Energetics and Vibrational Signatures of Nucleobase Argyrophilic Interactions

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This study investigates the interactions of both purine (adenine and guanine) and pyrimidine (cytosine, thymine, and uracil) nucleobases with a pair of silver atoms (Ag_2). Full geometry optimizations were performed on several structures of each nucleobase/Ag_2 complex and the corresponding isolated monomers using the M06-2X density functional method with a correlation consistent triple-ζ basis set augmented with diffuse functions on all atoms and a relativistic pseudopotential on Ag (aug-cc-pVTZ for H, C, N, and O and aug-cc-pVTZ-PP for Ag; denoted aVTZ). Harmonic vibrational frequencies were computed in order to confirm that each structure corresponds to a minimum on the M06-2X/aVTZ potential energy surface. Relative electronic energies for interactions between Ag_2 and each nucleobase were compared to elucidate energetic differences between isomers. Further analysis of the changes in vibrational frequencies, infrared intensities, and Raman scattering activities reveals how different Ag_2 binding sites might be identified spectroscopically. These results provide molecular-level insight into the interactions between nucleobases and silver, which may lead to better understanding and interpretation of surface-enhanced Raman spectroscopy (SERS) experiments on nucleobases and related systems.