Optical Diagnostics and Modeling of UHTC Volatilization in High-Enthaply Test Environments

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Mo-Si-B Alloys and Diboride Systems for High- Enthalpy Environments: Design and Evaluation

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Contract FA9550-11-1-0201 (09/2011-09/2015, Year 2 budget $143,049)

Developing Diagnostic Tools for Volatile Species Detection During High-Enthalpy Testing

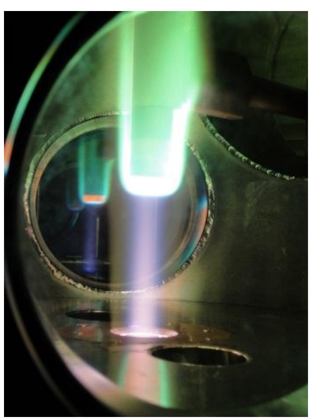
STATUS QUO

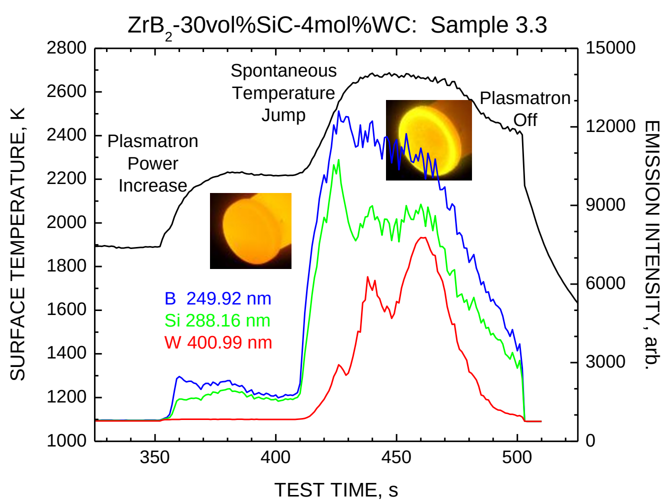
Materials testing in high-enthalpy facilities still relies largely on post-test sample characterization for materials response model development

- Microscopy and various materials analysis techniques provide valuable information about the *net result* of testing,.
- But, *in situ* measurements are needed to validate materials response models for predicting transient behavior.
- Need to move beyond temperature measurements and videos, to more sophisticated in situ measurements.

NEW INSIGTHS

Emission spectroscopy provides information about volatiles during high-enthalpy testing ; useful, but not a *spatially-resolved ground-state* probe.





RECENT PROGRESS

Laser-induced fluorescence diagnostics can probe the ground states of important volatile products like SiO and BO.

- *Spatially-resolved detection and routes towards species quantification*

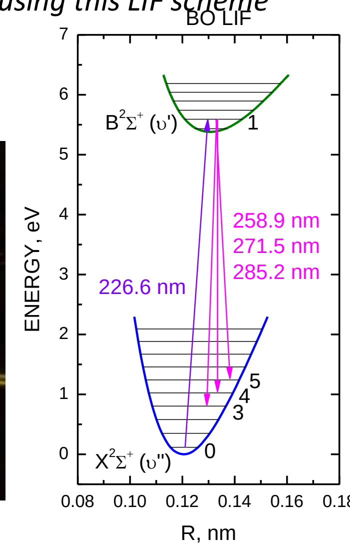
Development of a laboratory source for gaseous boron oxides

- Nitric-oxide-titrated nitrogen discharge with BCl_3 addition.
- Control of BO and BO_2 emission demonstrated
- Ground state BO confirmed

BO_2 (*A*-*X*) BO (*A*-*X*)

BO (*B*-*X*) LIF detection demonstrated

- *First measurement using this LIF scheme*



END-OF-PHASE GOAL

Planned Impact

- Implement LIF diagnostics for Si- and B- species in University of Vermont Inductively Coupled Plasma torch facility.
- Track volatile oxidation and sublimation products in situ and validate models for oxidation and volatilization of Si- and B- species .
- Payoff: Higher fidelity models leading to higher fidelity performance predictions for high-temperature aerospace ceramics and alloys based on silicon and boron constituents

Outline

- Introduction
- Laser-induced fluorescence (LIF) development for BO detection
- Volatility diagrams for dissociated environments

Mo-Si-B Alloys and Diboride Systems for High-Enthalpy Environments: Design and Evaluation

AFOSR Grant: FA9550-11-1-0201

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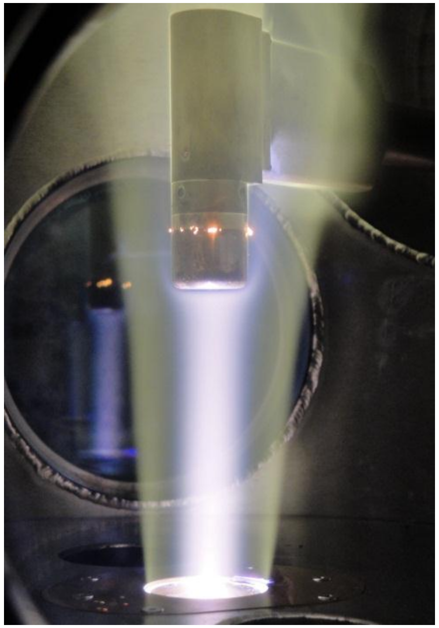
- Understand and control phase and microstructure stability in Mo-Si-B alloys through experiment and modeling.
- Develop coating strategies for Mo-Si-B/diboride composites based on thermodynamic and kinetic design strategies.
- Evaluate the thermal cycling and oxidation behavior of Mo-Si-B alloys, diboride-based materials, and their hybrids under various high-enthalpy aerothermal heating conditions in the UVM ICP facility.
- Develop and implement in situ optical diagnostics for the ICP facility, including: (i) simultaneous surface temperature and emittance measurement capability; (ii) emission FTIR spectroscopy for tracking specimen surface composition; and (iii) emission and LIF diagnostics for monitoring near-surface concentration gradients of key reactant and product species.
- Apply test results and diagnostic information to provide feedback for materials development and for the construction of materials response models of oxide formation, surface morphology, component volatilization, etc.



Volatile Products of UHTC Oxidation, Evaporation, and Sublimation

Si-O system: Si, Si_2, Si_3, SiO, SiO_2, Si_2O_2
B-O system: B, B_2, BO, BO_2, B_2O, B_2O_2, B_2O_3
C-O system: C, C_2, C_3, C_4, C_5, C_6, CO, CO_2

Passive oxidation:
$SiC(s) + 3/2O_2 = SiO_2(s,l) + CO$
$ZrB_2(s) + 5/2O_2 = ZrO_2(s) + B_2O_3(s,l)$

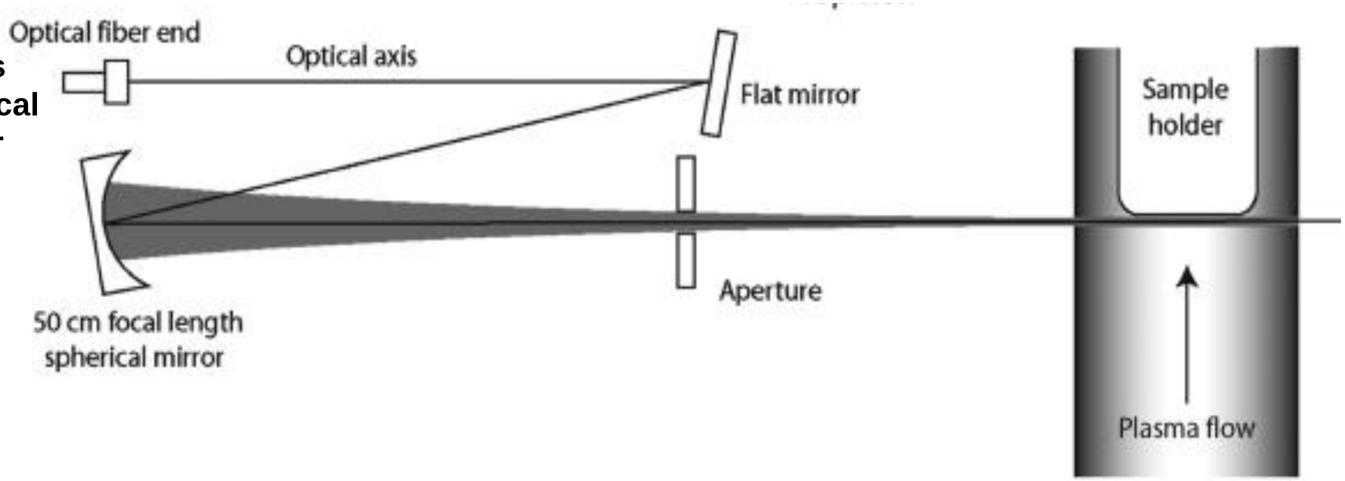
Active oxidation:
$SiC(s) + O_2 = SiO + CO$
$ZrB_2(s) + 2O_2 = ZrO_2(s) + 2BO$

Oxide volatilization:
$SiO_2(l) = SiO_2$ or $SiO + 1/2O_2$
$B_2O_3(l) = B_2O_3$
$B_2O_3(l) + 1/2O_2 = {}_2BO_2$

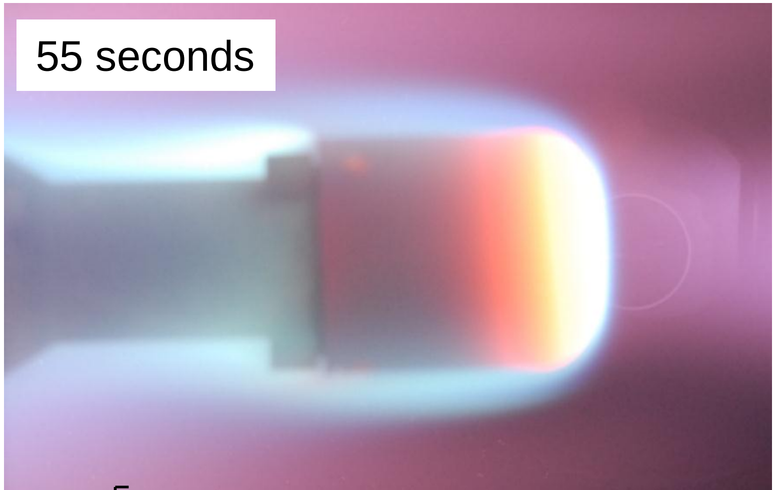

5 sec
15 sec
25 sec
35 sec
45 sec
55 sec
65 sec
75 sec
85 sec
95 sec
105 sec
115 sec
125 sec
135 sec
145 sec

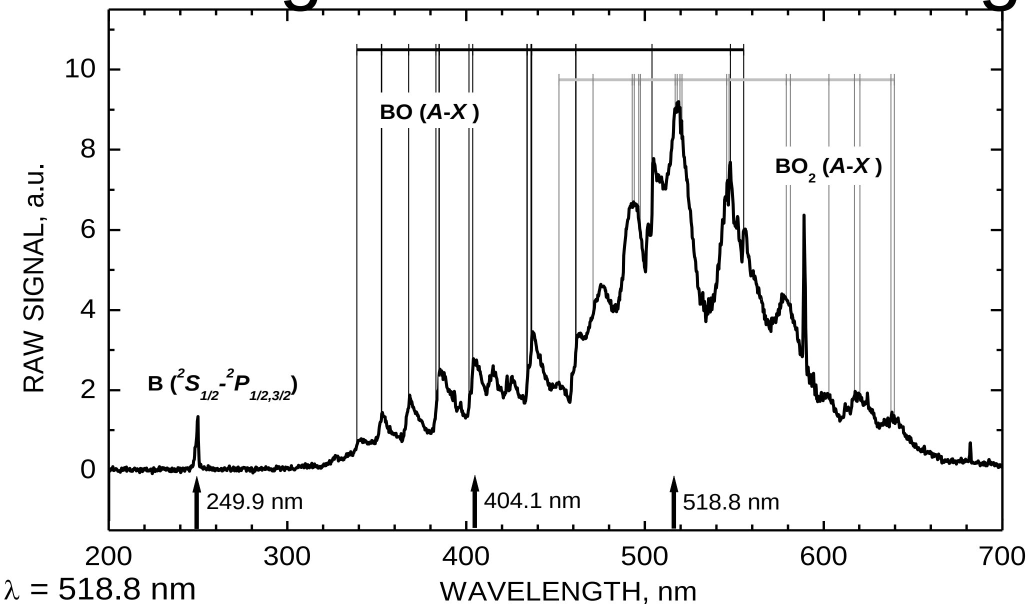
Emission Spectroscopy

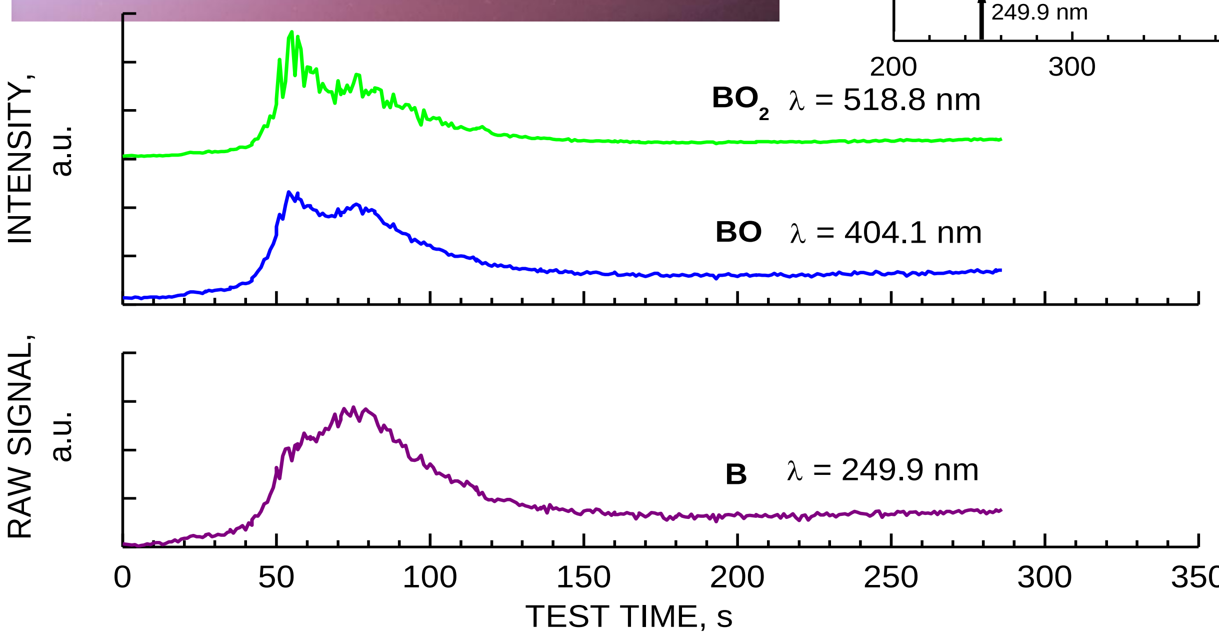
Fiber couples light to an optical spectrometer

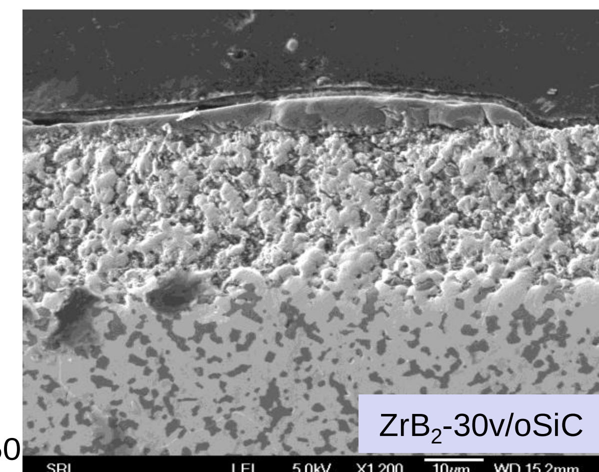


Boron Species Emission during Plasmatron Testing

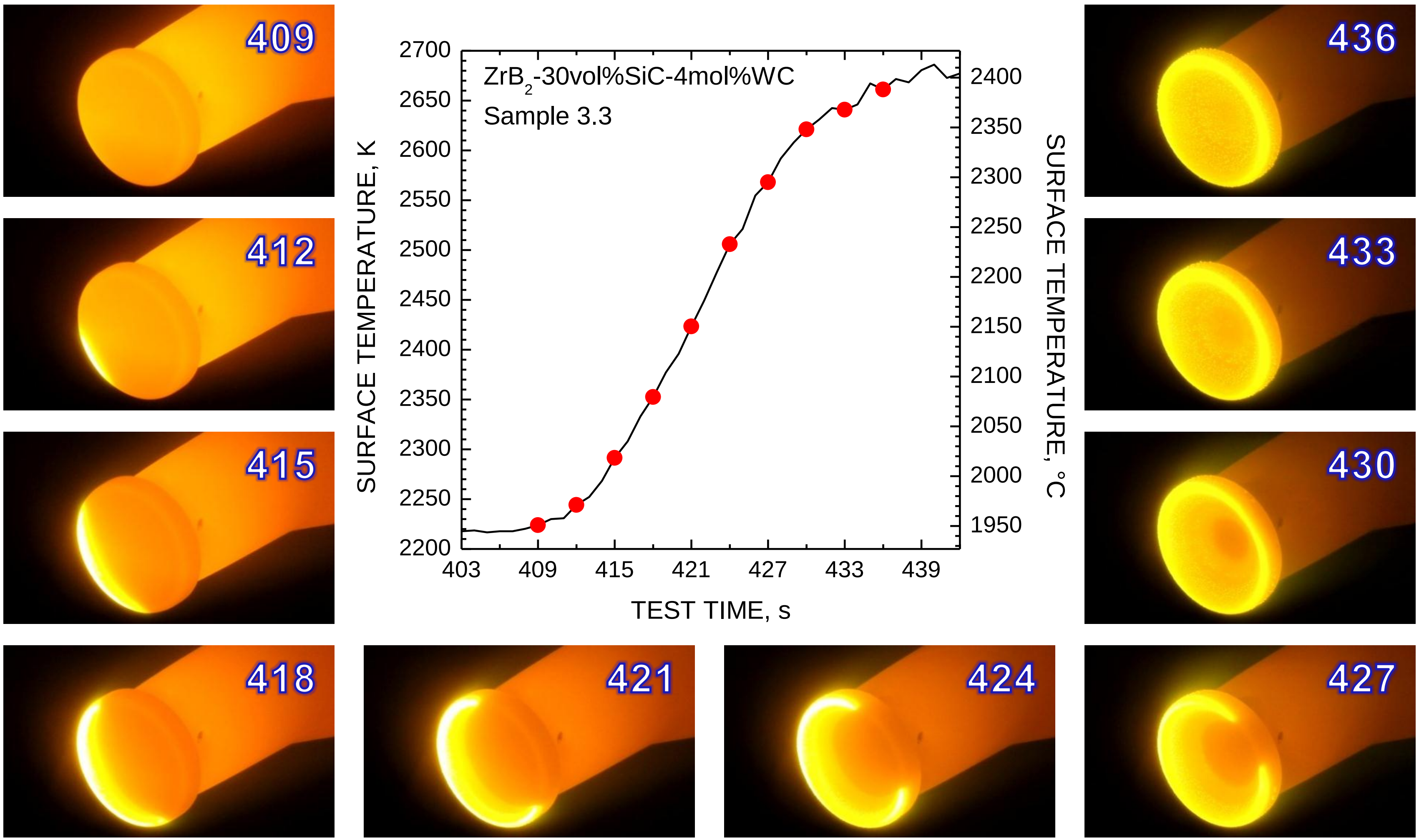




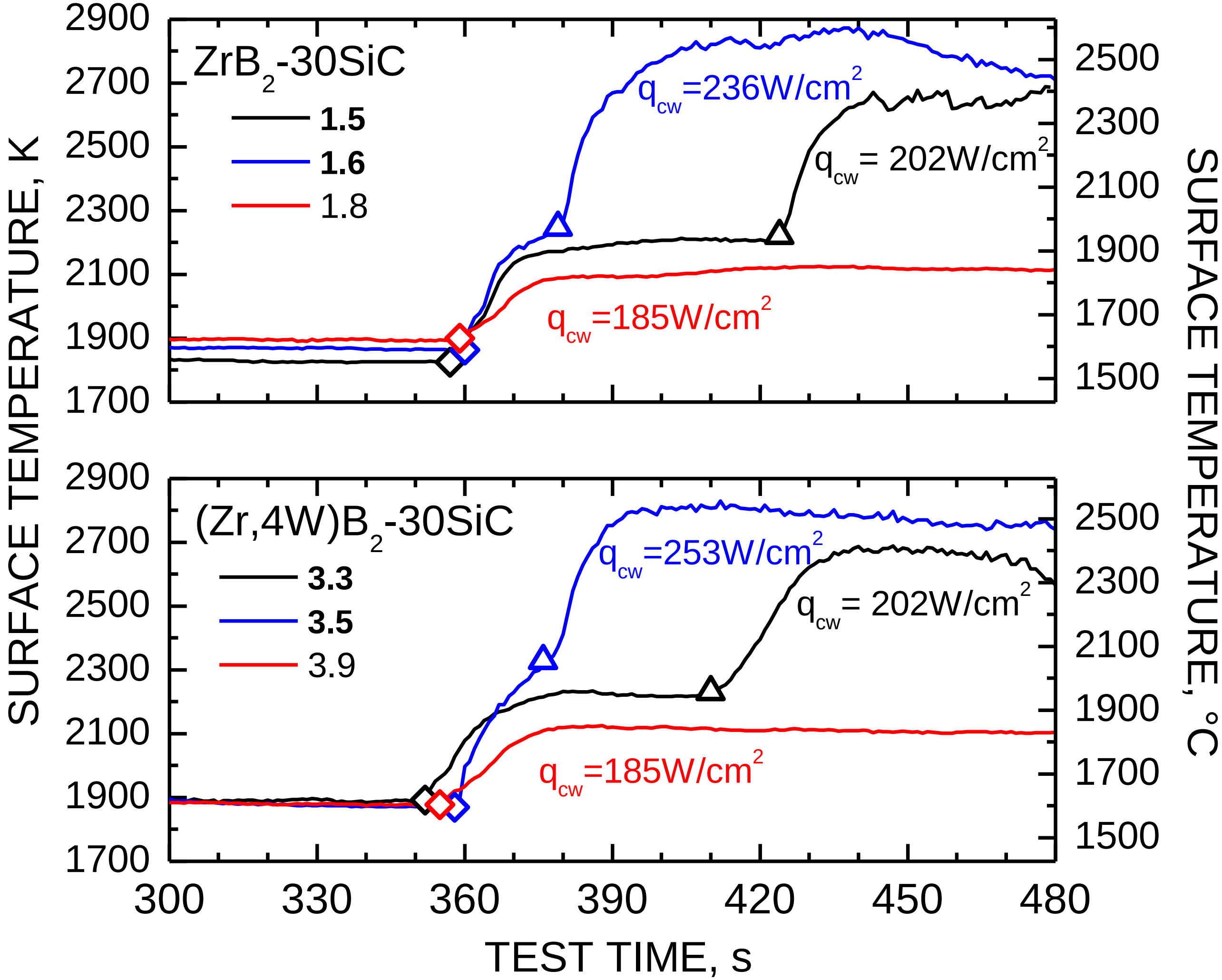




Spontaneous Temperature Jumps during Plasmatron Testing of ZrB_2-30v/oSiC Materials

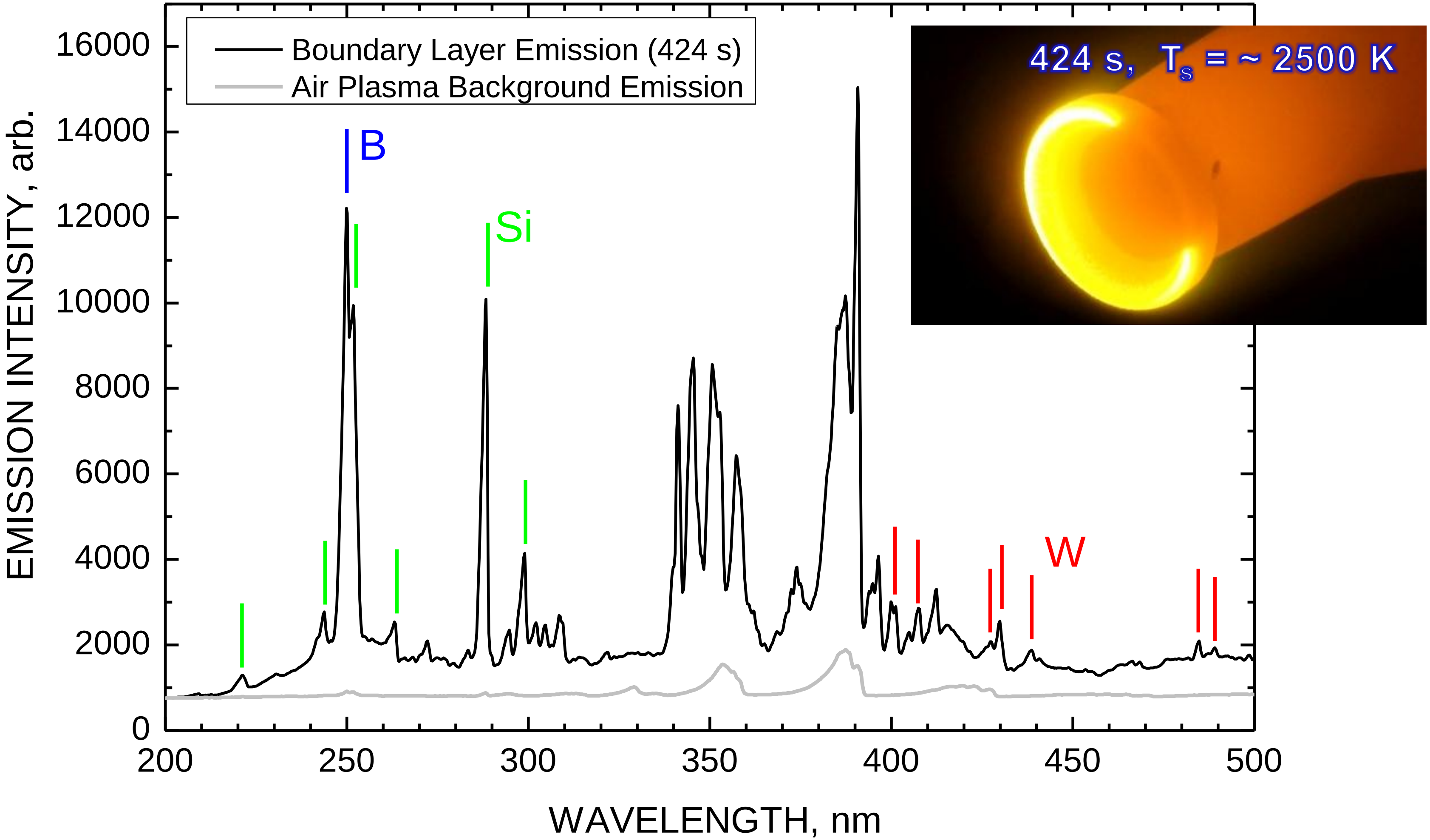


Heating Thresholds for Temperature Jumps

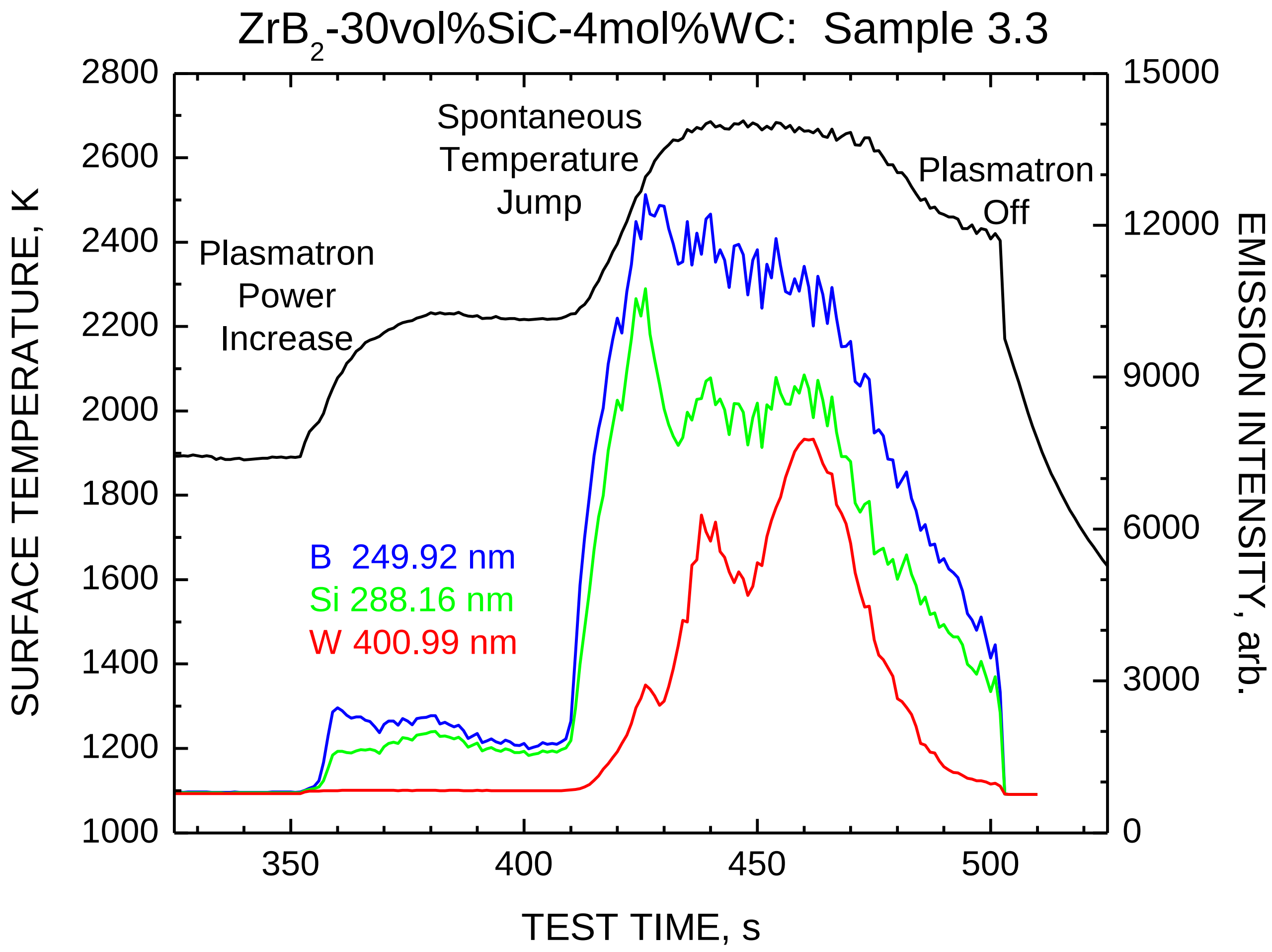


Emission Spectrum during Temperature Jump

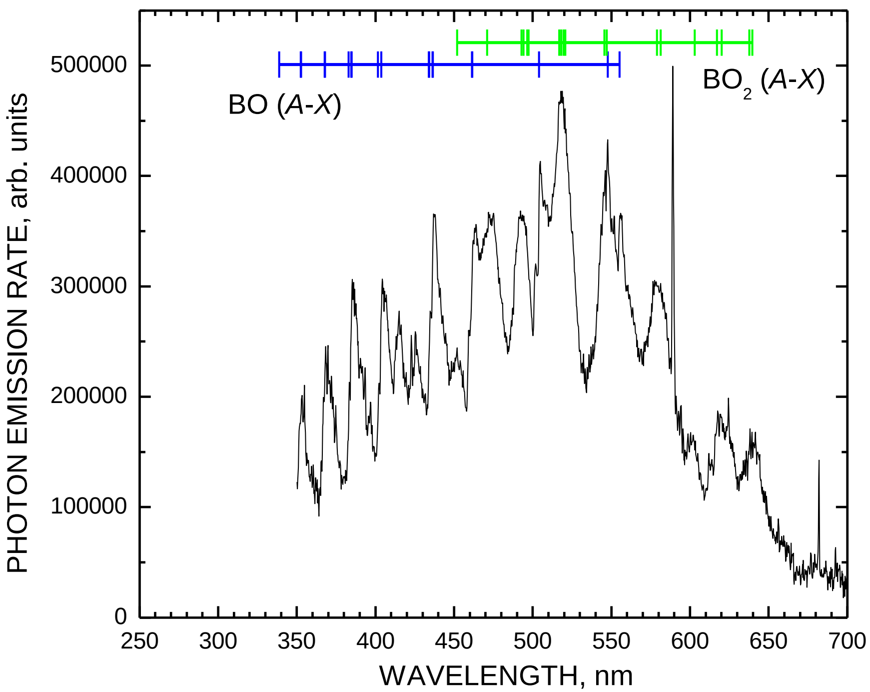
ZrB_2-30vol%SiC-4mol%WC: Sample 3.3



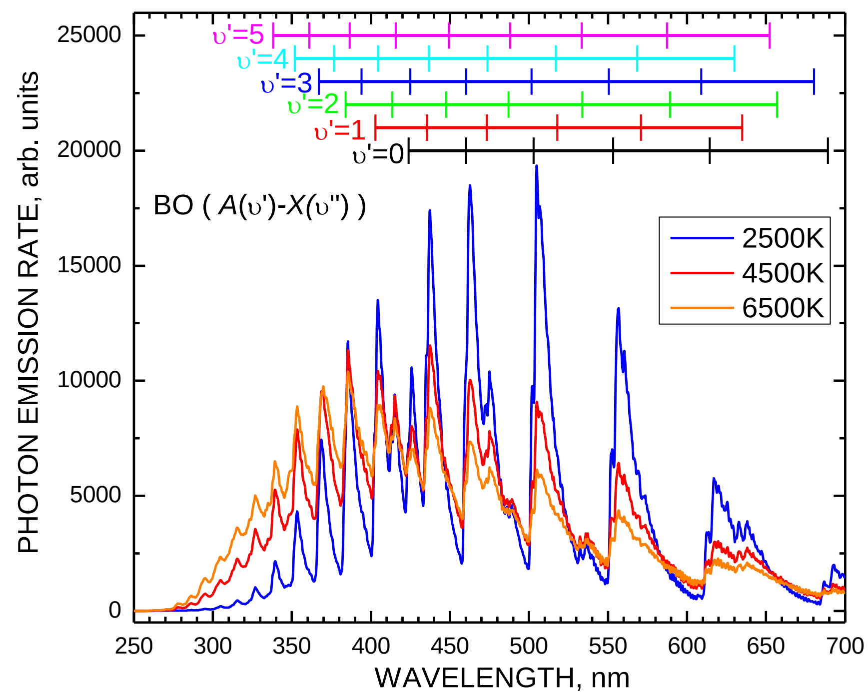
Transient Atomic Emission Signatures



BO Emission Simulation



Experimental intensity-calibrated spectrum

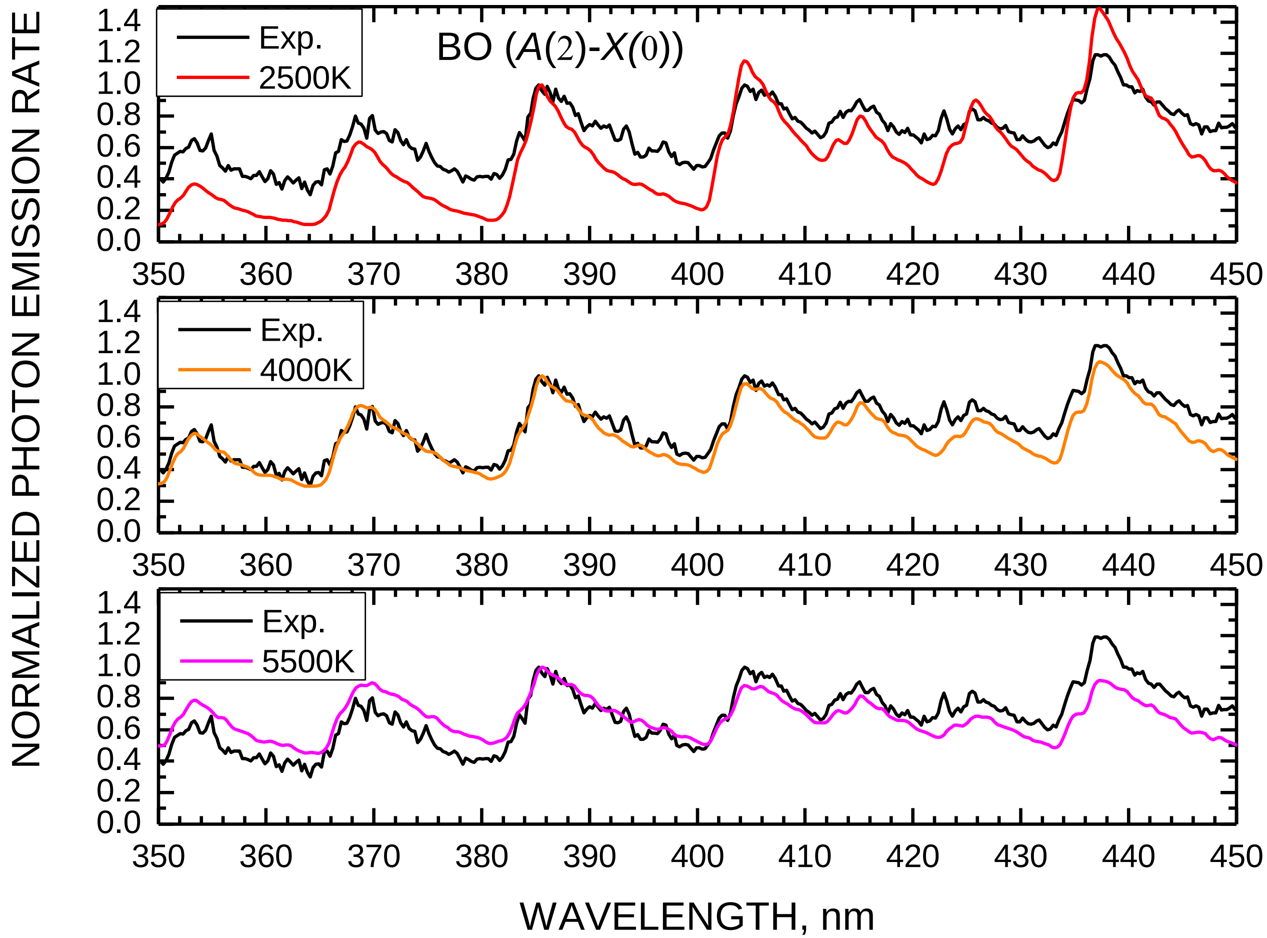


Computed spectrum using Pgopher program

PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk

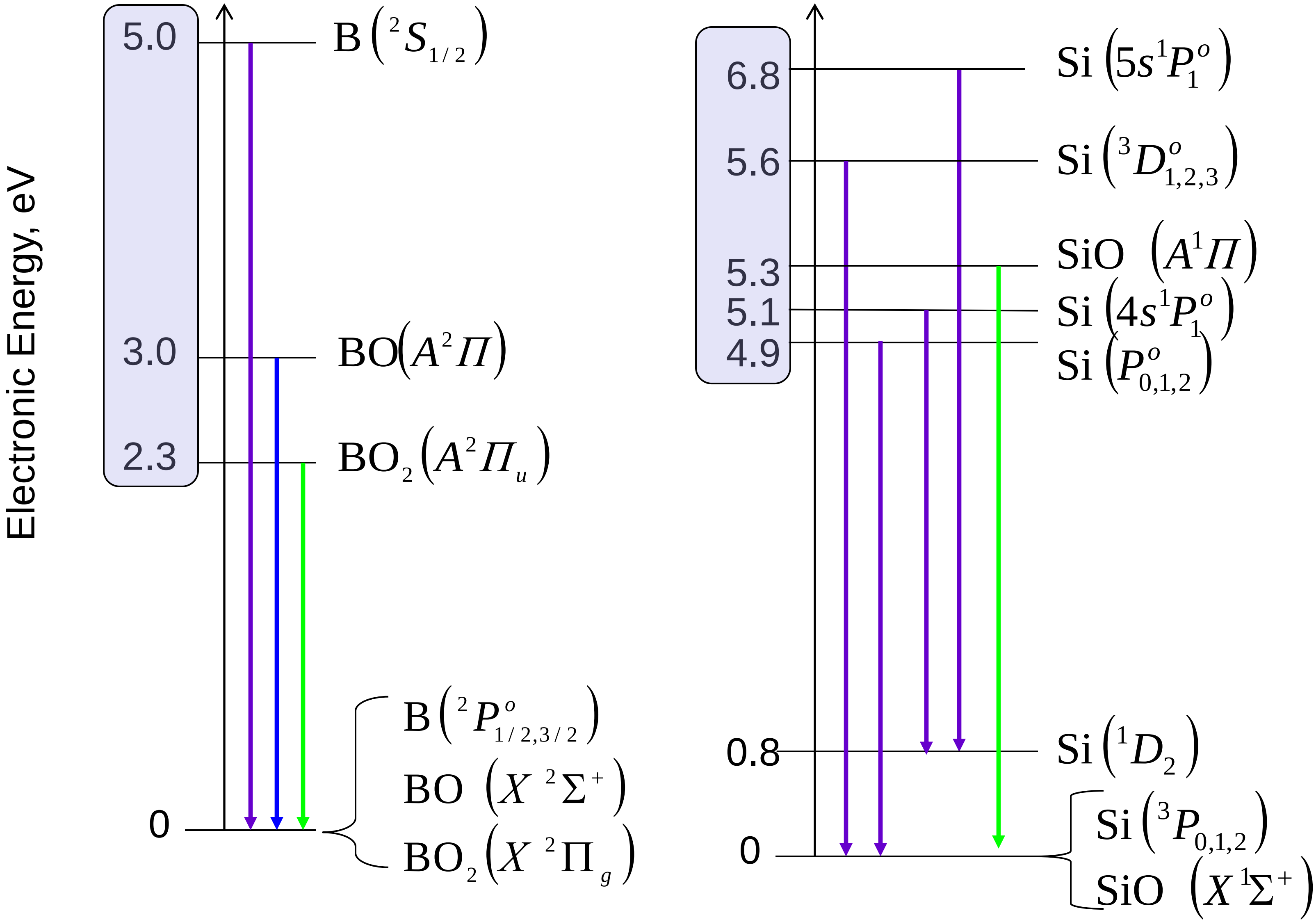
Frank-Condon factors from Liszt & Hyden Smith (1971) and spectral constants for ^{10}BO and ^{11}BO from Melen et al. (1985).

BO Emission Simulation



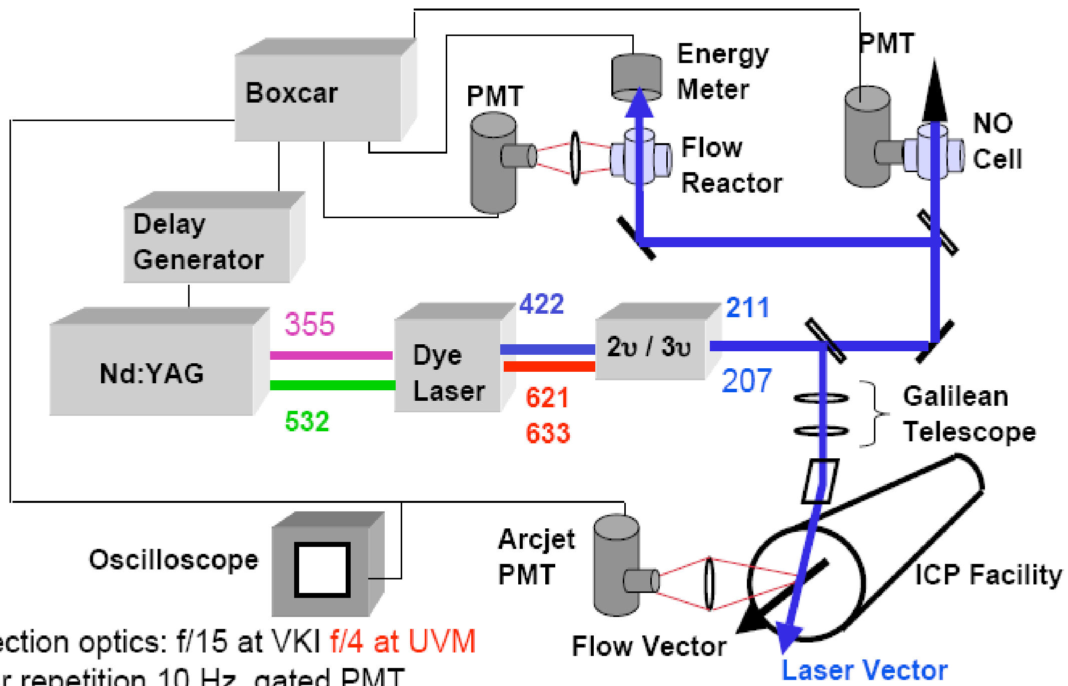
- Surface temperature measured as ~1725 K
- VKI CFD simulations predict ~6100 K free stream and ~ 3000 K 0.5 mm off surface

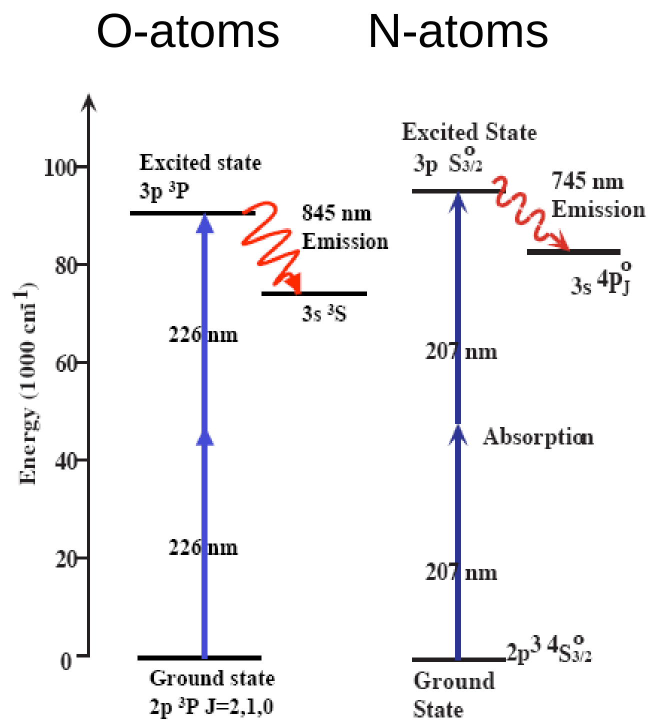
Emission Spectroscopy is Not a Ground-State Probe



One Approach: Laser Induced Fluorescence

Two-Photon LIF of Atomic Species





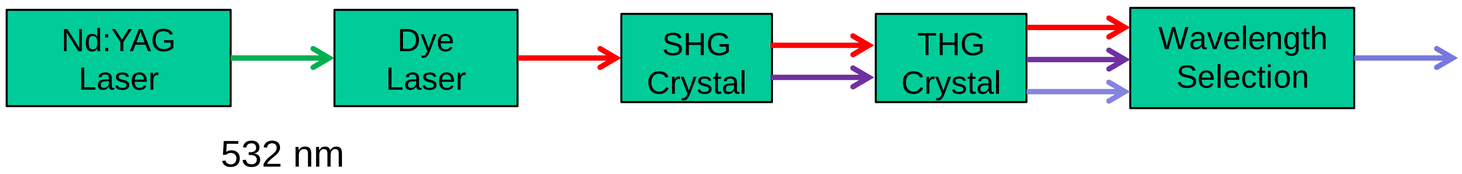
- Collection optics: f/15 at VKI f/4 at UVM
- Laser repetition 10 Hz, gated PMT
- Beam diameter 1-2 mm,
- Pulse energy at ICP is 0.1 to 0.25 mJ

Laser Induced Fluorescence for Volatile Product Detection and Quantification

Requirements:

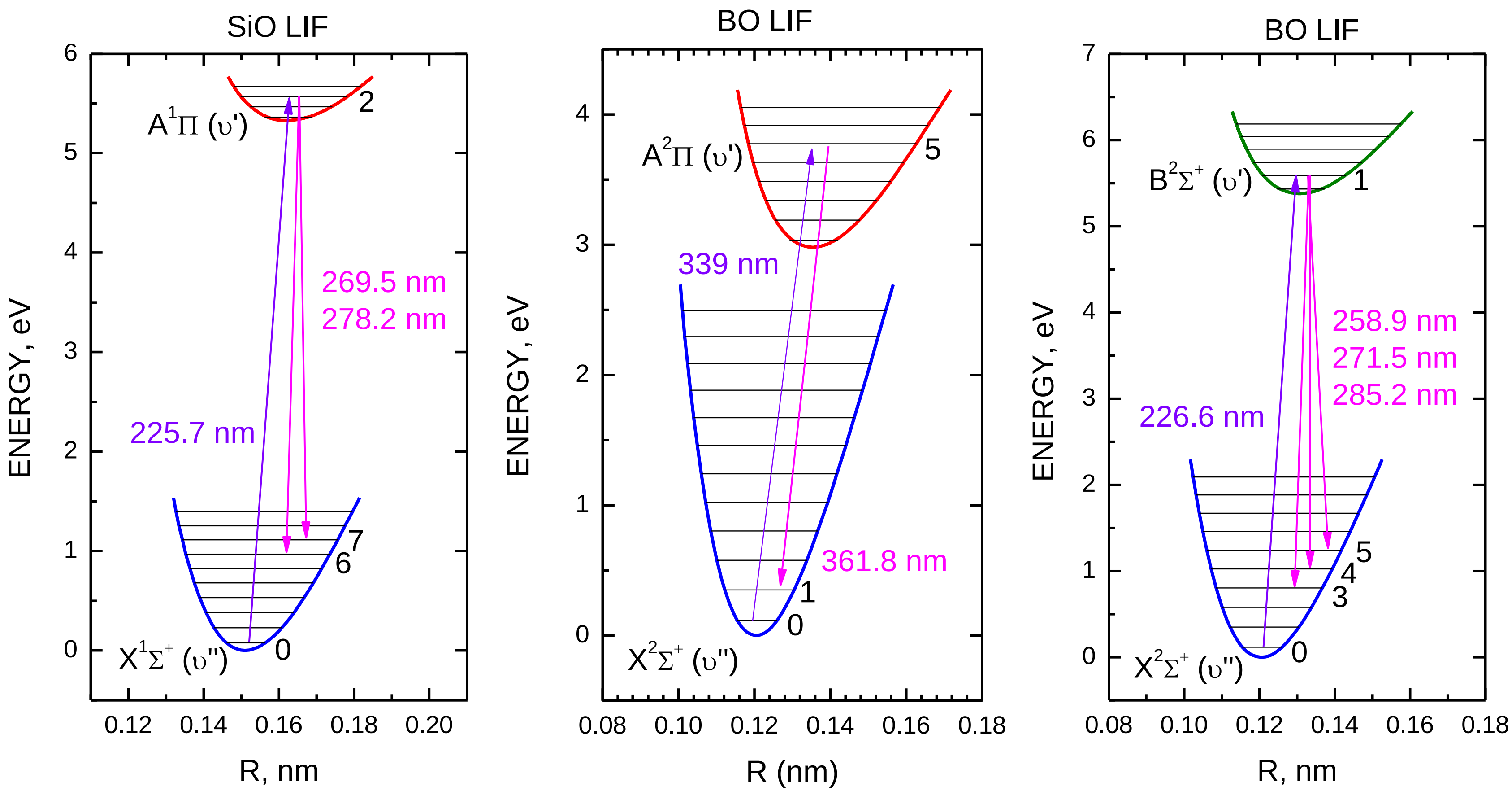
- LIF scheme for product detection
    - Understanding of spectroscopy
    - Characterization of interferences and sensitivities
- Laboratory source for product generation
    - Stable
    - Tunable
    - Quantifiable
- Both detection scheme and product source must be suitable for implementation at UVM

Generation of Excitation Wavelengths for Oxygen and Nitrogen Atom LIF



	Dye Laser	SHG Crystal	THG Crystal	Wavelength Selection
O-atom LIF	678 nm	678 nm 339 nm	678 nm 339 nm 226 nm	226 nm
N-atom LIF	633 nm	633 nm 316.5 nm	633 nm 316.5 nm 211 nm	211 nm
N-atom LIF	621 nm	621 nm 310.5 nm	621 nm 310.5 nm 207 nm	207 nm

Potentially Convenient SiO and BO LIF Schemes

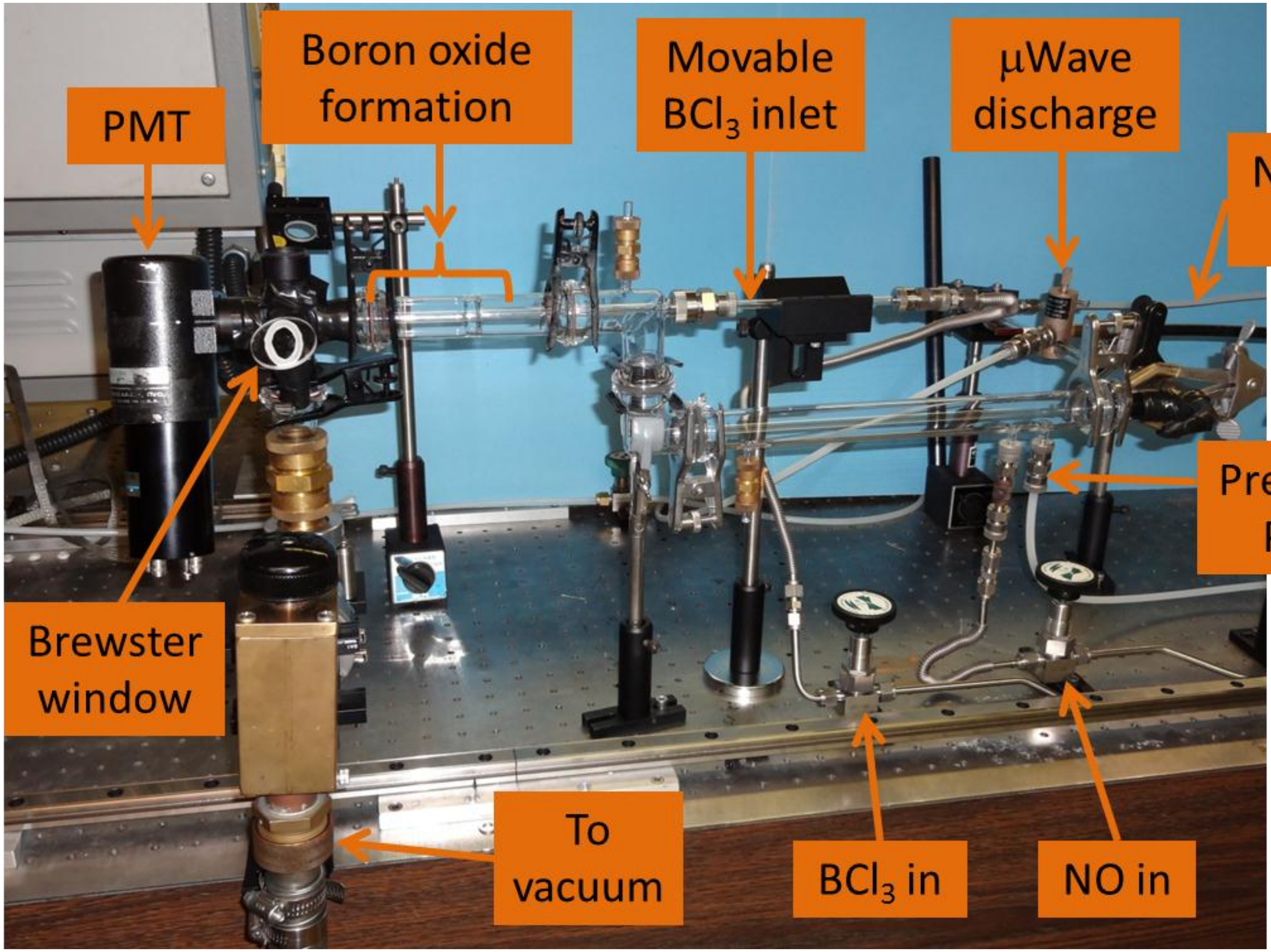


Goal: Implement and demonstrate BO and SiO detection in the UVM ICP

Laboratory Study of BO Emission and LIF Detection

First step: Source development

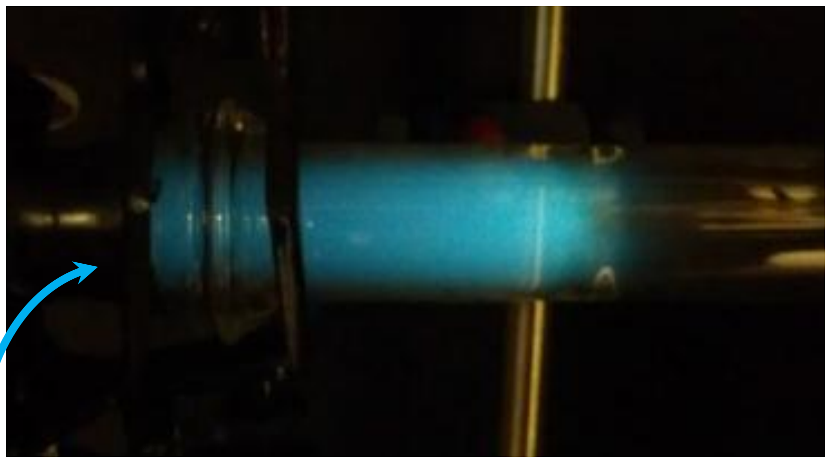
- React of atomic oxygen with boron trichloride to make gaseous boron oxides

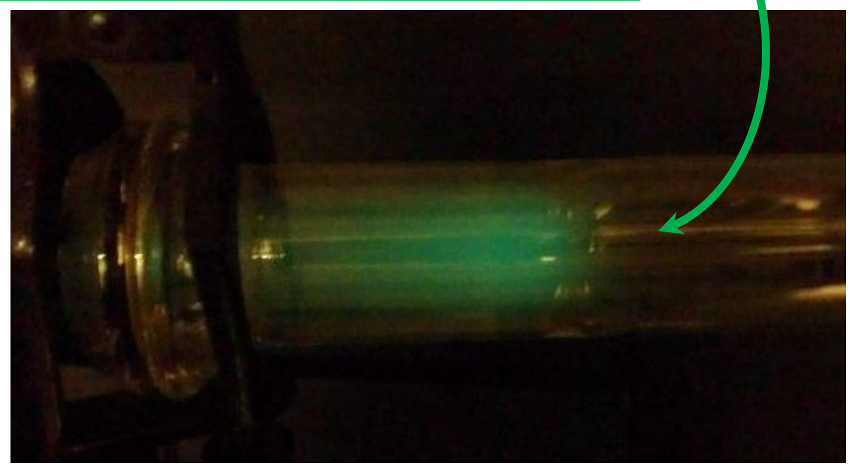


Emission for Two Different Discharge Schemes

- Generate BO by mixing BCl_3 with an oxygen discharge

O_2 → (μwave) → O_2,O → Boron oxides & other species
↑ N_2-5%BCl_3

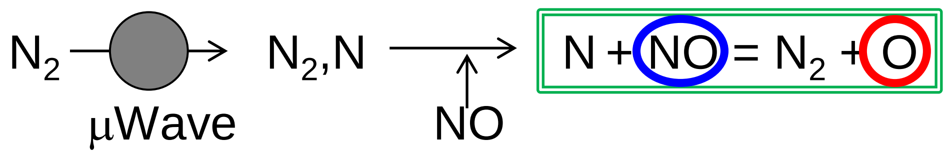


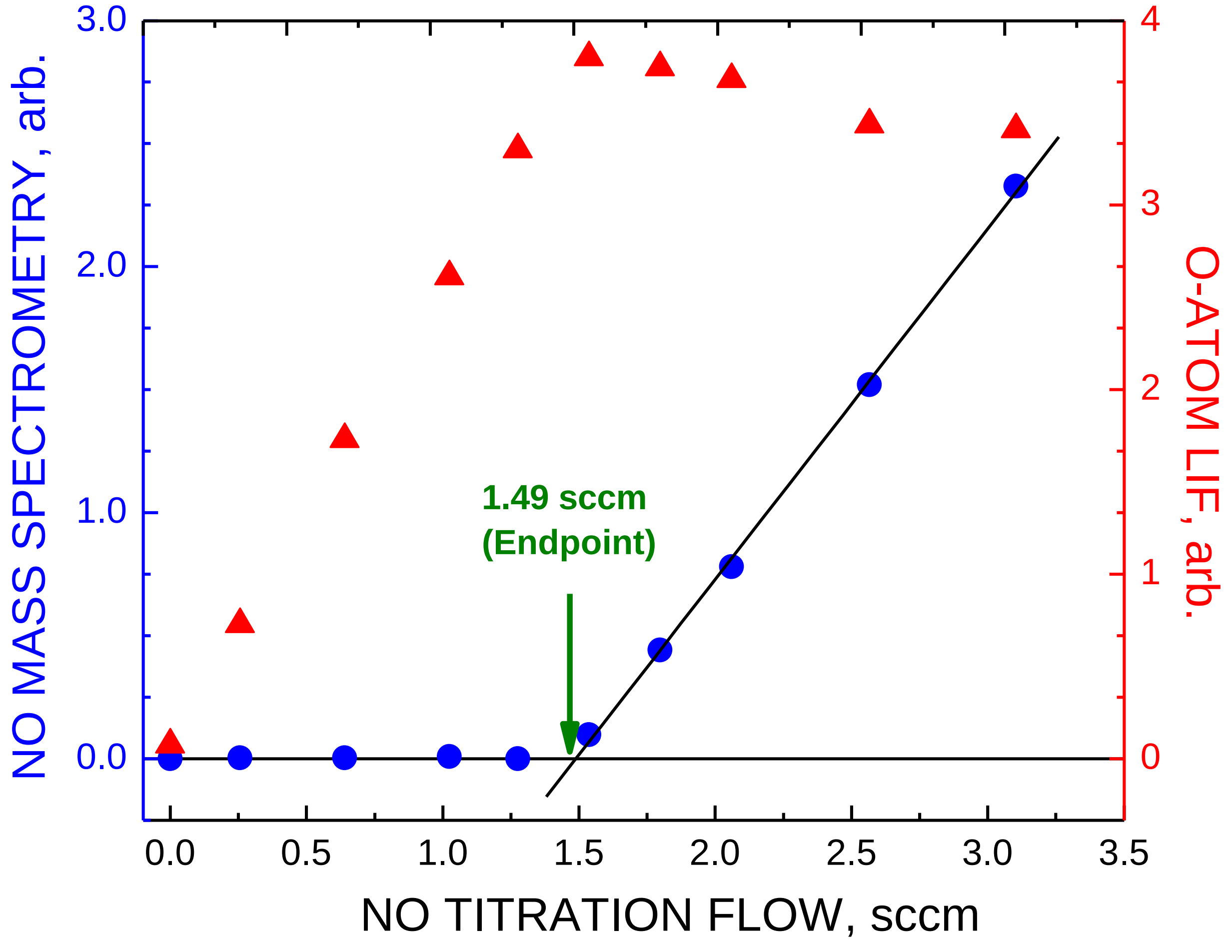


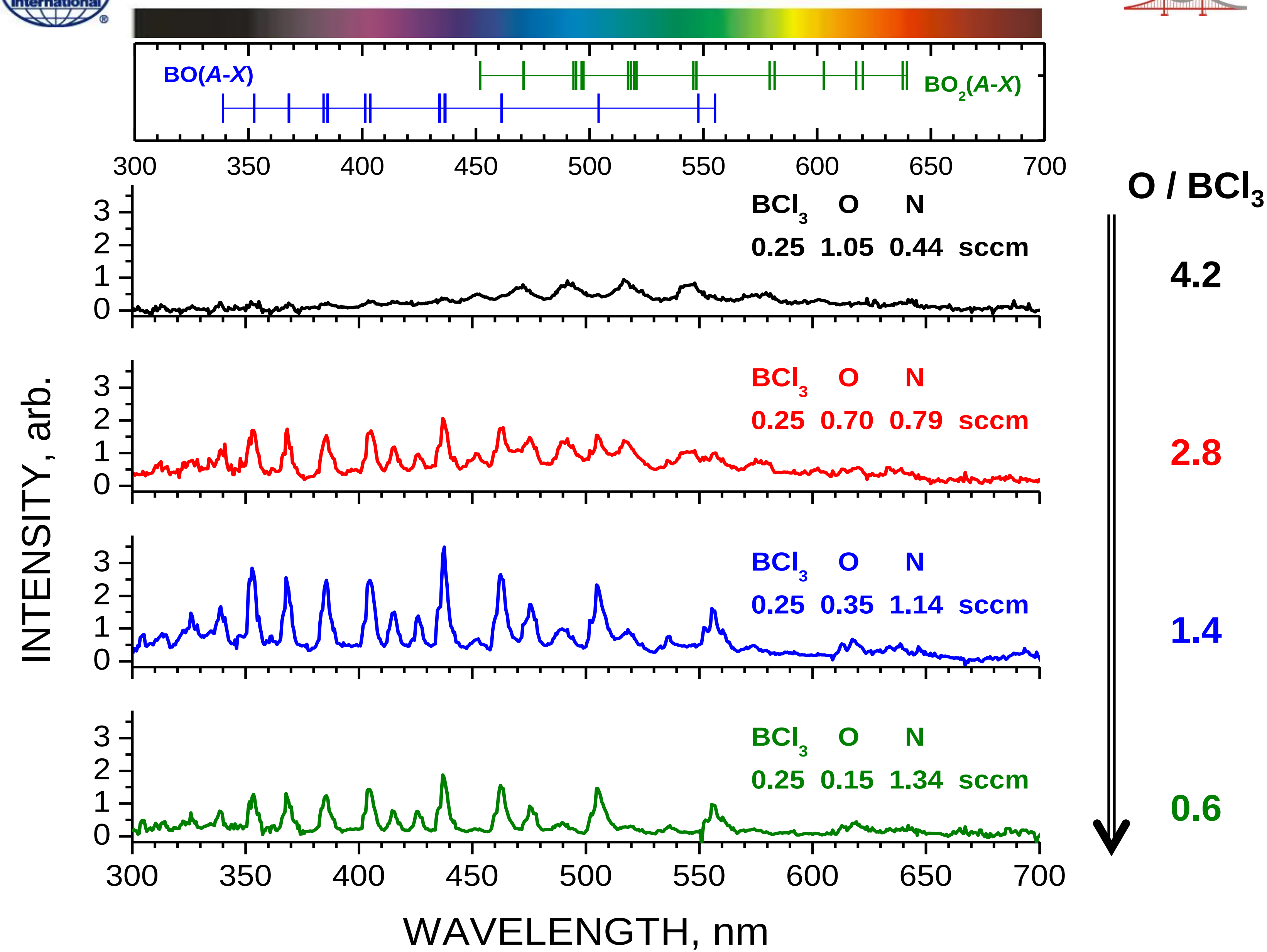
- Generate BO by mixing BCl_3 with a titrated nitrogen discharge

N_2 → (μWave) → N_2,N → N_2,N,O → Boron oxides & other species
↑ NO (first step); ↑ N_2-5%BCl_3 (second step)

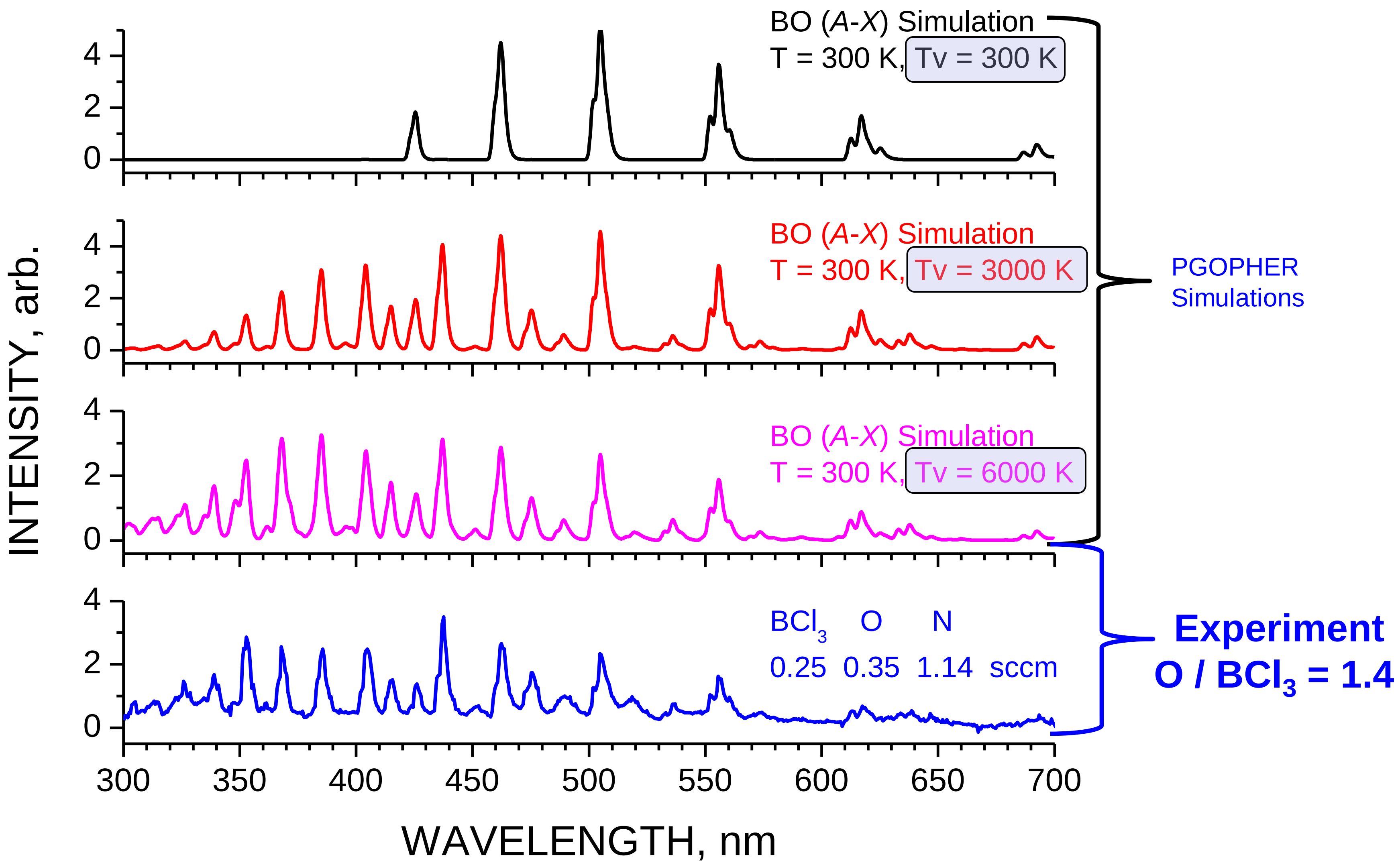
Control of O-atom Concentrations by Titration



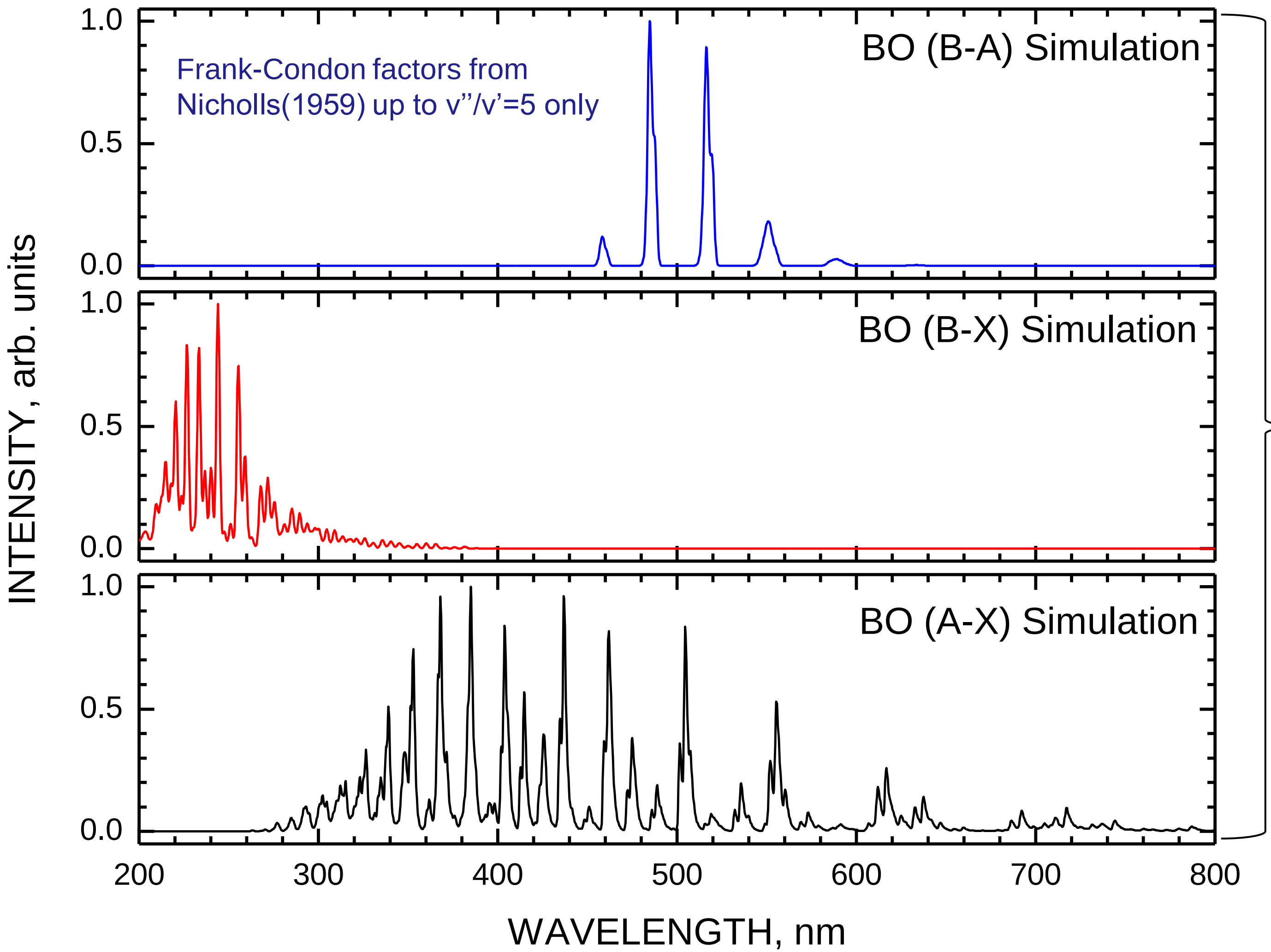



BO(A-X)
BO2(A-X)
300
350
400
450
500
550
600
650
700
O / BCl3
BCl3 O N
0.25 1.05 0.44 sccm
4.2
BCl3 O N
0.25 0.70 0.79 sccm
2.8
BCl3 O N
0.25 0.35 1.14 sccm
1.4
BCl3 O N
0.25 0.15 1.34 sccm
0.6
INTENSITY, arb.
0
1
2
3
WAVELENGTH, nm

Vibrational Non-Equilibrium in BO (*A*)



No BO *B*-state Emission in the Flow Reactor

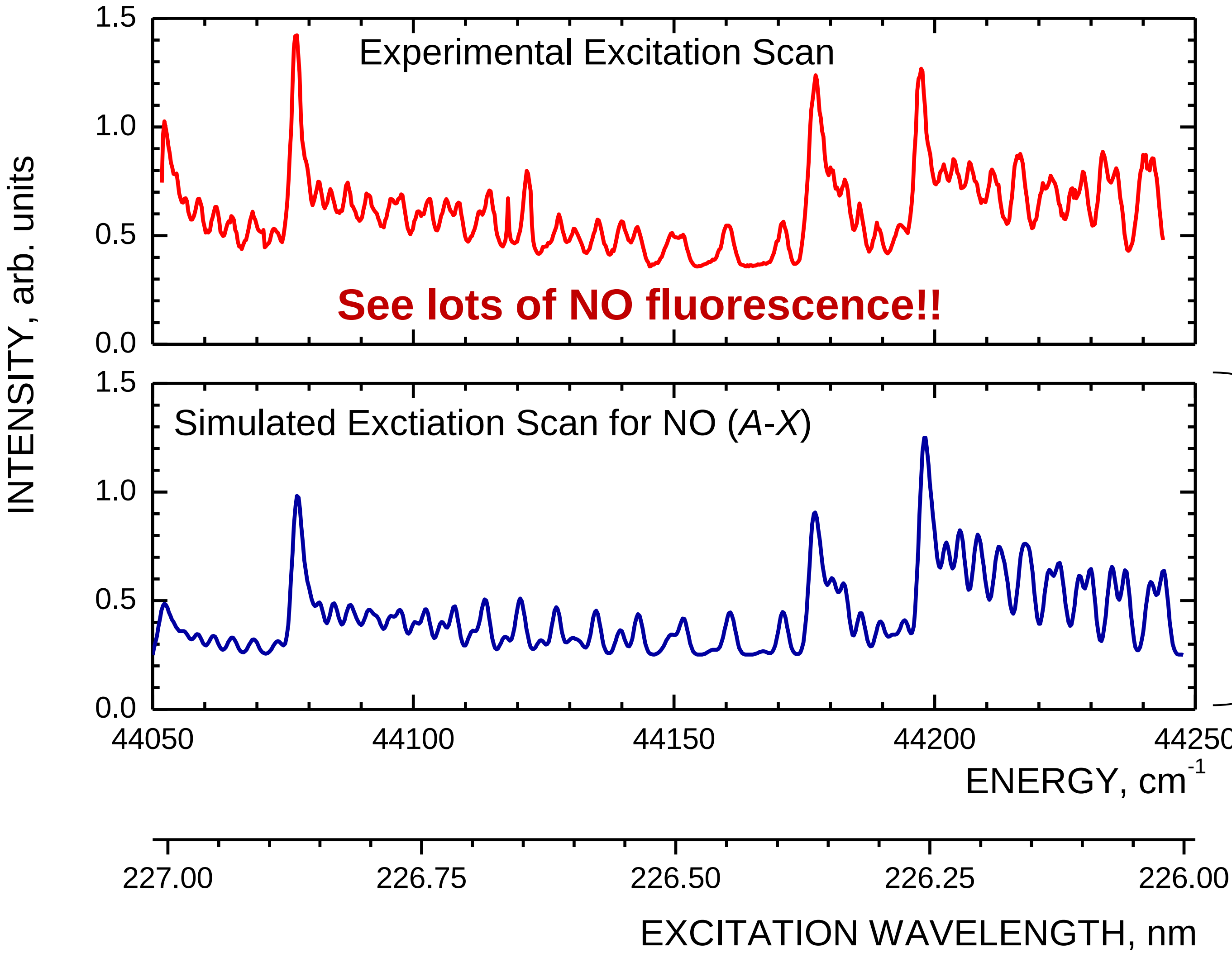


T = 300 K

T_V = 6000 K

PGOPHER, Simulations

First BO (*B*-*X*) LIF Attempt



Scan 226 to 227 nm range where BO *B*-*X*(0-0) band transitions are expected

LIFBASE, Luque, J. and Crosley, D.R., “LIFBASE: Database and Spectral Simulation for Diatomic Molecules,” MP-99-0099, www.sri.com/cem/lifbase, SRI International, 1999.

Where is NO coming from?

Most likely ←

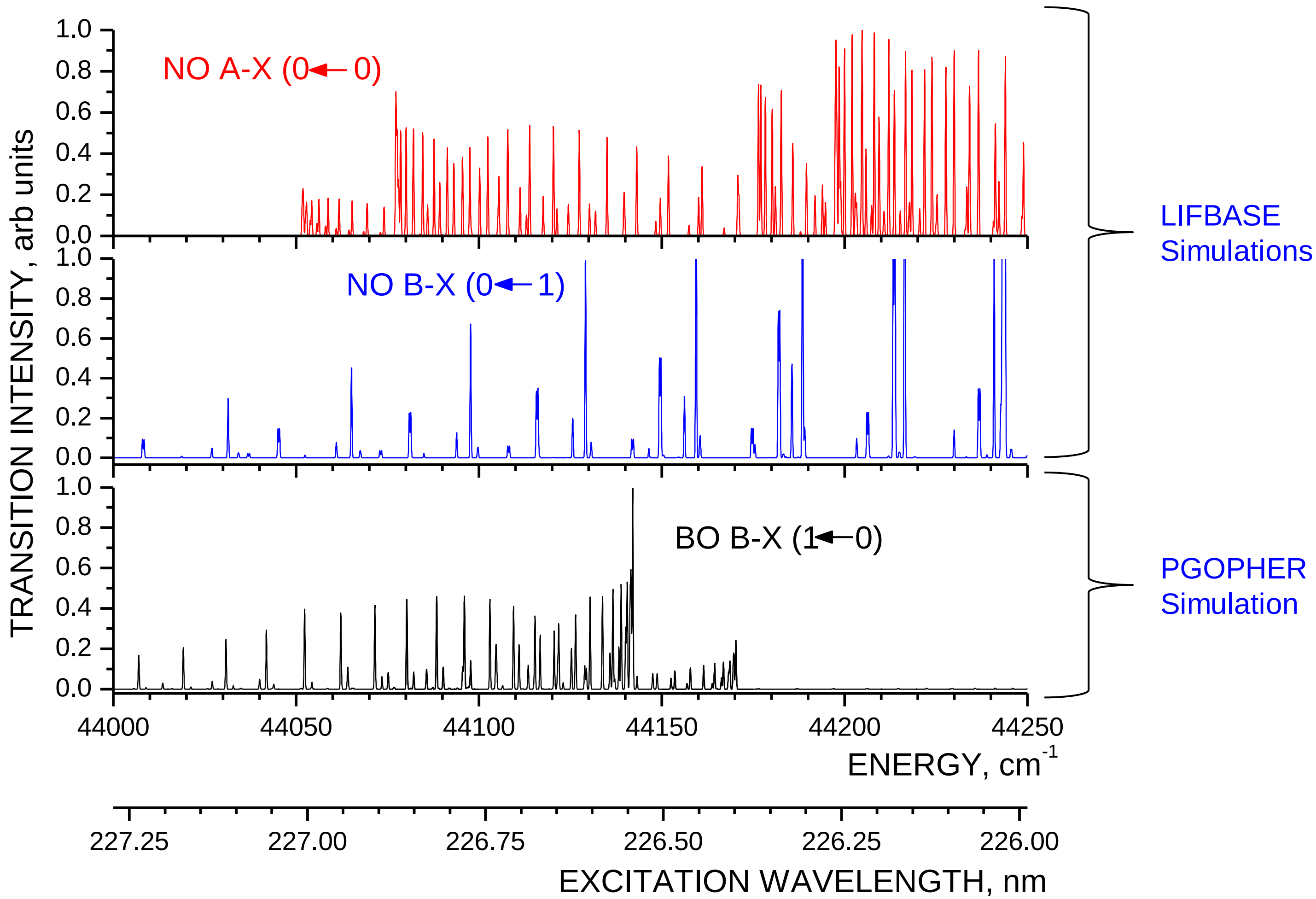
- Residual un-reacted NO added at titration port
- Surface recombination N(s) + O(s) = NO
- Gas phase recombination N + O = NO
- Unknown BCl_3 + O + N reactions

Why detection by LIF and not mass spectrometer?

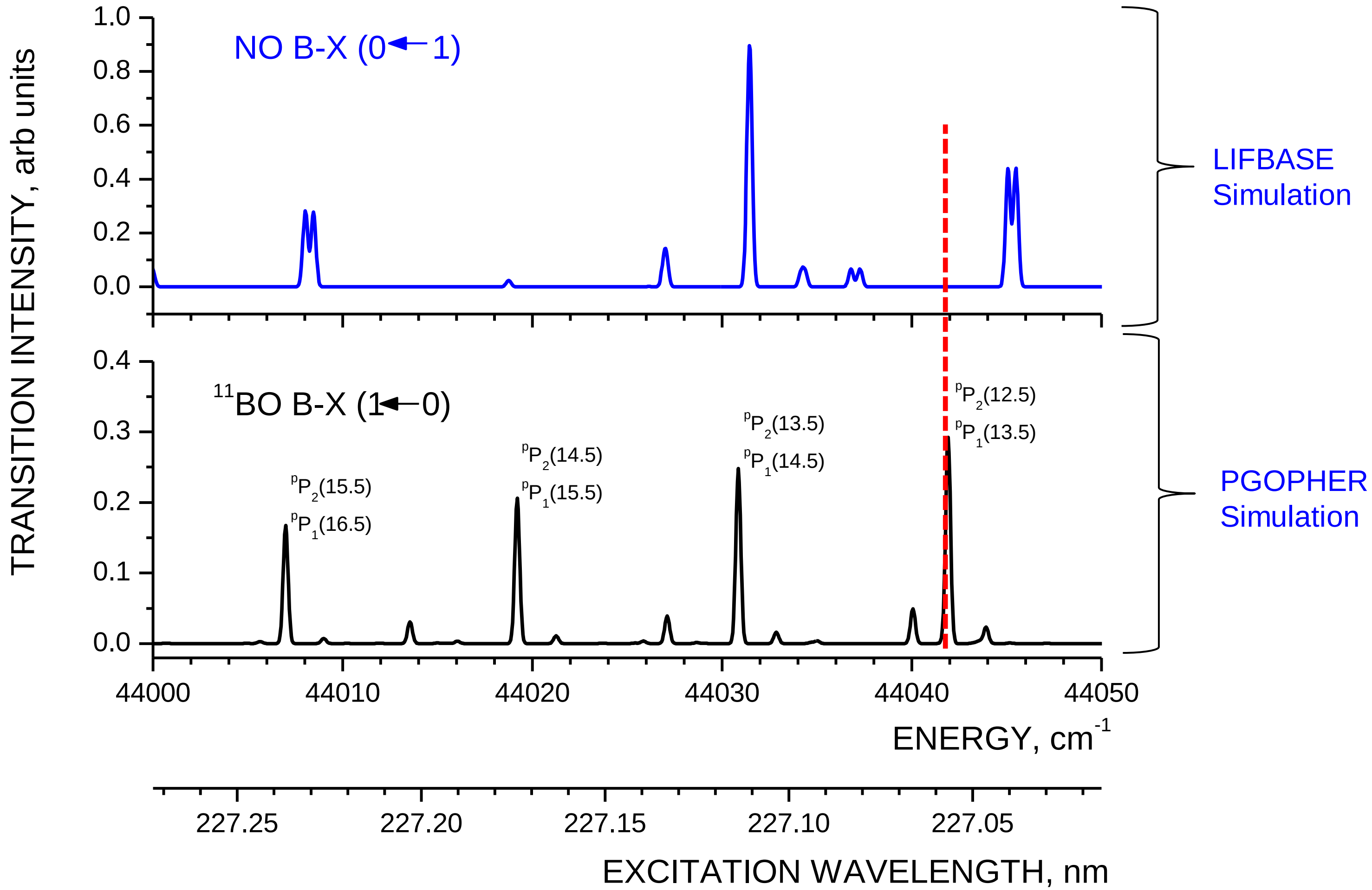
- Dilution factor of 10^6 sampling into mass spectrometer
- LIF probes NO inside reactor and is very sensitive for NO detection

NO has been detected in the UVM ICP by LIF, it could interfere with BO LIF there also.

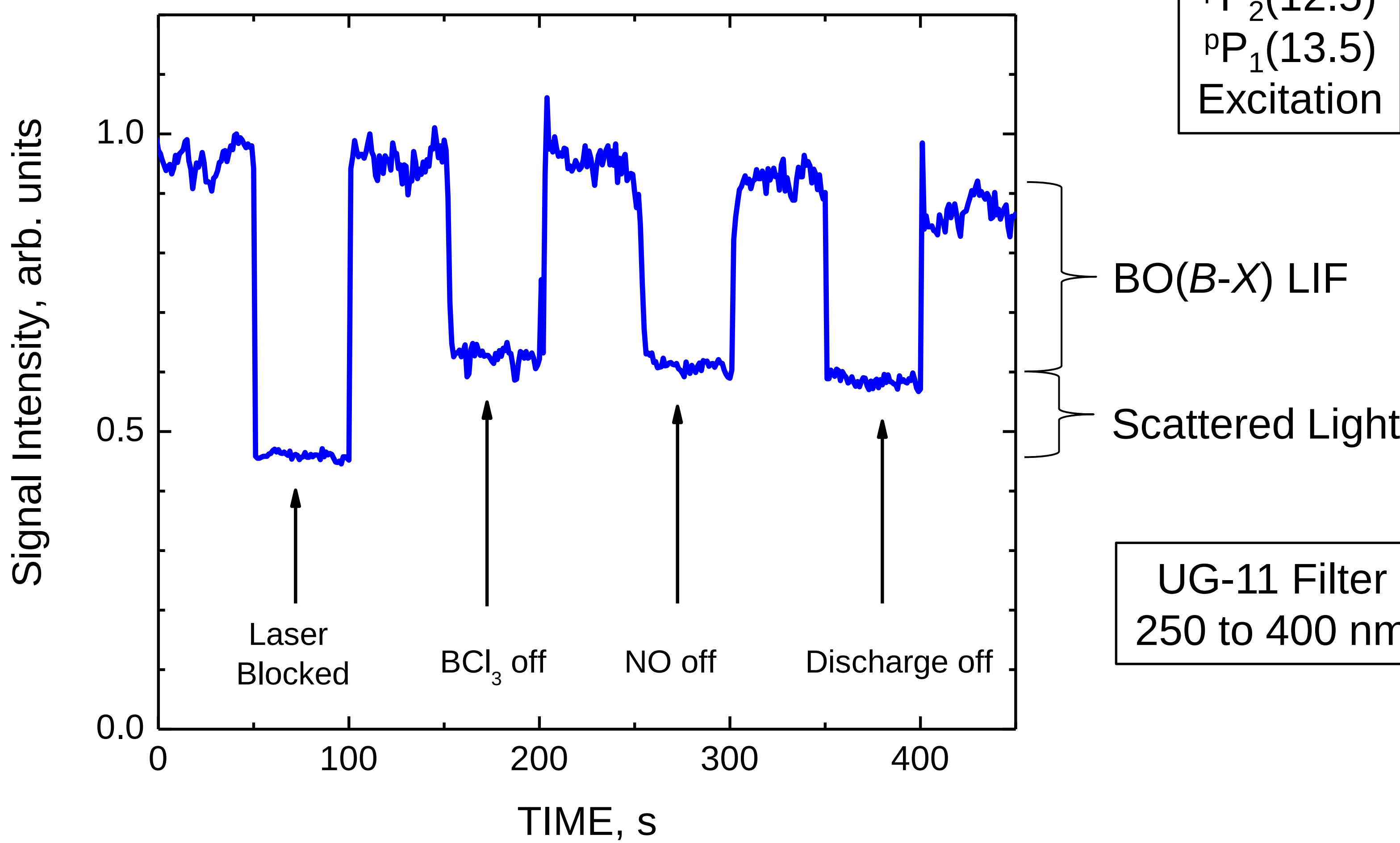
Nitric Oxide (*A*-*X*) and (*B*-*X*) Excitations



Choose BO(*B*-*X*) Excitation with Minimal Nitric Oxide Excitation Interference



First BO(*B*-*X*) LIF Detection



$^pP_2(12.5)$
$^pP_1(13.5)$
Excitation

UG-11 Filter
250 to 400 nm

Status of BO Emission and LIF Experiments

- Discharge source for gaseous boron oxides developed
- Production of BO and BO_2 excited states confirmed by emission
- Emission tuning by control of O-atom concentrations demonstrated
- First detection of BO via *B-X* LIF achieved

Next steps:

Characterize *B-X* LIF scheme thoroughly:
Radiative lifetime, quenching cross-sections, fluorescence branching

Quantify BO number density in the discharge source.

Volatility Diagrams for Dissociated Oxygen Environments?

Procedure in Equilibrium Environments:

- Identify stable condensed phases at a fixed temperature and a range of oxygen pressures
- Identify candidate gaseous species

- Compute species vapor pressures for equilibrium with oxygen and stable condensed phase
  - No gas-phase reactions
  - Specified condensed phase activity and oxygen pressure
  - Construct volatility diagrams from maximum species vapor pressures

Si-O System Volatility in O_2 Atmosphere

Si-O$_2$ System: Si(*s*,*l*), SiO$_2$(*s*,*l*), SiO$_2$, SiO, Si, Si$_2$, Si$_3$, and O$_2$

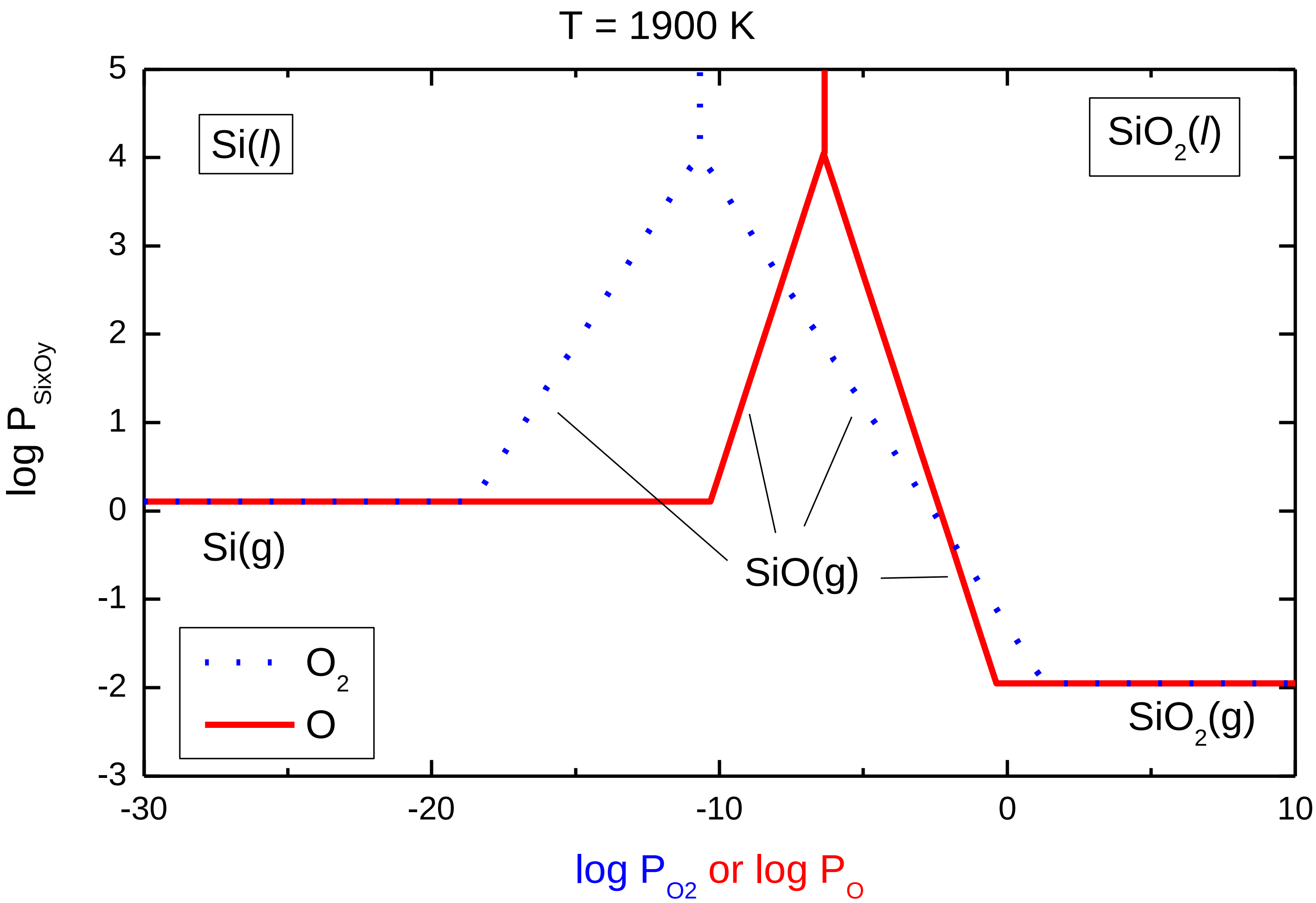
Group	Reaction	Equation	Expression
	R1	**Si(s,l) + O$_2$ → SiO$_2$(s,l)**	$\log P_{O2} = \log P_{ref} - \log K_1(T)$
Si(s,l)	**R2**	Si(s,l) → Si	$\log P_{Si} = \log P_{ref} + \log K_2(T)$
Si(s,l)	**R3**	2Si(s,l) → Si$_2$	$\log P_{Si2} = \log P_{ref} + \log K_3(T)$
Si(s,l)	**R4**	3Si(s,l) → Si$_3$	$\log P_{Si3} = \log P_{ref} + \log K_4(T)$
Si(s,l)	**R5**	Si(s,l) + O$_2$ → SiO$_2$	$\log P_{SiO2} = \log P_{O2} + \log K_5(T)$
Si(s,l)	**R6**	Si(s,l) + 1/2O$_2$ → SiO	$\log P_{SiO} = 1/2 \log P_{ref} + 1/2 \log P_{O2} + \log K_6(T)$
SiO$_2$(s,l)	**R7**	SiO$_2$(s,l) → SiO$_2$	$\log P_{SiO2} = \log P_{ref} + \log K_7(T)$
SiO$_2$(s,l)	**R8**	SiO$_2$(s,l) → SiO + 1/2O$_2$	$\log P_{SiO} = 3/2 \log P_{ref} - 1/2 \log P_{O2} + \log K_8(T)$
SiO$_2$(s,l)	**R9**	SiO$_2$(s,l) → Si + O$_2$	$\log P_{Si} = 2 \log P_{ref} - \log P_{O2} + \log K_9(T)$
SiO$_2$(s,l)	**R10**	2SiO$_2$(s,l) → Si$_2$ + 2O$_2$	$\log P_{Si2} = 3 \log P_{ref} - 2 \log P_{O2} + \log K_{10}(T)$
SiO$_2$(s,l)	**R11**	3SiO$_2$(s,l) → Si$_3$ + 3O$_2$	$\log P_{Si3} = 4 \log P_{ref} - 3 \log P_{O2} + \log K_{11}(T)$

Si-O System Volatility in O-atom Atmosphere

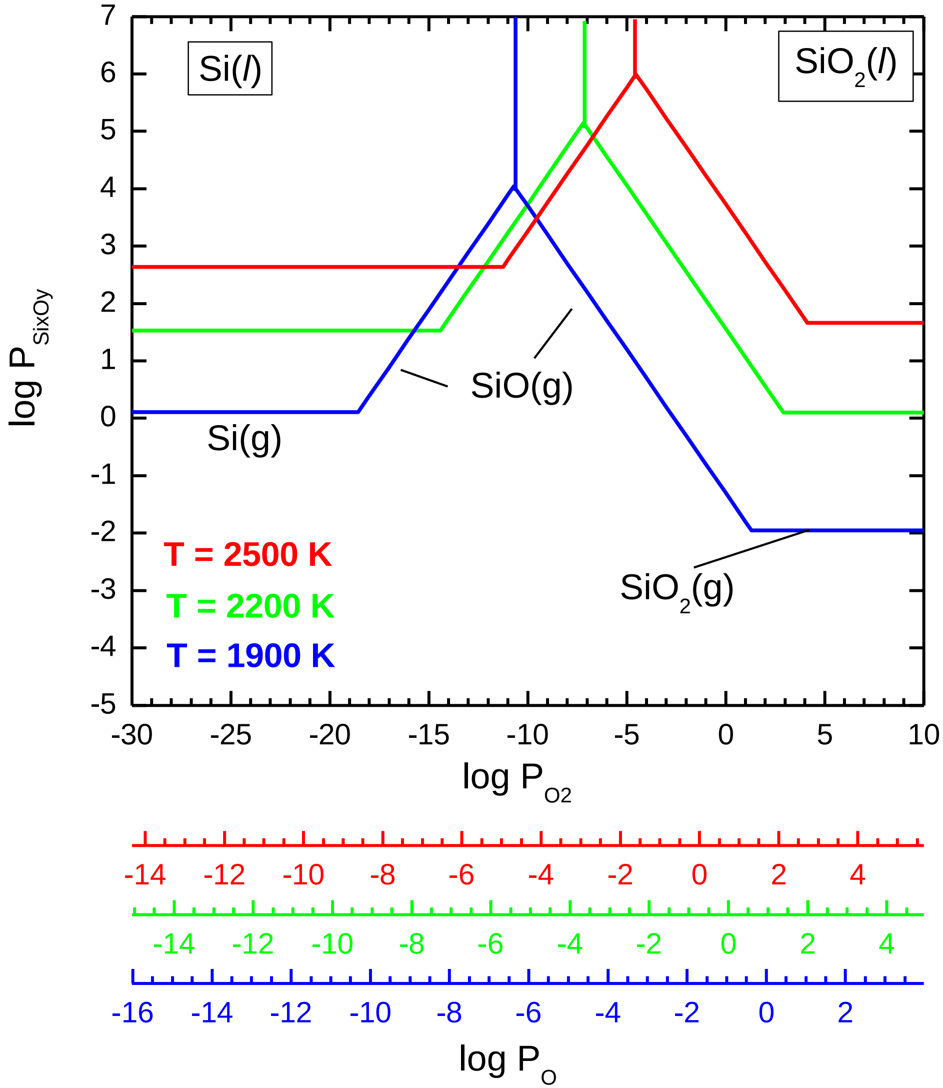
Si-O System: Si(*s*,*l*), SiO_2(*s*,*l*), SiO_2, SiO, Si, Si_2, Si_3, and O

	R1	**1/2Si(s,l) + O → 1/2SiO_2(s,l)**	$\log P_O = \log P_{ref} - \log K_1(T)$
Si(s,l)	**R2**	Si(s,l) → Si	$\log P_{Si} = \log P_{ref} + \log K_2(T)$
Si(s,l)	**R3**	2Si(s,l) → Si_2	$\log P_{Si2} = \log P_{ref} + \log K_3(T)$
Si(s,l)	**R4**	3Si(s,l) → Si_3	$\log P_{Si3} = \log P_{ref} + \log K_4(T)$
Si(s,l)	**R5**	Si(s,l) + 2O → SiO_2	$\log P_{SiO2} = -\log P_{ref} + 2\log P_O + \log K_5(T)$
Si(s,l)	**R6**	Si(s,l) + O → SiO	$\log P_{SiO} = \log P_O + \log K_6(T)$
SiO_2(s,l)	**R7**	SiO_2(s,l) → SiO_2	$\log P_{SiO2} = \log P_{ref} + \log K_7(T)$
SiO_2(s,l)	**R8**	SiO_2(s,l) → SiO + O	$\log P_{SiO} = 2\log P_{ref} - \log P_O + \log K_8(T)$
SiO_2(s,l)	**R9**	SiO_2(s,l) → Si + 2O	$\log P_{Si} = 3\log P_{ref} - 2\log P_O + \log K_9(T)$
SiO_2(s,l)	**R10**	2SiO_2(s,l) → Si_2 + 4O	$\log P_{Si2} = 5\log P_{ref} - 4\log P_O + \log K_{10}(T)$
SiO_2(s,l)	**R11**	3SiO_2(s,l) → Si_3 + 6O	$\log P_{Si3} = 7\log P_{ref} - 6\log P_O + \log K_{11}(T)$

Si-O System Volatility Diagrams for 1900 K



Si-O Volatility Diagrams for O_2-O in Equilibrium



Add gas-phase reaction
$1/2O_2 = O$

$$\log P_O = 1/2 \log P_{ref} + 1/2 \log P_{O2} + \log K_{ox}$$

What if O_2-O are not in Equilibrium?

Define atom to molecule ratio:

$$\beta \equiv \frac{P_O}{P_{O2}}$$

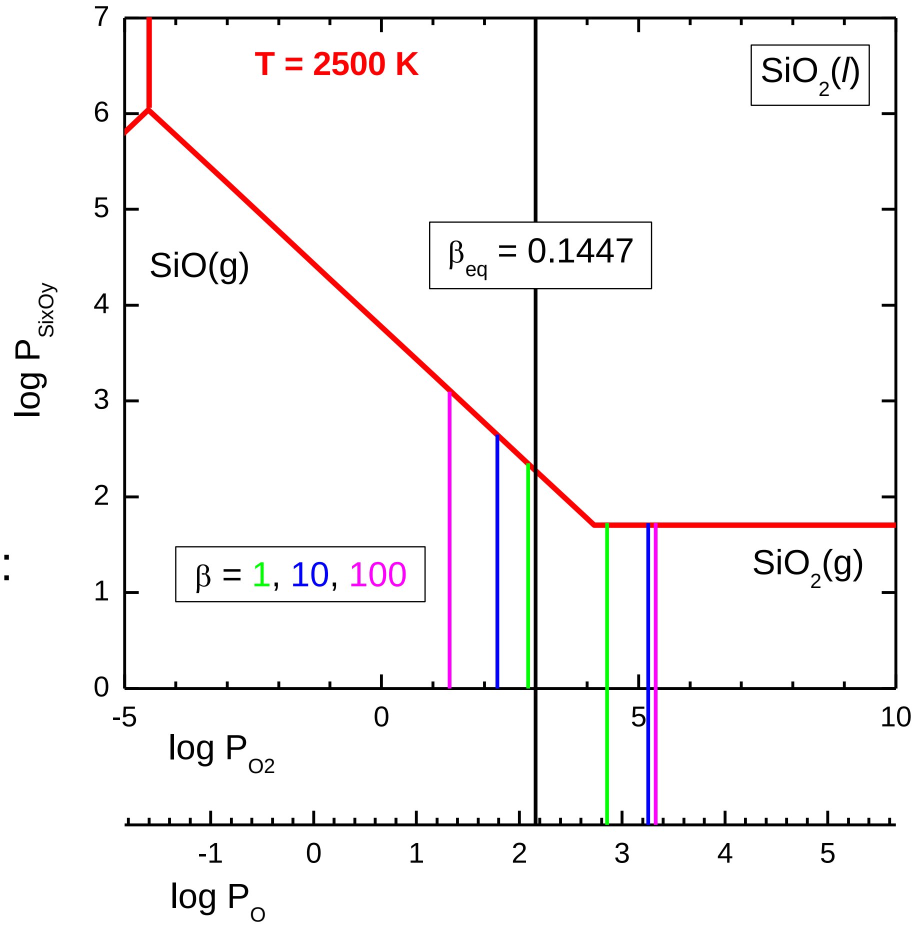
$$\beta_{eq} \equiv \frac{P_{O\,eq}}{P_{O2eq}} = K_{ox}(T)\sqrt{\frac{P_{ref}}{P_{O2eq}}}$$

Moving away from equilibrium conserving elemental O per volume:

:

$$\log P_{O2} = \log P_{O2eq} + \log\left(\frac{\beta_{eq}+2}{\beta+2}\right)$$

$$\log P_O = \log \beta + \log P_{O2}$$



Two different answers?!

Si-O System Volatility in O_2 – O Mixture

Add previous equation sets and solve for vapor pressures

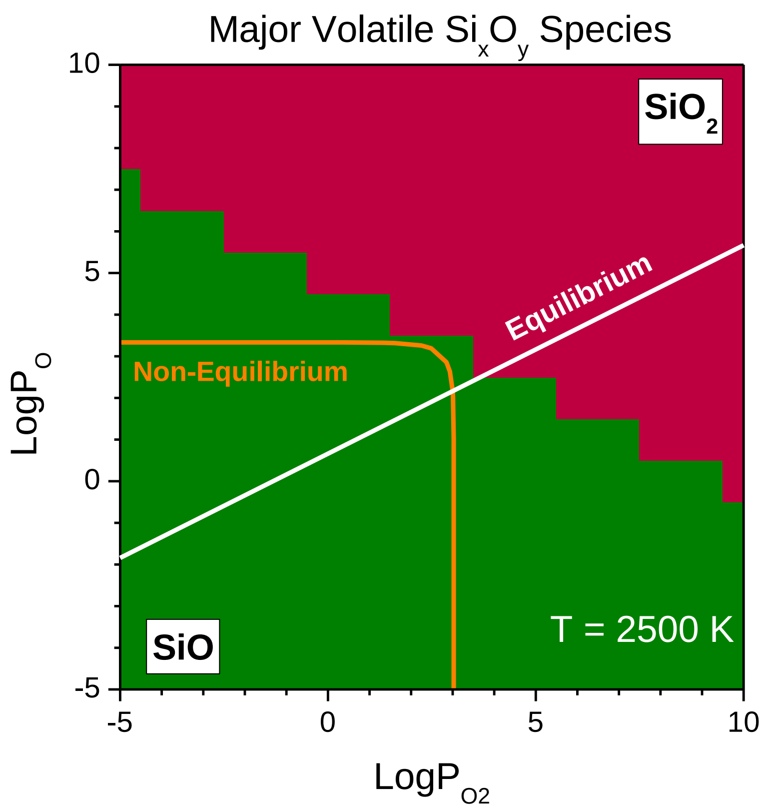
Si-O_2-O System: Si(*s*,*l*), SiO_2(*s*,*l*), SiO_2, SiO, Si, Si_2, Si_3, and O_2 and O

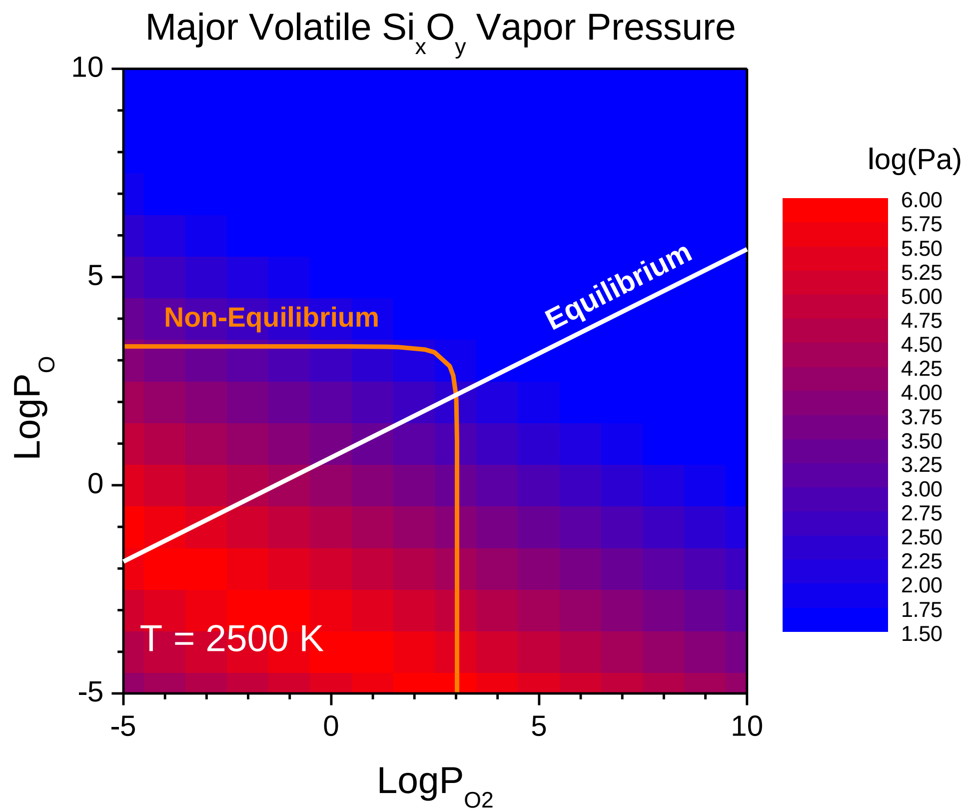
R1	**Si(s,l) + O + 1/2O_2 → SiO_2(s,l)**	$\log P_O^2 P_{O2} = 3\log P_{ref} - 2\log K_1(T)$
R2	Si(s,l) → Si	$\log P_{Si} = \log P_{ref} + \log K_2(T)$
R3	2Si(s,l) → Si_2	$\log P_{Si2} = \log P_{ref} + \log K_3(T)$
R4	3Si(s,l) → Si_3	$\log P_{Si3} = \log P_{ref} + \log K_4(T)$
R5	Si(s,l) + O + 1/2 O_2 → SiO_2	$\log P_{SiO2} = -1/2\log P_{ref} + 1/2\log P_O^2 P_{O2} + \log K_5(T)$
R6	Si(s,l) + 1/2O + 1/4 O_2→ SiO	$\log P_{SiO} = -1/4\log P_{ref} + 1/4\log P_O^2 P_{O2} + \log K_6(T)$
R7	SiO_2(s,l) → SiO_2	$\log P_{SiO2} = \log P_{ref} + \log K_7(T)$
R8	SiO_2(s,l) → SiO + 1/2O+ 1/4O_2	$\log P_{SiO} = 7/4\log P_{ref} - 1/4\log P_O^2 P_{O2} + \log K_8(T)$
R9	SiO_2(s,l) → Si + O+1/2O_2	$\log P_{Si} = 5/2\log P_{ref} - 1/2\log P_O^2 P_{O2} + \log K_9(T)$
R10	2SiO_2(s,l) → Si_2 + 2O + O_2	$\log P_{Si2} = 4\log P_{ref} - \log P_O^2 P_{O2} + \log K_{10}(T)$
R11	3SiO_2(s,l) → Si_3 + 3O +3/2O_2	$\log P_{Si3} = 11/2\log P_{ref} - 3/2\log P_O^2 P_{O2} + \log K_{11}(T)$

Si(s,l): R2–R6

SiO_2(s,l): R7–R11

Si-O System Volatility in O_2-O Mixture





Acknowledgments

This material is based on research sponsored by the Air Force Research Laboratory under agreement number FA9550-11-1-0201. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon.

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