# Pressure broadening of molecular transitions at high temperatures

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*Workshop « Abundance measurements in Exoplanetary Atmospheres »,*
*Grenoble, 12-14 may 2014*

# Motivation: water in exoplanets

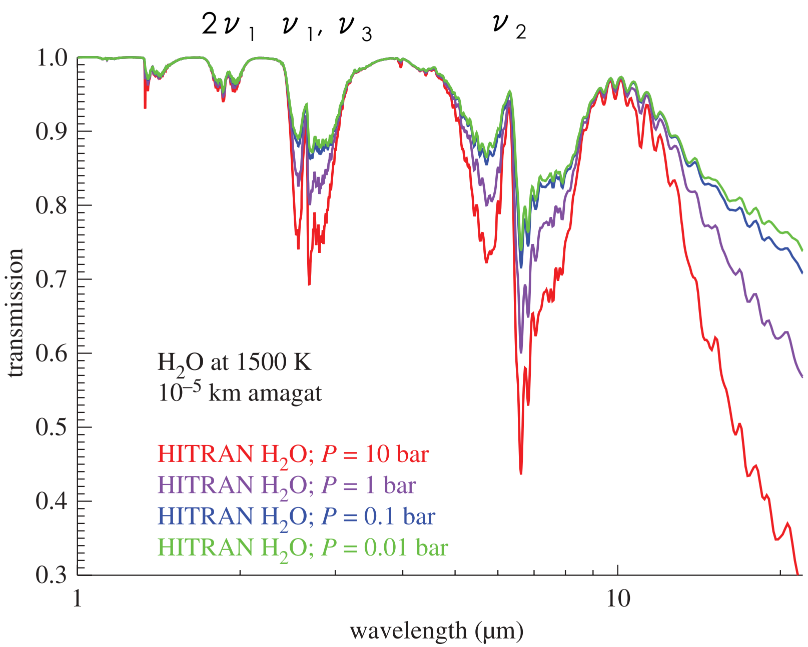



Figure 3. Transmission of stellar flux through a water vapour-containing planetary atmosphere as a function of the pressure of $H_2$ at a notional fixed temperature of 1500 K. (Online version in colour.)

- *« There appears to be a clear need to extend this work to deal with high temperature collisional broadening by hydrogen molecules. In the case of water, it would appear that broadening of the pure rotational transitions is of particular importance. »*

Tinetti et al. Phil. Trans. Roy. Soc. 2012

# Line shapes

- Line shape is determined from broadening mechanisms:

1. Natural line width from Heisenberg's uncertainty principle (negligible)

2. Doppler (thermal) broadening

3. Pressure (collisional) broadening

# Collisional broadening

- Broadening parameter (HWHM), e.g. in MHz/Torr

$$\gamma(f \leftarrow i;T) = \frac{\bar{v}\sigma^{\mathrm{PB}}(f \leftarrow i;T)}{2\pi k_b T} = 2.236\frac{\sigma^{\mathrm{PB}}(f \leftarrow i;T)}{\sqrt{\mu T}}$$

(1 $cm^{-1}$ = 30 GHz / 1 atm = 760 Torr)

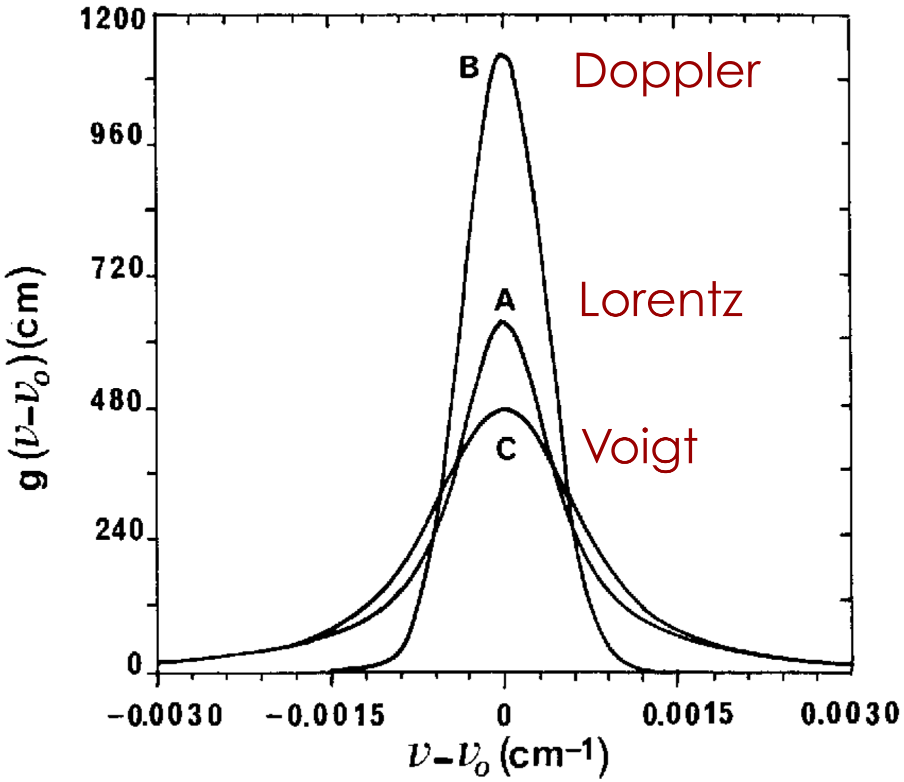
- Collisional line broadening causes Lorentz line shape:

$$f(\nu - \nu_0) = \frac{\gamma/\pi}{(\nu - \nu_0)^2 + \gamma^2}$$

# Voigt profile

- When Lorentz width becomes comparable to Doppler width, the broadening effects must be convolved to get the *Voigt* line shape.

- Extensively used to model line shapes in the Earth's and other atmospheres



# Theory of broadening

PHYSICAL REVIEW VOLUME 112, NUMBER 3 NOVEMBER 1, 1958

**General Impact Theory of Pressure Broadening***

MICHEL BARANGER
*Carnegie Institute of Technology, Pittsburgh, Pennsylvania, and the RAND Corporation, Santa Monica, California*
(Received July 8, 1958)

See also:

- A. Ben-Reuven Adv. Chem. Phys. 33 235 (1975)
- D. Robert & J. Bonamy J. Phys. 40 923 (1979)
- J. Schaefer & L. Monchick J. Chem. Phys. 87 171 (1987)

# General framework

- Born-Oppenheimer approximation
- Collisions are considered as binary
- The collision time is much shorter than the time interval between collisions
- No line mixing effects occur

# Two equivalent formulae
## (see Baranger's paper)

- 1) Coupling of *elastic* S-matrix elements

$$\sigma(j_i j_f; j_i j_f | E_{\mathrm{rel}}) = [\ldots] \left[ \delta_{ll'} \delta_{jj'} \delta_{\bar{j}\bar{j}'} \delta_{j_2} \delta_{j_2 j_2'} - S^{J}_{j_i j_2 j l \leftarrow j_i j_2' j' l'} S^{\bar{J}*}_{j_f j_2 \bar{j} l \leftarrow j_f j_2' \bar{j}' l'} \right]$$

- 2) Inelastic and elastic contributions

$$\begin{aligned} \sigma^{\mathrm{PB}}(f \leftarrow i; E_{\mathrm{coll}}) &= \frac{1}{2} \left[ \sum_{f' \neq i} \sigma^{\mathrm{in}}(f' \leftarrow i; E_{\mathrm{coll}}) + \sum_{f' \neq f} \sigma^{\mathrm{in}}(f' \leftarrow f; E_{\mathrm{coll}}) \right] \\ &\quad + \int \left| f_i(\Omega; E_{\mathrm{coll}}) - f_f(\Omega; E_{\mathrm{coll}}) \right|^2 \mathrm{d}\Omega, \end{aligned}$$

# The Random Phase approximation (RPA)

- Within the RPA, the elastic contribution is ignored:

$$\sigma^{\mathrm{PB}}(f \leftarrow i; E_{\mathrm{coll}}) = \frac{1}{2}\left[\sum_{f' \neq i} \sigma^{\mathrm{in}}(f' \leftarrow i; E_{\mathrm{coll}}) + \sum_{f' \neq f} \sigma^{\mathrm{in}}(f' \leftarrow f; E_{\mathrm{coll}})\right]$$

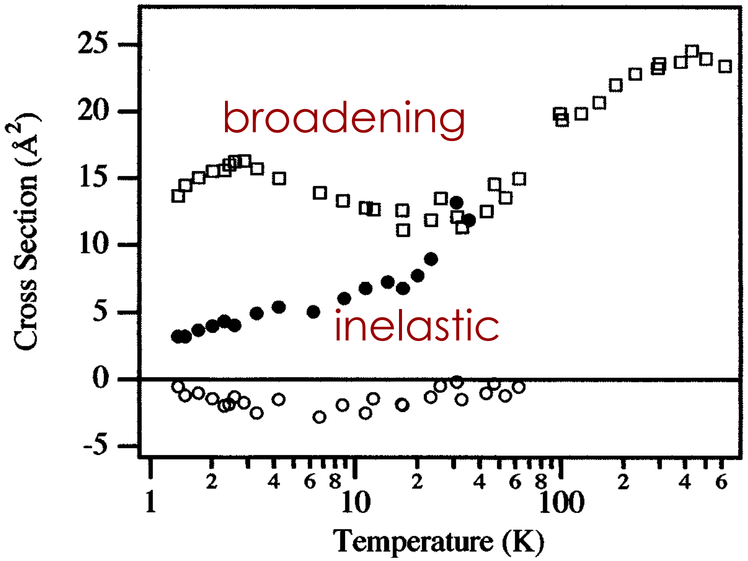
i.e. reorientation and dephasing collisions neglected

- Line widths are obtained as simple sums of inelastic cross sections

# Validity of RPA ?

- At low temperature, the elastic contribution (resonances) can dominate !

- Theoretically, RPA is expected to hold when the collision (or rotational) energy exceeds the depth of the potential well, i.e. about 300K




$H_2S$-He,  Ball & De Lucia PRL 1998

# Inelastic data for $H_2O$ and CO

- Extensive sets of inelastic rates made available recently for $H_2O$-$H_2$ and CO-$H_2$
  (Daniel et al. 2011, Yang et al. 2010)

- Data cover 5-1500K and 2-3000K and include the lowest 90 levels of $H_2O$ and 41 levels of CO, respectively.

- Ortho-to-para ratio of $H_2$ assumed to be 3:

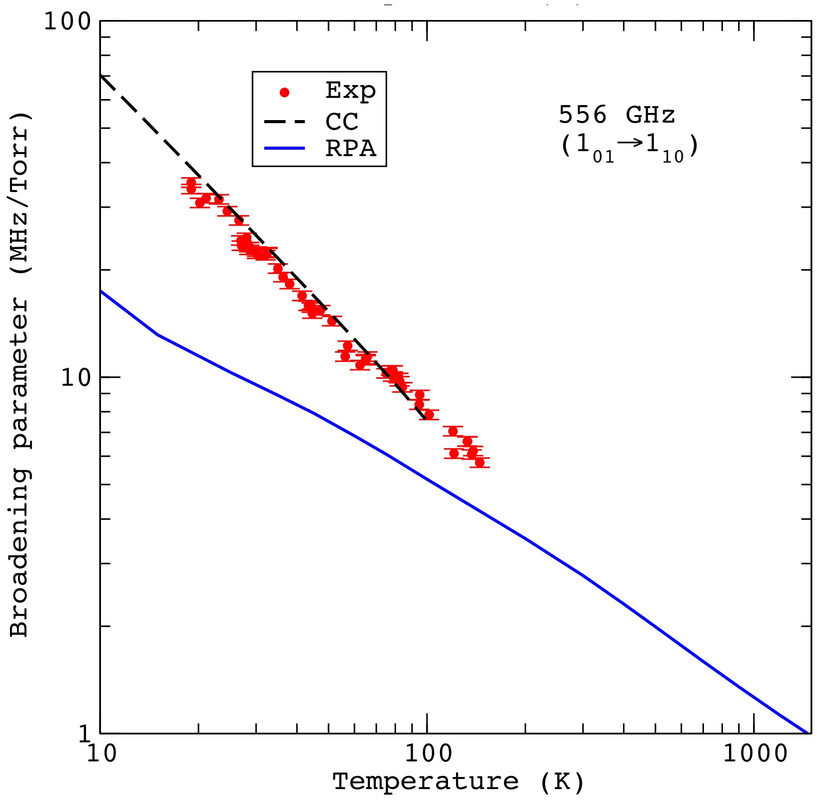
$$\sigma^{\mathrm{PB}}(f \leftarrow i; T) = \frac{1}{4}\sigma^{\mathrm{PB}}_{\mathrm{pH_2}}(f \leftarrow i, T) + \frac{3}{4}\sigma^{\mathrm{PB}}_{\mathrm{oH_2}}(f \leftarrow i; T),$$

- Averaged velocity

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi\mu}},$$

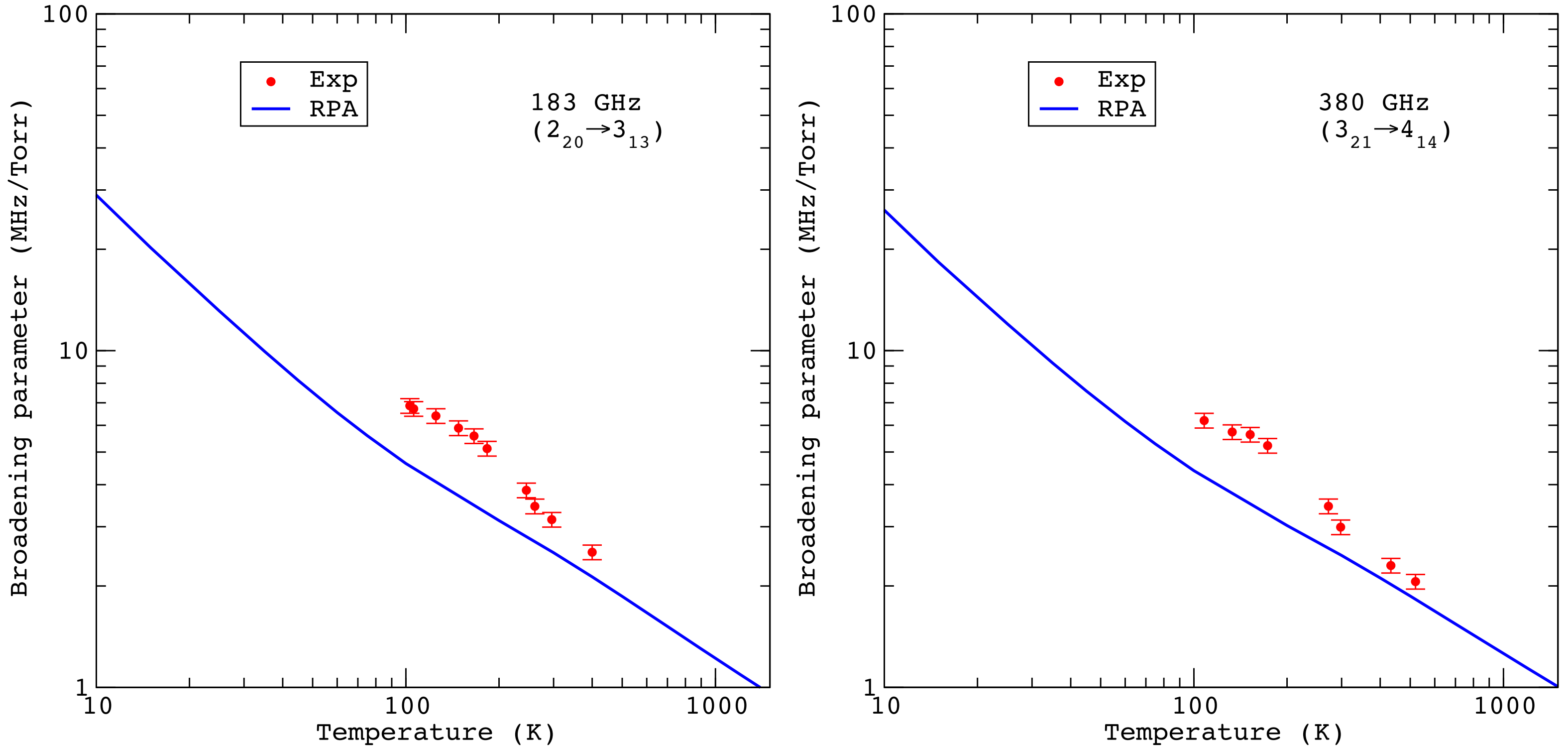
$$\sigma^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i; T) \approx k^{\mathrm{in}}_{\mathrm{pH_2}}(f \leftarrow i; T)/\bar{v}$$

# Water at low temperature



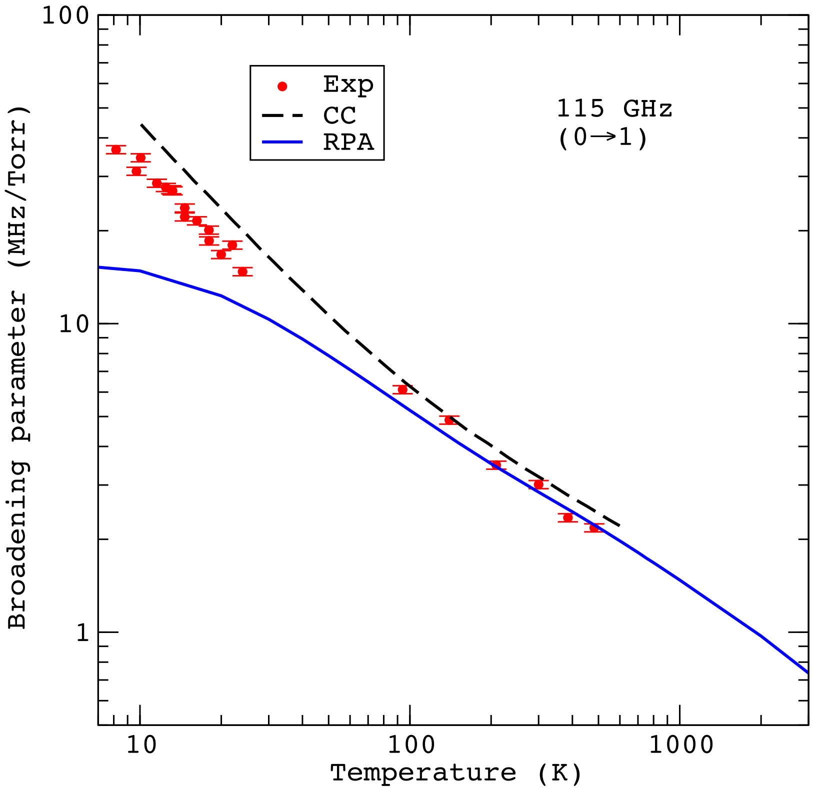

Faure et al. JQSRT (2013)
Experiment and CC calculations from Drouin & Wiesenfeld PRA (2012)

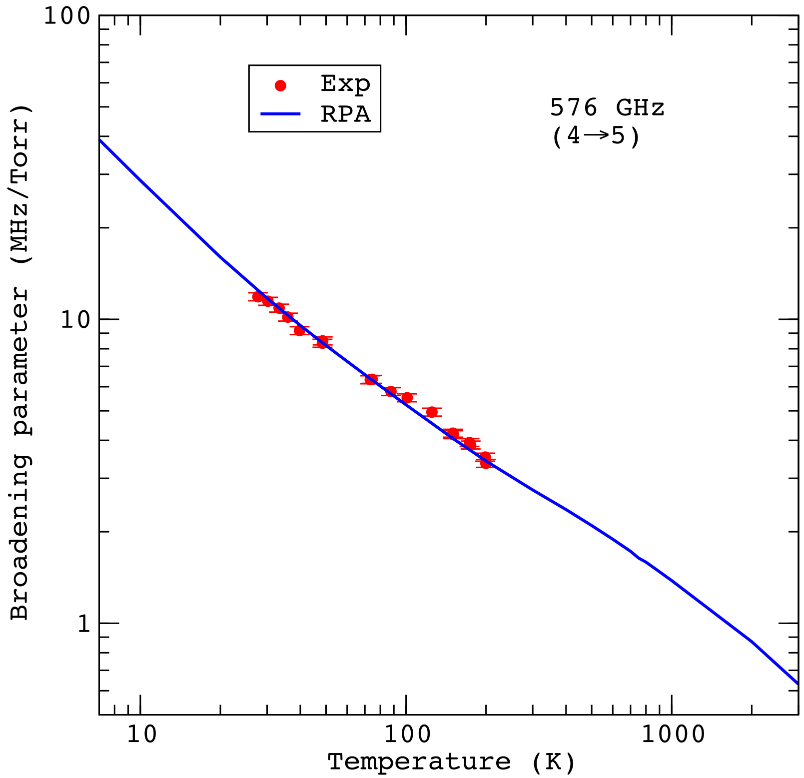
# Water at « high » temperature




Experiment from Dutta et al. (1993)

# CO in low and « high » *j*




Experiment and CC calculations from Mengel et al. (2000)
576 GHz measured by Dick et al. (2009)

# Modelling

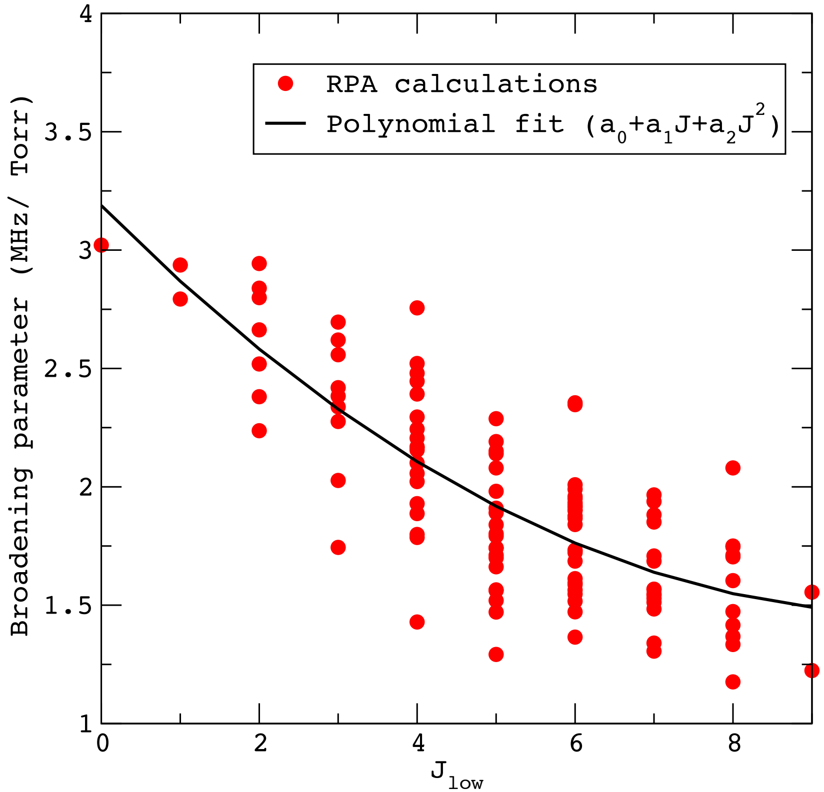
- Data include the lowest 71 ($J<10$) and 31 ($J<31$) levels of $H_2O$ and CO, respectively
- For modeling purpose,our data were fitted using the standard relation

$$\gamma(T) = \gamma_0 (T_0/T)^{\beta},$$

- The fits were found to reproduce our data within 10% or better

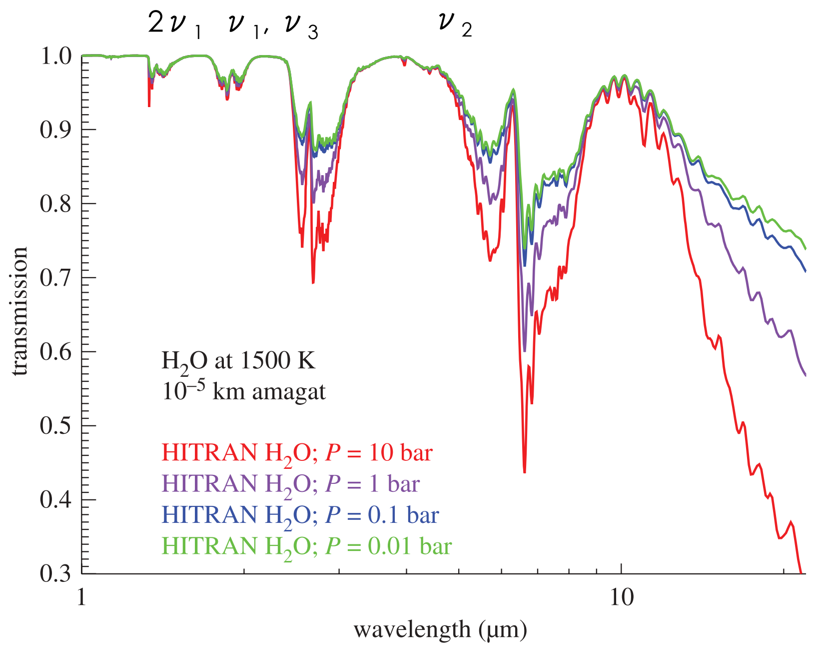
  - $\gamma_0$ = [2.6 - 3] MHz/Torr and $\beta$ = [0.5-0.7] for CO
  - $\gamma_0$ = [1 - 3] MHz/Torr and $\beta$ = [0.3-0.8] for $H_2O$

# Extrapolation ?




RPA calculations of Faure et al. JQSRT (2013) for $H_2O$-$H_2$ (T=296K)

# Vibrational dependence?

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# Ro-vibration vs. rotation

- Ro-vibrational transitions have much lower inelastic cross sections:

$$\sigma^{\text{in}}(f, v_f \leftarrow i, v_i; T) \ll \sigma^{\text{in}}(f, v_i \leftarrow i, v_i; T)$$

- Pure rotational cross sections do not strongly depend on the vibrational level:

$$\sigma^{\text{in}}(f, v_i \leftarrow i, v_i; T) \sim \sigma^{\text{in}}(f, v_0 \leftarrow i, v_0; T)$$

- As a result, the vibrational dependence is expected to be small:

$$\sigma^{\text{PB}}(f, v_f \leftarrow i, v_i; T) \sim \sigma^{\text{PB}}(f, v_0 \leftarrow i, v_0; T)$$

# Ro-vibrational transitions in water at 1.39 $\mu$m

Experimental data are from Zeninari et al. (2004) at room temperature

| Line number | Transition $(J'K'_aK'_c) \leftarrow (JK_aK_c)$ | Frequency ($cm^{-1}$) | Band | $\gamma(H_2)$ (MHz/Torr) Exp. | Calc. | Diff. (%) |
|---|---|---|---|---|---|---|
| 1 | $1_{01} \leftarrow 1_{10}$ | 7182.20910 | $2\nu_1$ | 3.282 | 2.776 | 15.4 |
| 2 | $2_{02} \leftarrow 3_{03}$ | 7181.15570 | $\nu_1 + \nu_3$ | - | 2.728 | - |
| 3 | $2_{12} \leftarrow 3_{13}$ | 7182.94955 | $\nu_1 + \nu_3$ | 2.872 | 2.680 | 6.7 |
| 4 | $3_{03} \leftarrow 3_{22}$ | 7175.98675 | $\nu_1 + \nu_3$ | 2.923 | 2.623 | 10.3 |
| 5 | $5_{15} \leftarrow 5_{14}$ | 7165.21504 | $\nu_1 + \nu_3$ | 2.690 | 2.180 | 18.9 |
| 6 | $6_{60} \leftarrow 6_{61}$ | 7185.59600 | $\nu_1 + \nu_3$ | 1.696 | 1.313 | 22.6 |

- Accuracy of RPA similar to pure rotation transitions, i.e. ~25%
- Small vibrational dependence in agreement with measurements by Brown & Plymate (1996)

# Conclusions

- Present data should help in estimating abundances (and C/O ratio !) in exoplanets
- Data available on the ExoMol website (ww.exomol.com)
- Extension of data in progress (high *J* and vibrational bands)