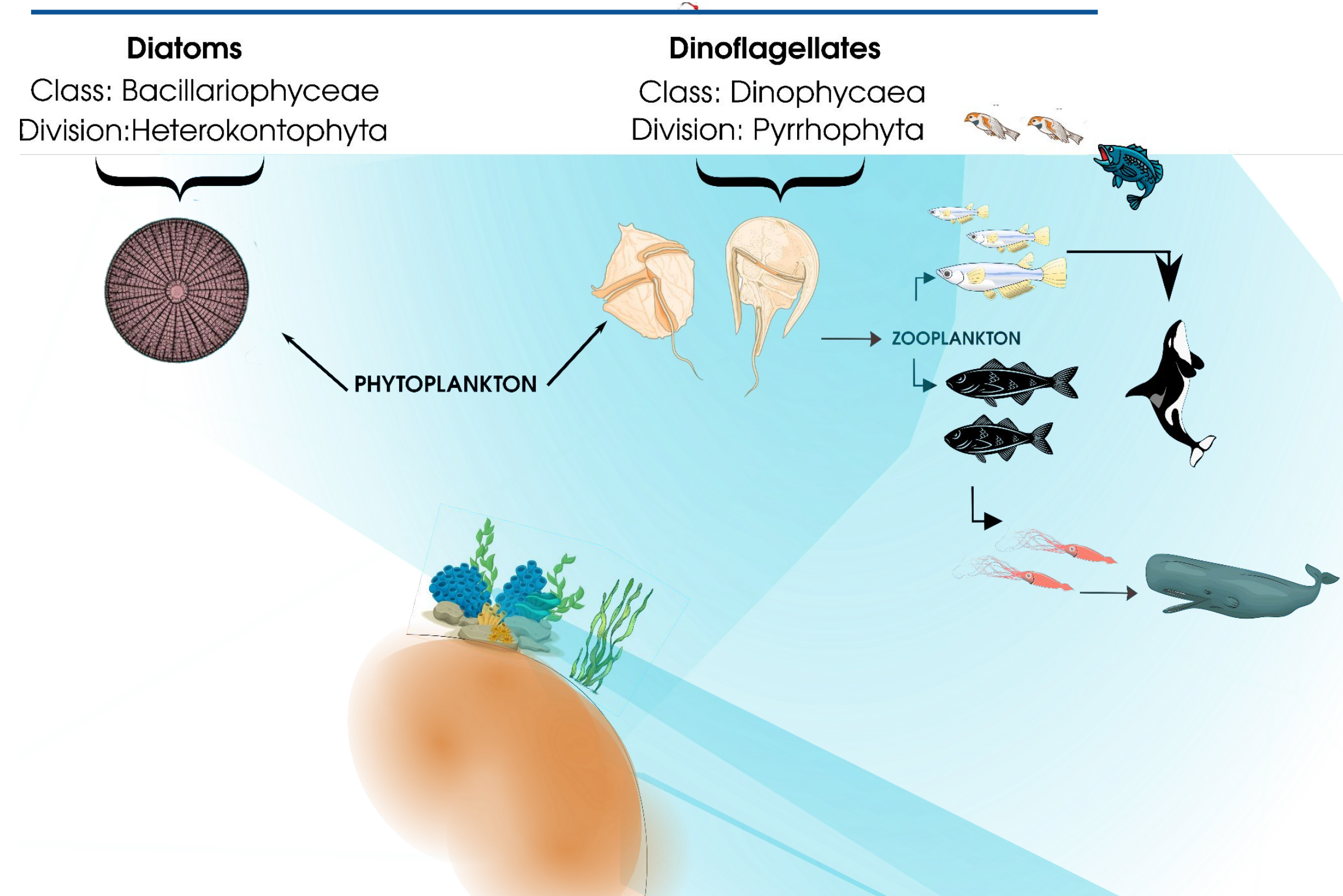


## Proton and Cation Affinities of Biosignature phytoplankton pigments and MALDI matrices from RI-MP2 quantum calculations

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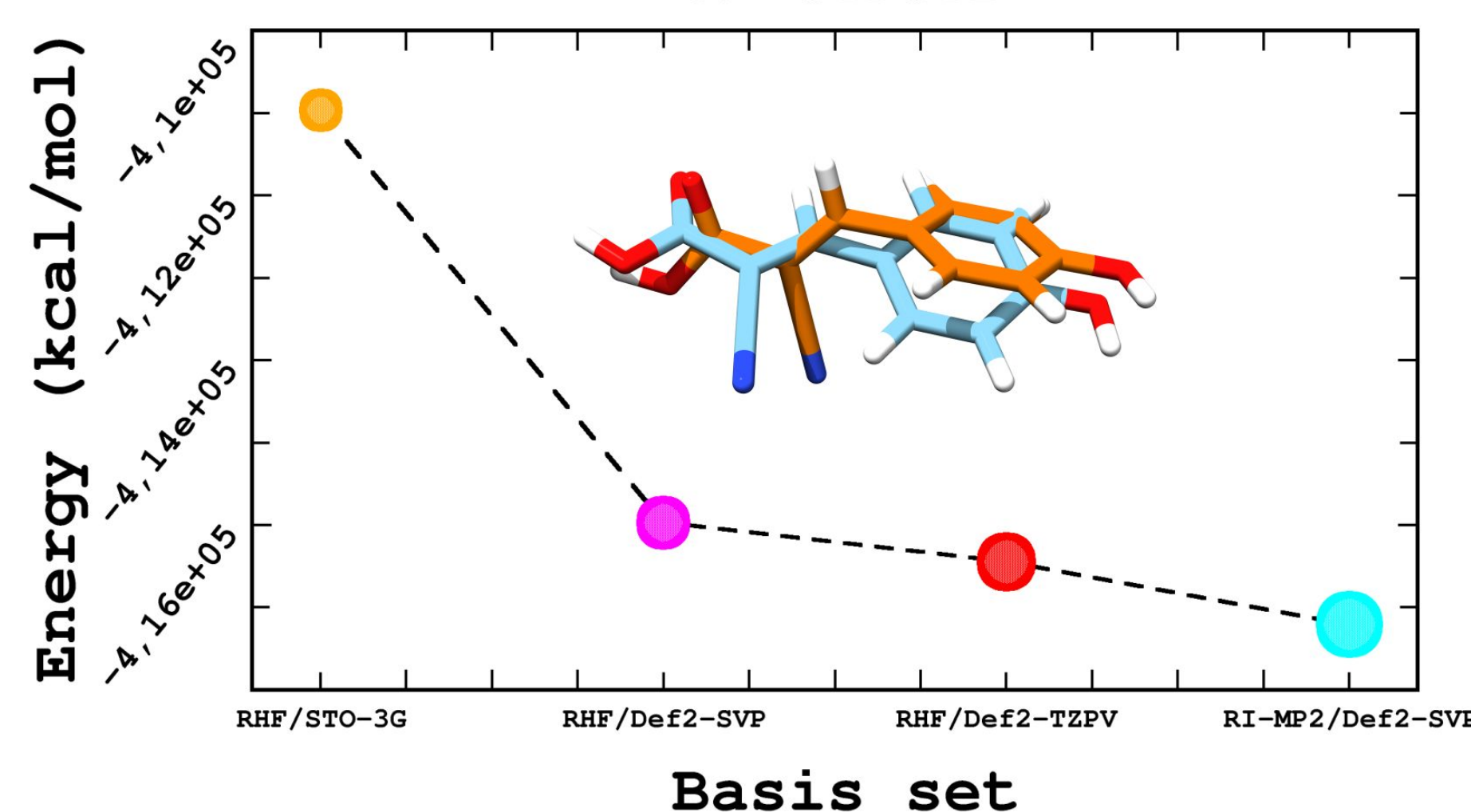
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### Aquatic Ecosystem



### Geometry Optimization

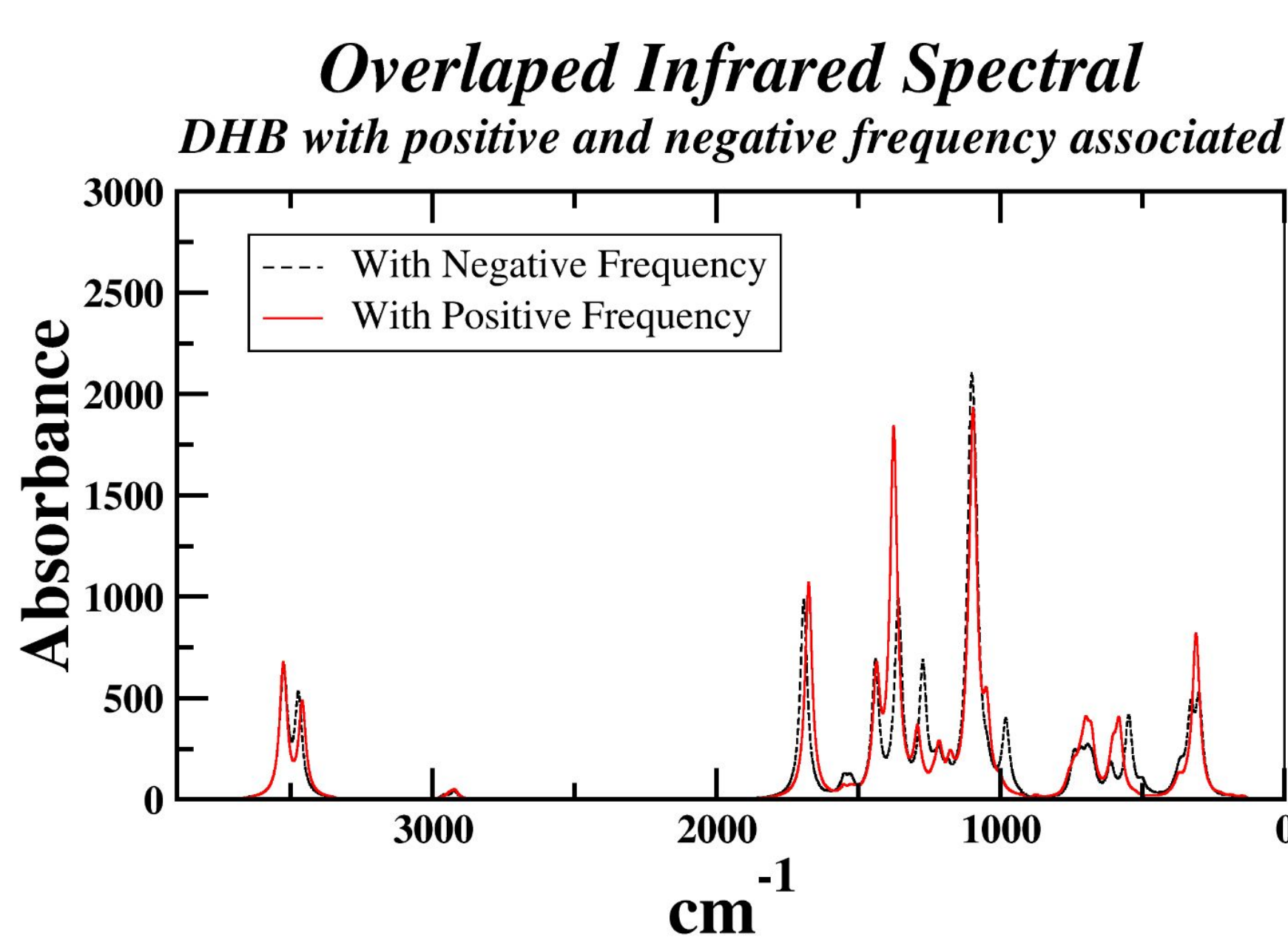
#### Single Point Energy vs Basis set $\alpha$ -CHCA



#### Optimization

Method: RI-MP2  
Basis set: Def2-TZVP  
ETol: 1E-08 a.u.

### Vibrational Frequency



Method: RI-MP2  
Basis set: Def2-TZVP  
Grapher: XMGRACE

Avoiding negative frequencies and comparing the IR spectral

The overlapped experimental and calculated IR have good agreement

### Proton Enthalpy Reaction

$$PA = -\Delta E_{Ele}^o - \Delta ZPE + 5/2RT \rightarrow \text{Absolute Temperature}$$

Electronic Energy Protonated - Ground

Gas Constant

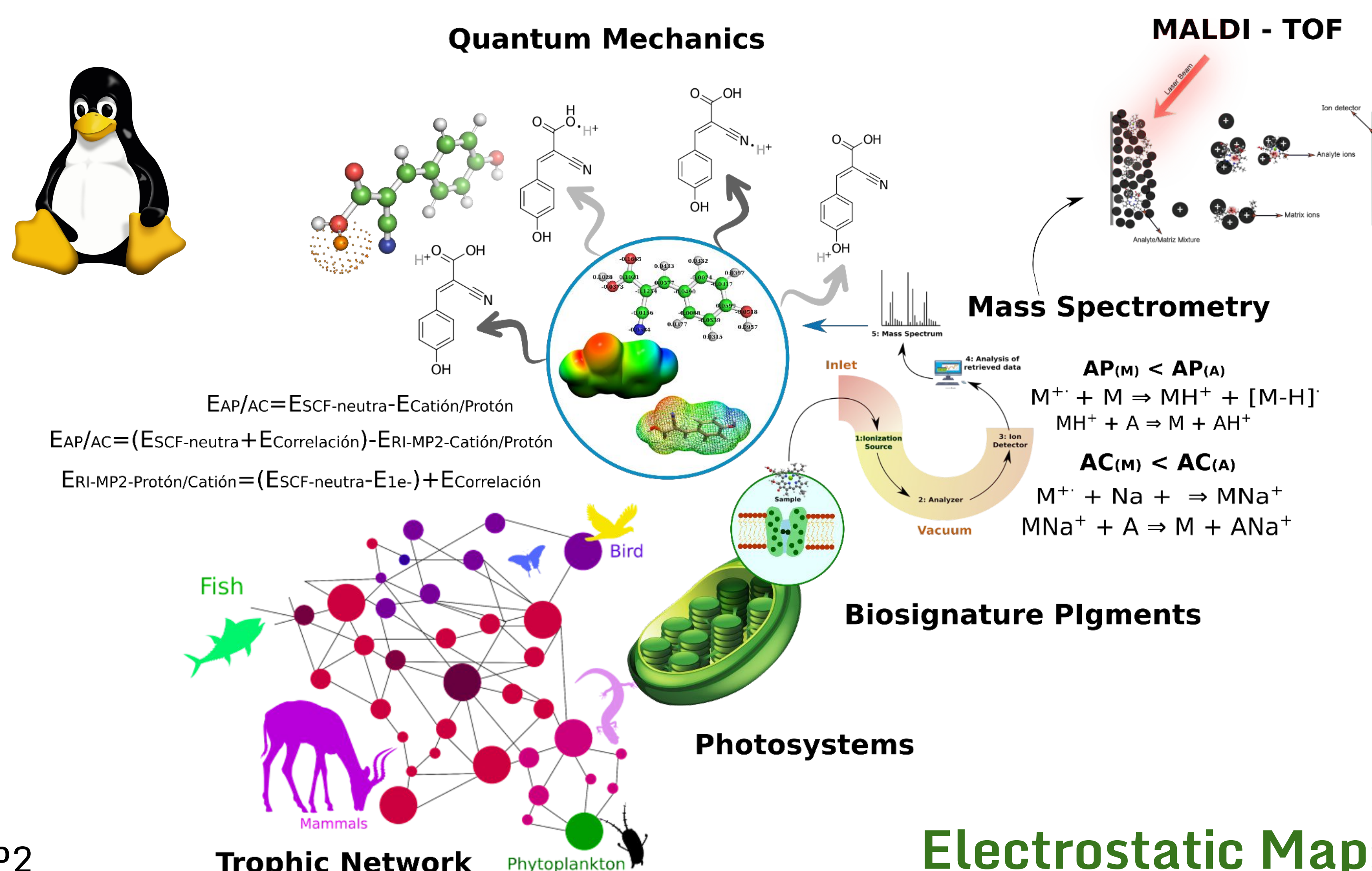
Zero Point Energy Protonated - Ground

### References

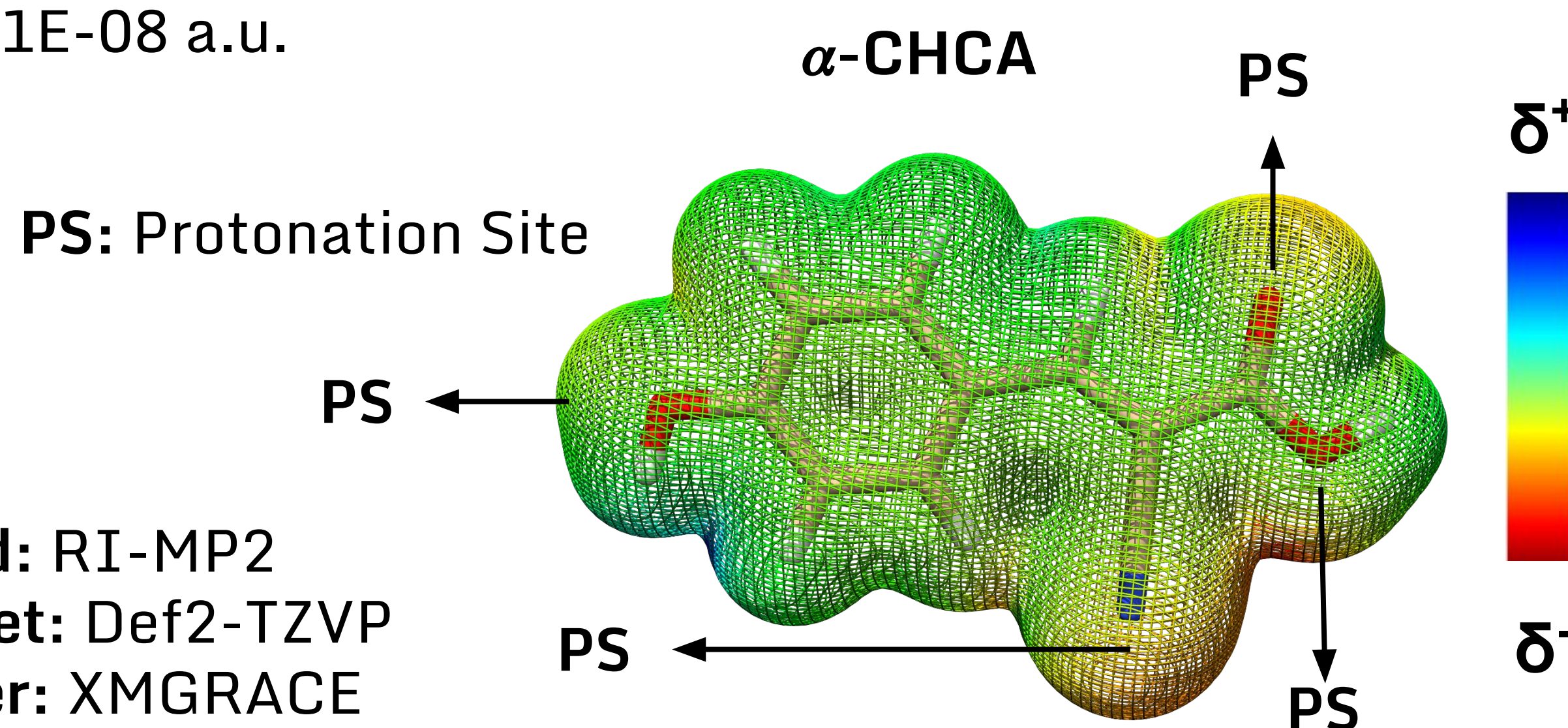
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Phytoplankton is a bioindicator useful to measure environmental health. Pigment-Biosignature compounds detection for these organisms by MALDI MS, allows its chemotaxonomic identification. Feasible MALDI matrices with thermochemical features (Proton/Cation Affinities -PA/CA- and Ionization Energies - $E_i$ -) guarantees a satisfactory ionization process. So, to establish these properties is a topical issue. We used quantum chemical methods (HF and Pos-HF) to calculate PA/CA energies of MALDI matrices and biosignature pigments.

### MALDI MS and Proton/Cation matrices



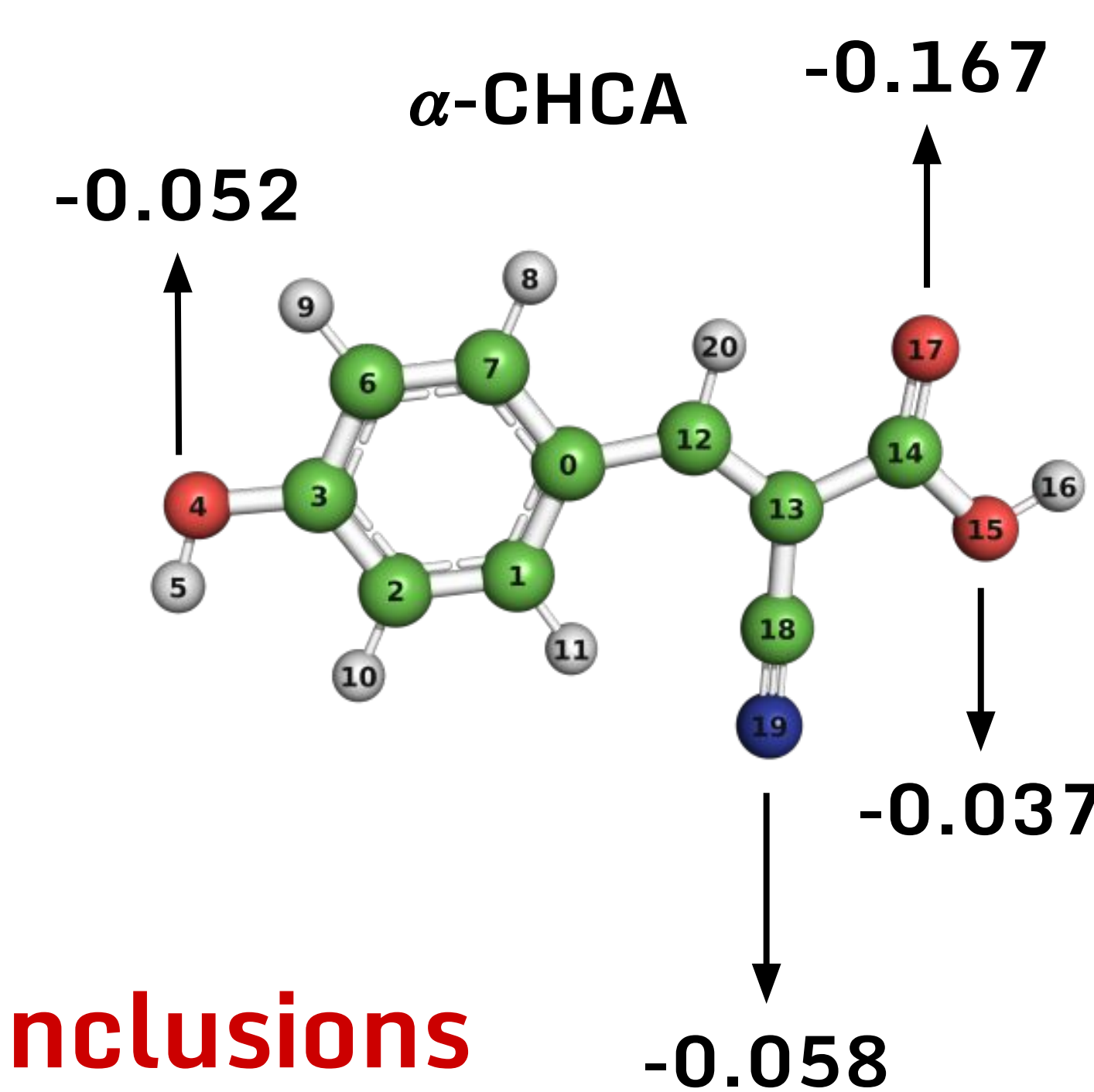
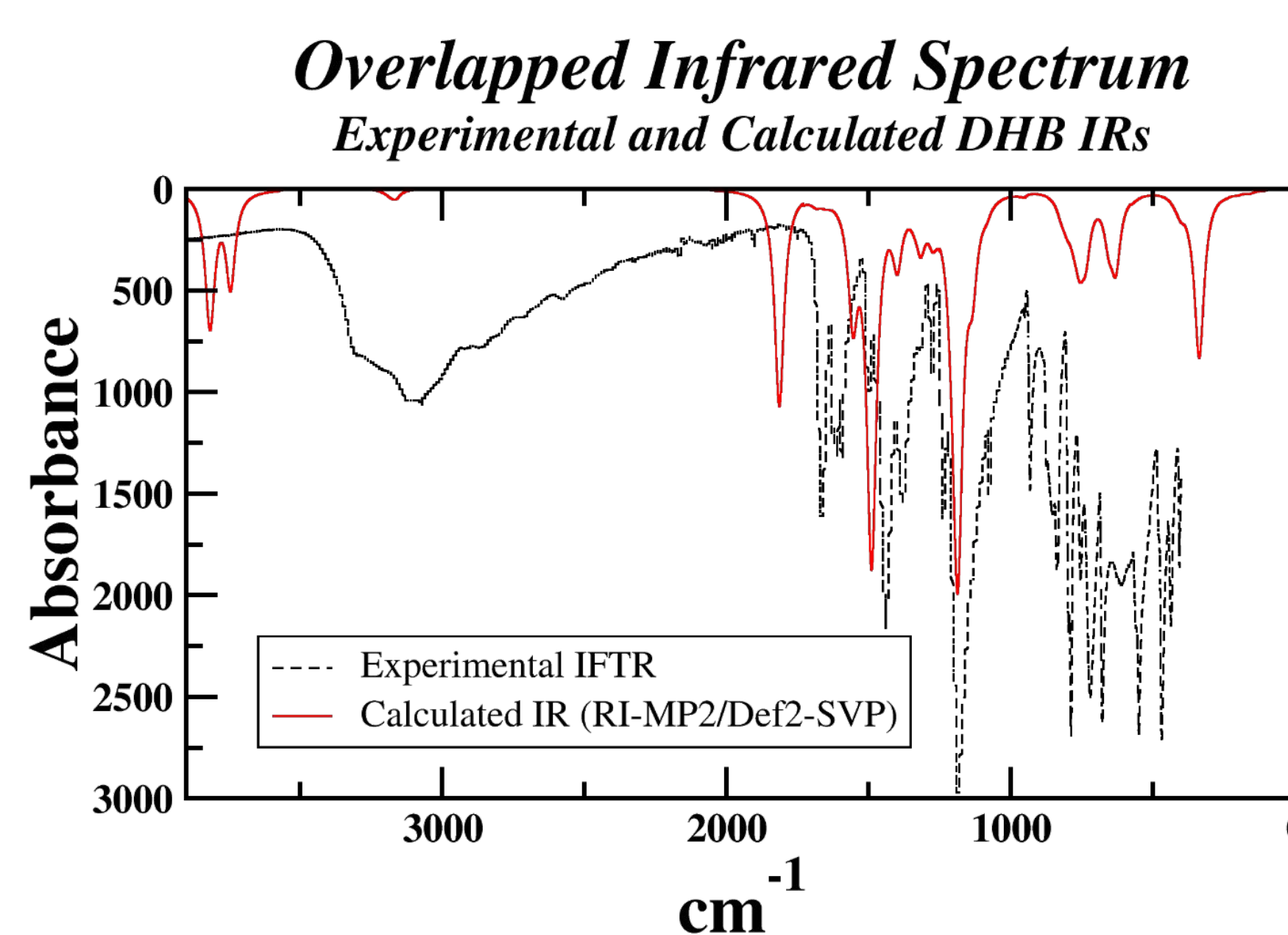
### Electrostatic Maps



MEP maps  
Method: RI-MP2  
Basis set: Def2-SVP  
IsoValue: 0.004



### Löwding Charge Analysis



### Conclusions

Geometry Setup protocol is feasible for our systems, and IR spectra are in agreement with experimental reports. From MEP it would be ideal to perform a Löwding population analysis for determining the protonation sites and associated charge. Next step is to optimize and calculate the SPE to build cation-structures.



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