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)
Absorption cross section measurements

Beer-Lambert Law

\[ A(\lambda) = \sigma(\lambda, T) \times L \times [\text{CFC-11}] \]

T range: 216–296 K, \( \lambda \) range: 190–230 nm

Typical precision: ± 0.5%, accuracy: ± 4% (2\( \sigma \))
Cross section results

- Systematic decrease in $\sigma$ with $T$
- Monotonic decrease in $\sigma$ with $\lambda$
- Manuscript in prep.
Cross section results

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

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

- Critical $\lambda$ range for atmospheric loss: 190–230 nm
- Most CFC-11 destruction between 15–30 km
- Local lifetime in the stratosphere $\sim$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)
**NF₃**

- Persistent greenhouse gas with a high GWP (~500 year lifetime)
- Mixing ratios are increasing in the atmosphere
- Previous studies focused on the room temperature $\sigma$ (biased model calculated lifetimes)
- $\text{NF}_3 \ \sigma(\lambda, T)$ measured using the same approach as was used for CFC-11
2-D modeling results

- Inclusion of temperature dependence in $\sigma$ is important
- Maximum atmospheric loss is between 25–50 km
- Papadimitriou et al. 2013 (GRL)
2-D modeling results

- Inclusion of temperature dependence in $\sigma$ is important
- Maximum atmospheric loss is between 25–50 km
- Papadimitriou et al. 2013 (GRL)
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($^1$D) 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?