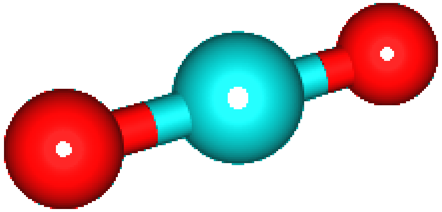
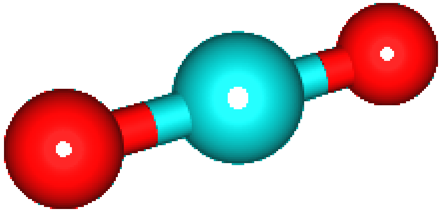


anti-sym



sym

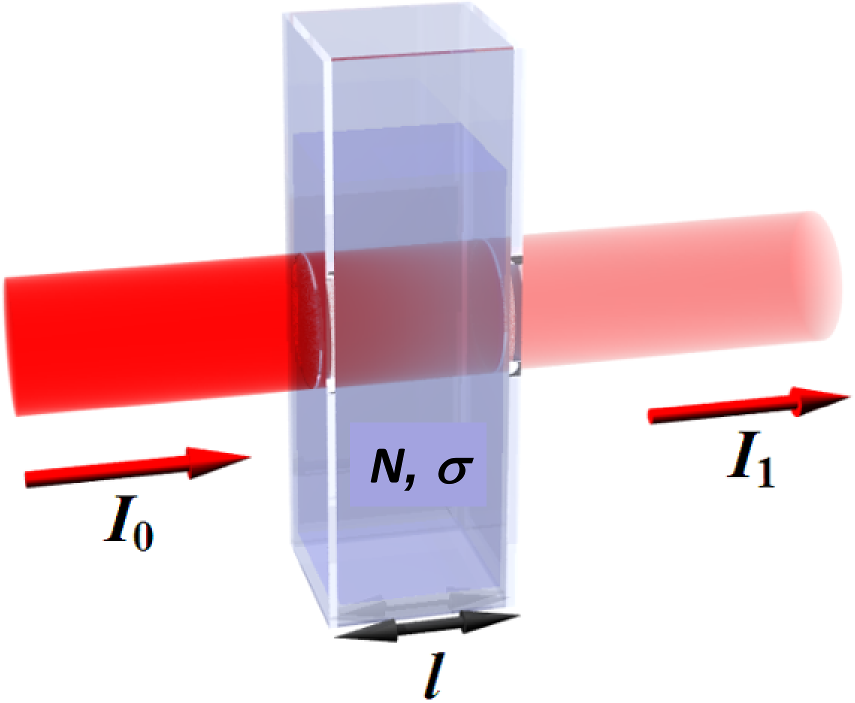
$\omega > \omega$

Combining IR spectroscopy with mass spectrometry

IR spectroscopy of extremely low-density samples
→ *Action spectroscopy in the IR*

- IR spectroscopy in molecular beams (lecture 1)
- IR spectroscopy of molecular ions (this lecture)
  - Combine IR spectroscopy with MS
  - <u>IR spectroscopy with the sensitivity of MS</u>
  - Analytical applications
  - Cryogenic ion spectroscopy
  - Dealing with conformational heterogeneity

Infrared spectroscopy



Typical values:

$$\sigma(\lambda)\, l\, N \sim 0.1 - 1$$

$\sigma \sim 10^{-20}\ \mathrm{cm}^2$

$l \sim 10\ \mathrm{cm}$

$\rightarrow N \sim 10^{19}$

$$T(\lambda) = I1 / I0 = e^{-\sigma(\lambda)\, l\, N}$$

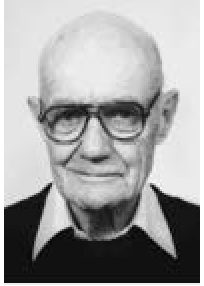
Lambert-Beer law

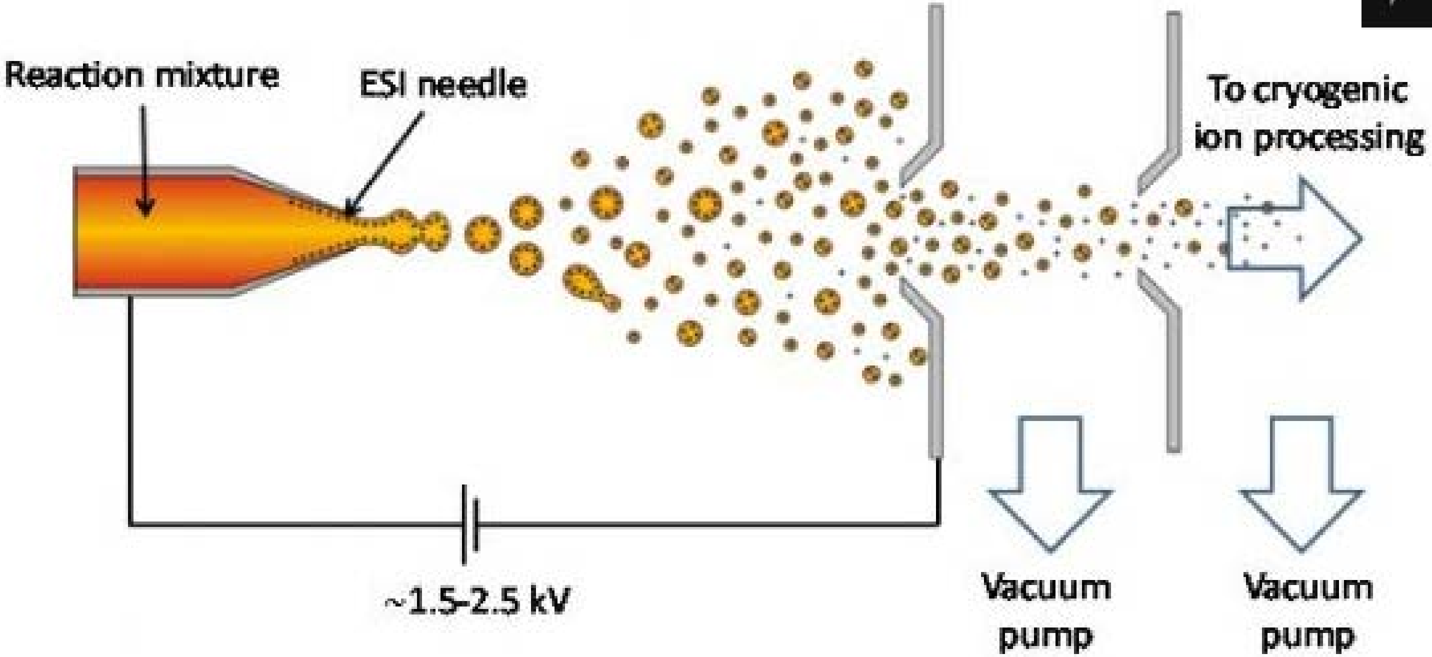
Tandem mass spectrometry

ion source → mass selection → ion chemistry → mass analysis → ion detector

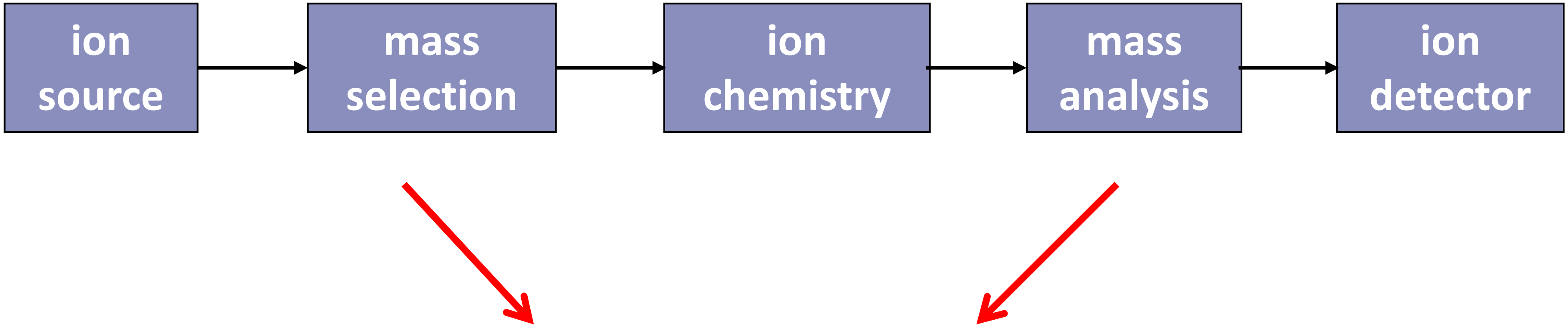
Electrospray Ionization (ESI)

John Fenn (NP Chemistry 2002)





Tandem mass spectrometry



ion source

mass selection

ion chemistry

mass analysis

ion detector

Electric fields

- Time of flight (TOF-MS)
- Quadrupole Mass Analyzer (QMS)
- Quadrupole ion traps

Magnetic fields

- Magnetic sector instruments
- Fourier Transform Ion Cyclotron Resonance (FTICR-MS)

Tandem mass spectrometry


ion source → mass selection → ion chemistry → mass analysis → ion detector

Ion chemistry:

- dissociation
  - collision induced (CID, CAD)
  - electron induced (ECD, ETD, EDD)
  - photon induced (IRMPD, BIRD, UVPD)
- ion-molecule reaction
  - hydrogen/deuterium exchange (HDX)
  - ligand exchange
  - H^+ transfer reaction
  - others
- ion-ion reaction (ETD, PTR)

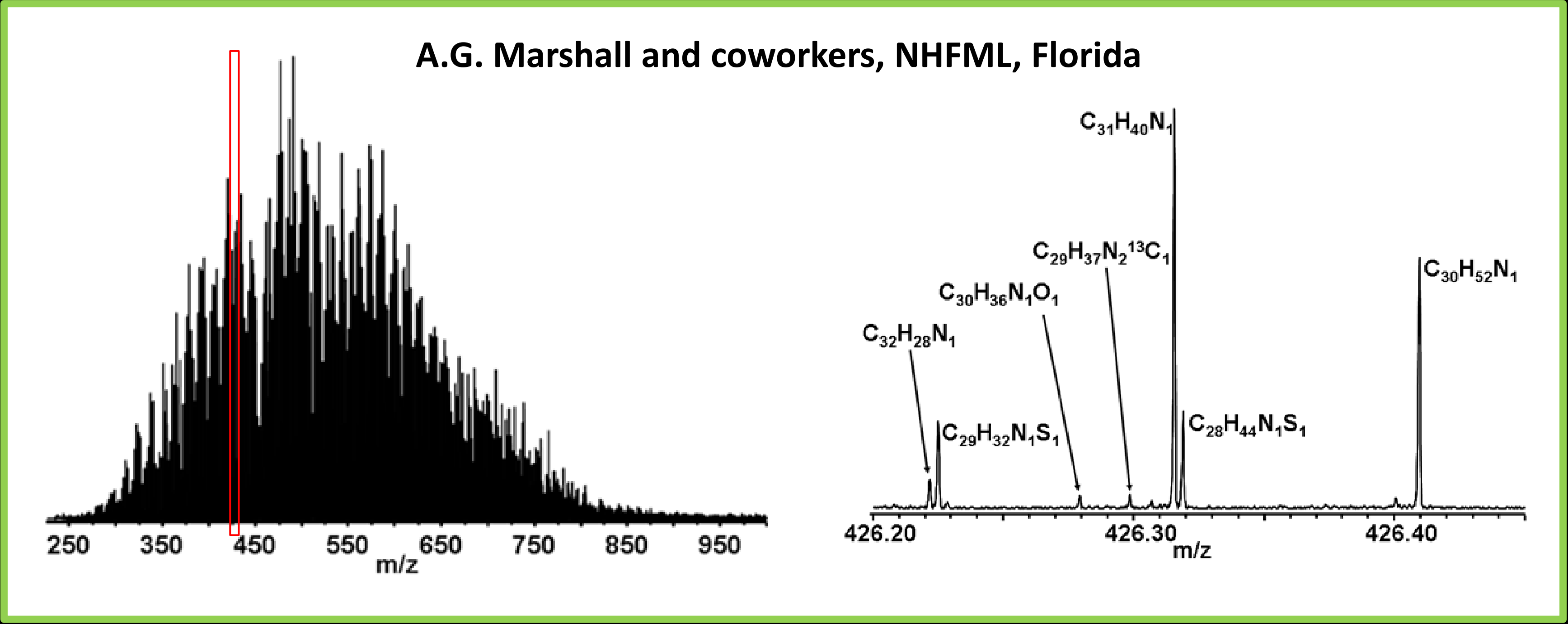
ion storage devices

Tandem mass spectrometry (MS^2, MS^n): in space, in time

Mass spectrometry as analytical tool

- metabolites
- environmental
- food analysis
- petreolomics
- illicit drug testing
- proteomics
- glycomics

- high sensitivity
- extremely high resolution



A.G. Marshall and coworkers, NHFML, Florida

molecular weight → molecular formula → molecular structure ?

The large diversity of organic molecules

$C_{16}H_{10}N2O2$

MW = 262.074

Search molecular formula

(= exact mass)

↓

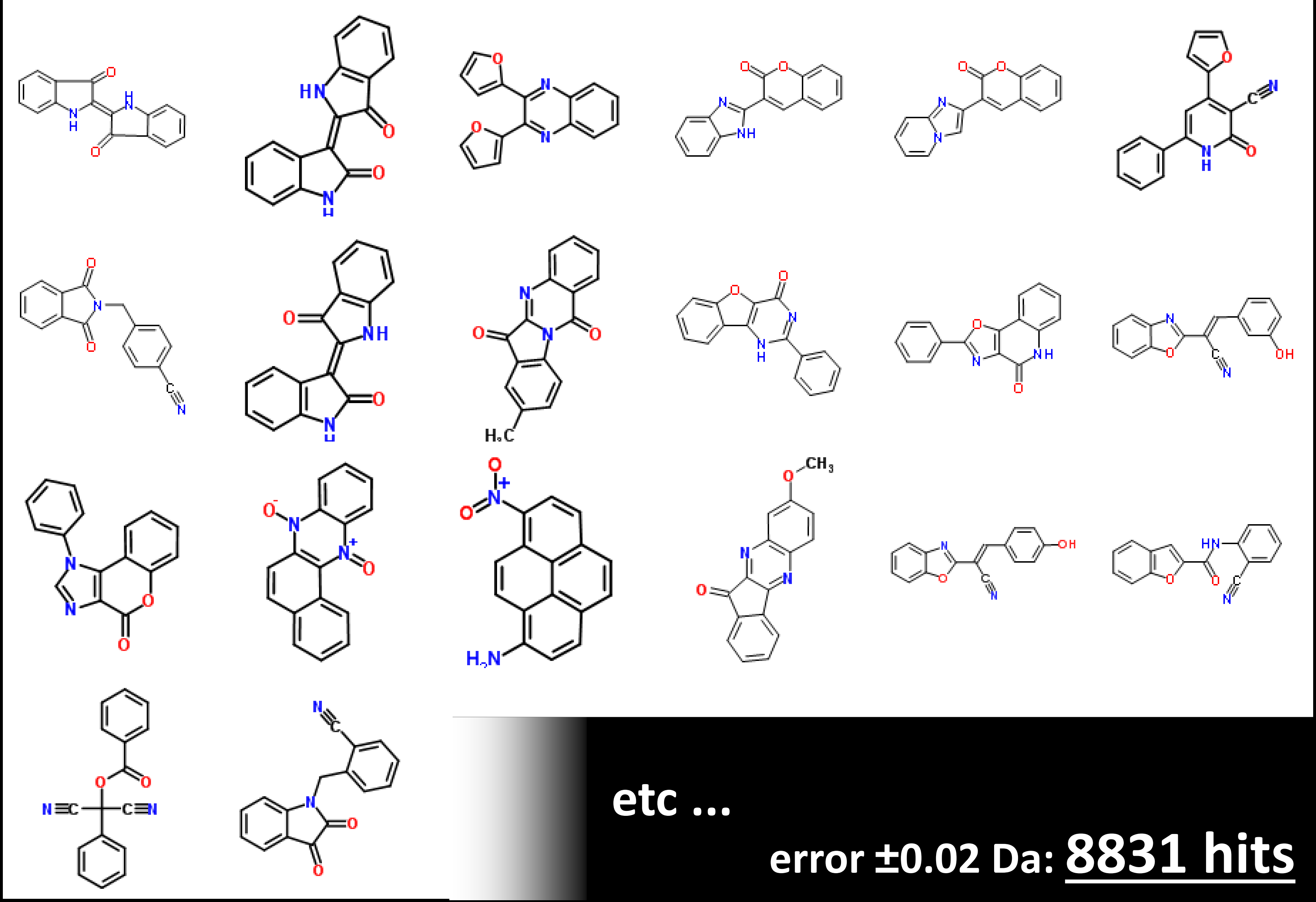
ChemSpider

Search and share chemistry

ROYAL SOCIETY OF CHEMISTRY

↓

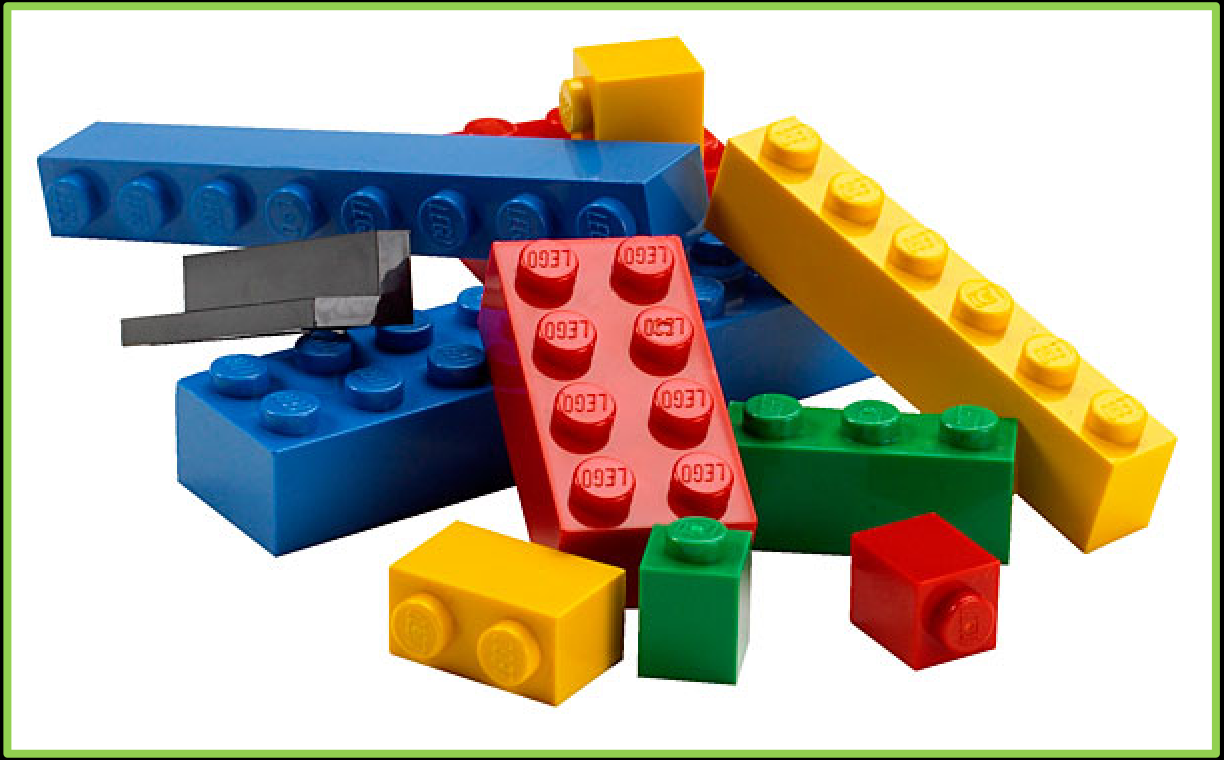
227 known isomers



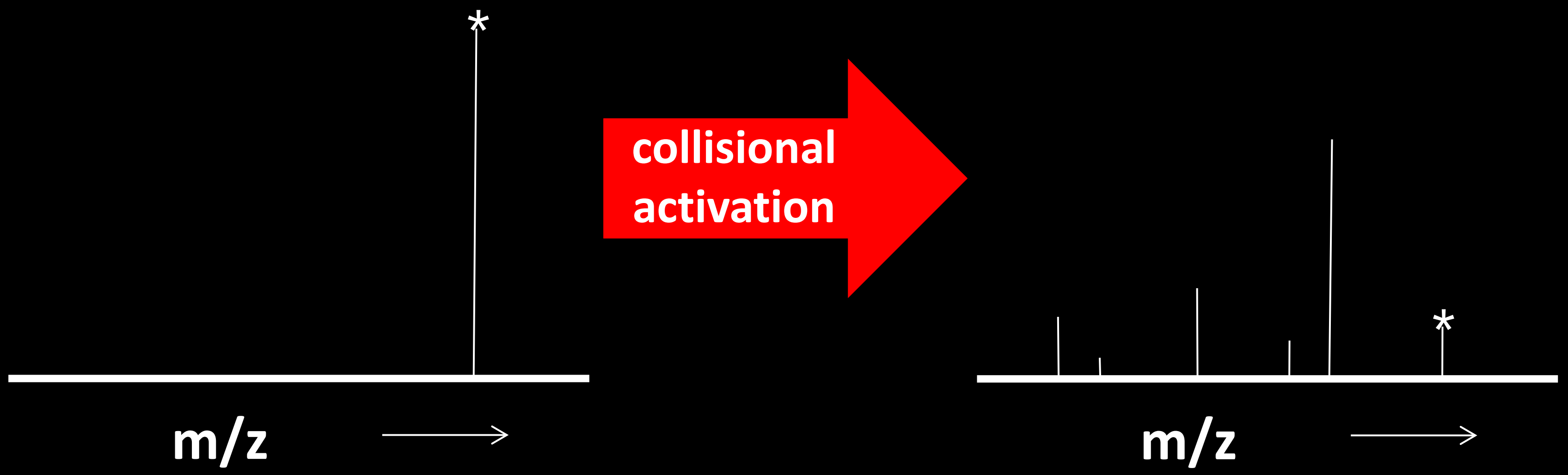
etc ...

error ±0.02 Da: <u>**8831 hits**</u>

How many different structures can you build?



Molecular structure from MS
Collision induced dissociation (MS/MS)



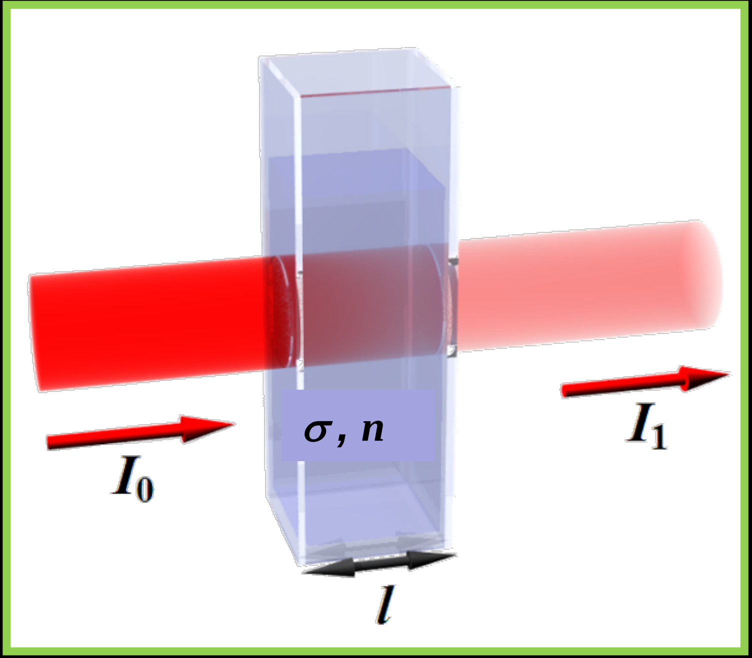
- **Fragment spectrum platform dependent**
- **Fragment spectrum not predictable from *first principles***

- **MS/MS database comparison**
- **Identify only *known unknowns***

Structural information from orthogonal methods

- retention time (LCMS)
- geometric cross section (ion mobility)
- # labile H-atoms (H/D exchange)
-
-
- IR spectroscopy
  - → connectivity
  - → intramolecular interactions
  - → predictable by QC
  - → database independent

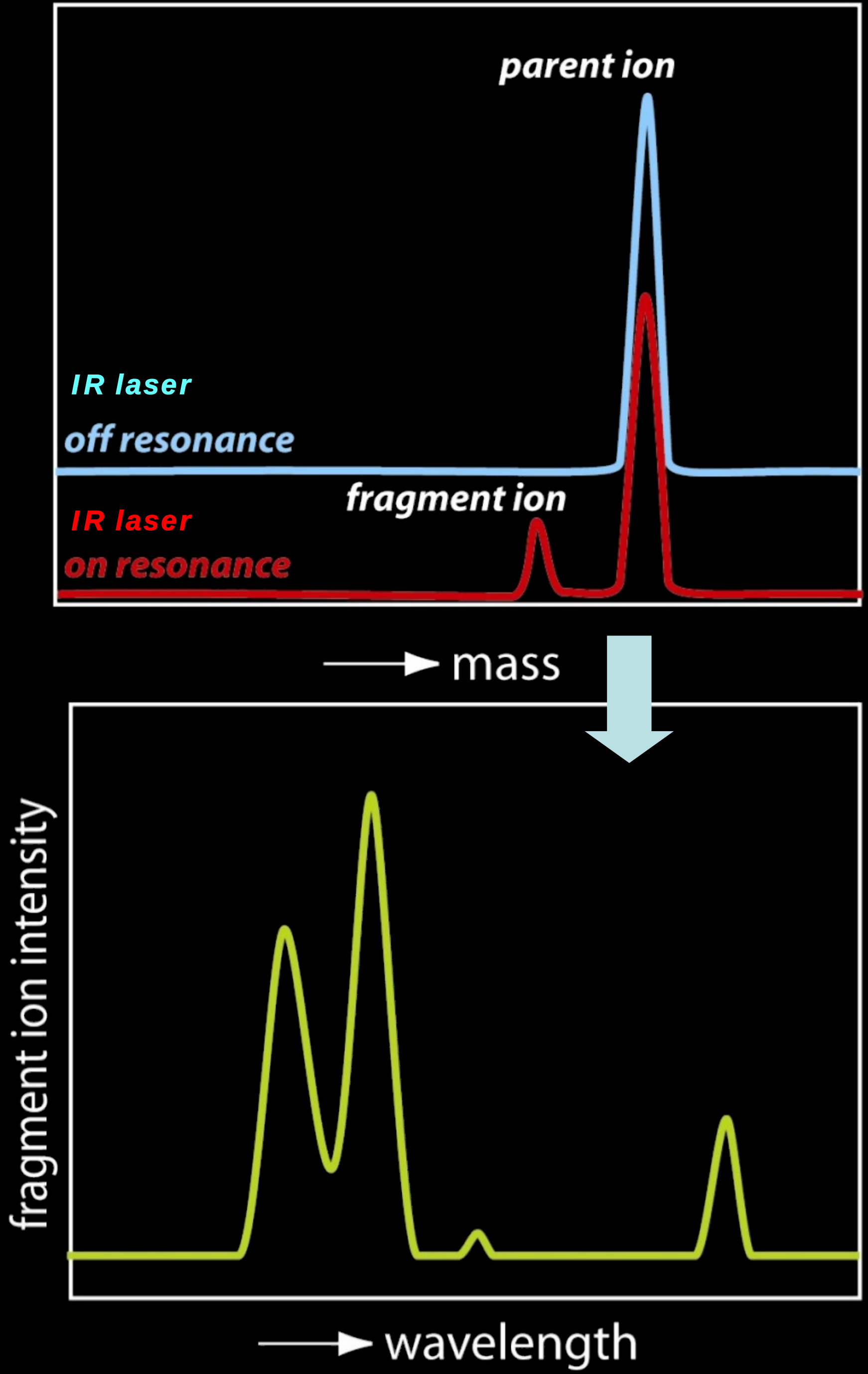
Can we record an infrared spectrum of the ions?



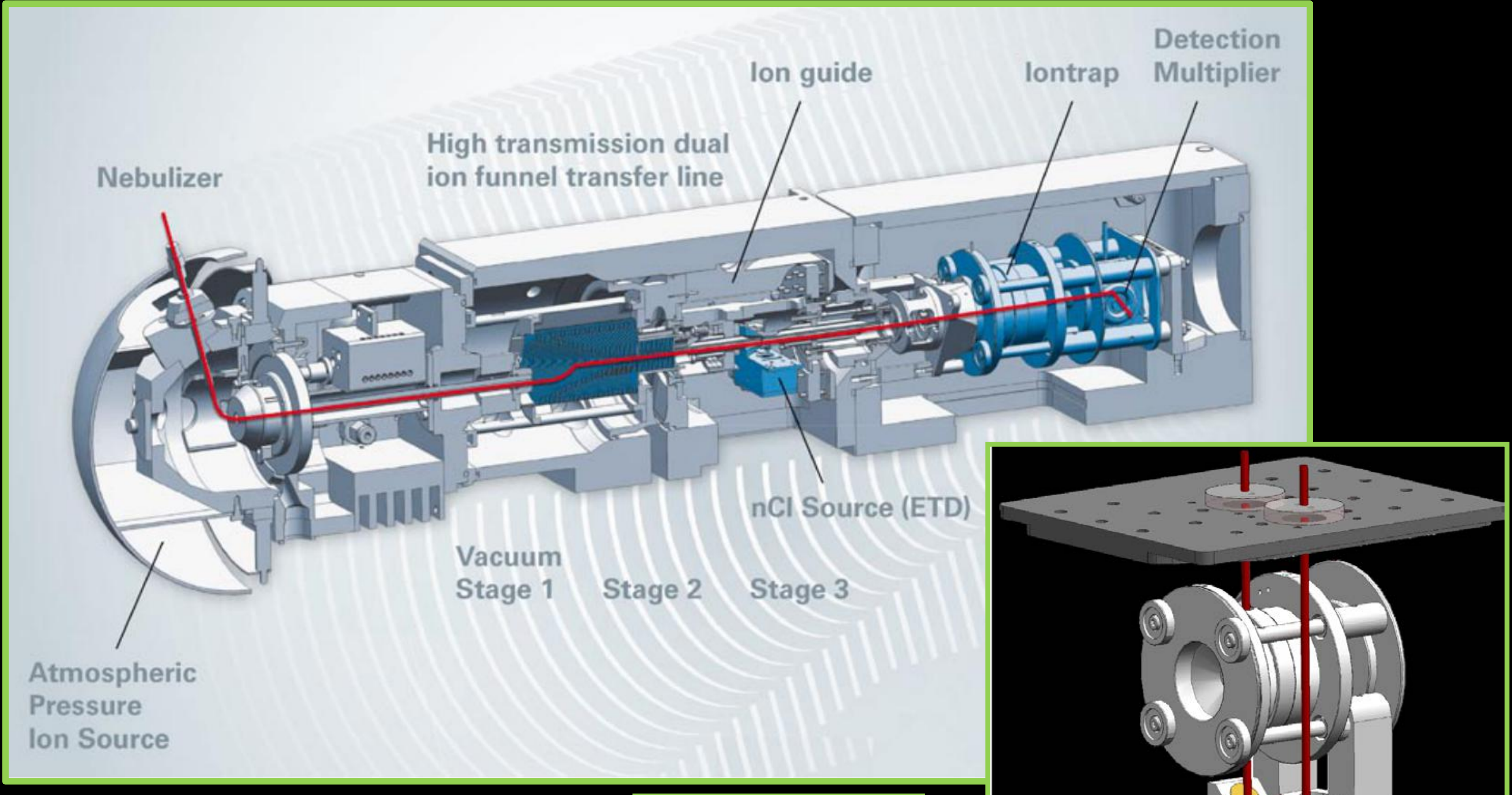
$$T(\lambda) = {}^{I_1}\!/_{I_0} = e^{-\sigma(\lambda)nl}$$

$n_{\text{ion}} < 10^{6}\ \text{cm}^{-3}$

$< 10^{-12}$ mbar



Experimental: modified Bruker Amazon Speed ETD



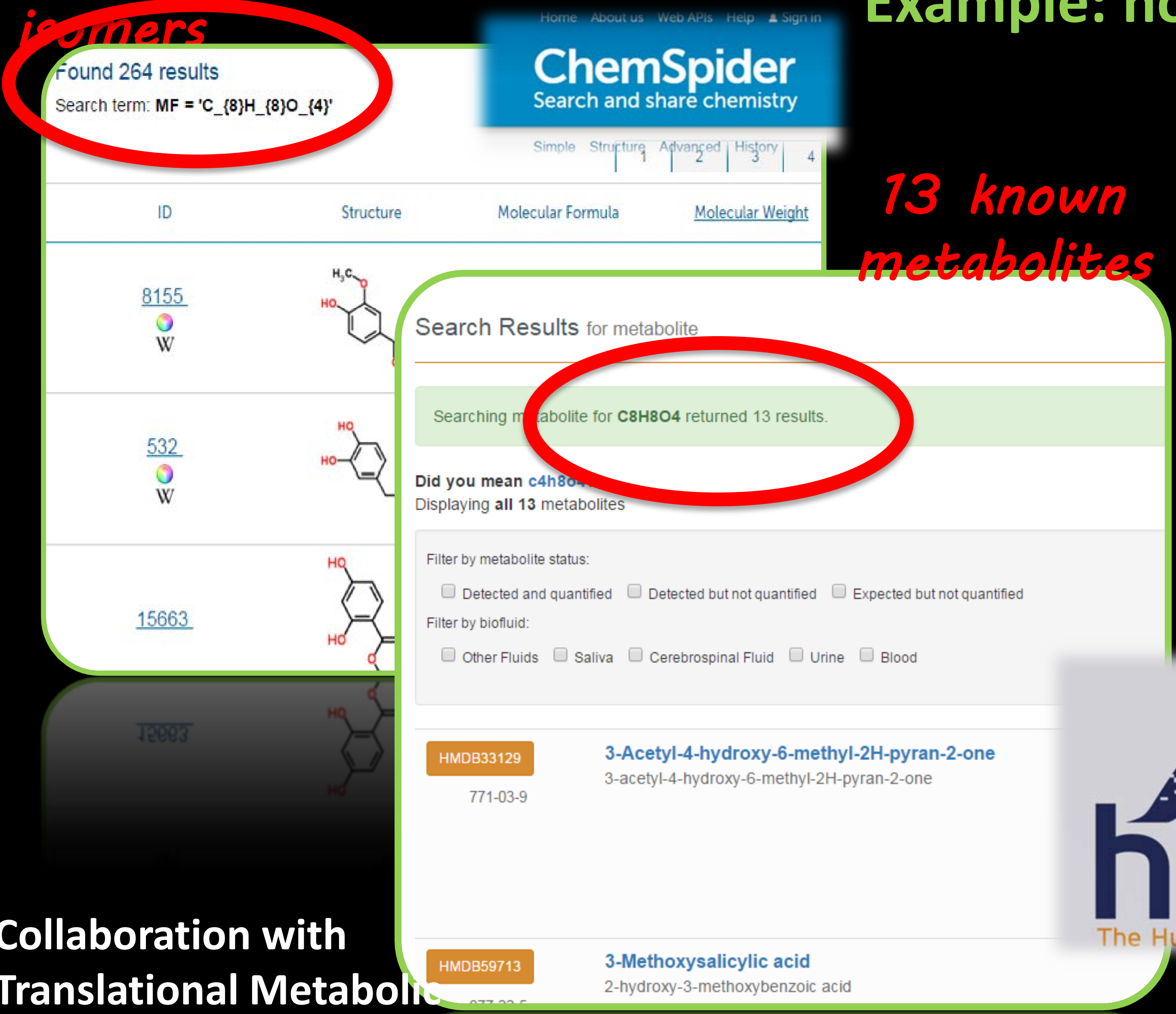
Thanks Christoph Gebhardt et al.
at Bruker!

Experimental: modified Bruker Amazon Speed ETD

Application to biomarker discovery in metabolomics

264 known isomers

Example: homogentisic acid



Home About us Web APIs Help Sign in

ChemSpider

Search and share chemistry

Simple Structure Advanced History

Found 264 results

Search term: **MF = 'C_{8}H_{8}O_{4}'**

ID	Structure	Molecular Formula	Molecular Weight
8155			
532			
15663			

13 known metabolites

Search Results for metabolite

Searching metabolite for **C8H8O4** returned 13 results.

Did you mean c4h8o4

Displaying **all 13** metabolites

Filter by metabolite status:

☐ Detected and quantified ☐ Detected but not quantified ☐ Expected but not quantified

Filter by biofluid:

☐ Other Fluids ☐ Saliva ☐ Cerebrospinal Fluid ☐ Urine ☐ Blood

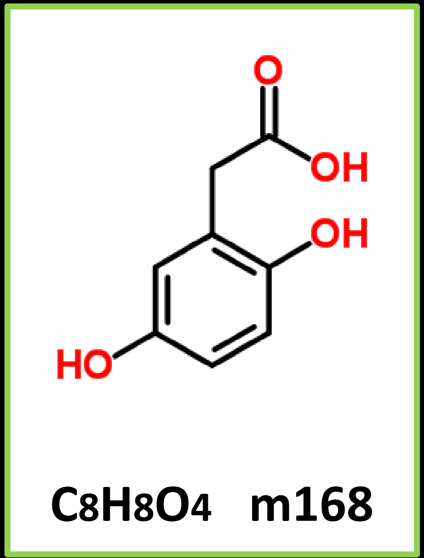
HMDB33129 3-Acetyl-4-hydroxy-6-methyl-2H-pyran-2-one

3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one

771-03-9

HMDB59713 3-Methoxysalicylic acid

2-hydroxy-3-methoxybenzoic acid



$C_8H_8O_4$ m168

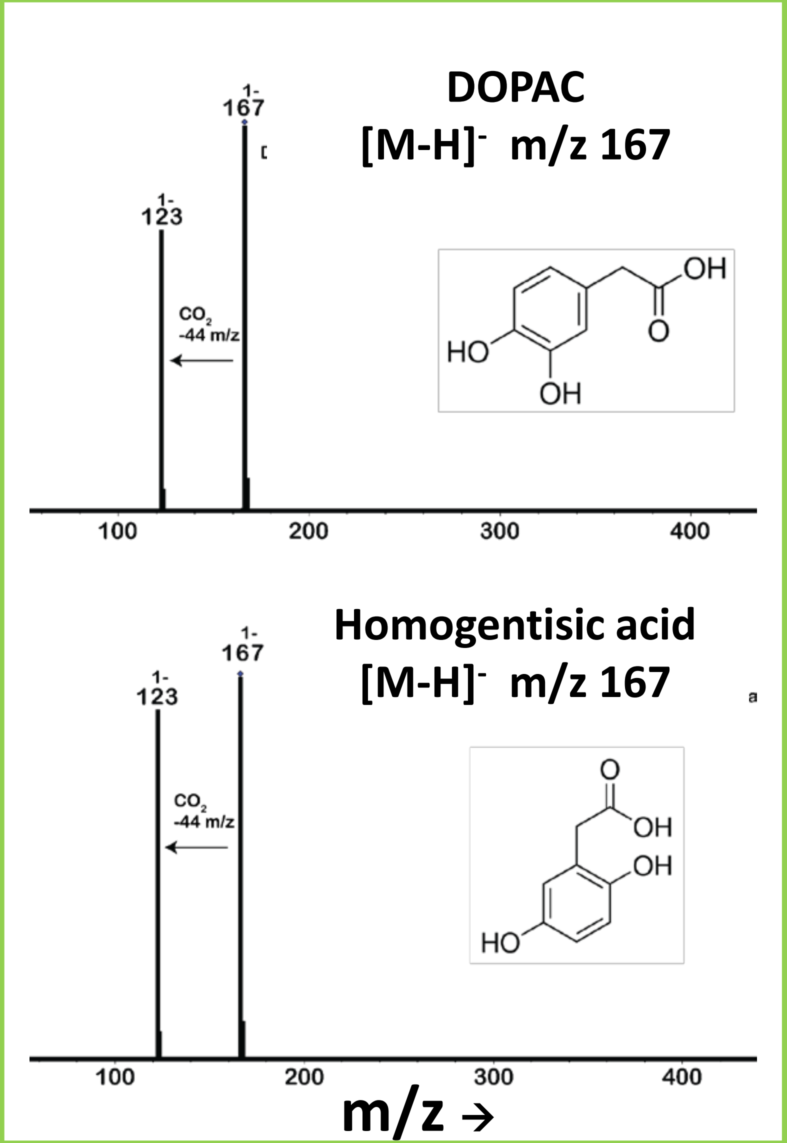
hmdb

The Human Metabolome Database

Collaboration with Translational Metabolic Laboratory at RU MC

Example: homogentisic acid

Tandem MS

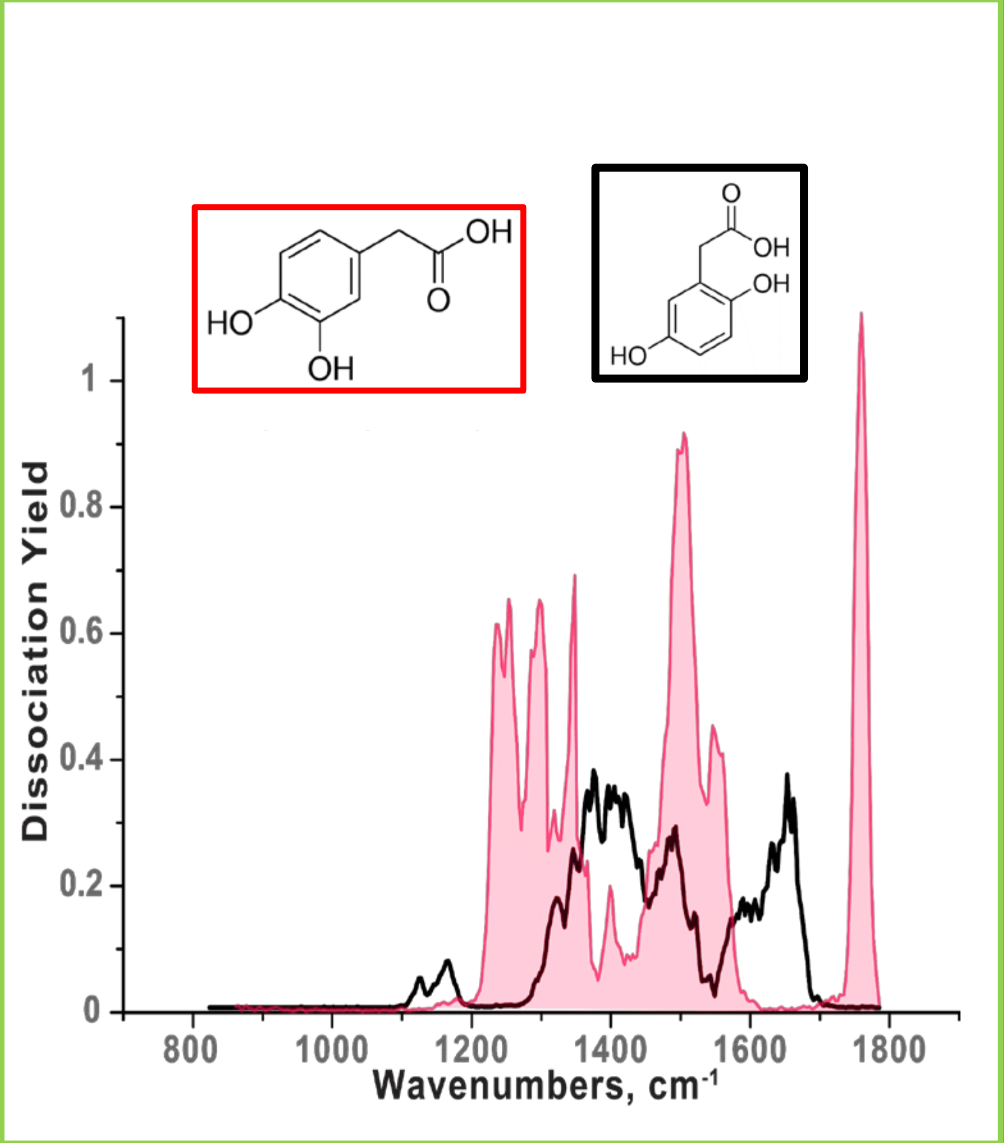


DOPAC
[M-H]$^-$ m/z 167

Homogentisic acid
[M-H]$^-$ m/z 167

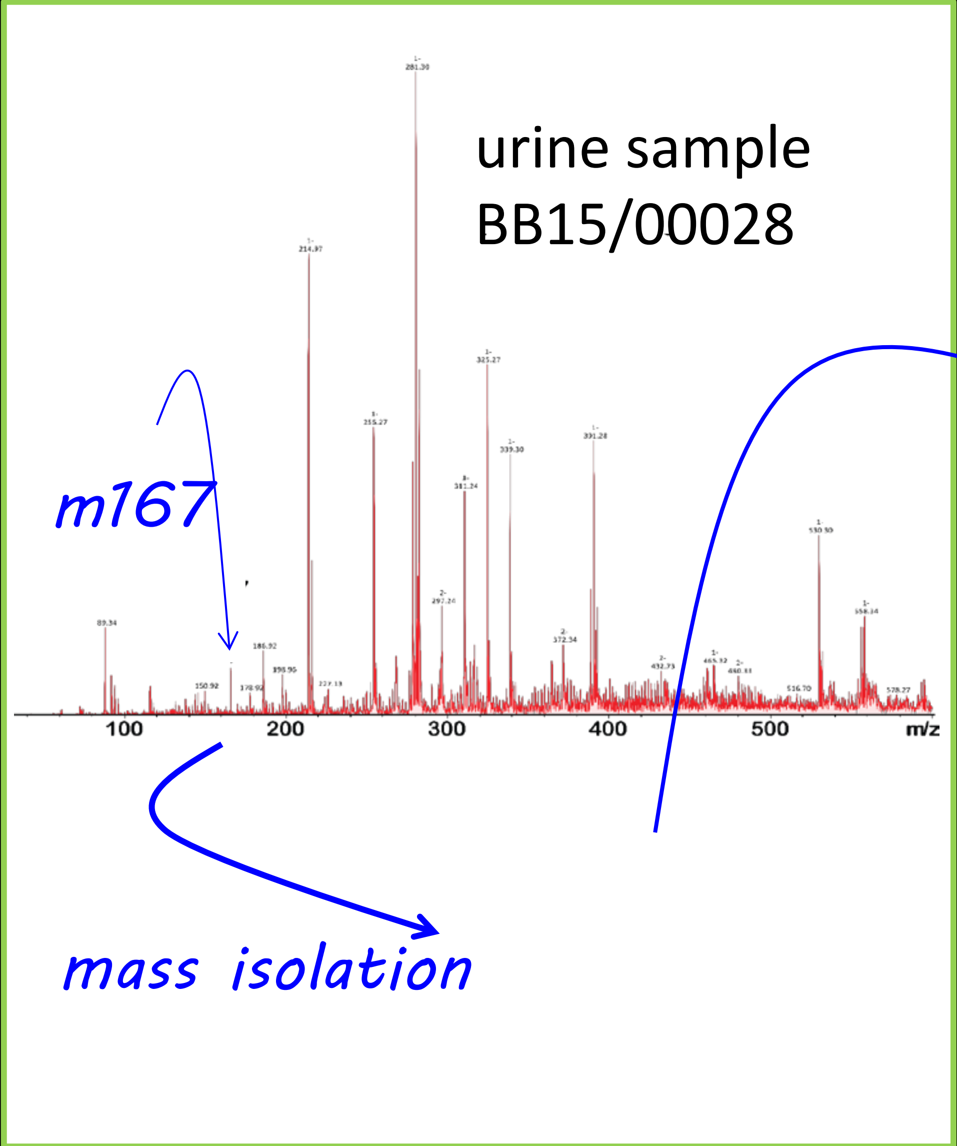
m/z →

IR ion spectroscopy



Example: homogentisic acid

in a complex biological matrix

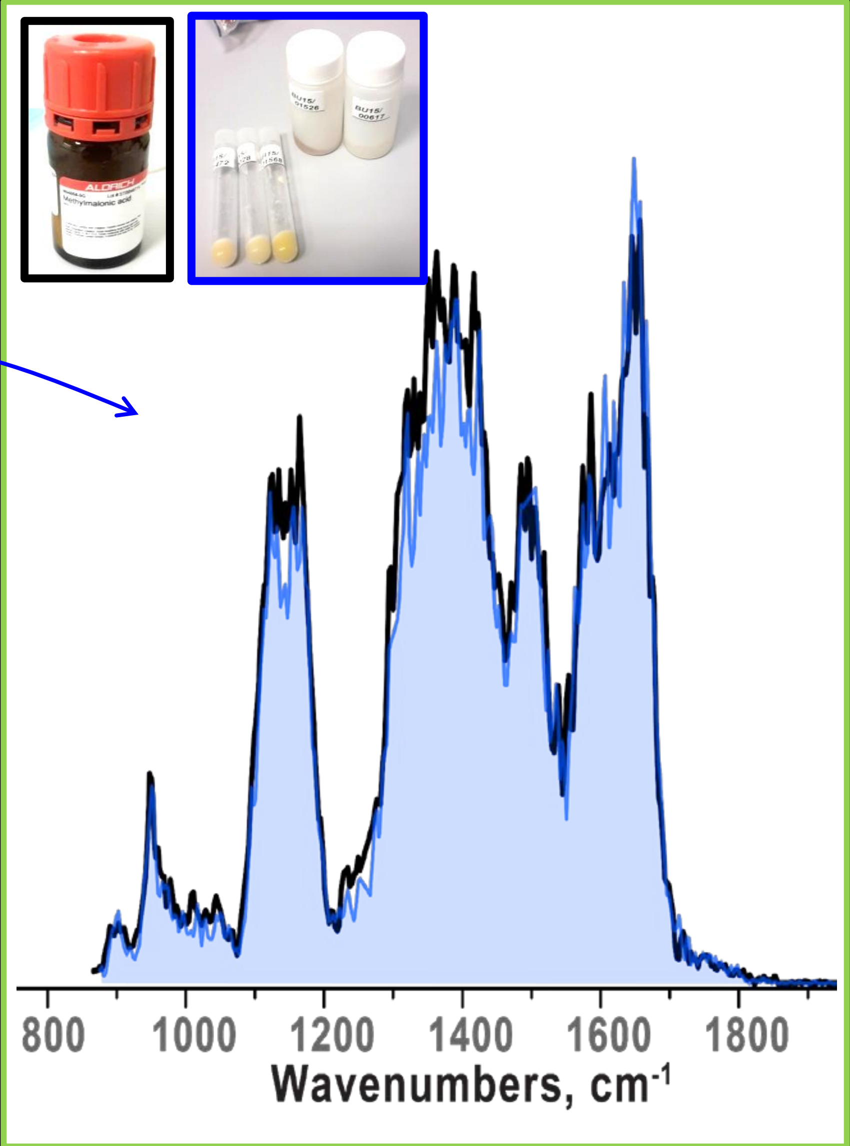


urine sample
BB15/00028

m167

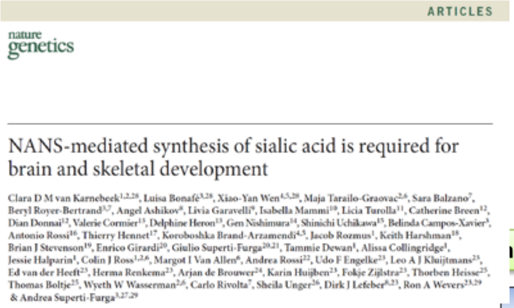
mass isolation

IR ion spectroscopy



Identification Inborn Errors of Metabolism

Collaboration with Translational Metabolic Laboratory



ARTICLES

nature genetics

NANS-mediated synthesis of sialic acid is required for brain and skeletal development

Clara D M van Karnebeek[1,2,28], Luisa Bonafé[3,28], Xiao-Yan Wen[4,5,28], Maja Tarailo-Graovac[2,6], Sara Balzano[7], Beryl Royer-Bertrand[3,7], Angel Ashikov[8], Livia Garavelli[9], Isabella Mammi[10], Licia Turolla[11], Catherine Breen[12], Dian Donnai[12], Valerie Cormier[13], Delphine Heron[13], Gen Nishimura[14], Shinichi Uchikawa[15], Belinda Campos-Xavier[3], Antonio Rossi[16], Thierry Hennet[17], Koroboshka Brand-Arzamendi[4,5], Jacob Rozmus[1], Keith Harshman[18], Brian J Stevenson[19], Enrico Girardi[20], Giulio Superti-Furga[20,21], Tammie Dewan[1], Alissa Collingridge[1], Jessie Halparin[1], Colin J Ross[1,2,6], Margot I Van Allen[6], Andrea Rossi[22], Udo F Engelke[23], Leo A J Kluijtmans[23], Ed van der Heeft[23], Herma Renkema[23], Arjan de Brouwer[24], Karin Huijben[23], Fokje Zijlstra[23], Thorben Heisse[25], Thomas Boltje[25], Wyeth W Wasserman[2,6], Carlo Rivolta[7], Sheila Unger[26], Dirk J Lefeber[8,23], Ron A Wevers[23,29] & Andrea Superti-Furga[3,27,29]

Radboudumc
university medical center

Next Generation Metabolic Screening Cerebrospinal fluid (CSF)

a

-resolution QTOF results

RI	Mass	RT
1	**244.07902**	**0.73**
2	204.08663	0.72
3	123.05511	1.38
4	219.11006	5.88
5	246.10811	0.78
6	168.06524	1.20
7	137.08057	0.76
8	138.05458	0.71
9	316.21164	4.78
10	99.04171	1.06
11	195.11299	4.80
12	221.01043	1.09
13	170.08089	1.74
14	220.97417	1.05
15	130.97859	1.07
16	429.31854	18.87
17	235.09380	5.77
18	206.10187	0.86
19	281.08261	1.10
20	327.10610	2.93

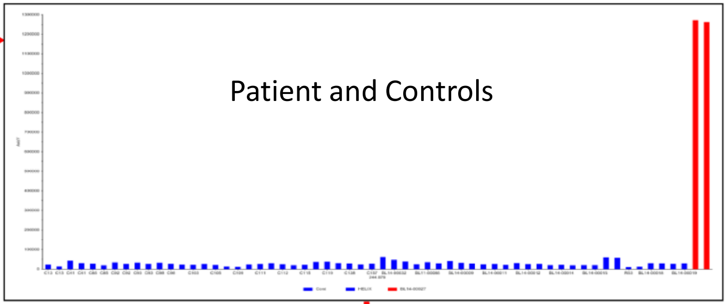
RI= position ranking intensity

Mass= measured mass

RT=retention time (min)

b

MS intensity plot of m/z 244.07902 in CSF of controls (blue) and the patient with NANS deficiency (red).



c

HMDB MS search results for 244.07902 m/z: multiple compounds possible

Compound	Name	Adduct	Adduct MW (Da)	Compound MW (Da)	Delta
HMDB01129	N-Acetylmannosamine	M+Na	244.079155	221.089937217	0.000135
HMDB00212	N-Acetylgalactosamine	M+Na	244.079155	221.089937217	0.000135
HMDB00215	N-Acetylglucosamine	M+Na	244.079155	221.089937217	0.000135

Three database hits are indistinguishable by both CID MS/MS and LC retention time

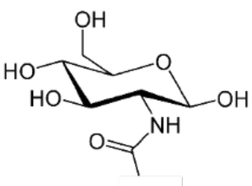
Identification Inborn Errors of Metabolism

Collaboration with Translational Metabolic Laboratory

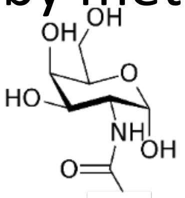
<10 microliters blood/urine used!

4 IR spectra ~ 2hrs

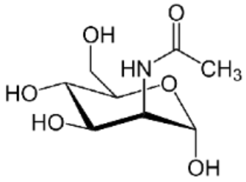
Possible database matches identified by metabolic screening



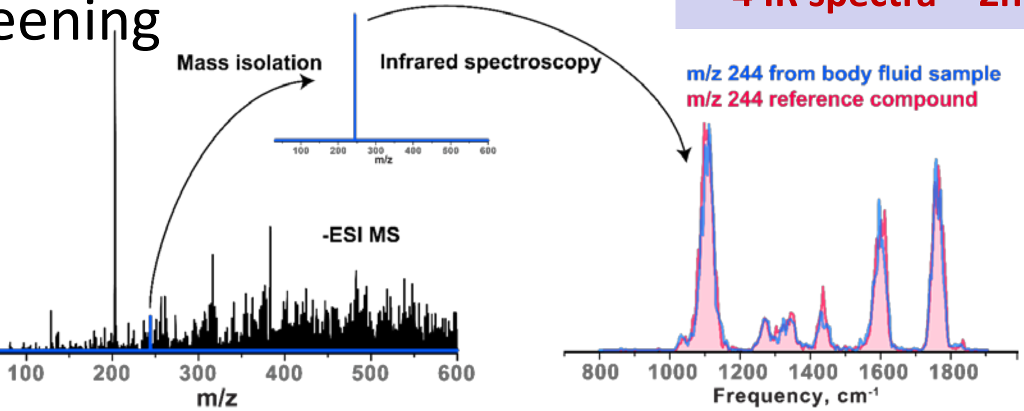
N-Acetylglucosamine
[M+Na]+ - m/z 244.07916



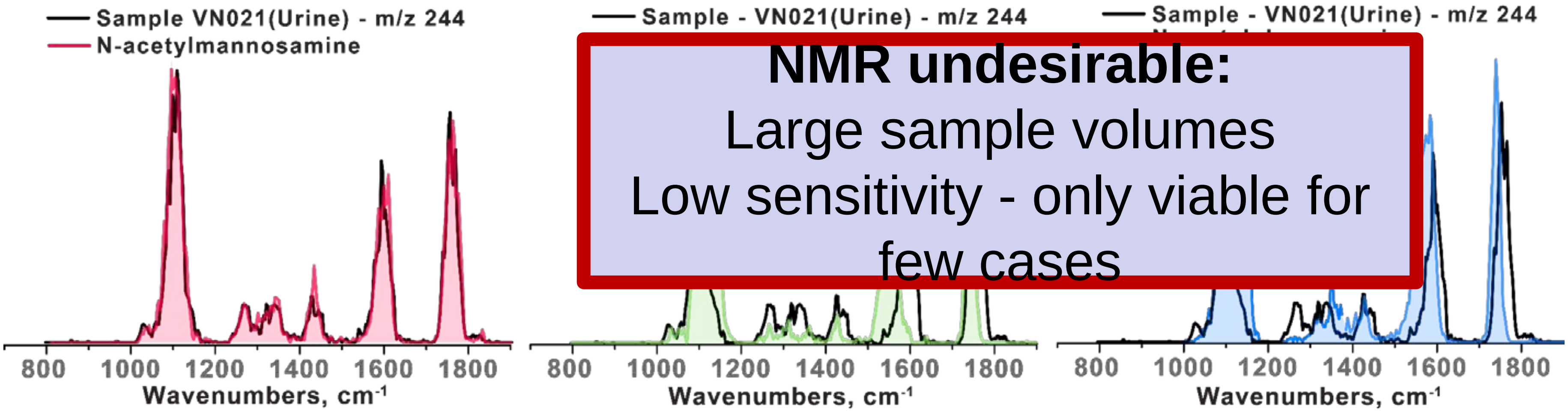
N-Acetylgalactosamine
[M+Na]+ - m/z 244.07916



N-Acetylmannosamine
[M+Na]+ - m/z 244.07916



~~MS~~, ~~MS/MS~~, ~~LC~~, NMR…



NMR undesirable:
Large sample volumes
Low sensitivity - only viable for few cases

IR multiple photon dissociation

IR photon energy << bond dissociation energy

Anharmonicity bottleneck

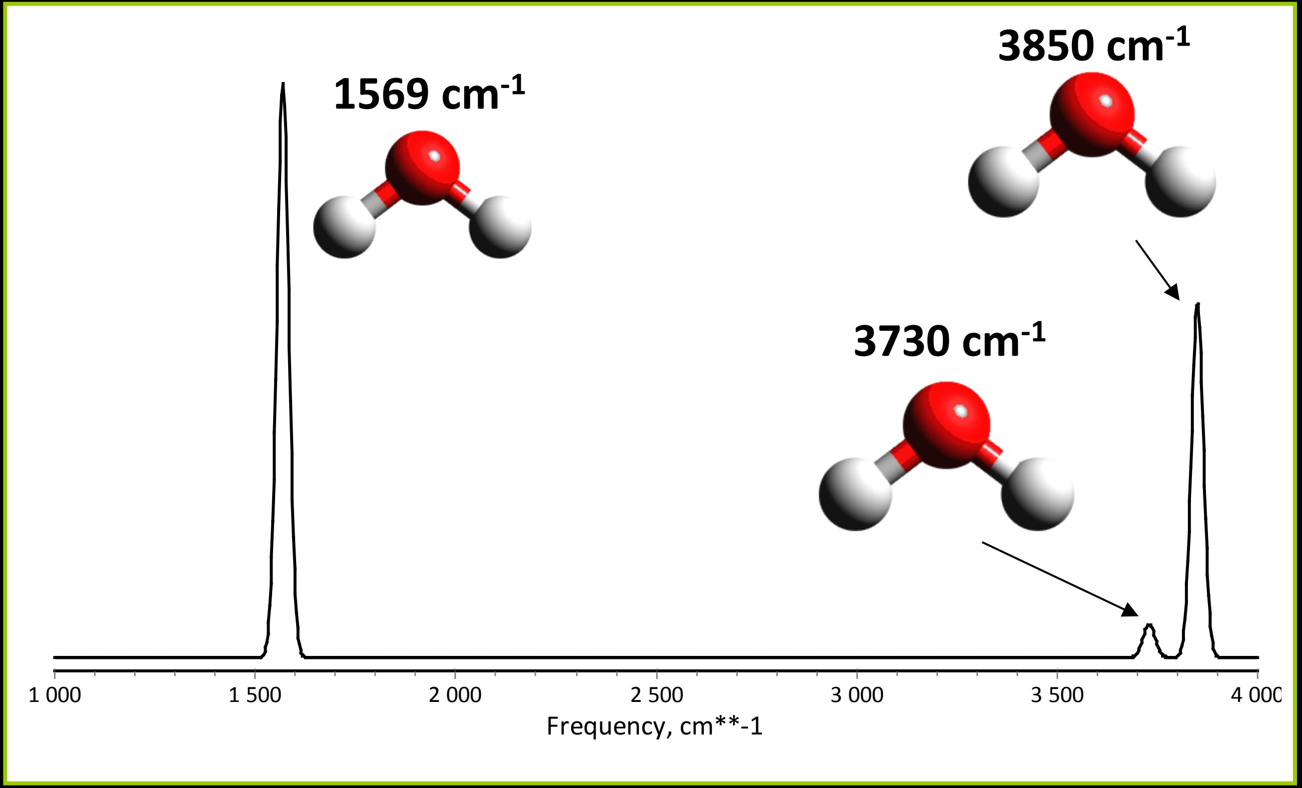
Manifestations of IRMPD

Vibrational structure of molecules

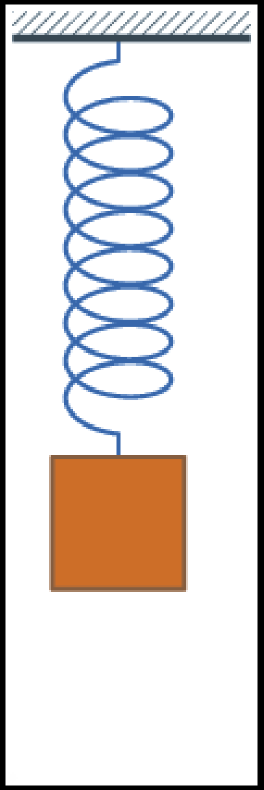
3N – 6 vibrational normal modes / frequencies

Complete orthogonal set

Vibrations are harmonic only approximately

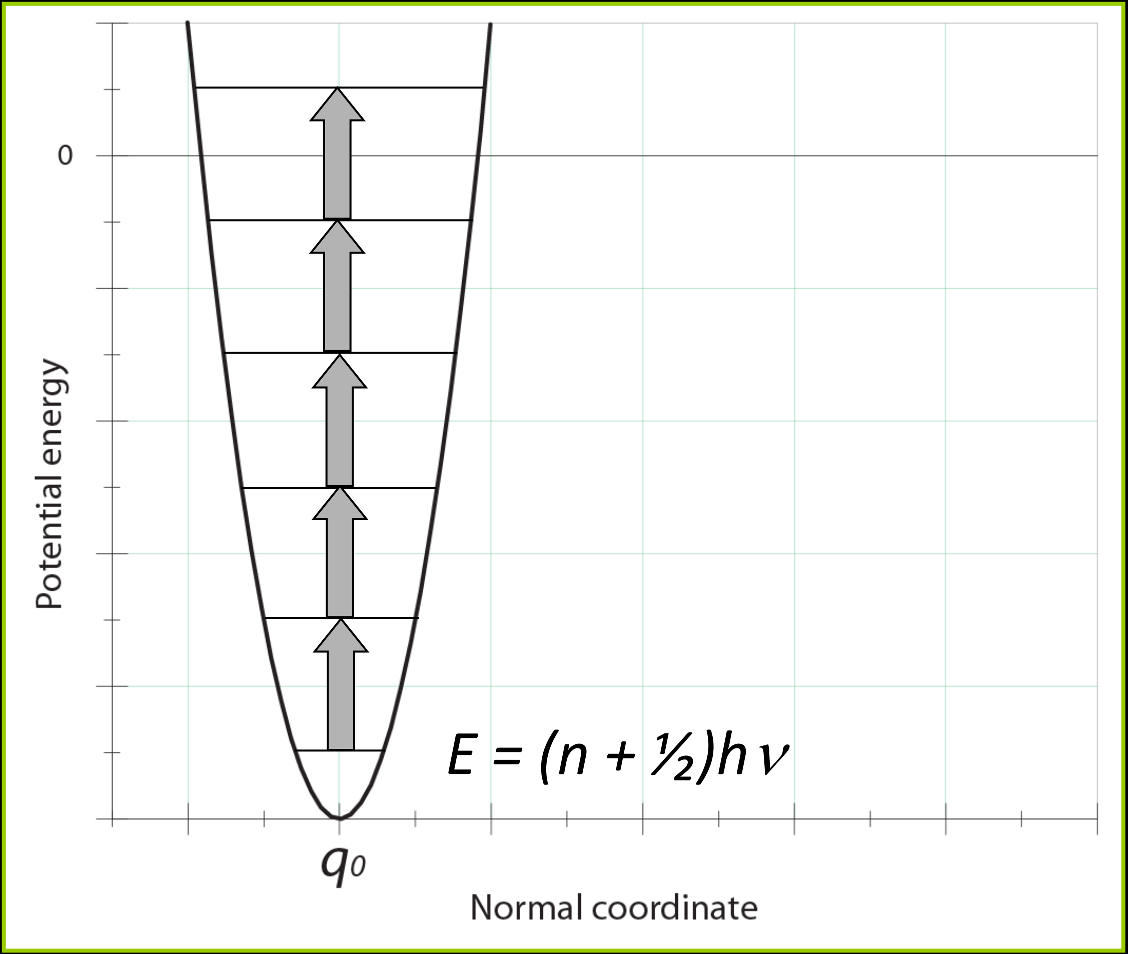


$F(z) = -kz$



Vibrational structure of molecules

Harmonic potential → levels equidistant

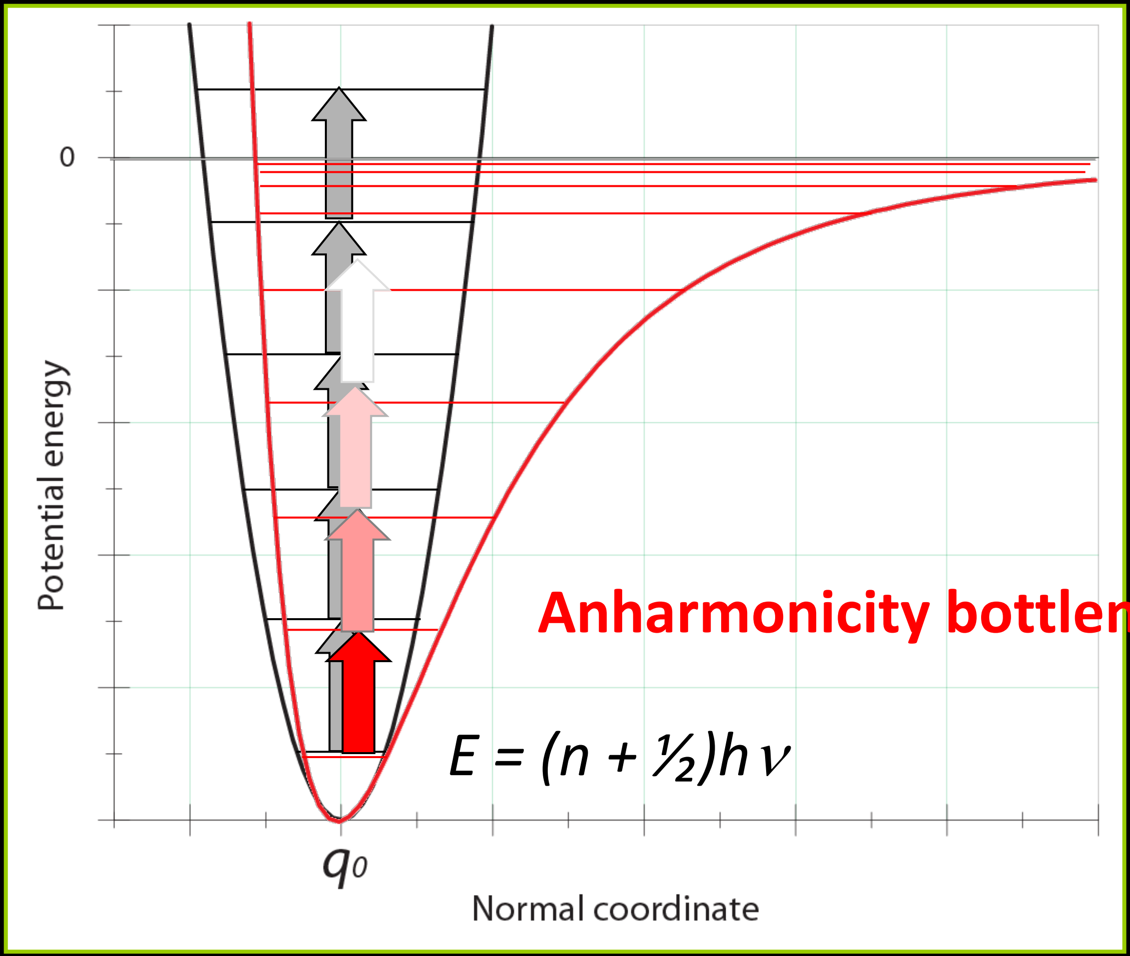


$$E = (n + ½)h\nu$$

Vibrational structure of molecules

Harmonic potential → levels equidistant

Anharmonic potential → levels converge to dissociation limit



Anharmonicity bottleneck

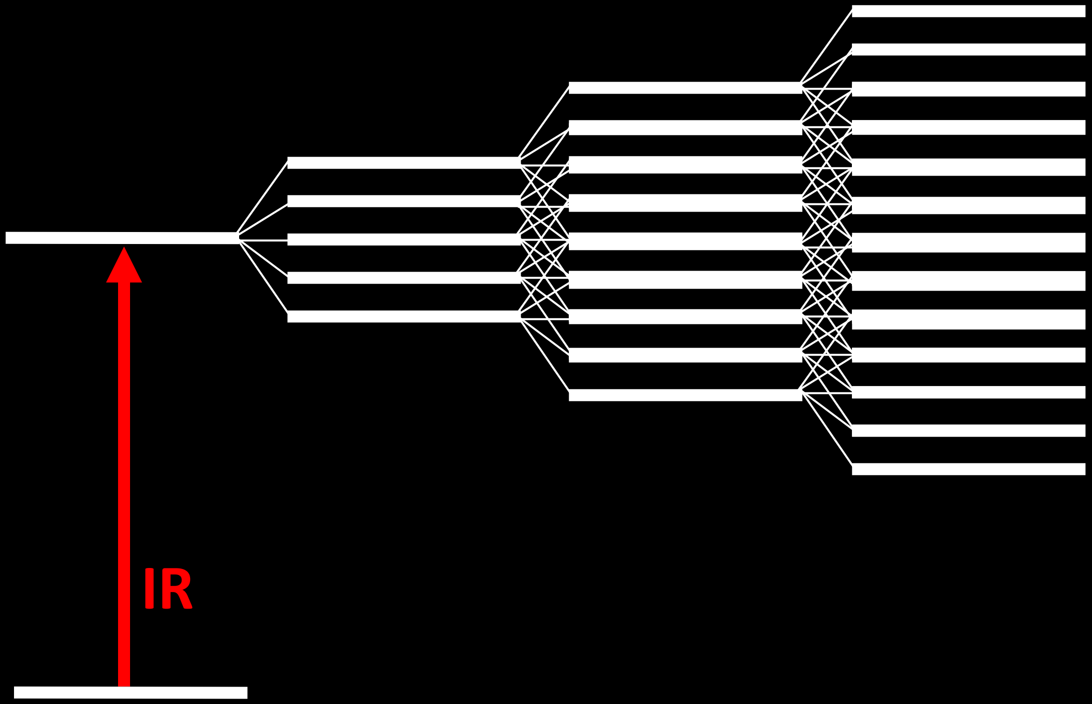
$$E = (n + \tfrac{1}{2})h\nu$$

Vibrational structure of molecules

Vibrational levels coupled

Vibrational level density increases rapidly

Intramolecular Vibrational Redistribution (IVR)



Vibrational structure of molecules

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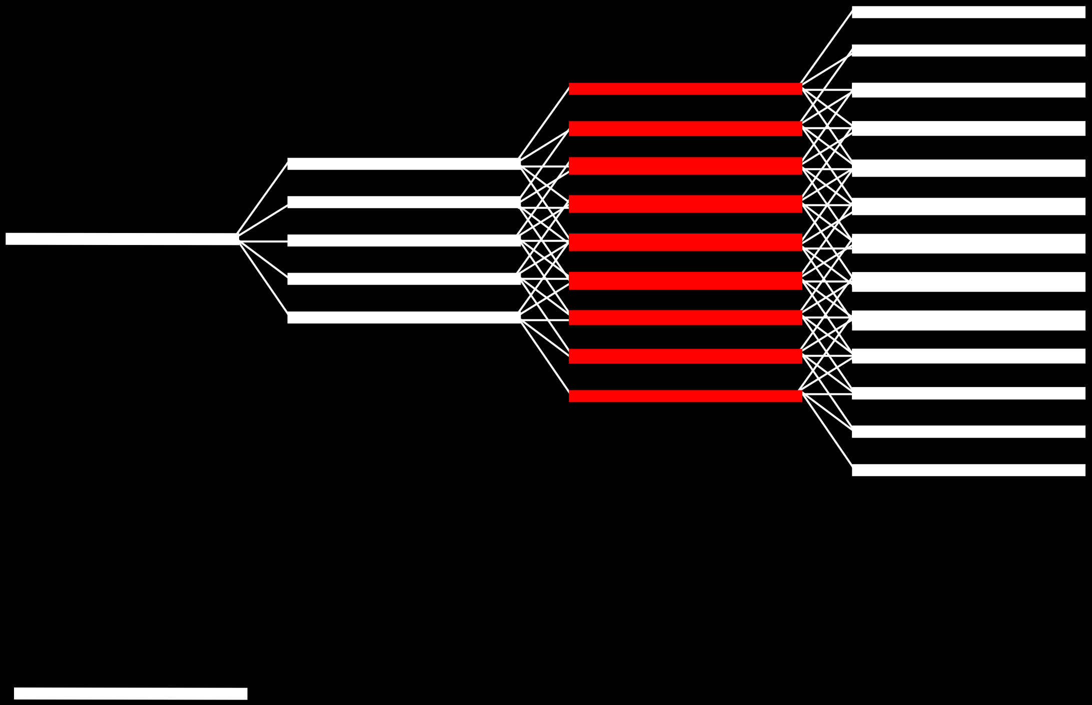
Intramolecular Vibrational Redistribution (IVR)



Vibrational structure of molecules

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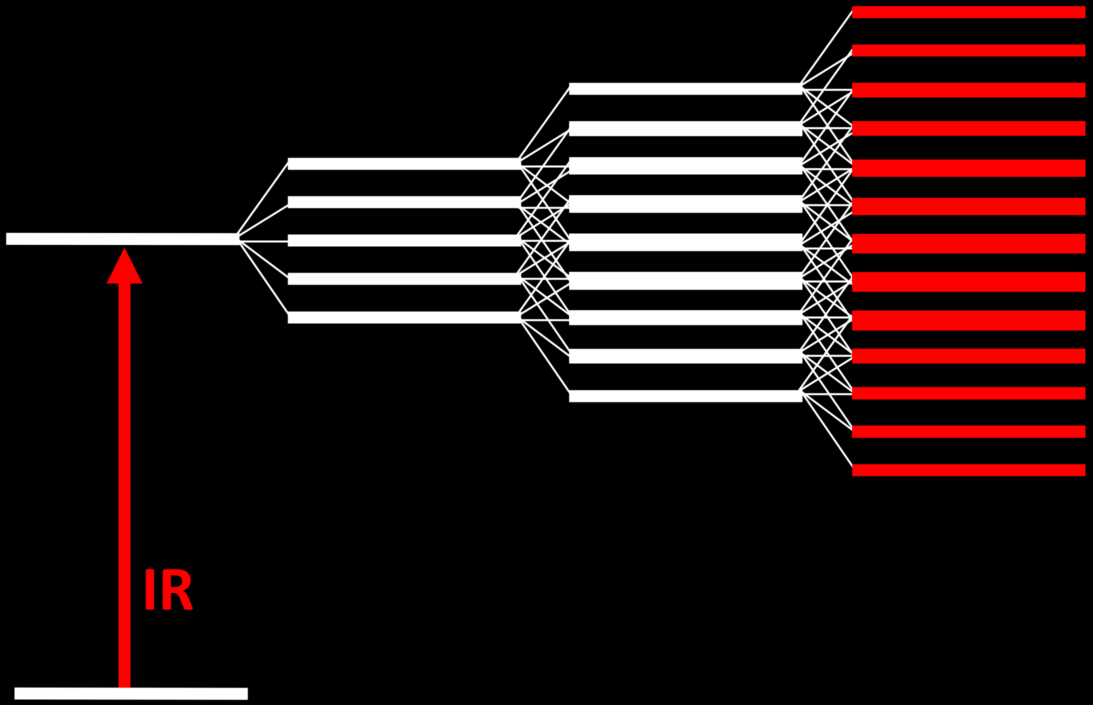
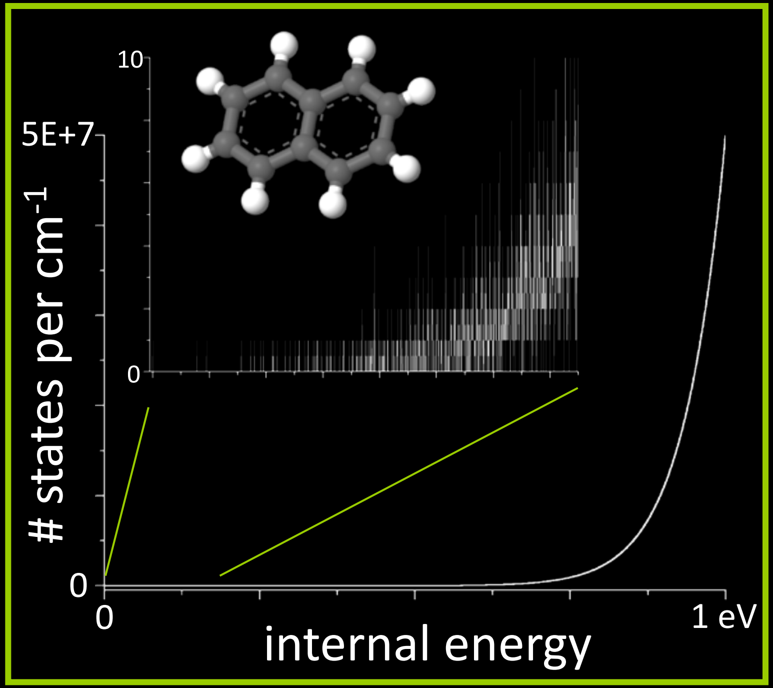
Intramolecular Vibrational Redistribution (IVR)





Beyer Swinehart algorithm

Count # vibrational states per energy interval

nu(i) i from 1 to k=3N – 6: *array containing the fundamental frequencies (as integers)*

P(j) j = 0 to energy range of interest: *array to be filled up with # states per cm^{-1} interval. initialize as (1, 0, 0, 0, 0 …)*

```
for i = 1 to k
        for j = 1 to 10 000                    calculate DoS up to 10 000 cm-1
                $P(j) = P(j) + P(j - nu(i))$
        next j
next i
```

Example: nu(1) = 3 cm^{-1}; nu(2) = 4 cm^{-1} ; nu(3) = 5 cm^{-1}

P(j=0 - 24)

init

(1,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0)

nu=3

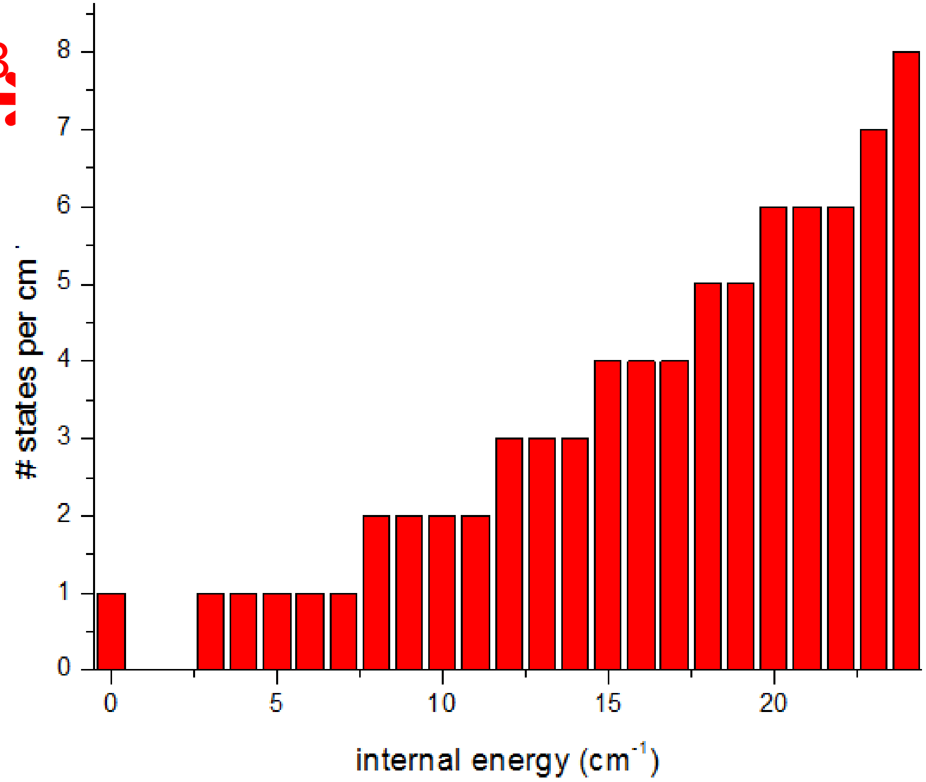
(1,0,0,1,0,0,1,0,0,1,0,0,1,0,0,1,0,0,1,0,0,1,0,0,1)

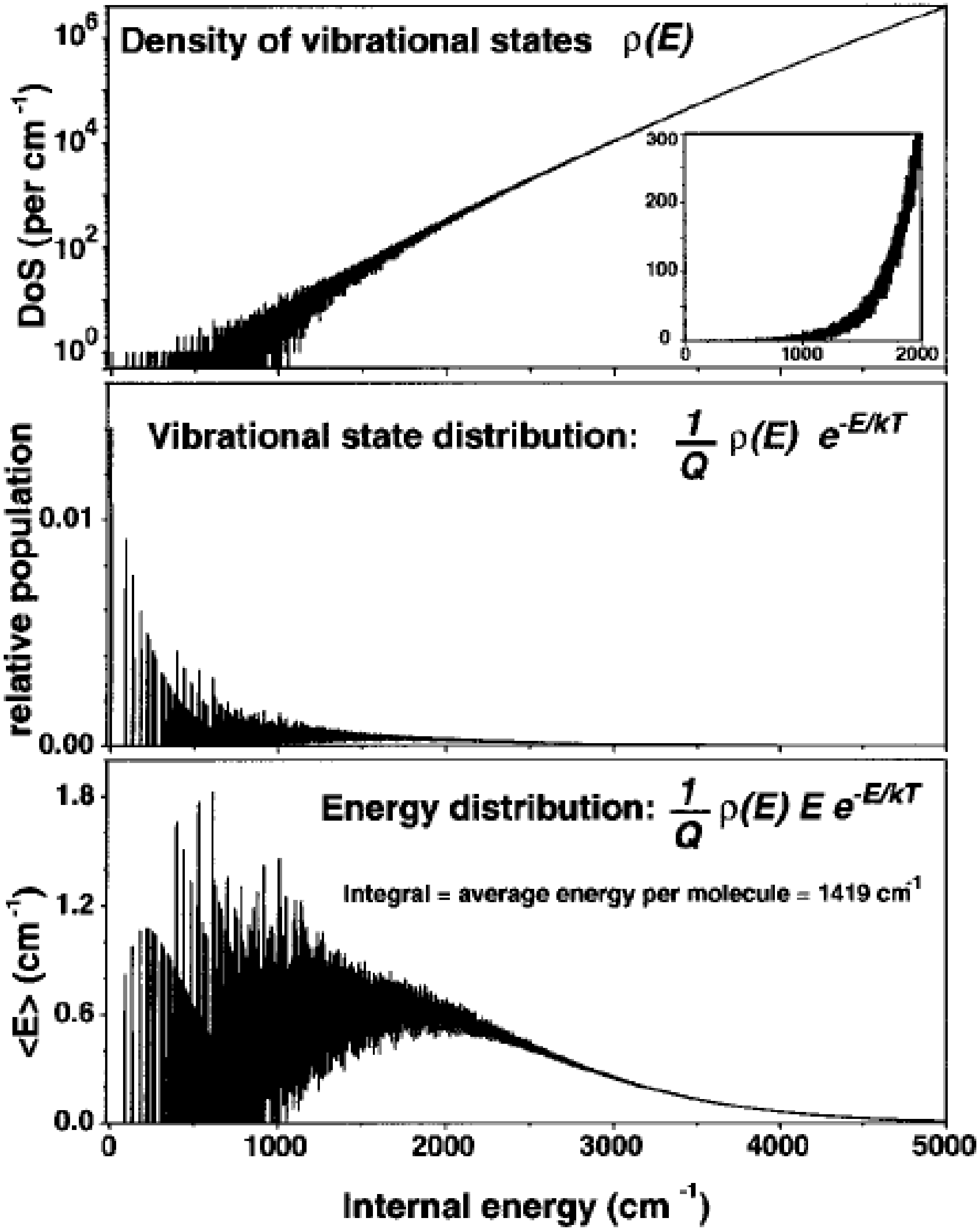
nu=4

(1,0,0,1,1,0,1,1,1,1,1,1,2,1,1,2,2,1,2,2,2,2,2,2,3)

nu=5

(1,0,0,1,1,1,1,1,2,2,2,2,3,3,3,



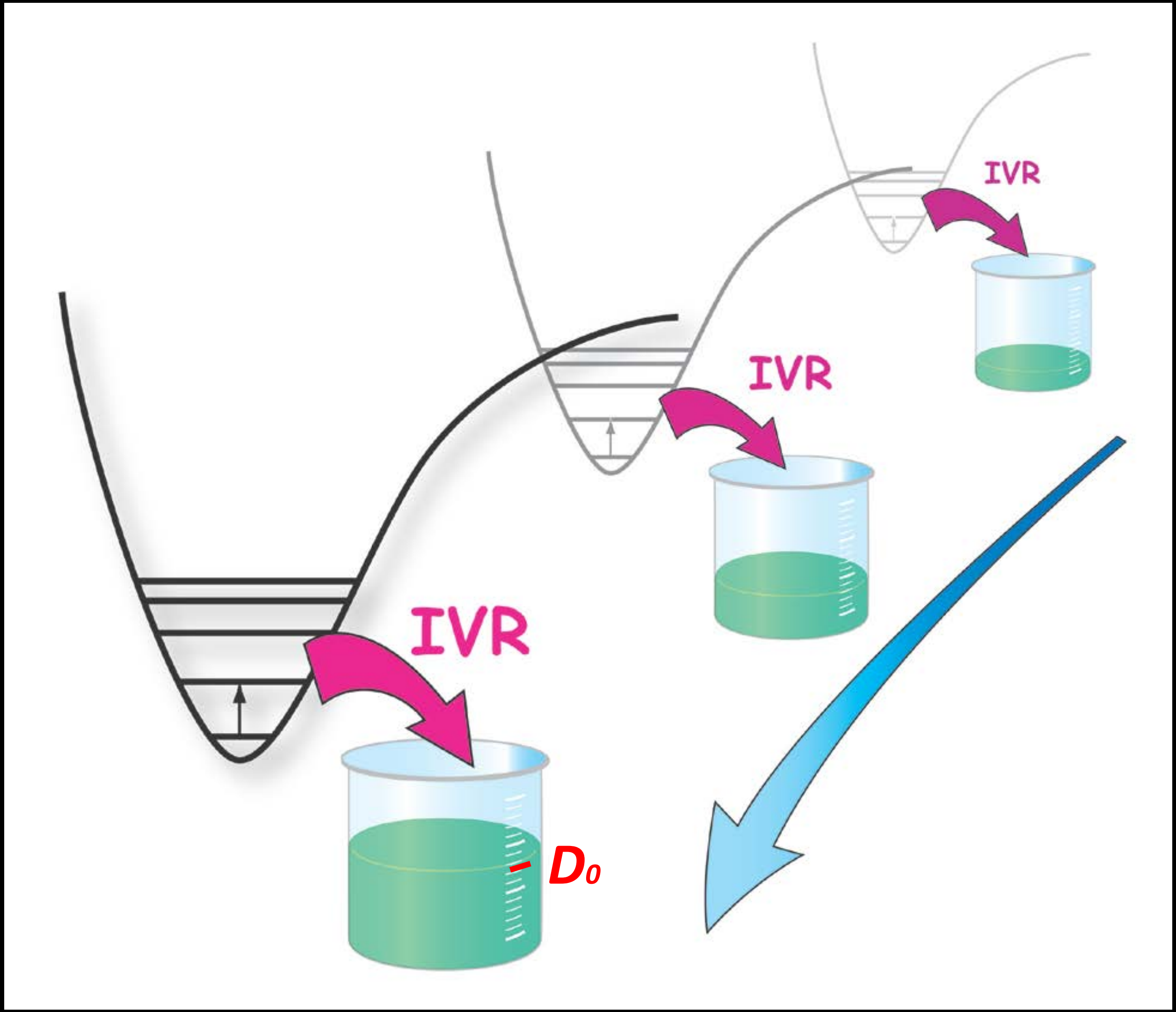


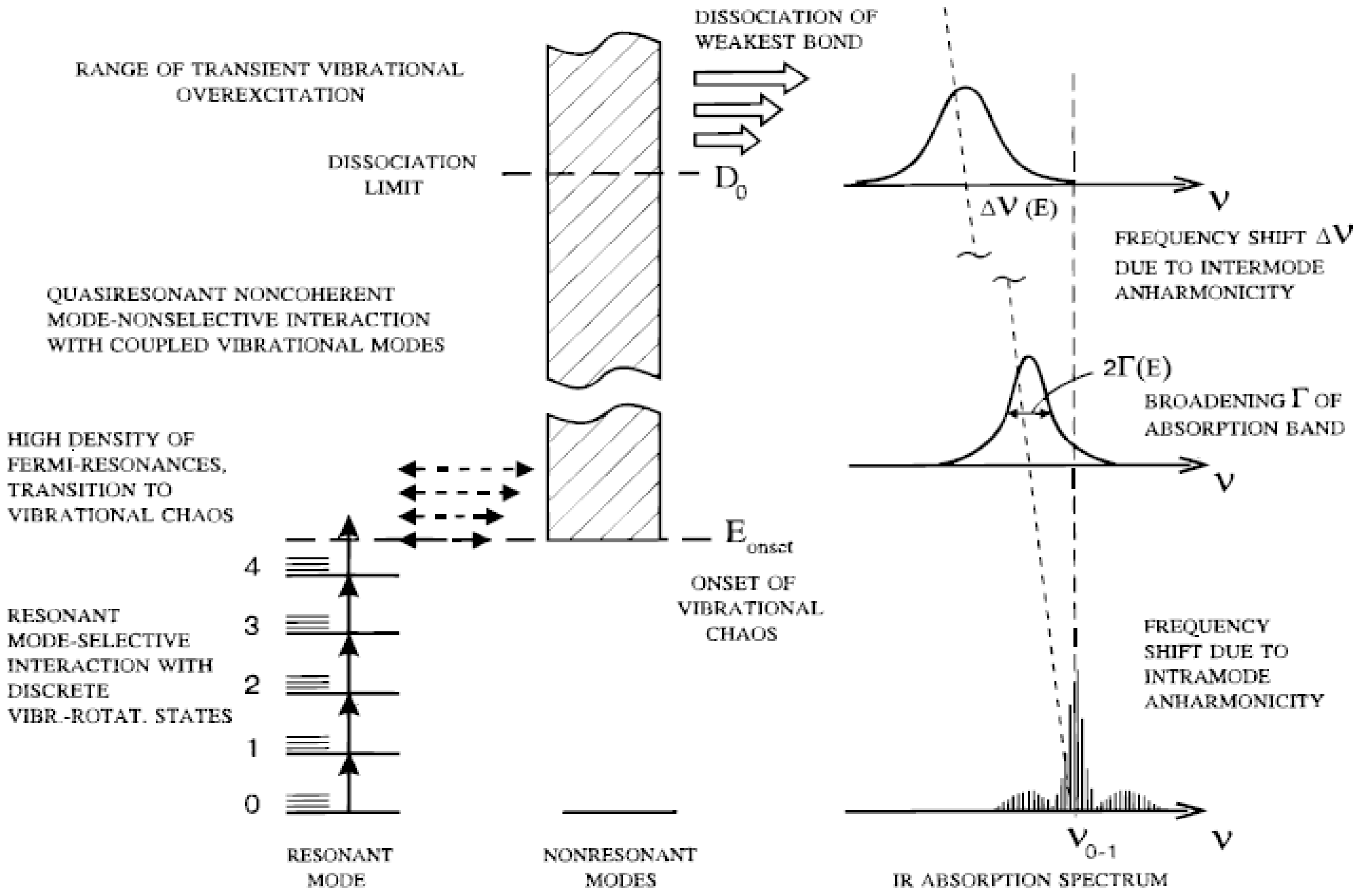
$$Q = \sum_{E=0}^{max} \rho(E) e^{-E/kT}$$

partition function

IVR mediated multiple photon excitation

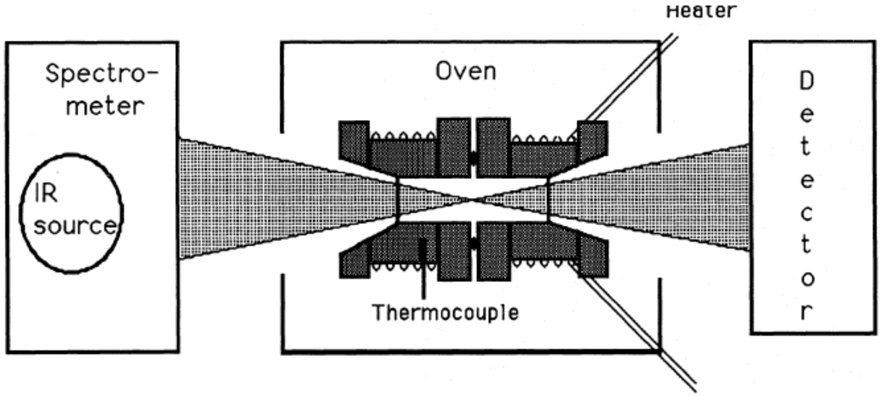
- Anharmonicity bottleneck avoided
- Moderate red-shift of transition

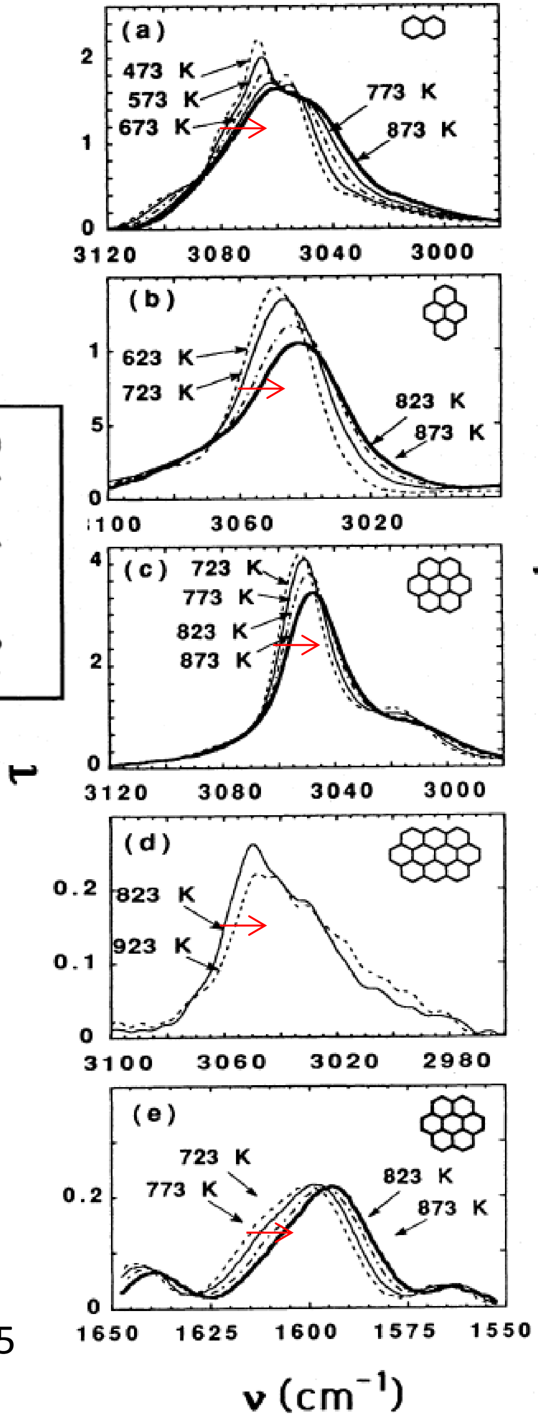


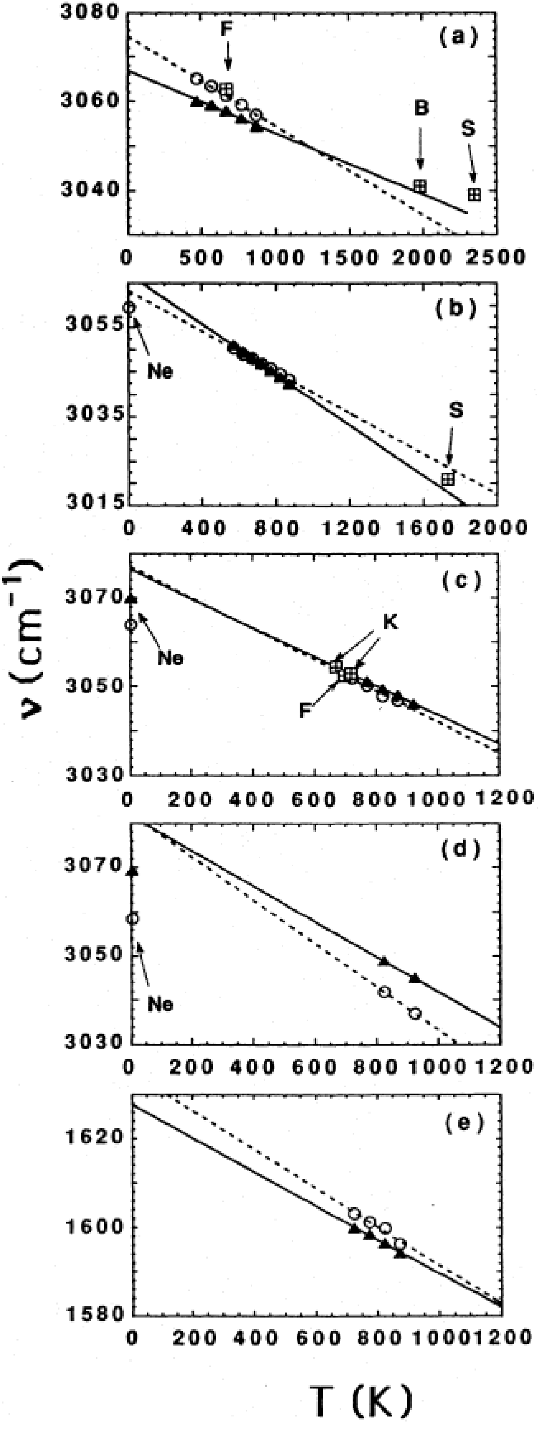


RANGE OF TRANSIENT VIBRATIONAL OVEREXCITATION
DISSOCIATION OF WEAKEST BOND
DISSOCIATION LIMIT
D_0
QUASIRESONANT NONCOHERENT MODE-NONSELECTIVE INTERACTION WITH COUPLED VIBRATIONAL MODES
HIGH DENSITY OF FERMI-RESONANCES, TRANSITION TO VIBRATIONAL CHAOS
E_{onset}
ONSET OF VIBRATIONAL CHAOS
RESONANT MODE-SELECTIVE INTERACTION WITH DISCRETE VIBR.-ROTAT. STATES
4
3
2
1
0
RESONANT MODE
NONRESONANT MODES
$\Delta\nu$ (E)
ν
FREQUENCY SHIFT $\Delta\nu$ DUE TO INTERMODE ANHARMONICITY
2Γ(E)
BROADENING Γ OF ABSORPTION BAND
ν
FREQUENCY SHIFT DUE TO INTRAMODE ANHARMONICITY
ν_{0-1}
ν
IR ABSORPTION SPECTRUM

IR spectra as function of T





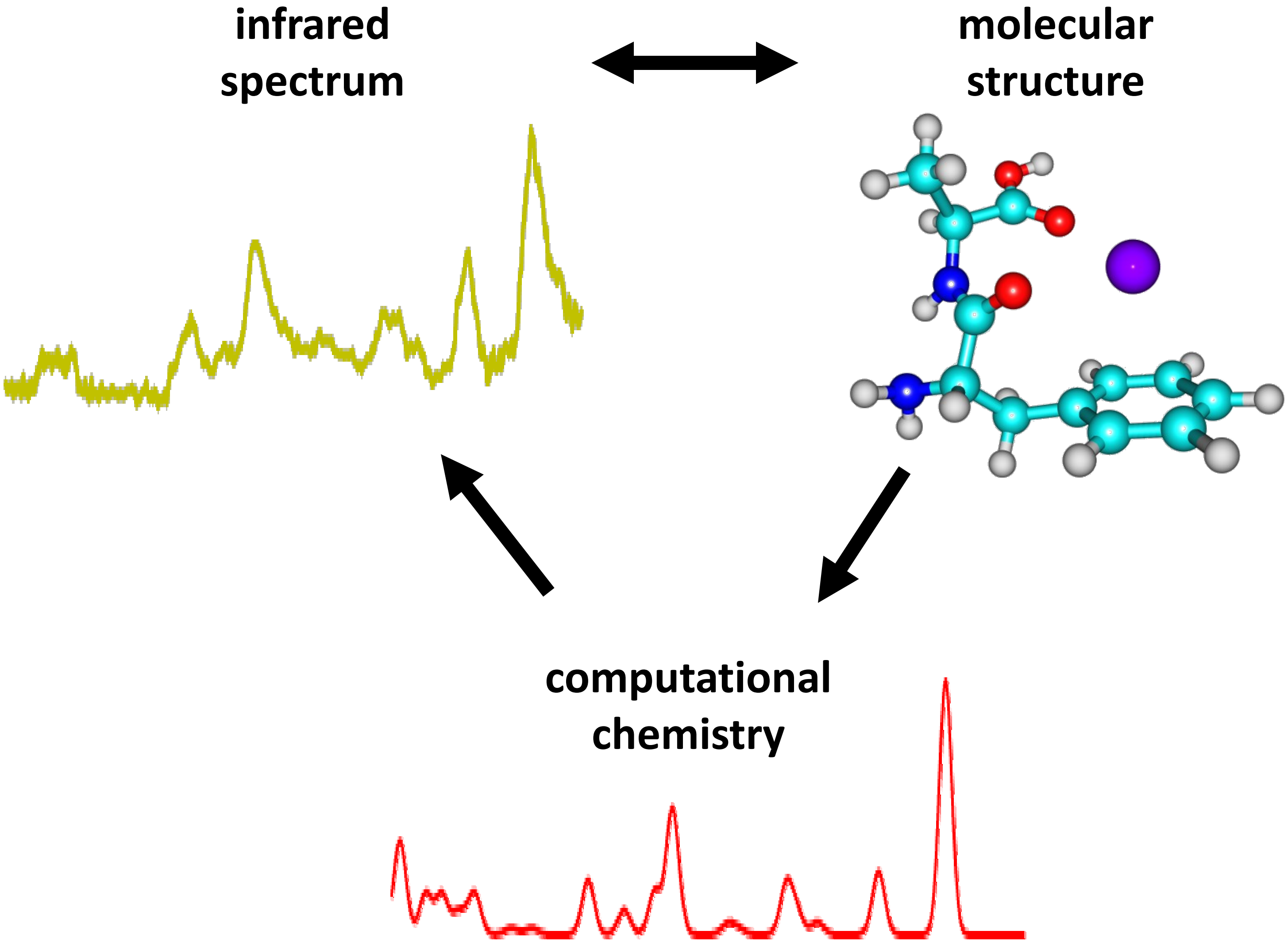


Red shift with increasing T due to anharmonicity

Joblin et al. A&A 299, 1995

Infrared spectroscopy – molecular structure

characteristic vibrations



infrared spectrum

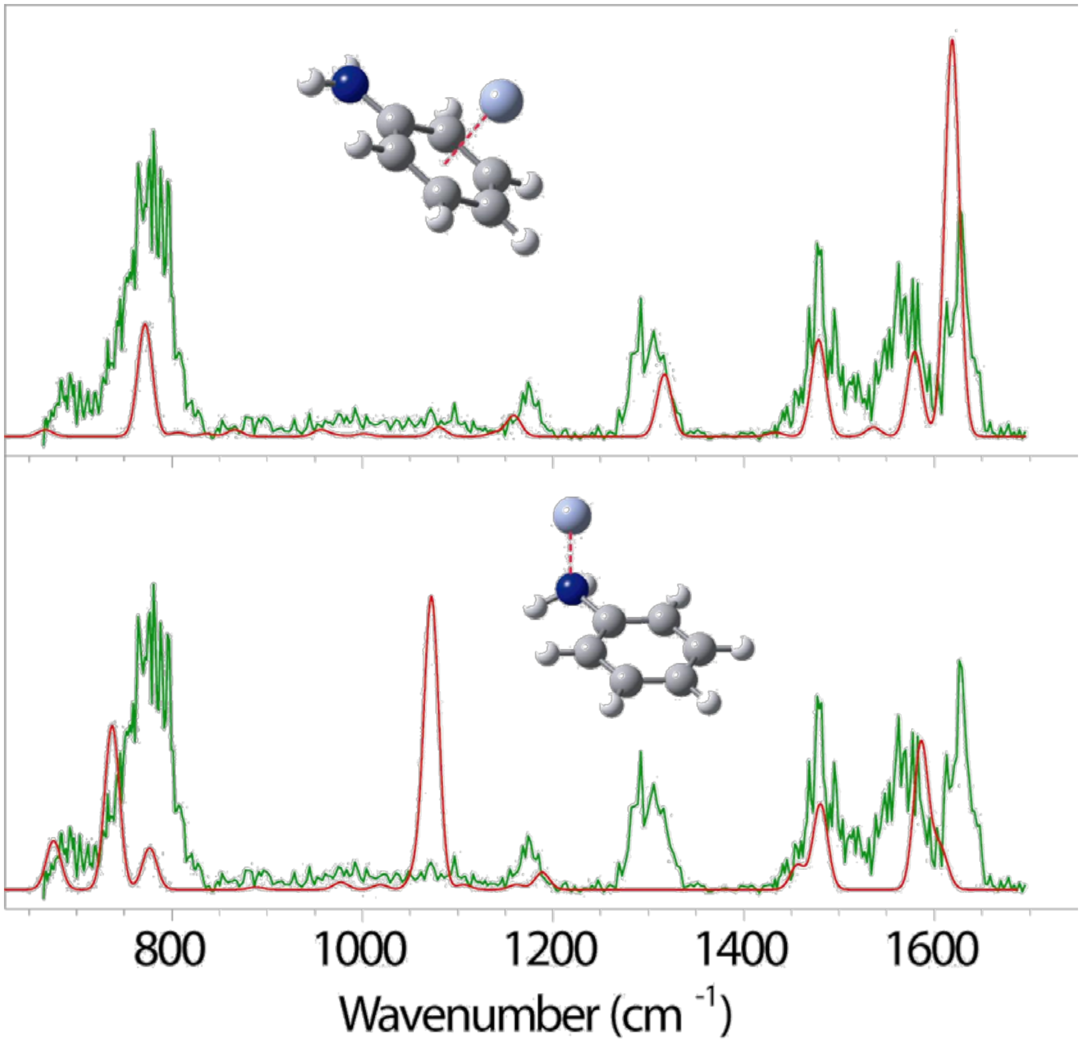
molecular structure

computational chemistry

Cr^+aniline: ring or nitrogen bound ?

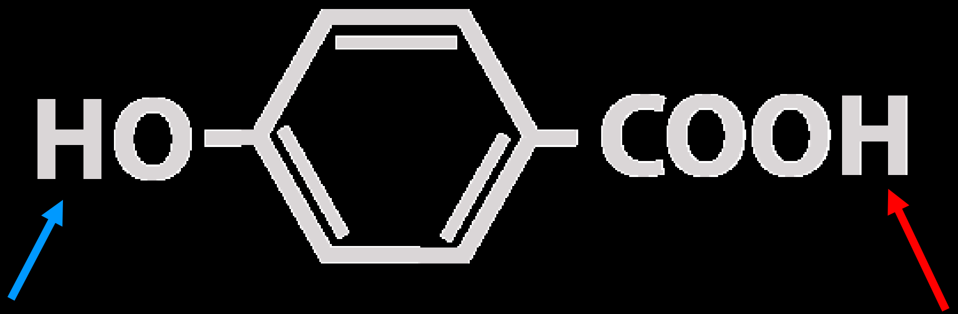
B3LYP: N-bound (ΔE = 7.2 kJ/mol)

MP1PW91: ring-bound (ΔE = 7.0 kJ/mol)



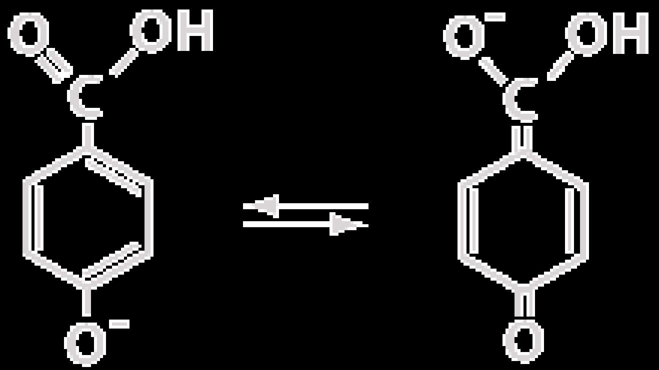
Site of deprotonation

***para*-hydroxy benzoic acid**



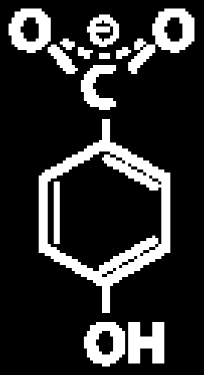
more acidic in gas phase

more acidic in solution



phenoxide

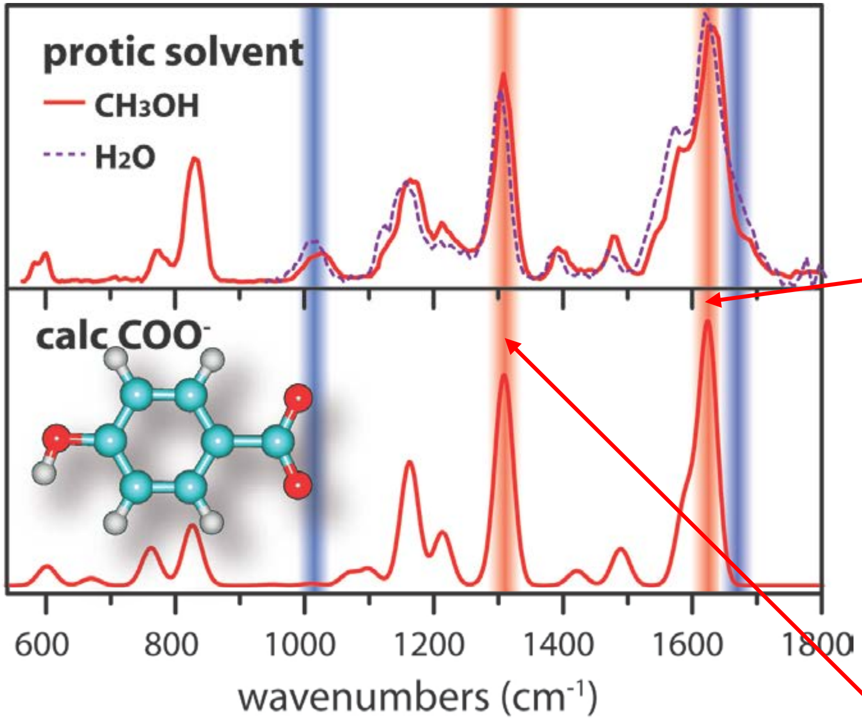
-33 kJ/mol

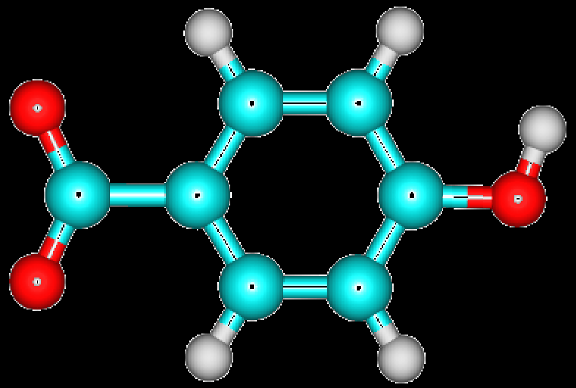


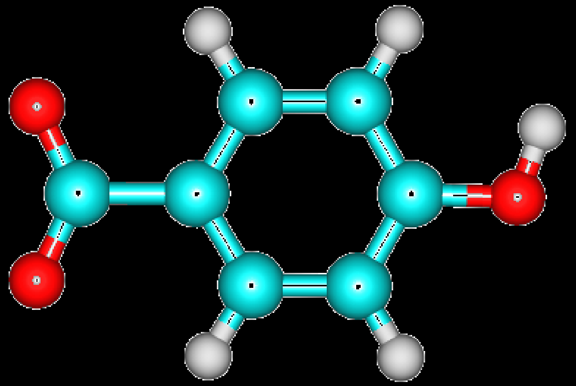
carboxylate

McMahon & Kebarle, *JACS* **1977**, *99*, 2222

Site of deprotonation

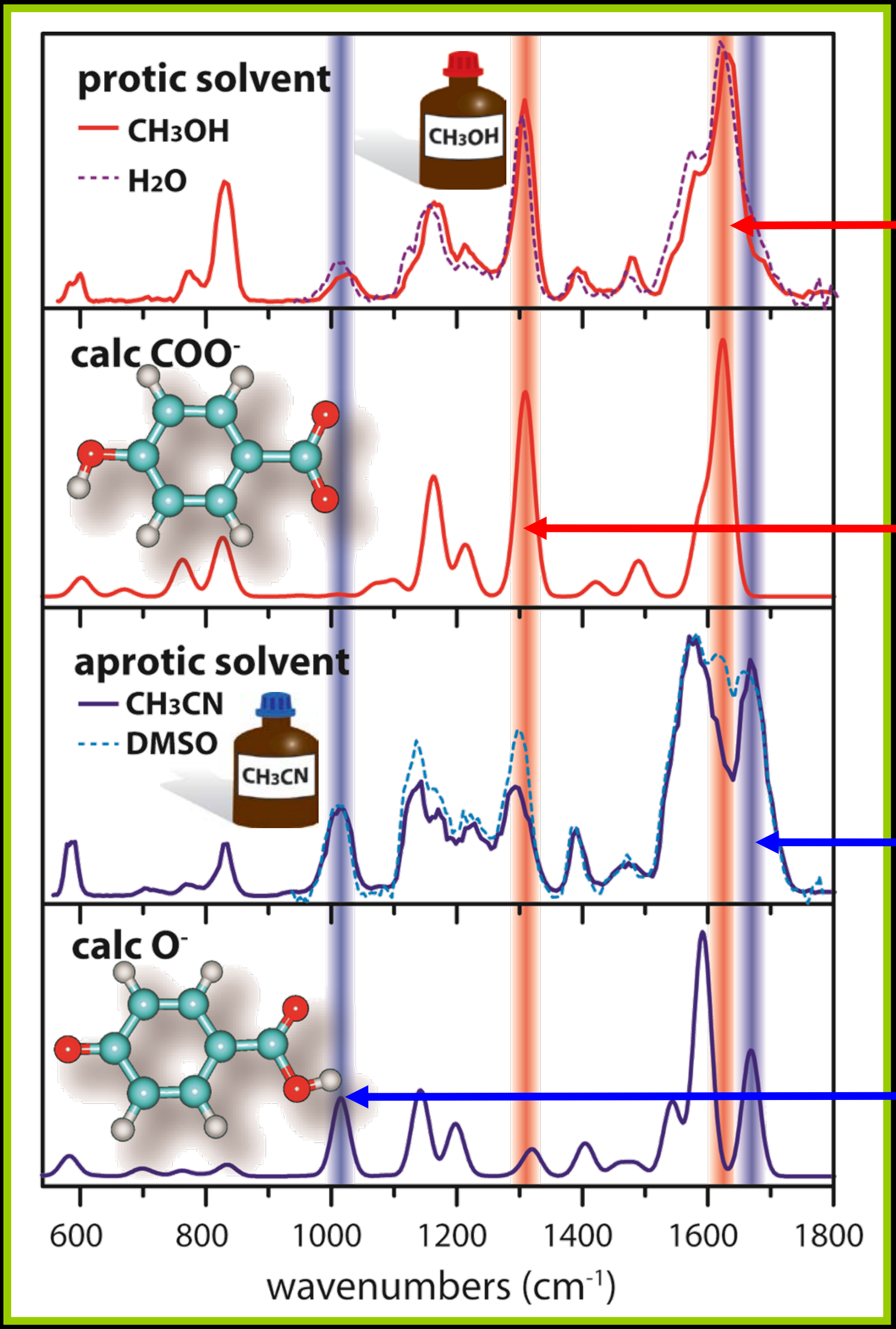


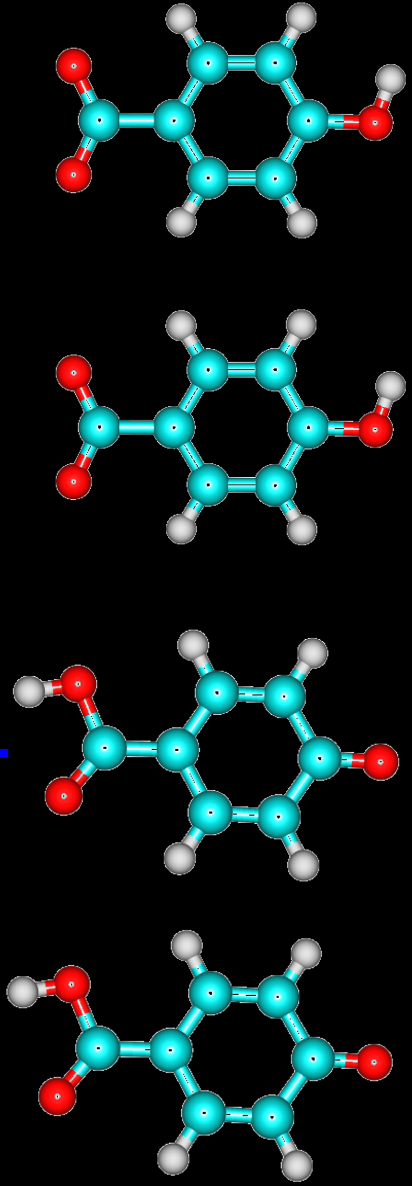




Steill & Oomens, *JACS* **2009**, *131*, 13570

Site of deprotonation



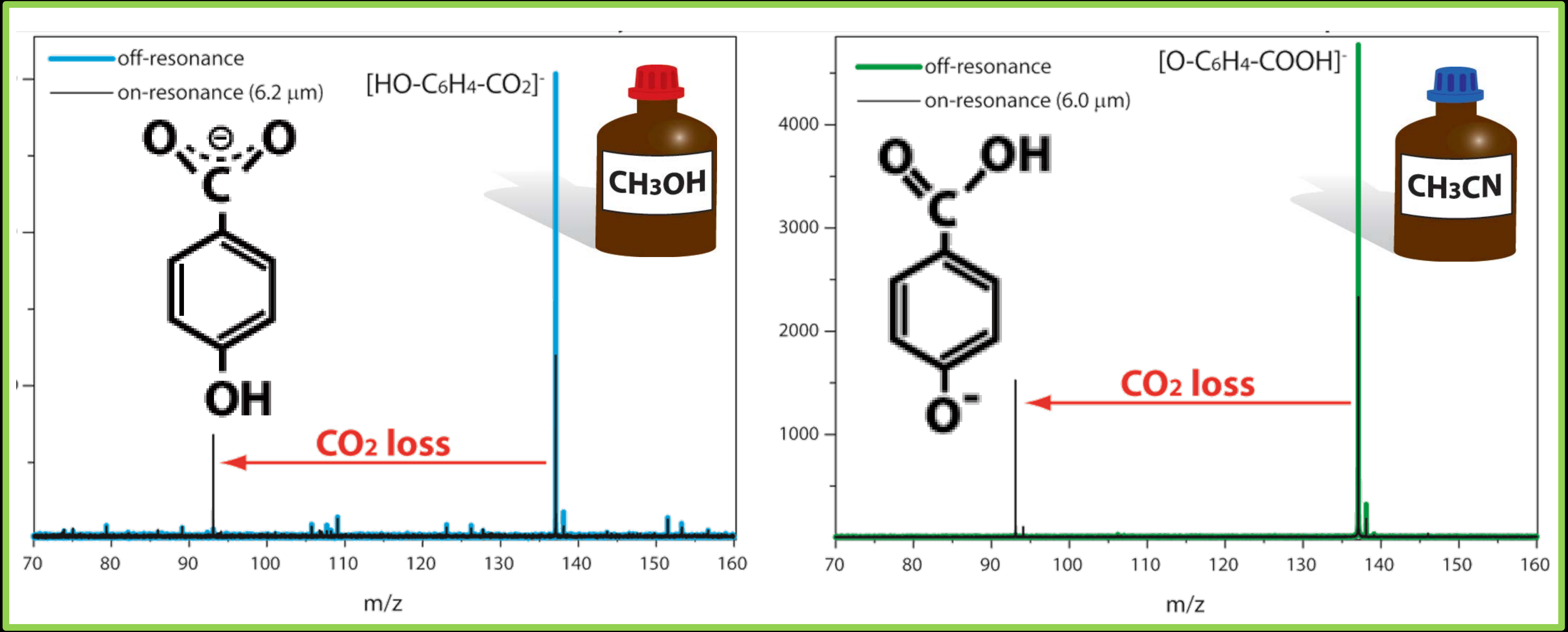


carboxylate

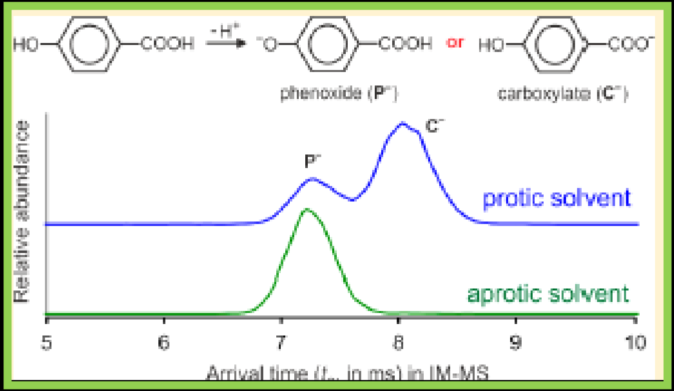
phenoxide

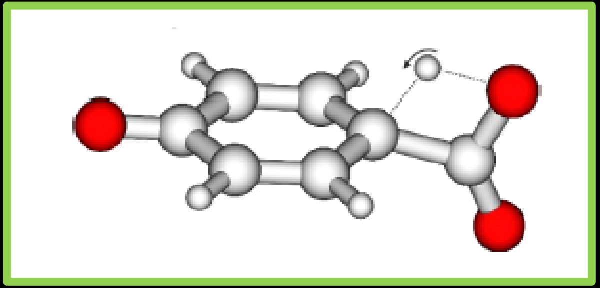
JACS **2009**, *131*, 13570

Mass spectra for *p*-HBA



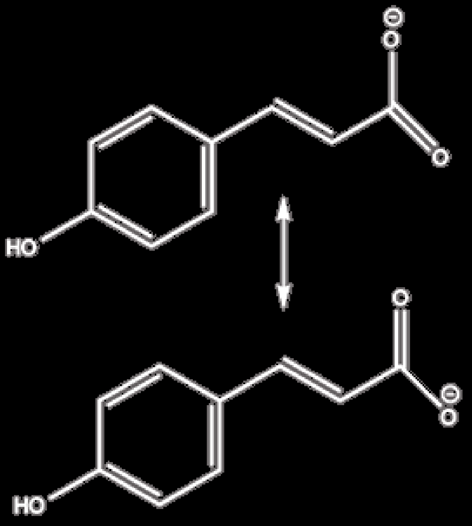
Tandem MS can be deceiving in structure determination !



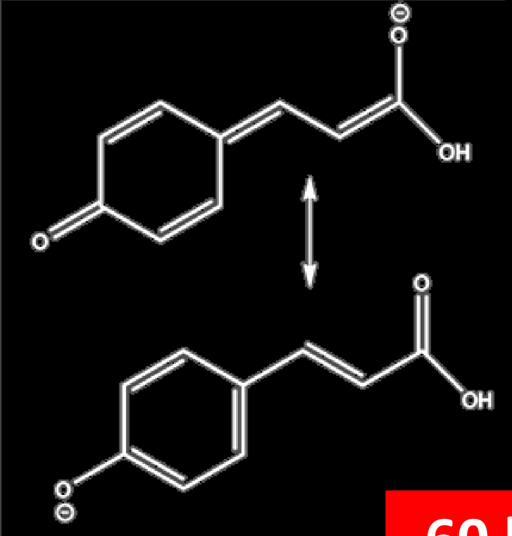


Schröder, Budesinski, Roithová, *JACS* **2012**, *134*, 15897

Deprotonation site: chromophore of PYP

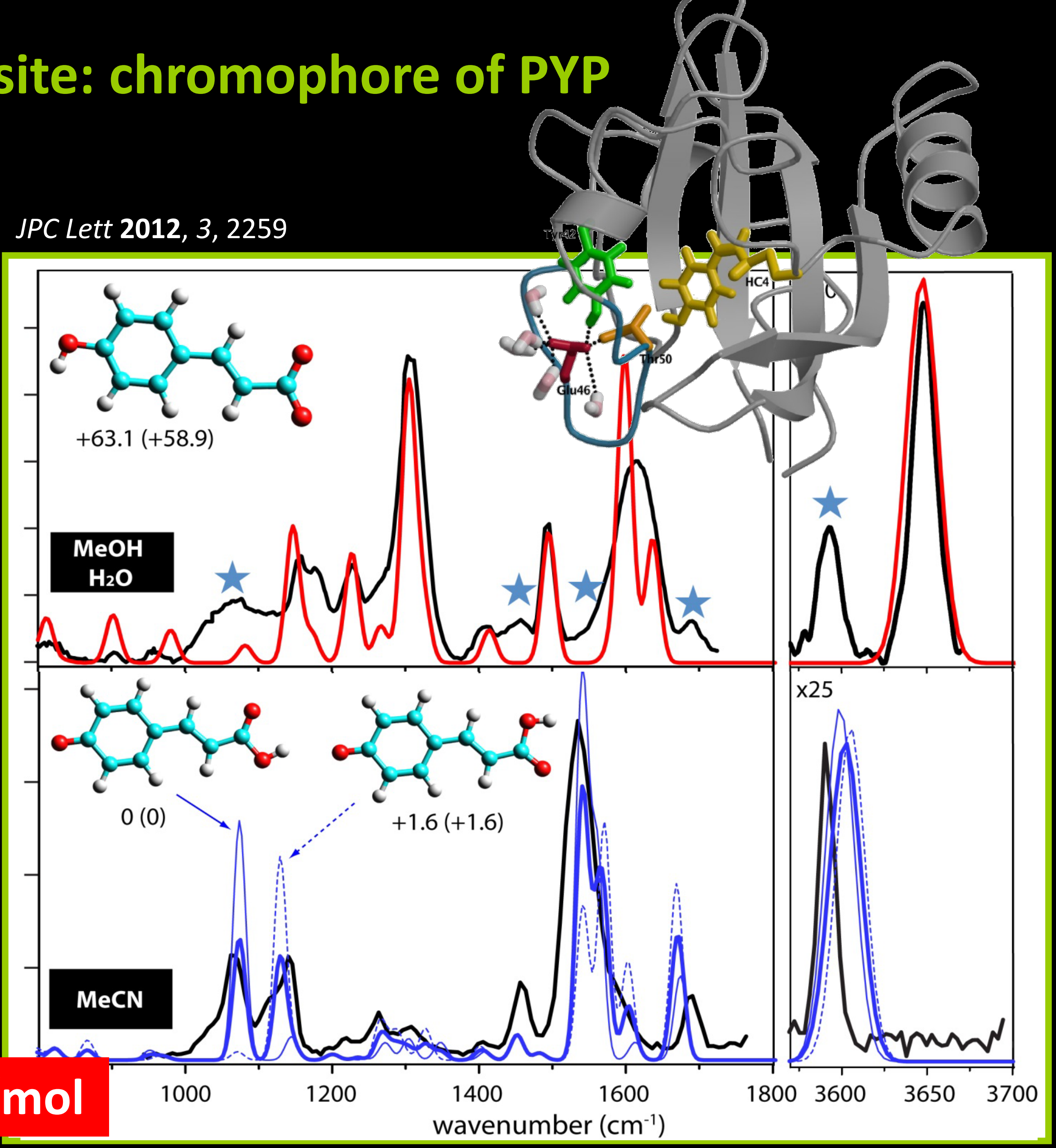


carboxylate



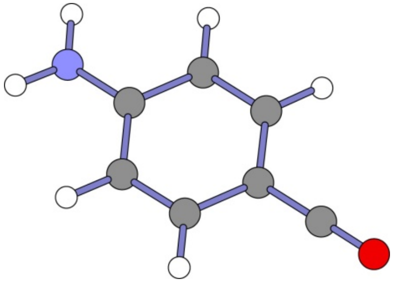
phenoxide

JPC Lett **2012**, *3*, 2259



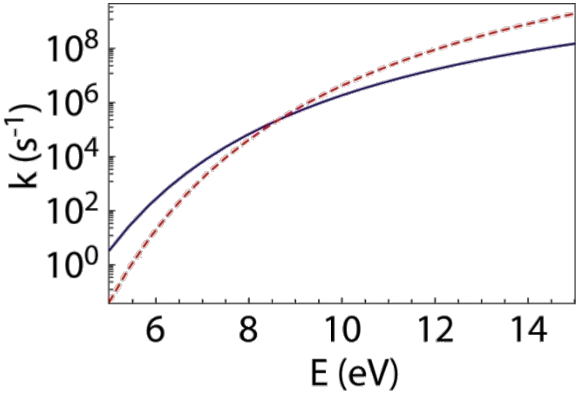
-60 kJ/mol

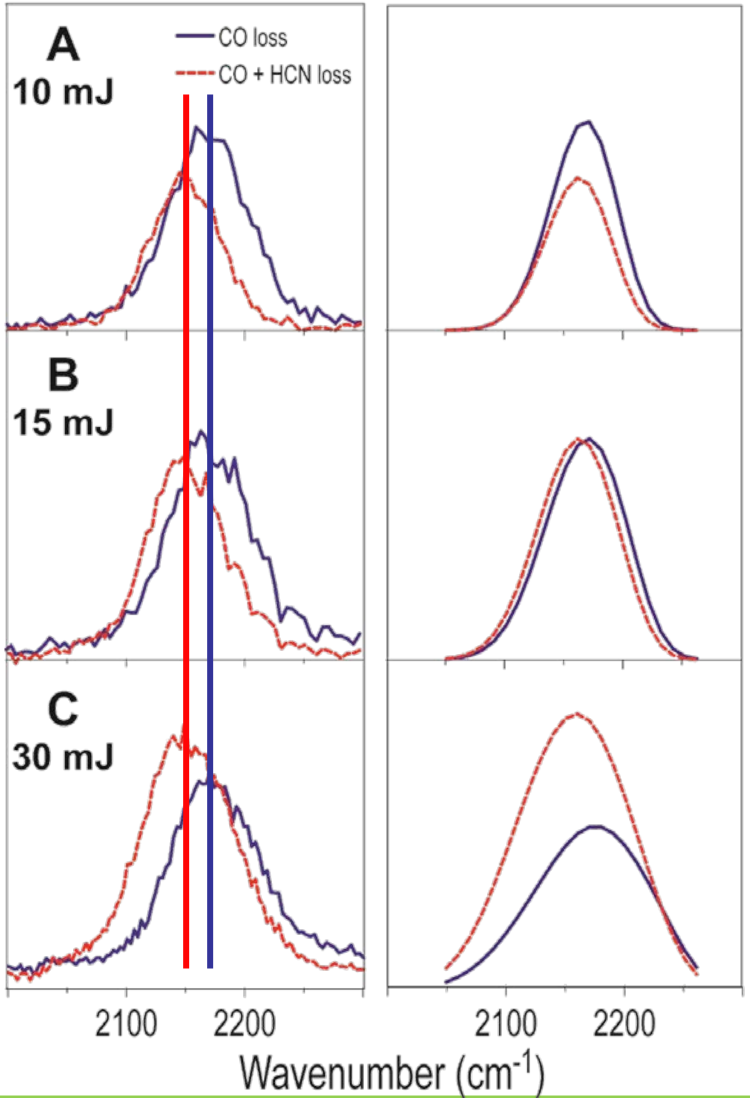
Exit channel dependent IRMPD spectra



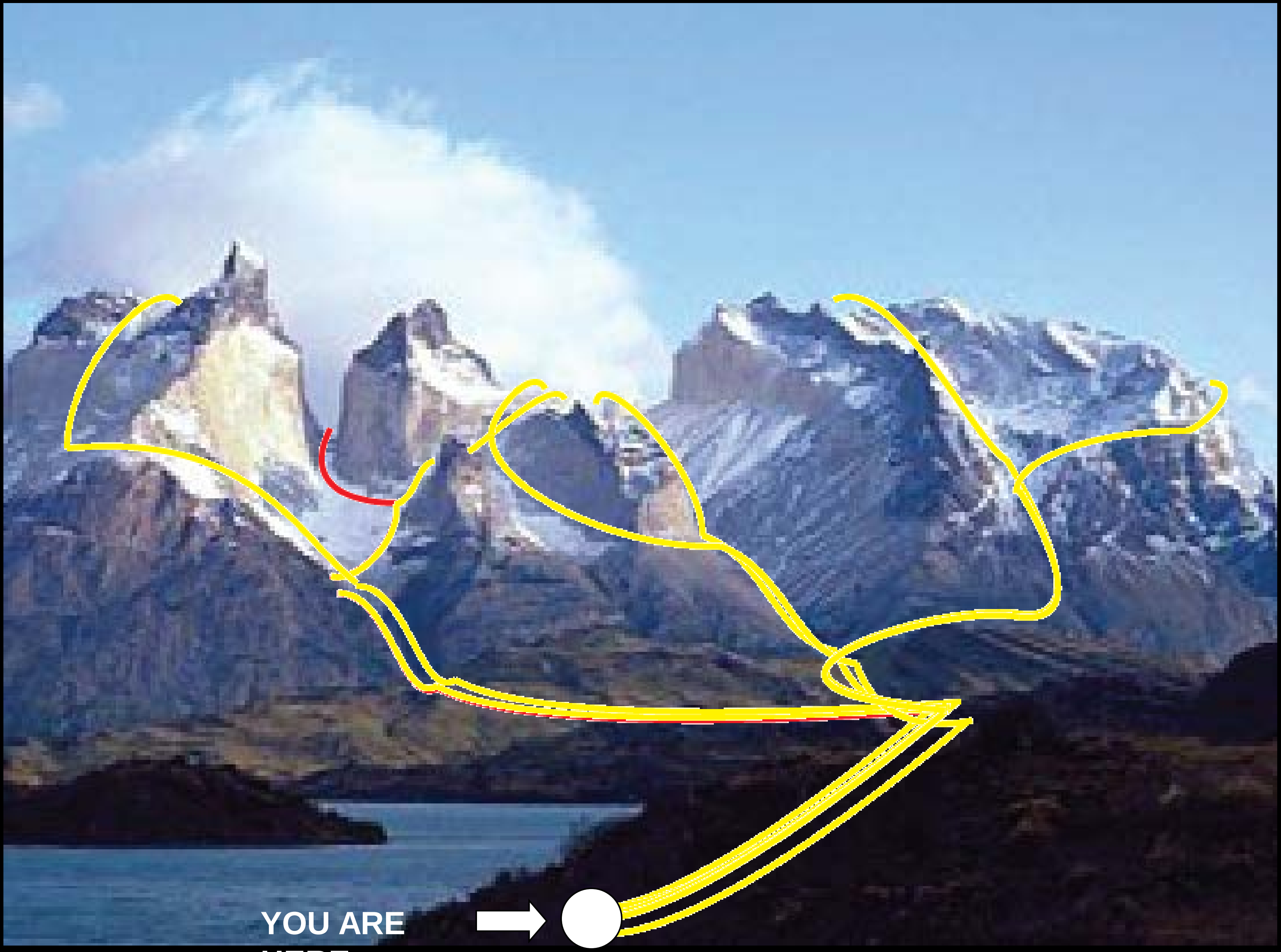
***para*-amino benzoyl ion**

CO loss	3.5 eV
CO+HCN loss	4.9 eV





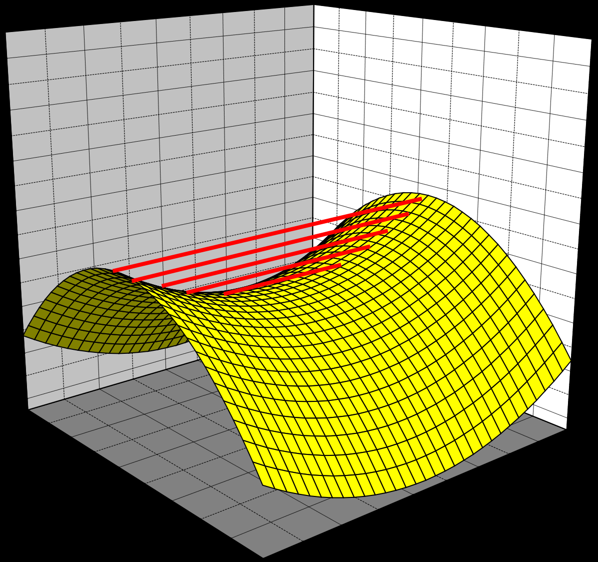
Unimolecular dissociation – transition state theory



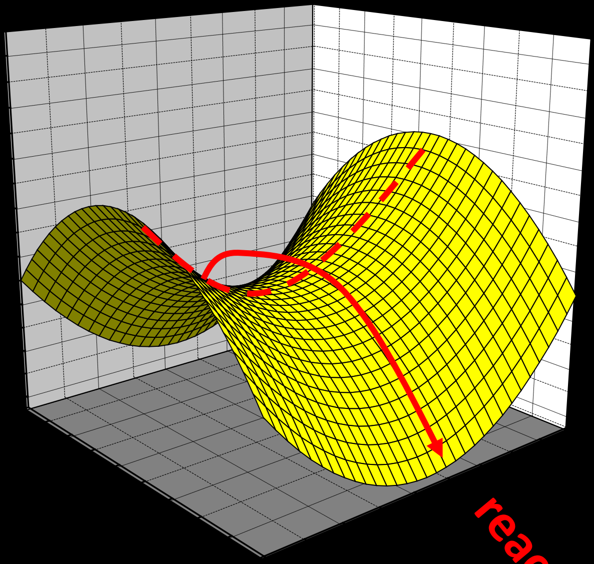
YOU ARE HERE

Unimolecular dissociation – transition state theory

Transition state: maximum along 1 coordinate
minimum along other coordinates

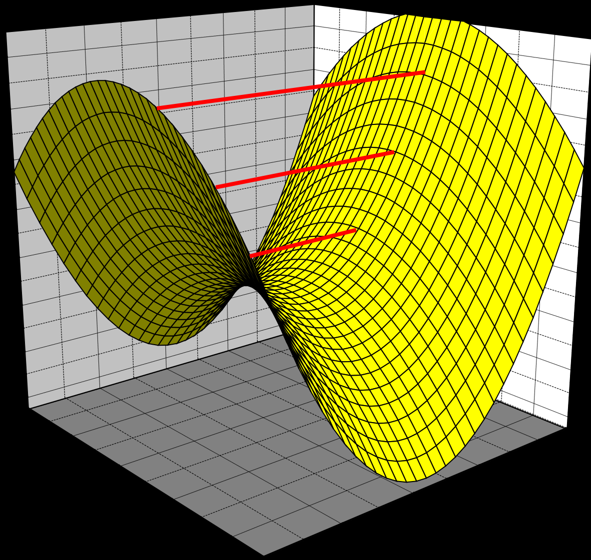


Loose TS
High state density
High entropy



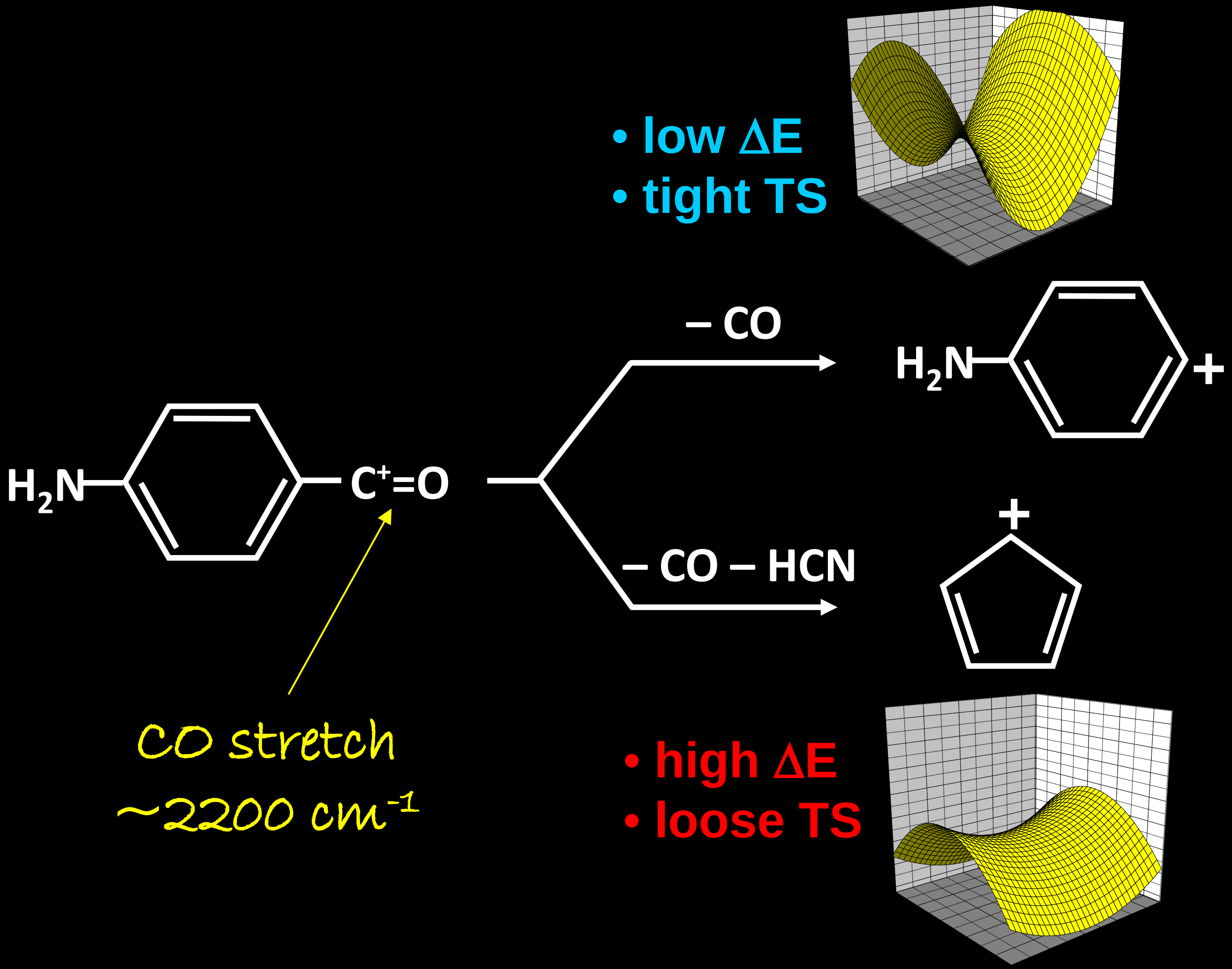
reaction coordinate

free energy
$\Delta G = \Delta E - T\Delta S$



Tight TS
Low state density
Low entropy

IRMPD spectra of *p*-ABz$^+$



- low ΔE
- tight TS

m/z 92

m/z 65

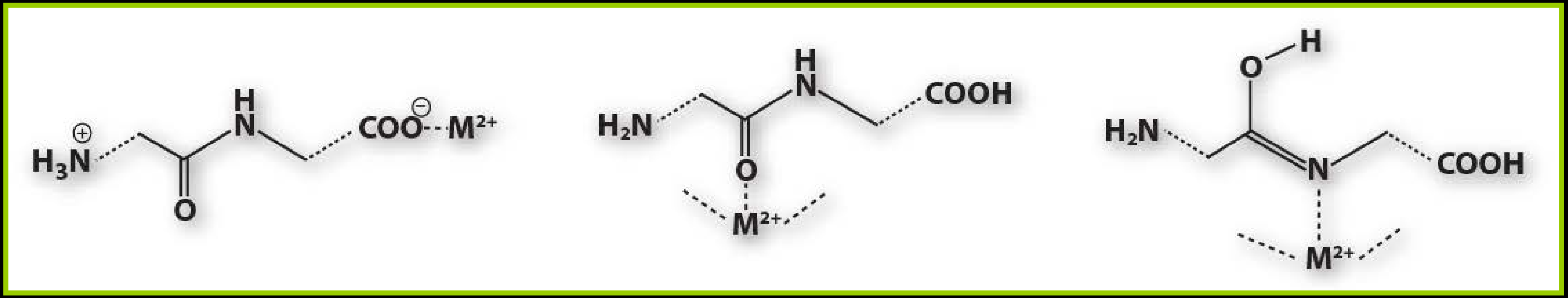
- high ΔE
- loose TS

CO stretch

~2200 cm^{-1}

Metal-ion peptide binding

How peptides chelate metal ions in the gas phase

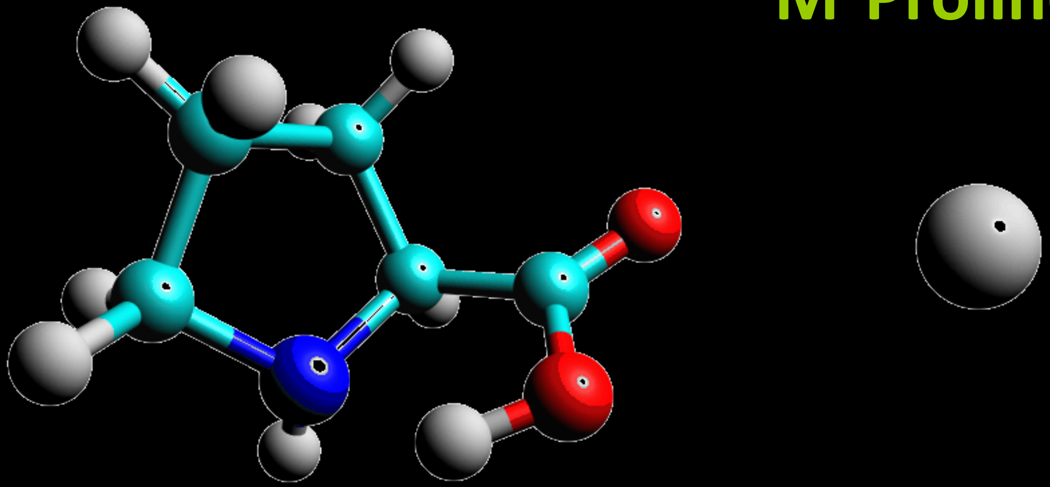


salt bridge
(zwitterion)

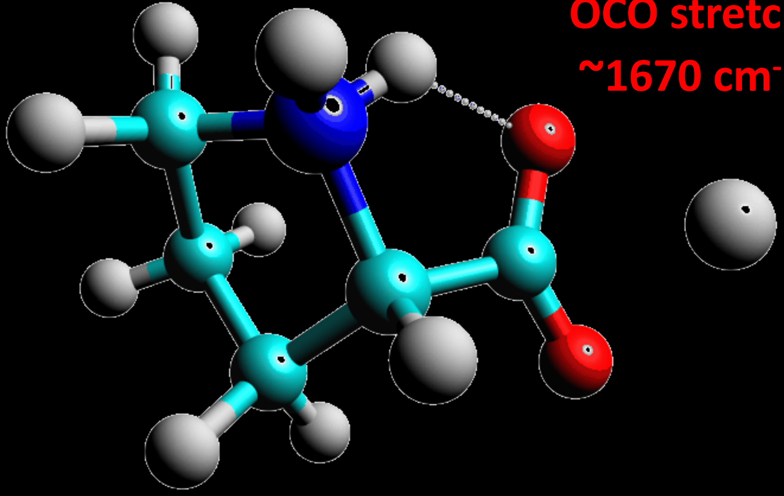
charge solvated
(‘keto’)

iminol
(‘enol’)

Charge-solvation or salt-bridge?
M$^+$Proline

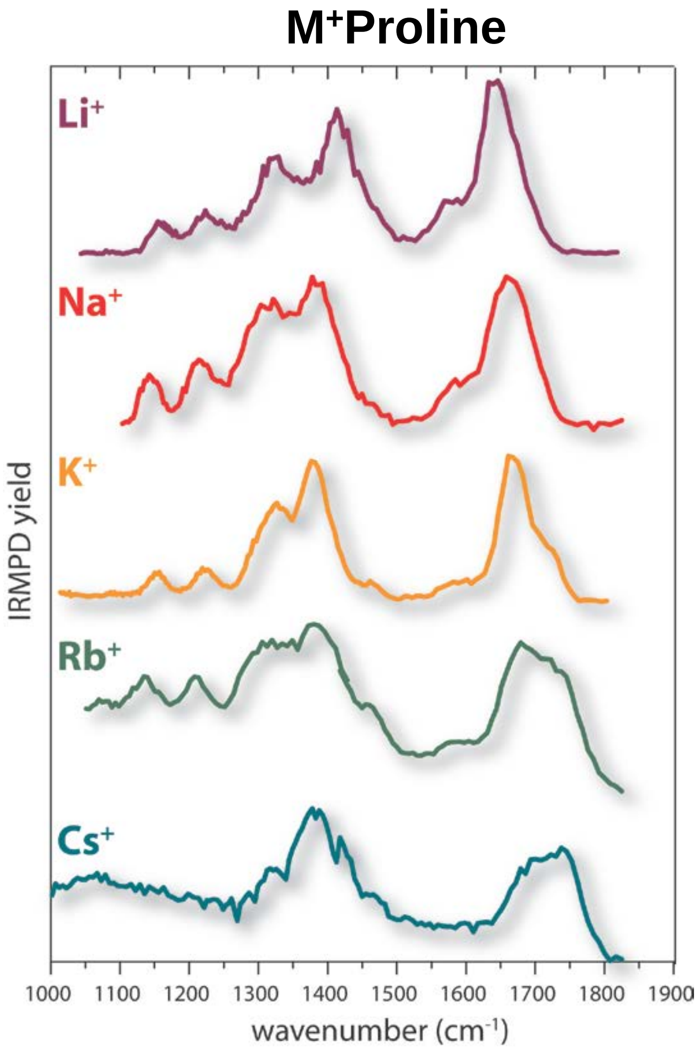


charge solvated
CO stretch
~1740 cm^{-1}



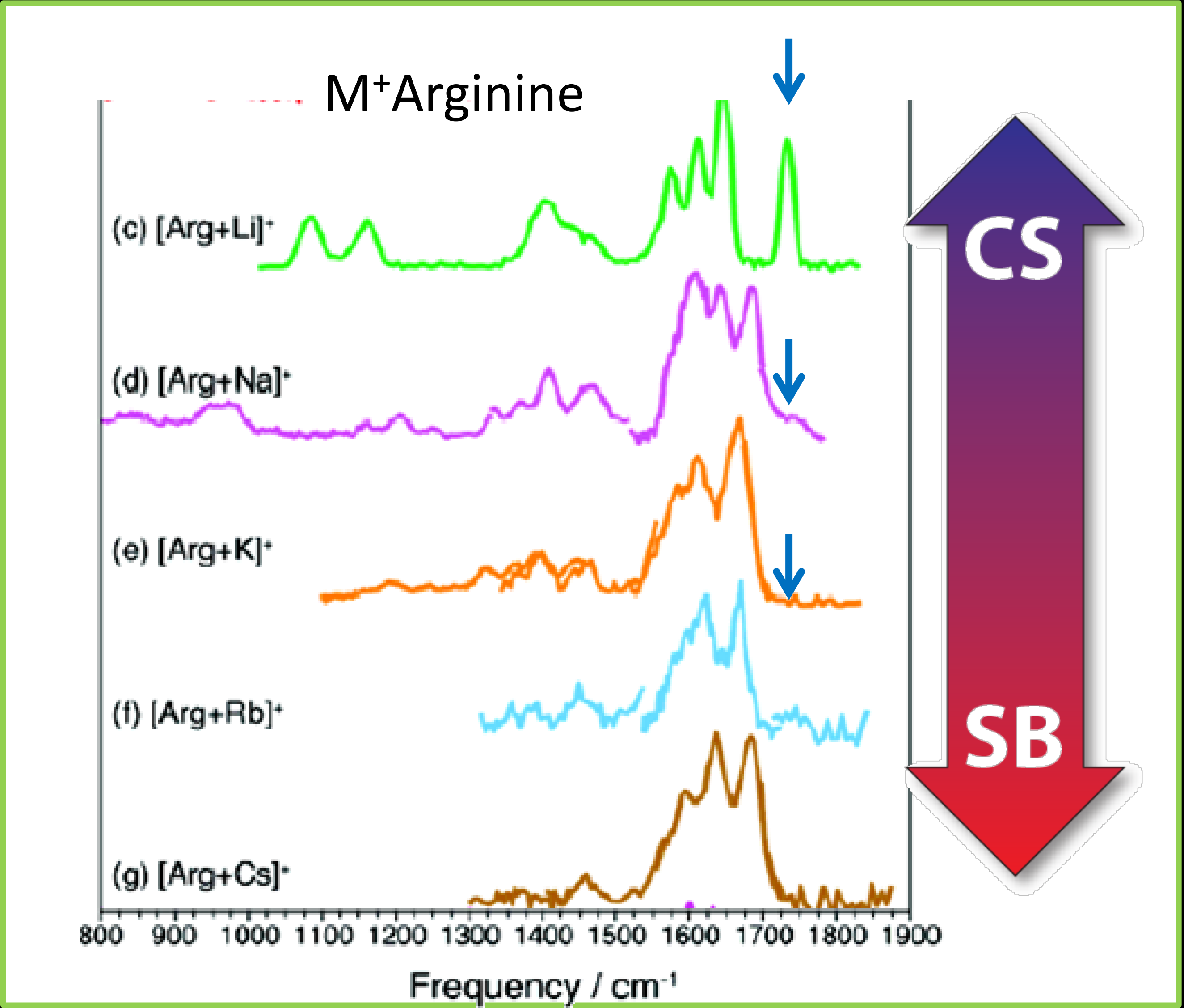
salt bridge
OCO stretch
~1670 cm^{-1}

Coordination: trends with metal ion size



Int J Mass Spectrom **2010**, *297*, 18

Coordination: trends with metal ion size



Forbes, Bush, Polfer, Oomens, Dunbar,
Williams, Jockusch, *JPC-A* **2007**, *111*, 11759

Coordination: trends with metal ion size

- **Smaller ion:**

dominates for aliphatic AA

→ higher charge density, more polarizing

→ induces charge separation more easily

→ tends to favor SB

- **Smaller ion:**

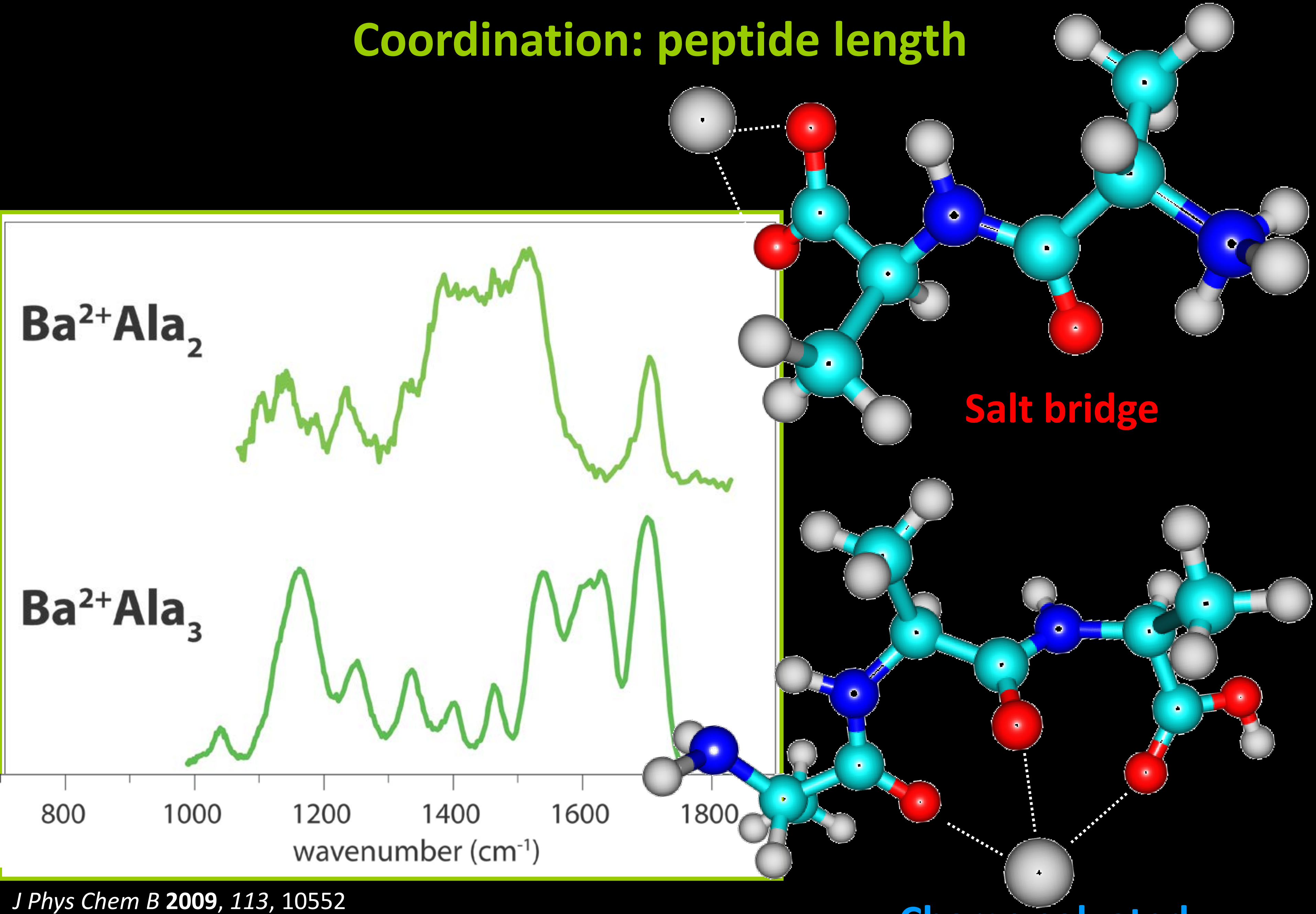
dominates for non-aliphatic AA

→ smaller ionic radius

→ sterically easier to solvate from all sides

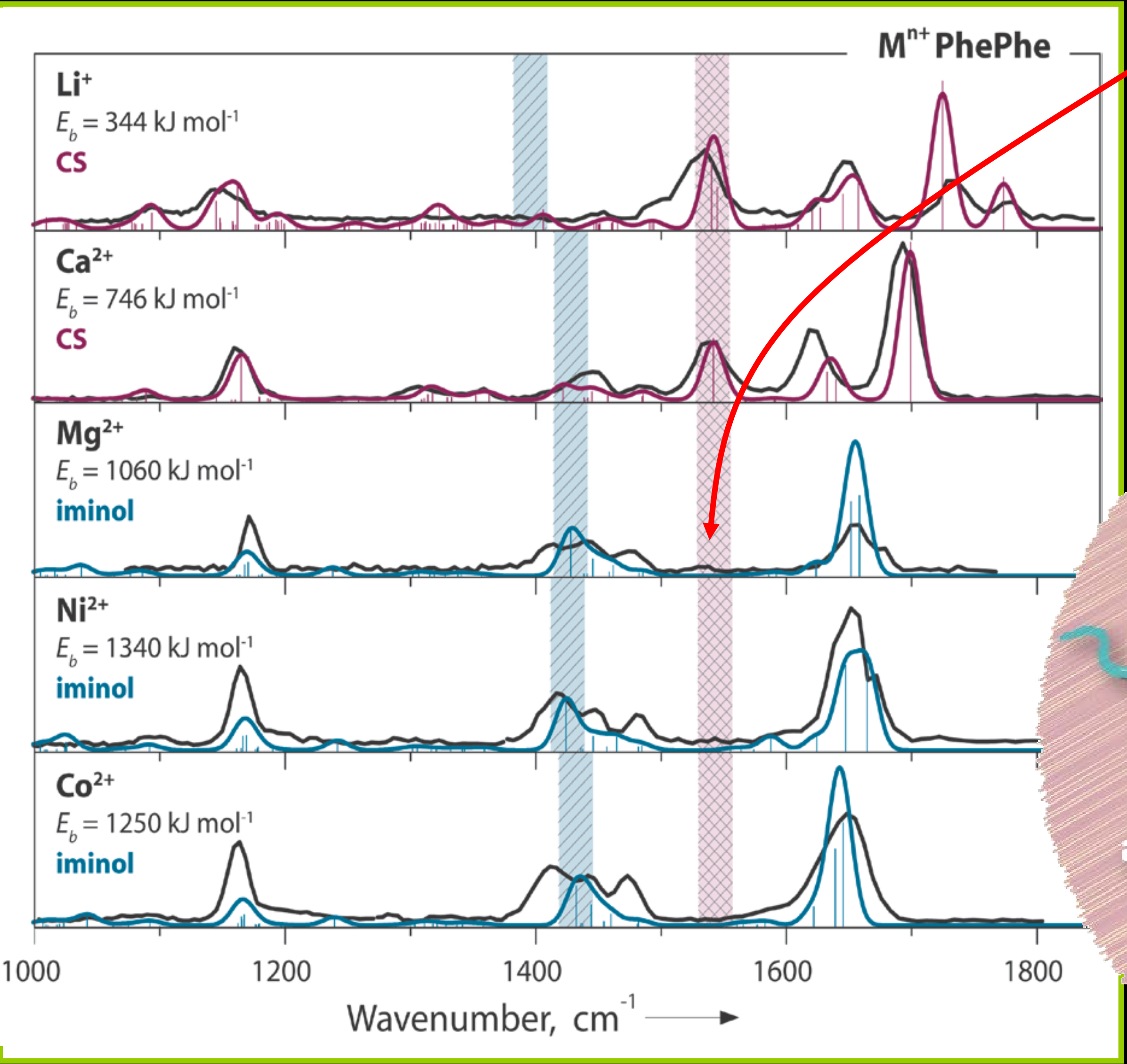
→ tends to favor CS

Coordination: peptide length



J Phys Chem B **2009**, *113*, 10552
Int J Mass Spectrom **2010**, *297*, 107

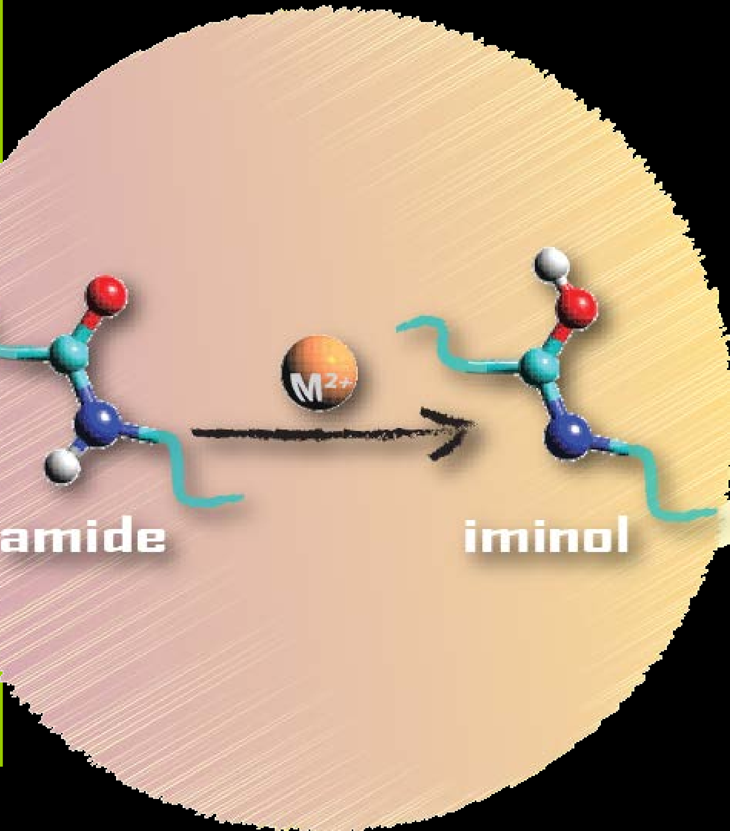
The iminol motif



No Amide II band

Strongly binding metals

Keto-enol tautomerization



Dunbar, Steill, Polfer, Berden, Oomens, *Angew Chem Int Ed* **2012,** *51*, 4591

ion chemistry: characterizing ion reactions

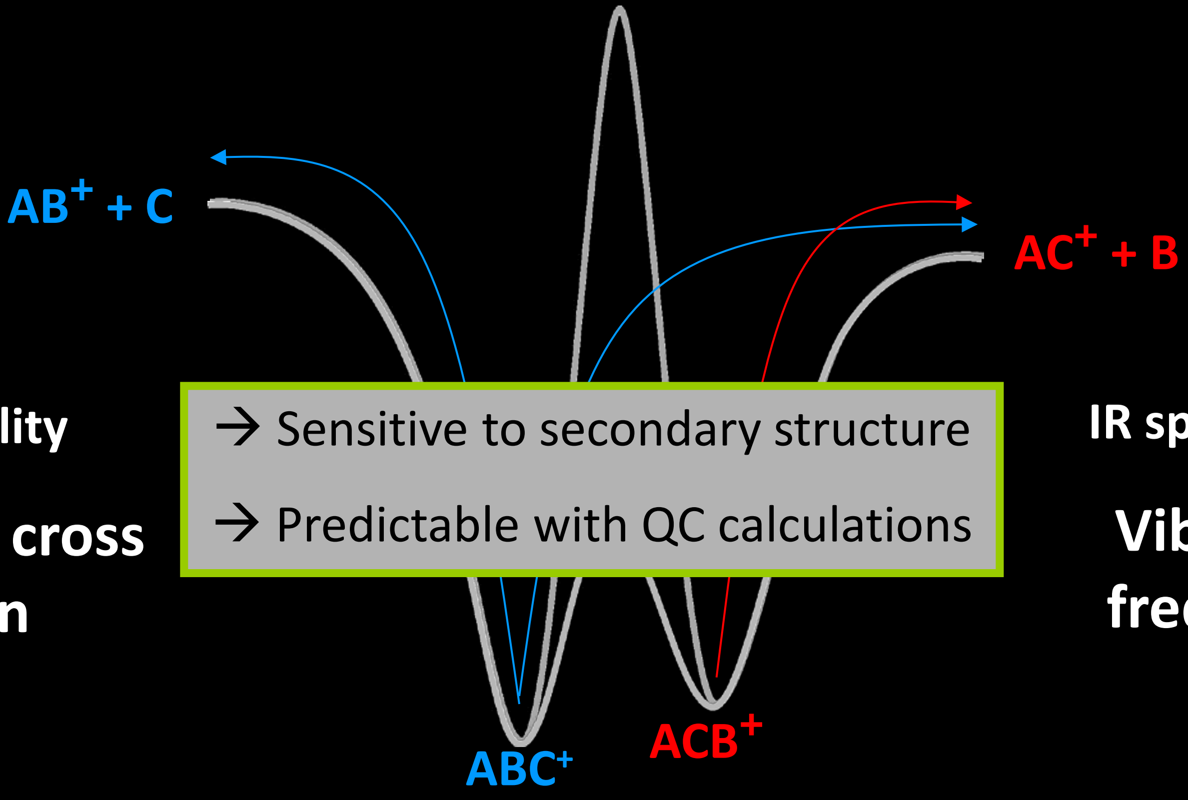
- Molecular structure determination
- Identification

Collision induced dissociation

Ion-molecule reaction

H/D exchange

Based on unknown reaction mechanisms



→ Sensitive to secondary structure

→ Predictable with QC calculations

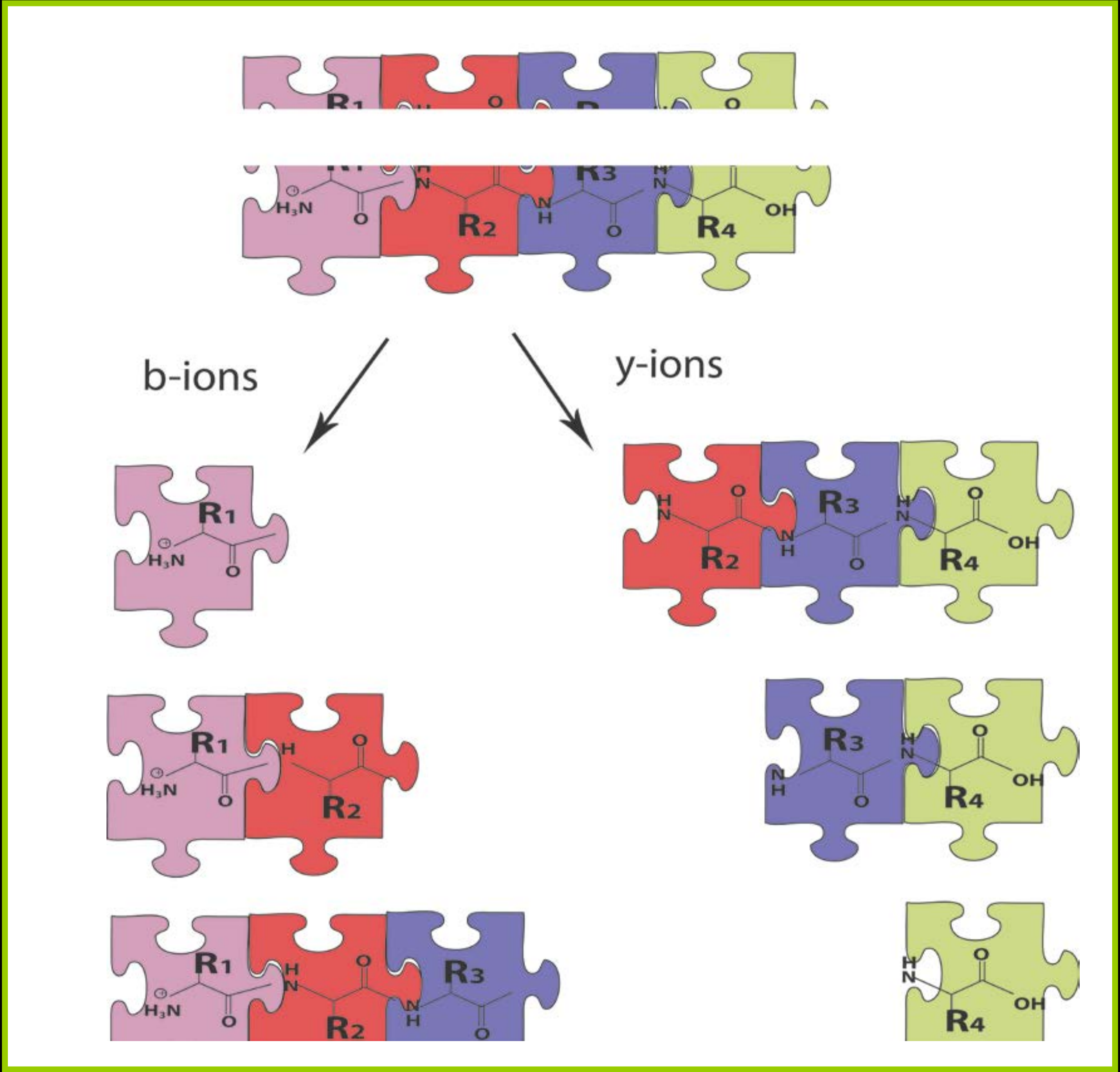
Ion mobility

Collisional cross section

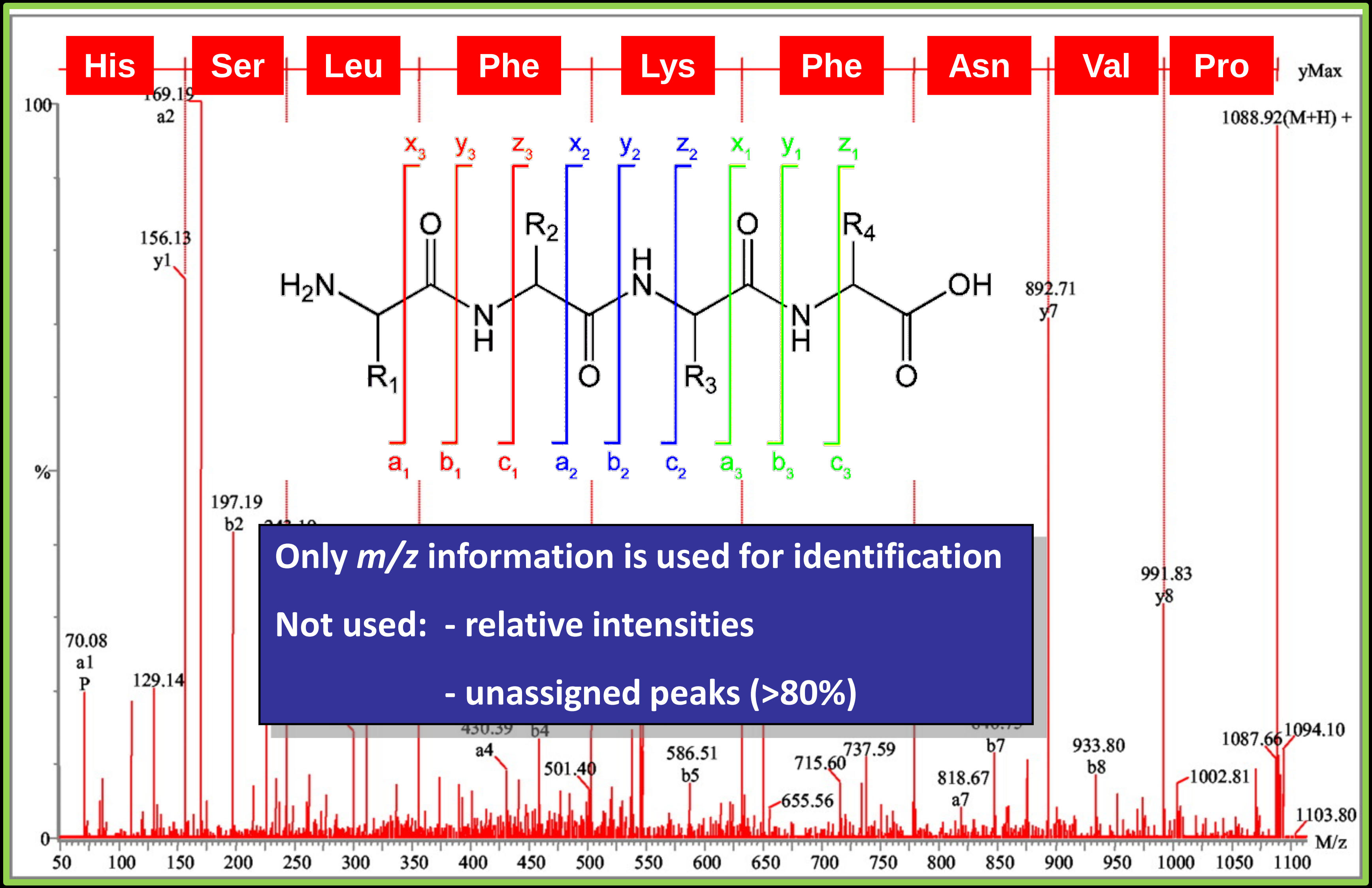
IR spectroscopy

Vibrational frequencies

Peptide sequencing by mass spectrometry



Peptide sequencing by mass spectrometry



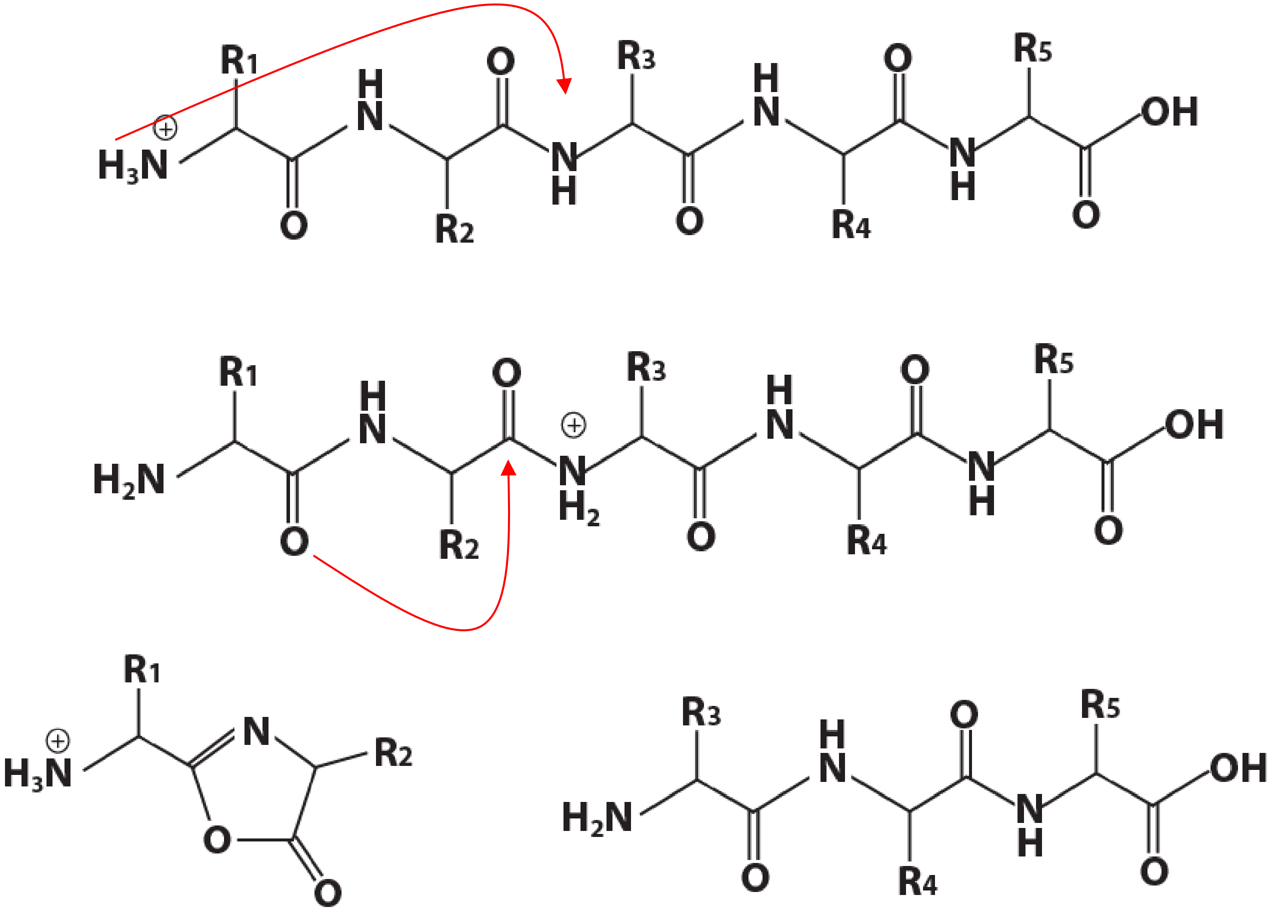
Only *m/z* information is used for identification

Not used: - relative intensities

- unassigned peaks (>80%)

MS/MS spectrum

b/*y* fragmentation pathway



mobile proton

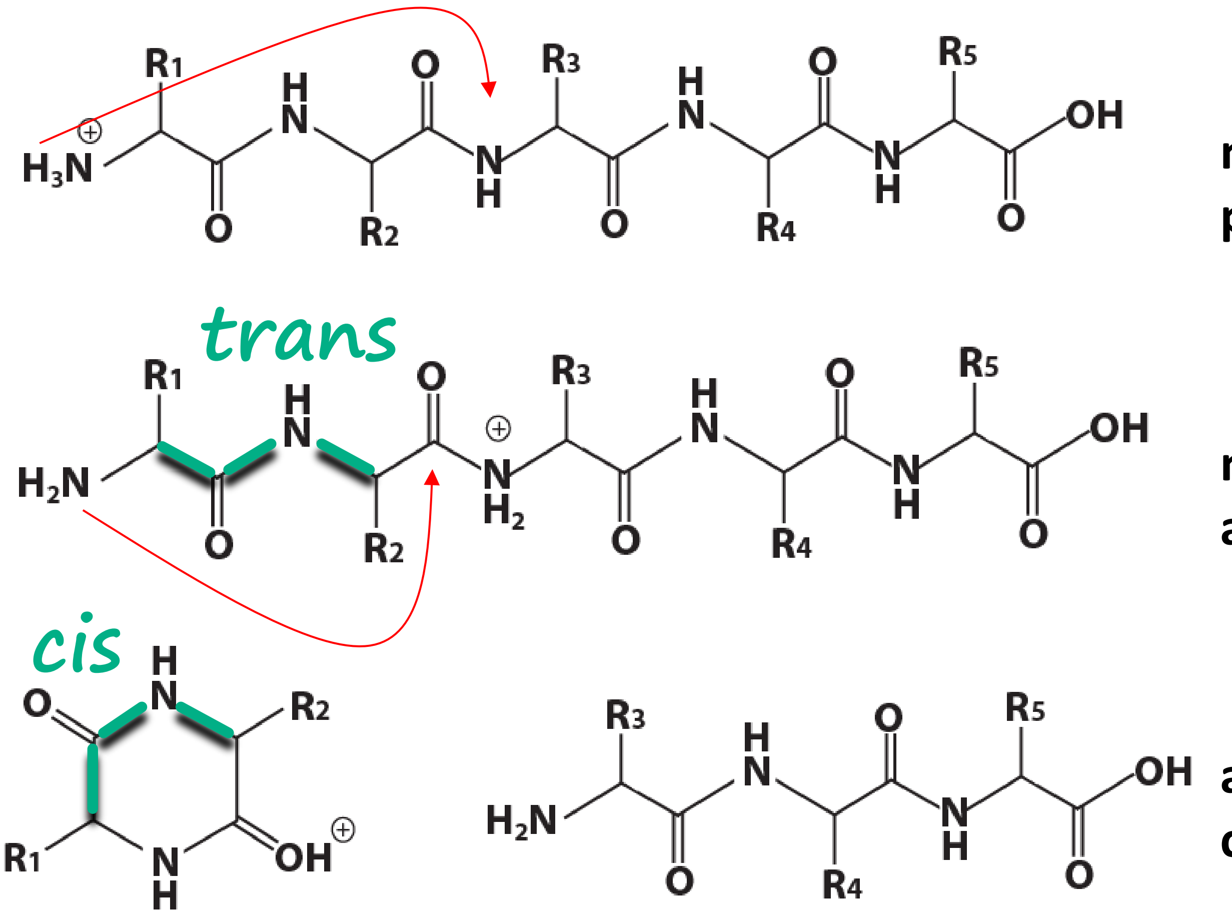
nucleophilic attack

amide bond cleavage

b-fragment: oxazolone

(*y*-fragment: truncated peptide)

Alternative *b/y* pathway: N-terminus as nucleophile



mobile proton

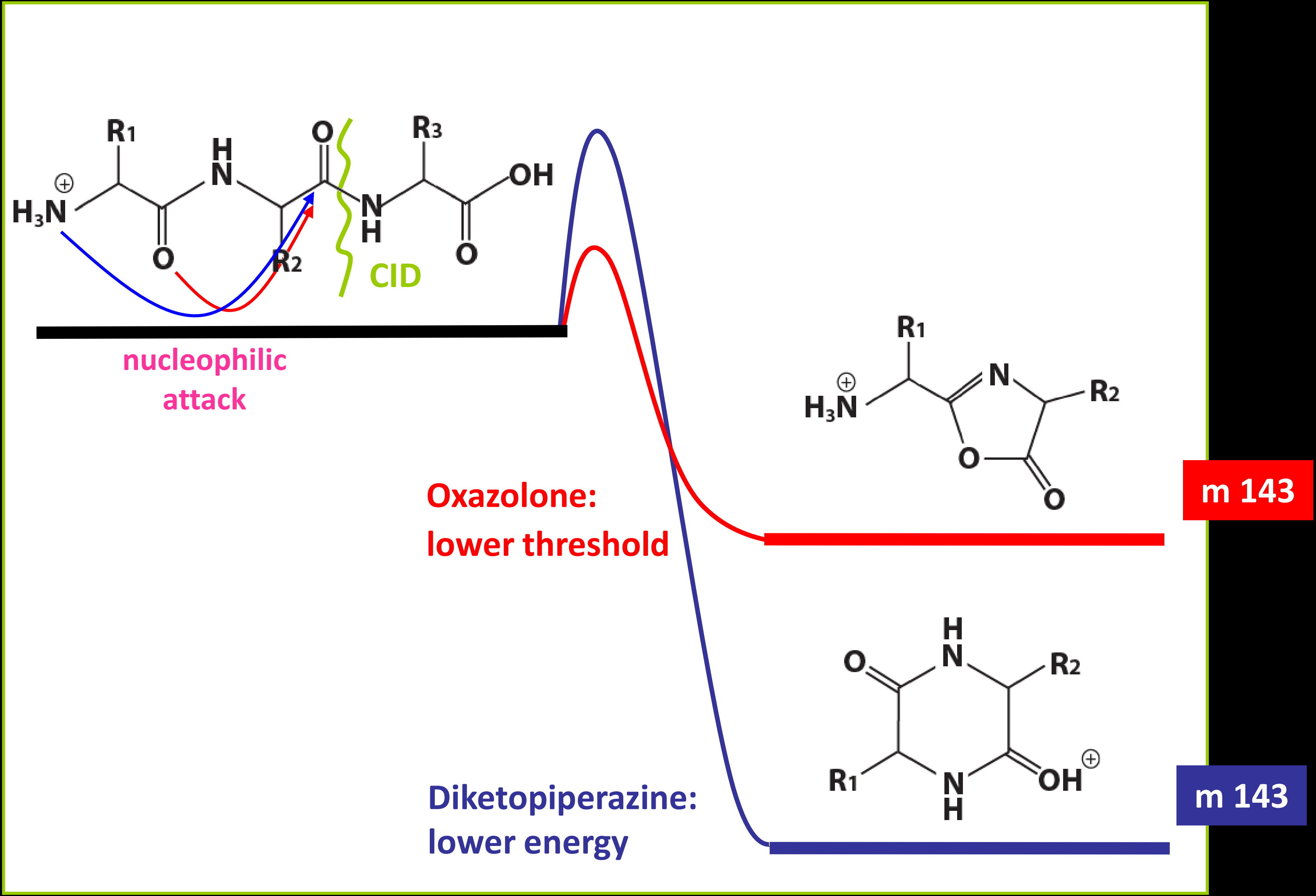
nucleophilic attack

amide bond cleavage

***b*-fragment: diketopiperazine** (*y*-fragment: truncated peptide)

Lower in energy than oxazolone !

Peptide fragmentation: *b*-type ions



nucleophilic attack

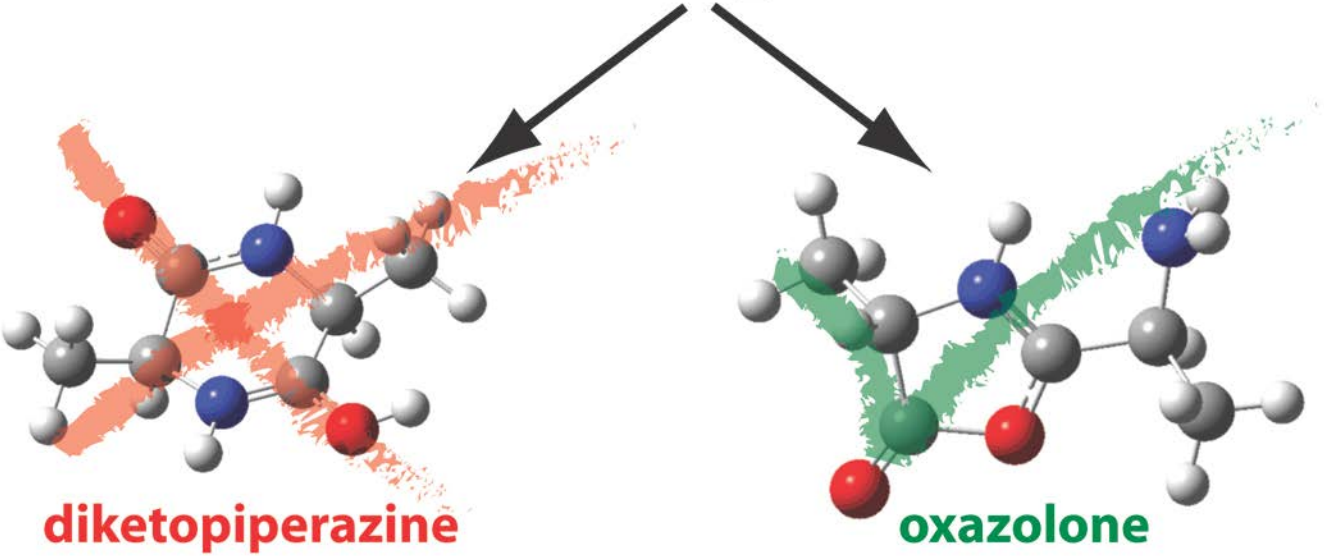
Oxazolone: lower threshold

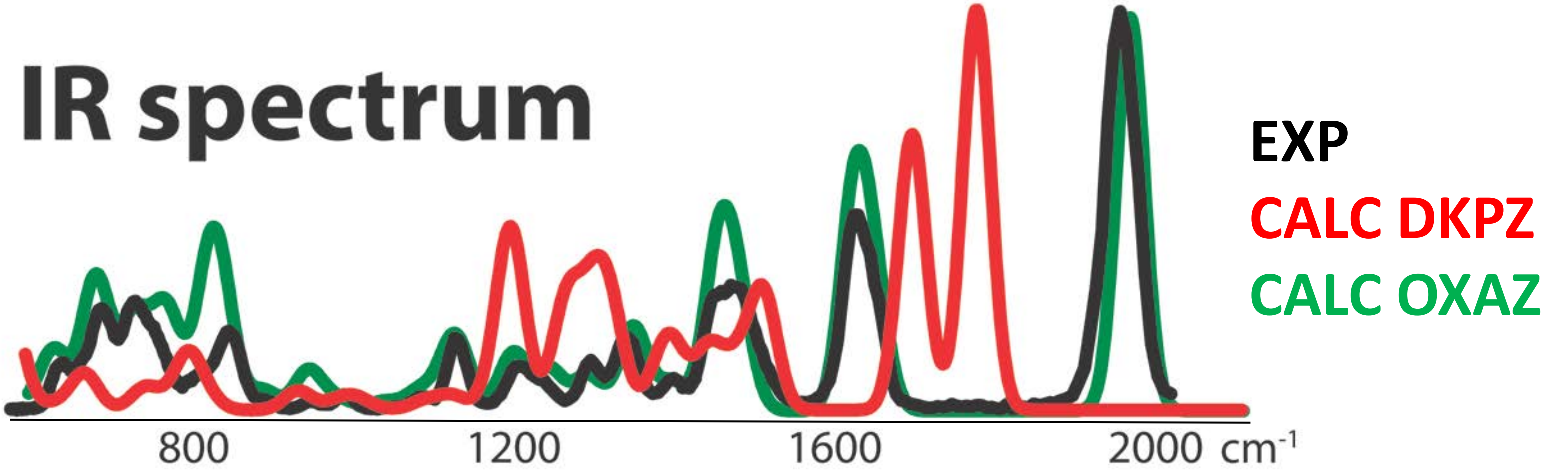
m 143

Diketopiperazine: lower energy

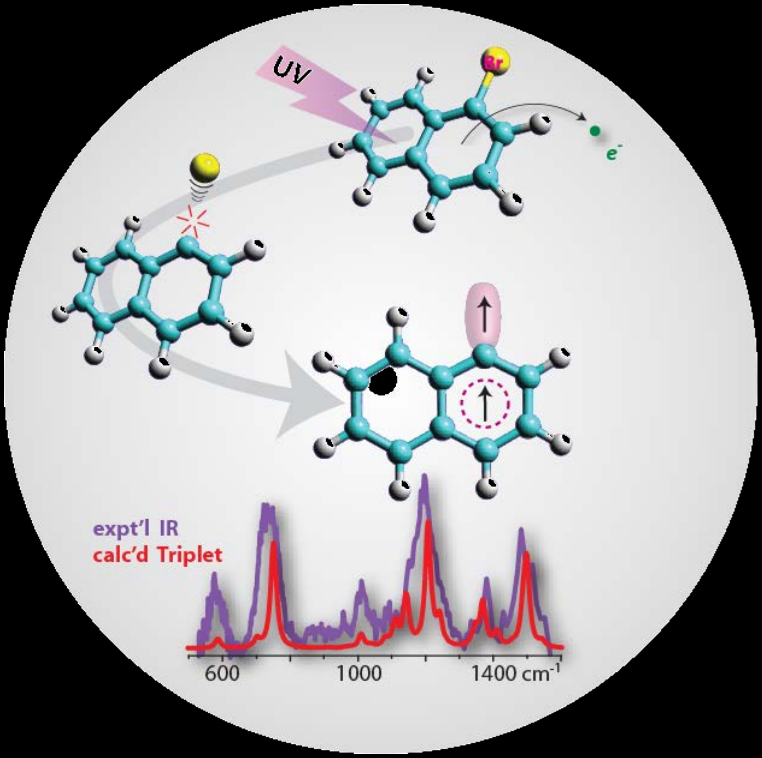
m 143

$\text{AlaAlaAlaH}^+ \xrightarrow{\text{CID}} b_2$

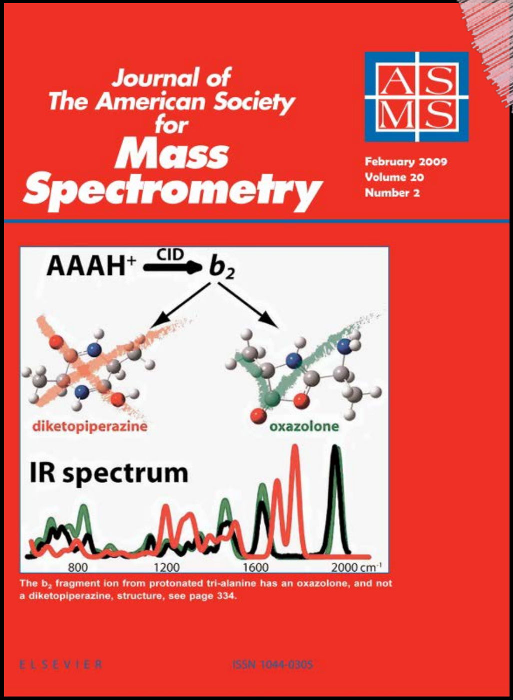




ion spectroscopy → ion structure



electronic state aryl cations



Journal of The American Society for Mass Spectrometry

AS MS

February 2009
Volume 20
Number 2

AAAH$^+$ $\xrightarrow{CID}$ b_2

diketopiperazine

oxazolone

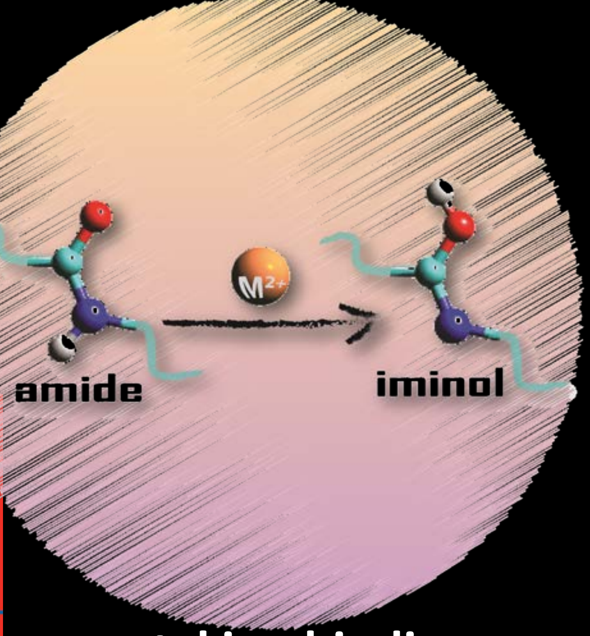
IR spectrum

The b_2 fragment ion from protonated tri-alanine has an oxazolone, and not a diketopiperazine, structure, see page 334.

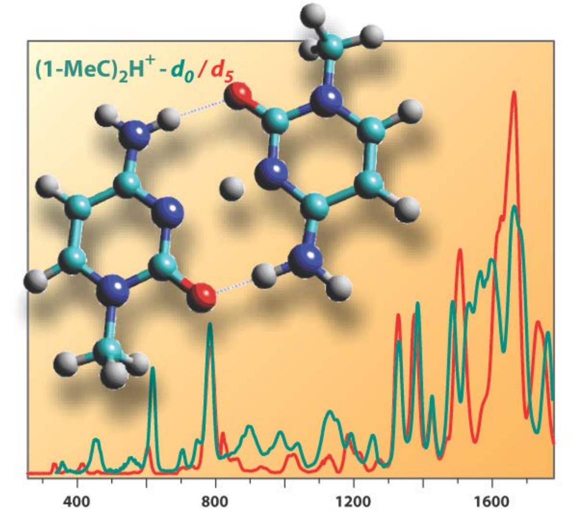
ELSEVIER

ISSN 1044-0305

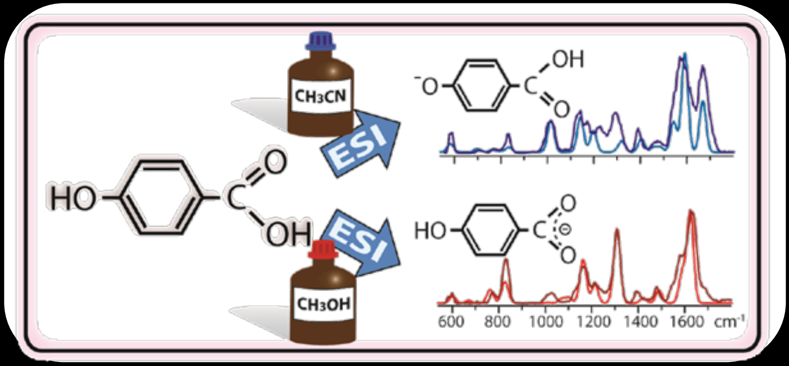
peptide fragment structures



metal ion binding

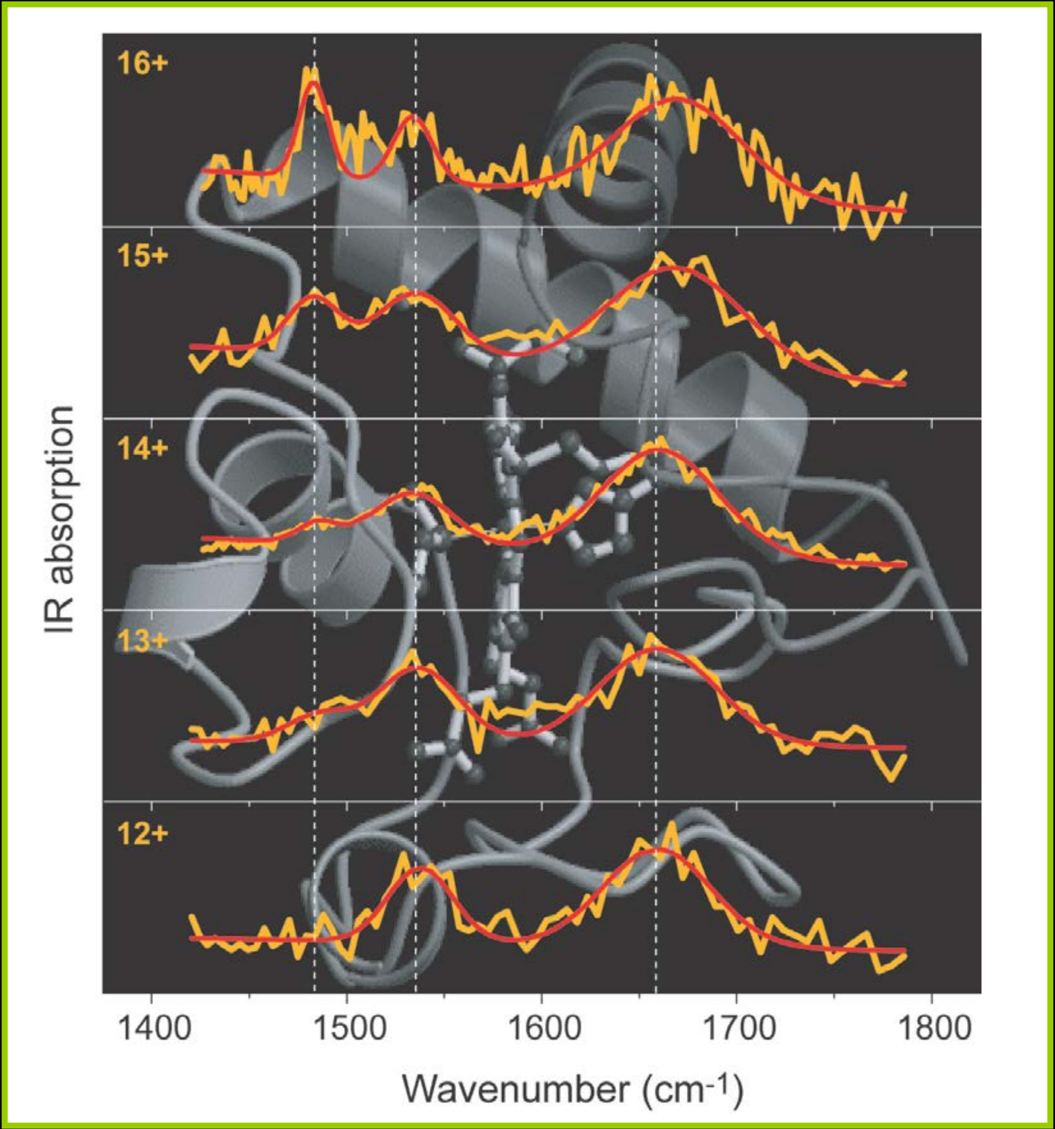


proton-bound dimers



deprotonation & tautomerization

Biochemistry: IR spectra of proteins



PCCP **2005,** *7,* 1345

Cytochrome C

~12.5 kDa

Amide I/II bands

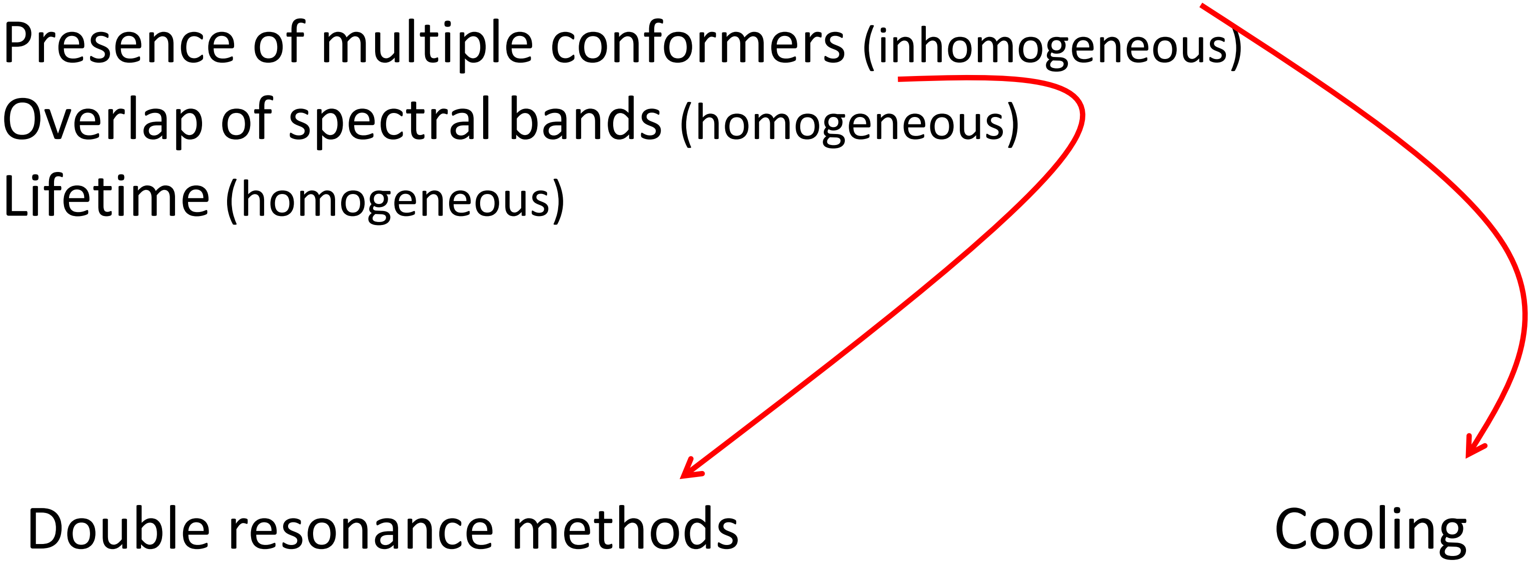
Charge-state resolved

No DFT spectra

Cryogenic ion spectroscopy

Sources of spectral broadening

- Multiple thermally populated lower states (inhomogeneous)
- Presence of multiple conformers (inhomogeneous)
- Overlap of spectral bands (homogeneous)
- Lifetime (homogeneous)



Double resonance methods

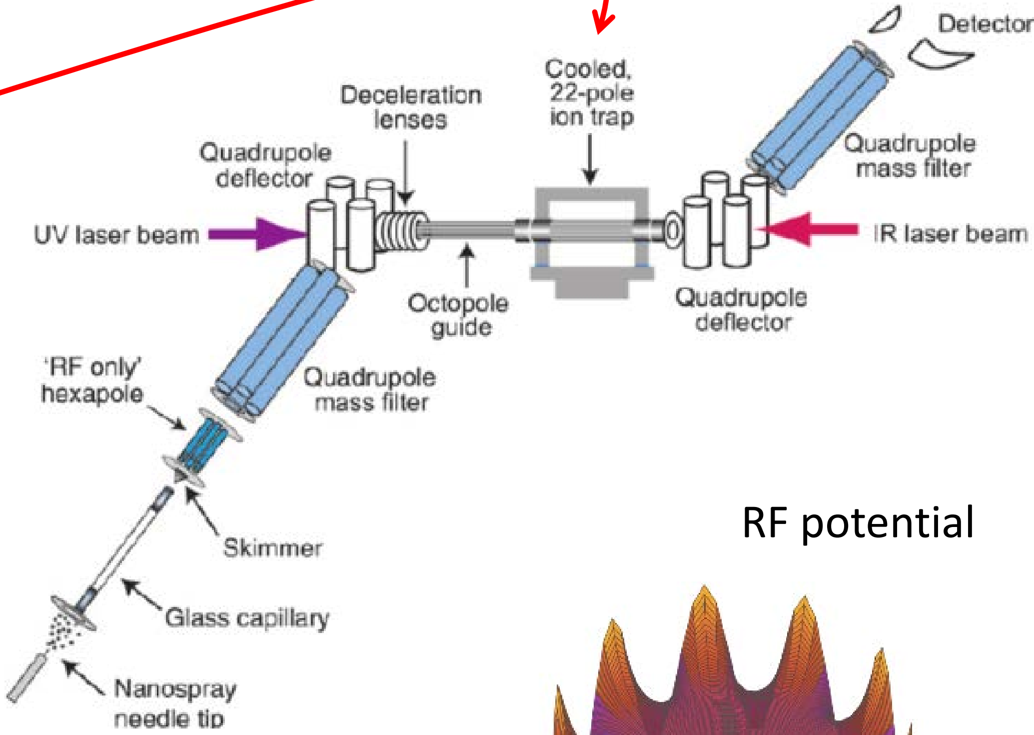
Cooling

Cryogenic ion spectroscopy

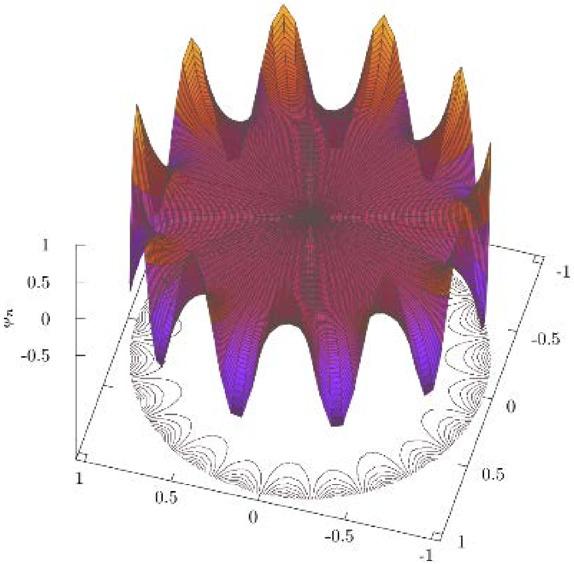
Buffer gas cooling

He buffer gas

LHe Cryostat



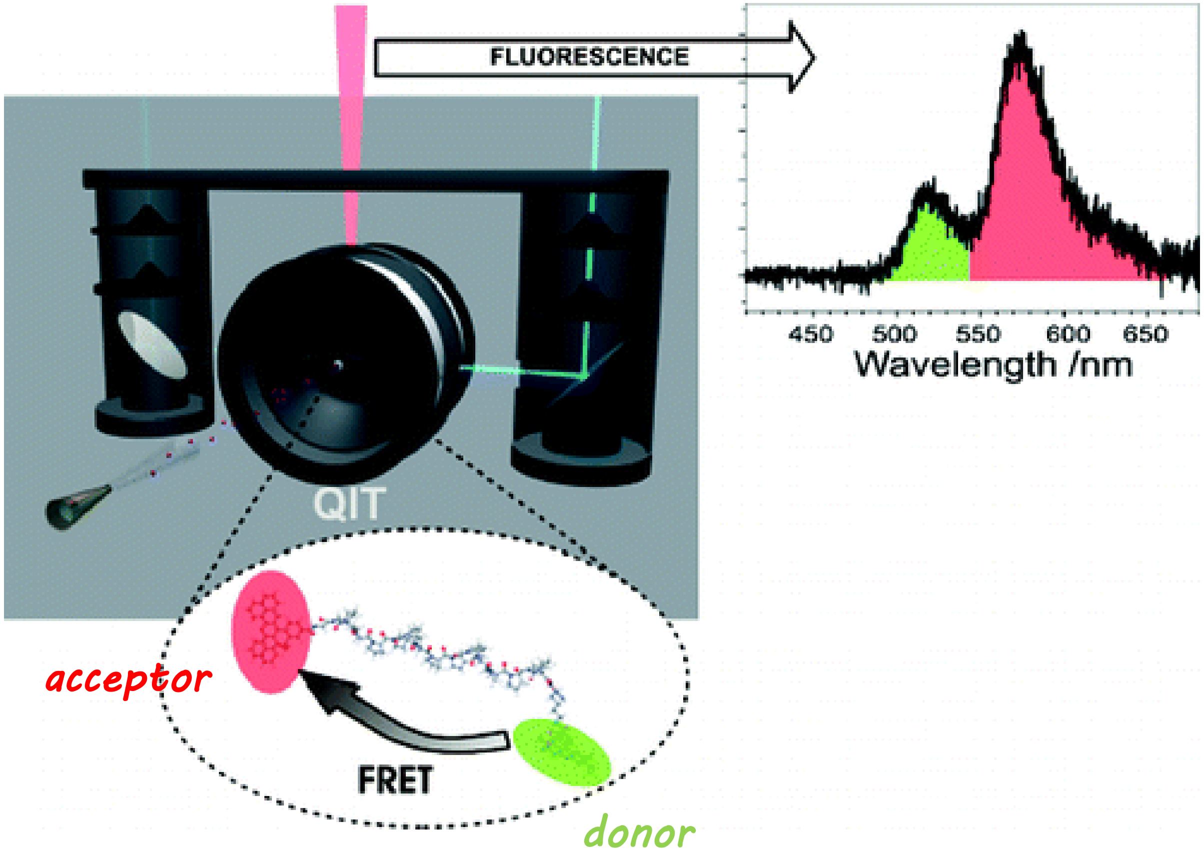
RF potential

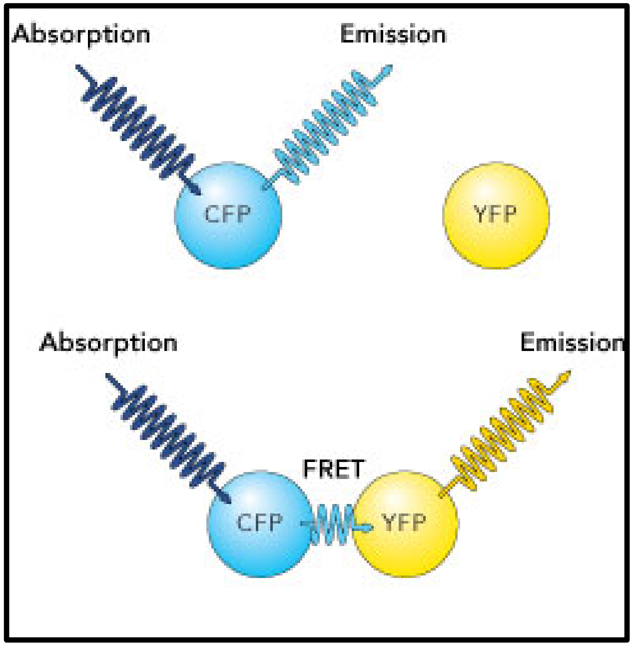


Cryogenic ion spectroscopy

Detection for IR or UV spectroscopies

- **Fluorescence (LIF)**



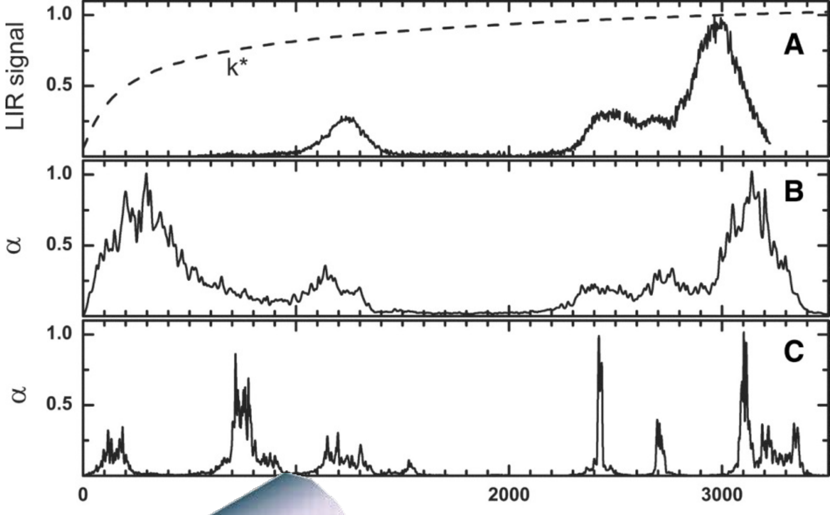


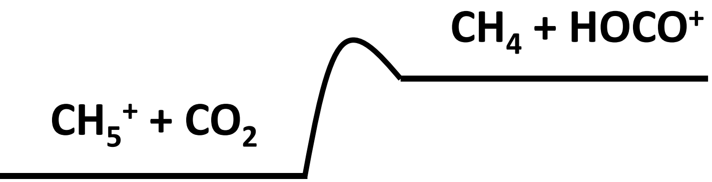
Jockusch et al. *J. Am. Chem. Soc.*, **2010**, *132*, 16156

Cryogenic ion spectroscopy

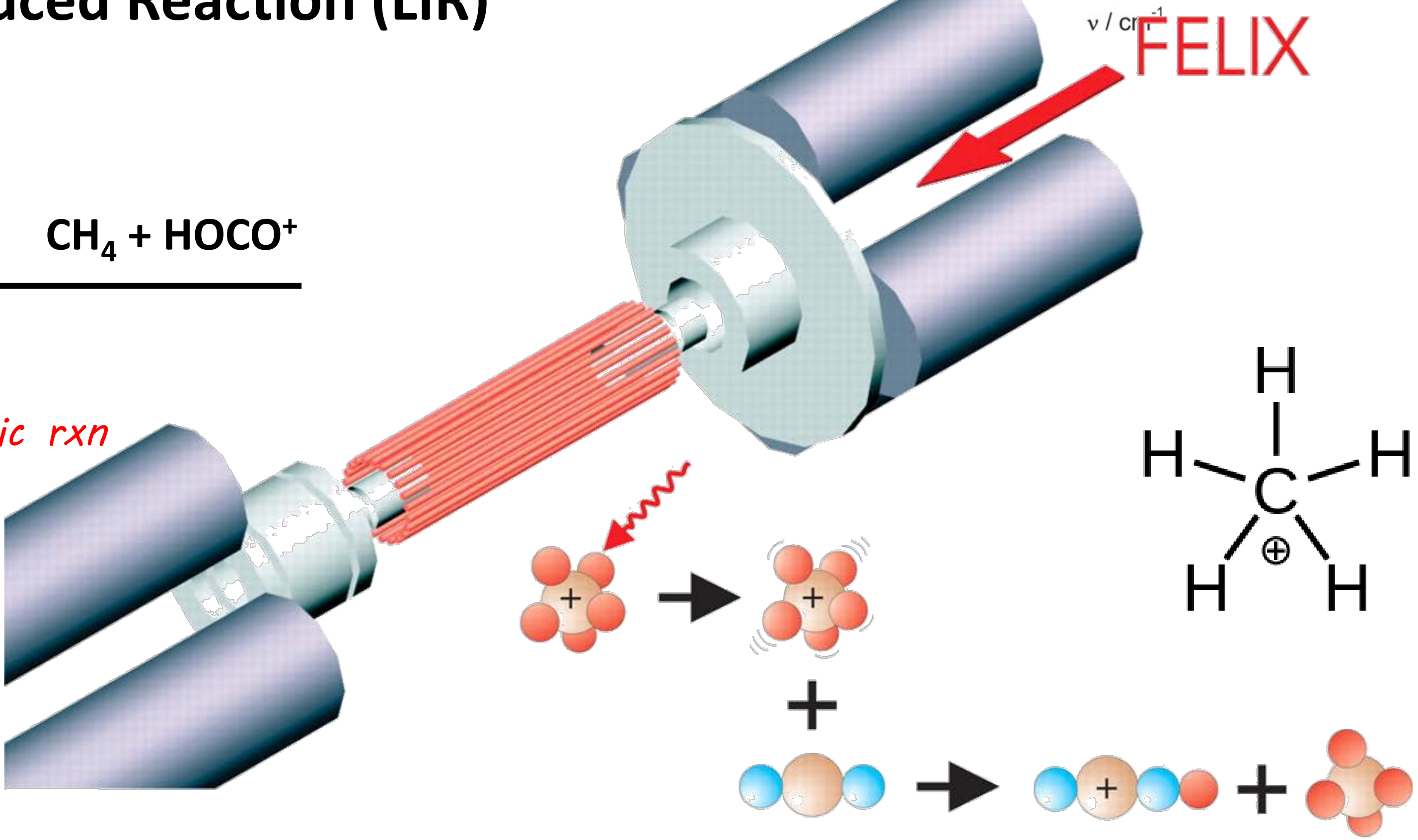
Detection for IR or UV spectroscopies

- Fluorescence (LIF)
- Laser Induced Reaction (LIR)





Slightly endothermic rxn

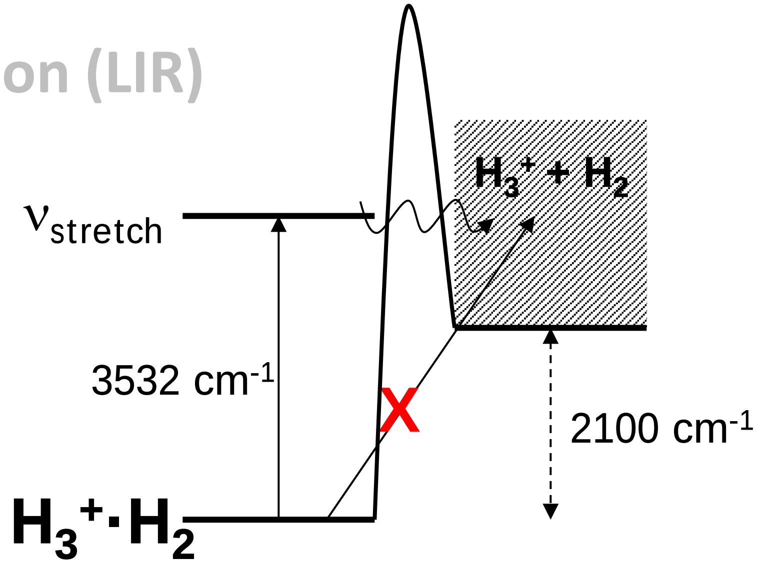


Asvany et al. *Science* **2005**;309:1219

Cryogenic ion spectroscopy

Detection for IR or UV spectroscopies

- Fluorescence (LIF)
- Laser Induced Reaction (LIR)
- **Messenger**



Yuan T Lee

The vibrational predissociation spectroscopy of hydrogen cluster ions[a)]

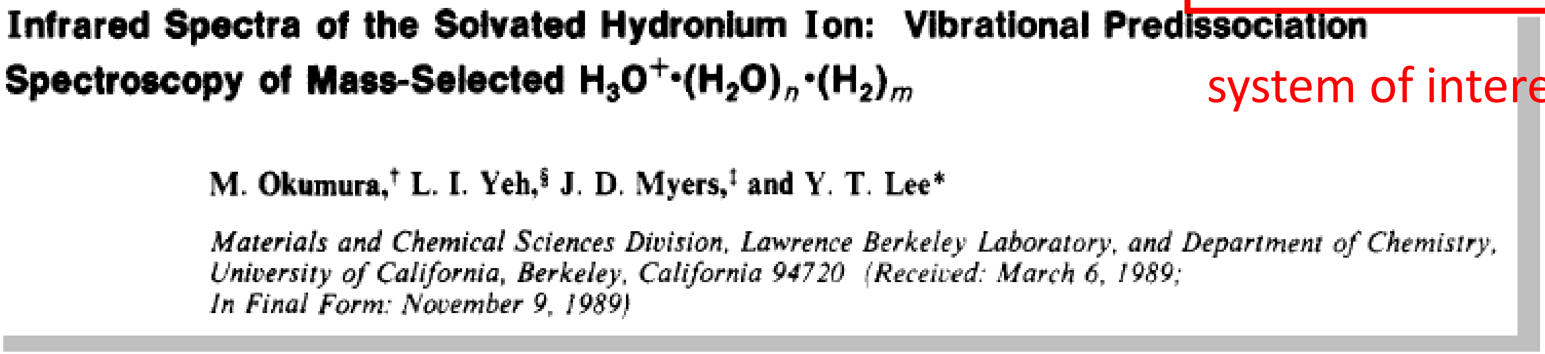
M. Okumura, L. I. Yeh,[b)] and Y. T. Lee

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

Weakly attached “messengers”

$H_3O^+\cdot(H_2O)_n\cdot(H_2)_m$

system of interest messenger



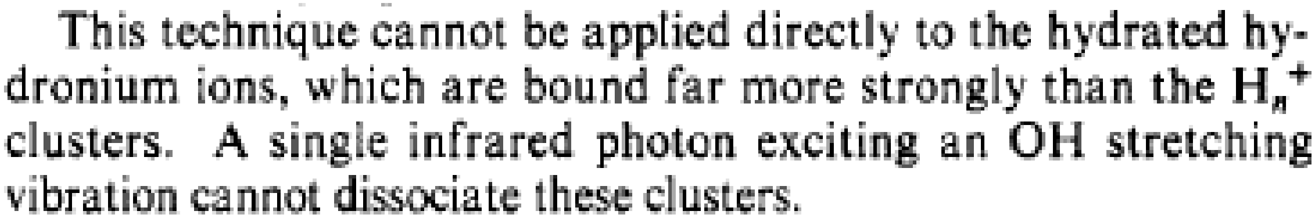
Infrared Spectra of the Solvated Hydronium Ion: Vibrational Predissociation Spectroscopy of Mass-Selected $H_3O^+\cdot(H_2O)_n\cdot(H_2)_m$

M. Okumura,[†] L. I. Yeh,[§] J. D. Myers,[‡] and Y. T. Lee*

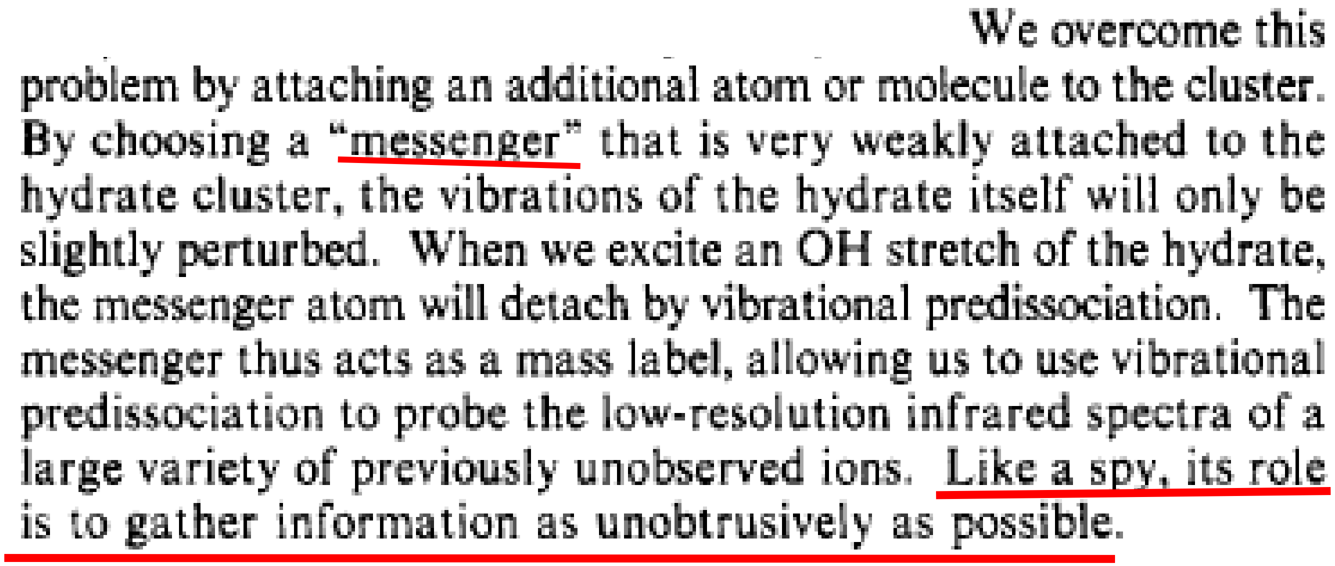
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

*(Received: March 6, 1989;
In Final Form: November 9, 1989)*

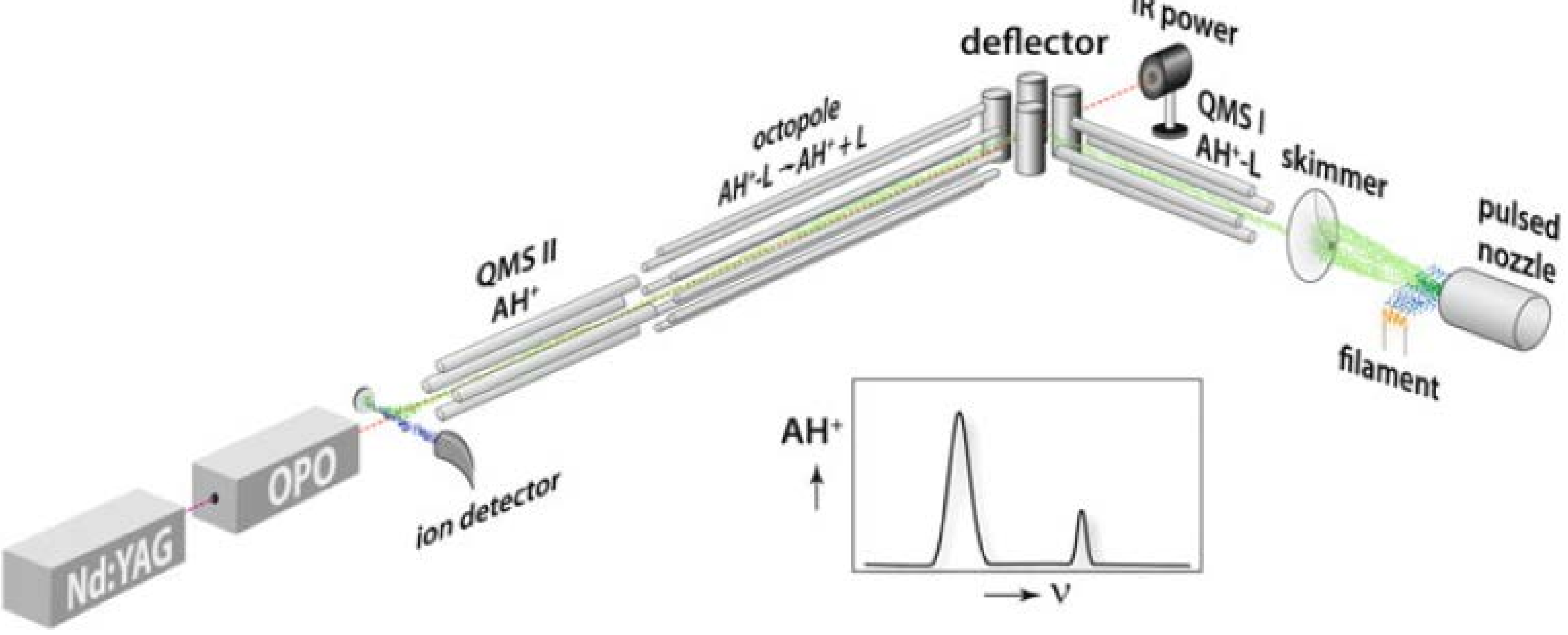
J. Phys. Chem. **94**, 3416 (1990)

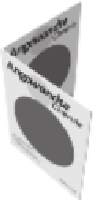


This technique cannot be applied directly to the hydrated hydronium ions, which are bound far more strongly than the H_n^+ clusters. A single infrared photon exciting an OH stretching vibration cannot dissociate these clusters.



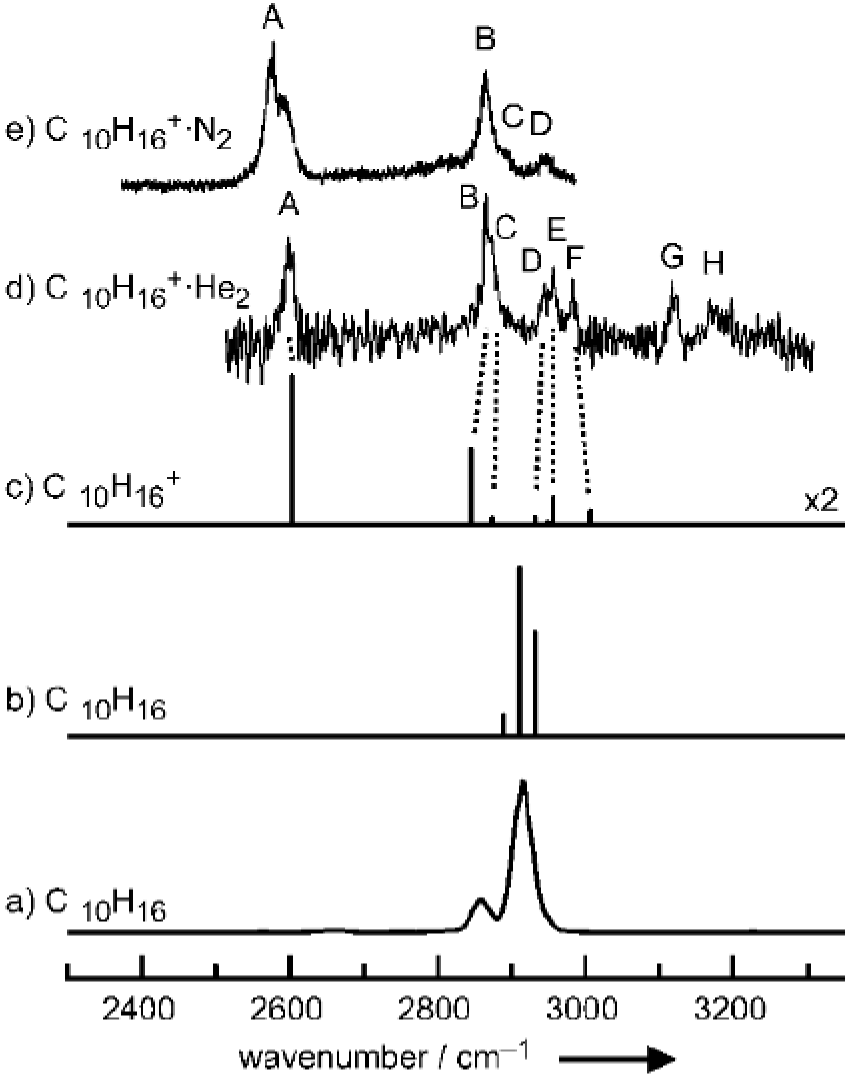
We overcome this problem by attaching an additional atom or molecule to the cluster. By choosing a “messenger” that is very weakly attached to the hydrate cluster, the vibrations of the hydrate itself will only be slightly perturbed. When we excite an OH stretch of the hydrate, the messenger atom will detach by vibrational predissociation. The messenger thus acts as a mass label, allowing us to use vibrational predissociation to probe the low-resolution infrared spectra of a large variety of previously unobserved ions. Like a spy, its role is to gather information as unobtrusively as possible.


IR power
deflector
QMS I
AH+-L
skimmer
pulsed
nozzle
filament
octopole
AH+-L → AH+ + L
QMS II
AH+
ion detector
OPO
Nd:YAG
AH+
↑
→ ν



Infrared Spectrum and Structure of the Adamantane Cation: Direct Evidence for Jahn–Teller Distortion**

*Alexander Patzer, Markus Schütz, Thomas Möller, and Otto Dopfer**



Angew. Chem. Int. Ed. **2012**, 51, 4925–4929

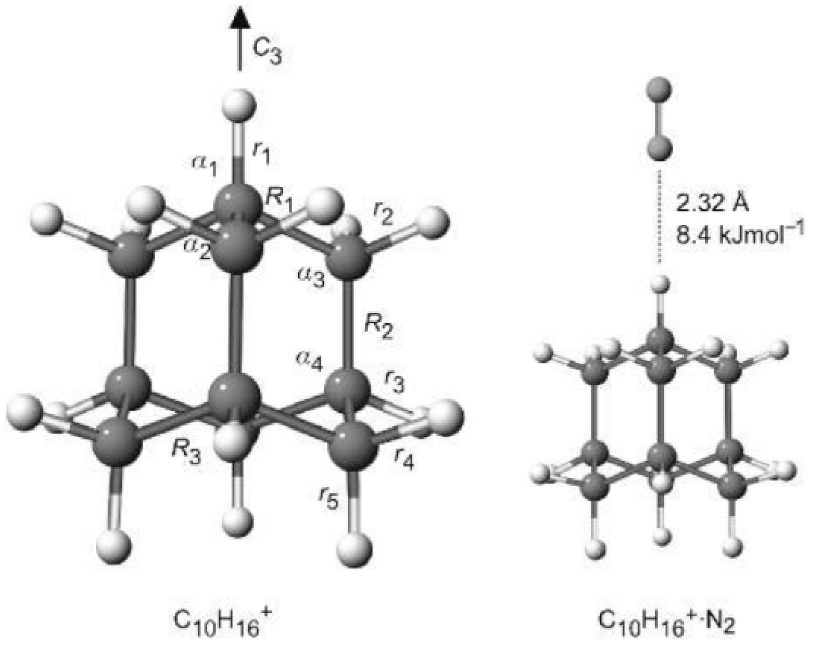
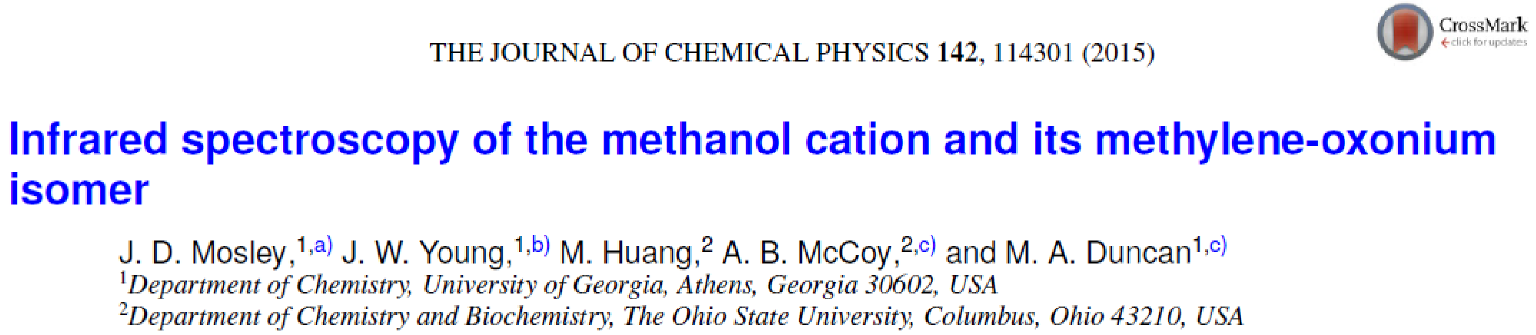


Figure 1. Structures of $C_{10}H_{16}^+$ and the most stable $C_{10}H_{16}^+{\cdot}N_2$ dimer calculated at the B3LYP/cc-pVDZ level. Relevant structural parameters are listed in Table T1 in the Supporting Information.

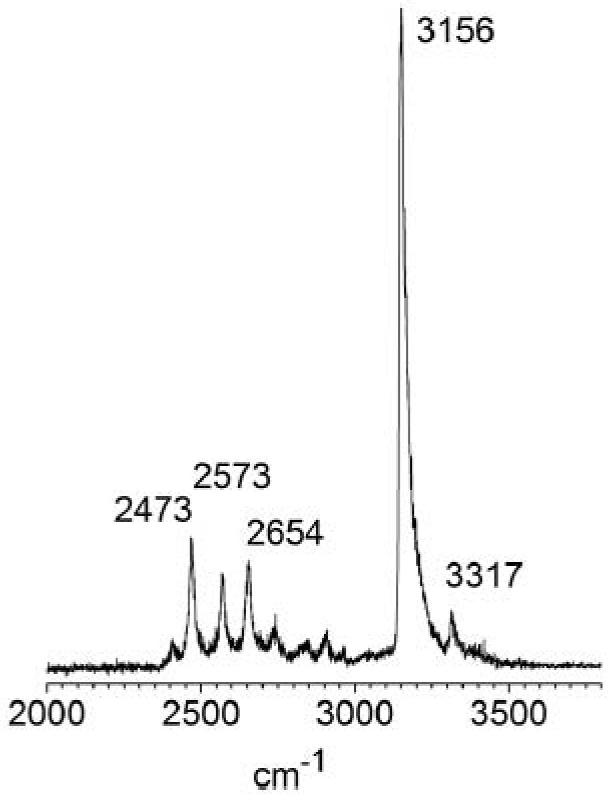


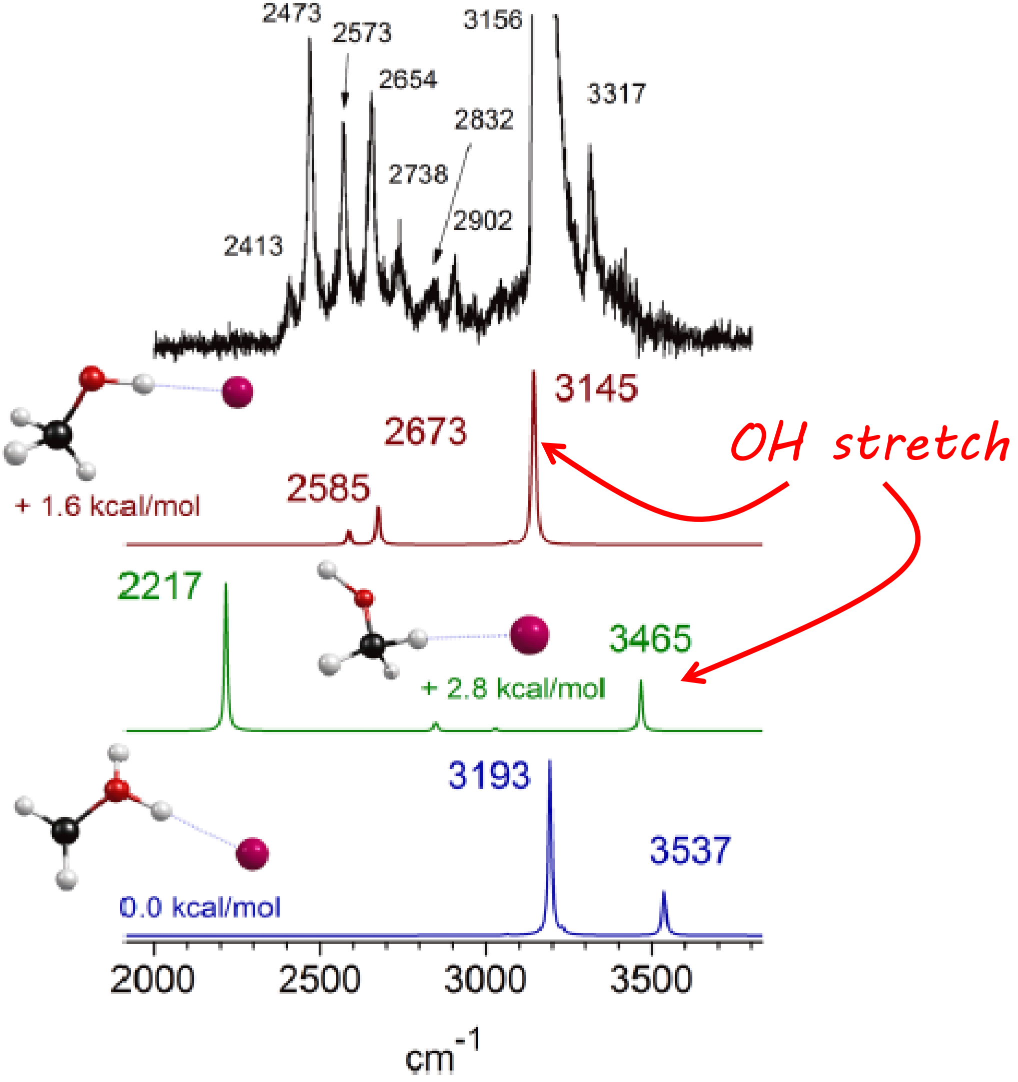
THE JOURNAL OF CHEMICAL PHYSICS **142**, 114301 (2015)

Infrared spectroscopy of the methanol cation and its methylene-oxonium isomer

J. D. Mosley,[1,a)] J. W. Young,[1,b)] M. Huang,[2] A. B. McCoy,[2,c)] and M. A. Duncan[1,c)]
[1]*Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA*
[2]*Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, USA*

Methanol radical cation
Ar messenger





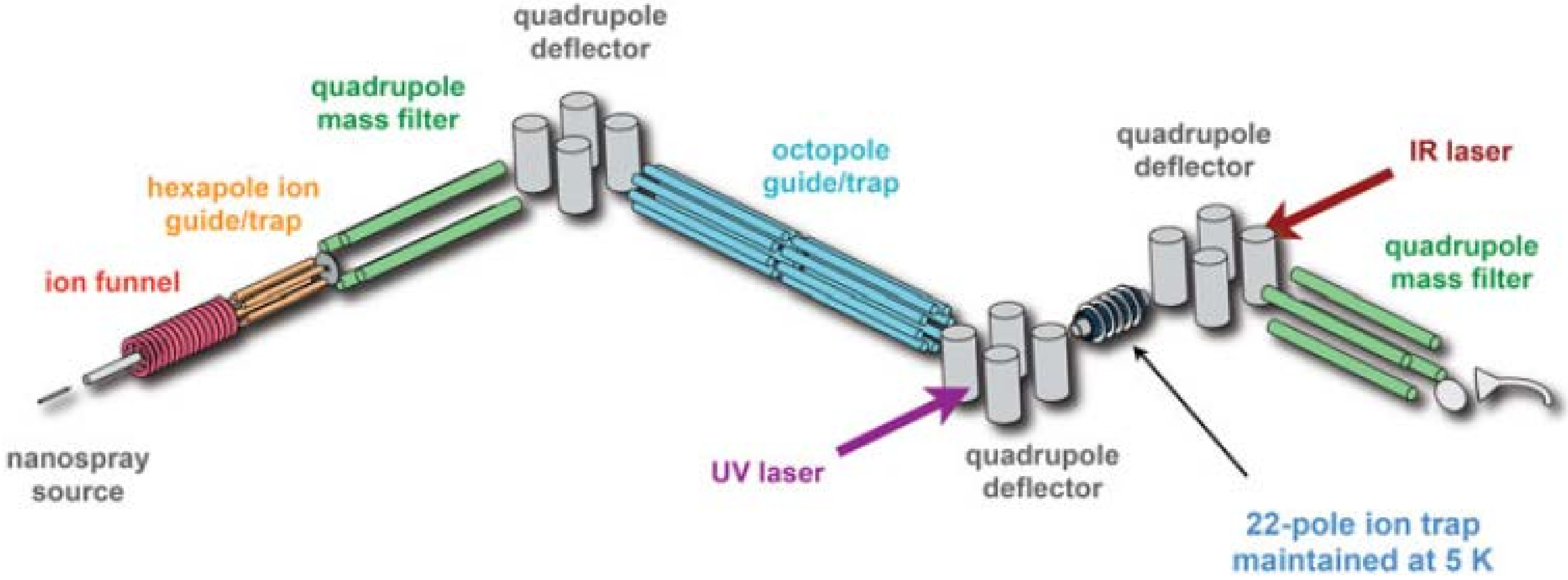


Fig. 7 The second generation Lausanne cold-ion photofragment spectrometer with a 22-pole ion trap [131]

Rizzo group, EPFL

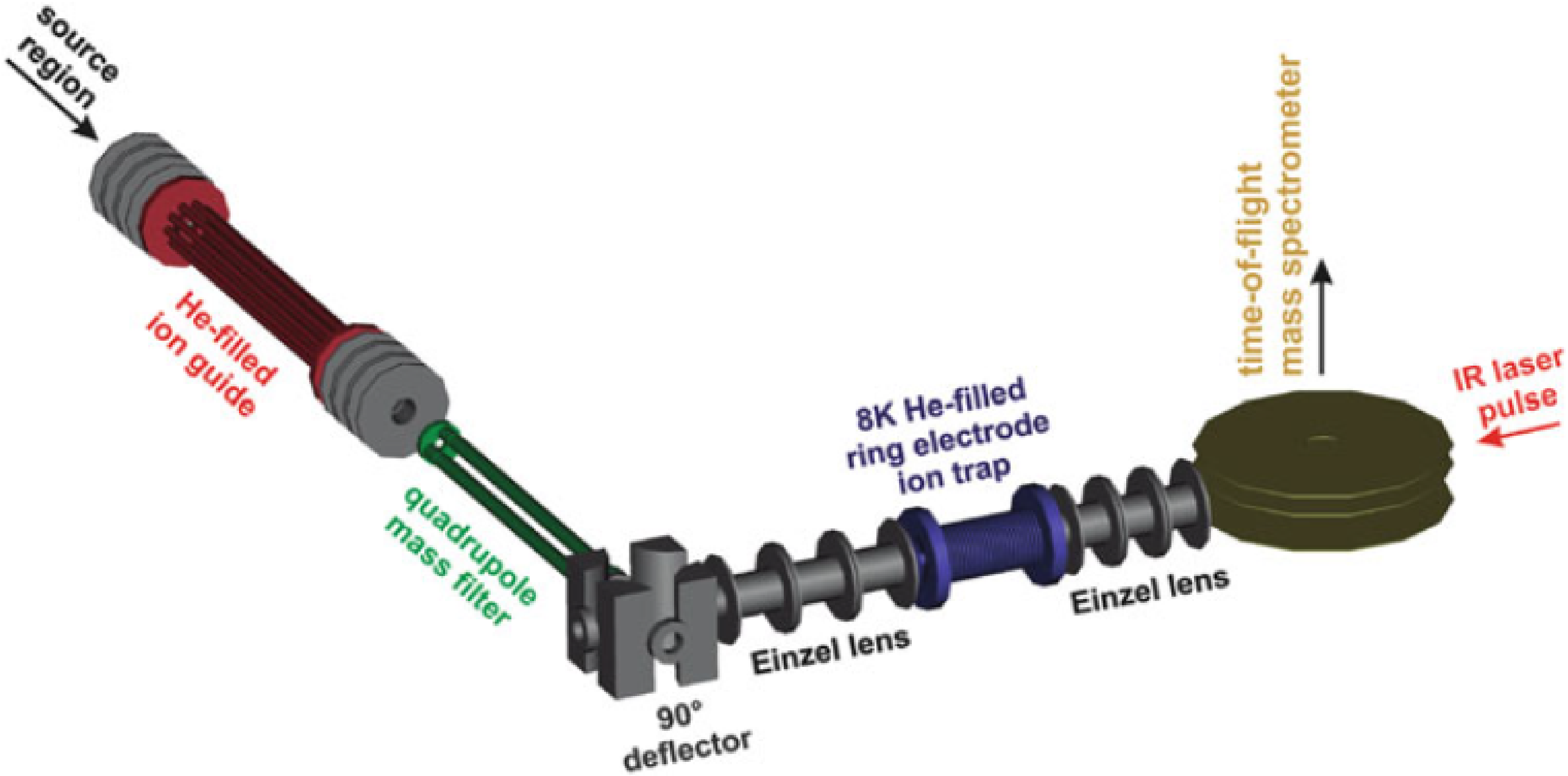


Fig. 8 Second-generation ion trap machine from the Asmis group [134]. The ion trap in this case is a ring-electrode trap, and fragment mass analysis is performed in a time-of-flight mass spectrometer. Reproduced with permission from [134]. Copyright (2009) ACS

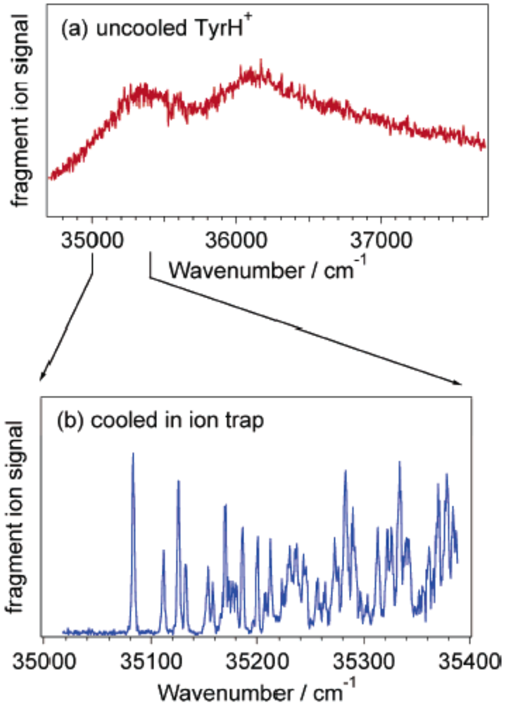
Asmis group, FHI Berlin

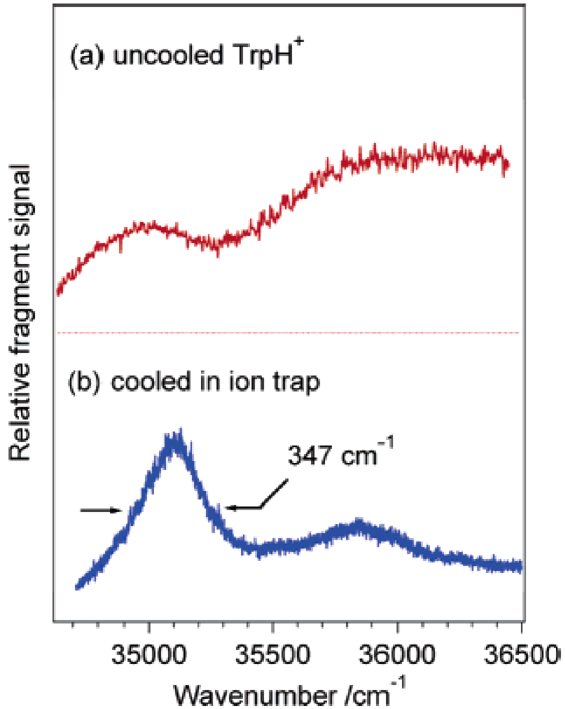
Cryogenic ion spectroscopy

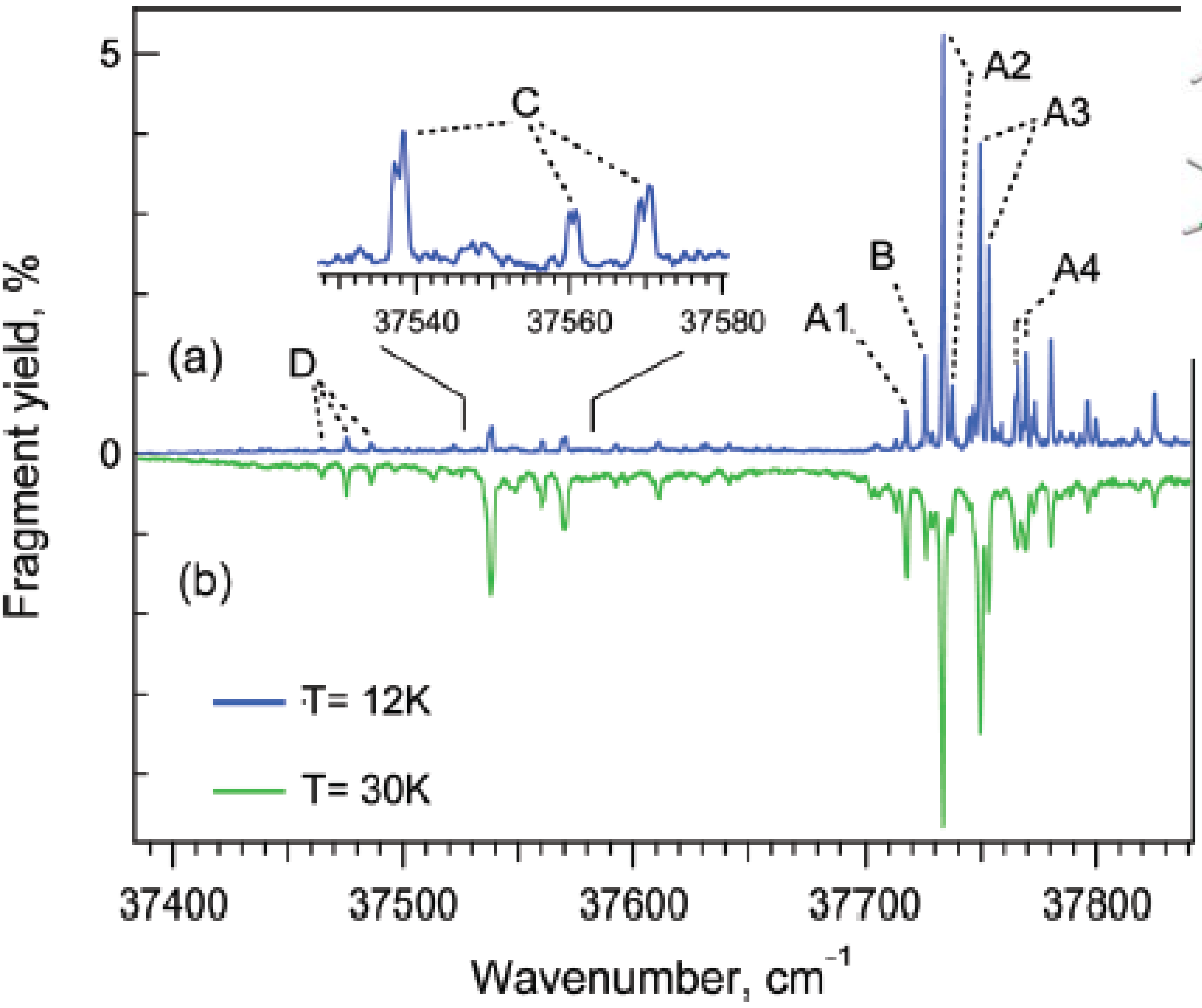
Detection for IR or UV spectroscopies

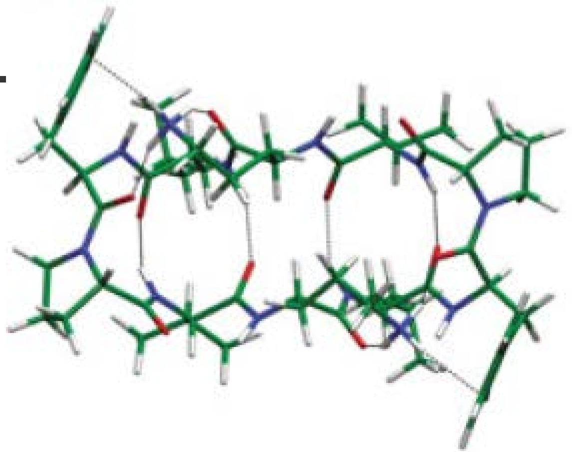
1. Electronic excitation
2. Internal conversion
3. Vibrational excitation
4. Dissociation
5. Detect fragment ion m/z

- Fluorescence (LIF)
- Laser Induced Reaction (LIR)
- Messenger
- **UV photodissociation**

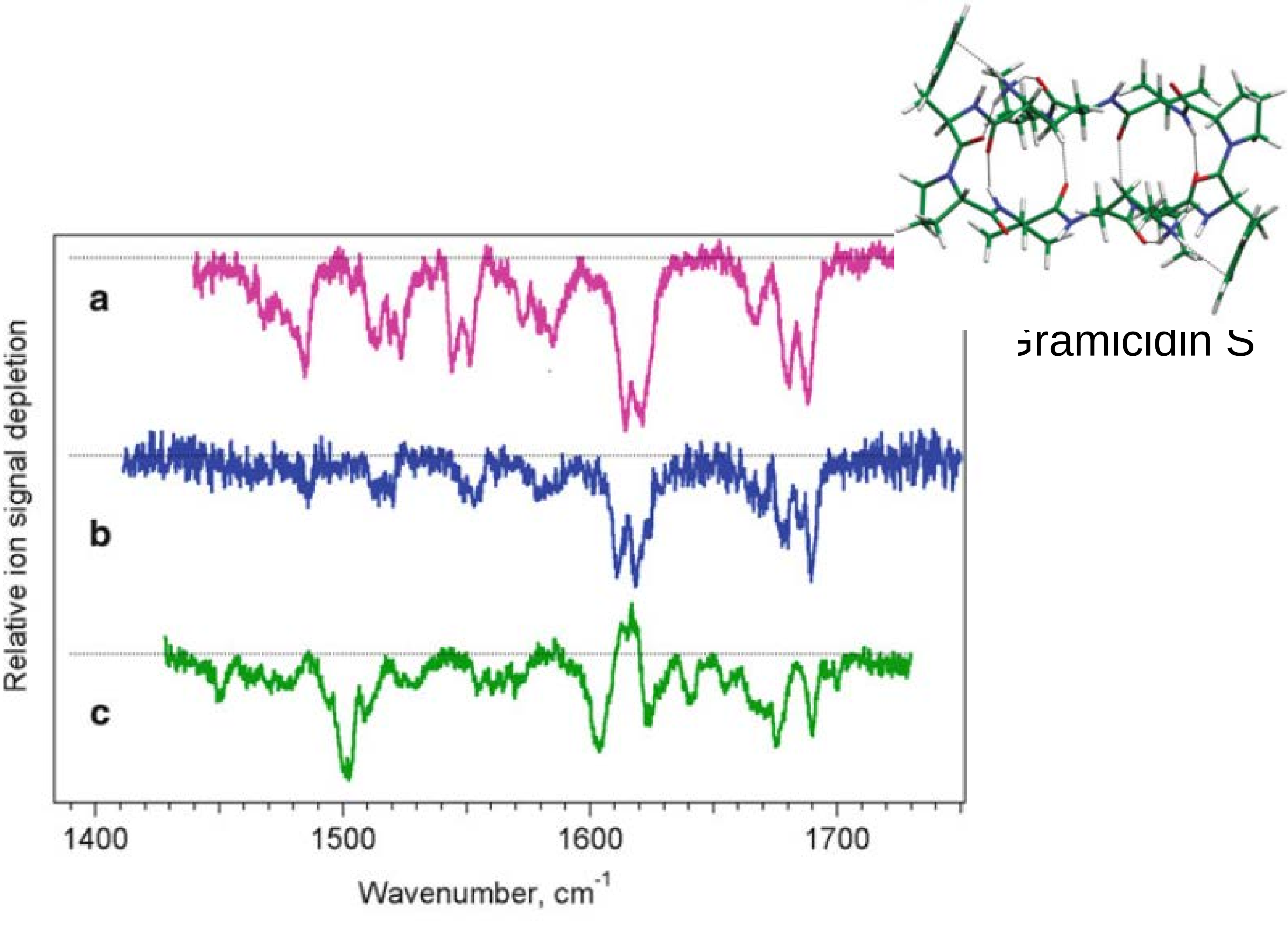








Gramicidin S

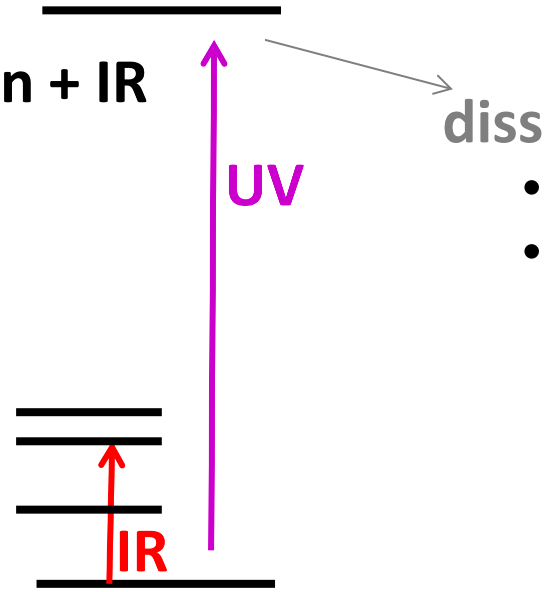

a
b
c
Relative ion signal depletion
1400
1500
1600
1700
Wavenumber, cm-1

ramicidin S

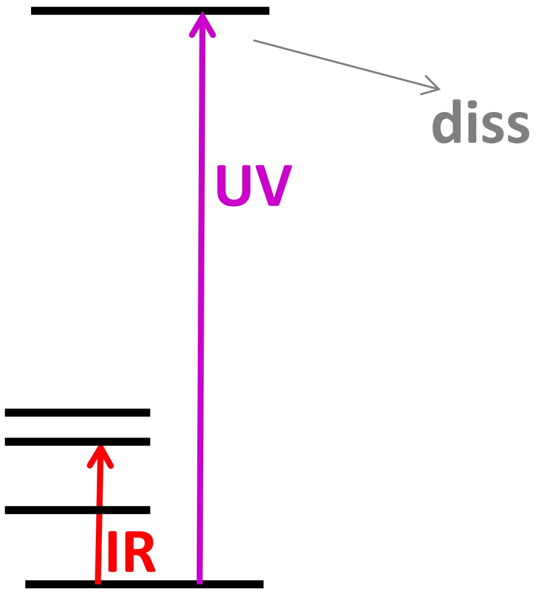
Cryogenic ion spectroscopy

Detection for IR or UV spectroscopies

- Fluorescence (LIF)
- Laser Induced Reaction (LIR)
- Messenger
- UV photodissociation + IR



- *Not conformer selective*
- *Gain*

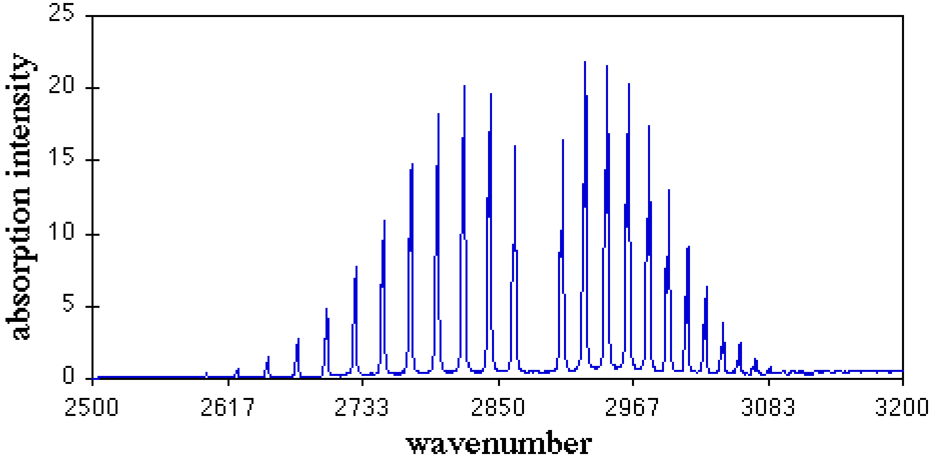


- *Conformer selective*
- *Depletion*

Cryogenic ion spectroscopy

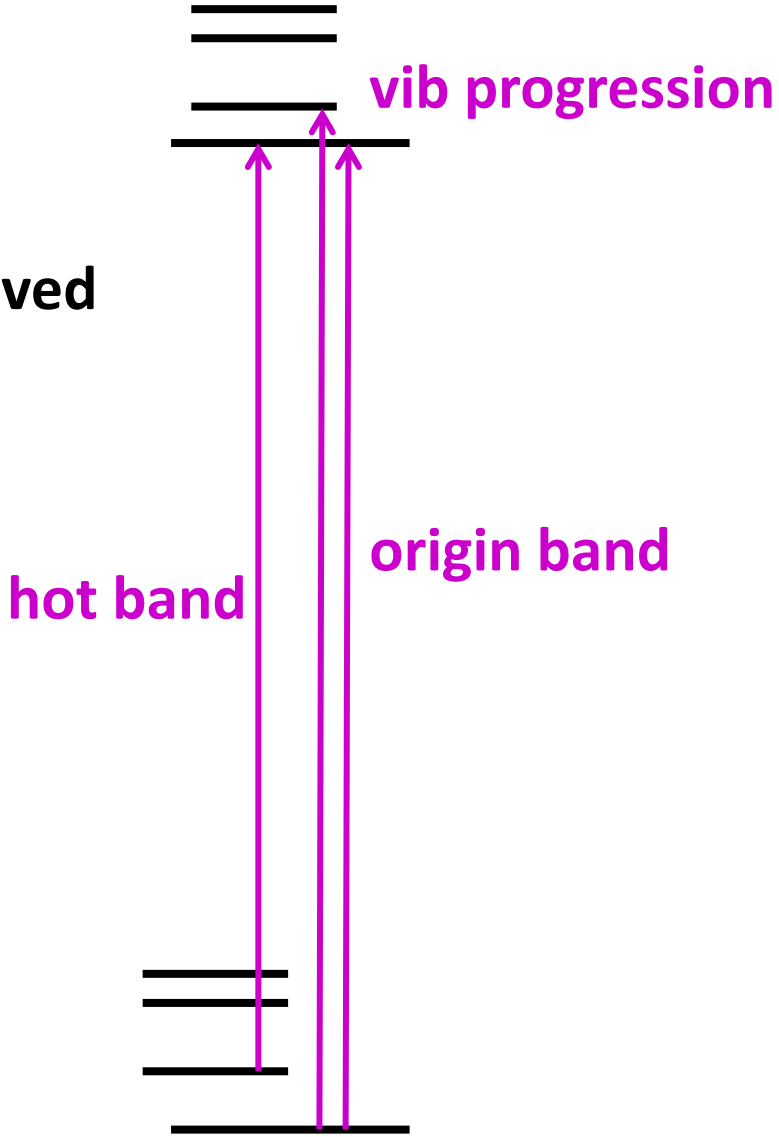
Determination of the ion temperature

- Clustering (with He) observed?
- Rotational resolution: highest J observed
- Rotational envelope
- Hot bands observed

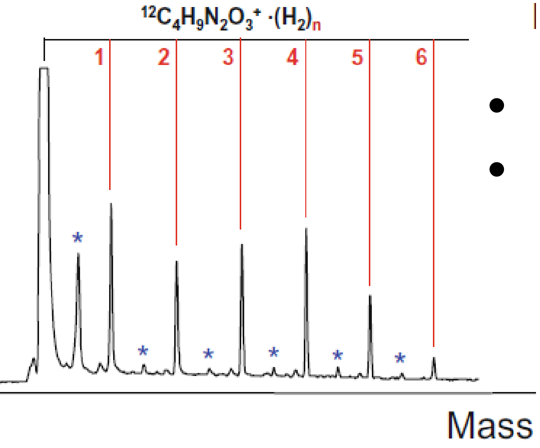


Experimental HCl Rotational-Vibrational Spectrum

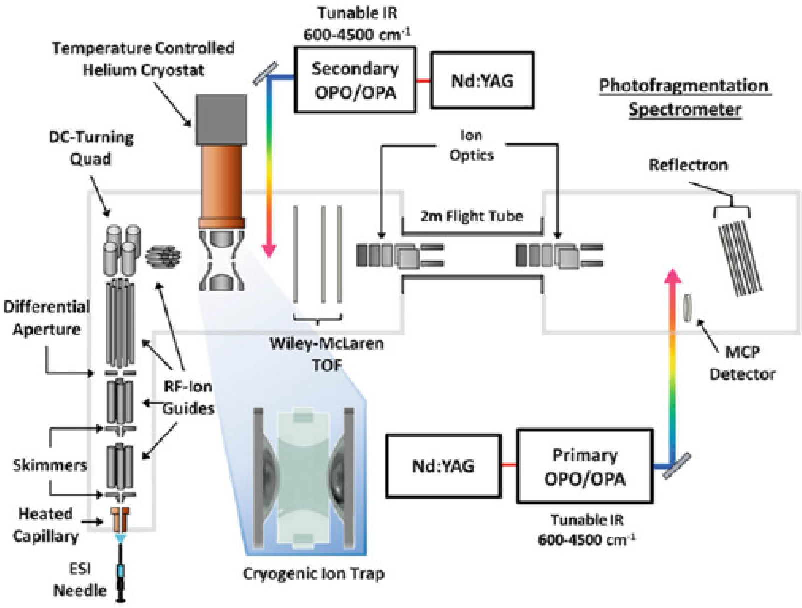
rotational: pop ~ $(2J+1)\exp[E_J/kT]$



Example: Messenger (H_2)

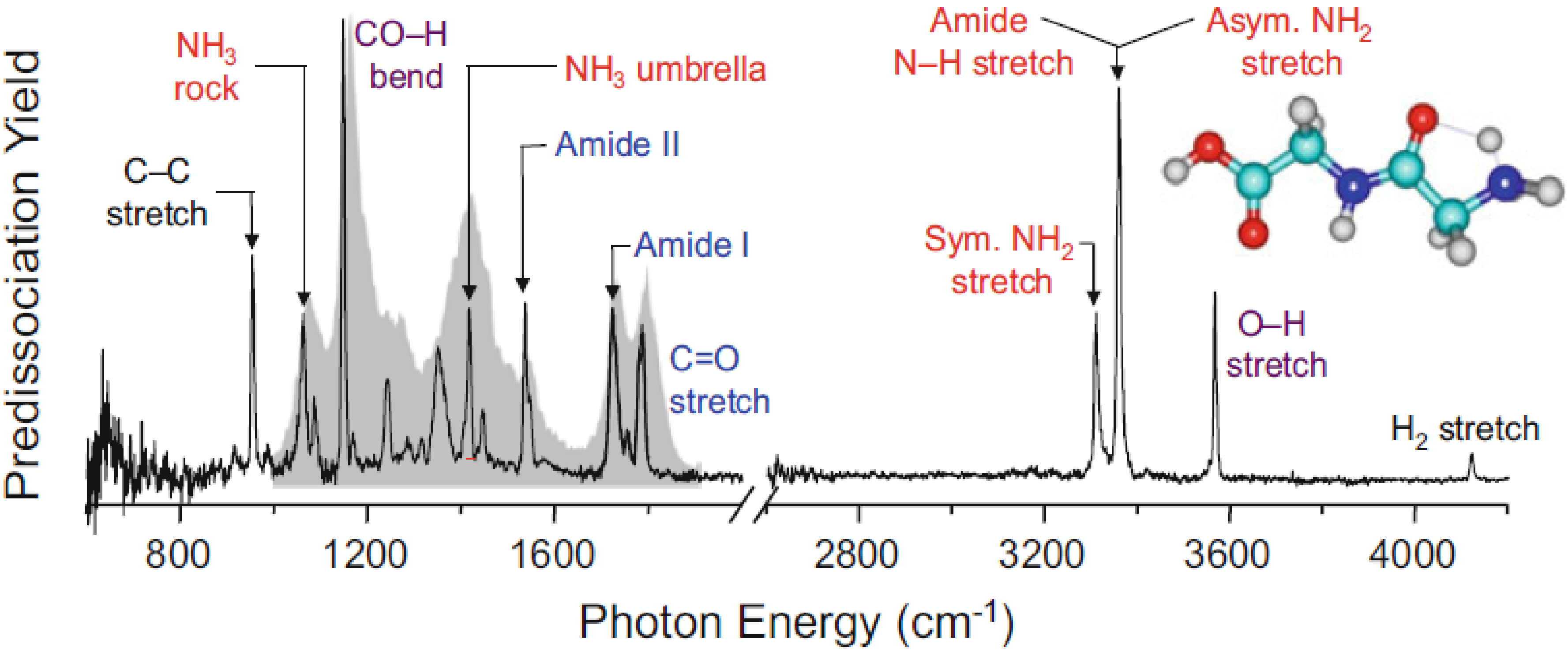


- no UV chromophore
- no conformer select



M.A. Johnson & co.

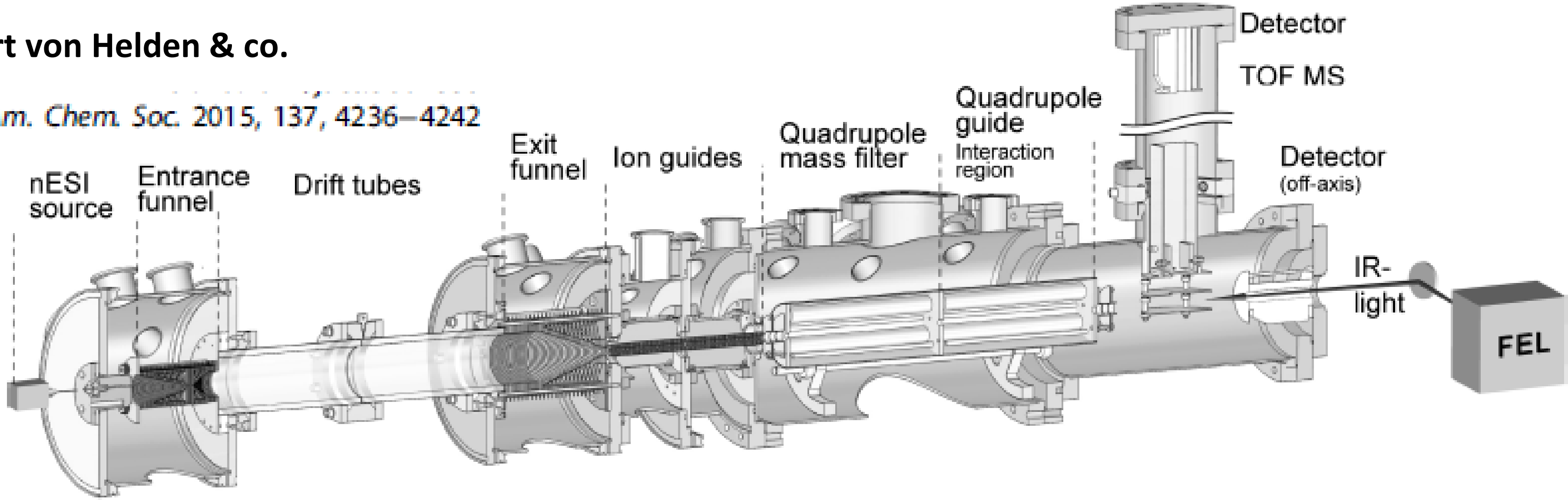
ACCOUNTS OF CHEMICAL RESEARCH ■ 202–210 ■ 2014 ■ Vol. 47,

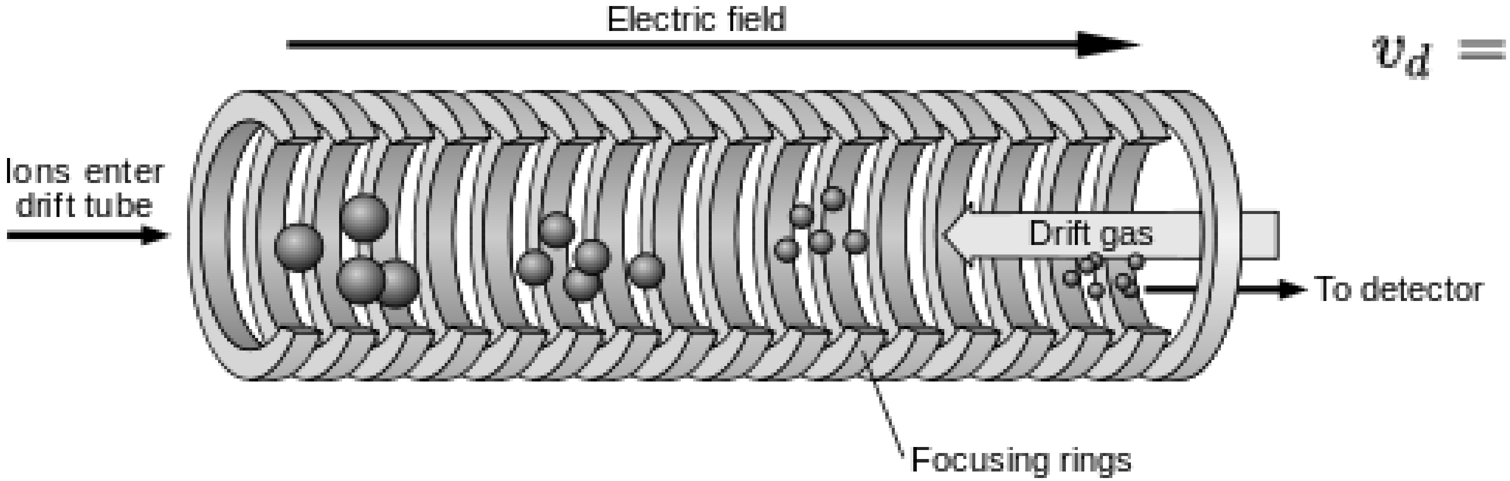


Dealing with conformational heterogeneity: ion mobility separation

Gert von Helden & co.

J. Am. Chem. Soc. 2015, 137, 4236−4242

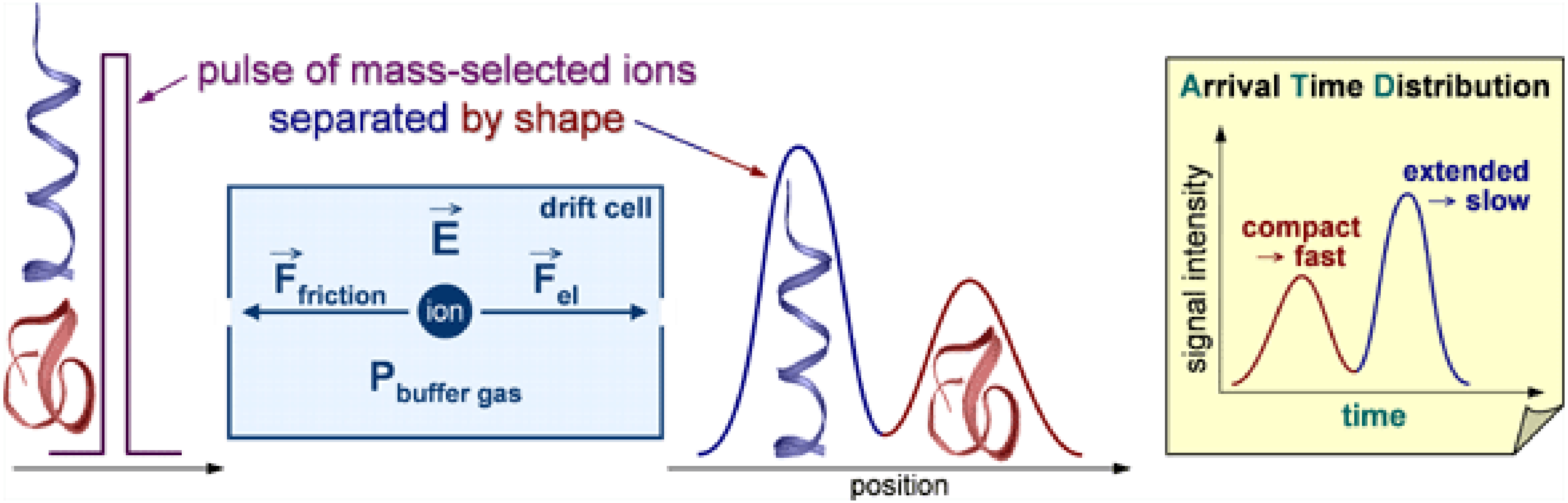




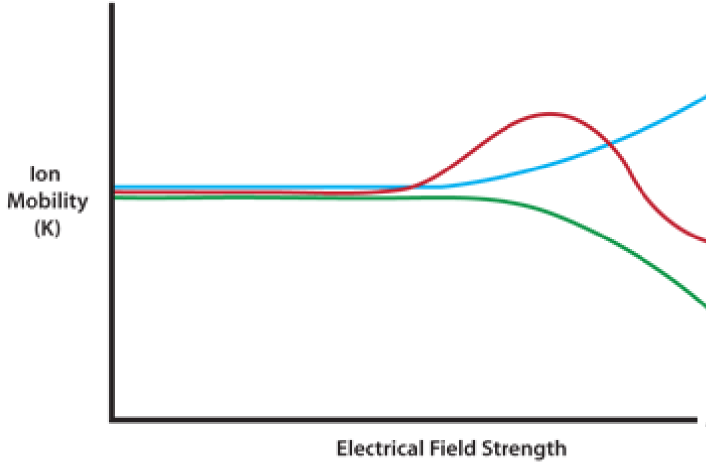
mobility

$$v_d = KE$$

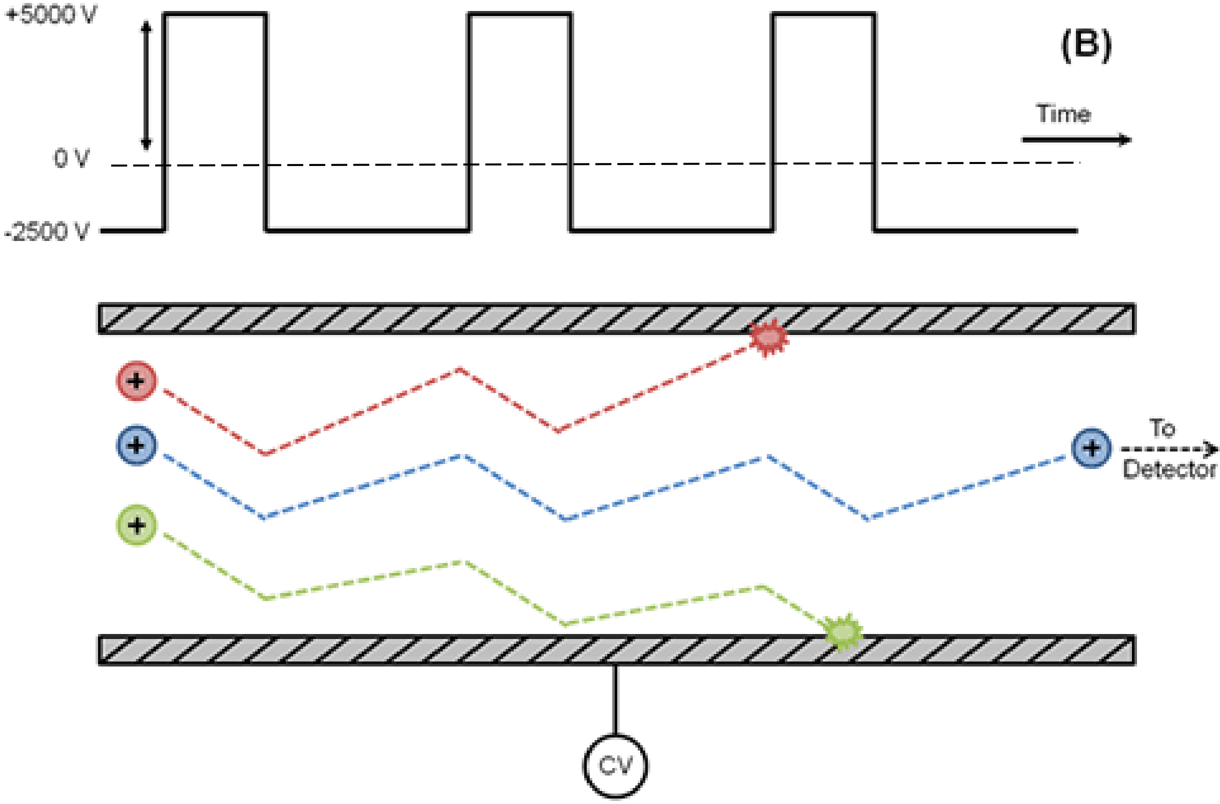
ion mobility spectrometry (IMS)



Differential ion mobility spectrometry (DIMS)



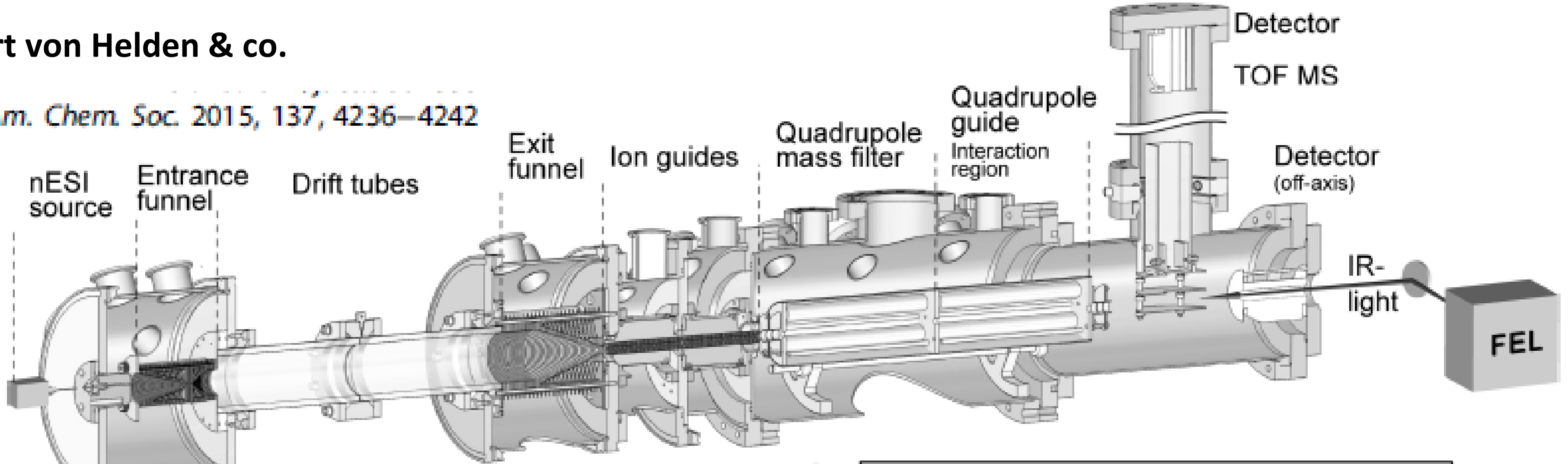
$$K = K_0\left(1 + a\frac{E}{n} + b\frac{E^2}{n^2} + \cdots\right)$$

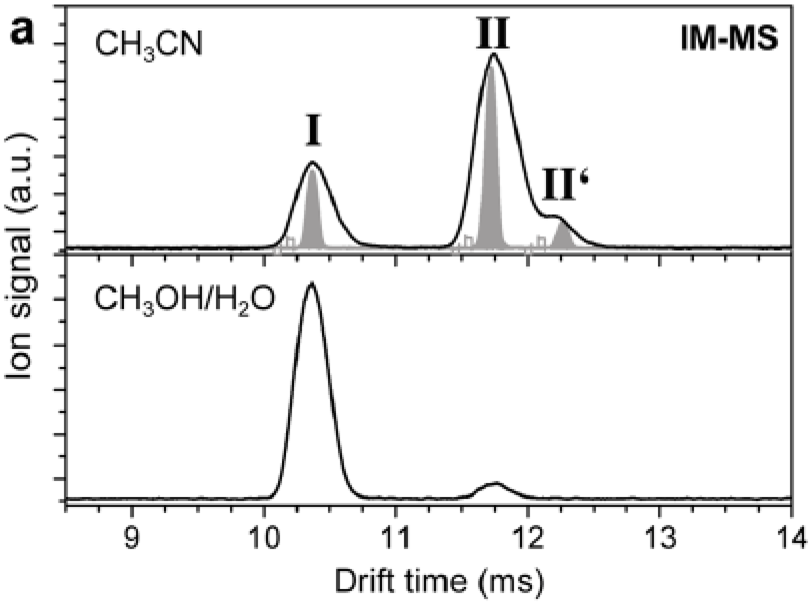


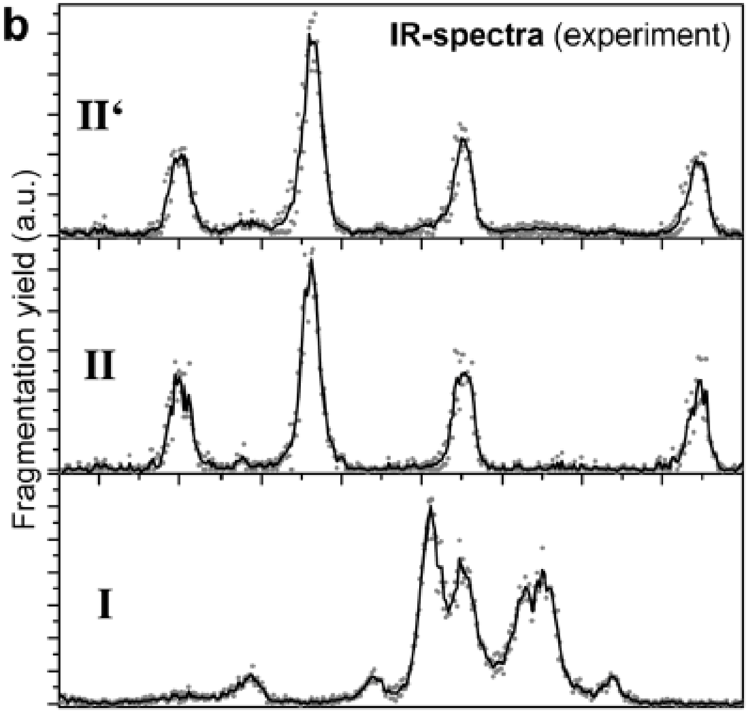
Dealing with conformational heterogeneity: ion mobility separation

Gert von Helden & co.

J. Am. Chem. Soc. 2015, 137, 4236−4242





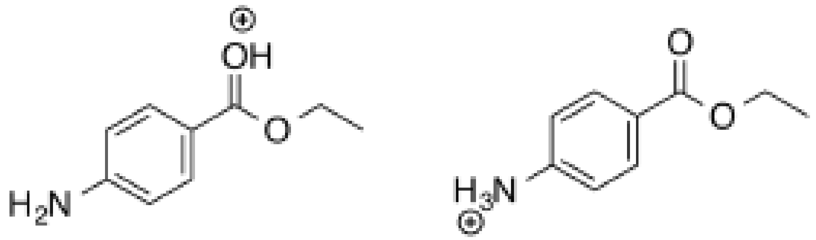


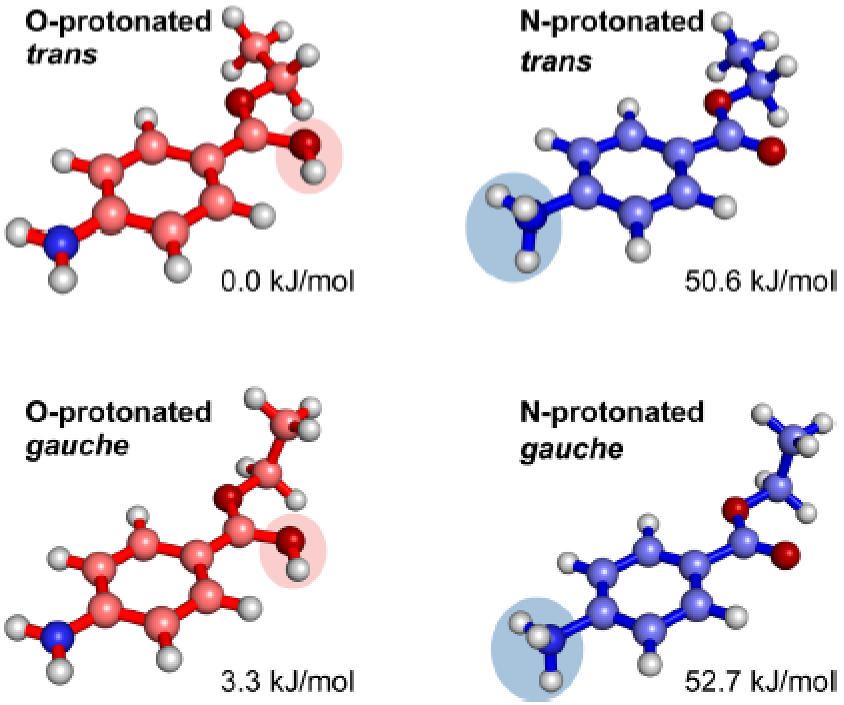
Conformer (protomer) selected IR spectroscopy

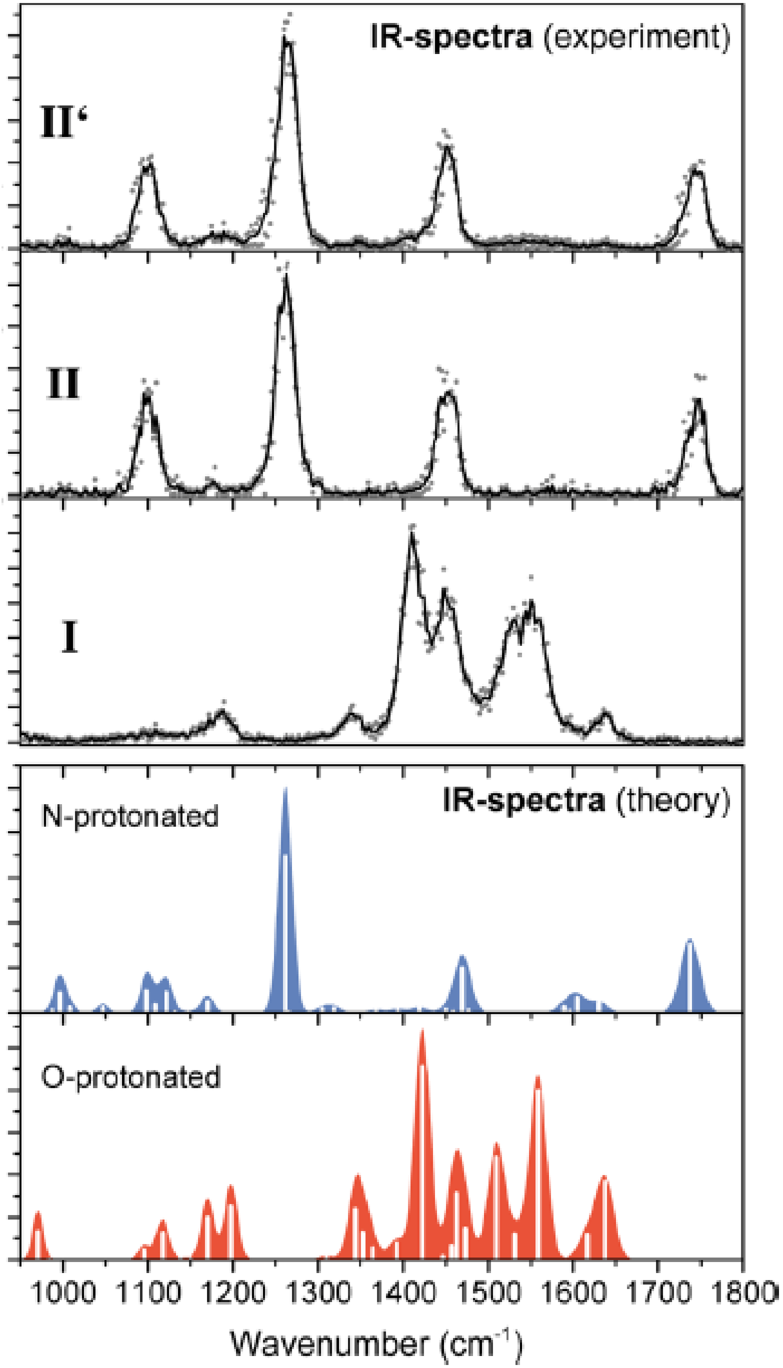
benzocaine

O-protonated

N-protonated



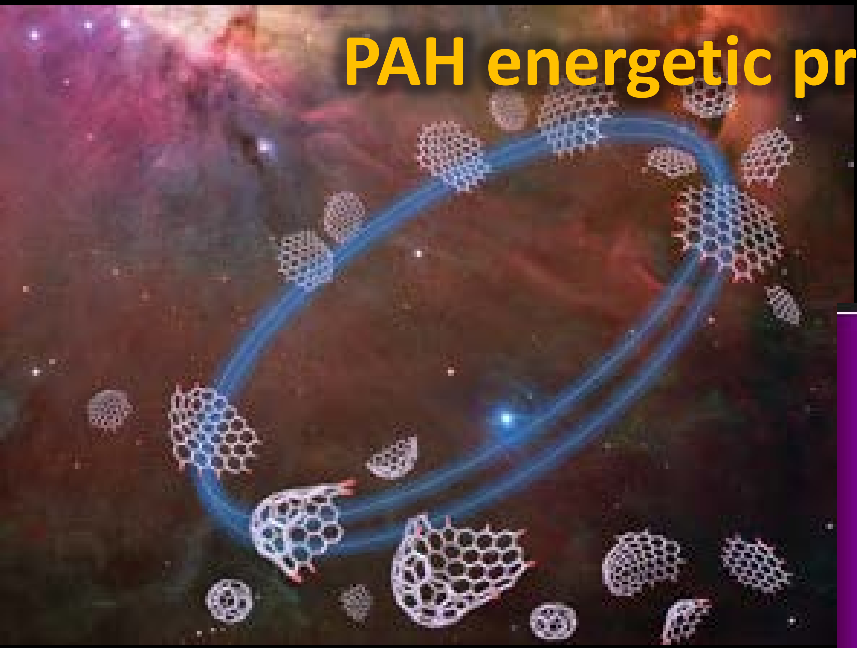




IR spectroscopy and chemistry of ionized polycyclic aromatic hydrocarbons (PAHs)

Applications in astrochemistry

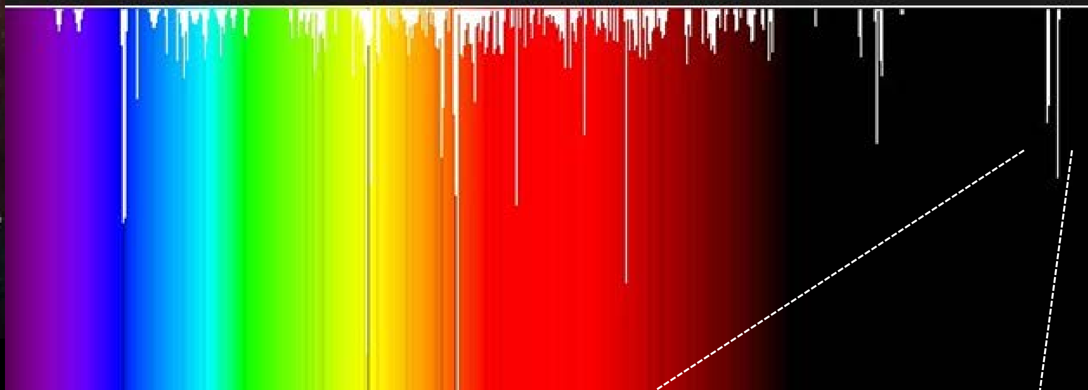
PAH energetic processing and fullerenes

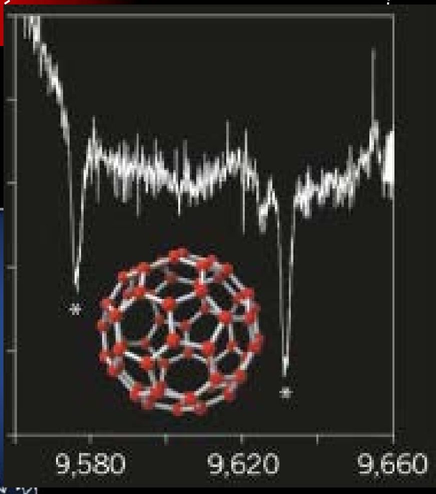


Diffuse Interstellar Bands (DIBs)

Recent identification of C_{60} and C_{70}

More large carbon species?



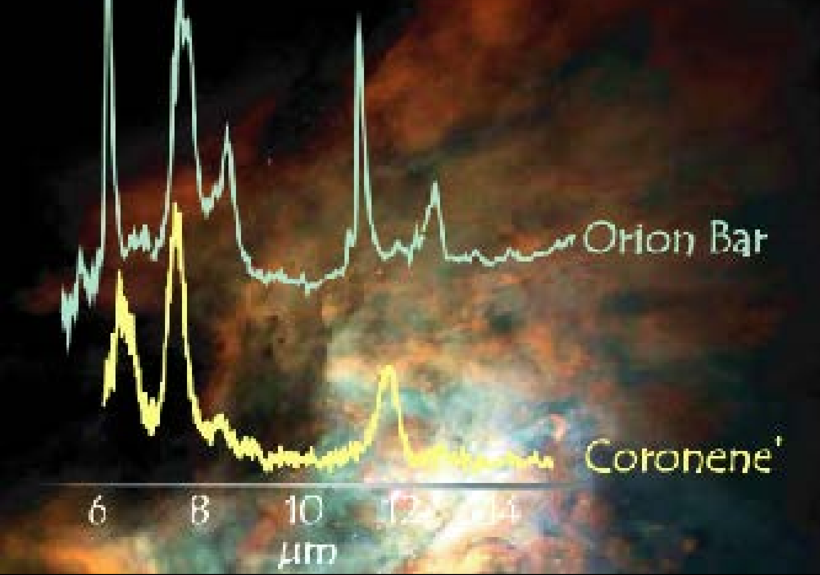


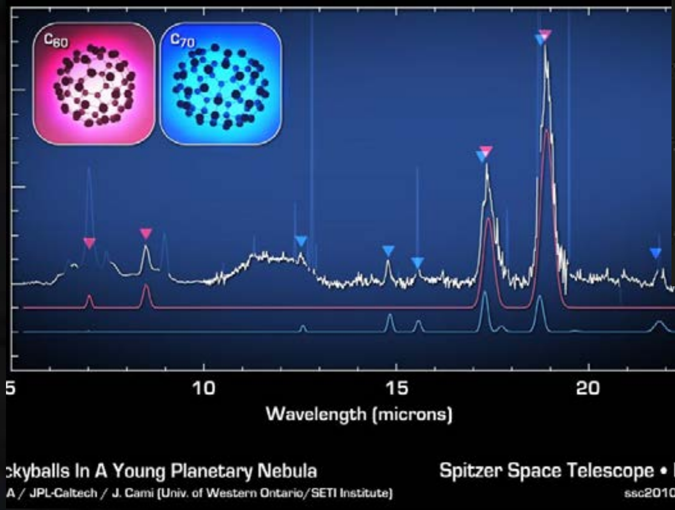
JP Maier & co

From UIRs to AIRs

Unidentified →Aromatic IR emission bands

But: no unique identification made





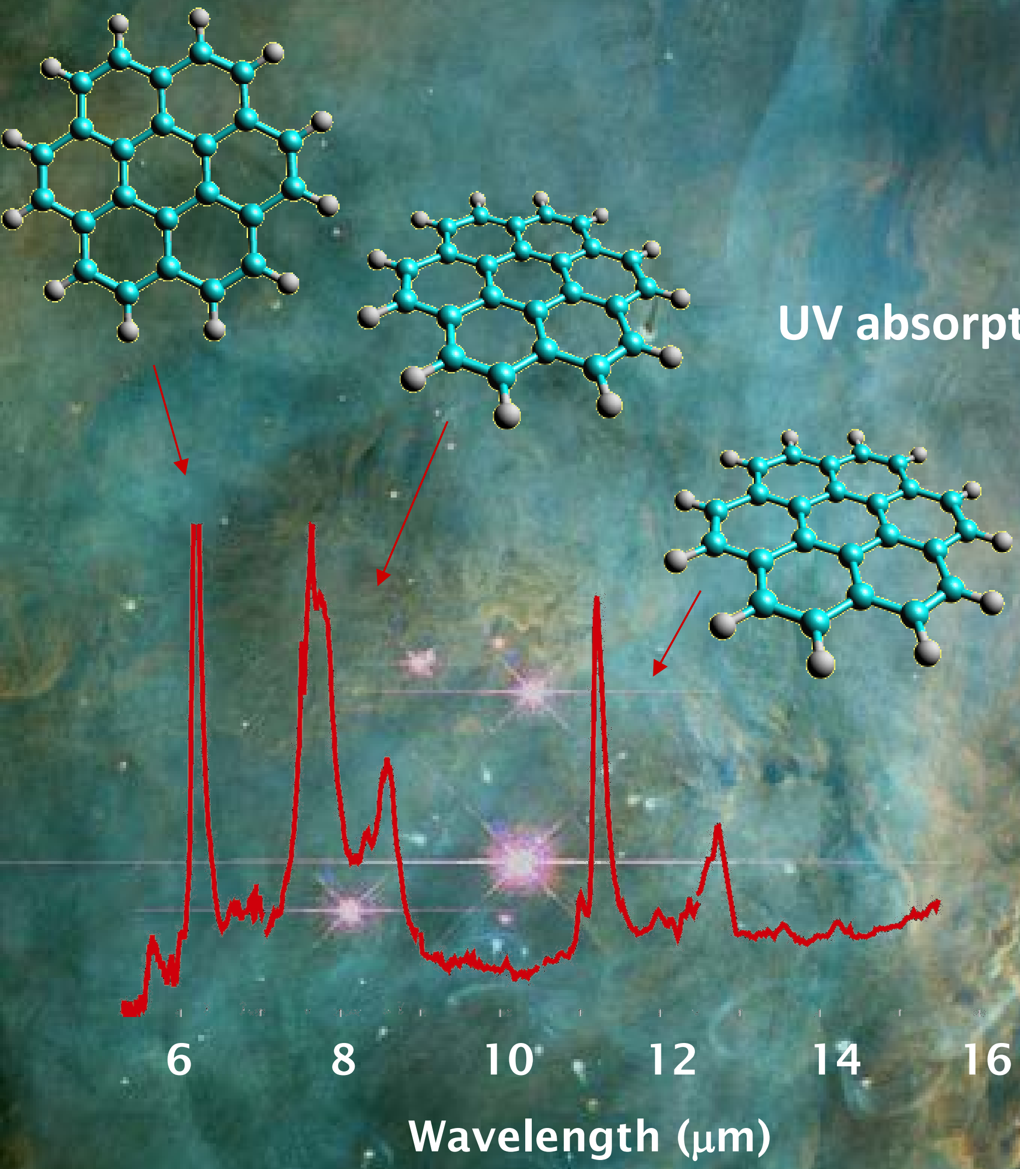
ckyballs In A Young Planetary Nebula

A / JPL-Caltech / J. Cami (Univ. of Western Ontario/SETI Institute)

Spitzer Space Telescope • IRS

ssc2010-06a

Unidentified infrared bands (UIRs)

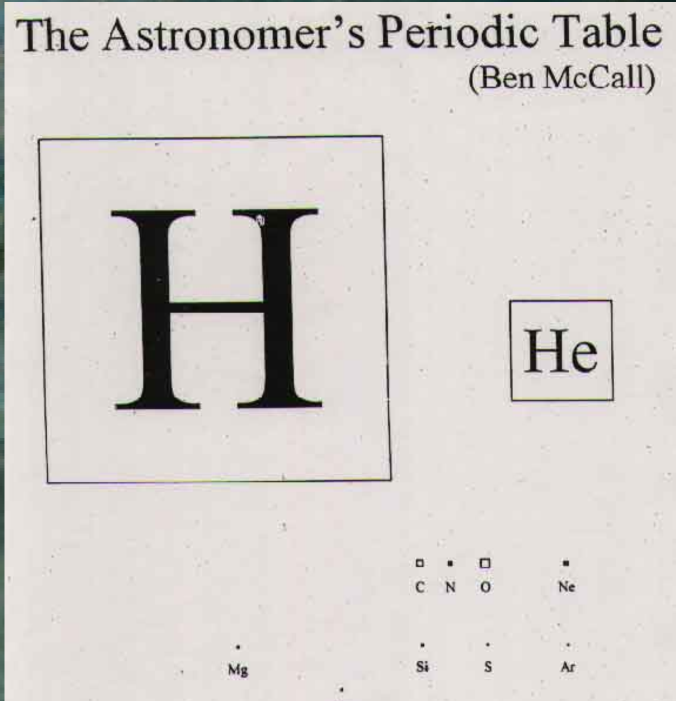


Abundantly present

Observed in emission

UV absorption followed by IR radiative cooling

→ Polyaromatic species - PAHs



The Astronomer's Periodic Table

(Ben McCall)

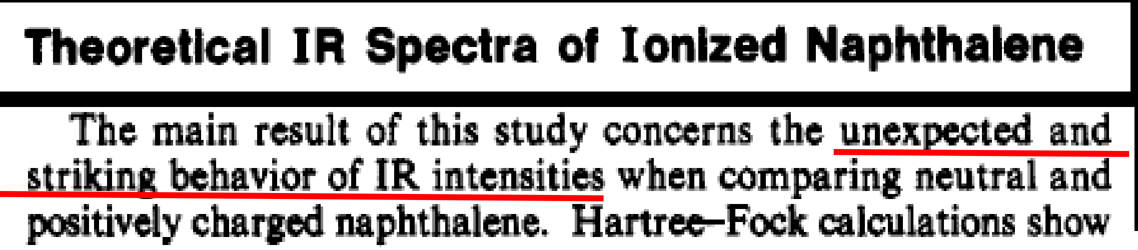
H He

C N O Ne

Mg Si S Ar

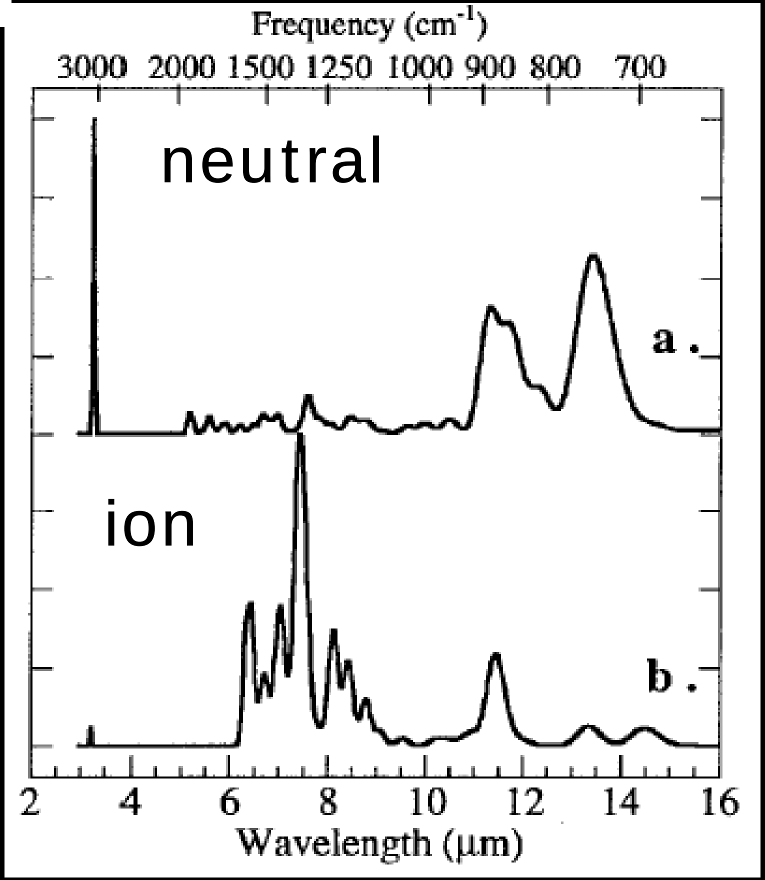
Neutral versus ionic PAHs

Pauzat, Talbi, Miller, DeFrees, Ellinger, JPC **96**, 7882 (1992)



Theoretical IR Spectra of Ionized Naphthalene

The main result of this study concerns the unexpected and striking behavior of IR intensities when comparing neutral and positively charged naphthalene. Hartree–Fock calculations show



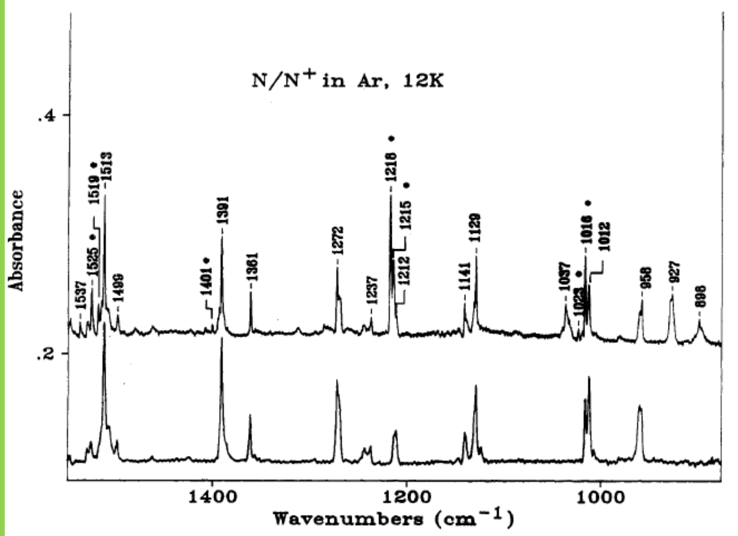
Allamandola, et al.

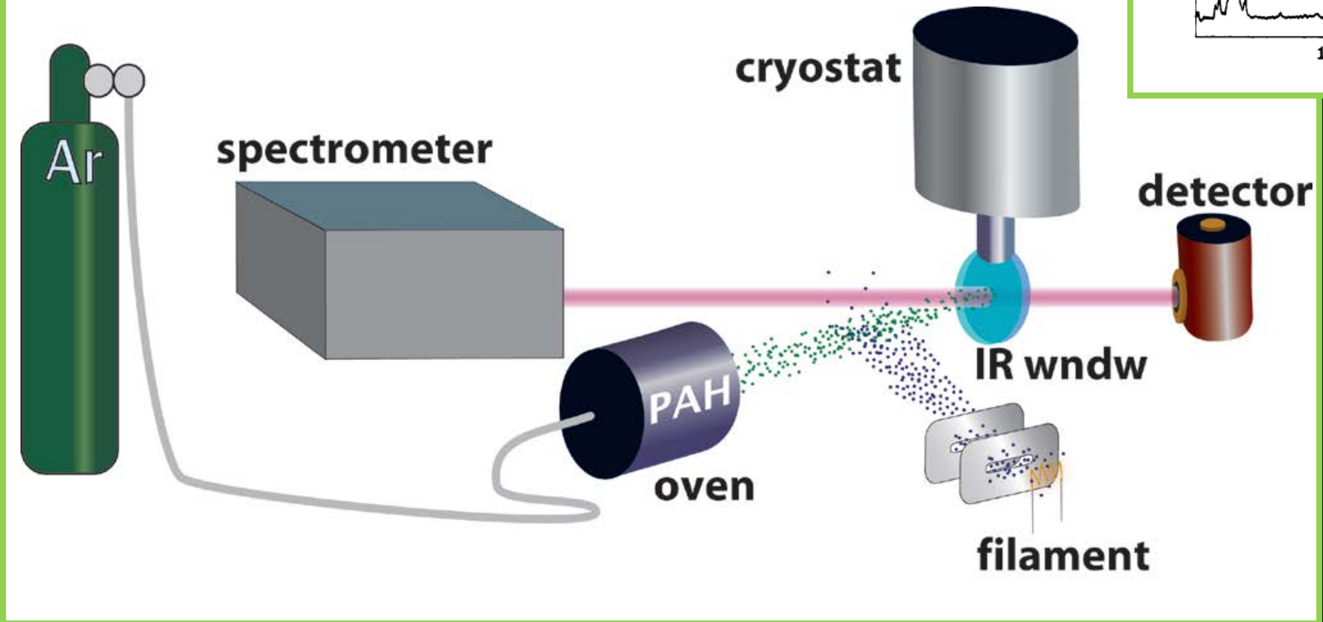
ApJ **511**, L115 (1999)

Neutral versus ionic PAHs

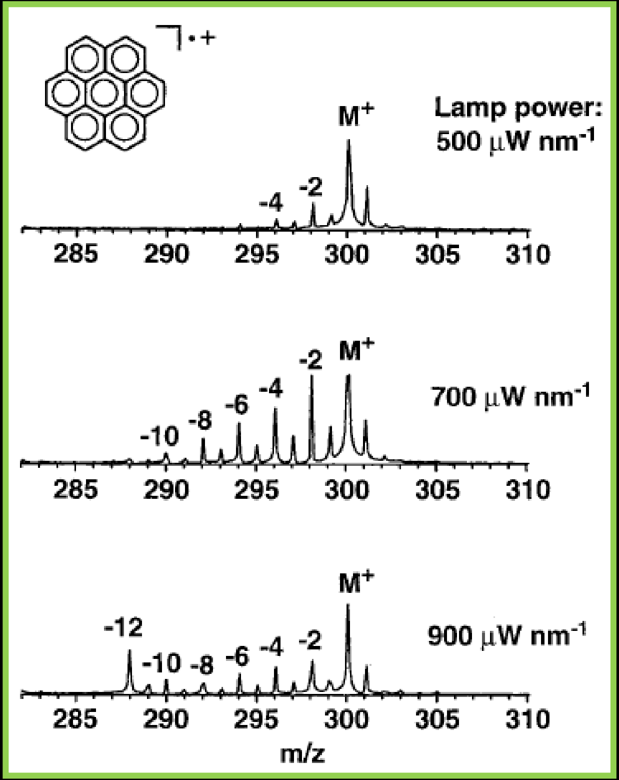
Infrared Spectrum of Matrix-Isolated Naphthalene Radical Cation

Szczepanski, Roser, Personnette, Eyring, Pellow, Vala,
JPC **96**, 7876 (1992)

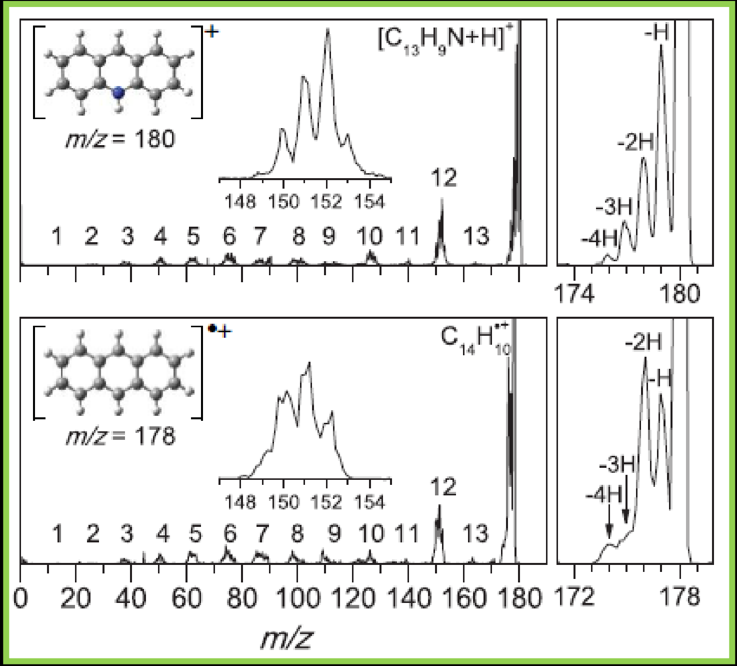




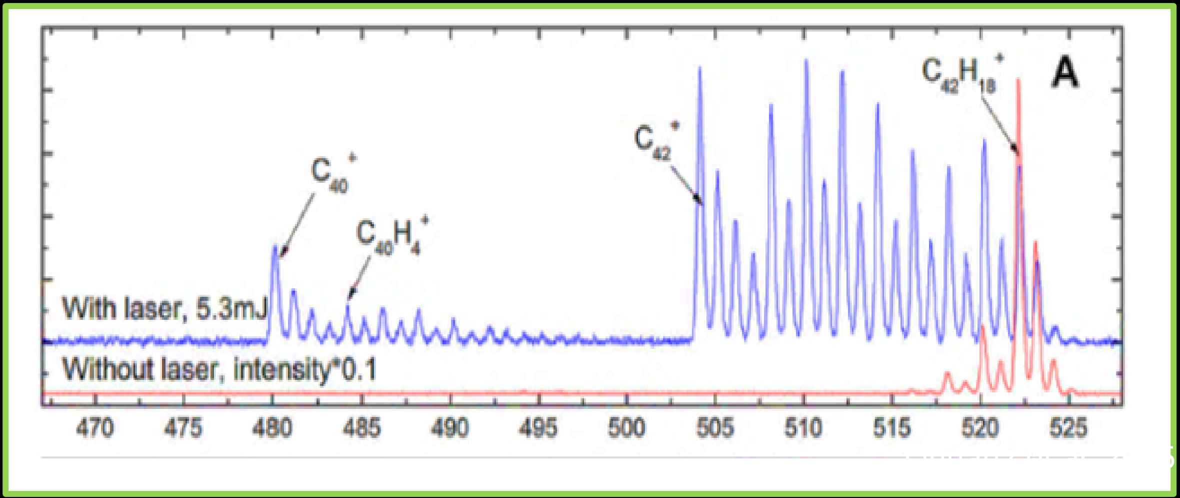
Hydrogen loss

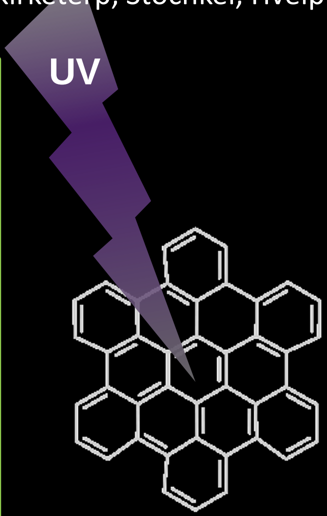


Ekern, Marshall, Szczepanski, Vala
ApJ **1997**, 488, L39



Johansson, Zettergren, Holm, Haag, Nielsen, Wyer, Kirketerp, Stochkel, Hvelplund, Schmidt, Cederquist
JCP **2011**, 135, 084304





$C_{42}H_{18}$

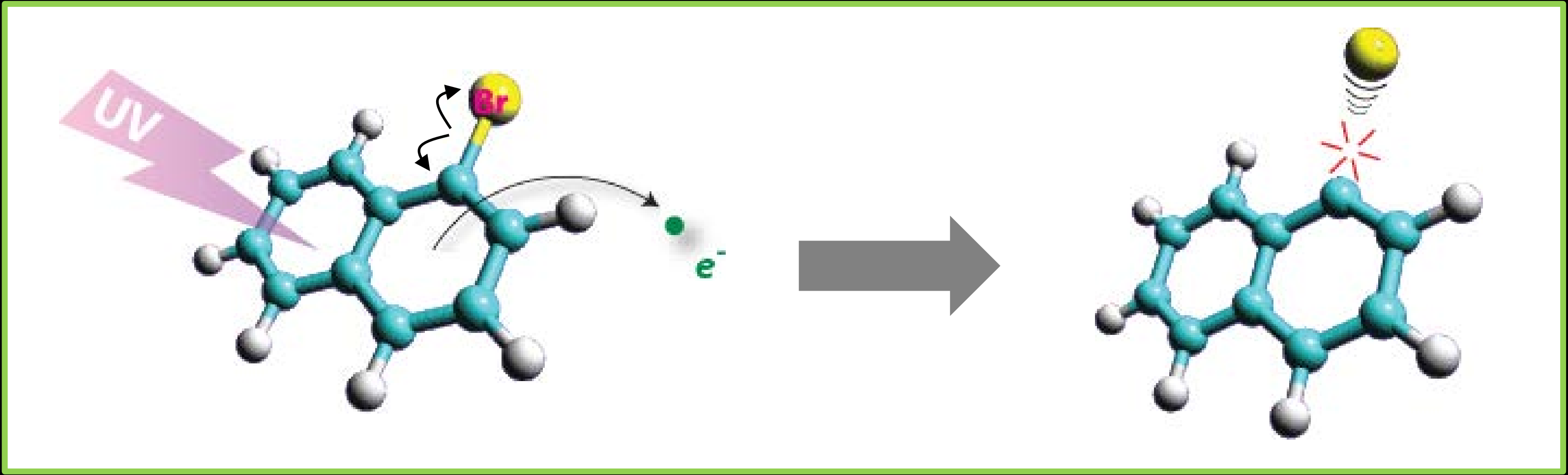
H-loss from radical cation PAHs

Aryl cations

- **Carbocation**
- **Even-electron**
- **Closed shell?**

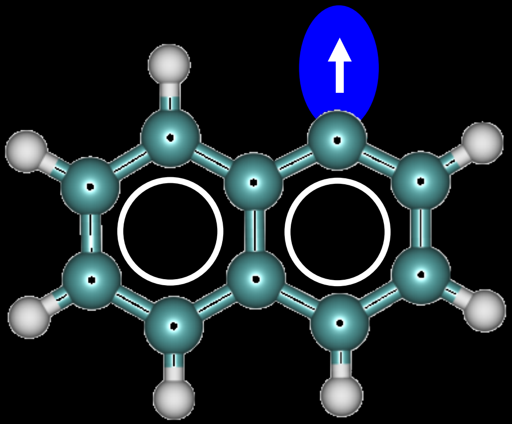
$$\mathrm{C10H7Br} \xrightarrow[\mathrm{UV}]{-\,e^-} [\mathrm{C10H7Br}^{+\bullet}]^* \xrightarrow{-\,\mathrm{Br}\bullet} \mathrm{C10H7}^+$$

bromonaphthalene *naphthyl carbocation*



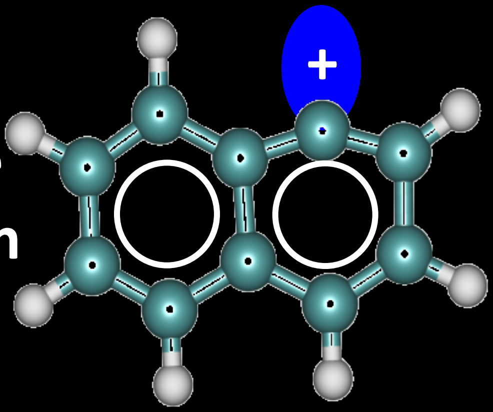
See e.g. Gotkis, Naor, Laskin, Lifshitz, Faulk, Dunbar, *JACS* **1993**, *114*, 7402

aryl cations: even-electron, but closed-shell?



Naphthyl radical $C_{10}H_7^{\bullet}$

remove electron



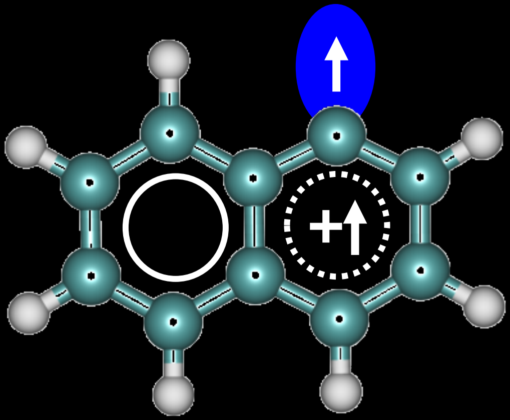
singlet: $\ldots\pi^{10}\sigma^{0}$

localized charge
closed shell
sp hybrid distorts

Naphthyl cation $C_{10}H_7^{+}$

$\Delta E(S - T) = 0$

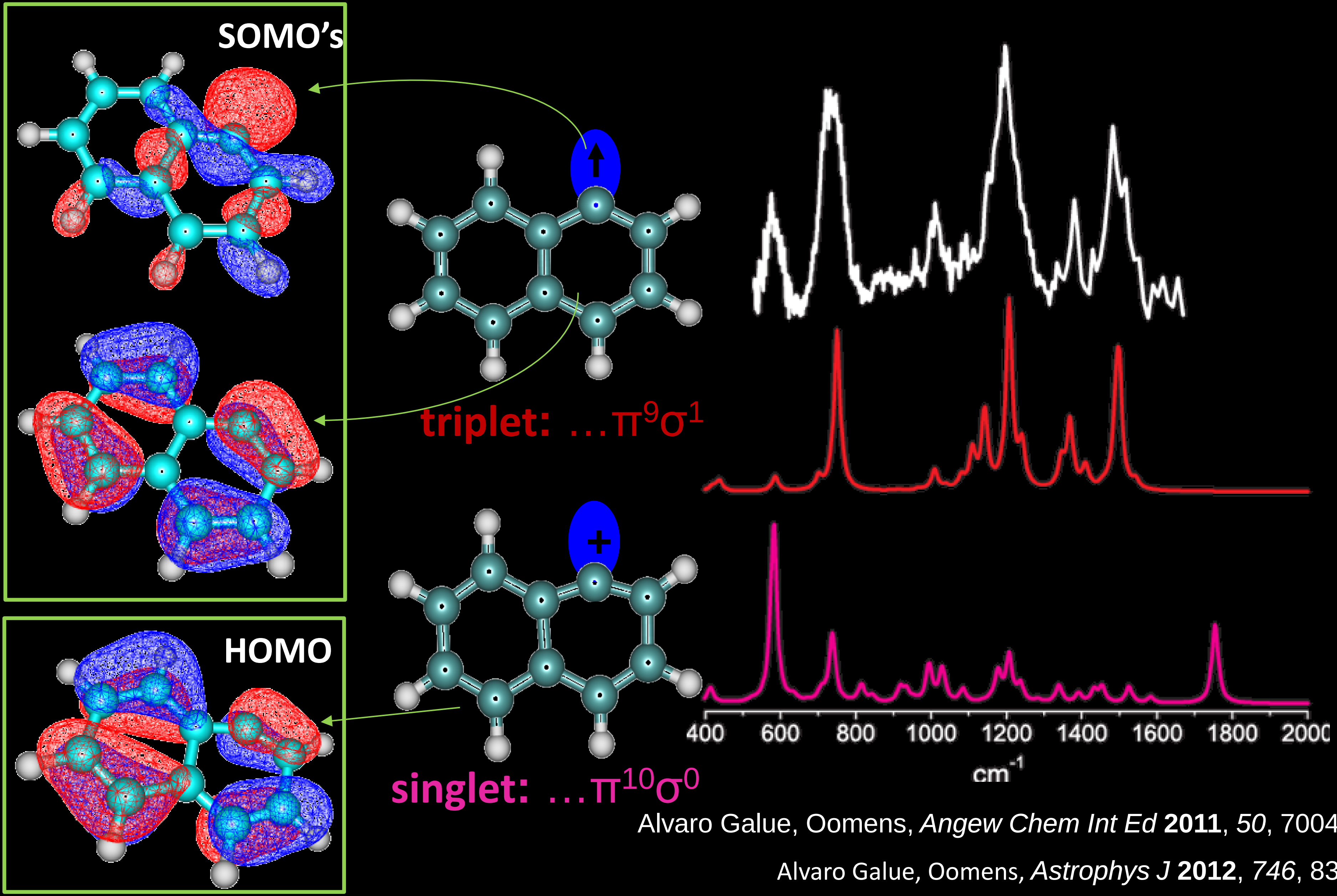
DFT level calculation



triplet: $\ldots\pi^{9}\sigma^{1}$

delocalized charge
open shell
all sp^2, no distortion

IR spectroscopy of the naphthyl cation



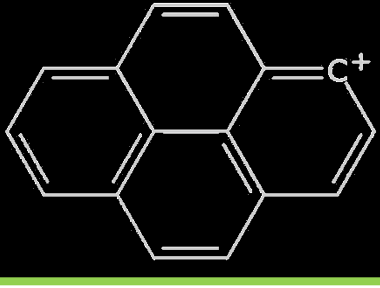
triplet: …$\pi^9\sigma^1$

singlet: …$\pi^{10}\sigma^0$

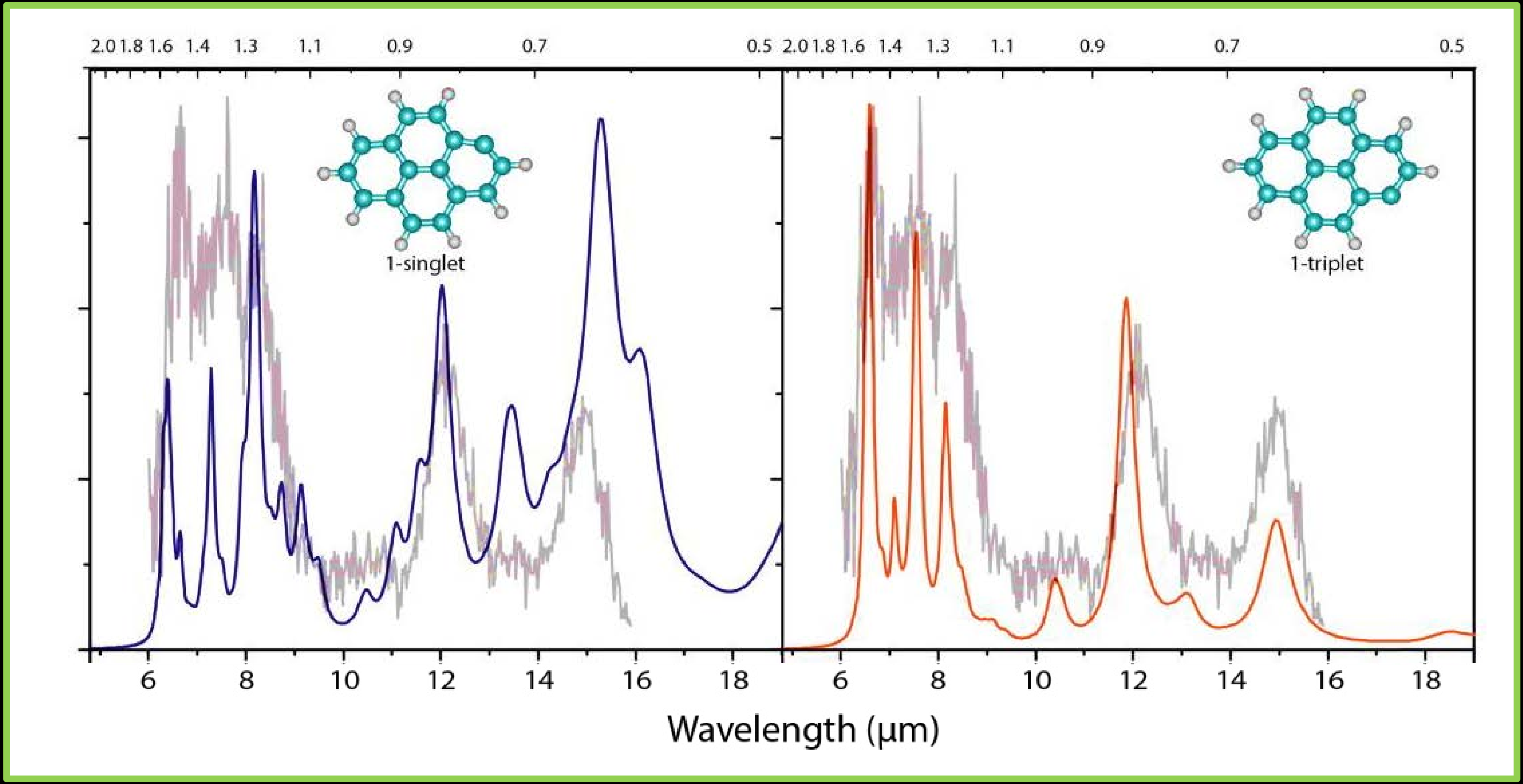
Alvaro Galue, Oomens, *Angew Chem Int Ed* **2011**, *50*, 7004

Alvaro Galue, Oomens, *Astrophys J* **2012**, *746*, 83

Larger PAHs



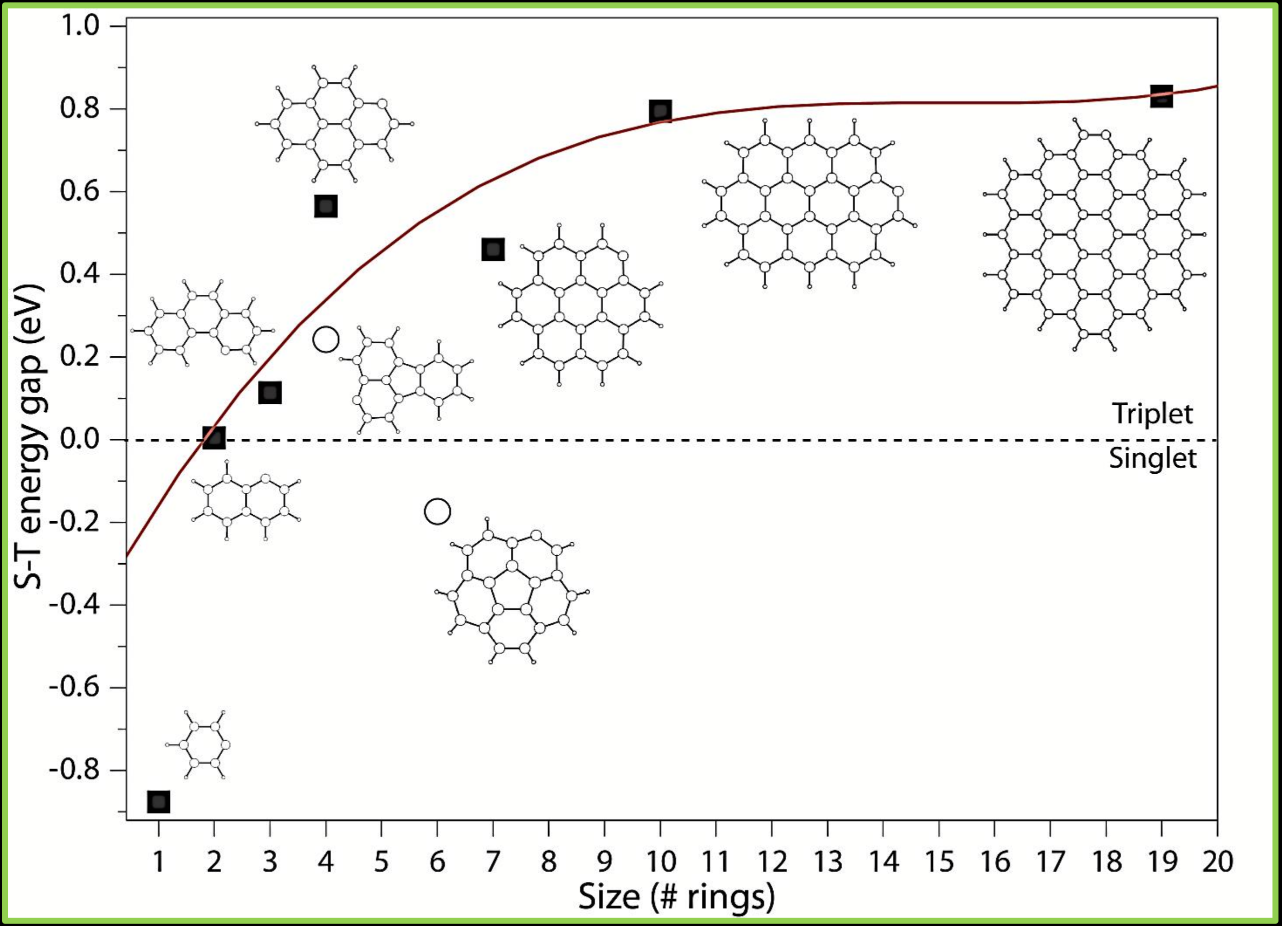
ΔE(S - T) = +0.56 eV



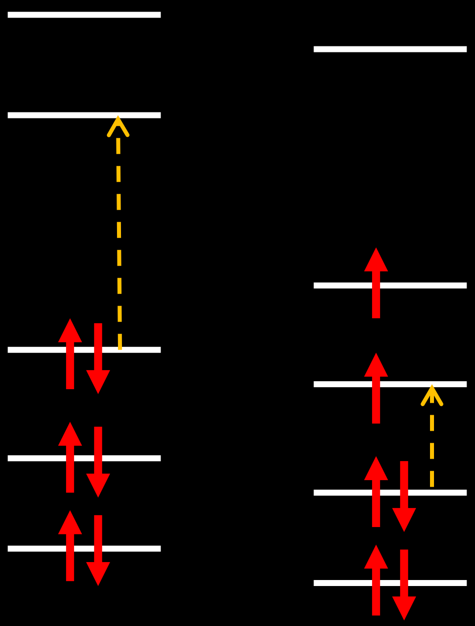
singlet

triplet

Aryl cations: triplet state more stable



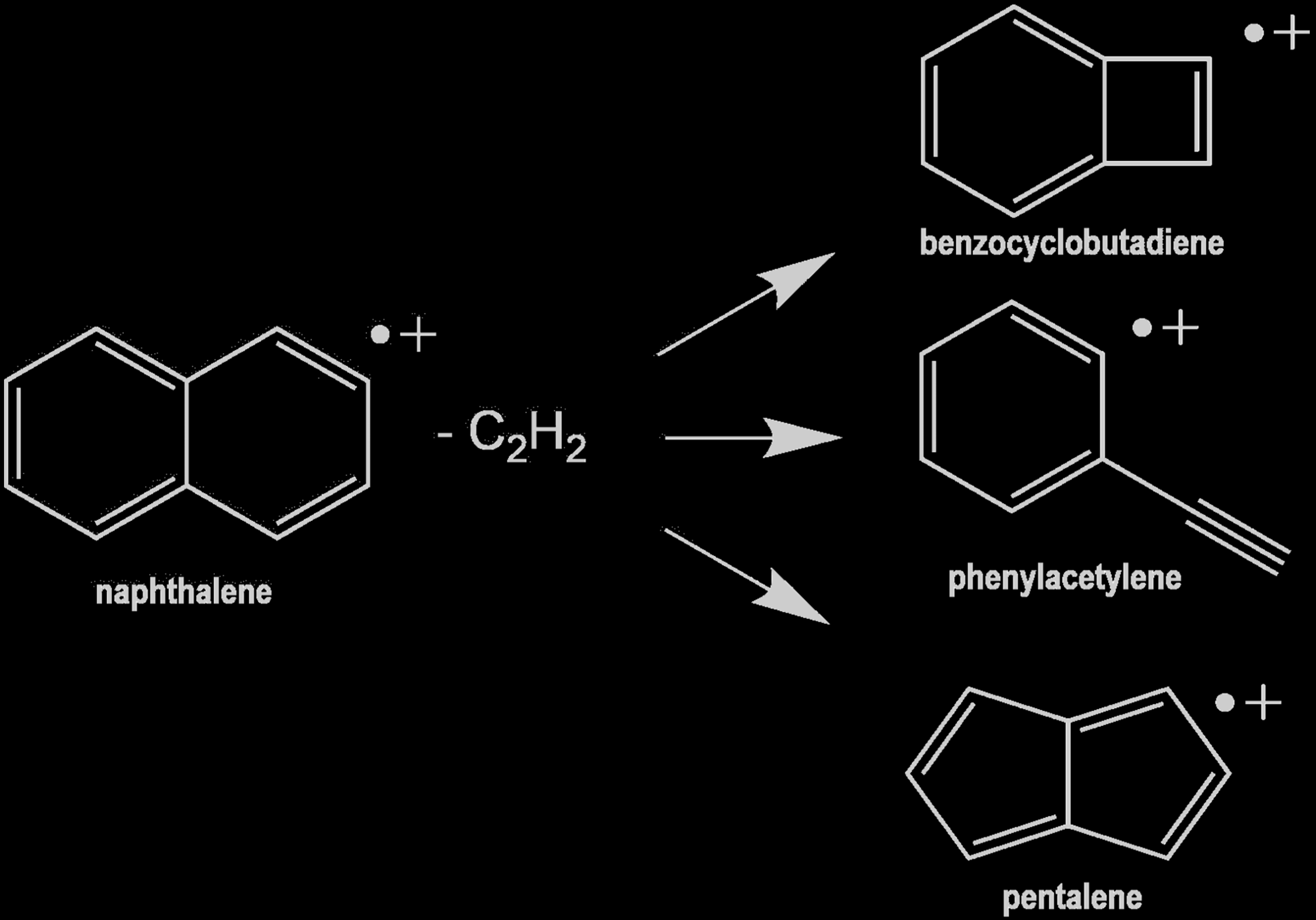
UV/vis spectra?



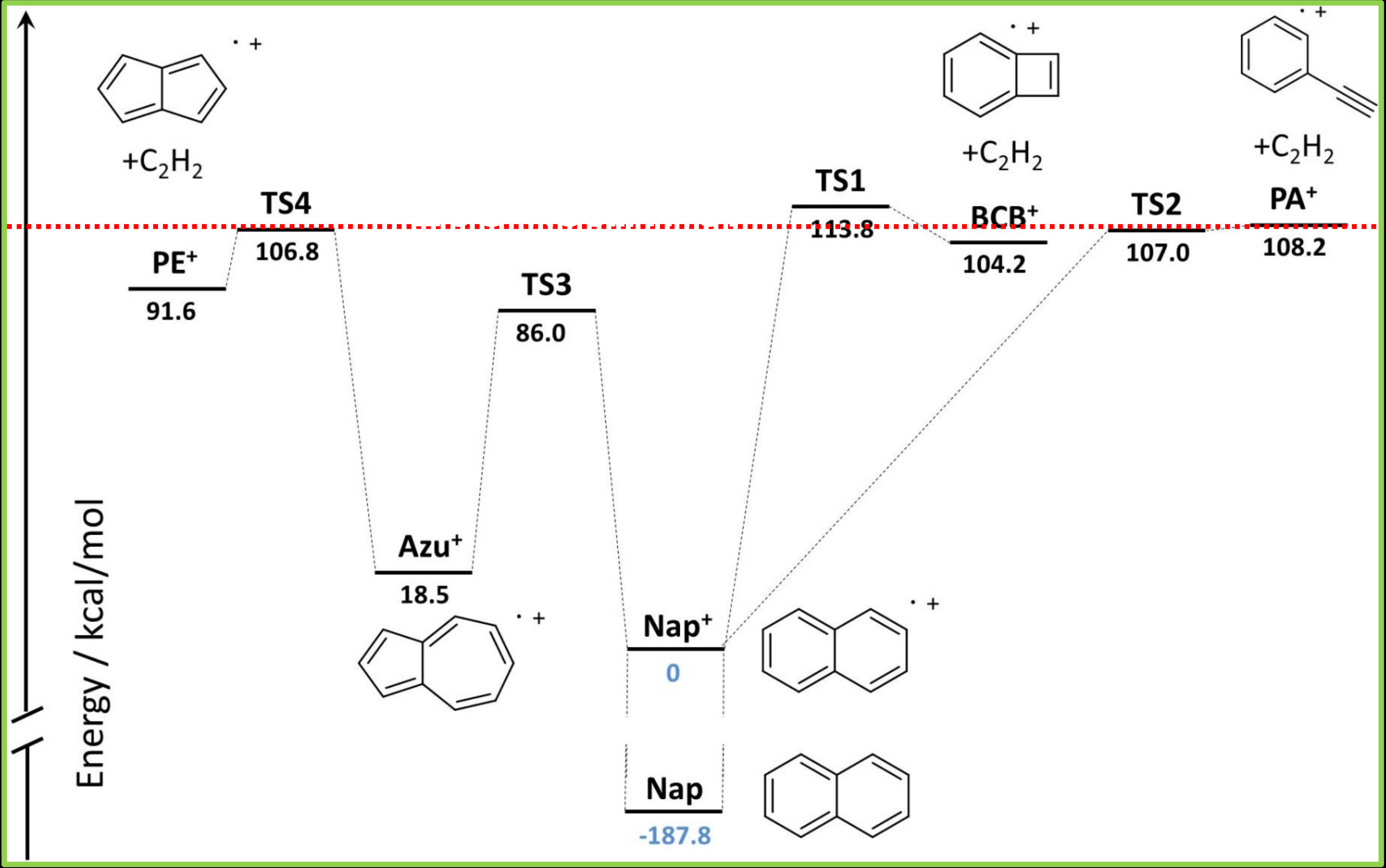
singlet
triplet

Alvaro Galue, Oomens, *Astrophys J* **2012**, *746*, 83

Naphthalene$^+$ dissociation: C_2H_2-loss

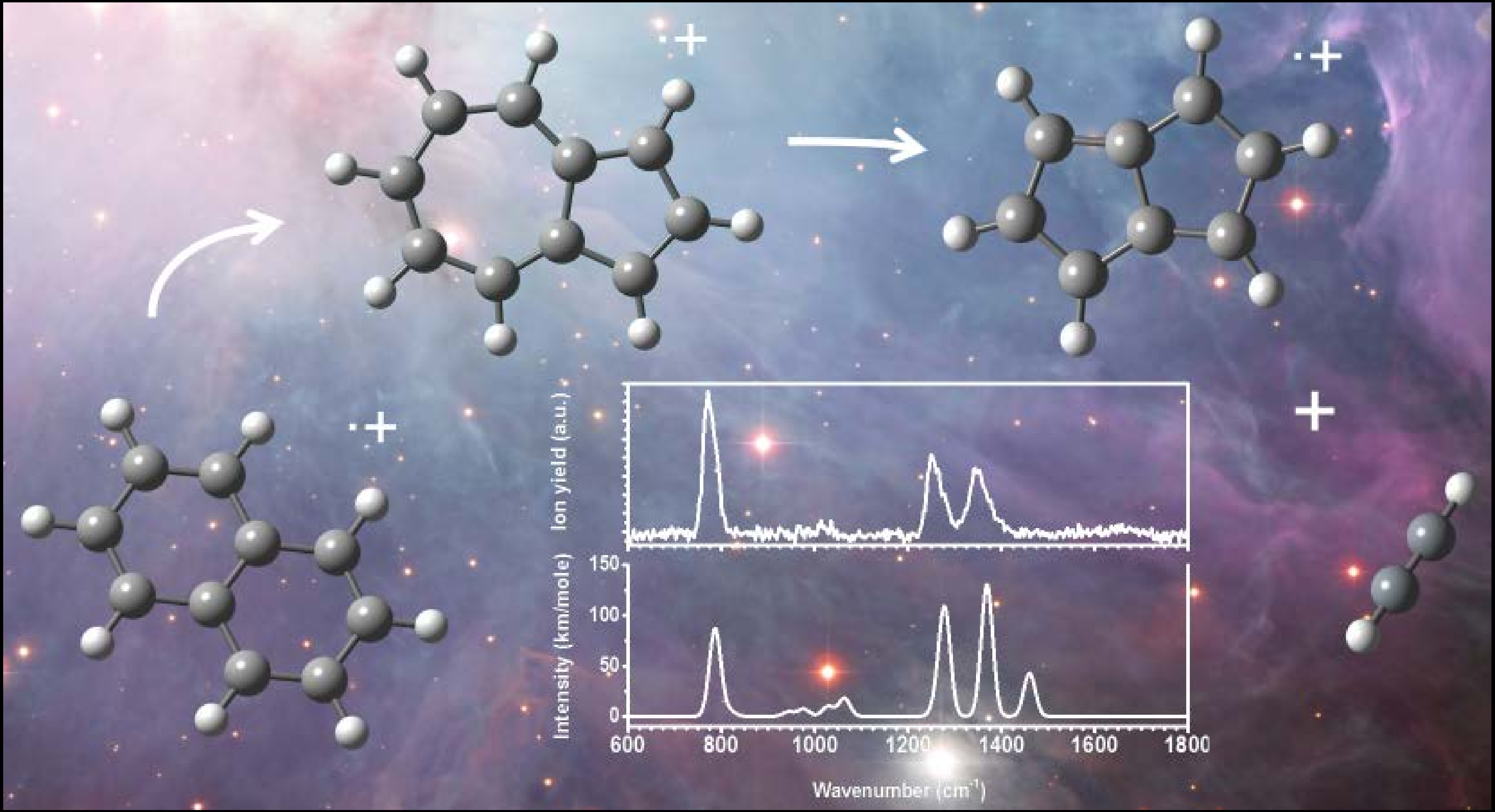


Naphthalene$^+$ Potential Energy Surface



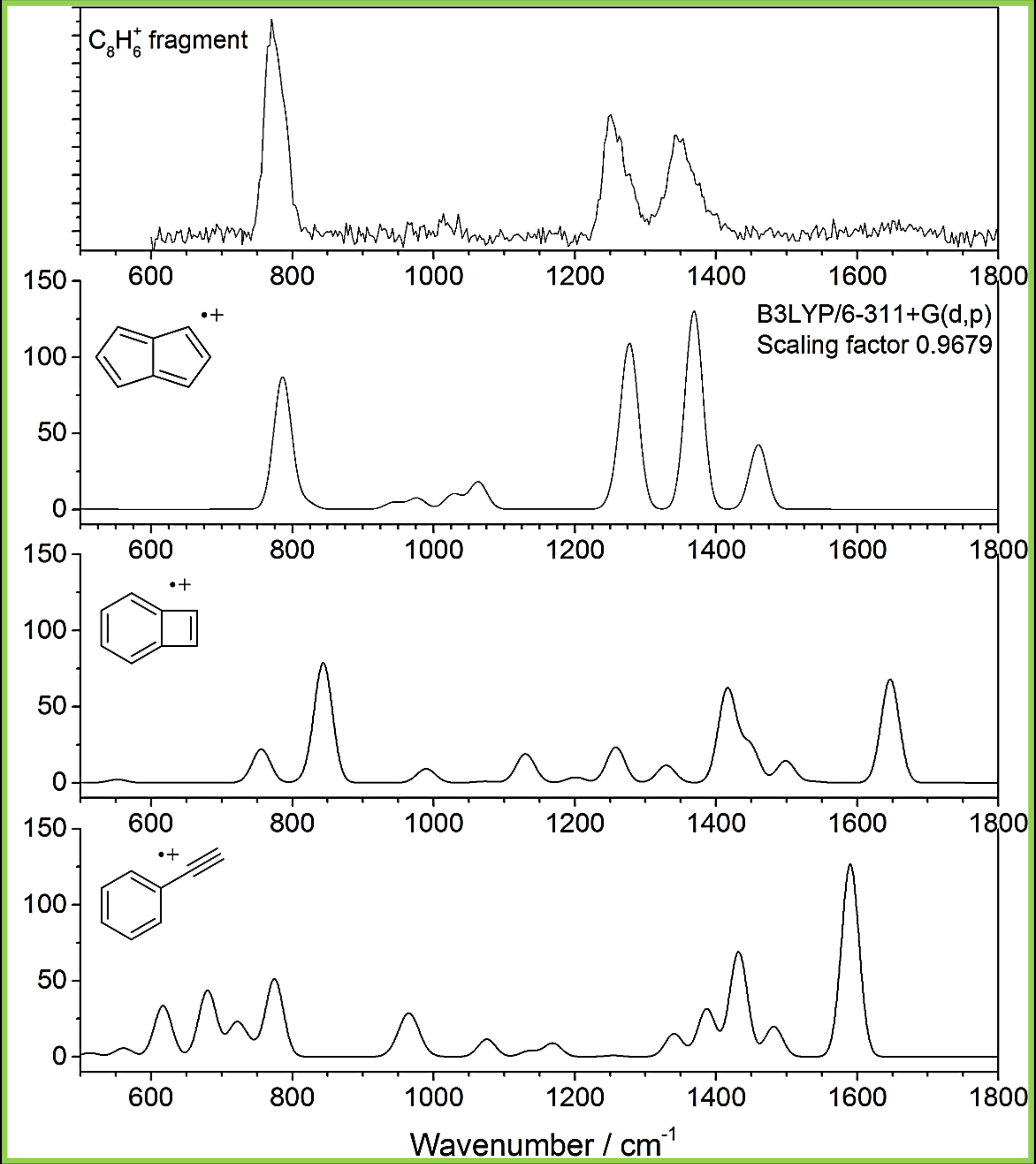
Dyakov, Ni, Lin, Lee and Mebel, PCCP, 2006, 8, 1404–1415.

Spectroscopic product ion identification



Bouwman, de Haas & Oomens, *Chem. Commun*. **2016**, *52*, 2636-2638

Spectroscopic product ion identification

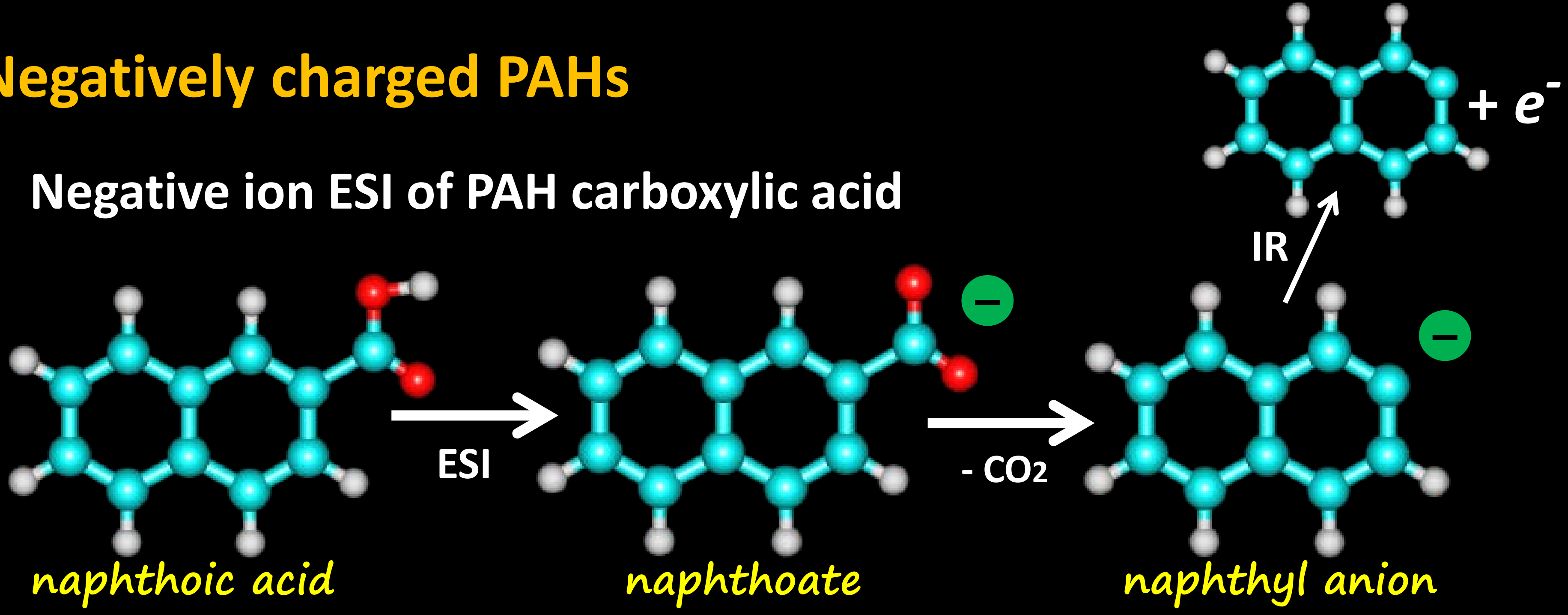


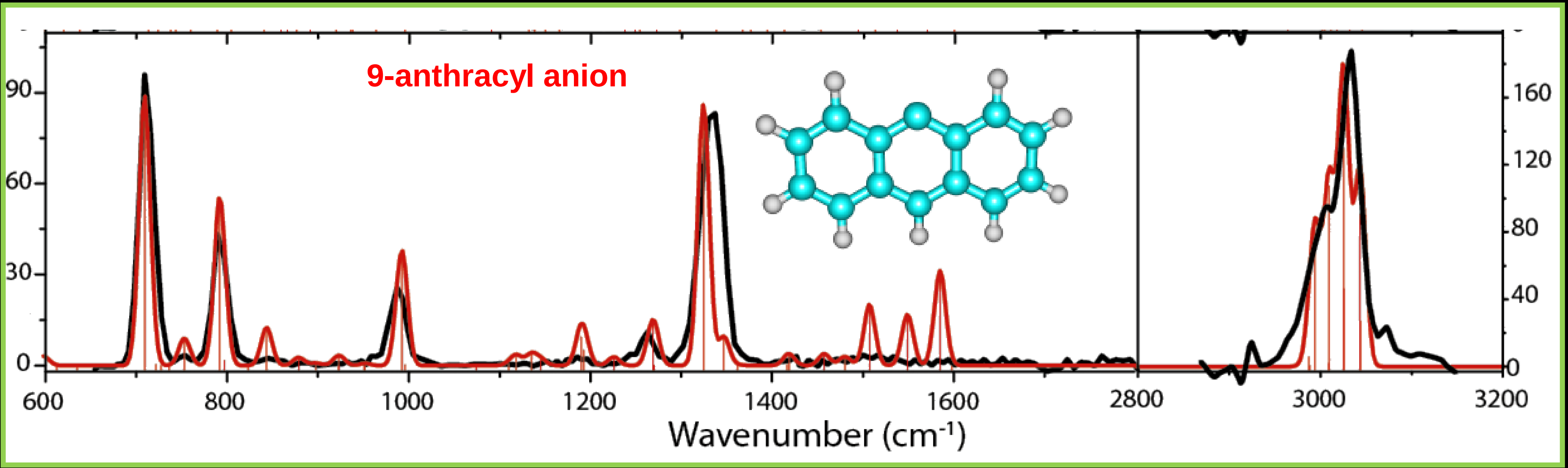
Facile formation of 5-membered ring species

Bouwman, de Haas & Oomens, *Chem. Commun*. **2016**, *52*, 2636-2638

Negatively charged PAHs

Negative ion ESI of PAH carboxylic acid

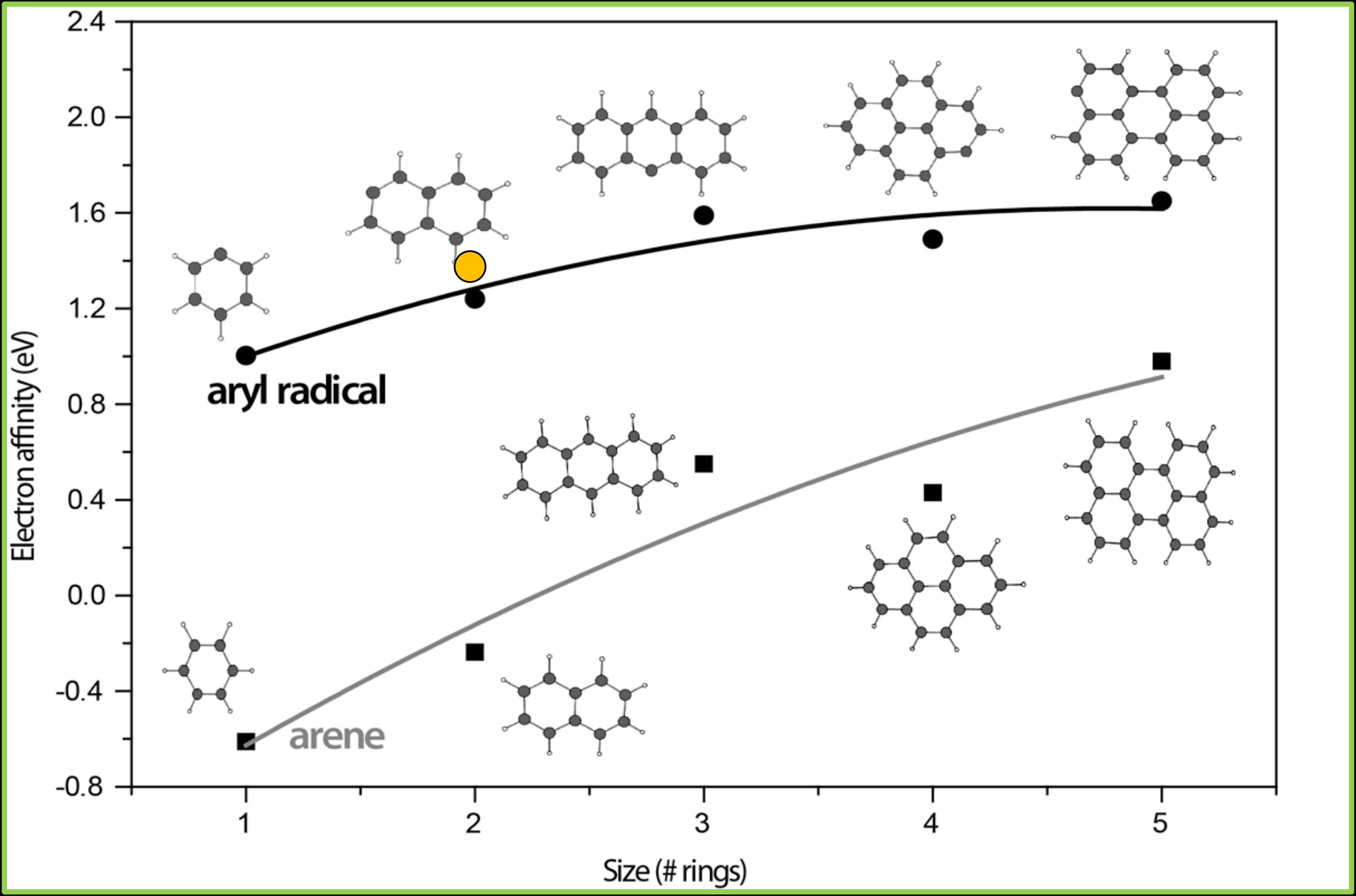




Gao, Berden, Oomens, *Astrophys J* **2014**, *787*, 170

Precursor: 9-anthroic acid

Electron affinities: radical vs deprotonated



● Exp value**: 1.37 eV (**Reed, Kass, *J. Mass Spectrom.* 2000, **35**, 534)

Deprotonated PAHs: large permanent dipole moment

	NAPH	ANTR	PHEN	PYR	TETR	CHRY	PERY	CORO
M	0.0	0.0	0.02	0.0	0.0	0.0	0.0	0.0
M^+	0.0	0.0	0.50	0.0	0.0	0.0	0.0	
MH^+	1.9 | 2.0	0.0 | 3.7	2.7 | 3.7	1.0 | 3.5	1.7 | 5.0	1.2 | 5.7	1.3 | 6.5	3.2
M^-	0.0	0.0	0.5	0.0	0.0	0.0	0.0	
$[M\text{-}H]^-$	6.0 | 8.2	4.2 | 11.3	6.0 | 11.3	7.8 | 10.0	5.0 | 14.5	5.2 | 14.7	6.7 | 9.9	9.9

Values in Debye