Atmospheric Lifetimes of CFC-11 and NF_3: Temperature dependent UV absorption cross sections

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Motivation for accurate laboratory measurements

- Experimental measurements of $\sigma(\lambda, T)$ represent a constraint on:
  - Atmospheric lifetimes
  - Global-warming potentials
  - Ozone-depletion potentials
- Interpretation of field data
- Increased accuracy/ reduces uncertainty in model calculated lifetimes

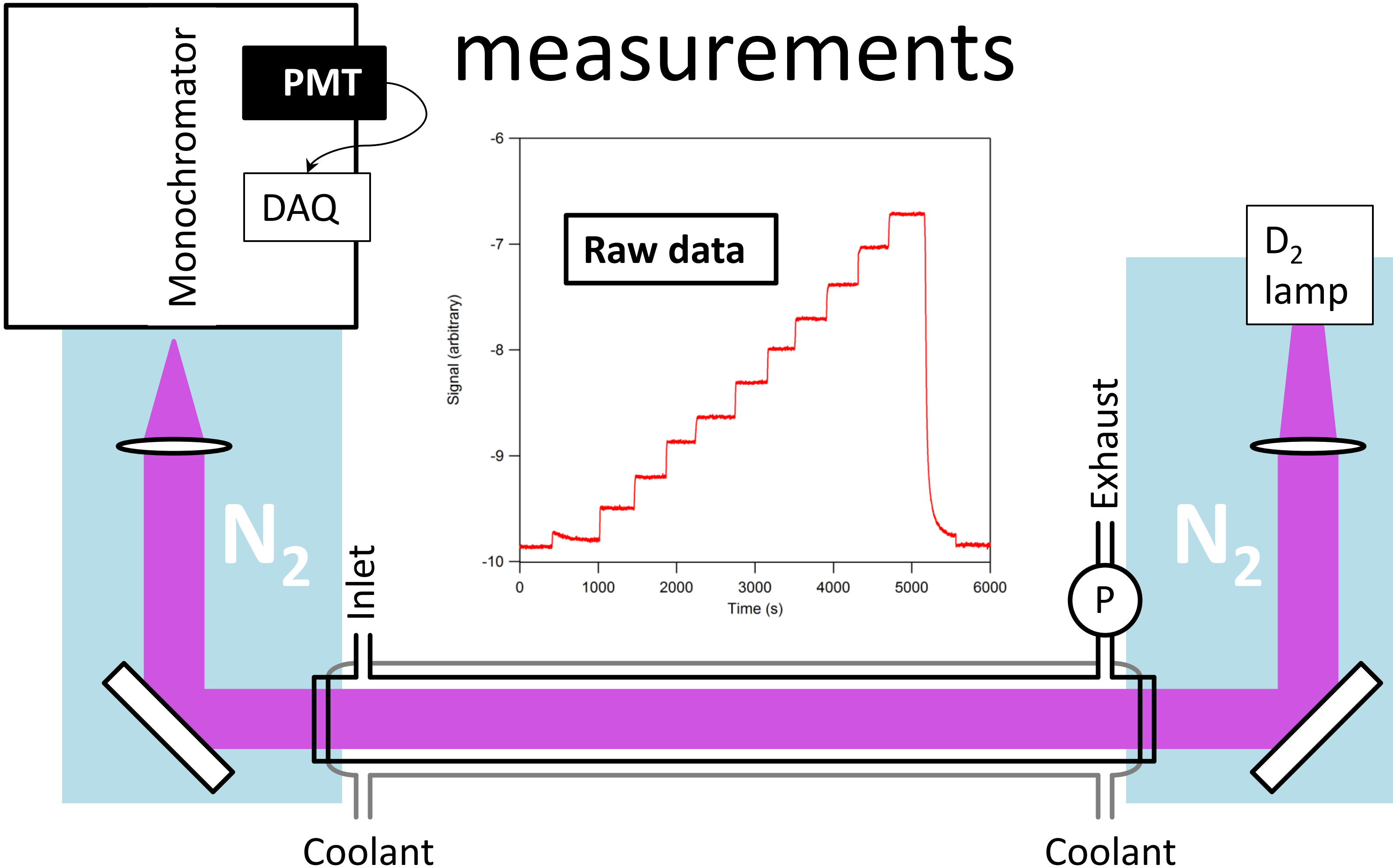
Outline

- Temperature dependent absorption cross section measurements presented for CFC-11 and NF_3
- Measurements are compared with current recommendations for modeling
- The impact of including these new data on 2-D modeled atmospheric lifetimes are discussed

Why measure CFC-11 $\sigma(\lambda, T)$?

- UV photolysis is the major loss process in the atmosphere
- Many room temperature measurements, but relatively few studies at stratospheric temperatures
- Model recommendations primarily based on two studies, but there is some discrepancy (as much as 25%)
- This level of uncertainty has an impact on calculated atmospheric lifetimes

Absorption cross section measurements



T range: 216–296 K, λ range: 190–230 nm

Typical precision: ± 0.5%, accuracy: ± 4% (2σ)

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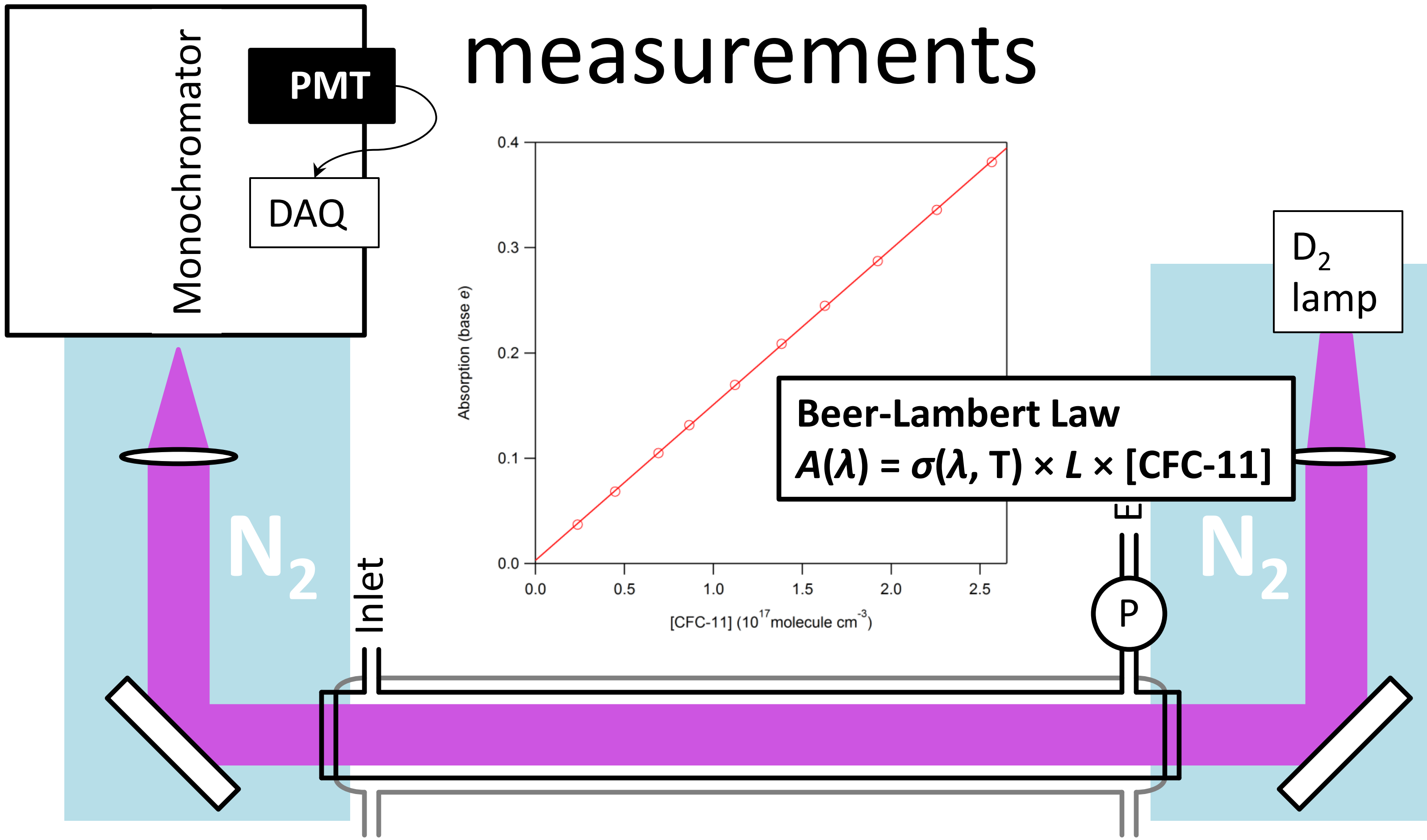

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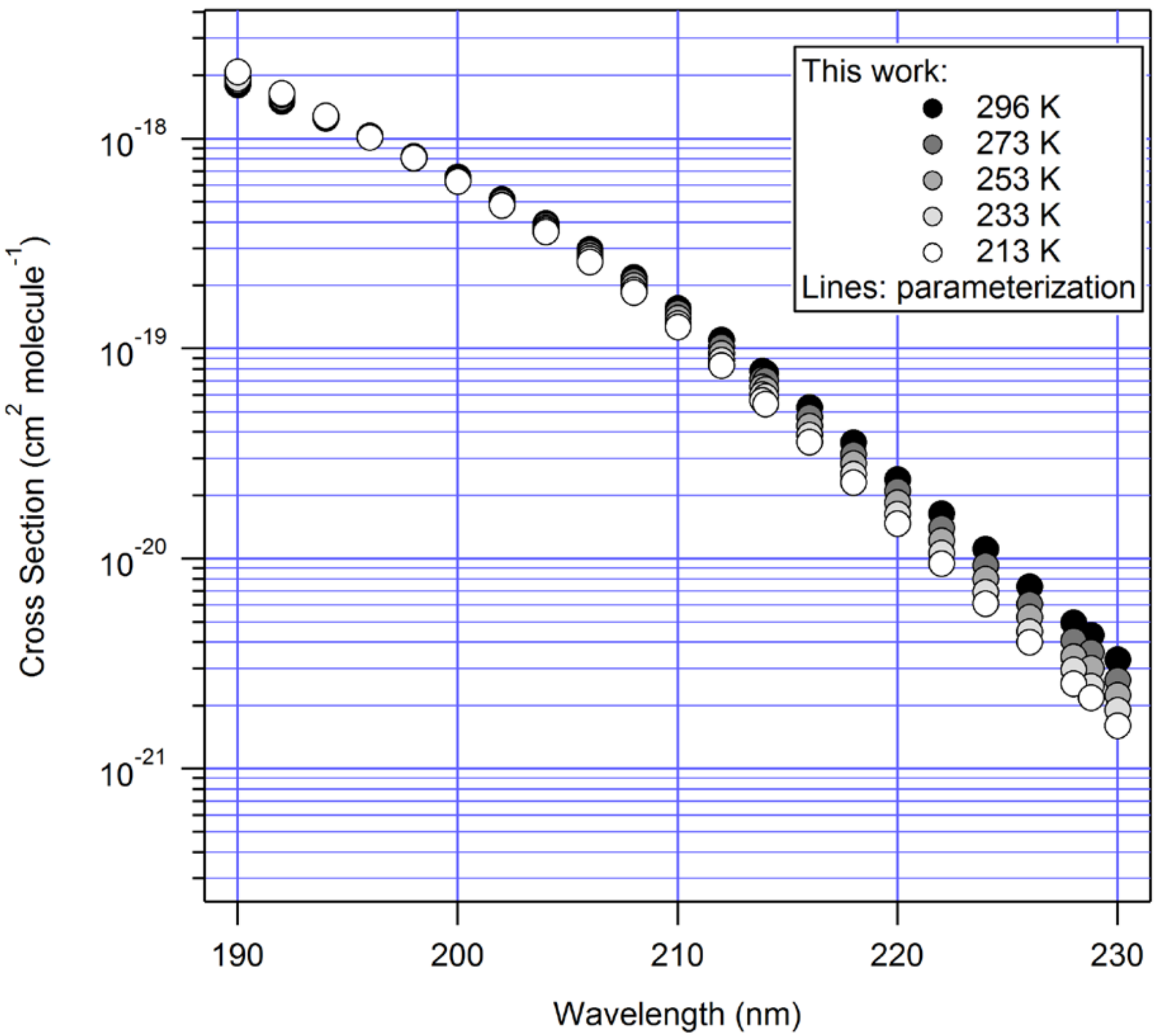
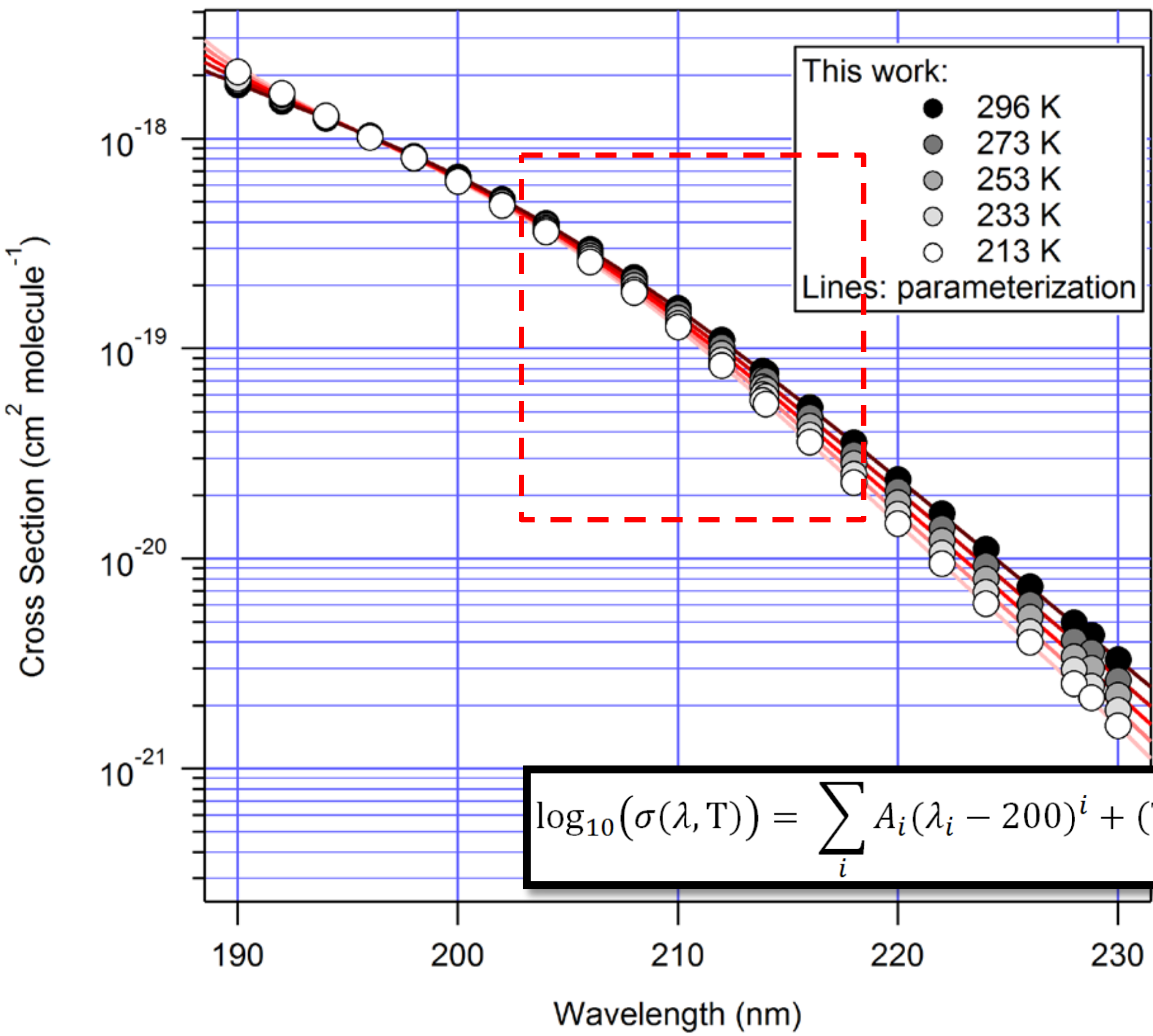
Cross section results



- Systematic decrease in σ with T
- Monotonic decrease in σ with λ

- *Manuscript in prep.*

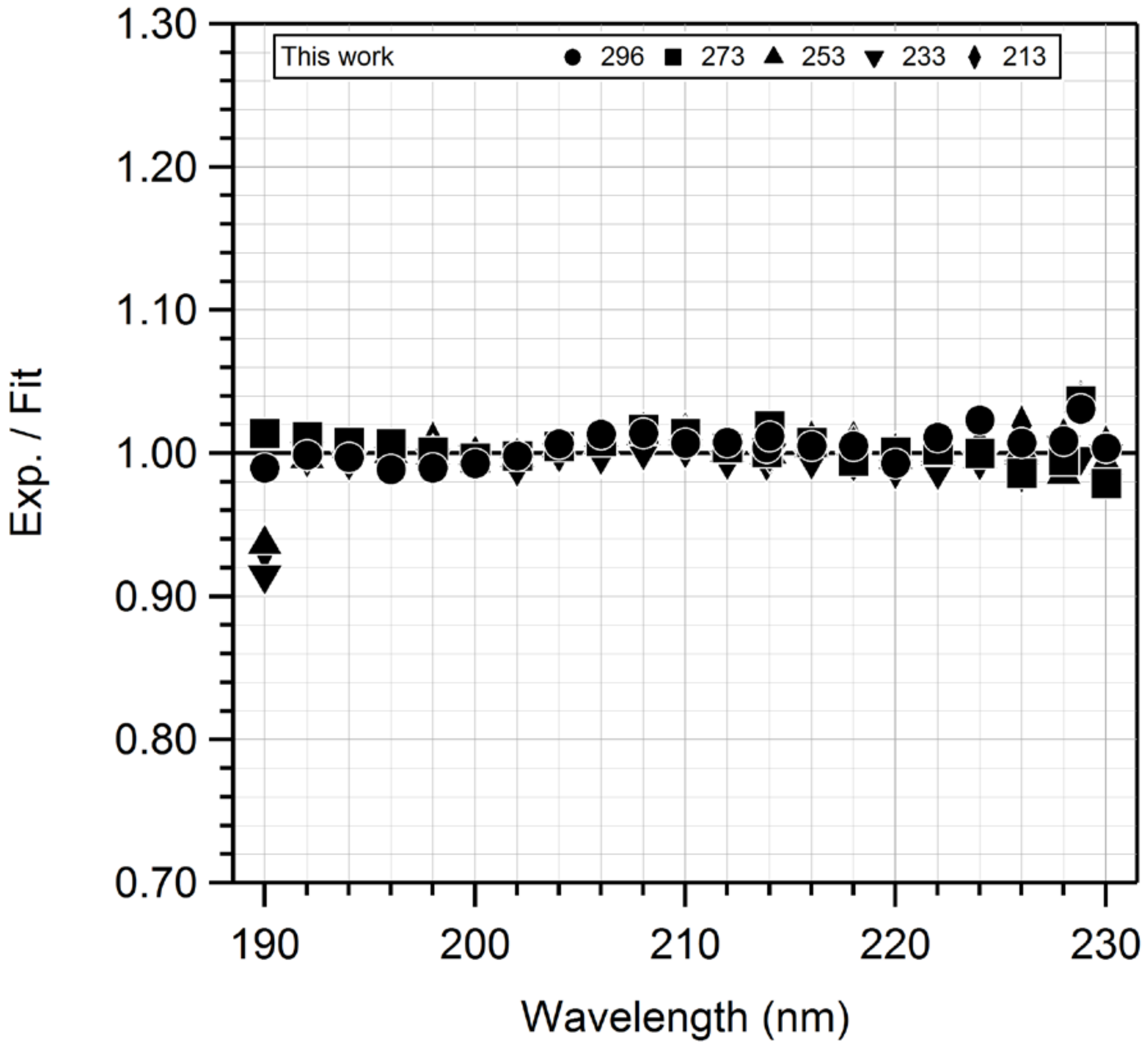
Cross section results



$$\log_{10}(\sigma(\lambda, \mathrm{T})) = \sum_i A_i(\lambda_i - 200)^i + (\mathrm{T} - 273)\sum_i B_i(\lambda_i - 200)^i$$

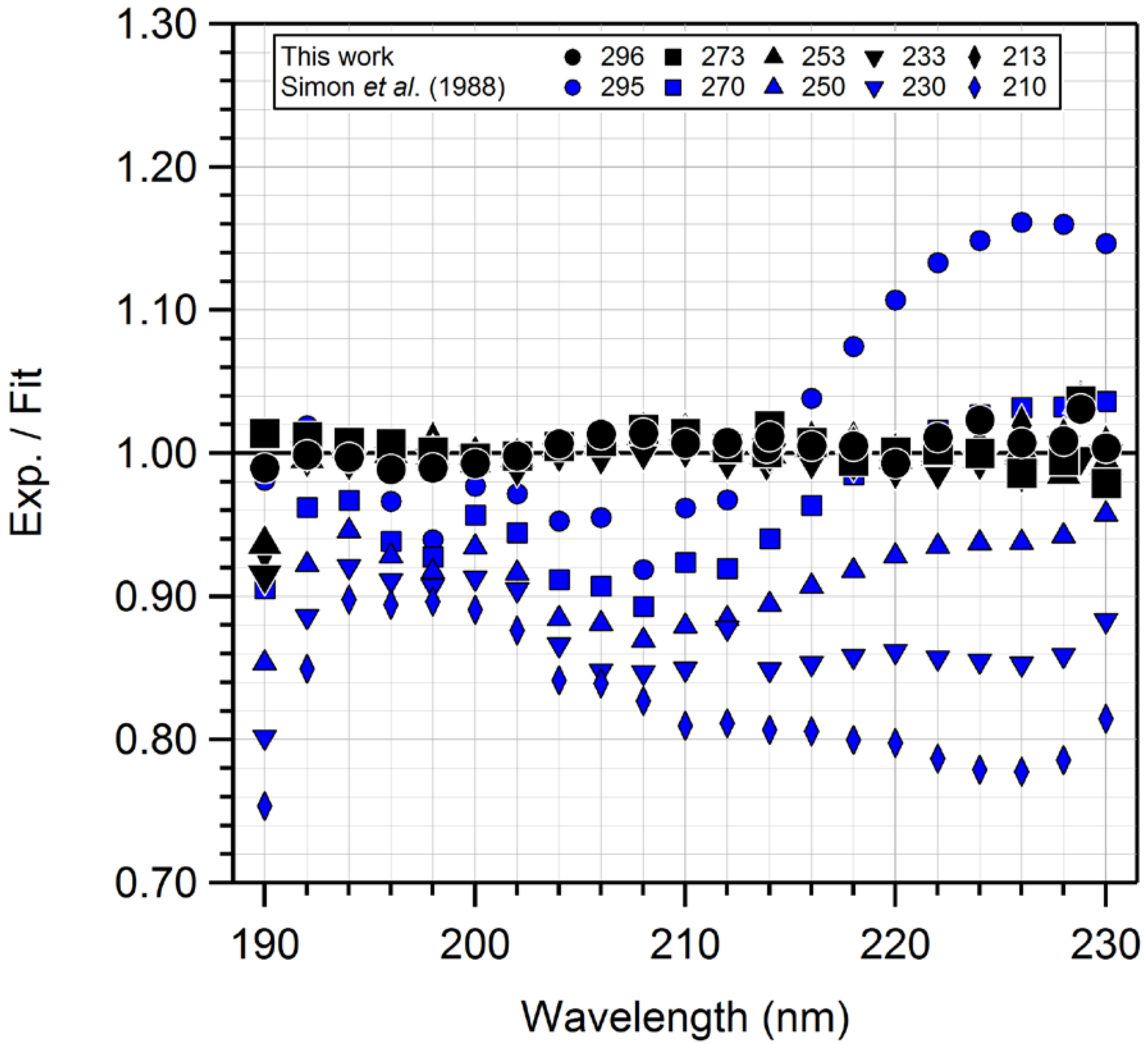
- Optimized fit with a 5th-order polynomial
- T-dependence is observed in the critical wavelength region

Comparison with parameterization



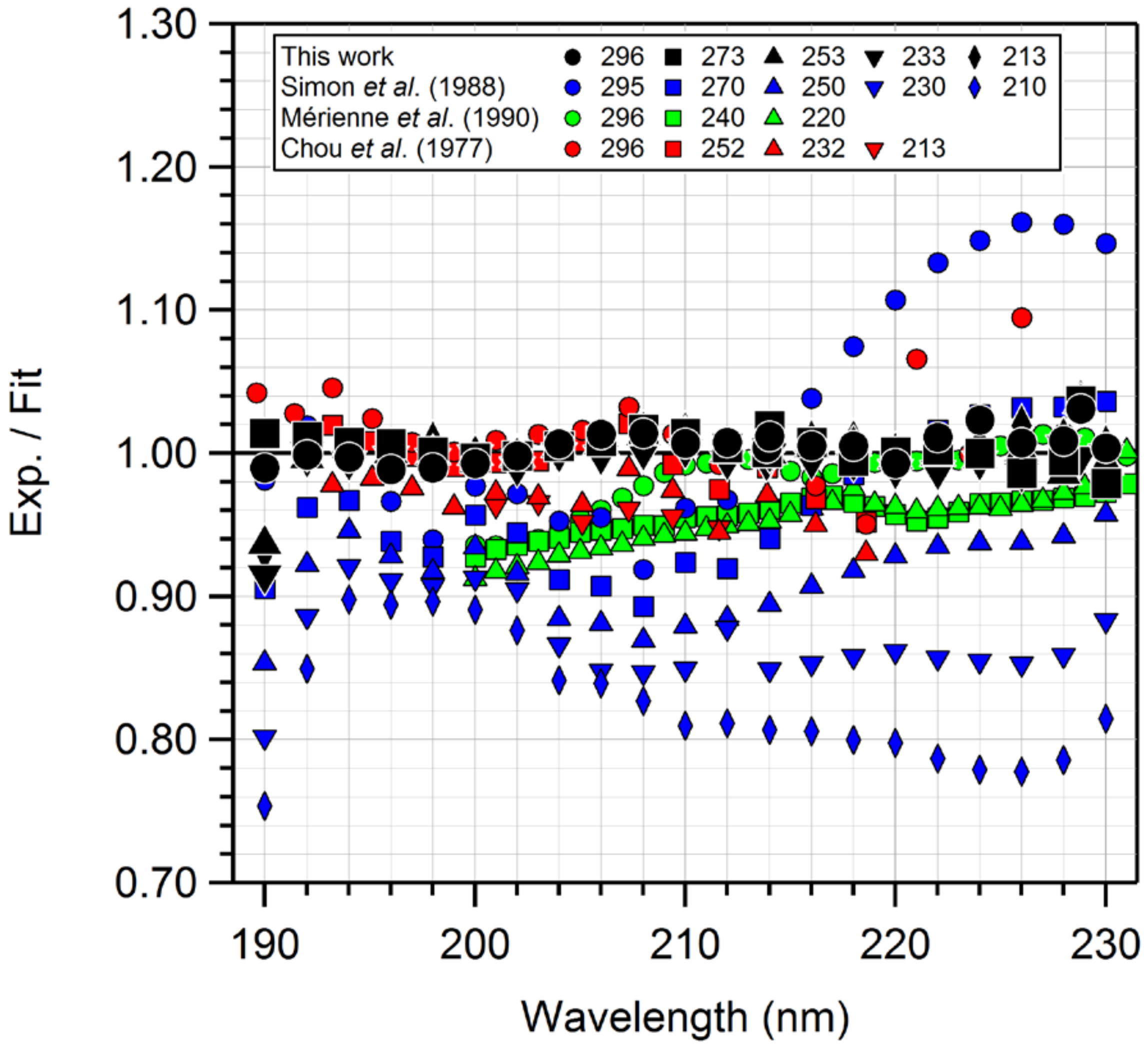
- Data is fitted well with the parameterization
- High-precision exp. data
- Appropriate fitting routine for model calcs.

Comparison with JPL recommendation



- Simon *et al*. is the current JPL recommendation
- Simon *et al*. data shows devation in T-dep, >20%

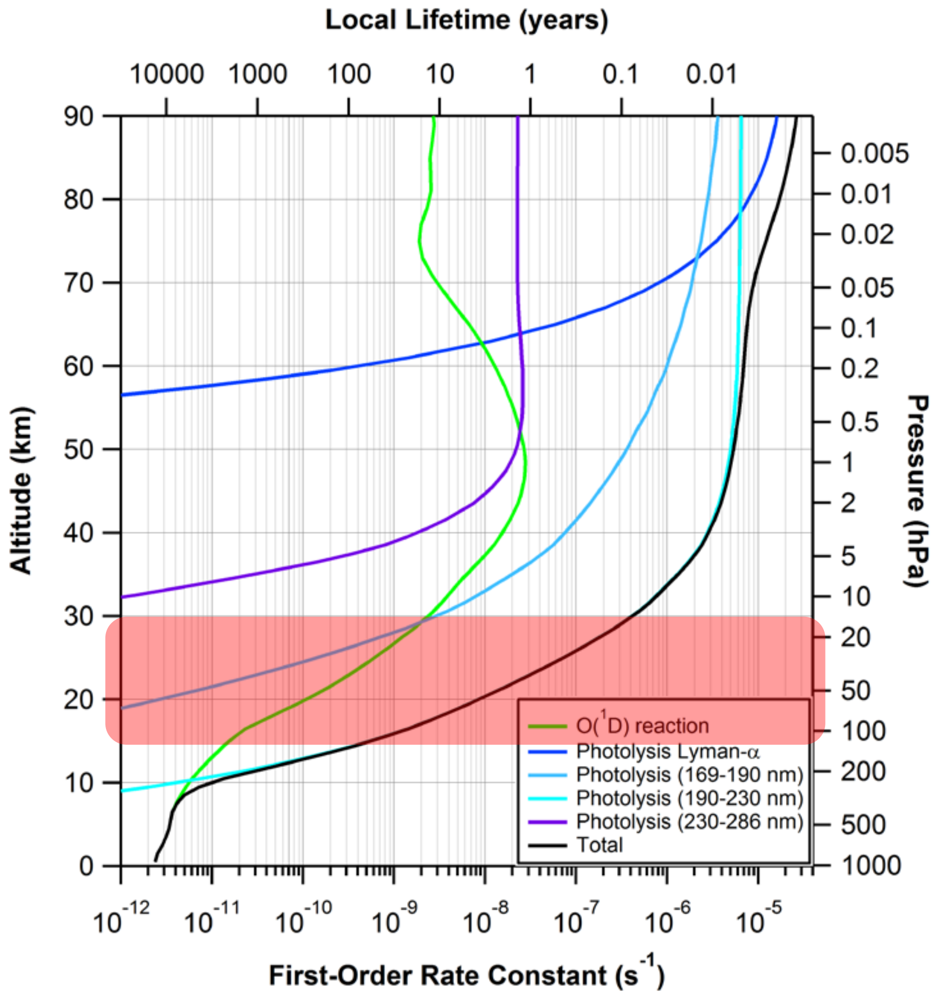
Comparison with literature



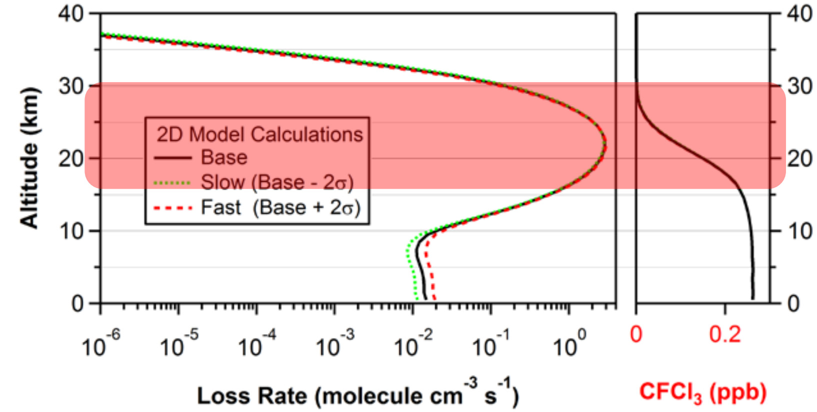
- Both Mérienne and Chou studies are found to be in good agreement
- Some systematic differences at shorter wavelengths

2-D modeling results

Loss processes



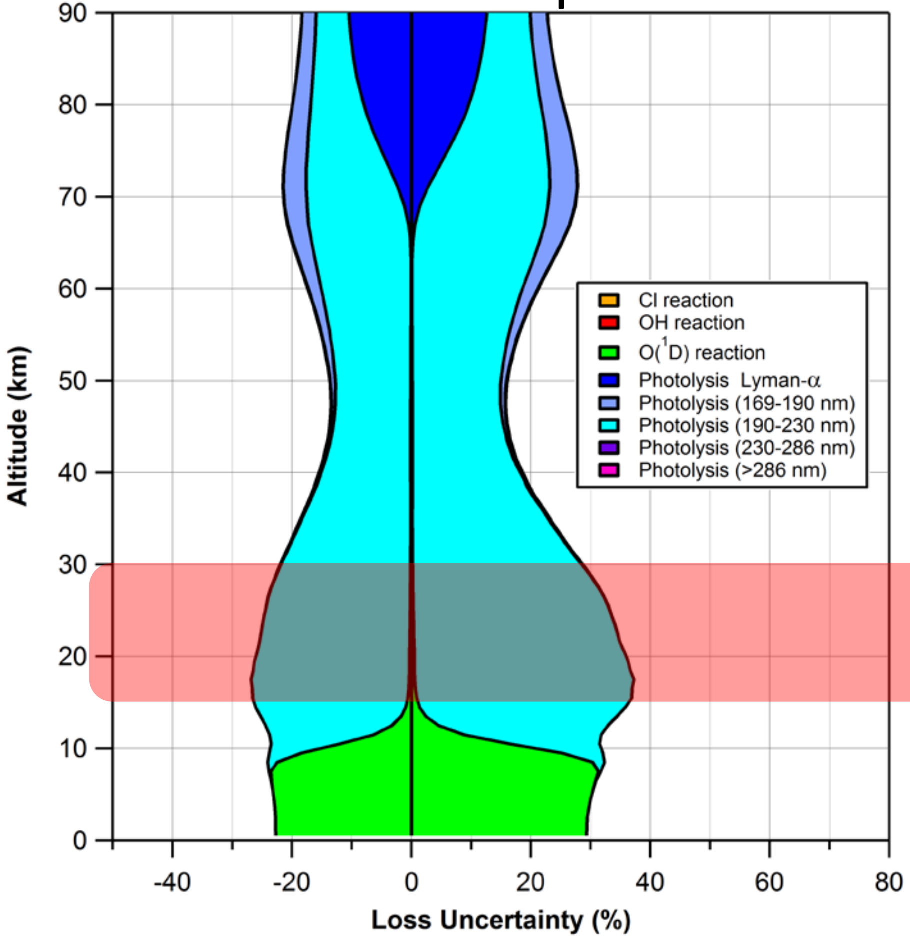
Molecular loss rates



- Critical λ range for atmospheric loss: 190–230 nm
- Most CFC-11 destruction between 15–30 km
- Local lifetime in the stratosphere ~1 year
- Calculated global lifetime: 58.1 years

2-D modeling results

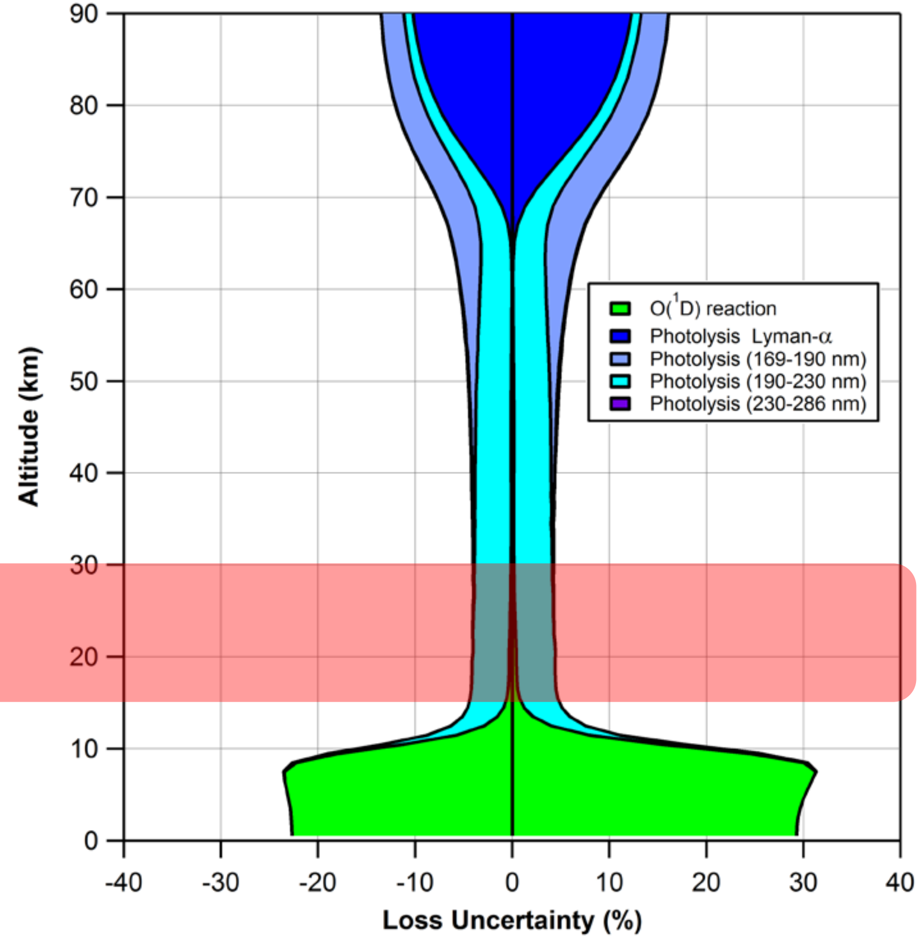
SPARC lifetime report



± 25% → 54.3 – 66.3 year lifetime

Global average lifetime: **60.2 years**

This work



± 4% → 57.4 – 58.8 year lifetime

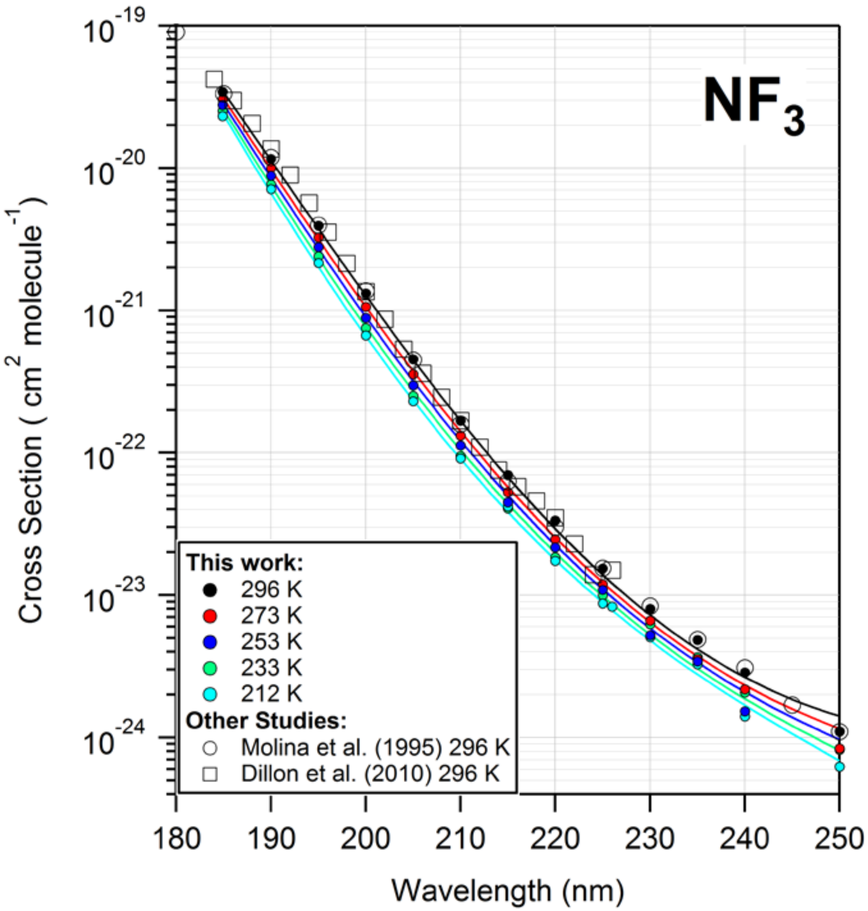
Global average lifetime: **58.1 years**

CFC-11 summary

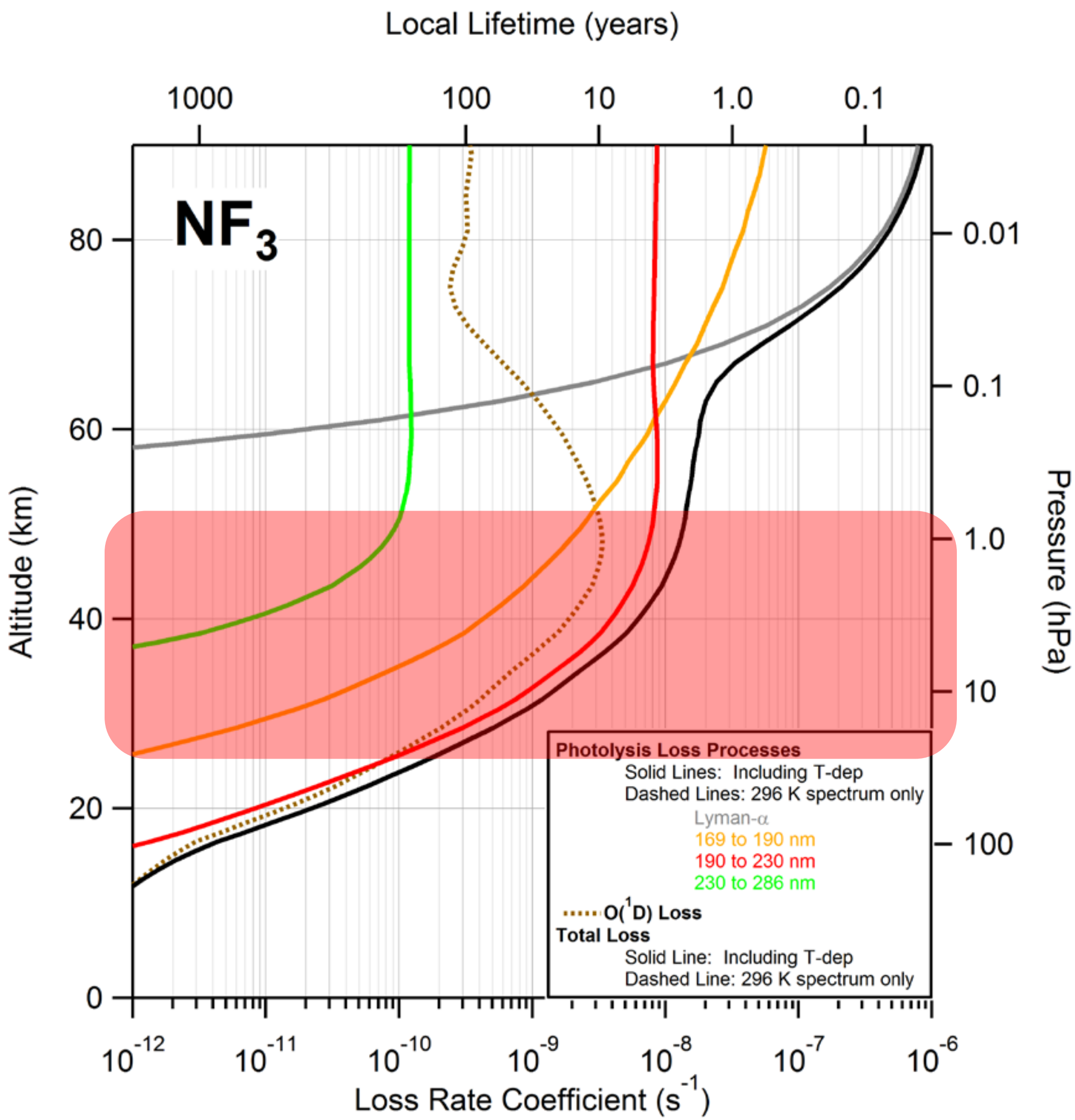
- Data impacts calc. lifetimes from current JPL
- Modeled lifetime decreased from 60.2 (SPARC) to 58.1 years (this work)
- Uncertainty in stratospheric photolysis rate decreased from ~25% to 4%
- Leading to a range in atmospheric lifetimes ±0.7 years (57.4 – 58.8 years)

NF_3

- Persistent greenhouse gas with a high GWP (~500 year lifetime)
- Mixing ratios are increasing in the atmosphere
- Previous studies focused on the room temperature σ (biased model calculated lifetimes)
- NF_3 $\sigma(\lambda, T)$ measured using the same approach as was used for CFC-11

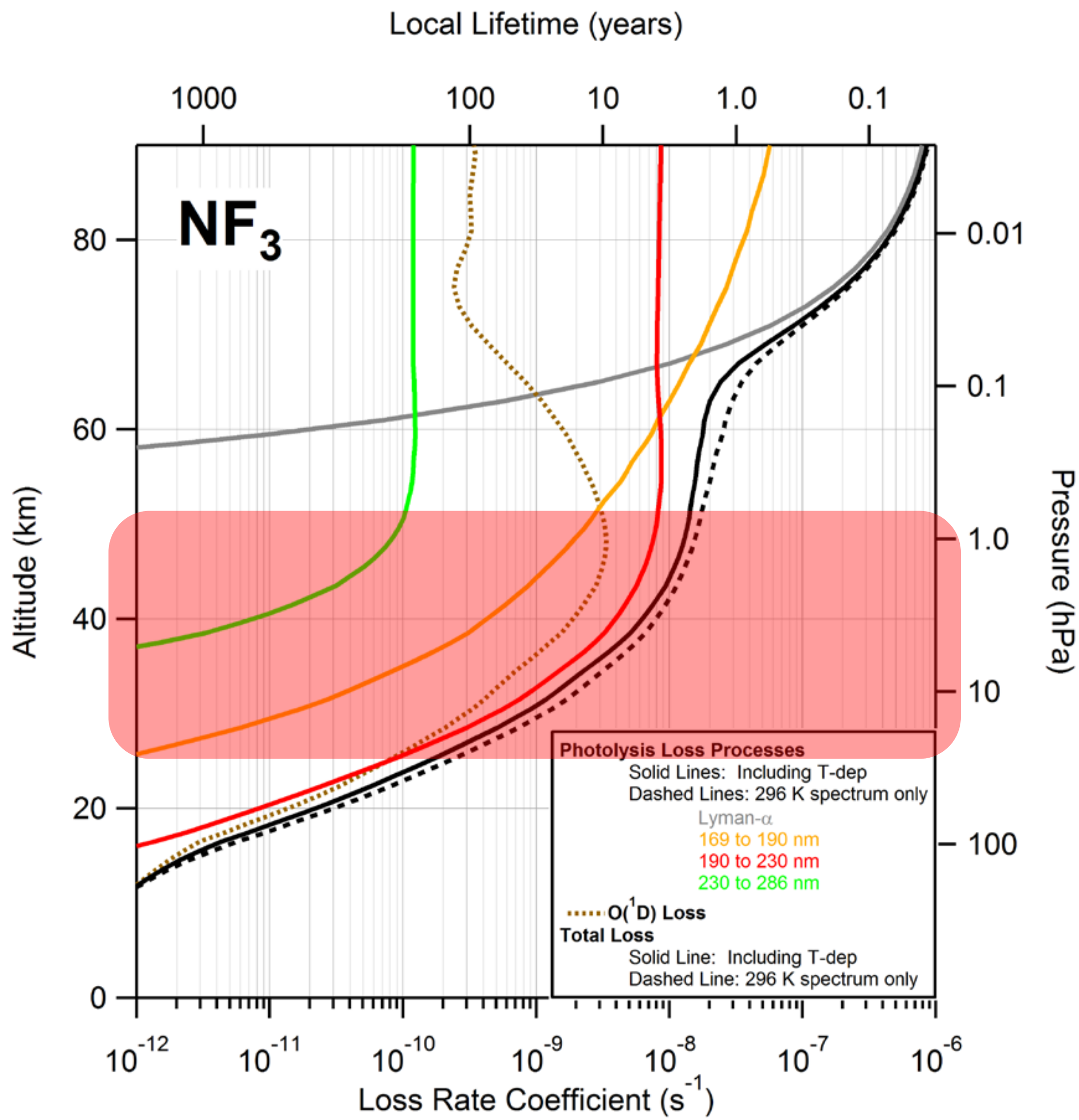


2-D modeling results



- Inclusion of temperature dependence in *σ* is important
- Maximum atmospheric loss is between 25–50 km
- Papadimitriou *et al.* 2013 (GRL)

2-D modeling results



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NF_3 summary

- Inclusion of temperature dependence of the NF_3 UV absorption spectrum, the calculated global lifetime is increased from 484 (without) to 585 (with) years (includes $O(^1D)$ losses 29%)
- NF_3 exhibits a strong temperature dependence to $\sigma(\lambda, T)$, ~45% decrease at 210 nm
- GWP $\rightarrow$ 100 yr time horizon = +1.1% (19,700)

  $\rightarrow$ 500 yr time horizon = +6.5% (17,700)

Any questions?