

# Structural Characterisation of Photoproducts by Vibrational Spectroscopy: Combining UV and IR Lasers in a Ion Trap.



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Principle : Tandem MS<sup>3</sup> mass spectrometry coupled with laser photofragmentation



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



**Pseudo-enantiomers** 







CdH<sup>+</sup>  $\rightarrow$  136<sup>+</sup> + 159 Hydrogen loss and C<sub>8</sub>C<sub>9</sub> cleavage Role of the  $\pi\sigma^*$  state

M=294

## 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<sup>+</sup>
- Photodissociation sensitive to chirality
- (Scuderi et al. J. Phys. Chem. A 2010)

### IRMPD spectrum of the UV photofragment m/z 453



#### Proposed mechanism

Coupled hydrogen and proton transfer within the dimer and cleavage of the  $C_8C_9$  bond





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