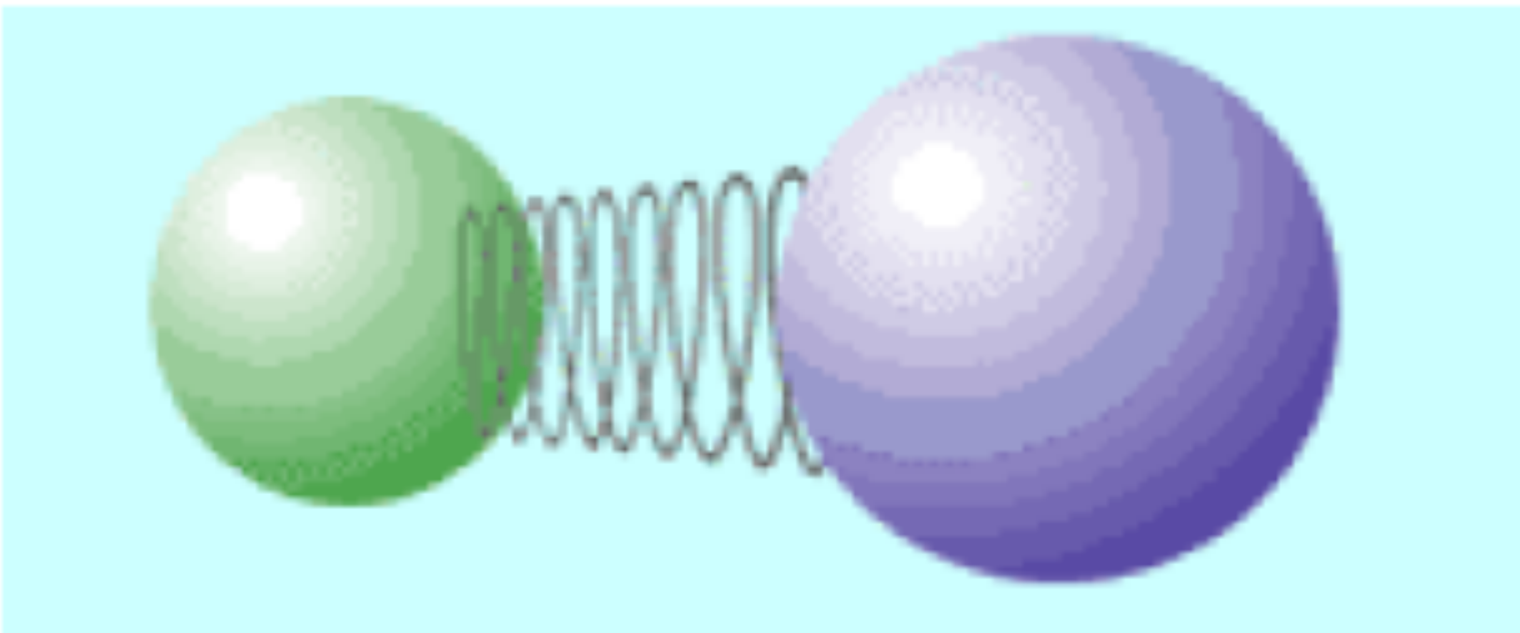
Vibrational Energy Structure

$$H\Psi = E\Psi$$

Hamiltonian is the kinetic and potential energy of the atoms vibrating in the potential set up by the positions of the nuclei.

Diatomic molecules

What is the possible vibrational motion?



Classically the frequency of oscillation for 2 atoms of mass m_1 and m_2 connected by a spring with constant k is

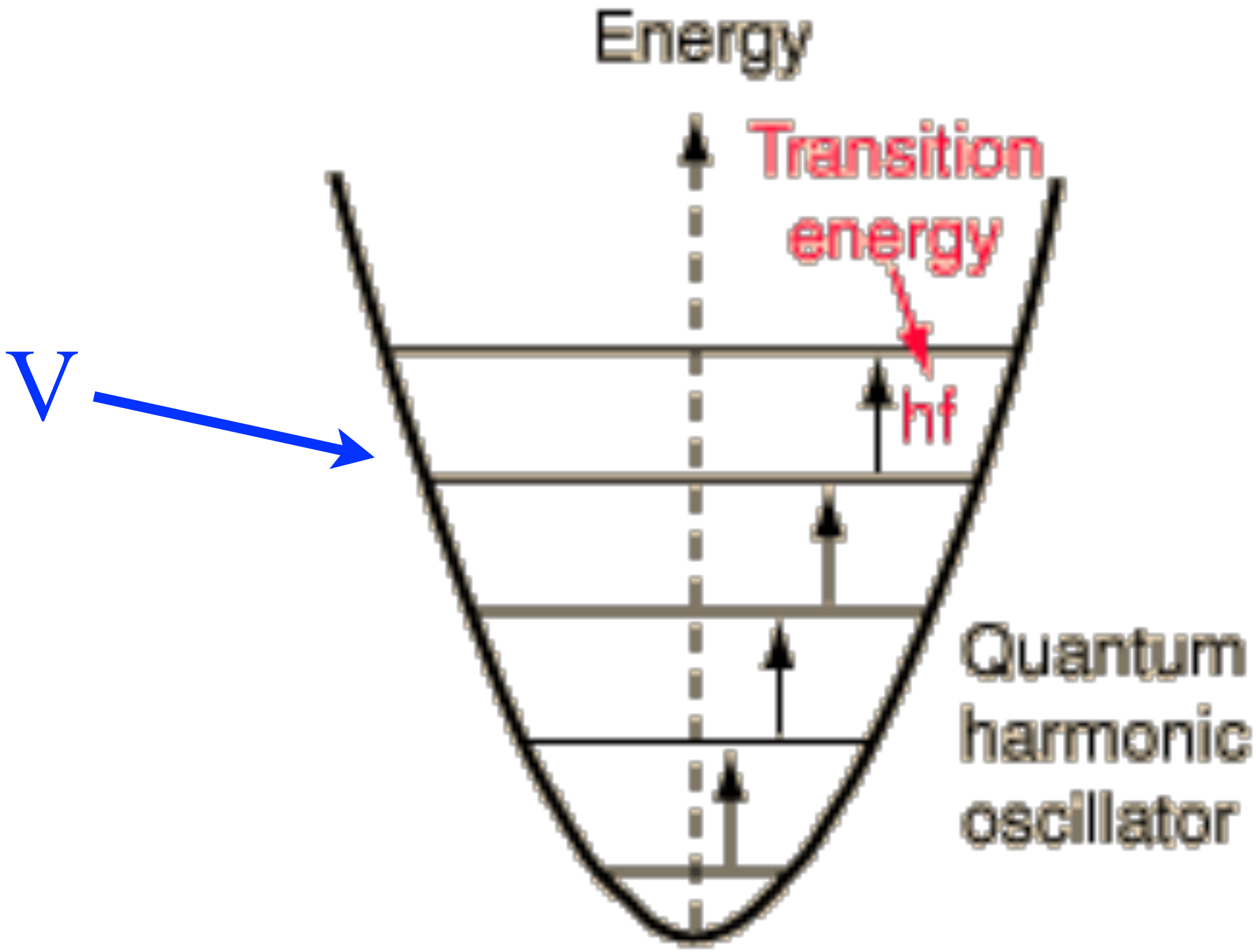
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass of the system

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Quantum Solution

solution is frequency ν_0 of a harmonic oscillator. This maps out a potential



Energy

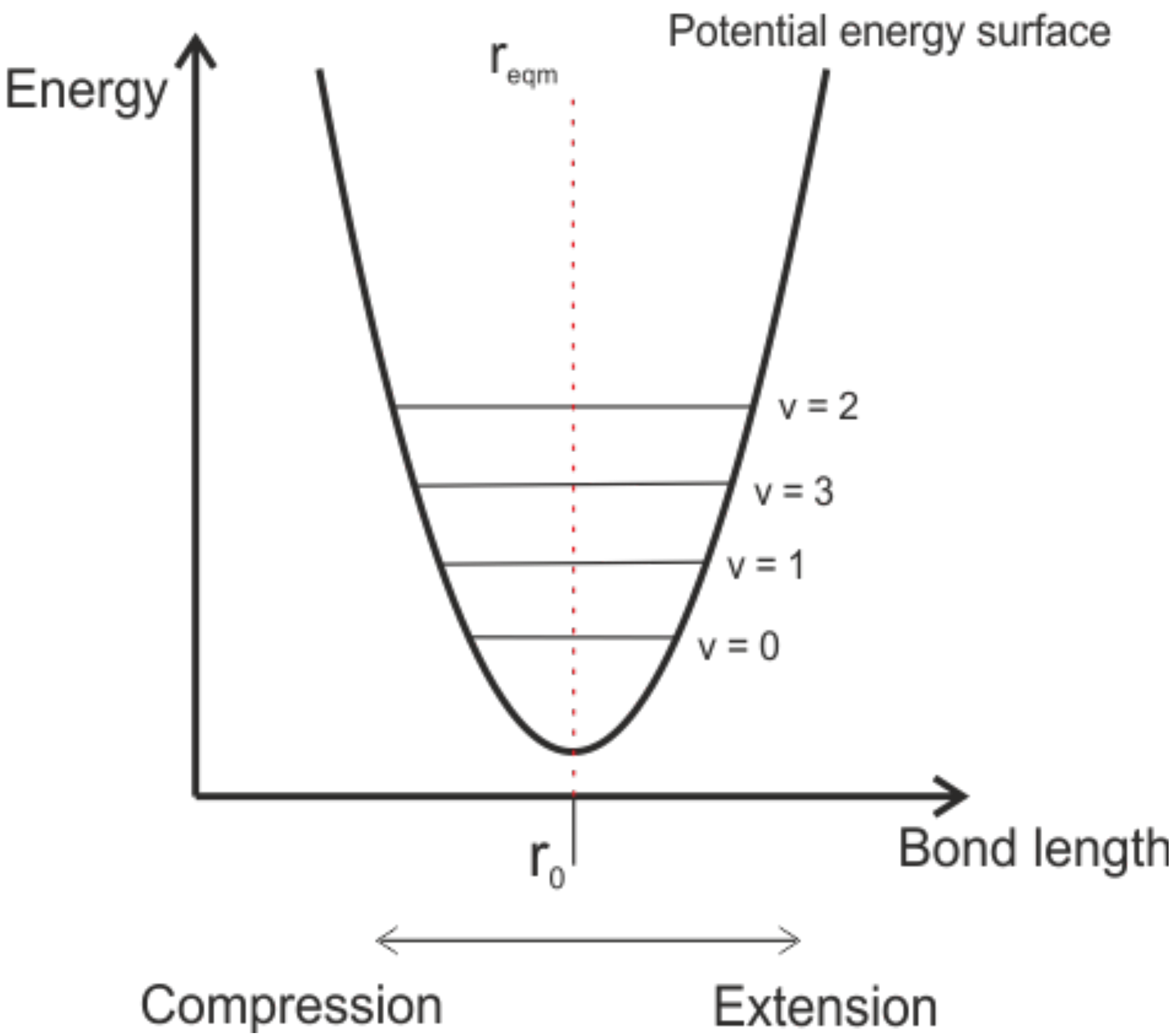
the energy of the harmonic oscillator *i* is

$$E_i = \left(\mathrm{v}_\mathrm{i} + \tfrac{1}{2}\right) h\nu_i$$

where v is an integer (quantum number)

v = 0, 1, 2, 3, …

The Simple Harmonic Oscillator

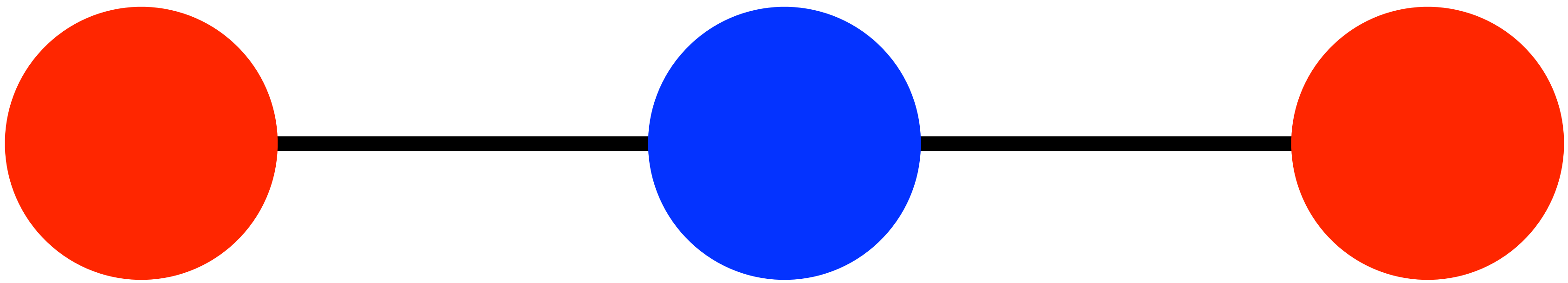


Vibrational Energy

$$E(\nu_1,\nu_2,\nu_3)=\left(\mathrm{v}_1+\tfrac{1}{2}\right)\omega_1+\left(\mathrm{v}_2+\tfrac{1}{2}\right)\omega_2+\left(\mathrm{v}_3+\tfrac{1}{2}\right)\omega_3\cdots$$

see Herzberg (Herzberg, G, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1960.) for details

Linear triatomic



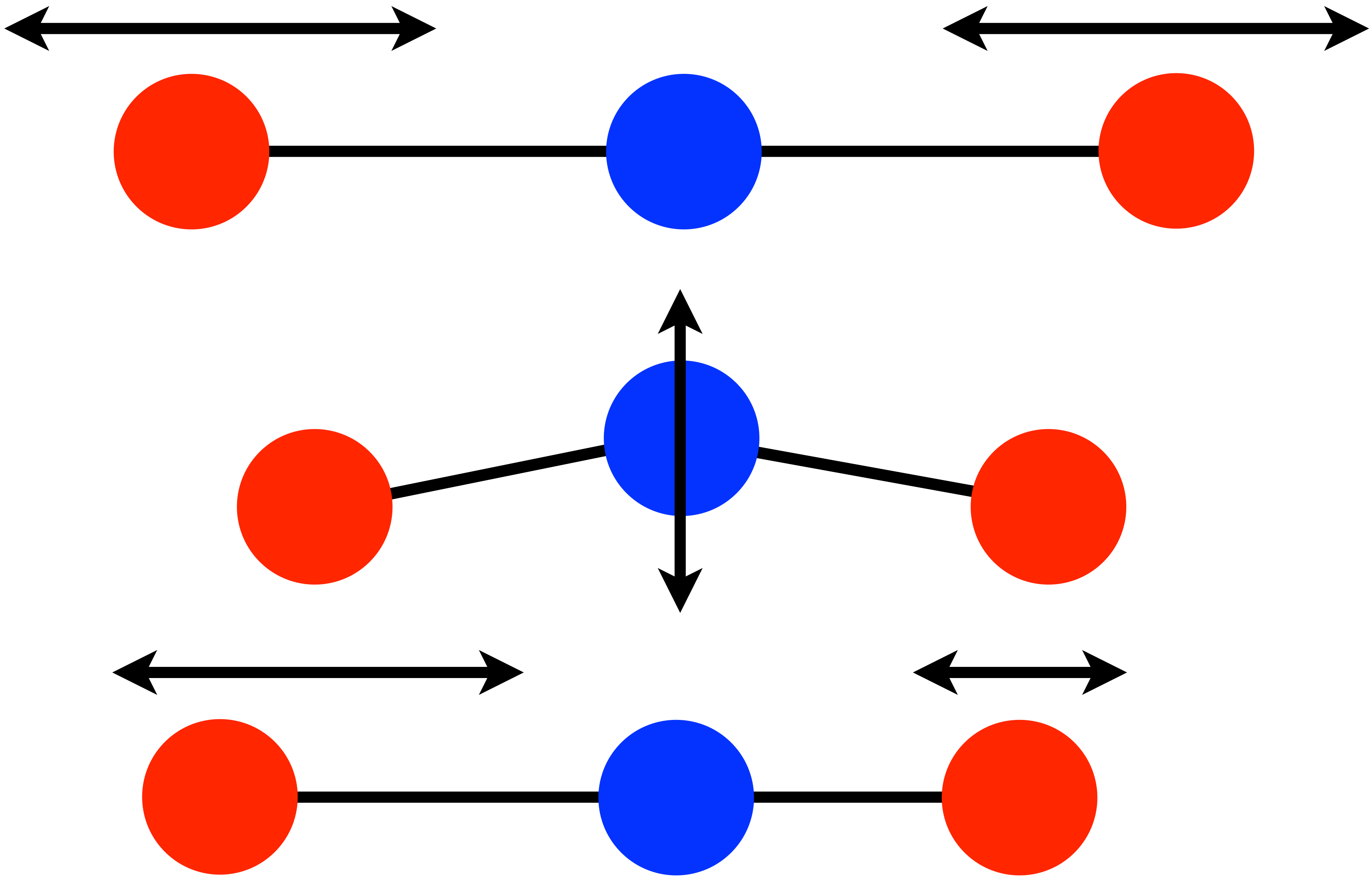
What motions are possible?

Basis Set

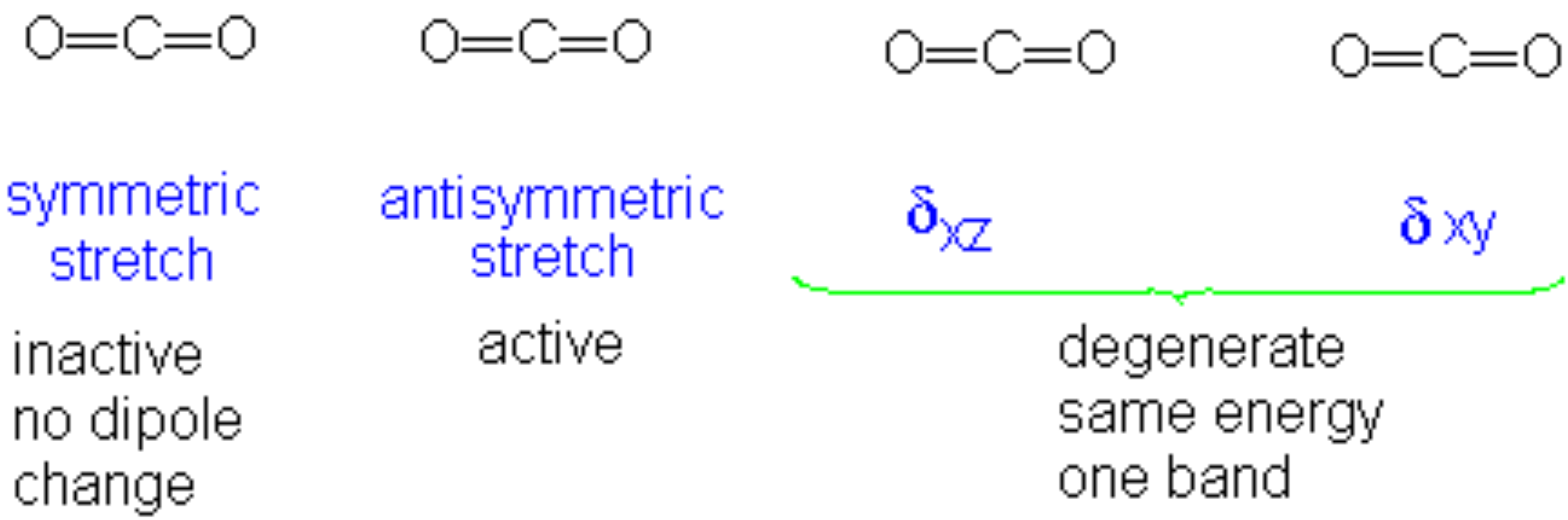
To map all motions is complicated.

Is there a set of basis vectors that will allow us to describe any motion?

normal modes



CO_2



O=C=O
O=C=O
O=C=O
O=C=O
symmetric stretch
antisymmetric stretch
δxz
δ xy
inactive
no dipole
change
active
degenerate
same energy
one band

Vibrational Energy

bend mode:

$\nu_2 = 667.37998\ \mathrm{cm}^{-1}$

symmetric stretch mode:

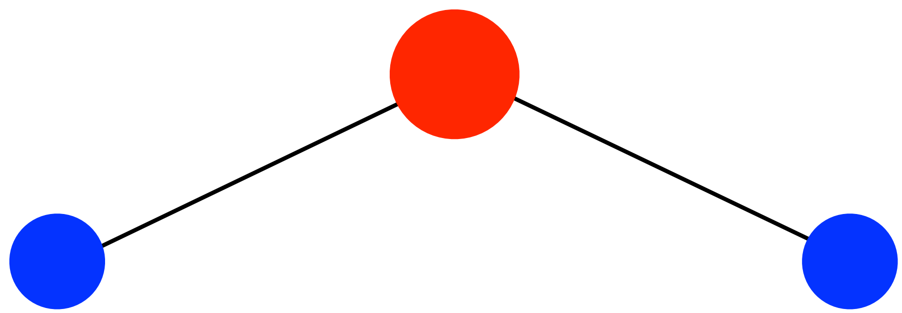
$\nu_1 = 1388.18435\ \mathrm{cm}^{-1}$

asymmetric stretch mode:

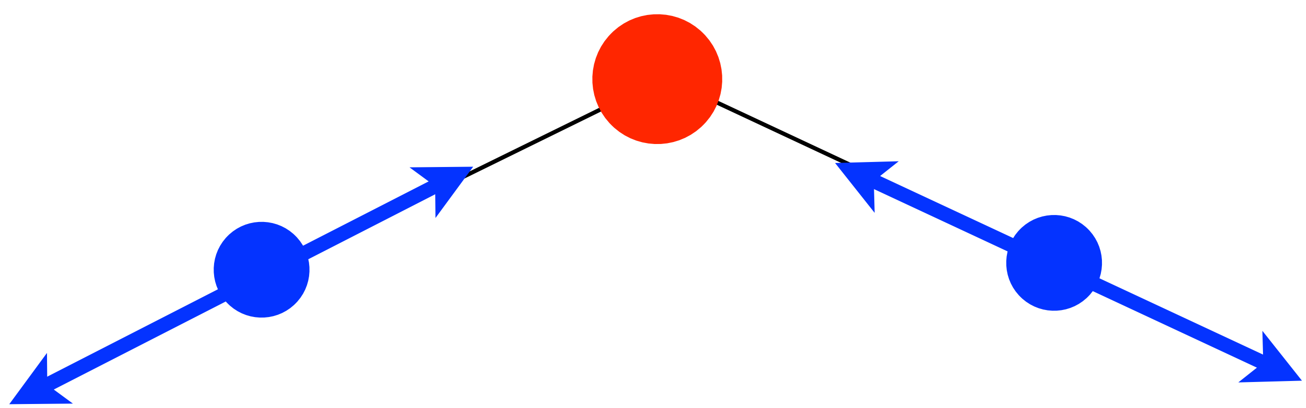
$\nu_3 = 2349.14295\ \mathrm{cm}^{-1}$

Non-linear triatomic

H_2O as an example



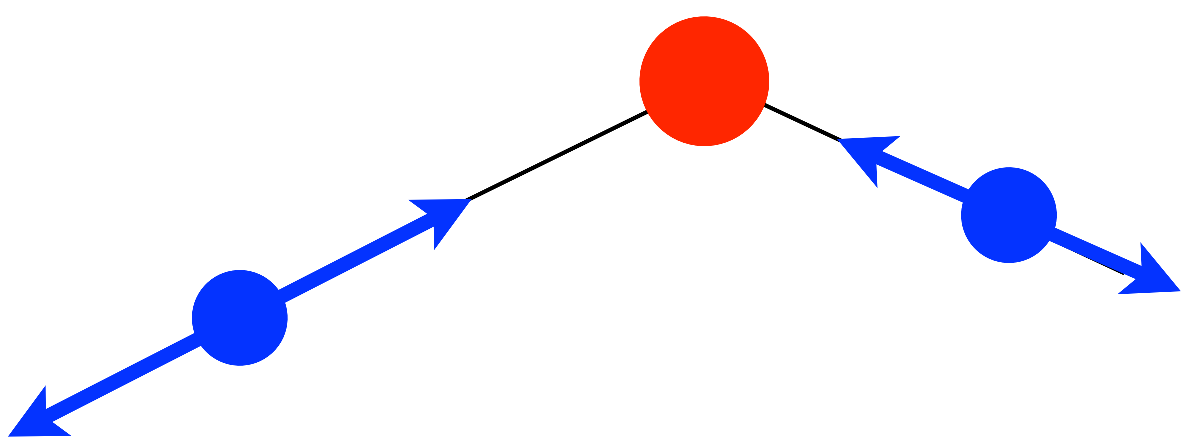
Vibrational basis vectors
symmetric stretch mode
$\nu_1 = 3657.0532 \text{ cm}^{-1}$



Vibrational basis vectors

asymmetric stretch mode

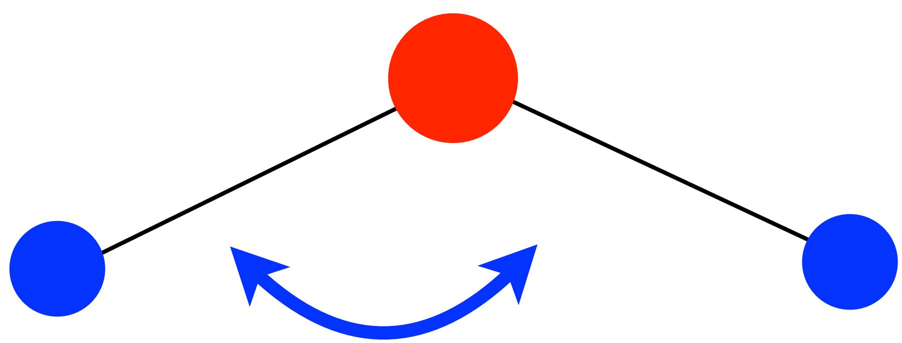
$\nu_3 = 3755.9287\ \text{cm}^{-1}$

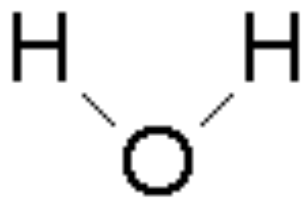


Vibrational basis vectors

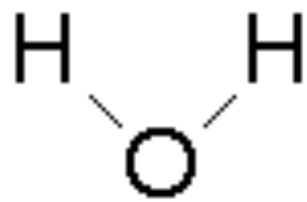
bend mode

$\nu_2 = 1594.7498\ \mathrm{cm}^{-1}$

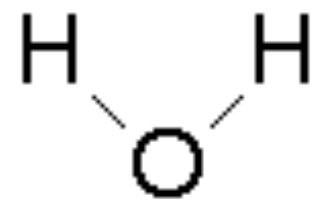




antisymmetric stretch

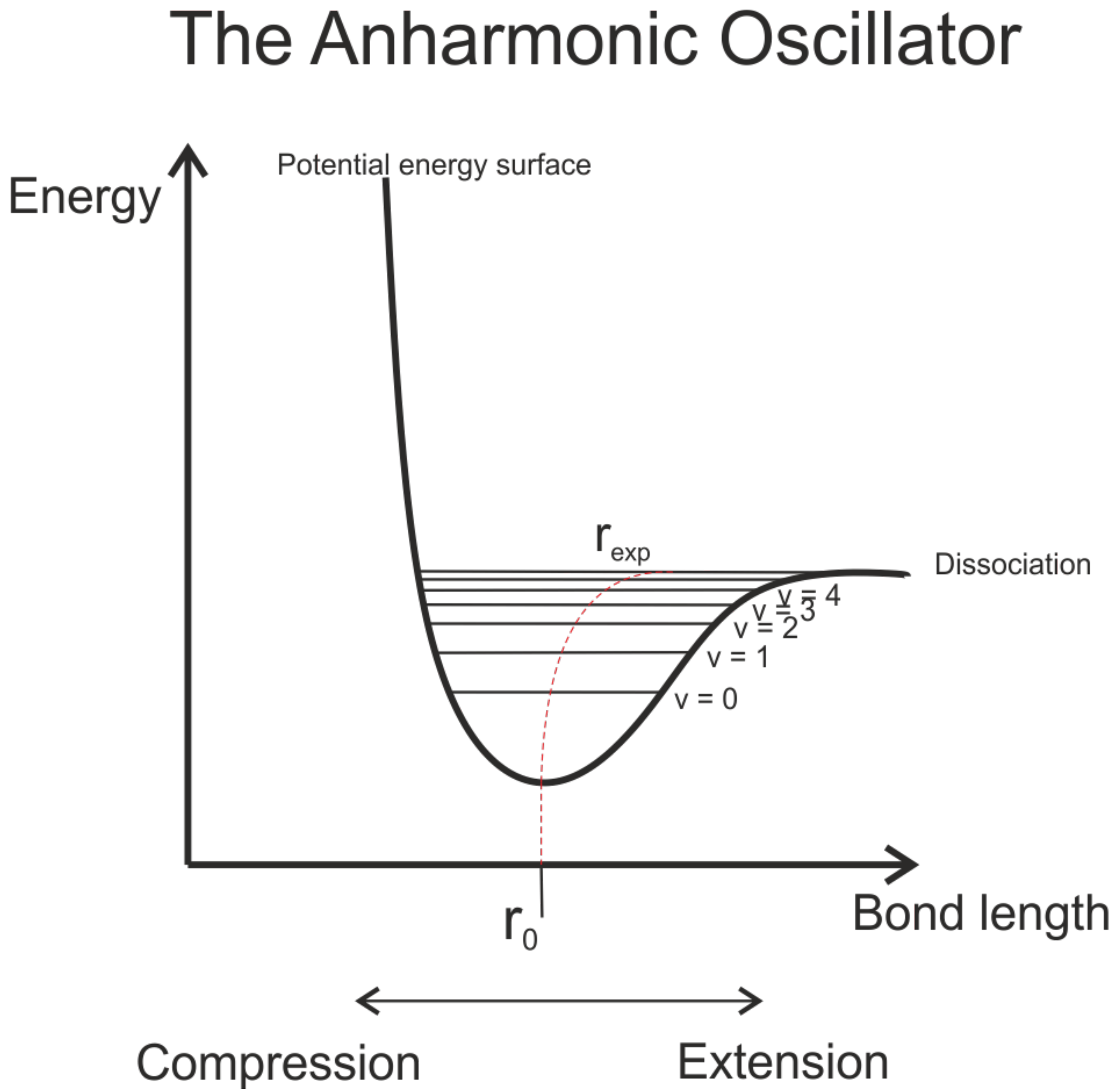


symmetric stretch



scissoring bend

Molecules are not harmonic oscillators



Anharmonic Corrections

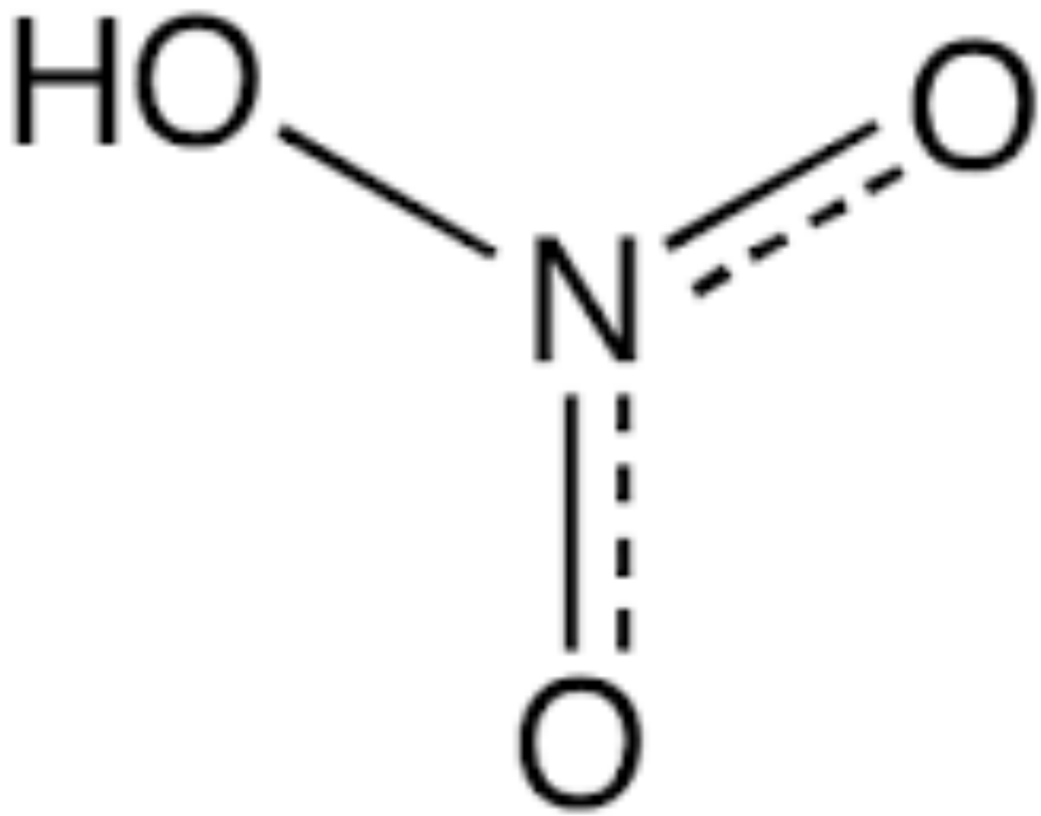
$$E(\nu_1, \nu_2, \nu_3) = \left(\mathrm{v}_1 + \tfrac{1}{2}\right)\omega_1 + \left(\mathrm{v}_2 + \tfrac{1}{2}\right)\omega_2 + \left(\mathrm{v}_3 + \tfrac{1}{2}\right)\omega_3 +$$

$$x_{11}\left(\mathrm{v}_1 + \tfrac{1}{2}\right)^2 + x_{22}\left(\mathrm{v}_2 + \tfrac{1}{2}\right)^2 + x_{33}\left(\mathrm{v}_3 + \tfrac{1}{2}\right)^2 +$$

$$x_{12}\left(\mathrm{v}_1 + \tfrac{1}{2}\right)\left(\mathrm{v}_2 + \tfrac{1}{2}\right) + x_{13}\left(\mathrm{v}_1 + \tfrac{1}{2}\right)\left(\mathrm{v}_3 + \tfrac{1}{2}\right) +$$

$$x_{23}\left(\mathrm{v}_2 + \tfrac{1}{2}\right)\left(\mathrm{v}_3 + \tfrac{1}{2}\right) + \cdots$$

Large molecules - HNO_3



Large molecules - HNO_3

normal modes in cm^{-1}

$\omega_1 = 3550.$ $\omega_6 = 647.$

$\omega_2 = 1710.$ $\omega_7 = 579.$

$\omega_3 = 1326.$ $\omega_8 = 762.$

$\omega_4 = 1303.$ $\omega_9 = 458.$

$\omega_5 = 879.$

Intensities

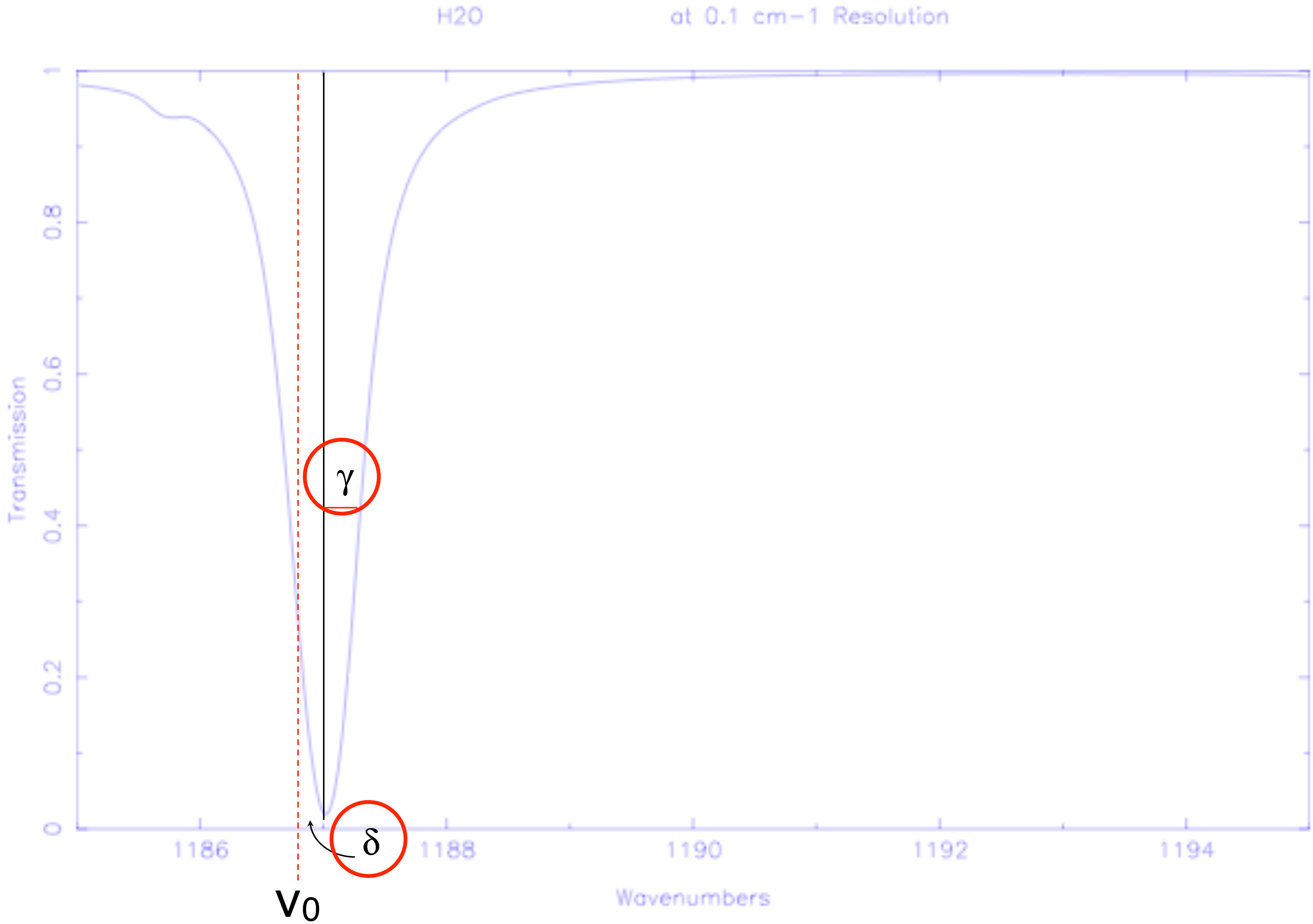
$$S_{f\leftarrow i}(T)=\frac{8\pi^3}{3hc}\frac{d_i e^{-E_i/kT}}{Q}\nu_{f\leftarrow i}\left(1-e^{-h\nu_{f\leftarrow i}/kT}\right)\frac{1}{d_i}\sum_{\xi,\xi'}\left|R_{f\xi\leftarrow i\xi'}\right|^2$$

units are cm^{-1}/(molecule cm^{-2})

S is temperature dependent

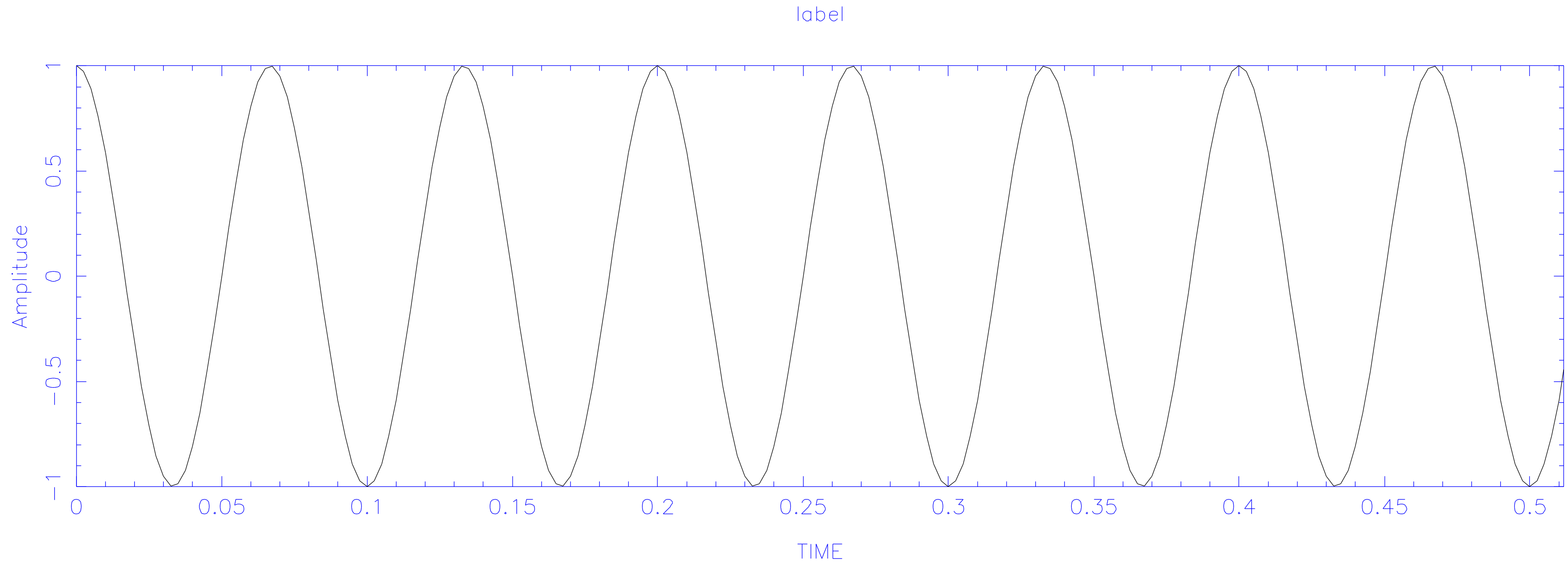
Line Shape

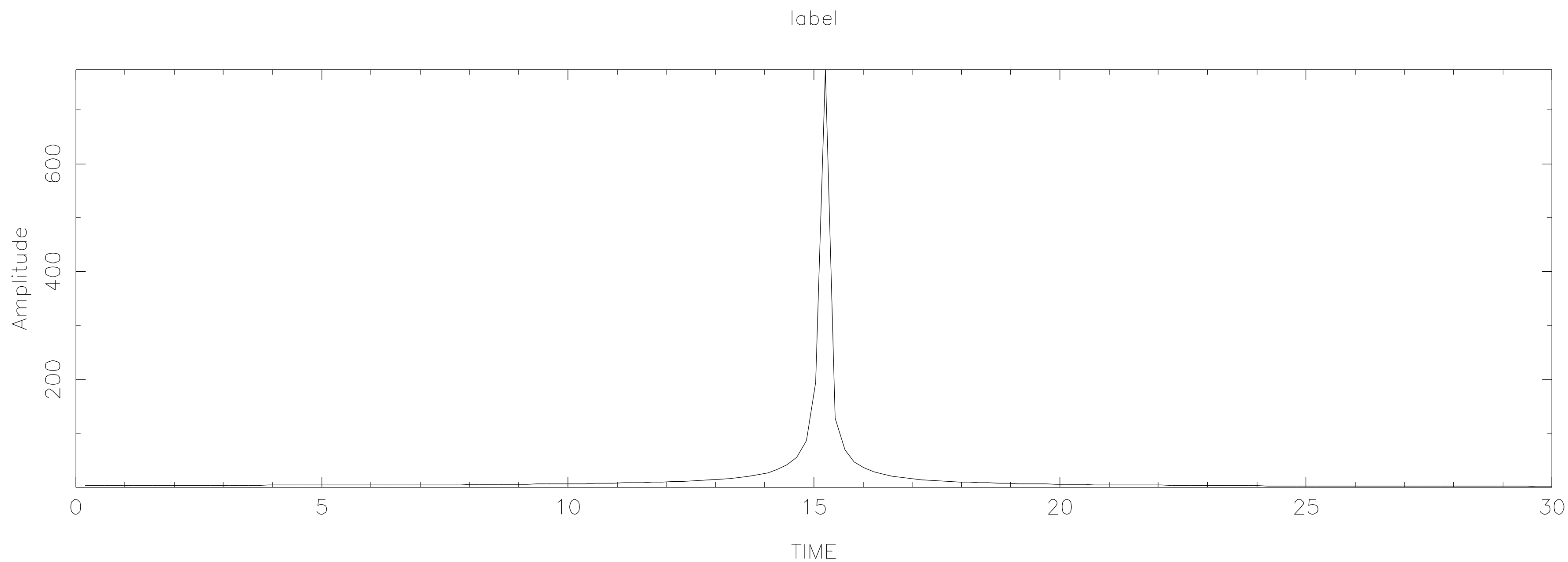
The lines we see in the spectra have a particular shape. The features can be understood in terms of line shape theory.



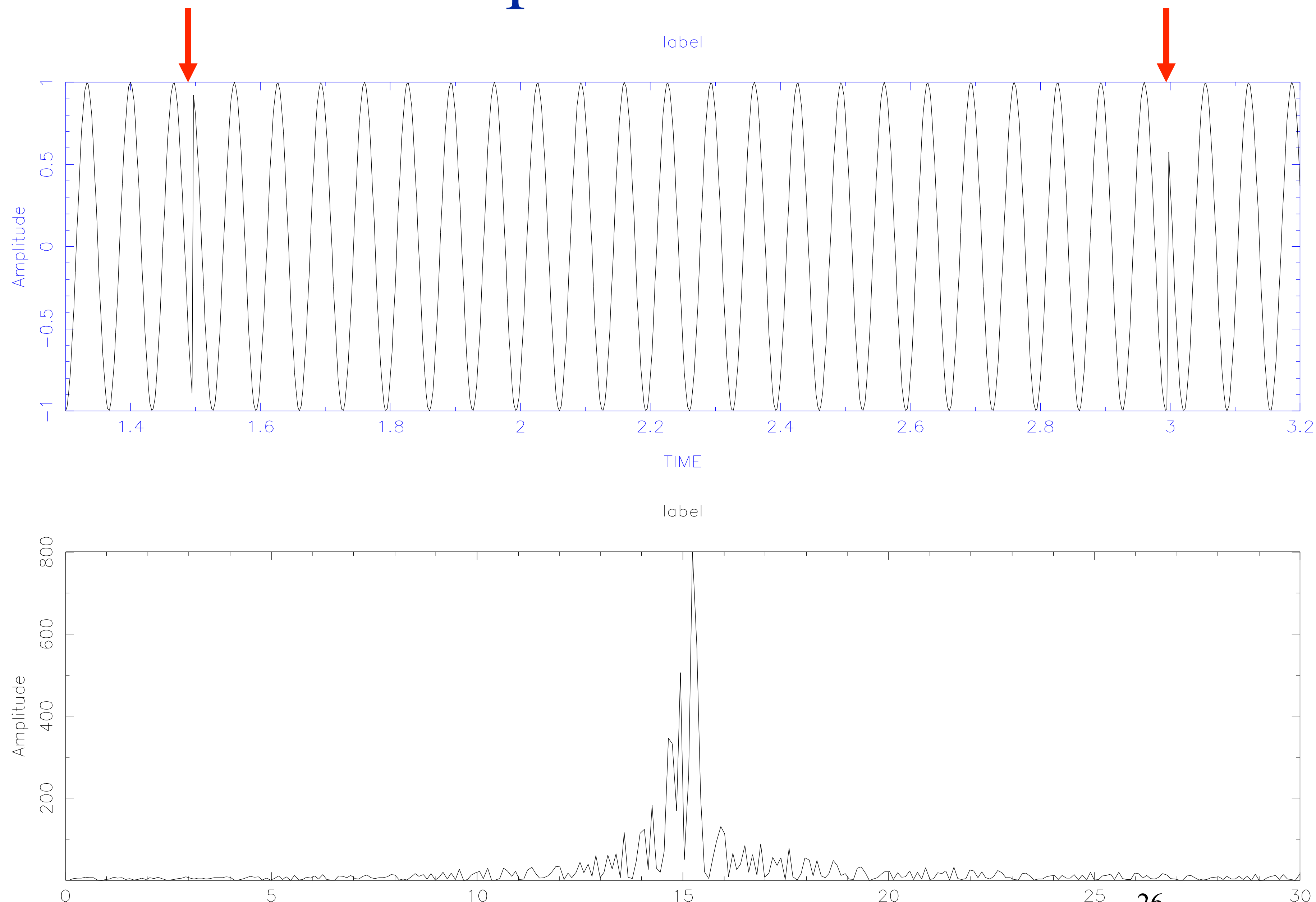
H2O
at 0.1 cm-1 Resolution
Transmission
0
0.2
0.4
0.6
0.8
1
1186
1188
1190
1192
1194
Wavenumbers
γ
δ
v0

A. A. Michelson in the 1890s



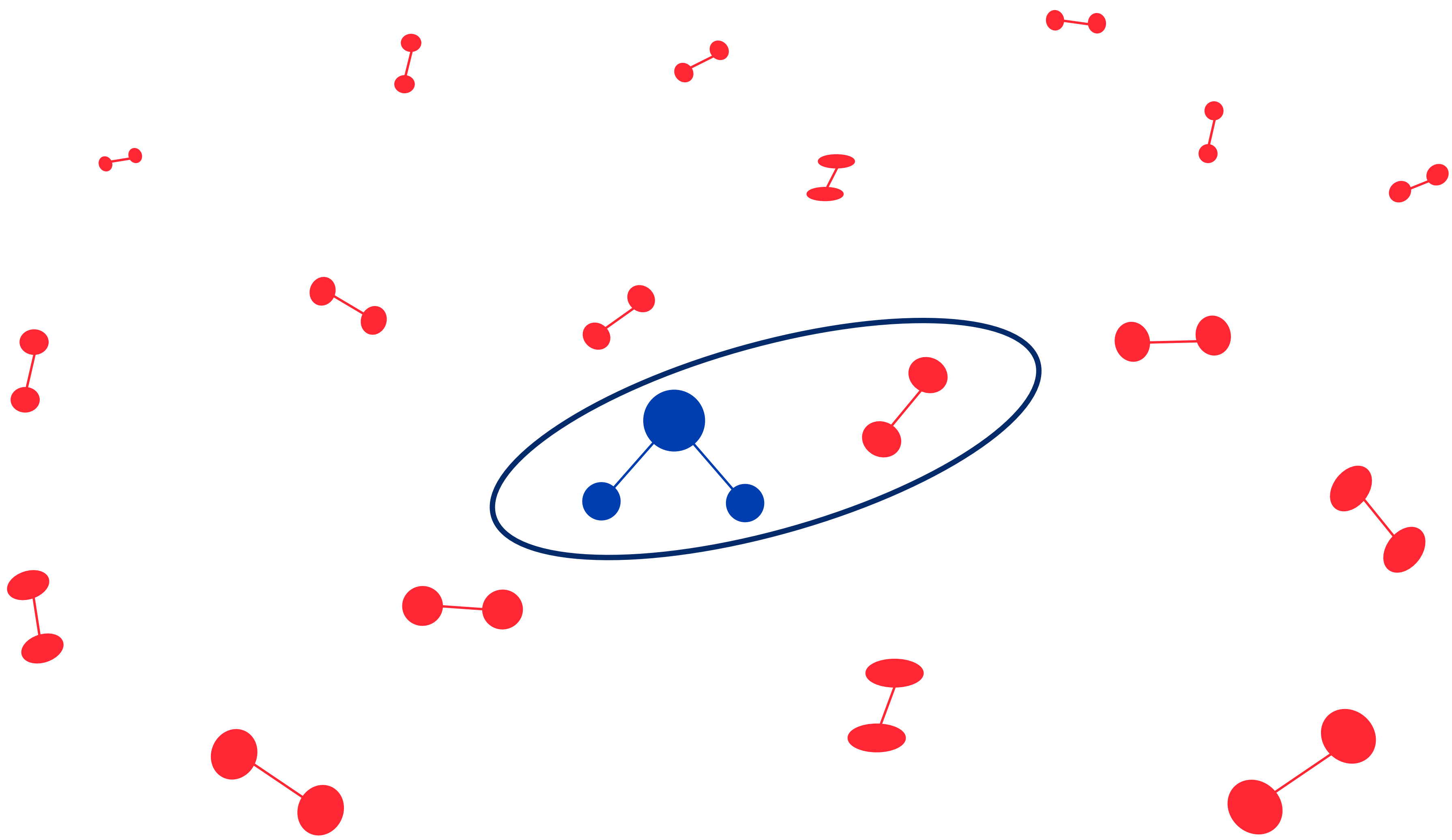


Interruption of radiation



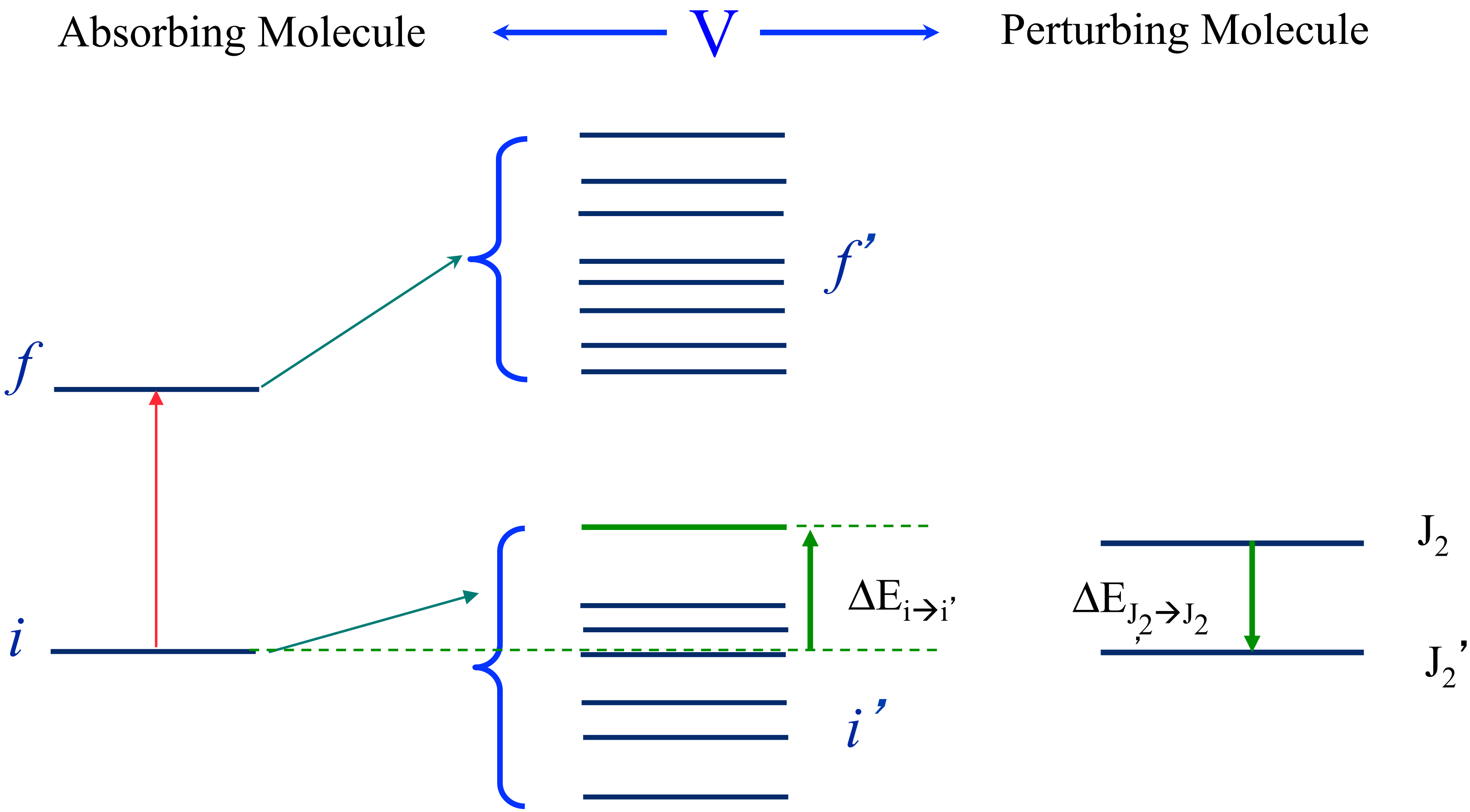
w cm^{-1}

The System



a single radiating molecule surrounded by a gas of perturbers

Connecting states



optical transitions

collisionally induced transitions

Semi-classical Robert-Bonamy formalism

$$\left(\gamma - i\delta\right)_{f \leftarrow i} = \frac{n_2}{2\pi c}\left\langle v \times \left[1 \quad - e^{-i\left\{{}^{I}S_1\left(f,i,J_2 v,b\right)+{}^{I}S_2\left(f,i,J_2 v,b\right)\right\}} e^{{}^{R}S_2}\right]\right\rangle_{v,b,J_2}$$

γ and δ are temperature dependent

By making calculations or measurements at different temperatures we can model the temperate dependence of the line shape parameters

Temperature Dependence of γ

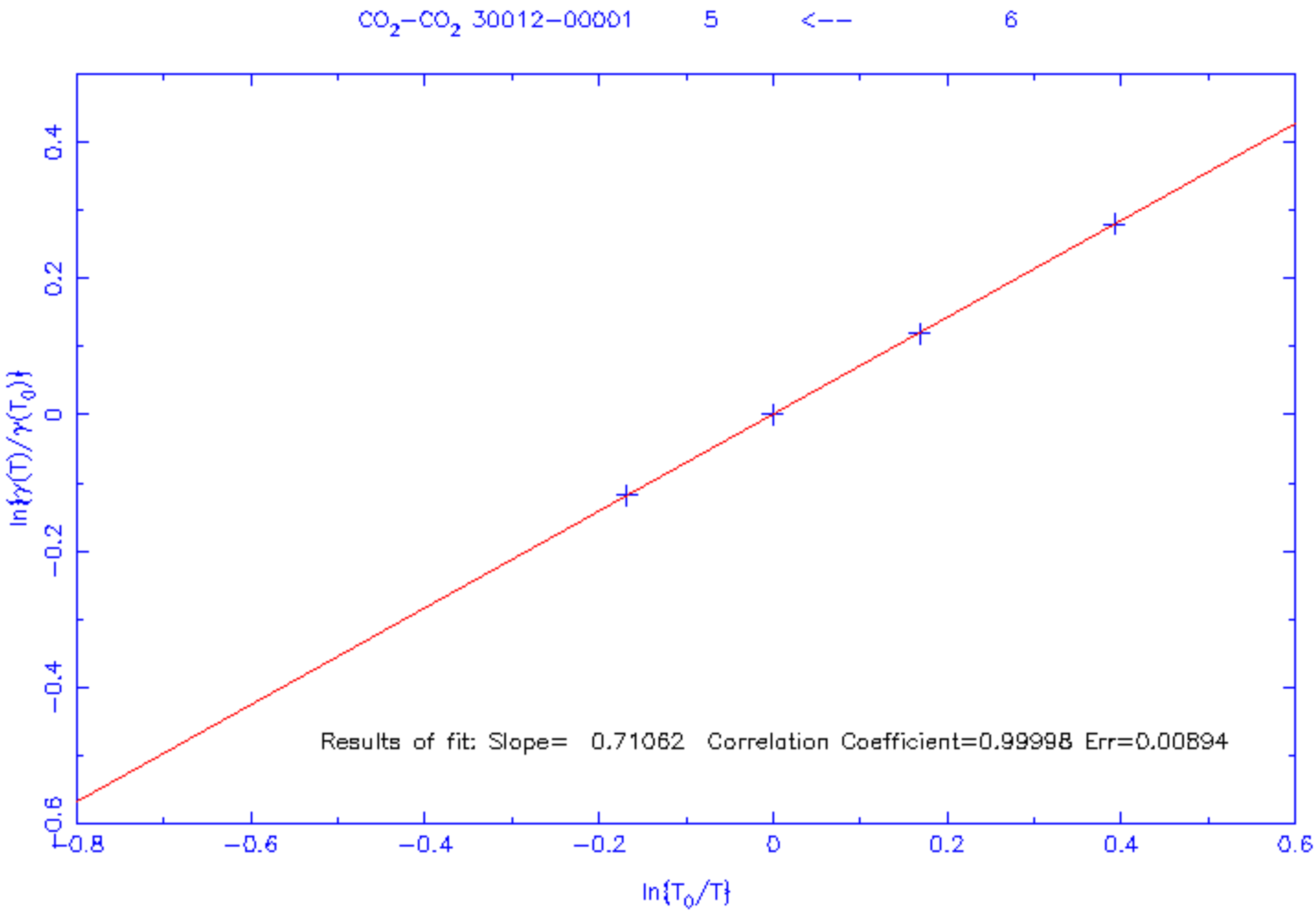
- Power law form

$$\gamma(T) = \gamma(T_0)\left[\frac{T_0}{T}\right]^N$$

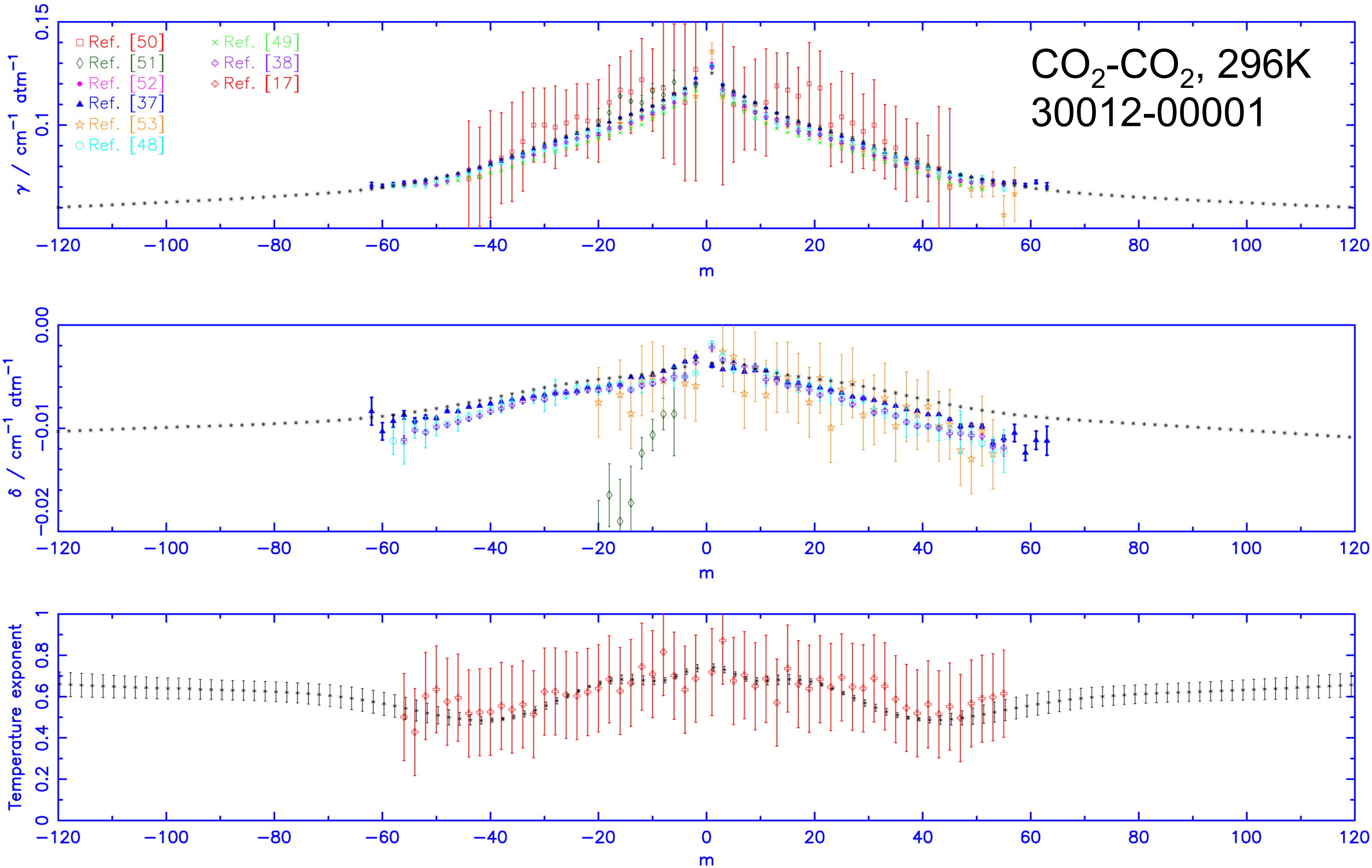
- In practice plot (fit)

$$\ln\left\{\frac{\gamma(T)}{\gamma(T_0)}\right\} = N\ \ln\left\{\frac{T_0}{T}\right\}$$

Temperature dependence of $\gamma(CO_2\text{-}N_2)$



Validation of the CRB Calculations



uncertainty

How well can we simulate a spectra?

How well can we do a retreival?

uncertainty

line positions - 4^{th} place after decimal or better

S generally between 1 and 5 percent for most molecules.

γ and δ least well known.

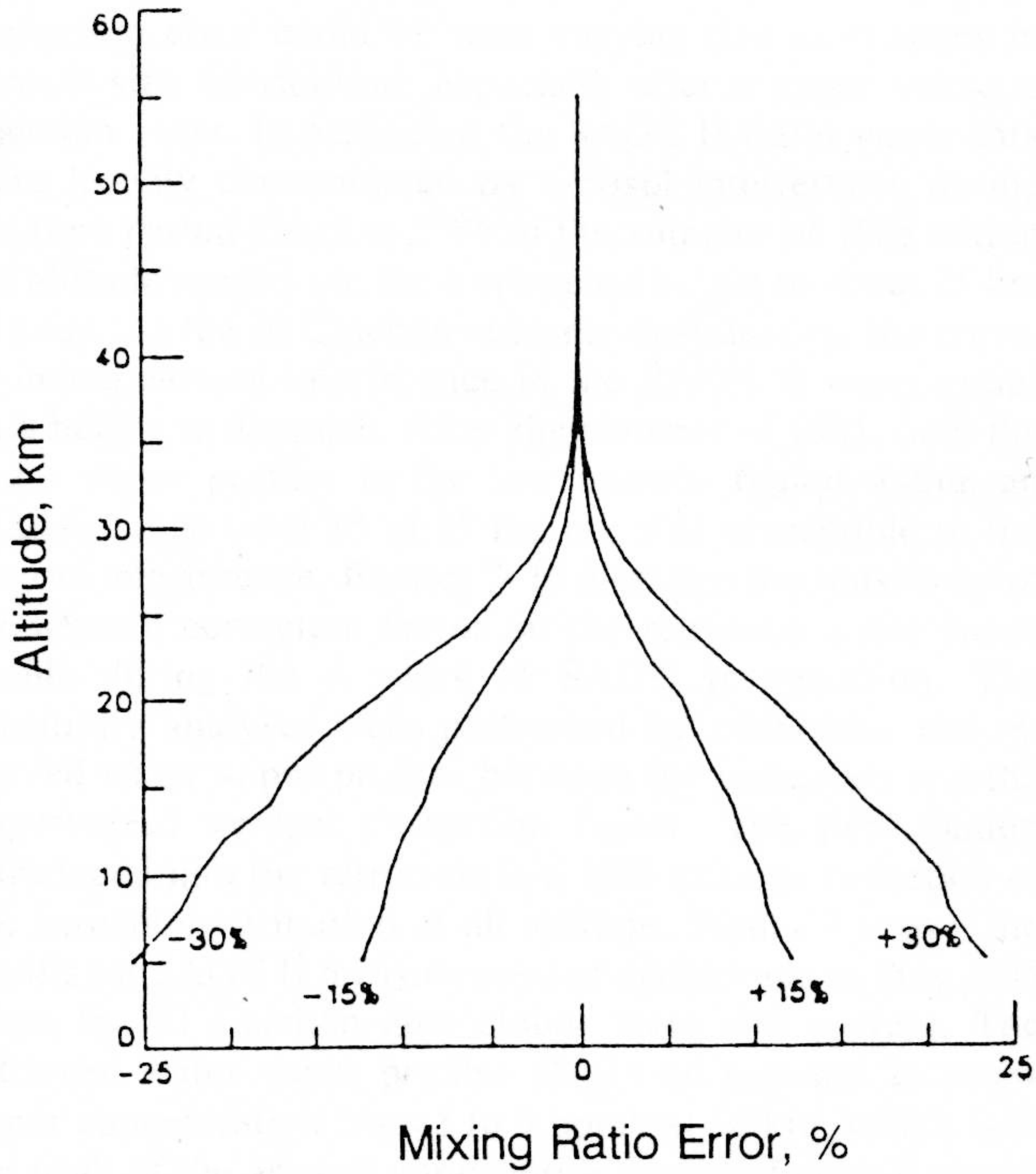


Fig. 4. Sensitivity study for SAGE II water vapor retrievals showing results obtained from uncertainties in the air broadened half widths of ±15 and ±30%.

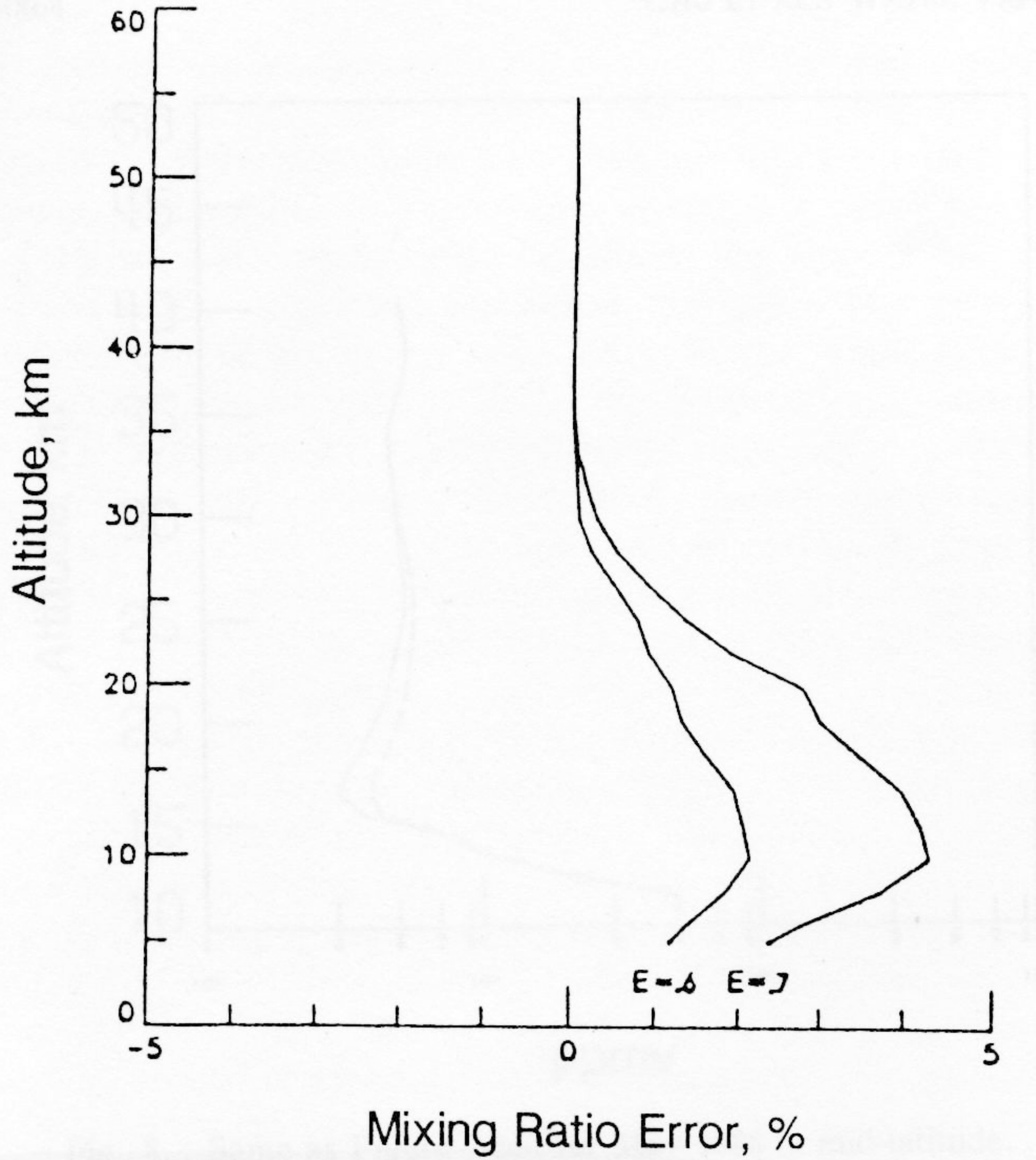


Fig. 5. Similar to Figure 4 except the sensitivity study is performed by varying the exponent in the air broadened half-width temperature correction factor from 0.5 to 0.6 and 0.7.

The Effect of the Half-Width of the 22-GHz Water Vapor Line on Retrievals of Temperature and Water Vapor Profiles With a 12-Channel Microwave Radiometer

James C. Liljegren, Sid-Ahmed Boukabara, Karen Cady-Pereira, and Shepard A. Clough

IEEE TRANSACTIONS ON GEOSCIENCE AND REMOTE SENSING, **43**, 1102-1108, 2005

***Abstract*—We show that observed biases in retrievals of temperature and water vapor profiles from a 12-channel microwave radiometer arise from systematic differences between the observed and model-calculated brightness temperatures at five measurement frequencies between 22 and 30 GHz. Replacing the value for the air-broadened half-width of the 22-GHz water**

In evaluating the MWRP for the ARM Program, Liljegren [3] observed significant biases, in comparison with radiosonde data, in the water vapor and temperature profiles retrieved from the MWRP with the artificial neural network algorithms supplied by the manufacturer [4], which were based on the Rosenkranz

Replacing the value for the air-broadened half-width of the 22-GHz water vapor line used in the Rosenkranz absorption model with the 5% smaller half-width from the HITRAN compilation largely eliminated the systematic differences in brightness temperatures. An *a priori* statistical retrieval based on the revised model demonstrated significant improvements in the accuracy and vertical resolution of the retrieved temperature and water vapor profiles.

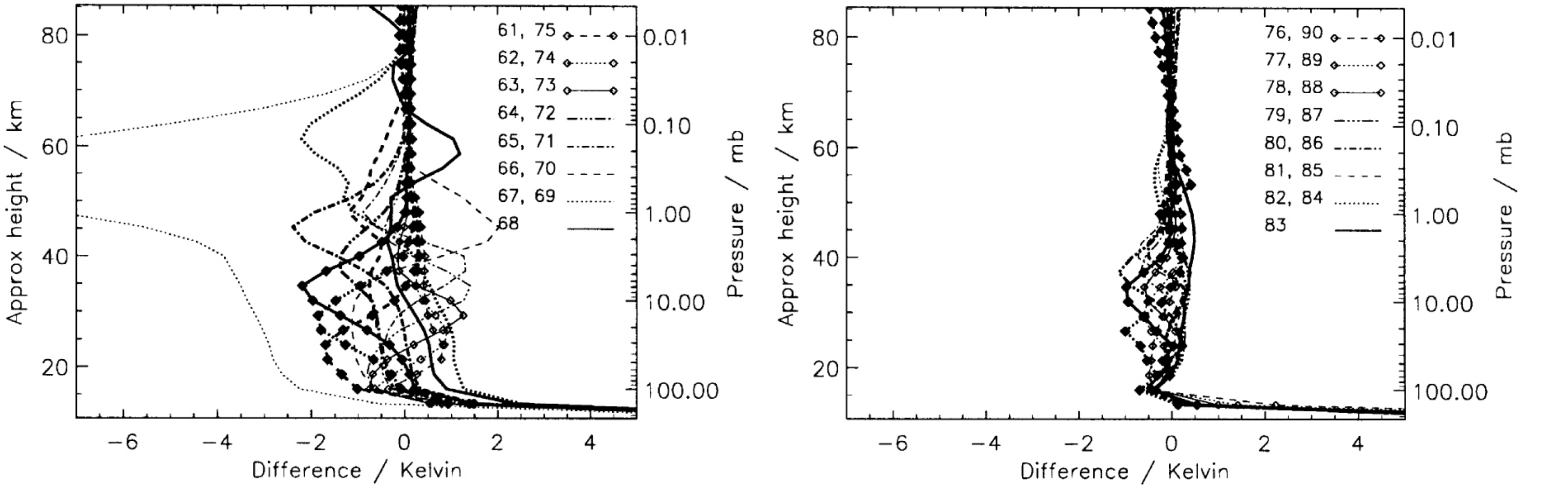


Fig. 5. Residuals (recalculated radiances – measured radiances) for a retrieval in which the sideband ratios are retrieved. Left panel: channels 61–75, the thin lines are for channels 69–75, the thick lines for channels 61–68. Right panel: channels 77–90, the thin lines are for channels 77–83, the thick lines for channels 84–90.

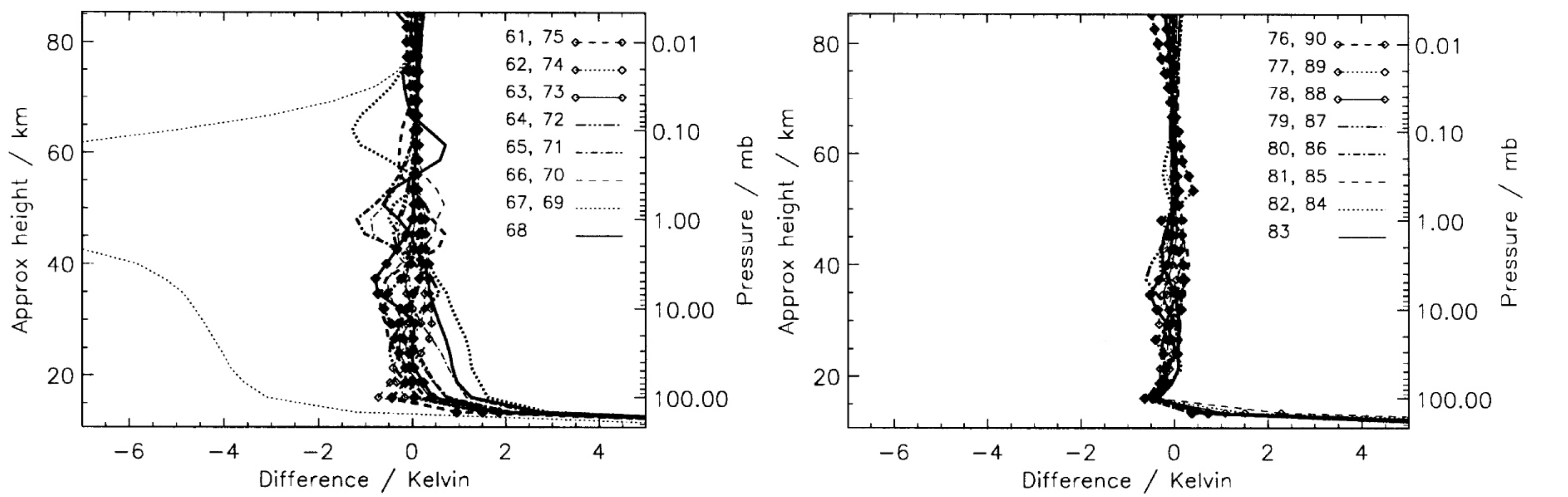


Fig. 8. Residuals (recalculated radiances – measured radiances) for a retrieval in which the sideband ratios and the pressure shift and broadening parameters are retrieved. Left panel: channels 61–75, the thin lines are for channels 69–75, the thick lines for channels 61–68. Right panel: channels 77–90, the thin lines are for channels 77–83, the thick lines for channels 84–90.

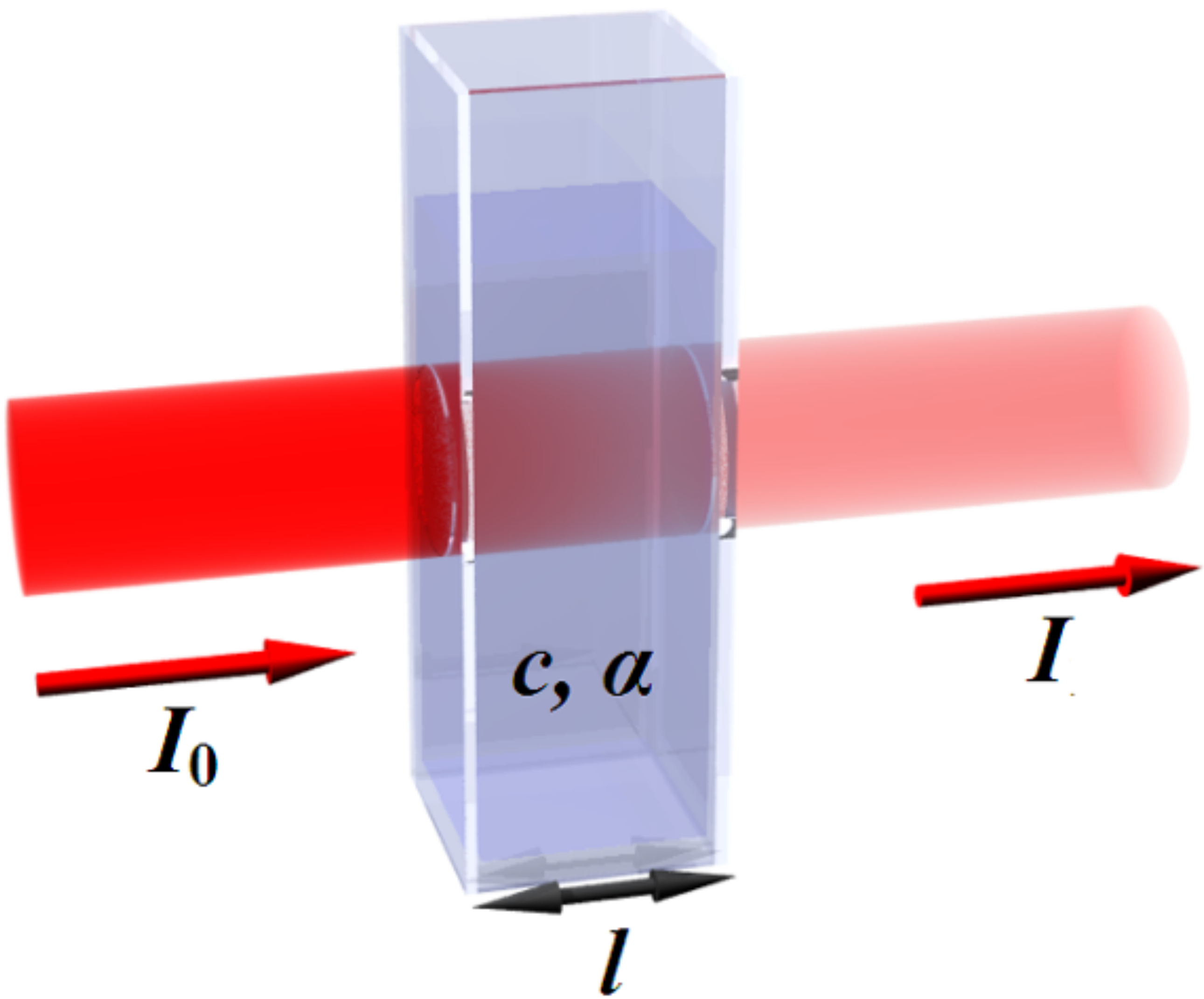
ν, S, γ, δ, E”

These are the spectral parameters needed to simulate a spectra.

Given these parameters how do we simulate a spectra?

What happens when light passes through a gaseous medium?

Absorption of Radiation



Observation

The intensity of the light is reduced after passing through a medium.

The reduction is a function of **frequency** (wavelength, wavenumber)

Proportional to **amount of molecules** in the path, **length** of the path, and **temperature**.

Beer–Lambert–Bouguer law

$$dI(\nu) = -k_{\mathrm{v}}(\nu) I(\nu) ds$$

the change in intensity along a path (of gas) ***ds*** is proportional to the amount of matter (gas) along the path.

$$I(\nu) = I_0(\nu) e^{-k_{\mathrm{v}}(\nu) ds}$$

where $k_{\mathrm{v}}(\nu)$ is the volume absorption coefficient

The **absorption coefficient** depends on the **density** of the gas

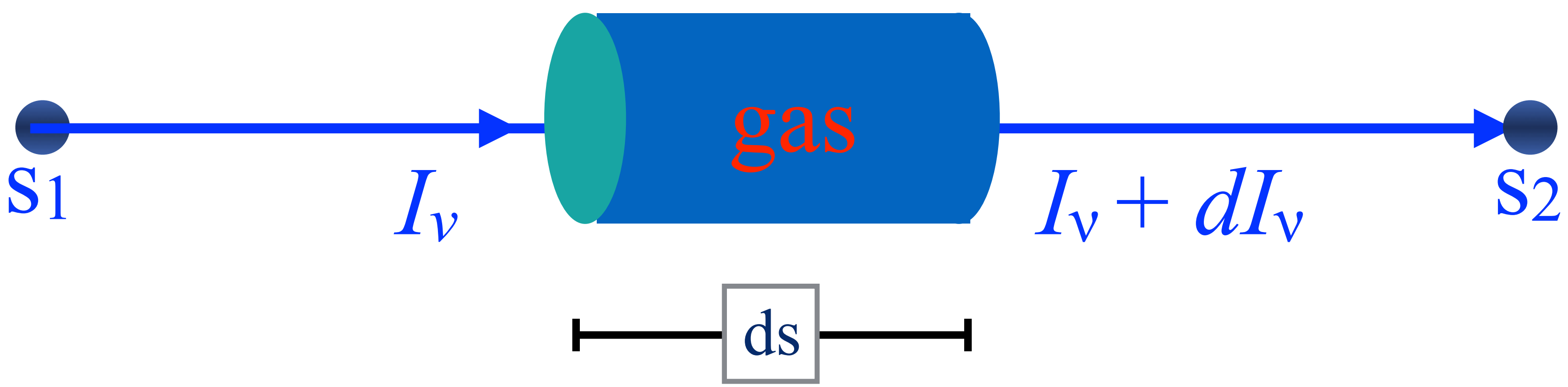
- the **molecular absorption coefficient**, $k_n(\nu) = k_\nu(\nu)/n$, where $\boldsymbol{n}$ is the number density of the absorbing molecules
- the **mass absorption coefficient**, $k_m(\nu) = k_\nu(\nu)/\rho_a$ where ρ_a is the density of the absorbing gas
- the **absorption coefficient at s.t.p**, $k_s(\nu) = k_\nu(\nu)n/n_s$, where n_s is Loschmidt's number ($n_L = N_A/V_m = 2.686\ 763 \times 10^{25}$ molecules/ m^3 at STP).

What is important is the product $\boldsymbol{k_{\mathrm{n}}(\mathrm{v})\,\mathrm{ds}}$ must be **unit less:**
So for each type of coefficient there is a corresponding **different measure of path length.**

we will rewrite

$$I(\nu) = I_0(\nu) e^{-k_\nu(\nu) ds}$$

to emphasize the path



$$I_\nu(s_2) = I_\nu(s_1) e^{-k_\nu(\nu) ds}$$

This equation is often written as

$$I_\nu(s_2) = I_\nu(s_1)\mathcal{T}_\nu(s_1, s_2)$$

where $\mathcal{T}_s(\nu)$ is the *monochromatic transmission function*

$$\mathcal{T}_\nu(s_1, s_2) = e^{-\int_{s_1}^{s_2} k_\nu(\nu)\,ds}$$

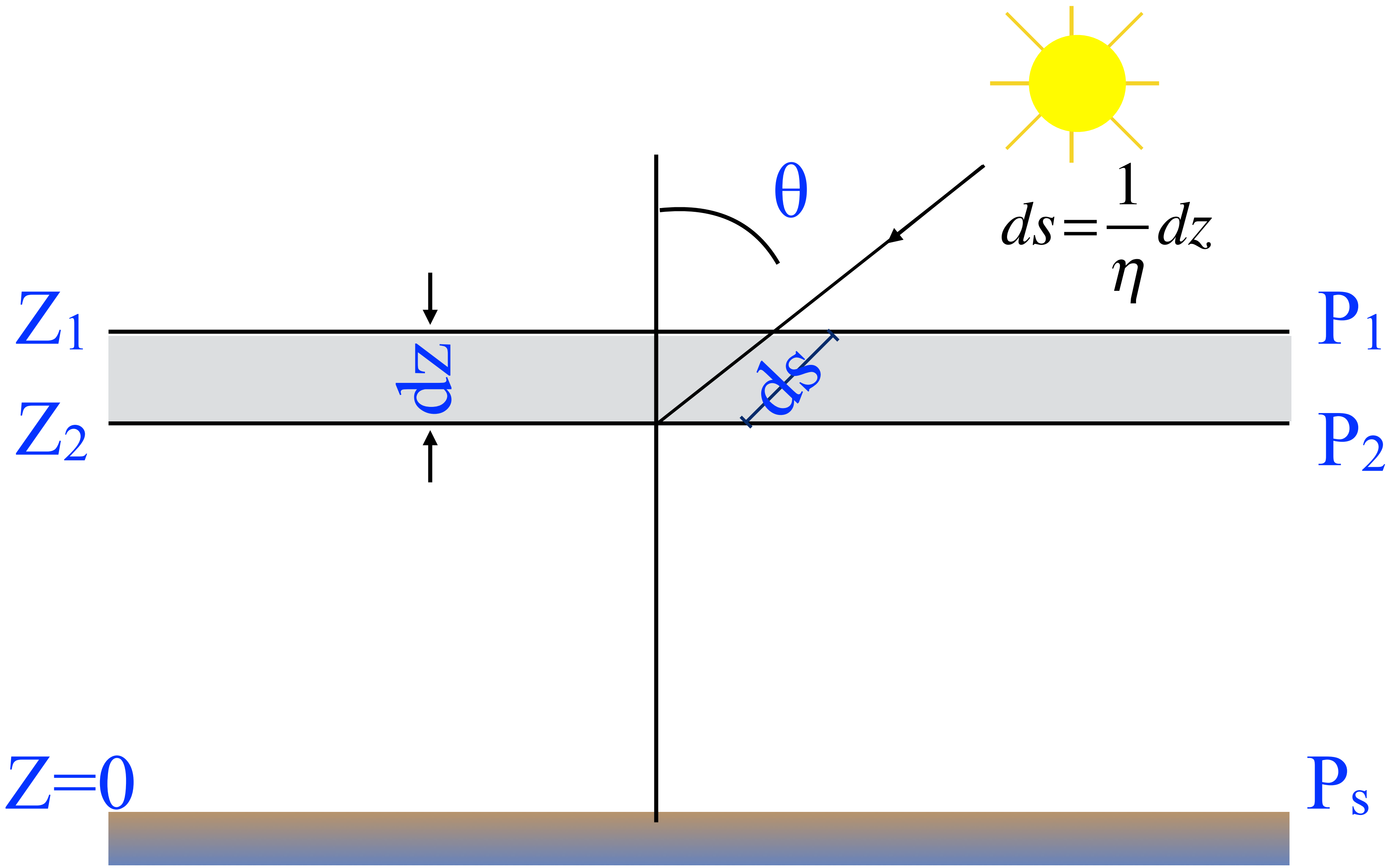
Assuming we know the radiation incident at some point along a path (i.e., at s_1) and we make a measurement of the radiation flowing from the atmosphere at some other level along this path (i.e., at s_2), this provides enough information to obtain the transmission.

At this point, it is convenient to introduce the quantity

$$\tau(s_1, s_2) = \int_{s_1}^{s_2} k_\nu(\nu)\, ds$$

which we refer to as the **optical path**. This quantity is basic to our mathematical description of how radiation interacts with matter.

To simplify the discussion we will consider an ideal atmosphere taken as a horizontally stratified medium.



The transmission along a path tilted from the vertical by an angle θ, the zenith angle, is simply related to the transmission along the vertical path according to

$$\mathcal{T}_\nu(s_1, s_2) = \mathcal{T}_\nu(z_1, z_2, \eta = \cos\theta) = e^{-\tau_\nu(z_1, z_2)/\eta}$$

where $\tau_\nu(z_1, z_2)$ is now measured along the vertical and is referred to as the **optical depth.**

It is common to use the **mass absorption coefficient** in the definition of optical depth in describing the transmission along a path through an absorbing gas.

From the previous Eqs. the slant path transmission function is

$$\mathcal{T}_{\nu}(s_1, s_2) = e^{\left(-\frac{1}{\eta}\int_{z1}^{z2} k_{\nu}(\nu)\rho_a\, dz\right)}$$

The optical mass is defined as

$$u(z_1, z_2) = \int_{z_1}^{z_2} \rho_a \, dz$$

which is often quoted in units of **grams per square centimeter**.

Using the **hydrostatic assumption,** dp/dz=-mg and the mixing ratio $r = \rho_a/\rho$, where ρ is the density of air gives

$$u(p_1, p_2) = \frac{1}{g}\int_{p_2}^{p_1} r\, dp$$

where **g** is the acceleration of gravity, and where $\mathbf{p_1}$ and $\mathbf{p_2}$ are the pressures associated with the altitudes $\mathbf{z_1}$ and $\mathbf{z_2}$, respectively

Take a path from a satellite to the ground

$$u\left(p_1, p_2\right) = \frac{r}{g}\int_0^{p_s} dp$$

when you apply the limits

$$u\left(p_1, p_2\right) = \frac{r\,p_s}{g}$$

The absorption path for a **uniformly mixed gas** is directly proportional to the **atmospheric surface pressure** p_s.

This relationship that has been proposed as a basis for the remote sensing of surface pressure.

For remote sensing, it is important to distinguish between ***monochromatic*** transmission functions and ***band*** transmission functions.

The former represents the transmission of radiation at **one selected wavelength**, whereas the latter is the transmission **averaged over a range of wavelengths** as specified, for example, by the spectral response of a particular instrument.

suppose that the radiation received at a detector is of the form

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

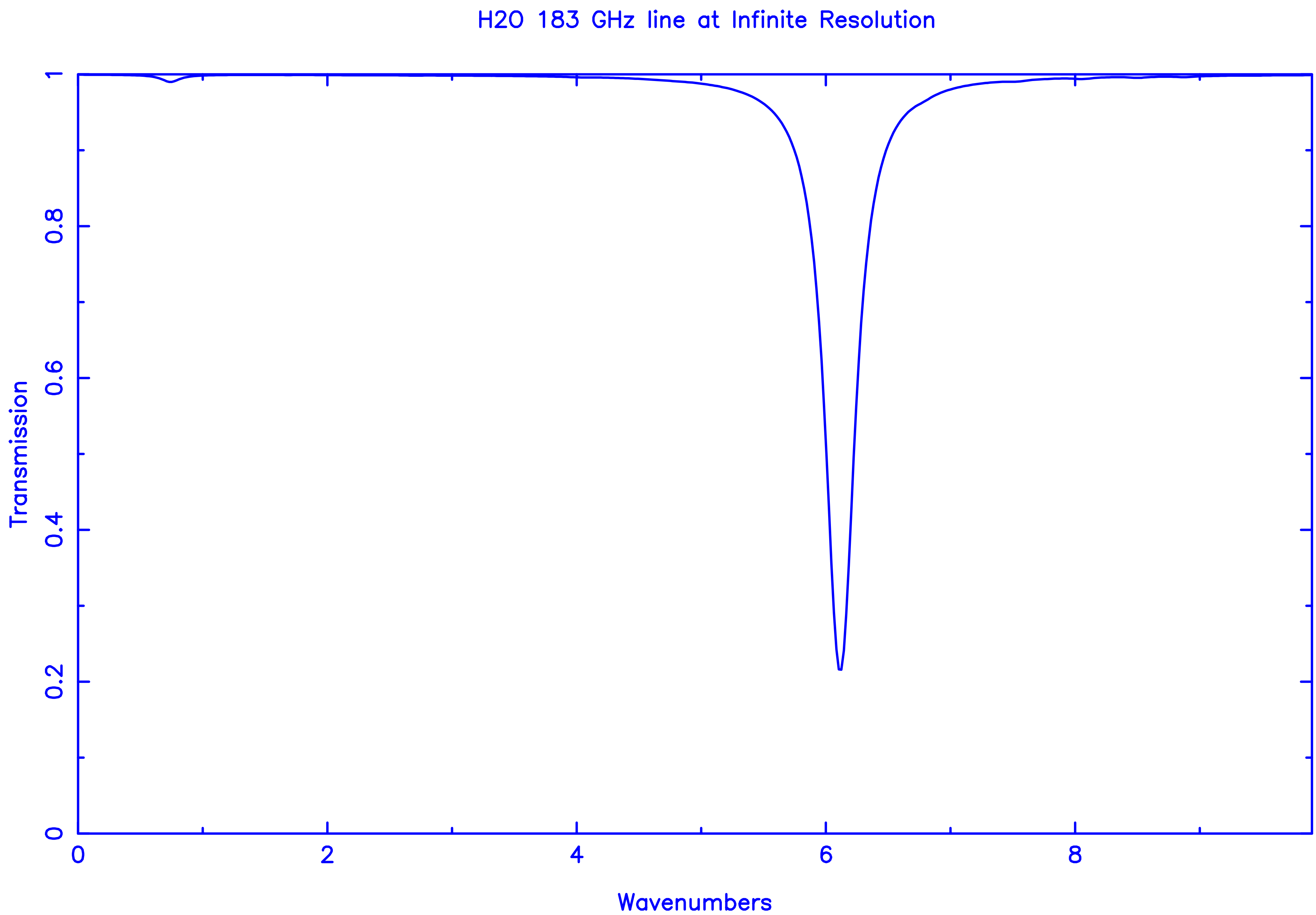
where g(ν) is the **spectral response function of the instrument** over its spectral band pass Δν. In terms of the transmission function, the intensity measured at s_2 is

$$I_{\Delta\nu}(s_2)=\int_{\Delta\nu} g(\nu) I_\nu(s_1) \mathcal{T}_\nu(s_1,s_2)\,d\nu$$

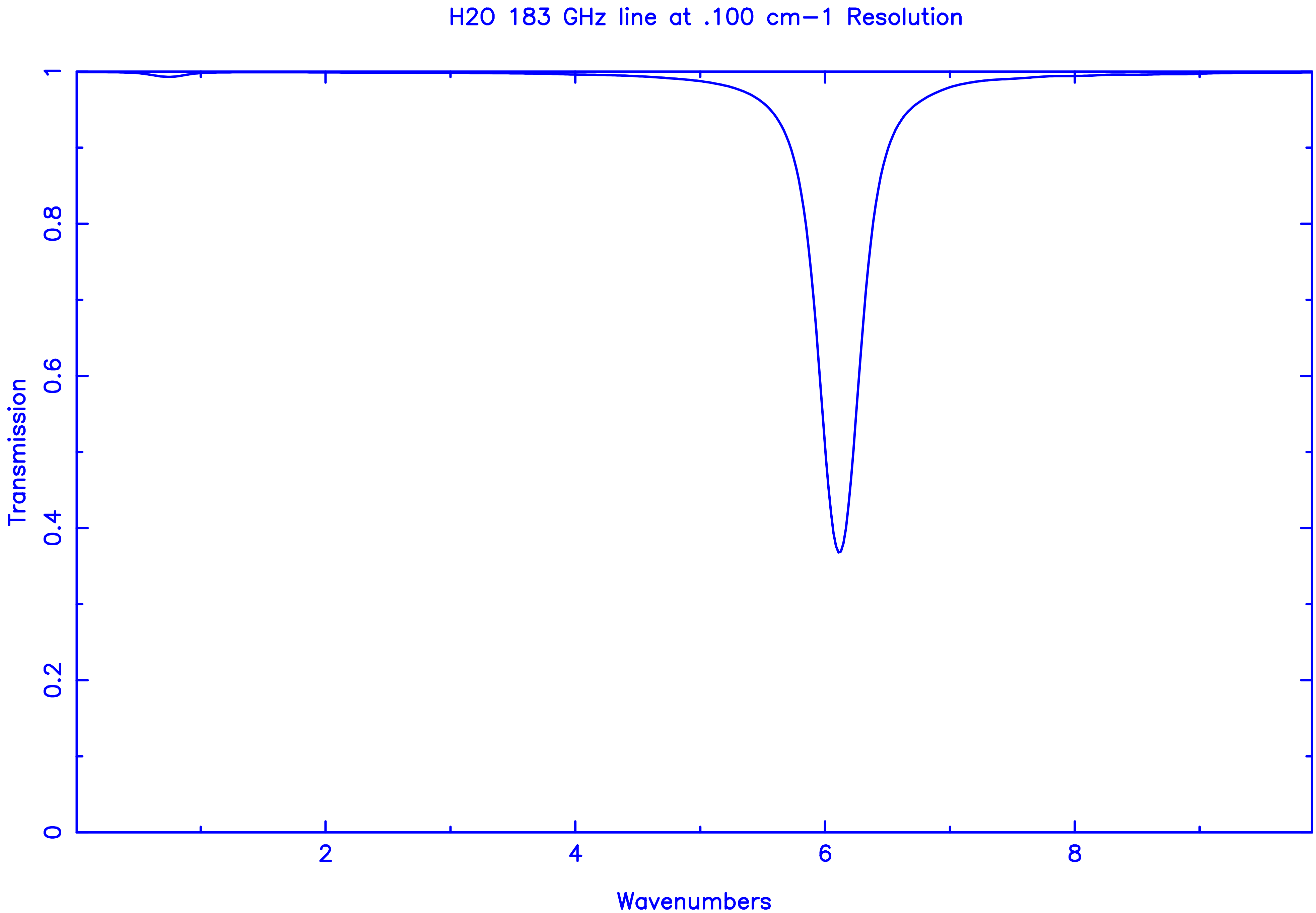
If the spectral band Δν is sufficiently narrow that the incident intensity is constant across the band, then the band transmission function becomes

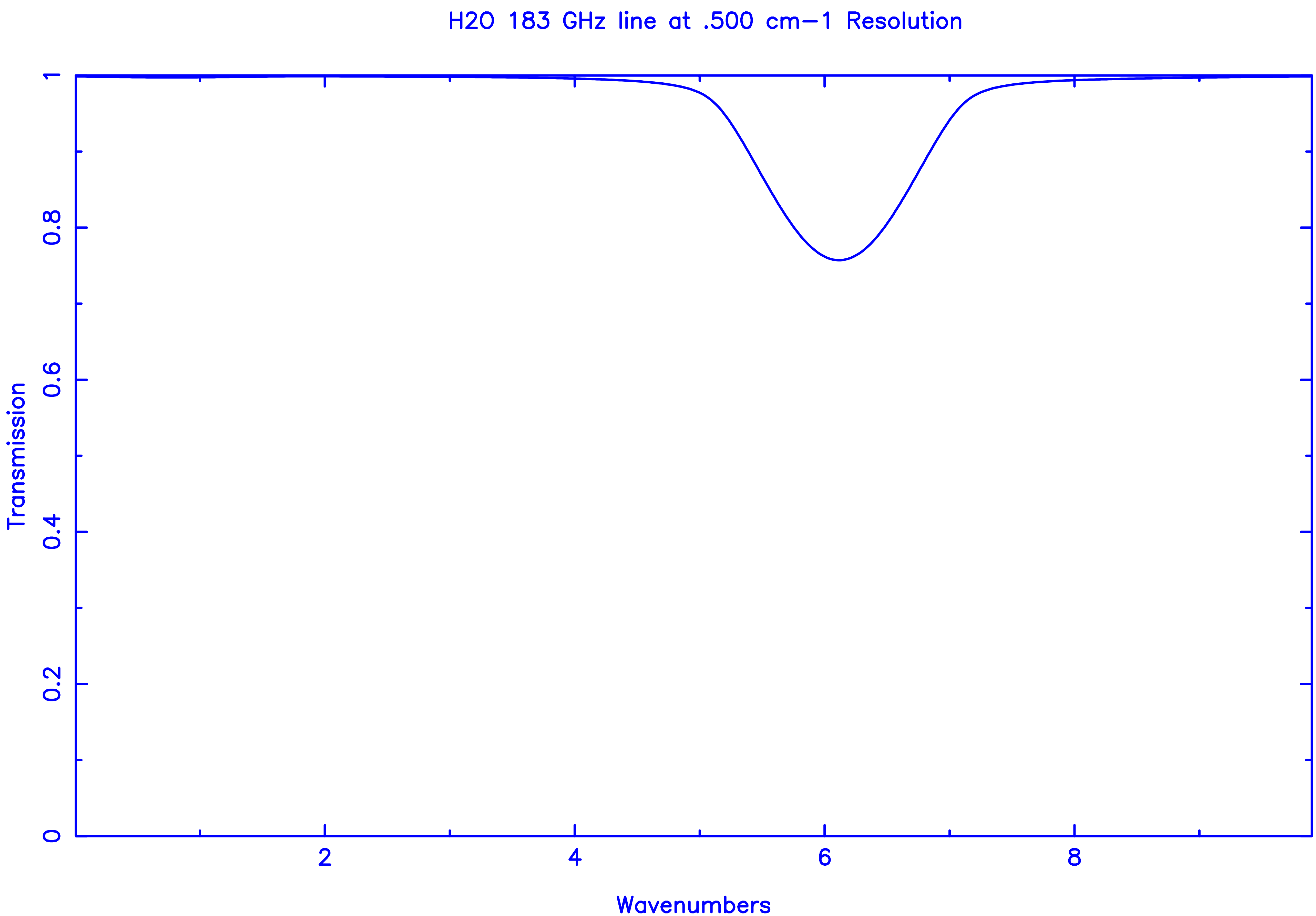
$$\left(\frac{I_{\Delta\nu}(s_2)}{I_{\Delta\nu}(s_1)}\right)=\mathcal{T}_{\Delta\nu}(s_1,s_2)=\int_{\Delta\nu} g(\nu)\,\mathcal{T}_\nu(s_1,s_2)\,d\nu$$

Therefore **instrument properties [in this case the response function g(v)] directly influence the transmission derived from measurements and must be accounted for in retrieval schemes.**

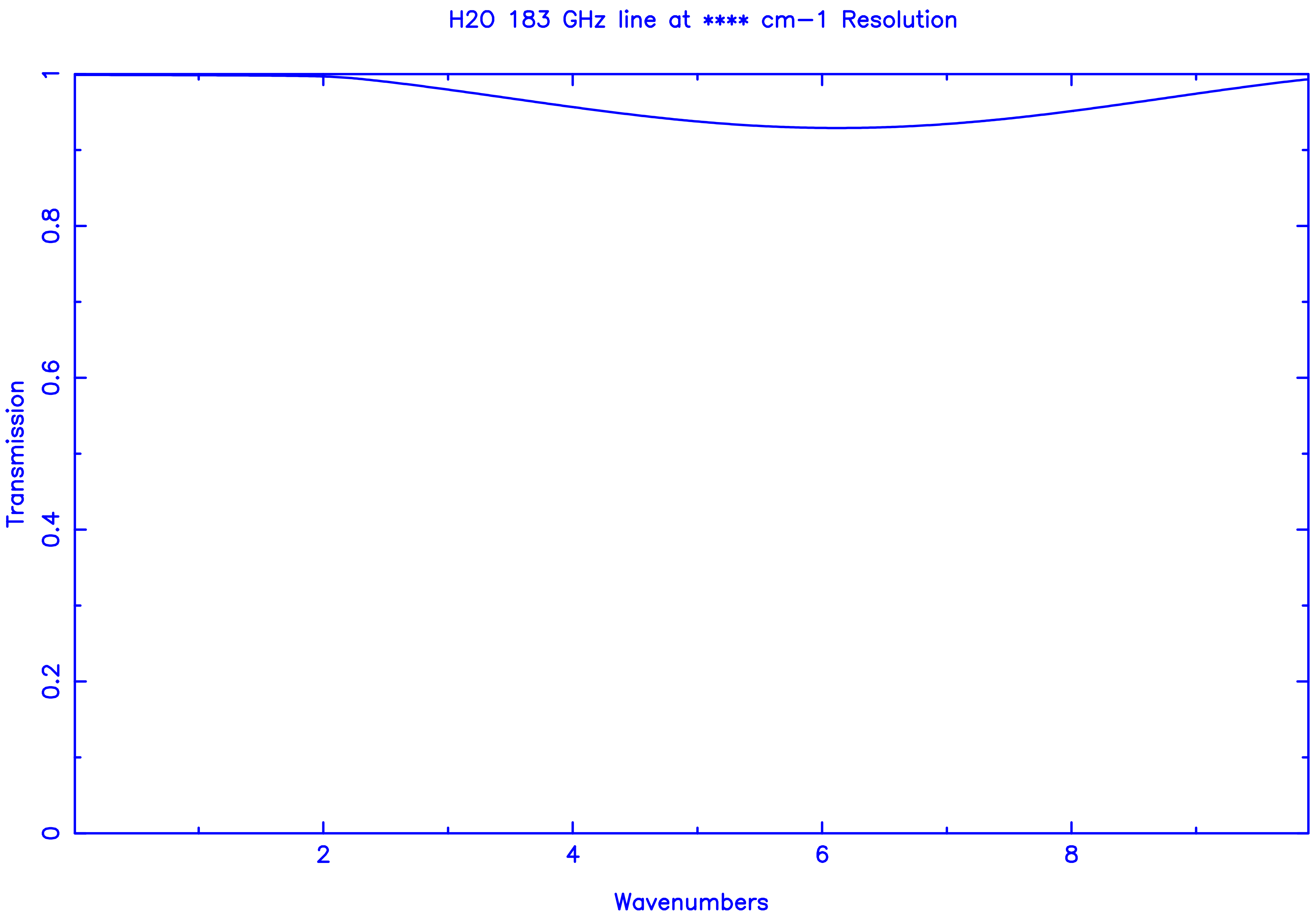


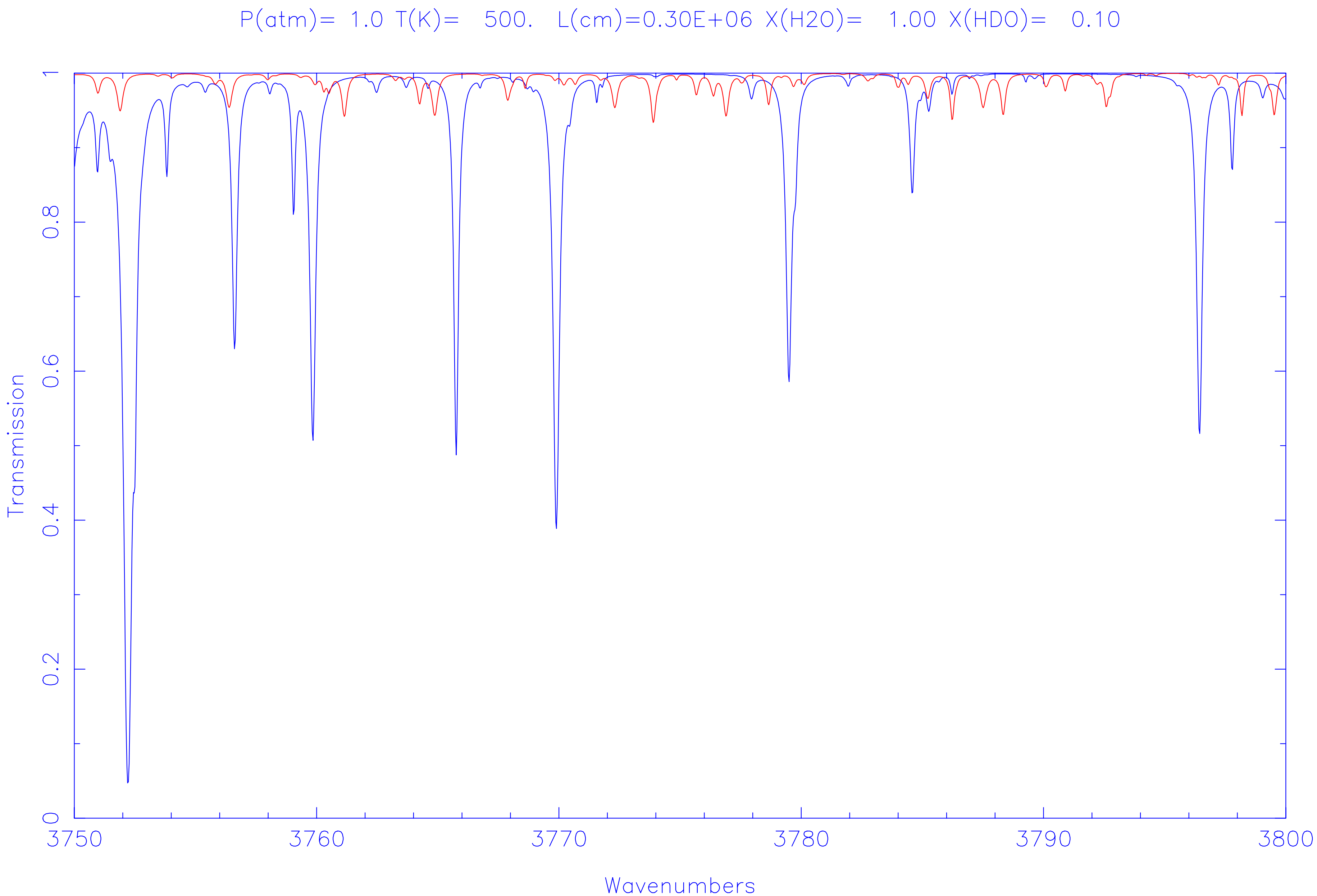
H2O 183 GHz line at Infinite Resolution
Transmission
Wavenumbers
0
0.2
0.4
0.6
0.8
1
0
2
4
6
8


H2O 183 GHz line at .100 cm−1 Resolution
Transmission
0
0.2
0.4
0.6
0.8
1
2
4
6
8
Wavenumbers

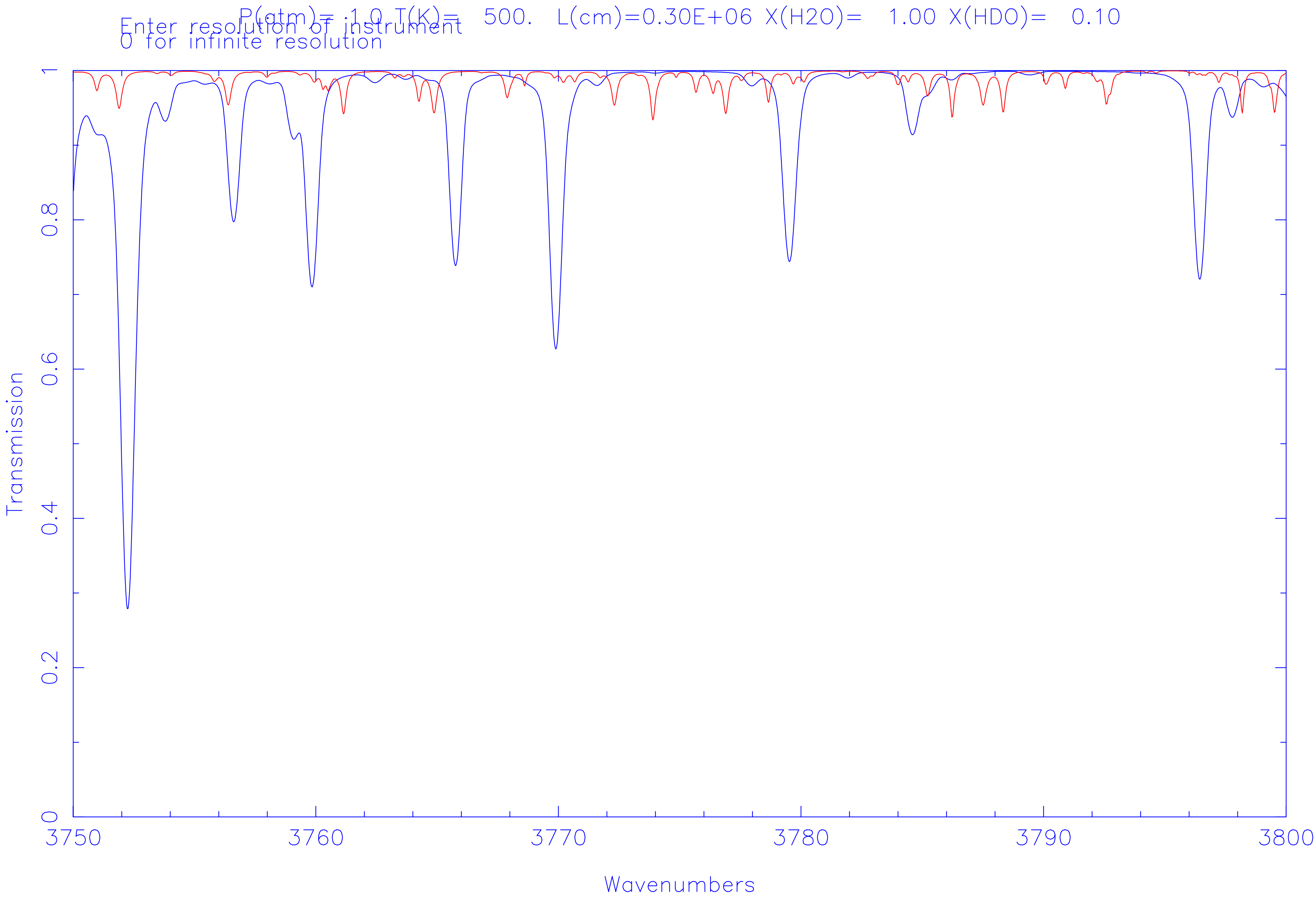


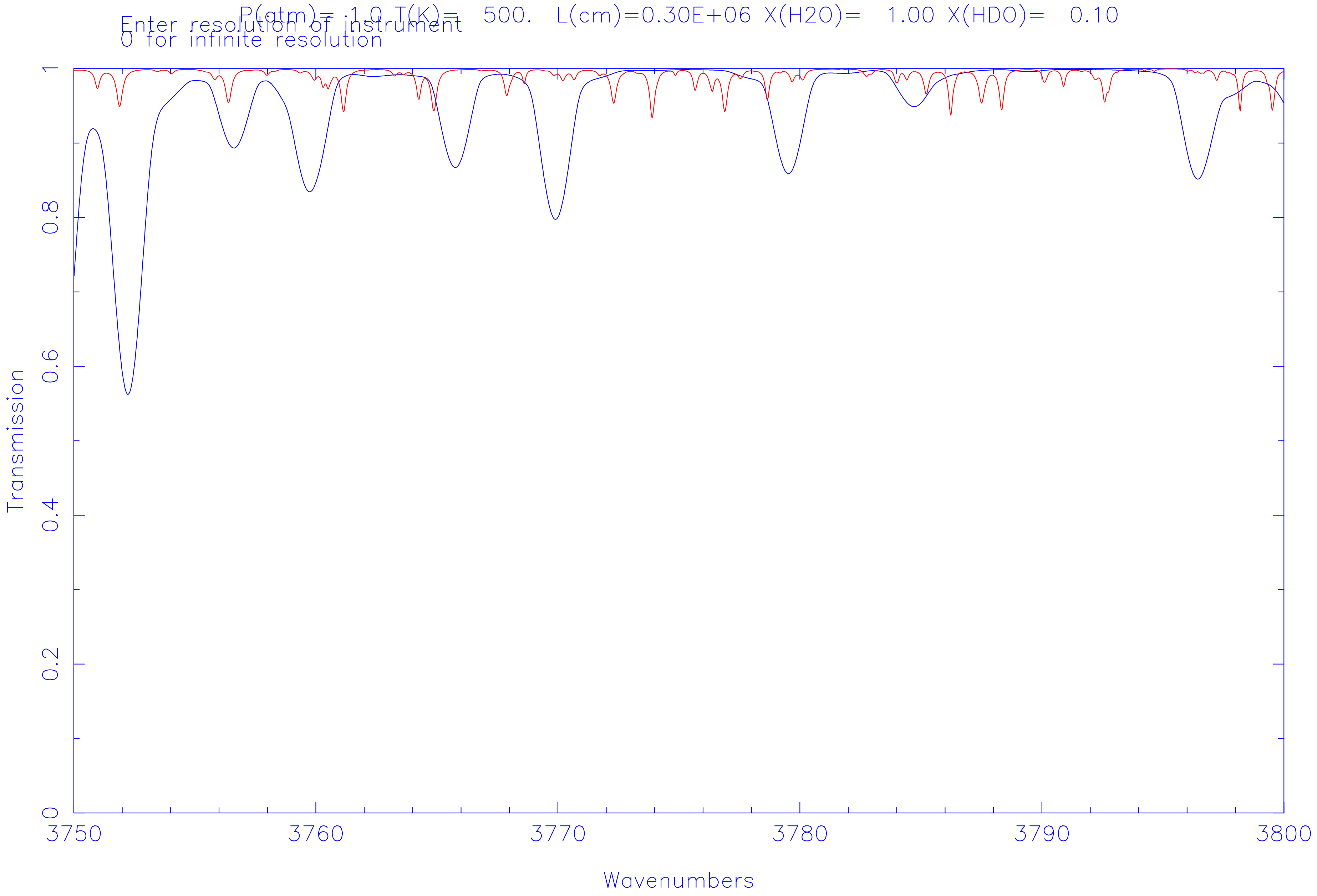
H2O 183 GHz line at .500 cm−1 Resolution
Transmission
Wavenumbers
0
0.2
0.4
0.6
0.8
1
2
4
6
8


H2O 183 GHz line at **** cm-1 Resolution
Transmission
0
0.2
0.4
0.6
0.8
1
2
4
6
8
Wavenumbers



P(atm)= 1.0 T(K)= 500. L(cm)=0.30E+06 X(H2O)= 1.00 X(HDO)= 0.10
Transmission
0
0.2
0.4
0.6
0.8
1
3750
3760
3770
3780
3790
3800
Wavenumbers


P(atm)= 1.0 T(K)= 500. L(cm)=0.30E+06 X(H2O)= 1.00 X(HDO)= 0.10
Enter resolution of instrument
0 for infinite resolution
Transmission
0
0.2
0.4
0.6
0.8
1
3750
3760
3770
3780
3790
3800
Wavenumbers



P(atm)= 1.0 T(K)= 500. L(cm)=0.30E+06 X(H2O)= 1.00 X(HDO)= 0.10
Enter resolution of instrument
0 for infinite resolution
Transmission
0
0.2
0.4
0.6
0.8
1
3750
3760
3770
3780
3790
3800
Wavenumbers