Atmospheric Lifetimes of CCl_3F (CFC-11) and NF_3: Temperature Dependent Ultraviolet (UV) Absorption Cross Sections

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Trichlorofluoromethane (CCl_3F, CFC-11) is a major ozone-depleting substance and a potent GreenHouse Gas (GHG). Nitrogen trifluoride (NF_3) is a persistent (long-lived) potent GHG. Both compounds are removed from the atmosphere primarily through UV photolysis in the stratosphere, and to a lesser extent, by reaction with $O(^1D)$. UV absorption cross sections, $\sigma(\lambda, T)$, of CFC-11 and NF_3 have been measured extensively around room temperature in previous studies, but the cross section temperature dependence remains a significant source of uncertainty in model calculated atmospheric lifetimes. The aim of this study was to address this issue through new and accurate measurements of the UV cross sections over the wavelength range 184.95 – 250 nm at temperatures in the range 212 – 296 K. A temperature dependence of the CFC-11 UV spectrum was observed in the wavelength region most relevant to atmospheric photolysis (200 – 220 nm) with a decrease in σ(210 nm, T) of ~20% between 296 and 216 K. For NF_3, the temperature dependence was more pronounced with a decrease in σ(210 nm, T) of ~45% between 296 and 212 K. The present results for CFC-11 indicate that the UV spectrum temperature dependence, currently recommended in the Jet Propulsion Laboratory (JPL) data evaluation for use in model calculations is too great (see Figure). The present data results in a decrease in the 2D model-calculated CFC-11 atmospheric lifetime from 60.2 (SPARC) to 58.1 (this work) years and a significant reduction in the uncertainty of its atmospheric photolysis rate (at stratospherically relevant temperatures the uncertainty is reduced from ~25 to 4%). For NF_3, the present study represents the first report of temperature dependent absorption cross sections. The Goddard Space Flight Center 2D model and a parameterization of $\sigma(\lambda, T)$ developed in this work were used to calculate atmospheric photolysis rates and the global annually averaged lifetime of NF_3. Including the UV absorption spectrum, temperature dependence substantially increases the stratospheric photolysis lifetime from 610 to 762 years and the total global lifetime from 484 to 585 years; the NF_3 global warming potentials on the 20-, 100-, and 500-year time horizons increased <0.3, 1.1, and 6.5% to 13,300, 17,700, and 19,700, respectively.

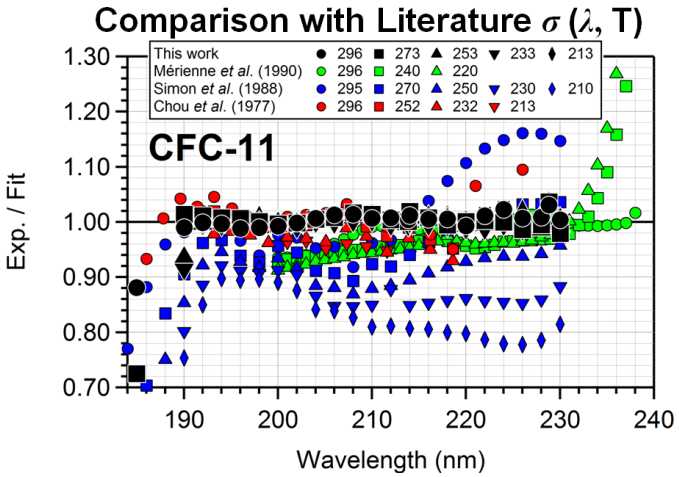

Figure 1. The ratio of experimentally determined CFC-11 UV absorption cross sections to the parameterization from this work. The work of Simon et al. (1988), which is currently recommended in the JPL evaluation, was found to significantly overestimate the temperature dependence of the UV absorption spectrum.