Quantum-Chemistry Theory Modeling of Chemical Warfare Agent/Adsorbent Interaction

Threat Agent Science – BA06TAS001
DTRA Program Manager: Dr. Frank Handler

Lt Jennifer Plourde
Air Force Research Lab

Tom J. Evans, Ph.D.
Cubic Defense Applications

Purpose for the Work

Experimental work with chemical warfare agents (CWA) is dangerous and expensive

- Only a few specially-equipped and –staffed laboratories perform CWA work
- High cost associated with CWA work
- Both factors limit the rate of study and characterization
- Increases the difficulty in dealing with the emergence of new threat agents (NTA)

Purpose for the Work

Experimental work often relies on the use of relatively-safe simulants

The degree to which these simulants correlate to specific agent behaviors is:

- Often unknown
- Directly correlated to specific properties/interactions
- Is never complete

Purpose for the Work

Goal: Gaining insight into the characteristics of CWA without the cost and risk.

Benefits of QCT

Quantum-Chemistry Theory (QCT) has been proven as a reliable approach for making *quantitative* predictions of molecular properties and characteristics

Benefits of QCT

QCT can be used to model the adsorption and reaction of CWA on surfaces

- Provides a means for understanding and predicting fate of agent
- Allows for the comparison of agents and simulants, leading to the evaluation, intelligent use and improvement of simulants
- Enables the quick assessment of new, previously-unknown CWAs
- Provides the enabling processes for a “materials-by-design” approach to CWA protection and remediation

Benefits of QCT

QCT is an aid to, not a replacement for, experimentation

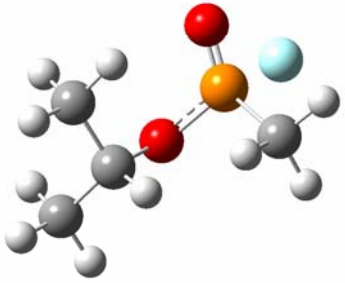
- QCT is a means for making the most efficient use of laboratories that can perform CWA work
- QCT calculations can easily be done to test ideas prior to experiment work

Approach

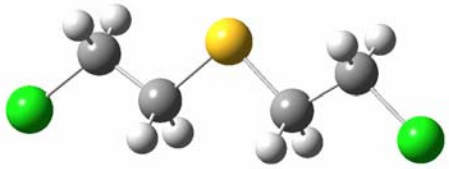
- Use Density Functional Theory (DFT) or post-Hartree Fock corrections (Møller-Plesset) to include electron correlation
- Utilize realistic models for reactive surface sites on operationally-relevant oxides: γ-Al_2O_3 and a-SiO_2
- Validate models by comparison of observed and calculated properties of species adsorbed on oxide surfaces
  - μ-wave Spectra
  - IR Spectra
  - ΔH_{ads}
  - Adsorption Geometries
- Compare adsorption behavior of real agents and simulants

Agents and Simulants of Interest

Agents

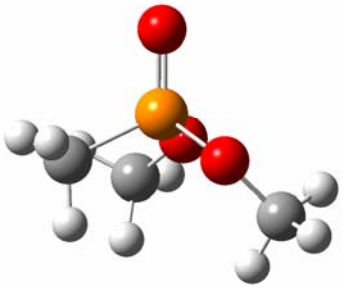


Sarin (GB)

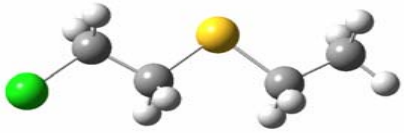


Sulfur Mustard (HD)

Simulants



DMMP

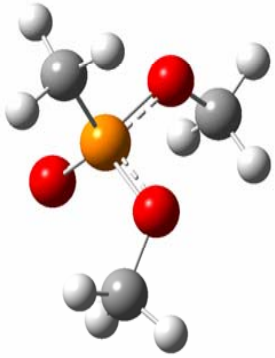


2-CEES

QCT Treatment of Free Molecules

How well do QCT methods calculate properties of free molecules?

DMMP



DMMP Rotational Constants (MHz)

Method	A	B	C
Experiment[1]	2828.753	1972.359	1614.268
B3LYP/6-31G*	2685.67	1943.79	1579.29
MP2/6-31G*	2714.42	1957.53	1600.19

Calculated vs. observed gas phase μ-wave spectra for DMMP

- Calculations use MP2 and DFT (B3LYP) approaches
- Relatively small basis sets (6-31G*)

→Good agreement with experimental results

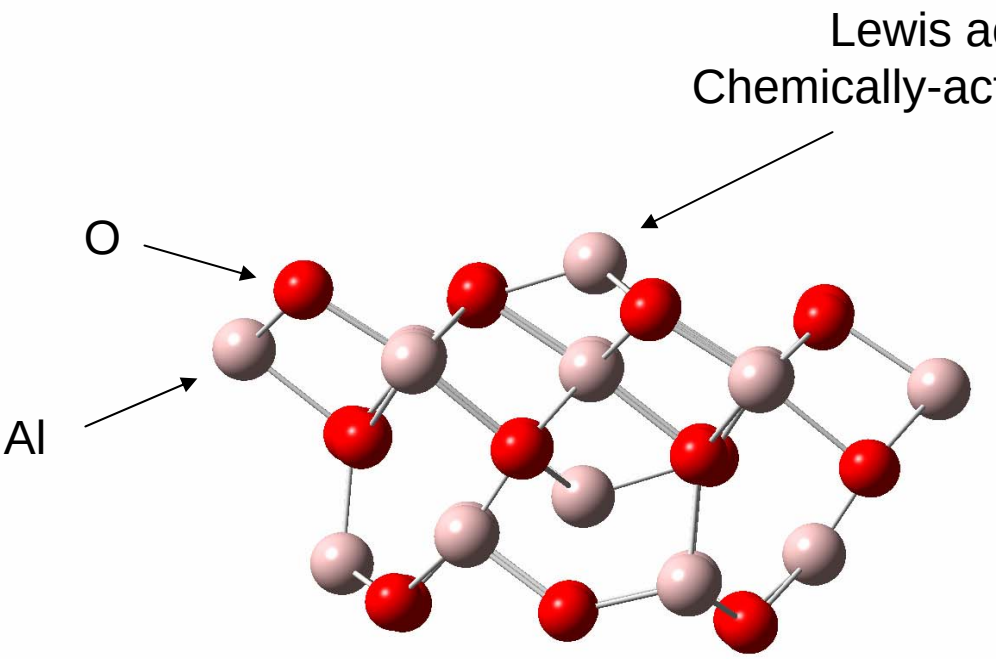
1. Suenram, et. al., *J. Mol. Spectrosc*. **211**, 110 (2002).

Systems of Interest

- Adsorption of agents and simulants on γ-Al_2O_3[2] and on OH-terminated a-SiO_2[3]
- Systems are fairly well understood – Calculated results can be compared to experiment[4-6]
- γ-Al_2O_3 and a-SiO_2 are important adsorbents – many other materials are based on a silicate or aluminosilicate chemical composition

2. Pinto and Elliott, *Phys. Rev. B* **70**, 125402 (2004).
3. Van Ginhoven et al., *Phys Rev B* **71**, 24208 (2005).
4. Mitchell, et al., *J. Phys. Chem. B* **101**, 11192 (1997).
5. Kuiper, et al., *J. Catal.* **43**, 154 (1976).
6. Kanan and Tripp, *Langmuir* **17**, 2213 (2001).

Model γ-Al_2O_3 Surface



- Cluster cut from semi-infinite crystal surface
- Different cluster sizes will be studied to evaluate size effects
  - Al_8O_{12} and $Al_{20}O_{30}$

Substrates on γ-Al_2O_3 Surface

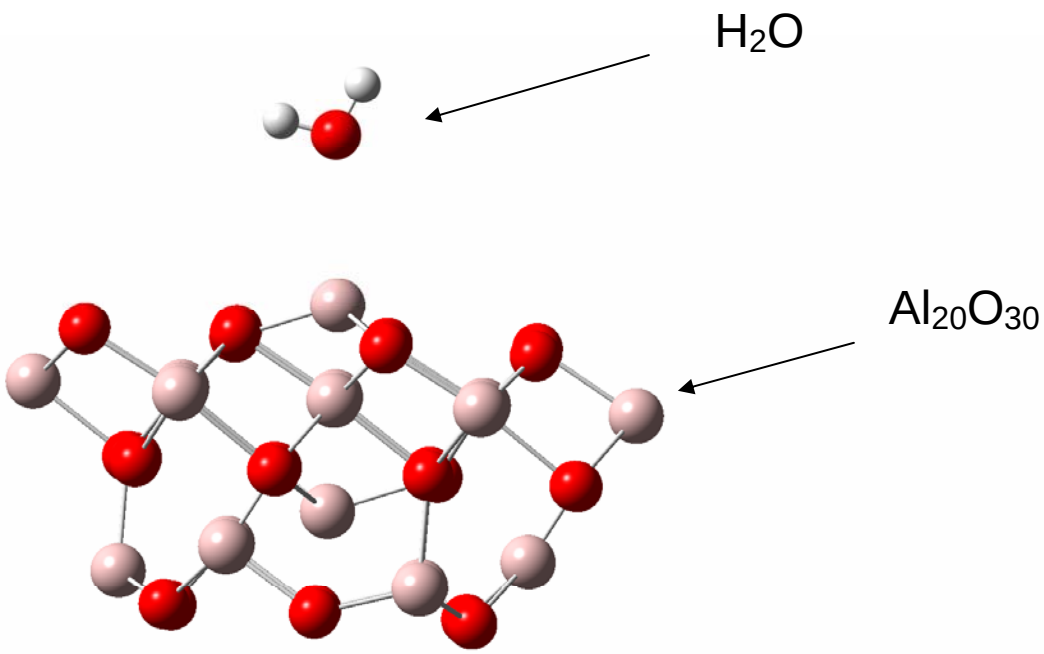
- Al active site allowed to relax during interactions with substrate
  - Displacement should be on the order of ~0.3 Å
- Heat of adsorption:
  - ΔH_{ads} = E(cluster + substrate) – E(cluster) - E(substrate) + E(BSSE)

E(BSSE) = Counterpoise correction for basis set superposition error

Testing γ-Al_2O_3
Physisorption of H_2O on γ-Al_2O_3

Cluster Calculation

- DFT (B3LYP)
- Optimize: relatively large basis for H_2O and Al_8O_{12} – small for the rest.
- Single-point calculation – large basis for all

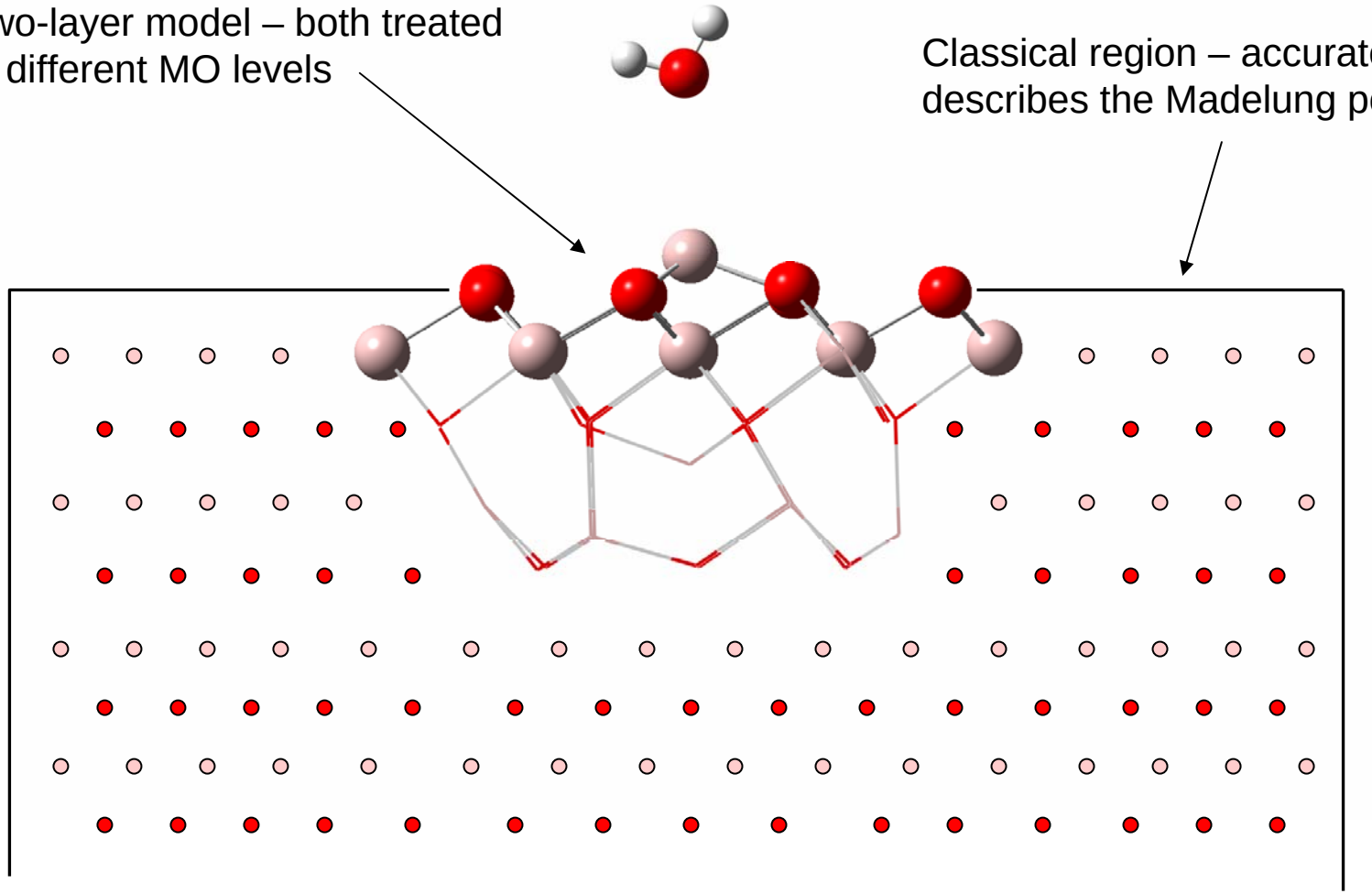


Difficult test case – polar adsorbent

ONIOM/SCREEP

Two-layer model – both treated at different MO levels

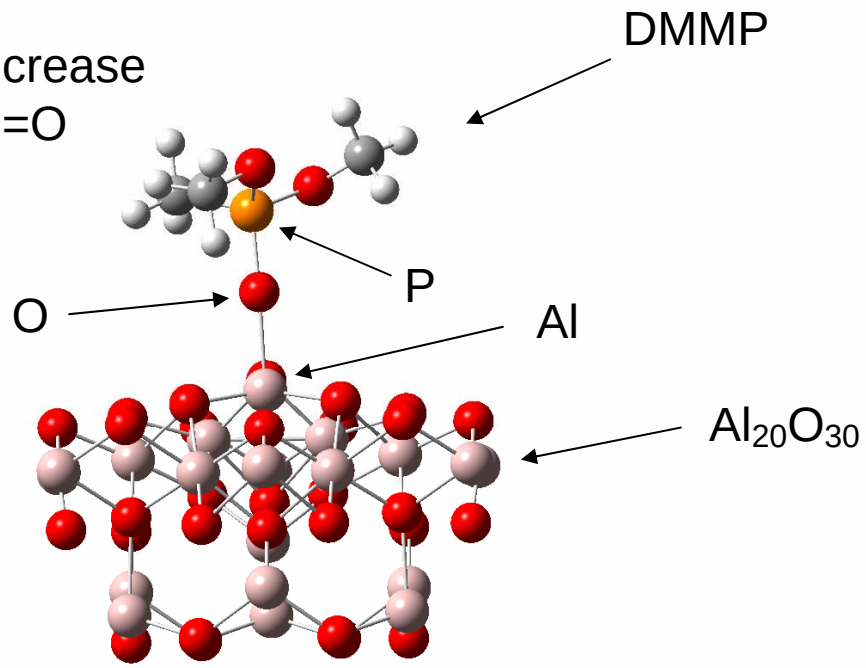
Classical region – accurately describes the Madelung potential



Agent/Simulant Interactions with γ-Al_2O_3

Comparison to experiment:
Adsorption should cause increase in frequency (red shift) of P=O

No other frequencies should undergo large changes



ΔH_{ads} calculations will be used to compare different adsorption geometries:
Lowest ΔH_{ads} indicates correct relative geometry

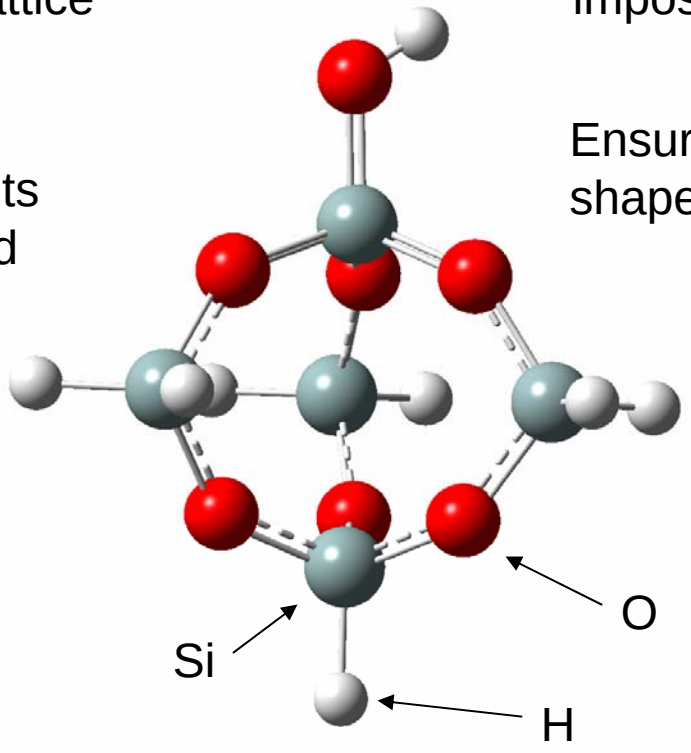
Model a-SiO_2 Surface

Cluster representation of the overall a-SiO_2 lattice

Without the bulk, structural constraints need to be imposed

C_s symmetry (plane) imposed during optimization

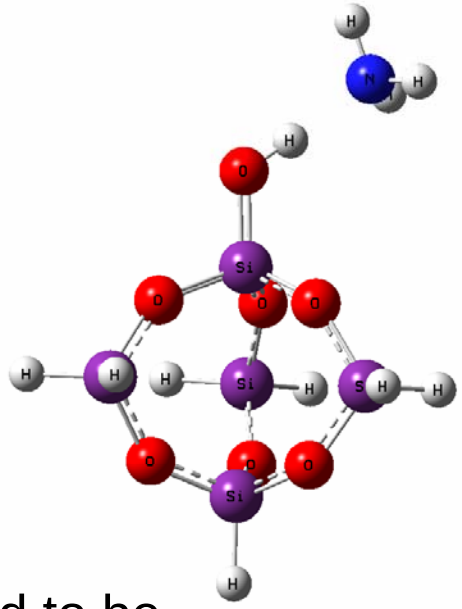
Ensures the cluster keeps the shape it would have in the bulk



Si_5O_7 Cluster

Model a-SiO_2 Surface

This system has C_s symmetry.



Almost any agent or simulant of interest will not have C_s symmetry.

Anharmonicity determined to be important.

Shortcoming of the B3LYP functional may be overcome with a better functional.

Future Directions

- Beyond free-standing Al_2O_3 clusters
  - Use embedding techniques to include lattice Madelung potential
  - Results to date suggest that substrate/cluster interactions are overestimated
  - Could affect absolute ΔH_{ads} but not agent/simulant comparison
- DMMP and Sarin SiO_2
  - Previous problems with getting shift of the SiO-H stretching mode solved by imposing C_s symmetry
  - Investigate DFT vs. MP2 treatments of hydrogen bonding
- Effects of Substrate Modification
  - Include hydration of Al_2O_3 surface to form –OH sites
    - Will permit studies of hydrolysis reactions relevant to agent fate
    - Sulfur Mustard (HD) and 2-CEES can be studied. 2-CEES reacts via

$$-CH_2Cl + HO\text{-}Al \rightarrow -CH_2\text{-}O\text{-}Al + HCl$$