SAND2010-4569P

Developing a Molecular Understanding of Water-CWA-Surface Interactions

CBS.FATE.03.10.SN.002

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Threat Agent Science
Technical Science Review

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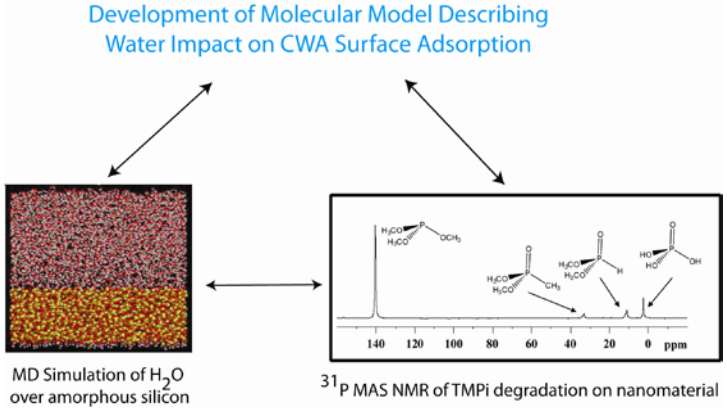
CBS.FATE.03.10.SN.02-
Developing a Molecular Understanding of Water-CWA-Surface Interactions

Todd M. Alam, Sandia National Labs

Objective: Develop a molecular level model to describe the role of water plays within water-CWA-surface interactions.

Description of Effort: Combined computational and experimental effort to describe the water-CWA-surface interactions. Initial efforts directed towards adsorption of Sarin (GB) and the DMMP simulant on hydrated SiO_2 surfaces. Molecular dynamics, Monte Carlo and quantum simulations will determine Sarin-water-surface and DMMP-water - surface energetics, along with experimental NMR chemical shift, chemical shift anisotropy (CSA) input.



Combined computational and experimental effort to model water-CWA-Surface interactions

Benefits of Proposed Technology: The final project deliverable will be a molecular model that describes interactions between Sarin and hydrated SiO_2 surfaces. This technical knowledge base can then be incorporated or extended to predict and understand future studies of water/CWA/surface interactions.

Challenges:
- Large computational effort involving multiple variables and conditions.
- Extension of results dependent on specific surface.

Maturity of Technology: TRL 2 – This proposal involves basic research and exploratory computations directed towards understanding the role water in CWA interactions with surfaces at the molecular level.

Research Area: Threat Agent Science.

Major goals/milestones by fiscal year:

FY10 –
- A.1 - Determine energetics of water-silica interactions.
- A.2 - Determine energetics of water-CWA interactions.
- B.1 – Calculate ^{31}P NMR for different phosphate binding.

FY11 –
- A.3 - Determine CWA-silica energetics.
- A.4 – Determine Role of water in Hydrolysis reaction.
- B.2 – Calculate ^{31}P NMR for different Sarin complexes.

Proposed Funding ($K):

	FY10	FY11
6.1	$650	$650

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Spend Plan

Date FY10 Funding Received	3/23/2010
Amount of FY10 Funding Received ($K)	$650K
FY10 Funds Obligated by 31 May 2010	$48K (7%)
Plans for Obligating Remaining FY10 Funds	$10K - direct
FY10 Funds Disbursed by 31 May 2010	$72K (11%)
Plans for Disbursing Remaining FY10 Funds	$520K*

* Current spend plan requires an extensive acceleration of expenditures to disperse remaining funds. This will be obtained by the recent addition of postdoctoral fellow (Jenkins) and students to the research project.

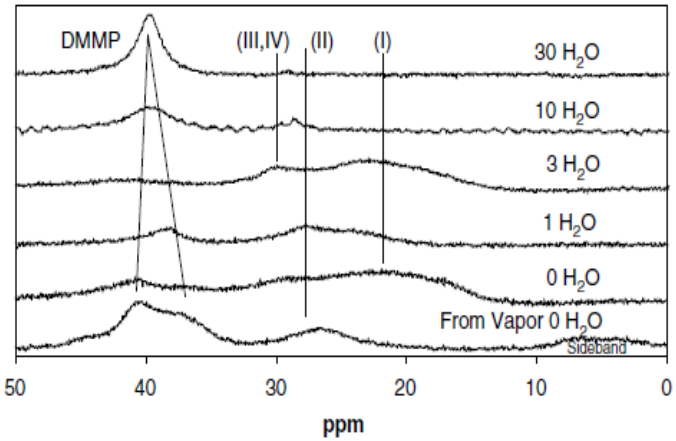
Program Objective

This proposal is aimed at developing a molecular level understanding into the role water plays on the interaction, lifetime and reaction kinetics of CWA, particularly nerve agents or organophosphate agents (OPA), on inorganic surfaces. The importance of water, including dissolved electrolytes, on CWA-surface interactions remains unclear and is the driving force of this proposed research.

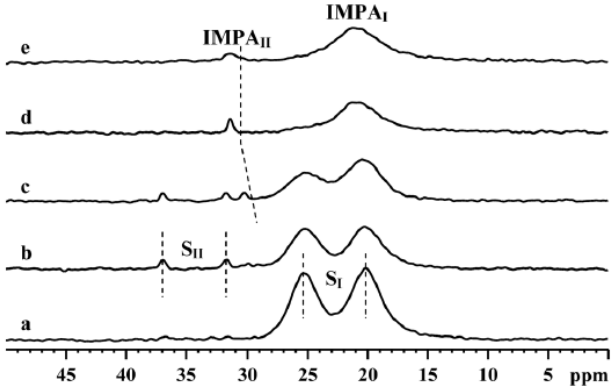
- Results impact future development of protective coatings, filtration devices, sensors and decontamination procedures.
- Computation efforts compatible with other research areas involving surface interactions.
- Results obtained from this project may be extended to investigations of catalytic surfaces.

Background and Significance

DMMP Decomposition on Zeolite



Sarin Adsorption on Carbon



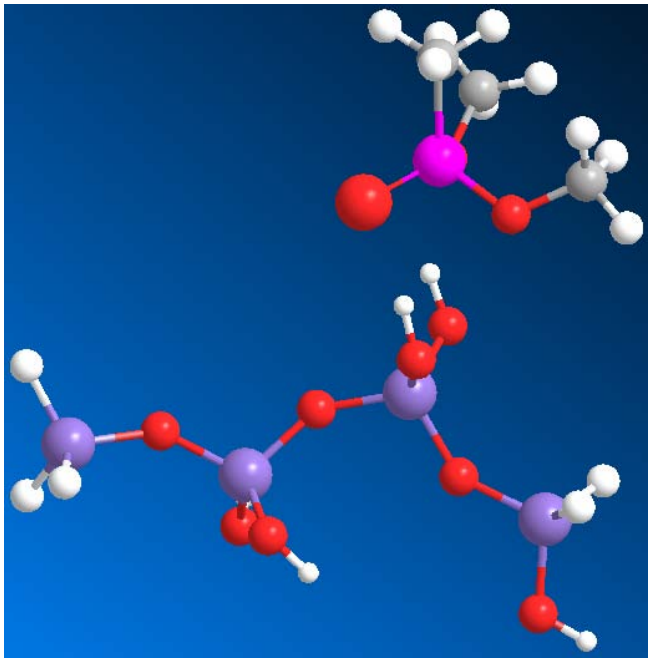
There are many experimental results, on a variety of materials, that clearly demonstrate that small amounts of water can impact the surface interaction of CWA.

- Water has been shown to increase/decrease decomposition rates.
- Impact transport properties through material.
- Leads to spectroscopically different binding environments?
- Electrolytes may be directly involved.

Do we understand how water influences the energetics of adsorption/desorption, the reaction coordinates profiles and kinetics, and diffusion rates or mechanisms??

1) Yang, S.-W., D. C. Doetschman, et al. (2006). "Sodium X-Type Faujasite Zeolite Decomposition of Dimethyl Methylphosphonate (DMMP) to Methylphosphonate: Nucleophilic Zeloite Reactions I." Microporous and Mesoporous Materials **92**: 56-60. 2) Kaplan, D., L. Shmueli, et al. (2007). "Degradation of Adsorbed Sarin on Activated Carbons: A ^{31}P-MAS-NMR Study." Clean: Soil, Air, Water **35**(2): 172-177

Background and Significance



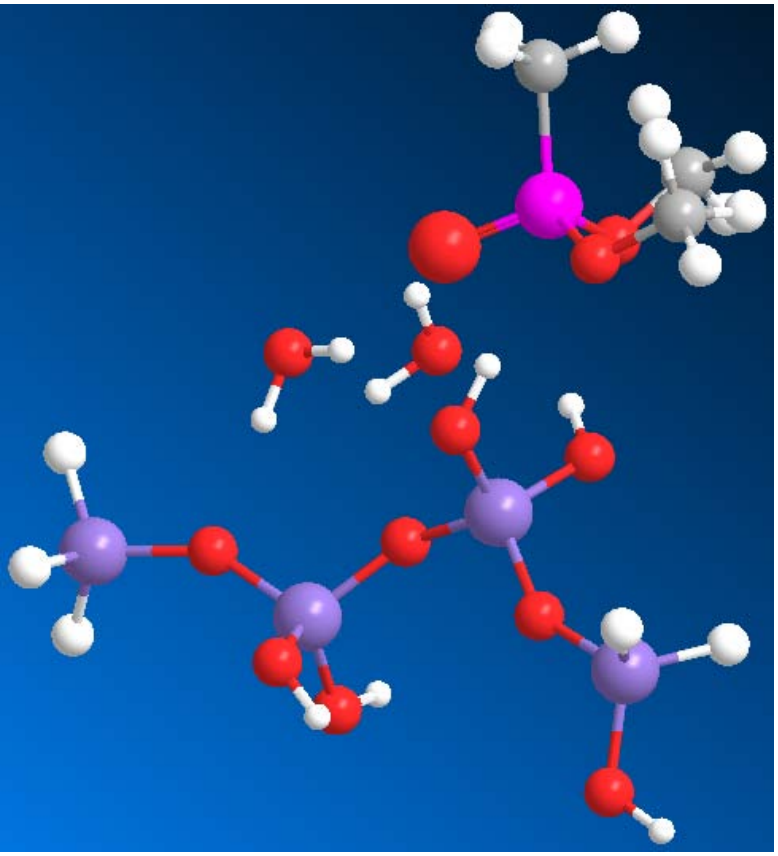
DMMP on Si Cluster

- **Numerous quantum level computational studies on adsorption of CWA on surfaces (from small to very-large sized clusters).***
- **Surfaces include SiO_2, TiO, Al_2O_3, CaO, MgO, clays and zeolites.**

*See the extensive work of J. Leszczynski (JSU) and V. M. Bermudez (NRL). For example see review by Michalkova, Gorb and Leszczynski (2007) "A Quest for Efficient Methods of Disintegration of Organophosphorus Compounds :Modeling Adsorption and decomposition Processes."

- **Computational studies into the role of water very limited!**
- **Passing comments using continuum methods (PCM), and a single report with an explicit water within the cluster (Ault, 2004).**
- **Need to explicitly include water!**

Technical Approach



•Will explicitly include water molecules in *ab initio* calculations to determine energies of adsorption and reactions.

- Cluster size could increase dramatically. How do we assure the conformational space is sampled?
- Combine these efforts with Monte Carlo and MD sampling to assure adequate sampling.
- Large computer clusters need to be utilized for efforts.

•Molecular dynamic (MD) simulations will be used to determine equilibrium structures/conformers and thermodynamic driving forces at the CWA/water/surface interface.

- Builds on previous work involving water at biological interfaces.
- Existing force fields limited/or questionable! Will incorporate results from *ab initio* calculations.

•Combine explicit water molecules with polarizable continuum methods (PCM) to evaluate impact of reaction coordinates.

- Need to evaluate from isolated water complexes (low %RH) to full solvation.

Technical Approach

4 Major Aims

1) Predict structural and energetic properties of Water/Silica surfaces.

$$[\text{Si surface}] + n\text{H}_2\text{O} \rightleftharpoons [\text{Si surface}] \bullet n\text{H}_2\text{O}$$

2) Predict Structural and Energetic properties of Water/CWA complexes

$$[\text{CWA}] + n\text{H}_2\text{O} \rightleftharpoons [\text{CWA}] \bullet n\text{H}_2\text{O}$$

3) Calculate role water has on adsorption/hydrolysis mechanisms

$$[\text{CWA}] \bullet n\text{H}_2\text{O} + [\text{Si surface}] \bullet m\text{H}_2\text{O} \rightleftharpoons [\text{CWA}] \bullet [\text{Si surface}] \bullet (n+m-y)\text{H}_2\text{O} + y\text{H}_2\text{O}$$

4) Correlate these structural properties with calculated ^{31}P NMR chemical shifts and chemical shift anisotropy (CSA).

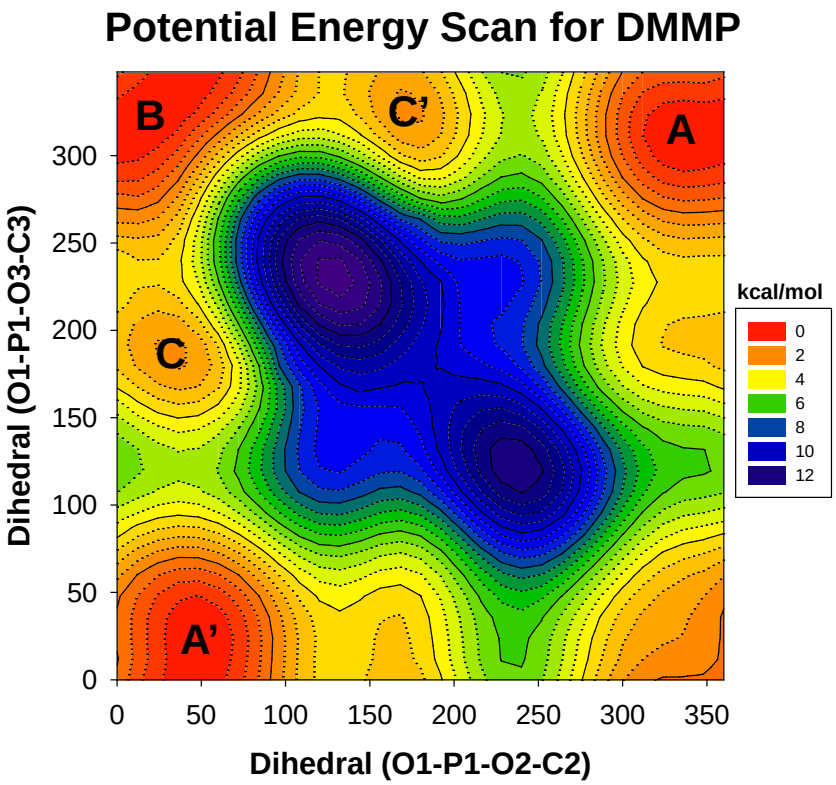
Strategy/Risk Mitigation

- **Most serious issue is the size of the cluster model employed and the ability to treat in a computationally efficient manner.**
  - Starting with small clusters and small MD cell size to help gauge the upper limit.
  - Will employ ONIOM methods (different levels of theory) for regions not crucial in the adsorption/reaction process.
  - Will combine explicit waters with implicit solvent (PCM) models. How many water need to be included to get converging results?
  - Utilize larger/faster computing facilities.

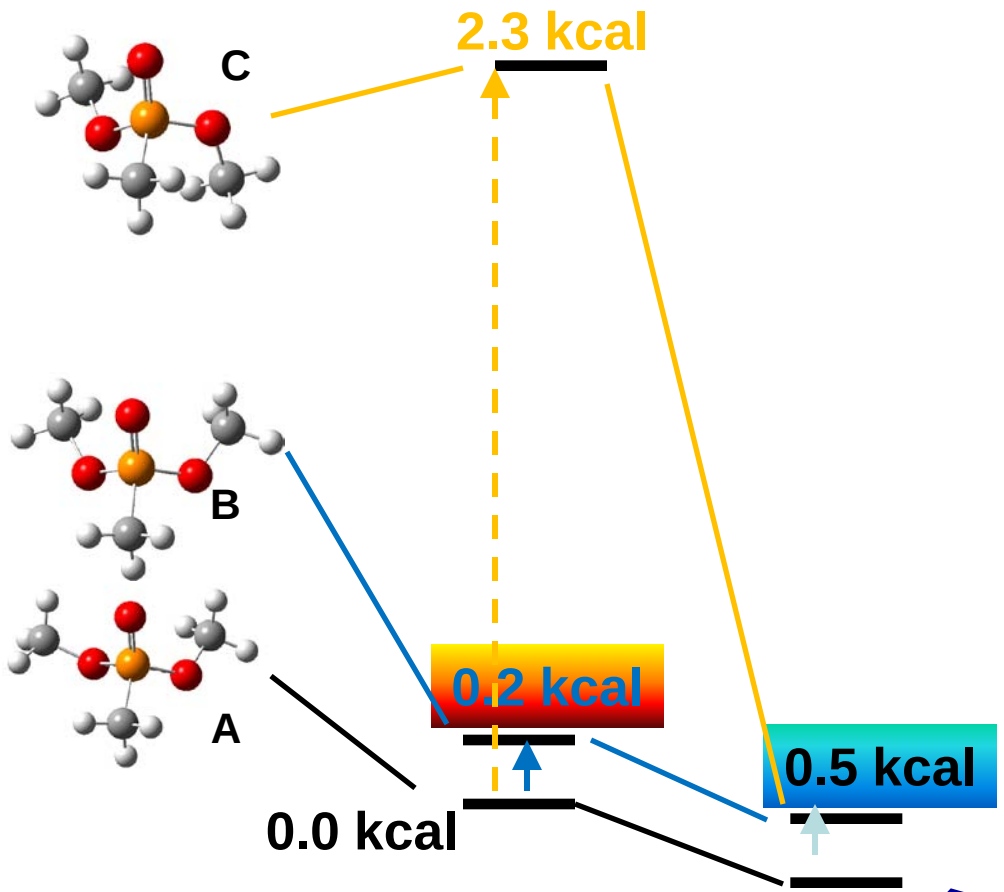
- **Need dynamic averaging to sample all conformers and to understand both equilibrium and kinetic process.**
  - Combine MD and *ab initio* calculations.
  - Investigate alternative methods to explore reaction pathways in water containing clusters.

Progress: *Water-CWA Interactions*

- **Water (explicit/implicit) plays role on conformer energetics!**

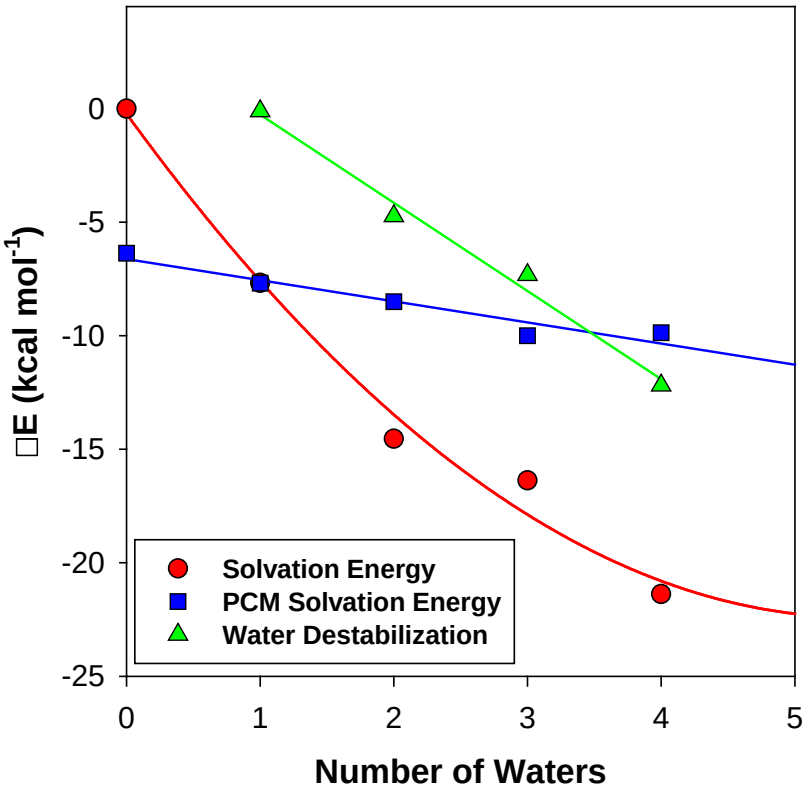


Alam, 2010, in preparation



Progress: *Water-CWA Complexation Energies*

DMMP/Water Complexes



- Have determined the energies of water complexation for DMMP and Sarin.
- Can compared these energies to solvation energies obtained using PCM.
- These cluster calculations also allow us to determined the energy of destabilization within the water hydrogen bonding network.
- These calculated energies provide basis to compare CWA/surface complexation and water/surface complexation energies.

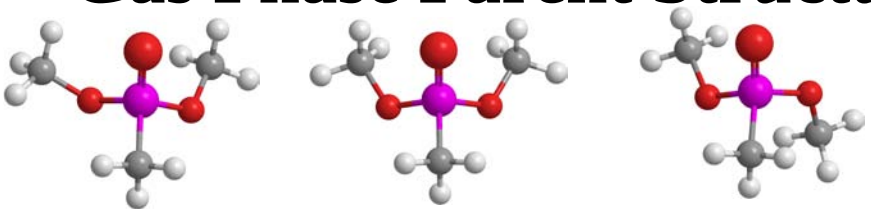
One issue noted: *A very rich and complex range of structures occurs when water is added explicitly. Need to develop a classification scheme to denote and describe these different structures.*

Progress: Implement "Evolutionary Generation Tree" for Classification of Water Clusters

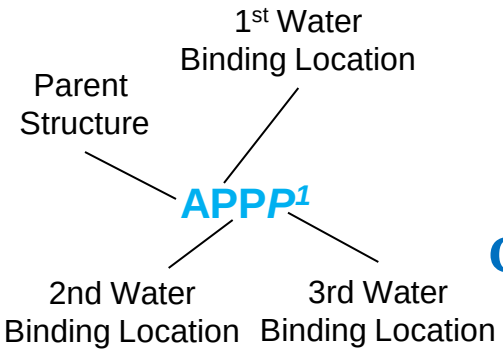
Gas Phase Parent Structures

Generation

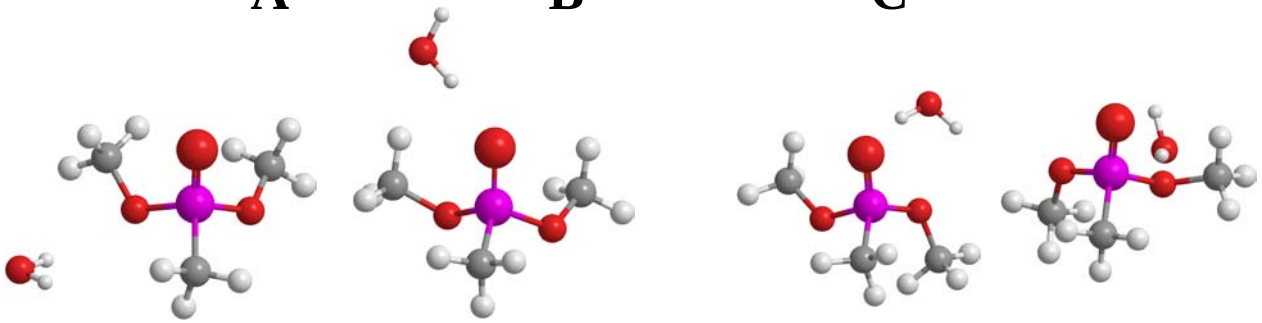
G0



A **B** **C**



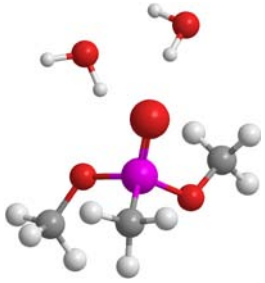
G1



AM **AP** **CP** **CM**

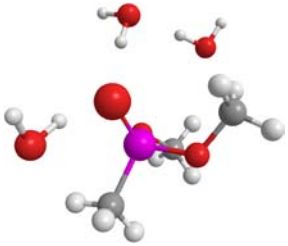
P – water bound to PO
M – water bound to OMe
Italic – water bound to another water in inner sphere.
Superscript - identifies which inner-sphere water

G2



CPP,…..CPM, CMP

G3

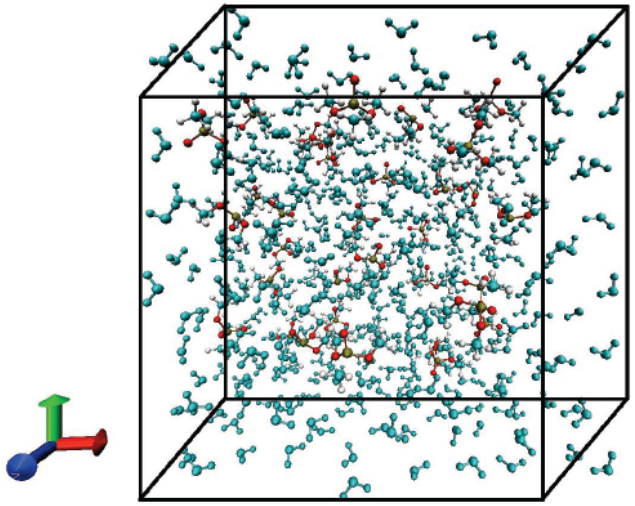


APP*P*[1], …….

Progress: *MD Simulations of Hydration*

- MD simulations of DMMP and Sarin in water performed to extract hydration and conformational information.

Simulation super-cell (periodic boundary conditions) for DMMP/water mixture

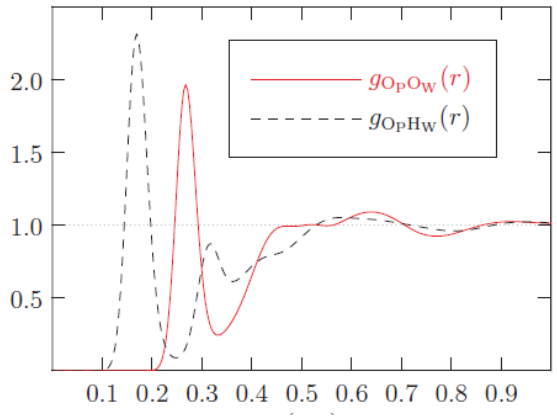


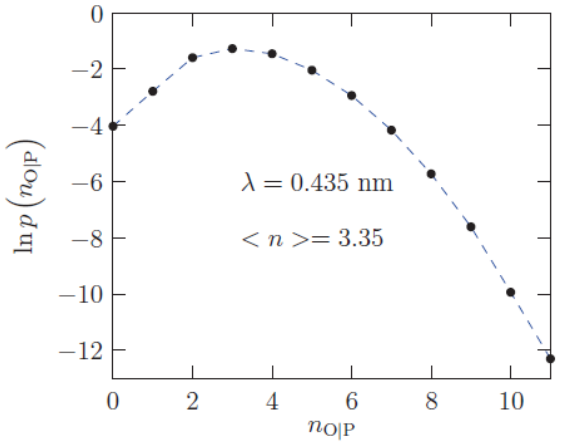
Thermodynamic state: $T = 300$K, $p = 1$ atm, $x = 33/433$ (mole fraction DMMP).

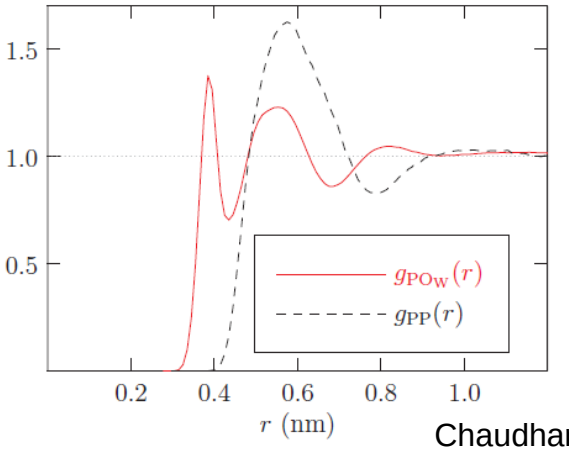
Chaudhari et al. (In preparation) 2010.

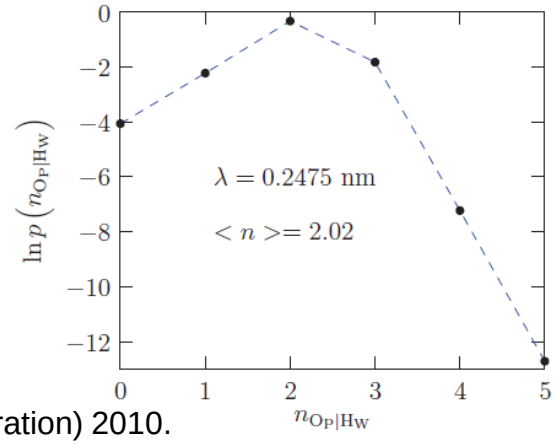
Progress: *Information Obtained from MD*

- MD simulations allowed extraction of the first solvation sphere and the number of waters coordinated to the P=O group.





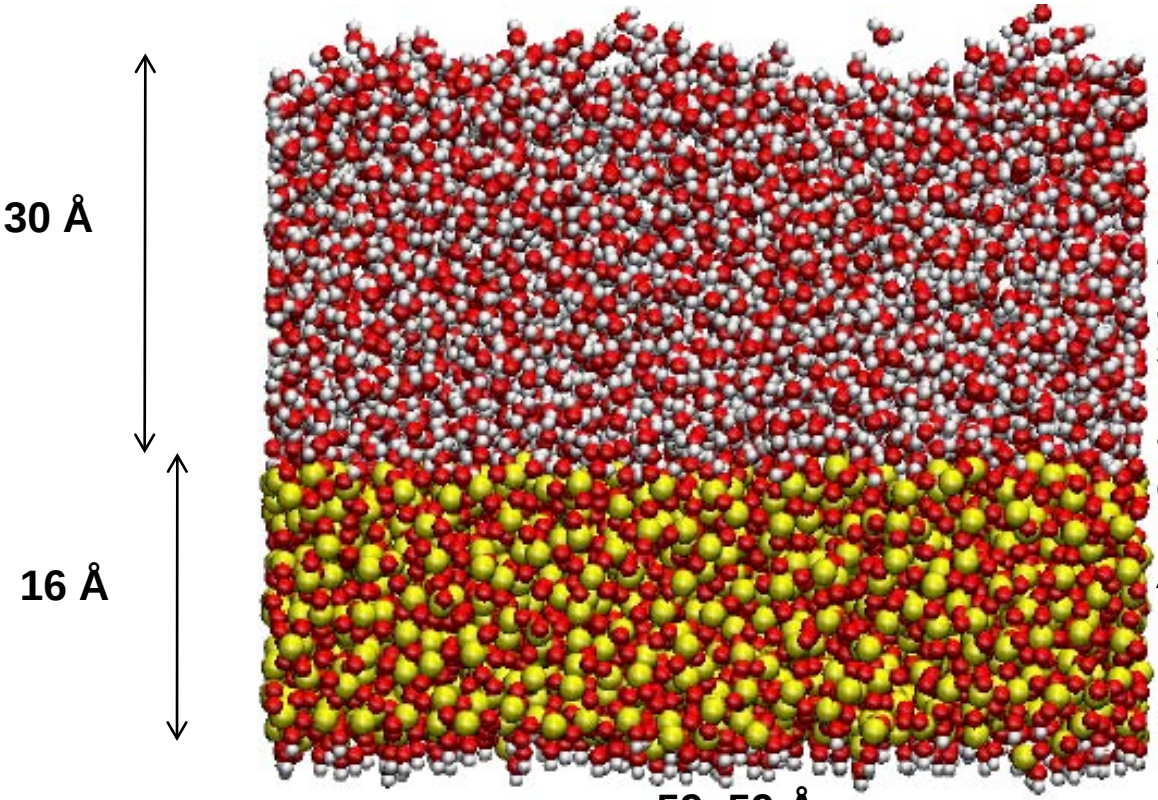




Chaudhari et al. (In preparation) 2010.

Progress: *MD Simulations of Silica*

- Water structure at the silica interface.



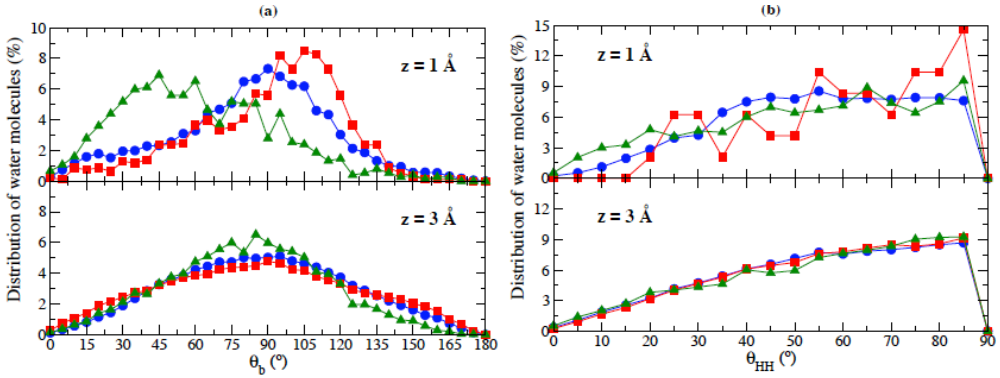
•Classical MD simulations of amorphous & crystalline surfaces with water film.

•*Ab initio* MD simulations of crystalline surfaces with monolayer water (10x9x16 Å slab)

Extend these result to systems with DMMP or Sarin

Progress: *Water Structure at Silica Surface*

a-quartz, b-cristobalite, amorphous

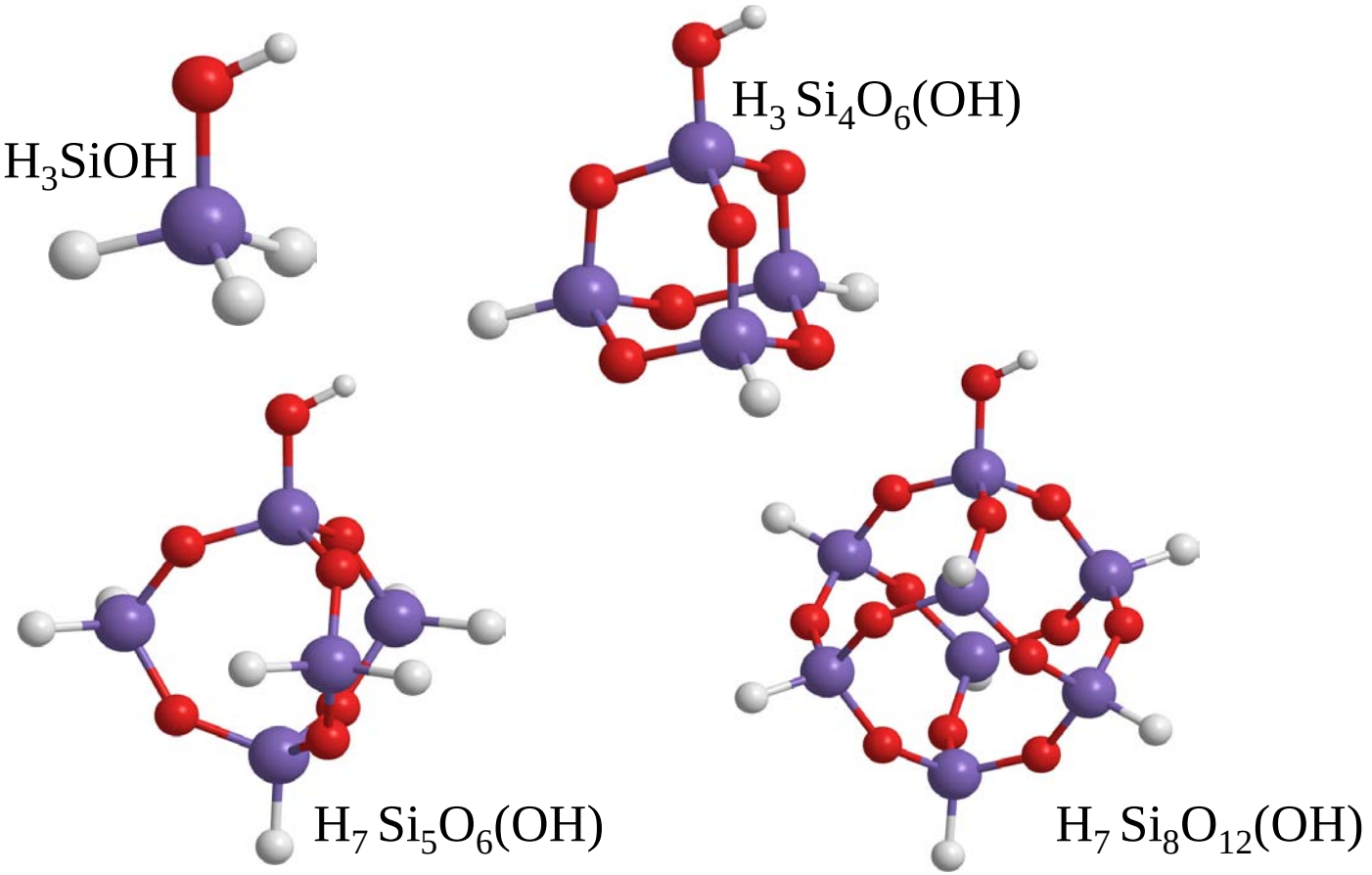


- *Waters at interface (3 Å) orient so hydrogen atoms interact with surface.*
- *Waters have reduced mobility at interface (6 Å) compared to bulk, but still are significantly mobile (not ice-like).*

Water bisector angle θ_b ,and angle connecting water HH θ_{HH} bonds with z-axis.θ_{HH} define parallel versus perpendicular orientations and amount of tilt toward surface.

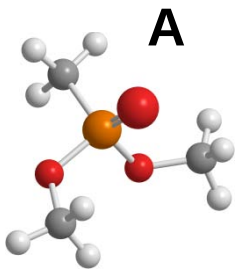
Progress: *Initial Cluster Models Targeted*

Small SiOH clusters



Progress: *Initial Cluster Models Targeted*

$$DMMP + H_xSi_yO_z(OH) \rightarrow DMMP{\cdot}H_xSi_yO_z(OH)$$

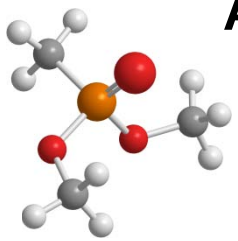


A

ΔE_{DMMP}

A, B, C

DMMP Structure	ΔE_{ads} kcal-mol^{-1}
A	-13.28
B	-11.85
C	-12.96



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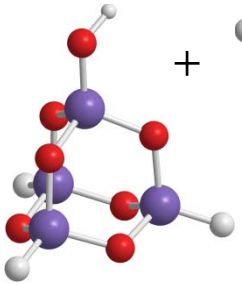
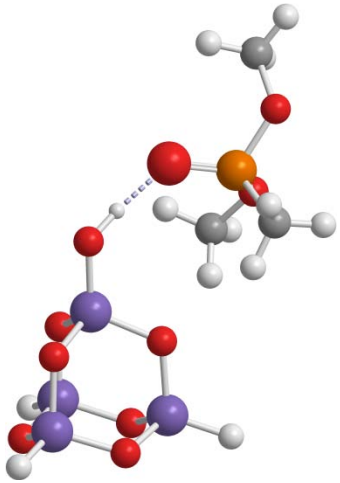


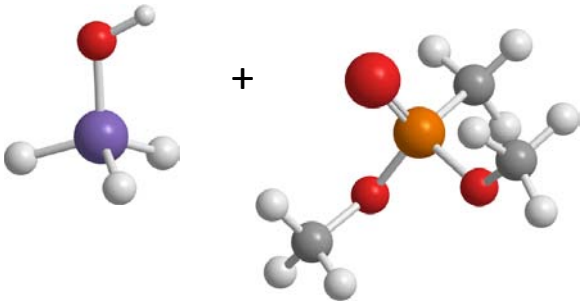
$H_3Si_4O_6(OH)$

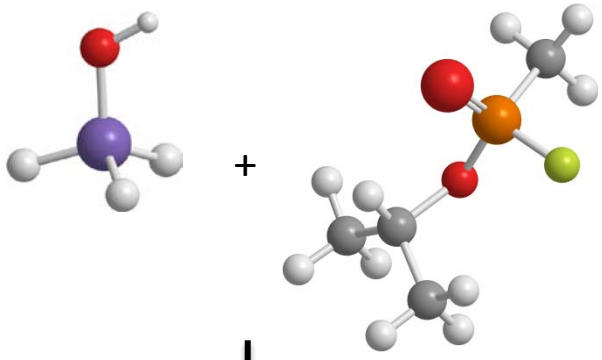
ΔE_{ads}



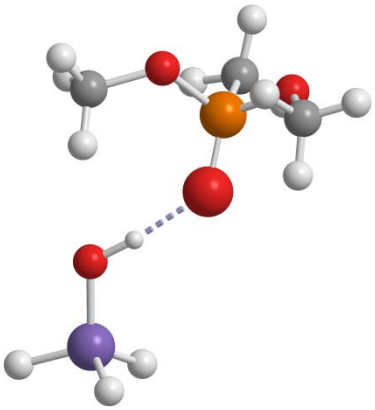
$DMMP{\cdot}H_3Si_4O_6(OH)$

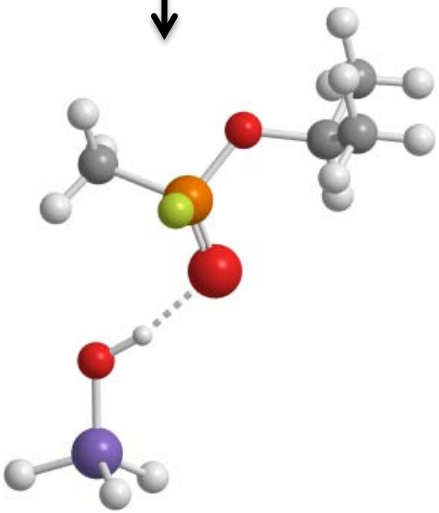
Progress: *Initial DMMP/Sarin Adsorption*





	ΔE_{ads} kcal-mol^{-1}
DMMP	-9.74
Sarin	-8.28



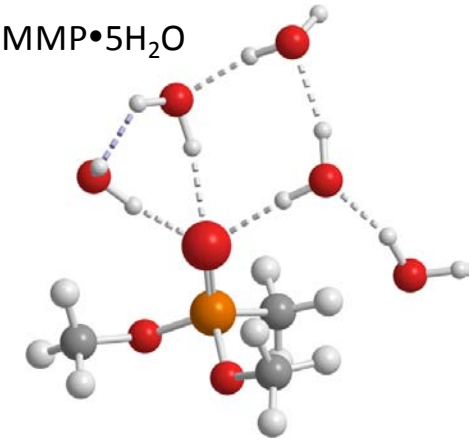


^{31}P Shielding (ppm)	
DMMP	-262.3
DMMP·H_3SiOH	-259.5
Sarin	-272.5
Sarin·H_3SiOH	-256.9

Progress: *Initial Water/Cluster Models*

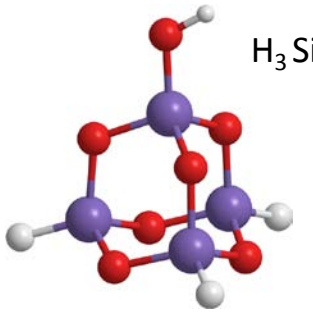
$$DMMP\bullet nH_2O + H_xSi_yO_z(OH) \rightarrow DMMP\cdot H_xSi_yO_z(OH) + H_2O$$

$DMMP\bullet 5H_2O$



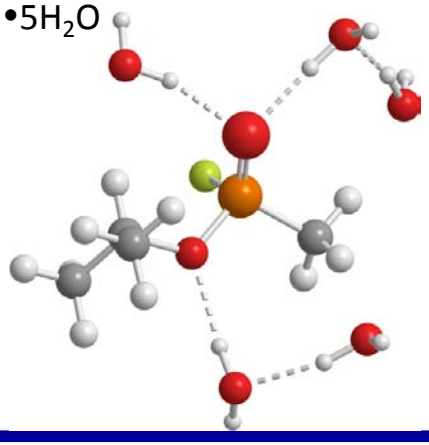
+

$H_3Si_4O_6(OH)$



→ $DMMP\cdot H_3Si_4O_6(OH) + 5H_2O$

$Sarin\bullet 5H_2O$



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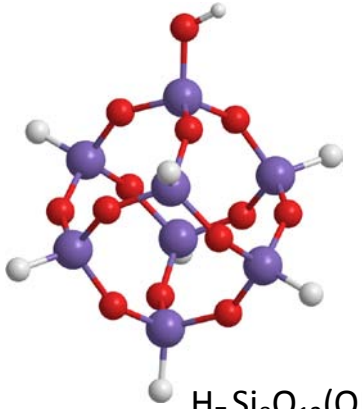


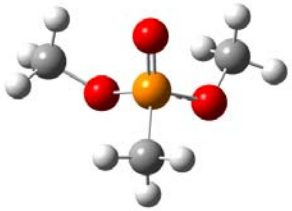
$H_7Si_8O_{12}(OH)$

→ $Sarin\cdot H_7Si_8O_{12}(OH) + 5H_2O$

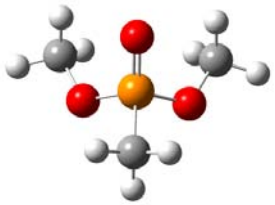
Progress: *Calculation of ^{31}P NMR*

Free

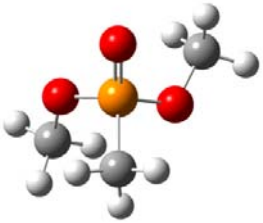
A



B



C



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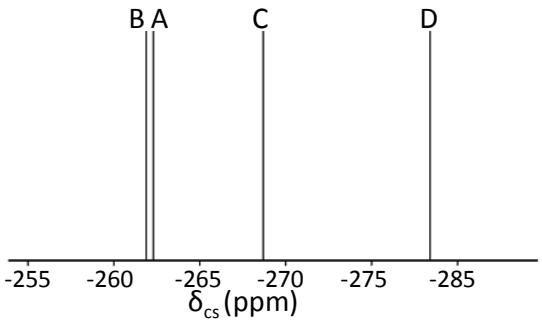
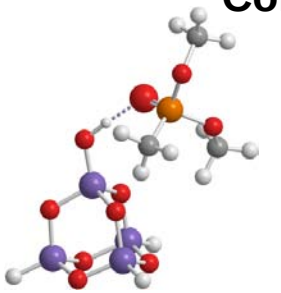
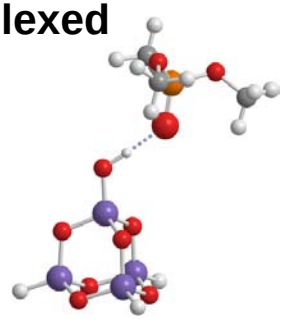


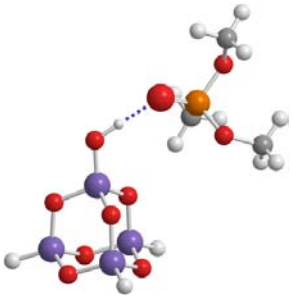
Complexed



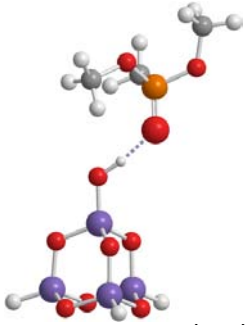
DMMPA·$H_3Si_4O_6(OH)$



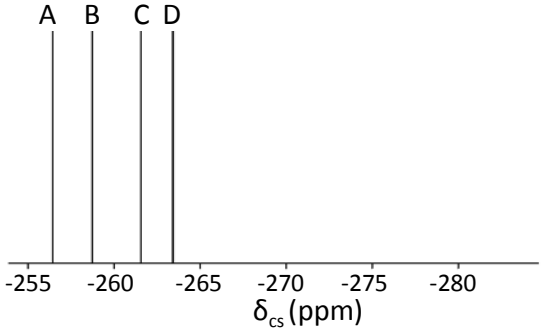
DMMPB·$H_3Si_4O_6(OH)$



DMMPC·$H_3Si_4O_6(OH)$

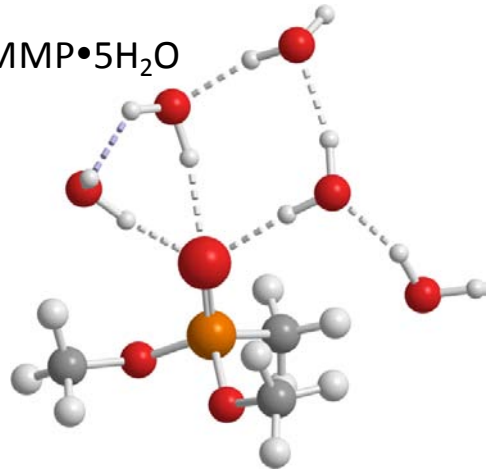


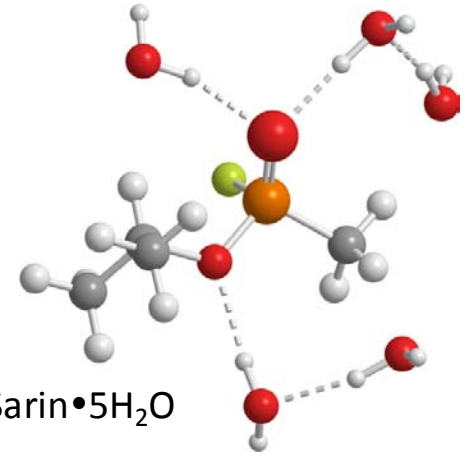
DMMPD·$H_3Si_4O_6(OH)$



Progress: *Impact of Water on ^{31}P NMR*

DMMP•5H_2O





Sarin•5H_2O

^{31}P Shielding (ppm)	
DMMP	-262.3
DMMP•H_2O	-261.3
DMMP•2H_2O	-257.9
DMMP•3H_2O	-257.9
DMMP•4H_2O	-251.2
DMMP•5H_2O	-250.6
Sarin	-272.5
Sarin•H_2O	-261.4
Sarin•2H_2O	-254.1
Sarin•3H_2O	-252.7
Sarin•4H_2O	-255.9
Sarin•5H_2O	-246.9

Progress based on results

- The initial results confirm that the explicit addition of water influences the adsorption energies of DMMP and Sarin to SiOH surfaces.
- We will continue to explore these interaction with larger surface clusters and compare to implicit PCM results.
- The Q1 have been meet and the Q2 milestones are in progress.

Conclusions

- Water does impact the adsorption energies of DMMP and Sarin to SiOH surfaces.
- If these results can be generalized of empirically described has yet to be determined or fully explored.
- This basic information has the potential to explain the impact of water on surface adsorption for different organophosphates.
- Concept and procedure should be extendable to other surfaces and compounds.

Future Directions

- Validate MD simulations. Implement quasi-chemical statistical thermodynamic theory of Rempe and Pratt

- Extend MD simulation to hydrated DMMP at amorphous silica surface and characterize surface interactions.

- Include simple electrolytes in MD simulations to evaluate impact on structure and thermodynamics.

- Expand *ab initio* energy and NMR calculations to larger surface clusters and multiple explicit hydration environments.

- Initiate calculation of transition state structures for DMMP and Sarin hydrolysis in the presence of explicit water and at SiOH surfaces.

Publications and Presentations

- Rempe et al/ “Simul;ation study of the Silicon dioxide and water interface (2010), *Journal of Computational and Theoretical Nanoscience,*Submitted.

Inter/Intra Agency Coordination/Collaboration

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  - Dr. Janelle Jenkins (Postdoctoral Fellow)
  - Amy Garner (Student Intern)
  - Emily Baldwin (Student Intern)
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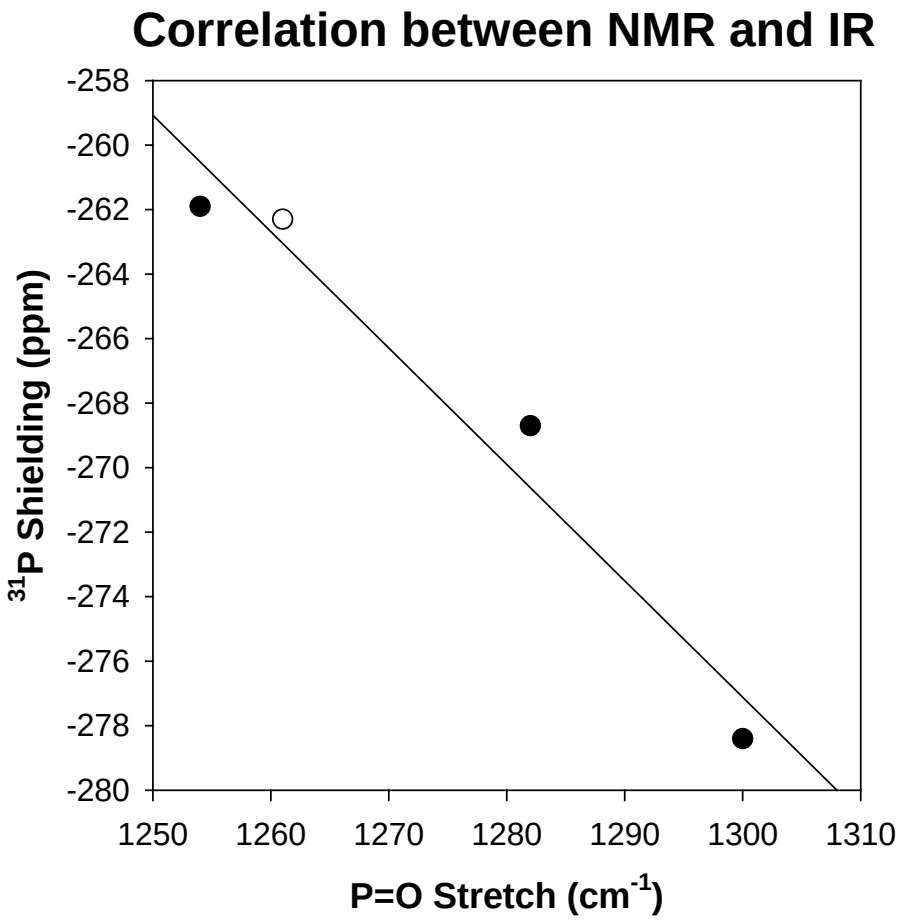
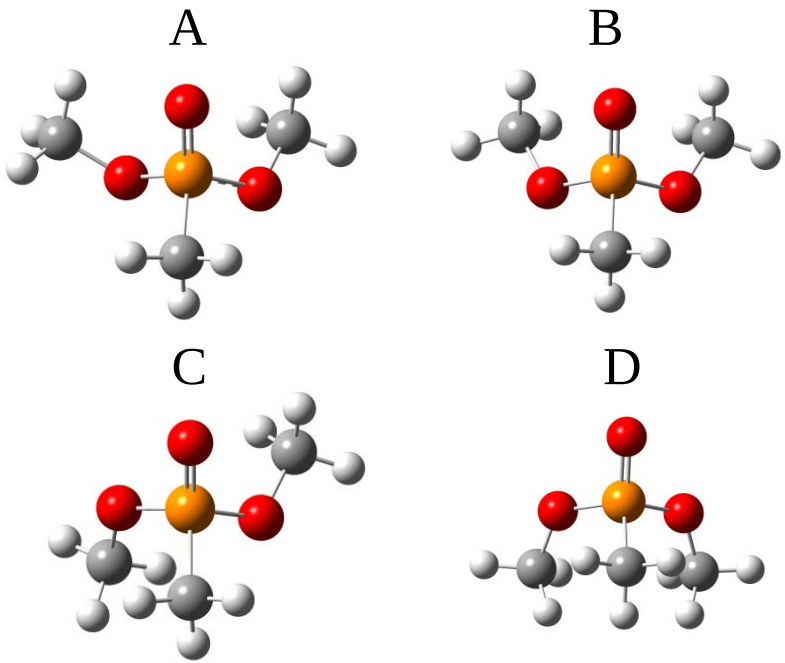
  - Prof. Lawrence Pratt
  - Dr. Mangesh Chaudari (Postdoctoral Fellow)
  - Wei Zhang (Graduate Student)
- **Physics Department**
  Fort Hays State University
  - Prof. Cathy Clewett (Visiting Professor/DOE FAST Team)
  - C. J. Pearce (Visiting Undergraduate Student)

Backups


Correlation between NMR and IR
-258
-260
-262
-264
-266
-268
-270
-272
-274
-276
-278
-280
31P Shielding (ppm)
1250
1260
1270
1280
1290
1300
1310
P=O Stretch (cm-1)


A
B
C
D