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CCSD(T) study on the structures and chemical bonds of AnO molecules (An = Bk–Lr)*

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The molecular geometries and dissociation energies of AnO (An = Bk–Lr) molecules were first obtained at the coupled-cluster single-, double-, and perturbative triple-excitations [CCSD(T)] level of theory. Four hybrid functionals, B3LYP, M06-2X, TPSSh, and PBE0, were also employed in the calculations for the sake of comparison. In comparison of the CCSD(T) results, B3LYP, TPSSh, and PBE0 functionals can obtain more appropriate results than M06-2X and MP2. The analyses on molecular orbitals show that the 7s, 6d, and 5f atomic orbitals of actinide (An) atoms participate in the bonding of An–O bonds. The partial covalent nature between An and O atoms is revealed by QTAIM analyses.

Keywords: *ab initio* calculation, AnO (Bk–Lr) molecules, density functional theory (DFT), chemical bonds

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1. Introduction

Actinides (An) are very heavy elements in the periodic table. Among the actinide elements, Th, U, and the transuranium elements of Np, Pu, Am and Cm have important applications and have been synthesized in appreciable quantities in nuclear reactors.[1–3] The other actinides are mostly used for research. Most of them are radioactive. Therefore, the experimental studies are not easy. Computational modeling is particularly useful for systems. Quantum chemistry can model molecular properties of species containing actinides, leading to an improved understanding. However, the studies for the latter actinides (Bk–Lr) are very rare because these elements are not present in nature. The energy levels and atomic spectra of neutral and ionized Bk, Cf, and Es have been determined in the spectroscopic study.[4] Moreover, the first ionization energies of Bk–Es were studied by resonance ionization mass spectroscopy (RIMS).[5]

Theoretical studies on the latter actinide compounds are also rare. The first and second ionization potentials of Bk–Lr atoms were obtained with multireference averaged coupled-pair functional (ACPF) calculations in conjunction with extended valence basis sets.[6] The bond lengths, binding energies, and vibrational constants of the monohydride, monoxide, and monofluoride of lawrencium (Lr) were determined at *ab initio* level of theory.[7] The bond distances and dissociation enthalpies of actinide oxides AnO and AnO_2 (An = Th–Lr) were predicted by density functional theory (DFT) methods in combination with the relativistic small-core pseudopotentials.[8] It is found that the high-level *ab initio* calculations were rare for the latter actinide oxides AnO (An = Th–Lr).

In the present work, we have performed the *ab initio* calculations, second-order Moller–Plesset perturbation theory (MP2) and coupled-cluster single-, double-, and perturbative triple-excitations [CCSD(T)], on the molecular structures, dissociation energies, bonding natures of AnO (An = Bk–Lr) molecules. Different DFT functionals were also employed for these species, and we would like to pick out the more appropriate functionals for the present species by comparing with CCSD(T) results.

2. Calculational details

The molecular geometries of AnO (Bk–Lr) molecules were optimized using the *ab initio* methods, MP2 and CCSD(T). The Cologne–Stuttgart small-core scalar relativistic effective core potential (SC-RECP) in combination with the associated basis set[6,7] was used to describe the heavy atoms (Bk–Lr), and the triple-ζ valence basis set of def2-TZVP[9] was used for the O atoms. The *ab initio* calculations were performed with the ORCA program.[10] Four hybrid functionals, including B3LYP,[11] M06-2X,[12] PBE0,[13] and TPSSh,[14] were also employed for comparison. We selected these four functionals because they were successful used in the studies related to the actinide complexes in previous works.[15,16] Furthermore, Hartree–Fock (HF) exchange proportions in these functionals are different, and they can be used to evaluate the influences from HF exchange proportion on the calculational results. The DFT calculations were performed with G09

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package,[17] in which the correlation-consistent cc-pVTZ basis set was applied for O atoms. The electronic states with different spin multiplicities were calculated for each system to determine the ground electronic state. In the CCSD(T) calculations, the DFT starting orbitals were used. The bonding nature of An–O chemical bonds was revealed by the quantum theory of atoms in molecules (QTAIM),[18] as implemented in the MULTIWFN program.[19] Natural bonding orbital (NBO) analyses[20] were performed with NBO version 3.1 incorporated in G09 package to obtain the charges, bond orders and orbital populations of titled molecules.

3. Results and discussion

The geometry optimizations of the titled AnO molecules were performed with MP2, CCSD(T), and four hybridization functionals (B3LYP, M06-2X, PBE0, and TPSSh), respectively. The predicted bond lengths, vibrational frequencies, and dissociation energies (D_0) of AnO (An = Bk–Lr) series were collected in Table 1. The dissociation energy D_0 defined as the difference between AnO molecules and free An and O atoms were calculated with the equation $D_0 = E(\mathrm{An}) + E(\mathrm{O}) - E(\mathrm{AnO})$, where E(An), E(O), and E(AnO) are the energies of free An and O atoms, and AnO molecule, respectively.

Table 1. The bonding lengths R_e, vibrational frequencies ω_e, and dissociation energies D_0, and spin multiplicity (M) of AnO (An = Bk–Lr) molecules predicted with different calculational methods.

Species	Properties	Methods						Theory[a]
		B3LYP	M06-2X	TPSSh	PBE0	MP2	CCSD(T)	
BkO	R_e (Å)	1.833	1.828	1.826	1.824	1.799	1.803	1.835
	ω_e (cm^{-1})	839	833	839	845	924	901	833
	D_0 (eV)	6.68	4.99	5.99	5.31	12.6	6.81	
	M	8	8	8	8	8	8	
CfO	R_e (Å)	1.825	1.804	1.824	1.805	1.814	1.819	1.822
	ω_e (cm^{-1})	826	850	807	857	855	849	833
	D_0 (eV)	4.83	4.79	5.67	4.72	6.61	5.73	
	M	5	7	5	5	7	7	
EsO	R_e (Å)	1.820	1.801	1.815	1.802	1.794	1.804	1.822
	ω_e (cm^{-1})	831	865	829	860	893	879	825
	D_0 (eV)	5.06	3.14	4.63	5.18	10.53	5.13	
	M	6	6	6	6	6	6	
FmO	R_e (Å)	1.877	1.880	1.817	1.850	1.850	1.858	1.850
	ω_e (cm^{-1})	671	725	790	714	747	739	735
	D_0 (eV)	3.67	3.08	4.47	3.87	8.77	7.70	
	M	3	3	5	3	3	3	
MdO	R_e (Å)	1.894	1.881	1.875	1.875	1.856	1.875	1.898
	ω_e(cm^{-1})	669	710	697	711	741	722	673
	D_0 (eV)	3.45	2.83	3.98	3.53	7.46	3.95	
	M	2	2	2	2	2	2	
NoO	R_e (Å)	1.917	1.919	1.900	1.898	1.886	1.913	1.923
	ω_e(cm^{-1})	661	674	689	690	689	651	650
	D_0 (eV)	3.00	2.25	3.47	3.03	12.53	3.43	
	M	1	1	1	1	1	1	
LrO	R_e (Å)	1.868	1.863	1.858	1.847	1.870	1.881	1.871
	ω_e (cm^{-1})	762	781	791	808	677	702	756
	D_0 (eV)	6.06	5.72	6.27	6.11	7.20	6.20	
	M	2	2	2	2	2	2	

[a]The results of theory are taken from Ref. [8].

To find the ground electronic state, different spin multiplicities were considered in the MP2 and DFT calculations. As shown in Table S1 of the Supplementary Material, MP2 predicted the ground electronic state of BkO to be octet with $(\sigma)^1(\delta)^2(\sigma)^1(\pi)^2(\sigma)^1$ 1-electron occupancy (see Table S2), in which all the 5f orbitals are occupied either by one or two electrons. In contrast, the 7s orbital is singly occupied. The MP2 predicted the bond length and frequency to be 1.799 Å and 924 cm^{-1}, respectively. The bond length and frequency of BkO predicted by CCSD(T) are 1.803 Å, 901 cm^{-1}, respectively. All of the DFT methods obtained a ground octet state for the BkO molecule, corresponding to the $(\pi)^1(\delta)^2(\pi)^2(\sigma)^1(\sigma)^1$ electron occupancy, which is different from the MP2 result. The bond lengths of BkO predicted at DFT level of theory are from 1.824 Å (PBE0) to 1.833 Å (B3LYP), and the frequencies in the range of 833 cm^{-1} (M06-2X) to 845 cm^{-1} (PBE0). The results of the present DFT methods are very close to the previous results.[8] It seems that the DFT obtains

the larger bond lengths and the lower frequencies than the CCSD(T) results. The D_0 value of BkO molecule predicted by CCSD(T) is 6.81 eV. The DFT methods obtained the lower dissociation energy, in the range of 4.99 eV–6.68 eV, and D_0 value obtained by B3LYP functional is most close to the result of CCSD(T). On the other hand, MP2 predicted the dissociation energy to be extremely high (12.6 eV).

CfO molecule has a ground septet state (MP2) with $(\varphi)^2(\sigma)^1\ (\pi)^2\ (\sigma)^1$ occupancy. The bond length and frequency of CfO predicted by CCSD(T) are 1.819 Å, and 849 cm^{-1}, respectively. M06-2X functional also obtained a ground septet state of CfO with $(\delta)^2(\pi)^2\ (\sigma)^1(\sigma)^1$ occupancy. On the other hand, the rest functionals, B3LYP, TPSSh, and PBE0 give a ground quintet state (see Table 1). M06-2X and PBE0 functionals predicted the bond length (frequency) to be shorter (larger) than that of CCSD(T). In contrast, the B3LYP and TPSSh functionals show the longer (lower) bond length (frequency) than CCSD(T). The dissociation energy of 5.67 eV evaluated by TPSSh functional is very close to the CCSD(T) result (5.73 eV).

For the EsO molecule, the MP2 and all of DFT functionals obtained a ground sextet state, and show a similar electron occupancy (see Table S2). The bond length and frequency predicted at the CCSD(T) level of theory are 1.804 Å, and 879 cm^{-1}, respectively. The calculational bond lengths and frequencies of M06-2X and PBE0 functionals are very close to these of CCSD(T). CCSD(T) obtains dissociation energy of 5.13 eV, which is consistent with the DFT results except for M06-2X. However, the dissociation energy predicted by MP2 is two times greater than the CCSD(T) result.

FmO molecule has a triplet ground state with $(\pi)^1\ (\sigma)^1$ 1-electron occupancy at MP2, B3LYP, M06-2X, and PBE0 levels of theory. On the other hand, the TPSSh functional places the ground at quintet spin multiplicity corresponding to the 5f occupancy of $(\pi)^1\ (\sigma)^1(\varphi)^2$ orbitals. At CCSD(T) level of theory, the ground triplet state corresponds to the bond length of 1.858 Å, and frequency of 739 cm^{-1}, respectively, and the CCSD(T) results agree with the previous theory results.[8] Compared to other functionals, the shorter bond length and higher frequency were obtained with the TPSSh functional because it could not obtain an appropriate ground state. Unexpectedly, the CCSD(T) gives very high dissociation energy (7.70 eV), which is much higher than the DFT results (3.08 eV–4.47 eV).

As for the MdO molecule, a ground doublet state was obtained by all of the calculational methods. All DFT methods obtained a σ^1 with one 5f electron occupancy. Nevertheless, MP2 shows a singly populated O 2p orbital which has a lone pair character. MP2 (CCSD(T)) predicted the bond length and frequency to be 1.856 Å (1.875 Å) and 741 cm^{-1} (722 cm^{-1}), respectively. The DFT methods predicted the bond length and frequency to be in the ranges of 1.875–1.894 Å and 669–711 cm^{-1}, respectively. The dissociation energies obtained by the DFT methods except for M06-2X functional are in the range of 3.45–3.98 eV, in agreement with the CCSD(T) result (3.95 eV).

NoO molecule has a closed-shell electronic configuration. As shown in Table 1, the bond lengths and frequencies obtained by the DFT methods are very close to the results of CCSD(T) (1.913 Å and 651 cm^{-1}). The M06-2X functional predicted the dissociation energy to be 2.25 eV, which is significantly lower than the value (3.43 eV) of CCSD(T). The rest functionals, B3LYP, TPSSh, and PBE0 obtained reasonable dissociation energy.

The ground state of LrO corresponds to a double state, the σ molecular orbital is singly occupied with An 7s. The bond lengths given by the DFT method (from 1.847 Å to 1.868 Å) are slightly shorter than the CCSD(T) result (1.881 Å). The frequencies predicted by the DFT methods are 60–106 cm^{-1} higher than that of CCSD(T) (702 cm^{-1}). The dissociation energies evaluated by the DFT methods are in excellent agreement with the value (6.20 eV) of CCSD(T). On the whole, the MP2 method generally overestimates the dissociation energy for all titled species. On the other hand, the M06-2X functional gives the lower D_0 values than CCSD (T). We also note that the rest functionals, B3LYP, TPSSh, and PBE0, predict the structures and dissociation energies in a reasonable error range.

Table 2. The NPA charges of An atoms, WBI of An–O bonds, and population in different shells of AnO (An = Bk–Lr) molecules.

			Population		
	Q (An)	WBI	7s	5f	6d
BkO	1.049	1.42	0.93	8.25	0.73
CfO	1.072	1.36	0.90	9.37	0.59
EsO	1.028	1.31	0.93	10.41	0.59
FmO	1.221	1.26	0.31	11.97	0.43
MdO	1.250	1.22	0.24	13.03	0.41
NoO	1.236	1.28	0.45	13.90	0.35
LrO	1.175	1.29	1.12	–	0.65

Table 2 shows the natural population analysis (NPA) charges of An atoms, Wiberg bond indexes (WBI), and population in different shells of AnO (An = Bk–Lr) molecules obtained at M06-2X level of theory. One can find that the An atoms in the titled species transfer more than $1|e|$ to the O atom, and act as the electron donor. The significant electron transfers from An to O atoms imply the ionic character of An–O bonds. The single bond characters of AnO bonds are revealed by the WBI values. The populations in different shells

of An atoms in the titled species are collected in Table 2. It can be found that the 7s orbitals in the studied molecules are single-electron occupation. Moreover, it is important to note that the 6d orbitals are also partially occupied. Thus, the 7s, 6d, and 5f atomic orbitals participate in chemical bonding of AnO (Bk–Lr) together.

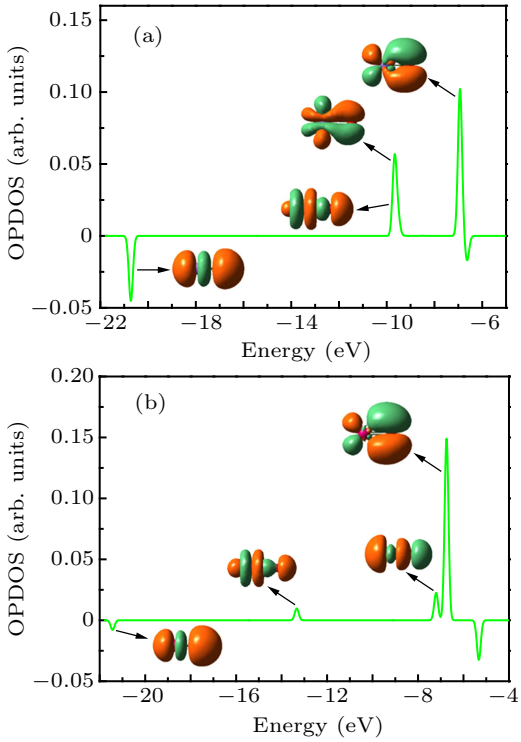


Fig. 1. The overlap population density of states (OPDOS) and molecular orbitals relevant to An–O bonds of BkO (a) and LrO (b) molecules.

The overlap population density of states (OPDOS) analyses[21–23] were performed to reveal the bonding nature of AnO (Bk–Lr) molecules. For BkO–NoO molecules, the bonding orbitals are similar (see Figs. S1–S5 in the Supplementary Material). Therefore, we only depict the OPDOS and relevant molecular orbitals in Fig. 1 for BkO and LrO, respectively. As shown in Fig. 1(a), two positive OPDOS peaks are localized around −10 eV and −7 eV, respectively. The peak at high energy level is identified as π bonds from the overlaps of Bk 6d and O 2p atomic orbitals. The 5f atomic orbitals of Bk are overlapped with O 2p, resulting in the π bond and σ bond at −10 eV. In addition to the bonding orbitals, the antibonding orbitals from Bk 6p and O 2s are also formed in the low-energy region. Previous work[22,23] also found this type of anti-bonding orbital in other actinide complexes. As for the LrO molecule, the predominant positive OPDOS peak shows that a π bond nature is mainly derived from the Lr 6d and O 2p atomic orbitals. The overlaps of Lr 7s and O 2p result in the σ bond near −7 eV. The weak OPDOS peak corresponding to the σ bond from Lr 5d and O 2p is found around −13 eV. The antibonding orbital is also formed.

The chemical bonding characters of AnO molecules were analyzed within the quantum theory of atoms in molecules (QTAIM)[18] framework. The wavefunction used in the QTAIM analyses was obtained at M06-2X level, which predicted the same ground electronic state as the MP2 method. The topological parameters relevant to (3, −1) bond critical points (BCP) of An–O bonds are shown in Table 3, and the 2D plots of electron density are depicted in Fig. 2. The topological parameters shown in Table 3 include the electron density at BCP ($\rho(r)$), Laplacian of electron density ($\nabla^2\rho$), the total electron energy density $H(r)$ (defined as the sum of local kinetic energy density $G(r)$ and the local potential energy density $V(r)$). Other important ratios ($H(r)/\rho(r), -V(r)/G(r)$), are used to assess the covalency. According to the criteria of QTAIM, the An–O bonds exhibit typical closed-shell characteristic, which can be concluded from the positive Laplacian $\nabla^2\rho(r)$ value. Meanwhile, we also note that the partial covalent interaction of An–O bonds is revealed by the negative $H(r)$ value and $-V(r)/G(r)$ ratio larger than 1. Energy density per electron, $H(r)/\rho(r)$, which is called "bond degree" parameter (BD).[24] The BD can render the covalence degree. The stronger the interaction, the greater the BD magnitude. From BkO to NoO, the absolute values of BD are gradually decreased, suggesting the weakened bonding strength. One can see from Fig. 2 that the electron density at BCP is also gradually decreased from BkO to NoO. The electron localization function (ELF)[25] and localized orbital locator (LOL)[26] at the BCP are also shown in Table 3. We can see that the ELF and LOL correlate excellently with electron density and total electron energy density $H(r)$. On the whole, the An–O bonds favor an ionic character in nature, and they also show partial covalent nature.

Table 3. The topological parameters of AnO (An = Bk–Lr) molecules.

	$\rho(r)$	$\nabla^2\rho$	$H(r)$	$H(r)/\rho(r)$	$-V(r)/G(r)$	ELF	LOL
BkO	0.237	0.661	−0.149	−0.629	1.475	0.407	0.453
CfO	0.235	0.669	−0.149	−0.634	1.470	0.398	0.448
EsO	0.232	0.630	−0.147	−0.634	1.483	0.405	0.452
FmO	0.192	0.641	−0.107	−0.557	1.400	0.320	0.407
MdO	0.176	0.621	−0.091	−0.517	1.370	0.297	0.392
NoO	0.164	0.624	−0.079	−0.482	1.337	0.226	0.376
LrO	0.193	0.727	−0.104	−0.539	1.365	0.296	0.393

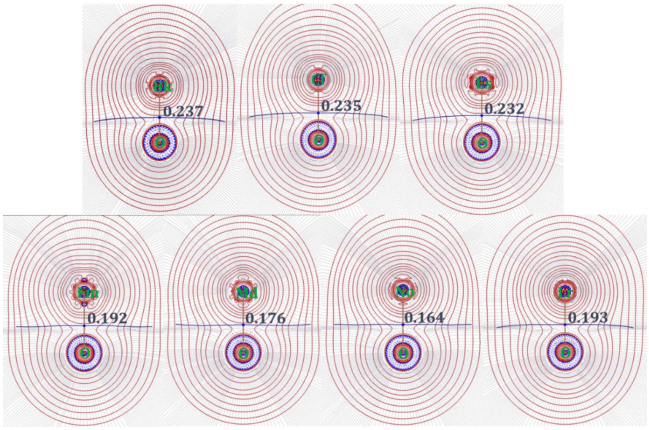


Fig. 2. The 2D plots for the electron density of AnO (An = Bk–Lr) molecules.

4. Conclusion

In summary, we have obtained the molecular geometries and dissociation energies of AnO (Bk–Lr) molecules at the CCSD(T) level of theory with MP2 starting orbitals. The DFT calculations have also been performed for these molecules with four HF/DFT hybridization functionals, B3LYP, M06-2X, TPSSh, and PBE0, for the sake of comparison. By comparing with CCSD(T) results, we conclude that the M06-2X functional generally gives the lower dissociation energies, on the other hand, the MP2 highly overestimates the dissociation energy. B3LYP, TPSSh, and PBE0 functionals always obtain reasonable molecular geometries and dissociation energies. The overlap population density of states (OPDOS) and molecular orbital analyses indicate that the 7s, 6d, and 5f atomic orbitals of An atoms participate into the bonding of An–O bonds. QTAIM analyses have been performed to reveal the bonding nature of An–O bonds. Our results indicate that An–O bonds are essentially closed-shell characteristic. Meanwhile, we also note that An–O bonds also show partial covalent nature revealed by the high electron density and negative electron energy density. From BkO to NoO, the bond strengths are gradually decreased.

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