AB INITIO STUDY OF THE BERKELYL AND CALIFORNYL IONS

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Actinyl ions, $AnO_2{}^{2+}$, and the corresponding $AnO_2{}^{+}$ ions, play an important role in the chemistry of the early actinide (An) metals. These hexa- and pentavalent dioxoactinide cations are characterized by very strong bonds to the two oxygens and exist for uranium through americium. The existence of oxidation states greater than IV for curium is unconfirmed. Uranyl is a closed shell dication. The ground and low lying excited states of the known actinyl ions involve the approximately degenerate $5f$ δ_u and ϕ_u orbitals. The intermediate coupling produces high spin ground states; the dioxocurium(V) cation ground state is $\delta_u^2\phi_u^2 3\pi_u^1\ {}^6\Pi_{3/2u}$. An open question is whether this trend will continue, resulting in septet and octet ground states for $BkO_2{}^{+}$ and $CfO_2{}^{+}$ ions, respectively. This study employs restricted Hartree-Fock and spin-orbit configuration-interaction methods. The actinides are modeled with relativistic effective core potentials and Gaussian correlation consistent double-zeta plus polarization basis sets. This year marks the tenth anniversary of the first presentations, at the International Symposium on Molecular Spectroscopy, by Pitzer group members on actinyl ions.