climate change initiative

LONG-LIVED GREENHOUSE GAS
PRODUCTS PERFORMANCES

Contribution of low-wavenumber absorption to halocarbon radiative forcing

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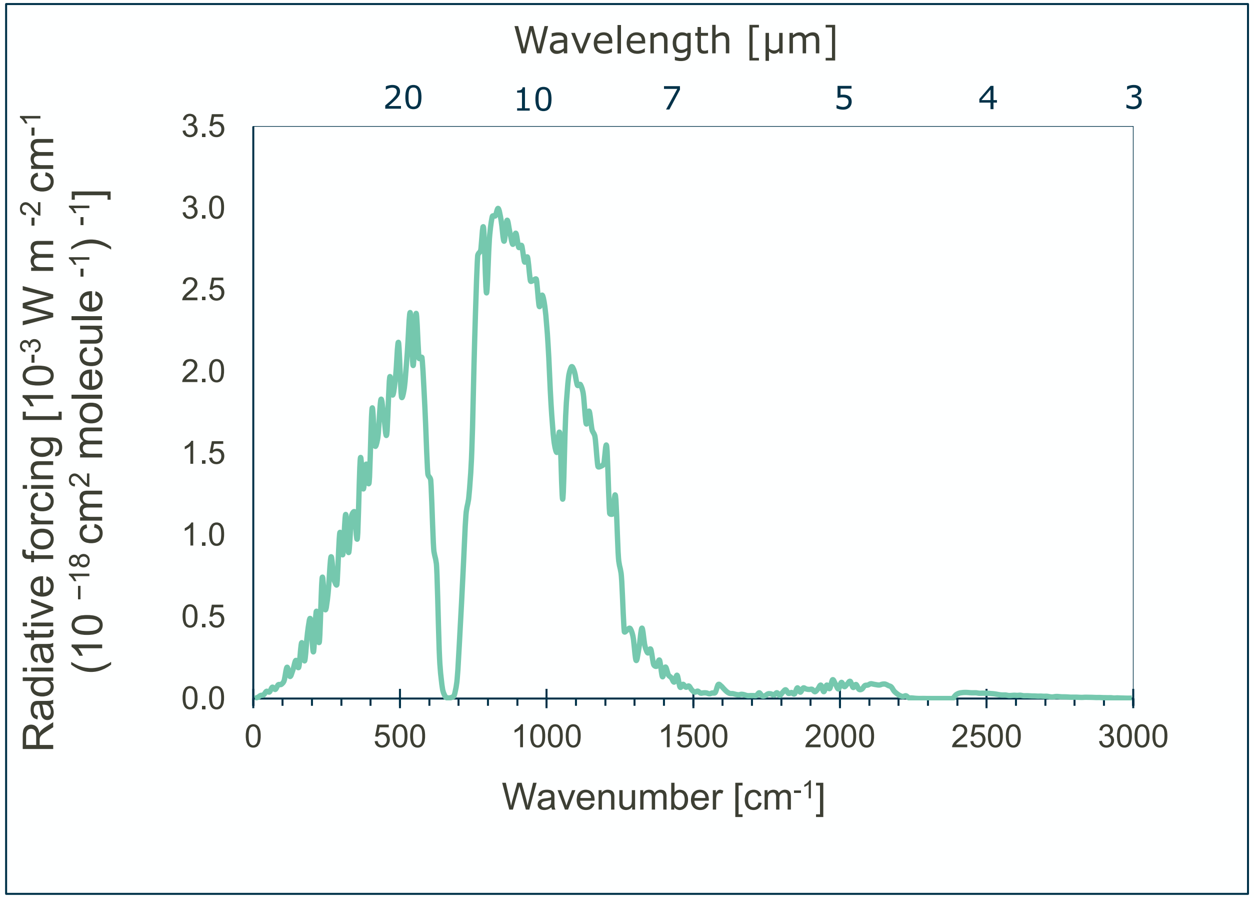
Pinnock Model (1995)



Radiative forcing (RF) for a 0–1 ppb increase in mixing ratio per unit cross-section.[2]

- The Pinnock Curve[1] highlights the wavenumber regions where weak absorbers (such as halocarbons) cause the greatest radiative forcing (RF).
- It is calculated using a narrow band radiative transfer code (including the main atmospheric gases and clouds).
- It allows the rapid calculation of halocarbon radiative efficiency directly from infrared (IR) absorption cross sections (σ, cm^2 $molecule^{-1}$) without the need for a radiation code.
- The most recent[2] Pinnock curve is a mixture of narrow band and line-by-line calculations

$$IRE = \sum_{i=1}^{n}\left[\int_{\nu_{1,i}}^{\nu_{2,i}} \sigma_i\,(\nu)d\nu\right] F_{\sigma}^{i}$$

F_{σ}^{i} : RF of the global annual mean atmosphere (GAM).

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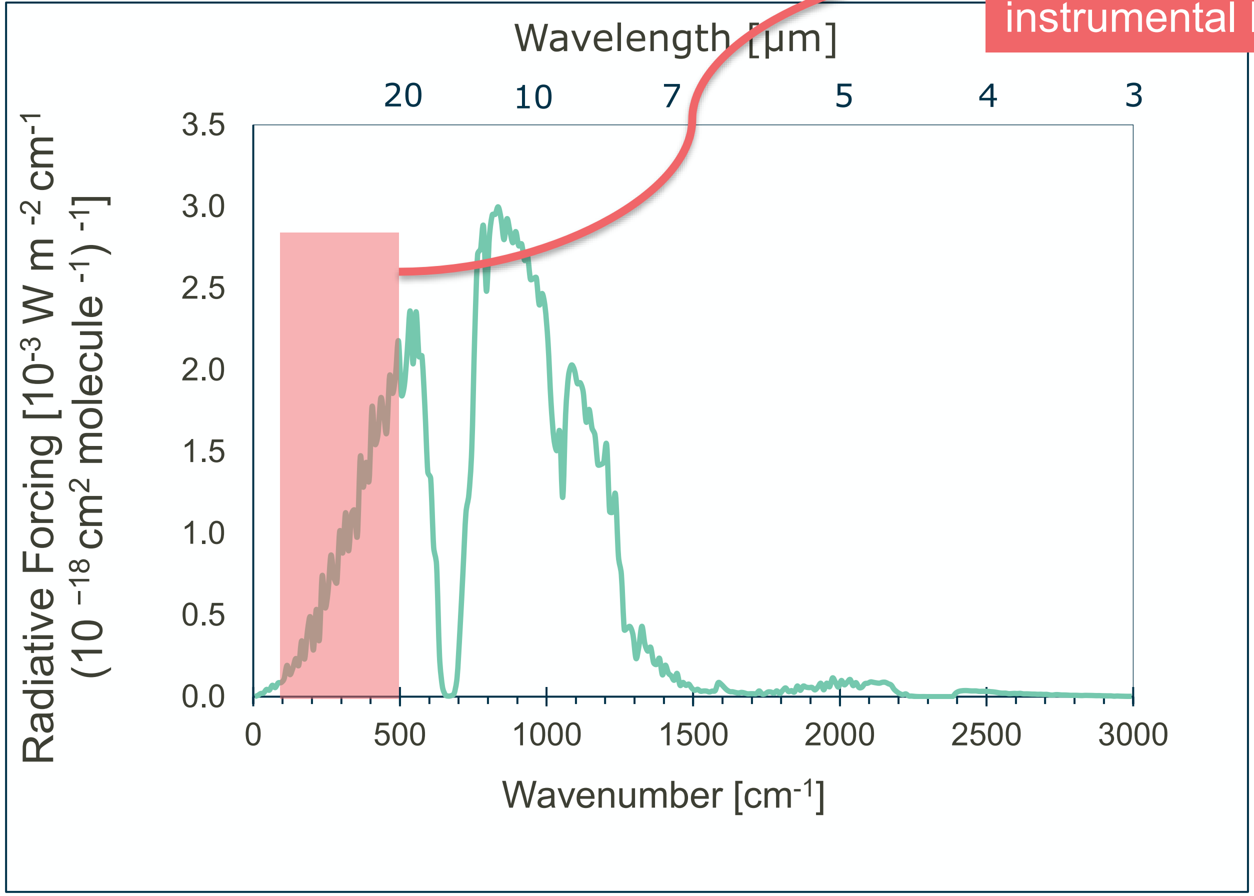
[1] Pinnock, et al., *J. Geophys. Res.* **1995**, 100, 23227.

[2] K. Shine & G. Myhre, *J. Adv. Model. Earth Syst.* **2020**, 12, e2019MS001951.

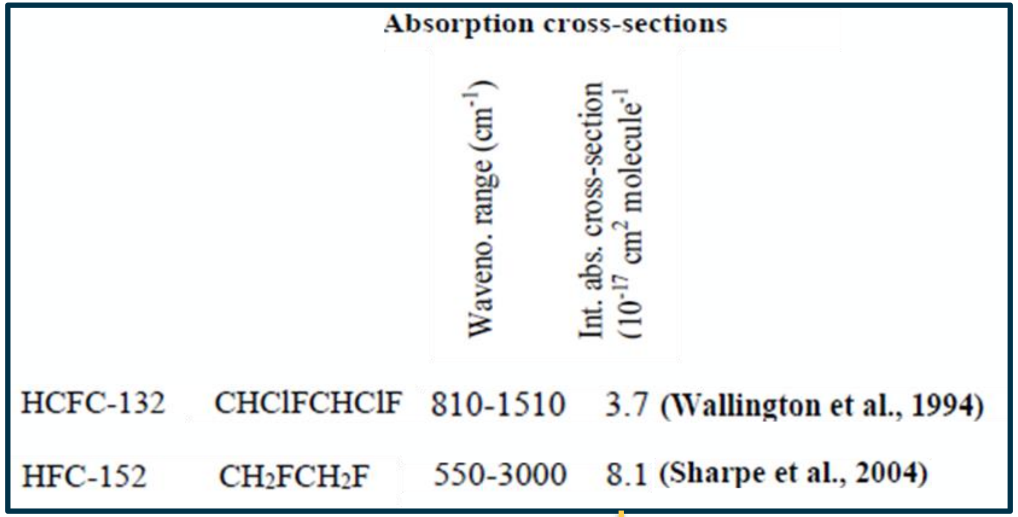
Pinnock Model (1995)

Few measurements of halocarbon cross-sections have been made at wavenumbers < 500 cm^{-1} because of instrumental limitations.



Radiative forcing (RF) for a 0–1 ppb increase in mixing ratio per unit cross section.[2]

E.g. **Hodnebrog, et al.**[3]



Absorption cross-sections

		Waveno. range (cm^{-1})	Int. abs. cross-section (10^{-17} cm^2 molecule^{-1})
HCFC-132	CHClFCHClF	810-1510	3.7 (Wallington et al., 1994)
HFC-152	CH_2FCH_2F	550-3000	8.1 (Sharpe et al., 2004)

$$RE = \sum_{i=1}^{n}\left[\int_{\nu_{1,i}}^{\nu_{2,i}} \sigma_i(\nu)\,d\nu\right] F_{\sigma}^{i}$$

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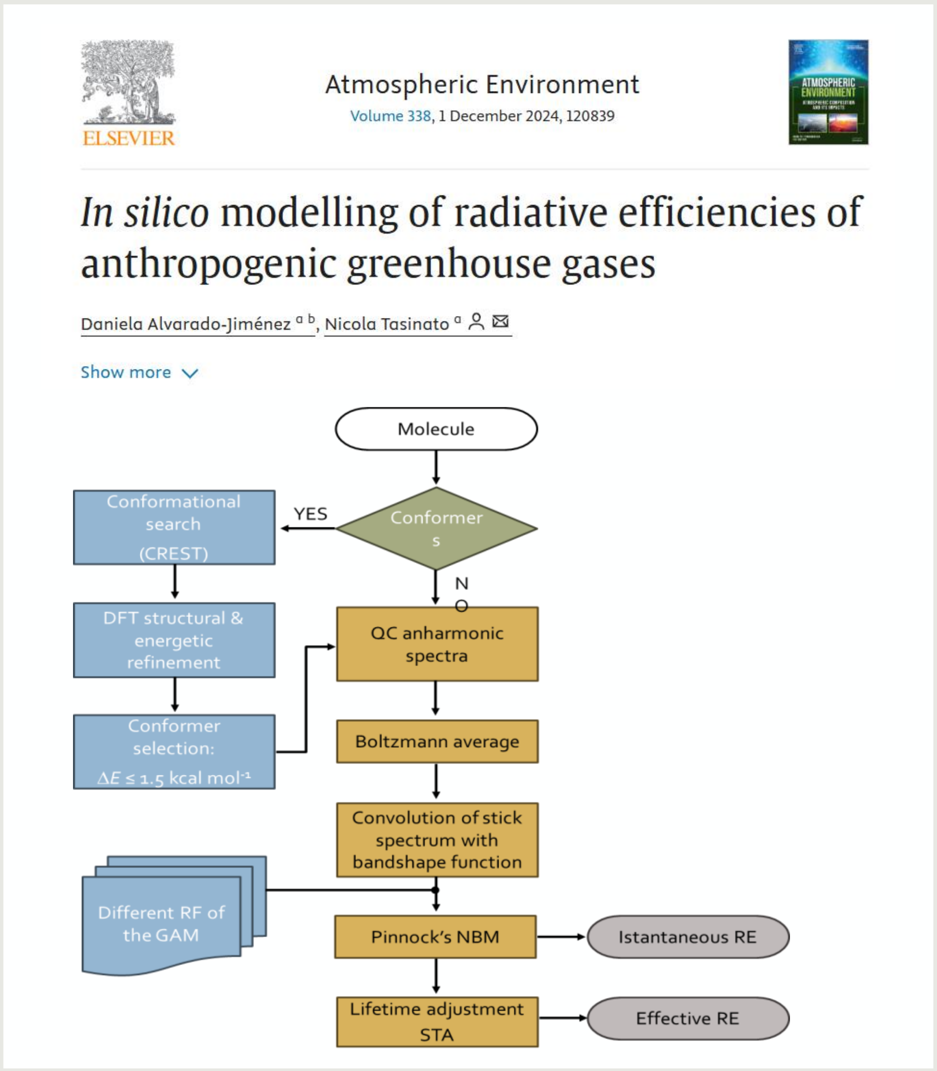
[1] Pinnock, et al., *J. Geophys. Res.* **1995**, 100, 23227.

[2] K. Shine & G. Myhre, *J. Adv. Model. Earth Syst*. **2020**, 12, e2019MS001951.

[3] Hodnebrog, et al., *Rev. Geophys*. **2020**, 58, e2019RG000691.

Quantum Chemical (QC) workflow to REs



Atmospheric Environment
Volume 338, 1 December 2024, 120839

In silico modelling of radiative efficiencies of anthropogenic greenhouse gases

Daniela Alvarado-Jiménez [a b], Nicola Tasinato [a]

Show more

Non-empirical inclusion of both mechanical- and electrical-anharmonicity.

Evaluation of low-frequency contributions to the radiative properties.

Consideration of conformational landscape.

VIBRATIONAL FREQUENCIES AND INTENSITIES

COMBINATION BANDS

OVERTONES

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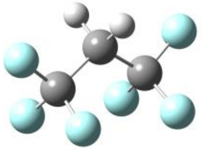
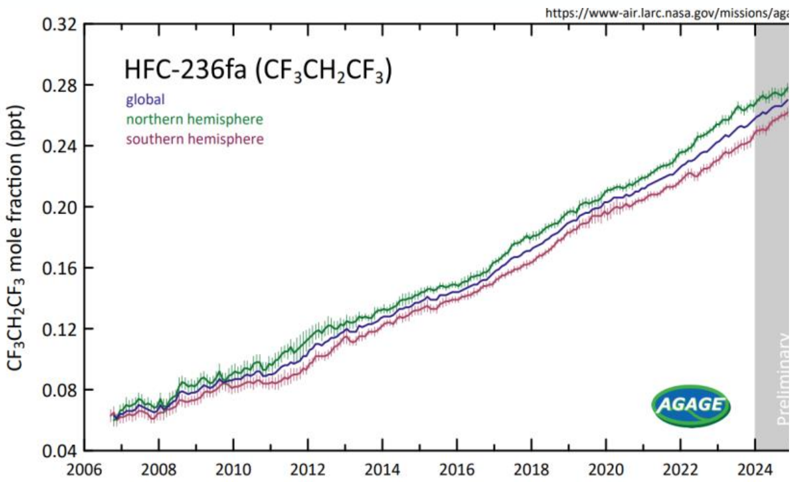
[1] Alvarado-Jiménez & N. Tasinato. Atmos. Environ. **2024**, 338, 120839.

Selected molecules

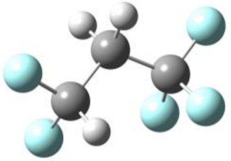
HFC-236fa



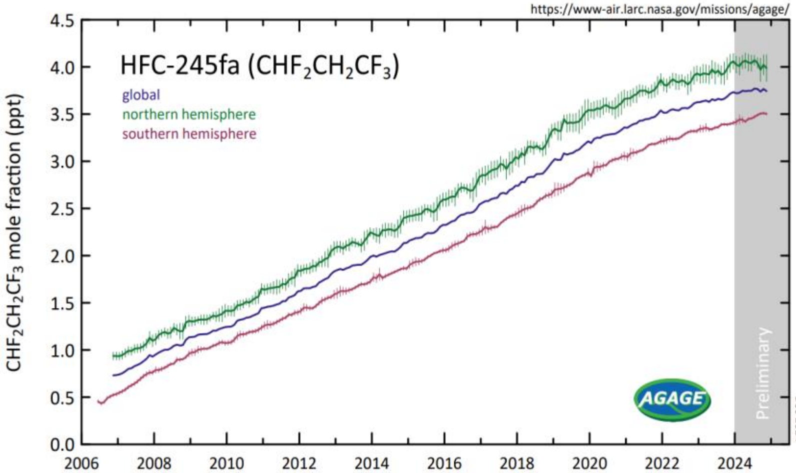
1,1,1,3,3,3-Hexafluoropropane



HFC-245fa

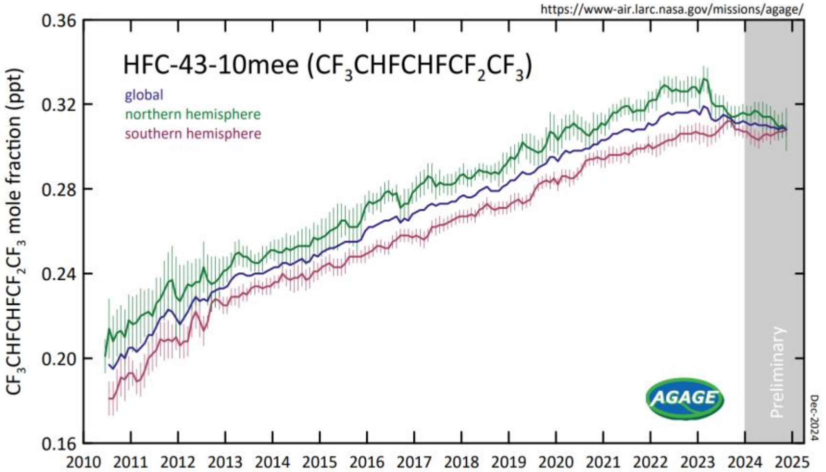


1,1,1,3,3-Pentafluoropropane



HFC-43-10mee

Decafluoropentane



IR Cross Sections: HFC-236fa

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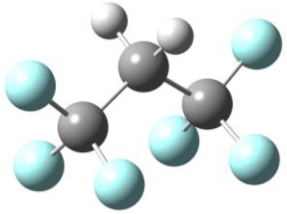
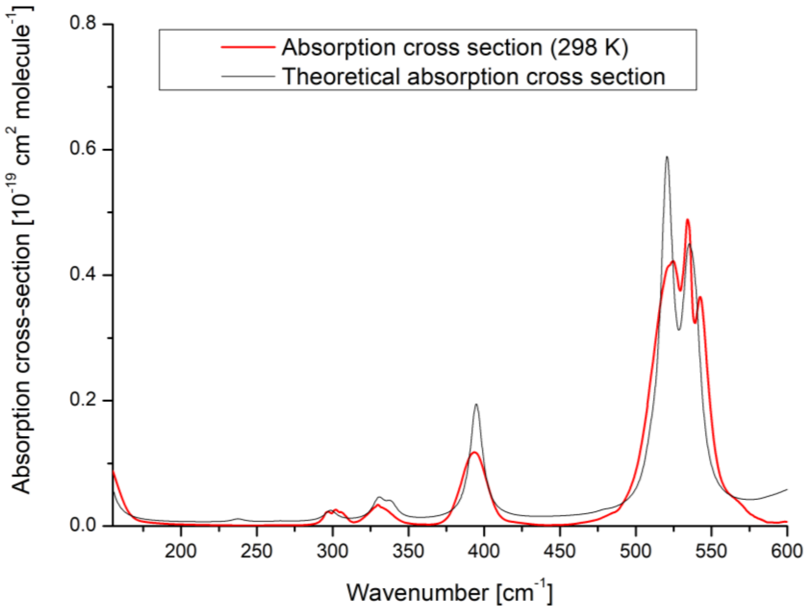
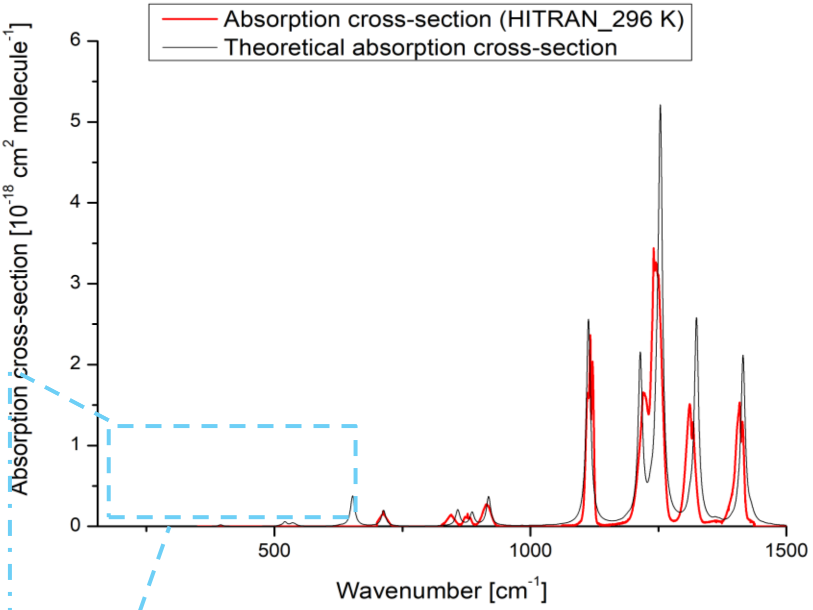


This work[1]





Some experimental details

- Measurements made at the RAL High-Resolution Spectroscopy Facility.
- Bruker IFS125 high-resolution Fourier-transform spectrometer with a 0.25 cm^{-1} spectral resolution.
- Temperature-controlled absorption cell (225 - 298 K).
- Adaptions for InHALE to measure at low wavenumbers are (i) a 6 μm Mylar Beamsplitter (30 - 680 cm^{-1}), (ii) 1 mm high-density polyethylene (HDPE) cell windows (10 - 700 cm^{-1}) and (iii) a DTGS (deuterated triglycine sulfate) detector (120 - 12000 cm^{-1}).

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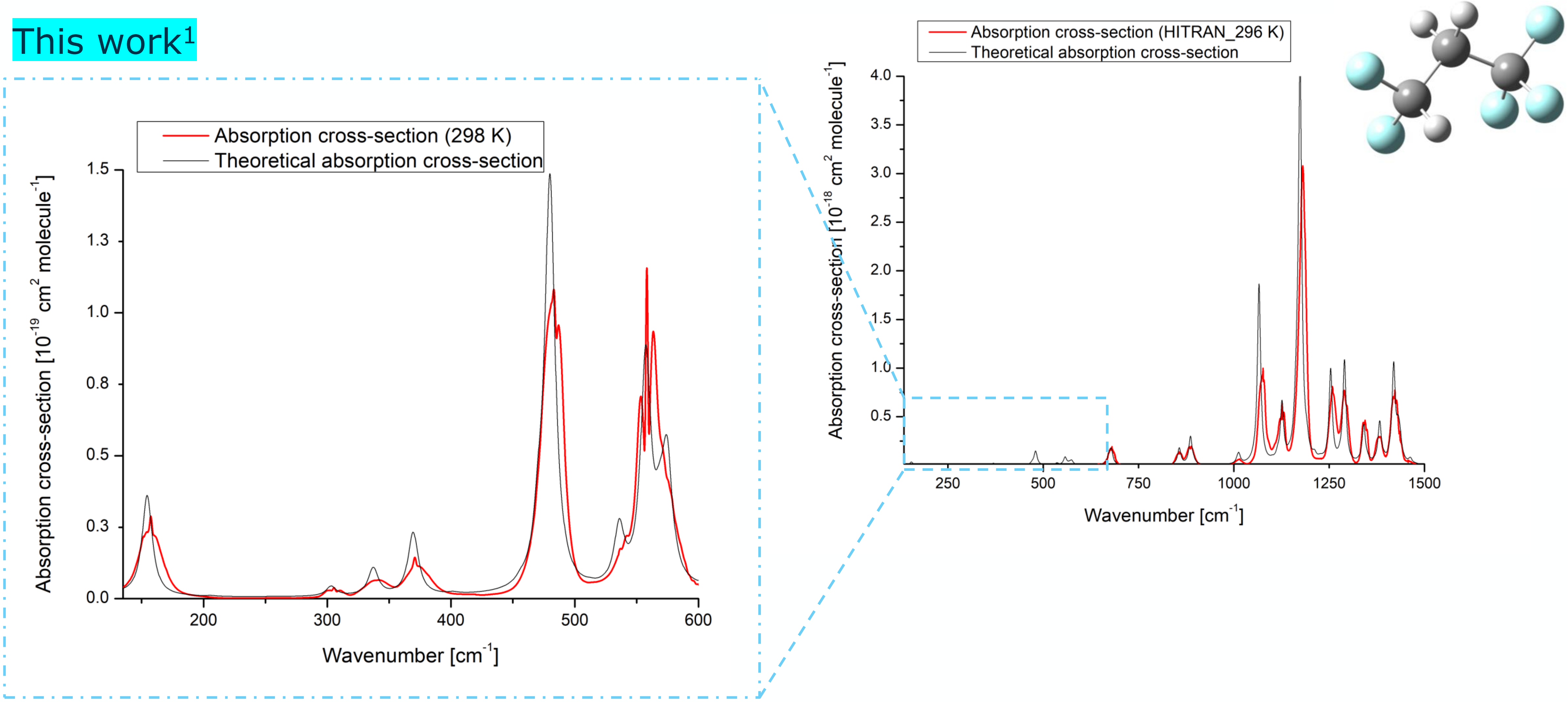
[1] D. Alvarado-Jiménez et al., J. Quant. Spectrosc. Radiat. Transfer, *In preparation.*

HITRAN_296 K: Gordon, et al. J. Quant. Spectrosc. Radiat. Transfer **2022**, 277, 107949.

IR Cross Sections: HFC-245fa

This work[1]



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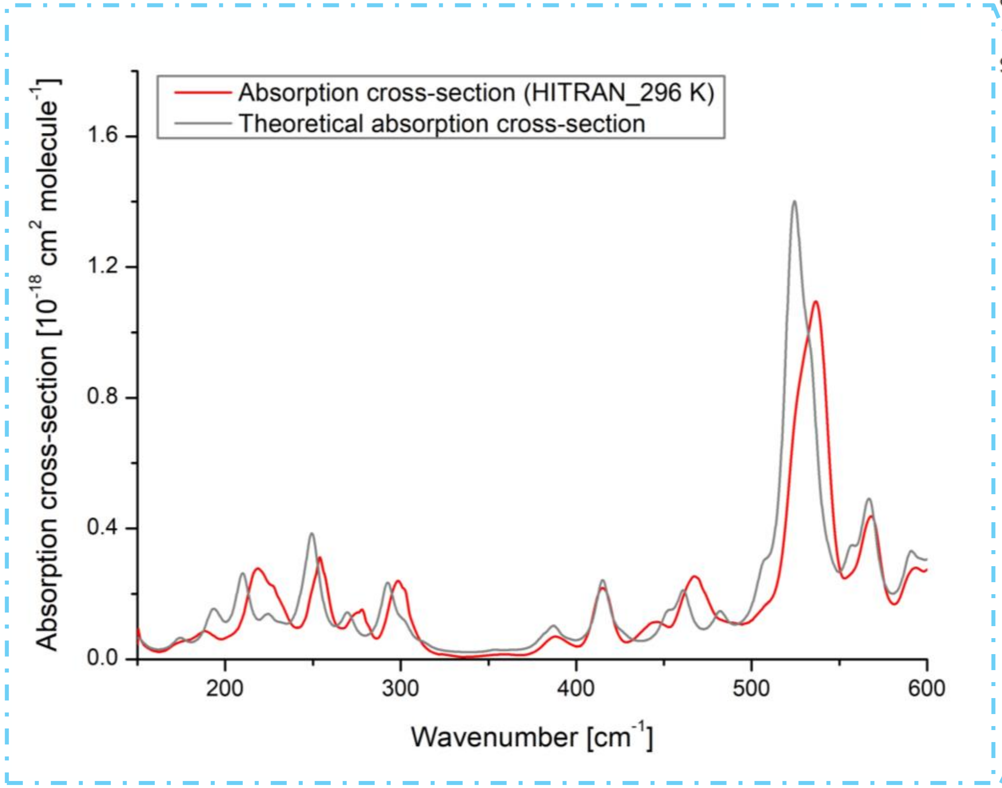
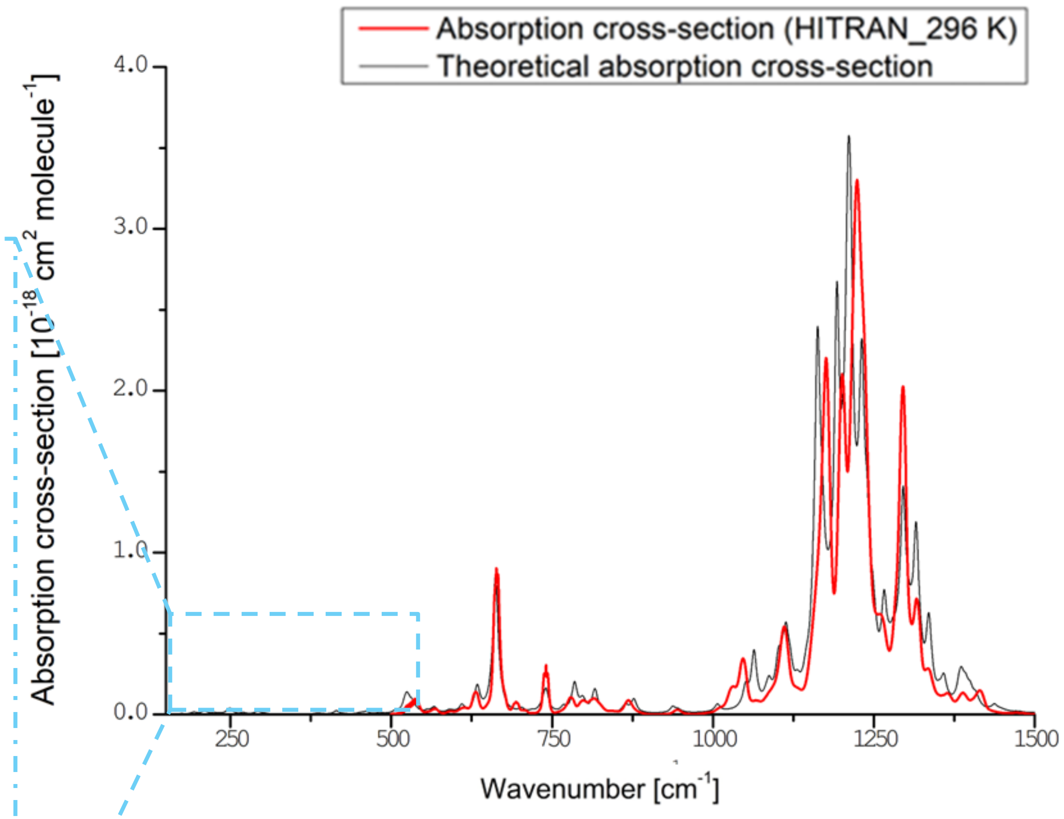
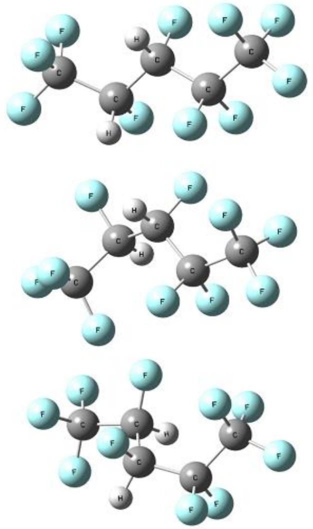
IR Cross Sections: HFC-43-10mee

This work[1]





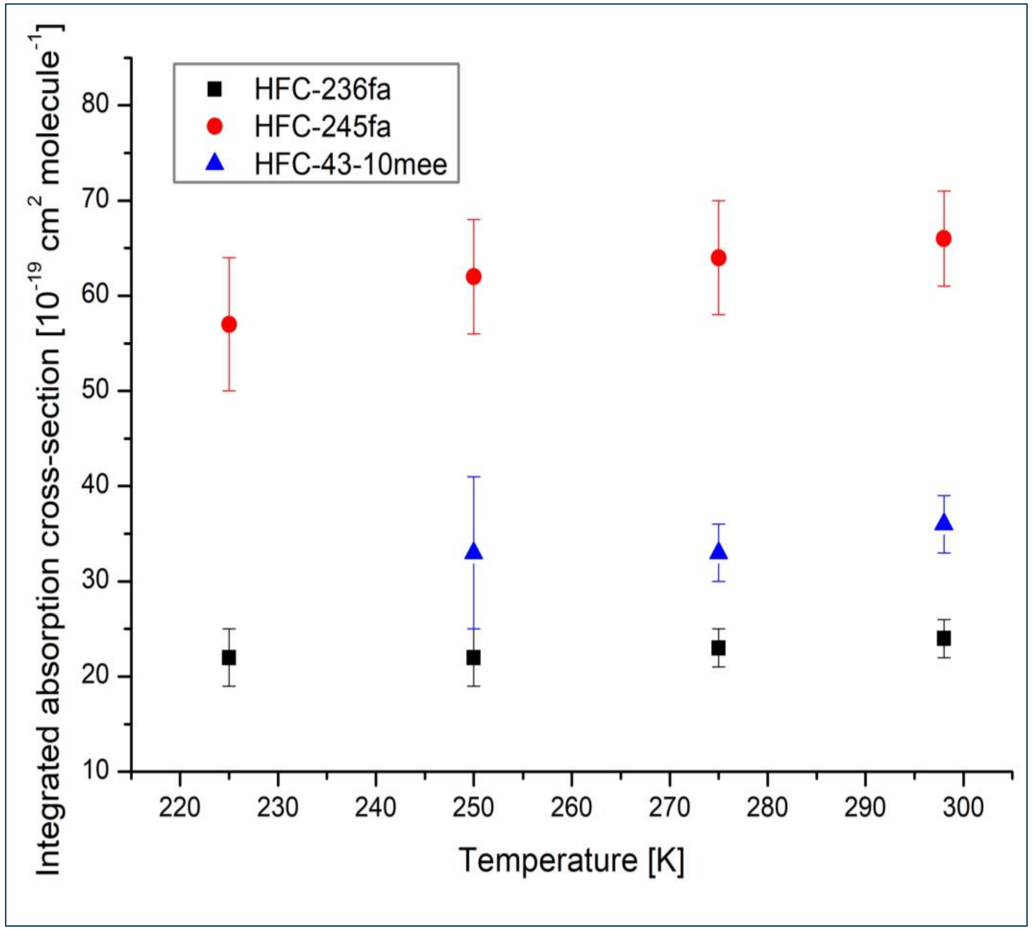


[1] D. Alvarado-Jiménez et al., J. Quant. Spectrosc. Radiat. Transfer, *In preparation.*

HITRAN_296 K: Gordon, et al. J. Quant. Spectrosc. Radiat. Transfer **2022**, 277, 107949.

Results: IR Cross Sections

Experimental integrated band strengths (10^{-19} cm molecule^{-1}) of HFC-236fa, HFC-245fa and HFC-43-10mee at T= 225, 250, 275 and 298 K and comparison with the QC counterpart.



Molecule	Integration limits (cm^{-1})	298 K	QC
HFC-236fa	285 - 350	1.1 (1)	1.5
	365-420	2.6 (2)	3.1
	465-585	19 (2)	17.5
	155-585	**24 (2)**	**26.1**
HFC-245fa	135-185	6.3 (5)	5.4
	285-405	5.7 (4)	6.4
	430-600	54 (4)	50.0
	135-600	**66 (5)**	**63.2**
HFC-43-10-mee	150-330	21 (1)	21.1
	340-500	15 (1)	14.7
	150-500	**36 (3)**	**36.1**

9% dev.

-5% dev.

-1% dev.

Results: Radiative Efficiencies

RE (W m^{-2} $ppbv^{-1}$) of HFC-236fa, HFC-245fa and HFC-43-10mee

Molecule	RE in the low freq.		Low freq. contribution (%)		Exp. ERE[c]	
	Exp.[a]	QC[b]	Exp.[a]	Literature[d]		
HFC-236fa	0.0009	0.0008	0.3%	4.8%	0.252	↓ ≈ -4%
HFC-245fa	0.0050	0.0048	1.9%	2.8%	0.249	↓ ≈ -1%
HFC-43-10mee	0.0031	0.0030	0.8%	0.5%	0.361	↑ ≈ 0.3%

QC estimates within the double-harmonic approximation.

Compared with values of the **Scientific Assessment of Ozone Depletion 2022.** World Meteorological Organization (WMO).

[a] From experimental IR absorption cross-section.
[b] From QC IR absorption cross-section.
[c] Sum REs over the 500 – 3000 cm^{-1} range from WMO and experimental REs here determined for the low frequency region.
[d] Van Hoomissen et al. *Molecular Physics* **2023**,122, e2273412.

World Meteorological Organization (WMO). *Scientific Assessment of Ozone Depletion: 2022, GAW Report No. 278*; WMO: Geneva, Switzerland, 2022.

Conclusions

We obtained **the first experimental IR absorption cross-sections < 500 cm^{-1}** for HFC-236fa, 245fa, and 43-10mee, with **good agreement between experimental and QC** results.

For the three molecules, our computational **results proved to be reliable** in predicting radiative efficiency in all the frequency range, particularly considering the challenges in the low-frequency region.

Including the low-frequency region enhances the accuracy of RE and GWP calculations, supporting more **informed and effective climate mitigation actions**.

Acknowledgements

Prof. Nicola Tasinato
(Scuola Normale Superiore, Italy)
Prof. Keith Shine
(University of Reading, United Kingdom)
Prof. Roberto Buizza
(Scuola Superiore Sant'Anna)
Dr. Richard Brownsword and Dr. Damien Weidmann
(Rutherford Appleton Laboratory, United Kingdom)

Spectroscopy, Thermochemistry
STARK
And Reaction Kinetics

The STARK group is acknowledged for high performace computing facilities

Scuola Normale Superiore for financial support
Project "Computational Modeling for Environmental Chemistry and Sustainability: from atmospheric monitoring to photo-catalysis".

PhD programme in Sustainable Development And Climate Change, with support of a scholarship co-financed by the Ministerial Decree no. 352.

Reading and RAL acknowledge funding from the UK Natural Environment Research Council Grant "Investigating Halocarbon Impacts on the global environment" (Grant Reference NE/X004198/1)"

Thank you for your attention!

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