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The atmospheric chemistry of sulphuryl fluoride, SO_2F_2

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Abstract. The atmospheric chemistry of sulphuryl fluoride, SO_2F_2, was investigated in a series of laboratory studies. A competitive rate method, using pulsed laser photolysis (PLP) to generate $O(^1D)$ coupled to detection of OH by laser induced fluorescence (LIF), was used to determine the overall rate coefficient for the reaction $O(^1D) + SO_2F_2 \rightarrow$ products (R1) of k_1 (220–300 K) = (1.3 ± 0.2) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Monitoring the $O(^3P)$ product (R1a) enabled the contribution (α) of the physical quenching process (in which SO_2F_2 is not consumed) to be determined as α (225–296 K)=(0.55 ± 0.04). Separate, relative rate measurements at 298 K provided a rate coefficient for reactive loss of $O(^1D)$, k_{1b}, of (5.8 ± 0.8) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} in good agreement with the value calculated from (1−α) × k_1=(5.9 ± 1.0) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Upper limits for the rate coefficients for reaction of SO_2F_2 with OH (R2, using PLP-LIF), and with O_3 (R3, static reactor) were determined as k_2 (294 K)<1 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} and k_3 (294 K)<1 × 10^{-23} cm^3 $molecule^{-1}$ s^{-1}. In experiments using the wetted-wall flow tube technique, no loss of SO_2F_2 onto aqueous surfaces was observed, allowing an upper limit for the uptake coefficient of γ(pH 2–12)<1 × 10^{-7} to be determined. These results indicate that SO_2F_2 has no significant loss processes in the troposphere, and a very long stratospheric lifetime. Integrated band intensities for SO_2F_2 infrared absorption features between 6 and 19 μm were obtained, and indicate a significant global warming potential for this molecule. In the course of this work, ambient temperature rate coefficients for the reactions $O(^1D)$ with several important atmospheric species were determined. The results (in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, $k_{(O^1D + N_2)}$=(0.33 ± 0.06); $k_{(O^1D + N_2O)}$=(1.47 ± 0.2) and $k_{(O^1D + H_2O)}$=(1.94 ± 0.5) were in good agreement with other recent determinations.

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