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# Laboratory Measurements of High Resolution Photoabsorption Cross-Sections of Isotopologues of $SO_2$

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The timing of the oxygenation of the Earth's atmosphere is a central issue in understanding the Earth's paleoclimate. The discovery of mass-independent fractionation (MIF) of sulphur isotopes deposited within Archean and Paleoproterozoic rock samples has given rise to a possible marker, through the transition between MIF in older rock samples ( $>$ 2.4 Gyrs) to mass-dependent fractionation (MDF) in younger samples, for the rise in oxygen concentrations in the Earth's atmosphere [Farquhar,2003]. Laboratory experiments [Farquhar,2001][Pen,2008] suggest isotopic self shielding during the gas phase photolysis as the dominant mechanism for MIF. Self shielding is present for $SO_2$ at wavelengths shorter than 220 nm where it undergoes partial predissociation. The UV absorption of $SO_2$ is dominated by the $\tilde{C}\ ^1B_2$ - $\tilde{X}\ ^1A_1$ electronic system which consists of strong vibrational bands extending from 170 - 230 nm. In an atmosphere consisting of low $O_2$ and $O_3$ concentrations, such as that predicted for the early Earth, UV radiation would penetrate deep into the ancient Earth atmosphere in the 180 - 220 nm range driving the photolysis of $SO_2$.

We have conducted the first ever high resolution measurements of the photo absorption cross sections of several isotopologues of $SO_2$, namely $^{32}SO_2$, $^{33}SO_2$, $^{34}SO_2$ and $^{36}SO_2$. The cross sections are being measured at Imperial College at initial resolutions of 1.0 $cm^{-1}$, and place special emphasis on the high relative accuracy of the measurements ($<$ 3%), vital for accurately modelling atmospheric processes. Further measurements at resolutions of $<$ 0.5 $cm^{-1}$ are scheduled for inclusion in photochemical models of the early Earth's atmosphere. The models will be used to more reliably identify the processes responsible for the sulphur isotope ratios found in ancient rock samples [Lyons, 2007]. 1.0 $cm^{-1}$ resolution measurements of the four isotopologues of $SO_2$ will be presented in addition to preliminary $<$ 0.5 $cm^{-1}$ photo absorption cross section measurements.

References:
Farquhar J & Wing BA, Earth and Planetary Science Letters, 213:1-13, 2003.
Farquhar J, Savarino J, Airieau S & Thiemens MH, JGR, 106:32829, 2001.
Pen A & Clayton RN, Geochimica et Cosmochimica Acta Supplement, 72:734, 2008.
Lyons JR, GRL 34:L22811, 2007.