

# Interfacial Matrix Stabilization Spectroscopy: Experimental Proof of Concept



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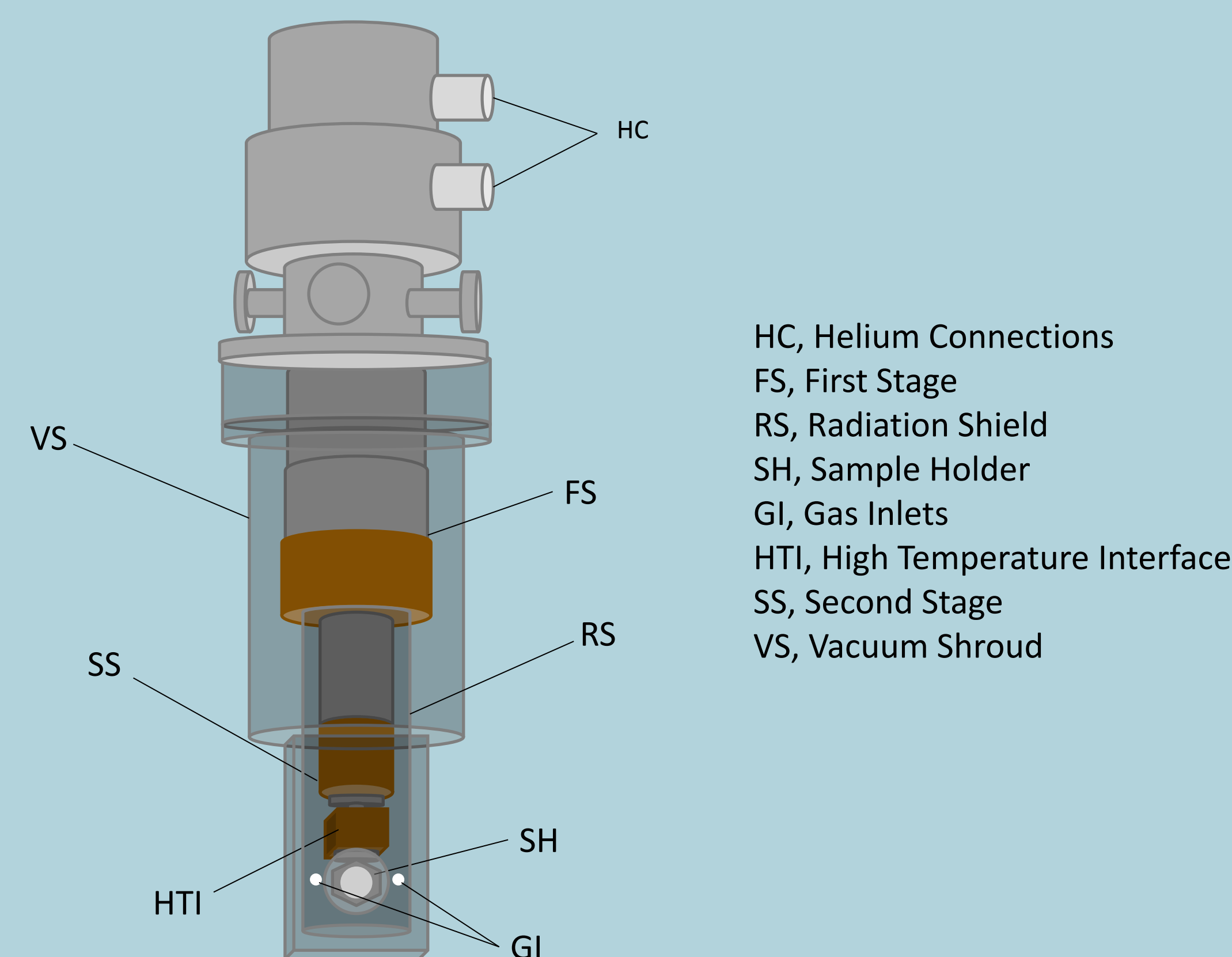
## Introduction

Gold nanoparticles are known to be catalytically active for CO oxidation.<sup>1</sup> These nanoparticles tend to be more catalytically active when supported on certain metal oxides. One of the most common supports for gold nanoparticles is titania. TiO<sub>2</sub> is known as an active support, due to its reducibility, which could allow the lattice oxygen to participate in reactions. The role of titania in the catalytic CO oxidation reaction is not yet fully understood. Here we report the interactions of CO with nanoparticle (NP) TiO<sub>2</sub> catalyst support that have been investigated using interfacial matrix stabilization spectroscopy (IMSS) and compare them with results obtained using World Gold Council (WGC) reference catalyst. IMSS is an adaptation of traditional matrix isolation spectroscopy to study the interactions at the interface between the cryogenic matrix and the substrate surface. We are developing this technique to probe interactions of molecules with real supported nanoparticle catalyst materials. We have taken care in our experiments to work at low temperatures and pressures in order to be able to study interactions of isolated molecules with the catalyst material.

## Experimental Protocol

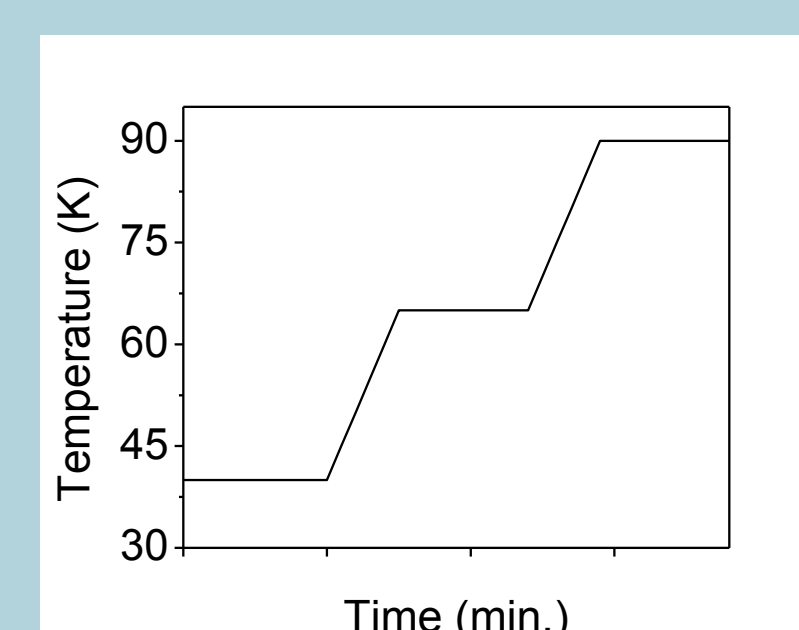
Commercial TiO<sub>2</sub> NP's (Degussa P25) were used in this study along with World Gold Council (WGC) Au/TiO<sub>2</sub> reference catalyst. Slurries of the samples were made in an acetone/water mix and sprayed onto a CaF<sub>2</sub> window held at 60° C, using an Aldrich® chromatography sprayer.

The samples were placed in a sample holder of a commercial Advanced Research Systems (ARS) DE-210SF cryostat (schematic below). The cryostat, equipped with KBr windows on the vacuum shroud, was positioned inside the cavity of a Nicolet 6700 FTIR so that the IR beam could pass through the radiation shield and the sample. "Clean" vacuum was maintained inside the system at ~4 x 10<sup>-7</sup> torr with an Edwards EXT70H turbo pump backed by an Edwards XDS 10 scroll pump. During experiments the base pressure of the system got to ~3 x 10<sup>-8</sup> torr due to cryopumping.



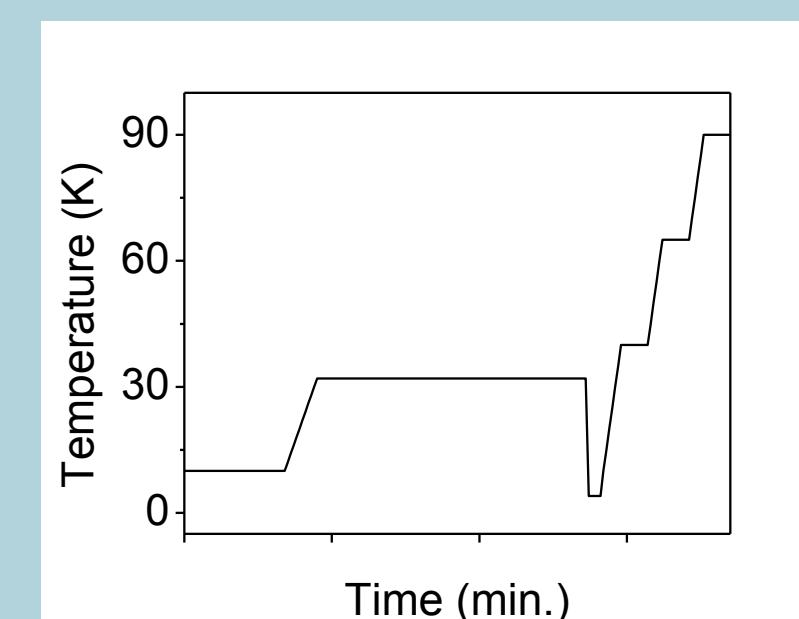
### Direct Adsorption:

- Cool sample down to 40 K
- Admit 30.67 mmol of 0.5% CO/Ar gas mix (average rate=1.8 mmol/min)
- Heat slowly to 65 K & 90 K



### Modified Matrix Isolation:

- Cool sample down to 10 K
- Deposit CO/Ar matrix
- Anneal at 32 K
- Destroy matrix by heating to 40 K
- Subsequently heat to 65 K & 90 K



### Frequency and assignment of spectral bands for CO/TiO<sub>2</sub>

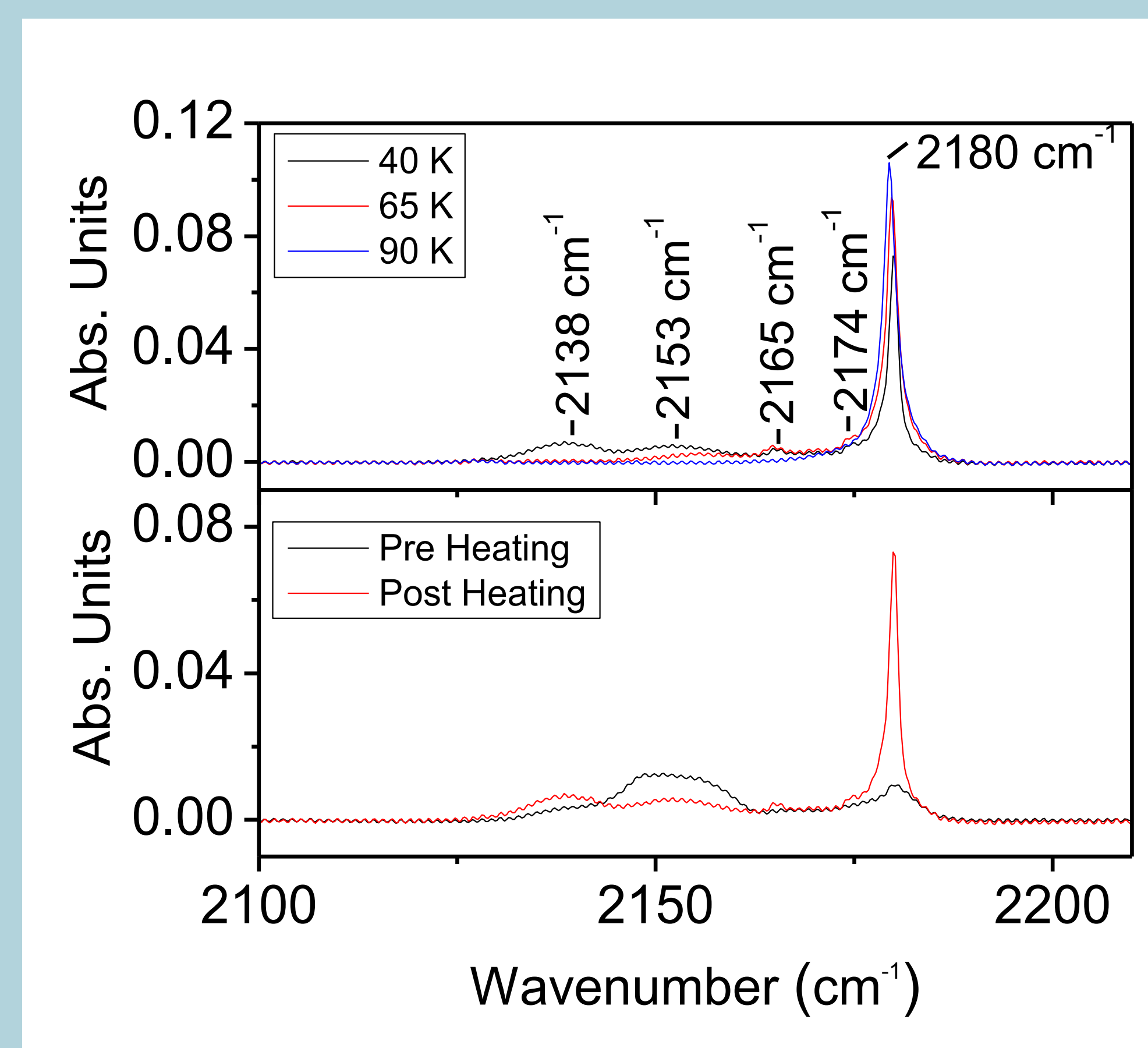
$\nu$ (cm <sup>-1</sup> )	Assignment
2138	CO trapped in an Ar matrix
2153 <sup>2</sup>	CO H-bonded to surface OH
2165 <sup>2</sup>	Ti <sup>4+</sup> —CO (Ti <sup>4+</sup> ions shielded by oxygen atoms)
2174 <sup>3</sup>	Ti <sup>4+</sup> —CO (Ti <sup>4+</sup> ions coordinately unsaturated)
2180 <sup>3</sup>	$\beta$ -Ti <sup>4+</sup> —CO (CO on Ti <sup>4+</sup> (0 1 0) faces)
3580 <sup>4,5</sup>	OH (str.) perturbed by CO
3633 <sup>5</sup>	OH (str.) on TiO <sub>2</sub> surface

## Results

### Direct Adsorption

- At 40 K system is too warm for Ar matrix to form, interactions shown are those of CO interacting with surface of TiO<sub>2</sub>
- Peak positions similar to higher temperature/pressure studies from literature<sup>2-5</sup>
- Upon heating up to 65 K we see growth of peak at 2165 cm<sup>-1</sup> and decrease of CO—OH peaks
- At 90 K CO—OH peak is absent and CO— $\beta$ -Ti<sup>4+</sup> is increased, suggesting population transfer at higher temperatures
- This population transfer implies that  $\beta$ -Ti<sup>4+</sup> sites are most stable
- From 40 to 65 K integrated peak areas do not change; at 90 K integrated area is 93% of low temp. value

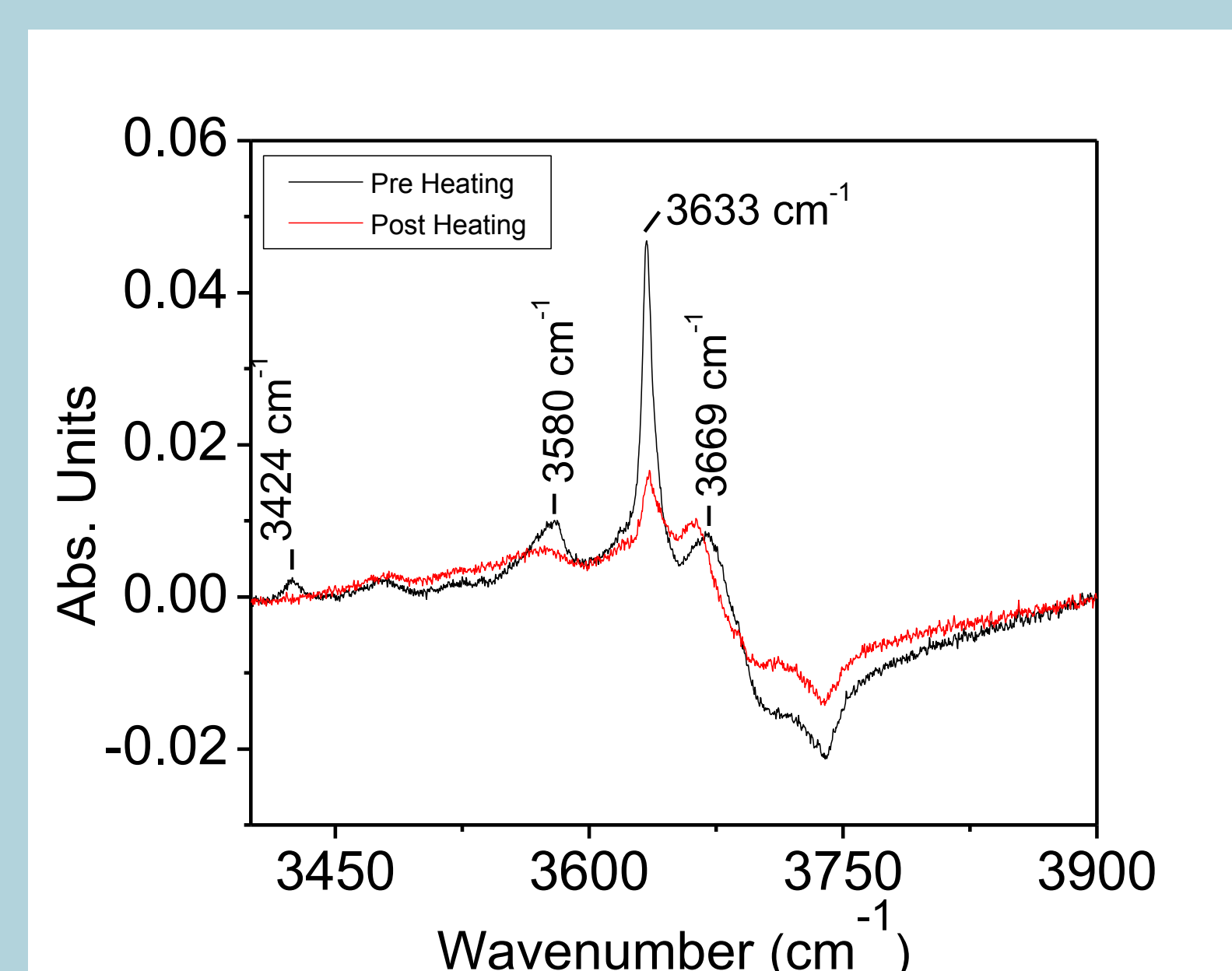
### FTIR spectra of direct adsorption of CO on TiO<sub>2</sub> NP's



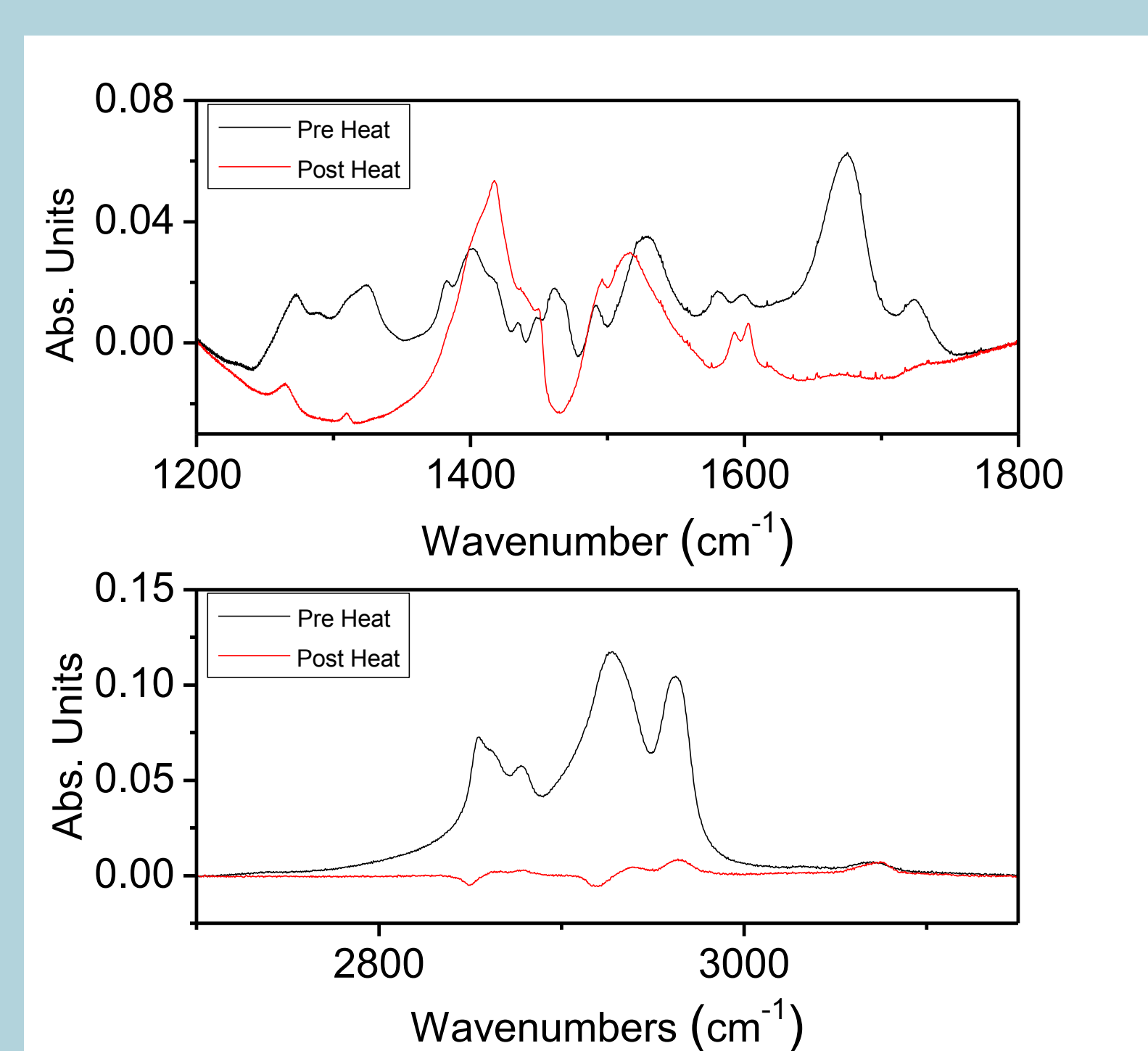
### Heat Treatment

- Peak grows in at 3580 cm<sup>-1</sup> upon direct adsorption of gas, assigned to perturbed OH stretch due to CO coordination
- Preheating sample to 650 K before gas adsorption reduces amount of surface OH, apparent by decrease in intensity of CO—OH bands and peak at 3580 cm<sup>-1</sup>
- Heat treatment of sample is also necessary to remove hydrocarbon contaminants from surface of sample
- Upon heat treatment we see changes in 1200-1800 cm<sup>-1</sup> region and see decrease in peak intensities in 2800-3000 cm<sup>-1</sup> region
- After cleaning, total number of CO binding sites increases, and ratios of different types of sites changes, favoring formation of CO— $\beta$ -Ti<sup>4+</sup> (see above)

### Spectra of OH stretch region before and after heat treatment



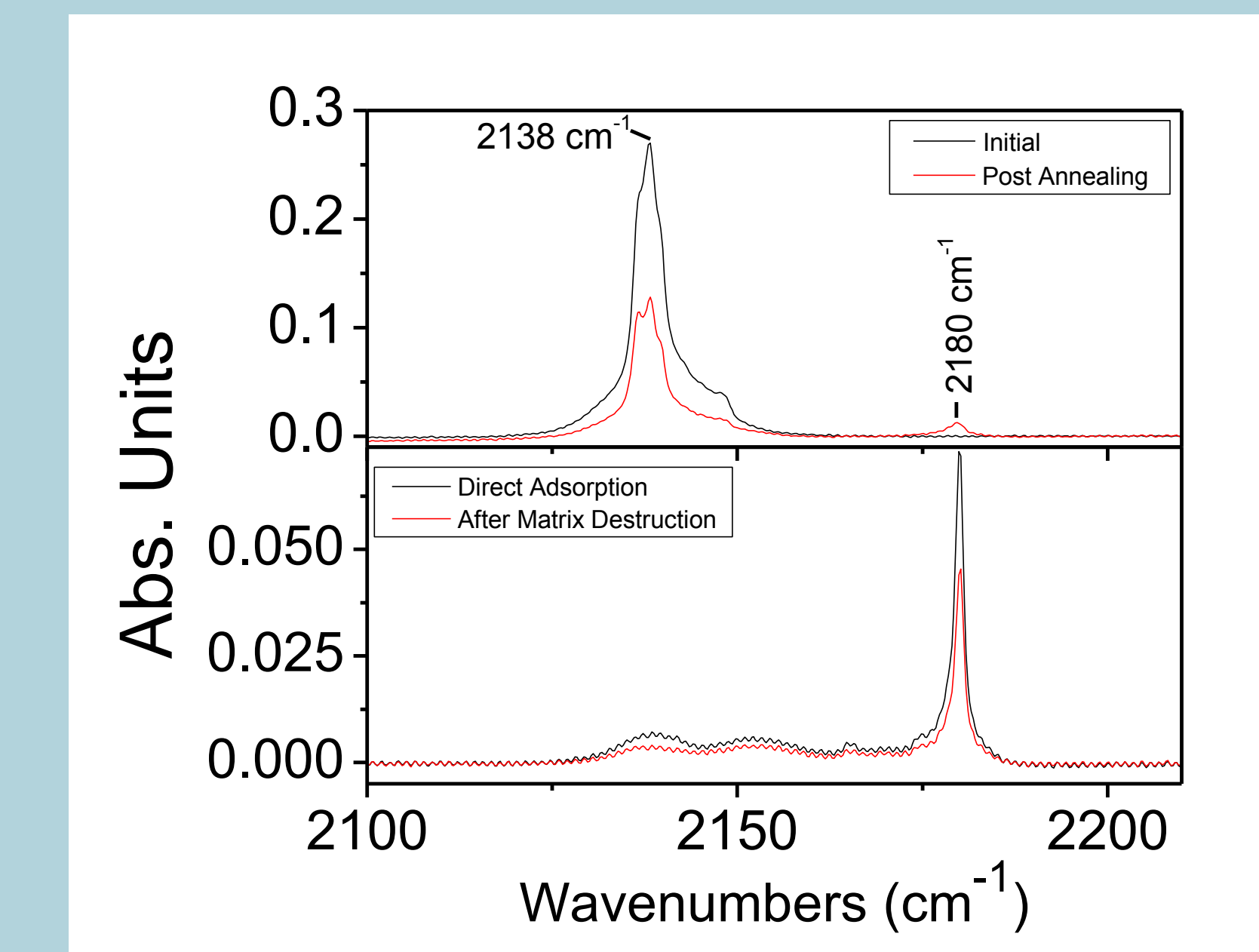
### Surface contamination pre/post heating



### Matrix Isolation

- After deposition at 10 K we only see peak for free CO at 2138 cm<sup>-1</sup> (no evidence of direct adsorption peaks)
- Annealing at 32 K allows for diffusion of CO through Ar matrix to TiO<sub>2</sub> surface as evident by peak at 2180 cm<sup>-1</sup> peak
- During annealing free CO peak goes down by about half while 2180 cm<sup>-1</sup> grows only slightly, showing some of matrix is lost during this process
- Upon heating to 40 K this peak remains present and showing that CO becomes bound to surface during annealing
- This peak as well as other peaks that show up upon heating match up with those from direct adsorption experiment

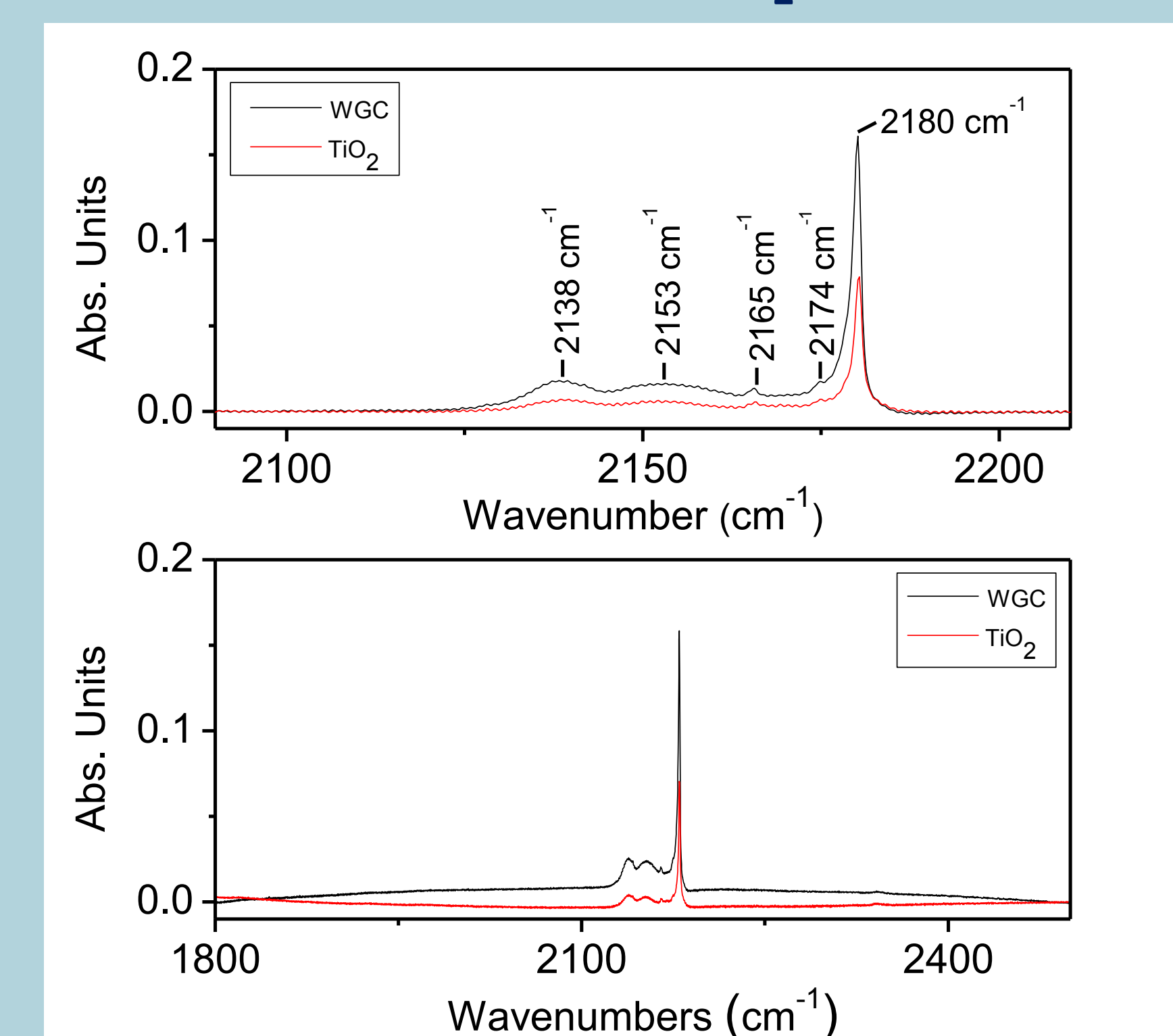
### IMSS spectrum of CO on TiO<sub>2</sub>



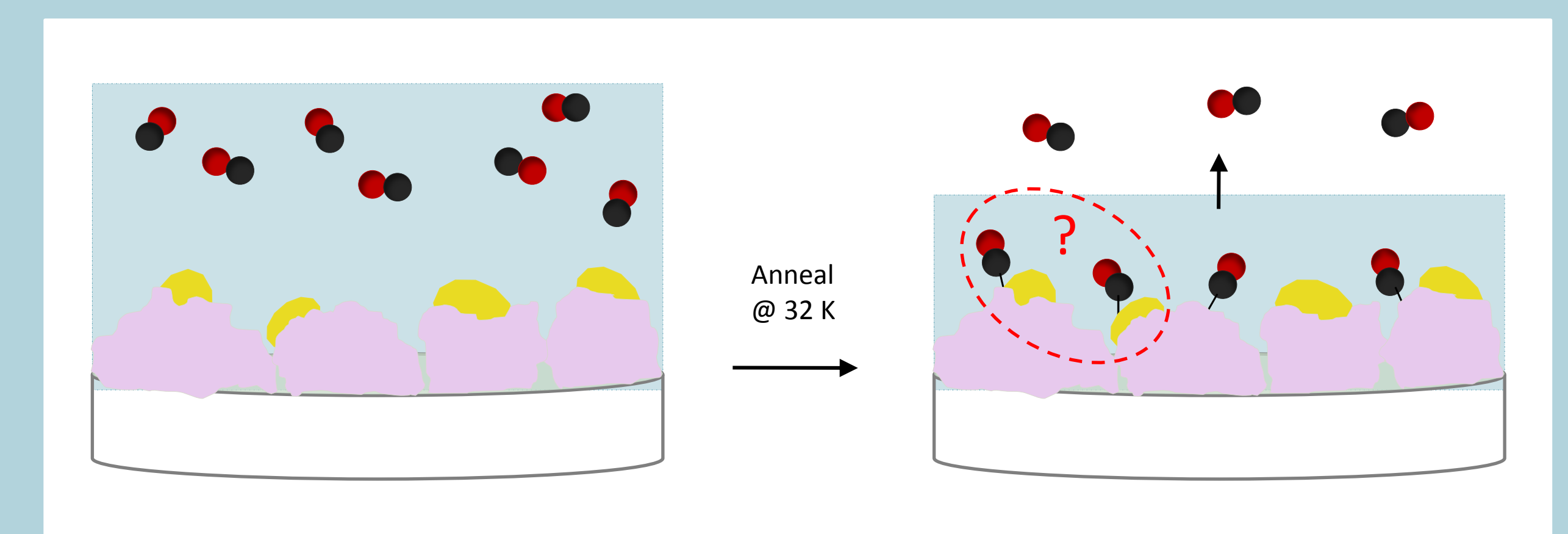
### TiO<sub>2</sub> vs. Au/TiO<sub>2</sub>

- Only see peaks assigned to interactions of CO with TiO<sub>2</sub> and surface OH
- All of the peaks seen on WGC match up perfectly with those seen on just TiO<sub>2</sub>

### Direct adsorption of CO at 40 K on WGC vs. bare TiO<sub>2</sub>



### Model:



## Conclusions and Future Work

The results discussed above show that we are able to see CO interacting with the TiO<sub>2</sub> surface at low temperatures. Most importantly, through our IMSS technique, we are able to see CO diffuse through the matrix and bind to the TiO<sub>2</sub> surface. An interesting aspect is that, despite conducting numerous control experiments, we see no evidence of CO interacting with the gold surface under the same experimental conditions as were carried out for the TiO<sub>2</sub> alone. Our working hypothesis is that the CO interaction with the gold is too weak for it to bind at 40 K. This result appears at odds with computational studies of CO binding to small gold clusters on TiO<sub>2</sub>.<sup>6</sup> Future experiments will use He/CO mixtures to investigate CO binding down to 4 K in order to confirm this.

### References:

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- Venkov, T.; Fajenweg, K.; Delannoy, L.; Klimev, H.; Hadjivanov, K.; Louis, C., *Applied Catalysis a-General* **2006**, 301 (1), 106-114.
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