

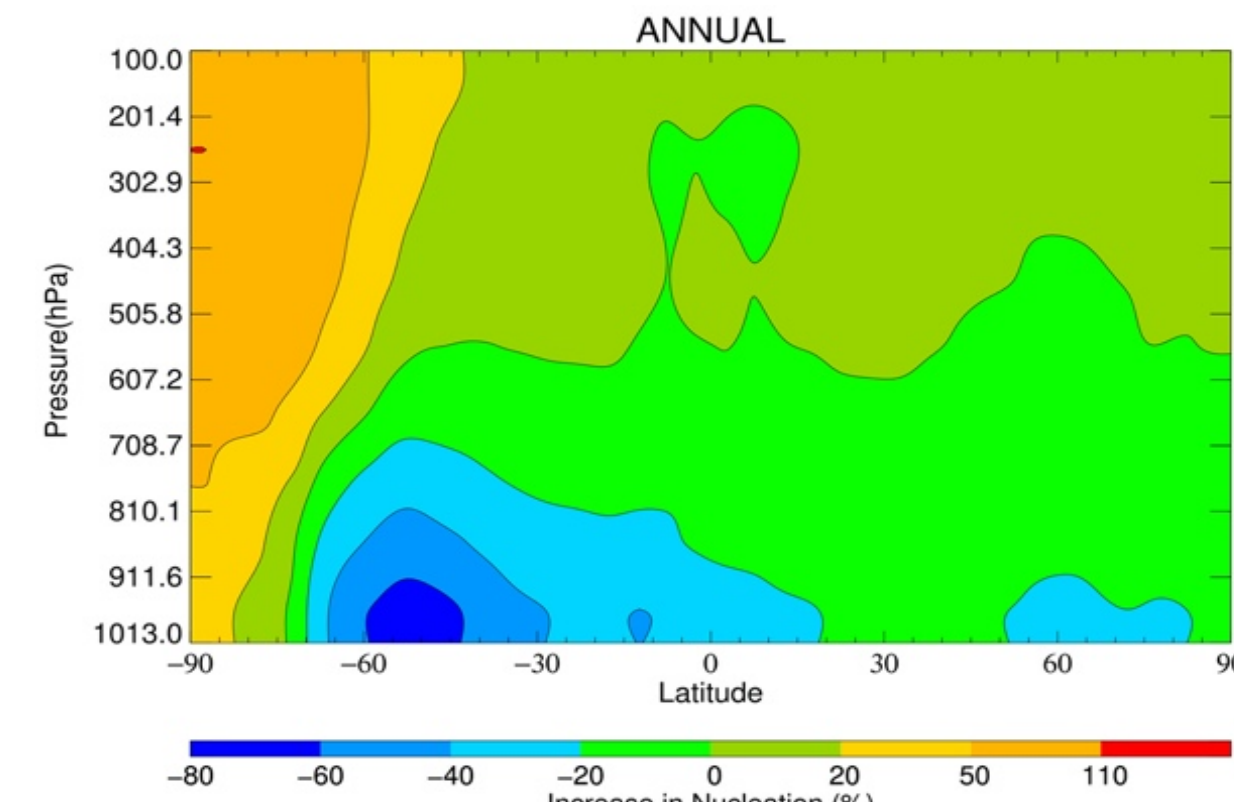
# Laboratory Measurements of Dimethyl Sulfide Oxidation Products

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## Background

- Dimethyl sulfide (DMS) is the largest contributor of natural sulfur to the atmosphere.
- The oxidation of DMS results in the formation of sulfate aerosols that can affect Earth's radiative balance by scattering solar radiation and serving as cloud condensation nuclei.
- Hydroperoxymethyl thioformate (HPMTF), is a newly identified major oxidation product of DMS and could potentially have a major impact on the atmospheric budget of sulfur.
- In a recent study modeling study, we have shown that accounting for HPMTF chemistry results in a significant decrease in boundary layer levels of sulfur dioxide (a known pollutant) and sulfuric acid (precursor for acid rain and aerosol formation) and increases in sulfate aerosol in the upper troposphere, with an associated 110% increase in sulfate aerosol nucleation rate.



The percentage change in the rate of nucleation rate (J) of sulfate aerosol after adding the chemistry of HPMTF in a global model

- However, the budget of HPMTF is poorly constrained as a consequence of a lack of kinetic data on its formation and fate in the atmosphere.

## Objectives

- Record and analyze the first ever formation kinetics data for Hydroperoxymethyl thioformate (HPMTF) at room-temperature,
- Develop a chemical kinetics simulation of the reaction system to facilitate the analysis of the experimental data.

## Approach

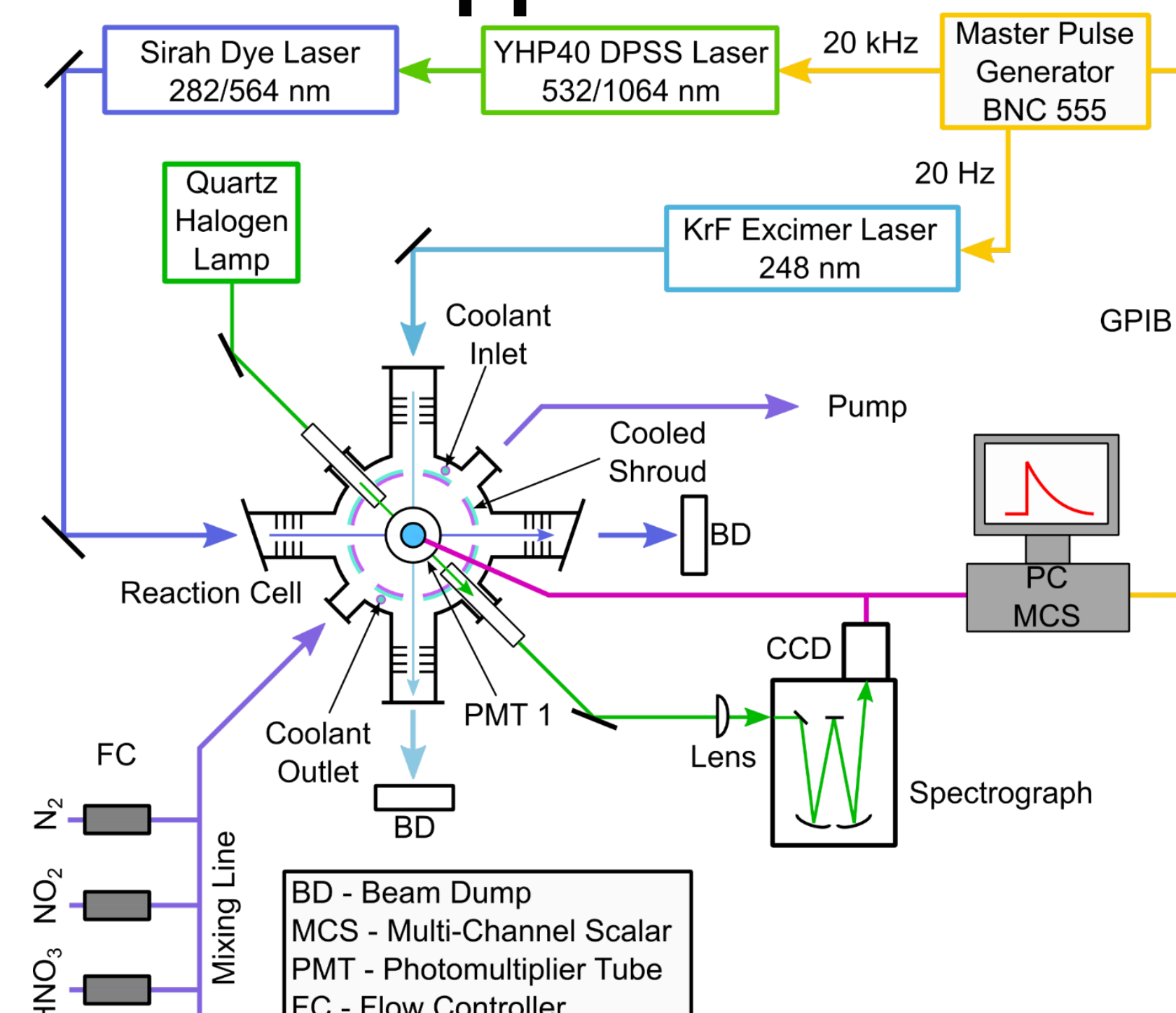


Fig 1. Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) apparatus

- The HPMTF formation rate coefficient was studied using the JPL-based Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) apparatus by examining the hydroxyl radical (OH) co-product.
- The PLP-LIF is a stainless-steel apparatus where light from probe source and photolysis laser beams are crossed in the center of the gas flow cell and fluorescence from excited OH is collected onto a photomultiplier tube. Time dependent signals were interfaced to a multichannel scalar/photon counting system for analysis as a function of time.
- OH is the co-product of HPMTF in this system, measuring the rate of OH production allowed us to estimate the rate of HPMTF production from this oxidation mechanism.

The OH was formed in the following reaction scheme:

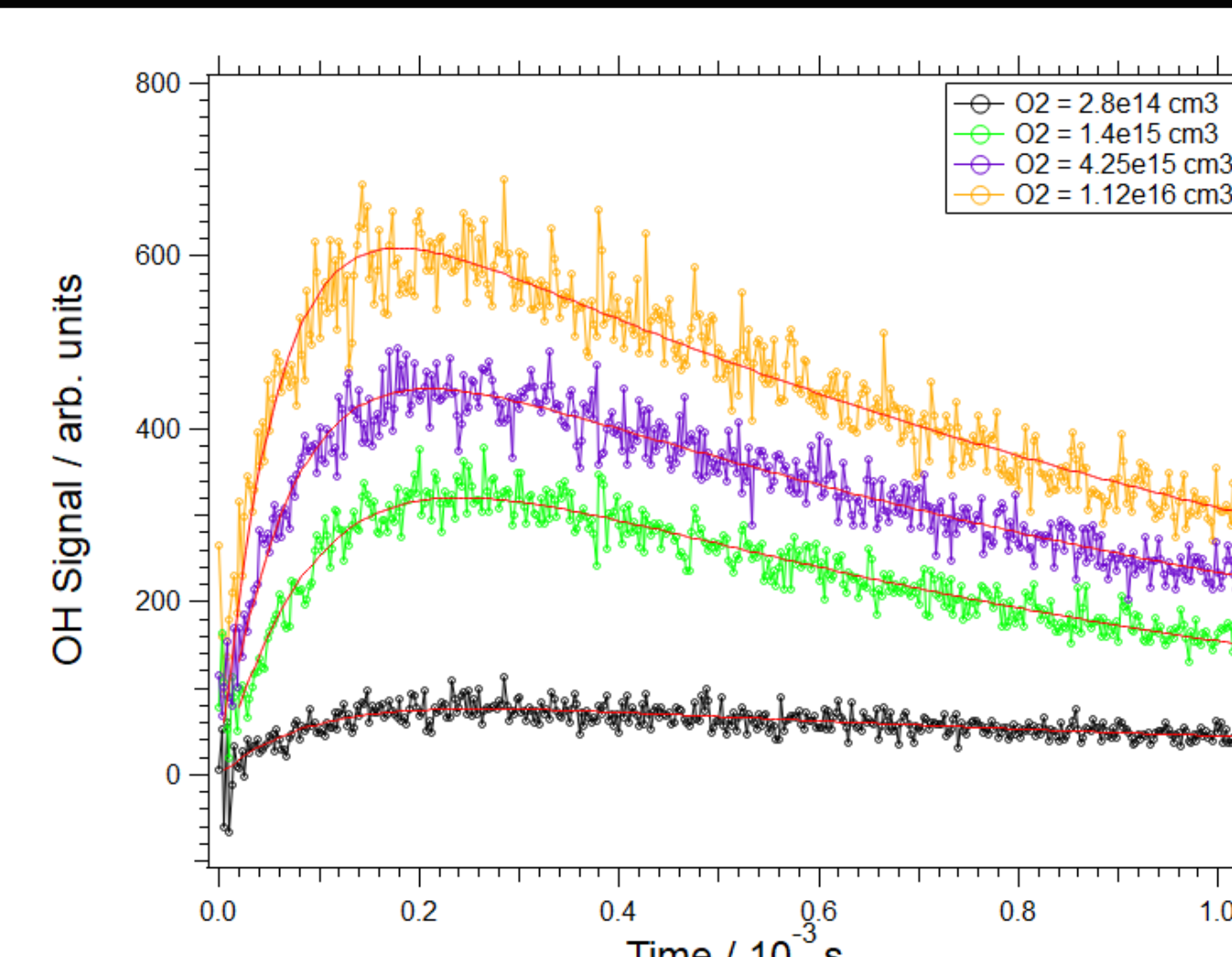
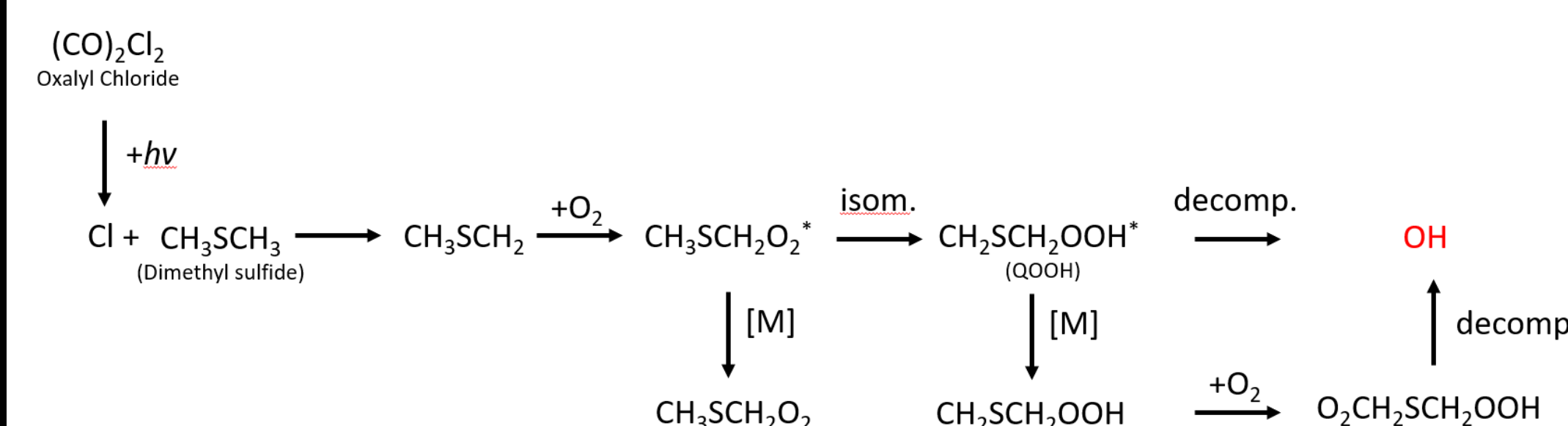


Fig 2. OH Signal as a function of time observed from the Cl+DMS+O<sub>2</sub> reaction system. Varying O<sub>2</sub> concentration allows the determination of rate coefficients. Reaction conditions: [DMS] = 3.5 × 10<sup>14</sup> cm<sup>-3</sup>, pressure = 50 Torr N<sub>2</sub>.

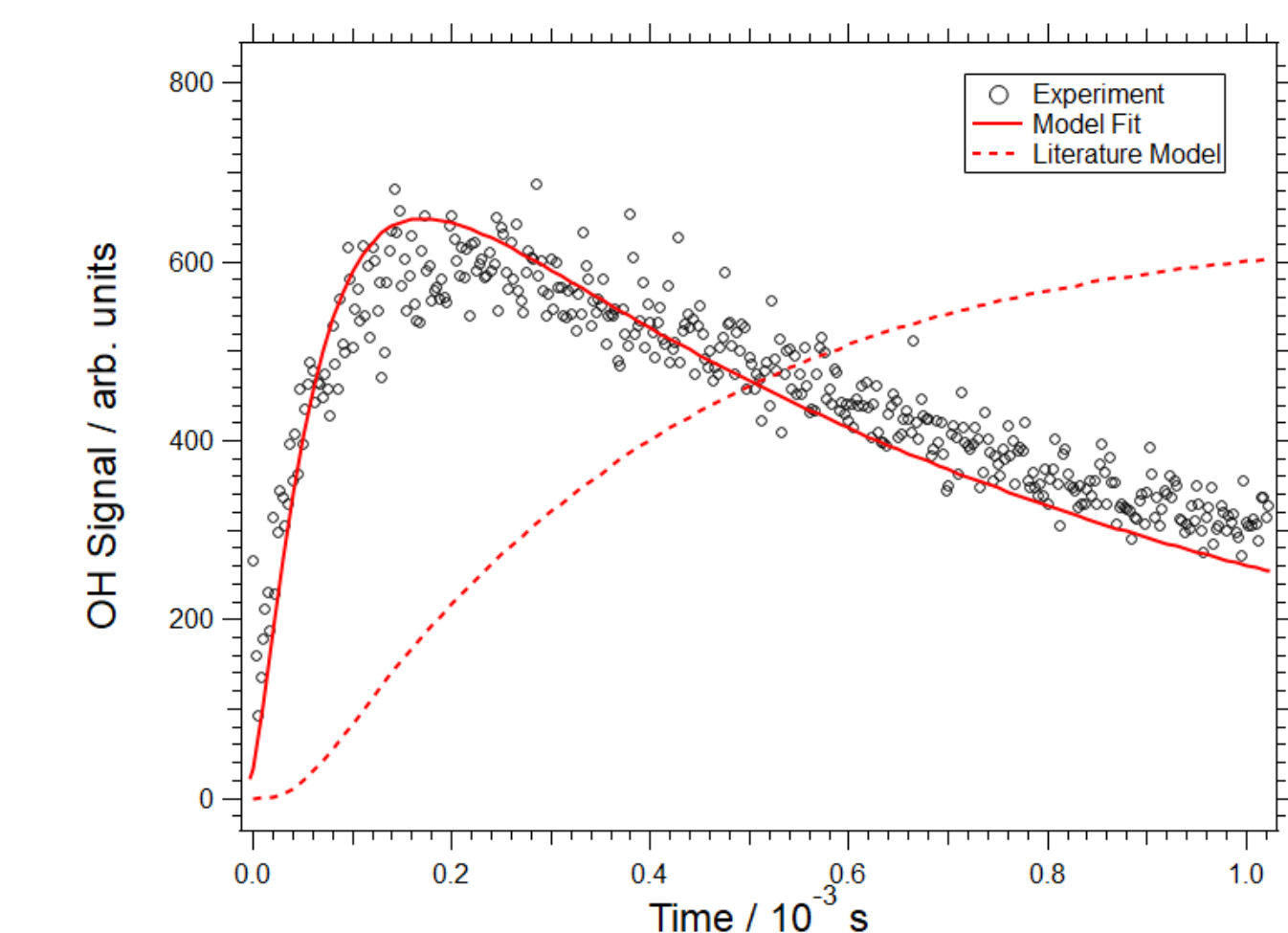


Fig 3. OH Signal as a function of time observed from the Cl+DMS+O<sub>2</sub> reaction system. Chemical simulations of OH temporal profile based on current literature rate coefficients (dashed line) and model adjusted to fit observations (solid line). Reaction conditions: [DMS] = 3.5 × 10<sup>14</sup> cm<sup>-3</sup>, [O<sub>2</sub>] = 1.1 × 10<sup>16</sup> cm<sup>-3</sup>, pressure = 50 Torr N<sub>2</sub>.

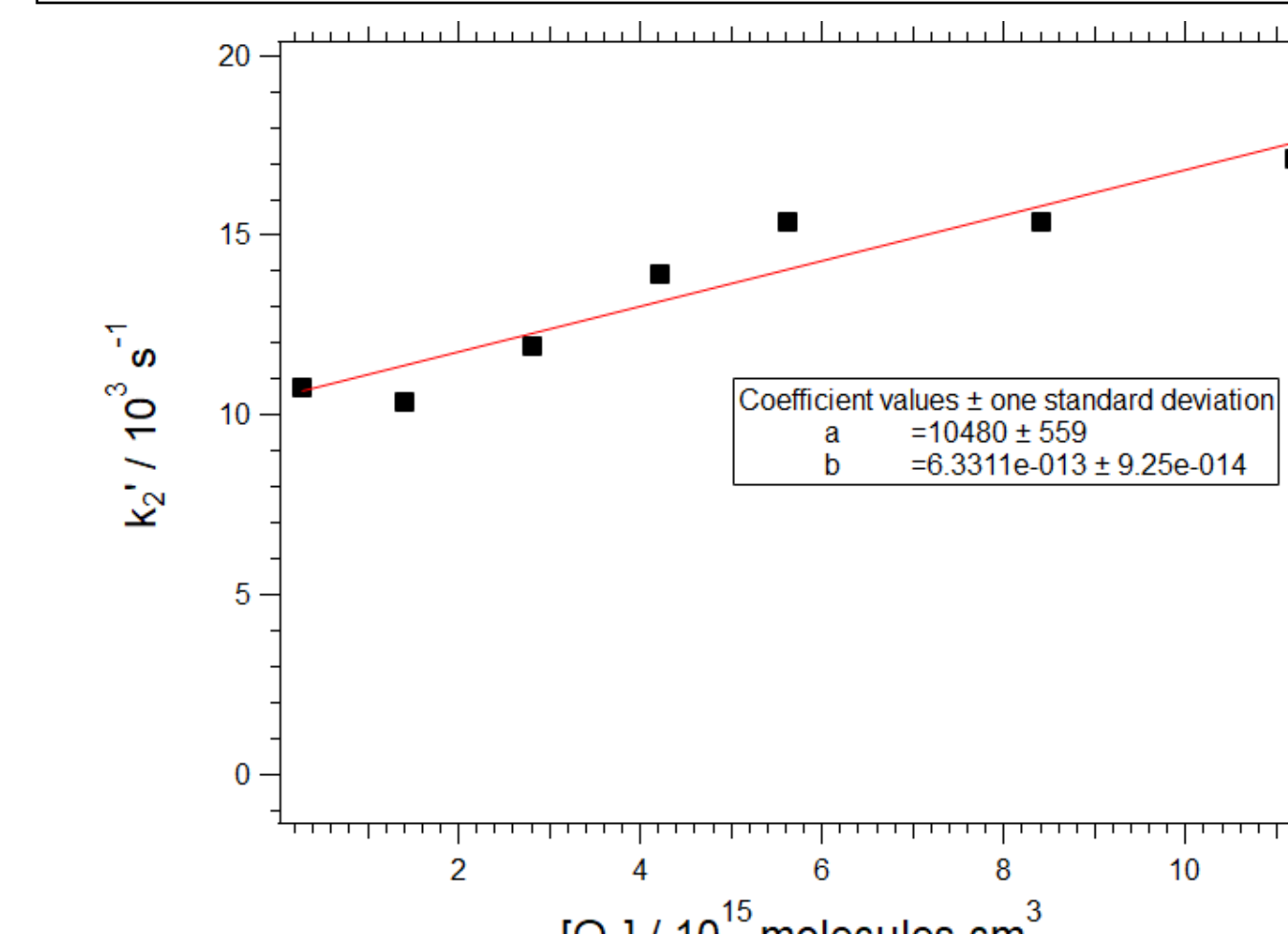


Fig 4. Bimolecular plot of  $K_2$  versus  $[\text{O}_2]$ , derived from fitting OH temporal profiles at 50 Torr N<sub>2</sub> total pressure. Observed rate coefficient is ~10x slower than current literature value ( $5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).

## Results

- Figure 2 shows a typical plot of OH fluorescence intensity as a function of time. As far as we are aware, this is the first time OH production has been observed from the oxidation of DMS.
- A comprehensive chemical kinetics simulation of the reaction system was developed, containing 13 chemical reactions.
- As OH is the co-product of HPMTF in this system, measuring the rate of OH production allowed us to estimate the rate of HPMTF production from this oxidation mechanism.
- The current chemical kinetic rate values used for the formation of HPMTF are derived from a theoretical research paper [1], and the simulated traces using these values can be seen in Figure 3 (dashed trace).
  - The chemical simulation was unable to accurately describe the OH signals observed.
  - We hypothesize that this is due to an over estimation of the stability of a reactive intermediate (QOOH, figure 1) involved in reaction R4, which could decompose under ambient conditions to yield OH.
  - Including this missing OH production dramatically improved the model/measurement agreement when included, as can be seen in the solid line trace in Figure 3.
- By changing oxygen (O<sub>2</sub>) concentrations in the system we were able to measure the rate coefficient,  $k_2$ , for reaction R2, based on the rate of OH signal rise as a function of O<sub>2</sub>.
- Figure 2 shows the temporal profiles of OH for 3 different O<sub>2</sub> concentrations [O<sub>2</sub>] with fitted profiles.
- Figure 4 shows the fitted rate as a function of [O<sub>2</sub>]. We measure the rate coefficient to be ~10x slower than that previously reported in the literature.
- Additionally, we have collected preliminary data on the OH yield (and therefore HPMTF yield) by studying the reaction of DMS with OH radicals (which is more representative of the oxidation mechanism in Earth's atmosphere). We estimate the OH yield at ~15% - the first measurement of the OH yield from this reaction.

[1] Runrun Wu, Sainan Wang, and Liming Wang, "New Mechanism for the Atmospheric Oxidation of Dimethyl Sulfide. The Importance of Intramolecular Hydrogen Shift in a CH<sub>3</sub>SCH<sub>2</sub>O Radical," The Journal of Physical Chemistry A, 119 (1), 2015, 112-117.

## Significance/Benefits to JPL and NASA

Research conducted as part of this Spontaneous Concept R&TD have facilitated the discovery of experimental conditions and provided preliminary results for expansion of the research into DMS auto-oxidation at different temperatures and pressures, providing HPMTF yields and formation rate coefficients over a range of conditions important for Earth's troposphere. The expansion of this research will serve as the basis for a peer-reviewed publication and form part of a proposal for the ROSES solicitation for Atmospheric Composition: Laboratory Studies.

Ultimately the results of this research will support the Tropospheric Composition and Aerosol and Clouds programs for Earth Science at JPL and will be incorporated into the NASA Data Evaluation- the standard reference source for critically evaluated rate constants, used in virtually every atmospheric chemical-transport model. These models are used in the analysis of atmospheric composition data from all past and present NASA suborbital missions and satellite instruments and missions including TOMS, UARS, TES, OMI, MLS, MOPITT, AIRS, MIRS, DISCOVER-AQ, and future missions such as TEMPO, MAIA and GEO-CARB.