

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236913603>

Static Electric Dipole Polarizabilities of Tri- and Tetravalent U, Np, and Pu Ions

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MAY 2013

Impact Factor: 2.69 · DOI: 10.1021/jp403078j · Source: PubMed

CITATION

1

READS

25

3 AUTHORS, INCLUDING:



[Kirk A Peterson](#)

Washington State University

273 PUBLICATIONS 16,137 CITATIONS

SEE PROFILE



[Aurora E Clark](#)

Washington State University

80 PUBLICATIONS 1,292 CITATIONS

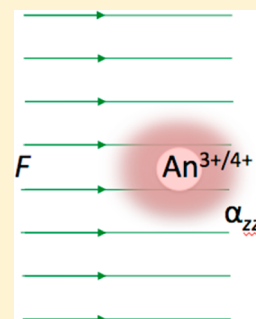
SEE PROFILE

Static Electric Dipole Polarizabilities of Tri- and Tetravalent U, Np, and Pu Ions

Payal Parmar,* Kirk A. Peterson,* and Aurora E. Clark*

Department of Chemistry, Washington State University, Pullman, Washington 99164, United States

ABSTRACT: High-quality static electric dipole polarizabilities have been determined for the ground states of the hard-sphere cations of U, Np, and Pu in the III and IV oxidation states. The polarizabilities have been calculated using the numerical finite field technique in a four-component relativistic framework. Methods including Fock-space coupled cluster (FSCC) and Kramers-restricted configuration interaction (KRCI) have been performed in order to account for electron correlation effects. Comparisons between polarizabilities calculated using Dirac–Hartree–Fock (DHF), FSCC, and KRCI methods have been made using both triple- and quadruple- ζ basis sets for U^{4+} . In addition to the ground state, this study also reports the polarizability data for the first two excited states of $U^{3+/4+}$, $Np^{3+/4+}$, and $Pu^{3+/4+}$ ions at different levels of theory. The values reported in this work are the most accurate to date calculations for the dipole polarizabilities of the hard-sphere tri- and tetravalent actinide ions and may serve as reference values, aiding in the calculation of various electronic and response properties (for example, intermolecular forces, optical properties, etc.) relevant to the nuclear fuel cycle and material science applications.



■ INTRODUCTION

The static electric dipole polarizability is a linear response property that is defined as the second derivative of the total energy with respect to a weak homogeneous external electric field.^{1,2} Polarizability is relevant to any atomic process where the most diffuse part of the electron density plays a crucial role, including the study of intermolecular forces,³ scattering phenomena,⁴ the optical properties of materials and clusters,^{5,6} charge transfer, and transition moment calculations.^{7,8} An updated list of calculated and experimental atomic polarizabilities is maintained at various centers across the globe, including the Center for Theoretical Chemistry and Physics at Massey University.⁹ However, few reports present the polarizabilities of atomic ions, where most data is tabulated in the Handbook of Atomic Data.¹⁰ Those values have been determined from variation-perturbation theory calculations, where relativistic effects are considered a minor perturbation. Of course, this method is not appropriate for heavy elements, and instead, a relativistic Hamiltonian is needed for high-quality results.¹¹ Of specific interest are values for the 5f ions, which are of great importance to the nuclear fuel cycle. Here, the polarizability dramatically alters the ion's interactions with nearby molecules and complexing ligands.

The 5f metals have a broad range of oxidation states. The open f shells in actinide ions give rise to a large number of close-lying electronic states in atomic or molecular spectra. The 5f, 6d, and 7s orbitals are very close in energy, leading to orbital mixing and an increased probability of having a multi-determinantal ground states. This work focuses on the tri- and tetravalent states of U, Np, and Pu, which have electron occupations that vary from two to five in their 5f shells. The strong spin-orbit coupling (SOC) significantly mixes terms of different configurations and LS values, leaving only the total angular momentum J as a good quantum number. In the

presence of an electric field, the unpaired valence electron configurations of these ions also cause anisotropy, that is, the perpendicular components of the polarizability differ relative to the symmetry axis ($\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$). This is significant for understanding long-range interatomic forces. The intense interest regarding the electronic structure of the 4f and 5f elements has inspired several recent reports of polarizabilities for heavy elements like trivalent lanthanide ions¹² and tetravalent Th, Pa, and U where the authors¹³ have utilized a (fully) relativistic Hamiltonian. Yet, data is still lacking for trivalent U, as well as $Np^{3+/4+}$ and $Pu^{3+/4+}$, which hinders our computational ability to understand the essential interactions of these ions. In this work, relativistic coupled cluster (CC) and configuration interaction (CI) approaches are utilized in the framework of the four-component Dirac–Coulomb Hamiltonian using the uncontracted basis sets of Dyall.¹⁴

■ METHODOLOGY

Modern methods for determining the dipole polarizability include analytical techniques, for example, the coupled perturbed Hartree–Fock method,^{15,16} yet numerical methods like finite-field perturbation are particularly convenient and involve taking the second derivative in the power series expansion of the total energy in a finite external electric field. The energy of the system in a static uniform electric field F acting in the z direction ($F_x = F_y = 0$, $F_z = F$) can be expanded in terms of the field strength

Special Issue: Curt Wittig Festschrift

Received: March 28, 2013

Revised: May 16, 2013

Published: May 16, 2013

$$E(F) = E(0) + \left. \frac{\partial E(F)}{\partial F} \right|_{F=0} F + \frac{1}{2} \left. \frac{\partial^2 E(F)}{\partial F^2} \right|_{F=0} F^2 + \dots \quad (1)$$

where the first derivative is the permanent dipole moment and the second derivative, which is expressed as $\alpha = -[\partial^2 E(F)/\partial F^2]|_{F=0}$ is the static dipole polarizability. The accuracy of a three-point fit (0.000, ± 0.002 – strength (in au) of the electric field along the z axis) and a five-point fit (0.000, ± 0.002 , ± 0.004) for the derivative was initially compared. Both fits yielded polarizability values within ~ 0.002 au³ of one another, and thus, the three-point fit has been utilized throughout. The data reported here are for the z component of the polarizability tensor (α_{zz}) in atomic units. As discussed previously,^{17,18} when the electric field is applied along the z axis of the atom, M_J (the projection of the total angular momentum J) is a good quantum number, the off-diagonal polarizability tensor components vanish, and the tensor components α_{xx} and α_{yy} are equal. The polarizability is expressed in terms of the total angular momentum J and its projection M_J as

$$\alpha_{zz}(M_J) = \alpha + \beta \left(M_J^2 - \frac{1}{3} J(J+1) \right) \quad (2)$$

where α is the mean polarizability and β is the polarizability anisotropy parameter (a measure of the difference between the various components of the dipole polarizability). The polarizability anisotropy is then defined for fixed J values as

$$\begin{aligned} \Delta\alpha(J, M_J) &= \alpha_{zz}(J, M_J) - \alpha_{xx}(J, M_J) \\ &= \beta(3M_J^2 - J(J+1)) \end{aligned} \quad (3)$$

The values of α and β for each ion have been calculated using eq 2 for different values of M_J .

■ COMPUTATIONAL DETAILS

The dipole polarizability calculations have been performed in the four-component (4c) Dirac–Hartree–Fock (DHF) framework because SOC is non-negligible¹³ and this approach includes both scalar and spin–orbit relativistic effects. All calculations have been performed using DIRAC12.¹⁹ In the 4c framework, the two-electron interaction is generally described by two terms, a simple Coulomb term and the Breit interaction. The latter contribution contains retardation effects, which are usually very small for chemical purposes and normally neglected, as well as the spin-other-orbit interactions. Inclusion of the latter interactions increases the computational cost significantly. The present implementation of the spin-other-orbit interactions, that is, the Gaunt interaction, is limited in the DIRAC12 program to essentially the 4c-DHF level. Inclusion of the Gaunt term at this level of theory for the atoms of the present work decreases the polarizabilities by 0.04–1.06%. Hence, in the present work, the two-electron interaction included only the Coulomb term, that is, the Dirac–Coulomb (DC) Hamiltonian. Because the full all-electron treatment is computationally expensive, contributions from the (SSIS)-type integrals (S denotes the small-component) have been replaced by a simple model correction,²⁰ which is the default within DIRAC12.

The relativistic Gaussian-type orbital (GTO) polarized triple- ζ (TZP) and quadruple- ζ (QZP) basis sets of Dyall¹⁴ have been utilized in their uncontracted form with inclusion of the polarizing functions for the 5f and 6d/7s electrons and the

correlating functions for 5f electrons. Thus, basis sets of sizes (33s29p20d13f3g2h) for TZP and (37s34p27d17f6g2h1i) for QZP have been used. While the 5d electrons have generally not been correlated so as to maintain a reasonable computational expense, the effect of 5d correlation has been investigated for the U⁴⁺ ion. In considering the correlation of 5d electrons, the size of the QZP basis set is the same as that mentioned above, that is, the 5d correlating functions have not been added to the basis set. It was unfortunately too computationally expensive to include the additional 5d correlating functions for these all-electron calculations given our computational resources. Thus, we would emphasize that the reader should use the data of the second column in Table 3 with care, keeping in mind that these were calculated as mentioned above. For all cases, the small-component basis functions have been generated through the restricted kinetic balance conditions.^{21,22}

The DHF polarizabilities and the Kramers pair spinors for the subsequent correlated calculations have been obtained from average-of-configurations open-shell DHF calculations. These calculations involved an open-shell state averaging over all possible electronic configurations of 5f electron occupations with various numbers of open-shell electrons according to the specific ion. The resulting average over many states was then resolved using a small CI in order to obtain polarizabilities for specific J and M_J states at the DHF level in order to more effectively compare to the correlated results described below.

The main challenge for studying the properties of U, Np, and Pu ions lies in the large number of electrons that must be correlated and the significant number of unpaired valence electrons. Systems having multiple unpaired electrons often cannot be adequately described by a single determinant,²³ and therefore, efficient multireference approaches are required. Hence, correlation effects in this work have been incorporated by using both Fock-space coupled cluster (FSCC)^{24–31} and multireference configuration interaction (MRCI).^{32,33} These approaches treat SOC and electron correlation on equal footing. The 4c Kramers restricted (KR)-CI^{34–36} method is based on the concept of generalized active spaces (GAS).^{34,37} The GAS CI method could be thought of as a generalization of the restricted active space (RAS) CI method.^{34–36,38,39} In principle, an arbitrary number of active orbital spaces with arbitrary electron occupation constraints can be used to determine the CI wave function, thus providing maximum flexibility for the electronic structure problem under consideration. The spinors 1s through 5d, that is, 78 electrons, were (typically) frozen after the SCF step, giving an active space of electrons varying from 10 to 16 in the correlation calculations. The virtual space was truncated by excluding spinors with energies larger than 10 au because higher-energy cutoffs were generally not feasible due to increased computational expense. The active space consisted of four GAS spaces using the notation GAS $n(x,y)$,⁴⁰ where n is the number of GAS spaces and (x,y) is the total number of active electrons and active orbitals, respectively. As an example, for the Pu³⁺ ion, GAS4(13,126) consists of four orbital spaces, the 6s orbital with 2 electrons, 6p with 6 electrons, 5f with 5 electrons, and the virtual orbitals up to 10 au, which yields a total of 126 orbitals. Single excitations from the first orbital space and single and double excitations from the second and third in the virtual space were taken into account.

The U⁴⁺ ion has only two unpaired electrons, and as such, electron correlation can also be treated by taking advantage of the 4c FSCC method. FSCC is one of the multireference CC

variants that can simultaneously calculate many states having different numbers of valence electrons. The FSCC method in the 4c DC framework accounts for both relativistic effects and electron correlation in an accurate manner. Within this method, the reference state is a closed-shell, single determinant, and the CC solution of this lowest (0,0) sector is a “parent” state that is used as the starting point for building higher-valence sectors (0,1) and (0,2) by adding or subtracting one or two electrons. The restriction in the present implementation of FSCC in DIRAC is that it cannot be applied to systems with >2 electrons or holes outside of the reference closed-shell system. We are therefore restricted to use this method only for U^{4+} . In most cases, the virtual space was truncated by excluding spinors with energies larger than 10 au so as to be consistent with the KRCI calculations; however, virtual spinors with energies as high as 30 au were included in some cases for calibration purposes.

RESULTS AND DISCUSSION

(i). U^{4+} Ion. The open-shell U^{4+} ion with its $5f^2$ electron configuration results in a 3H ground state term within the LS coupling scheme. SOC splits the ground state into $J = 4, 5$, and 6 levels. The first excited state is a 3F with $J = 2, 3$, and 4. The $J = 4$ ground-state level is separated by $\sim 4161\text{ cm}^{-1}$ from the next fine-structure level, $J = 2$ of the 3F state,⁴¹ and by about 6137 cm^{-1} from the $J = 5$ level of the ground 3H term, representing a large spin–orbit splitting between the various J levels.⁴¹ An energy level diagram for the lowest J levels of U^{4+} , obtained with the FSCC method and the QZP basis using a virtual spinor cutoff of 30 au (5d electrons not correlated) is presented in Figure 1. The calculated energy levels are first

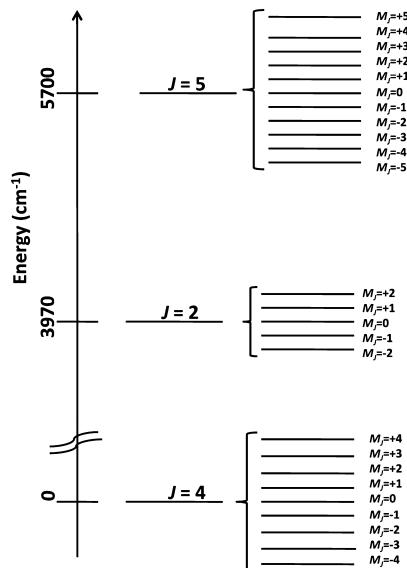


Figure 1. Energy level diagram for U^{4+} calculated at the 4c FSCC level with the QZP basis set, where the M_J states for the corresponding J levels are degenerate in the absence of an electric field. The zero of energy is defined as the $J = 4$, $M_J = 0$ ground state.

compared with the experimental values⁴¹ and other theoretical results.^{42,43} The first splitting observed with our calculations (3975 cm^{-1}) is between $J = 4$ and $J = 2$ and is calculated to be 185 cm^{-1} lower than experiment, while the second splitting at 5706 cm^{-1} (between $J = 2$ and $J = 5$) is 430 cm^{-1} lower.⁴¹ Previous theoretical studies^{42,43} reporting the energy spectrum of U^{4+} utilized FSCC with a higher virtual cutoff of 100 au, in

comparison to the 30 au in this work. Our reported first splitting (between $J = 4$ and $J = 2$) is 200 cm^{-1} lower, and the second splitting (between $J = 2$ and $J = 5$) is 330 cm^{-1} lower than those predicted values.^{42,43} A total of 9, 5, and 11 M_J states are obtained from $J = 4, 2$, and 5, respectively, when the electric field is applied. Table 1 reports the polarizabilities and anisotropies in the various M_J states of $J = 4, 5$, and 2 for U^{4+} , comparing DHF and FSCC results using the TZP and QZP bases. Increasing the basis set leads to only a $\sim 0.02\text{ au}^3$ increase at the DHF level and a $\sim 0.04\text{ au}^3$ increase with FSCC. Further, electron correlation is observed to increase the polarizability by $\sim 0.2\text{ au}^3$ at the QZP level (5d electrons not correlated). Interestingly, despite the large energy difference between the various J levels, the polarizabilities between two J states do not appreciably change ($<0.04\text{ au}^3$). Similar polarizabilities for different J levels have also been observed for Pa^{4+} .¹³ Table 2 presents the zz component of the polarizability for the lowest ($M_J = 0$) state of the ground $J = 4$ level with FSCC using two different virtual orbital cutoffs. At this level of theory with both the TZP and QZP basis sets, the 10 au cutoff does not yield appreciably different polarizabilities than the 30 au cutoff, which validates the choice of the smaller cutoff for the subsequent triple- ζ KRCI calculations. In fact, it was not computationally feasible to run KRCI calculations at the QZP level even using this 10 au cutoff with our current resources. Even obtaining all of the M_J states at the KRCI/TZP level was very computationally expensive. Therefore, we have only computed the polarizability of the lowest M_J state for the ground $J = 4$ level. One can see from Table 2 that the value of α_{zz} for $(J, M_J) = (4, 0)$ at the KRCI level is lower than that predicted by FSCC by 0.25 au^3 , yielding a result very similar to the DHF value.

Our best predicted value for the mean polarizability of the ground state of U^{4+} , as shown in Table 1, is 8.067 au^3 , which is $\sim 0.1\text{ au}^3$ higher than the previously calculated value¹³ of 7.97 au^3 , where the authors used the FSCC method. This difference is likely due to the relative sizes of basis sets employed. The basis sets used in the present work have three more d functions, two more f functions, four more g functions, and one more h. Further, we have included most of the correlating and polarizing (i.e., diffuse) functions, which are well-known to be required for the accurate calculation of dipole polarizabilities. Note too that the value reported here is significantly lower than that obtained by the much less accurate variation perturbation calculations,¹⁰ which predict 9.785 au^3 .

Table 3 presents the FSCC/QZP ground-state polarizabilities and anisotropies for U^{4+} with 5d electrons frozen (also presented in Table 1) and 5d electrons correlated. The correlation of the 5d electrons yields a decrease in the polarizabilities by $\sim 0.2\text{ au}^3$ as compared to when the 5d electrons are frozen. The anisotropies, however, exhibit much smaller effects. These results are consistent with similar calculations reported previously for the Pa^{4+} ion.¹³

(ii). U^{3+} , $Np^{3+/4+}$, and $Pu^{3+/4+}$. The isoelectronic ions U^{3+} and Np^{4+} have three open-shell 5f electrons, resulting in 4I ground states within the LS coupling scheme. Inclusion of SOC yields $J = 9/2, 11/2$, and $13/2$ levels. The spin–orbit energy splittings at the level of 4c DHF between various J levels have been calculated to be 8034 cm^{-1} for U^{3+} (8024 cm^{-1} experimentally^{44–46}) and 10537 cm^{-1} for Np^{4+} between the ground $J = 9/2$ and $J = 13/2$ levels. Np^{3+} and Pu^{4+} are isoelectronic ions with the electron configuration of $5f^4$, resulting in 5I ground-state terms in the LS coupling scheme.

Table 1. zz Component of the Polarizability Tensor (α_{zz}) and Anisotropies ($\Delta\alpha$) of U^{4+} for the Three Lowest J Levels and Their M_J States, the Mean Polarizability (α) (in au^3), and the Polarizability Anisotropy Parameter (β) for J Levels Using the 4c DHF and FSCC Methods with the TZP and QZP Basis Sets

J	4				5				2			
	DHF		FSCC		DHF		FSCC		DHF		FSCC	
	TZP	QZP	TZP	QZP	TZP	QZP	TZP	QZP	TZP	QZP	TZP	QZP
α_{zz}												
$M_J = 0$	8.116	8.142	8.345	8.391	8.188	8.215	8.416	8.464	7.769	7.790	7.901	7.937
± 1	8.077	8.102	8.297	8.342	8.159	8.186	8.381	8.429	7.827	7.849	7.981	8.018
± 2	7.959	7.983	8.154	8.196	8.073	8.098	8.276	8.321	8.000	8.025	8.218	8.261
± 3	7.762	7.784	7.915	7.953	7.928	7.957	8.100	8.143				
± 4	7.486	7.505	7.581	7.613	7.726	7.749	7.855	7.893				
± 5					7.467	7.487	7.540	7.573				
$\Delta\alpha$												
$M_J = 0$	0.394	0.398	0.478	0.486	0.433	0.437	0.525	0.535	−0.173	−0.176	−0.237	−0.244
± 1	0.335	0.338	0.406	0.413	0.389	0.393	0.473	0.482	−0.087	−0.088	−0.119	−0.122
± 2	0.158	0.159	0.191	0.194	0.260	0.262	0.315	0.321	0.173	0.176	0.238	0.244
± 3	−0.138	−0.139	−0.167	−0.170	0.043	0.043	0.052	0.053				
± 4	−0.552	−0.557	−0.669	−0.680	−0.259	−0.262	−0.315	−0.321				
± 5					−0.649	−0.655	−0.788	−0.802				
β	−0.020	−0.020	−0.024	−0.024	−0.014	−0.015	−0.017	−0.018	0.029	0.029	0.040	0.041
α	7.854	7.877	8.026	8.067 (7.97 ^a)	7.899	7.924	8.065	8.107	7.885	7.908	8.060	8.099

^aCalculated in ref 13 using lesser/no diffuse functions and a virtual cutoff of 25 au.

Table 2. zz Component of the Polarizability Tensor (α_{zz}) for the $J = 4$, $M_J = 0$ State of U^{4+} (in au^3) with Different Cutoffs for the 4c FSCC and KRCI Methods (5d not correlated)

basis set	cutoff (au)	KRCI	FSCC
TZP	10	8.100	8.350
TZP	30		8.345
QZP	10		8.399
QZP	30		8.391

Table 3. zz Component of the Polarizability Tensor (α_{zz}) and Anisotropies ($\Delta\alpha$) of the Ground $J = 4$ Level and Its M_J States, the Mean Polarizability (α) (in au^3), and the Polarizability Anisotropy Parameter (β) for $J = 4$ of the U^{4+} Ion for the 4c FSCC Method with Frozen and Correlated 5d Electrons with the QZP Basis Set

$J = 4$		
	5d-uncorrelated	5d-correlated
α_{zz}		
$M_J = 0$	8.391	8.189
± 1	8.342	8.143
± 2	8.196	8.007
± 3	7.953	7.781
± 4	7.613	7.464
$\Delta\alpha$		
$M_J = 0$	0.486	0.453
± 1	0.413	0.385
± 2	0.194	0.181
± 3	−0.170	−0.159
± 4	−0.680	−0.634
β	−0.024	−0.023
α	8.067	7.886

The J levels thus correspond to $J = 4, 5$, and 6 . The Pu^{3+} ion has five open-shell 5f electrons with a 6H ground-state term having $J = 5/2, 7/2$, and $9/2$. Tables 4 and 5 report the CI-resolved polarizabilities at the DHF level of theory using the QZP basis

sets. In all cases, 4c DHF predicts an increase in the polarizability by not more than 0.1 au^3 in going from one J level to the next, despite the large energy splittings between J states. This is the same trend discussed above in U^{4+} . Table 6 reports the zz component of the polarizability tensor of the lowest M_J states at the KRCI level using the TZP basis.

The polarizabilities for isoelectronic systems decrease with increasing charge, as seen in Tables 4 and 5. For instance, the polarizability of Np^{4+} is 7.528 au^3 , which is significantly lower than the polarizability of its isoelectronic counterpart U^{3+} , 11.660 au^3 . This effect decreases along the series because of the relativistic contraction of the 5f orbitals and is observed using DHF as well as KRCI methods. As anticipated, our values are significantly lower than those obtained using less accurate variational perturbation methods,¹⁰ though the trend of the change in polarizability along the series is similar. For example, the polarizability values for U^{3+} , Np^{3+} , and Pu^{3+} reported in ref 10 are 12.552, 12.012, and 11.540 au^3 , respectively, while our best ground-state DHF average values are 11.660, 10.533, and 9.709 au^3 . The difference in the polarizability values increases from 0.8 to 1.8 au^3 as one moves along the series for the three trivalent ions. In the case of tetravalent ions (Np and Pu), this difference in polarizabilities is larger and varies from 1.7 to 1.9 au^3 along the series for these three ions. The polarizabilities calculated in ref 10 for Np and Pu are 9.448 and 9.110, while our best values are on the order of 7 au^3 .

CONCLUSIONS

The static electric dipole polarizabilities and anisotropies of the ground and two lowest excited J levels have been computed for $An^{(3+/4+)}$, where $An = U, Np$, and Pu , using different relativistic all-electron methods. Relativistic and uncontracted basis sets of triple- and quadruple- ζ quality were used, including diffuse polarization and correlating functions, which are of significant importance in actinide ions. The polarizabilities and anisotropies of different J levels of U^{4+} were calculated using the FSCC method with two different virtual spinor cutoffs, leading

Table 4. zz Component of the Polarizability Tensor (α_{zz}) and Anisotropies ($\Delta\alpha$) of U^{3+} , Np^{4+} , and Pu^{3+} Ions for the Three Lowest J and Their M_J states, the Mean Polarizability (α) (in au^3), and the Polarizability Anisotropy Parameter (β) for J States Using the 4c DHF with the QZP Basis Set

J	U^{3+}			Np^{4+}			Pu^{3+}		
	9/2	11/2	13/2	9/2	11/2	13/2	5/2	7/2	9/2
α_{zz}									
$M_J = \pm 1/2$	11.743	11.899	12.026	7.581	7.618	7.655	9.400	9.508	9.548
$\pm 3/2$	11.722	11.876	12.002	7.568	7.607	7.644	9.632	9.599	9.599
$\pm 5/2$	11.681	11.830	11.955	7.541	7.584	7.623	10.10	9.782	9.704
$\pm 7/2$	11.619	11.762	11.884	7.502	7.550	7.592		10.057	9.859
$\pm 9/2$	11.535	11.670	11.789	7.448	7.505	7.550			10.068
$\pm 11/2$		11.555	11.671		7.449	7.498			
$\pm 13/2$			11.529			7.436			
$\Delta\alpha$									
$M_J = \pm 1/2$	0.124	0.203	0.284	0.080	0.100	0.125	−0.464	−0.343	−0.312
$\pm 3/2$	0.093	0.168	0.248	0.060	0.083	0.120	−0.116	−0.206	−0.234
$\pm 5/2$	0.031	0.099	0.177	0.020	0.049	0.078	0.580	0.069	−0.078
$\pm 7/2$	−0.061	−0.005	0.071	−0.040	−0.002	0.031		0.481	0.156
$\pm 9/2$	−0.187	−0.143	−0.071	−0.119	−0.071	−0.031			0.469
$\pm 11/2$		−0.316	−0.248		−0.156	−0.109			
$\pm 13/2$			−0.461			−0.203			
β	−0.005	−0.006	−0.006	−0.003	−0.003	−0.003	0.058	0.023	0.013
α	11.660	11.765	11.837	7.528	7.552	7.571	9.709	9.737	9.756

Table 5. zz Component of the Polarizability Tensor (α_{zz}) and Anisotropies ($\Delta\alpha$) of Np^{3+} and Pu^{4+} Ions for the Three Lowest J and their M_J States, the Mean Polarizability (α) (in au^3), and the Polarizability Anisotropy Parameter (β) for J States Using the 4c DHF with the QZP Basis

J	Np^{3+}			Pu^{4+}		
	4	5	6	4	5	6
α_{zz}						
$M_J = 0$	10.281	10.387	10.455	7.096	7.126	7.147
± 1	10.319	10.407	10.467	7.107	7.127	7.151
± 2	10.432	10.466	10.502	7.143	7.150	7.162
± 3	10.621	10.564	10.560	7.202	7.180	7.178
± 4	10.886	10.701	10.641	7.284	7.223	7.203
± 5		10.877	10.746		7.277	7.234
± 6			10.874			7.272
$\Delta\alpha$						
$M_J = 0$	−0.378	−0.294	−0.247	−0.118	−0.091	−0.074
± 1	−0.321	−0.265	−0.230	−0.100	−0.082	−0.069
± 2	−0.151	−0.176	−0.178	−0.047	−0.054	−0.053
± 3	0.132	−0.029	−0.091	0.041	−0.009	−0.028
± 4	0.529	0.176	0.030	0.165	0.055	0.009
± 5		0.441	0.186		0.136	0.056
± 6			0.376			0.113
β	0.019	0.010	0.006	0.006	0.003	0.002
α	10.533	10.583	10.623	7.174	7.186	7.198

Table 6. zz Component of the Polarizability (α_{zz}) at the KRCI/TZP Level for the Lowest M_J State of Each Ion under Consideration (in au^3)

state	$\alpha(M_J)$
$U^{3+} J = 9/2, M_J = 1/2$	11.692
$Np^{4+} J = 9/2, M_J = 1/2$	7.507
$Np^{3+} J = 4, M_J = 0$	10.184
$Pu^{4+} J = 4, M_J = 0$	7.011
$Pu^{3+} J = 5/2, M_J = 1/2$	9.306

to the conclusion that a 10 au virtual cutoff is sufficient. The FSCC method could not be utilized for ions other than U^{4+} due

to its present limitation for systems having one and two open-shell electrons. The KRCI method was utilized to calculate the polarizability for the lowest M_J state for all ions. Comparison of the KRCI and the FSCC values for the lowest state of U^{4+} leads to the result that the KRCI method underestimates the polarizability by about 0.25 au^3 (3%) in comparison to FSCC.

The static electric dipole polarizabilities follow the usual trend of negative slope along the series for actinides with the same oxidation states (i.e., they decrease with increasing atomic number) and also while going from lower to higher oxidation states. The values are significantly lower than the reported data¹⁰ as the latter were computed using relativistic effects as a variational perturbation. The polarizability value for U^{4+} is ~ 0.1

au^3 higher than that previously reported¹³ using the same level of theory but with a smaller set of basis functions. While this difference seems very small for U^{4+} , this may not be the case for other systems, and more importantly, the additional diffuse functions used in this work are strongly recommended for heavy systems in studying valence properties like polarizabilities. The polarizabilities of various J levels with the resolution of M_j for tri- and tetravalent actinide ions have not been studied before at the present level of theory. Our best estimated mean polarizabilities (in au^3) of the ground state are 11.660 and 8.067 for U^{3+} and U^{4+} ions, 10.533 and 7.528 for Np^{3+} and Np^{4+} ions, and 9.709 and 7.174 for Pu^{3+} and Pu^{4+} ions, respectively. In addition, the best α_{zz} polarizabilities (in au^3) reported for the lowest M_j states corresponding to the ground J level are 11.692 and 8.391 for U^{3+} and U^{4+} ions, 10.184 and 7.507 for Np^{3+} and Np^{4+} ions, and 9.306 and 7.011 for Pu^{3+} and Pu^{4+} ions, respectively. The values reported here are to date the most accurate all-electron calculations for the polarizabilities of the tri- and tetravalent actinide ions under consideration. In the future work, we will extend the relativistic calculation to compute the polarizabilities of the V and VI oxidation states for U, Np, and Pu in their molecular dioxo forms.

AUTHOR INFORMATION

Corresponding Author

*E-mail: payal.parmar@wsu.edu (P.P.); kipeters@wsu.edu (K.A.P.); auclark@wsu.edu (A.E.C.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors wish to thank the Dirac developers for fruitful discussions through the Dirac mailing list. This work was supported by a grant from the Department of Energy, Basic Energy Sciences, Heavy Element program (DE-SC0001815 to A.E.C. and DE-FG02-12ER16329 to K.A.P.). Parts of this work were performed at the William R. Wiley Environmental Science Laboratory using the Molecular Science Computing Facility (MSCF) therein, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for the Department of Energy by Battelle.

REFERENCES

- Dalgarno, A. Atomic Polarizabilities and Shielding Factors. *Adv. Phys.* **1962**, *11*, 281–315.
- Vleck, J. v. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University: Oxford, U.K., 1932.
- Buckingham, A.; Orr, B. Molecular Hyperpolarisabilities. *Q. Rev. Chem. Soc.* **1967**, *21*, 195–212.
- Kleinman, C. J.; Hahn, Y.; Spruch, L. Dominant Nonadiabatic Contribution to the Long-Range Electron–Atom Interaction. *Phys. Rev.* **1968**, *165*, 53–62.
- de Heer, W. A. The Physics of Simple Metal Clusters: Experimental Aspects and Simple Models. *Rev. Mod. Phys.* **1993**, *65*, 611–676.
- Miller, T. M.; Bederson, B. Electric Dipole Polarizability Measurements. *Adv. At., Mol., Opt. Phys.* **1988**, *25*, 37–60.
- Bonin, K. D.; Kresin, V. V. *Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters*; World Scientific: Singapore, 1997.
- Norcross, D. W. Photoabsorption by Cesium. *Phys. Rev. A* **1973**, *7*, 606–616.
- Schwerdtfeger, P. *An Updated List of Experimental and Calculated Polarizabilities*. <http://ctcp.massey.ac.nz/index.php?group=&page=dipole&menu=dipole> (2012).
- Fraga, S.; Karwowski, J.; Saxena, K. *Handbook of Atomic Data*; Elsevier Scientific: Amsterdam, The Netherlands, 1976.
- Dolg, M.; Cao, X. The Relativistic Energy-Consistent Ab-Initio Pseudopotential Approach and Its Application to Lanthanide and Actinide Compounds. *Recent Adv. Comput. Chem.* **2004**, *6*, 1–35.
- Clavaguéra, C.; Dognon, J. P. Accurate Static Electric Dipole Polarizability Calculations of +3 Charged Lanthanide Ions. *Chem. Phys.* **2005**, *311*, 169–176.
- Réal, F.; Vallet, V.; Clavaguéra, C.; Dognon, J. P. In-Silico Prediction of Atomic Static Electric-Dipole Polarizabilities of the Early Tetravalent Actinide Ions: $\text{Th}^{4+}(\text{5f}^0)$, $\text{Pa}^{4+}(\text{5f}^1)$, and $\text{U}^{4+}(\text{5f}^2)$. *Phys. Rev. A* **2008**, *78*, 052502–052502–8.
- Dyall, K. G. Relativistic Double-Zeta, Triple-Zeta, and Quadruple-Zeta Basis Sets for the Actinides Ac–Lr. *Theor. Chem. Acc.* **2007**, *117*, 491–500.
- Dalgarno, A.; Stewart, A. L. Perturbation Theory for Atomic Systems. *Proc. R. Soc. London, Ser. A* **1959**, *251*, 282–290.
- Markiewicz, E.; Meehan, R. P.; Stauffer, A. D. Polarizabilities and Shielding Factors for the $(\text{ns})^2$ Isoelectronic-Sequences. *J. Phys. B: At. Mol. Opt. Phys.* **1981**, *14*, 949–953.
- Bederson, B. R.; Beam, E. J. Measurements of Atomic Polarizabilities. *Adv. Chem. Phys.* **1966**, *10*, 1–27.
- Klos, J. Anisotropic Dipole Polarizability of Transition Metal Atoms: Sc(2d), Ti(3f,3p), V(4f,4p,6d), Ni(3f) and Ions: $\text{Sc}^{2+}(\text{2d})$, $\text{Ti}^{2+}(\text{3f,3p})$. *J. Chem. Phys.* **2005**, *123*, 024308/1–024308/7.
- DIRAC. *A Relativistic Ab-initio Electronic Structure Program*, Release DIRAC12 (2012), written by H. J. Aa. Jensen, Bast, R.; Saue, T.; Visscher, L. with contributions from Bakken, V.; Dyall, K. G.; Dubillard, S.; Ekström, U.; Eliav, E.; Enevoldsen, T.; Fleig, T.; Fossgaard, O.; Gomes, A. S. P.; Helgaker, T.; Lærdahl, J. K.; Lee, Y. S.; Henriksson, J.; Iliaš, M.; Jacob, Ch. R.; Knecht, S.; Komorovský, S.; Kullie, O.; Larsen, C. V.; Nataraj, H. S.; Norman, P.; Olejniczak, G.; Olsen, J.; Park, Y. C.; Pedersen, J. K.; Pernpointner, M.; Ruud, K.; Salek, P.; Schimmelpfennig, B.; Sikkema, J.; Thorvaldsen, A. J.; Thyssen, J.; van Stralen, J.; Villaume, S.; Visser, O.; Winther, T.; Yamamoto, S. <http://www.diracprogram.org> (2012).
- Visscher, L. Approximate Molecular Relativistic Dirac–Coulomb Calculations Using a Simple Coulombic Correction. *Theor. Chem. Acc.* **1997**, *98*, 68–70.
- Stanton, R. E.; Havriliak, S. Kinetic Balance: A Partial Solution to the Problem of Variational Safety in Dirac Calculations. *J. Chem. Phys.* **1984**, *81*, 1910–1918.
- Visscher, L.; Aerts, P. J. C.; Visser, O.; Nieuwpoort, W. C. Kinetic Balance in Contracted Basis-Sets for Relativistic Calculations. *Int. J. Quantum Chem.* **1991**, *40*, 131–139.
- Kaldor, U. The Fock Space Coupled Cluster Method: Theory and Application. *Theor. Chem. Acc.* **1991**, *80*, 427–439.
- Bartlett, R. J.; Musiał, M. Coupled-Cluster Theory in Quantum Chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291–352.
- Kaldor, U.; Eliav, E. High-Accuracy Calculations for Heavy and Super-Heavy Elements. *Adv. Quantum Chem.* **1998**, *31*, 313–336.
- Kutzelnigg, W. Quantum Chemistry in Fock Space. IV. The Treatment of Permutational Symmetry. Spin-Free Diagrams with Symmetrized Vertices. *J. Chem. Phys.* **1985**, *82*, 4166–4186.
- Lindgren, I. A Coupled-Cluster Approach to the Many-Body Perturbation Theory for Open-Shell Systems. *Int. J. Quantum Chem.* **1978**, *14*, 33–58.
- Lindgren, I.; Mukherjee, D. On the Connectivity Criteria in the Open-Shell Coupled-Cluster Theory for General Model Spaces. *Phys. Rep.* **1987**, *151*, 93–127.
- Mukherjee, D.; Moitra, R. K.; Mukhopadhyay, A. Correlation Problem in Open-Shell Atoms and Molecules. *Mol. Phys.* **1975**, *30*, 1861–1888.
- Mukherjee, D.; Moitra, R. K.; Mukhopadhyay, A. Applications of a Non-Perturbative Many-Body Formalism to General Open-Shell Atomic and Molecular Problems: Calculation of the Ground and the

Lowest π - π^* Singlet and Triplet Energies and the First Ionization Potential of Trans-Butadiene. *Mol. Phys.* **1977**, *33*, 955–969.

(31) Mukherjee, D. P.; S. Use of Cluster Expansion Methods in the Open-Shell Correlation Problem. *Adv. Quantum Chem.* **1989**, *20*, 291–373.

(32) Knecht, S.; Jensen, H. J. A.; Fleig, T. Large-Scale Parallel Configuration Interaction. I. Nonrelativistic and Scalar-Relativistic General Active Space Implementation with Application to (Rb–Ba)⁺. *J. Chem. Phys.* **2008**, *128*, 014108/1–014108/14.

(33) Knecht, S.; Jensen, H. J. A.; Fleig, T. Large-Scale Parallel Configuration Interaction. II. Two- and Four-Component Double-Group General Active Space Implementation with Application to BiH. *J. Chem. Phys.* **2010**, *132*, 014108/1–014108/13.

(34) Fleig, T.; Olsen, J.; Marian, C. M. The Generalized Active Space Concept for the Relativistic Treatment of Electron Correlation. I. Kramers-Restricted Two-Component Configuration Interaction. *J. Chem. Phys.* **2001**, *114*, 4775–4790.

(35) Fleig, T.; Olsen, J.; Visscher, L. The Generalized Active Space Concept for the Relativistic Treatment of Electron Correlation. II. Large-Scale Configuration Interaction Implementation based on Relativistic 2- and 4-Spinors and its Application. *J. Chem. Phys.* **2003**, *119*, 2963–2971.

(36) Fleig, T.; Jensen, H. J. A.; Olsen, J.; Visscher, L. The Generalized Active Space Concept for the Relativistic Treatment of Electron Correlation. III. Large-Scale Configuration Interaction and Multi-configuration Self-Consistent-Field Four-Component Methods with Application to UO₂. *J. Chem. Phys.* **2006**, *124*, 104106/1–104106/11.

(37) Olsen, J. The Initial Implementation and Applications of a General Active Space Coupled Cluster Method. *J. Chem. Phys.* **2000**, *113*, 7140–7148.

(38) Malmqvist, P. A.; Rendell, A.; Roos, B. O. The Restricted Active Space Self-Consistent-Field Method, Implemented with a Split-Graph Unitary Group Approach. *J. Phys. Chem.* **1990**, *94*, 5477–5482.

(39) Olsen, J.; Roos, B. O.; Jørgensen, P.; Jensen, H. J. A. Determinant Based Configuration Interaction Algorithms for Complete and Restricted Configuration Interaction Spaces. *J. Chem. Phys.* **1988**, *89*, 2185–2192.

(40) Ma, D. X.; Manni, G. L.; Gagliardi, L. The Generalized Active Space Concept in Multiconfigurational Self-Consistent Field Methods. *J. Chem. Phys.* **2011**, *135*, 044128/1–044128/11.

(41) Wyart, J. F.; Kaufman, V.; Sugar, J. Analysis of the Spectrum of Four-Times-Ionized Uranium (U⁵). *Phys. Scr.* **1980**, *22*, 389–396.

(42) Eliav, E.; Kaldor, U.; Ishikawa, Y. Relativistic Coupled-Cluster Method: Intrashell Excitations in the *f*² Shells of Pr⁺³ and U⁺⁴. *Phys. Rev. A* **1995**, *51*, 225–230.

(43) Infante, I.; Eliav, E.; Vilkas, M. J.; Ishikawa, Y.; Kaldor, U.; Visscher, L. A Fock Space Coupled Cluster Study on the Electronic Structure of the UO₂, UO₂⁺, U⁴⁺, and U⁵⁺ Species. *J. Chem. Phys.* **2007**, *127*, 124308/1–124308/12.

(44) Carnall, W. T.; Crosswhite, H. M. Optical Spectra and Electronic Structure of Actinide Ions in Compounds and in Solution. *Argonne Natl. Lab., [Rep.] ANL* **1985**, 84–90.

(45) Ruiperez, F.; Roos, B. O.; Barandiaran, Z.; Seijo, L. The 5*f*³ Manifold of the Free-Ion U³⁺: Ab-Initio Calculations. *Chem. Phys. Lett.* **2007**, *434*, 1–5.

(46) Carnall, W. T. A Systematic Analysis of the Spectra of Trivalent Actinide Chlorides in D_{3h} Site Symmetry. *J. Chem. Phys.* **1992**, *96*, 8713–8726.