
Unusual Ion UO_4^- Formed Upon Collision Induced Dissociation of $[\text{UO}_2(\text{NO}_3)_3]^-$, $[\text{UO}_2(\text{ClO}_4)_3]^-$, $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$ Ions

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The following ions $[\text{UO}_2(\text{NO}_3)_3]^-$, $[\text{UO}_2(\text{ClO}_4)_3]^-$, $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$ were generated from respective salts ($\text{UO}_2(\text{NO}_3)_2$, $\text{UO}_2(\text{ClO}_4)_3$, $\text{UO}_2(\text{CH}_3\text{COO})_2$) by laser desorption/ionization (LDI). Collision induced dissociation of the ions has led, among others, to the formation of UO_4^- ion (m/z 302). The undertaken quantum mechanical calculations showed this ion is most likely to possess square planar geometry as suggested by MP2 results or strongly deformed geometry in between tetrahedral and square planar as indicated by DFT results. Interestingly, geometrical parameters and analysis of electron density suggest it is an U^{VI} compound, in which oxygen atoms bear unpaired electron and negative charge. (J Am Soc Mass Spectrom 2010, 21, 1789–1794) © 2010 American Society for Mass Spectrometry

Uranium can occur at the oxidation states of II, III, IV, V, and VI [1], of which IV and VI are the most common. For example, in nature, the most abundant uranium compound is U_3O_8 , which can be considered as consisting of one molecule of UO_2 (U^{IV} oxide) and two molecules of UO_3 (U^{VI} oxide). In the laboratory, the most common uranium compounds are the salts of uranyl (UO_2^{2+} - U^{VI} -containing cation), e.g., $\text{UO}_2(\text{NO}_3)_2$, $\text{UO}_2(\text{CH}_3\text{COO})_2$. Uranium compounds with this element at other oxidation states (other than IV and VI) are also known, however, they are less stable, e.g., the U^{V} species in solutions easily undergo disproportionation reaction to U(IV) and U(VI) [2]. In nature, there are also uranyl peroxides $\text{UO}_2(\text{O}_2)$, but the respective minerals $\text{UO}_2(\text{O}_2)(\text{H}_2\text{O})_2$ and $\text{UO}_2(\text{O}_2)(\text{H}_2\text{O})_4$ do not exist in high abundances [3]. A number of more developed uranyl peroxides were obtained in labs [4–7].

Mass spectrometric studies of uranyl salts (mainly $\text{UO}_2(\text{NO}_3)_2$) have been reported, first by using FAB (fast atom bombardment) as ionization method [8], and then by electrospray ionization [9–15]. Most of the studies were performed in the positive ion mode; only Pasilis et al. have performed the ESI analysis in both positive and negative ion modes [10]. In this very excellent paper, the authors have systematically investigated the gas-phase uranyl-containing ions and they have examined ligand association/exchange and H/D exchange reactions of the species, using FT-ICR mass spectrometry to obtain accurate mass measurements.

In this communication, the collision induced dissociation (CID) of the ions $[\text{UO}_2(\text{NO}_3)_3]^-$, $[\text{UO}_2(\text{ClO}_4)_3]^-$, $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$ is discussed. The ions were generated from respective salts ($\text{UO}_2(\text{NO}_3)_2$, $\text{UO}_2(\text{ClO}_4)_3$, $\text{UO}_2(\text{CH}_3\text{COO})_2$) by laser desorption/ionization (LDI). As described further, the unusual formation of ion UO_4^- was detected upon decomposition of the ions subjected to CID.

Experimental

The LDI mass spectra and LDI MS/MS spectra were obtained on a Waters/Micromass (Manchester, UK) Q-TOF Premier mass spectrometer (software MassLynx ver. 4.1; Manchester, UK) fitted with a 200 Hz repetition rate Nd/YAG laser ($\lambda = 355$ nm, power density 10^7 W/cm²). For MS/MS experiments, argon was used as a collision gas at the flow-rate 0.5 mL/min in the collision cell. Collision energy (CE – the most important parameter for MS/MS experiments) is indicated in each MS/MS spectrum presented further.

To prepare the target spots, 1 μL of methanol solution containing uranyl salts was used (the concentration was of about 0.1 mol/dm [3]). After a few min at room temperature, the spot was dry and LDI mass spectra could be recorded. If the concentration was reduced, the target spots would not be properly covered by the compound analyzed and the abundances of ions would be small.

Uranyl nitrate and uranyl acetate (hydrates) were obtained from BDH, England (the company no longer exists). Uranyl perchlorate was prepared from uranyl nitrate (see Supplemental Information, which can be found in the electronic version of this article).

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Quantum mechanical calculations were performed as described in Supplemental Information.

Results and Discussion

Figure 1 shows the full scan LDI mass spectra of uranyl nitrate in positive and negative modes. The spectrum in the positive mode is dominated by singly charged ion UO_2^+ . In general, charge reduction is a well known process associated with the formation of gas-phase ions. Reduction of UO_2^{2+} to UO_2^+ ($\text{U}^{\text{VI}} \rightarrow \text{U}^{\text{V}}$) is also known from solution chemistry [16, 17] and was also observed upon ESI mass spectrometric studies [18].

The LDI mass spectrum obtained in the negative ion mode seems to be much more interesting. The most abundant ion is $[\text{UO}_2(\text{NO}_3)_3]^-$ at m/z 456. There are also ions in higher mass range, namely more complex cluster ions, (e.g., $[(\text{UO}_2)_2(\text{NO}_3)_3\text{O}]^-$ at m/z 742, $[(\text{UO}_2)_2(\text{NO}_3)_3\text{OH}_2\text{O}]^-$ at m/z 760, $[(\text{UO}_2)_2(\text{NO}_3)_5]^-$ at m/z 850) but they will not be discussed here.

The ion $[\text{UO}_2(\text{NO}_3)_3]^-$ and the ions detected in the lower mass range were subjected to CID MS/MS analysis (Figure 2). Decomposition of ion $[\text{UO}_2(\text{NO}_3)_3]^-$ yielded two fragment ions, namely ion $[\text{UO}_2(\text{NO}_3)_2\text{O}]^-$

at m/z 410 and $[\text{UO}_2(\text{NO}_3)\text{O}]^-$ at m/z 348. The latter ion was also formed from the former ion. This confirms the mass spectrometric fragmentation pathways described by Pasilis et al. [10]. However, the authors were not able to fragment the ion $[\text{UO}_2(\text{NO}_3)\text{O}]^-$ (“The stable $[(\text{UO}_2)(\text{O})(\text{NO}_3)]^-$ ion (m/z 348) cannot be further fragmented under our SORI-CID conditions”). We were able to fragment this ion, the observed decomposition yielded three fragment ions, namely ion $[\text{UO}_2\text{NO}_3]^-$ at m/z 332 (loss of oxygen atom), ion UO_4^- at m/z 302 (loss of NO_2), and ion NO_3^- at m/z 62 (loss of UO_3) as shown in Figure 2. This suggests that the energy deposited in our experiment is higher than in the case of the FT-ICR, or the ability to record fragment ions is better.

The ion UO_4^- seems to be especially interesting. The species composed of one uranium atom and four oxygen atoms are known, namely UO_4^{2-} ion [19–21], and the mentioned in the introduction uranyl peroxide $\text{UO}_2(\text{O}_2)$ (both contain U^{VI}). It is worth adding that complexation of O_2 by UO_2^+ is possible [22, 23].

It has to be stressed that Pasilis et al. have detected $[\text{UO}_4]^-$ ions on the full scan spectrum, but the ions were not discussed [10]. The ion UO_4^- was discussed in respect to the oxidation state of uranium and oxygen by

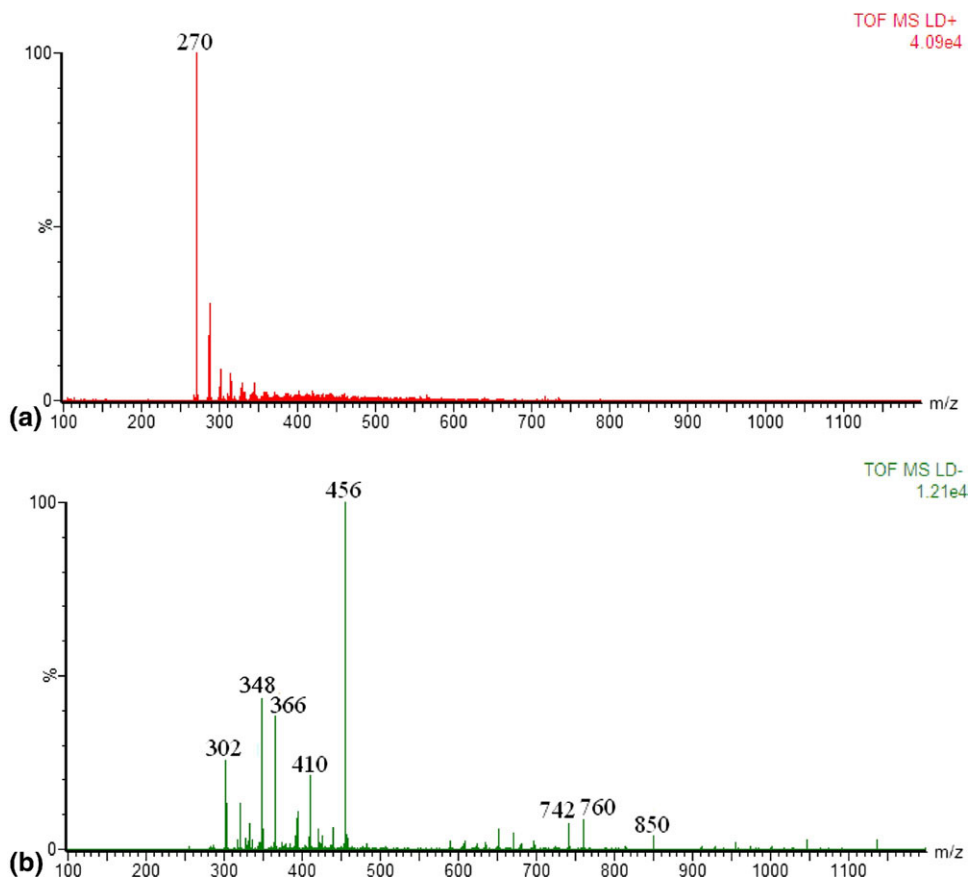


Figure 1. LDI full scan mass spectra of $\text{UO}_2(\text{NO}_3)_2$. (a) Mass spectrum of positive ion, UO_2^+ m/z 270; (b) mass spectrum of negative ion, $[\text{UO}_2(\text{NO}_3)_3]^-$ m/z 456, $[\text{UO}_2(\text{NO}_3)_2\text{O}]^-$ m/z 410, $[\text{UO}_2(\text{NO}_3)\text{O}(\text{H}_2\text{O})]^-$ m/z 366 (it is reasonable to assume that the water arises from trace impurities in the instrument), $[\text{UO}_2(\text{NO}_3)\text{O}]^-$ m/z 348, $[\text{UO}_4]^-$ m/z 302, $[(\text{UO}_2)_2(\text{NO}_3)_3\text{O}]^-$ m/z 742, $[(\text{UO}_2)_2(\text{NO}_3)_3\text{OH}_2\text{O}]^-$ m/z 760, $[(\text{UO}_2)_2(\text{NO}_3)_5]^-$ m/z 850.

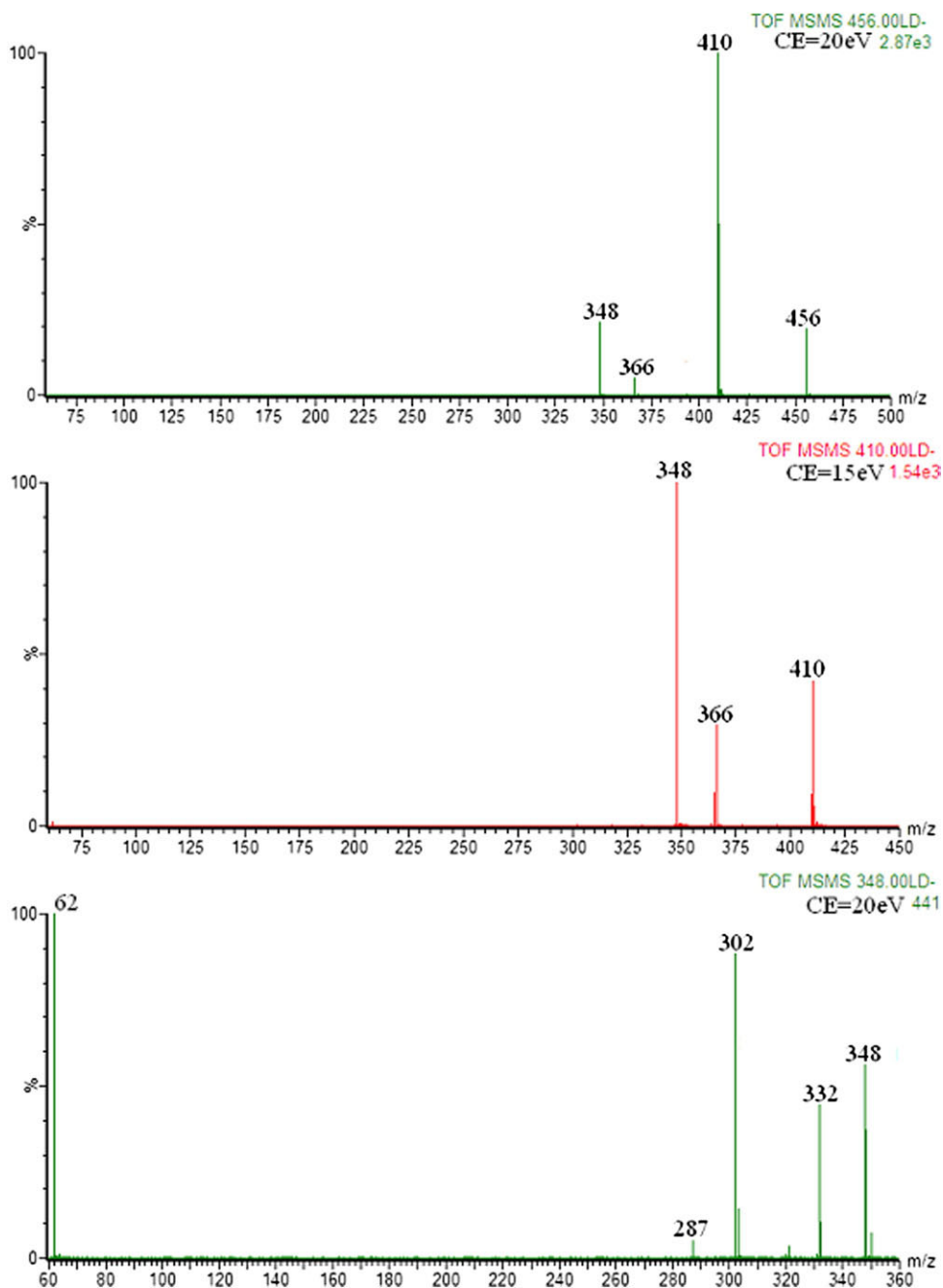


Figure 2. MS/MS spectra obtained for ions generated by LDI of $\text{UO}_2(\text{NO}_3)_2$. $[\text{UO}_2(\text{NO}_3)_3]^-$ m/z 456, $[\text{UO}_2(\text{NO}_3)_2\text{O}]^-$ m/z 410, $[\text{UO}_2(\text{NO}_3)\text{O}(\text{H}_2\text{O})]^-$ m/z 366 (it is reasonable to assume that the water arises from trace impurities in the instrument), $[\text{UO}_2(\text{NO}_3)\text{O}]^-$ m/z 348, $\text{UO}_2(\text{NO}_3)]^-$ m/z 332, $[\text{UO}_4]^-$ m/z 302, $[\text{UO}_2\text{OH}]^-$ m/z 303.

Marcalo et al., the authors generated the ion from solid UO_3 by laser ablation (laser desorption/ionization) [24]. At first, it would seem that UO_4^- contains U^{VII} , however, because uranium has six valence electrons, the oxidation state higher than VI cannot be expected. The first possibility is that this is an U^{V} -containing peroxide ion (which can be regarded as $[\text{UO}_2^+\text{O}_2^{2-}]^-$), the second possibility is that this is an U^{IV} -containing superoxide ion (which can be regarded as $[\text{UO}_2\text{O}_2^-]^-$), and the third possibility is that this is an U^{VI} -containing tetra-

oxo ion (thus formally three oxygen atoms are at -2 oxidation state and one at -1 oxidation state).

The ion UO_4^- was also subjected to CID experiment. As one can read in the paper by Marcalo et al. "... was inert in collision induced dissociation (CID) experiments ..." [24]. We were able to fragment this ion but the only observed decomposition consisted in the loss of oxygen yielding the fragment ion UO_3^- (U^{V} -containing ion). In the MS/MS spectra obtained (see Supplemental Information), the abundance of ion UO_3^- did not exceed

10% of that of ion UO_4^- . Even if collision energy was increased, the abundance of ion UO_4^- was decreased, but the fragment ions were not observed. It may be that at higher collision energy the ions lose electrons and form neutral species that cannot be detected, but this neutralization process will not be discussed here. Loss of oxygen atom is not structurally informative. It only suggests exclusion of the superoxide structure. In our opinion, for such structure loss of O_2 or formation of O_2^{2-} ion, could be expected [24].

The initial possible structures of UO_4^- presented in Figure 3 were subjected to quantum mechanical calcu-

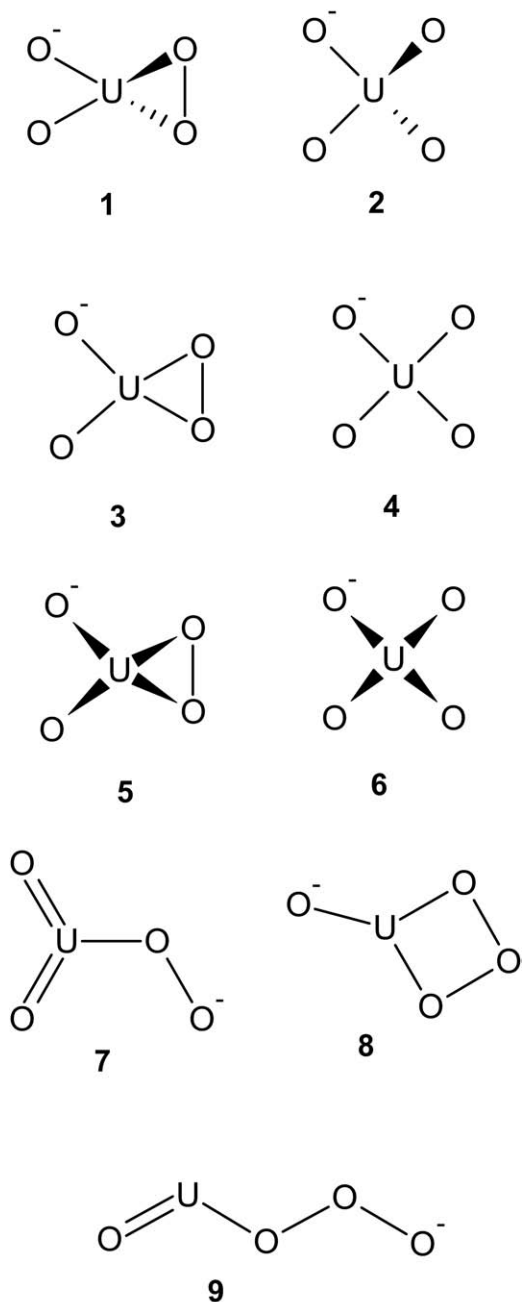


Figure 3. Initial structures of UO_4^- subjected to quantum mechanical optimization.

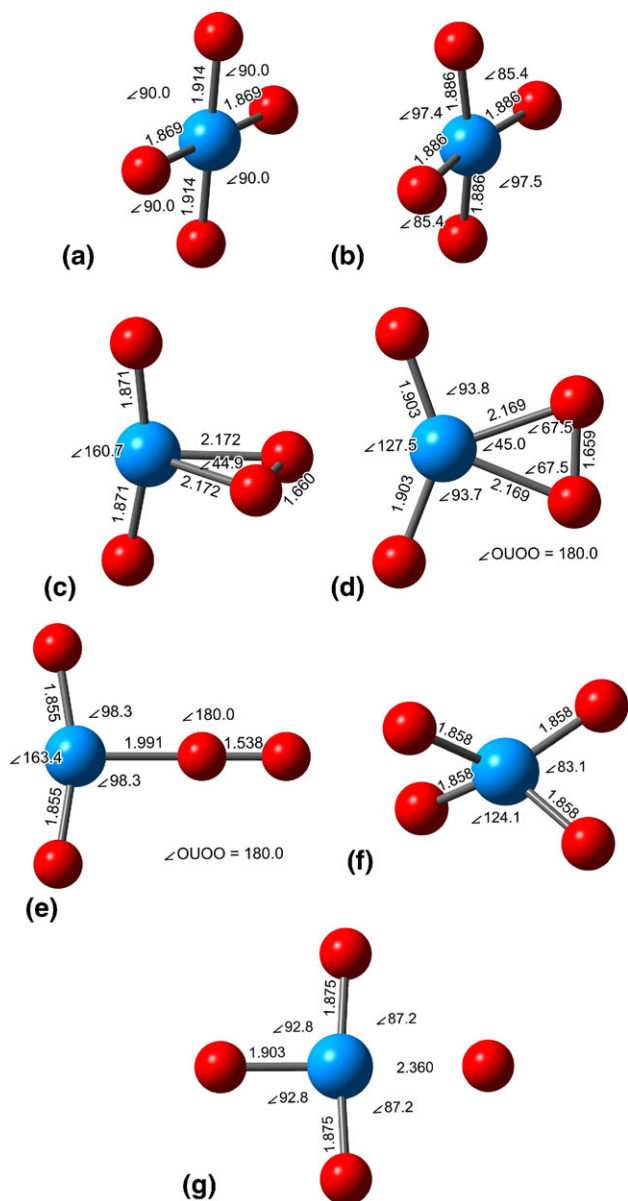


Figure 4. Unique structures of UO_4^- obtained after geometry optimization.

lations. Full geometry optimization performed at DFT level resulted in only six structures corresponding to potential energy minima shown in Figure 4. The energetically most favorable structures corresponded to doublet spin states, while quadruplet and sextuplet states were of about 20 and 40 kcal mol^{-1} higher in energy. Table 1 presents the calculated relative energies for the potential UO_4^- structures. Depending on the level of theory the lowest energy structure corresponds to the planar one favored at MP2 level, or strongly deformed tetrahedral geometry favored at DFT level (Structures A and B in Figure 4). The size of basis set seems to have only minor effects on the results as our deformed tetrahedral geometry B closely resembles the one suggested by Michelinini et al. [25] As the actual structure of UO_4^- anion is still unclear it is usually safer

to accept structures suggested by purely ab initio methods taking into account dynamic electron correlation like MP2 rather than the results from DFT calculations where various parameters were adjusted based mainly on the results for simple molecules of second period elements.

The analysis of electron densities for the Structures A and B (Figure 4) shows that Mulliken atomic spin densities calculated at MP2 level focused on oxygen atoms are essentially the same of about 0.29 elementary charge (e). (have the same three most significant digits although are not identical). The atomic charges ranged from $-0.45 e$ to $-0.51 e$ for oxygen atoms while they were ca $0.92 e$ for uranium atom. The Wiberg indices calculated for the structure A of UO_4^- are 1.07 for two UO atoms pairs and 1.20 for the other two UO. Interestingly, between two pairs of oxygen atoms Wiberg indices are 0.22 and 0.14, which may suggest some bonding between them. However, these oxygen atoms are essentially Trans to one another. The distances between U and O are 1.869 Å for one pair of bonds and 1.914 Å for the other and the OUO angles are almost equal to 90° . These results suggest the presence of uranium (VI) compound in which two UO bonds have double-bond character while the remaining two have single bond character (formally three oxygen atoms are at -2 oxidation state and one at -1 oxidation state, Figure 5). During energy optimization, we also found potential energy local minimum corresponding to a planar structure in which one of the UO bonds is significantly elongated to 2.360 Å (Figure 4, Structure G). Such structure had relative energy of ca 26 kcal mol^{-1} and spin density focused on the distant oxygen atom was 1.0 e . The presence of such structure among potential energy minima seems to explain the observed decomposition of UO_4^- consisting on oxygen atom loss.

It must be pointed out that the ions $[\text{UO}_4]^-$ were also obtained by subsequent CID of the ions $[\text{UO}_2(\text{ClO}_4)_3]^-$ and $[\text{UO}_2(\text{CH}_3\text{COO})_3]^-$. The mass spectra and their interpretation, obtained for uranyl perchlorate and uranyl acetate, are shown in Supplemental Information.

Table 1. The calculated relative energies (in kcal mol^{-1}) obtained for UO_4^-

Structure	E_{MP2}	E_{PBE}	E_{B3LYP}
A	0.0	4.8	5.8
B	7.5	0.0	0.0
C	68.2	42.6	29.4
D	76.1	48.2	35.4
E	115.8	73.7	67.2
F	24.0	3.3	1.2
G	26.0	—	—

MP2 stand for energy calculated at Møller-Plesset second order perturbation theory, PBE for energy calculated at Perdew-Burke-Ernzerhof functional, B3LYP for Becke three parameter method with Lee-Yang-Parr exchange correlation functional.

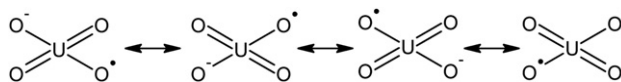


Figure 5. Proposed structure of UO_4^- based on geometry and electronic structure calculated at MP2 level.

Conclusion

UO_4^- ion was previously formed in the gas-phase by electrospray ionization from uranyl nitrate [10] and by laser desorption ionization from UO_3 [24]. In this work, UO_4^- ion was formed by laser desorption/ionization (and subsequent collision induced dissociation) from uranyl nitrate and others uranyl salts. Thus, the conclusion can drawn that formation of this ion is a feature of gas-phase uranium compounds, independent of the ionization method and independent of uranium compounds used. Inspection of the geometry and electronic structure of UO_4^- calculated quantum mechanically suggests it is a mixture of various resonance structures in which oxygen atoms bear formal negative charge and unpaired electron as presented in Figure 5.

Appendix A Supplementary Material

Supplementary material associated with this article may be found in the online version at doi:10.1016/j.jasms.2010.06.018.

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