FT-IR measurements of the O_2-O_2 collision-induced absorptions (cia) at high pressures

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Capturing the O_2 cia features in NIR/VIS

❑ Key optics components

(1) A broad-band spectrometer: JPL Bruker IFS-125HR

(2) A (heatable) high-pressure cell (HHPC) developed: Rated to 150 bars at 520 K

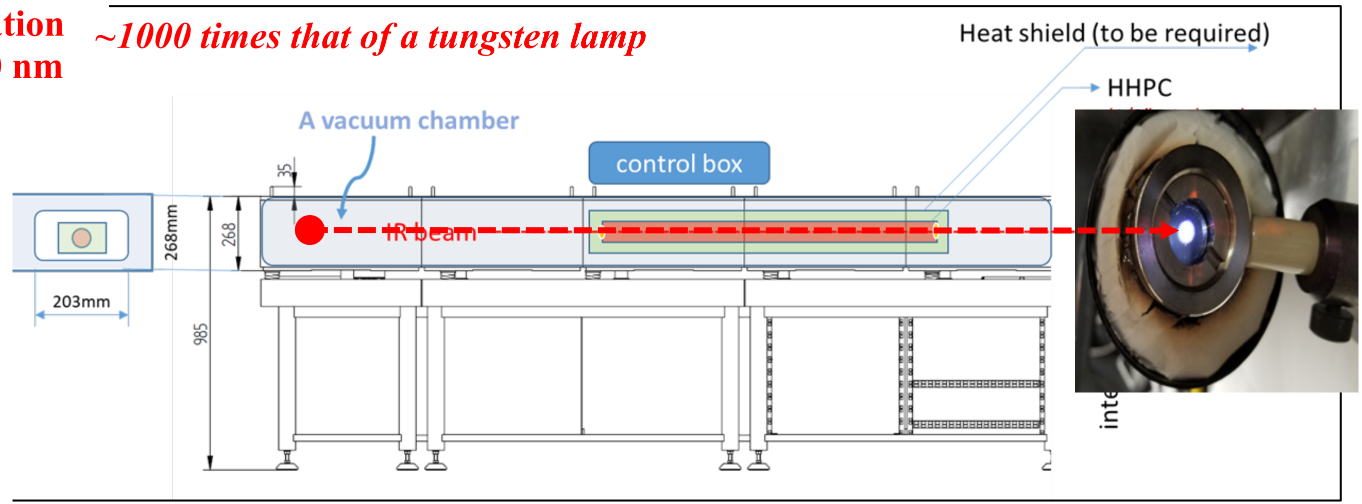
(3) A broad-band super-luminous light source: A Laser Driven Light Source.

All three components have been configured and employed for this work!

❑ HHPC inside an extension chamber

Broadband collimation in the 200 – 2400 nm

EQ-99FC LDLS with Fiber Collimator



Experimental conditions
- Number of molecules in the beam path

- **Gas samples**
  – O_2, 99.999%, normal sample [ε < 0.1%]
  – Dry air, 21(1)% O_2 [ε ~ 4.8%]

- **Path 1: HHPC**
  – Cell path = 0.999(1) m
  – Prs and Temp [δ=0.1 bar and 0.3K, respectively]
  – Pressure ranges, 3 – 131 bars
  – Departure from ideal gas law [up to 5.5%]

Pure O_2 [bars]	correction factors	Dry air	correction factors
116.4	1.055	131.2	1.043
83.0	1.045	130.9	1.043
57.3	1.034	101.8	1.033

- **Other paths (FT-IR & Ext. Chambers, Source box)**

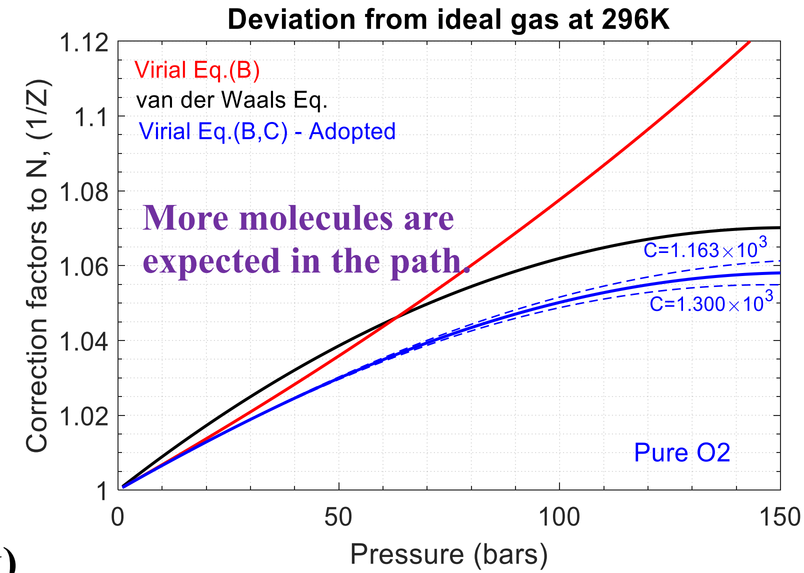
♣ Virial Eq. of State for real gases

The compressibility factor, Z, for a gas mixture is described by

$$Z = \frac{PV_m}{RT} = 1 + \frac{B_{mix}}{V_m} + \frac{C_{mix}}{V_m^2} + \cdots$$

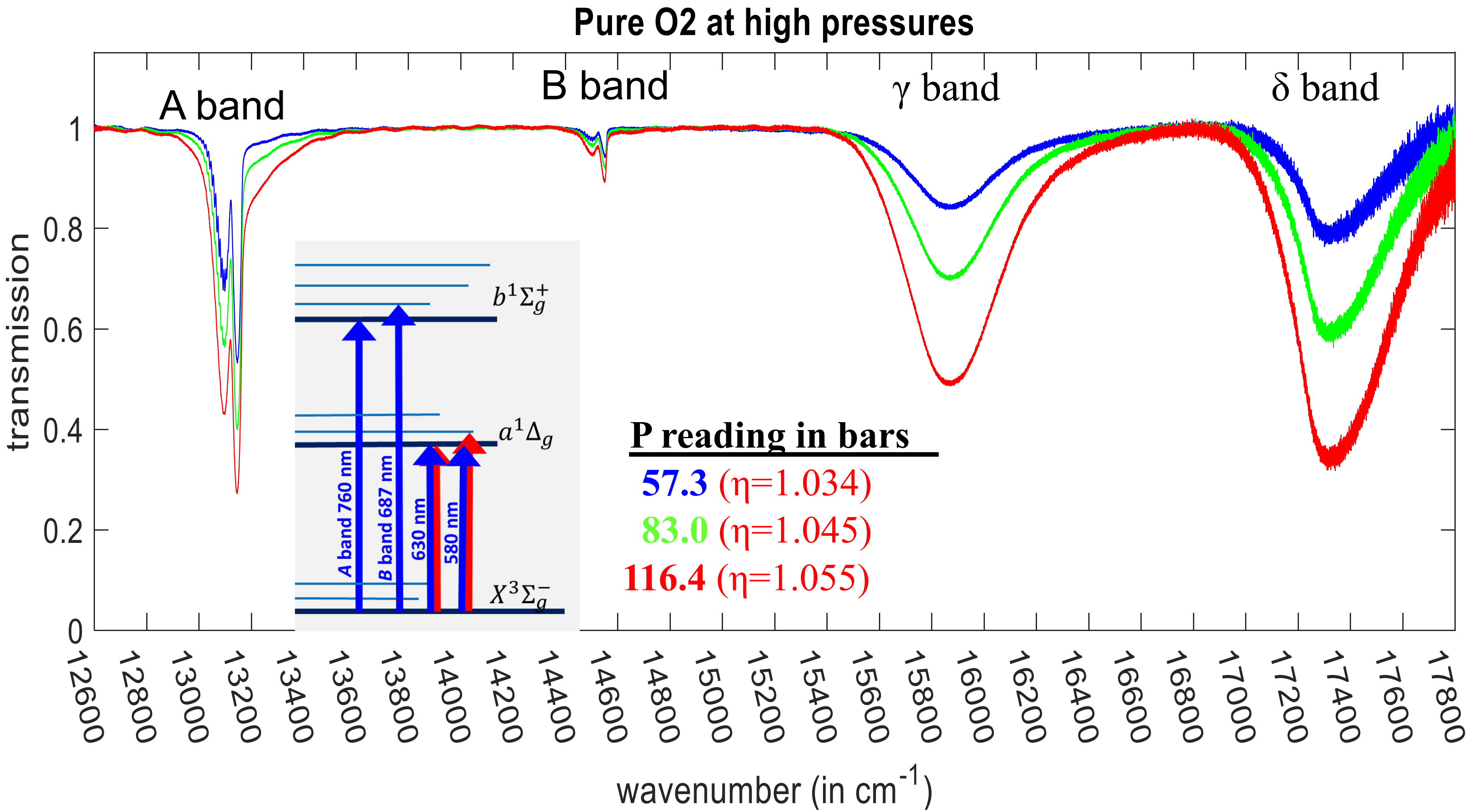
For a mixture,

$$B_{mix} = x_1^2 B_{11} + 2x_1x_2B_{12} + x_2^2 B_{22}$$



Note: The 2nd, 3rd Virial constants, *B* and *C*, are adopted from the CRC Handbook.

Spectra obtained at room Temp.



How to derive cia for O_2(B, γ, δ)

➢ What is measured:

Total extinction

RS = Rayleigh scattering (→ Ratioed out)

MD = magnetic dipole moments (Simulated)

- $\alpha_{tot} = \alpha_{RS} + \alpha_{MD} + \alpha_{cia}$
- $\alpha_{MD} = \alpha_{O2\_lines} (+ \alpha_{O2\_LM})$

➢ α_{MD}: Model & Assumptions:

(1) Widths and shifts at high pressures

→ Assumed proportional to Prs.

(2) Profile: SD-Voigt+LM (HITRAN)

Speed-dependence parameters

from Domyslawska et al.(2016)

(3) α_{LM}: Line mixing parameters

Rosenkranz parameters

Not available for O2(B) band

so we calculated them.

➢ Line mixing parameter calculations

- ***K*** = inelastic state-to-state collisional rotational transition (or transfer) rates;
- Upward transition modelled by EPG Law

$$K^{EPG}_{j\leftarrow k} = a\left|\frac{\Delta E_{jk}}{B}\right|^{-b} \exp\left(-c\left|\frac{\Delta E_{jk}}{k_B T}\right|\right)$$

- Downward transition by Detailed balance

$$K^{EPG}_{k\leftarrow j} = \frac{\rho_k}{\rho_j} K^{EPG}_{j\leftarrow k}$$

- ***W***, Real part of Relaxation Matrix

$$W_{jk} = -\frac{\epsilon}{2}\left[K^{EPG}_{j\leftarrow k} + K^{EPG}_{j'\leftarrow k'}\right]$$

- Model validation by Observed widths

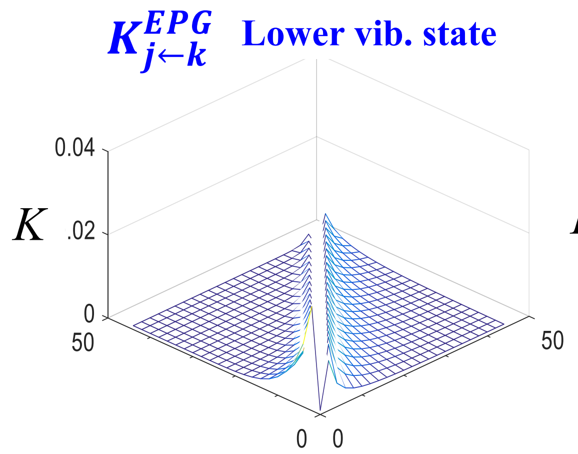
$$\gamma_l(obs) = \ll lk k' | Re[W] | l'_{jj'} \gg = W_{kk'}$$

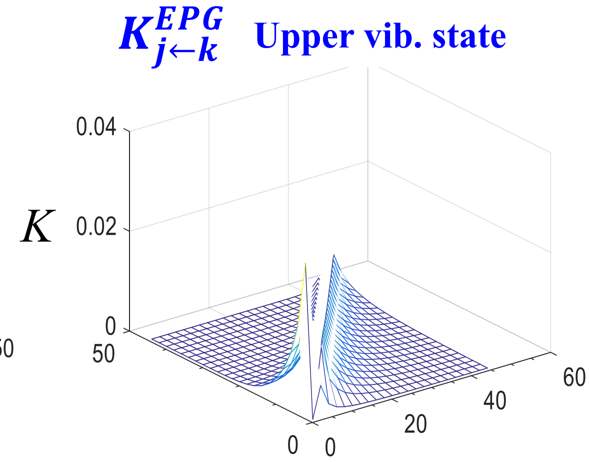
- Finally, first-order line mixing coefficient, **Rosenkranz parameter, *Y***

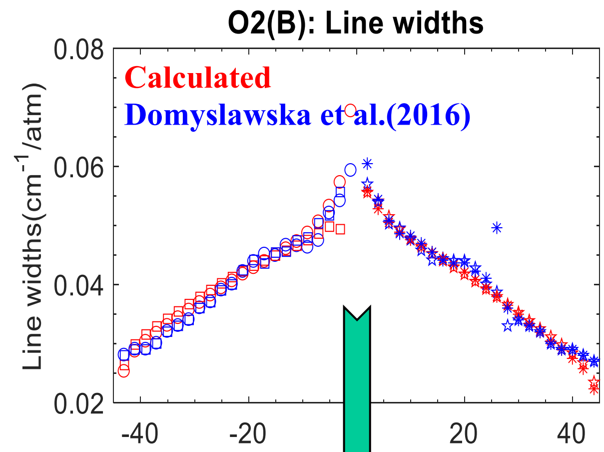
$$Y_k = 2\sum_{j\neq k} \frac{d_j}{d_k} \frac{W_{jk}}{\nu_j - \nu_k}$$

Observed line widths→[W]→Line mixing coeffs.

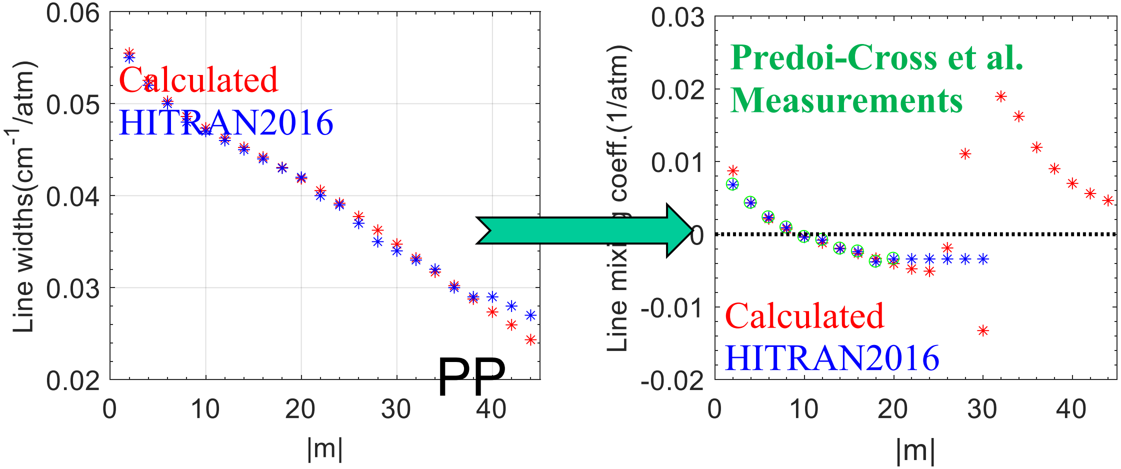
Treat PP, PQ, RQ, RR branches, separately.

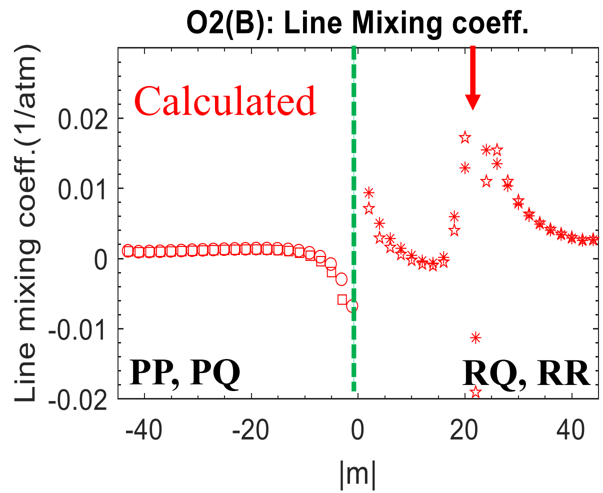




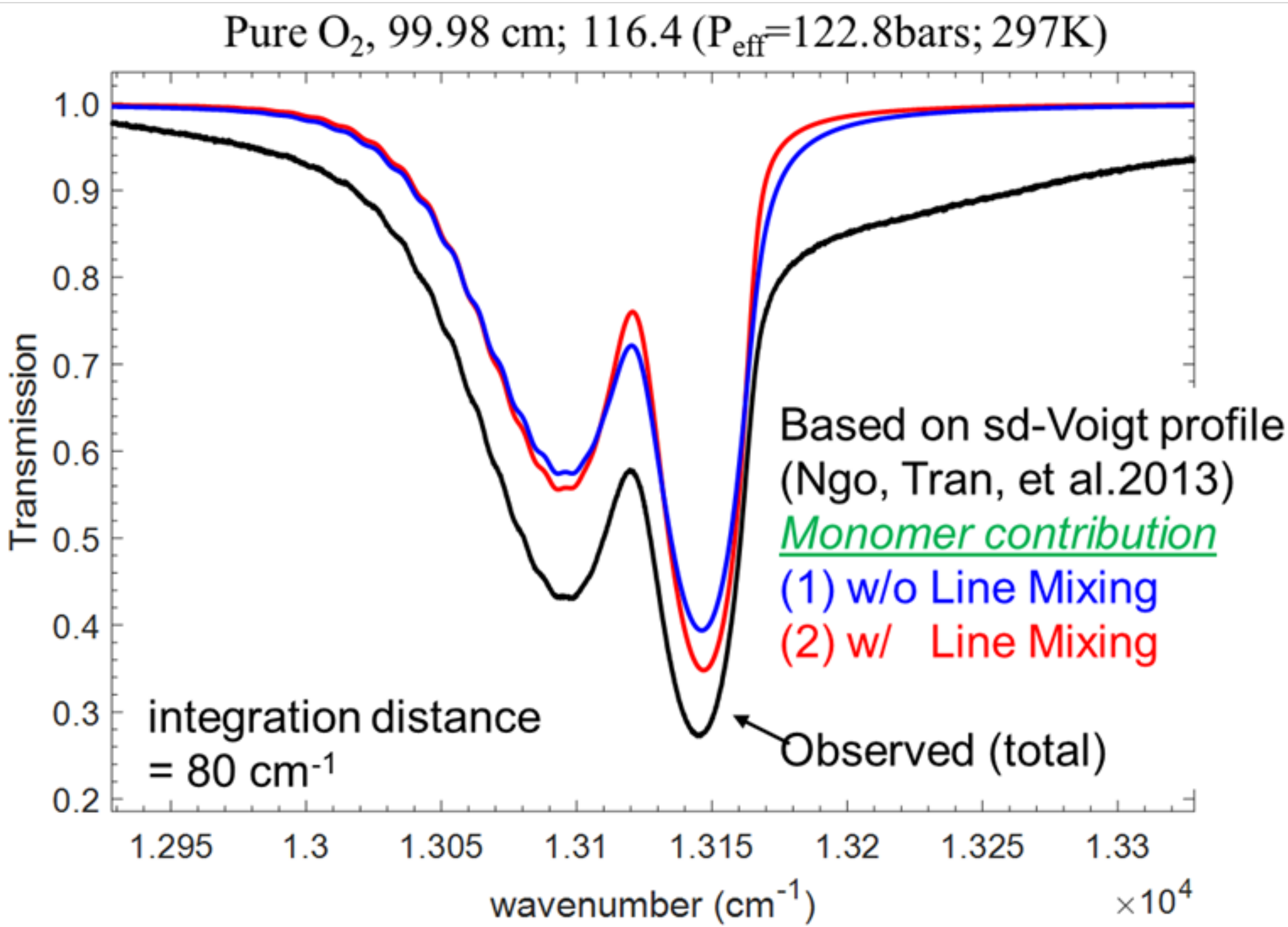


O_2(A) RR-branch

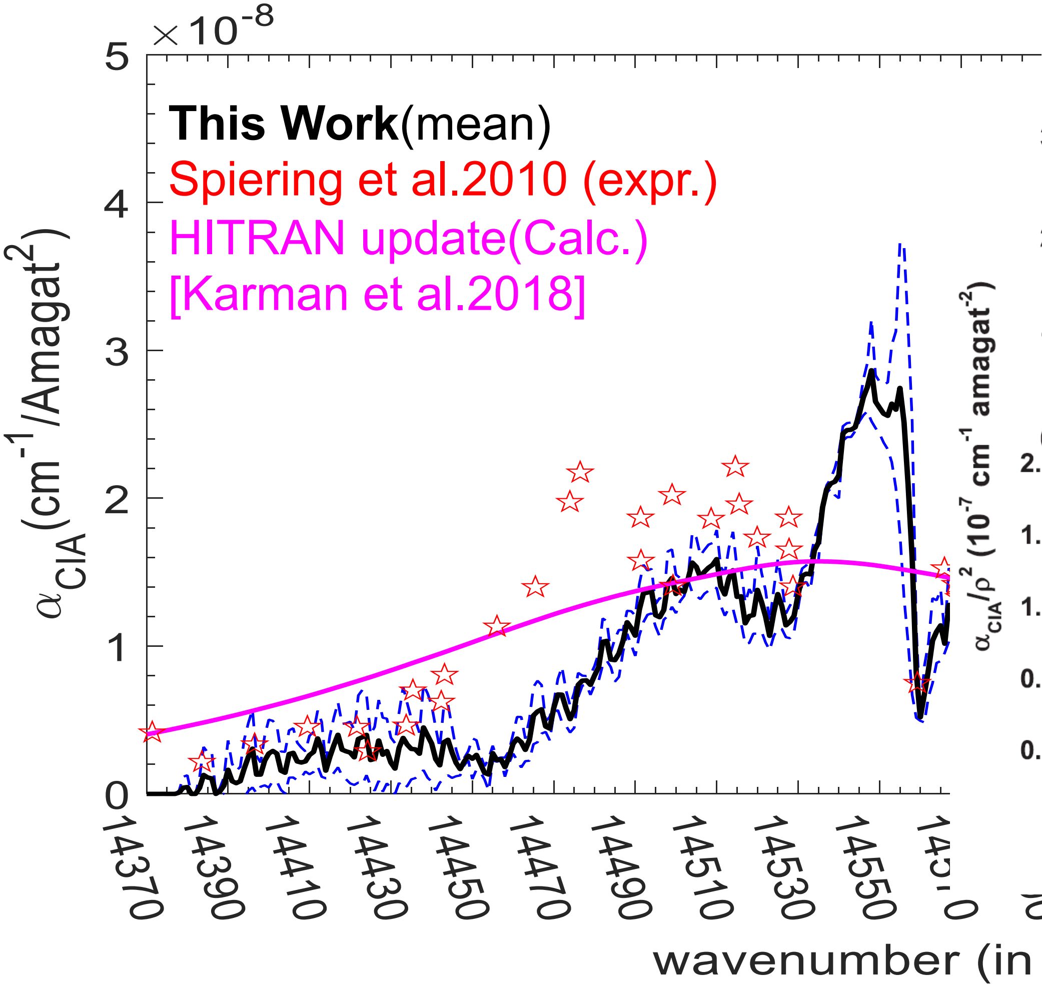




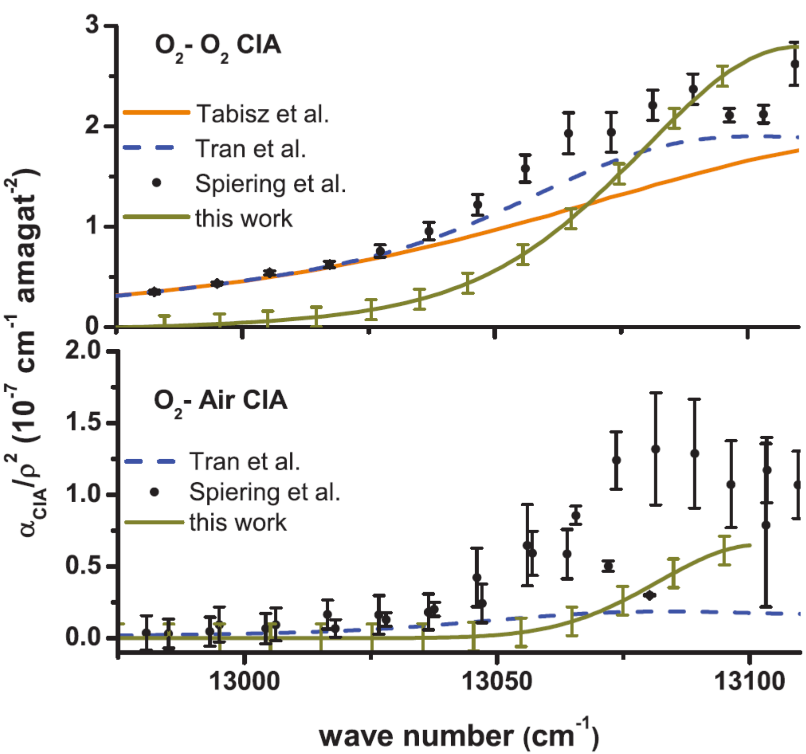
Impact of Line mixing – a sample case



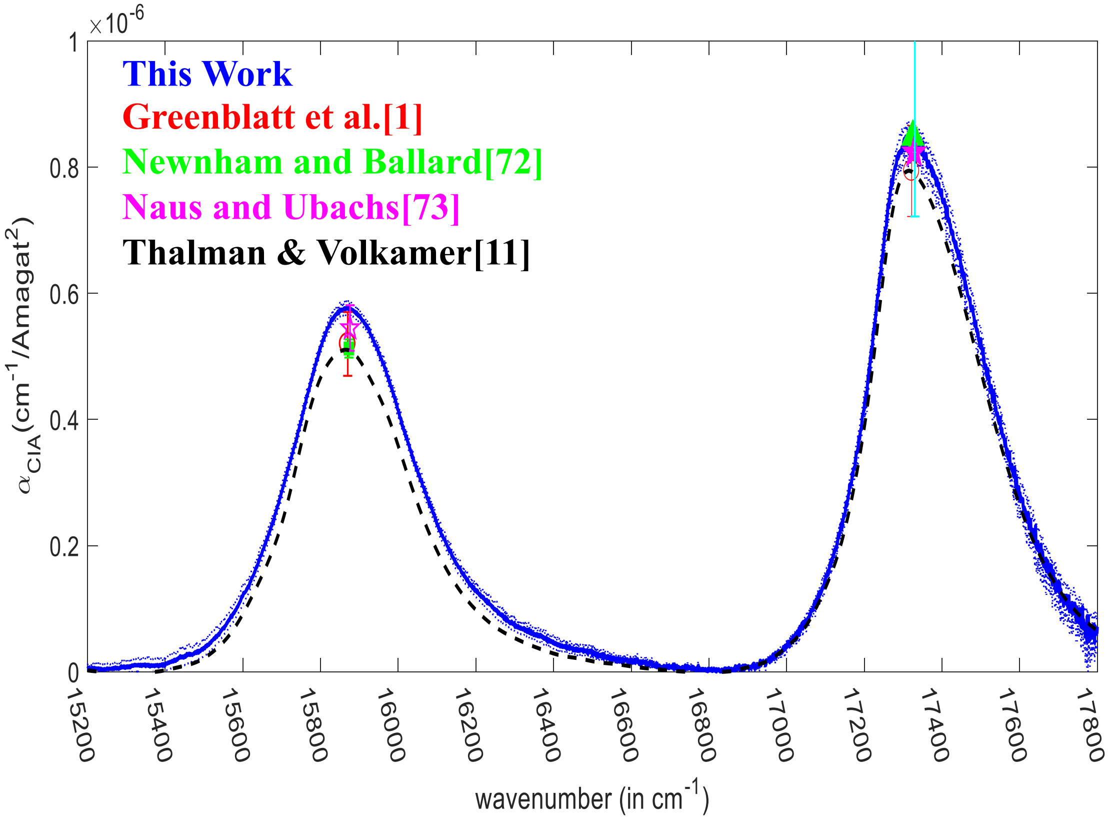
CIA in the O2(B) band based on sd-Voigt + 1st order line mixing (Rosenkranz)

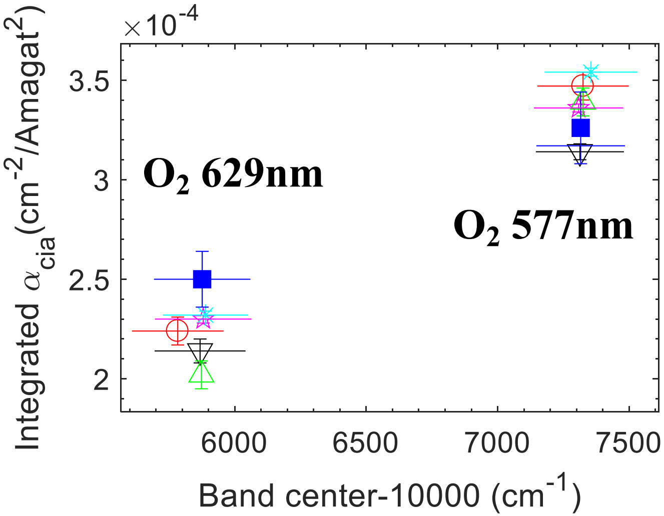


O_2(A) band cia [Long et al. 2012]



O_2–O_2 cia in the 629 & 577 nm regions





❑ **Comparison:**

- Peak frequency
- FWHM,
- Integrated CIA

(1) Agreed within combined uncertainties

(2) This work shows higher than others.

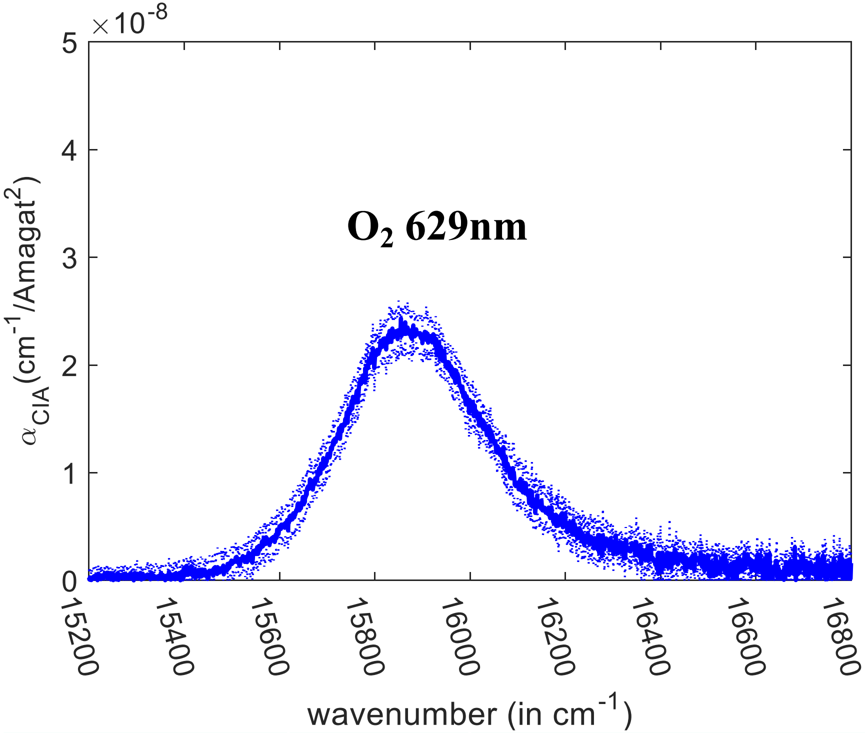
(3) Band shapes are different.

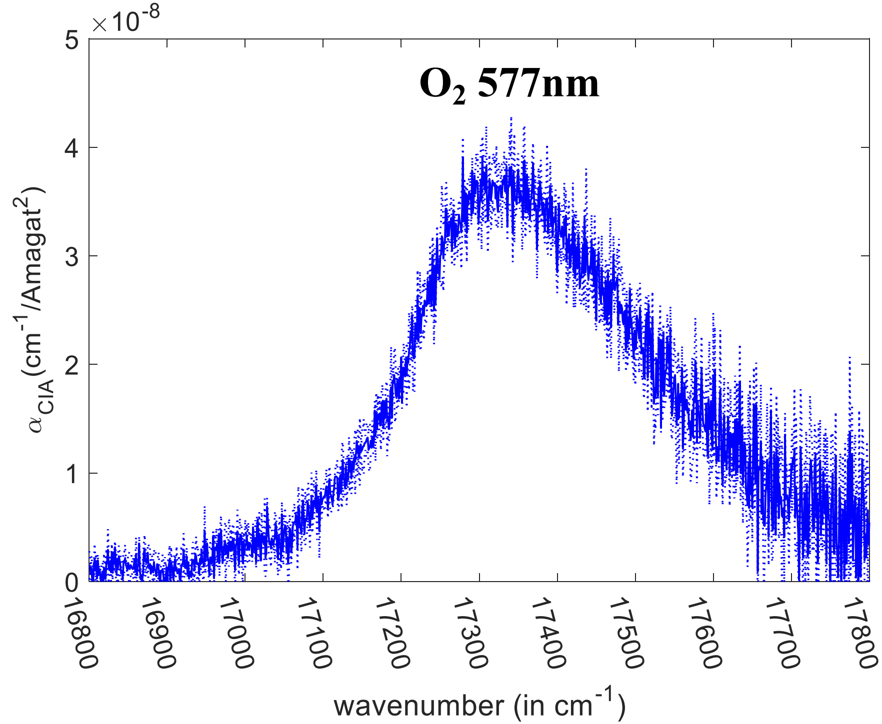
❑ **Spread, 629 and 577 nm bands**

- Band center ~ 106 & 43 cm-1
- FWHM ~ 47 & 18 cm^{-1}
- Integrated CIA ~ 8% & 4%

O_2-N_2 cia in the 629 and 577 nm regions

- Weaker than that of O_2-O_2 cia by a factor of ~30
- No measurements available for O_2-N_2 cia





Regions / Work	T (K)	$a^1\Delta_g(v=0) + a^1\Delta_g(v=0)$	$a^1\Delta_g(v=1) + a^1\Delta_g(v=0)$
band centers		629 nm	577 nm
Present work	296K	$1.03(\pm 0.21)\times 10^{-5}$	$1.48(\pm 0.20)\times 10^{-5}$

Summary and Acknowledgements

❑ Measured O_2-O_2 CIA in the O_2-B, γ, and δ band regions

- Simulate the resonance contribution with Line Mixing taken into account
- O_2(B): Integrated CIA = $0.32(6)\times10^{-5}$ cm^{-2}/Amg^2
  cf. Spiering et al.(2011): $S_{cia} = 0.44(4)\times10^{-5}$ cm^{-2}/Amg^2
- Ratio O_2: cia(A)/cia(B) = 16.7 cf. A-band/B-band = 16.9
  cf. Tran et al. (2006) Ratio = 10.7 ; Spiering et al.(2011), Ratio = 14.9
- **Integrated O_2-O_2 cia in the O2- γ and δ band regions:**
  $25.0(1.4)\times10^{-5}$ and $32.6(1.8)\times10^{-5}$, respectively.
- **Integrated O_2-N_2 cia in the O2- γ and δ band regions:**
  $1.03(0.21)\times10^{-5}$ and $1.48(0.20)\times10^{-5}$, respectively.

❑ Full line mixing element calculations for O_2(A) – on the way.

Acknowledgements

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