climate change initiative

LONG-LIVED GREENHOUSE GAS PRODUCTS PERFORMANCES

Atmospheric reactivity, infrared absorption cross section and climate metrics of HCFC-132b

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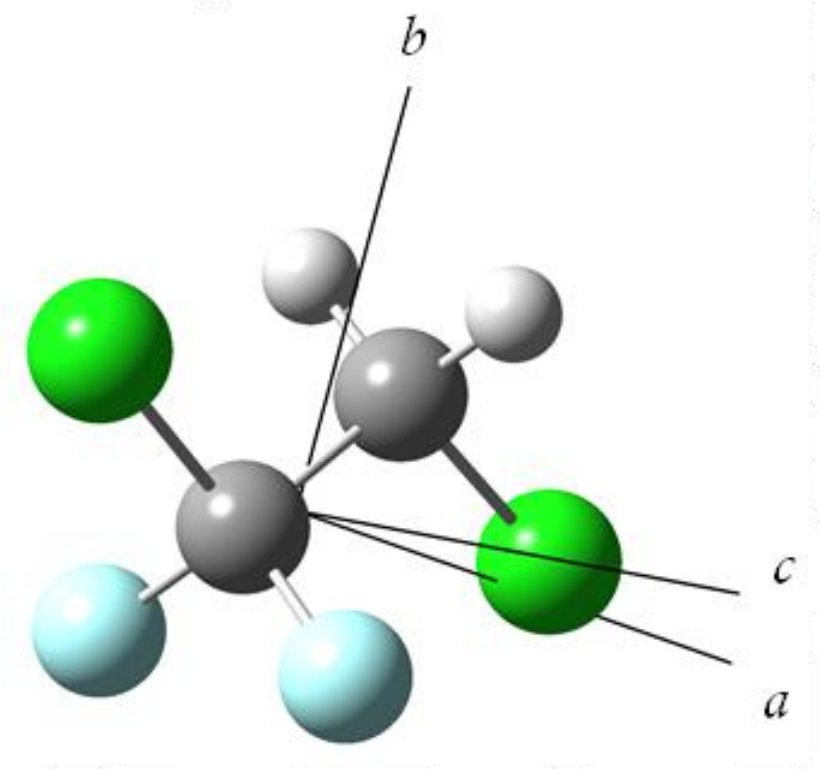
OUTLINE

HCFC-132b
(1,2-dichloro-1,1-difluoroethane)



- Introduction
- OH- and Cl-initiated atmospheric degradation
- Infrared absorption cross sections
- Climate metrics
- Conclusions

INTRODUCTION

Montreal protocol (1987) and subsequent amendments

- Regulate the phase-out of production and consumption of ozone depleting substances (ODSs).
- Full ban for end-use of CFCs set to the mid-1990s for developed countries and to 2010 globally.
- HCFCs and HFCs considered as replacement gases.

INTRODUCTION

Montreal protocol (1987) and subsequent amendments

- About HCFCs

Developed countries

2010
- Production and import of HCFC-142b and HCFC-22 were limited.

2020
- 100% phase-out of HCFC production and import was set.

Post-2020:
- Only recovered, recycled, or reclaimed HCFCs are available.

Developing countries

2013
- Consumption and production were frozen.

2015
- Reduction process began.

2020
- 35% reduction targeted.

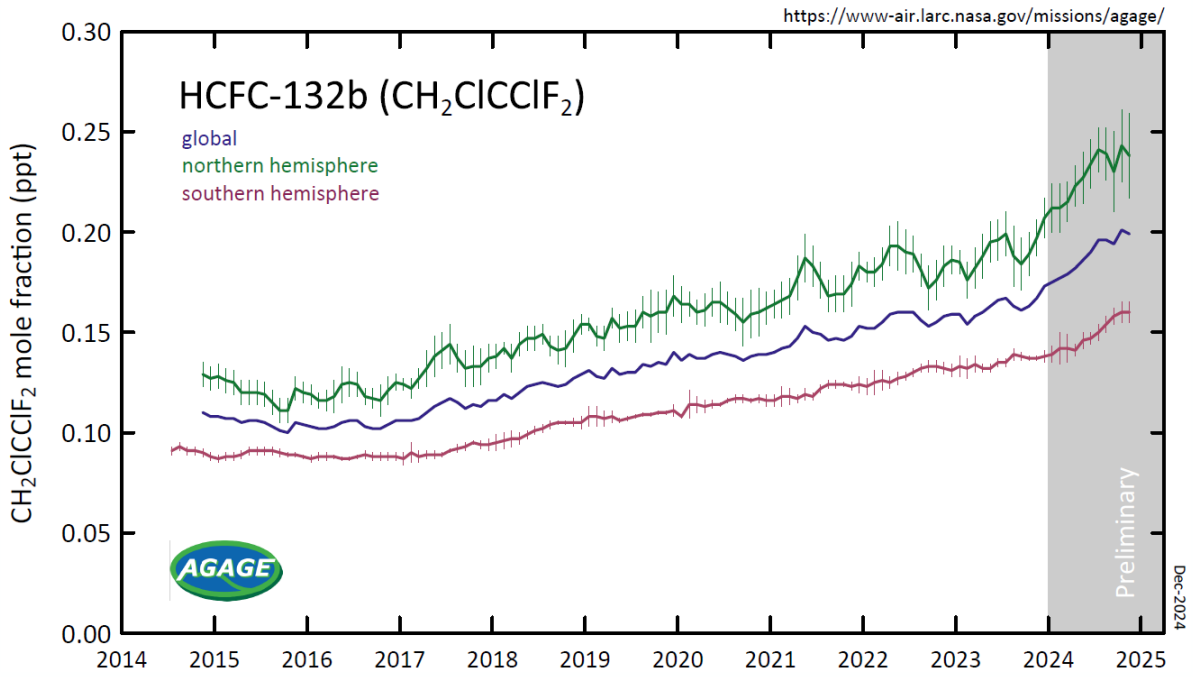
2025
- 67.5% reduction targeted.

2030
- 100% phase-out.

INTRODUCTION

HCFC-132b

- Long-term emissions in the atmosphere of $CH_2ClCClF_2$ (HCFC-132b), CH_2ClCF_3 (HCFC-133a) and CH_2ClF (HCFC-31) were reported.[1]
- HCFC-132b detected with an increasing mixing ratio over the period 2016 – 2019 (0.17 ppt at the end of 2019 in the northern hemisphere).[1]
- Not reported end-uses (likely formed during the synthesis of HFC-134a and other HFCs). Barely regulated by the Montreal protocol that focuses on ODSs with end-use applications.



[1] M. K. Vollmer, et al. *Proc.Natl. Acad. Sci. USA* **2021**, *118*, e2010914118.

HCFC-132b: atmospheric degradation

Reasons for investigating degradation of halocarbons in connection to climate change

- Understand how rapidly they degrade, and thus accumulate, in the atmosphere.
- Identify breakdown products with potentially harmful environmental impacts.
- Draw connections on where and when they degrade.
- Recognize possible chemical feedbacks.
- Provide data for chemical transport models (e.g. lifetimes).
- Determine climate metrics: radiative efficiency (RE) and global warming potential (GWP).

HCFC-132b: atmospheric degradation

Quantum chemical predictions of atmospheric oxidation processes

Experimental determination of rate constants difficult to perform under atmospheric conditions.

Some species cannot easily be observed/produced experimentally.

Can provide new insights and complement experimental information/data.

HCFC-132b: atmospheric degradation

COMPUTATIONAL PROTOCOL

THERMOCHEMISTRY

Accuracy: 0.3 kcal mol^{-1}

- Exploration of the reactive potential energy surface: B3LYP[2], M06-2X, M08-HX or PW6B95[3] in conjuction with jul-cc-pV(D+*d*)Z basis set.[4]
- Geometry and harmonic vibrational frequencies: (rev-)DSDPBEP86[5] or B2PLYP[6] with jun-cc-pV(T+*d*)Z.[4]
- Energy refinement: CCSD(T)-based composite schemes jChS or jChS-F12.[7]

KINETICS

Accuracy: factor of 2

- Variational transition state theory (VTST).[8]
- Variable-reaction coordinate variational transition state theory (VRC-VTST).[9]

SPECTROSCOPY

Accuracy: 5%

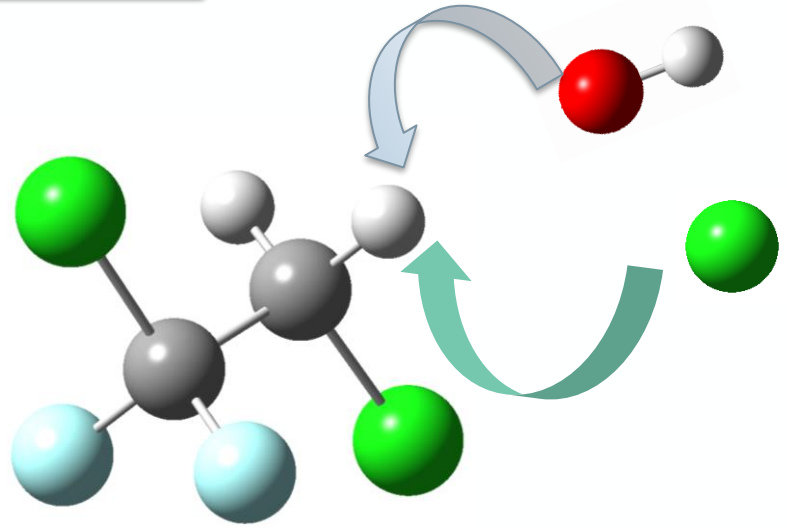
- Anharmonic infrared abosorption cross sections: DSDPBEP86/jun-cc-pV(T+d)Z. [10]

[2] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. [3] Y. Zhao & D. Truhlar, *Theor. Chem. Account* **2008**, *120*, 215; *J. Chem. Theory Comput.* **2008**, *4*, 1849; *J. Phys. Chem. A* **2005**, *109*, 5656. [4] E. Papajak, et al., *J. Chem. Theory Comp.* **2011**, *7*, 3027. [5] G. Santra, et al. *J. Phys. Chem.* **2019**, *123*, 5129. [6] S. Grimme. *Chem. Phys.* **2006**, *124*, 034108. [7] V. Barone et al. *J. Chem. Theory Comput.* **2021**, *17*, 4913. [8] J. L. Bao & D. Truhlar, *Chem. Soc. Rev.* **2017**, *46*, 7548. [9] S. Klippenstein, et al. *J. Chem. Phys.* **1992**, 96, 367. [10] D. Alvarado-Jiménez & N. Tasinato, *Atmos. Environ.* **2024**, *338*, 120839.

HCFC-132b: atmospheric degradation

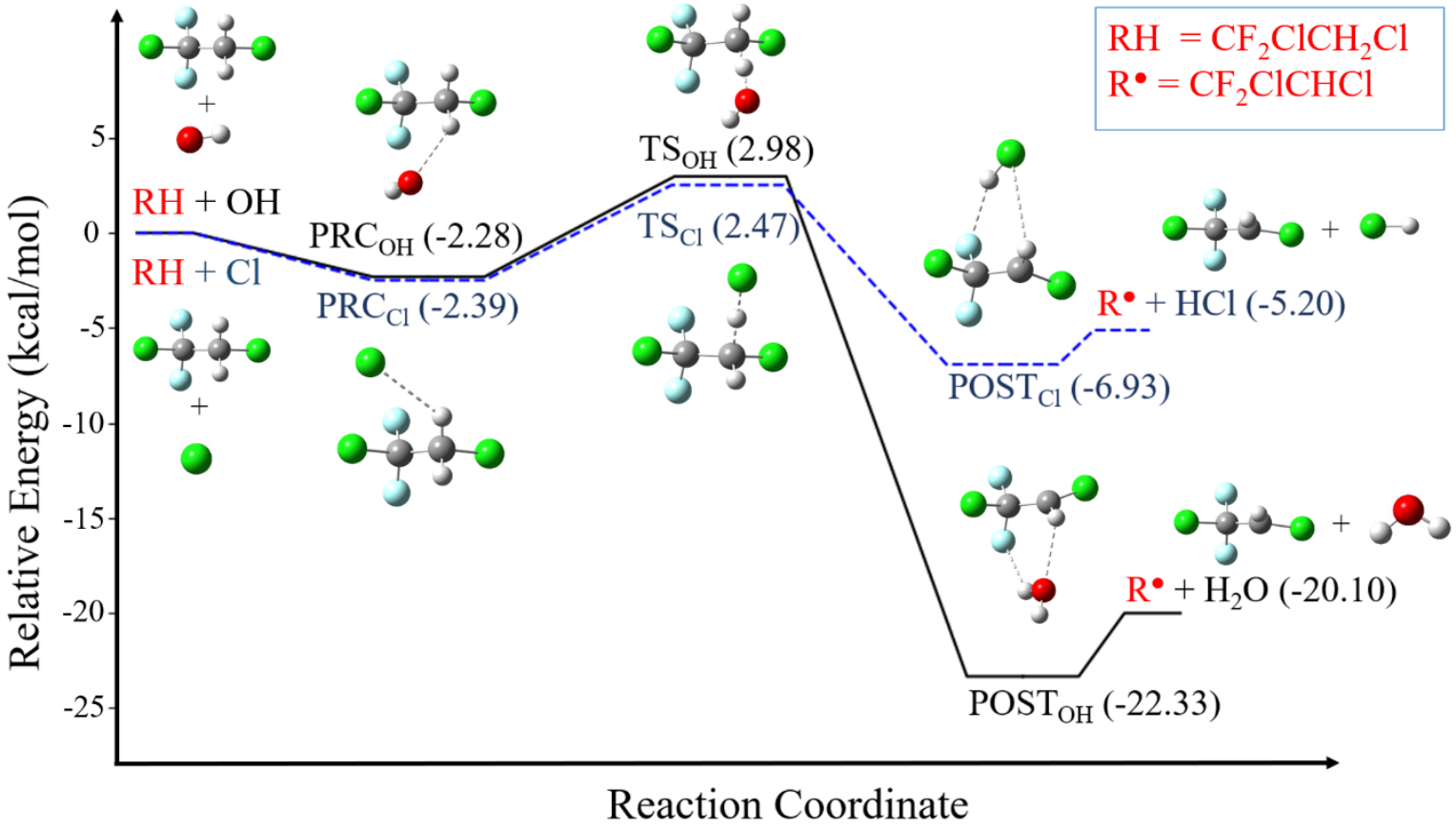
Atmospheric degradation pathways (gas phase)

- Photolysis → CFCs
- Reaction with atmospheric oxydants (OH, Cl, NO_3, O_3) → HCFCs, HFCs, HFOs, HFEs



J. B. Burkholder, et al. *Chem. Rev.* **2015**, *115*, 3704

HCFC-132b: atmospheric degradation

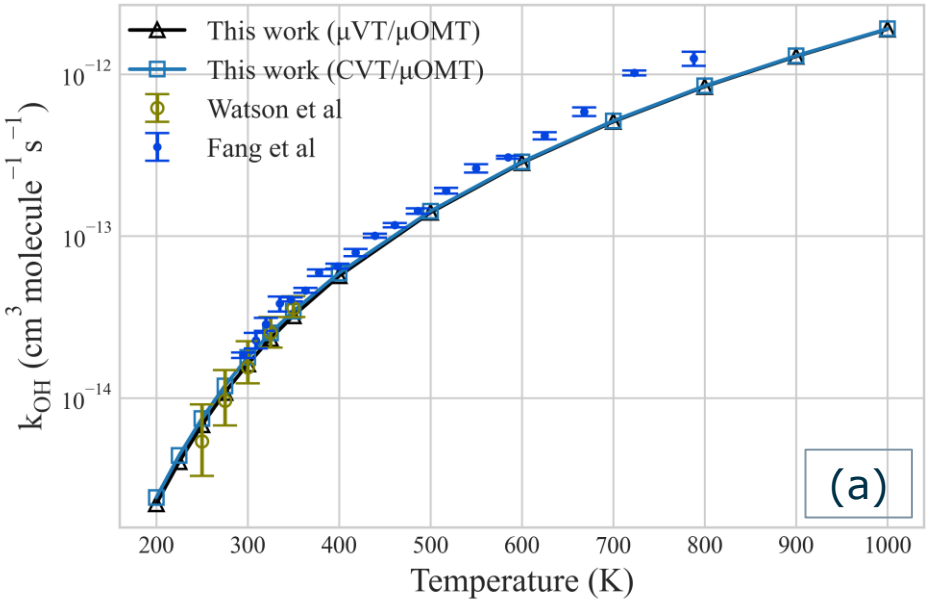


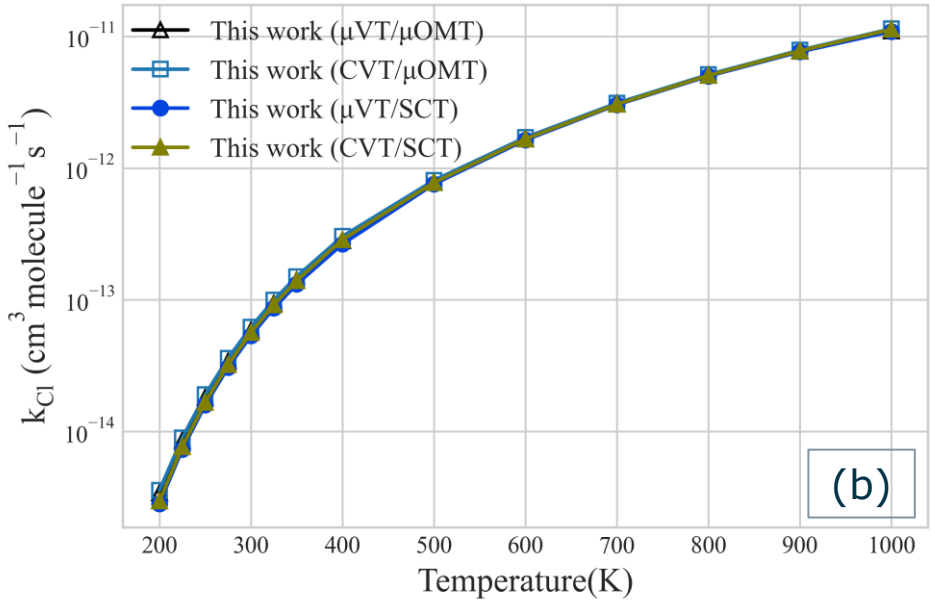
Reactive PES of the H-abstraction reactions from $CH_2ClCClF_2$ by the OH (black, solid) and Cl (blue, dashed) radicals, using the B2PLYP-D3 ZPE-corrected jChS relative energies (kcal mol^{-1}).[11]

[11] N. Rais, et al. *ACS Earth Space Chem.* **2023**, *7*, 892.

HCFC-132b: atmospheric degradation

Thermal rate constants calculated using VTST including multidimensional tunneling (OMT).[11]





Rate coefficients at the jChS//B2PLYP-D3/jun-cc-pV(T+*d*)Z level of theory between 200 and 1000 K for
(a) $CH_2ClCClF_2$ + OH
and
(b) $CH_2ClCClF_2$ + Cl
reactions.

$k_{HCFC\text{-}132b+OH}$ at 298 K [10^{-14} cm^3 molecule^{-1} s^{-1}]

This work	Fang et al.	Watson et al.
1.57	1.61	1.50

$k_{HCFC\text{-}132b+Cl}$ at 298 K: 5.65 × 10^{-14} cm^3 molecule^{-1} s^{-1}

[11] N. Rais, et al. *ACS Earth Space Chem.* **2023**, *7*, 892.

HCFC-132b: IR absorption cross sections

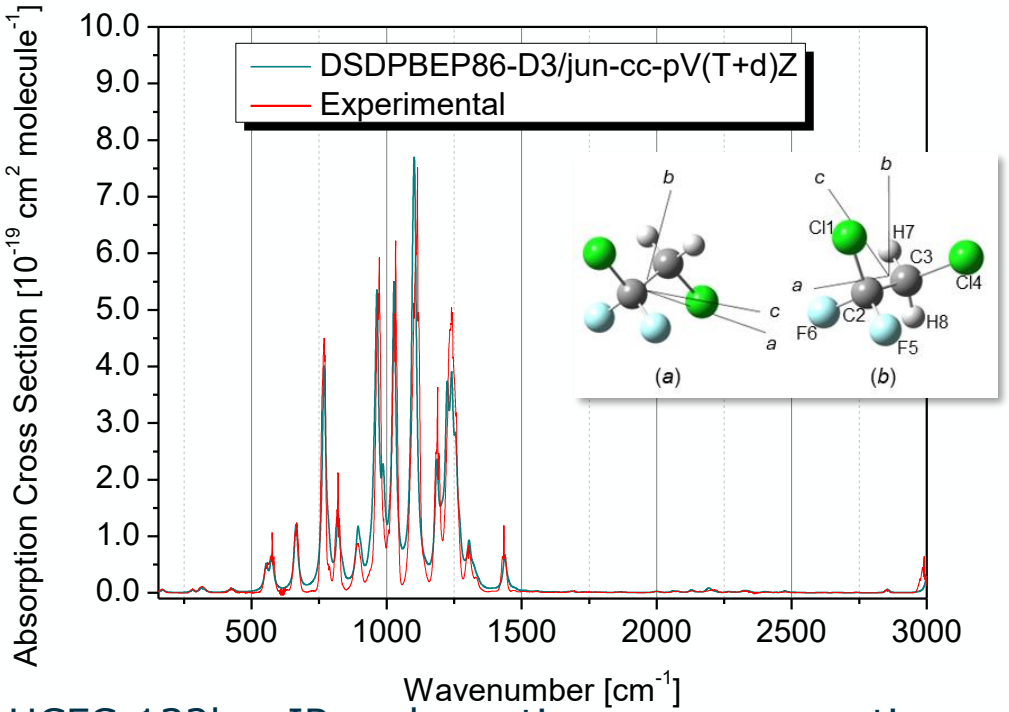
No previous spectroscopic investigations on HCFC-132b.

Experimental details

- Measurements made at Università Ca' Foscari, Venezia, Italy.
- IR spectral range:150 – 3500 cm^{-1}; Bruker Vertex70 Fourier Transform Infrared (FTIR) instrument at spectral resolutions of 0.5 and 1 cm^{-1}.
- Gas pressures in the range of 1.5 – 114.1 hPa and temperature of 295.2 ± 1.1 K.

Computational details

- *In silico* workflow to REs.[10]
- Non-empirical inclusion of anharmonic effects.
- 2 different conformers.
- DSDPBEP86-D3/jun-cc-pV(T+*d*)Z level of theory.



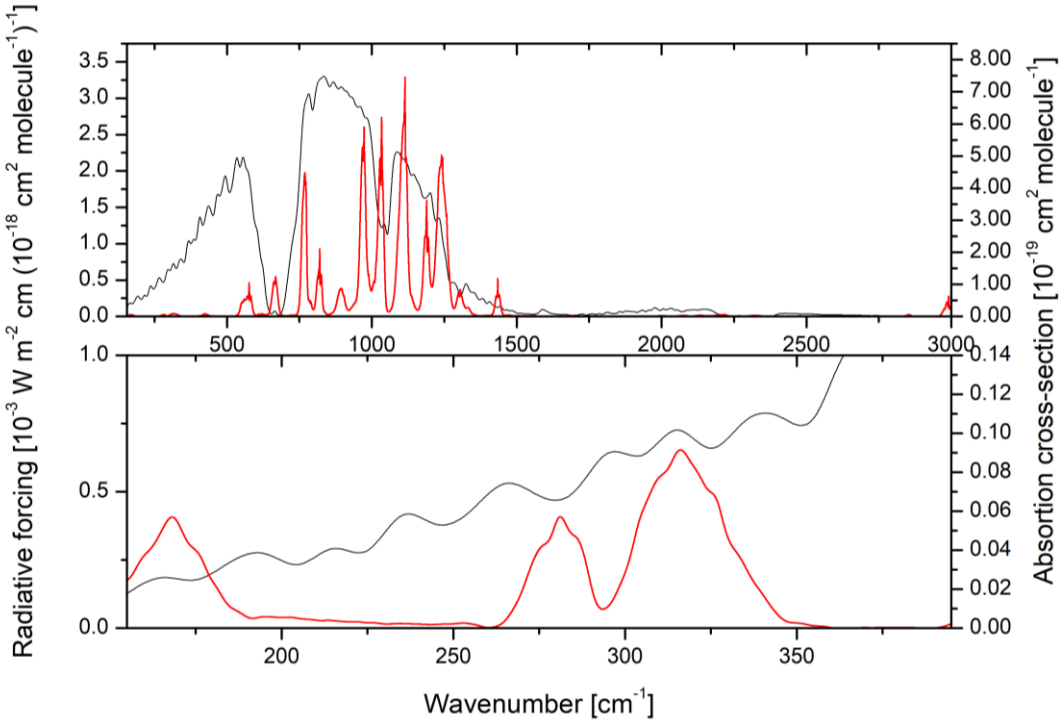
HCFC-132b IR absorption cross section spectrum from 150 to 3000 cm^{-1}.[12]

[10] D. Alvarado-Jiménez & N. Tasinato, *Atmos. Environ.* **2024**, *338*, 120839.
[12] D. Alvarado-Jiménez, et al. *ChemPhysChem* **2025**, *26*, e202400632.

HCFC-132b: climate metrics

Atmospheric lifetimes

	Present work	WMO 2022 [13]
HCFC-132b	3.4 years	3.5 years
HFO-1123	1.1 days [14]	1.6 days



Effective Radiative efficiency (W m^{-2} ppbv^{-1})

	Exp.	QC	WMO 2022 [13]
HCFC-132b	0.168 [12]	0.174 [12]	0.192
HFO-1123	0.002 [15]	0.002 [10]	0.0021

Harmonic QC calculations

Global Warming Potential

$$\mathrm{GWP}_i(\mathrm{H}) = \frac{ERE_i \tau_i \left[1 - exp\left(-\frac{H}{\tau_i}\right)\right]}{\int_0^H ERE_{co_2}(t)dt}$$

H: time horizon.
τ_i: atmospheric lifetime.

GWP-100	Exp.	QC	WMO 2022 [14]
HCFC-132b	275 [13]	285 [13]	332

[10] D. Alvarado-Jiménez & N. Tasinato, *Atmos. Environ.* **2024**, *338*, 120839.
[12] D. Alvarado-Jiménez, et al. *ChemPhysChem* **2025**, *26*, e202400632.
[13] W. M. O. (WMO)., Scientific Assessment of Ozone Depletion:2022.
[14] N. Rais, et al. *Phys. Chem Chem Phys.* **2024**, *26*, 19976.
[15] N. Tasinato, et al. *J. Phys. Chem A.* **2022**, *126*, 5328.

CONCLUSIONS

- Despite existing regulations, emissions of several ODSs are declining slowly, or even increasing, as in the case of HCFC-132b.
- Mechanistic insights into the OH- and Cl-initiated atmospheric degradation and the corresponding kinetic rate constants obtained by QC calculations, and lifetime derived.
- First measurements of the IR absorption cross sections over the 150 – 3500 cm^{-1} range.
- Retrieved HCFC-132b radiative efficiency and global warming potentials (20-, 100- and 500-time horizons).
- QC workflow to climate metrics (lifetimes and IR absorption cross-sections): accuracy on par with experimental measurements; usable for screening applications of replacement compounds and informed decision-making policies.

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