The UV Absorption Spectrum of the Simplest Criegee Intermediate CH_2OO

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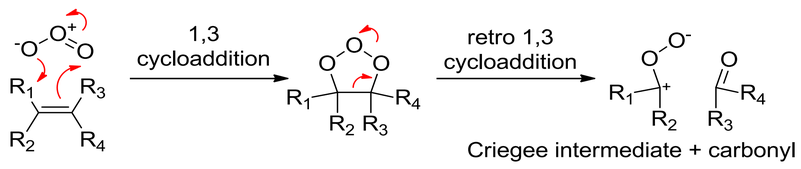
Introduction

Ozonolysis plays an important role in removal of unsaturated hydrocarbons in atmosphere. It is believed to produce Criegee intermediates.



◇ Why is Criegee intermediate important?

$CH_2OO + NO_2 \longrightarrow CH_2O + NO_3$

$CH_2OO + SO_2 \longrightarrow CH_2O + SO_3$

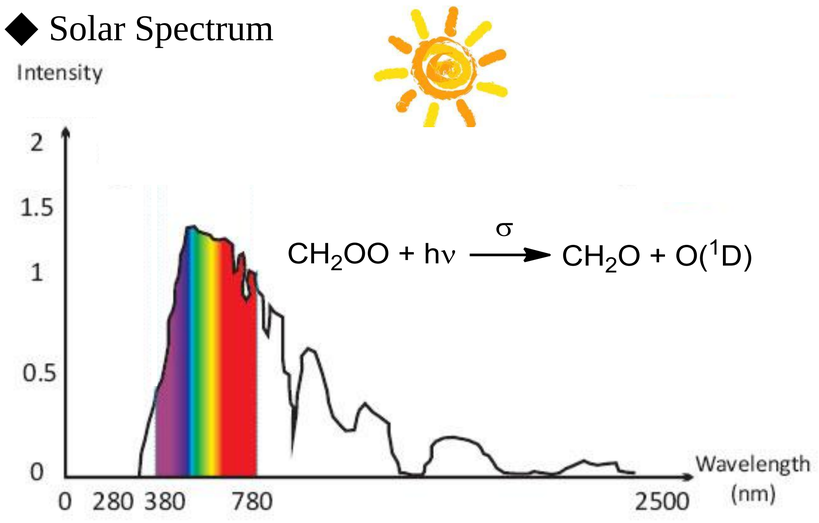
$CH_2OO + h\nu \longrightarrow CH_2O + O(^1D)$

$CH_2OO + CH_2OO \longrightarrow 2CH_2O + O_2$?

It is involved in many reactions linked to the change of earth's climate.

◇ In troposphere, CH_2OO absorbs UV light (> 300 nm) and dissociates.

◆ Solar Spectrum



In photolysis,

$$\frac{d[CH_2OO]}{dt} = -J[CH_2OO] \quad , \quad J = \int I(\lambda)\sigma(\lambda)\,d\lambda$$

J: 1st-order Photolysis rate constant, (sec^{-1})
I: Intensity of light, (photon · sec^{-1} · cm^{-2} · nm^{-1})
σ: absorption cross section (cm^2)

Simple Criegee intermediates (e.g., CH_2OO) can be synthesized through the reaction:

$CH_2I + O_2 \longrightarrow CH_2OO + I$

However, there is no quantitative measurement of σ to date.

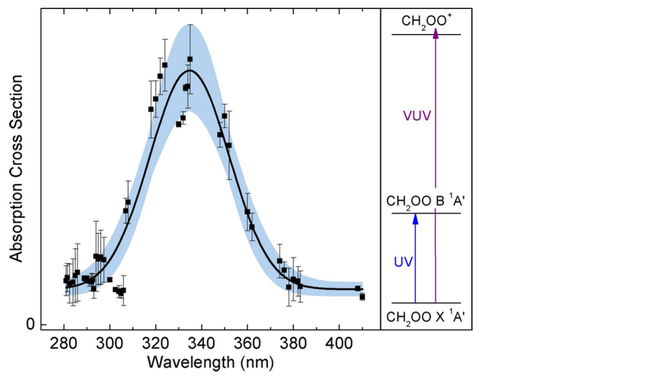


Figure 1. Experimental UV spectrum of CH_2OO isolated in a pulsed supersonic expansion. The absorption cross section was derived from the UV-induced depletion of the ground state and the corresponding VUV photoionization signal at m/z 46. The smooth curve is a fit to a simple Gaussian form; the uncertainty is illustrated by the blue-shaded region.

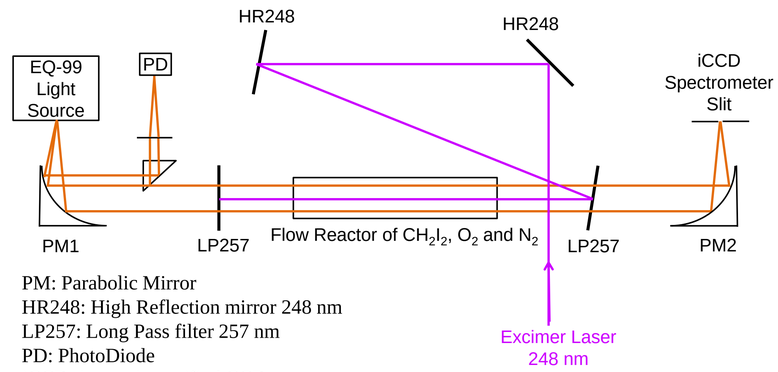
Beam et. al, *J. Am. Chem. Soc.* **2012**, *134*, 20045-20048

Our Work

1. Study the UV absorption spectrum of CH_2OO
2. Measure the absolute absorption cross section of CH_2OO

Experiment

1. UV transient absorption of CH_2OO



PM: Parabolic Mirror
HR248: High Reflection mirror 248 nm
LP257: Long Pass filter 257 nm
PD: PhotoDiode
iCCD: image-intensified CCD camera

	Pressure (torr)	Number density (cm^{-3})
CH_2I_2	0.023	7.6×10^{14}
O_2	22	7.2×10^{17}
N_2	86	2.8×10^{18}

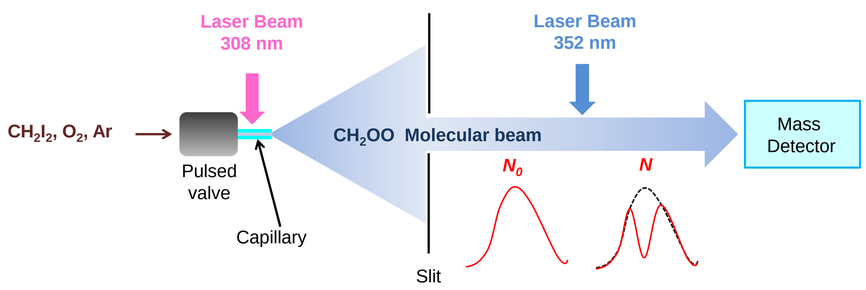
$CH_2I_2 + h\nu \longrightarrow CH_2I + I$ rxn(0)

$CH_2I + O_2 \longrightarrow CH_2OO + I$ rxn(1)

$CH_2OO + CH_2OO \longrightarrow$ Product rxn(2)

$CH_2OO + I \longrightarrow IO + CH_2O$ rxn(3)

2. Absorption cross section of CH_2OO



σ of CH_2OO can be quantified by comparison with known σ of CH_2I_2 :

◇ # of photons << # of molecules

$$A = \ln\frac{I_0}{I} = \sigma n L$$

◇ # of molecules << # of photons

$$-dN = dI \cdot \sigma \cdot N$$

$$\ln\frac{N_0}{N} = \sigma I \qquad N = N_0 \cdot e^{-\sigma I}$$

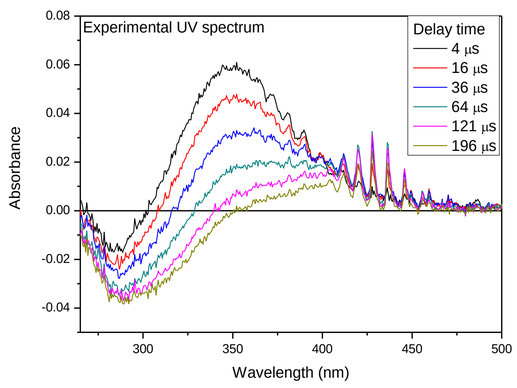
$$\frac{\sigma_{CH_2OO}}{\sigma_{CH_2I_2}} = \frac{I_{CH_2I_2}}{I_{CH_2OO}} \cdot \frac{\ln(\frac{N_0}{N})_{CH_2OO}}{\ln(\frac{N_0}{N})_{CH_2I_2}}$$

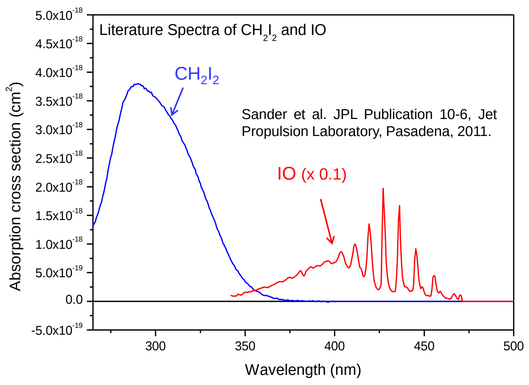
A: absorbance
σ: absorption cross section (cm^2)
n: number density (cm^{-3})
L: path length (cm)
I_0 and I: intensity of light before and after absorption

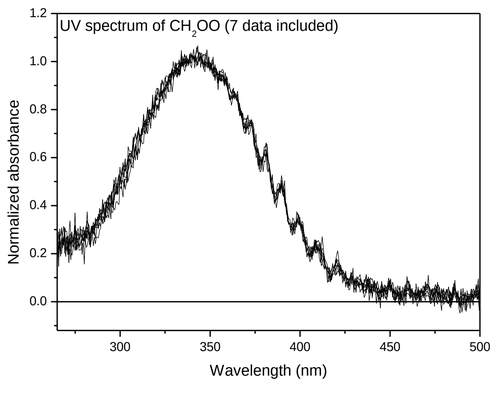
σ: absorption cross section (cm^2)
I: intensity of laser (photon · cm^{-2})
N_0 and N: numbers of molecules before and after the laser irradiation

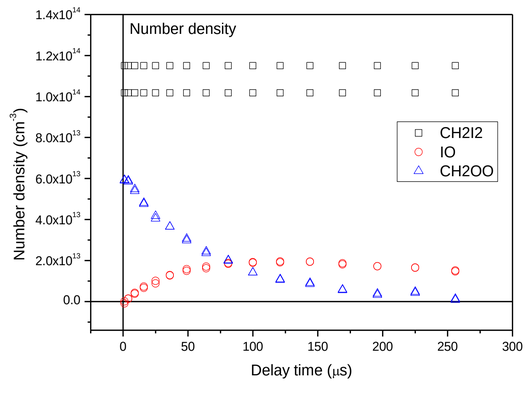
Results

1. UV spectrum of CH_2OO

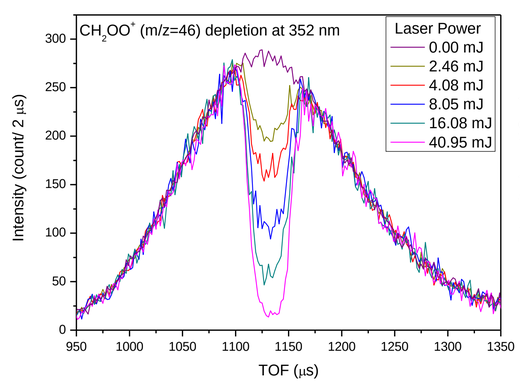


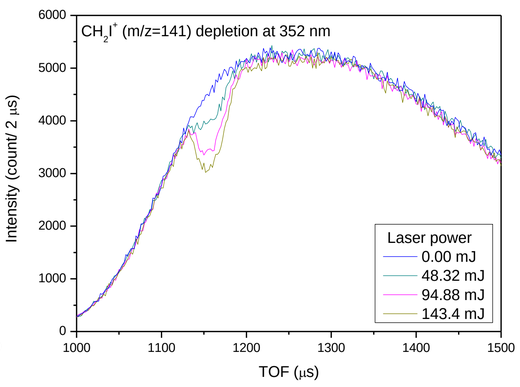


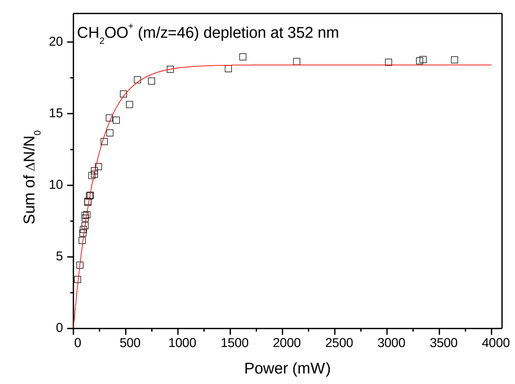


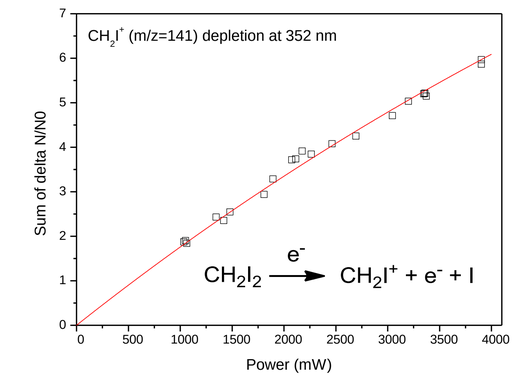


2. Absorption cross section of CH_2OO









@ 352 nm:

$$\frac{\sigma_{CH_2OO}}{\sigma_{CH_2I_2}} = 47.56 \qquad \sigma_{CH_2I_2} = 2.46\times10^{-19} cm^2$$

$$\rightarrow \quad \sigma_{CH_2OO} = 1.17\times10^{-17} cm^2$$

(Sander et al."Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011.)

Conclusions

The UV spectrum of CH_2OO has significant structures.

We determined its absorption cross section at 352 nm to be 1.17×10^{-17} cm^2.

We observed the kinetics involving rxn (2) and rxn (3).