

IR and UV Spectroscopy of Neutral Ion Pairs

Eric Gloaguen

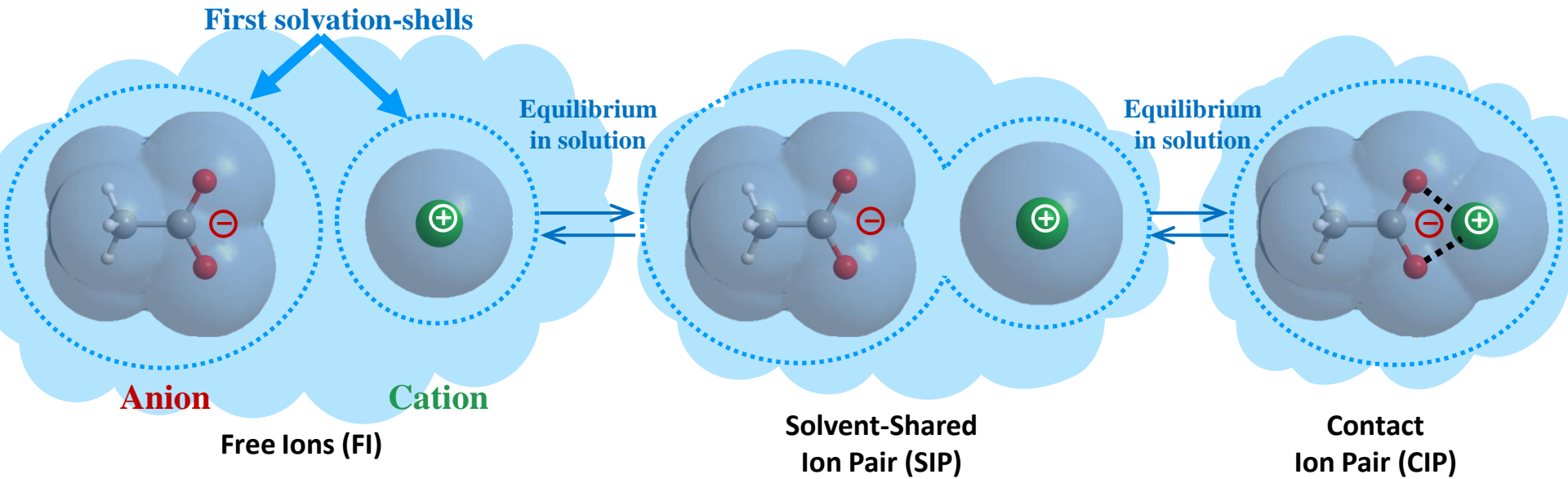


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Paris-Saclay University, France*



*Spectroscopy and Dynamics of Molecules and Clusters (SDMC) 2019
Shimla, 21-24 february 2019*

I. Ion pairing in solution



→ Pairing is favored by

- low permittivity
- low temperature
- high ion concentration
- high ionic charges

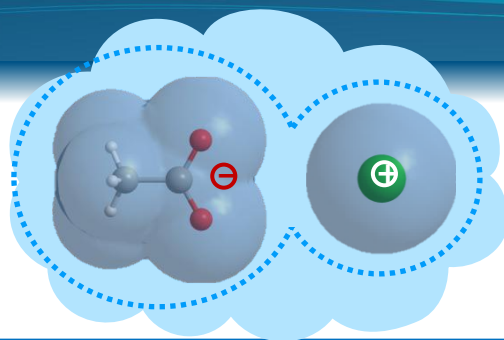
→ Ion pairs are found in sea water, aerosols, biological media...

→ Characterization of the ion pair distribution is challenging:

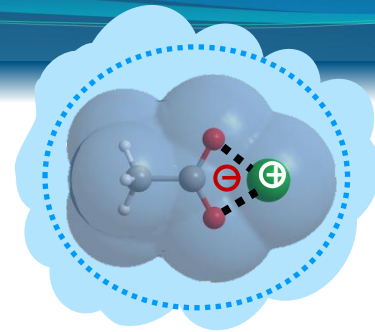
- Co-existence of all types of pairs and free ions
- Short lifetimes

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

SIP/SSIP



?



CIP

2008

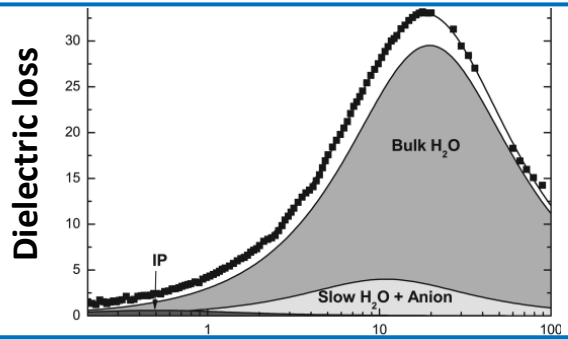
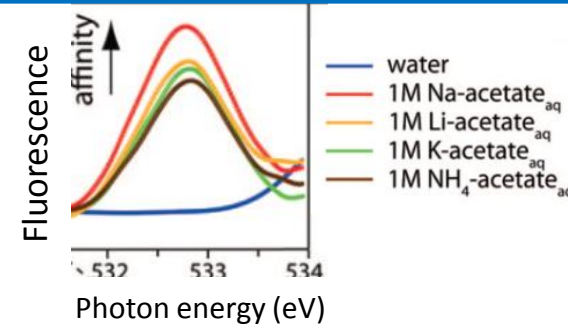
CIPs detected by X-ray absorption spectroscopy (XAS) in liquid microjet

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)



2012

SIPs detected by dielectric relaxation spectroscopy in solution

SIP >> CIP
à 1M

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

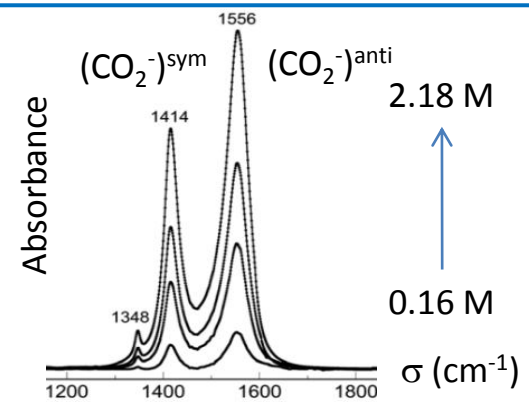
2014

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

SIP >> CIP à 1M

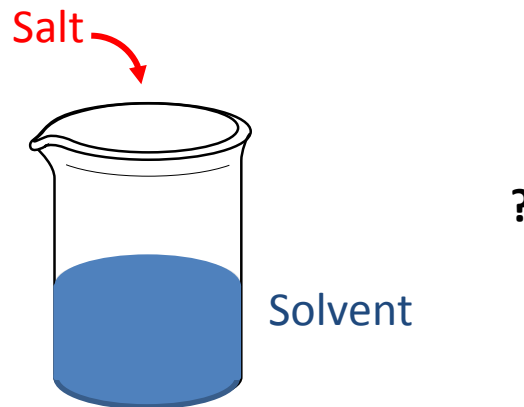
No CIP exists in solution at any concentration

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



I. Motivations

→ ***Supramolecular objects in electrolyte solutions are poorly known***



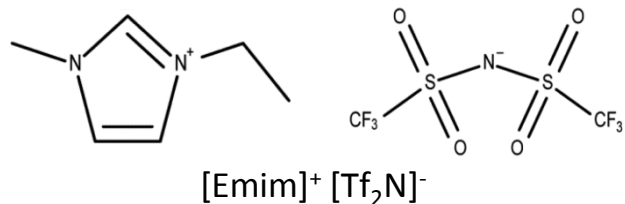
→ ***Experiments in solution document macroscopic effects, but struggle to characterize individual objects***

→ ***In turn, mass-selective and conformer-selective techniques in the gas phase can provide a characterization of these objects***

I. Neutral ion pairs in the gas phase

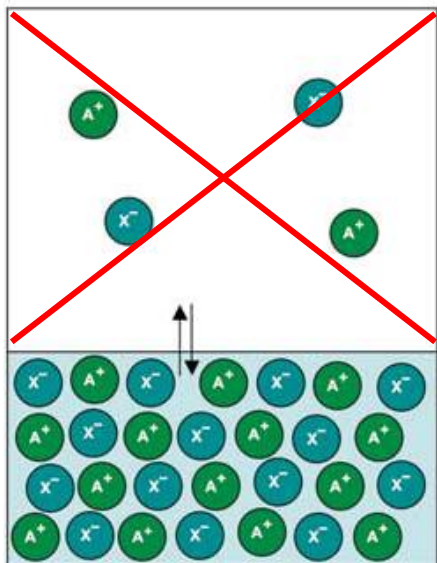
→ **Alkali Halides**
Heating

→ **Ionic liquid**



Distillation at 300°C under reduced pressure to purify ionic liquids

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



Microwave spectroscopy

Matrix isolation spectroscopy

Laser spectroscopy in molecular jet

*Groen Kovacs **Vibrational spectroscopy** (2010)*

*Dedonder-Lardeux, Grégoire, Juvet, Martrenchard, Solgadi **Chemical Review** (2000)*

Photoelectron spectroscopy

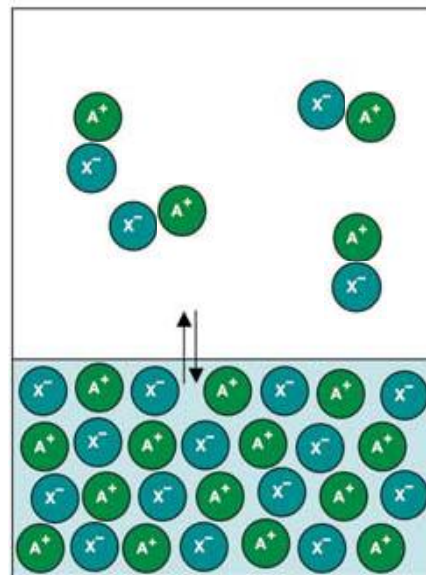
*Strasser, Goulay, Kelkar, Maginn, Leone **JPCA** (2007)*

He droplet IR spectroscopy

*Obi, Leavitt, Raston, Moradi, Flynn, Vaghjiani, Boatz, Chambreau, Douberly **JPCA** (2013)*

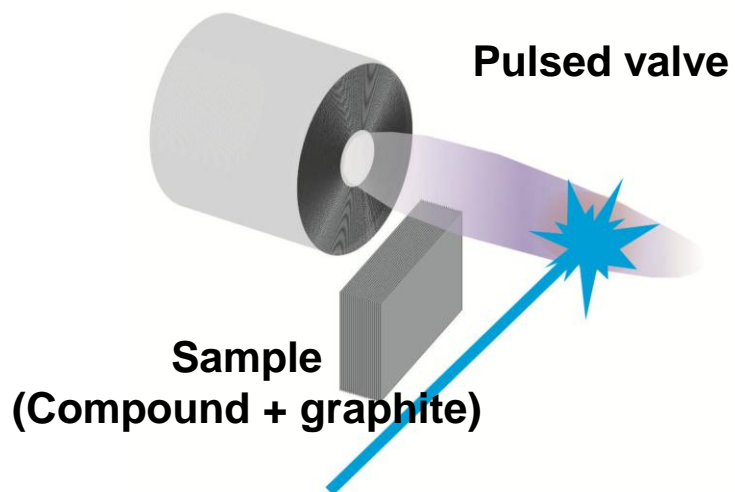
Double resonance IR/UV spectroscopy

*Cooper, Zolot, Boatz, Sporleder, Stearns **JPCA** (2013)*



II. Gas phase experiment

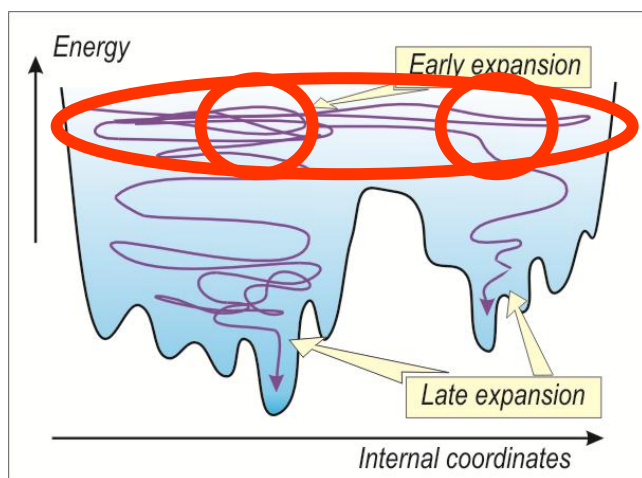
Vacuum chamber



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

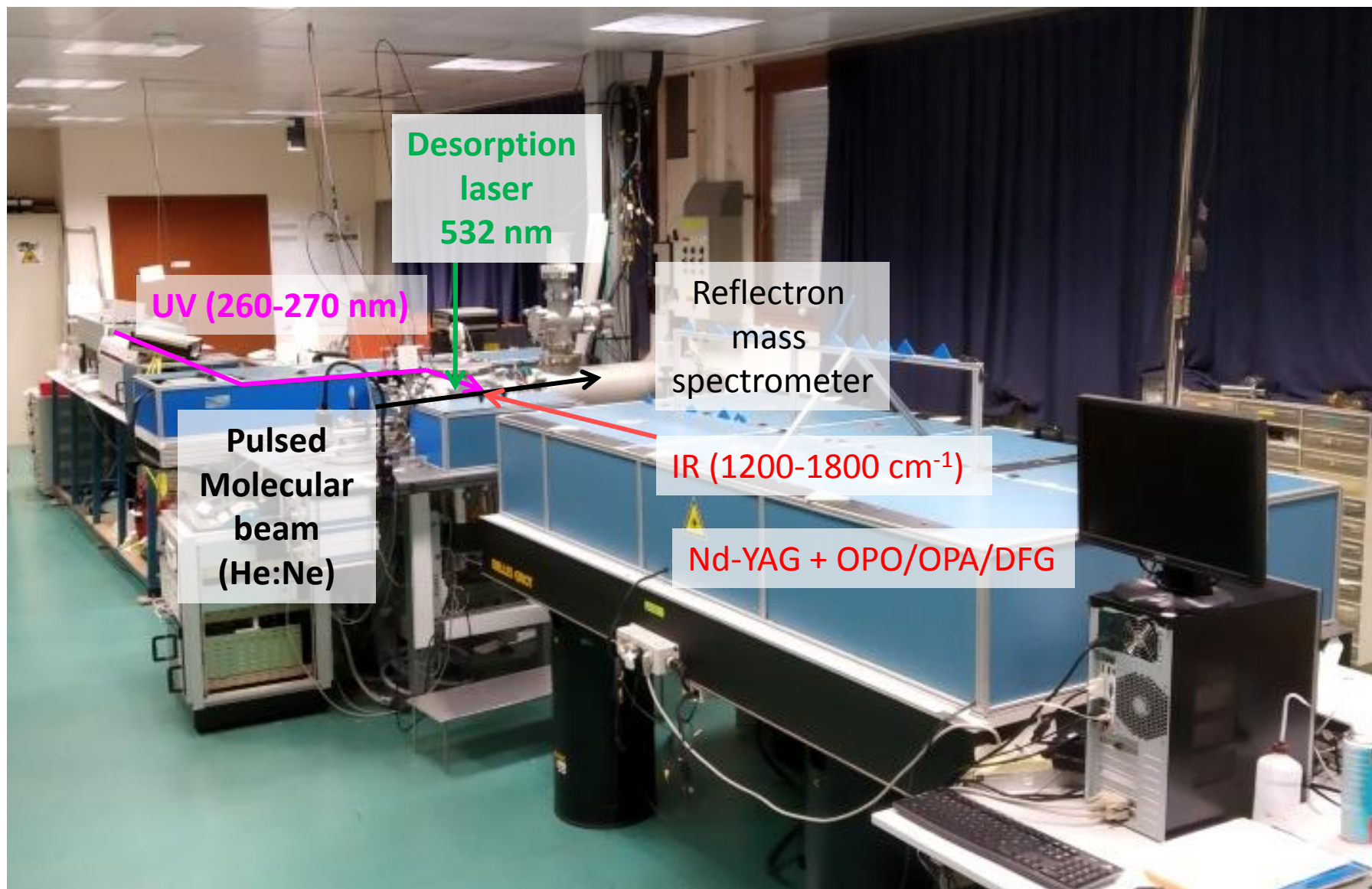
- Laser desorption: hot species in the gas phase with limited fragmentation

- 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

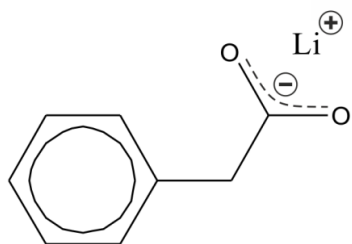
II. Gas phase experiment



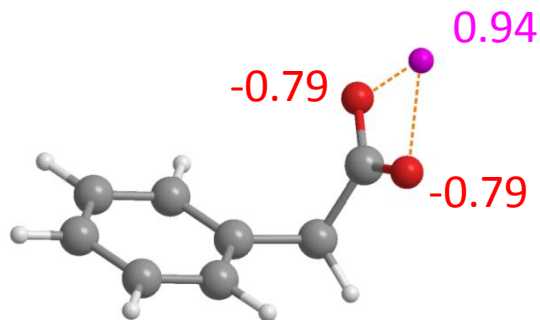
II. $(\text{Li}^+, \text{PA}^-)_g$

IR/UV double resonance spectroscopy

→ conformation-selectivity

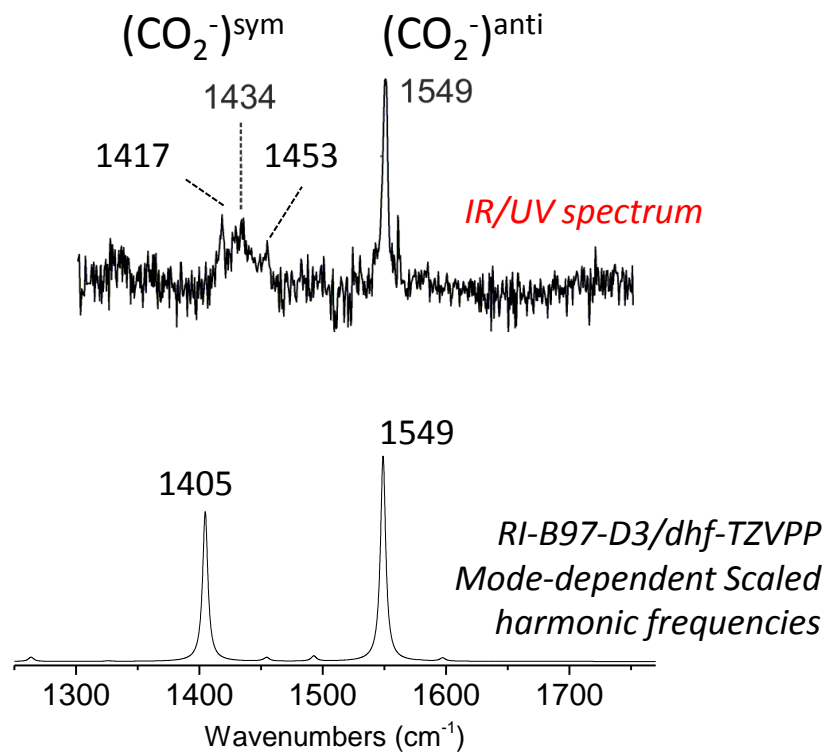
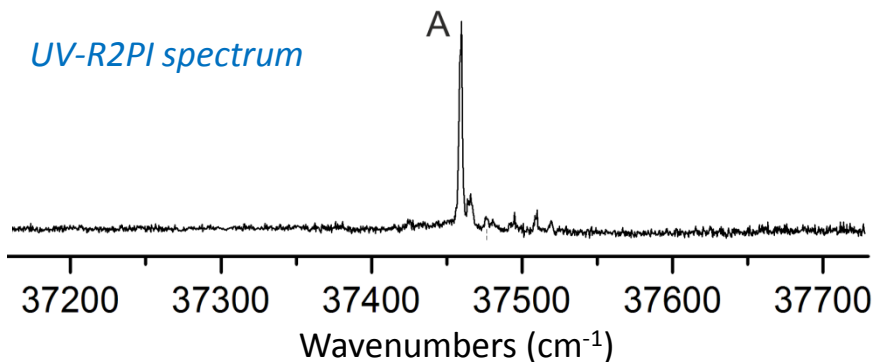


Lithium Phenylacetate
(Li^+ , PA^-)



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

UV-R2PI spectrum



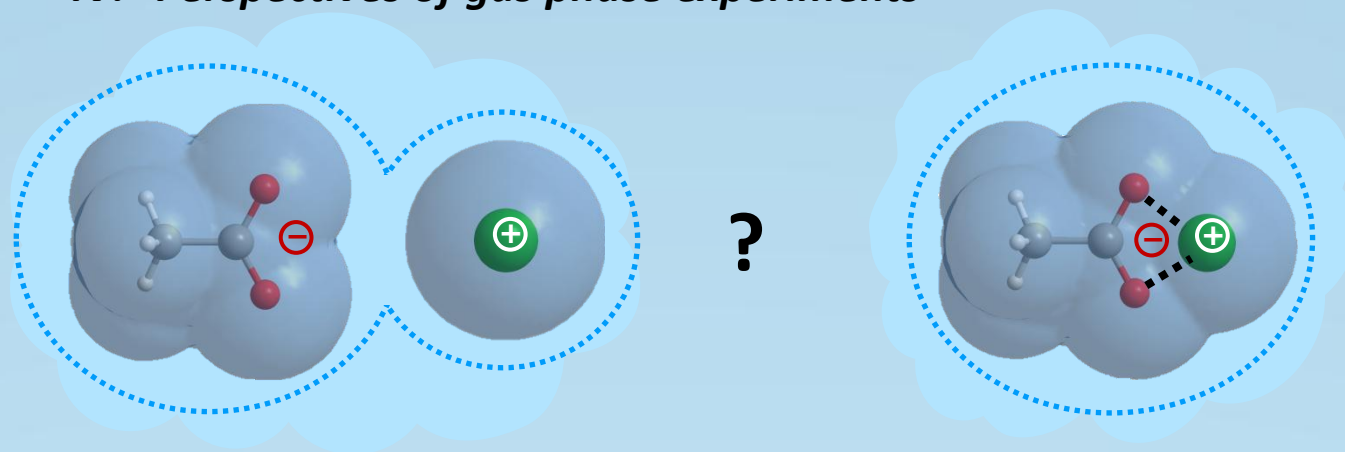
Gas phase ion pairs
are formed in our
experiment

I. Introduction

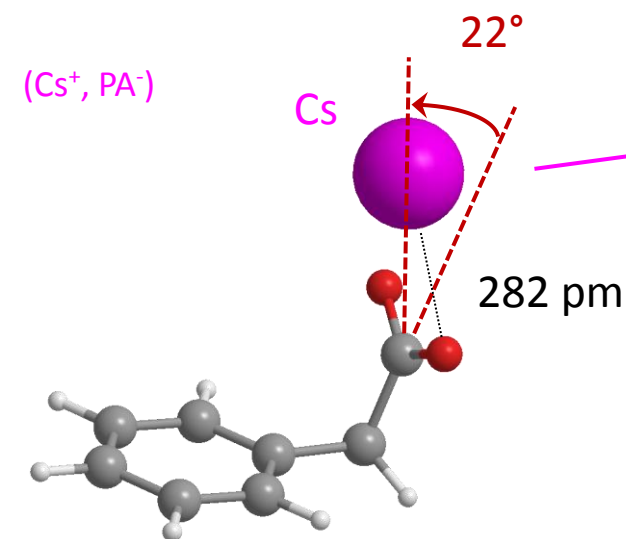
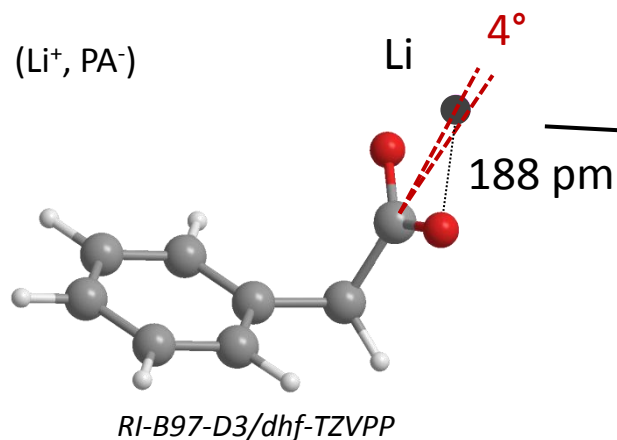
II. IR spectroscopy

III. UV spectroscopy

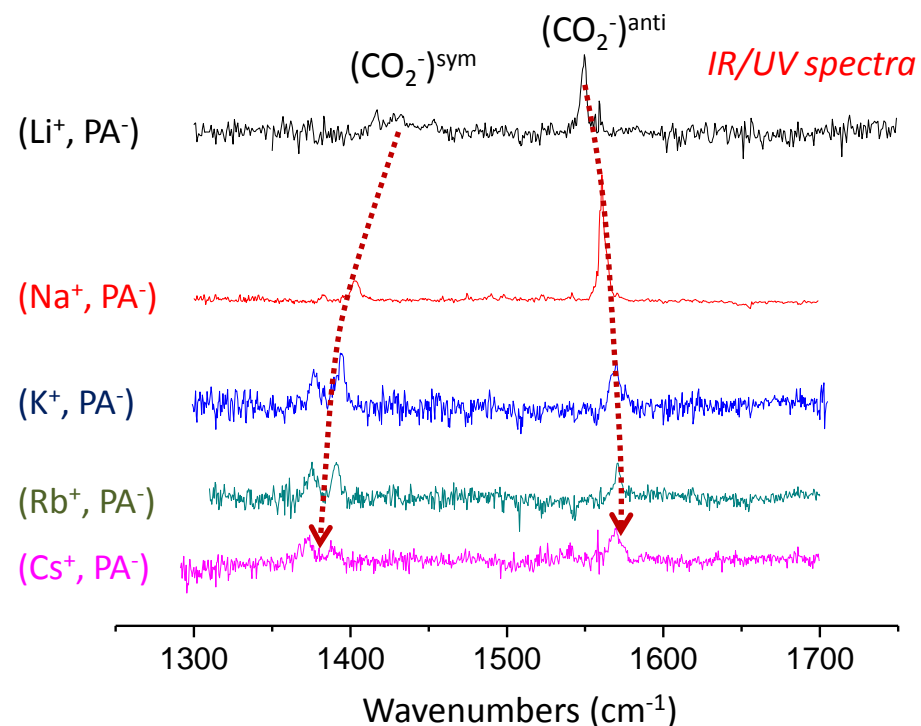
IV. Perspectives of gas phase experiments



II. IR spectroscopy of $(M^+, PA^-)_g$



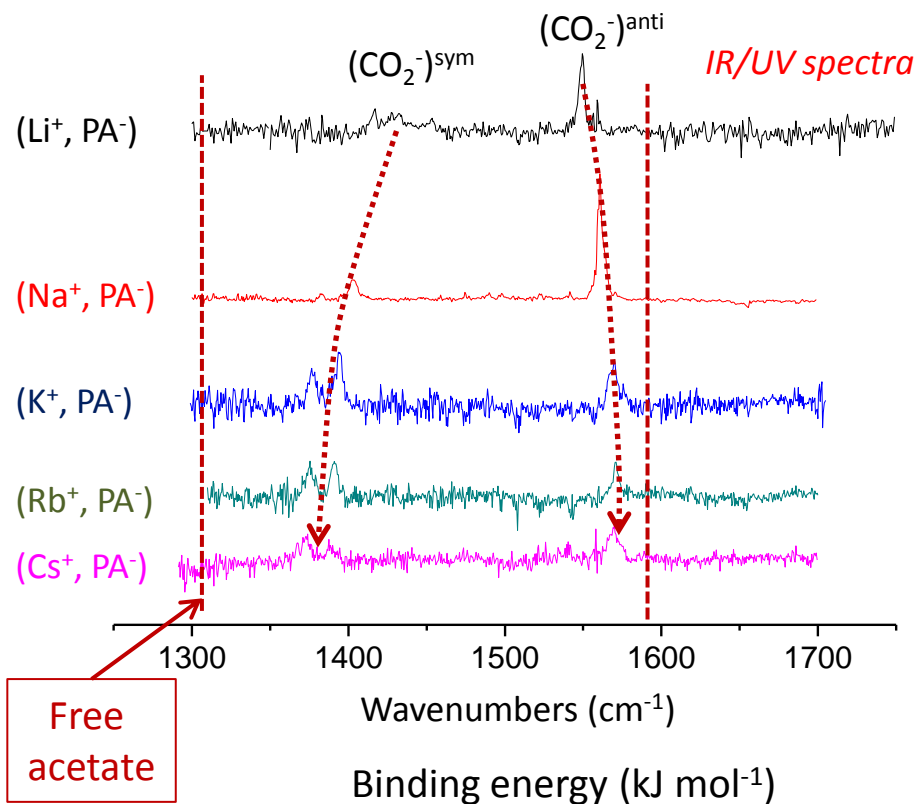
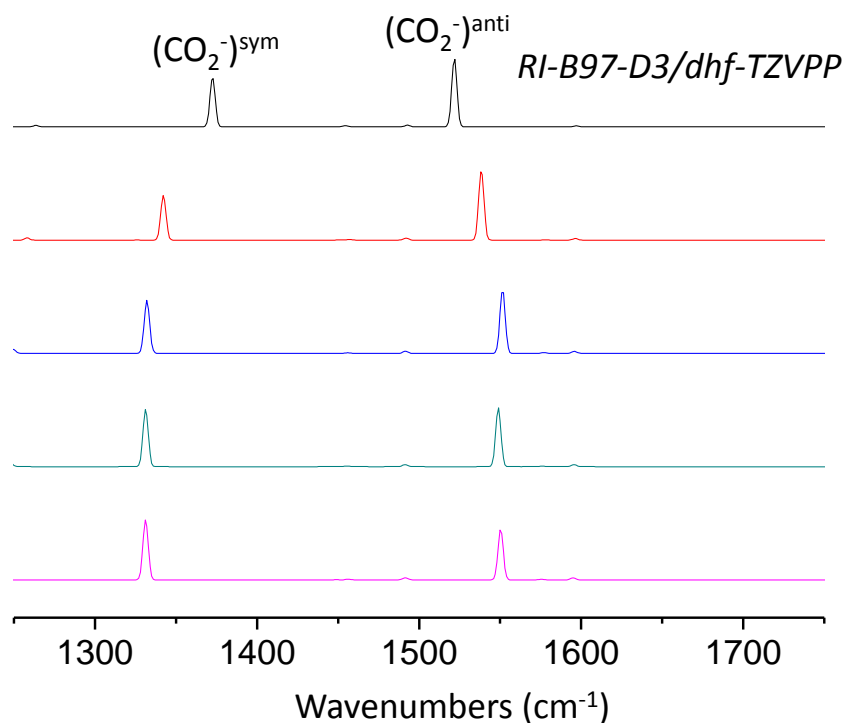
→ Large cations are attracted out-of-the carboxylate plane by the phenyl ring.



→ The multiplicity of the $(CO_2^-)^{sym}$ stretch reveals a coupling with the torsion around the C-CO₂⁻ bond

→ The (CO_2^-) stretch splitting ($\Delta\nu^{a-s}$) increases along the alkali series, and results mainly from the increase of the cation-anion distance.

II. IR spectroscopy of $(M^+, PA^-)_g$



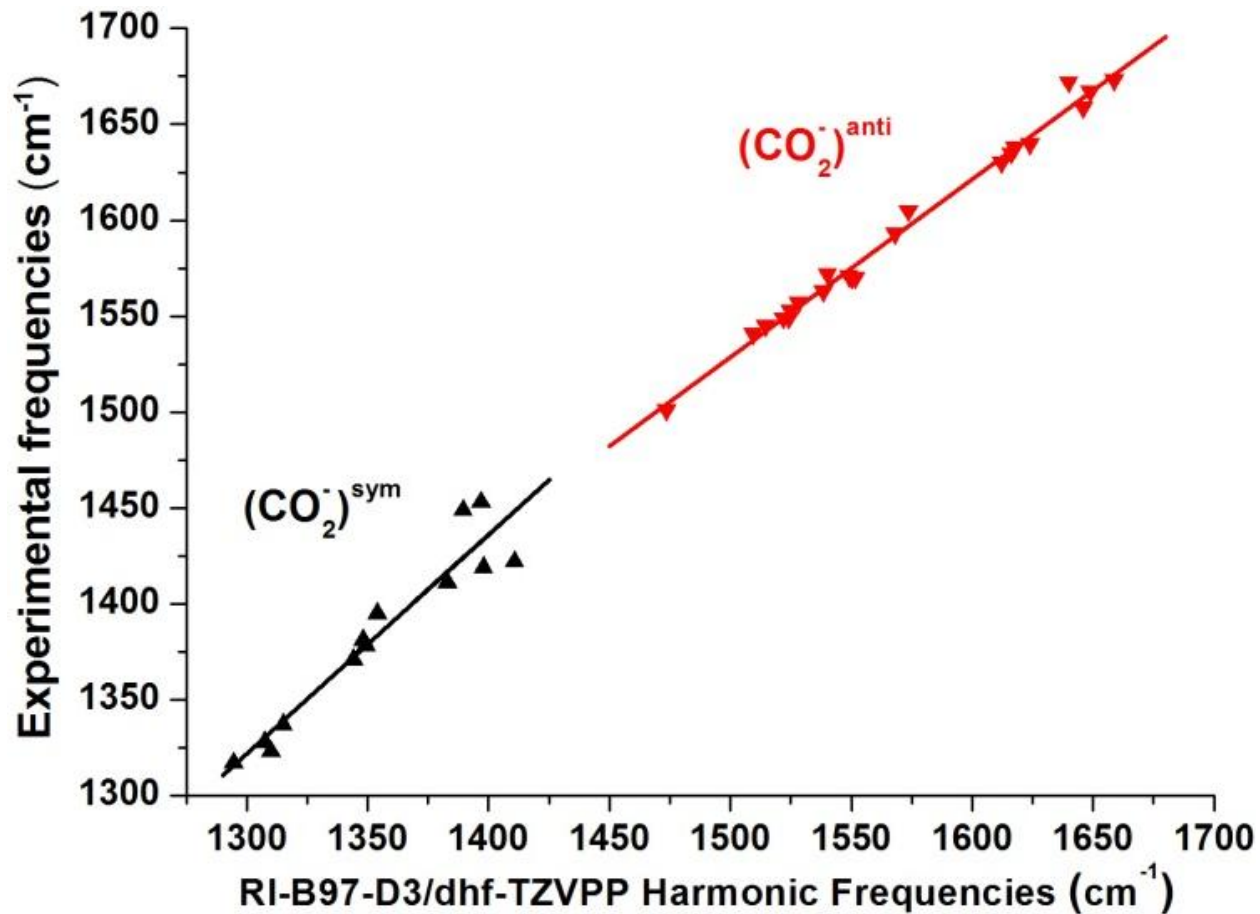
→ Calculations beyond the harmonic approximation are needed to reproduce the multiplicity of the $(CO_2^-)^{sym}$ stretch

→ The (CO_2^-) stretch splitting (Δv^{a-s}) increase is consistent with a weakening of the cation-anion interaction along the alkali series

(M^+, PA^-)	Binding energy (kJ mol ⁻¹)
(Li^+, PA^-)	643
(Na^+, PA^-)	582
(K^+, PA^-)	496
(Rb^+, PA^-)	491
(Cs^+, PA^-)	475

*BSSE-corrected-Full-CCSD(T)/dhf-TZVPP//
RI-B97-D3/dhf-TZVPP*

III. Accuracy of mode-dependent scaled vibrational frequencies



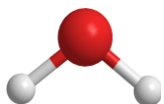
Standard deviations = Error between experiment and theory

15 cm⁻¹ for CO₂^{sym} stretch

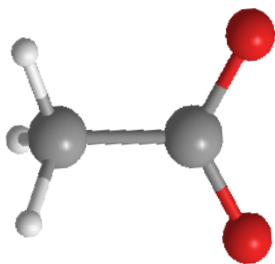
5 cm⁻¹ for CO₂^{anti} stretch

III. Conformational exploration of ion pairs in solution

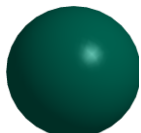
Biased Monte-Carlo Exploration
at the polarizable force field level (AMOEBA)



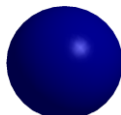
Explicit water molecules



Acetate



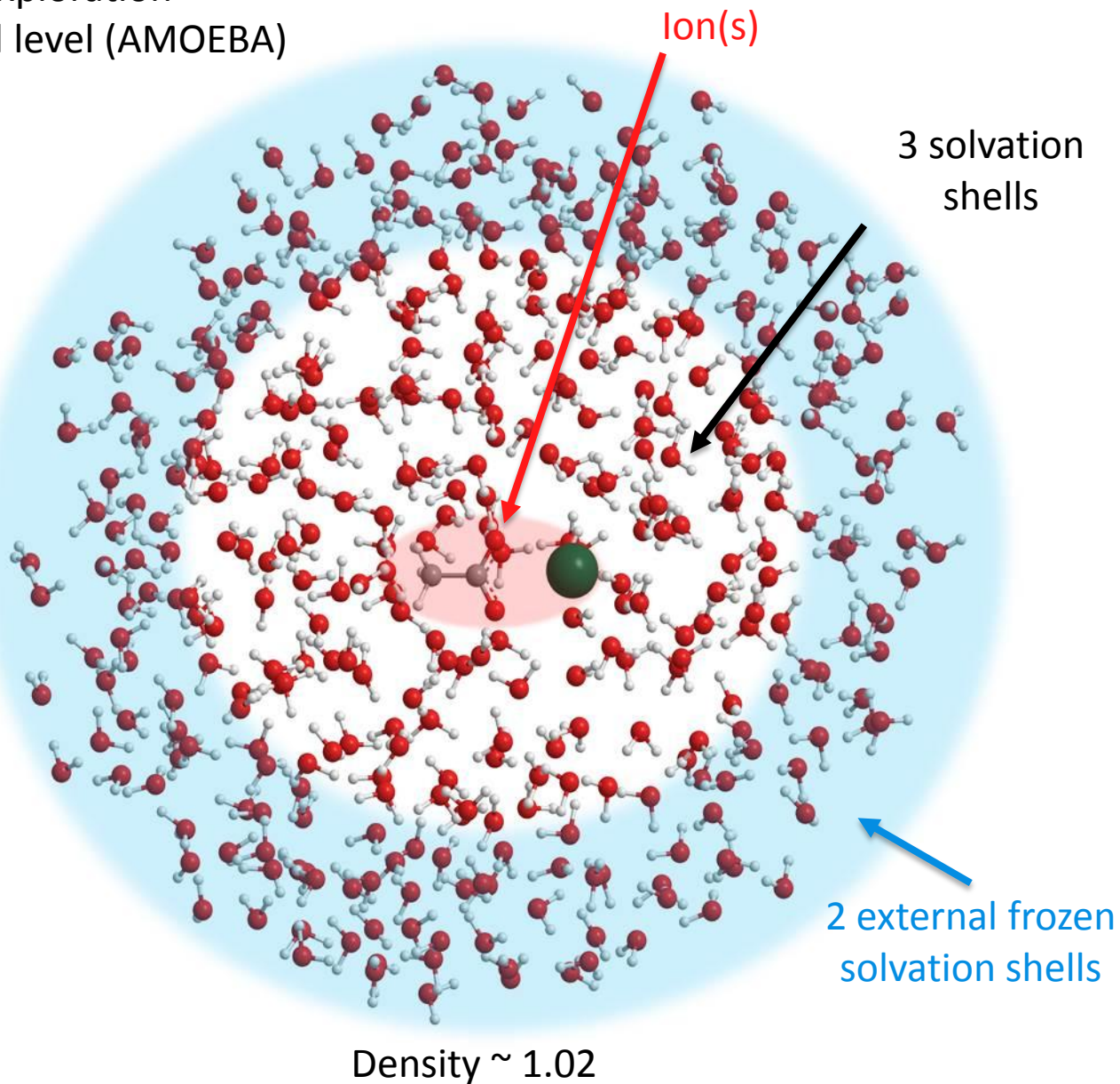
K⁺



Na⁺

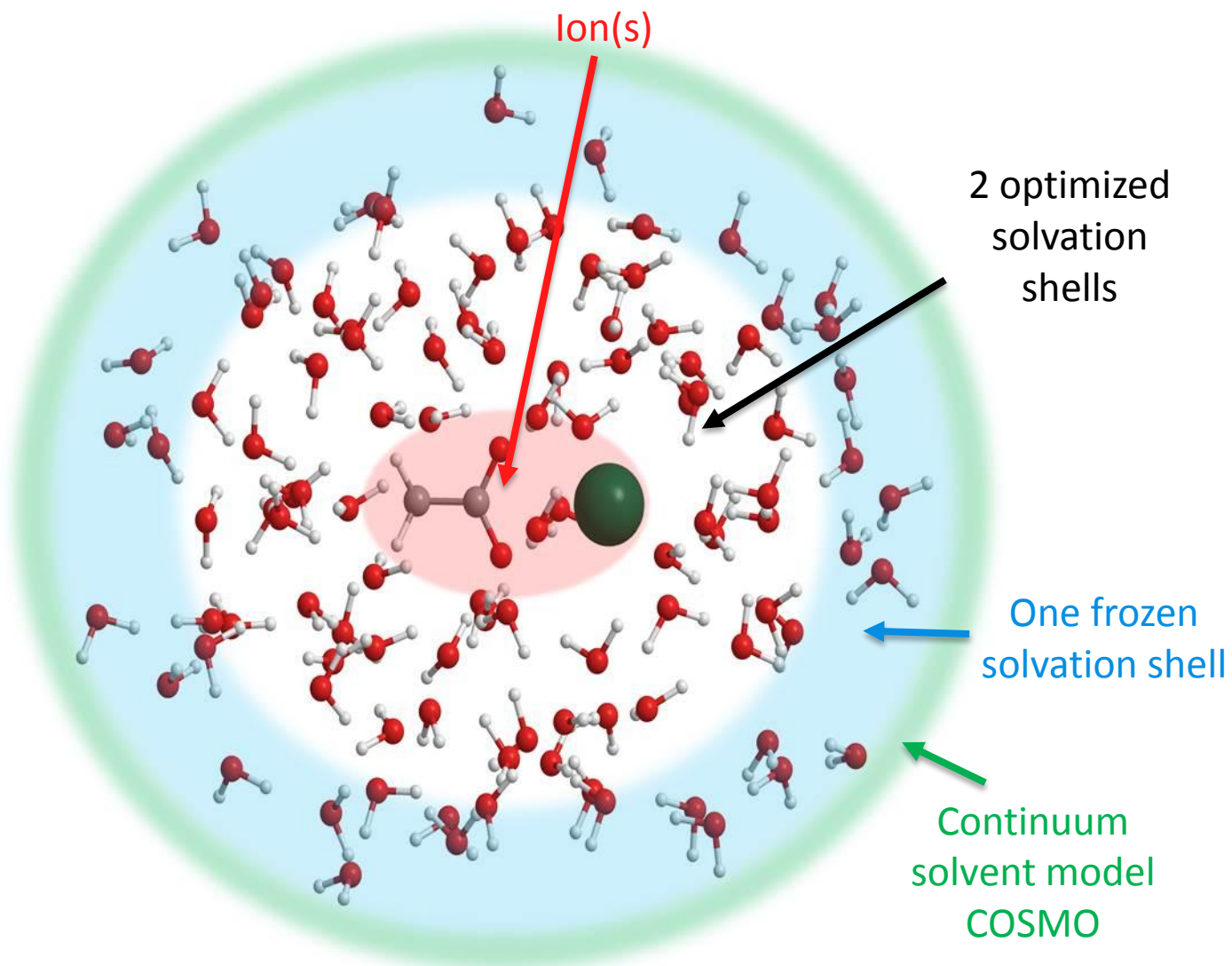


Li⁺



III. Geometry optimization – Frequency calculations

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



$\text{AcO}^- \text{M}^+ n\text{H}_2\text{O} ; n \in [100;140]$

Density ~ 1.02

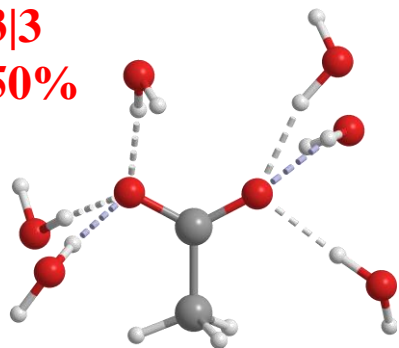
Concentration $\sim 0.4 \text{ mol L}^{-1}$

III. Free acetate ions

Carboxylate Coordination

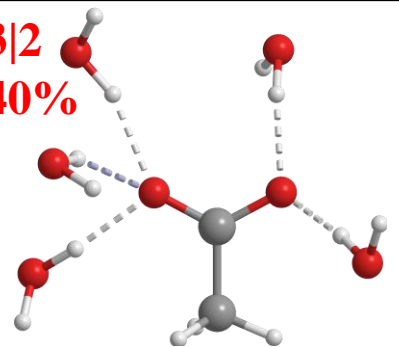
3|3

50%



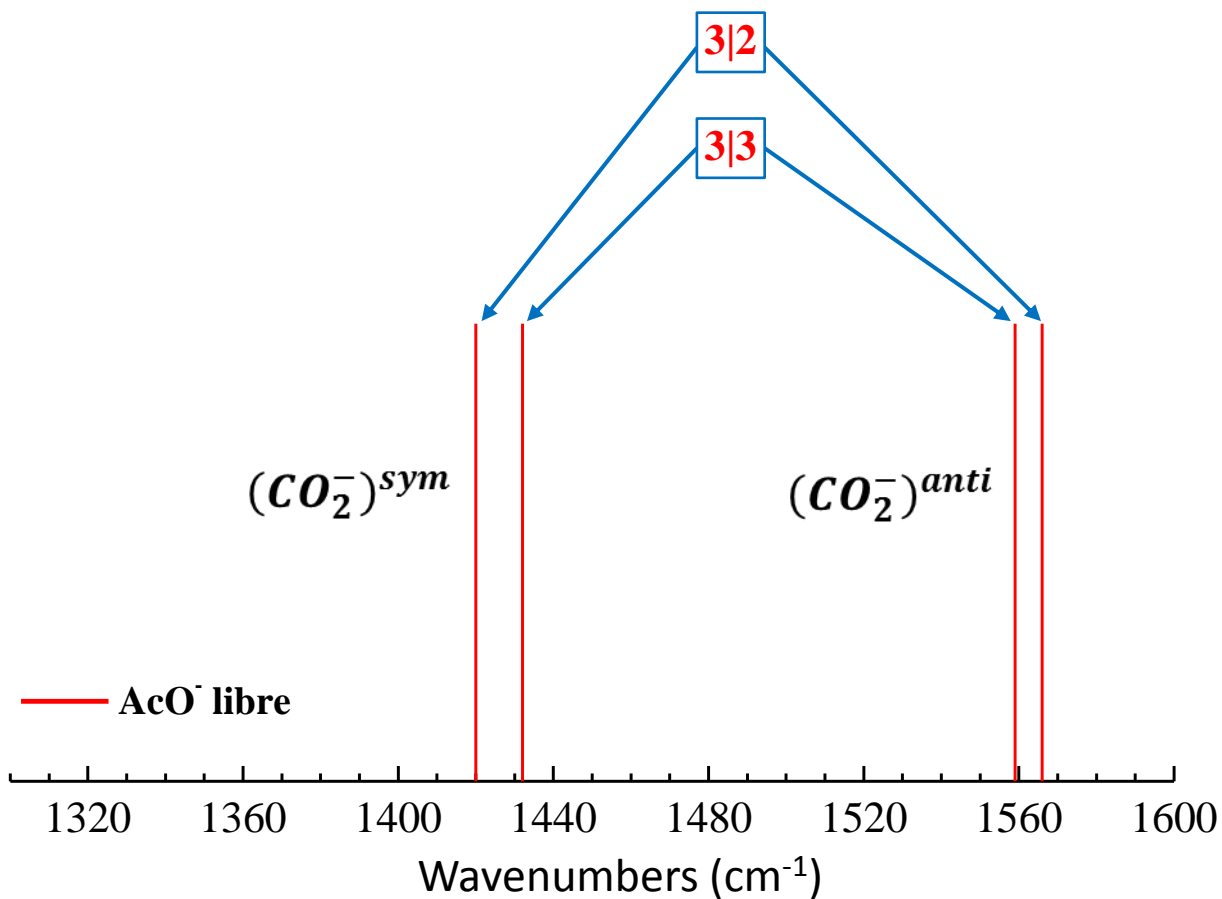
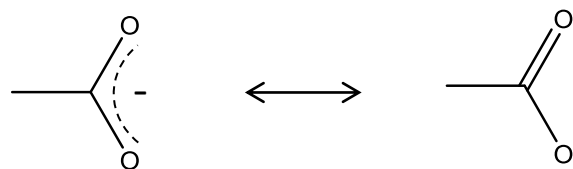
3|2

40%



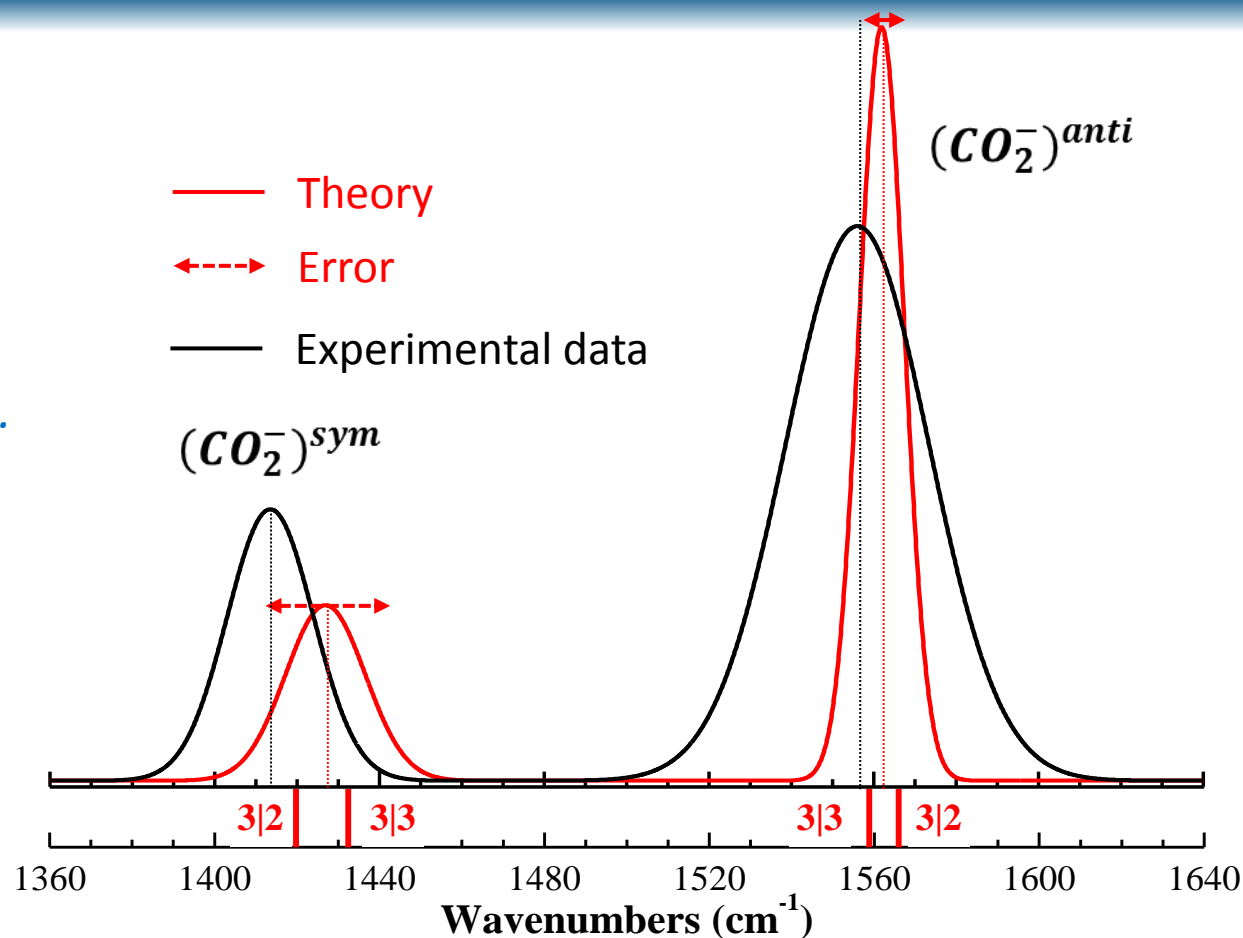
Structures
extracted from
larger clusters

The splitting Δv^{a-s} increases when the carboxylate group is in an increasingly asymmetric environment



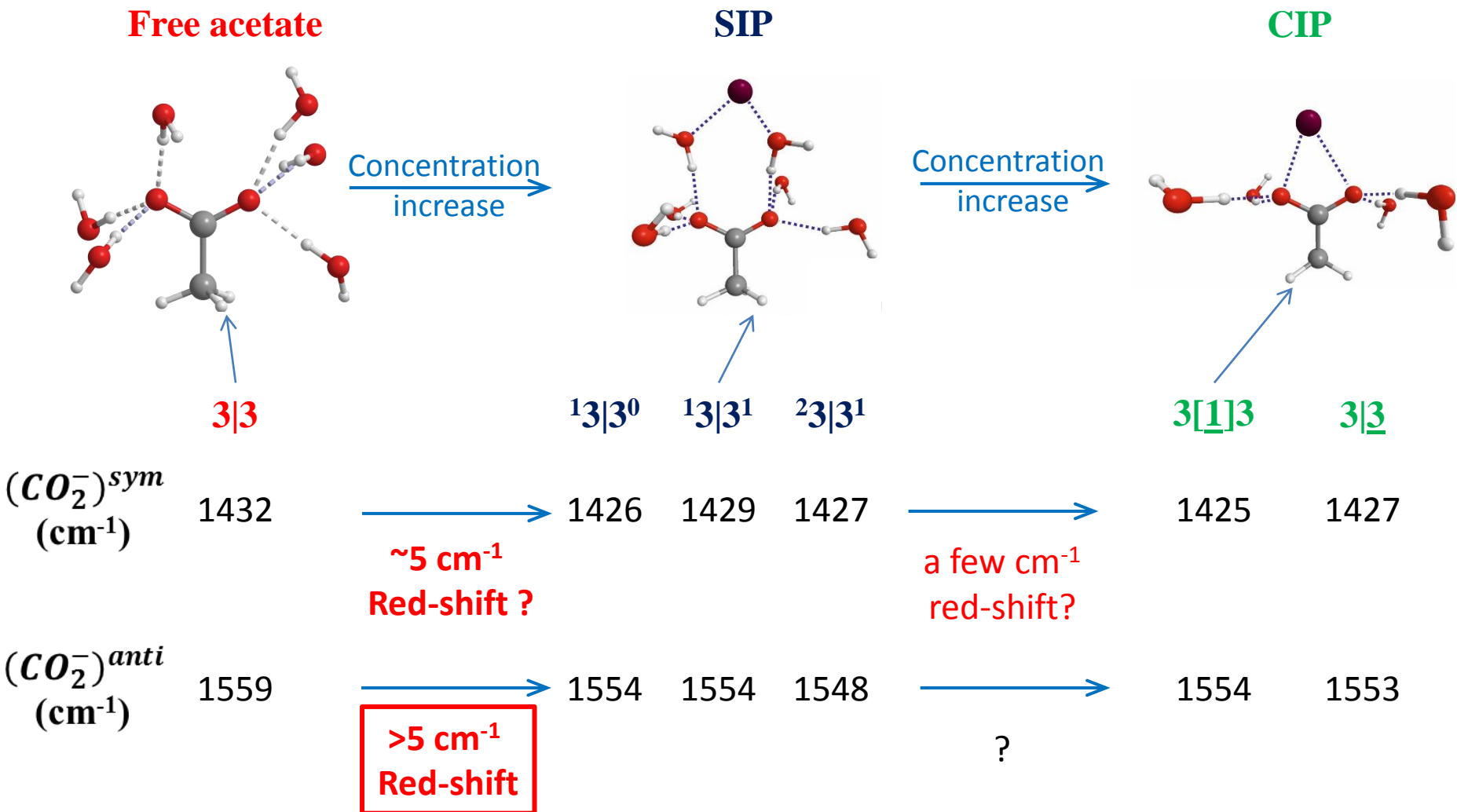
III. Free acetate ions

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)

III. Theoretical spectra of ion pairs: case of 3|3 structures with sodium



→ The formation of SIPs induces a red-shift of the $(CO_2^-)^{anti}$ stretch transition

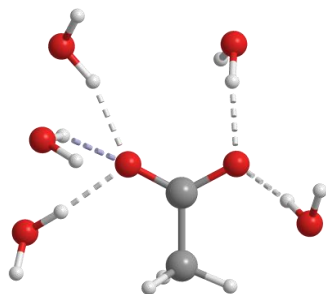
→ CIPs do not have necessarily a vibrational signature very different from SIPs

III. Theoretical spectra of ion pairs: case of 3|2 structures with sodium

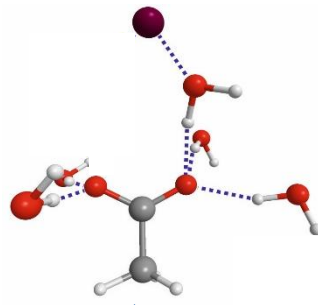
Free acetate

SIP

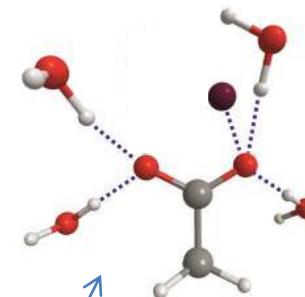
CIP



Concentration
increase →



Concentration
increase →



3|2

13|2⁰ 12|3⁰

3|2 3|2

$(CO_2^-)^{sym}$
(cm⁻¹)

1420

→

1421

1415

→

1429

1416

a few cm⁻¹
red-shift?

?

$(CO_2^-)^{anti}$
(cm⁻¹)

1566

→

1565

1564

→

1568

1573

a few cm⁻¹
red-shift?

~5 cm⁻¹
Blue-shift

→ The formation of CIPs induces a blue-shift of the $(CO_2^-)^{anti}$ stretch transitions

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

**Free
acetate**

SIP

CIP

$(CO_2^-)^{sym}$



**Measurable
red-shift ?**



?

Concentration
increase

Concentration
increase

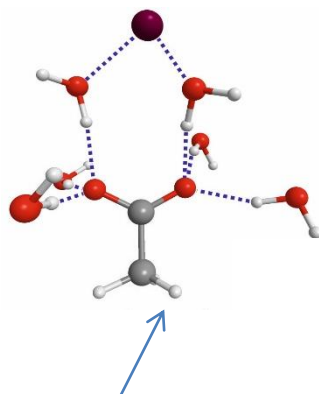
$(CO_2^-)^{anti}$



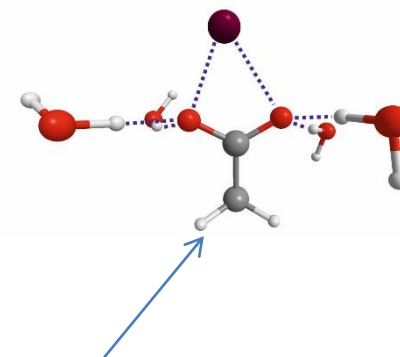
**Measurable
red-shift**



**Measurable
Blue-shift**

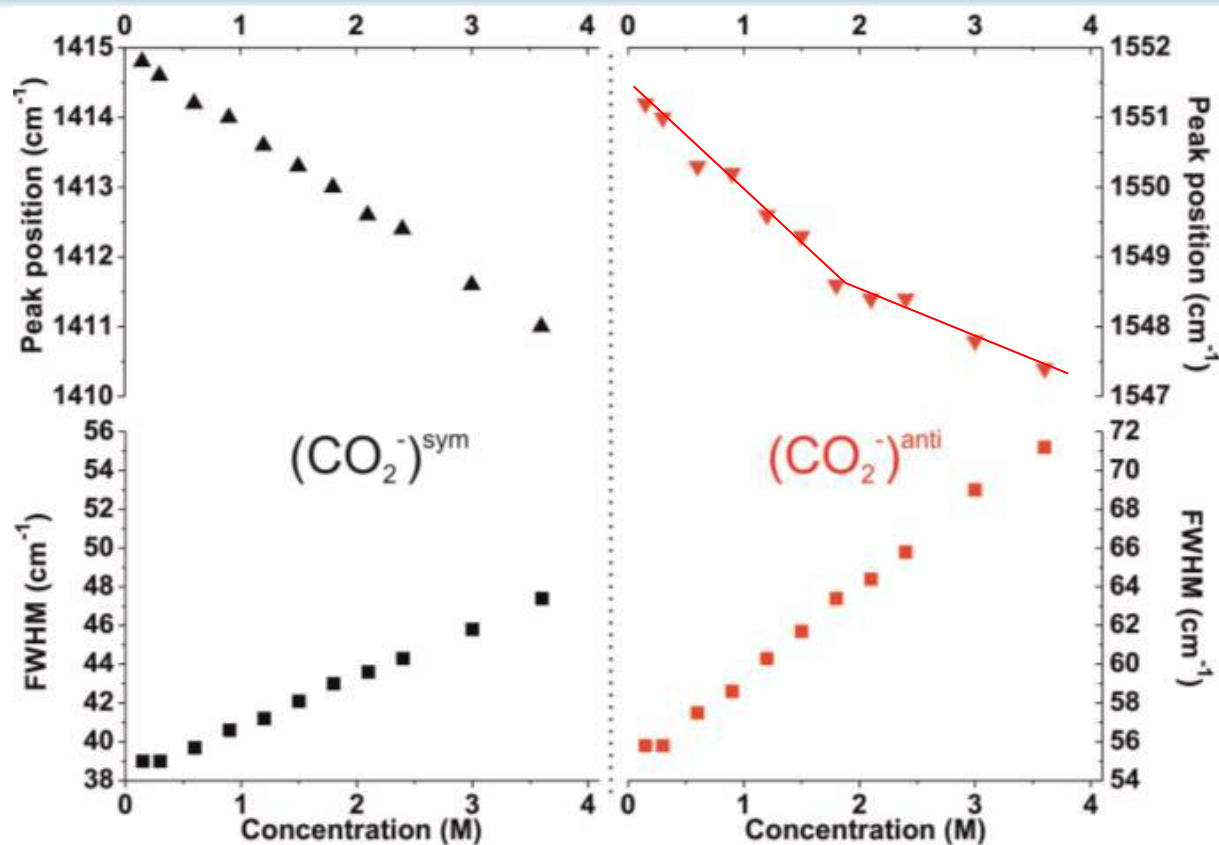
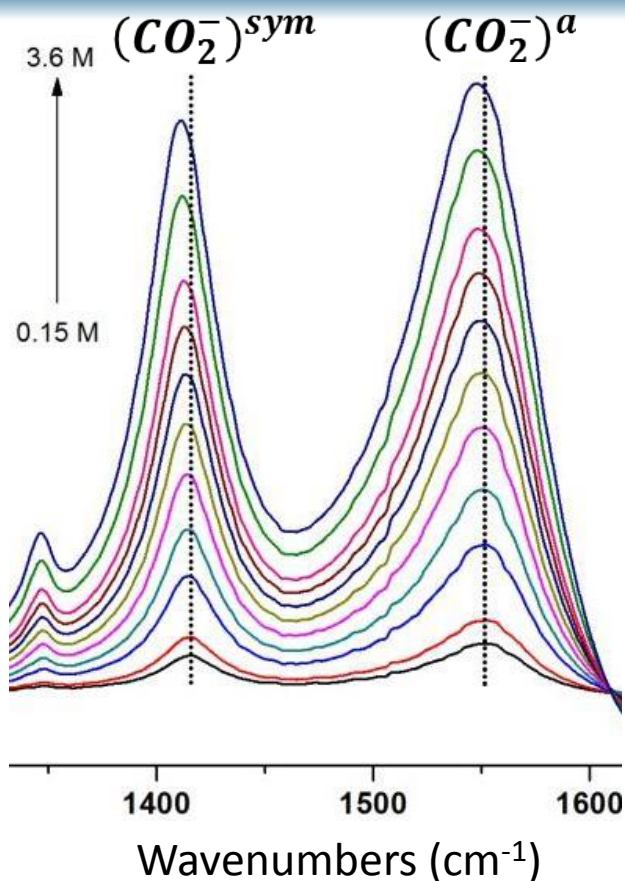


$13|3^0$ $13|3^1$ $23|3^1$



$3[\underline{1}]3$ $3|\underline{3}$

III. Theoretical vs experimental spectra



Habka, Very, Donon, Vaquero-Vara, Tardivel, Charnay-Pouget, Mons, Aitken, Brenner, Gloaguen (submitted)

- The red-shift observed from 0.3 M on both $(\text{CO}_2^-)^{\text{sym}}$ and $(\text{CO}_2^-)^{\text{anti}}$ is assigned to SIP formation
- The change of slope around 2 M is assigned to CIP formation

Conclusions

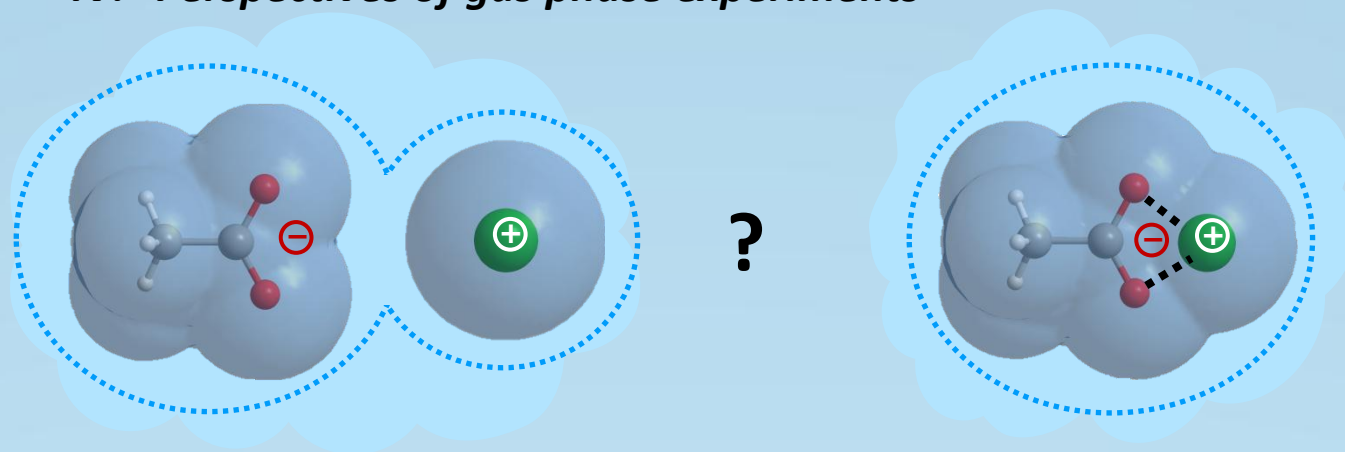
This approach enables us to assign specific supramolecular structures in solution and give typical concentration ranges

I. Introduction

II. IR spectroscopy

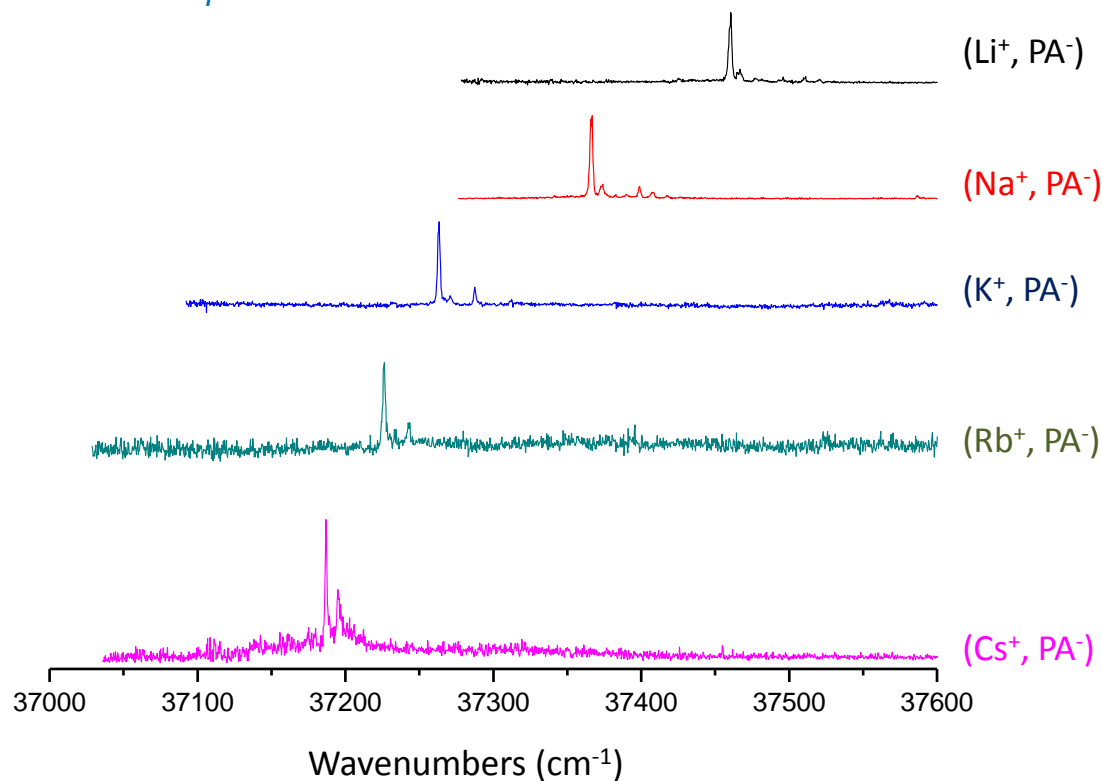
III. UV spectroscopy

IV. Perspectives of gas phase experiments

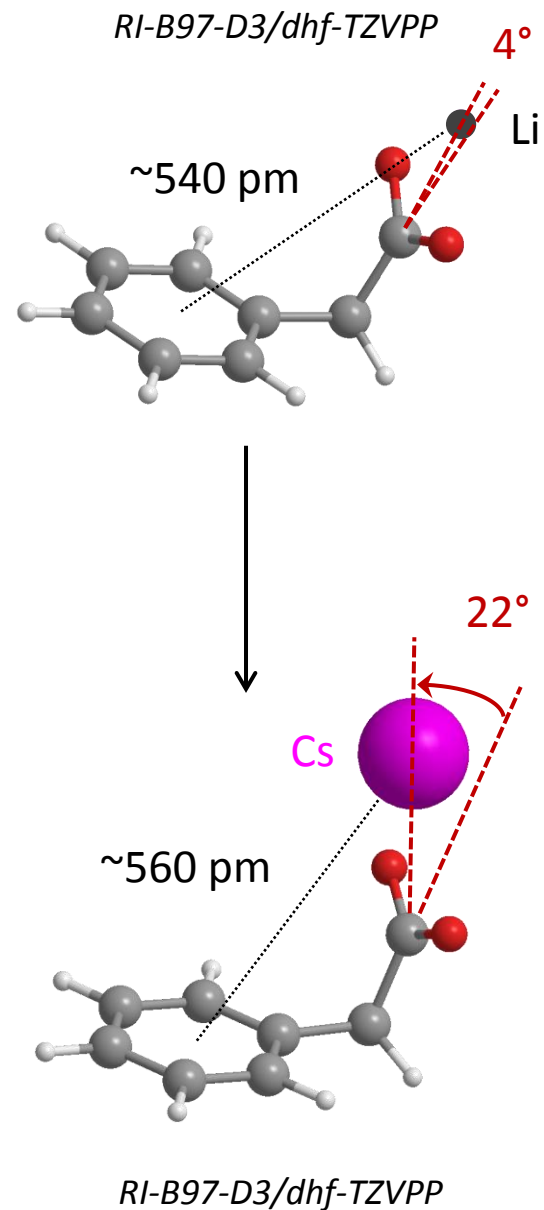


II. UV Spectroscopy of $(M^+, PA^-)_g$

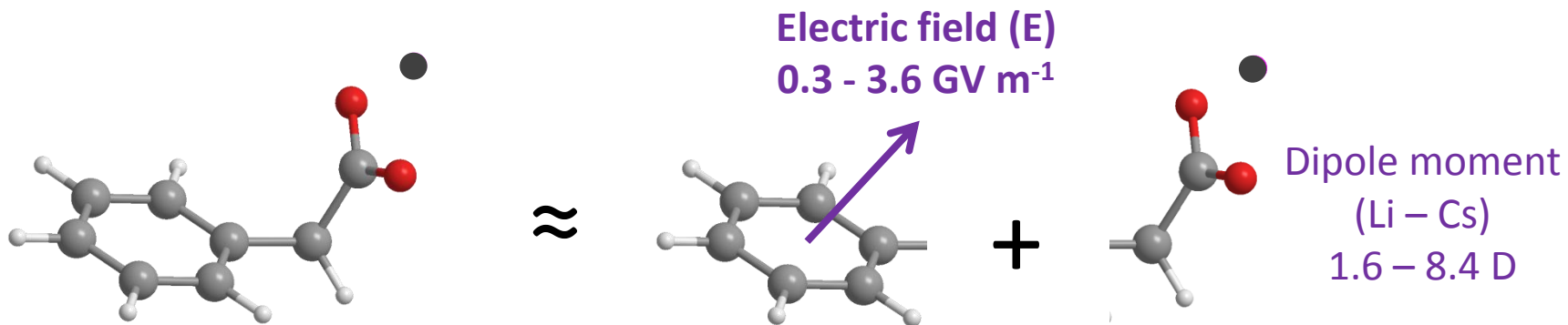
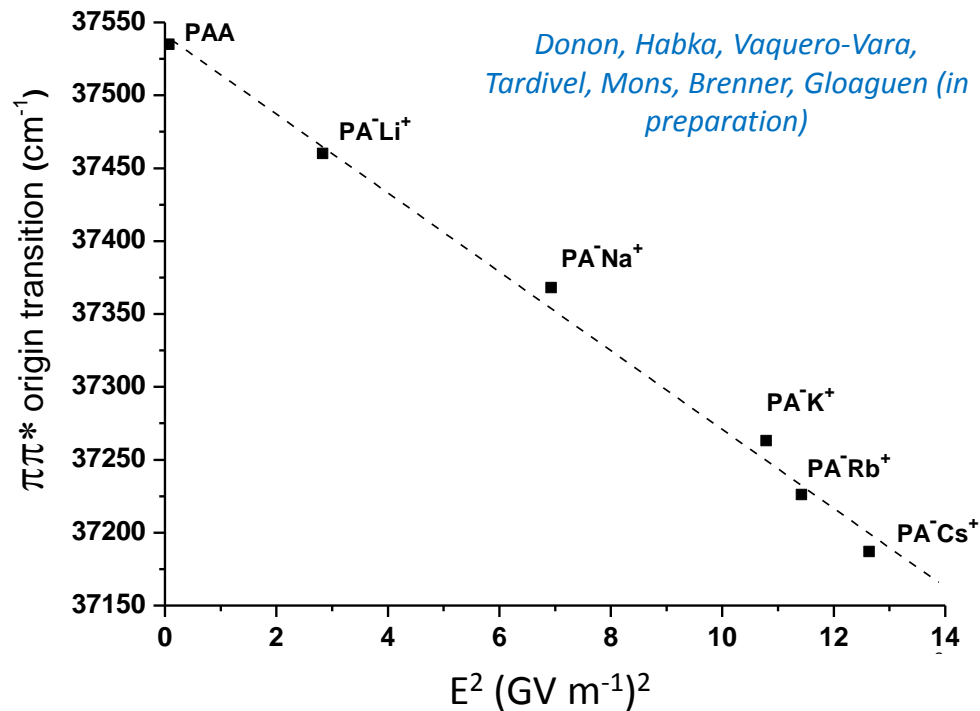
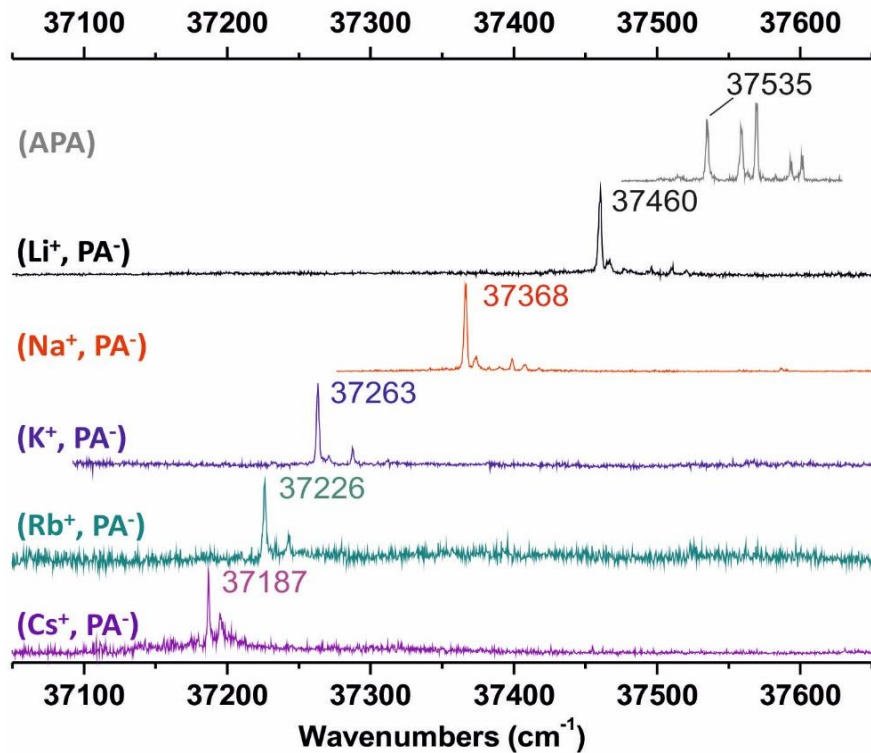
UV-R2PI spectra



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

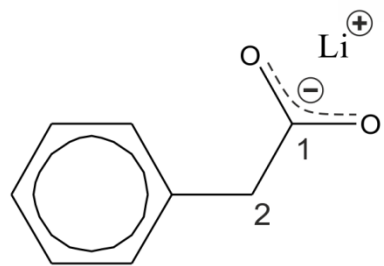


II. Internal Stark effect

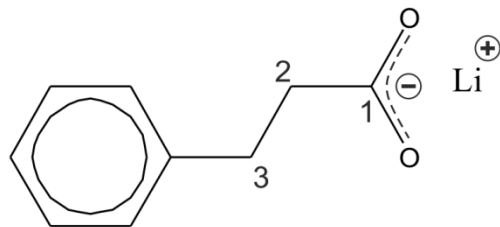


→ Stark spectroscopy of the phenyl ring at very high electric field (up to $\sim 4 \text{ GV m}^{-1}$)

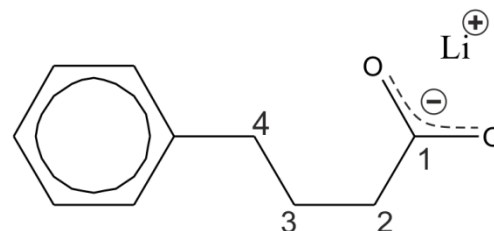
II. Molecular flexibility within ion pairs



Lithium Phenylacetate
(Li⁺, PA⁻)

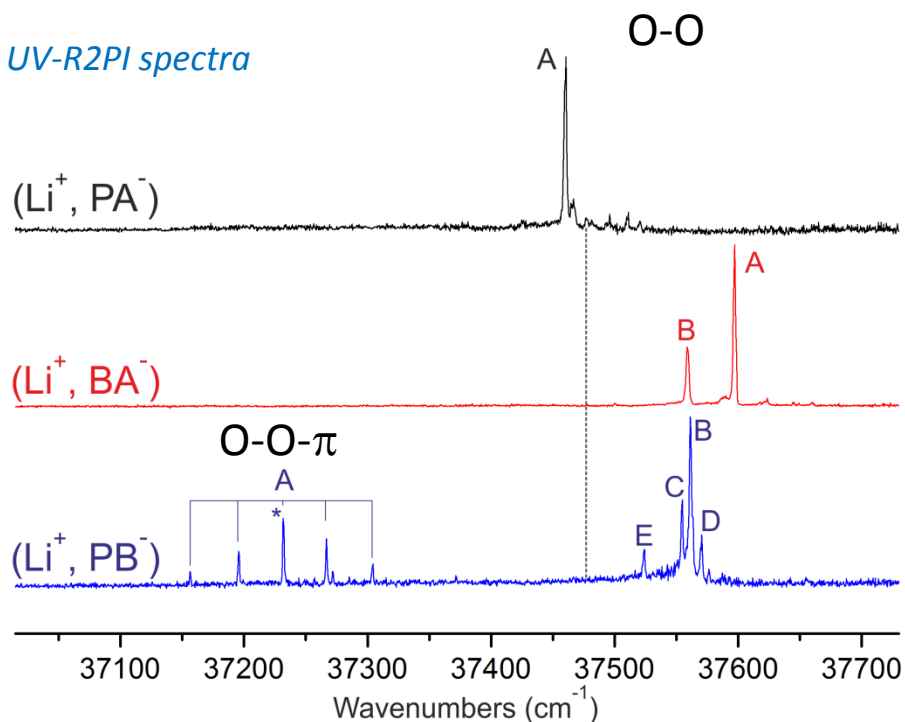


Lithium Benzylacetate
(Li⁺, BA⁻)

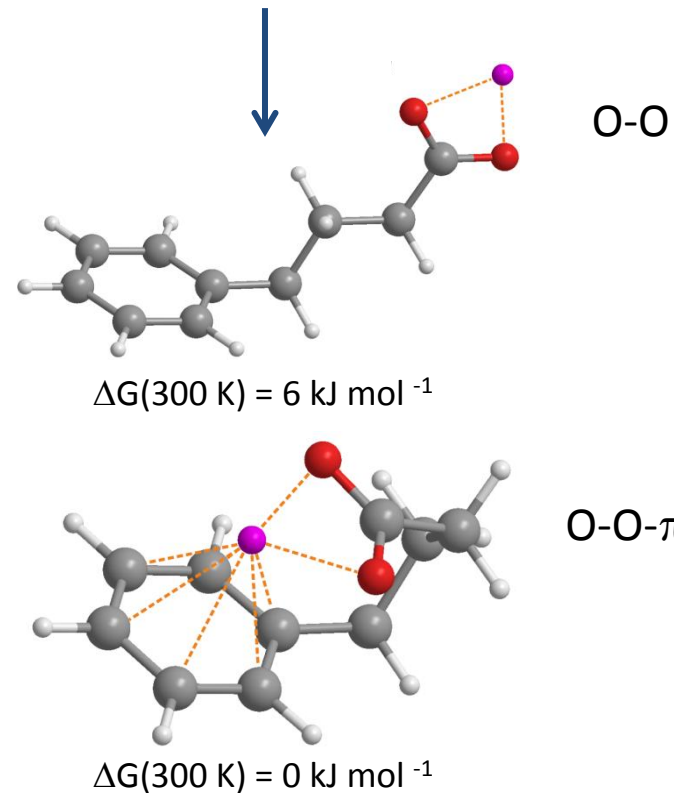


Lithium (4)-phenylbutyrate
(Li⁺, PB⁻)

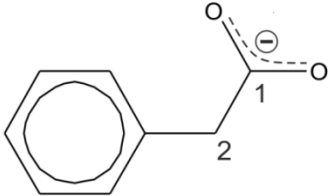
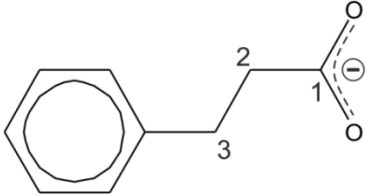
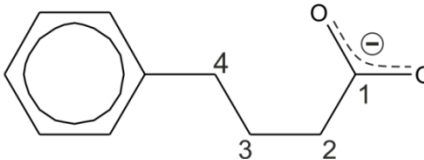
UV-R2PI spectra



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

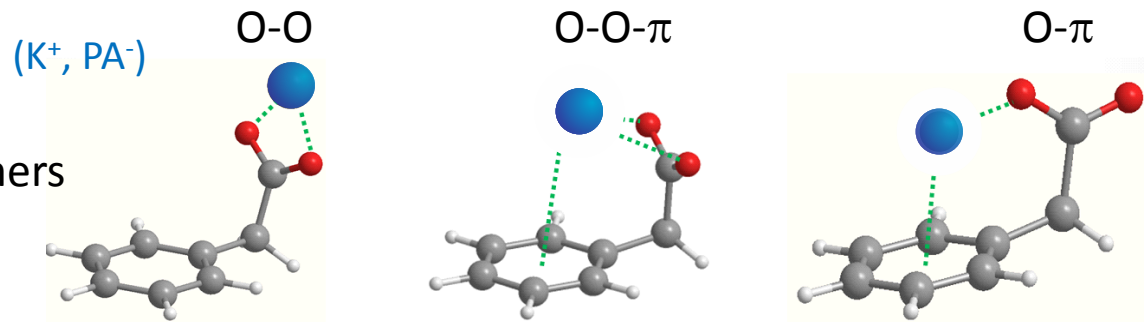


II. Experimental vs. Theoretical conformational landscape

Cations \ Anions						
Li ⁺	✓	Exp: O-O Th: O-O	✓	O-O O-O	✓	O-O + O-O- π O-O + O-O- π
Na ⁺	✓	O-O O-O	✗	O-O O-O + O-O- π	✓	O-O + O-O- π O-O + O-O- π
K ⁺	✗	O-O O-O + O-O- π	✓	O-O + O-O- π O-O + O-O- π		
Rb ⁺	✗	O-O O-O + O-O- π				
Cs ⁺	✗	O-O O-O + O-O- π				

➔ Inconsistent results between experiment and theory

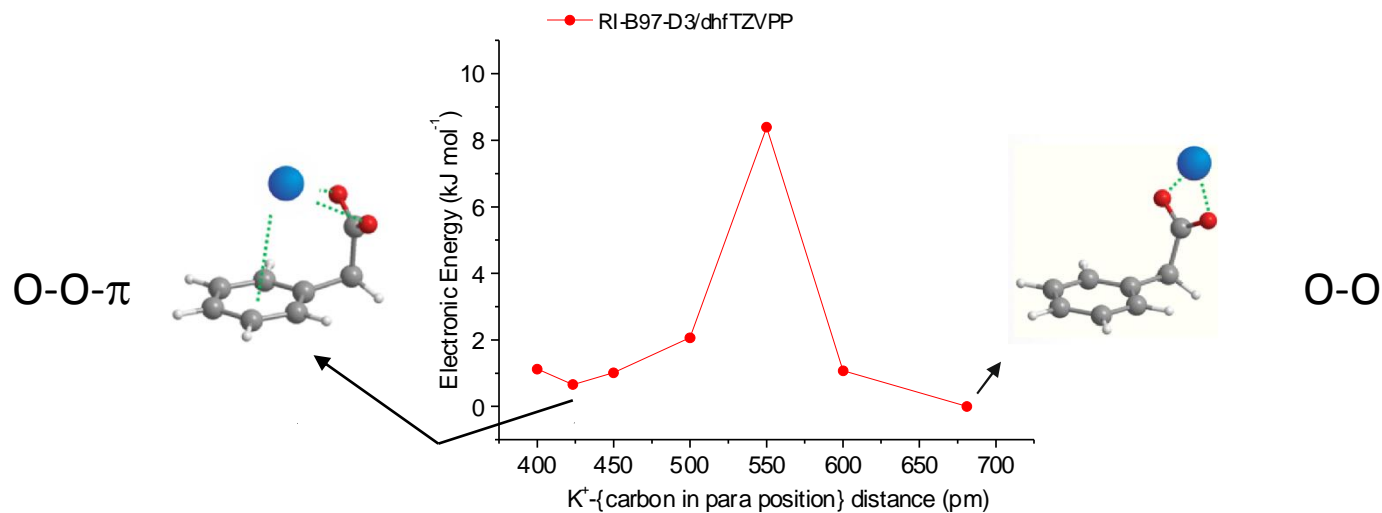
II. Benchmarks for quantum chemistry



Three most stable conformers

$\Delta G(300 \text{ K})$
RI-B97-D3/dhf-TZVPP

	O-O	O-O- π	O- π
Li ⁺ , PA ⁻	0	n/a	36
Na ⁺ , PA ⁻	0	n/a	29
K ⁺ , PA ⁻	0	6*	21
Rb ⁺ , PA ⁻	0	5*	20
Cs ⁺ , PA ⁻	0	3*	18



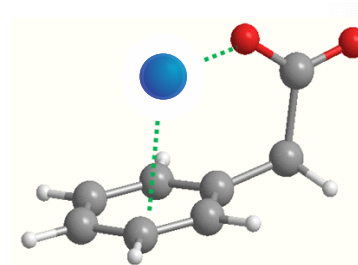
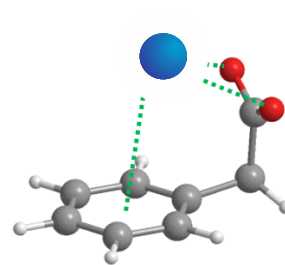
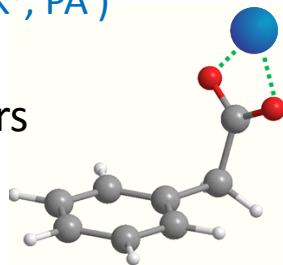
II. Benchmarks for quantum chemistry

(K⁺, PA⁻)

O-O

O-O- π

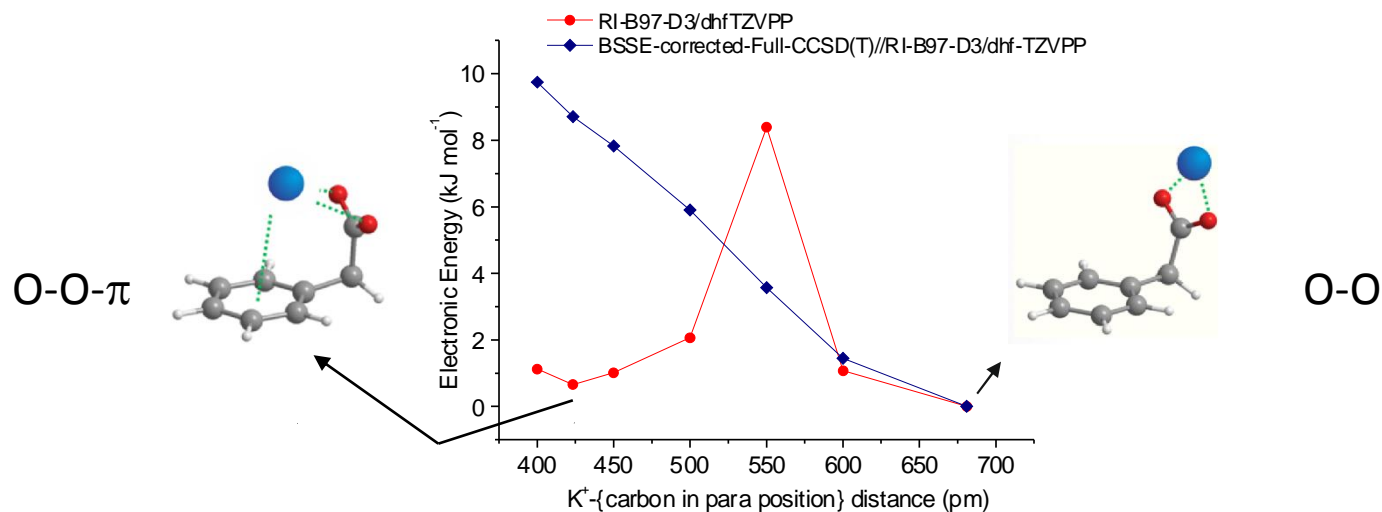
O- π



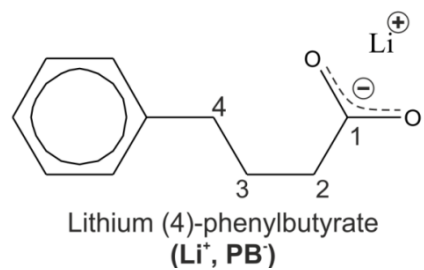
Three most stable conformers

$\Delta G(300\text{ K})$
RI-B97-D3/dhf-TZVPP

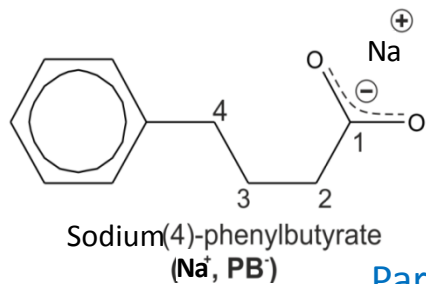
	O-O	O-O- π	O- π
Li ⁺ , PA ⁻	0	n/a	36
Na ⁺ , PA ⁻	0	n/a	29
K ⁺ , PA ⁻	0	6*	21
Rb ⁺ , PA ⁻	0	5*	20
Cs ⁺ , PA ⁻	0	3*	18



II. Fragmentation

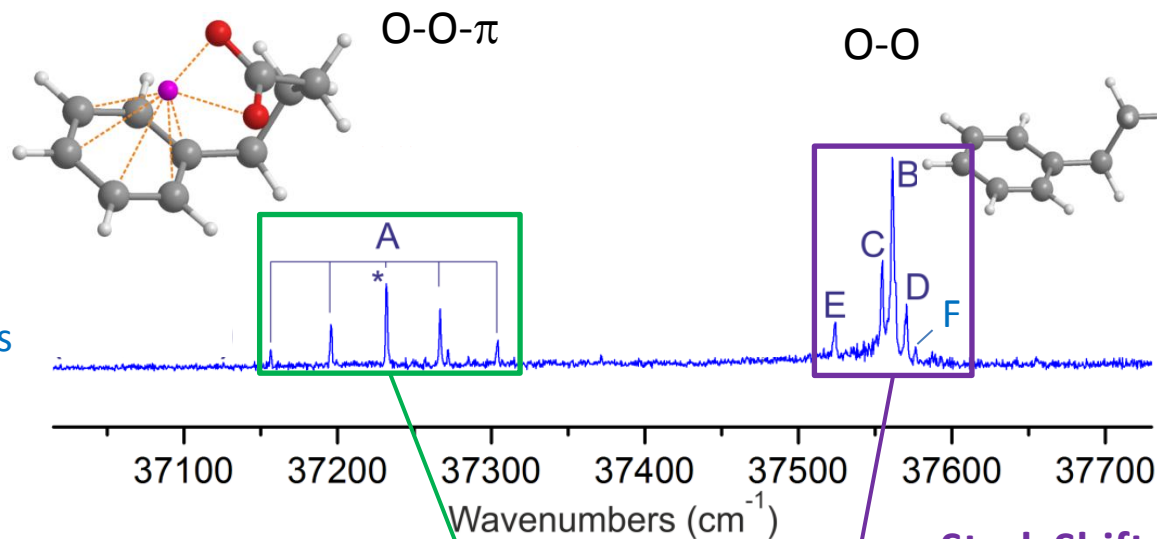


Parent ion mass
channel



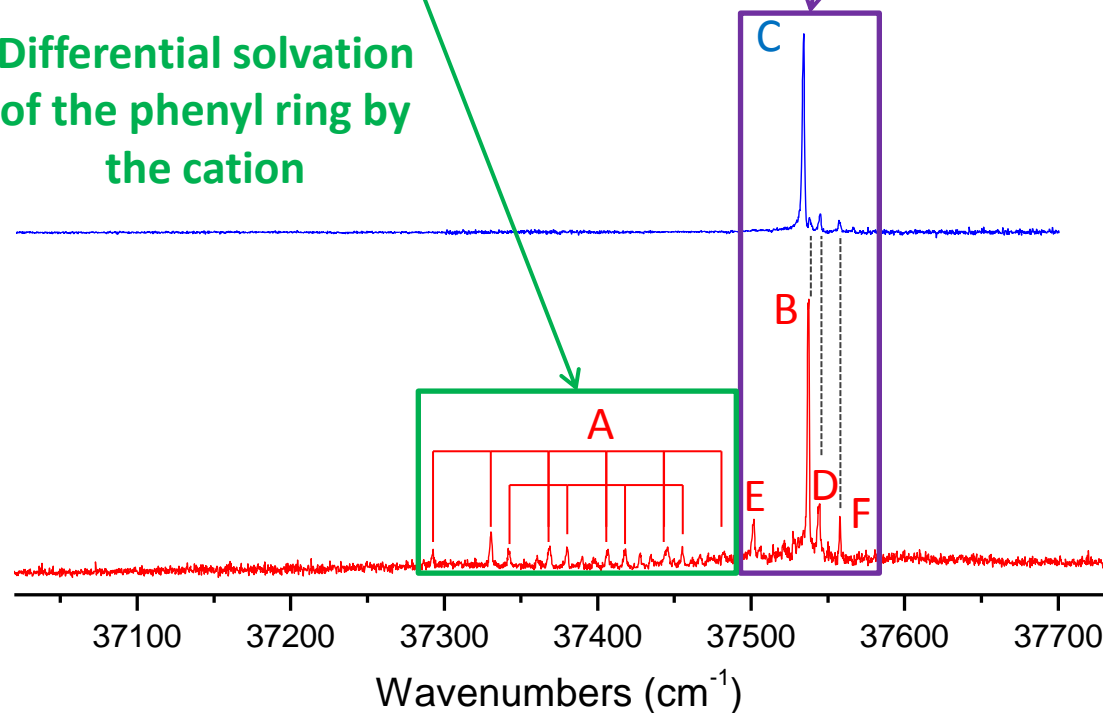
Parent ion mass
channel

Fragment
(CO₂ loss)



Differential solvation
of the phenyl ring by
the cation

Stark Shift



I. Introduction

II. IR spectroscopy

III. UV spectroscopy

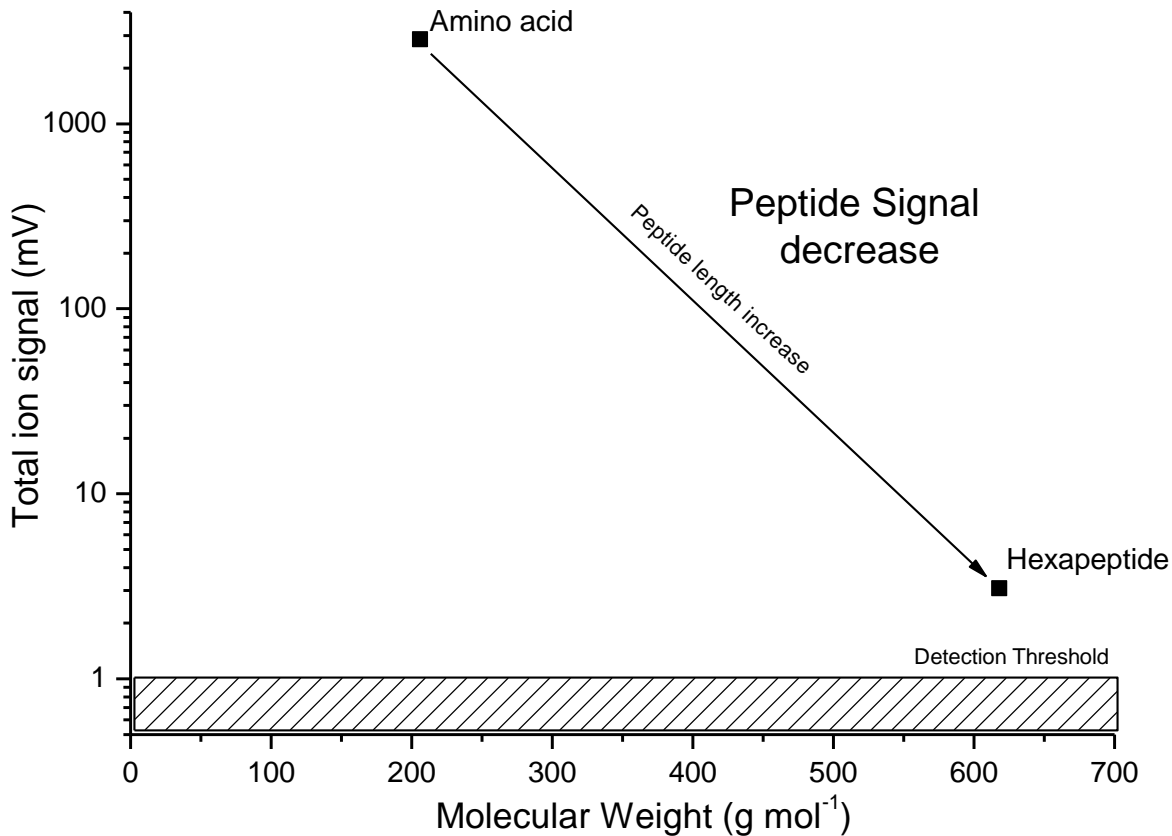
IV. Perspectives of gas phase experiments



Spectroscopy and Dynamics of Molecules and Clusters (SDMC) 2019

Shimla, 21-24 february 2019

Laser Desorption + R2PI : the peptide case

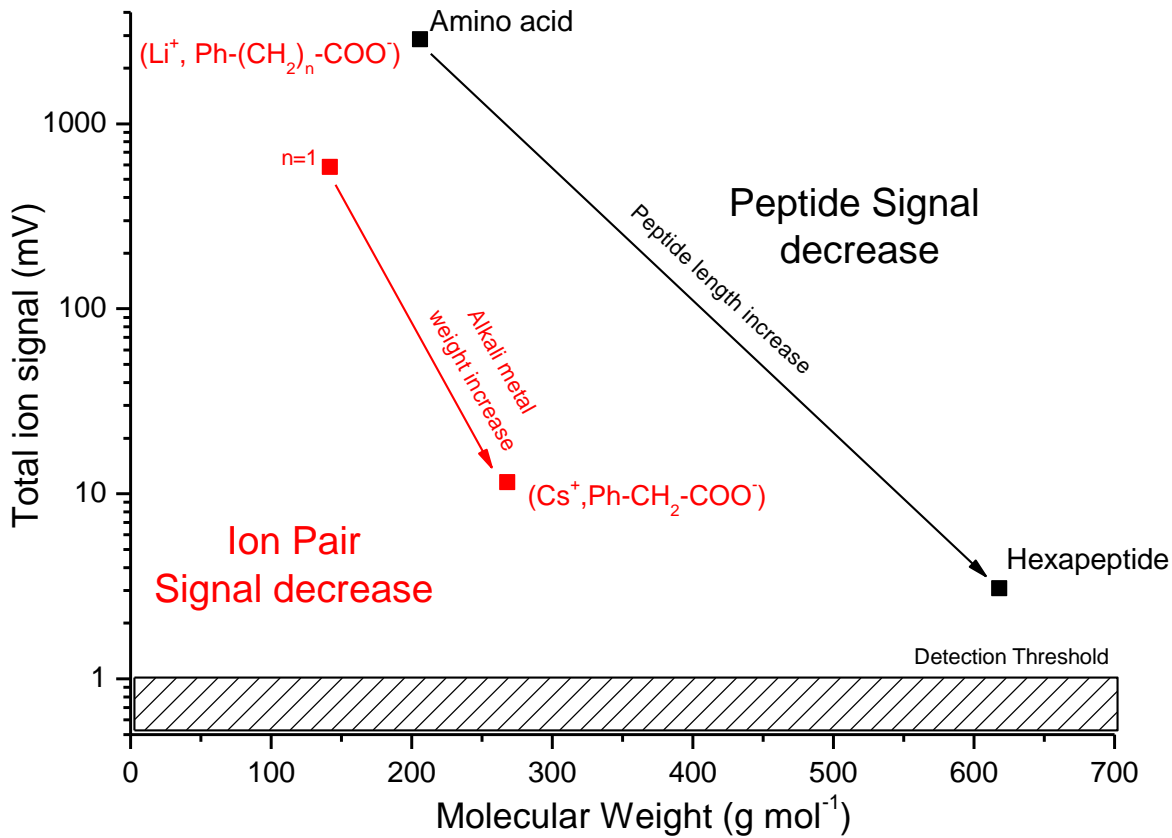


→ Not specific to R2PI

*Schlag, Grotemeyer, Levine
Chem. Phys. Lett. (1992)*

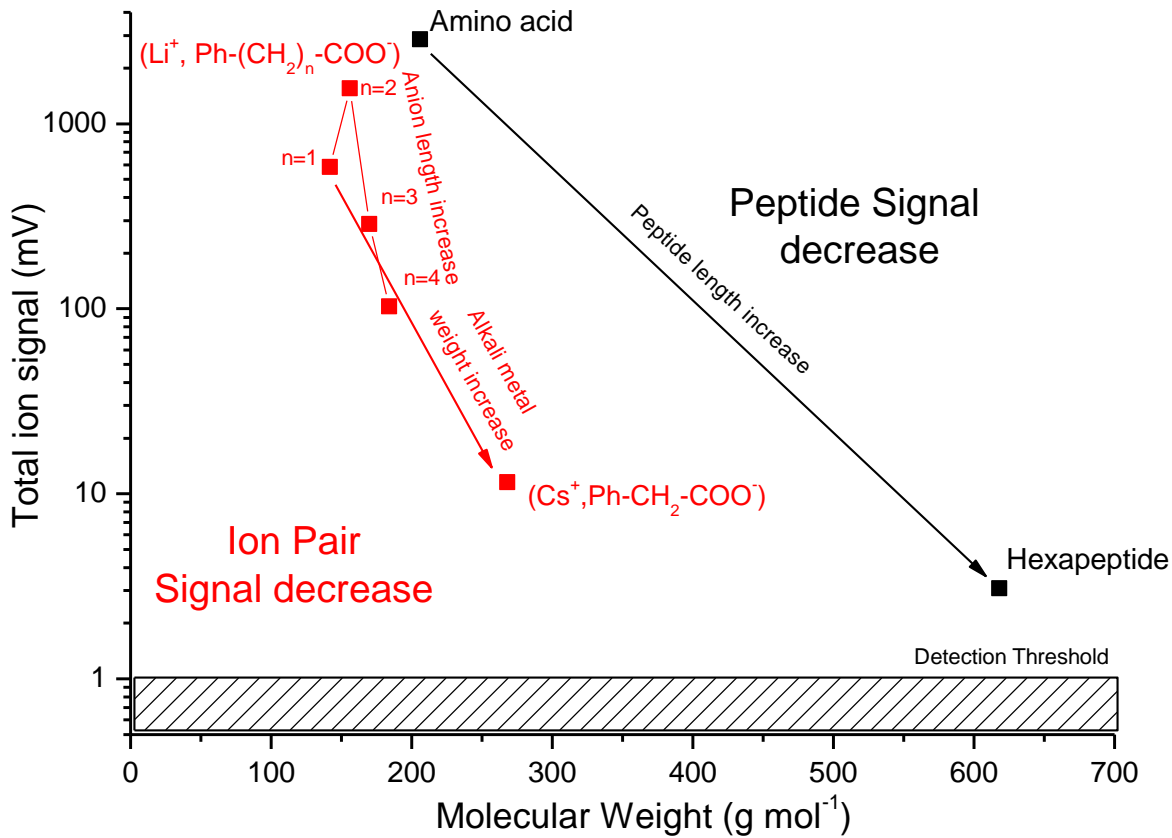
→ Excitation of states of the neutral followed by a rapid relaxation efficiently quenching ionization

Laser Desorption + R2PI : the ion pair case



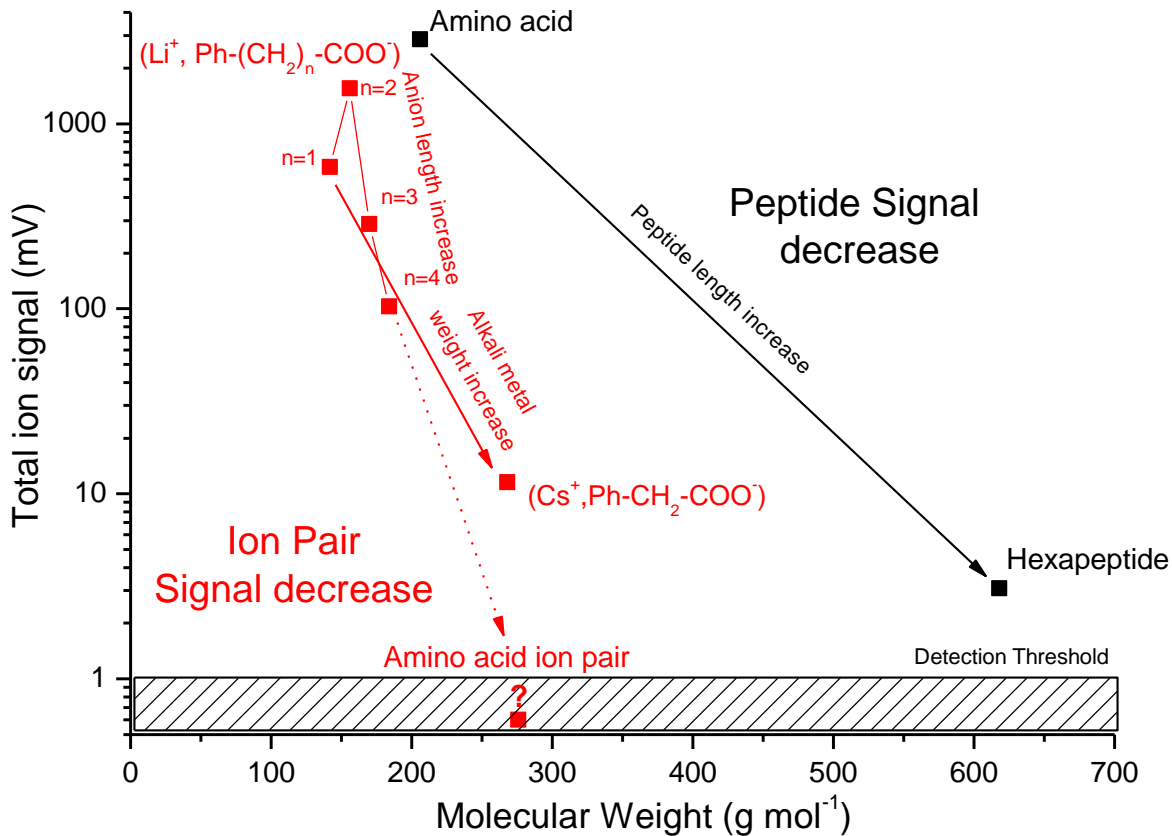
→ A more dramatic decrease is observed for ion pairs !

Laser Desorption + R2PI : the ion pair case



→ A more dramatic decrease is observed for ion pairs !

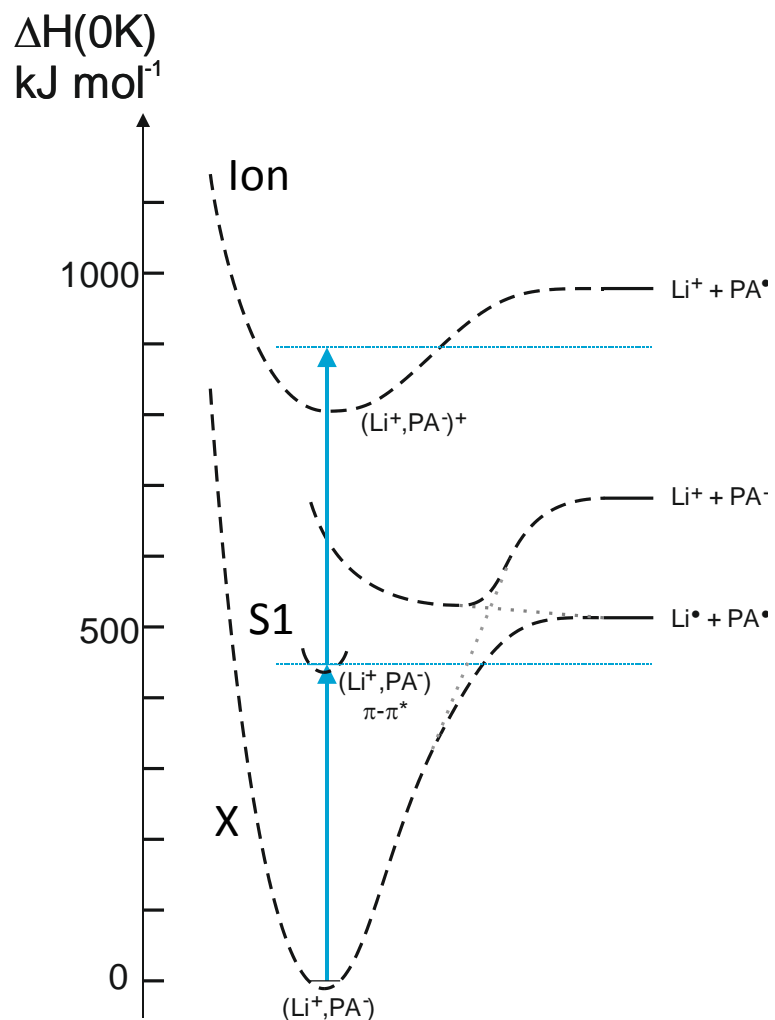
Laser Desorption + R2PI : the ion pair case



→ A more dramatic decrease is observed for ion pairs !

System window for ion pairs is very narrow...

IV. Energy Diagram of ion pairs



Why such a signal loss for ion pairs?

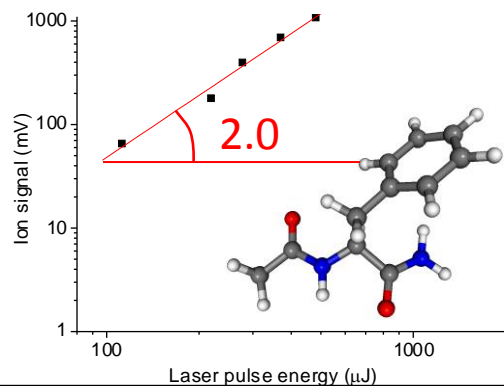
A. Quenching of ionization by relaxation of superexcited states of the neutral

B. Short lifetimes of the $\pi-\pi^*$ states

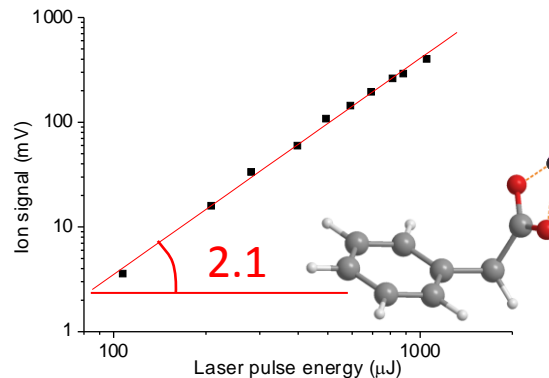
C. Vaporization efficiency

IV. Signal variations with the laser pulse energy

Ac-Phe-NH₂



(Li⁺, PA⁻)

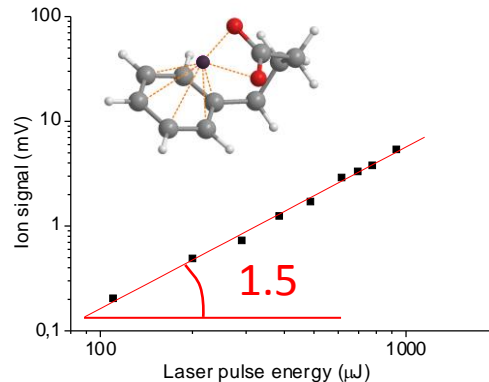
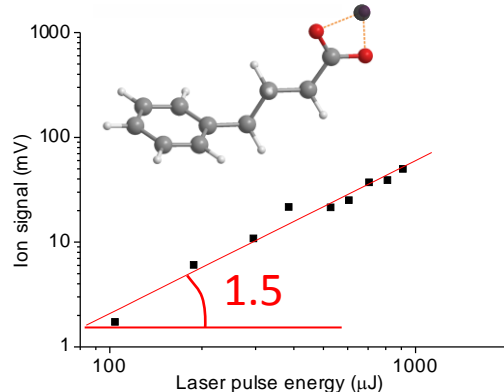


Apparent number of photon involved in the ionization process:

$$AN = 2$$

→ Equivalent absorption probability of both photons

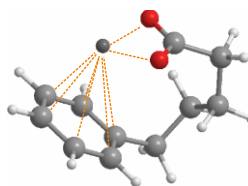
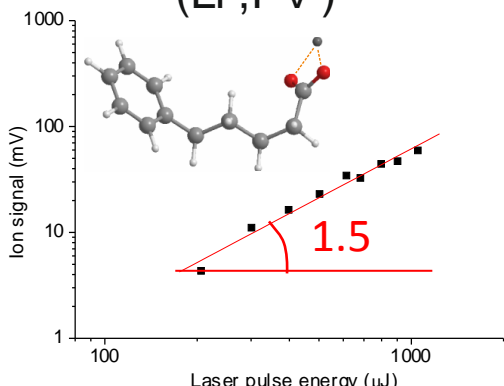
(Li⁺, PB⁻)



$$AN = 1.5$$

→ one absorption step is more probable than the other

(Li⁺, PV⁻)



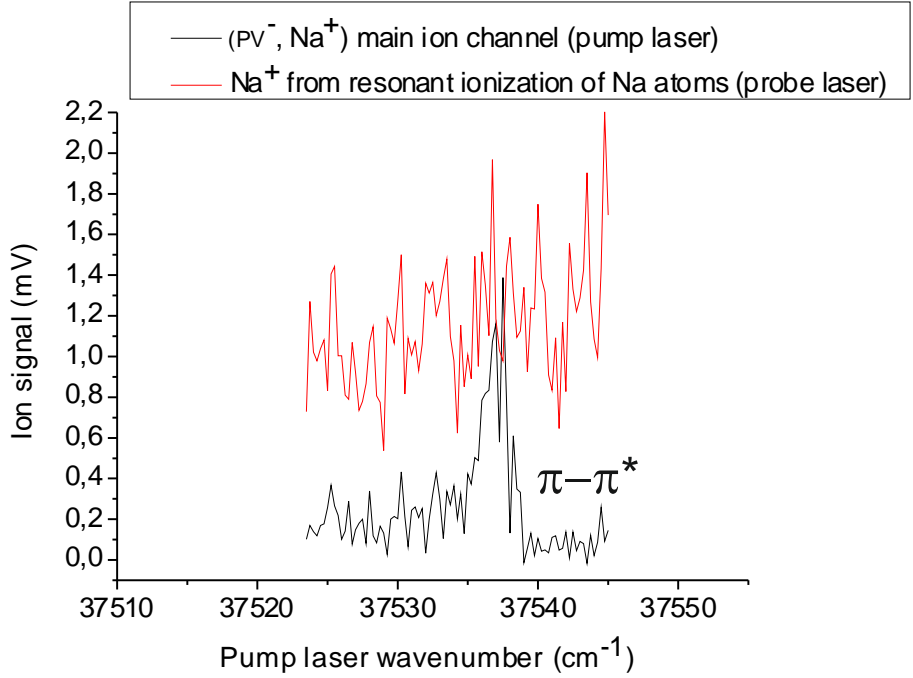
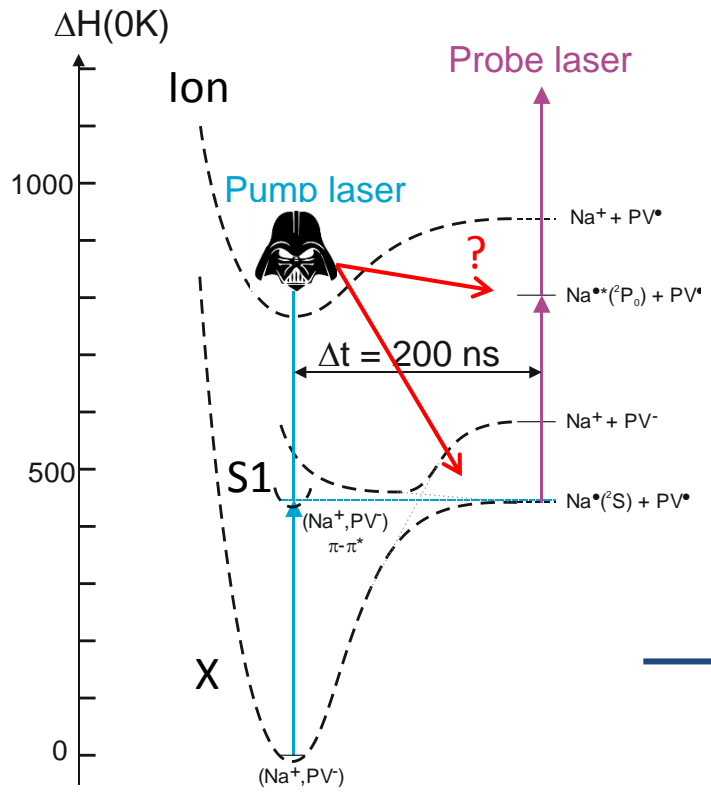
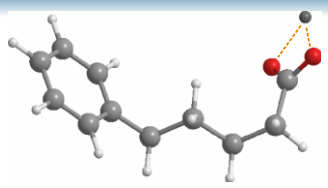
Lowest-energy conformer (missing)

AN < 2 combined with a huge decrease of the ion signal

→ Presence of dark states efficiently quenching ionization



IV. Shedding light on dark channels



No pump-probe signal

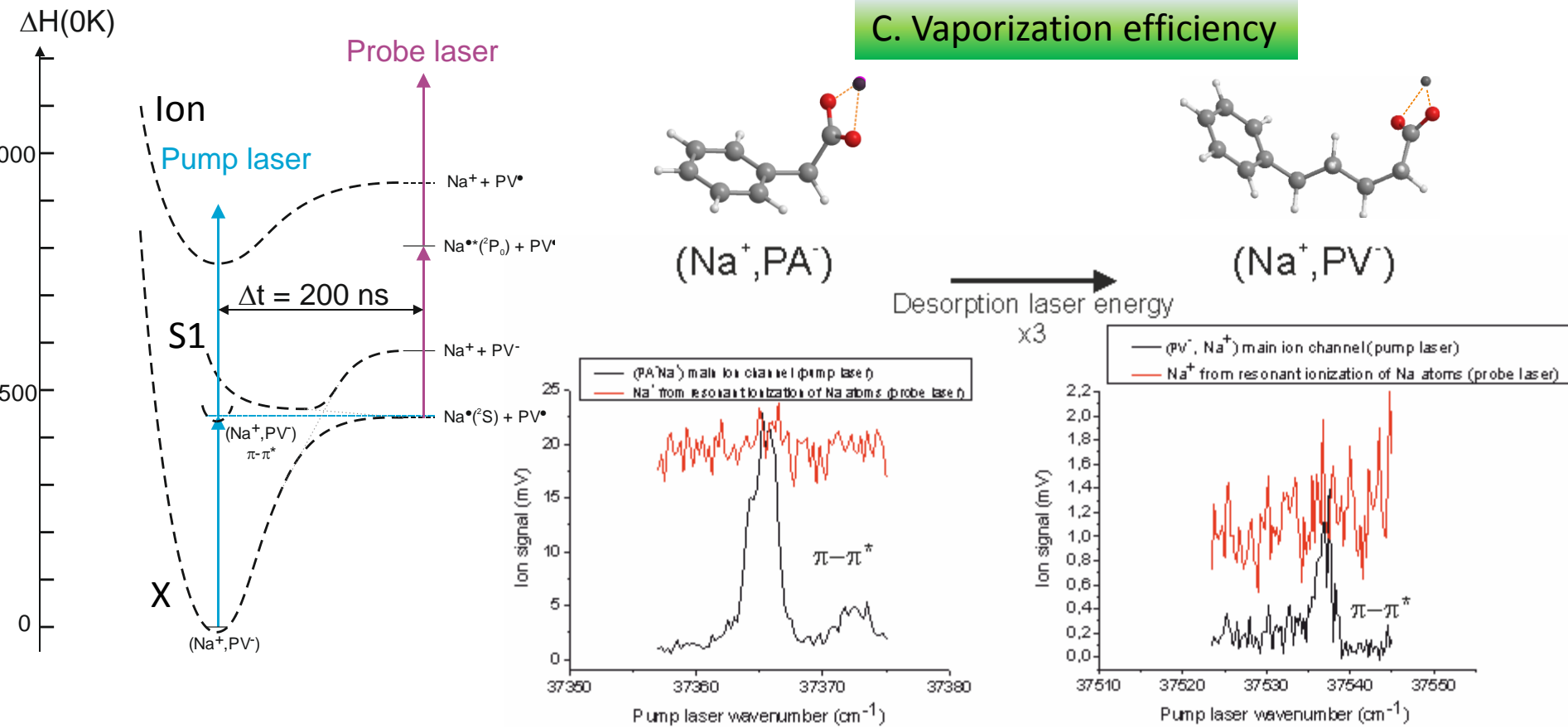
No relaxation to the most obvious non-ionic fragmentation channels

Conclusions

Dark states may not be the only explanation to the loss of ion signal

IV. Shedding light on dark channels

C. Vaporization efficiency



Ionization of sodium atoms in the molecular beam scale with the ion pair signal !

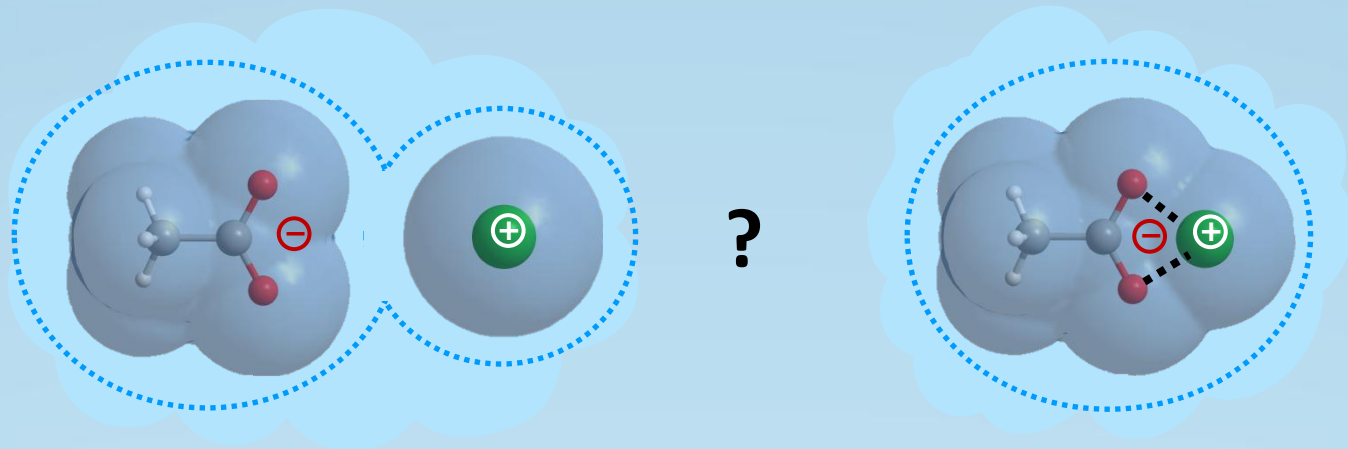
➔ Several parameters have been tested (solvent for sample preparation, graphite:salt ratio, way of mixing) but no improvement has been observed

Conclusions

Vaporization may be the main factor contributing to the loss of signal in the case of ion pairs, additional critical parameters need to be explored to improve vaporization efficiency

Conclusions

- ✓ *IR spectroscopy of gas phase neutral ions pairs are useful to solution phase studies*
- ✓ *The flexibility of molecular ions involved in strong interactions (500 kJ mol^{-1}) can be investigated by conformer-selective techniques*
- ✓ *Isolated ion pairs open an original approach for Electronic Stark Spectroscopy of UV chromophores at high electric field (4 GV m^{-1})*

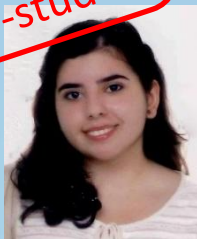


Acknowledgements



2014-2017
Sana Habka

PhD-student



PhD-student

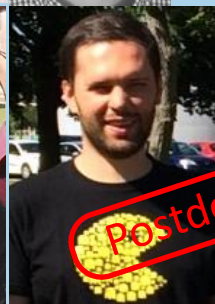


2017-2020
Jérémy Donon



2014-2015
Vanessa
Vaquero-Vara

Postdoc



Postdoc

2015-2016
Thibaut Very



2014-2018
5 undergraduate
students



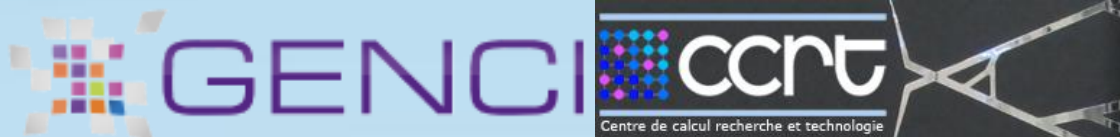
Ridha Elattar
Sarah de Lima-Barbosa
Samantha Bourg
Sentia Goursaud
Amani Ghandri



2016-2020
ANR JCJC IONPAIRS



2016-2018
TGCC





Marie GELEOC

Michel MONS

Eric GLOAGUEN

Gildas GOLDSZTEJN Valérie BRENNER Benjamin TARDIVEL

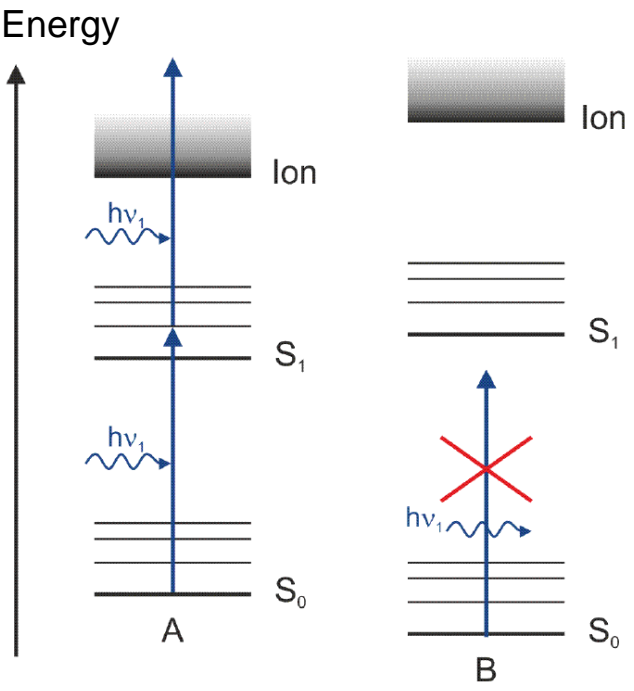
Jeremy DONON

Venkateswara-rao MUNDLAPATI

II. IR/UV double resonance spectroscopy

IR/UV

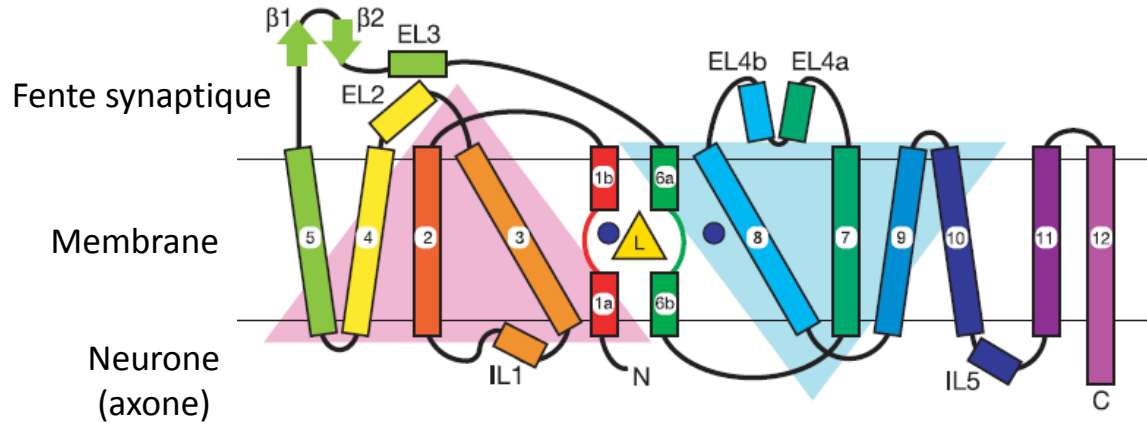
R2PI



I. Ion pairing at play in Biology

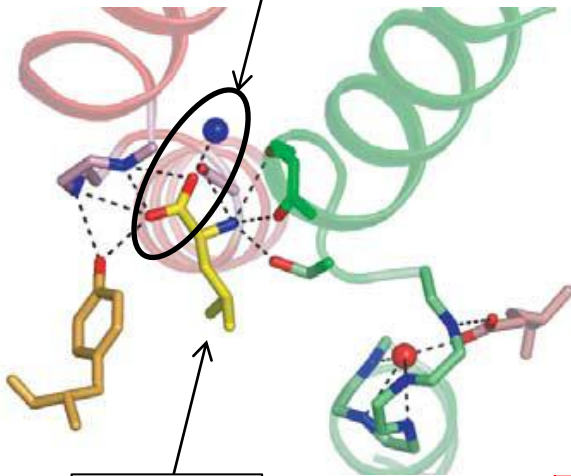
Protein LeuT_{Aa}
(PDB 2A65)

Fonction: recharger la vésicule synaptique après libération du neurotransmetteur (leucine)

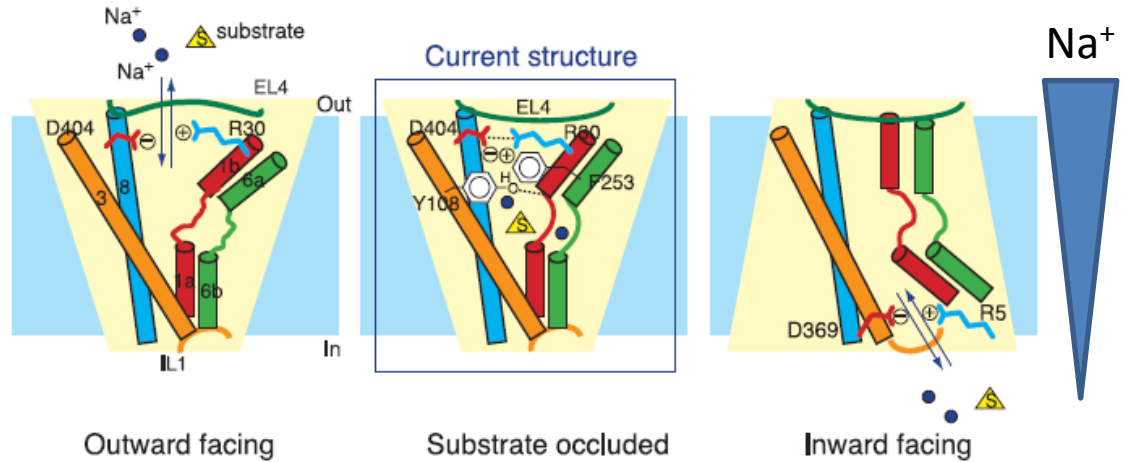


Yamashita, Singh, Kawate, Gouaux Nature (2005)

(R-COO⁻_{Leucine} , Na⁺) CIP



Leucine



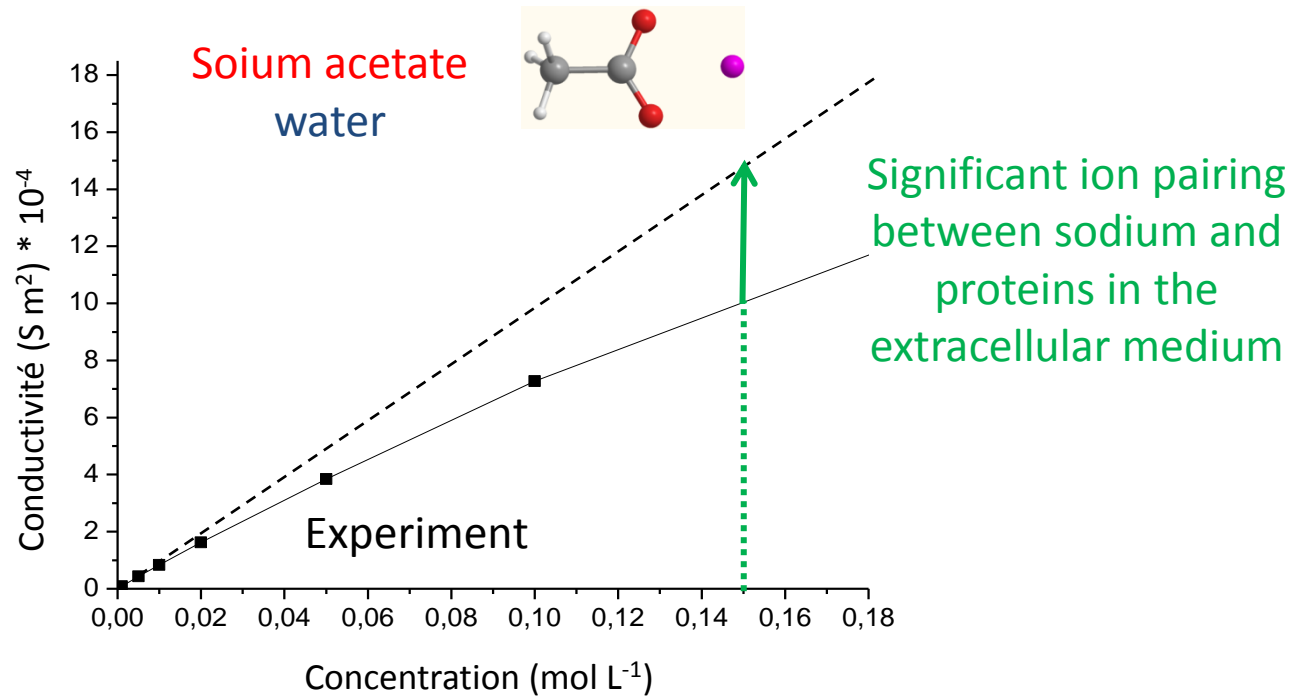
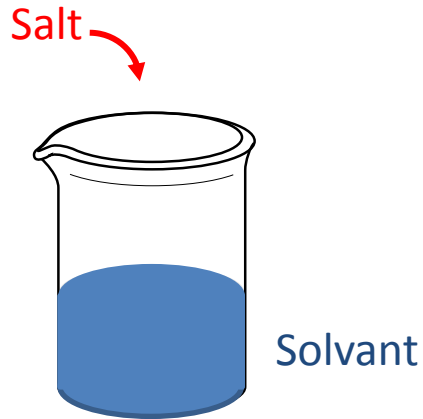
Le gradient de concentration en ion sodium est un élément moteur du transport de Leu au travers de la membrane

I. Conductivity of electrolyte solutions

Conductivity (κ) ?

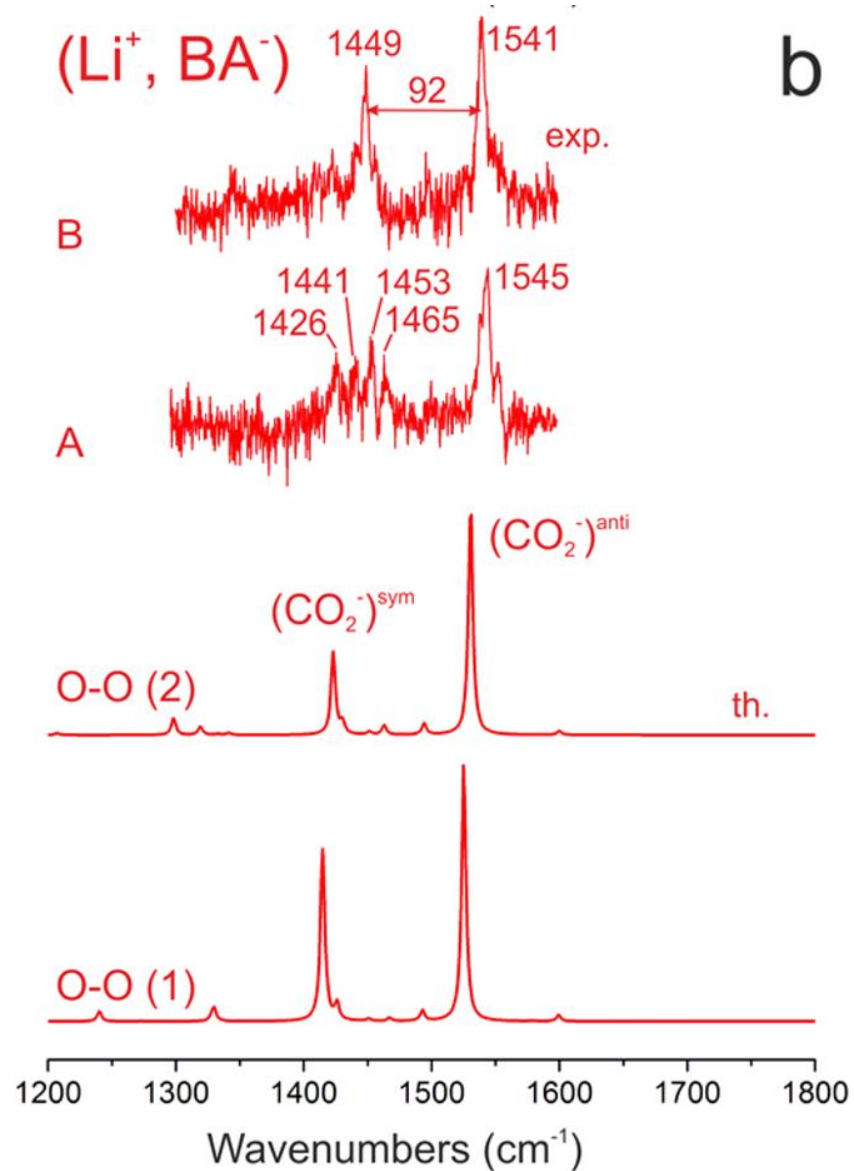
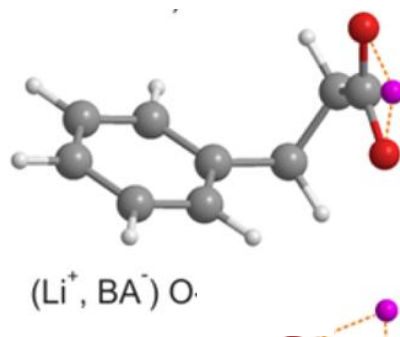
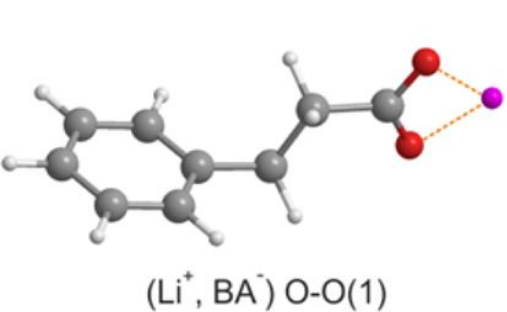
proportional to concentration (c) for free ions

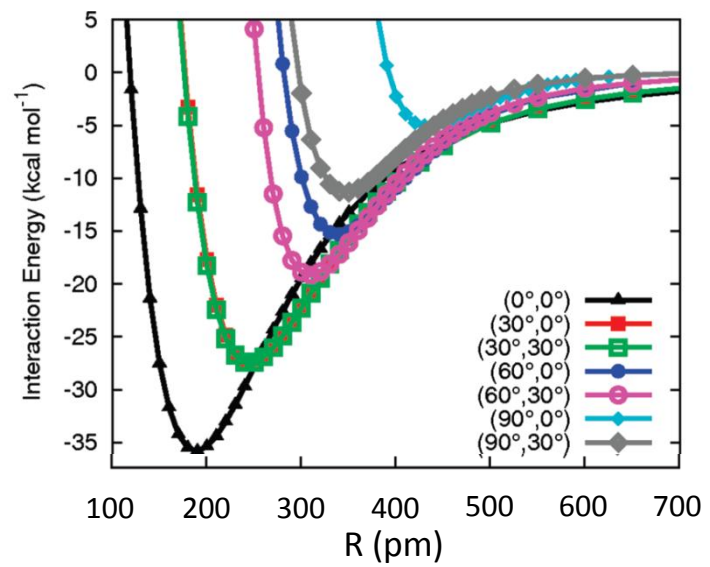
$$\kappa = \Lambda_m * c$$



→ The non-linear behaviour reveals the existence of ion pairs

→ Lack of knowledge of the microscopic properties of these systems, and their role in Biology

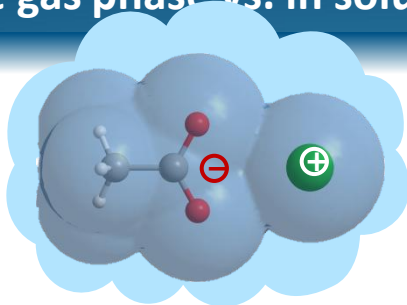




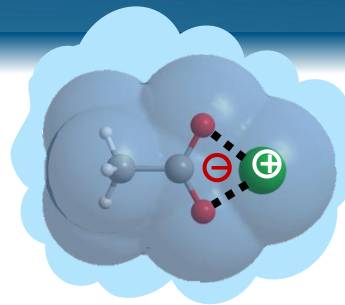
Marshall, Steele, Thanthiriwatte, Sherrill JPCA (2009)

III. Spectroscopy in the gas phase vs. in solution

CIP



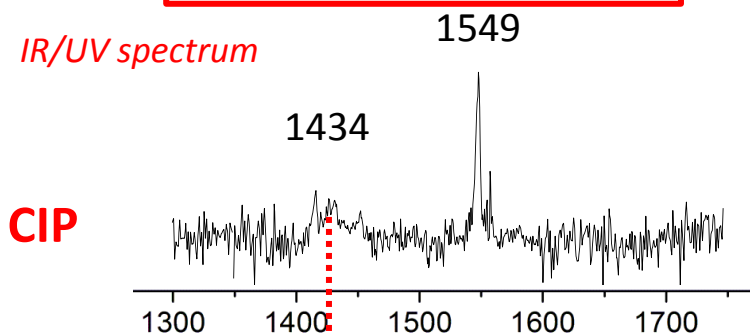
?



SIP/SSIP

Gas phase (M^+ , PA^-) CIPs

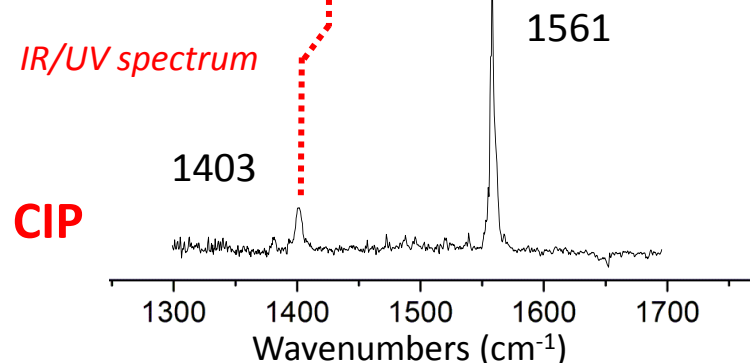
IR/UV spectrum



CIP

Li⁺

IR/UV spectrum

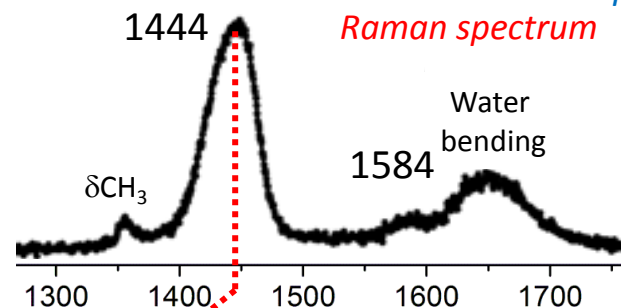


CIP

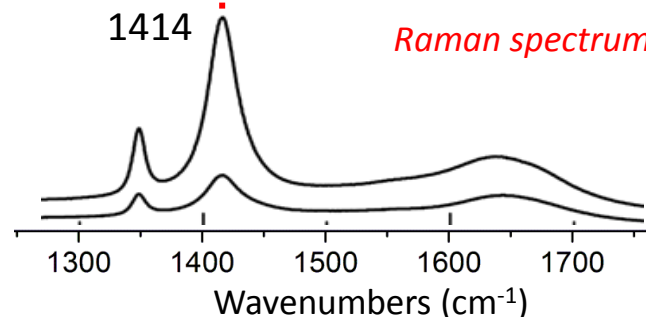
Na⁺

(M^+ , AcO^-) Solutions

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



CIP

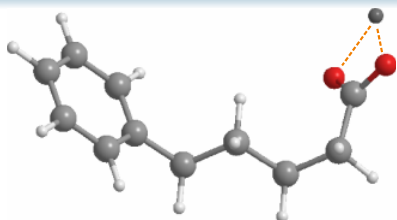


????

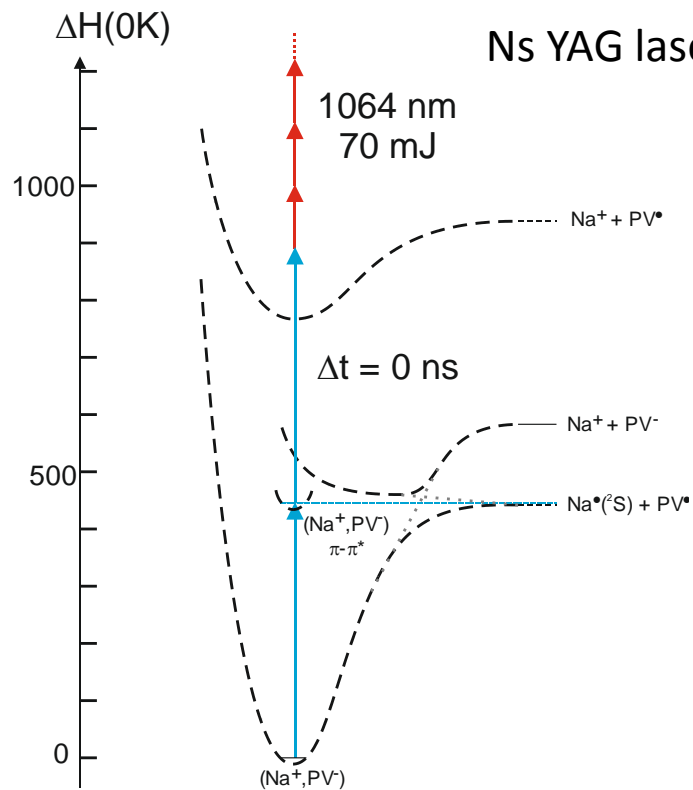
SIP/SSIP

→ Gas phase studies show that changing the cation lead to the same spectral shift that the one observed in solution which is assigned to a change of ion pair type.

IV. Flushing out dark states



Sodium phenylvalerate ($\text{Na}^+ \text{PV}^-$)



Ns YAG laser, mildly focused

→ Up to 40% signal increase of the parent ion!

→ Dark states quench ionization  !

→ Far to be enough to recover the order of magnitude of signal missing

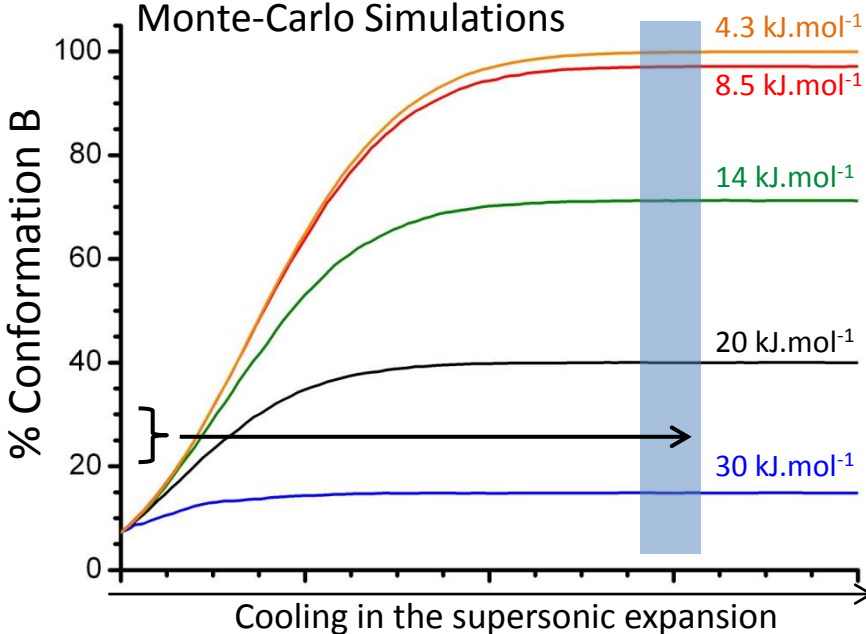
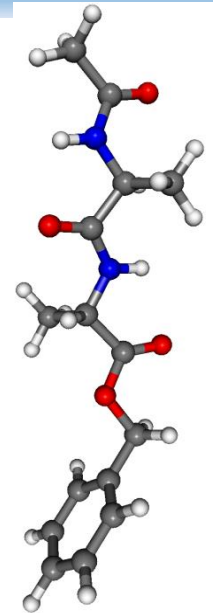
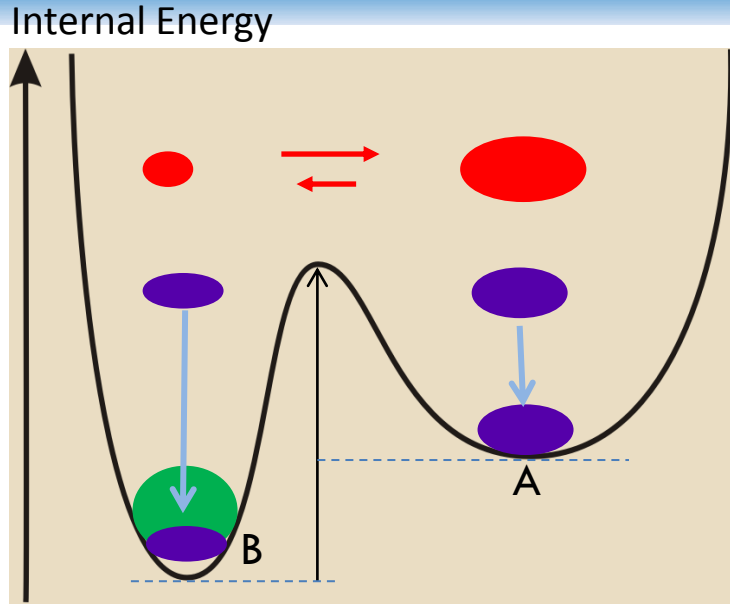
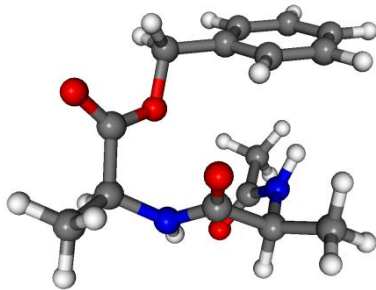
Conclusions

Ns lasers are probably not fast enough to compete efficiently with the relaxation process

3. Theoretical treatment of conformational cooling

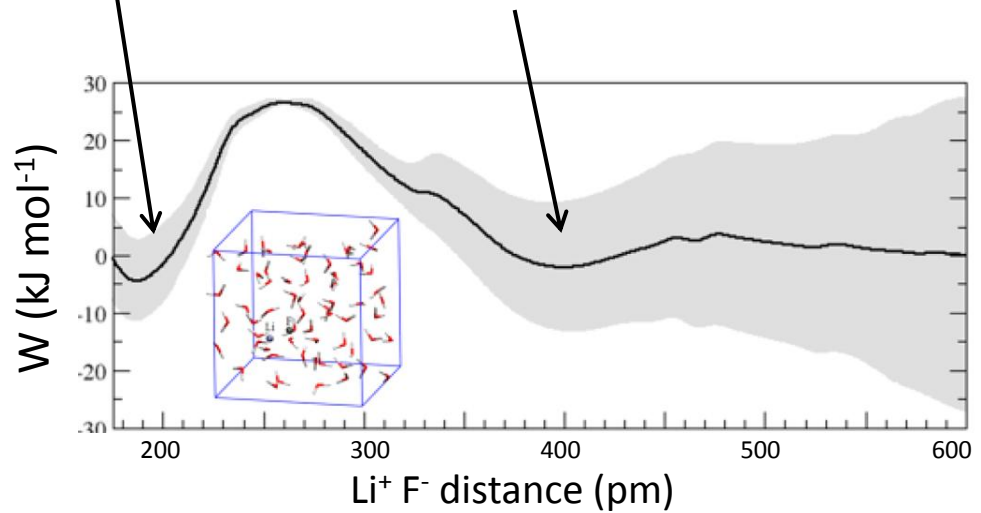
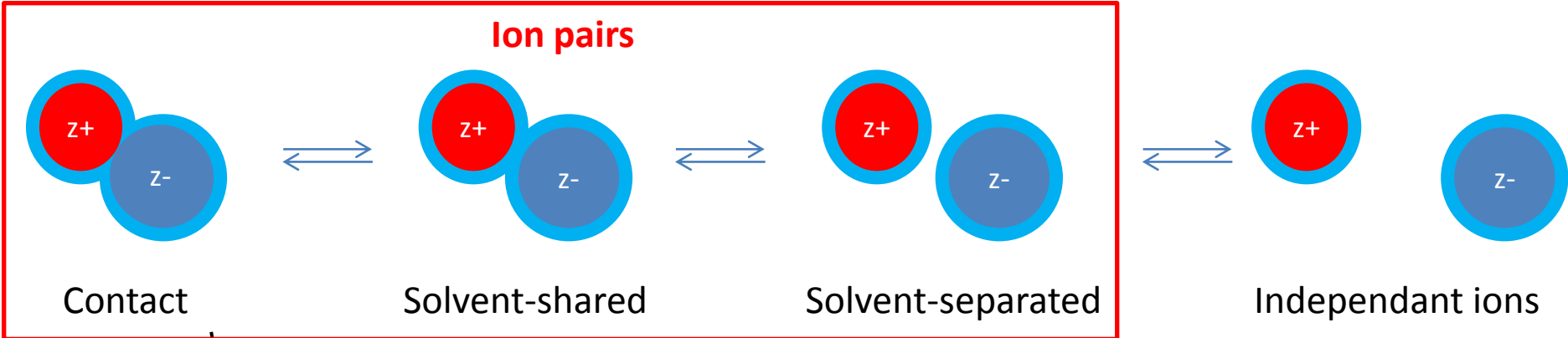
Spectroscopy is carried out at very low temperature where the time needed to reach a conformational equilibrium is much longer than the experimental timescale!

Ac-Ala-Ala-O-Bn



- The compromise between **cooling rate** and **isomerization rate** must be modeled in order to account for conformational distribution
- The « cheap » treatment of the interface experiment/theory on conformational distribution must be used with great care

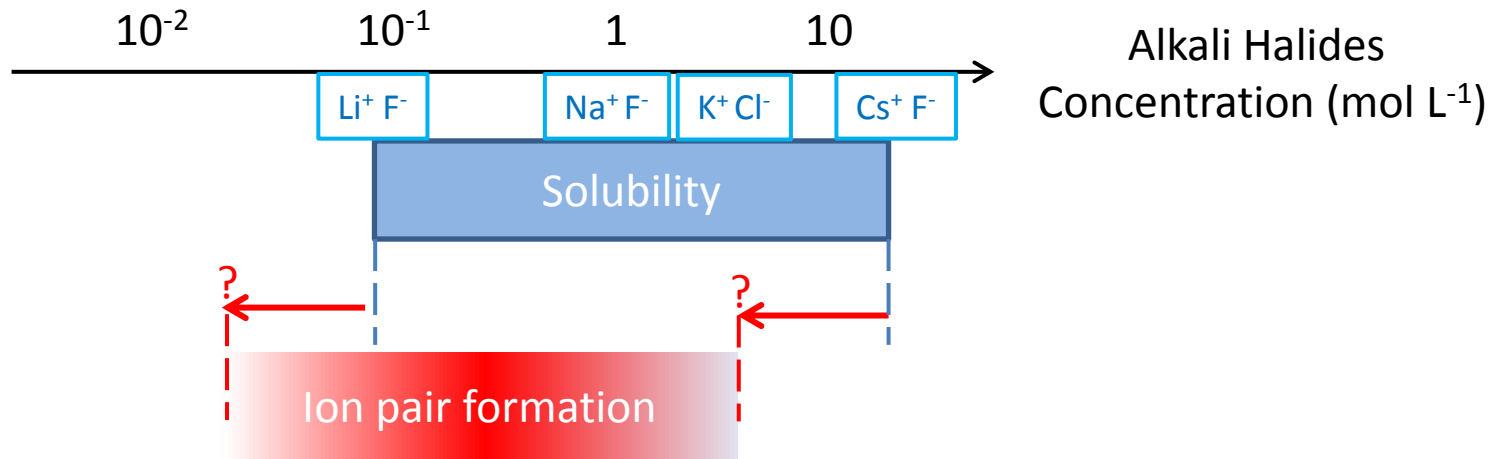
Eigen mechanism (1962) and current modelling: more than electrostatic



DFT Molecular Dynamics
Pluharova, Marsalek, Schmidt, Jungwirth
JPCL (2013)

- Explicit treatment of solvent molecules is needed to properly account for ion pairing
- The formation of ion pair is determined by
 - ✓ Concentration
 - ✓ Density of charge of the cation and the anion (Law of Matching Water Affinities)

Ion pairing and biomolecules



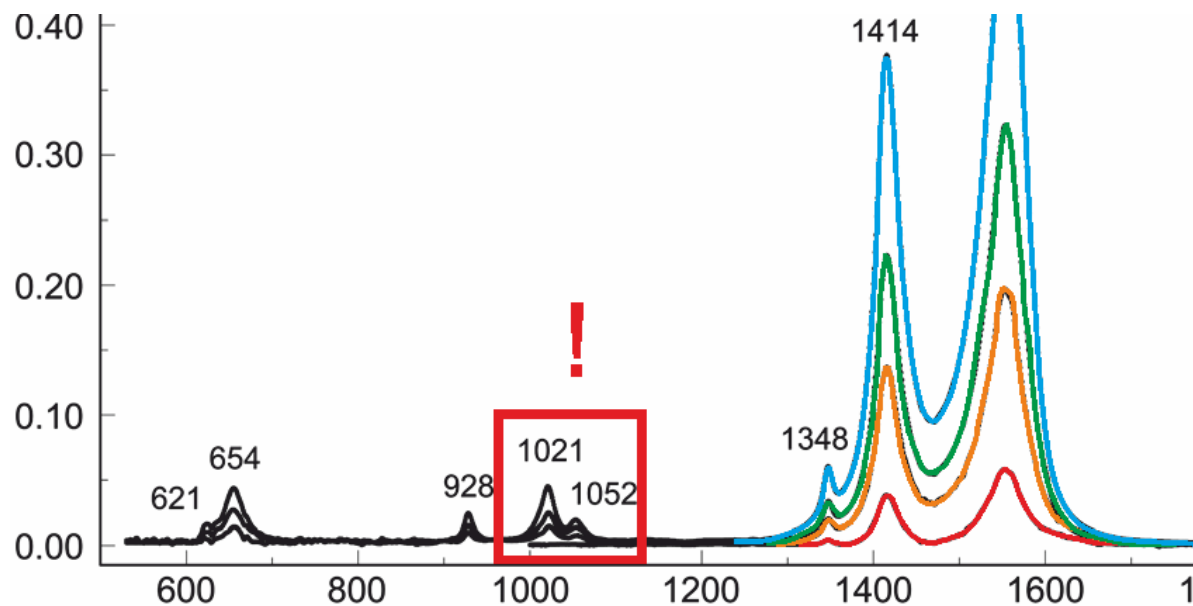
$$[\text{COO}^-_{\text{proteins}}]_{\text{intracellular}} \approx [\text{K}^+]_{\text{intracellular}} = 0,15 \text{ mol L}^{-1}$$

→ What about ion pairing with biomolecules?

- Molecular structure (Intramolecular salt bridges in proteins)
- Recognition (Intermolecular salt bridges between Protein-DNA)
- Crystallization (kidney stones)
- Protein crystallization /precipitation/salting out (neutralization by contact pairing)

IV. Paires d'ions

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



Quel crédit donner au spectre réalisé à basse concentration?

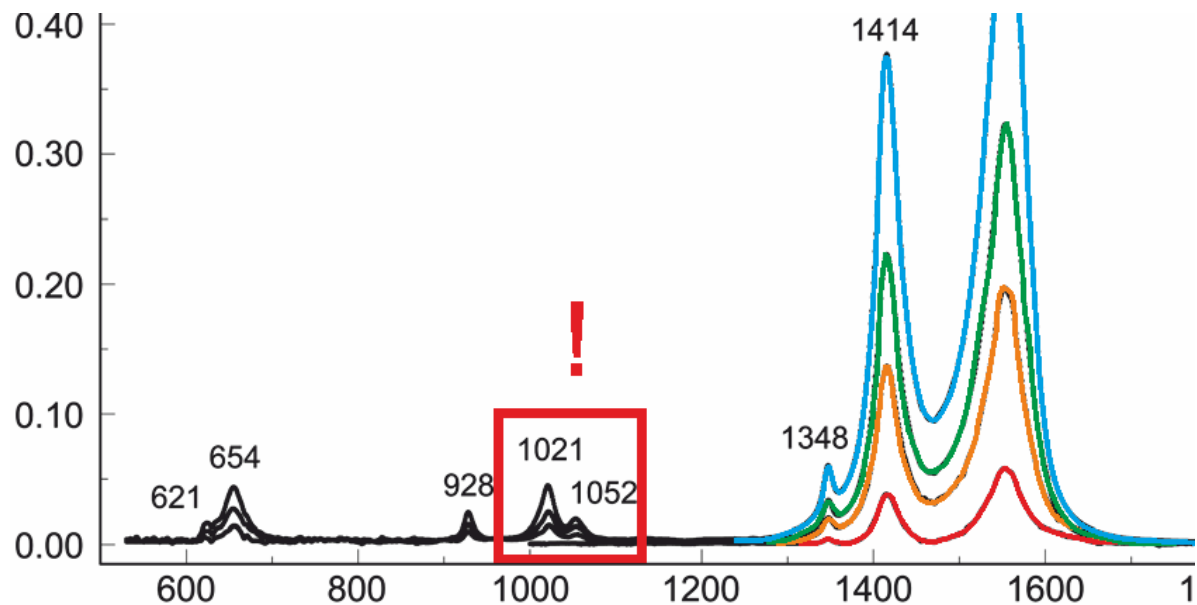
→ Expériences réalisées à l'ICMMO (Pr. D. J. Aitken): non reproductibilité des spectres publiés.

Conclusions

- Les espèces majoritaires à 2 M sont toujours les ions libres
- La non reproductibilité et les erreurs d'attribution viennent probablement des techniques de mesure employées (épaisseurs capillaires, fenêtres AgCl, techniques basées sur l'absorption des ondes évanescentes)

IV. Paires d'ions

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



Quel crédit donner au spectre réalisé à basse concentration?

→ Expériences réalisées à l'ICMMO (Pr. D. J. Aitken): non reproductibilité des spectres publiés.