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Relativistic and Crystal Field Effects in the Properties of the Actinides

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Relativisitic and crystal effects result in such an AnO_2^{2+} electronic configuration that the properties which are determined by the electronic structure change non-monotonously in the actinide series.

In recent years, there has been much interest in the relativistic effects (RE) [the relativistic contraction, the spin–orbit coupling (SOC) and the relativistic self-consistent expansion] for the p- and d-elements,[1-3] lanthanides (Ln) and actinides (An),[4-6] and transactinides.[7-9]

The essential aim of our investigation was to compare the chemistry of Ln and An in tri- and tetra-valent states.[4-6] The chemical difference between Ln and An seem to be caused mainly by RE.

The An and especially Ln compounds in oxidation states 0 are almost ionic and do not have a large crystal field effect (CFE). Both RE and CFE increase with increasing oxidation state. Our goal is to deduce the role of RE in the regulation of the properties of high oxidation state actinide compounds with increasing actinide atomic number Z_{An}. For our purposes, it would be of great interest to obtain information about the AnO_2^{2+} series (An = U, Np, Pu, Am). Among the numerous compounds for a given actinide the actinyl compounds seem to be more covalent. The question of whether a much stronger 'ligand effect' exists in AnO_2^{2+} than in AnO_6^{6-} or $AnHal_6$ has been conclusively proven.[6] The surprising result was that the properties P of actinyl compounds show three types of curves in plots of P *vs.* Z_{An}.[6,10] For the redox potentials $E^0(AnO_2^{2+}/AnO_2^{+})$, An = U sol Am; for the charge transfer energies in AnO_2^{2+}, E_{ch} gives a non-monotonous zigzag curve; for the refraction index and the molecular polarizability a monotonous curve is obtained; while the Gibbs free energy $G^O(AnO_2^{2+})$ and enthalpy of formation $H_f^O(AnO_2^{2+})$ gives a strictly monotonous curve. All three types of dependence were shown to occur in the structural and spectral properties of AnO_2^{2+}.[6,10,11]

The presence of much stronger 'axial oxygen field' effects than equatorial ligand field effects in actinyl compounds appears to be connected with the specific property of the $6p_{1/2}$-, 5f- and 6d-atomic orbitals (AO) to form multiple bonds $(O{=}An{=}O)^{2+}$ with the 2s- and 2p-AOs in a high oxidation state.[5]

Table 1 An—O bond distances in compounds **1–4**

	$R_{An—O}$/Å			
Compound	U	Np	Pu	Am
1	1.704	1.709	1.721	1.743
2	1.718	1.733	1.731	1.747
3	1.683	1.692	1.692	1.712
4	1.673	1.670	1.675	1.695

The nature of the non-monotonous variation in some properties and the monotonous variation in others has not yet been analysed in detail since molecular methods are still a long way from making accurate calculations. The electronic structure of UO_2^{2+} has been studied in detail.[12] In contrast, little is known about the electronic structure of NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+}, CmO_2^{2+} and all the monopositive ions AnO_2^{+}. Progress in the study of the behaviour of actinyl ions across the series has been slow to produce an adequate theory, because of the lack of these data. We have performed relativistic SCF MSW X_α[14] calculations on the actinyl cations UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+} and AmO_2^{2+} in the compounds $NaAnO_2Ac_3$ **1**, $Cs_2AnO_2Cl_4$ **2**, $Rb_2AnO_2(NO_3)_3$ **3** and $K_3AnO_2F_5$ **4**. The $R_{An—O}$ distances shown in Table 1 were used.[13]

In the $D_{\infty h}$ symmetry group the metal 5f-orbitals transform as φ_u, δ_u, π_u, σ_u and as φ_{5u}, φ_{7u}, δ_{3u}, δ_{5u}, π_{1u}, π_{3u}, σ_u with SOC taken into account. SCF X_α SW calculations using spin polarization result in the following ground state electronic configurations: $[X]3\sigma_u^2\varphi_{5u}^0$; $[X]3\sigma_u\varphi_{5u}^1\delta_{3u}^0$; $[X]3\sigma_u^2\varphi_{5u}^1\delta_{3u}^1(\varphi_{7u}\delta_{5u})^0$; $[X]3\sigma_u^2\varphi_{5u}^1\delta_{3u}^1(\varphi_{7u}\delta_{5u})^1$ for UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+} and AmO_2^{2+}, respectively. All φ_u and δ_u levels are almost completely An 5f in character and the next π_u, σ_u levels are derived from the 2s, 2p ligand and 5f metal orbitals. One can see that the electron affinity A of AnO_2^{2+} is in line with the energy of the $\varphi_{5u}(UO_2^{2+})$, $\delta_{3u}(NpO_2^{2+})$ and $\varphi_{7u}\delta_{5u}(PuO_2^{2+}, AmO_2^{2+})$ unoccupied levels. The computed electronic energies of these levels change non-monotonously with Z_n in all the compounds **1–4**

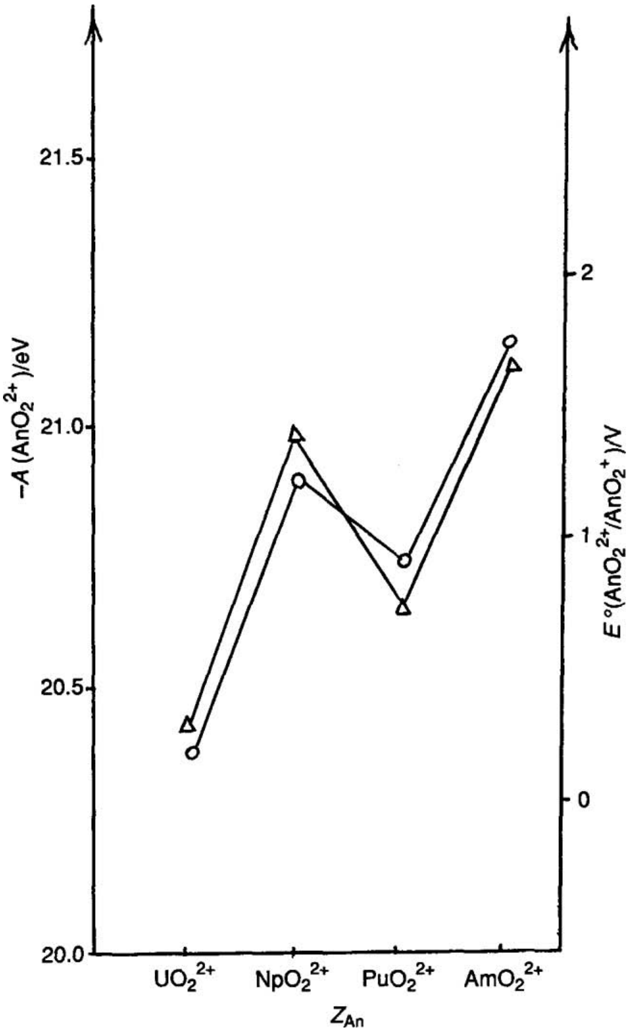

Fig. 1 Non-monotonous, zigzag dependence of $A(AnO_2^{2+})$ (○) and $E^0(AnO_2^{2+}/AnO_2^+)$ (△) on Z_{An}

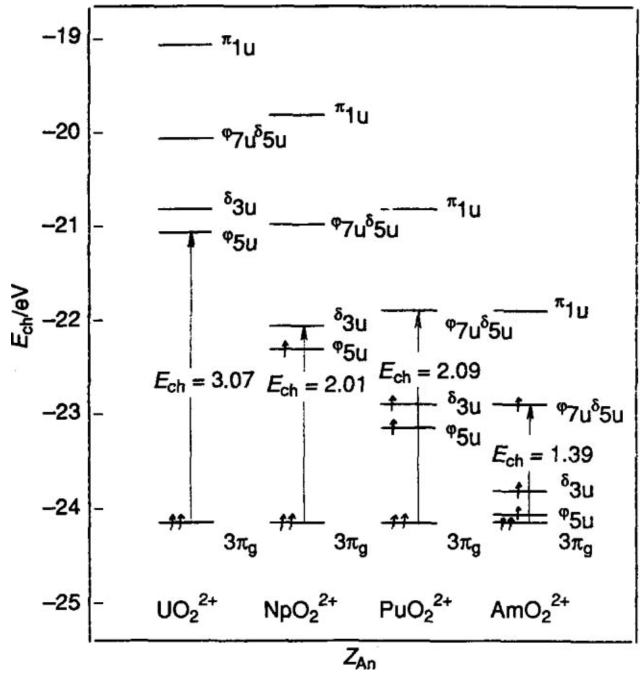

Fig. 2 Molecular orbital diagrams of AnO_2^{2+}, demonstrating the non-monotonous variation in E_{ch} with increasing Z_{An}

(Figs. 1, 2). We show this trend for our cation series. The values A/eV are: 20.4, 20.95, 20.66, 21.13 for UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+} and AmO_2^{2+}, respectively. The same regularity also occurs for other compounds.

For AnO_2^{2+} the levels φ_{5u} and δ_{3u} lie very close to the energy distance between which $\Delta_1 = \xi$, where ξ is a spin–orbit parameter. The next levels φ_{7u}, δ_{5u} occur $\Delta_2 = 2.5\xi$ above the δ_{3u} level. Even qualitatively, one sees that new aspects are introduced if the SOC is included in the scheme. The orbital shell effect for the φ_{5u} and δ_{3u} levels, together with the small splitting $\Delta_1 = \xi$, results in an increasing A of NpO_2^{2+} in comparison with that of UO_2^{2+}. Then A of PuO_2^{2+} is decreased in comparison with that of NpO_2^{2+} showing to the large spin–orbit destabilization of the $\varphi_{7u}\delta_{5u}$ levels ($\Delta_2 = 2.5\xi$), since an extra electron occupies the degenerate $\varphi_{7u}\delta_{5u}$ levels [eqn. (1)]

$$PuO_2^{2+}\{\sigma^1_{5u}\delta^1_{3u}\} + e^- \rightarrow PuO_2^+\{\varphi^1_{5u}\delta^1_{3u}(\varphi_{7u}\delta_{5u})^1\} \quad (1)$$

Finally, A of AmO_2^{2+} will be increased compared with that of PuO_2^{2+} owing to the shell effect. The next anomaly is the decrease of A for CmO_2^{2+} from that for AmO_2^{2+}.

In the hypothetical cations one would expect an anomalous decrease of A for CfO_2^{2+} from that for BkO_2^{2+}. So, summing up, a non-monotonous zigzag behaviour of $A(AnO_2^{2+})$ is seen across the actinide series (An = U–Cf). We conclude that this non-monotonous dependence is influenced by both CFE and SOC.

Obviously, $E^0(AnO_2^{2+}/AnO_2^+)$ depends on $A(AnO_2^{2+})$. The existing experimental data[15] of $E^0(AnO_2^{2+}/AnO_2^+)$ are in line with the values of A for AnO_2^{2+} (Fig. 1).

The same approach using the spin–polarization effect may be used to explain the non-monotonous change of the charge transfer energy, E_{ch}, in various compounds containing AnO_2^{2+}. The values of E_{ch} are determined by the energy difference between $1\pi_g$ occupied ligand MOs and the first unoccupied MOs. The first numbers change monotonously across the actinyl cations UO_2^{2+}–AmO_2^{2+}, but the latter follow the trend in the change of A. Calculated $E_{ch}/10^3$ cm^{-1}: 24.7, 16.2, 16.9 and 11.2. These values are in good agreement with the average experimental values: $E_{ch}/10^3$ cm^{-1} 20.4, 13.5, 15.4 and 10.0 for UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+} and AmO_2^{2+}, respectively. This results in a non-monotonous variation of E_{ch} for the cations UO_2^{2+}–AmO_2^{2+} with increasing Z_{An} and the monotonous dependence between $E^0(AnO_2^{2+}/AnO_2^+)$ and E_{ch} or E_{ch} and A.

It is interesting to ask how much of this anomalous behaviour does result from RE or CFE. The two effects are related, *i.e.* there are convincing reasons to expect both strong CFE and RE. In fact, firm confirmation of this conclusion is provided by the experimental and calculated redox-potentials E^0(III/II) and E^0(IV/III) for U, Np, Pu, Am. The variation of these potentials with Z_{An} follows a monotonous trend.[17] Moreover, the potentials E^0(III/II) and E^0 (IV/III)[17–19] obtained from the literature for the other actinide elements (Th, Pa, Bk–No) and all the lanthanides also follow the monotonous trend in each half of the series. From these data, we conclude that strong CFE and RE may result in non-variation of the properties of the f-element compounds, but if these effects are weak the dependence becomes monotonous as shown by the behaviour of the free ions.

The situation is, however, more complicated in the intermediate CFE, *e.g.* in the An^{V} compounds discussed. This case is more delicate.[19,20] The central factor in going from a monotonous to a non-monotonous dependence is that the SOC affects in the free or partly occupied 5f-levels of AnO_2^{2+} along the series. Reiterating, the relativistic element is the zigzag dependence of A, I (the ionization potentials), $F = I - A$ (the electronegativity), $E^0(AnO_2^{2+}/AnO_2^+)$ and E_{ch} in the AnO_2^{2+} series. Fig. 3 shows the dependence of F on Z_{An} for both existing and hypothetical cations.[21]

The opposite case is expected to arise when any property is determined by the total effect. For example, the enthalpy of formation $H^0(AnO_2^{2+})$ depends on the sum of the actinide

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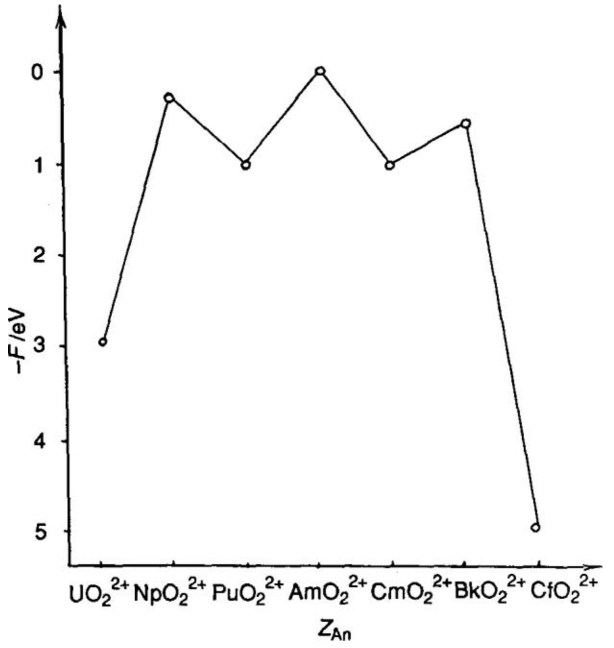

Fig. 3 Electronegativity of AnO_2^{2+} across the series U–Cf

ionization energies $\Sigma_{z=1}^{6} I(An^{z+})$. For total ionization the RE and CFE are small in comparison with the sum. In this case a monotonous dependence is observed. In fact, experimental values of $G^0(AnO_2^{2+})$ (kJ mol^{-1}: 952 ± 2; 796 ± 5; 756 ± 7; 587 ± 3 for An = U–Am, respectively, follow this trend.

We find the same effect in the electron density distribution. The effective charges on the actinides have been calculated as 2.58, 2.53, 2.46, 2.36 for UO_2^{2+}–AmO_2^{2+}, respectively.

We conclude that the non-monotonous zigzag behaviour of the redox-potentials, the charge transfer energies, and the electron affinities of AnO_2^{2+} are caused by relativistic and crystal field effects.

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