

SOLVENT-INDUCED STABILITY OF THE BENZENE RADICAL ANION

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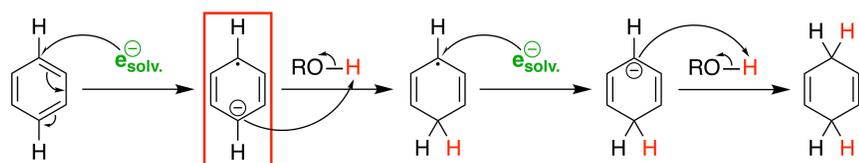
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INTRODUCTION

Benzene radical anion is a negatively charged species occurring as the first intermediate of the **Birch reduction of benzene** where benzene is converted into 1,4-cyclohexadiene in presence of **solvated electrons** and a proton source in **liquid ammonia**.

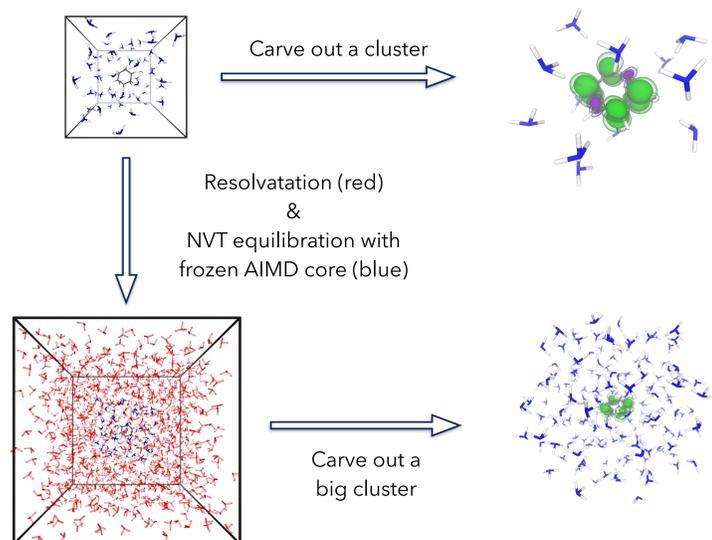


Beyond organic chemistry, the benzene radical anion has many intriguing properties from the point of view **physical** and **theoretical chemistry**.

- It was found to be a **meta-stable shape resonance in the gas phase** both experimentally [1] and computationally [2], however, recent *ab initio* molecular dynamics (AIMD) study and various spectroscopic measurements point to stability in solution [3].
- High level of theory is necessary due to its **non-trivial and diffuse electronic structure**.
- Here, a continuation of our previous work is presented and we address a detailed insight into the problem of **electronic stabilization** by solvent explicitly via **microsolvated clusters** and answer to these following questions:

1. **How many ammonia molecules stabilize the benzene radical anion?**
2. **What is the binding energy in the bulk liquid?**

METHODOLOGY & COMPUTATIONAL ASPECTS



Microsolvated clusters are prepared by **carving spherical subsystems** out of the simulation box by two approaches:

- Directly from the **AIMD bulk structures**.
- Method of **resolvation** in order to achieve larger cluster sizes beyond the original AIMD box.
- Every cluster size is sampled by 50 decorrelated thermal structures to provide converged statistics.
- Bulk liquid environment is represented by **non-equilibrium polarizable continuum model (PCM)** applied on the same clusters as in the gas phase.
- Once the microsolvated clusters are obtained, the **vertical binding energy** is calculated as a difference between the ground state energy of the anion (E_A) and

the neutral structure (E_N) at the geometry of the anion as

$$BE = E_A - E_N |_{\Delta(R)=0}$$

- For both the gas-phase and the PCM calculations, the reliable **revPBE0-D3** hybrid density functional together with **def2-TZVP** basis set was employed to calculate the binding energies.
- Individually, expenses per calculation vary **from minute to a few hundreds of core hours**.
- For larger systems, **memory demands** become the limiting parameter rather than the CPU time.
- To obtain statistically converged result, every system size needs to be **well sampled** which rises the expenses by order of the magnitude.

RESULTS

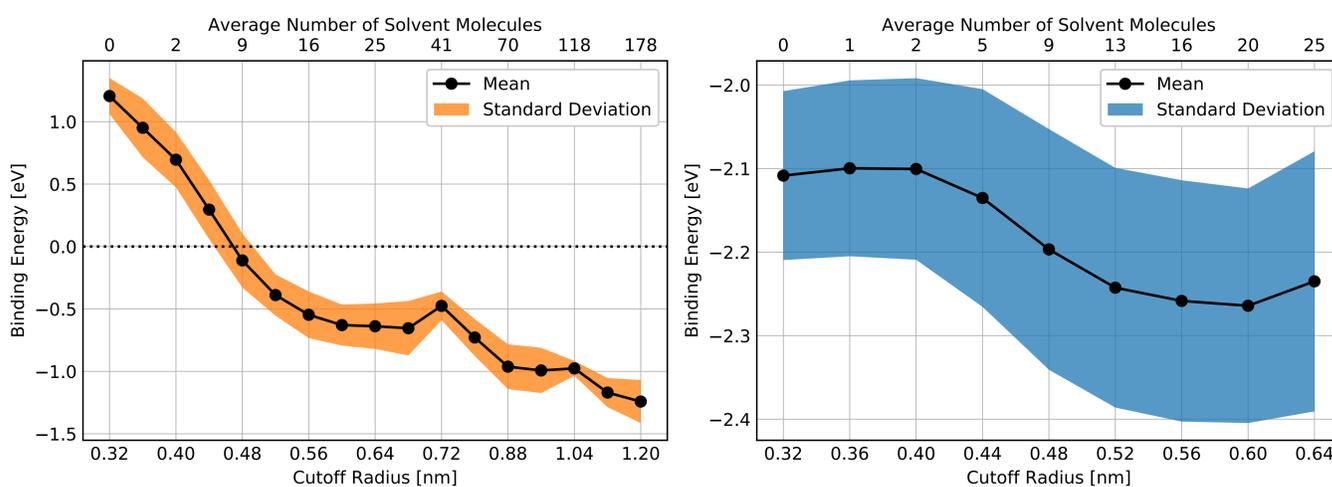


Figure: Convergence of the binding energy in the gas phase (left) and in the PCM (right)

We relate the binding energy of the excess electron and the size of the microsolvated cluster.

- In the gas phase we explicitly show the **transition** from the meta-stable state (positive binding energy) into the **electronically bound state**.

- Although the transition takes place within the first solvation shell, the absolute value of the binding energy converges slowly toward the bulk, where the value obtained from the PCM is **-2.2 eV**.

CONCLUSIONS

- Gas-phase calculations **bridge** the observation of the meta-stable state of the benzene radical anion in the gas phase and the bound state in solution.
- **10 ammonia molecules** are sufficient to stabilize the species, however, very large amount of solvent is needed to converge to the bulk properties.
- Convergence toward the bulk can be speeded up by employing the PCM resulting into the value of **-2.2eV**.
- The binding energy in bulk should be accessible experimentally by the **X-ray photoelectron spectroscopy of liquids** [4] and we are preparing the synchrotron measurement for spring 2021.

[1] Sanche L. Schulz G. J. *J. Chem. Phys.* 58, **1973**

[2] Bazante A. P et al. *J. Chem. Phys.* 148, **2015**

[3] Březina K. et. al. *J. Phys. Chem. Lett.* 11, **2020**

[4] Buttersack T. et al. *Science* 368, **2020**