VISIBLE PHOTODISSOCIATION SPECTRA OF THE 1-METHYL AND 2-METHYLNAPHTHALENE CATIONS: LASER SPECTROSCOPY AND THEORETICAL SIMULATIONS

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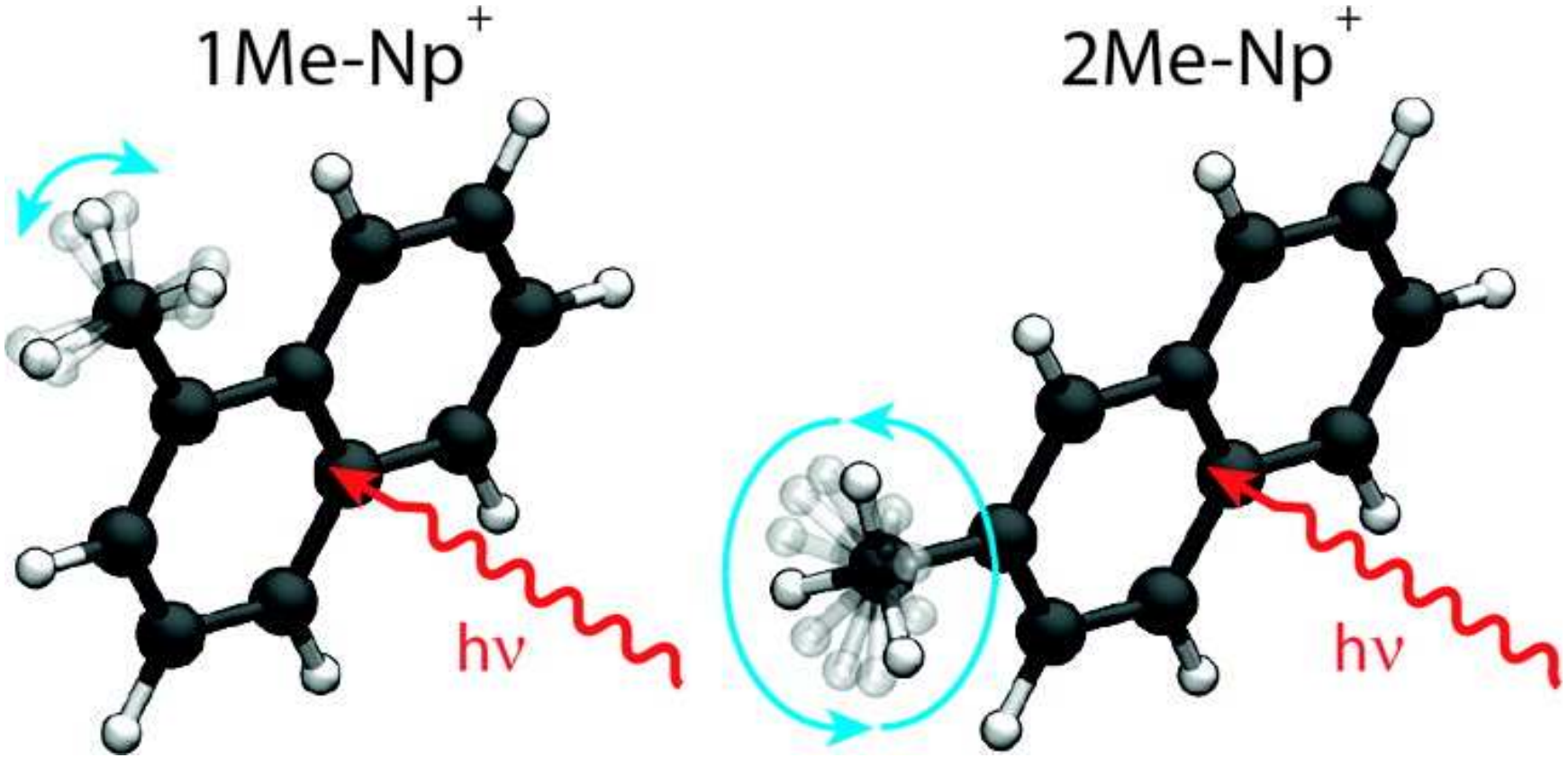
PAH cations in space and the DIB's spectra
Methyl substitution is relevant for astro-PAHs

Internal rotation

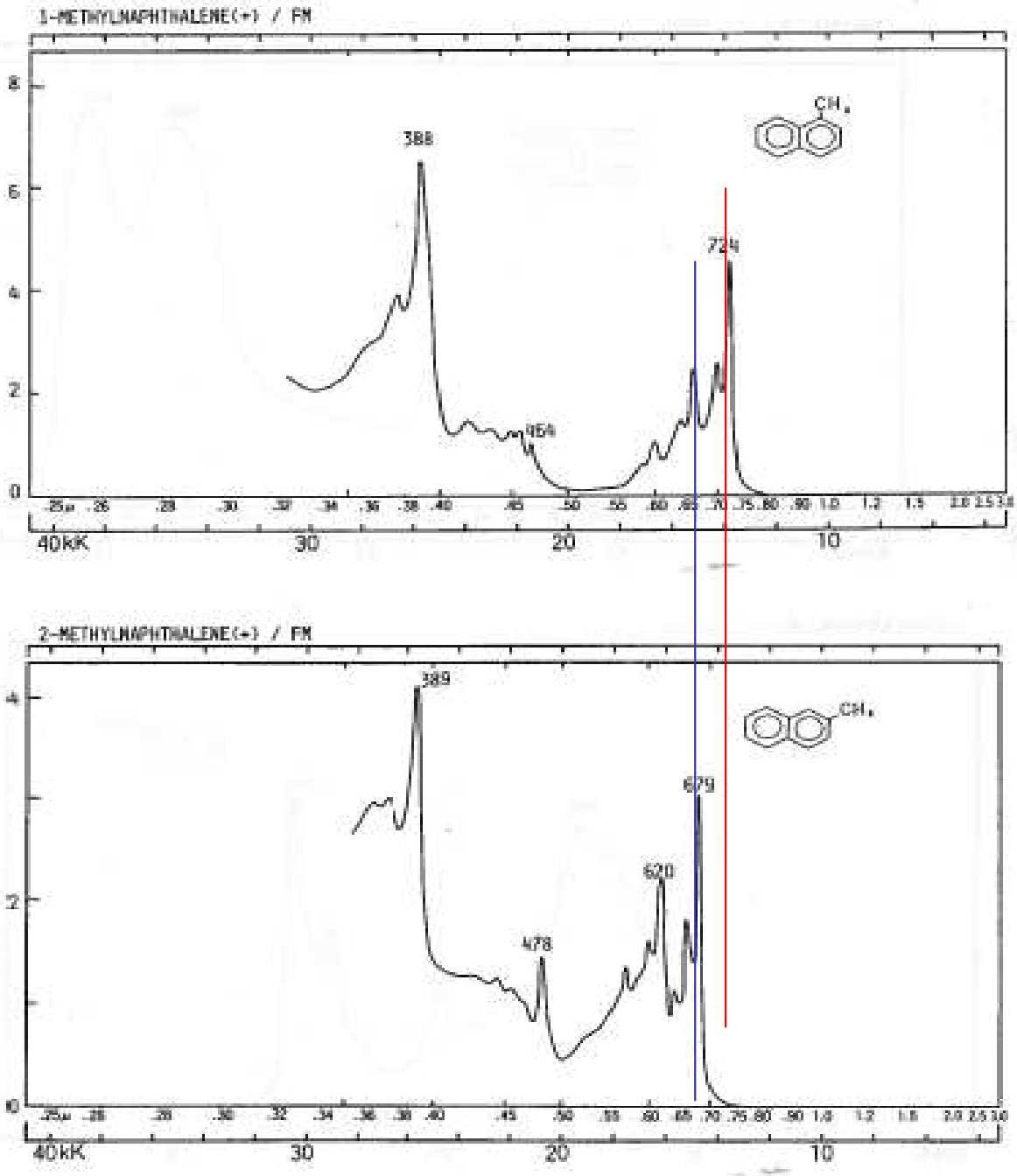


Tan, X.; Majewski, W.; Plusquellic, D.; Pratt, D.

Methyl-group torsional dynamics from rotationally resolved electronic spectra: 1-methylnaphthalene and 2-methylnaphthalene. NEUTRALS

J. Chem. Phys. 1991, 94, 7721−7733

The experimental challenge of PAH cations



Shida & Iwata, 1973

Low temperature
Freon matrix

Total spectral shift:
915 cm^{-1}

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Similar results in argon matrix

Andrews, L.; Kelsall, B.; Blankenship, T.

Vibronic absorption spectra of naphthalene and substituted naphthalene cations in solid argon.

J. Phys. Chem. 1982, 86, 2916−2926.

What about the gas-phase spectrum?

The experiment at Orsay

The « Argon tagging trick »

In the case of aromatic species, the electronic spectrum of the bare cation can be deduced by such tagging photodissociation spectroscopy when the properties of the aromatic chromophore M solvated by RG atoms are known in the $M^+-(RG)_n$ n=1,2 clusters.

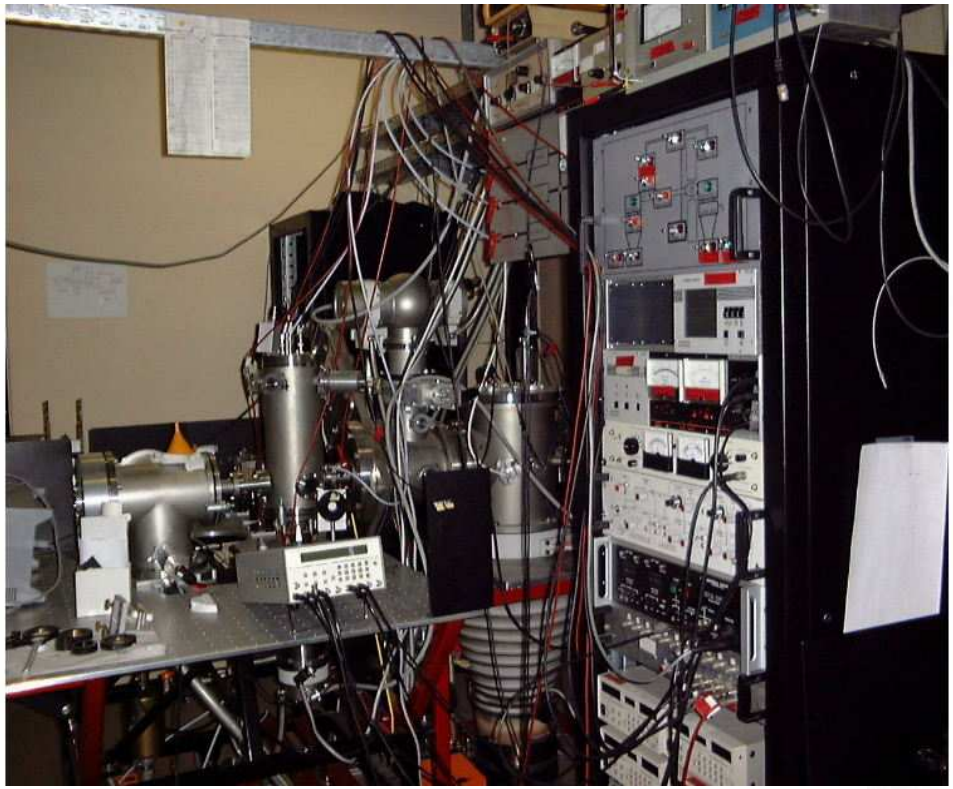
The observed perturbation, due to the solvation, is known as the electronic shift and is additive upon an increasing number of rare gas atoms.

Nowadays widely spread …

Experimental set-up

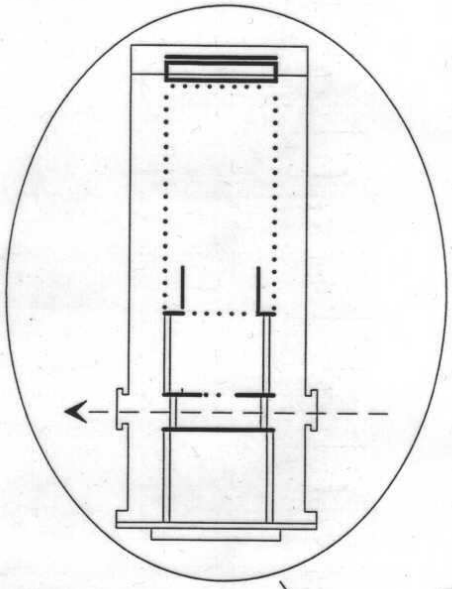
Molecular beam

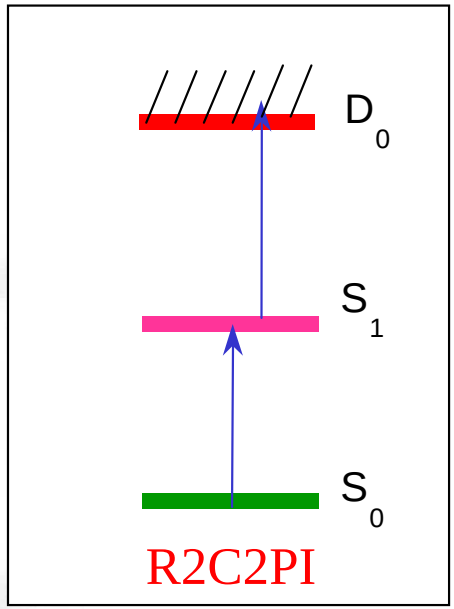
TOF

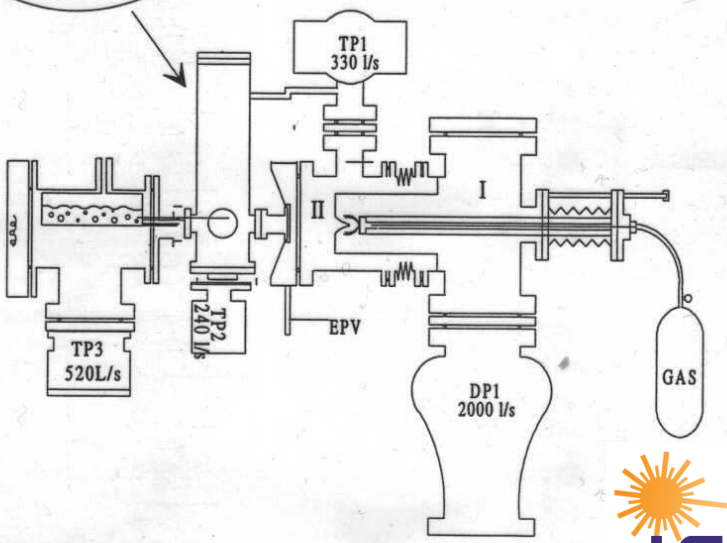


Preparation just above IP:

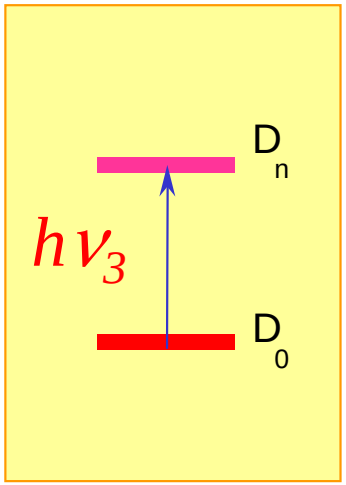
Cold cations

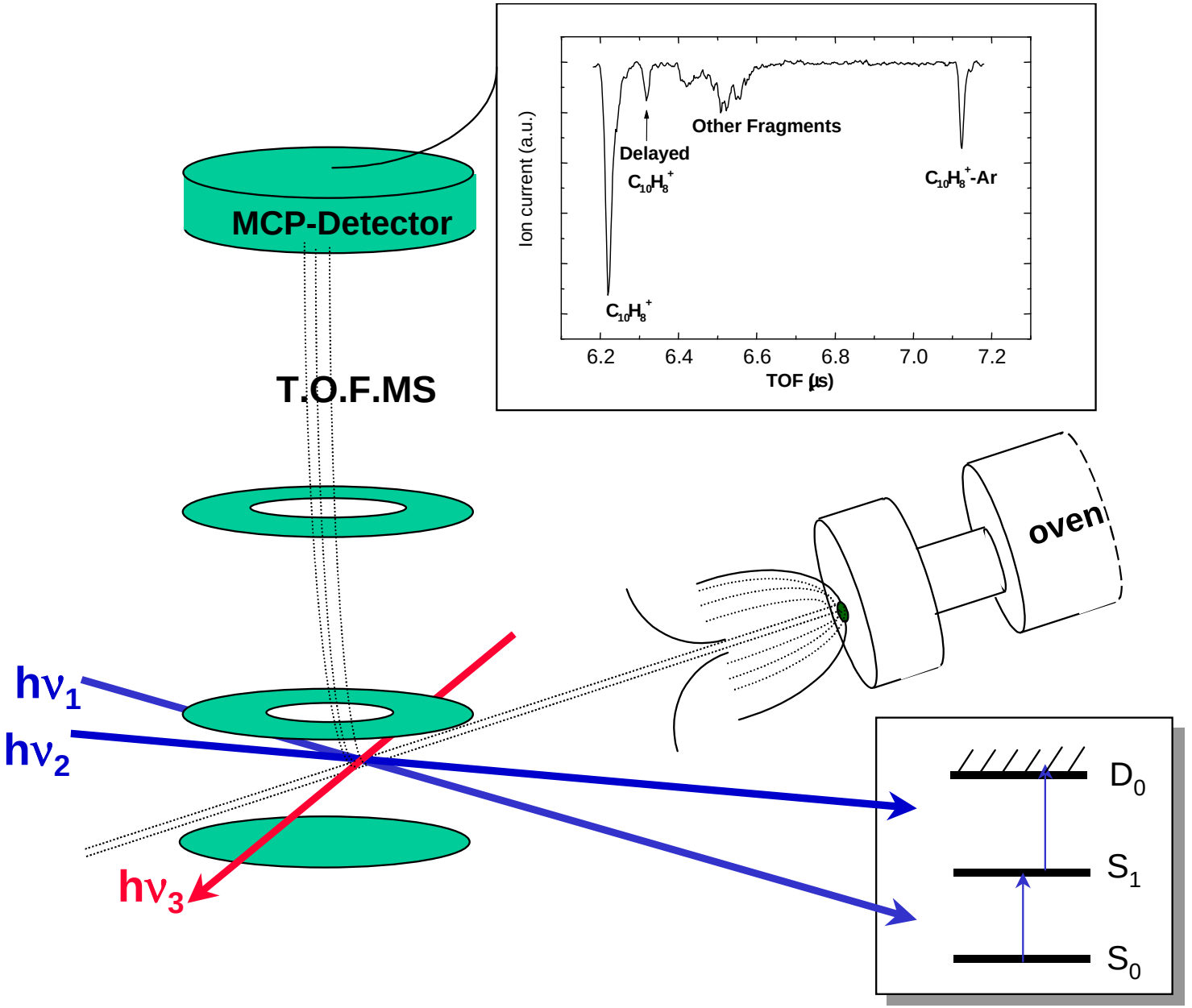




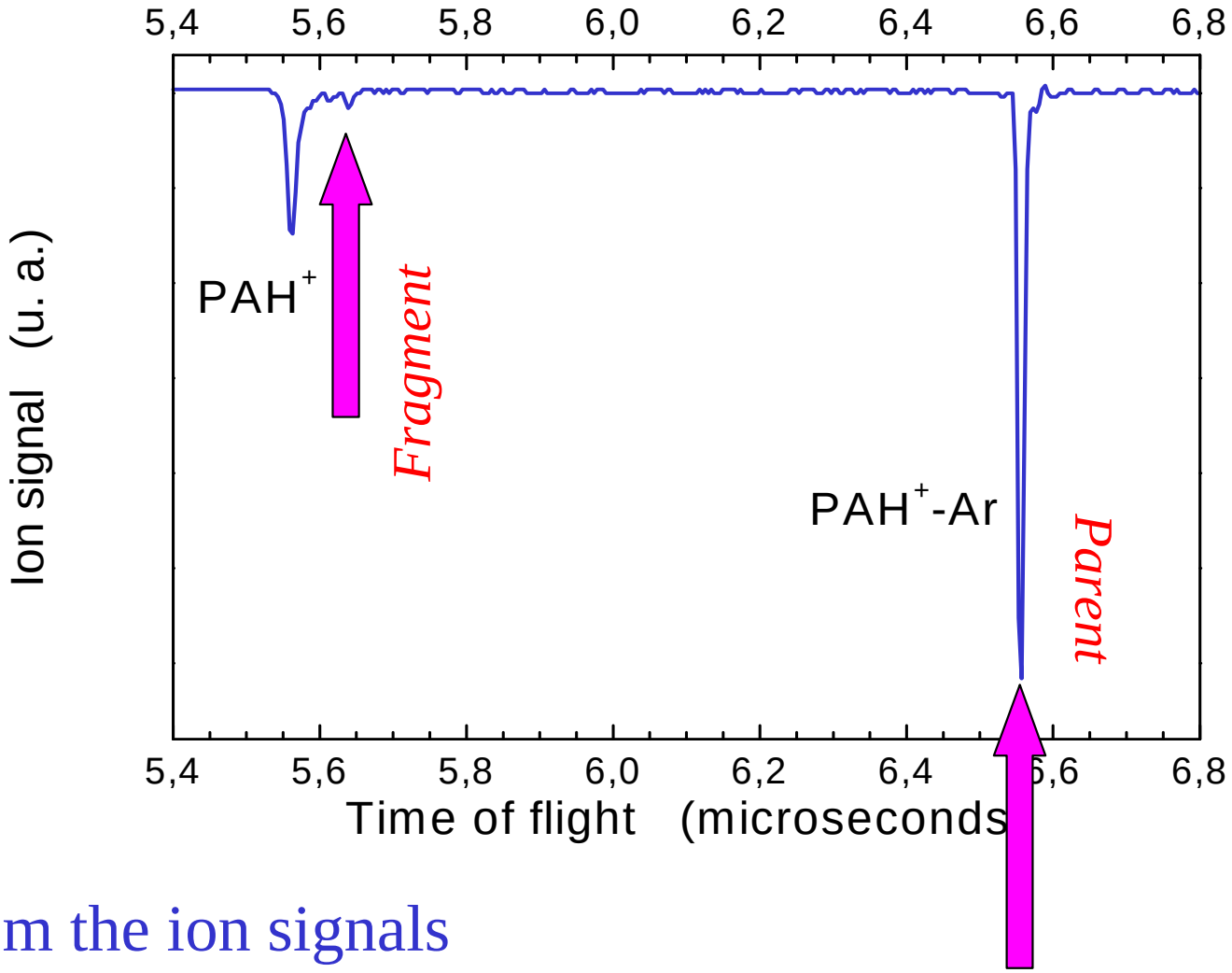


Principle of the technique





How to record a spectrum of PAH^+-argon?



From the ion signals

Spectrum = Fragmentation ratio versus laser wavelength

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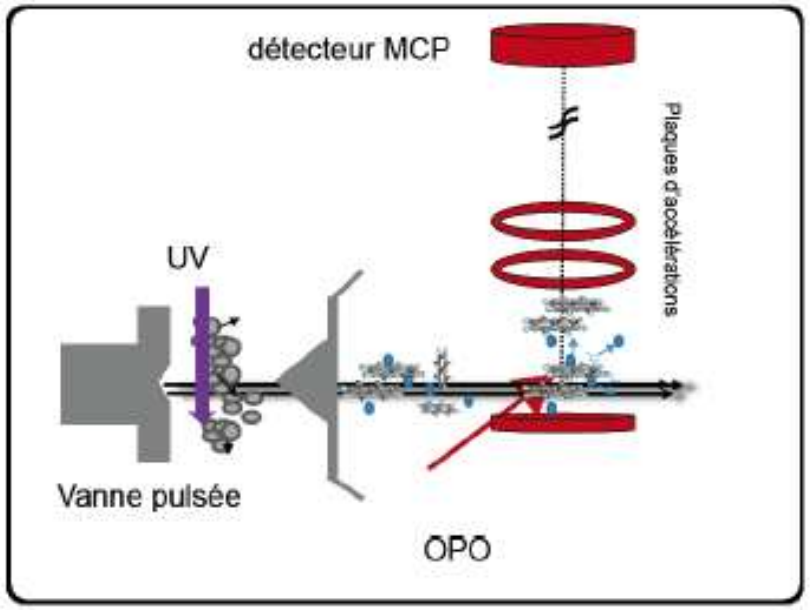
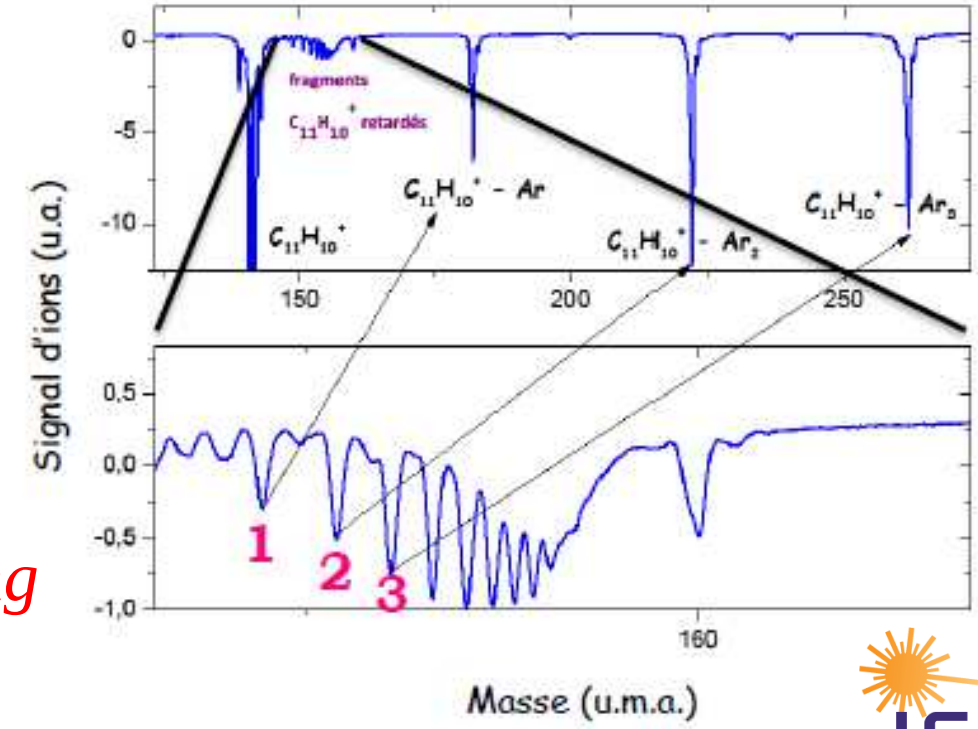
A change of protocol



Ions, formed right at the exit of the nozzle, freely fly until they are extracted by a delayed voltage pulse

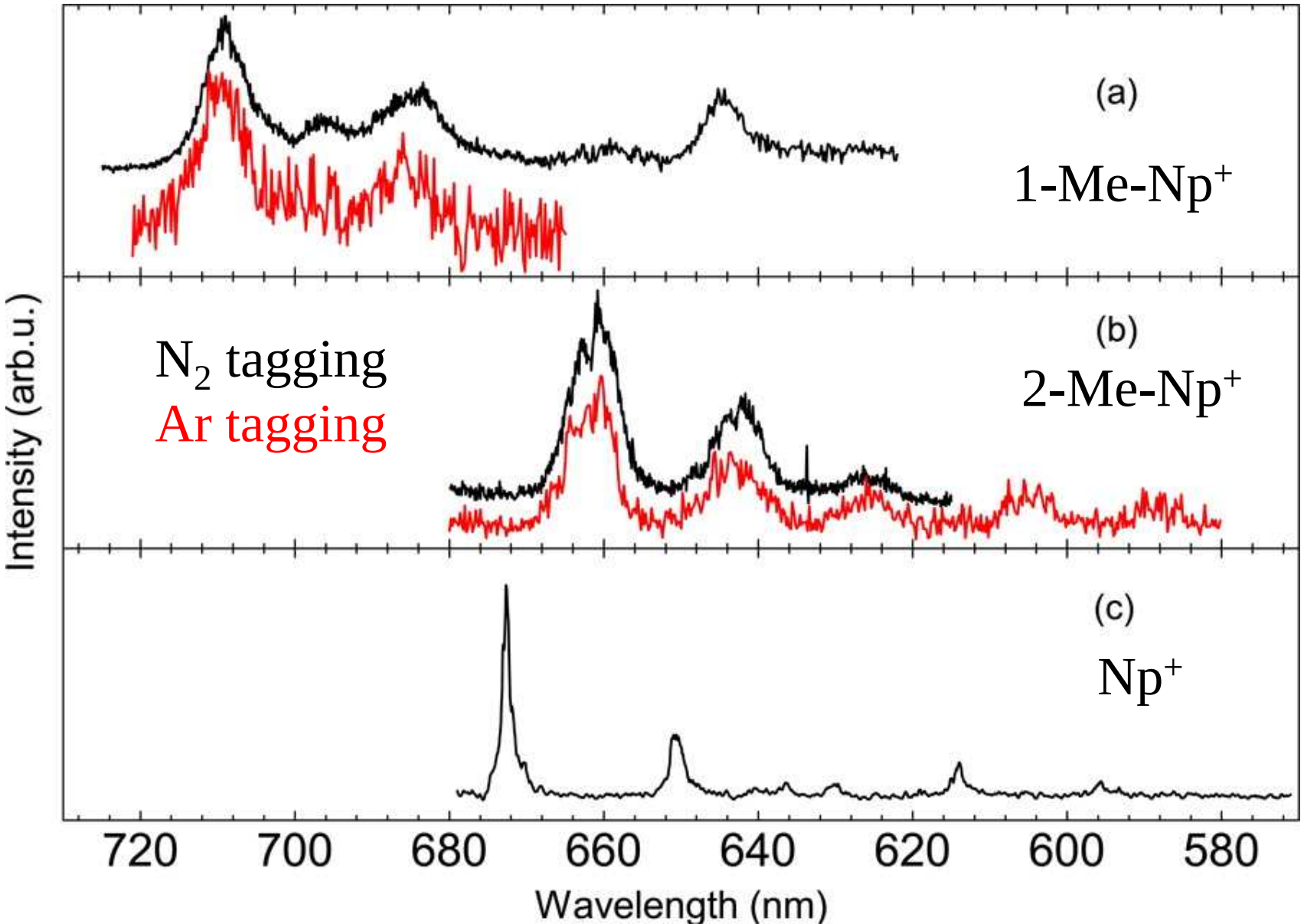
A typical TOF

Multiplex recording



The photodissociation spectra

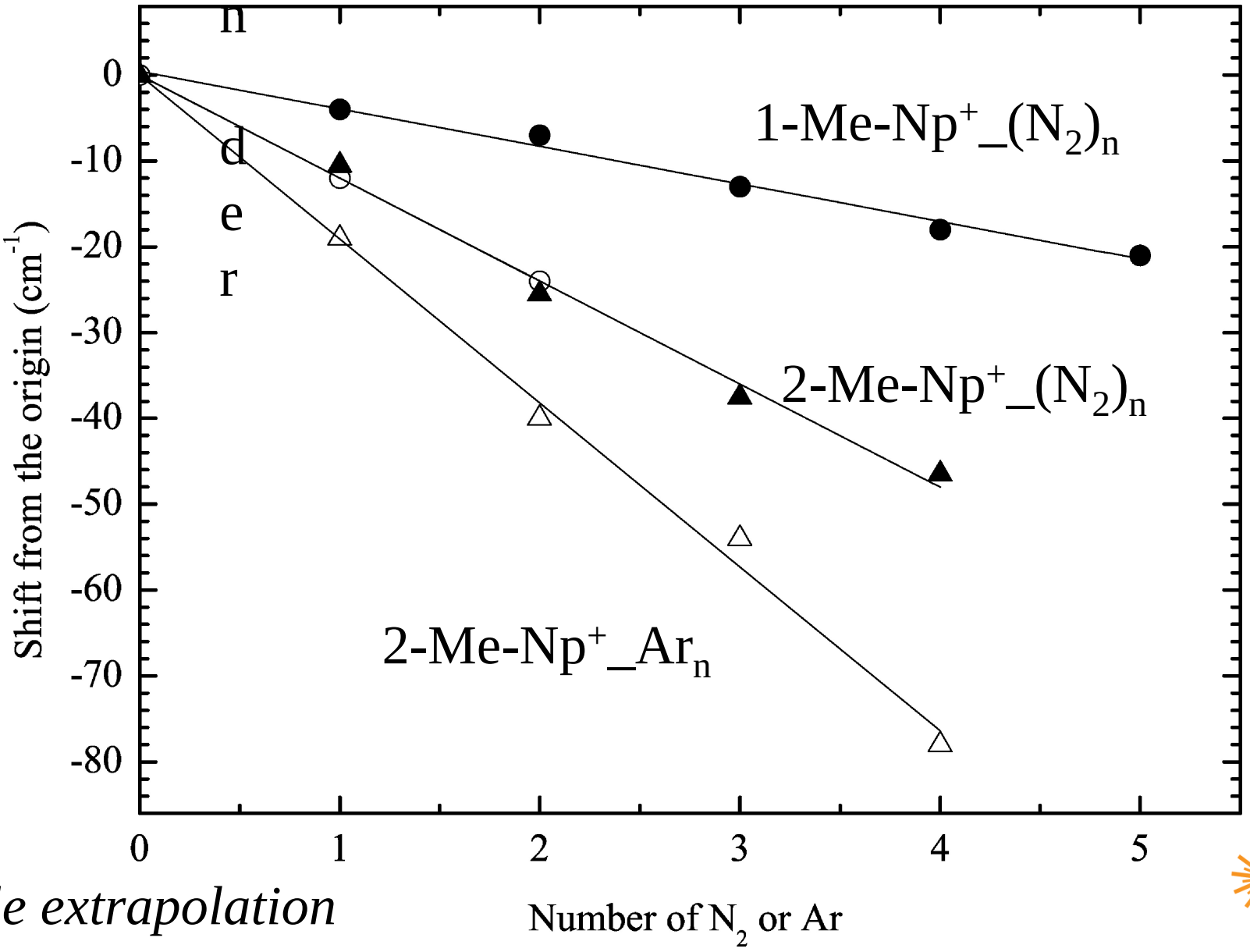
An Optical Parametric Oscillator (0.2 cm−1 bandwidth; Spectra-Physics) was used to photodissociate the cations in the 680−580 nm range.



FWHM
≈130 cm^{-1}

Intrinsic
FWHM
20-25 cm^{-1}

The Van der Waals spectral shifts : recovering the free gas-phase values

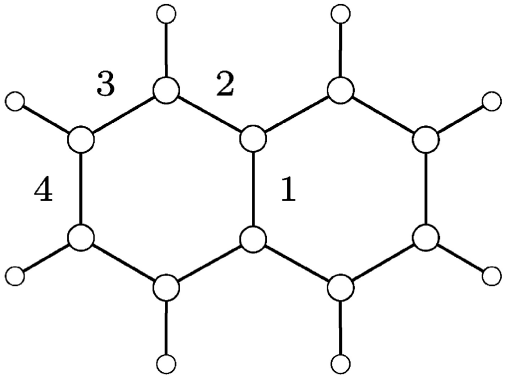


Simple extrapolation

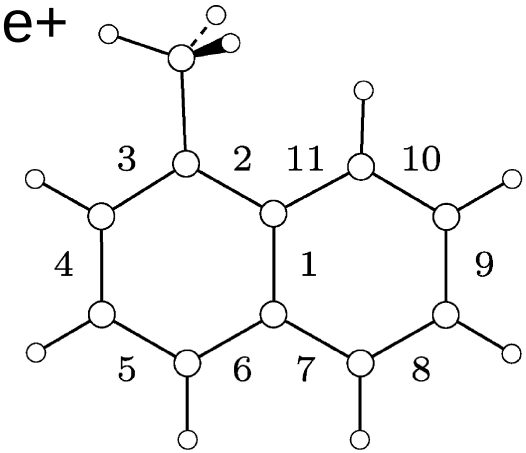
The main results

The 1-methylnaphthalene+ : red shift of 808 cm^{-1},
relative to the band of naphthalene+

D_2—D_0 at
14 906 cm^{-1}



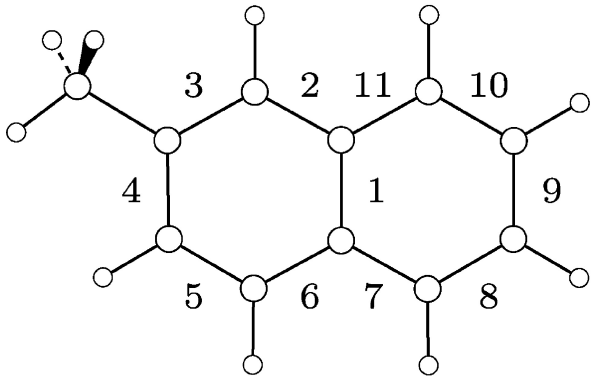
Np^+ (D_0)



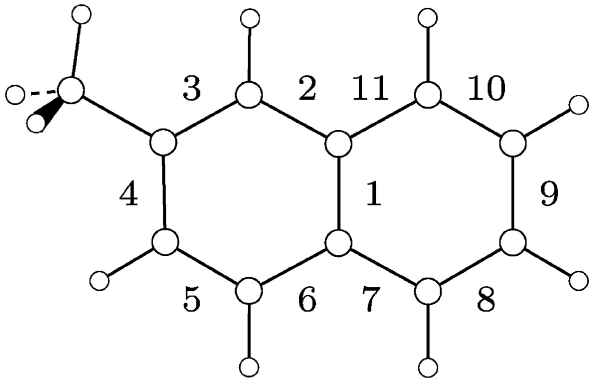
$1Me\text{-}Np^+$ (D_0)
s-e

Strong hindering

Staggered-Eclipsed
Φ = 0° 30°



$2Me\text{-}Np^+$ (D_0)
s-e



$2Me\text{-}Np^+$ (D_2)
e-s

Weak hindering

2-methylnaphthalene$^+$: blue shift of 226 cm^{-1}.

Theoretical treatment

Separation of the hindered rotor motion
from the other intramolecular modes

$H_\alpha(\theta,\mathbf{q})=H_\alpha^{rot}(\theta)+H_\alpha^{vib}(\mathbf{q})$ full decoupling of θ

Harmonic and Born−Oppenheimer approximations using the cumulant Gaussian fluctuations formalism (CGF)

(Franck-Condon-like)

- Mukamel, S. *Principles of nonlinear optical spectroscopy*; Oxford University Press: New York, 1995.
- Mukamel, S.; Abramavicius, D. *Many-Body Approaches for Simulating Coherent Nonlinear Spectroscopies of Electronic and Vibrational Excitons.* Chem. Rev. 2004, 104, 2073−2098.

DFT calculations B97-1 functional, 6-31G* basis set

Hindered rotation

$$H_{\alpha}^{\mathrm{rot}}(\theta) = -B_{\alpha}\frac{\partial^2}{\partial\theta^2} + V_{\alpha}(\theta)$$

$$V_{\alpha}(\theta) = \frac{1}{2}V_{\alpha,3}(1 - \cos(3\theta)) + \frac{1}{2}V_{\alpha,6}(1 - \cos(6\theta))$$

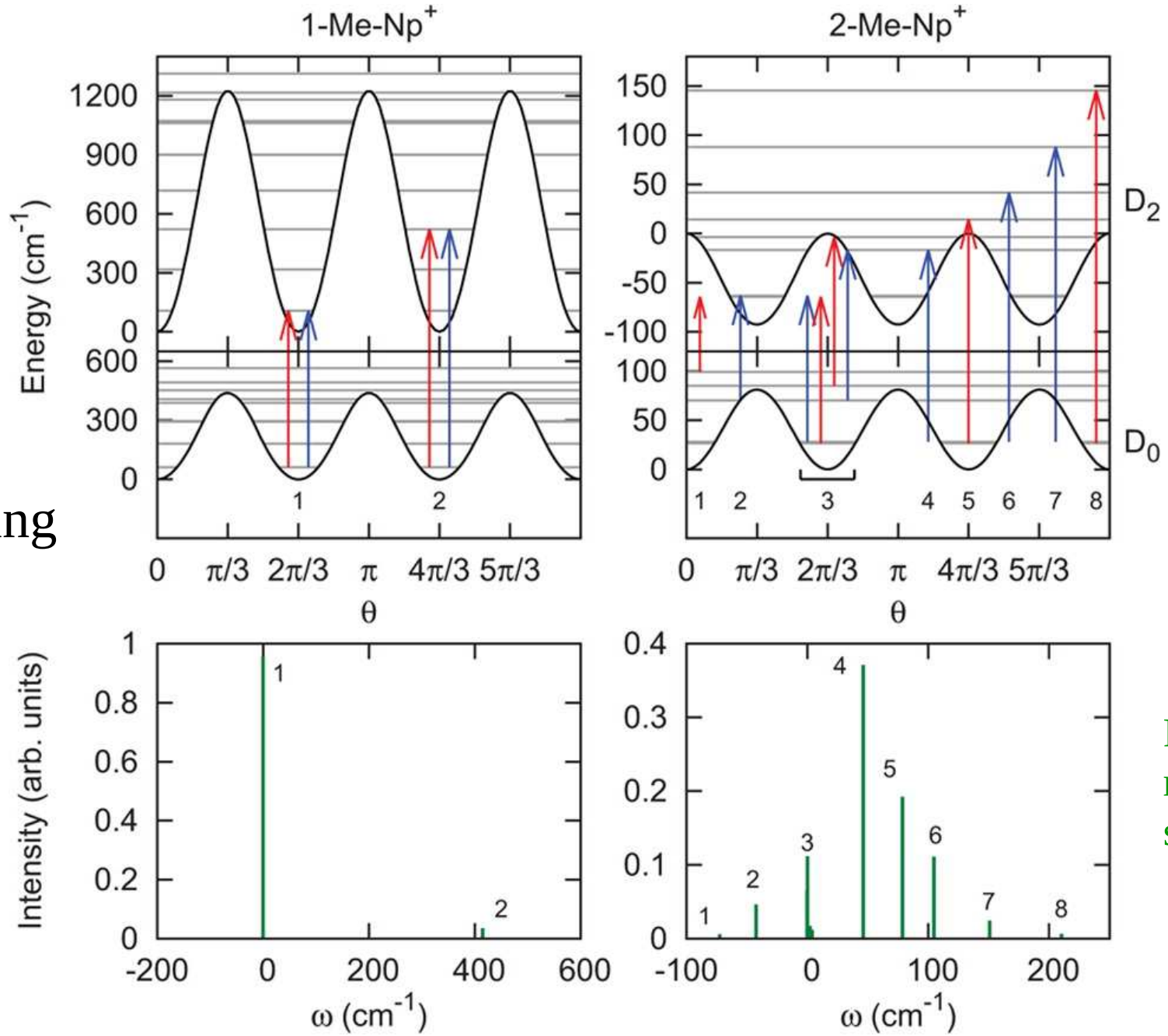
Fit of the Electronic Structure Data

	B_α (cm^{-1})	$V_{\alpha,3}$ (cm^{-1})	$V_{\alpha,6}$ (cm^{-1})
1Me−Np+ (D_0)	5.33	439.4	−31.5
1Me−Np+ (D_2)	5.30	1226.1	−64.1
2Me−Np+ (D_0)	5.31	81.3	−0.6
2Me−Np+ (D_2)	5.32	−92.7	−2.1

For comparison : Methylanthracene S_0 V_6 ~100 cm^{-1} or less (Baba, 2009)

Extension of the Cumulant Gaussian Fluctuations formalism to include the internal rotation.

Strong hindering



Weak hindering

Rich internal rotation structure

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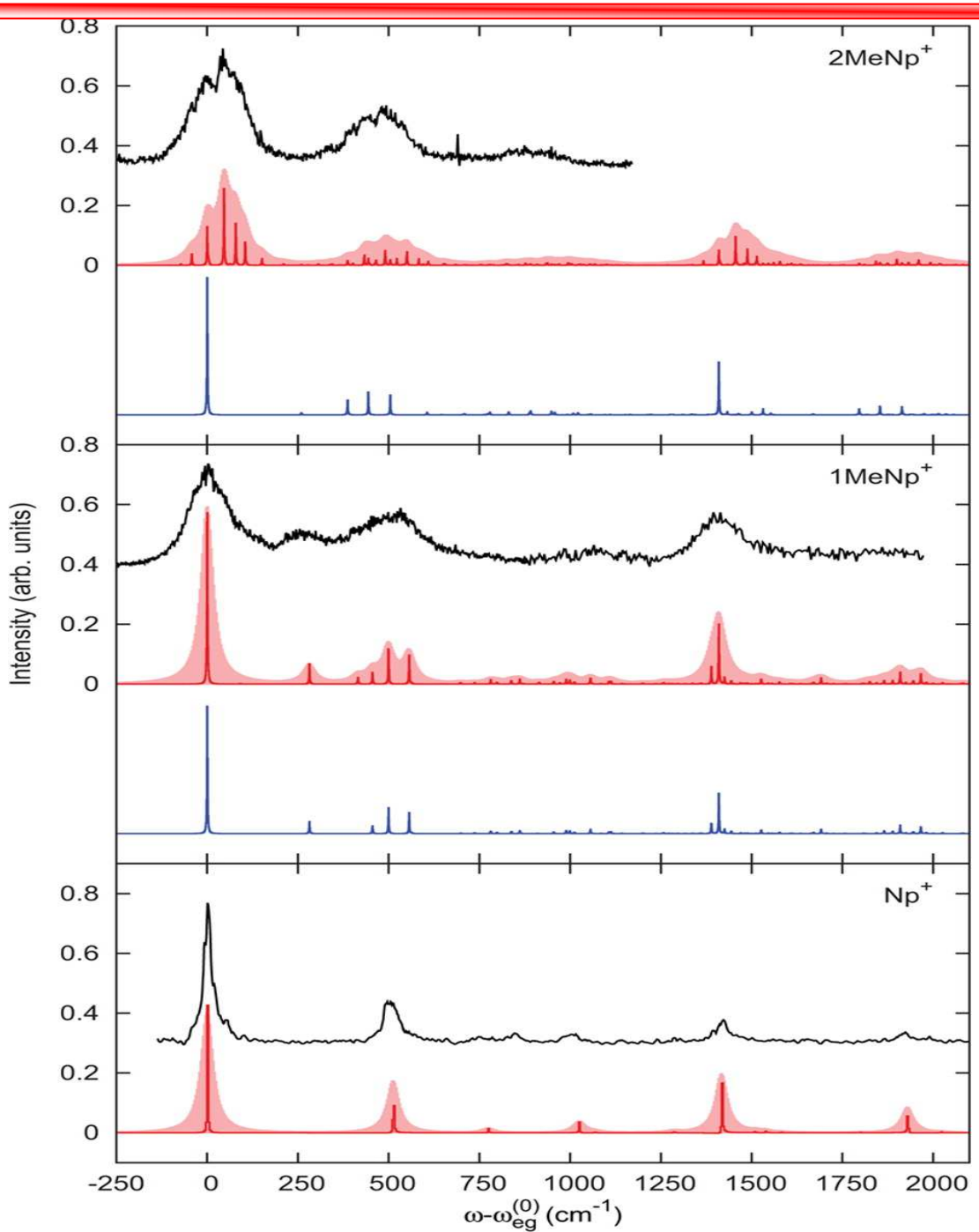
Comparison of experiment and theory



Internal rotation
at T=30 K

VdW modes not taken
into account

Lorentzian convolution δ=20 cm^{-1}
Intrinsic broadening due to
internal conversion rate

Excellent agreement !

Not a temperature effect

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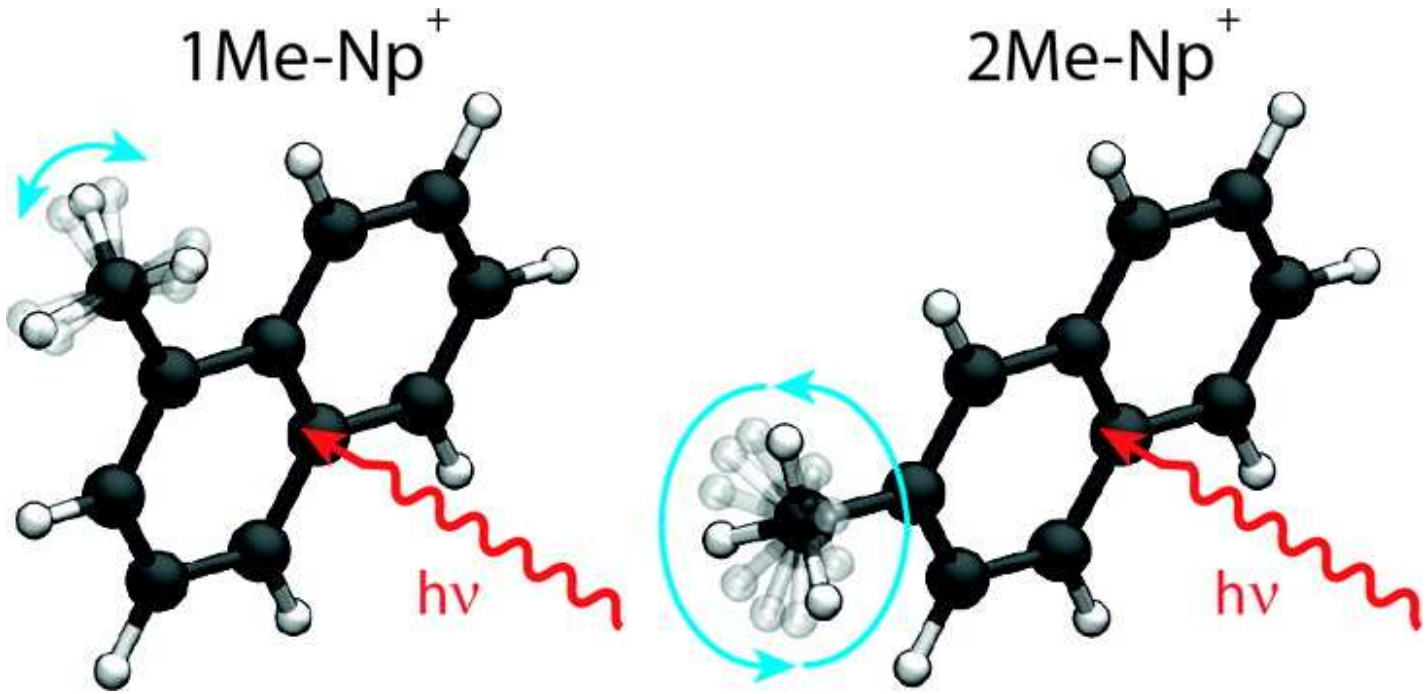

Thank you very much for your attention

Full reference for this work:
dx.doi.org/10.1021/jp407627x J. Phys. Chem. A 2013, 117, 13664