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Chlorine isotope fractionation during photolysis of difluorodichloromethane (CFC-12)

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Difluorochloromethane (CFC-12) is the most important ozone-depleting substance with a global mean tropospheric mixing ratio of about 530 pmol mol^{-1}. It is stable in the troposphere and only broken down in the stratosphere, mainly due to photolysis (≈ 95 %) and the reaction with O(^1D) (≈ 5 %).

In 2010, we reported on the first measurements of the chlorine isotope fractionation of stratospheric CFC-12 using mass spectrometers (Laube et al., Science 329:1167, 2010). We found an increase in the relative isotopic enrichment, $\delta(^{37}\mathrm{Cl})$, with altitude and a tight correlation between ln[1+ $\delta(^{37}\mathrm{Cl})$] and ln(mixing ratio). The derived apparent isotope effect at the tropical sampling location was (-12 ± 2) ‰. We speculated that, similar to stratospheric N_2O and CH_4, the intrinsic photochemical isotope effect could be up to twice this value, due to attenuating effects of mixing and diffusion.

We have now measured the isotope effect during CFC-12 photolysis under realistic temperature and light conditions, using a UV broadband lamp. Surprisingly, the derived photolysis isotope effect of (-12 ± 2) ‰ is identical to the apparent stratospheric isotope effect. The contribution due to the reaction of CFC-12 with O(^1D) to the overall isotope effect is small and in any case, the associated isotope effect is likely to be even smaller.

Therefore, this finding indicates that the photochemical lifetime at the tropical sampling location is much longer than the transport lifetime. N_2O has a similar global mean lifetime to CFC-12 (≈ 100 years) and it would be interesting to compare their apparent isotope effects at the same location (Teresina, Brasil, 5°S). Previous measurements for stratospheric N_2O were at least 17° in latitude away from the equator (Kaiser et al., Atmos. Chem. Phys. 6:3535, 2006).