

Photoionization of the three protonation forms of phosphate ion: From anion instability to stability upon moving to water

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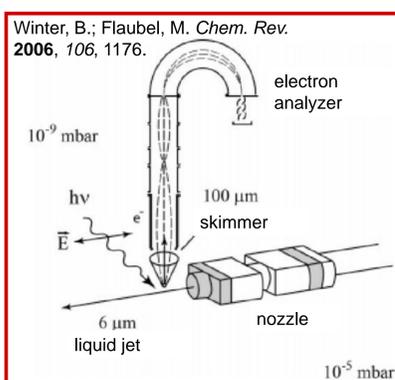
1. Motivation

- Phosphate is a significant structural building block of nucleotides and nucleic acids.
- Phosphate moiety is important in understanding the overall electronic structure of these biomolecules.
- Ionization energy is needed in assessing radiation damage and charge transfer in DNA.
- The ionization energies of the phosphate moiety and the aromatic bases of DNA are very close to each other.
- Phosphate is the dominant cellular buffer.
- Various protonation forms of phosphate can exist at different solution pH.
- Multiply charged phosphate ions are not stable in the gas phase with respect to spontaneous electron loss, hydration stabilizes them.
- Multiply charged ions do not exist as freely solvated species and there is substantial counter-ion association that is a strong function of ionic strength.

2. Experimental and theoretical methods

Photoelectron spectroscopy

of aqueous solutions using the microjet technique.

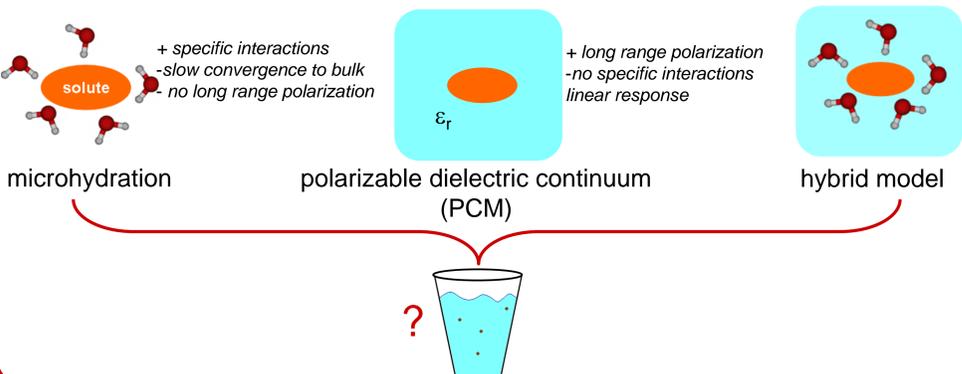


Ab initio calculations:

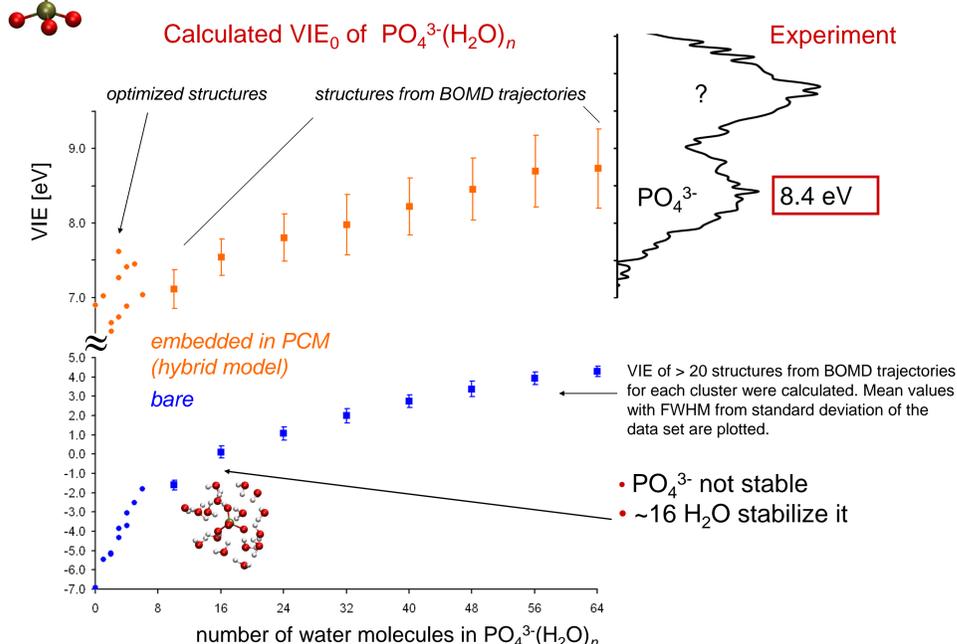
- Optimized structures of microhydrated anions (1-6 H₂O) at MP2/aug-cc-pVDZ level.
- Born-Oppenheimer molecular dynamics (BOMD) of Na⁺H_iPO₄⁽ⁱ⁻ⁱ⁻³⁾(H₂O)₆₄₋₈₃ for sampling geometries.
- “Carving out” clusters containing less water molecules from BOMD trajectories.
- Vertical IE of clusters (bare or embedded in polarizable dielectric continuum) at the DFT/BMK/6-31+g* level.
- Focused on the lowest ionization energy (IE).
- IE of tighter bound electrons = IE₀ + TDDFT excitation of ionized species.

3. Modeling of solvation

Ab initio calculations deal with individual molecules. Solution contains too many molecules to be treated explicitly ⇒ **compromises**

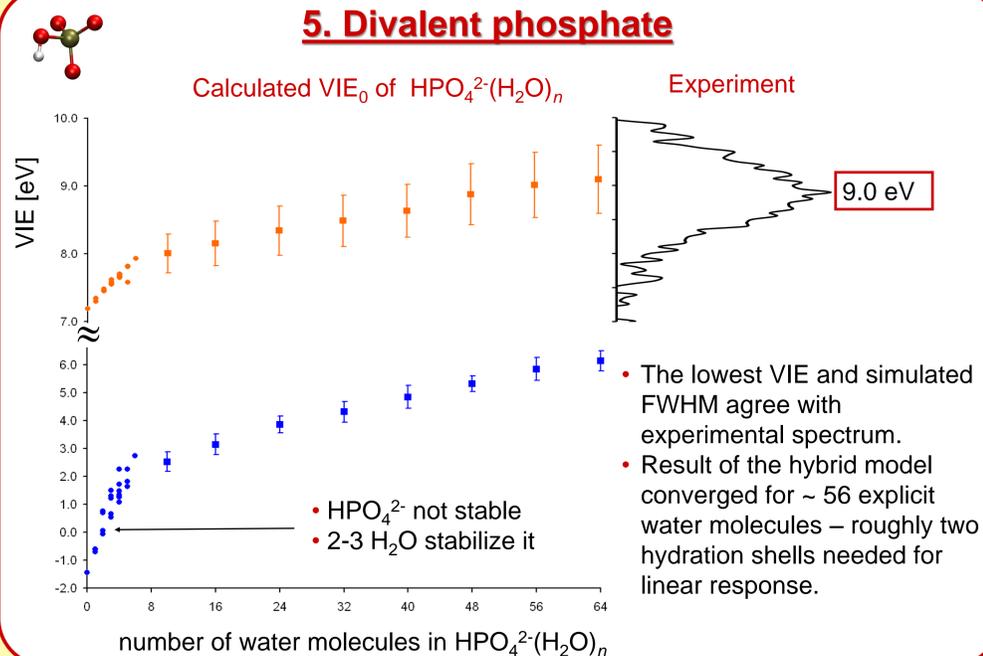


4. Trivalent phosphate



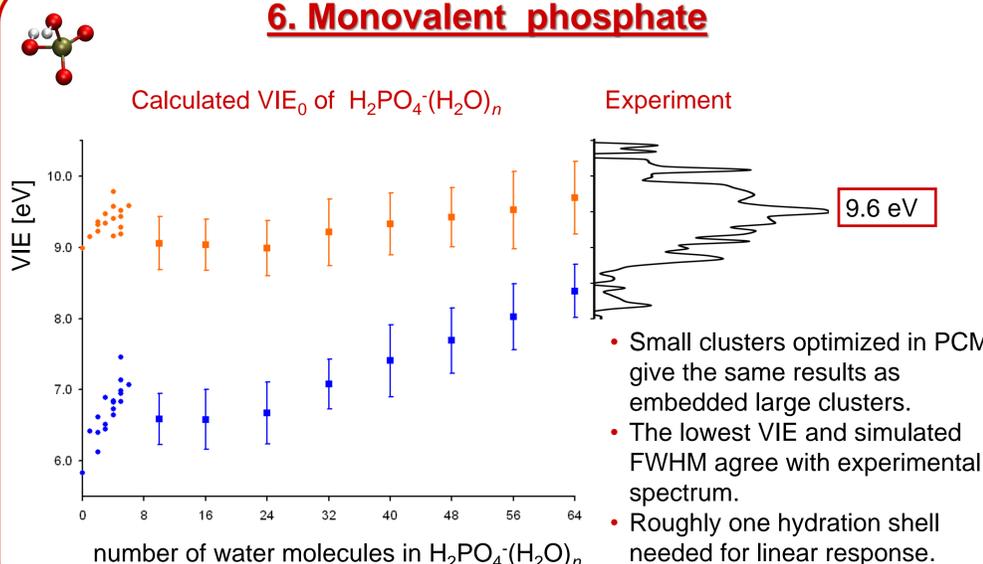
- The calculated value of the lowest VIE is slightly overestimated.
- Roughly two hydration shells are needed for linear response.
- The second peak probably due to ionization of tighter bound electrons, but cannot be proven because of limitation of TDDFT approach and hybrid model.

5. Divalent phosphate



- The lowest VIE and simulated FWHM agree with experimental spectrum.
- Result of the hybrid model converged for ~56 explicit water molecules – roughly two hydration shells needed for linear response.

6. Monovalent phosphate



- Small clusters optimized in PCM give the same results as embedded large clusters.
- The lowest VIE and simulated FWHM agree with experimental spectrum.
- Roughly one hydration shell needed for linear response.

7. Conclusions

- PO₄³⁻ and HPO₄²⁻ are not stable in the gas phase, about 16 water molecules are needed for stabilization of trivalent anion and 2-3 for divalent one.
- Employing a hybrid model, it is possible to establish, how many water molecules must be included explicitly so that the response of the rest of solvent to photoionization is in the linear regime. About two solvent shells are necessary for tri and divalent anions and about one for monovalent anion.

- VIEs of species present in measured solution: calculations employing hybrid model of solvation (1st row), experimental values for solution containing highlighted anion (2nd row).

PO ₄ ³⁻	NaPO ₄ ²⁻	Na ₂ PO ₄ ⁻	HPO ₄ ²⁻	NaHPO ₄ ⁻	H ₂ PO ₄ ⁻
8.7	8.6	8.7	9.0	9.0	9.7
	8.4		9.0		9.6

- Protonation (i.e. formation of covalent bond between H⁺ and the anion) increases the VIE of phosphate anion, while ion pairing with Na⁺ does not influence it due to the screening effect of water.
- Photoelectron spectroscopy is insensitive to ion pairing.
- Ionization energies of aqueous multivalent phosphate ions calculated within hybrid model are in a reasonable agreement with experimental results.

References

- Wang, X. B.; Wang, L. S. *Ann. Rev. Phys. Chem.* **2009**, *60*, 105.
- Winter, B.; Flaubel, M. *Chem. Rev.* **2006**, *106*, 1176.

Acknowledgements

