Hyperfine Structure in $^{229g}Th^{3+}$ as a Probe of the $^{229g}Th \rightarrow {}^{229m}Th$ Nuclear Excitation Energy

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We identify a potential means to extract the $^{229g}Th \rightarrow {}^{229m}Th$ nuclear excitation energy from precision microwave spectroscopy of the $5F_{5/2,7/2}$ hyperfine manifolds in the ion $^{229g}Th^{3+}$. The hyperfine interaction mixes this ground fine structure doublet with states of the nuclear isomer, introducing small but observable shifts to the hyperfine sublevels. We demonstrate how accurate atomic structure calculations may be combined with the measurement of the hyperfine intervals to quantify the effects of this mixing. Further knowledge of the magnetic dipole decay rate of the isomer, as recently reported, allows an indirect determination of the nuclear excitation energy.

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Thorium-229 is extraordinary among nuclei in that it possesses an isomer state ^{229m}Th lying within several eV of its ground state ^{229g}Th. The anomalously small nuclear excitation frequency is predicted to be within range of modern lasers, opening the door to a number of scientific possibilities. Proposed clocks based on this transition hold promise for unprecedented metrological performance, as the compact nuclear charge distribution (relative to the electron cloud in an atom) renders the ultranarrow transition frequency largely insusceptible to environmental influences [1–5]. Moreover, such a nuclear clock could be a valuable instrument for testing stability of fundamental constants, including the fine structure constant α, as the "accidental" near degeneracy of the two nuclear states (relative to typical nuclear energy scales) renders the transition frequency highly sensitive to fundamental constant variation [6]. Further still, it has been suggested that this transition could be used to realize a novel nuclear-based laser [7].

Presently, the nuclear excitation energy Δ_{nuc} has only been determined indirectly through differencing schemes, using γ radiation observed following α decay of ^{233}U into ^{229}Th. More than two decades ago, Reich and Helmer [8,9] deduced the result -1 ± 4 eV, following this a few years later with the refined value 3.5 ± 1 eV. After another decade, Barci *et al.* [10] and Guimarães-Filho and Helene [11] reported the results 3.4 ± 1.8 eV and 5.5 ± 1 eV, respectively. Finally, Beck *et al.* [12,13] presented the result 7.6 ± 0.5 eV, which they later modified slightly to 7.8 ± 0.5 eV. While the most recent value of Beck *et al.* is now largely accepted by the community, the large discrepancy with earlier results is not well understood. In a critique of the above works, however, Sakharov [14] suggested that the literature values suffer from systematic errors and underestimated uncertainties, further clouding precise knowledge of Δ_{nuc}. New, independent means of determining Δ_{nuc} could prove invaluable for efforts towards the laser excitation of the nucleus [2,3,15,16], either by providing improved results or through corroboration or dismissal of existing literature values.

In this Letter, we identify a potential means to extract Δ_{nuc} from precision microwave spectroscopy of the $5F_{5/2,7/2}$ hyperfine manifolds in the ion $^{229g}Th^{3+}$ (see Fig. 1). The proposed method further relies on capabilities

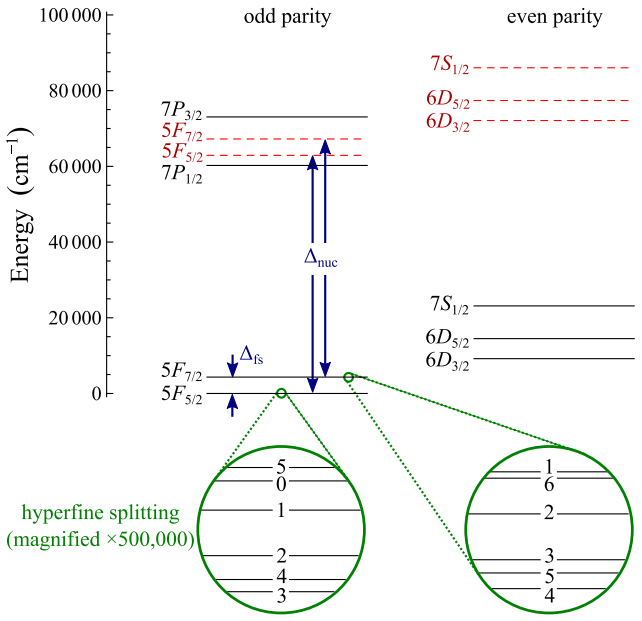

FIG. 1 (color online). Energy levels of $^{229}Th^{3+}$, including nuclear and electronic excitations. Solid-black and red-dashed lines distinguish levels associated with the ground and isomer nuclear states, ^{229g}Th ($I^\pi = \frac{5}{2}^+$) and ^{229m}Th ($I^\pi = \frac{3}{2}^+$), respectively. Hyperfine manifolds of the ground fine structure doublet are magnified, with sublevels labeled according to the total angular momentum F, where $|I - J| \leq F \leq I + J$. Hyperfine mixing between like-parity states has small but observable effects on these hyperfine manifolds, with the magnitude of mixing being dependent on level separation (e.g., Δ_{fs} and Δ_{nuc}). For the purpose of illustration, a nuclear excitation energy of $\Delta_{\mathrm{nuc}} = 7.8$ eV is assumed here.

of state-of-the-art atomic structure calculations for this system [17] as well as knowledge of the $^{229m}\mathrm{Th} \rightarrow {}^{229g}\mathrm{Th}$ magnetic dipole nuclear decay rate [18]. Campbell *et al.* [15] have demonstrated laser cooling of $^{229g}\mathrm{Th}^{3+}$ within a linear Paul trap and, furthermore, spectroscopically resolved $5F_{5/2,7/2}$ and $6D_{3/2,5/2}$ hyperfine sublevels. Their measurement precision was sufficient to deduce hyperfine constants A and B for all four states, though the optical spectroscopy employed ($5F_{5/2,7/2} \rightarrow 6D_{3/2,5/2}$) did not fully benefit from the long-lived nature of the $5F_{5/2,7/2}$ states, which makes the hyperfine intervals of these two states amenable to very high-precision microwave spectroscopy. In Ref. [17], it is argued that such measurements would not only be capable of yielding much-improved A and B constants, but also of revealing additional constants in the hierarchy of hyperfine constants. In principle, five constants are required to fully characterize the five intervals in each hyperfine manifold (refer to Fig. 1).

The hyperfine interaction accounts for electromagnetic coupling of atomic electrons with the nucleus, beyond that of the dominant electric monopole (Coulomb) interaction. Decomposed into multipolar contributions, the hyperfine interaction reads $V_{\mathrm{hfi}} = \sum_k \mathcal{M}^{(k)} \cdot \mathcal{T}^{(k)}$, where $\mathcal{M}^{(k)}$ and $\mathcal{T}^{(k)}$ are rank-k tensor operators acting in the nuclear and electronic subspaces, respectively, and the intervening dot signifies a scalar product. Expressions for $\mathcal{M}^{(k)}$ and $\mathcal{T}^{(k)}$ may be found, for example, in Refs. [19–22]. The summation runs over positive integers k, with terms ascending in k describing magnetic dipole ($M1$), electric quadrupole ($E2$), magnetic octupole ($M3$), electric hexadecapole ($E4$), etc., multipolar interactions. Hyperfine constants A, B, C, D, etc., quantify the effect of the respective interactions to first order. Following conventional definitions [19,21], hyperfine constants of the $5F_{5/2,7/2}$ states in $^{229g}\mathrm{Th}^{3+}$ read

$$
\begin{aligned}
A_{5/2} &\equiv \frac{2}{105}\mathcal{M}^{(1)}_{\downarrow\downarrow}\mathcal{T}^{(1)}_{\downarrow\downarrow}, \\
A_{7/2} &\equiv \frac{1}{21\sqrt{15}}\mathcal{M}^{(1)}_{\downarrow\downarrow}\mathcal{T}^{(1)}_{\uparrow\uparrow}, \\
B_{5/2} &\equiv \frac{5}{21}\mathcal{M}^{(2)}_{\downarrow\downarrow}\mathcal{T}^{(2)}_{\downarrow\downarrow}, \\
B_{7/2} &\equiv \frac{1}{3\sqrt{2}}\mathcal{M}^{(2)}_{\downarrow\downarrow}\mathcal{T}^{(2)}_{\uparrow\uparrow}, \\
C_{5/2} &\equiv \frac{5}{252}\mathcal{M}^{(3)}_{\downarrow\downarrow}\mathcal{T}^{(3)}_{\downarrow\downarrow}, \\
C_{7/2} &\equiv \frac{1}{12}\sqrt{\frac{5}{66}}\mathcal{M}^{(3)}_{\downarrow\downarrow}\mathcal{T}^{(3)}_{\uparrow\uparrow}, \\
D_{5/2} &\equiv \frac{1}{252}\mathcal{M}^{(4)}_{\downarrow\downarrow}\mathcal{T}^{(4)}_{\downarrow\downarrow}, \\
D_{7/2} &\equiv \frac{1}{36\sqrt{22}}\mathcal{M}^{(4)}_{\downarrow\downarrow}\mathcal{T}^{(4)}_{\uparrow\uparrow},
\end{aligned}
\tag{1}
$$

where $\mathcal{M}^{(k)}_{ij} \equiv \langle i||\mathcal{M}^{(k)}||j\rangle$ and $\mathcal{T}^{(k)}_{ij} \equiv \langle i||\mathcal{T}^{(k)}||j\rangle$ are reduced matrix elements with associations $|\downarrow\rangle = |^{229g}\mathrm{Th}\rangle$, $|\uparrow\rangle = |^{229m}\mathrm{Th}\rangle$ for the nuclear subspace and $|\downarrow\rangle = |5F_{5/2}\rangle$, $|\uparrow\rangle = |5F_{7/2}\rangle$ for the electronic subspace. Diagonal nuclear matrix elements appearing here are proportional to magnetic dipole $\mu \propto \mathcal{M}^{(1)}_{\downarrow\downarrow}$, electric quadrupole $Q \propto \mathcal{M}^{(2)}_{\downarrow\downarrow}$, magnetic octupole $\Omega \propto \mathcal{M}^{(3)}_{\downarrow\downarrow}$, and electric hexadecapole $\Pi \propto \mathcal{M}^{(4)}_{\downarrow\downarrow}$ moments of the $^{229g}\mathrm{Th}$ nucleus.

In principle, hyperfine constants may be determined spectroscopically by taking appropriate linear combinations of measured hyperfine energy intervals. However, spectroscopy does not differentiate between first order effects of the hyperfine interaction and all higher order effects, and for high-precision measurements it becomes necessary to distinguish *spectroscopic*, or "uncorrected," hyperfine constants from lowest order, or "corrected," hyperfine constants. While this distinction is only relevant at the ppm level for A and B constants, it becomes essential for the C and D constants, as second order $M1$-$M1$, $M1$-$E2$, or $E2$-$E2$ shifts to hyperfine sublevels may be comparable to the first order $M3$ or $E4$ shifts. In the remainder, a tilde is used to distinguish spectroscopic hyperfine constants $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$, as determined from the hyperfine intervals, from their lowest order counterparts, given by Eq. (1).

We illustrate the influence of higher order effects by initially focusing on the $\tilde{D}$ constants, writing each as the sum of the three terms

$$
\tilde{D}_J = D_J + D'_J + d'_J, \tag{2}
$$

where D_J is given by Eq. (1), D'_J includes dominant second order contributions, and d'_J subsumes all remaining higher order contributions. General angular considerations prohibit second order $M1$-$M1$ and $M1$-$E2$ effects from entering the $\tilde{D}$ constants [19], limiting the D'_J here to $E2$-$E2$ contributions. For the $5F_J$ state, we explicitly consider contributions attributed to mixing with (i) the neighboring $5F_{J'}$ state, (ii) the $5F_J$ state of the isomer, and (iii) the $5F_{J'}$ state of the isomer. The three contributions are proportional to $\Delta_{\mathrm{fs}}^{-1}$, $\Delta_{\mathrm{nuc}}^{-1}$, and $(\Delta_{\mathrm{nuc}} \pm \Delta_{\mathrm{fs}})^{-1}$, respectively, where Δ_{fs} is the fine structure splitting. For the third term, we take $(\Delta_{\mathrm{nuc}} \pm \Delta_{\mathrm{fs}})^{-1} \rightarrow \Delta_{\mathrm{nuc}}^{-1}$, as is valid in the limit $\Delta_{\mathrm{fs}} \ll \Delta_{\mathrm{nuc}}$; formally, the omitted part in this substitution is absorbed by the residual term d'_J. From a second order analysis, the contributions read

$$
\begin{aligned}
D'_{5/2} &\equiv \frac{\left|\mathcal{M}^{(2)}_{\downarrow\downarrow}\mathcal{T}^{(2)}_{\downarrow\uparrow}\right|^2}{20580\Delta_{\mathrm{fs}}} + \frac{\left|\mathcal{M}^{(2)}_{\downarrow\uparrow}\mathcal{T}^{(2)}_{\downarrow\downarrow}\right|^2}{3430\Delta_{\mathrm{nuc}}} - \frac{4\left|\mathcal{M}^{(2)}_{\downarrow\uparrow}\mathcal{T}^{(2)}_{\downarrow\uparrow}\right|^2}{46305\Delta_{\mathrm{nuc}}}, \\
D'_{7/2} &\equiv -\frac{\left|\mathcal{M}^{(2)}_{\downarrow\downarrow}\mathcal{T}^{(2)}_{\downarrow\uparrow}\right|^2}{2940\Delta_{\mathrm{fs}}} + \frac{\left|\mathcal{M}^{(2)}_{\downarrow\uparrow}\mathcal{T}^{(2)}_{\uparrow\uparrow}\right|^2}{2205\Delta_{\mathrm{nuc}}} - \frac{4\left|\mathcal{M}^{(2)}_{\downarrow\uparrow}\mathcal{T}^{(2)}_{\downarrow\uparrow}\right|^2}{6615\Delta_{\mathrm{nuc}}}.
\end{aligned}
$$

Introducing the off-diagonal hyperfine constant $B_{\mathrm{o.d.}} \equiv (5/36)\mathcal{M}^{(2)}_{\downarrow\downarrow}\mathcal{T}^{(2)}_{\downarrow\uparrow}$ and the dimensionless parameter

$$
\eta_k \equiv \frac{\mathcal{M}^{(k)}_{\downarrow\uparrow}/\mathcal{M}^{(k)}_{\downarrow\downarrow}}{\sqrt{\Delta_{\mathrm{nuc}}/\Delta_{\mathrm{fs}}}}, \tag{3}
$$

these expressions may be recast as

$$D'_{5/2} = \frac{3[72B^2_{\mathrm{o.d.}} + 147\eta_2^2 B^2_{5/2} - 128\eta_2^2 B^2_{\mathrm{o.d.}}]}{85750\Delta_{\mathrm{fs}}},$$
$$D'_{7/2} = \frac{2[-54B^2_{\mathrm{o.d.}} + 25\eta_2^2 B^2_{7/2} - 96\eta_2^2 B^2_{\mathrm{o.d.}}]}{6125\Delta_{\mathrm{fs}}}. \quad (4)$$

Note that the influence of the isomer state is contained within the parameter η_2.

Estimating the terms D_J and D'_J requires nuclear and electronic matrix elements, as well as the energy differences Δ_{fs} and Δ_{nuc}. Table I compiles the relevant properties, with values taken or inferred from the literature where available. Also included are present *ab initio* theoretical electronic matrix elements. The method starts by solving the self-consistent, fully relativistic Dirac-Hartree-Fock equations and includes important correlation corrections of the Brueckner orbital and random phase approximation type in the calculation of matrix elements (see, e.g., Refs. [20,30]). For diagonal rank-1 and rank-2 matrix elements, the present results may be compared with recent coupled-cluster results given by Safronova *et al.* [17], which include a more extensive treatment of correlation effects [31]. From Table I, contributions to the $\tilde{D}$ constants are estimated to be (in units of Hz) [32]

$$D_{5/2} \approx 0.6,$$
$$D'_{5/2} \approx 5 + 4\left(\frac{\eta_2}{0.15}\right)^2,$$
$$D_{7/2} \approx 3,$$
$$D'_{7/2} \approx -36 + 8\left(\frac{\eta_2}{0.15}\right)^2, \quad (5)$$

where entries in Table I yield values of η_2 spanning from 0.03 to 0.15. From the estimates given here, it is evident that higher order effects are non-negligible for the $\tilde{D}$ constants. Residual terms d'_J are further estimated to be suppressed by more than an order of magnitude relative to the respective D'_J.

In hypothetical absence of higher order effects, experimental $\tilde{D}$ constants could be readily combined with theoretical matrix elements to extract the nuclear hexadecapole moment $\Pi \propto \mathcal{M}^{(4)}_{\downarrow\downarrow}$, similar to what has been done for nuclear dipole and quadrupole moments using $\tilde{A}$ and $\tilde{B}$ constants [15,17]. The availability of two constants, $\tilde{D}_{5/2}$ and $\tilde{D}_{7/2}$, would provide a degree of redundancy for this process. In the actual case—wherein second order effects are not absent or negligible—the "extra" constant provides an opportunity to suppress uncertainty in Π resulting from these additional contributions. Hyperfine constants $B_{5/2}$ and $B_{7/2}$ appearing in Eq. (4) may be determined to high precision with microwave spectroscopy (recall, $B = \tilde{B}$ at the ppm level), while the off-diagonal constant $B_{\mathrm{o.d.}}$ can be expressed in terms of $B_{5/2}$ or $B_{7/2}$,

TABLE I. Nuclear and electronic properties contributing to spectroscopic (i.e., uncorrected) hyperfine constants $\tilde{C}_{5/2}$, $\tilde{C}_{7/2}$, $\tilde{D}_{5/2}$, and $\tilde{D}_{7/2}$. Many entries should be regarded as estimates only. Here e is the elementary charge, μ_N the nuclear magneton, and b the barn unit of area. Reference "p" denotes present *ab initio* theoretical electronic matrix elements (see text). Respective values of Δ_{nuc} correspond to 3.5(10), 3.4(18), 5.5(10), and 7.8(5) in units of eV.

Property (unit)		Values	References
	Nuclear properties		
$\mathcal{M}_1^{\downarrow\downarrow}$	(μ_N)	1.3(1), 1.04(2)	[23,17]
$\mathcal{M}_2^{\downarrow\downarrow}$	(eb)	6.45[a], 6.4(1)	[24,17]
$\mathcal{M}_3^{\downarrow\downarrow}$	(μ_Nb)	0.43[b]	
$\mathcal{M}_4^{\downarrow\downarrow}$	(eb^2)	1.4[a]	[24]
$\lvert\mathcal{M}_1^{\downarrow\uparrow}\rvert$[c]	(μ_N)	1.2, 0.85, 0.65	[25,10,26]
$\mathcal{M}_2^{\downarrow\uparrow}$	(eb)	0.80, 2.4	[10,26]
Δ_{nuc}	(10^{15} Hz)	0.8(2), 0.8(4), 1.3(2), 1.9(1)	[9,10,11,13]
	Electronic properties		
$\mathcal{T}_1^{\downarrow\downarrow}$	(10^9 Hz/μ_N)	4.15, 3.71	[17,p]
$\mathcal{T}_1^{\uparrow\uparrow}$	(10^9 Hz/μ_N)	2.42, 2.29	[17,p]
$\mathcal{T}_1^{\downarrow\uparrow}$	(10^9 Hz/μ_N)	1.13	[p]
$\mathcal{T}_2^{\downarrow\downarrow}$	(10^9 Hz/eb)	1.49, 1.47	[17,p]
$\mathcal{T}_2^{\uparrow\uparrow}$	(10^9 Hz/eb)	1.67, 1.73	[17,p]
$\mathcal{T}_2^{\downarrow\uparrow}$	(10^9 Hz/eb)	0.58	[p]
$\mathcal{T}_3^{\downarrow\downarrow}$	(10^3 Hz/μ_Nb)	15	[p]
$\mathcal{T}_3^{\uparrow\uparrow}$	(10^3 Hz/μ_Nb)	−12	[p]
$\mathcal{T}_4^{\downarrow\downarrow}$	(10^3 Hz/eb^2)	0.10	[p]
$\mathcal{T}_4^{\uparrow\uparrow}$	(10^3 Hz/eb^2)	0.31	[p]
Δ_{fs}	(10^{15} Hz)	0.129 682	[27]

[a]Inferred from intrinsic quadrupole and hexadecapole moments.
[b]From the theoretical value for ^{233}U [28].
[c]See note [29].

$$B_{\mathrm{o.d.}} = \frac{7}{12}\left(\frac{\mathcal{T}^{(2)}_{\downarrow\uparrow}}{\mathcal{T}^{(2)}_{\downarrow\downarrow}}\right)B_{5/2} = \frac{5}{6\sqrt{2}}\left(\frac{\mathcal{T}^{(2)}_{\downarrow\uparrow}}{\mathcal{T}^{(2)}_{\uparrow\uparrow}}\right)B_{7/2},$$

such that evaluation of $B_{\mathrm{o.d.}}$ is limited by theoretical uncertainty in the ratio $\mathcal{T}^{(2)}_{\downarrow\uparrow}/\mathcal{T}^{(2)}_{\downarrow\downarrow}$ or $\mathcal{T}^{(2)}_{\downarrow\uparrow}/\mathcal{T}^{(2)}_{\uparrow\uparrow}$. Using coupled-cluster techniques with empirical scaling, Safronova *et al.* [17] have demonstrated an evaluation of the diagonal matrix elements $\mathcal{T}^{(2)}_{\downarrow\downarrow}$ and $\mathcal{T}^{(2)}_{\uparrow\uparrow}$ to ~1%, and a similar accuracy could be expected for the above ratios. Moreover, the two expressions for $B_{\mathrm{o.d.}}$ allow separate evaluations and a further assessment of accuracy. With $B_{5/2}$, $B_{7/2}$, and $B_{\mathrm{o.d.}}$ known, an appropriate linear combination of $\tilde{D}_{5/2}$ and $\tilde{D}_{7/2}$ may be chosen to eliminate terms in Eq. (4) proportional to the poorly known factor η_2^2. Given theoretical values for $\mathcal{T}^{(4)}_{\downarrow\downarrow}$ and $\mathcal{T}^{(4)}_{\uparrow\uparrow}$, one may then solve the resulting expression for $\Pi \propto \mathcal{M}^{(4)}_{\downarrow\downarrow}$.

Perhaps a more intriguing prospect than obtaining Π is the alternative: combining $\tilde{D}_{5/2}$ and $\tilde{D}_{7/2}$ to solve for η_2, as this parameter contains information about the nuclear isomer state, ^{229m}Th. Taken in conjunction, Eqs. (2) and (4) yield an analytic solution for η_2 independent of the hexadecapole moment [29],

$$\eta_2 = \sqrt{2\frac{42875\Delta_{\mathrm{fs}}X - 108B_{\mathrm{o.d.}}^2(7\rho_D+1)}{441B_{5/2}^2 - 700\rho_D B_{7/2}^2 + 384B_{\mathrm{o.d.}}^2(7\rho_D-1)}},$$
$$X = (\tilde{D}_{5/2} - d'_{5/2}) - \rho_D(\tilde{D}_{7/2} - d'_{7/2}), \quad (6)$$

where $\rho_D \equiv D_{5/2}/D_{7/2} = (\sqrt{22}/7)(\mathcal{T}^{(4)}_{\downarrow\downarrow}/\mathcal{T}^{(4)}_{\uparrow\uparrow})$. Borrowing values from Table I, we estimate that η_2 could potentially be determined to ~5% using Eq. (6). To arrive at this conclusion, we ascribed plausible uncertainties to parameters on the right-hand side of Eq. (6), assuming their precise evaluation with microwave spectroscopy and state-of-the-art theoretical techniques (e.g., Ref. [17]). Namely, we assumed uncertainties of ~1% for $B_{\mathrm{o.d.}}$, ~20% for ρ_D, and ~1% for $(\tilde{D}_J - d'_J)$. Uncertainty propagation into η_2 was tracked by Monte Carlo evaluation of Eq. (6) with normally distributed parameters. While a ~5% evaluation of η_2 is deemed a distinct possibility, we stress that accuracy at this level is not assured, even with the assumed uncertainties. For example, whereas a quasiparticle-plus-phonon model calculation predicts 2.4 eb for $\mathcal{M}^{(2)}_{\downarrow\uparrow}$, a semiempirical analysis predicts 0.80 eb (see Table I). Relative to the former, the latter value implies an order-of-magnitude reduction in the signal provided by η_2^2, with a corresponding reduction in the accuracy to which η_2 may be determined. Acknowledging the possibility of a larger $\mathcal{M}^{(2)}_{\downarrow\uparrow}$, on the other hand, suggests potentially better resolution of η_2.

In analogy to the $\tilde{D}$ constants, the $\tilde{C}$ constants are likewise split into three terms,

$$\tilde{C}_J = C_J + C'_J + c'_J, \quad (7)$$

where C_J is given by Eq. (1), C'_J includes dominant second order contributions, and c'_J subsumes residual higher order contributions. For $\tilde{C}$ constants, second order $M1$-$E2$ contributions emerge along with $E2$-$E2$ contributions, while $M1$-$M1$ contributions remain absent from angular considerations [19]. Written analogously to Eq. (4), the dominant second order contributions are

$$C'_{5/2} = \frac{3}{49000\Delta_{\mathrm{fs}}}[2100\sqrt{3}A_{\mathrm{o.d.}}B_{\mathrm{o.d.}} - 792B_{\mathrm{o.d.}}^2 + 3675\sqrt{14}\eta_1\eta_2 A_{5/2}B_{5/2} + 147\eta_2^2B_{5/2}^2 - 700\sqrt{42}\eta_1\eta_2 A_{\mathrm{o.d.}}B_{\mathrm{o.d.}} - 352\eta_2^2B_{\mathrm{o.d.}}^2],$$
$$C'_{7/2} = \frac{1}{7000\Delta_{\mathrm{fs}}}[-3150\sqrt{3}A_{\mathrm{o.d.}}B_{\mathrm{o.d.}} - 324B_{\mathrm{o.d.}}^2 + 2625\sqrt{14}\eta_1\eta_2 A_{7/2}B_{7/2} + 50\eta_2^2B_{7/2}^2 - 1050\sqrt{42}\eta_1\eta_2 A_{\mathrm{o.d.}}B_{\mathrm{o.d.}} + 144\eta_2^2B_{\mathrm{o.d.}}^2], \quad (8)$$

where we have introduced the off-diagonal constant $A_{\mathrm{o.d.}} \equiv (1/21)\sqrt{2/5}\mathcal{M}^{(1)}_{\downarrow\downarrow}\mathcal{T}^{(1)}_{\downarrow\uparrow}$ and where η_1 is defined by Eq. (3). From Table I, contributions to the $\tilde{C}$ constants are estimated to be (in units of Hz) [32]

$$C_{5/2} \approx 130,$$
$$C_{7/2} \approx -120,$$
$$C'_{5/2} \approx -70 + 60\left(\frac{\eta_1}{0.46}\right)\left(\frac{\eta_2}{0.15}\right) + 7\left(\frac{\eta_2}{0.15}\right)^2,$$
$$C'_{7/2} \approx -200 + 20\left(\frac{\eta_1}{0.46}\right)\left(\frac{\eta_2}{0.15}\right) + 9\left(\frac{\eta_2}{0.15}\right)^2, \quad (9)$$

where entries in Table I yield values of $|\eta_1|$ spanning from 0.13 to 0.46. The hyperfine constants $A_{5/2}$ and $A_{7/2}$ in Eq. (8) may be determined to high precision with microwave spectroscopy, while $A_{\mathrm{o.d.}}$ satisfies

$$A_{\mathrm{o.d.}} = \sqrt{\frac{5}{2}}\left(\frac{\mathcal{T}^{(1)}_{\downarrow\uparrow}}{\mathcal{T}^{(1)}_{\downarrow\downarrow}}\right)A_{5/2} = \sqrt{6}\left(\frac{\mathcal{T}^{(1)}_{\downarrow\uparrow}}{\mathcal{T}^{(1)}_{\uparrow\uparrow}}\right)A_{7/2}.$$

Safronova *et al.* [17] have demonstrated ~1% evaluation of $\mathcal{T}^{(1)}_{\downarrow\downarrow}$ and $\mathcal{T}^{(1)}_{\uparrow\uparrow}$, and a similar accuracy could be expected for the ratios appearing here. Equations (7) and (8) may be combined to yield a solution for η_1 dependent upon $C_{5/2}$ and $C_{7/2}$ only through the ratio $\rho_C \equiv C_{5/2}/C_{7/2} = (1/7)\sqrt{110/3}(\mathcal{T}^{(3)}_{\downarrow\downarrow}/\mathcal{T}^{(3)}_{\uparrow\uparrow})$ and, thus, independent of the nuclear octupole moment $\Omega \propto \mathcal{M}^{(3)}_{\downarrow\downarrow}$. The resulting analytic solution is lengthy and is not presented here. Borrowing values from Table I and taking plausible uncertainties of ~1% for $A_{\mathrm{o.d.}}$, ~20% for ρ_C, and ~1% for $(\tilde{C}_J - c'_J)$, assuming their evaluation with microwave spectroscopy and state-of-the-art theoretical techniques, we find that η_1 can potentially be determined to ~20%.

Zhao *et al.* [18] recently reported an observation of $^{229m}\mathrm{Th} \rightarrow {}^{229g}\mathrm{Th}$ nuclear relaxation with a lifetime $\tau = 8.7 \pm 1.4$ hr, attributing the mechanism to radiative decay while ruling out internal conversion. We note that this result has been met with some skepticism [33]. Radiative decay is dominated by the $M1$ multipolar channel [22], with the decay rate depending on the off-diagonal matrix element $\mathcal{M}^{(1)}_{\downarrow\uparrow}$, as well as Δ_{nuc}. Expressed in terms of η_1 in favor of $\mathcal{M}^{(1)}_{\downarrow\uparrow}$, this rate reads [22,34] $\tau^{-1} = (14/5)\hbar^{-4}c^{-3}\Delta_{\mathrm{fs}}^{-1}\Delta_{\mathrm{nuc}}^4\eta_1^2\mu^2$, where $\hbar$ is the reduced Planck constant and c is the speed of light. Rearranging for Δ_{nuc}, this expression gives the proportionality relation $\Delta_{\mathrm{nuc}} \propto \tau^{-1/4}|\eta_1|^{-1/2}|\mu|^{-1/2}$. With τ and μ given to ~15% [18] and ~1% [17], respectively, and assuming η_1 to be evaluated to ~20% following the above prescription, we conclude that Δ_{nuc} can potentially be determined to ~10%. Thus, by utilizing alternative experimental and theoretical input, the present method has potential to obtain Δ_{nuc} with

accuracy comparable to the γ-ray differencing schemes of Refs. [9–13].

In summary, here we have identified a potential means to extract the $^{229g}\mathrm{Th} \rightarrow {}^{229m}\mathrm{Th}$ nuclear excitation energy using a combination of precision microwave spectroscopy together with state-of-the-art theoretical methods of atomic structure. The triply ionized species $^{229g}\mathrm{Th}^{3+}$ lends itself well to the present proposal. First, the long-lived ground fine structure doublet $5F_{5/2,7/2}$ has a multitude of hyperfine intervals, with spectroscopic constants $\tilde{C}_{5/2}$, $\tilde{C}_{7/2}$, $\tilde{D}_{5/2}$, and $\tilde{D}_{7/2}$ having sizable fractional contributions attributed to hyperfine mixing with states of the nuclear isomer. Second, the single-valence character of $^{229g}\mathrm{Th}^{3+}$ greatly aids in its theoretical description (i.e., calculation of electronic properties), especially by comparison to the complex four-valence neutral system. Finally, foundations of this proposal have already been demonstrated in recent works focused on this ion, including cooling, trapping, and spectroscopic interrogation within a Paul trap [15] and accurate calculation of electronic hyperfine matrix elements [17]. The present work motivates continued efforts in these directions as well as efforts towards improved characterization of the $M1$ decay rate of the isomer [18,33]. A new, independent determination of the nuclear excitation energy could prove to be an essential step in ultimately realizing direct laser excitation of the thorium-229 nucleus.

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