

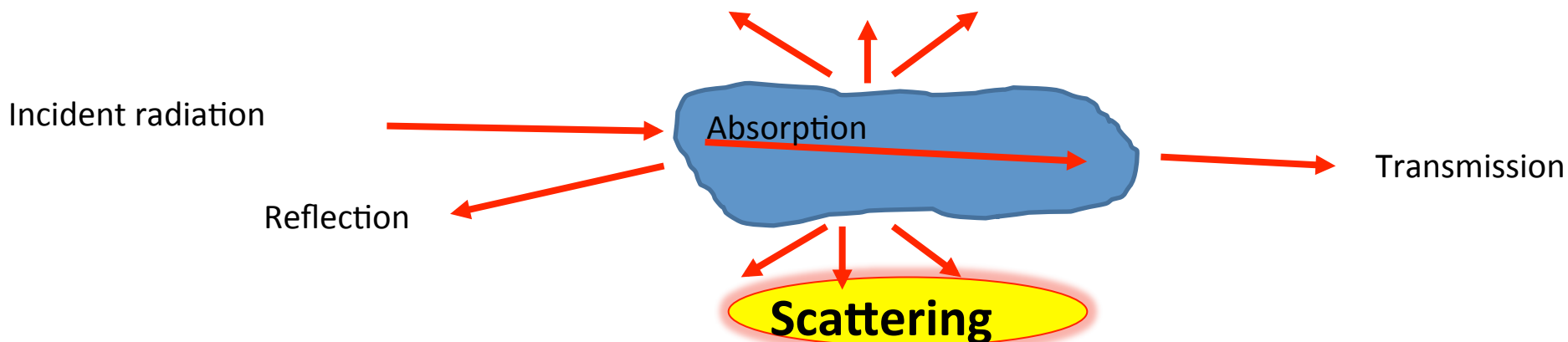
Experiments vs simulations: a comparison between collected and simulated Raman spectra of simple organic molecules, pure and in aqueous solutions

Francesco D'Amico

Beamline IUVS

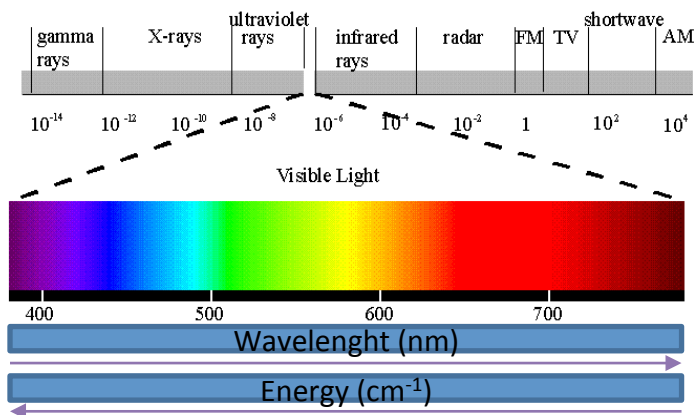
Interaction of radiation with matter

When the electromagnetic radiation interacts with matter and its energy is not in resonance with any energy level difference, absorption does not take place but **scattering processes** can occur at second order in perturbation theory

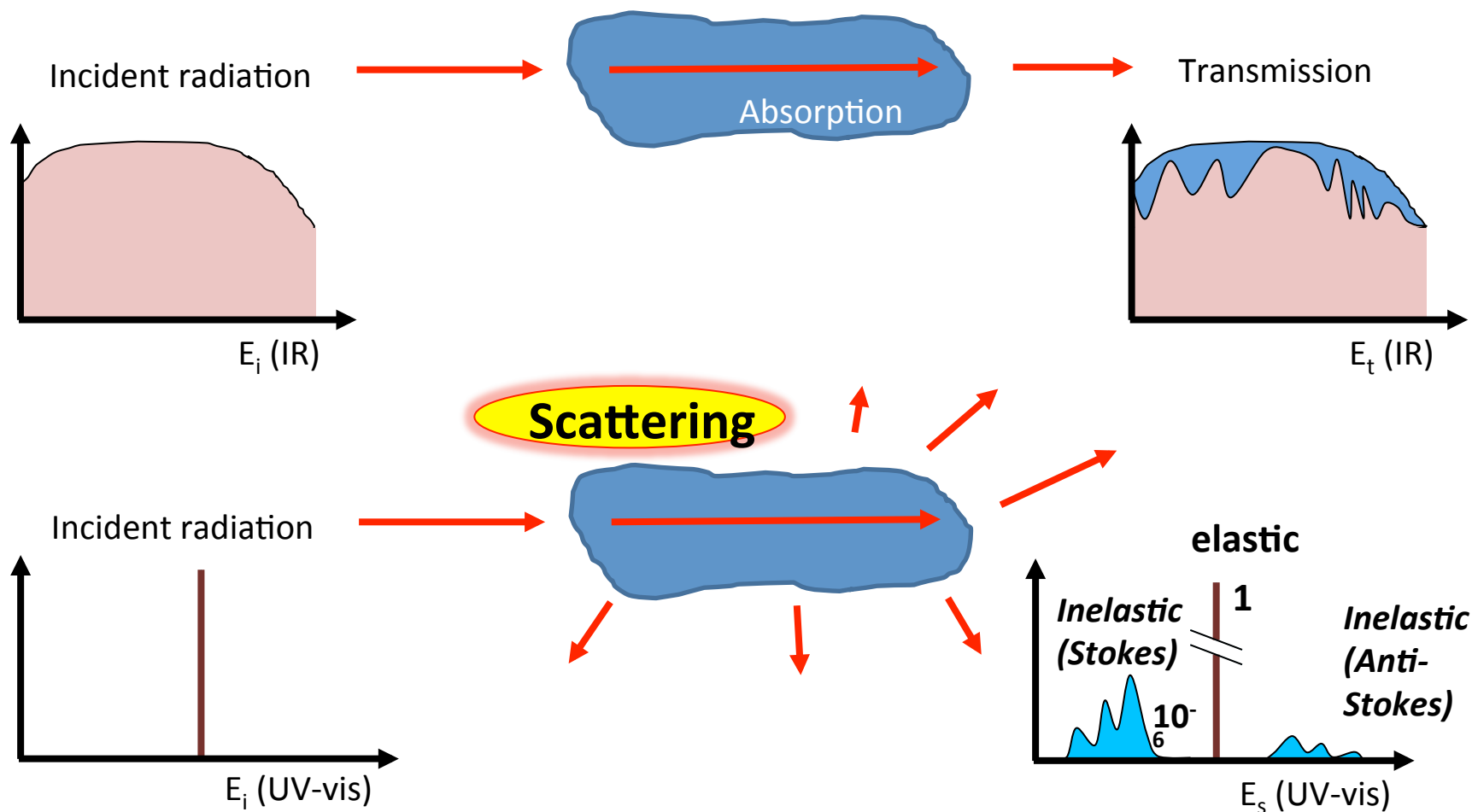


By the analysis of the characteristic of radiation (wavelength and intensity) before and after its interaction with the system under investigation, we can study the elementary excitations of a molecular and atomic system

Optical spectroscopy techniques includes all the experimental techniques which use the electromagnetic radiation as a probe

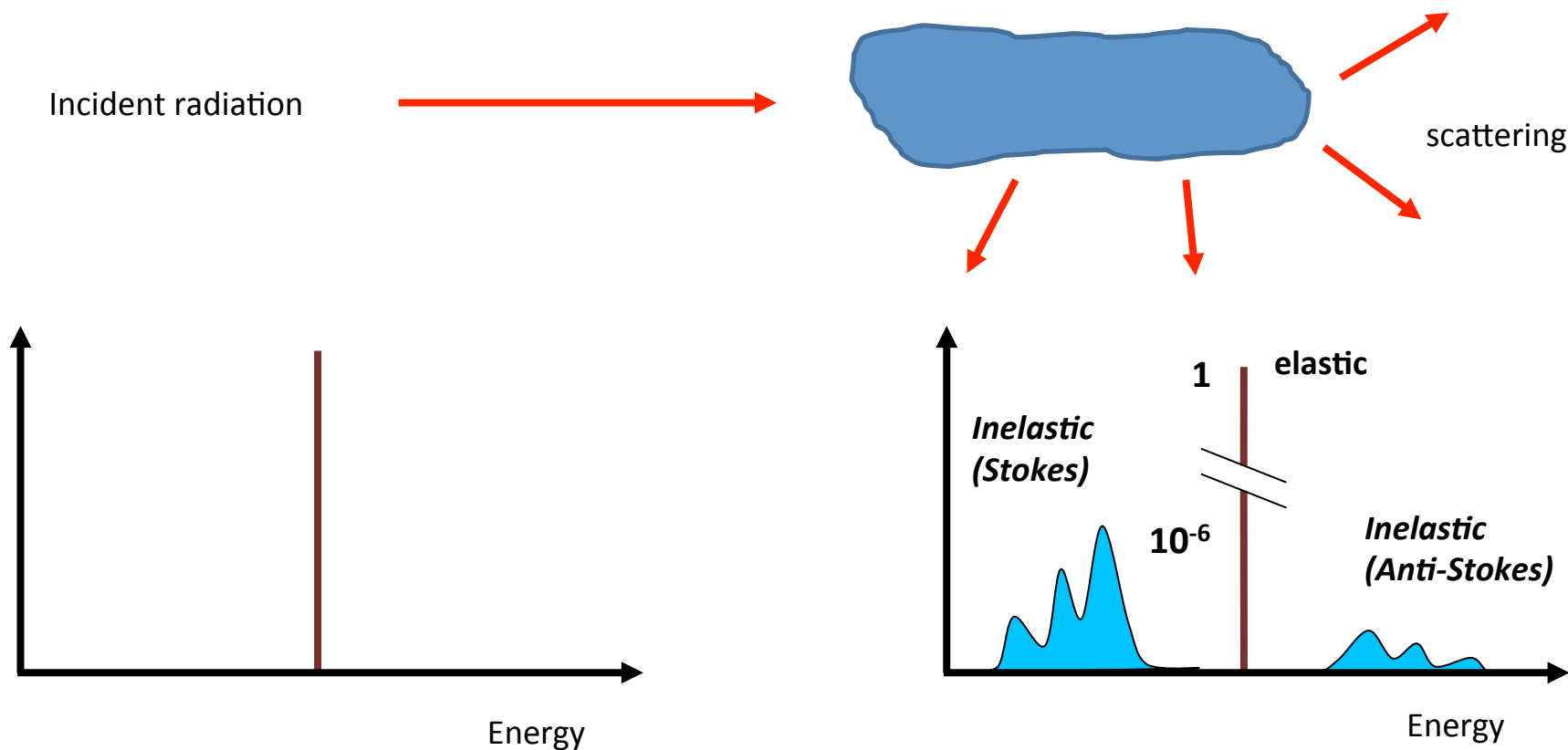


Vibrational spectroscopies: IR vs Raman

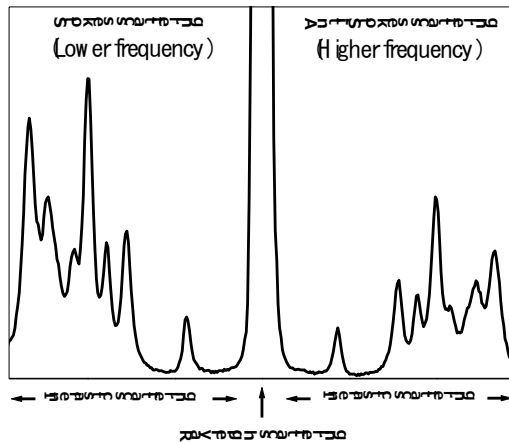


Raman scattering

*When the electromagnetic radiation interacts with matter and its energy is not in resonance with any energy level difference, absorption does not take place but **scattering processes** can occur at second order in perturbation theory*

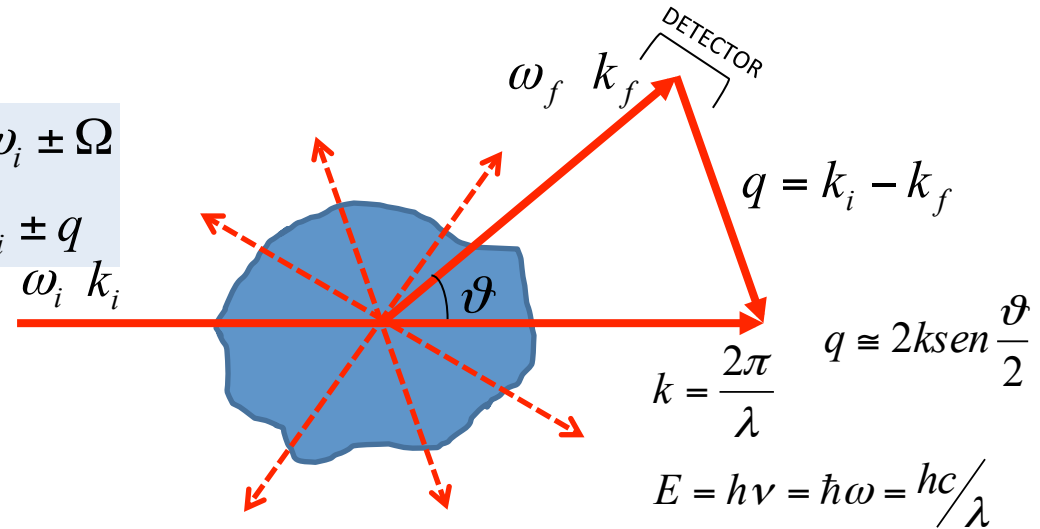


Inelastic scattering experiments



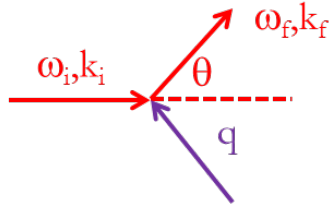
$$\omega_f = \omega_i \pm \Omega$$

$$k_f = k_i \pm q$$



ANTI-STOCKES PROCESS

absorption of phonon Ω, q

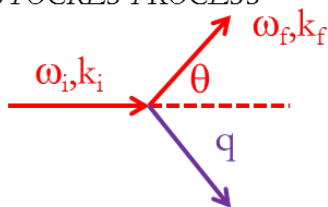


$$\omega_f = \omega_i + \Omega$$

$$k_f = k_i + q$$

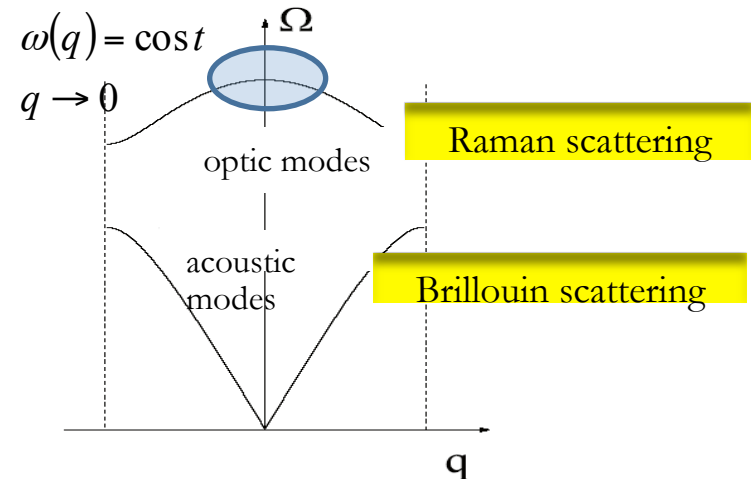
STOCKES PROCESS

emission of phonon Ω, q

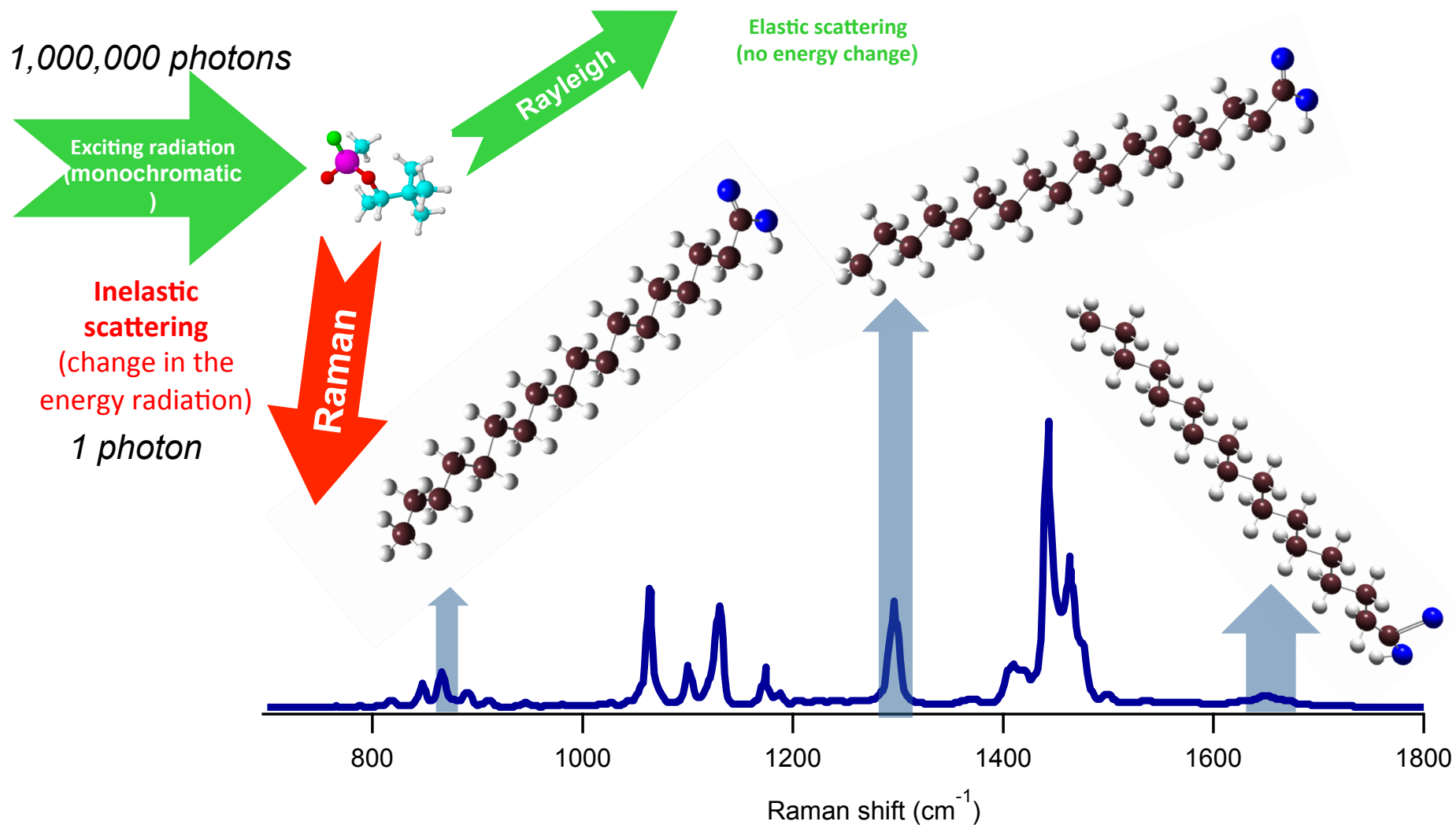


$$\omega_f = \omega_i - \Omega$$

$$k_f = k_i - q$$



Raman scattering



Raman effect

Raman bands arise from **changes in the molecular polarizability** during the vibrations

$$P(t) = \alpha_0 E_0 \cos \omega_0 t + \frac{1}{2} \delta \alpha_k Q_k^0 E_0 [\cos(\omega_0 - \omega_k)t - \phi_k + \cos(\omega_0 + \omega_k)t + \phi_k]$$

$$= P(\omega_0) + P(\omega_0 - \omega_k) + P(\omega_0 + \omega_k)$$

$$P(\omega_0) \propto \cos \omega_0 t$$

Rayleigh or elastic scattering

Raman scattering total intensity:

$$P(\omega_0 - \omega_k) \propto \cos(\omega_0 - \omega_k)t - \phi_k$$

Stokes Raman scattering

$$P(\omega_0 + \omega_k) \propto \cos(\omega_0 + \omega_k)t + \phi_k$$

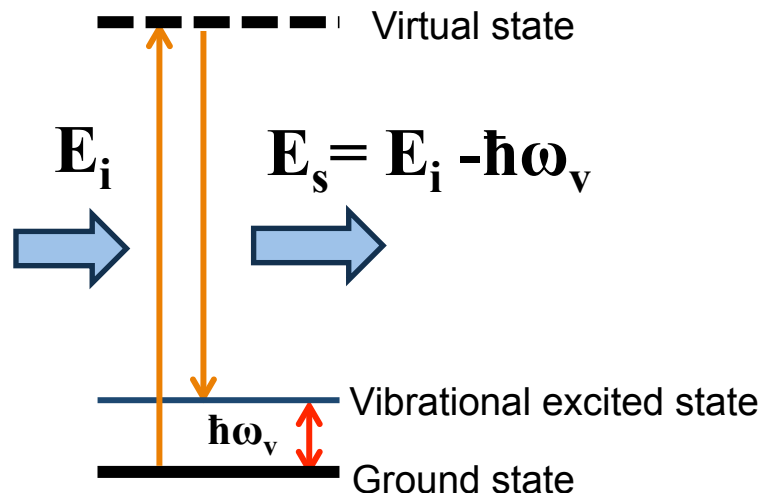
Anti-Stokes Raman scattering

$$I(\theta)_{av} = B(\nu_0 \pm \nu)^4 I_0 \left(\frac{\partial \alpha_{xx}}{\partial Q_1} \right)_0^2 \sin^2 \theta$$

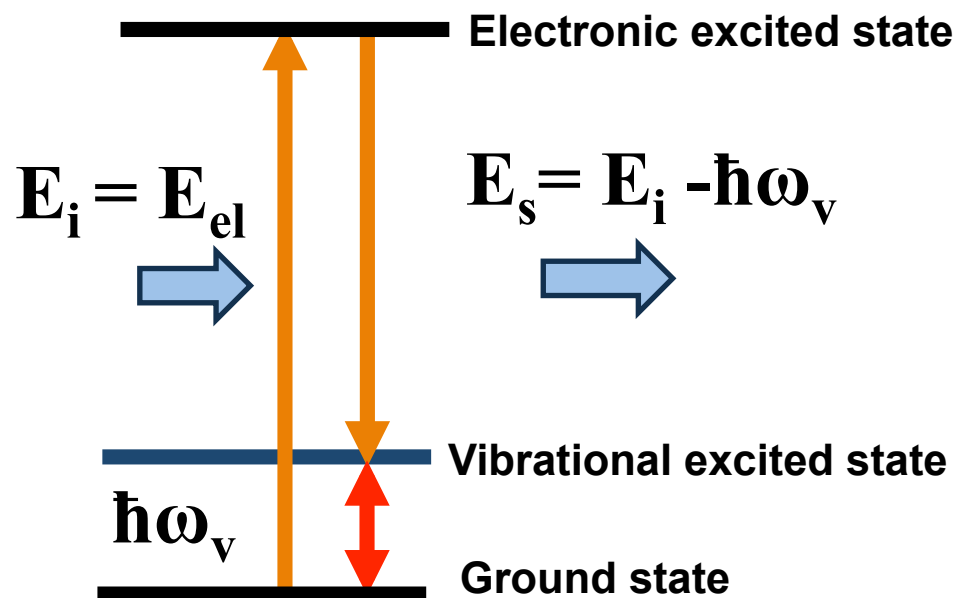
derived polarizability tensor

Resonant Raman scattering

Spontaneous Raman

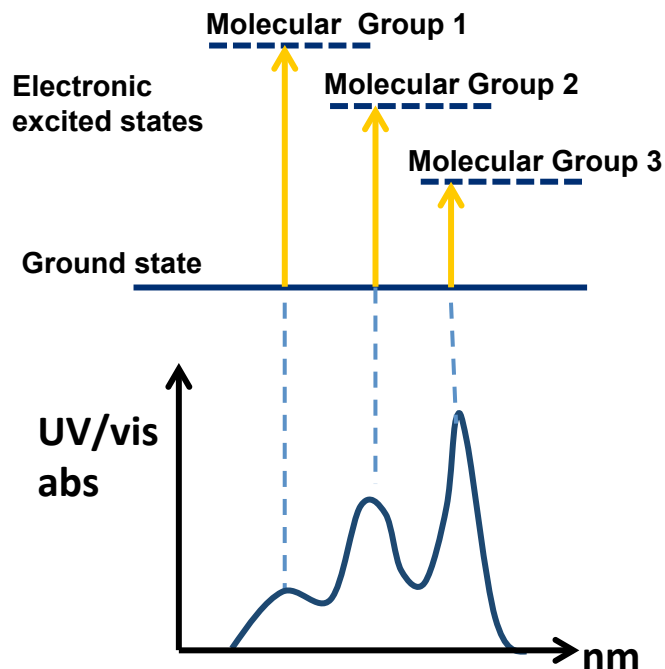


Resonant Raman

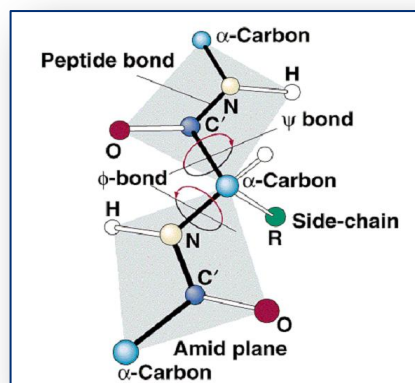


Raman cross section increased

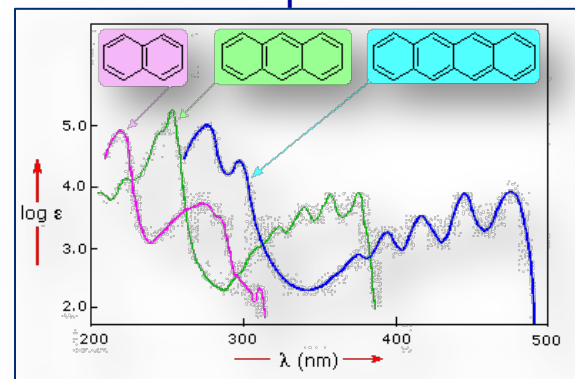
UV Resonant Raman scattering



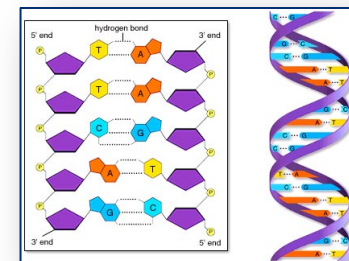
200-220 nm Peptide bonds



200-300 nm Aromatic compounds



225-300 nm DNA nitrogenous bases



S. A. Oladepo et al. *Chem. Rev.* 2012.

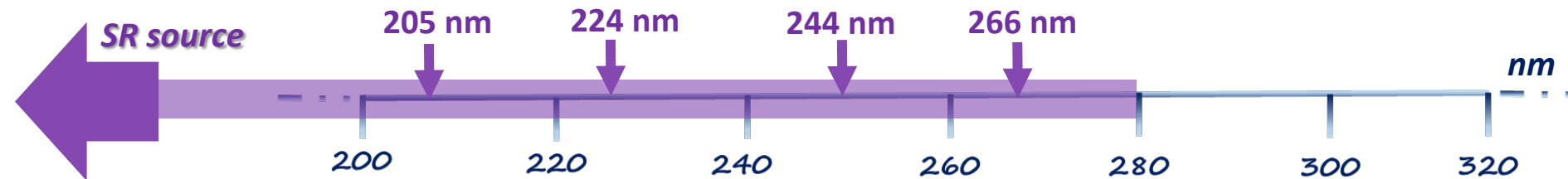
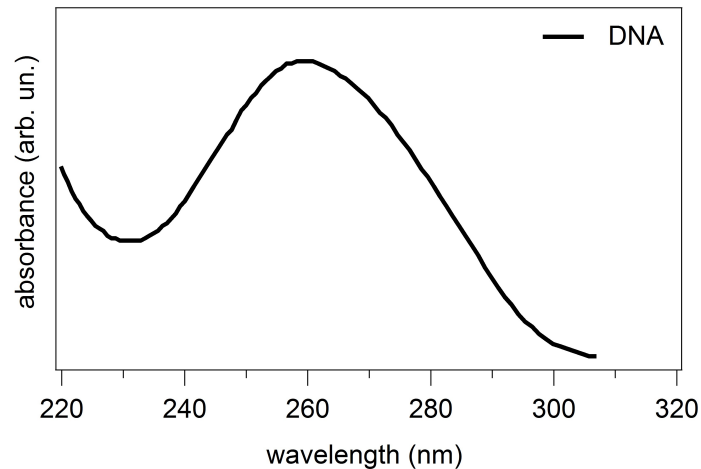


Further advantages on the use of UVRR

- **Absence** of *fluorescence background* on the spectra
- Measurements in **water** and/or **buffer solutions** at low solute concentrations
- **Higher Raman cross section** with respect to the Raman scattering performed exploiting visible near/IR laser sources

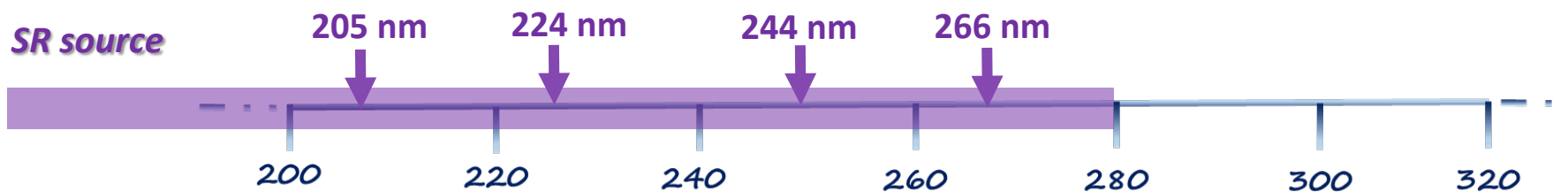
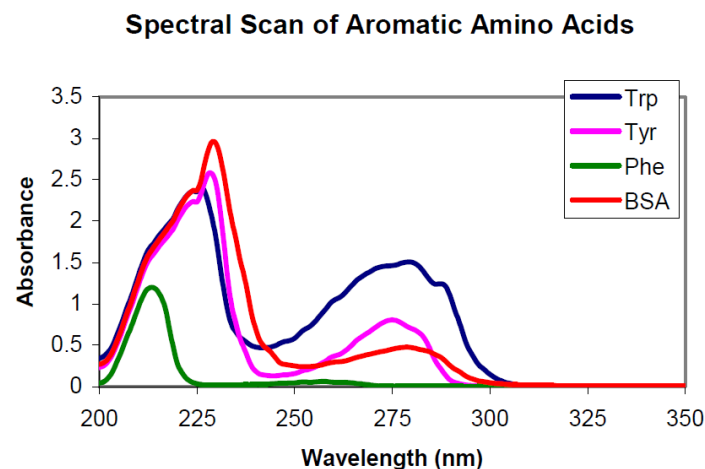
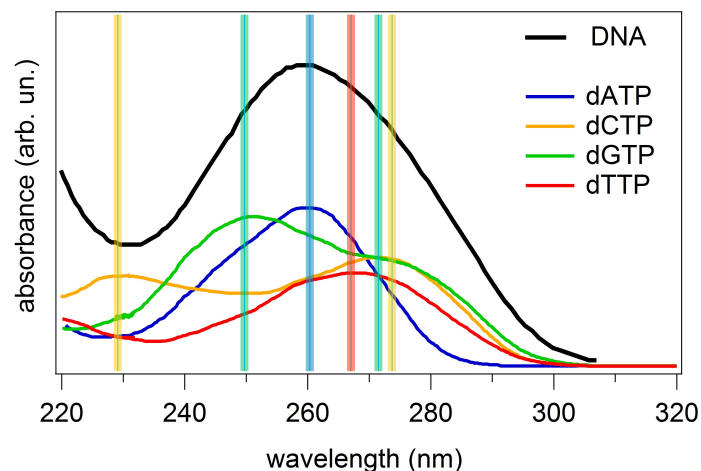
Exciting wavelength selectivity

- *Laser: **fixed** wavelength sources*
- *SR: **tunable** CW wavelength source → better selectivity*

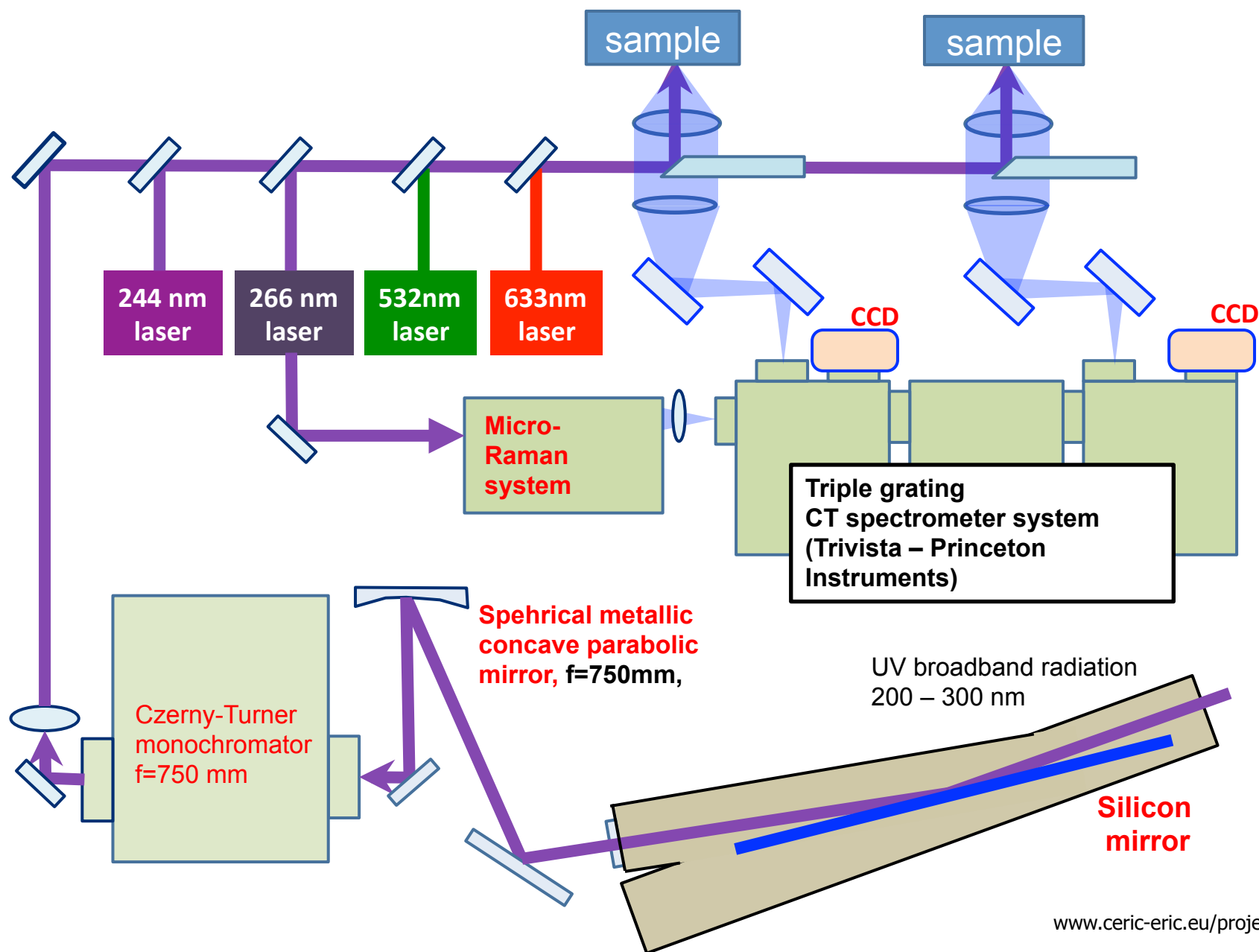


Exciting wavelength selectivity

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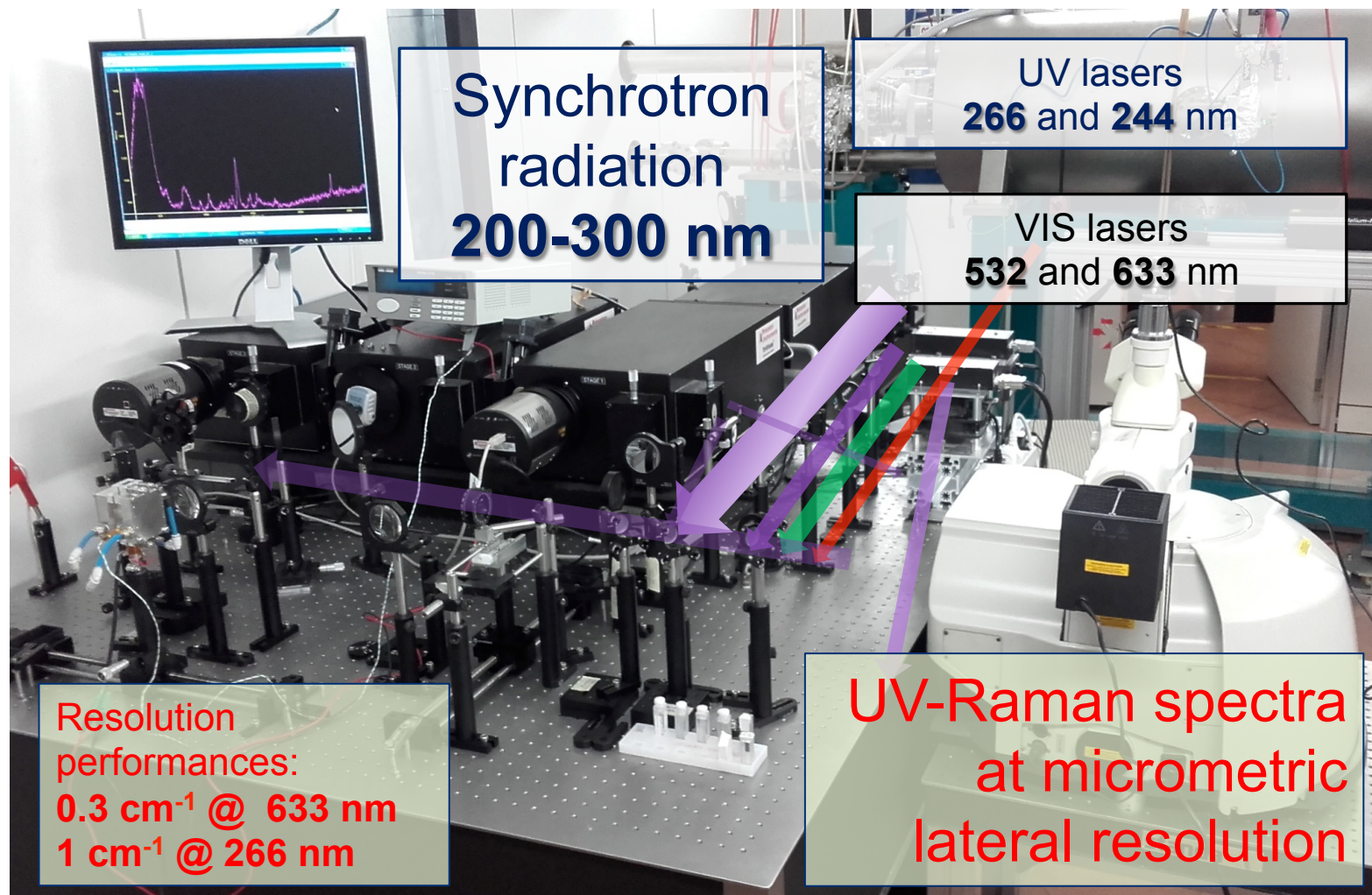


UVRR set-up, IUUVS at Elettra

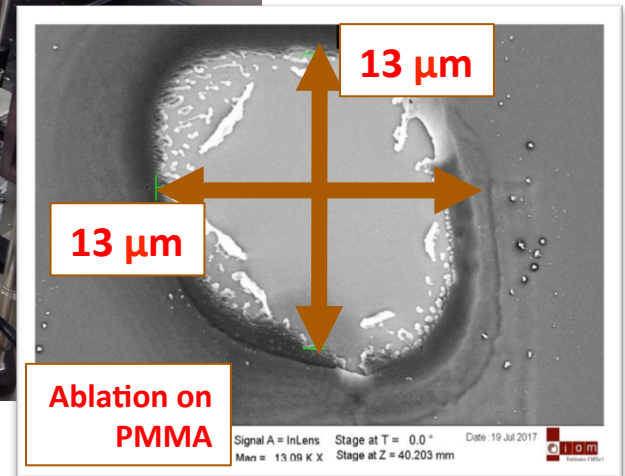
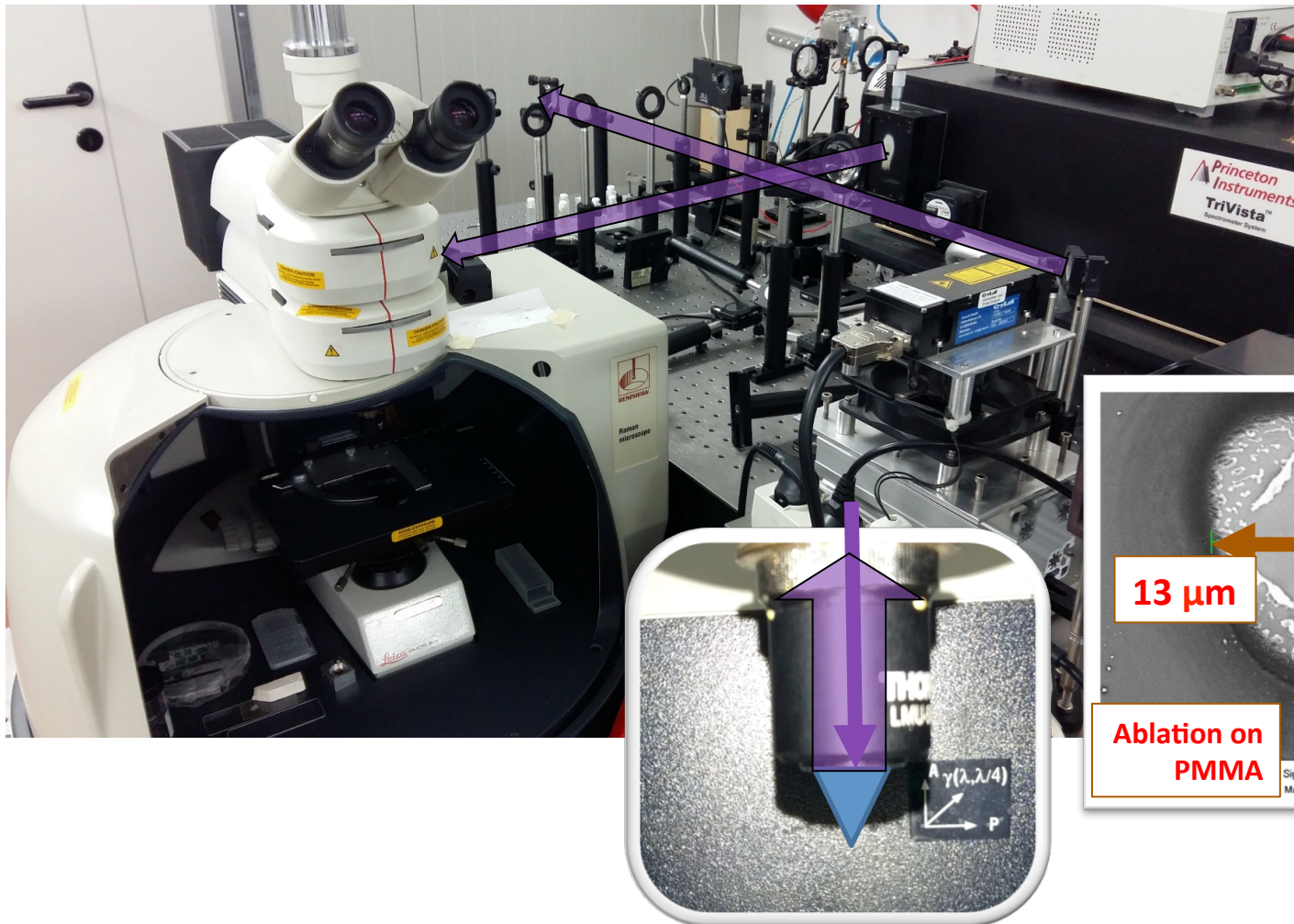


UVRR set-up, IUUVS at Elettra

F. D'Amico et al. *NIMA* 2013.



UV micro Raman system



<https://www.acdlabs.com/resources/freeware/chemsketch/>

ORCA

An ab initio, DFT and semiempirical SCF-MO package



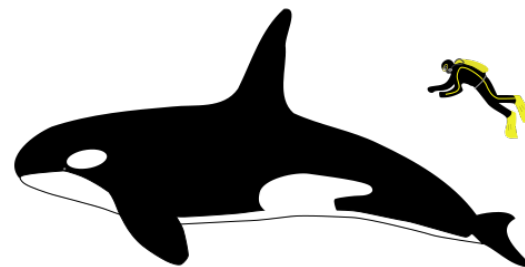
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[https://en.wikipedia.org/wiki/ORCA_\(quantum_chemistry_program\)](https://en.wikipedia.org/wiki/ORCA_(quantum_chemistry_program))



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AVOGADRO

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Avogadro

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Manual

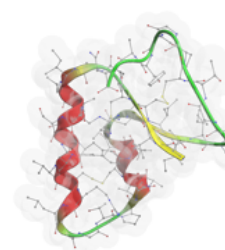
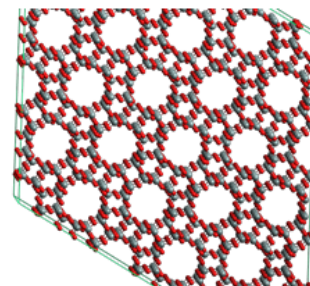
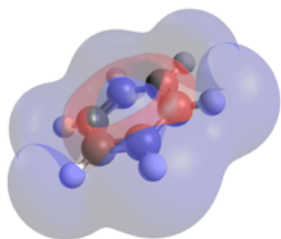
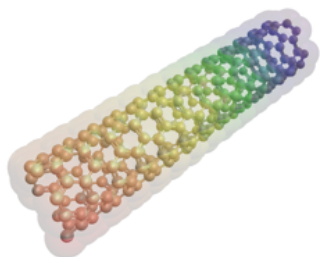
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