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Computational Studies of Nonstoichiometric Sodium Auride Clusters

Ying-Chan Lin[†] and Dage Sundholm*[,‡]

[†]Department of Chemistry, The Centre for Theoretical and Computational Chemistry, 9037 Tromsø, Norway
[‡]Department of Chemistry, University of Helsinki, P.O. Box 55 (A. I. Virtanens plats 1), FIN-00014 Helsinki, Finland

S *Supporting Information*

ABSTRACT: The molecular structures of low-lying isomers of anionic and neutral sodium auride clusters have been studied computationally at the second-order Møller−Plesset perturbation theory level using quadruple-ζ basis sets augmented with a double set of polarization functions. The first vertical detachment energies were calculated at the Møller−Plesset level as the energy difference between the cluster anion and the corresponding neutral cluster. The photodetachment energies of higher-lying ionization channels were calculated by adding electronic excitation energies of the neutral clusters to the first vertical detachment energy. The excitation energies were calculated at the linear response approximate coupled-cluster singles and doubles level using the anionic cluster structures. The obtained ionization energies for $NaAu^-$, $NaAu_2^-$, $NaAu_3^-$, $NaAu_4^-$, $Na_2Au_2^-$, $Na_2Au_3^-$, $Na_3Au_3^-$, and $Na_2Au_4^-$ were compared to values deduced from experimental photoelectron spectra. Comparison of the calculated photoelectron spectra for a few energetically low-lying isomers shows that the energetically lowest cluster structures obtained in the calculations do not always correspond to the clusters produced experimentally. Spin-component-scaled second-order Møller−Plesset perturbation theory calculations shift the order of the isomers such that the observed clusters more often correspond to the energetically lowest structure, whereas the spin-component-scaled approach does not improve the photodetachment energies of the sodium aurides. The potential energy surface of the sodium aurides is very soft, with several low-lying isomers requiring an accurate electron correlation treatment. The calculations show that merely the energetic criterion is not a reliable means to identify the structures of the observed sodium auride clusters; other experimental information is needed to ensure a correct assignment of the cluster structures. The cluster structures of nonstoichiometric anionic sodium aurides have been determined by comparing calculated ionization energies for low-lying structures of the anionic clusters with experimental data.
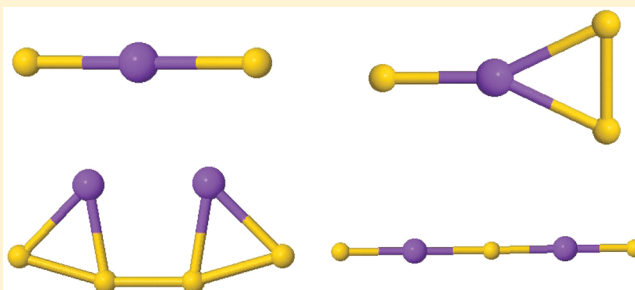
1. INTRODUCTION

Analogies between gold and halogens have been proposed because gold has a large electron affinity due to the relativistic stabilization of the 6s orbital.[1−3] The stabilization leads to formation of alkali−gold compounds, where Au acts as electron acceptor. The most simple sodium auride compound is diatomic NaAu, which was observed for the first time 30 years ago by Piacente et al.[4] NaAu was later thoroughly investigated by Stangassinger et al., who were able to determine the dissociation energy and molecular constants of its three lowest excited states.[5] Molecular structures and bonding energies of other diatomic alkali−gold and alkaline earth−gold compounds have also been obtained in gas-phase measurements.[6−10] Studies on alkali auride solids have shown that the electric properties change along the alkali metal series from Na to Rb. CsAu and RbAu alloys are ionic semiconductors, whereas the lighter alkali auride solids are metallic.[11]

Bimetallic sodium auride clusters have been studied experimentally[12−14] and computationally.[15,16] Schumacher et al. produced mixed sodium−gold clusters consisting of up to five gold atoms and with an excess of sodium atoms.[12,13] Hoshino et al. produced neutral sodium−gold clusters with the composition of Na_mAu_n ($6 \leq m \leq 13$; $0 \leq n \leq 10$) and measured their ionization potentials.[14] Heiz et al. performed a similar study on gold-doped alkali−metal clusters with the compositions of Na_nAu and Cs_nAu.[12] We recently reported a combined computational and experimental study of anionic stoichiometric $Na_nAu_n^-$ ($n = 1 − 3$) clusters,[17] where the molecular structures of the anionic clusters were determined by comparing experimental and computational photoelectron spectroscopy (PES) spectra. The calculations showed that the clusters have many low-lying isomers, making an identification of sodium auride clusters based merely on energetic criteria difficult. However, the calculations showed that the PES spectra of the isomers significantly differ, rendering computational determinations of cluster structures feasible when having access to experimental photoelectron spectra. Explicit calculations of the electron density showed that the excess electron of the anionic clusters is basically shared by the gold atoms, yielding a preference for the formation of extended cluster structures with separated gold atoms to minimize the Coulomb repulsion.[17] A

similar study of the sodium coinage metal clusters $NaCu_4^-$, $NaAg_4^-$, and $NaAu_4^-$ showed that the Cu and Ag species are pyramidal, whereas a planar $NaAu_4^-$ structure was found to be the energetically lowest isomer, as also observed in the experiment.[18] Calculations of magnetically induced ring currents for the Cu_4^{2-} moiety yielded current strengths of the same size as those obtained for Al_4^{2-}, suggesting that the Cu_4^{2-} ring is stabilized by aromaticity,[19] whereas for $NaAu_4^-$, the energy gain due to the spread of the extra electron is larger than the aromatic stabilization energy.[20] The molecular structures of alkaline earth auride clusters (Au_4M, with M = Mg, Ca, Sr, and Ba) have been studied computationally by Pichierri.[21] The obtained results suggest formation of a Au_4^{2-} isomer with D_{4h} symmetry when the Au_4^{2-} cluster has formally doubly positively charged alkaline earth metals as the counterion.

This work is a continuation of our previous study of the sodium auride clusters[17] by extending it to identification of low-lying isomer structures for nonstoichiometric sodium auride clusters such as $NaAu_2^-$, $NaAu_3^-$, $Na_2Au_3^-$, and $Na_2Au_4^-$. The cluster structures of the corresponding neutral clusters are also reported, even though there are no experimental data available with which to compare.

This article is organized as follows. The computational methods are briefly described in section 2. The calculated cluster structures of the lowest isomers of the neutral and anionic clusters are discussed in the section 3. In section 4, the calculated photoelectron spectra of the sodium auride clusters are compared to experimental data for determining the cluster structures.[22−24] The main conclusions are summarized in section 5.

2. COMPUTATIONAL METHODS

The molecular structures of the studied neutral Na_mAu_n and anionic $Na_mAu_n^-$ clusters were optimized at the second-order Møller−Plesset perturbation level (MP2) using the resolution-of-the-identity (RI) approach.[25] Different initial geometries were manually constructed for the structure optimizations. The stationary points obtained in the structure optimizations were checked by calculating the vibrational frequencies. The ground-state energies at the stationary points were also calculated using the spin-component-scaled MP2 method (SCS-MP2)[26] because recent studies on gold clusters and gold complexes showed that MP2 tends to overbind,[27−31] whereas at the SCS-MP2 level, the relative energies are often close to those obtained in accurate coupled-cluster calculations. The vertical electron detachment energies of the PES spectra were obtained by combining calculated values for the electronic excitation energies of neutral clusters with the ground-state detachment energy calculated at the MP2 level. Thus, it is assumed that the final state consists of an excited neutral cluster and a free electron, the kinetic energy of which can be measured. The electronic excitation energies were calculated for the neutral clusters at the approximate coupled-cluster singles and doubles (CC2) level[32] using the RI approach.[33,34]

The ground-state vertical detachment energies (VDEs), that is, the electron affinities of the neutral clusters calculated for the anionic structures, were calculated as the energy difference between the ground-state energies of the anionic and neutral clusters using the optimized molecular structures of the anionic clusters. The ground-state adiabatic detachment energies (ADEs) were analogously obtained using the fully optimized structures of both the anionic and the neutral species. The energies of the higher photodetachment transitions were

obtained by adding excitation energies of the neutral clusters to the ground-state VDE. For open-shell anions in a spin doublet state, the removal of an electron can result in a final singlet or triplet state of the neutral cluster. The PES spectra of these systems were simulated by adding the CC2 singlet and triplet excitation energies to the ground-state VDE. For closed-shell anionic clusters, the ionization leads to an open-shell neutral cluster, the state of which is assumed to be a spin doublet. Higher multiplets were not considered in the calculations of the PES spectra because they are expected to be appear high in energy and to be rare as they involve spin−flip excitations of one valence electron with a simultaneous ionization of another electron.

Four different basis sets were employed. The largest basis set consists of the more recently optimized standard Karlsruhe quadruple-ζ quality valence basis set augmented with double polarization functions (def2-QZVPP).[35] The smallest Au basis set, denoted TZVPP, consists of a 7s5p3d Au basis set optimized for the neutral gold trimer[36,37] and augmented with 2f, as suggested by Pyykkö et al.[38] The smaller basis set for Na was the standard Karlsruhe triple-ζ valence basis set augmented with double polarization functions (def-TZVPP).[39] The effect of diffuse functions was assessed using the def2-TZVPPD and def2-TZVPP basis sets[35,40] In the following, we omit def and def2 in the basis set notation.

The corresponding auxiliary basis sets for the RI-MP2 and RI-CC2 calculations were used[33,41] For Au, the effective core potentials (ECP) from the Stuttgart group were employed.[42] The small-core ECP replaces 60 of the core electrons. All 19 electrons per gold atom and all sodium electrons were correlated. The calculations have been performed with Turbomole.[43]

3. CLUSTER STRUCTURES

The molecular structures of stoichiometric $Na_nAu_n^-$ clusters and of $NaAu_4^-$ have previously been determined by comparing calculated photoelectron spectra for low-lying isomers with experimental data.[17,18] In those studies, the TZVPP basis sets augmented with polarization functions were employed. However, in the present study, we noticed that it is in some cases necessary to use at least QZVPP quality basis sets in order to obtain the correct cluster structures. The same conclusion was drawn in a recent coupled-cluster study on gold clusters.[27] The accuracy of the previous study on $NaAu^-$, $Na_2Au_2^-$, $Na_3Au_3^-$, and $NaAu_4^-$ is therefore assessed using the larger QZVPP basis sets. The most significant differences in comparison to our previous results are discussed. The main focus of this study though is to elucidate the structure of the nonstoichiometric $Na_mAu_n^-$ clusters. Determination of the structures of the sodium auride clusters is a challenge because the energy differences between the isomers are small. Our previous studies showed that the photoelectron spectra are very sensitive to the cluster structure, rendering reliable structure determinations feasible by comparing the computed photo-detachment energies with values deduced from experimental photoelectron spectra.[24] Cui, Li, and Wang have produced nonstoichiometric $Na_mAu_n^-$ clusters in beam experiments by laser vaporization of a compressed disk target made from Au and Na and measured the photoelectron spectra.[24] The experimental methods have previously been described in detail.[17,22,23]

The structures obtained for the energetically lowest isomers of $NaAu_2^-$, $Na_2Au_2^-$, $NaAu_3^-$, $Na_2Au_3^-$, $NaAu_4^-$, $Na_2Au_4^-$, and

$Na_3Au_3^-$ are shown in Figures 1−7. The Cartesian coordinates of the optimized MP2/QZVPP structures of the anionic
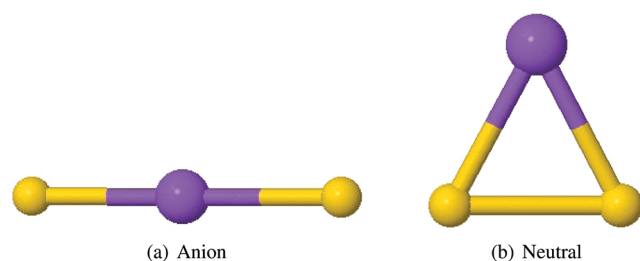

(a) Anion   (b) Neutral

Figure 1. The molecular structures of the lowest isomers of (a) $NaAu_2^-$ and (b) $NaAu_2$ optimized at the MP2/QZVPP level. The figures have been made with Jmol.[48]

sodium auride clusters and the corresponding neutral ones are given as Supporting Information. The relative energy differences for the lowest isomers of the anionic clusters are given in Table 1.

Table 1. Lowest Isomers of the Studied Anionic and Neutral Sodium auride Clusters Optimized at the MP2/QZVPP Level[a]

cluster	isomer I[b]	isomer II	MP2	SCS-MP2
$Na_2Au_2^-$	bent stick (C_s)	ring (D_{2h})	−8.4	2.0
$NaAu_3^-$	Y-shaped (C_{2v})	quadrangular (C_{2v})	−1.5	22
$NaAu_4^-$	planar (C_{2v})	pyramidal (C_{4v})	9.5	36
$Na_2Au_3^-$	linear ($D_{\infty h}$)	star (D_{3h})	−20	−6.4
$Na_2Au_4^-$	planar (C_{2v})	triangular (C_{2v})	−23	−37
$Na_3Au_3^-$	pyramid with two wings (C_s)	star with a Na bridge (C_s)	2.2	13
$NaAu_4$	planar (C_s)[c]	pyramid (C_{2v})	−6.5	11
Na_2Au_3	four-ring with a Au$_2$ (C_{2v})	planar (C_s)	21	40
Na_2Au_4	triangular (C_{2v})	planar (C_{2v})	−1.6	23
Na_3Au_3	star with a Na bridge (C_s)[d]	ring (D_{3h})	17	4.9

[a]The cluster structures are shown in Figures 1−7. The energy differences (in kJ/mol) are calculated at the MP2/QZVPP and SCS-MP2/QZVPP levels. [b]Isomer I is observed in the experiment. Negative relative energy values means that isomer II is the energetically lowest structure in the calculation. [c]The planar C_{2v} isomer is 52 and 31 kJ/mol above the lowest one at the MP2 and SCS-MP2 levels, respectively. [d]The planar isomer is 13 and 5.8 kJ/mol above the lowest one at the MP2 and SCS-MP2 levels, respectively.

Optimization of the cluster structures using the TZVPP and QZVPP basis sets yielded significantly different geometries for $Na_2Au_3^-$. At the MP2/TZVPP level, a bent structure of C_{2v} symmetry was obtained, whereas the MP2/QZVPP calculations yielded a minimum for a linear structure and a global minimum for a three-dimensional (3D) structure of D_{3h} symmetry. Reoptimization of $Na_3Au_3^-$ at the MP2/QZVPP level using the QZVPP basis sets resulted in a similar structure as that obtained when using the TZVPP basis. However, the MP2/QZVPP structure has a more pronounced trigonal pyramidal 3D structure than the MP2/TZVPP one. The lowest $Na_3Au_3^-$ cluster has C_s symmetry and can be considered to consist of a Na$_3$ triangle with one Au forming the top of a trigonal pyramid. The other Au atoms are attached to two of the base edges of the pyramid and are slightly bent downward. For the $NaAu^-$, $Na_2Au_2^-$, and $NaAu_4^-$ species, the structure optimizations at the MP2/TZVPP and MP2/QZVPP levels yielded practically identical structures.

The bent $Na_2Au_3^-$ structure obtained at the MP2/TZVPP level is probably due to the two-electron basis set incompleteness error that recently was found to result in nonplanar benzene at ab initio correlation levels when too small basis sets were employed.[44] The two-electron basis set incompleteness error can make bent structures artificially lower in energy than planar and linear ones, which probably is the reason why $Na_2Au_3^-$ is bent at the MP2/TZVPP level and linear in the MP2/QZVPP calculations.

3.1. $NaAu_2^-$ and $NaAu_2$. The linear structure of the anionic $NaAu_2^-$ cluster (Figure 1a) is the lowest-lying isomer, whereas neutral $NaAu_2$ has a triangular structure of C_{2v} symmetry (Figure 1b). The anion does not have any minimum corresponding to the triangular structure of C_{2v} symmetry. The linear structure of the anion is stabilized because the excess charge is mainly distributed on the Au atoms. The excess charge is split and separated as far as possible from each other, thereby reducing the Coulomb repulsion. For the neutral cluster, the Au−Au bond and the possibility to form an electron delocalization pathway around the triangle stabilize the closed structure. The neutral $NaAu_2$ cluster can be described as a Au$_2$ molecule with a sodium atom attached to the bond center as the Au−Au distance is only 2.54 Å.

3.2. $Na_2Au_2^-$. The lowest $Na_2Au_2^-$ isomer obtained in the MP2/QZVPP calculation is a quadrangular ring of D_{2h} symmetry. The $Na_2Au_2^-$ cluster of D_{2h} symmetry is not the observed one because it has a very small VDE of 0.357 eV, or about 5 times smaller than the experimental one. The observed isomer has a planar quasi-linear structure at the MP2/QZVPP level, as also obtained in our previous study using the MP2/
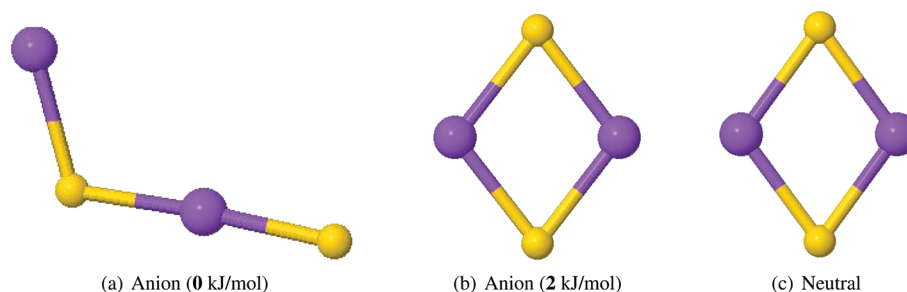

(a) Anion (**0** kJ/mol)   (b) Anion (**2** kJ/mol)   (c) Neutral

Figure 2. The two lowest molecular structures of the $Na_2Au_2^-$ anion are shown in (a) and (b). The energetically lowest structure of the neutral Na_2Au_2 cluster is shown in (c). The cluster structures were optimized at the MP2/QZVPP level. The relative energies given in parentheses were obtained in single-point SCS-MP2/QZVPP calculations.

(a) Anion (**0** kJ/mol)   (b) Anion (**22** kJ/mol)   (c) Neutral

Figure 3. The two energetically lowest molecular structures of the $NaAu_3^-$ anion are shown in (a) and (b). The energetically lowest structure of neutral $NaAu_3$ is shown in (c). The structures were optimized at the MP2/QZVPP level. The relative energies given in parentheses were obtained in single-point SCS-MP2/QZVPP calculations.
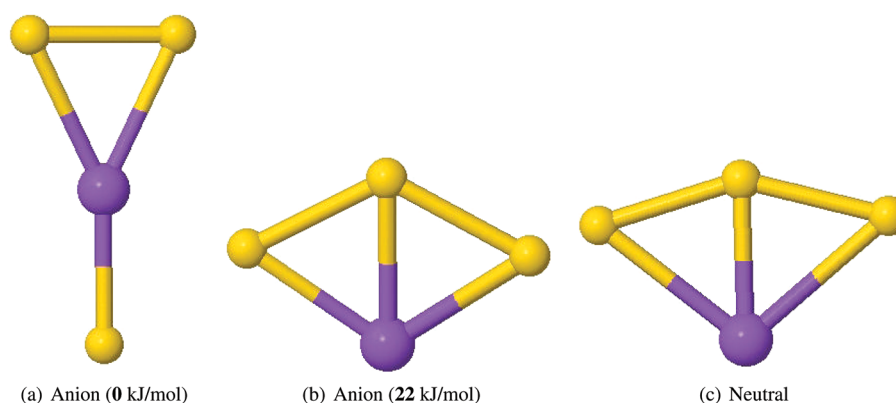

(a) Anion (**0** kJ/mol)   (b) Anion (**-6.4** kJ/mol)

(c)
Neutral (**0** kJ/mol)   (d) Neutral (**40** kJ/mol)

Figure 4. The two energetically lowest molecular structures of the $Na_2Au_3^-$ anion are shown in (a) and (b). The two energetically lowest structures of neutral Na_2Au_3 are shown in (c) and (d). The structures were optimized at the MP2/QZVPP level. The relative energies given in parentheses were obtained in single-point SCS-MP2/QZVPP calculations. The relative energy of the observed anion is set to zero.
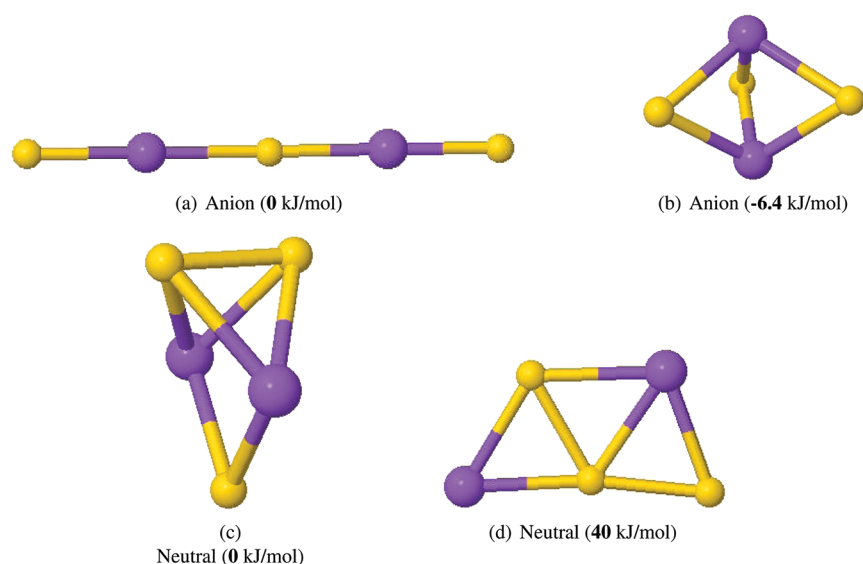
TZVPP basis sets.[17] The D_{2h} structure is 8.4 kJ/mol below the stick at the MP2/QZVPP level, and at the SCS-MP2/QZVPP level, the quadrangle ring is 2.0 kJ/mol higher in energy. Higher-order electron correlation effects as well as the zero-point vibrational energy contributions shift the order of the isomers.[17] Optimization of neutral Na_2Au_2 using the QZVPP basis set did not yield any quasi-linear structure corresponding to the $Na_2Au_2^-$ stick. The lowest isomer of neutral Na_2Au_2 is a rhombic ring-shaped species of D_{2h} symmetry.[17] Thus, the use of the larger basis set could not explain why the experimental ADE and VDE are almost equal, which would suggest that the cluster structures of the anionic and neutral $Na_2Au_2^-$ species are similar. The lowest $Na_2Au_2^-$ and Na_2Au_2 isomers are shown in Figure 2.

3.3. $NaAu_3^-$ and $NaAu_3$. The structure optimization of $NaAu_3^-$ yielded two low-lying structures of C_{2v} symmetry. See Figure 3a and b. The lowest isomer obtained at the MP2/QZVPP level has a planar quadrangular, almost rhombic, structure with Au−Au distances of 2.75 Å. The Au−Na distances at the edges are 2.58 Å, and the one in the center is 2.75 Å. The three Au atoms form an angle of 124°. The second-

lowest isomer is Y-shaped and planar with Na at the center. The two isomers are separated by only 1.5 kJ/mol. In single-point SCS-MP2 calculations, the Y-shaped isomer is 22 kJ/mol lower than the quadrangular one. The anionic cluster prefers the Y-shaped structure to reduce the Coulomb repulsion of the negatively charged Au atoms. The energy differences obtained at the SCS-MP2/QZVPP level are given in Table 1 and Figure 3.

For the neutral $NaAu_3$ cluster, only one low-lying isomer was obtained. It has a quadrangular structure similar to the second-lowest isomer of the $NaAu_3^-$ anion but with a larger Au−Au−Au angle of 149°. The $NaAu_3$ cluster is shown in Figure 3c. The quadrangular structure is stabilized by the Au−Au bonds and possibly by the electron delocalization pathway around the ring as for $NaAu_2$. Structure optimization of neutral $NaAu_3$ did not yield any isomer corresponding to the Y-shaped one.

3.4. $Na_2Au_3^-$ and Na_2Au_3. The lowest isomer of the $Na_2Au_3^-$ anion is a 3D structure of D_{3h} symmetry with the two Na atoms along the symmetry axis. At the MP2/QZVPP level, it lies 20 kJ/mol below the second isomer, which is a linear cluster of $D_{\infty h}$ symmetry. At the SCS-MP2/QZVPP level, the
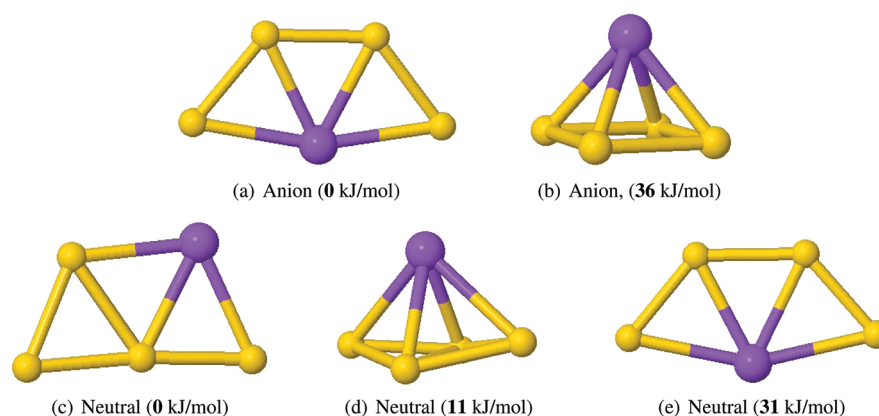
(a) Anion (**0** kJ/mol)   (b) Anion, (**36** kJ/mol)

(c) Neutral (**0** kJ/mol)   (d) Neutral (**11** kJ/mol)   (e) Neutral (**31** kJ/mol)

Figure 5. The two energetically lowest molecular structures of the $NaAu_4^-$ anion are shown in (a) and (b). The three energetically lowest structures of neutral $NaAu_4$ are shown in (c)−(e). The structures were optimized at the MP2/QZVPP level. The relative energies given in parentheses were obtained in single-point SCS-MP2/QZVPP calculations.

D_{3h} structure is only 6.4 kJ/mol below the linear one, which is observed in the photodetachment experiment. The two lowest isomers of $Na_2Au_3^-$ are shown in Figure 4a and b. The lowest isomer of the neutral cluster, shown in Figure 4c, has a 3D structure of C_{2v} symmetry. The planar structure of the neutral Na_2Au_3 cluster, shown in Figure 4d, lies 22 kJ/mol higher in energy at the MP2 level and 40 kJ/mol in the SCS-MP2 calculations. The planar neutral Na_2Au_3 clusters seem to be stabilized by formation of Au−Au bonds. The structures of the two energetically lowest isomers of the neutral Na_2Au_3 cluster can be obtained by formally adding a Na^+ cation to the two lowest $NaAu_3^-$ isomers. The Na_2Au_3 structure derived from the Y-shaped $NaAu_3^-$ cluster has a 3D structure of C_{2v} symmetry (Figure 4c). The addition of Na^+ to the quadrangular $NaAu_3^-$ isomer yields the planar structure of C_s symmetry shown in Figure 4d. The energy differences obtained at the MP2/QZVPP and SCS-MP2/QZVPP levels are given in Table 1.

3.5. $NaAu_4^-$ and $NaAu_4$. Previous calculations on $NaAu_4^-$ clusters suggested that a planar isomer is the energetically lowest one with the pyramidal isomer of C_{4v} symmetry as the second-lowest isomer. The repeated calculations on $NaAu_4^-$ at the MP2 and SCS-MP2 levels using the QZVPP basis sets show that the larger basis set favors the planar structure. The planar structure is also stabilized at the SCS-MP2 level. The planar isomer is 9.5 kJ/mol below the pyramidal one at the MP2/QZVPP level. In the SCS-MP2/QZVPP calculations, the planar isomer is 36 kJ/mol below the pyramidal one. MP2/QZVPP optimizations of neutral $NaAu_4$ isomers suggest that the most stable isomer is a pyramid-shaped isomer of C_{2v} symmetry. However, the SCS-MP2 single-point calculations on $NaAu_4$ indicate that the planar isomer of C_s symmetry shown in Figure 5a is 10.5 kJ/mol below the pyramid-shaped one. The lowest $NaAu_4^-$ and $NaAu_4$ isomers are shown in Figure 5.

3.6. $Na_2Au_4^-$ and Na_2Au_4. The lowest isomer of the anionic $Na_2Au_4^-$ cluster obtained at the MP2/QZVPP level has the planar triangular-shaped structure of C_{2v} symmetry shown in Figure 6b. The triangular-shaped cluster is 23 kJ/mol below the planar isomer of C_{2v} symmetry consisting of a quasi-linear gold chain with the two Na atoms attached to the same side of the gold chain, as shown in Figure 6a. At the SCS-MP2/QZVPP level, the triangular-shaped isomer is even lower in energy, or 37 kJ/mol below the isomer with the gold chain. The isomer with the gold chain though is observed in the electron detachment experiment. The neutral Na_2Au_4 cluster has also
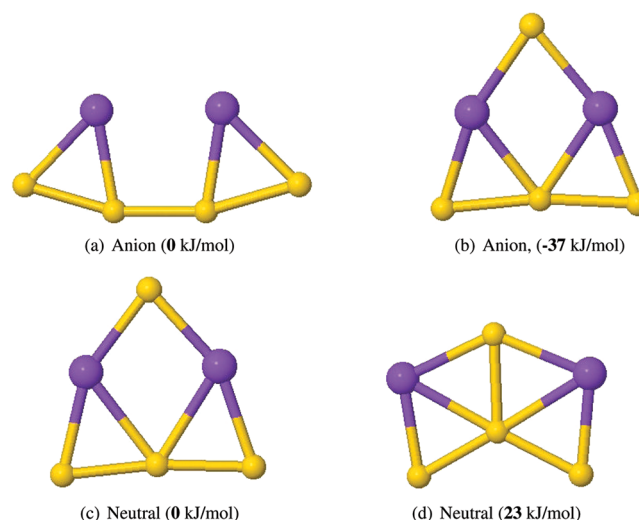

(a) Anion (**0** kJ/mol)   (b) Anion, (**-37** kJ/mol)

(c) Neutral (**0** kJ/mol)   (d) Neutral (**23** kJ/mol)

Figure 6. The two energetically lowest molecular structures of the $Na_2Au_4^-$ anion are shown in (a) and (b). The two energetically lowest structures of neutral Na_2Au_4 are shown in (c) and (d). The structures were optimized at the MP2/QZVPP level. The relative energies given in parentheses were obtained in single-point SCS-MP2/QZVPP calculations. The relative energy of the observed anion is set to zero.

two low-lying isomers. The lowest isomer shown in Figure 6c has a similar planar triangular-shaped structure as the energetically lowest anionic $Na_2Au_4^-$ cluster obtained at the MP2 level. The other Na_2Au_4 isomer, shown in Figure 6d, has C_{2v} symmetry. It consists of a connected D_{3h}-shaped Au star with the Na atoms at the opposite edges. At the MP2/QZVPP level, the neutral triangular-shaped Na_2Au_4 isomer is 1.6 kJ/mol below the planar one with the connected Au framework. Single-point SCS-MP2 calculations stabilize the triangular-shaped cluster, which is 23 kJ/mol lower in energy at the SCS-MP2/QZVPP level.

The effect of diffuse functions was assessed using the TZVPPD and TZVPP basis sets[35,40] in calculations on the charged and neutral Na_2Au_4 isomers. The diffuse functions reduced the relative energy between the two anionic clusters by only 5 kJ/mol, implying that the reversed relative stability of the $Na_2Au_4^-$ isomers is not due to basis set effects. The significant difference between the SCS-MP2 and MP2 energies suggests that higher-order electron correlation effects must be taken into account for obtaining the observed order of the
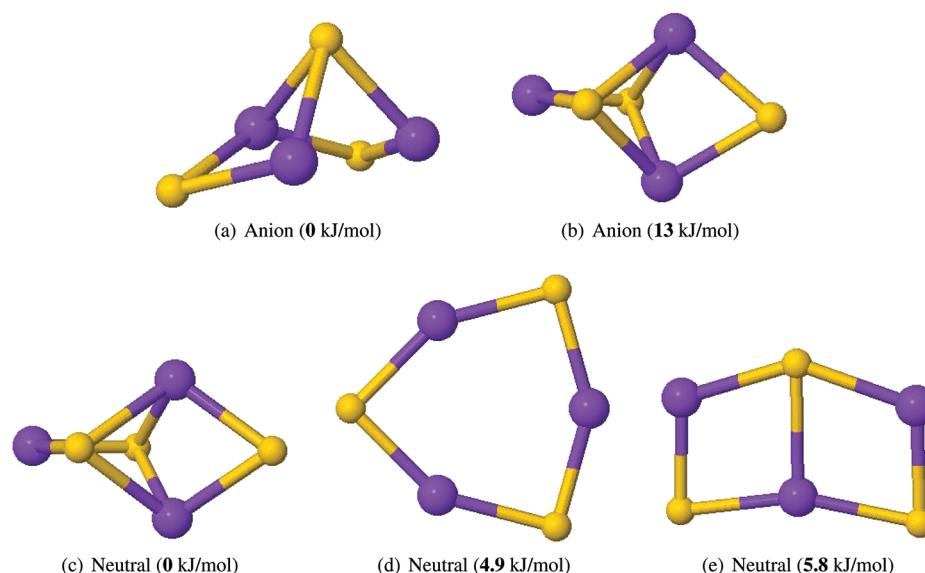
(a) Anion (**0** kJ/mol)   (b) Anion (**13** kJ/mol)

(c) Neutral (**0** kJ/mol)   (d) Neutral (**4.9** kJ/mol)   (e) Neutral (**5.8** kJ/mol)

Figure 7. The two energetically lowest molecular structures of the $Na_3Au_3^-$ anion are shown in (a) and (b). The three lowest isomers of neutral Na_3Au_3 are shown in (c)−(e). The structures were optimized at the MP2/QZVPP level. The energy difference calculated at the SCS-MP2/QZVPP level is given within parentheses.

Table 2. VDE and ADE (in eV) for the Studied Clusters[a]

cluster	structure	VDE			ADE		
		MP2	SCS-MP2	exp.[24]	MP2	SCS-MP2	exp.[24]
$NaAu^-$	linear ($C_{\infty v}$)	0.722	0.685	0.77 ± 0.03^b	0.667	0.685	0.62 ± 0.03^b
$NaAu_2^-$	linear ($D_{\infty h}$)	4.266	4.138	4.0	2.490	2.652	3.9
$Na_2Au_2^-$	planar (C_s)	1.511	1.464	1.54 ± 0.03^b	0.256	0.277	1.46 ± 0.03^b
	ring (D_{2h})	0.357	0.267		0.343	0.257	
$NaAu_3^-$	Y-shaped (C_{2v})	3.231	3.042	3.2	1.075	1.207	2.9
	quadrangular (C_{2v})	1.292	1.129		1.091	0.979	
$NaAu_4^-$	planar (C_{2v})	3.371	3.190	2.98^c	3.245	3.099	2.82^c
	pyramidal (C_{4v})	3.104	2.900		2.613	2.510	
$Na_2Au_3^-$	linear ($D_{\infty h}$)	5.021	4.908	4.8	2.044	2.264	4.5
	star (D_{3h})	4.130	4.012		2.250	2.330	
$Na_2Au_4^-$	planar (C_{2v})	2.104	2.038	1.9	1.155	0.826	1.7
	triangular (C_{2v})	1.510	1.319		1.378	0.549	
$Na_3Au_3^-$	"pyramid" (C_s)	1.193	1.114	1.20 ± 0.05^b	0.604	0.591	0.79 ± 0.06^b
	"bipyramid" (C_s)	0.619	0.495		0.582	0.454	

[a]The calculated VDEs and ADEs are compared to the experimental values. The molecular structures and the detachment energies were calculated at the (SCS)-MP2/QZVPP and CC2/QZVPP levels, respectively. The cluster structures are shown in Figures 1−7. [b]Reference 17. [c]Reference 18.

$Na_2Au_4^-$ isomers. Diffuse functions affected the ground-state VDEs by less than 0.02 eV, implying that diffuse functions are not crucial for identifying the sodium auride clusters.

3.7. $Na_3Au_3^-$. In our previous study, several low-lying structures for the anionic $Na_3Au_3^-$ were obtained in the MP2/TZVPP calculations.[17] Here, we reoptimized the structure of the two lowest isomers of the $Na_3Au_3^-$ at the MP2/QZVPP level because the structures of the larger sodium auride clusters might depend on the size of the employed basis sets, even though the rather large TZVPP basis sets were employed in the previous study. At the MP2/QZVPP level, the lowest $Na_3Au_3^-$ cluster has a trigonal-pyramid structure, with the Na atoms forming the base and a Au atom at the top. The two remaining Au atoms at the edges of the Na_3 triangle are bent out of the plane formed by the Na atoms. The structure is shown in Figure 7a. The lowest $Na_3Au_3^-$ structure is very typical for the sodium auride clusters with the almost neutral Na atoms at the center and the negatively charged Au atoms separated far away

from each other to reduce the Coulomb repulsion of the excess charge. The energetically lowest neutral Na_3Au_3 cluster consists of the D_{3h}-shaped $Na_2Au_3^-$ cluster with Na^+ added between two of the Au atoms. It can alternatively be seen as a trigonal-bipyramid with a Na_3 base and Au atoms at the tops. The third Au atom is attached to an edge of the Na_3 base plane. The second-lowest Na_3Au_3 anionic cluster has a structure that is very reminiscent of that for the lowest neutral one. The second-lowest neutral Na_3Au_3 cluster is a six-membered ring of D_{3h} symmetry, shown in Figure 7b. It lies only 4.9 kJ/mol higher in energy at the SCS-MP2/QZVPP level. The third neutral Na_3Au_3 cluster is a planar structure that is only 5.8 kJ/mol above the lowest Na_3Au_3 cluster. The energy separations between the neutral clusters are thus much smaller than the accuracy of the employed computational methods. The combination of structure optimization and the photodetachment experiment provides information about the structures of anionic clusters, whereas no useful experimental data are

Table 3. Calculated VDEs (in eV) for NaAu⁻, NaAu₂⁻, and NaAu₃⁻ Compared to Experimental Data[a]

	NaAu⁻			NaAu₂⁻			NaAu₃⁻	
assign.	exp.[17]	calc.	assign.	exp.[24]	calc.	assign.	exp.[24]	calc.
X	0.77 ± 0.03	0.722 (S)	X	4.0	4.266	X	3.2	3.231 (S)
A	3.42 ± 0.03	3.575 (T)	A	4.4	4.642	A	4.1	4.268 (S)
B	3.89 ± 0.03	4.046 (S)	B	5.3	5.906			4.270 (T)
C	4.32 ± 0.03	4.406 (T)			5.909	B	5.1	5.350 (S)[b]
D	~4.6	4.569 (T)[b]	C	5.7	6.058			5.351 (T)[b]
		4.590 (S)[b]			6.075	C	5.5	5.532 (T)
					6.107			5.537 (S)
					6.247			5.539 (T)
								5.540 (T)
								5.571 (T)
								5.582 (T)
								5.601 (T)
								5.634 (S)

[a]For NaAu⁻ and NaAu₃⁻, the singlet and triplet final states are indicated by (S) and (T), respectively. The degeneracy of the detachment channels is also indicated when it deviates from 1. [b]Two nearly degenerate states.

available for the neutral ones, rendering reliable structure determinations of nearly degenerate neutral sodium auride clusters difficult. The energetically lowest structures of the Na₃Au₃ and Na₃Au₃⁻ clusters are shown in Figure 7.

4. SPECTRAL ASSIGNMENTS AND DISCUSSION

The error bars of the calculated VDEs can be estimated by comparing the calculated and measured values for NaAu⁻. The first VDE is about 0.05 eV smaller than the experimental value whose uncertainty is ±0.03 eV.[17] The calculation of the second and third VDEs yields values that are 0.16 eV larger than those obtained in the measurement. The fourth VDE is 0.09 eV larger than the experimental value. The first VDE is in good agreement with experiment, whereas the excitation energies and hence the higher VDEs seem to be up to 0.2 eV larger than the experimental values. Comparison of the calculated and measured VDEs for the other clusters shows that the MP2/CC2 approach to determine the PES spectra tends to provide slightly too large values for the higher VDEs. However, the differences between calculated and measured VDEs are much smaller than the difference between the VDEs of the different isomers, rendering the assignment of the PES spectra possible provided that the correct cluster structure was obtained in the structure optimization.

The anionic clusters consisting of an odd number of atoms are closed-shell species because each Na and Au atom contributes with one valence electron each. The anionic clusters with an even number of atoms are analogously open-shell species. The closed-shell clusters are generally more stable than the open-shell ones, thus possessing significantly larger VDEs. One exception among the studied clusters is NaAu₃⁻ which has a ground-state VDE of 3.2 eV. This value is almost as large as the VDEs for the closed-shell anions.

The experimental ADEs and VDEs of the anionic clusters are compared to the computed values in Table 2. The excellent agreement between the calculated and experimental PES data provide credence for the identified structures of the Na_mAu_n⁻ clusters. The bandwidth of the first transition and the corresponding ADE might indicate whether the electron detachment process leads to large structural changes of the neutral cluster.[22] However, complete optimizations of some of the structures of the neutral clusters lead to significant geometrical and energetical changes when the optimized

structure of the anionic clusters is the initial geometry. Thus, the bandwidth of the peaks in the PES spectra and the complete relaxation of the neutral cluster obtained in the calculations seem in those cases to have little in common.

4.1. NaAu⁻. The lowest VDE for NaAu⁻ of 0.722 eV calculated at the MP2/QZVPP level is about 0.05 eV smaller than the value of 0.77 ± 0.03 eV deduced from the experiment.[17] The corresponding ADE is 0.667 eV, calculated at the MP2/QZVPP level, as compared to the experimental ADE of 0.62 ± 0.03 eV.[17] Previous studies on Au clusters showed that MP2 generally overestimate binding energies, whereas the SCS-MP2 often provides relative ground-state energies for gold-containing clusters that are in good agreement with coupled-cluster values.[27] For NaAu⁻, the SCS-MP2 calculations employing QZVPP basis sets yield a VDE and ADE of 0.685 and 0.643 eV, respectively. The ADE obtained at the SCS-MP2/QZVPP level agrees well with the value deduced from experiment, whereas the VDE obtained at the SCS-MP2 level is 0.10 eV too small as compared to experiment. The accuracy of the VDE and ADE values calculated at the SCS-MP2 level is not generally better than those obtained using conventional MP2 calculations. The relative energy differences obtained at the MP2 and SCS-MP2 levels are small. The relative ground-state energies are significantly affected by the SCS approach, eventually leading to changes in the energetic order of the isomers of the larger sodium auride clusters.

The higher VDE values are obtained by adding excitation energies of neutral NaAu to the first VDE. The accuracy of the CC2 excitation energies is generally ±0.3 eV,[45] implying that one can expect such error bars for the calculated values of the higher VDEs. For strongly multiconfigurational cases, the uncertainties in the CC2 excitation errors might be much larger.[46] The approximate treatment of relativistic effects using effective core potentials and the omission of spin−orbit effects also affects the accuracy of the VDEs. However, comparison of the calculated VDEs for NaAu⁻ with those deduced from the laser vaporization experiment shows that the calculated VDEs deviate at most 0.15 eV from experiment. Thus, the combination of energy differences calculated at the MP2 level and CC2 excitation energies seems to be a powerful tool for structure determination of mixed alkali metal gold clusters. The calculated and measured photodetachment energies of NaAu⁻ are compared in Table 3.

Table 4. Calculated VDEs (in eV) for Na$_2$Au$_2^-$, Na$_2$Au$_3^-$, and NaAu$_4^-$ Compared to Experimental Data[a]

Na$_2$Au$_2^-$			Na$_2$Au$_3^-$			NaAu$_4^-$		
assignment	exp.[17]	calc.	assignment	exp.	calc.	assignment	exp.	calc.
X	1.54 ± 0.03	1.511 (S)	X	4.8	5.021	X	2.98	3.371
A	4.37 ± 0.03	4.427 (T)			5.119	A	4.12	4.401
		4.485 (S)	A	5.9	6.060	B	4.79	4.991
B	4.76 ± 0.03	4.798 (T)			6.234	C	4.98	5.039
		4.930 (T)			6.432			5.536
		5.112 (T)						
		5.201 (T)						
		5.210 (S)						

[a]For Na$_2$Au$_2^-$ the singlet and triplet final states are indicated by (S) and (T), respectively.

4.2. NaAu$_2^-$. Calculations of the first detachment energies of NaAu$_2^-$ yielded MP2 values of 4.27 and 2.53 eV for VDE and ADE, respectively. The corresponding SCS-MP2 values are 4.14 and 2.65 eV. The structural change between the anion and the neutral species results in a significant difference between the VDE and ADE values. The VDE obtained in the SCS-MP2 calculation is in somewhat better agreement with the experimental one of 4.0 eV than the MP2 value. The discrepancy of 0.27 eV between calculated and measured VDEs is within the error bars of the employed methods. The experimental values are taken from a preliminary and unpublished study by Cui, Li, and Wang.[24] The calculated value for the second VDE of 4.64 eV confirms that the observed NaAu$_2^-$ is indeed linear. The two first peaks in the experimental spectrum are very well resolved. A larger discrepancy between calculated and measured VDE values appears at 5.3 eV. However, the experimental spectrum consists of a broad double peak with lots of fine structure between 5.2 and 5.9 eV. The spectrum is very congested and not very well resolved. The computational methods are probably not accurate enough to describe the high-lying excited states of NaAu$_2$. The combined CC2/MP2 calculations yield values for the two lowest VDEs of NaAu$_2^-$ that are systematically about 0.25 eV larger than the ones deduced from the laser vaporization experiment. The calculated and measured photodetachment energies of NaAu$_2^-$ are compared in Table 3.

4.3. NaAu$_3^-$. Calculations of the VDEs for NaAu$_3^-$ show that the Y-shaped isomer is the cluster observed in the experiment. MP2 calculations yield the first VDEs of 3.23 and 1.29 eV for the Y-shaped and the quadrangular isomers, respectively. The SCS-MP2 calculations yield slightly smaller values of 3.04 and 1.13 eV. The experimental VDE is 3.2 eV, which indicates that the Y-shaped isomer is the main NaAu$_3^-$ cluster observed experimentally, whereas a broad small peak at around 1.5 eV might originate from the quadrangular NaAu$_3^-$ cluster. The experimental VDEs are taken from a preliminary and unpublished study.[24] The ADE for the quadrangular isomer is 1.09 and 0.98 eV at the MP2 and SCS-MP2 levels. The structural relaxation of the Y-shaped isomer yields small ADEs of 1.08 and 1.21 eV at the MP2 and SCS-MP2 levels, respectively. The calculated VDEs are in close agreement with the experimental values. The first VDE value calculated at the SCS-MP2 level seems to be slightly smaller than the experimental one, whereas the VDE calculated at the MP2 level agrees better with experiment. The calculated and measured photodetachment energies of NaAu$_3^-$ are compared in Table 3.

4.4. NaAu$_4^-$. MP2/QZVPP calculations of the first VDE for the two lowest NaAu$_4^-$ isomers yield values of 3.37 and 3.10 eV

for the planar and the pyramidal isomers, respectively. The corresponding MP2 values for the ADEs are 3.25 and 2.61 eV. At the SCS-MP2 level, the VDEs are 3.19 and 2.90 eV for the two isomers. The ADEs calculated at the SCS-MP2 level are 3.10 and 2.51 eV. In the laser vaporization experiment, the first VDE and ADE are 2.98 and 2.82 eV, respectively.[18] The excitation spectrum of the planar neutral NaAu$_4$ isomer has three relevant states for the photodetachment spectrum, whereas for the pyramidal cluster, six excited states can contribute to the PES spectrum. Comparison of the calculated VDEs with the experimental spectrum rules out the pyramidal isomer, even though the calculated and measured values for its first VDE largely agree. The energetically lowest planar NaAu$_4^-$ cluster is most likely the observed one. The simulated and experimental PES spectra for NaAu$_4^-$ agree qualitatively with discrepancies up to 0.4 eV. The first VDE calculated at the SCS-MP2 level deviates only 0.2 eV from experiment, leading to an overall good agreement between calculated measured PES spectra. The calculated and measured photodetachment energies of NaAu$_4^-$ are compared in Table 4.

4.5. Na$_2$Au$_3^-$. The lowest VDE calculated at the MP2 level is 5.02 eV, which is in good agreement with the experimental value of 4.8 eV. At the SCS-MP2 level, a slightly smaller VDE of 4.91 eV is obtained. The CC2 excitation energies for neutral Na$_2$Au$_3$ yielded a second VDE of 6.06 eV, which agrees well with the corresponding experimental VDE value of 5.9 eV. The experimental VDEs are taken from a preliminary and unpublished study.[24] The CC2 calculations also suggest a second VDE at 5.12 eV, which is almost degenerate with the lowest one and might be difficult to resolve experimentally. The first peak of the experimental PES spectrum is split into two at the top, which might be due to the two almost degenerate states. Comparison of the calculated PES spectrum with experiment suggests that the observed Na$_2$Au$_3^-$ has a linear structure. The calculated ADE of 2.04 eV is much smaller than the experimental value of about 4.5 eV. A broad and weak peak at around 4 eV in the experimental spectrum might originate from the Na$_2$Au$_3^-$ cluster of D_{3h} symmetry, whose first VDE is 4.13 eV at the MP2/QZVPP level. The calculated and measured photodetachment energies of Na$_2$Au$_3^-$ are compared in Table 4.

4.6. Na$_2$Au$_4^-$. The lowest isomer of Na$_2$Au$_4^-$ is a triangular-shaped planar cluster of C_{2v} symmetry. At the MP2/QZVPP level, the calculated value for the first VDE is 1.51 eV, which is about 0.4 eV smaller than that obtained experimentally. The second isomer, which also has C_{2v} symmetry, lies 23 kJ/mol higher in energy at the MP2/QZVPP level. Its first VDE is 2.10 eV, which agrees well with the experimental one of 1.9 eV. Apparently, the second isomer is observed in the photodetach-

ment experiment measured by Cui, Li, and Wang.[24] The calculated VDEs for the higher transitions are also slightly larger than those obtained in the measurement. The calculated value for the second VDE of 3.36 eV is 0.26 eV larger than the experimental value of 3.1 eV. The fourth peak at 3.7 eV seems to consist of four transitions. Two detachment channels contribute to the band at 4.2 eV. The close agreement between calculated and measured PES spectra indicates that the energetically second isomer is observed in the experiment. The calculated ADE of 1.16 eV is much smaller than the experimental ADE value of 1.7 eV.[24] The calculated and measured photodetachment energies of $Na_2Au_4^-$ are compared in Table 5.

Table 5. Calculated VDEs (in eV) for $Na_2Au_4^-$ and $Na_3Au_3^-$ Compared to Experimental Data[a]

	$Na_2Au_4^-$			$Na_3Au_3^-$	
assignment	exp.[24]	calc.	assignment	exp.[17]	calc.
X	1.9	2.104 (S)	X	1.20 ± 0.05	1.193 (S)
A	3.1	3.359 (T)	A	4.03 ± 0.03	4.088 (T)
B	3.4	3.419 (T)	B	4.25 ± 0.03	4.363 (T)
C	3.7	3.834 (S)			4.380 (S)
		3.836 (T)	C	4.61 ± 0.05	4.646 (S)
		3.842 (T)			4.834 (T)
		3.864 (S)			4.892 (T)
D	4.2	4.185 (T)			4.926 (T)
		4.197 (S)			
		4.555 (T)			

[a]The singlet and triplet final states are indicated by (S) and (T), respectively.

4.7. $Na_3Au_3^-$. The PES spectrum for $Na_3Au_3^-$ calculated using the MP2/QZVPP structure is in excellent agreement with experiment. The four lowest VDEs calculated at the MP2/QZVPP level agree within 0.1 eV with the experimental values. Thus, reoptimization of the $Na_3Au_3^-$ structure did not significantly change the calculated PES spectrum even though the use of the larger basis sets slightly affects the cluster structure. The higher PES transitions are slightly larger than those obtained experimentally.[17] The first VDE calculated at the SCS-MP2 level is somewhat smaller than the experimental value. The calculated and measured photodetachment energies of $Na_3Au_3^-$ are compared in Table 5.

5. SUMMARY AND CONCLUSIONS

The present study shows that PES measurements of electron detachment energies of anionic sodium auride clusters combined with high-level ab initio calculations are a powerful tool to determine the cluster structures. The molecular structures were optimized at the MP2 level using QZVPP. The excitation energies of the neutral clusters using the corresponding anionic structures were calculated at the linear response approximate coupled-cluster singles and doubles (CC2) level. The relative energies of the sodium auride clusters, and the first VDEs were also calculated at the SCS-MP2 level. The combined MP2 and CC2 calculations yield computed PES spectra of the anionic clusters. The molecular structures of the anionic sodium auride clusters were identified by comparing calculated VDEs with values deduced from experimental PES spectra.

Comparison of the calculated PES spectra for a few energetically low-lying isomers of the sodium auride clusters shows that the lowest structures obtained in the MP2 calculations are not always the ones produced in the laser vaporization experiment. For $NaAu_3^-$, $Na_2Au_2^-$, $Na_2Au_3^-$, and $Na_2Au_4^-$, the energetically second isomer at the MP2 level is detected. The SCS-MP2 calculations shift the order of the isomers such that the observed ones in most cases become more stable. The only exception is $Na_2Au_4^-$. The observed $Na_2Au_3^-$ and $Na_2Au_4^-$ species are the second-lowest isomers at the MP2 and SCS-MP2 levels. The potential energy surface of the sodium aurides is very soft, with several low-lying isomers, requiring high-level electron correlation treatment in combination with large basis sets. The calculations on the sodium aurides show that the relative energy is not a reliable means to determine the cluster structures; other experimental information is needed to ensure that the correct cluster structures have been obtained. Higher-order correlation effects seem to be significant for some of the clusters. However, more accurate ab initio methods cannot come into question because of the size of the clusters and the basis set requirements. Density functional theory (DFT) is not an option because DFT calculations yielded negative energy gaps for some of the anions and too small VDEs as compared to experiment for other clusters. For example, the VDEs of the two lowest isomers of $Na_2Au_3^-$ calculated at the DFT level using the Tao−Perdew−Staroverov−Scuseria (TPSS)[47] functional are 3.54 and 3.13 eV, which can be compared to the experimental value of 4.8 eV. The large deviation from the experimental VDE value and the rather close agreement between the two calculated VDEs render identification of the observed clusters using the TPSS functional difficult. The SCS-MP2 calculations improved the relative energies of the isomers, whereas the shifted VDE values obtained using single-point SCS-MP2 calculations are generally too small as compared to experiment. Thus, the SCS approach does not improve the VDEs of the sodium auride clusters. The bandwidth of the first peak in the PES spectrum generally provides information about the structural differences between the anionic and neutral clusters. However, relaxation of the molecular structures of the neutral clusters leads in many cases to large geometrical changes and huge relaxation energies that are unrelated to the peak widths.

The employed methods yield unambiguous identification of the studied sodium auride clusters because the lowest VDE values of the isomers differ by 0.5−3.5 eV, which is larger than the estimated error bars of the MP2 calculations. The only exception is $NaAu_4^-$, whose higher photodetachment channels have to be considered in order to identify the observed species. For the rest of the studied sodium aurides, the energetically higher photodetachment channels can be used to verify that the correct cluster structures have indeed been found.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total energies (in hartree) and Cartesian coordinates (in bohr) of the sodium auride clusters optimized at the MP2/QZVPP level. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: sundholm@chem.helsinki.fi.

Notes
The authors declare no competing financial interest.

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