

# Gas phase reactions of uranyl with α-hydroxyisobutyric acid using electrospray ionization mass spectrometry and density functional theory

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Abstract Electrospray ionization mass spectrometry (ESI-MS) technique was used to find out the type of species of uranyl with  $\alpha$ -hydroxyisobutyric acid in positive and negative ion modes. It was found that the singly charged monomeric and doubly charged dimeric species were present in soft ionization conditions. The molecular level understanding on the structures and energetics were investigated using density functional theory based calculations. It was found that ML<sub>3</sub>, the most intense species observed in ESI-MS were energetically more favorable as compared to ML<sub>1</sub> and ML<sub>2</sub>.

Keywords Uranyl · HIBA · ESI-MS · DFT

# Introduction

The formations of different species of hydroxycarboxylic group containing ligands with uranyl ion have gained significant attention in view of its application in separation

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processes in nuclear industries and environmental science [1]. Studies on the formation of different species are important to understand the migration behavior and to design the methodology for the separation of lanthanides and other fission product from the irradiated fuel samples [2]. The hydroxycarboxylic acids are also used as the model compound for humic substances which are present in nature [3, 4]. Out of the several analytical separation methods, high performance liquid chromatography (HPLC) is an efficient method for separation of actinides and lanthan ides [5]. In HPLC, complexing agent like  $\alpha$ -hydroxyisobutyric acid (HIBA) is commonly used for the separation of uranium and other fission products in irradiated fuel samples [6, 7]. Thus, understanding the nature of various species responsible for their retention on a given stationary phase would be very helpful to fine-tune the separation conditions.

Electrospray ionization (ESI) being a soft ionization technique has been utilized for the studies of identification of metal ligand species [8]. The two techniques (HPLC and ESI-MS) are commonly used to understand the speciation of heavy metal ion in solution (HPLC) and in gas phase (ESI-MS). HPLC is a commonly used technique for the separation of metallic complexes, which in turn depends on the speciation of the metal ions. Thus, it provides indirect evidence towards the speciation. Whereas, ESI-MS technique can directly reveal the type of species formed in the gas phase. However, the orientation and the geometry of the species can be revealed by density functional theory (DFT) [9, 10]. Previously we had reported the formation of different species of uranyl with HIBA in positive and negative ion modes [11]. Electrospray ionization and desolvation process may cause artifacts in the distribution of ions in the mass spectra. The major species of uranyl with HIBA were identified and it was found that the distribution

of species depends on mobile phase composition, instrumental parameters and electrolyte concentration.

In this paper we report the complexation of uranyl with HIBA in different solvents and the behavior of uranyl(V) in the presence of different solvents in gas phase. DFT calculations were performed to provide the insight to experimental result, possible pathways for the formation of these species along with the optimized geometry. The theoretically calculated values of structural parameters were in good agreement with the experimentally reported values [12]. The preferable binding mode along with potential surface diagram is helpful for understanding the experimental observation about the change in intensities observed for various species.

# **Experimental**

Uranyl nitrate hexahydrate (BDH, Poole, UK), α-hydroxvisobutyric acid (Alfa Aeser) were used as received. Water purified by Milli-Q system (Millipore, Bengaluru, India) and isopropyl alcohol, methanol, acetone (Sigma-Aldrich, Bengaluru, India) were used for the dilutions and also as the mobile phase for sample introduction into ESI. About  $5 \times 10^{-6}$  M of uranyl solution was prepared by dissolving appropriate quantity of uranyl nitrate hexahydrate in methanol, followed by addition of different solvents to obtain the required mobile phase composition. 0.1 M of HIBA was prepared by dissolving the appropriate quantity in methanol followed by further dilution to the required concentration. The mixing of metal and ligand was done on the volume basis. Solutions of uranyl nitrate and HIBA in 1:1 methanol-water mixture containing  $10^{-5}$  M NaClO<sub>4</sub> were introduced into the ESI-MS system at a flow rate of 3 µL/min.

## Instrumentation

An electrospray mass spectrometer with Quadruple-Timeof-Flight analyzer (model micrOTOFQ-II, Bruker Daltonics GmbH) was used for the studies. Compass Isotope Pattern software was used to obtain theoretically predicted spectra. Bruker Compass Data Analysis software (supplied by Bruker Daltonics GmbH) was used to process the data obtained in the MS as well as MS/MS modes. Samples taken in a 500  $\mu$ L syringe (Hamilton) were infused into the ESI-MS system using a syringe pump (NEMESYS, Cetrol GmbH). Capillary potentials of -4500 and +3800 V were employed for the measurements performed in the positive ion mode and in the negative ion mode, respectively.

#### **Computational details**

For the accurate description of structures and energetics, BP86 functional [13, 14] in conjunction with triple  $\zeta$ quality TZVP basis set [15, 16] is used for geometry optimization. The core electrons of uranium are treated with relativistically contracted small core effective potential, whereas the valence electrons are treated with def-TZVP basis set. The lighter atoms are treated with all electron TZVP basis set. Binding free energies are computed with hybrid B3LYP functional [17, 18] with the same basis set. This combination of method and basis set tend to predict accurate geometries and energetics which was tested for several uranyl complexes [19, 20]. All structures are verified as minima by computing the harmonic vibrational frequencies using the AOFORCE module as implemented in TURBOMOLE 6.3.1 version [21]. All reported energies are corrected for thermodynamics, thus they are free energies.

# **Results and discussion**

Uranyl solutions in different solvents along with HIBA were infused in ESI-MS and mass spectra were acquired in positive and negative ion modes. The general observation of mass spectra obtained for uranyl ion in different solvents is that the most abundant peak is due to the solvent having higher gas phase basicity. For example when the methanol water composition was varied from 10 to 90 % (V/V) it was found that the peak of  $[UO_2(CH_3O)]$ ; m/z 301.05 was the most dominating in all the proportions. The higher coordinated species viz.  $[UO_2(H_2O)_5(CH_3O)]^+$ , [UO<sub>2</sub>(OH)(H<sub>2</sub>O)<sub>3</sub>(CH<sub>3</sub>OH)]<sup>+</sup> having uranyl coordination more than 4 were also found in the mass spectra. However, as seen in the spectrum (Fig. 1), peaks were deformed in shape indicating instability of these high coordinated species. In order to ascertain the influence of gas phase basicity, different aprotic solvents with change in basicity e.g. isopropyl alcohol (IPA), acetone (Aco) and acetonitrile were also used as mobile phase. As presented in Tables S1 and S2 the most dominating peak is due to the uranyl species containing solvent of higher gas phase basicity. It is established that in gas phase the ligand with higher basicity binds strongly with the metal ion. MeOH and IPA are having higher gas phase basicity than water hence the complexation is preferred with these solvents. For example, in case of isopropyl alcohol-methanol mobile phase, the different species identified in positive mode are  $[UO_2(IPA-H)]^+$ ,  $[UO_2(IPA)(OH)]^+$ ,  $[UO_2(IPA)(IPA-H)]^+$ ,  $[UO_2(IPA)(NO_3)]^+$ ,  $[UO_2(IPA)_2(OH)]^+$ ,  $[UO_2(IPA)(H_2O)$  $(NO_3)$ ]<sup>+</sup>,  $[UO_2(IPA)_2(OH)(H_2O)]^+$ ,  $[UO_2(IPA)_2(NO_3)]$  $(H_2O)$ ]<sup>+</sup>,  $[UO_2(IPA)_2(NO_3)]^+$  and  $[UO_2(IPA)_3(OH)]^+$ .



Fig. 1 ESI-MS spectrum of  $[UO_2(H_2O)_5(CH_3O)]^+$  at m/z 391.11

When acetone-methanol was used as mobile phase, in contrast to the previous other solvents, doubly charged species were also observed as seen in Table S2. The singly charged species were  $[UO_2(Aco)(OH)]^+$ ,  $[UO_2(Aco)_2]$ (OH)]<sup>+</sup>, [UO<sub>2</sub>(Aco)<sub>3</sub>(OH)]<sup>+</sup>, [UO<sub>2</sub>(Aco)<sub>4</sub>(OH)]<sup>+</sup>, [UO<sub>2</sub>  $(Aco)_5(OH)]^+$ ,  $[UO_2(Aco)_6(OH)]^+$ , and the doubly charged species were  $[UO_2(Aco)_4]^{2+}$ ,  $[UO_2(Aco)_5]^{2+}$ . The observation of doubly charged species is due to the dispersal of charge on uranyl ion by the aprotic solvent. As shown in Table S1, in presence of more basic solvent IPA, it was found that the species due to coordination of IPA to uranyl were dominating over the methanol in gas phase. In case of methanol, nitrate containing species were absent in the positive ion mode. However, in case of IPA as solvent, the species containing nitrate ion viz. [UO2(IPA)2  $(H_2O)(NO_3)$ <sup>+</sup>,  $[UO_2(IPA)_2(H_2O)(NO_3)]$ <sup>+</sup> and  $[UO_2(IPA)_2(IPA$  $(NO_3)$ <sup>+</sup> were found with appreciable abundances.

Effect of different solvents on oxidation states of uranium was also observed. These studies were carried out with respect to the +5 oxidation state of uranium at m/z270 of UO<sub>2</sub><sup>+</sup>. U(V) was not stabilize in solution but was observed in the gas phase. U(V) was observed in gas phase as a result of reduction of U(VI) under ESI-MS conditions. Existence of uranyl as UO<sub>2</sub><sup>+</sup> has been reported in positive ion mode [22]. As shown in the Fig. 2, with increase in water percentage in the mobile phase the relative



Fig. 2 Effect of solvent composition on +5 oxidation states of uranium

abundances of species corresponding to uranium(V) are increasing. However, when the proportion of isopropyl alcohol (IPA) or acetone is increased in the mobile phase, it resulted in the reduction of relative abundance of uranium +5 species. This may be due to the preferential stabilization of charge of uranium(VI) in aprotic solvent compared to the water.

#### Complexation of uranyl with HIBA

In order to study the complexation behavior of HIBA with uranyl, mixture of uranyl ion and HIBA with an amount ratio 10:1 prepared in 1:1 water-methanol medium was infused. The pH of this solution was 5.0. The different species in the positive ion mode are  $ML_1$ ,  $ML_1(H_2O)$ ,  $ML_1(CH_3OH)$ ,  $ML_1(H_2O)(CH_3OH)$ ,  $ML_2$ ,  $ML_2(H_2O)$ ,  $ML_3$  as per the earlier reported data [10]. Detailed analysis carried out during the present study revealed the existence of dimeric species viz. M<sub>2</sub>L<sub>4</sub> in singly as well as doubly charged states. Similarly when the solutions were analyzed in negative ion mode, the different species reported are  $[UO_2(NO_3)_3]^-$ ,  $[UO_2(NO_3)_2L]^-$ ,  $[UO_2(NO_3)L(OH)]^-$ ,  $[UO_2(NO_3)L_2]^-$ ,  $[UO_2L_3]^-$ ,  $[UO_2(OH)L_2]^-$  and  $[UO_2$ (L)(L-H)]<sup>-</sup>. Among these species, ML<sub>3</sub> was found to be the base peak. It may be worth mentioning that before optimization of ionization and desolvation conditions in ESI,  $ML_2$  was the most abundant species. The existence of the species ML<sub>1</sub>, ML<sub>2</sub> and ML<sub>3</sub> was established in solution phase employing extended X-ray absorption fine structure (EXAFS) by Moll et al. [12].

## **Computational results**

Based on experimental m/z ratio, a viable reaction scheme is proposed to understand the gas phase speciation of various uranyl complexes. The ligand HIBA has two types of acidic protons namely proton attached to the carboxylate site (IBA<sub>a</sub>) and the other located at the hydroxy group site (IBA<sub>b</sub>). These two functional groups have

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different gas phase proton affinity (PA) values such as  $IBA_a$  as -332.9 kcal mol<sup>-1</sup> and  $IBA_b$  as -368.7 kcal mol<sup>-1</sup>. There also exists another site which is doubly deprotonated ( $IBA_c$ )

with PA value -811.0 kcal mol<sup>-1</sup>. Thus, HIBA can exhibit the following deprotonation equilibrium with the varying proton affinity values (Scheme 1).Thus depending upon the modes of ionization in ESI-MS and variable deprotonation state, positive as well as negative species can be formed in positive and negative ion modes, respectively. The optimized structure of uranyl nitrate (species 1) with BP86 functional is consistent with the X-ray structure. For instance the U–O<sub>yl</sub> bond lengths are very close to the experimental data within 0.02 Å.

## **Negatively Charged Species**

In Scheme 2, possible reaction pathways in the negative ion mode, their computed potential free energy surface (Fig. 3) and most stable optimized structures are shown in Fig. 4. As scheme 2 suggests, upon deprotonation, HIBA can successively replace the nitrate ligand to form uranyl-HIBA complexes of variable stoichiometry (1:1; species 2, 1:2; species 3 and 1:3; species 4). In the mono-negative charged 1:1 uranyl nitrate-HIBA complexes, singly deprotonated HIBA i.e. IBA<sub>a</sub> and IBA<sub>b</sub> can either coordinate via carboxylate with bi-dentate motif or via bi-dentate chelating binding mode where both hydroxyl and carboxylate functional groups can directly coordinate to uranyl. Of these two binding motifs, we find that chelating mode is more preferable by ~19 kcal mol<sup>-1</sup>. The

Scheme 1 Structure of HIBA and its deprotonated species

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HIBA	IBA <sub>a</sub>	IBA <sub>b</sub>	IBA <sub>c</sub>
PA	-332.9 kcal mol <sup>-1</sup>	-368.7 kcal mol <sup>-1</sup>	-811.0 kcal mol <sup>-1</sup>



$$1)[UO_{2}(NO_{3})_{3}]^{1} \xrightarrow{+HIBA} (2)[UO_{2}(NO_{3})_{2} (IBA_{b})]^{1} \xrightarrow{+HIBA} (3)[UO_{2}(NO_{3}) (IBA_{b})_{2}]^{1} \xrightarrow{-HNO_{3}} (4)[UO_{2}(IBA_{b})_{3}]^{1} \xrightarrow{+HIBA} (4)[UO_{2}(IBA_{b})_{3}]^{1} \xrightarrow{-HNO_{3}} (4)[UO_{2}(IBA_{b})_{3}]^{1} \xrightarrow{-HNO_{3}} (4)[UO_{2}(IBA_{b})_{3}]^{1} \xrightarrow{-HIO_{3}} (4)[UO_{2}(IBA_{b})_{3}]^{1}$$







Fig. 4 Optimised structure (Å) urany complex with  $\alpha$ -hydroxyisobutyric acid in negative mode

observed preference for chelate mode over bidentate carboxylate mode can be accredited to the reduction of steric strain in complex and involvement of basic hydroxyl group in binding for former. Further, the computed U=O<sub>yl</sub> bond of the chelate binding mode is slightly longer (by 0.01 Å) as compared to carboxylate binding mode. These variations prompt us to consider IBA<sub>b</sub> deprotonated state for the higher stoichiometric complexes.

Further, in agreement with our experimental observations, successive addition of two more  $IBA_b$  at the primary coordination sphere is noted to be energetically favorable as evident from the computed potential energy surface (Fig. 3). Further, water can also react with the uranyl centre to form hydroxylated species (species 5 and 7). The reaction free energies for these complexes are found to be considerably more favorable (>-78 kcal mol<sup>-1</sup>) as compared to 1:3 (U: HIBA) complex ( $\sim -65 \text{ kcal mol}^{-1}$ ). For the formation of species 8, one of the ligand is doubly deprotonated leading to the favorable free energy of formation ( $\sim -108.4 \text{ kcal mol}^{-1}$ ). Addition of HIBA in the metal coordination center led to marginal elongation (up to 0.04 Å) of U=O<sub>yl</sub> bond which caused significant reduction in the computed asymmetric vibrational frequency  $v_{asym}$ (847 cm<sup>-1</sup>) of U=O<sub>yl</sub> bond and hence is in accord to the previous experimental reports of Moll et al. [12]. Further, O=U=O bond is also observed to deviate from linearity as we approach towards higher stoichiometric complex. Nevertheless, computed U–O<sub>OH</sub> bond length was shorter than the U–O<sub>COOH</sub> suggesting weaker participation of carboxylate group than the hydroxyl in case of chelate binding mode.

#### Positively charged species

In positive ion mode, mono and di positive metal species were identified. The possible formation processes (Scheme 3), thermodynamic and structural parameters are shown in Figs. 5 and 6. In contrast to the negative ion mode, U remains in V oxidation state (m/z 270 of UO<sub>2</sub><sup>+</sup>). Here, formation of different species can be considered as combination of two processes viz (a) oxidation of U(V) to U(VI) (b) coordination of ligand/solvent to the U(VI). As evident from the computed free energies, carboxylate binding of IBA<sub>a</sub> to uranyl center via bi-dentate motif is unfavorable (~+10 kcal mol<sup>-1</sup>) (species 10). Further chelate binding of IBA<sub>a</sub> with UO<sub>2</sub><sup>+</sup> is noted to be thermodynamically unfavorable by ~+8 kcal mol<sup>-1</sup>. However,

Scheme 3 Positive ion mode

Positive species formation Scheme for singly charged species

90-100-





Fig. 6 Optimised structure (Å) of uranyl complex with  $\alpha$ -hydroxyisobutyric acid in positive mode



the chelation binding of IBAb was more favorable  $(\sim 42 \text{ kcal mol}^{-1})$  due to the charge neutralization. Akin to negative ion mode, successive addition to form 1:2 and 1:3 uranyl-HIBA complexes (species 11 & 12) are become progressively favorable because of increasing charge compensation of highly positive uranium center. Calculated negative reaction free energies for the solvent coordinated uranyl complexes provide further support to the experimental observation of solvent effect. The species (10) can undergo solvolysis by combining with methanol and water resulting into  $[UO_2(IBA)(CH_3OH)]^{1+}$  and  $[UO_2(IBA)(CH_3OH)(H_2O)]^{1+}$ , respectively. On the other hand subsequent addition of H<sub>2</sub>O will lead to the formation of  $[UO_2(IBA)(H_2O)]^{1+}$ and (16)  $[UO_2(IBA)(H_2O)_2]^{1+}$ . In order to assess the favorability of dimeric species formation, we extended our calculations on optimized dimeric (18)  $[UO_2(HIBA)(IBA)]_2^{2+}$  species (Fig. 6). Indeed, computed potential energy surface finds higher stability of the complex as compared to 1:2 complex (species 11) and thus provide structural insights to our experimental findings. Computed U=O<sub>y1</sub> bond length on complex (species 11) is significantly shorter (1.71 Å) as compared to UO<sub>2</sub><sup>2+</sup>. Expectedly, with ligand binding, this bond is seen to elongate by 0.8 Å. The same is reflected with the reduction of v(U=O) value as compared to bare UO<sub>2</sub><sup>+</sup>. O=U=O bond angle is also noticed to get bent (by almost ~13°) upon ligand binding. For the dimeric species, U–U bond distance is 3.85 Å. The uranyl oxygen of one uranyl center is seen to be slightly bent towards to the other uranyl center which resulted in elongation of U<sub>1</sub>=O bond (2.54 Å) as compared to U<sub>2</sub>=O bond (1.86 Å) (Fig. 6) [23, 24].

# Conclusion

ESI-MS studies along with DFT calculations were carried out to understand the speciation of various uranyl species in gas phase. Quantum chemical calculations have complimented the experimental studies which tracks possible pathways for the formation of different species of uranyl with HIBA. Computational analyses of positive and negative species were carried out and it was found that  $ML_3$  species is more energetically favorable over the  $ML_2$ which in turn more favorable than  $ML_1$ . This observation also corroborates the difference in intensity of  $ML_1$ ,  $ML_2$ and  $ML_3$  in ESI-MS.

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## References

- Metz V, Geckeis H, González-Robles E, Loida A, Bube C, Kienzler B (2012) Radionuclide behaviour in the near-field of a geological repository for spent nuclear fuel. Radiochim Acta 100:699–713
- Lochny M, Odoj R (1998) Separation of actinides by means of HPLC. J Radioanal Nucl Chem 228:165–169
- 3. Sachs S, Bernhard G (2011) Influence of humic acids on the actinide migration in the environment: suitable humic acid model substances and their application in studies with uranium—a review. J Radioanal Nucl Chem 290:17–29
- Sundararajan M, Rajaraman G, Ghosh SK (2011) Speciation of uranyl ions in fulvic acid and humic acid: a DFT exploration. Phys Chem Chem Phys 13:18038–18046
- Nash KL, Jensen MP (2001) Analytical-scale separations of the lanthanides: a review of techniques and fundamentals. Sep Sci Technol 36:1257–1282
- Jaison PG, Raut NM, Aggarwal SK (2006) Direct determination of lanthanides in simulated irradiated thoria fuels using reversedphase high-performance liquid chromatography. J Chromatogr A 1122:47–53
- Datta A, Sivaraman N, Viswanathan KS, Ghosh S, Srinivasan TG, Vasudeva Rao PR (2013) Correlation of retention of lanthanide and actinide complexes with stability constants and their speciation. Radiochim Acta 101:81–92
- Keith-Roach MJ (2010) A review of recent trends in electrospray ionisation–mass spectrometry for the analysis of metal–organic ligand complexes. Anal Chim Acta 678:140–148
- Yu X, Xu X, Chen Z (2008) ESI-MS and theoretical study on the coordination structures and reaction modes of the diperoxovanadate complexes containing histidine-like ligands. Int J Mass Spectrom 269:138–144
- Kumar P, Jaison PG, Sundararajan M, Telmore VM, Ghosh SK, Aggarwal SK (2013) Speciation of platinum-benzoylthiourea in the gas phase using electrospray ionization mass spectrometry

and density functional theory. Rapid Commun Mass Spectrom 27:947-954

- 11. Jaison PG, Kumar P, Telmore VM, Aggarwal SK (2013) Electrospray ionization mass spectrometric studies on uranyl complex with a-hydroxyisobutyric acid in water–methanol medium. Rapid Commun Mass Spectrom 27:1105–1118
- Moll H, Geipel G, Reich T, Bernhard G, Fanghanel T, Grenthe I (2003) Uranyl(VI) complexes with alpha-substituted carboxylic acids in aqueous solution. Radiochim Acta 91:11–20
- Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38:3098–3100
- Perdew JP (1986) Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys Rev B 33:8822–8824
- Schäfer A, Huber C, Ahlrichs R (1994) Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. J Chem Phys 100:5829–5835
- 16. Weigend F, Ahlrichs R (2005) Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. Phys Chem Chem Phys 7:3297–3305
- 17. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98:5648–5652
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 37:785–789
- Verma PK, Pathak PN, Kumari N, Sadhu B, Sundararajan M, Aswal VK, Mohapatra PK (2014) Effect of successive alkylation of N,N-dialkyl amides on the complexation behavior of uranium and thorium: solvent extraction, small angle neutron scattering, and computational studies. J Phys Chem B 118:14388–14396
- 20. Verma PK, Kumari N, Pathak PN, Sadhu B, Sundararajan M, Aswal VK, Mohapatra PK (2014) Investigations on preferential Pu(IV) extraction over U(VI) by N,N-dihexyloctanamide versus tri-n-butyl phosphate: evidence through small angle neutron scattering and DFT studies. J Phys Chem A 118:3996–4004
- 21. Ahlrichs R, Bar M, Baron H-P, Bauernschmitt R, Bocker S, Ehrig M, Eichkorn K, Elliot S, Furche F, Haase F, Haser M, Horn H, Huber C, Huniar U, Kattannek M, Kolmel C, Koolwitz M, May K, Ochsenfeld C, Ohm H, Schafer A, Schneider U, Treutler O, von Arnim M, Weigend F, Weis P, Weiss H TURBOMOLE V6.3.1 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBO-MOLE GmbH, since 2007. http://www.turbomole.com
- Van Stipdonk MJ, Chien W, Bulleigh K, Wu Q, Groenewold GS (2006) Gas-phase uranyl-nitrile complex ions. J Phys Chem A 110:959–970
- 23. Austin JP, Sundararajan M, Vincent MA, Hillier IH (2009) The geometric structures, vibrational frequencies and redox properties of the actinyl coordination complexes ([AnO<sub>2</sub>(L)<sub>n</sub>]<sub>m</sub>; An=U, Pu, Np; L=H<sub>2</sub>O, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, CH<sub>3</sub>CO<sup>2-</sup>, OH<sup>-</sup>) in aqueous solution, studied by density functional theory. Dalton Trans 30:5902–5909
- 24. Sundararajan M, Campbell AJ, Hillier IH (2008) Catalytic cycles for the reduction of [UO<sub>2</sub>]<sup>2+</sup> by cytochrome c7 proteins proposed from DFT calculations. J Phys Chem 112(19):4451–4457