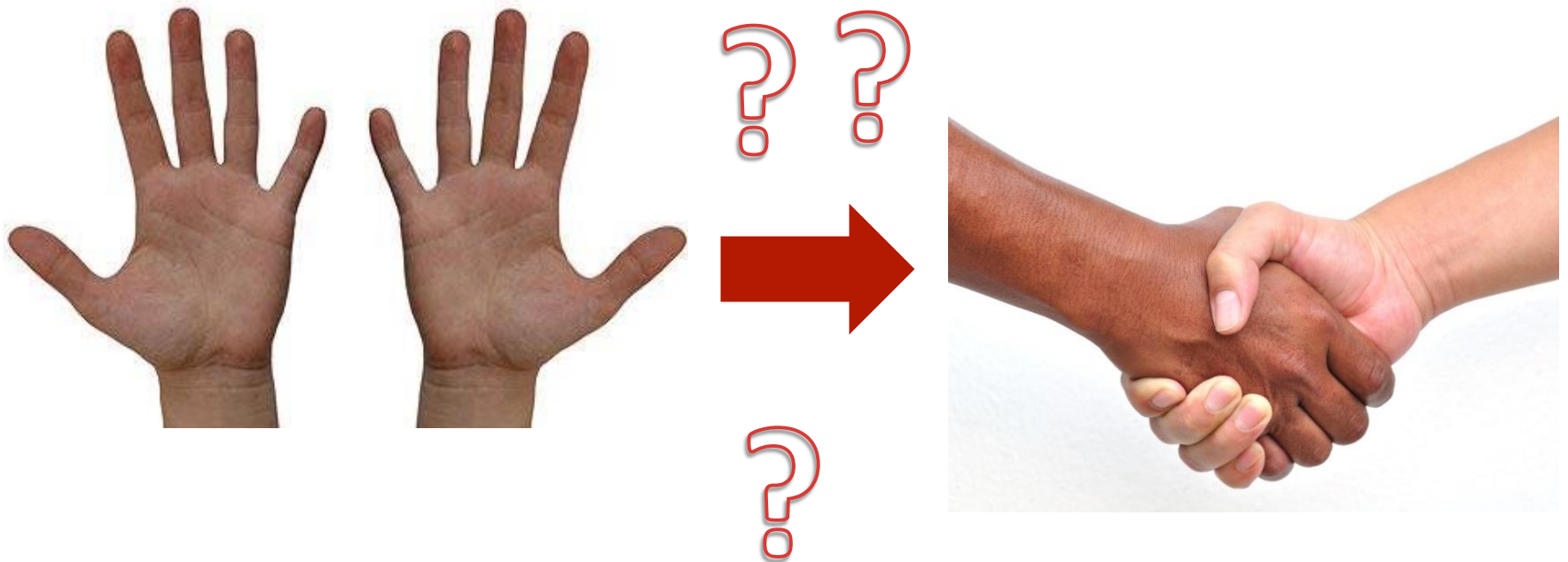


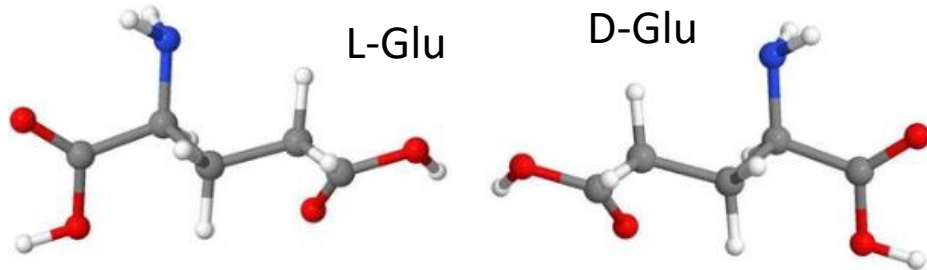
Probing **chirality recognition** of protonated glutamic acid dimers by gas-phase vibrational spectroscopy and first-principles simulations



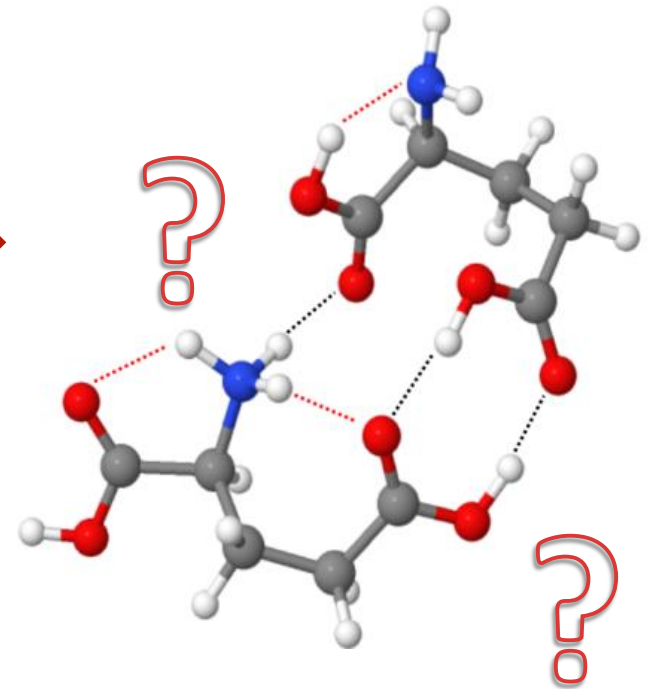
Stereo-specific interaction?

Glutamic acid (Glu)

naturally occurring α -amino acid
principal excitatory neurotransmitter



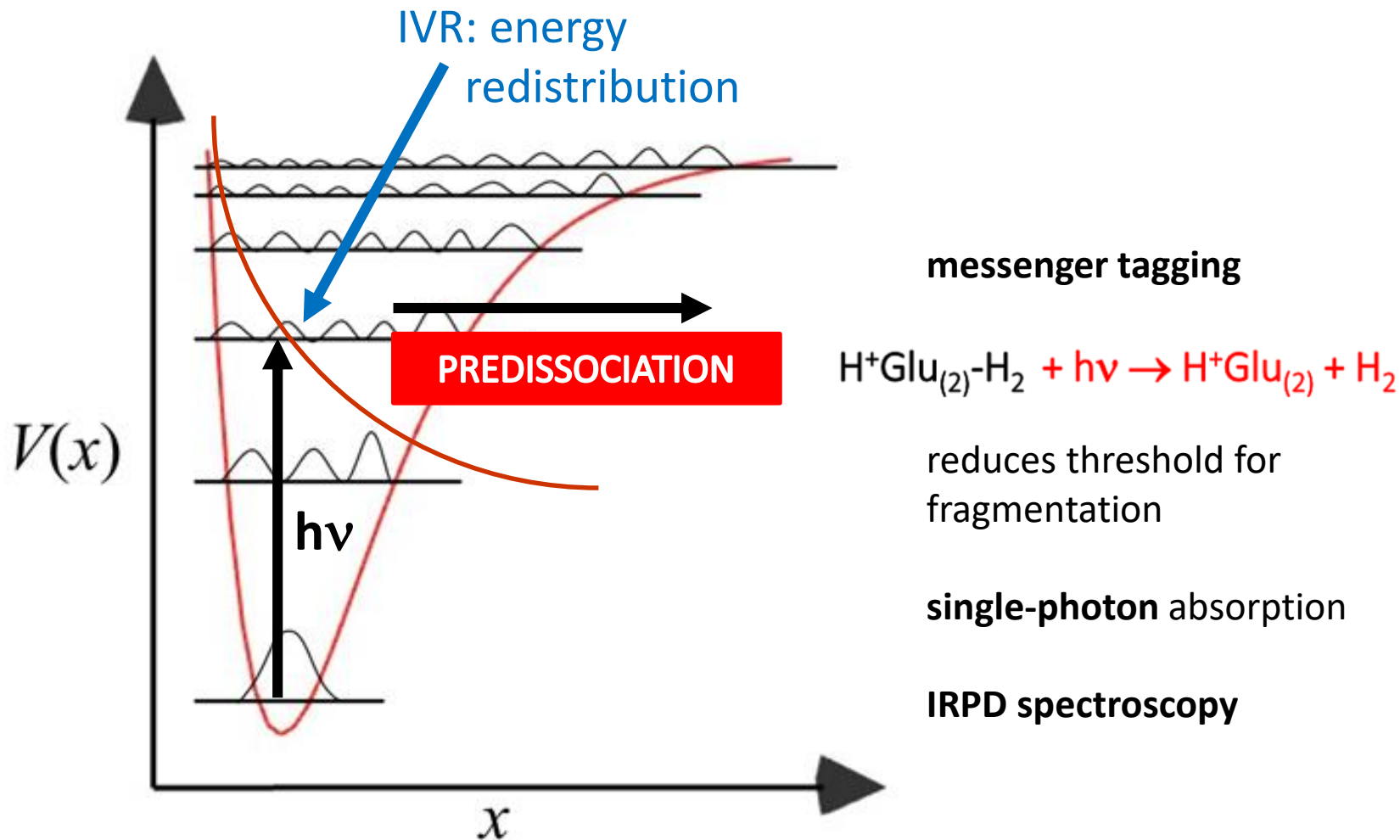
Protonated dimers of glutamic acid (Glu_2H^+)



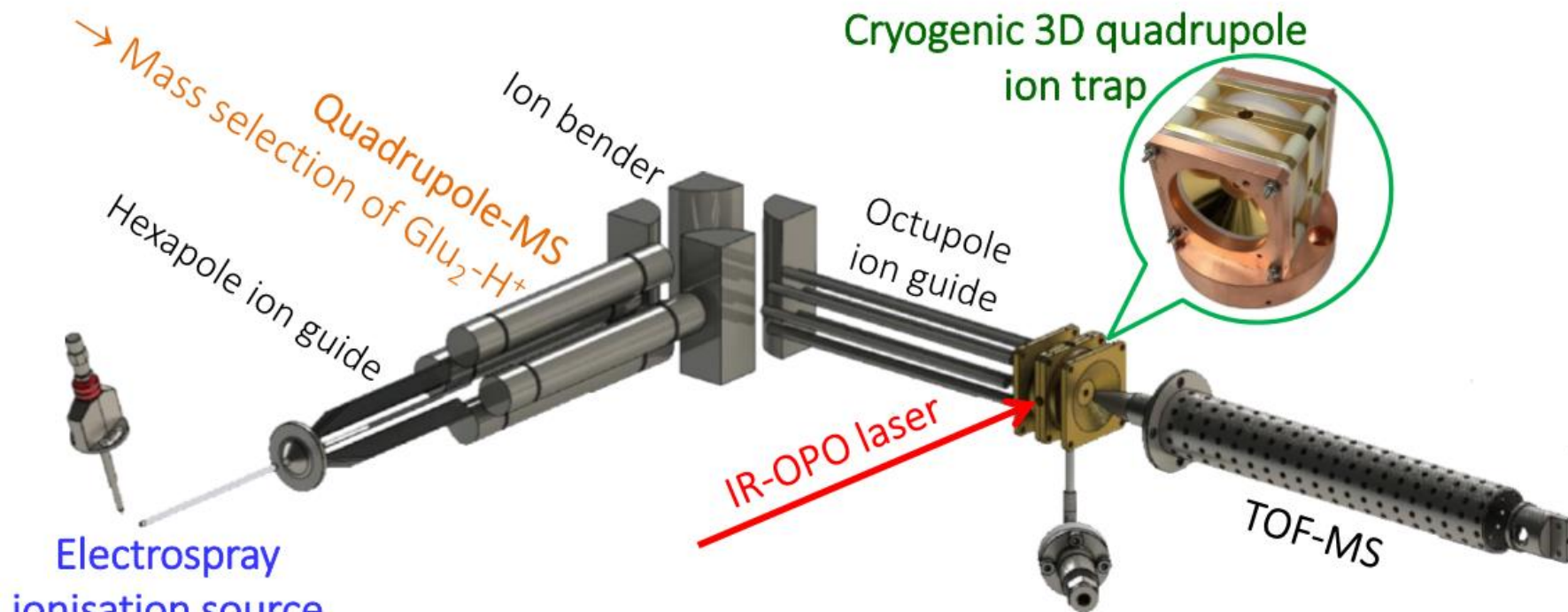
homochiral (LL) vs. heterochiral (LD)

- a) different interaction?
- b) how many gas-phase conformers?
- c) structure?
- d) stability?

Experimental Method: Gas-Phase Vibrational Spectroscopy



IRPD Spectroscopy



Pulsed valve: He/H₂ injection (80%/20%)
Formation of H₂-tagged clusters

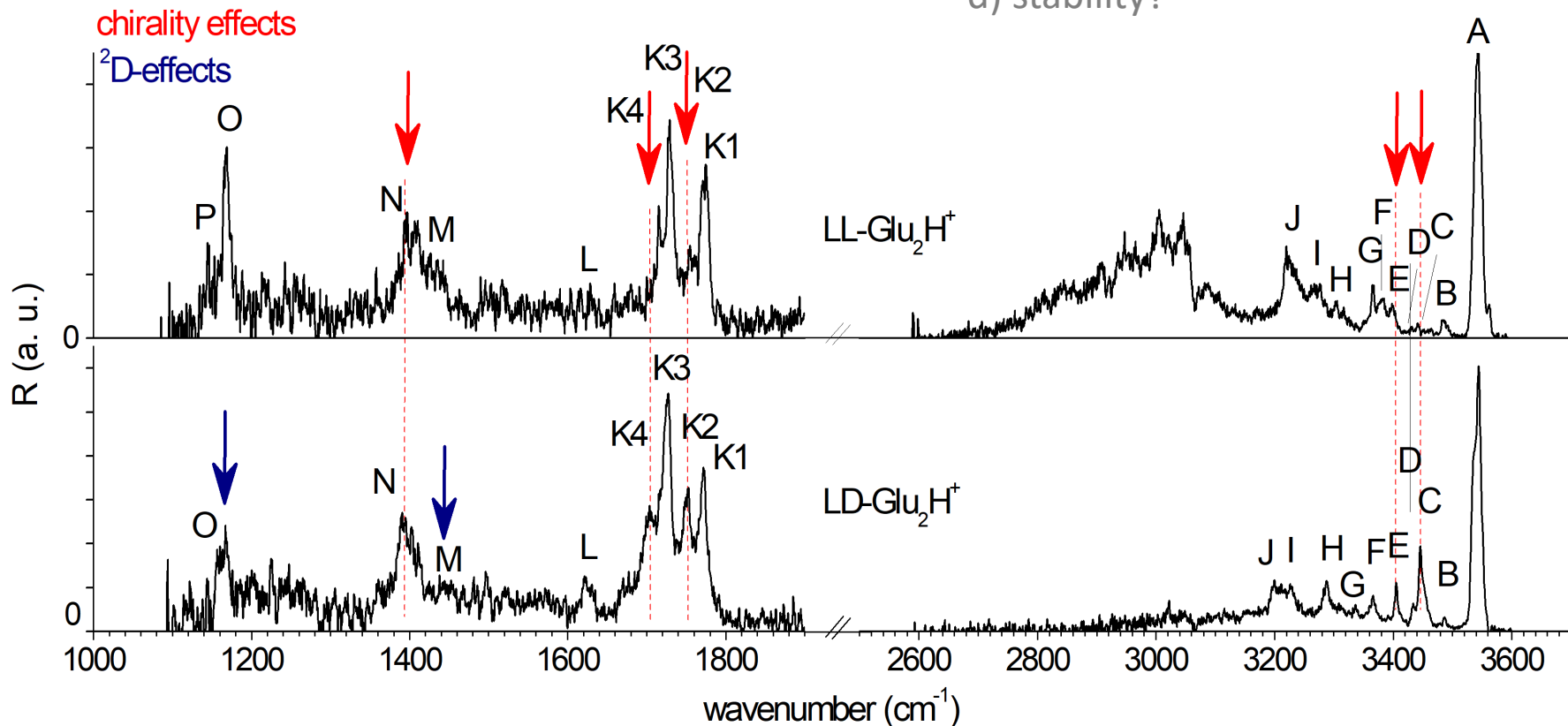


Results IRPD

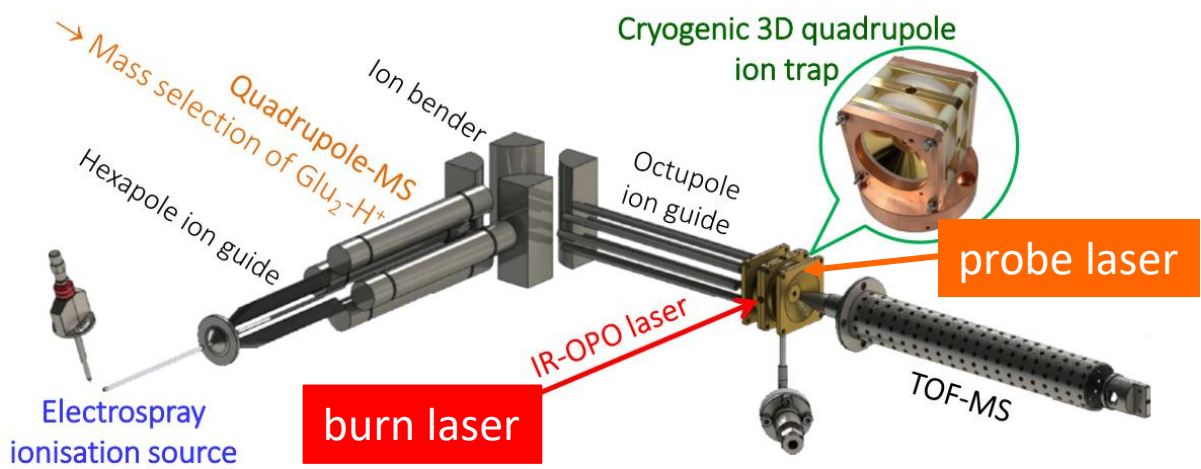
stereospecific IRPD spectra



- a) different interaction?
- b) how many conformers?
- c) structure?
- d) stability?



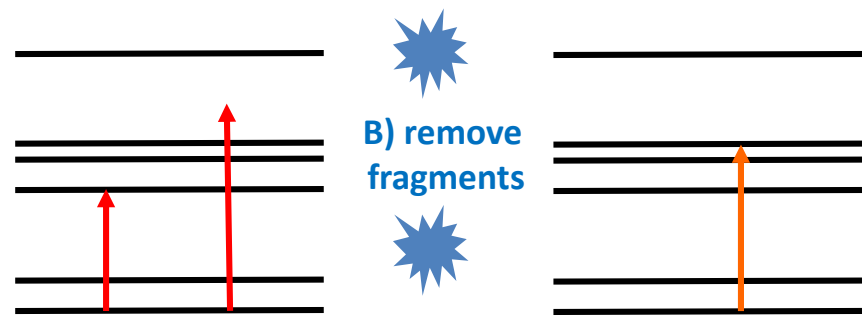
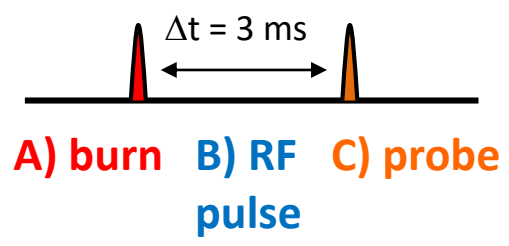
IR-IR-hole burning spectroscopy



conformer selective!

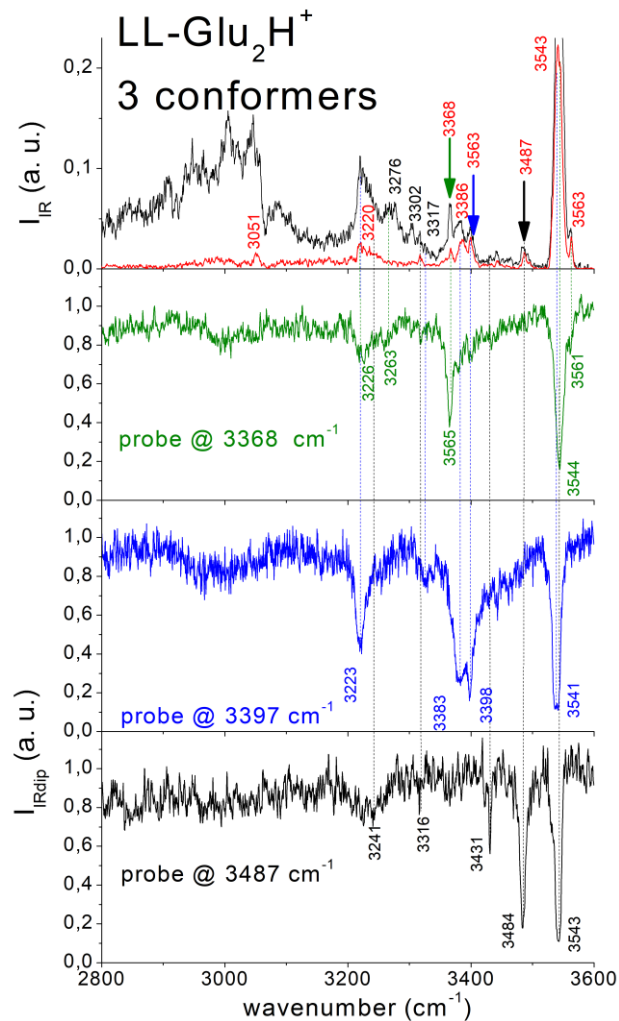
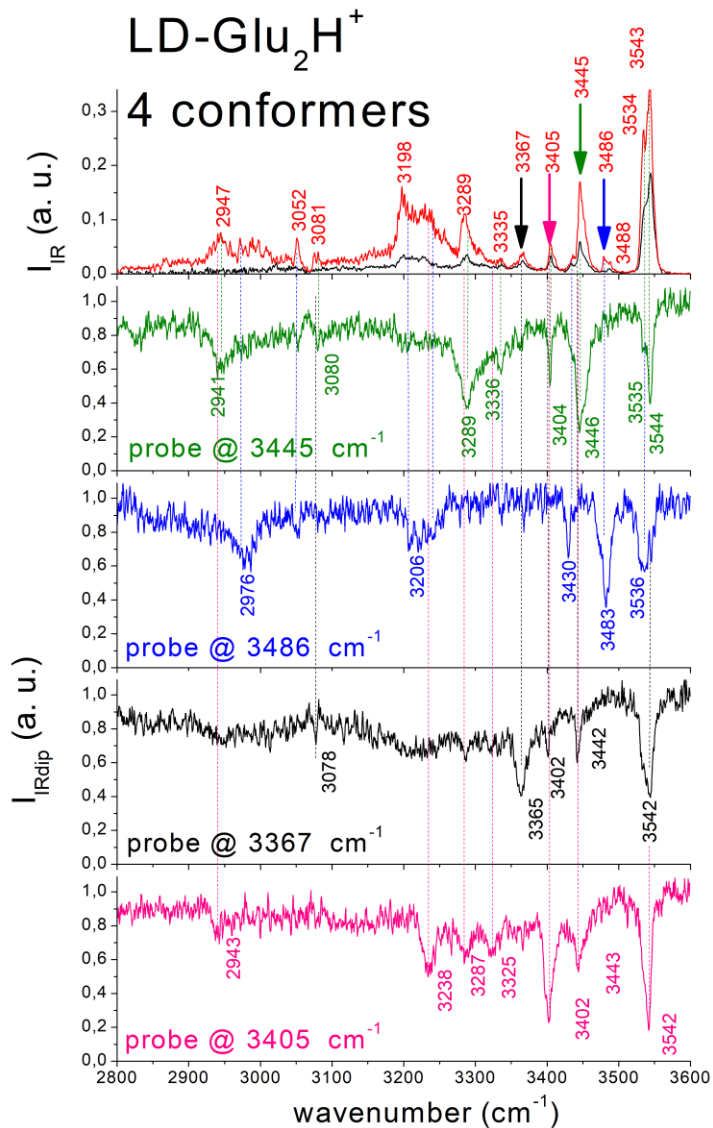
A) burn laser scanned
depletion of constant
fragmentation **ONLY** if
SAME conformer

C) probe laser set at
 $\Delta E = h\Delta\nu$ (conformer-specific)
constant fragmentation



Results IR-IR-hole burnig

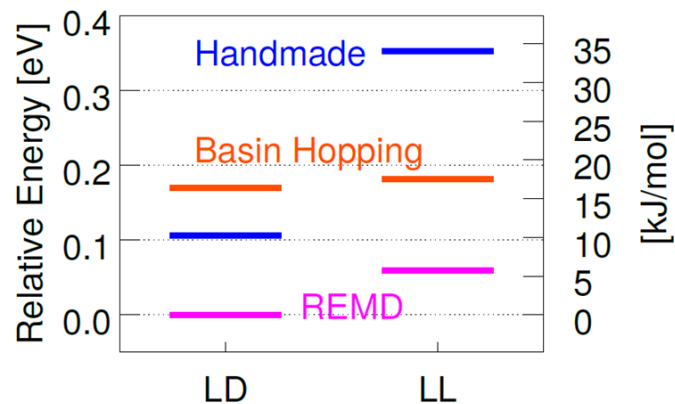
- 😊 a) different interaction?
- 😊 b) how many conformers?
- c) structure?
- d) stability? **THEORY**



First-Principles Simulations (what I do here)

Presampling

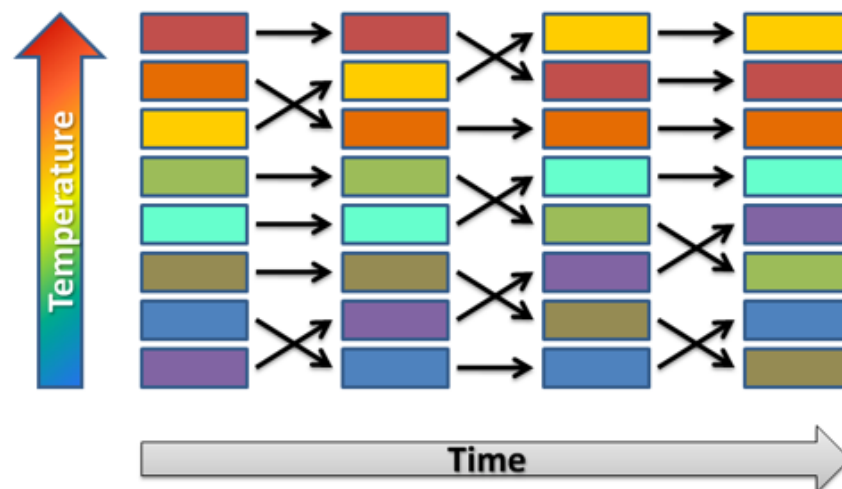
- by hand
 - basin hopping
- (MM3Pro force field)



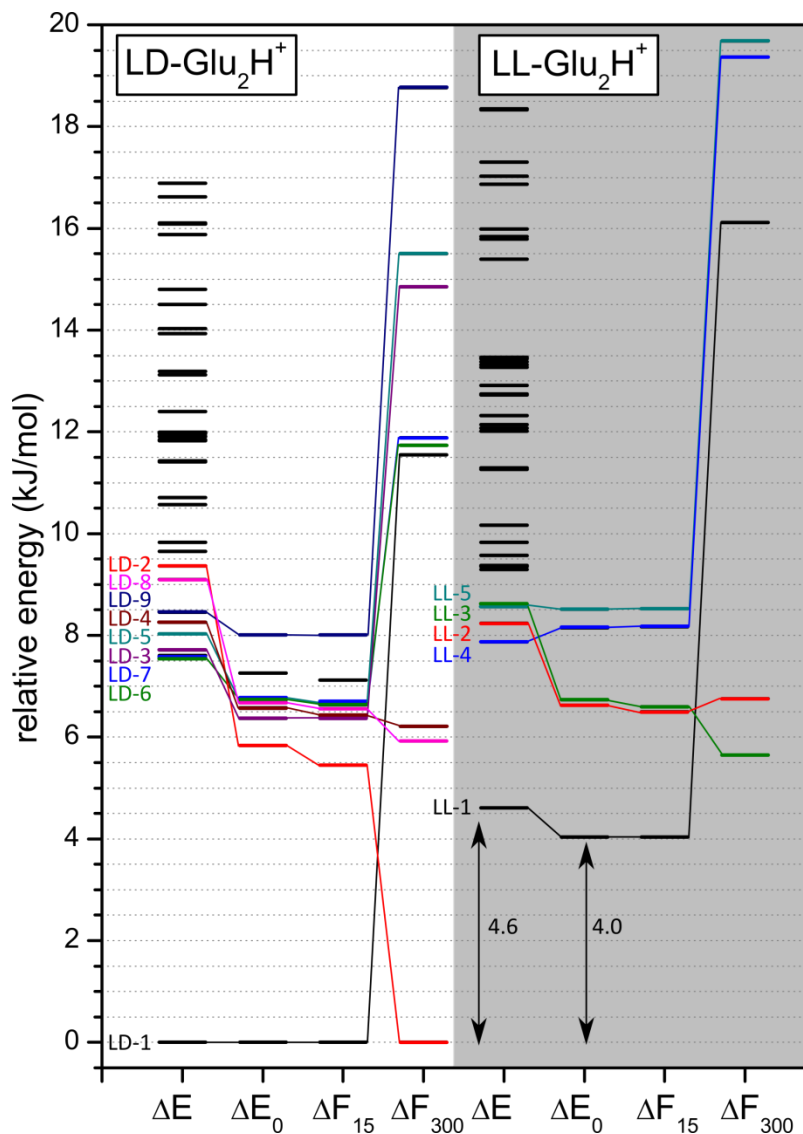
Full sampling

- Replica Exchange Molecular Dynamics (REMD) simulation
- DFT + Vibrational Analysis

$$P(1 \leftrightarrow 2) = \min \left(1, \exp \left[\left(\frac{1}{k_B T_1} - \frac{1}{k_B T_2} \right) (U_1 - U_2) \right] \right)$$

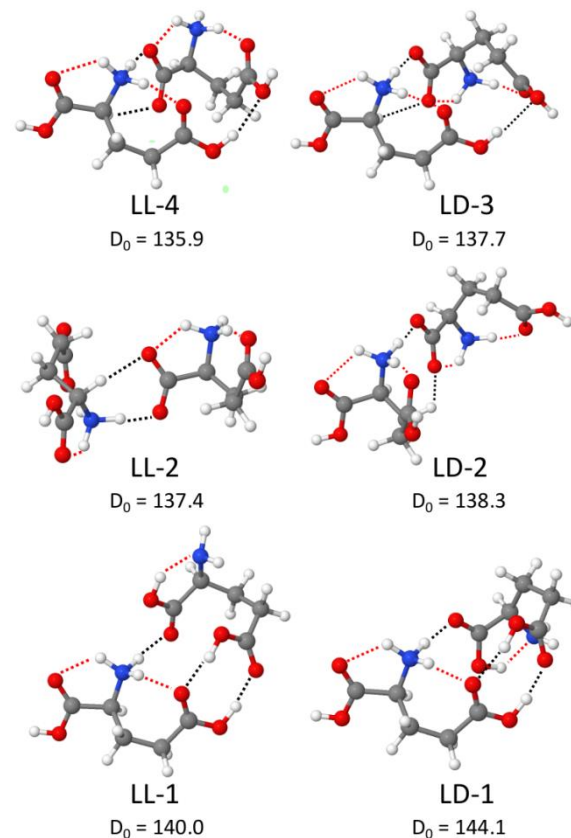


Results from Simulations



- a) different interaction?
- b) how many conformers?
- c) structure?
- d) stability?

assignment by comparison of calc. and exp. spectra



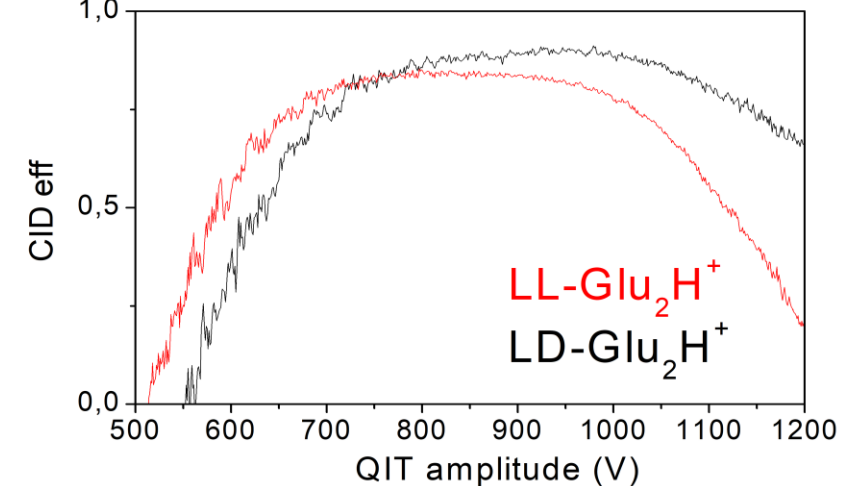
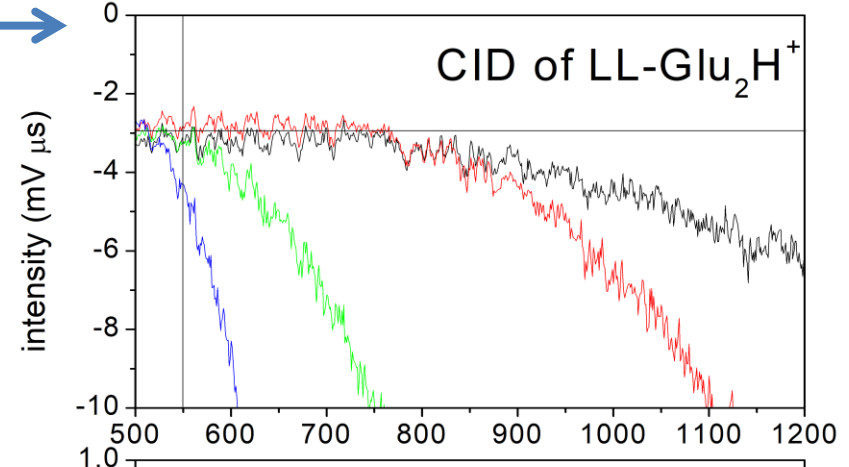
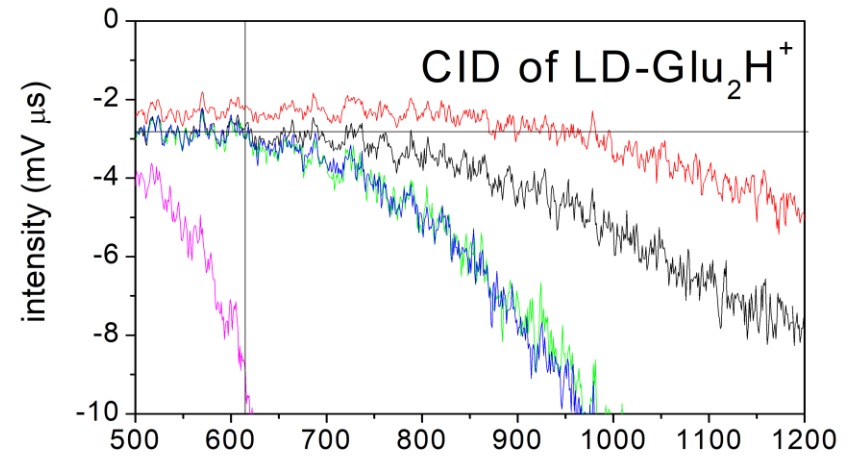
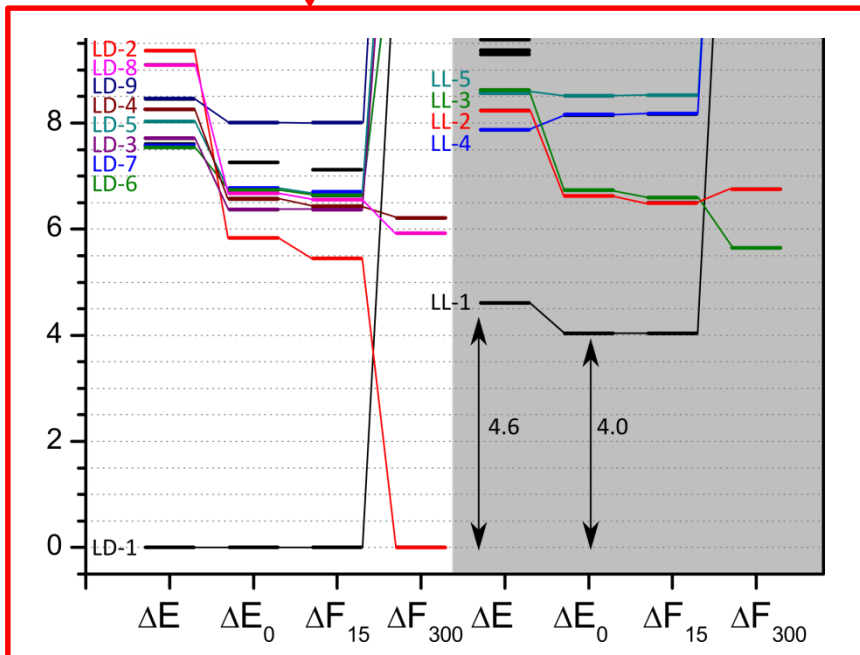
$$D_0 = E_0(\text{Glu}_2\text{H}^+) - E_0(\text{GluH}^+) - E_0(\text{Glu})$$

binding energy

About stability...

Theory: LD more stable than LL

Can we verify by experiment?



Summary

- specific ν_{NH_2} ($\approx 3450 \text{ cm}^{-1}$) and ν_{CO} ($\approx 1750 \text{ cm}^{-1}$) are **fingerprints of chirality recognition**
- **LD-Glu₂H⁺ more stable** than LL-Glu₂H⁺ by $> 4 \text{ kJ/mol}$
- conformer-selective IR-IR double resonance spectroscopy:
3 LL-Glu₂H⁺ conformers
4 LD-Glu₂H⁺ conformers
- **assignment of spectra?**
- **conformer population (300 K s. 15 K)?**
kinetic trapping or cooling?

How does chirality recognition work?
Compare to other systems?



Thank you for your attention!

Aude Bouchet, Shun-ichi Ishiuchi,
Masaaki Fujii, Otto Dopfer,
Markus Schneider, Carsten Baldauf



DFG

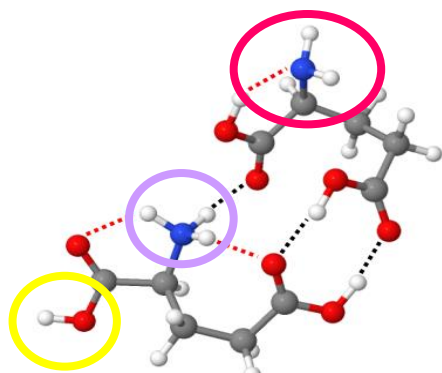


Results IRPD

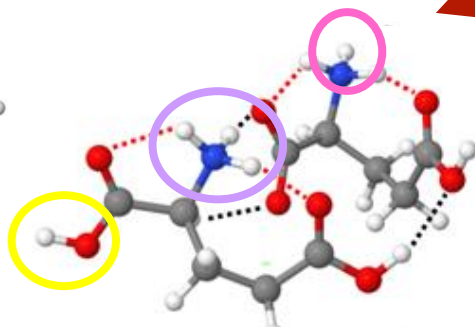
isotope labeling helps assign transitions in IRPD spectra



relation to structure?!



LL-1
 $D_0 = 140.0$



LL-4
 $D_0 = 135.9$

