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Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry: a New Tool for Gas-Phase Chemical Kinetics

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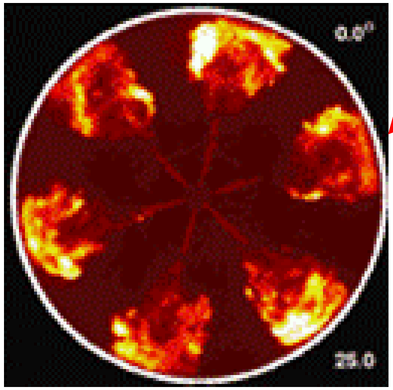
Tailored experimental probes

for gas-phase chemistry

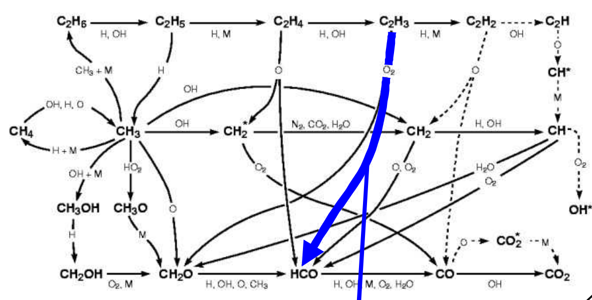


In-cylinder ignition
C. G. Mueller, CRF

Complex chemistry

Tailored experimental probes
for gas-phase chemistry

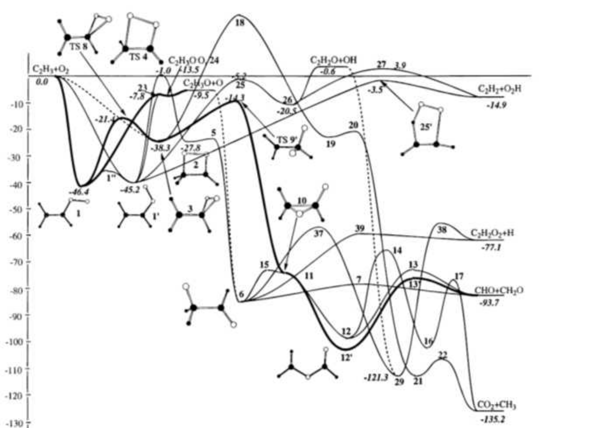
Fuel + O_2



Najm *et al.* PS *Combust. Flame* 1998, 113:312.

CO_2 + H_2O + energy

NO_x?
soot?
timing?
engine knock?
P and *T* dependence?



At least 8 papers on the reaction kinetics of vinyl + O_2!

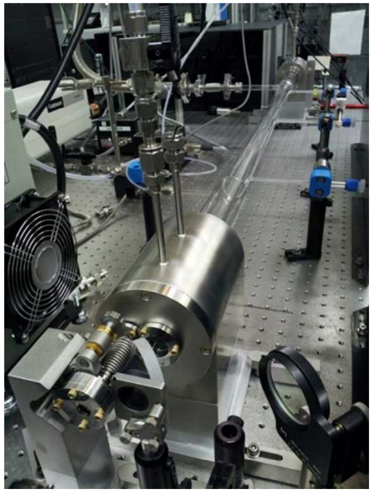
Mebel et al., JACS, **118** (1996) *9759*

What is a perfect experimental method?

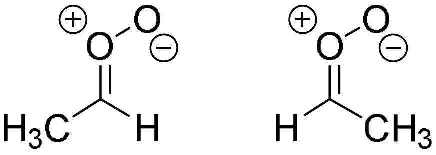
Time-resolved laser-initiation studies

- Non-intrusive *in situ* probe — transient absorption
- Sensitivity — path length enhancement
- Multiplexed — broadband absorption
- Real-time measurement — μs time resolution

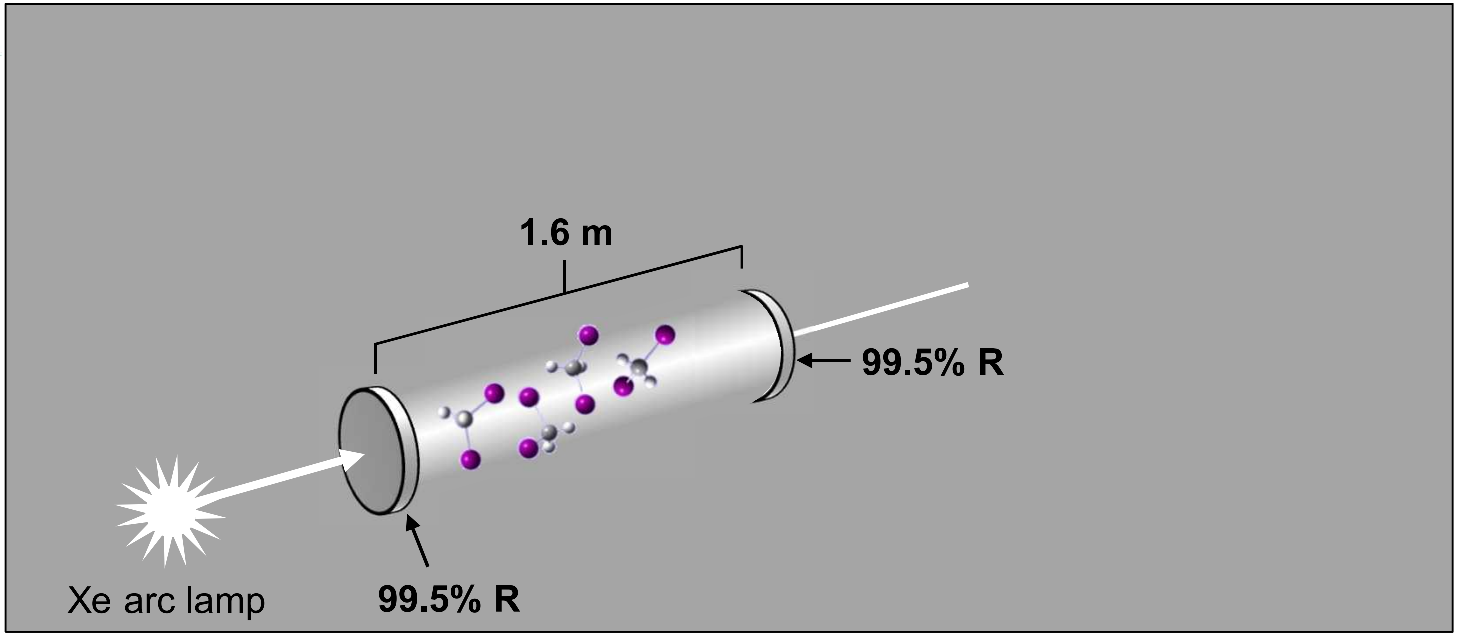
I. Development of Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry



II. The search for UV spectrum of CH_3CHOO



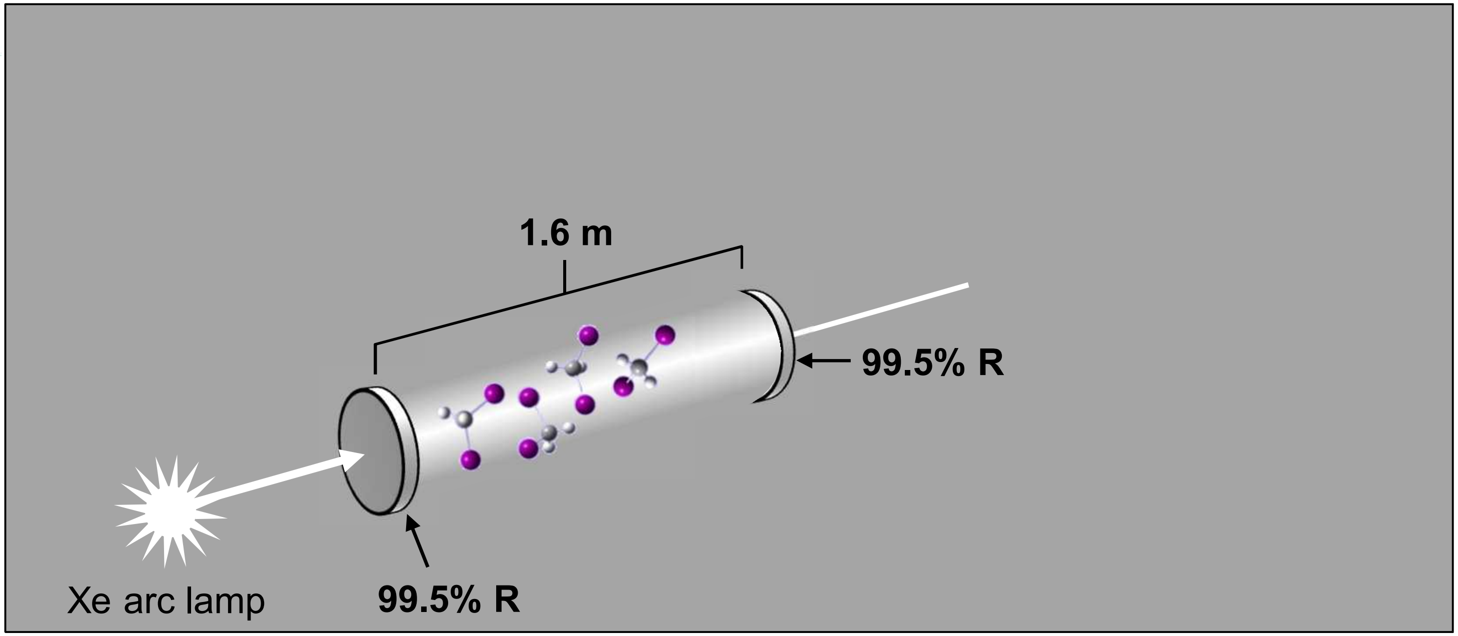
anti- *syn-*



Broadband, low-finesse optical cavity

- Xe arc lamp source (250 – 2400 nm)
- Overall length 1.6 m
- Cavity mirrors 99.5% R (300 – 700 nm)

$L_{eff} \approx D \cdot (1-R)^{-1}$ ~200x path length enhancement



Two sets of mirrors:

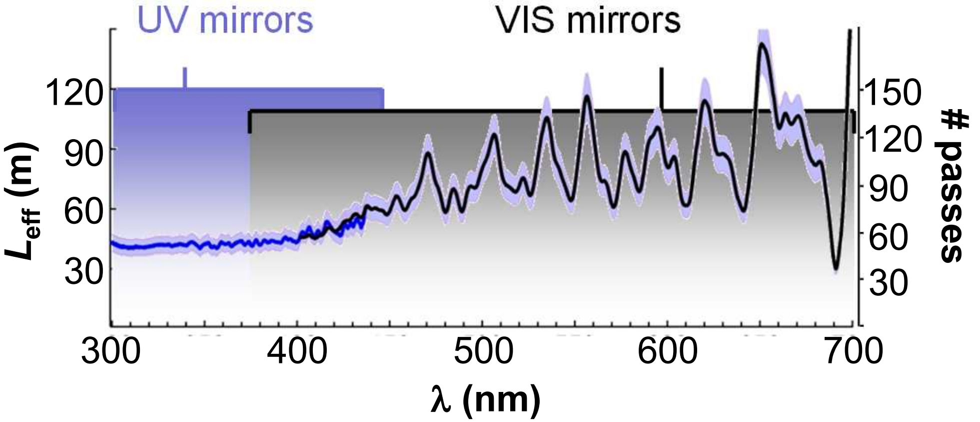
UV 300 – 450 nm R = 99.5±0.2%

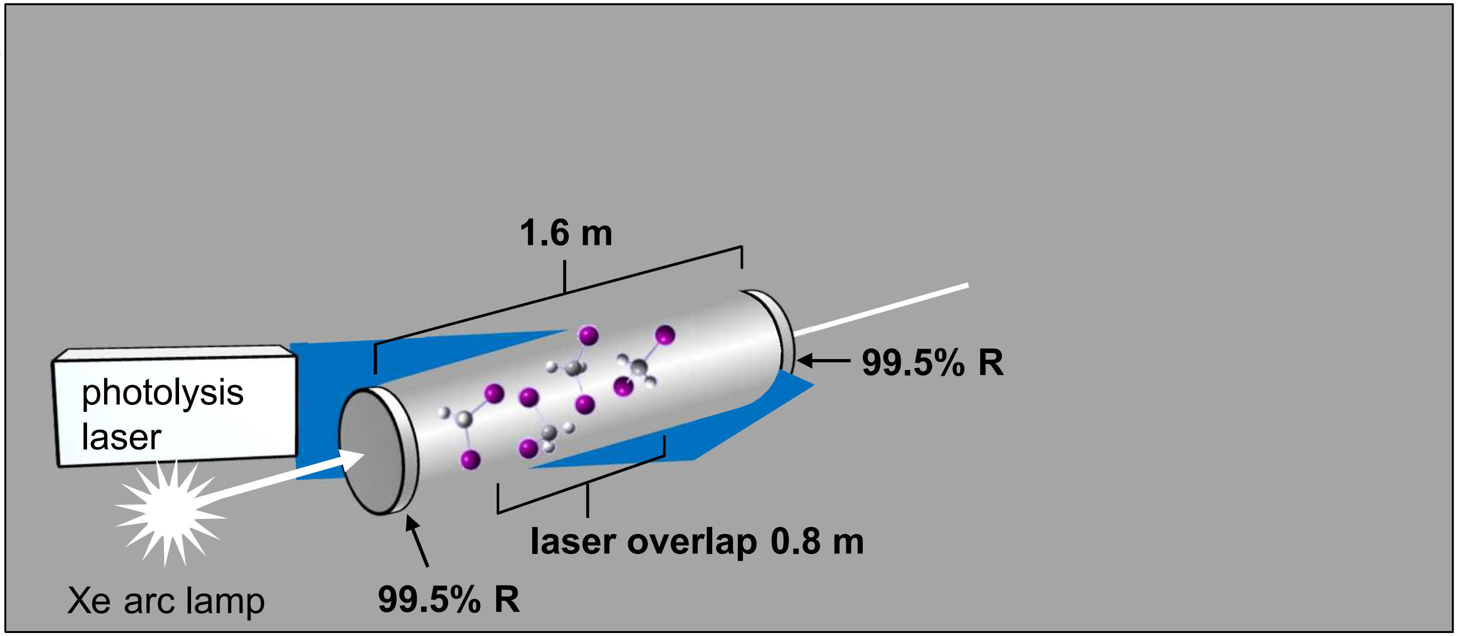
VIS 370 – 700 nm R = 99.5±0.2%

$L_{eff}(\lambda)$ measured using absorption "standards" – NO_2 and CH_2I_2

~ 50 – 80 passes for UV

~ 70 – 150 passes for VIS

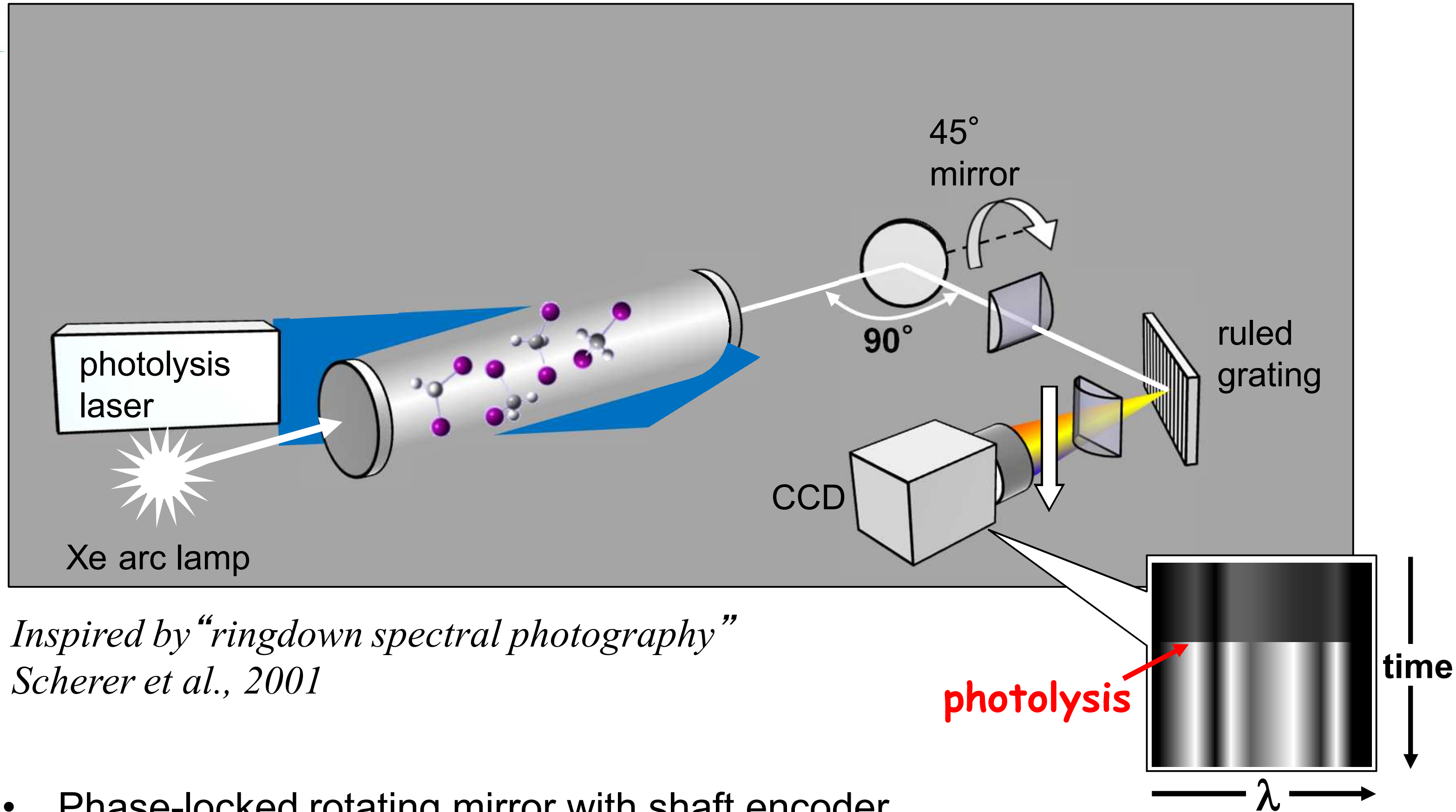




Optical cavity integrated into laser photolysis reactor

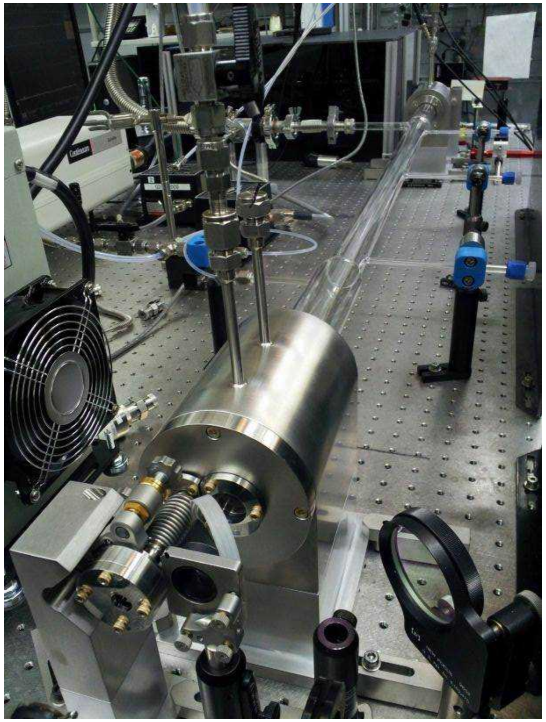
- Laser – CW probe cross at 2° (overlap length 0.8 m)
- Active *T* and *P* control: *T* up to ~ 600 K
  P up to 1 atm
- Precision metered gas flows
- Homogeneous reaction mixture

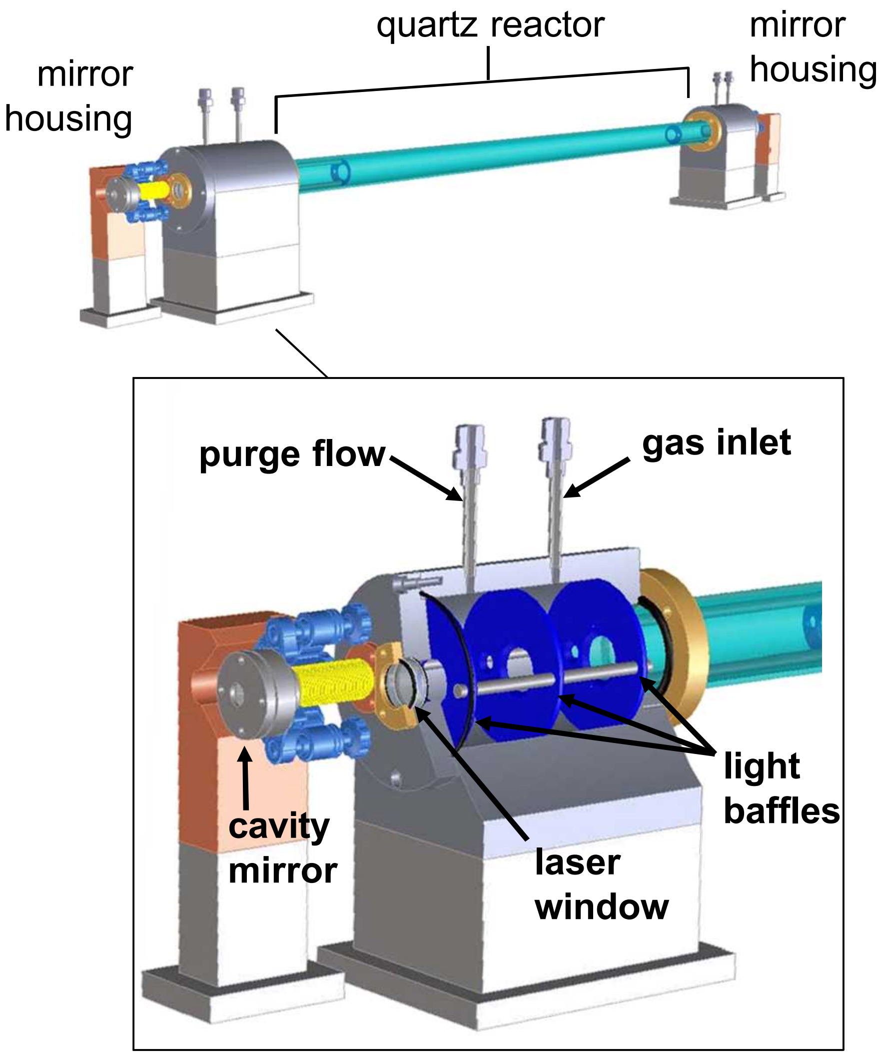
- Photolysis laser reaction initiation; continuous absorption probing



Inspired by "ringdown spectral photography"
Scherer et al., 2001

- Phase-locked rotating mirror with shaft encoder
- ruled grating: **X–axis ↔ probe λ**
  mirror rotation: **Y–axis ↔ time**
- Image recorded on megapixel CCD (1024x1024)
- Photolysis synchronized with mirror rotation: transient absorption in one shot
- Average 10s to 1000s of laser shots in "long exposure"

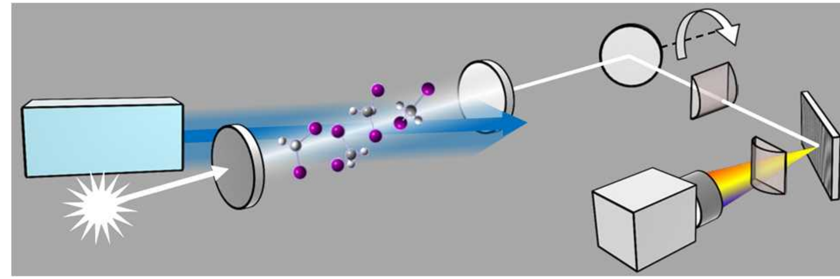




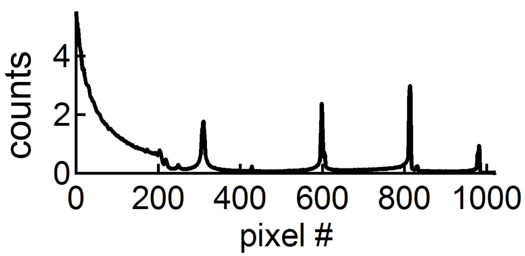
quartz reactor
mirror housing
mirror housing
purge flow
gas inlet
light baffles
cavity mirror
laser window

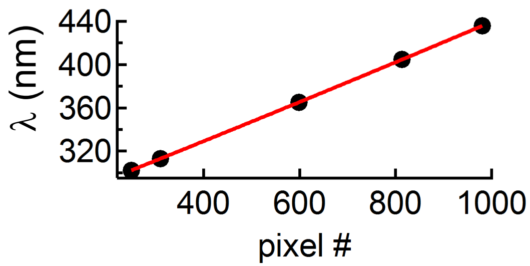
Spectrometer calibration

1. **Wavelength**
2. Kinetic time

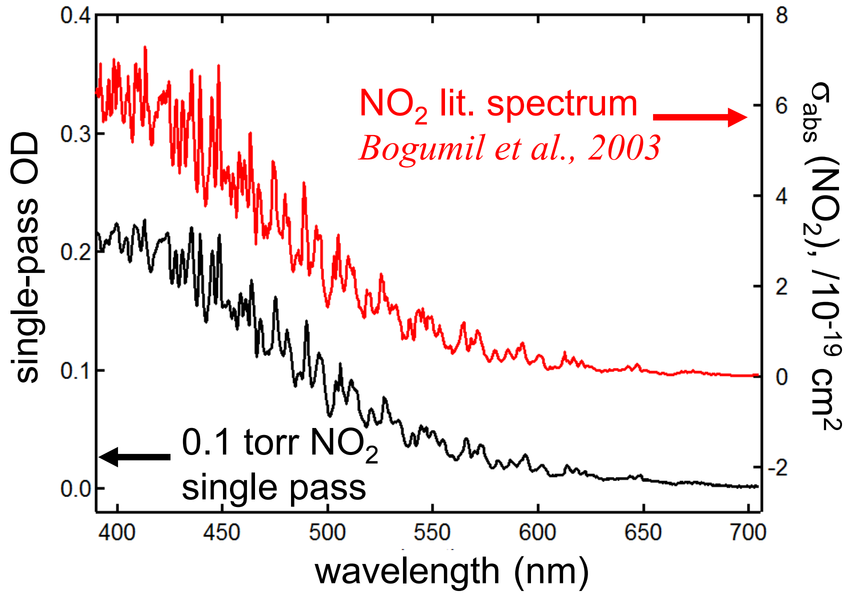


Hg(Ne) lamp spectrum





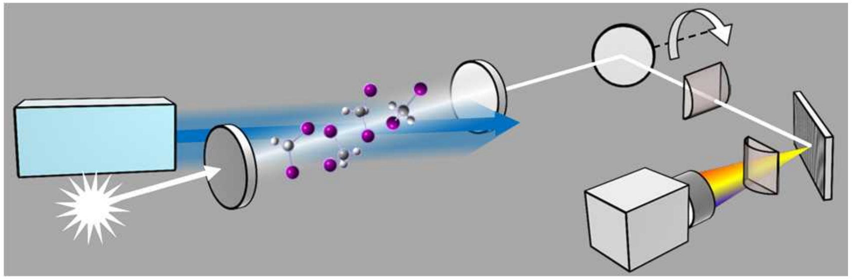
single-pass absorption spectrum of NO_2



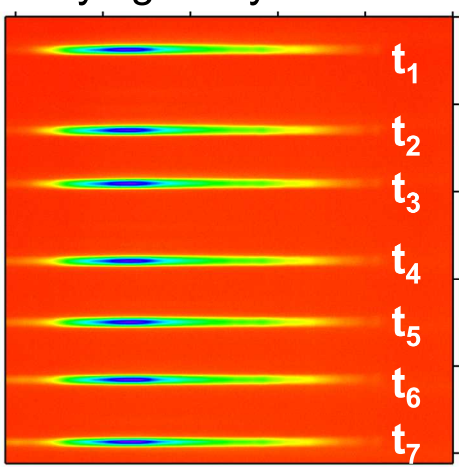
- Example: 600 grooves/mm:
  ~0.4 nm/pixel, ~2 nm resolution

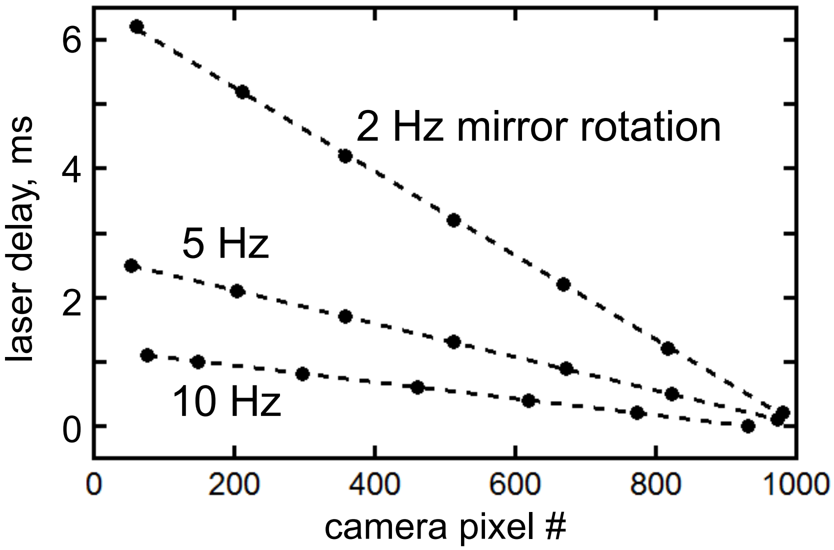
Spectrometer calibration

1. Wavelength
2. **Kinetic time**



Imaging laser scatter, varying delay times



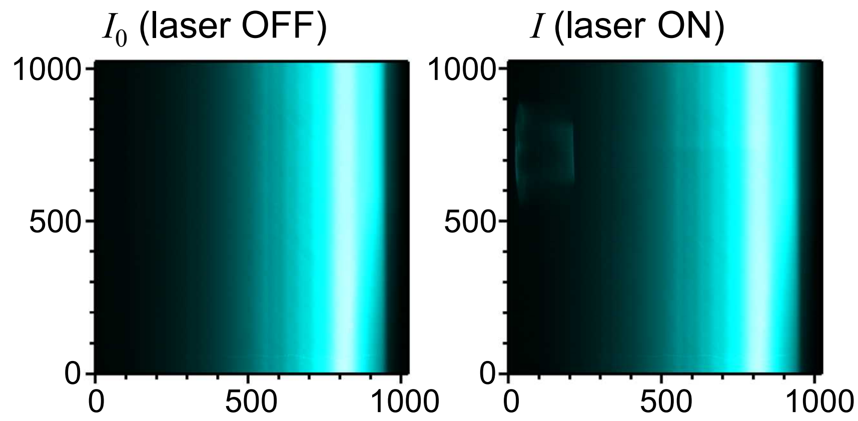


- Example: 10 Hz operation
  ~1.3 μs/pixel, ~6 μs resolution

Data acquisition

Active background subtraction

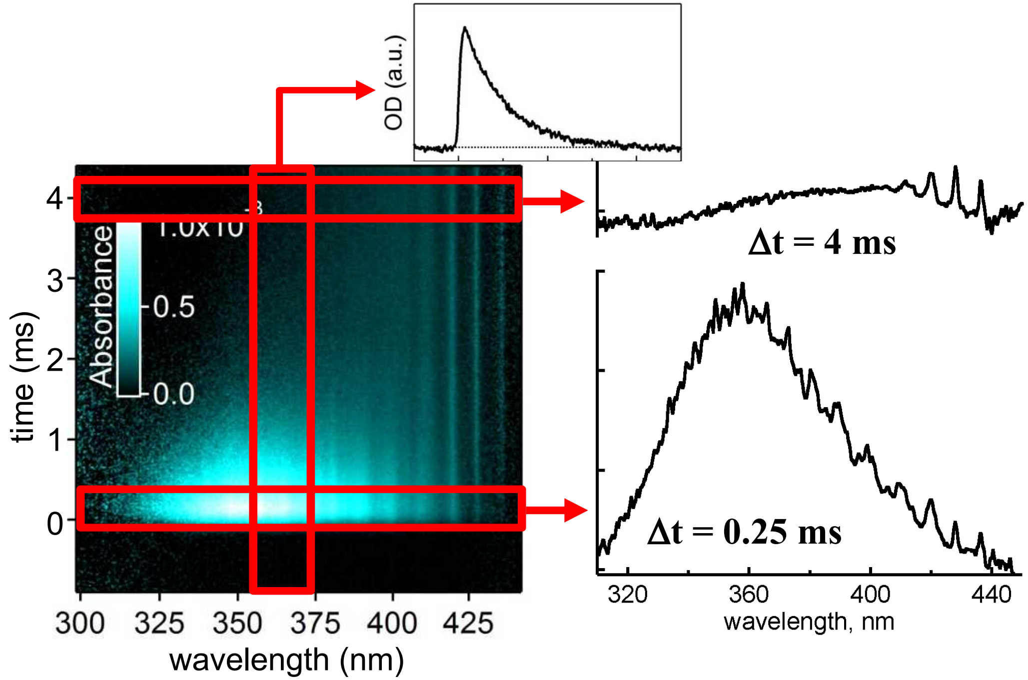
- Alternating laser ON / OFF exposures



Transient absorption

$$OD = -\ln\left(\frac{I}{I_0}\right) = L_{\text{eff}} \cdot C \cdot \sigma_{abs}$$

UV spectroscopic study of CH_2OO (2014)



Experimental Sensitivity

Detection limit of stable species

α_{min} (300 – 700 nm) ~$3\cdot10^{-8}$ cm^{-1} $Hz^{-1/2}$

Chemical kinetics studies

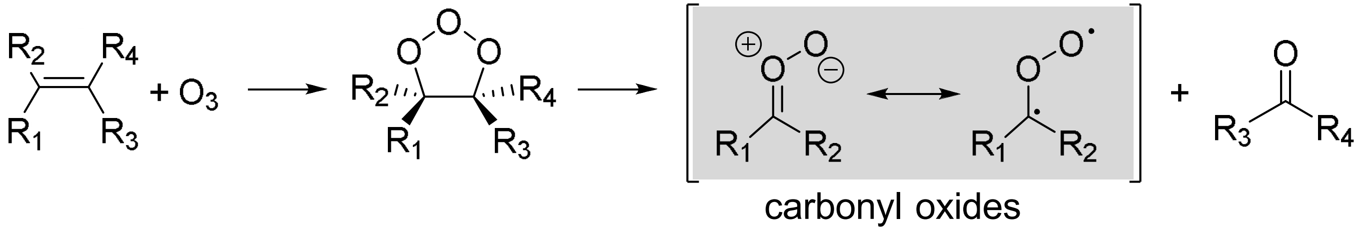
- Initial radicals <10^{14} cm^{-3}

Some practical examples (total experimental effort = 10 minutes):

HCO	σ_{614nm} ~$4\cdot10^{-18}$ cm^2	detection limit: ~$8\cdot10^{10}$ cm^{-3}
C_2H_3	σ_{404nm} ~$1\cdot10^{-18}$ cm^2	~$3\cdot10^{11}$ cm^{-3}
CH_2O	σ_{325nm} ~$7\cdot10^{-20}$ cm^2	~$4\cdot10^{12}$ cm^{-3}
CH_2OO	σ_{355nm} ~$1\cdot10^{-17}$ cm^2	~$3\cdot10^{10}$ cm^{-3}

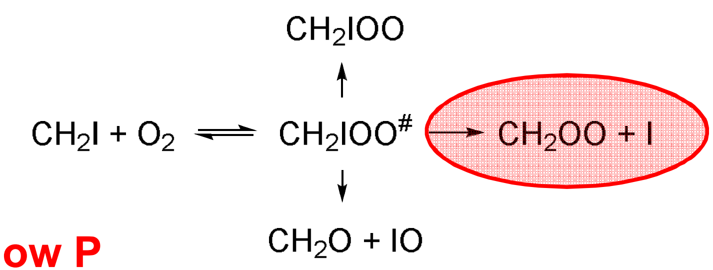
Spectroscopy and reaction kinetics of Criegee intermediates

1949 R. Criegee postulated that carbonyl oxides are intermediates in ozonolysis



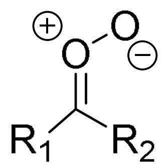
2012 **A simple new method of CI production in the lab:**
Taatjes and co-workers

CH_2OO formation dominates at low P
Yield approaches 1 (!)



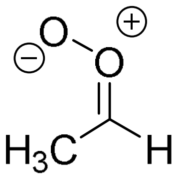
Spectroscopy and reaction kinetics of Criegee intermediates

- Criegee intermediates are major oxidants of trace atmospheric species and potential OH sources

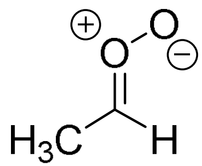


+ SO_2	→	H_2SO_4	$k \sim 1\cdot10^{-11}$ cm^3s^{-1}
+ NO_2	→	NOx	$k \sim 1\cdot10^{-11}$ cm^3s^{-1}
+ organic acids	→	OVOC	$k \sim 1\cdot10^{-10}$ cm^3s^{-1}
	→	OH	

- Some Criegee intermediates have conformer-dependent reactivity

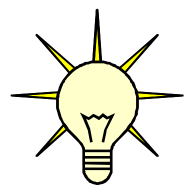


syn-CH_3CHOO



anti-CH_3CHOO

acetaldehyde oxide



- **Can we use UV spectroscopy to characterize CH_3CHOO?**
- **UV transient absorption for direct kinetics studies?**

Two groups measured strong UV absorption for CH_3CHOO near ~330 nm
M. Lester and co-workers (2103), J. Lin and co-workers (2014)

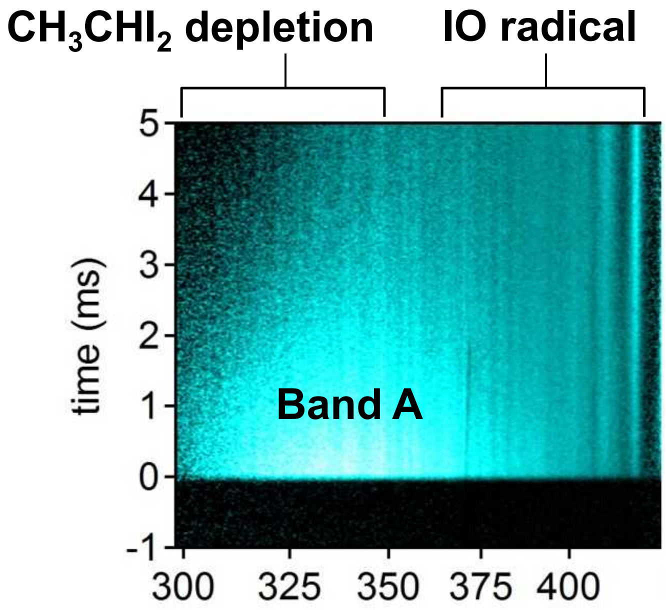
UV spectroscopy of CH_3CHOO

$$CH_3CHI_2 \xrightarrow{h\nu} CH_3CHI + I$$

$$CH_3CHI + O_2 \longrightarrow I + \textit{syn}\text{-}CH_3CHOO$$
$$\textit{anti}\text{-}CH_3CHOO$$

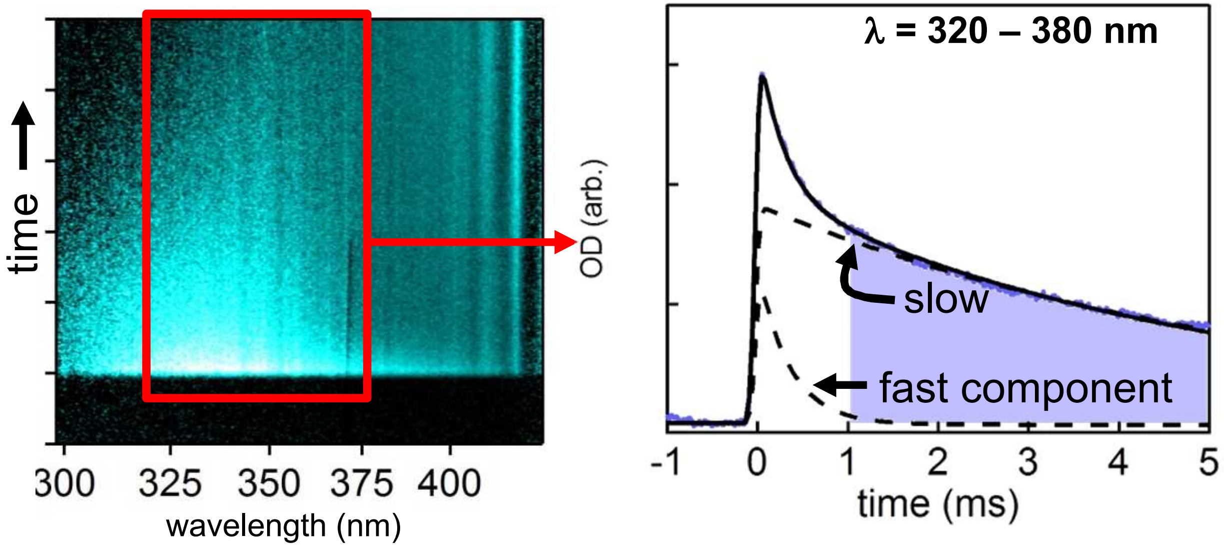
UV spectroscopy of CH_3CHOO

P = 20 torr, *T* = 293K
He bath



UV spectroscopy of CH_3CHOO

Transient absorption in the presence of H_2O

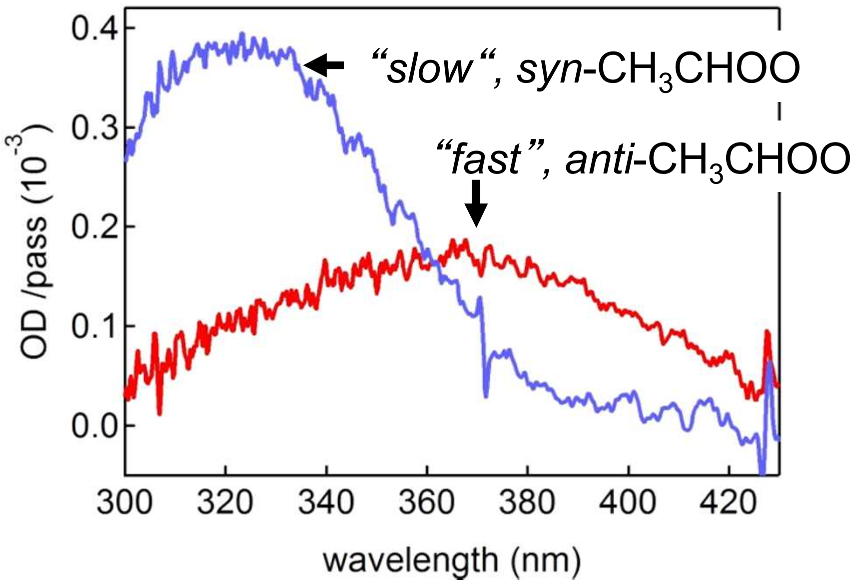


- Two decay components

Spectral assignment based on

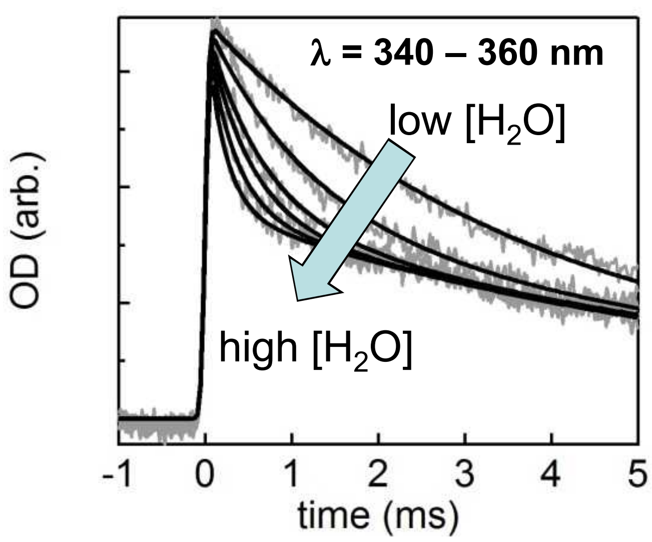
- Measured reaction kinetics with SO_2, H_2O, other species
- Calculated band maximum shift, *syn*- vs. *anti*

Peak σ_{abs} *(syn-* and *anti-)* ~$1 \cdot 10^{-17}$ cm^2

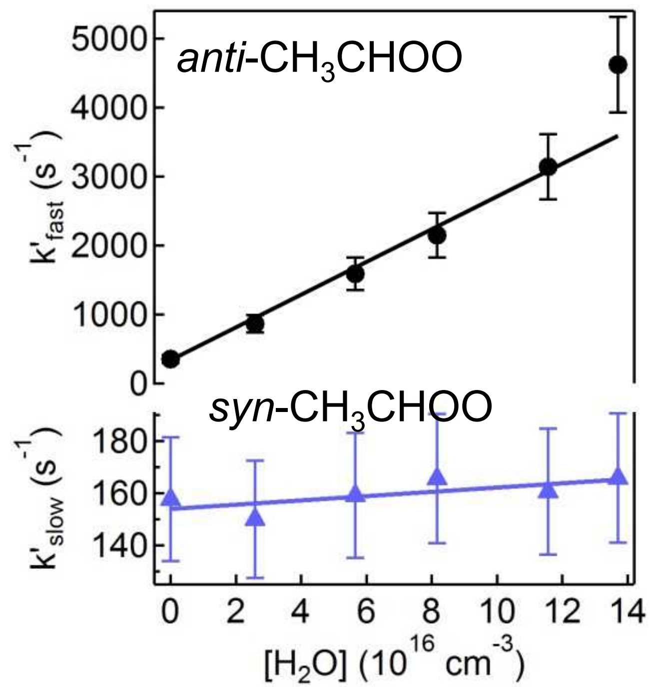


Direct measurements of conformer-dependent reactivity

Reaction with H_2O



- Sum of 2 kinetic components
- Only k'_{fast} depends on $[H_2O]$



The bimolecular rate coefficients:

•$k_{fast} = (2.4 \pm 0.4) \cdot 10^{-14}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$

•$k_{slow} < 1 \cdot 10^{-16}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$

Summary

New experimental capability for transient absorption probing of gas-phase chemistry

- **~100x path length enhancement**
- **near-UV – VIS spectral coverage**
- **μs time resolution**
- **efficient data acquisition**

- **robust, insensitive to alignment**
- **price tag: $40K (excluding photolysis laser)**

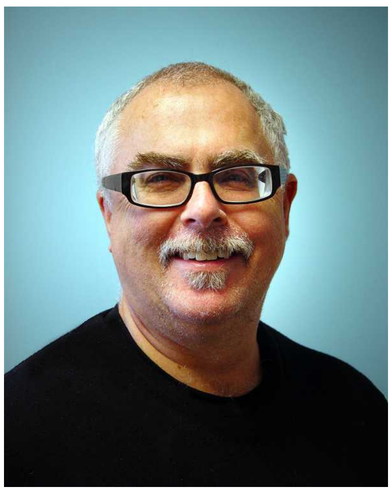
Acknowledgemenrts

Funding:

U.S. DEPARTMENT OF ENERGY | Office of Science

Development of TR-BB-CEAS experimental apparatus

LDRD Laboratory Directed Research & Development



David Chandler

Kendrew Au Ashley M. Scully

UV spectroscopy of CH_3CHOO

Thank you