Density functional study of uranyl (VI) amidoxime complexes*

Chi Fang-Ting(匙芳廷)[a)b)], Li Peng(李 鹏)[c)], Xiong Jie(熊 洁)[a)], Hu Sheng(胡 胜)[a)], Gao Tao(高 涛)[c)], Xia Xiu-Long(夏修龙)[a)], and Wang Xiao-Lin(汪小琳)[a)b)†]

[a)] *Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang* 621900, *China*

[b)] *College of Chemistry, Sichuan University, Chengdu* 610064, *China*

[c)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

(Received 12 December 2011; revised manuscript received 26 April 2012)

Uranyl (VI) amidoxime complexes are investigated using relativistic density functional theory. The equilibrium structures, bond orders, and Mulliken populations of the complexes have been systematically investigated under a generalized gradient approximation (GGA). Comparison of (acet) uranyl amidoxime complexes ($[UO_2(AO)_n]^{2-n}$, $1 \leq n \leq 4$) with available experimental data shows an excellent agreement. In addition, the U–O(1), U–O(3), C(1)–N(2), and C(3)–N(4) bond lengths of $[UO_2(CH_3AO)_4]^{2-}$ are longer than experimental data by about 0.088, 0.05, 0.1, and 0.056 Å. The angles of N(3)–O(3)–U, O(2)–N(1)–C(1), N(3)–C(3)–N(4), N(4)–C(3)–C(4), and C(4)–C(3)–N(3) are different from each other, which are due to existing interaction between oxygen in uranyl and hydrogen in amino group. This interaction is found to be intra-molecular hydrogen bond. Studies on the bond orders, Mulliken charges, and Mulliken populations demonstrate that uranyl oxo group functions as hydrogen-bond acceptors and H atoms in ligands act as hydrogen-bond donors forming hydrogen bands within the complex.

Keywords: uranyl amidoxime complexes, intra-molecular hydrogen bonds, bond order, Mulliken populations

PACS: 31.15.es, 21.60.Jz **DOI:** 10.1088/1674-1056/21/9/093102

1. Introduction

To recognize the uranyl ion (UO_2^{2+}) is a long-standing goal for purposes of environmental remediation, metallurgical extraction, and water purification from seawater.[1] Uranium is one of the most valuable metals existing in seawater. The concentration of uranium in seawater is always 3.3 mg/m^3.[2] Extracting uranium from seawater is one of challenging problems that require knowledge in chemical, kinematical, and process-design aspects. Many adsorbents have been developed and tested for the extraction of uranium from seawater. Among them, amidoxime (AO) group containing adsorbents are shown to be more effective for the extraction of uranium from seawater.[3–5] Comparison of experimental U-loading capacity with calculated functional group density indicates that UO_2^{2+} ions could form a complex with AO groups with a ratio of 1:4. There are many other reported coordination numbers between UO_2^{2+} and AO groups.[6–9] To the best of our knowledge, the complexes of uranyl and AO have been rarely investigated using quantum chemistry. The description of the electronic structures of uranium and AO is essential for understanding their chemical and physical properties, and thus for the development of applications.

Similar to many other areas of quantum chemistry, density functional methods have been successfully applied to study actinide systems.[10,11] Up to now, density functional theory (DFT) applied in 5f element chemistry has been widely discussed.[12–20] Most of them have been aimed to provide some contribution to actinide chemistry relevant to actinide separation, complexes, and sequestration in mesoporous materials. The investigation strongly advances the understanding and prediction of actinide transport in the environment specially related to the safety of nuclear waste repositories. The development of ligands capable of selectively and effectively binding of uranyl ion has been motivated by applications including uranium mining and purification, nuclear fuel cycle pro-

*Project supported by the Science and Technology Development Foundation of China Academy of Engineering Physics (Grant No. 2011A0301003).

†Corresponding author. E-mail: xlwang@caep.ac.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

cess chemistry, chelation therapy for metal poisoning, and uranium recovery from seawater. Typically, the short U=O bonds are inert, indicating that, as a rule, all ligands are situated in an equatorial plane perpendicular to the O=U=O axis in tetragonal, pentagonal, and hexagonal bipyramidal geometries.[21−24]

Motivated by the above consideration, we have studied the complex behaviours of amidoxime functional group toward uranyl ions systematically, in particular the coordination symmetry and the kind of donor atoms. In the present study, we have systematically examined the bond orders, Mulliken populations, vibrational properties, and ligand effects of several uranyl complexes with amidoxime using the relativistic density functional theory. Moreover, we compare our findings with other theoretical and experimental results, and discuss their possible impacts on understanding of uranyl coordination.

2. Computational method

Recently, there have been significant developments in improving the accuracy and applicability of the DFT methods in the chemistry of uranium complexes. It is proved that the choices of the basis set and density functional are essential for the accurate description of spin states of the ligand and uranium complexes.[25] The geometries, vibrational frequencies, and electronic structures of the potential uranium product complexes have been calculated using relativistic DFT with the Amsterdam density functional (ADF) code,[26,27] where the scalar relativistic is incorporated by the zero-order regular approximation (ZORA).[28] Generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) functionals were used. Geometry optimizations have been calculated with standard Slater-type-orbital (STO) basis sets and triple-zeta-polulation (TZP) functions for all the atoms. Since the 5f and 6d semicore orbitals are important for actinide bonding, they are included explicitly in the variational space along with the 5f, 6s, 6d, 6p, and 7s valence orbitals, whereas frozen-core approximation was applied to the U [$1s^2$–$5d^{10}$] atomic core. The frozen-core approximation was also utilized on C, N, and O for the 1s electrons.

Population-based bond orders were calculated with the ADF–PBE approach. Atomic charges and bond orders are not quantum-mechanical observables. However, we have found that the calculated charges and bond orders are consistent with chemically meaningful models for various actinide compounds and various strengths of bonds.

3. Results and discussion

3.1. Calculated geometries and vibrational frequencies

Calculated optimized geometries and vibrational frequencies of deprotonated species in gas phase are shown in Table 1. Antisymmetric uranyl stretching frequencies for different UO_2^{2+} species are also given in Table 1. There is a good inverse correlation between U–O_{oxo} bond lengths and stretching frequencies. As the bond length increase, the stretching vibration frequency decrease. It is known that the coordination energy of complexes arises from electrostatic attraction, repulsion, ligand polarization, uranyl polarization, charge transfer from the ligand to the uranyl, and reverse charge transfer.[29,30] We note that the antisymmetric stretching frequency decreases from 981 to 884 cm^{-1} when $[UO_2(AO)]^+$ changes to $[UO_2(CH_3AO)_4]^{2-}$. This shift is consistent with donation of additional electron density to the uranium center by each additional ligand, repelling the axial O atoms and weakening the U=O bonds. This interpretation is supported by the results of the computational modeling (Table 1) which shows the lengthening of the U=O bond as more amidoxime or acetamidoxime ligands are added.

Table 1. Calculated bond angles, bond lengths (in units of Å), and uranyl stretching frequencies (in units of cm^{-1}) of different species in the gas phase (ADF TZP-PBE). The O_{oxo} is oxygen atoms of Uranyl (VI) oxo group. The O_{li} and N_{li} are oxygen and nitrogen atoms of (acet) amidoxime. The υ_{asym} is the asymmetry vibration of O=U=O.

Complex	d(U–O_{oxo})	d(U–O_{li})	d(U–N_{li})	d(U–O(2))	d(U–O(3))	angle(O=U=O)	υ_{asym}
$UO_2(AO)^+$	1.779	2.097	2.592	–	–	169.4°	981
$UO_2(CH_3AO)^+$	1.781	2.091	2.570	–	–	168.7°	971
$UO_2(AO)_2$	1.813	2.227	2.675	–	–	180.0°	908
$UO_2(CH_3AO)_2$	1.817	2.219	2.669	–	–	180.0°	907
$UO_2(AO)_3^-$	1.827	2.462	2.636	–	–	180.0°	889
$UO_2(CH_3AO)_3^-$	1.829	2.462	2.622	–	–	180.0°	882
$UO_2(AO)_4^{2-}$	1.860	–	–	2.324	2.260	179.9°	890
$[UO_2(CH_3AO)_4]^{2-}$	1.880	–	–	2.268	2.211	180.0°	884

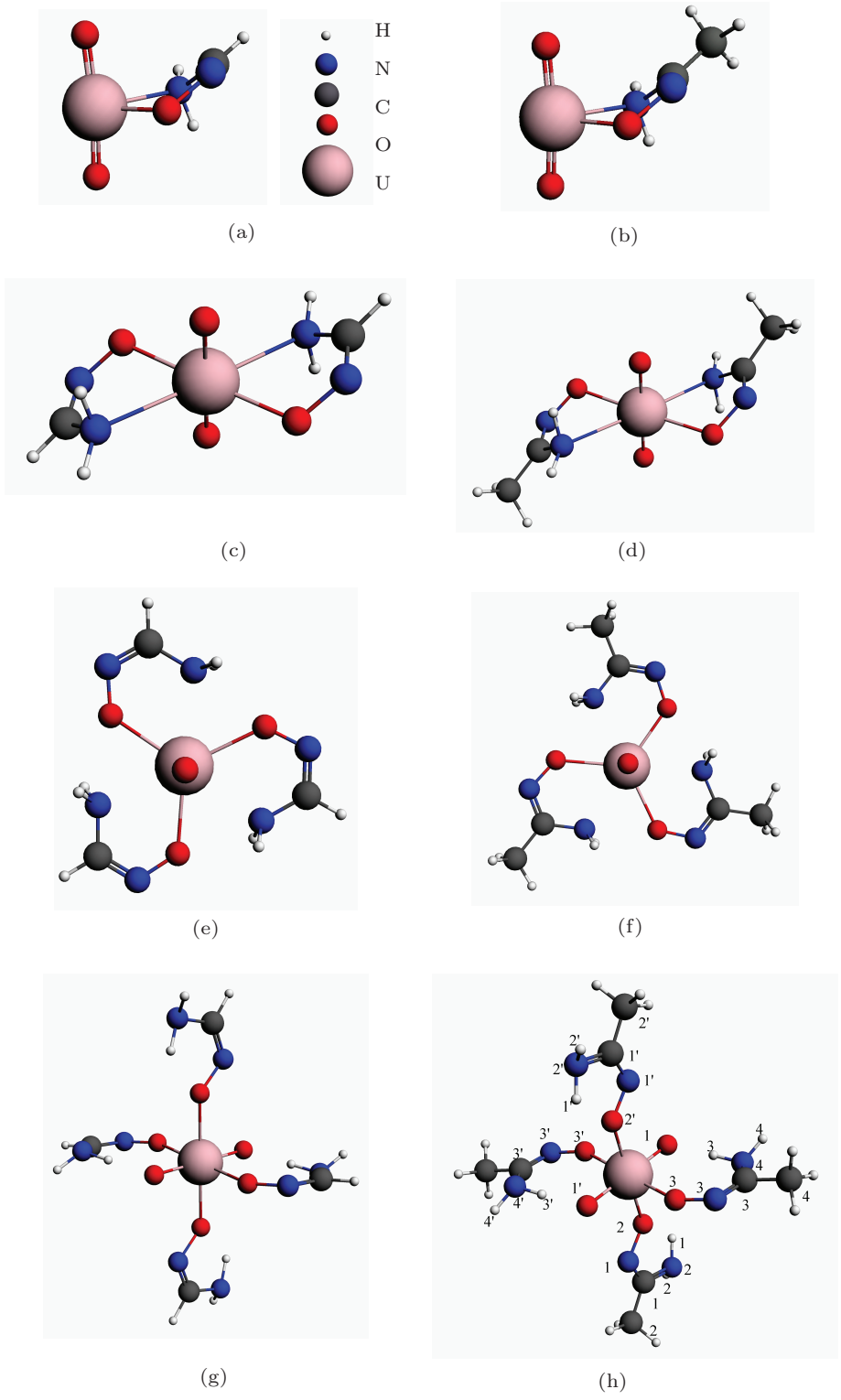


Fig. 1. (colour online) Structures of uranyl amidoxime complexes with different symmetries. (a) $[UO_2(AO)]^+$ (C_1); (b) $[UO_2(CH_3AO)]^+$(C_1); (c) $[UO_2(AO)_2]$ (C_i); (d) $[UO_2(CH_3AO)_2]$ (C_i); (e) $[UO_2(AO)_3]^-$ (C_{3h}); (f) $[UO_2(CH_3AO)_3]^-$ (C_{3h}); (g) $[UO_2(AO)_4]^{2-}$ (C_i); (h) $[UO_2(CH_3AO)_4]^{2-}$ (C_i).

For one, two, and three coordinated amidoxime complexs, the band lengths of U–O_{li} and U–N_{li} increase with the increase in the ligands, indicating that the electron density per ligand donated to the metal center is greater in complexes containing fewer ligands. This conclusion concurs with the general observation that ligand binding energies in noncovalent metal–ligand complexes decrease as the number of lig-

ands increases.[31] However, for the four AO^- and CH_3AO^- complexes, the distance between O_{li} donor and uranyl is short compared with the three complexes. The modest band length decrease may reflect a slight steric crowding of the equatorial ligands. O and N atoms coordinate together with uranyl in tri (acet) amidoxime complexe. In fact, the bond lengths for the N_{li} of the $n = 1$, 2, 3 (acet) amidoxime complexes are found to be longer than the O_{li} donor of the corresponding complexes. These results support the expectation that oxygen is a stronger nucleophile than nitrogen, which in turn indicates that uranyl is classified as a hard Lewis acid, and hence it has an enhanced affinity for oxygen donor atoms.[32−34] The calculated bond lengths of O(2) of the four coordinated (acet) amidoxime complexes are about 0.06 Å longer than that of O(3) of the same complexes (see Fig. 1(f) and Table 1). The U–O_{li} bond distance does not suffer any significant variation, compared with complexes with AO^- and CH_3AO^- ligands, which indicates that electron-donating effect of the methyl group is slight.

The equilibrium structures of the different species are shown in Fig. 1. In the optimized GGA structures of the di-, tri-, and tetra (acet) amidoxime complexes, the uranyl unit is linear, and the (acet) amidoximes are symmetrically distributed in the equatorial plane. All oxygen and nitrogen atoms of ligands lie in the equatorial plane. The O=U=O angles of one coordinated species is slightly bent. While O=U=O angles of two, three, and four coordinated species is essentially linear.

3.2. Comparison between calculated and experimental data

In Tables 2 and 3, we make a comparison between our calculated data and experimental data.[35] For the one, two, and three coordinated species, they are calculated for the first time. There is a good agreement between calculated U–O(2), N(1)–O(2), N(3)–O(3), C(1)–N(1), C(3)–N(3), C(1)–C(2), and C(3)–C(4) bond lengths (see Fig. 1(h)) and experimental bond lengths for the four coordinated uranyl amidoximes, which proves the validity of our approach. However, with regard to our gas-phase calculations, the U–O(1), U–O(3), C(1)–N(2), and C(3)–N(4) bond lengths of $[UO_2(CH_3AO)_4]^{2-}$ are longer than experimental data by about 0.088, 0.05, 0.1, and 0.056 Å, respectively. The calculated angles of N(3)–O(3)–U and N(3)–C(3)–N(4) are larger than experimental data by 34.6° and 10.0°, respectively. By contrast, O(2)–N(1)–C(1), N(4)–C(3)–C(4), and C(4)–C(3)–N(3) is slightly less. This phenomenon may be understood as follows. Firstly, in gas phase, the interaction between O(1) and H(3) atoms increases the lengths of U–O(1), C(1)–N(2), and C(3)–N(4). A gas-phase environment offers a great degree of control, which might enable the measurement of calculated parameters. However, in Ref. [36], nitrate ions of uranyl nitrate play an important role in the crystallization process: nitrate ions provide the specific intermolecular contacts. Because nitrate is an anion of the crystal system of uranyl (VI) amidoxime complexs, it can interact with hydrogen, making the intramolecular hydrogen weak, or even disappear. Secondly, this also corresponds to the tendency of GGA functionals to overestimate bond lengths that has been observed for various actinide species.[36]

In order to explore the possible interaction between uranyl ions and amine groups of amidoxime, Choi and Nho[37] compared amidoxime and acrylamide grafted to the polyethylene file by radiation. The acrylamide-grafted PE film does not adsorb uranyl ion, which indicates that =N–O groups of the grafted copolymer are coordinated with uranyl. Hence, in tetra coordination, it is oxygen not nitrogen that coordinates with uranyl. In Table 3, a comparison is made between our calculated N–O stretching frequencies and experimental ones. The calculated vibrational frequencies for (acet) amidoxime-uranyl complexes agree with experimental data. For a given bare N–O stretch in the range of 920–940 cm^{-1}, the N–O of uranyl amidoxime complex will be red shifted to 899–920 cm^{-1}. Electron density transfers to uranium and weakens N–O bond. Compared with experimental data, the calculated O=U=O stretches are shifted toward lower frequencies.[38,39] This shift is consistent with the transfer of additional electron density to the uranium center in gas phase, repelling the axial O atoms, and thus weakening the U=O bonds.

Table 2. Selected bond lengths and bond angle of the $[UO_2(CH_3AO)_n]^{2-}$ $(n = 4)$.

Bond	Bond length/Å		Bond	Bond angle/(°)	
	This work	Ref. [35]		This work	Ref. [35]
U–O(1)	1.863	1.775	O(1)–U–O(1')	180.0	180
U–O(2)	2.308	2.301	O(1)–U–O(2)	88.3	91.19
U–O(3)	2.263	2.313	O(1)–U–O(2')	91.7	88.81
N(1)–O(2)	1.380	1.366	O(1)–U–O(3)	89.3	88.91
N(3)–O(3)	1.378	1.383	O(1)-U–O(3')	90.7	91.10
C(1)–N(1)	1.297	1.300	O(2)–U–O(2')	180.0	180
C(1)–N(2)	1.414	1.314	O(2)–U–O(3)	89.7	89.64
C(3)–N(3)	1.299	1.299	O(2)–U–O(3')	90.3	90.36
C(3)–N(4)	1.391	1.335	O(3)–U–O(3')	180.0	180
C(1)–C(2)	1.433	1.448	N(1)–O(2)–U	129.6	121.8
C(3)–C(4)	1.468	1.472	N(3)–O(3)–U	152.8	118.2
			O(2)–N(1)–C(1)	110.5	121.1
			O(3)–N(3)–C(3)	117.3	120.5
			N(1)–C(1)–N(2)	123.4	121.5
			N(2)–C(1)–C(2)	119.0	120.4
			C(2)–C(1)–N(1)	119.0	118.2
			N(3)–C(3)–N(4)	130.1	120.1
			N(4)–C(3)–C(4)	115.7	120.5
			C(4)–C(3)–N(3)	114.2	119.4

Table 3. Stretching vibration of sample before and after adsorbing U (VI).

	O–N		C=N		υ_{asym}	
	Before	After	Before	After	Before	After
This work	927	920	1709	1581–1609		884
Ref. [35]			1656	1577		915
Ref. [38]	922	913	1650			
Ref. [39]	927	899				904
Ref. [37]	940		1650			
Ref. [40]	920		1650			

3.3. Bond orders, Mulliken charges, and populations

Bond order measures the stability of a bond. It is also an indication of bond strength. The G–J bond orders of one, two, three, and four coordinated species are given in Table 4. It is found that U–O(1) bond orders are about 2.0 in all species, which agrees well with double bond of U–O_{oxo}. Due to the involvement of the uranyl orbital bonding to the equatorial ligands, all of U–O_{oxo} values are significantly reduced from 2.4947 to 2.0785. It is a good approximation that the sum of the total bond order per metal surface atom is conserved. The increase in the coordination number decreases the bond order per bond, and also the bond strength of the atom bonds. The bond orders of U–N(2) are about 0.4, while those of U–O(2) are about 1. This indicates that the bond of U–O_{li} is stronger than that of U–N_{li}, and also supports the expectation that oxygen is a stronger nucleophile than nitrogen. Uranyl is classified as a hard Lewis acid, and it has an enhanced affinity for oxygen donor atoms.

Typically, two hydrogens of amido group (NH_2) have the same bond orders. The bond orders of N(4)–H(3) and N(4')–H(3') are smaller than N(4)–H(4) and N(4')–H(3'), indicating some amount of electron donation from the H(3) and H(3') atoms to other atoms nearby. The geometry shown in Fig.1 demonstrates that the distance between the uranyl oxo and one of amide H atoms is close enough (1.812 Å) to form H-bond. Therefore, H(3) and H(3') transfer their elec-

trons to oxygen of uranyl, resulting in the decrease of bond orders. The bond order is also an evidence of intramolecular hydrogen bonds between the ligands to uranyl. Uranyl oxo group acts as hydrogen bond acceptors. H atoms of NH_2 in (acet) amidoxime acts as hydrogen bond. Intramolecular hydrogen could enhance stability and selectivity of the four coordinated species.

Table 4. Bond orders of the one, two, three and four coordinated species.

$[UO_2(AO)_n]^{2-n}$	U–O(1)	U–N(2)	U–O(2)	U–O(3)	N(4)–H(3)	N(4)–H(4)	N(4')–H(3')	N(4')–H(4')
n=1	2.495	0.469	1.323	–	–	–	–	–
	2.486	0.481	1.344	–	–	–	–	–
n=2	2.352	0.330	0.978	–	–	–	–	–
	2.342	0.330	0.997	–	–	–	–	–
n=3	2.297	0.371	0.581	–	–	–	–	–
	2.288	0.374	0.589	–	–	–	–	–
n=4	2.148	–	0.721	0.888	0.792	0.902	0.791	0.904
	2.078	–	0.753	0.937	0.763	0.904	0.764	0.905

To understand the relative roles of the U 6p, 5f, and 6d orbitals and their chemical bonds, a series of theoretical analyses have been performed.[40] Tables 5 and 6 lists the Mulliken charges and populations calculated for the uranyl and (acet) amidoxime complexes. The Mulliken analysis reveals that U carries highly positive charges in these U (VI) complexes, which helps to form stable molecules by both covalent and ionic interactions. The charge transfer analysis corroborates that the electron donation occurs from the ligands to the metal center. For the case of one, two, and three coordinated complexes, the addition of a new ligand slightly increases the charge transfer. Charge shift from the ligand to the empty f orbitals is therefore obviously favored. In other words, the interaction between UO_2^{2+} and ligands has some covalent character and it is possible that the coordination energy will be influenced by the charge transfer and the electrostatic and polarization terms.[41] Typically, in the tetra-coordianted complex, the Mulliken charges of H(3) and H(3') are about 0.23, which indicates that H(3) interacts with O of UO_2^{2+}. This is also supported by the analysis of the band order (Table 4). However, the Mulliken charges of H(4) and H(4') are about 0, which indicates that H(4) does not interact with O of UO_2^{2+}.

If hydrogen bond are able to contact uranyl oxo group within the ligand, intramolecular hydrogen bond can enhance to both the stability and selectivity of complexation.[53] In order to display the intramolecular H-bond visually, the diagram of the $[UO_2(CH_3AO)_4]^{2-}$ is drawn (see Fig. 2). Obviously, there are hydrogen bonds between oxygen of uranyl and hydrogen of NH_2.

Table 5. Orbital occupation of $[UO_2(CH_3AO)_n]^{2-}$ $(1 \leq n \leq 4)$.

n	U	O(2)	N(1)	O(3)	H(3)	H(4)
1	$5f^{2.72}$ $(6s+7s)^2$ $6p^{5.68}$ $6d^{1.45}$	$2s^{1.92}$ $2p^{4.51}$	$2s^{1.48}$ $2p^{3.80}$			
	$5f^{2.73}$ $(6s+7s)^2$ $6p^{5.69}$ $6d^{1.46}$	$2s^{1.92}$ $2p^{4.60}$	$2s^{1.49}$ $2p^{3.81}$			
2	$5f^{2.72}$ $(6s+7s)^2$ $6p^{5.70}$ $6d^{1.48}$	$2s^{1.91}$ $2p^{4.59}$	$2s^{1.46}$ $2p^{3.79}$			
	$5f^{2.73}$ $(6s+7s)^2$ $6p^{5.70}$ $6d^{1.49}$	$2s^{1.92}$ $2p^{4.60}$	$2s^{1.46}$ $2p^{3.80}$			
3	$5f^{2.57}$ $(6s+7s)^2$ $6p^{5.74}$ $6d^{1.52}$	$2s^{1.90}$ $2p^{4.63}$	$2s^{1.46}$ $2p^{3.77}$			
	$5f^{2.58}$ $(6s+7s)^2$ $6p^{5.73}$ $6d^{1.52}$	$2s^{1.90}$ $2p^{4.64}$	$2s^{1.48}$ $2p^{3.78}$			
4	$5f^{2.62}$ $(6s+7s)^2$ $6p^{5.76}$ $6d^{1.49}$	$2s^{1.90}$ $2p^{4.63}$		$2s^{1.91}$ $2p^{4.67}$	$1s^{0.62}2p^{0.15}$	$1s^{0.92}2p^{0.11}$
	$5f^{2.60}(6s+7s)^2$ $6p^{5.74}$ $6d^{1.51}$	$2s^{1.90}$ $2p^{4.63}$		$2s^{1.92}$ $2p^{4.68}$	$1s^{0.61}2p^{0.17}$	$1s^{0.94}2p^{0.12}$

Table 6. Net charge of $[UO_2(CH_3AO)_n]^{2-}$ $(1 \leq n \leq 4)$.

n	U	O(2)	N(1)	H(3)	H(4)
1	2.10	–0.49	–0.32		
	2.08	–0.51	–0.34		
2	2.06	–0.56	–0.30		
	2.03	–0.58	–0.30		
3	2.07	–0.58	–0.29		
	2.06	–0.60	–0.31		
4	2.05	–0.58	–0.64	0.23	–0.034
	2.07	–0.59	–0.65	0.22	–0.058

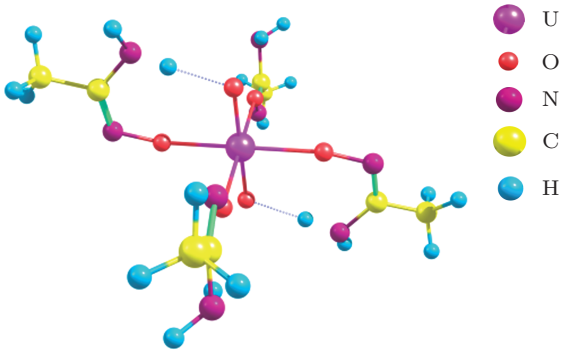


Fig. 2. (colour online) Structures of uranyl acetamidoxime complexes. Dotted line denotes the band between hydrogen of ligand NH_2 group and oxygen of uranyl oxo group.

4. Conclusions

In this paper, the DFT theory has been applied to model uranyl-amidoxime complexes in gas phase. The mechanistic properties of $[UO_2(CH_3AO)_4]^{2-}$ were also explored intramolecular hydrogen bonds between uranium and ligands.

Calculated geometries and vibrational frequencies reveal that the oxygens of uranyl ion are chemically inert. There are generally 4–6 additional donor atoms around uranium. Uranyl (VI) ion is a hard Lewis acid and prefers to interact with hard oxygen donors. Therefore, compared with nitrogen, oxygen of amidoxime prefers coordinating with U atoms.

Our calculated results are reasonably consistent with experimental data for $[UO_2(CH_3AO)_4]^{2-}$. Compared with the experimental data, the U–O(1), U–O(3), C(1)–N(2), and C(3)–N(4) bond lengths are longer by about 0.088, 0.05, 0.1, and 0.056 Å. The angles of N(3)–O(3)–U and N(3)–C(3)–N(4) is 34.6° and 10.0° larger than experimental data. In contrast, O(2)–N(1)–C(1), N(4)–C(3)–C(4), and C(4)–C(3)–N(3) is slightly less. These deviations can be attributed to existing interaction between oxygen of uranyl and hydrogen of amino. It is supposed that the interaction is intramolecular hydrogen bond.

Investigations into the bond orders, Mulliken charges, and populations further testify that uranyl oxo group acts as hydrogen bond acceptors, and H atom of NH_2 acts as the hydrogen-bond donor forming hydrogen bands within $[UO_2(CH_3AO)_4]^{2-}$. Thus, the tetra (acet) amidoxime complexes are much more acceptable. Unusual phenomenon of tetra-coordination uranyl amidoxime complex clearly requires further experimental and theoretical studies.

References

[1] Sather A C, Berryman O B and Rebek J Jr 2010 *J. Am. Chem. Soc.* **132** 13572
[2] Davies R V, Kennedy J and Mcllroy R W 1964 *Nature* **203** 1110
[3] Egawa H, Nakayama M, Nonaaka T, Yamamoto H and Uemura K 1987 *J. Appl. Polym. Sci.* **34** 1557
[4] Egawa H, Kabay N, Shuto T and Jyo A 1992 *J. Appl. Polym. Sci.* **46** 129
[5] Egawa H, Nonaka T, Abe S and Nakayama M 1992 *J. Appl. Polym. Sci.* **45** 837
[6] Kumar V, Bhardwaj Y K, Dubey K A, Chaudhari C V, Goel N K, Biswal J, Sabharwal S and Tirumalesh K 2006 *Sep. Sci. Technol.* **41** 3123
[7] Zhang A, Uchiyama G and Asakura T 2005 *React. Funct. Polym.* **63** 143
[8] Badawy S M, Sokker H H and Dessouki A M 2006 *J. Appl. Poly. Sci.* **99** 1180
[9] Choi S H and Nho Y C 2000 *Radiat. Phys. Chem.* **57** 187
[10] Liu S P, Gong J, Hao F H and Hu G C 2008 *Chin. Phys.* B **17** 1674
[11] Xu H B, Peng X K and Chen C B 2010 *Chin. Phys.* B **19** 062901
[12] Bühl M, Kabrede H, Diss R and Wipff G 2005 *J. Am. Chem. Soc.* **127** 13506
[13] Jia T T, Gao T, Zhang Y G, Lei Q H and Luo D L 2011 *Chin. Phys.* B **20** 113601
[14] García-Hernández M, Willnauer C, Krüger S, Moskaleva L V and Rösch N 2006 *Inorg. Chem.* **45** 1356
[15] Tian X F, Long C S, Zhu Z H and Gao T 2010 *Chin. Phys.* B **19** 057102
[16] Zhang Y G and Li Y D 2010 *Chin. Phys.* B **19** 033302
[17] Stipdonk M J V, Chien W, Bulleigh K, Wu Q and Groenewold G S 2006 *J. Phys. Chem.* A **110** 959
[18] Hagberg D, Karlström G, Roos B O and Gagliardi L 2005 *J. Am. Chem. Soc.* **127** 14250
[19] Groenewold G S, Gianotto A K and Cossel K C 2006 *J. Am. Chem. Soc.* **128** 4802
[20] Vallet V, Wahlgren U, Schimmelpfennig B, Szabó Z and Grenthe I 2001 *J. Am. Chem. Soc.* **123** 11999
[21] Weck P F, Kim E, Masci B, Thuéry P and Czerwinski K R 2010 *Inorg. Chem.* **49** 1465
[22] Watson L A and Hay B P 2011 *Inorg. Chem.* **50** 2599
[23] Pan Q J and Schreckenbach G 2010 *Inorg. Chem.* **49** 6509

[24] Shamov G A and Schreckenbach G 2006 *J. Phys. Chem.* A **110** 9486

[25] Schreckenbach G and Shamov G A 2010 *Acc. Chem. Res.* **43** 19

[26] te Velde G, Bickelhaupt F M, Baerends E J, Guerra C F, van Gisbergen S J A, Snijders J G and Ziegler T J 2001 *Comput. Chem.* **22** 931

[27] Fonseca G C, Snijders J G, te Velde G and Baerends E J 1998 *Theor. Chem. Acc.* **99** 91

[28] van Lenthe E, Baerends E J and Snijders J G 1993 *J. Chem. Phys.* **99** 4597

[29] Clavaguera-Sarrio C, Hoyau S, Ismail N and Marsden C J 2003 *J. Phys. Chem.* A **107** 4515

[30] Hagberg D, Karlstrom G, Roos B O and Gagliardi L 2005 *J. Am. Chem. Soc.* **127** 14250

[31] Rodgers M T and Armentrout P B 2000 *Mass Spectrom. Rev.* **19** 215

[32] van Horn J D and Huang H 2006 *Coord. Chem. Rev.* **250** 765

[33] Antonisse M M G and Reinhoudt D N 1998 *Chem. Commun.* **4** 443

[34] Dai S, Shin Y S, Barnes C E and Toth L M 1997 *Chem. Mater.* **9** 2521

[35] Witte E G, Schwochau K S, Henkel G and Krebs B 1984 *Inorg. Chim. Acta* **94** 323

[36] Shamov G A and Schreckenbach G 2005 *J. Phys. Chem.* A **109** 10961

[37] Chio S H and Nho Y C 2000 *Radiat. Phys. Chem.* **57** 187

[38] Das S, Pandey A K, Athawale A A and Manchanda V K 2009 *J. Phys. Chem.* B **113** 6328

[39] Kavaklı P A and Güven O 2004 *J. Appl. Polym. Sci.* **93** 1705

[40] Lyon J T, Hu H S, Andrews L and Li J 2007 *PNAS* **104** 8919

[41] Sarrio C C, Hoyau S, Ismaail N and Marsden C J 2003 *J. Phys. Chem.* A **107** 4515

[42] Franczyk T S, Czerwinski K R and Raymond K N 1992 *J. Am. Chem. Soc.* **114** 8138