Supplementary Materials for

Interplay of Intra- and Intermolecular H Bonding in a Progressively Solvated Macrocyclic Peptide

Natalia S. Nagornova, Thomas R. Rizzo, Oleg V. Boyarkin*

*To whom correspondence should be addressed. E-mail: oleg.boiarkin@epfl.ch

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Interplay of Intra- and Intermolecular H-Bonding in a Progressively Solvated Macrocyclic Peptide

Natalia S. Nagornova, Thomas R. Rizzo and Oleg V. Boyarkin*

Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

* To whom correspondence should be addressed. E-mail: oleg.boiarkin@epfl.ch

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S1
Experimental method

We generate water complexes of doubly protonated gramicidin S in the gas phase from $5 \cdot 10^{-5}$ M solution of the peptide in pure water using a nanospray ion source. To generate complexes of GS with H$_2^{18}$O isotopologue we dissolve GS in water, which is isotopically enriched to 95% of $^{18}$O. In addition to this, the whole volume, which includes the electrospray needle and the capillary entrance, was sealed by a plastic cover to ensure no ambient air flow through the capillary. Dry nitrogen gas bubbled through a flask with H$_2^{18}$O was purged into the cover to maintain the inside pressure slightly above the atmospheric one. It took the whole night of purging to replace near 90% of the normal water, which likely sits on walls of the capillary and plastic cover, by its isotopologue. This isotopic replacement was evident from a change of relative intensities of the mass-peaks, corresponding to the clusters of the same size with H$_2^{16}$O and H$_2^{18}$O.

Protonated species pass through a quadrupole mass filter, which selects parent ions of a particular mass-to-charge ratio ($m/z$). The resolution of our mass-filter allows us unambiguously select only isotopically substituted clusters of n=8. After the m/z selection, the ions are transferred into a 22-pole ion trap, which is cooled to 6 K by a closed-cycle refrigerator. Clusters are cooled in collisions with a pulse of helium, which is introduced into the trap before the arrival of the ion packet. After about 80 ms, when the sample ions are cold and He has been pumped out, we interrogate our sample with IR and UV pulses that are sent through the trap. UV photofragmentation is performed using the 2-3 mJ output of a frequency-doubled dye laser pumped by 7 ns pulses of a Nd:YAG laser at 355 nm. Absorption of UV laser light by the parent ions leads to their fragmentation, which we monitor by measuring a particular charged fragment, selected by the second quadrupole mass filter and detected by a channeltron electron multiplier. For n≥16 clusters the most abundant charged fragments are those, which loose 15-17 water molecules. The fragmentation of smaller clusters yields doubly protonated bare GS, which we detect to monitor UV and IR absorption.

For IR spectroscopy we use the 3–5 mJ output of an optical parametric oscillator (OPO), which is pumped by 8 ns pulses of a Nd:YAG laser. To record conformer-selective IR spectra we employ IR-UV double resonance detection (30-35) where an IR pulse precedes a UV pulse by approximately 200 ns. In this scheme IR absorption spectra of parent cluster ions are generated by fixing the wavenumber of the UV laser on a photofragmentation transition of a particular conformer and monitoring the reduction of UV fragmentation as a function of the IR laser wavenumber.
The only exception is the IR spectrum of singly solvated \([\text{GS}+2\text{H}]^{2+}\), for which we did not detect any charged UV-induced fragments. We therefore measured conformer non-selective IR spectra of this cluster using 12 mJ output of IR OPO only and by detecting bare \([\text{GS}+2\text{H}]^{2+}\), which is the only IR-induced charged fragment that we see.

**Figure S1.**
Calculated structure of the most stable \([\text{GS}+2\text{H}]^{2+}\) conformer (27). Hydrogen and \(\text{NH}_3^+\)-\(\pi\) electron bonds are shown by dashed lines.
Figure S2.
Snapshot of a mass-spectrum, showing distribution of $[\text{GS}+2\text{H}]^{2+}(\text{H}_2\text{O})_n$ clusters, produced by a nano-electrospray under the conditions, optimized for low-size clusters. Appropriate adjustments of voltages and of drying gas flow of the electrospray allow some control of the cluster size distribution.
Figure S3.

All measured electronic spectra of cold, doubly protonated gramicidin S and its complexes with n water molecules, \([\text{GS}+2\text{H}]^{2+}(\text{H}_2\text{O})_n\) \((2 \leq n \leq 50)\), obtained by detecting the fragment complexes \([\text{GS}+2\text{H}]^{2+}(\text{H}_2\text{O})_m\) with \(m=n-16\pm1\) for \(n>16\), but \([\text{GS}+2\text{H}]^{2+}\) for \(2 \leq n \leq 15\).
References


