



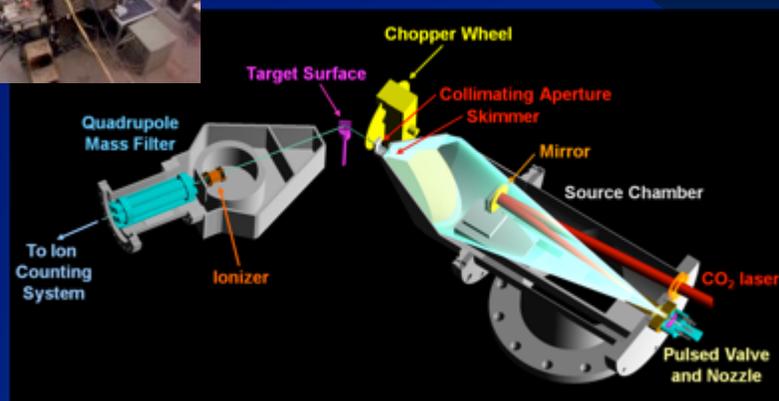
Beam-Surface Scattering Studies on Hot Surfaces

Timothy K. Minton

Molecular Beam Scattering



configuration for beam-
surface scattering



GOAL

- Chemical/inelastic interaction mechanisms between O, O₂, N, and N₂ and surfaces or gases

PAYOFF

- New knowledge of reactivity and energy transfer in gas-surface and gas-phase collisions under hypersonic conditions
- Input data for models

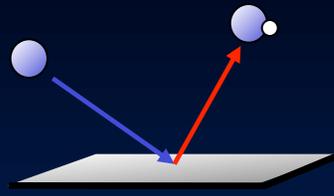
METHODOLOGY

- Hyperthermal neutral beam scattering
 - beam-surface, crossed-beams
- Surface topographical analysis
 - AFM, SEM, profilometry
- Surface chemical analysis
 - XPS, FTIR

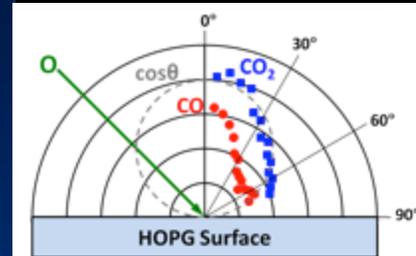
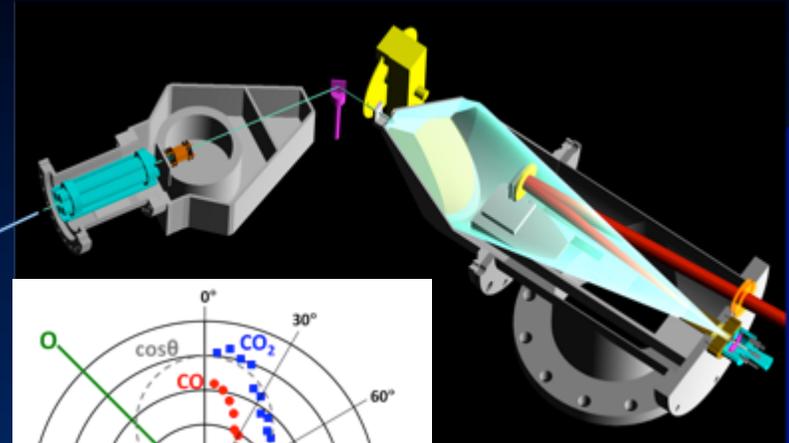
Molecular Beam Studies of Surface Oxidation and Erosion

(Based on laser-detonation source of ~5 eV O atoms)

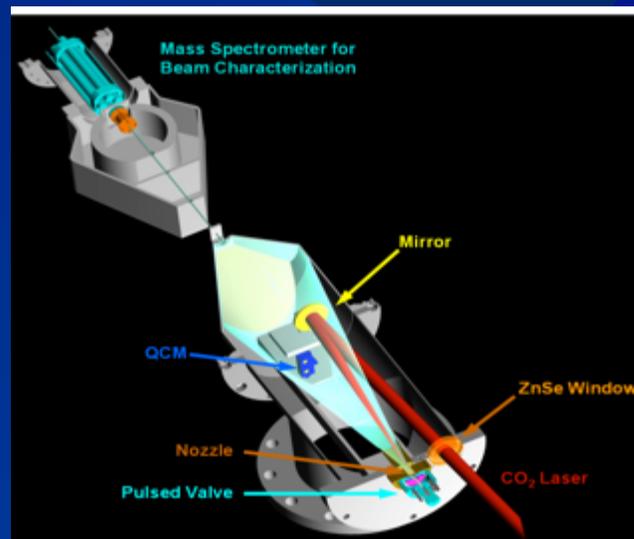
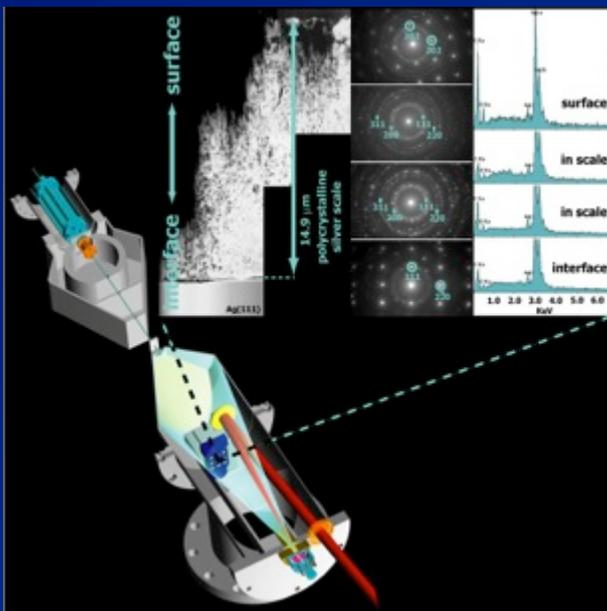
crossed-beams apparatus



Beam-Surface Scattering



Exposure and post-exposure characterization

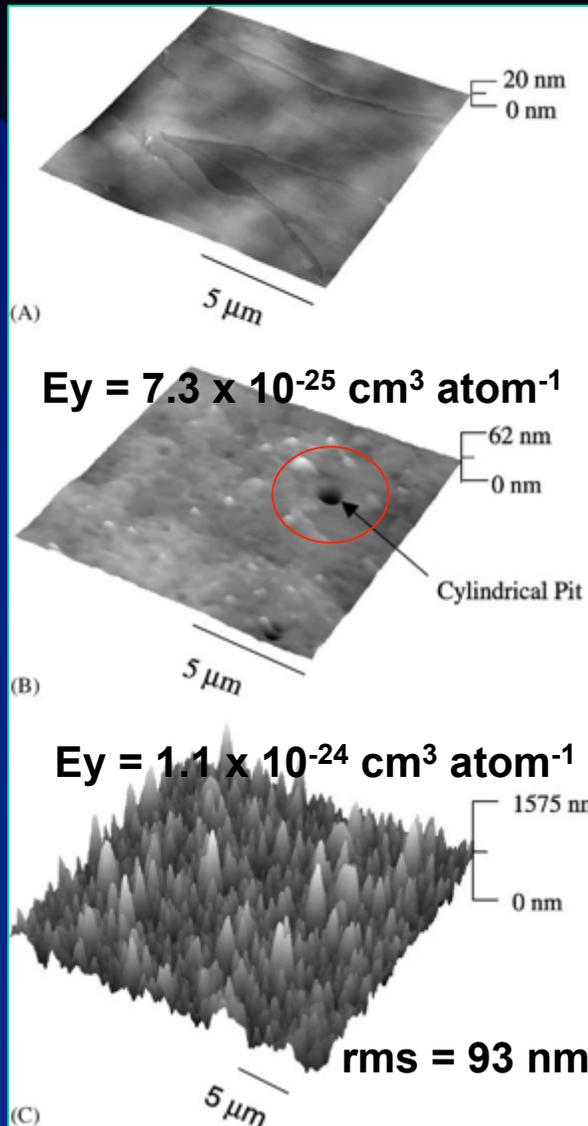


In situ measurements of mass loss with QCM

Surface Topography of Eroded HOPG

Laboratory
Conditions:

pristine



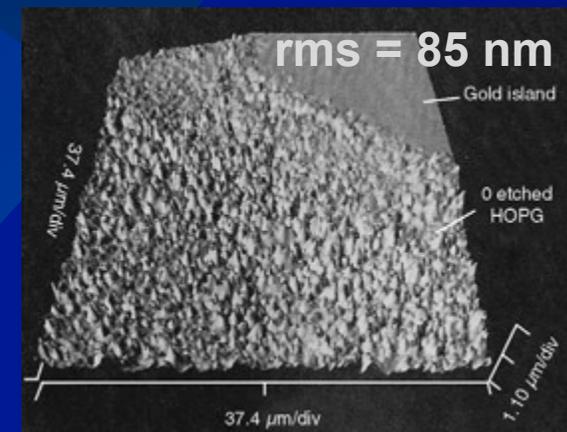
exposed
 $1.8 \times 10^{20} \text{ cm}^{-2}$
25 °C

exposed
 $2.0 \times 10^{20} \text{ cm}^{-2}$
220 °C

Significant temperature dependence: etch pits at lower temps and random roughness at higher temps.

Close agreement between 220 °C exposure and low Earth orbit (LEO) result.

LEO, EOIM-3
 $2.0 \times 10^{20} \text{ cm}^{-2}$

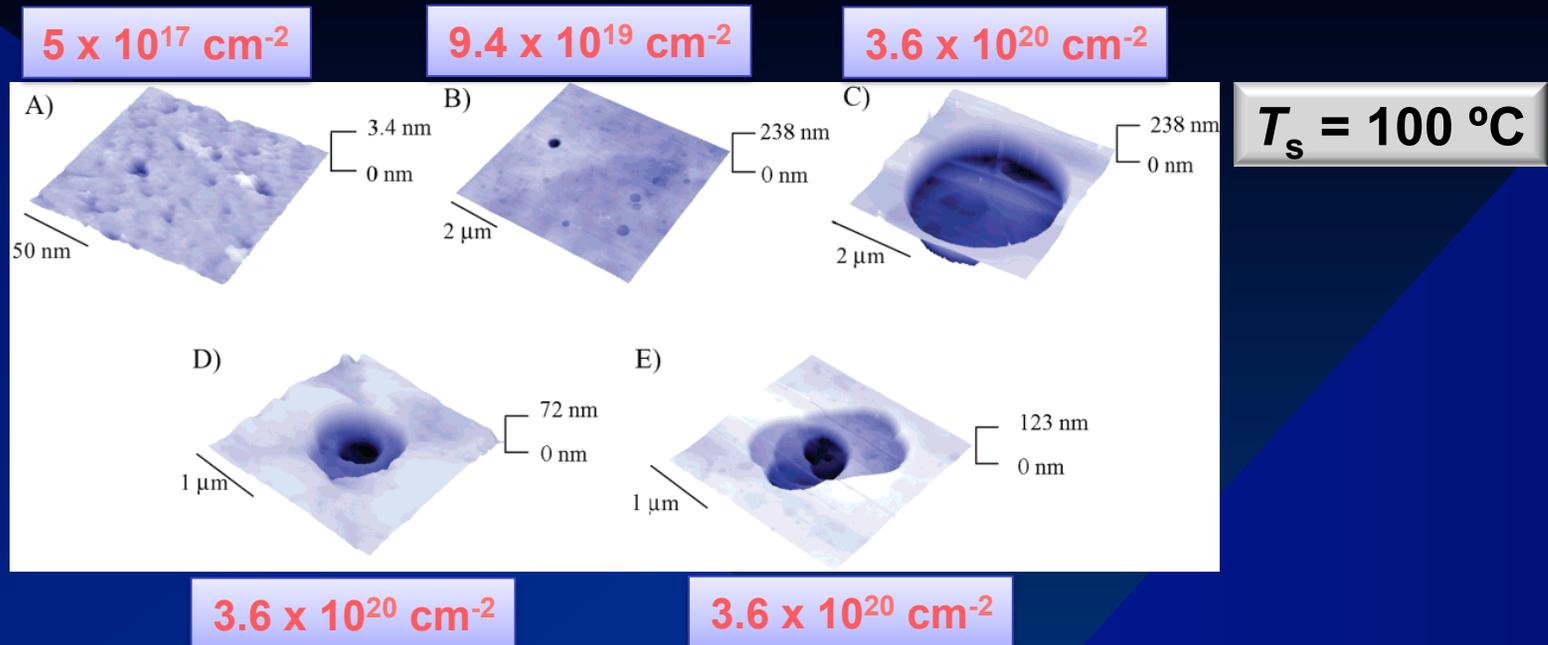


$E_y = 1.1 \times 10^{-24} \text{ cm}^3 \text{ atom}^{-1}$

Minton, *Prog. Org. Coat.* **47**, 443 (2003)

Investigation of Etch Pits

STM
images of
exposed
HOPG



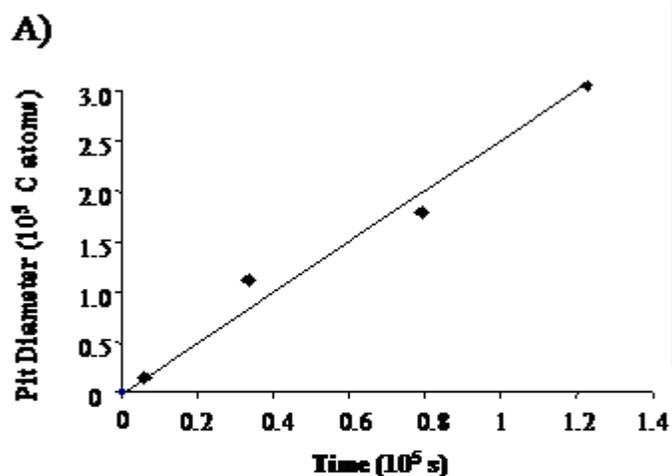
After ~100 monolayers of hyperthermal O atoms, no pristine areas of the surface remain [similar to Tagawa, *Surf. Sci.* **440**, 49 (1999)].

Shallow, circular etch pits grow in diameter linearly with O-atom fluence.

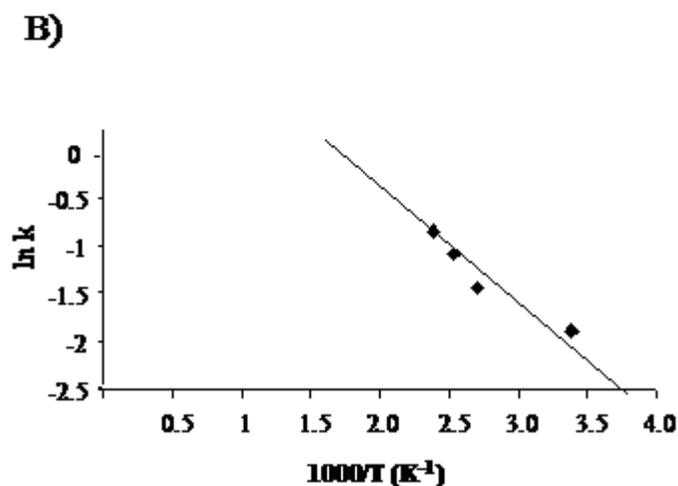
Pits frequently overlap, especially with higher O-atom fluences.

Minton, *J. Phys. Chem. B* **109**, 8476 (2005)

Erosion Kinetics of Edge Carbon Atoms



Linear growth of pit diameter gives effective zero-order rate constant for the reaction probability between O atoms and edge carbon atoms: 1 C atom removed for every 2.3 O atoms ($3.8 \times 10^{-24} \text{ cm}^3 \text{ atom}^{-1}$).

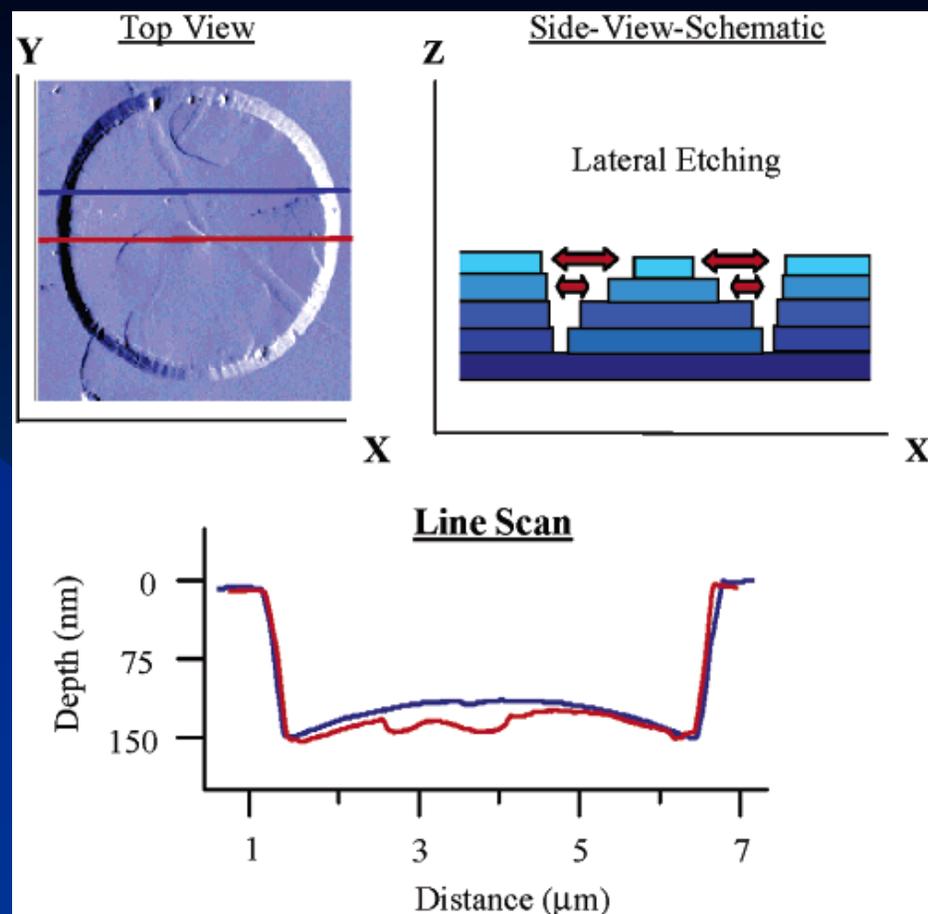


Zero-order rate constant is temperature dependent, and Arrhenius plot gives an activation energy of $E_a = 10.5 \text{ kJ mol}^{-1}$ (0.11 eV).

Curvature of Etch Pit Bottoms

Grazing-angle scattering of O atoms from the emerging pit sidewall probably leads to a relatively high flux of energetic O atoms around the peripheral edge of the pit, thus enhancing the rate of carbon atom removal in this localized region.

Edge carbon atoms are exposed inside and outside the “foot” of the sidewall, and lateral etching can be both inward and outward.



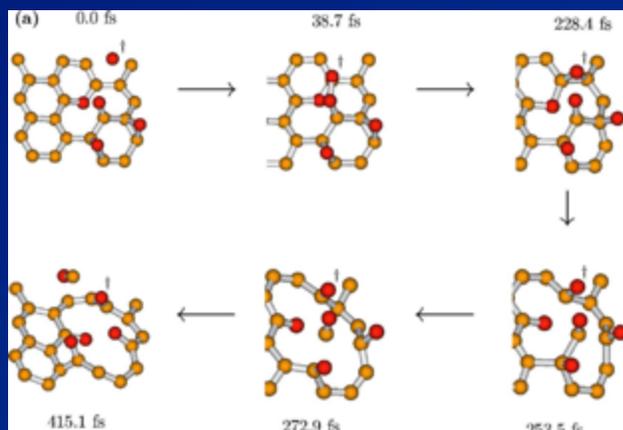
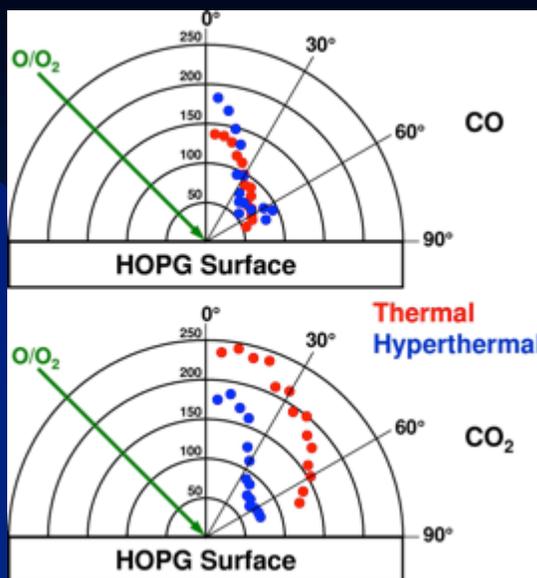
Hyperthermal O-Atom Reactions on Graphite

Reactive scattering dynamics

When hyperthermal O atoms strike a graphite surface, CO and CO₂ are formed via non-equilibrium mechanisms, as indicated by angular and translational energy distributions.

Experiment →

Theory ↙



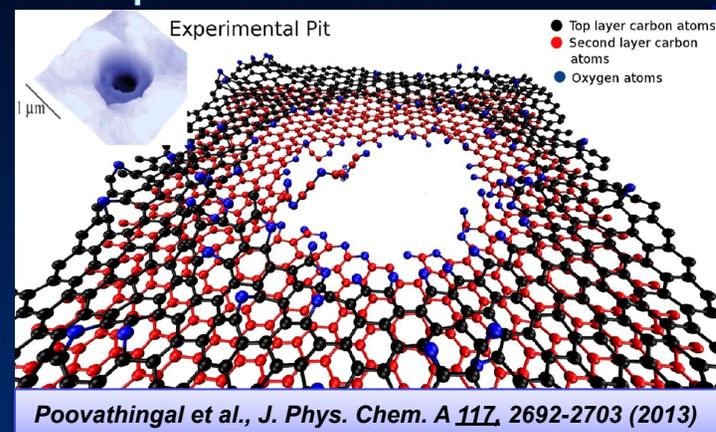
Direct dynamics calculations (using DFT) reveal complex mechanisms, with release of CO and CO₂ from the surface following surface functionalization with oxygen.

Paci et al., J. Phys. Chem. A **113**, 4677-85 (2009)

Paci et al., Accts. Chem. Res. DOI 10.1021/ar200317y (2012)

ReaxFF Calculations

ReaxFF calculations are validated by earlier direct dynamics calculations and experimental results.



Conclusions

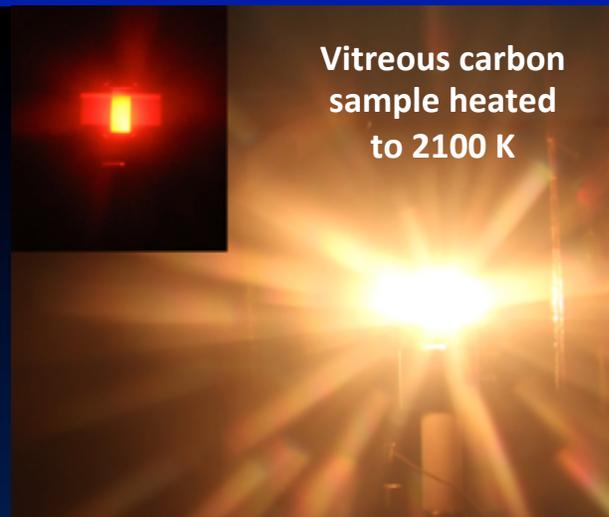
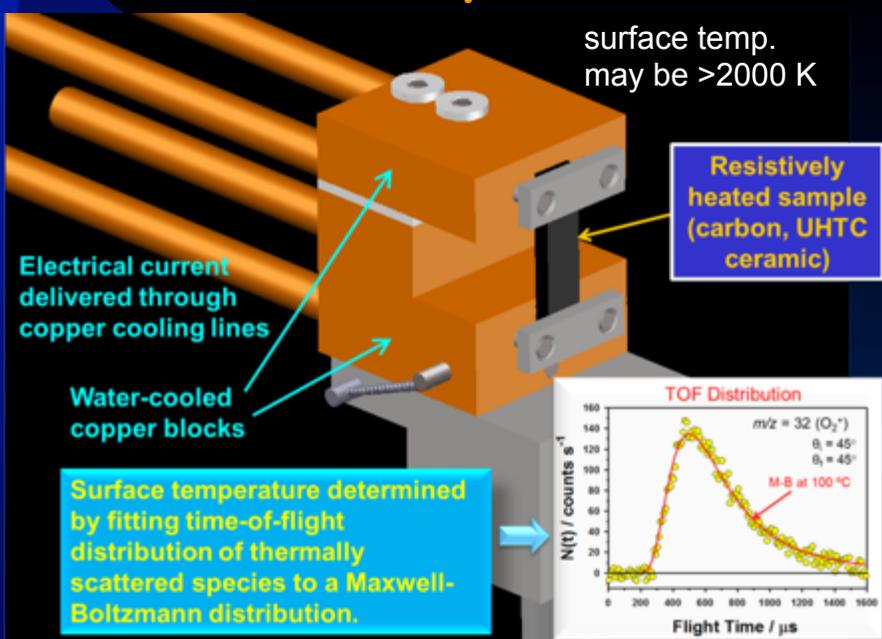
Anisotropic etching on HOPG: lateral etch rate much higher than downward etch rate.

At higher surface temperatures, ~200 °C, downward etching competes with lateral etching, and surface topography changes from etch pits to random roughness.

No reaction at all between O atoms and undefected graphene sheet.

CO and CO₂ mainly formed when epoxide groups diffuse to holes on the surface where carbonyl groups are already present.

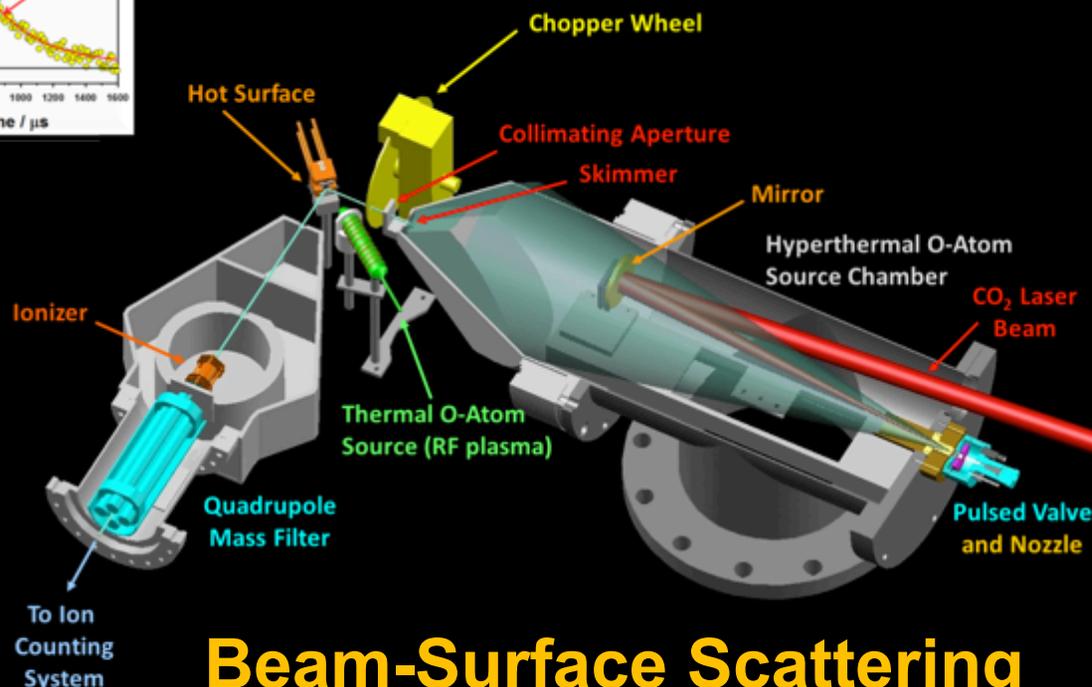
Heated Sample Mount



Grad student, Vanessa Murray inspects hot carbon sample

Hyperthermal O or thermal O and O_2 beams can be directed at high-T surfaces.

Volatile products and their dynamical behavior can be explored with a rotatable mass spectrometer detector.



Beam-Surface Scattering Experiments

Vitreous (Glassy) Carbon

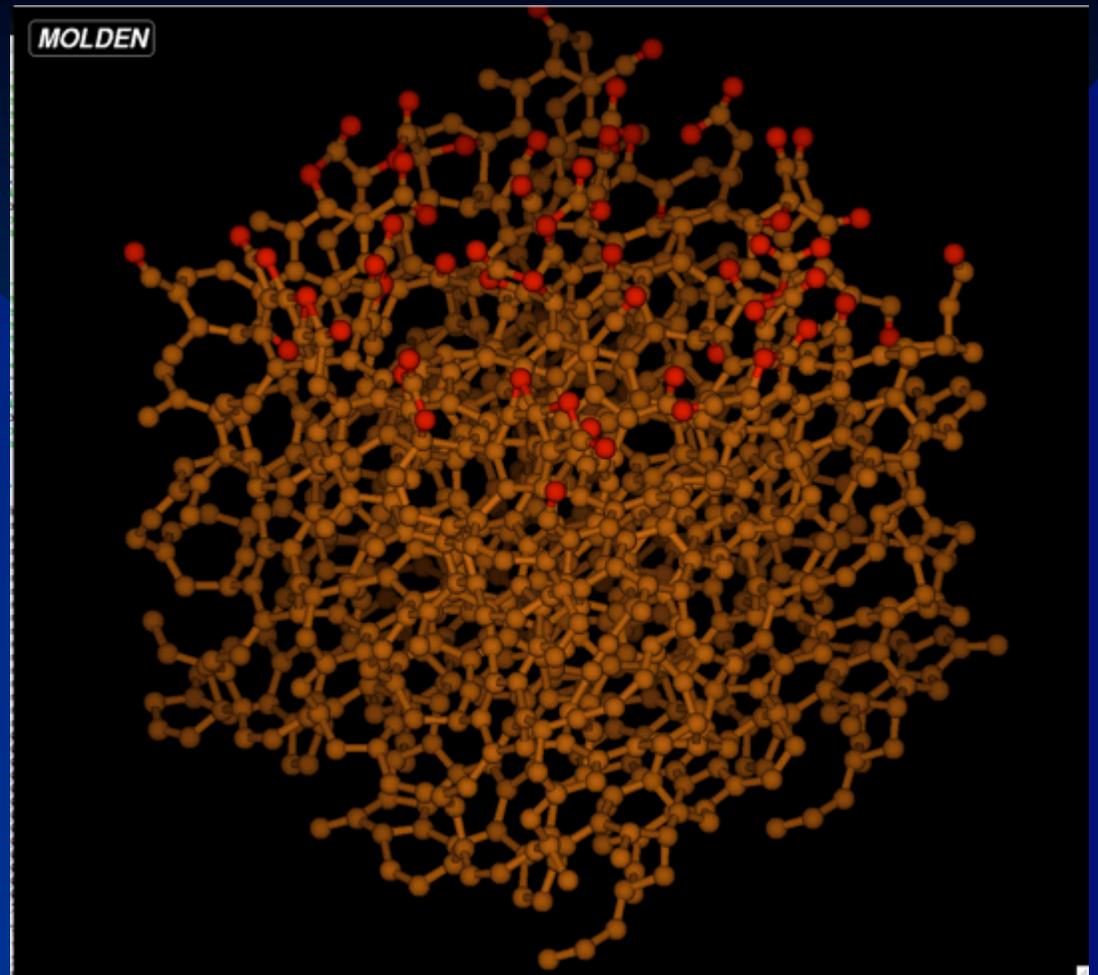
sp^2 carbon, with fullerene-related structure.

Isotropic, electrically conducting, impermeable to gases and a low coefficient of thermal expansion.

Lower density ($1.3\text{-}1.5\text{ g/cm}^3$) than graphite (2.27 g/cm^3) or diamond (3.52 g/cm^3).

May undergo similar atomic-level reactions as graphite with oxygen.

Vitreous carbon and HOPG can be two limiting cases for the study of the oxidation of sp^2 carbon.

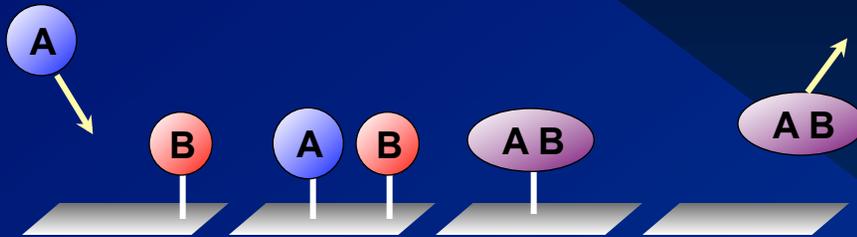


Model of partially oxidized vitreous carbon provided by Adri van Diun's group

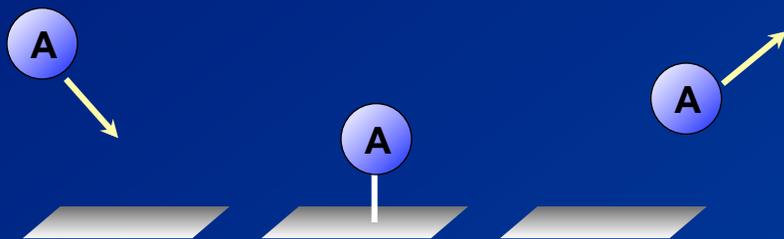
Gas - Surface Interactions

Thermal Mechanisms

Langmuir-Hinshelwood reactive

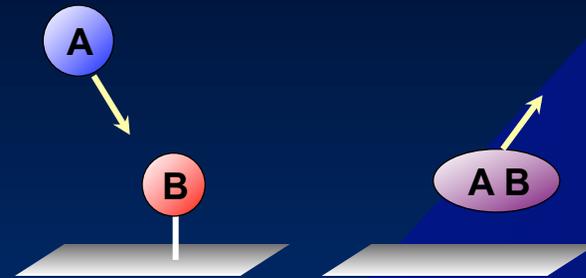


Trapping (thermal) Desorption nonreactive



Non-thermal Mechanisms

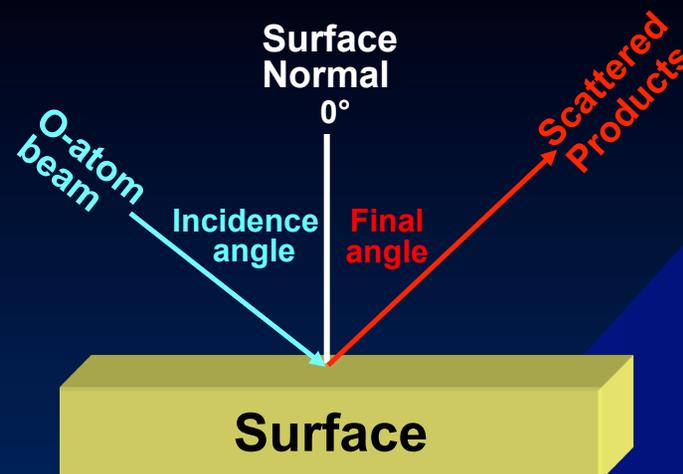
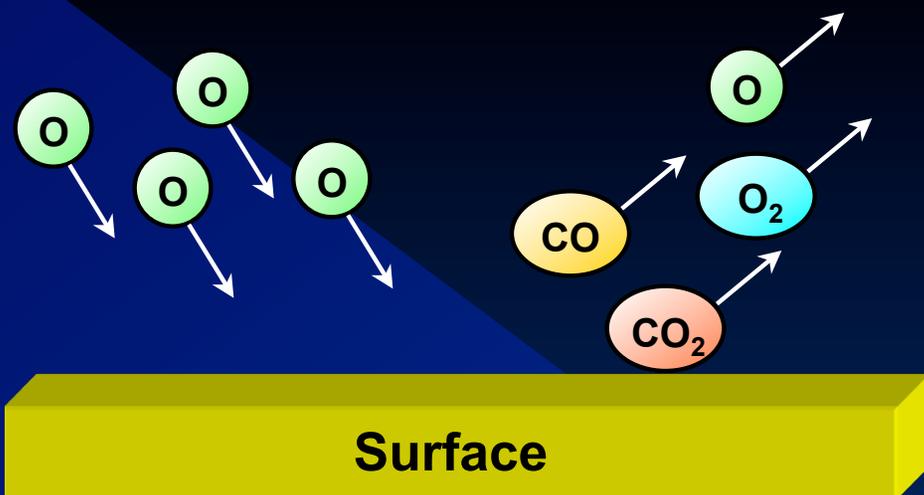
Eley-Rideal reactive



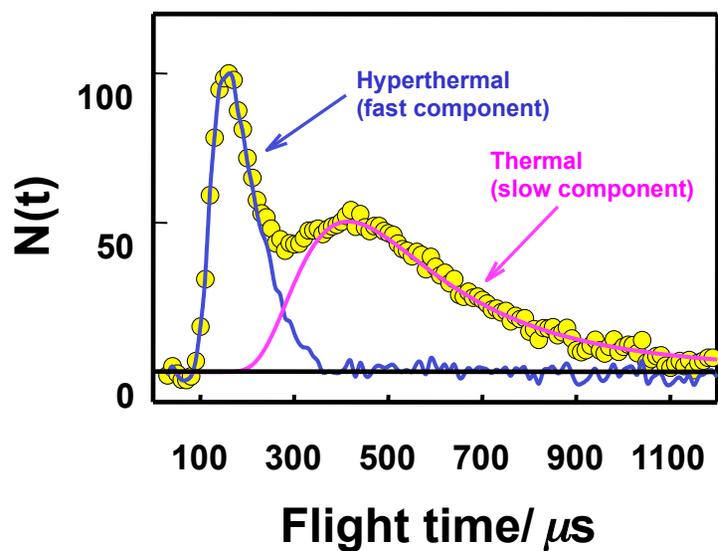
Inelastic (impulsive) Scattering nonreactive



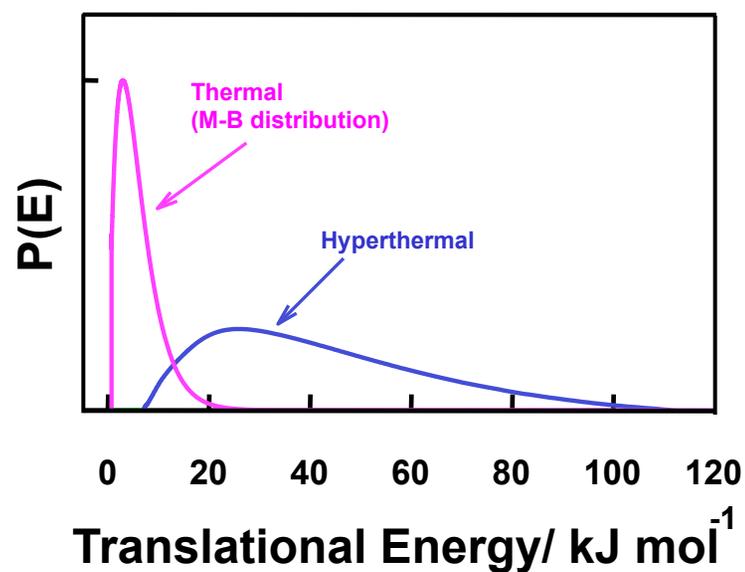
Beam-Surface Scattering



TOF Distribution



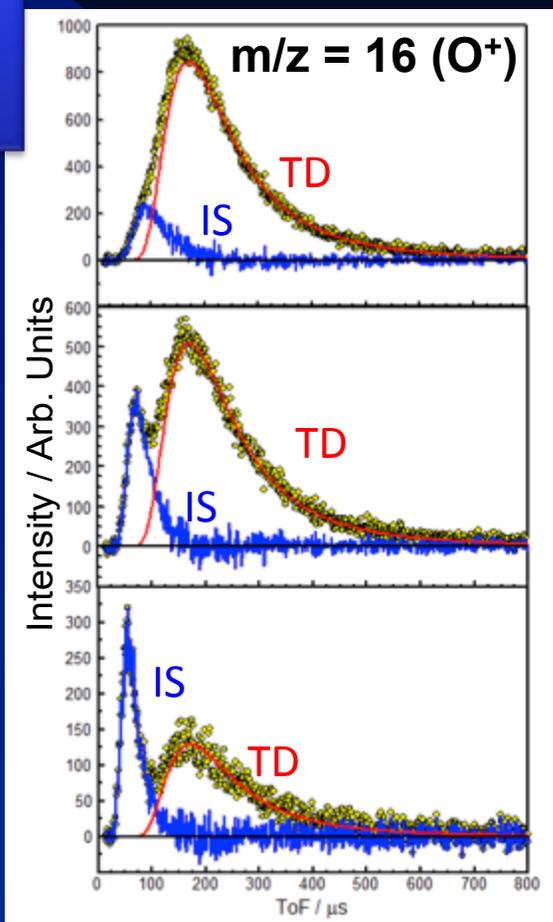
Translational Energy Distribution



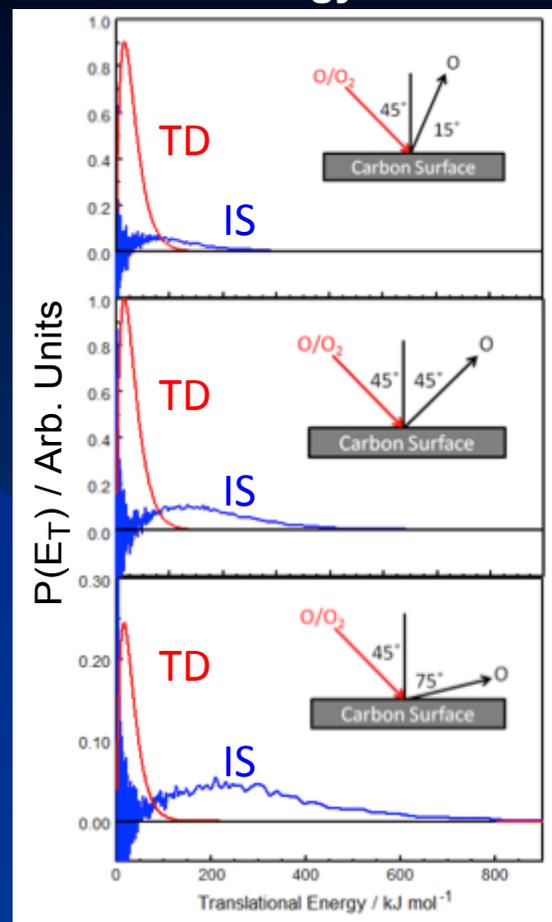
Time-of-Flight and Translational Energy Distributions at 1875 K: *inelastic scattering of O atoms*

$E_{inc} =$
494 kJ mol⁻¹
(5.1 eV)

TOF distributions



Translational energy distributions

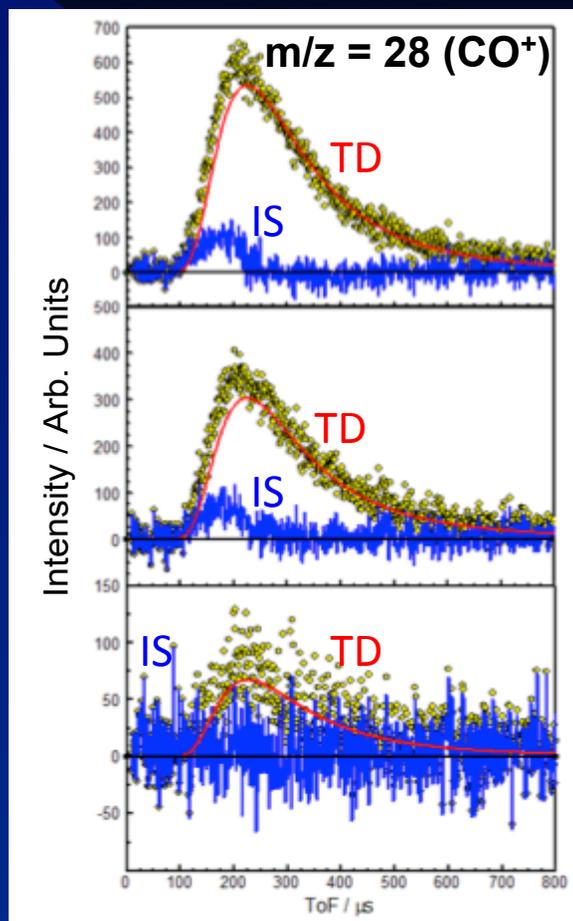


Significant thermal and non-thermal scattering; ratio depends on scattering angle.
Non-thermal scattering has broad energy distribution.

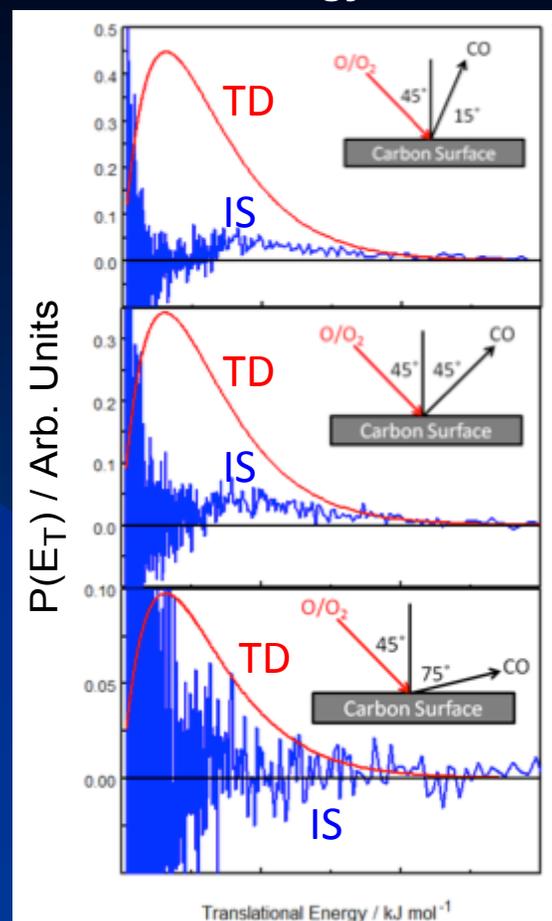
Time-of-Flight and Translational Energy Distributions at 1875 K: reactive scattering of CO

$E_{\text{inc}} =$
494 kJ mol⁻¹
(5.1 eV)

TOF distributions



Translational energy distributions

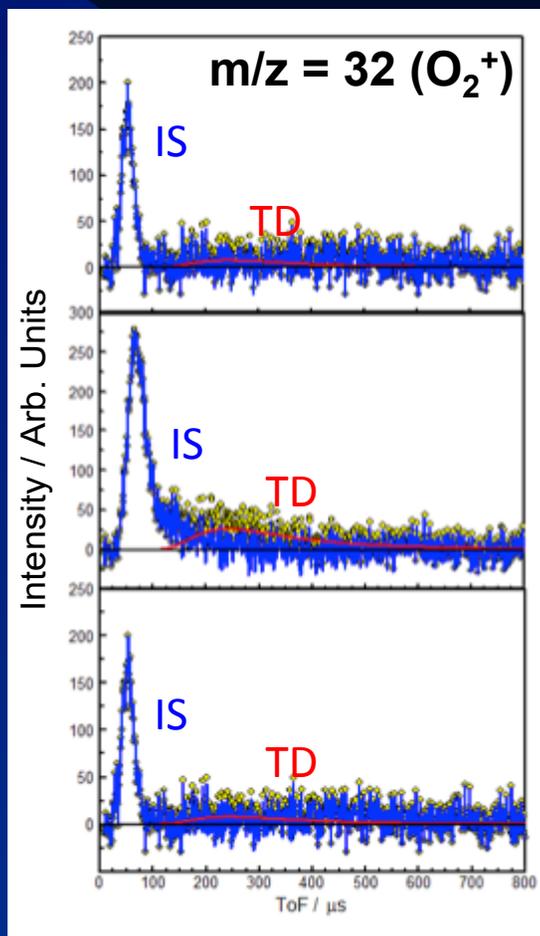


Thermal scattering is dominant; CO is produced in reaction that is in thermal equilibrium with the surface.

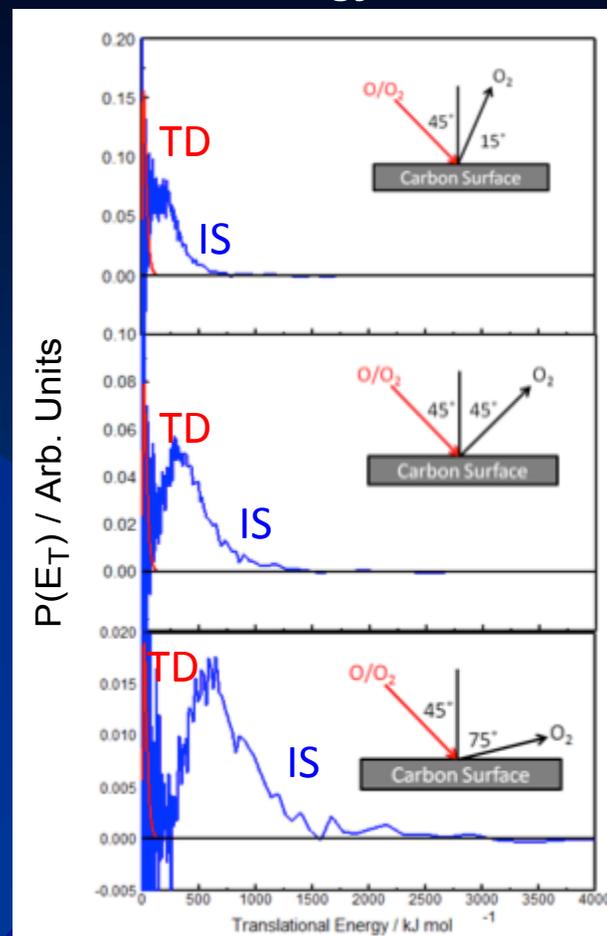
Time-of-Flight and Translational Energy Distributions at 1875 K: reactive scattering of O_2

$E_{inc} =$
494 kJ mol⁻¹
(5.1 eV)

TOF distributions



Translational energy distributions



Non-thermal scattering is dominant; suggests direct reaction of incident O-atom with surface O atom.

Angular Distributions

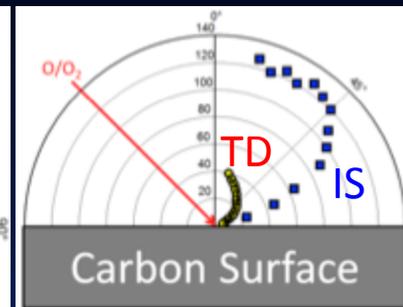
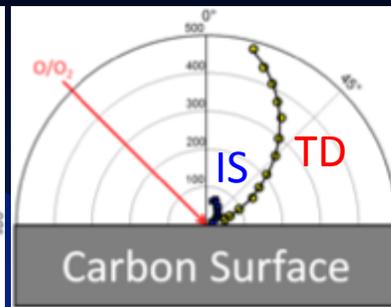
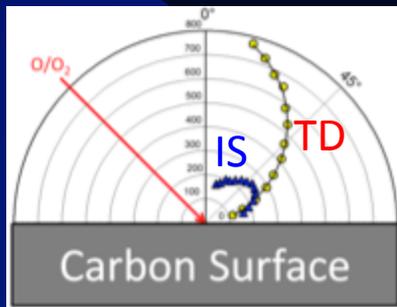
$m/z = 16$ (O^+)

$m/z = 28$ (CO^+)

$m/z = 32$ (O_2^+)

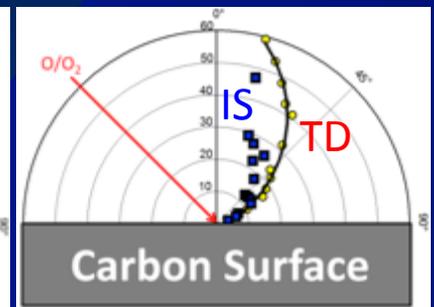
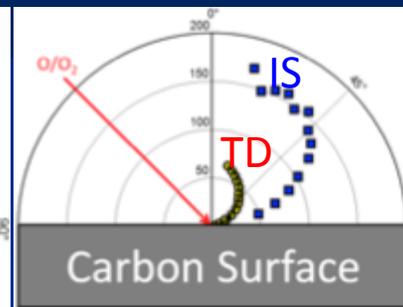
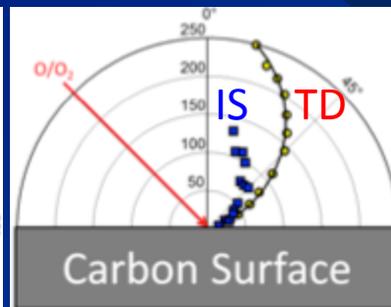
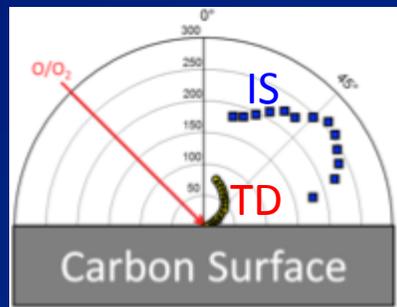
$m/z = 44$ (CO_2^+)

1875 K



Hyperthermal beam: $O/O_2 = 9$

750 K



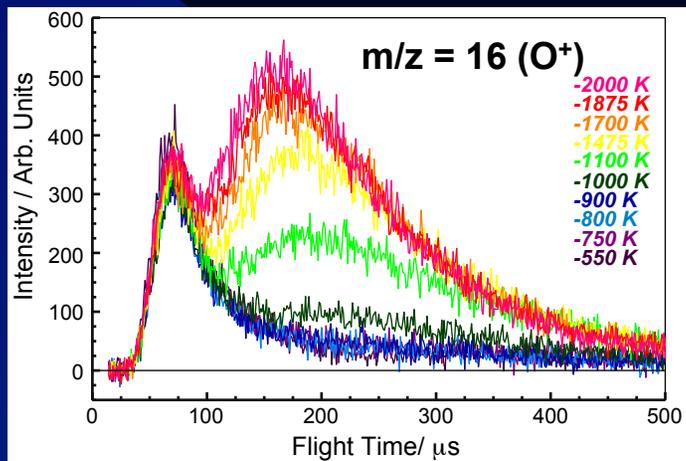
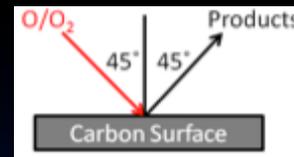
Inelastically scattered O atoms dominated by IS at low temperatures and TD at high temperatures; mainly because of large increase in TD product intensity at high temperatures.

CO signal increases as temperature increases; mainly because of increase in TD products.

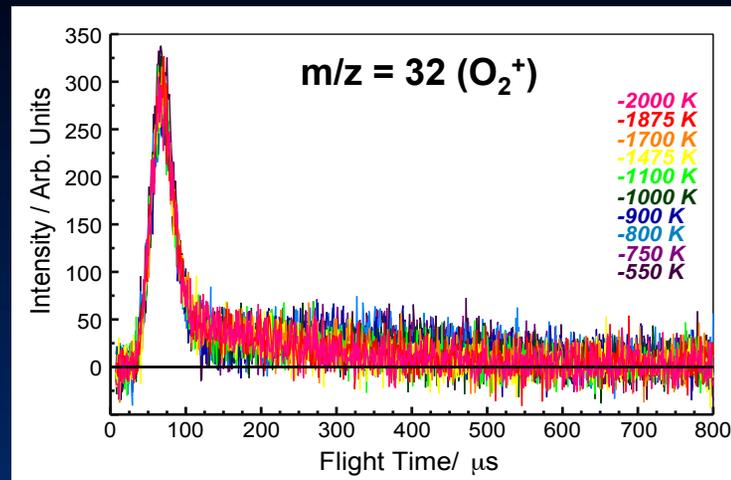
O_2 products largely independent of surface temperature; majority IS. Mixture of reactive and inelastic.

CO_2 is not produced at higher temperatures; possibly suppressed by $CO_2 + C \rightarrow CO + O$ reaction.

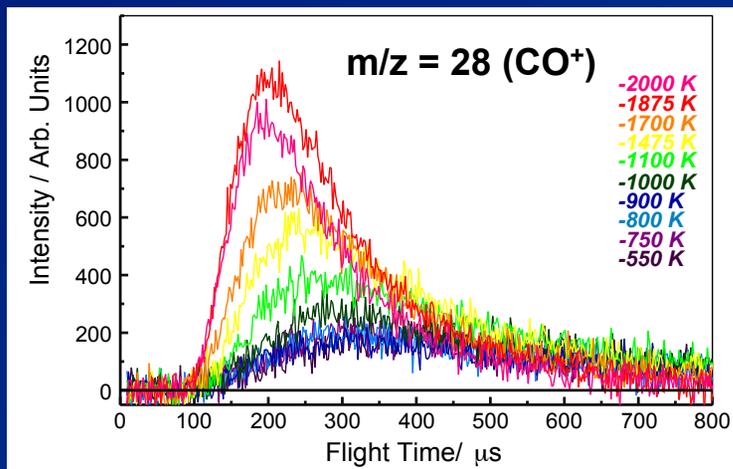
Temperature Survey



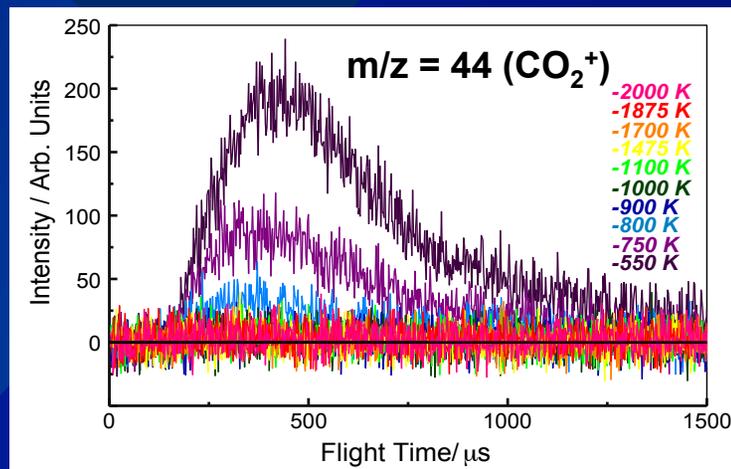
Inelastic scattering of O atoms exhibits hyperthermal and thermal components. The thermal component grows dramatically with increasing surface temperature.



Inelastic scattering of O_2 exhibits both hyperthermal and thermal components, with hyperthermal dominating.

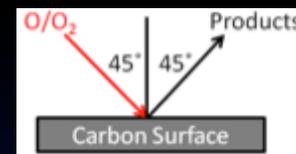


CO is by far the dominant reactive product, and it scatters mostly thermally with a small hyperthermal component.

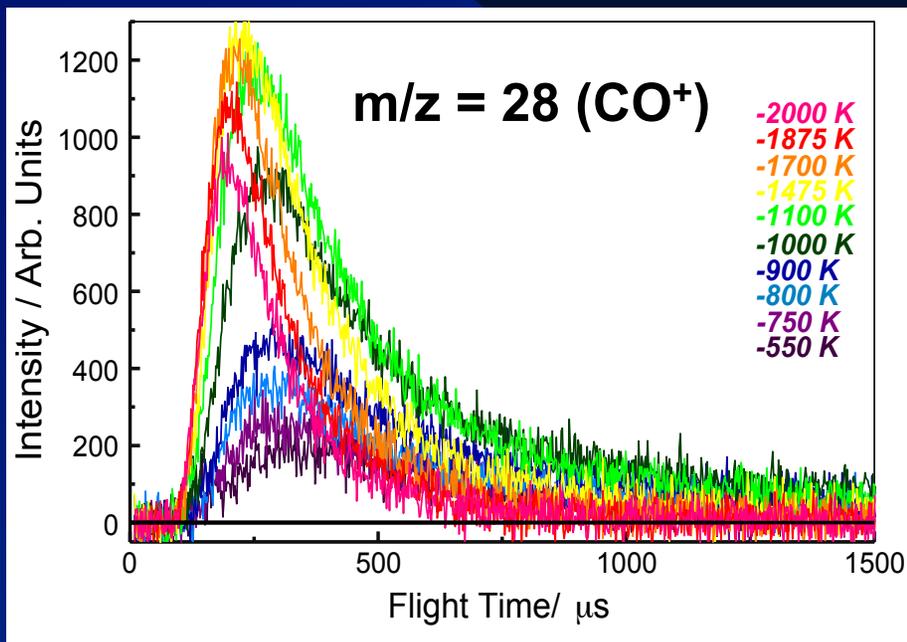


CO_2 is a major product at lower surface temperatures and becomes negligible at higher temperatures. CO_2 scatters mostly thermally.

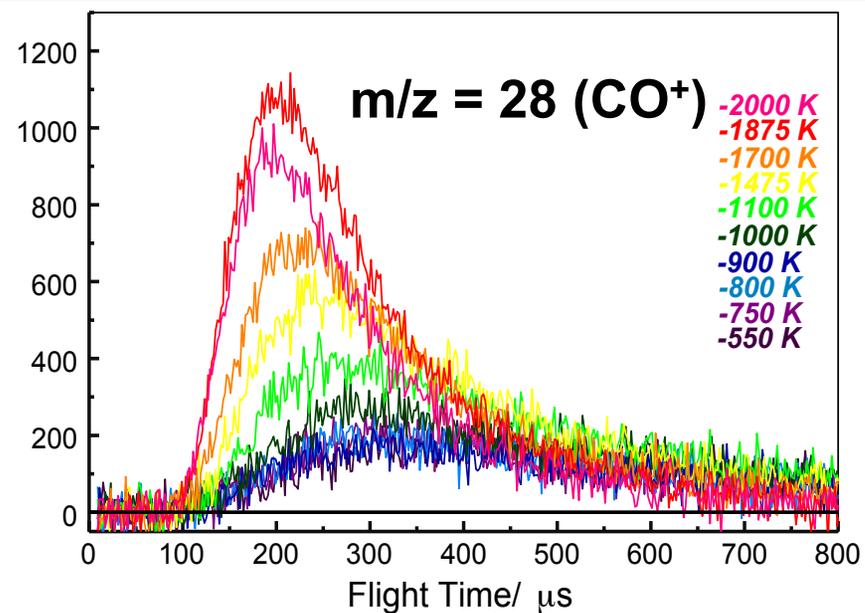
Hysteresis in Temperature Dependence



Increasing Surface Temperature

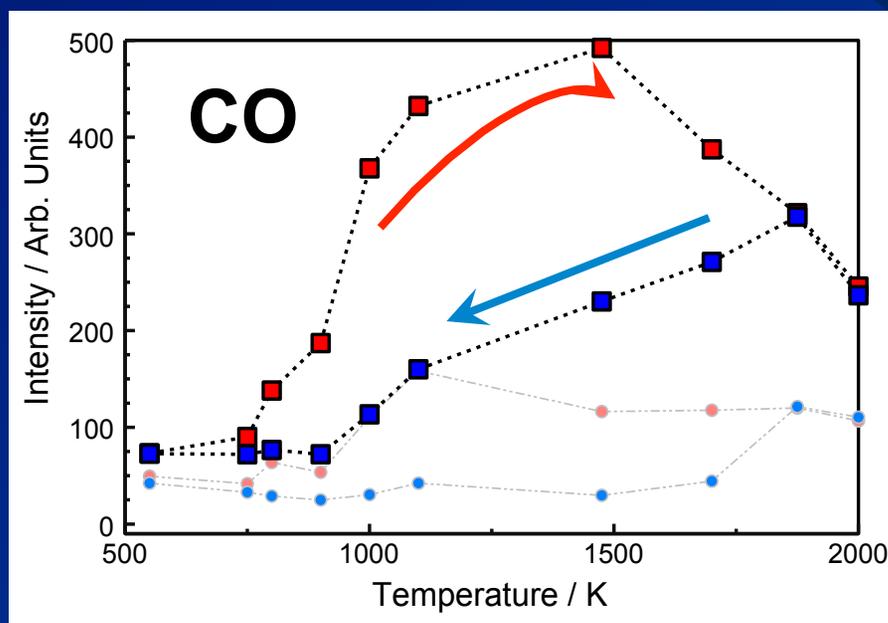
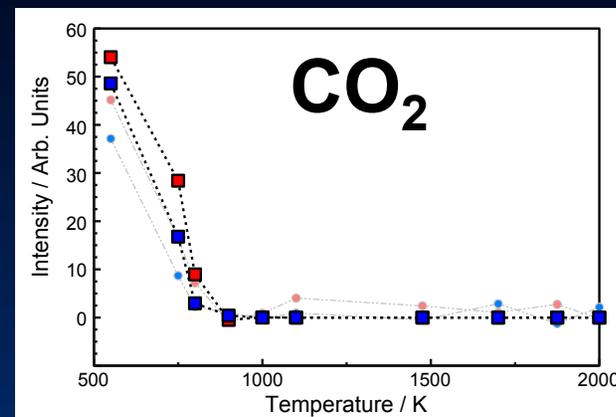
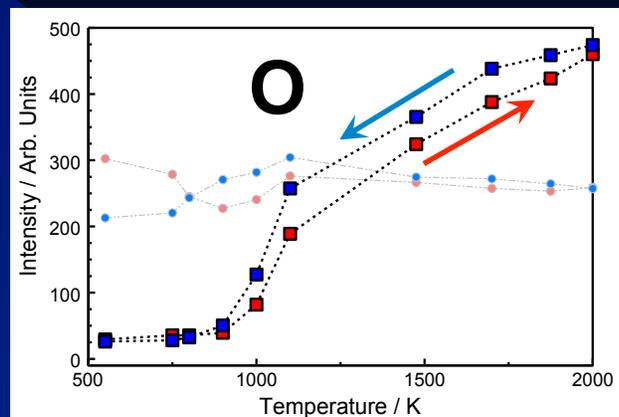
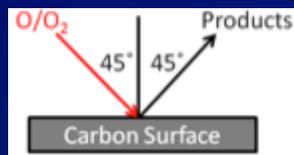


Decreasing Surface Temperature



The CO signal intensity increases with surface temperature up to 1475 K and then decreases. However, there is a hysteresis in CO production depending on whether the surface temperature is increasing or decreasing.

Exploring hysteresis in temperature dependence of scattered flux of O, CO, and CO₂



Small hysteresis in inelastically scattered O atoms, mainly in the TD component.

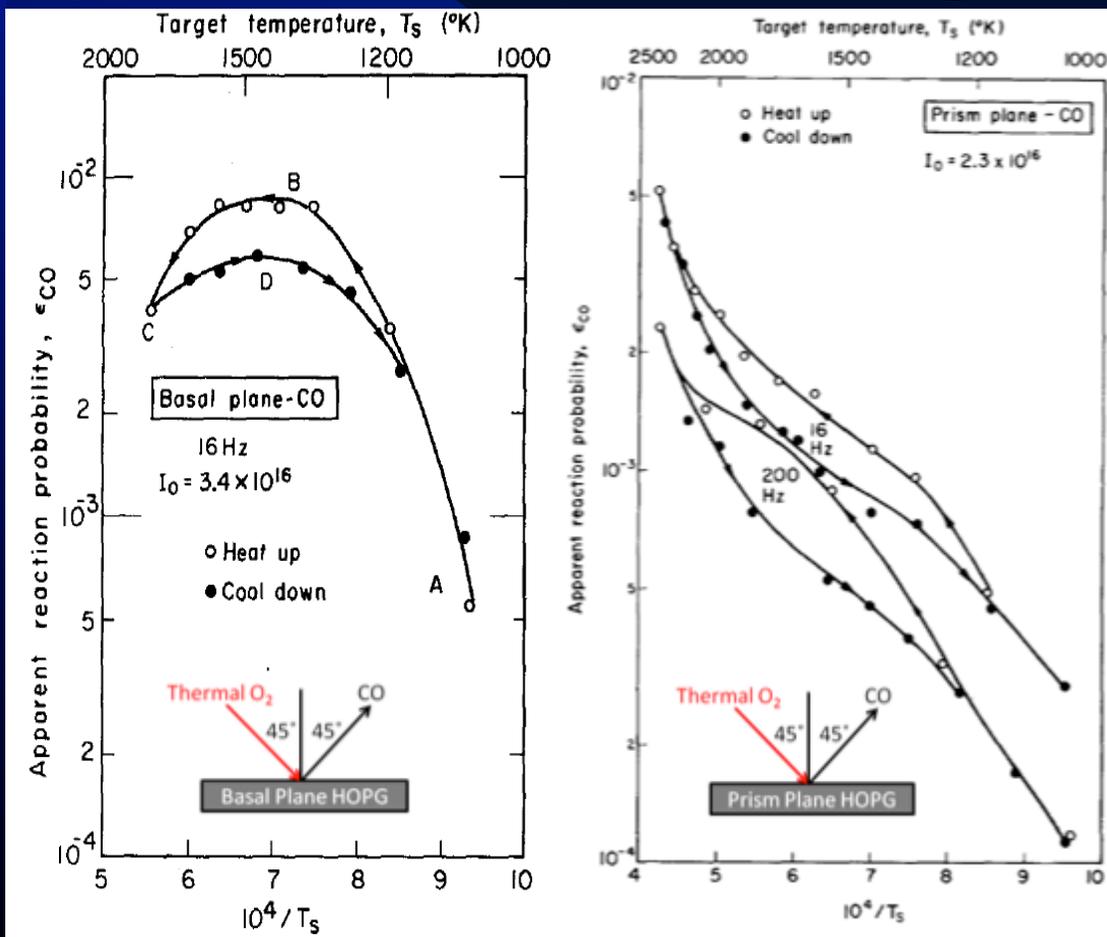
No hysteresis in reactively scattered CO₂, within experimental uncertainty.

Large hysteresis in reactively scattered CO, in both the IS and TD components.

Hysteresis in Temperature Dependence

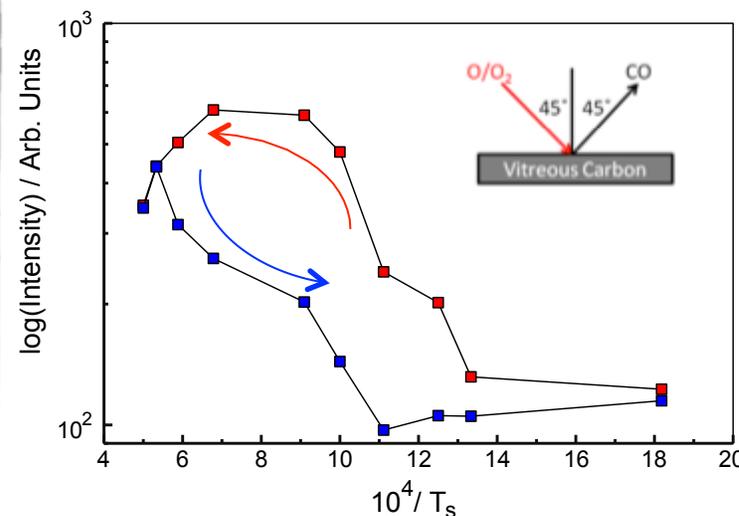
Earlier molecular beam experiment also showed hysteresis in CO signal when basal and prism planes of HOPG were exposed to thermal O₂.

New results with 5.1 eV O atoms striking a vitreous carbon surface.



Olander et al. J. Chem. Phys. 57, 408 (1972)

Olander et al. J. Chem. Phys. 57, 408 (1972)

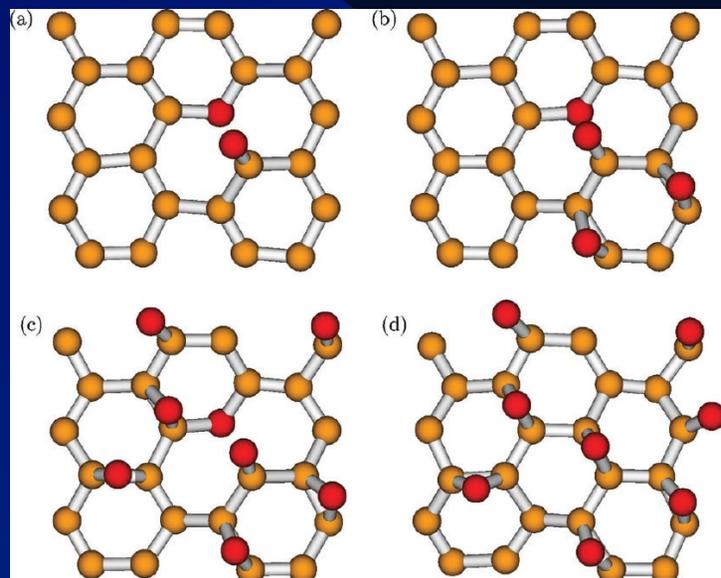


Oxidation of carbon surface at lower temperatures makes the surface more reactive.

“Cooking” the surface for ~1 hr during O or O₂ bombardment at higher temperatures brings CO product flux down to lower curve, where flux remains stable.

Theoretical Calculations of O + Graphite Interactions

Methods: SCC-DFTB-based and PBE/DZP-based direct dynamics calculations using a graphene model.



Reaction	Model A	Model B	Model C	Model D
ring opening	68	26	25	0
epoxide formation	151	147	62	24
epoxide migration	58	80	33	38
carbonyl formation	5	1	0	0
O ₂ formation	1	34	108	155
CO ₂ formation	0	4	3	0
CO formation	0	1	6	0
dioxirane formation	0	2	2	0
inelastic O	0	7	14	4
sheet damage	0	0	0	5

Model surfaces with different amounts of oxidation – **no reaction of 5 eV O atoms on defect-free graphene sheet**

Paci et al., *J. Phys. Chem. A* **113**, 4677-85 (2009)

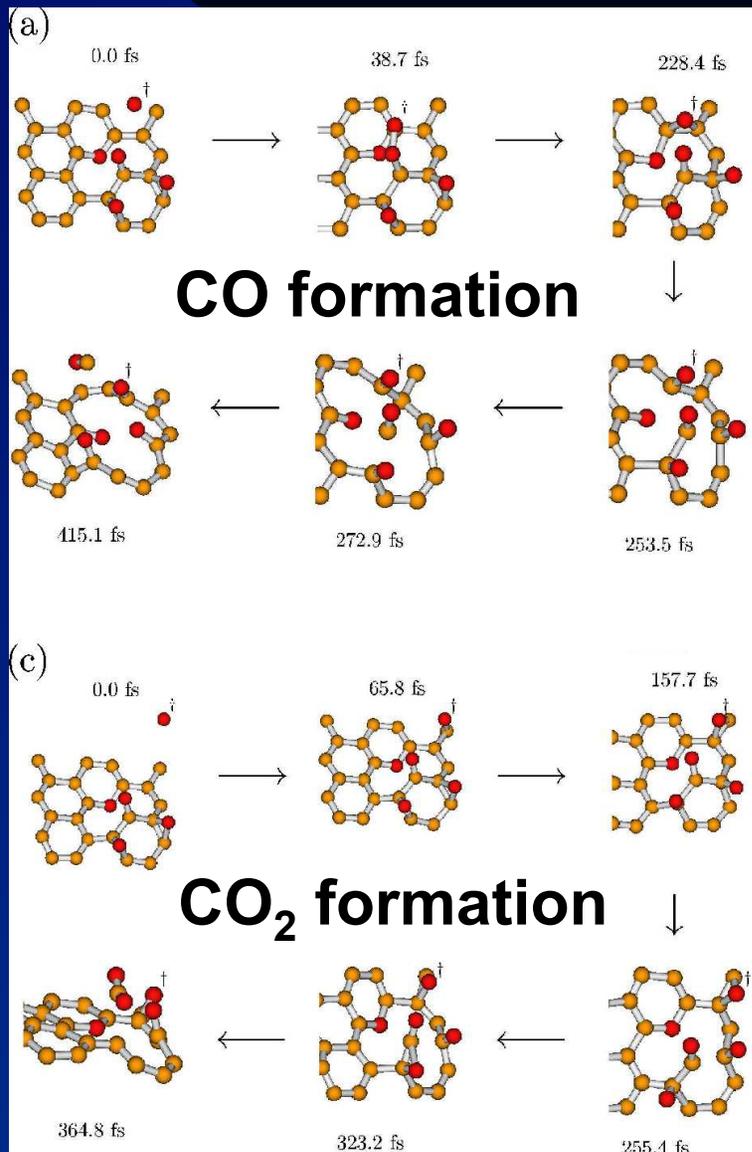
Paci et al., *Accts. Chem. Res.* DOI 10.1021/ar200317y (2012)

Epoxide formation is highly probable.

Direct reaction of incident O atom with surface O atom to produce O₂ becomes likely on oxidized surface.

Formation of CO and CO₂ become more probable on oxidized surface with defects (or “holes”).

CO and CO₂ Formation on Graphite



CO and CO₂ arise when epoxide groups diffuse to holes on the surface where carbonyl groups are already present. CO and CO₂ form when these carbonyl groups dissociate from the surface, resulting in larger holes.

CO and CO₂ are formed indirectly, and they are likely to desorb along the surface normal, in agreement with experiment.

Reaction at defect sites on graphene sheet and growing size of holes resulting from reactions that produce CO and CO₂ is consistent with observation of lateral etching vs. downward etching.

Summary and Speculations – 1

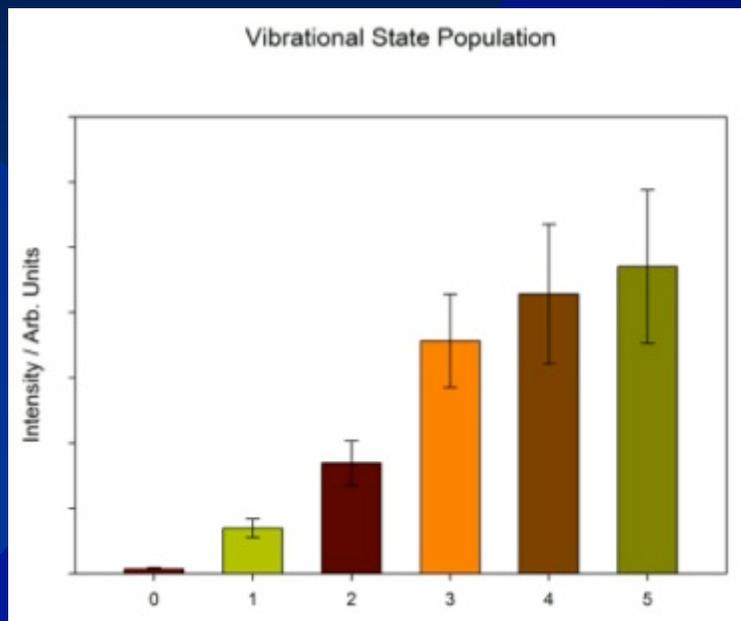
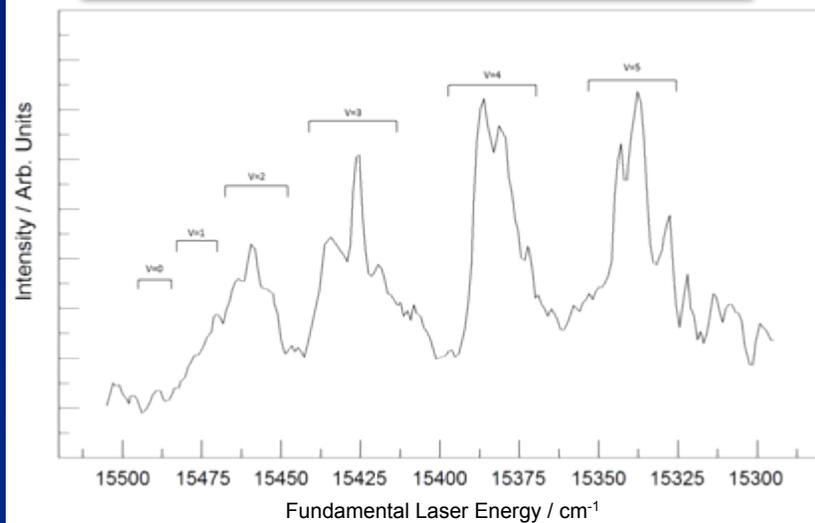
- **Increasing thermal O-atom scattering at higher temperatures.**
Chemisorbed O atoms may be more easily desorbed as T increases.
- **Non-thermal O₂ scattering at all temperatures.**
Incident O atom picks off a surface O atom in direct (Eley-Rideal) reaction, consistent with theoretical calculations.
- **CO₂ and CO have comparable intensities at ~550 K, but CO₂ is essentially gone above 1000 K.**
 - Possibly the result of the Boudouard reaction: $\text{CO}_2 + \text{C} \rightarrow \text{CO} + \text{O}$.
 - At elevated T , the full oxidation of carbon to CO₂ may be “short-circuited” by desorption of CO.
- **CO₂ and CO have significant non-thermal scattering components at lower T that become relatively unimportant at higher T .**
Hyperthermal collisions lead to ejection of CO and CO₂, but at higher T , slower, thermal reactions apparently become dominant.

Summary and Speculations – 2

- **Hysteresis in dominant reactive product (CO).**
 - Surface apparently oxidizes more at lower T and is therefore more reactive; higher T reduces the oxide and thus the reactivity.
 - Consistent with theory, which finds more reactivity on more highly oxidized surface.
 - Consistent with larger thermal O-atom scattered flux at higher T .
 - Consistent with decrease in CO scattered flux as T becomes very high: increased reactivity to produce CO is counter-balanced by reduction of O atoms available for reaction.
- **Similar behavior in CO product from thermal O₂ reactions with HOPG and from hyperthermal O-atom reactions with vitreous carbon; suggests that rate limiting processes may be similar.**
 - It was found that dissociative chemisorption of O₂ is not rate limiting in the thermal oxidation of HOPG at high T : thermal O-atom reactions must dominate.
 - Observation of mostly thermal O and CO implies that non-equilibrium reactions are minor even under hyperthermal O-atom bombardment.
 - Consistent with larger thermal O-atom scattered flux at higher T .
 - Theory and experiment suggest that oxidation occurs at edges of graphene sheets in a thermal, activated process.

Further Molecular Beam Studies of Oxygen-Carbon Reactions

- In-depth analysis of existing data and comparison with ongoing theoretical simulations in Adri van Duin's group.
- Additional experiments on the reactions of thermal O_2 with vitreous carbon and thermal O_2 and hyperthermal O with HOPG, coupled with additional theoretical calculations.
- Gas-phase reactions of oxygen with carbon clusters: $C + O_2$, $O + C_2$, $O + C_3$.



**Vibrational population inversion
in CO products**