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Density Functional Study of AuX^q (X = O, S, Se, Te, q = +1, 0, −1) Molecules

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Bond distances, vibrational frequencies, electron affinity, ionization potential, and dissociation energies of the title molecules were studied by use of density functional methods B3LYP, B3P86, B3PW91, BHLYP, BLYP, BP86, mPW1PW91, and PBE1PBE. It was found that the ground electronic state is doublet for neutral species, singlet for the anion, and triplet for the cation, in agreement with experiments and previous theoretical studies. The calculated properties are highly dependent on the functionals employed, in particular for the dissociation energy. The predicted bond distances and vibrational frequencies are in agreement with experiments and previous theoretical results. BP86 and BLYP have relatively good performance in reproducing the experimental results, while BHLYP is the worst functional method compared with the other density functional methods used for the title molecules.

1. Introduction

Clusters containing gold have attracted considerable attention because of their importance for wide applications in catalysis, microelectronics, and optical materials. However, the mechanism of the cluster growth in such systems could not be simply understood as ionic or covalent type of bonding. This has provided a challenge in experimental science, computational chemistry, and computational physics to reproduce the experimental data and produce accurate predictions of reactivity and properties.[1−11] A thorough and excellent review concerning the theoretical chemistry of gold was recently given by Pyykkö.[1] Stimulated by that work, presented here is a theoretical study of AuX (X = O, S, Se, Te) with neutral and charged species based on density function theory (DFT). For these molecules, theoretical[1,4−9] and experimental studies[2,3] are still far and few between. Experimentally, photoelectron spectroscopy of AuO^- and AuS^-[2] and near-infrared electronic spectroscopy of AuO[3] have been conducted recently. It has been found that the bond distance of AuO is 1.912 Å[2] and that of AuO^- is 1.899 Å.[2] Electron affinity (EA) of 2.374 ± 0.007 eV for AuO and 2.469 ± 0.006 eV for AuS were obtained.[2] For AuS and AuS^-, vibrational frequency of 400 ± 30 cm^{-1} and 380 ± 60 cm^{-1} was assigned.[2] From theory, a CCSD(T) (single and double excitation coupled cluster with perturbative triples) study presented the bond distance of AuO, AuO^-, AuS, and AuS^- and the EA of AuO and AuS.[2] Density functional study at B3PW91 (explanation for the notation see the second part of the paper) with LANL-E (extended version of LANL2DZ, which is the double-ξ type effective core potential developed by Los Alamos National Laboratory) basis set was conducted on the anion and cation of AuX (X = O, S, Se, Te) molecules, and bond distances of the charged species, electron affinity, ionization potential (IP), and dissociation energy were reported.[4] In addition, CISD/SC (configuration interaction with single and double excitations corrected by size-consistency effects),[5] DFT,[6,8,9] and ZORA (zero-order regular approximation)[6] calculations were conducted on AuO and AuS, in which bond distance, vibrational frequency, and dissociation energy were obtained. A study by MP2 (second-order perturbative Mϕller−Plesset) method on AuS showed that quartet state ($^4\Sigma^-$) was the ground state,[7] which contradicts both experiments[2,3] and other theoretical (including ours) results[4,5,8] in which the doublet state ($^2\Pi$) was predicted to be the ground state. For AuSe and AuTe, the available studies are rare,[4] although there were a few studies on Au_2Te[10] and Au_2Se.[11]

DFT is currently widely used to determine structures and reaction energy diagrams for a wide variety of molecules. Compared to high-level ab initio molecular orbital theories, DFT has the advantage of applicability anywhere in the periodic table and inherent computational efficiency, that is, it requires less computational time and storage memory. This makes it particularly effective for those molecules involving heavy metal elements. On the other hand, till now, many density functional methods have been developed during the past decade. It is known that each density functional method is different from the others on theoretical aspect. Therefore, it is necessary and meaningful to test these density functional methods when applied on different systems, especially for systems containing transition metals because different density functional methods may produce quite different properties for a given system.[12] In this study, the availability of accurate experimental data coupled with the advances in density functional theory motivated us to examine the ground state of the AuX molecules by use of diverse density functional methods. The results are compared with experiments and previous theoretical studies. The performance among different density functional methods is compared. We hope this work could stimulate more research on transition metals with different ligands and provide reference in choosing the reliable density functional method in future study.

2. Computational Methods

All geometry optimizations were performed using the Gaussian03 suite of programs.[13] Bond distance, vibrational frequency, EA, IP, and dissociation energies were determined for the title molecules by use of eight different exchange-correlation functionals, denoted as B3LYP, B3P86, B3PW91, BHLYP, BLYP,

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TABLE 1: Calculated Bond Distances *d* (Å), Vibrational Frequency ω_e (cm^{-1}), and Relative Energy ΔE (eV) of AuX (X = O, S, Se, Te) Molecules at the B3LYP Level for Various Spin Multiplicities *S*

		AuO			AuS			AuSe			AuTe		
	S	d	ωe	ΔE	d	ωe	ΔE	d	ωe	ΔE	d	ωe	ΔE
neutral	2	1.922	538.8	0.00	2.232	363.0	0.00	2.353	242.5	0.00	2.583	183.8	0.00
	4	1.989	414.4	1.30	2.311	293.5	1.43	2.448	185.7	1.40	2.742	125.4	1.20
anion	1	1.898	611.0	0.00	2.251	355.4	0.00	2.373	233.9	0.00	2.606	174.3	0.00
	3	2.086	359.5	0.21	2.374	260.4	0.66	2.507	166.5	0.71	2.794	113.4	0.64
cation	1	1.863	629.5	1.92	2.182	392.2	1.37	2.309	260.4	1.27	2.553	189.6	1.27
	3	1.945	437.9	0.00	2.218	352.1	0.00	2.341	237.1	0.00	2.587	176.8	0.00

BP86, mPW1PW91, and PBE1PBE.[14−24] For these density functional methods, the correlation functional is from either Lee, Yang, and Parr (LYP),[14] Perdew−Wang 1991 (PW91),[15] or Perdew 86 (P86),[16] while the exchange functional is from either Becke's three-parameter HF/DFT hybrid exchange fuinctional (B3),[17] pure DFT exchange functional of 1988 (B),[18] a modification of the half-and-half HF/DFT hybrid method (BH),[19] Perdew−Wang 1991 (PW91),[15] or Barone's modified PW91 (MPW1).[20] PBE1PBE is the GGA exchange-correlation functionals of Perdew, Burke, and Ernzerhof.[21] The basis set used is CEP-121G (compact effective potential)[22] for Au and Te. In CEP-121G, the spin−orbit (SO) effects was averaged out, that is, only effective SO was considered. Since SO effects could be very important for heavy metals such as Au and Te, the results may differ compared with the case that SO effects were considered explicitly. In this aspect, more work both on theory and its applications is clearly necessary. The valence electrons considered in CEP-121G are $5s^25p^65d^{10}6s^1$ for Au and $5s^25p^4$ for Te. For O, S, and Se, the all electron basis set 6-311++G(3df) is used. To avoid trapping at local minima of the potential energy surface, different initial geometries (bond distances) were adopted. The calculated dissociation energies were corrected by the zero-point vibrational energies.

3. Results and Discussion

The calculated results are listed in Tables 1 and 2. Because of the spin polarization, the molecules were first calculated by use of B3LYP at various spin multiplicities, that is, double and quartet for the neutral and singlet and triplet for the charged species, to find the lowest spin state for each molecule (including the charged species). The calculated results are listed in Table 1. Table 2 lists the bond distances, vibrational frequency, EA, IP, and dissociation energy from the lowest spin multiplicity of the title molecules at various density functional methods, B3LYP, B3P86, B3PW91, BHLYP, BLYP, BP86, mPW1PW91, and PBE1PBE.

From Table 1, it is seen that for the neutral molecule, the doublet (electronic state cannot be determined; the experimentally observed eletronic state is $^2\Pi$ [2,3]) is the most stable. For the charged species, singlet ($^1\Sigma$) and triplet ($^3\Sigma$) are the most stable for anion and cation, respectively. These conclusions are in agreement with both experiments[2,3] and previous theoretical studies.[4,5,8] For the anion, the triplet state has smaller energy difference (less than 1.0 eV) compared with the singlet state (global minimum), for instance, 0.21 eV for AuO^- (Table 1). This indicates that the triplet state is a competitive candidate of the ground state for AuO^-. For the neutral and cation, the energy difference for the two considered spin states is a bit large (larger than 1.0 eV).

AuO^q. This is the most studied molecule among the title molecules. For the neutral, the experimentally observed bond distance is 1.912 Å,[3] in agreement with our calculation in which the calculated bond distance is from 1.889 Å at BP86 to 1.955 Å at BHLYP (Table 2). Our results are also in agreement with previous theoretical study at CCSD(T) (1.907 Å),[2] CISD/SC (1.946 Å),[5] and BPW91 (1.9 Å)[8] and better than those from BP (1.831 Å)[6] and ZORA (1.864 Å).[6] Our calculated vibrational frequency is from 512.4 cm^{-1} at BHLYP to 603.5 cm^{-1} at BP86, comparable to the previous theoretical value 532.1 cm^{-1} at BPW91,[8] larger than the one (497 cm^{-1}) obtained at CISD/SC level,[5] but smaller than those from BP (695 cm^{-1})[6] and ZORA (632 cm^{-1}).[6] For EA, our calculated values are from 1.42 eV at BHLYP to 2.62 eV at B3P86, in which BP86 (2.37 eV) and BLYP (2.20 eV) have the best performance in reproducing the experimental value 2.374 eV[2] and the previous theoretical study at CCSD(T) (2.26 eV)[2] and B3PW91 (2.36 eV).[4] BHLYP has the worst performance. The calculated IP is from 9.34 eV at BHLYP to 10.47 eV at B3P86, in fair agreement with the previous theoretical value 9.82 eV at B3PW91,[4] in particular for our B3PW91 IP value (9.84 eV). The calculated dissociation energy is from 1.25 eV at BHLYP to 2.44 eV at BP86, in which BP86 (2.44 eV) and BLYP (2.32) perform best in reproducing the experimental data 2.26 eV[23] and 2.33 eV;[24] others underestimate the experimental value. Except for the dissociation energy at BHLYP (1.25 eV), the values from other DFT methods are comparable to the previous theoretical study at B3PW91 (1.92 eV).[4] Compared with previous theoretical DFT results by LANL2DZ basis set (BLYP 2.04 eV, B3LYP 1.60 eV, and B3PW91 1.50 eV),[9] our calculation with combined basis set (CEP-121G for Au, 6-311++G(3df) for O) gives better results (BLYP 2.32 eV, B3LYP 1.86 eV, and B3PW91 1.98 eV, compared with experimental value 2.26 eV[23] and 2.33 eV[24]). This conclusion also applies for AuS. The improvement of our combined basis set over that of LANL2DZ may be because we use pseudopotentials (PP) for Au and an all electron basis set 6-311++G(3df) for O, while at LANL2DZ, PP is used for Au and double-ζ basis set (D95) is used for O (and valence double-ζ basis set D95V for S). To confirm this conclusion, we calculated the dissociation energy of AuO at the BLYP level by use of LANL2DZ basis set on Au and 6-311++G(3df) on O. It is found that the calculated dissociation energy 2.38 eV is quite close to 2.32 eV from the combined basis set CEP-121G on Au and 6-311++G(3df) on O. This supports our conclusion.

For AuO^-, our calculated bond distance changes in a narrow range for different methods, which is from 1.880 Å at B3P86 and mPW1PW91 to 1.914 Å at BLYP, in excellent agreement with the experimental value 1.889 Å[2] and a previous theoretical study at CCSD(T) (1.888 Å)[2] and B3PW91 (1.910 Å).[4] The calculated vibrational frequency is from 588.2 cm^{-1} at BLYP to 646.0 cm^{-1} at PBE1PBE, larger than their corresponding values in neutral species. For the dissociation energy, BHLYP gives the smallest value 1.60 eV, while BP86 gives almost double the value (3.00 eV). For AuO^+, the calculated bond distance shown in Table 2 is comparable to the previous theoretical value 1.981 Å.[4] The calculated vibrational frequency oscillates in a wide range from 257.5 cm^{-1} at BHLYP to 570.8 cm^{-1} at BP86. The calculated dissociation also shows that BHLYP gives the smallest value 0.73 eV. Therefore, from our

TABLE 2: Calculated Bond Distances d (Å), Vibrational Frequency ω_e (cm^{-1}), Electron Affinity EA (eV), Ionization Potential IP (eV), and Dissociation Energy D_e, D_{e1}, D_{e2} (eV) for AuX (X = O, S, Se, Te) Molecules at Lowest Spin Multiplicity[n]

		B3LYP	B3P86	B3PW91	BHLYP	BLYP	BP86	mPW1PW91	PBE1PBE	expt	theor[e]	theor[f]	theor[g]	theor	theor
AuO	d	1.922	1.902	1.908	1.955	1.911	1.889	1.913	1.909	1.912[a]	1.907		1.946	1.831[h] 1.864[i]	1.9[k]
	ω_e	538.8	572.0	558.9	512.4	566.6	603.5	554.0	556.9				497	695[h] 632[i]	532.1[k]
	EA	2.11	2.62	2.01	1.42	2.20	2.37	1.89	1.88	2.374 ± 0.007[b]	2.26	2.36			
	IP	9.92	10.47	9.84	9.34	9.87	10.06	9.76	9.74			9.82			
	D_e	1.86	1.98	1.81	1.25	2.32	2.44	1.75	1.81	2.26[c] 2.33[d]		1.92	1.52	2.81[h] 2.84[i]	2.04,[l] 1.96[l] 1.60,[l] 1.50[l]
AuO^-	d	1.898	1.880	1.883	1.889	1.914	1.892	1.880	1.877	1.899[b]	1.888	1.910			
	ω_e	611.0	644.8	637.5	615.8	588.2	628.0	641.7	646.0						
	D_{e1}	2.37	2.53	2.40	1.60	2.81	3.00	2.30	2.37						
AuO^+	d	1.945	1.918	1.931	2.149	1.913	1.889	1.949	1.943			1.981			
	ω_e	437.9	481.6	452.9	257.5	529.2	570.8	410.4	423.1						
	D_{e2}	1.26	1.36	1.23	0.73	1.85	1.98	1.14	1.19						
AuS	d	2.232	2.204	2.210	2.245	2.237	2.206	2.209	2.206		2.219		2.260	2.57[j]	
	ω_e	363.0	382.8	379.0	358.3	361.0	383.2	379.8	381.8	400 ± 30[b]			350	141[j]	
	EA	2.36	2.88	2.30	2.01	2.30	2.50	2.24	2.23	2.469 ± 0.006[b]	2.43	2.39			
	IP	8.92	9.46	8.87	8.63	8.81	9.01	8.82	8.79			8.92			
	D_e	2.25	2.45	2.34	1.93	2.43	2.65	2.32	2.38	2.59[d]		2.44	1.93	0.28[j]	1.94,[m] 2.01[m] 1.76,[m] 1.82[m]
AuS^-	d	2.251	2.222	2.226	2.242	2.268	2.235	2.222	2.218		2.233	2.260			
	ω_e	355.4	375.3	372.6	363.7	344.4	364.9	376.9	380.0	380 ± 60[b]					
	D_{e1}	2.42	2.63	2.52	2.01	2.63	2.85	2.49	2.55						
AuS^+	d	2.218	2.190	2.196	2.258	2.215	2.185	2.198	2.194			2.228			
	ω_e	352.1	374.7	368.7	312.0	363.0	387.2	364.7	367.5						
	D_{e2}	2.64	2.83	2.71	2.12	3.03	3.24	2.65	2.71						
AuSe	d	2.353	2.324	2.330	2.360	2.360	2.329	2.328	2.325						
	ω_e	242.5	255.9	253.1	241.3	240.0	254.5	254.1	255.4						
	EA	2.40	2.91	2.33	2.08	2.33	2.52	2.28	2.26			2.38			
	IP	8.63	9.15	8.56	8.35	8.50	8.70	8.50	8.48			8.56			
	D_e	2.19	2.35	2.24	1.89	2.34	2.53	2.23	2.28						
$AuSe^-$	d	2.373	2.342	2.347	2.362	2.393	2.357	2.342	2.339			2.379			
	ω_e	233.9	248.1	245.8	240.5	225.2	240.5	248.7	250.2						
	D_{e1}	2.38	2.56	2.45	2.00	2.60	2.76	2.43	2.49						
$AuSe^+$	d	2.341	2.312	2.312	2.373	2.342	2.310	2.320	2.317			2.342			
	ω_e	237.1	251.7	247.7	215.4	242.5	258.5	245.9	247.4						
	D_{e2}	2.87	3.04	2.93	2.36	3.24	3.43	2.88	2.93						
AuTe	d	2.583	2.557	2.563	2.583	2.594	2.565	2.561	2.559						
	ω_e	183.8	192.2	190.6	185.3	180.4	189.9	191.7	192.5						
	EA	2.24	2.80	2.24	1.98	2.12	2.38	2.19	2.18			2.48			
	IP	8.04	8.60	8.02	7.77	7.92	8.16	7.97	7.95			7.88			
	D_e	1.92	2.10	1.99	1.66	2.05	2.25	1.98	2.03						
$AuTe^-$	d	2.696	2.576	2.582	2.593	2.626	2.593	2.578	2.574			2.556			
	ω_e	174.3	184.0	182.7	178.5	168.2	179.4	184.8	185.9						
	D_{e1}	2.17	2.42	2.35	2.07	2.14	2.42	2.38	2.43						
$AuTe^+$	d	2.587	2.559	2.567	2.609	2.589	2.557	2.568	2.566			2.516			
	ω_e	176.8	185.8	183.2	168.5	179.3	189.2	182.7	183.4						
	D_{e2}	2.58	2.76	2.65	2.42	2.69	2.89	2.66	2.69						

[a] Reference 3. [b] Reference 2. [c] Reference 23. [d] Reference 24. [e] Reference 2. Values in this column are from the theoretical study at the CCSD(T) level. For the basis set, Stuttgart small core energy consistent relativistic pseudopotentials are used for Au and augmented-cc-pVTZ for O and S. The bond distance for AuO (1.907 Å) is the average of the two spin−orbit states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. The same applies for the bond distance of AuS (2.219 Å). [f] Reference 4. Values in this column are from the theoretical study at the B3PW91/LANL-E level. [g] Reference 5. Values in this column are from the theoretical study at the CISD/SC level. [h] Reference 6. Theoretical study by the Becke−Perdew functional. [i] Reference 6. Theoretical study by the ZORA method. [j] Reference 7. Theoretical study by the MP2 method and Hay and Wadt double-ζ basis set. Spin state at quartet ($^4\Sigma^-$) was predicted to be the most stable. [k] Reference 8. Theoretical study at the BPW91 level. For basis set, LANL2DZ for Au, 6-311+G(d) for O. [l] Reference 9. DFT studies with LANL2DZ basis set. The value 2.04 eV is from BLYP, 1.96 eV from BPW91, 1.60 eV from B3LYP, and 1.50 eV from B3PW91. [m] Reference 9. DFT studies with LANL2DZ basis set. The value 1.94 eV is from BLYP, 2.01 eV from BPW91, 1.76 eV from B3LYP, and 1.82 eV from B3PW91. [n] For the dissociation energy, D_{e1} represents the channel $AuX^- = Au + X^-$ for X = O, S, and Se, and $AuX^- = Au^- + X$ for X = Te. For D_{e2}, the channel is $AuX^+ = Au^+ + X$ for X = O, S, and Se, and $AuX^+ = Au + X^+$ for X = Te.

study it is seen that for both neutral and charged species, BP86 and BLYP have the best performance in reproducing the experimental data, while BHLYP is the worst. Other methods are in-between.

AuS^q. The calculated bond distance is around 2.2 Å for neutral species, in agreement with the results at the CCSD(T) level (2.219 Å)[2] and the CISD/SC level (2.260 Å).[5] These bond distances are smaller than the one obtained by the MP2 method (2.57 Å) in which $^4\Sigma^-$ was predicted to be the ground state for neutral species. This conclusion (i.e., $^4\Sigma^-$ being the ground state) is in sharp contrast to experimental observation[2] and previous theoretical studies[2,5] in which the doublet ($^2\Pi$) was the ground state. For vibrational frequency, the experimentally observed value is 400 ± 30 cm^{-1}, close to our calculated values which are from 358.3 cm^{-1} at BHLYP to 383.2 cm^{-1} at BP86. Our results are better than that at the CISD/SC level (350 cm^{-1}).[5] For EA, the best performance from our calculation is at BP86 (2.50 eV), which is in excellent agreement with experimental

data 2.469 eV[2] and theoretical results at the CCSD(T) level (2.43 eV)[2] and at the CISD/SC level (2.39 eV).[5] Besides BP86, the performance of B3LYP (2.36 eV) is also satisfactory, followed by BLYP (2.30 eV) and B3PW91 (2.30 eV). B3P86 overestimates the experimental value by 0.311 eV, while BHLYP, mPW1PW91, and PBE1PBE underestimate the experimental value by 0.459 eV, 0.229 eV, and 0.239 eV, respectively. The calculated IP is in good agreement with the previous theoretical value at the CISD/SC level (8.92 eV). Exactly the same result is obtained at the B3LYP level (8.92 eV). For the dissociation energy, the worst performance is from BHLYP (1.93 eV, compared with the experimental value 2.59 eV[24]). The remaining seven functionals are satisfactory in reproducing the experimental data, in which BP86 (2.65 eV) performs the best, followed by B3P86 (2.45 eV) and BLYP (2.43 eV). Except at the BHLYP level, our calculated dissociation energy is also better than those at the CISD/SC level (1.93 eV)[5] and at the MP2 level (0.28 eV).[7] As mentioned before in neutral AuO, our calculation with combined basis set (CEP-121G for Au, 6-311++G(3df) for S) gives better results (BLYP 2.43 eV, B3LYP 2.25 eV, and B3PW91 2.34 eV, compared with the experimental value 2.59 eV[24]) than those with LANL2DZ (PP for Au and double-ζ valence basis set for S) basis set (BLYP 1.94 eV, B3LYP 1.76 eV, and B3PW91 1.82 eV).[9]

For AuS^-, it is seen from Table 2 that our calculated bond distance is in fair agreement with other theoretical studies 2.233 Å[2] and 2.260 Å.[4] For vibrational frequency, the experimentally observed value is 380 ± 60 cm^{-1}, comparable with our calculated results from 344.4 cm^{-1} at BLYP to 380.0 cm^{-1} at PBE1PBE. The calculated dissociation energy changes from 2.01 eV at BHLYP to 2.85 eV at BP86. For AuS^+, the calculated bond distance is in good agreement with the previous theoretical result at the B3PW91/LANL-E level (2.228 Å).[4]

$AuSe^q$. Information on this dimer is less. The previous theoretical study at B3PW91 with LANL-E basis set predicted that EA of AuSe is 2.38 eV and IP is 8.56 eV.[4] Our calculated EA (from 2.08 eV at BHLYP to 2.91 eV at B3P86) and IP (8.35 eV at BHLYP to 9.15 eV at B3P86 eV) are comparable to these previous theoretical values.

For $AuSe^-$, all functionals have good performance in the calculation of bond distance compared with the previous study at the B3PW91/LANL-E level (2.379 Å).[4] This is also true for $AuSe^+$.

$AuTe^q$. Unlike the other three dimers, 6-311++G(3df) basis set is not available for Te. Therefore, we use CEP-121G for element Te. Since only six valence electrons ($5s^25p^4$) are considered, deviation of the calculated values from experiment (if any) will be expected for this large core basis set. It is seen from Table 2 that our calculated EA and IP is in good agreement with the previous study at the B3PW91/LANL-E level (2.48 eV for EA and 7.88 eV for IP),[4] in particular at the BP86 level (2.38 eV) for EA.

For $AuTe^-$ and $AuTe^+$, our calculated bond distance is in agreement with the theoretical study at the B3PW91/LANL-E level (2.556 Å for $AuTe^-$ and 2.516 Å for $AuTe^+$).[4] For the dissociation energy D_{e1}, there are two channels available, that is, $AuX^- = Au^- + X$ and $AuX^- = Au + X^-$. For X = O, S, and Se, Mulliken charge analysis suggests that the latter is preferred because the extra electron is located on X. While for X = Te, Au and Te have the equal ability to gain the electrons, that is, nearly half-and-half ($Au^{-0.47}Te^{-0.53}$). In this case, both channels are possible, and indeed the two channels give almost the same dissociation energy. Here, we only listed one of them ($AuTe^- = Au^- + Te$) because in this channel the dissociation energy is slightly lower than that of the other channel ($AuTe^- = Au + Te^-$). For D_{e2}, it is clear from Mulliken charge analysis that Te tends to lose more electrons compared with Au ($Au^{0.24}Te^{0.76}$), and indeed, the channel $AuX^+ = Au + X^+$ is preferred to $AuX^+ = Au^+ + X$ because of the higher dissociation energy of the latter. We hope this conclusion can be confirmed by a higher level study with an elaborate basis set.

4. Conclusions

Density functional methods B3LYP, B3P86, B3PW91, BHLYP, BLYP, BP86, mPW1PW91, and PBE1PBE have been tested in the study of the spectroscopic constants for the title molecules. The calculated properties are dependent on the functionals employed. BP86 and BLYP have relatively good performance in reproducing the experimental results, while BHLYP is the worst. For neutral AuX from O to Te, the calculated bond distance increases with the increasing atomic size, while vibrational frequency and IP decrease. EA slightly increases from O to Se and then decreases at Te. The trends in the change of the properties apply also for the anion and cation species. We hope this study can serve as a useful guide for future experimental studies, especially for those molecules for which no other data is available, and provide guidance in choosing the reliable density functional methods in further theoretical study.

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