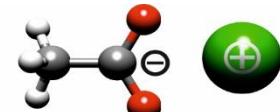
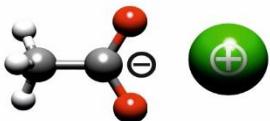


Spectroscopie de paires d'ions isolées

Eric Gloaguen

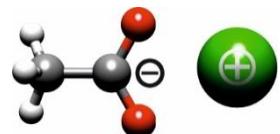


Groupe Structures Biomoléculaires
LIDYL UMR 9222 (CEA-CNRS)
Université Paris-Saclay



Séminaire ISMO
Orsay, 10 septembre 2019

Gas phase



Motivations:

- Explore a class of molecular objects poorly documented in the gas phase
- Document the intrinsic properties of supramolecular objects typically found in condensed phase, but poorly known



Condensed phase (ion pairs, mainly neutral)

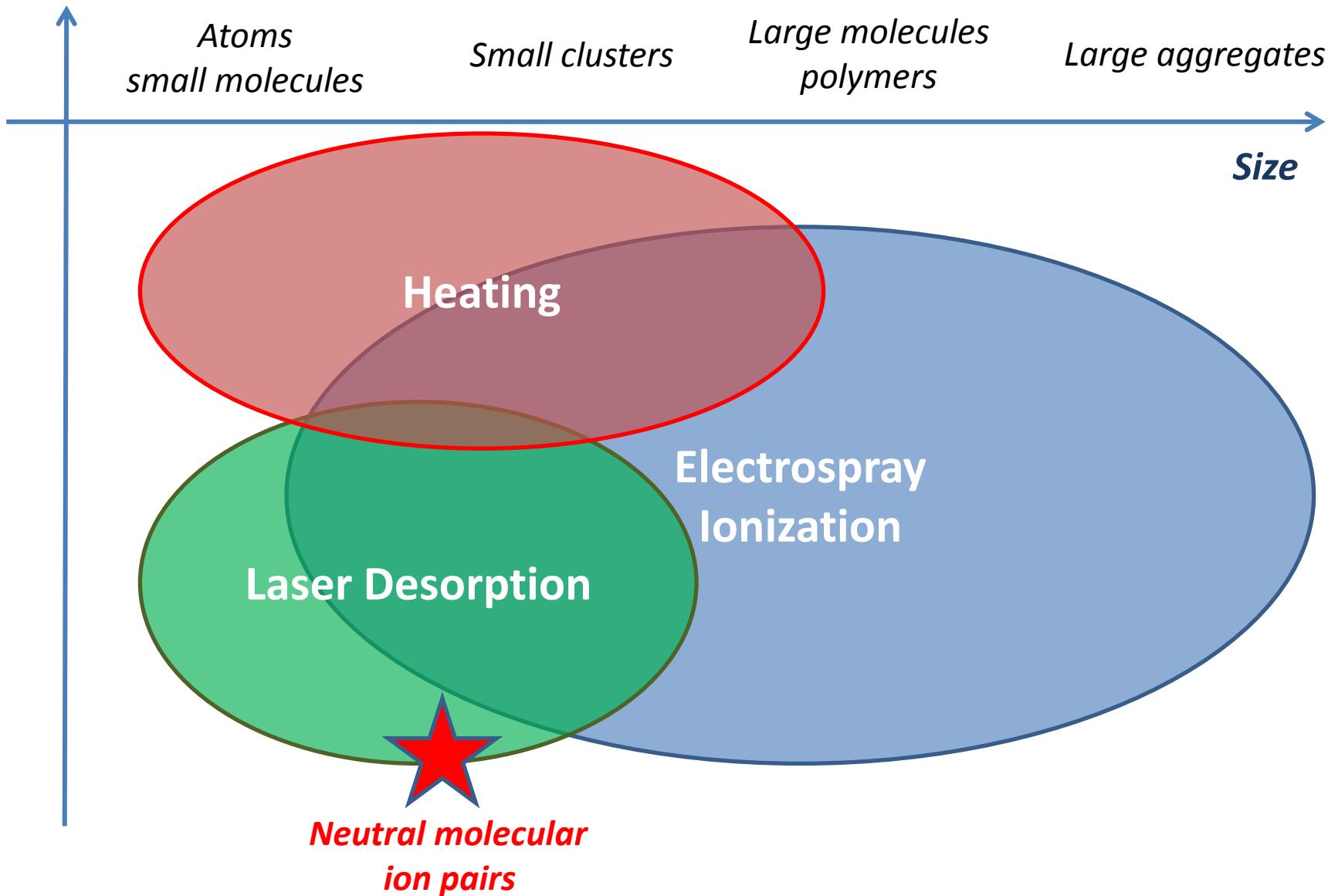
- Electrolytes (sea water, biological media, batteries)
- Ionic liquids (solvent)
- Aerosol particles (atmosphere)
- Cristallization/precipitation
- Viscosity
- Particle nucleation

Issues:

- Very hard to detect: ion pair type distributions are often unknown
- Poor structural characterization

Neutral ion pairs in the gas phase: a frontier of science

Volatility



Neutral ion pairs in the gas phase

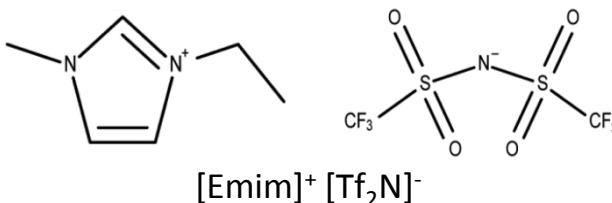
Alkali Halides
(Heating)

- Microwave spectroscopy
- Matrix isolation spectroscopy
- Laser spectroscopy in molecular jet

Groen Kovacs *Vibrational spectroscopy* (2010)
Dedonder-Lardeux, Grégoire, Jouvet,
Martrenchard, Solgadi *Chemical Review* (2000)

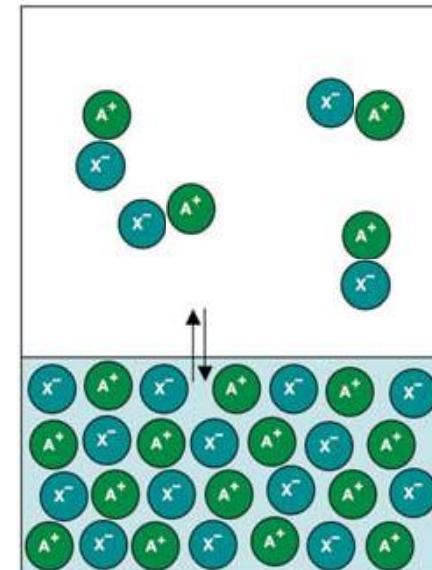
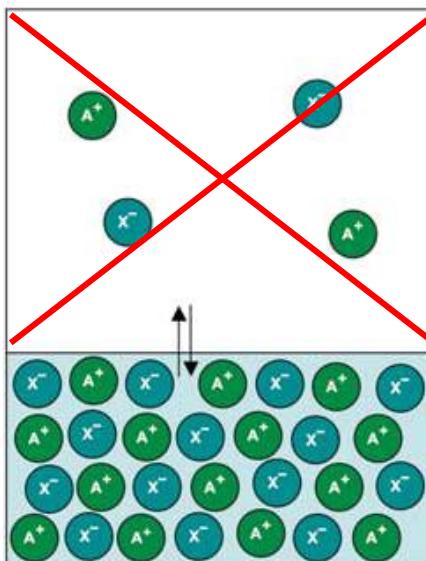
Ionic liquid

(Distillation at 300°C under reduced pressure)



Earle, Esperança, Gilea, Canongia Lopes, Rebelo,
Magee, Seddon, Widegren *Nature* (2006)

- Photoelectron spectroscopy
Strasser, Goulay, Kelkar, Maginn, Leone JPCA (2007)
- He droplet IR spectroscopy
Obi, Leavitt, Raston, Moradi, Flynn, Vaghjiani, Boatz, Chambreau, Douberly JPCA (2013)
- Double resonance IR/UV spectroscopy
Cooper, Zolot, Boatz, Sporleder, Stearns JPCA (2013)



I. Molecular folding
of isolated ion pairs

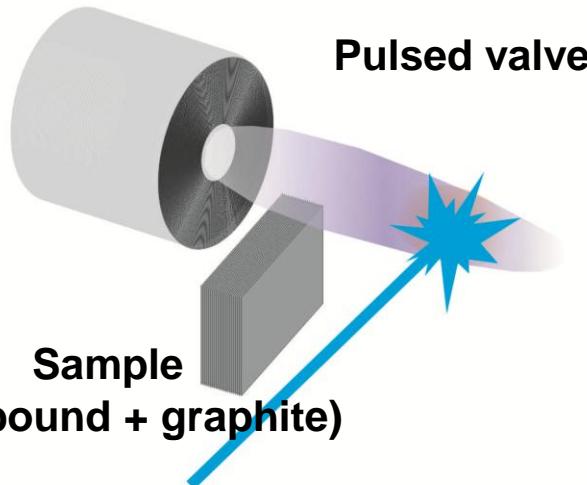
III. Stark spectroscopy
at very high electric
field using ion pairs

II. Characterization of
ion pairs in solution
assisted by gas phase
spectroscopy



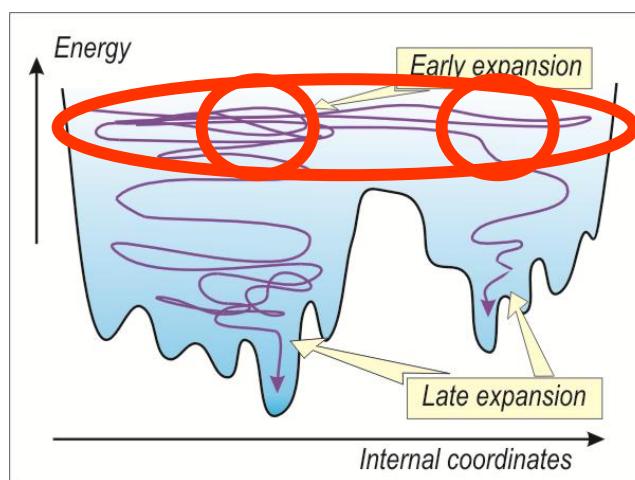
I. Gas phase experiment

Vacuum chamber



Sample preparation: compound mixed with graphite, and pressed into a solid pellet

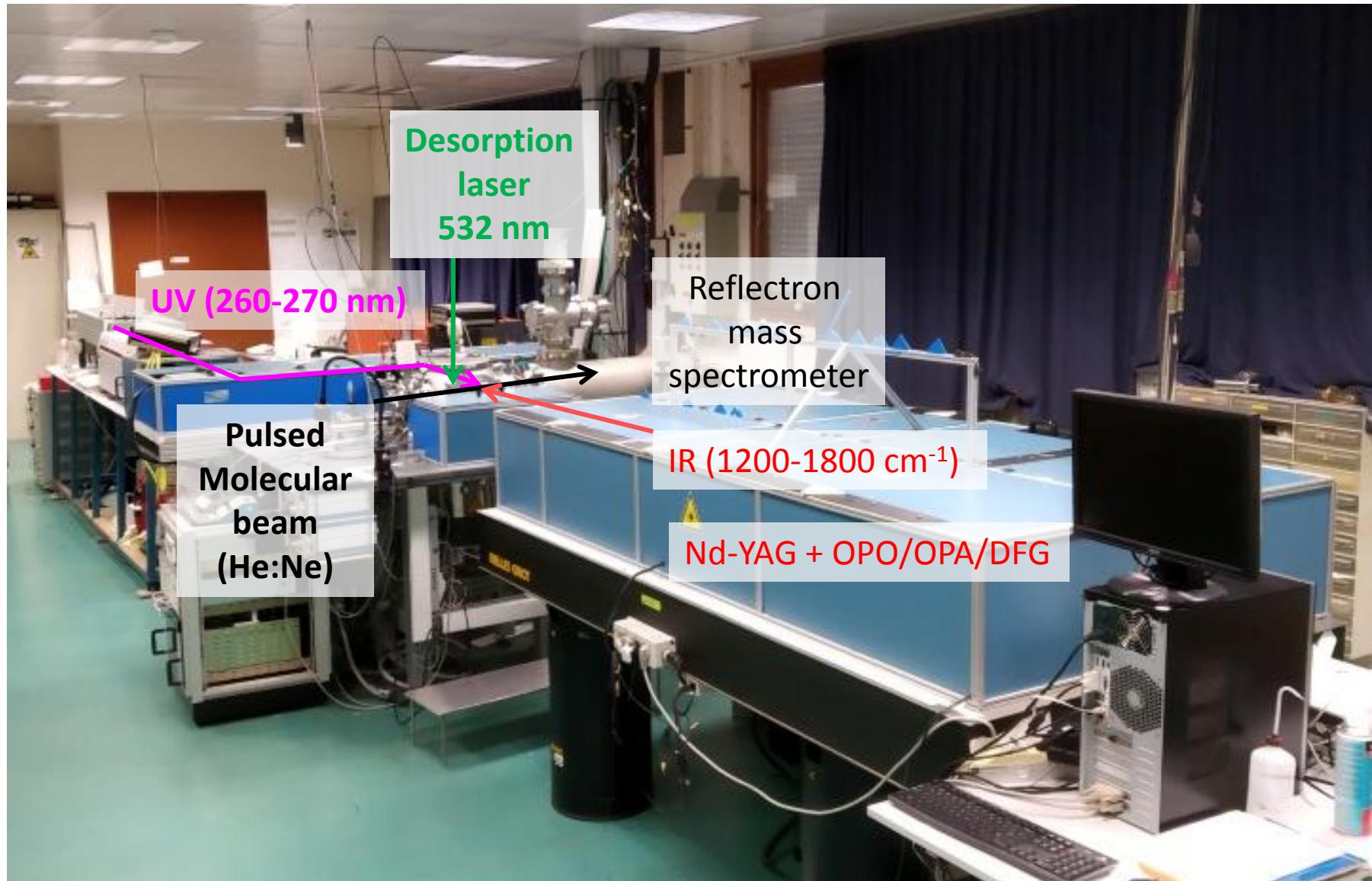
Laser desorption: hot species in the gas phase with limited fragmentation



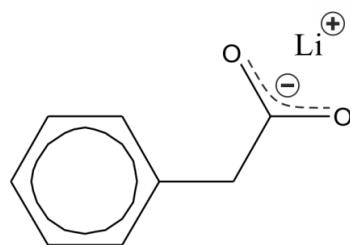
Cooling in the supersonic expansion (He/Ne): complexes are trapped in one or more conformations

Analysis of the conformational populations by IR and UV spectroscopy in the interaction region of a time-of-flight mass spectrometer

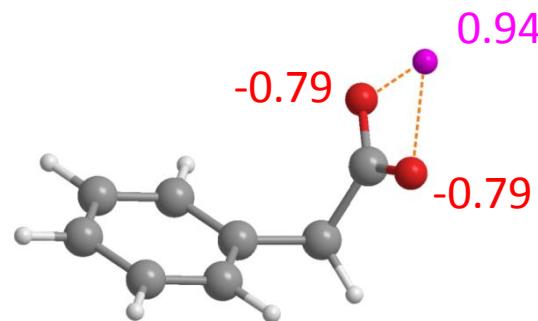
I. Gas phase experiment



IR/UV double resonance spectroscopy
→ conformation-selectivity

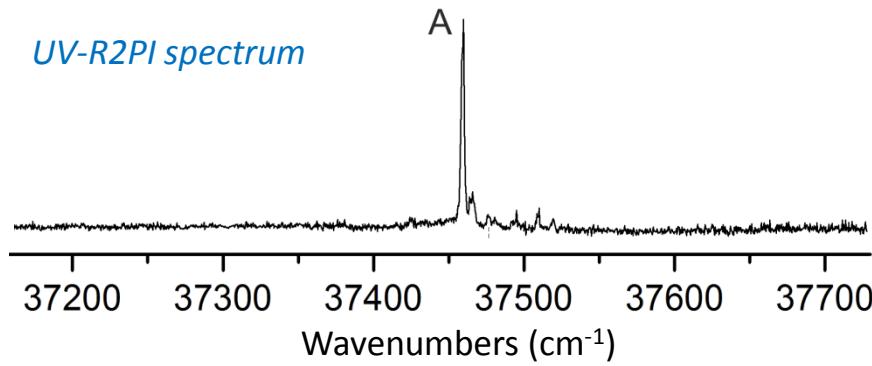


Lithium Phenylacetate
 $(\text{Li}^+, \text{PA}^-)$

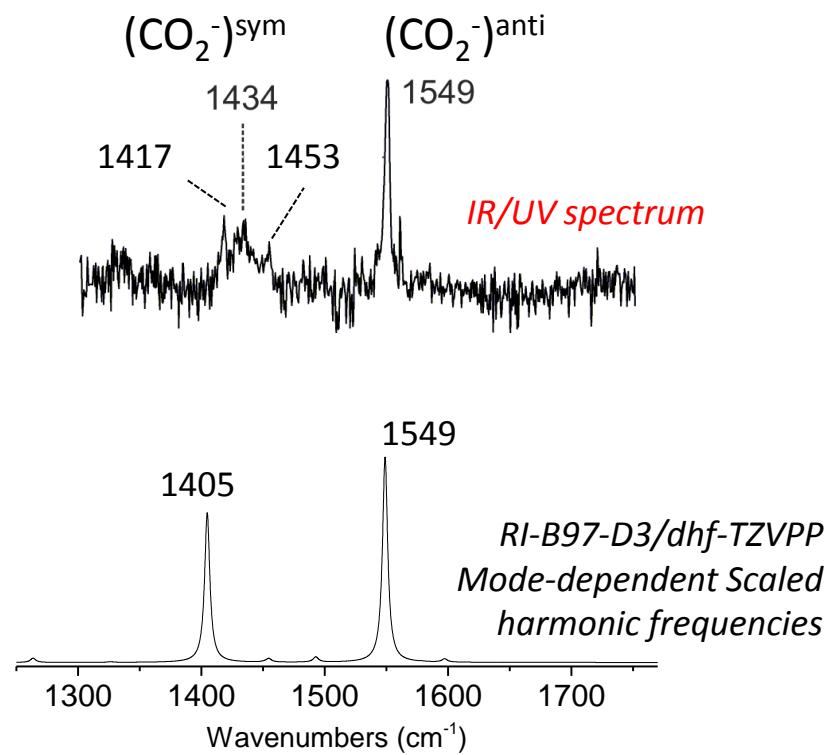


RI-B97-D3/dhf-TZVPP
Natural Bond Orbital Analysis

UV-R2PI spectrum

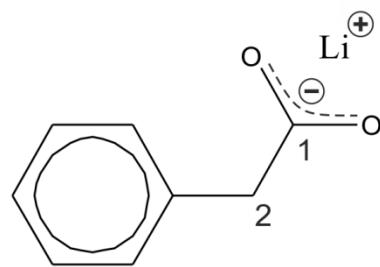


Habka, Brenner, Mons, Gloaguen *JPCL* (2016)

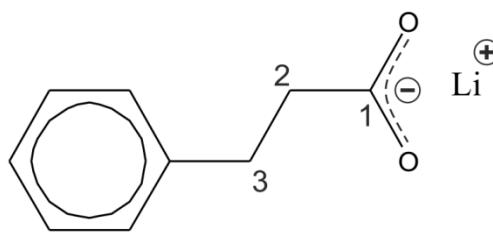


Gas phase ion pairs
are formed in our
experiment

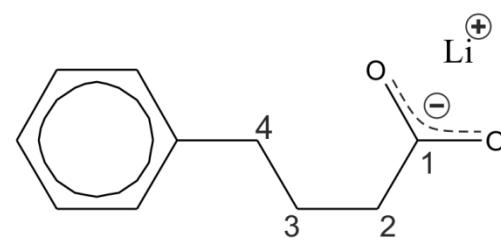
II. Molecular flexibility within ion pairs



Lithium Phenylacetate
(Li^+ , PA^-)

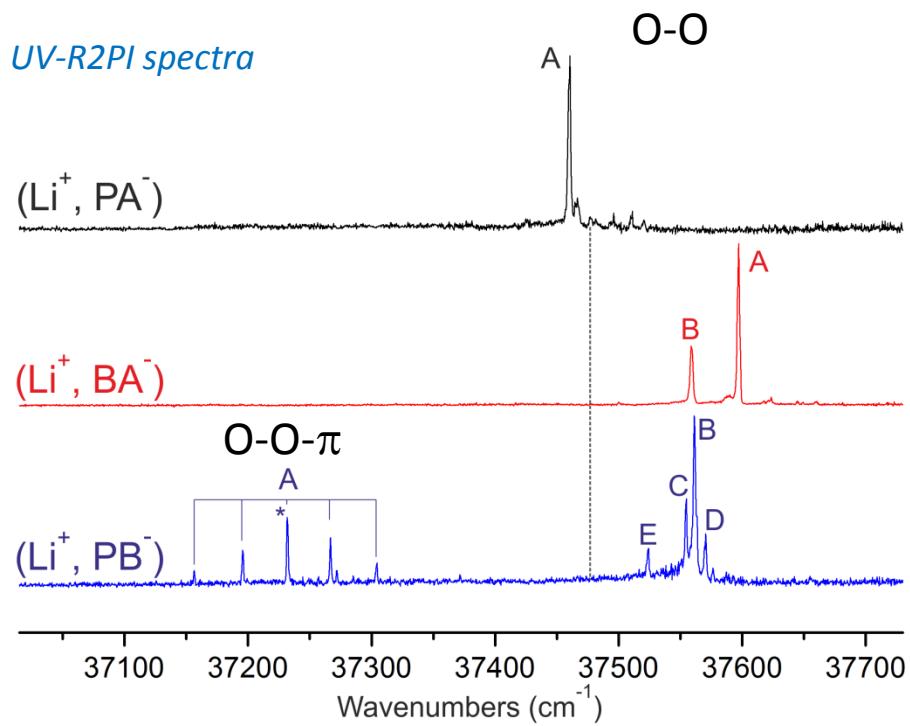


Lithium Benzylacetate
(Li^+ , BA^-)

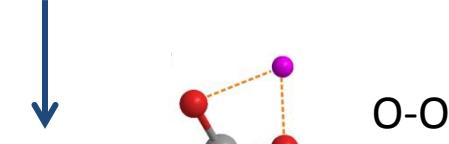


Lithium (4)-phenylbutyrate
(Li^+ , PB^-)

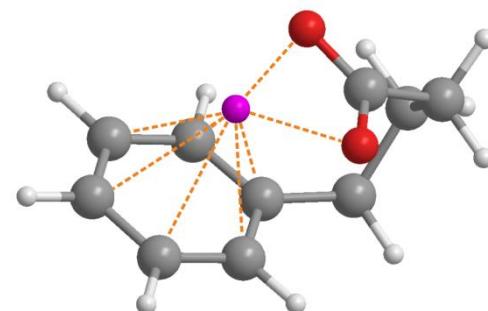
UV-R2PI spectra



Habka, Brenner, Mons, Gloaguen *JPC* (2016)



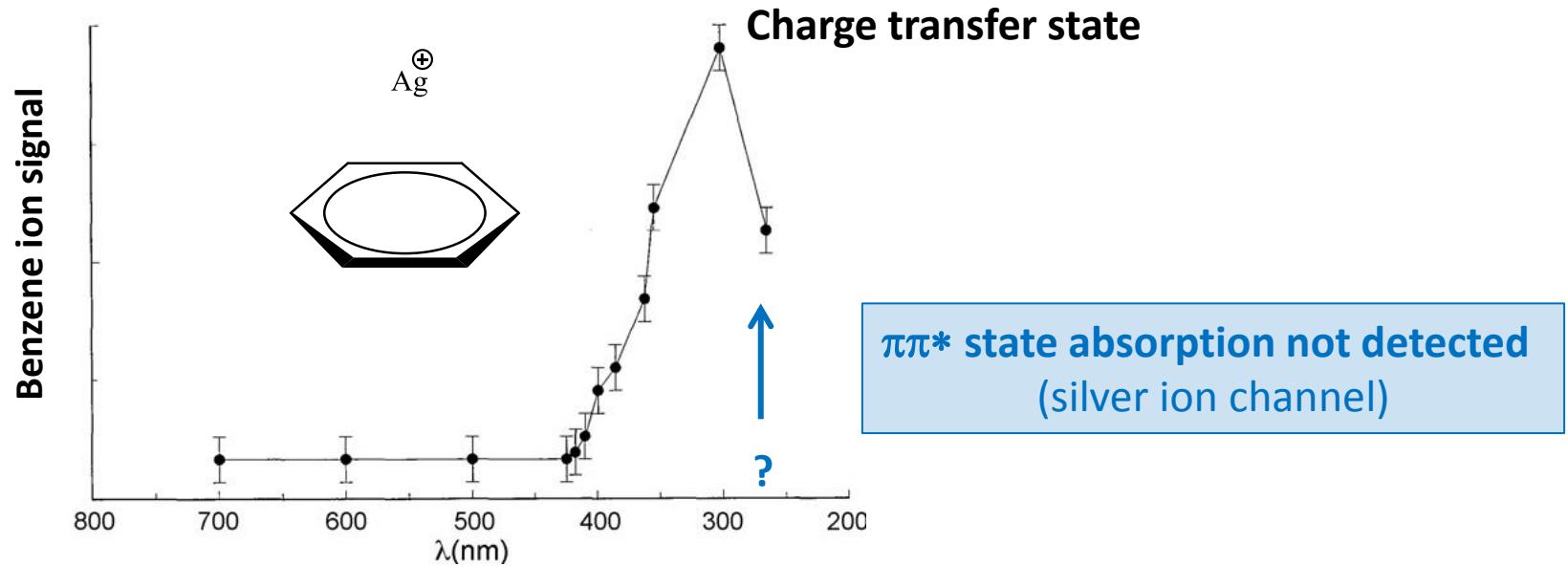
$$\Delta G(300 \text{ K}) = 6 \text{ kJ mol}^{-1}$$



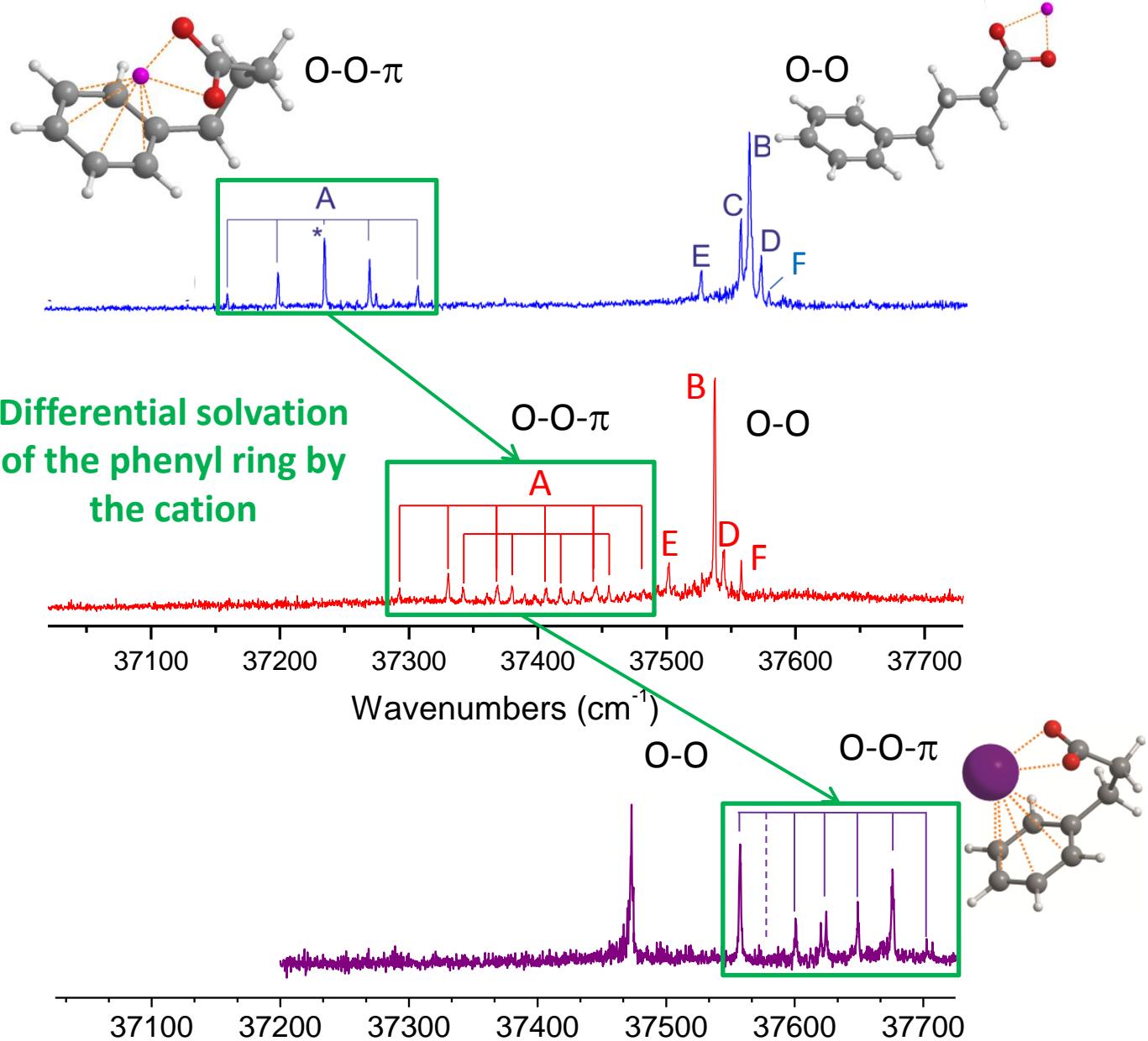
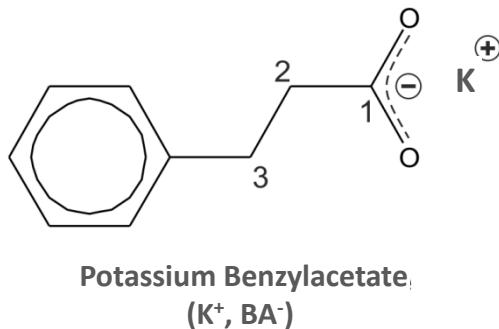
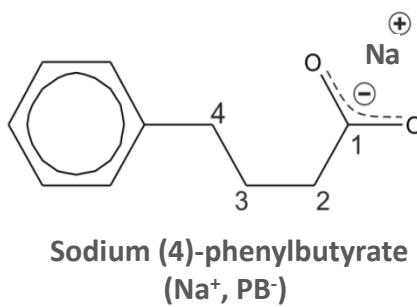
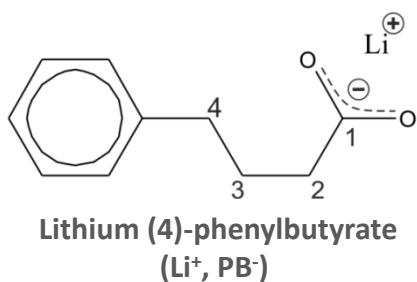
$$\Delta G(300 \text{ K}) = 0 \text{ kJ mol}^{-1}$$

I. 1st characterization of the $\pi\pi^*$ state of a phenyl ring + cation system

Willey, Cheng, Bishop, Duncan **JACS** (1991)



I. Cation- π interactions with Na^+ and K^+



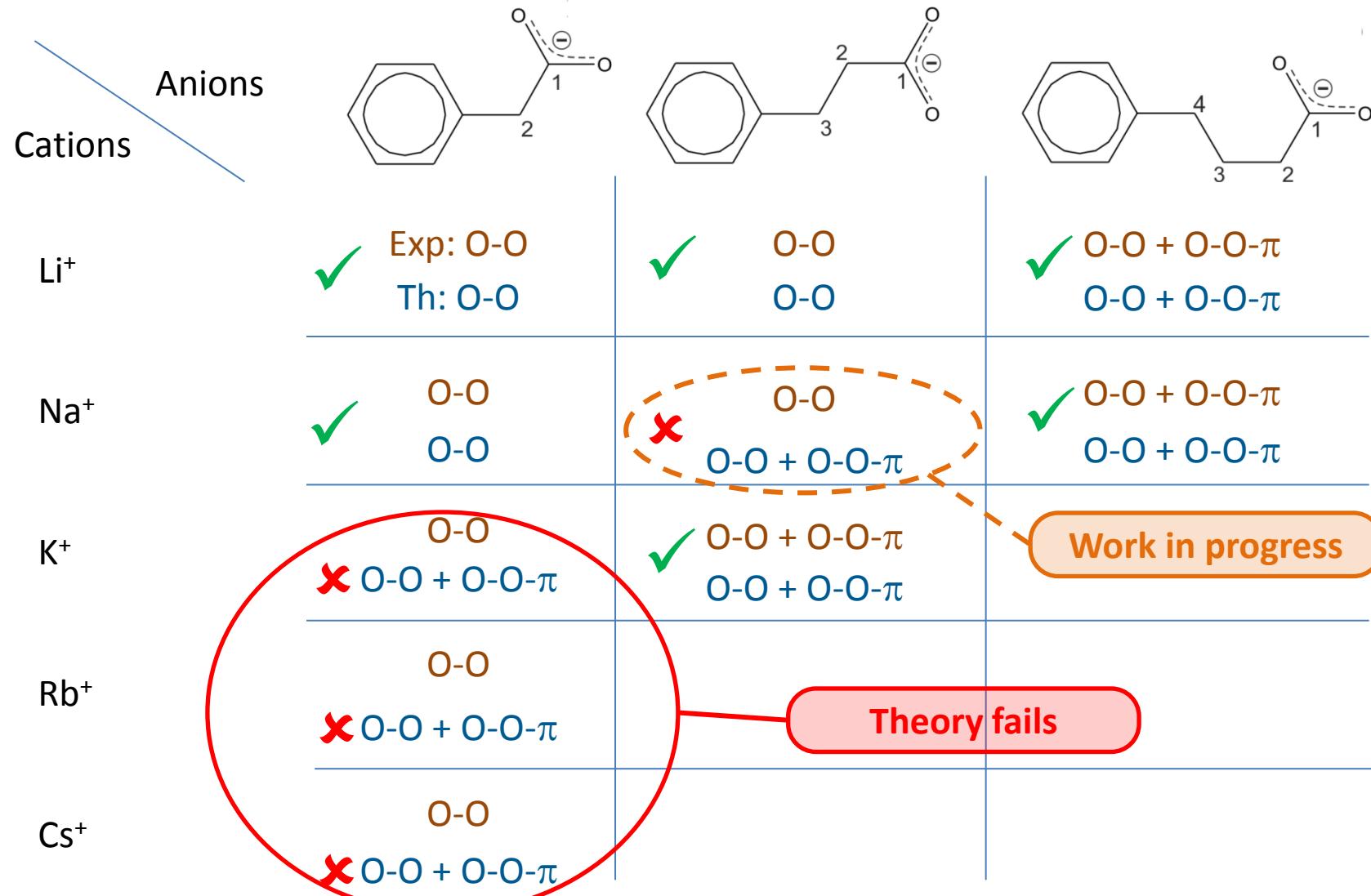
I. Experimental vs. Theoretical conformational landscape

Experiment:

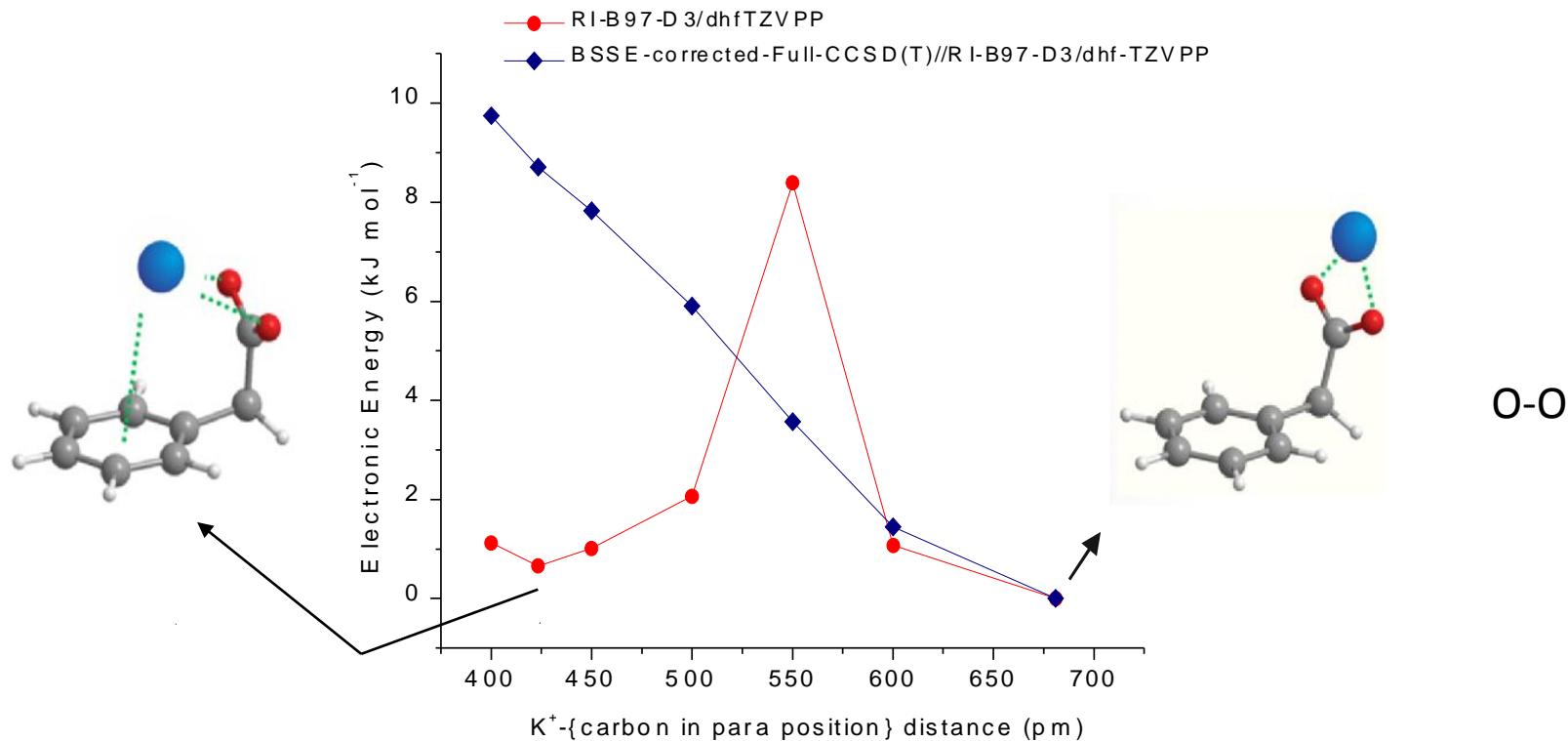
Apparent conformational distribution from R2PI spectra

Theory:

Conformational distribution from $\Delta G(300K)$ at the RI-B97-D3/dhf-TZVPP level



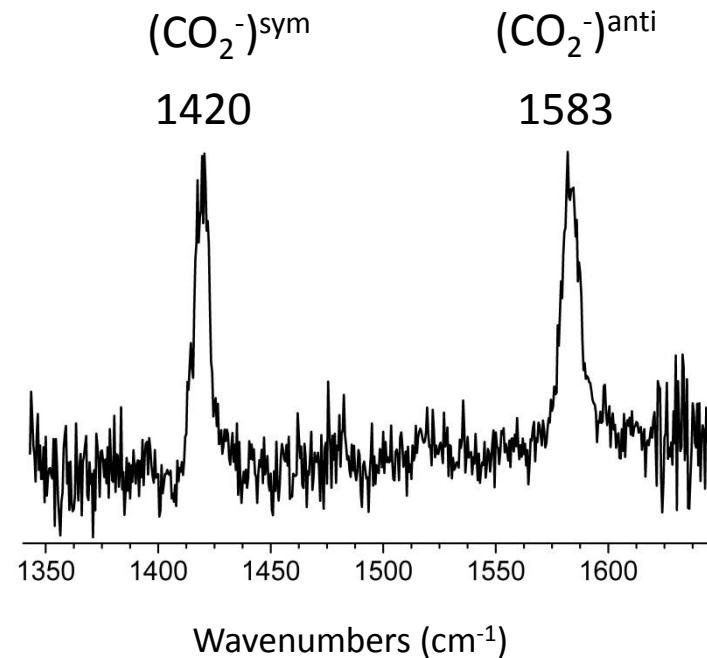
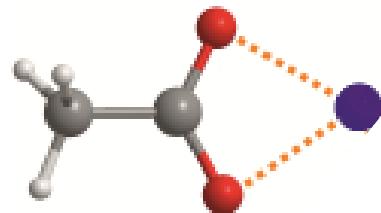
I. Experimental vs. Theoretical conformational landscape



The relative description of cation-anion ($\sim 500 \text{ kJ mol}^{-1}$) and cation- π ($\sim 100 \text{ kJ mol}^{-1}$) interactions at the RI-B97-D3/dhf-TZVPP level of theory is poor

Gas phase ion pairs reveal flaws in theoretical methods that would be otherwise difficult to detect in systems dealing with weaker non covalent interactions

I. Ion pairs without UV chromophore



First experimental IR signature of a contact ion pair between sodium and acetate
No coupling of the $(CO_2^-)^{sym}$ stretch

Common organic salt can be laser desorbed and investigated by spectroscopic techniques in the gas phase

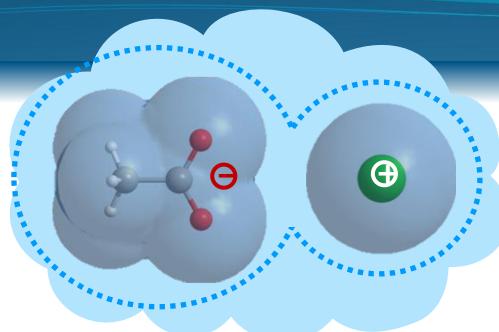
I. Molecular folding
of isolated ion pairs

III. Stark spectroscopy
at very high electric
field using ion pairs

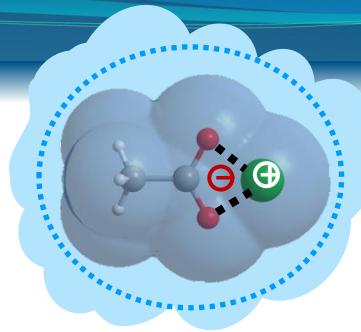
II. Characterization of
ion pairs in solution
assisted by gas phase
spectroscopy

II. $(\text{Na}^+, \text{AcO}^-)_{\text{aq}}$ 1M

SIP/SSIP



?



CIP

2008

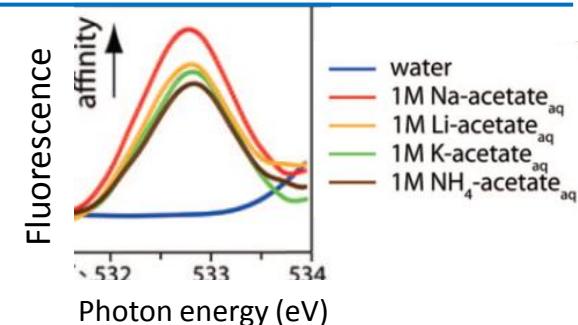
CIPs detected by X-ray absorption spectroscopy (XAS) in liquid microjet

Carbon K-edge

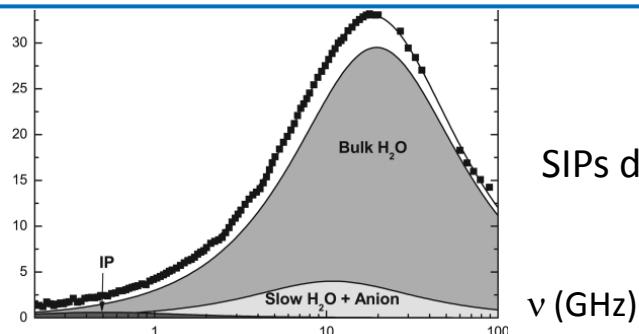
Ueijo, Schwartz, Muffin, Drisdell, Cohen, Saykally PNAS (2008)

Oxygen K-edge

Aziz, Ottosson, Eisebitt, Eberhardt, Jagoda-Cwiklik, Vácha, Jungwirth, Winter JPCB (2008)



Dielectric loss



2012

SIPs detected by dielectric relaxation spectroscopy in solution

**SIP > CIP
à 1M**

*Rahman, Hefter, Buchner JPCB (2012)
Rahman, Buchner JML (2012)*

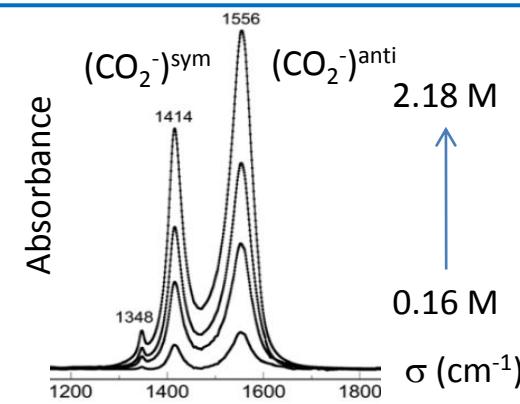
2014

SIPs detected by Fourier-Transformed IR (FTIR) in solution

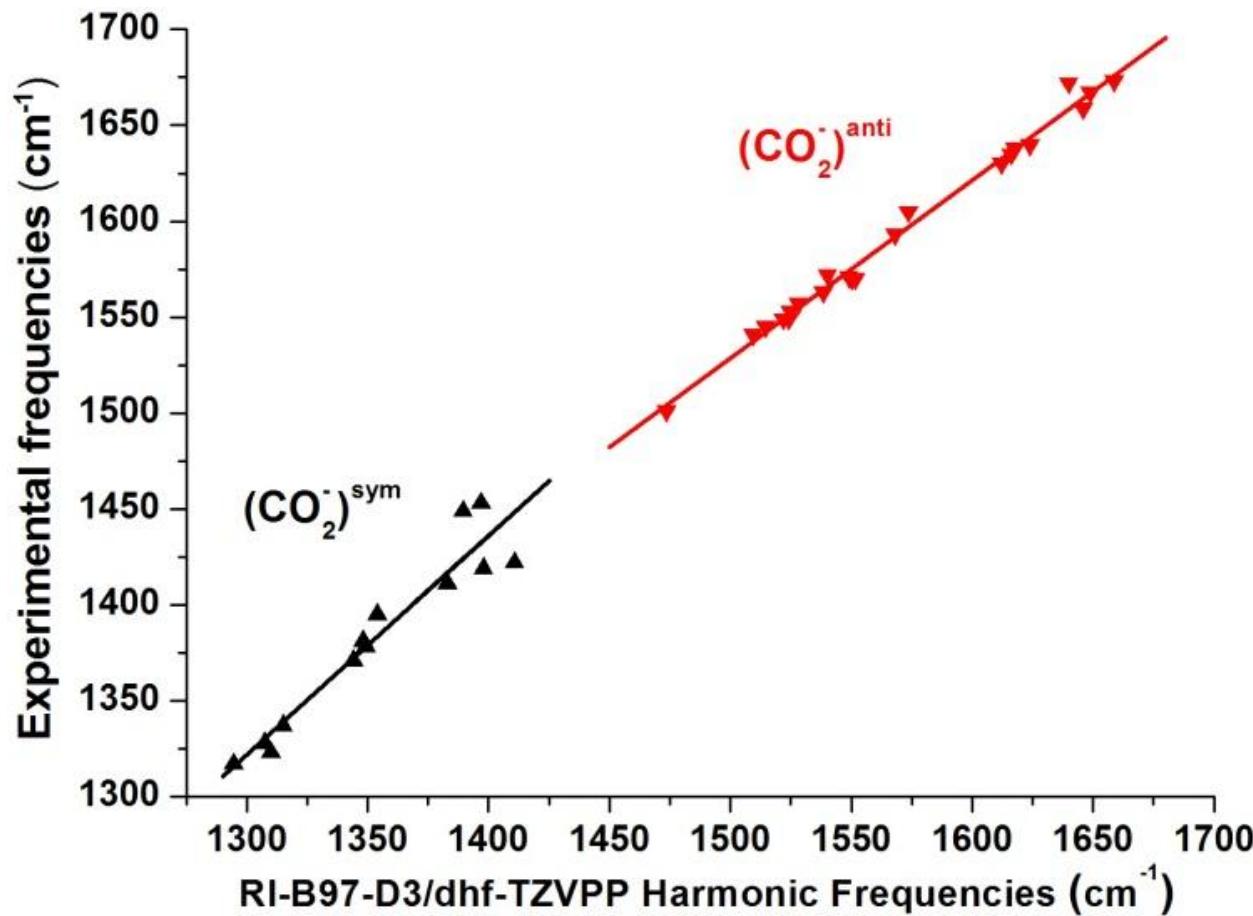
SIP > CIP à 1M

No CIP exists in solution at any concentration

*Rudolph, Fischer, Irmer Dalt. Trans. (2014)
Rudolph, Irmer RSC Adv. (2015)*



II. Accuracy of mode-dependent scaled vibrational frequencies



Standard deviations = Error between experiment and theory

15 cm^{-1} for CO_2^{sym} stretch

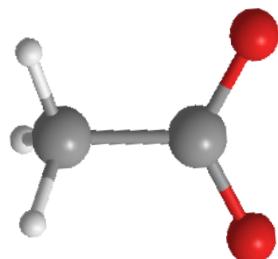
5 cm^{-1} for $\text{CO}_2^{\text{anti}}$ stretch

II. Conformational exploration of ion pairs in solution

Biased Monte-Carlo Exploration
at the polarizable force field level (AMOEBA)



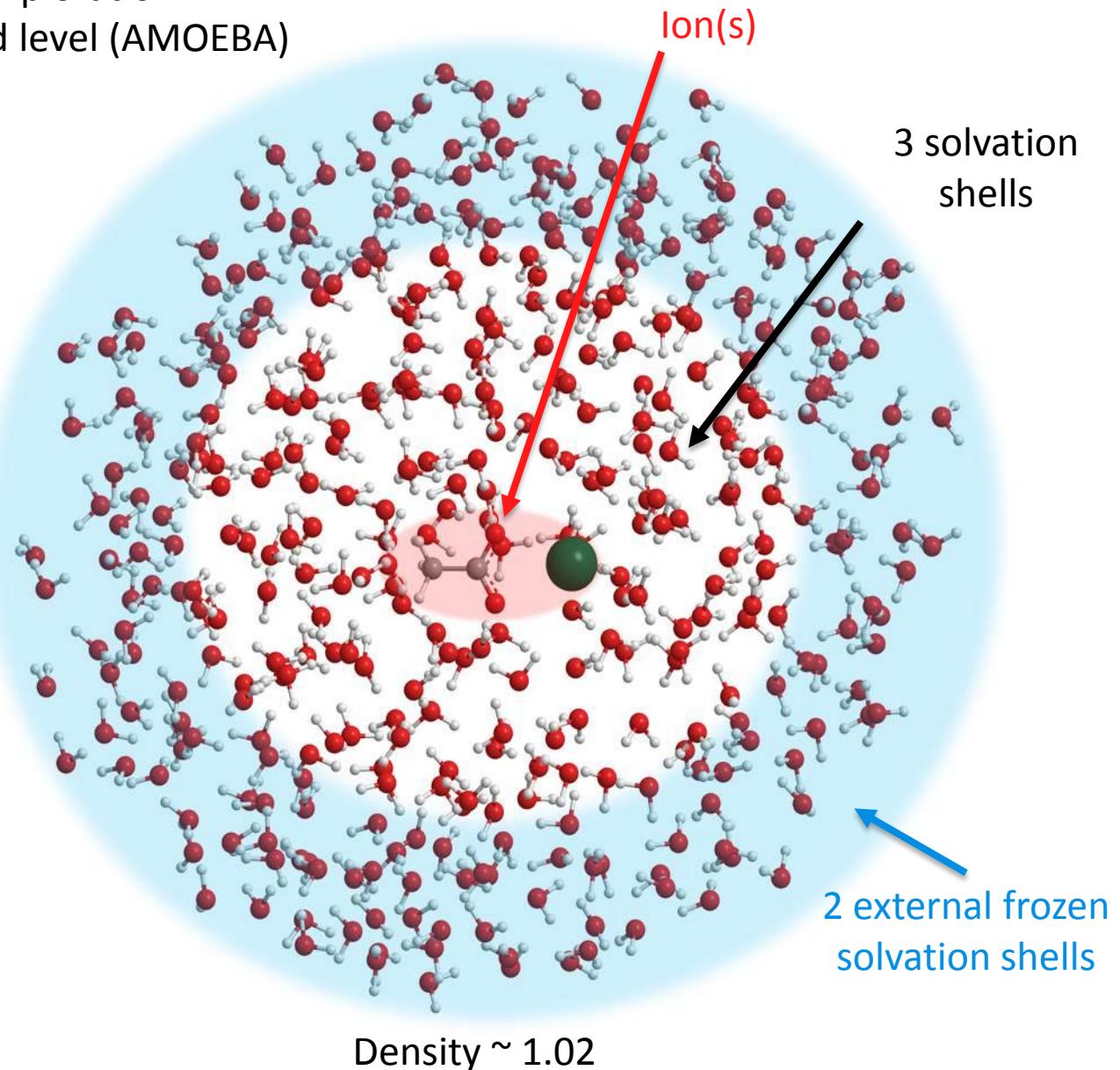
Explicit water molecules



Acetate

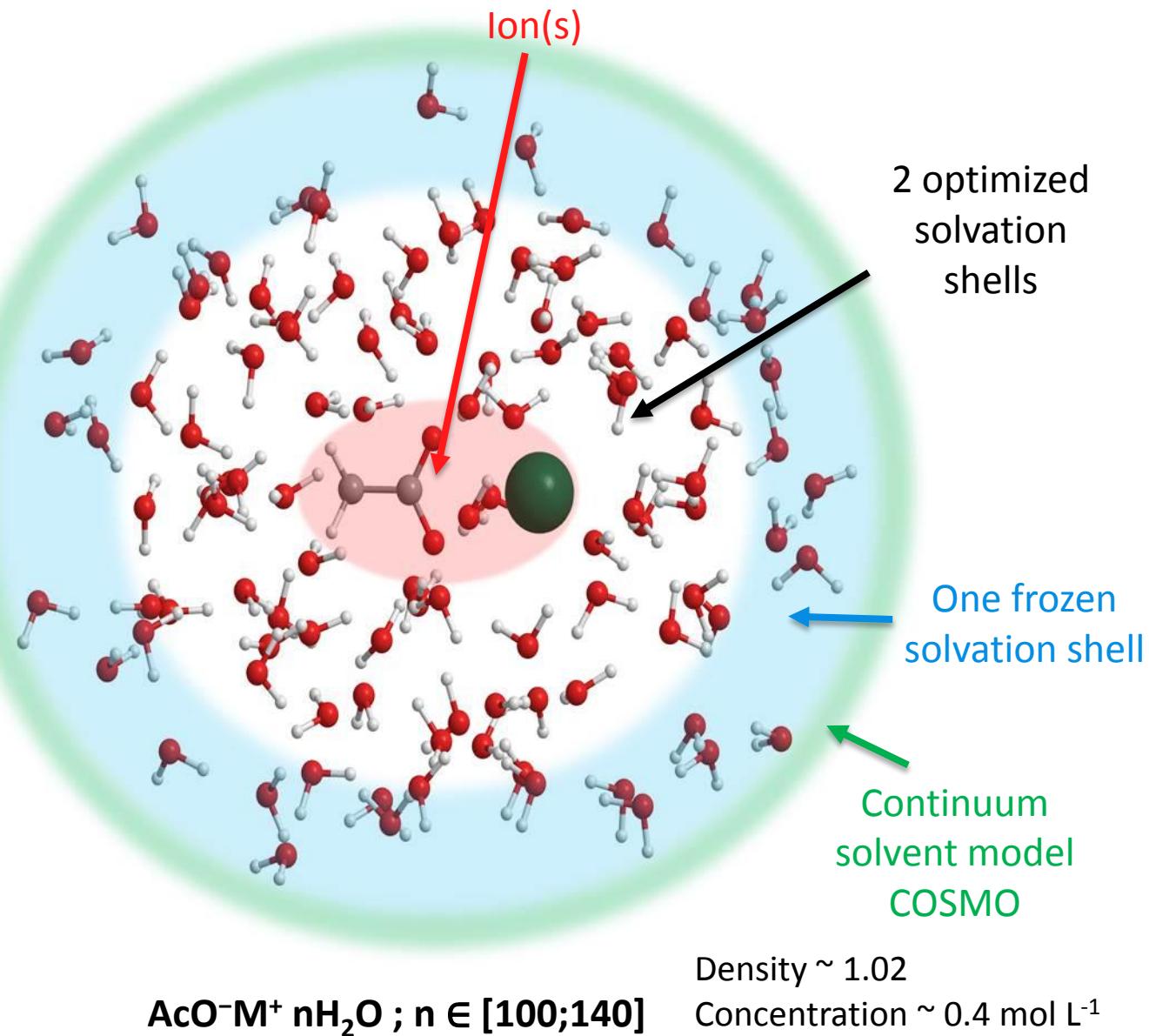


Li^+ Na^+ K^+ Rb^+ Cs^+



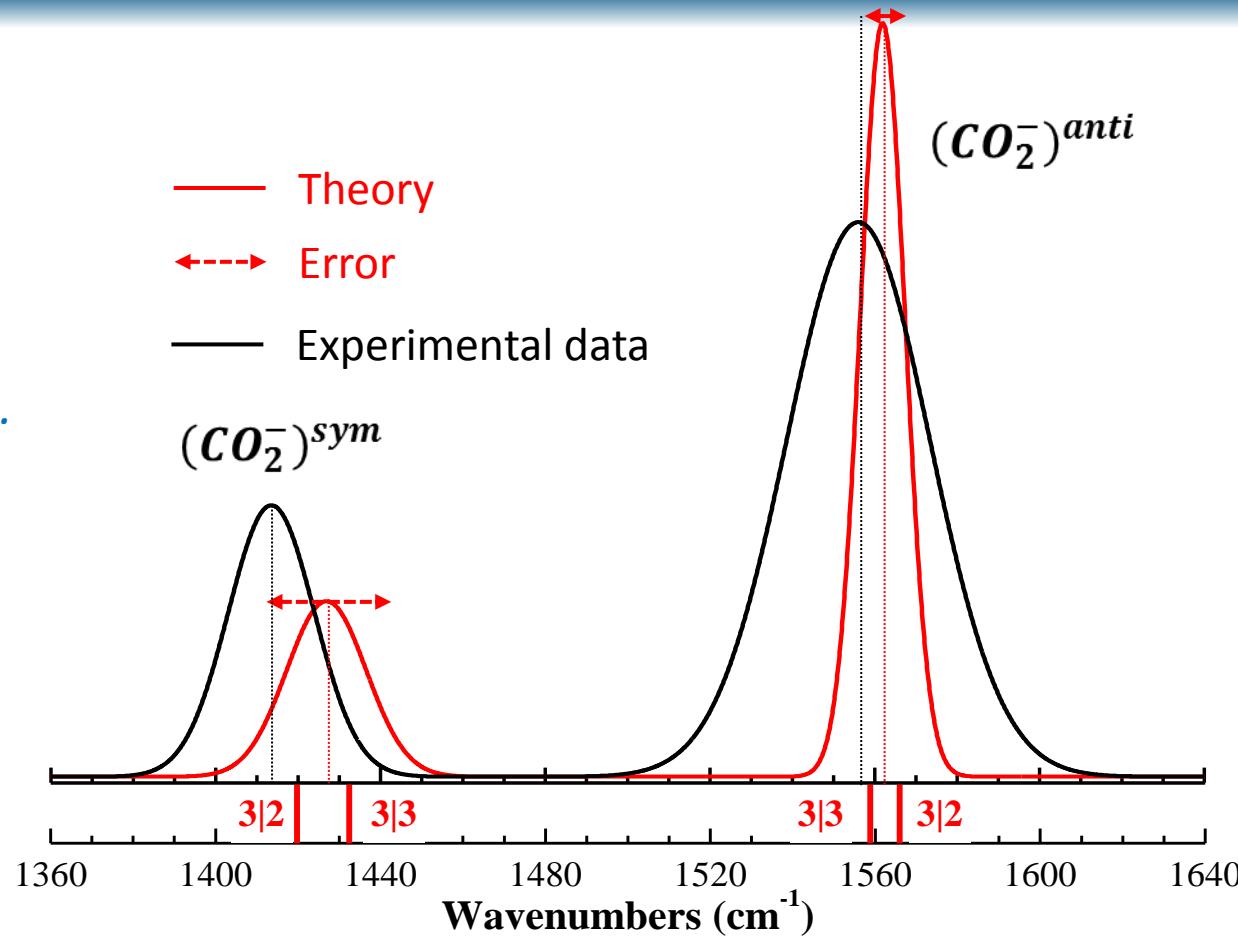
II. Geometry optimization – Frequency calculations

Sampling
↓
Geometry optimizations
Frequency calculations
(RI-B97-D3/dhf-TZVPP)
↓
Averaged frequencies
Averaged intensities
Spectral width



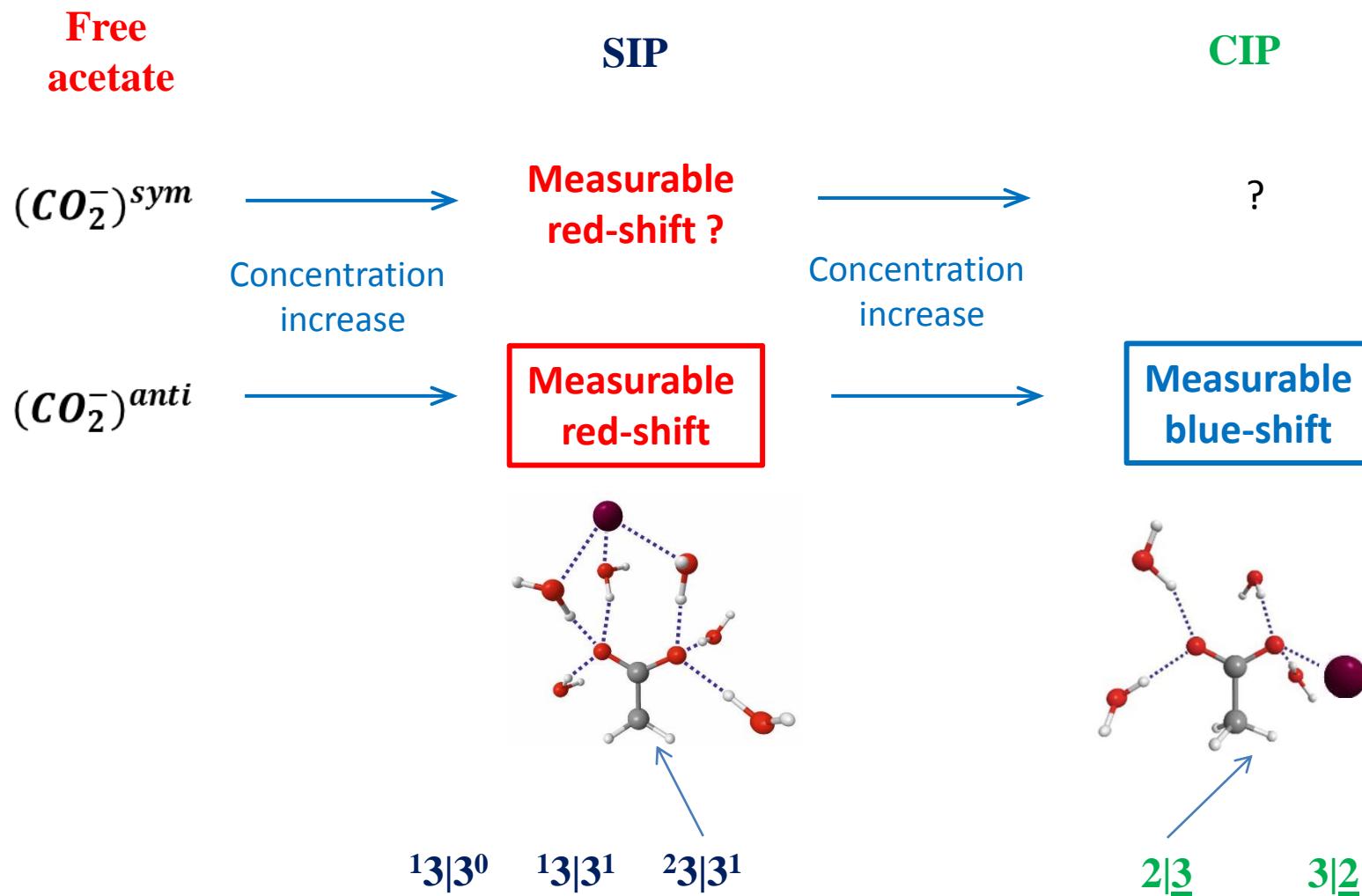
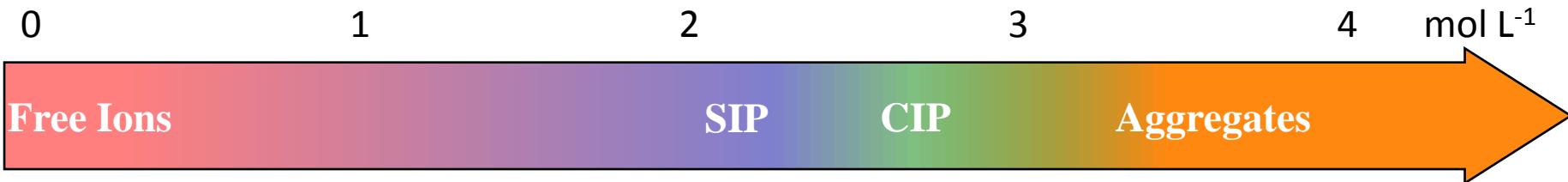
II. Free acetate ions

Rudolph, Fischer,
Irmer *Dalt. Trans.*
(2014)

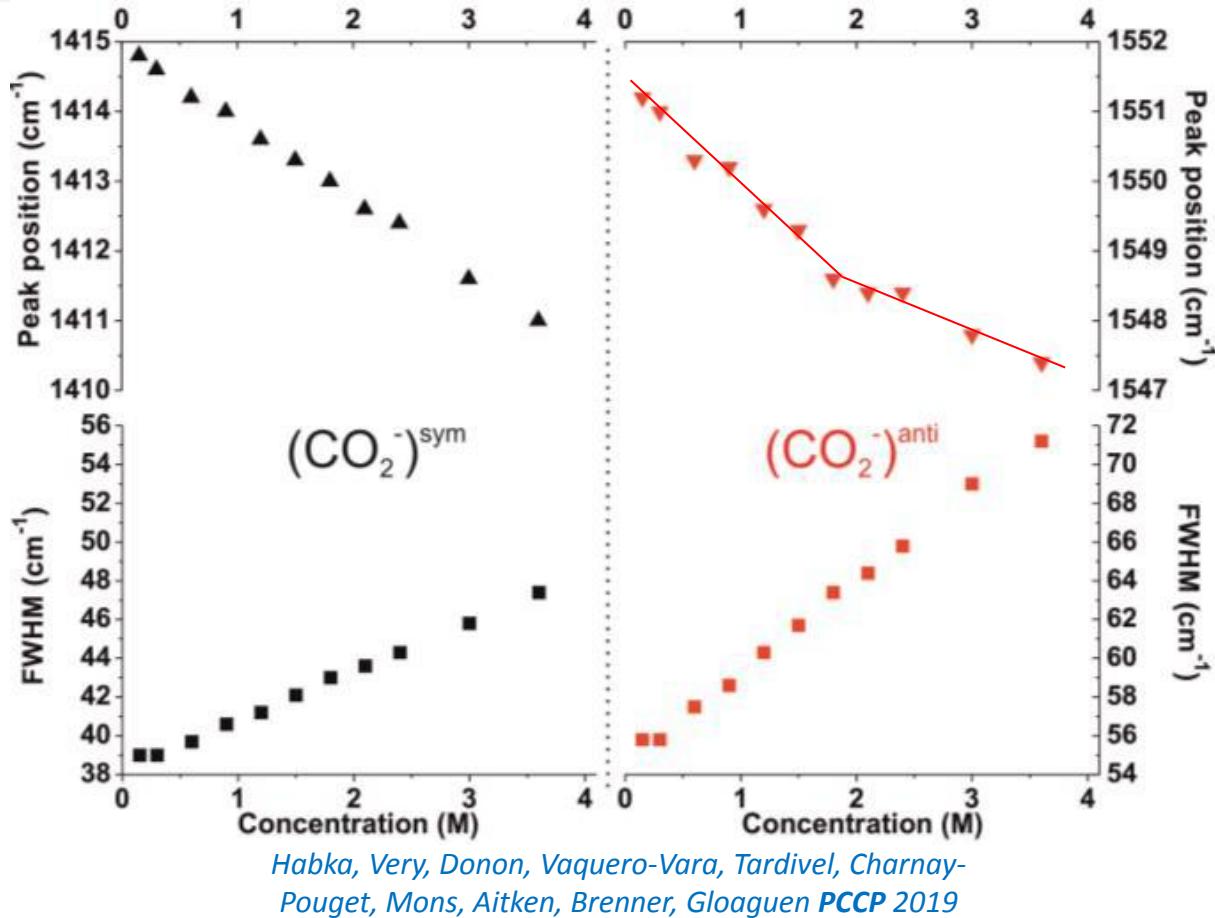
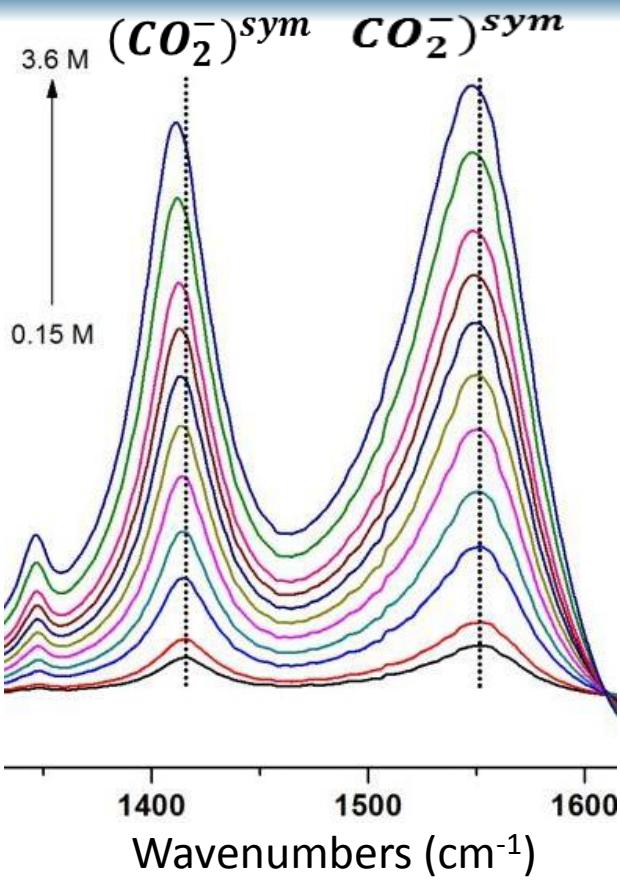


- Theoretical frequencies and intensities (area) reproduce the experimental data within the expected error
- Theoretical spectral width of the antisymmetric is underestimated (temperature effects are not included in the theoretical model)

II. Theoretical spectra of ion pairs between acetate and sodium: Conclusions



II. Theoretical vs experimental spectra



Habka, Very, Donon, Vaquero-Vara, Tardivel, Charnay-Pouget, Mons, Aitken, Brenner, Gloaguen PCCP 2019

The red-shift observed from 0.3 M on both $(CO_2^-)^{sym}$ and $(CO_2^-)^{anti}$ is assigned to SIP formation
The change of slope around 2 M can be assigned to CIP formation

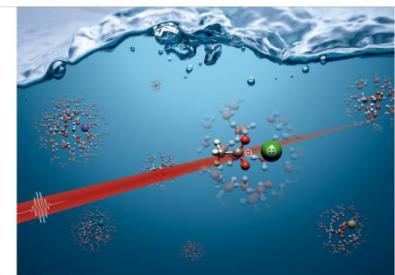
This approach enables us to interpret spectral shifts in solution and assign specific supramolecular structures at different concentration ranges

Identification of ion pairs in solution by IR spectroscopy: crucial contributions of gas phase data and simulations

Sana Habka, Thibaut Very, Jeremy Donon, Vanesa Vaquero-Vara, Benjamin Tardivel, Florence Charnay-Pouget, Michel Mons, David J. Aitken, Valérie Brenner and Eric Gloaguen

Phys. Chem. Chem. Phys., 2019, **21**, 12798-12805.

DOI: 10.1039/c9cp00700h

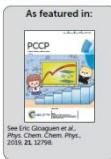


Showcasing research from the Biomolecular Structures Group,
Dr Eric Gloaguen, CNRS, CEA-Saclay, Université Paris-Saclay,
France

Identification of ion pairs in solution by IR spectroscopy: crucial

contributions of gas phase data and simulations

This work explores an original approach where accurate gas phase data are combined with quantum mechanics/molecular mechanics calculations of ion pairs in solution, resulting in an unprecedented level of accuracy in vibrational frequency prediction. As an application of this methodology to the interpretation of solution phase IR spectra of sodium acetate, this work illustrates the potential of the approach for the elucidation of supramolecular structures in electrolyte solutions.



As featured in:
PCCP
See Eric Gloaguen et al.,
Phys. Chem. Chem. Phys.,
2019, **21**, 12798

rsc.li/pccp
Supplementary material

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ROYAL SOCIETY
OF CHEMISTRY

CELEBRATING
IYPT 2019



I. Molecular folding
of isolated ion pairs

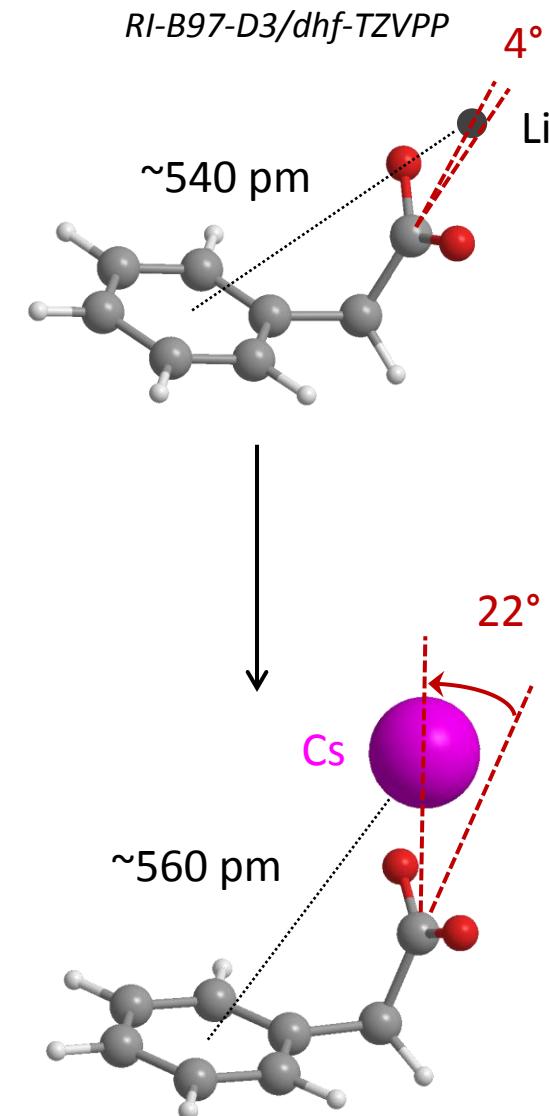
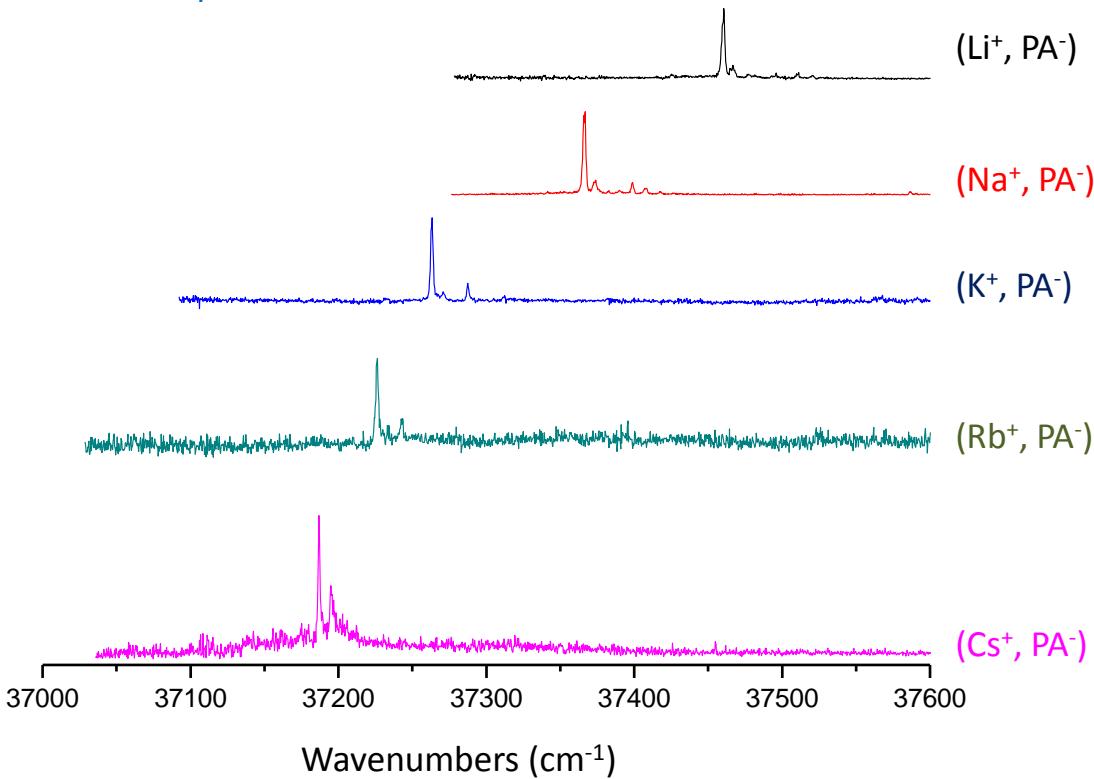
III. Stark spectroscopy
at very high electric
field using ion pairs

II. Characterization of
ion pairs in solution
assisted by gas phase
spectroscopy



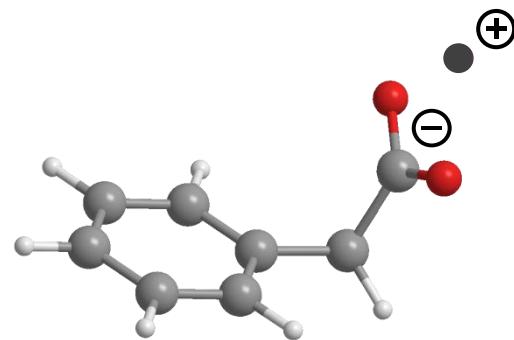
III. UV Spectroscopy of $(M^+, PA^-)_g$

UV-R2PI spectra



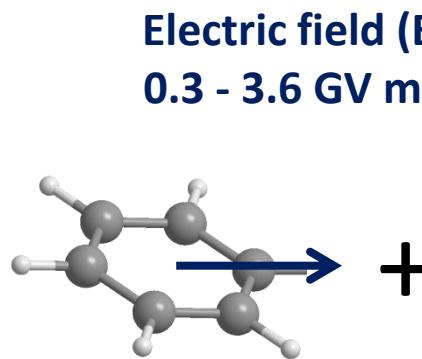
→ The change of geometry does not explain the red-shift of the $\pi \rightarrow \pi^*$ transition

III. Electric field and ion pairs

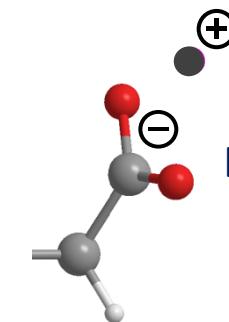


RI-B97-D3/dhf-TZVPP

\approx

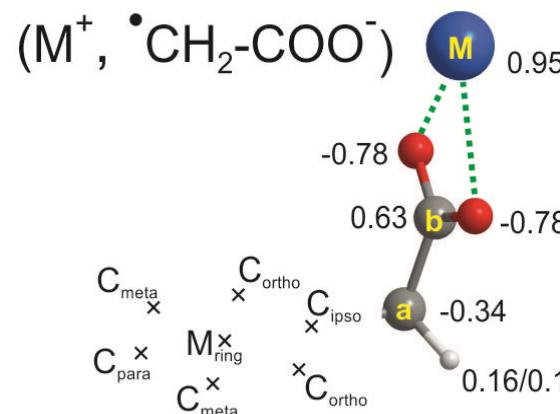
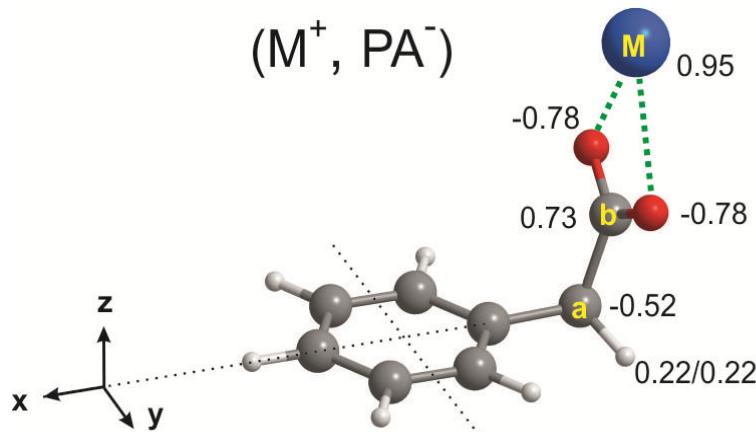


Electric field (E)
0.3 - 3.6 GV m⁻¹



Dipole moment
(Li – Cs)
1.6 – 8.4 D

Electronic Stark effect on the phenyl ring?



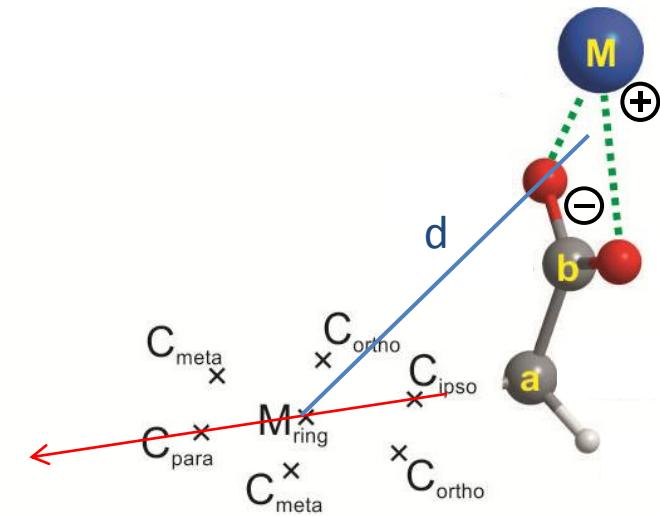
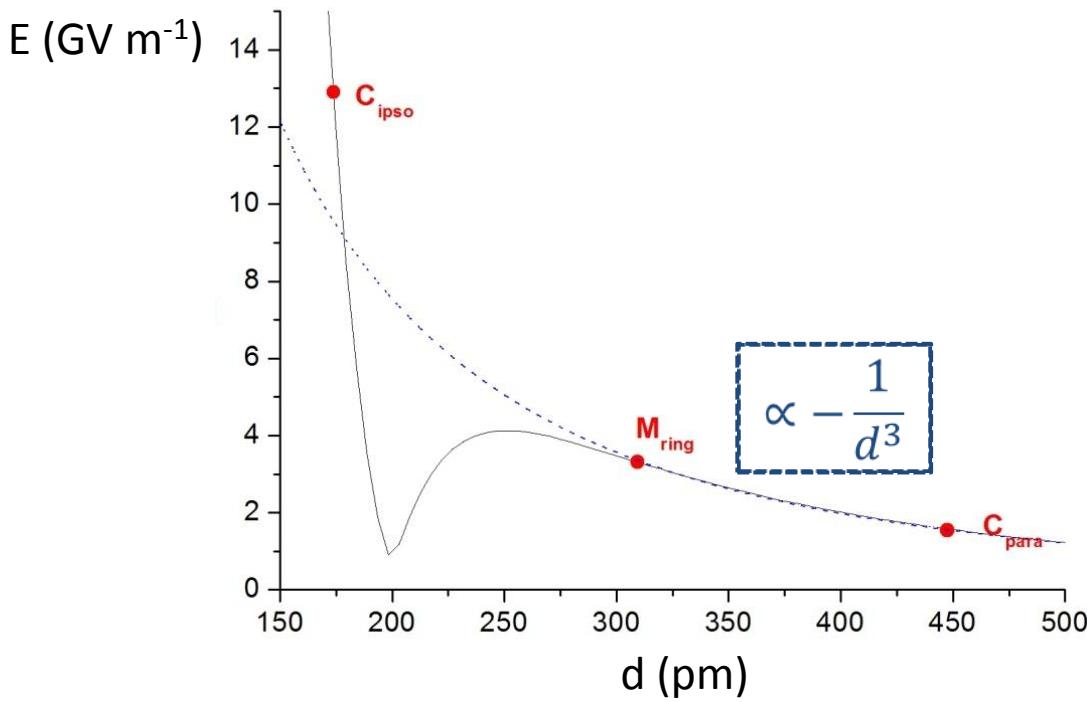
C_{meta}
 C_{para}

C_{ortho}
 M_{ring}^x

C_{ipso}
 C_{ortho}

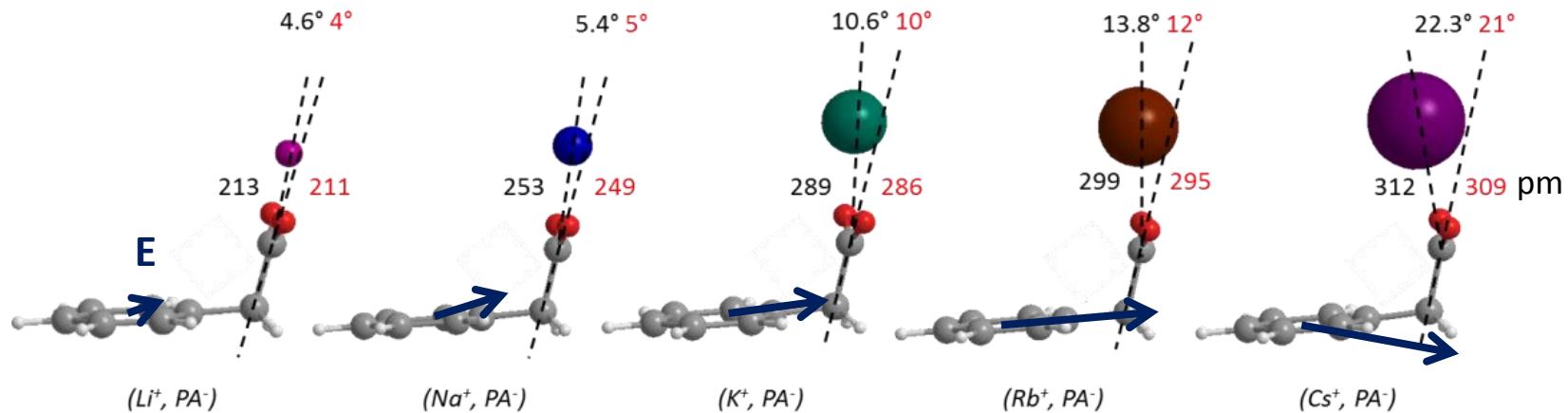
NBO analysis
RI-B97-D3/def2-QZVPP

III. Electric field profile and orientation



RI-B97-D3/dhf-TZVPP

BSSE-corrected-Full-RI-CCSD(T)/dhf-TZVPP



III. Stark effect

$$\Delta\nu = -\frac{1}{h} \left(\Delta\mu \cdot E + \frac{1}{2} E \cdot \Delta\alpha \cdot E \right)$$

Spectral shift

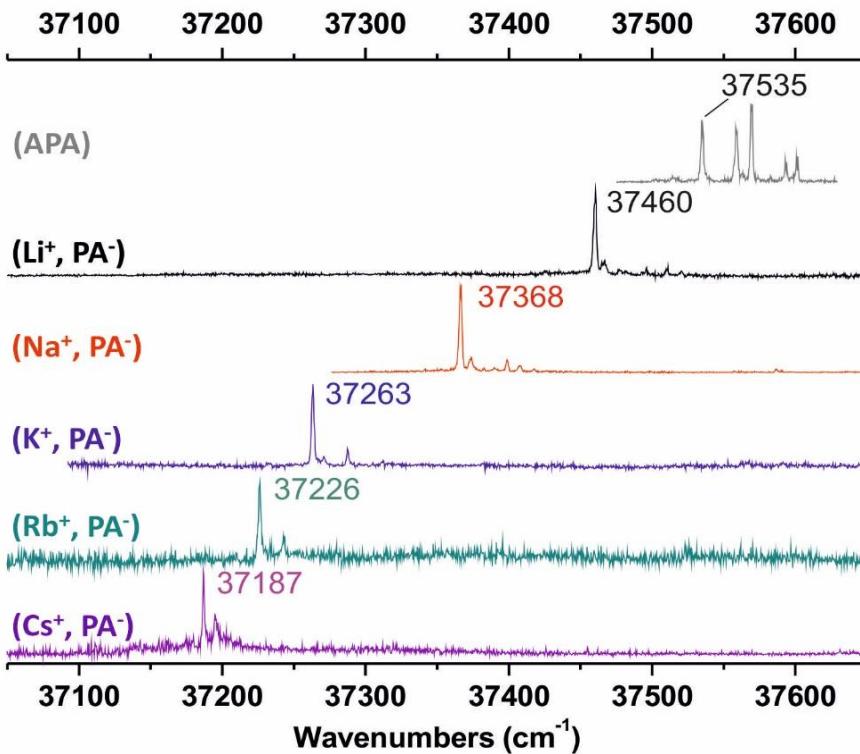
Dipole moment difference between the excited and ground states

$$E_z \approx E_y \approx 0$$

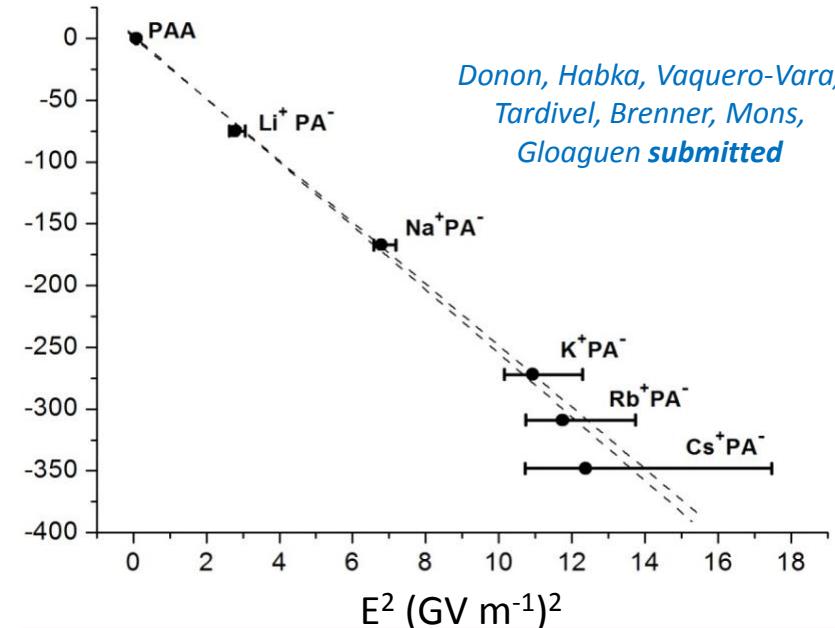
$$\Delta\nu \approx -\frac{1}{h} \left(\Delta\mu_x E_x + \frac{\Delta\alpha_{xx}}{2} E_x^2 \right)$$

Phenyl ring weakly polarized by photoexcitation

$$\Delta\nu \approx -\frac{1}{h} \frac{\Delta\alpha_{xx}}{2} E_x^2$$

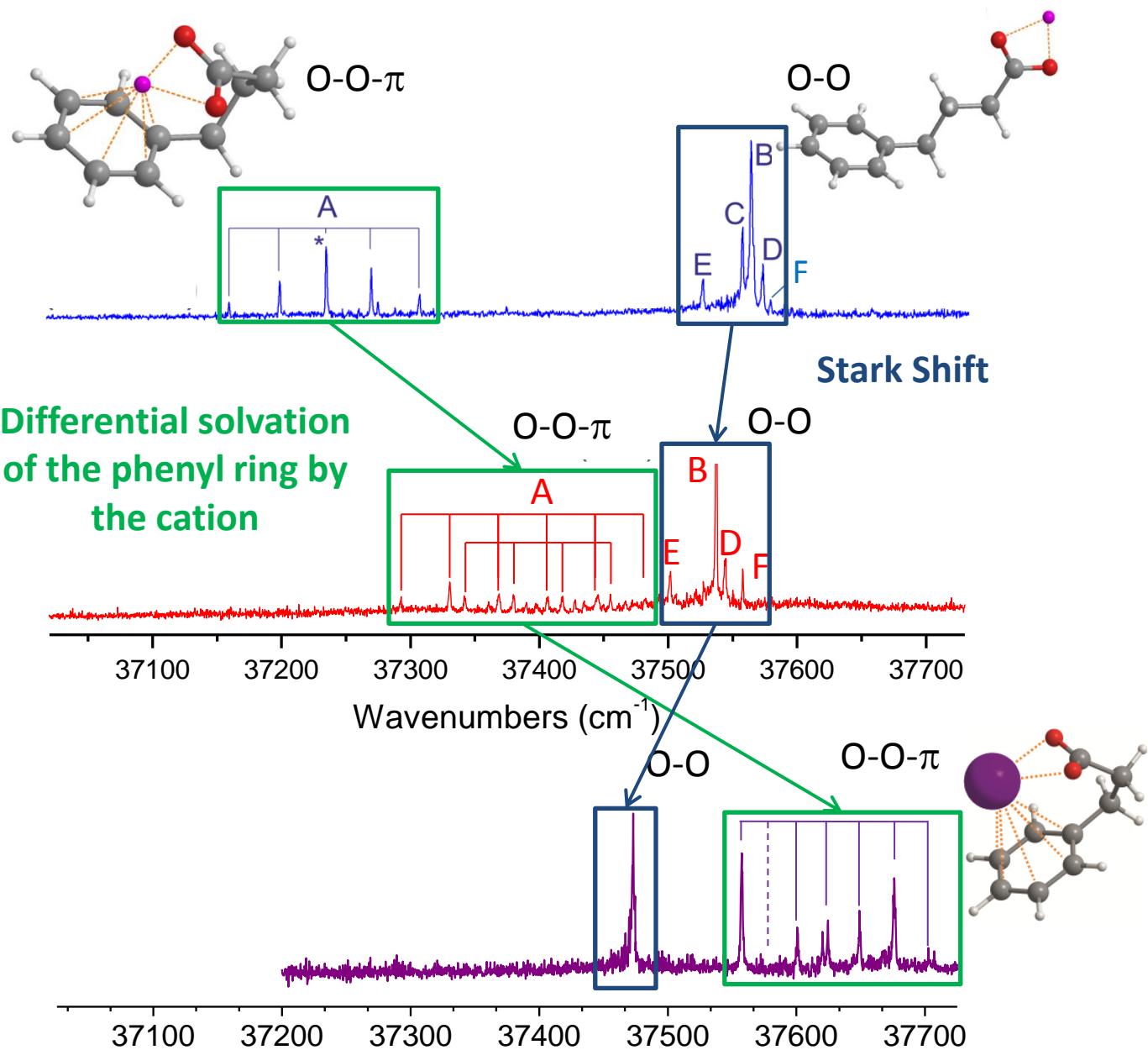
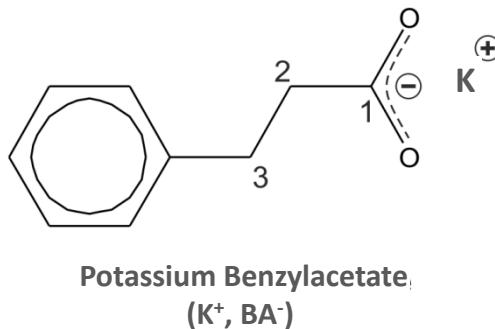
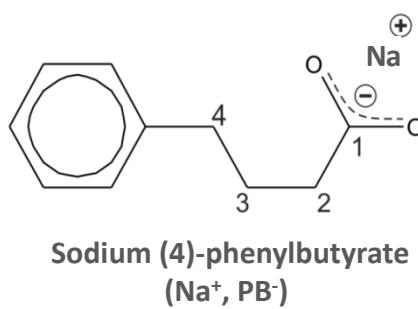
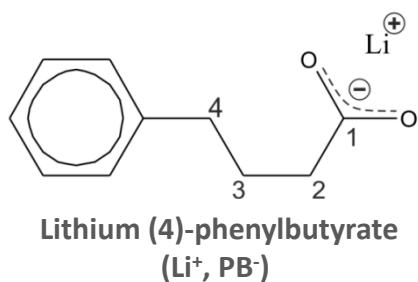


$$\Delta\nu (\text{cm}^{-1})$$

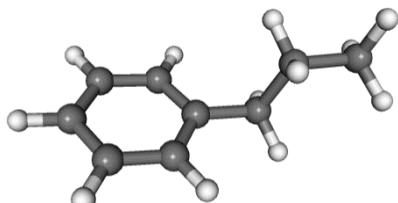
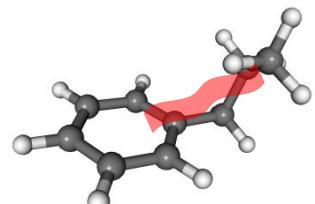


The electronic red-shift can be assigned to a Stark effect

III. UV spectroscopy rationalization – Stark Shift

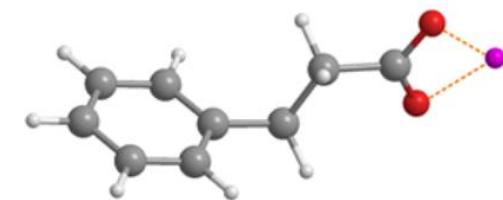
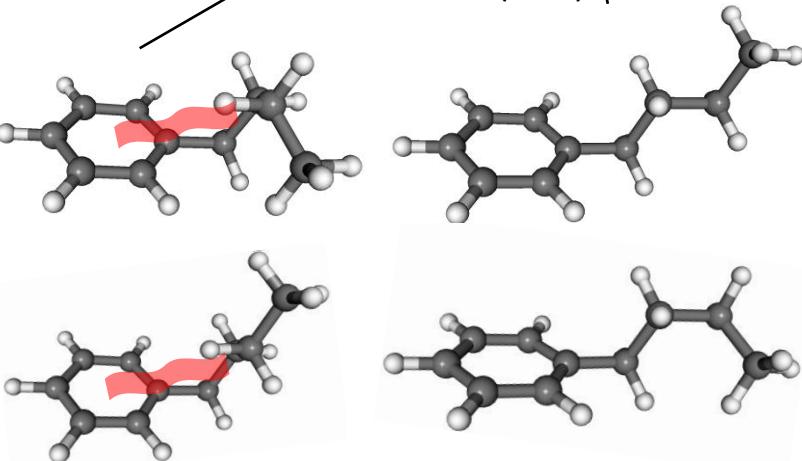
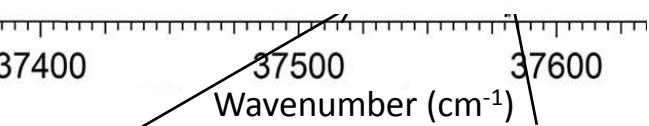


III. UV spectroscopy rationalization – Stark splitting



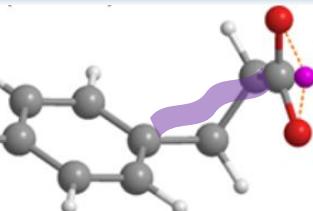
Hewett, Bocklitz, Tabor,
Sibert III, Suhm, Zwier
Chem. Sci. 2017

Propylbenzene

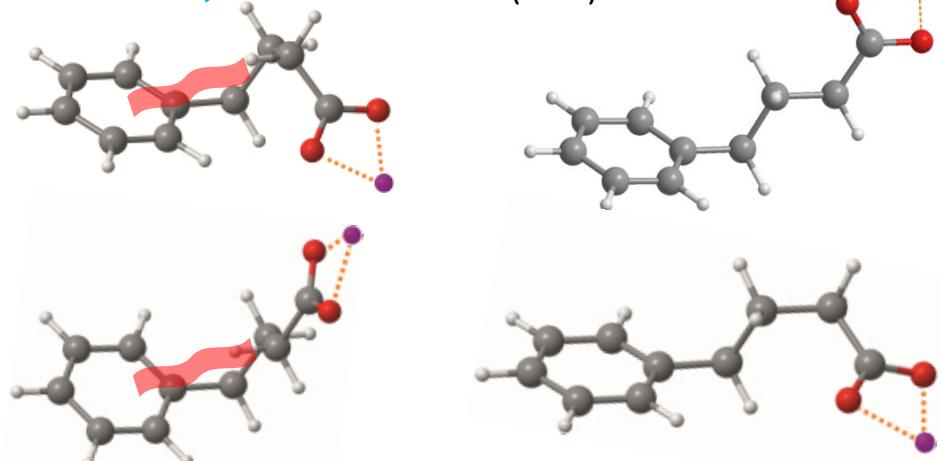
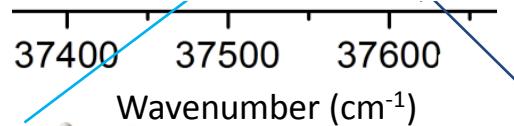


Lithium Benzylacetate
(Li^+ , BA^-)

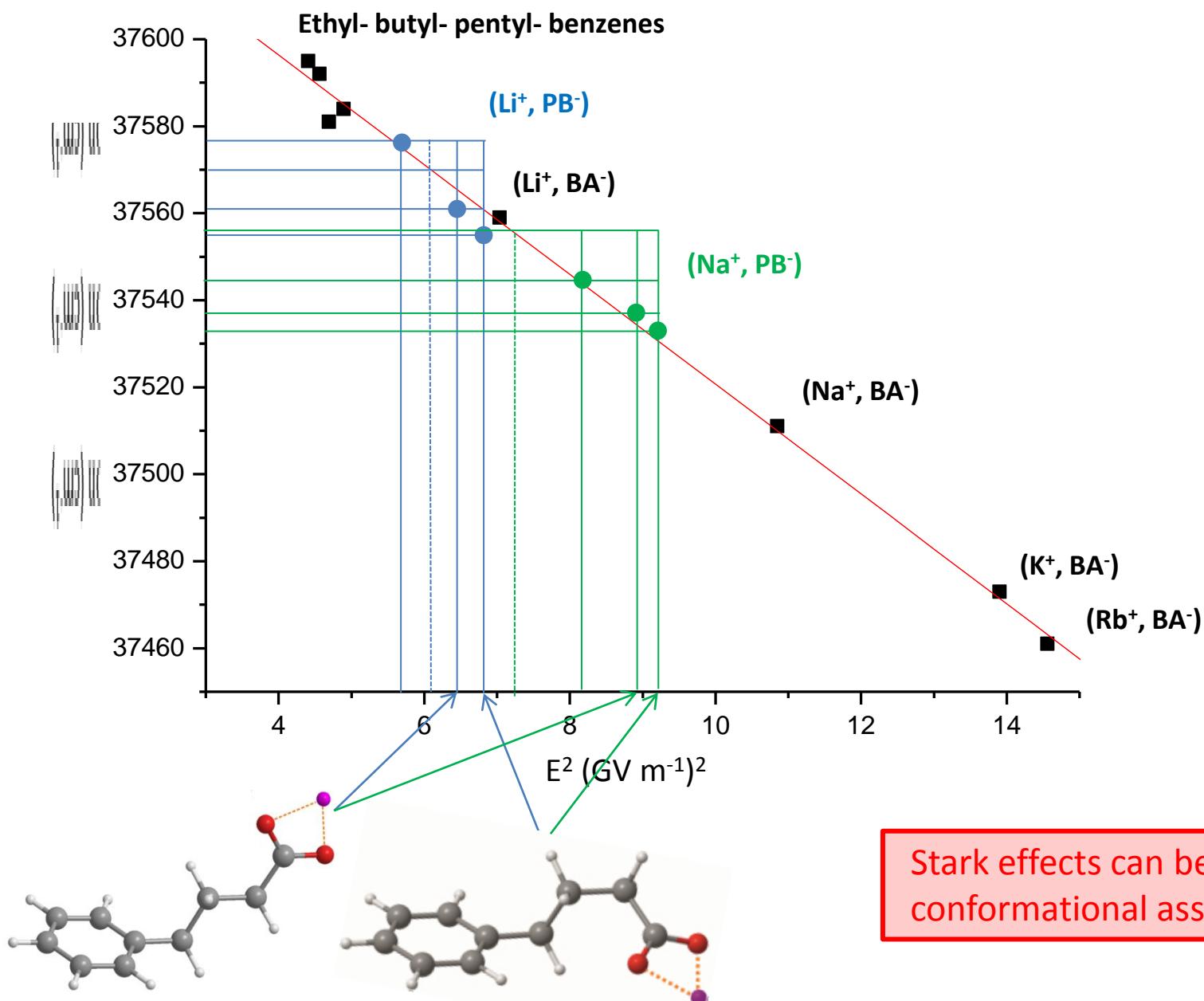
Lithium (4)
(I)



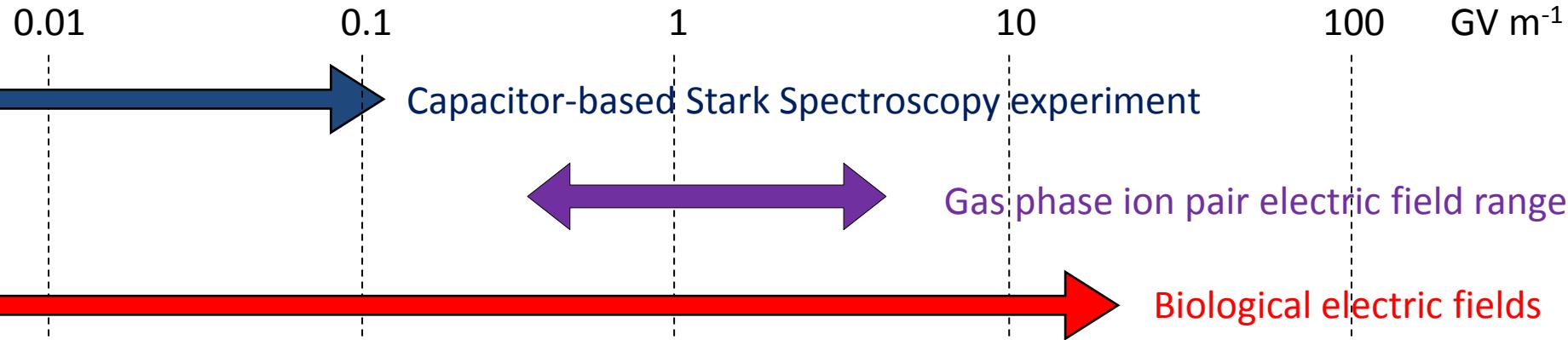
Stark
splitting



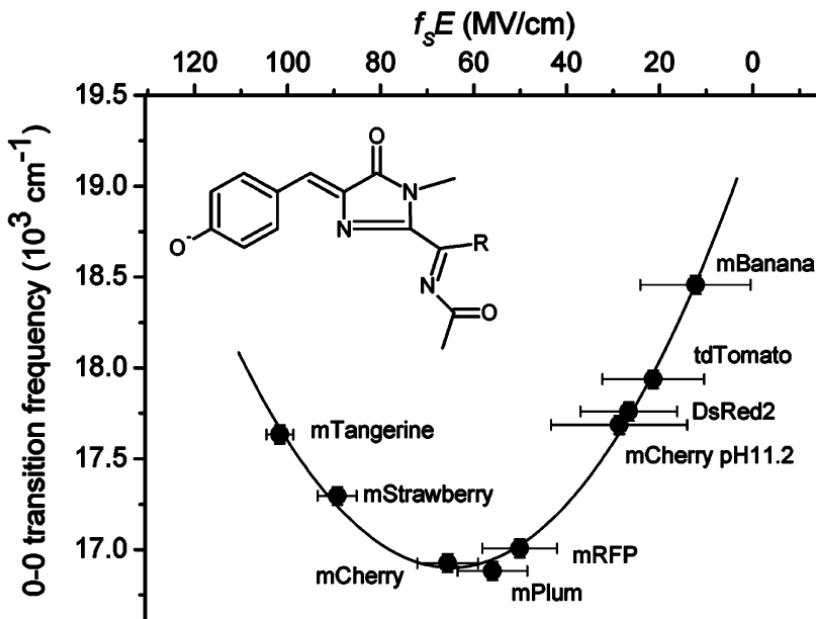
III. Conformational assignment assisted by Stark effects



III. Electric field measurement

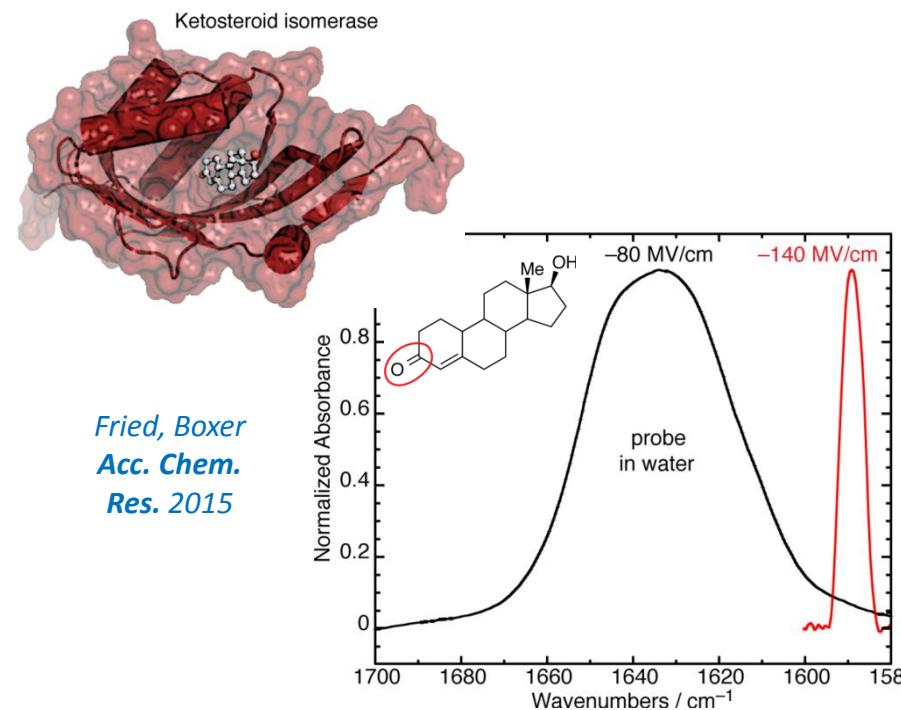


Electronic Stark effect (ESE) in red fluorescent proteins

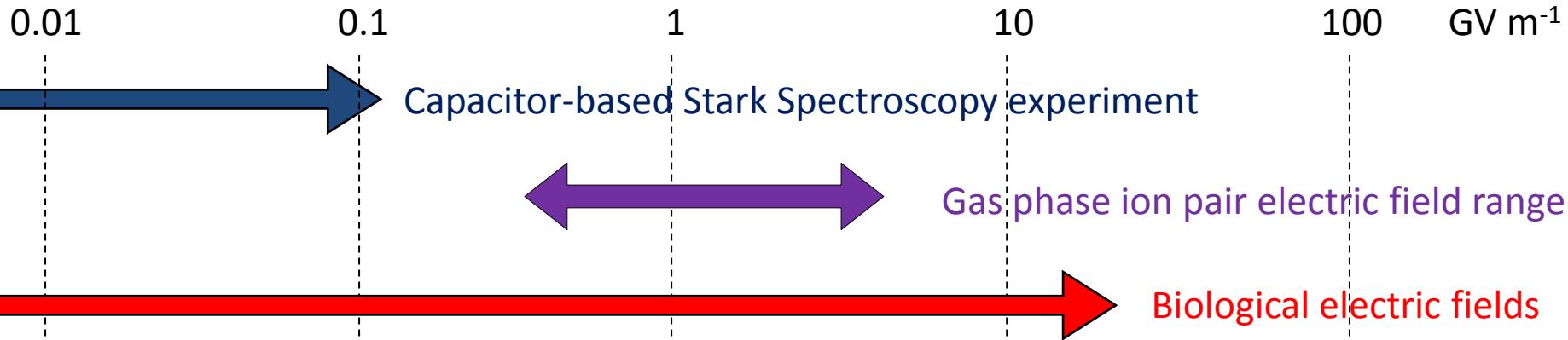


Drobizhev, Tillo, Makarov, Hughes,
Rebane JPCB 2009

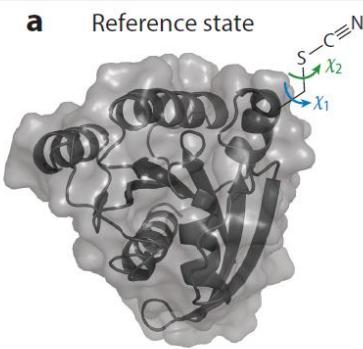
Vibrational Stark effect (ESE) to characterize ligand binding



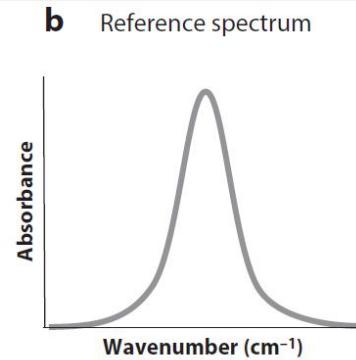
III. Electric field measurement



a Reference state

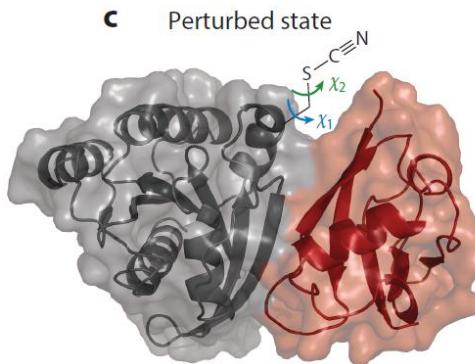


b Reference spectrum

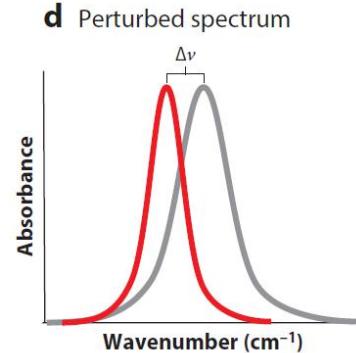


Slocum, Webb *Annu. Rev. Phys. Chem.* 2018

c Perturbed state



d Perturbed spectrum



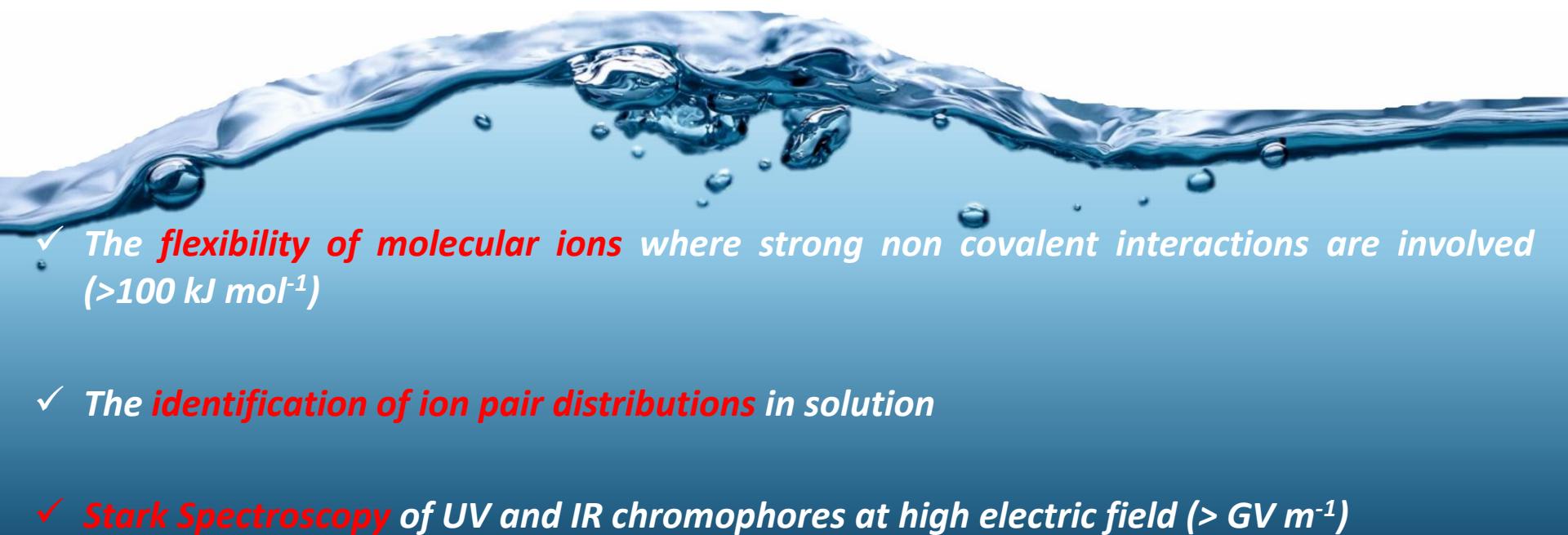
Local electric field measurement using a vibrational Stark effect (VSE) probe, provided a calibration

Future direction: characterization of VSE at high electric field

Conclusions

Neutral ion pairs are original objects in the gas phase that can be investigated by the arsenal of laser spectroscopic techniques

Gas phase ion pairs enable us to tackle various issues from an original point of view:

- 
- ✓ The flexibility of molecular ions where strong non covalent interactions are involved ($>100 \text{ kJ mol}^{-1}$)
 - ✓ The identification of ion pair distributions in solution
 - ✓ Stark Spectroscopy of UV and IR chromophores at high electric field ($> \text{GV m}^{-1}$)

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Postdoc

Thibaut Very



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students

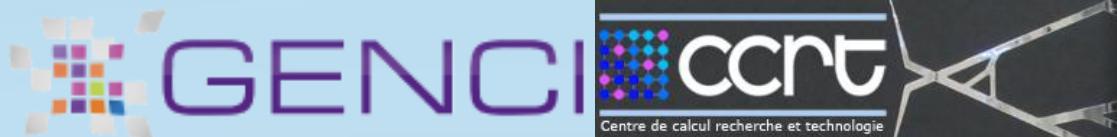


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TGCC



Biomolecular structures group



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