

Structural and Thermodynamical Studies of Aqueous Arsenic by First Principles



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Motivation



www.leighday.co.uk

Exposed to > 0.01 mg/L:

-45-57 million in Bangladesh

-13 million in USA:

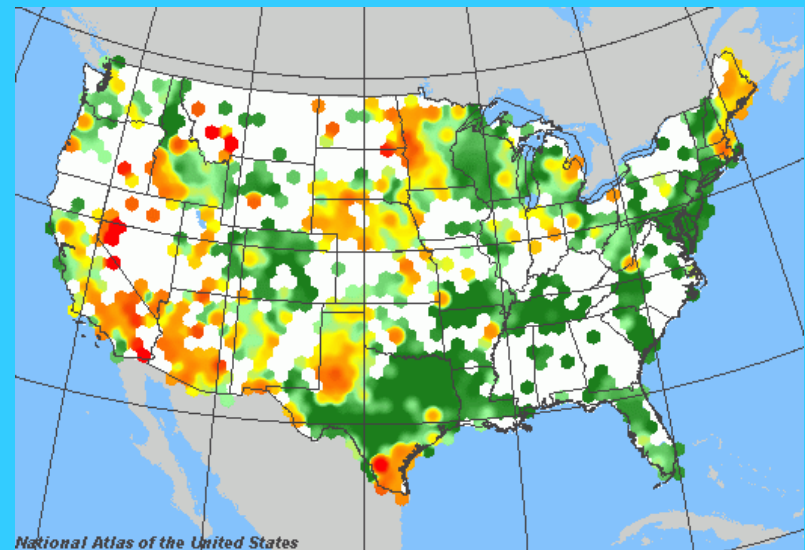
also:

Argentina, Australia, Chile, Hungary, India

Mexico, Peru, Thailand, China, West Bengal

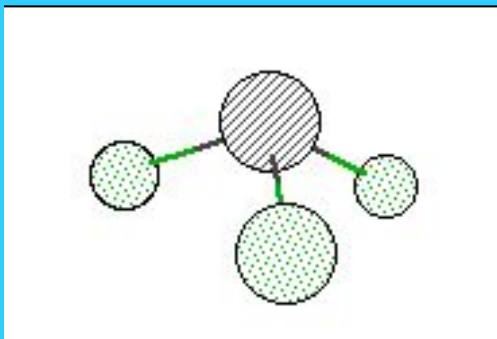
Impact on Health:

- cancers: skin, lungs, bladder, kidneys
- hypertension
- cardiovascular disease
- diabetes
- reproductive difficulties

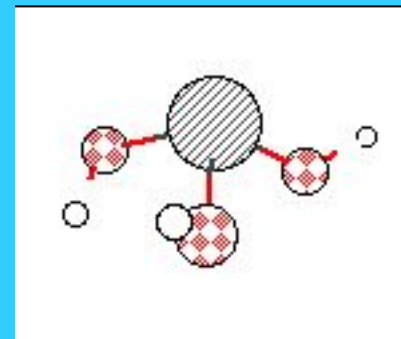


US Geological Survey, 2004

Developing a Model



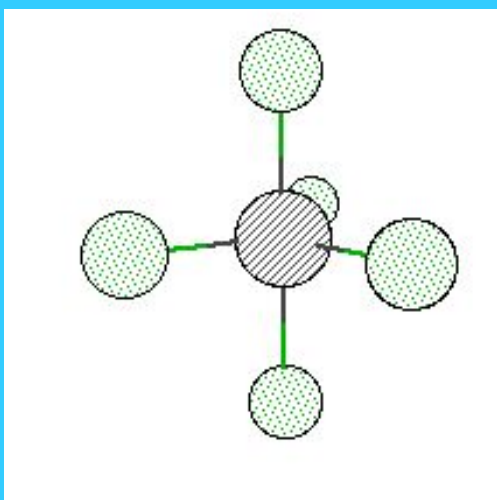
AsCl₃



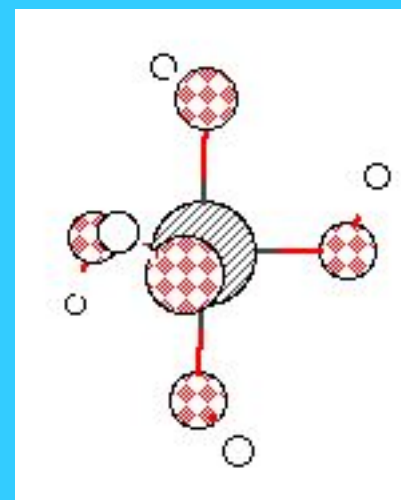
As(OH)₃

As (III)

Or

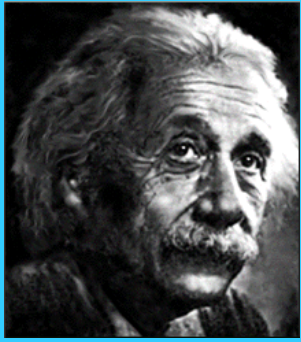


AsCl₅

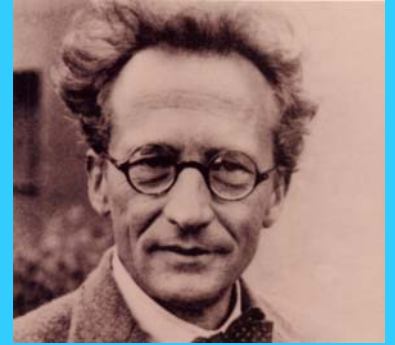


As(OH)₅

As (V)



Methods



First Principle Methods: (ab initio)

- Hartree Fock (HF)
- Moller-Plesset 2nd order perturbation (MP2)
- Density Functional (DFT or PBE)

Basis Sets:

cc-pvDz, cc-pvTz, cc-pvQz

Correlation Consistent Polarized Valence ___ Zeta set

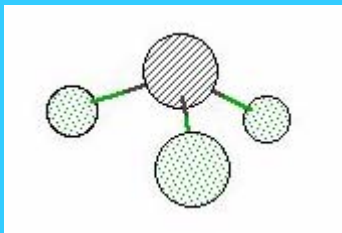
Conditions:

Gas & Continuum Water



Optimized Geometries

Most 'agreeable' geometries:



AsCl₃ cc-pvTz HF_{water}

	<u>Calculated:</u>	<u>Experimental</u>
Bond Length (As-Cl)	2.169 Å	2.161 Å
Bond angle:	98.5° & 97.5 °	98.7°

Trends:

- HF_{water} and MP2_{gas} best agreement for all cases, except AsCl₃ pvDz
- DFT is worst for: AsCl₅ and As(OH)₅
- For cc-pvTz, range of deviation:

HF_w = 0.05-5.34% MP2 = 0.05-6.82% DFT = 3.61-13.1%

Vibrational Spectra: Best Fits

<u>Molecule</u>	<u>Calc. Type</u>	<u>Calc. value</u>	<u>Exp. value</u>	<u>Deviation</u>
AsCl ₃	HF _{water} vDz	966.37 cm ⁻¹	966 cm ⁻¹	0.038 %
AsCl ₃	HF _{water} vTz	412.06 cm ⁻¹	416 cm ⁻¹	1.07 %
AsCl ₅	HF _{water} vDz	367.75 cm ⁻¹	369.5 cm ⁻¹	0.47 %
AsCl ₅	HF _{gas} vTz	400.16 cm ⁻¹	403.9 cm ⁻¹	0.926 %
As(OH) ₃	MP2 _{gas} vDz	694.25 cm ⁻¹	700 cm ⁻¹	0.821 %
As(OH) ₃	MP2 _{gas} vTz	702.44 cm ⁻¹	700 cm ⁻¹	0.292 %
As(OH) ₅	HF _{water} vDz	746.15 cm ⁻¹	745 cm ⁻¹	0.154 %
As(OH) ₅	HF _{water} vTz	840.54 cm ⁻¹	843 cm ⁻¹	0.292 %

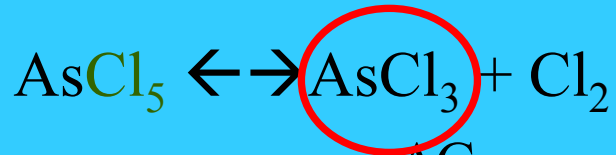
Experimental results used for comparison from: Efremov 2002, Haupt & Seppelt 2002, Tossell et al. 1997, Loehr & Plane 1968, and Gout et al. 1997.

Vibrational Spectra: Method Comparison

<u>Calc. Method</u>	<u>Range of Deviation</u>	<u>Average Deviation</u>
HF	0.038 % -- 24.7 %	4.24 %
MP2	0.292 % -- 13.8 %	4.27 %
DFT	2.32 % -- 41 %	17.7 %

Improved match: HF_{gas} average correction factor = 1.04
vs 0.893 found by Helz 1995
4 % < 10.7 %

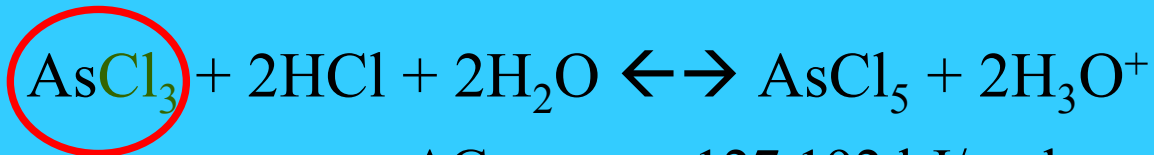
Coordination Chemistry



$$\Delta G_{\text{HFwater}} = -51.611 \text{ kJ/mol}$$

$$\Delta G_{\text{MP2gas}} = -51.591 \text{ kJ/mol}$$

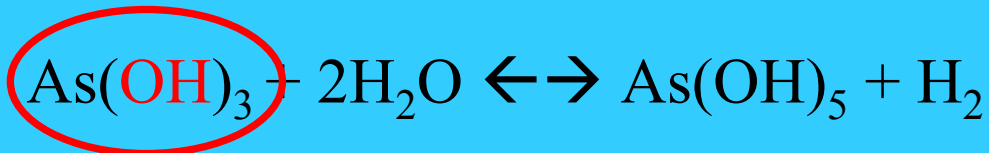
$$\Delta G < 0$$



$$\Delta G_{\text{HFwater}} = 127.192 \text{ kJ/mol}$$

$$\Delta G_{\text{MP2gas}} = 120.140 \text{ kJ/mol}$$

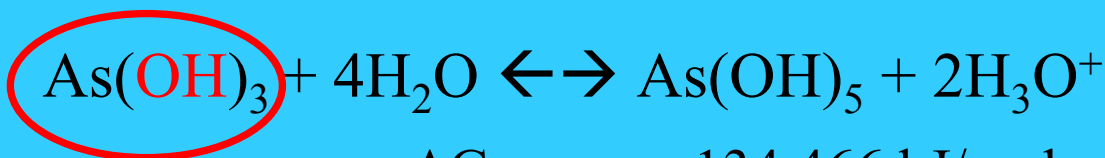
$$\Delta G > 0 \quad !!!$$



$$\Delta G_{\text{HFwater}} = 59.622 \text{ kJ/mol}$$

$$\Delta G_{\text{MP2gas}} = \quad \text{kJ/mol}$$

$$\Delta G > 0$$



$$\Delta G_{\text{HFwater}} = 134.466 \text{ kJ/mol}$$

$$\Delta G_{\text{MP2gas}} = \quad \text{kJ/mol}$$

$$\Delta G > 0$$

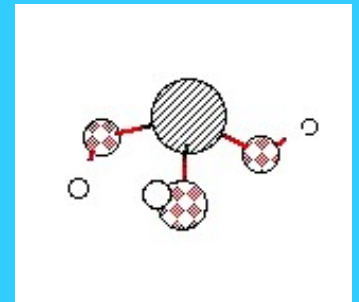
Conclusions

- HF_{water} and MP2_{gas} results give best agreement

	<u>HF</u>	<u>MP2</u>
Range of deviation in geometry:	0.05-5.34%	0.005-6.82%
Range deviation in vib. freq.:	0.038-24.7%	0.29-13.8%

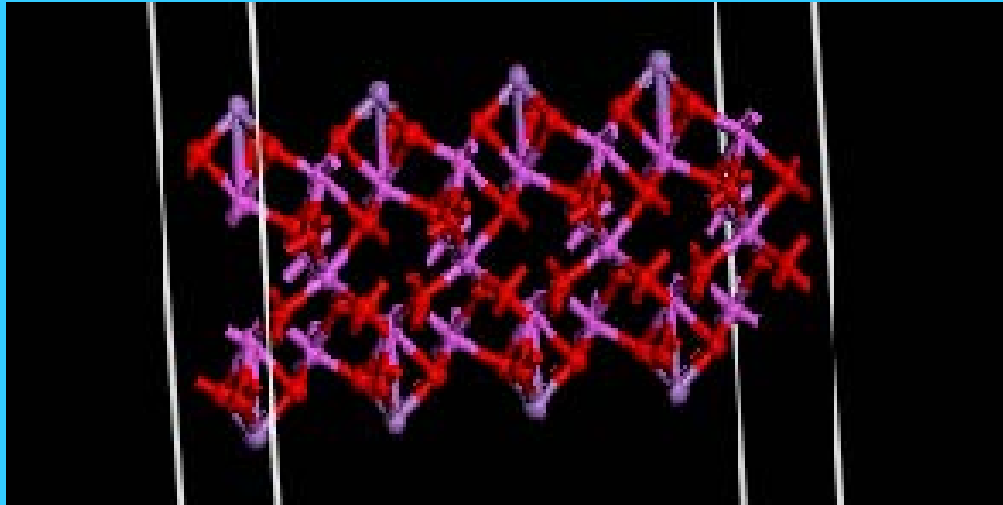
- Structure:
 - AsCl₅ is bipyramidal in structure
 - As(OH)₅ between bipyramidal and square pyramidal

- As (III) is favored



Proceeding Work

- Explicit water first principle calculations for
 $\text{As}(\text{Cl})_{3,5}$ & $\text{As}(\text{OH})_{3,5}$
- Surface calculations on $\alpha\text{-Al}_2\text{O}_3$ (0001)



- P. Engel, O. Coskuner, A. Chaka to be submitted

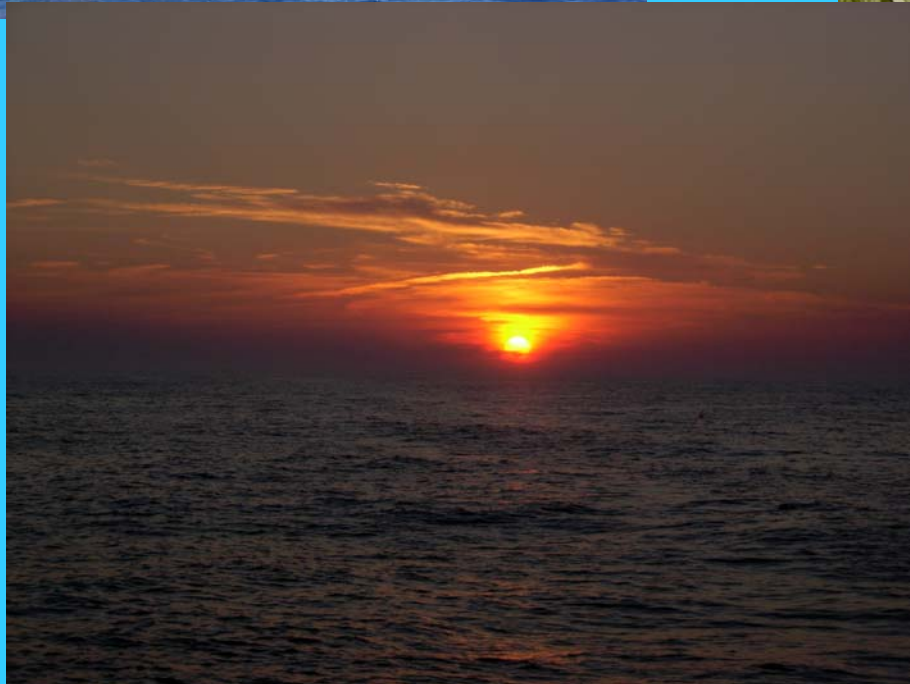
Acknowledgments

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- Dr. Orkid Coskuner – Dr. Cynthia Lo

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My Future



MIT – WHOI
PhD in
Physical Oceanography

Disclaimer

In discussions following the presentation of this study, I have found the following errors:

- $\text{As}(\text{Cl})_5$ is unstable at room temperature
- $\text{As}(\text{OH})_5$ does not exist in nature, instead, the correct As(V) aqueous species is AsO_4^{3-}
- The vibrational spectra should have only been compared to the asymmetric stretch peak, and
- Some of the calculations were done under less stringent convergence criteria and thus give worst agreement. The fits of these can not be compared to the fits of those performed with more strict criteria.
- With these in mind, the new conclusions point to MP2 and DFT as the better calculation methods.

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