A THEORETICAL MODEL FOR WIDE-BAND IR-ABSORPTION MOLECULAR SPECTRA AT ANY PRESSURE:

FICTION OR REALITY?

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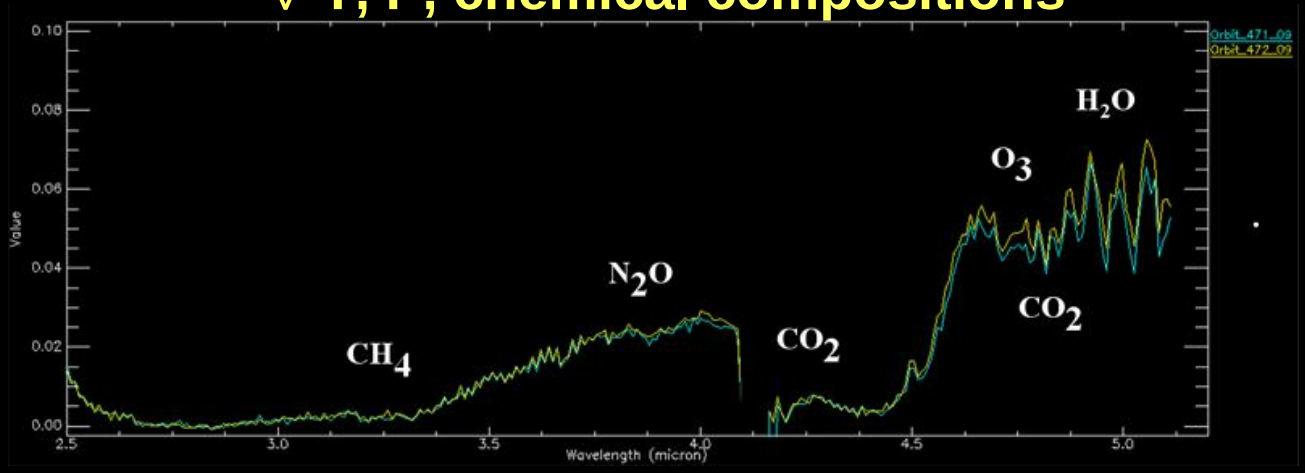
Plan

1. Outline of the needs
2. Non-Markovian Energy-Corrected Sudden approach
3. Applications to high-density IR spectra
4. Applications to CO_2 IR spectra at low densities
5. Conclusions & perspectives

❶ Outline of the needs

Mars **Earth** **Venus**

∀ T, P, chemical compositions

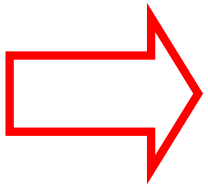


Planets: http://www.space.com/11187-earth-magnetic-field-solar-wind.html

Outline of the needs

Absorption coefficient as a function of frequency

for each spectroscopically active molecule



Atmospheric radiative transfer codes

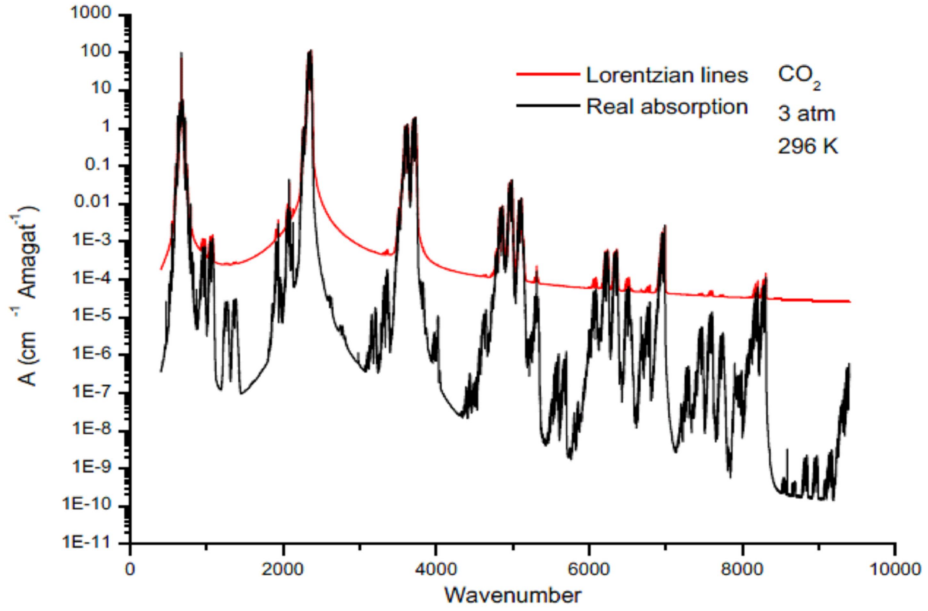
Retrieval of geophysical parameters (temperature, humidity,…)

Weather/climate models

Optimization of solar photovoltaic systems

...

1 Outline of the needs



Courtesy : N.N. Filippov

Absorption coefficients as functions of frequency

- Region of molecular resonances
  - low pressures: +
  - high pressures: + / -
- Spectral wings
  - near: + / -
  - far: -
- Contributions from Collision-Induced Absorption: - / +
- Contributions from dimers and higher-order clusters: - / +

Outline of the needs

STANDARD APPROACH for allowed absorption

Niro et al., JQSRT 88, 483 (2004)

$$\alpha(\sigma) = \frac{8\pi^3}{3hc}\sigma\, n_1 (1 - e^{-\frac{hc\sigma}{kT}})\frac{1}{\pi}\mathrm{Re}\sum_{k,k'}\rho_k d_k d_{k'}[i(\sigma-\sigma_k)] + n_2 W]^{-1}_{kk'}$$

- absorption coefficient at wavenumber σ
- Active-gas density
- Rotational populaton
- Dipole matrix element
- Isolated-line positions
- Bath-gas density
- Rotational relaxation matrix

$\mathrm{Re}\,W_{kk'}$ Modelled by the Energy-Corrected Sudden approach for «downward» transitions + detailed-balance relation $\mathrm{Re}W_{kk'}\rho_k = \mathrm{Re}W_{k'k}\rho_{k'}$ for « upward » ones

$\mathrm{Im}\,W_{kk'}$ One-parameter empirical modelling using the detailed balance

$\mathrm{Re}\,W_{kk}$

$\mathrm{Im}\,W_{kk}$ Calculated by sum rules $W_{kk} = -\sum_{k'}\frac{d_{k'}}{d_k}W_{k'k}$

In the 1st-order impact approx

❶ Outline of the needs

STANDARD APPROACH: PROBLEMS

❶

ECS parameters fitted to experimental LW
Sum rules for calculation of diag. elements

⇨ Recalculated LW ≠ experimental LW

« Renormalization procedure »

1) Lines sorted in decreasing intensity order
2) Expt LW imposed on the diagonal
3) Off-diagonal elements scaled to satisfy the detailed balance

❷ Empirical modeling of Im W

❸ Far spectral wings:
break down of the impact approximation ⇨ Empirical corrections to the Lorentzian shape: « χ-factors »

❹ Far spectral wings: violation of the detailed balance

$$\Phi(-\omega) = \Phi(\omega)\exp(-\beta\hbar\omega)$$

Filippov & Tonkov, JCP 108, 3608 (1998)

❺ One-sided sum rules → asymptotic behavior σ^{-3} in the far wing

→ negative intensities in low-frequency wing

General sum rules hold ONLY in the non-Markovian case

Bulanin et al., JQSRT 31, 521 (1984)

❷ Non-Markovian Energy-Corrected Sudden approach

Symmetrized spectral density:

$$S^{(r)}(\sigma) = \frac{1}{\pi} \mathrm{Re} \sum_{k,k'} A_k^{(r)} \left[i(\sigma - \sigma_k) + n_2 \Gamma^{(r)}(\sigma) \right]^{-1}_{k,k'} A_{k'}^{(r)}$$

r - rank of the coupling tensor

σ_k - proper frequencies of the free active molecule

n_2 - gas density

$A_k^{(r)\ 2}$ - intensities of separate lines $A_k^{(r)} = (-1)^{J_i} \sqrt{(2J_i+1)(2J_f+1)} \begin{pmatrix} J_i & r & J_f \\ 0 & 0 & 0 \end{pmatrix} \sqrt{\frac{\rho_i + \rho_f}{2}}$

$\langle J_f \| C^{(r)} \| J_i \rangle$

n_{if}

General form of the off-diagonal relaxation matrix elements:

$$\Gamma^{(r)}_{if,i'f'}(\sigma) = -\left[1 + \exp(-hc\sigma / kT)\right] / 2 n_{if} n_{i'f'} \times \sum_L (2L+1) F^{Lr}_{if,i'f'} \left[\rho_i \, \Phi_L(\sigma - \sigma_{f'i}) + \rho_{i'} \, \Phi_L(\sigma - \sigma_{fi'}) \right]$$

Kouzov, PRA 60, 2931 (1999)

Properties of the non-Markovian relaxation matrix

Symmetry (detailed balance):

$$\Gamma^{(r)}_{if,i'f'}(\sigma) = \Gamma^{(r)}_{i'f',if}(\sigma)$$

Time-reversal symmetry:

$$\Gamma^{(r)}_{if,i'f'}(\sigma) = \Gamma^{(r)*}_{fi,f'i'}(-\sigma)$$

Double-sided sum rules:

$$\sum_{i'f'\neq if} \Gamma^{(r)}_{if,i'f'}(\sigma) A^{(r)}_{i'f'} = \sum_{i'f'\neq if} A^{(r)}_{i'f'} \Gamma^{(r)}_{i'f',if}(\sigma) = -\Gamma^{(r)}_{if,if}(\sigma) A^{(r)}_{if}$$

Positive definition:

$$\sum_{if,i'f'} B^{(r)}_{if}\ \Gamma^{(r)}_{if,i'f'}(\sigma)\ B^{(r)}_{i'f'} \geq 0\,,\ \forall\ B^{(r)}$$

❷ Non-Markovian Energy-Corrected Sudden approach

ECS modeling of the correlation function

Buldyreva & Bonamy, PRA 60, 370 (1999)

$$\mathrm{Re}\ \Phi_L(\sigma) = \frac{2}{1+\exp\left(-hc\,\sigma/kT\right)}\,\Phi_L^{class}(\sigma)$$

$$\Phi_L^{class}(\sigma) = Q_L^{'}\ \Omega(\sigma)$$

$$\Omega(\sigma) = \left(1+\frac{(2\pi c b_c \bar{\sigma})^2}{12\ n\bar{v}^2}\right)^{-n} \quad , \quad n = 1\ or\ \ 2$$

Standard ECS parameters

ECS-EP: $A(T), \alpha, \gamma, b_c$
ECS-P : $A(T), \alpha, b_c$
ECS-E : $A(T), \gamma, b_c$

Spectroscopy-independent

$$Q_L = \frac{A(T)}{\left[L(L+1)\right]^{\alpha}}\exp\left[-\gamma\frac{B}{kT}L(L+1)\right]$$

❷ Non-Markovian Energy-Corrected Sudden approach

Modifications for IR absorption bands

$r = 1$

Buldyreva & Daneshvar, JCP 139, 164107 (2013)

Linear molecule with a bending mode $(v_1 v_2^l v_3)$
can be considered as a symmetric top with $K \equiv l$

IOSA: Green, JCP 70, 816 (1979); JCP 90, 3603 (1989)

(I) Isolated-line intensities

$$A_k^{(r)} = (-1)^{J_i + l_f} \sqrt{(2J_i+1)(2J_f+1)} \begin{pmatrix} J_i & r & J_f \\ l_i & l_f - l_i & -l_f \end{pmatrix} \sqrt{\frac{\rho_i + \rho_f}{2}}$$

(II) Relaxation matrix

$$F_{if,i'f'}^{Lr} = (-1)^{r+l_i+l_f} \begin{pmatrix} J_i' & L & J_i \\ -l_i & 0 & l_i \end{pmatrix} \begin{pmatrix} J_f & L & J_f' \\ l_f & 0 & -l_f \end{pmatrix} \begin{Bmatrix} J_i & J_f & r \\ J_f' & J_i' & L \end{Bmatrix}$$

❷ Non-Markovian Energy-Corrected Sudden approach

(III) Vibration-rotation interactions:

(A) Isolated-line intensities:

Correction via Herman-Wallis factors

$$F(m) = (1 + a_1 m + a_2 m^2 + a_3 m^3)^2$$ *P*- & *R*-

$$F(m) = (1 + b_2 m^2)^2$$ *Q*-

$$m = -J \quad (P); \quad m = J \quad (Q); \quad m = J + 1 \quad (R)$$

$$A_k^{(1)} \rightarrow A_k^{(1)\,HW} = A_k^{(1)} \sqrt{F(m)}$$

Coriolis interactions between vibrational levels:

Hartmann et al., JCP 110, 7733 (1999)

- If sum rules are restricted to one band, unperturbed dipole elements should be used
- Modifications of rel. matr. for Coriolis effects have no influence on the absorption shape

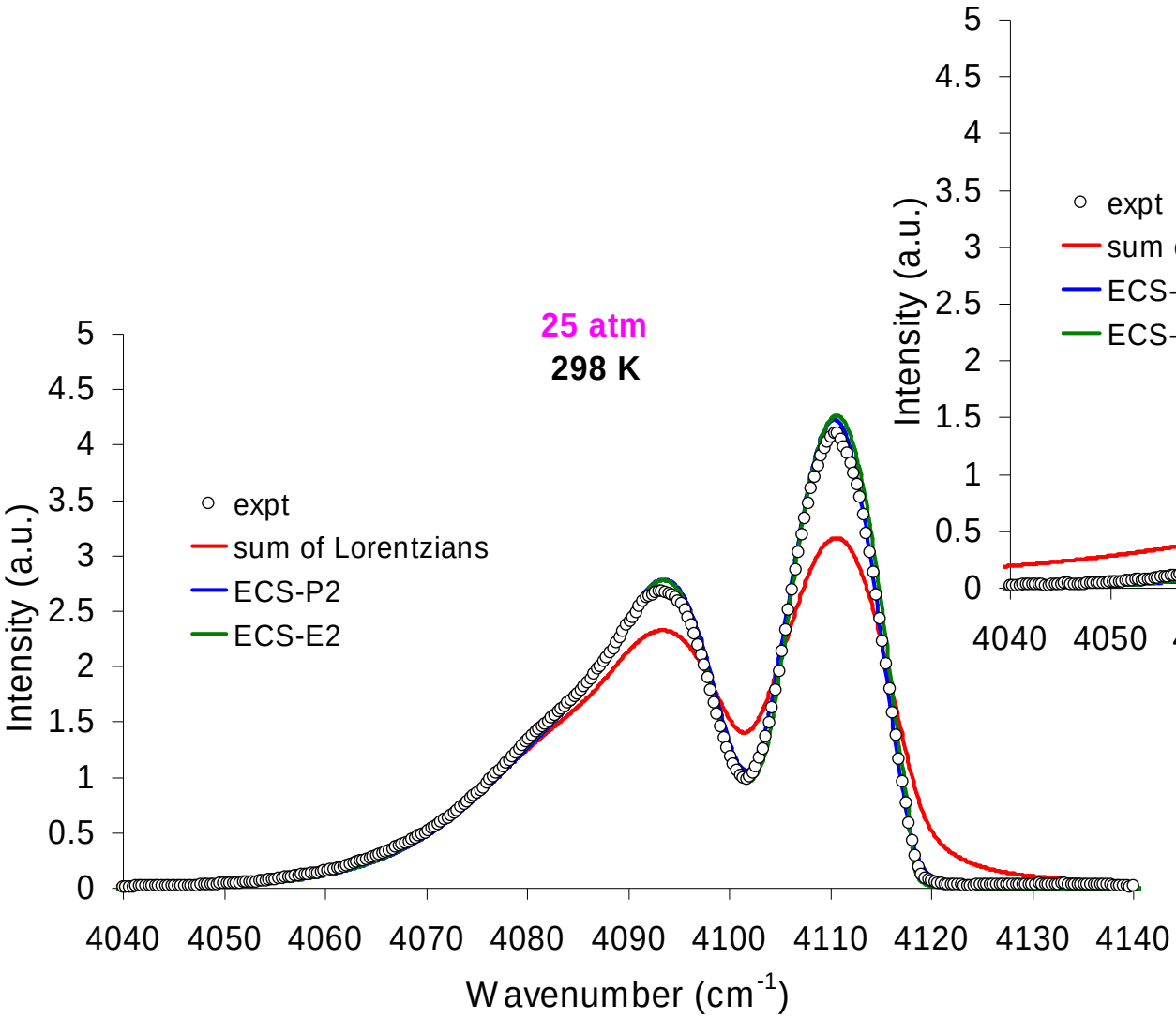
(B) Relaxation matrix modeling:

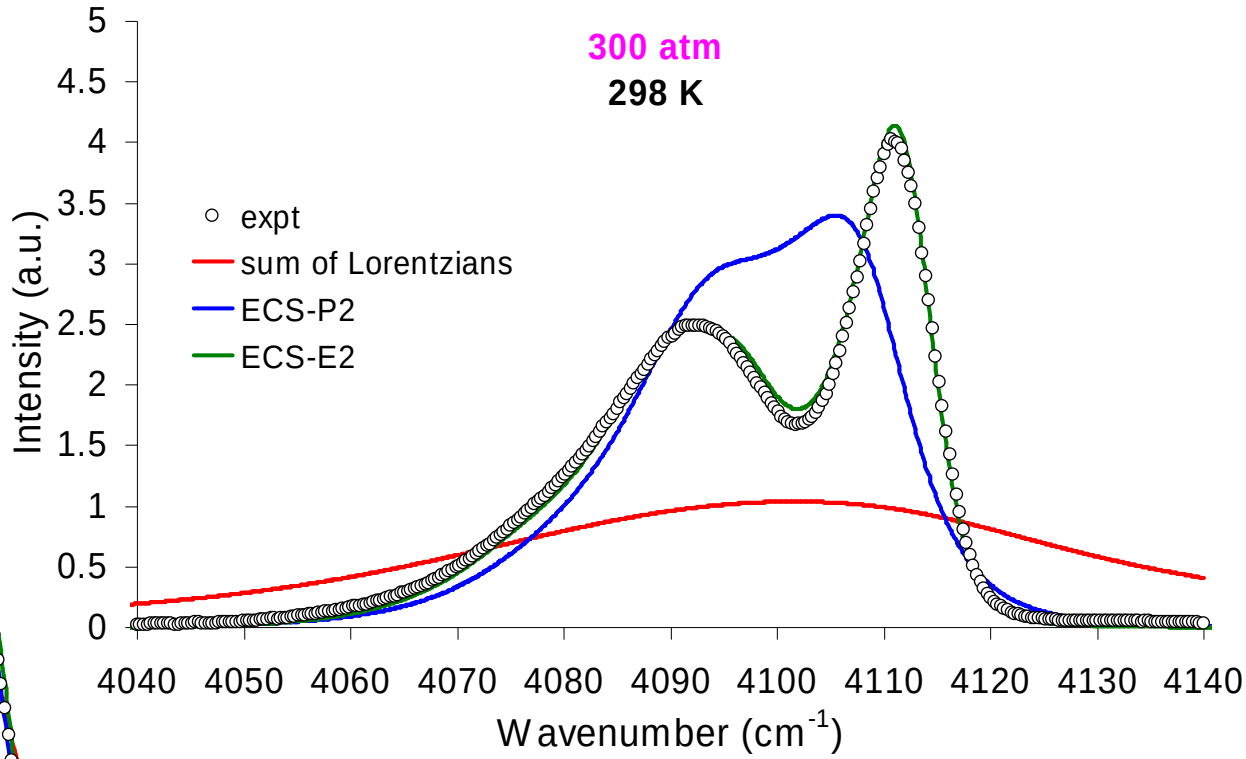
$$A_k^{(1)}$$

CO_2: Effective correction allowed for diagonal elements

❸ Applications to high-density IR spectra

OCS-He $2\nu_3$

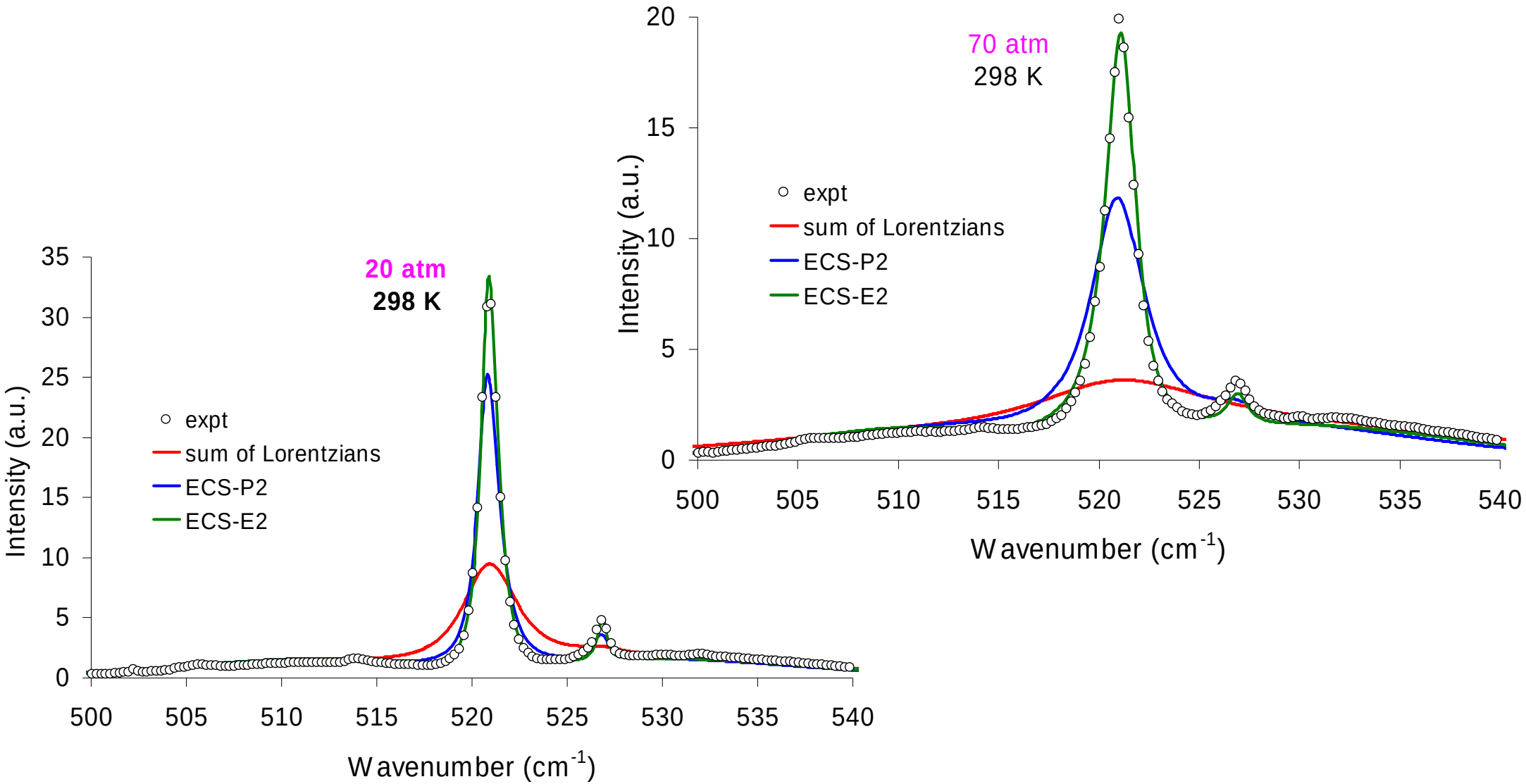




Buldyreva et al., JCP 138, 164117 (2013)

❸ Applications to high-density IR spectra

OCS-He ν_2



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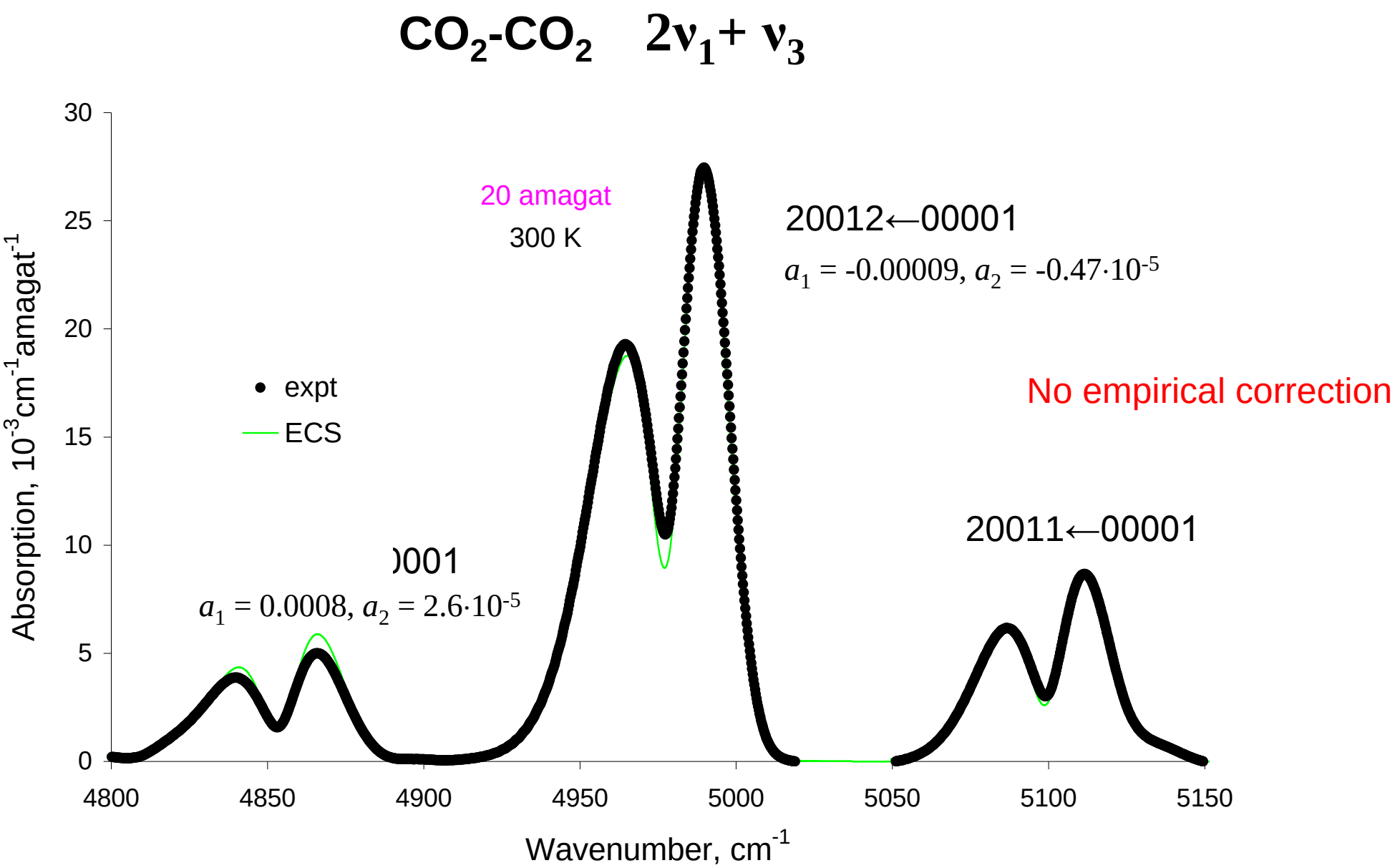
❸ Applications to high-density IR spectra

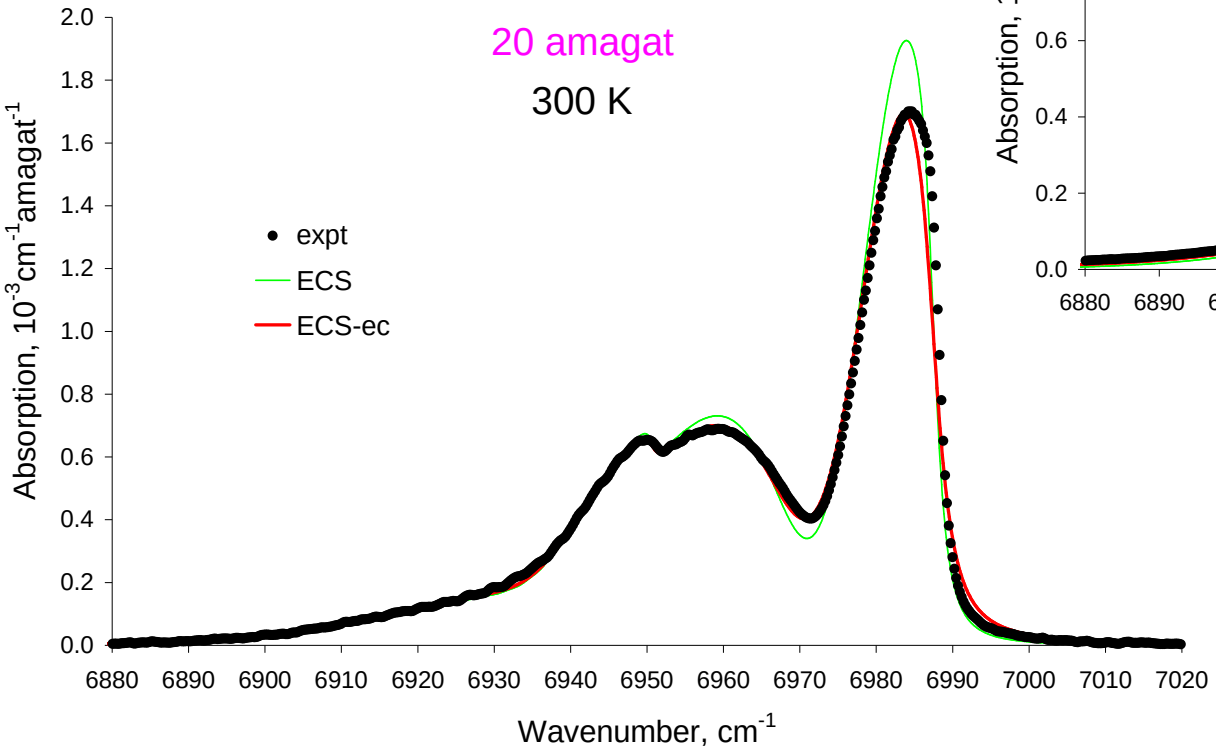


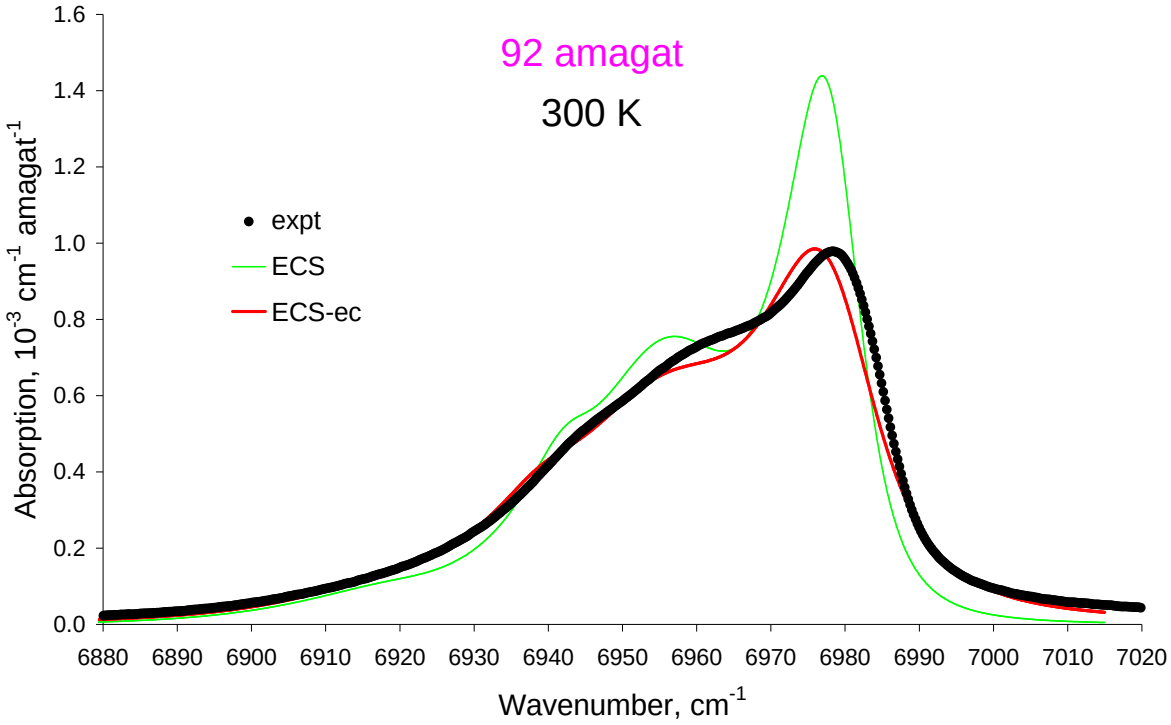
Filippov et al., PCCP 15, 13826 (2013)

HW factors: Rothman et al., JQSRT 48, 537 (1992)

❸ Applications to high-density IR spectra

CO_2-CO_2 $3\nu_3$





Empirical correction
$\gamma'_v = 0.040$ cm^{-1} amagat^{-1}

a_1 = -0.000215

HW factors: Rothman et al., JQSRT 48, 537 (1992)

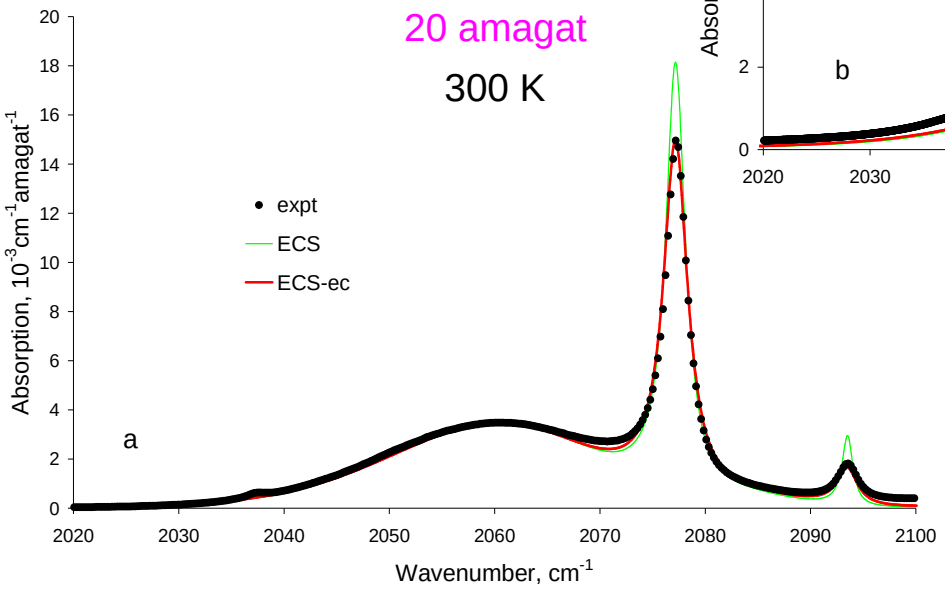
Filippov et al., PCCP 15, 13826 (2013)

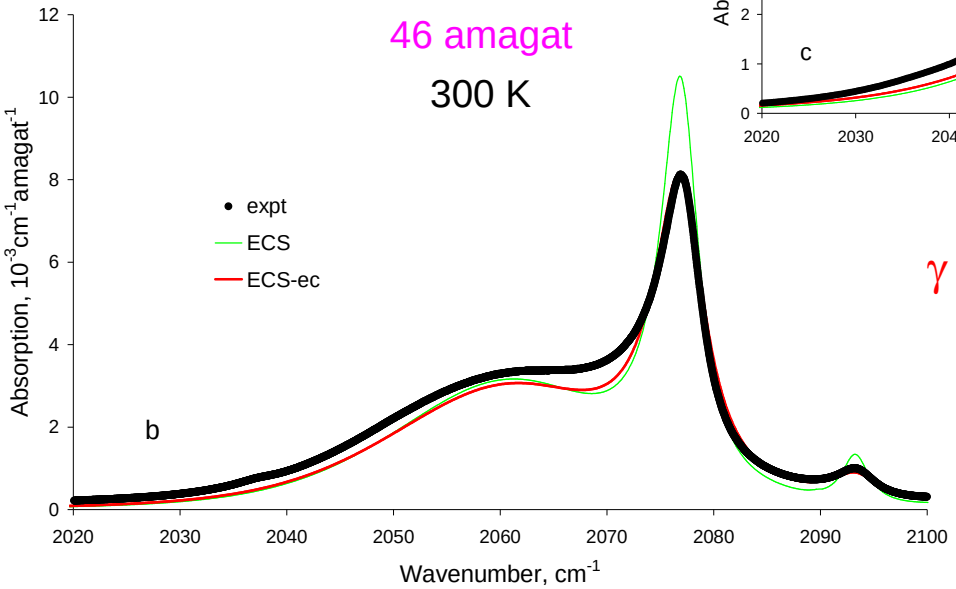
❸ Applications to high-density IR spectra

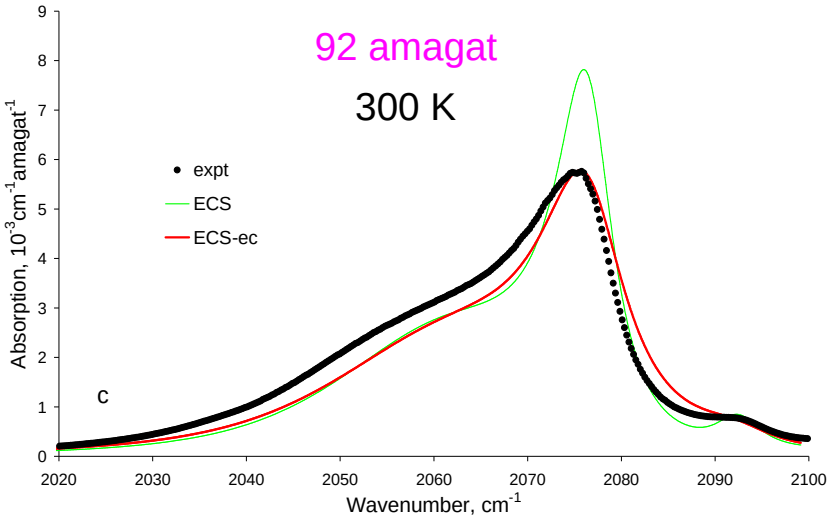
CO_2-CO_2 $(\nu_1 + \nu_2)_I$

$a_1 = -0.3772$, $a_2 = 0.52 \cdot 10^{-5}$, $b_2 = -0.58 \cdot 10^{-5}$

HW factors: Rothman et al., JQSRT 48, 537 (1992)







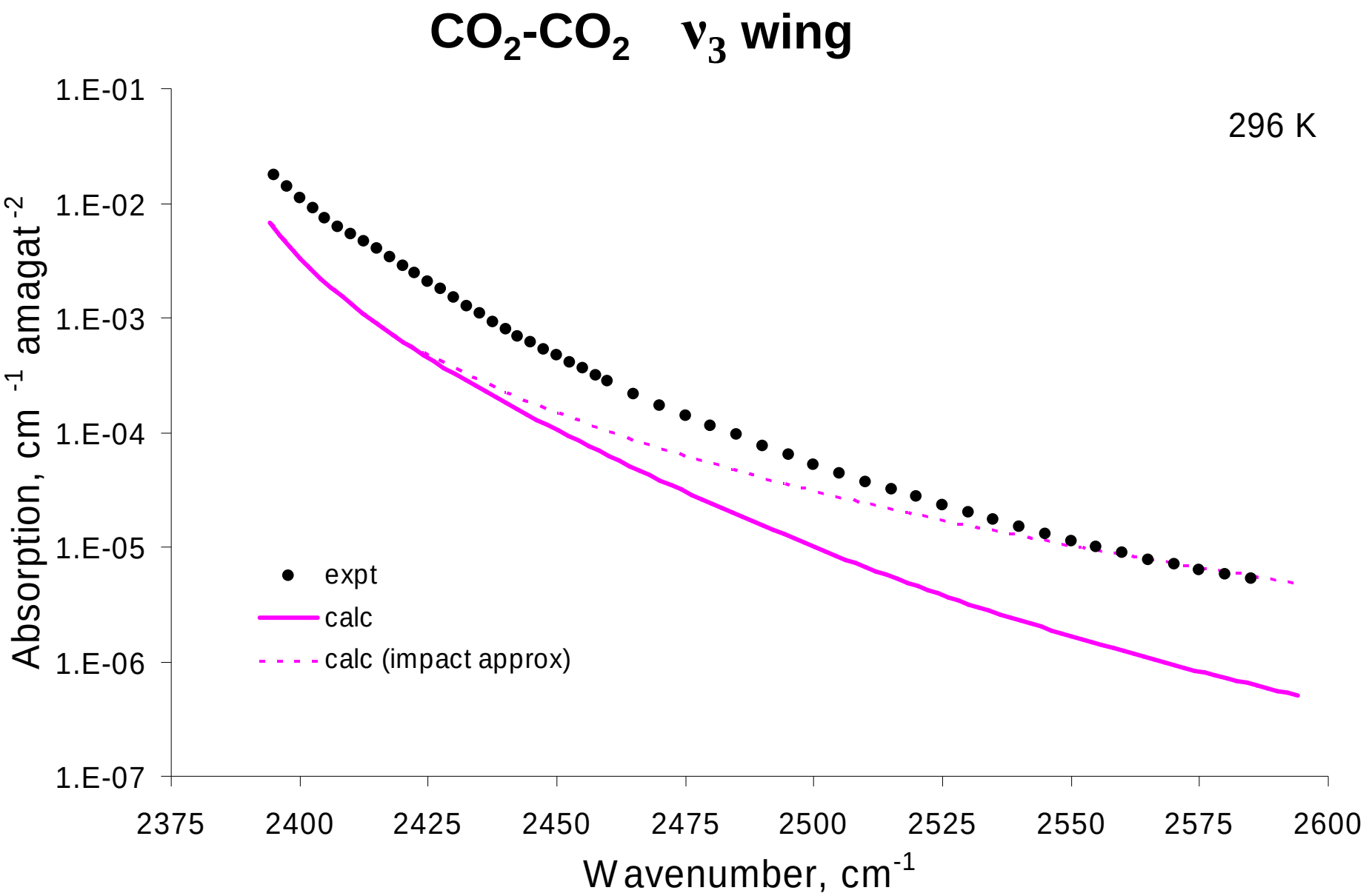
$\gamma'_v = 0.020$ cm^{-1} amagat^{-1}

$\gamma'_v = 0.016$ cm^{-1} amagat^{-1}

$\gamma'_v = 0.013$ cm^{-1} amagat^{-1}

Filippov et al., PCCP 15, 13826 (2013)

❸ Applications to high-density IR spectra

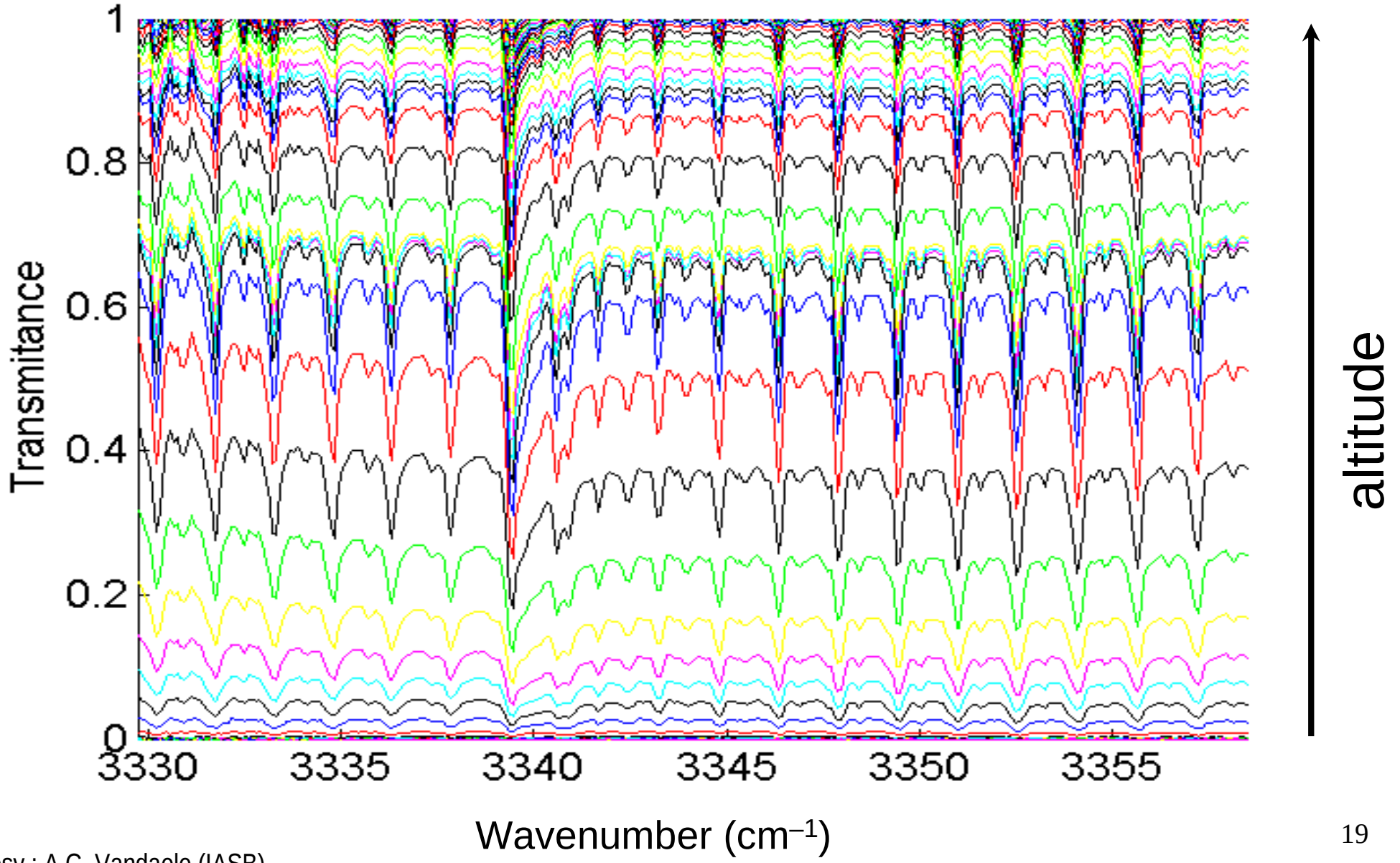


Buldyreva & Daneshvar, JCP 139, 164107 (2013)

expt: Le Doucen et al., Appl. Opt. 24, 897 (1985)

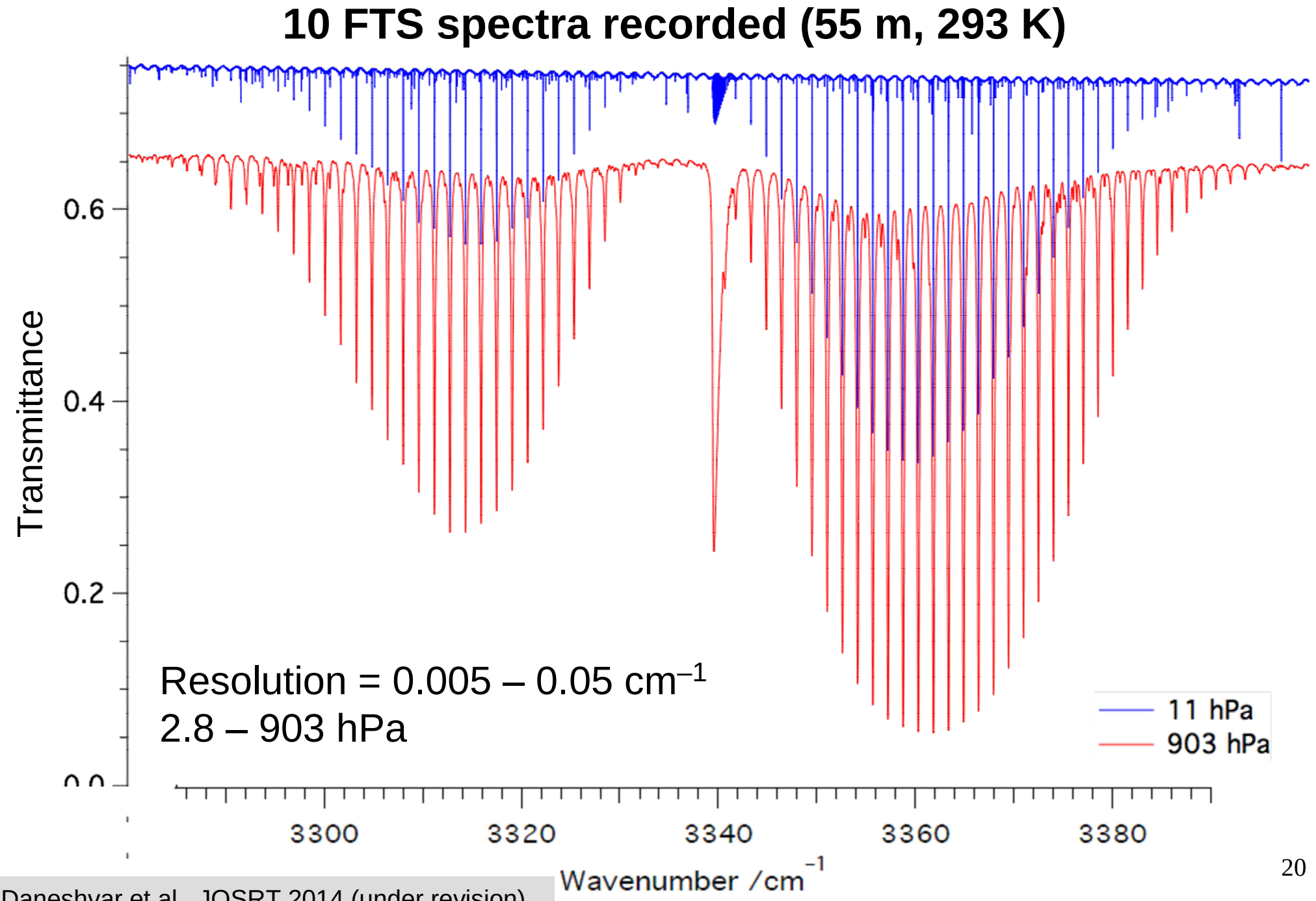
❹ Applications to CO_2 IR spectra at low densities

SOIR spectra of the atmosphere of Venus (Venus Express)



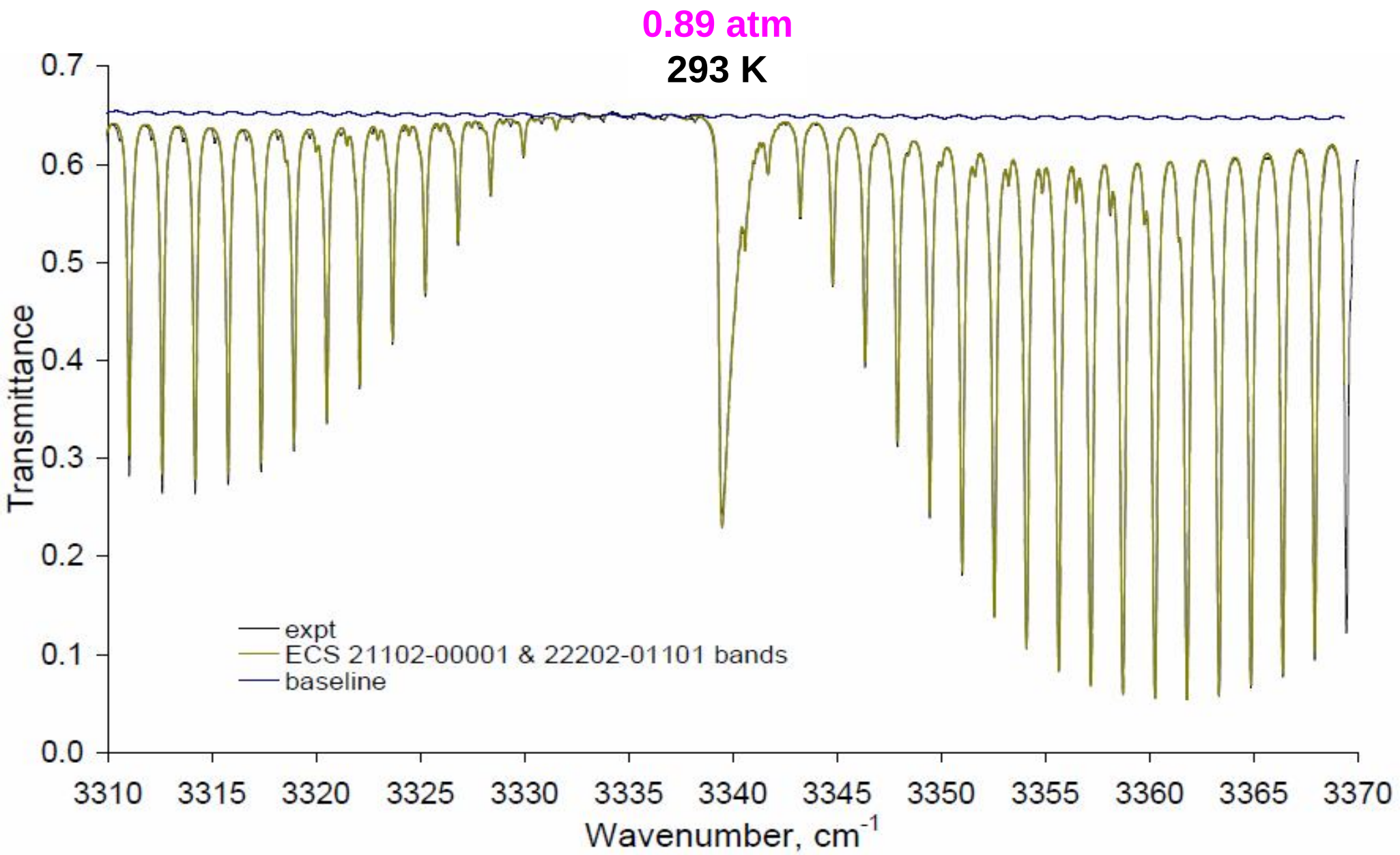
Courtesy : A.C. Vandaele (IASB)

❹ Applications to CO_2 IR spectra at low densities



Daneshvar et al., JQSRT 2014 (under revision)

❹ Applications to CO_2 IR spectra at low densities



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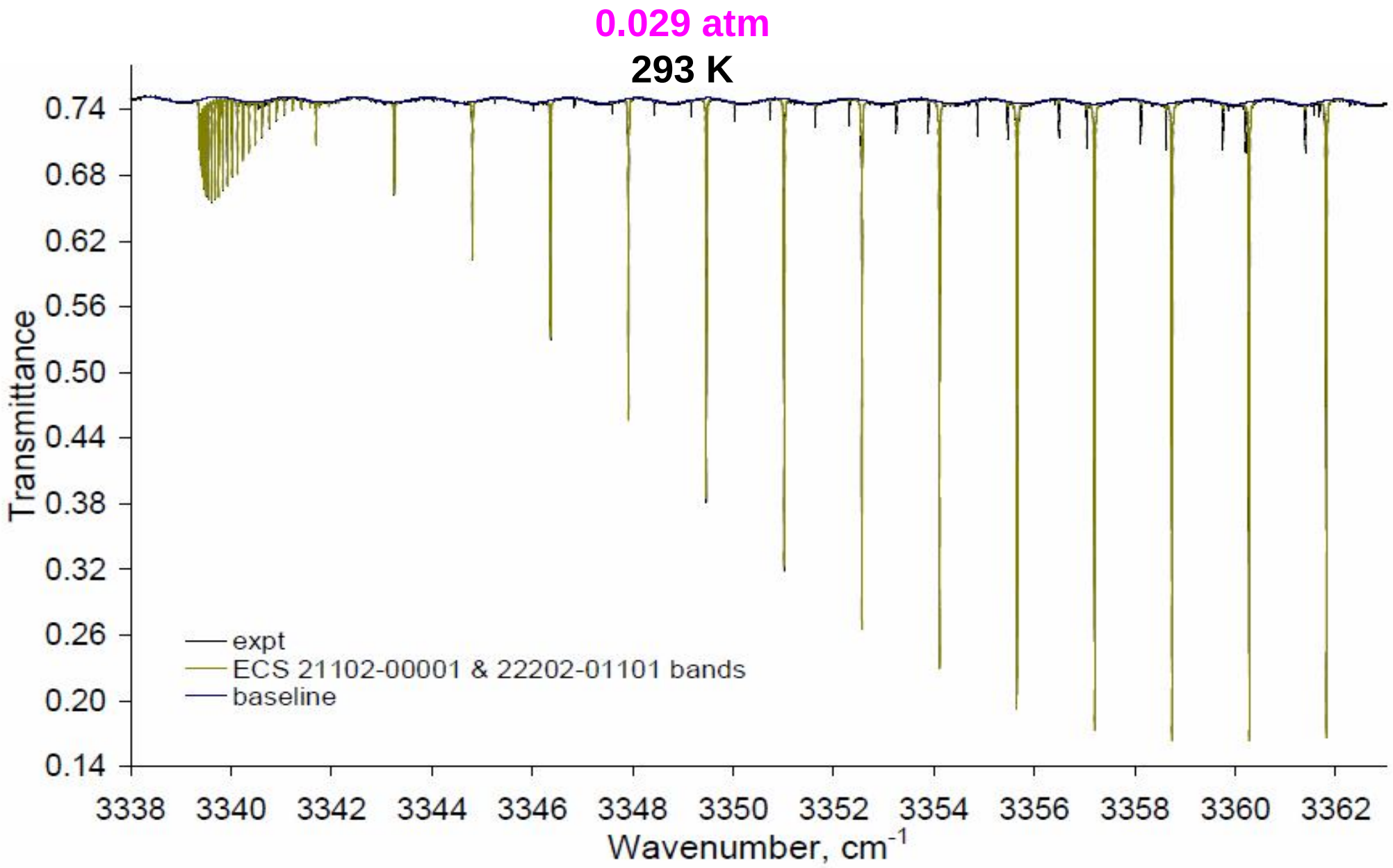
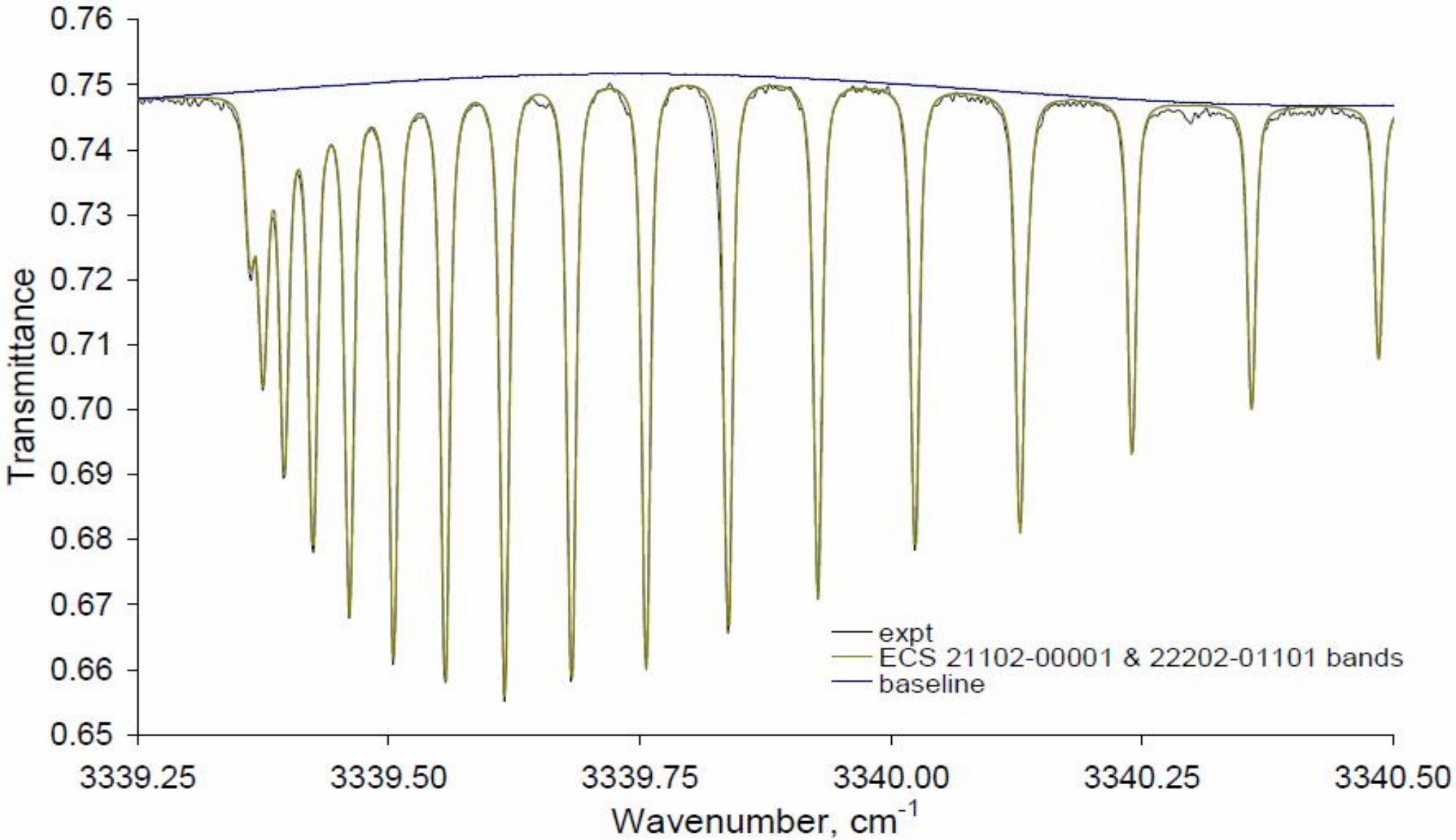
❹ Applications to CO_2 IR spectra at low densities



Daneshvar et al., JQSRT 2014 (under revision)

❹ Applications to CO_2 IR spectra at low densities

0.029 atm **Q-branch zoom**



Daneshvar et al., JQSRT 2014 (under revision)

❺ Conclusions & perspectives

Main results

- Immediate good agreement with expt OCS-He spectra up to 300 atm **without any additional fitting parameter**
- Satisfactory agreement for CO_2 up to nearly liquid phase (**+ 1 fitting parameter**)
- Excellent agreement with low-density expt CO_2 spectra down to 0.03 atm
- The model has **a universal character** (IR, Raman iso, aniso)

Further improvements/tests/applications

- Studies of extremely low pressures (narrowing effects)
- Modeling of Im Γ
- Studies of **far wings (non-Markovian effects)**
- Modeling of temperature dependences
- Calculations of correlation functions from *ab initio* PES
- Studies of other bands and other molecular systems