

# Raman spectroscopic study of 6-amino-7-deazapurine



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## ABSTRACT

We used Raman spectroscopy to perform an adsorption study on 6-amino-7-deazapurine (6A-7DAP) on gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs). Unlike the adenine purine unit, the 6A-7DAP ring does not have a nitrogen atom in its N7 position. Density functional theory (DFT) calculations predicted that the amino-9H tautomeric form would be most stable among the conformers of 6A-7DAP including amino and imino conformers. Surface-enhanced Raman scattering spectra were analyzed with appropriate vibrational assignments to estimate the binding modes based on DFT calculations. After considering the enhancement factors, the Raman spectra of adenine and 6A-7DAP on AgNPs and AuNPs were dissimilar, suggesting that the different nitrogen atoms of the adenine and 6A-7DAP molecule may be significantly involved in the binding on AgNPs and AuNPs. Our Raman study indicates that the purine analog nitrogen atoms' positions may play a significant role in coordinating metal surfaces.

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## 1. Introduction

Much attention has been given to the use of nanoparticulate intracellular delivery of anticancer drugs [1]. Surface-enhanced Raman scattering (SERS) has been used to estimate the presence of adsorbates on metal nanostructures [2–5]. To explain the complexity of various tautomeric forms of purine bases by energetic stabilities and hydrogen bonding interactions, quantum chemical calculations have been introduced [6].

DNA base analogs have attracted much attention due to their important roles in molecular biology and genetics [7–9]. Analogs of purine bases have been implicated in the prebiotic system as drug molecules for therapy [10]. A compound of deazapurines as a purine-based metabolite has diverse functions ranging from secondary metabolism to RNA modification [11]. 6-Amino-7-deazapurine (6A-7DAP)-consisting nucleosides have been identified as a novel inhibitor of cyclin-dependent kinases (CDKs) [12]. Unlike the adenine purine unit, this 6A-7DAP ring does not have a nitrogen atom in its N7 position, whereas the pentose ring attaches to the N1 atom of the CDK compounds.

Numerous studies have investigated the adsorption of adenine on metal nanoparticles (NPs) [13–15]. It has been reported that N7 of adenine has a significant role in binding silver nanoparticles (AgNPs)

[16]. It is not certain yet whether the absence of the nitrogen atom at the “7” position in the purine ring of 6A-7DAP would cause dissimilar binding schemes on metal surfaces, which leads to different adsorption geometries. In this work, we performed a SERS study of adenine and 6A-7DAP on AuNPs and AgNPs. The energetic stabilities of several tautomeric forms of 6A-7DAP were calculated to estimate its most stable conformer to discuss the adsorption behaviors to explain the experimental Raman spectra. Our study indicates that the positions of the nitrogen atoms in the purine analog rings, may play a significant role in coordinating metal surfaces, resulting in different Raman spectra features.

## 2. Experimental

### 2.1. Sample preparation and physical characterization

Adenine ( $\geq 99\%$ ) and 6A-7DAP (97%) were purchased from Sigma–Aldrich (St. Louis, USA). Colloidal AuNPs were synthesized by the citrate reduction method. Concisely, 3 mL of 1% sodium citrate solution was added quickly to 30 mL of 1.4 mM HAuCl<sub>4</sub> solution under vigorous stirring, and the mixture was then boiled for 1 h. For AgNPs, 50 mL of triply distilled water was added to 1 mL of AgNO<sub>3</sub> (55 mM) on the heating and stirring plate. We also maintained the level of liquid in the flask wall for 1 h by adding triply distilled water. UV–vis spectroscopy, transmission electron microscopy, and dynamic light scattering particle size analysis were used to characterize colloidal AuNPs and AgNPs.

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## 2.2. DFT calculations

The most stable geometries of the amino 1H-, 3H-, and 9H-tautomeric forms of 6A-7DAP were selected to compare the vibrational spectra. The imino forms of (9H, 1H) and (9H, 3H) tautomeric forms were also calculated, as well as the amino forms. Raman frequencies and assignments were calculated at the fully optimized geometry with the minima on potential energy surfaces. The Raman frequencies of the most stable tautomer of the amino-9H form were calculated to correlate the experimental spectra. DFT calculations were performed using Gaussian 09 software [17].

## 2.3. SERS and Raman spectroscopy

All Raman experiments were performed using a Renishaw Raman Microscope System 1000 spectrometer equipped with an integral microscope (Leica DM LM), and a 632.8 nm HeNe laser was used for excitation [18,19]. The SERS spectra were obtained using spectroscopic glass tubes after either adenine or 6A-7DAP was introduced into the AuNP and AgNP solutions. In order to assess standard deviation, three independent measurements were performed. In the SERS measurements, the concentrations of adenine and 6A-7DAP on AuNPs were 10  $\mu$ M, and up to 500  $\mu$ M on AgNPs.

## 3. Results and discussion

### 3.1. Quantum mechanical calculations of tautomeric forms of 6A-7DAP

Fig. 1 illustrates the molecular structures of 6A-7DAP and adenine. No nitrogen atom is present at the “7” position of the imidazole part of the purine ring in 6A-7DAP, which differs from the case of adenine. The atomic numbering is based on Ref. [20]. DFT calculations were used to examine the energetic stabilities of the three amino tautomers of (9H), (3H), and (1H) of the 6A-7DAP aromatic ring. The amino-9H form was found to be the most stable, as it was in the case of adenine. The relative energies of amino (3H) and (1H) were estimated to be higher by 11.92 and 24.12 kcal/mol, respectively, as summarized in Table 1. We also calculated the imino (1H, 9H) and (3H, 9H) forms of the 6A-7DAP tautomers. Their

**Table 1**

Relative optimized energies of three amino (1H, 3H, 9H) and two imino (1H, 9H) and (3H, 9H) tautomeric 6A-7DAP.

Configurations	B.E. (kcal/mol)
Amino	
1H	24.12
3H	11.92
9H	0.0
Imino	
(1H, 9H)	14.22
(3H, 9H)	26.22

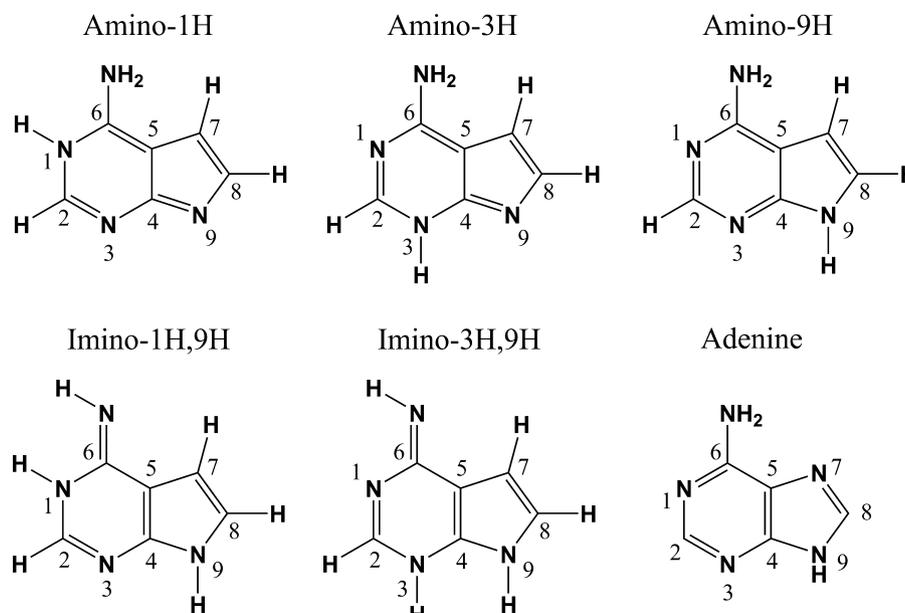
1H-amino gas phase optimized energy =  $-451.26750734$  au.  
 3H-amino gas phase optimized energy =  $-451.28695354$  au.  
 9H-amino neutral gas phase optimized energy =  $-451.30594804$  au, (1H, 9H imino form) =  $-451.28328448$ , (3H, 9H imino form) =  $-451.26416103$  au.

energies were predicted to be higher by 14.22 and 26.22 kcal/mol, respectively, than that of the amino-9H form. We chose to use the most stable amino-9H form to interpret our experimental Raman spectra. Our calculations indicate that adenine and 6A-7DAP have some common characteristics in terms of tautomeric stabilities. We performed Raman measurements to estimate the plausible adsorption geometries on Ag and Au.

It has been determined that the excitation wavelength at 632.8 nm is more suitable for AuNPs because the aggregated AuNPs exhibited the absorption at  $\sim 650$  nm. Our compiled data [22] proved that the 632.8 nm wavelength is also applicable in the study of adsorption on AgNPs when the absorption becomes redshifted after the occurrence of aggregation as revealed in Fig. 2. The excitation wavelength at 632.8 nm appeared to be adequate in obtaining the SERS spectra of the aggregated AgNPs and AuNPs. It must be mentioned that the concentrations of adenine and 6A-7DAP on AgNPs at 500  $\mu$ M appeared to be much larger than those on AuNPs at 10  $\mu$ M.

### 3.2. Raman spectra of adenine

Fig. 3 shows the normal Raman (NR) and SERS spectra of adenine. The ring breathing band at  $\sim 730$   $\text{cm}^{-1}$ , was prominent as



**Fig. 1.** Tautomeric forms of 6A-7DAP and most stable amino-9H form of adenine. Please note that there is no nitrogen atom at the “7” position in 6A-7DAP, which differs from the case of adenine. Atomic numbering is based on Ref. [20].

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