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Systematics of hyperfine interactions in actinyl compounds (*)

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Résumé. — On présente les mesures des interactions hyperfines quadrupolaire et magnétique obtenues par spectroscopie Mössbauer dans les complexes (AnO₂)⁻ des actinides où An = U, Np, Pu, et dans (UO₂)⁺ avec An = Np, Pu, Am. A l’exception de l’interaction quadrupolaire dans les complexes (NpO₂)⁺ et (PuO₂)⁺ dont la configuration est 5f, les données sont interprétées à l’aide d’un modèle simple considérant l’addition d’électrons non liants à un noyau uranyle. Dans le cas des configurations 5f, le modèle prévoit un gradient de champ électrique trop grand d’un facteur environ trois par rapport au résultat expérimental.

Abstract. — Hyperfine interactions in several actinyl complexes are presented. The electric quadrupole and magnetic hyperfine interaction constants are calculated within a simple model whereby non-bonding electrons, perturbed by an axial crystal field, are added to a uranyl core. This approach provides reasonable agreement for all cases except the quadrupole interaction in 5f⁺ systems, where the measured values are about three times smaller than those calculated.

The electronic properties of the actinyl ions have been frequently discussed [1-3]. Although details of various models differ, especially with regard to the correct molecular orbitals in uranyl ions, the following results for the actinyls as a whole are generally accepted: the uranyl complex (UO₂)⁺⁺ contains twelve electrons which exactly fill the available bonding orbital. This then forms a core for other actinyl species, with the additional electrons falling into non-bonding orbitals. These electrons in turn are treated in a framework of Russell-Saunders coupling which is perturbed by the strong axial crystal-field interactions due to the axial oxygen ions. Crystalline field and ligand field effects with equatorial ions are considered to be much less influential than those with the axial ions.

At present the most extensive discussions have been with regard to (UO₂)⁺⁺ and (NpO₂)⁺⁺ complexes. Except for spectroscopic data, very little work is available which attempts to systematically discuss physical properties of a number of species [1-3]. Recently, Mössbauer effect measurements in U, Np, Pu and Am have made it possible to obtain hyperfine interaction data in the complexes (UO₂)⁺⁺, (NpO₂)⁺⁺, (PuO₂)⁺⁺ and (AmO₂)⁺⁺ [6-7]. These include the electronic configurations 5f⁺, n = 0 to 4, with the exception of n = 3, where data are not yet available. Representative data obtained at 4.2 K for the principal component of the electric field gradient tensor, eq, and for the magnetic hyperfine field, Hₚ, are given in table I. Elementary considerations for the calculation of these quantities, along with the tabulation of appropriate electronic parameters, have been given previously [6].

Within the framework for the actinyls discussed above, the electric field gradient can be written [6, 8]

\[ eq = eq_{\text{uranyl}} - ea \left( 3 J^2 - 2j(j + 1) \right) r^{-3} (1 - R_j) \]  

(1)

where eq_{uranyl} is the value observed in the uranyl ion, α, is a reduced matrix element, R_j = 0.35 is a Sternheimer factor, and (r⁻³) is a 5f electron radial average. At present, no calculation for eq_{uranyl} has been performed which both explains the observed magnitude as well as the sign of the interaction [9]. Therefore we must currently adopt this simply as an empirical value. Assuming a strong crystal field within a single J manifold, the crystal field ground states \(|J, J_z\rangle\) in the remaining cases are taken as \(|5/2, ±5/2\rangle\) for 5f, \(|4, ±4\rangle\) for 5f², and \(|4, 0\rangle\) for 5f⁴. In the last case, one requires J_z = 0 rather than J_z = ±J due to a change in the signs of the Stevens factors occurring in the crystal field Hamiltonian. The results of the calculations are shown in table I. The agreement is seen to be satisfactory in all cases except for the 5f² ions.

Magnetic hyperfine interactions are also seen in some cases (table I). The magnetic hyperfine field is given by

\[ H_p = [2 \mu_n N_f \langle r^{-3} \rangle + \chi (g_s - 1)] J_z \]  

(2)

The first term arises from the orbital momentum of electrons in unfilled valence shells, and the second term is due to polarization of the core electrons by the outer electrons. The quantity N_f is a reduced matrix element, and \(\chi\) is approximately a constant with the value -600 kOe. Calculated values are

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Table I. — Experimental and calculated values for the principal component of the electric field gradient tensor, $eq$, and the magnetic hyperfine field, $H_m$, in various actinyl ions.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ion</th>
<th>Measured $eq$ (10$^5$ V/cm$^2$)</th>
<th>Calculated $eq$ (10$^5$ V/cm$^2$)</th>
<th>Measured $H_m$ (kOe)</th>
<th>Calculated $H_m$ (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5f^0$</td>
<td>(UO$_2$)$^+$</td>
<td>7.7</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$5f^1$</td>
<td>(NpO$_2$)$^{''}$</td>
<td>12.0</td>
<td>11.0</td>
<td>2 500</td>
<td>3 000</td>
</tr>
<tr>
<td>$5f^2$</td>
<td>(NpO$_2$)$^{''}$</td>
<td>4.7</td>
<td>10.8</td>
<td>6 000</td>
<td>5 100</td>
</tr>
<tr>
<td>$5f^3$</td>
<td>(PuO$_2$)$^{''}$</td>
<td>4.1</td>
<td>11.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$5f^4$</td>
<td>(AmO$_2$)$^+$</td>
<td>9.5</td>
<td>8.7</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

given in table I. For the $5f^1$ and $5f^2$ configurations, $|J_z|$ was estimated using $g$ values measured by EPR [10, 11]. The hyperfine field vanishes for the $5f^0$ ions due to the filled f shell. Similarly one has $H_m = 0$ for the $5f^0$ case since the crystal field establishes a $J_z = 0$ ground state.

From an investigation of table I, one sees that in general the simple approach described here reproduces the observed hyperfine interactions to within 15%. The predominant exception is the case of $5f^2$ ions. Here the calculated magnetic hyperfine field is acceptable, while the calculated quadrupole interaction is about three times larger than that observed. This does not appear to be an experimental error, since the same value is obtained both for (NpO$_2$)$^+$ and (PuO$_2$)$^{''}$ complexes. While it is admitted that the approach taken here is very simple, the agreement in all other cases speaks for its essential correctness. Therefore the inadequacy of the calculation in this one isolated case is not presently understood. The most likely explanation is that the assumption of a purely axial crystal field with only the ground state occupied is inadequate.

References