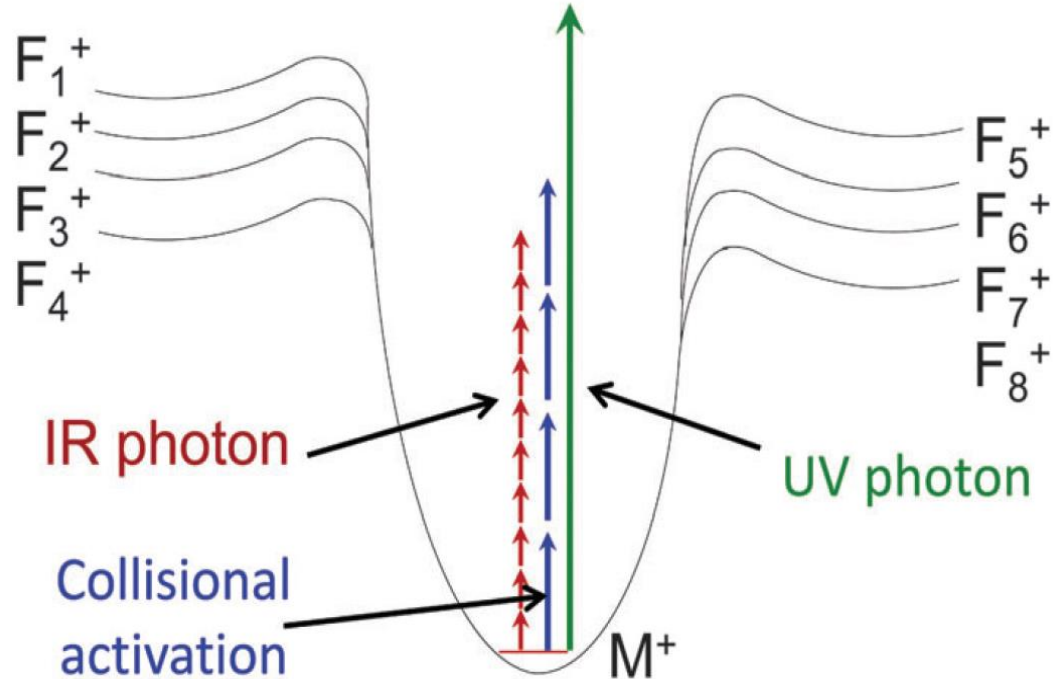
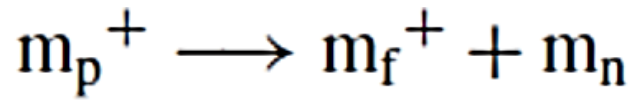


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Métodos espectroscópicos acoplados à MS – Instrumentação

Espectroscopia de íons



Avaliação da taxa de dissociação em função do comprimento de onda do fóton gera uma medida indireta da absorção dos fótons

Faixas espectrais (e fontes de radiação) diferentes podem ser utilizadas, com mecanismos diferentes:

- IR, UV, UV de vácuo

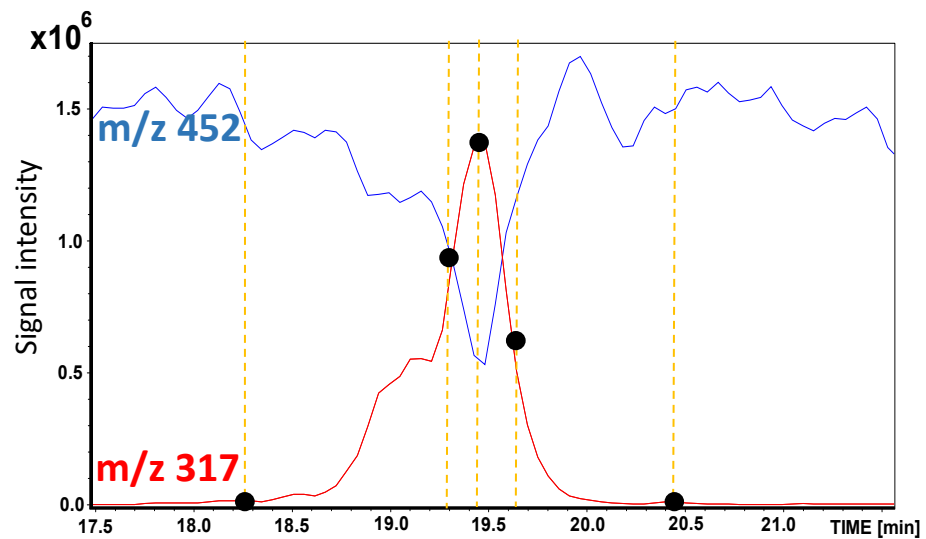
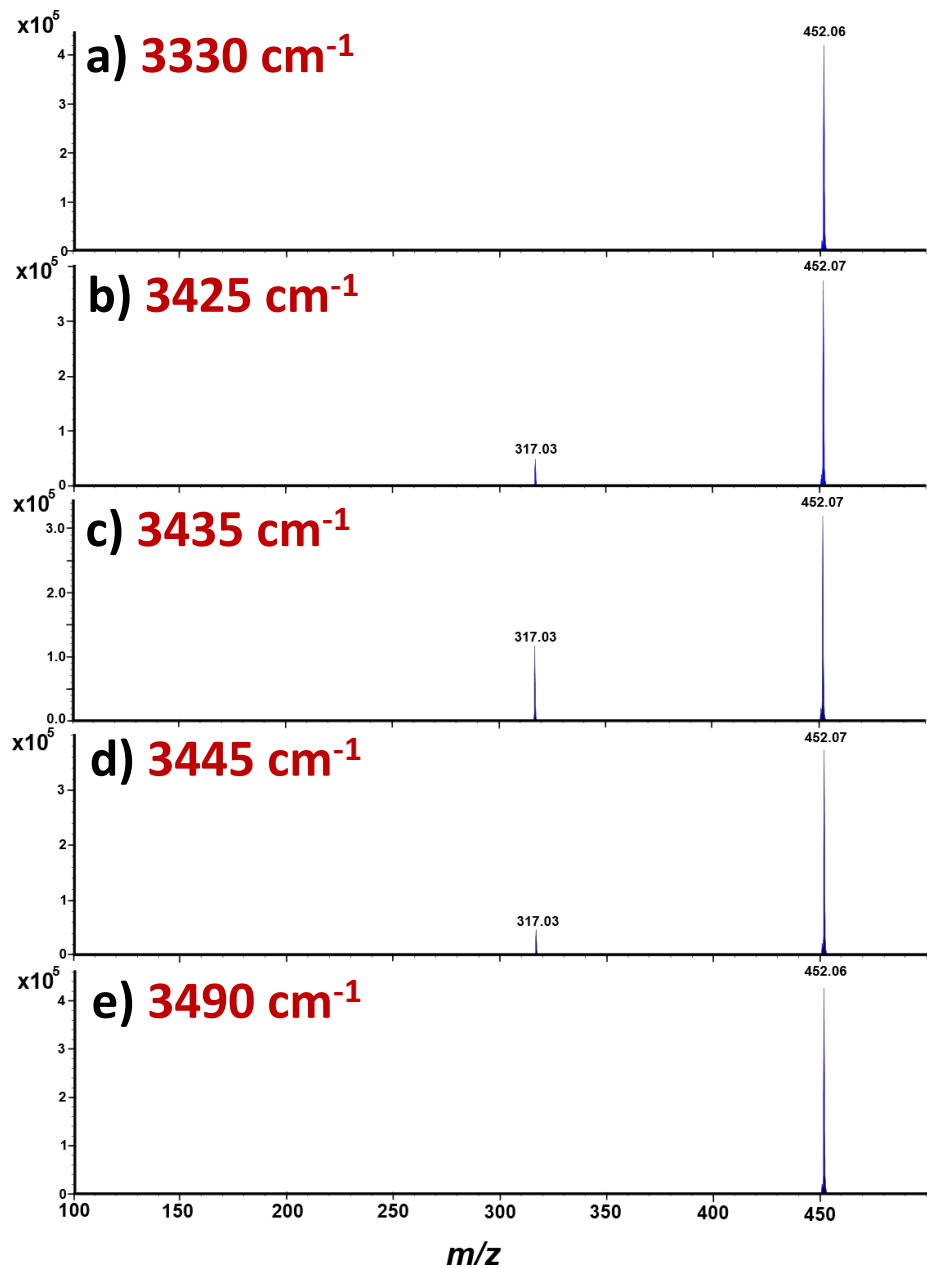
Em técnicas diversas:

- Dupla ressonância (IR-IR), FRET, fótons em faixas espectrais diferentes (UV-IR, UV-IR²)

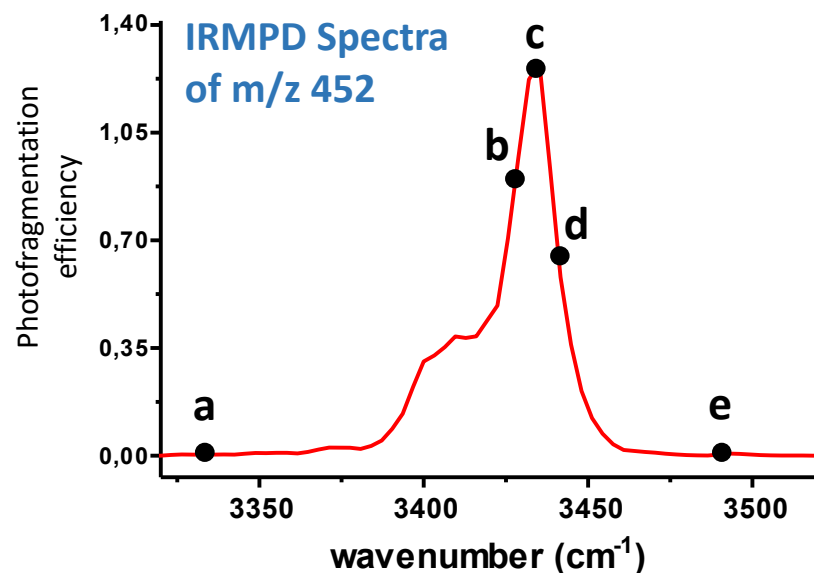
Fontes diversas:

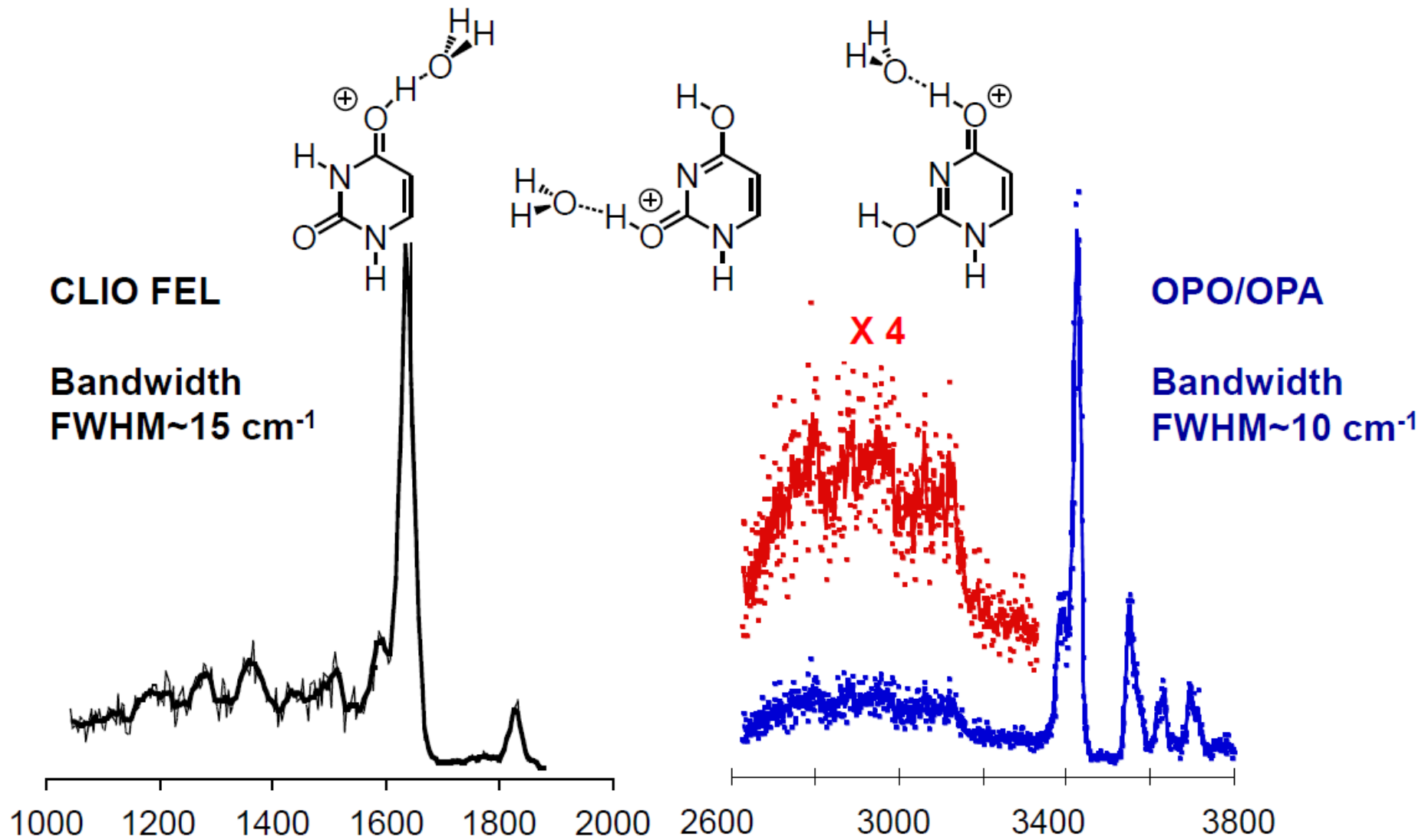
- OPO/OPA, FEL, Sincrotron (sobretudo para PEPICO)

Espectroscopia de íons – IRMPD



$$\text{eff} = -\ln\left(\frac{I_P}{I_P + \sum I_{F_n}}\right) = -k_{\text{obs}}t$$





J.M. Bakker et al., *J. Phys. Chem. A* **2008**, 112, 12393

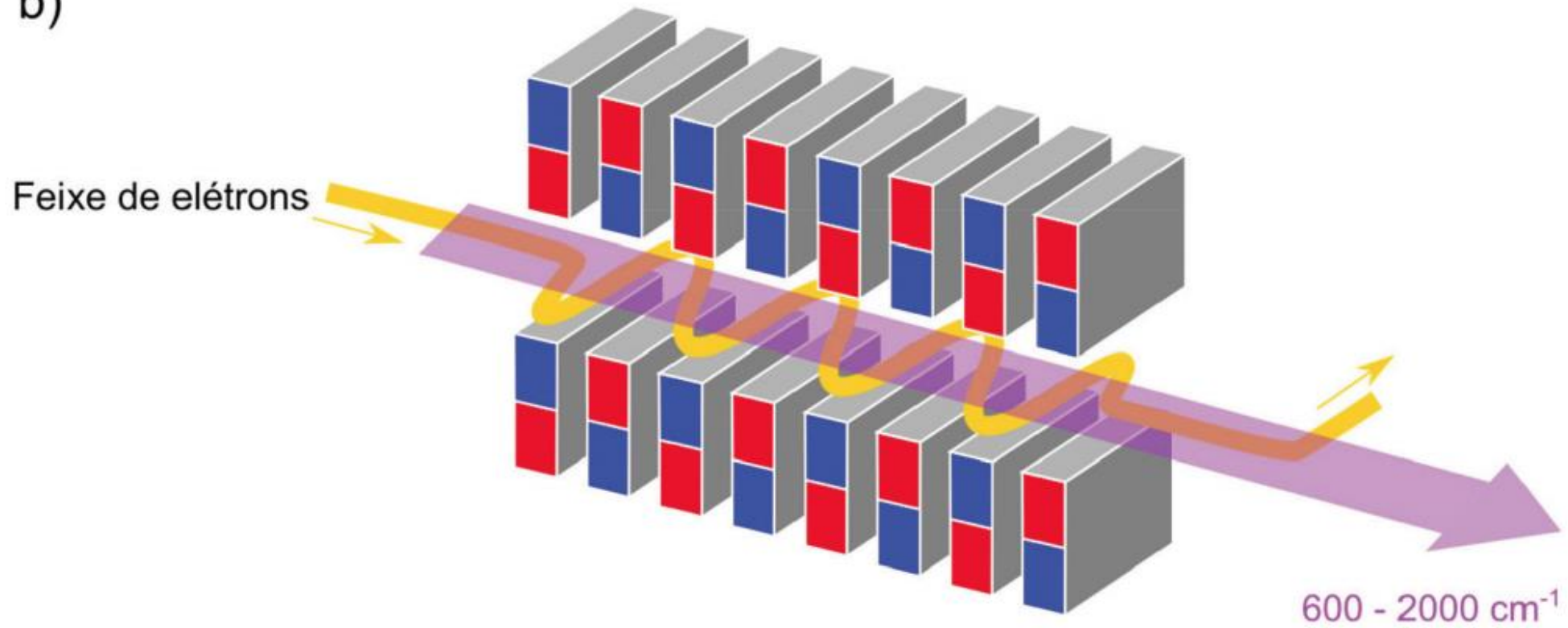
Fontes de radiação para IRMPD

Laser system	Type	Range/cm ⁻¹	Peak power	Energy per second/J
CO ₂	Gas discharge	925–1085	5–15 W	5–15
CO	Gas discharge	1600–1900	1–10 W	1–10
FELIX	Free electron laser	500–2000 ^a	10 MW	0.1–0.6 (10 Hz)
CLIO	Free electron laser	600–2500	20 MW	≤0.6 (25 Hz)
OPO/A	Non-linear optics	2500–4000	0.5–2 MW	0.06–0.1 (10 Hz)
OPO/A	Non-linear optics	2500–4000	50–100 mW	0.05–0.1

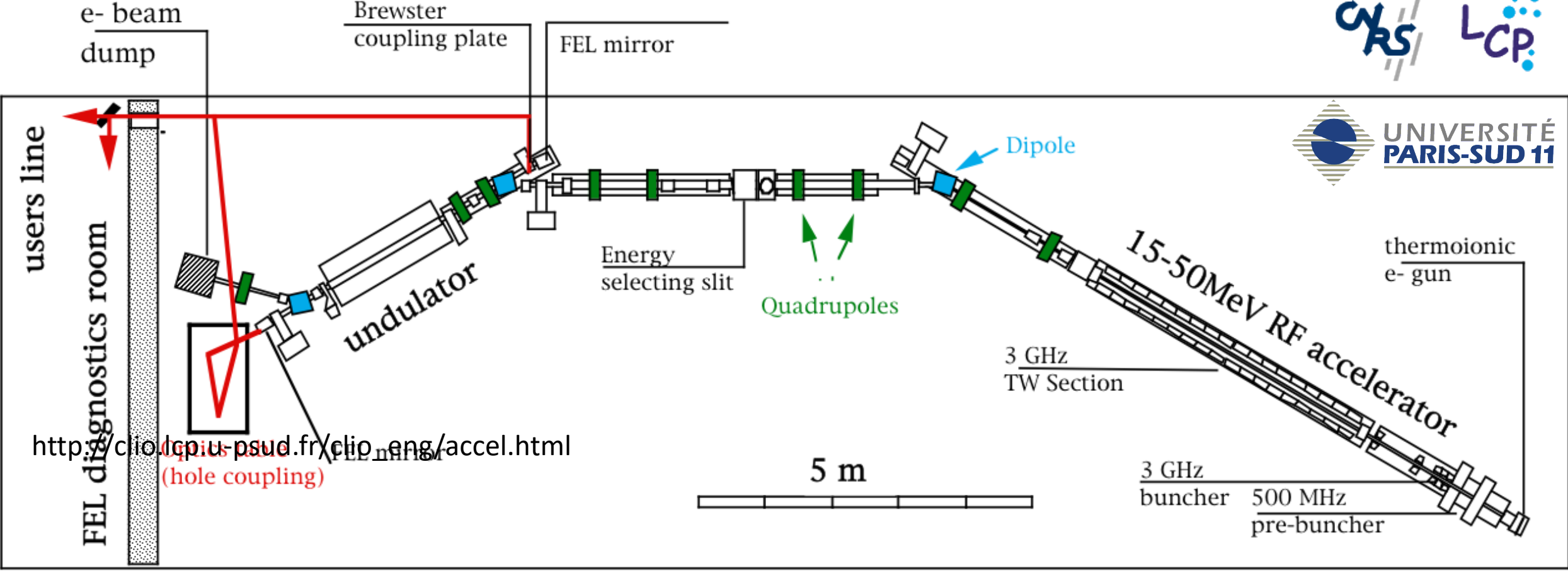
FELIX and CLIO abrem chamadas semestrais
“Novo” FEL: FHI – 2013!

Free electron laser - FEL

b)

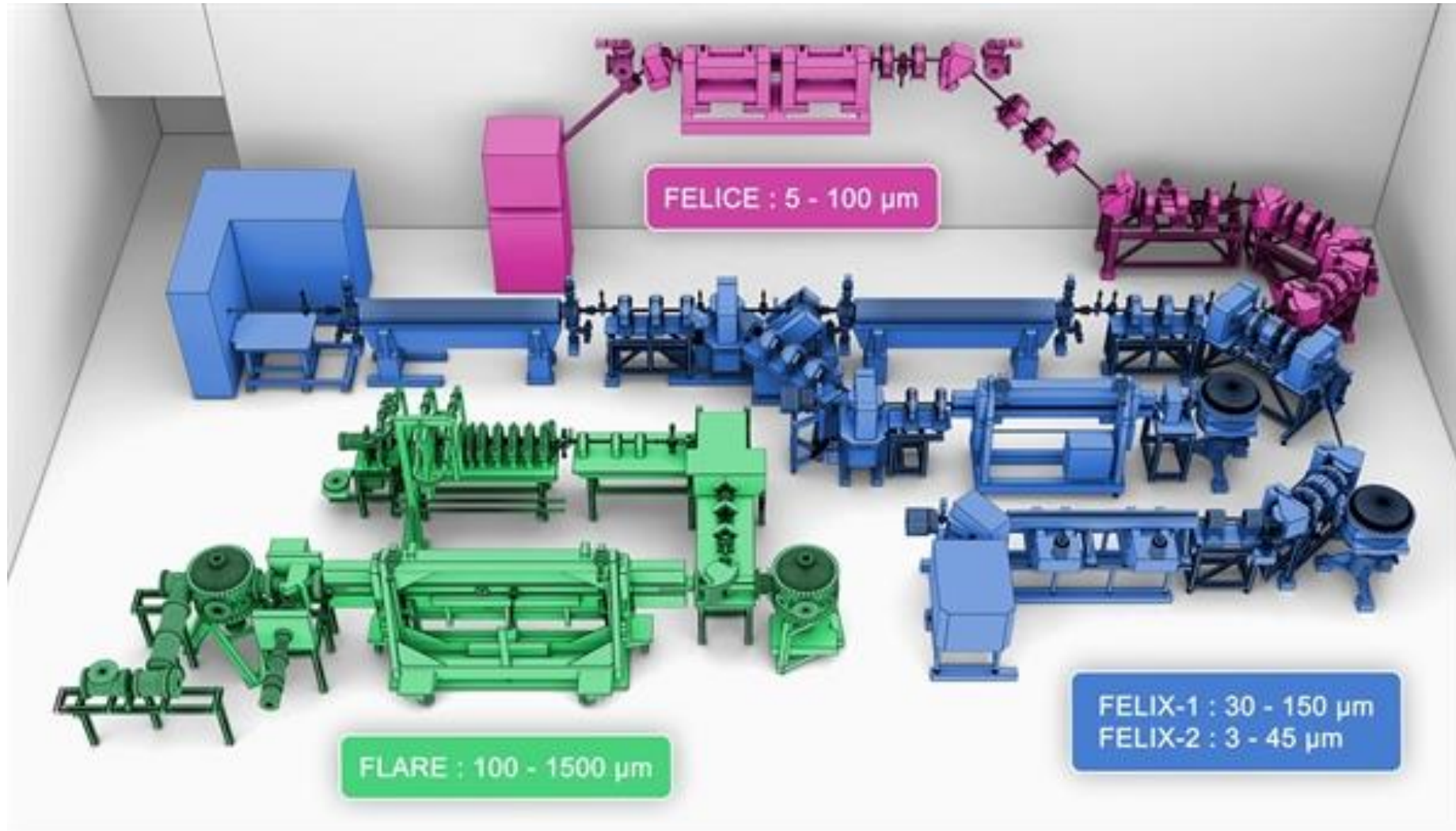


Clio - França

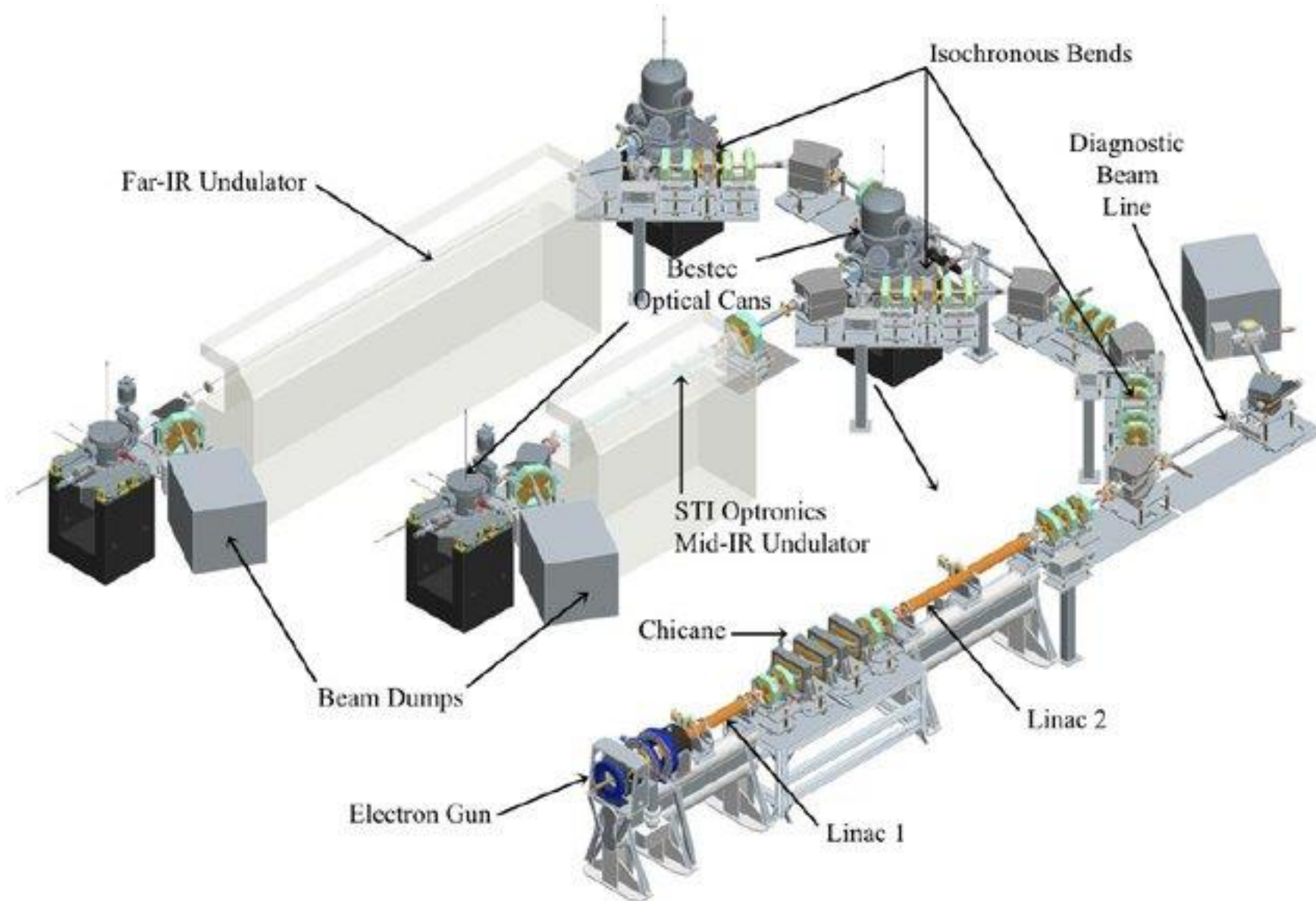


http://clio.lcp.u-psud.fr/clio_eng/accel.html

Felix - Holanda



FHI-FEL - Alemanha

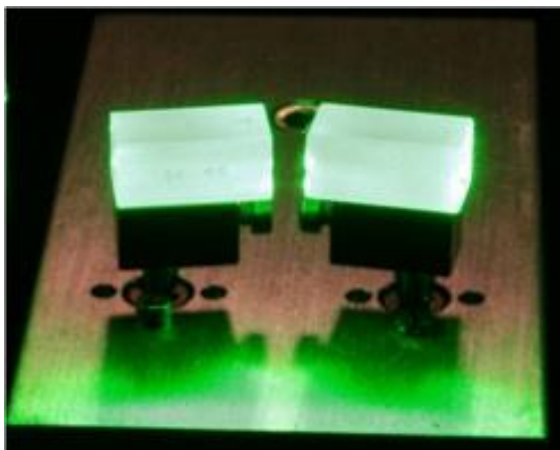
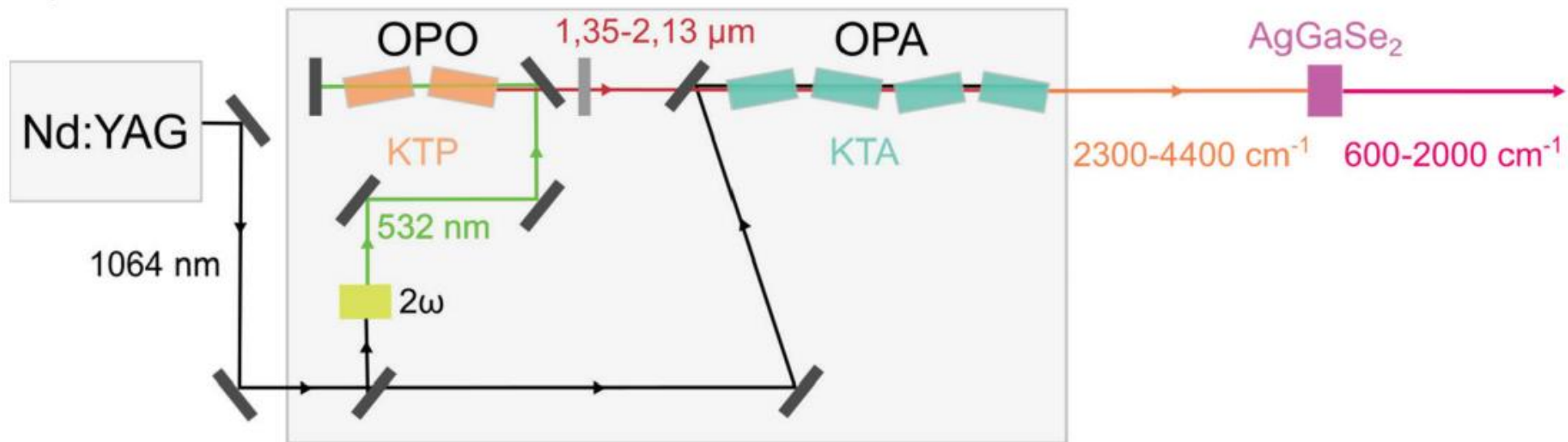


[Commissioning Status of the Fritz Haber Institute THz FEL](#)

[Conference Paper](#) Jan 2011, Proceedings of IPAC2011, San Sebastián, Spain

a)

OPO/OPA



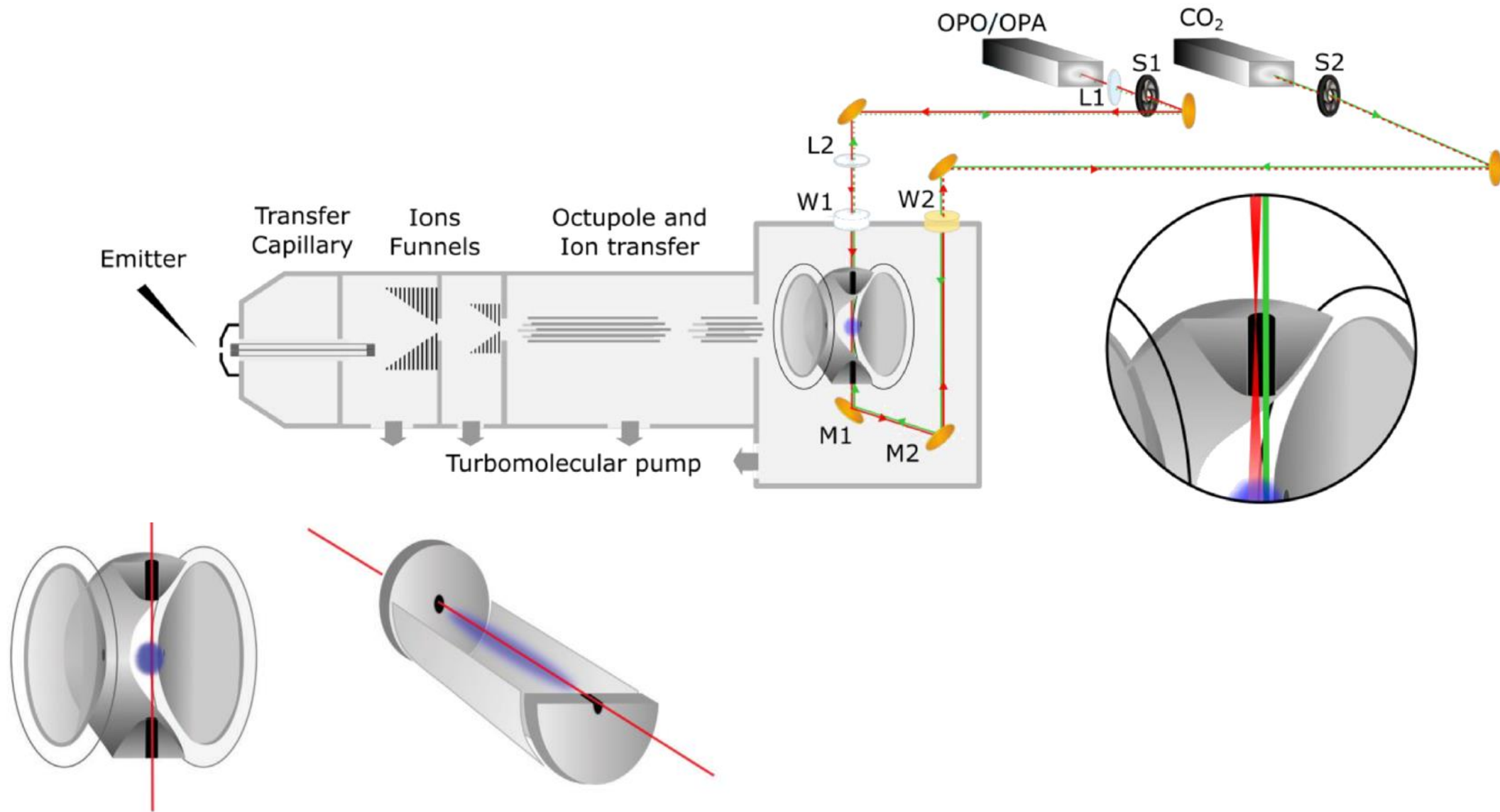
$$\vec{P}(t) = \epsilon_0 (X_1 \vec{E}(t) + X_2 \vec{E}^2(t) + \dots)$$

$$\omega_p = \omega_i + \omega_s$$

$$2\omega_1, \omega_1 + \omega_2, \omega_1 - \omega_2$$

$$\omega(1965 \text{ a } 4686 \text{ cm}^{-1}) = \left(\frac{1}{880 \text{ a } 710 \text{ nm}} - \frac{1}{1064 \text{ nm}} \right) \times 10^7$$

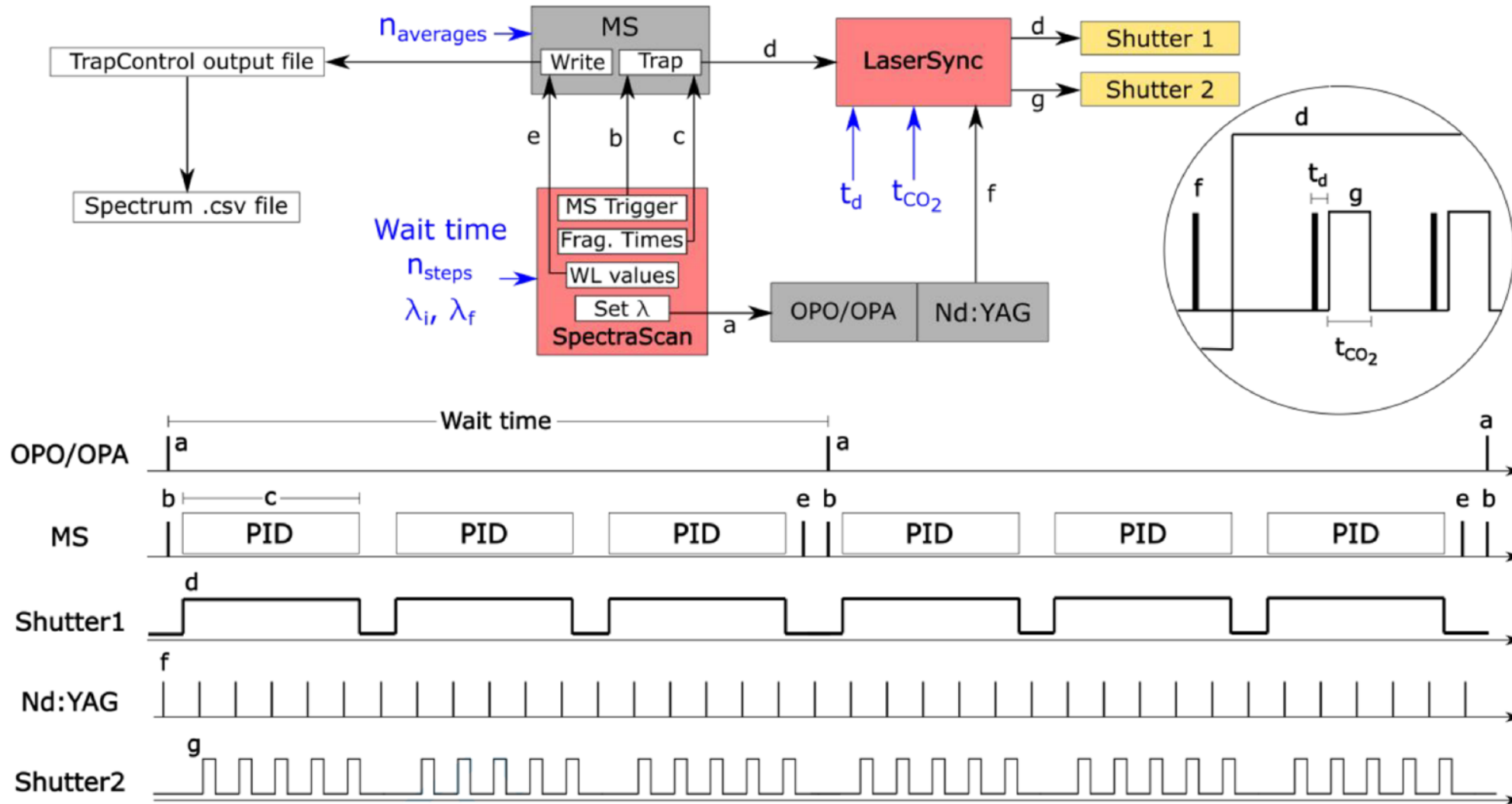
Acoplamento físico das fontes de radiação



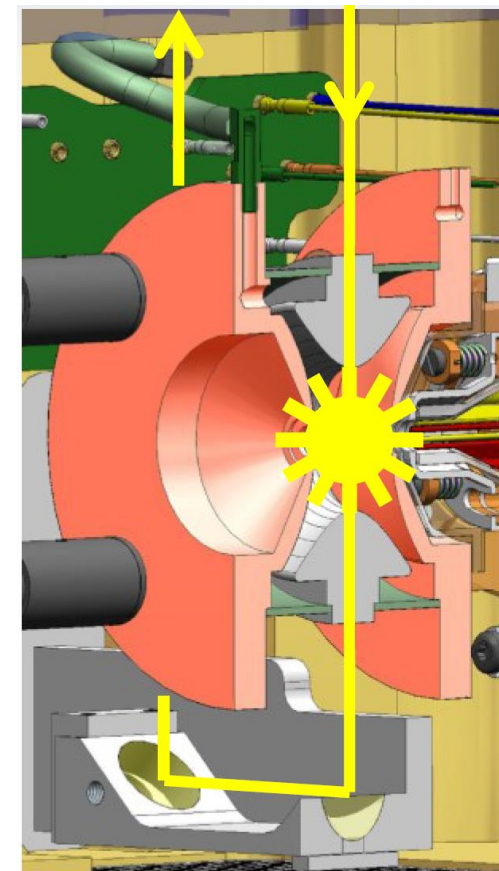
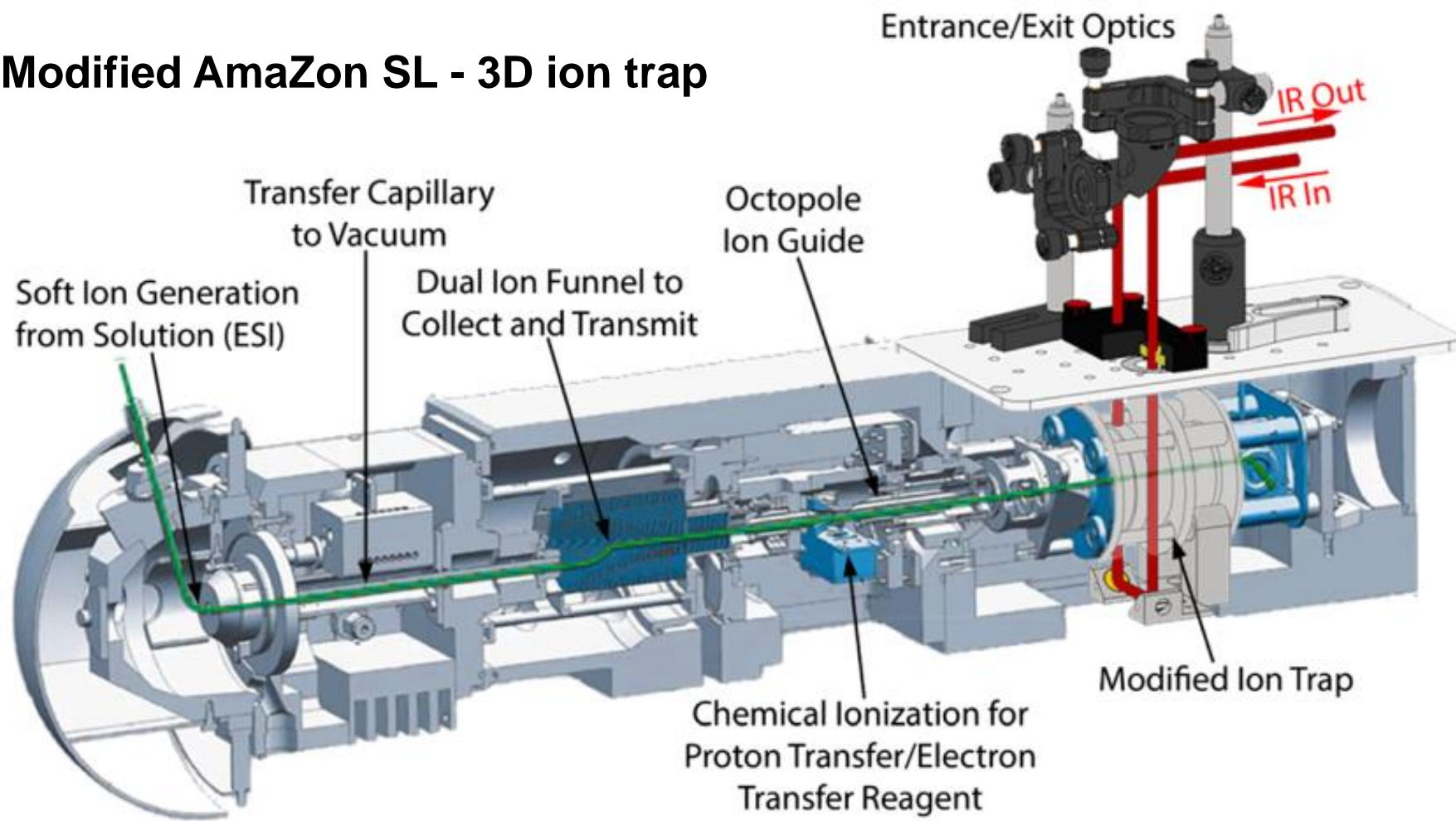
Quim. Nova, Vol. 43, No. 8, 1125-1137, 2020 <http://dx.doi.org/10.21577/0100-4042.20170582>

Penna, T. C. et. al. Rapid Commun. Mass Spectrom. 2020, 34 (e8635).

Sincronização e pulsação dos lasers



Modified AmaZon SL - 3D ion trap





Continuum

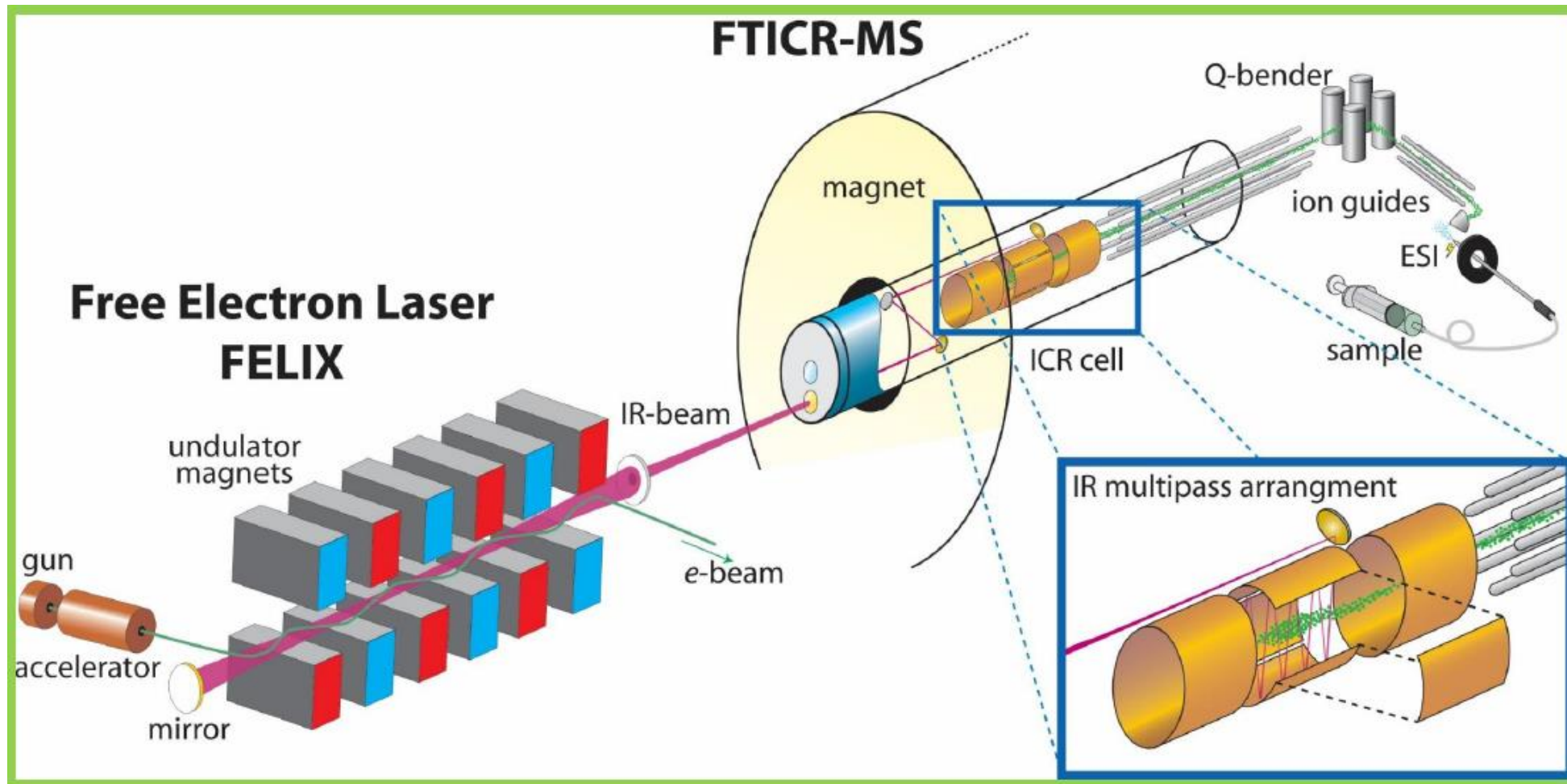
LaserVision

Newport

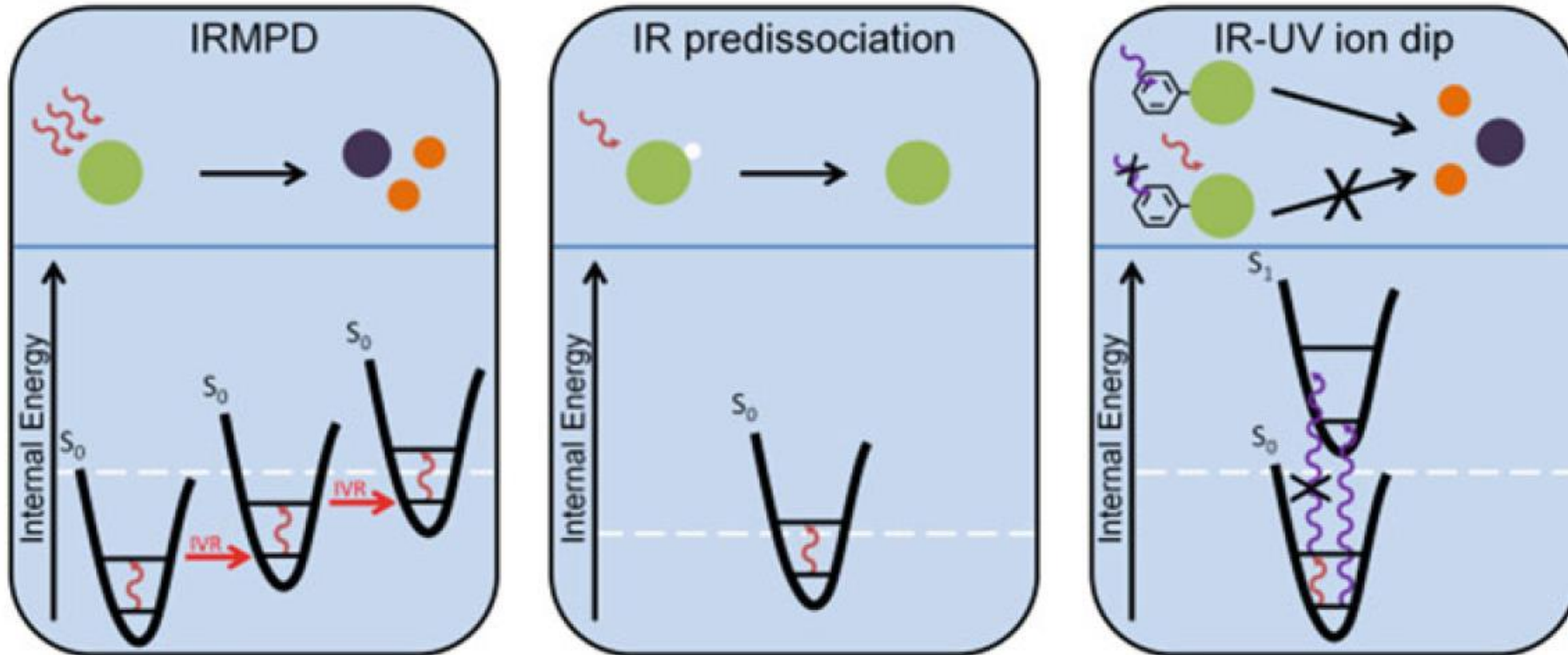
Continuum

Technical document with handwritten notes and a table.

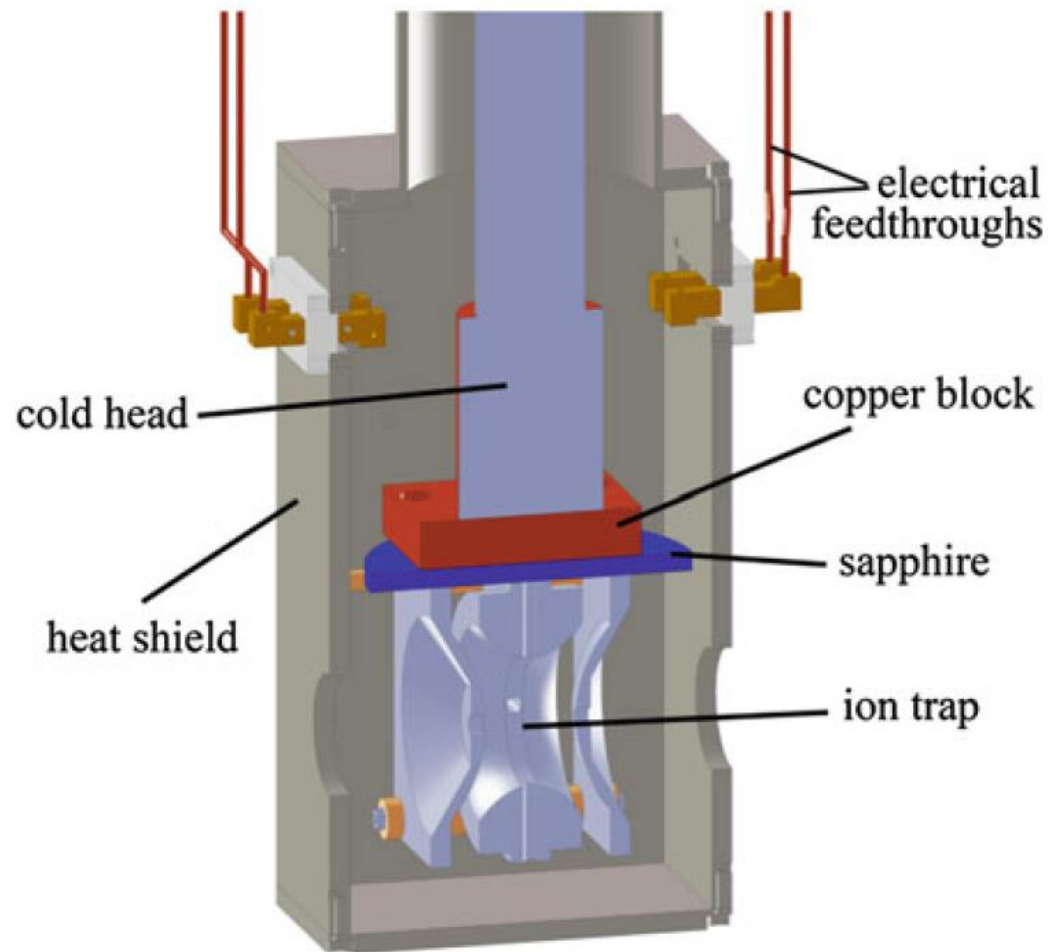
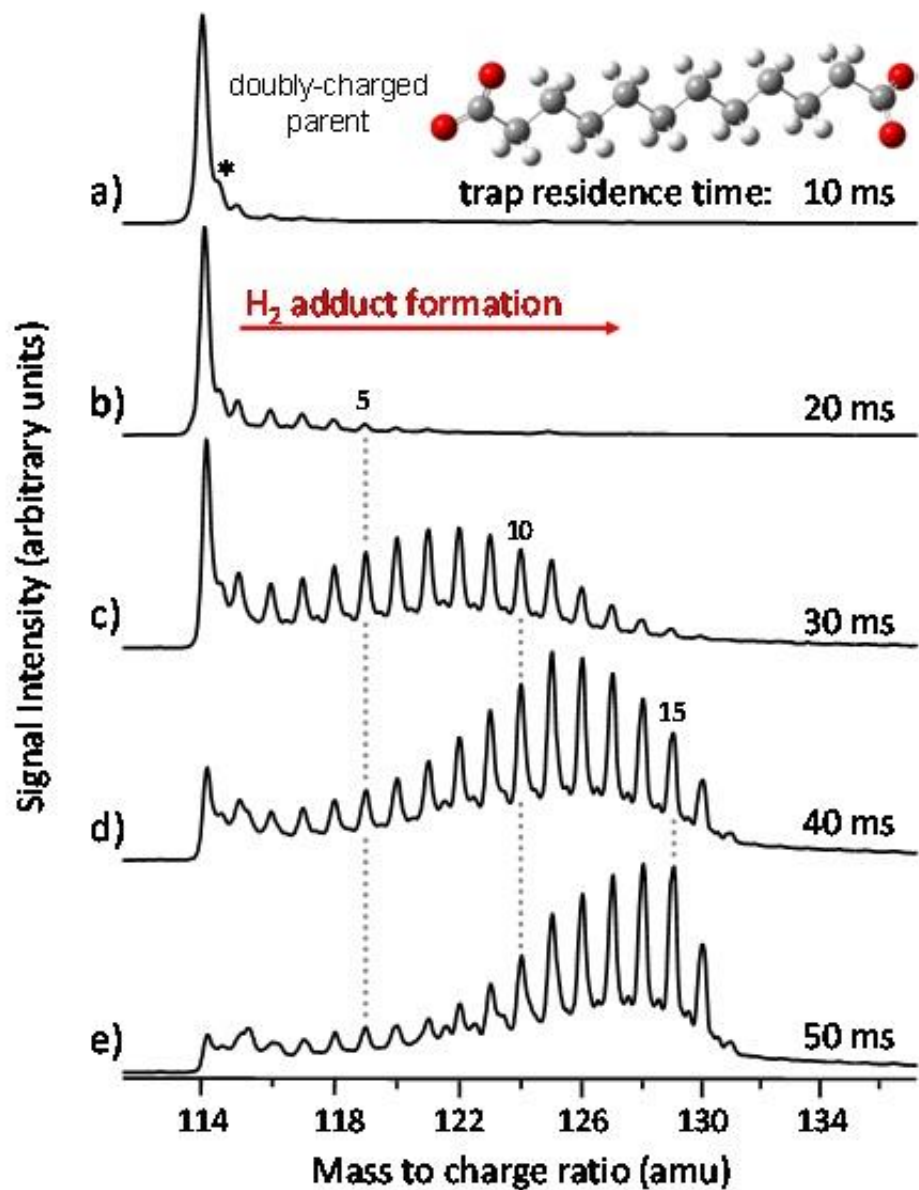
FELIX – acoplamento com FT-ICR



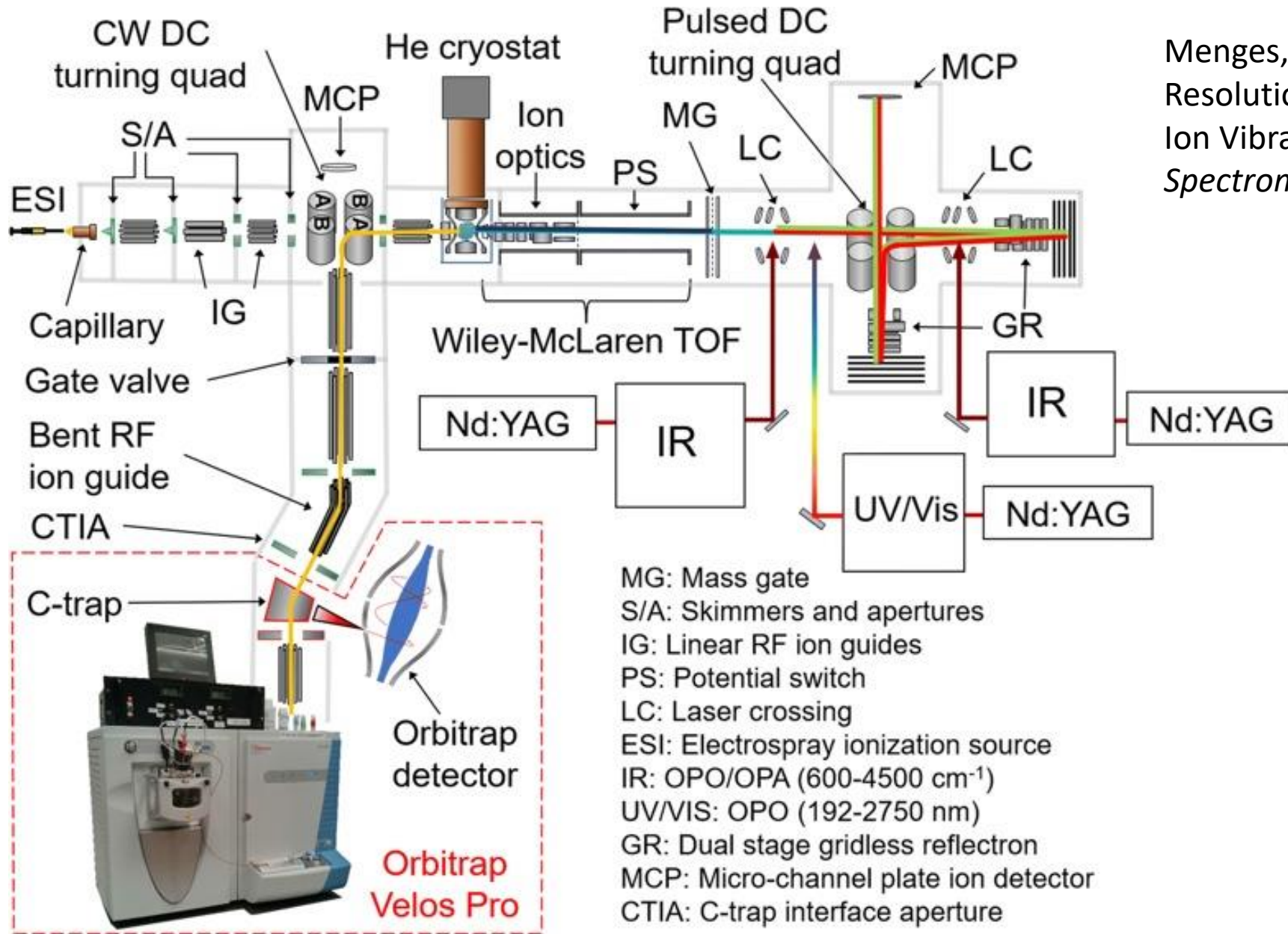
Técnicas alternativas para aquisição de espectros IR



Espectroscopia de pré-dissociação criogênica



Acoplamento com instrumentos de alta resolução

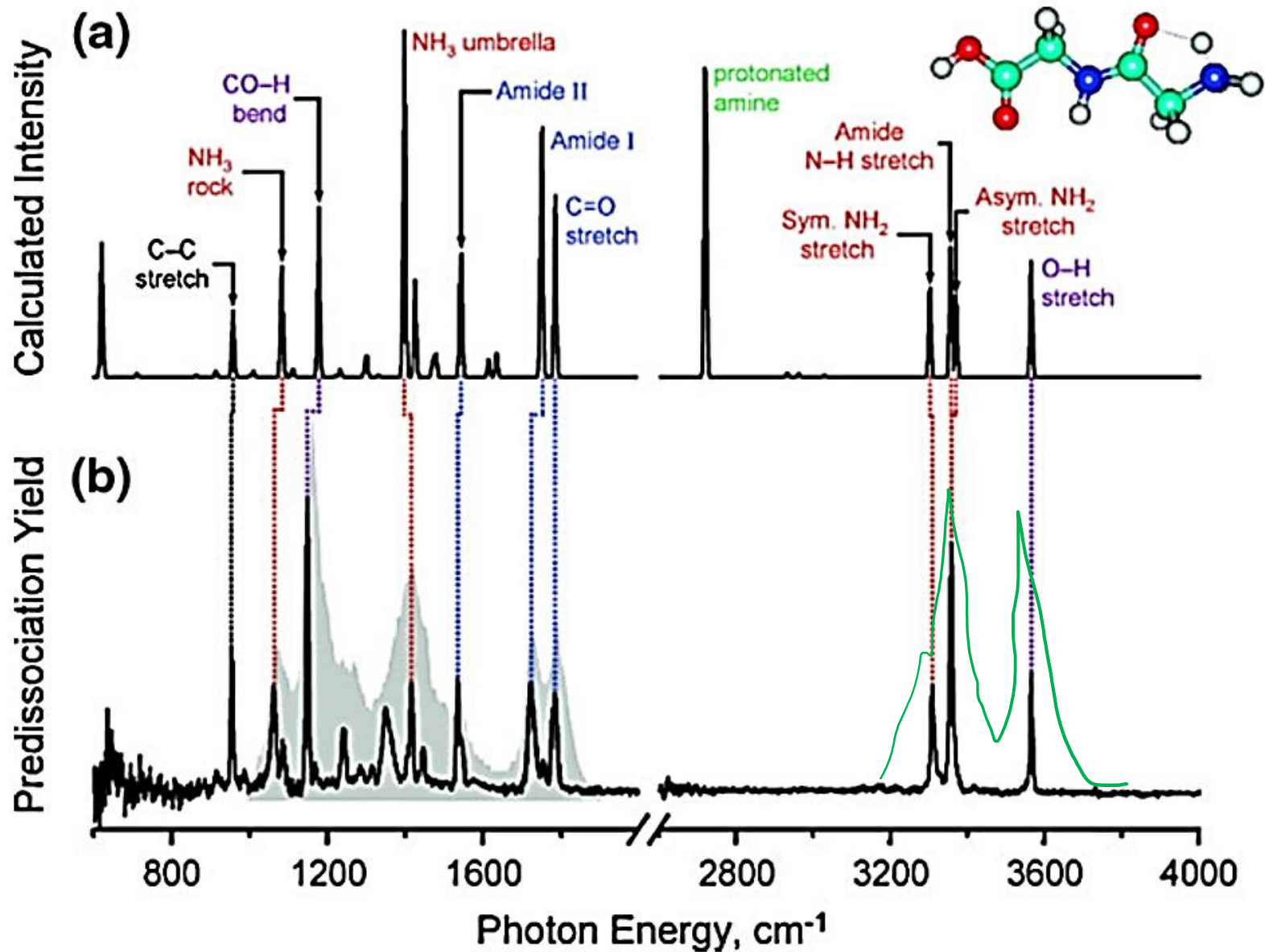


Menges, F. S. et. al. Integration of High-Resolution Mass Spectrometry with Cryogenic Ion Vibrational Spectroscopy. *J. Am. Soc. Mass Spectrom.* **2019**, 30 (9), 1551–1557.

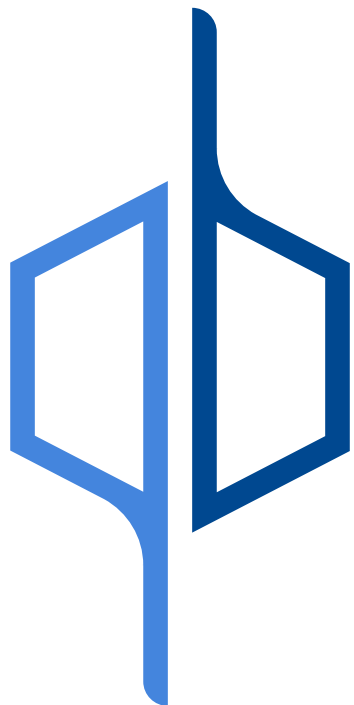
A



IRPD vs. IRMPD



(1) Cismesia, A. P.; et. al. *J. Am. Soc. Mass Spectrom.* **2016**, 27 (5), 757–766.
<https://doi.org/10.1007/s13361-016-1366-4>.



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