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: $\gamma$-Al$_2$O$_3$ and a-SiO$_2$
• Validate models by comparison of observed and calculated properties of species adsorbed on oxide surfaces
  • $\mu$-wave Spectra
  • IR Spectra
  • $\Delta H_{ads}$
  • 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
How well do QCT methods calculate properties of free molecules?

### DMMP

#### DMMP Rotational Constants (MHz)

<table>
<thead>
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<th>Method</th>
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<th>B</th>
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<tr>
<td>Experiment¹</td>
<td>2828.753</td>
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<td>B3LYP/6-31G*</td>
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<td>MP2/6-31G*</td>
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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

Systems of Interest

• Adsorption of agents and simulants on $\gamma$-Al$_2$O$_3$ and on OH-terminated α-SiO$_2$

• Systems are fairly well understood – Calculated results can be compared to experiment$^{4-6}$

• $\gamma$-Al$_2$O$_3$ and α-SiO$_2$ are important adsorbents – many other materials are based on a silicate or aluminosilicate chemical composition

Model $\gamma$-$\text{Al}_2\text{O}_3$ Surface

- Cluster cut from semi-infinite crystal surface
- Different cluster sizes will be studied to evaluate size effects
  - $\text{Al}_8\text{O}_{12}$ and $\text{Al}_{20}\text{O}_{30}$

Lewis acid $\text{Al}(T_d)$
Chemically-active surface site
Substrates on $\gamma$-Al$_2$O$_3$ Surface

- Al active site allowed to relax during interactions with substrate
  - Displacement should be on the order of $\sim 0.3$ Å

- Heat of adsorption:
  - $\Delta H_{\text{ads}} = E(\text{cluster + substrate}) - E(\text{cluster}) - E(\text{substrate}) + E(\text{BSSE})$
  - $E(\text{BSSE}) = \text{Counterpoise correction for basis set superposition error}$
Testing $\gamma$-Al$_2$O$_3$
Physisorption of H$_2$O on $\gamma$-Al$_2$O$_3$

Cluster Calculation
• DFT (B3LYP)
• Optimize: relatively large basis for H$_2$O and Al$_8$O$_{12}$ – 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-Al₂O₃

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

No other frequencies should undergo large changes

$\Delta H_{ads}$ calculations will be used to compare different adsorption geometries:
Lowest $\Delta H_{ads}$ indicates correct relative geometry
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
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$_2$O$_3$ clusters
  • Use embedding techniques to include lattice Madelung potential
  • Results to date suggest that substrate/cluster interactions are overestimated
  • Could affect absolute $\Delta H_{ads}$ 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$_2$O$_3$ 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
      $-\text{CH}_2\text{Cl} + \text{HO-Al} \rightarrow -\text{CH}_2\text{-O-Al} + \text{HCl}$