High-resolution measurements of the simplest Criegee Intermediate (CH$_2$OO) with mid-infrared absorption spectroscopy

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1. Introduction

Criegee intermediates are energy-rich carbonyl oxides with two free radical centres which act independently of each other (**Figure.1**). More than 60 years ago, Criegee intermediate was first postulated by Rudolf Criegee [1]. Cycloaddition of ozone to the C=C double bond of a alkene forms a cyclic trioxolane intermediate, and the large exothermicity of this reaction leads to a rapid cleavage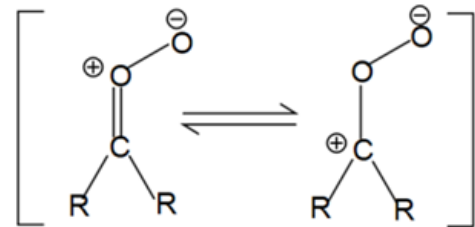 of the C−C bond and one O−O bond to form a carbonyl compound and a carbonyl oxide, R$_1$R$_2$COO, which is known as a Criegee intermediate.

Figure.1 Criegee intermediate

Beside the OH radical, O$_3$, the NO$_3$ radical, and Cl atoms, Criegee intermediate was recognized as another oxidant, due to its rich reactivity in the atmosphere (**Figure.2**).
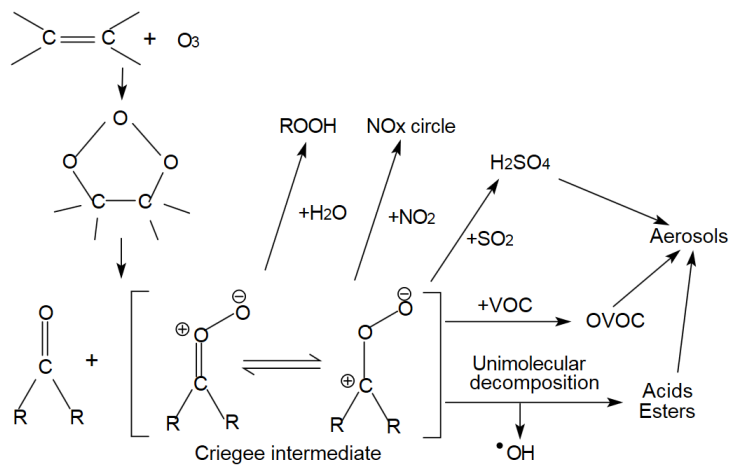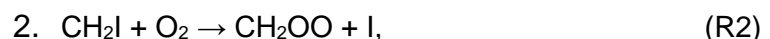
Criegee intermediate has been eluding from direct

Figure.2 The reactivity of Criegee intermediate in the atmosphere

observation for decades, until a breakthrough was made by Welz et al [2], the simplest Criegee intermediate, CH$_2$OO produced with processes：

$$1.\ \ CH_2I_2 + h\nu \rightarrow CH_2I + I \qquad\qquad (R1)$$
$$2.\ \ CH_2I + O_2 \rightarrow CH_2OO + I, \qquad\qquad (R2)$$

succesfully, which means the direct measurements of Criegee intermediate had become possible in laboratories.

2. Research purpose

The purpose of this study is to establish measuring the absorption spectra of CH_2OO in the range of 1273 cm^{-1} to 1278 cm^{-1} and to study the kinetics of the CH_2OO. Even though, the absorption spectra of CH_2OO have been observed with a FTIR [3], the linewidth is no less than 0.1 cm^{-1} if an absorption spectrum was taken with a FTIR, which is not sufficient in observation of individual absorption lines of CH_2OO. Compared with FTIR, our device could take a spectrum at higher resolution linewidth 0.0005 cm^{-1}, and the absorption spectrum measured with our device, was able to show every absorption lines individually, which is more precise and ideal than the FTIR in kinetic study of CH_2OO.

3. Simulation

The simulated absorption spectra of CH_2OO were carried out with a PGOPHER [4] program. Positions of the IR absorption lines of CH_2OO were determined by vibrational and rotational transitions.

Vibrational transition: $v = 0$(ground) $\rightarrow$ $v_4 = 1$(excited, $v_0 = 1285.9$ cm^{-1}).

Rotational transitions are described with three rotational constants A, B, and C of the both state. Ground state, $A'' = 2.59355$ cm^{-1}, $B'' = 0.41580$ cm^{-1}, and $C'' = 0.35762$ cm^{-1} [5]. Excited state, $A' = 2.59365$ cm^{-1}, $B' = 0.41495$ cm^{-1}, $C' = 0.35806$ cm^{-1} [6].

Gaussian distribution halfwidth $\gamma_D = 0.0017$ cm^{-1}, Lorentz distribution halfwidth $\gamma_L = 0.01$ cm^{-1}.

Centrifugal distortion constants, $\Delta_J = 4.54271676 \times 10^{-7}$, $\Delta_{JK} = -1.84605222 \times 10^{-6}$, $\Delta_K = 2.11661213 \times 10^{-4}$, $\delta_J = 6.97966080 \times 10^{-8}$, $\delta_K = 3.23308015 \times 10^{-6}$ of the ground ($v = 0$) state, and $\Delta_J = 4.55845583 \times 10^{-7}$, $\Delta_{JK} = -1.79144386 \times 10^{-6}$, $\Delta_K = 2.32871940 \times 10^{-4}$, $\delta_J = 6.80608000 \times 10^{-8}$, $\delta_K = 3.2429863 \times 10^{-6}$ of the excited($v_4 = 1$) state were used in the spectral simulation.

4. Experiment

The apparatus of this experiment was set up as in **Figure.3**. We used a CH_2I_2-O_2 photolysis technique in our experiment. A mixture of CH_2I_2/N_2/O_2 (1/20/250) flowed into the cell with
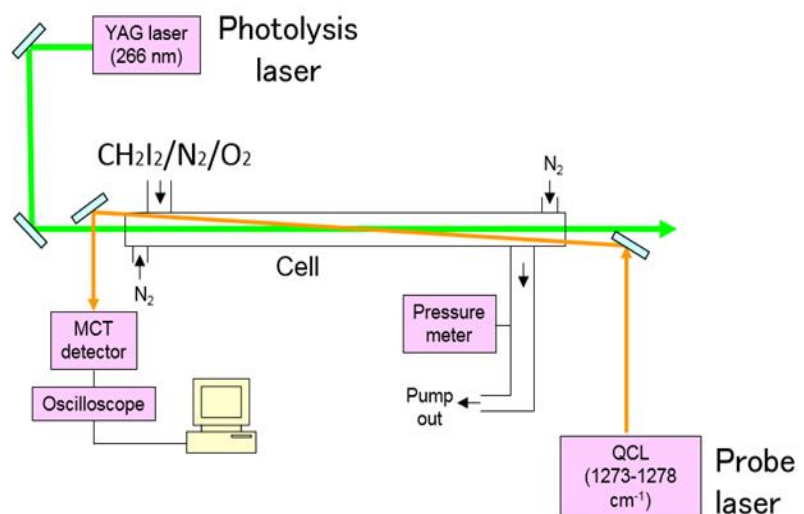

Figure.3 Experiment apparatus

purge gas (N₂) injected in both sides in order to keep lens mounted on both sides clean. A fourth harmonics of YAG laser (λ = 266 nm), decomposed CH_2I_2 into CH_2I and I. CH_2I would react with O_2 immediately, with CH_2OO produced. Opposite to the direction of YAG laser beam, rays of light of a QCL (quantum cascade laser, wavenumber 1273-1278 cm⁻¹) went through the cell, then directed into a MCT detector. The QCL was used to detect the presence of CH_2OO and the wavenumber of the light emitted by the QCL could be adjusted by changing the current and temperature. The temperature and the Pressure inside the cell are T = 298 K and P = 45 Torr.

5. Results and discussion

The absorption lines of CH_2OO were observed successfully compared with a simulated absorption spectrum in **Figure.4**(c). The detection limitation in our experiment for the concentration of CH_2OO was estimated to be 2×10^{12} molecule cm⁻³. Some modification had been made in simulation results with Centrifugal distortion constants inputted, for example, the orientation of the second peak, and small absorption lines appeared in (b), which consist with the situations in (c). A variation Δ = 0.15 cm⁻¹ was noticed in the QCL's operation, which might lead to the misalignment between results of the simulation and the experiment.
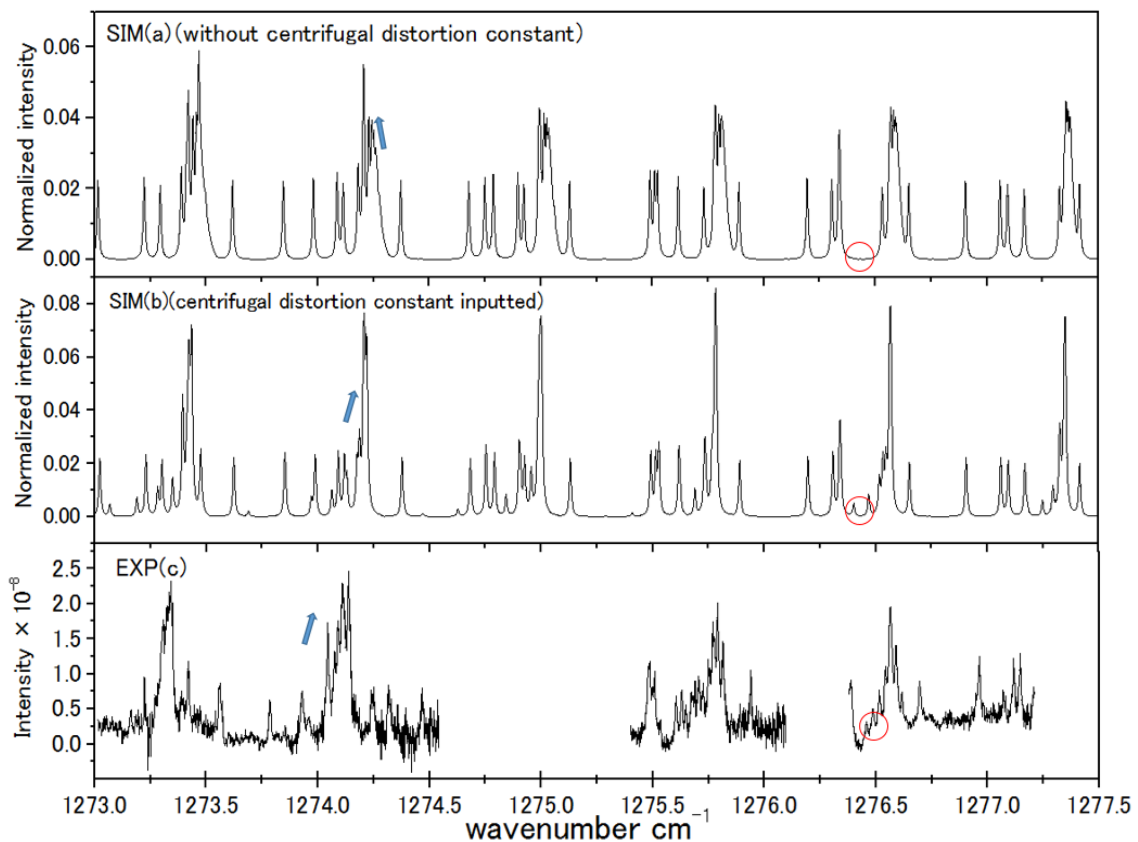

Figure.4 Experiment results compared with a simulated spectrum of CH_2O

6. The rate coefficient for the reaction of CH_2OO with SO_2

The reaction of Criegee intermediate with SO_2 leads to the formation of H_2SO_4 in the atmosphere, triggering secondary aerosol formation. The rate coefficient for the reaction of Criegee intermediate with SO_2 varies according to direct and indirect measurements. We prefer the direct observation in the reaction of CH_2OO with SO_2, for the reason that the rate of CIs generated from the reaction of alkene with O_3 is very slow, and the reaction of SO_2 with other oxidants is complicated. Singals of CH_2OO(**Figure.5**) were recorded with the concentration of SO_2 incresed gradually inside the cell and the rate coefficient for the reaction of CH_2OO with SO_2 was fitted to be 4.16×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (**Figure.6**)in this experiment, which was reported to be 3.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1} in Welz et al's research[2].
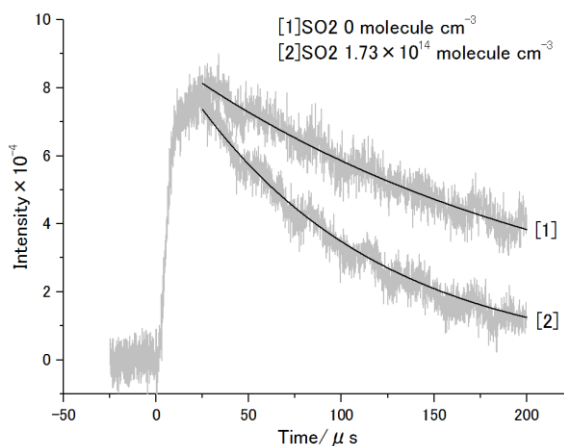

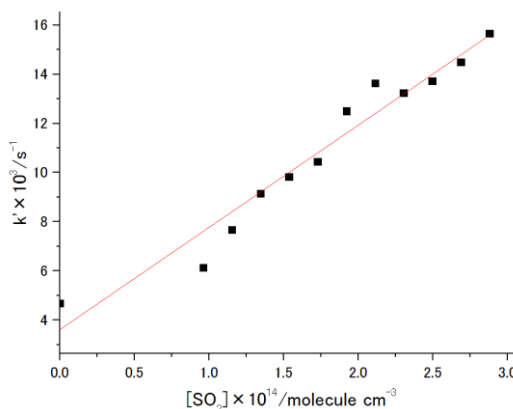Figure.5 Time profile of CH_2OO

Figure.6 Linear fit to CH_2OO+SO_2 data, where the slope is the rate coefficient for CH_2OO+SO_2

7. Conclusion and future plan

The absorption lines of CH_2OO has been observed successfully, and the rate coefficient for the reaction of CH_2OO with SO_2 was measured with this new high-resolution approach.

Research on kinetics of CH_2OO with this high-resolution new method will be made further, for example, the reaction of CH_2OO with water vapor, which determines the fate of Criegee intermediate in the atmosphere.

References
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