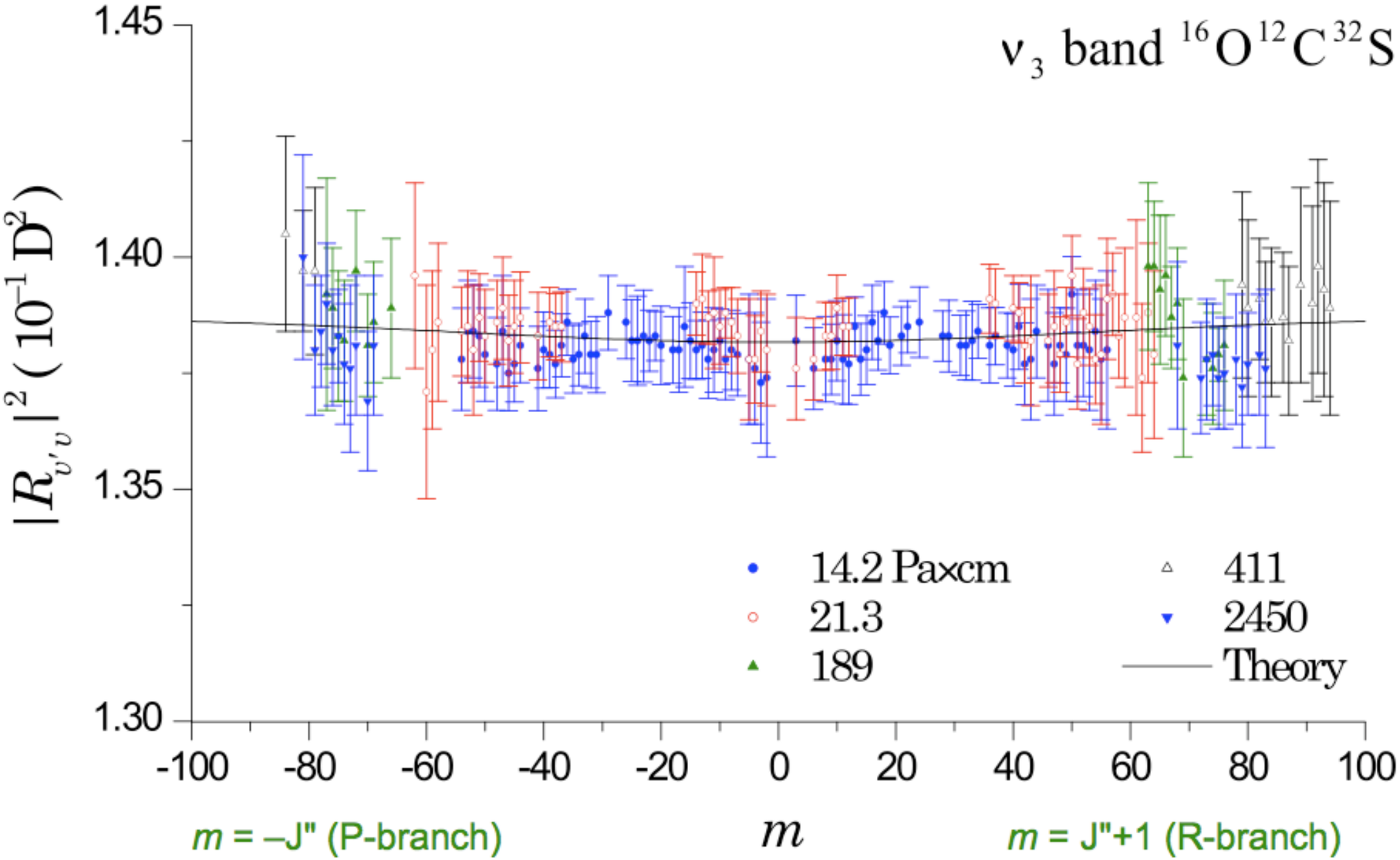
Hönl-London factor

vibronic transition moment $R_{v'v}$ ($\sum_\alpha$ included)

Band strength :

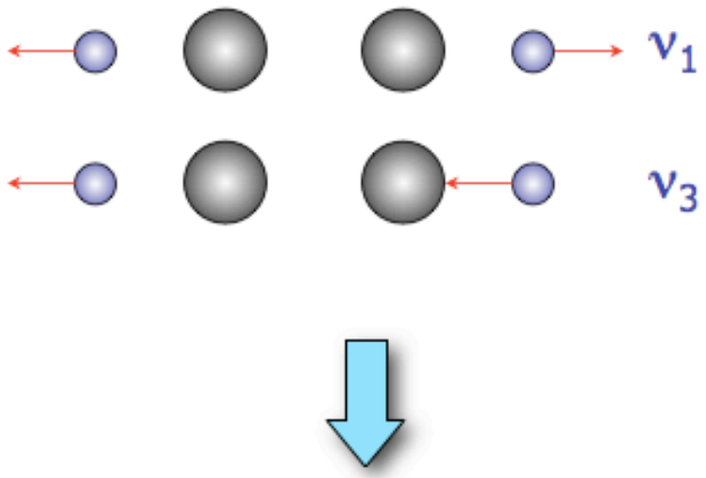
$$S_v = \sum_{\text{all lines}} \sigma_{ji} = \frac{8\pi^3}{3hc}\frac{1}{4\pi\epsilon_0}\frac{\tilde{\nu}_0}{Q_v(T)} I_a\, e^{-hcE_v/kT}\,|R_{v'v}|^2$$

Vibrational transition dipole moment

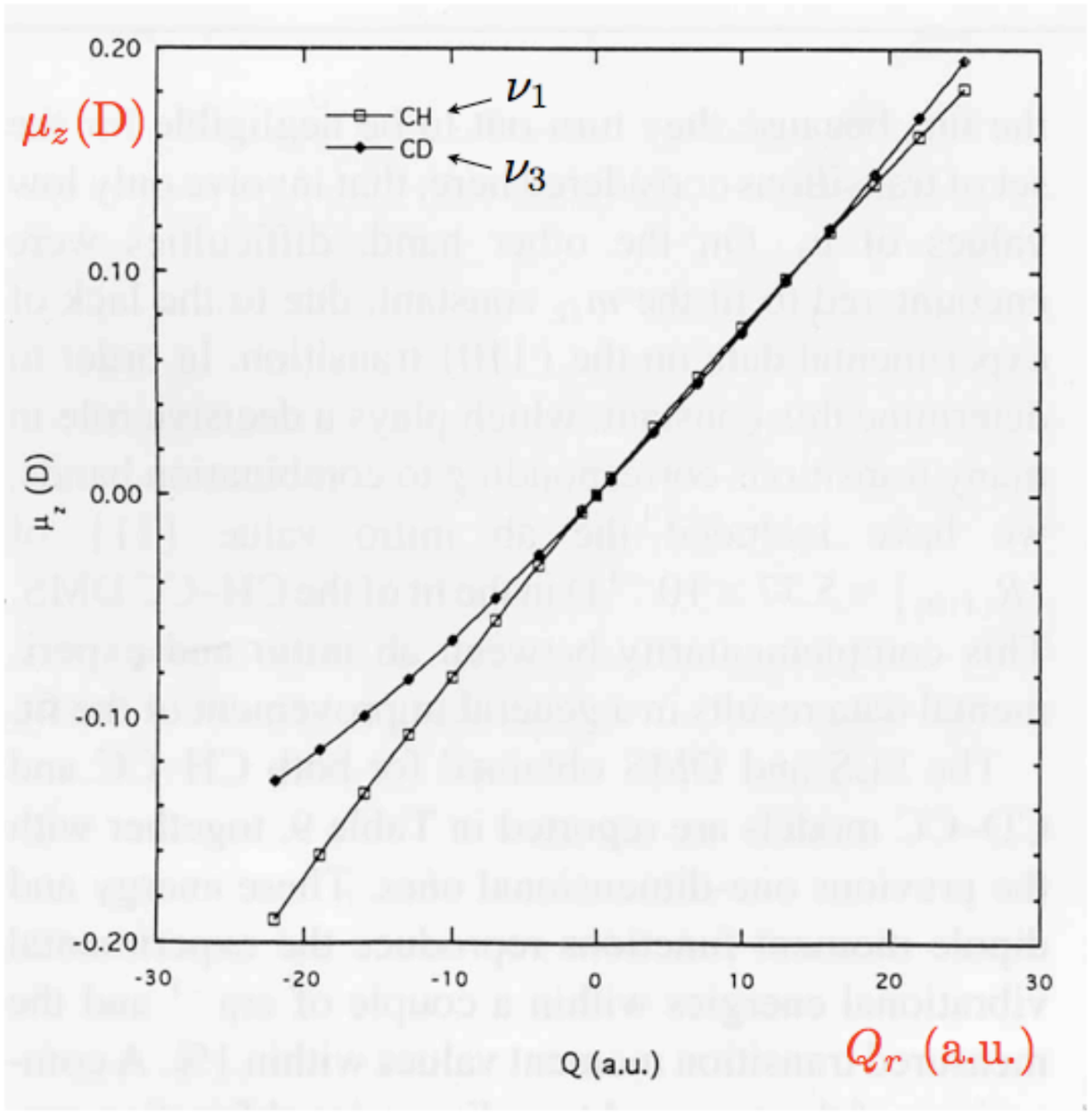


Vibrational motion and dipole moment

2 stretching modes of vibration of **C_2HD**

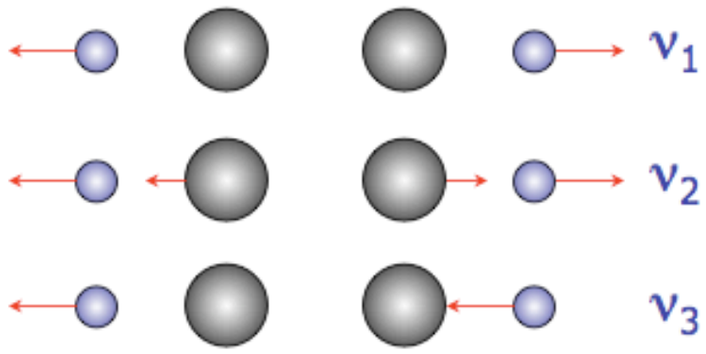


"Parallel" bands (transitions)

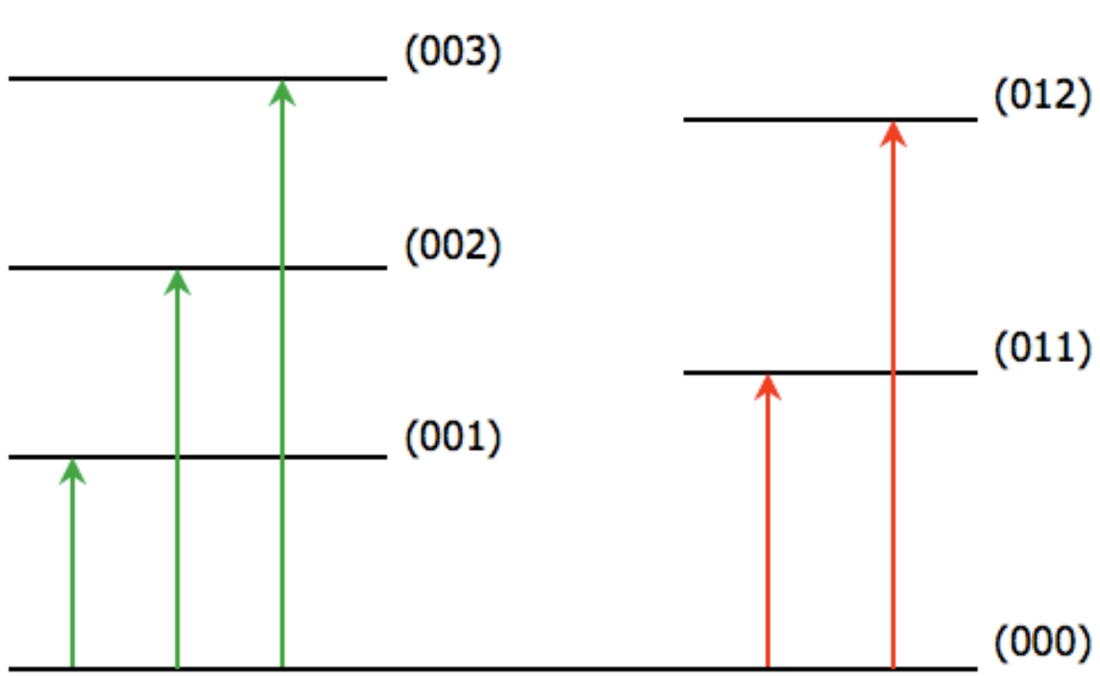


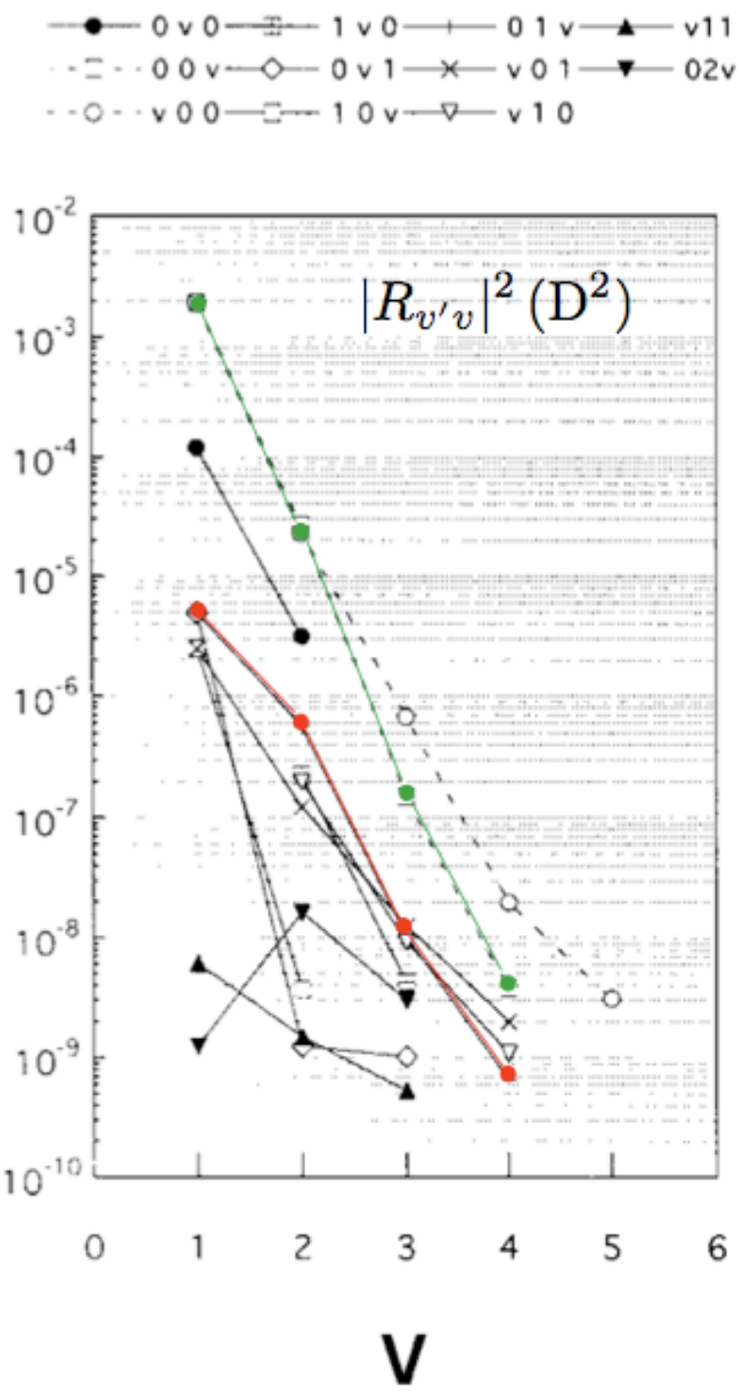
Band intensities

Transitions in C_2HD (stretching vibrations)



$(\nu_1\nu_2\nu_3)$



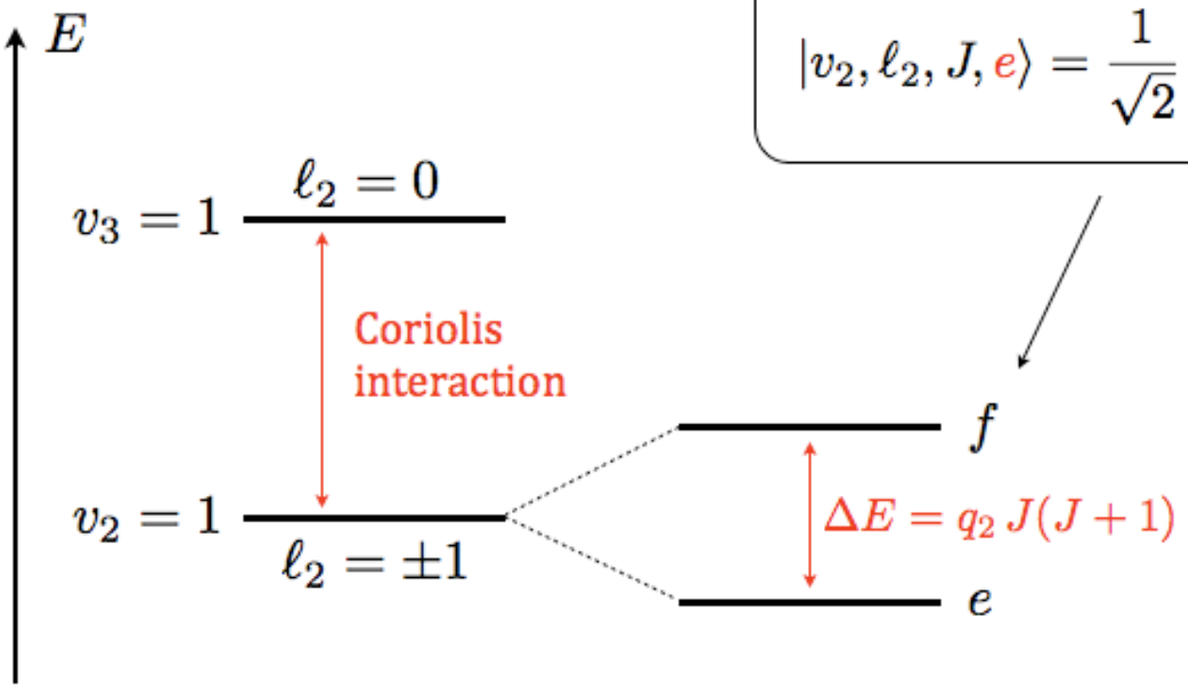


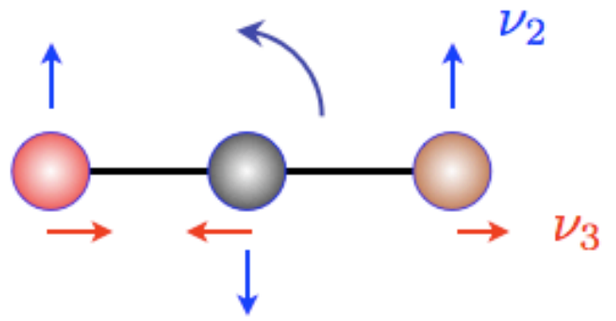
Vibration-rotation interaction

ℓ-doubling in linear (triatomic) molecules

$$|v_2, \ell_2, J, f\rangle = \frac{1}{\sqrt{2}}\left[|v_2, \ell_2, J\rangle - (-1)^{\ell_2}|v_2, -\ell_2, J\rangle\right]$$

$$|v_2, \ell_2, J, e\rangle = \frac{1}{\sqrt{2}}\left[|v_2, \ell_2, J\rangle + (-1)^{\ell_2}|v_2, -\ell_2, J\rangle\right]$$

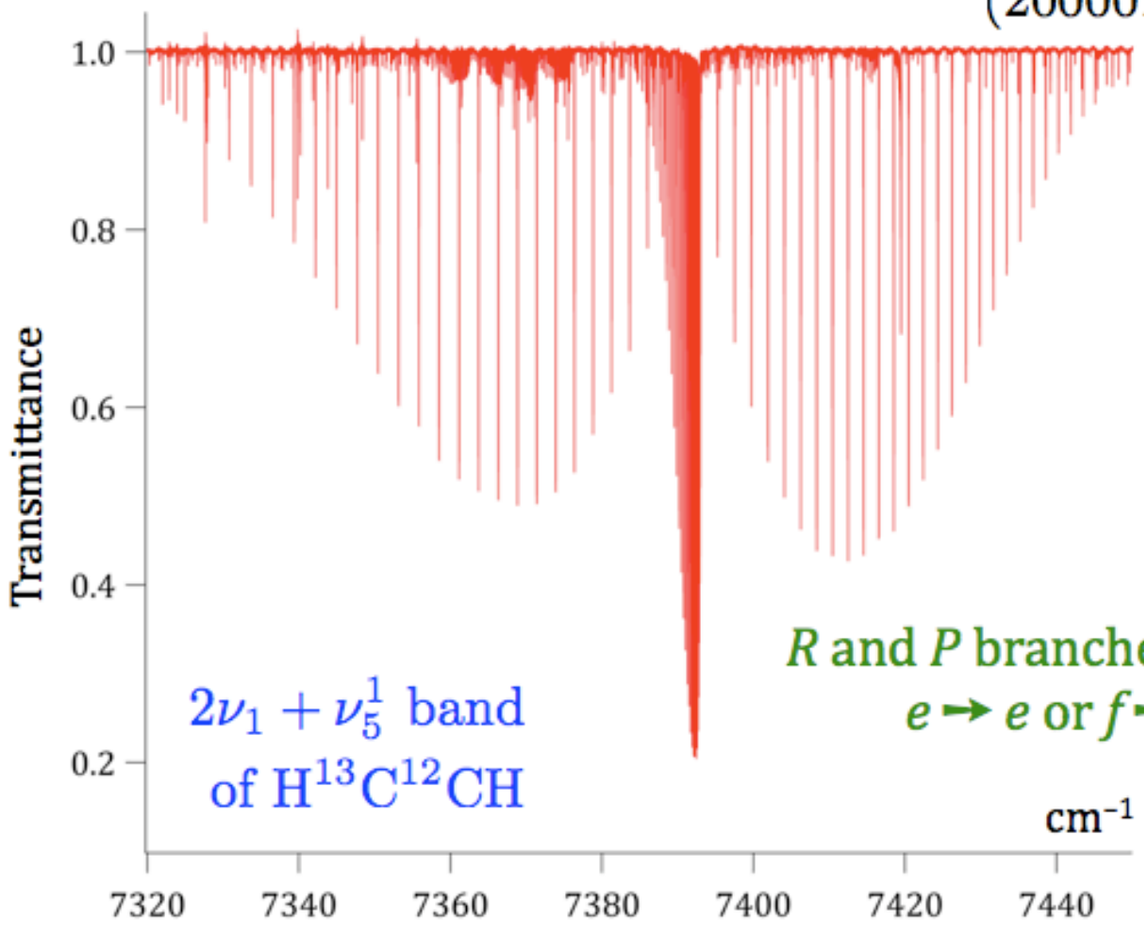




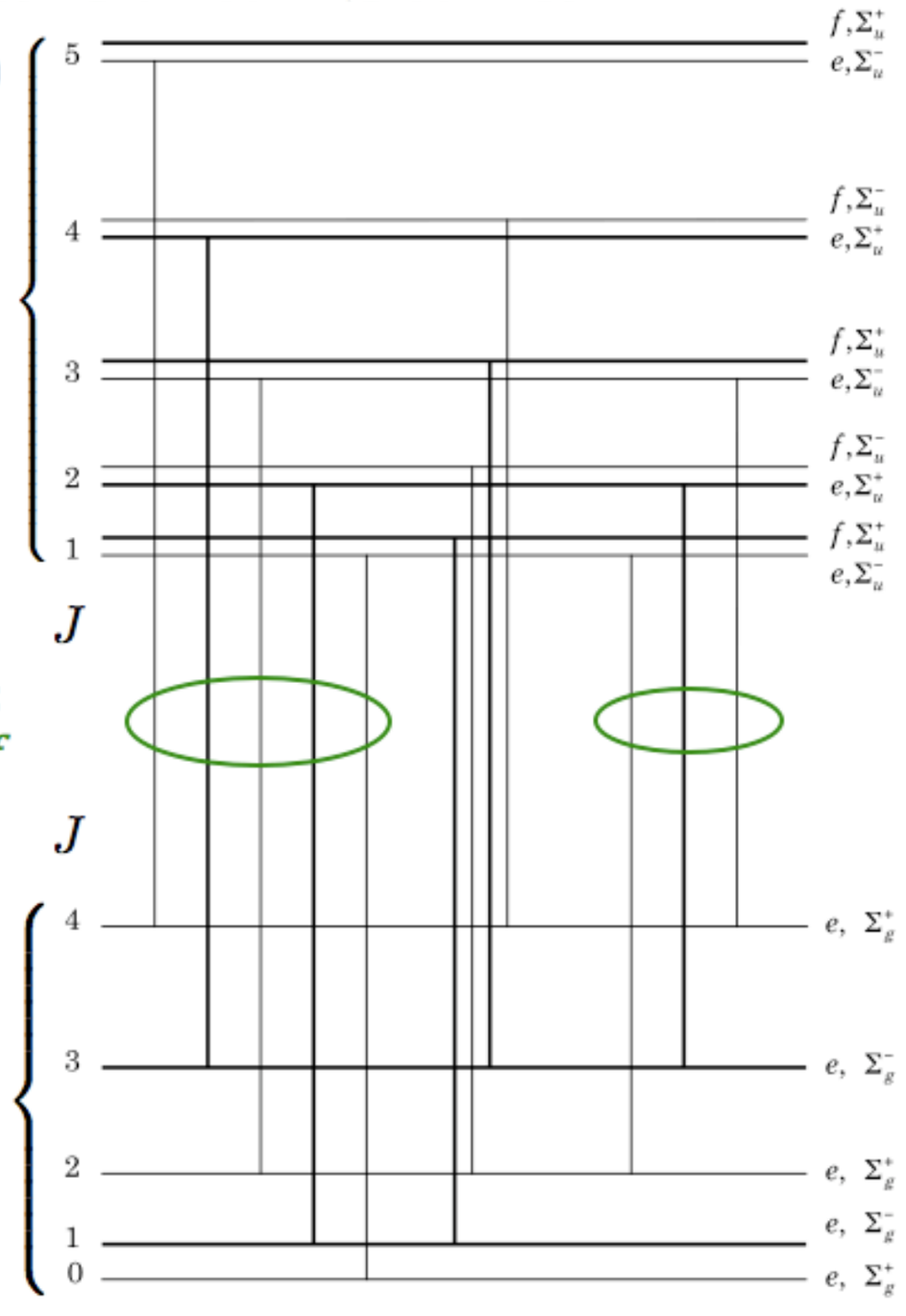
$q_2 \approx 0.001$ cm^{-1} (N_2O)

Before After diagonalisation

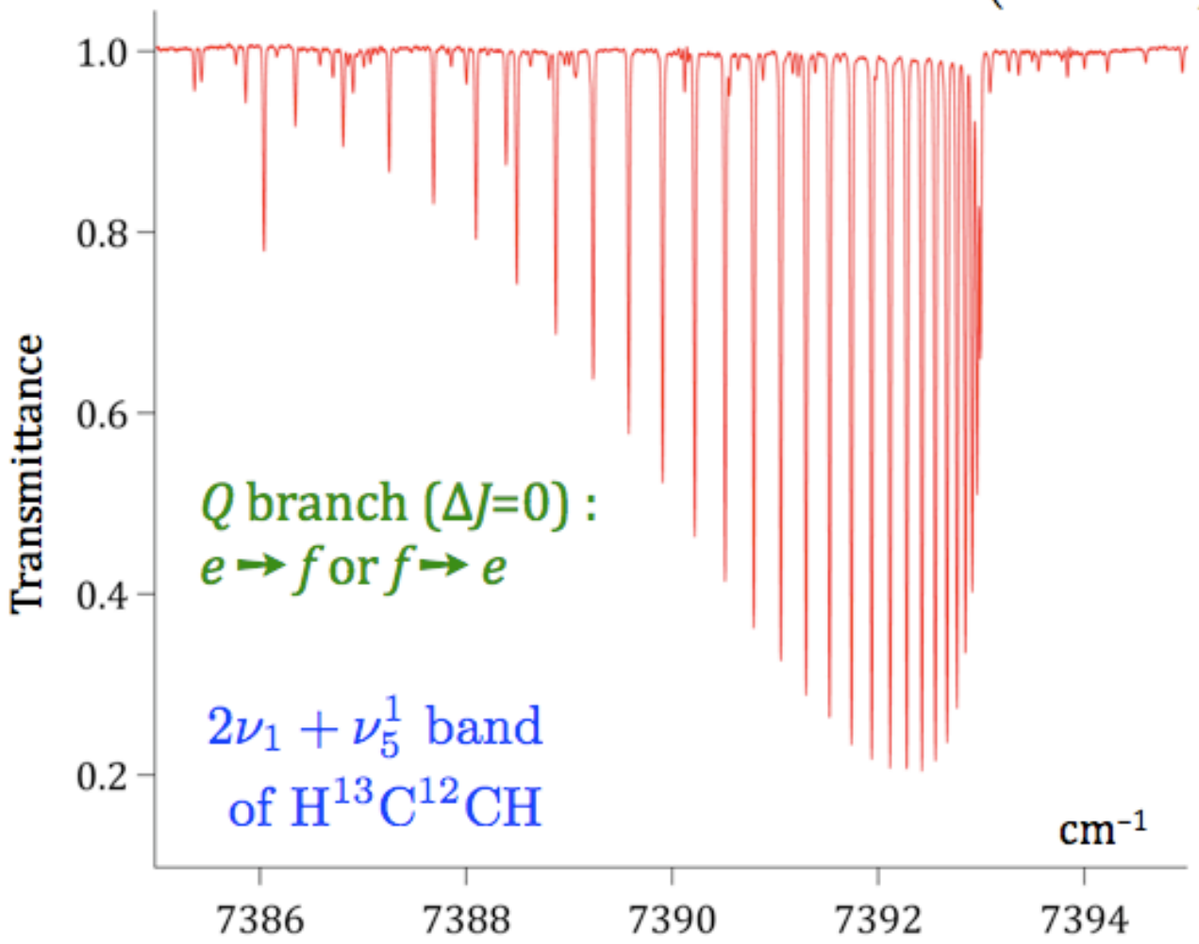
Structure of a perpendicular band



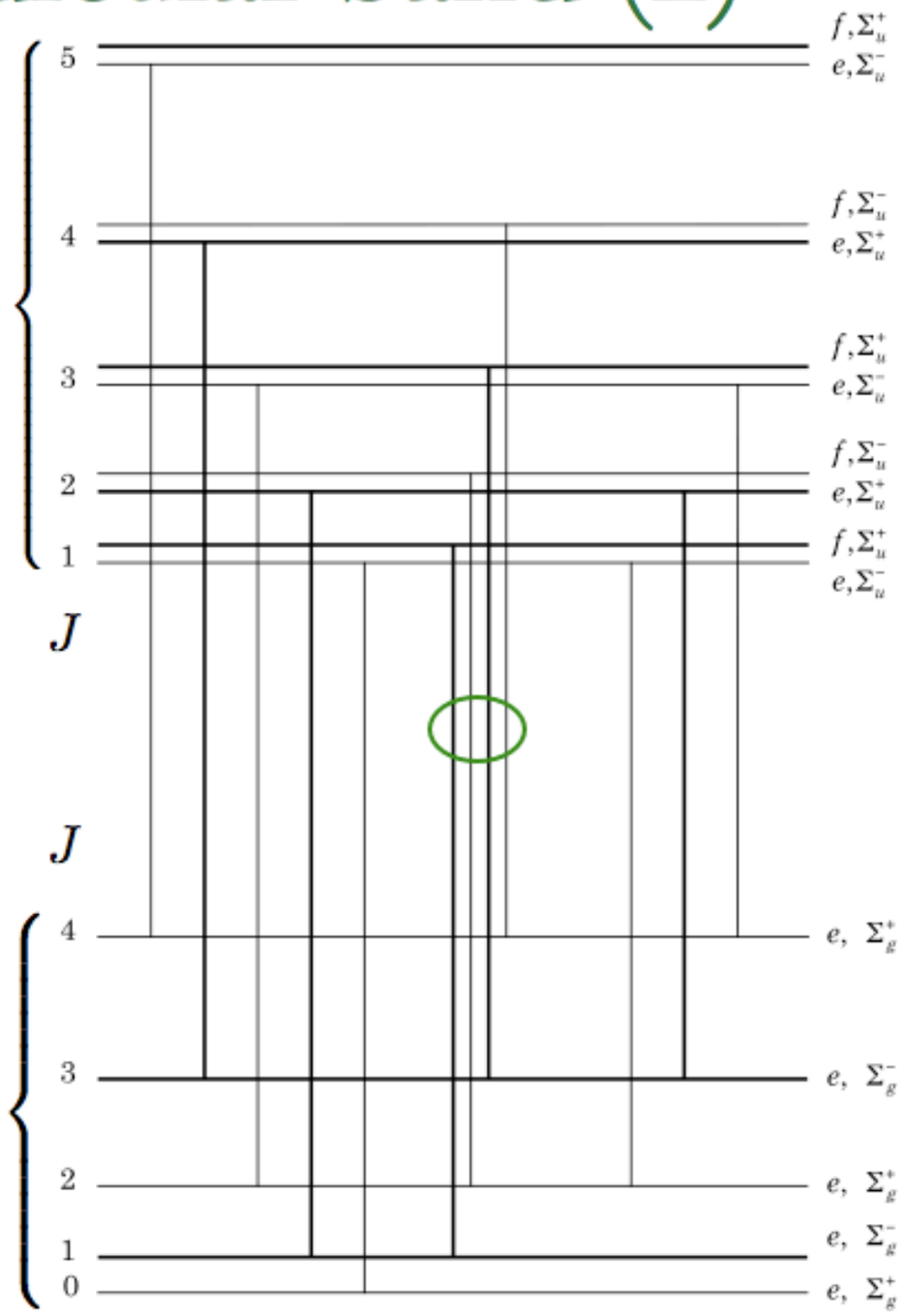
R and *P* branches :
$e \rightarrow e$ or $f \rightarrow f$



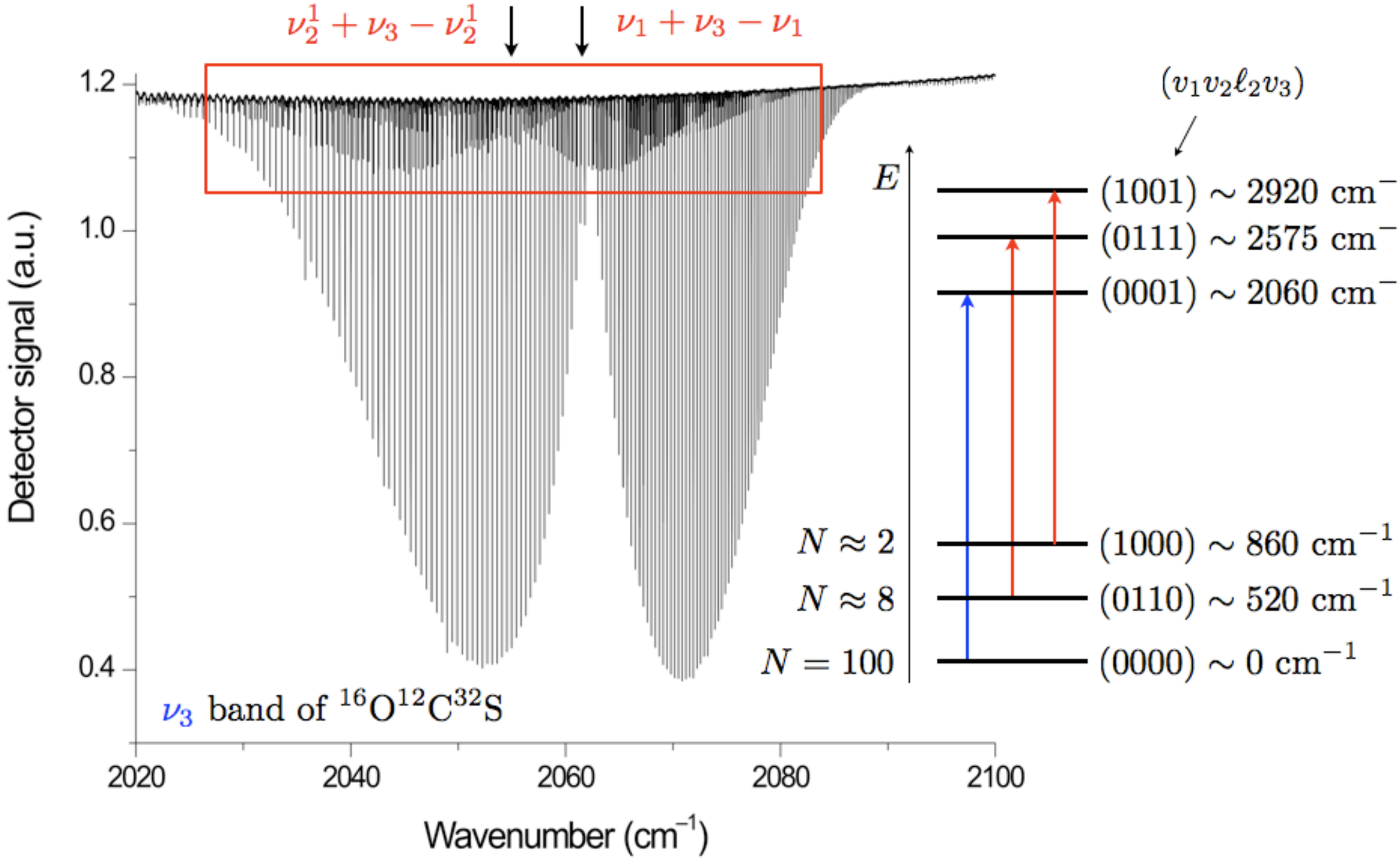
Structure of a perpendicular band (2)



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

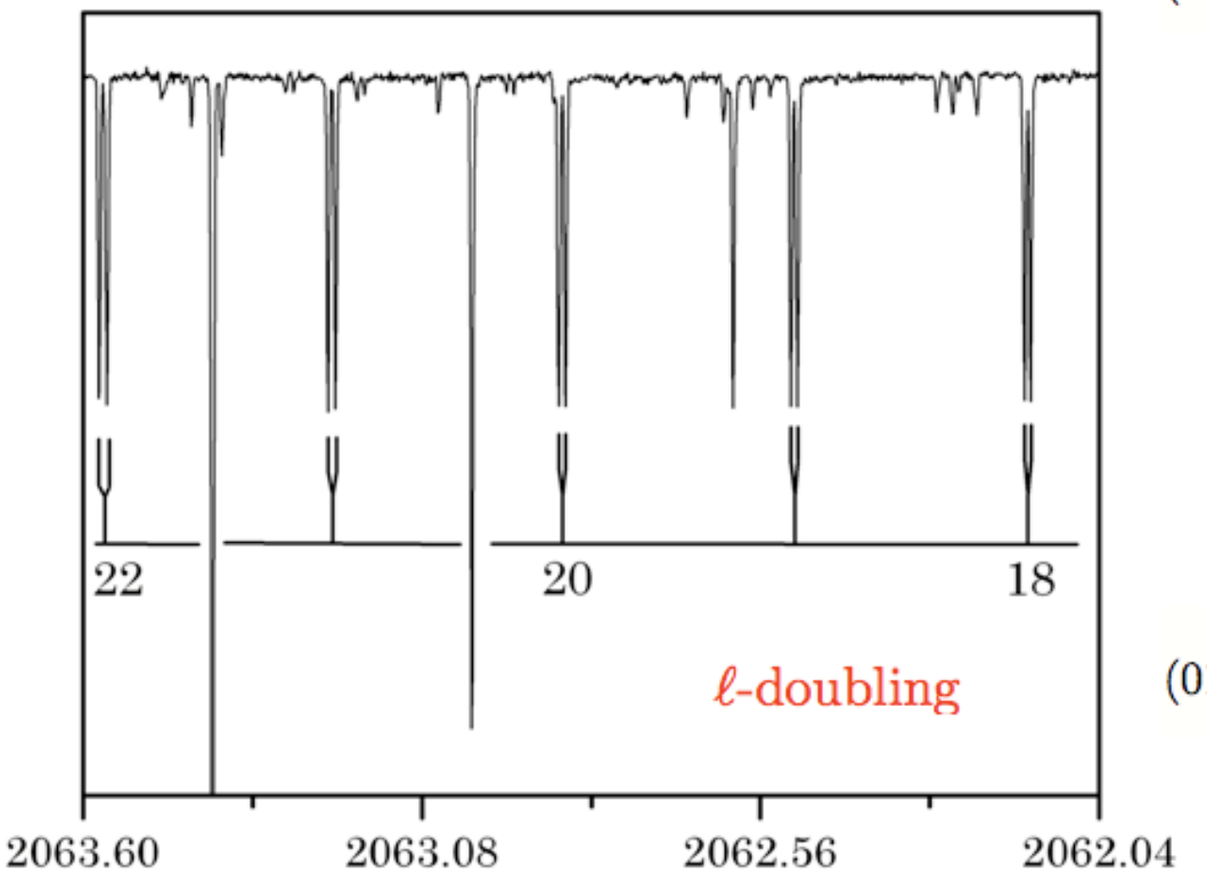


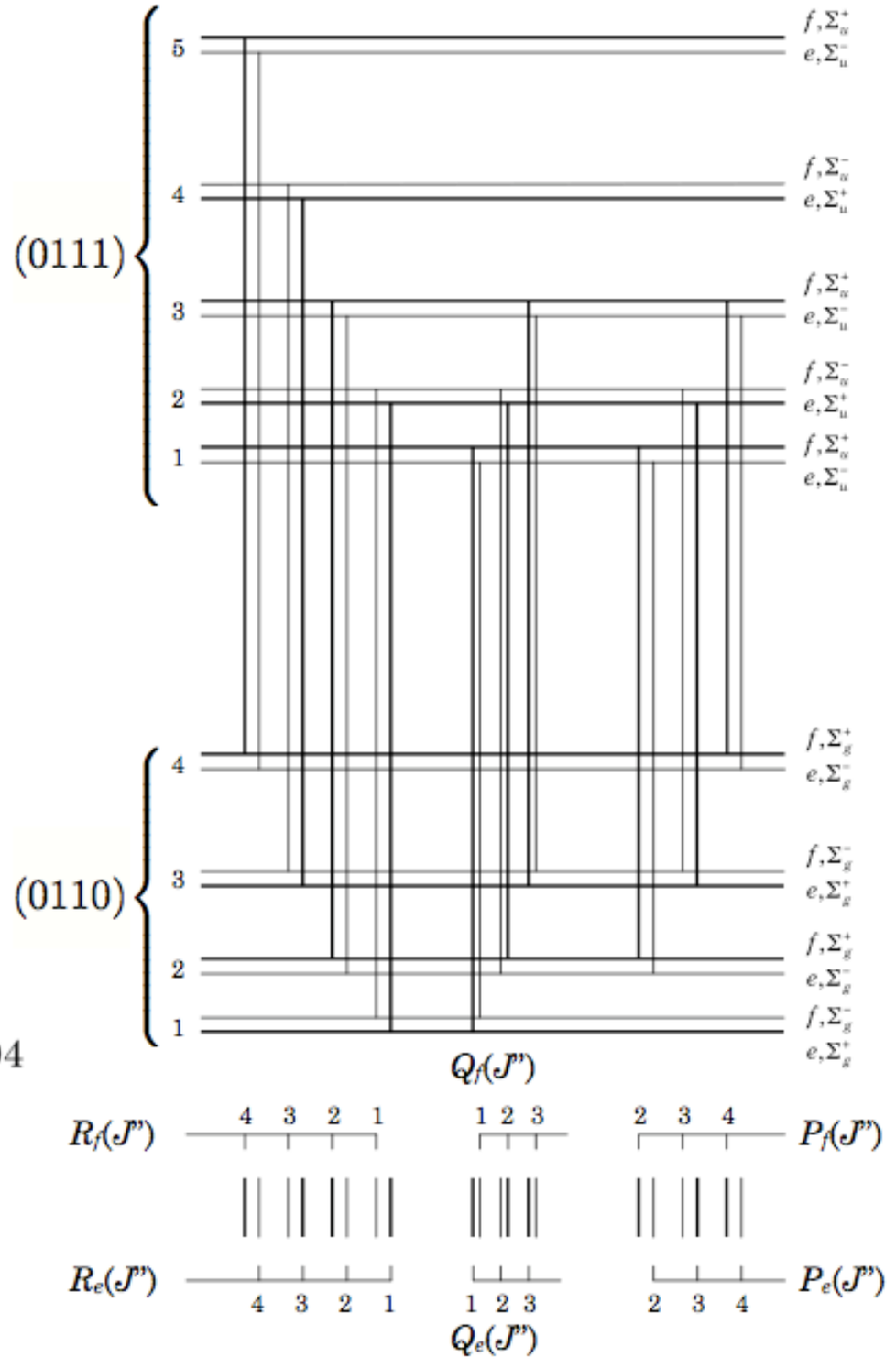
Hot bands


$\nu_2^1 + \nu_3 - \nu_2^1$
$\nu_1 + \nu_3 - \nu_1$
Detector signal (a.u.)
1.2
1.0
0.8
0.6
0.4
ν_3 band of $^{16}O^{12}C^{32}S$
2020
2040
2060
2080
2100
Wavenumber (cm^{-1})
$(v_1 v_2 \ell_2 v_3)$
E
$(1001) \sim 2920$ cm^{-1}
$(0111) \sim 2575$ cm^{-1}
$(0001) \sim 2060$ cm^{-1}
$N \approx 2$
$N \approx 8$
$N = 100$
$(1000) \sim 860$ cm^{-1}
$(0110) \sim 520$ cm^{-1}
$(0000) \sim 0$ cm^{-1}

Hot bands (2)

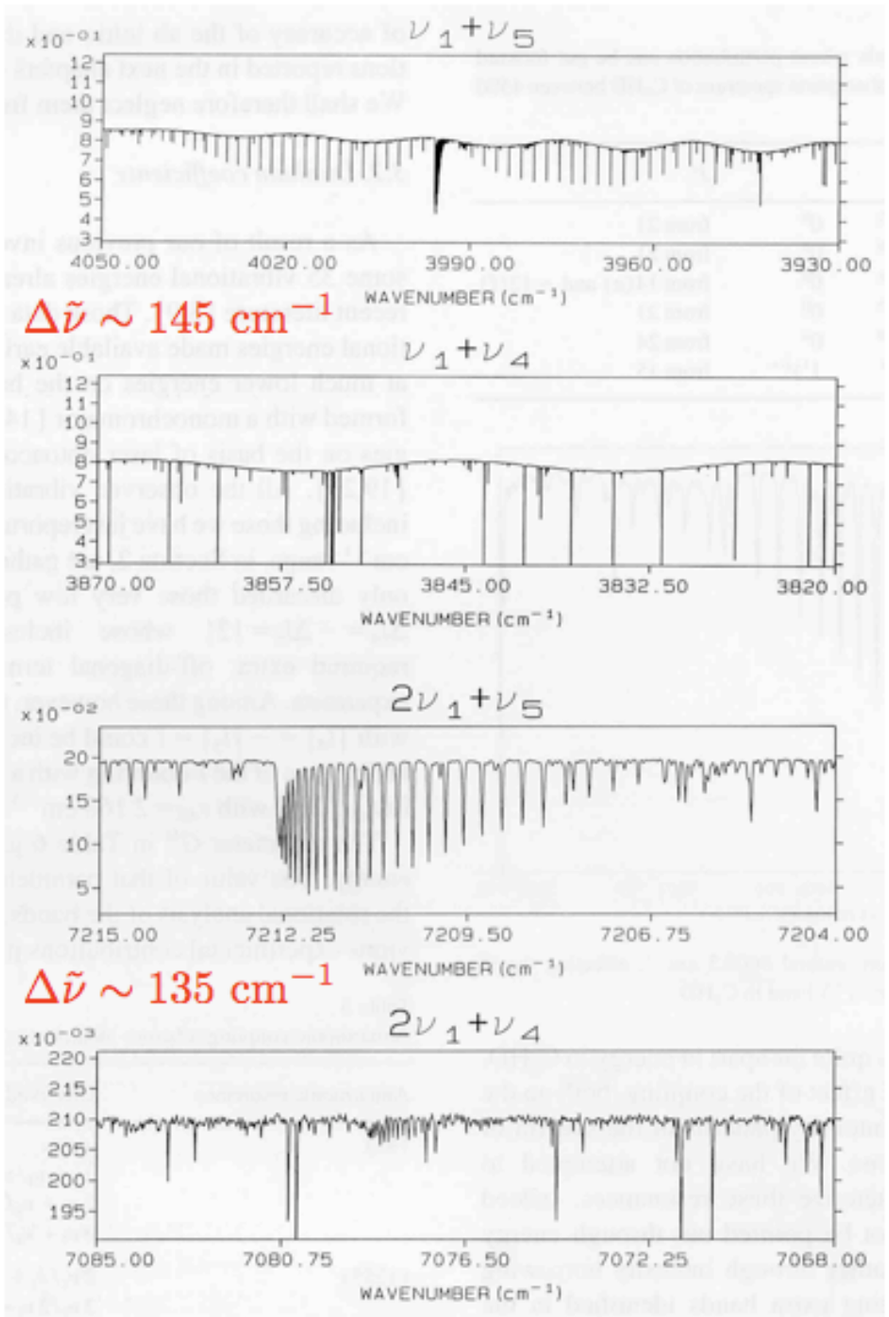
$\nu_2^1 + \nu_3 - \nu_2^1$ band of $^{16}O^{12}C^{32}S$ (R-branch)



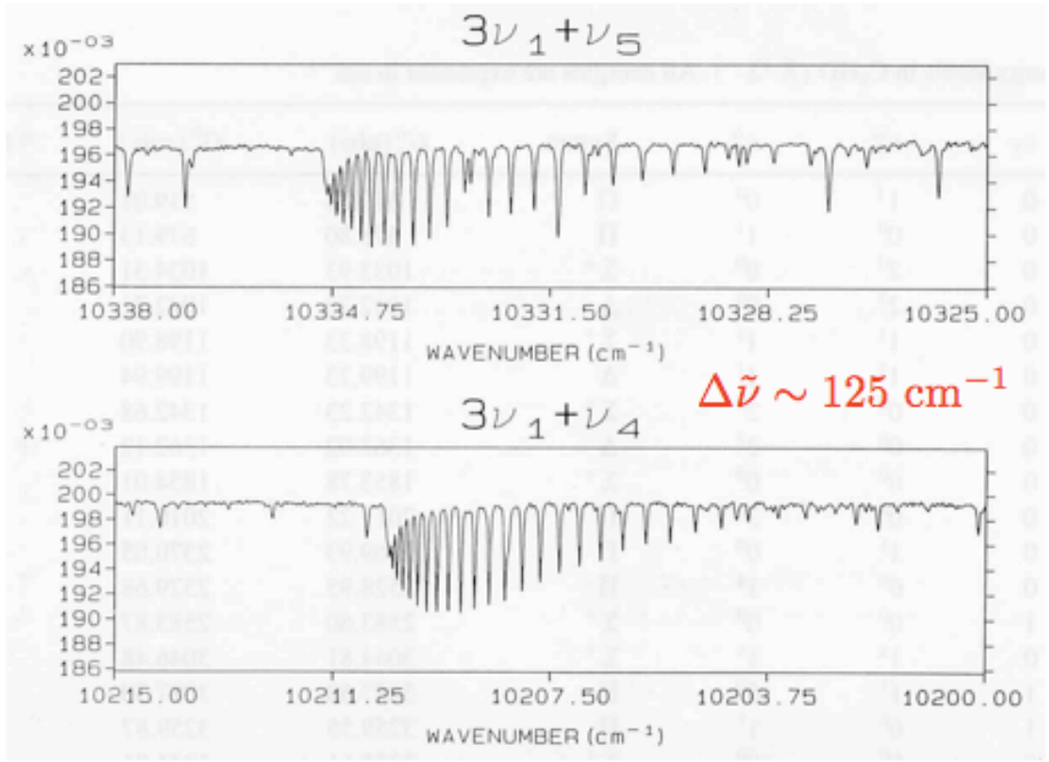


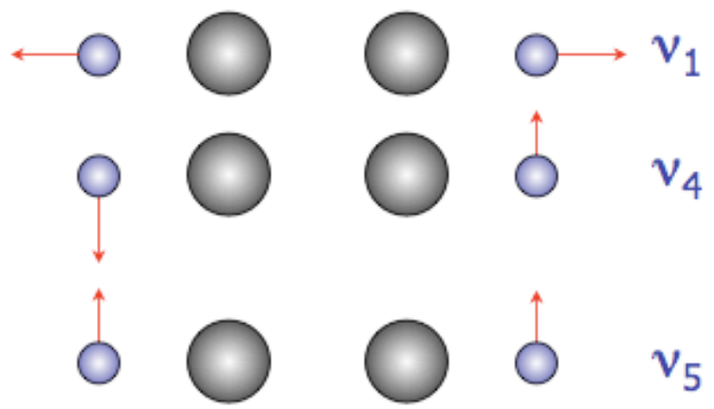
- R and P branches : $e \rightarrow e$ or $f \rightarrow f$
- Q branch : $e \rightarrow f$ or $f \rightarrow e$

Anharmonic resonances



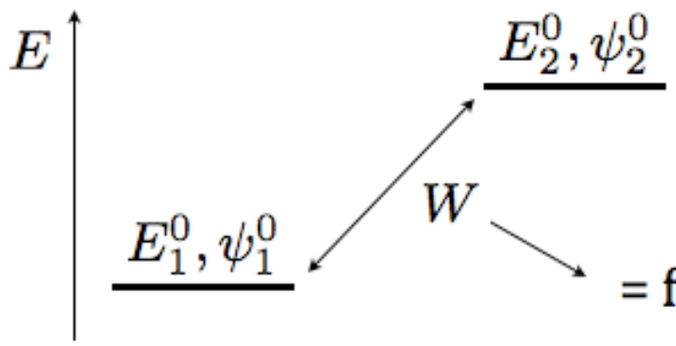
Near infrared absorption spectrum of C_2HD





Anharmonic resonances (2)

- **Energy levels and corresponding Hamiltonian matrix :**



= function of the *force constants*

$$\hat{H} = \begin{pmatrix} E_1^0 & W \\ W & E_2^0 \end{pmatrix}$$

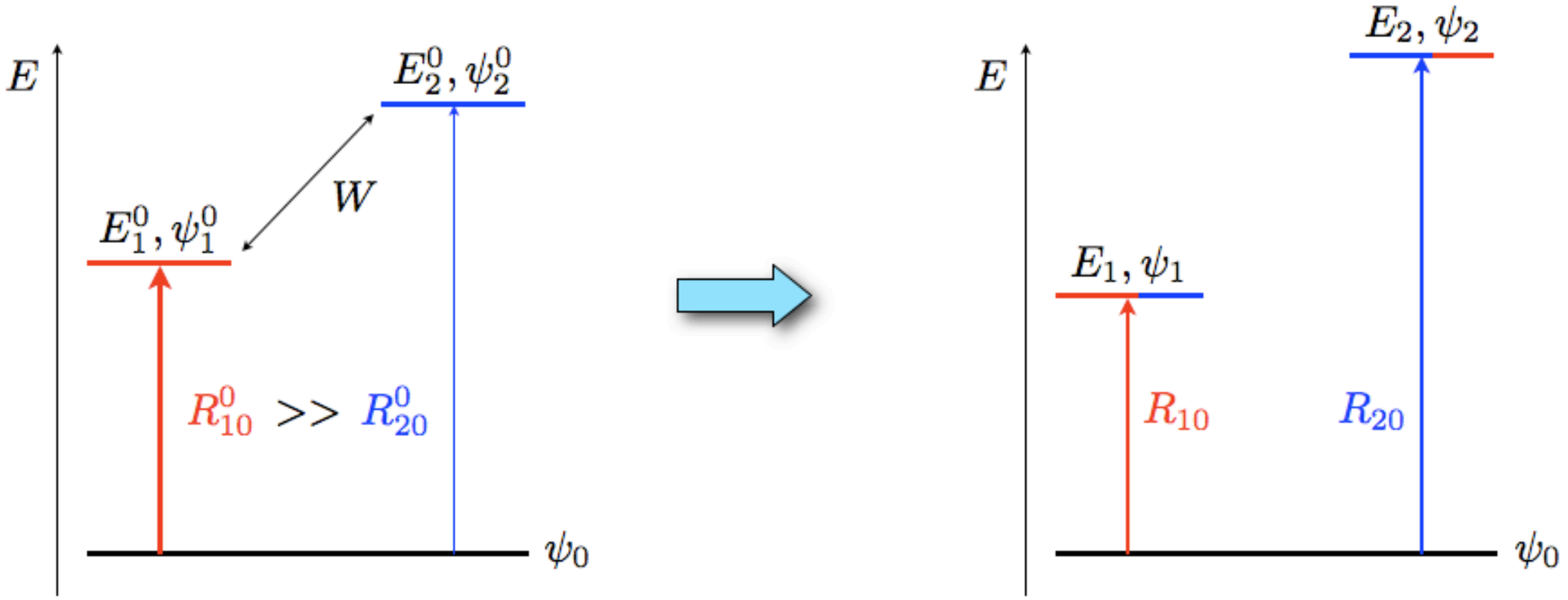
- **Effects of the perturbation :**

Energies : $E_{1,2} = \frac{E_1^0 + E_2^0}{2} \pm \frac{\Delta}{2}$ $\quad \Delta = \sqrt{\delta^2 + 4W^2}$ $\quad \delta = E_2^0 - E_1^0$

Wavefunctions : $\psi_1 = a\,\psi_1^0 + b\,\psi_2^0$ $\quad \psi_2 = b\,\psi_1^0 - a\,\psi_2^0$ $\quad a = \sqrt{\frac{1}{2} + \frac{\delta}{2\Delta}}$ $\quad b = \sqrt{\frac{1}{2} - \frac{\delta}{2\Delta}}$

(mixing of the properties of the states)

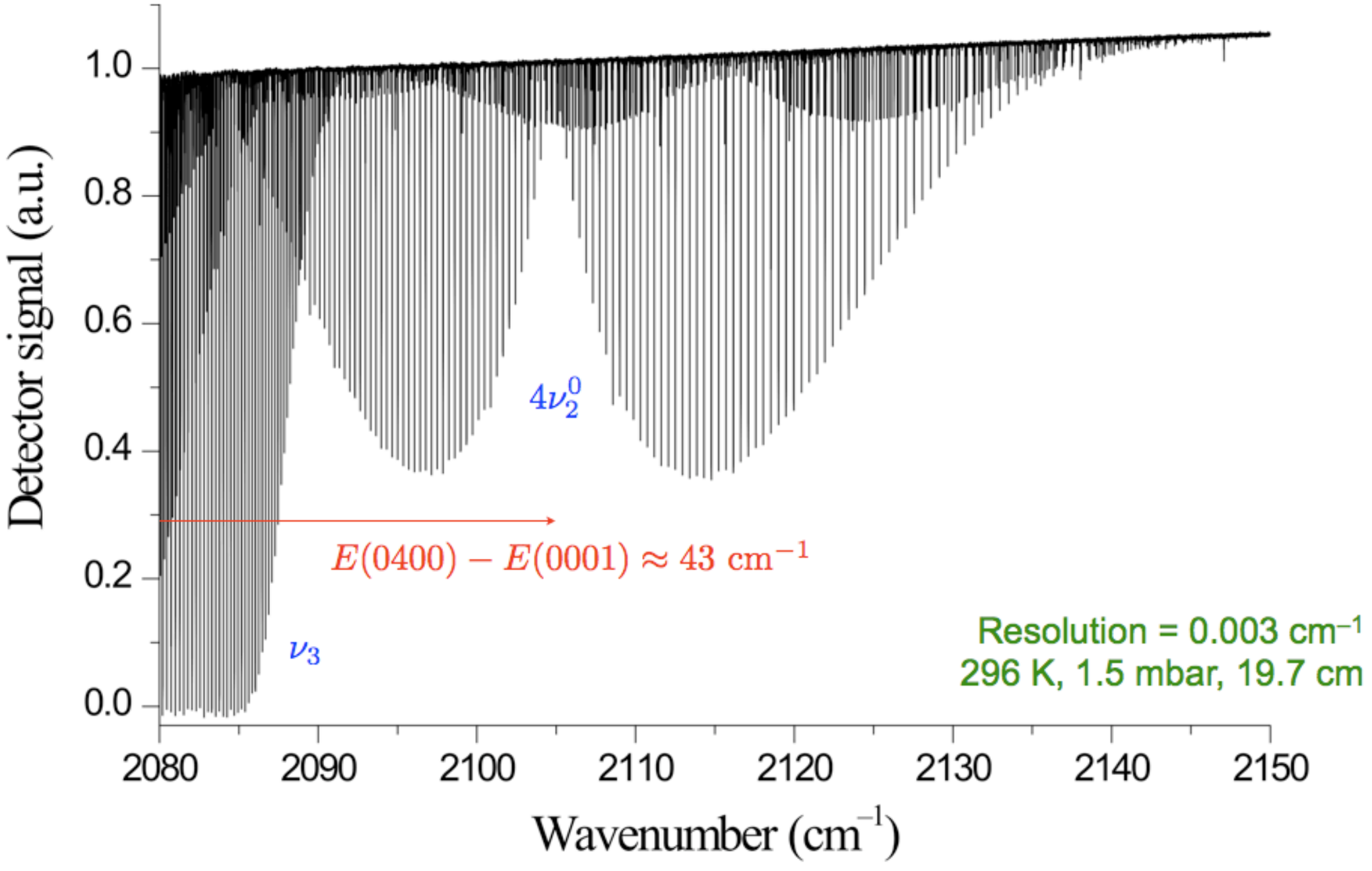
Intensity borrowing



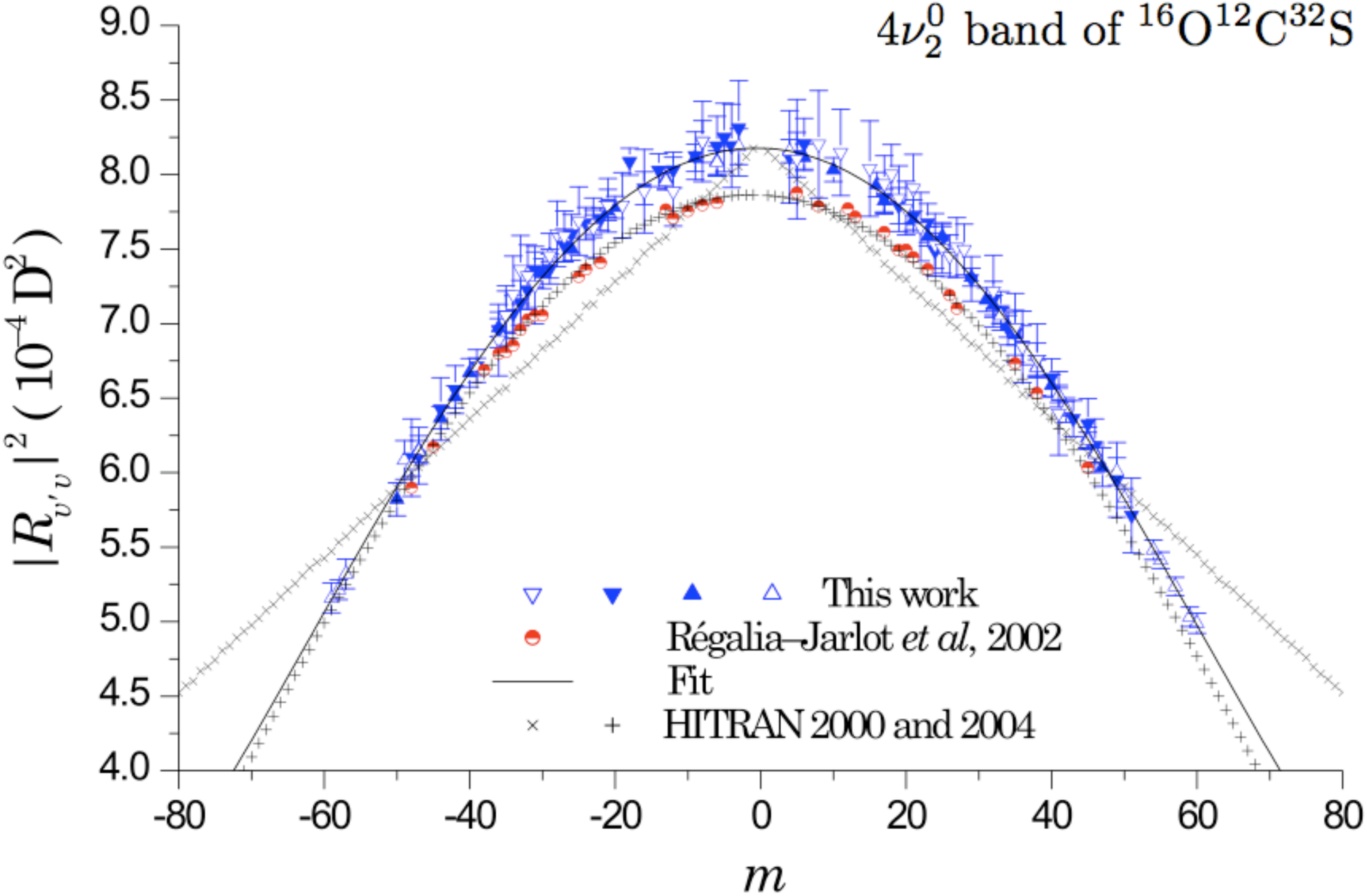
$$R_{10} = \langle \psi_1 | \mu_\alpha^{(v)} | \psi_0 \rangle = \langle a\,\psi_1^0 + b\,\psi_2^0 | \mu_\alpha^{(v)} | \psi_0 \rangle = a \langle \psi_1^0 | \mu_\alpha^{(v)} | \psi_0 \rangle + b \langle \psi_2^0 | \mu_\alpha^{(v)} | \psi_0 \rangle$$

$$\Rightarrow \begin{aligned} R_{10} &= aR_{10}^0 + bR_{20}^0 \approx aR_{10}^0 \\ R_{20} &= bR_{10}^0 - aR_{20}^0 \approx bR_{10}^0 \end{aligned} \Rightarrow \frac{S_v(1-0)}{S_v(2-0)} \approx \frac{a^2}{b^2}$$

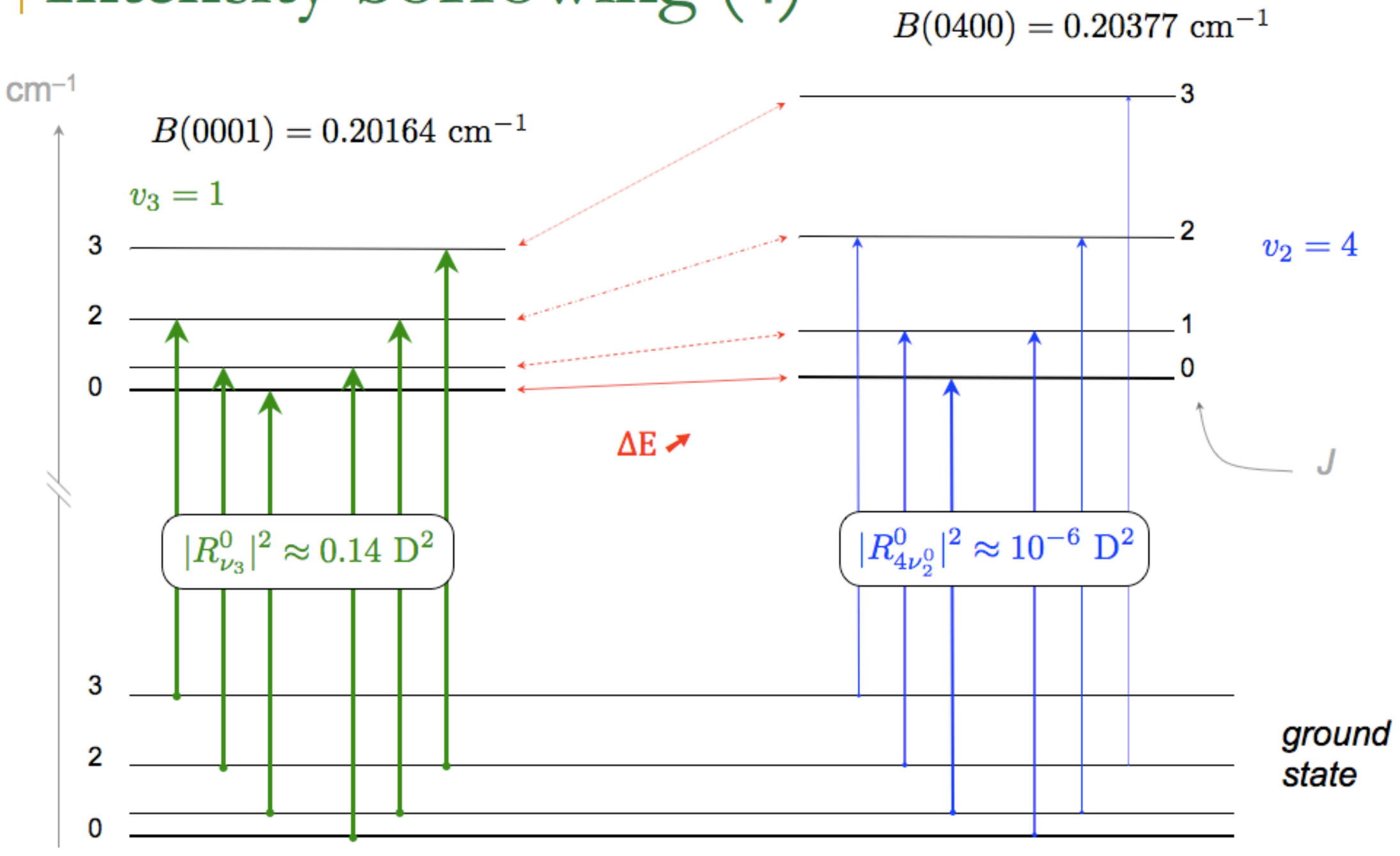
Intensity borrowing (2)



Intensity borrowing (3)



Intensity borrowing (4)

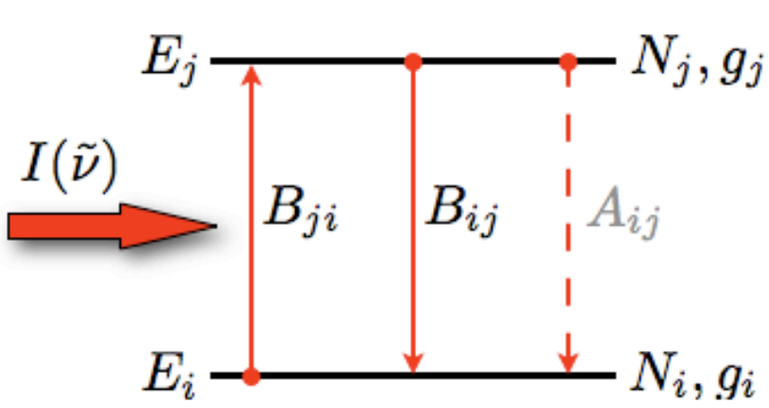


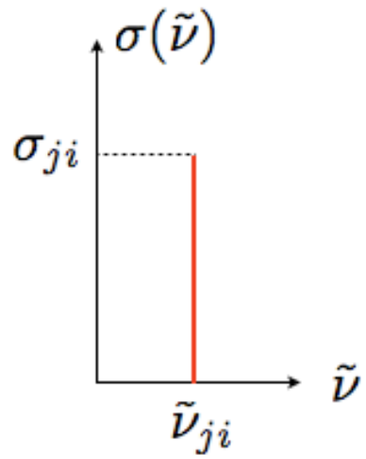
Principes de la spectroscopie

Line profiles

Basic line profiles (line shape functions)

Absorption in a two-levels system :



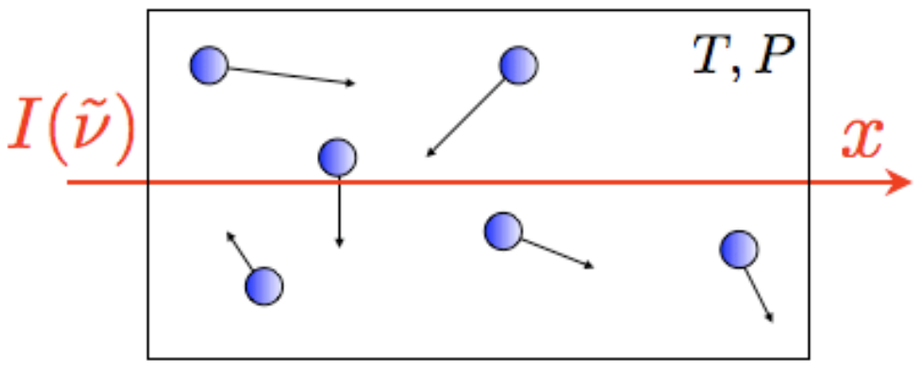


$$\tilde{\nu}_{ji} = E_j - E_i$$

$$\sigma(\tilde{\nu}) = \sigma_{ji}\,\delta(\tilde{\nu} - \tilde{\nu}_{ji})$$

$$\gamma_{ji} = 0$$

Homogeneous gas at thermodynamical equilibrium



P ~ 10 – 10000 Pa, T ~ 200 – 300 K

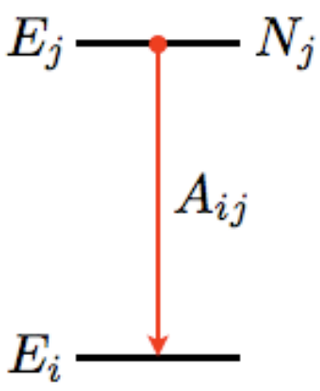
- Lifetime
- Motion
- Collisions

Line broadening

$$A(\tilde{\nu}) = \alpha_{ji}\, g(\tilde{\nu} - \tilde{\nu}_{ji})\, \ell = \sigma_{ji}\, g(\tilde{\nu} - \tilde{\nu}_{ji})\, N\ell$$

Natural broadening

- Spontaneous emission :



Population of level *j*

$$dN_j/dt = -A_{ij} N_j \quad \Rightarrow \quad N_j(t) = N_j(0)\, e^{-A_{ij} t}$$

$$A_{ij} = 1/\tau_j \text{ with } \tau_j = \text{ Lifetime of level } j$$

Emitted radiation

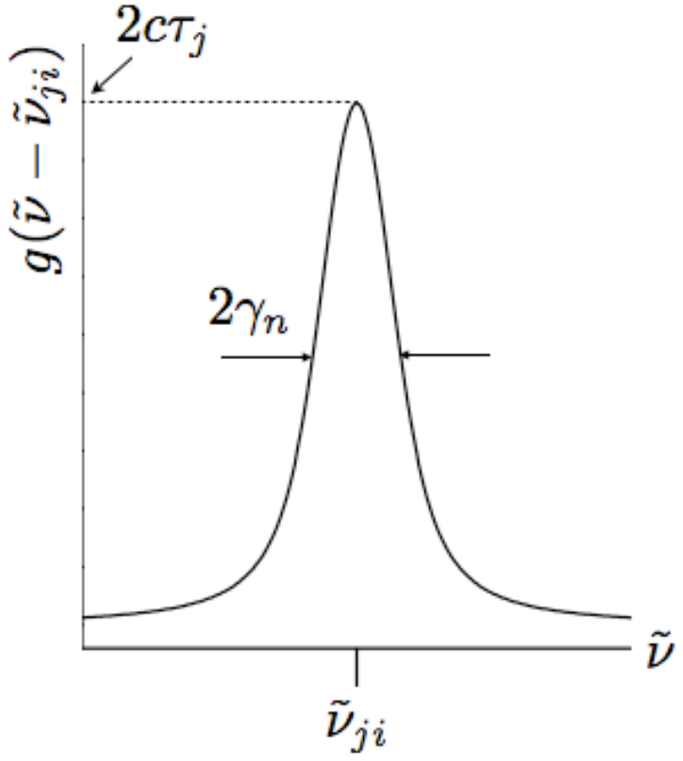
$$E(t) = E_0 \cos(2\pi c \tilde{\nu}_{ji} t)\, e^{-A_{ij} t}$$

- Line profile (Fourier transformation) :

$$F(\omega) = \int_{-\infty}^{\infty} E(t)\, e^{-i 2\pi c \tilde{\nu} t}\, dt$$

$$\Rightarrow \quad g(\tilde{\nu} - \tilde{\nu}_{ji}) = \frac{1}{\pi} \frac{\gamma_n}{\gamma_n^2 + (\tilde{\nu} - \tilde{\nu}_{ji})^2}$$

with the natural line width : $\gamma_n = \dfrac{1}{2\pi c} \dfrac{1}{\tau_j}$

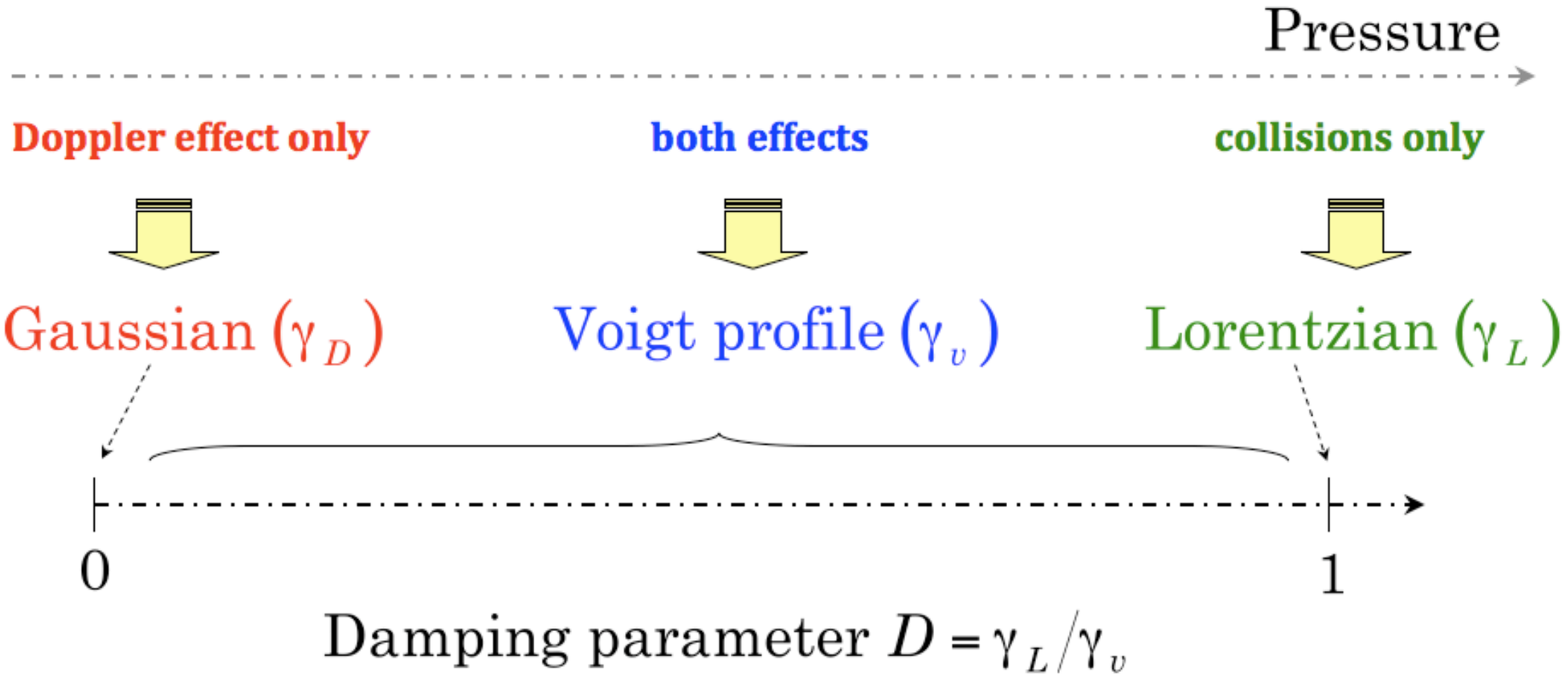


In the infrared range : $\tau_j \sim 10^{-3}$ s $\Rightarrow$ $\gamma_n \sim 5 \times 10^{-9}\ \text{cm}^{-1}$

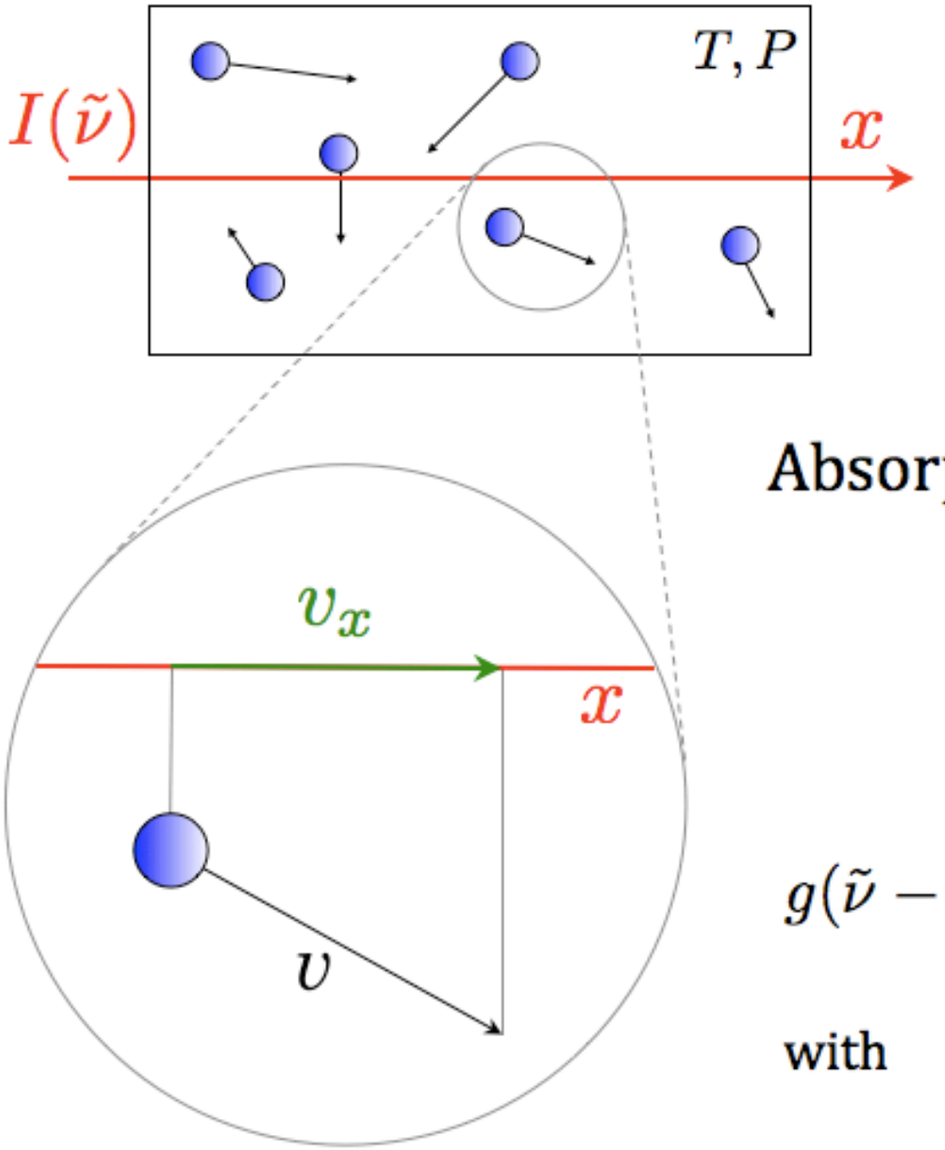
Effects of motion and collisions

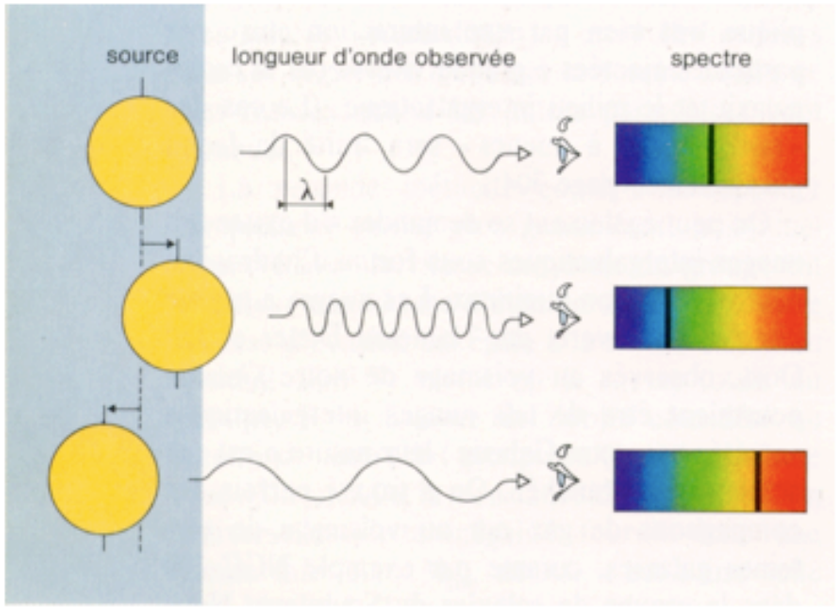
Assumptions :

- collisions = binary impacts
- they have no effect on molecular translation



Doppler broadening





Absorption if $\tilde{\nu} = \tilde{\nu}_{ji}[1 + (v_x/c)]$

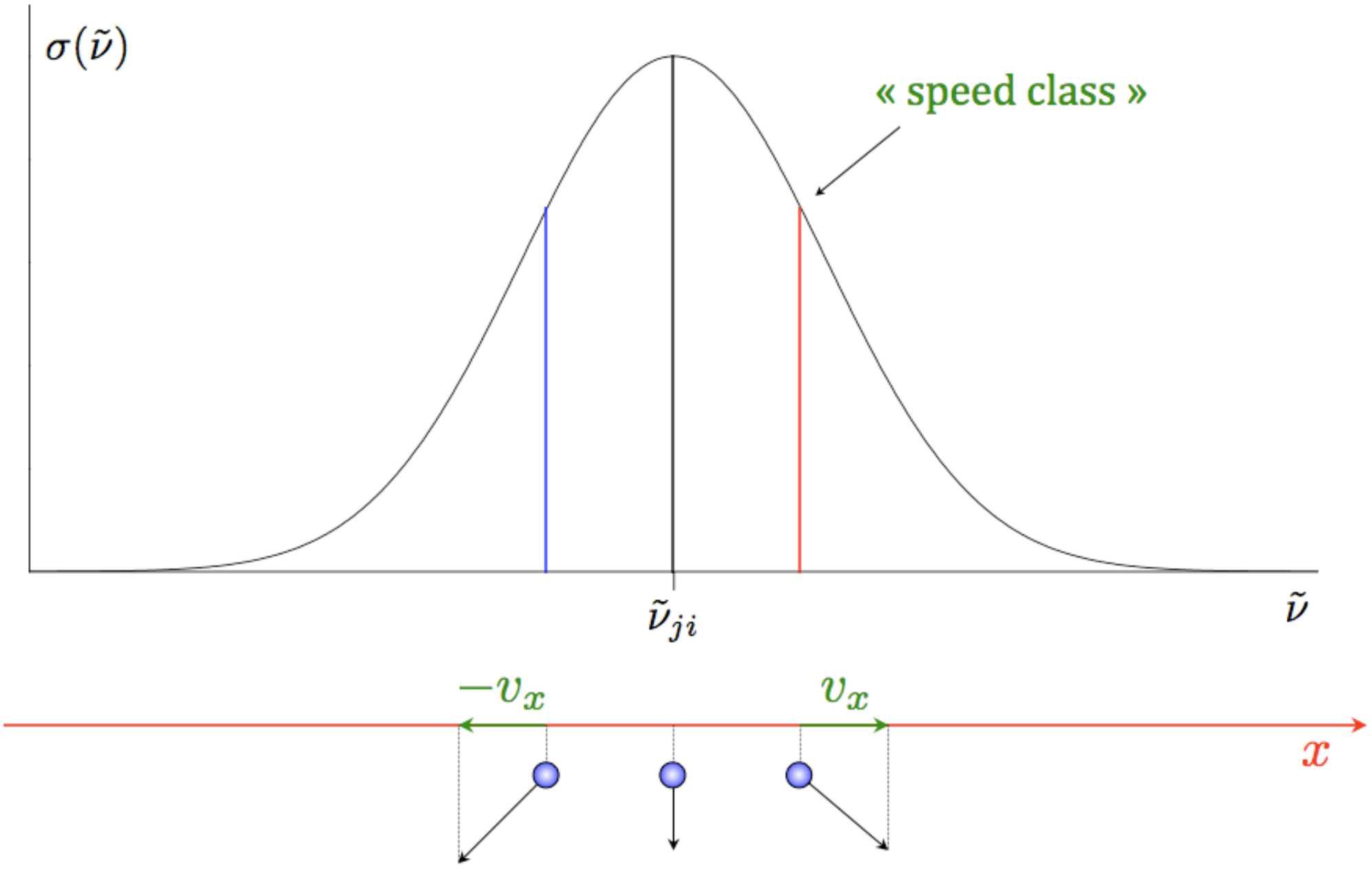
one dimension *Maxwell-Boltzmann* distribution

$$g(\tilde{\nu} - \tilde{\nu}_{ji}) = \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\gamma_D} \exp\left\{ - \ln 2 \left(\frac{\tilde{\nu} - \tilde{\nu}_{ji}}{\gamma_D} \right)^2 \right\}$$

with

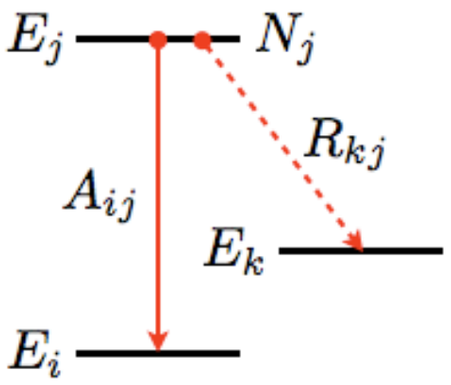
$$\gamma_D = \sqrt{\ln 2}(v_p/c)\tilde{\nu}_{ji} = 3.581 \times 10^{-7} \tilde{\nu}_{ji} \sqrt{\frac{T}{M}}$$

Heterogeneous line profile



Pressure broadening

- Spontaneous emission **+ inelastic collisions** :



$$dN_j/dt = -(A_{ij} + R_{kj})N_j \quad \Rightarrow \quad N_j(t) = N_j(0)\, e^{-(A_{ij}+R_{kj})t}$$

$$\Rightarrow \tau_j^{eff} = \frac{1}{A_{ij} + R_{kj}}$$

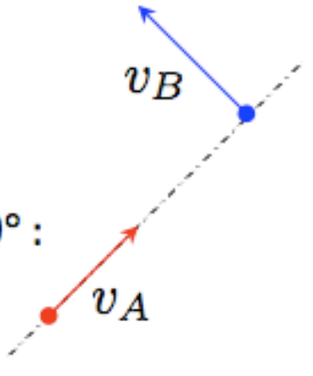
- Collision-induced rate of transition in gas kinetic theory (*the active molecule **A** collides with a buffer of molecules **B***) :

$$R_{kj} = Z(1A, B) = N_B\, \bar{v}_{AB}\, \sigma_{AB}$$

N_B : particle density of B

$\bar{v}_{AB}$: Average speed of A relative to B : $\bar{v}_{AB}^2 = v_A^2 + v_B^2 + 2\, v_A v_B \cos\theta$

on average, collisions occur at 90° :



σ_{AB} : Collision cross section : $\sigma_{AB} = \pi(d_A + d_B)^2/4$

For a collision to occur, the center of B must be within the cylinder of diameter $(d_A+d_B)/2$.

Note. $\bar{v}_{AB}\sigma_{AB}$ = Volume traveled per second by A relative to molecules B.

Pressure broadening and shift

- Effective lifetime of the upper level j :

$$\frac{1}{\tau_j^{eff}} = \frac{1}{\tau_j^{spont}} + N_B\,\bar{v}_{AB}\,\sigma_{AB}$$

$$\bar{v}_{AB} = \sqrt{\frac{8kT}{(\pi\mu)}} \text{ with } \frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

$$N_B = P_B/kT$$

$$\Rightarrow \quad \frac{1}{\tau_j^{eff}} = \frac{1}{\tau_j^{spont}} + \sigma_j^{inel}\sqrt{\frac{8}{\pi\mu kT}}\,P_B$$

- Pressure broadening :

⇒ **Lorentzian profile with HWHM :** $\gamma_L = \gamma_n + \gamma_0\,P_B$ (*Stern-Vollmer*)

"pressure broadening parameter" : $\gamma_0(T) = \gamma_0(T_0)\left(\frac{T_0}{T}\right)^n$ ← "temperature dependence exponent"

Pressure broadening by **air** :

$$\begin{aligned}\gamma_L &= [\gamma_0^{self}x + \gamma_0^{air}(1-x)]P_{tot} \\ &= [\gamma_0^{self}x + (0.79\gamma_0^{N_2} + 0.21\gamma_0^{O_2})(1-x)]P_{tot}\end{aligned}$$

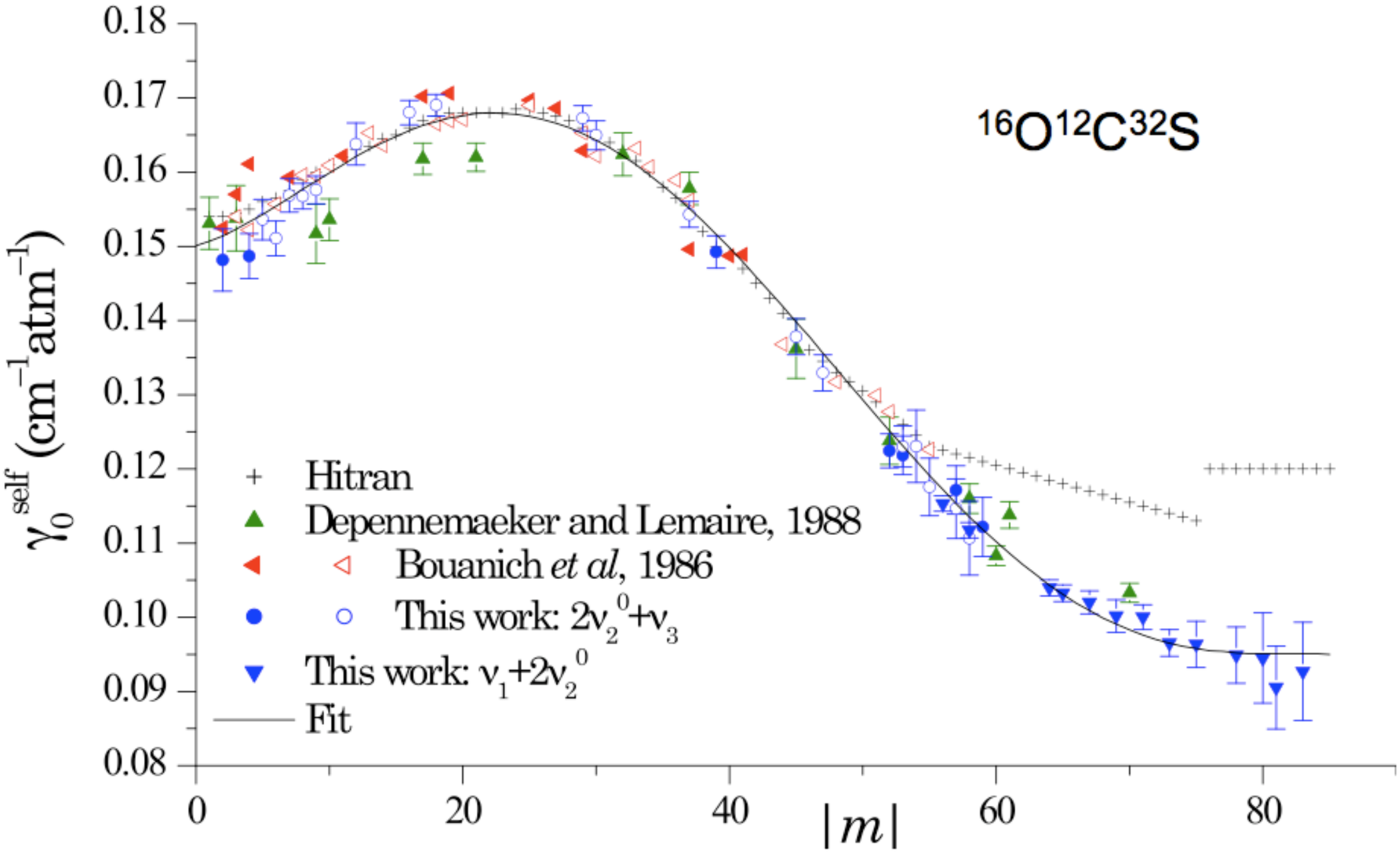
$x = \frac{N}{N + N_{O_2} + N_{N_2}}$

- Pressure shift :

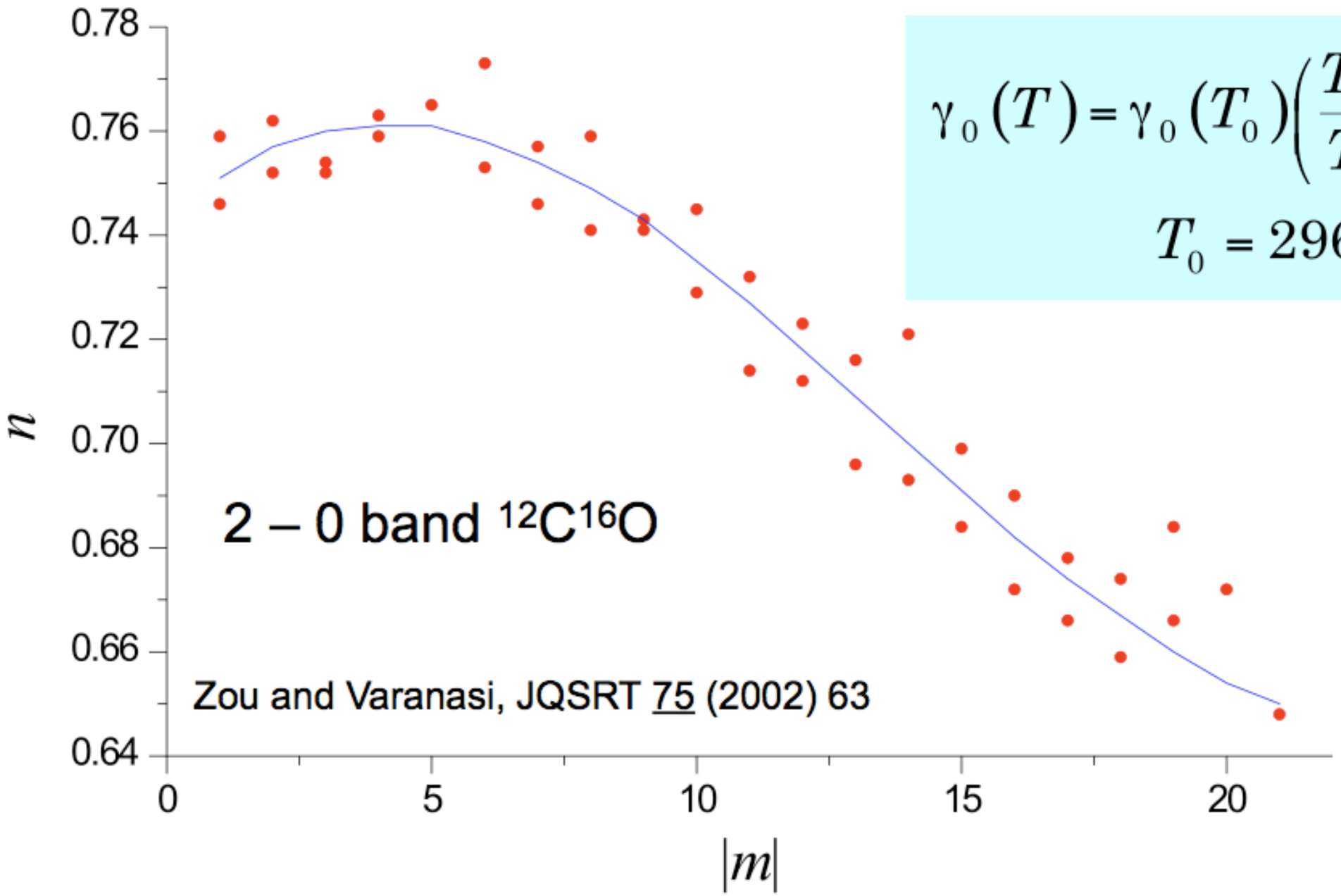
$$g(\tilde{\nu} - \tilde{\nu}_{ji}) = \frac{1}{\pi}\,\frac{\gamma_n}{\gamma_n^2 + (\tilde{\nu} - \tilde{\nu}_{ji} - \Delta\tilde{\nu})^2} \qquad \Delta\tilde{\nu} = \delta_0\,P$$

← "pressure shift parameter"

Pure gas: Self-broadening parameter



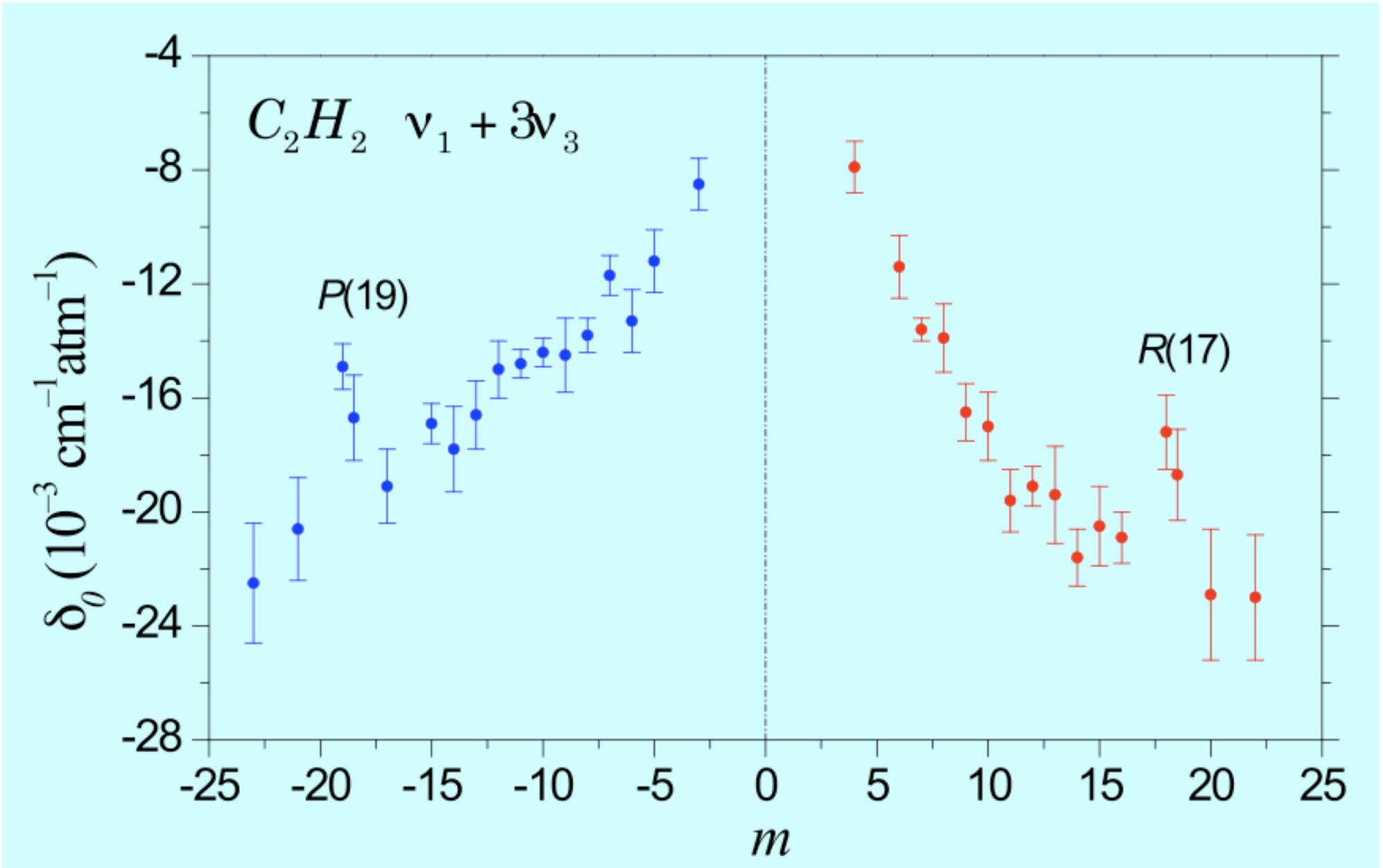
Temperature dependence of γ_0



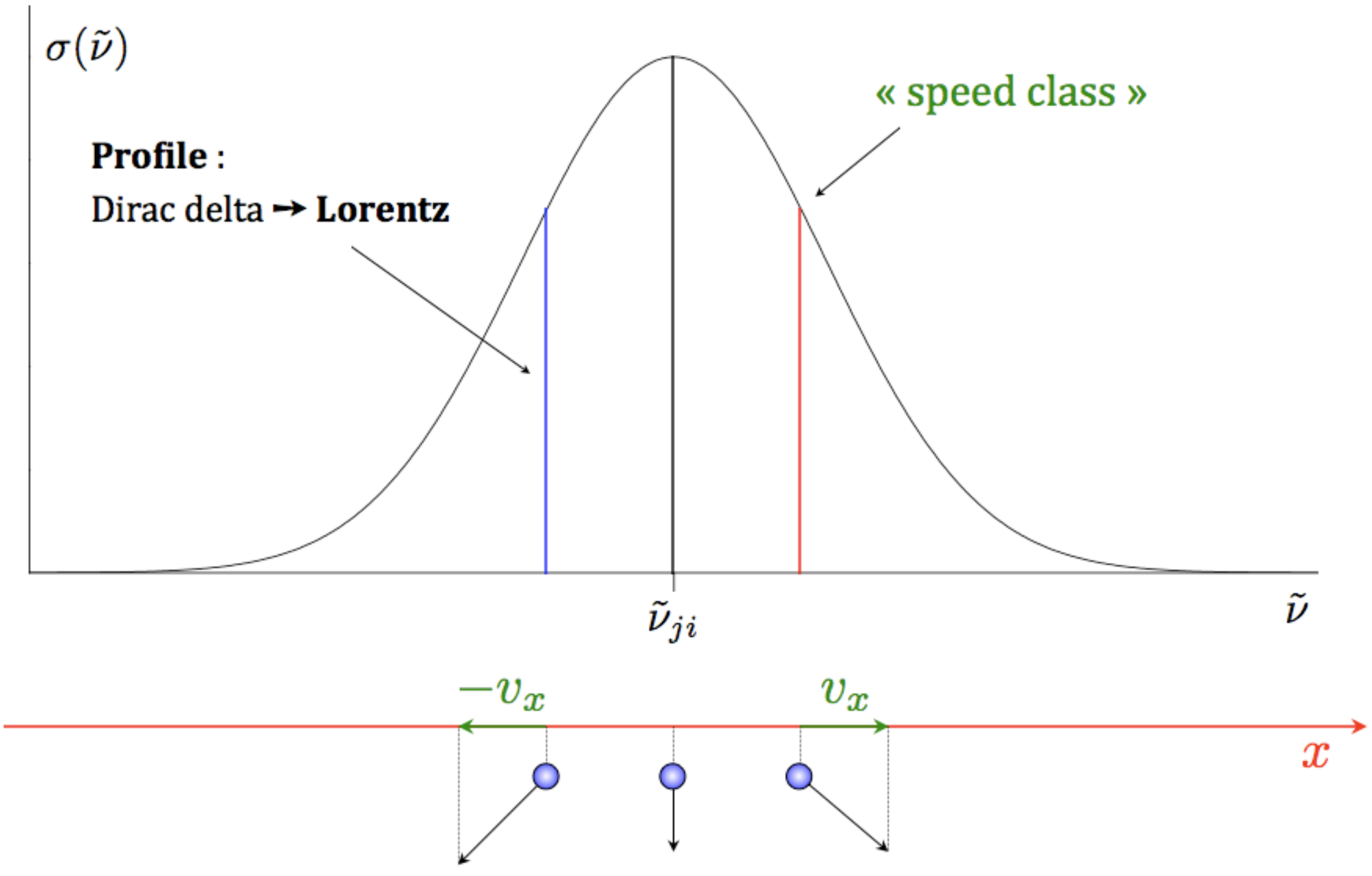
$$\gamma_0(T) = \gamma_0(T_0)\left(\frac{T_0}{T}\right)^n$$

$$T_0 = 296\ \mathrm{K}$$

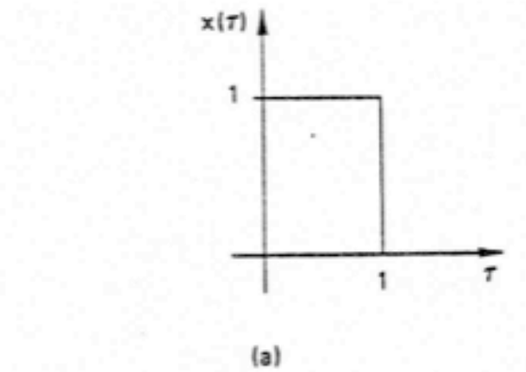
Pressure shift



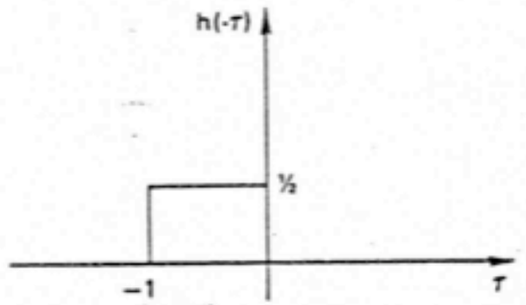
Doppler *and* pressure broadening

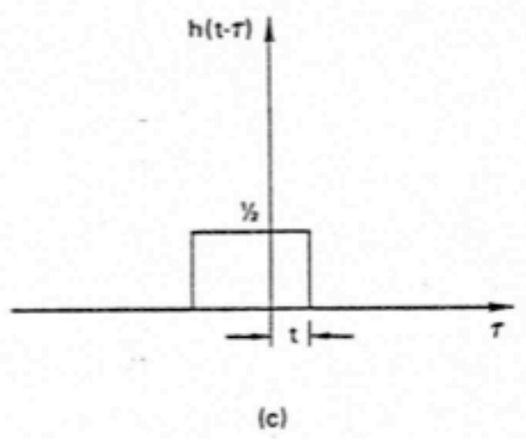


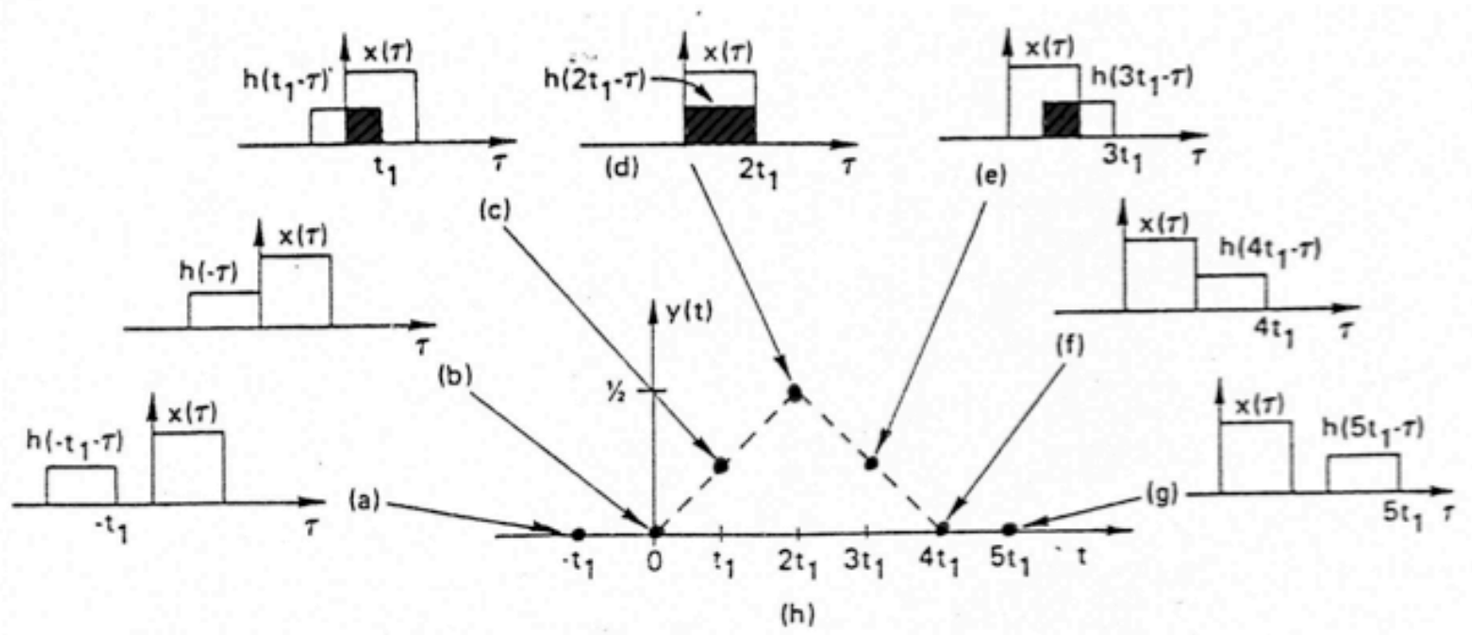
Convolution of two functions



$$y(t) = \int_{-\infty}^{\infty} x(\tau)h(t-\tau)d\tau = x(t) * h(t)$$

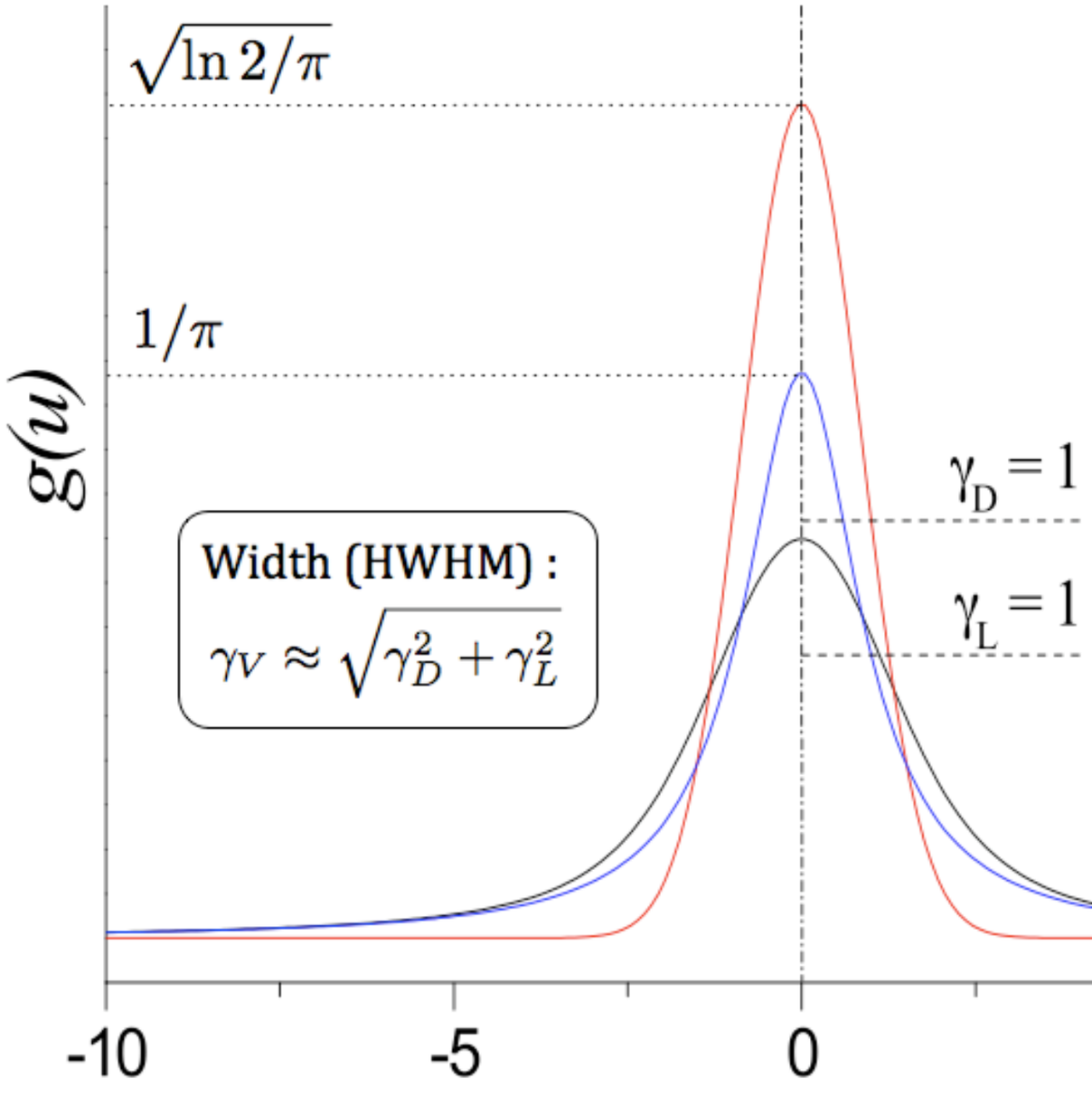






The Voigt profile

$$
\begin{aligned}
g_V(\tilde{\nu} - \tilde{\nu}_{ji}) &= g_D(\tilde{\nu}) * g_L(\tilde{\nu} - \tilde{\nu}_{ji}) \\
&= \int_{-\infty}^{\infty} g_D(\tilde{\nu}')\, g_L(\tilde{\nu} - \tilde{\nu}_{ji} - \tilde{\nu}')\, d\tilde{\nu} \\
&= \frac{1}{\gamma_D}\sqrt{\frac{\ln 2}{\pi}}\, K(x,y)
\end{aligned}
$$



Reduced Voigt profile :

$$K(x,y) = \frac{y}{\pi}\int_{-\infty}^{\infty} \frac{e^{-t^2}}{y^2 + (x-t)^2}\, dt$$

$$x = \sqrt{\ln 2}\,(\tilde{\nu} - \tilde{\nu}_{ji})/\gamma_D$$

$$y = \sqrt{\ln 2}\,(\gamma_L/\gamma_D)$$

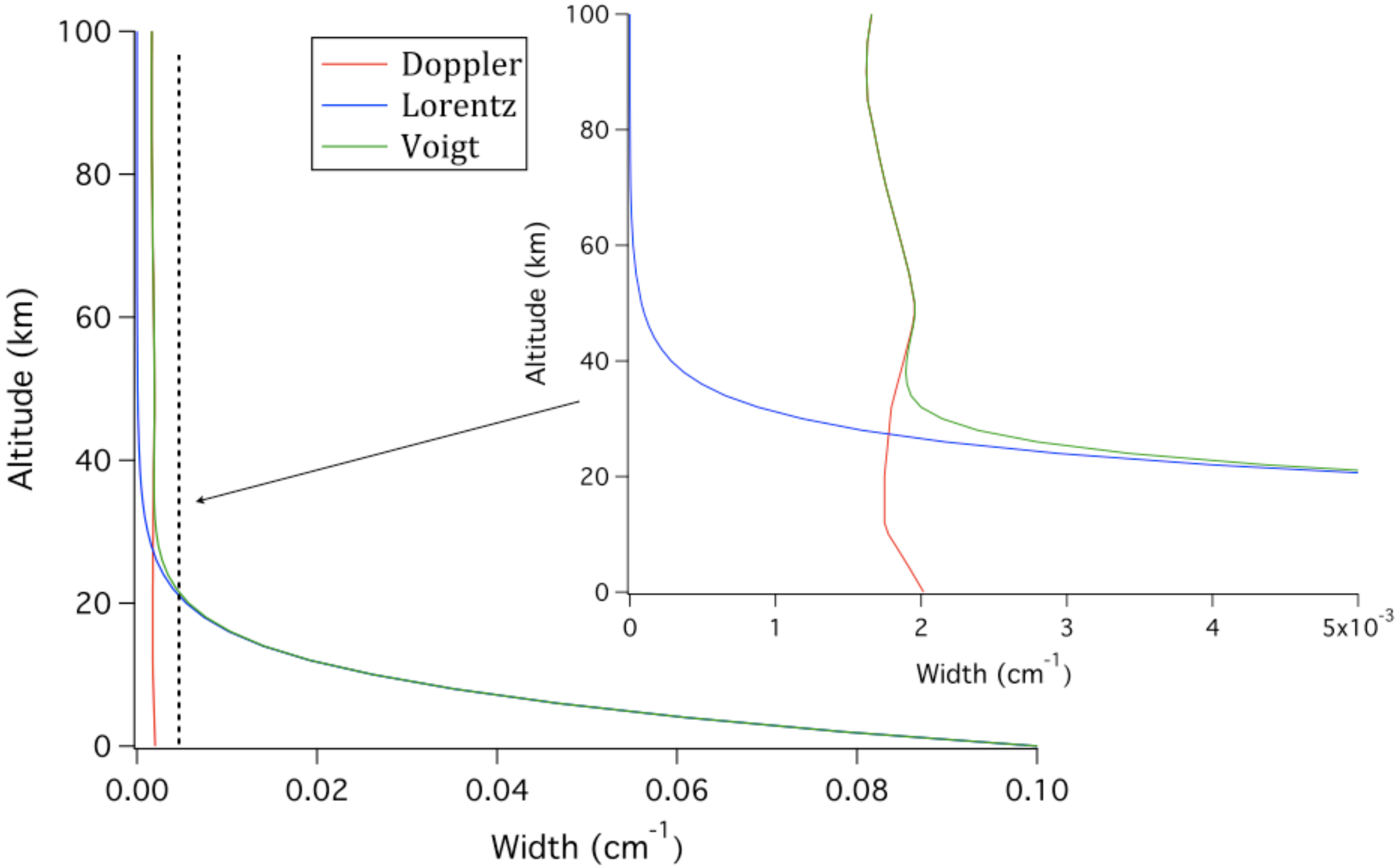
Some numbers...

N_2O (44 g/mol)

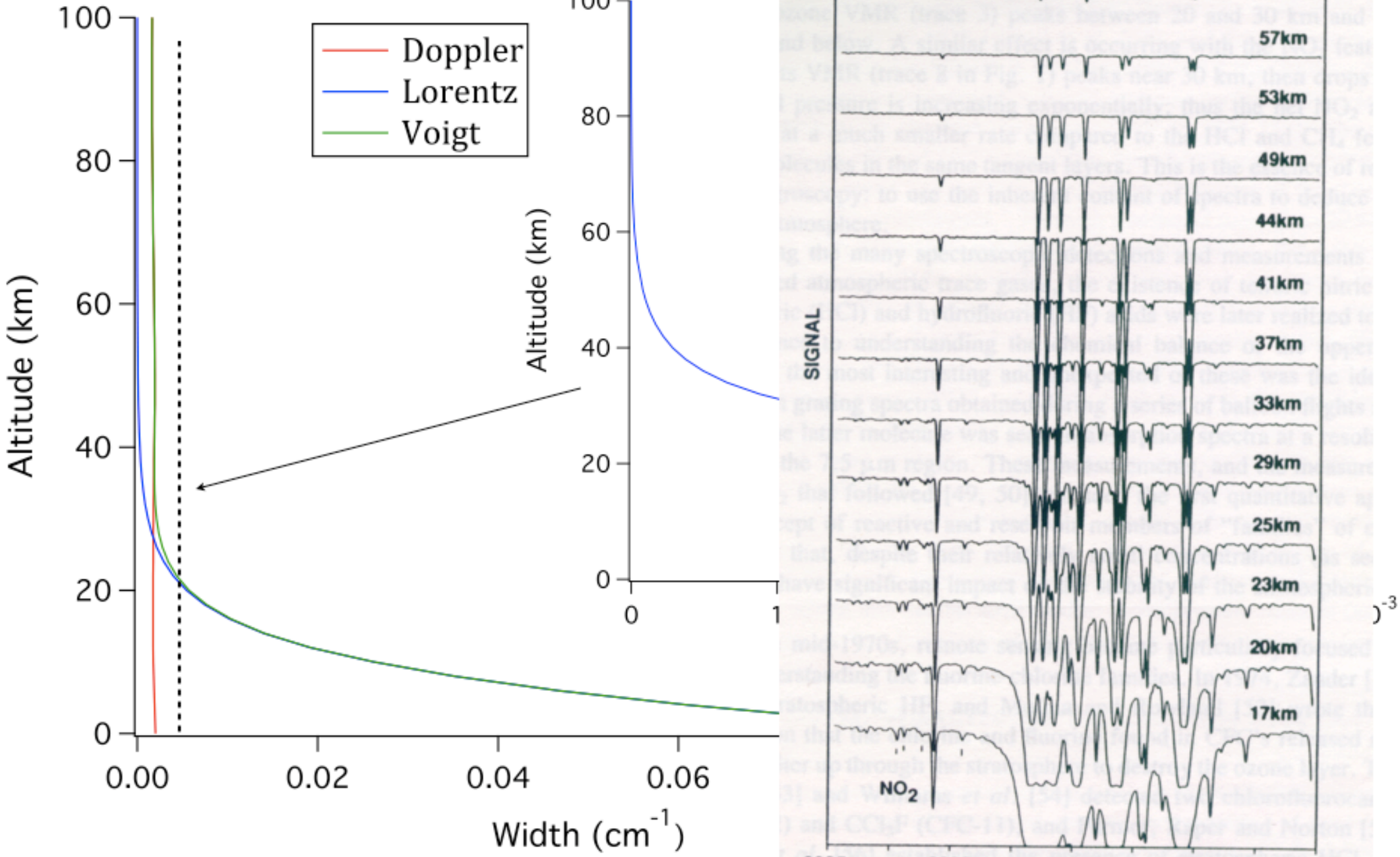
T = 296 K, $\tilde{\nu}_k$ = 2200 cm^{-1}, γ_0 = 0.1 $cm^{-1}atm^{-1}$

γ (cm^{-1})	P = 1 mbar	P = 100 mbar
Gauss	2.04×10^{-3}	2.04×10^{-3}
Lorentz	9.87×10^{-5}	9.87×10^{-3}
Voigt	2.09×10^{-3}	1.03×10^{-2}

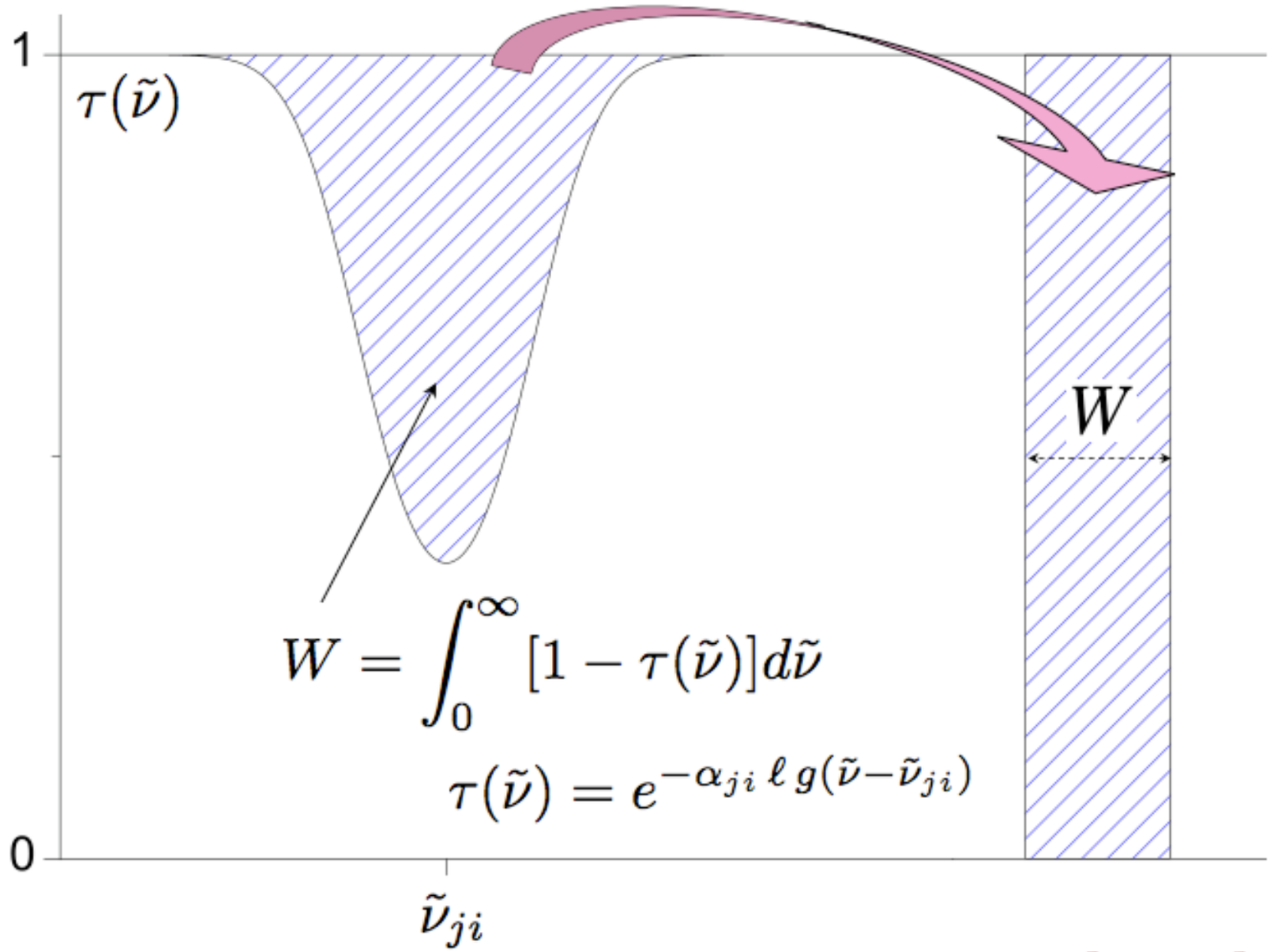
Evolution of widths with altitude



Evolution of widths w

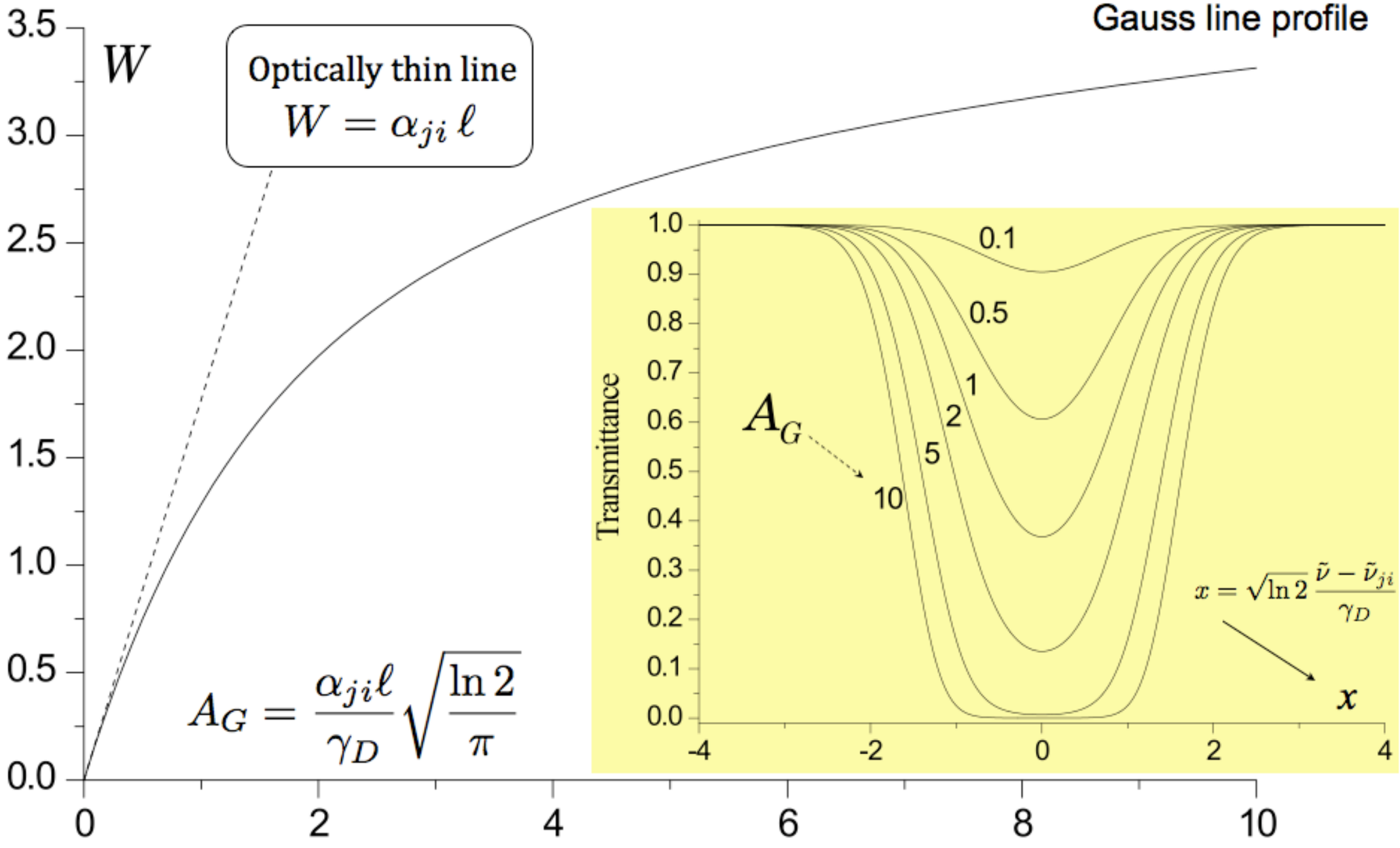


Equivalent width

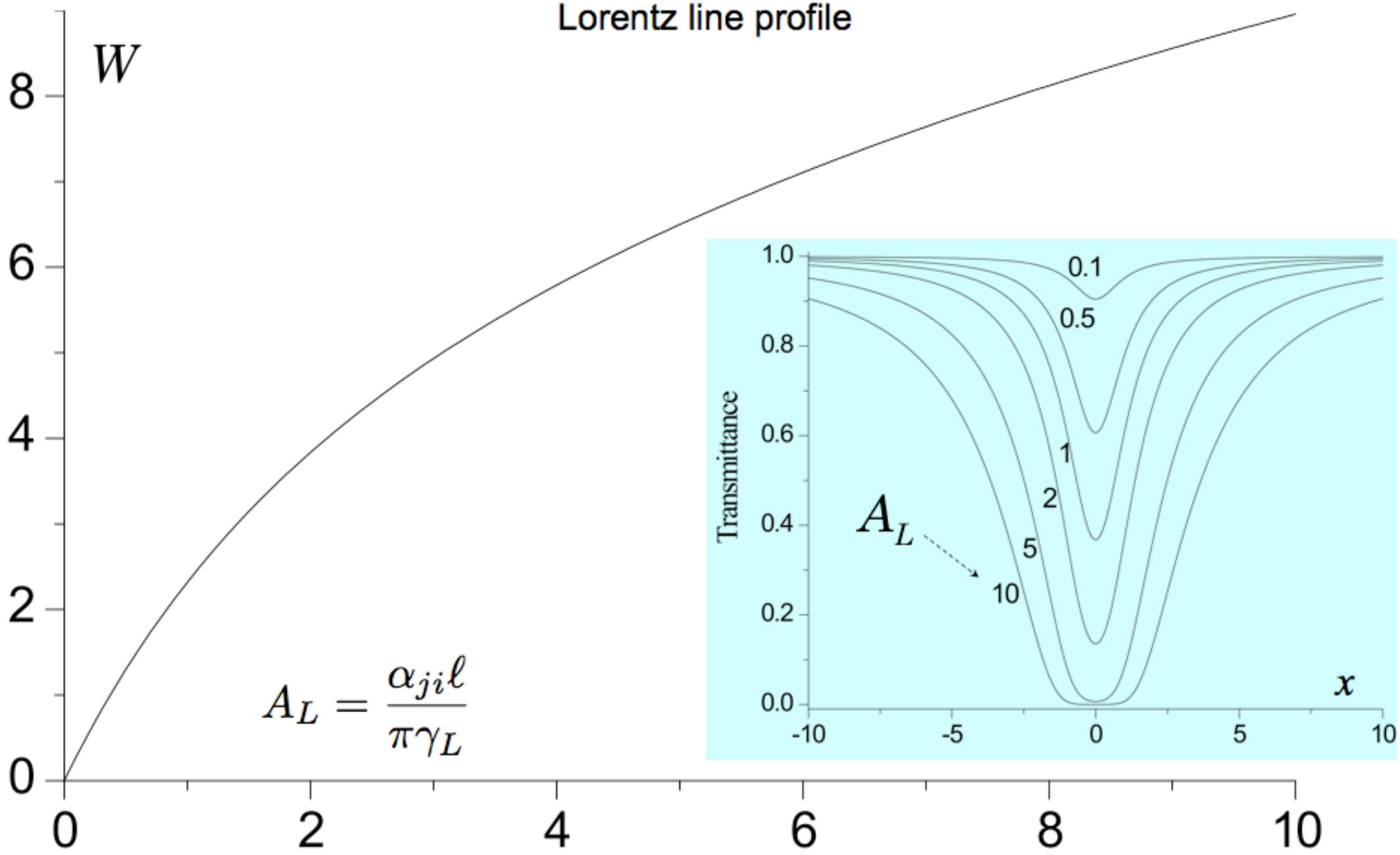


Link with line intensity ?

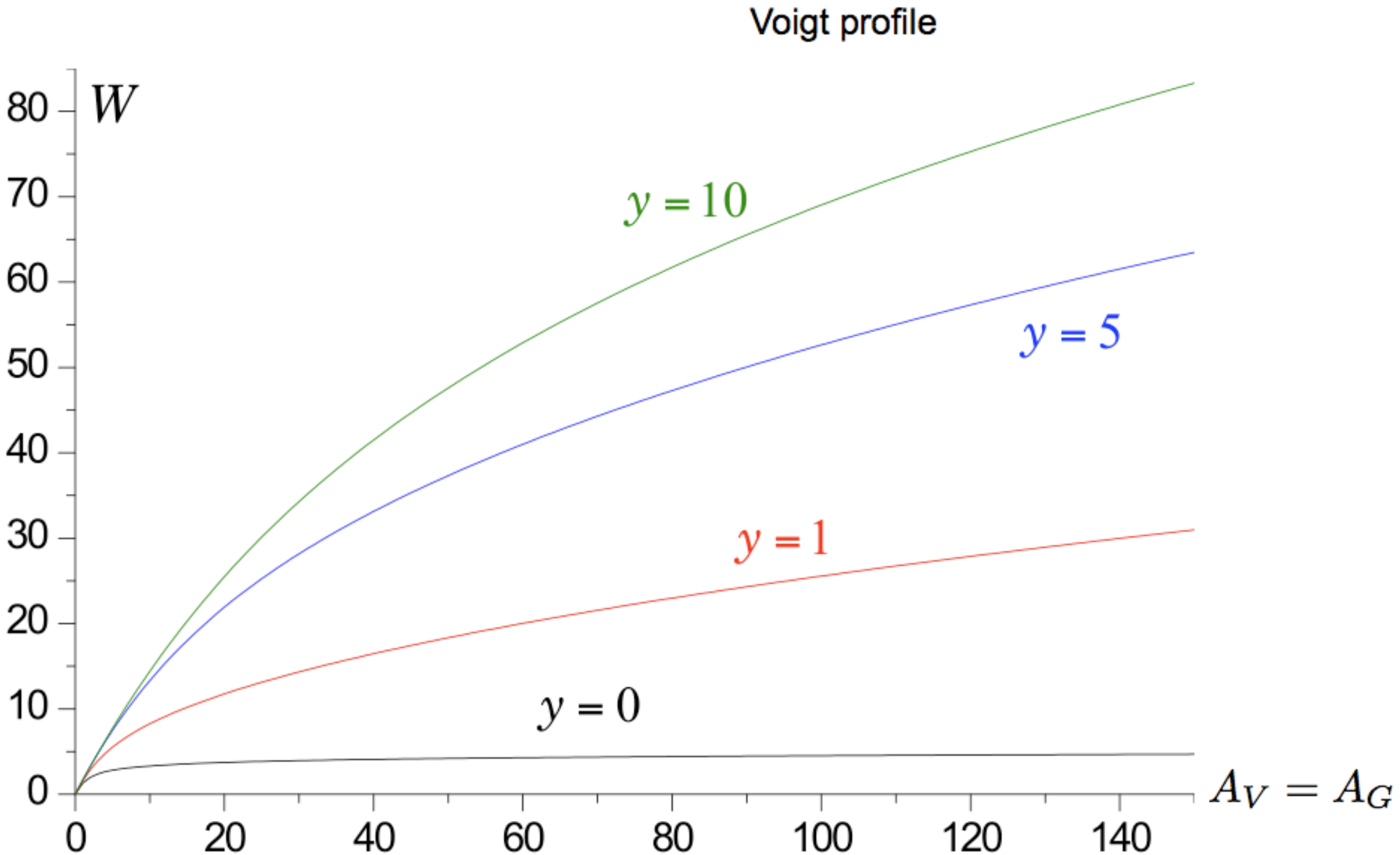
Equivalent width – Curve of grow



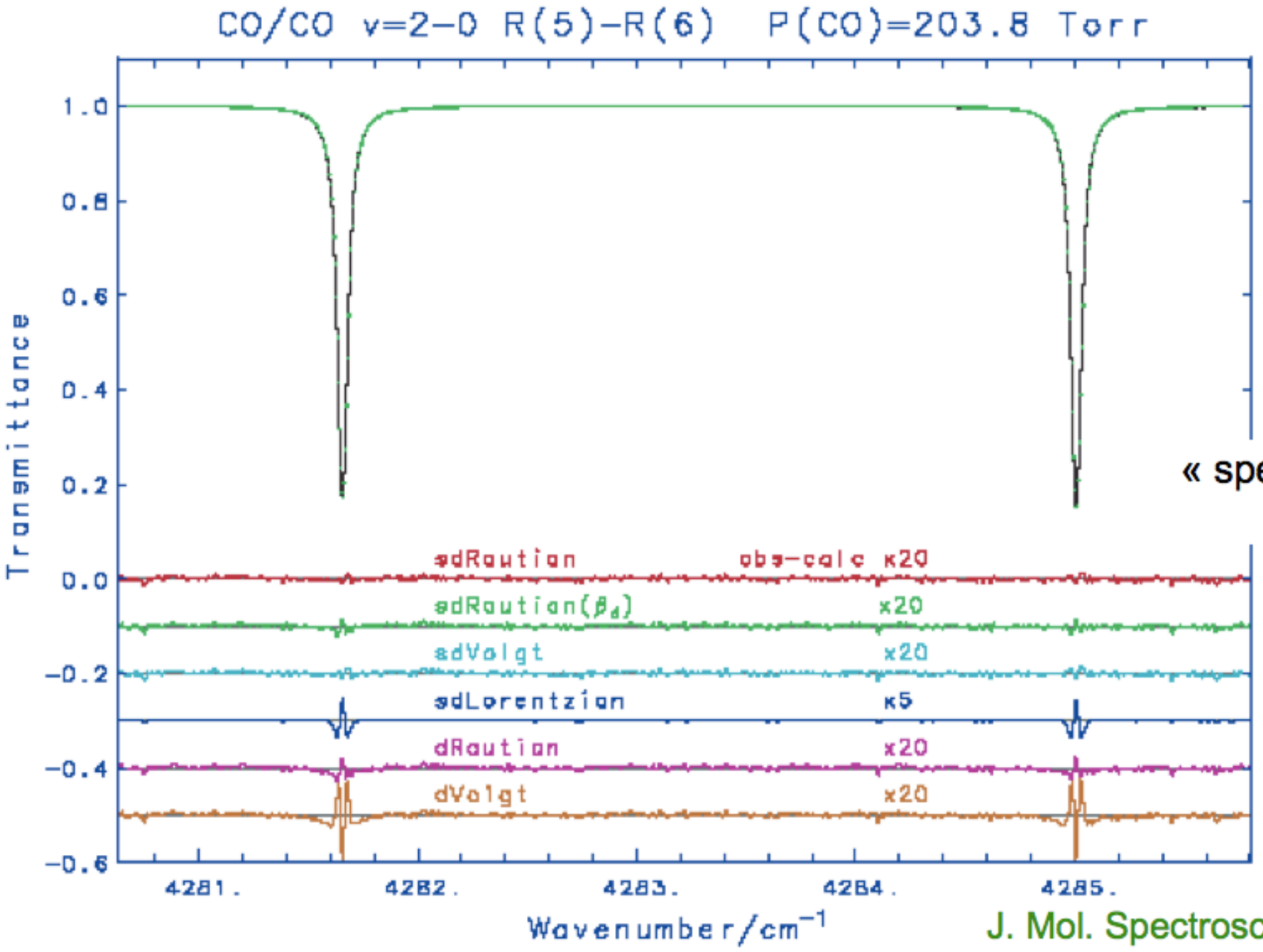
Equivalent width – Curve of grow



Equivalent width – Curve of grow



Departure from the Voigt profile



« speed-dependent »
profiles

Rautian
Voigt

Brault *et al*,
J. Mol. Spectrosc. 222 (2003) 220

non-Voigt profiles

collisions = binary impacts
no effect on molecular translation } **Voigt**

collisions → motion
(diffusion)

motion → collisions
$(\gamma_L \not\propto \overline{v}_{rel})$

Dicke narrowing

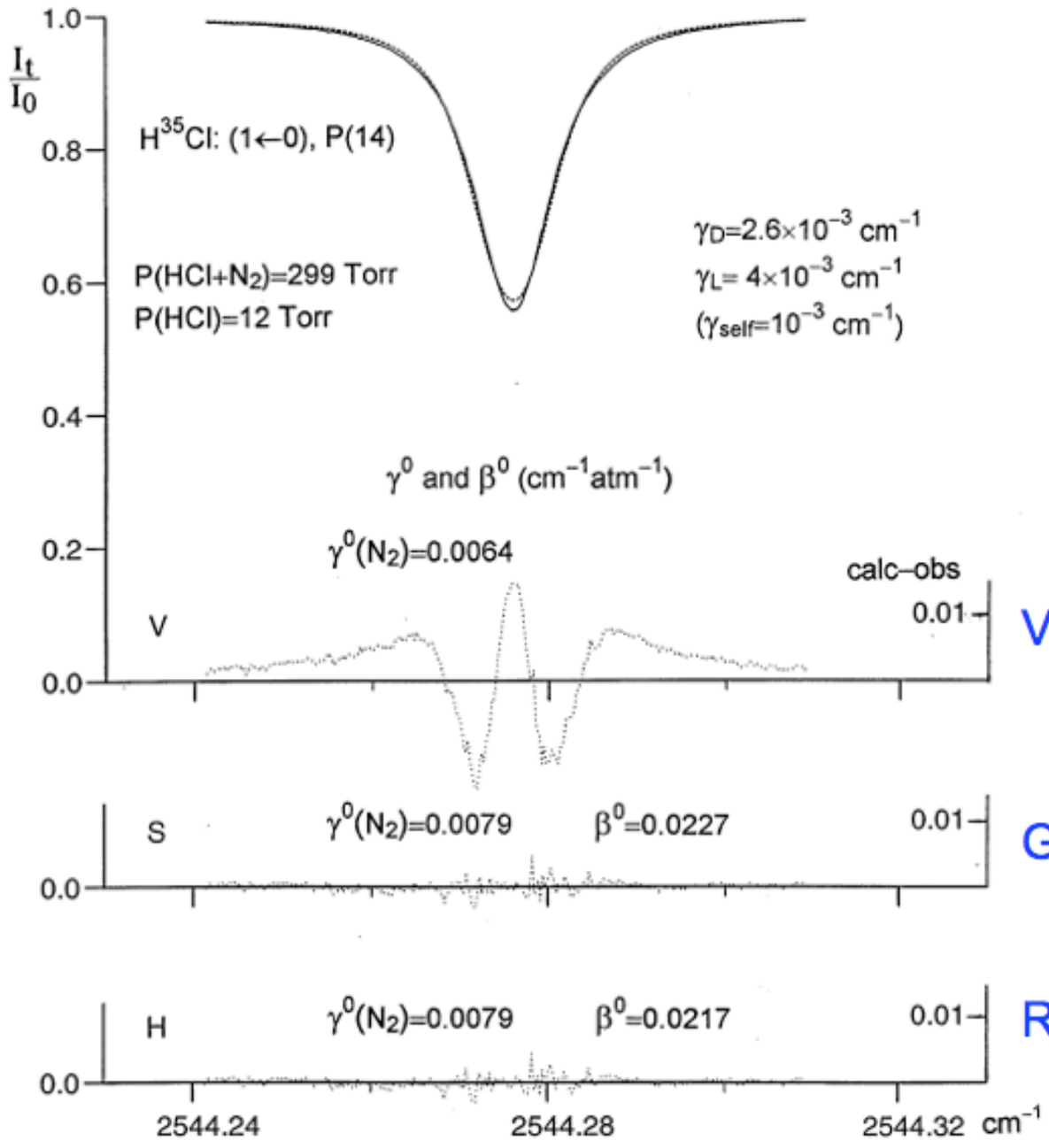
« soft » collisions
Galatry profile

« hard » collisions
Rautian profile

« speed-dependent »
profiles

Henry *et al*, JQSRT 56 (1996) 647; Pine, JQSRT 62 (1999) 397.

Dicke narrowing

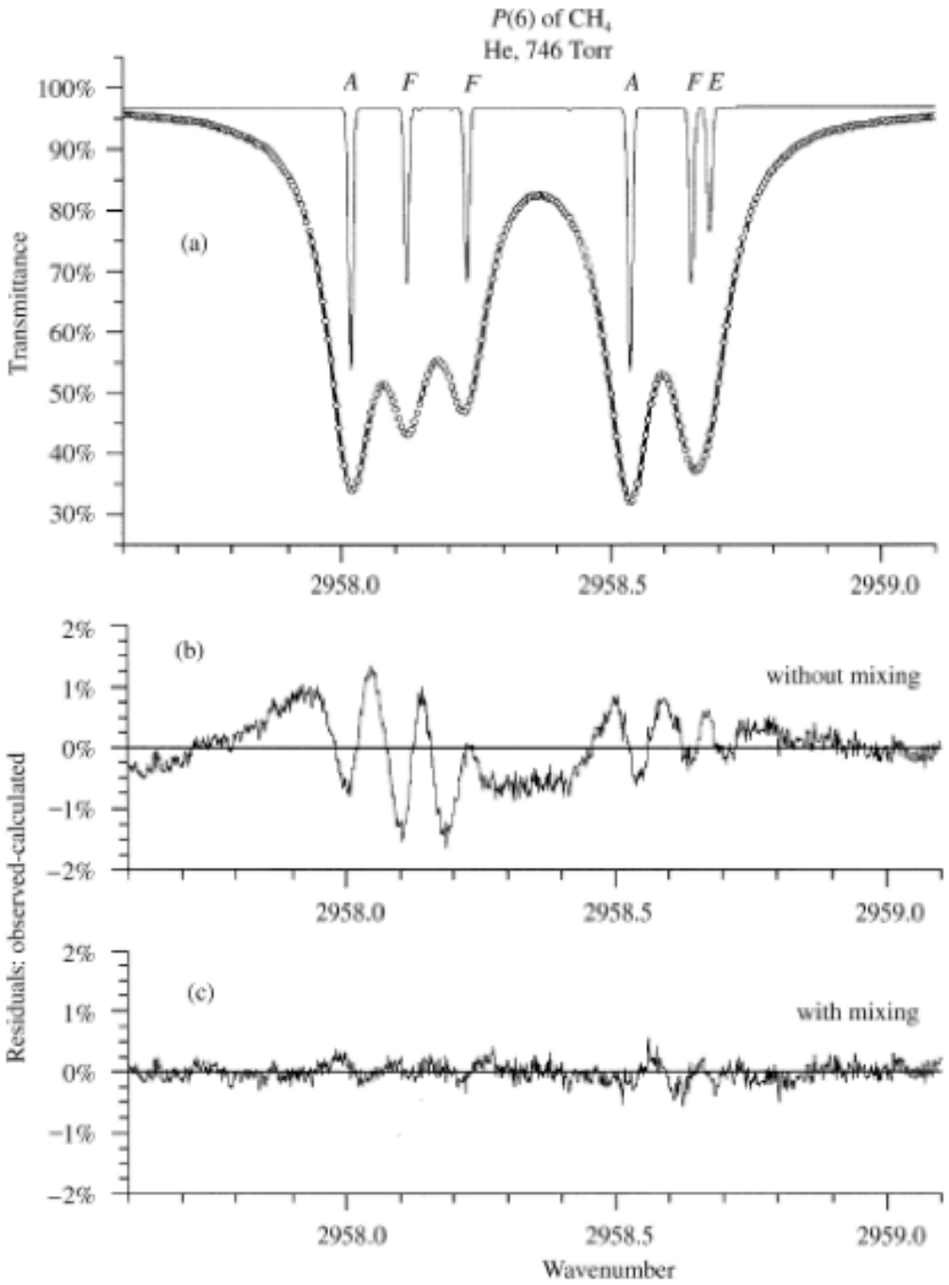


Henry and Hurtmans, Spectrochim. Acta 55 (1999) 1967

TDL spectrum

β^0 = « narrowing parameter »

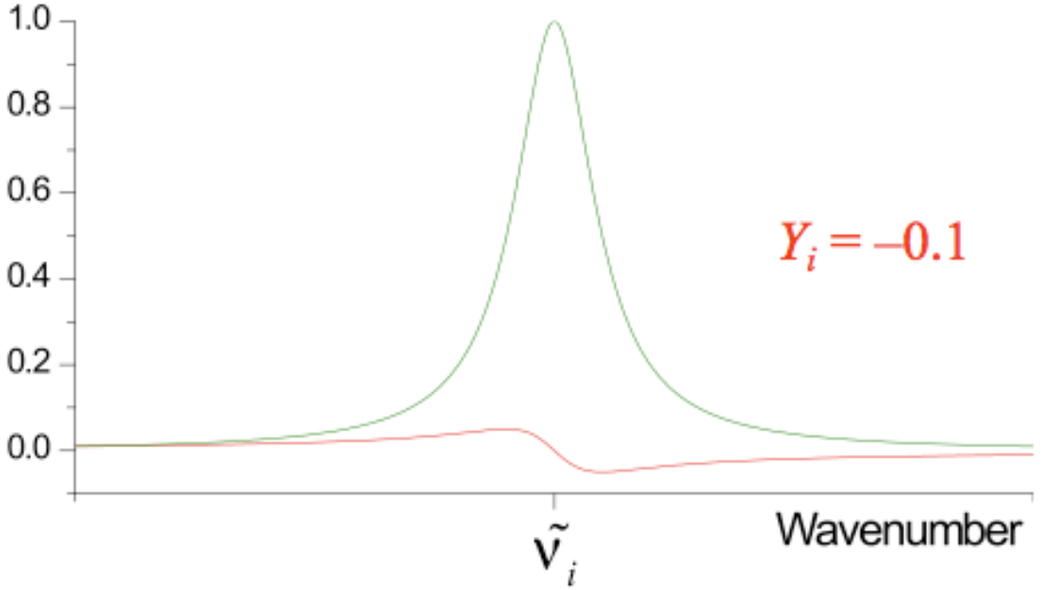
Line-mixing



Lévy, Lacome, Chackerian, in "*Spectroscopy of the Earth's atmosphere and interstellar medium*", Academic Press (1992)

P. Rosenkranz, IEEE Trans. Antennas Propag. **23**, 498 (1975)

$$g\left(\tilde{\nu}-\tilde{\nu}_i\right)=\frac{1}{\pi}\frac{\gamma_L+Y_i\left(\tilde{\nu}-\tilde{\nu}_i\right)}{\left(\tilde{\nu}-\tilde{\nu}_i-\Delta\tilde{\nu}\right)^2-\gamma_L^{\,2}}$$



Grigoriev *et al.*, JQSRT 69 (2001) 189

Conclusion

- **Lecture** = *Overview of **some** of the building blocks of molecular spectra*
- Summary
  - Vibration-rotation energies, transitions and intensities
  - Coriolis and anharmonic resonances
  - Line profiles
- Much more to say
  - Instrumental contributions
  - Molecular symmetry, electronic transitions, interactions
  - …

The end