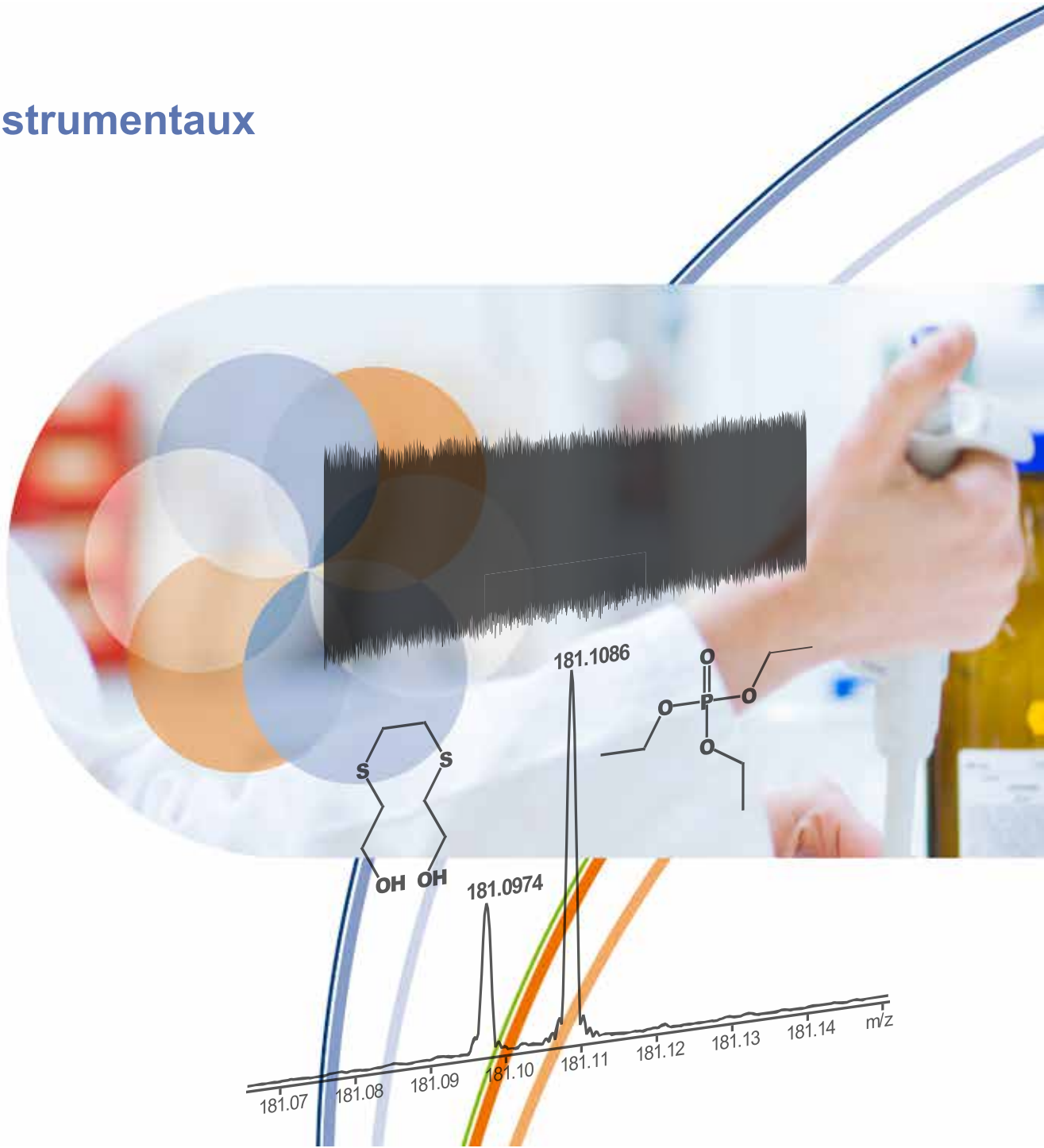


FT-ICR : Aspects Instrumentaux

Carlos Afonso



Mouvement cyclotronique

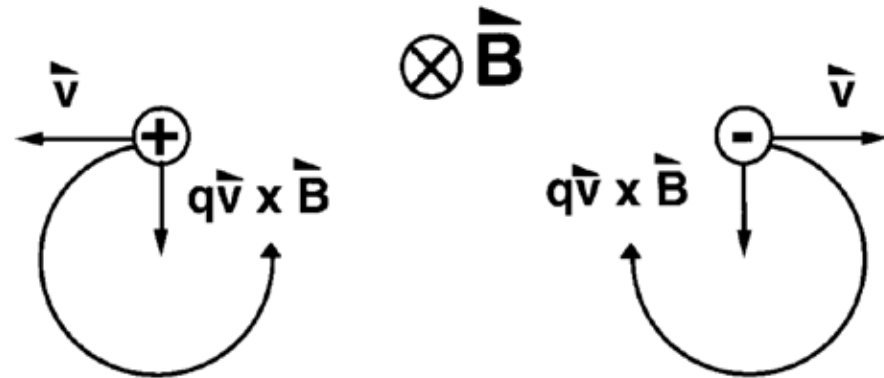
- Force de Lorentz

$$\vec{F} = q\vec{v} \times \vec{B}$$

- Force centripète

$$F = ma_c = \frac{mv^2}{r}$$

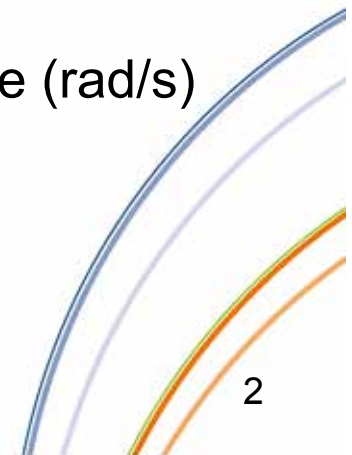
$$v = \omega_c r$$



$$\omega_c = \frac{qB}{m} \rightarrow \nu_c = \frac{qB}{2\pi m}$$

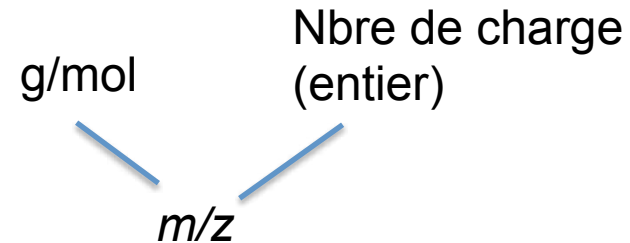
ν_c : Fréquence (Hz)

ω_c : Vitesse angulaire (rad/s)



Conversion SI/unités usuelles

- SI
 - kg, Hz, Tesla, Coulomb
- Unités usuelles
 - m/z , T



$$N_a = 6.022 \times 10^{23} \text{ mol}^{-1}$$

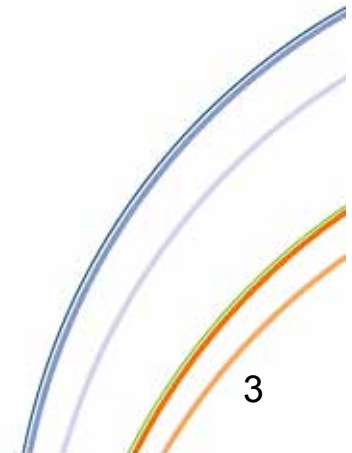
$$m(\text{kg}) = M(\text{g/mol}) / (6.02214129 \times 10^{23} \times 10^3)$$

$$q = ze = z \times 1.60217657 \times 10^{-19} \text{ C}$$

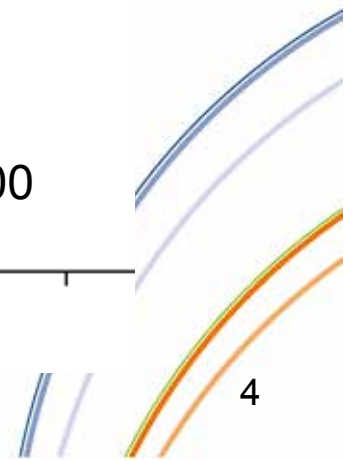
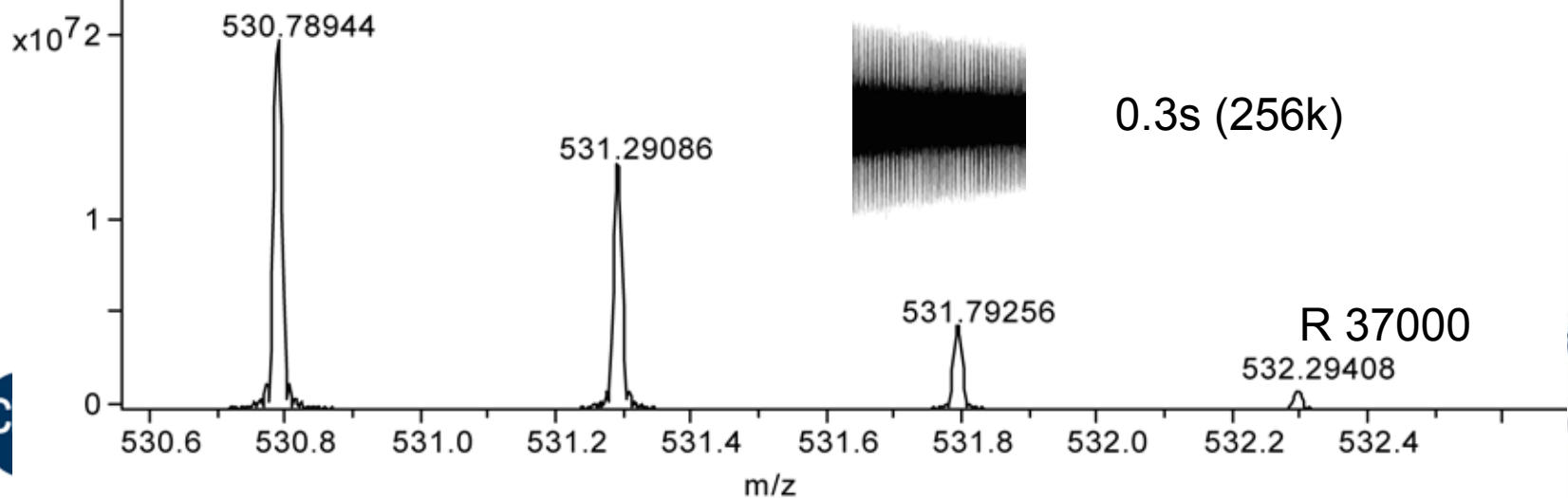
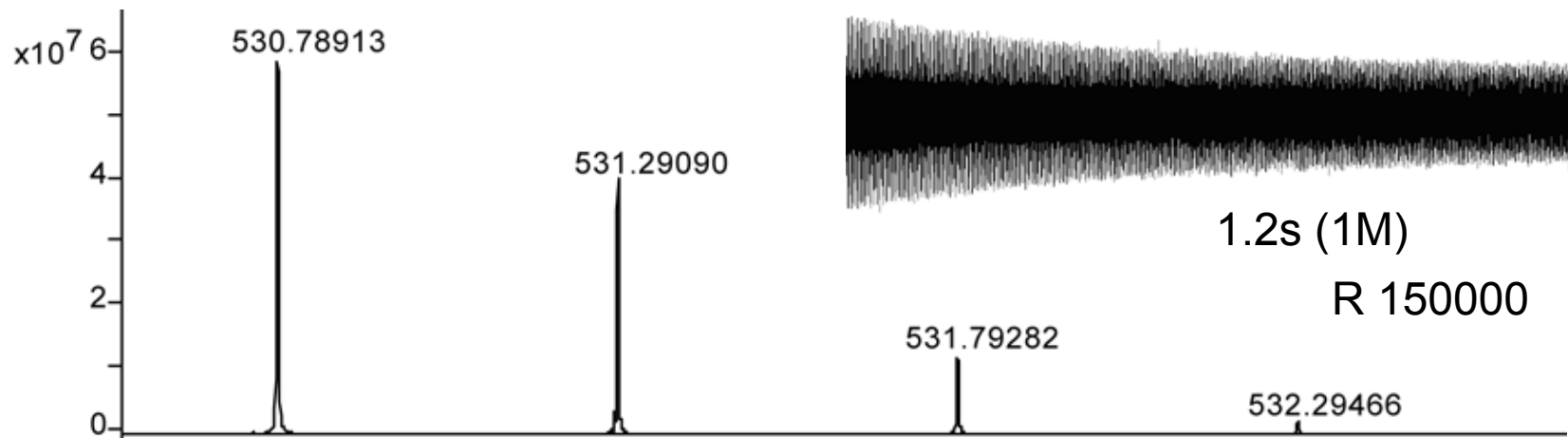
$$v_c = \frac{qB}{2\pi m}$$

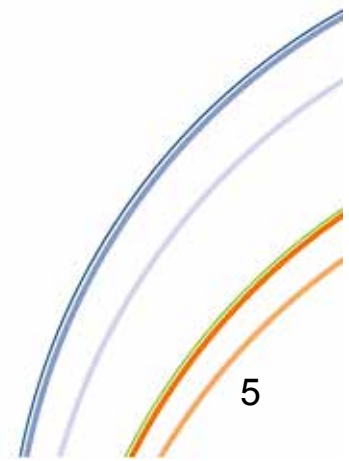
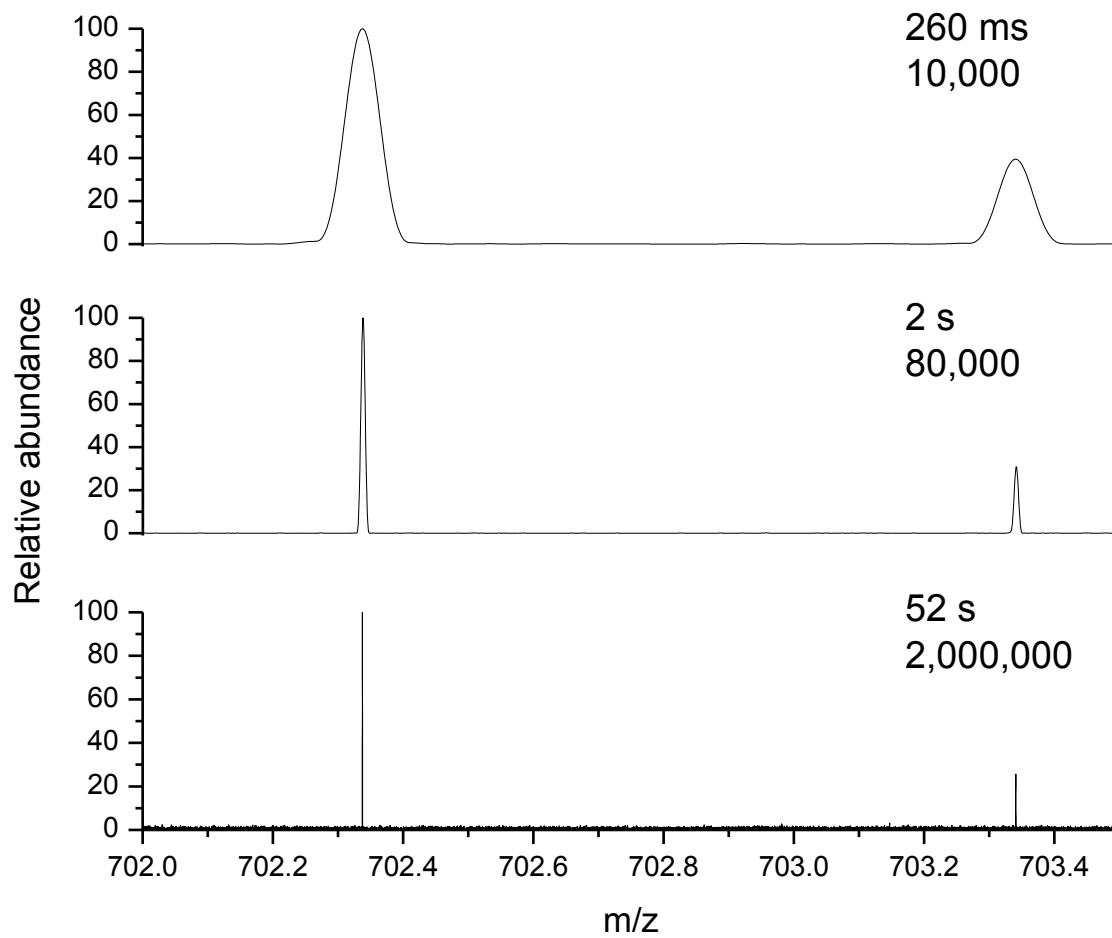
$$v_c = \frac{z \times 1.6 \times 10^{-19} B \times 6.022 \times 10^{23} \times 10^3}{2\pi m(u)}$$

$$v_c = \frac{1.535611 \times 10^7 B}{m/z}$$

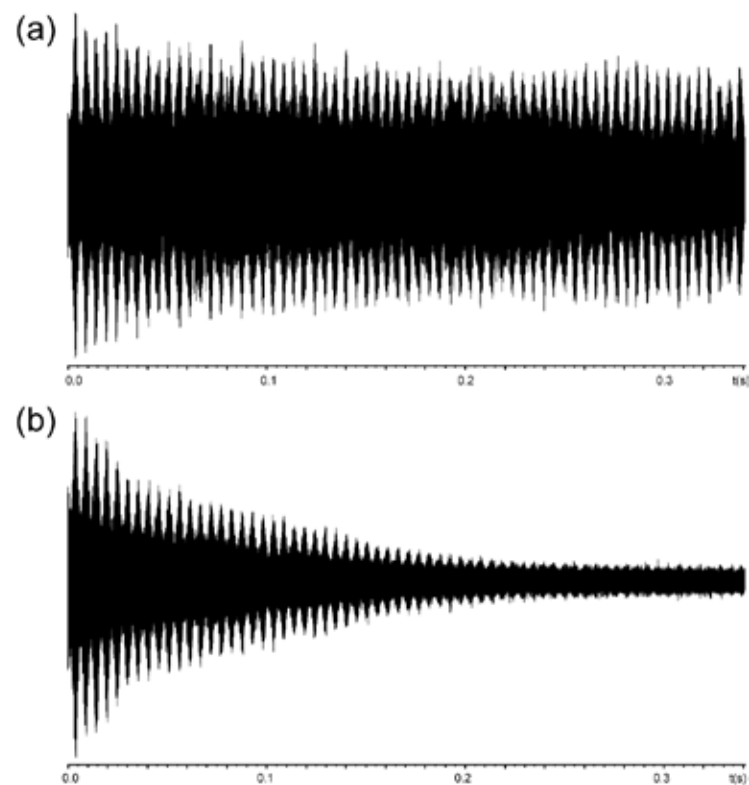


Temps de détection





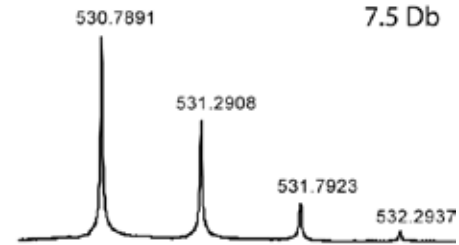
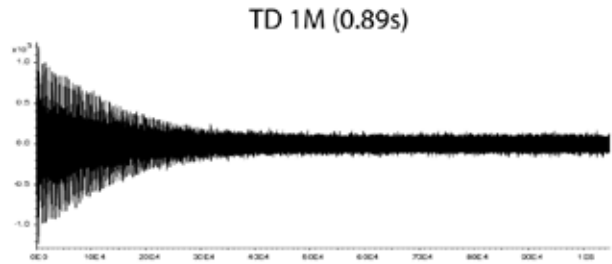
Effet de la pression



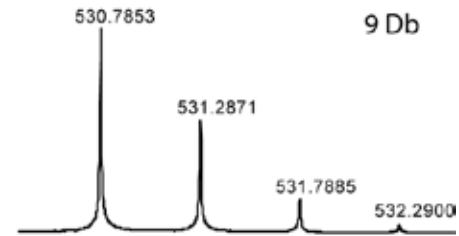
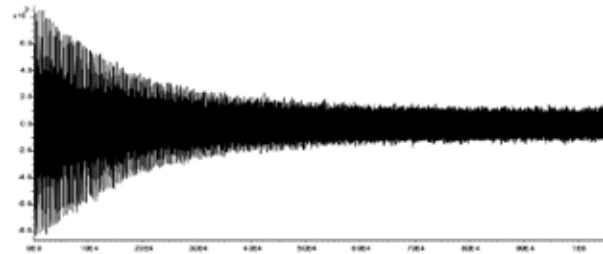
Signal transitoire de 0.32 s (512k) correspond à l'enregistrement de l'ion m/z 531 de la bradykinine (a) sans et (b) avec introduction d'argon dans la cellule suivi d'un temps de pompage de 1 s.

$$V_{exc} = 250 \times 10^{-20} \frac{A}{(V_{P-P})}$$

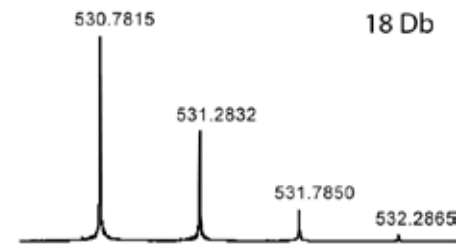
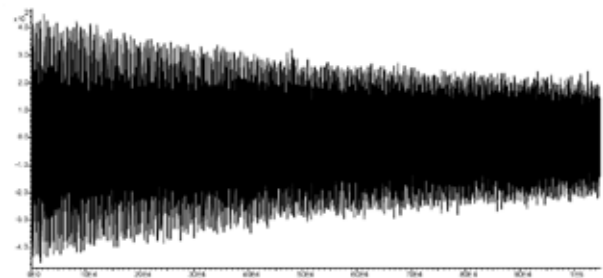
Excitation



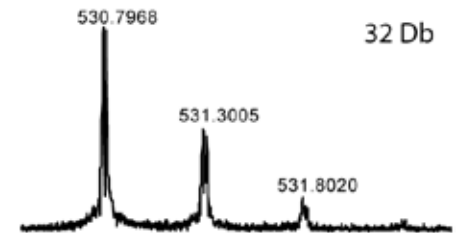
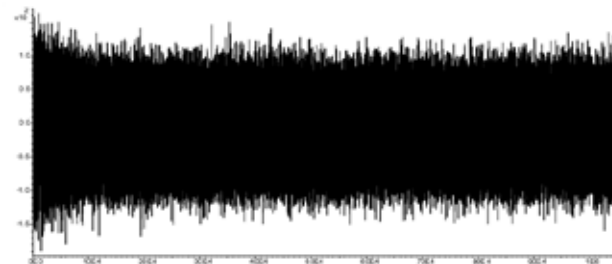
105 V_{pp}



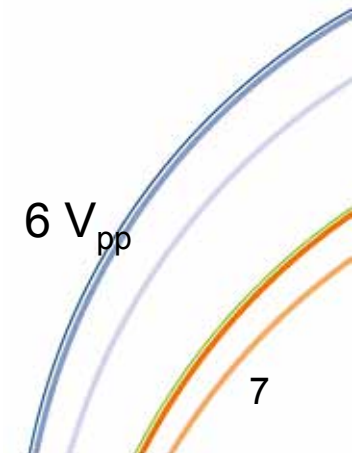
89 V_{pp}



31 V_{pp}

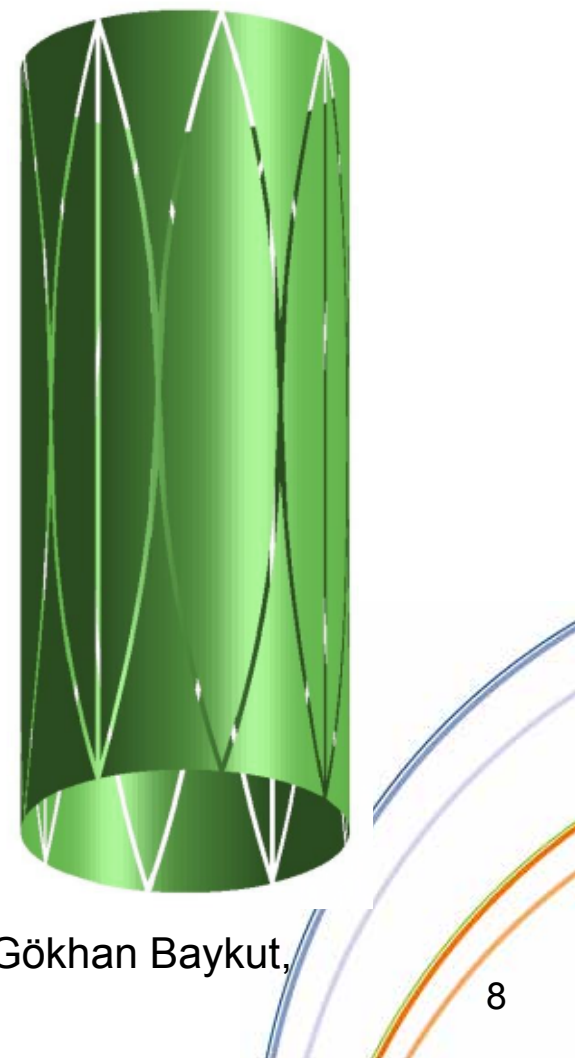


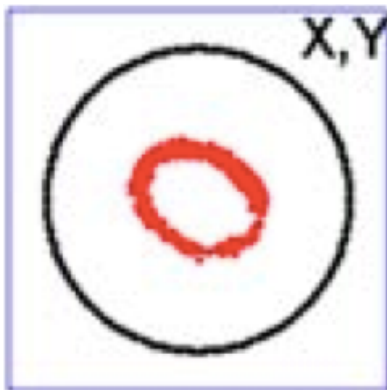
6 V_{pp}



Comment augmenter la résolution ?

- Eugene Nikolaev



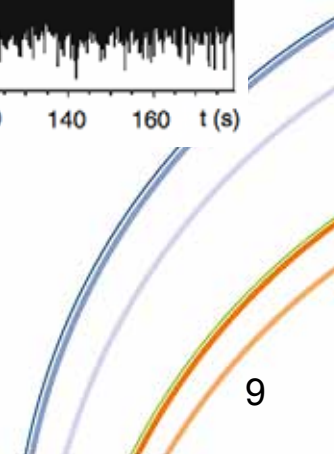
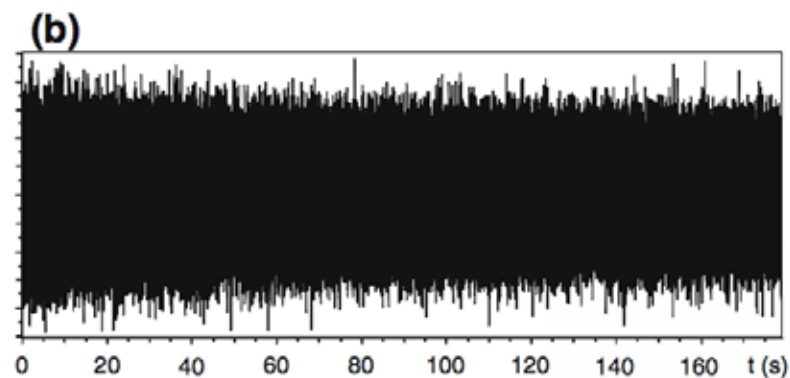
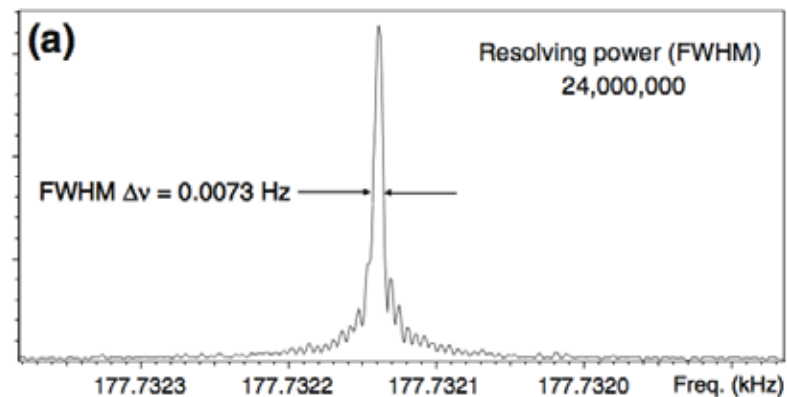


T=0.6s
B=7 T
m/z 500

cellule Thermo

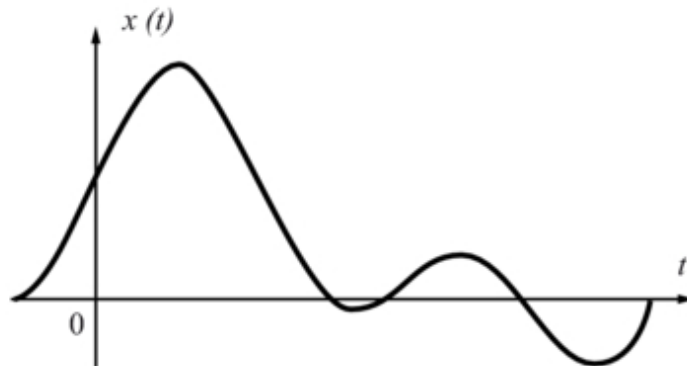
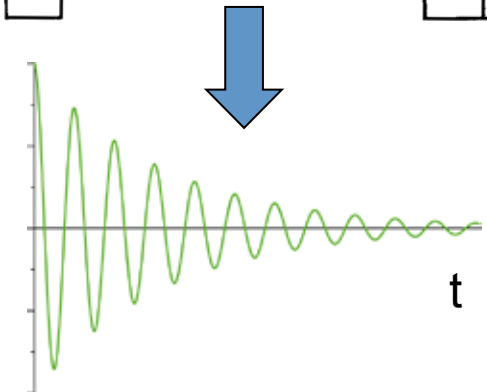
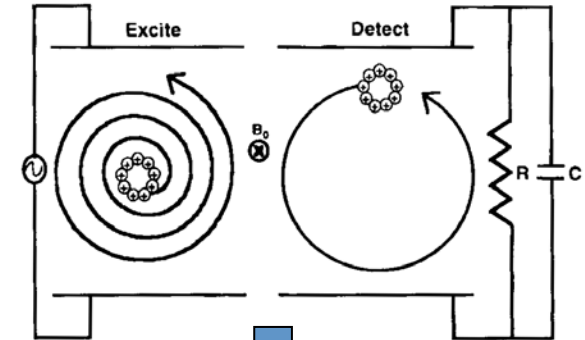


PNNL
geometry

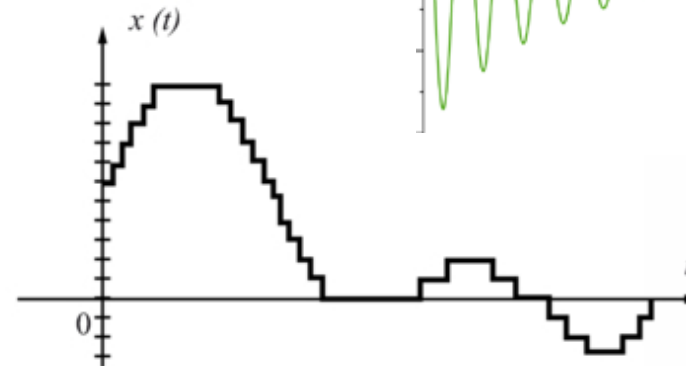


Le signal transitoire : un signal analogique

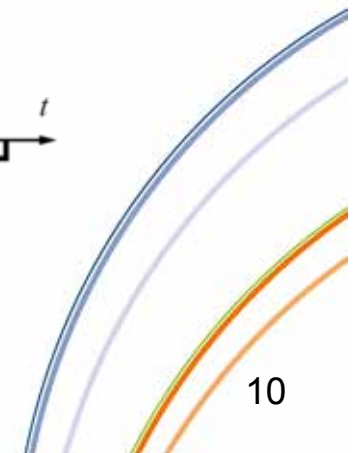
- Courant alternatif continu
 - L'informatique nécessite un signal numérique
 - Convertisseur analogique/numérique
- Contraintes
 - Hautes fréquences
 - Tailles de fichier



Signal analogique
de départ



Signal recomposé
présentant des échelottes

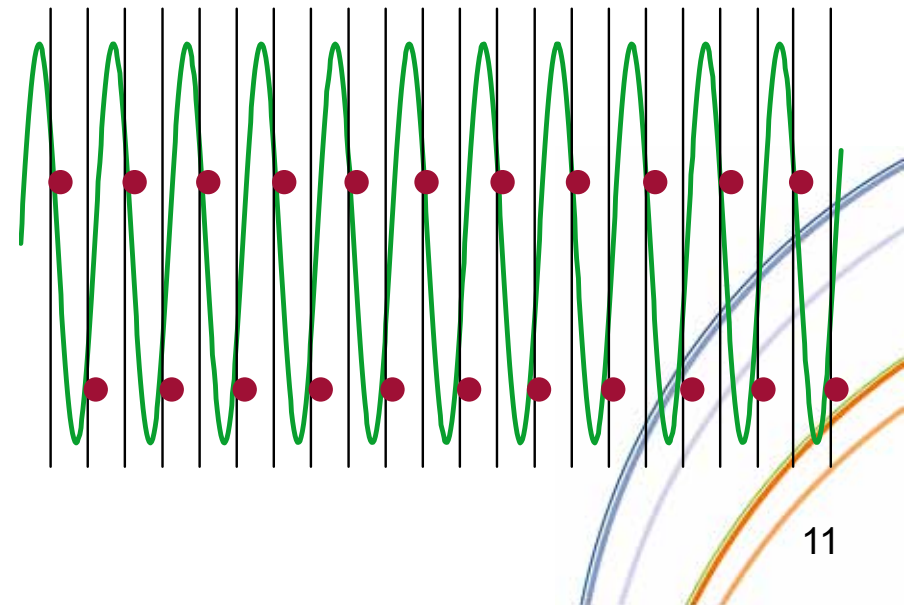
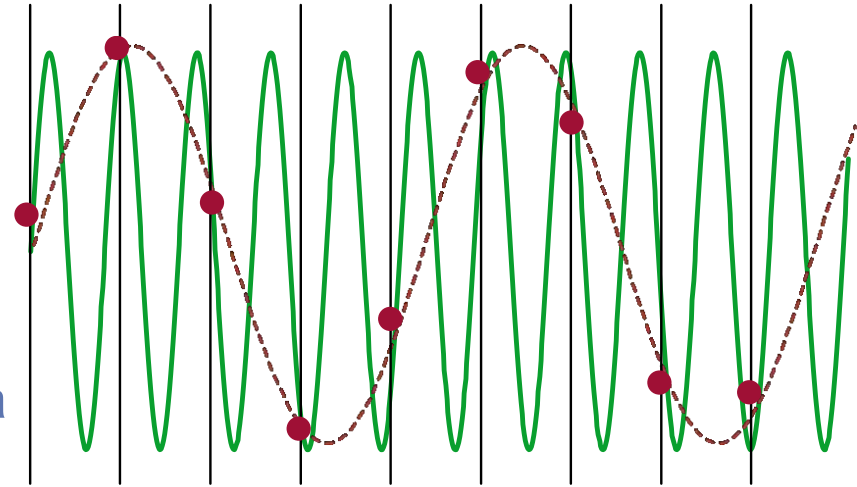




Nyquist

Echantillonnage

- Convertir un signal analogique (continu) en signal numérique (discret)
 - ADC (analog to digital converter)
- Exemple : un CD audio contient des données musicales échantillonnées à 44,1 kHz (44 100 échantillons par seconde).
- Critère de Nyquist (1928)
 - la fréquence d'échantillonnage d'un signal doit être égale ou supérieure à 2 fois la fréquence maximale contenue dans ce signal, afin de convertir ce signal d'une forme analogique à une forme numérique.



Echantillonnage et photo

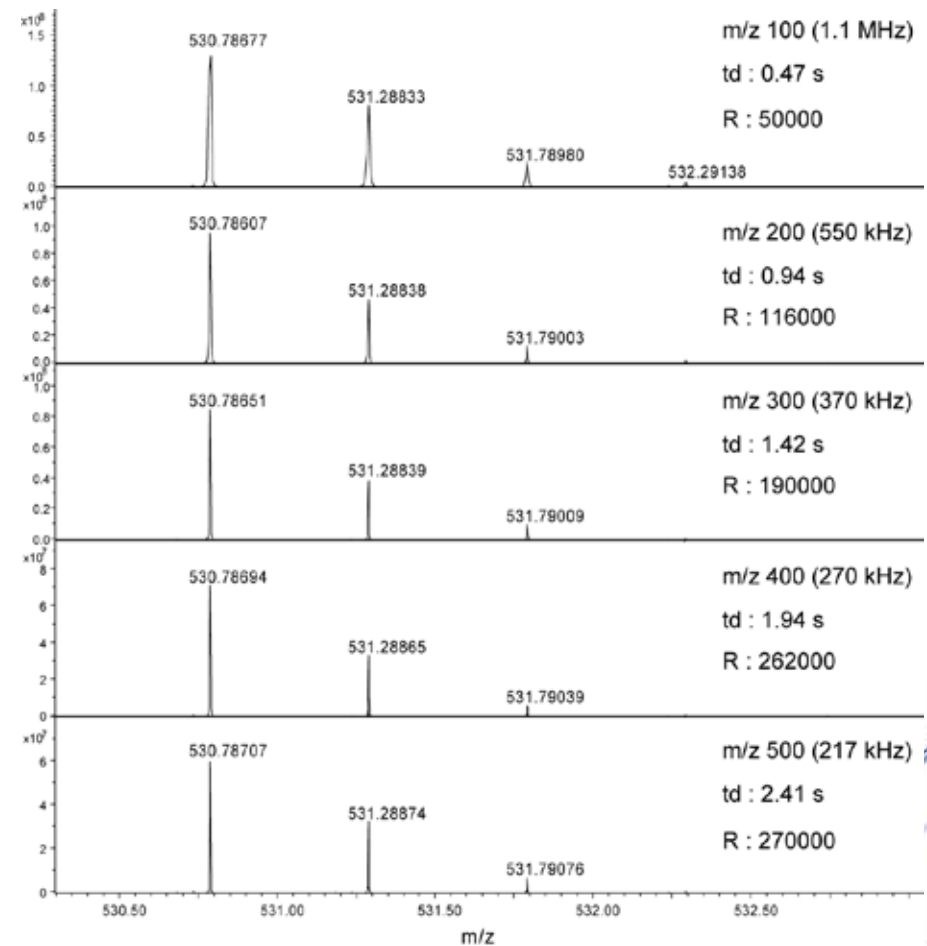


- Image sous échantillonnée
 - Effet de moiré



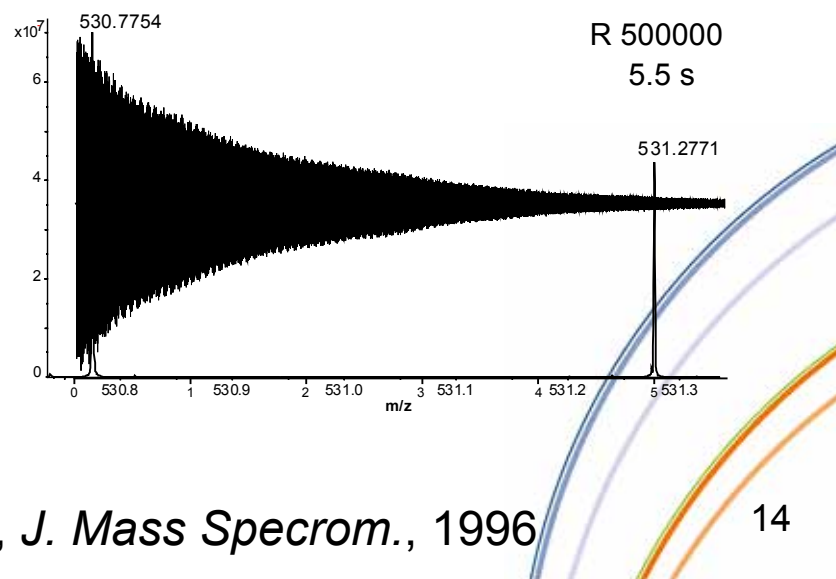
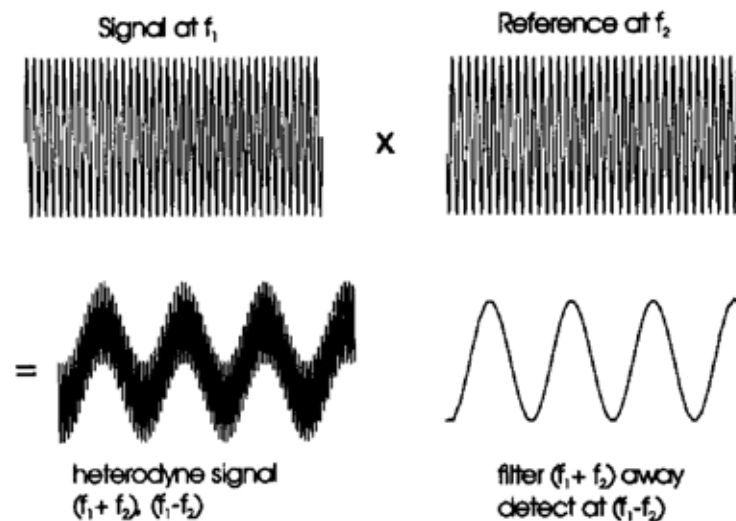
Importance des basses masses

- Critère de Nyquist
 - m/z 100 (1.1 MHz)
 - Echantillonnage 2.2 MHz
 - 1 M \Rightarrow 0.47s
- Pour une taille de fichier donné (ex. 1M) la longueur du signal transitoire sera lié à la valeur des bas m/z .
- Facteur limitant si l'on veut avoir de très hautes résolutions tout en détectant



Détection Hétérodyne

- Ultra haute résolution
 - Limité par la longueur du signal transitoire
 - m/z 430 (250 kHz, 7T)
 - Échantillonnage 500 kHz
 - 1M \Rightarrow 2s
- Mode « narrowband »
 - 250 kHz x 265 kHz
 - Signal composite
 - 15 kHz et 515 kHz
 - Échantillonnage 30 kHz
 - 1M \Rightarrow 33 s



Détails du calcul

- Broadband

$$v_c = \frac{1.535611 \times 10^7 B}{m/z} = \frac{1.535611 \times 10^7 \times 7}{430} = 250000 \text{ Hz}$$

$$= 250 \text{ kHz}$$

- Echantillonnage 500 kHz soit 0,5 MHz
- Avec 1 Million de points durée du transient :
- $T=1/0.5= 2 \text{ s}$

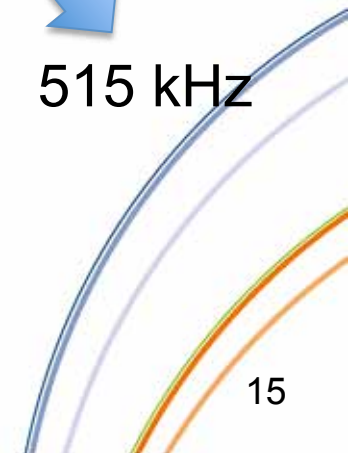
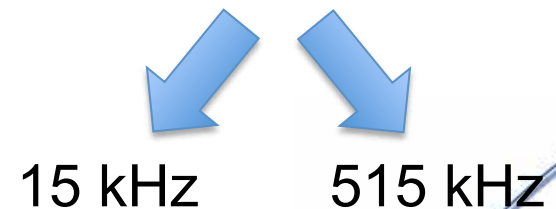
- Hétérodyne (narrowband)

- Echantillonnage 30 kHz soit (0.03 MHz)
- 1M : $T=1/0.03 = 33 \text{ s}$

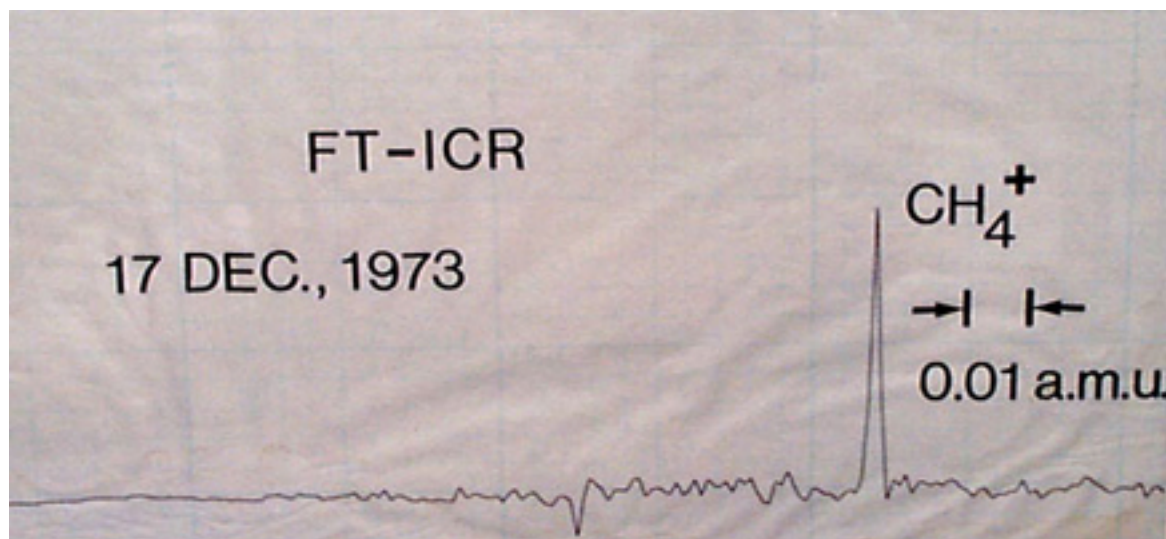
- Conséquences ?

- Gamme de m/z de $430 \times 15/250=26$

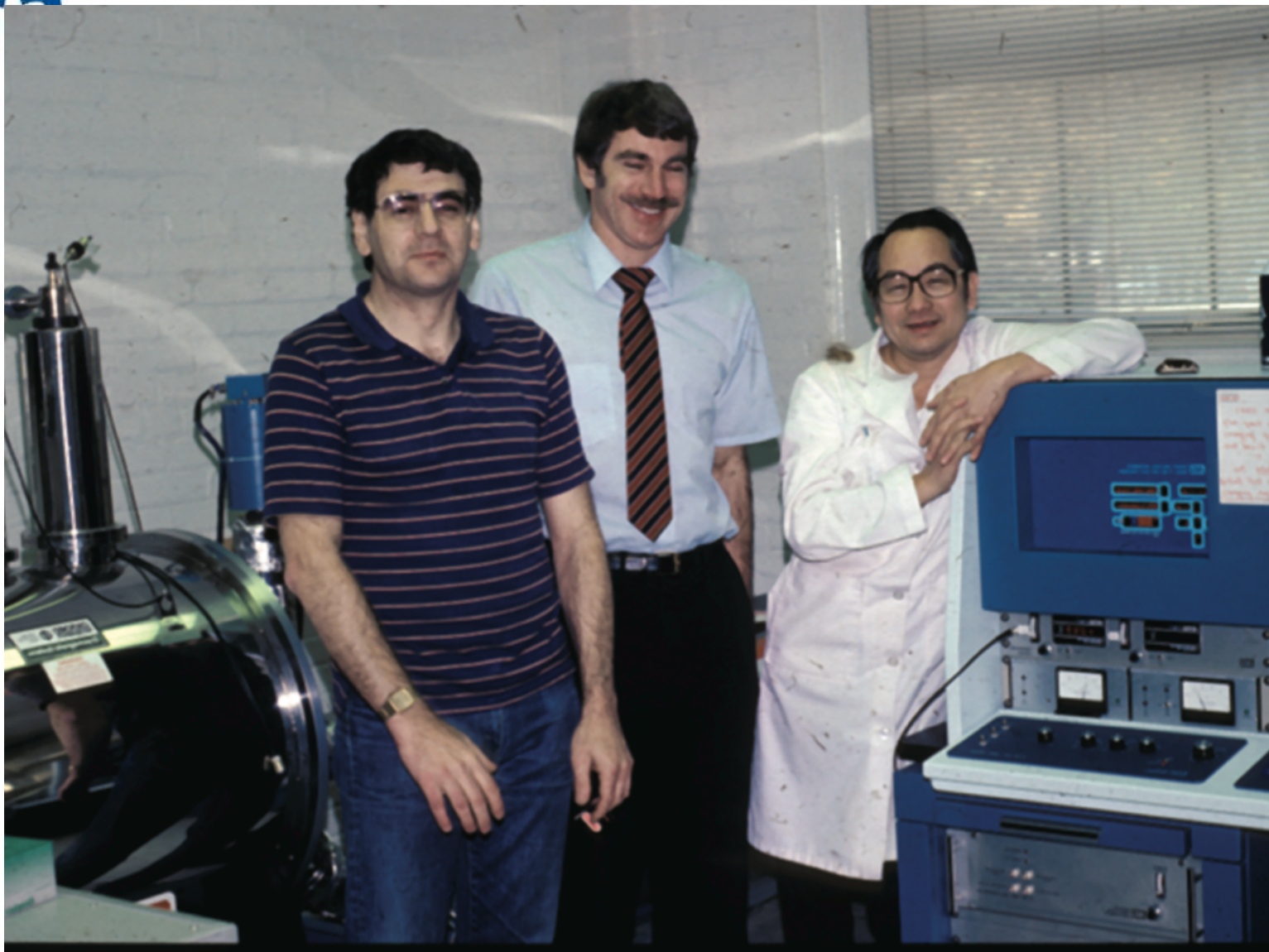
$$250 \text{ kHz} \times 265 \text{ kHz}$$



Exemple : premier FT-ICR



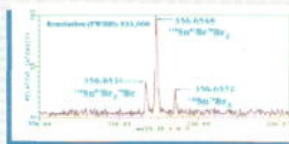
Ion cyclotron motion was excited by a 2.8 msec, 20 mV(p-p) rf electric field pulse at a frequency of 307.126 kHz, which corresponds to an applied **magnetic field of 0.32 tesla**. The excited ion cyclotron motion is converted to an alternating voltage at the resonance frequency by the ICR cell; **this voltage was then amplified by a broad-band (10 kHz to 2 MHz) rf amplifier and mixed with the output of a second rf oscillator (see below). The difference frequency was extracted using a 1.5 kHz low pass filter, and the resultant signal was then digitized at a rate of 10 kHz using a 1024-channel signal averager** to give the digitized (time-domain) response shown in fig. 1. The first 256 data points in fig. 1 were then recorded on magnetic tape and a discrete transformation of that array was carried out by a digital computer to yield the ICR absorption spectrum shown in fig. 2.



Transforming Mass Spectrometry

200 (1976)

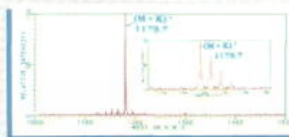
Ultra-high resolution



This FTMS spectrum of tin bromide contains a triplet at nominal mass 356, **never before resolved by any other mass spectrometer!** The triplet is shown here with clear baseline separation, demonstrating a resolving power of 833,000!

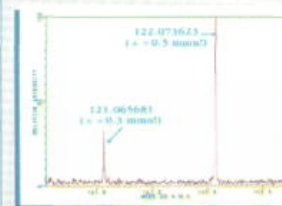
Sample courtesy of Professor E. W. McLafferty, Cornell University.

Laser desorption of large molecules



This FTMS spectrum of the cyclic polypeptide Gramicidin-S (molecular weight 1141 amu) shows very soft ionization. The base peak is the pseudo-molecular ion $(M + K)^+$ formed due to potassium attachment (favored by addition of KBr). The expanded region inset illustrates the high resolution (7000 FWHH) easily achieved with the FTMS-2000.

New high-resolution GC/MS



The FTMS-2000 now easily achieves high mass resolution and accurate mass measurement under capillary GC conditions. This high-resolution (11,000 FWHH) spectrum here was obtained on-the-fly from a Grob-type activity mixture. Mass measurement deviations are only 2.8 ppm and 3.8 ppm without use of internal calibrant!

New FTMS-2000 general-purpose ultra-high resolution mass spectrometer advantages:

Versatility

Unmatched experimental versatility, instant switching between modes.

Sensitivity At ultra-high resolution, for high masses and labile compounds.

Speed For pulsed (laser and Cs SIMS) experiments and fast GC/MS.

Stability For accurate mass measurement and long-term mass calibration.

Productivity Intrinsic computer-based productivity.



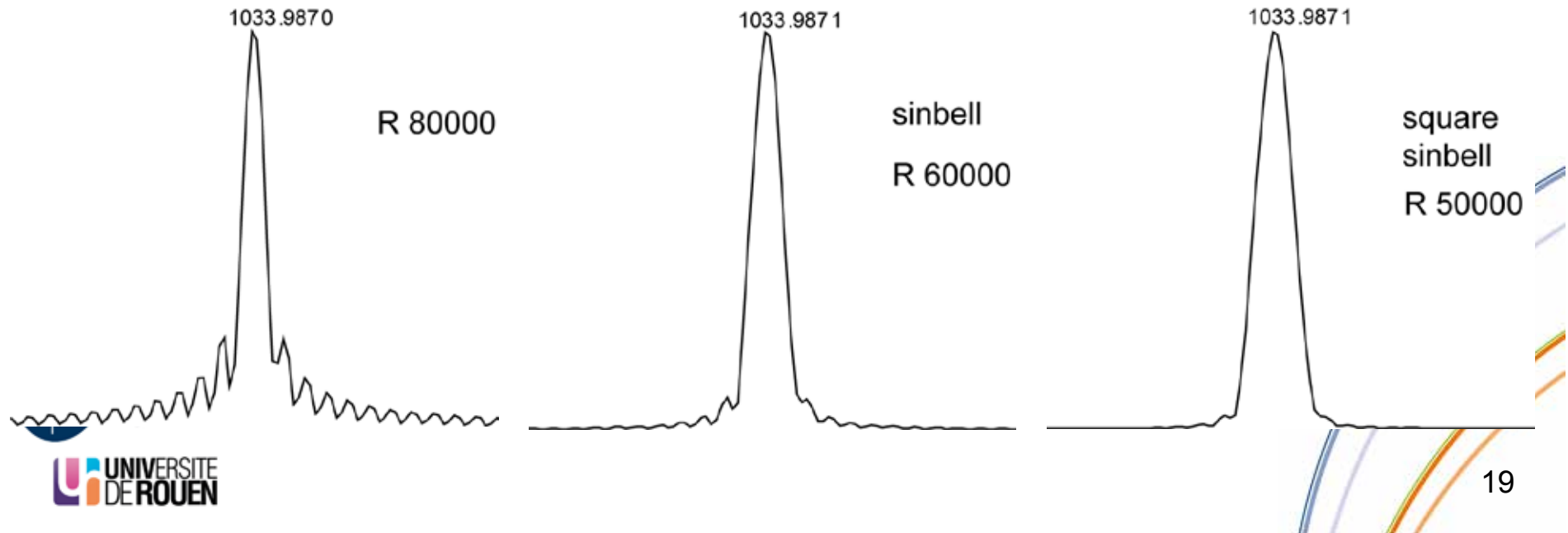
Nicolet
The FT Spectroscopy People

Nicolet Analytical Instruments/5225-1 Verona Road Madison, WI 53711/608-273-5004/Telex: 910-286-2736

CIRCLE 151 ON READER SERVICE CARD

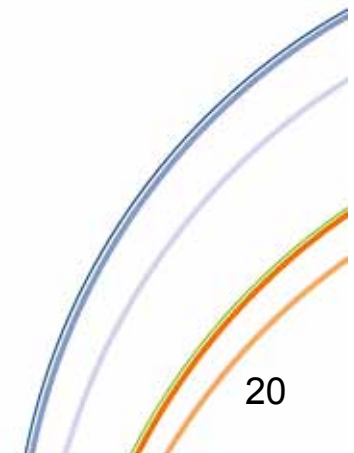
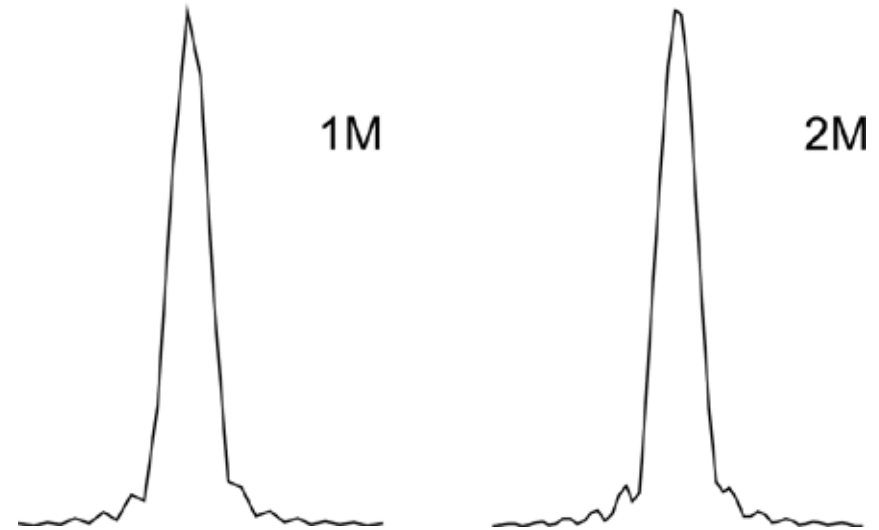
Traitement du signal « Apodisation »

- « Apodisation »
 - Suppression de pieds de pics
 - Fonction sinusoidale



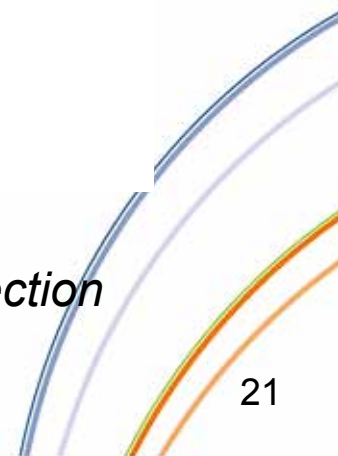
Traitement du signal “zero filling”

- Augmenter, avant la FFT, la taille du fichier de données
 - 1M \Rightarrow 2M
- Améliore la forme des signaux
 - Mesure de m/z
 - Améliore la mesure de l'intensité des signaux (quantification)



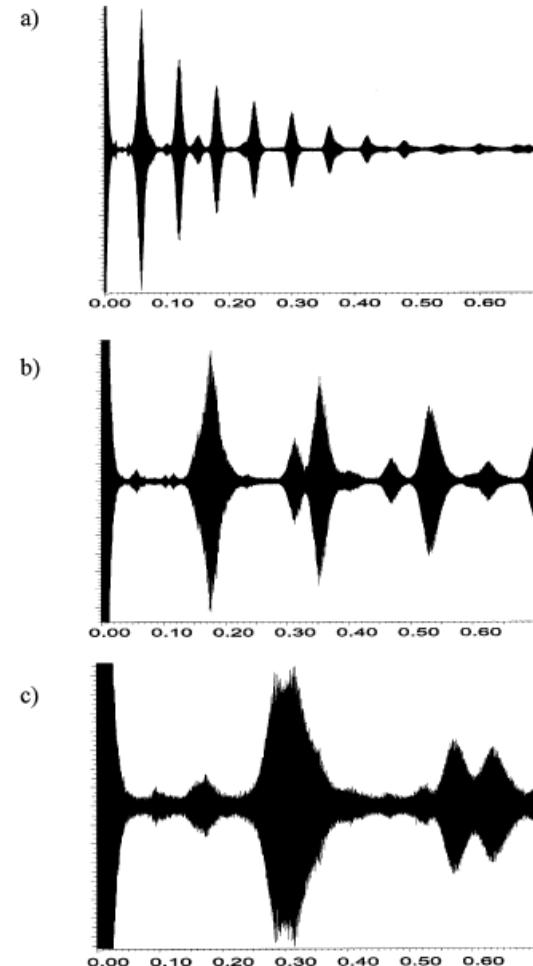
Isotope beating

Spectres de masse d'isolement de l'ion m/z 531 avec une fenêtre (a) de m/z 5, et (b) de m/z 0.5 conduisant à la sélection de l'ion monoisotopique uniquement.



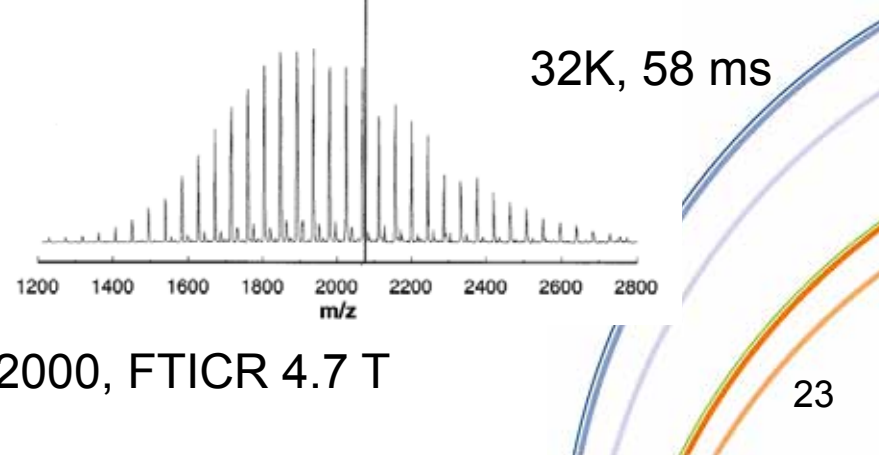
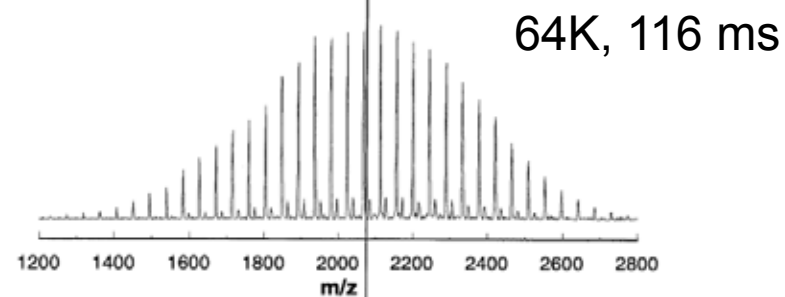
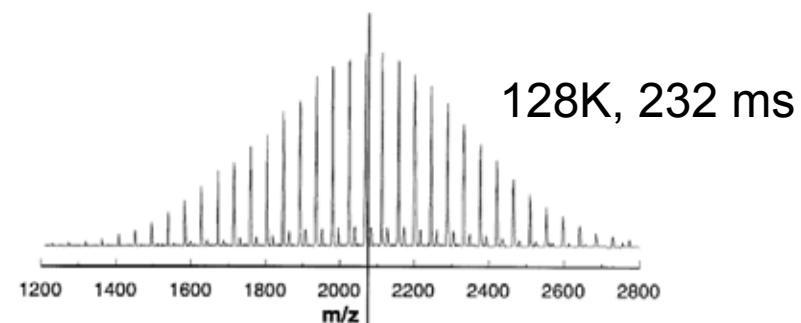
Isotope beating (2)

- (a) bovine insuline avec un état de charge +5 (Mw 5729)
- (b) cytochrome c avec un état de charge +8 (Mw 12360)
- (c) myoglobine avec un état de charge +10 (Mw 17554)



Isotope beating (3)

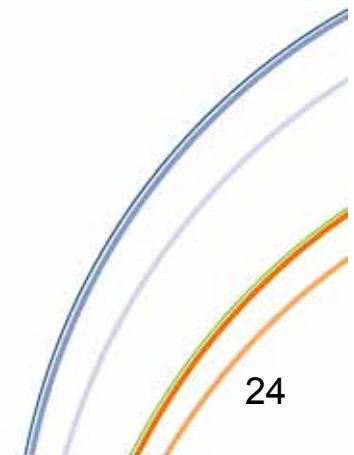
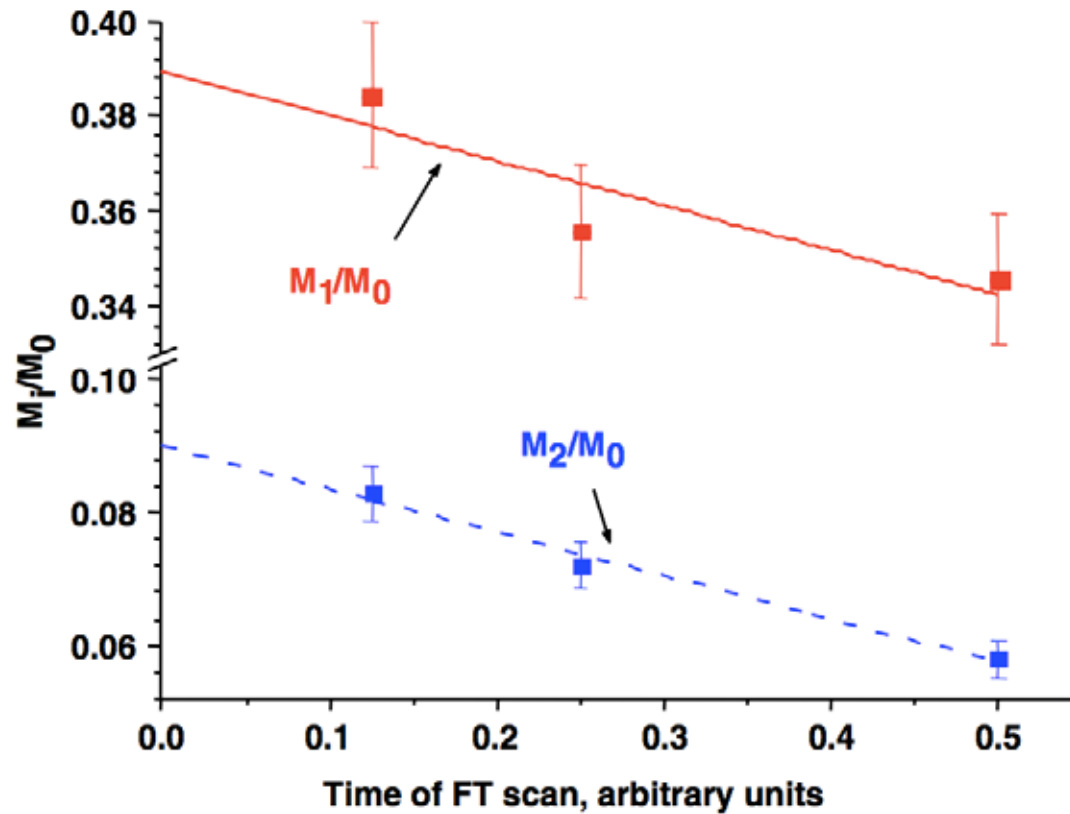
- Attention pour la quantification !



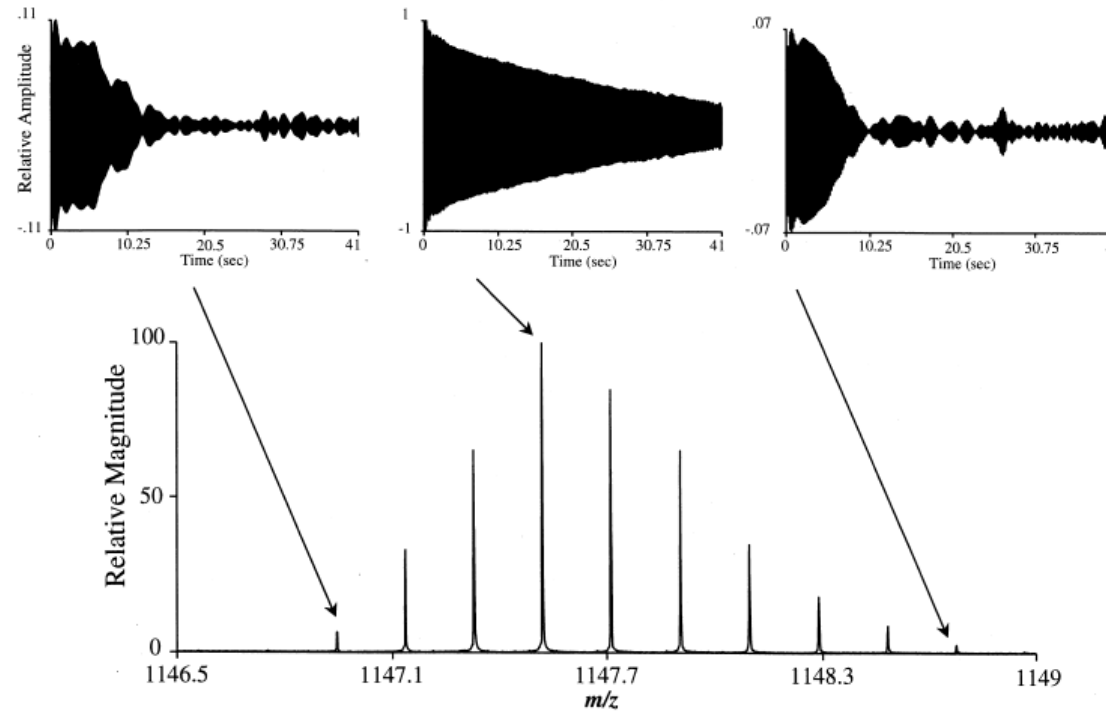
PEG 2000, FTICR 4.7 T

Rapport isotopique et FT-ICR

- Abondance des isotopes systématiquement trop bas
 - Erreur augmente avec le temps de détection



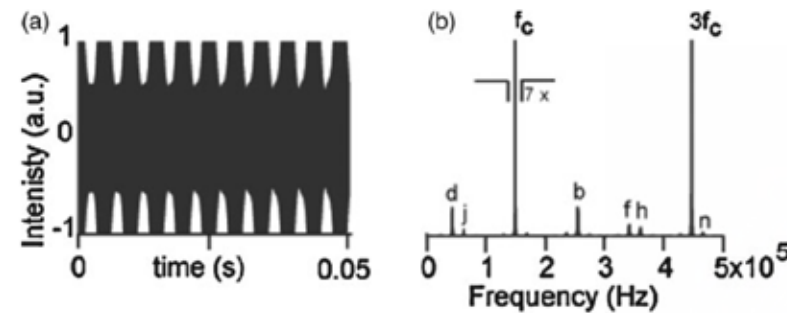
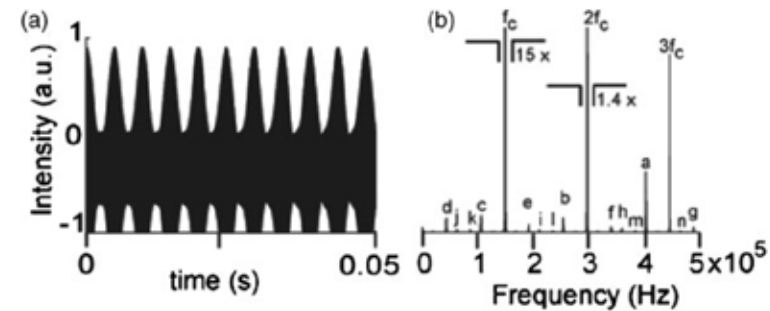
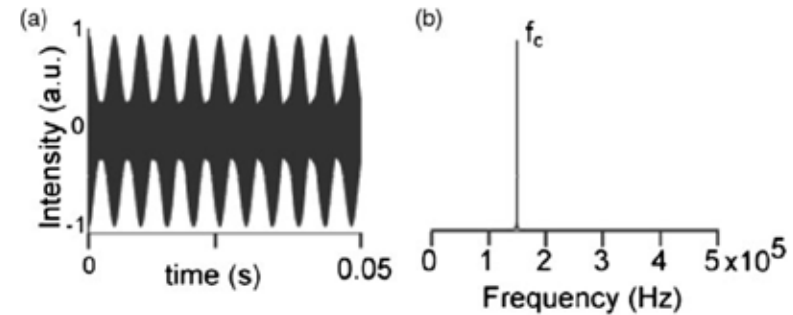
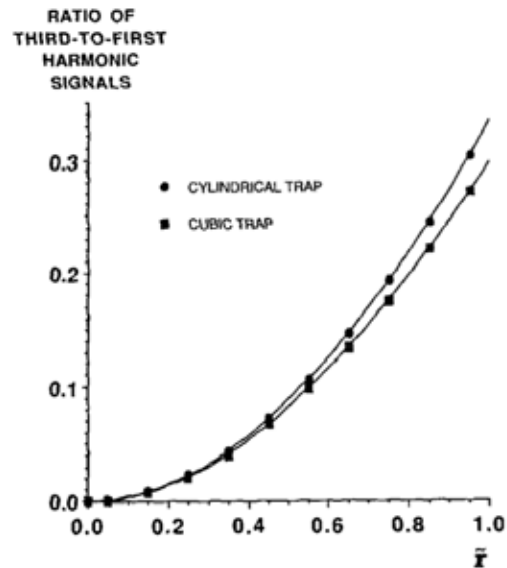
Quantification en FTMS ?



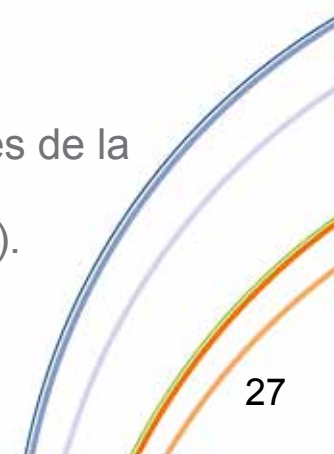
Extracted time-domain signals for individual isotopic peaks from the 51 charge state of bovine insulin. The differences in signal damping vary with the abundances of the isotopic species

Harmoniques

- Les harmoniques sont des artéfacts qui apparaissent lorsque le signal n'est pas tout à fait sinusoïdal
- Cellule finie : Harmoniques impaires

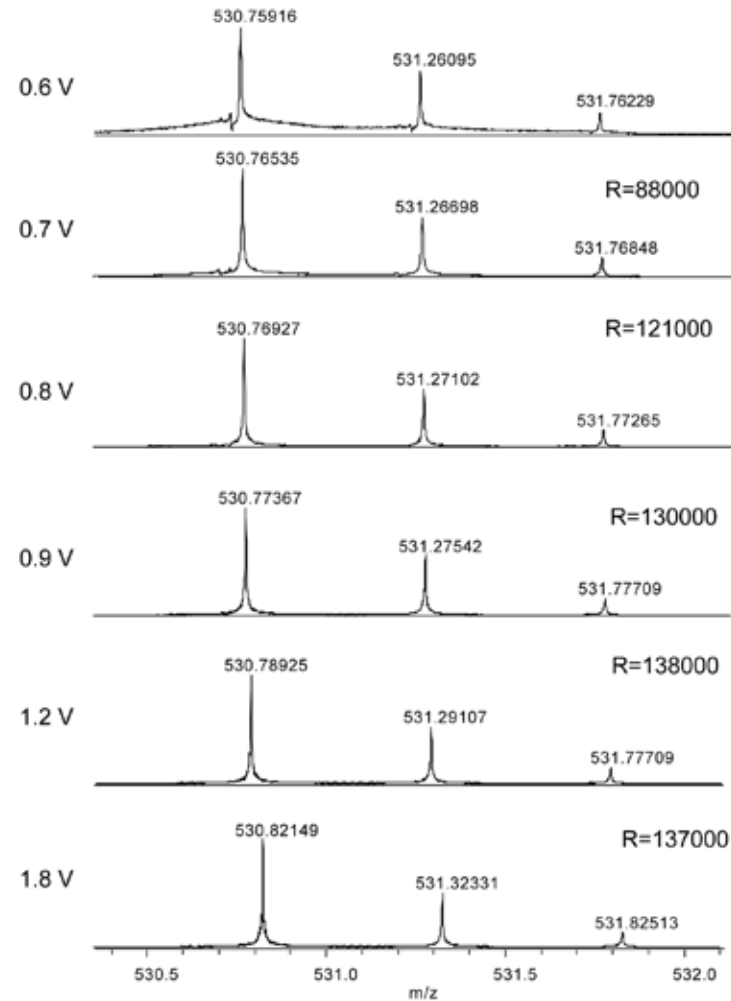


- Etalonnage
 - Lorsque l'on a changé le mouvement des ions dans la cellule
 - Pression (pulse de gaz en SORI).
 - Excitation des ions (pour la détection)
 - Voltage appliqué sur les plaques de piégeage.
 - Sidekick
 - Changement de la gamme de m/z
- Etalonnage interne vs externe
 - Interne
 - Le plus fiable et précis < 1ppm
 - Mélange d'un étalon
 - Bon étalonnage quelque soit les paramètres utilisés.
 - Externe
 - Simple mais nécessite de ne pas changer les paramètres de la cellule.
 - Nombre d'ions doit être constant (un ordre de grandeur).



Paramètres influençant la mesure de m/z

- Paramètres de la cellule
 - V_{RF} excitation
 - V piégeage
 - \Rightarrow changement important des m/z
- Nombre ions dans la cellule



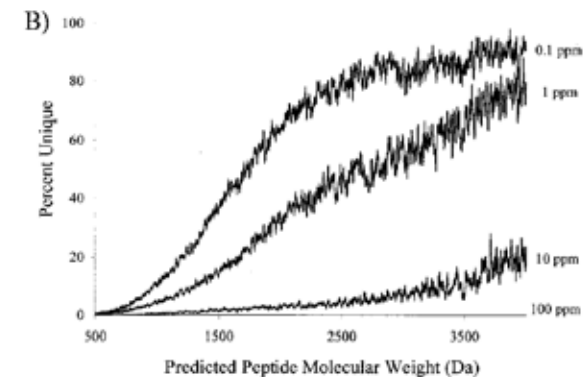
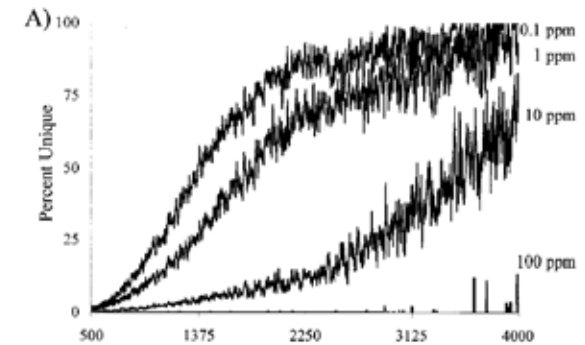
Augmenter la précision

m/z	3 ppm	1 ppm
200	1	1
300	2	1
400	6	1
500	11	5
600	26	10
700	45	16

- **Autres critères**

- Ajout de restrictions (Nature et nombre des éléments à considérer)

Massif isotopique (\Rightarrow nbre de C, Cl...)



Recherche formule élémentaire

Generate Molecular Formula

Min:

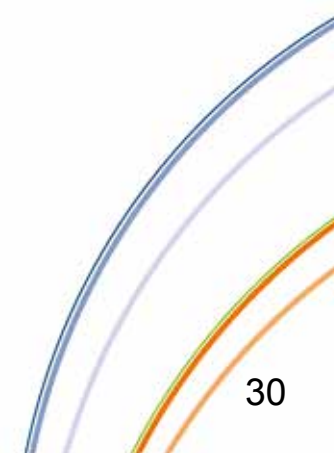
Max:

Note: for m < 2000 the elements C, H, N, and O are considered implicitly.

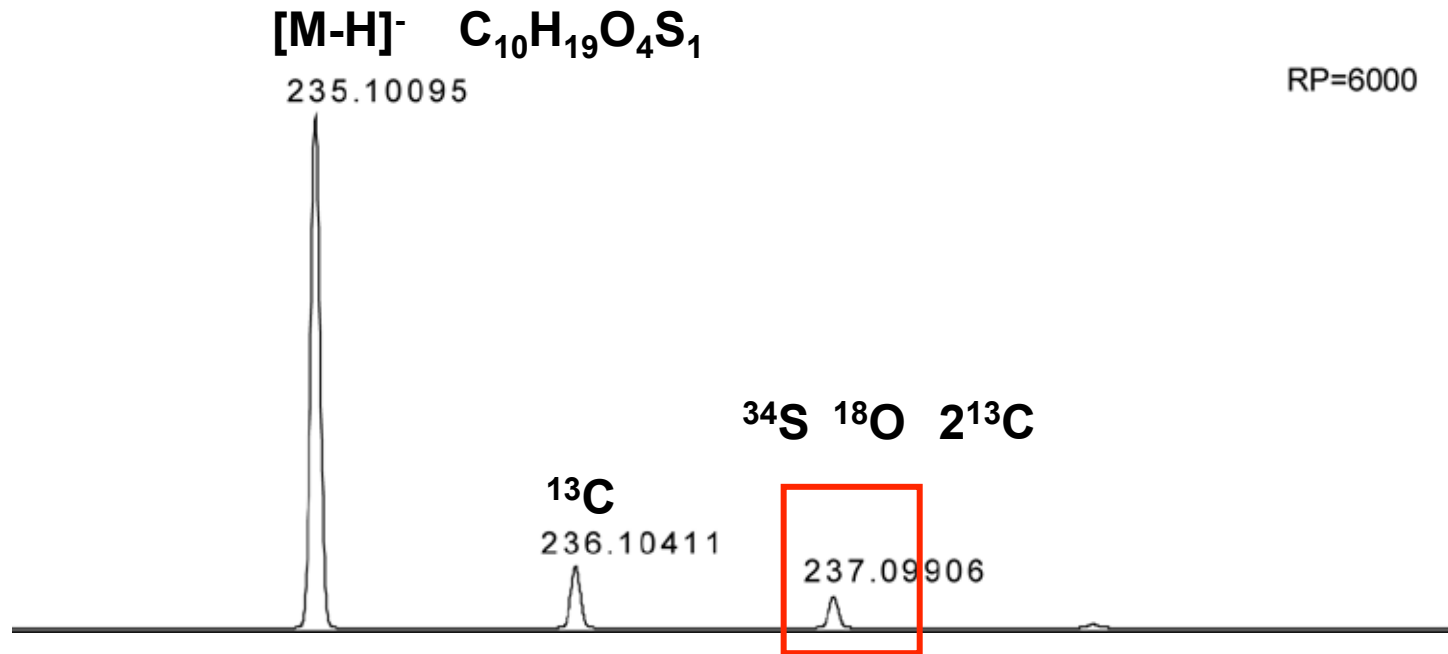
Measured m/z: Tolerance: mDa Charge:

#	Mol. Formula	m/z	err [mDa]	lenl [ppm]	err [ppm]	mean err [ppm]
1	C 10 H 33 Cu 1 O 7	328.15168	-0.01	0.0	-0.0	-0.0
2	C 7 H 25 Cu 1 N 10 O 1	328.15033	-1.36	4.1	-4.1	-4.1
3	C 8 H 31 Cu 1 N 3 O 6	328.15034	-1.36	4.1	-4.1	-4.1
4	C 9 H 27 Cu 1 N 7 O 2	328.15168	-0.02	0.1	-0.1	-0.1
5	C 11 H 29 Cu 1 N 4 O 3	328.15302	1.32	4.0	4.0	4.0

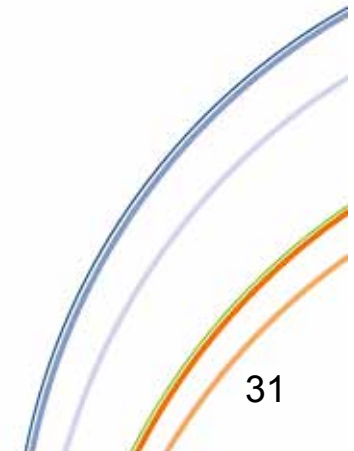
Automatically locate monoisotopic peak Maximum number of formulas:
 Check rings plus double bonds Minimum: Maximum:
 Apply nitrogen rule Electron configuration:
 Filter H/C element ratio Minimum H/C: Maximum H/C:
 Estimate carbon number Generate immediately

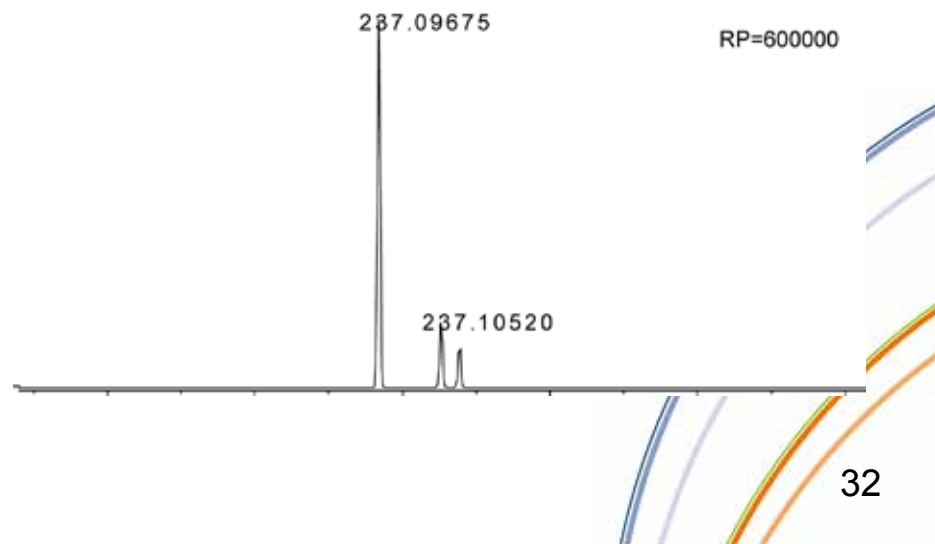
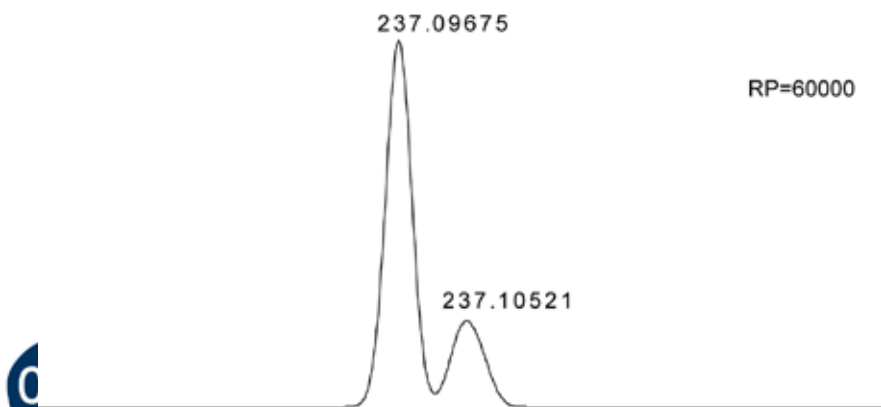
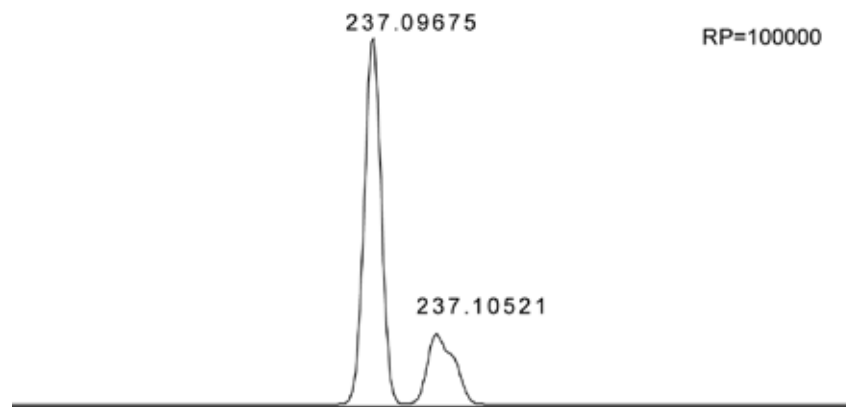
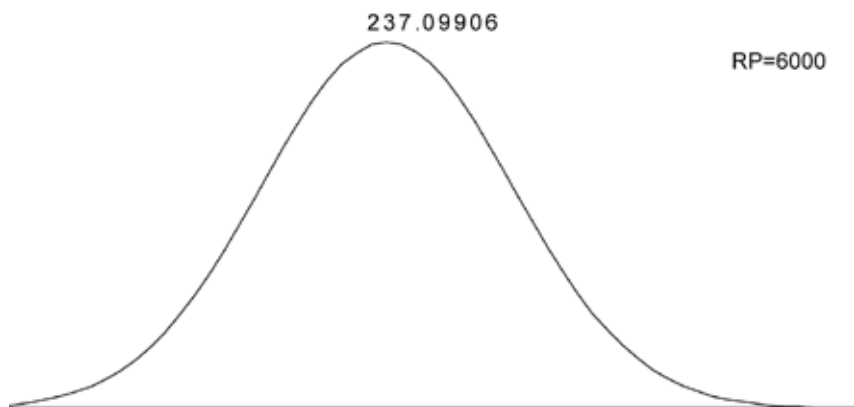


La haute résolution : pourquoi ?

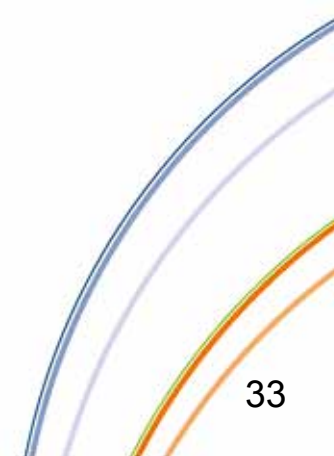
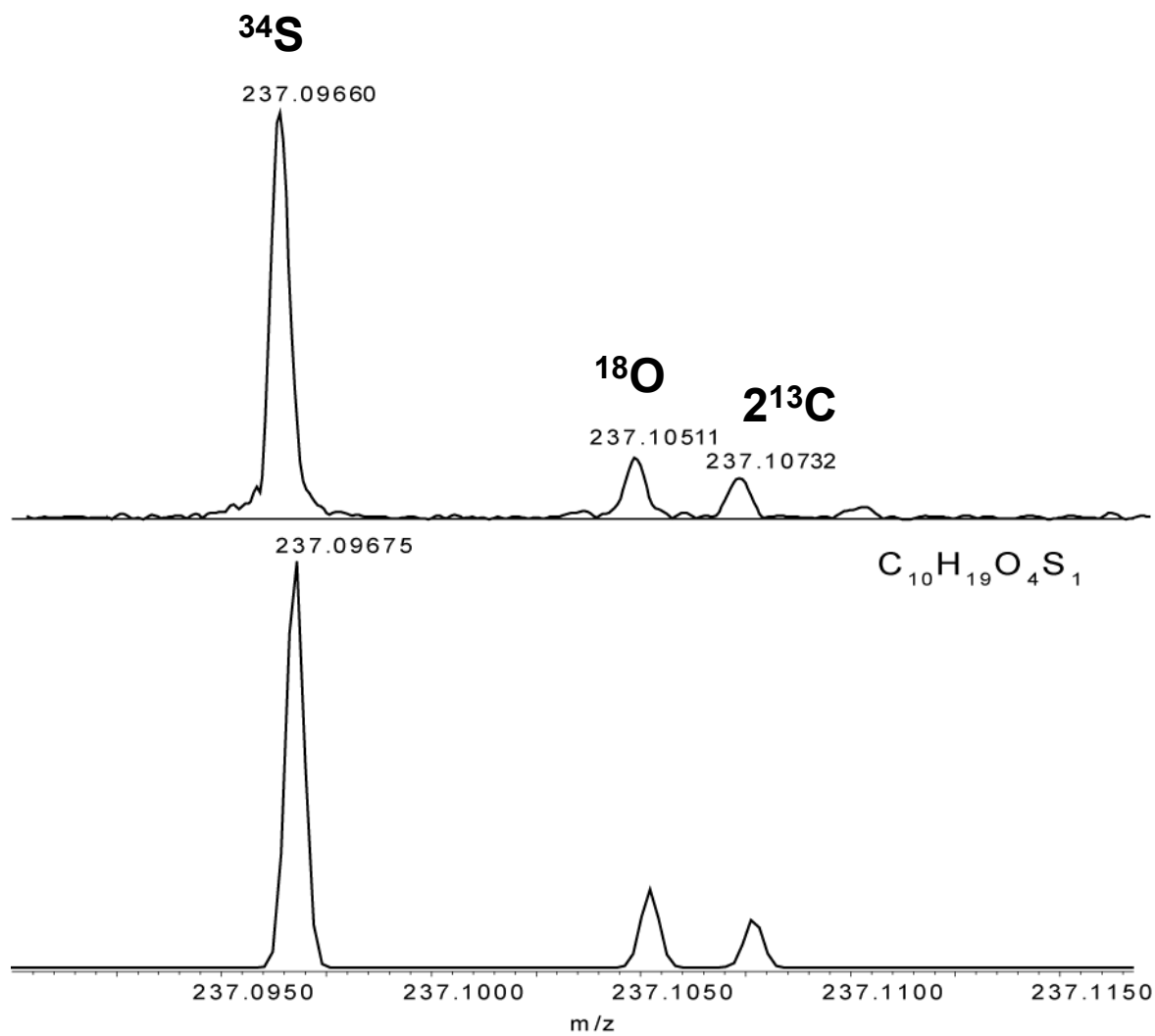


	0	+1	+2
S (32)	95.00	0.76	4.22
O (16)	99.76	0.04	0.20

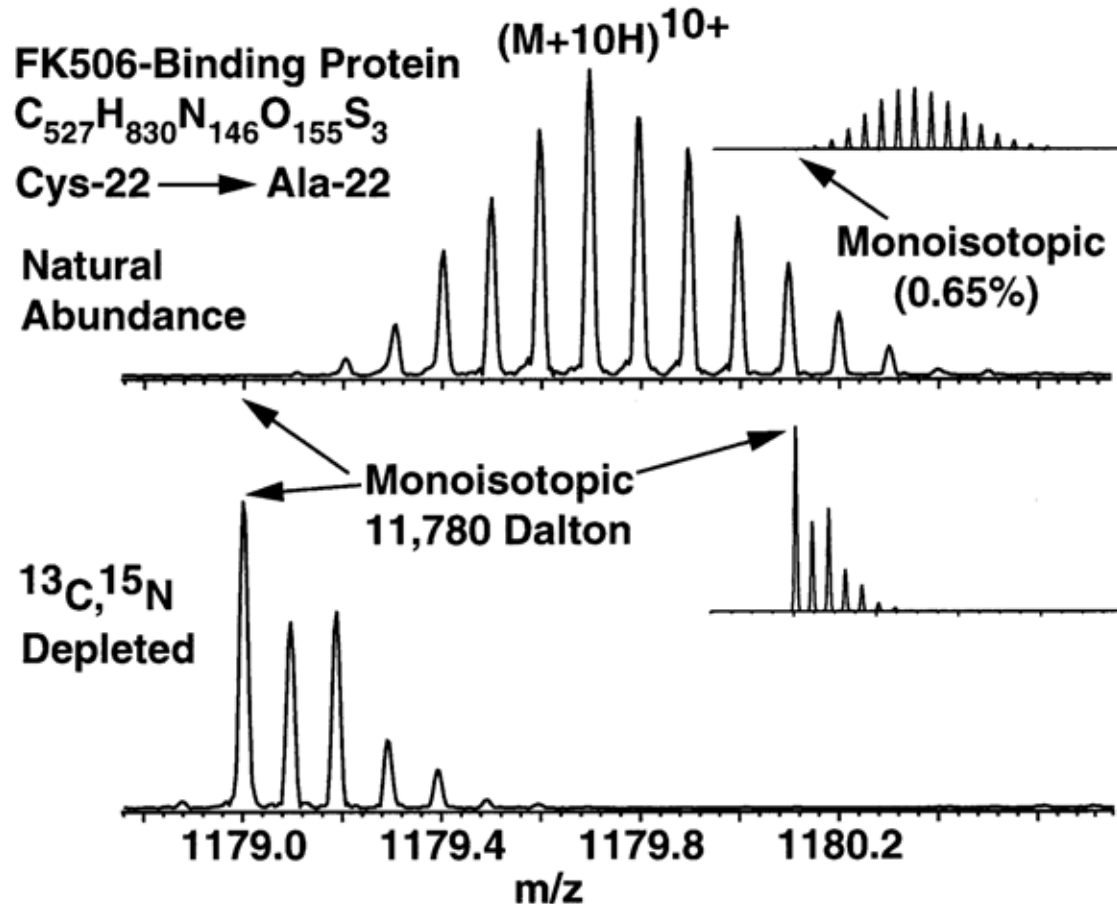




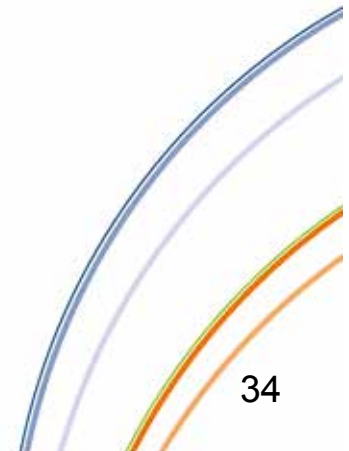
Expérimentalement



Isotope depletion



- FK506-binding protein.
- Natural-abundance isotopic distribution (98.89% ^{12}C , 99.63% ^{14}N).
- Distribution Isotopique dans un milieu de culture contenant 99.95% ^{12}C and 99.99% ^{14}N .



- Proportionnel au nombre de périodes enregistrées.

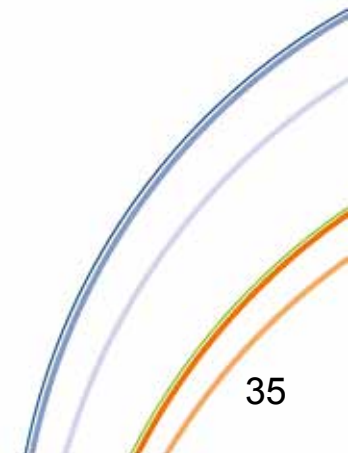
$$R = \frac{m}{\Delta m} = \frac{\omega}{\Delta \omega} \quad \Delta \omega \propto \frac{k}{T}$$

- FT-ICR

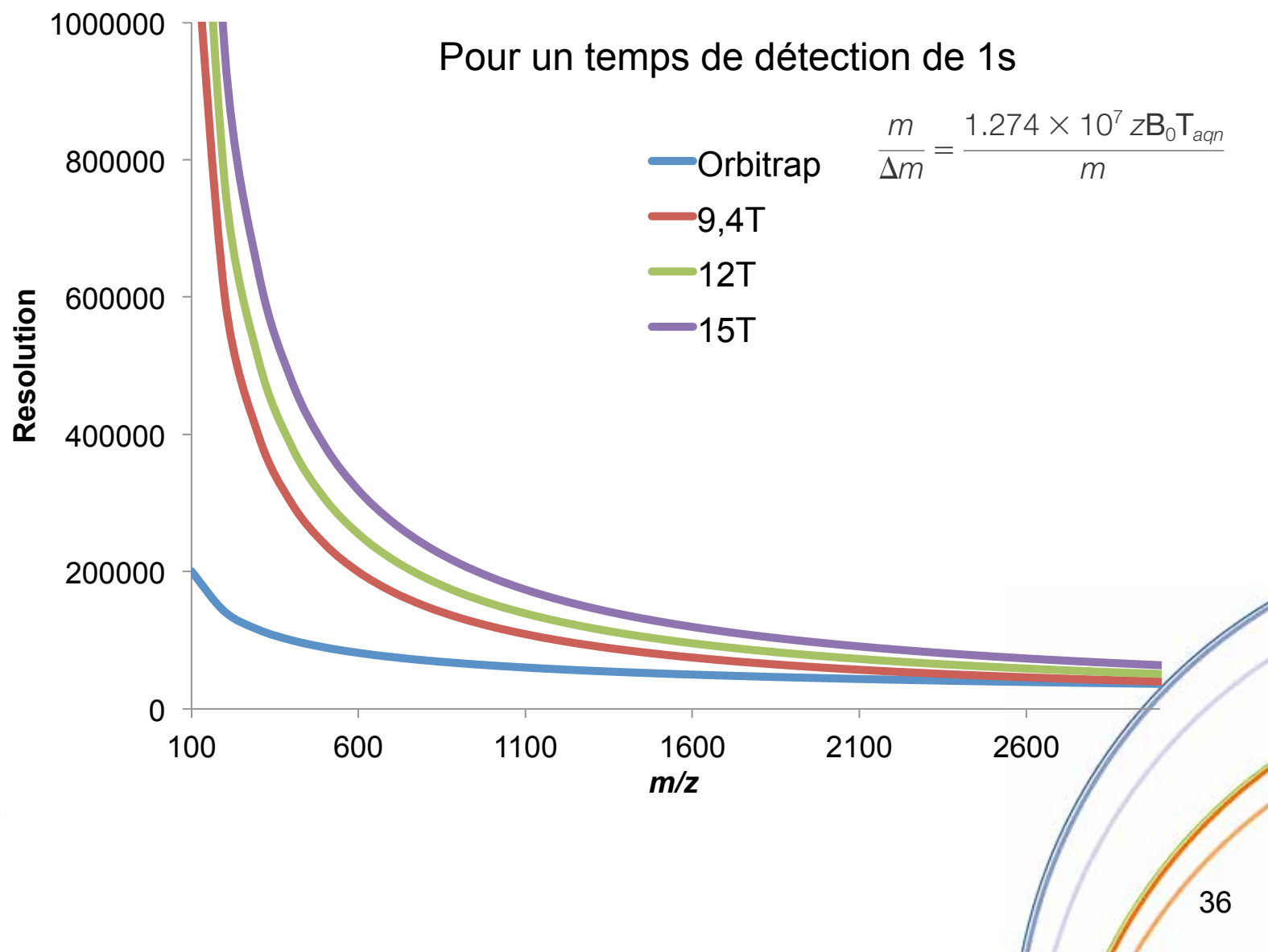
$$\omega_c = \frac{qB}{m} \quad R = \frac{qB}{\Delta \omega} \propto \frac{qBT}{mk} \quad \rightarrow \quad \frac{1}{m/z}$$

- Orbitrap

$$\omega = \sqrt{\frac{k}{m/z}} \quad R \propto K \sqrt{\frac{1}{m/z}} T \quad \rightarrow \quad \sqrt{\frac{1}{m/z}}$$

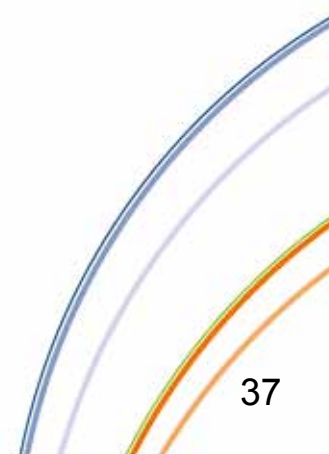


Comparaison FT-ICR/Orbitrap



Si le temps n'est pas un problème

- Limiter la détection à 1s
 - Couplage chromatographique
- ESI en infusion ou MALDI
 - Le temps n'est pas une limitation
- Sur un FT-ICR des temps de détection de plusieurs minutes sont possibles.
 - $R > 10 \cdot 10^6$ avec un 7 T



Pourquoi le vide est nécessaire ?

- Spectromètres de masse
 - vide poussé
 - Les collisions conduisent à des pertes d'ions.
 - Libre parcours moyen (L)

$$L = \frac{kT}{\sqrt{2}p\sigma}$$

- L = 1 m \Rightarrow vide de $6.6 \cdot 10^{-5}$ mBar

k: Constante de Boltzmann

T: Température

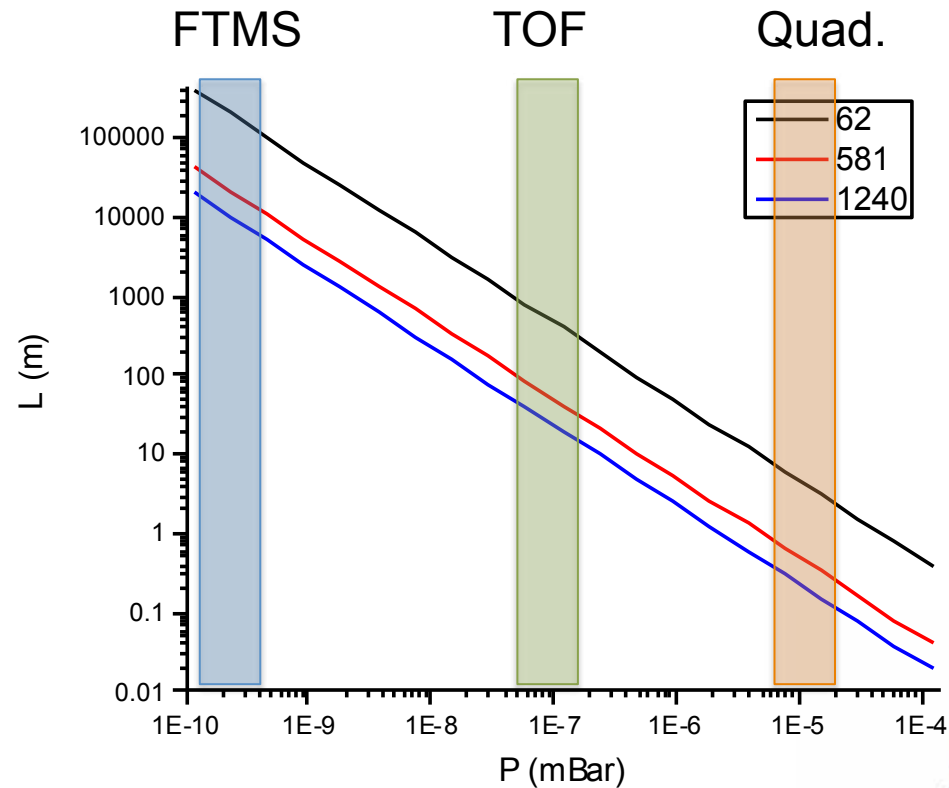
p: Pression

σ : section efficace de collision



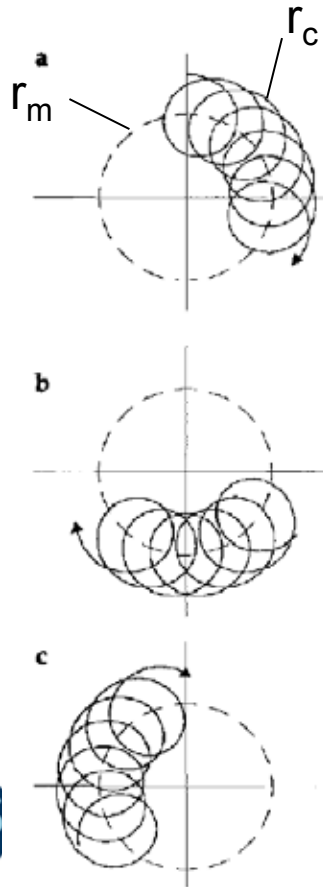
Libre parcours moyen et pression

- Exemples
 - Gly₂ (1+) 62 Å²
 - Melittin (3+) 581 Å²
 - Cytochrome c (+6) 1240 Å²
- FTMS
 - Ultravide < 10⁻⁷ mBar
 - Implique l'utilisation de matériaux spéciaux
 - Extrême propreté
 - Dégazage du système (Bake out)
 - éliminer traces d'humidité...
 - 10⁻⁹ mBar, Libre parcours moyen 40km !

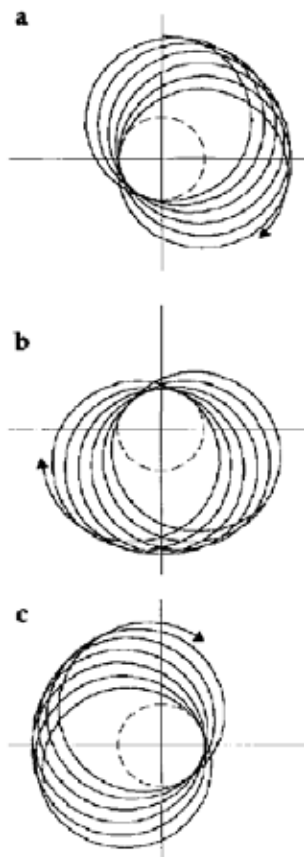


Mouvement des ions cyclotron + magnetron

Sans excitation

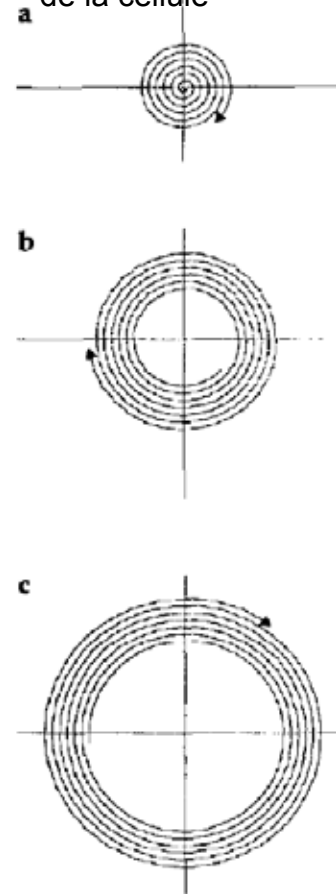


Avec excitation

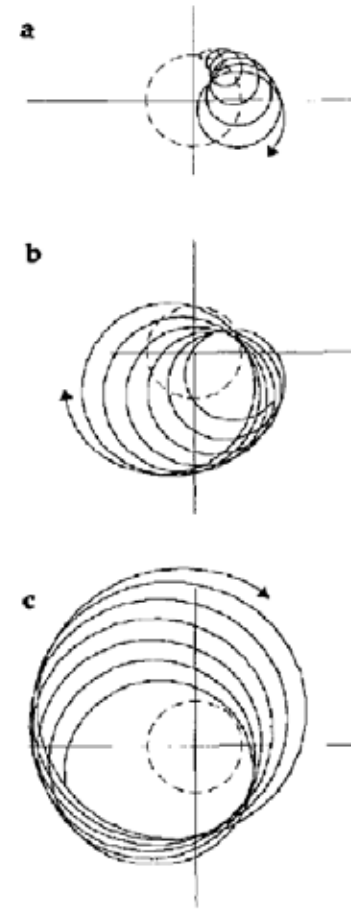


Magnetron nul

Ion initialement au centre de la cellule



Magnetron non nul



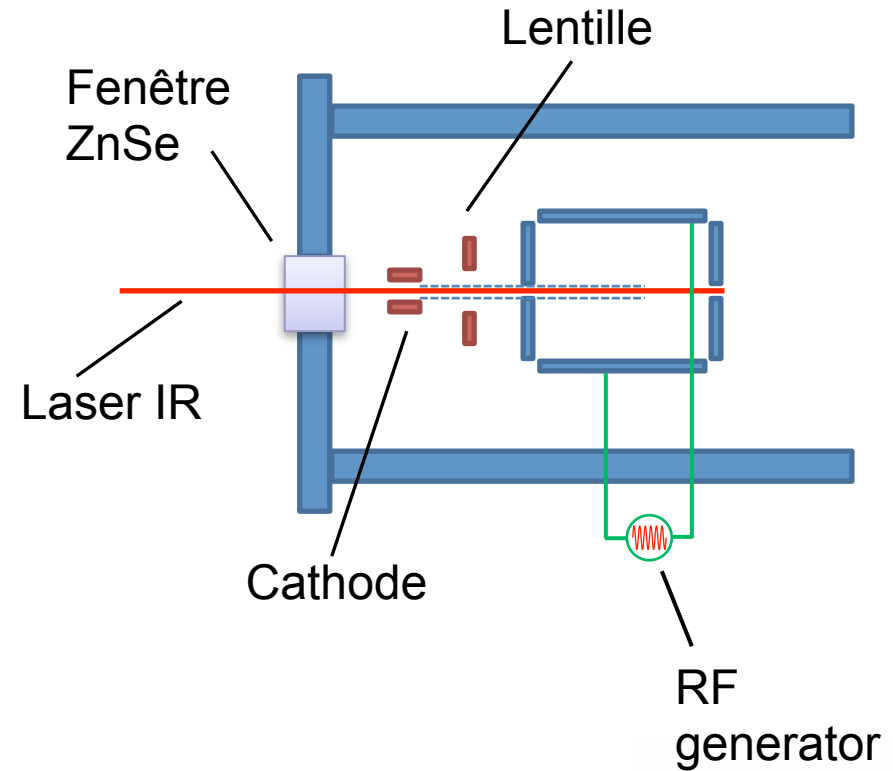
- Séquences temporelles

- EXD (ECD/EDD/EID)
- IRMPD
- Excitation résonante
- MSⁿ
- Ex: ECD puis SORI/CID

- Doubles résonances

- IRMPD + excitation résonante (DR-IRMPD)
- ECD + excitation résonante (DR-ECD)

Modes d'activation



Mode d'activation (il y a le choix)

- SORI (sustained off-resonance irradiation)
- $\Delta\nu = 1000 - 2000$ Hz (Offset)
- A optimiser en fonction du précurseur.
- Nécessite d'introduire un gaz (Ar et N_2) et donc implique un temps de pompage avant la détection
- Cycle $\sim 2-4$ s

• IRMPD

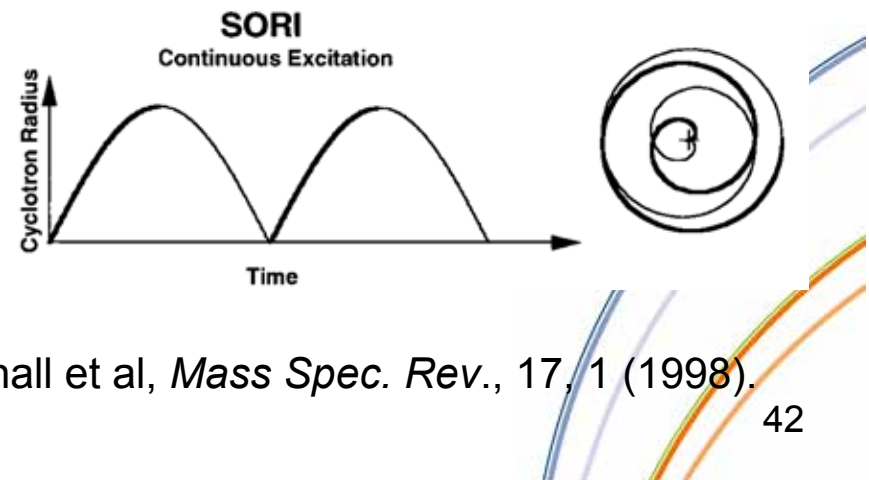
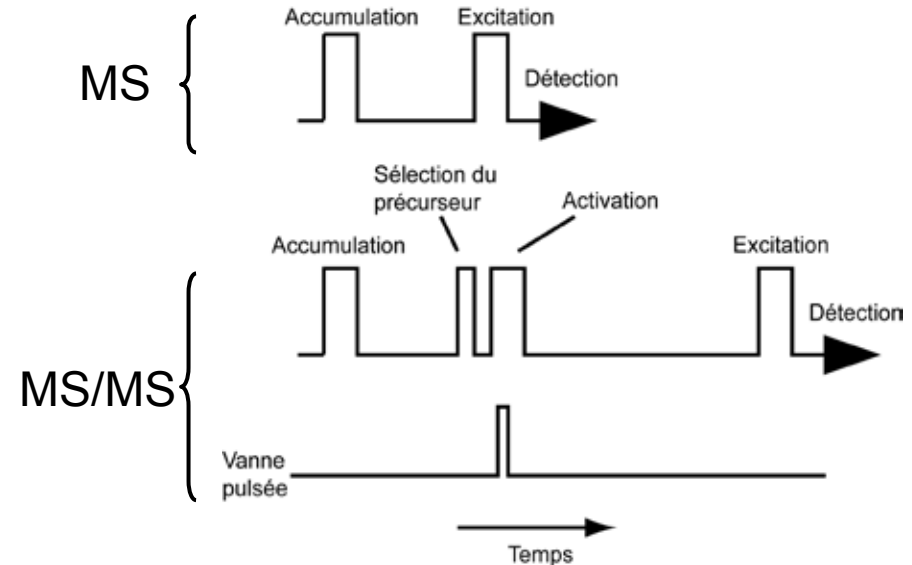
- Irradiation par laser IR
 - Laser CO_2 25-45W
 - Typiquement irradiation 1s à 10 W
- Pas de gaz de collision
 - Temps d'activation $\sim 100-1000$ ms

• BIRD

- «Blackbody Infrared Multiphoton Dissociation»
- Chauffage de la cellule 100-200 °C
 - plusieurs dizaines de secondes

- Dissociation par capture d'électron dissociative

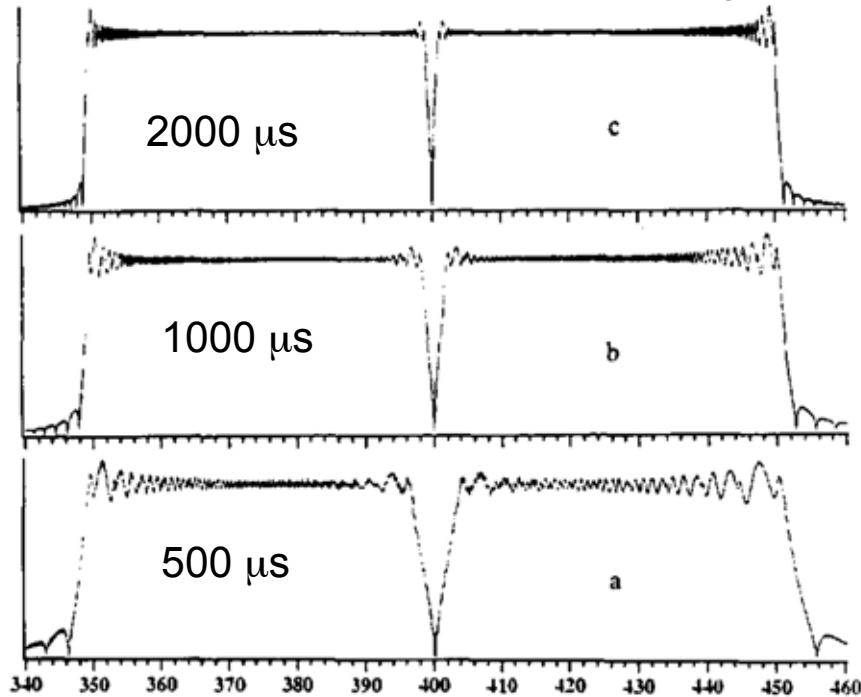
UNIVERSITÉ DE ROUEN
Temps d'activation $\sim 10-100$ ms



Marshall et al, *Mass Spec. Rev.*, 17, 1 (1998).

Sélection d'un ion précurseur

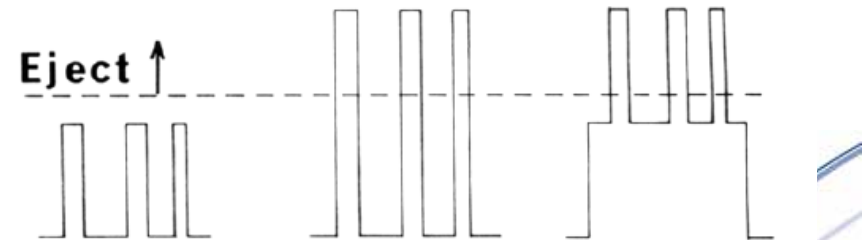
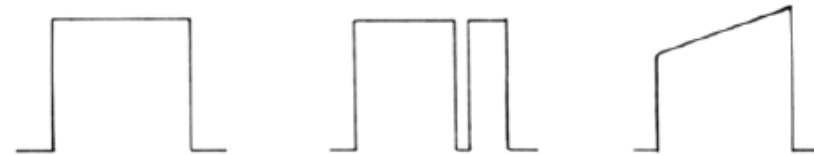
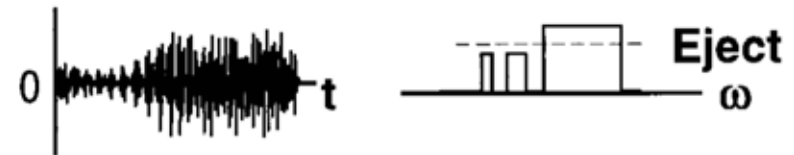
correlated swept-frequency



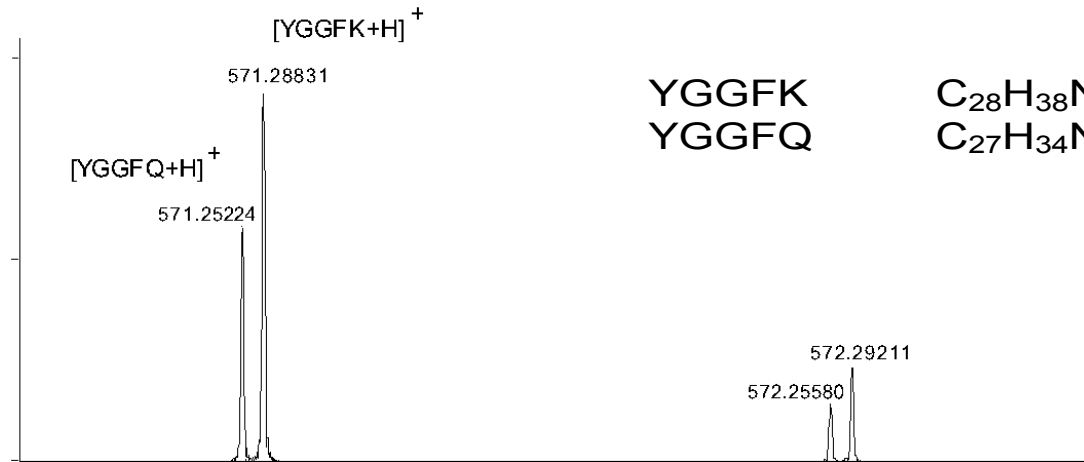
Sélection m/z 400.00000

SWIFT

Stored waveform inverse Fourier transform



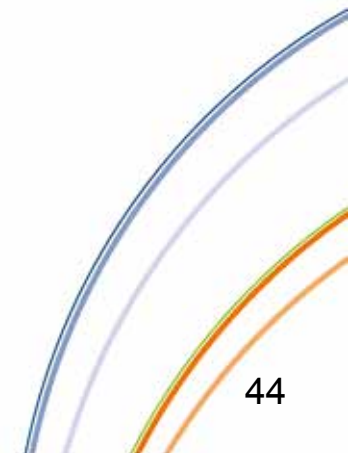
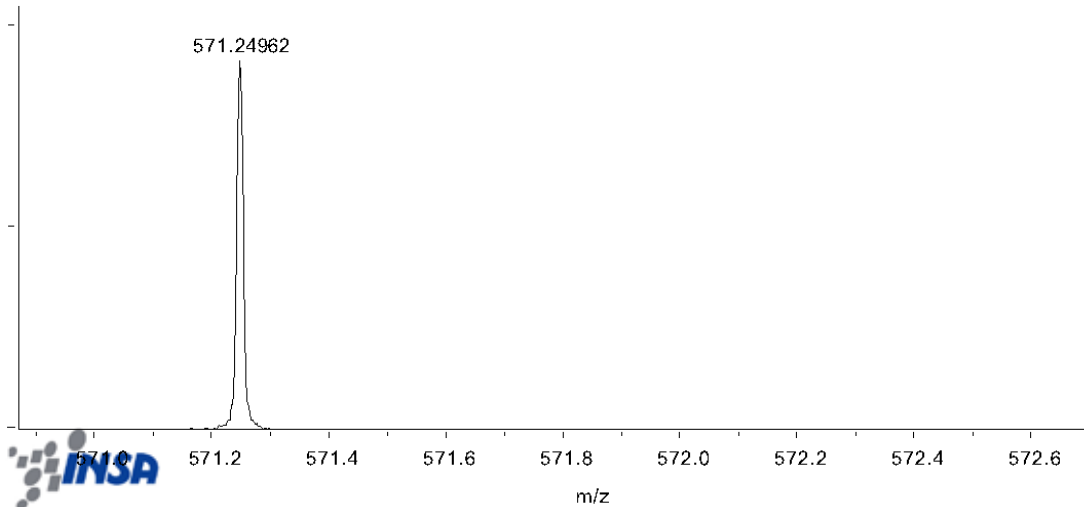
Composés Isobares : Sélection en Haute Résolution



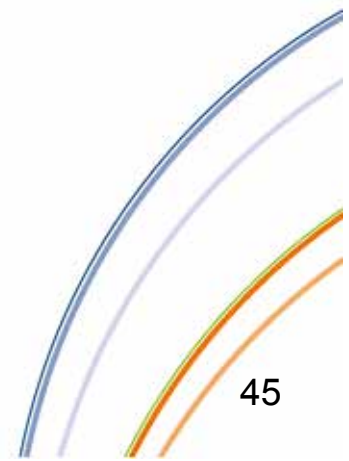
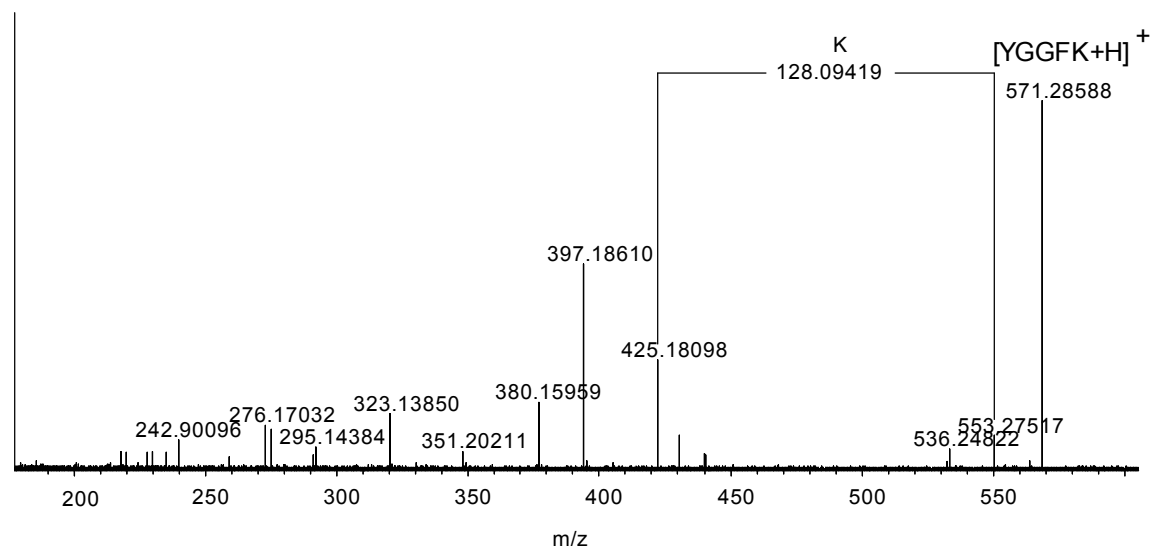
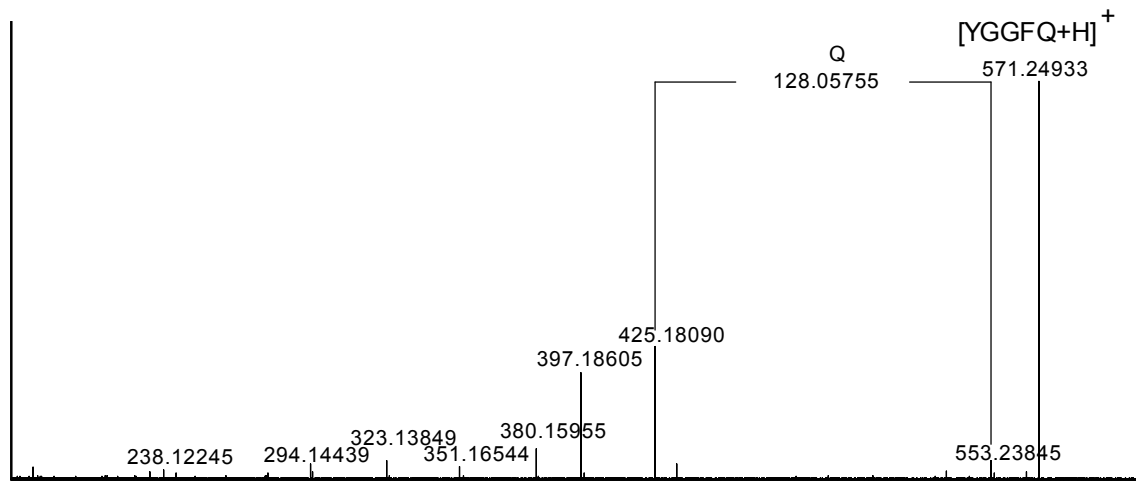
YGGFK
YGGFQ

$C_{28}H_{38}N_6O_7$
 $C_{27}H_{34}N_6O_8$

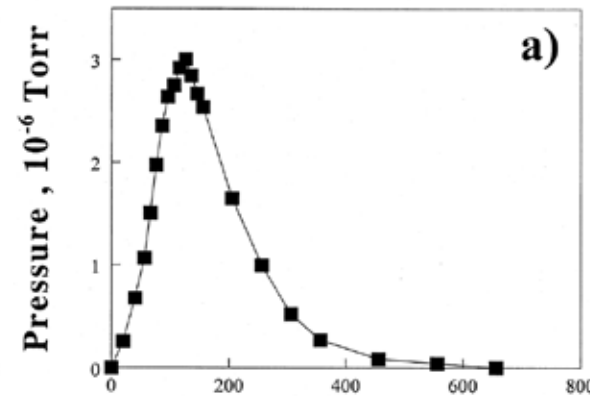
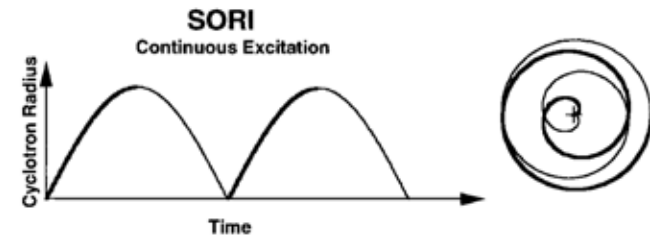
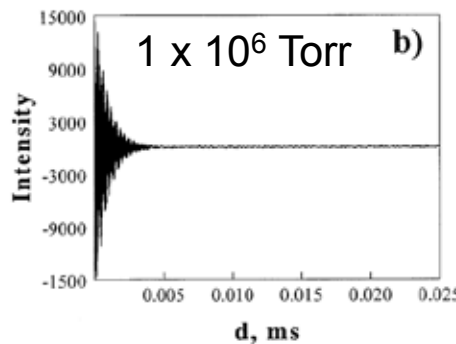
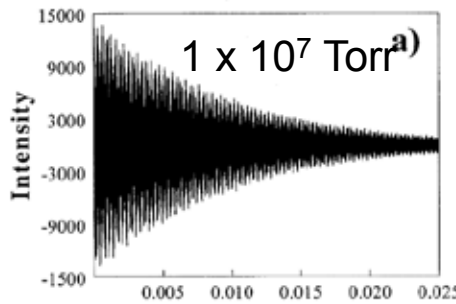
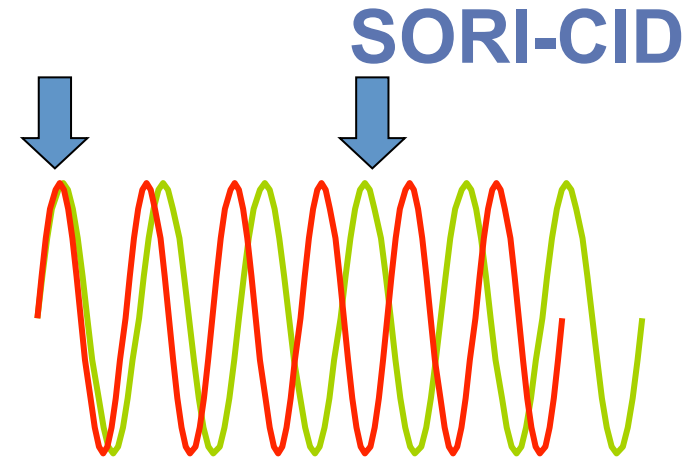
571.2875
571.2511



Sélection en Haute Résolution



- Sustained Off-Resonance Irradiation
- $\Delta\nu = 500 - 2000$ Hz (Offset)
 - A optimiser en fonction du précurseur.
- Nécessite d'introduire un gaz (Ar ou N₂)
 - $\sim 10^{-6}$ Torr
 - implique un temps de pompage avant la détection
- Cycle $\sim 2-4$ s

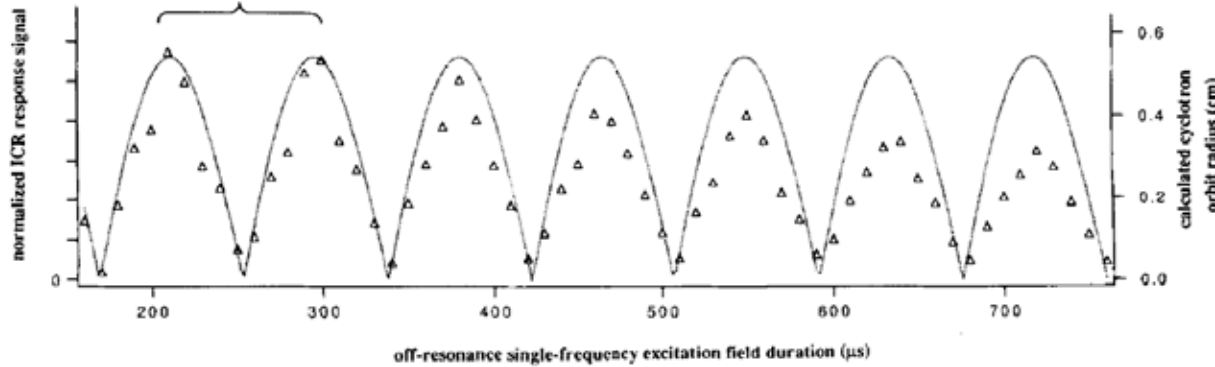
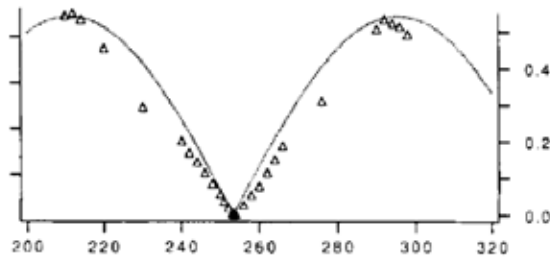


Mouvement des ions

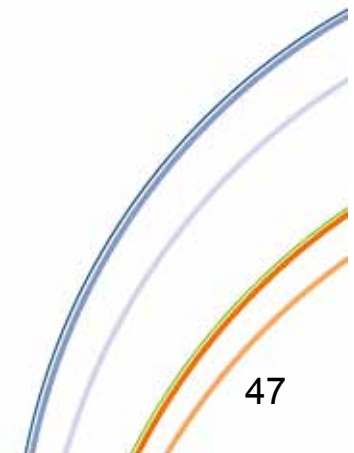
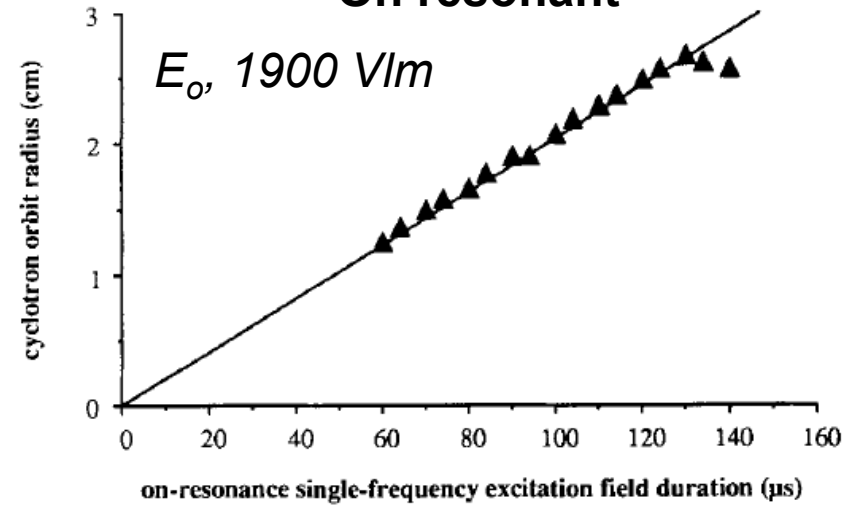
$$E_0 = \frac{V_{p-p}}{d} S_{E1}^1$$

$$r = \frac{E_0 T_{exc}}{2B}$$

Off resonant

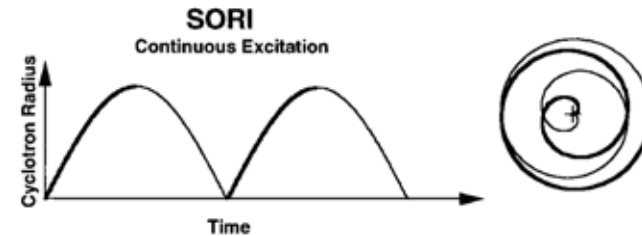


On resonant



Énergie interne

- SORI
 - Multiples collisions
 - Temps d'activation \gg temps entre deux collisions
 - 100-200 ms (0.5-10 V)
 - Inconvénients
 - Perte de résolution (gaz)
 - Distorsion du massif isotopique



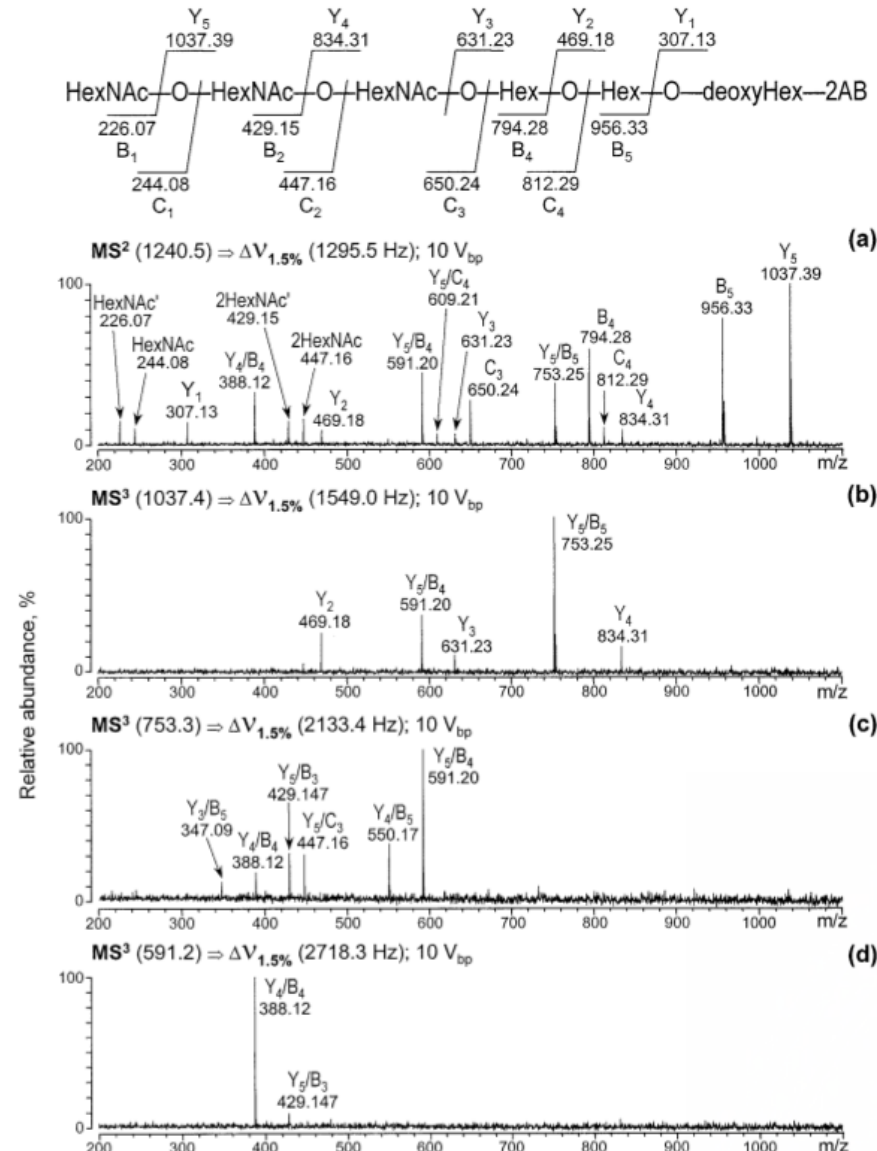
$$E_{\text{lab}} = \frac{\beta^2 q^2 V_{\text{p-p}}^2}{16 m d^2 \Delta \omega^2} [1 - \cos(\omega - \omega_c) t]$$

- On resonance
 - Si collision multiples
 - Atténuation du signal
 - Limité aux petits systèmes
 - $< 500 \mu\text{s}$ (50-300 V)
 - Perte de résolution en raison de la de la distorsion du nuage d'ions

$$E_{\text{lab}} = \frac{\beta^2 q^2 V_{\text{p-p}}^2}{8 m d^2 \Delta \omega^2} \quad E_{\text{lab}} \text{ max.}$$

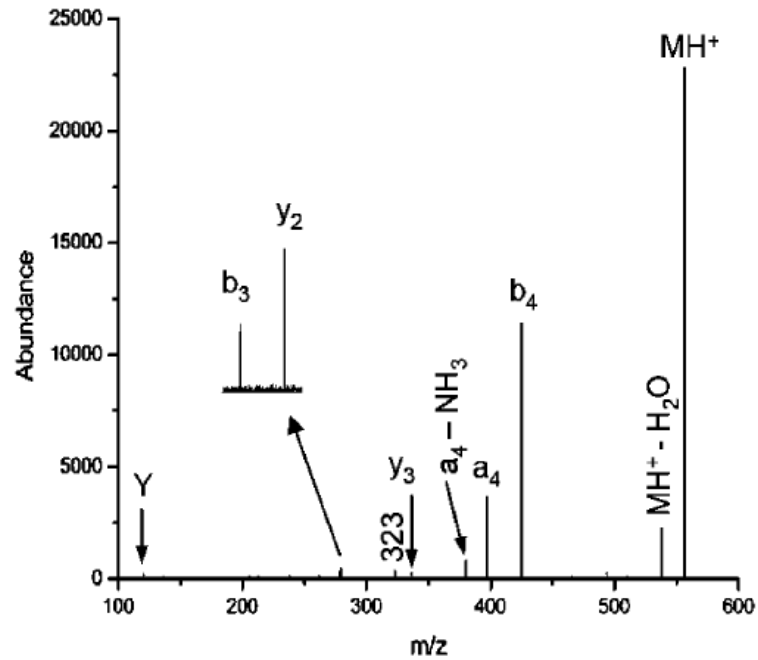
$$E_{\text{lab}} = \frac{\beta^2 q^2 V_{\text{p-p}}^2 t^2}{32 m d^2} \quad (\text{on resonance})$$

- Optimisation
 - Fréquence de l'Offset
 - Amplitude
- P.B. O'Connor
 - Offset fixe : exemple 1.5 %
 - Corrige la la difference d'efficacité lors de l'étude de composés de masse différente

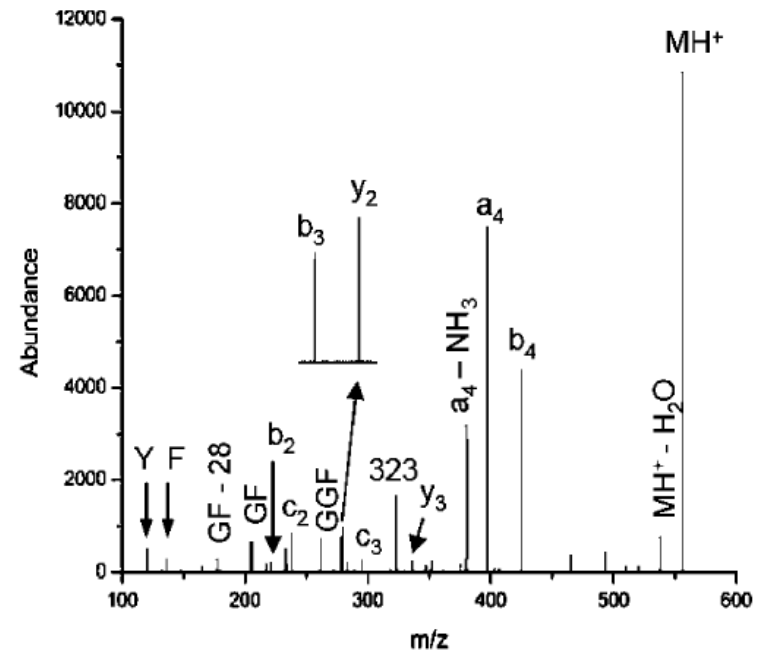


Exemple YGGFL

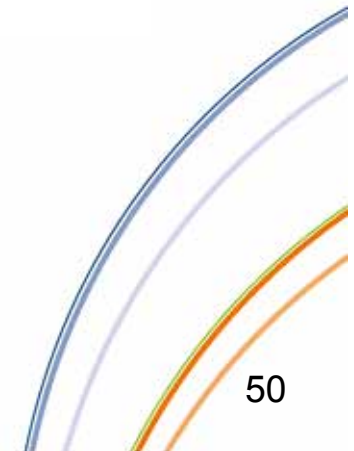
a) Experimental, SORI only: 500 ms, 2.0 V



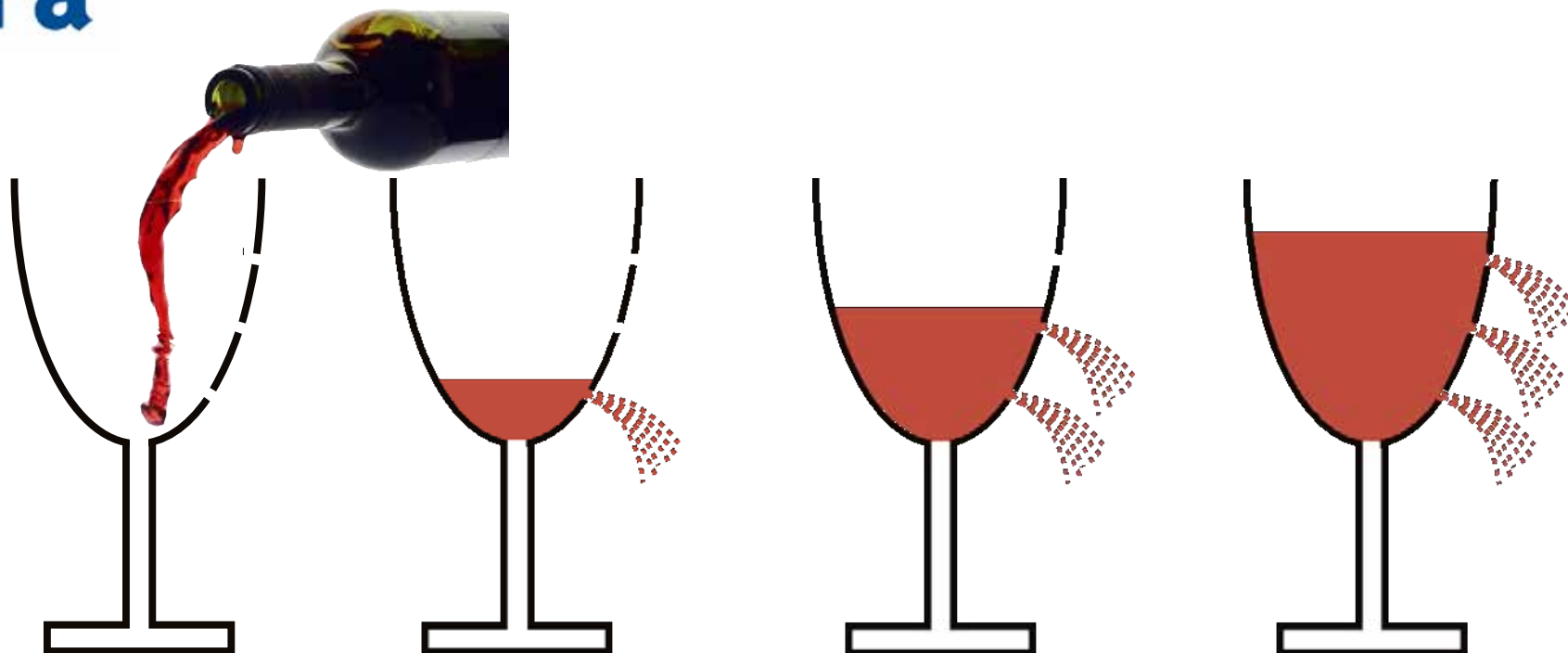
b) Experimental, RE only: 10 μ s, 120 V



$\Delta\nu = +1000\text{Hz}$



Conditions d'activations

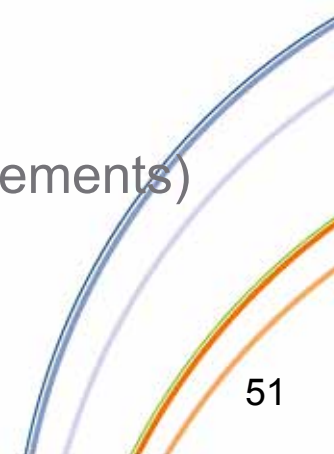


- **Chauffages lents**

- Favorisent les chemins de plus faible énergie (réarrangements)

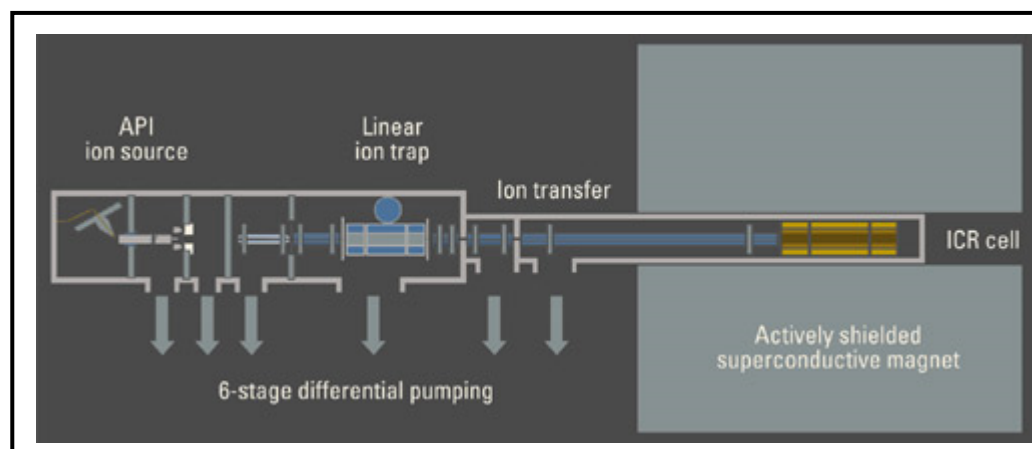
- **Chauffages rapides**

- Donnent accès à des chemins de haute énergie



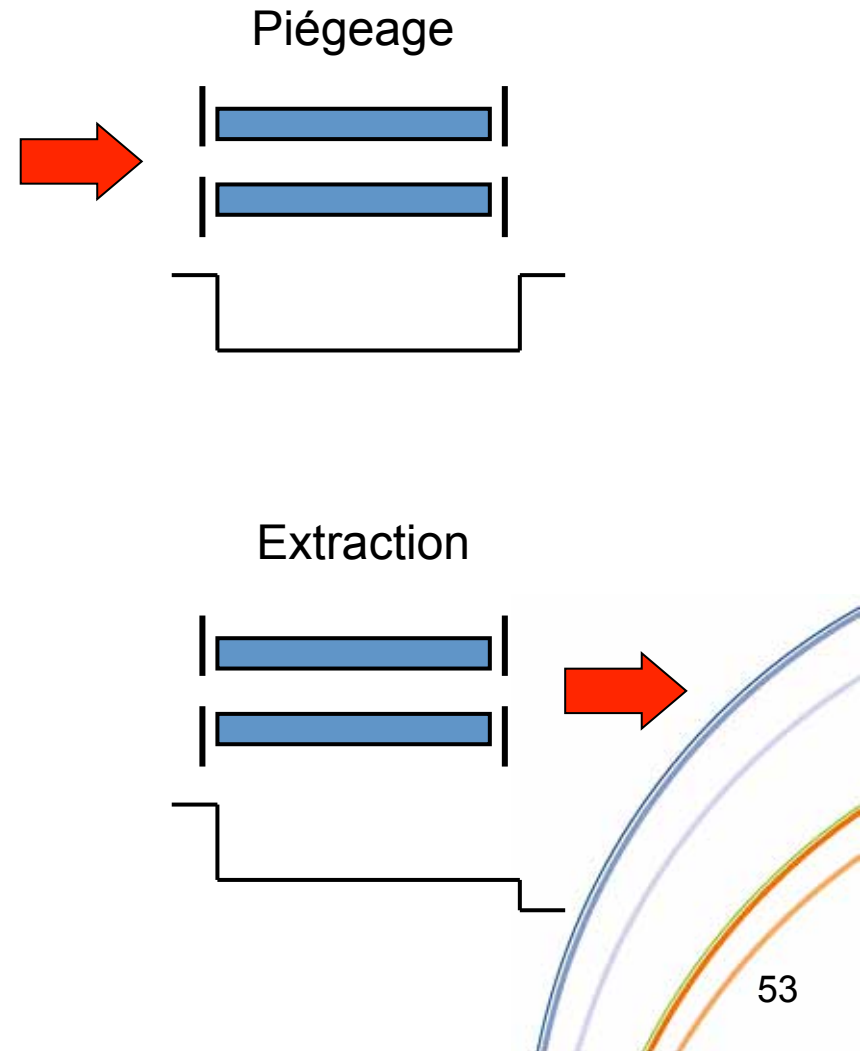
Instruments hybride

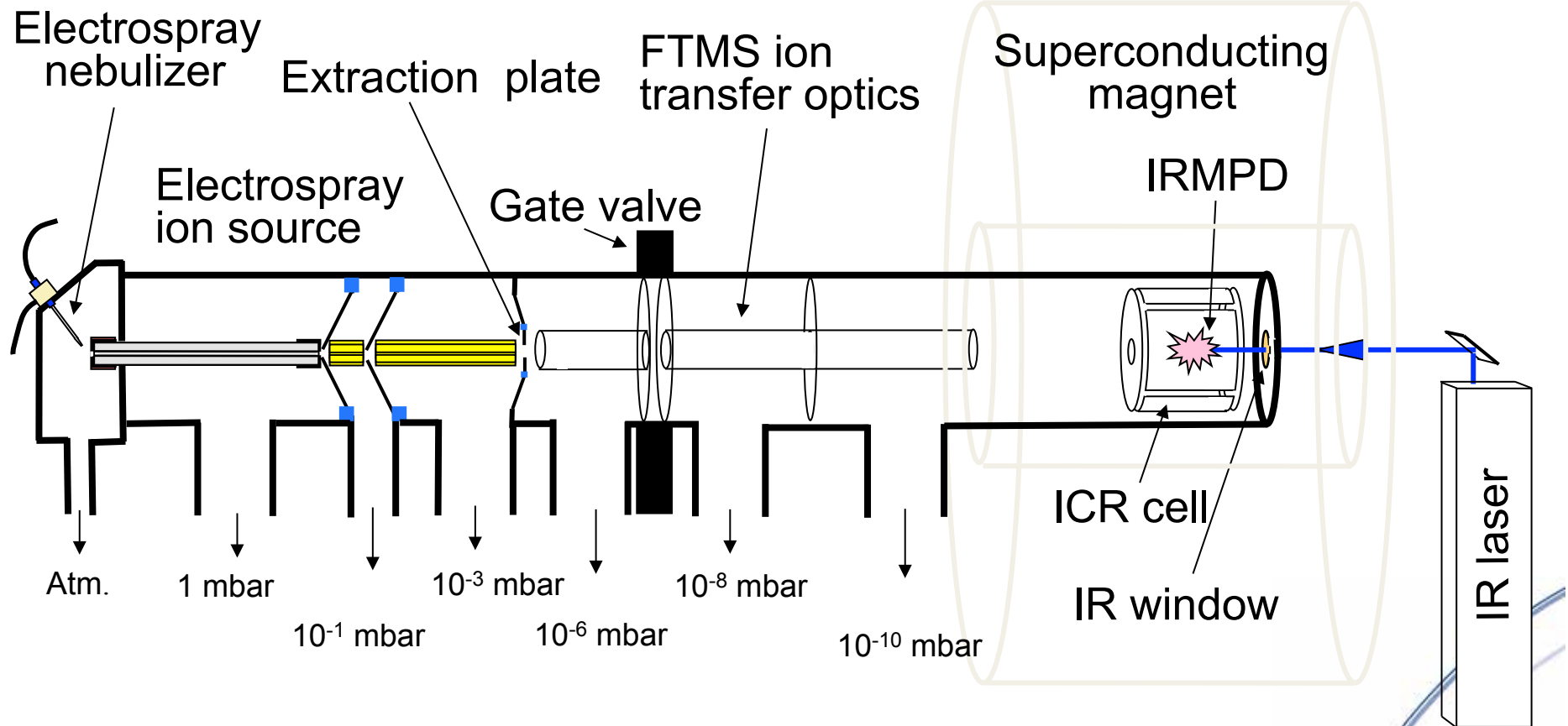
- Instrument hybride
 - Piège-FT/ICR
 - MSⁿ, Prescan,
 - Qq-FT/ICR
 - Pas de problème de seuil de basse masse
 - Faire la MS/MS dans une cellule de collision (ou piège à ions) avant l'analyse des ions fils en haute résolution dans le FT/ICR
 - Pas de temps de pompage



FTMS hybride - piège 2D

- Accumulation externe des ions.
 - Meilleure gamme dynamique
- Instruments hybrides
 - Piège-2D-Orbitrap
 - MSⁿ
 - Prescan
 - Qq-FT/ICR
 - Pas de problème de seuil de basse masse
 - Faire la MS/MS dans une cellule de collision (ou piège à ions) avant l'analyse des ions fils en haute résolution dans le FT/ICR



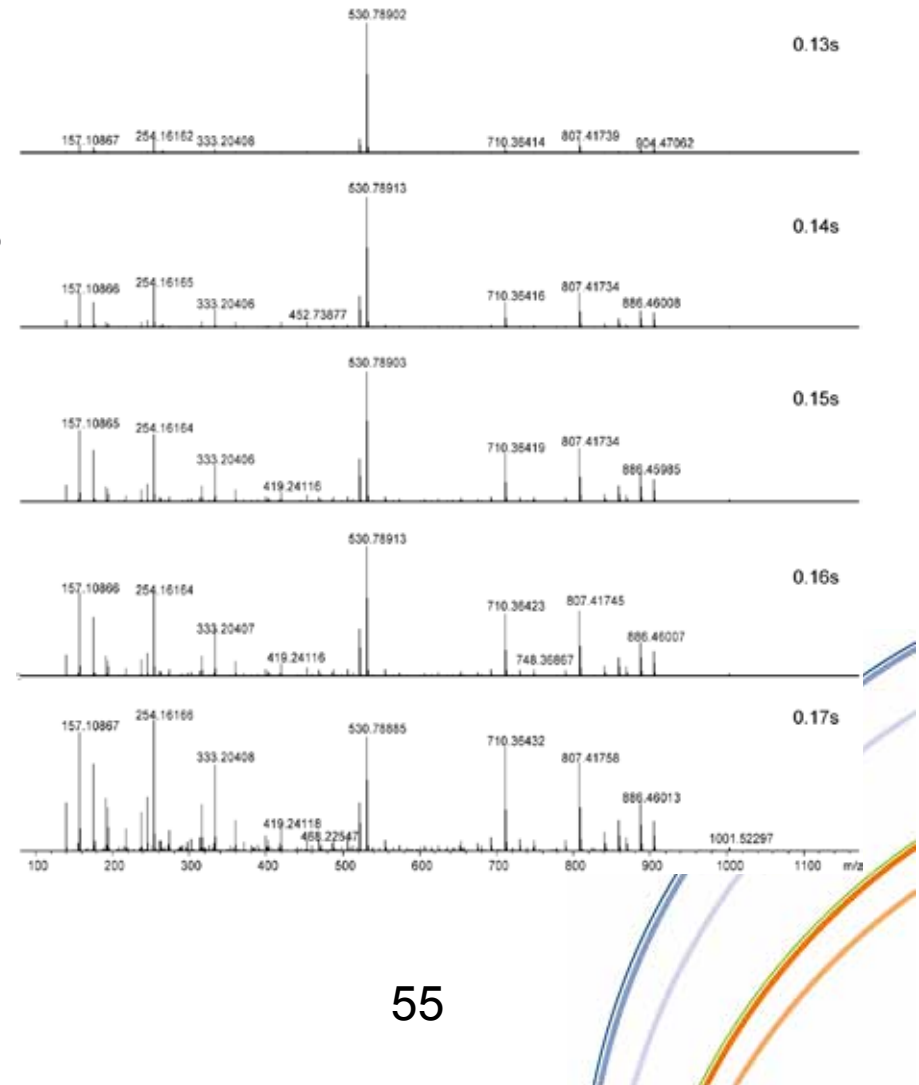


Laser à CO₂ continu (10.6 μm, 25 W)

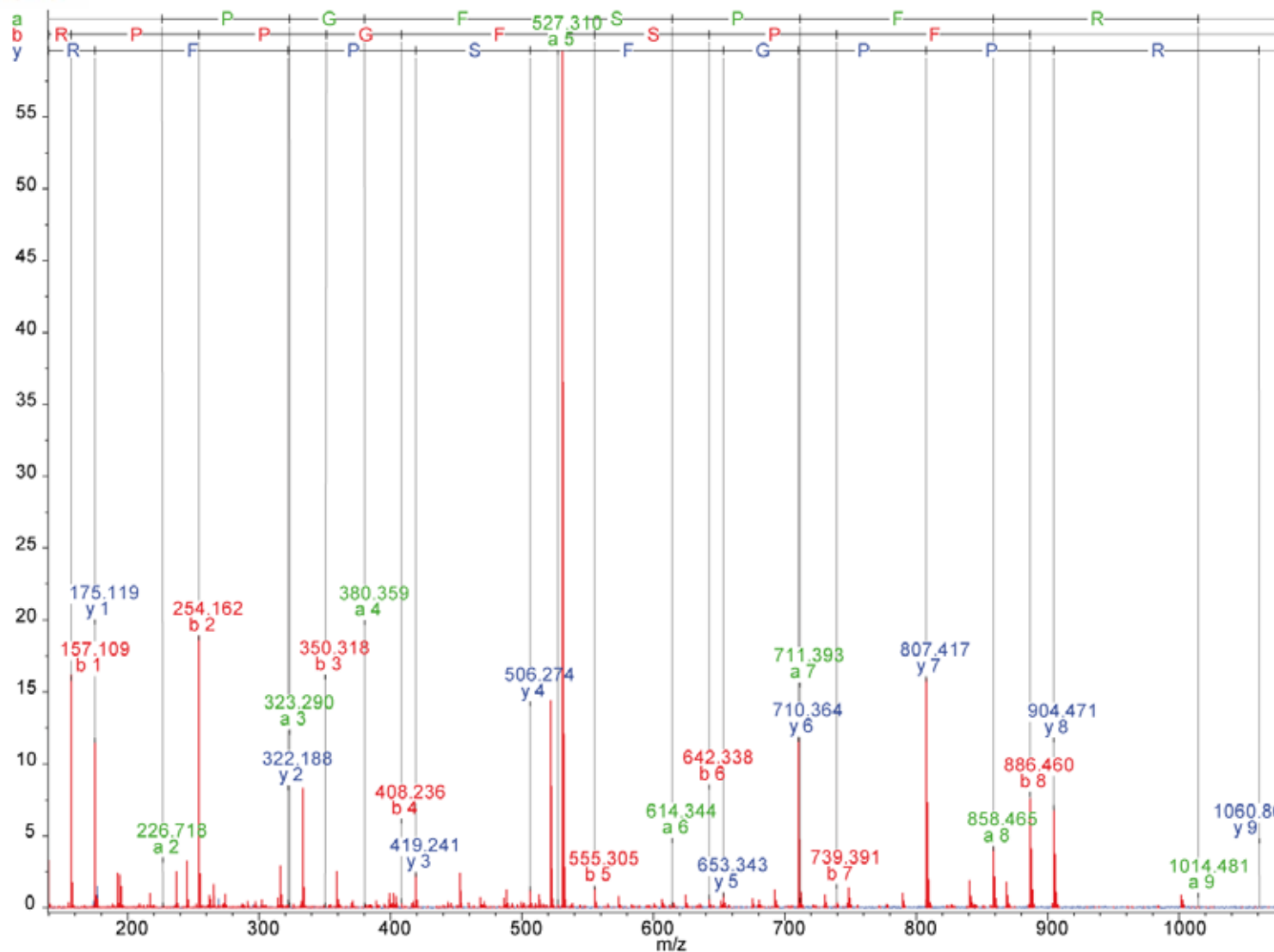
– Control de la puissance et du temps d'irradiation

FTMS masse précise en MS/MS

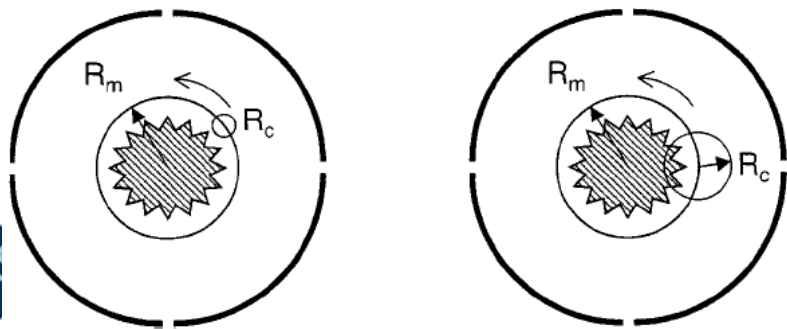
- Peptide (RPPGFSPFR)
 - IRMPD
 - Présence de nombreuses fragmentations consécutives
 - Pas de gaz
 - Permet de conserver une précision < 2 ppm en étalonnage externe



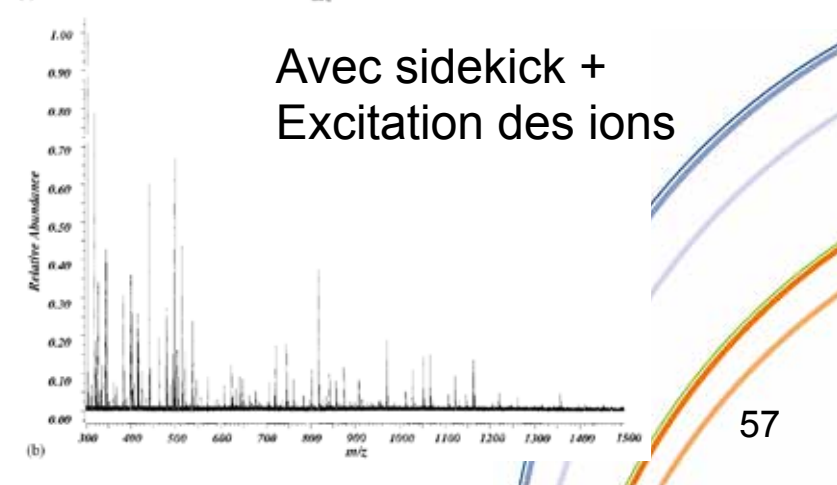
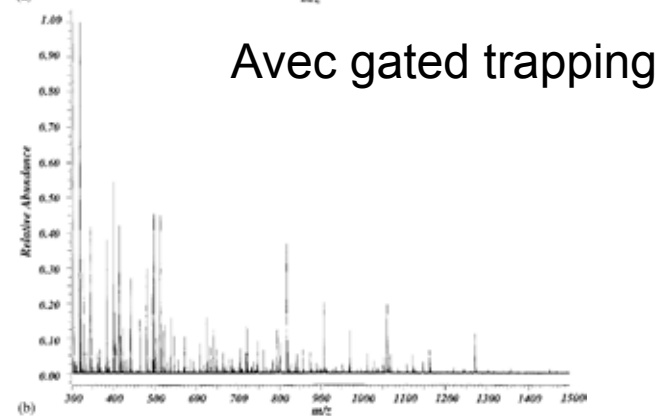
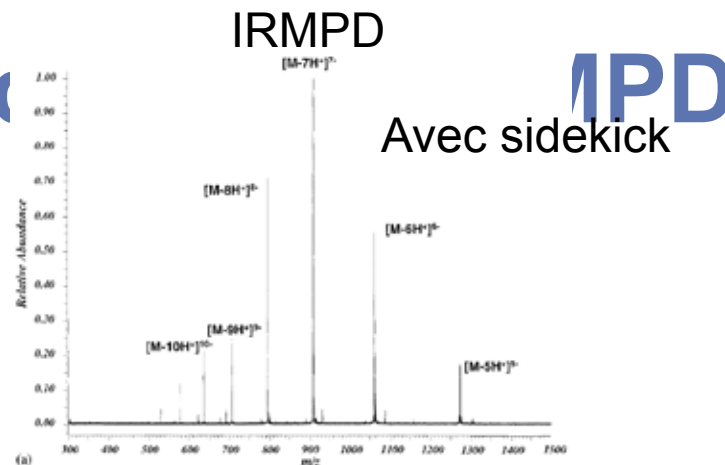
Séquençage *de novo* automatique



- Dissociation d'ADN
 - Avec sidekick les ions possèdent un plus grand rayon magnétronique
 - Il n'y a pas un bon recouvrement entre le laser et les ions donc pas de dissociation.
 - Solution : augmenter le rayon cyclotronique par une excitation.



Sidekick

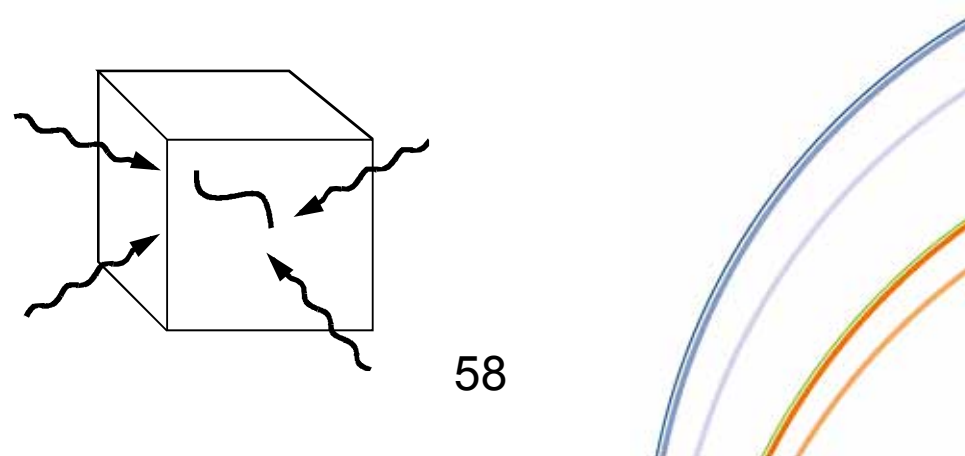
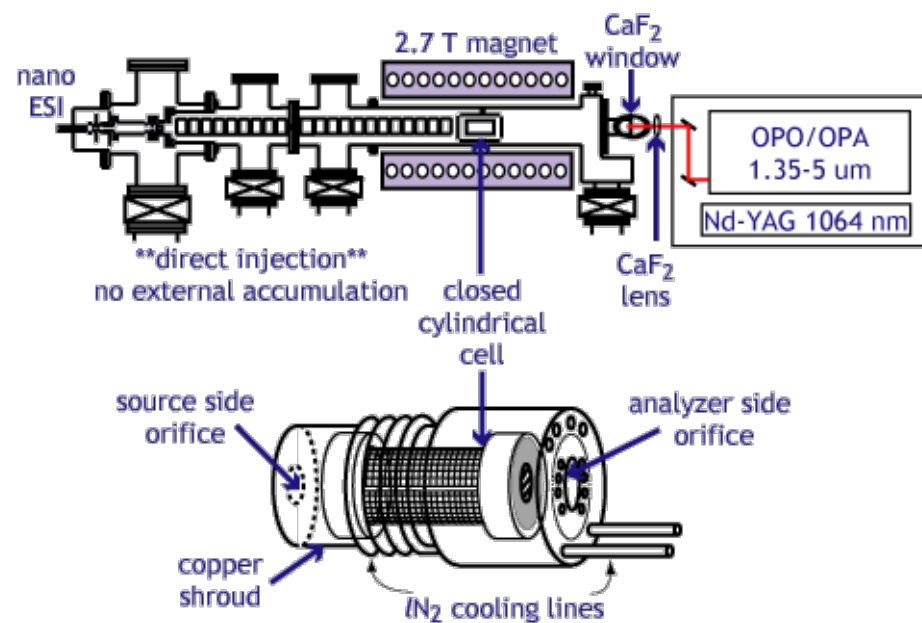


- Blackbody Infrared radiation dissociation Collisions (CID)

- FT/ICR
- Emission photon IR
- Energie d'activation

$$\ln k = A - \frac{E_a}{RT}$$

- Forces/nature des liaisons

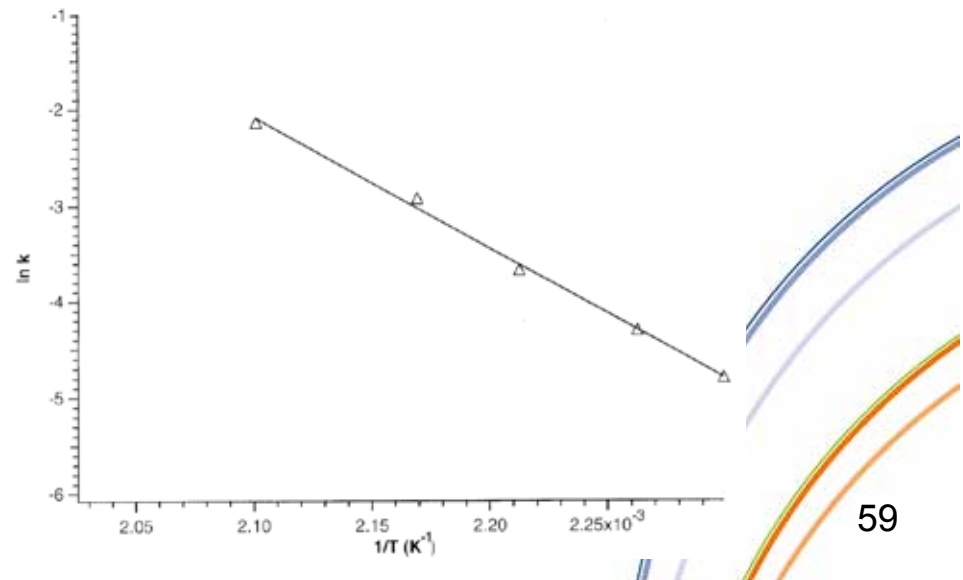
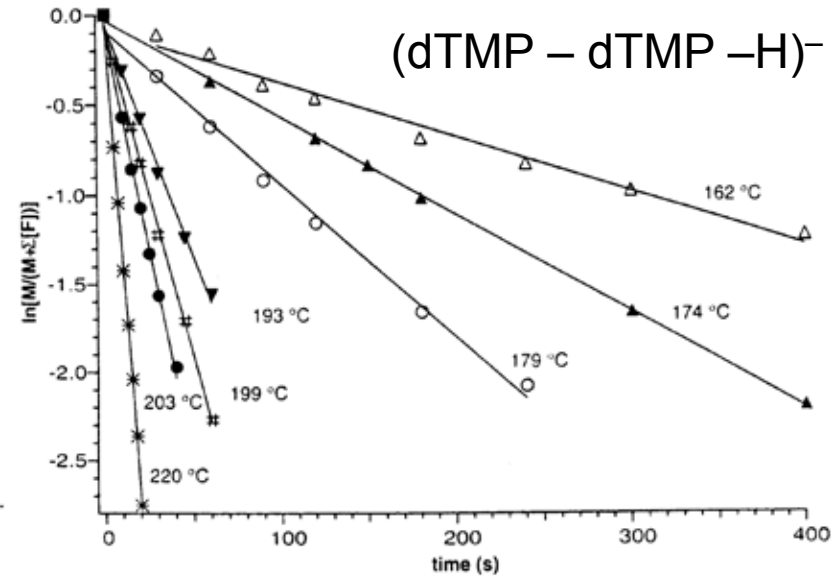


Exemple : étude ADN par BIRD

Espèce	E_a (eV)	LogA
dAMP.dAMP ⁻	1.18 ± 0.05	11.4 ± 0.7
dCMP.dCMP ⁻	1.22 ± 0.06	11.5 ± 0.8
dTMP.dTMP ⁻	1.28 ± 0.04	12.2 ± 0.4
dGMP.dGMP ⁻	1.26 ± 0.09	12.2 ± 1.1
dGMP.dCMP ⁻	1.59 ± 0.098	15.4 ± 0.9
dAMP.dTMP ⁻	1.17 ± 0.04	8.2 ± 0.2

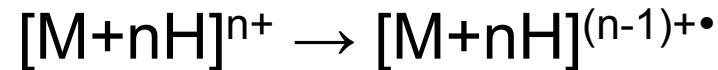
- dGMP.dCMP⁻

- E_a plus élevée
- Liaisons Watson-Crick conservées en phase gazeuse

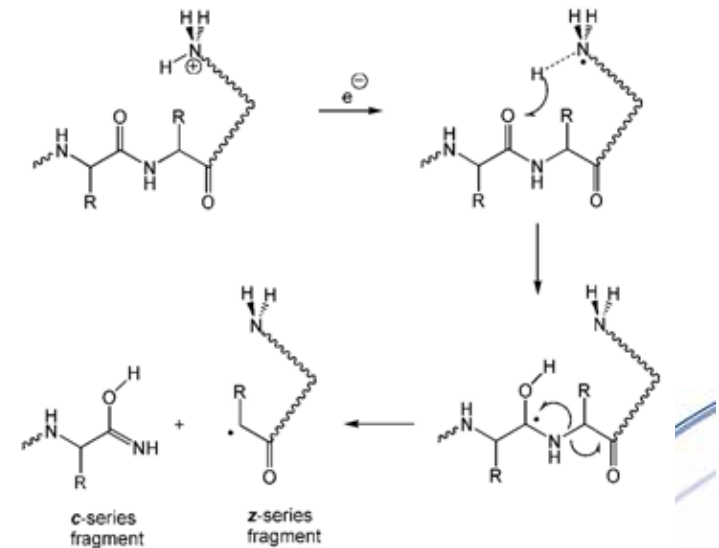


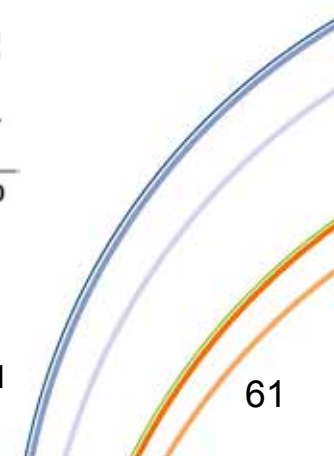
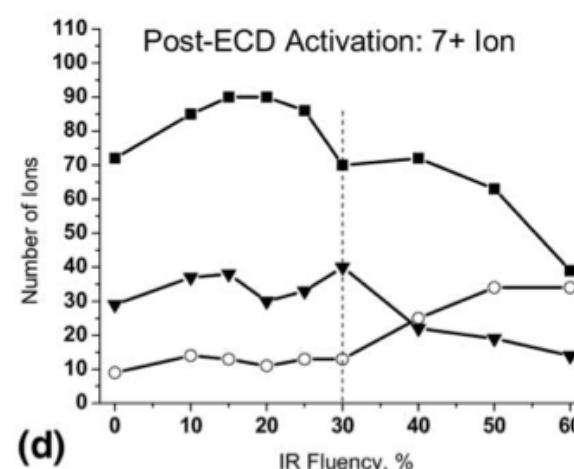
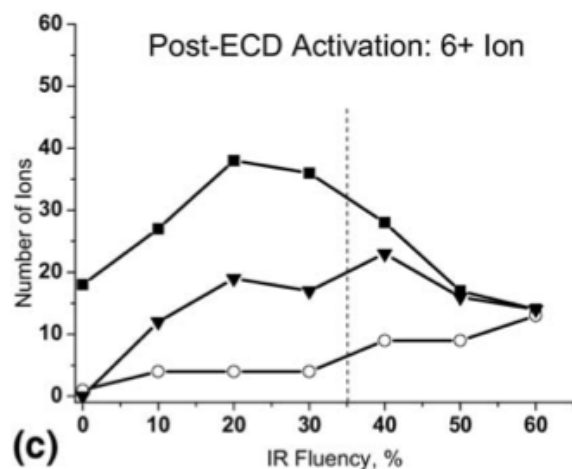
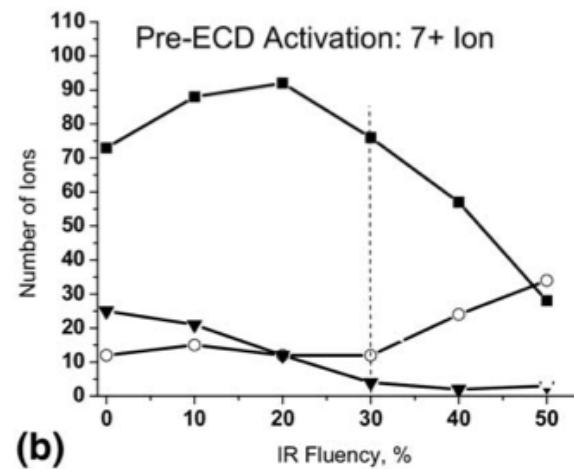
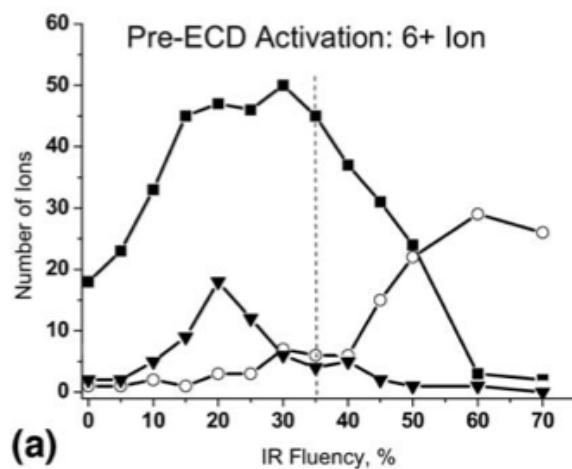
Méthodes alternatives de dissociation : ECD

- ECD (electron capture dissociation) - McLafferty et Zubarev
 - FT-ICR
 - capture d'électrons lents (<0.2 eV) par des ions multichargés.



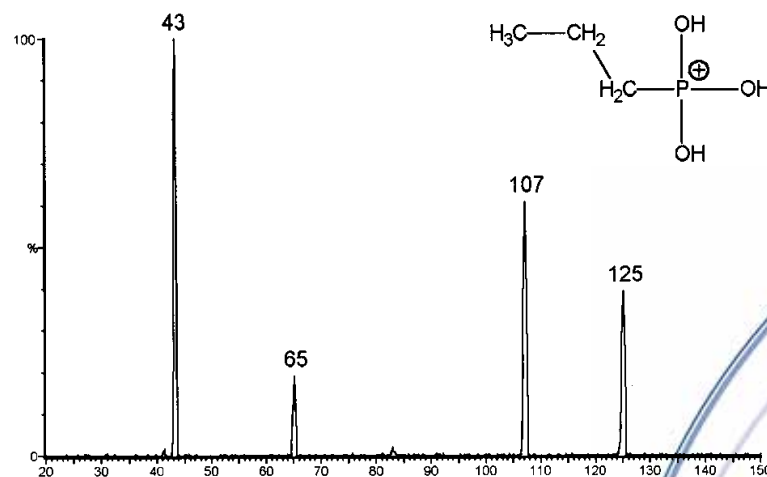
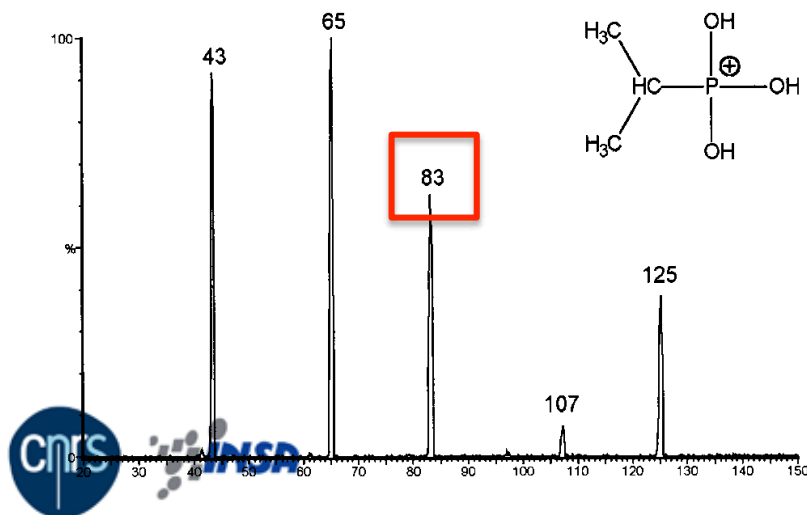
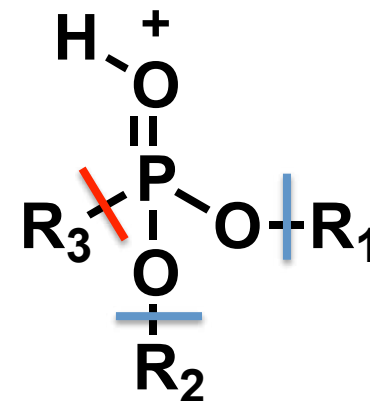
- Formation d'espèces radicalaires
 - Décomposition non ergodique
 - Pas de répartition statistique de l'énergie
 - Fragments c' / z'
- Intérêt
 - Voie de décomposition alternative (ions c' et z')
 - Décomposition de haute masse moléculaire
 - Approche « top-down »





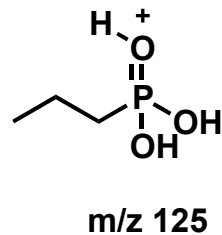
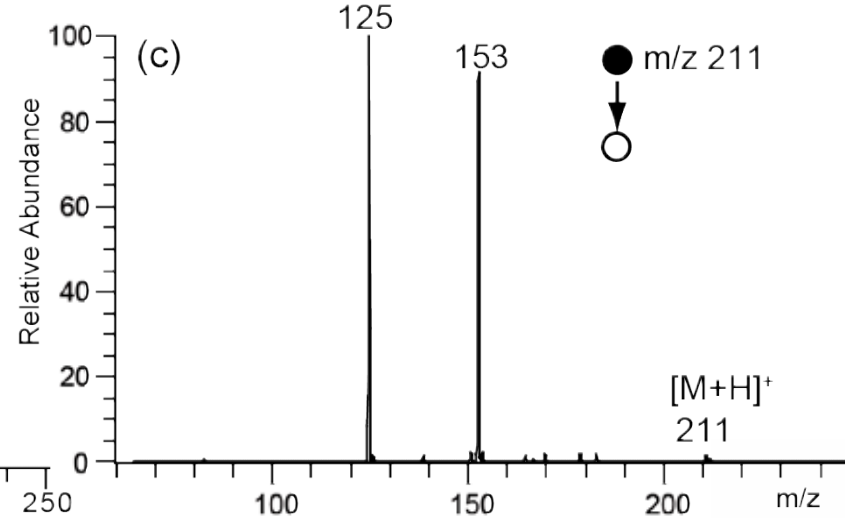
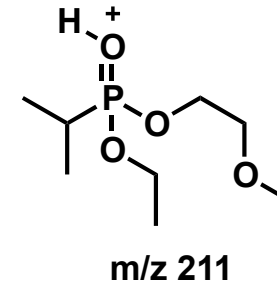
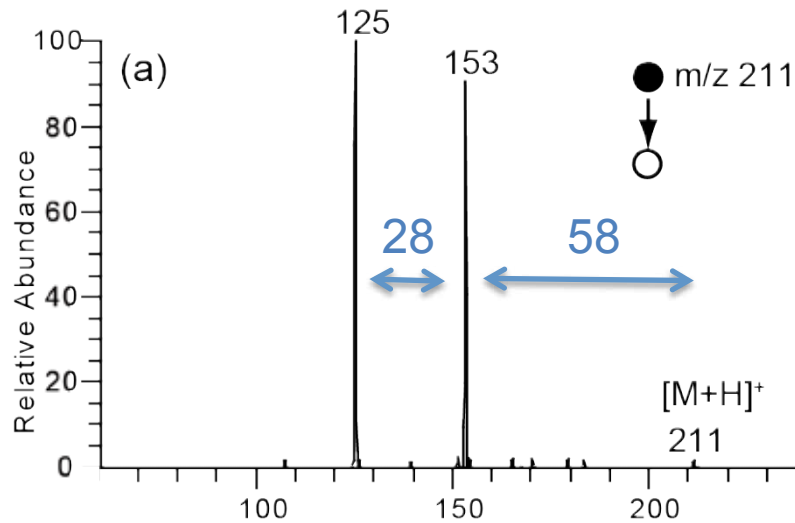
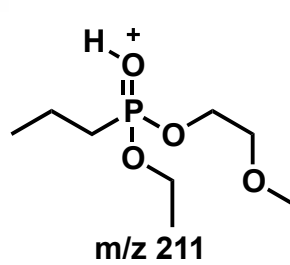
Exemple : organophosphorés

- Pesticides ou d'armes chimiques
 - Liaison OR fragile
 - Liaison OP stable
- Information sur le groupement RP
 - Exemple : Propyl isopropyl

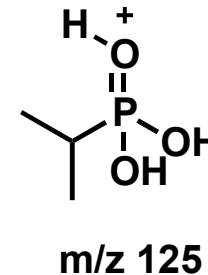


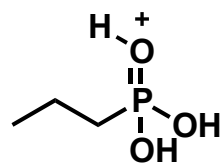
van Baar, J. Mass Spectrom. 33, 1104-1108 (1998)

Exemple : organophosphorés

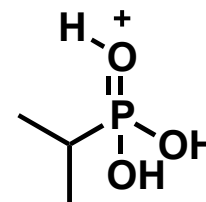


Très stable

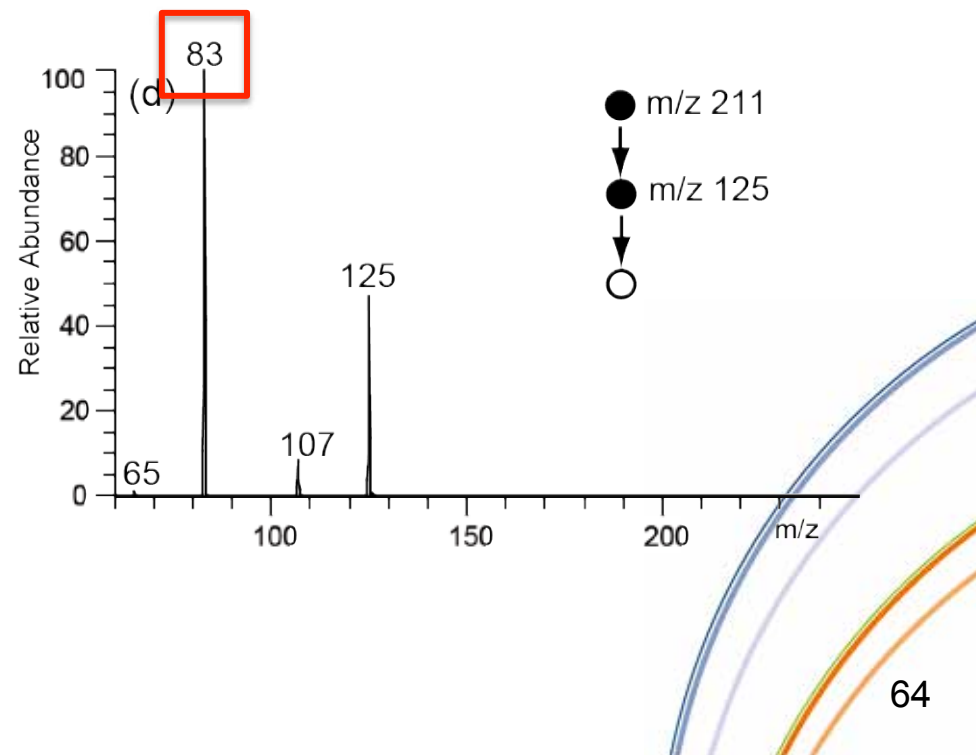
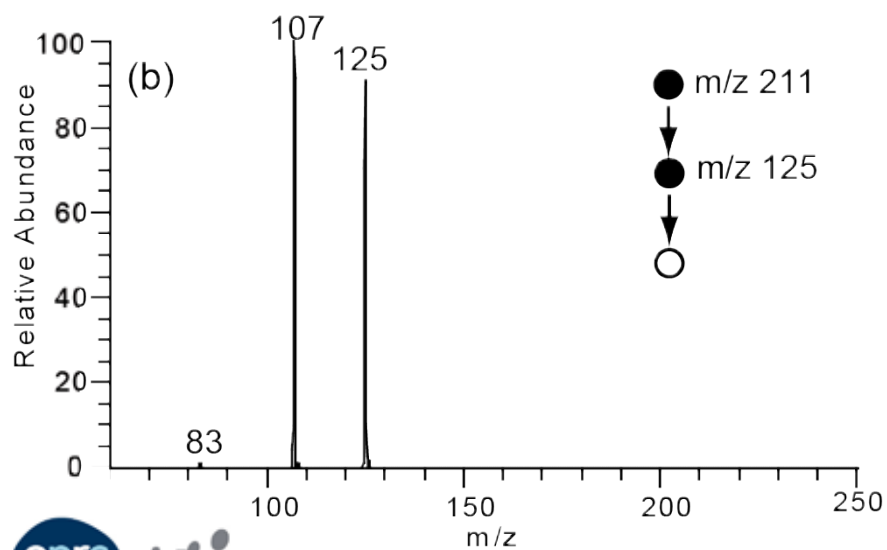




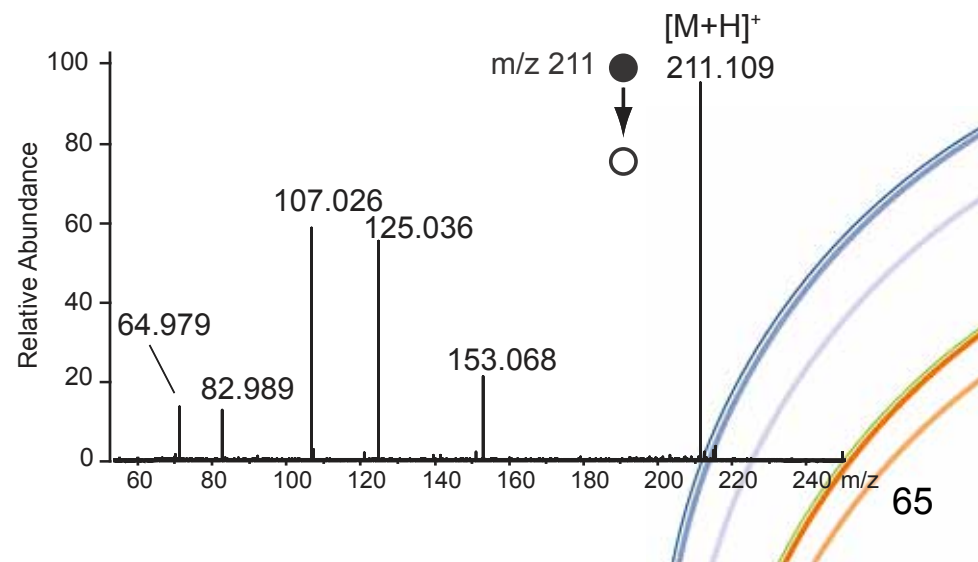
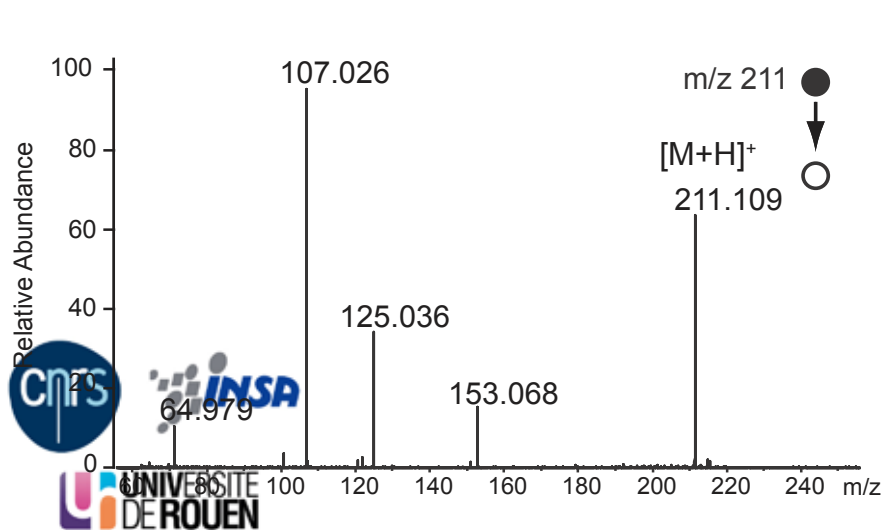
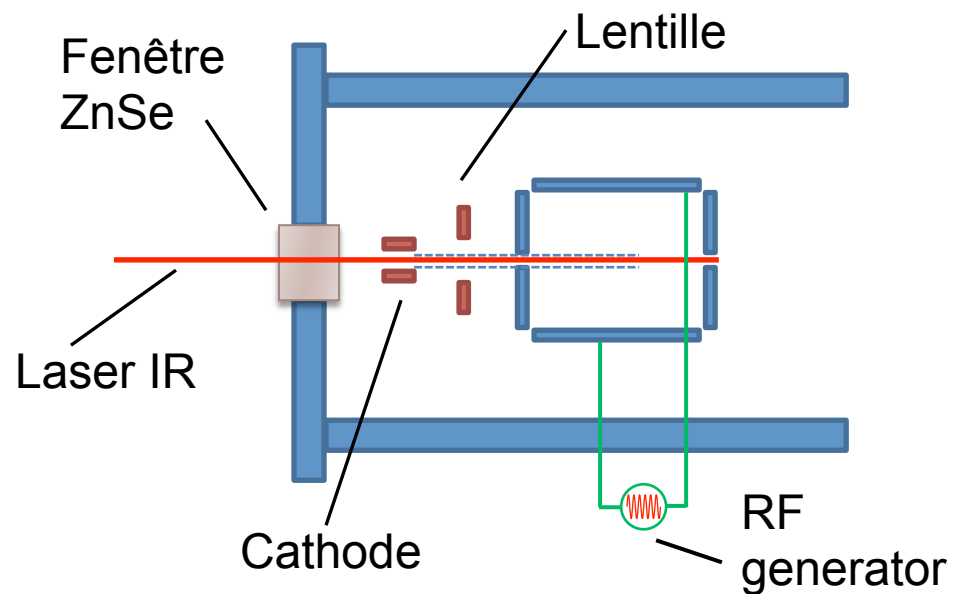
m/z 125

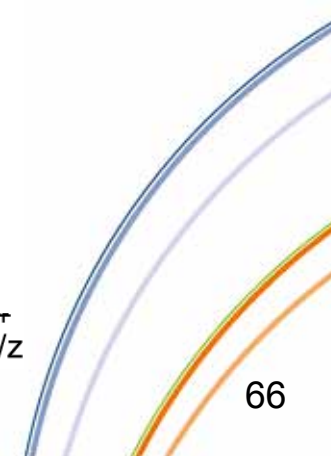
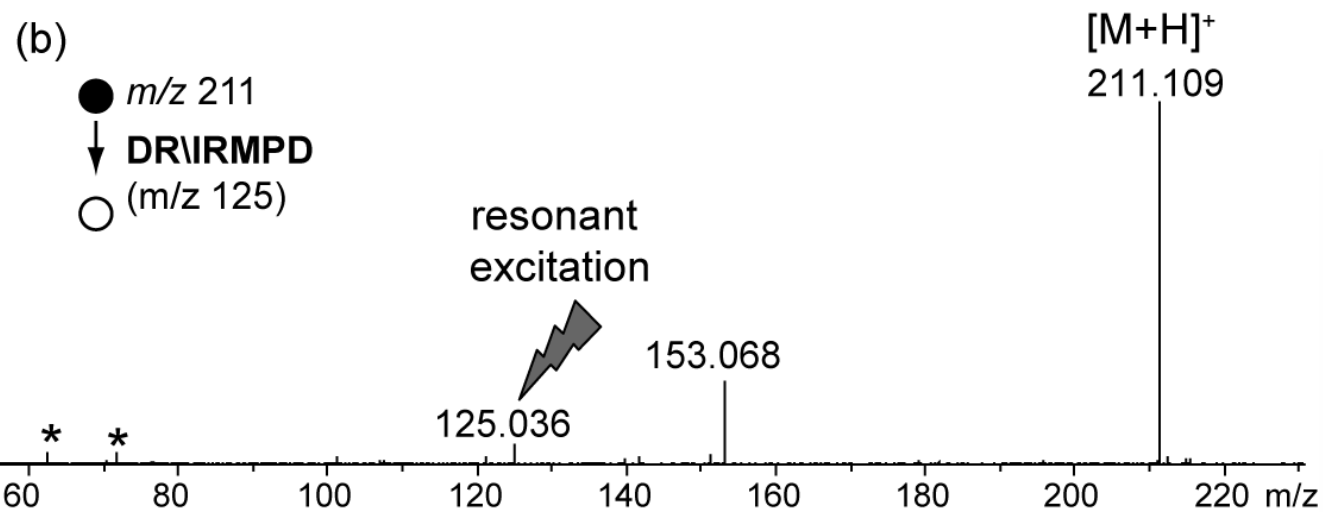
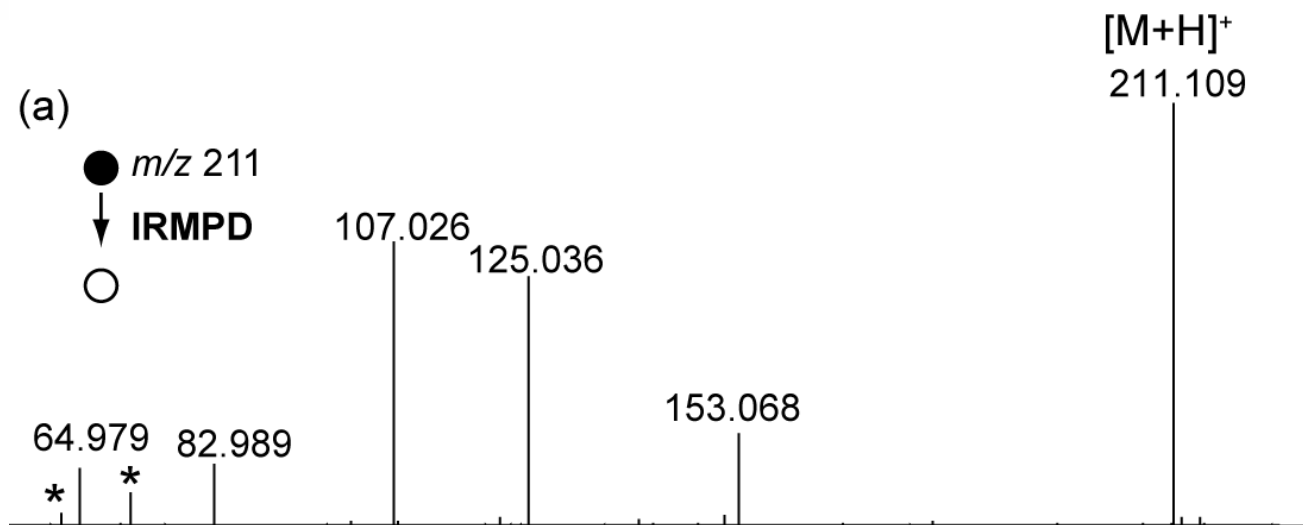


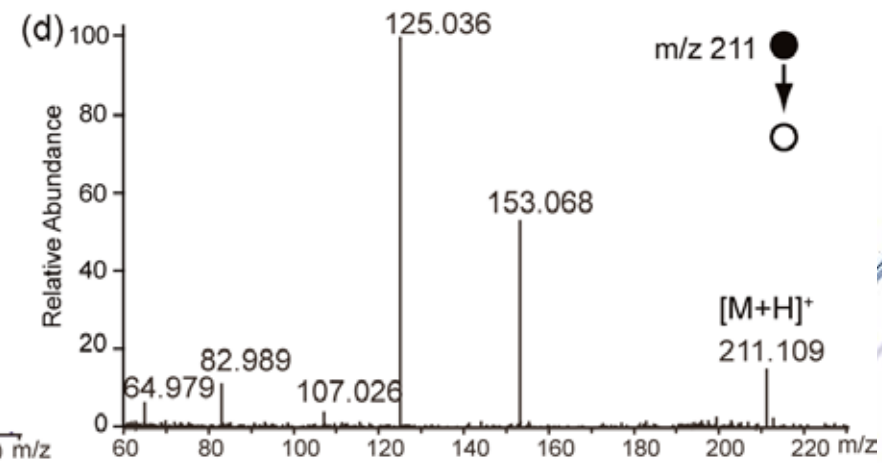
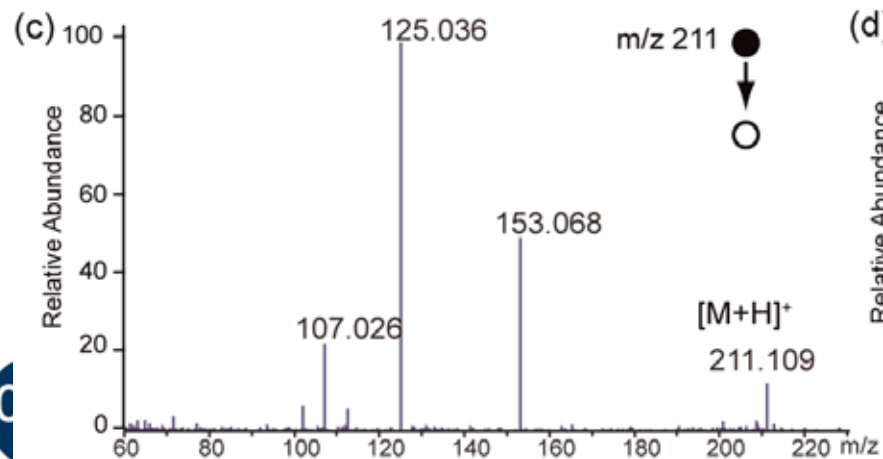
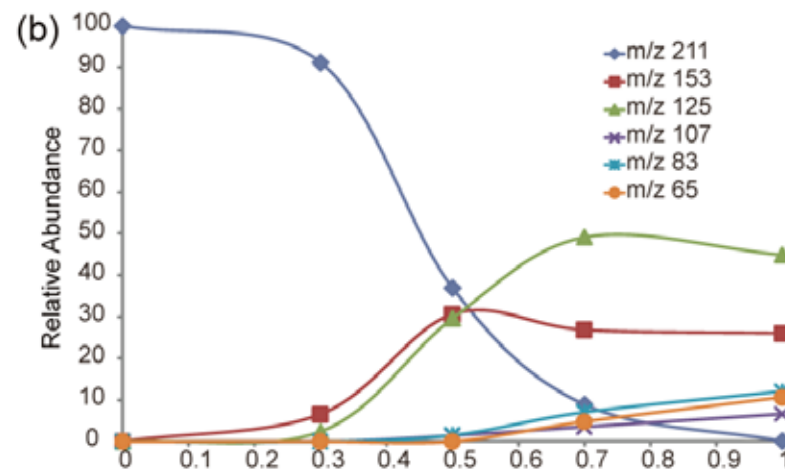
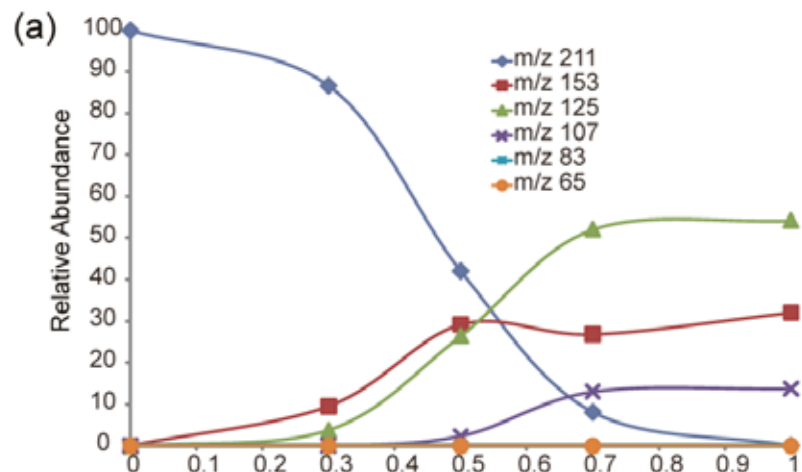
m/z 125



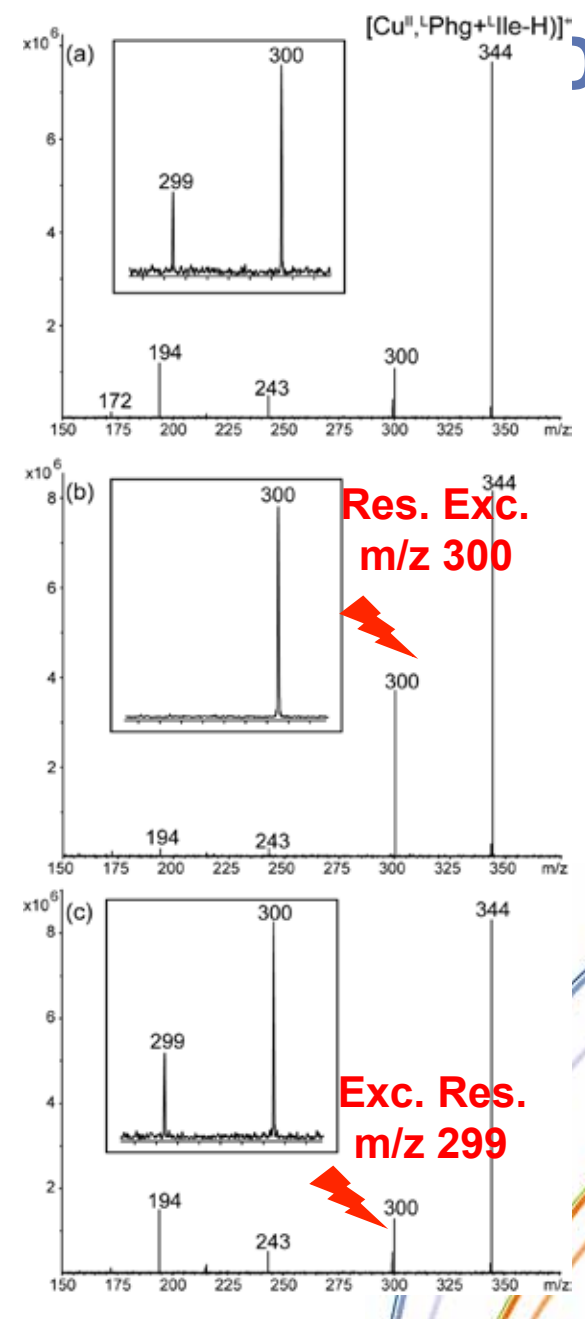
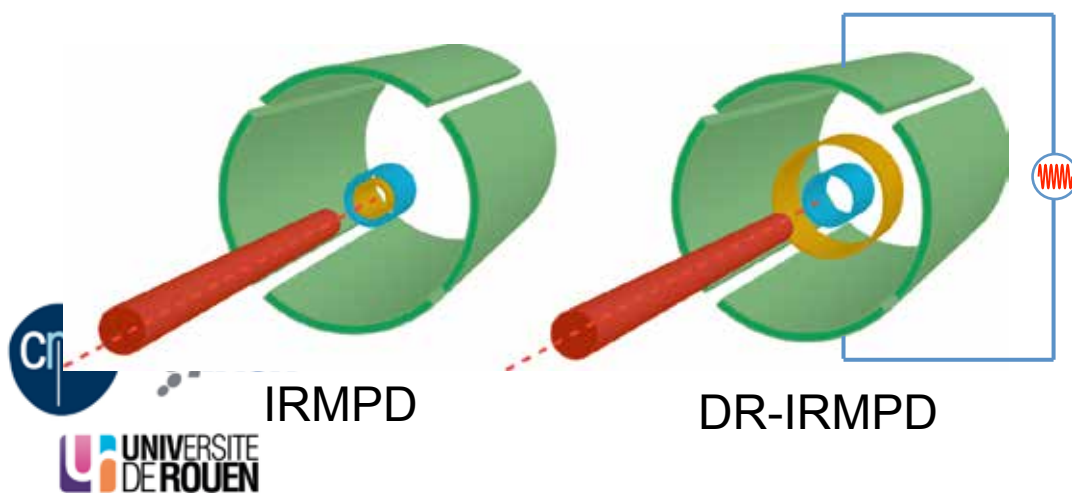
IRMPD (FTICR)



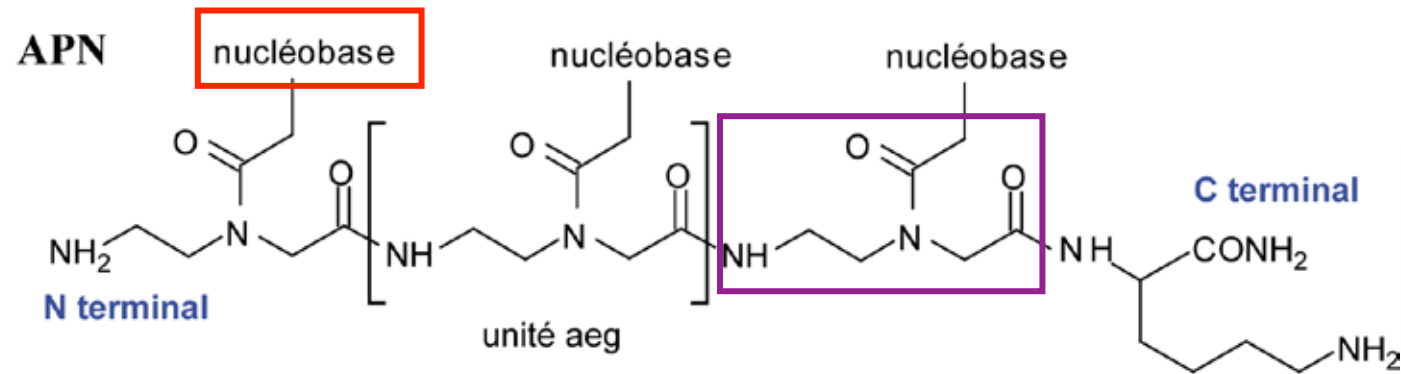
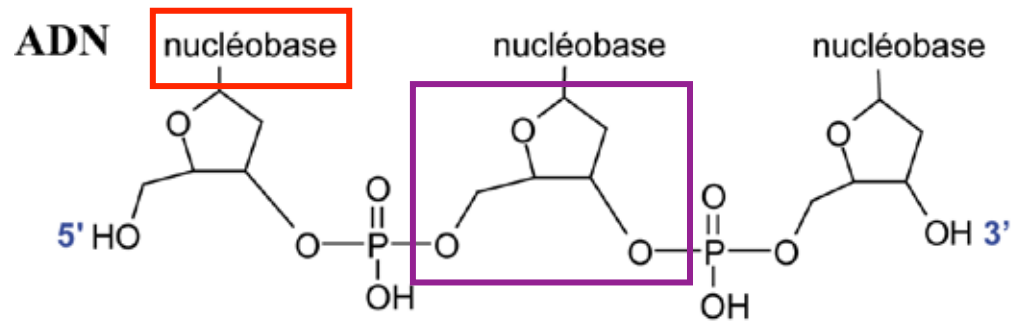


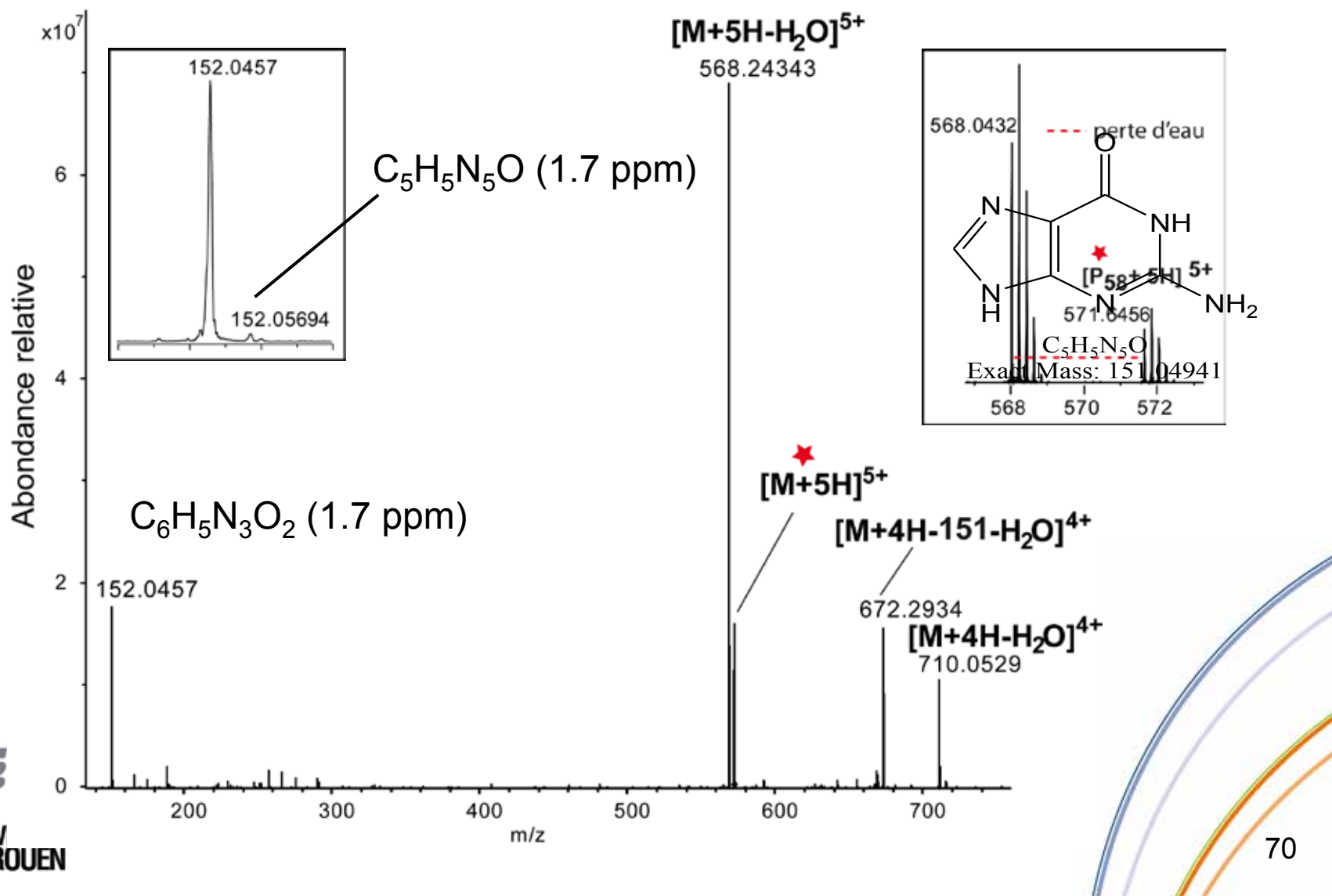


- IRMPD
 - m/z 300 perte de CO_2
 - m/z 299 perte de HCO_2^- ?
- DR-IRMPD
 - m/z 300 $0.6 V_{p,p}$
 - Augmentation du rayon cyclotronique,
 - Plus de superposition avec le faisceau laser
 - Perte de décompositions consécutives
 - m/z 299 produit par perte de H^+ à partir de m/z 300 !

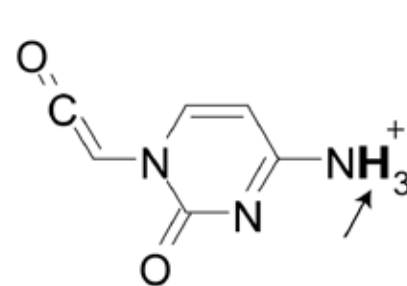
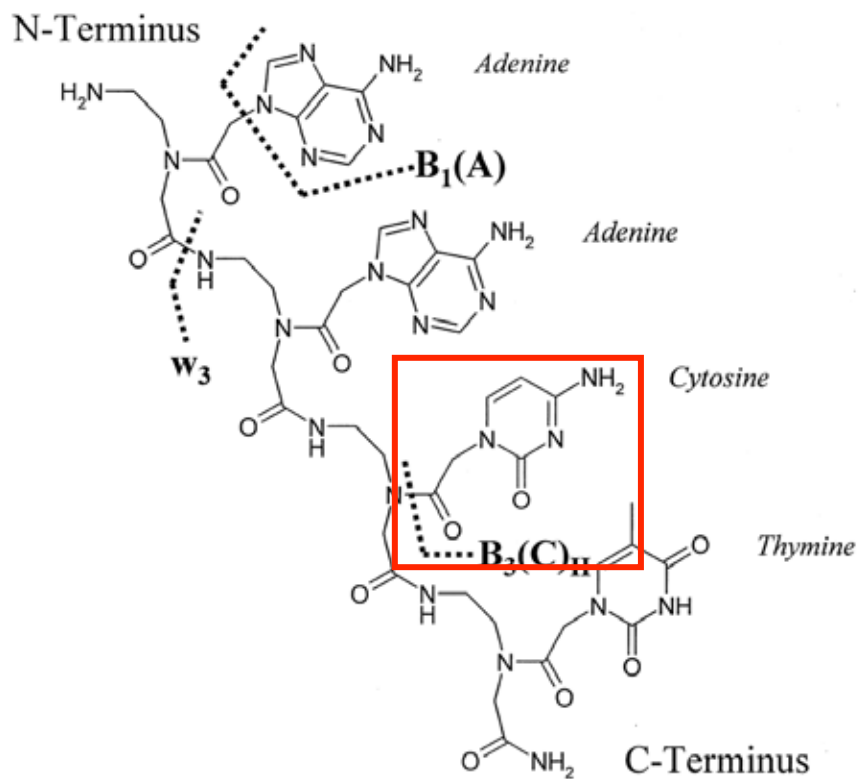


Etude structurale d' APNs

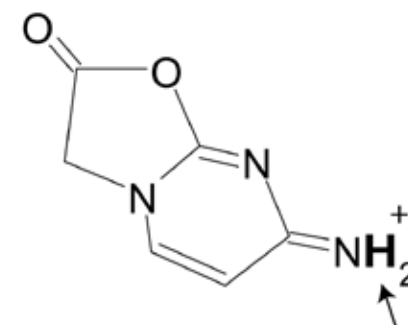




Attribution



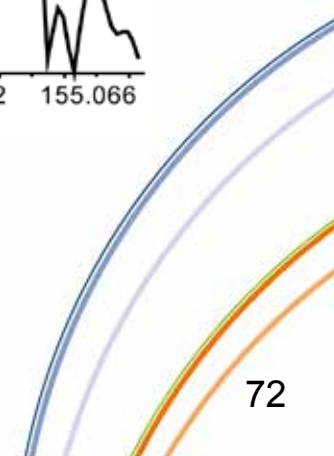
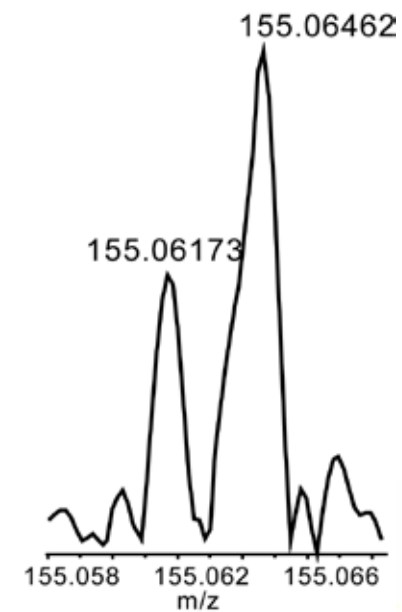
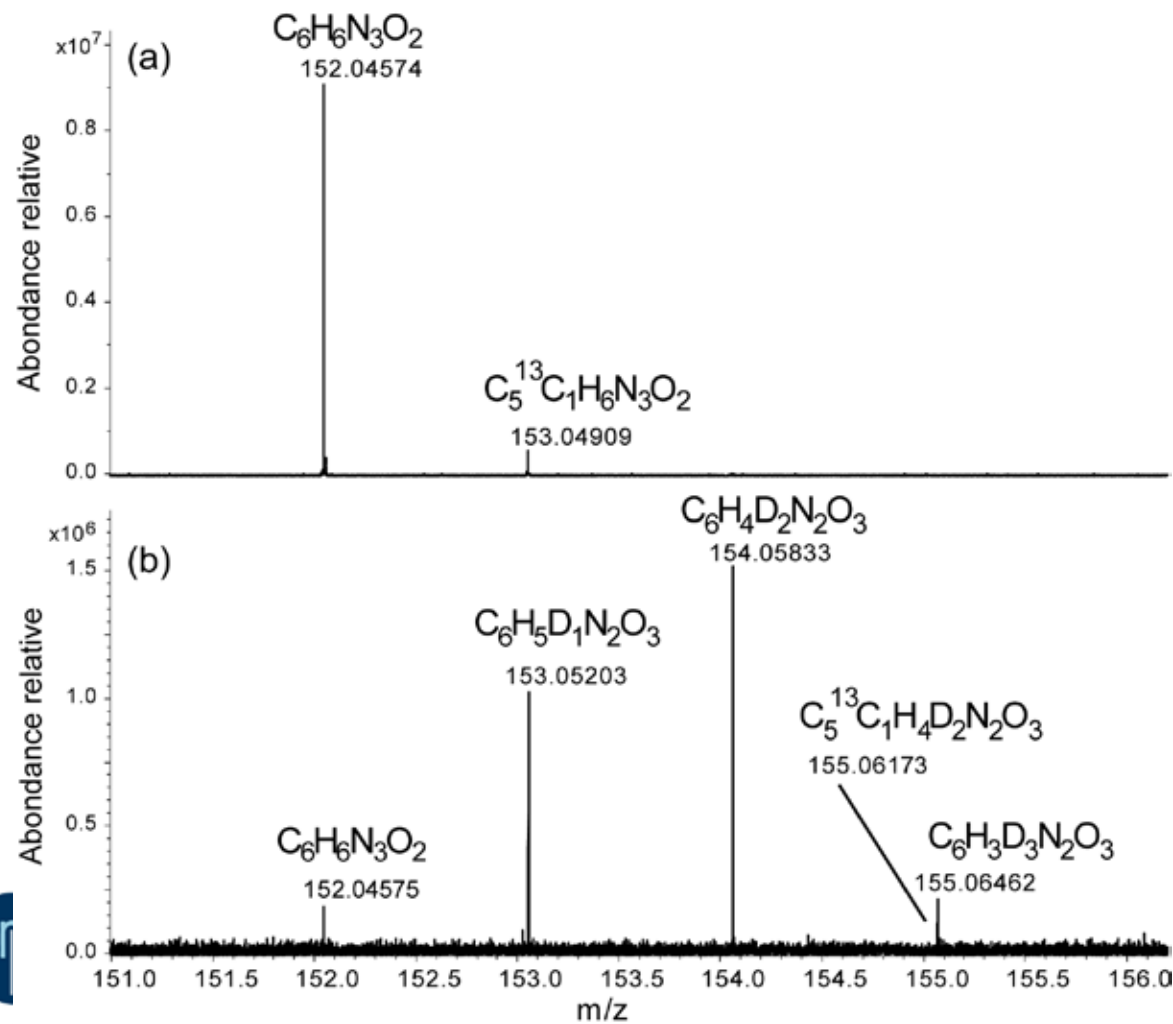
$[B_n(C)_{II}+H]^+$



$[B_n(C')_{II}+H]^+$

$C_6H_5N_3O_2$

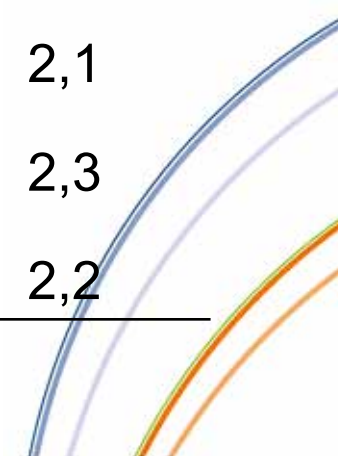
Echanges H/D



Attribution par les mesures de masse précises

Mesures de masses précises des espèces observées après échange H/D données pour l'ion MH⁺.

Formule brute	nbre D	m/z exp.	m/z theo.	erreur (ppm)
$C_6H_6N_3O_2$	0	152,04575	152,04545	1,9
$C_6H_5D_1N_3O_2$	1	153,05203	153,05194	1,9
$C_6H_4D_2N_3O_2$	2	154,05833	154,05821	2,1
$C_5^{13}C_1H_4D_2N_3O_2$	2	155,06173	155,06136	2,3
$C_6H_3D_3N_3O_2$	3	155,06462	155,06428	2,2



- FT-ICR
 - Ultra haute résolution $>10^6$
 - Mesure de masse précise en MS et MSⁿ.
 - Indispensable pour interpréter des systèmes complexes (Biopolymères...)
 - Etalonnage externe très stable
 - Etalonnage interne 200 ppb
 - Flexible
 - DR-ECD, DR-IRMPD
 - MSⁿ dans la cellule ICR
 - IRMPD/CID/EXD

