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Energetics and Vibrational Signatures of Nucleobase Argyrophilic Interactions

by

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A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

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Approved by

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Abstract

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 theory (DFT) method with a correlation consistent triple-$\zeta$ 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 frequency computations indicate that each optimized 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.
1 Introduction

1.1 Nucleobases

The groundbreaking discovery of DNA and RNA structures was the result of astonishing scientific research over several decades from the first discovery of nucleic acid by Miescher to the famous double helix model by Watson and Crick using Franklin’s X-ray crystallography work.1–3 DNA and RNA are found in the form of nucleotides, which are composed of a phosphate group, a pentose sugar (ribose for RNA and deoxyribose for DNA), and one of five nucleobases. Nucleobases can exist in multiple tautomeric forms, different from one another based on the position of the protons and double bonds.4 Figure 1 depicts the optimized structures of the most common resonance structures of purine (adenine and guanine) and pyrimidine (cytosine, thymine, and uracil) nucleobases in the tautomeric forms that can be found in DNA and RNA.5 The common numbering convention for atoms in the ring of nucleobases represented in Figure 1 is used throughout this study.
As the only varying component of nucleotides, nucleobases constitute the most important pieces of genetic information and are involved in many cellular processes. Thus, the ability to detect and identify individual nucleobase is a significant asset to many fields of science such as biology, biochemistry, analytical chemistry, and medicine.6–10

1.2 Vibrational Spectroscopy

Vibrational spectroscopy is a powerful analytical tool that provides a way to elucidate the structures of interaction in specific molecular systems as changes in the vibrational spectra of interacting molecules indicate which and to what extent atoms and bonds are affected by weak intermolecular interactions.11 This is possible because the vibrational energy levels are quantized and molecules have vibrations with each
vibrational mode having different energy.$^{12}$

Spectroscopy is regarded as the study of light-matter interactions as spectroscopic techniques are based on transitions that occur between different energy states of molecules when they interact with electromagnetic radiation. The two types of these interactions are absorption and scattering. Absorption occurs when the energy of the photon matches that of a vibrational, rotational, or electronic transition, whereas scattering occurs when the energy does not match. Infrared spectroscopy utilizes the absorption interaction, and Raman spectroscopy utilizes the scattering interaction.$^{12}$

1.3 Raman Spectroscopy

Raman spectroscopy can be used to study biomolecules because the Raman spectrum created by scattered light due to a change in polarizability can provide a structural fingerprint of a particular molecule.$^{13–16}$ Three different forms of scattering can occur: Rayleigh scattering, Stokes scattering, and anti-Stokes scattering shown in Figure 2.
Rayleigh scattering is elastic meaning that there is no energy change between the incident light and scattered light. On the other hand, there are energy changes in inelastic scattering, which are Stokes scattering and anti-Stokes scattering. In Stokes scattering, the molecule in the vibrational ground state is excited to the virtual state and relaxed to the vibrational excited state. In anti-Stokes scattering, the molecule in the vibrational excited state is excited to the virtual state and relaxed down to the vibrational ground state. Raman spectroscopy utilizes these inelastic scattering forms; thus, they are known as Raman scattering. The identification of biomolecules using Raman spectroscopy presents a difficult problem in which biomolecules have a small scattering cross-section and are found in low concentrations due to their low
solubility in water.\textsuperscript{15,17–19}

1.4 Surface-Enhanced Raman Spectroscopy

First discovered in 1974 through pyridine adsorbed at a silver electrode, surface-enhanced Raman spectroscopy (SERS) provides the solution for weak scattering.\textsuperscript{20} The weak Raman activity can be greatly enhanced by a factor of up to $10^{14}$, which provides a sufficient SERS cross section for single molecule detection, when the molecule is adsorbed onto a specially prepared metal surface or nanoparticles that can function as the antenna.\textsuperscript{16,21–28} This high enhancement factor allows for the acquisition of high resolution vibrational spectra of biomolecules from very diluted aqueous solutions down to $10^{-8} \text{ M}$.\textsuperscript{14,17,29} As such, the detection and identification of nucleotides are made possible due to the unique SERS spectra of nucleobases.\textsuperscript{13,22,29,30}

There are two widely accepted mechanisms for the SERS effect: electromagnetic enhancement (resonance between the incident or Raman scattered light with surface plasmons of the metal substrate) and chemical enhancement (a charge transfer between the metal and the adsorbate).\textsuperscript{8,13,16,18,19,23,25–27,31} The physical-chemical phenomena present in SERS can be understood better by theoretical studies, which can provide information on relationship between the molecular level properties of the interfacial structure and the SERS process.\textsuperscript{27,32,33}

Unfortunately, a detailed knowledge of the interactions between nucleobases and metal surface is difficult to obtain because the adsorption and Raman properties depend strongly on adsorption site, and multiple binding sites are available in nucleobases.\textsuperscript{34,35} The knowledge of the preferred adsorption site of silver on each nucleobase can provide molecular-level insight into the interactions between nucleobases and silver because varying interacting sites lead to different structural modulations, which can change the electron distribution force constants, polarizability, dipole moment, and vibrational spectra.\textsuperscript{36} For these reasons, a theoretical investigation of the inter
actions between nucleobases and silver using computational chemistry is presented in this study.

1.5 The Schrödinger Equation

Computational chemistry utilizes simulation and modeling in many different ways to predict molecular properties for various chemical systems. One way to do this is solving the Schrödinger equation. Erwin Schrödinger was the first to formulate an equation that integrated an appropriate wave function needed to be solved for the wave-particle duality necessary for understanding physical phenomena at the atomic level. The Schrödinger equation ($\hat{H}\Psi = E\Psi$) contains three terms: the Hamiltonian operator ($\hat{H}$), the wave function ($\Psi$), and the total energy ($E$). $\hat{H}$ is the total energy energy operator that describes the kinetic and potential energies for each particle, and $\Psi$ is the $n$-electron wave function that depends on the identities and positions of the nuclei and on the total number of electrons. By solving the Hamiltonian operator and the wave function, it is possible to obtain the total energy of the system.$^{12}$

The Schrödinger equation has been successfully solved exactly for the hydrogen atom with only one electron. The presence of electron correlation in multi-electron atoms or molecules results in a loss of spherical symmetry, and the Schrödinger equation cannot be solved exactly for these multi-electron systems. The electrons dictate the most important aspects of the interactions; thus, computational chemists developed numerical methods that calculate approximate wave functions and values for observables such as energy, bond lengths and angles, and dipole moments.$^{12}$

1.6 Level of Theory

The selection of the level of theory, which is comprised of a method and basis set, is crucial to have the correct balance between the accuracy of the results and the computational demands. *Ab initio* methods attempt to solve the Schrödinger equation
as accurately as possible. This can be extremely challenging and computationally demanding, so density functional theory replaces the correlated motions of electrons with a physical observable, the electron density, allowing the computational demands to be much cheaper than the \textit{ab initio} methods. Of many different possible density functionals, M06-2X has been proven to adequately describe a variety of non-covalent interactions.\textsuperscript{18,37} A basis set mathematically describes the space in which the electrons reside. The basis set of choice (aug-cc-pVTZ-PP) utilizes a pseudopotential (PP) for Ag. Due to the large molecular weight and size of Ag, classical basis sets cannot be used. The pseudopotential replaces the core electrons to account for relativistic effects and helps to reduce the high computational demands of Ag. The level of theory used in this study was chosen specifically because the same level of theory was found to be the most effective at reproducing the experiment frequencies in the previous study of pyrimidine and its interactions with Ag\textsubscript{2} and H\textsubscript{2}O molecules.\textsuperscript{18}
2 Computational Details

Full geometry optimizations were performed on several structures of each nucleobase/Ag₂ complex and the corresponding isolated monomers using the M06-2X density functional theory (DFT) 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 as well as infrared intensities (IR) and Raman scattering activities (RA) were computed in order to confirm that each optimized structure corresponds to a minimum on the M06-2X/aVTZ potential energy surface and to investigate vibrational spectra of the nucleobase before and after complex formation.

A pair of silver atoms (Ag₂) is utilized to probe the interactions between the nucleobases and silver as well as the resulting spectroscopic perturbations. Even though, the number of silver atoms affects the adsorption and Raman properties, the adsorption site is more important in determining the binding interactions. The enhancement mechanism for small and large clusters of silver is similar, and the Raman enhancement decreases as the distance between the molecule and the silver cluster increases.

The electronic energetics of each nucleobase/Ag₂ complex with various binding sites are computed to determine the interaction strength of each nucleobase with Ag₂ depending on the binding site. This interaction strength will be referred to as binding energy \( E_{\text{bind}} = E_{\text{nucleobase/Ag}_2} - E_{\text{nucleobase}} - E_{\text{Ag}_2} \). The difference in \( E_{\text{bind}} \) in each nucleobase/Ag₂ complex with various binding sites will be referred to as relative energy \( \Delta E = E_{\text{nucleobase/Ag}_2} - E_{\text{minimum/nucleobase/Ag}_2} \).

Moreover, the vibrational signatures of nucleobase/Ag₂ complexes are examined because the analysis of changes in the vibrational spectra can provide detailed infor-
mation on the interaction between each nucleobase and silver as well as adsorption mechanism.\textsuperscript{11, 44}

All computations were performed using analytic gradients and Hessians available in the Gaussian 09 software package.\textsuperscript{45} Pure angular momentum ($5d$, $7f$, etc.) atomic orbital basis functions were used in place of their Cartesian counterparts ($6d$, $10f$, etc.) functions. Additionally, a pruned numerical integration grid having 99 radial shells and 590 angular points per shell was used. All electronic energies were converged to at least $1.0 \times 10^{-10}$ E$_h$, and the maximum Cartesian forces in the optimized structures were below $1.2 \times 10^{-5}$ E$_h$ a.u.$^{-1}$. 
3 Results and Discussion

3.1 Structures and Energetics

A variety of interactions between Ag$_2$ and electron rich regions of the nucleobases ($\pi$, N, and O) were examined because the adsorption process is thought to involve an interaction of the $\pi$-electron system of the heteroaromatic ring with a silver electrode.$^{46}$ Nevertheless, all initial structures collapsed during the geometry optimization to those shown in Figure 3 exhibiting either N or O interactions with the Ag$_2$ unit. Using these structures, intermolecular distances were defined by the shortest distance between an Ag atom and a nucleobase atom, denoted by the dashed lines in each structure.
Figure 3. Structures of each nucleobase/Ag$_2$ complex with varying binding sites optimized at the M06-2X/aVTZ level of theory.
Table 1 compares electronic binding energies ($E_{\text{bind}}$), relative energies ($\Delta E$), and intermolecular distances (R) of each nucleobase/Ag$_2$ complex shown in Figure 3.

**Table 1.** Electronic binding and relative energies ($E_{\text{bind}}$ and $\Delta E$ in kcal mol$^{-1}$) of nucleobase/Ag$_2$ complexes with varying binding sites computed at the M06-2X/aVTZ level of theory as well as intermolecular distances (R in Å) denoted by the dashed lines in Figure 3.

| Nucleobase | Binding Site | $E_{\text{bind}}$ | $\Delta E$ | R  |
|------------|--------------|-------------------|------------|----|
| Adenine    | N1           | −15.2             | +0.2       | 2.35 |
|            | N3           | −15.4             | 0.0        | 2.34 |
|            | NH$_2$ @ C6  | −8.2              | +7.2       | 2.50 |
|            | N7           | −14.8             | +0.6       | 2.33 |
| Guanine    | NH$_2$ @ C2  | −7.4              | +7.7       | 2.50 |
|            | N3           | −14.0             | +1.1       | 2.35 |
|            | O @ C6       | −13.6             | +1.4       | 2.36 |
|            | N7           | −15.1             | 0.0        | 2.35 |
| Cytosine   | O @ C2       | −14.4             | +3.0       | 2.33 |
|            | N3           | −17.4             | 0.0        | 2.35 |
|            | NH$_2$ @ C4  | −7.7              | +9.7       | 2.51 |
| Thymine    | O @ C2/N1    | −11.3             | 0.0        | 2.39 |
|            | O @ C2/N3    | −9.9              | +1.4       | 2.38 |
|            | O @ C4/N3    | −10.3             | +1.0       | 2.38 |
|            | O @ C4/C5    | −10.7             | +0.6       | 2.38 |
| Uracil     | O @ C2/N1    | −10.9             | 0.0        | 2.39 |
|            | O @ C2/N3    | −9.5              | +1.4       | 2.39 |
|            | O @ C4/N3    | −10.2             | +0.7       | 2.38 |
|            | O @ C4/C5    | −10.6             | +0.3       | 2.39 |

In the adenine/Ag$_2$ complex, four potential binding sites were identified (Figure 3). The one with Ag$_2$ interacting with N3 has the lowest electronic energy and therefore exhibits the strongest binding. The three $sp^2$ hybridized N binding sites (N1, N3, and N7) have $E_{\text{bind}}$ around $−15$ kcal mol$^{-1}$ (within ±0.5 kcal mol$^{-1}$ of each other). On the other hand, the out-of-plane binding at the $sp^3$ N (NH$_2$ @ C6) is 7 kcal mol$^{-1}$ higher in energy than that of the $sp^2$ hybridized N binding sites. In addition, intermolecular distance for the NH$_2$ site increases by 0.15 Å. This same trend in $E_{\text{bind}}$, $\Delta E$, and R
can be seen in the guanine/Ag$_2$ and cytosine/Ag$_2$ complexes as well.

The guanine/Ag$_2$ complex also exhibits the strongest binding at the $sp^2$ hybridized N sites, around $-14$ kcal mol$^{-1}$ at N3 and $-15$ kcal mol$^{-1}$ at N7, and R is virtually identical at all three of these structures. Another energetically competitive site is at $sp^2$ O @ C6 with $E_{\text{bind}}$ approaching $-14$ kcal mol$^{-1}$. The $sp^3$ N (NH$_2$ @ C2) is again the weakest binding site with $E_{\text{bind}}$ of only $-7.4$ kcal mol$^{-1}$ and an R value of $2.50$ Å compared to $2.35$ Å or $2.36$ Å for the other binding sites.

Each structure of the cytosine/Ag$_2$ complex shows a clear difference in the energetics. There is only one $sp^2$ hybridized N site (N3) with a marked decrease in $E_{\text{bind}}$ to more than $-17$ kcal mol$^{-1}$. The $sp^2$ O @ C2 site exhibits binding similar to the $sp^2$ O site available in guanine with $E_{\text{bind}}$ of approximately $-14$ kcal mol$^{-1}$. The binding at the $sp^3$ NH$_2$ @ C4 site is around $-8$ kcal mol$^{-1}$, which is much weaker than the lowest energy binding site (N3) with $\Delta E$ over $9$ kcal mol$^{-1}$. The large differences in the energetics among the three possible binding sites in the cytosine/Ag$_2$ complex indicate that the silver will most likely to bind to the N3 binding site.

The thymine/Ag$_2$ and uracil/Ag$_2$ complexes show a synonymous trend in the energetics due to their similarities in structures. There are no $sp^2$ hybridized or $sp^3$ N sites and only $sp^2$ O sites. It is important to note that an oxygen atom provides two possible binding sites with its two lone pairs of valence electrons as observed in the optimized structures of the thymine/Ag$_2$ and uracil/Ag$_2$ complexes in Figure 3. Nevertheless, Ag$_2$ ignores the possible binding site located on the oxygen side close to N7 in the guanine/Ag$_2$ complex and converges to the N7 binding site instead despite starting its initial geometry optimization unarguably closer to the oxygen atom. The same phenomenon happens in the cytosine/Ag$_2$ complex, which silver ignores the oxygen binding site close to N3. Silver only binds to oxygen when the nearby nitrogen is protonated, and $\Delta E$ is higher when the silver binds to oxygen compared to nitrogen. Thus, it is quite evident that silver prefers in-plane binding at $sp^2$ hy-
bridized nitrogen instead of oxygen. The most difficult problem in the thymine/Ag₂
and uracil/Ag₂ complexes is the proximity of ∆E in every binding site. In both cases
of the thymine/Ag₂ and uracil/Ag₂ complexes, the largest difference in ∆E among
various binding sites is less than 1.5 kcal mol⁻¹ when compared to the lowest en-
ergy binding site, O @ C2/N1. Experimentally, thymine has been found to have the
weakest interaction with silver when compared to adenine, guanine, and cytosine. The
same interaction strength trend can be predicted for uracil due to its similarities
with thymine. This agrees with the overall weaker $E_{\text{bind}}$ of the thymine/Ag₂ and
uracil/Ag₂ complexes (around $-11$ kcal mol⁻¹) compared to the guanine/Ag₂ and
cytosine/Ag₂ complexes with $sp^2$ O sites (around $-14$ kcal mol⁻¹).

The energetics of each nucleobase/Ag₂ complex with varying binding sites allowed
the elimination of the $sp^3$ N amino group as a possible binding site from all complexes
because of the large ∆E. However, the analysis of the energetics was not sufficient
to determine the most preferred binding site of Ag₂ because other binding sites ($sp^2$
hybridized N and $sp^2$ O) displayed the similarities in the energetics. This supports
the necessity of examining the vibrational signatures of each nucleobase/Ag₂ complex
upon complexation.

### 3.2 Vibrational Signatures

The binding of Ag₂ affects the vibrational frequency, infrared intensity, and Raman
scattering activity of a nucleobase, while the magnitude and direction of the changes
depend on the location of Ag₂. The examination of these vibrational perturbations
complement the information presented in the previous section and provide further
insight into the interaction between each nucleobase/Ag₂.

Table 2 shows the vibrational frequencies (Freq), Raman scattering activities
(RA), and corresponding changes ($\Delta$Freq and $\Delta$RA, respectively) associated with
the nucleobase/Ag₂ complexation depicted in Figure 3.
| Nucleobase | Binding Site | Freq  | RA  | ∆Freq | ∆RA | Freq  | RA  | ∆Freq | ∆RA | Freq  | RA  | ∆Freq | ∆RA | Freq  | RA  | ∆Freq | ∆RA | Freq  | RA  | ∆Freq | ∆RA |
|------------|--------------|-------|-----|--------|-----|-------|-----|--------|-----|-------|-----|--------|-----|-------|-----|--------|-----|-------|-----|-------|-----|
| Adenine    | Isolated     | 1532  | 1   | 1430  | 26  | 1340  | 39  | 1021   | 6   | 952   | 5   | 906    | 2   |       |     |        |     |       |     |        |     |
|            | N1           | +6    | +39 | 0     | +23 | +18   | +29 | +7     | +9  | +3    | 0   | +11    | +6  |       |     |        |     |       |     |        |     |
|            | N3           | 0     | +2  | +12   | +29 | +1    | +15 | +2     | +5  | +3    | -1  | +18    | 0   |       |     |        |     |       |     |        |     |
|            | NH$_2$ @ C6  | -5    | +6  | -3    | +2  | -10   | +19 | +43    | 0   | -3    | +1  | -2     | 0   |       |     |        |     |       |     |        |     |
|            | N7           | 0     | +12 | +8    | +11 | -5    | -11 | -3     | -3  | +23   | -4  | 0      | 0   |       |     |        |     |       |     |        |     |
| Guanine    | Isolated     | 1841  | 54  | 1342  | 6   | 1156  | 4   | 1081   | 7   | 956   | 6   | 845    | 1   |       |     |        |     |       |     |        |     |
|            | NH$_2$ @ C2  | +13   | -14 | -5    | -1  | +8    | -1  | +3     | -3  | +1    | 0   | -10    | 0   |       |     |        |     |       |     |        |     |
|            | N3           | +14   | +15 | +6    | +22 | -10   | +6  | +6     | +6  | +1    | +1  | +18    | 0   |       |     |        |     |       |     |        |     |
|            | O @ C6       | -73   | +95 | +31   | +61 | +19   | -2  | -3     | +8  | -2    | +5  | 0      | +2  |       |     |        |     |       |     |        |     |
|            | N7           | +3    | +22 | +6    | -1  | +2    | -1  | +15    | -2  | +22   | -4  | +4     | 0   |       |     |        |     |       |     |        |     |
| Cytosine   | Isolated     | 1815  | 30  | 1454  | 4   | 1284  | 22  | 1101   | 3   | 994   | 3   | 940    | 3   |       |     |        |     |       |     |        |     |
|            | O @ C2       | -76   | +102| +7    | +112| +34   | +4  | +16    | +1  | +4    | +2  | +17    | -1  |       |     |        |     |       |     |        |     |
|            | N3           | -3    | -15 | +11   | +8  | +10   | +6  | +22    | +1  | +13   | +5  | +25    | +10 |       |     |        |     |       |     |        |     |
|            | NH$_2$ @ C4  | +13   | +11 | +1    | +1  | -34   | -13 | +38    | +1  | +10   | 0   | +9     | +3  |       |     |        |     |       |     |        |     |
| Thymine    | Isolated     | 1840  | 25  | 1806  | 41  | 1446  | 3   | 1413   | 1   | 1216  | 0   | 980    | 6   |       |     |        |     |       |     |        |     |
|            | O @ C2/N1    | -70   | +33 | +14   | +48 | +21   | +51 | 0      | +2  | +11   | +4  | +11    | 0   |       |     |        |     |       |     |        |     |
|            | O @ C2/N3    | -65   | +49 | +20   | +9  | +15   | +5  | +5     | +52 | +52   | +52 | 0      | 0   | +13    | 0   |       |     |        |     |       |     |
|            | O @ C4/N3    | +13   | -8  | -61   | +231| +3    | +12 | +10    | +40 | +13   | +2  | +5     | +12 |       |     |        |     |       |     |        |     |
|            | O @ C4/C5    | +11   | +2  | -52   | +217| +4    | +2  | +5     | +1  | +11   | +4  | +3     | 0   |       |     |        |     |       |     |        |     |
| Uracil     | Isolated     | 1846  | 34  | 1821  | 46  | 1435  | 2   | 1424   | 2   | 1213  | 0   | 984    | 3   |       |     |        |     |       |     |        |     |
|            | O @ C2/N1    | -72   | +35 | +17   | +63 | +22   | +25 | +2     | +9  | +18   | +2  | +4     | -1  |       |     |        |     |       |     |        |     |
|            | O @ C2/N3    | -67   | +47 | +21   | +9  | +18   | +1  | +3     | +29 | +4    | +4  | +5     | 0   |       |     |        |     |       |     |        |     |
|            | O @ C4/N3    | +12   | -12 | -58   | +206| +5    | +3  | +8     | +30 | +3    | +2  | +16    | +6  |       |     |        |     |       |     |        |     |
|            | O @ C4/C5    | +9    | -5  | -58   | +165| +7    | +8  | +4     | +2  | +5    | +4  | +8     | +2  |       |     |        |     |       |     |        |     |
These modes were selected from the region around 800 cm\(^{-1}\) to 2000 cm\(^{-1}\) because these vibrations primarily involve the motion of non-hydrogen atoms and produce intense Raman bands, while containing a significant amount of vibrational information about nucleobases.\(^{47}\) In addition, this region has been found to be the most effective at reproducing the experiment in the previous study of pyrimidine and its interactions with Ag\(_2\) and H\(_2\)O molecules using the same level of theory (M06-2X/aVTZ).\(^{18}\) Figure 4-8 show the simulated Raman spectra of isolated nucleobase with each nucleobase/Ag\(_2\) complex. The simulated Raman spectra were created by fitting computed harmonic frequencies to the Lorentzian curve with half width of 2 cm\(^{-1}\).

In the adenine/Ag\(_2\) complex, the mode at 906 cm\(^{-1}\) presents a symmetrical N1-C2-N3 stretching of the six-membered ring. When Ag\(_2\) binds to the N1 or N3 site of this mode, there is an increase in frequency (+11 cm\(^{-1}\) and +18 cm\(^{-1}\), respectively) since both N1 and N3 are the constituents of the six-membered ring. However, the binding of Ag\(_2\) to the two other sites, N7 and NH\(_2\) C6, results in no change or a decrease (−2 cm\(^{-1}\)) in frequency. A symmetrical N7-C8-N9 stretching of the five-membered ring is at 952 cm\(^{-1}\) and exhibits a frequency shift of +23 cm\(^{-1}\) only with the adsorption of Ag\(_2\) to the constituent of the N7 site. Even though the NH\(_2\) site has been eliminated as a competitive binding site energetically, the mode with the NH\(_2\) rocking at 1021 cm\(^{-1}\) is worth mentioning due to the large frequency shift of +43 cm\(^{-1}\) as Ag\(_2\) binds to the NH\(_2\) group. Therefore, an increase in frequency is present when Ag\(_2\) binds to an atom or a group within the motion of the modes. The most interesting mode of the adenine/Ag\(_2\) complex is present at 1340 cm\(^{-1}\) with an asymmetrical N1-C2-N3 stretching. A similar change in frequency and Raman scattering activity is expected whether Ag\(_2\) binds to the N1 or N3 site because of the trend examined in the modes with a symmetrical stretching. However, a shift to higher energy (+18 cm\(^{-1}\)) is present when Ag\(_2\) adsorbs to the N1 site, but barely
changes when Ag₂ adsorbs to the N3 site, which is most likely due to the involvement of the amino group adjacent to N1. It has been found experimentally that the modes dominated by motion of the amino group causes a strong Raman enhancement when the amino group is close to the metal surface.²⁵ This explanation can be supported by the mode at 1532 cm⁻¹ characterized as the scissoring of the NH₂ group. There is a significant Raman enhancement (×40) when Ag₂ binds to the N1 site but almost no Raman enhancement with the addition of Ag₂ to the N3 site instead.

![Figure 4. Simulated Raman spectra of isolated adenine with each adenine/Ag₂ complex.](image)

The guanine/Ag₂ complex has three modes that can distinguish the O @ C6 binding site from the other binding sites. The mode at 1841 cm⁻¹ with the C=O stretching experiences a substantial shift to lower energy (−73 cm⁻¹) and an enhancement of Raman scattering activity (around ×3) when Ag₂ binds to the O @ C6 site. In several experiments, this was found to be caused by a loss in the double bond character of the carbonyl group as electrons are donated to the silver surface.
from the carbonyl group. The same phenomenon can also be observed in the cytosine/Ag$_2$, thymine/Ag$_2$, and uracil/Ag$_2$ complexes, which all contain a carbonyl group. Experimentally, the presence of a decrease in frequency and enhancement in Raman of the C=O stretching band revealed the proximity of the carbonyl group to the silver surface. Two alternate modes of the guanine/Ag$_2$ complex at 1342 cm$^{-1}$ and 1156 cm$^{-1}$ contain a wagging motion of N1-H. These modes shift to much higher energy when Ag$_2$ binds to the O @ C6 site compared to other binding sites with a large Raman enhancement (around $\times 11$) at 1342 cm$^{-1}$. The N7 binding site can be differentiated through a solitary increase in frequency when Ag$_2$ binds to the N7 site at 1081 cm$^{-1}$ and 956 cm$^{-1}$ that consist of the stretching inside the five-membered ring. On the other hand, the N3 binding site can be distinguished from other binding sites through the frequency shift of $+18$ cm$^{-1}$ at the 845 cm$^{-1}$ mode.

Figure 5. Simulated Raman spectra of isolated guanine with each guanine/Ag$_2$ complex.
The cytosine/Ag$_2$ complex shows a clear difference in the energetics for each binding site, and fortunately, this characteristic also applies to the vibrational signatures. All of the six selected modes have noticeable change in frequency with either varying magnitude or direction. The most noticeable mode is at 1454 cm$^{-1}$ with a N1-H wagging motion. When Ag$_2$ binds to the O @ C2 site, Raman scattering activity is enhanced significantly ($\times 29$), whereas the binding of Ag$_2$ to other sites causes no substantial enhancement. Three modes at 1101 cm$^{-1}$, 994 cm$^{-1}$, and 940 cm$^{-1}$ all share the NH$_2$ rocking and stretching within the ring. All sites exhibit a shift to higher energy, and in a higher magnitude when Ag$_2$ adsorbs to the N3 site. On the other hand, at the 1284 cm$^{-1}$ mode with a C2-N3 stretching and a N1-H wagging, a greater increase in frequency is predicted with the addition of Ag$_2$ to the O @ C2 site (+34 cm$^{-1}$) compared to the N3 (+10 cm$^{-1}$) and NH$_2$ @ C4 ($-34$ cm$^{-1}$).

![Simulated Raman spectra of isolated cytosine with each cytosine/Ag$_2$ complex.](image)

**Figure 6.** Simulated Raman spectra of isolated cytosine with each cytosine/Ag$_2$ complex.
In the thymine/Ag\(_2\) complex, the mode at 1840 cm\(^{-1}\) includes a C2=O stretching, whereas the mode at 1806 cm\(^{-1}\) includes a C4=O stretching. When Ag\(_2\) binds to the two binding sites present at the oxygen atom involved in a C=O stretching, the frequency decreases significantly, while the Raman scattering activity is notably enhanced for both sites. On the contrary, when Ag\(_2\) binds to the oxygen atom not involved in a C=O stretching, the mode shifts to higher energy, and Raman scattering activity is slightly affected. The mode at 1446 cm\(^{-1}\) is characterized as an asymmetrical N1-C2-N3 stretching and a N1-H wagging. The adsorption of Ag\(_2\) to the O @ C2/N1 site causes a shift to higher energy and a large Raman enhancement (\(\times 18\)). In comparison, the mode at 1413 cm\(^{-1}\) with a N3-C4 stretching and a N3-H wagging shifts to higher energy and enhances Raman scattering activity significantly when Ag\(_2\) interacts with the O @ C2/N3 (\(\times 53\)) or the O @ C4/N3 site (\(\times 41\)). The frequency shifts and Raman enhancement computed for both modes are influenced greatly by the wagging motion of N1-H and N3-H.
Figure 7. Simulated Raman spectra of isolated thymine with each thymine/Ag\textsubscript{2} complex.

Experimentally, the SERS spectra of cytosine and uracil have been found to be similar due to the same ring structure and a similar geometry on the surface\textsuperscript{50}. Even more so, the thymine/Ag\textsubscript{2} and uracil/Ag\textsubscript{2} complexes share similarities in structures, energetics, and vibrational signatures. The previously discussed trends in the thymine/Ag\textsubscript{2} complex apply directly to the uracil/Ag\textsubscript{2} complex modes at 1846 cm\textsuperscript{-1}, 1821 cm\textsuperscript{-1}, 1435 cm\textsuperscript{-1}, and 1424 cm\textsuperscript{-1}. The 1216 cm\textsuperscript{-1} and 980 cm\textsuperscript{-1} modes of the thymine/Ag\textsubscript{2} complex in comparison to 1213 cm\textsuperscript{-1} and 984 cm\textsuperscript{-1} modes of the uracil/Ag\textsubscript{2} complex are particularly interesting. Despite all the similarities shared between the two nucleobase/Ag\textsubscript{2} complexes, the methyl group of the thymine/Ag\textsubscript{2} complex, which does not form any coordination bond with silver, is clearly affecting these two modes differently from the hydrogen atom of the uracil/Ag\textsubscript{2} complex\textsuperscript{48}. For example, the thymine/Ag\textsubscript{2} complex mode at 980 cm\textsuperscript{-1} shifts to higher energy with a larger magnitude when Ag\textsubscript{2} binds to the O @ C2/N1 or O @ C2/N3 site. However, a
larger increase in frequency is present in the uracil/Ag$_2$ complex mode at 984 cm$^{-1}$ when Ag$_2$ interacts with the O @ C4/N3 or O @ C4/C5 site.

![Simulated Raman spectra of isolated uracil with each uracil/Ag$_2$ complex.](image)

**Figure 8.** Simulated Raman spectra of isolated uracil with each uracil/Ag$_2$ complex.

Various trends in the vibrational signatures of each nucleobase/Ag$_2$ complex have been identified. When Ag$_2$ binds to the site in motion or the substituent of atoms in motion, especially in the case of a symmetrical stretching, an increase in frequency is expected. This trend was observed experimentally in which the totally symmetrical ring mode shifts to higher energy in all derivatives of adenine once these molecules are adsorbed to the silver surface.$^{51}$ The NH$_2$ group motion such as rocking and scissoring shifts the mode to higher energy and enhances the Raman scattering activity when Ag$_2$ binds to a nearby binding site. A similar phenomenon is present with the wagging motion of N-H. The addition of Ag$_2$ to the oxygen atom involved in a C=O stretching causes a significant decrease in frequency and enhancement of Raman scattering activity.
4 Conclusions

The nature of the interaction between the molecule and a metal surface is unclear; thus, a theoretical study of the interaction between each nucleobase and silver was presented in this work. By modeling the silver surface with Ag$_2$, the optimized structures of each nucleobase/Ag$_2$ complex with various possible binding sites ($sp^2$ hybridized N, $sp^2$ O, and $sp^3$ N) were found. The electronic binding energies of each nucleobase/Ag$_2$ complex were compared to determine the most energetically favored binding site. Only the $sp^3$ N amino group binding site could be eliminated energetically because the complexation of Ag$_2$ through this site increased the binding energy by approximately 7 kcal mol$^{-1}$ to 9 kcal mol$^{-1}$ compared to the lowest energy binding site. In some cases, $sp^2$ hybridized N was more favorable than $sp^2$ O; however, both were found to be equally energetically competitive, making them essentially isoenergetic. Because of this ambiguity in the energetics, vibrational signatures of each nucleobase/Ag$_2$ complex upon complexation were examined.

The enhancement in Raman scattering activity upon complexation was not as large as a factor of up to $10^{14}$. Nevertheless, the change in frequency and Raman scattering activity upon complexation differed noticeably depending on the binding site in several modes such as a symmetrical stretching, an NH$_2$ group motion, an wagging motion of N-H, and a C=O streching. These modes could be used qualitatively to discriminate between particular binding motifs experimentally.
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Appendix

A 1. Cartesian coordinates in angstroms (Å) for the Ag$_2$ structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Ag   | 3.537134 | 0.187469 | 0.000000 |
| Ag   | 6.007358 | 1.176673 | 0.000000 |

A 2. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for Ag$_2$ with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA |
|------|----|----|
| 153  | 0  | 56 |
A 3. Cartesian coordinates in angstroms (Å) for the adenine structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| N    | -2.169804 | 0.005311 | 0.024898 |
| C    | -0.936389 | 0.603158 | 0.016711 |
| C    | -0.037666 | -0.452755 | -0.003999 |
| N    | -0.690095 | -1.668313 | -0.008566 |
| C    | -1.950598 | -1.349580 | 0.008990 |
| C    | 1.322168  | -0.103550 | -0.016099 |
| N    | 1.651559  | 1.188145  | -0.007117 |
| C    | 0.671396  | 2.098554  | 0.013090 |
| N    | -0.638705 | 1.902742  | 0.026146 |
| H    | 0.999169  | 3.131007  | 0.019540 |
| N    | 2.294167  | -1.034730 | -0.036332 |
| H    | -3.055669 | 0.480707  | 0.039704 |
| H    | -2.769034 | -2.051038 | 0.011405 |
| H    | 2.055980  | -2.009447 | -0.043599 |
| H    | 3.253510  | -0.740211 | -0.044772 |
A 4. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in $\text{A}^4$ amu$^{-1}$) for adenine with the M06-2X method/aVTZ level of theory.

| Freq | IR  | RA | Freq | IR  | RA |
|------|-----|----|------|-----|----|
| 17   | 175 | 0  | 1092 | 18  | 8  |
| 171  | 23  | 0  | 1161 | 25  | 2  |
| 224  | 0   | 0  | 1262 | 15  | 8  |
| 277  | 11  | 3  | 1279 | 33  | 11 |
| 307  | 0   | 0  | 1340 | 57  | 39 |
| 522  | 4   | 3  | 1380 | 12  | 4  |
| 534  | 2   | 2  | 1388 | 63  | 72 |
| 547  | 20  | 1  | 1430 | 10  | 26 |
| 555  | 29  | 0  | 1462 | 36  | 5  |
| 594  | 73  | 0  | 1532 | 54  | 1  |
| 623  | 1   | 6  | 1551 | 46  | 84 |
| 681  | 6   | 0  | 1624 | 39  | 4  |
| 708  | 0   | 0  | 1674 | 144 | 25 |
| 737  | 3   | 25 | 1683 | 673 | 12 |
| 845  | 10  | 1  | 3198 | 15  | 130|
| 900  | 7   | 1  | 3266 | 0   | 116|
| 906  | 15  | 2  | 3628 | 119 | 169|
| 952  | 14  | 5  | 3678 | 111 | 128|
| 1012 | 3   | 0  | 3766 | 76  | 43 |
| 1021 | 5   | 6  |      |     |    |
**A 5.** Cartesian coordinates in angstroms (Å) for the guanine structure with the M06-2X/aVTZ level of theory.

| Atom | x        | y        | z        |
|------|----------|----------|----------|
| N    | 2.050657 | 1.518243 | −0.026025|
| C    | 2.834905 | 0.484927 | −0.029729|
| N    | 2.144635 | −0.706368| −0.009409|
| C    | 0.820355 | −0.390822| 0.009271 |
| C    | 0.780450 | 0.990981 | −0.002236|
| N    | −0.205186| −1.278475| 0.023808 |
| C    | −1.365987| −0.694547| 0.050512 |
| C    | −0.500698| 1.641283 | 0.021019 |
| N    | −1.532907| 0.658647 | 0.048637 |
| O    | −0.796602| 2.810436 | 0.025900 |
| N    | −2.505605| −1.450662| 0.131059 |
| H    | 3.911751 | 0.513039 | −0.046690|
| H    | 2.524142 | −1.637574| −0.006324|
| H    | −2.461355| 1.048380 | 0.124046 |
| H    | −2.350674| −2.430672| −0.041175|
| H    | −3.347881| −1.076816| −0.272664|
A 6. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for guanine with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 142  | 3  | 0  | 1065 | 8  | 3  |
| 166  | 1  | 0  | 1081 | 17 | 7  |
| 206  | 11 | 0  | 1100 | 19 | 1  |
| 319  | 6  | 1  | 1156 | 33 | 4  |
| 336  | 71 | 1  | 1190 | 45 | 1  |
| 343  | 13 | 2  | 1319 | 1  | 13 |
| 371  | 2  | 1  | 1342 | 58 | 6  |
| 490  | 8  | 3  | 1380 | 14 | 12 |
| 531  | 42 | 3  | 1406 | 27 | 84 |
| 543  | 198| 3  | 1466 | 32 | 18 |
| 568  | 92 | 1  | 1540 | 1  | 94 |
| 620  | 63 | 2  | 1583 | 73 | 45 |
| 638  | 10 | 27 | 1630 | 64 | 9  |
| 674  | 8  | 0  | 1637 | 313| 98 |
| 680  | 19 | 0  | 1681 | 537| 49 |
| 728  | 39 | 0  | 1841 | 799| 54 |
| 760  | 6  | 0  | 3273 | 0  | 119|
| 820  | 23 | 1  | 3601 | 71 | 159|
| 845  | 11 | 1  | 3615 | 69 | 107|
| 870  | 8  | 1  | 3674 | 99 | 121|
| 956  | 8  | 6  | 3714 | 54 | 54 |
A7. Cartesian coordinates in angstroms (Å) for the cytosine structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | −0.685348 | 0.903846 | −0.000546 |
| C    | 0.559525  | 1.420268 | −0.002037 |
| N    | 1.631483  | 0.602846 | −0.001869 |
| C    | 1.533992  | −0.809033 | −0.000171 |
| N    | 0.269614  | −1.326723 | 0.001334 |
| C    | −0.769569 | −0.530944 | 0.001165 |
| O    | 2.557095  | −1.454550 | −0.000163 |
| N    | −1.990725 | −1.108345 | 0.002706 |
| H    | −2.040996 | −2.111957 | 0.003905 |
| H    | −2.831925 | −0.564763 | 0.002696 |
| H    | 0.756736  | 2.483009  | −0.003402 |
| H    | −1.561277 | 1.531237  | −0.000638 |
| H    | 2.571405  | 0.965120  | −0.002960 |
### Vibrational frequencies, infrared intensities, and Raman scattering activities for cytosine with the M06-2X method/aVTZ level of theory.

| Freq | IR  | RA | Freq | IR  | RA |
|------|-----|----|------|-----|----|
| 48   | 176 | 0  | 1101 | 36  | 3  |
| 144  | 1   | 0  | 1137 | 3   | 8  |
| 207  | 14  | 0  | 1219 | 56  | 8  |
| 365  | 3   | 1  | 1284 | 27  | 22 |
| 410  | 15  | 1  | 1366 | 47  | 8  |
| 542  | 5   | 2  | 1454 | 108 | 4  |
| 547  | 2   | 1  | 1520 | 129 | 6  |
| 549  | 3   | 0  | 1602 | 217 | 23 |
| 581  | 2   | 6  | 1634 | 244 | 11 |
| 644  | 56  | 0  | 1721 | 525 | 16 |
| 742  | 32  | 0  | 1815 | 802 | 30 |
| 786  | 4   | 28 | 3223 | 2   | 82 |
| 796  | 6   | 0  | 3258 | 0   | 102|
| 814  | 50  | 0  | 3628 | 124 | 133|
| 940  | 4   | 3  | 3644 | 85  | 127|
| 994  | 1   | 3  | 3771 | 67  | 49 |
| 1001 | 0   | 1  |      |     |    |
**A 9.** Cartesian coordinates in angstroms (Å) for the thymine structure with the M06-2X/aVTZ level of theory.

| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | 0.707102  | 0.235115  | −0.043948 |
| C    | 0.465964  | −1.081457 | 0.004370  |
| N    | −0.803187 | −1.605711 | 0.086008  |
| C    | −1.945790 | −0.835578 | 0.126020  |
| N    | −1.684353 | 0.516006  | 0.075678  |
| C    | −0.440406 | 1.144481  | −0.007429 |
| O    | −3.056753 | −1.303073 | 0.197713  |
| C    | 2.068302  | 0.842142  | −0.132713 |
| O    | −0.364114 | 2.351028  | −0.044013 |
| H    | 1.263255  | −1.811603 | −0.018353 |
| H    | −0.955618 | −2.599711 | 0.120912  |
| H    | −2.493842 | 1.120307  | 0.102443  |
| H    | 2.836999  | 0.072132  | −0.152841 |
| H    | 2.247667  | 1.501490  | 0.716225  |
| H    | 2.154784  | 1.454413  | −1.030072 |
A 10. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for thymine with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 114  | 0  | 0  | 1171 | 6  | 2  |
| 158  | 2  | 0  | 1216 | 156| 0  |
| 170  | 0  | 0  | 1250 | 7  | 5  |
| 280  | 3  | 0  | 1387 | 7  | 32 |
| 302  | 1  | 0  | 1413 | 3  | 1  |
| 398  | 23 | 1  | 1424 | 8  | 6  |
| 407  | 18 | 1  | 1446 | 89 | 3  |
| 464  | 20 | 4  | 1474 | 8  | 5  |
| 552  | 7  | 4  | 1497 | 4  | 5  |
| 562  | 61 | 0  | 1521 | 149| 17 |
| 613  | 2  | 5  | 1744 | 67 | 49 |
| 697  | 63 | 1  | 1806 | 784| 41 |
| 747  | 5  | 16 | 1840 | 725| 25 |
| 781  | 19 | 0  | 3070 | 15 | 216|
| 800  | 49 | 1  | 3130 | 5  | 70 |
| 814  | 6  | 4  | 3154 | 9  | 56 |
| 941  | 15 | 1  | 3219 | 3  | 89 |
| 980  | 12 | 6  | 3615 | 82 | 75 |
| 1030 | 3  | 2  | 3662 | 121| 101|
| 1079 | 1  | 1  |      |    |    |
A 11. Cartesian coordinates in angstroms (Å) for the uracil structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 1.322552 | 0.510483 | −0.072101 |
| C    | 1.110199 | −0.806809 | 0.032585  |
| N    | −0.150499 | −1.338623 | 0.104719  |
| C    | −1.303469 | −0.573539 | 0.076364  |
| N    | −1.056115 | 0.775734  | −0.031623 |
| C    | 0.185357  | 1.420555  | −0.111786 |
| O    | −2.407877 | −1.054307 | 0.140677  |
| O    | 0.242378  | 2.623151  | −0.203879 |
| H    | 1.916590  | −1.525021 | 0.066219  |
| H    | −0.298261 | −2.331052 | 0.183278  |
| H    | −1.873361 | 1.369838  | −0.055626 |
| H    | 2.312506  | 0.929591  | −0.128857 |
A 12. Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for uracil with the M06-2X method/aVTZ level of theory.

| Freq  | IR  | RA | Freq  | IR  | RA |
|-------|-----|----|-------|-----|----|
| 155   | 2   | 0  | 1004  | 0   | 2  |
| 169   | 0   | 0  | 1099  | 6   | 5  |
| 396   | 24  | 1  | 1213  | 112 | 0  |
| 404   | 22  | 1  | 1238  | 6   | 19 |
| 523   | 21  | 2  | 1395  | 11  | 17 |
| 549   | 8   | 5  | 1424  | 30  | 2  |
| 567   | 4   | 2  | 1435  | 100 | 2  |
| 581   | 43  | 0  | 1520  | 145 | 12 |
| 686   | 75  | 1  | 1711  | 96  | 34 |
| 742   | 14  | 0  | 1821  | 970 | 46 |
| 784   | 4   | 22 | 1846  | 536 | 34 |
| 788   | 38  | 0  | 3231  | 2   | 87 |
| 838   | 65  | 0  | 3279  | 3   | 96 |
| 984   | 9   | 3  | 3612  | 82  | 68 |
| 996   | 8   | 1  | 3662  | 125 | 91 |
A 13. Cartesian coordinates in angstroms (Å) for the adenine/Ag$_2$ complex (N1) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| N    | 2.364572| 0.503418| 0.042805|
| C    | 1.020043| 0.750550| 0.019164|
| C    | 0.433838| −0.504641| 0.035057|
| N    | 1.381958| −1.502570| 0.067561|
| C    | 2.513333| −0.861256| 0.071141|
| C    | −0.969501| −0.541754| 0.016051|
| N    | −1.622752| 0.628229| −0.015620|
| C    | −0.919945| 1.777076| −0.027830|
| N    | 0.386936| 1.927271| −0.012354|
| H    | −1.517005| 2.680468| −0.053588|
| N    | −1.646450| −1.696947| 0.028747|
| H    | 3.092752| 1.197642| 0.039688|
| H    | 3.488202| −1.320297| 0.093667|
| H    | −1.139287| −2.564079| 0.052539|
| H    | −2.653914| −1.700524| 0.014655|
| Ag   | −3.972794| 0.689777| −0.049832|
| Ag   | −6.623403| 0.457678| −0.082648|
A 14. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the adenine/Ag$_2$ complex (N1) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 19   | 0  | 0  | 955  | 20 | 5  |
| 20   | 0  | 5  | 1009 | 2  | 1  |
| 57   | 0  | 12 | 1029 | 19 | 14 |
| 92   | 1  | 9  | 1091 | 15 | 11 |
| 99   | 2  | 9  | 1166 | 23 | 2  |
| 171  | 1  | 1  | 1266 | 99 | 9  |
| 174  | 13 | 50 | 1274 | 31 | 10 |
| 224  | 41 | 0  | 1358 | 45 | 69 |
| 265  | 93 | 9  | 1389 | 60 | 58 |
| 292  | 24 | 3  | 1391 | 17 | 43 |
| 309  | 0  | 1  | 1430 | 34 | 49 |
| 531  | 6  | 4  | 1470 | 25 | 23 |
| 541  | 7  | 2  | 1538 | 21 | 40 |
| 544  | 14 | 2  | 1551 | 43 | 118|
| 563  | 30 | 0  | 1632 | 67 | 12 |
| 600  | 77 | 2  | 1667 | 155| 22 |
| 641  | 17 | 2  | 1694 | 644| 4  |
| 680  | 3  | 2  | 3201 | 3  | 59 |
| 709  | 0  | 0  | 3271 | 0  | 167|
| 738  | 2  | 29 | 3583 | 139| 307|
| 842  | 7  | 0  | 3670 | 146| 192|
| 906  | 7  | 1  | 3725 | 161| 45 |
| 917  | 11 | 8  |      |    |    |
A 15. Cartesian coordinates in angstroms (Å) for the adenine/Ag$_2$ complex (N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z        |
|------|---------|---------|----------|
| N    | 1.835865| 0.426575| -0.090976|
| C    | 0.475465| 0.532220| -0.063966|
| C    | 0.019559| -0.748381| 0.198774 |
| N    | 1.069662| -1.630185| 0.332189 |
| C    | 2.126573| -0.893883| 0.153445 |
| C    | -1.373466| -0.909178| 0.278284 |
| N    | -2.156309| 0.161115| 0.099225 |
| C    | -1.590068| 1.337292| -0.147229|
| N    | -0.292633| 1.614181| -0.245788|
| H    | -2.265907| 2.172075| -0.284614|
| N    | -1.937507| -2.099085| 0.527306 |
| H    | 2.484810 | 1.181896| -0.259179|
| H    | 3.144497 | -1.246133| 0.185899 |
| H    | -1.361026| -2.909950| 0.663542 |
| H    | -2.938269| -2.167502| 0.575347 |
| Ag   | 0.818040 | 3.628677| -0.672805|
| Ag   | 2.600693 | 5.558010| -1.106803|
A 16. Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for the adenine/Ag\(_2\) complex (N3) with the M06-2X method/aVTZ level of theory.

| Freq  | IR | RA | Freq  | IR | RA |
|-------|----|----|-------|----|----|
| 16    | 1  | 4  | 955   | 10 | 5  |
| 21    | 0  | 0  | 1010  | 3  | 0  |
| 62    | 0  | 12 | 1024  | 5  | 10 |
| 79    | 2  | 5  | 1098  | 12 | 19 |
| 102   | 4  | 13 | 1170  | 60 | 2  |
| 169   | 1  | 0  | 1263  | 18 | 12 |
| 173   | 15 | 48 | 1286  | 17 | 44 |
| 212   | 52 | 0  | 1341  | 178| 54 |
| 256   | 139| 0  | 1385  | 44 | 23 |
| 280   | 11 | 3  | 1398  | 89 | 42 |
| 316   | 1  | 1  | 1442  | 9  | 55 |
| 531   | 4  | 1  | 1475  | 44 | 4  |
| 545   | 10 | 2  | 1532  | 52 | 3  |
| 568   | 0  | 1  | 1548  | 24 | 77 |
| 572   | 7  | 2  | 1632  | 23 | 2  |
| 612   | 66 | 7  | 1671  | 125| 18 |
| 623   | 2  | 7  | 1687  | 1166| 47 |
| 682   | 6  | 0  | 3206  | 3  | 68 |
| 709   | 2  | 0  | 3272  | 0  | 100|
| 743   | 22 | 35 | 3611  | 176| 219|
| 841   | 7  | 1  | 3622  | 180| 298|
| 906   | 7  | 0  | 3759  | 82 | 57 |
| 924   | 33 | 2  |       |     |    |
**A 17.** Cartesian coordinates in angstroms (Å) for the adenine/Ag$_2$ complex (NH$_2$ @ C6) structure with the M06-2X/aVTZ level of theory.

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| N    | 2.080713 | 0.599980 | 0.059774 |
| C    | 0.728196 | 0.809163 | 0.094409 |
| C    | 0.177719 | −0.468070 | 0.057336 |
| N    | 1.156859 | −1.436625 | 0.005176 |
| C    | 2.266714 | −0.759327 | 0.006760 |
| C    | −1.215553 | −0.524224 | 0.073059 |
| N    | −1.916075 | 0.596979 | 0.133931 |
| C    | −1.252743 | 1.761837 | 0.169419 |
| N    | 0.057012  | 1.955287 | 0.151129 |
| H    | −1.870477 | 2.649193 | 0.219118 |
| N    | −1.890131 | −1.728831 | −0.041565 |
| H    | 2.790283  | 1.313025 | 0.064654 |
| H    | 3.254715  | −1.188939 | −0.029653 |
| H    | −1.370591 | −2.531226 | 0.288385 |
| H    | −2.844790 | −1.686524 | 0.288209 |
| Ag   | −1.977839 | −2.122889 | −2.504829 |
| Ag   | −2.069148 | −2.593288 | −5.120306 |
A 18. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the adenine/Ag$_2$ complex (NH$_2$ @ C6) with the M06-2X method/aVTZ level of theory.

| Freq | IR  | RA  | Freq | IR  | RA  |
|------|-----|-----|------|-----|-----|
| 12   | 1   | 10  | 949  | 11  | 6   |
| 18   | 0   | 12  | 1006 | 4   | 1   |
| 39   | 0   | 3   | 1065 | 13  | 6   |
| 46   | 0   | 2   | 1093 | 22  | 6   |
| 112  | 13  | 9   | 1156 | 26  | 6   |
| 162  | 10  | 49  | 1271 | 44  | 9   |
| 224  | 5   | 7   | 1274 | 27  | 5   |
| 230  | 17  | 6   | 1330 | 11  | 58  |
| 272  | 13  | 1   | 1361 | 55  | 8   |
| 315  | 1   | 2   | 1390 | 61  | 69  |
| 506  | 2   | 3   | 1427 | 15  | 28  |
| 535  | 5   | 1   | 1454 | 59  | 4   |
| 554  | 26  | 5   | 1527 | 89  | 8   |
| 563  | 9   | 9   | 1554 | 58  | 77  |
| 595  | 86  | 2   | 1617 | 23  | 8   |
| 629  | 1   | 5   | 1670 | 425 | 26  |
| 672  | 45  | 14  | 1691 | 152 | 7   |
| 684  | 89  | 11  | 3208 | 11  | 133 |
| 733  | 33  | 27  | 3270 | 0   | 116 |
| 762  | 422 | 2   | 3544 | 60  | 173 |
| 848  | 49  | 7   | 3654 | 56  | 36  |
| 904  | 7   | 2   | 3671 | 138 | 155 |
| 912  | 5   | 2   |      |     |     |
A 19. Cartesian coordinates in angstroms (Å) for the adenine/Ag$_2$ complex (N7) structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| N    | 2.101436 | 0.759610 | −0.003926 |
| C    | 0.740472  | 0.946345  | 0.018954  |
| C    | 0.203630  | −0.331633 | 0.010890  |
| N    | 1.215896  | −1.273872 | −0.016288 |
| C    | 2.323018  | −0.582771 | −0.024242 |
| C    | −1.203022 | −0.413080 | 0.031072  |
| N    | −1.894665 | 0.728251  | 0.055930  |
| C    | −1.237046 | 1.889920  | 0.060695  |
| N    | 0.072329  | 2.096097  | 0.043565  |
| H    | −1.859488 | 2.775977  | 0.081297  |
| N    | −1.876035 | −1.573876 | 0.026545  |
| H    | 2.794108  | 1.489631  | −0.005139 |
| H    | 3.314445  | −1.004006 | −0.044517 |
| H    | −1.407405 | −2.465199 | 0.008205  |
| H    | −2.880379 | −1.540764 | 0.042104  |
| Ag   | 1.001746  | −3.594737 | −0.042408 |
| Ag   | 0.373188  | −6.178551 | −0.065572 |
Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for the adenine/Ag\(_2\) complex (N7) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 19   | 0  | 5  | 975  | 27 | 1  |
| 20   | 0  | 0  | 1013 | 3  | 0  |
| 53   | 1  | 10 | 1018 | 5  | 3  |
| 80   | 1  | 4  | 1114 | 35 | 6  |
| 111  | 2  | 15 | 1162 | 20 | 5  |
| 172  | 0  | 1  | 1258 | 26 | 2  |
| 177  | 14 | 41 | 1283 | 40 | 25 |
| 215  | 27 | 1  | 1335 | 61 | 28 |
| 245  | 92 | 12 | 1381 | 1  | 9  |
| 305  | 9  | 2  | 1393 | 60 | 48 |
| 310  | 3  | 0  | 1438 | 37 | 36 |
| 527  | 3  | 5  | 1461 | 67 | 4  |
| 532  | 1  | 4  | 1532 | 154 | 13 |
| 534  | 7  | 2  | 1557 | 96 | 87 |
| 563  | 10 | 1  | 1629 | 1  | 10 |
| 603  | 106| 1  | 1673 | 177 | 18 |
| 626  | 4  | 7  | 1684 | 600 | 8  |
| 679  | 2  | 1  | 3201 | 16 | 183 |
| 709  | 0  | 0  | 3277 | 5  | 67 |
| 737  | 1  | 33 | 3579 | 262 | 444 |
| 843  | 11 | 0  | 3667 | 158 | 243 |
| 900  | 6  | 0  | 3721 | 187 | 136 |
| 906  | 15 | 1  |      |    |    |
A 21. Cartesian coordinates in angstroms (Å) for the guanine/Ag₂ complex (NH₂ @ C2) structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| N    | −2.067365 | 0.673783 | −0.815340 |
| C    | −2.673596 | −0.457044 | −0.616009 |
| N    | −1.860783 | −1.399891 | −0.031297 |
| C    | −0.648088 | −0.809689 | 0.146946 |
| C    | −0.793733 | 0.473292 | −0.342776 |
| N    | 0.447083 | −1.388968 | 0.709028 |
| C    | 1.463091 | −0.591597 | 0.735139 |
| C    | 0.337752 | 1.362818 | −0.308026 |
| N    | 1.456471 | 0.684267 | 0.268522 |
| O    | 0.459541 | 2.502068 | −0.674308 |
| N    | 2.687762 | −1.059202 | 1.221651 |
| H    | −3.698928 | −0.672790 | −0.866516 |
| H    | −2.096127 | −2.345820 | 0.217105 |
| H    | 2.315574 | 1.217650 | 0.251667 |
| H    | 2.561145 | −1.948204 | 1.688952 |
| H    | 3.177148 | −0.400818 | 1.814544 |
| Ag   | 4.286241 | −1.409385 | −0.669194 |
| Ag   | 6.080831 | −1.562060 | −2.619593 |
**A 22.** Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the guanine/Ag$_2$ complex (NH$_2$ @ C2) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 12   | 0  | 9  | 867  | 322| 6  |
| 14   | 1  | 9  | 877  | 9  | 1  |
| 40   | 1  | 3  | 957  | 7  | 6  |
| 48   | 2  | 3  | 1069 | 15 | 6  |
| 97   | 2  | 5  | 1084 | 21 | 4  |
| 153  | 1  | 24 | 1100 | 53 | 1  |
| 164  | 2  | 32 | 1164 | 24 | 3  |
| 202  | 6  | 4  | 1191 | 54 | 2  |
| 222  | 27 | 6  | 1307 | 10 | 24 |
| 320  | 2  | 1  | 1338 | 56 | 4  |
| 339  | 2  | 1  | 1382 | 15 | 14 |
| 387  | 1  | 3  | 1412 | 34 | 111|
| 454  | 44 | 15 | 1472 | 55 | 24 |
| 491  | 4  | 2  | 1532 | 20 | 109|
| 533  | 1  | 4  | 1578 | 99 | 142|
| 579  | 73 | 1  | 1628 | 55 | 17 |
| 616  | 115| 10 | 1631 | 330| 209|
| 634  | 15 | 22 | 1687 | 446| 52 |
| 675  | 11 | 1  | 1854 | 712| 39 |
| 678  | 19 | 4  | 3272 | 0  | 147|
| 703  | 57 | 40 | 3538 | 52 | 192|
| 740  | 73 | 7  | 3594 | 61 | 74 |
| 820  | 8  | 1  | 3632 | 47 | 48 |
| 835  | 146| 1  | 3670 | 112| 126|

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**A 23.** Cartesian coordinates in angstroms (Å) for the guanine/Ag$_2$ complex (N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| N    | -2.265598 | 1.073597 | -0.002022 |
| C    | -2.741987 | -0.132454 | -0.024391 |
| N    | -1.754514 | -1.094038 | -0.031756 |
| C    | -0.570516 | -0.428815 | -0.012472 |
| C    | -0.900790 | 0.910173  | 0.006527  |
| N    | 0.666782  | -0.997917 | -0.005583 |
| C    | 1.642207  | -0.125043 | 0.008266  |
| C    | 0.157282  | 1.882284  | 0.027005  |
| N    | 1.424406  | 1.214631  | 0.026285  |
| O    | 0.131197  | 3.084526  | 0.040134  |
| N    | 2.930955  | -0.547813 | -0.034992 |
| H    | -3.785790 | -0.398022 | -0.036451 |
| H    | -1.869164 | -2.096005 | -0.045676 |
| H    | 2.210794  | 1.848140  | -0.000705 |
| H    | 3.085030  | -1.535701 | 0.095461  |
| H    | 3.665209  | 0.065346  | 0.271974  |
| Ag   | 0.904721  | -3.330565 | 0.029160  |
| Ag   | 1.117151  | -5.975867 | 0.120277  |
A 24. Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for the guanine/Ag\(_2\) complex (N3) with the M06-2X method/aVTZ level of theory.

\[
\begin{array}{cccccc}
\text{Freq} & \text{IR} & \text{RA} & \text{Freq} & \text{IR} & \text{RA} \\
17 & 1 & 6 & 863 & 29 & 1 \\
20 & 2 & 0 & 878 & 9 & 1 \\
49 & 5 & 9 & 957 & 5 & 7 \\
77 & 4 & 3 & 1066 & 11 & 2 \\
94 & 3 & 12 & 1087 & 15 & 11 \\
145 & 1 & 2 & 1101 & 23 & 3 \\
167 & 1 & 0 & 1145 & 46 & 10 \\
174 & 10 & 48 & 1194 & 90 & 1 \\
208 & 6 & 1 & 1321 & 4 & 12 \\
288 & 135 & 1 & 1348 & 27 & 28 \\
326 & 9 & 2 & 1385 & 49 & 11 \\
355 & 11 & 3 & 1410 & 38 & 70 \\
373 & 2 & 3 & 1475 & 51 & 25 \\
437 & 92 & 8 & 1545 & 1 & 96 \\
498 & 1 & 4 & 1589 & 48 & 26 \\
540 & 2 & 1 & 1630 & 93 & 38 \\
587 & 51 & 5 & 1645 & 381 & 50 \\
624 & 61 & 1 & 1675 & 493 & 86 \\
639 & 30 & 34 & 1855 & 1036 & 68 \\
674 & 7 & 0 & 3277 & 0 & 113 \\
683 & 19 & 1 & 3588 & 103 & 204 \\
723 & 33 & 1 & 3609 & 74 & 186 \\
756 & 0 & 1 & 3631 & 118 & 146 \\
816 & 17 & 1 & 3719 & 133 & 57 \\
\end{array}
\]
A 25. Cartesian coordinates in angstroms (Å) for the guanine/Ag₂ complex (O @ C6) structure with the M06-2X/aVTZ level of theory.

| Atom | x    | y    | z     |
|------|------|------|-------|
| N    | -2.519512 | 0.398844 | -0.022440 |
| C    | -2.927765  | -0.827746 | 0.065334  |
| N    | -1.890415  | -1.734938 | 0.118460  |
| C    | -0.737662  | -1.016040 | 0.058025  |
| C    | -1.146235  | 0.306029  | -0.029275 |
| N    | 0.515838   | -1.518451 | 0.089428  |
| C    | 1.427092   | -0.590918 | 0.008823  |
| C    | -0.142148  | 1.314141  | -0.105818 |
| N    | 1.140403   | 0.742102  | -0.087068 |
| O    | -0.270230  | 2.530649  | -0.181223 |
| N    | 2.743421   | -0.925228 | -0.022641 |
| H    | -3.956451  | -1.146580 | 0.096387  |
| H    | -1.952278  | -2.736522 | 0.187814  |
| H    | 1.906942   | 1.405280  | -0.160896 |
| H    | 2.953736   | -1.880649 | 0.209174  |
| H    | 3.439048   | -0.234536 | 0.202457  |
| Ag   | 1.610205   | 3.957603  | -0.105824 |
| Ag   | 4.264308   | 4.226391  | 0.044897  |
A 26. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in A$^4$ amu$^{-1}$) for the guanine/Ag$_2$ complex (O @ C6) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 10   | 2  | 4  | 844  | 19 | 3  |
| 17   | 0  | 0  | 880  | 8  | 1  |
| 47   | 3  | 7  | 954  | 15 | 11 |
| 72   | 2  | 7  | 1068 | 2  | 1  |
| 102  | 9  | 6  | 1078 | 12 | 14 |
| 145  | 1  | 0  | 1115 | 2  | 1  |
| 160  | 10 | 44 | 1174 | 18 | 2  |
| 183  | 2  | 1  | 1204 | 52 | 2  |
| 208  | 7  | 1  | 1329 | 2  | 12 |
| 319  | 134| 5  | 1374 | 67 | 67 |
| 335  | 8  | 1  | 1382 | 29 | 11 |
| 368  | 5  | 0  | 1408 | 75 | 129|
| 380  | 46 | 5  | 1457 | 14 | 111|
| 452  | 100| 2  | 1545 | 15 | 195|
| 498  | 7  | 5  | 1587 | 34 | 36 |
| 543  | 5  | 6  | 1630 | 54 | 55 |
| 579  | 102| 0  | 1641 | 197| 92 |
| 650  | 15 | 25 | 1680 | 414| 101|
| 657  | 10 | 12 | 1768 | 1423| 149|
| 676  | 6  | 6  | 3273 | 0  | 161|
| 688  | 27 | 4  | 3488 | 372| 1081|
| 735  | 18 | 6  | 3608 | 85 | 206|
| 756  | 3  | 1  | 3671 | 123| 178|
| 823  | 18 | 1  | 3730 | 103| 32 |
**A 27.** Cartesian coordinates in angstroms (Å) for the guanine/Ag$_2$ complex (N7) structure with the M06-2X/aVTZ level of theory.

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| N    | -1.986130 | 0.247185 | 0.027946 |
| C    | -2.471813 | -0.960111 | -0.007330 |
| N    | -1.483232 | -1.906653 | -0.046007 |
| C    | -0.288758 | -1.244801 | -0.034733 |
| C    | -0.621953 | 0.090432  | 0.012115  |
| N    | 0.941145  | -1.807318 | -0.055699 |
| C    | 1.896078  | -0.920730 | -0.046483 |
| C    | 0.418970  | 1.076005  | 0.028280  |
| N    | 1.682196  | 0.428527  | -0.006451 |
| O    | 0.344271  | 2.278751  | 0.059958  |
| N    | 3.193662  | -1.329491 | -0.122439 |
| H    | -3.518323 | -1.213829 | -0.006935 |
| H    | -1.600549 | -2.905683 | -0.078655 |
| H    | 2.467899  | 1.062185  | -0.047009 |
| H    | 3.329426  | -2.318435 | 0.005877  |
| H    | 3.916792  | -0.733695 | 0.241659  |
| Ag   | -3.058443 | 2.341505  | 0.112008  |
| Ag   | -4.702168 | 4.443165  | 0.211835  |
Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the guanine/Ag$_2$ complex (N7) with the M06-2X method/aVTZ level of theory.

| Freq | IR  | RA | Freq | IR  | RA |
|------|-----|----|------|-----|----|
| 15   | 1   | 0  | 849  | 8   | 1  |
| 19   | 0   | 6  | 881  | 7   | 0  |
| 49   | 1   | 3  | 978  | 16  | 2  |
| 53   | 1   | 15 | 1057 | 6   | 2  |
| 99   | 1   | 12 | 1096 | 16  | 5  |
| 152  | 7   | 1  | 1107 | 45  | 2  |
| 168  | 0   | 1  | 1157 | 43  | 3  |
| 171  | 17  | 52 | 1199 | 86  | 4  |
| 204  | 7   | 1  | 1325 | 3   | 13 |
| 314  | 111 | 2  | 1348 | 89  | 5  |
| 328  | 32  | 0  | 1387 | 4   | 17 |
| 345  | 5   | 2  | 1418 | 37  | 68 |
| 373  | 2   | 1  | 1471 | 67  | 9  |
| 486  | 152 | 1  | 1544 | 14  | 107|
| 498  | 51  | 7  | 1587 | 135 | 49 |
| 540  | 11  | 3  | 1630 | 72  | 4  |
| 595  | 65  | 3  | 1651 | 446 | 180|
| 625  | 81  | 2  | 1679 | 666 | 44 |
| 640  | 17  | 32 | 1844 | 697 | 76 |
| 673  | 3   | 1  | 3282 | 8   | 67 |
| 681  | 21  | 1  | 3607 | 72  | 107|
| 726  | 29  | 0  | 3612 | 121 | 217|
| 758  | 3   | 0  | 3665 | 137 | 236|
| 820  | 20  | 1  | 3725 | 63  | 59 |
**A29.** Cartesian coordinates in angstroms (Å) for the cytosine/Ag$_2$ complex (O @ C2) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -1.483704 | 1.085043 | -0.120606 |
| C    | -0.325437 | 1.772078 | -0.072569 |
| N    | 0.847440  | 1.117100 | 0.063348  |
| C    | 0.929312  | -0.276067 | 0.159900  |
| N    | -0.227269 | -0.973834 | 0.112694  |
| C    | -1.372331 | -0.340498 | -0.019605 |
| O    | 2.034025  | -0.800103 | 0.281923  |
| N    | -2.487387 | -1.092547 | -0.059993 |
| H    | -2.391837 | -2.090731 | 0.012128  |
| H    | -3.396817 | -0.683540 | -0.158999 |
| H    | -0.270536 | 2.849131  | -0.137782 |
| H    | -2.434087 | 1.581221  | -0.228508 |
| H    | 1.723757  | 1.624360  | 0.100503  |
| Ag   | 4.046240  | 0.368196  | 0.367037  |
| Ag   | 5.788030  | 2.383401  | 0.375846  |
\textbf{A 30.} Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the cytosine/Ag$_2$ complex (O@C2) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 15   | 1  | 5  | 957  | 1  | 2  |
| 21   | 0  | 0  | 998  | 3  | 4  |
| 53   | 3  | 9  | 1009 | 0  | 1  |
| 78   | 2  | 6  | 1116 | 23 | 3  |
| 120  | 12 | 14 | 1140 | 3  | 18 |
| 159  | 1  | 1  | 1238 | 52 | 3  |
| 175  | 26 | 41 | 1318 | 11 | 25 |
| 206  | 81 | 0  | 1377 | 73 | 36 |
| 217  | 101| 0  | 1461 | 68 | 117|
| 383  | 26 | 1  | 1521 | 327| 19 |
| 425  | 7  | 0  | 1602 | 145| 18 |
| 550  | 7  | 4  | 1636 | 566| 40 |
| 560  | 9  | 1  | 1720 | 642| 19 |
| 566  | 9  | 0  | 1740 | 1302| 132|
| 599  | 32 | 10 | 3233 | 2  | 43 |
| 674  | 23 | 20 | 3261 | 0  | 152|
| 743  | 19 | 1  | 3539 | 390| 883|
| 799  | 1  | 29 | 3623 | 146| 267|
| 804  | 4  | 2  | 3764 | 73 | 70 |
| 819  | 44 | 0  |      |    |    |
**A 31.** Cartesian coordinates in angstroms (Å) for the cytosine/Ag$_2$ complex (N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x        | y        | z        |
|------|----------|----------|----------|
| C    | −1.049176| 1.349835 | 0.030564 |
| C    | 0.170462 | 1.922214 | 0.004748 |
| N    | 1.285916 | 1.161513 | −0.015367|
| C    | 1.256671 | −0.242373| −0.010961|
| N    | 0.013945 | −0.817386| 0.015324 |
| C    | −1.082194| −0.084694| 0.035132 |
| O    | 2.290956 | −0.867495| −0.029833|
| N    | −2.261754| −0.719147| 0.060312 |
| H    | −2.281341| −1.729457| 0.063451 |
| H    | −3.125646| −0.210281| 0.076102 |
| H    | 0.315240 | 2.993032 | −0.001050|
| H    | −1.951543| 1.937913 | 0.046905 |
| H    | 2.205716 | 1.573054 | −0.034784|
| Ag   | 0.081016 | −3.171068| 0.020397 |
| Ag   | −0.820391| −5.685753| 0.045175 |
A 32. Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in \(\AA^4\) amu\(^{-1}\)) for the cytosine/Ag\(_2\) complex (N3) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 19   | 2  | 6  | 965  | 1  | 13 |
| 22   | 1  | 0  | 1007 | 2  | 7  |
| 63   | 3  | 12 | 1008 | 0  | 1  |
| 71   | 7  | 1  | 1122 | 45 | 4  |
| 102  | 1  | 13 | 1137 | 3  | 6  |
| 155  | 1  | 1  | 1227 | 56 | 15 |
| 169  | 15 | 43 | 1294 | 56 | 27 |
| 208  | 3  | 3  | 1380 | 24 | 14 |
| 307  | 117| 9  | 1465 | 177| 12 |
| 385  | 10 | 5  | 1530 | 84 | 28 |
| 421  | 20 | 0  | 1599 | 340| 52 |
| 542  | 7  | 4  | 1650 | 159| 28 |
| 557  | 7  | 1  | 1717 | 431| 17 |
| 570  | 0  | 9  | 1812 | 521| 16 |
| 595  | 4  | 7  | 3231 | 1  | 109|
| 652  | 52 | 1  | 3262 | 0  | 167|
| 744  | 34 | 1  | 3555 | 193| 340|
| 795  | 1  | 32 | 3642 | 128| 195|
| 800  | 0  | 1  | 3734 | 144| 71 |
| 812  | 47 | 2  |      |    |    |
**A 33.** Cartesian coordinates in angstroms (Å) for the cytosine/Ag$_2$ complex (NH$_2$ @ C4) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -1.110812 | 1.060567 | 0.161617 |
| C    | -0.014266 | 1.573885 | -0.437790 |
| N    | 1.105593  | 0.833790 | -0.541272 |
| C    | 1.220494  | -0.487631 | -0.054451 |
| N    | 0.096347  | -1.002261 | 0.548948 |
| C    | -0.977010 | -0.278438 | 0.642933 |
| O    | 2.267647  | -1.070476 | -0.185454 |
| N    | -2.095213 | -0.890091 | 1.199242 |
| H    | -1.863558 | -1.740623 | 1.695894 |
| H    | -2.718208 | -0.280427 | 1.709129 |
| H    | 0.018510  | 2.569487  | -0.856802 |
| H    | -2.032804 | 1.612610  | 0.240895 |
| H    | 1.934376  | 1.195987  | -0.986847 |
| Ag   | -3.533844 | -1.392515 | -0.791876 |
| Ag   | -5.214801 | -1.600591 | -2.839377 |
Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in \(\text{Å}^4\) amu\(^{-1}\)) for the cytosine/Ag\(_2\) complex (NH\(_2\) @ C4) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 15   | 0  | 9  | 950  | 8  | 6  |
| 20   | 6  | 9  | 1004 | 3  | 3  |
| 40   | 0  | 2  | 1007 | 0  | 2  |
| 50   | 5  | 2  | 1135 | 25 | 14 |
| 118  | 13 | 11 | 1138 | 17 | 3  |
| 146  | 0  | 5  | 1216 | 74 | 18 |
| 170  | 18 | 46 | 1250 | 7  | 9  |
| 249  | 12 | 5  | 1342 | 92 | 23 |
| 362  | 4  | 1  | 1455 | 174| 5  |
| 422  | 9  | 1  | 1514 | 95 | 15 |
| 520  | 52 | 6  | 1615 | 221| 27 |
| 545  | 3  | 3  | 1628 | 69 | 16 |
| 554  | 36 | 5  | 1720 | 522| 21 |
| 579  | 2  | 5  | 1828 | 896| 42 |
| 660  | 19 | 7  | 3228 | 1  | 78 |
| 717  | 354| 10 | 3260 | 1  | 66 |
| 760  | 48 | 9  | 3548 | 62 | 167|
| 779  | 17 | 36 | 3635 | 125| 137|
| 809  | 18 | 1  | 3657 | 46 | 41 |
| 825  | 238| 4  |      |    |    |
**A 35.** Cartesian coordinates in angstroms (Å) for the thymine/Ag$_2$ complex (O @ C2/N1) structure with the M06-2X/aVTZ level of theory.

| Atom | x          | y          | z         |
|------|------------|------------|-----------|
| C    | -1.297362  | -0.465153  | 0.007722  |
| C    | -0.522761  | -1.555712  | -0.050582 |
| N    | 0.854256   | -1.494089  | -0.076689 |
| C    | 1.550120   | -0.319788  | -0.045568 |
| N    | 0.760675   | 0.793301   | 0.013917  |
| C    | -0.640211  | 0.842005   | 0.044796  |
| O    | 2.772096   | -0.254974  | -0.068343 |
| C    | -2.789619  | -0.488528  | 0.037696  |
| O    | -1.209362  | 1.905066   | 0.097781  |
| H    | -0.932817  | -2.555352  | -0.080847 |
| H    | 1.409659   | -2.339338  | -0.120948 |
| H    | 1.244197   | 1.680907   | 0.038319  |
| H    | -3.163487  | -1.509607  | 0.005851  |
| H    | -3.194760  | 0.066303   | -0.808144 |
| H    | -3.158586  | -0.001462  | 0.939943  |
| Ag   | 4.097653   | -2.237006  | -0.172606 |
| Ag   | 4.654072   | -4.835299  | -0.284843 |
**A 36.** Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the thymine/Ag$_2$ complex (O@C2/N1) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 13   | 1  | 6  | 991  | 8  | 5  |
| 18   | 3  | 0  | 1036 | 4  | 6  |
| 46   | 0  | 7  | 1079 | 1  | 1  |
| 71   | 1  | 5  | 1170 | 9  | 4  |
| 111  | 12 | 8  | 1227 | 184| 5  |
| 122  | 0  | 0  | 1257 | 1  | 9  |
| 154  | 0  | 0  | 1396 | 4  | 73 |
| 169  | 14 | 46 | 1413 | 5  | 3  |
| 169  | 2  | 1  | 1425 | 3  | 5  |
| 280  | 4  | 1  | 1467 | 80 | 54 |
| 312  | 1  | 0  | 1473 | 8  | 5  |
| 415  | 7  | 0  | 1496 | 0  | 6  |
| 420  | 38 | 1  | 1523 | 125| 61 |
| 473  | 67 | 7  | 1744 | 59 | 95 |
| 560  | 4  | 8  | 1770 | 1819| 57 |
| 616  | 16 | 17 | 1820 | 445| 90 |
| 621  | 7  | 13 | 3072 | 12 | 264|
| 701  | 60 | 3  | 3132 | 4  | 83 |
| 751  | 3  | 14 | 3159 | 7  | 58 |
| 781  | 6  | 2  | 3229 | 4  | 54 |
| 801  | 50 | 0  | 3558 | 392| 916|
| 818  | 28 | 7  | 3607 | 96 | 89 |
| 939  | 14 | 2  |      |    |    |
**A 37.** Cartesian coordinates in angstroms (Å) for the thymine/Ag$_2$ complex (O @ C2/N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | −1.449426 | −0.531928 | 0.014836 |
| C    | −0.833400 | −1.712865 | −0.113061 |
| N    | 0.539465  | −1.832819 | −0.168205 |
| C    | 1.390895  | −0.765793 | −0.097941 |
| N    | 0.763716  | 0.439881  | 0.032580  |
| C    | −0.619177 | 0.672289  | 0.098337  |
| O    | 2.604164  | −0.906218 | −0.149823 |
| C    | −2.929775 | −0.352302 | 0.078899  |
| O    | −1.042033 | 1.795355  | 0.214725  |
| H    | −1.377085 | −2.644582 | −0.180842 |
| H    | 0.981608  | −2.732162 | −0.264736 |
| H    | 1.361301  | 1.258261  | 0.088254  |
| H    | −3.441959 | −1.309475 | 0.007775  |
| H    | −3.268181 | 0.294859  | −0.729822 |
| H    | −3.212164 | 0.135497  | 1.011462  |
| Ag   | 4.196415  | 0.863544  | −0.039073 |
| Ag   | 5.556784  | 3.138830  | 0.125403  |
Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for the thymine/Ag\(_2\) complex (O @ C2/N3) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 15   | 0  | 6  | 993  | 4  | 6  |
| 15   | 3  | 0  | 1036 | 4  | 2  |
| 44   | 0  | 8  | 1079 | 1  | 1  |
| 57   | 0  | 4  | 1164 | 3  | 1  |
| 114  | 4  | 12 | 1215 | 151| 0  |
| 122  | 0  | 2  | 1257 | 2  | 3  |
| 164  | 0  | 0  | 1394 | 5  | 28 |
| 165  | 0  | 1  | 1418 | 8  | 53 |
| 174  | 13 | 47 | 1426 | 4  | 4  |
| 281  | 0  | 0  | 1461 | 132| 3  |
| 310  | 0  | 0  | 1473 | 8  | 6  |
| 410  | 10 | 1  | 1496 | 2  | 6  |
| 418  | 73 | 3  | 1519 | 193| 43 |
| 468  | 25 | 6  | 1747 | 51 | 58 |
| 557  | 17 | 6  | 1775 | 1689| 73 |
| 574  | 63 | 1  | 1826 | 375| 50 |
| 621  | 2  | 3  | 3072 | 13 | 250|
| 708  | 30 | 8  | 3133 | 3  | 68 |
| 751  | 5  | 22 | 3157 | 8  | 65 |
| 781  | 9  | 1  | 3228 | 3  | 130|
| 801  | 41 | 1  | 3543 | 195| 374|
| 821  | 28 | 10 | 3656 | 136| 112|
| 934  | 15 | 1  | 68   |    |    |
A 39. Cartesian coordinates in angstroms (Å) for the thymine/Ag$_2$ complex (O @ C4/N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z        |
|------|-------|-------|----------|
| C    | -1.031393 | -0.479525 | 0.001224 |
| C    | -0.317277  | -1.615447  | -0.006425 |
| N    | 1.053748   | -1.631392  | -0.007643 |
| C    | 1.832248   | -0.492941  | -0.001196 |
| N    | 1.082144   | 0.670526   | 0.006652  |
| C    | -0.295212  | 0.777096   | 0.008439  |
| O    | 3.035583   | -0.510426  | -0.002288 |
| C    | -2.523728  | -0.418108  | 0.002824  |
| O    | -0.841603  | 1.871976   | 0.015696  |
| H    | -0.789873  | -2.587946  | -0.012089 |
| H    | 1.565551   | -2.498559  | -0.013455 |
| H    | 1.617214   | 1.533272   | 0.011582  |
| H    | -2.951434  | -1.418424  | -0.003049 |
| H    | -2.884838  | 0.126829   | -0.868896 |
| H    | -2.883409  | 0.115939   | 0.881844  |
| Ag   | 0.235631   | 3.991309   | 0.028003  |
| Ag   | 1.874926   | 6.081335   | 0.039676  |
A 40. Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the thymine/Ag$_2$ complex (O @ C4/N3) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 14   | 0  | 7  | 986  | 12 | 17 |
| 16   | 2  | 0  | 1030 | 9  | 3  |
| 53   | 1  | 11 | 1080 | 1  | 0  |
| 58   | 0  | 4  | 1182 | 30 | 2  |
| 100  | 4  | 8  | 1228 | 118| 2  |
| 117  | 0  | 0  | 1247 | 11 | 21 |
| 169  | 8  | 52 | 1382 | 23 | 74 |
| 171  | 0  | 1  | 1424 | 3  | 41 |
| 172  | 0  | 1  | 1427 | 3  | 12 |
| 300  | 19 | 2  | 1449 | 90 | 15 |
| 304  | 1  | 1  | 1475 | 9  | 5  |
| 412  | 70 | 3  | 1498 | 1  | 4  |
| 413  | 15 | 1  | 1534 | 125| 15 |
| 469  | 23 | 4  | 1736 | 5  | 19 |
| 557  | 13 | 4  | 1746 | 1312| 272|
| 596  | 67 | 0  | 1853 | 717| 17 |
| 623  | 11 | 7  | 3071 | 12 | 210|
| 708  | 20 | 6  | 3132 | 4  | 56 |
| 757  | 2  | 14 | 3156 | 10 | 68 |
| 781  | 18 | 0  | 3223 | 2  | 146|
| 803  | 38 | 3  | 3538 | 195| 315|
| 816  | 4  | 7  | 3655 | 156| 152|
| 946  | 12 | 1  |      |    |    |
Cartesian coordinates in angstroms (Å) for the thymine/Ag\(_2\) complex (O @ C4/C5) structure with the M06-2X/aVTZ level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -0.803365 | -0.591118 | -0.048421 |
| C    | -0.095225  | -1.731812  | -0.059741  |
| N    | 1.267668   | -1.768619   | 0.084437   |
| C    | 2.047283   | -0.644550   | 0.254952   |
| N    | 1.305384   | 0.521397    | 0.264568   |
| C    | -0.064983  | 0.652346    | 0.126823   |
| O    | 3.244528   | -0.675212   | 0.381736   |
| C    | -2.287743  | -0.531390   | -0.203936  |
| O    | -0.561129  | 1.768267    | 0.159099   |
| H    | -0.570381  | -2.694906   | -0.185040  |
| H    | 1.769872   | -2.641369   | 0.071511   |
| H    | 1.833102   | 1.375334    | 0.387142   |
| H    | -2.703081  | -1.529891   | -0.325550  |
| H    | -2.566283  | 0.068198    | -1.072236  |
| H    | -2.753782  | -0.065526   | 0.666014   |
| Ag   | -2.708209  | 2.789599    | 0.006437   |
| Ag   | -5.127716  | 3.879282    | -0.170256  |
Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the thymine/Ag$_2$ complex (O @ C4/C5) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 10   | 0  | 0  | 984  | 17 | 6  |
| 20   | 0  | 5  | 1029 | 5  | 1  |
| 48   | 0  | 13 | 1074 | 2  | 1  |
| 65   | 0  | 3  | 1183 | 28 | 5  |
| 94   | 7  | 6  | 1227 | 217| 4  |
| 117  | 0  | 0  | 1249 | 12 | 14 |
| 168  | 14 | 60 | 1382 | 7  | 73 |
| 170  | 1  | 1  | 1418 | 9  | 2  |
| 224  | 0  | 0  | 1423 | 2  | 5  |
| 291  | 3  | 0  | 1450 | 59 | 5  |
| 303  | 1  | 0  | 1475 | 13 | 5  |
| 411  | 25 | 1  | 1493 | 27 | 39 |
| 412  | 18 | 1  | 1533 | 177| 16 |
| 468  | 38 | 2  | 1734 | 38 | 47 |
| 567  | 26 | 8  | 1754 | 1576| 258|
| 587  | 60 | 0  | 1851 | 949| 26 |
| 616  | 1  | 16 | 3057 | 12 | 315|
| 697  | 53 | 1  | 3112 | 1  | 48 |
| 754  | 7  | 17 | 3150 | 20 | 63 |
| 780  | 21 | 0  | 3222 | 2  | 87 |
| 803  | 46 | 2  | 3604 | 90 | 71 |
| 816  | 2  | 13 | 3652 | 167| 158|
| 946  | 11 | 1  |      |    |    |
A 43. Cartesian coordinates in angstroms (Å) for the uracil/Ag$_2$ complex (O @ C2/N1) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | 1.422776| 0.970992| −0.084344|
| C    | 0.361092| 1.782287| −0.021149|
| N    | −0.92209| 1.300760| 0.065481 |
| C    | −1.216016| −0.038057| 0.093953 |
| N    | −0.123818| −0.853732| 0.028799 |
| C    | 1.227556| −0.471502| −0.061572|
| O    | −2.356041| −0.471763| 0.170955 |
| O    | 2.089626| −1.311942| −0.111599|
| H    | 0.444564| 2.859060| −0.034116|
| H    | −1.713709| 1.930744| 0.112429 |
| H    | −0.310145| −1.847426| 0.047856 |
| H    | 2.429129| 1.347688| −0.152278|
| Ag   | −4.230255| 1.014224| 0.282132 |
| Ag   | −5.505059| 3.347483| 0.348495 |
Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the uracil/Ag$_2$ complex (O @ C2/N1) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 14   | 1  | 5  | 843  | 61 | 0  |
| 21   | 3  | 0  | 988  | 5  | 3  |
| 48   | 0  | 7  | 1006 | 6  | 1  |
| 74   | 1  | 5  | 1010 | 0  | 2  |
| 112  | 13 | 8  | 1102 | 1  | 10 |
| 161  | 2  | 0  | 1231 | 137| 3  |
| 168  | 14 | 45 | 1239 | 16 | 32 |
| 183  | 0  | 0  | 1405 | 3  | 38 |
| 413  | 10 | 0  | 1426 | 2  | 11 |
| 417  | 55 | 2  | 1457 | 103| 26 |
| 527  | 37 | 3  | 1518 | 152| 63 |
| 560  | 30 | 13 | 1716 | 117| 51 |
| 576  | 4  | 1  | 1774 | 1654| 69 |
| 613  | 12 | 18 | 1837 | 556| 110|
| 707  | 63 | 3  | 3236 | 3  | 47 |
| 742  | 4  | 2  | 3278 | 5  | 139|
| 788  | 16 | 23 | 3546 | 414| 872|
| 794  | 31 | 1  | 3608 | 98 | 85 |
A 45. Cartesian coordinates in angstroms (Å) for the uracil/Ag₂ complex (O @ C2/N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | 1.123916| 1.595441| 0.118722|
| C    | −0.166190| 1.845485| 0.363344|
| N    | −1.117380| 0.855056| 0.324418|
| C    | −0.826543| −0.454957| 0.035266|
| N    | 0.493015| −0.696002| −0.212195|
| C    | 1.548105| 0.238028| −0.199738|
| O    | −1.699009| −1.308495| 0.009814|
| O    | 2.672856| −0.117637| −0.438704|
| H    | −0.537000| 2.830823| 0.604162|
| H    | −2.087775| 1.050009| 0.509702|
| H    | 0.744435| −1.655093| −0.429795|
| H    | 1.873805| 2.367519| 0.147777|
| Ag   | −0.387081| −6.034219| −1.073587|
| Ag   | −1.326164| −3.622283| −0.479283|
A 46. Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for the uracil/Ag\(_2\) complex (O @ C2/N3) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 12   | 4  | 0  | 843  | 59 | 0  |
| 17   | 0  | 6  | 989  | 7  | 3  |
| 51   | 0  | 9  | 1004 | 0  | 2  |
| 58   | 0  | 4  | 1007 | 8  | 3  |
| 116  | 4  | 13 | 1098 | 5  | 5  |
| 158  | 1  | 0  | 1217 | 99 | 4  |
| 174  | 12 | 45 | 1239 | 16 | 10 |
| 179  | 0  | 1  | 1403 | 5  | 33 |
| 406  | 15 | 1  | 1427 | 4  | 31 |
| 411  | 63 | 3  | 1453 | 231| 3  |
| 528  | 19 | 2  | 1514 | 154| 25 |
| 550  | 17 | 4  | 1718 | 79 | 32 |
| 578  | 49 | 0  | 1779 | 1519| 80 |
| 580  | 23 | 2  | 1842 | 443| 56 |
| 700  | 40 | 8  | 3238 | 2  | 120|
| 743  | 9  | 0  | 3275 | 5  | 157|
| 789  | 8  | 33 | 3538 | 196| 335|
| 791  | 25 | 2  | 3654 | 139| 104|
A 47. Cartesian coordinates in angstroms (Å) for the uracil/Ag₂ complex (O @ C4/N3) structure with the M06-2X/aVTZ level of theory.

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | 0.861951 | 1.589743 | 0.538388 |
| C    | -0.414594 | 1.899547 | 0.270848 |
| N    | -1.292192 | 0.981978 | -0.232122 |
| C    | -0.950980 | -0.331523 | -0.507912 |
| N    | 0.370813 | -0.620815 | -0.222000 |
| C    | 1.328517 | 0.241306 | 0.287600 |
| O    | -1.730623 | -1.132354 | -0.950702 |
| O    | 2.469290 | -0.142330 | 0.496545 |
| H    | -0.819581 | 2.887224 | 0.436955 |
| H    | -2.249716 | 1.223712 | -0.430163 |
| H    | 0.657864 | -1.576210 | -0.411794 |
| H    | 1.559213 | 2.307338 | 0.934777 |
| Ag   | 3.309418 | -2.335740 | 0.111169 |
| Ag   | 3.730173 | -4.888487 | -0.492234 |
Vibrational frequencies (Freq in cm\(^{-1}\)), infrared intensities (IR in km mol\(^{-1}\)), and Raman scattering activities (RA in Å\(^4\) amu\(^{-1}\)) for the uracil/Ag\(_2\) complex (O @ C4/N3) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 15   | 3  | 0  | 841  | 54 | 1  |
| 18   | 0  | 6  | 995  | 17 | 9  |
| 53   | 1  | 11 | 1000 | 7  | 9  |
| 61   | 0  | 4  | 1009 | 0  | 1  |
| 119  | 6  | 13 | 1107 | 6  | 5  |
| 164  | 1  | 0  | 1216 | 109| 3  |
| 175  | 16 | 45 | 1247 | 2  | 29 |
| 177  | 0  | 2  | 1395 | 49 | 87 |
| 409  | 20 | 1  | 1432 | 0  | 32 |
| 414  | 75 | 2  | 1440 | 88 | 5  |
| 529  | 28 | 3  | 1533 | 128| 11 |
| 559  | 19 | 6  | 1705 | 66 | 41 |
| 576  | 1  | 2  | 1762 | 1394| 252|
| 596  | 52 | 0  | 1858 | 620| 22 |
| 701  | 26 | 7  | 3236 | 1  | 142|
| 745  | 20 | 0  | 3281 | 5  | 105|
| 790  | 29 | 2  | 3531 | 207| 335|
| 793  | 0  | 24 | 3649 | 160| 146|
### A 49. Cartesian coordinates in angstroms (Å) for the uracil/Ag\(_2\) complex (O @ C4/C5) structure with the M06-2X/aVTZ level of theory.

| Atom | x          | y          | z          |
|------|------------|------------|------------|
| C    | 0.948911   | 0.922814   | 0.100882   |
| C    | −0.205697  | 1.589335   | −0.043000  |
| N    | −1.399118  | 0.946779   | −0.215431  |
| C    | −1.525566  | −0.430502  | −0.257015  |
| N    | −0.320127  | −1.088512  | −0.106123  |
| C    | 0.933249   | −0.524900  | 0.072993   |
| O    | −2.578824  | −0.991731  | −0.409093  |
| O    | 1.905138   | −1.255595  | 0.191077   |
| H    | −0.256582  | 2.668369   | −0.030650  |
| H    | −2.260161  | 1.458454   | −0.322472  |
| H    | −0.366955  | −2.098498  | −0.130428  |
| H    | 1.892286   | 1.427617   | 0.237126   |
| Ag   | 4.128668   | −0.450624  | 0.505347   |
| Ag   | 6.452755   | 0.796333   | 0.841052   |
Vibrational frequencies (Freq in cm$^{-1}$), infrared intensities (IR in km mol$^{-1}$), and Raman scattering activities (RA in Å$^4$ amu$^{-1}$) for the uracil/Ag$_2$ complex (O @ C4/C5) with the M06-2X method/aVTZ level of theory.

| Freq | IR | RA | Freq | IR | RA |
|------|----|----|------|----|----|
| 13   | 1  | 0  | 843  | 47 | 4  |
| 19   | 1  | 6  | 992  | 13 | 6  |
| 53   | 0  | 12 | 999  | 12 | 1  |
| 65   | 0  | 4  | 1011 | 1  | 4  |
| 108  | 12 | 8  | 1113 | 19 | 23 |
| 166  | 1  | 1  | 1218 | 146| 5  |
| 171  | 18 | 53 | 1251 | 9  | 63 |
| 176  | 0  | 0  | 1394 | 21 | 13 |
| 409  | 21 | 1  | 1428 | 3  | 4  |
| 416  | 37 | 2  | 1443 | 81 | 9  |
| 533  | 62 | 4  | 1532 | 229| 19 |
| 560  | 5  | 7  | 1703 | 75 | 20 |
| 576  | 8  | 3  | 1762 | 1579| 212|
| 599  | 48 | 0  | 1855 | 860| 29 |
| 698  | 61 | 1  | 3233 | 2  | 72 |
| 748  | 11 | 0  | 3250 | 4  | 177|
| 790  | 39 | 0  | 3603 | 98 | 78 |
| 792  | 1  | 28 | 3648 | 163| 165|