

Probing the Molecular Dissociation Channel of Oxalyl Chloride Photodissociation at 248 nm by Cavity Ring-Down Spectroscopy

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Cavity ring-down spectroscopy (CRDS) is an ultra-sensitive absorption spectroscopy technique. In CRDS, an optical cavity and a pair of high-reflectivity mirrors are used, and a pulse of laser light is then directed into the cavity. By measuring the decay rate of the laser light leaking out from the cavity, it is possible to obtain the absorbance and absorption spectrum. In this work, we demonstrate that molecular chlorine (Cl_2) is formed following photolysis of oxalyl chloride at 248 nm. First, the absorption spectrum of Cl_2 is obtained by measuring chlorine gas by CRDS. Comparing the spectrum of Cl_2 with the photolysis spectrum of oxalyl chloride, we confirm that molecular chlorine is formed. Pressure-dependence experiments show that Cl_2 formation is first-order with respect to oxalyl chloride. Energy-dependence experiments show that the reaction proceeds via a single-photon pathway. Vibrational analysis shows that the chlorine molecules formed are vibrationally hot, with a vibrational branching ratio of 1: 0.19: 0.012, corresponding to a vibrational temperature of 372 ± 29 K assuming room rotational temperature. The quantum yield of molecular chlorine is determined by the reference method to be 0.8 ± 0.4 , in which some secondary reactions may be present.

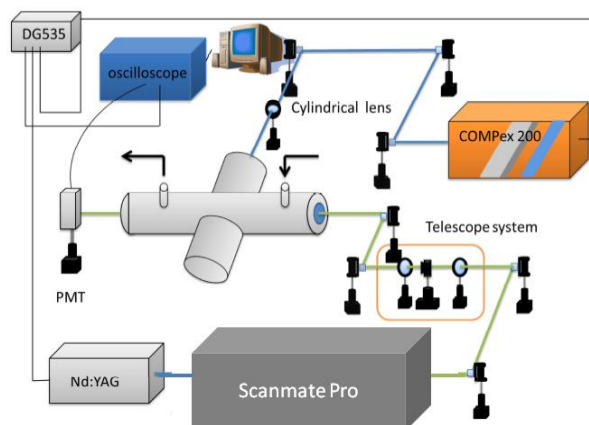


Figure 1: Experimental setup of CRDS.

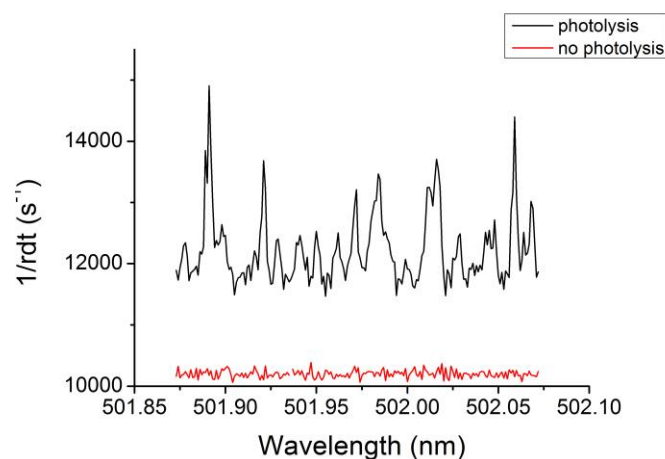


Figure 2: Photolysis spectrum of $(\text{COCl})_2$.

References

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