Infrared Absorption Cross-sections of Fluorinated Molecules for Improved Global Warming Potential Calculations (A33L-3349)

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1. Introduction

Fluorinated compounds contain C-F bonds, which results in their absorbing strongly in the optically thin region of the atmosphere known as the atmospheric window (750-1250 cm^{-1}), causing positive radiative forcing. The calculation of the radiative efficiencies and global warming potentials of these molecules relies on precise knowledge of their absorption cross-sections, but experimental measurements of these cross-sections are often limited.

Scientific Objectives:

1. To measure infrared absorption cross-sections over a range of temperatures.
2. To perform DFT calculations and calibrate them against experimental spectra.
3. To improve RE and GWP calculations of the species studied.

Definitions:

- **Radiative forcing (RF)** is a measure of how much a species can alter the radiation budget of the atmosphere (units of Wm^{-2}).
- An instantaneous **radiative efficiency (RE)** is the RF per unit mixing ratio.
- **Global warming potential (GWP)** quantifies how much energy a gas will absorb over a given period of time H, relative to the same amount of CO$_2$.
- The GWP of a gas can be calculated using the RE, which can be derived from a measured or theoretical **absorption cross-section**.

$$\mathrm{GWP}(H) = \frac{\int_0^H \mathrm{RF}_i(t)\mathrm{d}t}{\int_0^H \mathrm{RF}_{CO_2}(t)\mathrm{d}t} = \frac{\mathrm{AGWP}_i(H)}{\mathrm{AGWP}_{CO_2}(H)}$$

where τ is the gas lifetime, and the RF per unit mass is the absolute GWP:

$$\mathrm{AGWP}(H) = \mathrm{RE}\cdot\tau(1 - exp(-\frac{H}{\tau}))$$

The RE and GWP are useful metrics for evaluating emission polices.

2. Radiative Efficiencies & Global Warming Potentials

Pinnock *et al.* [1995] showed that the instantaneous RE can be calculated directly from the cross-sections and the instantaneous cloudy-sky RF per unit cross-section for the global annual mean atmosphere (the "Pinnock curve"). We use an updated Pinnock curve calculated by Hodnebrog *et al.* [2013], shown in Figure 1. The RE is calculated by integrating the product of a molecule's cross-section with Pinnock's curve.

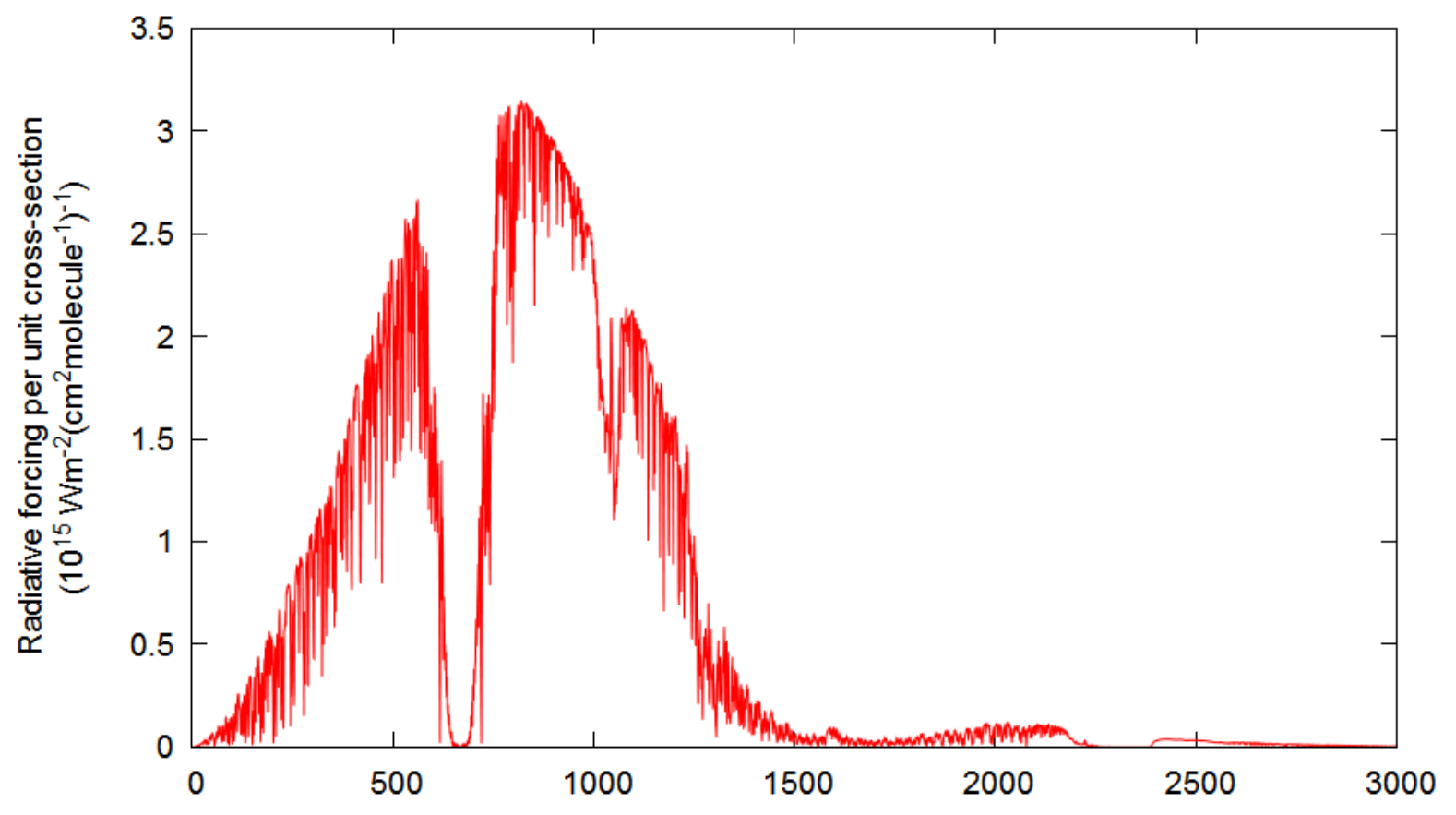


Figure 1: Pinnock's curve [from Hodnebrog et al., 2013].

Pinnock's method assumes that a gas is well mixed, and so corrections are applied to account for non-uniform mixing ratios. Fractional corrections are based on empirically derived expressions that depend on whether the atmospheric removal process is primarily photolysis in the stratosphere or reactions with OH in the troposphere. The RE is also increased by 10% to account for stratospheric temperature adjustment. See Godin [2017] for details.

3. Experimental Set-Up

Absorption cross-sections are derived from spectra measured from 530-3400 cm^{-1} at 0.1 cm^{-1} resolution, using a Bomem DA8 Fourier transform infrared spectrometer (with globar source, KBr beamsplitter, and MCT detector). Gas samples are from Sigma-Aldrich, and are typically certified as 99% pure. A heatable cell with an optical pathlength of 10 cm is used. Spectra are recorded at temperatures from 296 to 365 K (measured with an in-line thermocouple of <1 K accuracy) and pressures from 0.1 to 7 Torr (measured with an MKS 10-Torr Baratron having a resolution of ±0.01 Torr). The set-up is shown in Figure 2.

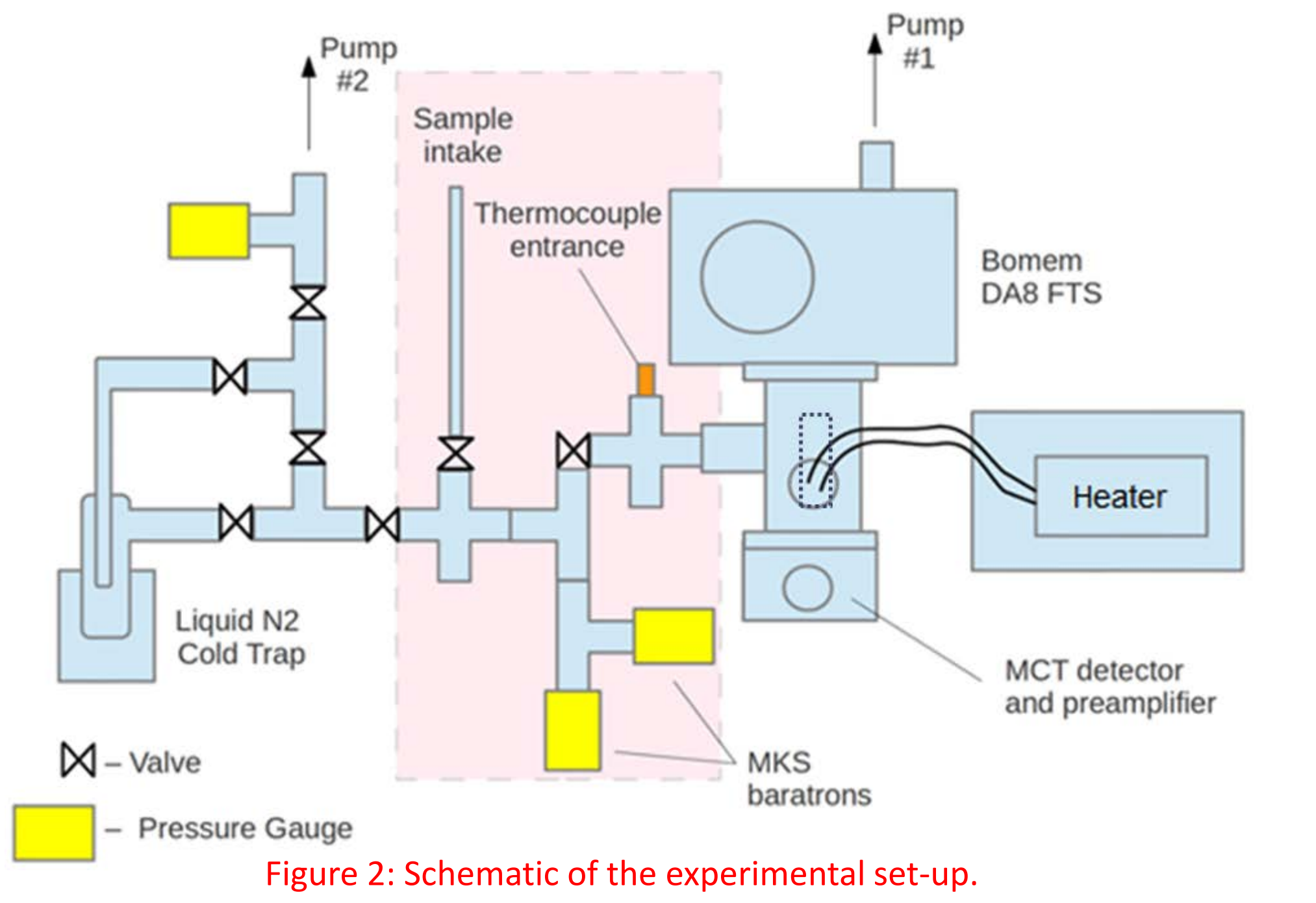


Figure 2: Schematic of the experimental set-up.

4. Density Functional Theory (DFT) Calculations

Density functional theory provides a semi-empirical method for calculating the electronic structure of molecules and obtaining band strength and fundamental vibrational frequencies. Theoretical DFT calculations are performed here using the B3LYP method and a minimum basis set of 6-311++G(2d,p). DFT calculations for PFPO (see below) are taken from Badawi and Fomer [2008].

As the population of each configuration changes with temperature, differences between spectra can be used to make accurate line assignments. DFT spectra have systematic offsets and need to be calibrated against the experimental spectra to ensure the accuracy of band positions.

5. Data Analysis

Experimental absorption cross-sections are obtained from the Beer-Lambert law:

$$I(\nu) = I_o(\nu)e^{-\chi(\nu)} \quad \text{where the optical depth is:} \quad \chi(\nu) = \frac{PT_o}{TP_o}N_L L\sigma(\nu)$$

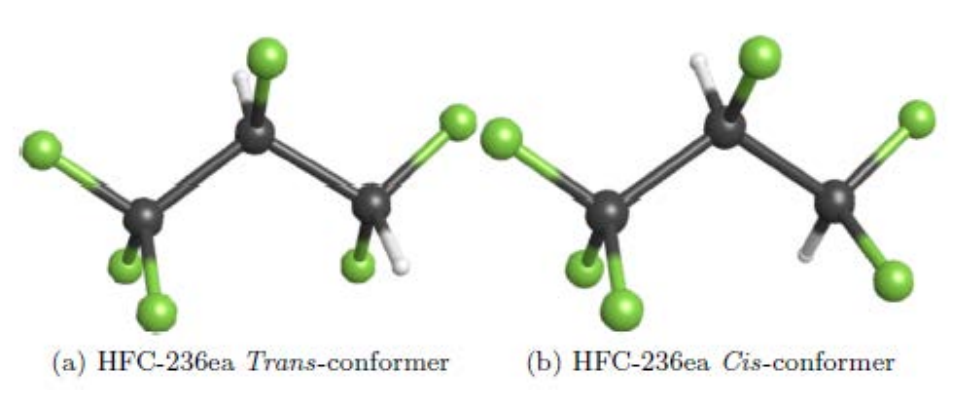
and N_L is the Loschmidt's constant, and T_o and P_o are standard temperature and pressure.

- Linear fits of optical depth vs. pressure are used to find the zero-Torr absorption cross-section.
- Differences in spectra with temperature are used to assign bands to the proper conformer.
- DFT spectra are linearly scaled to better match the experimental spectra.
- RE and GWP are calculated using the experimental cross-section, supplemented with DFT spectra to extend the spectral range to 0 cm^{-1} where relevant.

1,1,1,2,3,3-hexafluoropropane (HFC-236ea) [Ref. 1]

- HFC-236ea is commonly used as a refrigerant
- Atmospheric lifetime of 11.0 years
- Only one published spectrum, recorded at room temperature [Gierczak et al., 1996]
- No reported measurements in the atmosphere, but included in the IPCC Fifth Assessment Report as a possible greenhouse gas [Myhre et al., 2013]

Figure 3: HFC-236ea conformers.
F atoms are green, H white, and C grey.



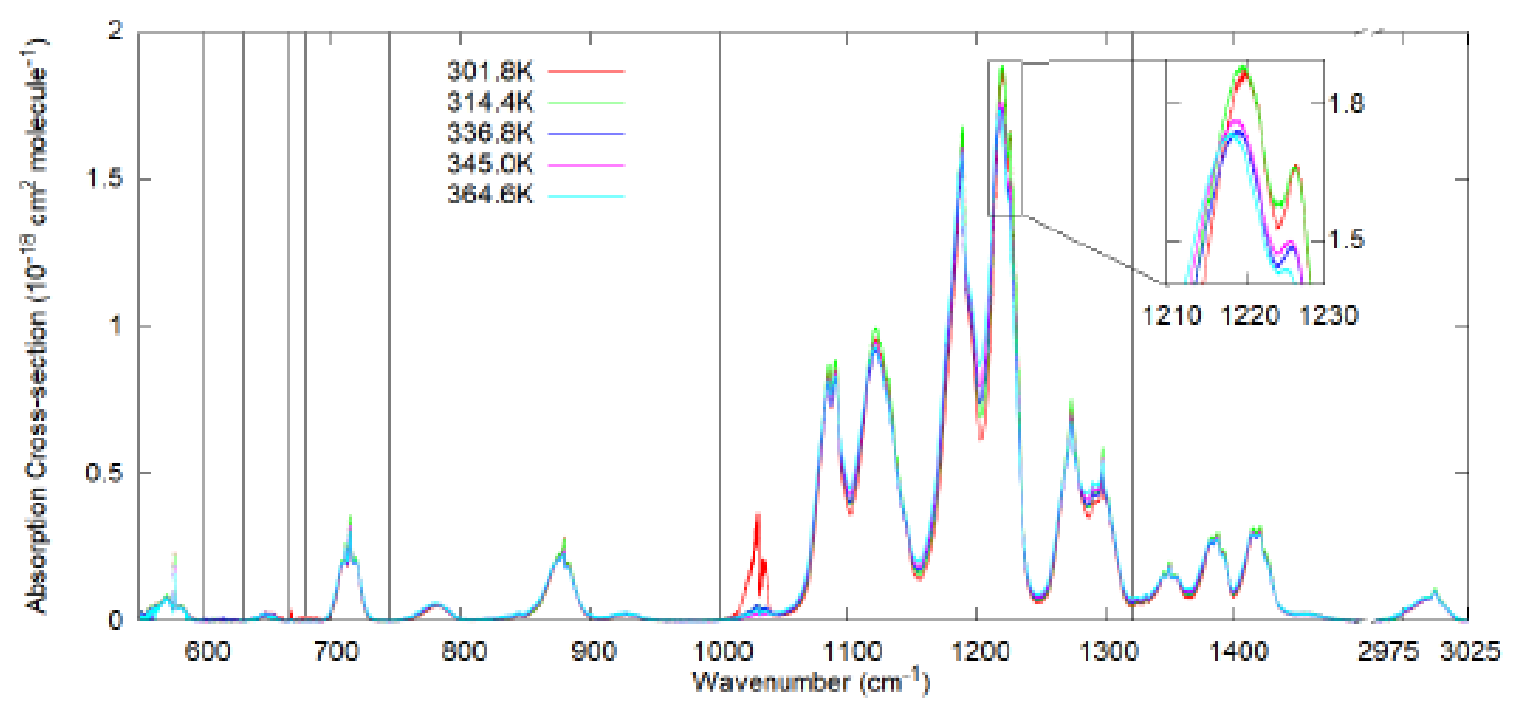


Figure 4: Absorption cross-sections of HFC-236ea.

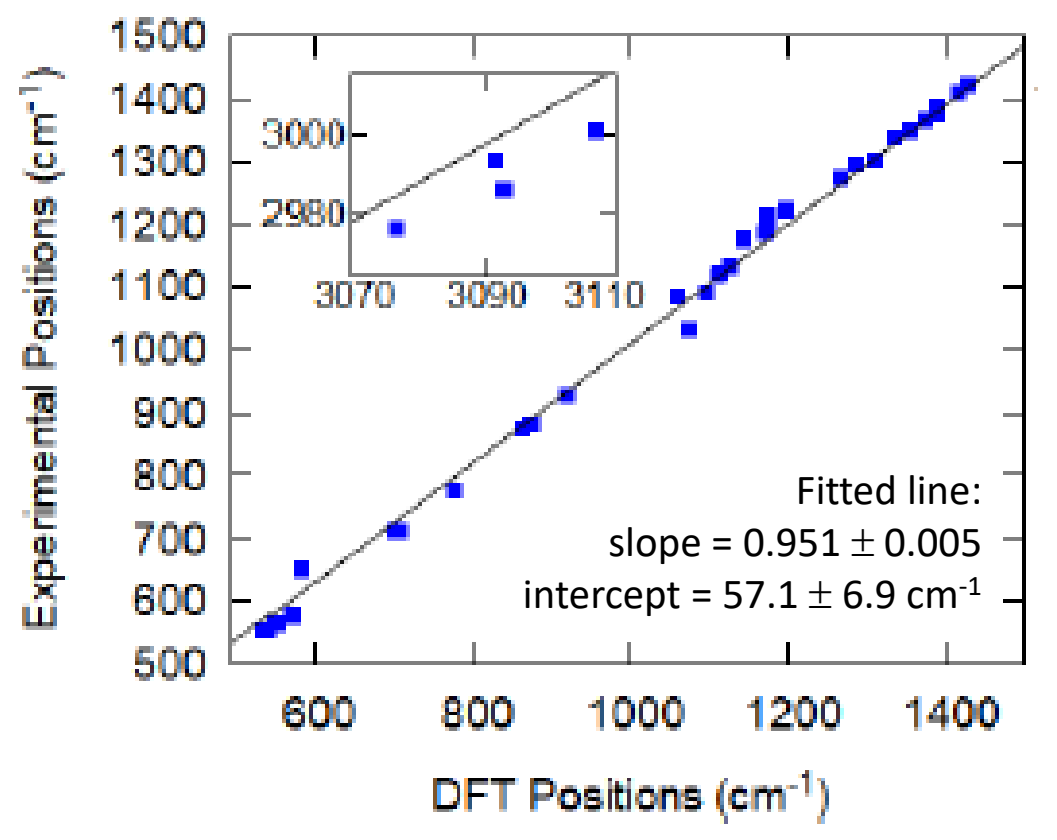


Figure 5: Experimental absorption peak positions versus DFT peak positions for HFC-236ea .

Data Set	Temp. (K)	Range (cm^{-1})	Uncorrected RE (Wm^{-2}ppb^{-1})	Corrected RE (Wm^{-2}ppb^{-1})	GWP$_{100}$
IPCC AR5	296	600-1350	0.24*	0.30	1335
Exp	301.8	550-3000	0.243±0.028	0.256±0.034	1141±402
Combined Exp and DFT	301.8	0-3000	0.252±0.029	0.265±0.035	1181±417

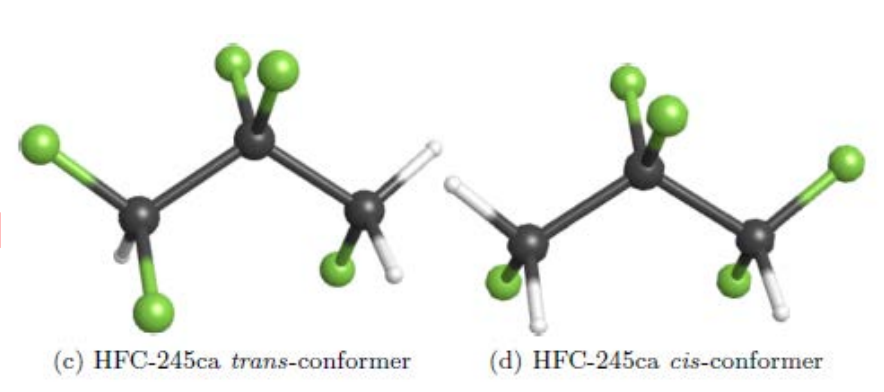
*Implied by Gierczak *et al.* that the RE is 1.10 relative to the RE of CFC-11

Table 1: Summary of RE and GWP$_{100}$ values for HFC-236ea at room temperature. IPCC AR5 is Myhre et al. (2013).

1,1,2,2,3-pentafluoropropane (HFC-245ca) [Ref. 1]

- HFC-236ea is used as a refrigerant and as a foam-blowing agent
- Atmospheric lifetime of 6.5 years
- No published spectra
- No reported measurements in the atmosphere, but included in the IPCC Fifth Assessment Report as a possible greenhouse gas [Myhre et al., 2013]

Figure 6: HFC-245ca conformers.
F atoms are green, H white, and C grey.



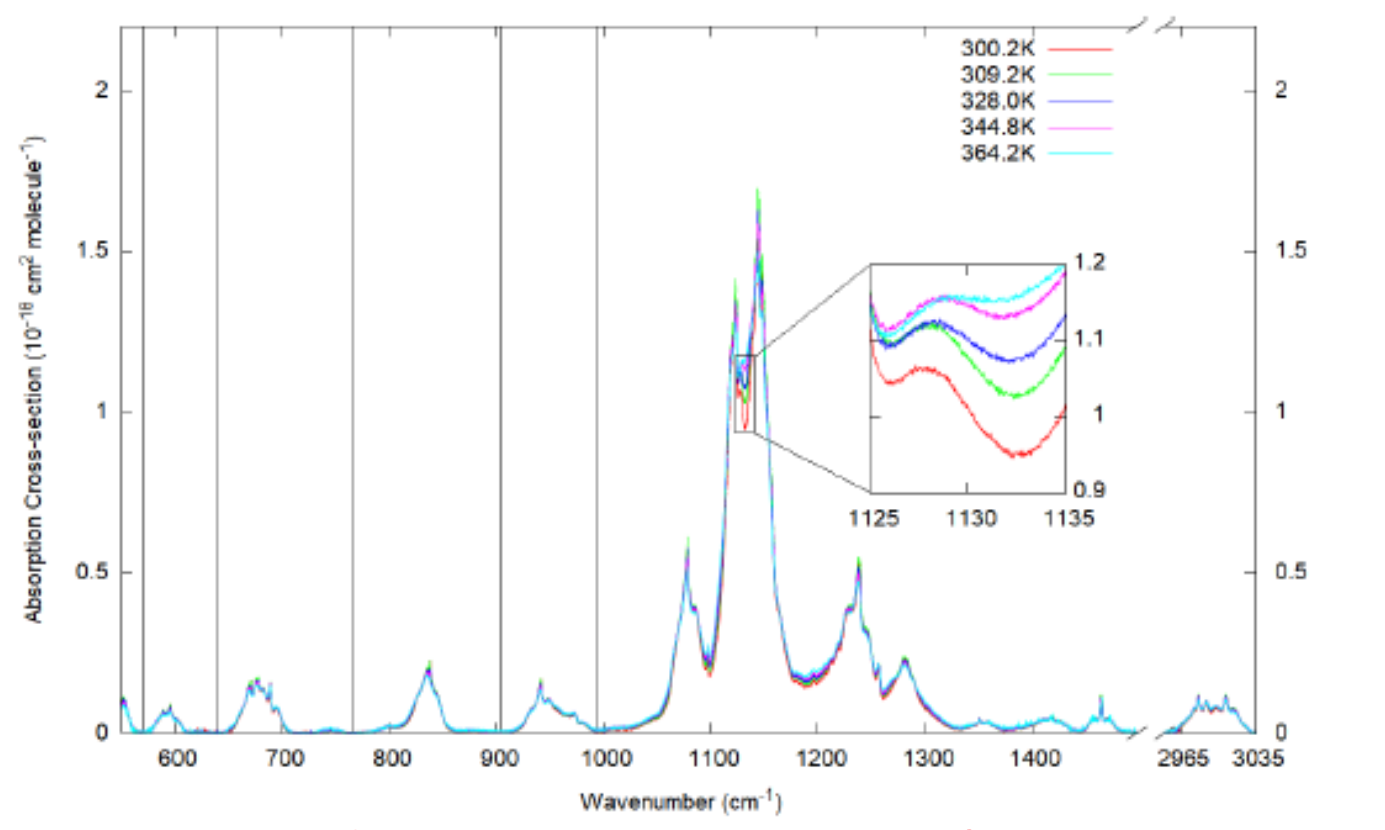


Figure 7: Absorption cross-sections of HFC-245ca.

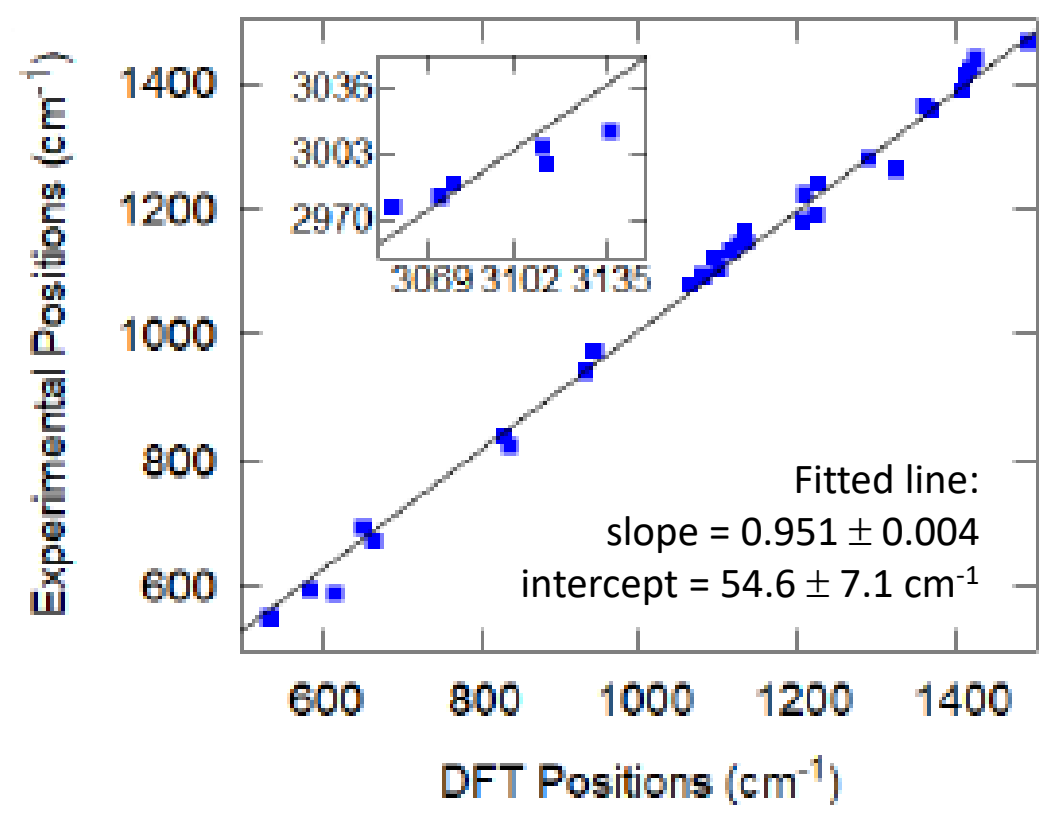


Figure 8: Experimental absorption peak positions versus DFT peak positions for HFC-245ca.

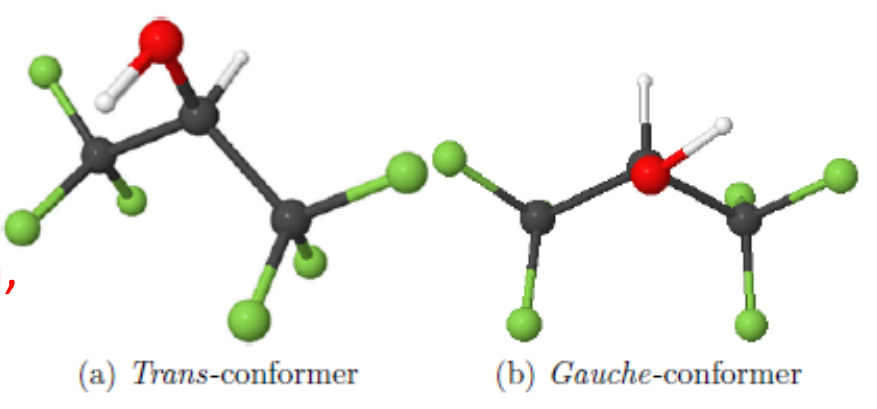
Data Set	Temp. (K)	Range (cm^{-1})	RE (Wm^{-2}ppb^{-1})	Uncorrected RE (Wm^{-2}ppb^{-1})	GWP$_{100}$
IPCC AR5				0.24	716
Exp	300.2	550-3000	0.191±0.019	0.197±0.023	588±205
Combined Exp and DFT	300.2	0-3000	0.196±0.020	0.202±0.027	602±210

Table 2: Summary of RE and GWP$_{100}$ values for HFC-245ca at room temperature. IPCC AR5 is Myhre et al. (2013).

1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) [Ref. 2]

- HFIP is a specialty solvent for some polar polymers and used in production of anesthetics
- Atmospheric lifetime of 1.9 years
- Has two stable ground state conformations based on positions of OH internal rotor: *trans* and *gauche*

Figure 9: HFIP conformers.
O atoms are red, F green, H white, and C grey.



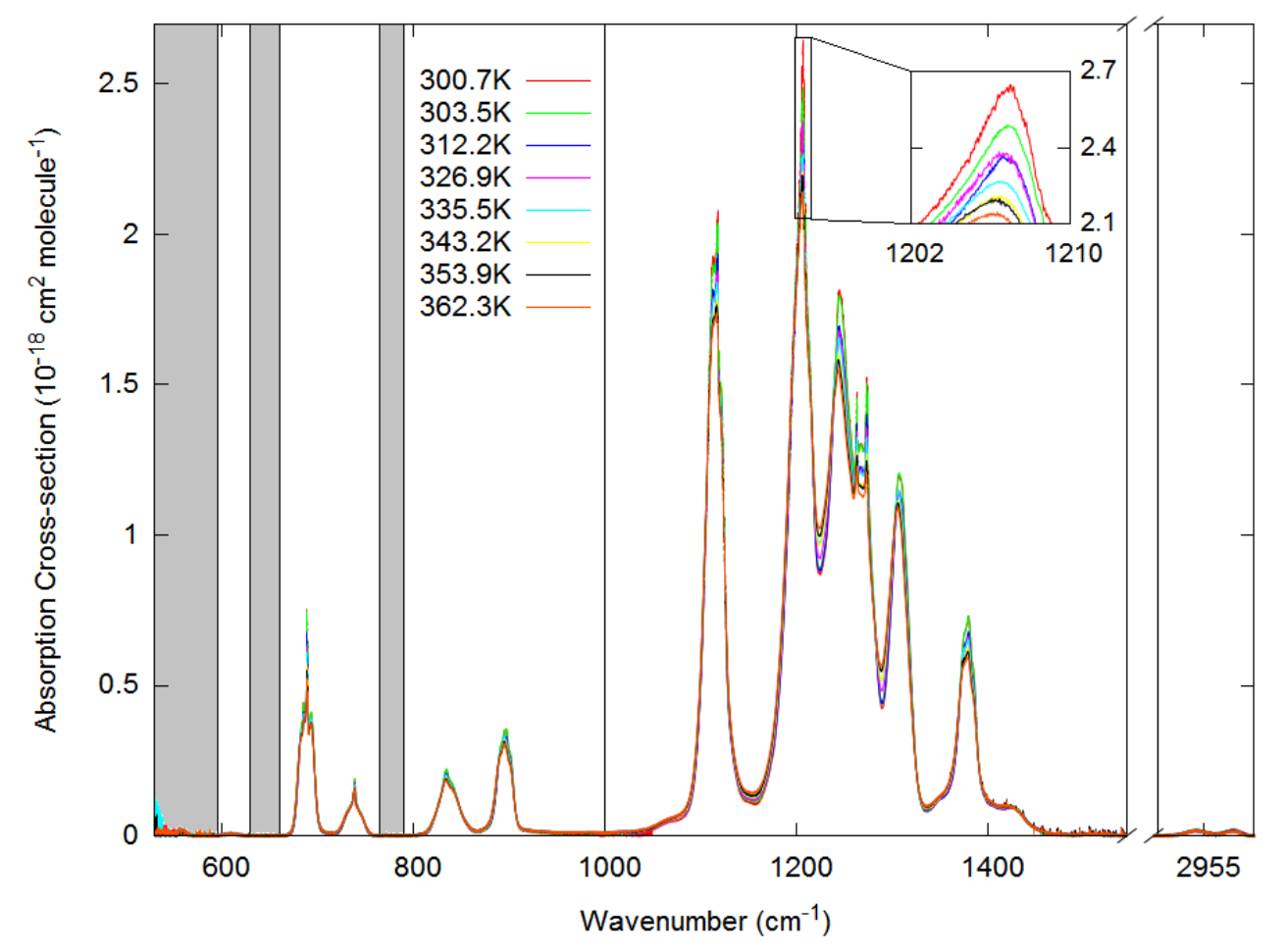


Figure 10: Absorption cross-sections of HFIP.

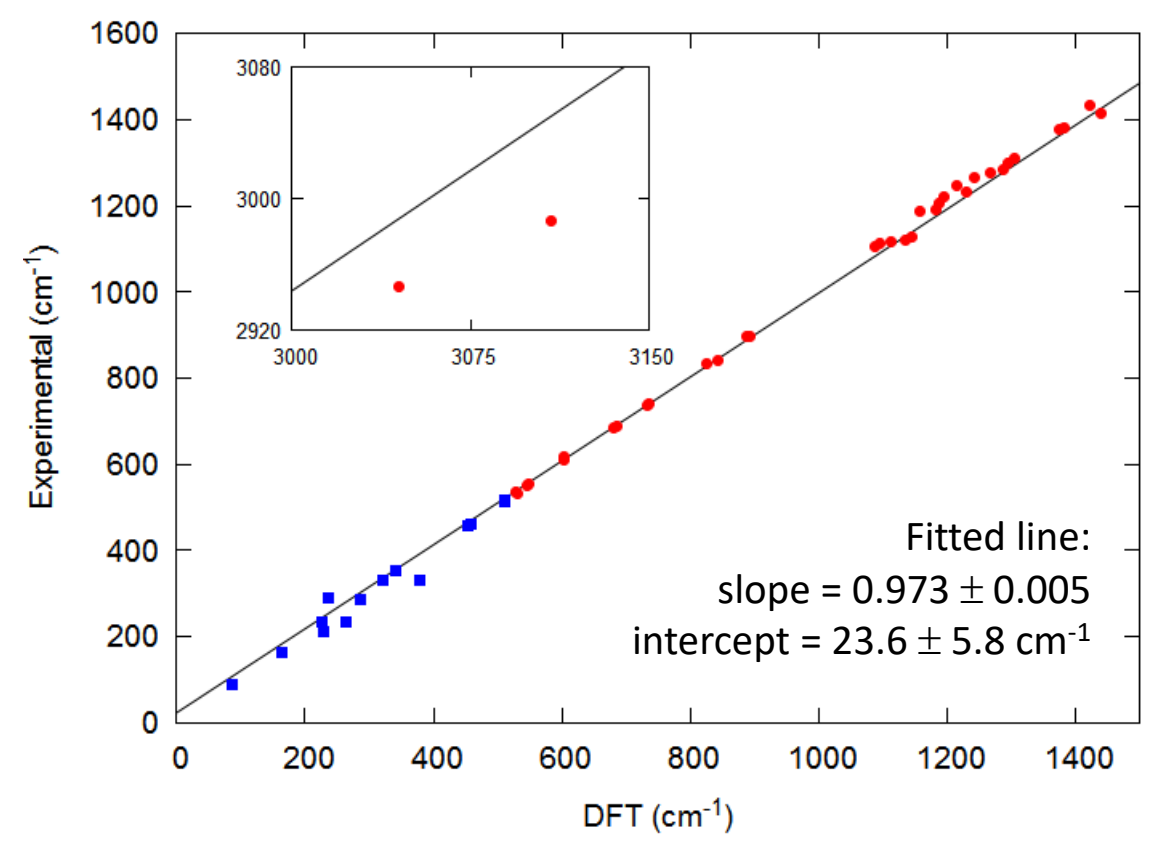


Figure 11: Experimental absorption peak positions versus DFT peak positions for HFIP. Red circles are from this work. Blue squares are experimental data below 530 cm^{-1} taken from [Barns & Murto, 1972; Murto et al., 1973 ; Durig et al., 1988].

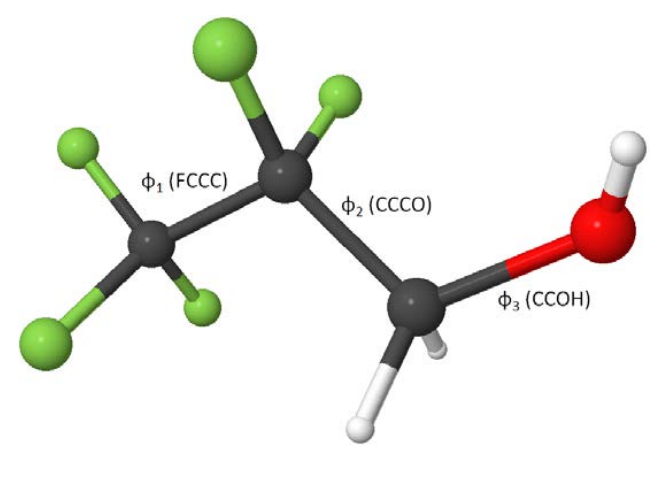
Data Set	Temp. (K)	Range (cm^{-1})	RE (Wm^{-2}ppb^{-1})	GWP$_{100}$
Imasu *et al.*	296	700-1500	0.31±0.062	100
Hodneborg *et al.*				182
Exp	300.6	530-3000	0.293±0.059	188
DFT	300.6	0-3000	0.348±0.070	223
Exp+DFT	300.4	0-3000	0.317±0.063	203

Table 3: Summary of RE and GWP$_{100}$ values for HFIP at room temperature.

2,2,3,3,3-pentafluoropropanol (PFPO) [Ref. 3]

- PFPO is used to increase volatility of an analyte and to introduce fluorine atoms for better detection limits in gas chromatography
- Atmospheric lifetime of 0.33 years
- Has three stable ground state conformations based on positions of internal rotors

Figure 12: The *trans-trans-gauche* conformer of PFPO.
O atoms are red, F green, H white, and C grey.



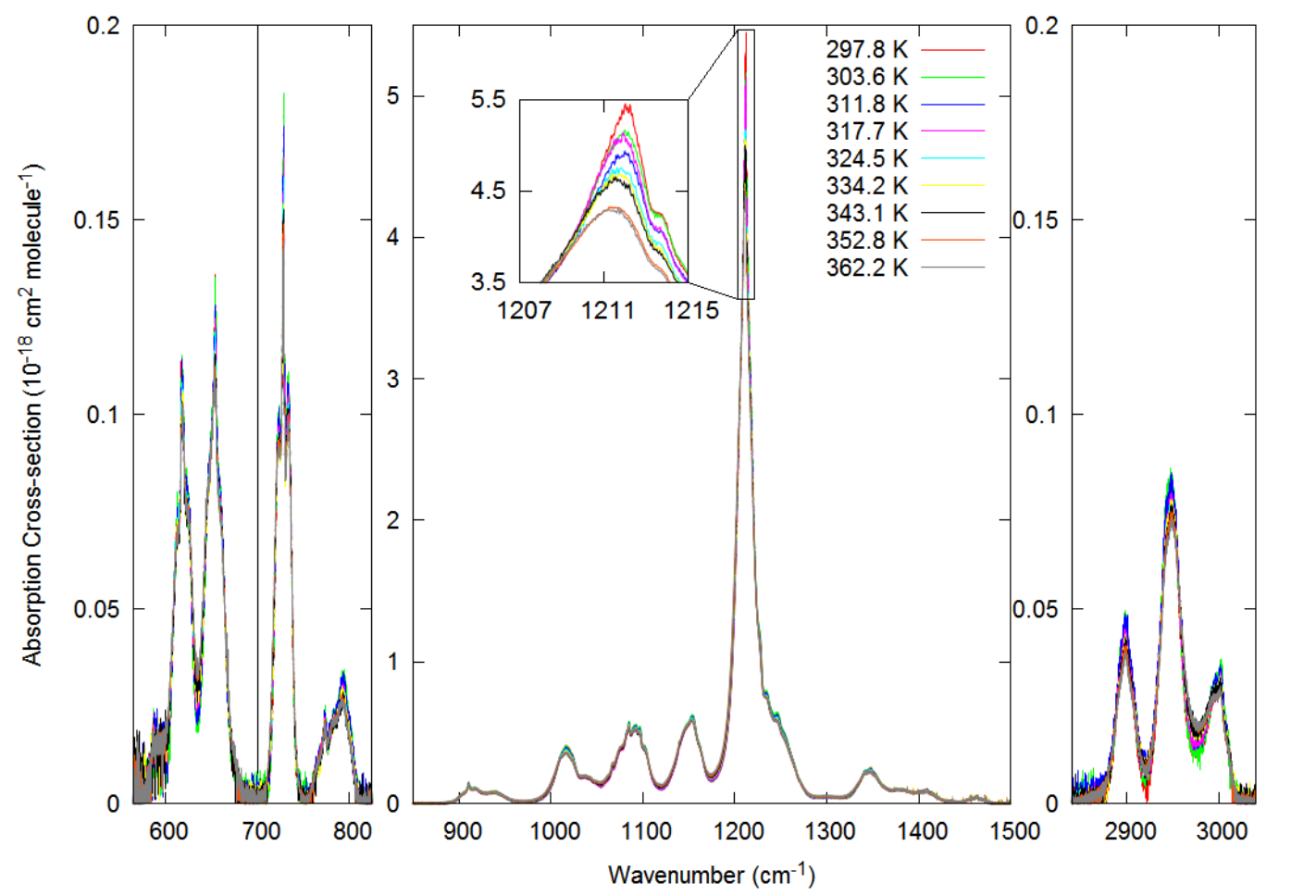


Figure 13: Absorption cross-sections of PFPO.

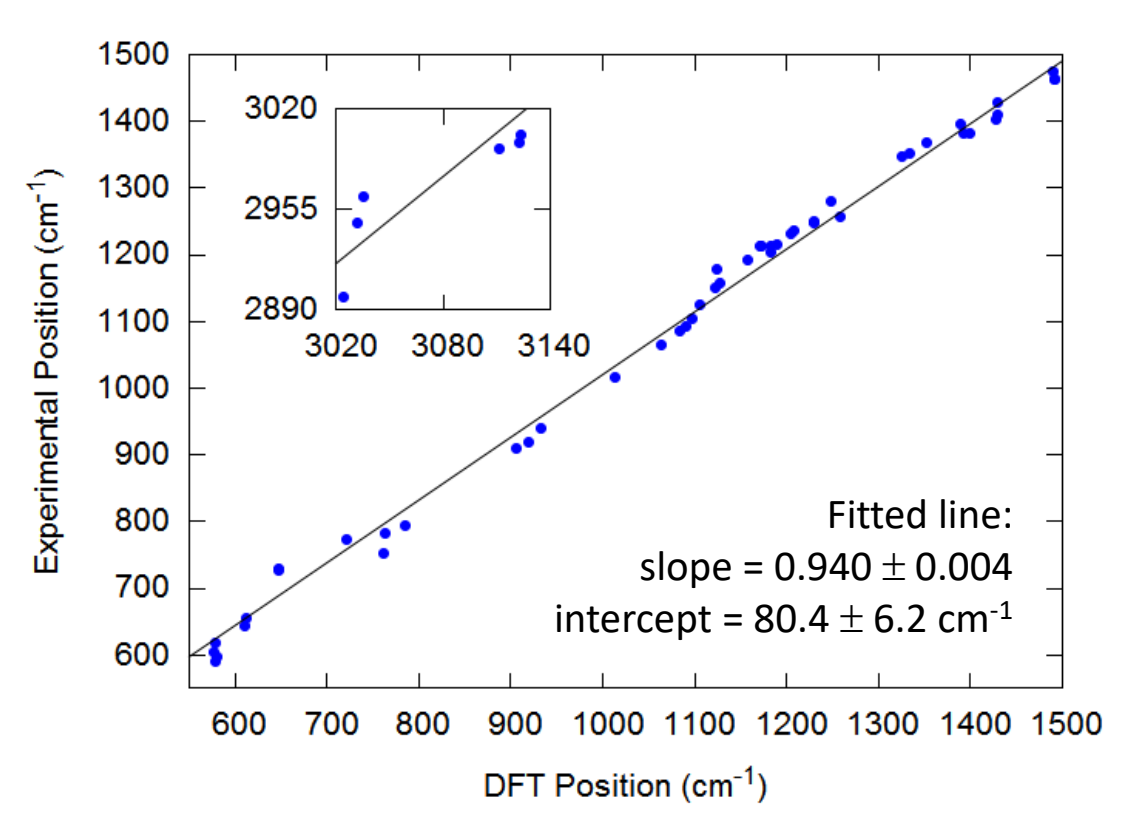


Figure 14: Experimental absorption peak positions versus DFT peak positions for PFPO.

Data Set	Temp. (K)	Range (cm^{-1})	RE (Wm^{-2}ppb^{-1})	GWP$_{100}$
Imasu *et al.*	296	700-1500		18
Sellevåg *et al.*	298	490-1500	0.252±0.05	23.1
Antiñolo *et al.*	298	500-4000	0.26±0.052	25.0
Hodnebrog *et al.*			0.27±0.054	19
Experimental	297.8	565-3000	0.257±0.051	19.8
DFT	0-3000	297.8	0.344±0.069	23.2
Experimental+DFT	297.8	0-3000	0.300±0.06	23.1

Table 4: Summary of RE and GWP$_{100}$ values for PFPO at room temperature.

Perfluorotributylamine (PFTBA) [Ref. 4]

- Used in electronic reliability and quality testing
- No known sinks in the atmosphere, resulting in lifetimes of hundreds of years and well-mixed atmospheric distributions
- Atmosphere VMR of 0.18 ± 0.01 pptv
- Has the highest radiative efficiency of any compound detected in the atmosphere

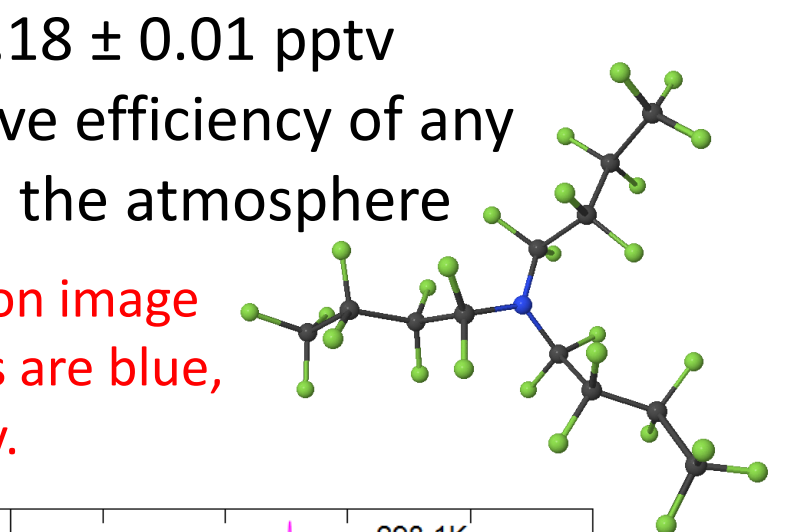


Figure 15: Projection image of PFTBA. N atoms are blue, F green, and C grey.

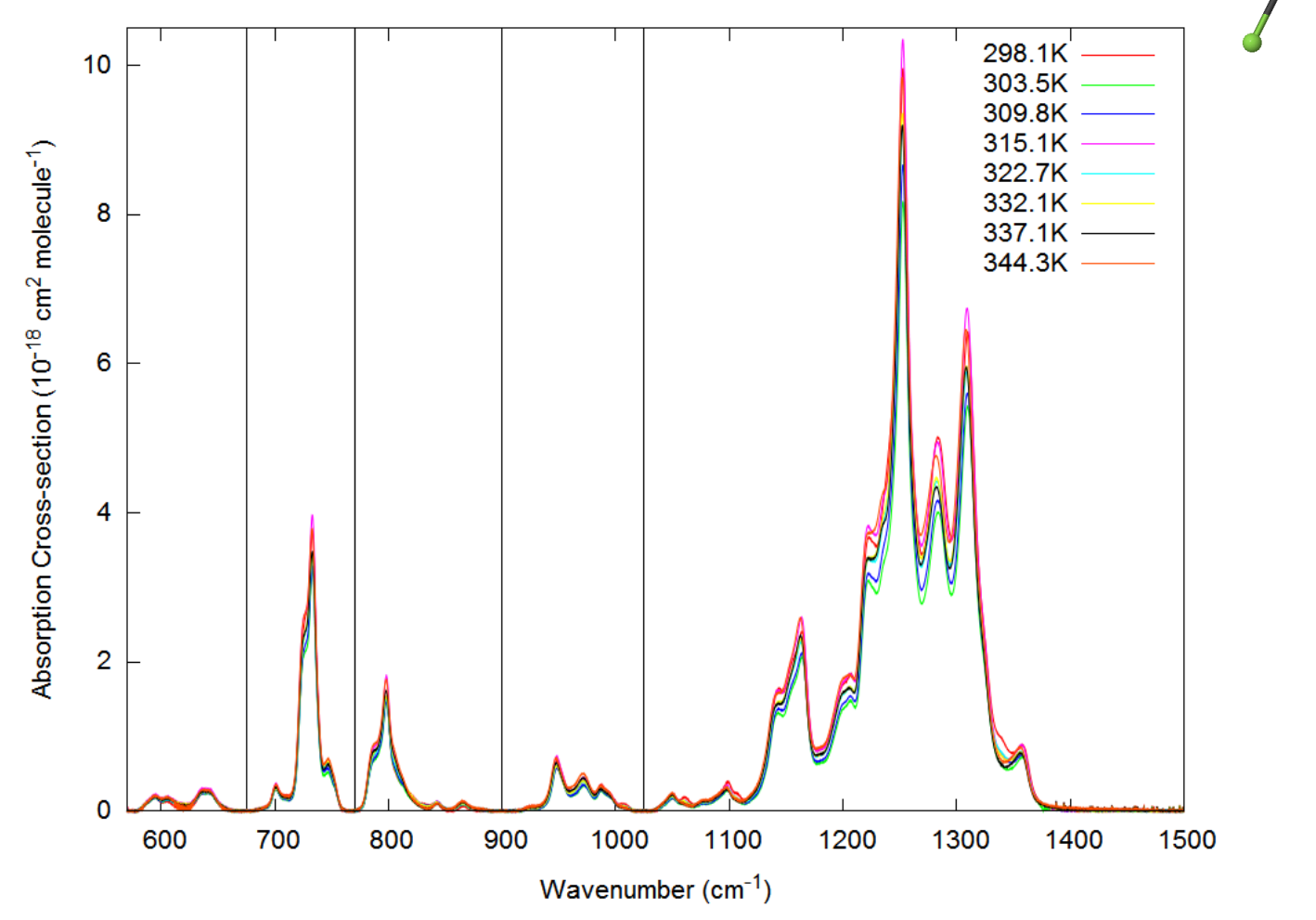


Figure 16: Absorption cross-sections of PFTBA.

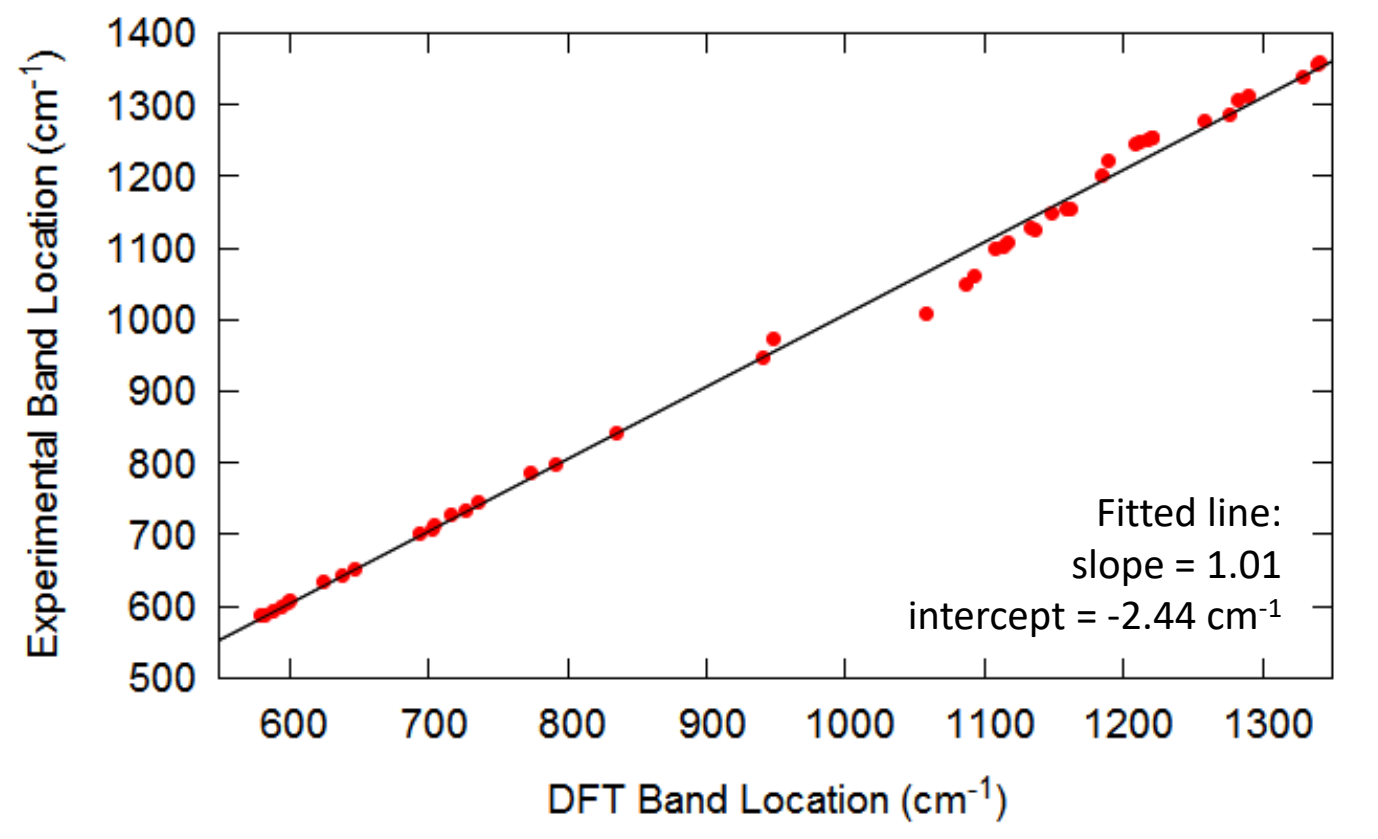


Figure 17: Experimental absorption peak positions versus DFT peak positions for PFTBA.

Data Set	Lifetime (yr)	Temp. (K)	Range (cm^{-1})	RE (Wm^{-2}ppb^{-1})	GWP$_{100}$
Hong *et al.*	500	296.0	600-1500	0.86±0.17	7100
3M	2000				7200
Experimental	500(2000)	298.2	550-3000	0.782±0.156	6982(7580)
DFT	500(2000)	298.2	0-3000	0.928±0.186	8282(8990)
DFT+Exp	500(2000)	298.2	0-3000	0.803±0.161	7170(7783)

Table 5: Summary of RE and GWP$_{100}$ values for PFTBA at room temperature. Hong et al. (2013) and Costello et al. (2004: "3M") estimate the lifetime as 500 and 2000 years, respectively. GWP values for both lifetimes are shown, with the values in parentheses for a lifetime of 2000 years.

Perfluorodecalin (PFDC) [Ref. 5]

- Powerful medical solvent
- Atmospheric lifetime of 2000 years

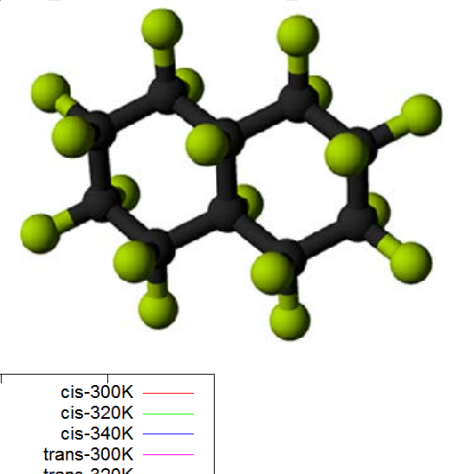


Figure 18: The *trans* conformation of PFDC. F atoms are green and C gray.

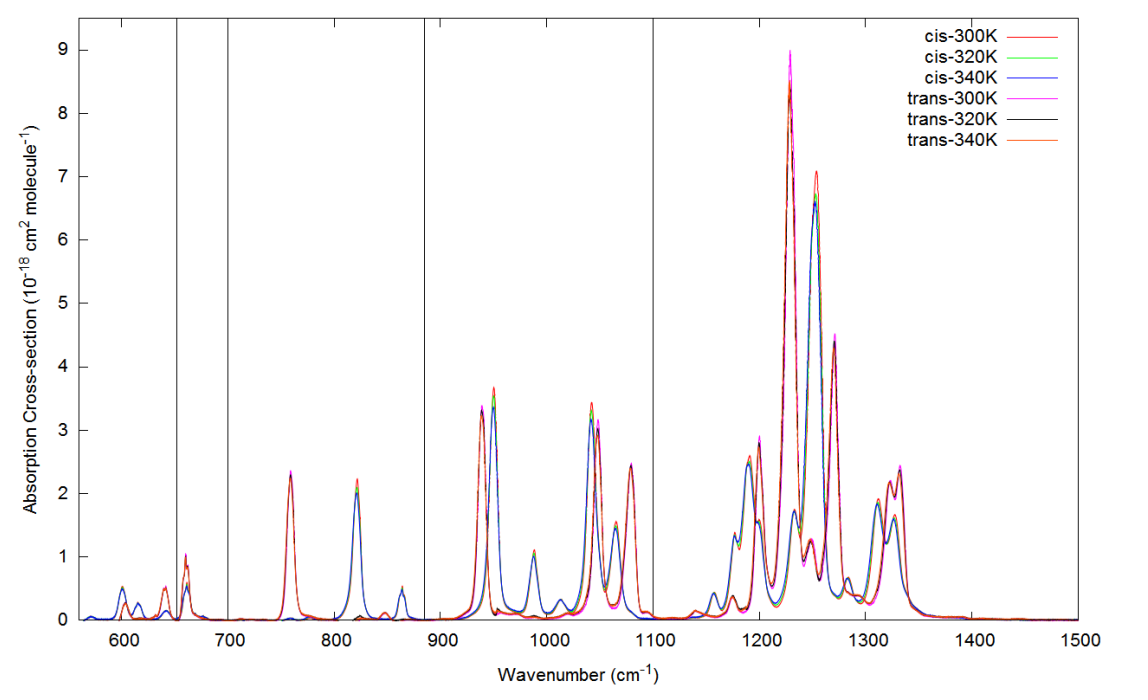


Figure 19: Absorption cross-sections of PFDC.

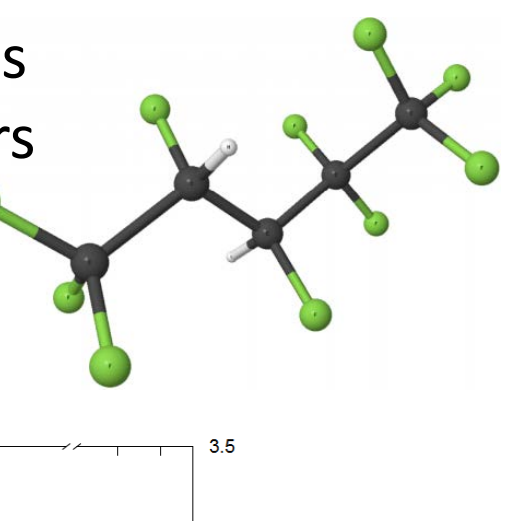
Data Set	Range (cm^{-1})	RE	GWP$_{100}$
Shine *et al.*	560-1500	0.45±0.049	6290±1890
Experimental	560-1500	0.50±0.055	7060±2120
DFT	0-3000	0.58±0.081	8170±2450
Experimental+DFT	0-3000	0.53±0.058	7440±2230

Table 6: Summary of RE and GWP$_{100}$ values for *trans*-PFDC at 296K [Shine et al., 1996] and 300 K..

2H,3H-perfluoropentane (HFC-43-10mee) [Ref. 6]

- Used as a solvent in electronics and for the recovery of radioactive elements
- Atmospheric lifetime of 6.1 years

Figure 20: Projection image of the *threo* diastereomer of HFC-43-10mee. F atoms are green, H white, and C grey.



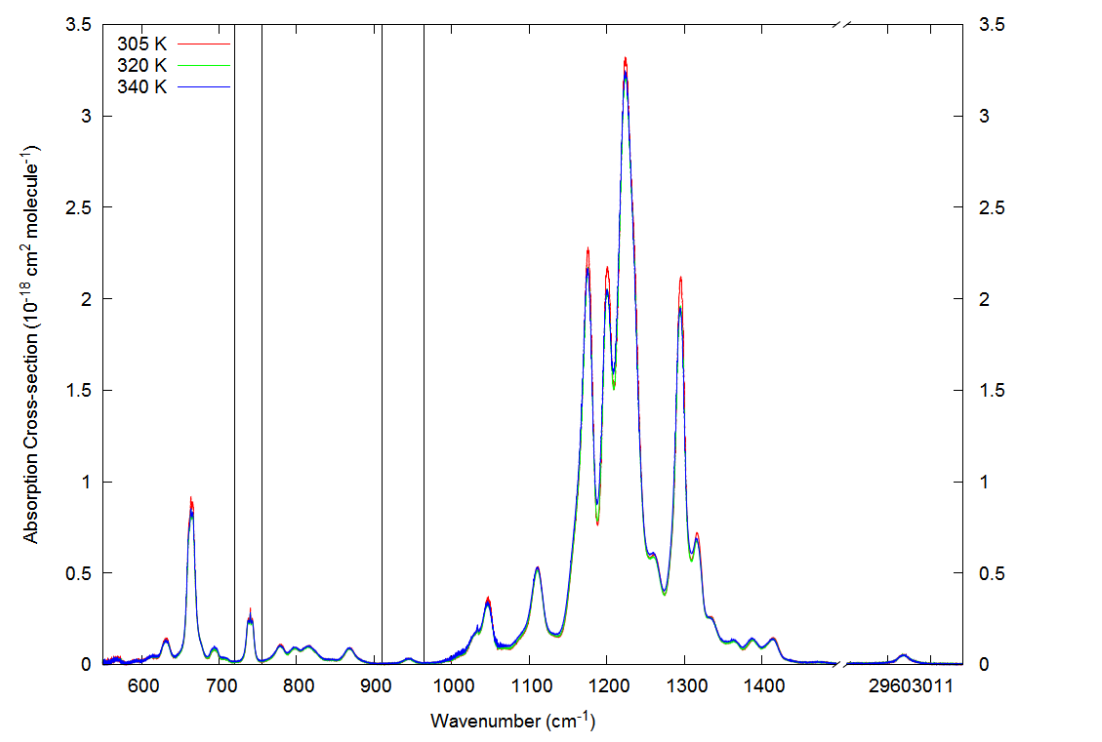


Figure 21: Absorption cross-sections of HFC-43-10mee.

Data Set	Range (cm^{-1})	RE	GWP$_{100}$
PNNL	500-3000	0.332±0.036	1385±485
Hodneborg *et al.*		0.40±0.044	1650±578
Experimental	550-3000	0.329±0.036	1375±481
DFT	0-3000	0.435±0.061	1817±636
Experimental+DFT	0-3000	0.359±0.039	1410±494

Table 7: Summary of RE and GWP$_{100}$ values for HFC-43-10mee at 298K [Sharpe et al., 2004: "PNNL"] and 300 K.

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Results presented here can be found in these publications:

[1] Godin, P.J., K. Strong, K. Le Bris, H. Johnson, and R. Piunno. Conformational analysis and global warming potentials of 1,1,1,2,3,3-hexafluoropropane and 1,1,2,2,3-pentafluoropropane from absorption spectroscopy, J. Quant. Spectrosc. Rad. Transfer, in review, 2018.
[2] Godin, P.J., K. Le Bris, and K. Strong. Conformational analysis and global warming potentials of 1,1,1,3,3,3-hexafluoro-2-propanol from absorption spectroscopy, J. Quant. Spectrosc. Rad. Transfer, 203, 522-529, 2017.
[3] Godin, P.J., A. Cabaj, L.-H. Xu, K. Le Bris, and K. Strong. A study of the temperature dependence of the infrared absorption cross-sections of 2,2,3,3,3-pentafluoropropanol in the range of 298-362 K, J. Quant. Spectrosc. Rad. Trans., 186, 150-157, 2017.
[4] Godin, P.J., A. Cabaj, S. Conway, A.C. Hong, K. Le Bris, S.A. Mabury, and K. Strong. Temperature-dependent absorption cross-sections of perfluorotributylamine, J. Mol. Spec., 323, 53-58, 2016.
[5] Le Bris, K., J. DeZeeuw, P.J. Godin, and K. Strong. Cis- and trans-perfluorodecalin: infrared spectra, radiative efficiency and global warming potential, J. Quant. Spectrosc. Rad. Transfer, 203, 538–541, 2017.
[6] Le Bris, K., J. DeZeeuw, P.J. Godin, and K. Strong. Infrared absorption cross-sections, radiative efficiency and global warming potential of HFC-43-10mee, J. Mol. Spec., 348, 64-67, 2018.

7. Summary

- New temperature-dependent infrared absorption cross-sections were measured for seven fluorinated molecules.
- First known temperature-dependent study of HFC-236ea, HFC-245ca, HFIP, PFPO, PFTBA, and PFDC.
- Density functional theory calculations were performed for HFC-236ea, HFC-245ca, HFIP, PFTBA, PFDC, and HFC-43-10mee.
- Integrated band strengths (not shown), radiative efficiencies, and global warming potentials of all seven molecules were derived.
- Experimental RE and GWP values are consistent with previously published data and strengthen our confidence in these numbers.
- The RE and GWP values are higher (~1 to 20%) when the experimental spectral range is extended to 0 cm^{-1} with DFT, suggesting that current radiative impacts derived from spectra typically measured at wavenumbers above ~500 cm^{-1} may be underestimated.

Acknowledgements

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