

# IR and UV Spectroscopy of Neutral Ion Pairs

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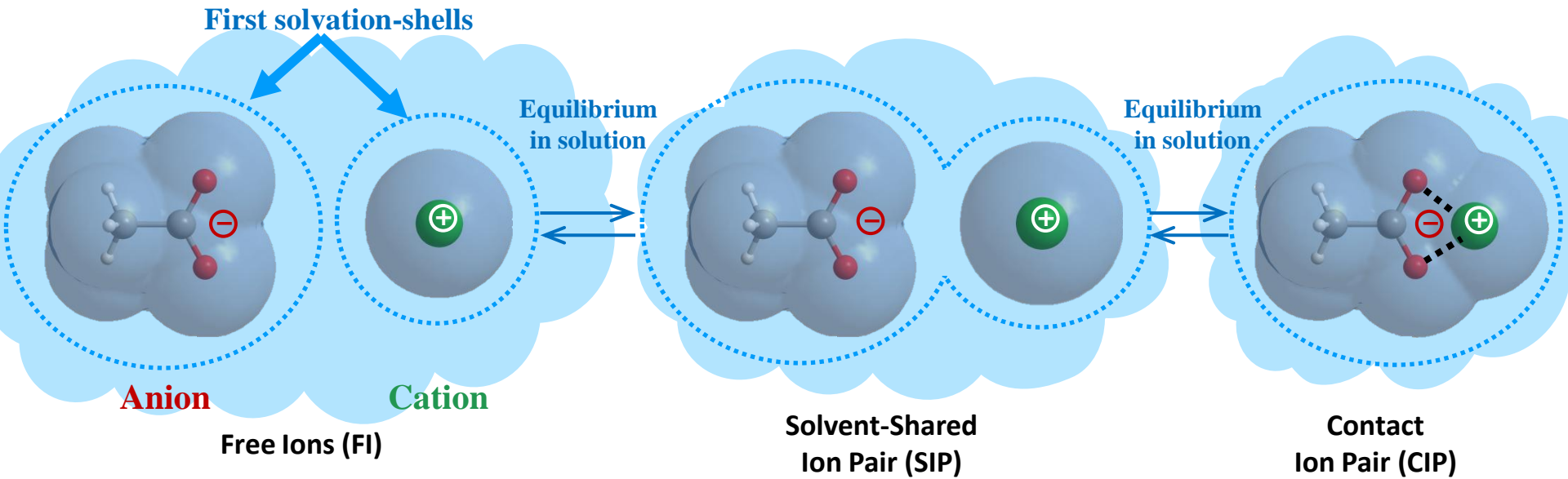
***NISER Seminar**  
Bhubaneswar, 25 february 2019*

# I. Université Paris-Saclay





# I. Ion pairing in solution



→ Pairing is favored by

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

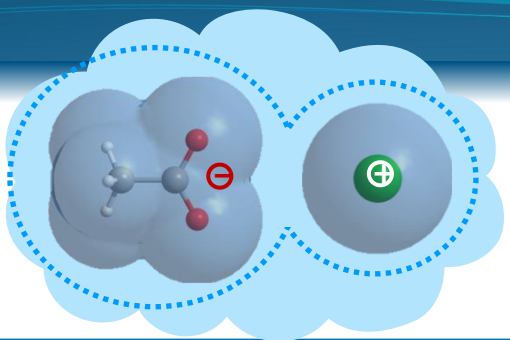
→ Ion pairs are found in sea water, aerosols, biological media...

→ Characterization of the ion pair distribution is challenging:

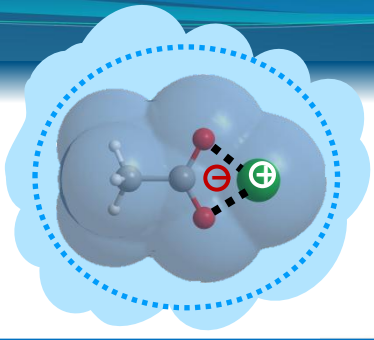
- Co-existence of all types of pairs and free ions
- Short lifetimes

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

SIP/SSIP



?



CIP

2008

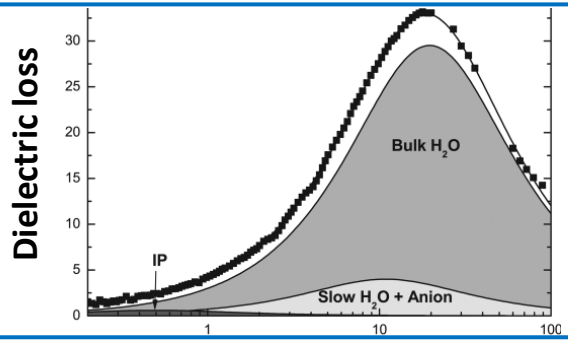
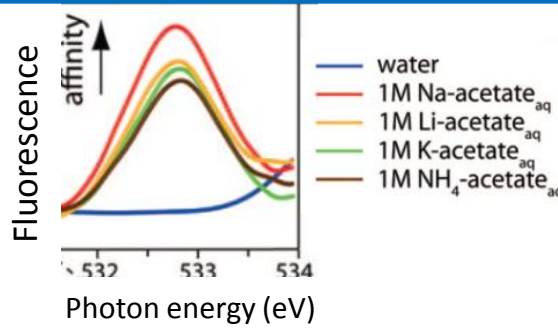
CIPs detected by X-ray absorption spectroscopy (XAS) in liquid microjet

Carbon K-edge

*Uejo, 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)*

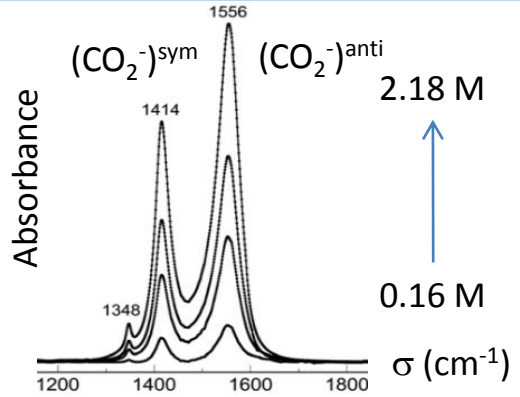
2014

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

SIP >> CIP à 1M

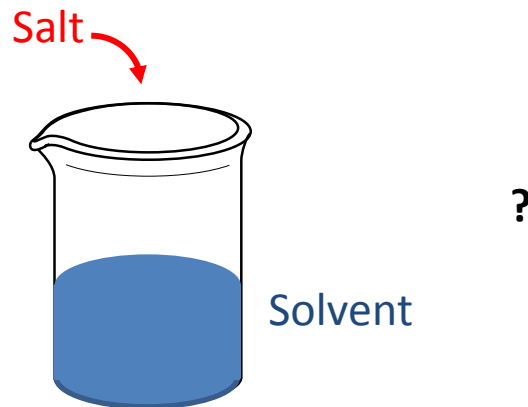
No CIP exists in solution at any concentration

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



# I. Motivations

→ *Supramolecular objects in electrolyte solutions are poorly known*



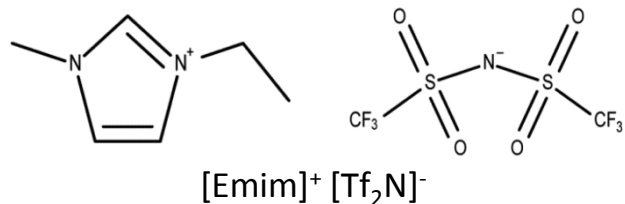
→ *Experiments in solution document macroscopic effects, but struggle to characterize individual objects*

→ *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

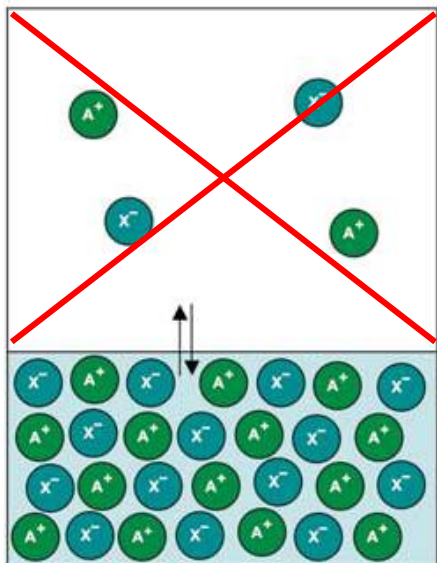
→ **Alkali Halides**  
Heating

→ **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, Jouvét, Martrenchard, Solgadi **Chemical Review** (2000)*

Photoelectron spectroscopy

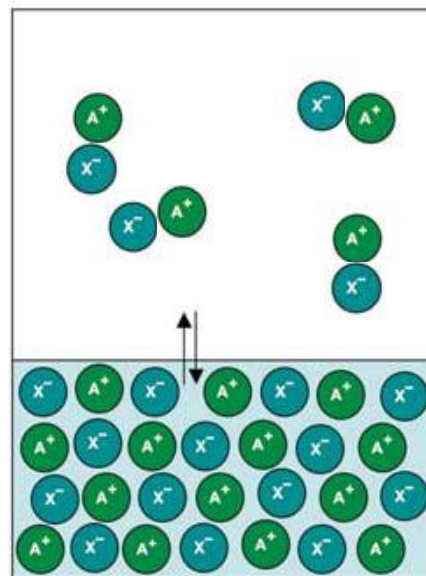
*Strasser, Goulay, Kelkar, Maginn, Leone **JPCA** (2007)*

He droplet IR spectroscopy

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

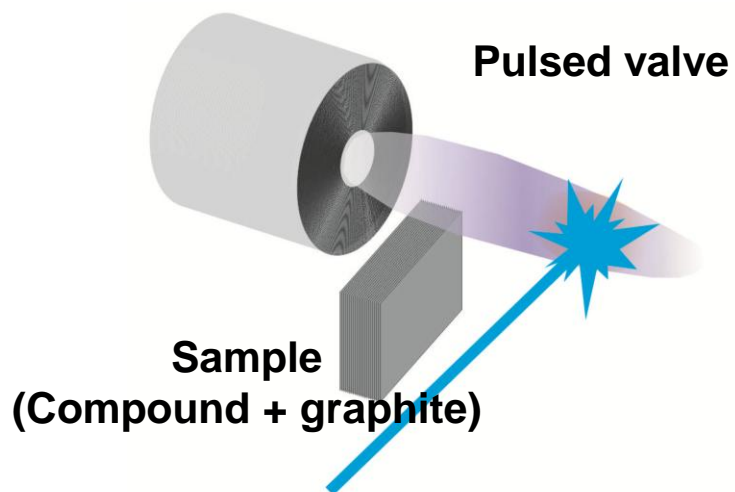
Double resonance IR/UV spectroscopy

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



## II. Gas phase experiment

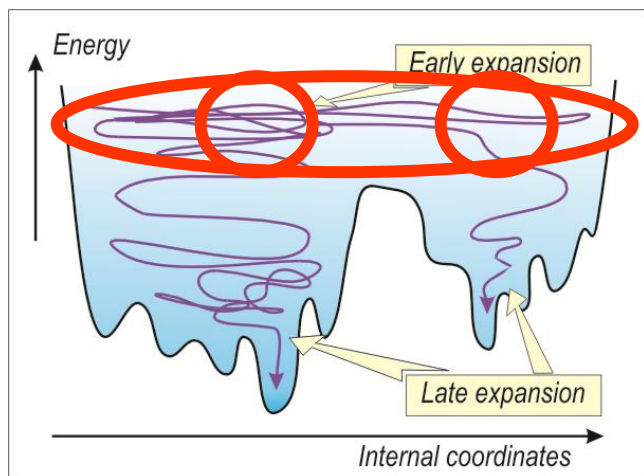
### Vacuum chamber



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

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

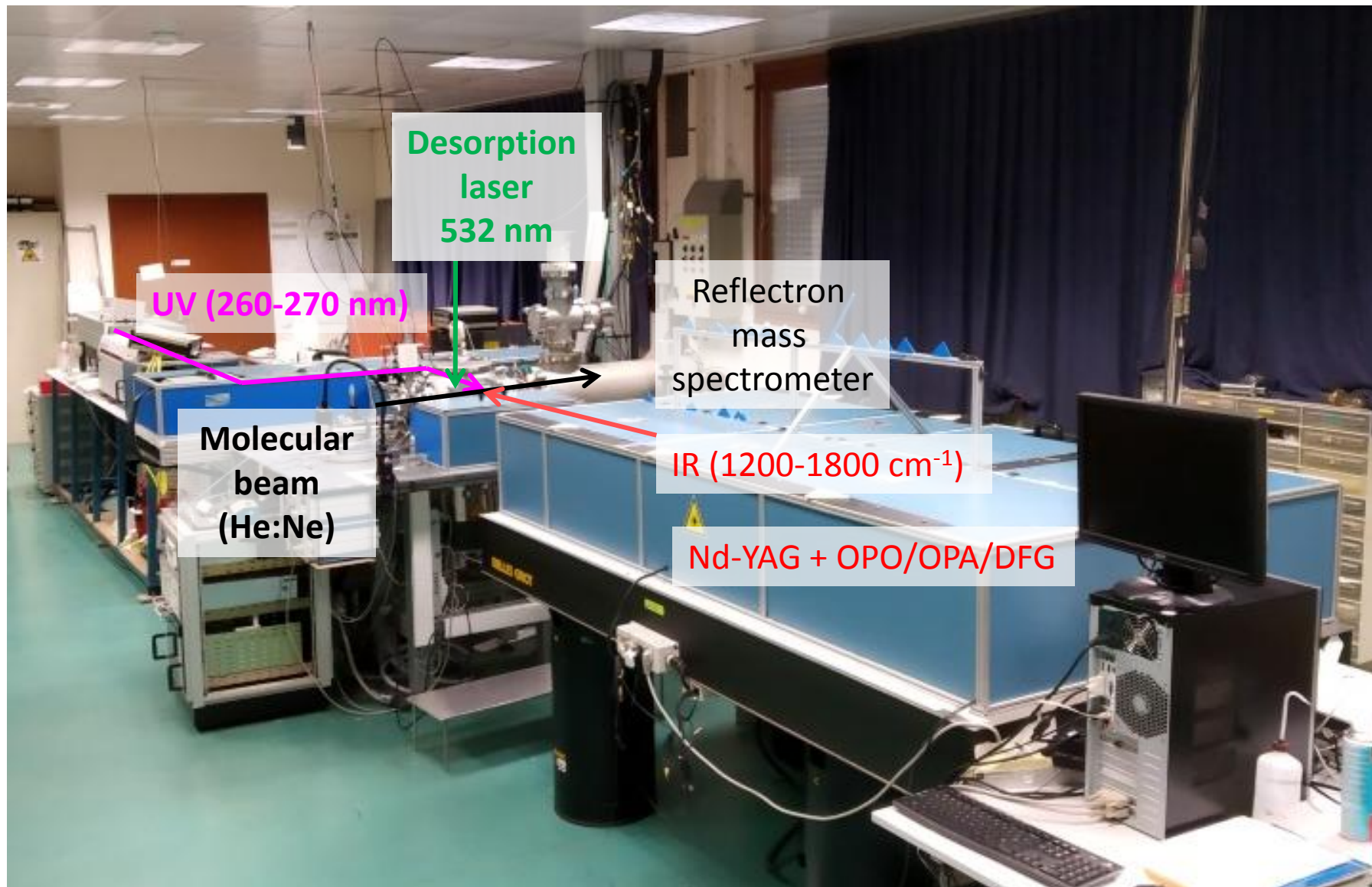
- Cooling in the supersonic expansion (He/Ne): complexes are trapped in one or more conformations



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



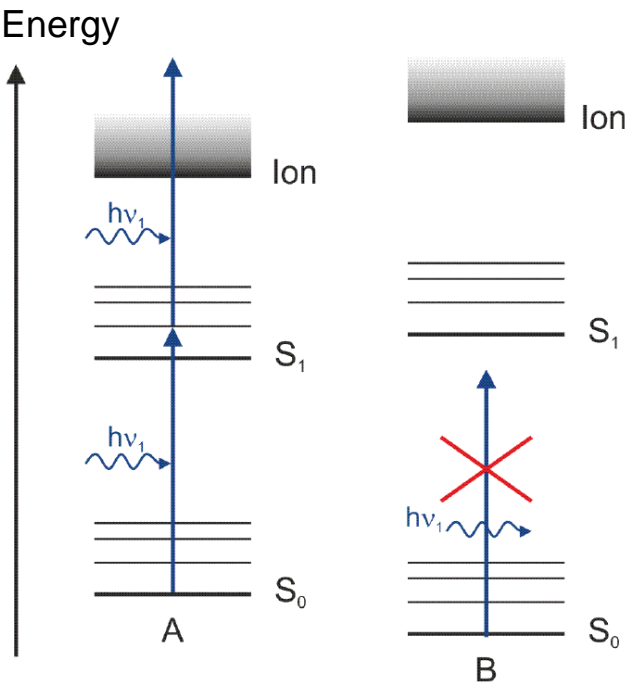
## II. Gas phase experiment



# II. IR/UV double resonance spectroscopy

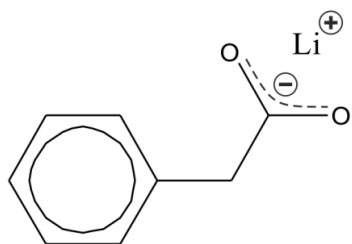
IR/UV

R2PI

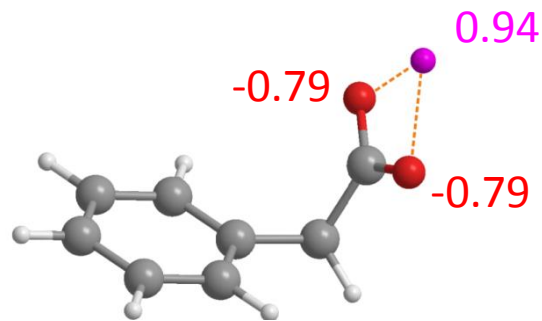


## II. $(\text{Li}^+, \text{PA}^-)_g$

IR/UV double resonance spectroscopy  
→ conformation-selectivity

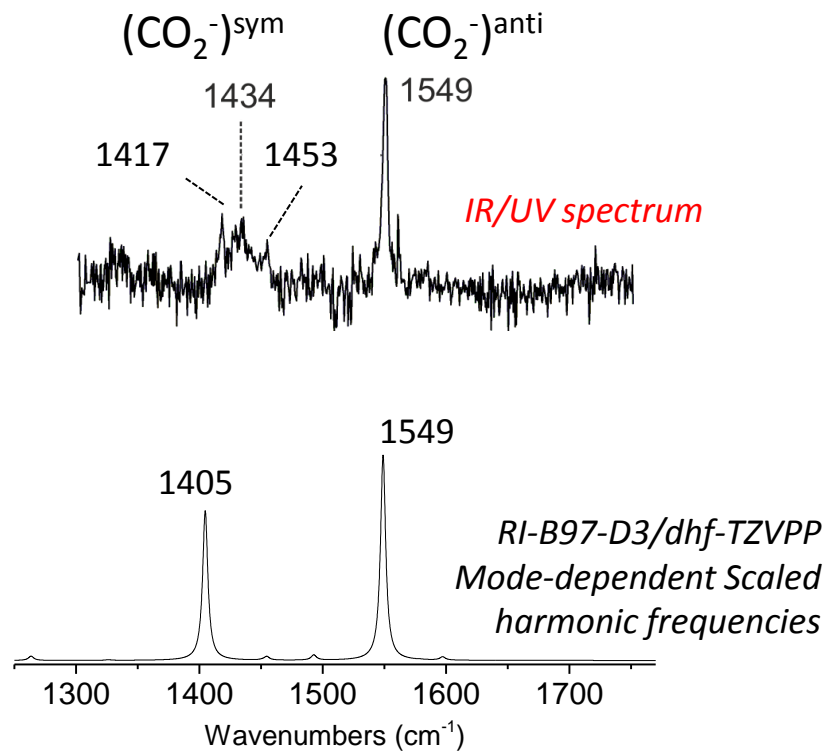
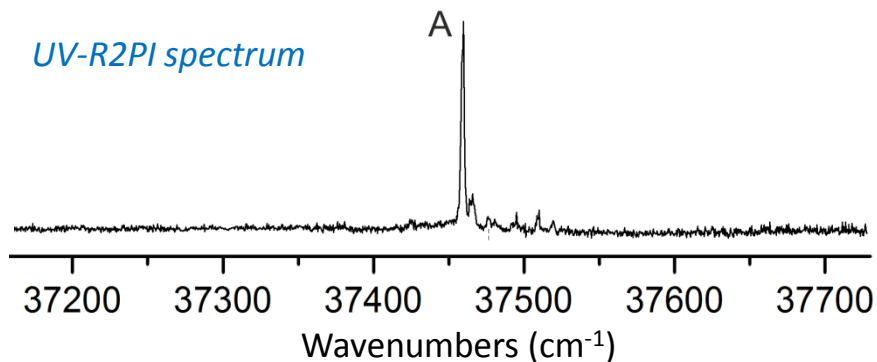


Lithium Phenylacetate  
( $\text{Li}^+$ ,  $\text{PA}^-$ )



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

UV-R2PI spectrum



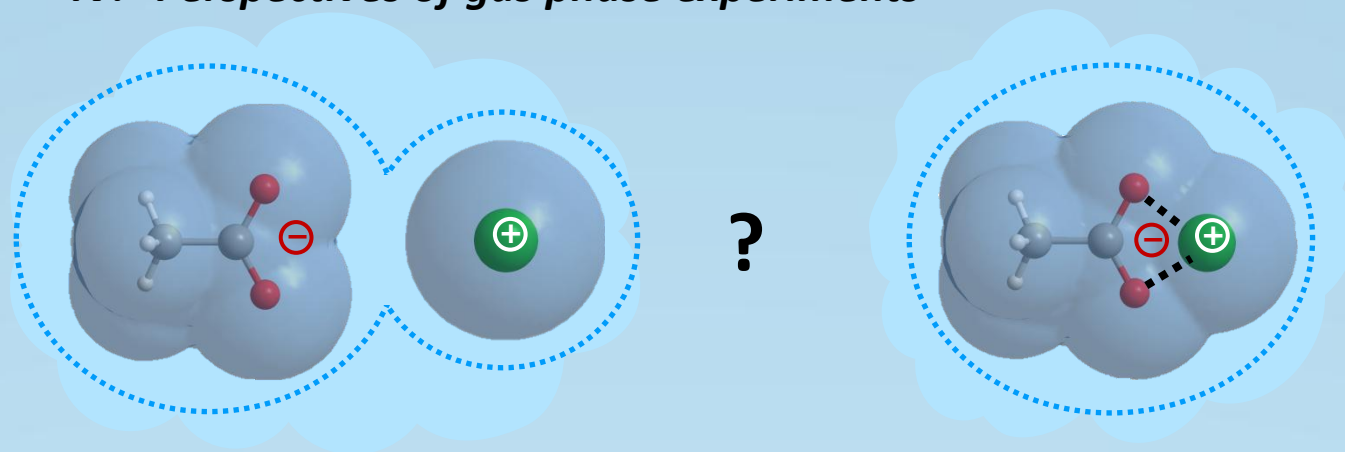
Gas phase ion pairs  
are formed in our  
experiment

## ***I. Introduction***

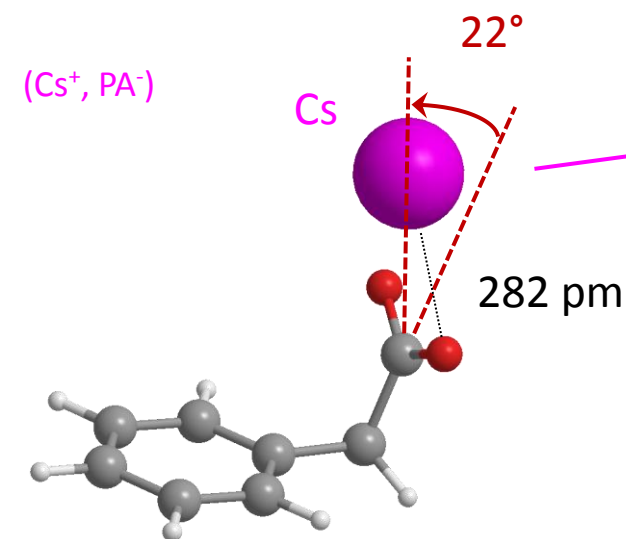
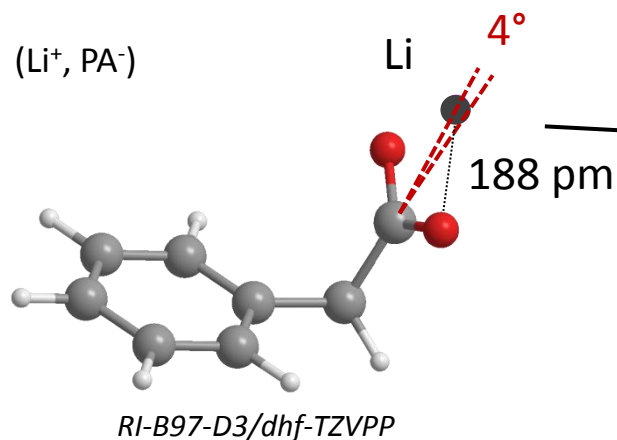
## ***II. IR spectroscopy***

## ***III. UV spectroscopy***

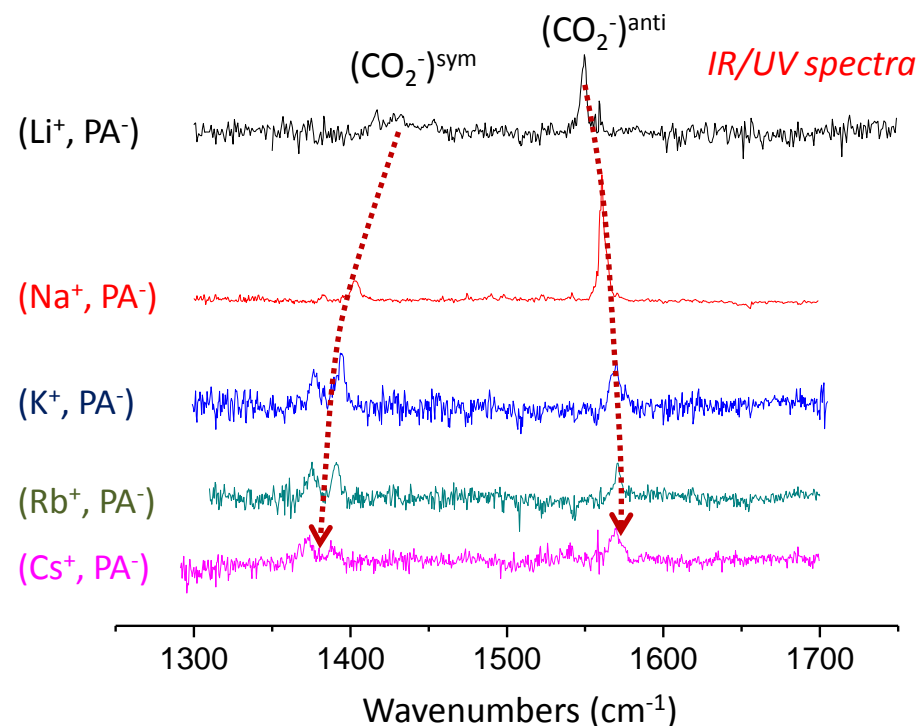
## ***IV. Perspectives of gas phase experiments***



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



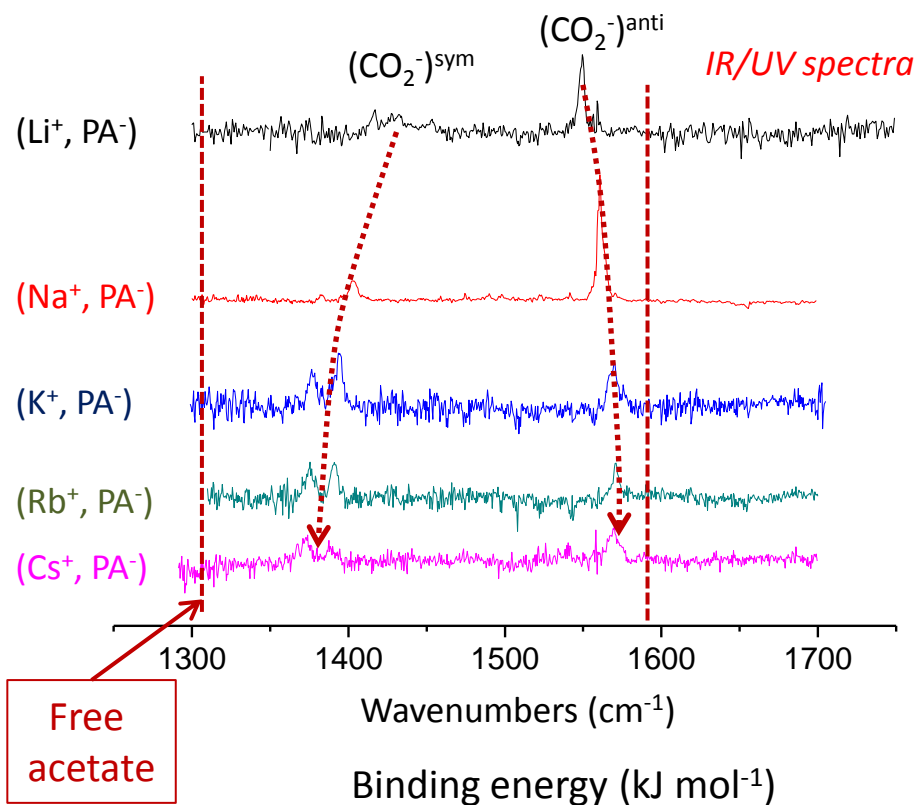
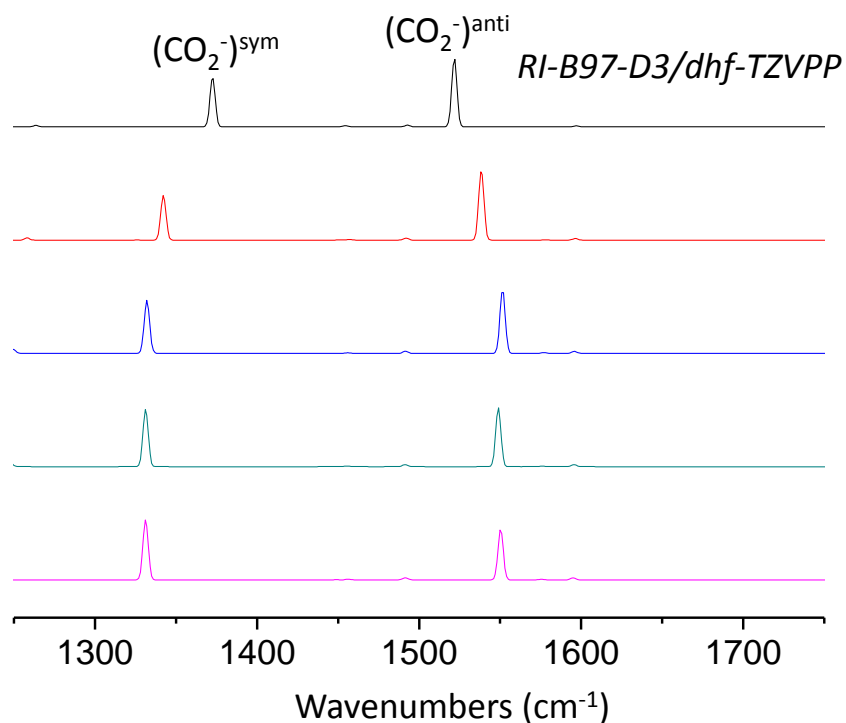
→ Large cations are attracted out-of-the carboxylate plane by the phenyl ring.



→ The multiplicity of the  $(CO_2^-)^{sym}$  stretch reveals a coupling with the torsion around the C-CO<sub>2</sub><sup>-</sup> 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 $(M^+, PA^-)_g$



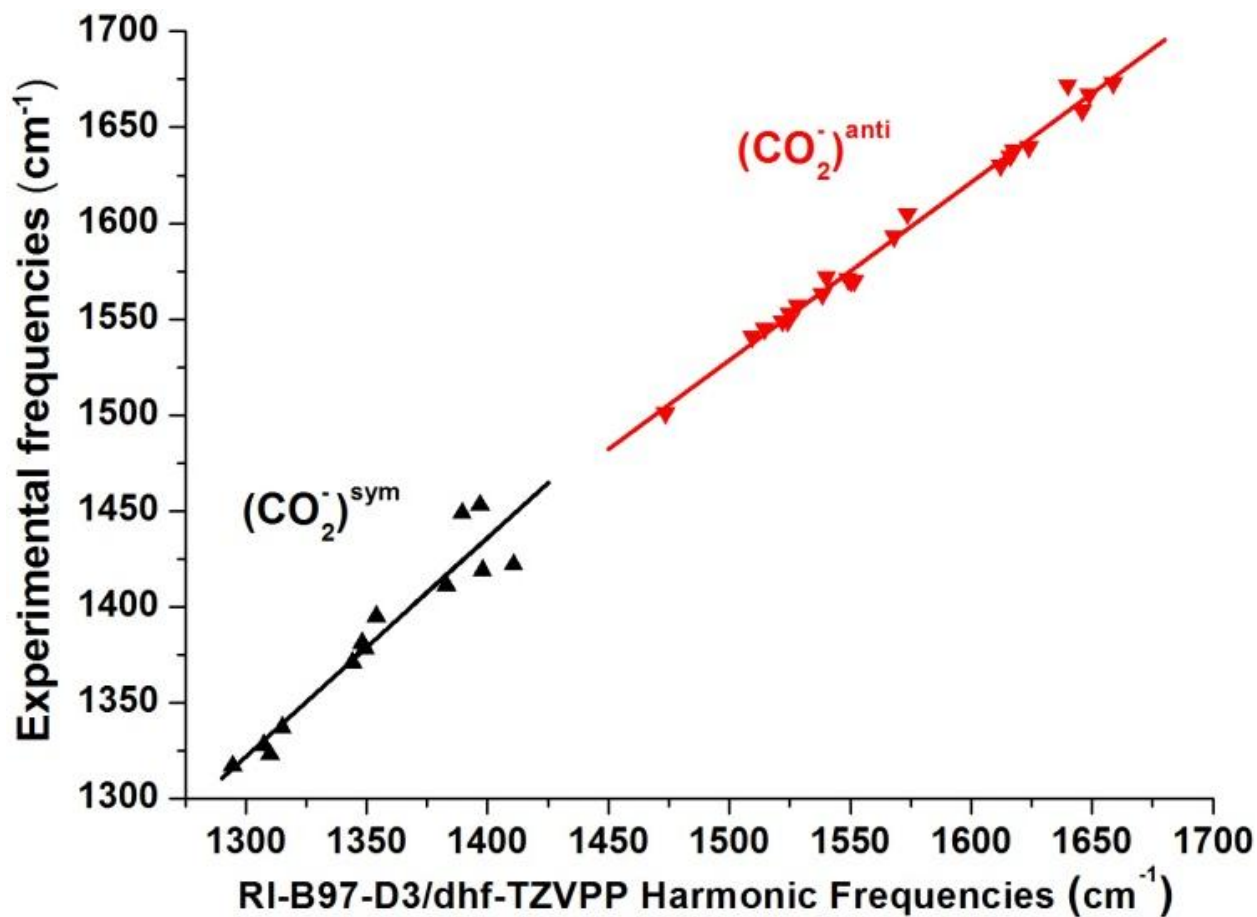
→ Calculations beyond the harmonic approximation are needed to reproduce the multiplicity of the  $(CO_2^-)^{sym}$  stretch

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

$(Li^+, PA^-)$	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



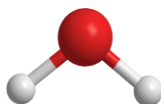
Standard deviations = Error between experiment and theory

15 cm<sup>-1</sup> for CO<sub>2</sub><sup>sym</sup> stretch

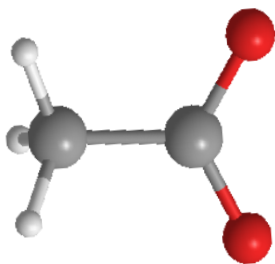
5 cm<sup>-1</sup> for CO<sub>2</sub><sup>anti</sup> stretch

### III. Conformational exploration of ion pairs in solution

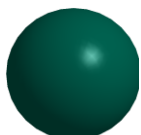
Biased Monte-Carlo Exploration  
at the polarizable force field level (AMOEBA)



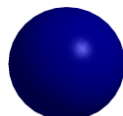
Explicit water molecules



Acetate



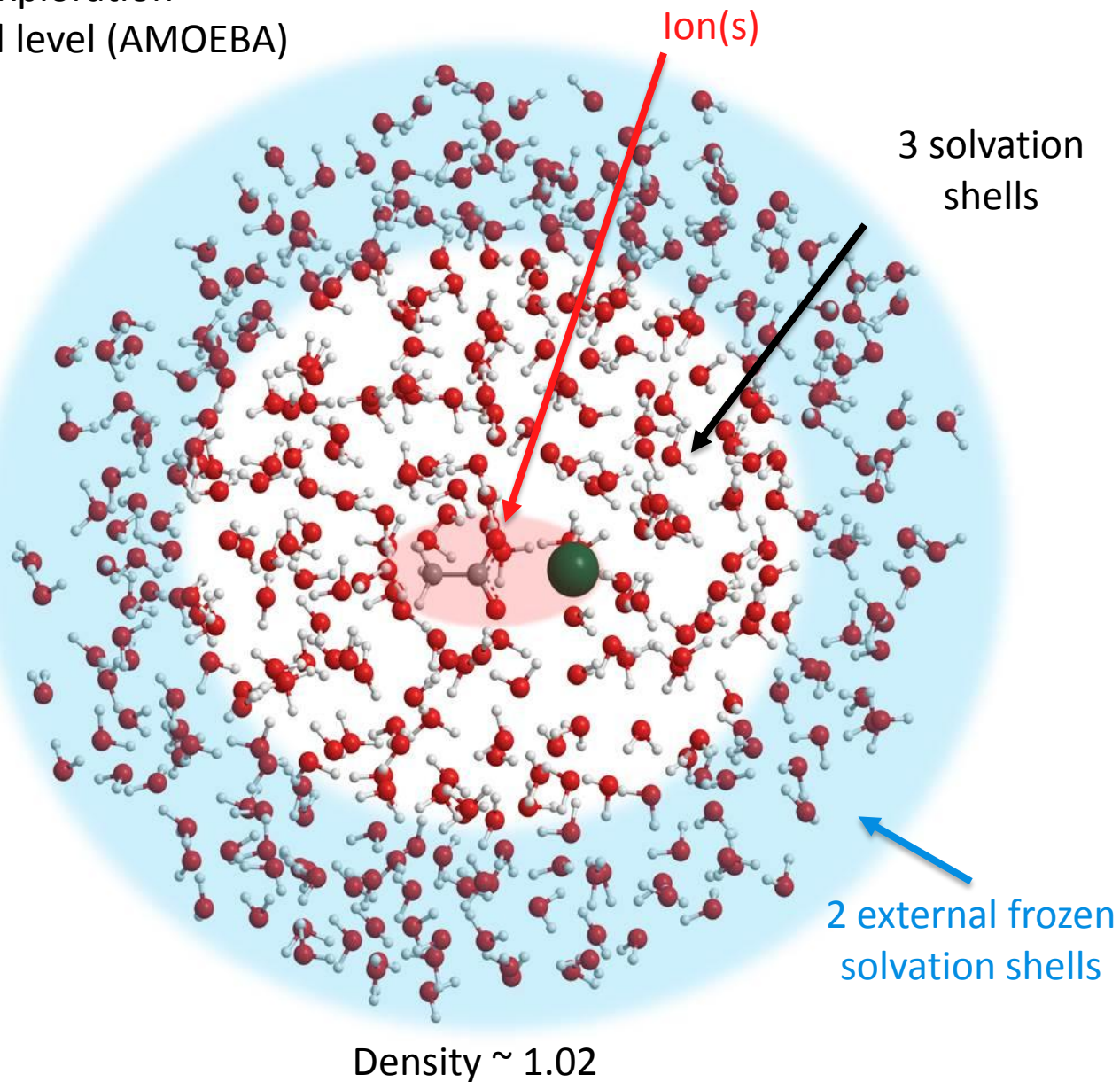
K<sup>+</sup>



Na<sup>+</sup>



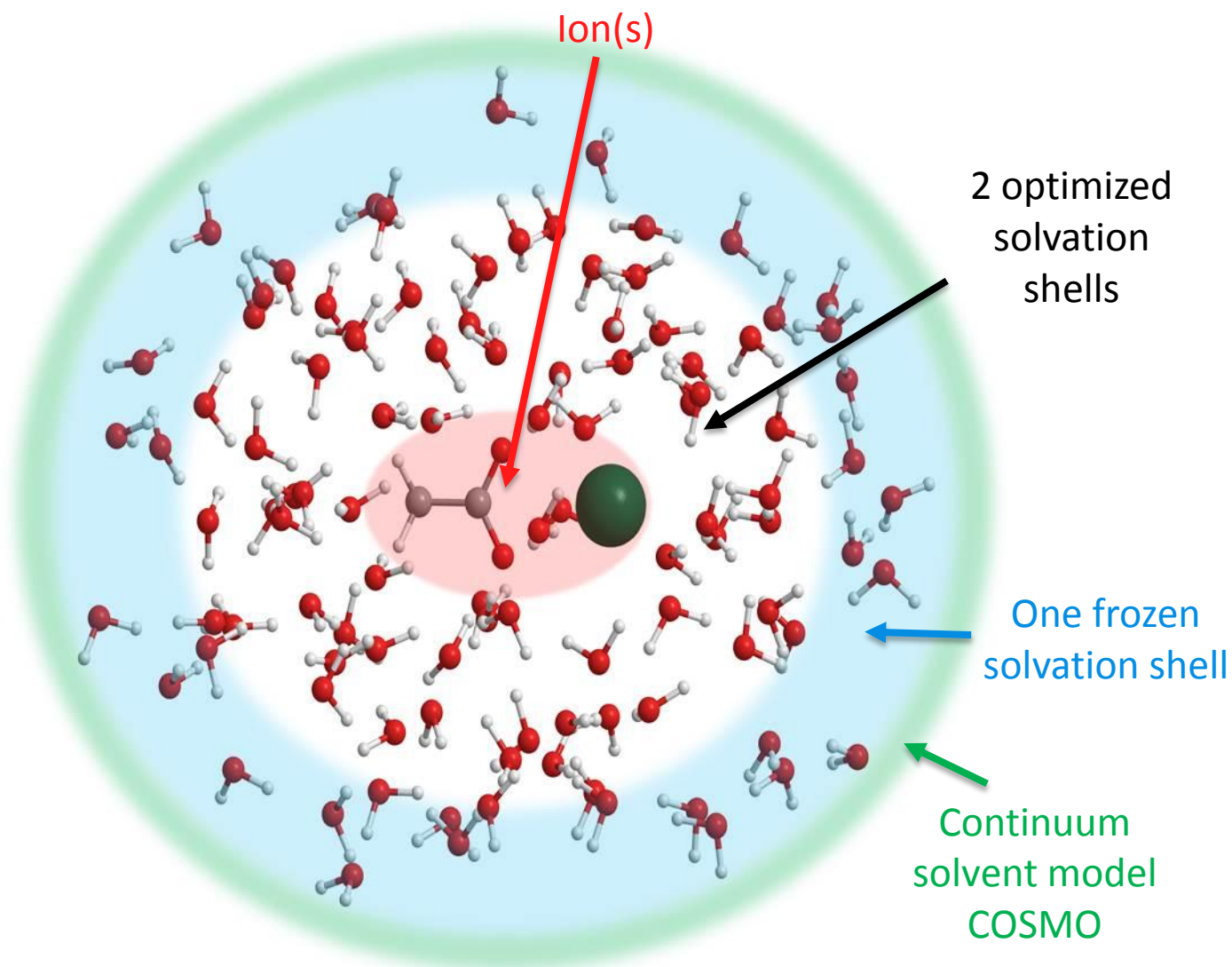
Li<sup>+</sup>





### 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  $\sim 1.02$

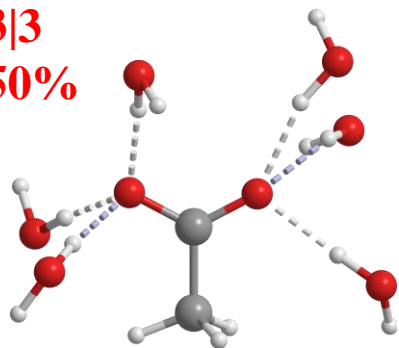
Concentration  $\sim 0.4 \text{ mol L}^{-1}$

### III. Free acetate ions

#### Carboxylate Coordination

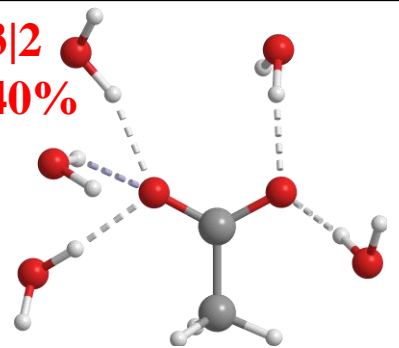
3|3

50%



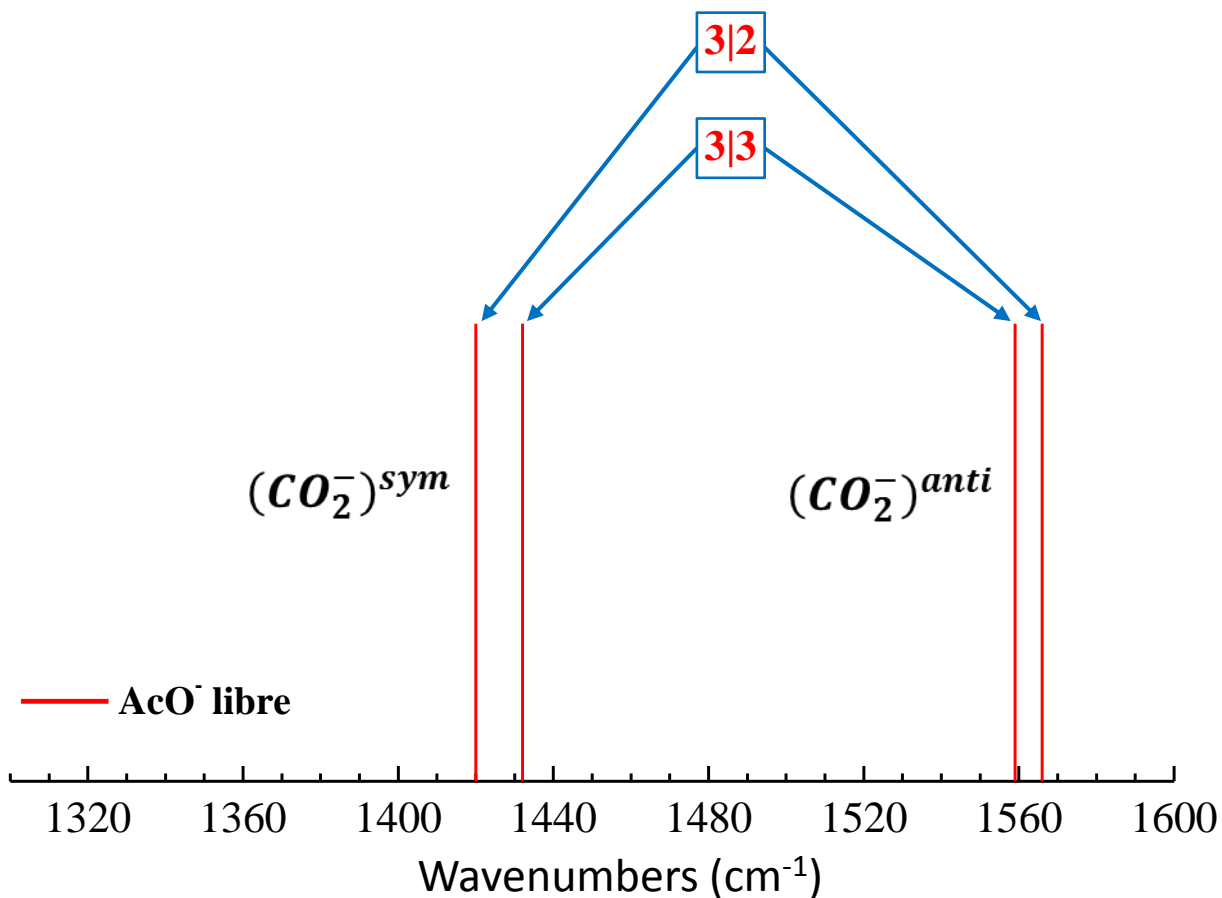
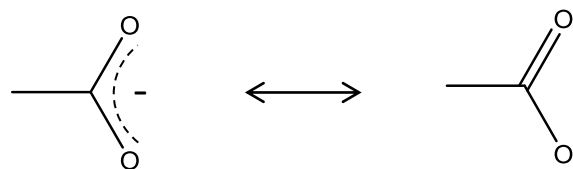
3|2

40%



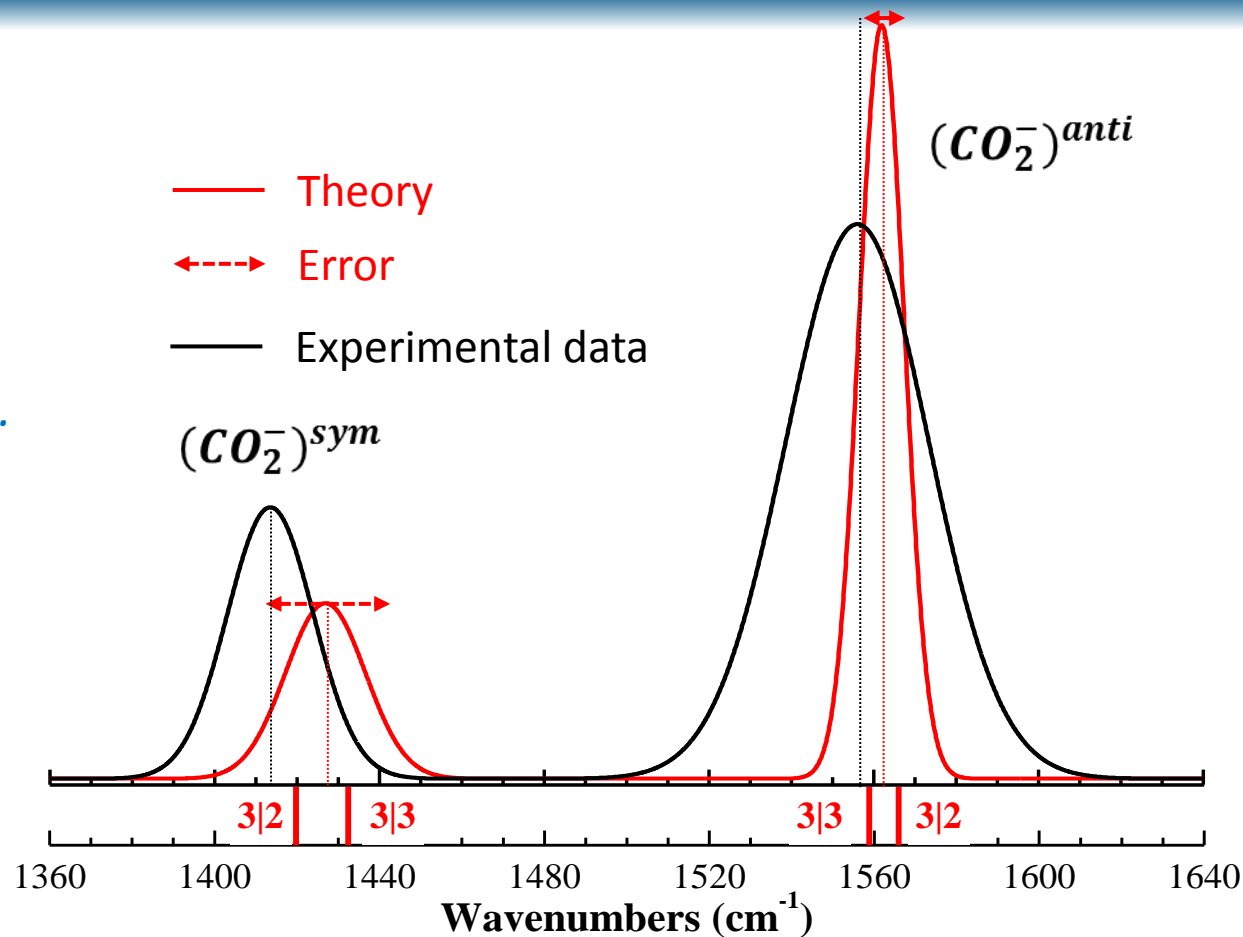
Structures  
extracted from  
larger clusters

The splitting  $\Delta v^{a-s}$  increases when the carboxylate group is in an increasingly asymmetric environment



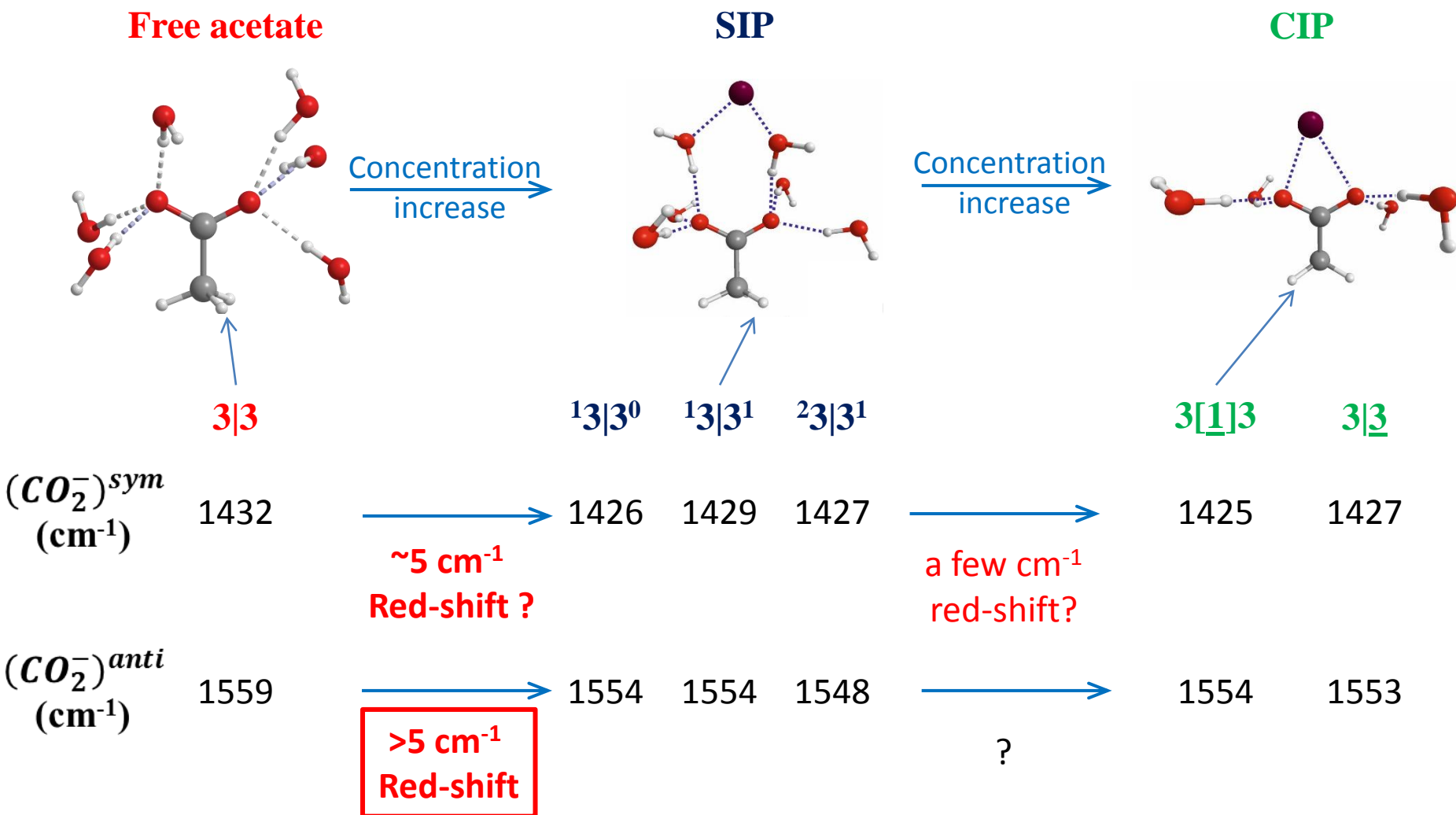
### III. Free acetate ions

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

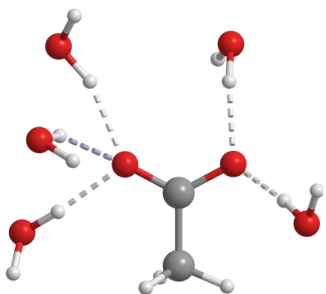


→ The formation of SIPs induces a red-shift of the  $(CO_2^-)^{anti}$  stretch transition

→ 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



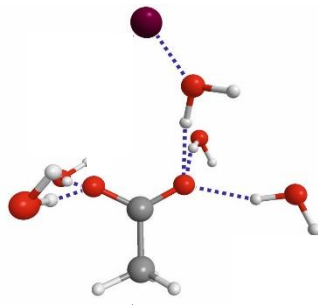
3|2

$(CO_2^-)^{sym}$   
(cm<sup>-1</sup>)

1420

Concentration  
increase →

SIP



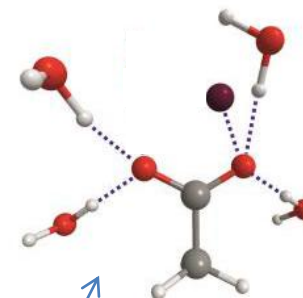
13|2<sup>0</sup> 12|3<sup>0</sup>

1421 1415

→ a few cm<sup>-1</sup>  
red-shift?

Concentration  
increase →

CIP



3|2 3|2

1429 1416

?

$(CO_2^-)^{anti}$   
(cm<sup>-1</sup>)

1566

→ a few cm<sup>-1</sup>  
red-shift?

1565 1564

→ ~5 cm<sup>-1</sup>  
Blue-shift

1568 1573

→ 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

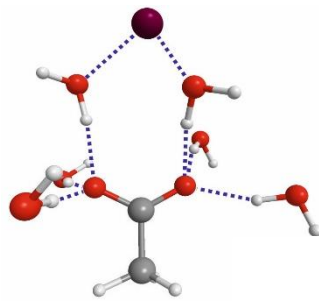
$(CO_2^-)^{anti}$



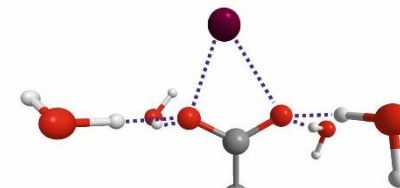
**Measurable  
red-shift**



**Measurable  
Blue-shift**

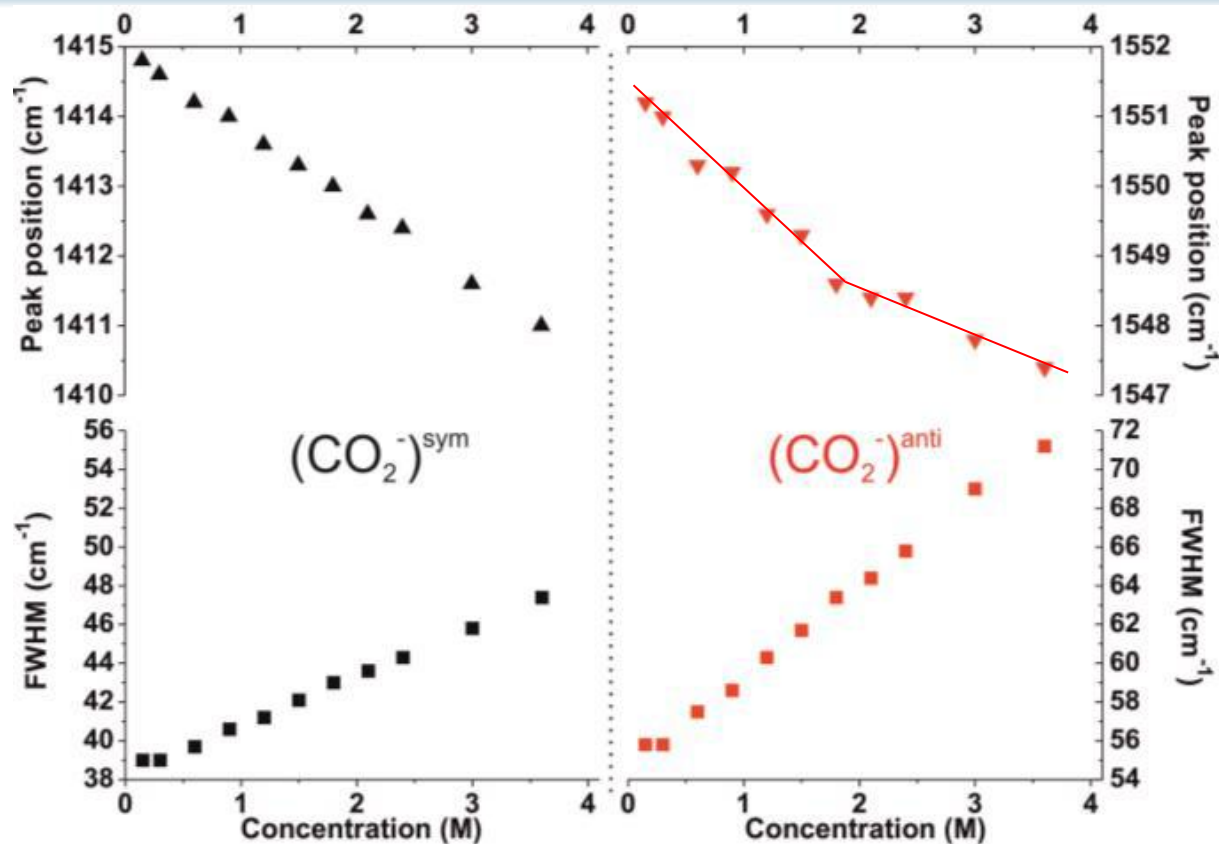
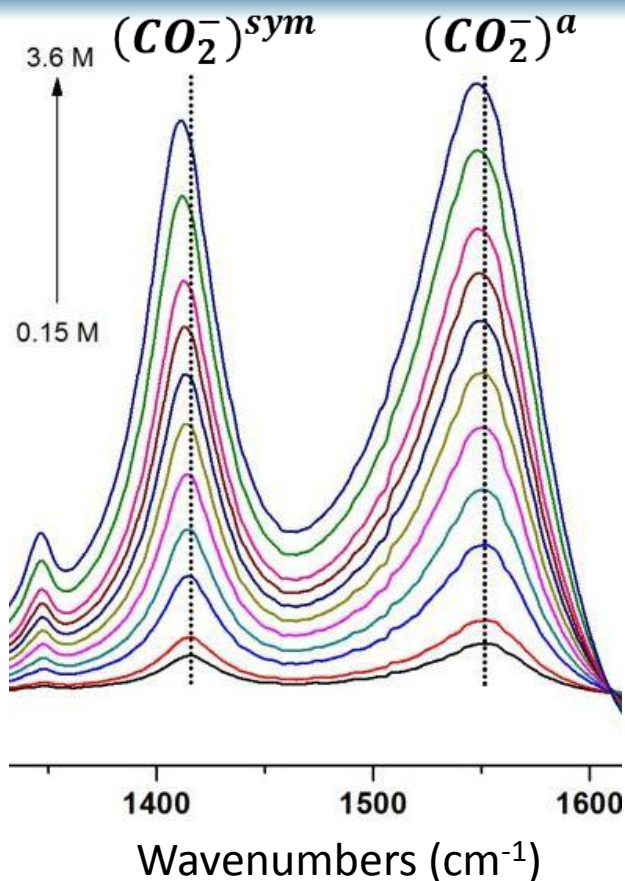


$^{13}C|^{30}S$     $^{13}C|^{31}S$     $^{23}S|^{31}C$



$^3C|^{13}S$     $^3C|^{33}S$

### 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

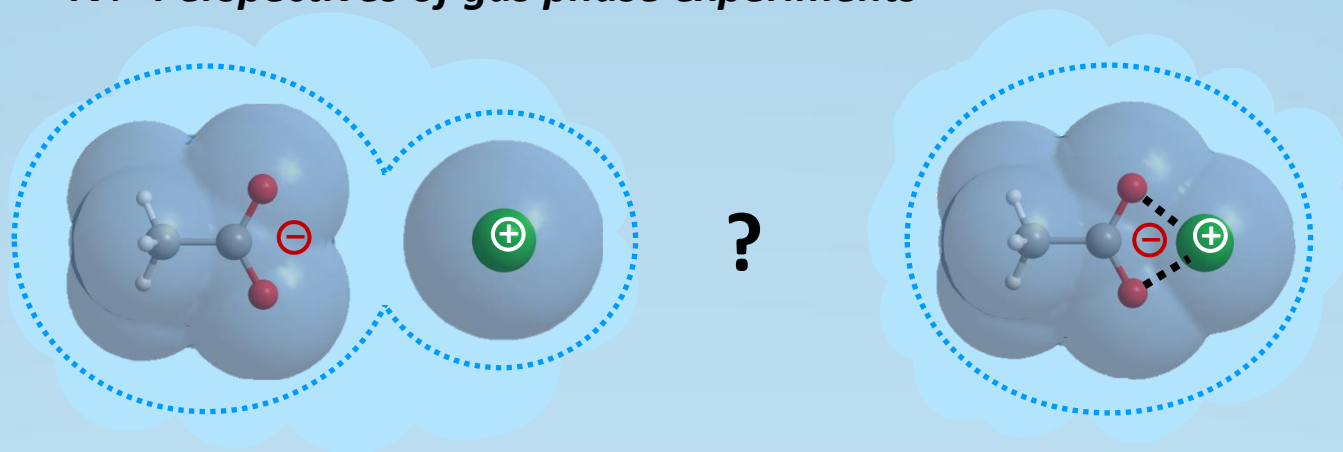
This approach enables us to assign specific supramolecular structures in solution and give typical concentration ranges

**I. Introduction**

**II. IR spectroscopy**

**III. UV spectroscopy**

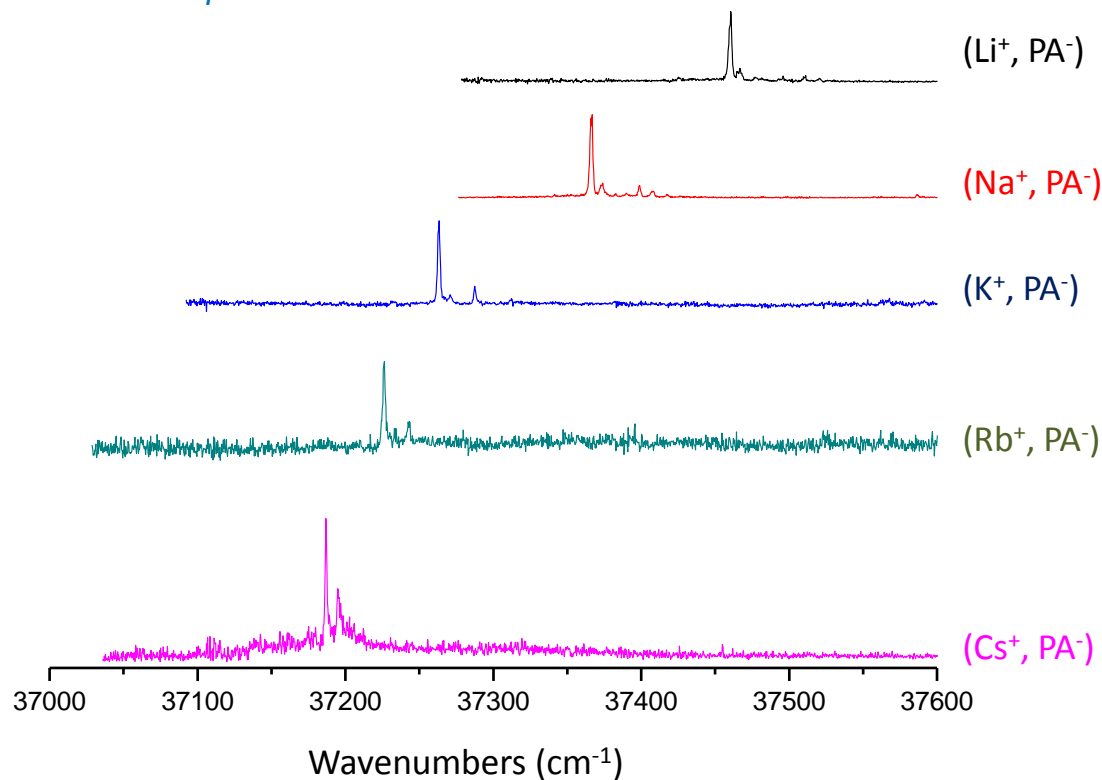
**IV. Perspectives of gas phase experiments**



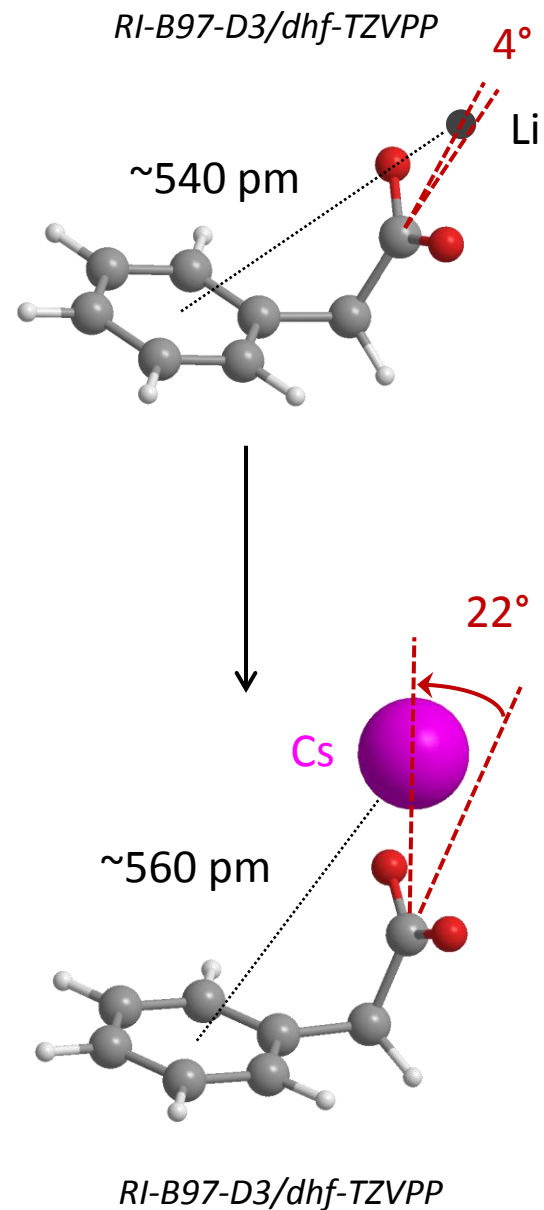


## II. UV Spectroscopy of $(M^+, PA^-)_g$

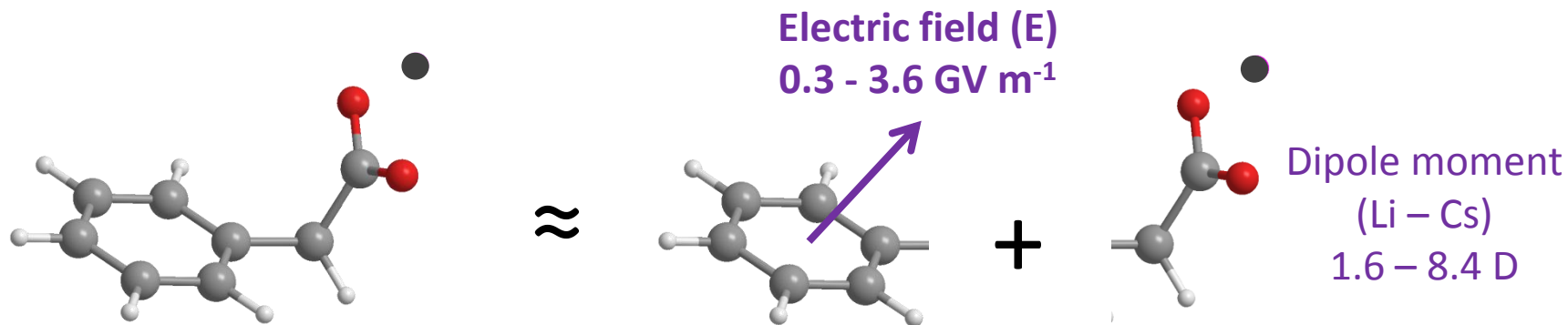
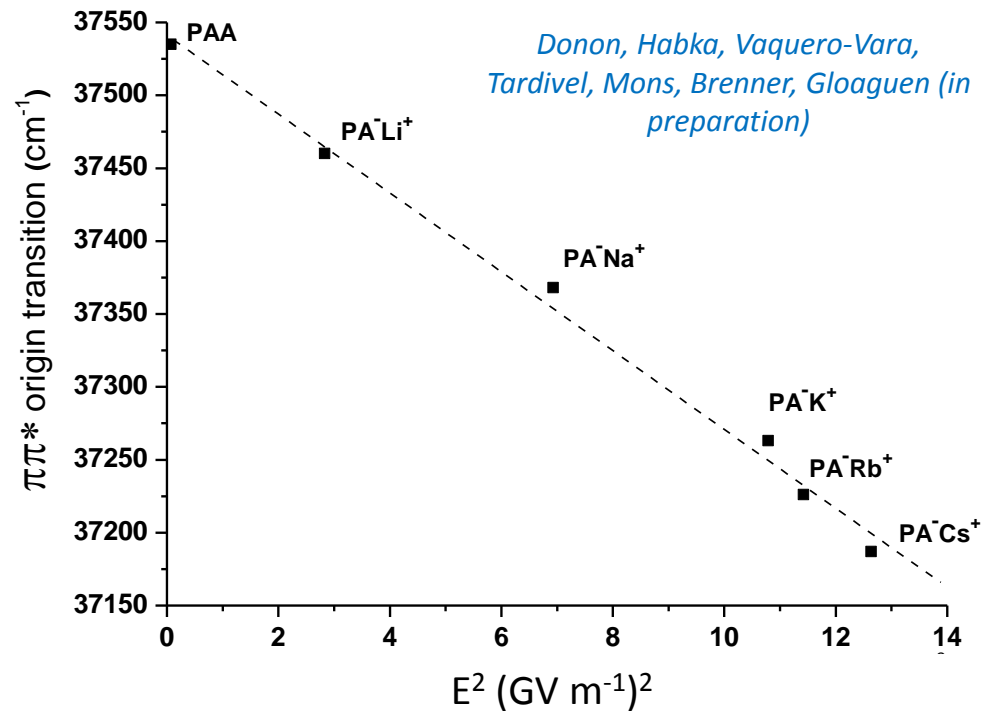
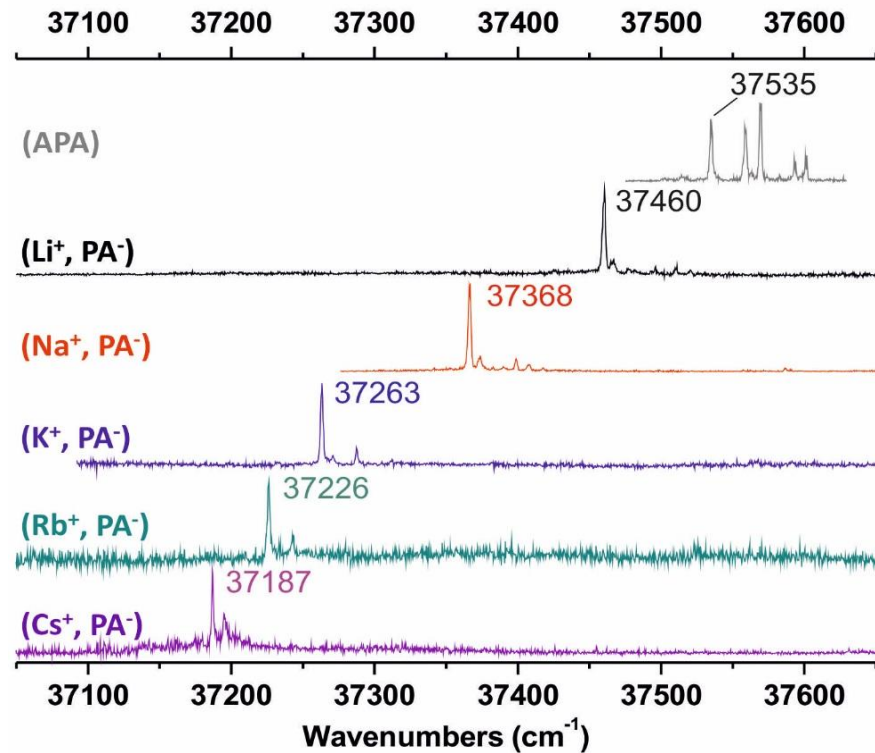
UV-R2PI spectra



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

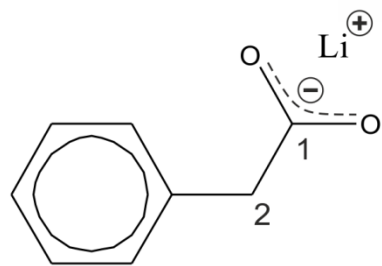


## II. Internal Stark effect

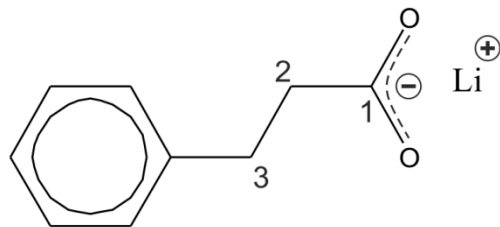


→ Stark spectroscopy of the phenyl ring at very high electric field (up to  $\sim 4 \text{ GV m}^{-1}$ )

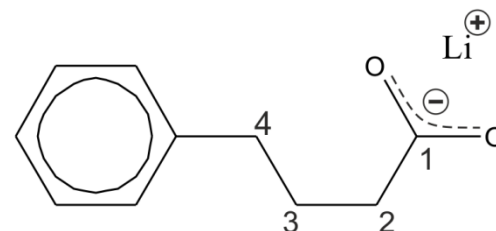
## II. Molecular flexibility within ion pairs



Lithium Phenylacetate  
(Li<sup>+</sup>, PA<sup>-</sup>)

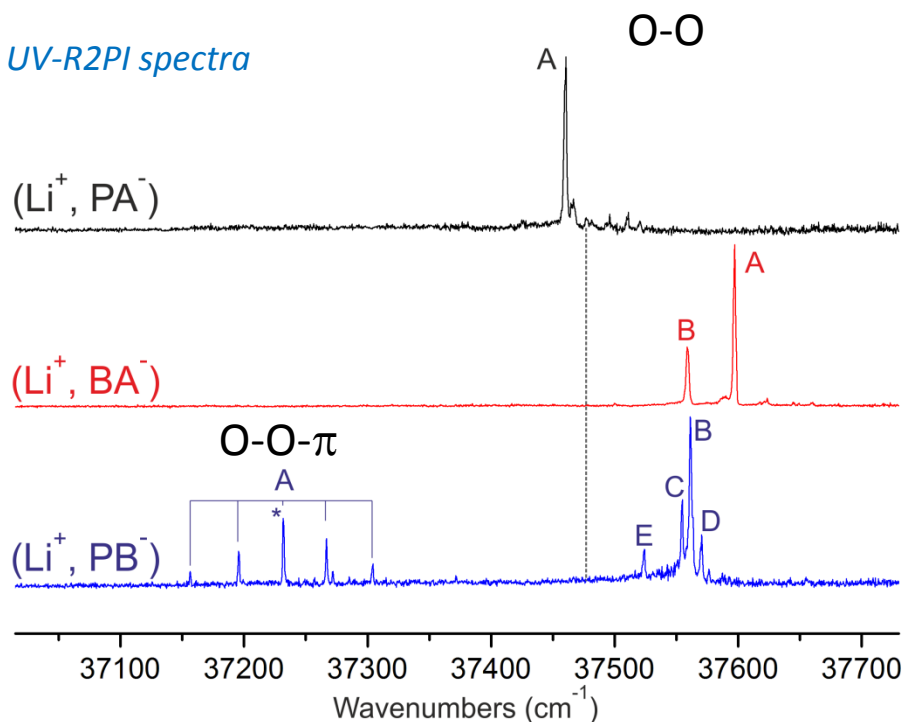


Lithium Benzylacetate  
(Li<sup>+</sup>, BA<sup>-</sup>)

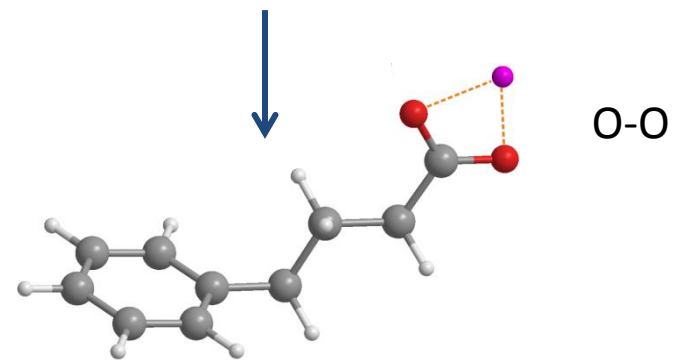


Lithium (4)-phenylbutyrate  
(Li<sup>+</sup>, PB<sup>-</sup>)

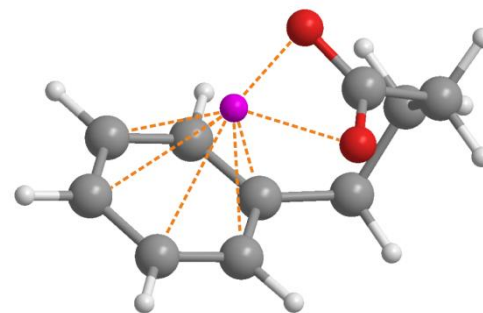
UV-R2PI spectra



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



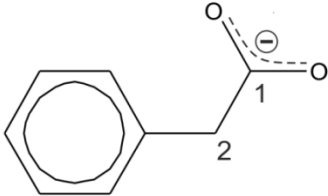
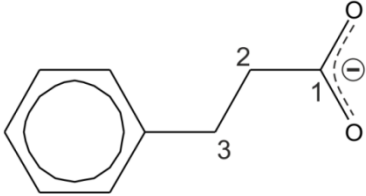
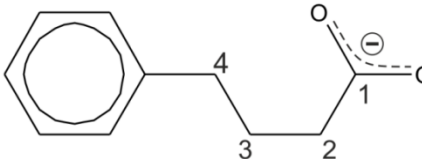
$$\Delta G(300 \text{ K}) = 6 \text{ kJ mol}^{-1}$$



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

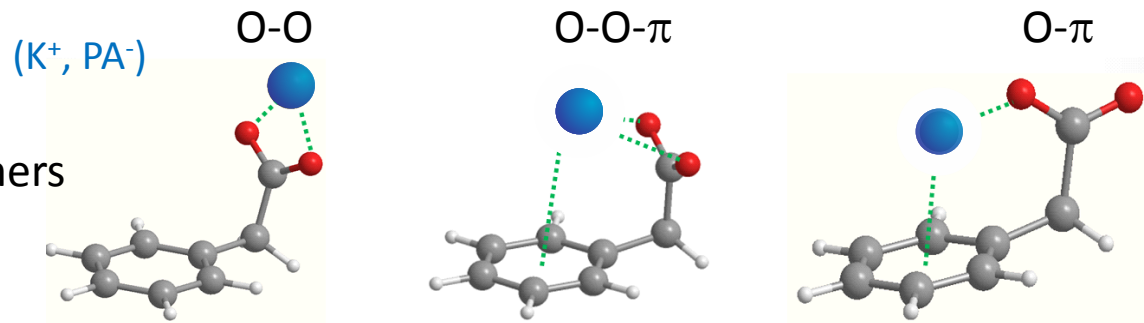
RI-B97-D3/dhf-TZVPP

## II. Experimental vs. Theoretical conformational landscape

Cations \ Anions						
Li <sup>+</sup>	✓	Exp: O-O Th: O-O	✓	O-O O-O	✓	O-O + O-O- $\pi$ O-O + O-O- $\pi$
Na <sup>+</sup>	✓	O-O O-O	✗	O-O O-O + O-O- $\pi$	✓	O-O + O-O- $\pi$ O-O + O-O- $\pi$
K <sup>+</sup>	✗	O-O O-O + O-O- $\pi$	✓	O-O + O-O- $\pi$ O-O + O-O- $\pi$		
Rb <sup>+</sup>	✗	O-O O-O + O-O- $\pi$				
Cs <sup>+</sup>	✗	O-O O-O + O-O- $\pi$				

➔ Inconsistent results between experiment and theory

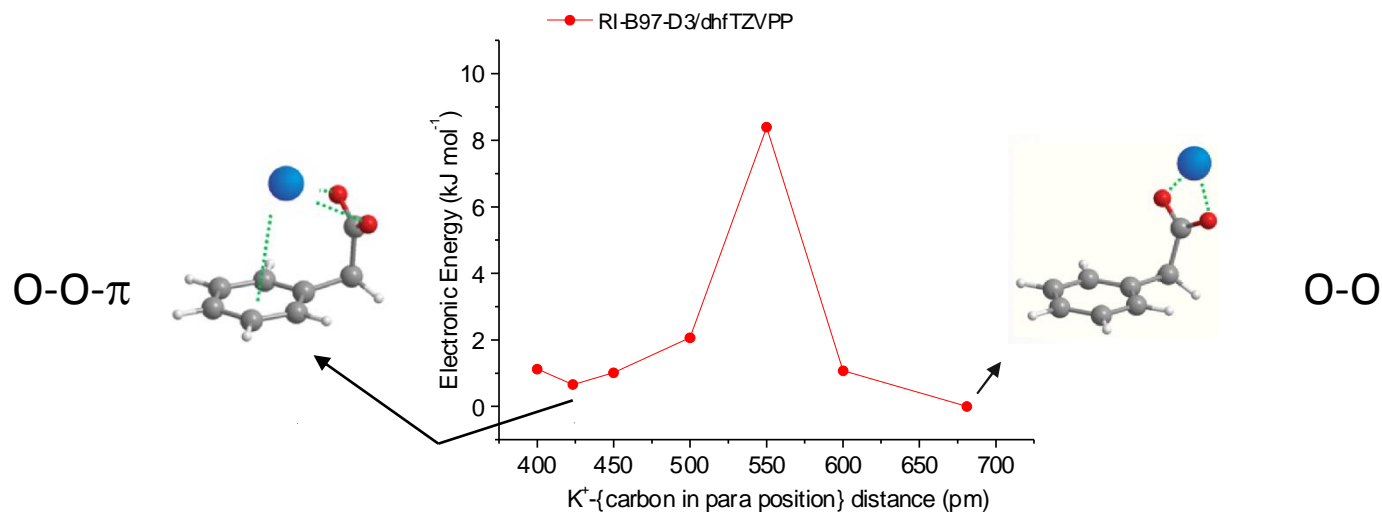
## II. Benchmarks for quantum chemistry



Three most stable conformers

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

	O-O	O-O- $\pi$	O- $\pi$
Li <sup>+</sup> , PA <sup>-</sup>	0	n/a	36
Na <sup>+</sup> , PA <sup>-</sup>	0	n/a	29
K <sup>+</sup> , PA <sup>-</sup>	0	6*	21
Rb <sup>+</sup> , PA <sup>-</sup>	0	5*	20
Cs <sup>+</sup> , PA <sup>-</sup>	0	3*	18



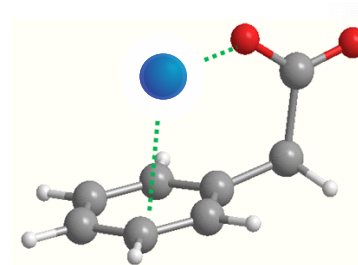
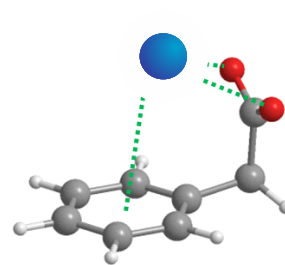
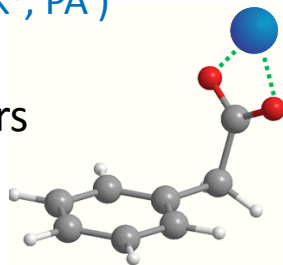
## II. Benchmarks for quantum chemistry

(K<sup>+</sup>, PA<sup>-</sup>)

O-O

O-O- $\pi$

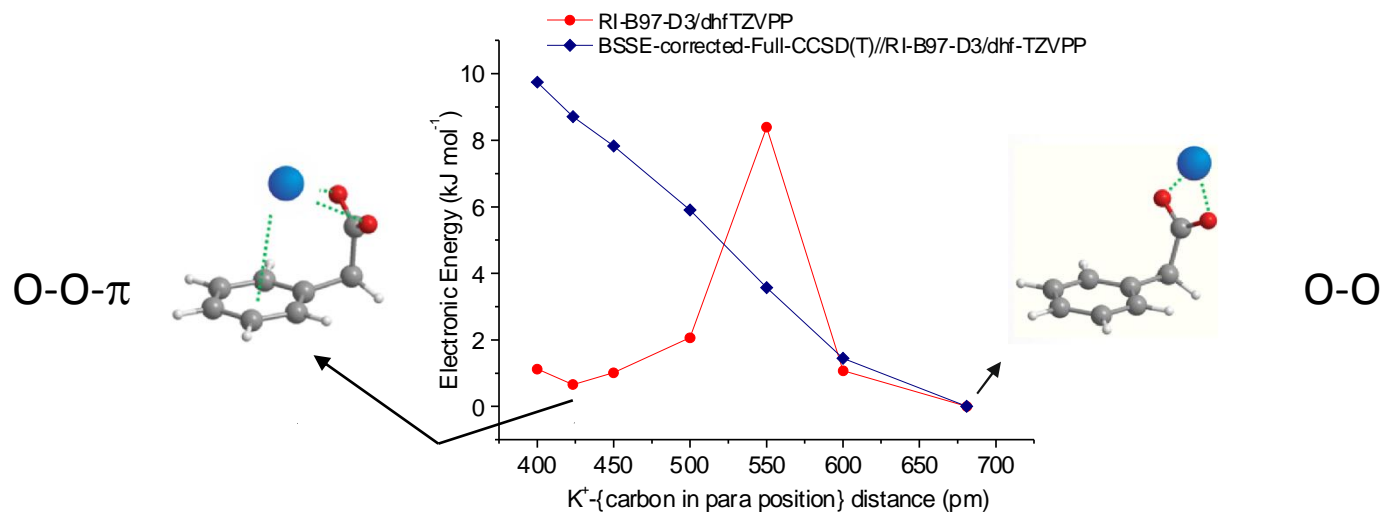
O- $\pi$



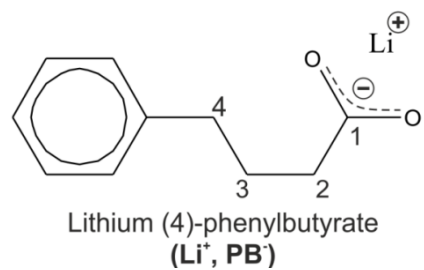
Three most stable conformers

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

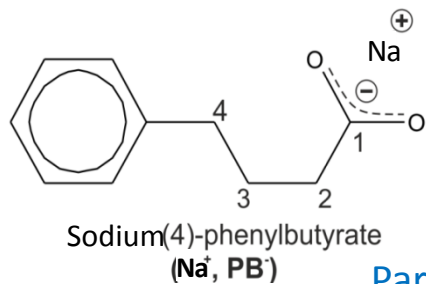
	O-O	O-O- $\pi$	O- $\pi$
Li <sup>+</sup> , PA <sup>-</sup>	0	n/a	36
Na <sup>+</sup> , PA <sup>-</sup>	0	n/a	29
K <sup>+</sup> , PA <sup>-</sup>	0	6*	21
Rb <sup>+</sup> , PA <sup>-</sup>	0	5*	20
Cs <sup>+</sup> , PA <sup>-</sup>	0	3*	18



## II. Fragmentation

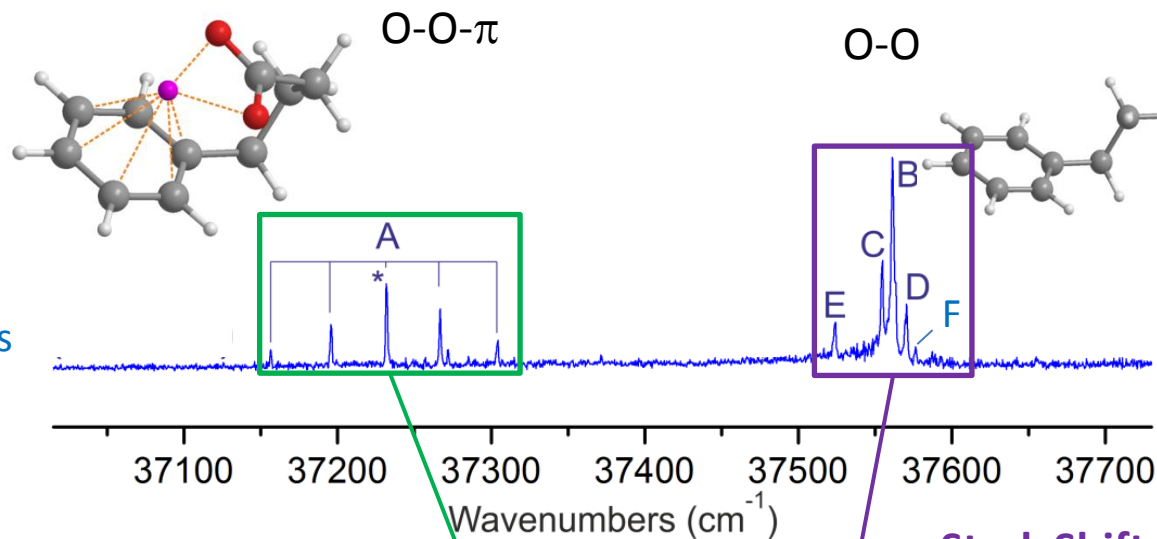


Parent ion mass  
channel



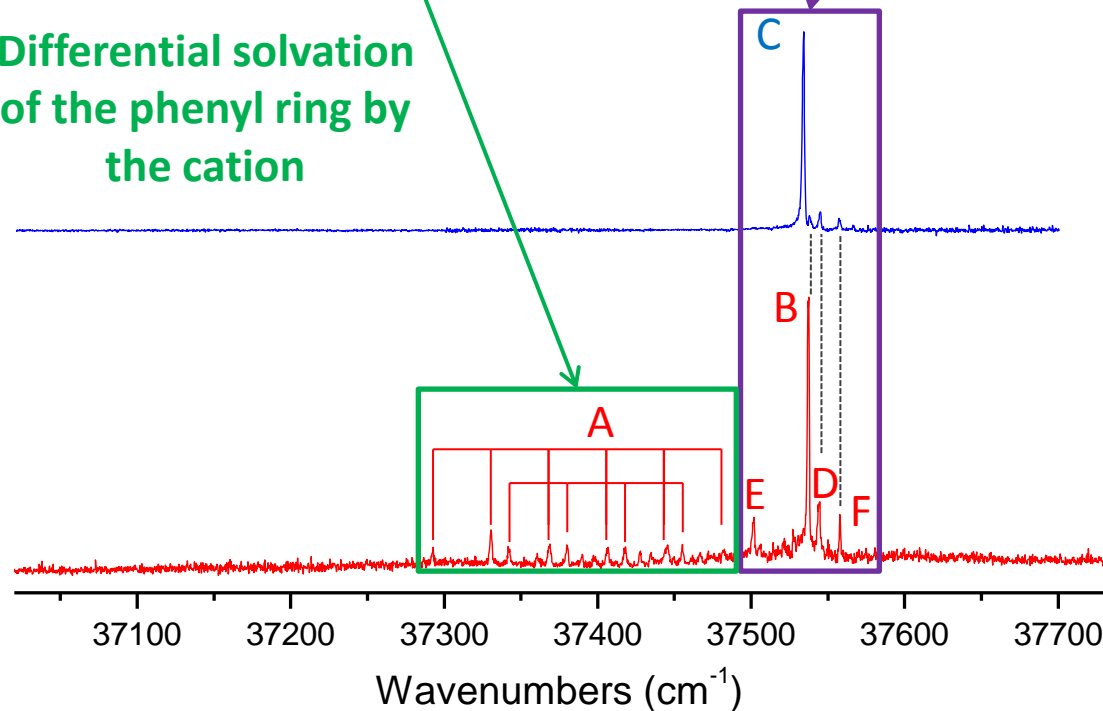
Parent ion mass  
channel

Fragment  
(CO<sub>2</sub> loss)



Differential solvation  
of the phenyl ring by  
the cation

Stark Shift



***I. Introduction***

***II. IR spectroscopy***

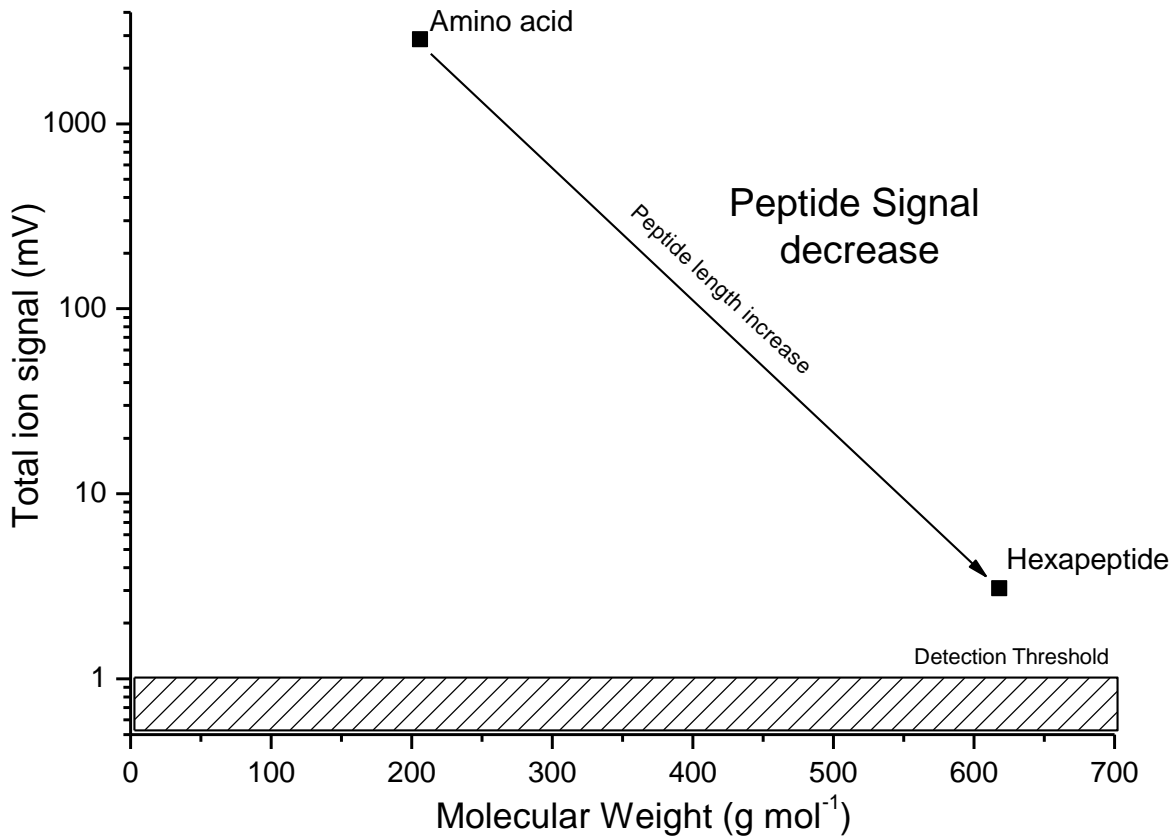
***III. UV spectroscopy***

***IV. Perspectives of gas phase experiments***





## Laser Desorption + R2PI : the peptide case

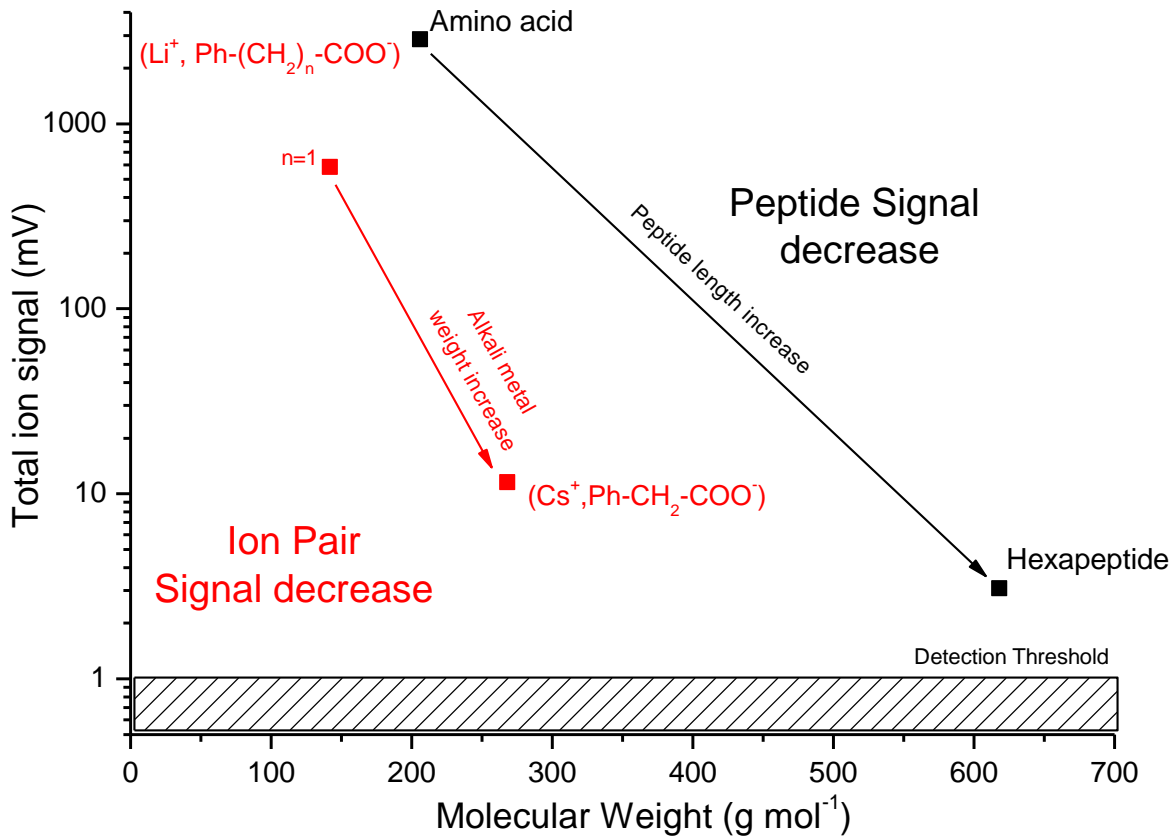


→ Not specific to R2PI

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

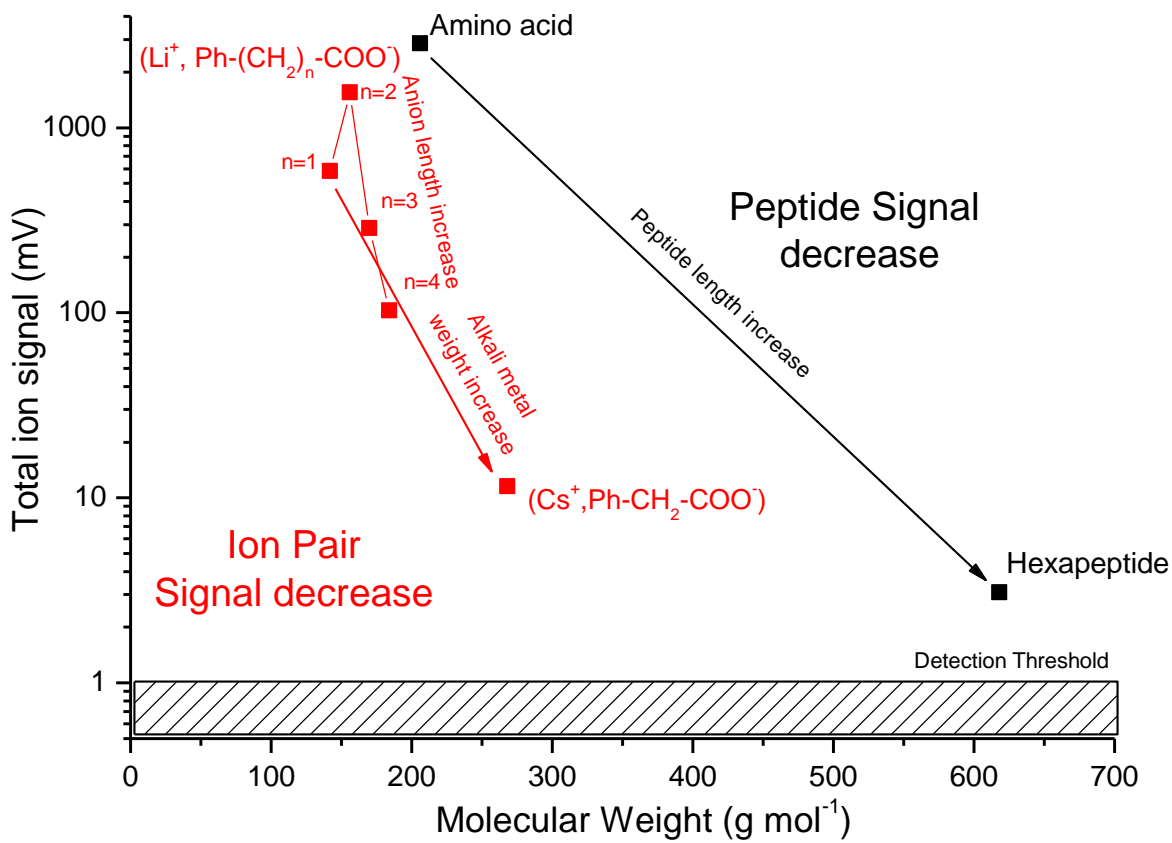
→ Excitation of states of the neutral followed by a rapid relaxation efficiently quenching ionization

## Laser Desorption + R2PI : the ion pair case



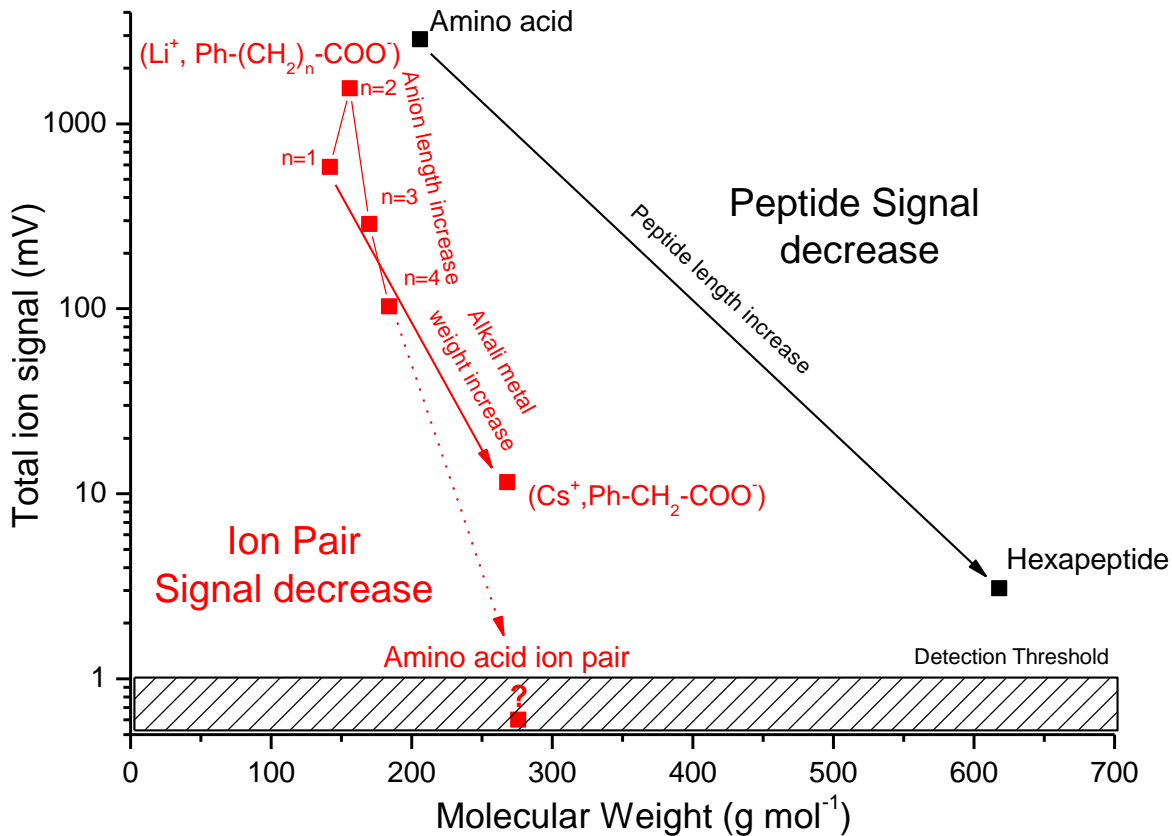
→ A more dramatic decrease is observed for ion pairs !

## Laser Desorption + R2PI : the ion pair case



→ A more dramatic decrease is observed for ion pairs !

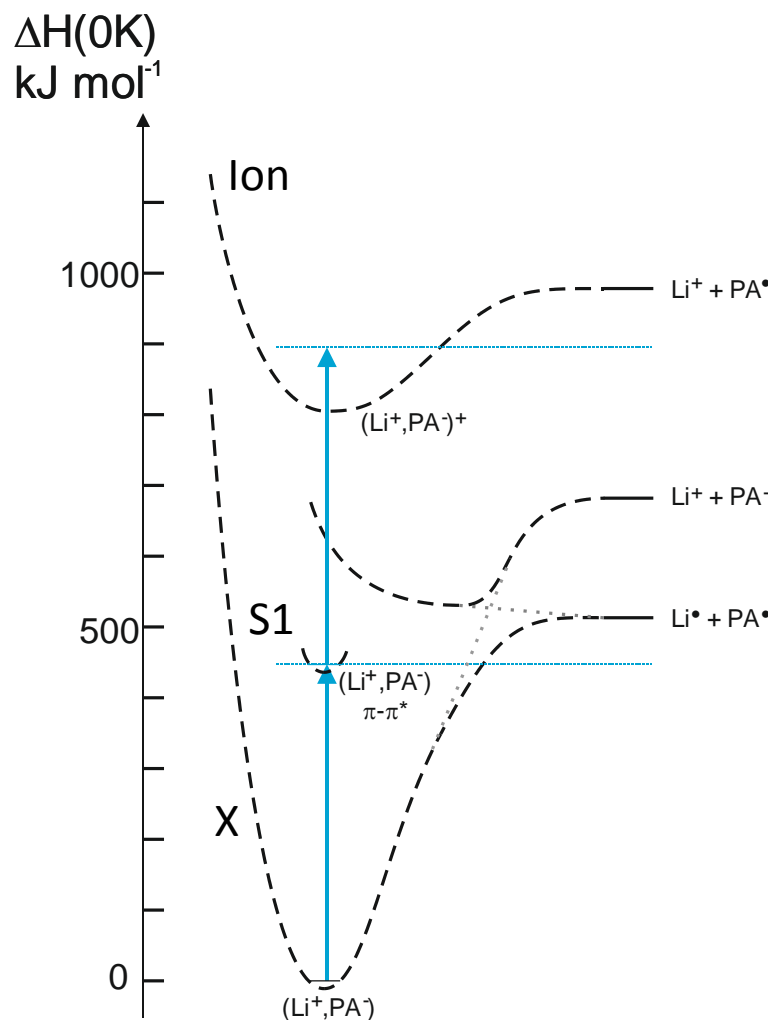
## Laser Desorption + R2PI : the ion pair case



→ 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?

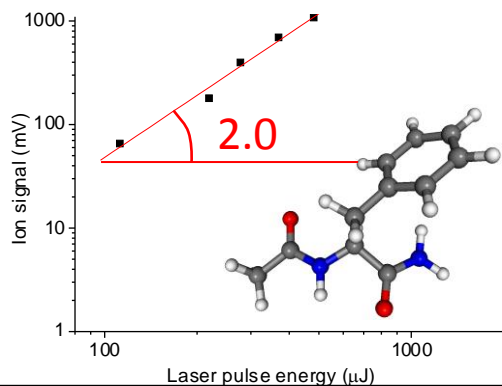
A. Quenching of ionization by relaxation of superexcited states of the neutral

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

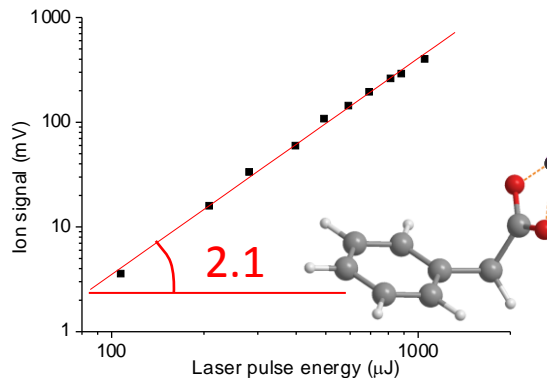
C. Vaporization efficiency

## IV. Signal variations with the laser pulse energy

Ac-Phe-NH<sub>2</sub>



(Li<sup>+</sup>, PA<sup>-</sup>)

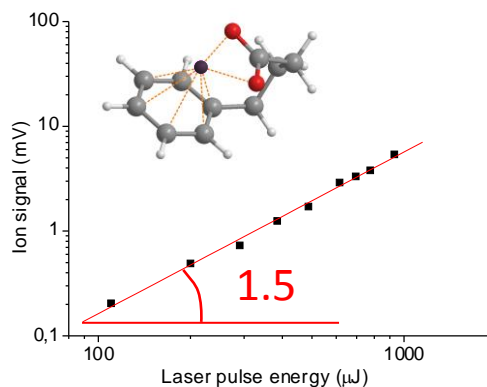
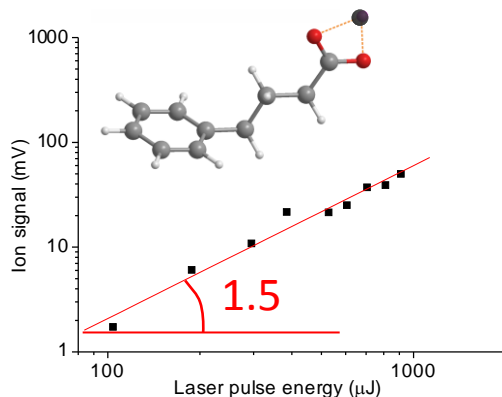


Apparent number of photon involved in the ionization process:

$$AN = 2$$

→ Equivalent absorption probability of both photons

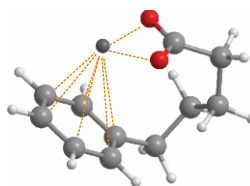
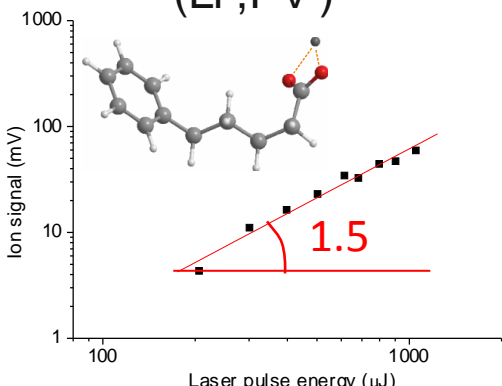
(Li<sup>+</sup>, PB<sup>-</sup>)



$$AN = 1.5$$

→ one absorption step is more probable than the other

(Li<sup>+</sup>, PV<sup>-</sup>)



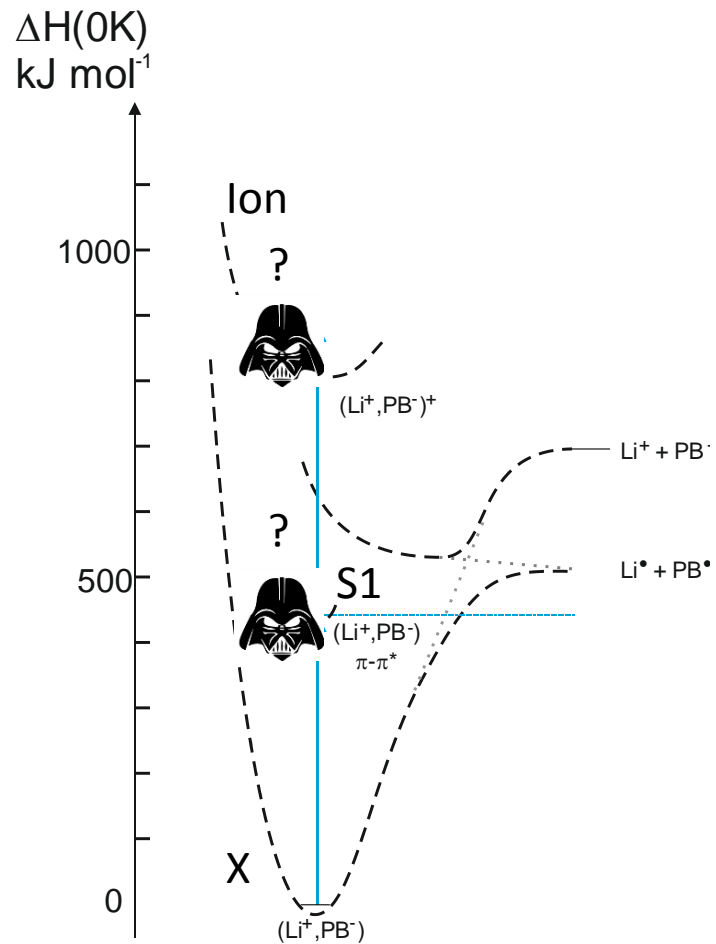
Lowest-energy conformer (missing)

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

→ Presence of dark states efficiently quenching ionization



## IV. How to fight against dark states ?



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

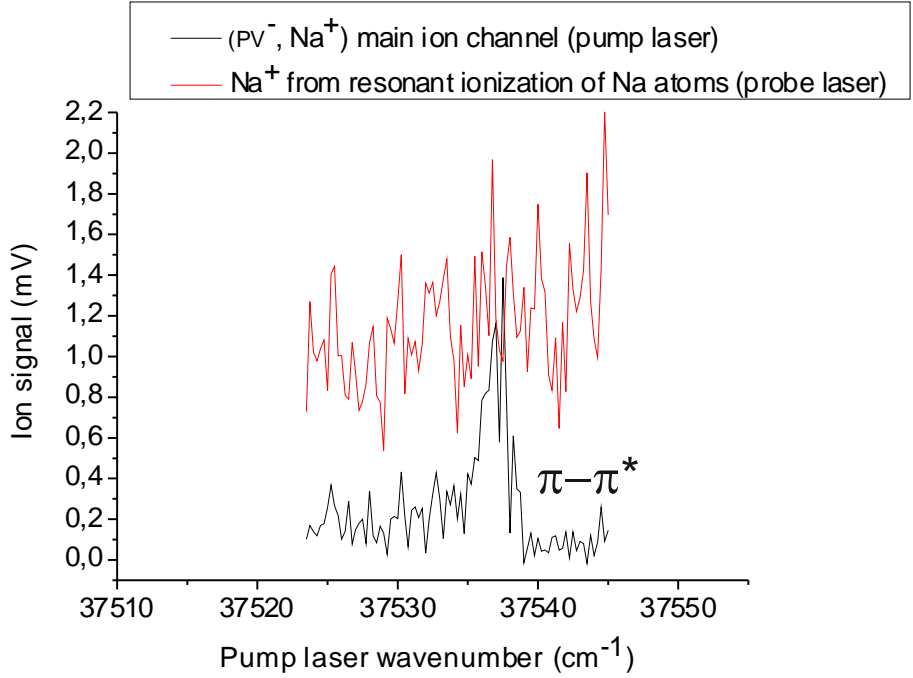
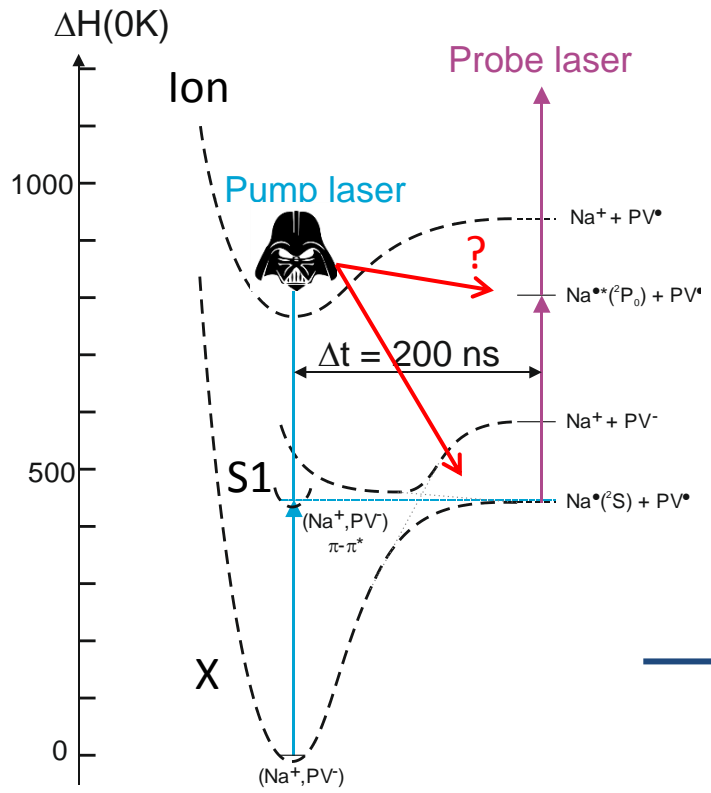
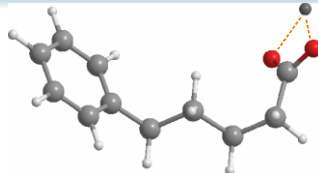
→ Add an IR laser to improve the ionization signal  
*...40% increase only, work in progress...*

→ Monitoring the fragmentation channels leading to neutral atoms  
*... next slide ...*

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

→ Lifetime measurements  
*...work in progress...*

# IV. Shedding light on dark channels



No pump-probe signal

No relaxation to the most obvious non-ionic fragmentation channels

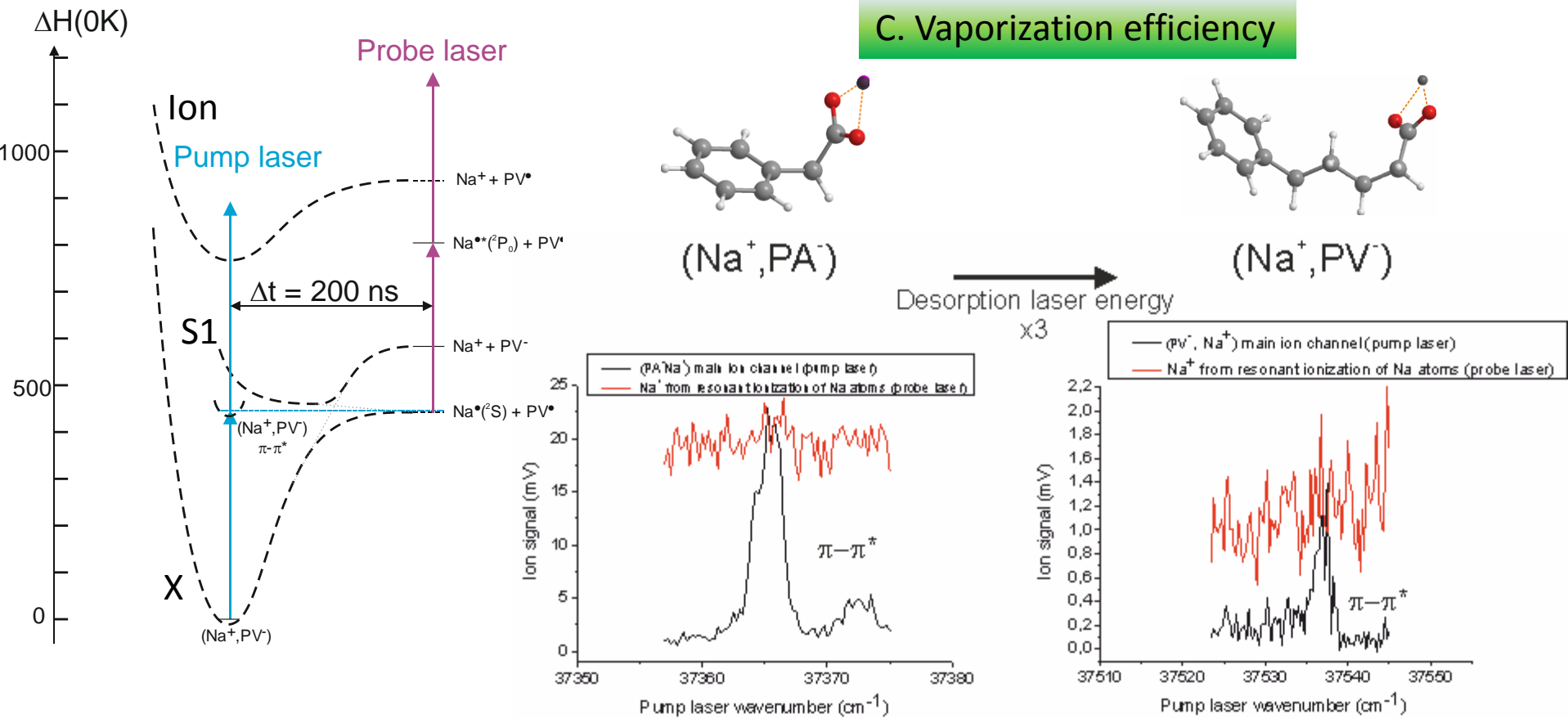
## Conclusions

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 ( $500 \text{ kJ mol}^{-1}$ ) 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 ( $4 \text{ GV m}^{-1}$ )*



# 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



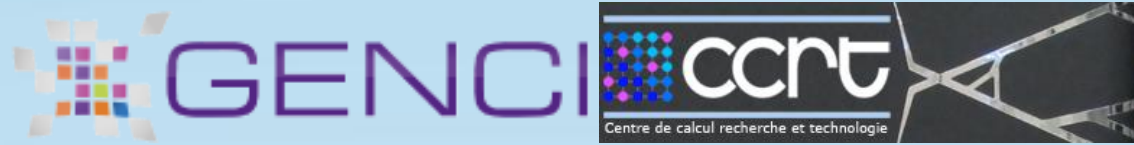
Ridha Elattar  
Sarah de Lima-Barbosa  
Samantha Bourg  
Sentia Goursaud  
Amani Ghandri



2016-2020  
ANR JCJC IONPAIRS



2016-2018  
TGCC





**Marie GELEOC**

**Michel MONS**

**Eric GLOAGUEN**

**Gildas GOLDSZTEJN Valérie BRENNER Benjamin TARDIVEL**

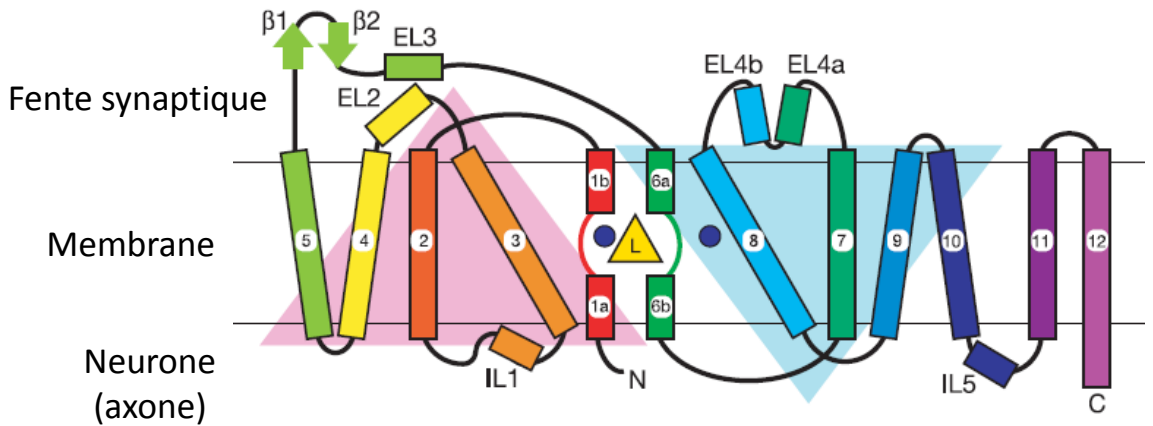
**Jeremy DONON**

**Venkateswara-rao MUNDLAPATI**

# I. Ion pairing at play in Biology

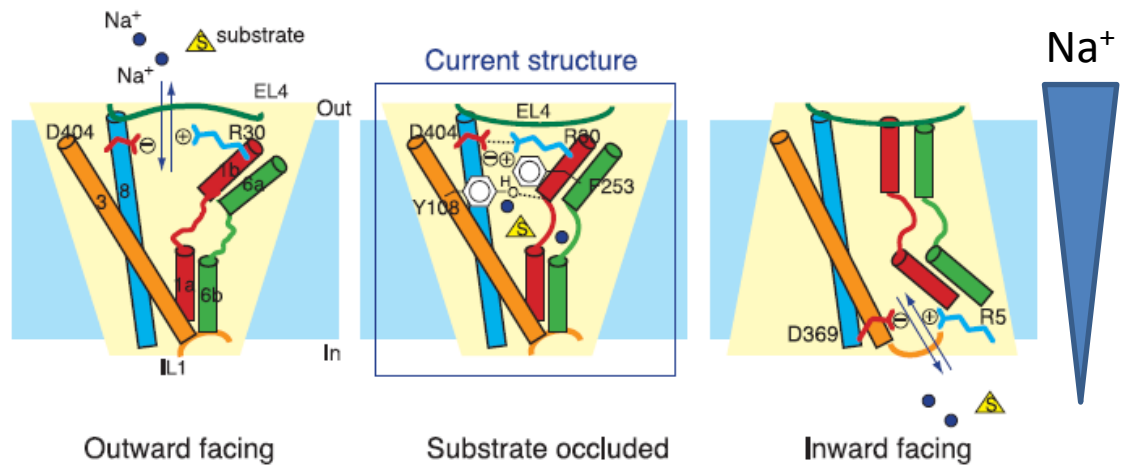
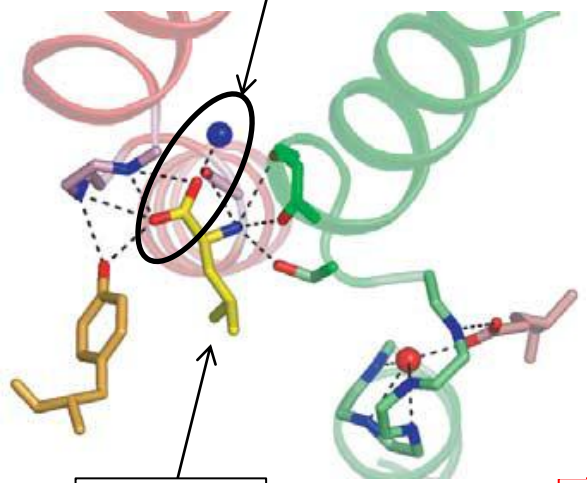
**Protein LeuT<sub>Aa</sub>**  
(PDB 2A65)

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



*Yamashita, Singh, Kawate, Gouaux Nature (2005)*

$(R-COO^-_{Leucine}, Na^+)$  CIP



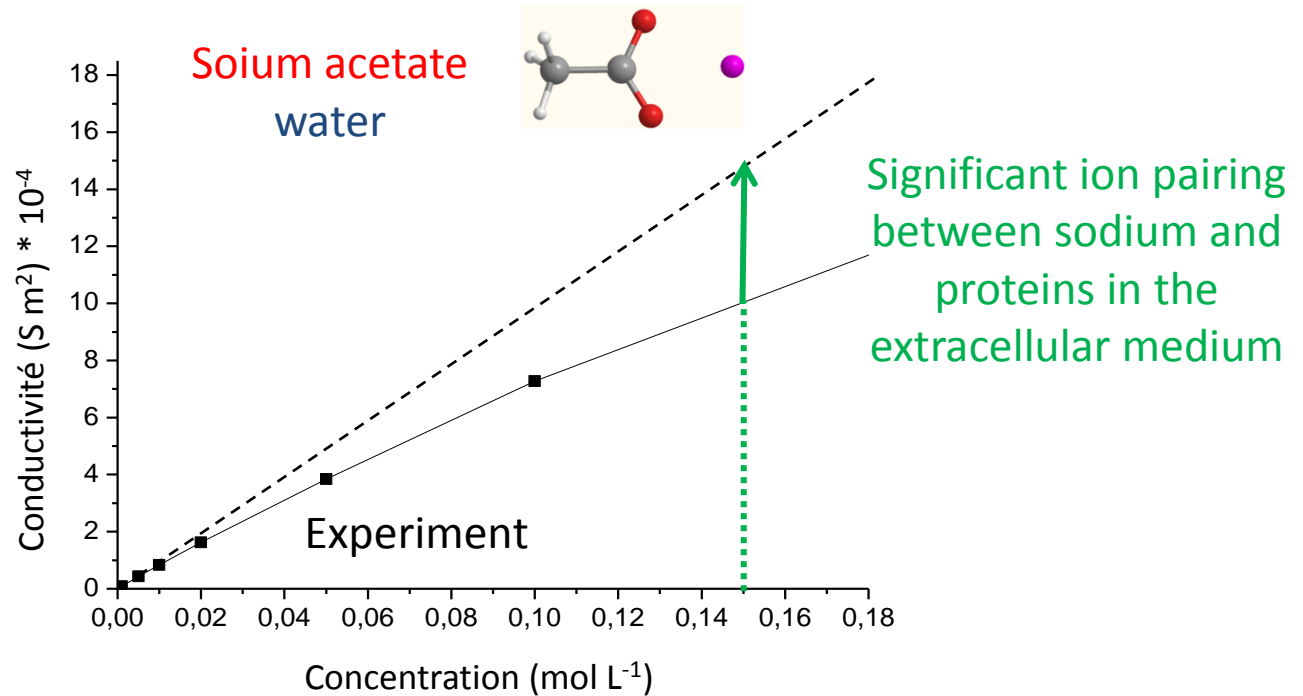
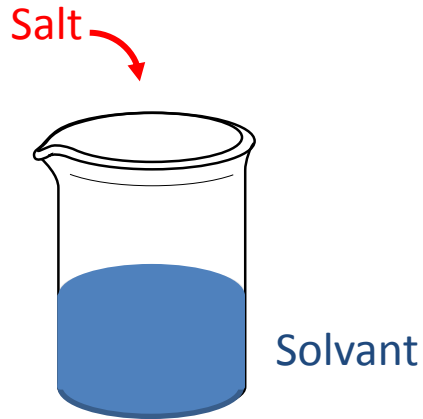
Le gradient de concentration en ion sodium est un élément moteur du transport de Leu au travers de la membrane

# I. Conductivity of electrolyte solutions

Conductivity ( $\kappa$ ) ?

proportional to concentration ( $c$ ) for free ions

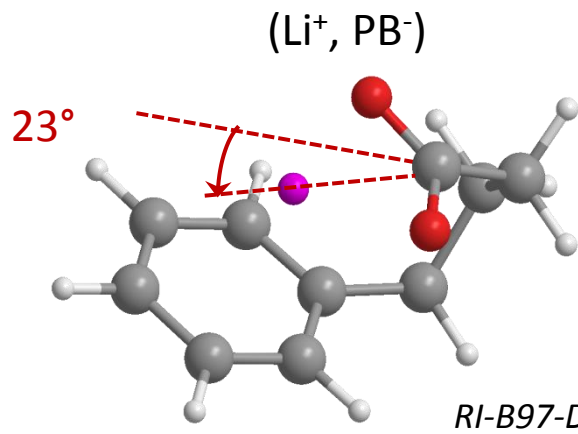
$$\kappa = \Lambda_m * c$$



→ 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

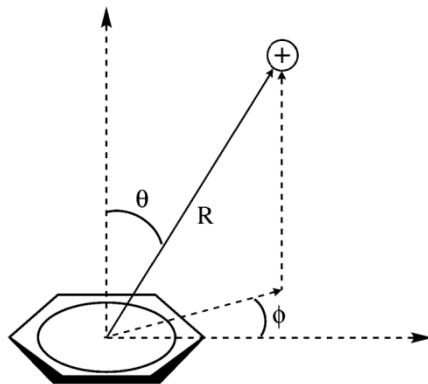
## II. Competition between cation-anion and cation- $\pi$ interactions



RI-B97-D3/dhf-TZVPP

The cation-anion interaction is frustrated

Interaction cation- $\pi$



CCSD(T)/6-311++G(2d,2p)

Benzene- $\text{Li}^+$

$R = 190 \text{ pm}$

$\theta = 0^\circ$

$150 \text{ kJ mol}^{-1}$

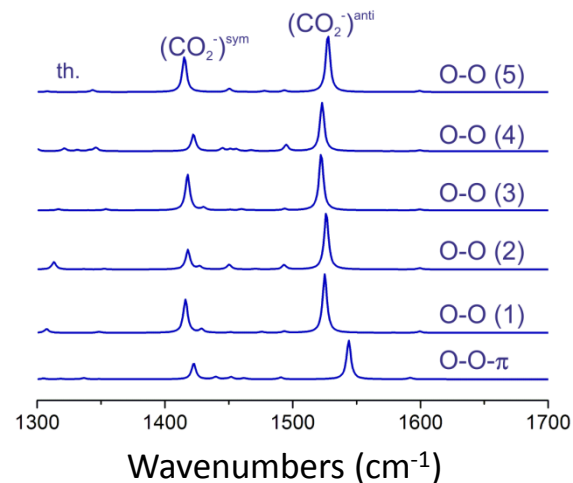
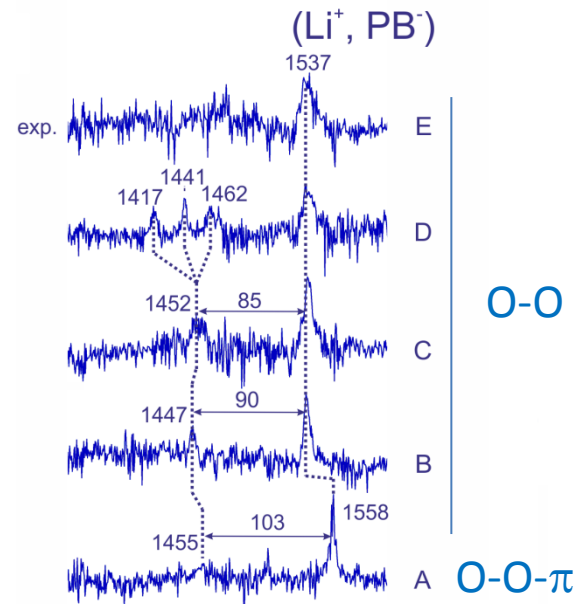
Marshall, Steele,  
Thanthiriwatte, Sherrill  
JPCA (2009)

$(\text{Li}^+, \text{PB}^-)$

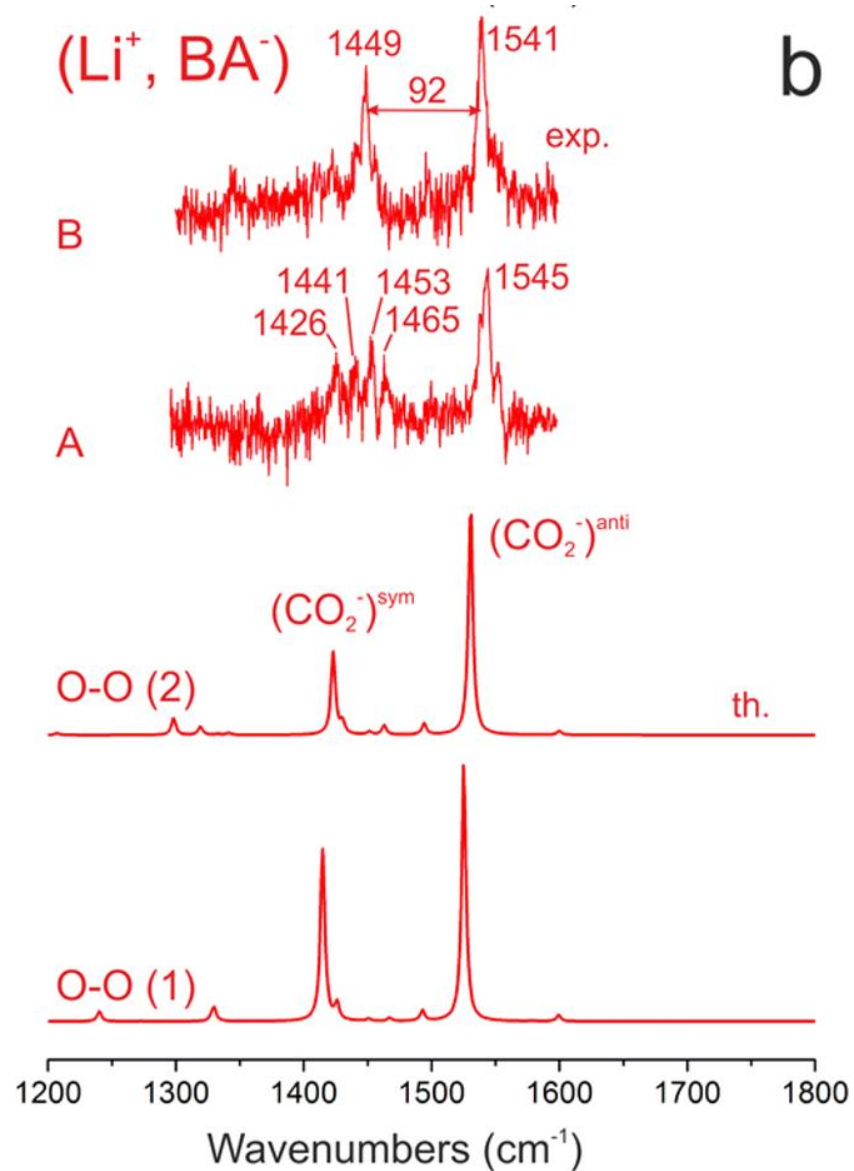
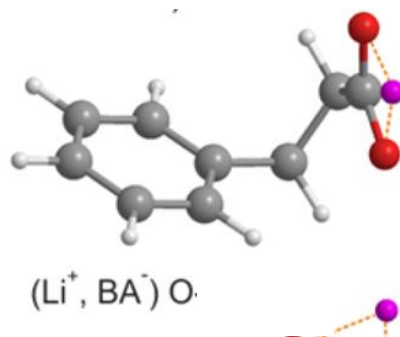
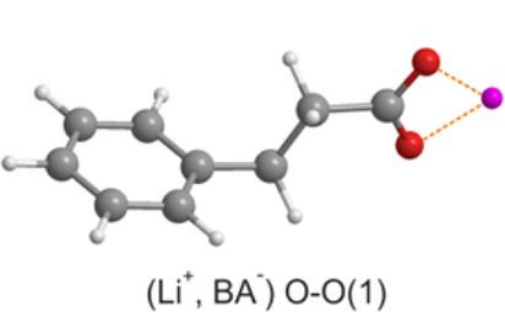
$R = 280 \text{ pm}$

$\theta = 15^\circ$

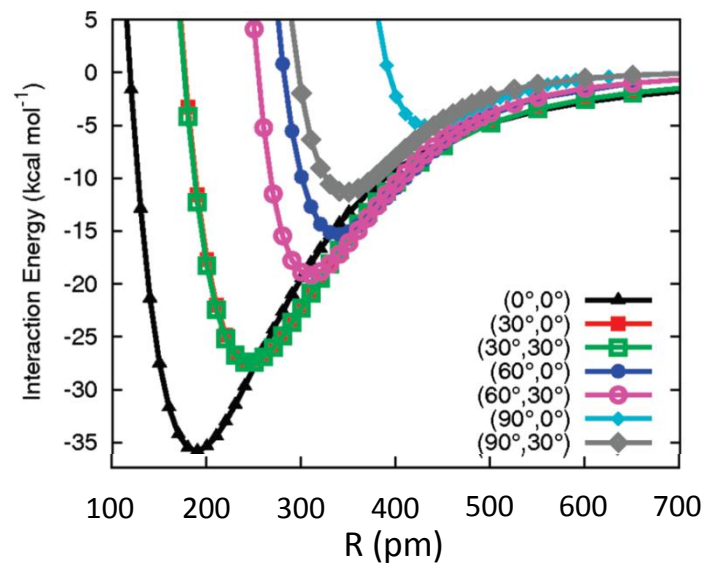
$\sim 100 \text{ kJ mol}^{-1}$



→ B97-D structures are accurate enough les signatures vibrationnelles caractéristiques des familles O-O et O-O- $\pi$



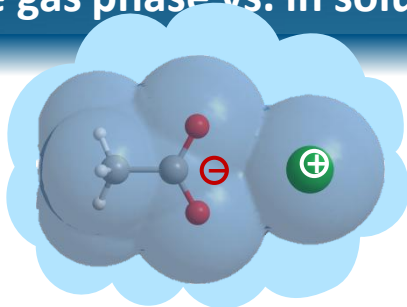




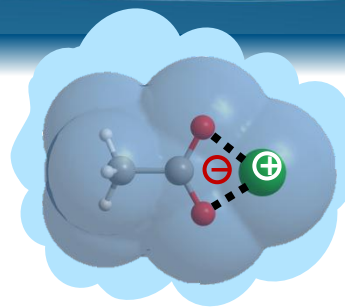
*Marshall, Steele, Thanthiriwatte, Sherrill JPCA (2009)*

### III. Spectroscopy in the gas phase vs. in solution

CIP



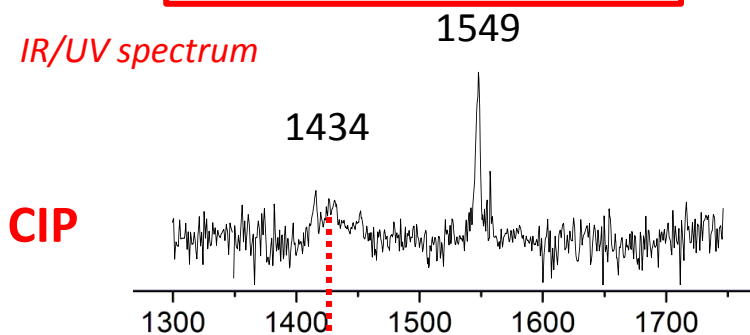
?



SIP/SSIP

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

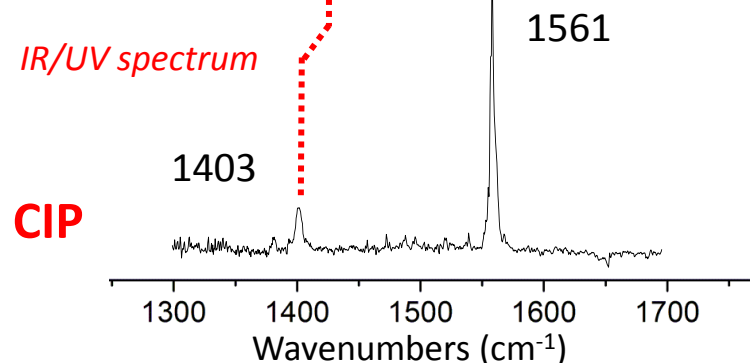
IR/UV spectrum



CIP

$Li^+$

IR/UV spectrum

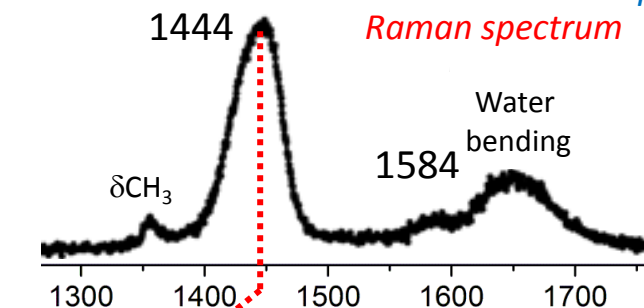


CIP

$Na^+$

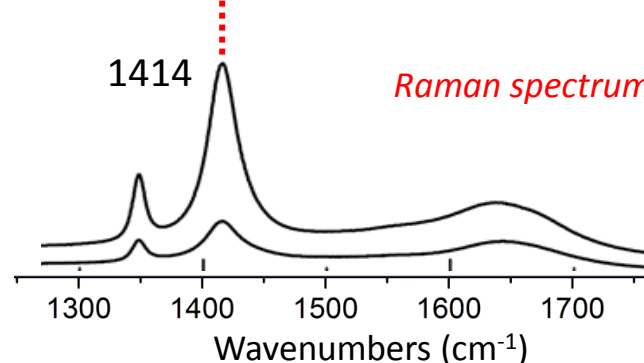
( $M^+$ ,  $AcO^-$ ) Solutions

Raman spectrum



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

CIP

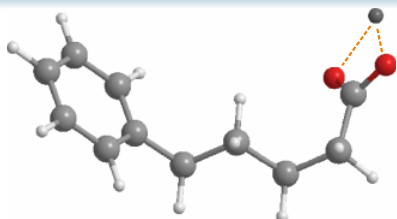


????

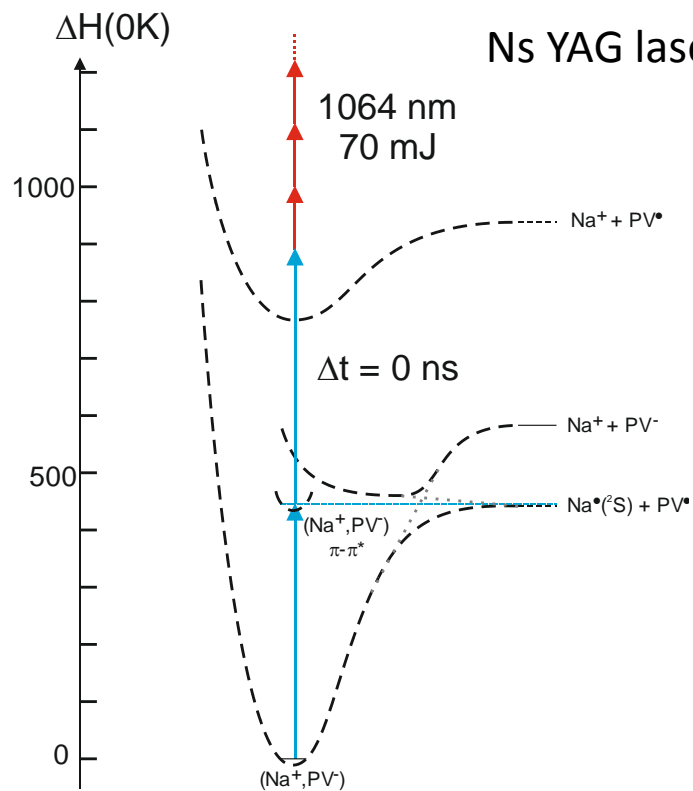
SIP/SSIP

→ 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

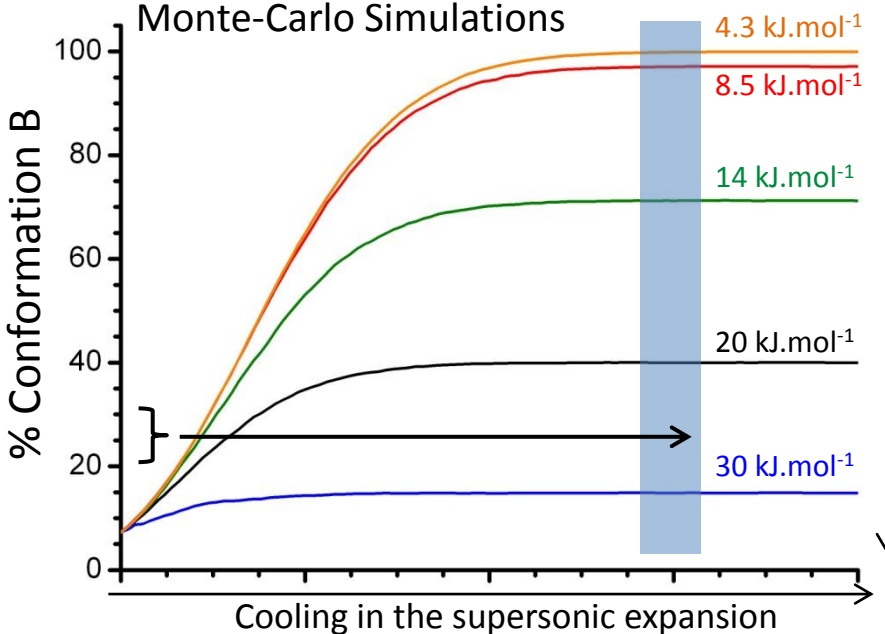
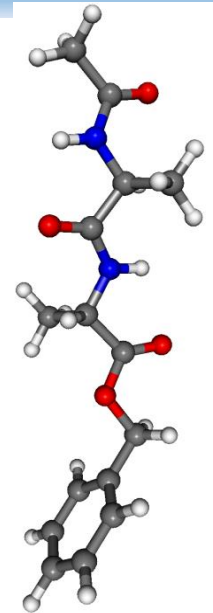
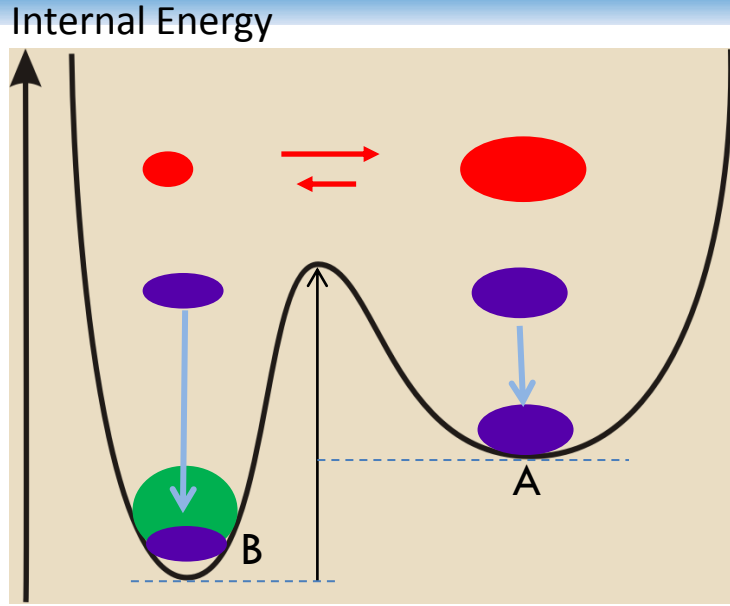
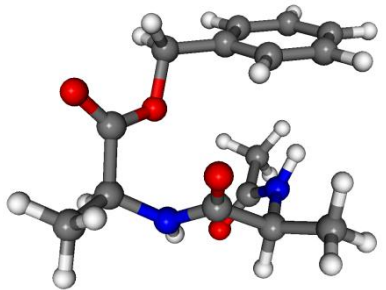
### Conclusions

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

# 3. Theoretical treatment of conformational cooling

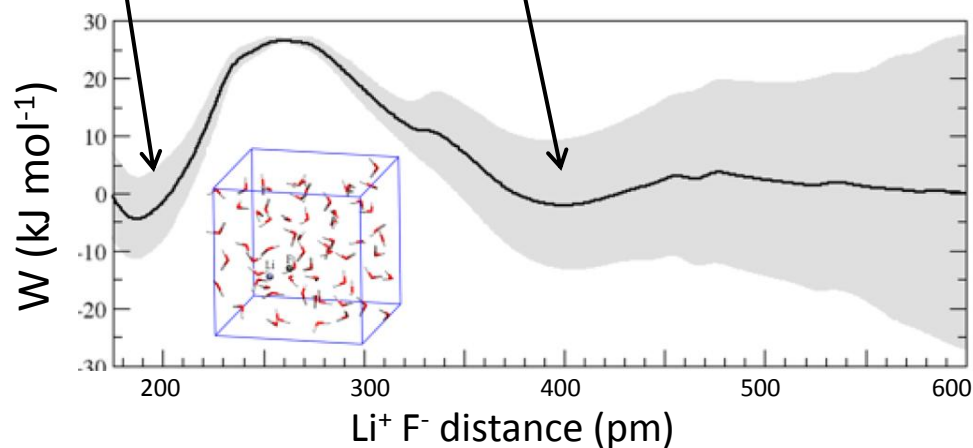
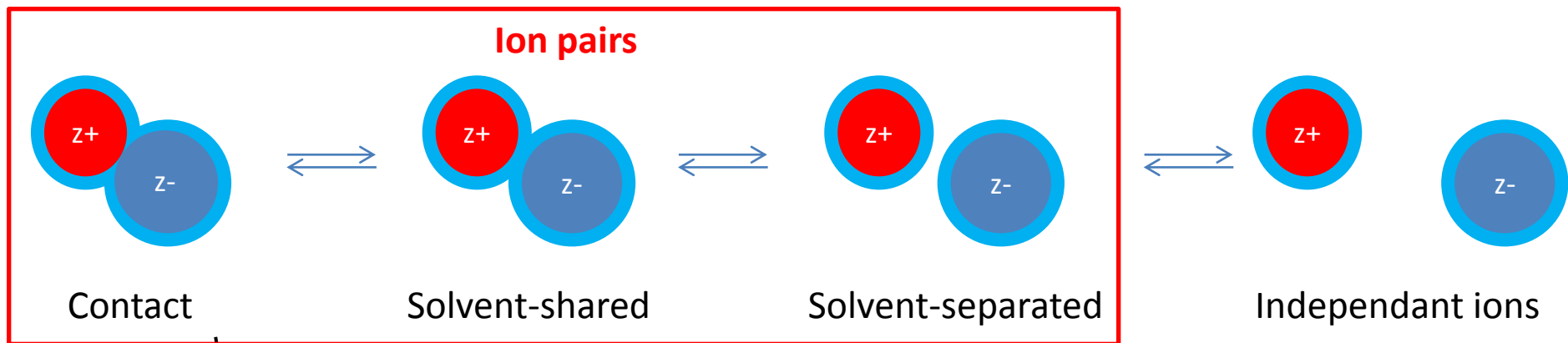
Spectroscopy is carried out at very low temperature where the time needed to reach a conformational equilibrium is much longer than the experimental timescale!

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

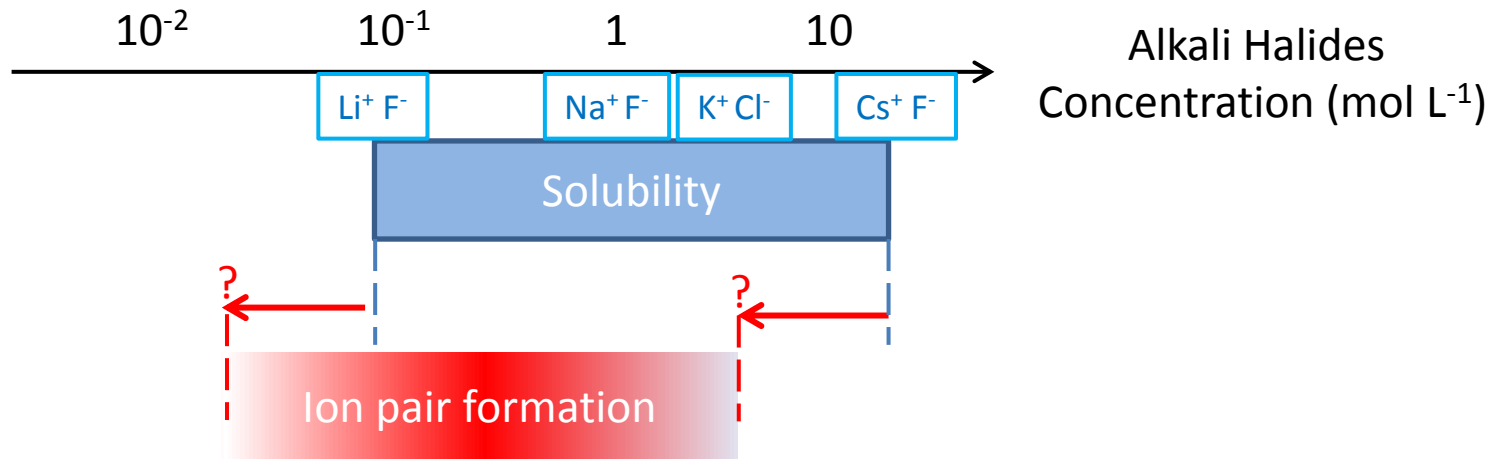
# Eigen mechanism (1962) and current modelling: more than electrostatic



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



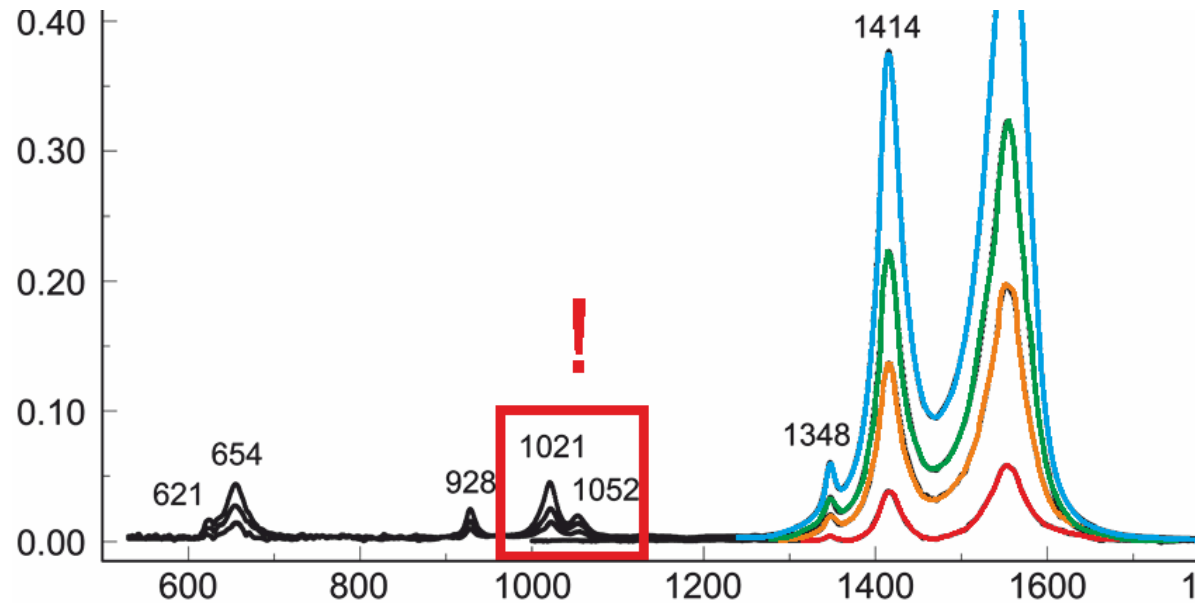
$$[\text{COO}^-_{\text{proteins}}]_{\text{intracellular}} \approx [\text{K}^+]_{\text{intracellular}} = 0,15 \text{ mol L}^{-1}$$

→ 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?

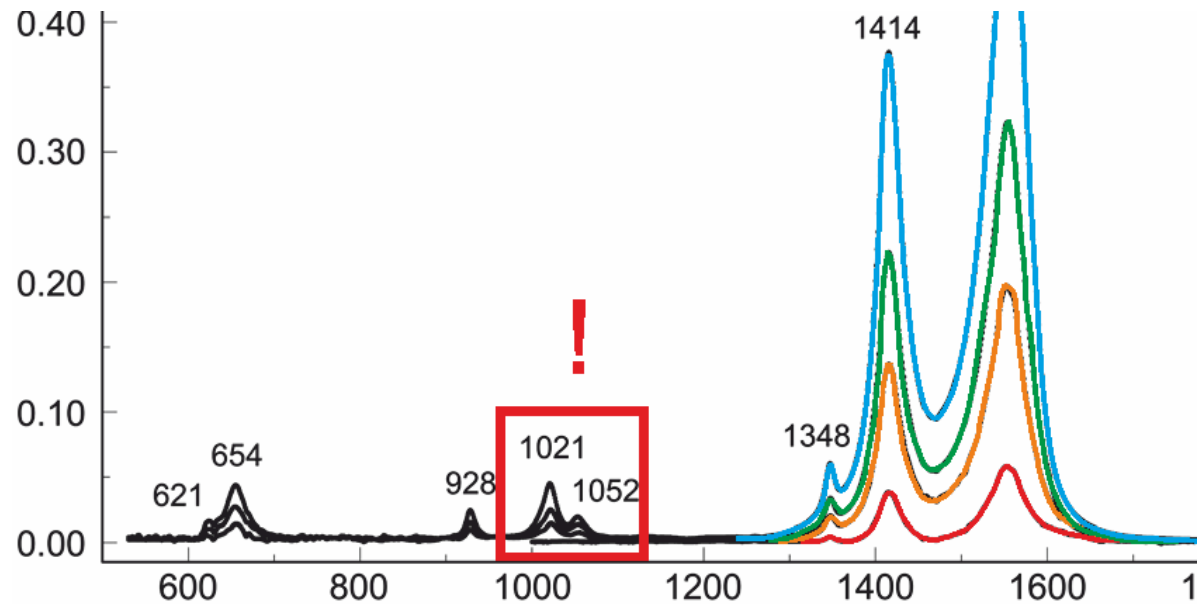
→ Expériences réalisées à l'ICMMO (Pr. D. J. Aitken): non reproductibilité des spectres publiés.

### 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.