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

Supplementary information for

"Proton in the ring: spectroscopy and dynamics of proton bonding in macrocycle cavities"

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Animation of BOMD trajectories

Animated configuration sequences extracted from the BOMD trajectories illustrating the proton sharing effects discussed throughout the paper are available in gif format. Please, contact the corresponding author Bruno Martínez-Haya (bmarhay@upo.es) to access the animation files.

The proton sharing effects represented the animations are as follows:

Anim1.gif: proton sharing between opposite oxygen atoms in 12c4-H^+

Anim2.gif: proton sharing between opposite nitrogen atoms in cyclen-H^+

Anim3.gif: rotation of NH_2^+ group in cyclen-H^+

Anim4.gif: migration of proton to a different intracavity bond (D1 to D2) in 15c5-H^+

Anim5.gif: migration of proton to a different intracavity bond (D2 to D3) in 15c5-H^+

Anim6.gif: migration of proton to a different intracavity bond (D4 to D3) in 15c5-H^+

Anim7.gif: migration of proton to a different intracavity bond (E1 to E2) in 18c6-H^+

BOMD spectra of 12c4-H+ and cyclen-H$^+$ conformers inconsistent with experiment

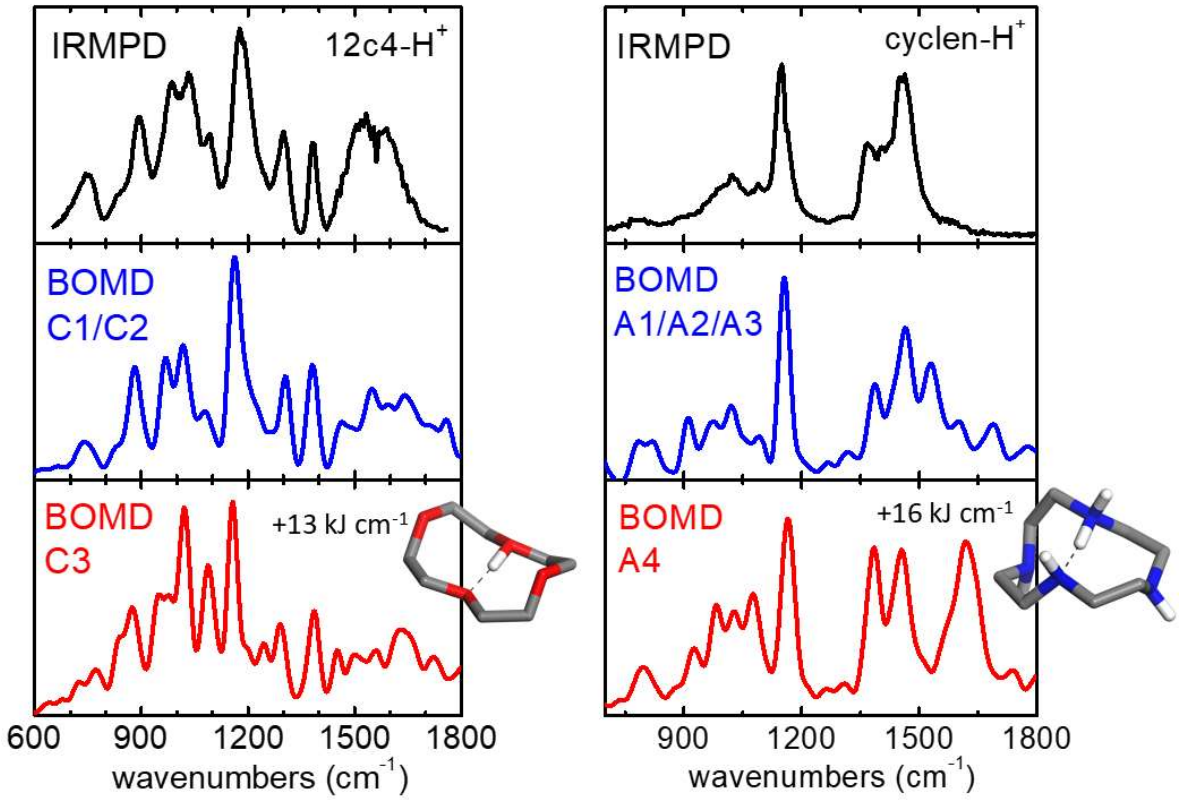

Fig. S1: BOMD infrared spectra computed for additional conformers of the 12c4-H$^+$ (left) and cyclen-H$^+$ (right) systems. These conformers, denoted C3 and A4, lie at B3LYP-D3 DFT energies 13 and 16 kJ mol^{-1} above the most stable conformers C1 and A1, respectively, due to unfavorable backbone configurations. Their BOMD spectra (bottom panels) display appreciable differences with the IRMPD experiment (top panels), particularly in the 1000-1100 cm^{-1} and 1300-1700 cm^{-1} regions, which rules out a relevant contribution of these conformers to the experimental observations. In this work, the dynamics of the 12c4-H$^+$ and cyclen-H$^+$ systems are rationalized in terms of the joint contribution of the C1/C2 and A1--A3 conformations, respectively (see Fig. 2), whose BOMD spectra provide a fairer match to the IRMPD experiment (middle panels, see also Fig. 6).