

ANGULAR OVERLAP TREATMENT OF THE ELECTRONIC SPECTRA OF ACTINIDE COMPLEXES OF TETRAGONAL SYMMETRY

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ABSTRACT

The electronic spectra of the f^1 systems $\text{Ba}_3\text{NpO}_6(O_h)$, $\text{Li}_3\text{UO}_4(\sim O_h)$, $\text{Na}_2\text{NpO}_4(D_{4h})$ and $\text{Li}_4\text{NpO}_5(D_{4h})$ are interpreted and assigned within the angular overlap model and radial parameters of interest are extracted from the spectra. The relationship between the angular overlap model parameters and the conventional ligand-field parameters is derived. For comparison molecular orbital calculations are performed on NpO_6^{6-} and UO_6^{7-} ions using the relativistic X_α approach.

INTRODUCTION

THE angular overlap model (AOM) was first introduced by Jørgensen *et al*¹ to understand the weak ligand field observed for various complexes of the lanthanide series. In the early model, only the σ -type interactions between the metal f and ligand orbitals were considered. Later other types of interactions (π , δ , ...) were incorporated in the theory^{2,3}. The model is also applied to the d -transition metal complexes. A full description of the AOM can be found elsewhere^{4,5}. According to this approach, the matrix elements between the metal orbitals ψ_M , due to the perturbation of the ligands, are expressed in terms of certain radial parameters e_μ ($\mu = \sigma, \pi, \delta, \dots$):

$$\langle \psi_M || \psi_{M'} \rangle = \sum_{\mu} \sum_w C_{\mu}^w e_{\mu}(w).$$

Summation over w is carried out when different ligands are present. Here C_{μ}^w are the angular parts of the above integral, which are determined from the symmetry of the complex via group theory. The radial integrals e_{μ} are related to the group overlap integrals $G_{ML}(\mu)$ between the metal and the ligand group orbitals by the relation⁴

$$e_{\mu} = H_L^2 \cdot G_{ML}(\mu)^2 / (H_M - H_L),$$

where H_L and H_M are the orbital energies of the ligand and the metal respectively. The advantage of using this model in the treatment of f^n systems over the conventional ligand field model is evident from the following discussion especially for systems of lower symmetry. Optical spectra of f^1 systems of the D_4 symmetry are described within the ligand-field approach by using five radial parameters⁶ (Δ , θ , τ , γ ,

δ). In most cases the relative magnitude of these parameters cannot be guessed beforehand. It is possible within the AOM to restrict the interaction between the metal and the ligands to the σ and π types only; the other types of interactions (δ , ϕ) are expected to be weak, and sometimes the ligands are not capable of forming the δ and ϕ types of bonding (e.g. oxygen, fluorine). Thus, by adopting this approximation, the parameters can be reduced to four (two for the axial and two for the equatorial ligands). On the other hand, the e_{μ} parameters are generally expected to exhibit the trend $e_{\sigma} > e_{\pi} > e_{\delta}$.

RESULTS AND DISCUSSION

Since the D_4 symmetry is common among the actinide complexes, e.g. UOX_3^{2-} ($X = \text{F}, \text{Cl}, \text{Br}$)⁷, $\text{Cs}_2\text{NpO}_2\text{Cl}_4^8$ and MO_6^{n-} ($M = \text{U}, \text{Np}, \text{Pu}$)⁹, we will concentrate on this type of symmetry; other symmetry types can be treated in an analogous manner. Each of these complexes can be considered to have an octahedral configuration with an axial distortion (either elongation or compression). The matrix elements for the f orbitals in $\text{MX}_6(D_4)$ were constructed by adding together the matrices of the axial field case $\text{MX}_2(D_{\infty h})$ and those of the tetragonal case $\text{MX}_4(D_{4h})$ (because the additivity principle is readily applied within the AOM). Apart from a constant term the matrix elements for the D_4 case are:

$$\langle \pm 3 || \pm 3 \rangle = 5/4 e_{\sigma}(\text{eq}) + 15/8 e_{\pi}(\text{eq}) \quad (1)$$

$$\langle \pm 2 || \pm 2 \rangle = 5/4 e_{\pi}(\text{eq}) \quad (2)$$

$$\langle \pm 1 || \pm 1 \rangle = 2 e_{\pi}(\text{ax}) + 3/4 e_{\sigma}(\text{eq}) + 1/8 e_{\pi}(\text{eq}) \quad (3)$$

$$\langle 0 || 0 \rangle = 2e_{\sigma}(\text{ax}) + 3/2 e_{\pi}(\text{eq}) \quad (4)$$

$$\langle \pm 2 || \mp 2 \rangle = 5/4 e_{\pi}(\text{eq}) \quad (5)$$

$$\langle \pm 3 || \mp 1 \rangle = 15/4 [e_{\sigma}(\text{eq}) - 1/2 e_{\pi}(\text{eq})]. \quad (6)$$

Here, $e_{\mu}(\text{eq})$ and $e_{\mu}(\text{ax})$ are the parameters corresponding to the equatorial and the axial ligands respectively. By comparing the orbital energy differences in this model with those previously expressed in terms of Δ , θ , τ , γ and δ^6 , the following interrelations can be obtained:

$$\Delta = 5/2 e_{\pi}(\text{eq}), \quad \theta = 2 e_{\sigma}(\text{eq}) - e_{\pi}(\text{eq}),$$

$$\tau = (2/21)d_{\sigma} + (1/7)d_{\pi},$$

$$\gamma = (6/77)d_{\sigma} + (2/7)d_{\pi},$$

$$\delta = (10/231)d_{\sigma} - (5/77)d_{\pi},$$

where Δ and θ are the Reisfeld and Crosby parameters¹⁰ for the O_h case, and d_{μ} stands for $[e_{\mu}(\text{ax}) - e_{\mu}(\text{eq})]$.

Optical spectra of f^1 octahedral complexes

Before discussing the spectra of the tetragonally distorted systems, we will first mention the more symmetric structures of the O_h symmetry. In this case, three radial parameters including one effective spin-orbit coupling constant are needed to describe the spectrum. Four electronic transitions can take place in this symmetry between the split components of the f manifold. These are, in order of increasing energy, $\Gamma_7 \rightarrow \Gamma_8$, $\Gamma_7 \rightarrow \Gamma_7$, $\Gamma_7 \rightarrow \Gamma_6$ and $\Gamma_7 \rightarrow \Gamma_6$. Denoting these transitions by E_1 , E_2 , etc. and utilizing the previously published crystal field and spin-orbit coupling matrices^{9, 11}, we get the following relations:

$$\Delta = (E_2^2 - 12\xi^2)^{1/2} + 1/2\xi = 5/2 e_{\pi}$$

and

$$\theta = [(E_3 - E_1)^2 - 45/4\xi^2]^{1/2} + \xi = (2e_{\sigma} - e_{\pi})$$

where ξ is the effective spin-orbit coupling parameter. A good fit between the experimentally observed transitions and the parameters Δ , θ and ξ can be obtained by varying the value of ξ from which Δ and θ are calculated, then using the set (Δ, θ, ξ) to calculate the electronic transitions, and repeating the whole process until we get the best fit between the calculated and observed spectra. The electronic spectra of Ba_3NpO_6 (O_h) and Li_3UO_4 ($\sim O_h$) were treated by the above approach; the results are shown in table 1. For the sake of comparison, MO calculations were performed on NpO_6^{6-} and UO_6^{7-}

Table 1 Ligand-field and angular overlap parameters for Ba_3NpO_6 and Li_3UO_4 . (All values are in cm^{-1} .)

	Ba_3NpO_6			Li_3UO_4		
	exp. ^a	calc. ^b	X_{σ}	exp. ^a	calc. ^b	X_{σ}
$\Gamma_7 \rightarrow \Gamma_8$	7690	7696	4677	4283, 4821	5021	4358
$\Gamma_7 \rightarrow \Gamma_7$	9390	9390	6758	7072	7072	6164
$\Gamma_7 \rightarrow \Gamma_6$	11760	14356	12461	10386	10858	11748
$\Gamma_7 \rightarrow \Gamma_6$	16500	16500	15072	12647	12640	14204
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Δ	7959	3620		5093	3325	
θ	4702	6760		3714	6616	
e_{π}	3184	1448		2037	1330	
e_{σ}	3943	4104		2876	3973	
ξ		1785			1625	

^aReference 9; ^bCalculated using the parameters obtained from the fitting of experimental data.

anions by using the relativistic version of the X_{σ} method¹². The different $f-f$ transition energies were calculated by assuming a spin-orbit parameter $\xi(5f)$ of 1625 cm^{-1} for U and 1785 cm^{-1} for Np. The results of these calculations are also presented in table 1. The parameters extracted from experi-

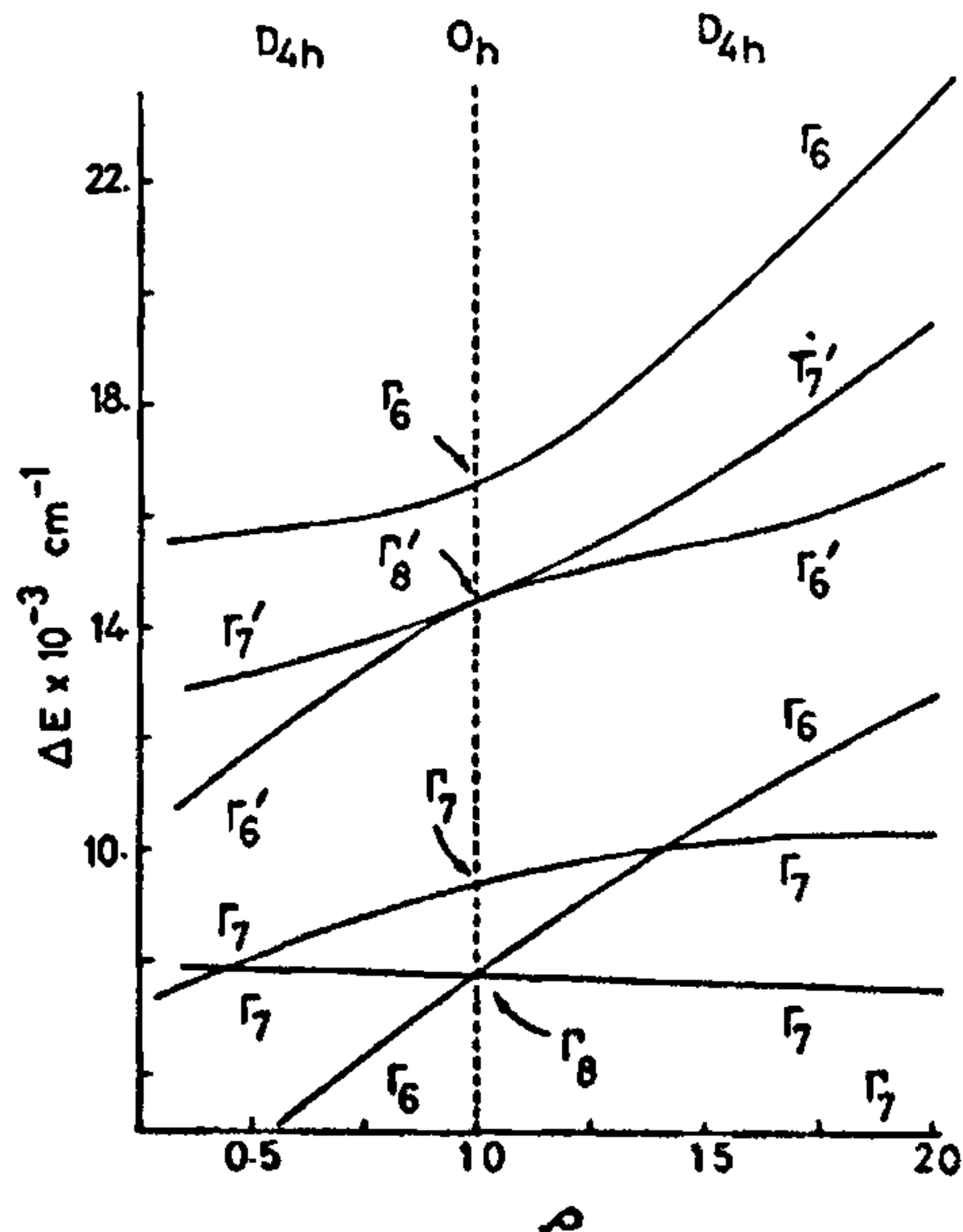


Figure 1. Transition energies of f^1 systems as a function of the extent of tetragonal distortion.

Table 2 Angular overlap parameters for some tetragonal complexes. (Values are in cm^{-1} .)

	Li_4NpO_5		Na_2NpO_4		Li_3UO_4	
	exp. ^a	calc. ^b	exp. ^a	calc. ^b	exp. ^a	calc. ^b
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8)$	6116	5987	8130	7796	4283	4328
$\Gamma_7 \rightarrow \Gamma_7$	8547	8856	9615	8603	7072	6844
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8)$	10363	9416	—	4429	4821	5016
$\Gamma_7 \rightarrow \Gamma'_6(\Gamma'_8)$	12210	13759	10310	10434	10386	{ 10343
$\Gamma_7 \rightarrow \Gamma'_7(\Gamma'_8)$	15152	15153	12500	12956		{ 10419
$\Gamma_7 \rightarrow \Gamma_6$	18700	18482	15150	15003	12647	12346
$e_\sigma(\text{eq}) =$	3408		3465		2498	
$e_\sigma(\text{ax}) =$	5919		764		3143	
$e_\pi(\text{eq}) =$	2532		3320		1800	
$e_\pi(\text{ax}) =$	4382		2100		2079	
$\xi =$	1785		1785		1625	

^{a,b}See footnote of table 1.

mental data and those obtained theoretically are in agreement with the expected trend $\text{Np}^{6+} > \text{U}^{5+}$. It is observed that the X_a method underestimates the e_π parameter in both UO_6^{7-} and NpO_6^{6-} .

Optical spectra of f^1 tetragonal complexes

The splitting pattern due to the symmetry descent $O_h \rightarrow D_4$ follows the scheme

$$\begin{aligned}\Gamma_7 &= \Gamma_7, \Gamma_8 = \Gamma_7 + \Gamma_6, \\ \Gamma'_8 &= \Gamma'_7 + \Gamma'_6 \text{ and } \Gamma_6 = \Gamma_6.\end{aligned}$$

From equations (1–6), it is clear that if the AOM is used to parametrize the optical transitions in D_4 systems, only five parameters including one effective spin-orbit coupling constant are required to describe the spectra (compare with the conventional ligand-field approach where six parameters are required to describe the transition energies¹³), even though it is difficult to extract reliable values for the AOM parameters from experimental transition energies. In order to get a qualitative estimate of these parameters we propose the following scheme. As a first step of approximation, we assume that the ratio $\rho = e_\sigma(\text{ax})/e_\sigma(\text{eq})$ will not be far from the $e_\pi(\text{ax})/e_\pi(\text{eq})$ ratio. In figure 1, a plot of the energies of the split levels of the f manifold as functions of ρ for the NpO_6^{6-} system characterized by the e_σ and e_π parameters previously obtained for $\text{Ba}_3\text{NpO}_6(O_h)$ is displayed. From the figure one finds that the first transition is always of the type $\Gamma_7 \rightarrow \Gamma_7$ for the case $\rho > 1$, but for the second transition one has the possibility of either $\Gamma_7 \rightarrow \Gamma_7$ or $\Gamma_7 \rightarrow \Gamma_6$ depending on the extent of distortion from the O_h symmetry. An interesting result is also evident from figure 1; the

ground state is of the Γ_6 type under the condition $\rho < 0.6$. The extent of distortion can also be judged from the difference $\Gamma'_7(\Gamma'_8) - \Gamma'_6(\Gamma'_8)$ observed experimentally while no crossing is expected between the $\Gamma'_7(\Gamma'_8)$ and $\Gamma'_6(\Gamma'_8)$ levels. For example, for Li_3UO_4 the $\Gamma_7 \rightarrow \Gamma'_7(\Gamma'_8)$ and $\Gamma_7 \rightarrow \Gamma'_6(\Gamma'_8)$ are observed experimentally (table 2) as one absorption peak at 10386 cm^{-1} , and we may conclude that the extent of distortion is weak. By utilizing a plot like figure 1, we can assign the different $f-f$ transitions of the tetragonal complexes, based on our estimate of the extent of distortion expected in the system under consideration. Then we can fit the observed energies with the AOM parameters. In this step the condition $e_\sigma(\text{ax})/e_\sigma(\text{eq}) = e_\pi(\text{ax})/e_\pi(\text{eq})$ can be relaxed. The above approach was performed for Li_3UO_4 , Li_4NpO_5 and Na_2NpO_4 systems, all of which are known to have MO_6^{n-} tetragonal structures⁹. The results of the fitting are given in table 2. The fitting was done using the complete AOM plus spin-orbit coupling matrices for the tetragonal case. The AOM parameters obtained in table 2 are in good agreement with the X-ray data¹⁴ for the compounds. In Li_4NpO_5 , the axial Np–O bond is shorter than the equatorial bonds; so it is expected that $e_\sigma(\text{ax}) > e_\sigma(\text{eq})$ and $e_\pi(\text{ax}) > e_\pi(\text{eq})$. Note that the reverse situation is observed in Na_2NpO_4 , where the axial Np–O bond is longer than the equatorial bonds.

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