A comparative theoretical study of bonding in UO$_{2}^{++}$, UO$_{2}^{+}$, UO$_{2}$, UO$_{2}^{-}$, OUCO, O$_{2}$U(CO)$_{2}$, and UO$_{2}$CO$_{3}$

D. Majumdar $^{a}$, K. Balasubramanian $^{a,b,c,*}$, H. Nitsche $^{c,d}$

$a$ Department of Applied Science, Hertz Hall, Bldg 661, Davis College of Engineering, University of California at Davis, P.O. Box 808, L-794, Livermore, CA 94550, USA

$b$ Chemistry and Material Science Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550, USA

$c$ Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

$d$ Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720, USA

Received 8 May 2002; in final form 29 May 2002

Abstract

Extensive ab initio calculations have been carried out to study the structure and bonding characteristics of UO$_{2}^{++}$, UO$_{2}^{+}$, UO$_{2}$, UO$_{2}^{-}$, OUCO, O$_{2}$U(CO)$_{2}$, and UO$_{2}$CO$_{3}$ using various methods including complete active space multiconfiguration self consistent filed (CASMCSCF) and multireference singles plus doubles configuration (MRSDCI) techniques. The calculated vibrational frequencies of these species are compared with the matrix spectra of Andrews and coworkers. The nature of bonding in these species is discussed. © 2002 Published by Elsevier Science B.V.

1. Introduction

Investigations of the structures and coordination chemistry of actinide complexes are of fundamental importance as these are central to the understanding the mechanisms of aqueous migration of actinides under environmental conditions. The vast majority of actinide wastes is produced in commercial nuclear reactors from uranium-based fuels [1], and is expected to be stored in deep geologic repositories. The sorption of the actinides on mineral and bacterial interfaces plays a major role in actinide transport.

Carbonates are common anions found in significant concentrations in natural ground water and they are exceptionally strong complexation agents for actinide ions [1–4]. They play an important role in the process of radioactive transport [5]. The stability of actinide carbonate complexes is reflected in the formation of naturally occurring carbonate minerals such as rutherfordine [UO$_{2}$ (CO$_{3}$)] [6], liebigite [Ca$_{3}$[UO$_{2}$ (CO$_{3}$)$_{3}$] · 10–11H$_{2}$O], and andersonite [Na$_{2}$Ca[UO$_{2}$ (CO$_{3}$)$_{3}$] · 6H$_{2}$O] [8].

The uranyl carbonate system is experimentally by far the most extensively studied among the carbonate systems [9–13]. The tris-carbonato uranyl complex [UO$_{2}$ (CO$_{3}$)$_{3}^{-}$] is strongly stabilized in
solutions of high ionic strength and it is thought to be responsible for the very high solubility of An₂CO₃ (An = U, Np, Pu, Am) in carbonate solutions and thus may be important in the aquatic transport of actinyl ions via carbonate complexation. The study of the complexation of actinide ions with carbonates can provide significant insight into their properties in solution as well as in isolated (gas-phase) conditions.

The molecular structure of UO₂(CO₃)⁴⁻ was established through single crystal X-ray diffraction [8]. Allen et al. [12] studied ¹³C and ¹⁷O NMR spectra of UO₂(CO₃)⁴⁻ and (UO₂)₃(CO₃)₆⁻ in aqueous solution as a function of pH, ionic strength, carbonate concentration, uranium concentration, and temperature. Their extended X-ray absorption fine structure (EXAFS) spectroscopic studies on both solid [C(NH₂)₆][UO₂(CO₃)₆] and aqueous (UO₂)₃(CO₃)₆⁻ suggest that the same uranium species are present in the solid and the solution phase. They have further predicted the geometrical parameters of uranyl carbonate clusters from their experimental studies [13].

Andrews and his coworkers [14–16], have studied the matrix-isolated spectra of several uranium containing species like UO, UO₂, UO₃, UO₂⁺, UO₂⁻, OUCO, OUCO⁺, OUCO⁻, and O₂U (CO)₃ by reacting laser-ablated U with O₂ and CO₂. They have obtained the IR spectra and vibrational frequencies and have also carried out density functional (DFT) level computations. The geometries of UO₂⁺ and UO₂⁻ were studied further at the CASMCSCF level. The full active space of UO₂CO₃ consists of 44 orbitals (17 a₁, 12 b₂, 10 b₁, and 5 a₂). If all of the orbitals and 48 electrons were considered, the total number of configuration spin functions (CSFs) becomes excessively large. Thus a restricted active space approach was used for the CASMCSCF calculations. The final active space consisted of four a₁, two b₂, three b₁, and one a₂

2. Methods of computation

The calculations presented here were carried out using the DFT [19], second order Möller–Plesset perturbation (MP2) [20], coupled cluster doubles (CCD), complete active space multiconfiguration self consistent field (CASMCSF) and multireference singles and doubles configuration interaction (MRSDCI) approaches. The electronic structure calculations of O₂U(CO)₂ and UO₂CO₃ were carried out in the C₃v symmetry and the structure calculations of OUCO were carried out in C₃ symmetry. UO₂⁺, UO₂⁺, and UO₂⁻ are linear molecules and the structure calculations of these molecules were carried out in D₂h symmetry.

The DFT approach utilized Becke's three-parameter functional [21] with Vosko et al.'s [22] local correlation part and Lee et al.'s [23] nonlocal part (abbreviated as B3LYP). The geometry searches were carried out at the DFT and MP2 levels using the Berny algorithm with redundant internal coordinates [24]. All the calculations were carried out using relativistic effective core potentials (RECPs) that retained the outer 6s²6p⁵f¹6d¹7s² shells of uranium [25]. The corresponding optimized Gaussian (5s5p4d4f) basis set [25] contracted to (3s3p3d2f) was used. An extended basis set with an augmentation of a set of g polarization functions with α_g = 0.516 labeled U (5s5p4d4f1g/ 3s3p4d2f1g) was further used to gauge the accuracy of the basis set. For the carbons and oxygens, RECPs were employed retaining the outer 2s, and 2p shells in the valence space [26]. The corresponding basis sets for the elements were taken from Pacios and Christiansen [26], and were augmented with a six component 3d Gaussian function (α_d = 0.75 for carbon, and 0.85 for oxygen) adopted from Dunning and Hay [27].

The geometries of UO₂CO₃, UO₂⁺, UO₂⁺, and UO₂⁻ were studied further at the CASMCSCF level. The full active space of UO₂CO₃ consists of 44 orbitals (17 a₁, 12 b₂, 10 b₁, and 5 a₂). If all of the orbitals and 48 electrons were considered, the total number of configuration spin functions (CSFs) becomes excessively large. Thus a restricted active space approach was used for the CASMCSCF calculations. The final active space consisted of four a₁, two b₂, three b₁, and one a₂.
orbitals. Eight a₁, four b₂, four b₁ and one a₂ orbitals were kept in the core. No excitations were allowed from the core orbitals, but they were allowed to relax. Fourteen electrons were distributed among the active space orbitals of different symmetries.

The CASMCSCF calculations were carried out using restricted active space (in C₂ᵥ symmetry) for UO₂, UO₂⁺, UO₂⁺⁺, and UO₂. All electrons were included in the active space of our CAS-MCSCF computations of these molecules. All of the electrons were distributed among seven a₁, four b₂, four b₁, and one a₂ orbitals. These orbital combinations were chosen through several trial calculations on UO₂⁺⁺, using different combinations of a₁, b₂, b₁, and a₂ orbitals. The electronic states of these molecules are then reassigned according to D₁h symmetry. The maximum number of CSFs in the CASMCSCF calculation was 37,236. The MRSDCI calculations were used to calculate the dissociation energy of UO₂⁺⁺ using the CASMCSCF configurations. The maximum number of CSFs used for this purpose was 5.5 million. The MP2, DFT and CCD [28] calculations were carried out using GAUSSIAN 98 package of codes [29]. The CASMCSCF and MRSDCI calculations were made using GAMESS [30] and a modified version of ALCHEMY II package to include RECPs [31,32].

3. Results and discussion

3.1. The gas-phase structures of UO₂⁺⁺, UO₂, UO₂⁺, UO₂⁻, UOCO, O₂U(CO)₂, and UO₂CO₃

Tables 1 and 2 contain the geometries of UO₂⁺⁺, UO₂, UO₂⁺, UO₂⁻ (Table 1), UOCO, and O₂U(CO)₂ (Table 2) in their lowest electronic states using CASMCSCF, CCD, MP2, and DFT/B3LYP level of theories. The results obtained by Andrews and coworkers [14,15] at the DFT/B3LYP level are also included for comparison. The results show that the structures in their lowest electronic states are in overall agreement with ours. Both the geometrical parameters and the vibrational frequencies agree quite well. The tables also contain the observed vibrational frequencies of these molecules. Our computed results agree with the experimentally observed frequencies, and thereby support the validity of the calculated structures. Only the MP2 calculations on UOCO and O₂U(CO)₂ show some differences with respect to the previous DFT/B3LYP bond angles (Table 2). In the case of UOCO, although the predicted geometries are similar in both the methods, the predicted ground state in the MP2 method (5A¹) is different from that of the DFT/B3LYP (5A²). Our MP2 results on O₂U(CO)₂ vary from those of the DFT/B3LYP calculations, especially with respect to the C–U–C bond angle. The DFT calculations of Andrews et al. [15] predict an acute angle (65.1°), whereas our MP2 calculation predicts an obtuse C–U–C angle (142.7°). But the MP2 calculations in this geometry predict more accurate vibrational frequencies (Table 2) and compare better with the experiment.

The first and second ionization potentials (IPs) of UO₂ are known experimentally to be 5.4 (0.1) and 15.4 (2.6) eV, respectively, [33,34]. Andrews and coworkers have calculated these parameters to be 6.27 and 15.31 eV at the DFT/B3LYP level. They have also calculated the electron affinity (EA) of UO₂ (108 kJ/mol). We have computed all these parameters at the MP2 and CCD levels and they are presented in the footnote of Table 1. The second IP of UO₂ appears to be overestimated at both the MP2 and CCD levels. The rest of the calculated parameters are quite good.

Table 3 contains the optimized geometric parameters of UO₂CO₃ obtained at the DFT/B3LYP, MP2, CCD, and CASMCSCF level of theories. The DFT/B3LYP and MP2 results are presented under two different basis sets viz., (5s5p4d4f/3s3p3d2f) and (5s5p4d4f1g/3s3p3d3f1g). The results presented in Table 3 show that the uranium–oxygen distance for the uranyl part (U–O₁, Fig. 1) does not change much with the basis set size. Moreover, our RECP basis sets results agree with those of Andrews and coworkers [14,15] in the lowest energy electronic state at different levels of theory. Thus the reliability of our basis sets for the calculations of the UO₂CO₃ structure should be quite good. The uranium–oxygen distance for the carbonate part (U–O₃) is slightly smaller in the larger basis, but the distance is within the tolerance limit. The calculated
minimum energy structures at the DFT/B3LYP, MP2 and CCD levels are presented in Fig. 1. The uranyl part is almost linear in the monocarbonate structure and it is oriented vertically above and below the plane containing the uranium atom and the carbonate group. In the CASMCSCF calculation (Table 1), the U–O' bond length of the minimum energy geometry (1A1) is slightly shorter (1.697 Å) than the corresponding MP2/DFT results, but the U–C distance is slightly longer (2.656 Å). The calculated U–O' distance in the CASMCSCF calculation is also shorter than that in the DFT/MP2 calculations. The most important feature in the CASMCSCF calculation is that the O–U–O bond angle is much wider (173.8°) than those calculated in DFT and MP2 levels. This indicates that this method accounts for the linearity of the O–U–O bond more satisfactorily than the other methods.

### 3.2. Comparison of the vibrational frequencies of UO$_2$CO$_3$ and other selected molecules

There is no infrared (IR) spectral study for UO$_2$CO$_3$ in solution as such, although this species has been observed in equilibrium with other species. But the IR and Raman studies on some related compounds in the solid state and aqueous solution are available [12]. Our predicted uranyl frequencies could be compared with such data. The IR spectra were studied for the solid hydrated

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Method</th>
<th>Bond length (Å)</th>
<th>Bond angle (Deg.)</th>
<th>Frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$$^{2+}$</td>
<td>1Σ$_g^+$</td>
<td>CAS</td>
<td>1.671</td>
<td>180.0</td>
<td>1100 ($\sigma_g$), 194 ($\pi_u$), 1179 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCD</td>
<td>1.678</td>
<td>180.0</td>
<td>923 ($\sigma_g$), 126 ($\pi_u$), 1024 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MP2</td>
<td>1.728</td>
<td>180.0</td>
<td>1027 ($\sigma_g$), 144 ($\pi_u$), 1126 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>1.687</td>
<td>180.0</td>
<td>1041 ($\sigma_g$), 161 ($\pi_u$), 1140 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[14]</td>
<td>1.705</td>
<td>180.0</td>
<td>874, 161, 962</td>
</tr>
<tr>
<td>UO$_2^+$</td>
<td>2Φ$_u$</td>
<td>CAS</td>
<td>1.700</td>
<td>180.0</td>
<td>971 ($\sigma_g$), 146 ($\pi_u$), 1031 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCD</td>
<td>1.744</td>
<td>180.0</td>
<td>901 ($\sigma_g$), 101 ($\pi_u$), 955 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MP2</td>
<td>1.780</td>
<td>180.0</td>
<td>916 ($\sigma_g$), 191 ($\pi_u$), 1001 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>1.746</td>
<td>180.0</td>
<td>936 ($\sigma_g$), 148 ($\pi_u$), 1010 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[14]</td>
<td>1.764</td>
<td>180.0</td>
<td>874, 161, 962</td>
</tr>
<tr>
<td>UO$_2^-$</td>
<td>3Φ$_u$</td>
<td>CAS</td>
<td>1.832</td>
<td>180.0</td>
<td>927 ($\sigma_g$), 168 ($\pi_u$), 958 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCD</td>
<td>1.766</td>
<td>180.0</td>
<td>896 ($\sigma_g$), 149 ($\pi_u$), 913 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MP2</td>
<td>1.795</td>
<td>180.0</td>
<td>880 ($\sigma_g$), 222 ($\pi_u$), 933 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>1.764</td>
<td>180.0</td>
<td>874 ($\sigma_g$), 138 ($\pi_u$), 931 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[14]</td>
<td>1.800</td>
<td>180.0</td>
<td>874, 161, 962</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expt.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO$_2$$^{2+}$</td>
<td>2Φ$_u$</td>
<td>CAS</td>
<td>1.765</td>
<td>180.0</td>
<td>872 ($\sigma_g$), 160 ($\pi_u$), 895 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCD</td>
<td>1.797</td>
<td>180.0</td>
<td>869 ($\sigma_g$), 150 ($\pi_u$), 856 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MP2</td>
<td>1.825</td>
<td>180.0</td>
<td>832 ($\sigma_g$), 223 ($\pi_u$), 875 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>1.791</td>
<td>180.0</td>
<td>825 ($\sigma_g$), 136 ($\pi_u$), 874 ($\sigma_u$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[14]</td>
<td>1.828</td>
<td>180.0</td>
<td>874, 161, 962</td>
</tr>
</tbody>
</table>

Calculated ionization potentials (IP), and electron affinity of UO$_2$ (at the CCD and MP2 levels) are included in the footnote. Previous results at the DFT/B3LYP level and experimental frequencies are also included for comparison.

*a* [35].

*b* [14].

crystal of the compound \([\text{C(NH}_2\text{)}_2]\)\textsubscript{3}\text{[UO}_2\text{(CO}_3\text{)]_6}\),
and an unresolved shoulder for the O–U–O asymmetric stretch was observed at 915 cm\(^{-1}\) [12].
This was masked by a strong carbonate out-of-plane deformation mode at 892 cm\(^{-1}\).
Using the relationship between Raman active and IR active stretching modes, the IR stretching mode of O–U–O was assigned at 911 cm\(^{-1}\) [12].
In our DFT/B3LYP calculations, the O–U–O stretching frequencies are obtained at 882 and 898 cm\(^{-1}\) in two different uranium basis sets.
In the case of MP2 calculations, the corresponding values are 846 cm\(^{-1}\) (smaller U basis) and 859 cm\(^{-1}\) (larger U basis). The calculated gas-phase results are quite close to the experimental values.

In the case of UO\(_4^{2+}\), UO\(_2^+\), UO\(_3^+\), and UO\(_2^-\), the calculated O–U–O symmetric stretching frequency increases continuously from UO\(_2^-\) (856 cm\(^{-1}\), MP2) to UO\(_2^{2+}\) (1024 cm\(^{-1}\), MP2). This is consistent with the increasing O–U strengths in these uranyl oxide compounds.

The available experimental frequencies also follow the same trend.
(Table 1). This trend is also observed in the asymmetric stretching frequencies of these molecules. In the case of $\text{O}_2\text{U} (\text{CO})_2$, the O–U–O asymmetric stretch has been observed experimentally (889 cm$^{-1}$). The calculated values at the MP2 (918 cm$^{-1}$) and DFT/B3LYP (908 cm$^{-1}$) agree quite well with the experimental data. The results further show that the bonding characteristics of O–U–O in $\text{O}_2\text{U} (\text{CO})_2$ should be quite comparable with uranyl bond of UO$_2$CO$_3$ and UO$_2^+$.

3.3. Nature of bonding in UO$_2$CO$_3$ and other uranyl containing compounds chosen

The UO$_2^{2+}$ ion has the HOMO (highest occupied molecular orbital) configuration of $\sigma_g^2$. The first virtual orbital is $\phi_u$, and it is composed of uranium 5f orbital. The ground state of UO$_2^{2+}$ ($^3\Phi_u$) has the configuration $\sigma_g^2\phi_u^1$. The two other uranyl compounds UO$_2$($^3\Phi_u$) and UO$_2$($^5\Phi_u$) have the configurations $\sigma_g^2\phi_u^1\phi_u^1\phi_u^1$ and $\sigma_g^2\phi_u^1\phi_u^1\phi_u^1\phi_u^1$. Since UO$_2$, UO$_2^{2+}$ and UO$_2^{2+}$ configurations involve $\sigma_g$ (containing contribution from both uranium and oxygen orbitals), it is expected that there would be charge delocalization in these molecules. The calculated gross Mulliken population analyses (MP2 level) show that the charge on U in UO$_2^{2+}$ is 1.966 e. In the case of UO$_2^{2+}$ the net charge on U and O (1.522 e and −0.261 e) suggest that the excess electron is almost 50% delocalized on oxygen. Similar charge distribution pattern was observed in previous DFT/B3LYP calculation. In the case of UO$_2$ (U: 0.739 e, O: −0.370 e) and UO$_2^+$ (U: −0.123 e, O: −0.438 e), the charge distribution pattern suggests that the excess electrons are more localized on oxygen.

The charge distribution pattern of UO$_2^{2+}$ indicates that the U–O bond in this molecule could be very strong. We have calculated the dissociation energy of UO$_2^{2+}$ at the MRSDCI level for the following dissociation process relative to the lowest atoms:

$$\text{UO}_2^{2+}(^1\Sigma_g^+) \rightarrow \text{U}^{2+}(\text{quintet, 5f}^36d^1) + 2\text{O}(^3\text{P})$$

The MRSDCI and the MRSDCI +Q (Davidson-corrected) values for the dissociation energies are 11.81 and 12.76 eV, respectively. The results show that the U–O bonds in UO$_2^{2+}$ are quite strong.

We have computed the dissociation energies of UO$_2^{2+}$, UO$_2^+$, and UO$_2$ at the CCD level. The cal-
culated UO\(^{++}\) dissociation energy at the CCD level is 11.96 eV. This is very close to the MRSDCI result of 11.81 eV. The dissociation energies of UO\(^{+}\) and UO\(^2\) have been calculated for the reactions UO\(^{+}\) \(\rightarrow\) U\(^{+}\) (quartet, 5\(f^87s^2\)) + 2O\(^{(3P)}\) and UO\(^2\) \(\rightarrow\) U (quintet, 5\(f^66d^17s^2\)) + 2O\(^{(3P)}\), respectively. The calculated CCD dissociation energies are 13.83 and 14.11 eV for UO\(^{+}\) and UO\(^2\), respectively. This shows that the U–O bond strengths in these molecules follow the order UO\(^2\) > UO\(^{+}\) > UO\(^{++}\). We have further compared the \(\Delta E\) value of the process U + O\(_2\) \(\rightarrow\) O\(_2\)U (\(-980\) kJ) obtained by Andrews et al. [14] using DFT/ B3LYP, with our CCD result (\(-959\) kJ/mol). The similarity of both the results shows that the U–O bond strength order as obtained in our CCD calculation is quite reasonable.

In the case of O\(_2\)U(CO)\(_2\), the HOMO (7\(b_2\)) and HOMO-1 (5\(b_1\)) orbitals have the following compositions at the MP2 level.

\[\psi(\text{HOMO}) = U[6p_y - 6d_{yz} - 5f_{(5\sigma^2 - 3\pi^2)}] \]
\[= (C_1 - C_2)[2s + 2p_y - 2p_z] \]
\[-(O_1 + O_2)[2s - 2p_z] \]

In both HOMO and HOMO-1 orbitals, the uranium 5f orbitals are involved in the bonding. The HOMO-1 orbital of UO\(_2\)(CO)\(_2\) involves pure uranyl binding, and it shows that it is mostly of \(\pi\) character. The calculated MP2 charges (Mulliken) on U (0.898 e) and O (\(-0.295\) e) connected to U show that the charges are delocalized and thereby support \(\pi\)-type bonding.

The analysis of the bonding characteristics of UO\(_2\)CO\(_3\) could be made through consideration of its molecular orbitals (MO) and the Mulliken populations. For this purpose we consider the active space natural orbitals of UO\(_2\)CO\(_3\) obtained through the CASM/CSCF/MRSDCI calculations. The active space of UO\(_2\)CO\(_3\) (at the CASM/CSCF level) has seven occupied orbitals (two \(a_1\), two \(b_2\), three \(b_1\), and one \(a_2\)) and three unoccupied orbitals (two \(a_1\) and one \(b_1\)). Fig. 2 contains the MO pictures of six occupied active space orbitals of UO\(_2\)CO\(_3\)(\(2a_1\), \(1b_2\), \(2b_2\), \(1b_1\), \(2b_1\), and \(1a_2\)) for its \(^1\text{A}_1\) ground state. The compositions of seven active space occupied molecular orbitals could be represented in the following way (considering the molecule to be ascribed in the \(yz\) plane).

\[\psi(2a_1) = -[U](7s - 6p_z + 6d_{z^2}) \]
\[= [C](2s - 2p_z) + [O_1 - O_2](2p_y) \]
\[+ [O_1 + O_2 - O_3 - O_4 + O_5](2p_z) \]

\[\psi(1b_2) = -[U](6p_y - 6d_{yz} - 5f_{(5\sigma^2 - 3\pi^2)}) \]
\[= [C - O_1 - O_2 + O_3 + O_4 - O_5](2p_y) \]
\[+ [O_1 - O_2](2p_z) \]

Fig. 2. Three-dimensional representation of the \(1b_1\), \(1b_2\), \(2b_1\), \(1a_2\), \(1b_1\), \(2b_1\), \(2b_2\), and \(1a_2\) active space occupied molecular orbitals of UO\(_2\)CO\(_3\) (\(^1\text{A}_1\)) (From CASM/CSCF/MRSDCI calculations). The molecular orientations are in \(yz\) plane. They are then rotated to get better view.
The chargedistribution pattern is similar to those of trons. The MO compositions of the active orbitals due to exchange of electrons with the uranium 2p orbitals and deficient in the 2s orbitals. Thus there would be a strong overlap between the 2p orbitals and deficient in the 2s orbitals. The MO compositions of the active orbitals show the presence of such an overlap in the uranyl bonding of UO$_2$CO$_3$.

4. Conclusions

Carbonate formation is one of the most important processes governing the actinide migration from the repositories. We have theoretically studied the structure of the simplest carbonate compound of uranium [uranyl carbonate (UO$_2$CO$_3$)] together with other small compounds containing uranium–oxygen bonds viz., UO$_2$$^{2+}$, UO$_2$, UO$_2^+$, OUCO and O$_2$U(CO)$_2$ that have been studied by Andrews and coworkers in the matrix. The structures and frequencies of UO$_2$$^{2+}$, UO$_2$, UO$_2^+$, and UO$_2$ were computed at the CASMCSCF, MP2, and DFT/B3LYP levels of theories. The results agree with the previous DFT/B3LYP calculations regarding ground electronic states and geometries. The calculations on OUCO and O$_2$U(CO)$_2$ have been carried out at the MP2 level. Our results are similar to the previous DFT/B3LYP calculations of Andrews et al. [15], but the predicted ground state of OUCO at the MP2 level is different (³A'). The calculated vibrational frequencies at both the levels are consistent with the experimental values.

The gas-phase calculations on UO$_2$CO$_3$ were carried at the DFT/B3LYP, MP2, CASMCSCF, and MRSDCI levels. The calculations show that analogous to higher uranyl carbonate complexes, the gas-phase structure of the uranyl part in UO$_2$CO$_3$ is almost linear, especially at the CASSCF level. Comparison of the vibrational frequencies and the orbital nature of UO$_2$CO$_3$ with other molecules studied here, indicates that the uranyl bonding in this molecule is similar to those of O$_2$U(CO)$_2$ and UO$_2$$^{2+}$ and has considerable π character.

Acknowledgements

The research at UC Davis was supported by DOE office of basic energy sciences, chemical sciences division, and the work at LLNL was performed under the auspices of the US department.
of Energy by the University of California, LLNL under contract number W-7405-Eng-48. The work at LBNL was supported by in part by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division of the US Department of Energy (DOE) under Contract DE-AC03-76SF00098.

References

[31] The major authors of ALCHEMY II are B. Liu, B. Reesfield, M. Yoshinime.