Ionization of nucleic acid components: From the gas phase to the aqueous environment

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1. Motivation

- All molecules within the cell can be ionized by highly energetic radiation.
- Aqueous DNA is damaged in several ways: ionized base, sugar, strand breaks, DNA-protein crosslinks.
- Electron can be ejected by various mechanisms.
- Resulting radical cation – "hole" migrates along the helix.
- The hole usually ends up on guanine.
- For understanding of the charge mobility vertical and adiabatic ionization potentials of each of the nucleic acid component within realistic environment (in solution) are needed.

2. Experimental and theoretical methods

- Photoelectron spectroscopy of aqueous solutions became possible recently using microjet technique.
- Calculations of ionization potentials of nucleic acid components
  - Monobasic phosphate group in the gas phase decreases the lowest VIP by 1.3 eV.
  - Calculated VIP of PnO)4n is excitation to SOMO + IP of the non-ionized particle.
- Optimized structures of guanine tautomers, adenine, conformers of nucleosides and nucleotides, microhydrated bases (1-6 H2O).
- Calculations of ionization potentials of phosphate anions
  - Focused on the lowest IP.
  - Optimized structures of microhydrated anions (1-6 H2O).
  - Born-Oppenheimer molecular dynamics of HPO42- (H2O)6 for sampling geometries.
  - "Cutting" cluster containing less water molecules.
  - Vertical IP of clusters (bare or embedded in dielectric continuum) at the DFT/BMKS-31+g* level.

3. Modeling of solvation

Ab initio calculations deal with individual molecules. Solution contains too many molecules to be treated explicitly. Compromises include:
- Microhydration
- Microhydrated dielectric continuum (PCM)
- Hybrid model

Further reading

4. Modeling of photoionization - guanine

- Addition of sugar to the gaseous base does not change the lowest VIP. It increases the intensity in the higher binding energy region.
- Monobasic phosphate group in the gas phase decreases the lowest VIP by 2-3 eV depending on the conformer. Spectrum changes dramatically.
- In solution, monobasic phosphate group almost does not affect the lowest VIP.
- Photoelectron spectrum of complex compounds can be decomposed into contributions of its constituents due to the screening effect of the solvent.
- Differences between conformers become less pronounced upon solvation.

5. Photoelectron spectra of aqueous nucleotides

- Experimental and modelled PE spectra agree in the onset, the position of the maximum of modelled spectrum is underestimated by 0.5 - 1 eV.
- The lowest VIP is separated from others by 1 eV.
- Similar conclusions as for pyrimidines. Guanine compounds have the lowest IPs.

6. Monovalent phosphate

- Calculated VIP of HPO42- (H2O)6
- Small clusters optimized in PCM give the same results as embedded large clusters.
- The lowest VIP and simulated FWHM agree with experimental spectrum.
- Roughly one hydration shell needed for linear response.

7. Divalent phosphate

- Experimental spectrum of aqueous HPO42-
- The lowest VIP and simulated FWHM agree with experimental spectrum.
- Roughtly two hydration shells needed for linear response.

8. Trivalent phosphate

- Calculated VIP of PO43- (H2O)6
- The lowest VIP is slightly overestimated.
- Roughly 2 hydration shells needed for linear response.

9. Conclusions

- The effect of water on photoinization of neutral molecules is described well by PCM. For monovalent anions – one and for multivalent anions – two explicit hydration shells are needed to achieve linear response.
- Water increases IP of anions and decreases IP of neutral and cations in comparison to the gas phase.
- Water screens the interactions. It allows for decomposition of the PE spectra of nucleotides into contributions of its constituents and diminishes the influence of ion pairing.

10. Future work

- Interpret the second peak of solution containing PO43-.
- Calculate VIPs of tighter bound electrons in aqueous phosphates.
- Study larger systems, e.g. guanine tetradec, dinucleotides.

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