Multiscale Dynamics in Molecular Systems - GDRs EMIE & UP summer school
Ecole de Physique des Houches
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Electron and proton transfers

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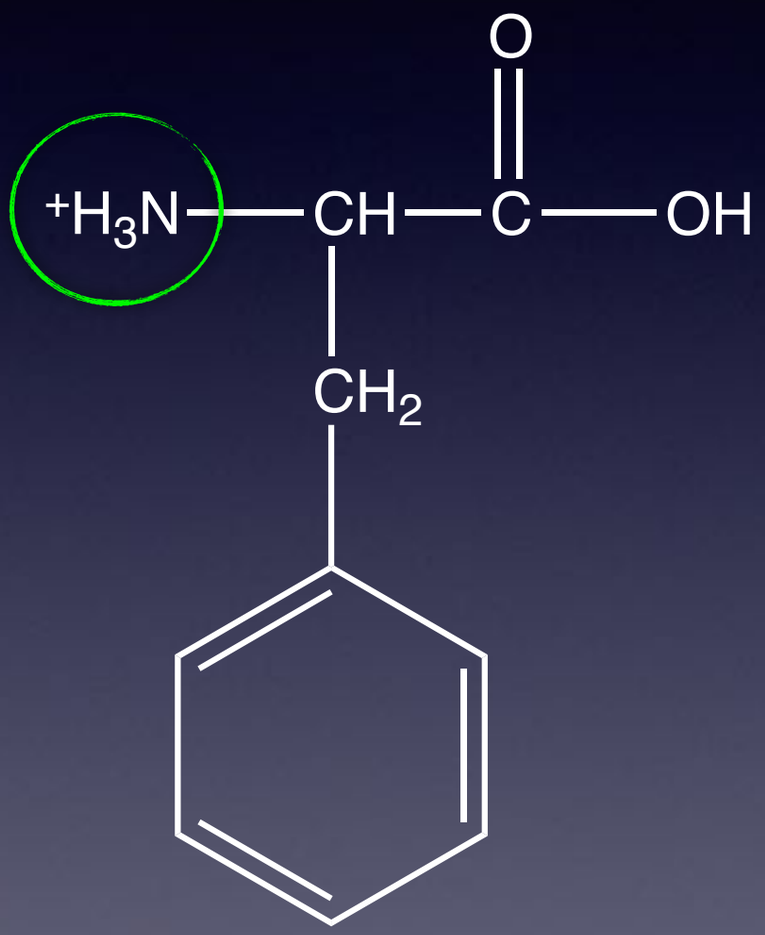
Outline

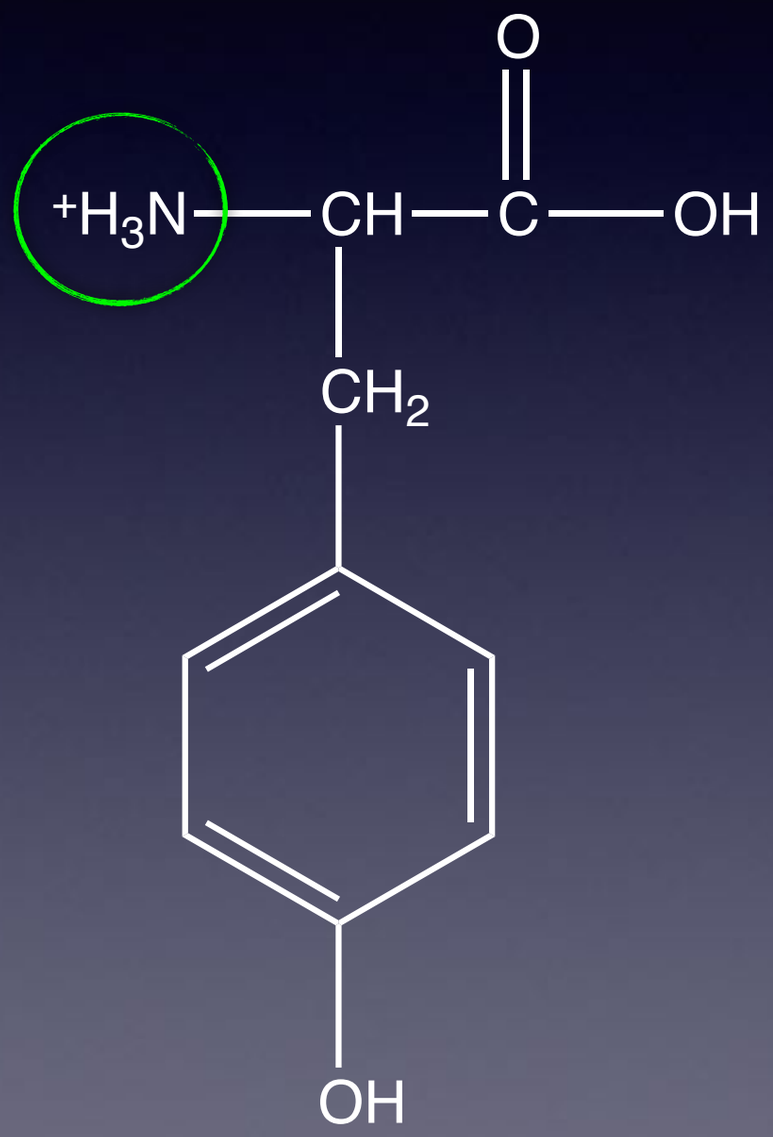
- Protonated species
- Experimental setup : cold ion trap
- UV photofragmentation spectroscopy
- Pump-probe experiments
- **Multiscale relaxation dynamics**

Protonated aromatic amino acids

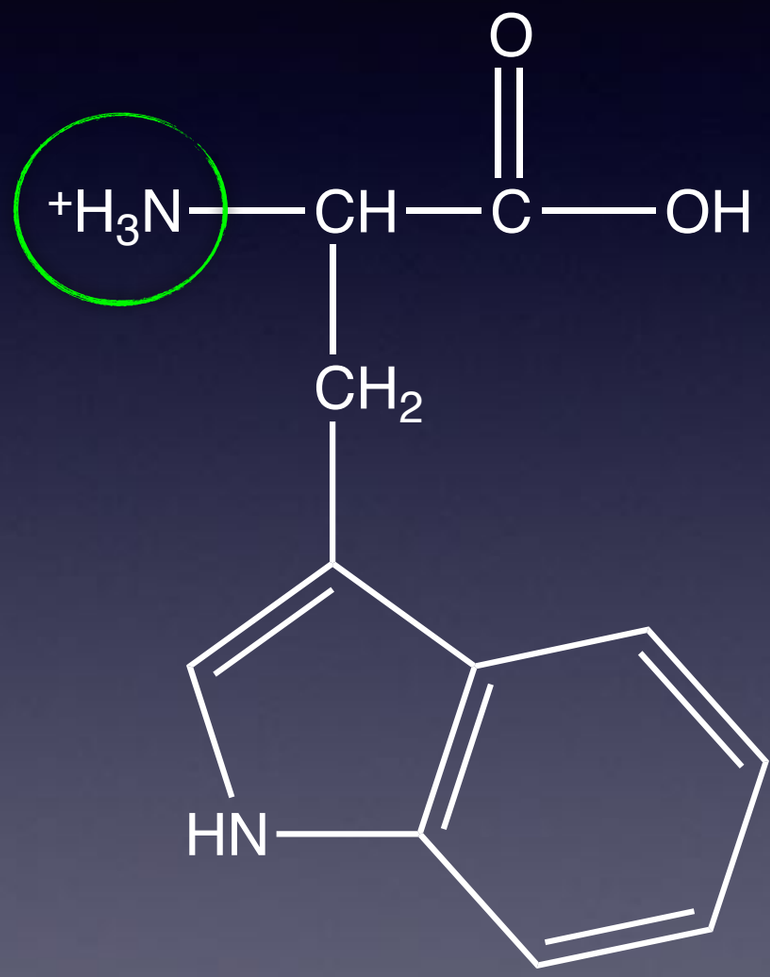
Phenylalanine(H^+)



Tyrosine(H^+)



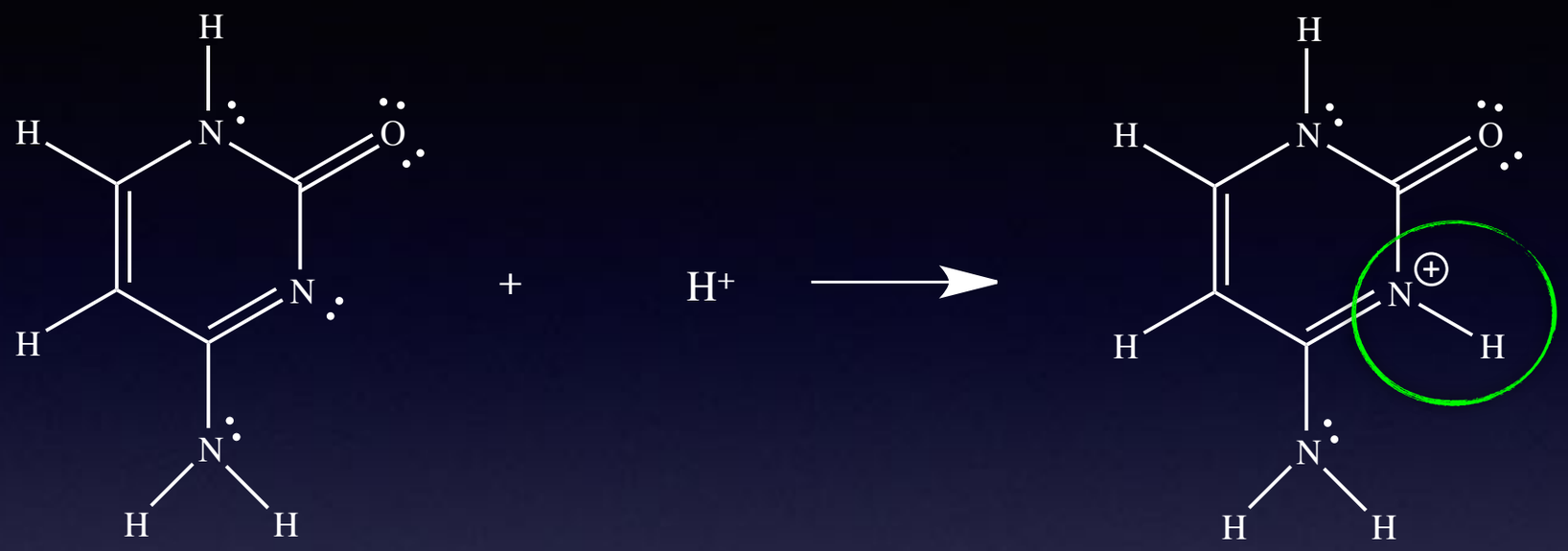
Tryptophan(H^+)



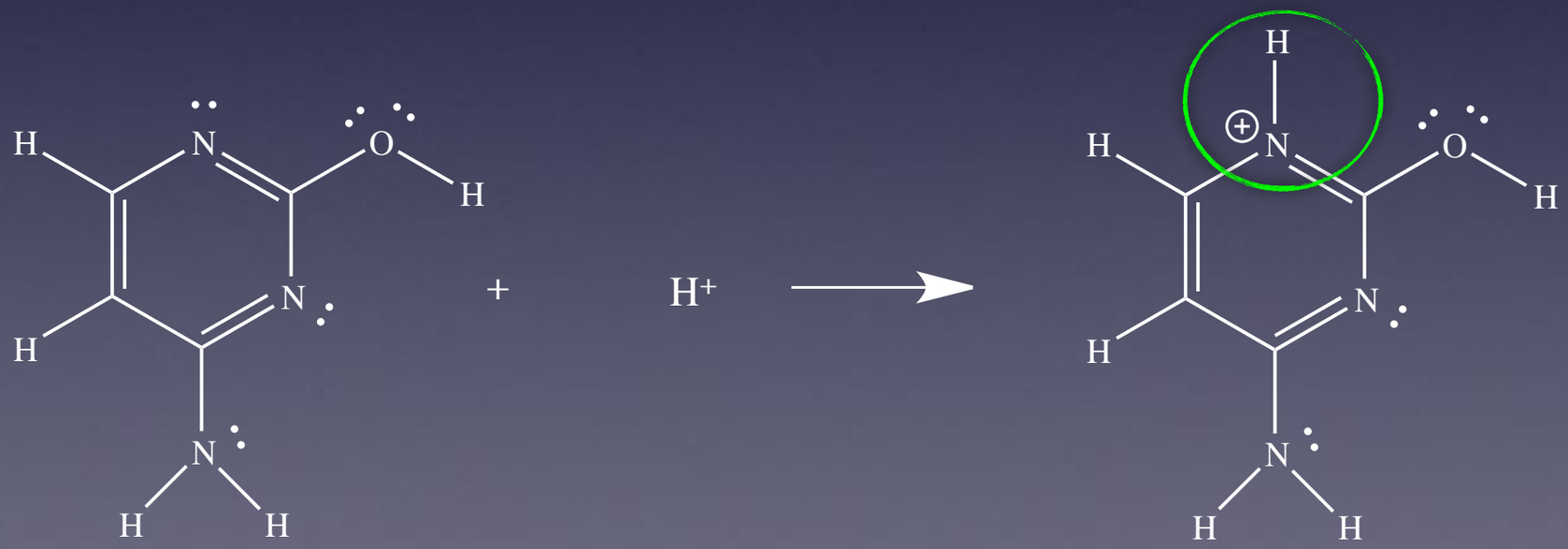
H^+ on the primary amine ($-NH_2$) group

Protonated Cytosine

Keto



Enol



Tautomers

Protonation

- **Protonation** : addition of a proton to an atom, molecule or ion
- **Protonation** : different from hydrogenation in that during protonation a **change** in **charge** of the protonated species **occurs**, while the charge is unaffected during hydrogenation

Protonation

- … occurs in many catalytic reactions
- …occurs in acid-base reactions
- … leads to mass and charge change
- **Chemical properties are altered** :
  - hydrophobicity
  - reactivity
  - **optical properties**

Protonation

- Example : formation of ammonium ion by protonation of ammonia

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

Bulk solution (water)* : pK_a (NH_4^+/NH_3) = 9.25

*The solvent is an active partner in the proton equilibrium process, and so **pK_a** does **not** represent **an intrinsic property** of the molecule in isolation.

Proton affinity

The proton affinity of an anion or a neutral atom or molecule is the **negative** of the **enthalpy change** (ΔH) in the reaction between above species and proton in the gas phase :

$$A^- + H^+ \rightleftharpoons AH$$

$$B + H^+ \rightleftharpoons BH^+$$

The property related to proton affinity is the **gas-phase basicity**, i.e. **negative of Gibbs energy** (ΔG), which means that the gas-phase basicity includes entropic terms (ΔS) in contrast to proton affinity.

Gas phase ⟷ Condensed phase

« The factors which account for the enormous discrepancies between these two different worlds of chemistry are operationally defined as *solvation*. »

Gas-Phase Proton Transfer - a Breakthrough for Solution Chemistry - E. M. Arnett, Acc. Them. Res., 1973, 6, 12, 404

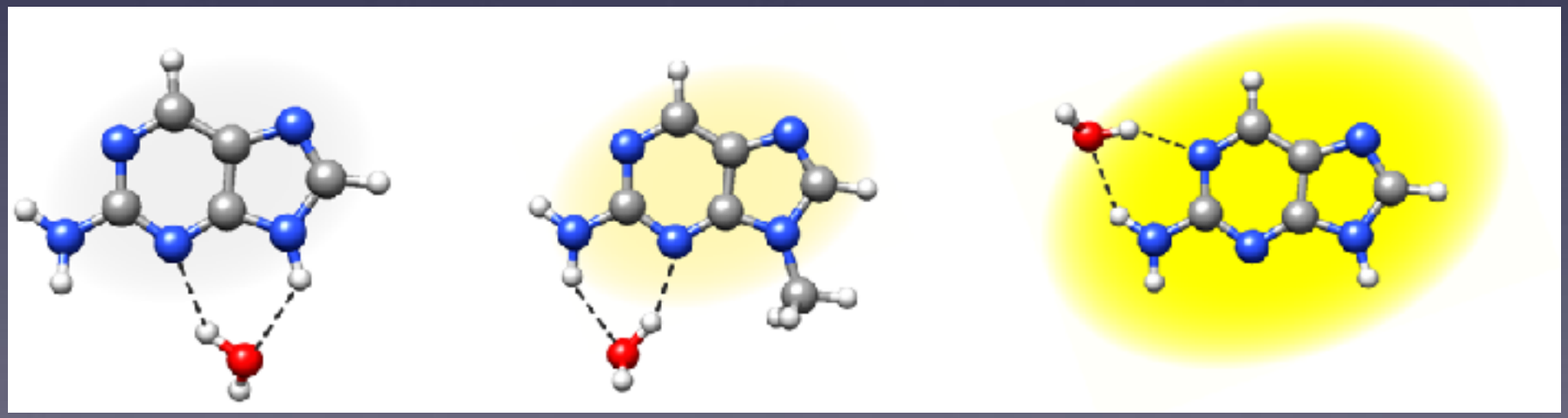
Gas phase studies - Isolated conditions

Molecules of biological interest :

- Link between **structure** and **function/reactivity**
- **Isolation** most stable **conformations**
- **Determination** of their **structures**
- Access to intrinsic properties

Environment effects

- Microsolvatation -> towards the condensed phase



« Switching on the fluorescence of 2-aminopurine by site-selective microhydration »
S. Losbiger, S. Blaser, R. K. Sinha, H.M. Frey and S. Leutwyler Nature Chemistry, 6, 2014, 989

Structural information

Mass spectrometry …

- Study of biological systems :
  - Proteins; peptides …

- Identification of sequences/structures of peptides
  - Fragmentation techniques : CID, ETD ….

… coupled to laser spectroscopy :

IR Multiphoton dissociation (IRMPD)

- Localized excitation : **vibrational modes of the ground state (S_0)**
- Access to structures
- MS^n : parents and fragments

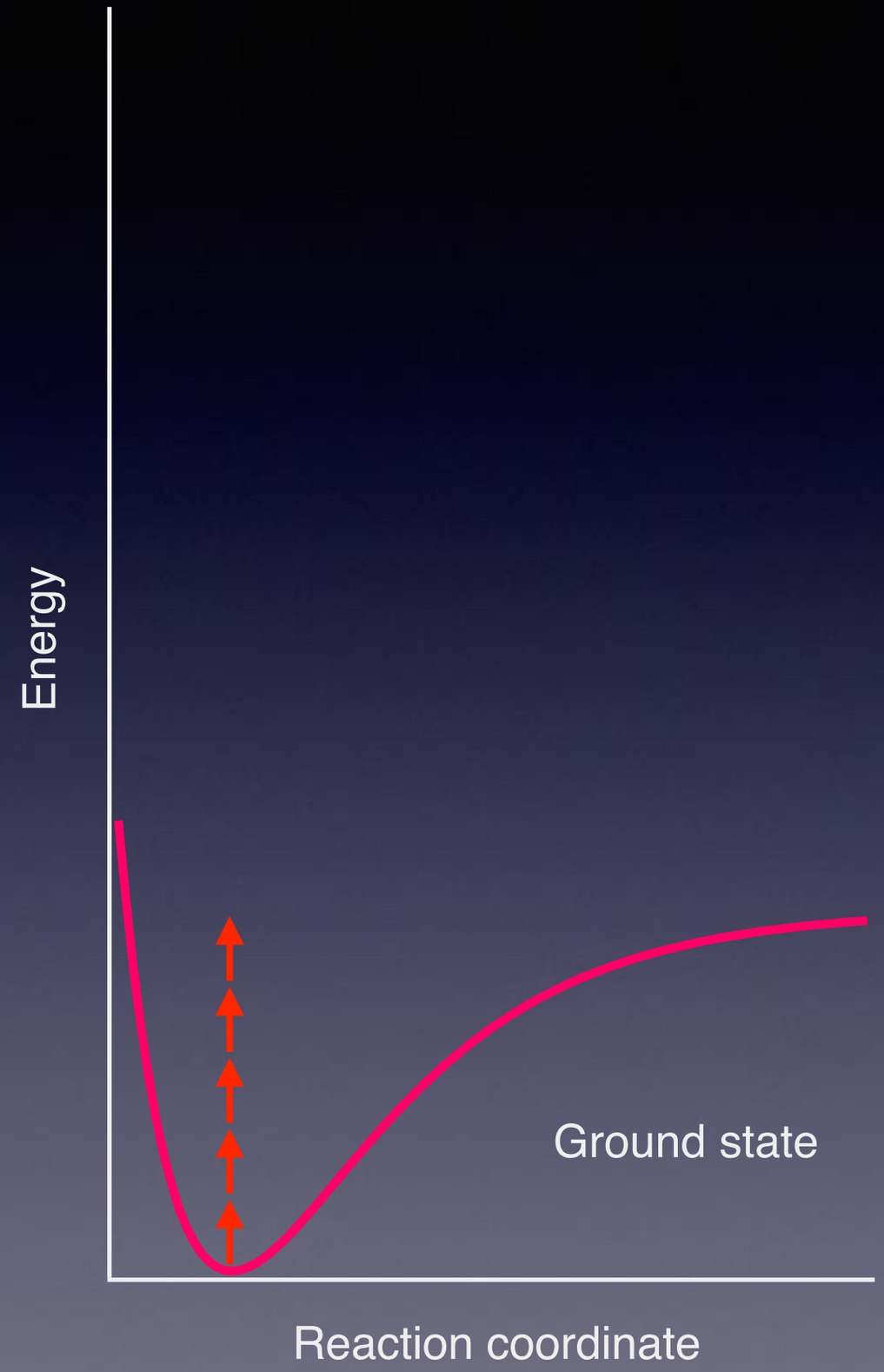
Ultraviolet Photodissociation (UVPD)

- Localized excitation : **excited state**
- Photospecific ruptures
- Rapid fragmentation -> structural information

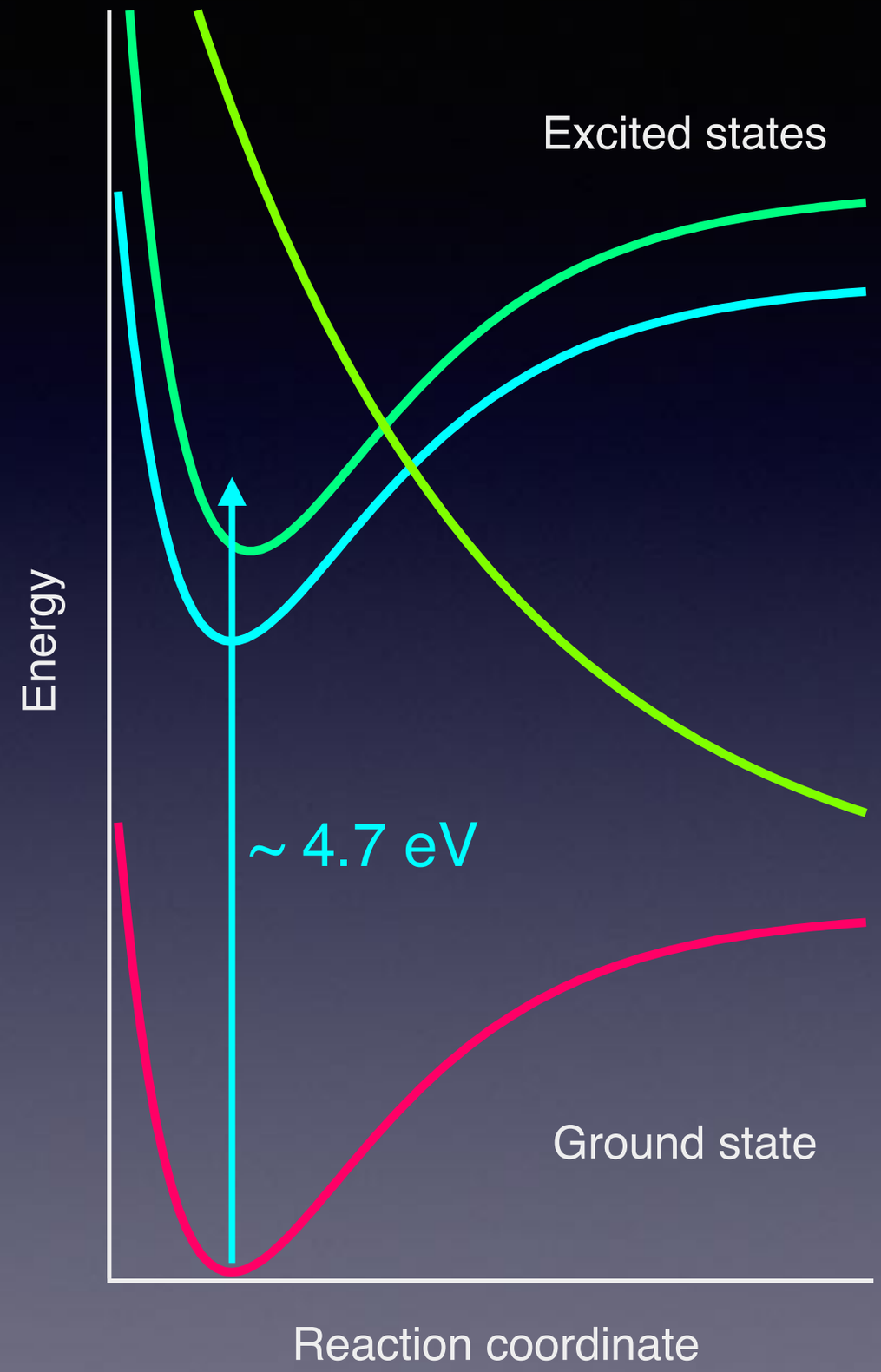
Activation

IR photons / Collisions
Gradual increase in internal energy

Statistical dissociation - slow



Activation



IR photons / Collisions
Gradual increase in internal energy

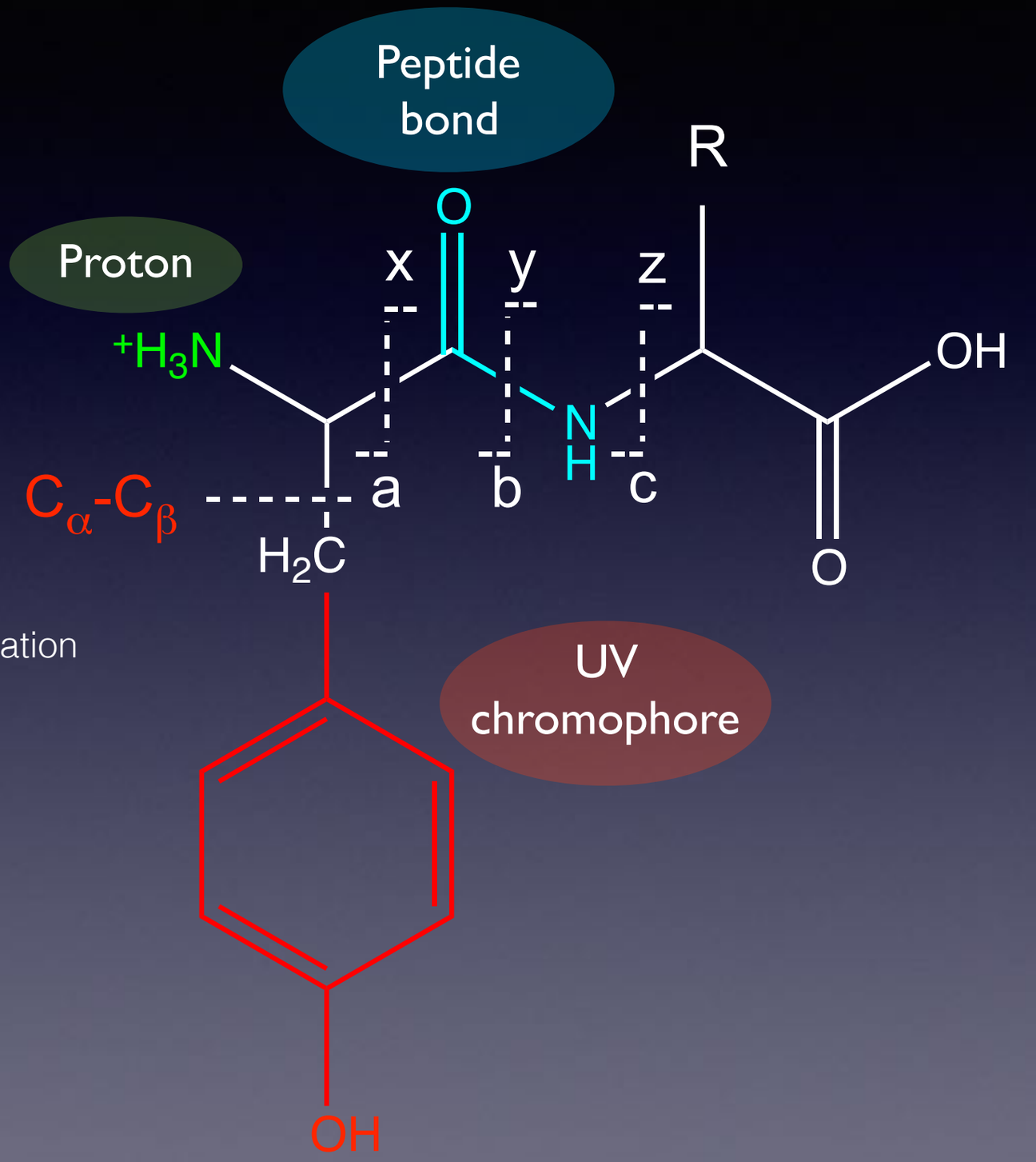
Statistical dissociation - slow

UV photons
Sudden increase in internal energy

Direct dissociation - fast

UV photodissociation as a probe of the structure

Complementary information



IRMPD
IR Multi-**P**hoton **D**issociation

EID
Electron **I**nduced **D**issociation

UVPD
UV Photoinduced **D**issociation

CID
Collisions **I**nduced **D**issociation

After electronic excitation

Radiative processes

v/s

Non-radiative processes

- Internal Conversion to the ground state S_0
- Coupling with a charge transfer state
- Intersystem crossing to a triplet state T_n

Observable : fragments

Experimental setups in Orsay

- Combination of laser spectroscopy and mass spectrometry :
    - **Control** over **entrance channel** (m/z)
    - **Control** over **energy** (photon)
    - **Control** over **exit channel(s)** (fragments)

Multicoincidence Arc-en-Ciel

- Detection ion + neutral(s)
- Access to fragmentation times (from 20 ns to ms)

Fragmentation mechanism
Binary / Sequential

Cryogenic ion trap (10 K)

- Isolation of conformers
- Energy- and Time-resolved spectroscopy
- Direct comparison with quantum chemistry calculations

Structure, Excited States Dynamics and Mechanisms

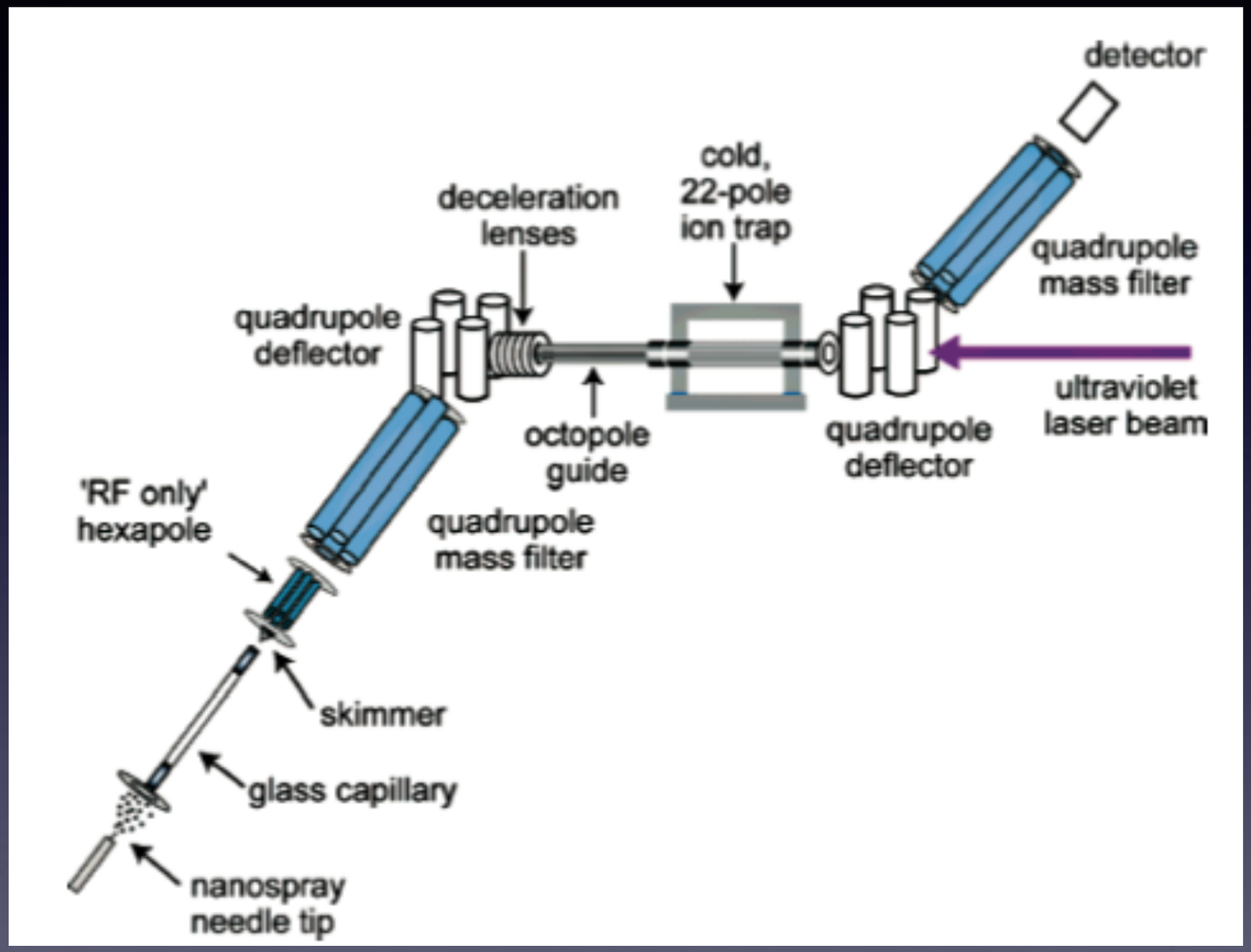
Cryogenic Ion Trap

Photofragmentation spectroscopy and Multiscale relaxation dynamics

Cryogenic Ion Trap

SELA, Centre Laser de l’Université Paris-Sud
Bâtiment 520, ISMO, Orsay

Photofragmentation spectroscopy of cold ions



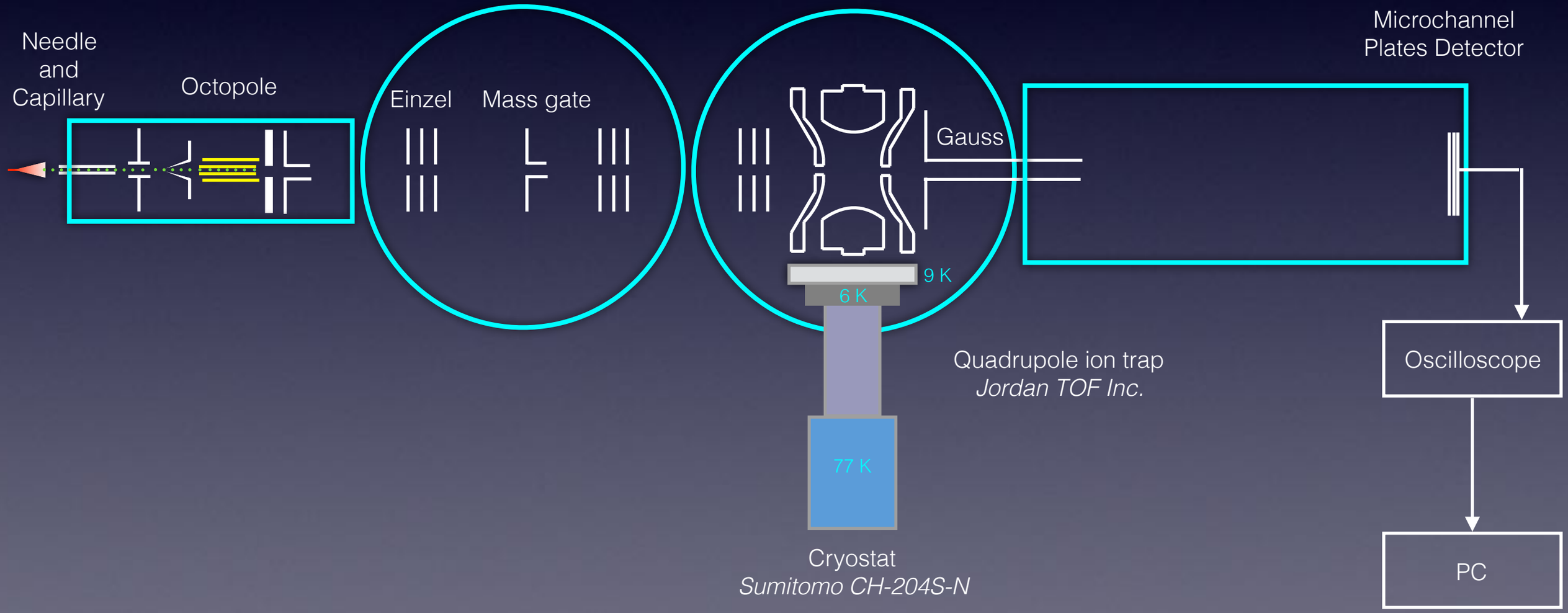
*Boyarkin et al., J. Am. Chem. Soc. 2006, **128**, 2816*

*D. Gerlich, Adv. Chem. Phys. 1992, **82**, 1-176*

Group of Thomas Rizzo (EPFL)

- First spectrum of Tyrosine(H^+) in 2006

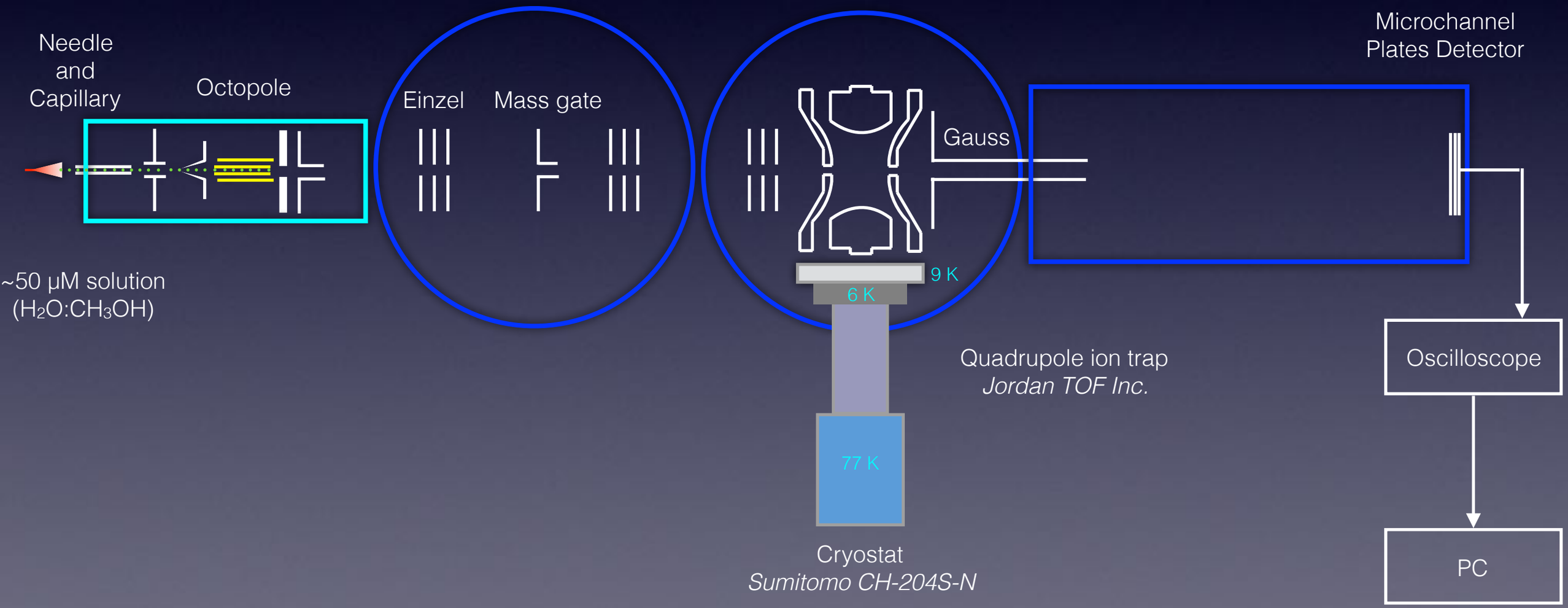
Experimental setup



*Alata et al., J. Phys. Chem. A, 2013, **117**, 4420, Féraud et al., Phys. Chem. Chem. Phys., 2014, **16**, 5250*

Experimental setup

Electrospray Ionization source (ESI)



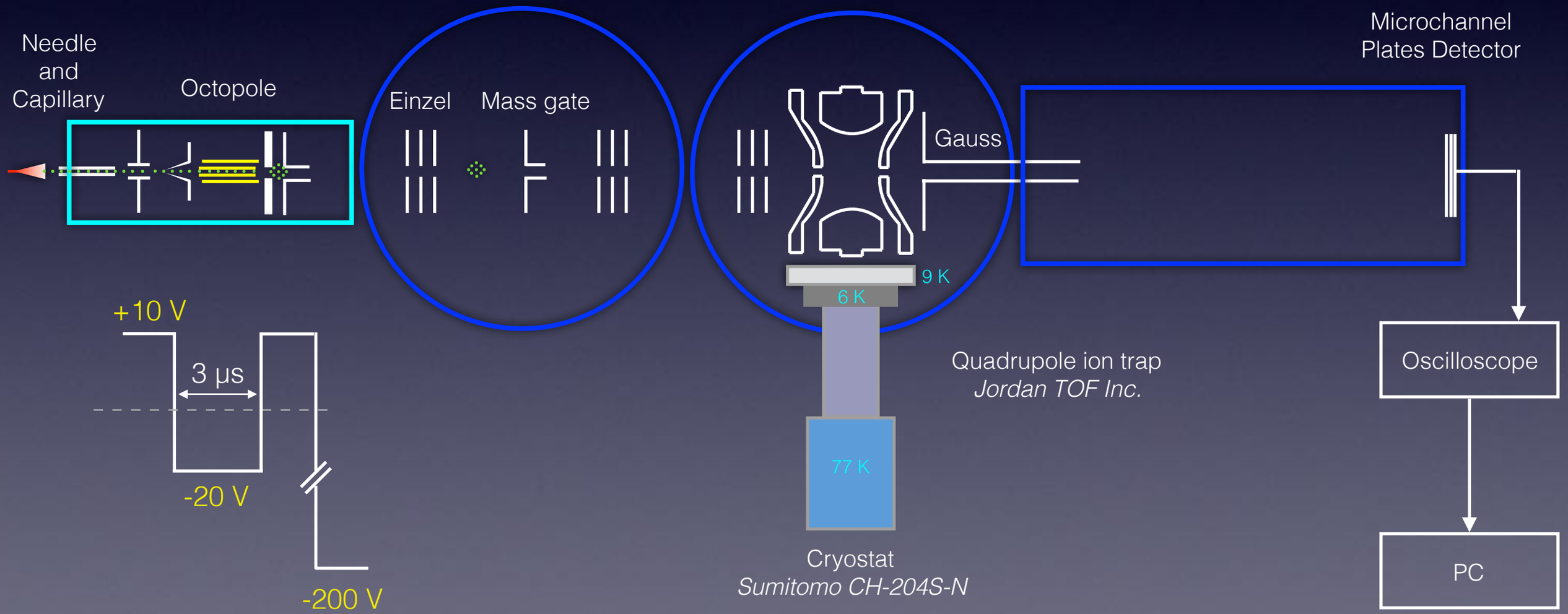
~50 μM solution (H_2O:CH_3OH)

Quadrupole ion trap
Jordan TOF Inc.

Cryostat
Sumitomo CH-204S-N

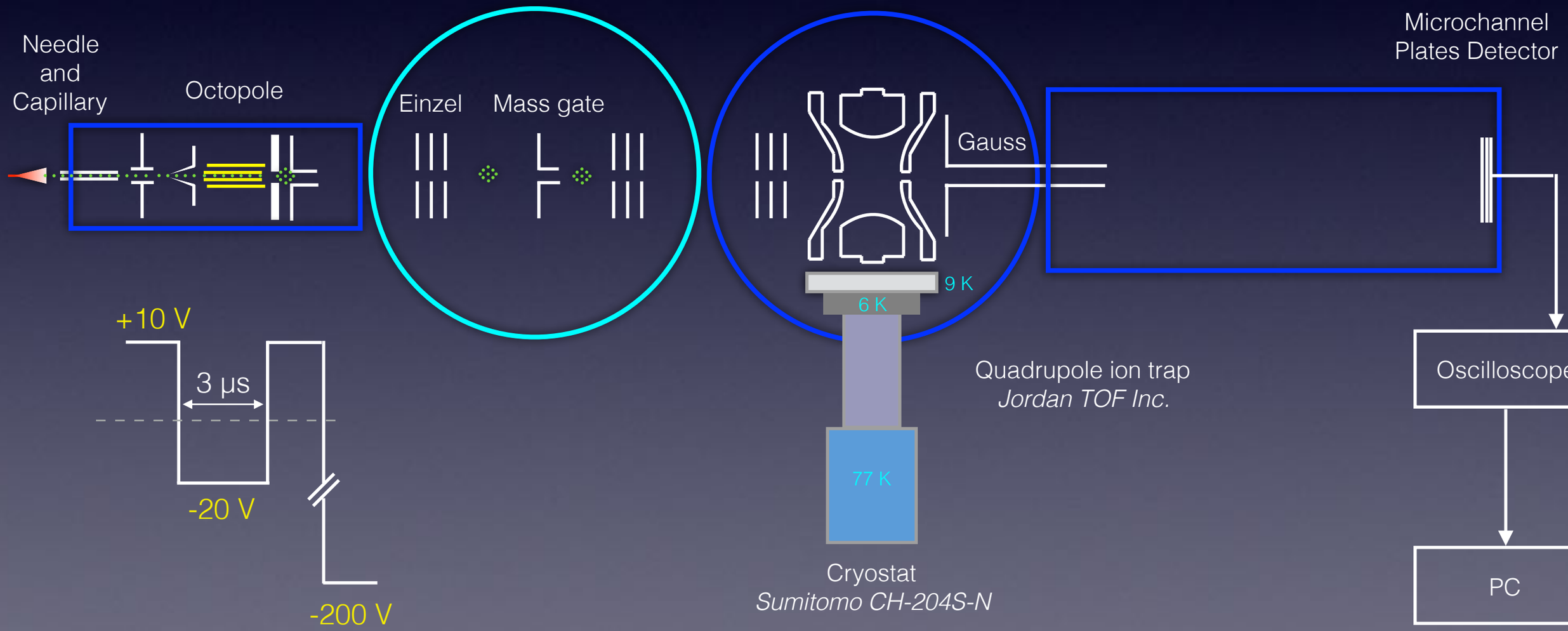
Experimental setup

Electrospray Ionization source (ESI) → Bunching



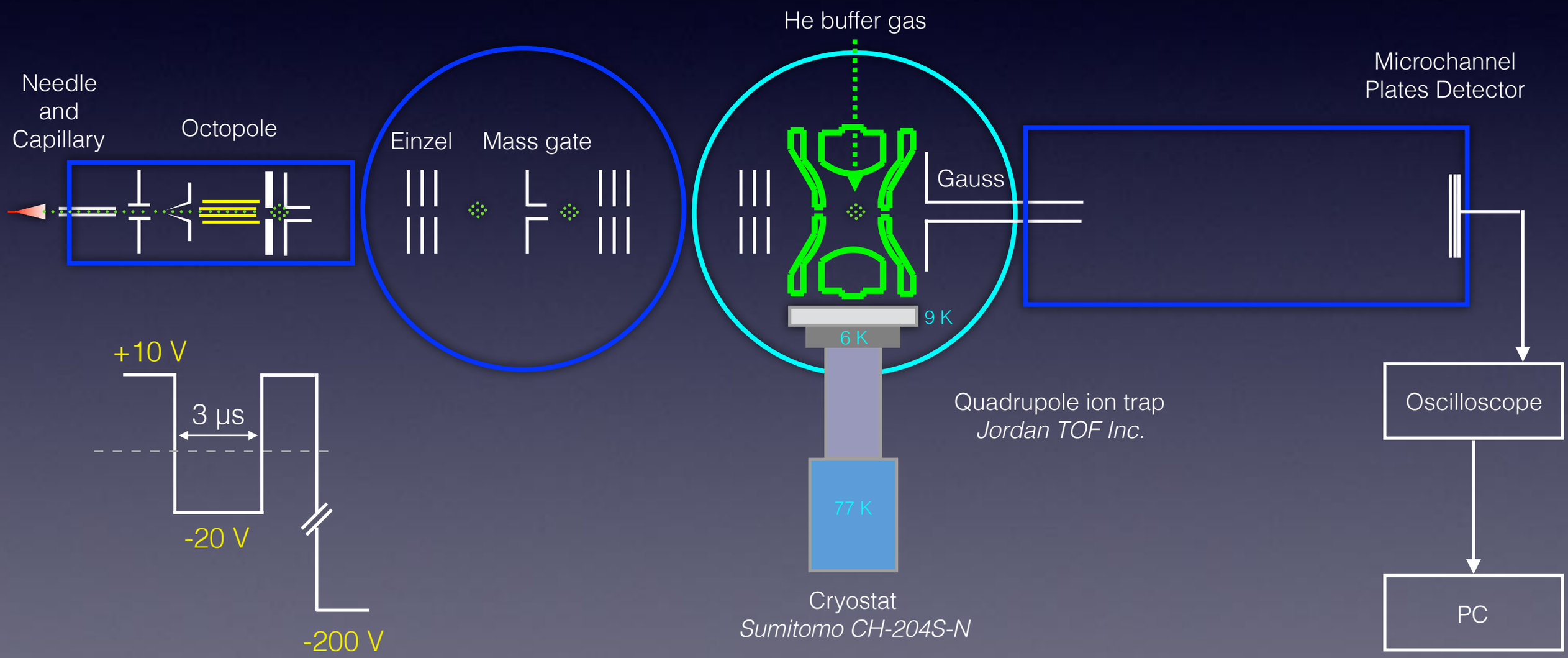
Experimental setup

Electrospray Ionization source (ESI) → Bunching → Mass selection



Experimental setup

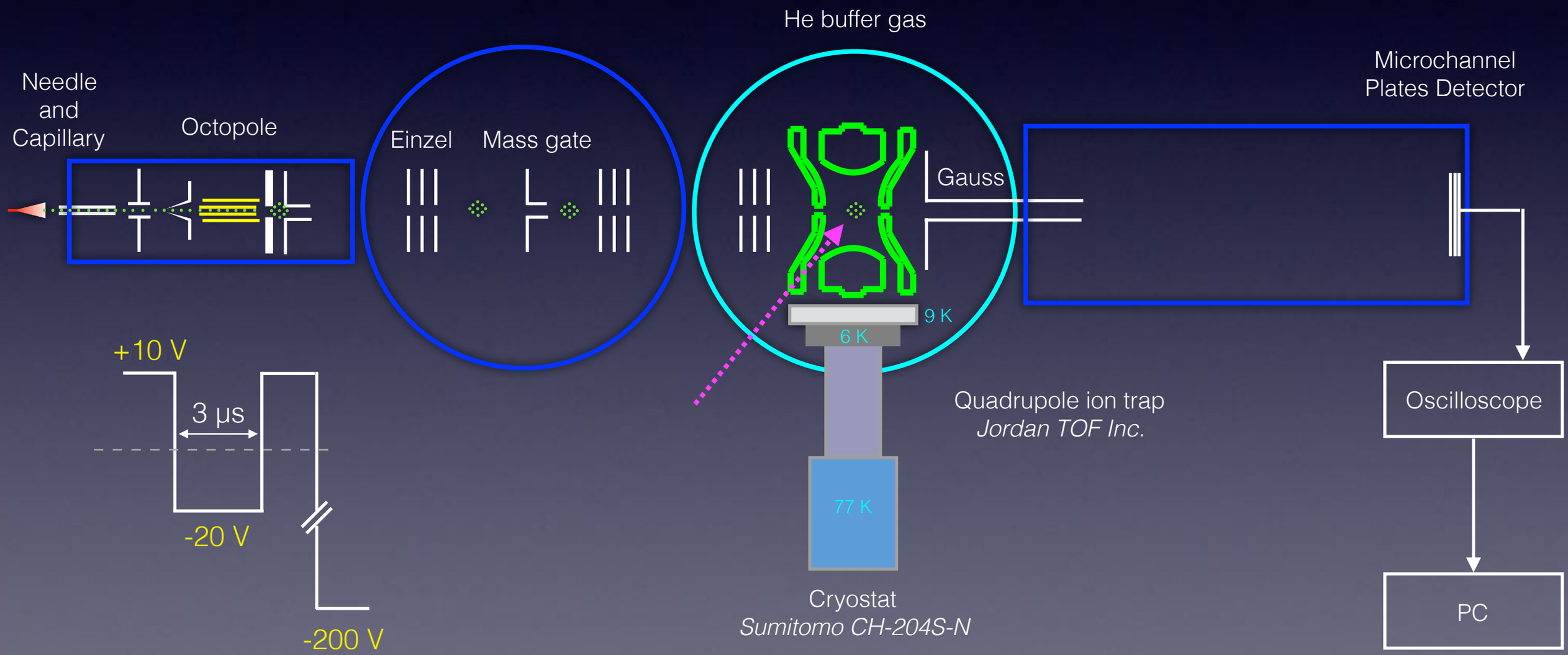
Electrospray Ionization source (ESI) → Bunching → Mass selection → Trapping and Cooling



Experimental setup

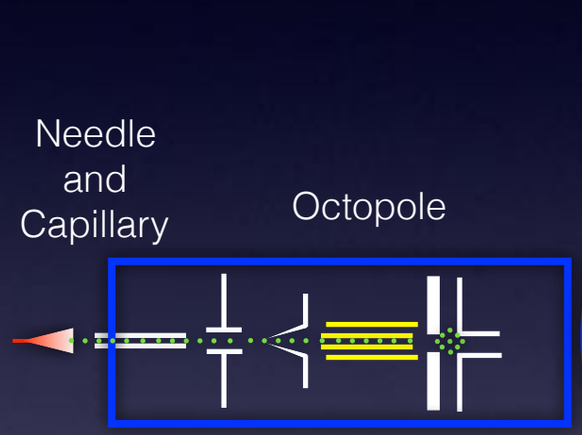
Electrospray Ionization source (ESI) → Bunching → Mass selection → Trapping and Cooling

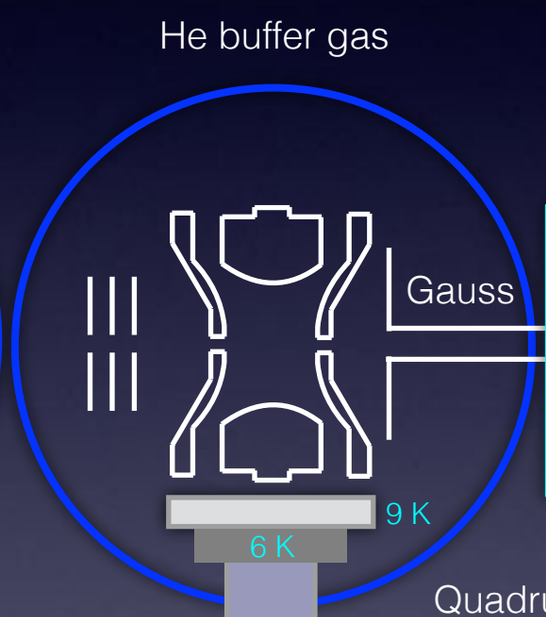
Photodissociation

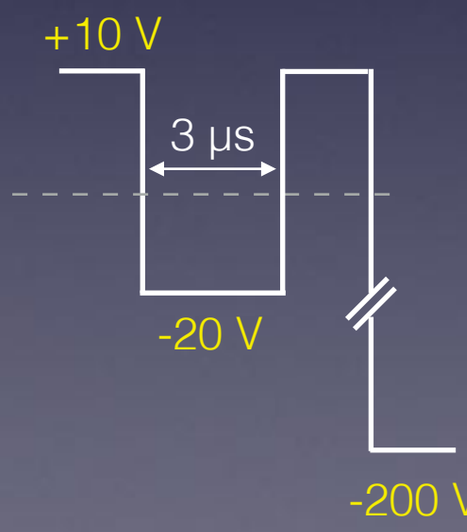


Experimental setup

Electrospray Ionization source (ESI) → Bunching → Mass selection → Trapping and Cooling / Photodissociation → Time-of-Flight Mass Spectrometry

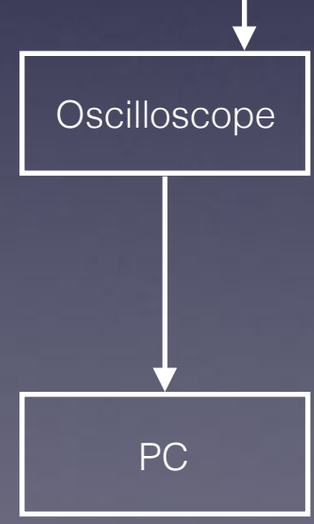


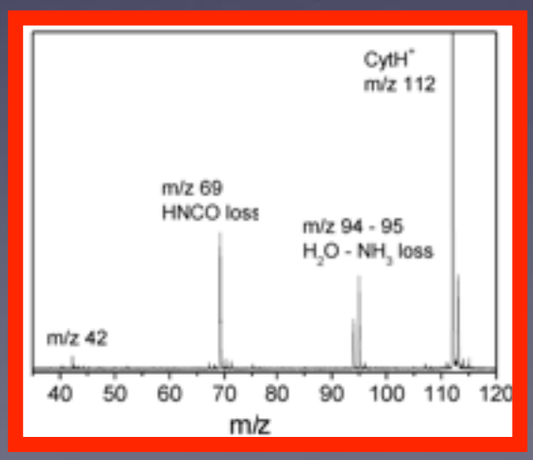




Quadrupole ion trap
Jordan TOF Inc.

Cryostat
Sumitomo CH-204S-N





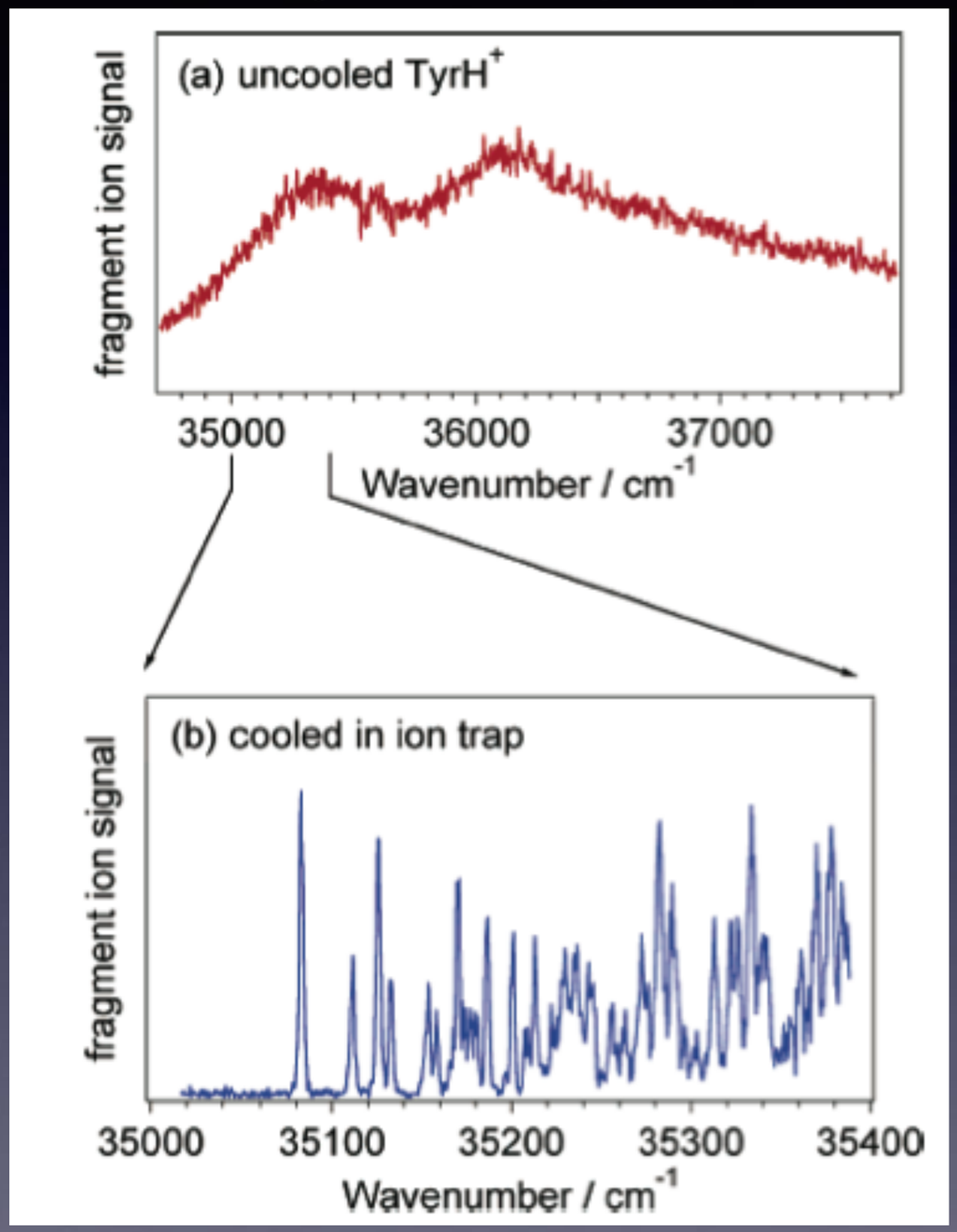
Action spectroscopy

Pump-probe

Fragmentation kinetics

Experimental setup

Tyrosine(H^+)



West Lafayette
New Haven
Providence
Madison

Marseille
Orsay

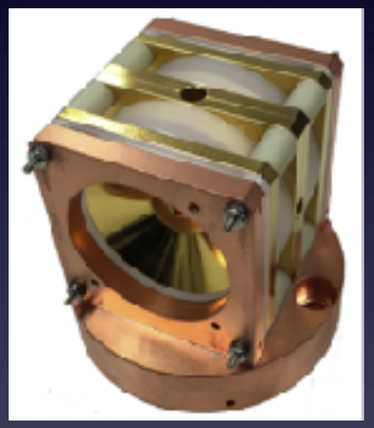
Lausanne
Bâle

Berlin

Innsbruck

Tokyo

22 pôles



Paul trap

Photofragmentation spectroscopy

Resolved vibronic spectrum -> Structural information

*Boyarkin et al., J. Am. Chem. Soc. 2006, **128**, 2816*

Experimental setup

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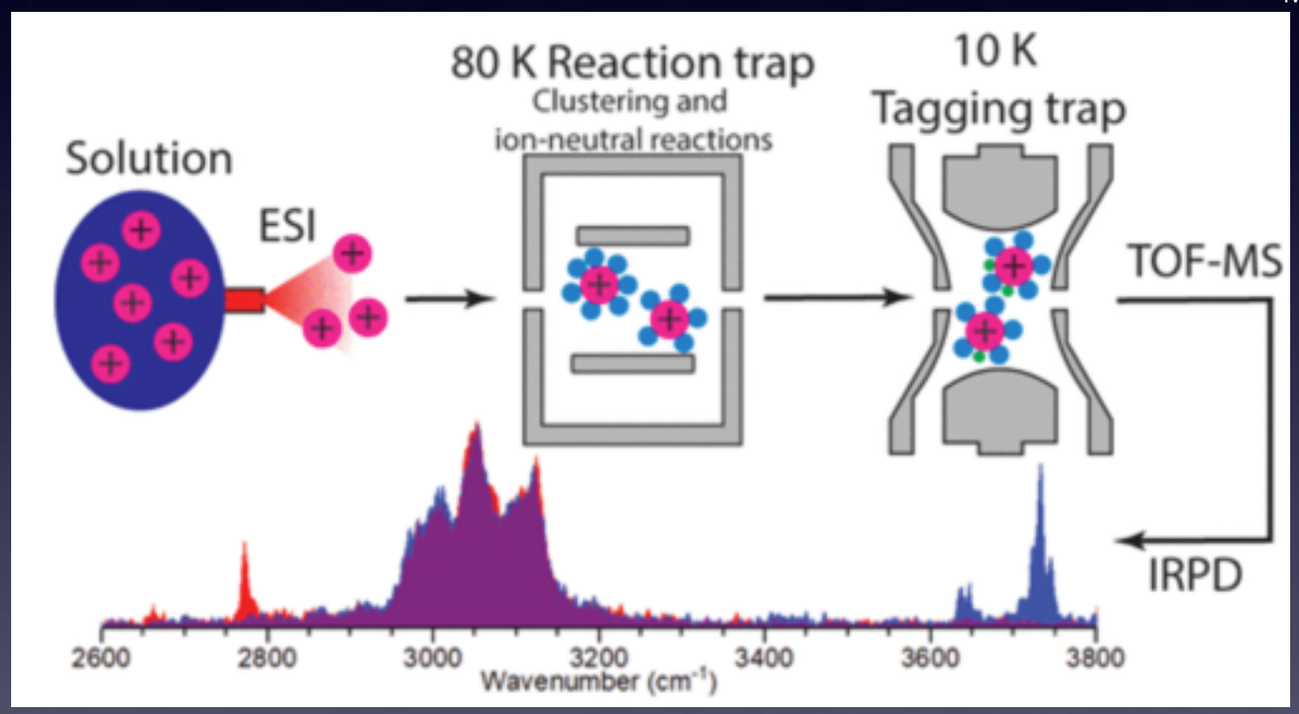
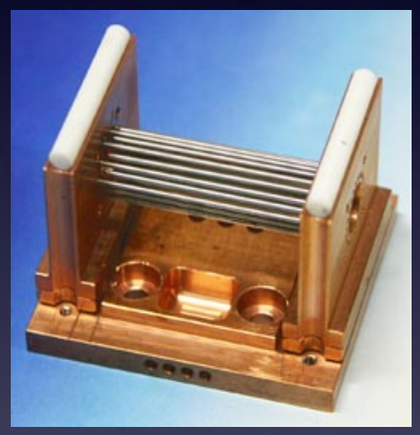
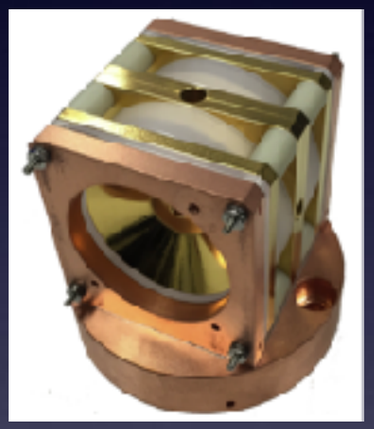




22 pôles



Paul trap

Clusters and Reactivity

E. Garand, J. Phys. Chem. A 2018, ***122****, 6479*

Experimental setup

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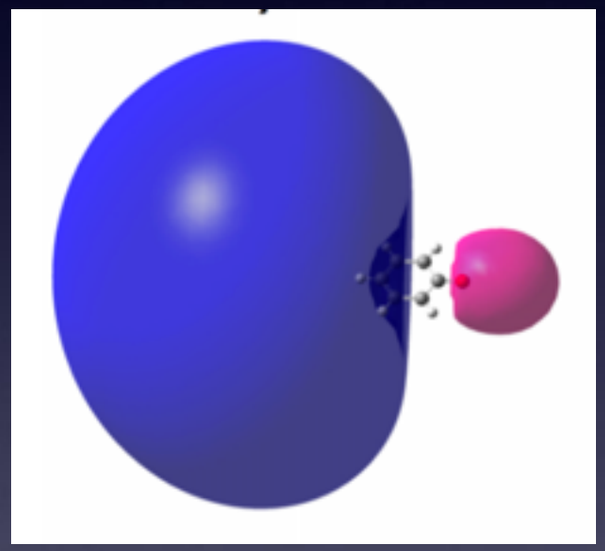
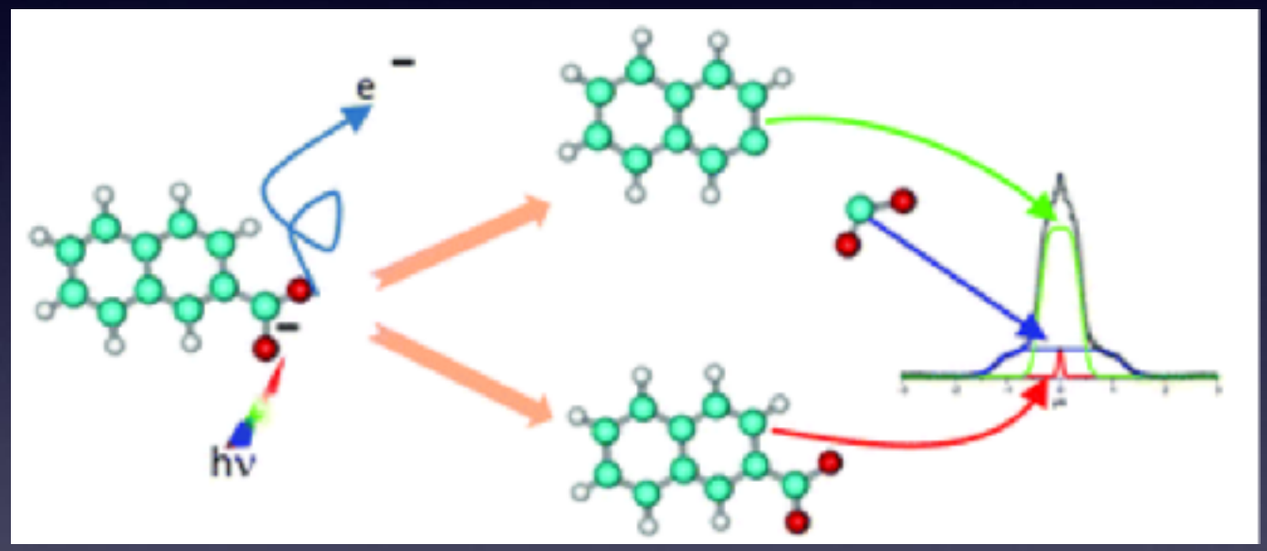


The wavefuntion of dipole bound state of the phenoxide anion.

L. S. Wang - USA

Photodetachment spectroscopy

*L. S. Wang, J. Chem. Phys. 2015, **143**, 040901*



Competition between dissociative photodetachment and photodissociation of the naphthoate anions.

J. Noble, C. Dedonder and C. Jouvet - France

Photodetachment v/s Photofragmentation

*Pino et al., Phys. Chem. Chem. Phys. 2019, **21**, 1797*

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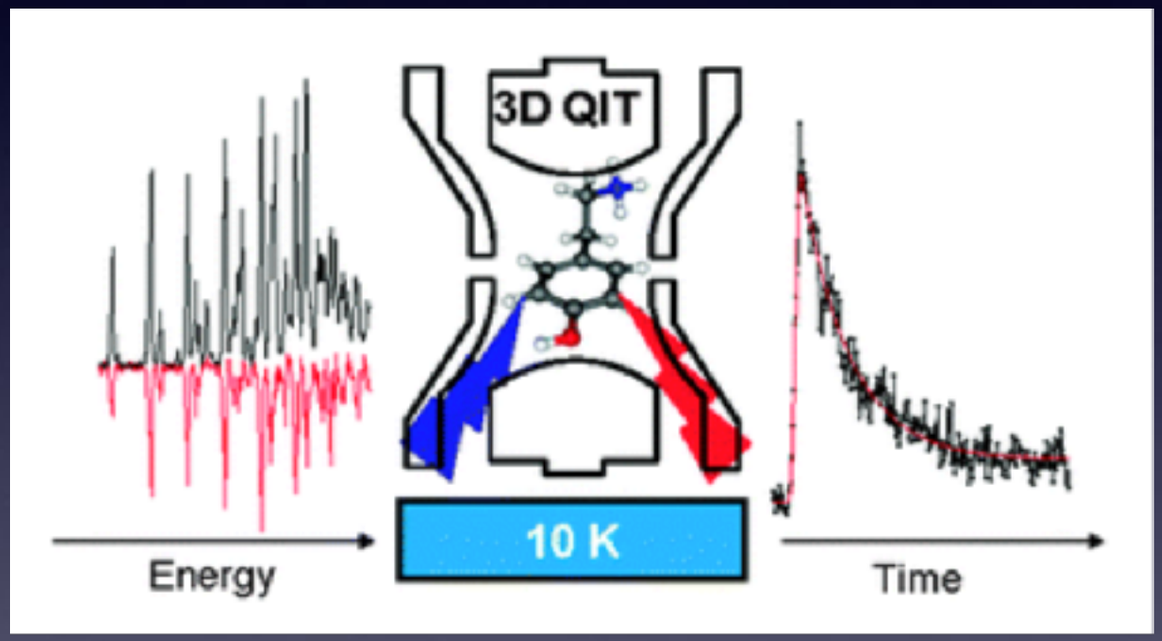

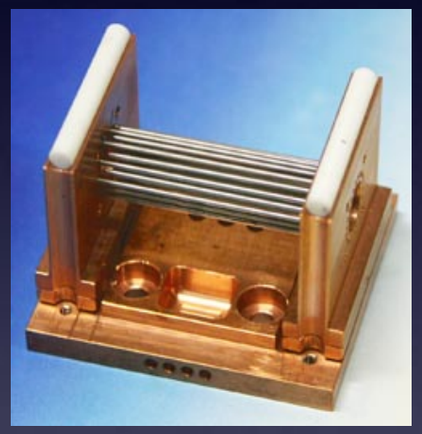

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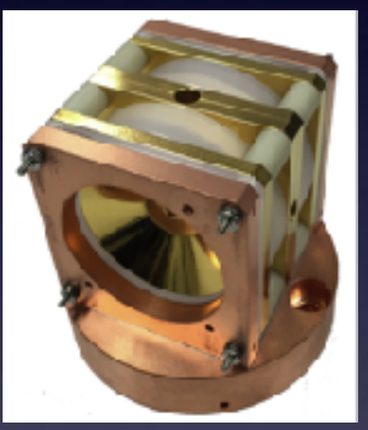


Paul trap

Orsay

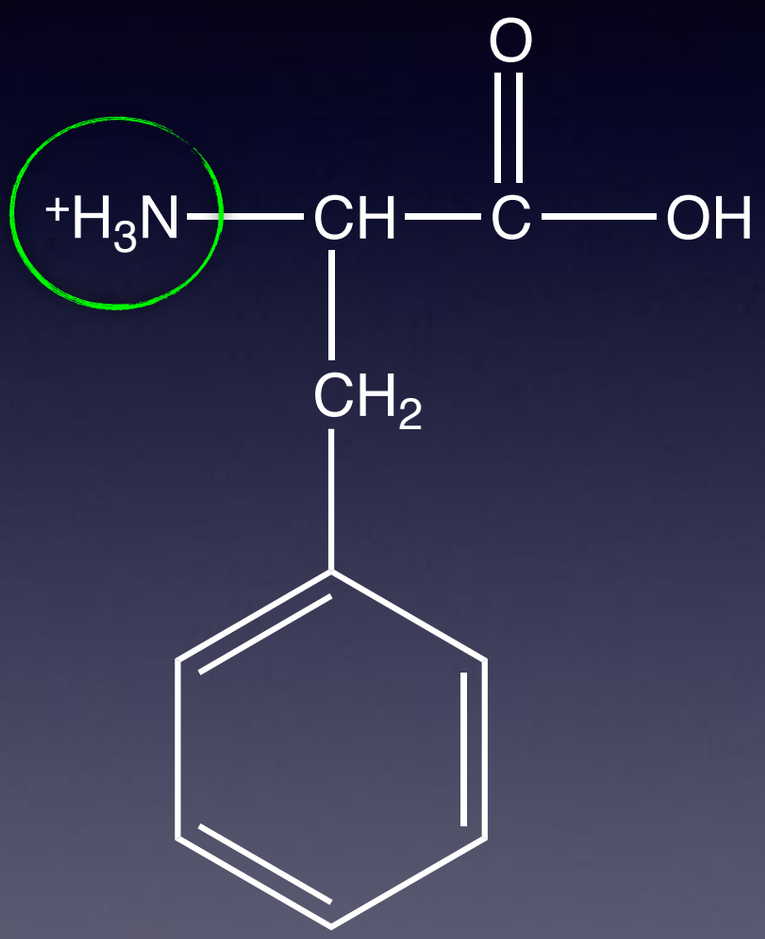
Photofragmentation mechanisms - Multiscale dynamics

Protonated aromatic amino acids

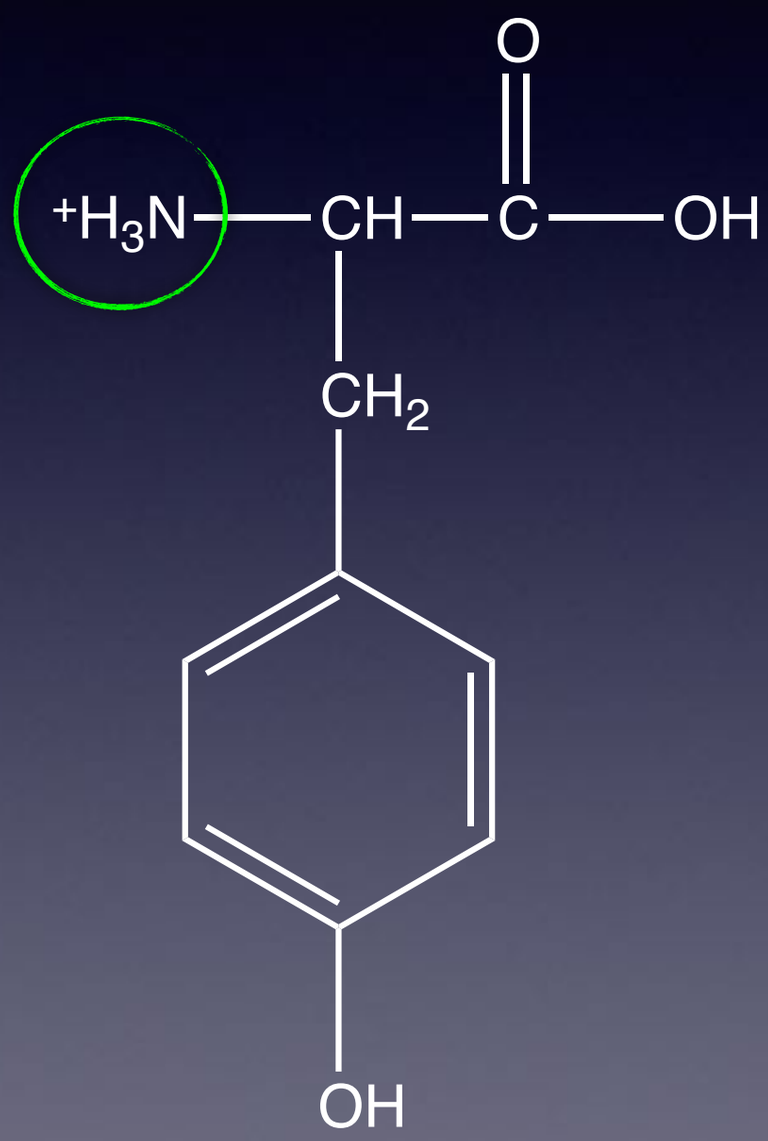
Phenylalanine(H^+)
Tyrosine(H^+)
Tryptophan(H^+)

Aromatic amino acids

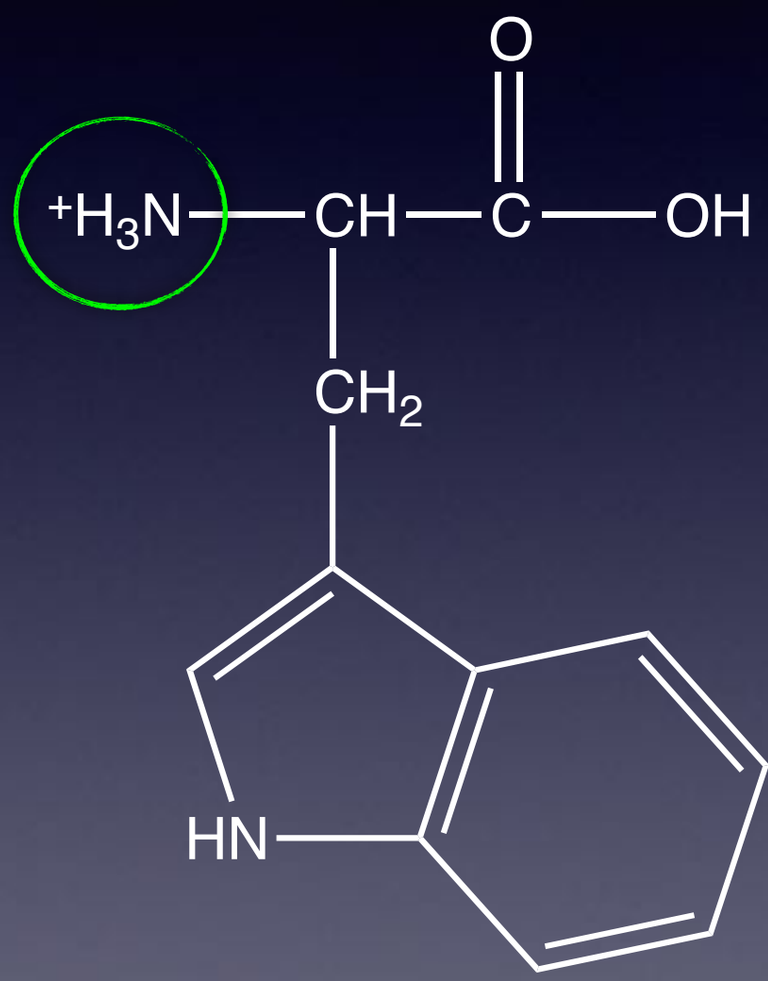
Phenylalanine(H^+)



Tyrosine(H^+)

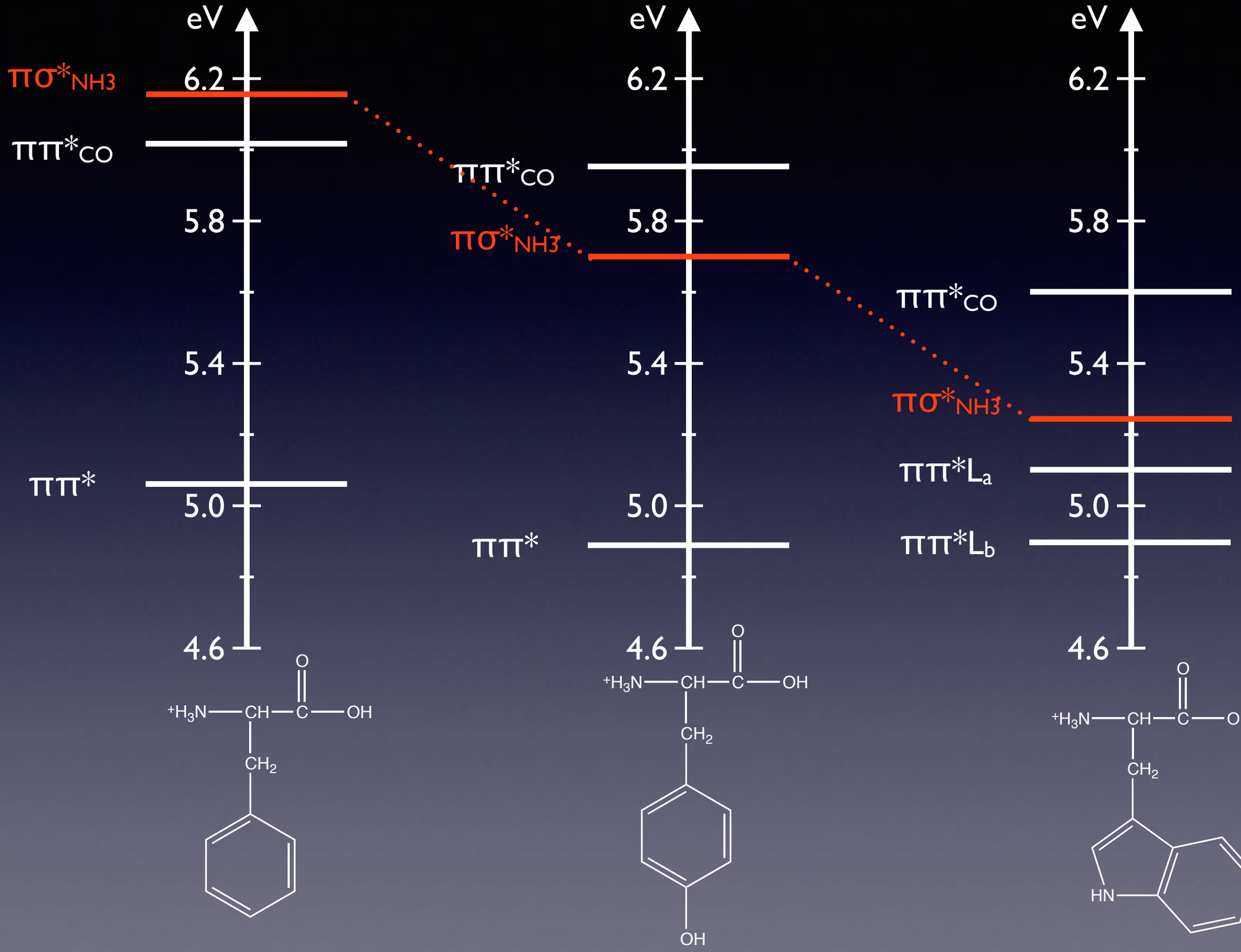


Tryptophan(H^+)



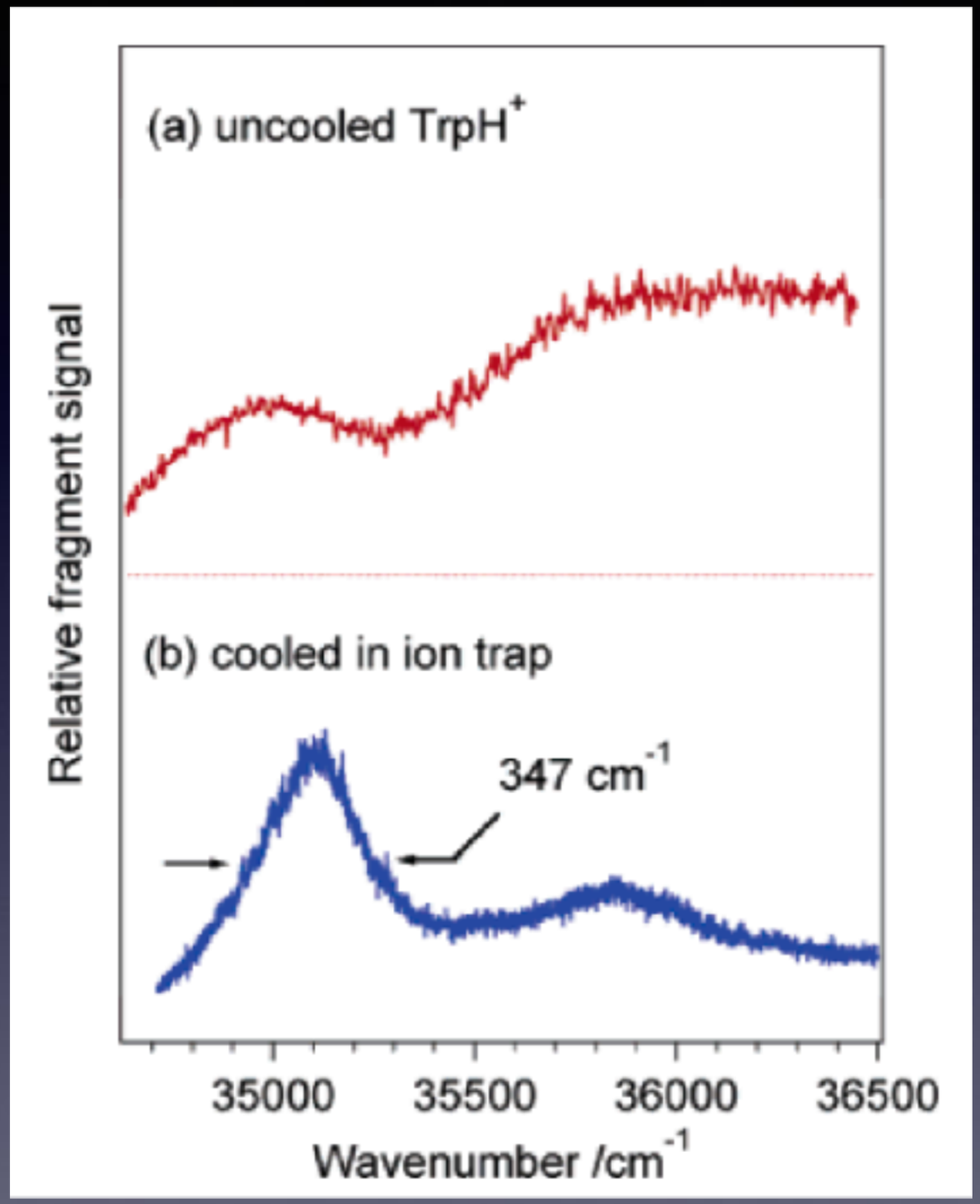
ππ*, ππ*CO and πσ*NH3 states

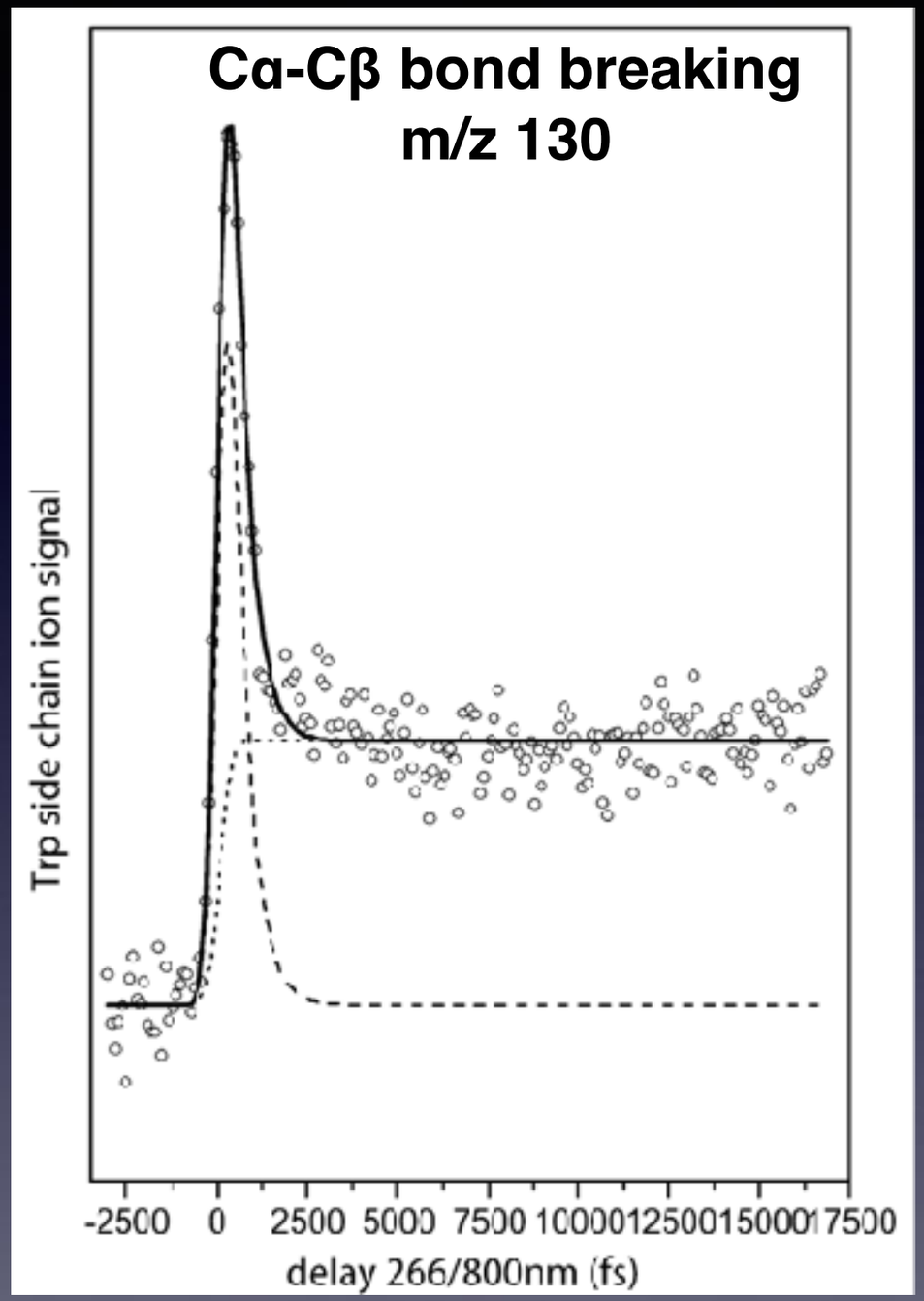
Gregoire et al.
JACS 2007, **129**, 6223



Phenylalanine(H^+) Tyrosine(H^+) Tryptophan(H^+)

Tryptophan(H+)





ππ* state decays in < 100 fs

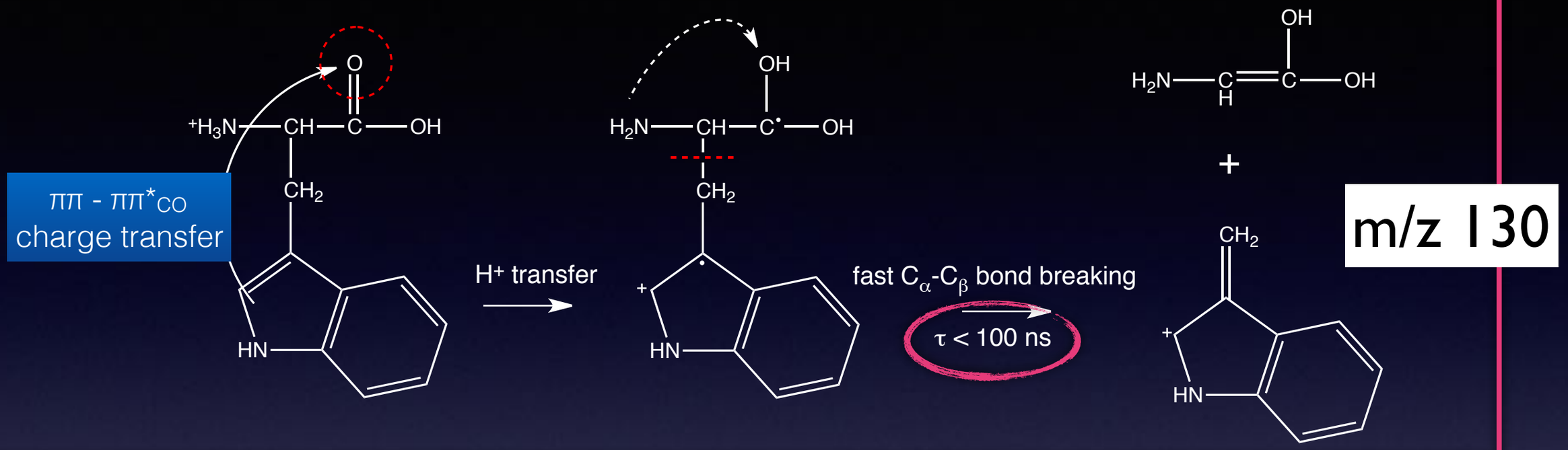
Efficient ππ* - πσ*coupling

Boyarkin et al., J. Am. Chem. Soc. 2006, ***128****, 2816*

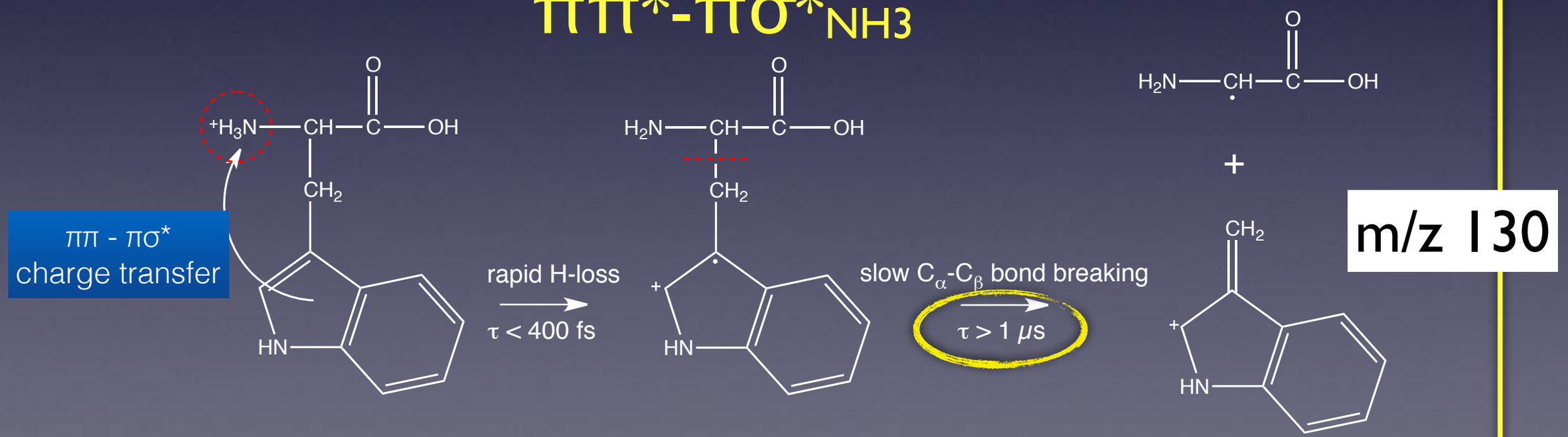
Kang et al., Phys. Chem. Chem. Phys. 2005, ***7****, 394*

Tryptophan(H+)

ππ*-ππ*$_{CO}$

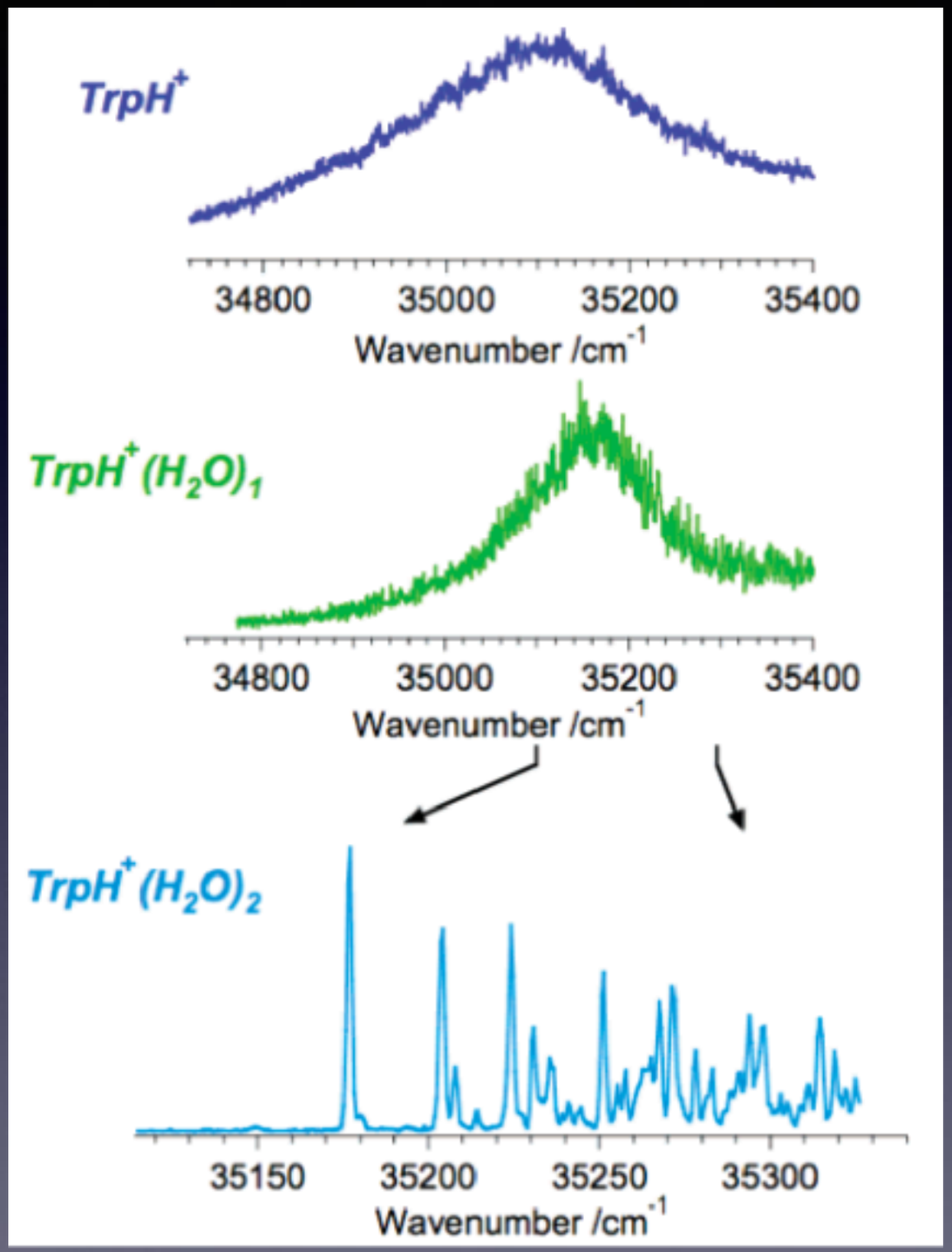


ππ*-πσ*$_{NH3}$



Same m/z - > two different fragmentation mechanisms!

Tryptophan(H+)

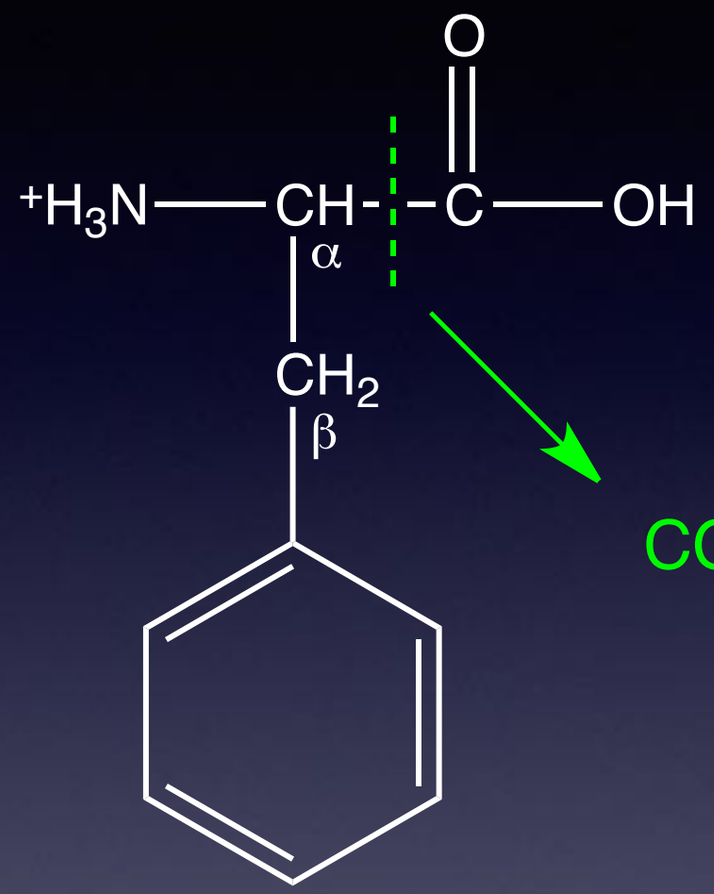


Microsolvation of NH_3^+ group by as few as two H_2O molecules is sufficient to decouple ππ* - πσ*

Longer lived excited state
->
Highly resolved spectra

*Mercier et al., J. Am. Chem. Soc. 2006, **128**, 16938*

CID* of Phenylalanine(H+)



m/z 166

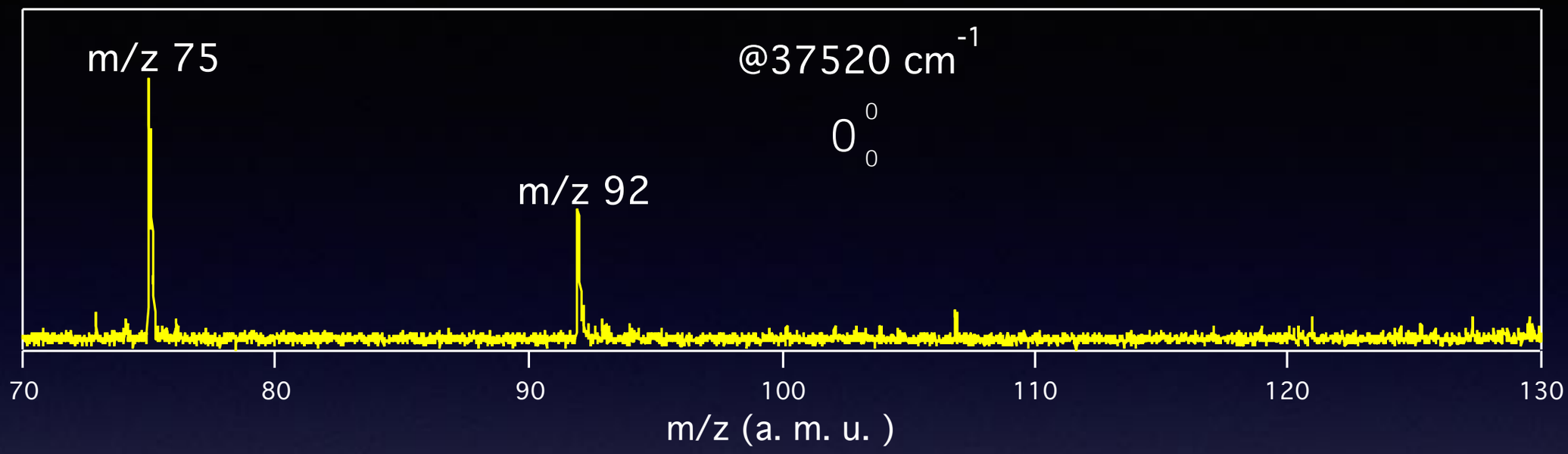
CO + H_2O loss

m/z 120

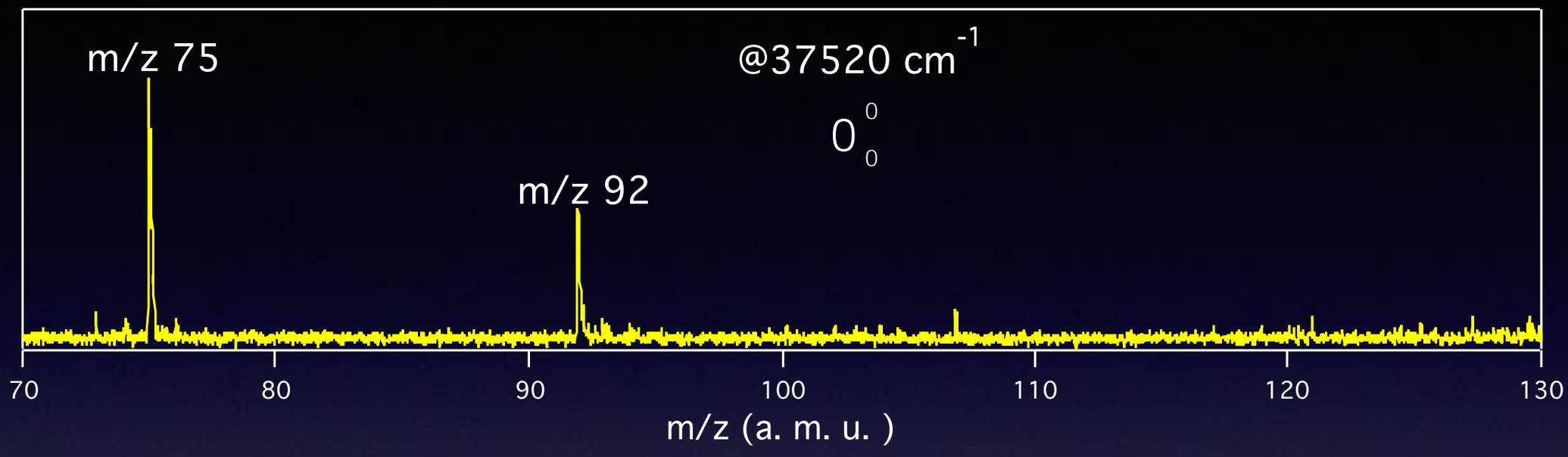
- m/z 120 - CO + H_2O loss

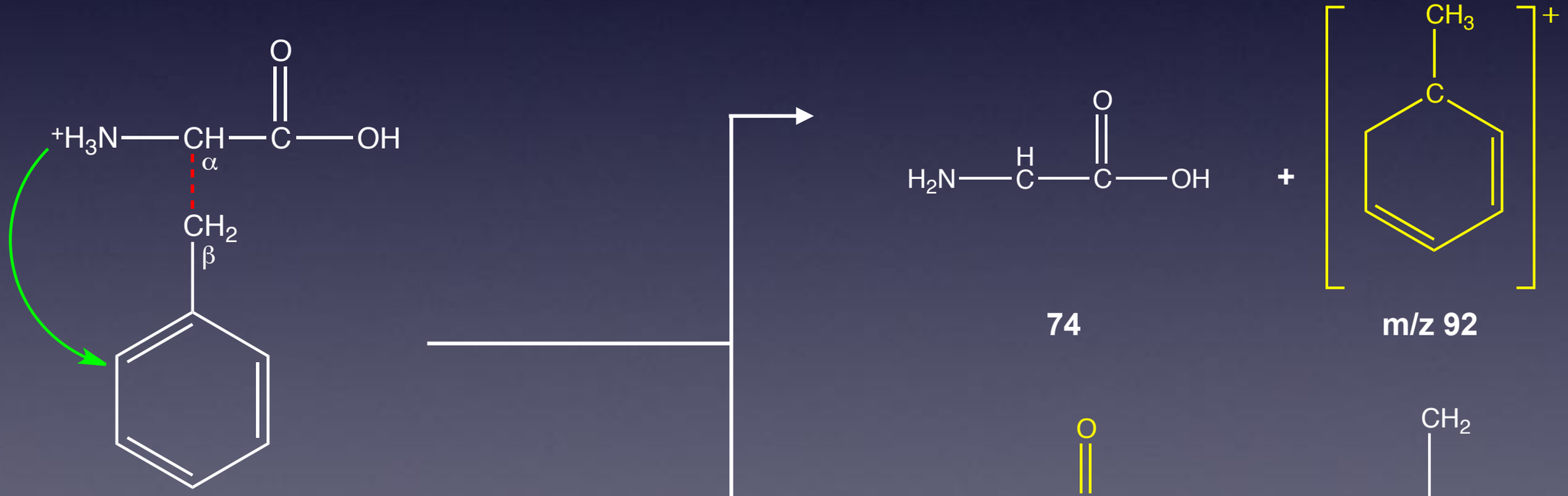
*CID : Collisions-Induced Dissociation

UVPD* of Phenylalanine(H+)

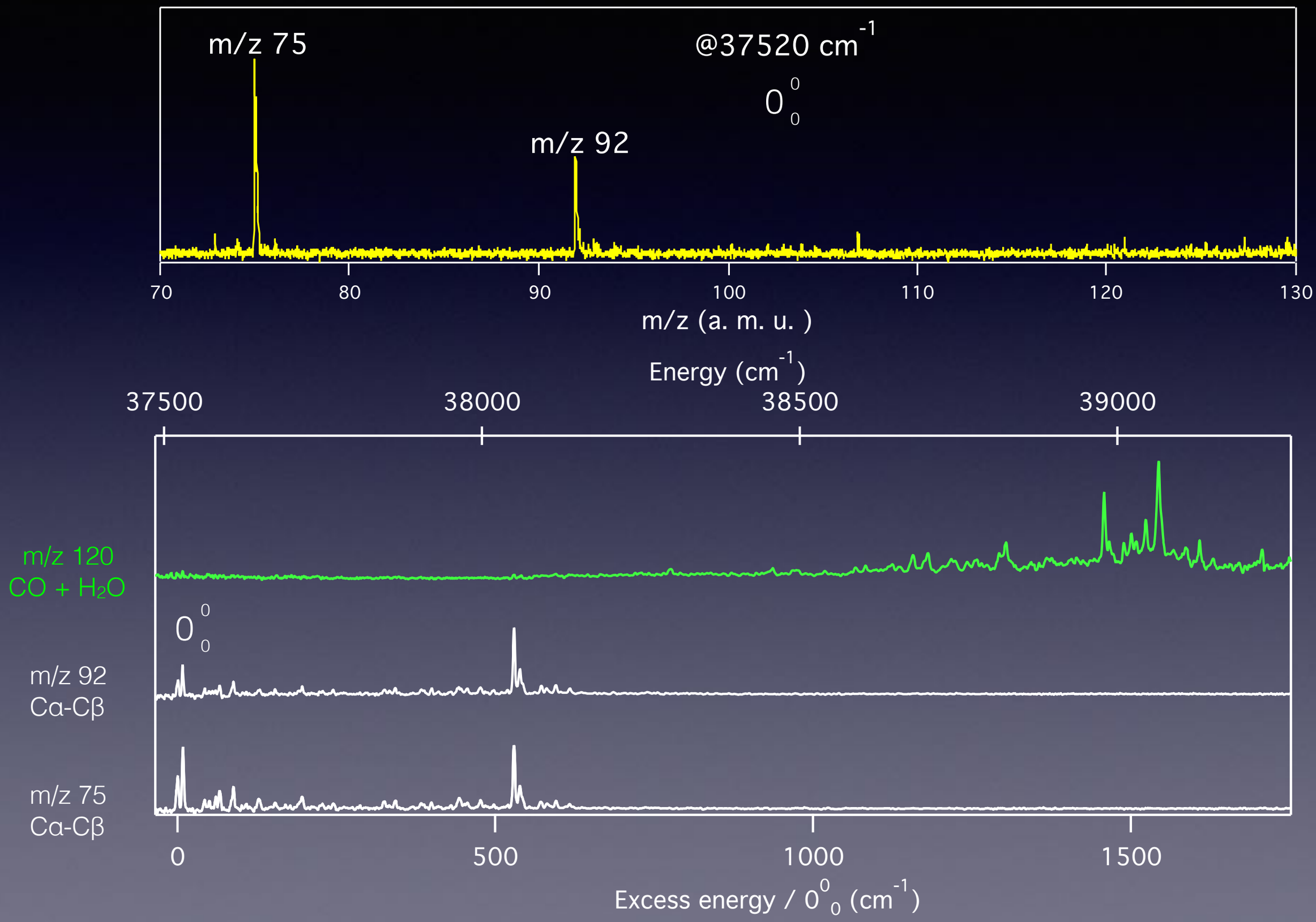


UVPD of Phenylalanine(H+)

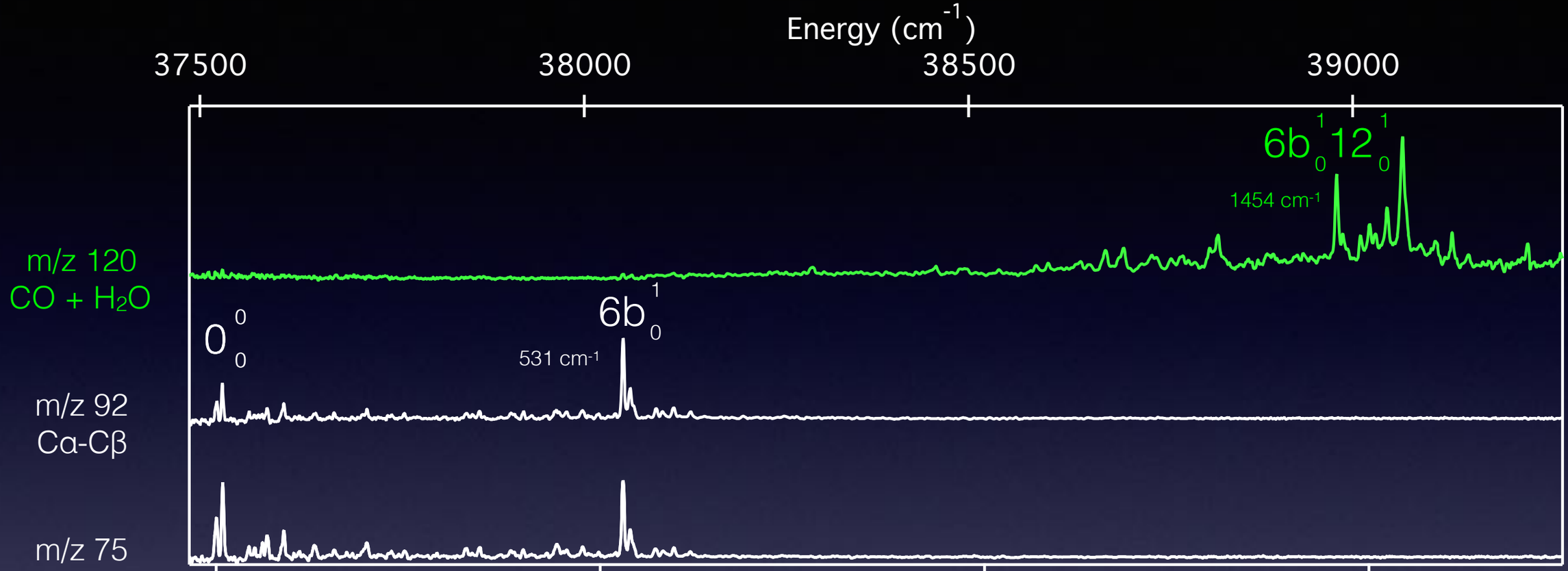




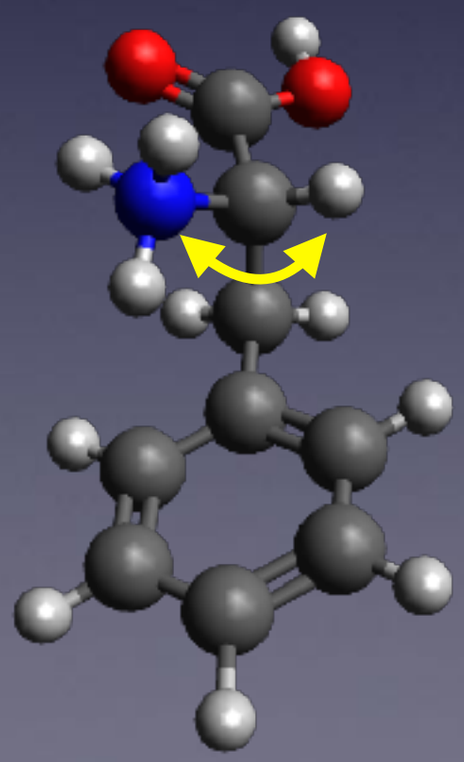
UVPD of Phenylalanine(H+)

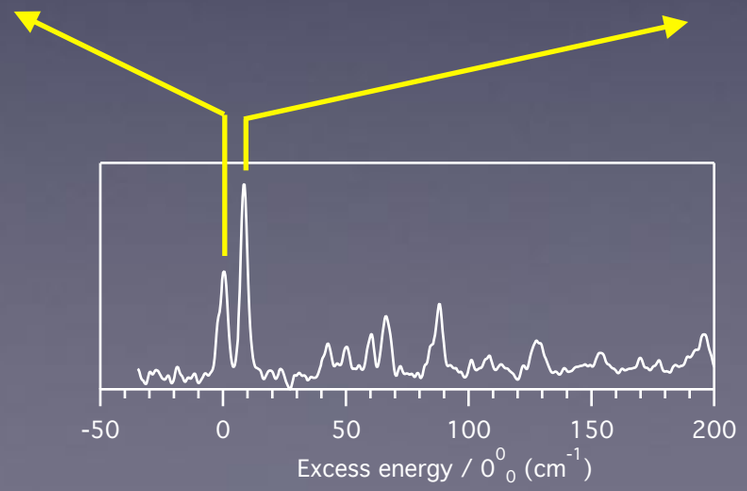


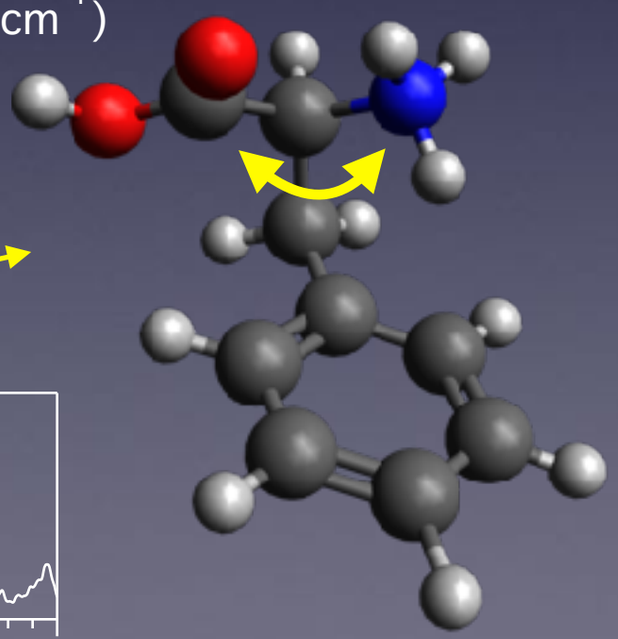
UVPD of Phenylalanine(H+)



Rot conformer

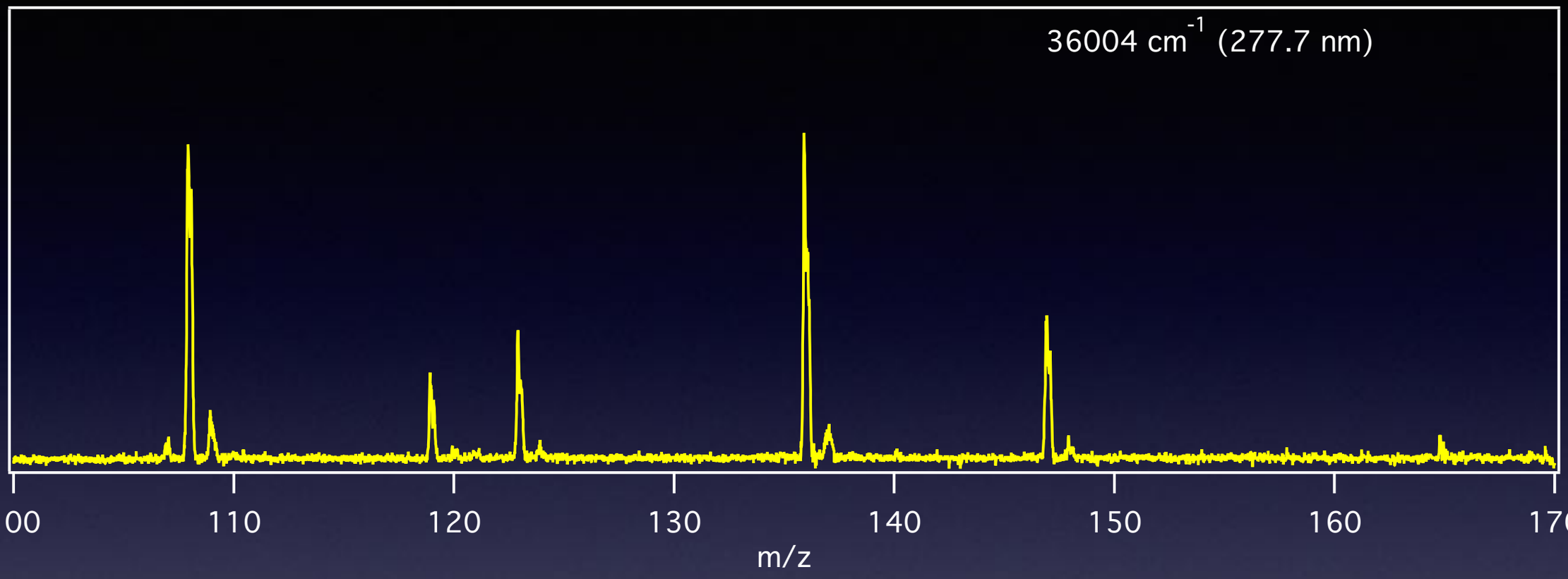




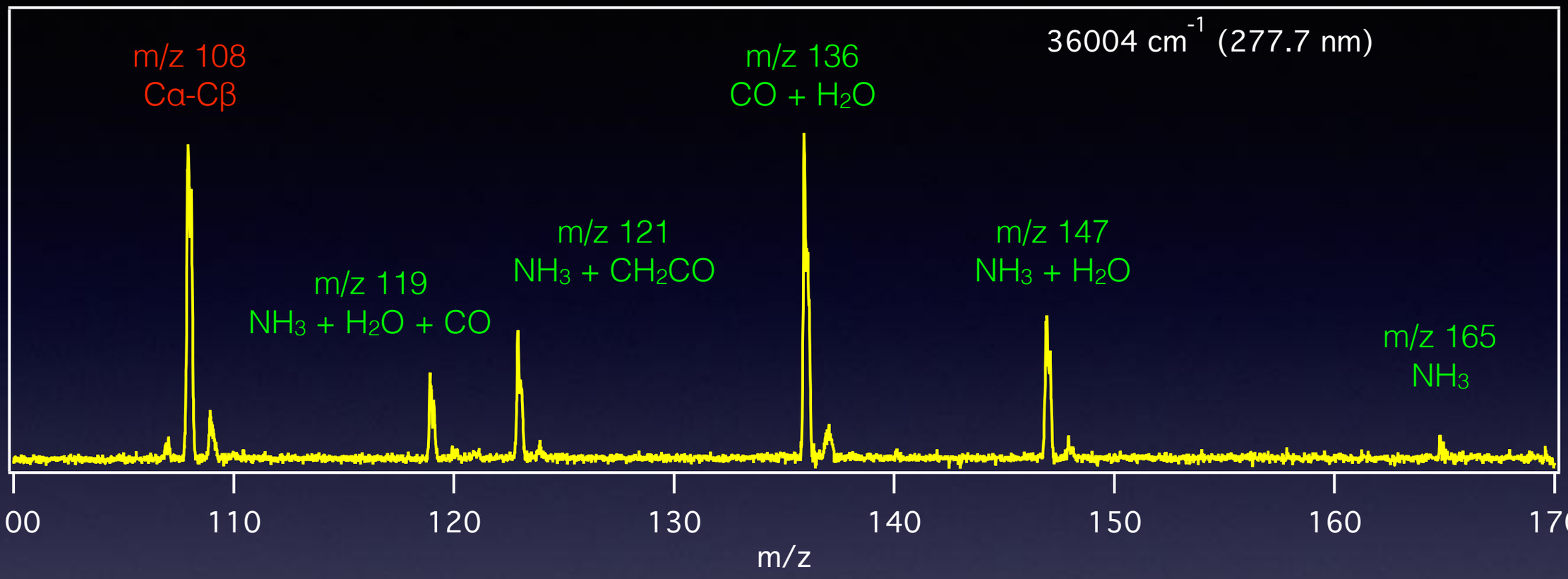


Stack conformer

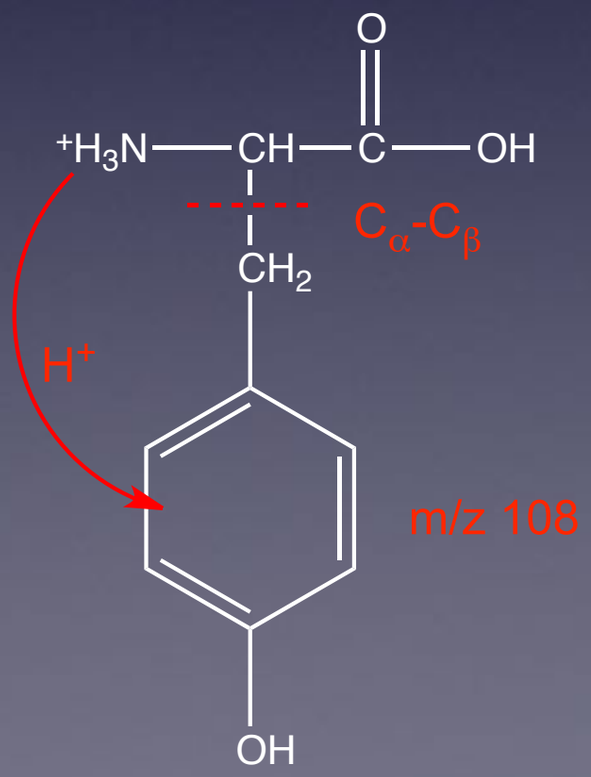
UVPD of Tyrosine(H^+)



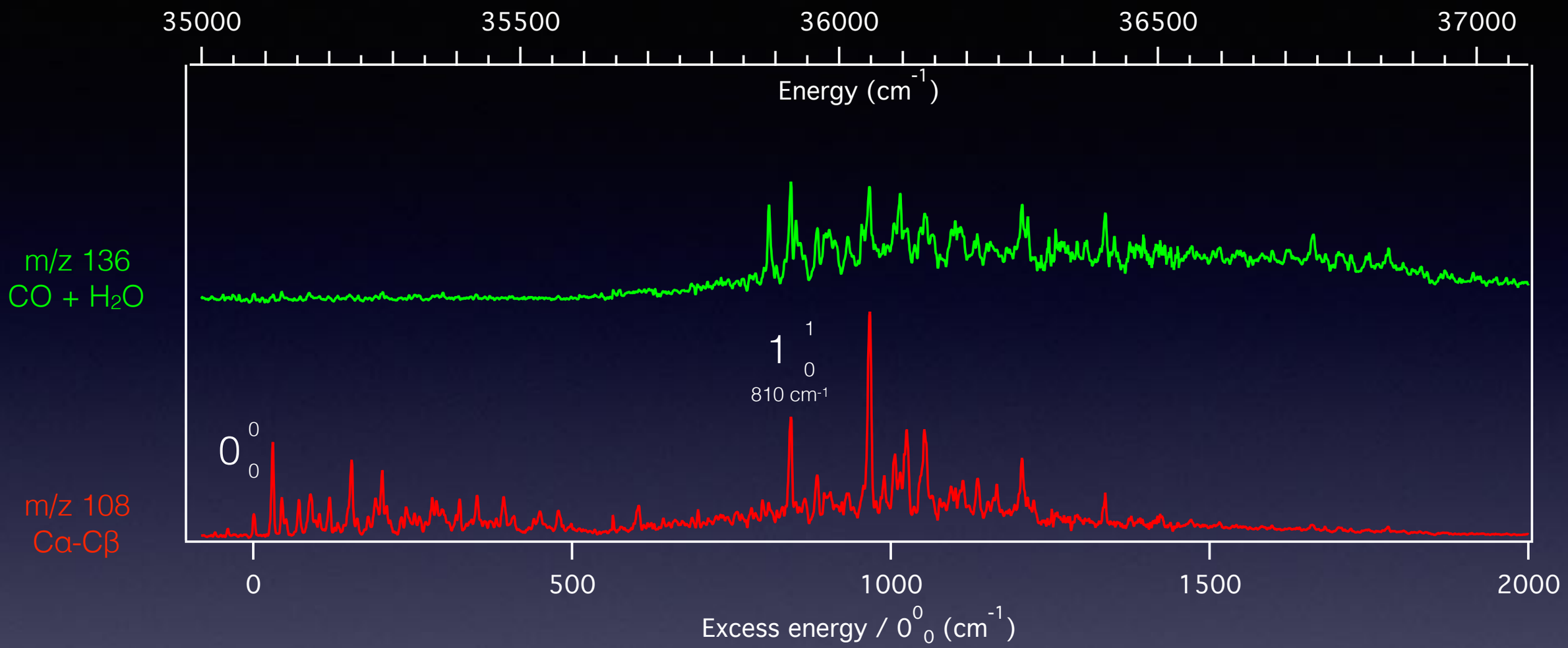
UVPD of Tyrosine(H+)



- Cα-Cβ bond rupture (m/z 108)
- Proton transfer to ring
- CID-like fragments

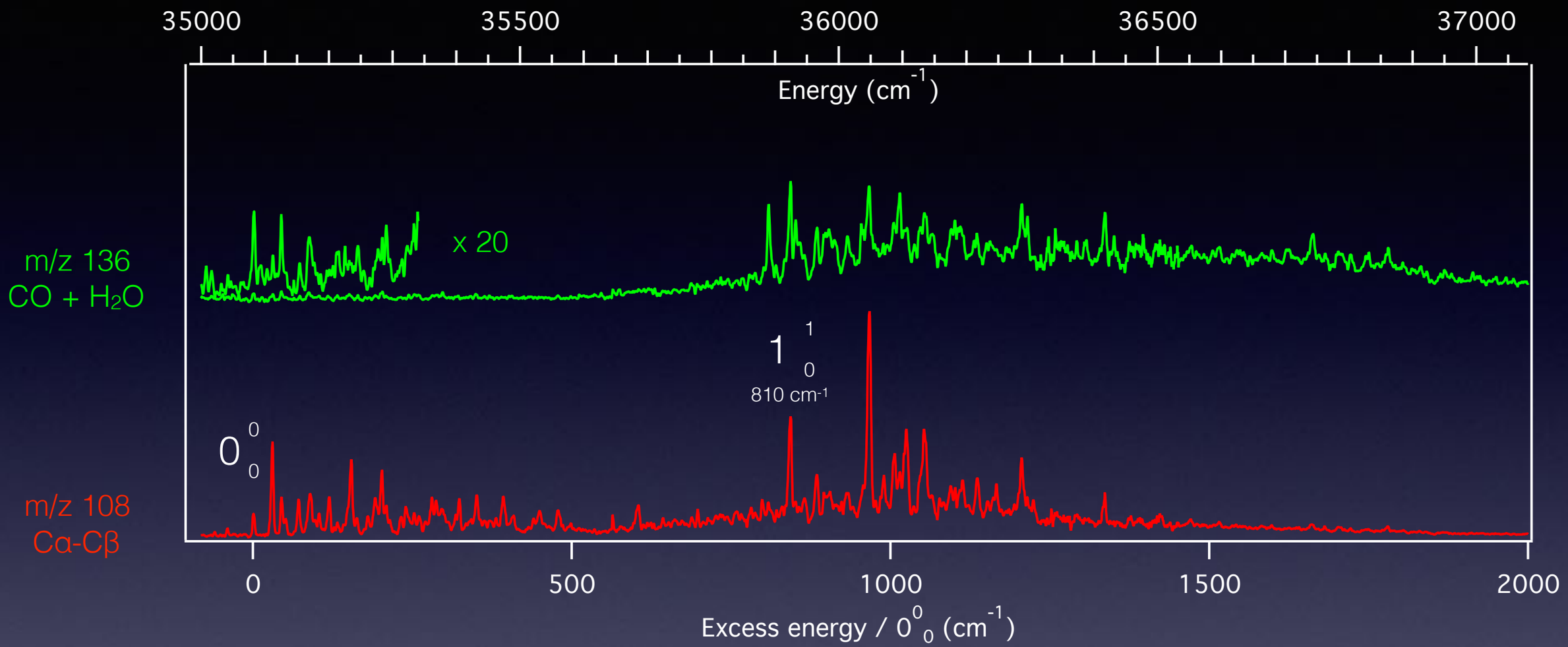


UVPD of Tyrosine(H+)



- ππ* is the bright state
- At the band origin : m/z 108 most intense fragment

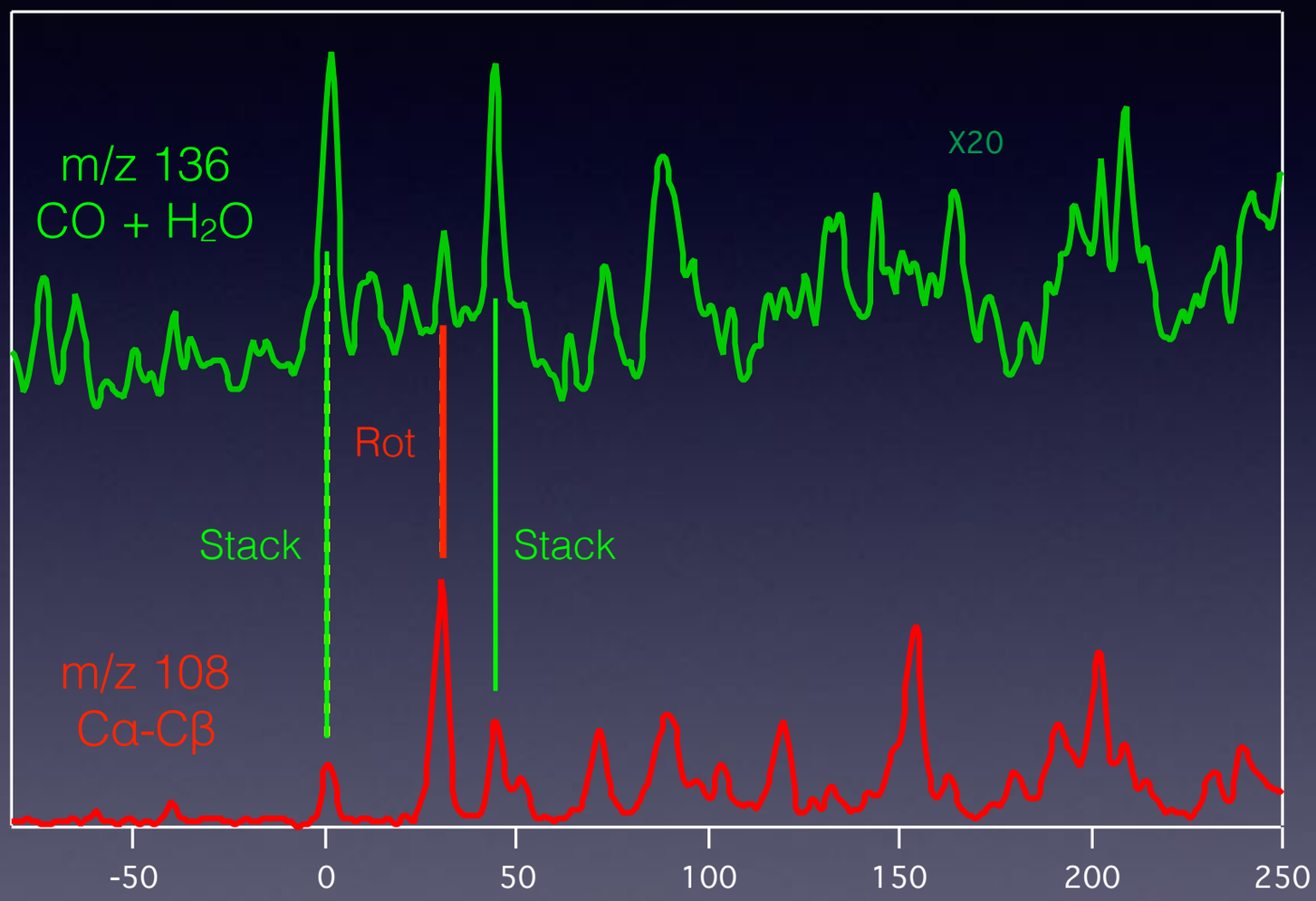
UVPD of Tyrosine(H+)

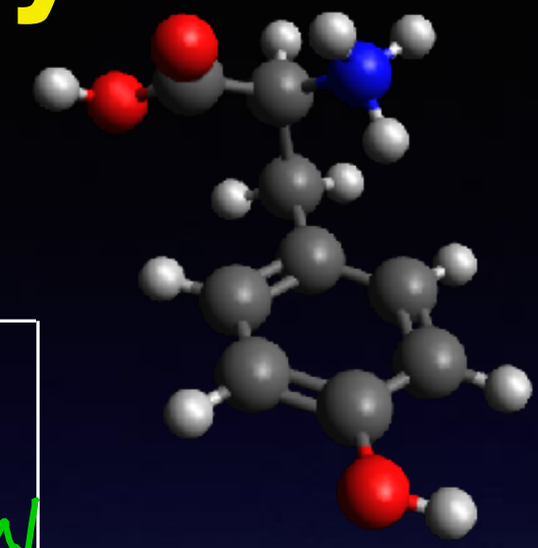


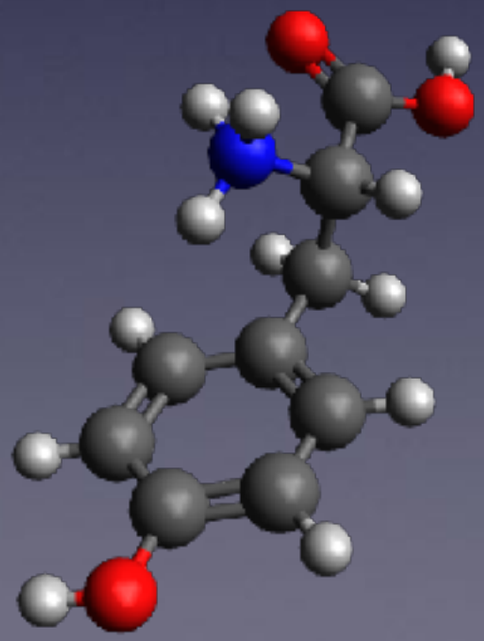
- ππ* is the bright state
- At the band origin : m/z 108 most intense fragment

Conformer selectivity

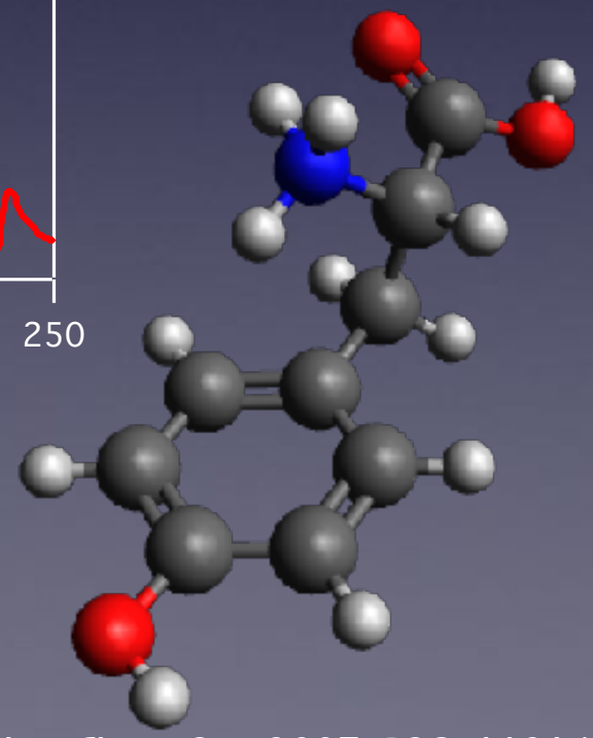
Stack conformers
m/z 136





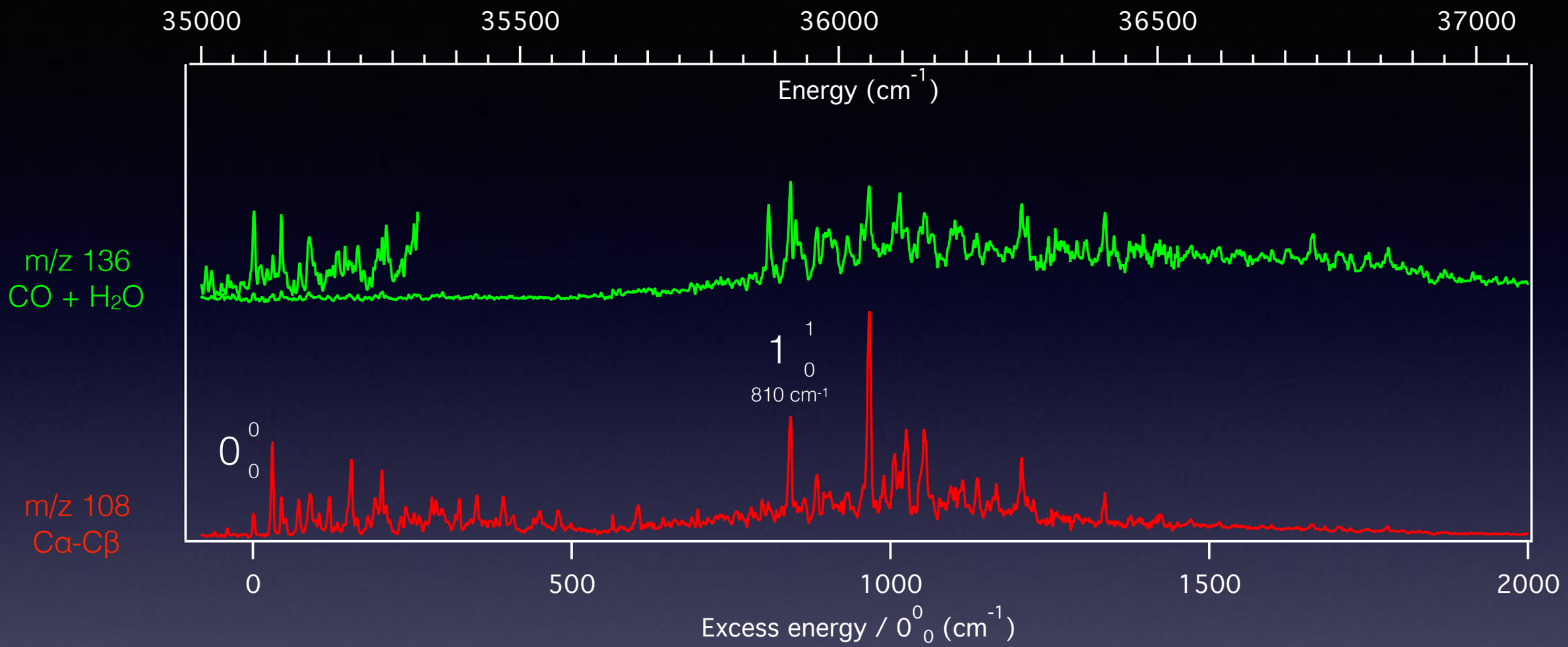


Rot conformers
m/z 108



*Stearns et al., J.Am. Chem. Soc. 2007, **129**, 11814*

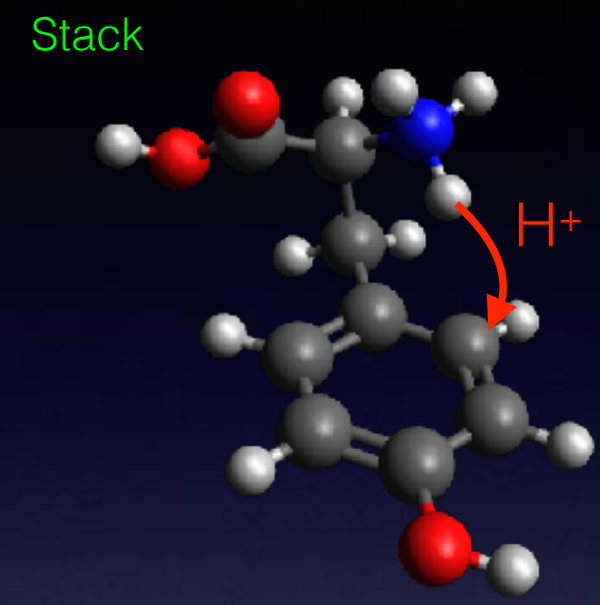
UVPD of Tyrosine(H+)



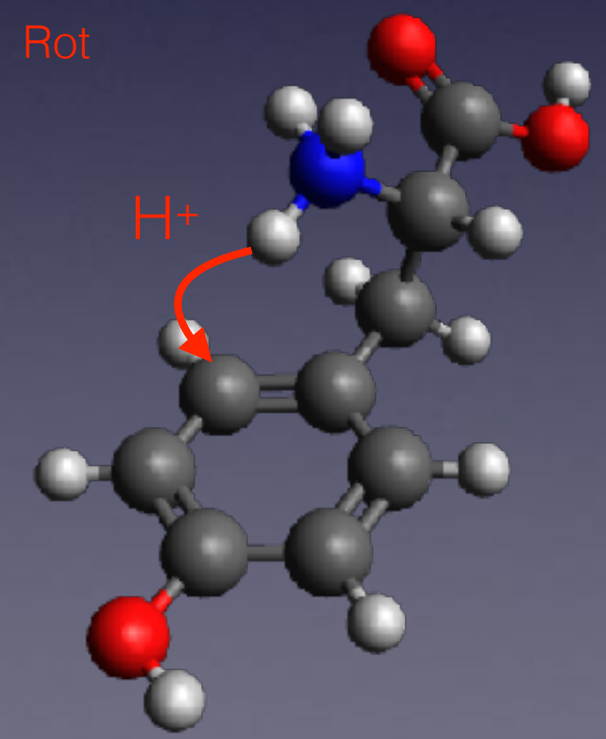
- ππ* transition
- At the band origin : m/z 108 most intense fragment
- Higher in energy : competition

Excited state relaxation processes

- Barrier for H^+ transfer to ring : ~0.2 eV



- $\pi\pi^*$ - $\pi\pi^*_{CO}$ charge transfer :
  - Stack conformers : 0.4 eV
  - Rot conformers : 0.6 eV

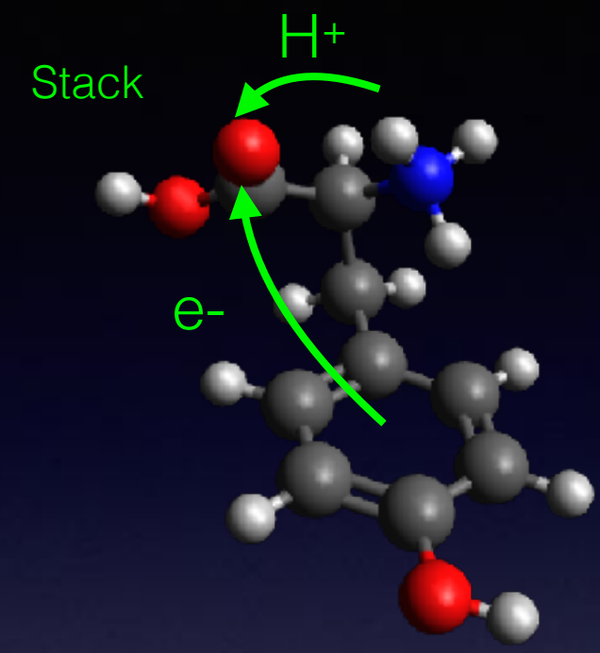


- Conformer selectivity :
  - Stack conformers : CO + H_2O loss
  - Rot conformers : Cα-Cβ rupture

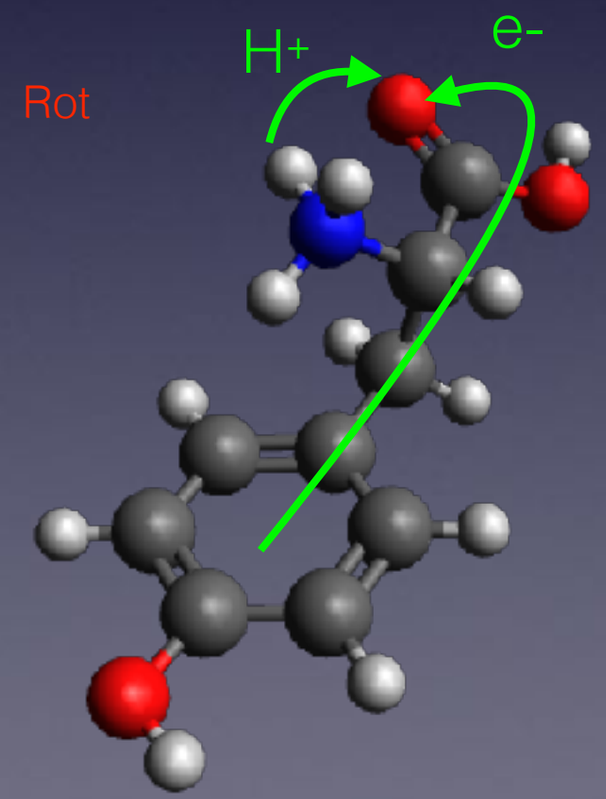
*Féraud et al., J. Phys. Chem. 2015, **119**, 5914*

Excited state relaxation processes

- Barrier for H^+ transfer to ring : ~0.2 eV



- $\pi\pi^*$ - $\pi\pi^*_{CO}$ charge transfer :
  - Stack conformers : 0.4 eV
  - Rot conformers : 0.6 eV

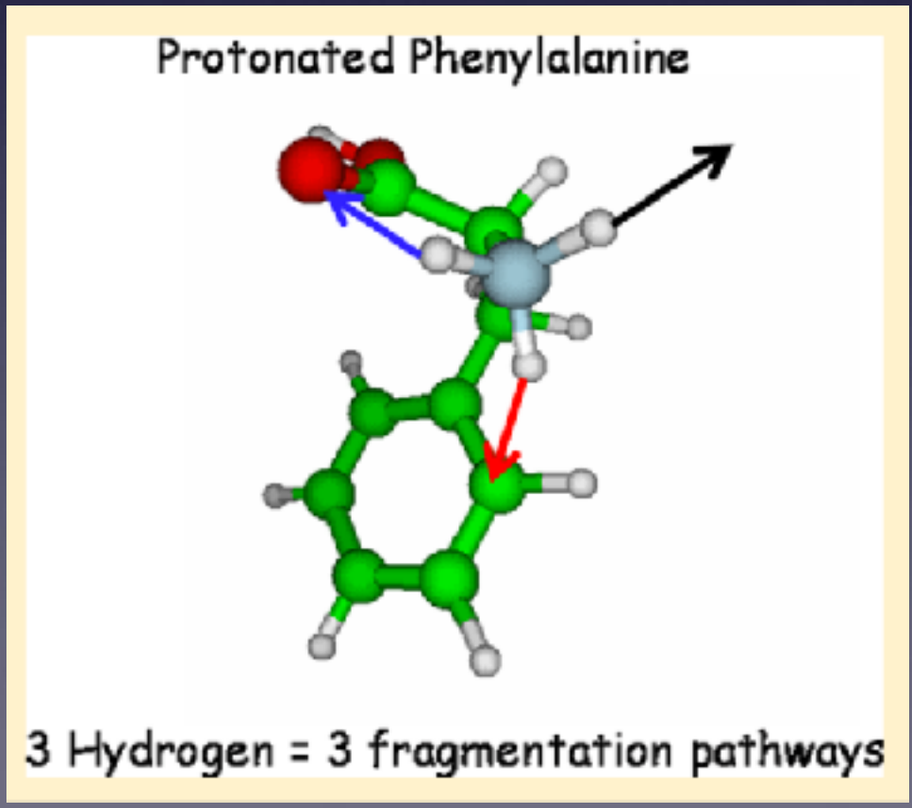


- Conformer selectivity :
  - Stack conformers : CO + H_2O loss
  - Rot conformers : Cα-Cβ rupture

*Féraud et al., J. Phys. Chem. 2015, **119**, 5914*

Conclusions

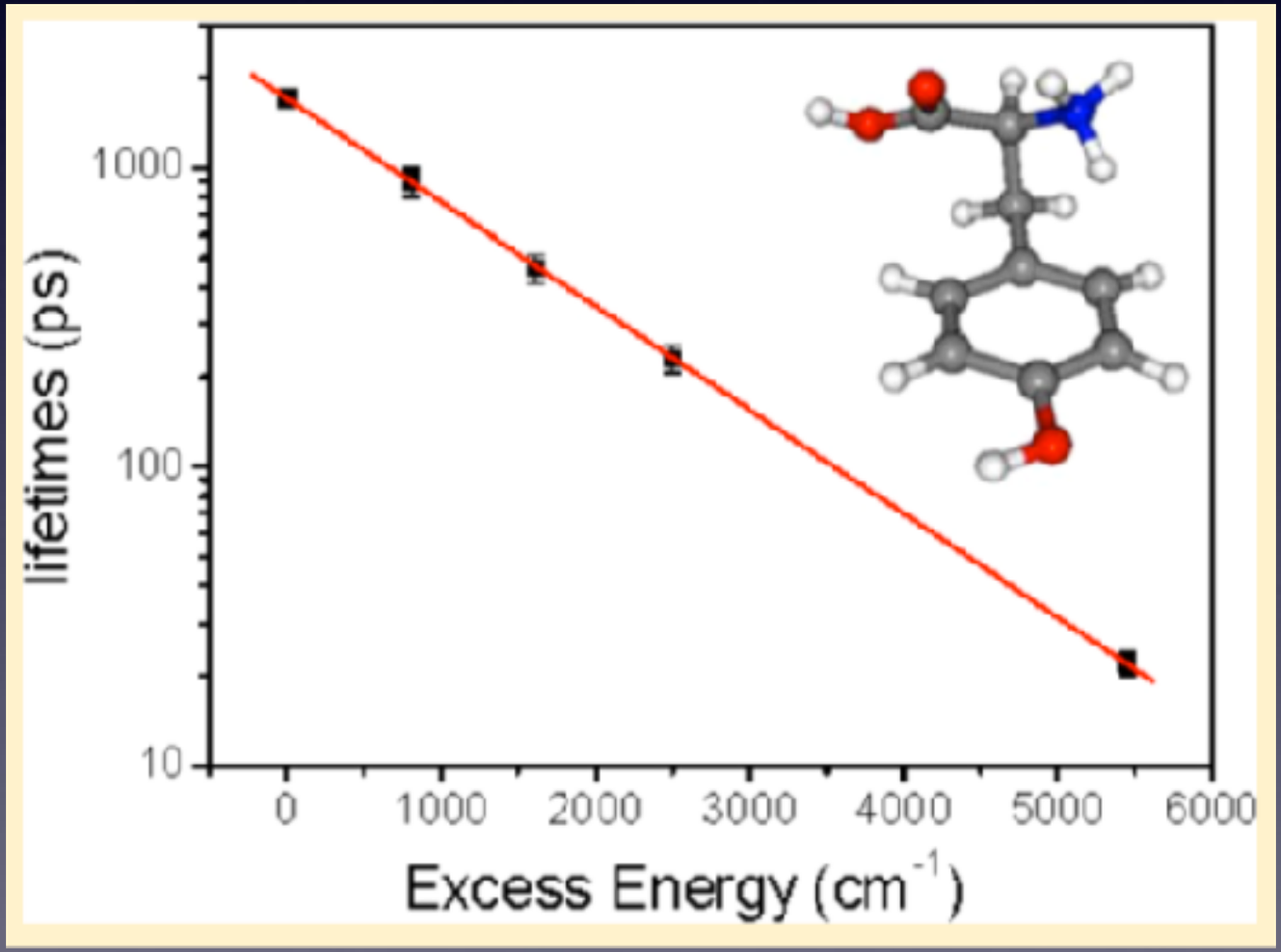
- ππ* state is the locally excited state
- Cα-Cβ bond rupture at the band origin
- Higher in energy : CID-like fragments (e.g. CO + H_2O loss)
- Tyrosine(H^+) : competition / Phenylalanine(H^+) : no competition
- Coupling with higher CT states - conformation selectivity



*Féraud et al., J. Phys. Chem. 2015, **119**, 5914*

Conclusions

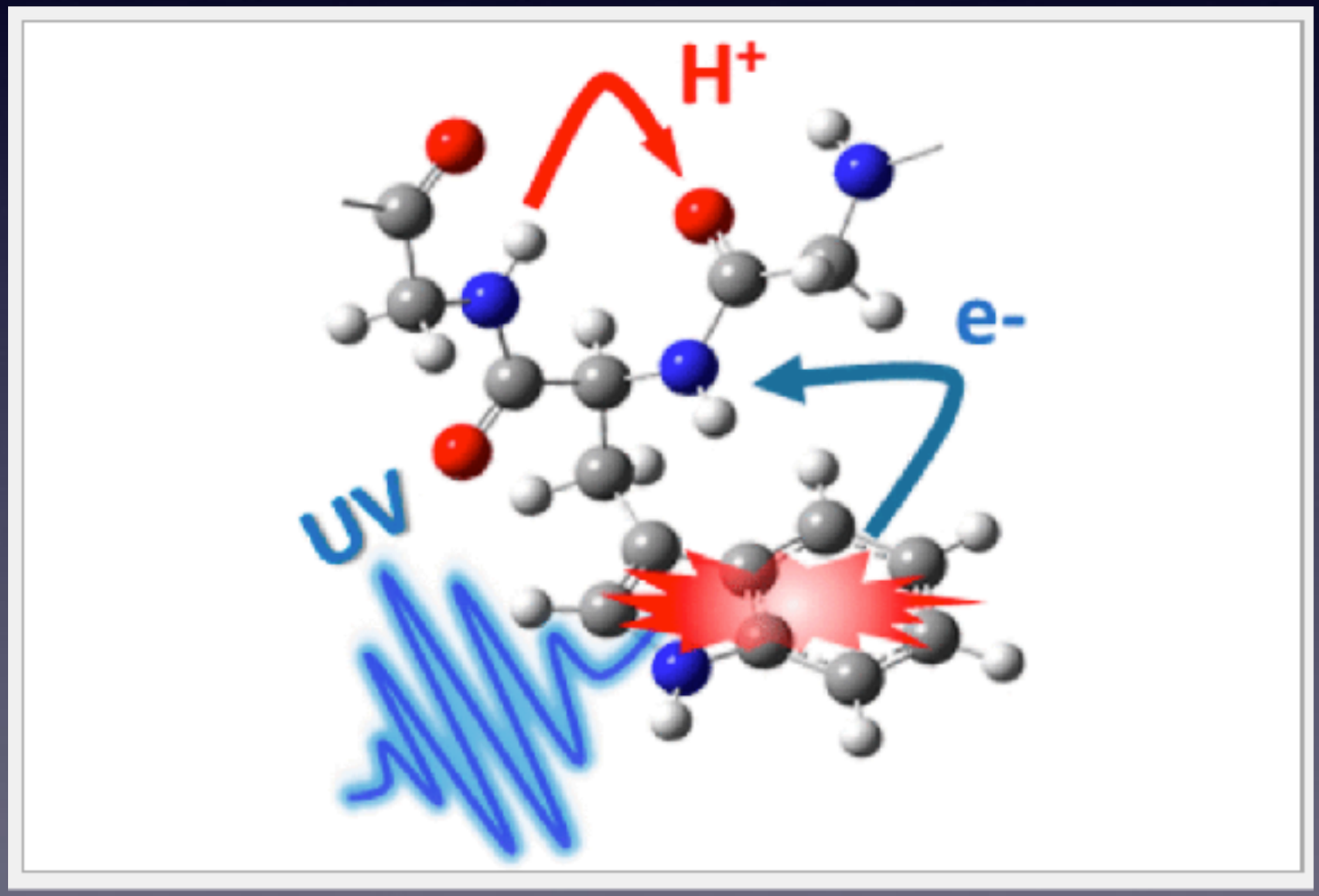
- Conformer- and mode-specific excited state lifetimes of cold protonated tyrosine ions



*Soorkia et al., J. Phys. Chem. Lett. 2014, **5**, 4349*

Conclusions

- UV photo induced dynamics of conformer-resolved aromatic peptides

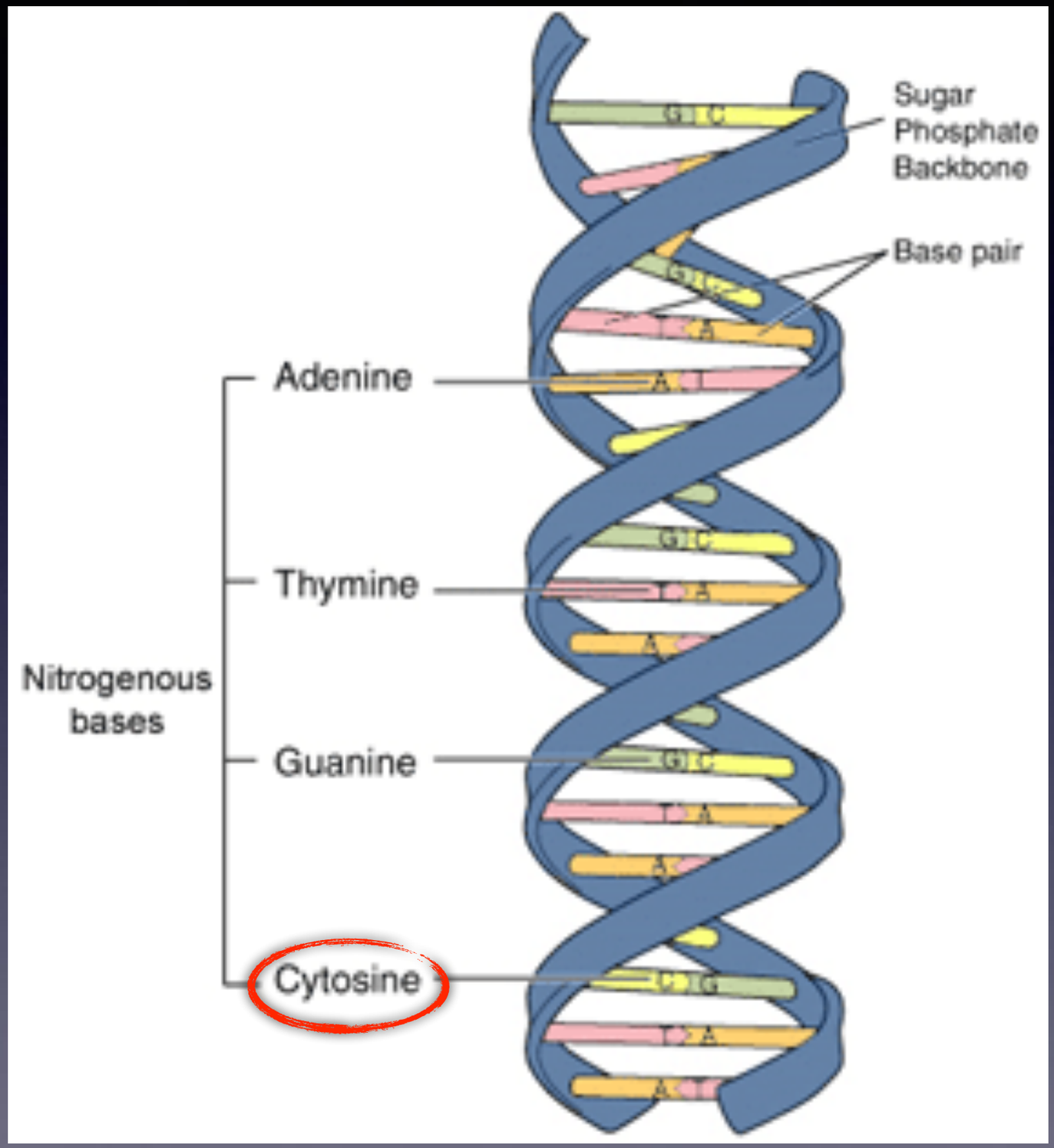


S. Soorkia, C. Jouvet and G. Grégoire, Chem. Rev. 2019 DOI: 10.1021/acs.chemrev.9b00316

Protonated DNA Bases

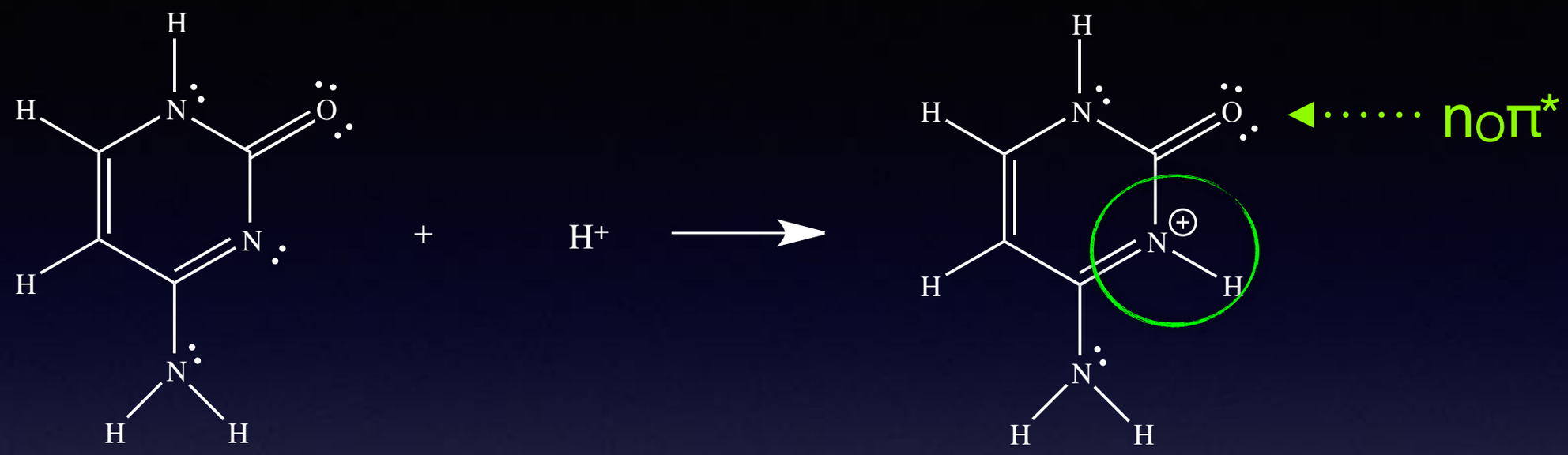
Cytosine(H^+)

DNA/RNA bases

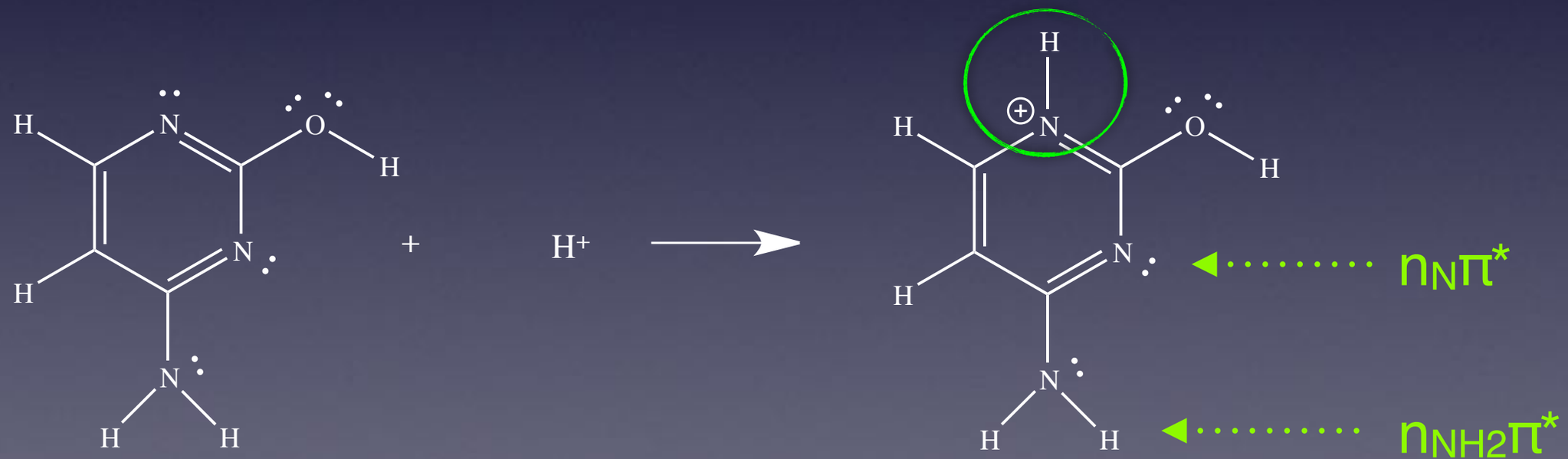


Neutral v/s Protonated

Keto



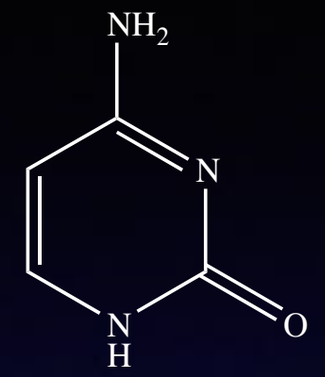
Enol



- Locally excited state is still a $\pi\pi^*$
- Lone pairs : charge transfer states

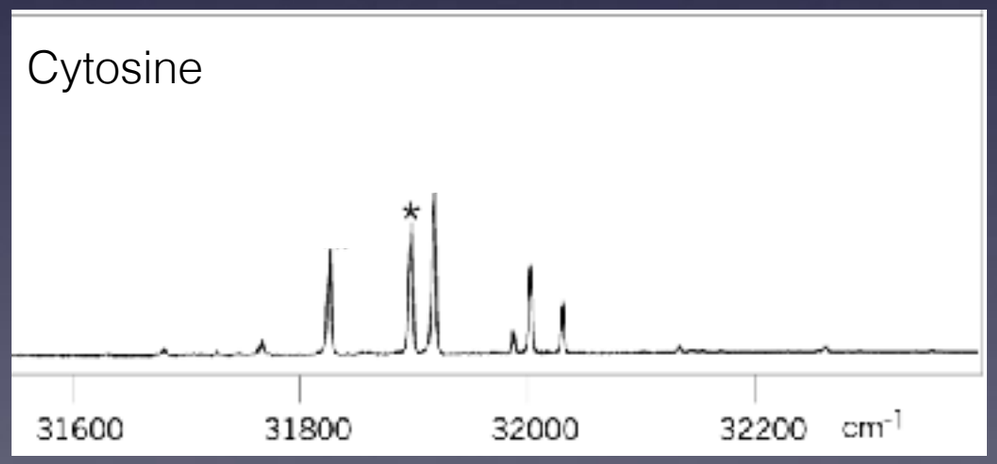
DNA bases : a long-standing story

- Absorption in the UV (230 - 290 nm)
- Gas phase and condensed phase (solution) studies :
  - S. K. Kim, M. de Vries, M. Mons, T. Gustavsson, D. Markovitsi, T. Schultz, S. Leutwyler …
- Paradigm : relaxation of S_1 ($^1\pi\pi^*$) to ground state is ultrafast
  - relaxation without inducing dommage - thermalisation
- Short lifetimes -> Theory / Calculations



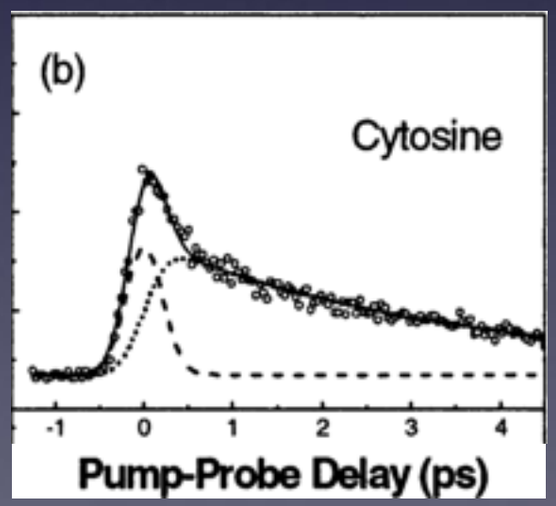
Cytosine

316.5 310.6 nm



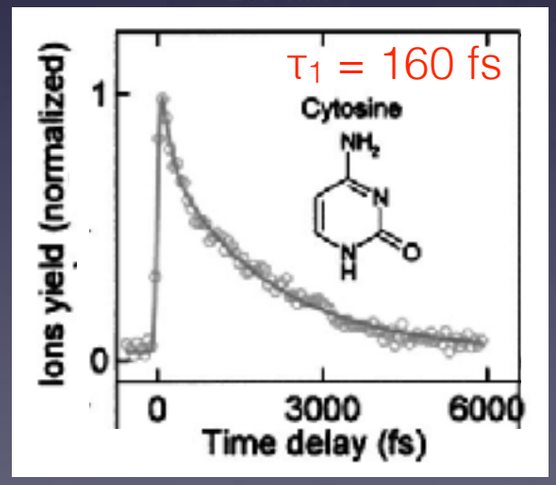
de Vries et al. CPL 2002

267 nm



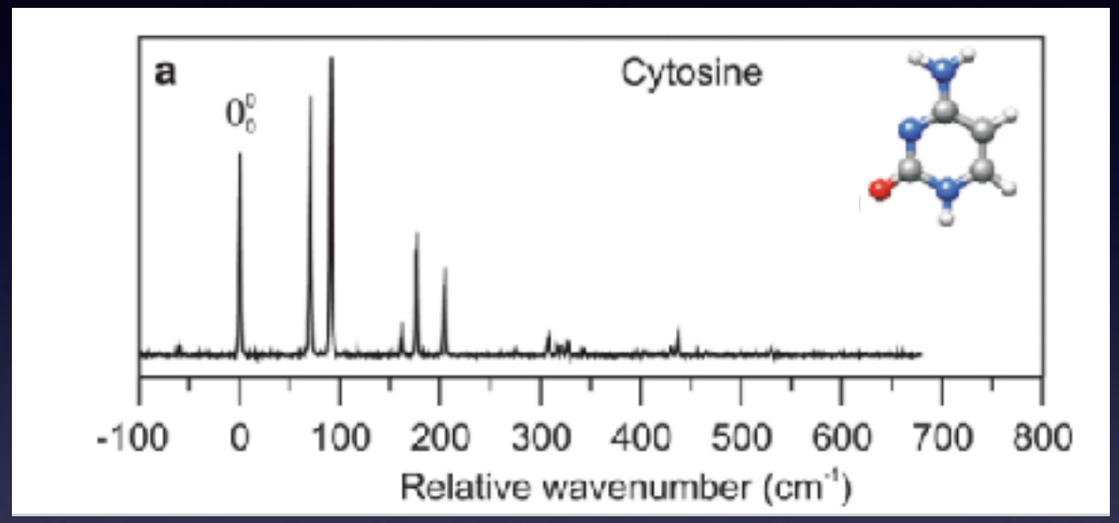
Kim et al. JACS 2002

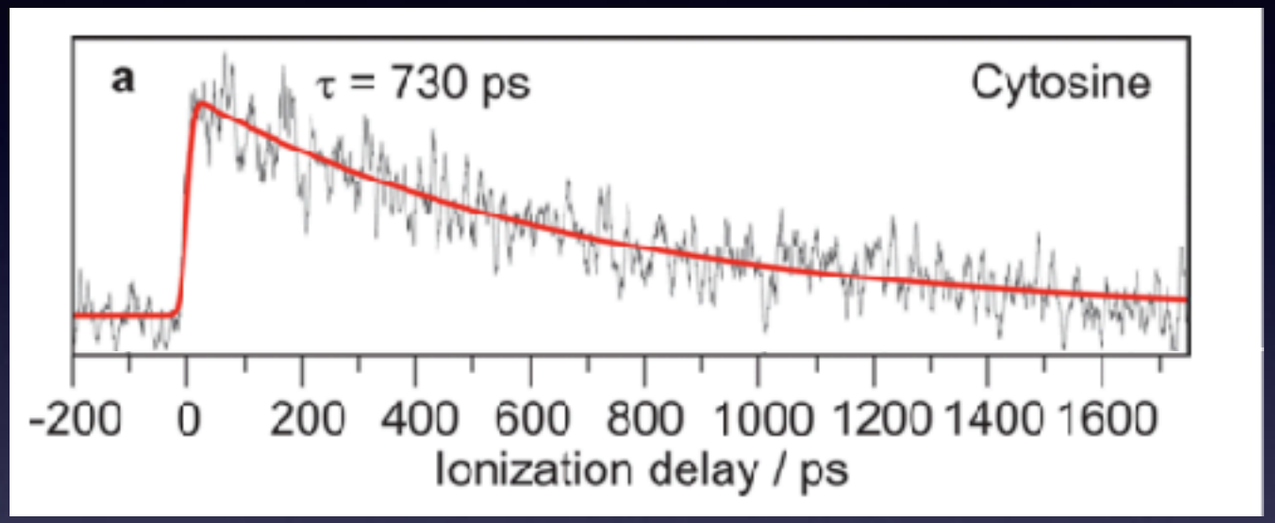
267 nm



Canuel et al. JCP 2005

Neutral Cytosine





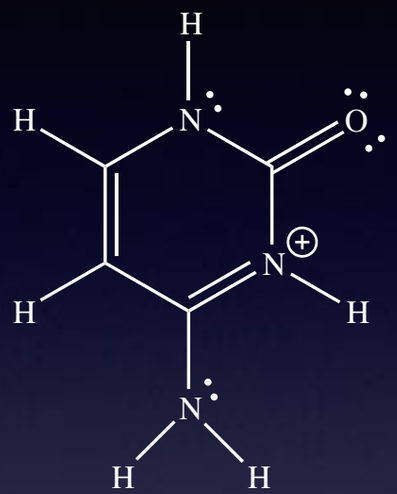
Excited state lifetime of $^1\pi\pi^*$: 730 ps

~700 x longer than time constants extracted from femtosecond experiments

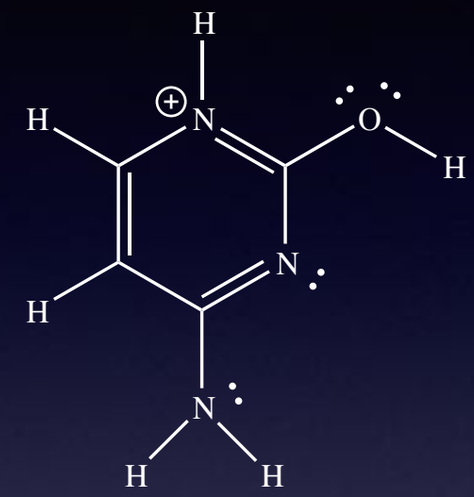
« Gas-phase Cytosine-N1-Derivatives have 0.1 - 1 ns lifetimes near the S1 state minimum »
S. Blaser, M. A. Trachsel, S. Lobsiger, T. Woedmer, H.-M. Frey and S. Leutwyler J. Phys. Chem. Lett., 7, 2016, 752

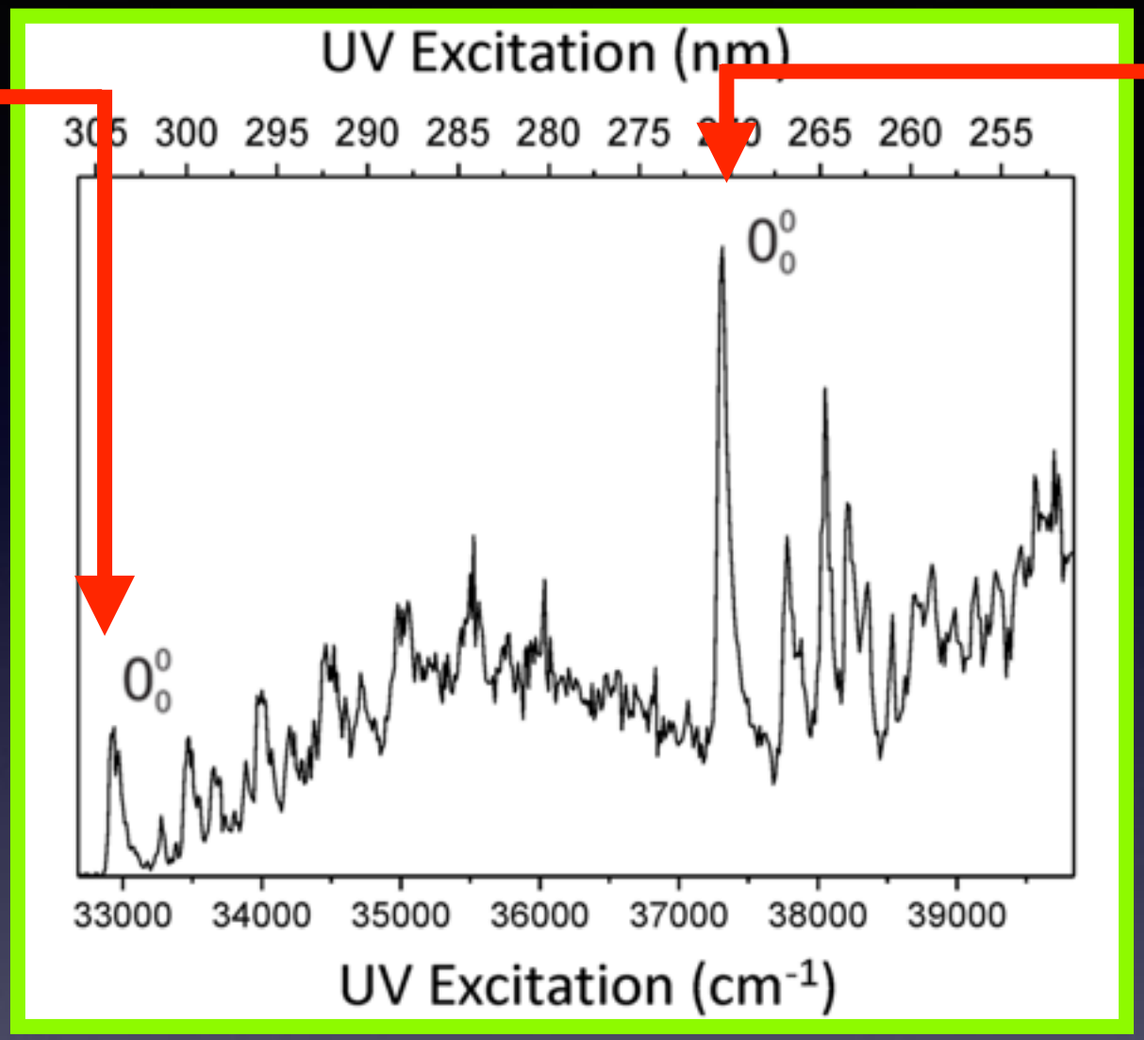
Protonated Cytosine

Keto



Enol



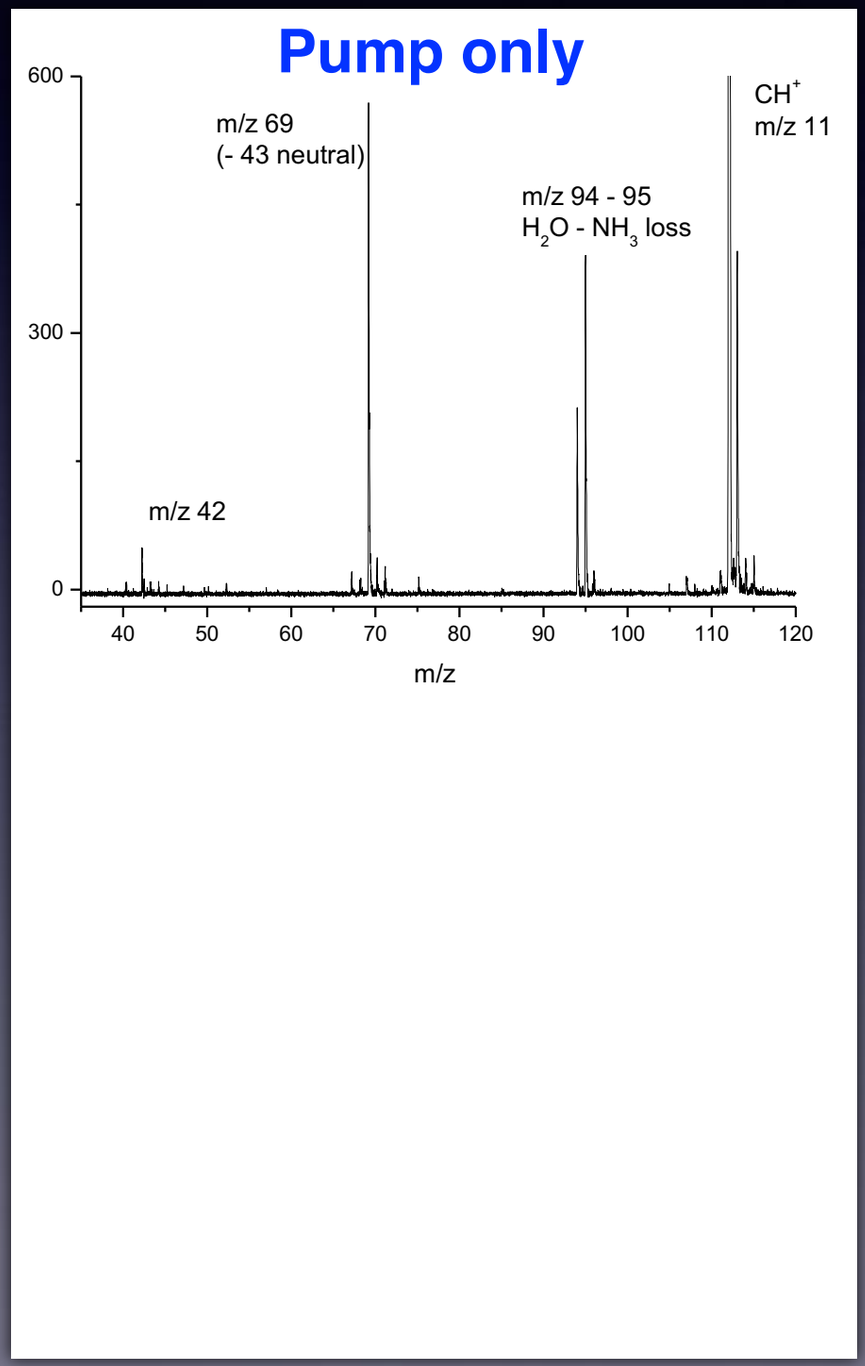


« Non-radiative processes in protonated diazines, pyrimidine bases and an aromatic azine »
Pino et al. Phys. Chem. Chem. Phys., 18, 2016, 20126

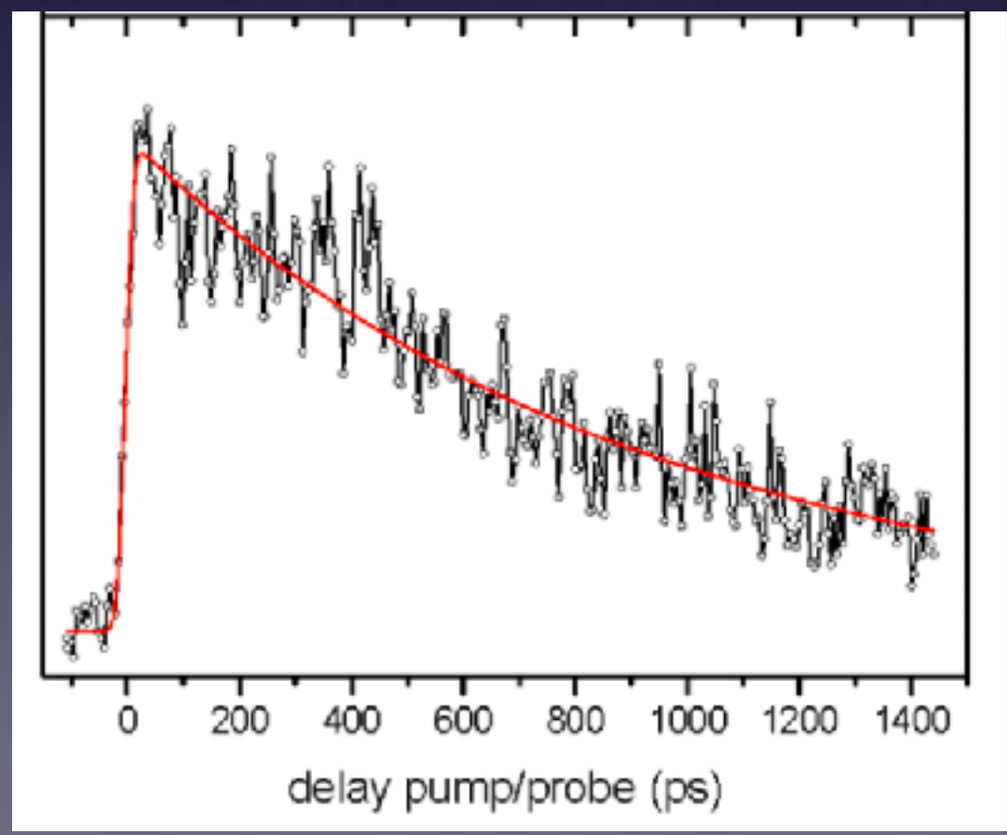
- Locally excited state : $\pi\pi^*$
- Peak broadening :
  - Short lifetimes : 130 (keto) et 100 (enol) fs

Principle of pump-probe experiment on a photofragmentation signal

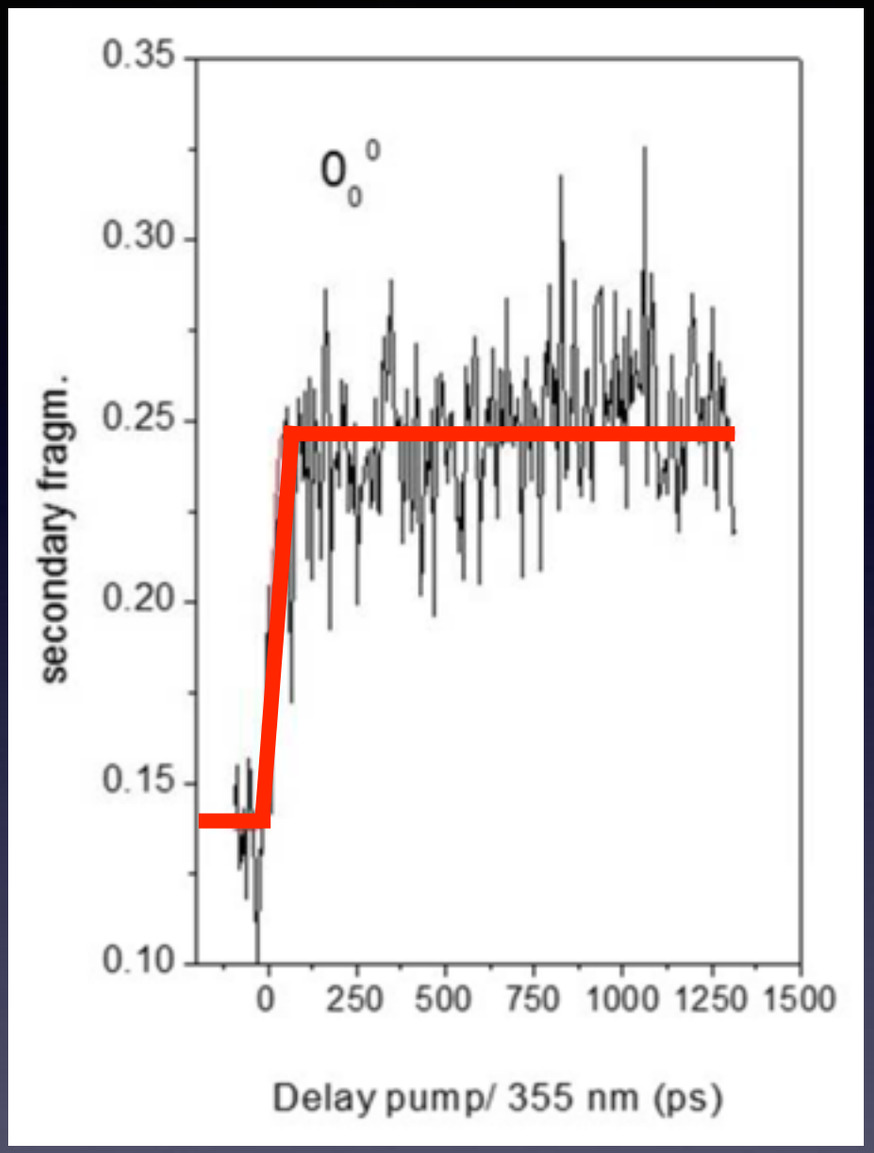
- Pump laser on one vibronic transition -> fragments
- Probe laser (@ 355 nm)
  - not absorbed by parent ions and fragments



- Fragmentation yield as a function of the delay between pump and probe pulses



Enol (pump-probe on ps timescale)

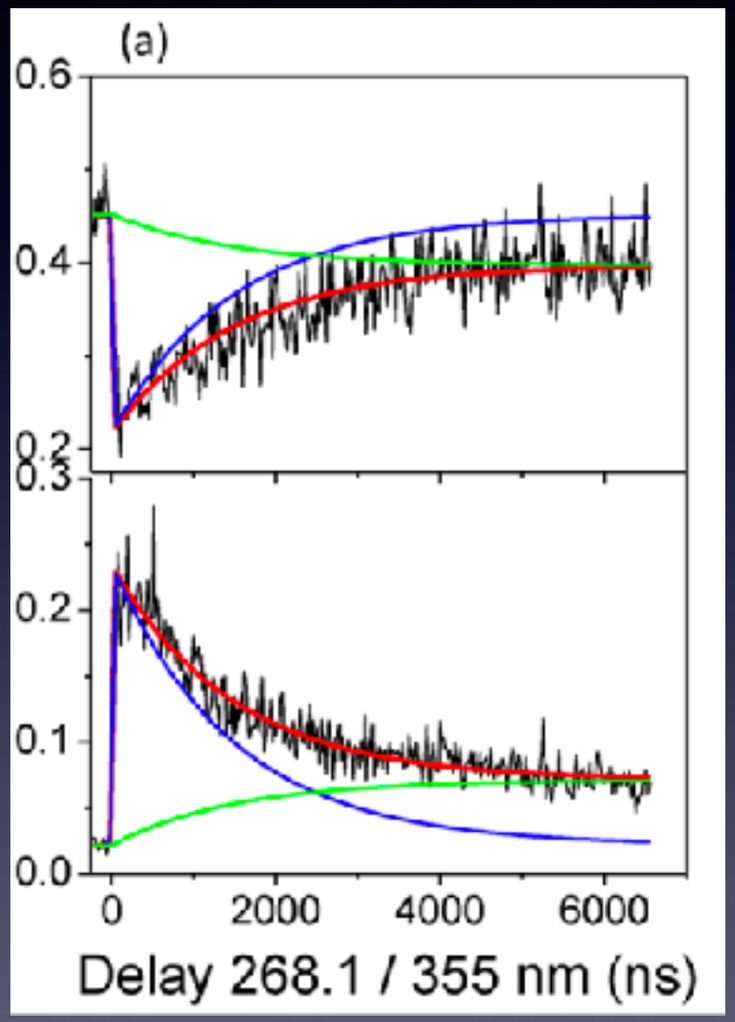


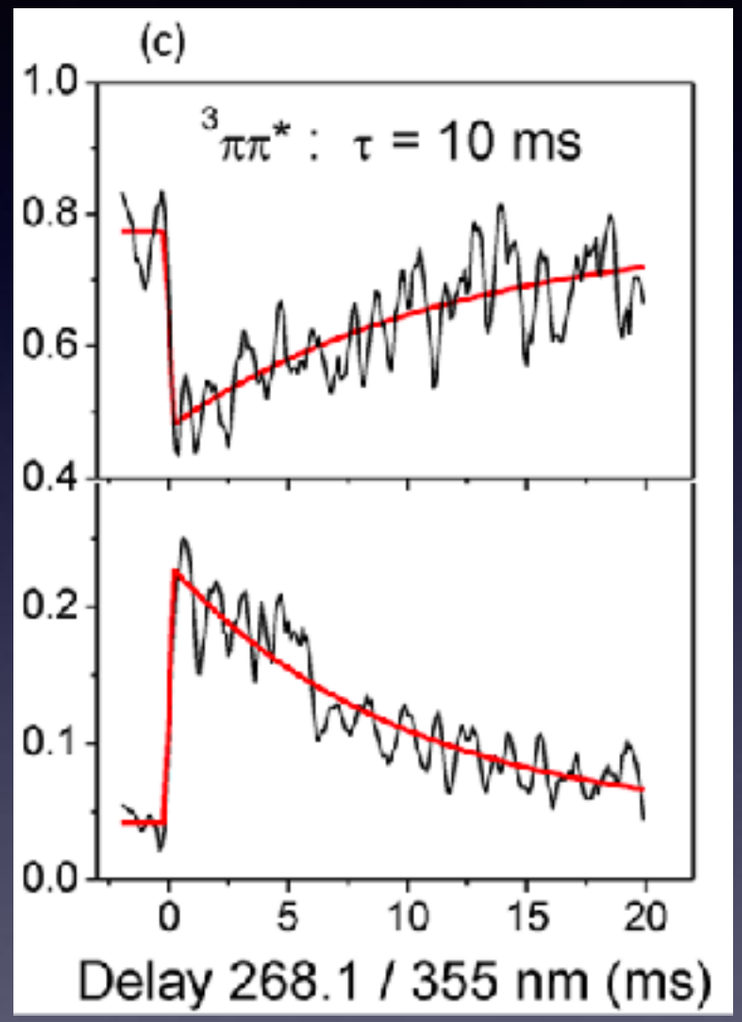
- Time constant that cannot be measured on 1.5 ns timescale
- … not the lifetime of the locally excited state (c.f ~100 fs)

What are we measuring ?

Enol (longer timescale …)

- 2 colour signal over ten orders of magnitude



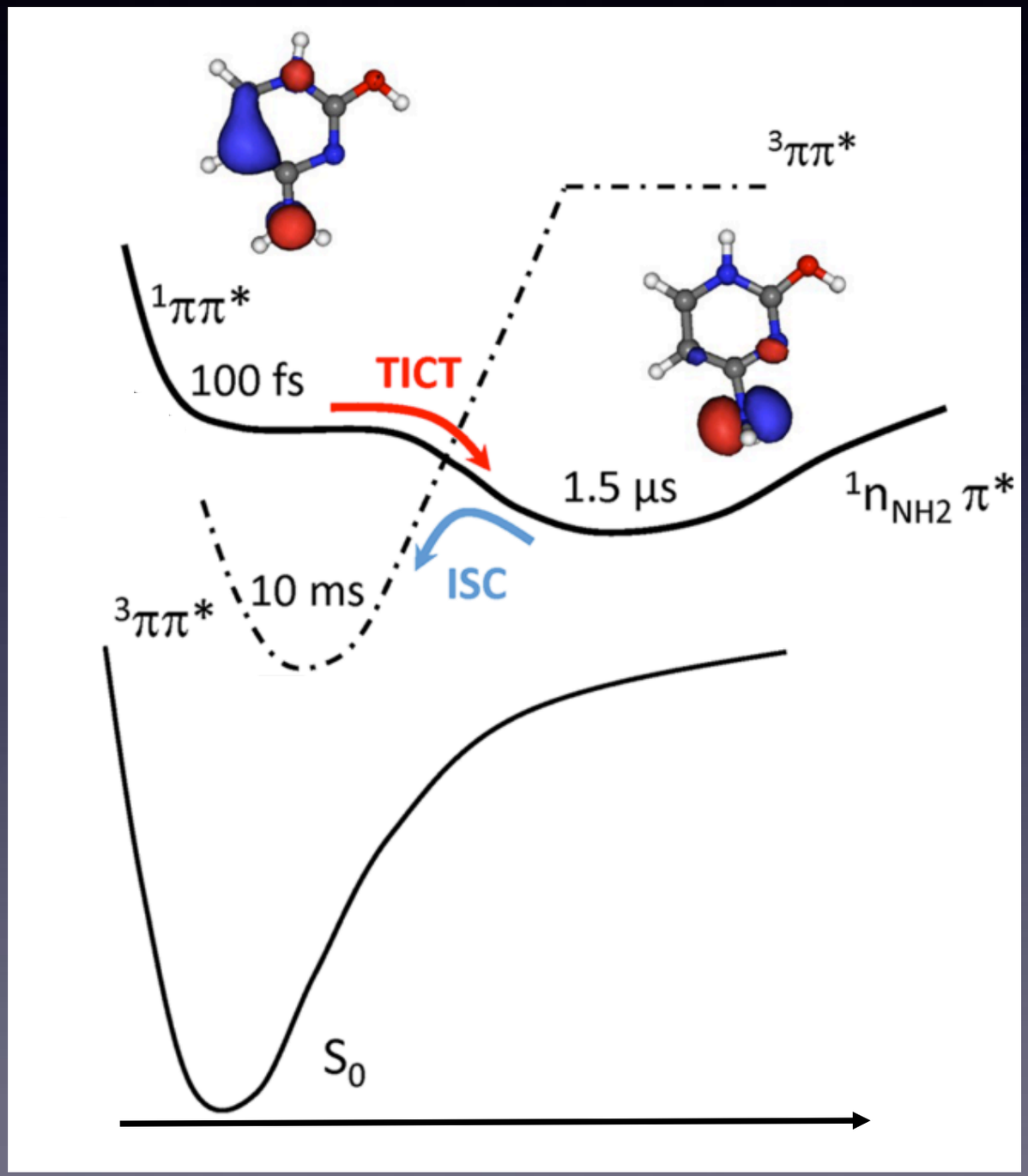


$$S(t) = A_0 + A_1 \times \exp^{-(t-t_0)/\tau} + A_2 \times (1 - \exp^{-(t-t_0)/\tau})$$

Schematic representation of the PES

- CC2/aug-cc-pVDZ calculations
  - Relative energies of the states involved in the dynamics

Enol

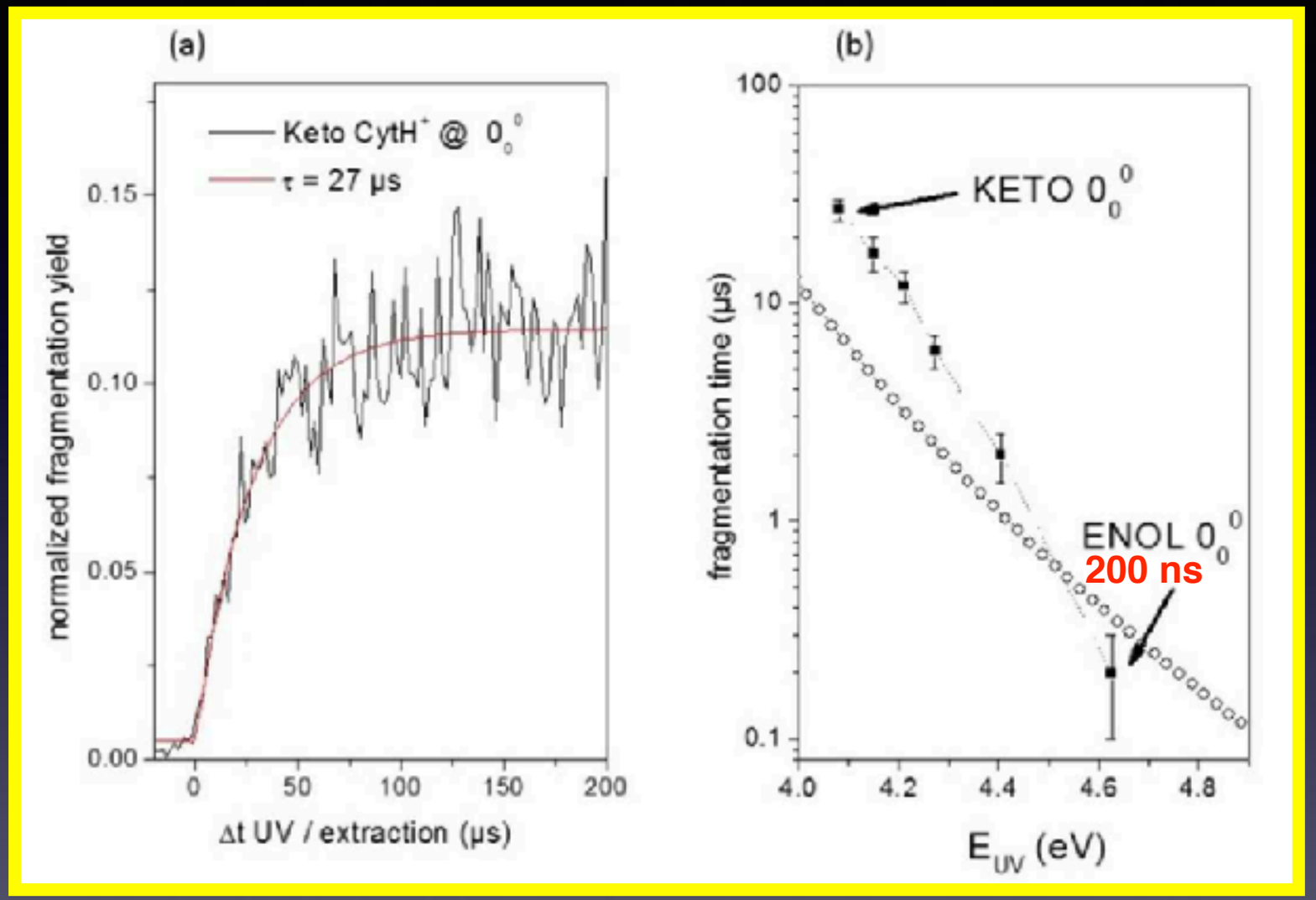


Excited states dynamics

Information on exit channels ?

TICT : Twist Intramolecular Charge Transfer

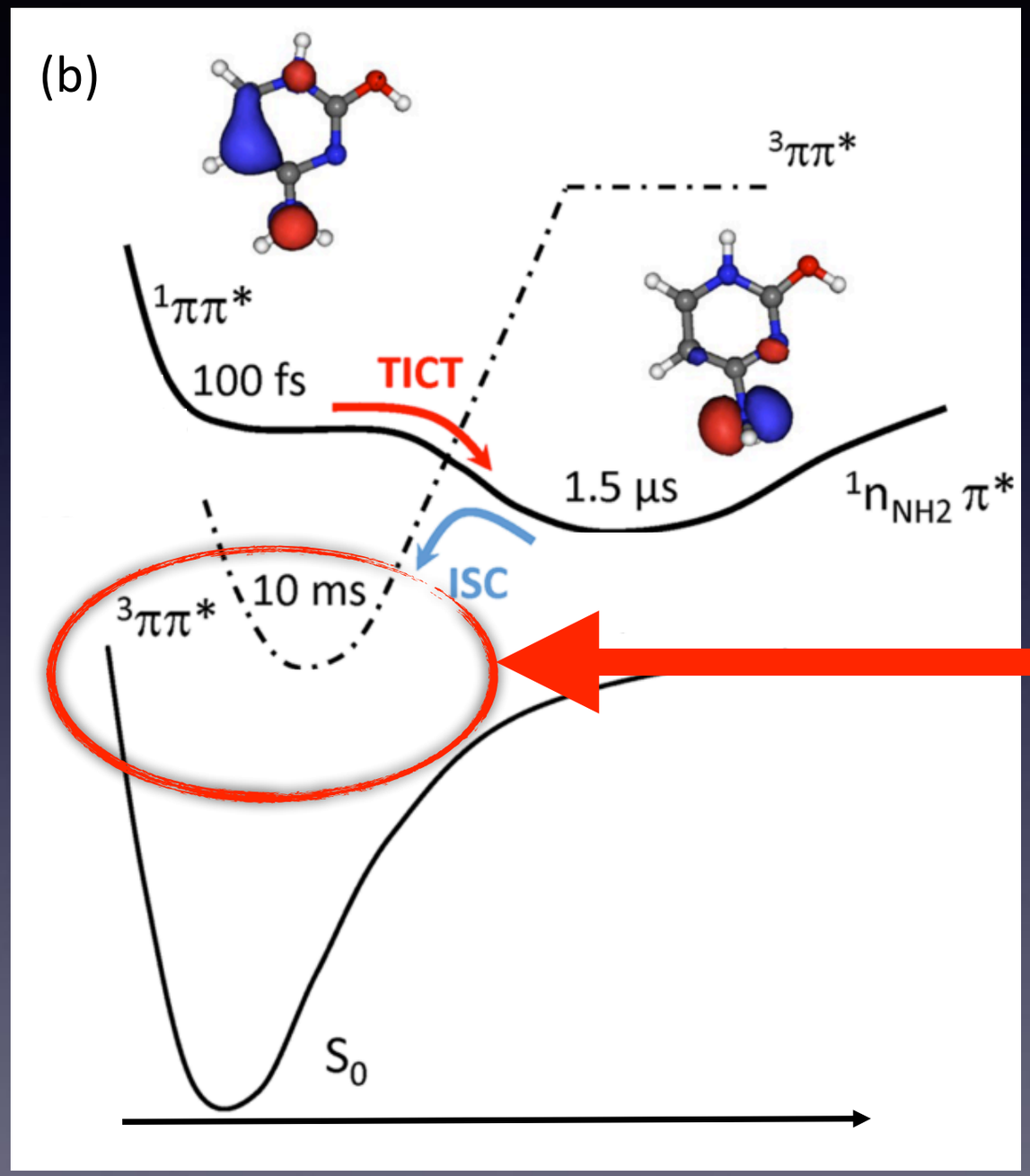
Fragmentation kinetics



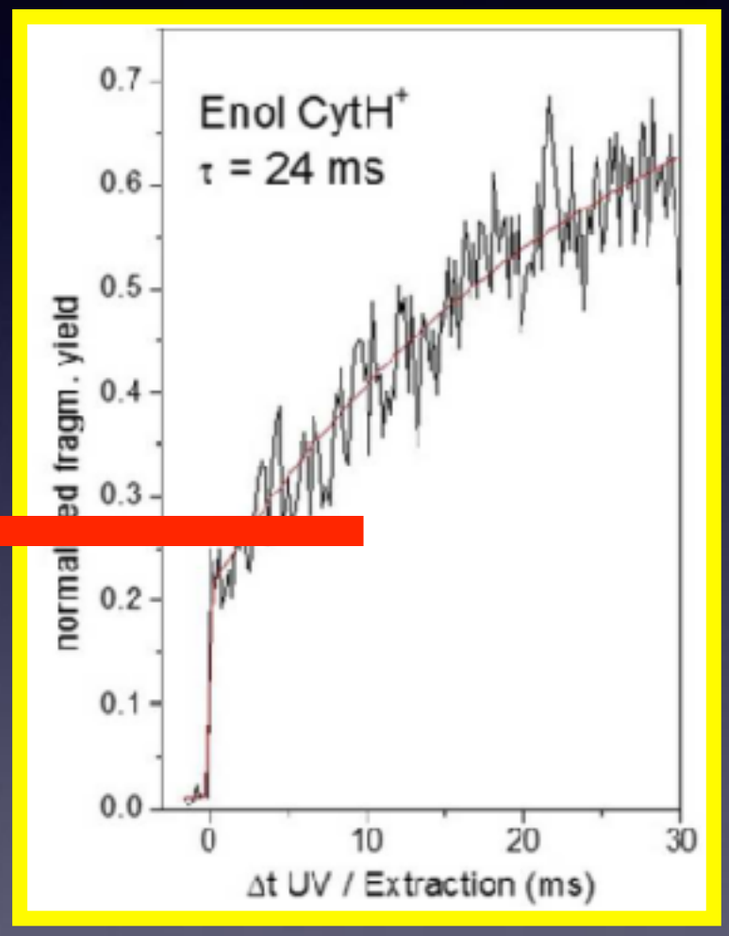
- Same kinetics for all fragments
- Same fragments as in CID
- RRKM calculation → statistical fragmentation in S_0 after Internal Conversion

… back to the ground state

Enol



- Internal Conversion

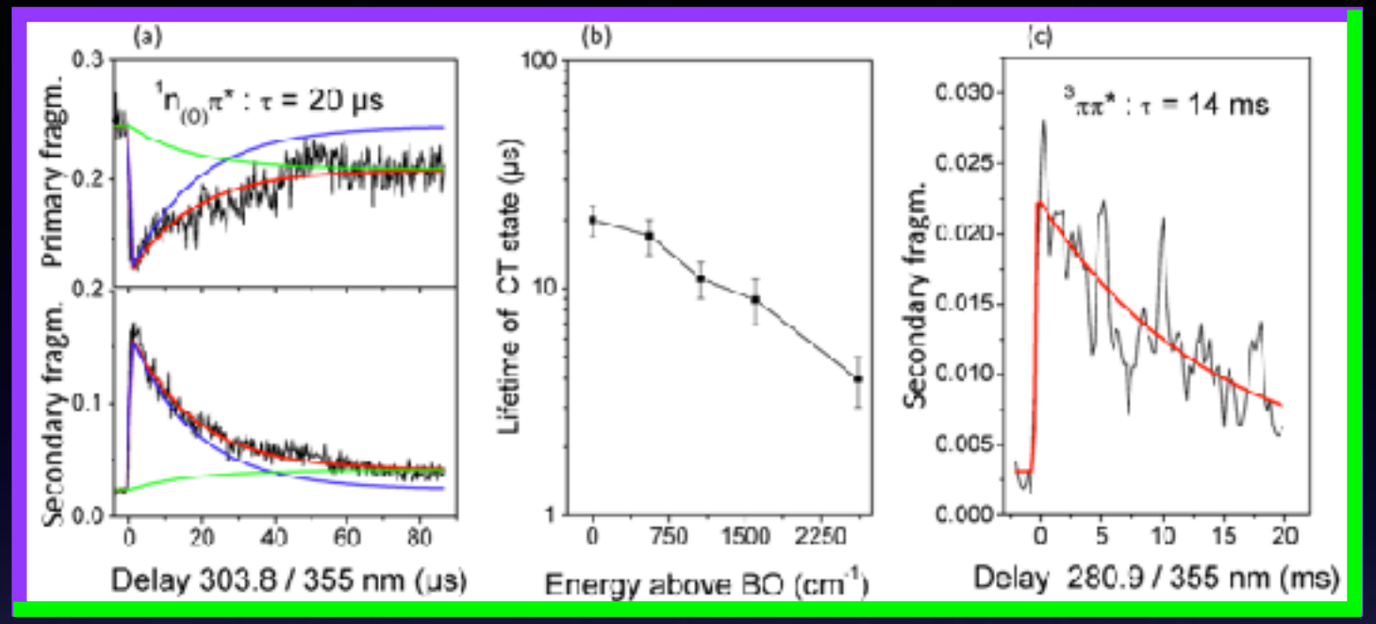


- Intersystem crossing

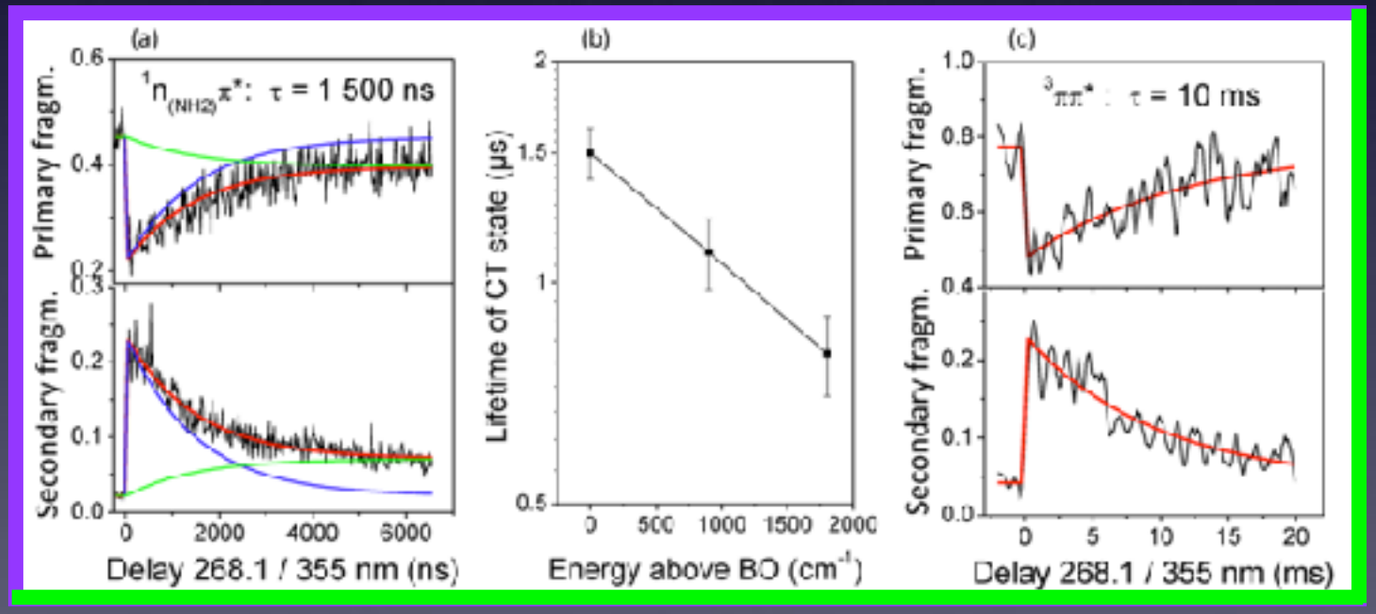
- **> 50% population leading to fragmentation passes through $^3\pi\pi^*$!**

Summary of multi scale dynamics

Keto



Enol



- ππ* decays (in the sub picosecond time scale) to a …
- Second excited state (keto 20 - 4 μs; enol 1.5 to 0.8 μs) - CT states
- Long-lived component (~10 ms) - T state following ISC

THANK YOU ...