

# Infrared Multiphoton Dissociation Spectroscopy of Protonated Uracil and Thiouracils: Effects of Thioketo-substitution on Gas-Phase Conformation

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The gas-phase structures of protonated complexes of uracil (U) and five thiouracils including: 2-thiouracil (2SU), 5-methyl-2-thiouracil (5Me2SU), 6-methyl-2-thiouracil (6Me2SU), 4-thiouracil (4SU), and 2,4-dithiouracil (24dSU) are examined via infrared multiple photon dissociation (IRMPD) action spectroscopy and theoretical electronic structure calculations. The IRMPD action spectra of these six protonated complexes exhibit both similar and distinct spectral features over the range of  $\sim 1000$  to  $1900$   $\text{cm}^{-1}$  such that the complexes are easily differentiated by their IRMPD action spectra (see Figure). Absence of the carbonyl stretch at  $\sim 1825$   $\text{cm}^{-1}$  in the IRMPD spectra for the  $\text{H}^+(\text{U})$ ,  $\text{H}^+(2\text{SU})$ ,  $\text{H}^+(5\text{me}2\text{SU})$ , and  $\text{H}^+(6\text{Me}2\text{SU})$  complexes suggests that the binding of a proton reduces the carbonyl functional groups in these complexes. In contrast, the intense band at  $\sim 1825$   $\text{cm}^{-1}$  in the IRMPD action spectrum of  $\text{H}^+(4\text{SU})$  indicates that the carbonyl group is not reduced in this complex. Measured IRMPD action spectra are compared to linear IR spectra calculated at the B3LYP/6-31G\* level of theory to identify the structures accessed in the experimental studies. On the basis of these comparisons and energetics derived from the calculations, it is clear that binding of a proton stabilizes a minor tautomer of the nucleobase in the  $\text{H}^+(\text{U})$ ,  $\text{H}^+(2\text{SU})$ ,  $\text{H}^+(5\text{me}2\text{SU})$ , and  $\text{H}^+(6\text{Me}2\text{SU})$  complexes, where the diketo, thioketo-oxo, dithioketo groups are reduced by proton binding and transfer of the N3H proton. In contrast, the proton preferentially binds at the 4-thioketo position to the canonical oxo-thioketo tautomer in the  $\text{H}^+(4\text{SU})$  complex. Additional bands are present in the IRMPD action spectra of the  $\text{H}^+(\text{U})$  and  $\text{H}^+(4\text{SU})$  complexes that suggest that a small population of excited low-energy conformers are also accessed in the experiments.

