The recent improvements in the air- and self- broadened CO_2 and N_2O spectroscopic line-shape parameters in HITRAN2020 database

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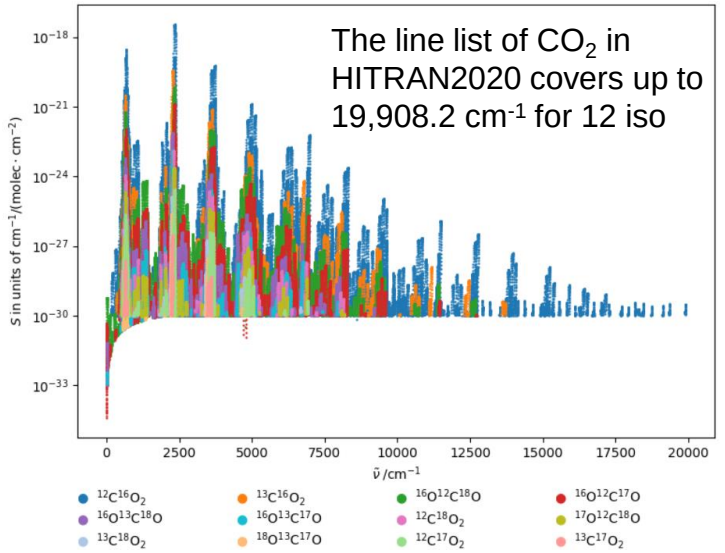
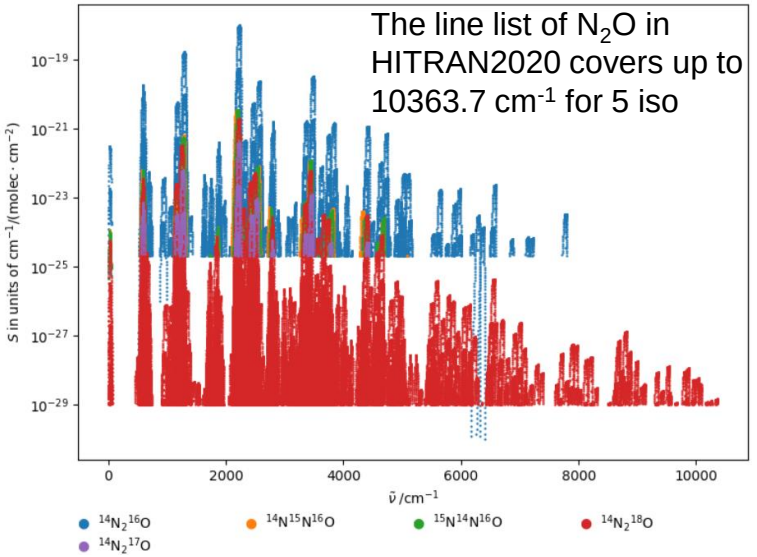
Overview of CO2 and N2O line lists in HITRAN2020

- The HITRAN database is an excellent resource for reference spectroscopic data for atmospheric applications.
- For each transitions of CO_2 & N_2O, the line-shape parameters were updated using the Voigt and speed-dependent Voigt (SDV) profiles.

Why CO_2 and N_2O line-shape parameters were revised with respect to HITRAN2016

- Vibrational dependence of line widths was excessive for some of the bands due to the semi-classical calculations.
- In the spectral region covered by the OCO-2 mission, the line widths were based on the SDV profile, with no speed-dependence parameter provided.
- The model for predicting the pressure shifts (δ) assumed they were the same for the P and R branch lines (where m = −J for the P branch lines and m = J + 1 for the R branch).
- No SDV parameters for line widths were provided
- No first-order line-mixing parameters provided in the database explicitly, although a FORTRAN routine for calculating line mixing was provided.
- The Voigt (VP) line- shape parameters of N_2O had not been modified since the release of HITRAN2004.
- Also, for efficient applicability of the database, it is important that the advanced line-shape parameters be available for as many lines as possible and not just for selected transitions





HITRAN2016: Gordon et al., JQSRT 203 (2017) 3-69

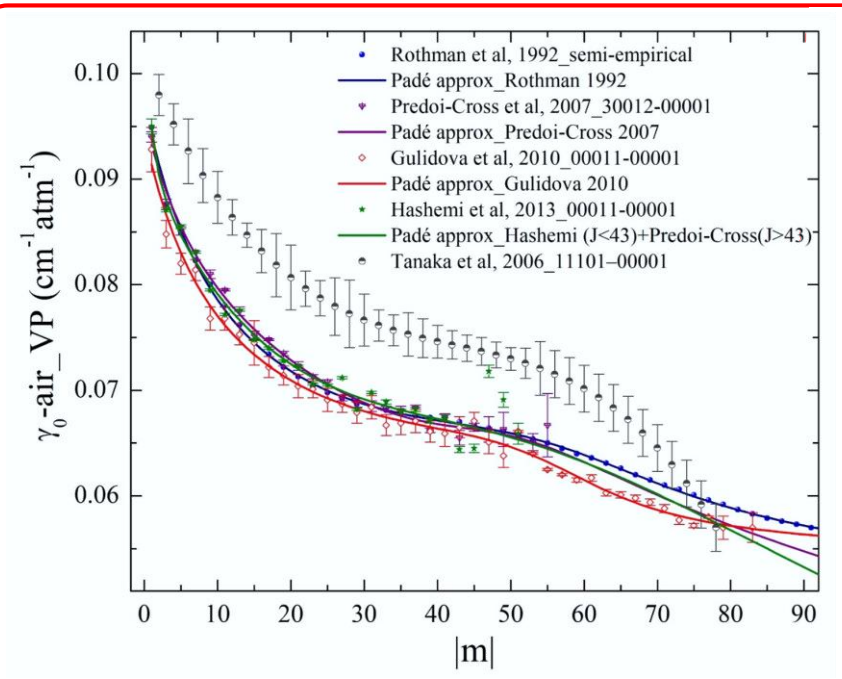
General approach for revising the line-shape parameters for CO_2 and N_2O

1. Selected broadening parameters with their temperature dependence, and speed dependence from different studies in different bands were compared.
2. A negligible vibrational dependence was observed for broadening, and semi-empirical models (using the Padé approximants) were used to interpolate/extrapolate the data.
3. The results were validated against laboratory and/or atmospheric spectra
4. The Voigt (VP) and SDV parameters were populated in separate data tables.

Description	Symbol
Air-broadening	γ_0-air
Self-broadening	γ_0-self
Temp. exponent of air-width	n-air
Temp. exponent of self-width	n-self
Air-shift	delta_air
Self-shift	delta-self

The Voigt (VP) parameters

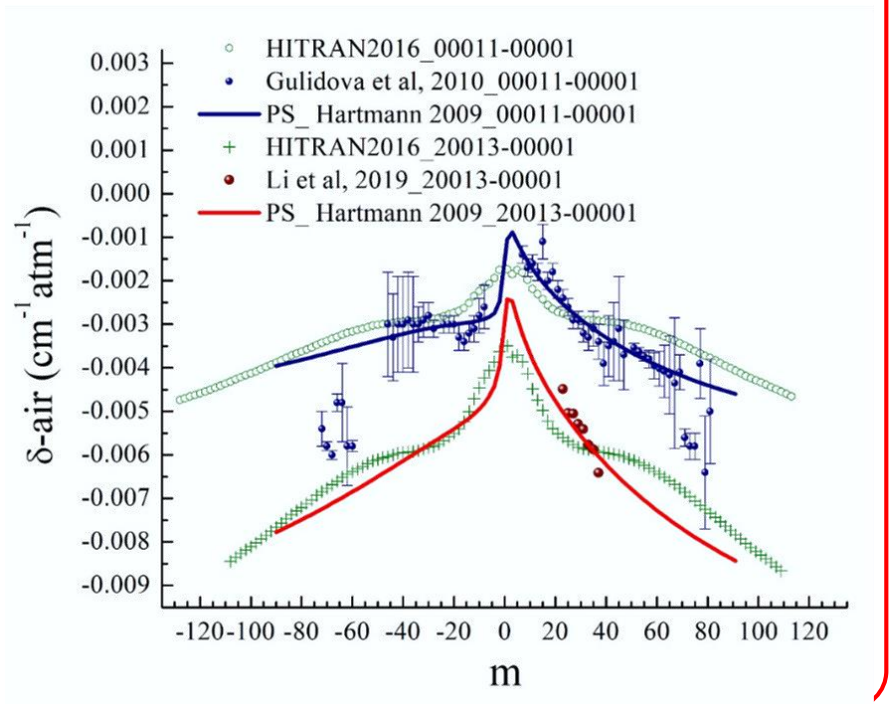
[1]: Hashemi et al, JQSRT, 256,107283.
[2]: Hartmann, JQSRT 110 (2009) 2019-2026



$$\gamma_0 = \frac{(c_0 + c_1 \times |m| + c_2 \times |m|^2 + c_3 \times |m|^3)}{(1 + d_1 \times |m| + d_2 \times |m|^2 + d_3 \times |m|^3 + d_4 \times |m|^4)}$$

The air-broadening half widths of CO_2 deduced using the VP and fitted using the Padé function.

$$\delta[(\nu_1 + \Delta\nu_1, \nu_2 + \Delta\nu_2, \nu_3 + \Delta\nu_3, J_f) \leftarrow (\nu_1, \nu_2, \nu_3, J_i)] = (J_i - J_f)\delta_{rot}(|m|) + (a_1\Delta\nu_1 + a_2\Delta\nu_2 + a_3\Delta\nu_3)\delta_{vib}(|m|).$$

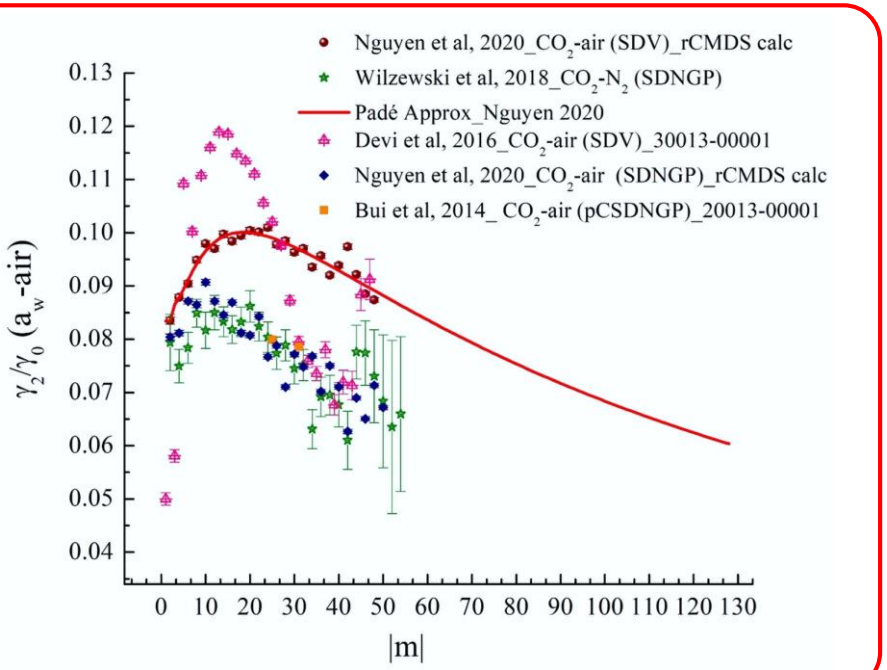


The air-shifts estimated calculated using Hartmann's approach[2] (the solid line), the experimental measurement at the same band and compared to those in HITRAN2016 versus |m|.

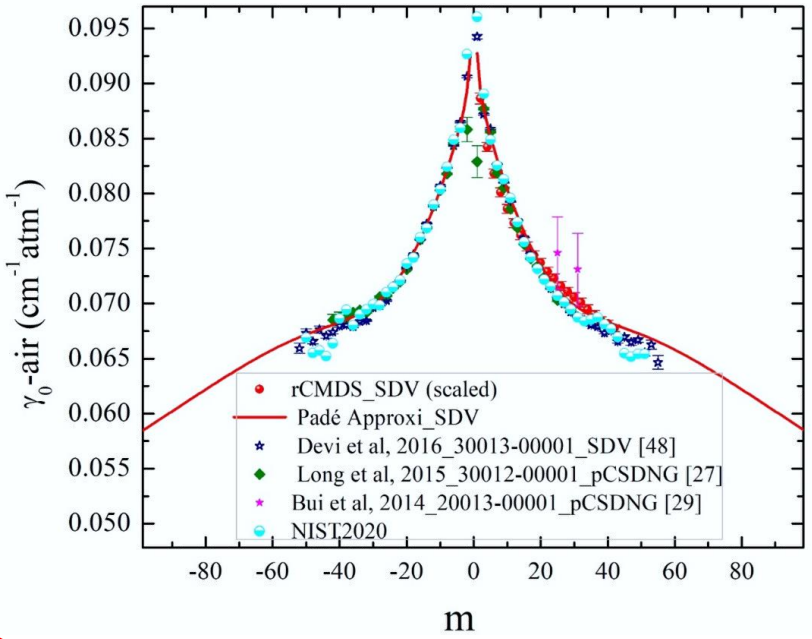
The speed-dependent parameters

Description	Symbol
Broadening half width	γ_0-air ($cm^{-1}atm^{-1}$)
	γ_0-self ($cm^{-1}atm^{-1}$)
Temp. dep. of half width	n_{γ_0}-air (unitless)
	n_{γ_0}-self (unitless)
Speed dep. of half width	γ_2-air ($cm^{-1}atm^{-1}$)
	γ_2-self ($cm^{-1}atm^{-1}$)
Temp. dep. of speed dep.	n_{γ_2}-air (unitless)
	n_{γ_2}-self (unitless)
Line shifts	δ-air ($cm^{-1}atm^{-1}$)
	δ-self ($cm^{-1}atm^{-1}$)

The speed dependence of air-broadening half widths of CO_2 versus |m| using the SDV and speed-dependent Nelkin-Gatak (SDNG) profiles.

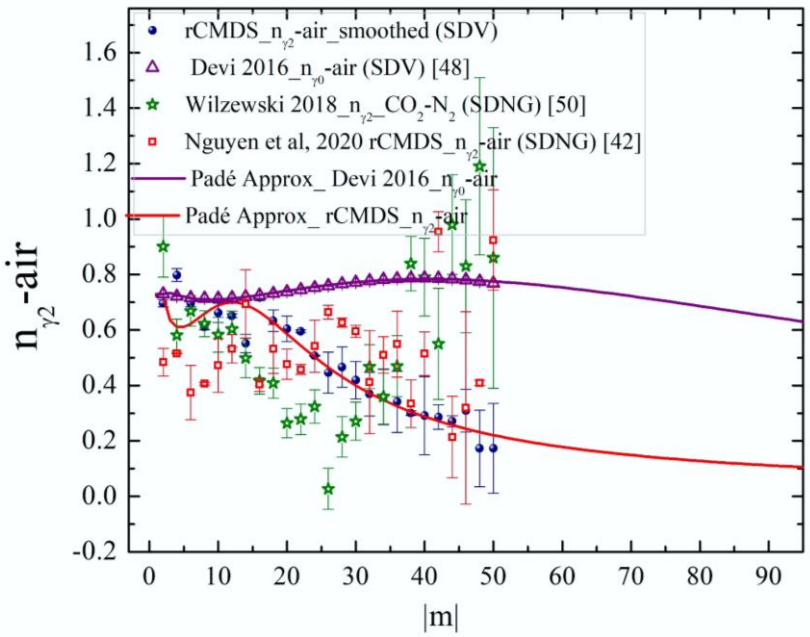


Nguyen et al, JQSRT,242 (2020) 106729.
Bui et al, JCP, 141 (17) (2014) 174301
Devi et al, JQSRT, 177 (2016) 117-144 .
Wilzewski et al, JQSRT, 206 (2018) 296-305.
Birk et al, 2021, Private communication
Daneshvar et al, JQSRT, 2014;149:258–74



The air-broadening half widths of CO_2 versus |m| deduced using the SDV profile and fitted using the Padé function.

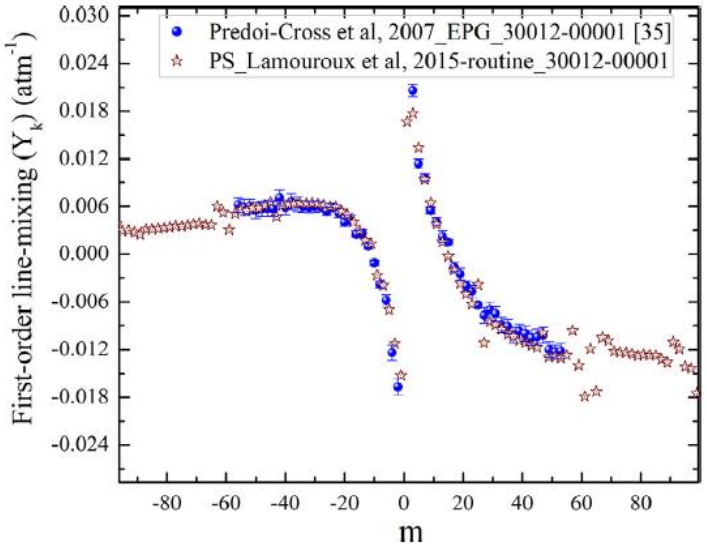
The smoothed temperature dependence of γ_2-air of CO_2 lines versus |m| deduced with the SDV profile



Update of the CO LM package:

The line mixing package for CO_2 was updated. The approach by Lamouroux et al.[1] is used for predicting the line-mixing effect in all the bands of CO_2 either accounting for the full line mixing (W) or the first-order approximation (Y):

1) VP+ first order LM
2) VP+ full LM
3) SDV+ first-order LM. This Fortran package is available at HITRAN*online*: https://hitran.org/supplementary/

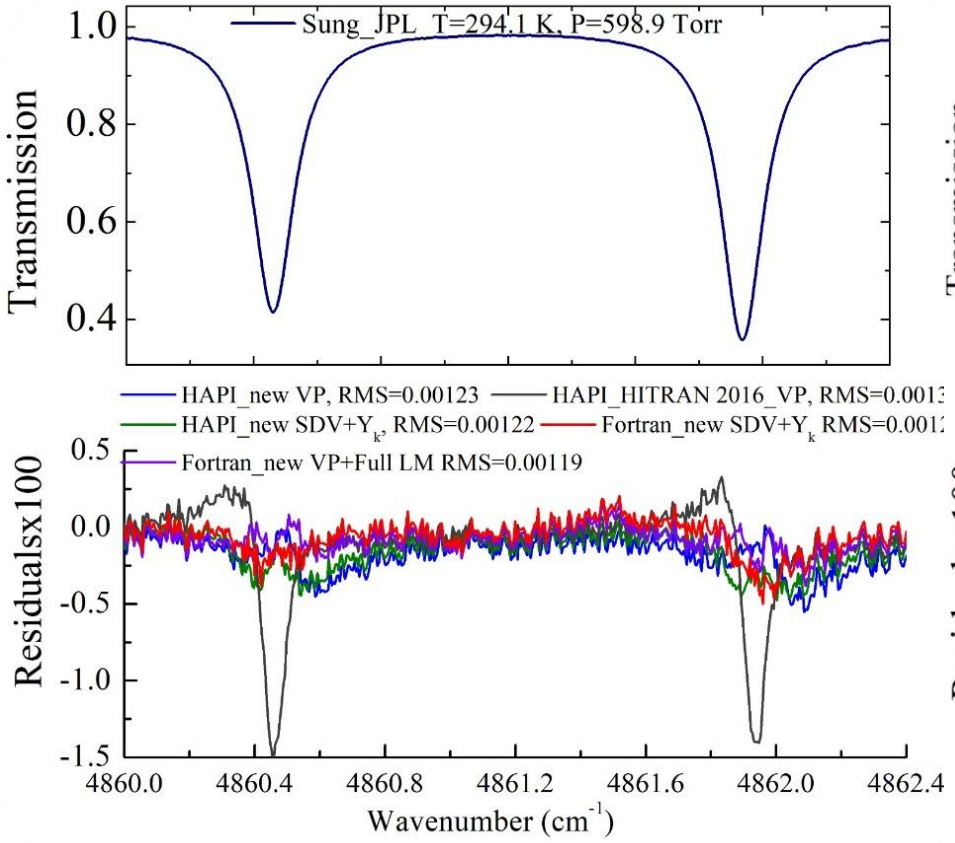


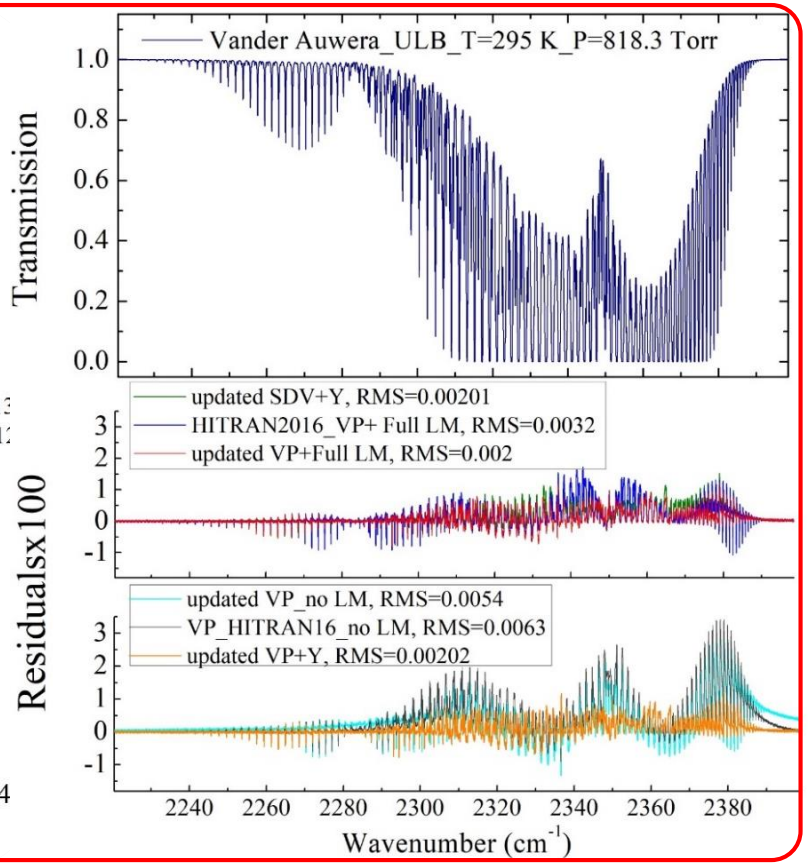
[1] Lamouroux et al., 2321-2331, JQSRT 151(2015), 88–96

Validation using laboratory spectra

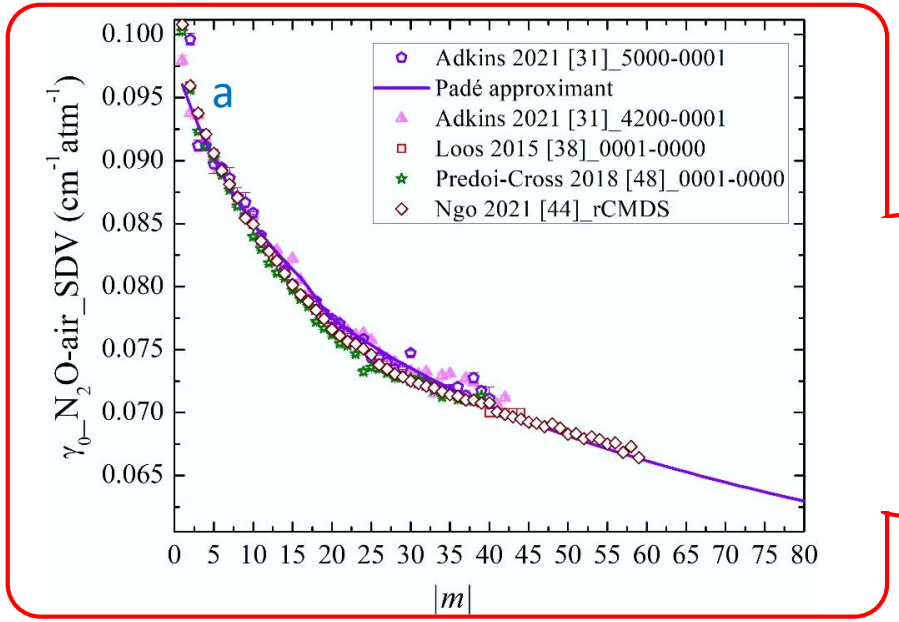
- The HITRAN Application Programming Interface (HAPI) was adopted to include Y parameters.
- In both regions shown here, the highest residuals were obtained when using HITRAN2016 VP parameters. Using the new VP and SDV parameters led to improvements in residuals
- Best residuals:

i) Voigt+Full line mixing
ii) Speed dependent Voigt+First-order line mixing





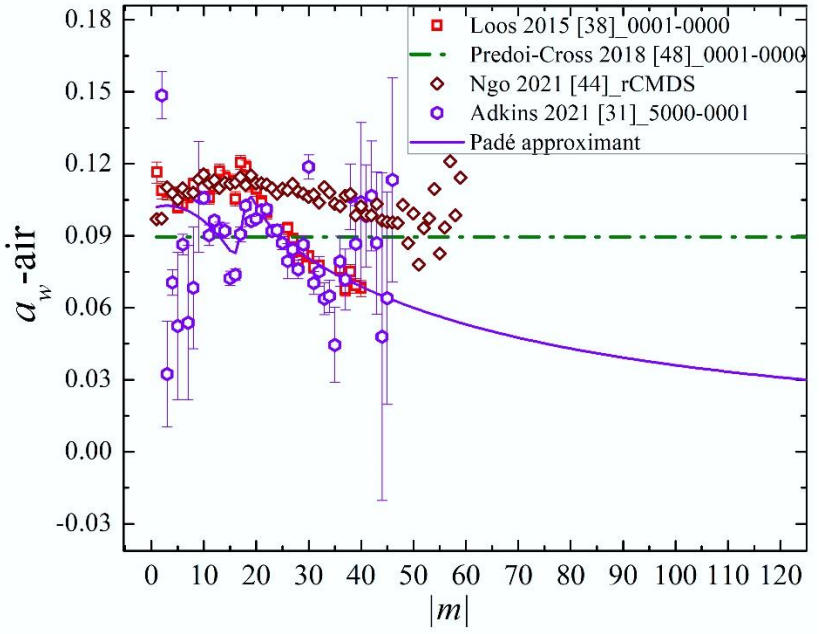
Updating the SDV parameters group for N_2O

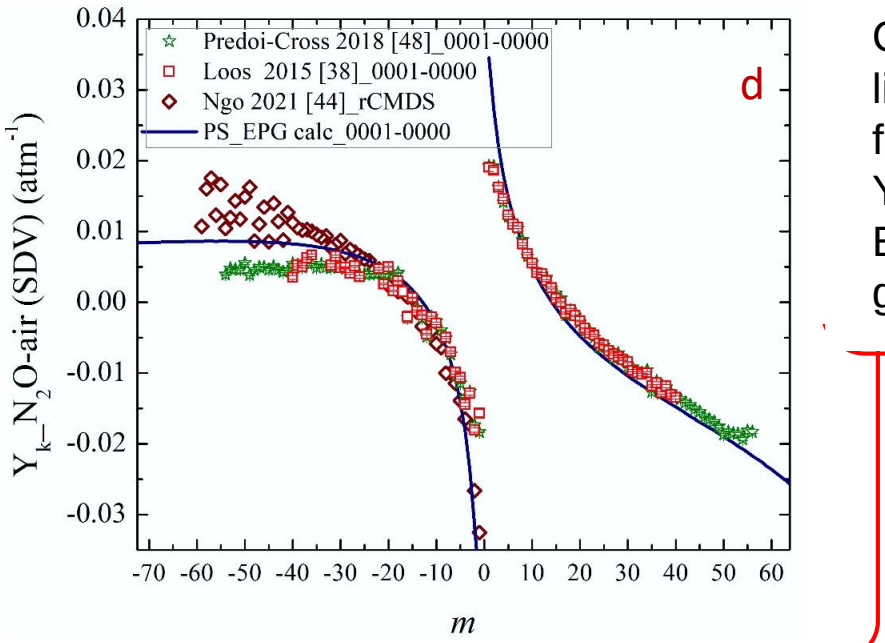


The air-broadening half widths of N_2O deduced using the SDV profile and fitted using the Padé approximants

Hashemi et al, JQSRT, 271 (2021) 107735

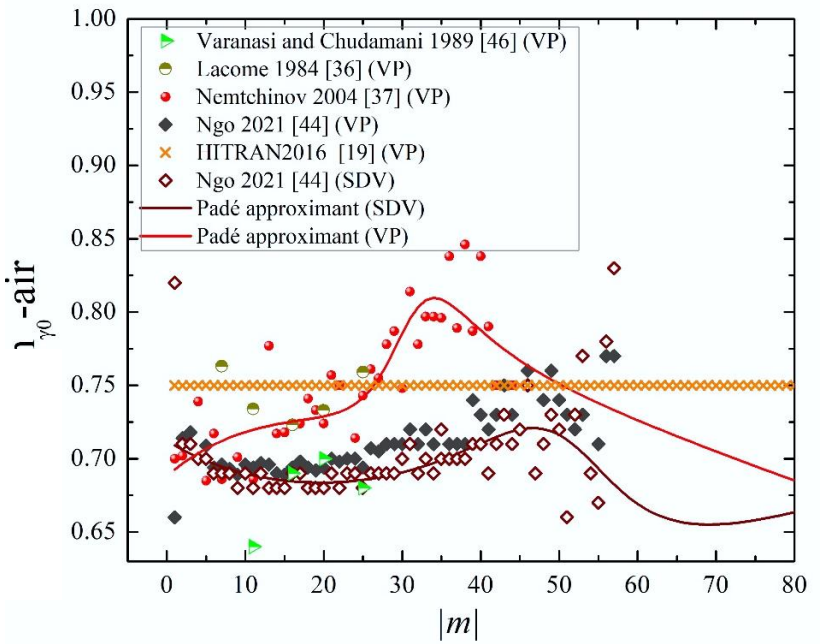
The speed dependence of air-broadening half widths of N_2O versus | m |.





Comparison of the first-order line-mixing parameter versus *m* for the v_3 band. The estimated Y_k parameters using the Exponential Power Gap law is given by the solid line.

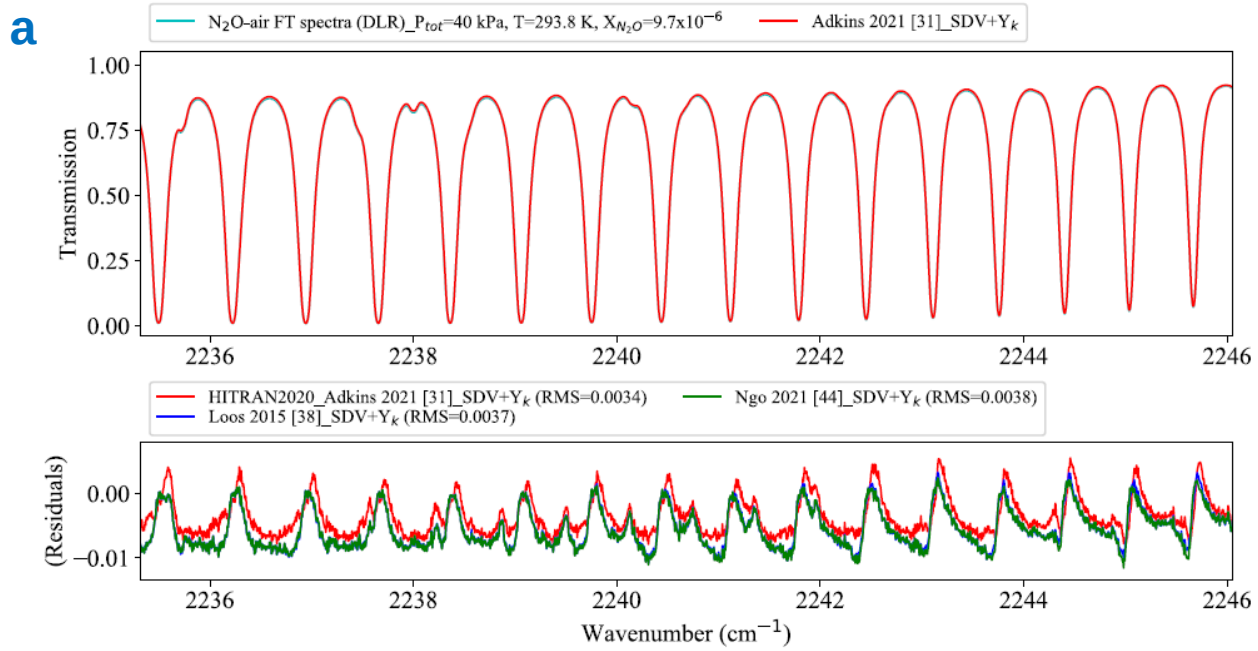
The temperature dependence of air-broadening of N_2O lines, using the VP and the SDV profile

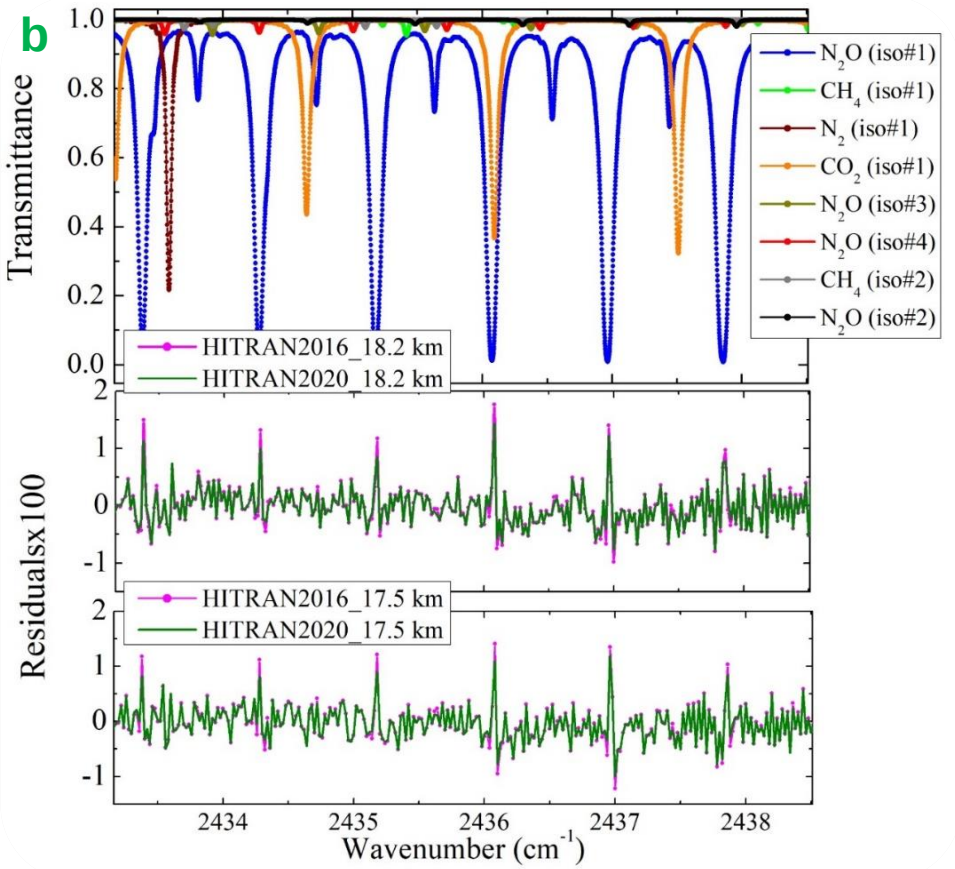


Validation N_2O spectroscopic parameters

ACE-FTS analysis results

a: The FT transmission spectra of N_2O-air at T = 293.8 K, total P = 40 kPa The bottom panel shows the improved residuals when using HITRAN2020 parameters
b:ACE-FTS analysis results from occultation sr10063. Fitted residuals for a tangent height near 18.2 km and 17.5 km using VP parameters from HITRAN2016 (in pink) and SDV parameters from HITRAN2020 (in green).





ref: Hashemi et al, JQSRT, 271 (2021) 107735 and the references therein.

Conclusions and acknowledgement:

- Revision of line broadening and line shifts of the air and self-broadening CO_2 and N_2O lines with their temperature dependence parameters.
- Addition of the speed dependence of the broadening with their temperature dependence for every transition.
- Addition of the first order line mixing and their temperature dependence for each of the allowed transition.
- Improvements for both line lists in HITRAN2020 when validated using the laboratory and atmospheric spectra.

- We would like to thank all collaborators who helped in providing us with data and validating the results.
- Also, we thank our funding resource, NASA HITRAN grants.