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

SUPPLEMENTARY INFORMATION

Characterization of the ion trap temperature

The experimental spectrum of protonated benzaldehyde, recorded in the ion trap under the same experimental conditions as the spectra of the protonated DNA bases, is shown in the following figure together with the Franck-Condon simulation at different temperatures. It is clearly observed that the temperature of the ions is around or lower than 50K considering the signal to noise ratio. Benzaldhyde was chosen since it is one molecule for which the Franck-Condon analysis is working the best.[1]

(1) Alata, I.; Omidyan, R.; Dedonder-Lardeux, C.; Broquier, M.; Jouvet, C. Electronically excited states of protonated aromatic molecules: benzaldehyde. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11479–86.

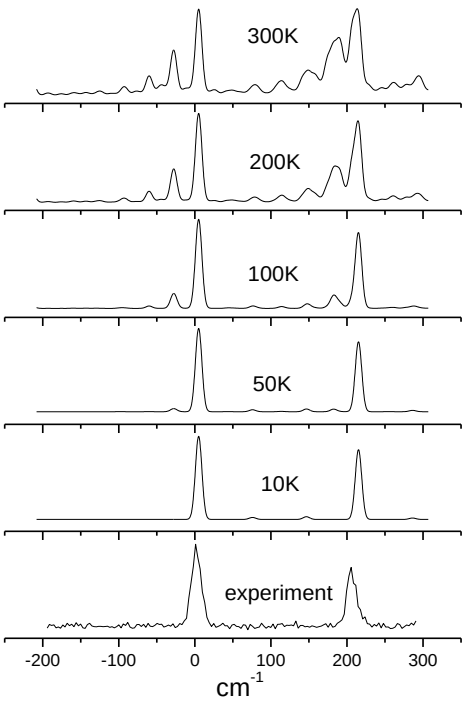

Figure SI1: (Bottom) Experimental spectrum of protonated benzaldehyde, recorded under the same experimental conditions as the spectra of the protonated DNA bases. Franck-Condon simulation at different temperatures.

Low resolution extended spectral range for TH^+

Since the time to record a spectrum is quite long, we first recorded the spectra in the whole spectral range in a fast mode and then, in the spectral regions where we observed transitions, the spectra were recorded again with small scanning steps.

In the case of TH^+, the fast mode spectrum did not show any transition in the 290 – 330 nm spectral region, as shown in the following Figure. Therefore, we did not explore this region with higher resolution and we only showed in the ms the region recorded at small scan steps where the transitions appear.

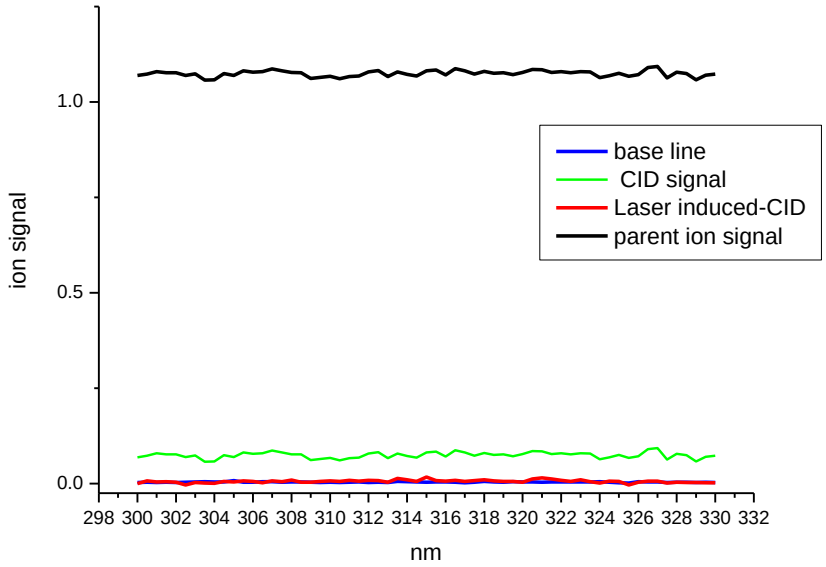

Figure SI2: TH^+ signal recorded in the (290 -330) nm spectral region, in black parent ion signal, in green photon induced + collision induced dissociation signal, in red photon induced signal. Thus there is no detectable transition in this spectral region.