THE ELECTRONIC SPECTRA OF THE AMERICYL AND CURYL IONS

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Large graphical unitary group approach (GUGA) spin–orbit multireference configuration interaction (SOCI) singles and doubles calculations have been performed on Am^{2+}, AmO_2^{+}, CmO_2^{2+}, and CmO_2^{+}. The ground state of the americyl cation is $\delta_u^2 \phi_u^1 \ ^4\Phi_{3/2u}$. The first ligand to metal charge transfer (LMCT) state is $3\sigma_u^1 \delta_u^2 \phi_u^2 \ ^6\Sigma_{5/2u}$. The ground and first LMCT states of the isoelectronic dioxoamericium(V) and curyl cations are $\delta_u^2 \phi_u^2 \ ^5\Sigma_{0+\ g}^{+}$ and $3\sigma_u^1 \delta_u^2 \phi_u^2 3\pi_u^1 \ ^7\Pi_{0+\ g}$. The dioxocurium(V) cation ground state is $\delta_u^2 \phi_u^2 3\pi_u^1 \ ^6\Pi_{3/2u}$. Agreement with experimental LMCT excitation energies is good. Other intense electronic transitions are $f \longleftarrow f$. Recent software developments have enabled the calculation of electric dipole transition moments from GUGA SOCI wavefunctions[a]. Tentative assignments[b] of the $f \longleftarrow f$ transitions have been reevaluated with the new software. Calculations are planned to search for nonlinear minima of these ions. The actinides are modeled with relativistic effective core potentials and Gaussian correlation consistent double-zeta plus polarization (cc-pVDZ) basis sets.

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[a]S. Matsika and R. M. Pitzer, unpublished, 1999.

[b]S. R. Brozell and R. M. Pitzer, 53rd Ohio State University International Symposium, Paper RB05, p. 207, 1998.