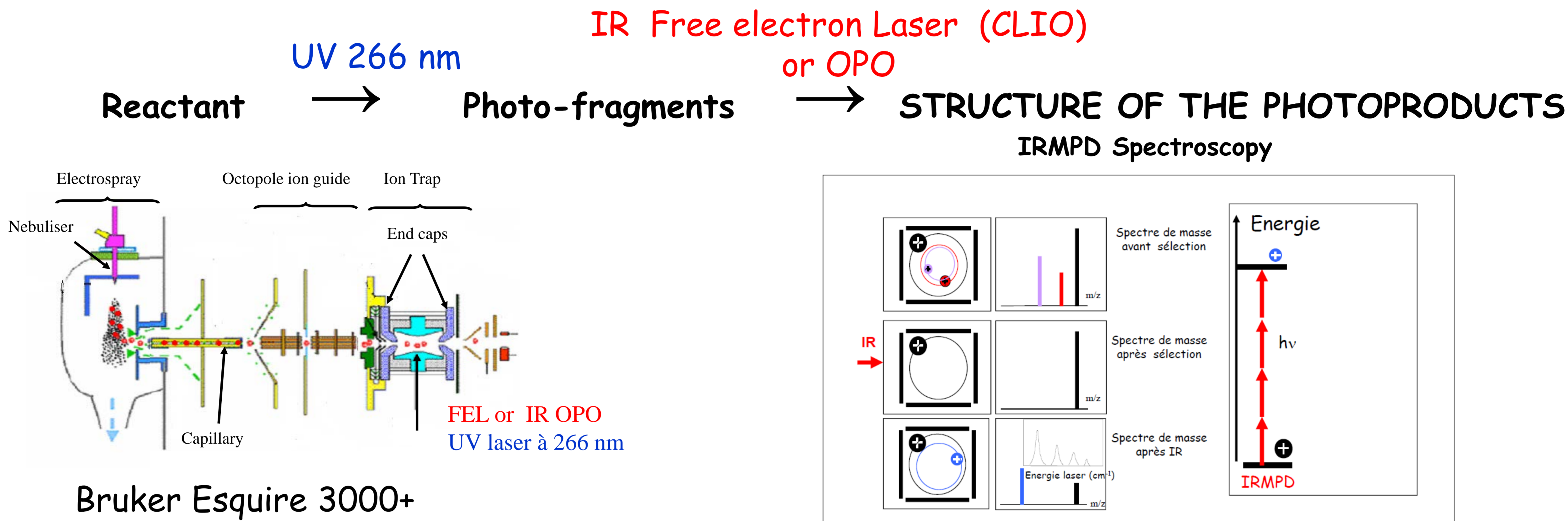
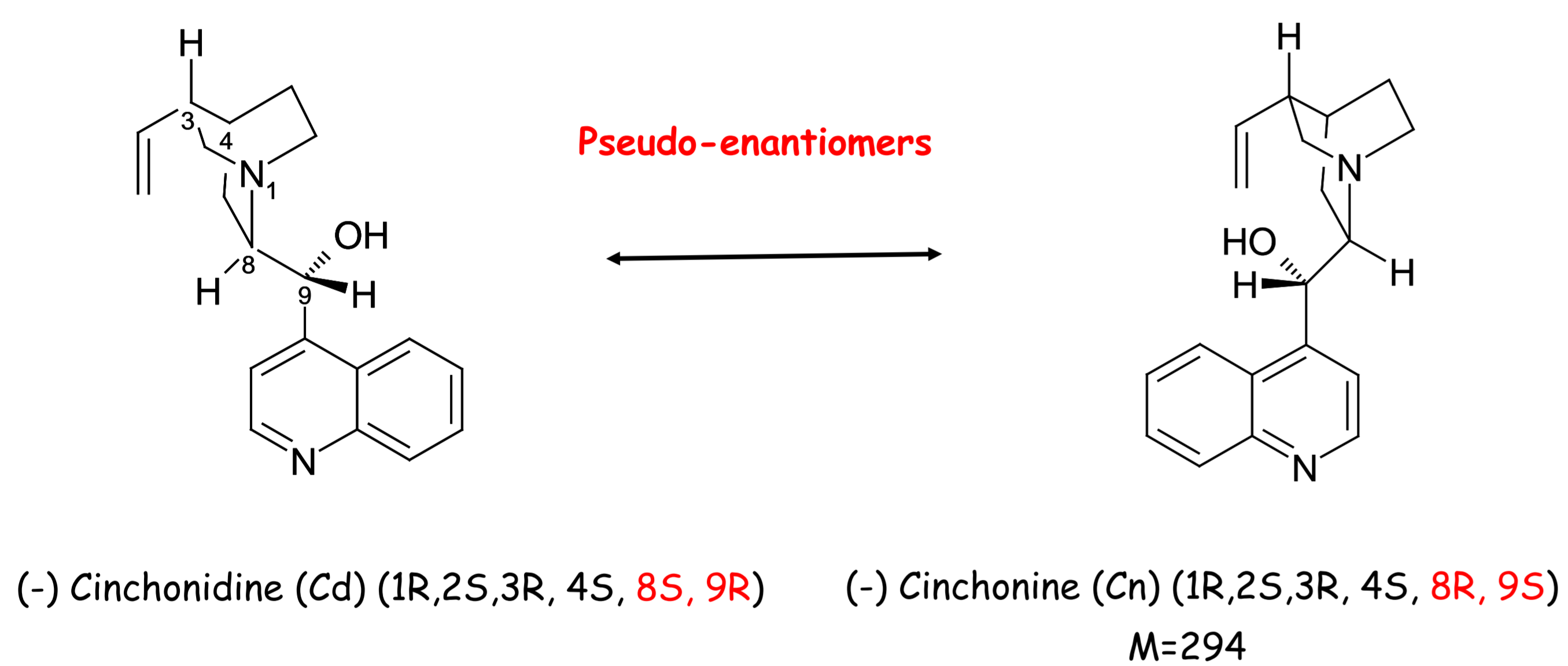


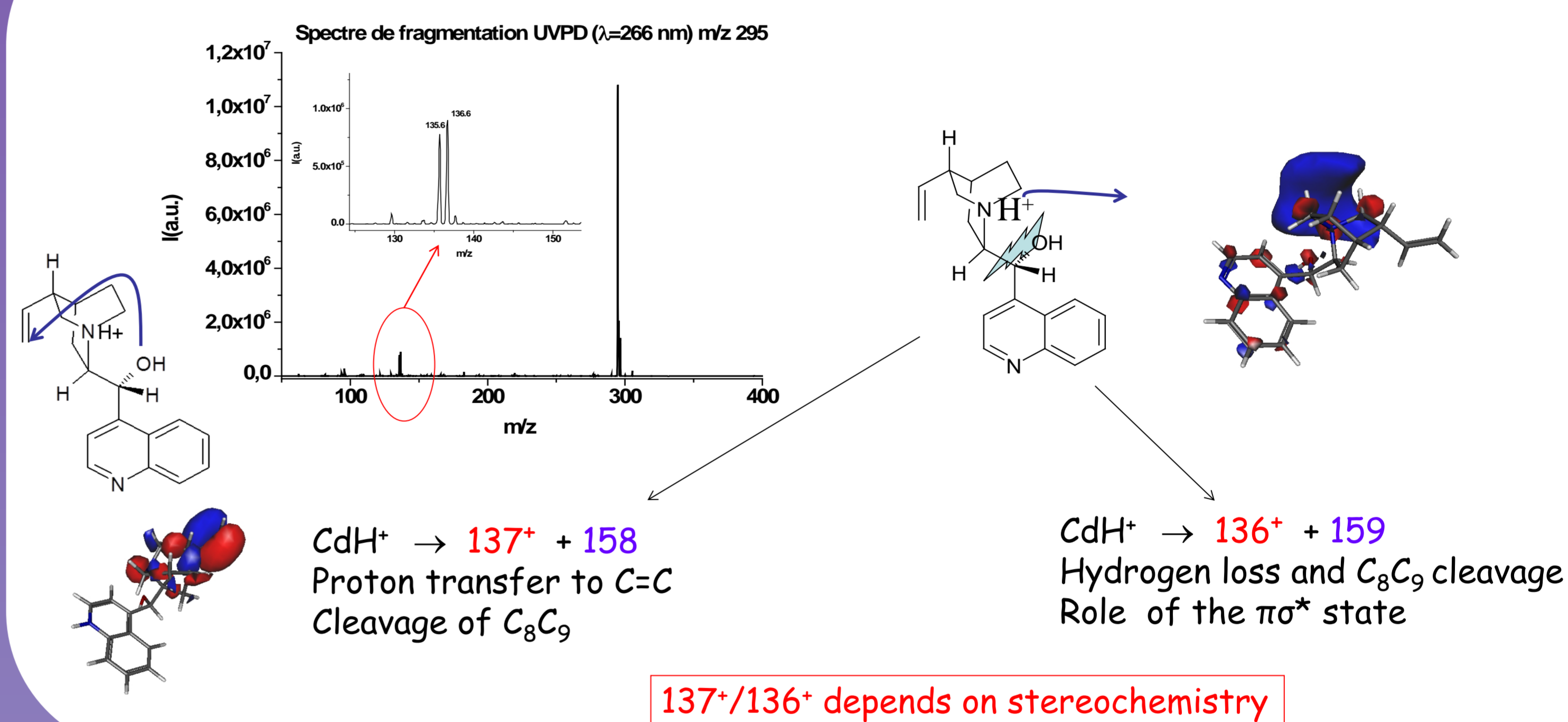
Principle : Tandem MS³ mass spectrometry coupled with laser photofragmentation



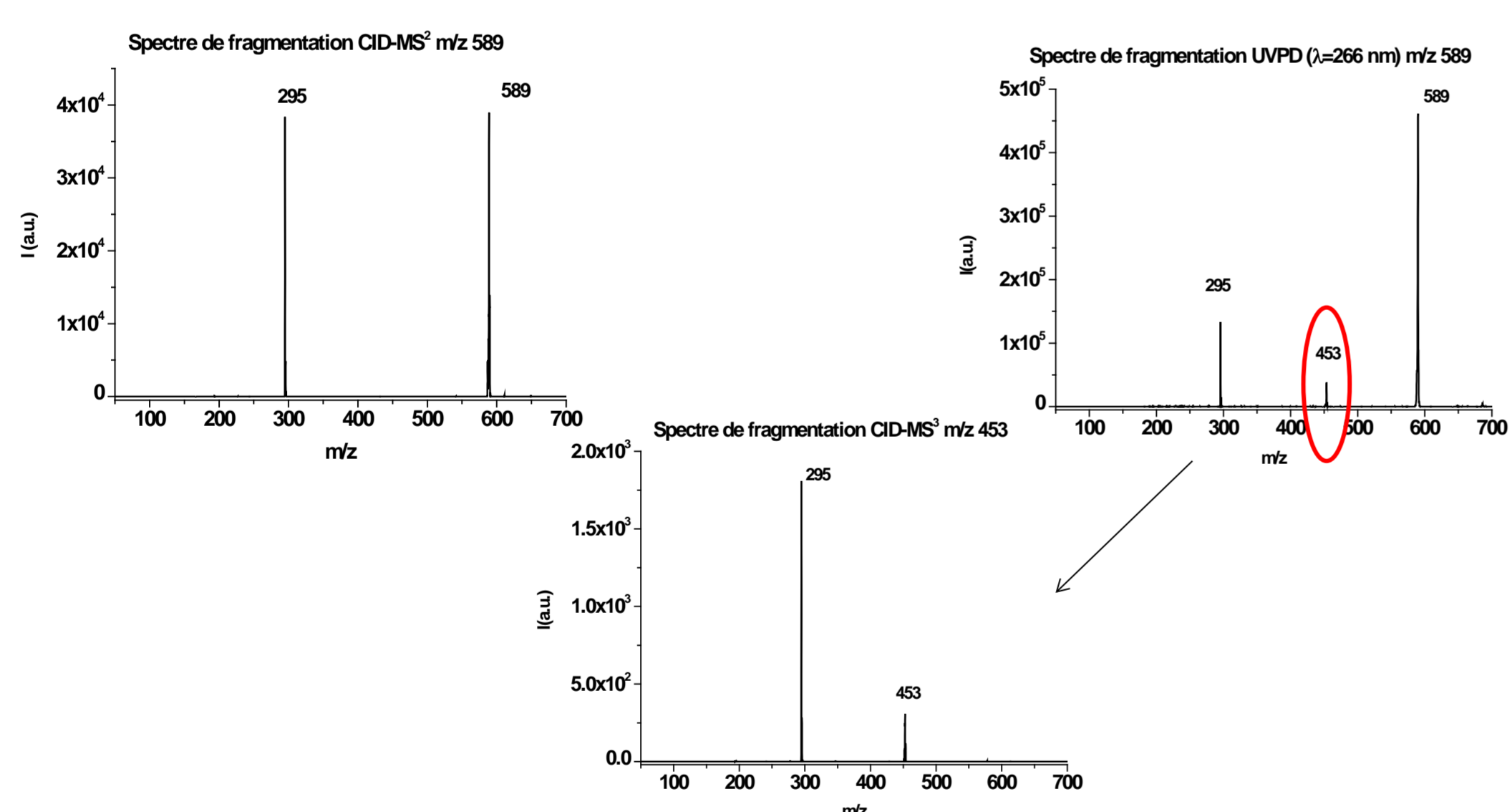
Studied systems: Cinchona alkaloid (quinine derivatives) and their protonated dimers



Protonated monomer m/z 295

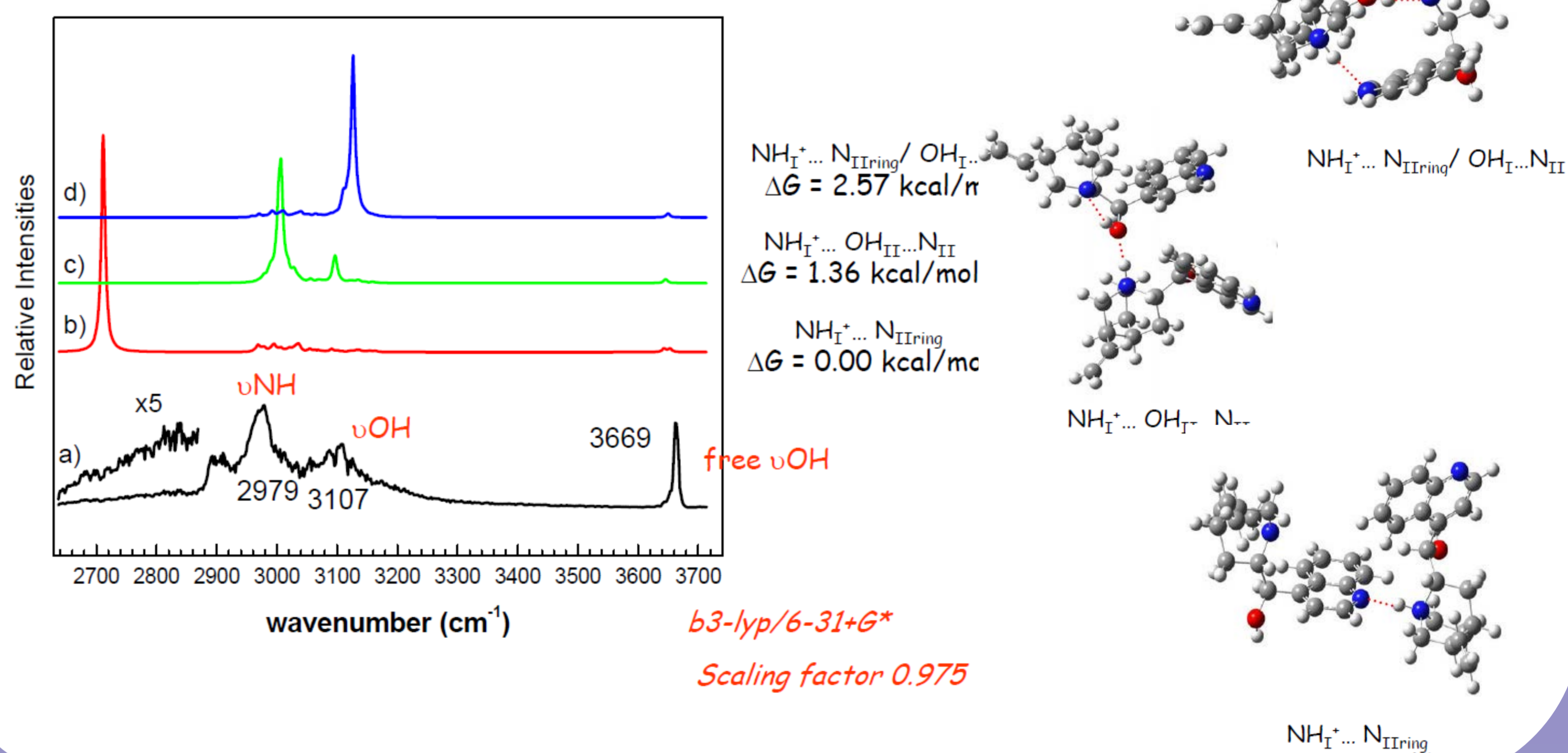


UV fragmentation of the cinchonidine protonated dimer Cd_2H^+ m/z 589

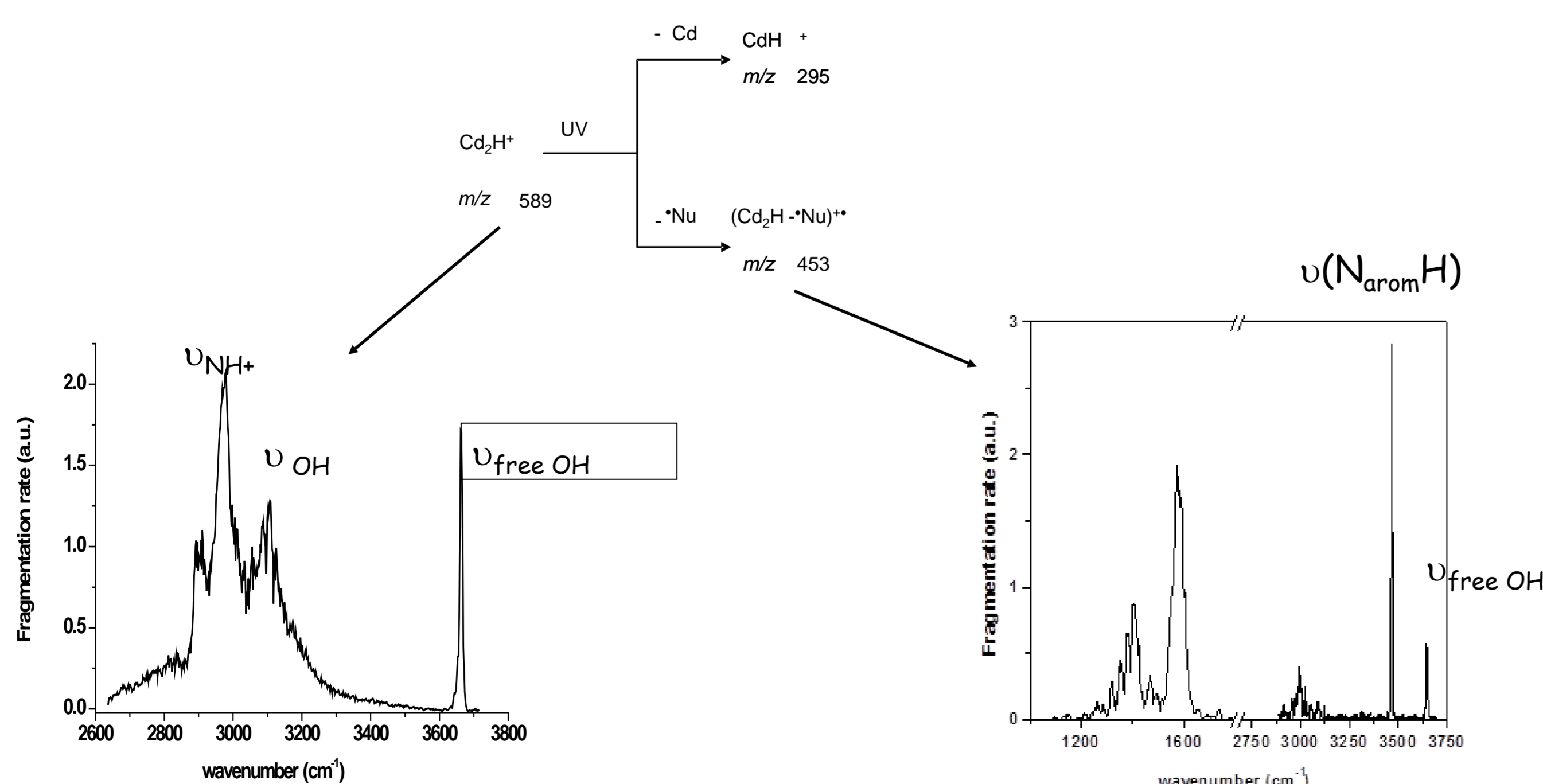


- UV photo-fragmentation results to different fragments from those formed by collision-induced dissociation or IRMPD
- The photo-products contains CdH^+
- Photodissociation sensitive to chirality (Scuderi et al. J. Phys. Chem. A 2010)

IRMPD Spectroscopy of the parent m/z 589 and DFT calculations

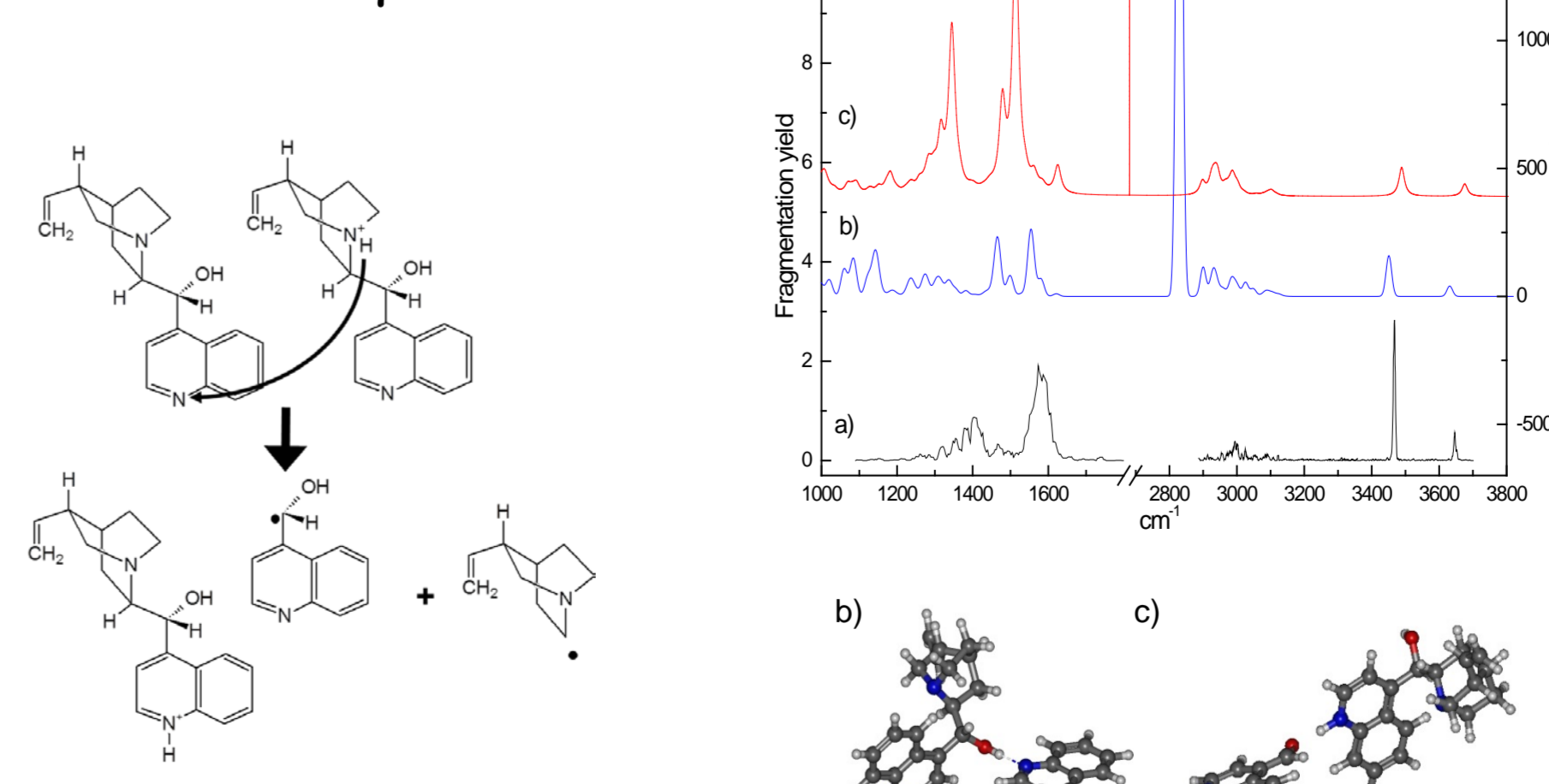


IRMPD spectrum of the UV photofragment m/z 453



Proposed mechanism

Coupled hydrogen and proton transfer within the dimer and cleavage of the C₈C₉ bond ⇒ Proton located on quinoline N



Structures of the radical compatible with the experiment (DFT b97-d/TZVPP) (Scuderi et al. J. Phys. Chem. Letters 2014)

Conclusions and perspectives

Coupling these two techniques provides a new tool for the study of photo-fragmentation mechanisms by probing the structure of the UV photo-fragments. Extension to other systems showing specific fragmentation scheme in the UV, like protonated peptides. Role of stereochemistry and chirality in progress