

## Supporting information of the manuscript:

### Photodissociation Electronic Spectra of Cold Protonated Quinoline and Isoquinoline in the Gas-Phase

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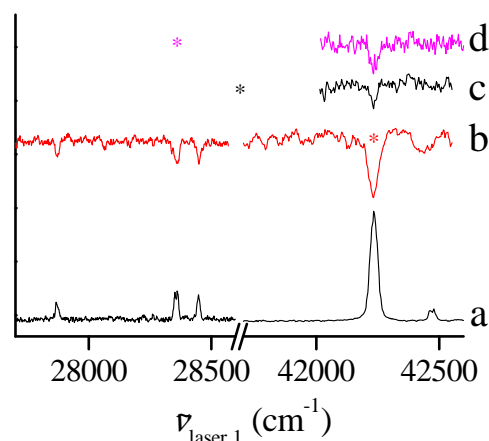
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### Double Resonance Experiments:

We have performed UV–UV ion-dip spectra by scanning the wavelength  $\lambda_1$  of a so-called burn laser pulse, fired across the ion trap about 40 ms earlier than a second laser pulse (probe laser) that is kept at a fixed  $\lambda_2$ . The selection of a given conformer is done by setting the probe wavelength on one specific transition. The burn-induced population depletion of the probed conformer causes signal dips in the spectrum whenever  $\lambda_1$  is resonant with any transition of this ion. However, in order to exclusively collect the ion signal produced by the probe laser, the fragments generated earlier by the burn pulse must be removed from the trap. This is done by destabilizing their trajectories using specific auxiliary dipolar radiofrequencies following the procedure described in a previous publication.<sup>1</sup> The laser wavelengths  $\lambda_1$  and  $\lambda_2$  are selected within  $8\text{ cm}^{-1}$  by use of two optical parametric oscillators (EKSPLA, model-NT342B) that operate with scanning steps up to 0.02 nm, pulse energies of  $\sim 0.5\text{ mJ}$  and a duty cycle of 10 Hz.

In Figure S1, the  $m/q = 77$  mass channel photofragmentation spectrum of  $\text{QH}^+$  (a) is compared with the UV–UV ion-dip spectrum for the same ion (b), with the latter being

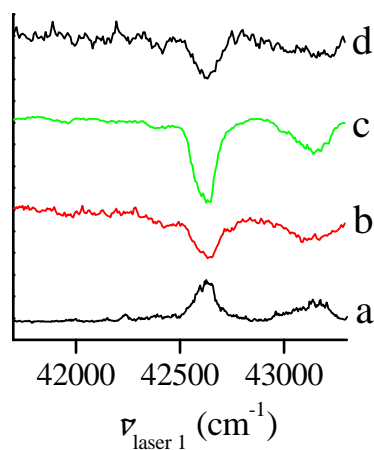
probed on the  $\tilde{\nu}_{0-0}$  band of the  $S_3$  state ( $\tilde{\nu}_{\text{laser } 2} = 42230 \text{ cm}^{-1}$ ). Ion yield dips appear whenever  $\text{QH}^+$  absorbs energy, not only while scanning the probed excited state but also in the  $S_1$  spectral region. Likewise, UV–UV ion-dip spectra for  $m/q = 103$  ions show evident dips at the  $\tilde{\nu}_{0-0}$  band of the  $S_3$  state ( $42230 \text{ cm}^{-1}$ ) when probed on the first broad peak of  $S_2$  (c) or on the  $\tilde{\nu}_{32}$  vibrational band of  $S_1$  (d). Ion extraction has to be delayed 20 ms to collect sufficiently large  $m/q = 103$  signal upon  $S_3$  excitation (spectra c and d). These results are a clear indication that the three vibronic transitions ( $S_1 \leftarrow S_0$ ,  $S_2 \leftarrow S_0$  and  $S_3 \leftarrow S_0$ ) shown in Figure S1 are originating from excitation of same  $\text{QH}^+$  tautomer.



**Figure S1.** Photofragmentation (a) and UV–UV ion-dip spectra of protonated quinoline recorded on the  $m/q = 77$  (b) and 103 (c, d) mass channels as a function of the excitation frequency ( $\tilde{\nu}_{\text{laser } 1}$ ,  $\text{cm}^{-1}$ ). Probe laser (\*) fixed at: (b),  $42230 \text{ cm}^{-1}$  ( $\tilde{\nu}_{0-0}$  band of the  $S_3$  state); (c),  $31908 \text{ cm}^{-1}$  (first broad peak of the  $S_2$  state); (d),  $28353 \text{ cm}^{-1}$  ( $\tilde{\nu}_{32}$  band of the  $S_1$  state).

A similar result is obtained for protonated isoquinoline. In Figure S2 it is shown a portion of the  $S_3 \leftarrow S_0$  photofragmentation spectrum of  $\text{iQH}^+$  recorded on the  $m/q = 77$  mass channel (a), and the UV–UV ion-dip spectra recorded for the same ion probed on the  $30_0^1$  band of the  $S_3$  state at  $42644 \text{ cm}^{-1}$  (b) and on the  $0_0^0$  band of the  $S_1$  state at  $28043 \text{ cm}^{-1}$  (c). A signal dip at  $\tilde{\nu}_{\text{laser } 1} = 42644 \text{ cm}^{-1}$  is found not only for  $\tilde{\nu}_{\text{laser } 2}$  tuned on the  $30_0^1$  band of the  $S_3$  state (b) but also on the  $0_0^0$  band of the  $S_1$  state (c). The same signal dip at  $\tilde{\nu}_{\text{laser } 1} = 42644 \text{ cm}^{-1}$  is observed in the UV–UV ion-dip spectrum for  $m/q = 103$  probing the  $0_0^0$  band

of the  $S_1$  state (d). These observations imply that the  $iQH^+$  electronic spectra presented in Figure 5 correspond to a single tautomer.



**Figure S2.** Photofragmentation (a) and UV–UV ion-dip spectra of protonated isoquinoline recorded on the  $m/q = 77$  (b, c) and 103 (d) mass channels as a function of the excitation frequency ( $\tilde{\nu}_{\text{laser } 1}$ ,  $\text{cm}^{-1}$ ). Probe laser fixed at: (b), 42644  $\text{cm}^{-1}$  ( $30_0^1$  band of the  $S_3$  state); (c) and (d), 28043  $\text{cm}^{-1}$  ( $0_0^0$  band of the  $S_1$  state).

## Bibliography:

1. Kang, H.; Féraud, G.; Dedonder-Lardeux, C.; Juvet, C. New Method for Double-Resonance Spectroscopy in a Cold Quadrupole Ion Trap and Its Application to UV–UV Hole-Burning Spectroscopy of Protonated Adenine Dimer. *J. Phys. Chem. Lett.* **2014**, *5*, 2760–2764.