

# Equilibrium Adsorption of $(\text{O}_2)_m$ on Gold Anions $\text{Au}_n^-$

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2005 Gordon Conference: Clusters and Nanoparticles

# Overview

## Objective

Measure equilibrium adsorption of oxygen molecules on gold cluster anions in the size range  $n = 7-26$

## Methods

- Sputter ion gas aggregation cluster source
- Radio frequency ion trap
  - temperature controlled (120-400 K)
  - cluster storage ( $t \leq 600$  s)
  - mass spectrometry ( $R=M/\Delta M \leq 500$ )

## Results

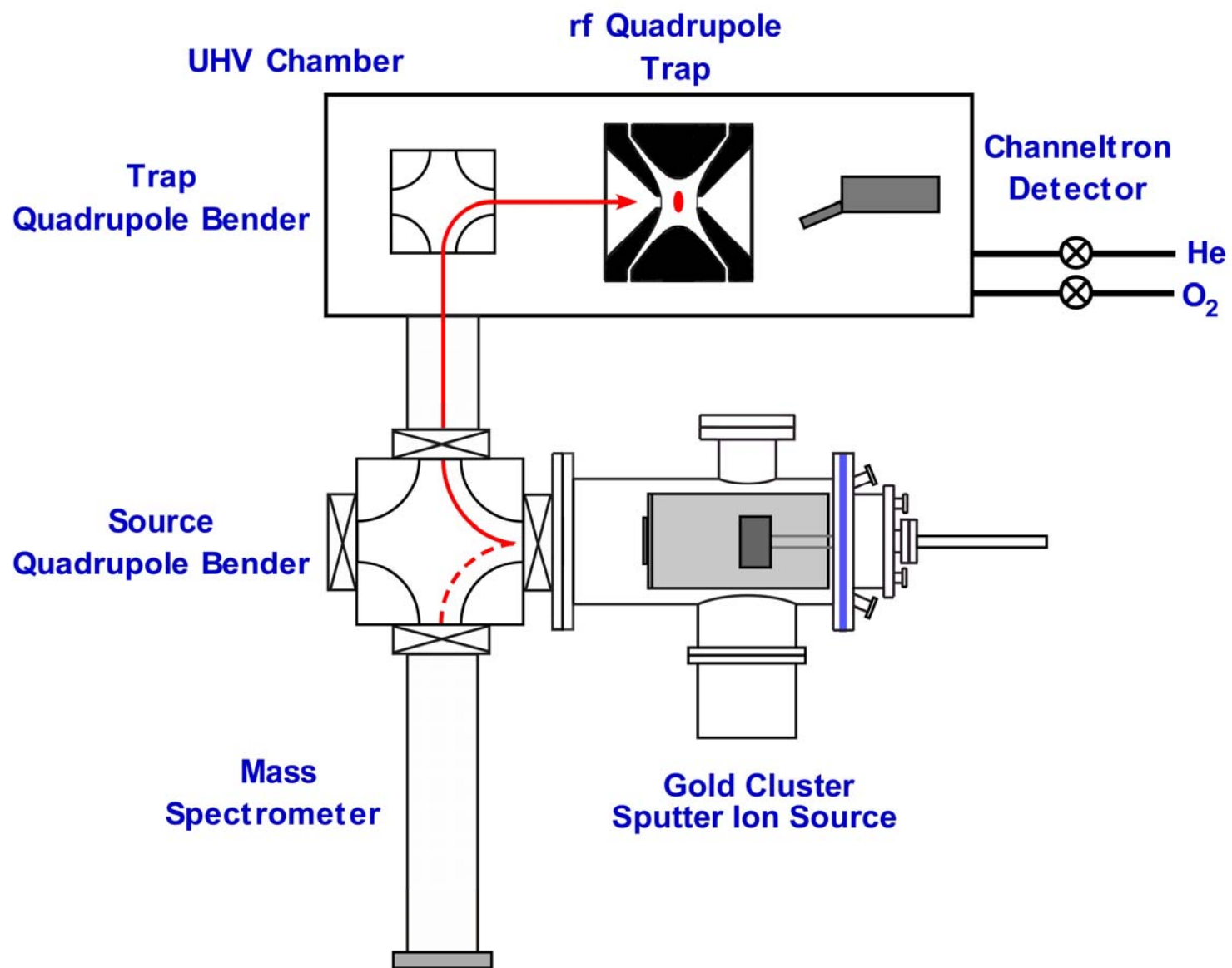
- Equilibrium formation of  $[\text{Au}_n(\text{O}_2)_m]^-$  observed for  $m=1-3$ 
  - dependence of  $K_{\text{equil}}$  on  $n$
  - formation/relaxation rates

# Introduction

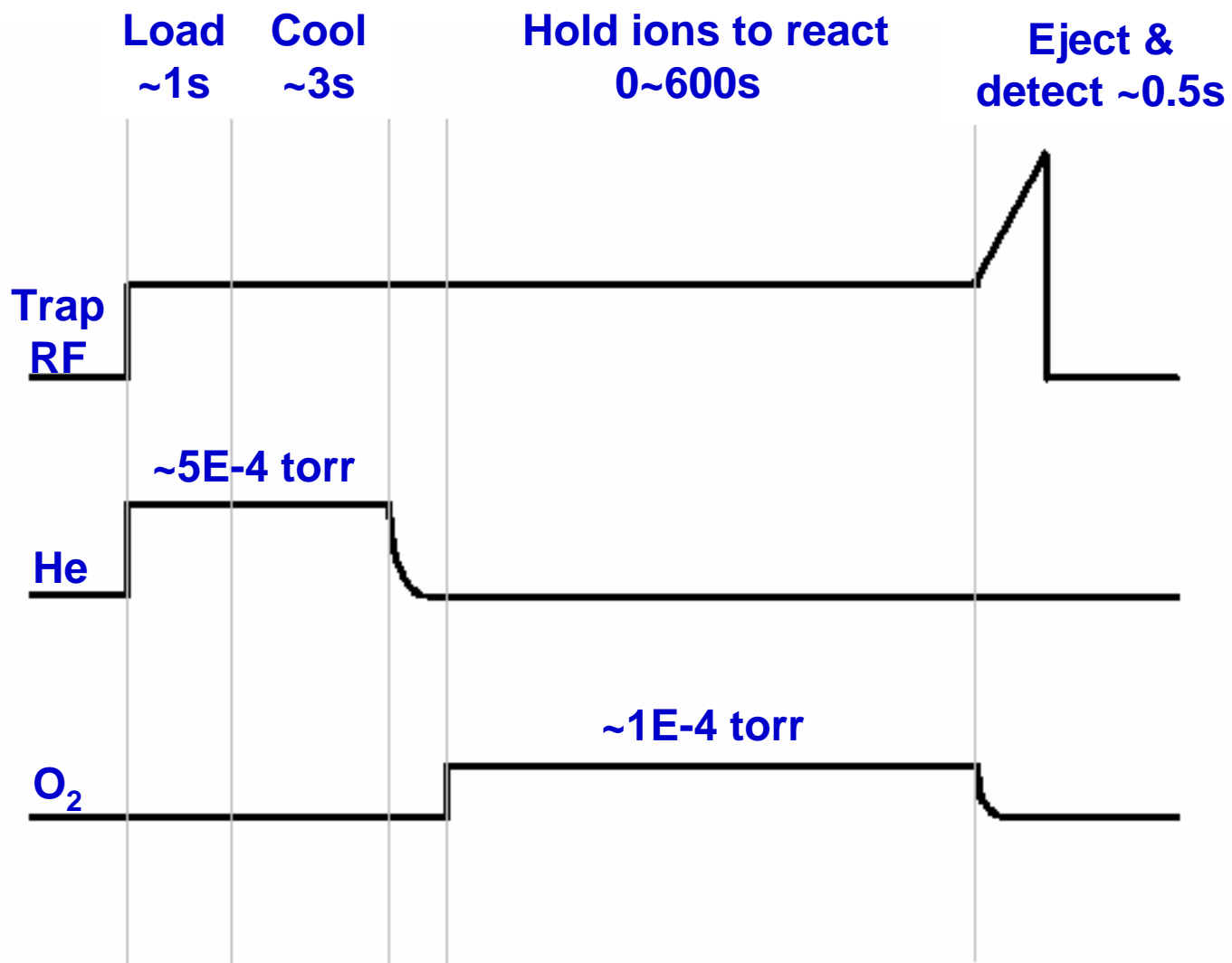
The catalytic reactivity of gold clusters has been an active area of research since experiments<sup>1,2</sup> and analysis<sup>3</sup> demonstrated the formation of CO<sub>2</sub> following co-adsorption of O<sub>2</sub> and CO on supported gold clusters. In particular the back donation of electrons to the gold clusters supported on MgO substrates<sup>2,3</sup> motivated gas phase measurements of the adsorption of O<sub>2</sub> and CO on gold cluster anions<sup>4</sup> and also calculations<sup>5</sup> of O<sub>2</sub> adsorption on gas phase anions. The anion measurements were performed in a the pulsed flow-reactor and observed single molecule uptake of O<sub>2</sub> throughout the even number cluster size range n=2-22. However calculations<sup>6,7</sup> suggested that adsorption on the odd ones or multiple O<sub>2</sub> molecules adsorption were expected.

Measurements of the diffraction of small gold anions have been underway in our laboratory during the past year. This ongoing research will concentrate on the changes in cluster structure induced by the adsorption of O<sub>2</sub> which has been discussed<sup>3,5,9</sup> previously. It has been necessary to determine the O<sub>2</sub> adsorption parameters required by the planned diffraction experiments. This poster describes the preliminary results of these measurements.

# Experiment Instrument

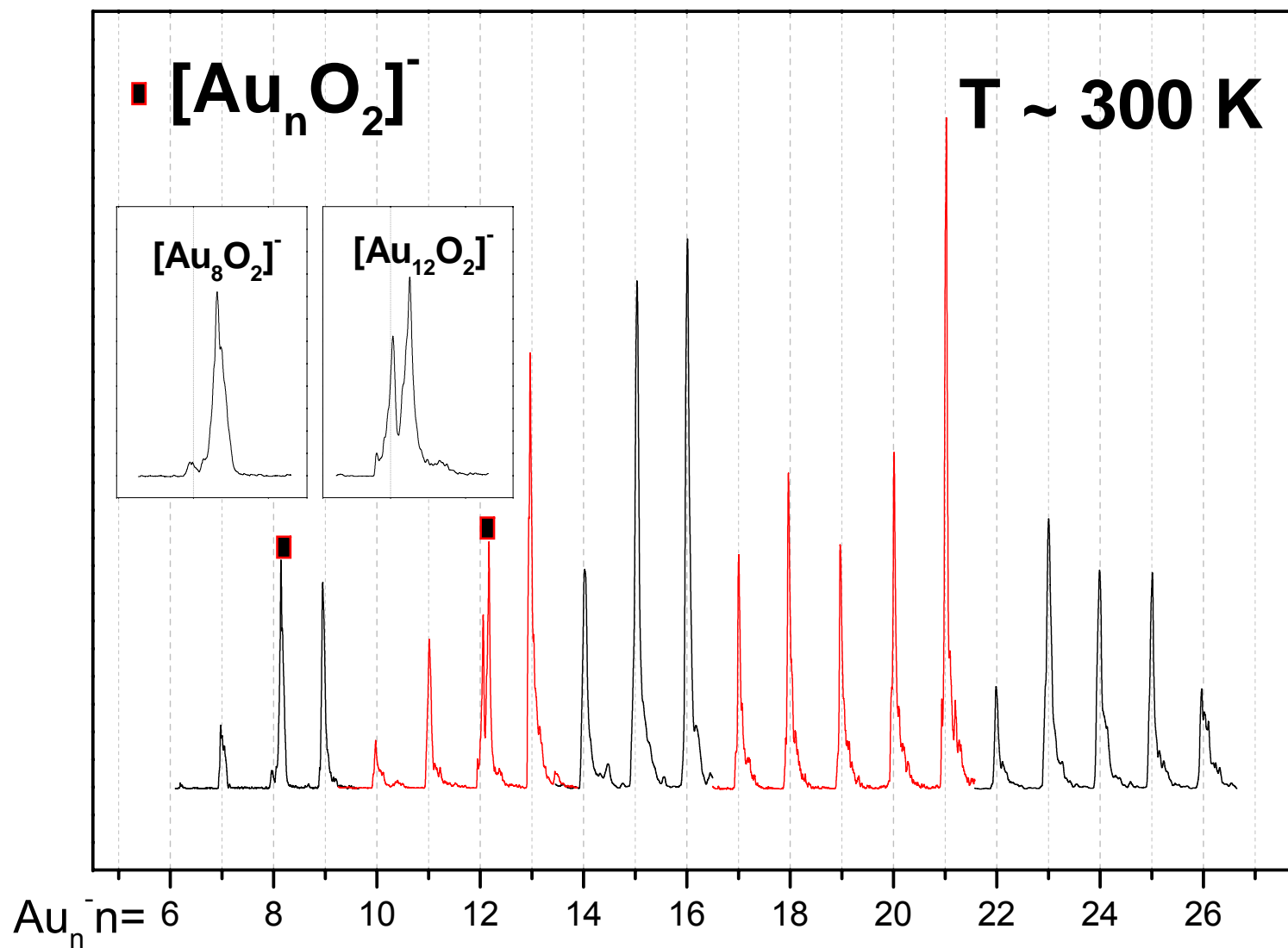


# Experimental Data Sequence



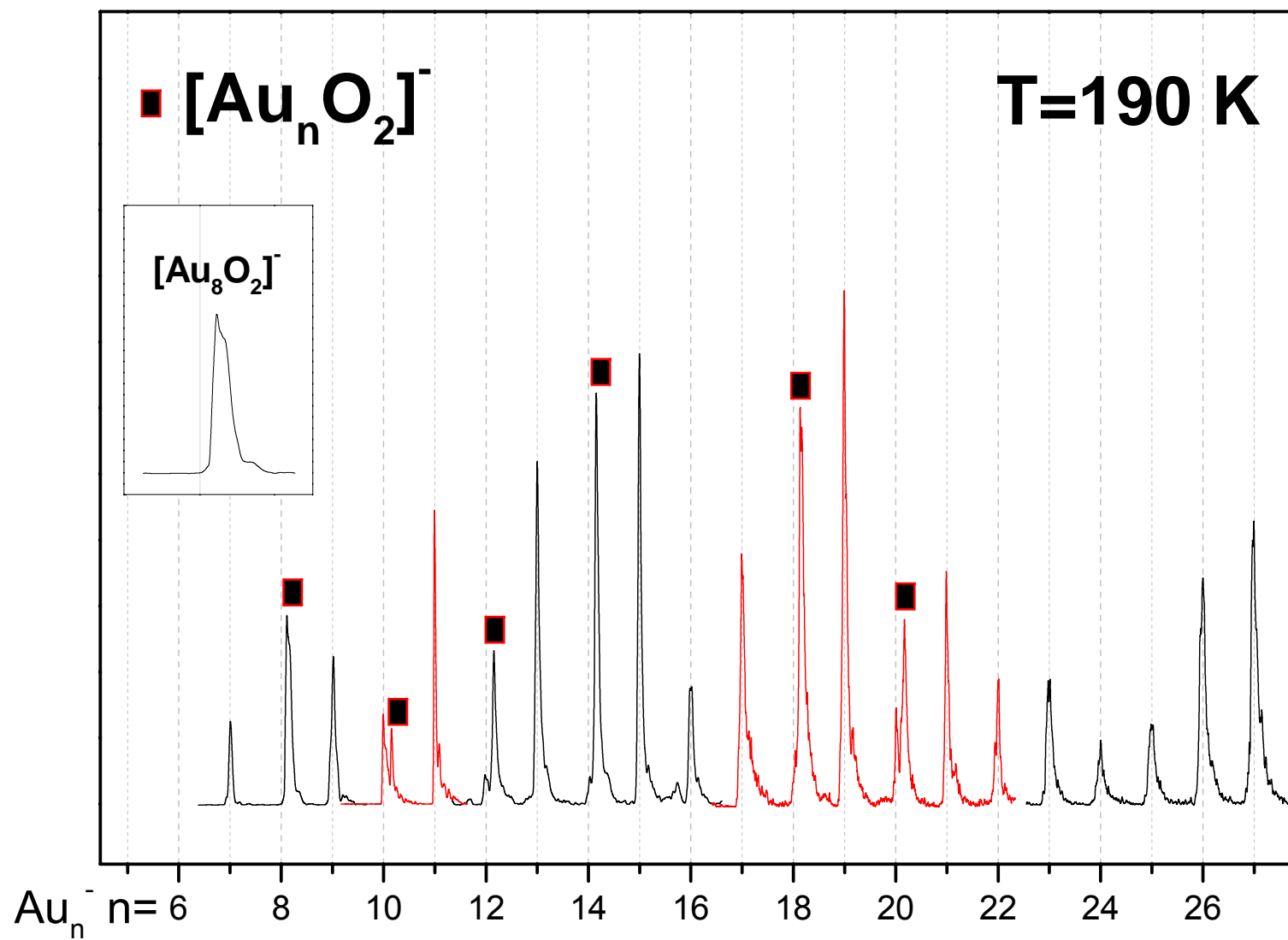
# O<sub>2</sub> Adsorption vs Au<sub>n</sub><sup>-</sup>

P(O<sub>2</sub>) ≈ 10E-4 torr    Hold ≈ 50s



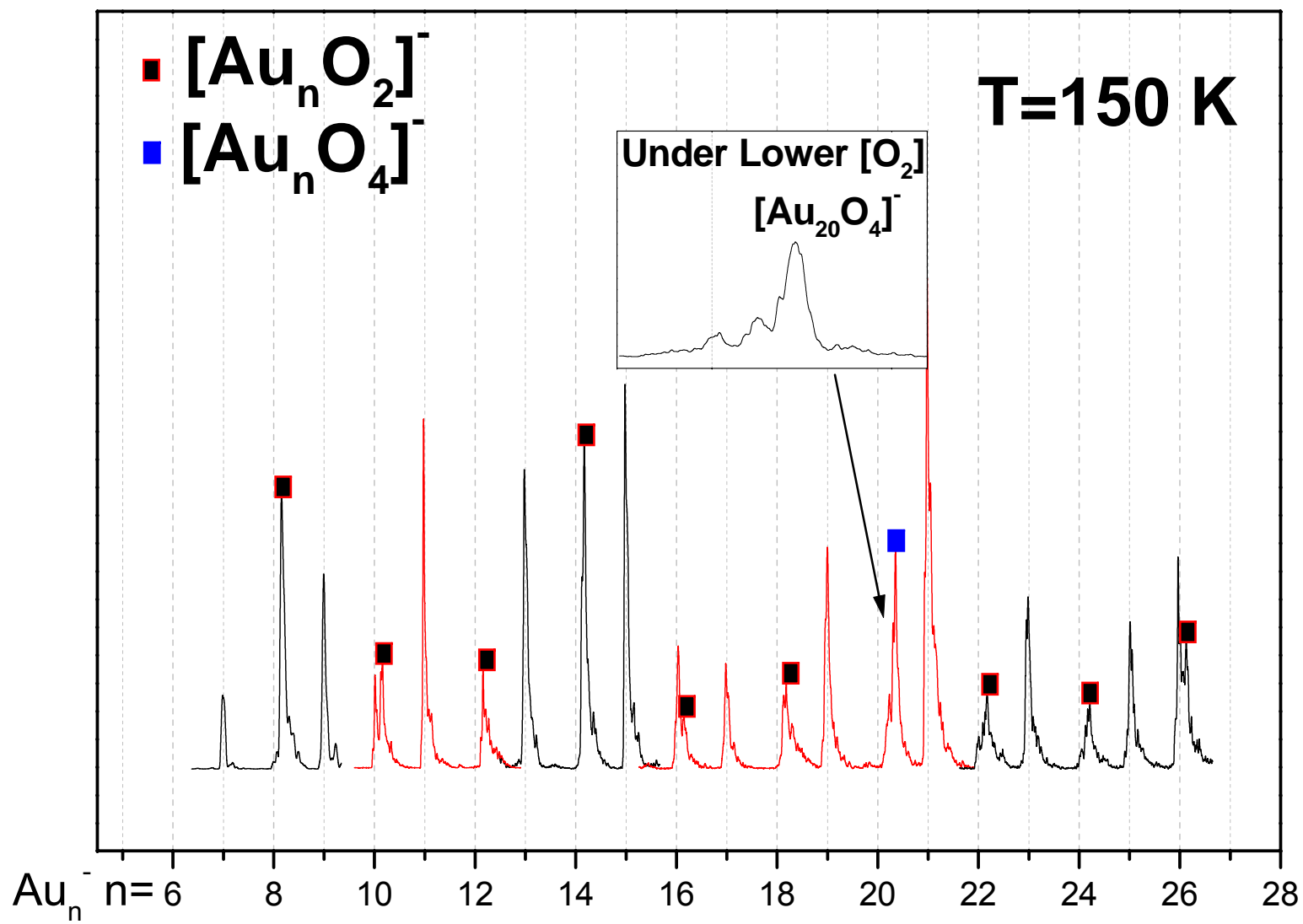
# O<sub>2</sub> Adsorption vs Au<sub>n</sub><sup>-</sup>

P(O<sub>2</sub>) ≈ 10E-4 torr    Hold ≈ 50s



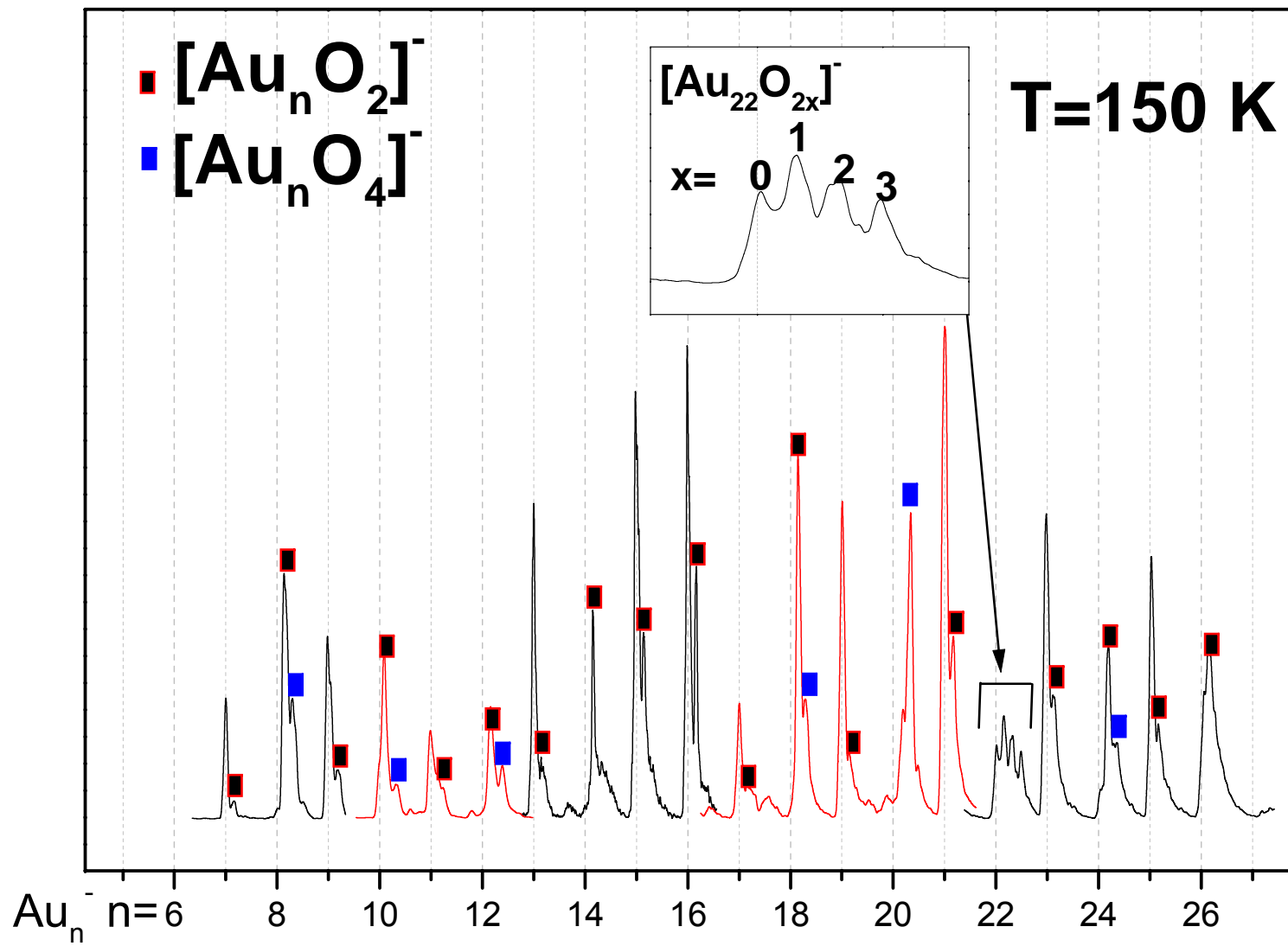
# O<sub>2</sub> Adsorption vs Au<sub>n</sub><sup>-</sup>

P(O<sub>2</sub>) ≈ 10E-4 torr    Hold ≈ 50s

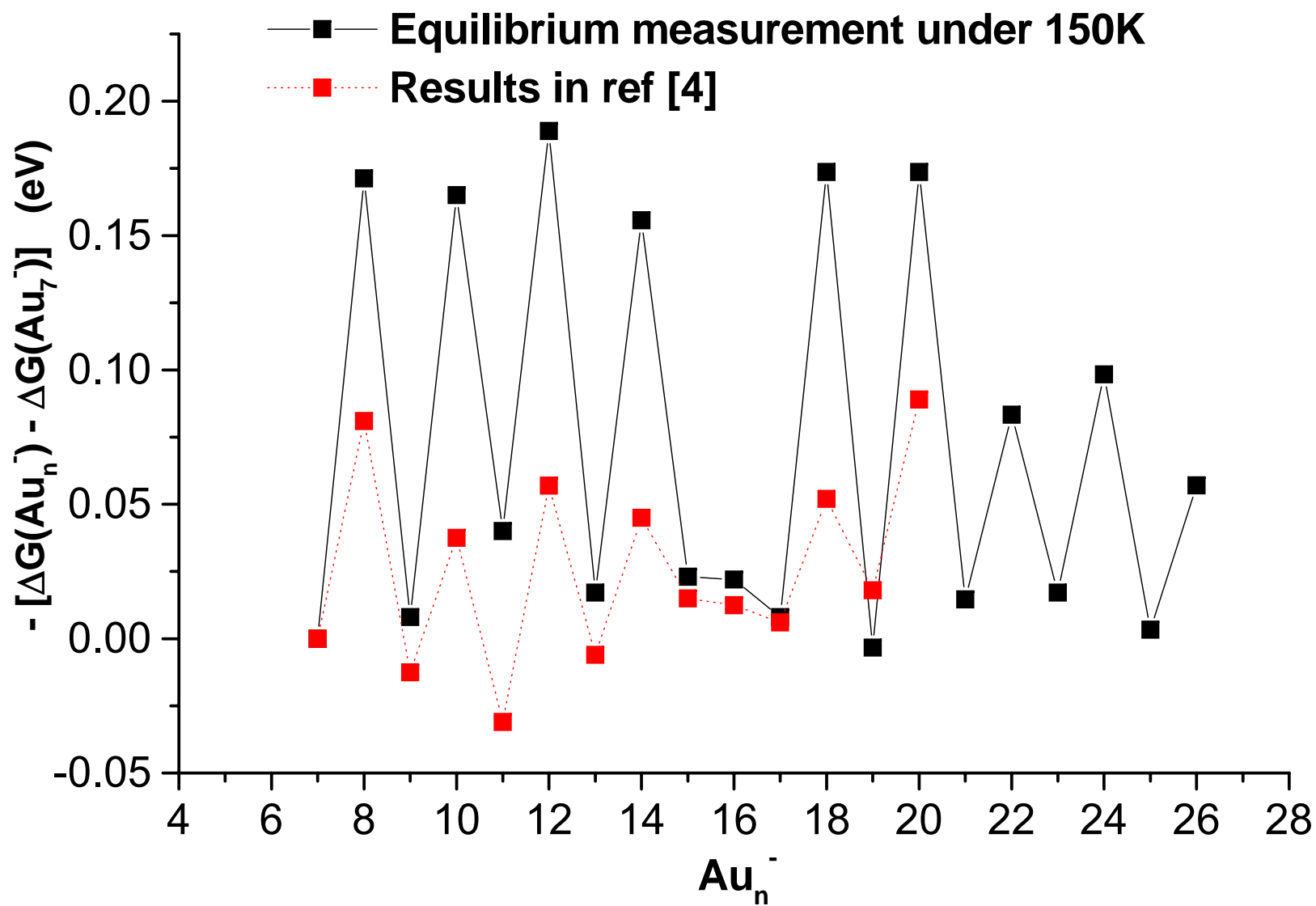


# O<sub>2</sub> Adsorption vs Au<sub>n</sub><sup>-</sup>

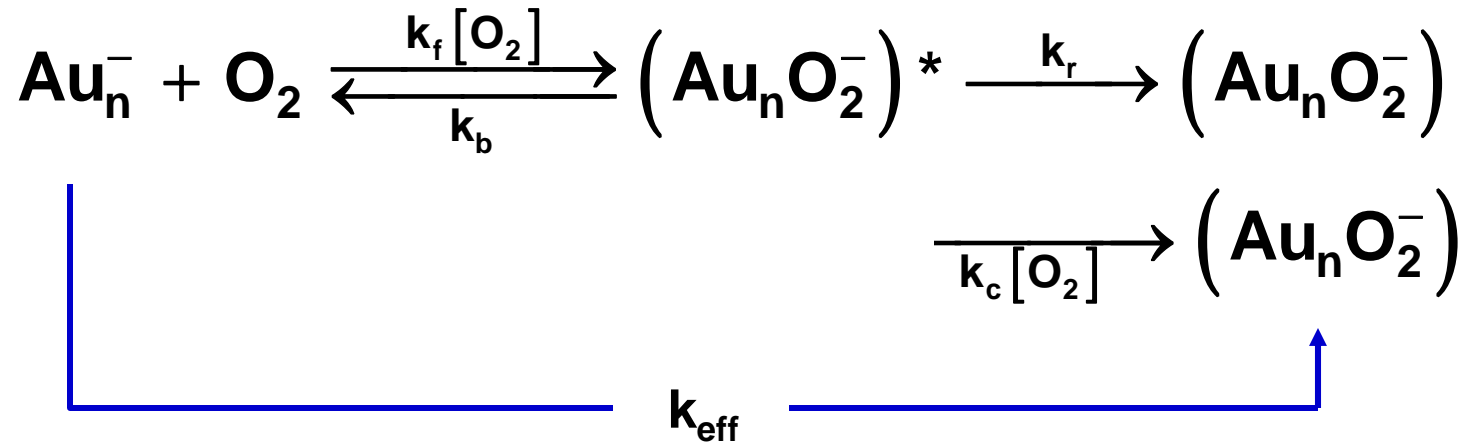
P(O<sub>2</sub>) ≈ 10E-4 torr Hold ≈ 50s



## Relative $\Delta G$ for single $O_2$ absorption: Size dependence



## Kinetics of O<sub>2</sub> Adsorption on Au<sub>n</sub><sup>-</sup>



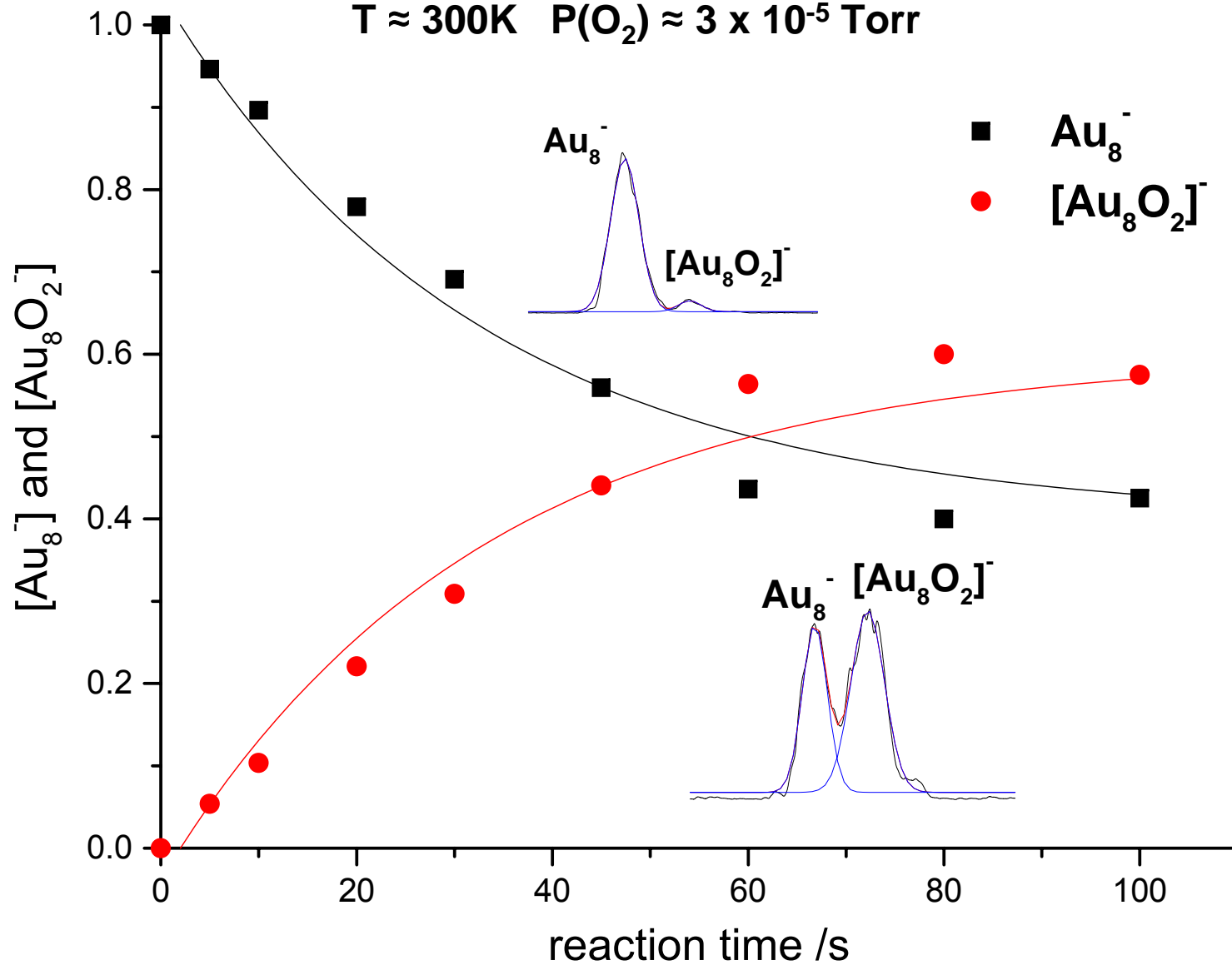
$$\frac{d}{dt} \text{Au}_n^- = -k_{\text{eff}} \text{Au}_n^-$$

$$\frac{d}{dt} (\text{Au}_n \text{O}_2^-) = k_{\text{eff}} \text{Au}_n^-$$

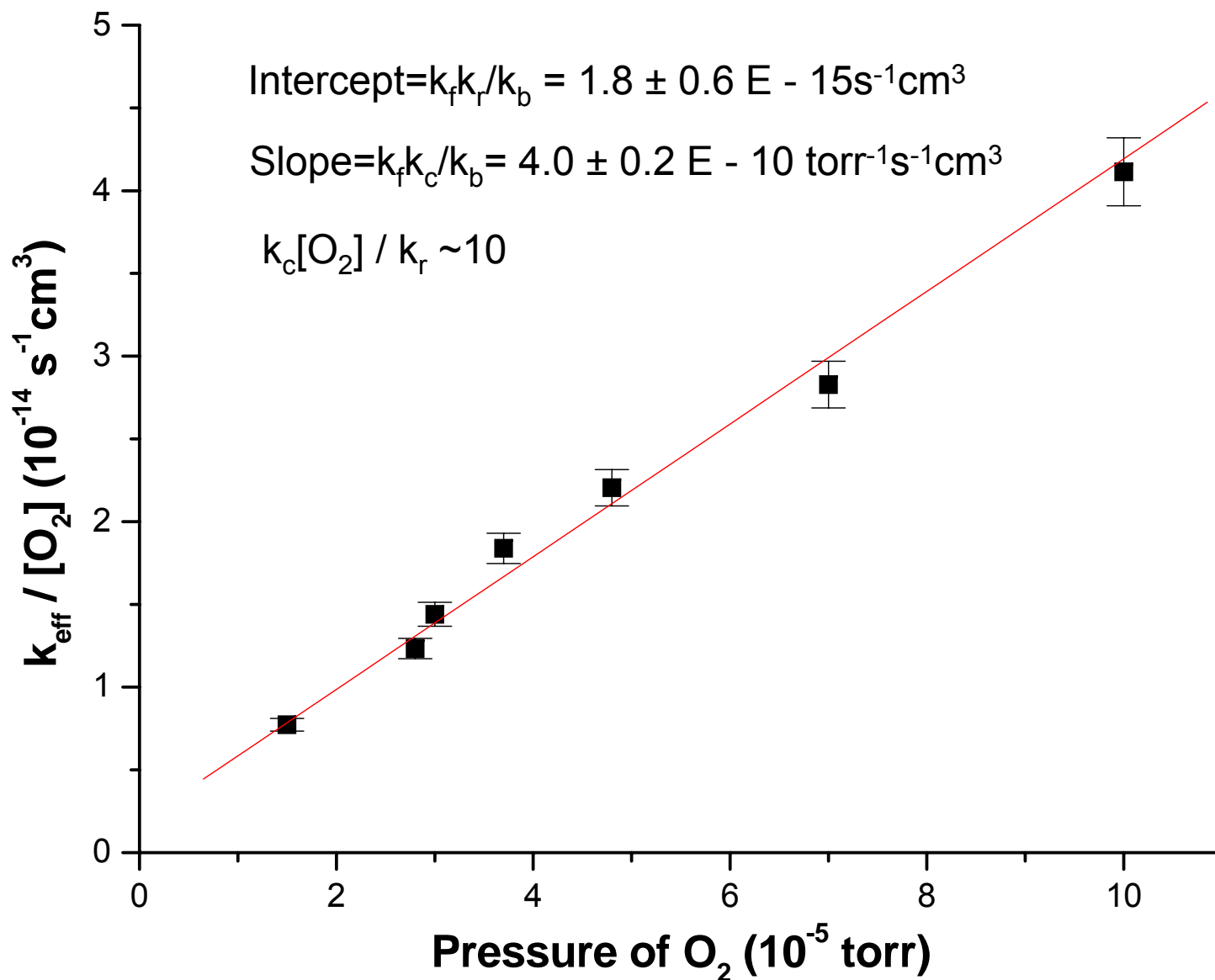
$$k_{\text{eff}} = \frac{k_f [\text{O}_2] (k_c [\text{O}_2] + k_r)}{k_b + k_c [\text{O}_2] + k_r}$$



$T \approx 300\text{K}$   $P(\text{O}_2) \approx 3 \times 10^{-5} \text{Torr}$

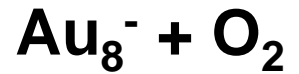


## Pressure Dependence: $\text{Au}_8^- + \text{O}_2 \rightarrow (\text{Au}_n\text{O}_2)^-$



## Comparison of Reaction Rates

radiative limit: pressure  $\rightarrow 0$



$$k_{\text{eff}} = k_f k_r / k_b \rightarrow 1.8 \pm 0.6 \text{ E } -15 \text{ s}^{-1} \text{cm}^3$$



$$k_{\text{eff}} \rightarrow 1 \text{ E } -11 \text{ s}^{-1} \text{cm}^3$$

$k_b$  increase ,  $k_r$  decrease with similar  $k_f$

## Summary

- Measured equilibrium adsorption of single oxygen molecule on gold cluster anions in the size range  $n = 7-26$
- Observed multiple adsorption of oxygen molecules on certain special size, such as  $n=20$  and  $22$ .
- Vibrational relaxation is about 10 times as radiative rates under experimental conditions
- Effective formation rates for  $[\text{Au}_n(\text{O}_2)]^-$  are significantly less than for  $[\text{Au}_n(\text{CO})]^+$

# References

1. M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. 34, 405 (1987).
2. A. Sanchez, S. Abbet, U. Heiz, et al., J. Phys. Chem. A 103, 9573 (1999).
3. Bokwon Yoon, Hannu Häkkinen, Uzi Landman, Anke S. Wörz, Jean-Marie Antonietti, Stéphane Abbet, Ken Judai, Ueli Heiz, Science 307 403, (2005).
4. B.E. Salisbury, W.T. Wallace, R.L. Whetten, Chem. Phys. 262, 131 (2000).
5. Bokwon Yoon, Hannu Häkkinen, and Uzi Landman, J. Phys. Chem. A107, 4066 (2003).
6. Greg Mills, Mark S.Gordon, Horia Metiu, Chem. Phys. Lett. 359, 493 (2002).
7. Sergey A. Varganov, Ryan M. Olson, and Mark S. Gordon, Horia Metiu J. Chem. Phys.119, 2531 (2003).
8. Hannu Häkkinen, Bokwon Yoon, and Uzi Landman, Xi Li, Hua-Jin Zhai, and Lai-Sheng Wang, J. Phys. Chem. A107, 6168 (2003).
9. Häkkinen, H.; Abbet, S.; Sanchez, A., Heiz, U.; Landman, U. Angew. Chem. Int. Ed. 42, 1297 (2003).
10. Marco Neumaier, Florian Weigend, Oliver Hampe, Manfred M. Kappes, J. Chem. Phys. 122, 104702 (2005)

# Acknowledgment

**Support:** Michael Burns, Ryan Danell

**Funding:** The Rowland Institute at Harvard and NSF