Chemistry in Action: Space Shuttle Fuel Chemistry

Ghanshyam L. Vaghjiani

Space and Missile Propulsion Division
Propellant Branch
Air Force Research Laboratory
AFRL/PRSP
10 E Saturn Blvd
Edwards AFB, CA 93524, USA

Tel: 661 275 5657
Fax: 661 275 6245
Email: ghanshyam.vaghjiani@edwards.af.mil

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Outline

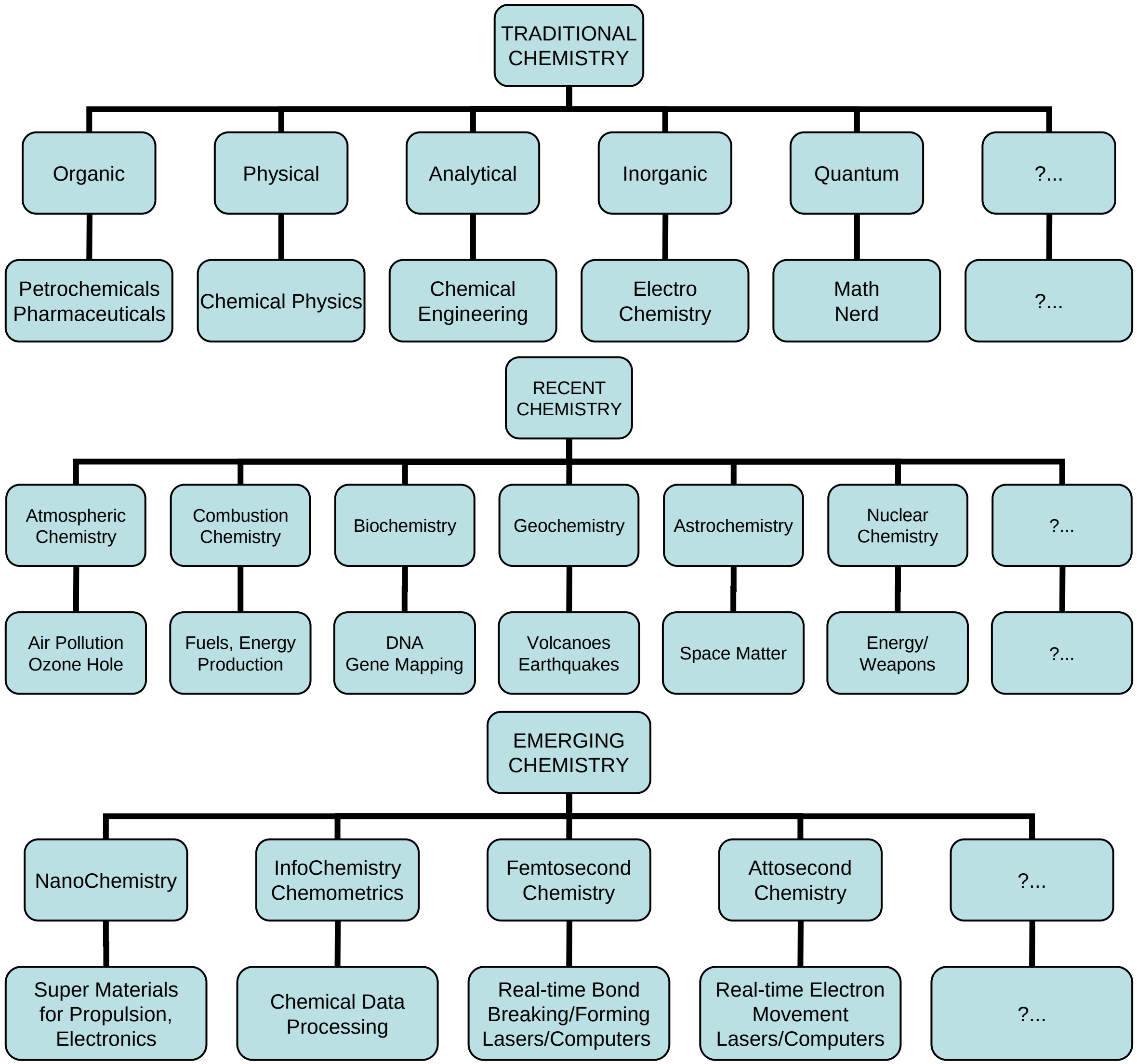
- Student’s Perception of Chemistry
- Role In Science and Technology
  - Traditional Areas
  - Recent and Emerging Technologies
- Space Shuttle-Atmospheric Interactions
- New Hypergolic Fuels
- Closing Remarks
  - Acknowledgements
  - Career in the Government
  - Web Resources

Student's Perception of Chemistry

- It is too Hard! Too Much Math! I do not Like Cooking!
- It is Only for Academicians!
- What use is it for Getting Good Jobs?
- I Also Thought This! Until I met my Mentor, Ian Worthington

- Definition:
  - Study of MATTER and the Changes That Take Place With That MATTER
- Importance:
  - MATTER is Everywhere! Therefore it Matters a lot!
    - To Understand the Energetics of Breaking and Making Chemical Bonds
    - We Seek Microscopic Explanation of Macroscopic Changes we Experience

Role in Science and Technology



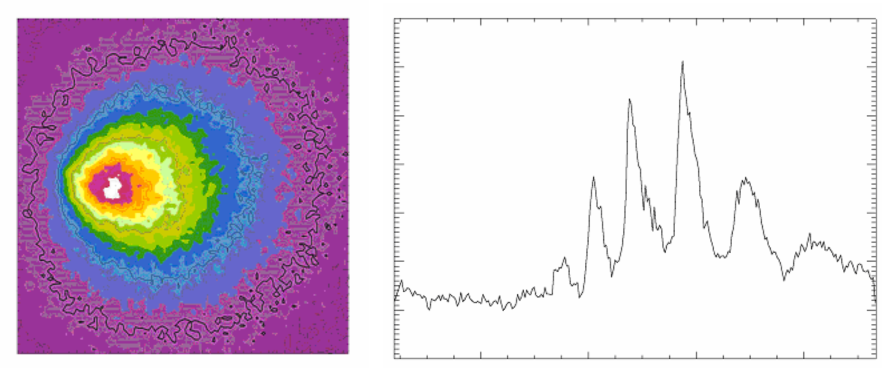
Space Shuttle Propulsion System

- Space Propulsion (PRC, OMS, Veneers):
  - Hypergolic Liquids
    - $CH_3NHNH_2 + N_2O_4 \rightarrow$ products + ΔH
      - NO External Ignition Required!
- Boost Phase (2 x 3.1 Mlb):
  - Solids
    - HTPB + $NH_4ClO_4 \rightarrow$ products + ΔH
      - One-time Squib
- Launch (3 x 0.4 Mlb):
  - Cryogenic Liquids
    - $2H_2 + O_2 \rightarrow 2H_2O + \Delta H$
      - One-time Torch

Space Shuttle-Atmospheric Interactions

- **AFRL's Motivation:**
  - **Understand Chemiluminescent Processes at ≥ 200 Km**

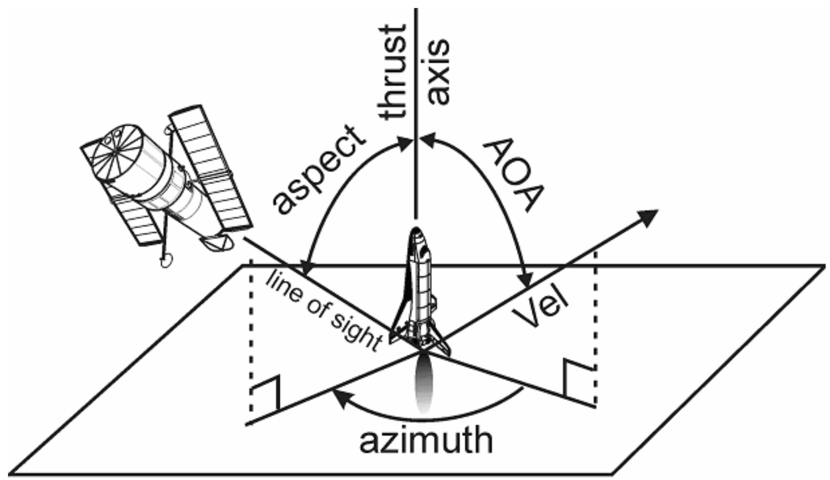
- Strong Emissions From CO(a):



- Cause of Chemiluminescence:
  - Rocket Plume-Atmospheric Interactions

- UV-Chemistry Questions:
  - Precursors?
  - Its Formation?
  - Its Reactions?

- Space Experiment



Observation Platforms	Thrusters
Space Shuttle	Space Shuttle
Mir Space Station	Progress-M
MSX	Soyuz-TM

Proposed CO(a) Source Chemistry

- Unreacted $CH_3NHNH_2 \rightarrow\rightarrow$ Precursor(s)
- Precursor(s) + O $\rightarrow$ Products

  $\rightarrow CO(a_{(v')}) + R$

  $\rightarrow CH_2 + OR'$

  $\rightarrow CH + OR''$

- ❑ 200 km-Thermosphere
  - ❑ $[O] >> [O_2]$

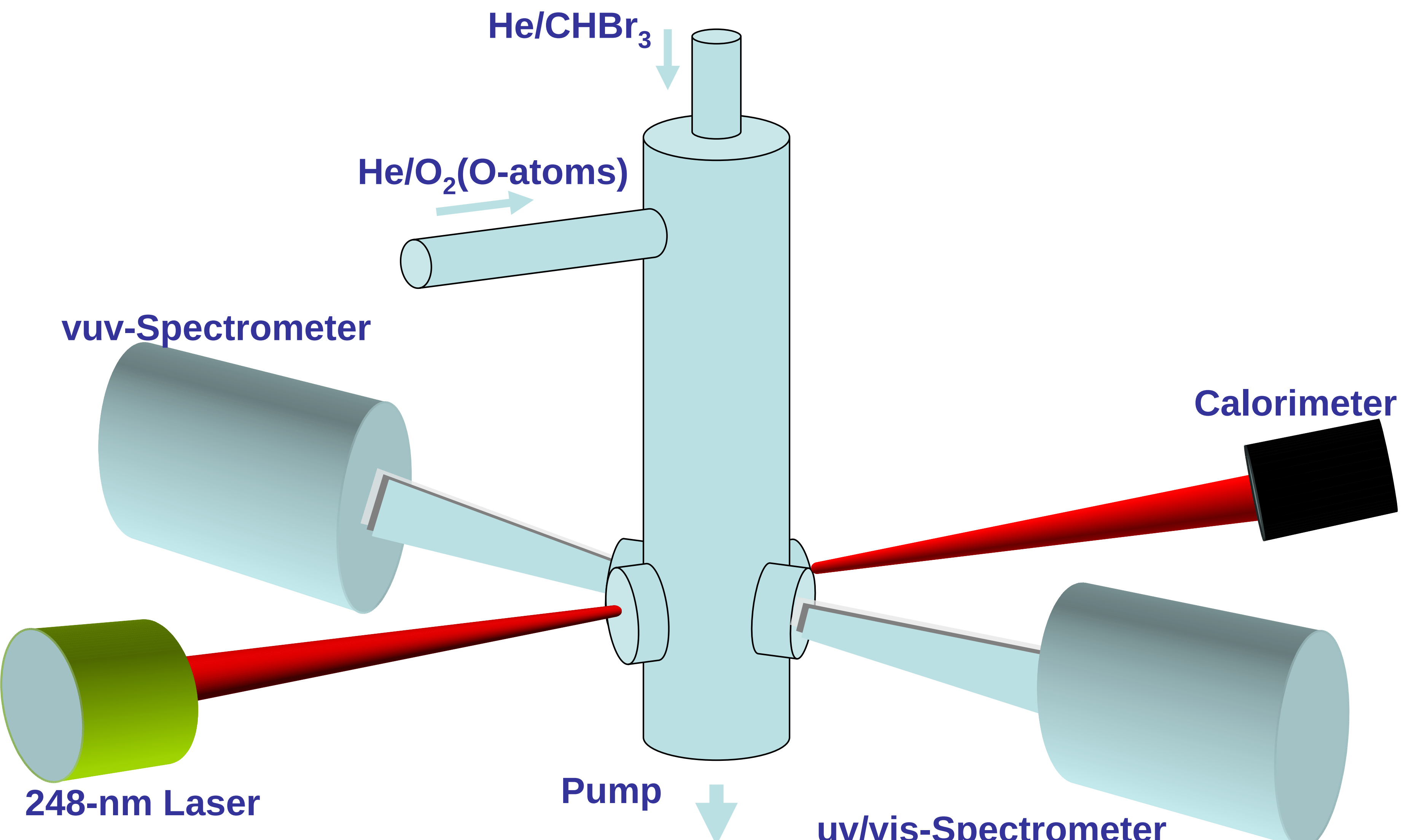
- $CH_2 + O \rightarrow$ Products ($k = 1.3 \times 10^{-10}$) → { $CO + H_2$ (Main); $2H + CO$ (~ 20%); $H + HCO$ (HCO*); $CH + OH$ (~ 6%) }

  $\rightarrow CO(a_{(v'\leq 8)}, a'_{(v'\leq 5)}, d_{(v'\leq 1)}) + H_2$

- $CH + O \rightarrow$ Products ($k = 9.5 \times 10^{-11}$) → { $CO + H$ (Main); HCO (HCO*); $HCO^+ + e^-$ (~ 0.03%); $C + OH$ (? +ve E_a) }

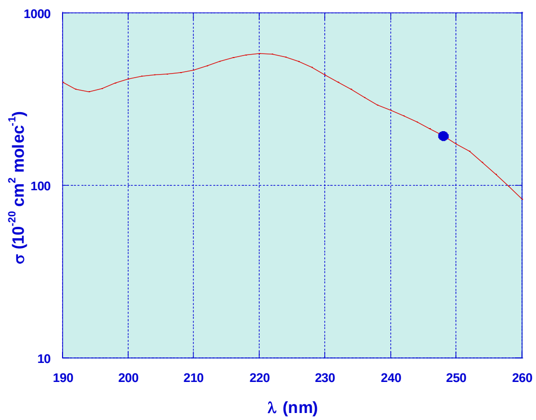
  $\rightarrow CO(a_{(v'\leq 8)}, a'_{(v'\leq 5)}, d_{(v'=0)}) + H$

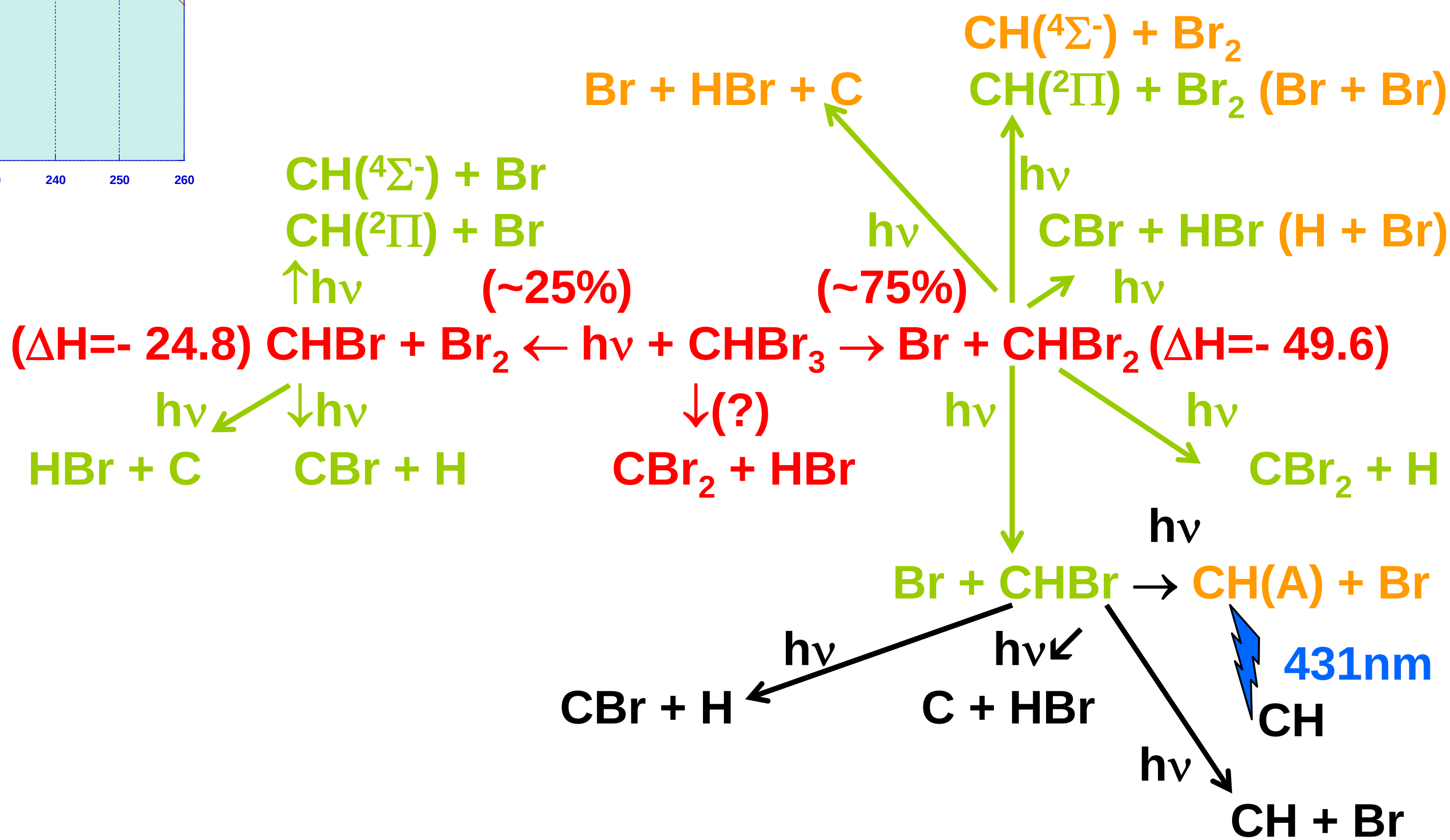
Apparatus



He/CHBr3
He/O2(O-atoms)
vuv-Spectrometer
Calorimeter
248-nm Laser
Pump
uv/vis-Spectrometer

$CHBr_3$ Photolysis To Produce CH Radicals





CO(A) Source Reactions

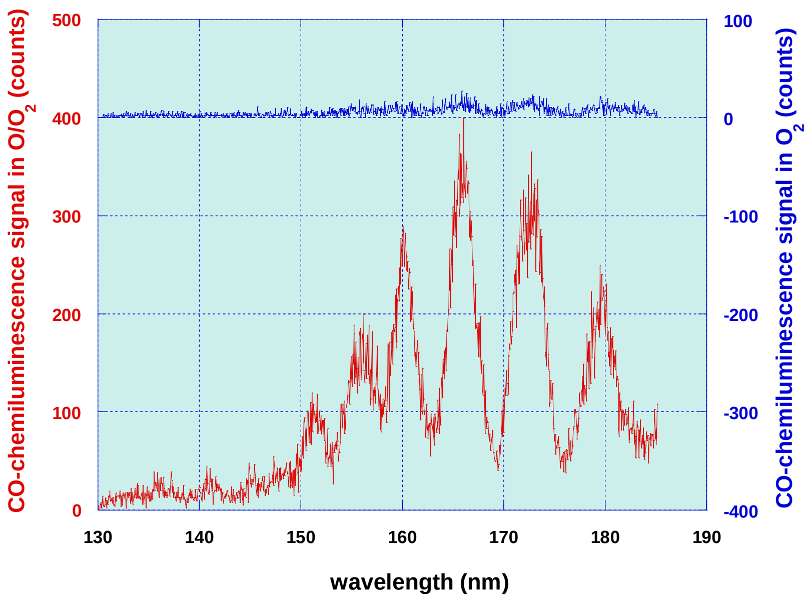
- Chemiluminescence Intensity Varied as $(\text{Laser Fluence})^2$

Reaction	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

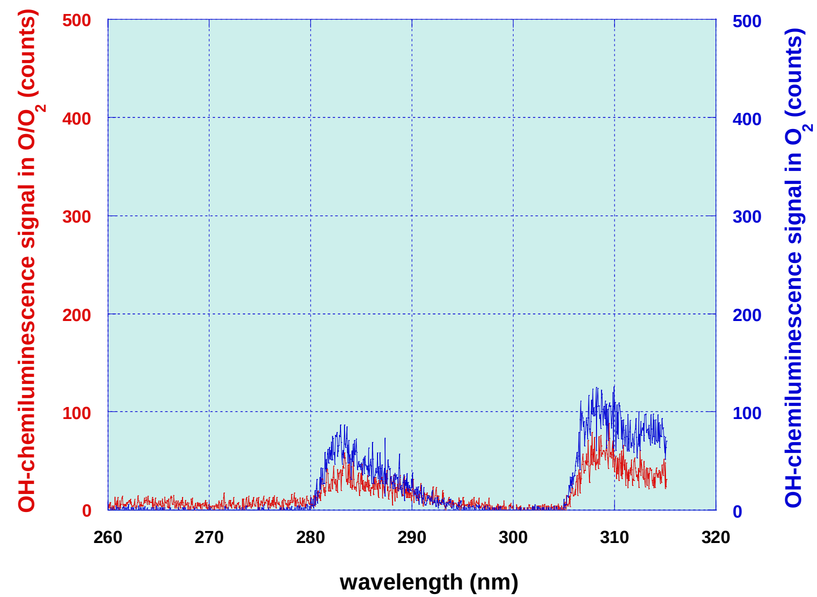
Comparison of CO & OH-Chemiluminescence

Strong CO(A) Signal in O/O_2



Very Weak CO(A) Signal in O_2 only

Weakened OH(A) Signal in O/O_2



Strong OH(A) Signal in O_2 only

$k = (2.3\text{-}5.9) \times 10^{-11}$

CH + $O_2 \rightarrow$ Products

$\rightarrow CO(a_{(v' \leq 4)}, a'_{(v'=0)}) + OH$

- CO + OH (~ 20%)
- CO_2 + H (~ 30%)
- HCO + O (~ 20%)
- H + CO + O (~ 30%)
- CO + OH(A) (~ 0.48%)

Time-Resolved CO(A)-Chemiluminescence

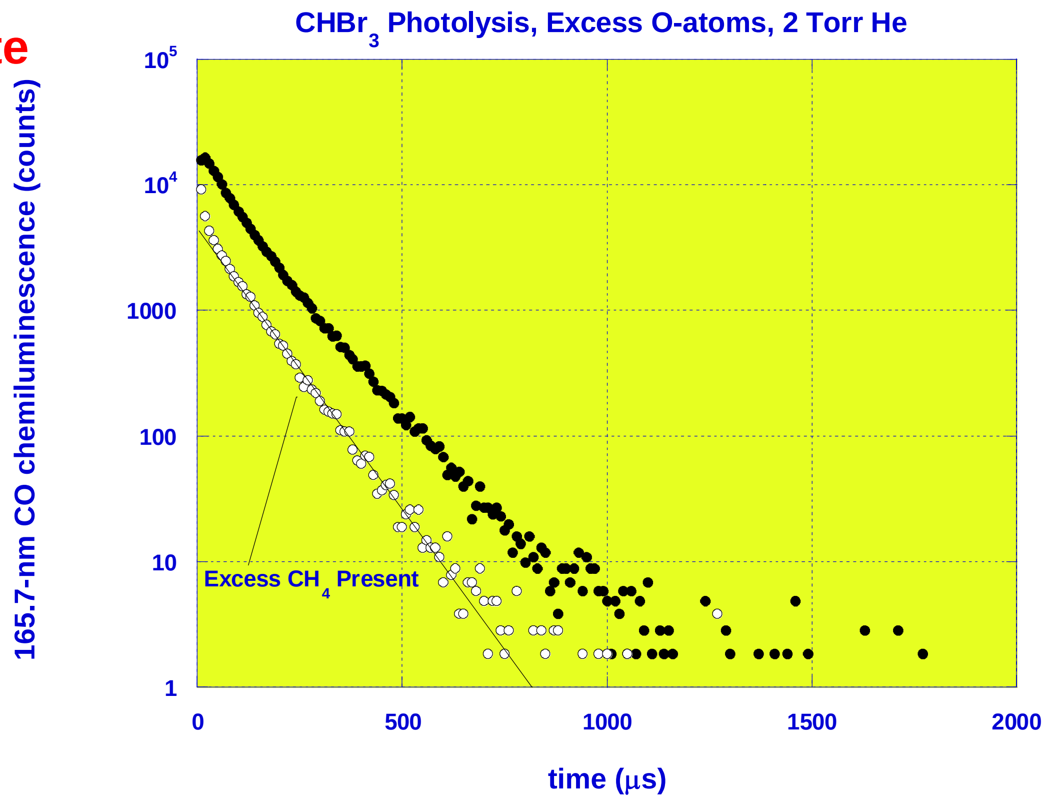
- **Bimolecular Reaction Rate Coefficients of Added Substrate When CH_4 Present**

↓

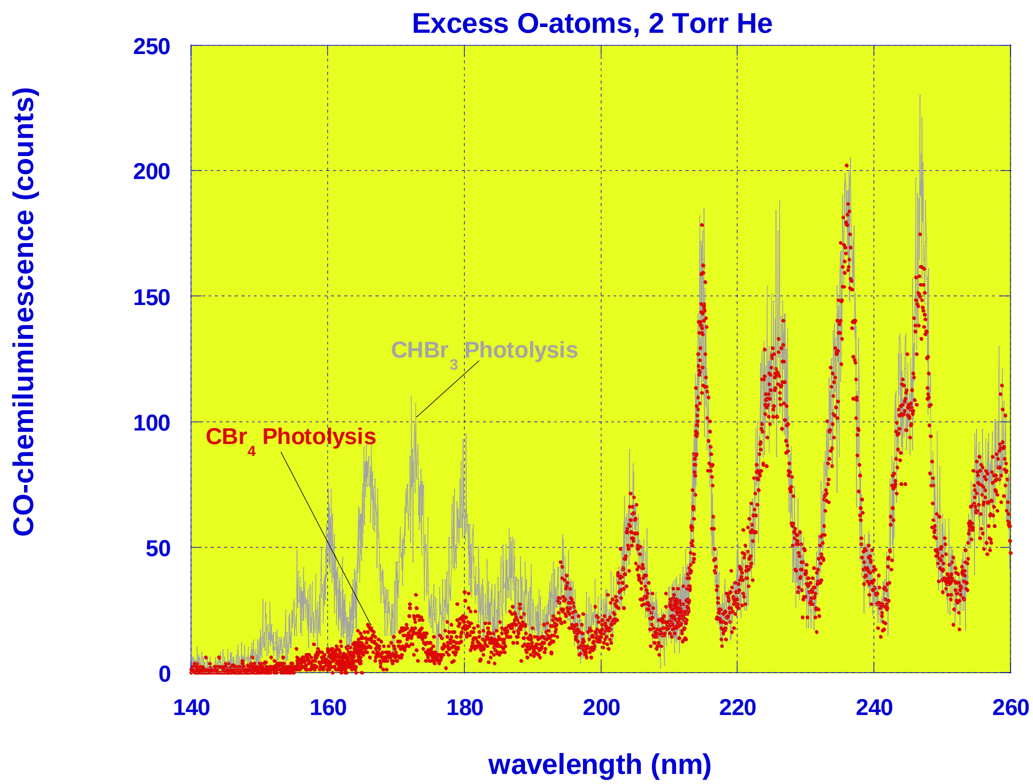
$k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$
$k_{N_2O} < 7 \times 10^{-14}$
$k_{NO} = (3.4 \pm 0.5) \times 10^{-11}$
$k_{H_2} < 2 \times 10^{-13}$
$k_{CH_4} < 6 \times 10^{-14}$

↓

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



$CHBr_3$ Versus CBr_4 Photolysis



- **Stronger VUV Signal in $CHBr_3$ Photolysis**

↓

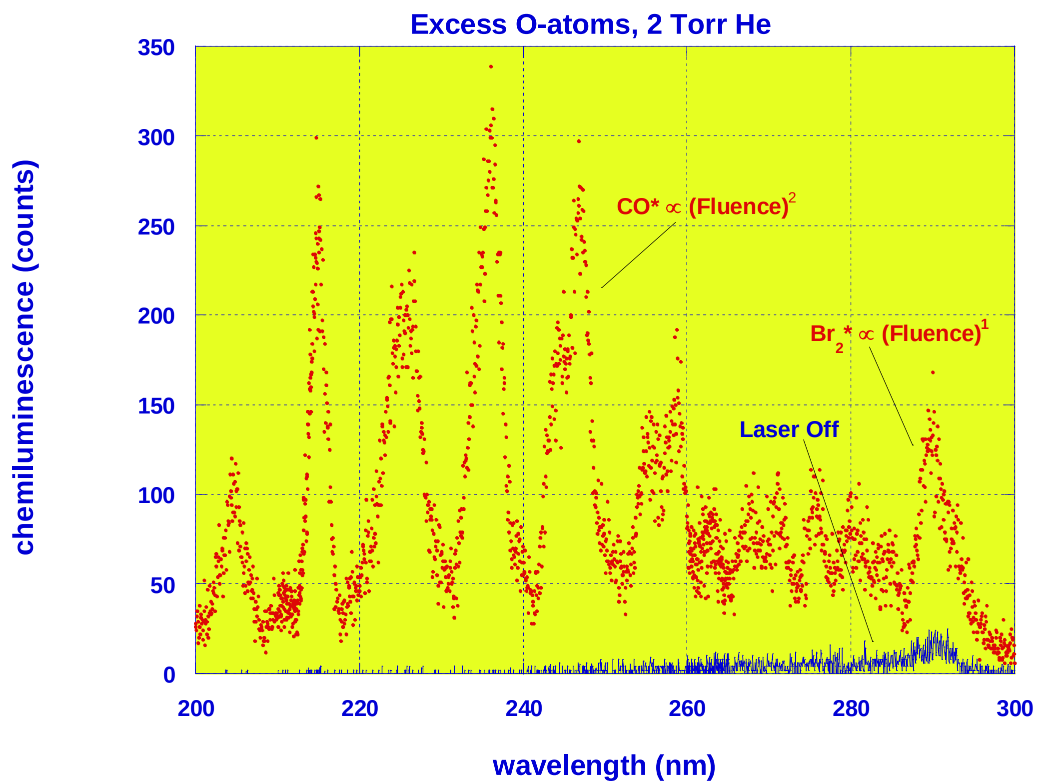
($CH^{\#}$ (or $CHBr^{\#}$) + O) Important

- **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

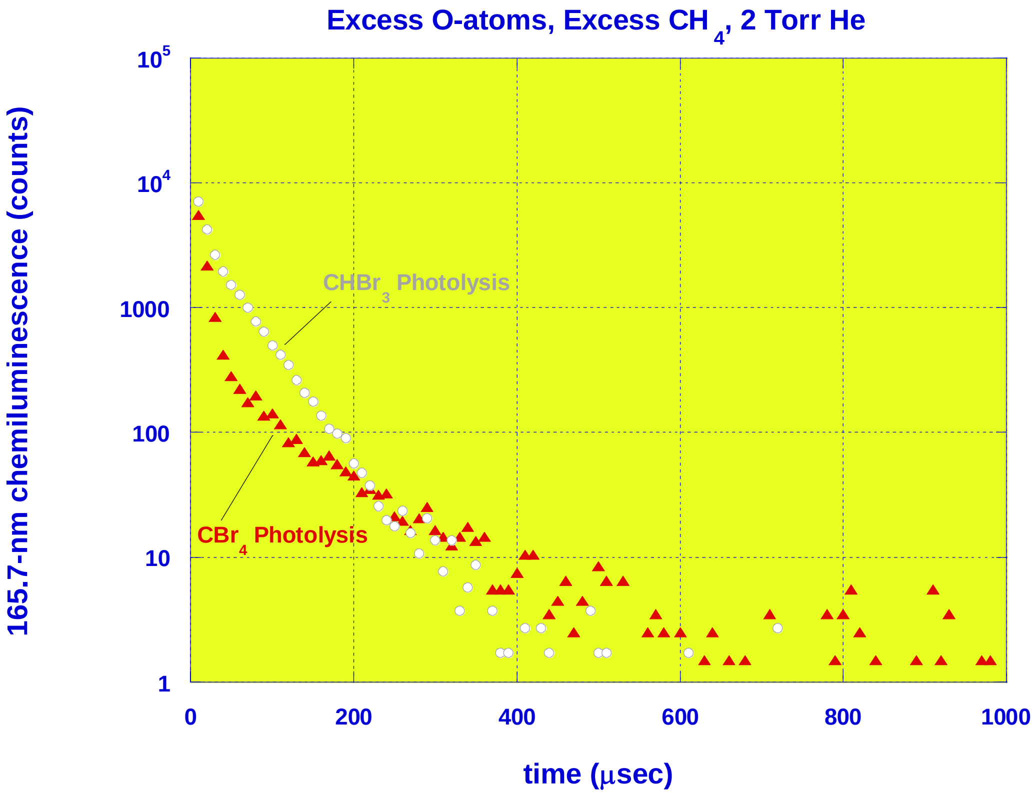


- $CBr_2 + O \rightarrow CO + Br_2^*$
- CBr_2 Formed in Absence of Photolysis
- CBr_2 Formed in Photolysis
- $CBr + O \rightarrow CO^* + Br$

↓

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

$CHBr_3$ Versus CBr_4 Photolysis



- $CHBr_3$
  $k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$
- CBr_4
  $k_{O_2} = (2.4 \pm 0.4) \times 10^{-12}$

↓

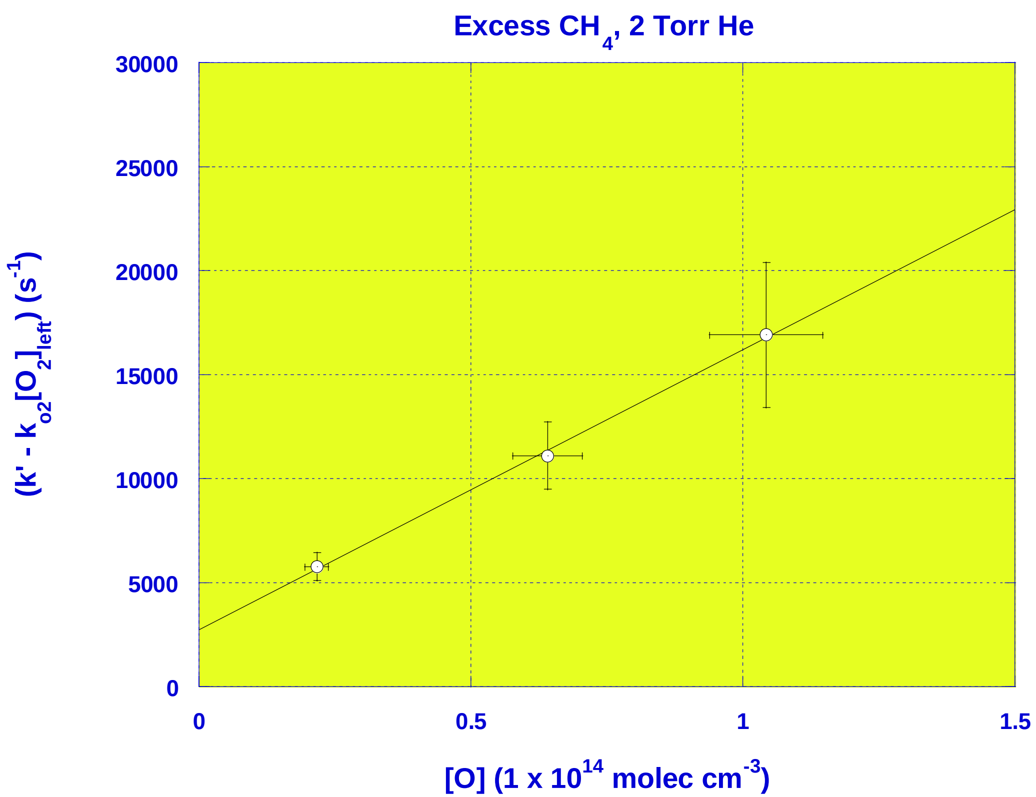
($CBr^{\#}$ + O) Source is not as Important as ($CH^{\#}$ + O) in $CHBr_3$ Photolysis

- $CHBr^{\#}$ has Very Short Lifetime (~ 5 µs) 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:

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

Space Shuttle-Atmospheric Interaction: Conclusions

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

Strong Emissions From:

- CO(A), CO(a)
- OH(A) when O_2 Present
- Br_2(D)

Kinetic & Laser Fluence Trend Analyses of the Chemiluminescence:

- CH($X^2\Pi$, $a^4\Sigma^-$) + O
- CBr_2 + O

- **Plume Fragments (CH) + Thermosphere (O-atoms) $\rightarrow$ UV Emissions**

New Hypergolic Fuels

- **AFRL's Motivation:**
  - **Replace Highly Toxic CH_3NHNH_2 (MMH)**
  - **Design Better Performing Fuels**

- **AFRL's Approach:**
  - **Tune Fuel Structure for;**
    - **Energy Content: High Heat of Combustion**
    - **Oxygen Balance: Lower Spacecraft Mass**
    - **Physical Properties: Higher ρ, Lower mp, Reduced Sensitivities**
    - **Ignition/Combustion Behavior: Short ID Time**

Scape Suit

Cost Reduction in Launch/Health/ Environment

Splash Shield

- **Propellant Performance (I_{sp})**

Fuel + Oxidizer $\rightarrow$ Products + ΔH

$$\Delta H = K.E = \tfrac{1}{2}mv^2$$

$$I_{sp} = (1/g)\int F(t)dt / \int \dot{M}(t)dt = (1/g)(2\Delta H/m)^{1/2}$$

Search For Hypergolic Fuels

- **CEA-Evaluation:** **Identify Better Fuels**

	N_2O_4/MMH	N_2O_4/HEHN	N_2O_4/HEATN
KE($MJ\ kg^{-1}$)	4.7	3.9	4.0
ρ($kg\ m^{-3}$)	1189	1424	1454
FOM	1.0	1.03	1.05

- **Definition:** **A Pair of Compounds, Upon Contact, Chemically React and Release Sufficient Heat to Spontaneously Ignite**

- **Discovery/Research of Hypergolic Propellants:** **1930's, Germany (e.g. BMW)**

- **No *a Priori* Method to Predict Hypergolicity:** **NEW Fuel & Oxidizer Hypergol Pair Must be Experimentally Verified!**

Screening Fuels For Hypergolicity

Drop-test Apparatus Employed: O/F = ~ 20

Fuel	IRFNA	N_2O_4	WFNA
CH_3NHNH_2 (L) (MMH)	HGI	HGI	HGI
$HOCH_2CH_2N^+H_2NH_2\ NO_3^-$ (L) (HEHN)	HGI*	VR	HGI*
(1-ethan-2-ol)-4-amino-1,2,4-triazolium nitrate (L) (HEATN)	SR	VR	
1H-1,2,3-triazole (L)	SR	SR	
1-amino-1,2,3-triazole (M)	HGI*		
3-methyl-1-amino-1,2,3-triazolium nitrate (S)	VR	VR	
▽–≡–H (L)	VR	VR	VR
▽–≡–▽ (L)	HGI*	HGI*	HGI*
▽–≡–≡–▽ (L)	HGI*	HGI*	HGI*

HGI=hypergolic ignition, VR=vigorous reaction, SR=slow reaction. At room temperature, fuel is solid (S), liquid (L), or heated to its melting point (M)
*New hypergols

Fuel Functionality Affects Ignition

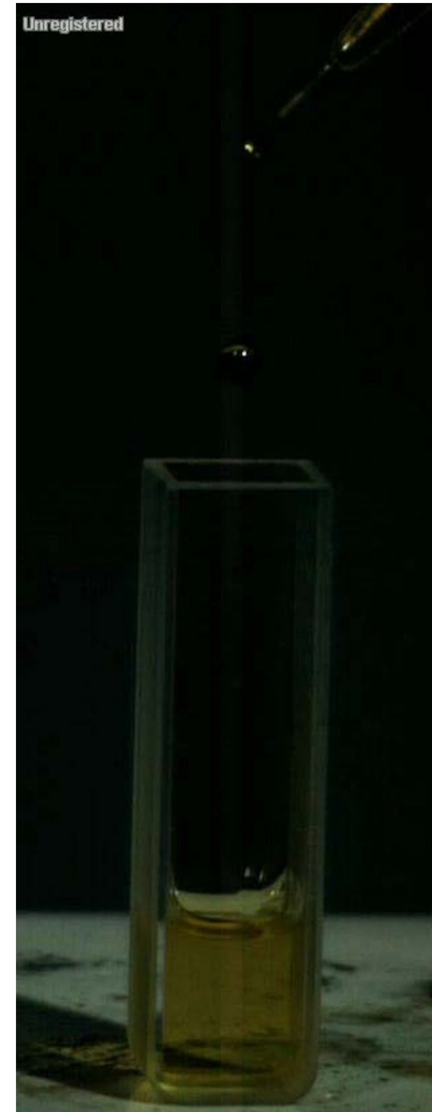
WFNA / ▿–≡–▿ is Hypergolic

▿–≡–H

Not Hypergolic

▿–≡–≡–▿

Is Hypergolic;
ID = 5.0 ms



Complexity of the Pre-ignition Chemistry

▿−≡−▿ / N_20_4

ID = 40.6 ms

New Hypergolic Fuels: Conclusions

- Characterization of Pre-ignition Chemistry is the Key for Designing new Hypergols

- Apply Spectroscopic Probing Tools
  - Rapid-Scan FTIR
  - Time-Resolved Raman
  - Time-Resolved Emission
  - High Speed Video
- Develop Global Initiatory Mechanism
- Construct Pre-Ignition Models
- Kinetic Modeling of Ignition
- Tune Fuel Chemical Functionalities

- Apply Quantum Chemistry Tools
  - ΔH of Intermediates
  - PES (Reaction Coordinates)
  - Reaction Rates
- Provide Initial Rationale to Experimental Observations

Focused/Intelligent Approach to new Synthesis of Hypergolic Fuels

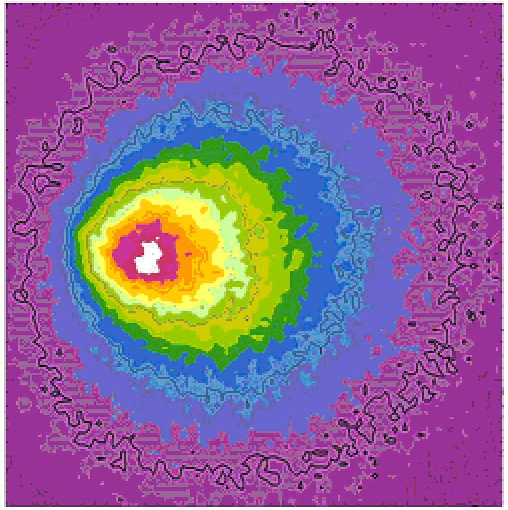
Closing Remarks

- Acknowledgements:
  - AFOSR
    - Drs. M. Berkin & M. Berman ($$$$)
  - AFRL/PRSP
    - Drs. Alfano (Experimental), Mills & Boats (Theory), Suri & Hawkins (Synthesis)
- Career in the Government:
  - DoD
    - AFRL, ONR, ARL, etc
  - DoE
    - LLNL, ANL, ONL, LANL, etc
  - DoC
    - NOAA, NIST, etc
  - NASA
    - Dryden, Ames, JPL, etc
  - And Many More ....
- Web Resources:
  - American Chemical Society www.chemistry.org
  - Edwards AFB www.edwards.af.mil
  - NASA www.nasa.gov
  - New Scientist www.sciencesjob.com

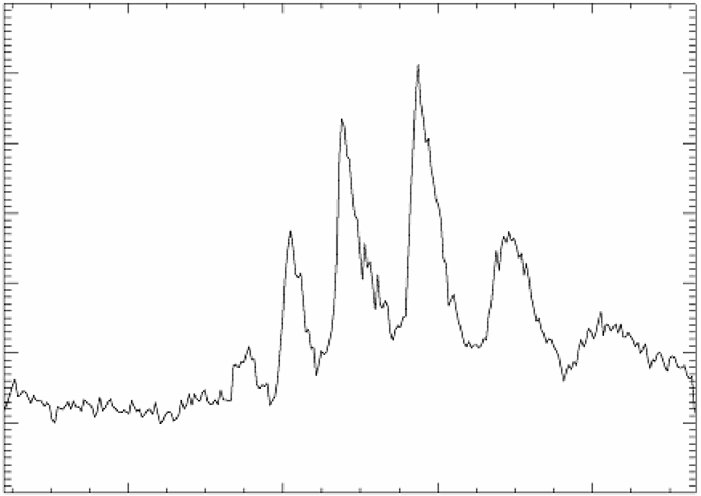
Backup Slides

UV/Vis Plumes

Radiance Data



Spectral Data



⇔ **Plume Data** ⇔

⇳

Modeling Studies

⇳

Laboratory Studies

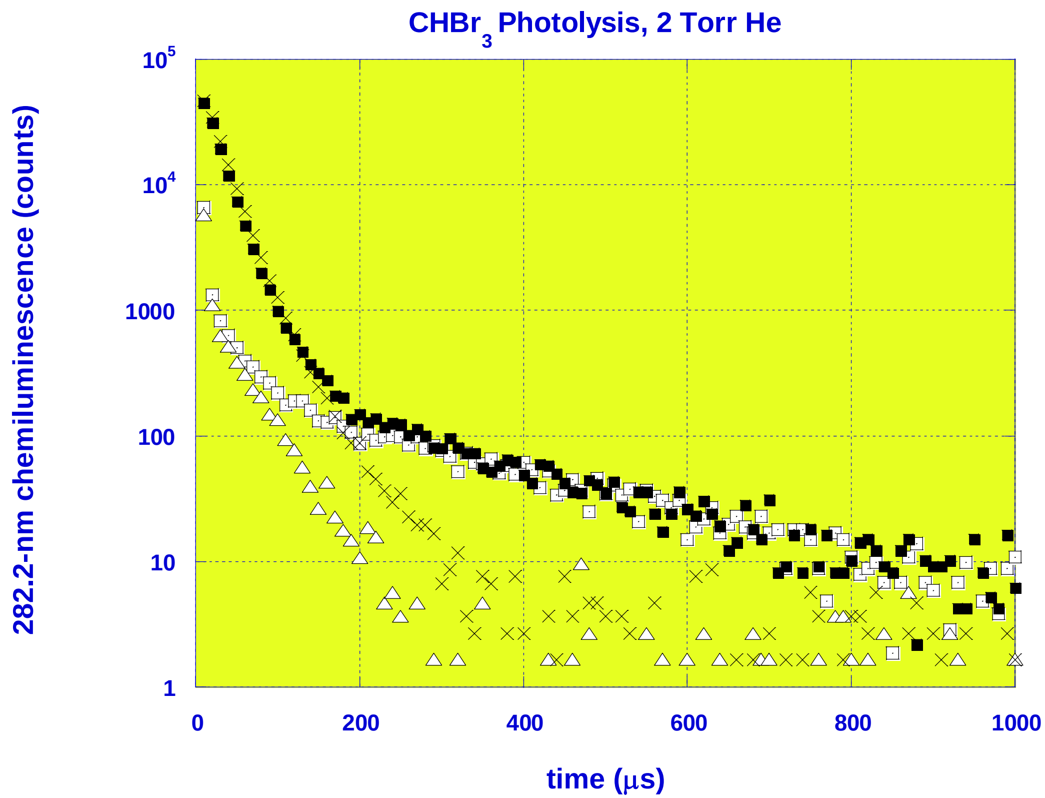
⇳

Chemiluminescent Processes

⇳

Identify Spacecraft Atmospheric Interactions

282.2-nm Signal



❑ **Absence of O-atoms**

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

↓

$CH(X^2\Pi) + O_2 \rightarrow CO + OH(A)$

$CH(a^4\Sigma^-) + O_2 \rightarrow CO + OH(A)$

❑ **5.0 x 10^{13} of O-atoms**

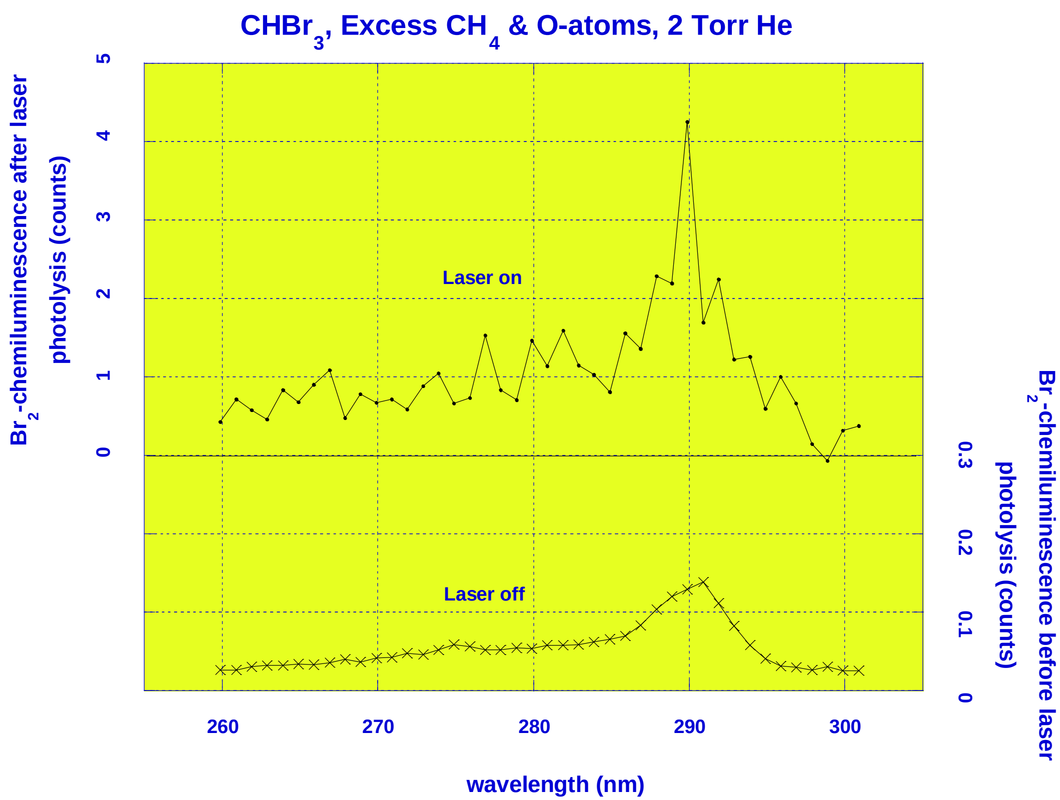
■-trace: (O_2, 8.8 x 10^{14})
□-trace: (O_2) + (CH_4, 5.0 x 10^{15})

↓

$CBr_2 + O \rightarrow CO + Br_2(D)$

(CBr_2 + CH_4) Slow Reaction

Br_2*-Chemiluminescence



- Laser off

$CHBr_3 + O \rightarrow CBr_3 + OH$

$CBr_3 + O \rightarrow CBr_2 + BrO$

↓

$CBr_2 + O \rightarrow Br_2^* + CO$

- Laser on

$Br_2^* \propto (\text{Fluence})^1$

↓

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

$CHBr_3 + h\nu \xrightarrow{?} CBr_2 + HBr$

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

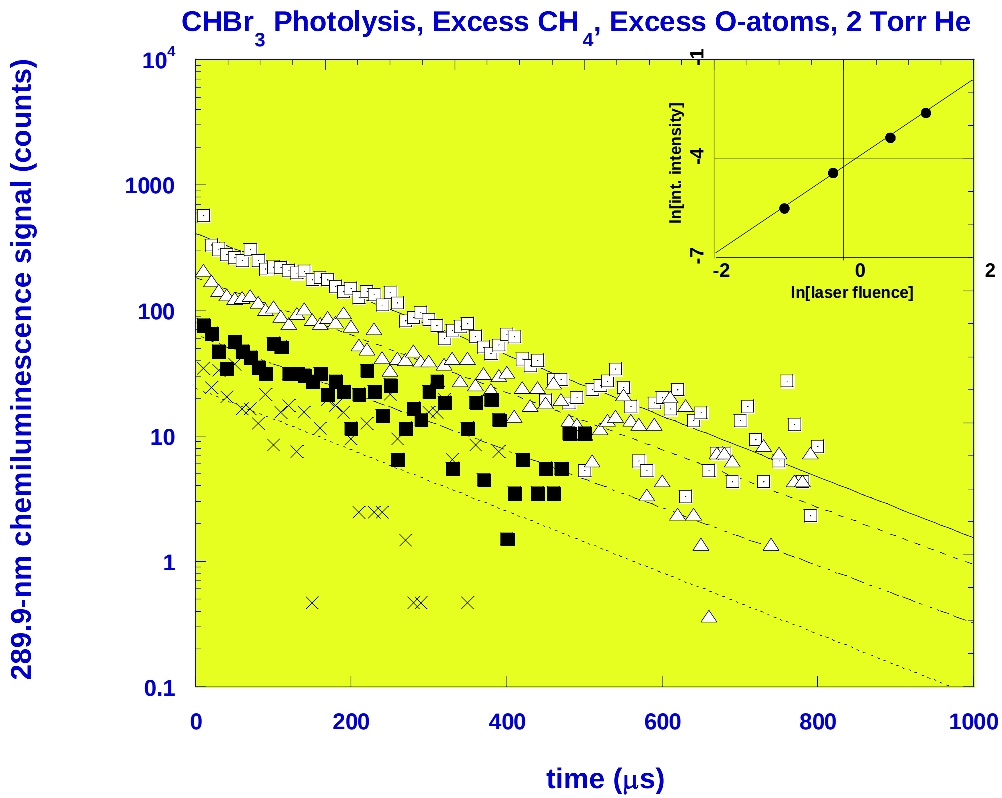
$CHBr_2^* + O \nrightarrow Br_2^* + HCO$

$CHBr_2 + O \rightarrow CBr_2 + OH$

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

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

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:

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

↓

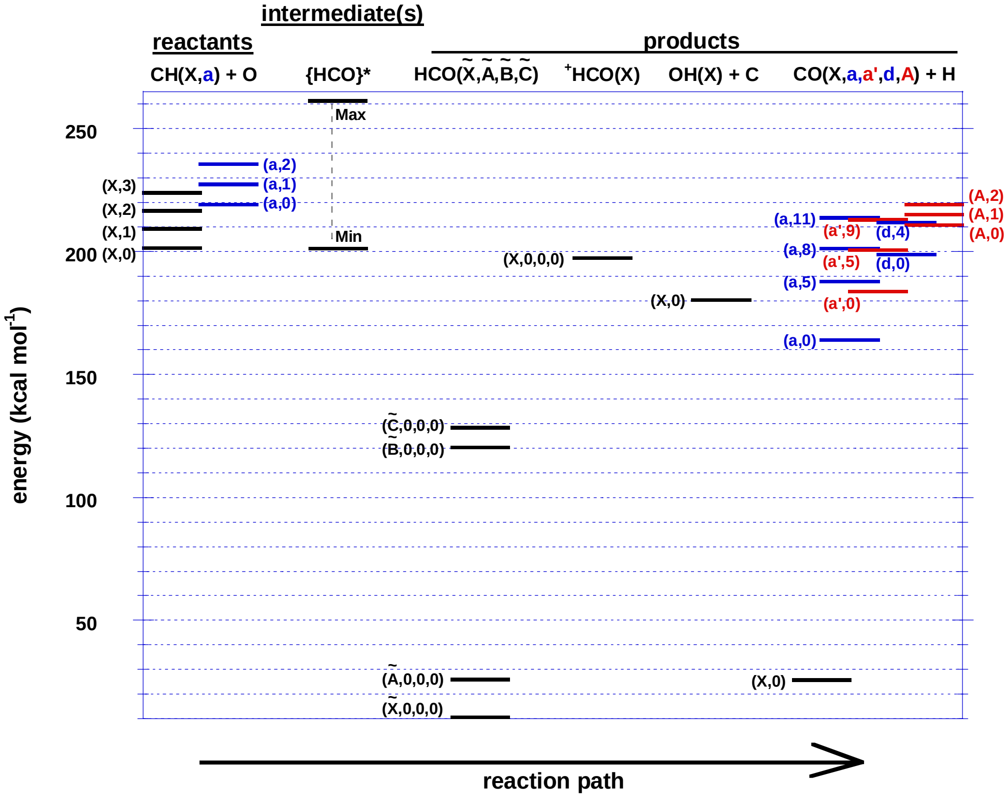
$CBr_2 + Br$ { ϕ?

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

CO* Production Mechanism

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

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



Hypergolic Action

- **No *a Priori* Method:** Hypergolicity Between any Pair of Fuel & Oxidant System Must be Experimentally Verified

- **Know Your Calories:** < 0.05 cc of a Fuel can Lead to a Spectacular Interaction With an Oxidizer

$$2N_2H_4 + N_2O_4 \rightarrow 3N_2 + 4H_2O \quad \Delta H = -279 \text{ kcal/mol } (51 \text{ mg} = 220 \text{ calories})$$