

Anomalies in the Process of Ionization of Analytes in MALDI Electronic Transfer Vs. Proton Transfer Via Quantum Chemistry

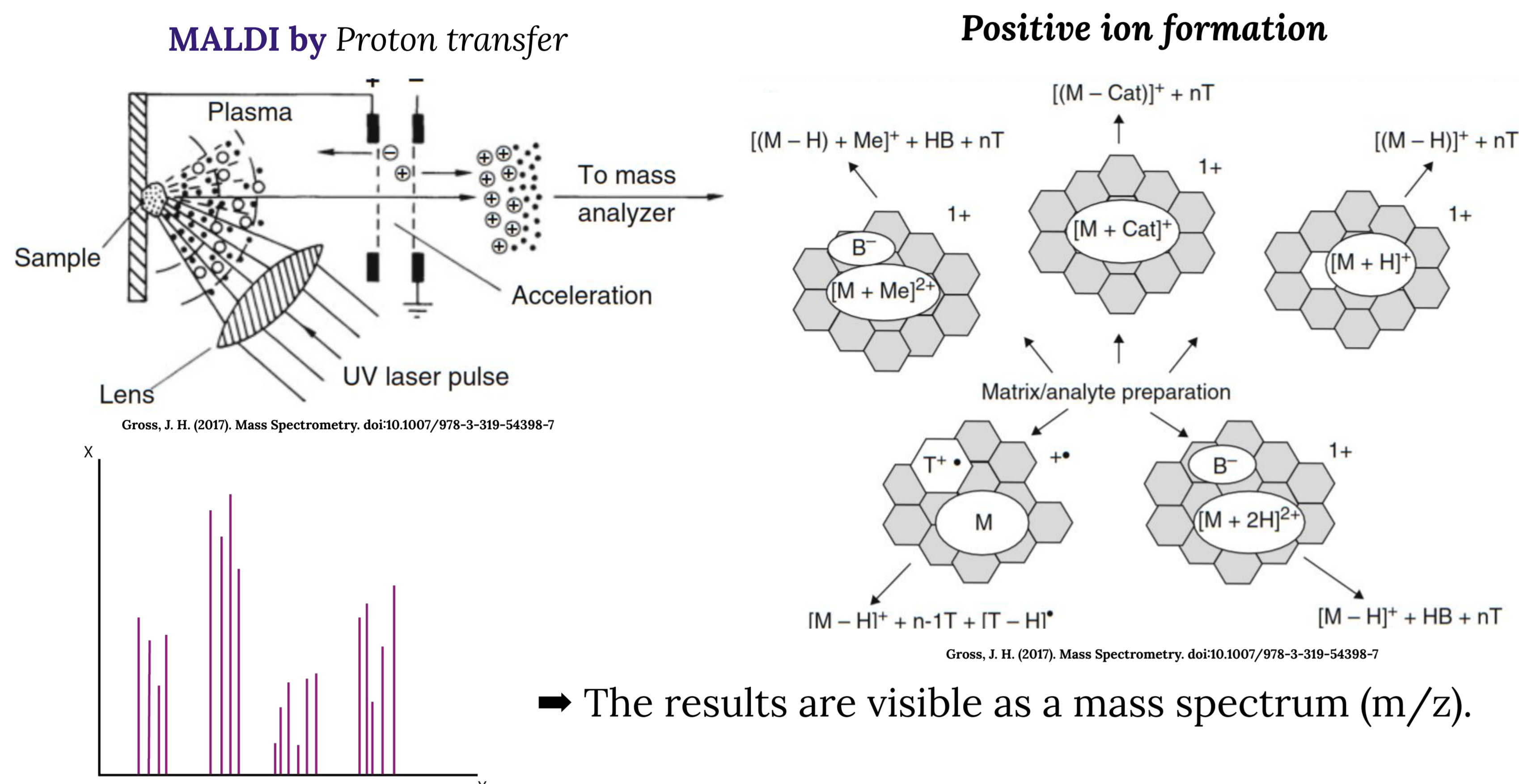
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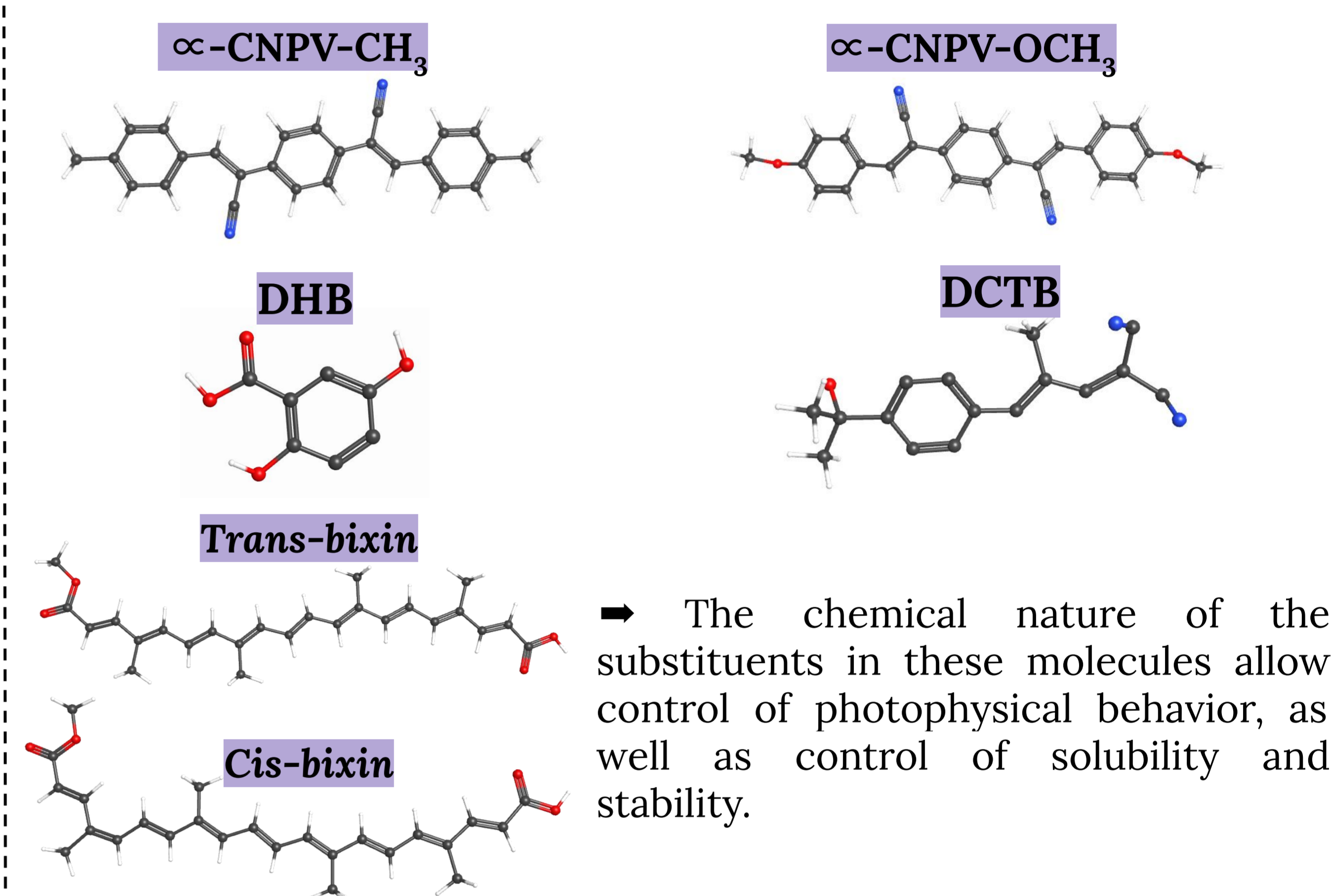
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Matrix-Assisted Laser Ionization/Desorption (MALDI) makes possible to ionize any target molecule (with low or high molecular weight and/or with low or high concentration) indirectly, mediated by analyte interaction with an organic compound that serves as a matrix. The FisicoQuímica Teórica y Experimental (GIFTEX) Research Group of the Universidad Industrial de Santander (UIS) have been working for years on the development of MALDI matrices for the analysis of a broad spectrum of chemical species. Matrixes developed by GIFTEX-RG, such as α -cyanophenylenevinylene (α -CNFV), are suggested as better analytical medators than commercial matrixes, such as DCTB. Therefore, we propose the use of mechano-quantum methods to calculate physical-chemical parameters of the compounds involved in the study (matrixes and analytes) to evaluate CNFV as possible Proton Transfer (PT) matrixes. The first step is to obtain the geometries of matrix and analyte structures, followed by geometry optimization, using the quantum chemistry software ORCA, both in neutral and protonic chemical state. Geometry optimizations will be performed using *ab initio* (RHF/6-311G(2d,2p)) and DFT (B3LYP/6-311G(2d,2p)) theory levels. Later on, the system energy and the most favorable protonation site will be evaluated. Calculations will be performed in gaseous phase, subtracting the energy difference between the neutral optimised structure and the protonate optimised structure. The results will be analyzed to explain the anomalous protonation of analytes using electron transfer matrixes.

Matrix-Assisted Laser Desorption/Ionization (MALDI)



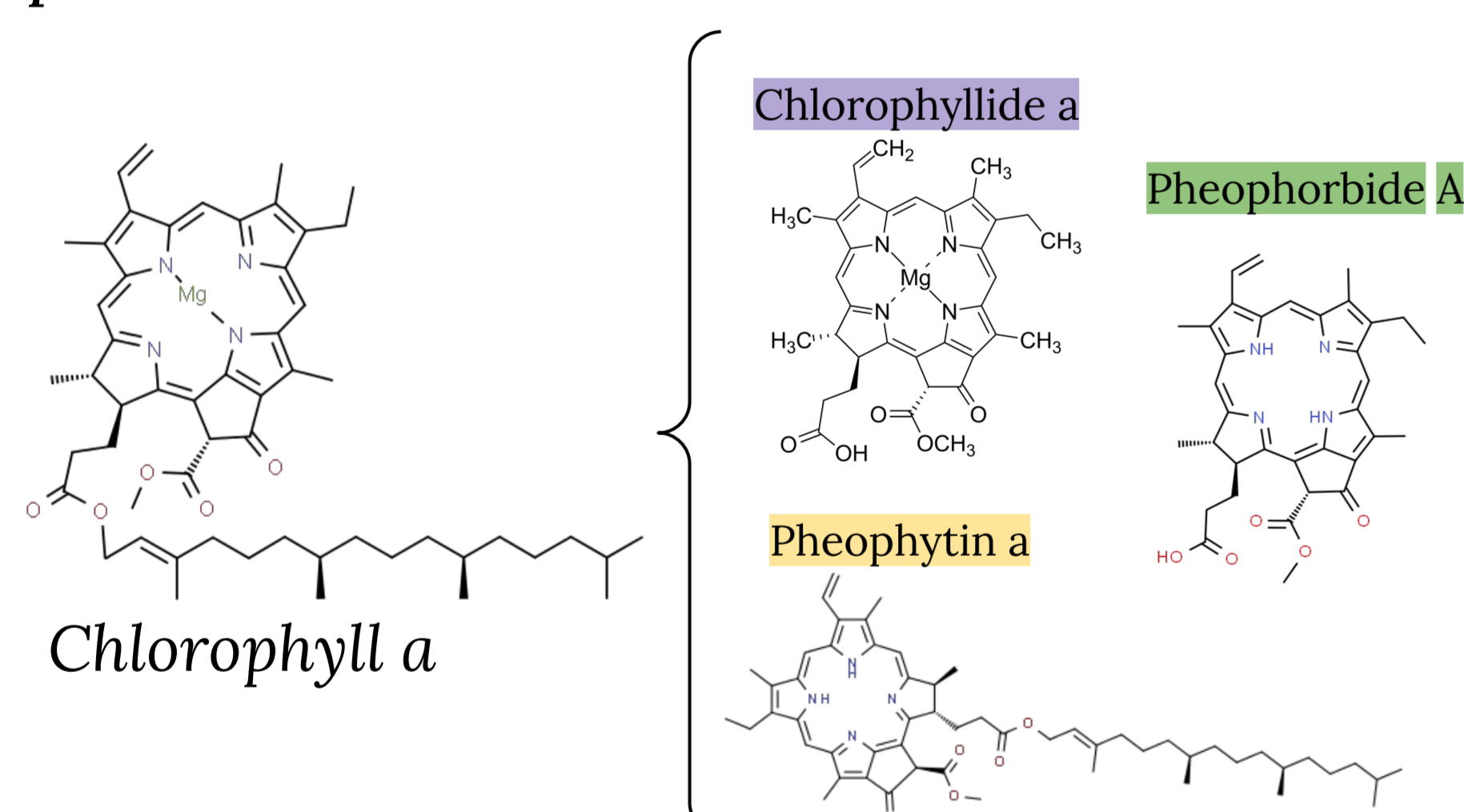
α -Phenylenevinylene (α -CNPV-): Electron Transfer (ET) Matrixes



Methodology: Quantum Calculations

Comp. Chem. calculation: Protonic Affinities (PA)

Molecular Structures → Analytes: Phytoplankton pigments and their protonated derivatives



Proton Affinity (PA) calculation → Hoppilliard y Bourcier

FUNCTIONAL DENSITY		
Basis sets	6-31 + G (d, p)	6-311 + G (2d, 2p)

$$PA = -\Delta H = -(\Delta E + \Delta nRT), \Delta n = -1$$

$$\Delta E = [E_T(MH^+) - E_T(M)] + [ZPVE(MH^+) - ZPVE(M)] - 3/2RT$$

$$PA = -(\Delta E_T + \Delta ZPVE - 5/2RT)$$

Geometric optimizations → Methods

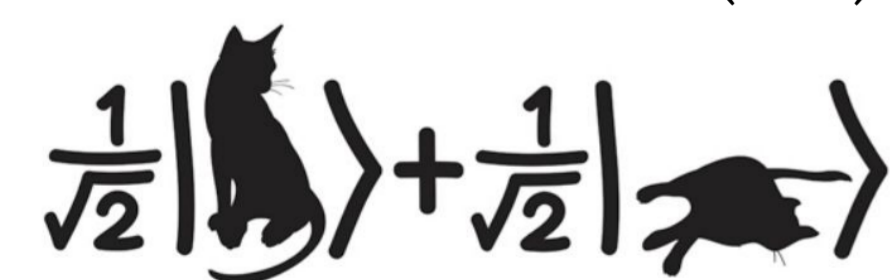
Low levels of theory

→ Hartree-Fock (HF)

Precise levels of theory

→ Møller Plesset (MP)

→ Coupled-Cluster (CC)



$$H_e(r;R)\Psi_e(r;R) = E_e(R)\Psi_e(r;R)$$

$$[T_e + V_{e-e} - V_{n-e}]\Psi_e(r;R) = E_e(R)\Psi_e(r;R)$$

HPC Resources



Main Software



.sh file (script)

```
#!/bin/bash
#PBS -l nodes=1:ppn=24 *to specify the number of nodes and ppn
#PBS -l walltime=00:00:00 *to specify the job elapsed time
#PBS -M correo@correo.com *email to sent the job results
#PBS -l mem=XXgb *to specify, in GB, the RAM memory request
```

Reported Empirical Data

PROPERTIES: MOLECULES TARGET		
Molecules	pka (Strongest Basic)	pkb (Strongest Acidic)
Chlorophyll a	6.92	-1.2
Pheophytin a	7.24	-0.71
Pheophorbide A	6.92	-1.2
β -Carotene	-4.3	UNKNOW
Lutein	-0.91	18.22

$$pH = pka + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pKa = -\log Ka$$

Theoretical value: proton affinity (PA)	
DHB (neutral)	852.9 kJmol ⁻¹
DCTB	UNKNOW
Bixine	UNKNOW
α -CNPV-OCH ₃	UNKNOW
α -CNPV-CH ₃	UNKNOW
Chlorophyll a	UNKNOW
Carotenoids	UNKNOW

Bibliography

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