

Conformational Structures of Jet-cooled Acetaminophen–water Clusters: A Gas Phase Spectroscopic and Computational Study

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Acetaminophen (AAP) is a widely used over-the-counter antipyretic and analgesic, a major ingredient in various cold and flu drugs, Tylenol®. On the basis of the results with AAP monomer, we would like to step further on the study of AAP–water clusters. For the acetaminophen (AAP)–water clusters (AAP–(H₂O)₁) have been investigated by mass-selected resonant two-photon ionization (R2PI), ultraviolet-ultraviolet hole-burning (UV–UV HB), infrared-dip (IR-dip), and infrared-ultraviolet hole-burning (IR–UV HB) spectroscopy. Each *syn*- and *anti*-AAP rotamer has three distinctive binding sites (–OH, >CO, and >NH) for a water molecule, thus 6 different AAP–(H₂O)₁ conformers are expected to exist in the molecular beam. The origin bands of the AAP(OH)–(H₂O)₁ and AAP(CO)–(H₂O)₁ conformers (including its *syn*- and *anti*-conformers) in the R2PI spectrum are shifted to red and blue compared to those of the AAP monomer, respectively. The spectral assignments of the origin bands in the R2PI spectrum and the IR vibrational bands in the IR-dip spectra for the four lowest-energy conformers of AAP–(H₂O)₁, [*syn*- and *anti*-AAP(OH)–(H₂O)₁ and *syn*- and *anti*-AAP(CO)–(H₂O)₁], are aided by *ab initio* and time-dependent density functional theory (TDDFT) calculations. Further investigation on the IR-dip spectra has revealed a hydrogen-bonded NH stretching mode, supporting the presence of the *syn*-AAP(NH)–(H₂O)₁ conformer. Moreover, by employing IR–UV HB spectroscopy, we have reconfirmed the existence of the *syn*-AAP(NH)–(H₂O)₁ conformer, which happened to be buried underneath the broad background attributed from the AAP(OH)–(H₂O)₁ conformers

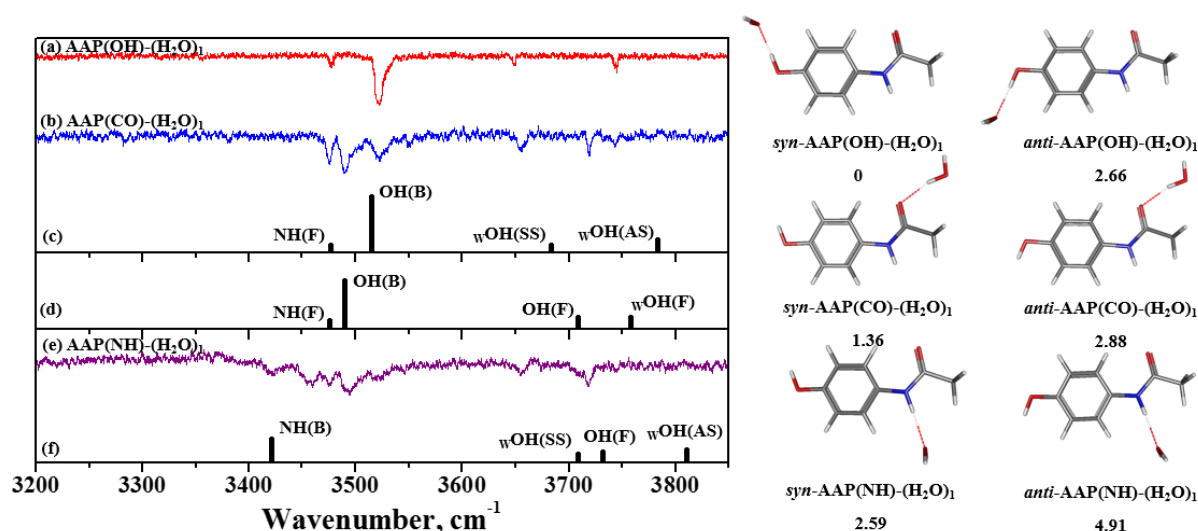


Figure 1. IR-dip and calculated IR bar spectra of three major *syn*-AAP–(H₂O)₁ conformers. The optimized structures of 6 different conformers of AAP–(H₂O)₁ in the ground state. The relative energies are shown below the corresponding structure (kJ/mol, zero-point energy corrected).