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# Ligand effect on uranium isotope fractionations caused by nuclear volume effects: An *ab initio* relativistic molecular orbital study

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We have calculated the nuclear volume term ( $\ln K_{nv}$ ) of the isotope fractionation coefficient ( $\epsilon$ ) between  $^{235}\text{U}$ – $^{238}\text{U}$  isotope pairs by considering the effect of ligand coordination in a U(IV)–U(VI) reaction system. The reactants were modeled as  $[\text{UO}_2\text{Cl}_3]^-$  and  $[\text{UO}_2\text{Cl}_4]^{2-}$  for U(VI), and  $\text{UCl}_4$  for U(IV). We adopted the Dirac–Coulomb Hartree–Fock method with the Gaussian-type finite nucleus model. The result obtained was  $\ln K_{nv}=0.001\,90$  at 308 K, while the experimentally estimated value of  $\ln K_{nv}$  is 0.002 24. We also discuss how the ligand affects the value of  $\ln K_{nv}$ , especially for the various structures of different compounds, and different ligands within the halogen ion series (F, Cl, and Br). © 2010 American Institute of Physics. [doi:10.1063/1.3463797]

## I. INTRODUCTION

Nuclear volume effects in isotope fractionations have been recognized since 1996, from the uranium enrichment experiment of Nomura *et al.*<sup>1</sup> and the theoretical explanation by Bigeleisen.<sup>2</sup> The importance of nuclear volume effects has increased, especially in geochemistry, environmental chemistry, and cosmochemistry, as a source of mass independent isotope fractionations.<sup>3–8</sup> For example, Fujii *et al.*<sup>3</sup> suggested that some isotope anomalies in meteorites from the early solar system are attributable to nuclear volume effects. Recently, two papers have reported that instruments used for observing isotope ratios, such as a multiple collector inductively coupled plasma mass spectrometer and a thermal ionization mass spectrometer, can cause artificial mass independent isotope fractionation, and this is possibly attributable to nuclear volume effects.<sup>4,5</sup> The number of such reports will increase in the near future, and consideration of nuclear volume effects will become very important in various analyses using isotope ratios.

Even though Bigeleisen<sup>2</sup> introduced a formula for the nuclear volume term ( $\ln K_{nv}$ ) of the fractionation coefficient ( $\epsilon$ ) in 1996, quantum chemical calculations for  $\ln K_{nv}$  using finite nucleus models have only appeared recently. In 2007, Schauble<sup>6</sup> calculated isotope fractionation coefficients by considering both molecular vibrational and nuclear volume effects for Hg and Tl compounds, which are important isotopes in geochemistry. In 2008, we explained experimental  $\epsilon$  values for the U(III)–U(IV) reaction system, calculating  $\ln K_{nv}$  for  $\text{U}^{3+}$  and  $\text{U}^{4+}$  atomic models employing a relativistic Dirac–Coulomb multiconfigurational Hartree–Fock method.<sup>9</sup> In 2008, we also calculated  $\ln K_{nv}$  for the U(IV)–U(VI) reaction system using  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$  molecular models employing the relativistic Dirac–Coulomb Hartree–Fock

(DCHF) method.<sup>10</sup> In our paper, we discussed the validity of our molecular orbital method because molecular orbital calculations usually include more approximations than atomic orbital calculations do. We tested three types of basis sets, and compared the data with the results from atomic numerical calculations in the  $\text{U}^{3+}$ – $\text{U}^{4+}$  system. We also compared the Gaussian-type and Fermi-type finite nucleus models in the  $\text{U}^{3+}$ – $\text{U}^{4+}$  system and showed that the molecular orbital method can provide comparable quality to the atomic orbital method.<sup>10,11</sup>

In experiments on the U(IV)–U(VI) system, the reactions occur in a 5M  $\text{Cl}^-$  ion aqueous solution and hence, water or  $\text{Cl}^-$  ligands coordinate to both  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$  species.<sup>1</sup> Because  $\text{UO}_2^{2+}$  is absorbed on the anionic exchange resin, the total charge of the U(VI) species is negative, and the expected coordination number of the  $\text{Cl}^-$  ions is three or four. The  $\text{U}^{4+}$  species remain in the aqueous solution, and are assumed to form a neutral molecule,  $\text{UCl}_4$ , from the stability constant of  $\text{U}^{4+}$  and the acidity of the solution. Although  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$  are the basic forms of the U(VI) and U(IV) reactants, respectively, and are good models for initial calculations, the ligand coordination may change the value of  $\ln K_{nv}$  to some extent. In addition, Schauble<sup>12</sup> presented a poster at the AGU2006 conference that reproduced the experimental  $\epsilon$  values of the U(IV)–U(VI) system by calculating both the molecular vibrational and nuclear volume terms, using  $[\text{UO}_2\text{Cl}_3(\text{H}_2\text{O})_2]^-$  and  $[\text{U}(\text{H}_2\text{O})_9]^{4+}$  model compounds. Note that Schauble's method and our method are different in the adaptation of the basis sets: Schauble adopted a one-component-type basis set based on the DIRAC04 software package,<sup>13</sup> while we adopted a two-component-type basis set based on the REL4D software package.<sup>14</sup> REL4D can handle general contracted-type basis sets for both large and small components, while DIRAC04 needs to use uncontracted basis sets for small components.

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Thus, our method was generally faster in terms of computational time than Schauble's method was.<sup>15,16</sup>

Based on this background, we performed calculations on  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$  with  $\text{Cl}^-$  ligands using our own method, and estimated the value of  $\ln K_{nv}$  for the U(IV)–U(VI) system. Our aim was to obtain a basic understanding of the effect of the ligand on the nuclear volume term. Therefore, we used simple model compounds with a high symmetry without any water ligands:  $[\text{UO}_2\text{Cl}_3]^-$  or  $[\text{UO}_2\text{Cl}_4]^{2-}$  for U(VI), and  $\text{UCl}_4$  for U(IV). We studied the relationship between the molecular geometry of the compounds and the value of  $\ln K_{nv}$ . We also considered other ligands,  $\text{F}^-$  and  $\text{Br}^-$ , to discuss how the strength of ligand coordination affects the value of  $\ln K_{nv}$ .

## II. COMPUTATIONAL DETAILS

For the U(IV)–U(VI) system with 235 and 238 isotope pairs, the value of  $\ln K_{nv}$  is expressed as

$$\ln K_{nv} = (kT)^{-1} \{ [E(^{238}\text{U(VI)}) - E(^{235}\text{U(VI)})] - [E(^{238}\text{U(IV)}) - E(^{235}\text{U(IV)})] \}, \quad (1)$$

where  $T$  is the absolute temperature,  $k$  is the Boltzmann constant, and  $E$  is the total energy of a compound.<sup>10</sup> Hence, we obtained the total energies of  $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{X}_4^{2-}$ ,  $\text{UX}_4$  ( $\text{X} = \text{Cl}$ ,  $\text{F}$ , and  $\text{Br}$ ), and  $\text{UO}_2\text{Cl}_3^-$  for  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes using the DCHF method. We only focused on the nuclear volume effects in this paper and do not discuss molecular vibrational effects, which is experimentally estimated as  $-0.00114$  for  $^{235}\text{U}$ – $^{238}\text{U}$  pair (see Ref. 10 for more details). The effect of the size of the nucleus was considered using the Gaussian-type finite nucleus model, with the nuclear charge radius set as 5.8266 fm for  $^{235}\text{U}$  and 5.8514 fm for  $^{238}\text{U}$ , as reported in literature.<sup>17</sup> We used the REL4D software package, which is the relativistic part of the UTCHEM software package.<sup>14</sup> The convergence criterion in the self-consistent-field procedures was  $1.0 \times 10^{-6}$  a.u. for the density matrices and  $1.0 \times 10^{-9}$  a.u. for the total energy. We modified Faegri's contracted basis spinors for the uranium and bromine basis sets.<sup>18</sup> For oxygen basis sets, we optimized the contraction coefficients at the four-component multiconfigurational Dirac-Coulomb Hartree-Fock (MCDCHF) level using the exponents of Roos' double-zeta atomic natural orbital (ANO) basis sets.<sup>19</sup> We optimized the contraction coefficients at the four-component MCDCHF level for fluorine and chlorine,<sup>20</sup> using the exponents of the third-order Douglas–

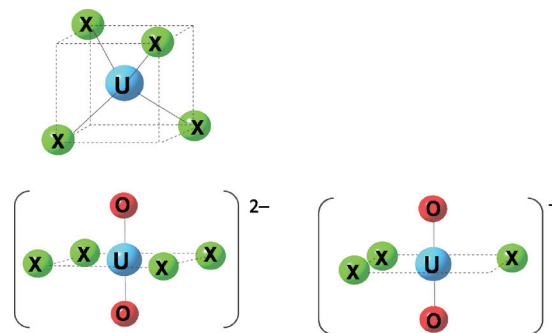


FIG. 1. Molecular structures of  $\text{UX}_4$ ,  $\text{UO}_2\text{X}_4^{2-}$ , and  $\text{UO}_2\text{X}_3^-$ .

Kroll–Hess basis sets.<sup>21</sup> The lowest one or two exponents of these basis sets were added as primitive basis sets to give these basis sets to be valence double-zeta (DZ) or triple-zeta (TZ) quality, respectively. We modified the basis sets to be valence TZ quality for uranium. The basis sets for the other elements were modified to be valence DZ quality. We also added two polarization functions for oxygen, fluorine, and chlorine from Roos' DZ ANO basis set.<sup>19,22</sup> The basis set data are described in supplementary material.<sup>23</sup>

Regarding the molecular geometries of the reactants, we assumed that  $\text{UO}_2^{2+}$  was linear and symmetrical ( $D_{\infty h}$ ),  $\text{UO}_2\text{X}_4^{2-}$  was tetragonal bipyramidal ( $D_{4h}$ ), and  $\text{UX}_4$  was a tetrahedral ( $T_d$ ) structure. We also assumed that  $\text{UO}_2\text{Cl}_3^-$  had a tetragonal bipyramid structure with a vacant site. A water molecule could coordinate to this vacant site but we disregarded any water ligands in this work for simplicity of the calculations. A schematic drawing of the molecular structures is shown in Fig. 1.

The geometry optimization was carried out for  $\text{UO}_2\text{Cl}_3^-$  and  $\text{UO}_2\text{X}_4^{2-}$  as follows. The bond length of  $\text{UX}$  ( $R_{\text{UX}}$ ) was optimized using the fixed bond length of  $\text{UO}$  ( $R_{\text{UO}}$ ) as 1.7 Å, and after we obtained the optimized value of  $R_{\text{UX}}$ ,  $R_{\text{UO}}$  was optimized using the fixed value of  $R_{\text{UX}}$ . We drew local potential curves by changing the  $\text{UO}$  or  $\text{UX}$  distance using a step size of 0.1 Å around the equilibrium distance, and obtained the minimum energies and the stable  $\text{UO}$  and  $\text{UX}$  bond distances by fitting cubic polynomials. We used only  $^{238}\text{U}$  isotopologues for the geometry optimizations. Basis set superposition errors are disregarded in this work. Further details are provided in a previous publication.<sup>10</sup>

TABLE I. Optimized  $\text{UO}$  and  $\text{UCl}$  bond lengths and total energies of the reactants.

	$R_{\text{UO}}$ (Å) <sup>a</sup>	$R_{\text{UCl}}$ (Å) <sup>a</sup>	Total energy (a.u.)	
			$^{235}\text{U}$	$^{238}\text{U}$
$\text{U}^{4+}$	...	...	−28 050.244 826 987	−28 050.134 824 754
$\text{UCl}_4$	...	2.549 380	−29 896.913 208 371	−29 896.803 204 649
$\text{UO}_2^{2+}$	1.660 627	...	−28 201.936 010 112	−28 201.826 006 922
$[\text{UO}_2\text{Cl}_3]^-$	1.709 850	2.702 425	−29 585.881 851 726	−29 585.771 846 155
$[\text{UO}_2\text{Cl}_4]^{2-}$	1.713 710	2.816 056	−30 046.889 311 832	−30 046.779 306 260

<sup>a</sup>We rounded off the bond length (in Å) to the seventh decimal place to provide an accuracy that corresponds with the listed total energies.

TABLE II. Calculated nuclear volume terms ( $\ln K_{nv}$ ) of 235–238 isotope pairs in the U(IV)–U(VI) system at 308 K for each reactant model. The corresponding experimental value is 0.002 24 (see Ref. 24).

	$\text{UO}_2^{2+}$	$[\text{UO}_2\text{Cl}_3]^-$	$[\text{UO}_2\text{Cl}_4]^{2-}$
$\text{U}^{4+}$	0.000 98	0.003 42	0.003 42
$\text{UCl}_4$	−0.000 55	0.001 90	0.001 90

### III. RESULTS AND DISCUSSIONS

#### A. The value of $\ln K_{nv}$ in the U(IV)–U(VI) system with $\text{Cl}^-$ ligands

Table I lists the optimized bond lengths of UO and/or UCl (in angstroms) and the total energy of each compound in hartree (atomic units). The value of  $R_{\text{UO}}$  increases from 1.66 to 1.71 Å when  $\text{Cl}^-$  ligands coordinate to uranium. The coordination of  $\text{Cl}^-$  ligands decreases the bonding strength of UO. The values of  $R_{\text{UCl}}$  in  $\text{UO}_2\text{Cl}_3^-$  and  $\text{UO}_2\text{Cl}_4^{2-}$  are approximately 2.7 and 2.8 Å, which are much longer than the value of 1.7 Å of  $R_{\text{UO}}$ . In  $\text{UCl}_4$ , the value of  $R_{\text{UCl}}$  is shorter, approximately 2.5 Å, than the value of  $R_{\text{UCl}}$  in  $\text{UO}_2\text{Cl}_3^-$  and  $\text{UO}_2\text{Cl}_4^{2-}$  compounds.

Using the energies shown in Table I, we calculated the value of  $\ln K_{nv}$  of the 235–238 isotope pair at 308 K, as shown in Table II. The comparable experimental value is 0.002 24.<sup>24</sup> If we ignore  $\text{Cl}^-$  ligands for both U(IV) and U(VI), i.e., the  $\text{U}^{4+}$ – $\text{UO}_2^{2+}$  system, the value of  $\ln K_{nv}$  (0.000 98) is smaller than the experimental value (0.002 24). If we consider  $\text{Cl}^-$  ligands for both U(IV) and U(VI), then the value of  $\ln K_{nv}$  is 0.001 90 for both  $\text{UCl}_4$ – $\text{UO}_2\text{Cl}_3^-$  and  $\text{UCl}_4$ – $\text{UO}_2\text{Cl}_4^{2-}$ , and this value is consistent with the experimental value (0.002 24). If we only add  $\text{Cl}^-$  ligands to U(IV), then the value of  $\ln K_{nv}$  becomes negative, and if we only add  $\text{Cl}^-$  ligands to U(VI), then the value of  $\ln K_{nv}$  overestimates the experimental value. Hence, the influence of  $\text{Cl}^-$  ligands is significant, and it is essential to consider  $\text{Cl}^-$  ligands for both species in a well-balanced manner.

Table III shows the value of  $\ln K_{nv}$  for several geometries of the U(IV) and U(VI) models. Note that the value of  $\ln K_{nv}$  in this system is proportional to the difference in the isotopic energy ( $\Delta E_{\text{isotope}}$ ) of U(VI) and the isotopic energy of U(IV). Hence, the larger value of  $\Delta E_{\text{isotope}}$  of U(VI) provides the larger value of  $\ln K_{nv}$ , whereas the larger value of  $\Delta E_{\text{isotope}}$  of U(IV) provides the smaller value of  $\ln K_{nv}$ . If we compare  $[\text{UO}_2\text{Cl}_4]^{2-}$  and  $[\text{UO}_2\text{Cl}_3]^-$  with the same values of  $R_{\text{UO}}$  and  $R_{\text{UCl}}$ , then  $[\text{UO}_2\text{Cl}_4]^{2-}$  shows a larger value of  $\ln K_{nv}$  than  $[\text{UO}_2\text{Cl}_3]^-$  does. In other words, the additional

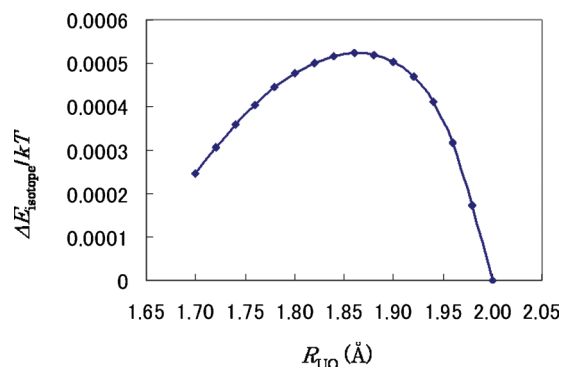


FIG. 2. Correlation between  $R_{\text{UO}}$  and  $\Delta E_{\text{isotope}}/kT$  of the  $\text{UO}_2^{2+}$  molecule ( $T=308$  K).

coordination of  $\text{Cl}^-$  ligands enhances the value of  $\Delta E_{\text{isotope}}$  of U(VI). The longer bond length of  $R_{\text{UO}}$  in U(VI) enhances the value of  $\ln K_{nv}$  and  $\Delta E_{\text{isotope}}$  of U(VI). In contrast, the shorter bond length of  $R_{\text{UCl}}$  in U(VI) enhances the value of  $\ln K_{nv}$  and  $\Delta E_{\text{isotope}}$  in U(VI). When we consider the effect of  $\text{Cl}^-$  ligands on U(IV) species, the longer bond length of  $R_{\text{UCl}}$  provides a larger value of  $\ln K_{nv}$  and a smaller value of  $\Delta E_{\text{isotope}}$  for U(IV). This means the coordination of  $\text{Cl}^-$  in U(IV) enhances the value of  $\Delta E_{\text{isotope}}$  for U(IV).

In summary, we observed a tendency that  $\text{Cl}^-$  coordination increases the value of  $\Delta E_{\text{isotope}}$  for both U(IV) and U(VI) in our results. In contrast, the shorter bond length of  $R_{\text{UO}}$  in U(VI) around the equilibrium distance decreases the value of  $\Delta E_{\text{isotope}}$  for U(VI). For reference, we show the dependence of  $\Delta E_{\text{isotope}}/kT$  on  $R_{\text{UO}}$  in  $\text{UO}_2^{2+}$  in Fig. 2, where  $T$  is 308 K. The maximum value of  $\Delta E_{\text{isotope}}/kT$  was found to occur approximately  $R_{\text{UO}}=1.86$  Å, which is longer than the equilibrium distance of  $R_{\text{UO}}$  (1.66–1.71 Å) obtained in our study.

We used the Dirac–Coulomb Hartree–Fock method and disregarded electron correlation in our study because we consider the electron correlation gives minor change to the value of  $\ln K_{nv}$ . The value of  $\ln K_{nv}$  described in Eq. (1) is proportional to the double subtractions of four similar energies. Most of their energies are canceled in the subtractions and small portion of the energy differences remains, in the order of  $10^{-6}$  or  $10^{-7}$  a.u. Generally, the HF energy in a total energy is much greater than the electron correlation energy and this should be also valid in the value of  $\ln K_{nv}$ . Moreover, contribution of the correlation energy to the value of  $\ln K_{nv}$  comes from only molecular orbital changes of two types of different nuclear potentials. In contrast, the contribution of the HF energy to the value of  $\ln K_{nv}$  comes from both the

TABLE III. Value of  $\ln K_{nv}$  for several modeled compounds.

Geometries of U(VI) models	$\text{U}^{4+}$	$\text{UCl}_4: R_{\text{UCl}}=2.7$ (Å)	$\text{UCl}_4: R_{\text{UCl}}=2.5$ (Å)
$[\text{UO}_2\text{Cl}_4]^{2-}: R_{\text{UO}}=1.8$ (Å), $R_{\text{UCl}}=2.5$ (Å)	0.004 63	0.003 37	0.002 98
$[\text{UO}_2\text{Cl}_4]^{2-}: R_{\text{UO}}=1.8$ (Å), $R_{\text{UCl}}=2.7$ (Å)	0.003 98	0.002 72	0.002 33
$[\text{UO}_2\text{Cl}_4]^{2-}: R_{\text{UO}}=1.7$ (Å), $R_{\text{UCl}}=2.7$ (Å)	0.003 69	0.002 43	0.002 04
$[\text{UO}_2\text{Cl}_3]^-: R_{\text{UO}}=1.8$ (Å), $R_{\text{UCl}}=2.5$ (Å)	0.004 23	0.002 97	0.002 57
$[\text{UO}_2\text{Cl}_3]^-: R_{\text{UO}}=1.8$ (Å), $R_{\text{UCl}}=2.7$ (Å)	0.003 67	0.002 42	0.002 02
$[\text{UO}_2\text{Cl}_3]^-: R_{\text{UO}}=1.7$ (Å), $R_{\text{UCl}}=2.7$ (Å)	0.003 39	0.002 13	0.001 73



TABLE IV. Optimized geometries of the  $UX_4$  and  $UO_2X_4^{2-}$  complexes, where  $X=F$ ,  $Cl$ , and  $Br$ . [We rounded off the bond length (in Å) to seven decimal places to provide an accuracy that corresponds with the listed total energies in Table V.]

Ligand	$UX_4$	$UO_2X_4^{2-}$	
	$R_{UX}$ (Å)	$R_{UX}$ (Å)	$R_{UO}$ (Å)
$X=F$	2.060 953	2.229 704	1.772 999
$X=Cl$	2.549 380	2.816 056	1.713 710
$X=Br$	2.693 600	2.991 288	1.706 907

molecular orbital changes and direct energy changes of one-electron energies of two different nuclear potentials. However, the HF method cannot describe dispersion interactions and molecular geometries can differ in between the HF and electron correlation calculations. In this case, the electron correlation might affect the value of  $\ln K_{nv}$  via molecular geometry change, as our results show the dependence of  $\ln K_{nv}$  on molecular geometry. In the relativistic effective core potential (ECP) calculations with LANL2DZ (Ref. 25) by GAUSSIAN 03,<sup>26</sup> the bond lengths of  $R_{UCl}$  in  $UCl_4$  are 2.585 and 2.574 Å, optimized by the HF and CCSD method, respectively. Similarly in  $[UO_2Cl_4]^{2-}$ , the bond lengths of  $R_{UO}$  are 1.727 and 1.795 Å, and the bond lengths of  $R_{UCl}$  are 2.825 and 2.793 Å, by the HF and CCSD method, respectively. The difference of  $\ln K_{nv}$  value from the molecular geometry change (i.e.,  $\Delta R_{UCl} = -0.01$  Å in  $UCl_4$  and  $\Delta R_{UCl} = -0.03$  Å and  $\Delta R_{UO} = 0.07$  Å in  $[UO_2Cl_4]^{2-}$ ) is roughly estimated as  $3 \times 10^{-4}$  from the data of Table III, while the  $\ln K_{nv}$  value of DCHF is about  $2 \times 10^{-3}$ . Hence, the molecular geometry corrections from electron correlations may provide some change to the value of  $\ln K_{nv}$  (in the order of 10%), but the value of  $\ln K_{nv}$  at the DCHF level is still dominant.

### B. Comparison of the effect of $F^-$ , $Cl^-$ , and $Br^-$ ligands on $\ln K_{nv}$

Table IV shows the optimized bond lengths of  $UX_4$  and  $UO_2X_4^{2-}$ , where  $X=F$ ,  $Cl$ , and  $Br$ . For both  $UX_4$  and  $UO_2X_4^{2-}$ , the trend in  $R_{UX}$  is  $R_{UF} \leq R_{UCl} \leq R_{UBr}$ , which reflects the order of electronegativity of the halogen atoms. In contrast, the stronger coordination of the halogen atoms increases the  $R_{UO}$  bond length:  $R_{UO}(X=F) > R_{UO}(X=Cl) > R_{UO}(X=Br)$ . Table V shows the value of  $\ln K_{nv}$  of  $UX_4-UO_2X_4^{2-}$  in the optimized structures shown in Table IV. The order of electronegativity of the halogen atoms was also preserved in the value of  $\ln K_{nv}$ , as  $\ln K_{nv}$  increased when the ligand coordination became stronger. In  $UX_4$ , the

value of  $\Delta E_{\text{isotope}}$  decreased when the ligand coordination became stronger ( $\Delta E_{\text{isotope}} = 0.110\,003\,39$  a.u. for  $X=F$ ,  $0.110\,003\,72$  a.u. for  $X=Cl$ , and  $0.110\,003\,79$  a.u. for  $X=Br$ ). In contrast, for  $UO_2X_4^{2-}$ , the value of  $\Delta E_{\text{isotope}}$  increased when the ligand coordination became stronger ( $\Delta E_{\text{isotope}} = 0.110\,006\,71$  a.u. for  $X=F$ ,  $0.110\,005\,57$  a.u. for  $X=Cl$ , and  $0.110\,005\,44$  a.u. for  $X=Br$ ). Hence, both effects increased the value of  $\ln K_{nv}$  for stronger halogen ligands. As a comparison, we calculated the value of  $\ln K_{nv}$  using a common geometry for three ligands,  $UX_4$ ,  $R_{UX} = 2.5$  Å and  $UO_2X_4^{2-}$ ,  $R_{UX} = 2.7$  Å and  $R_{UO} = 1.7$  Å. The value of  $\ln K_{nv}$  obtained was  $0.002\,31$  ( $X=F$ ),  $0.002\,04$  ( $X=Cl$ ), and  $0.001\,93$  ( $X=Br$ ), i.e., similar values. From this result, we supposed that the larger value of  $\ln K_{nv}$  for stronger halogen ligands comes from the shorter bond length between the uranium atoms and the ligand.

A relevant ligand exchange experiment on a U(VI) species was reported in 1984,<sup>27</sup> although it did not include any U(IV) species and the ligands used in the experiment were chloride, perchlorate, and various carboxylate ions within the U(VI) species. This experiment observed that a stronger ligand coordination decreased the strength of the UO bond and decreased the asymmetric vibrational frequency of  $UO_2$  ( $\nu_3$ ). It was observed that the value of  $\epsilon$  increased almost linearly as the value of  $\nu_3$  decreased. The effect of the molecular vibration from  $\nu_3$  only explains one-third of the value of  $\epsilon$ , and the other two-thirds of the value of  $\epsilon$  possibly come from nuclear volume effects. In that case, a stronger coordination of the ligand should increase the value of  $\ln K_{nv}$ . The trend in our calculations shows that the stronger halogen ligand enhances the value of  $\ln K_{nv}$ , and matches the experimental evidence.

## IV. CONCLUSIONS

We have obtained the value of  $\ln K_{nv}$  for the U(IV)–U(VI) system for the  $^{235}\text{U}$ – $^{238}\text{U}$  isotope pair from relativistic molecular orbital calculations of  $UO_2^{2+}$  and  $U^{4+}$  with  $Cl^-$  ligands. When we considered  $Cl^-$  ligands for both  $UO_2^{2+}$  and  $U^{4+}$  species, the calculated value of  $\ln K_{nv}$  was  $0.001\,90$ , which is reasonably close to the experimental value of  $\ln K_{nv}$  ( $0.002\,24$ ). We found non-negligible effects in both  $\ln K_{nv}$  and  $\Delta E_{\text{isotope}}$  arising from the coordination of the ligand, the bond length between the ligand and the uranium atom, coordination number of the ligand, and the type of ligand. The observed tendency of the effect of different ligands is consistent with previous experimental data on ligand exchange fractionation of uranyl carboxylates. The change in molecular orbitals due to ligand coordination should be much smaller than the change in molecular orbitals due to oxidation-reduction processes or covalent bond formation.

TABLE V. Total energies and  $\ln K_{nv}$  values of the  $UX_4-UO_2X_4^{2-}$  systems ( $X=F$ ,  $Cl$ , and  $Br$ ).

Ligand	Total energy for $^{235}UX_4$ (a.u.)	Total energy for $^{238}UX_4$ (a.u.)	Total energy for $^{235}UO_2X_4^{2-}$ (a.u.)	Total energy for $^{238}UO_2X_4^{2-}$ (a.u.)	$\ln K_{nv}$ (308 K)
$X=F$	−28 451.246 202 763	−28 451.136 199 368	−28 601.072 974 827	−28 600.962 968 119	0.003 40
$X=Cl$	−29 896.913 208 371	−29 896.803 204 649	−30 046.889 311 832	−30 046.779 306 260	0.001 90
$X=Br$	−38 473.155 398 494	−38 473.045 394 699	−38 623.165 311 688	−38 623.055 306 245	0.001 69

Nevertheless, the change in molecular orbitals due to ligand coordination unexpectedly enhances the large isotope nuclear volume effects. It is important to consider what type of molecular orbital enhances the nuclear volume effect, and we are now working on such an analysis to obtain information on molecular orbital structures. In addition, the isomer shift in the Mössbauer spectroscopy is relevant to the present nuclear volume effects of isotope fractionations. Hence, the theoretical or experimental information of isomer shifts might be also helpful to understand the mechanism of the nuclear volume effects in molecules.

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