QUANTIFICATION OF STRUCTURAL ISOMERS VIA MODE-SELECTIVE IRMPD

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Mixtures of structural isomers can pose a challenge for vibrational ion spectroscopy. In cases where particular structures display diagnostic vibrations, these structures can be selectively ”burned away”. In ion traps, the ion population can be subjected to multiple laser shots, in order to fully deplete a particular structure, in effect allowing a quantification of this structure. Protonated para-amino benzoic acid (PABA) serves as an illustrative example. PABA is known to preferentially exist in the N-protonated (N-prot) form in solution, but in the gas phase it is energetically favorable in the O-protonated (O-prot) form. As shown in Figure 1, the N-prot structure can be kinetically trapped in the gas phase when sprayed from non-protic solvent, whereas the O-prot structure is obtained when sprayed from protic solvents, analogous to results by others [1,2]. By parking the light source on the diagnostic 3440 cm^{-1}mode, the percentage of the O-prot structure can be determined, and by default the remainder is assumed to adopt the N-prot structure. It will be shown that the relative percentages of O-prot vs N-prot are highly dependent on the solvent mixture, going from close to 0% O-prot in non-protic solvents, to 99% in protic solvents. Surprisingly, water behaves much more like a non-protic solvent than methanol. It is observed that the capillary temperature, which aids droplet desolvation by black-body radiation in the ESI source, is critical to promote the appearance of O-prot structures. These results are consistent with the picture that a protic bridge mechanism is at play to facilitate proton transfer, and thus allow conversion from N-prot to O-prot, but that this mechanism is subject to appreciable kinetic barriers on the timescale of solvent evaporation. 1. J. Phys. Chem. A 2011, 115, 7625. 2. Anal. Chem. 2012, 84, 7857.