Quadrupole antishielding factors for actinide ions

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Perturbation-numerical calculations have been performed using nonrelativistic Hartree-Fock-Slater wave functions to obtain the Sternheimer quadrupole antishielding factor γ_∞ for all the tetrapositive ions in the actinide series ($90 \le Z \le 103$). For these ions, the nonrelativistic γ_∞ values seem to be constant at ~ -95. It is estimated that the relativistic effects would increase the $|\gamma_\infty|$ value by ~65%.

The repercussions of the induced effects in the core electrons, respectively due to the external point charges and the valence electrons on the total electric field gradient q_{total} acting at the nuclear site, were first represented by Sternheimer[1] as

$$q_{\text{total}} = (1-\gamma_\infty) q_{\text{ion}} + (1-R) q_{\text{valence}}, \tag{1}$$

where q_{ion} and q_{valence} define the electric field gradient due to the external point charges and the valence electrons respectively. The constants γ_∞ and R are commonly known as Sternheimer antishielding (or shielding) factors.

During recent years a few nuclear quadrupole coupling data on actinide nuclei ($90 \leqslant Z \leqslant 103$) have become available, mainly through Mössbauer-effect[2] and atomic-beam magnetic-resonance[3] experiments. In the interpretation of such data it is essential to have a knowledge of reliable theoretical values of Sternheimer antishielding factors, corresponding to the atom or ion under investigation. In this paper we report the results of our perturbation-numerical calculations of γ_∞ for all tetrapositive actinide ions using nonrelativistic Hartree-Fock-Slater[4] (HFS) wave functions for the unperturbed state. In view of the fact that the elements in the actinide series occur in several valence states we have also calculated γ_∞ values for U^{3+}, U^{5+}, U^{6+}, and Am^{2+} ions.

The perturbed radial functions $u_1'(nl \to l')$ were obtained by directly solving the following nuclear moment-perturbed Schrödinger equation[1]:

$$\left(-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0(r) - E\right) u_1'(nl \to l') = u_0'(nl)\left(\frac{1}{r^3} - \left\langle\frac{1}{r^3}\right\rangle_{nl} \delta_{ll'}\right). \tag{2}$$

Excluding the consistency and correlation effects,[5] the quadrupole antishielding factor γ_∞ is given to zeroth order by

$$\gamma_\infty = \sum_{nl} c(nl \to l') \int_0^\infty u_0'(nl) u_1'(nl \to l') r^2\, dr. \tag{3}$$

The constants $c(nl \to l')$ involving angular integrals have been tabulated by Sternheimer.[6] For each ion, the coefficients corresponding to the perturbations of the $5f$ orbital were multiplied by the fraction to which the $5f$ orbital is occupied. All calculations were carried out by a method reported earlier[7] using the IBM 7044/1401 system at the Indian Institute of Technology, Kanpur.

TABLE I. Nonrelativistic total γ_∞ values to zeroth order for the ions in actinide series ($90 \le Z \le 103$). The electronic configuration considered in each case is shown in column 2.

Ion	Config. (Rn)−	Present calc.	Other calcs.
$_{90}Th^{4+}$	$5f^0$	−107.170	−177.5 [a]
$_{91}Pa^{4+}$	$5f^1$	−105.325	
$_{92}U^{3+}$	$5f^3$	−117.987	
$_{92}U^{4+}$	$5f^2$	−103.805	
$_{92}U^{5+}$	$5f^1$	−95.530	
$_{92}U^{6+}$	$5f^0$	−85.155	−143.9 [a]
$_{93}Np^{4+}$	$5f^3$	−102.170	
$_{94}Pu^{4+}$	$5f^4$	−100.970	
$_{95}Am^{2+}$	$5f^7$	−132.867	−137.3 [b]
$_{95}Am^{4+}$	$5f^5$	−99.786	
$_{96}Cm^{4+}$	$5f^6$	−98.842	
$_{97}Bk^{4+}$	$5f^7$	−97.985	
$_{98}Cf^{4+}$	$5f^8$	−96.890	
$_{99}E^{4+}$	$5f^9$	−96.47	
$_{100}Fm^{4+}$	$5f^{10}$	−96.40	
$_{101}Md^{4+}$	$5f^{11}$	−95.417	
$_{102}No^{4+}$	$5f^{12}$	−95.210	
$_{103}Lw^{4+}$	$5f^{13}$	−94.211	

[a] Reference 9.
[b] Reference 8.

Our results are given in Table I along with the earlier available[8,9] results for purposes of comparison. Sternheimer[8] calculated $\gamma_\infty = -137$ for Am^{2+} by using HFS wave functions corresponding to the neutral atom. He had predicted that the use of actual ionic wave functions for Am^{2+} should reduce $|\gamma_\infty|$ by ~5%. The present value of $\gamma_\infty = -133$ confirms this prediction. Feiock and Johnson[9] have performed uncoupled calculations similar to those of ours using relativistic HFS wave functions and obtained γ_∞ as -177.5 and -143.9 for Th^{4+} and U^{6+} ions, respectively. A comparison of these values with the present nonrelativistic values show that the relativistic effects increase $|\gamma_\infty|$ by ~65% and ~69% for Th^{4+} and U^{6+} ions, respectively. The present nonrelativistic γ_∞ values, however, appear to be constant and ~ -95 for the tetrapositive ions in the actinide series.

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