

Supporting Information

Exploring the Relevance of Gas-phase Structures to Biology: Cold Ion Spectroscopy of the Decapeptide Neurokinin A.

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Chemicals

Neurokinin A (Abcam Biochemicals) was purchased and used without further purification. Peptide solution at 50 μM concentration was prepared in mixtures of 100/0, 50/50 and 0/100 water/methanol solvents with 1% of acetic acid.

Photofragmentation mass spectrum of NKA

Figure S1 shows photofragmentation mass spectrum for doubly protonated NKA. UV laser wavenumber is fixed at 37431 cm^{-1} . The lightest of the detected fragments (Figure S1) corresponds to the loss of the Phe side chain, which is a well-known prompt fragmentation channel, specific to electronic excitation of Phe chromophore. The two most abundant fragments correspond to the loss of neutrals with the masses correspond

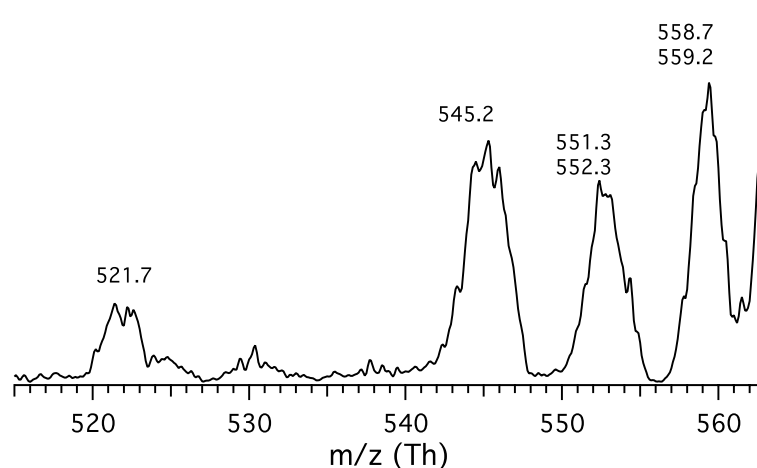


Figure S1. UV-induced photofragmentation mass spectrum of doubly protonated NKA. The rising edge of the largely prevailing parent ion ($m/z=567.7\text{ Th}$) is visible on the right.

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to the loss of NH_3 (ammonia) from the Lys side chain, H_2O loss from Asp or Ser side chains and COOH loss from Asp side chain. The peak near 552 Th might correspond to $[\text{b}_5 - \text{NH}_3]^{1+}$ or $[\text{b}_5 - \text{H}_2\text{O}]^{1+}$ fragment.

UV spectrum of NKA dissolved in 1:1 water-methanol solution.

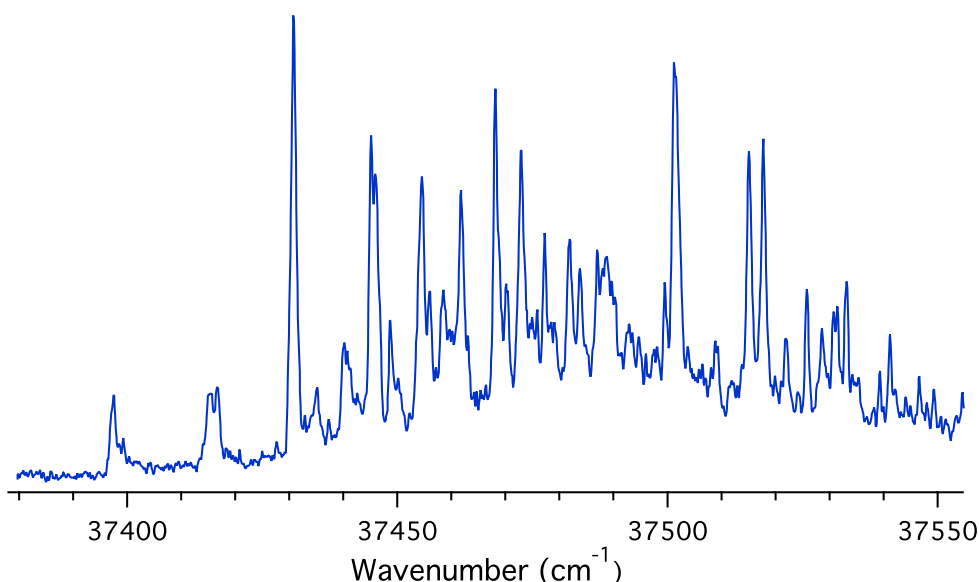


Figure S2. UV photofragmentation spectra of doubly protonated NKA dissolved in 50:50 water-methanol solution with 1% of acetic acid. The spectra were measured by detecting all fragments within 540 to 556 Th window of m/z .

IR-UV “hole-burning” spectroscopy

Figure S3 shows IR depletion spectra of five NKA conformers in the $3400\text{-}3700\text{ cm}^{-1}$ region, where vibrational transitions are well resolved. For each of the five conformers, except the conformer IV, we have chosen a unique vibrational transition, labelled in figure S3 with the corresponding numbers. The corresponding hole-burning spectra are shown in figure S4.

All well-resolved vibrational transitions of conformer IV strongly overlap with transitions of other conformers. We therefore recorded the “hole-burning” spectra of these conformers while exciting the transition that belongs to both conformers I and IV. Provided that we have already identified all the UV peaks, associated with conformer I, we may assume that the additionally removed electronic transitions belong to the conformer IV.

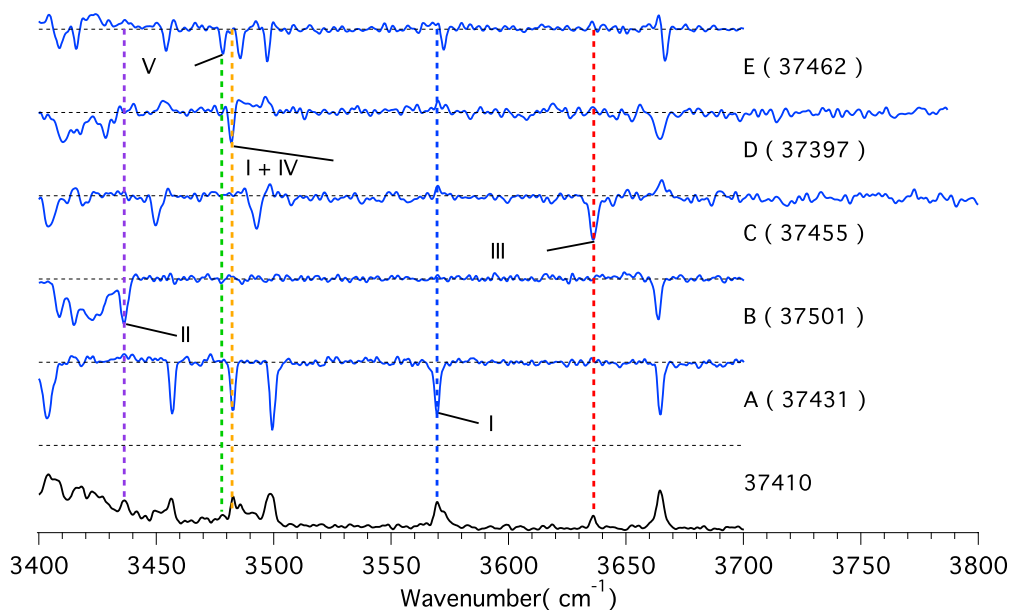


Figure S3. Unique vibrational peaks of each conformer, used for IR-UV "hole-burning" spectroscopy.

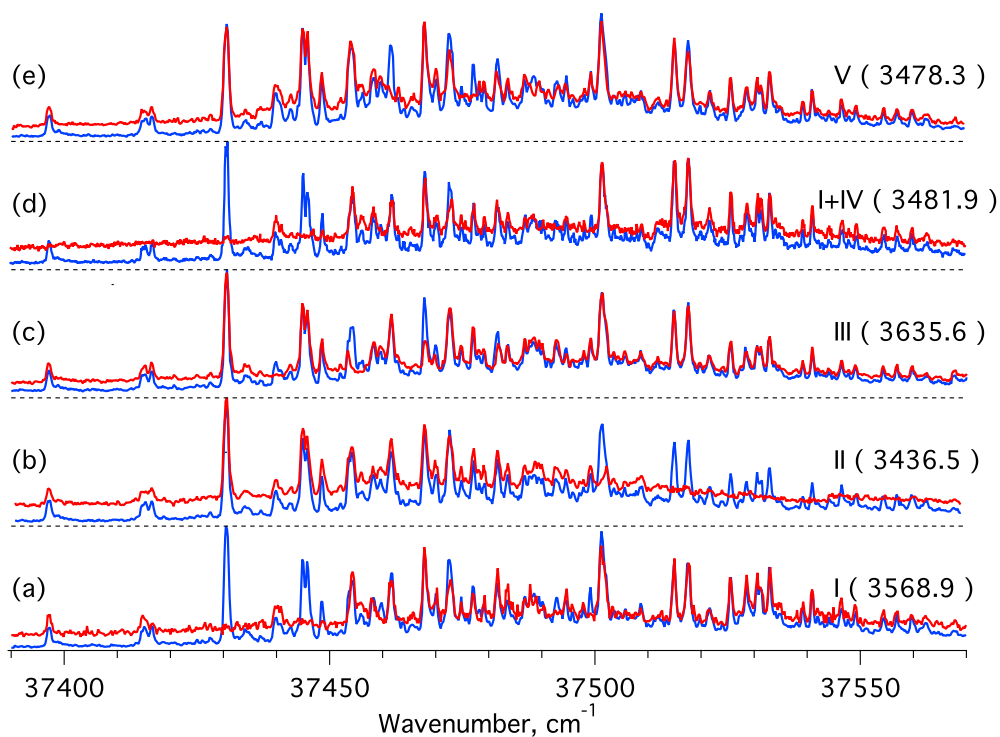


Figure S4. IR-UV "hole-burning" spectra of NKA. (a)-(e) correspond to IR laser wavenumber fixed at vibrational transitions, marked I – V in Fig. S3, respectively.