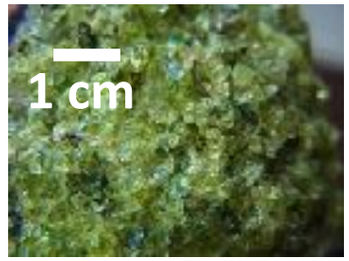
Cluster as a model for chemistry in the interstellar environment

Protoplanetary disk

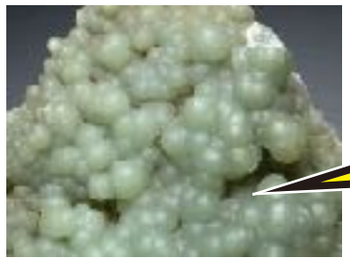
CO, H_2, H_2O

+

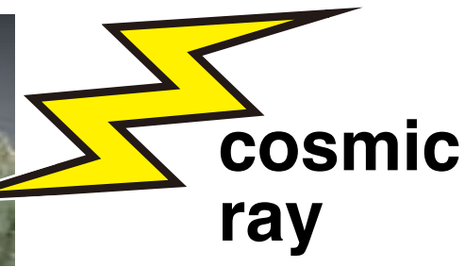
Mineral particles and ions

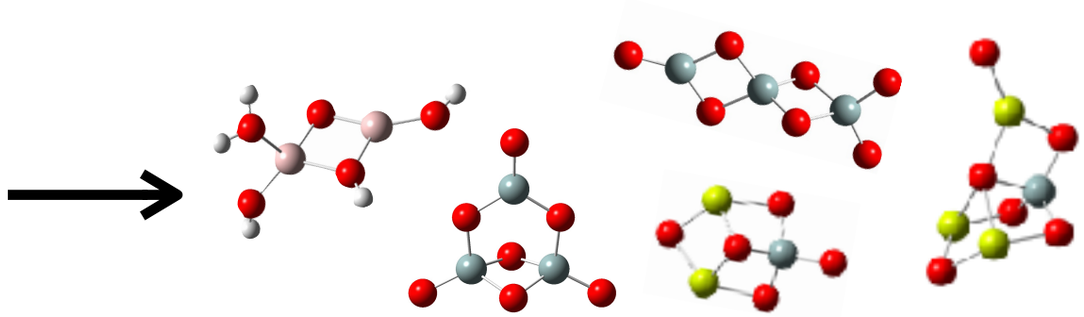


olivine
$(Mg,Fe)_2SiO_4$



gibbsite
γ-$Al(OH)_3$





Cluster ions consisting of Mg, Fe, Al, Si, O

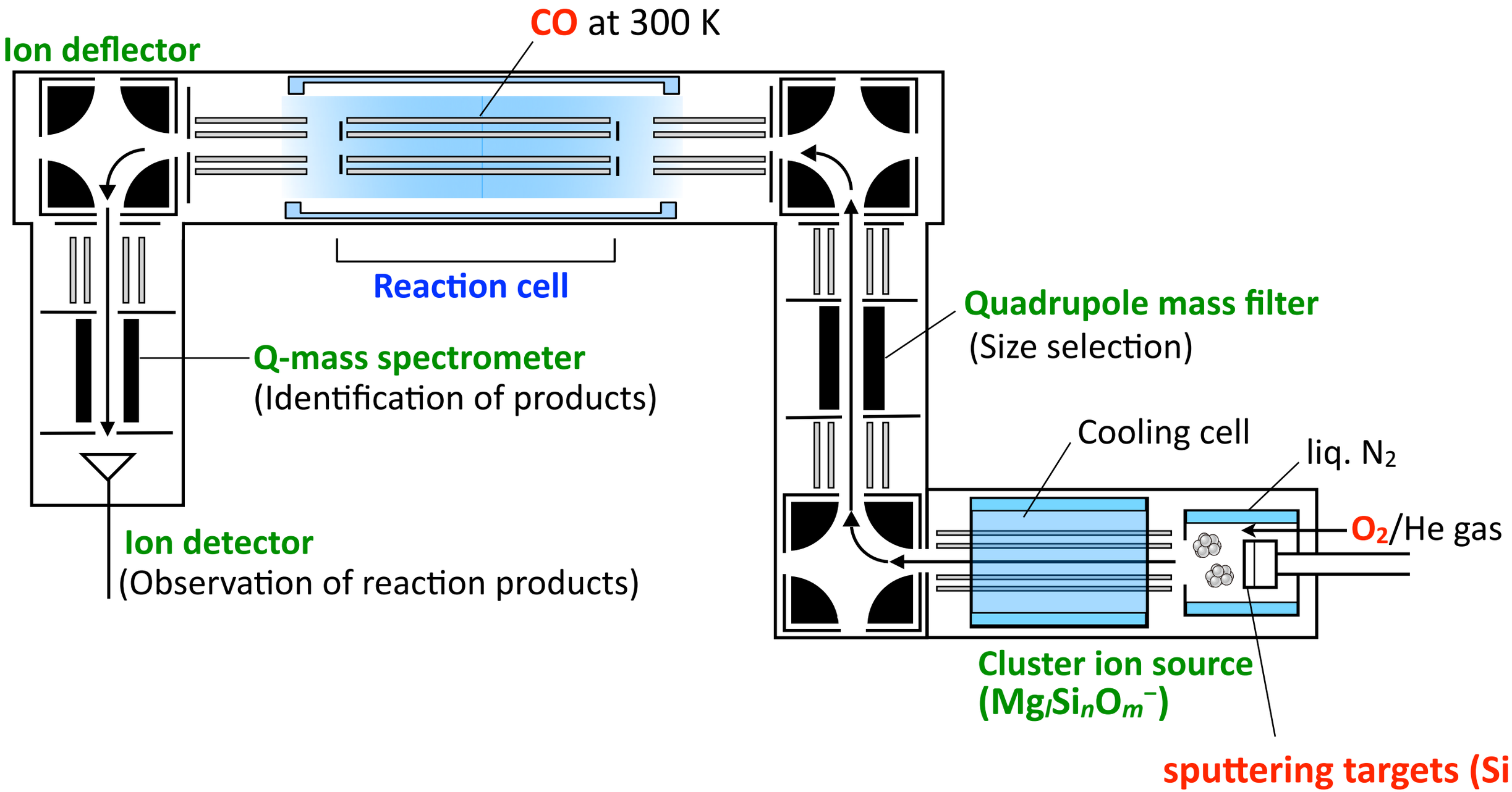
Fischer-Tropsch reaction e.g., Fe, Ni /Al_2O_3, MgO, Si

$$(2n+1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O$$

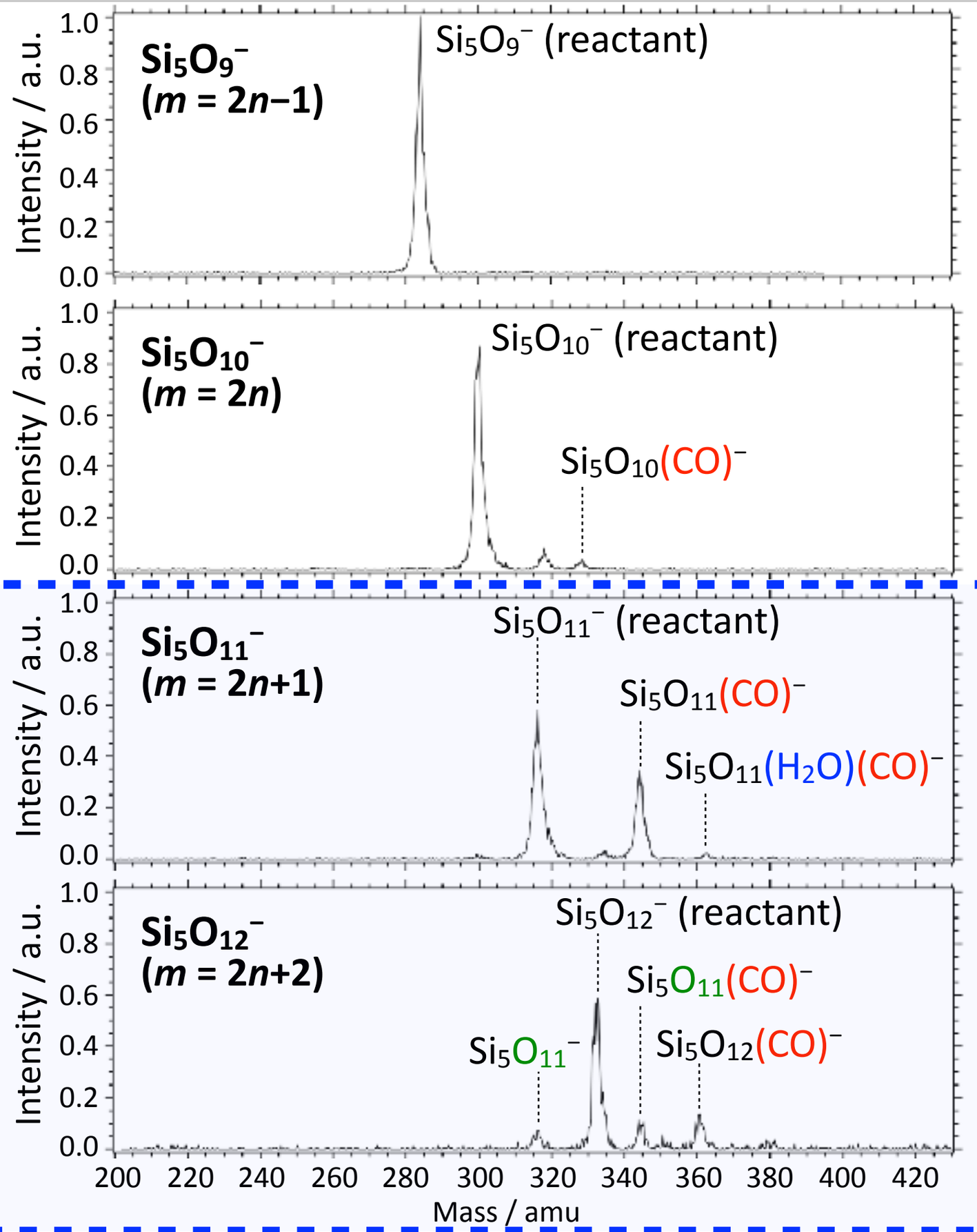
Reaction of mineral clusters with CO, H_2O, H_2 and N_2…

Experiment

$Si_nO_m^-$ + H_2O → ?



Reaction of $Si_nO_m^-$ with CO: n = 5



$Si_5O_9^-$ ($m = 2n-1$)

$Si_5O_{10}^-$ ($m = 2n$)

$Si_5O_{11}^-$ ($m = 2n+1$)

$Si_5O_{12}^-$ ($m = 2n+2$)

$P_{CO} = 7.4\times10^{-1}$ Pa
E_{col} with CO was 0.8 eV

no reaction products

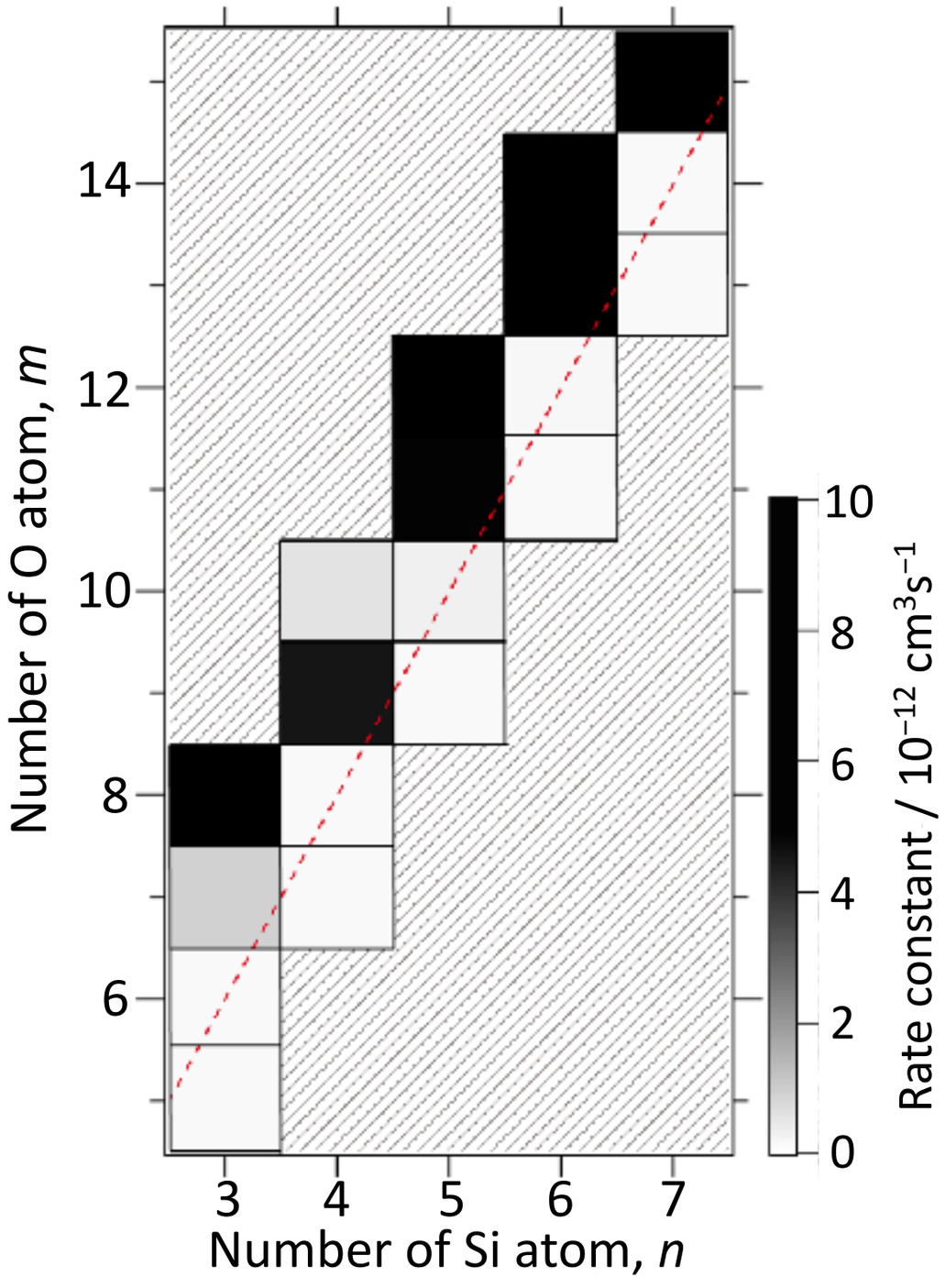
small peaks

high reactivity toward CO

CO adducts

CO adducts
generation of CO_2

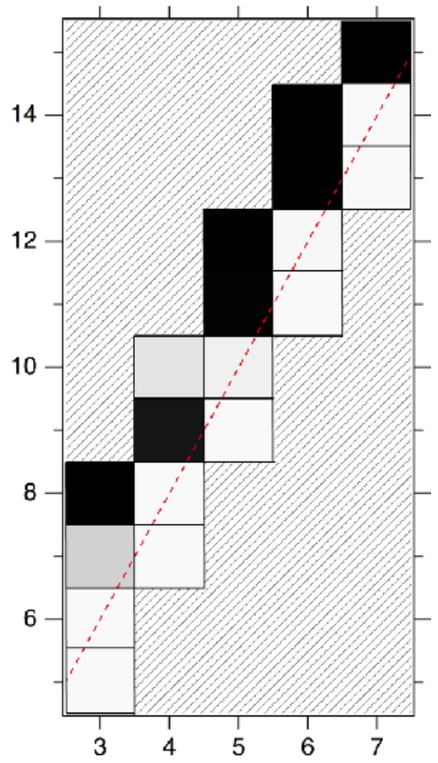
Rate constants of the adsorption reaction



Rate constants were high for

$$m \geq 2n + 1$$

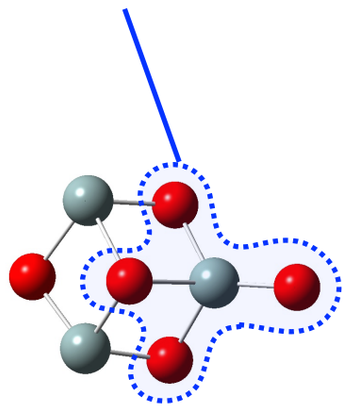
Adsorption sites of a CO molecule on $Si_nO_m^-$: n = 3



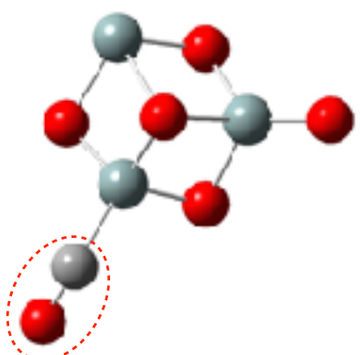
$m \geq 2n + 1$

$Si_3O_m^-$

four-fold coordination
forming a SiO_4 tetrahedron



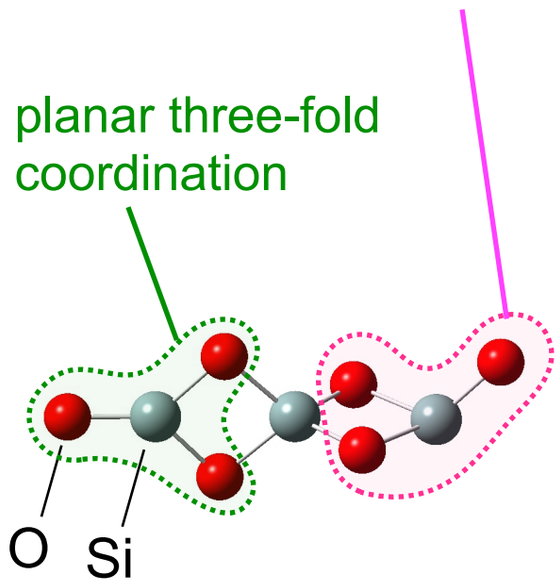
3a $Si_3O_5^-$
(non reactive)



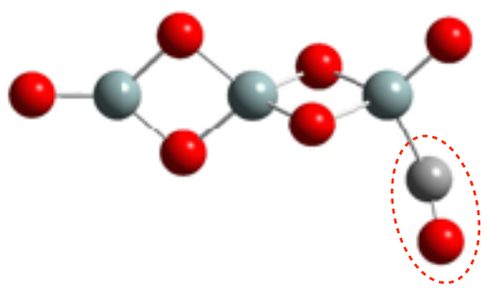
3a' $S_3O_5(CO)^-$
(D_0 = 0.31 eV)

triangular-pyramidal
three-fold coordination

planar three-fold
coordination

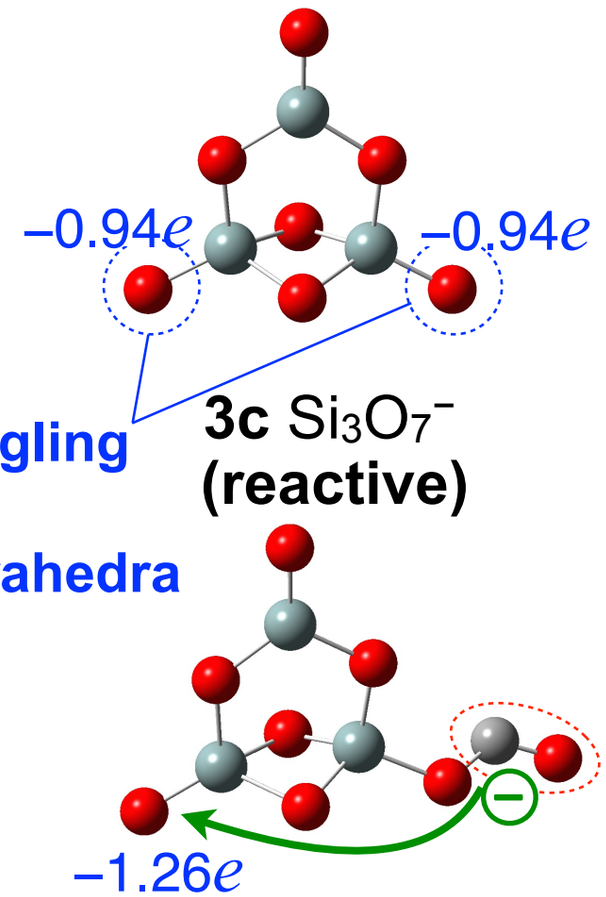


3b $Si_3O_6^-$
(non reactive)



3b' $S_3O_6(CO)^-$
(D_0 = 0.45 eV)

Local charges of O atoms are typically −1.2e–−1.3e. (NBO analysis)



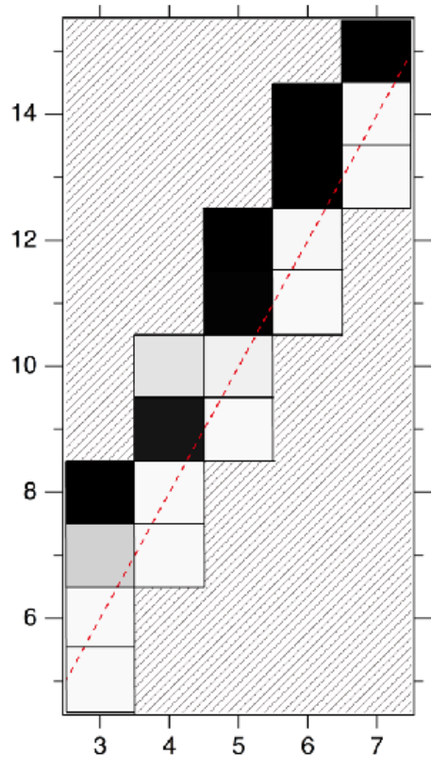
3c $Si_3O_7^-$
(reactive)

3c' $Si_3O_7(CO)^-$
(D_0 = 1.12 eV)

Adsorption site of CO:
A dangling O atom of the pair appearing in $Si_nO_{2n+1}^-$

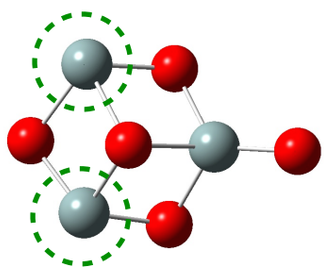
(Optimized using the Gaussian09 package, B3LYP/aug-cc-pVDZ)

Site selectivity: Location of SOMO

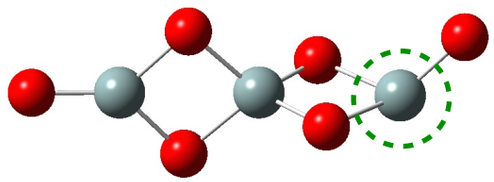


$m \geq 2n + 1$

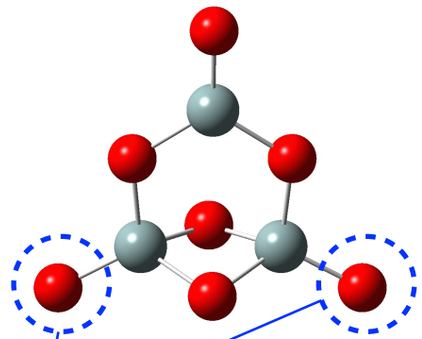
$Si_3O_m^-$



3a $Si_3O_5^-$

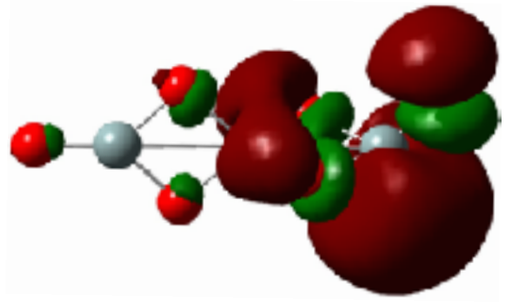


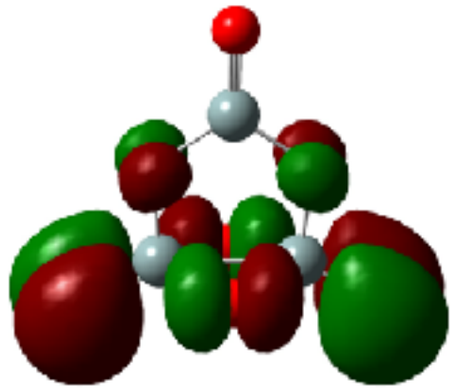
3b $Si_3O_6^-$



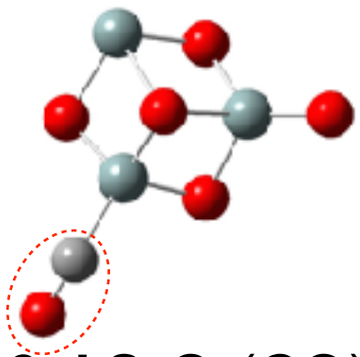
3c $Si_3O_7^-$

pair of dangling O atoms

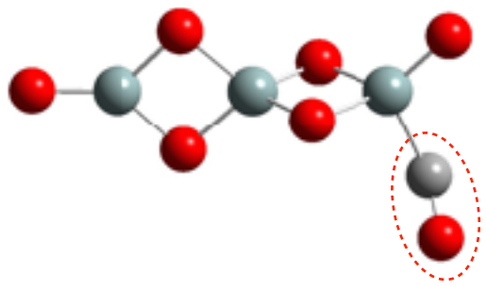




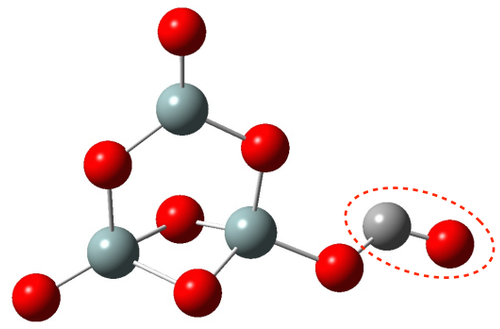
Isosurfaces of SOMOs



3a' $S_3O_5(CO)^-$



3b' $S_3O_6(CO)^-$



3c' $Si_3O_7(CO)^-$

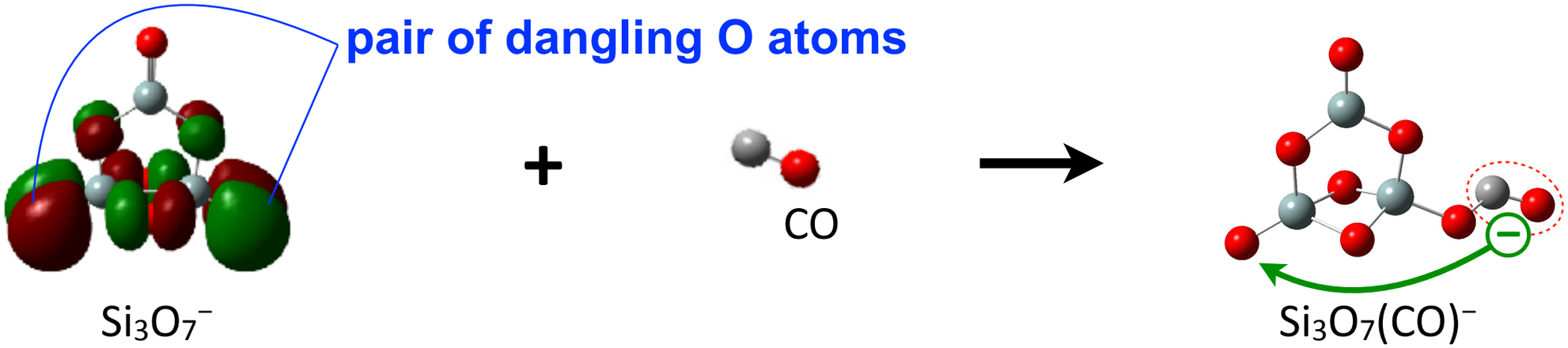
(Optimized using the Gaussian09 package, B3LYP/aug-cc-pVDZ)

Summary

✺ **Reaction of $Si_nO_m^-$ with a CO molecule**

✶ **A pair of dangling O atoms** on four-fold coordinated Si atoms, which appears in $Si_nO_{2n+1}^-$, plays a key role for CO adsorption

✶ **The site selectivity** is governed by the **location of SOMO** on $Si_nO_m^-$



(M. Arakawa, R. Yamane, and A. Terasaki, *J. Phys. Chem. A* **120**, 139, 2016)