Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

UV spectroscopy of cold ions as a diagnostics of the protonation site.

Géraldine Féraud, Natalia Esteves-López, Claude Dedonder-Lardeux, Christophe Jouvet

Supplementary information

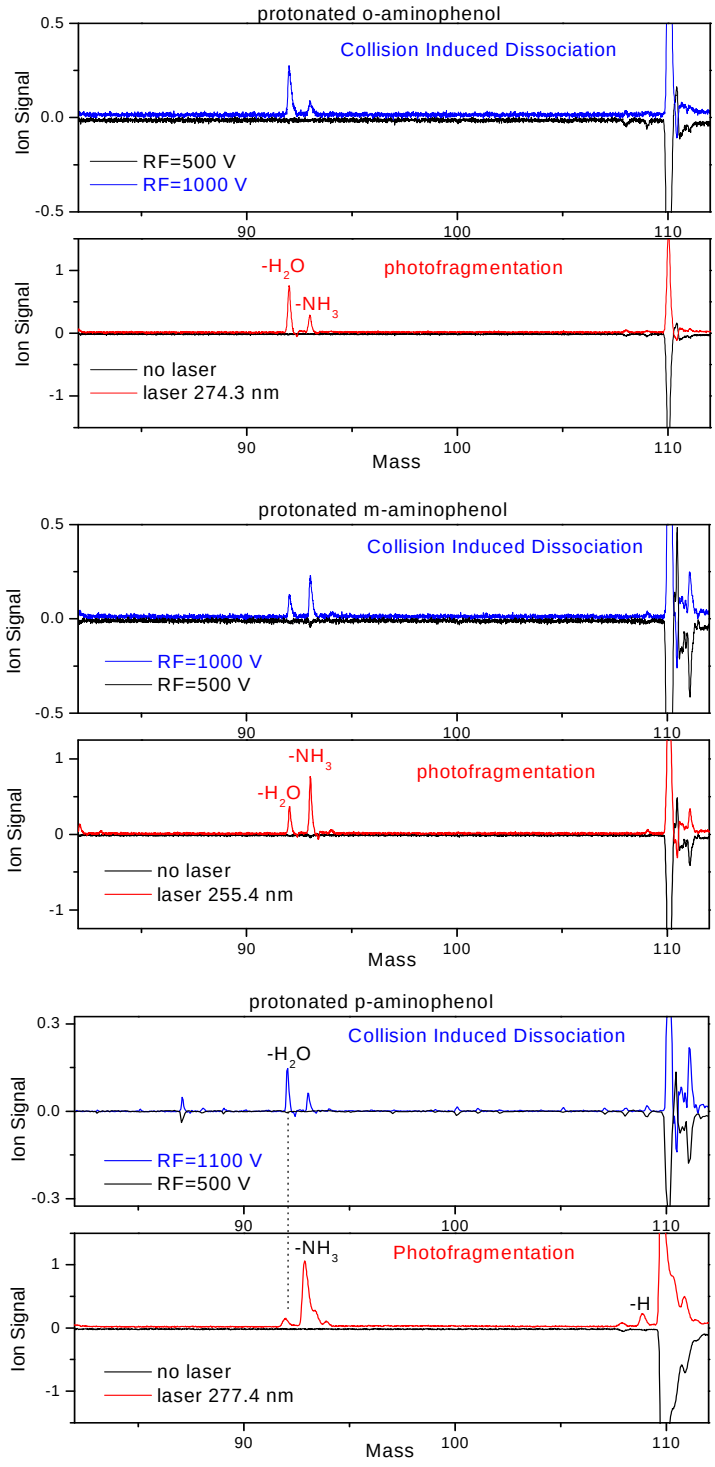

Figure SI.1: Mass spectra of photon induced fragmentation for protonated aminophenol isomers compared with collision induced fragmentation. The H loss channel, specific of the UV fragmentation, is observed only for the *para* isomer.

Evaluation of the temperature of the ions in the cold ion trap

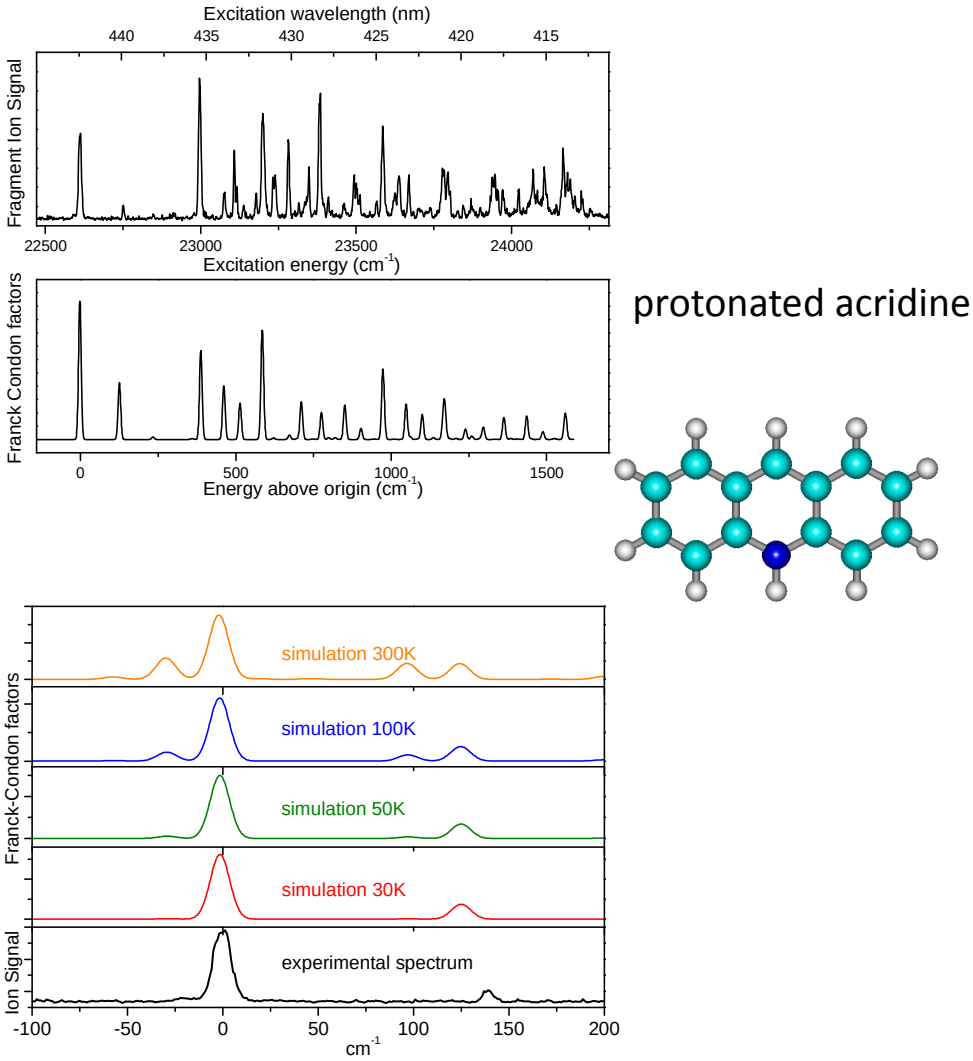

Figure SI.2: protonated acridine was chosen since its vibrational spectroscopy is well reproduced by Franck-Condon simulations using ground and excited state calculated frequencies as can be seen in the upper part of the figure: comparison between the experimental (upper trace) and calculated (lower trace) spectra. In the lower part of the figure: comparison between the experimantal spectrum (lower trace) and spectra calculated at different temepratures. The hot band at -25 cm^{-1} is not observed in the experimental spectrum, which sets an upper limit for the ion tempetature at 50K.

Table SI.1: Calculated ground state energies for the trans *ortho*-aminophenolH^+ and *para*-aminophenolH^+ at the DFT/B3LYP/cc-pVDZ level.

DFT/B3LYP/cc-PVDZ		
Trans *ortho*-aminophenolH^+		
tautomer	Calculated energy (Hartree)	Energy relative to the most stable tautomer(eV)
NH3	- 362.9946	0
C3	- 362.9830	0.30
C4	- 362.9714	0.61
C5	- 362.9810	0.36
C6	- 362.9830	0.30
para-aminophenolH^+		
NH3	- 362.9894	0
C2	- 362.9656	0.65
C3	- 362.9805	0.24

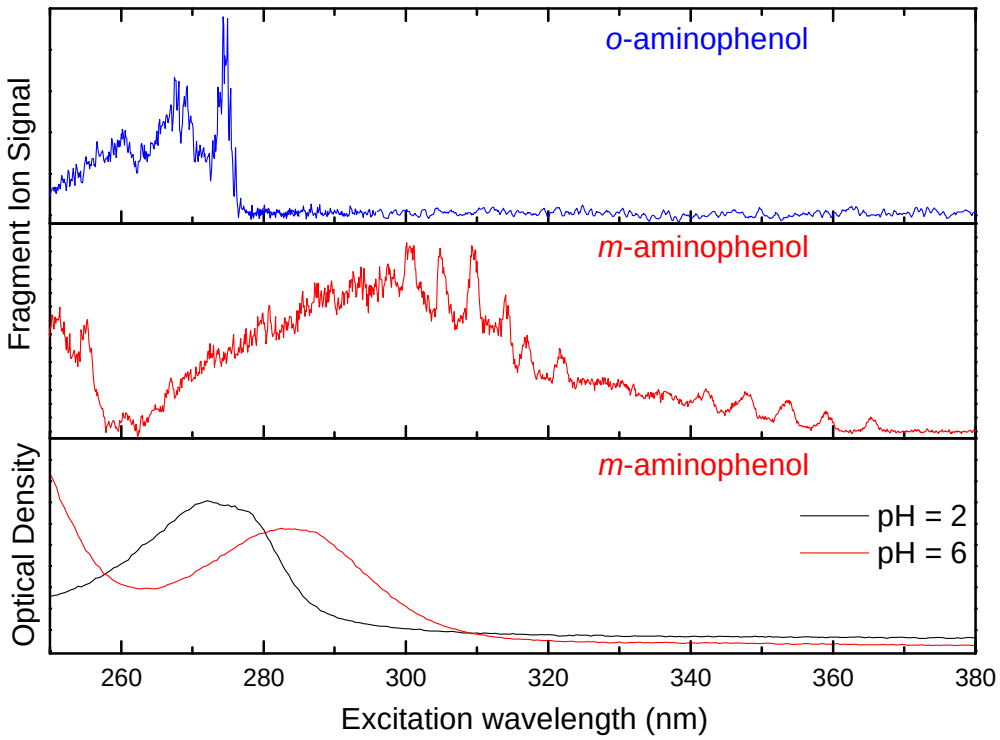

Figure SI.3: Comparison between gas phase photofragmentation spectra of protonated aminophenols and liquid phase absorption spectra for *m*-aminophenol at different pHs. The condensed phase spectra have been recorded with a CARY spectrophotometer, the solution being 10^{-4} molar in a 50/50 methanol/water solvent, as that used in the electrospray source. At low pH, *m*-aminophenol is expected to be protonated and the spectrum exhibits a band at 275 nm, the signature of protonation on the amino group, which is in good agreement with calculations.