

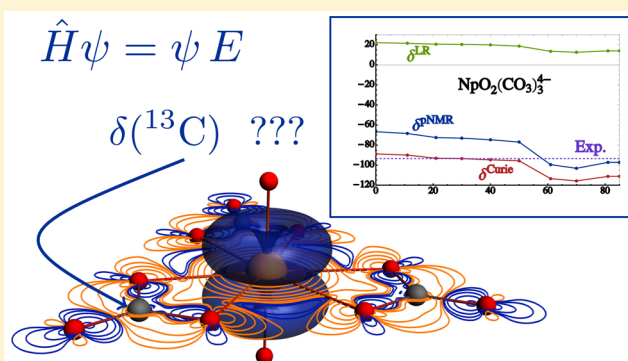
Calculating NMR Chemical Shifts for Paramagnetic Metal Complexes from First-Principles

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S Supporting Information

ABSTRACT: Paramagnetic effects on NMR shifts (pNMR) for paramagnetic metal complexes are calculated from first-principles, without recourse to spin Hamiltonian parameters. A newly developed code based on complete active space (CAS) and restricted active space (RAS) techniques in conjunction with treating spin-orbit (SO) coupling via state interaction is applied to ^{13}C NMR shifts of actinyl tris-carbonate complexes, specifically $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ and $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$. The experimental pNMR shifts as well as the sizable difference of the ^{13}C NMR shift for these iso-electronic species are well reproduced by the calculations. Approximations to the pNMR shift equations using spin Hamiltonian parameters or the magnetic susceptibility are calculated for the same systems at the same level of theory, and it is shown how the approximations relate to the ab initio data.



The treatment of paramagnetic open-shell species is a frontier in quantum chemistry.^{1–5} Paramagnetic systems can be characterized experimentally in great detail by magnetic resonance techniques, among others. Consequently, the interest in calculations of NMR chemical shifts for systems with electron paramagnetism (pNMR)—particularly for paramagnetic metal complexes—has been rising quickly in recent years.^{6–16} pNMR spectra can be very difficult to interpret without theoretical support. In the past, attempts at modeling pNMR theoretically have typically relied on approximate expressions for the chemical shift utilizing electron paramagnetic resonance (EPR) pseudo-spin Hamiltonian parameters or the magnetic susceptibility (examples are discussed below), and often some or all of these parameters were obtained using density functional theory (DFT). For systems with (i) orbital degeneracies, or (ii) low-energy excited states, or (iii) strong spin-orbit (SO) coupling, it has so far been somewhat unclear to what extent approximate pNMR expressions are applicable and/or to what extent Kohn–Sham DFT calculations with common approximate functionals can be applied without running into severe problems. Ab initio methods capable of treating open-shell systems reliably are needed in combination with a compatible theoretical formulation for pNMR shielding.

Herein, we present a theoretical ab initio approach for calculations of pNMR chemical shifts that does not resort to calculated EPR parameters or magnetic susceptibilities. It is applied to a rather challenging application scenario where all three of the aforementioned categories (i) to (iii) apply simultaneously, namely, pNMR ligand shifts in actinide complexes. Specifically, $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ and $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$ are considered for this pilot application. Experimental isotropic

^{13}C NMR shifts are available from measurements in aqueous solution.^{17,18} Both complexes exhibit sizable ^{13}C pNMR shifts (–62 and –94 ppm, respectively) relative to the analogous diamagnetic U(VI) complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, but they are also surprisingly different given that the U(V) and Np(VI) complexes are iso-electronic.

Our approach takes advantage of a recent derivation by Soncini and van den Heuvel (SvH) for the NMR shielding tensor as a temperature- (T -) dependent bilinear derivative of the Helmholtz free energy.^{19,20} Using the notation of a recent paper by our group further elaborating on the SvH formalism and the T -dependence of pNMR chemical shifts,¹⁶ the shielding tensor elements of a paramagnetic or diamagnetic system are given by the following sum-over-states (SOS) expression:

$$\sigma_{ij}^N(T) = \frac{1}{Q} \sum_{\lambda} e^{-E_{\lambda}/(k_B T)} \left[\sum_a \langle \lambda | \hat{H}_{Nij}^{\text{DS}} | \lambda a \rangle + 2 \text{Re} \sum_{\lambda' \neq \lambda} \sum_{a, a'} \frac{\langle \lambda | \hat{H}_i^Z | \lambda' a' \rangle \langle \lambda' a' | \hat{H}_{Nj}^{\text{HyF}} | \lambda a \rangle}{E_{\lambda'} - E_{\lambda}} + \frac{1}{k_B T} \sum_{a, a'} \langle \lambda | \hat{H}_i^Z | \lambda a' \rangle \langle \lambda a' | \hat{H}_{Nj}^{\text{HyF}} | \lambda a \rangle \right] \quad (1)$$

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In eq 1, $Q = \sum_{\lambda,a} \exp(-E_{\lambda}/(k_B T))$ is the partition function in the absence of the external field or the fields from nuclear spin magnetic moments, $ij \in \{x,y,z\}$, λ counts the electronic states, a counts the components of degenerate states, and k_B is the Boltzmann constant. Further, N indicates the nucleus of interest, Z is notation for the Zeeman operator derivative with respect to a component of the external magnetic field, HyF is the notation for the nuclear hyperfine field operator derivative with respect to the components of the nuclear spin magnetic moment, and DS indicates the bilinear derivative representing the diamagnetic shielding operator in case the formalism affords diamagnetism explicitly. The last term in eq 1 is the Curie term, and proportional to $1/T$. As pointed out previously by SvH and by us, the shielding expression is general in the sense that the wave functions and operators may include relativistic effects to all orders. As such, it can be applied directly in an ab initio framework, either as-is in SOS form or as a Boltzmann average of suitably defined linear response functions. The formalism also covers indirect nuclear spin–spin coupling and the magnetizability, upon suitable substitutions of the operators. For a nondegenerate ground state (GS), negligible Boltzmann populations of excited states, and for a nonrelativistic quantum mechanical framework, eq 1 is equivalent to the famous expression for NMR shielding published in 1952 by Norman Ramsey.^{21,22}

We implemented eq 1 in SOS form into a developer's version of the Molcas package.²³ Optimized XYZ structures of the complexes were taken from ref 24. The integrals for DS, Z , and HyF were evaluated for a set of SO wave functions determined by state interaction from scalar relativistic complete active space (CAS) wave functions obtained with the second order Douglas Kroll Hess all electron relativistic Hamiltonian and ANO-RCC basis sets contracted to triple- ζ quality. Additional spin-polarization was generated as explained in recent work by our group on hyperfine coupling (HFC),²⁵ by augmenting the CAS principal active space ("ras2") by restricted active spaces allowing for 1 hole in the "ras1" space of occupied orbitals and 1 electron in the "ras3" space of unoccupied orbitals. The notation $\text{RAS}[n,m]$ is used in the following to indicate the size of the ras1 (n) and ras3 (m) space. To keep the memory requirements low, the RAS calculations used a (1,6) ras2 space including the $5f$ orbitals (except for the $5f_{\sigma}$ orbital, which is too destabilized by the "yl" ligands), but state energies from CAS(7,10) in the SO state interaction including solvent effects. For further analysis of the results, EPR g -tensors, hyperfine tensors, and magnetic susceptibilities were calculated along the same lines using the Molcas modules described in refs 25–29. Solvent effects were considered via a polarizable continuum model. Dynamic electron correlation, estimated by CAS second-order perturbation theory, were previously found to increase the energetic separation between the ground state and first excited state in gas phase by about 60 wavenumbers for the U complex and very slightly reduce the energy gap for the Np system;²⁴ the solvent model gave comparably small energy corrections. Additional computational details can be found in the Supporting Information (SI). As explained in ref 25, the current use of a nonrelativistic HyF operator allows for reliable calculations for hyperfine integrals for lighter ligand atoms. An implementation of relativistic hyperfine operators is under way but not essential for the present study.

The SOS formulation prevents a truly efficient calculation of the full ligand shielding. However, the pNMR ligand chemical shifts of paramagnetic metal complexes in reference to analogous diamagnetic systems are primarily caused by the low-energy

electronic states derived from the metal open shell generating the electronic magnetic moment and net spin density at the ligand atoms. The isotropic chemical shift with respect to an analogous diamagnetic reference is therefore predominantly given by

$$\delta_{\text{pNMR}}^N = \sigma_{\text{ref,dia}}^N - \sigma^N(T) = -\frac{1}{3} \sum_i \frac{1}{Q} \sum_{\lambda} e^{-E_{\lambda}/(k_B T)} \times \left[2\text{Re} \sum_{\lambda' \neq \lambda} \sum_{a,a'} \frac{\langle \lambda a | \hat{H}_i^Z | \lambda' a' \rangle \langle \lambda' a' | \hat{H}_{\text{Ni}}^{\text{HyF}} | \lambda a \rangle}{E_{\lambda'} - E_{\lambda}} + \frac{1}{k_B T} \sum_{a,a'} \langle \lambda a | \hat{H}_i^Z | \lambda a' \rangle \langle \lambda a' | \hat{H}_{\text{Ni}}^{\text{HyF}} | \lambda a \rangle \right] \quad (2)$$

where the sums now run over low-energy electronic states related to the metal open shell. For non-hydrogen atoms, a close similarity of the DS contributions to the shielding in the probe and reference is expected, and it was verified numerically. Consequently, the DS is omitted from eq 2 and not discussed further.

The matrix elements of $\hat{H}_{\text{Ni}}^{\text{HyF}}$ are critical for the pNMR shielding. The HyF operator has three contributions:^{30,31} Fermi-contact (FC), spin-dipole (SD), and paramagnetic spin-orbital (PSO). The pNMR shift in eq 2 as well as the hyperfine coupling tensor introduced below can be partitioned in the same way. Relativistic operator expressions differ from the nonrelativistic ones. For instance, there is no actual "contact" term with a δ distribution even for point nuclei. However, the physical mechanisms are similar, and therefore we use the familiar acronyms and further note that for light nuclei the relativistic operators behave very similar to the nonrelativistic ones. In the limit of vanishing SO coupling, the FC mechanism is isotropic and is responsible for the pNMR contact shifts. A contact shift requires a net magnetization around and at the probe nucleus and consequently indicates metal–ligand covalency if the only source of electron paramagnetism is the metal center. The term "magnetization" is used here in place of "spin density" or "spin magnetization" because for our actinide samples both spin and orbital angular momenta are important, as evidenced by the contributions from all mechanisms, FC+SD and PSO, to the ligand pNMR shifts (vide infra). The SD mechanism is anisotropic and causes dipolar (pseudocontact) shifts via interaction of the magnetization around the metal center with the probe nucleus. The PSO mechanism in the hyperfine coupling vanishes in the absence of SO coupling, while it is the main driver of the chemical shift for diamagnetic compounds. If the effects from SO coupling are pronounced, the PSO mechanism can become a major driver for pNMR shifts, while at the same time the association of FC with contact and SD with dipolar shifts weakens.^{16,32}

For each electronic multiplet (the reader is reminded that the inclusion of SO interactions in the wave functions means that these are not pure spin-multiplets), the Curie term in the isotropic pNMR shielding can be expressed in terms of EPR parameters^{6,16,20} as

$$\delta_{\text{pNMR}}^N(\text{Curie}) = \frac{\beta_e}{g_N \beta_p} \frac{S(S+1)}{3k_B T} \frac{1}{3} \text{tr}[\mathbf{g} \mathbf{a}_N] \quad (3)$$

where S is the pseudospin chosen to match the $2S+1$ -fold degeneracy of the multiplet, β_e and β_p are the Bohr and nuclear magneton, respectively, \mathbf{g} is the g -tensor, \mathbf{a}_N is the HFC tensor of the probe nucleus, and tr indicates the sum of diagonal elements

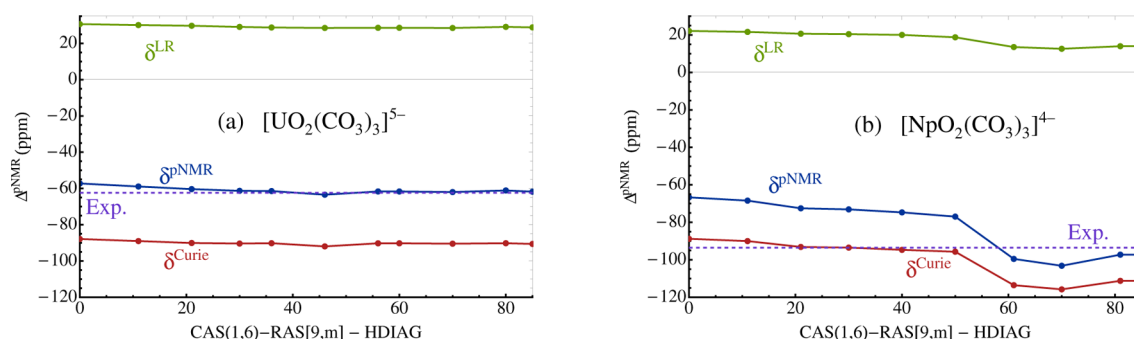


Figure 1. Convergence of RAS[n,m] calculations of the ^{13}C pNMR shift of eq 2 with the size of the active space used to generate spin polarization. $T = 273\text{ K}$. Experimental shifts of $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ (a, -62.4 ppm)¹⁸ and of $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$ (b, -93.5 ppm)¹⁷ with respect to diamagnetic uranyl(VI)-tris-carbonate are indicated by horizontal dashed lines. “LR” indicates the term with the energy denominators in eq 2, “Curie” the term with the $1/(k_B T)$ factor, and “pNMR” their sum.

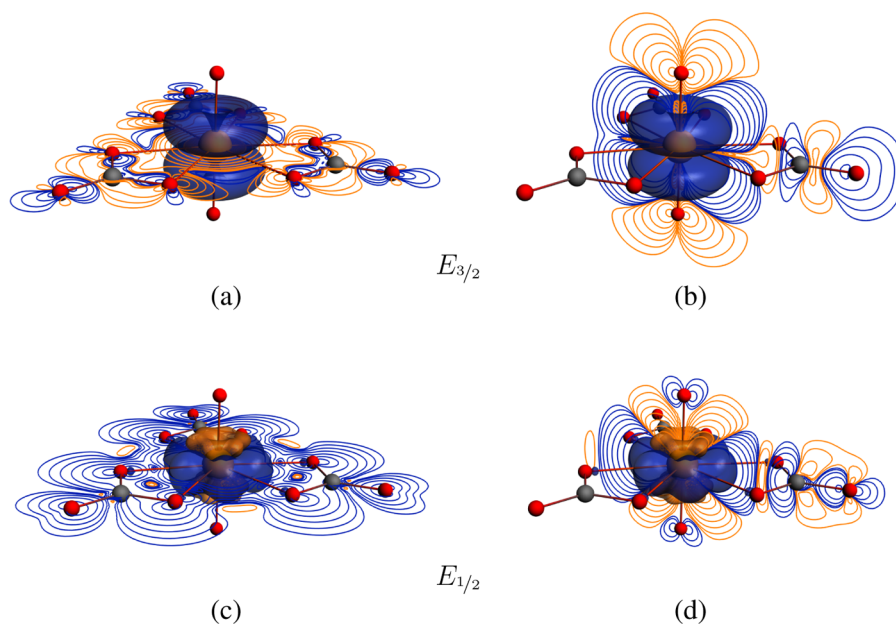


Figure 2. $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$: Spin magnetization $m_{\parallel}^S(r)$ for the GS $E_{3/2}$ (top, a and b) and first excited state $E_{1/2}$ (bottom, c and d) doublet components with $\langle S_{\parallel} \rangle > 0$. Isosurface values: $\pm 0.001\text{ au}$. Contour lines for cuts within (a,c) and perpendicular (b,d) to the equatorial plane, respectively. RAS[9,85] calculation.

of the matrix product. Equation 3 is the aforementioned frequently used expression of the pNMR shielding in terms of EPR parameters. For systems with orbitally nondegenerate ground states, absence of low-energy excited states, and relatively weak SO coupling, the expression gives reasonable results as evidenced, for example, by the good agreement of the large calculated pNMR ligand shifts of $3d$ metallocenes with experiment.^{8,15} A modification to treat spin-multiplets split by zero-field splitting in eq 3 is possible, which influences the T -dependence.^{16,20}

Another frequently used approximate pNMR expression is useful when there is weak or no metal–ligand covalency. In this case, the SD term in the HyF operator plays a decisive role. If the magnetization around the metal can be approximated by a point magnetic dipole, by absorbing it into a δ distribution times the integrated magnetization,¹⁴ the hyperfine interaction for different ligand atoms is determined simply by a geometric factor. The electronic magnetic anisotropy can be calculated from the anisotropy of the susceptibility tensor χ for the high- T limit. Bertini et al.³³ have derived different variants of the resulting expression; one that we recently used to study pNMR shifts in

the two carbonate complexes²⁴ reads for a system with axial symmetry

$$\delta_{\text{pNMR}}^{\text{N}}(\text{SD, Bertini}) = \frac{1}{12\pi R_{\text{N}}^3} \Delta\chi_{\text{ax}} (3 \cos^2 \theta - 1);$$

$$\Delta\chi_{\text{ax}} = \chi_{\parallel} - \chi_{\perp} \quad (4)$$

Here, \parallel indicates the direction of the principal axis of symmetry, \perp the plane orthogonal to it, R_{N} the distance of the probe nucleus with respect to the paramagnetic center, and θ the angle of the probe nucleus position with respect to the symmetry axis. For a given multiplet, without magnetic coupling to other states, the susceptibility relates to the corresponding EPR g -factors as

$$\chi_i = \mu_0 \mu_{\text{B}}^2 g_i^2 \frac{S(S+1)}{3kT} \quad (5)$$

A direct connection between eqs 3 and 4 can be made, by assuming that the HFC tensor is calculated for a point magnetic moment at the metal and scaled by the g -tensor elements divided by g_{e} in order to reflect relativistic effects, as previously suggested

Table 1. Comparison of the Calculated pNMR Shift Curie Terms (ppm, All Times -1 Representing σ_{Curie}) for the Two Lowest Kramers Doublets of $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ from Eqs 2, 3, and 4^a

	Curie shielding from eq 2				from eq 3				from eq 4	
	total	FC	SD	PSO	total	FC	SD	PSO	χ^b	χ^c
$[\text{NpO}_2(\text{CO}_3)_3]^{4-}$										
$E_{3/2}$	109.65	22.79	28.43	58.42	109.78	22.82	28.46	58.49	32.24	28.06
$E_{1/2}$	130.06	-47.94	32.86	145.14	130.21	-47.99	34.54	144.21	124.43	
$[\text{UO}_2(\text{CO}_3)_3]^{5-}$										
$E_{3/2}$	82.71	3.39	25.30	54.01	82.80	3.39	25.33	54.07	30.69	39.24
$E_{1/2}$	113.05	-60.70	33.10	140.65	113.18	-60.77	34.88	139.82	115.69	

^aRAS[9,85] calculations. The Curie terms and the HFC contributions of eq 3 are also broken down into the FC, SD, and PSO mechanisms. ^b χ calculated using eq 5. ^c χ is the calculated Van Vleck susceptibility calculated as in ref 24 (see SI for details).

by Atherton³⁴ and detailed in ref 14. However, we note that for actinyl complexes the condition of a high- T limit connected with eq 4 is not met because the states deriving from $^2\Pi$ and $^2\Sigma$ are far too high in energy.

The pNMR shifts of the U(V) and Np(VI) actinyl tris-carbonate complexes are negative relative to the analogous U(VI) complex. The sign can be rationalized by the Bertini equation due to the fact that for the two lowest electronic states $\Delta\chi_{\text{ax}}$ is large and positive, while at the same time the $3\cos^2\theta-1$ for the equatorial (\perp) plane is negative. However, the magnitudes of the results from eq 4 are much too small to account for the experimentally observed pNMR shifts and therefore only provide a weak rationale.²⁴

Figure 1 shows for the two actinide complexes the convergence of the pNMR shift of eq 2, along with the Curie and the linear response (LR, the sum with the energy denominators) contributions plotted separately. The present calculations for the largest RAS spaces agree much better with experiment than the previous estimates based on eq 4.

The electronic states contributing to the Curie and LR term are the two doublets deriving from the $^2\Delta$ and $^2\Phi$ states of the actinyl moieties (see the Supporting Information (SI) and ref 24 for further details regarding the electronic spectra). The two doublets are separated by 142 (U) and 356 (Np) cm^{-1} , respectively, with the state of $^2\Delta$ parentage being the GS. A detailed breakdown of the data (see SI) shows that contact (FC) shifts are sizable, in particular for the excited doublet of $^2\Phi$ parentage, where the unpaired electron density at the metal is largest in the equatorial (eq) plane. A $5f^4$ scalar relativistic $^2\Delta$ state has a node in the eq plane for the unpaired density, but some in-plane magnetization is present in the GS of the complexes due to SO induced mixing of Δ and Φ spatial symmetries. The spin magnetizations corresponding to a quantization axis of the magnetic moment in the \parallel direction (corresponding to the usual spin density if SO coupling were absent³⁵) are visualized in Figure 2 and clearly exhibit the Δ and Φ parentage of the states and the extent of spin polarization in the eq plane.

Figure 1 indicates increasingly negative shift contributions as additional spin polarization is generated by opening up larger RAS[n,m] spaces. The changes remain overall less important compared to the total pNMR shift for the U complex, but for Np the inclusion of higher lying unoccupied orbitals in the active space is clearly beneficial, as it creates a sizable FC contribution in the ground state. The LR term follows the trend for the Curie term, because FC contributions also enter the LR matrix elements in a similar way. We did expect a degree of oscillatory behavior upon increasing the active spaces, because different orbitals contribute differently to the FC mechanism depending

on their s/σ character. At the size of the active spaces attainable in the calculations, the results appear to be reasonably well converged.

A breakdown of the Curie terms for the two lowest electronic states in comparison with eqs 3 and 4, collected in Table 1, reveals the relations between the approximate pNMR shift equations and the ab initio calculation:

(i) For a given multiplet, the Curie term of eq 2 agrees numerically well with the $\text{tr}[\mathbf{g} \mathbf{a}_\text{N}]$ -based shift of eq 3, both in terms of the total as well as in terms of the individual contributions FC, SD, and PSO. A Boltzmann average of the shifts generated by each multiplet and calculated with eq 3 from EPR parameters determined ab initio would closely correspond to δ^{Curie} in Figure 1. This gives the dominant contributions to the pNMR shift for our samples.

(ii) The SD contribution from either eq 2 or 3 is much too small to account for the observed shifts. A purely dipolar mechanism can neither explain the magnitude of the shifts nor their difference for the two complexes.

(iii) Magnetic coupling between the low-energy electronic states produces a LR Boltzmann average of opposite sign to the Curie contributions, but smaller in magnitude, which brings the total close to the experimental shifts. The LR term is also responsible for some of the difference in the ^{13}C shifts between the two complexes. The difference is further amplified by the more pronounced spin polarization contributions generated for the Np system with the larger RAS spaces.

(iv) The Bertini equation, eq 4, assumes a dipolar mechanism and vanishing spatial extension of the magnetization. For the ground state, where $g_{\parallel} \simeq 2$, $g_{\perp} \simeq 0$ (see SI and ref 24), the Bertini equation indeed gives a result close to the SD-only contributions obtained with the other equations. Therefore, the point-magnetic dipole approximation underlying eq 4 appears to be—for our samples—much less severe than neglecting the PSO and FC contributions in the hyperfine tensor.

Using the calculated van Vleck susceptibility, obtained from an equation similar to 1, yields similar Bertini shifts as when using the GS g -factors in eq 5. We showed already in ref 24 that LR coupling terms in the susceptibility counter-act the larger magnetic anisotropy of the excited state.²⁴ The excited state affords $g_{\parallel} \simeq 4$, $g_{\perp} \simeq 0$. Evaluating χ from these g -factors gives a Bertini shift close to the total Curie contributions for the excited state obtained ab initio and from eq 3 with ab initio EPR parameters. This is likely a coincidence, as the Bertini eq 4 only includes the SD contribution of the hyperfine interaction but the g -factors enter quadratically while eq 3 is linear in \mathbf{g} . We tentatively attribute the discrepancies to the fact that eq 4 should apply for the high- T limit, which is not established for the actinyl samples.

(v) PSO contributions to the terms entering the pNMR shifts, both in the ab initio eq 2 and in the EPR-parameter-based eq 3, are large for our samples. This underlines the fact that SO coupling in 5f shells can take a strong influence on magnetic (and other) properties. A calculation of the ligand chemical shifts without inclusion of SO interactions would therefore unlikely produce reasonable answers for the right reasons.

In summary, the calculations show that the SvH NMR shielding expression is in principle applicable to cases even as challenging as ligand shifts in actinide complexes. The combination of SO coupling in the actinide 5f shell with the presence of very low-energy excited states and orbital degeneracies renders such systems difficult for a theoretical treatment. The current implementation utilizes the restricted active space paradigm and includes SO coupling via state interaction. A present limitation of the approach is the large number of configurations that would have to be treated for systems with several unpaired electrons, in particular, when the ras1 and ras3 spaces are opened up to generate additional spin polarization. Alternative routes such as density matrix renormalization group techniques appear promising in this regard.³⁶ The doublet states of the two complexes investigated herein require comparatively low computational resources. The largest contributions to the ¹³C pNMR shifts in our samples stem from the T-dependent Curie terms, which can alternatively be modeled based on calculated EPR g-tensors and hyperfine coupling tensors. However, given that the latter require the same matrix elements that enter the SvH expression, there appears no advantage in taking the EPR “detour” except for analysis purposes and model building. For our actinyl samples, the Bertini expression does not appear to be a suitable approximation. The present calculations very likely benefit from error cancellation. Fully quantitative agreement with experiment will not only require an improved treatment of spin polarization, and inclusion of dynamic electron correlation, but very likely also solvent effects and dynamics, affecting the wave functions as well as the state energies entering eq 1.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional data regarding the electronic states, additional calculated magnetic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00932.

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Notes

The authors declare no competing financial interest.

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