248-nm Laser Photolysis of $CHBr_3$/O-atom Mixtures: Kinetic Evidence for UV CO(A)-Chemiluminescence in the Reaction of Methylidyne Radicals With Atomic Oxygen

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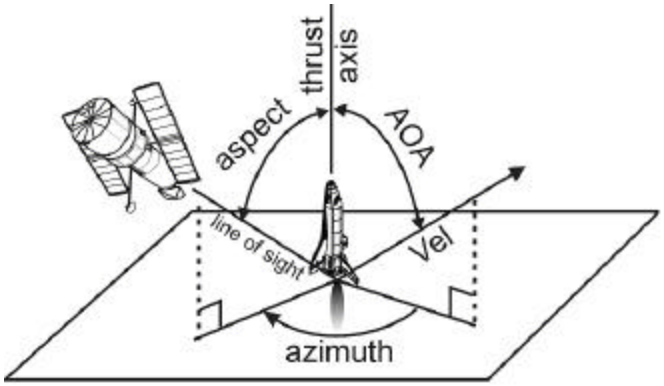
AFRL's Motivation

- **Spacecraft Atmospheric Interactions**
- **Chemiluminescent Combustion Processes**

- Strong Emissions From:
  - $O(^1D)$, $O(^1S)$
  - NH(A)
  - OH(A)
  - CO(a)
- Cause of Chemiluminescence:
  - Plume-Atmospheric Interactions
- Source Chemistry:
  - Precursors? & Formation?
  - O-atom Reactions
  - Other Reactions

- Space Experiment



Observation Platforms

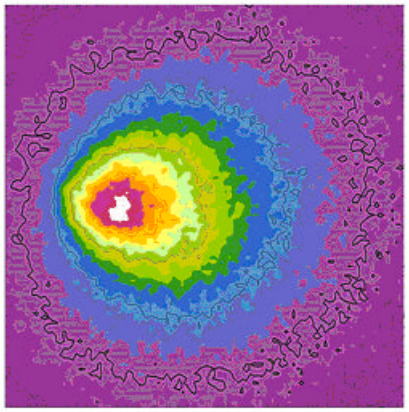
Space Shuttle
Mir Space Station
MSX

Thrusters

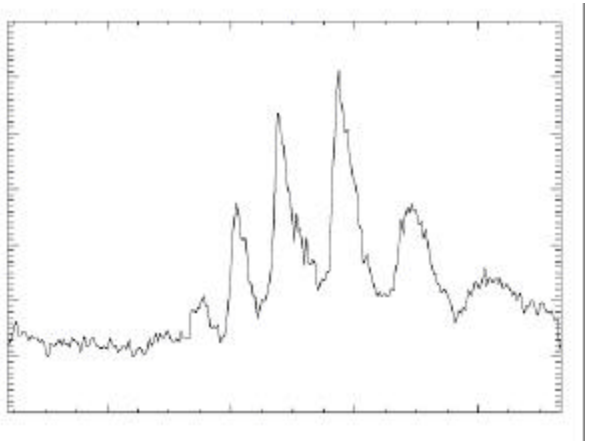
Space Shuttle
Progress-M
Soyuz-TM

UV/Vis Plumes

Radiance Data



Spectral Data



Plume Data

⇕

Modeling Studies

⇕

Laboratory Studies

⇕

Chemiluminescent Processes

⇕

Identify Spacecraft Atmospheric Interactions

Proposed CO(a) Source Chemistry

- Unreacted Fuel ® ® Precursor(s)
- Precursor(s) + O ® Products

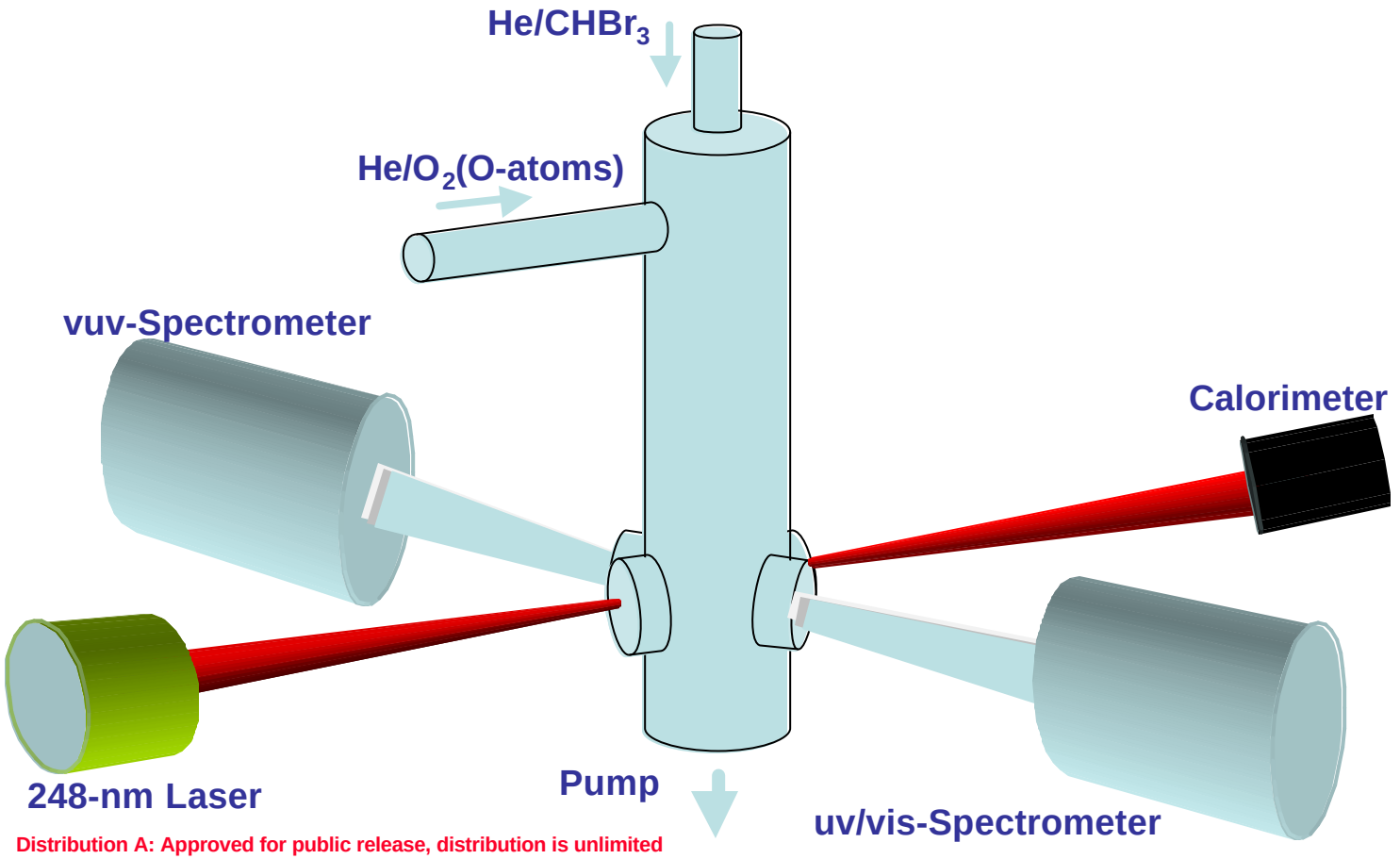
® $CO(a_{(v')})$ + R

® CH_2 + OR'

® CH + OR''

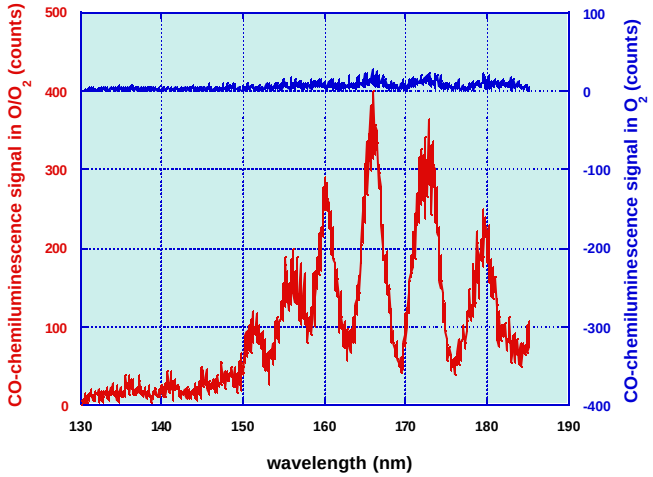
- CH_2 + O ® Products ($k = 1.3 \times 10^{-10}$)
  - ® $CO(a_{(v'\pounds 8)}, a'_{(v'\pounds 5)}, d_{(v'\pounds 1)}) + H_2$
  - CO + H_2 (Main)
  - 2H + CO (~ 20%)
  - H + HCO (HCO*)
  - CH + OH (~ 6%)
- CH + O ® Products ($k = 9.5 \times 10^{-11}$)
  - ® $CO(a_{(v'\pounds 8)}, a'_{(v'\pounds 5)}, d_{(v'=0)}) + H$
  - CO + H (Main)
  - HCO (HCO*)
  - $HCO^+ + e^-$ (~ 0.03%)
  - C + OH (? +ve E_a)

Apparatus

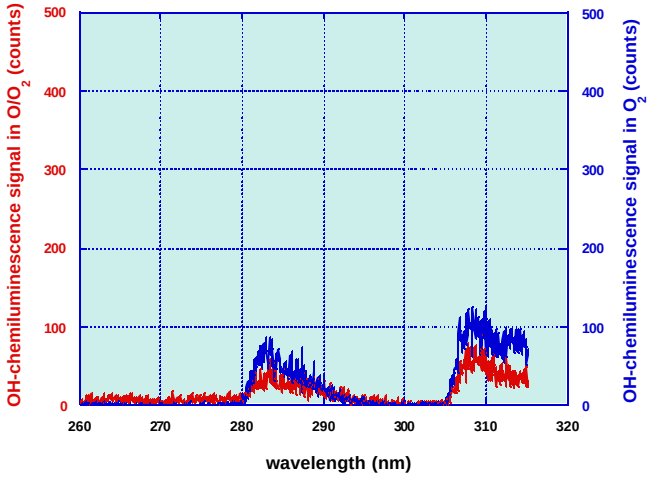


Comparison of CO & OH-Chemiluminescence

Strong CO(A) Signal in O/O_2



Weakened OH(A) Signal in O/O_2

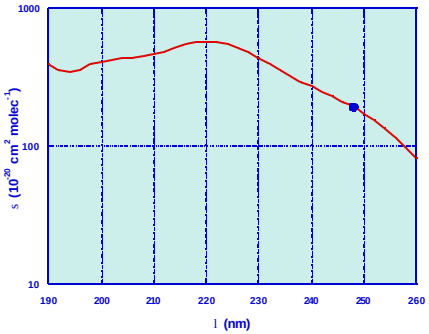


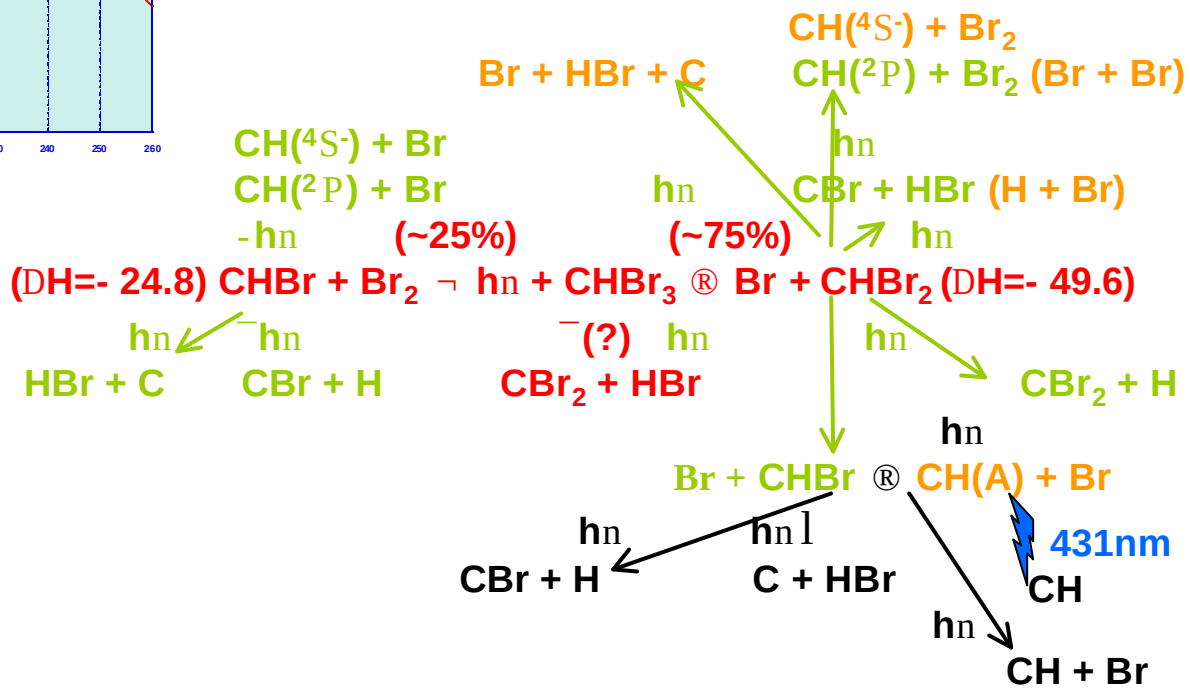
Very Weak CO(A) Signal in O_2 only

Strong OH(A) Signal in O_2 only

- CH + O_2 ® Products ($k = (2.3\text{-}5.9) \times 10^{-11}$)
  - ® CO($a_{(v' \pounds 4)}$, $a'_{(v'=0)}$) + OH
    - CO + OH (~ 20%)
    - CO_2 + H (~ 30%)
    - HCO + O (~ 20%)
    - H + CO + O (~ 30%)
    - **CO + OH(A) (~ 0.48%)**

Bromoform Photolysis





CO(A) Source Reactions

- Chemiluminescence Intensity Varied as (Laser Fluence)^2

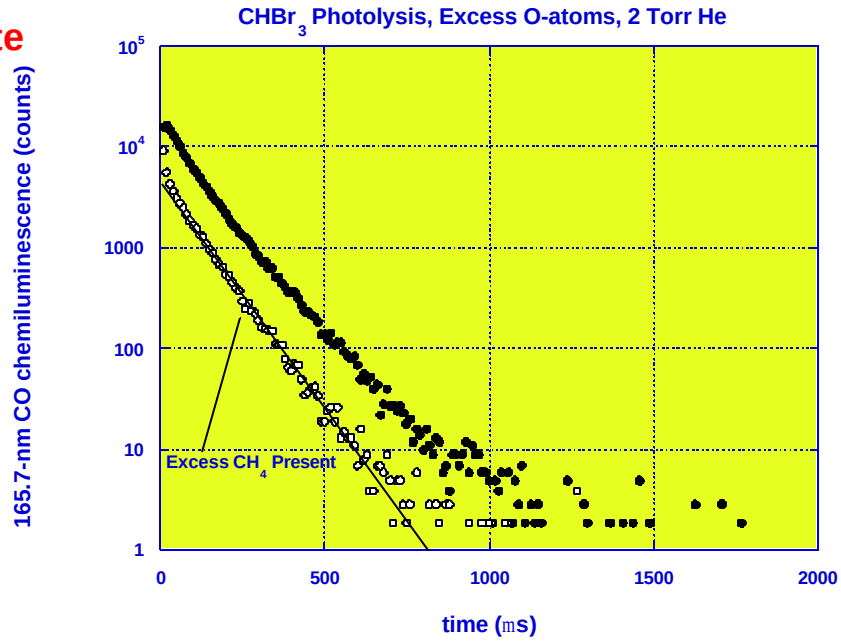
	ΔH^o_{298K}(kcal mol^{-1})
$C(^3P) + O(^3P) \rightarrow CO(A^1\Pi)$	(-71.8)
$CHBr + O(^3P) \rightarrow HBr(X^1\Sigma^+) + CO(A^1\Pi)$	(+1.3)
$CH + O(^3P) \rightarrow H(^2S) + CO(A^1\Pi)$	(+9.2)
$CBr + O(^3P) \rightarrow Br(^2P_{3/2}) + CO(A^1\Pi)$	(+3.8)
$CBr_2 + O(^3P) \rightarrow Br_2(^1\Sigma^+_g) + CO(A^1\Pi)$	(+29.1)

- Diatomics or Triatomics Need to be Internally Excited

Time Resolved CO(A)-Chemiluminescence

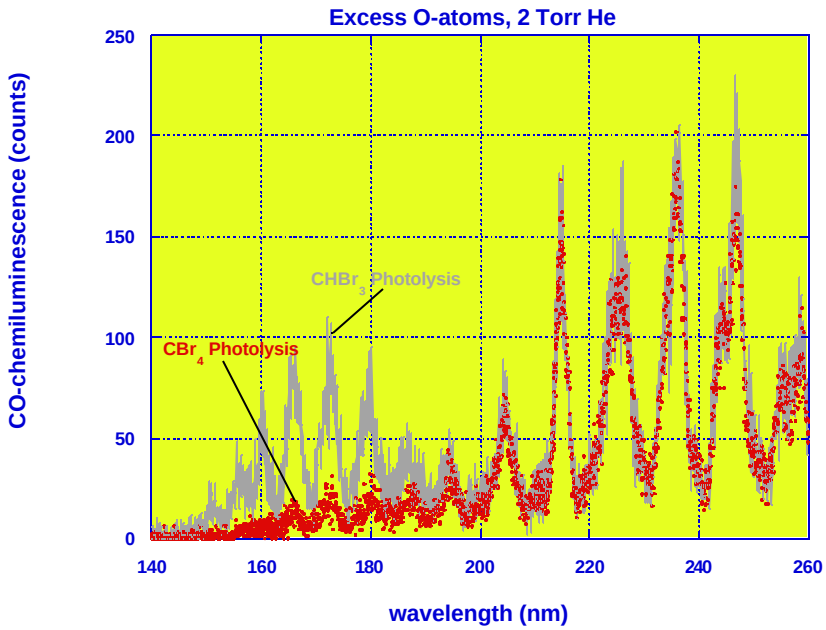
- **Bimolecular Reaction Rate Coefficients of Added Substrate When CH_4 Present**

$k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$
$k_{N_2O} < 7 \times 10^{-14}$
$k_{NO} = (3.4 \pm 0.5) \times 10^{-11}$
$k_{H_2} < 2 \times 10^{-13}$
$k_{CH_4} < 6 \times 10^{-14}$



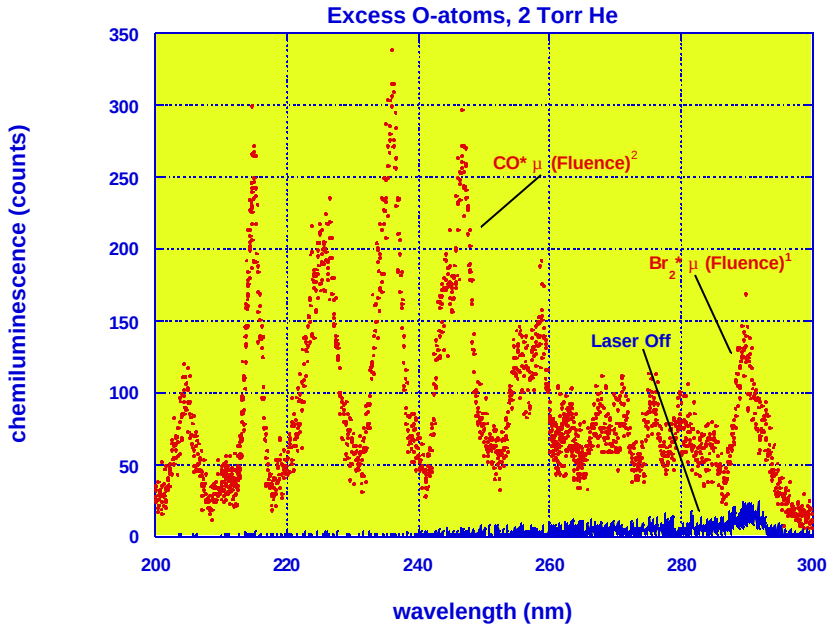
- **(C + O) Not the Source**

$CHBr_3$ Versus CBr_4 Photolysis



- **Stronger VUV Signal in $CHBr_3$ Photolysis**
  - **($CH^{\#}$ (or $CHBr^{\#}$) + O) Important**
- **Signal in CBr_4 Photolysis Varies as (Fluence)^2**
  - **($CBr_2^{\#}$ + O) not Important, Since Br_2* Signal Varies as (Fluence)^1**

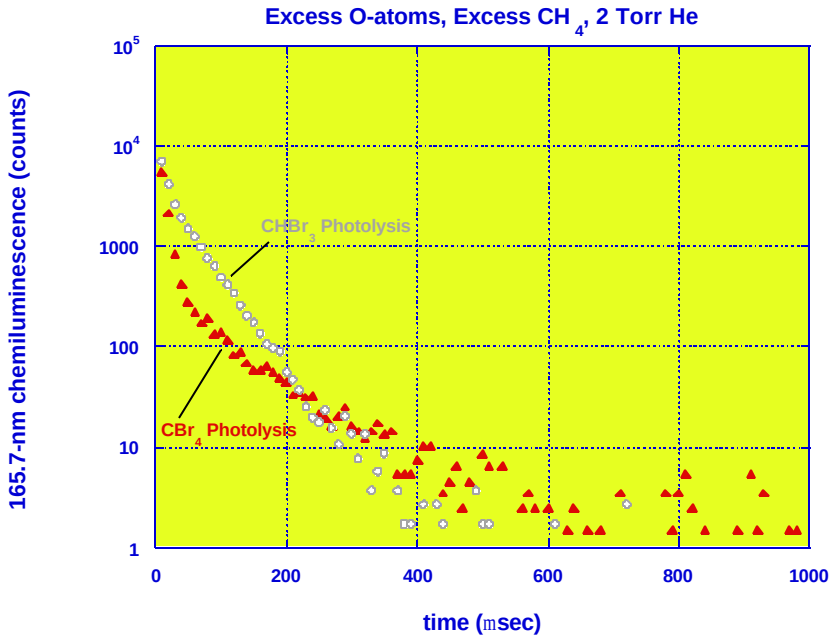
CBr_4 Photolysis



- $CBr_2 + O \rightarrow CO + Br_2^*$
- CBr_2 Formed in Absence of Photolysis
- CBr_2 Formed in Photolysis
- $CBr + O \rightarrow CO^* + Br$

$CBr_2 + O \rightarrow CO^* + Br_2$ not Important

$CHBr_3$ Versus CBr_4 Photolysis



- $CHBr_3$
  $k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$

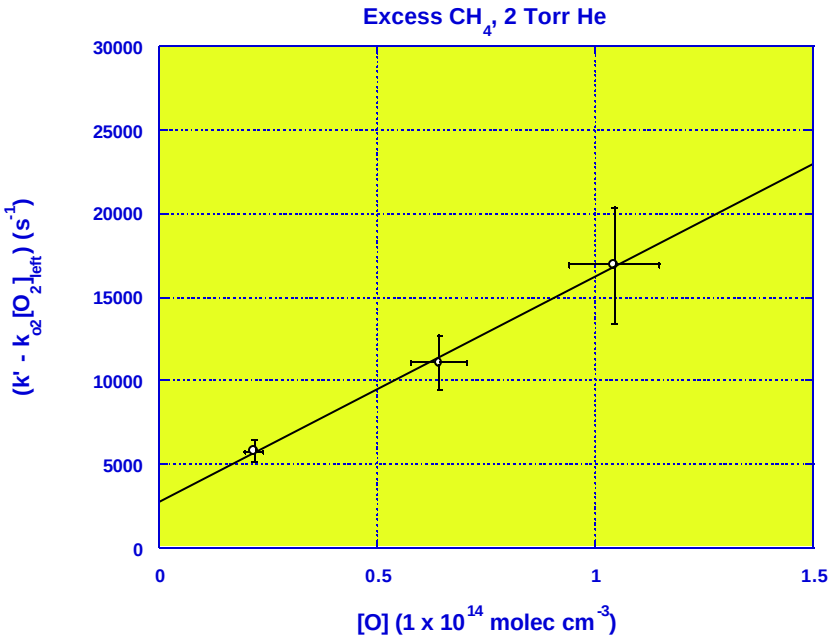
- CBr_4
  $k_{O_2} = (2.4 \pm 0.4) \times 10^{-12}$

($CBr^{\#}$ + O) Source is not as Important as ($CH^{\#}$ + O) in $CHBr_3$ Photolysis

- $CHBr^{\#}$ has Very Short Lifetime (~ 5 ms) and
  $k_{(CHBr + O_2)} < 2 \times 10^{-14}$

($CHBr^{\#}$ + O) Source not Important in $CHBr_3$ Photolysis

CH($a^4\Sigma^-$) + O Reaction Rate Coefficient

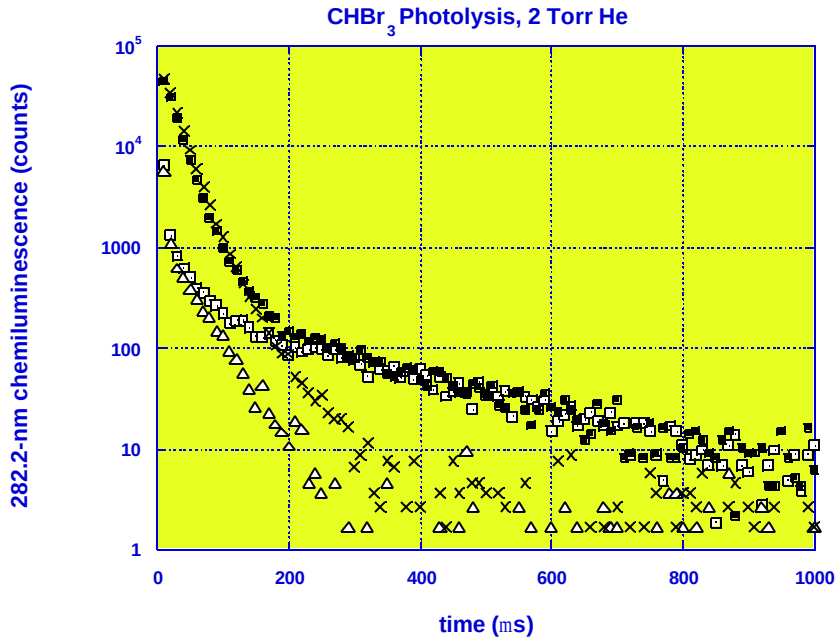


- $k_{(CH(a) + O)} = (1.35 \pm 0.47) \times 10^{-10}$

Previously:

- $k_{(CH(X) + O)} = (9.5 \pm 1.4) \times 10^{-11}$

282.2-nm Signal



- **Absence of O-atoms**

X-trace: (O_2, 8.8 x 10^{14})
D-trace: (O_2) + (CH_4, 5.0 x 10^{15})

–

$CH(X^2P) + O_2$ ® CO + OH(A)

$CH(a^4S^-) + O_2$ ® CO + OH(A)

- **5.0 x 10^{13} of O-atoms**

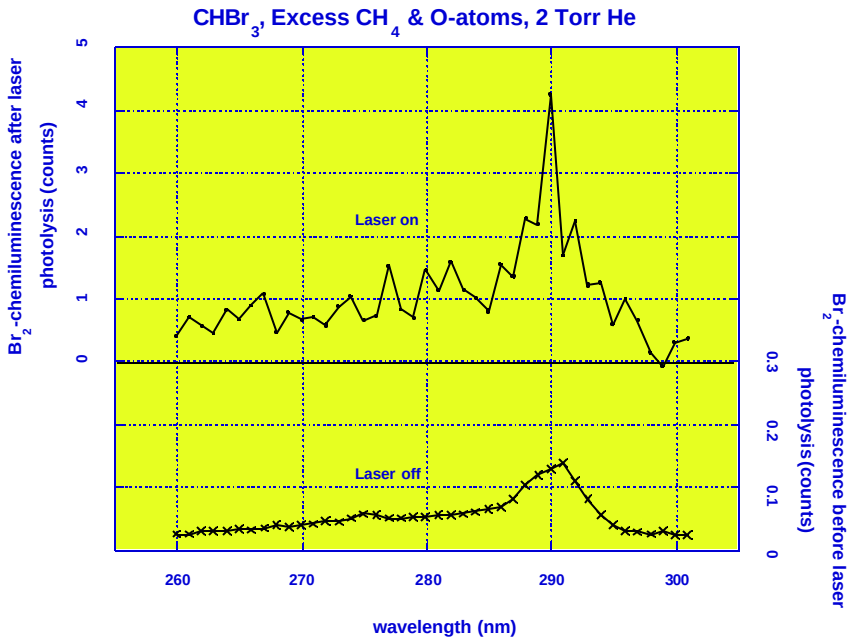
• -trace: (O_2, 8.8 x 10^{14})
? -trace: (O_2) + (CH_4, 5.0 x 10^{15})

–

$CBr_2 + O$ ® CO + Br_2(D)

($CBr_2 + CH_4$) Slow Reaction

Br_2*-Chemiluminescence



❑ **Laser off**

$CHBr_3 + O$? $CBr_3 + OH$

$CBr_3 + O$ • $CBr_2 + BrO$

–

$CBr_2 + O$ • $Br_2^* + CO$

❑ **Laser on**

Br_2^* μ (Fluence)^1

–

$CHBr_3 + h\nu \rightarrow CHBr_2^* + Br$

$CHBr_3 + h\nu \rightarrow CBr_2 + HBr$

$CHBr_2^* + h\nu \rightarrow CBr_2 + H$

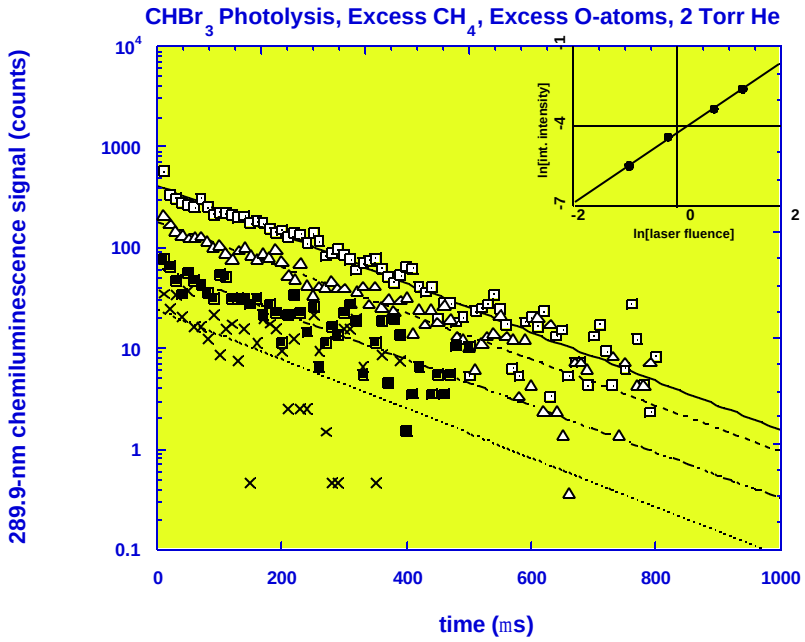
$CHBr_2^* + O \rightarrow Br_2^* + HCO$

$CHBr_2 + O \rightarrow CBr_2 + OH$

$CHBr_2^* + O \rightarrow CBr_2 + OH(A)$

$CHBr^* + O \rightarrow CBr + OH(A)$

Time Resolved Br_2*-Signal



- Fast Br_2* Rise
- Also:

$k_{O_2} < 9 \times 10^{-14}$

$k_{CH_4} < 7 \times 10^{-14}$

$k_O = (5.4 \pm 1.0) \times 10^{-11}$

$CHBr_3 + h\nu \rightarrow CBr_2 + HBr$

Less Important

$CBr_3 + h\nu \rightarrow CBr_2 + Br$

- Since:

$CBr_4 + h\nu \rightarrow CBr_3^* + Br$

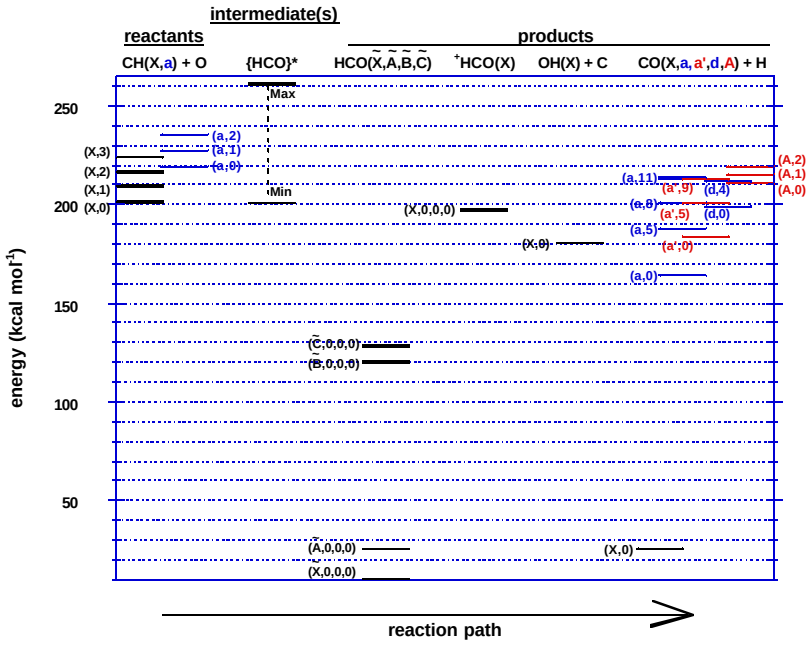
$CBr_3^* \rightarrow CBr_2 + Br$ } f ?

$CBr_4 + h\nu \rightarrow CBr_2 + Br_2$ { f ?

CO* Production Mechanism

$CH^{\#} + O \rightarrow \{HCO\}^* \rightarrow CO^* + H$

$CO^* \xrightarrow{M} CO(X,a,a',d,A)$



Conclusions

- 248-nm Photolysis of $CHBr_3$/O-atom Mixtures

Strong Emissions From:

  - CO(A), CO(a)
  - OH(A) when O_2 Present
  - NH(A) when NO Present
  - $Br_2(D)$

Kinetic & Laser Fluence Trend Analyses of the Chemiluminescence:

  - CH + O
  - CH + O_2 (NO)
  - CBr_2 + O

- 248-nm Photolysis of CBr_4/O-atom Mixtures
  - CBr + O
  - CBr_2 + O

- Thermospheric O-atoms + Plume Fragments (CH) ® UV Emissions