THE UV-VIS SPECTRUM OF ClSO RADICAL FROM THE PHOTOLYSIS of THIONYL CHLORIDE AT 248 nm

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Sulfinyl radicals (R-SO) play a critical role in various fields, from biology to atmospheric chemistry, such as aerosol formation in which chlorine atoms was proposed to potentially catalyze the oxidation of sulfur species in Venus' atmosphere. In this study, we performed a Pulsed Laser Photolysis experiment to detect ClSO from Cl_2SO photolysis at 248 nm in a gas flow reactor using time-resolved UV-Vis transient absorption spectroscopy. A strong absorption near 303 nm and a weak one around 385 nm, with a vibrational progression of about 658 $\mathrm{cm}^{-1}$and 227 cm^{-1}, was recorded. Ab initio calculations at the EOMEE-CCSD/ano-pVQZ level revealed that the strong and weak band corresponds to the 1^2A" $\leftarrow$ X^2A" and the 2^2A' $\leftarrow$ X^2A" transitions. Further analysis showed that there might be a conical intersection between the 1^2A' and 2^2A' state near the ground-state geometry, which poses a challenge for further theoretical work. Furthermore, we constructed a molecular orbital diagram analysis to understand the electronic structure of the sulfinyl functional group. The analysis suggested that sulfinyl radicals tend to form chemical bonds with other radicals. As an example, a fast recombination rate coefficient of Cl + ClSO $\rightarrow$ Cl_2SO reaction was investigated to be $k_{Cl+ClSO}$ = (1.48 $\pm$ 0.42)$\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 292 K and 90 Torr utilizing the strong absorption band. These results suggest that the Cl-containing SO_x species might act as radical reservoirs in sulfur oxide-rich environments such as Venus' atmosphere.

Refernce:

1.Wen Chao, Gregory H. Jones, Mitchio Okumura, Carl J. Percival, and Frank A. F. Winiberg*, Spectroscopic and Kinetic Studies of the ClSO Radical from Cl_2SO Photolysis, J. Am. Chem. Soc, 2022, 144, 44, 20323-20331. DOI: 10.1021/jacs.2c07912