

Proton transfer in nucleobases is mediated by water

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I. EXPERIMENTAL DETAILS

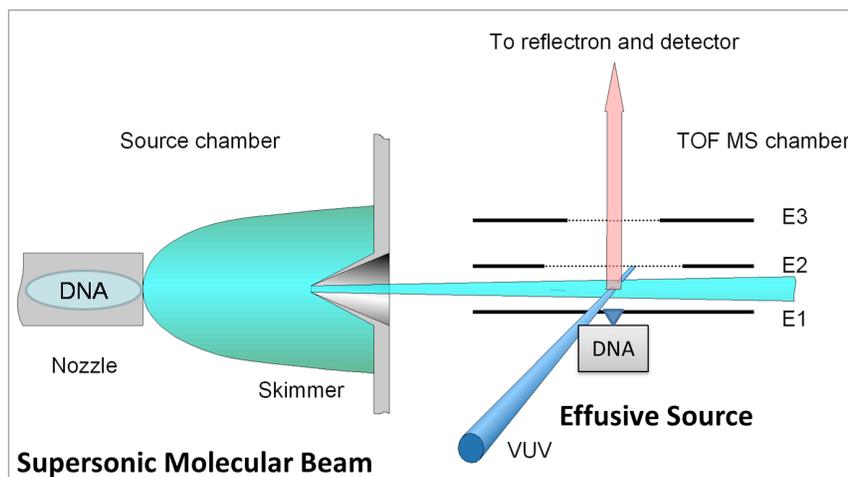


FIG. S1: Schematic of experimental apparatus.

The experiments were performed on a molecular beam apparatus coupled to a 3 meter VUV monochromator on the Chemical Dynamics Beamline at the Advanced Light Source. The experimental apparatus is described in Fig. S1 and in Ref. [1]. To generate monomers and dimers in a supersonic jet expansion, a small sample is placed in a thermal vaporization source (3/8" tube with 100 μm orifice) and heated to generate sufficient vapor pressure.

Argon gas at 600 Torr was bubbled through water (D_2O) and then passed over the sample vapors (1,3-mU from Sigma-Aldrich, at 112 $^\circ\text{C}$) before expanding to vacuum through a 100 μm orifice and a 2 mm skimmer (1 cm downstream) to produce a molecular beam at the interaction region of a reflectron mass spectrometer (R. M. Jordan) where it is ionized by the

VUV light. As the synchrotron light is quasi-continuous (500 MHz), pulsing the electrical fields of the ion optics forms the ion packet in the mass spectrometer. Measurements are taken at photon energies between 8 eV and 12 eV with a step size of 50 meV. The ion signals from the microchannel plate detector are collected with a multichannel-scalar card (FAST Comtec 7889) and accumulated over multiple (e.g., 300,000) sweeps at each point of the scan[2]. We repeated the experiments with H₂O vapors and d6-1,3-mU, the latter is unavailable commercially, and therefore it was synthesized according to the procedure developed by Davidson and Baudisch (Davidson and Baudisch 1926) and we described in detail in our previous paper[3].

II. RELEVANT STRUCTURES OF METHYLATED URACIL CLUSTERS AND MICROHYDRATES

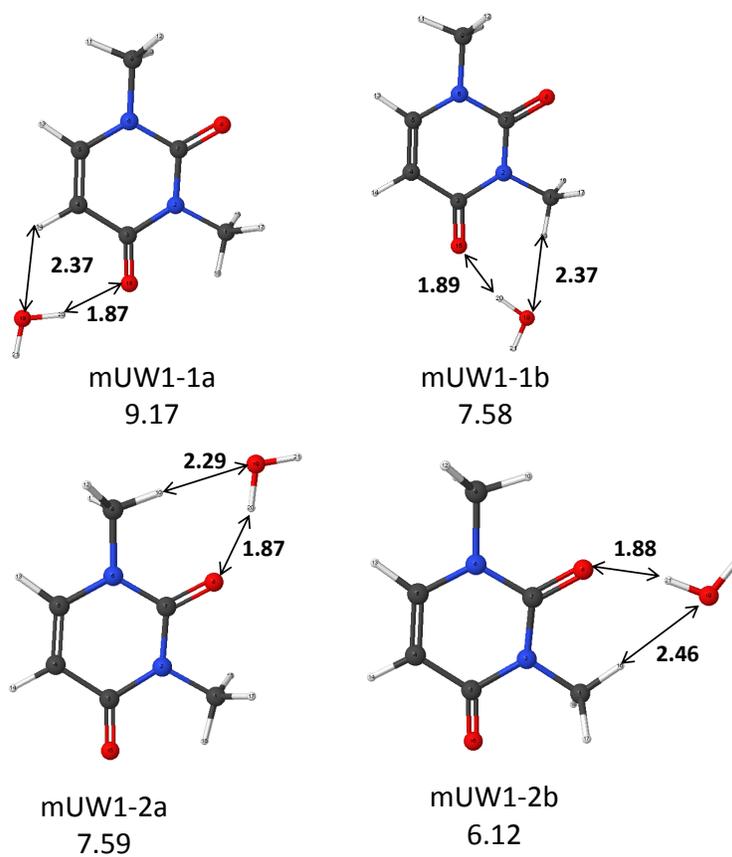


FIG. S2: Monohydrated structures. Distances in angstroms and binding energies in kcal/mol are given for each structure. The lowest-energy isomer is mUW1-1a. mUW1-1b, mUW1-2a, and mUW1-2b are 1.59, 1.58 and 3.06 kcal/mol higher, respectively.

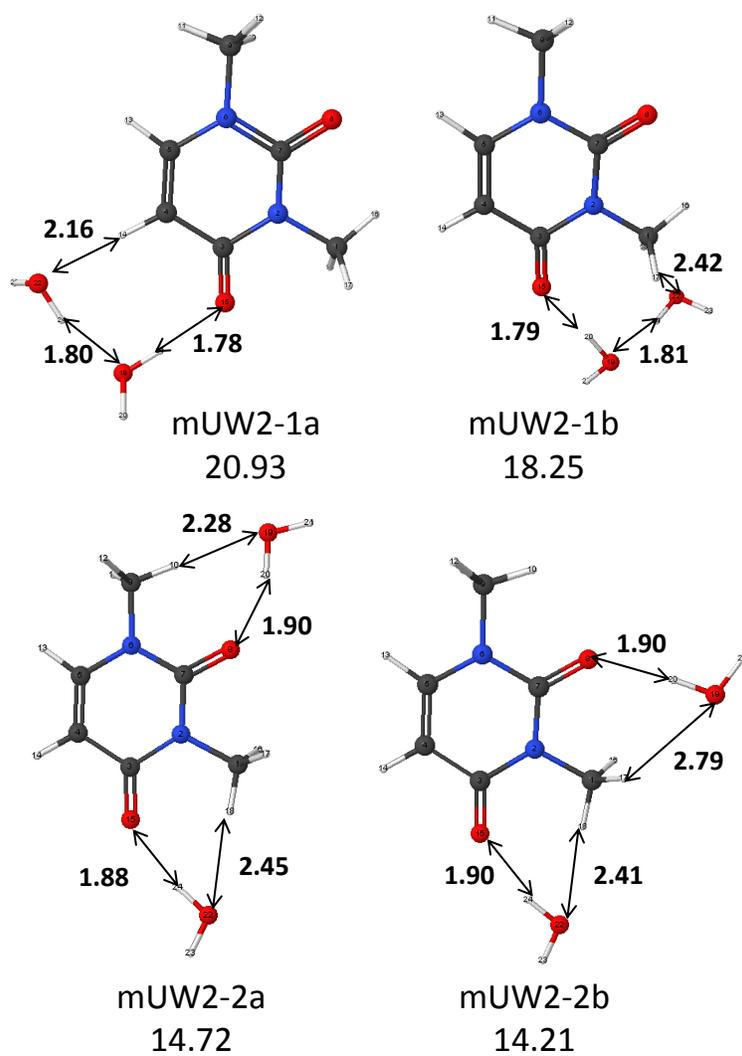


FIG. S3: Dihydrated structures. Distances in angstroms and binding energies in kcal/mol are given for each structure. The lowest-energy isomer is mUW2-1a.

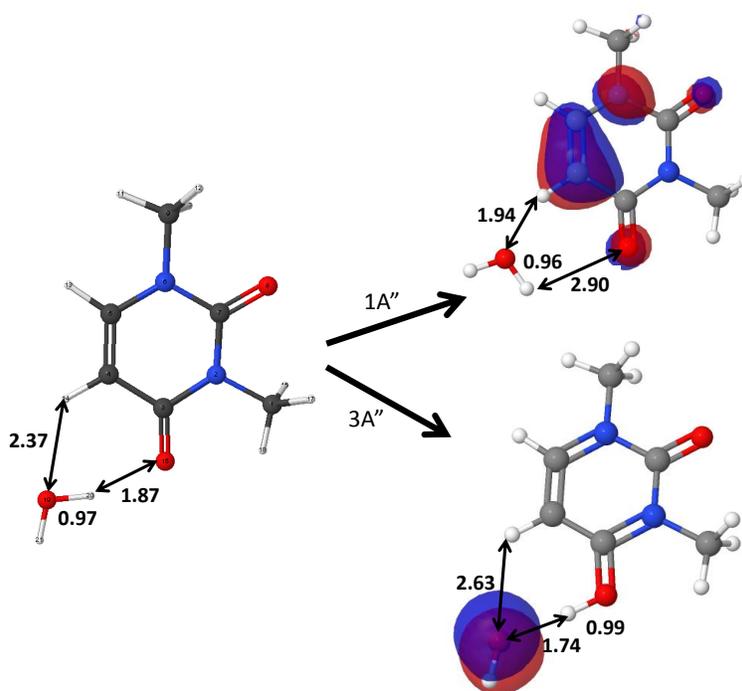


FIG. S4: Structural changes in ionized mUW1-1a. Left: optimized neutral state. Top right: Franck-Condon optimized structure of the 1^{st} ($1A''$) adiabatic state of the cation. Bottom right: optimization of the 5^{th} ($3A''$) adiabatic state of the cation gives optimized proton-transferred structure of the cation.

III. THYMINE CLUSTERS

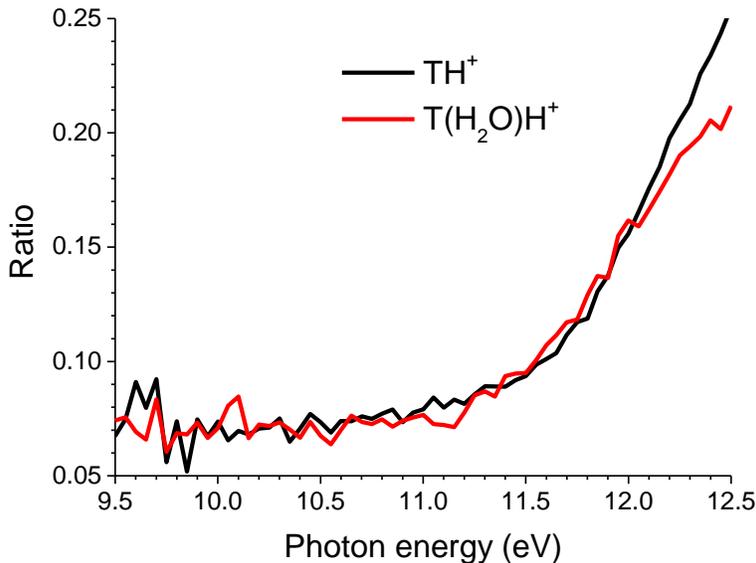


FIG. S5: Yield of protonated thymine (TH) and thymine-water (T(H₂O)H⁺) clusters.

Fig. S5 shows the yield of protonated thymine (TH⁺) and thymine-water (T(H₂O)H⁺) clusters as a function of ionization energy. We observe that the onsets for TH⁺ and T(H₂O)H⁺ are the same, which is similar to the mU(H₂O)_nH⁺ appearance energies that do not depend on the cluster size. Note that in the absence of water, PT in thymine occurs at 9.20 eV, with a major rise in signal between 9.7 and 9.9 eV[4]. Thymine provides an interesting comparison since we have demonstrated previously[4], hydrogen bonded and π -stacked dimers populate the molecular beam in contrast to dimethyluracil, where only π -stacked dimers exist. The calculations suggest that it is hydrogen bonded thymine dimers which give rise to this signal, while the lower onset is explained by a dimer with π -stacked geometry. Upon solvation, PT switches off at these lower energies, as is evidenced in the signal for TH⁺ and T(H₂O)H⁺ shown in Fig. S5. Using a similar analysis as performed for mU, a constant ratio of 0.073 is due to isotopes while the onset of PT begins around 10.6 eV, with a major rise at 11.2 eV. Both the onset and the shapes of the appearance curves are very similar to those for mU shown in Fig. 6 of the main manuscript, suggesting that a similar PT mechanism from the solvent is occurring. This means, whether one has hydrogen bonded or π -stacked nucleobase dimers and higher clusters, upon solvation, PT which was quite effective from cluster fragmentation shuts down completely from the base itself. It is

only when the solvent is ionized that PT begins again.

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