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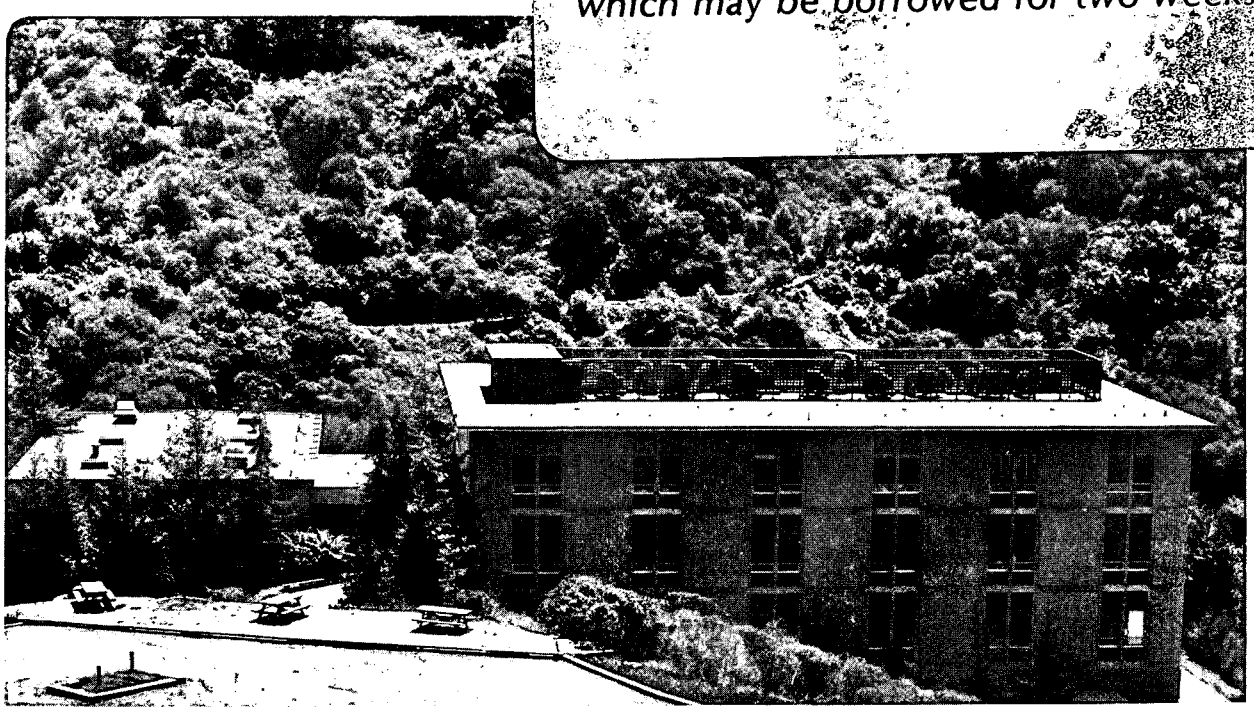

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Multinuclear NMR Spectroscopy of the Tetrahedral U(IV) Complex: $U(BH_3CH_3)_4$

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Abstract

The temperature dependence of the ^{1}H, ^{11}B, and ^{13}C-NMR spectra of T_d $U(BH_3CH_3)_4$ in solution is reported. The paramagnetic shifts are interpreted as originating from purely spin delocalization mechanisms with no contribution from the metal-orbital dipolar interaction. It is shown that the temperature dependence of both ^{1}H shifts (bridging and terminal protons) is identical with that calculated from a polarizataion theory which assumes the shift is proportional to the average value of electron spin in the inner 5f orbitals. The proportionality constant is -5.64 MHz for the bridging protons and -0.59 MHz for the terminal protons. The temperature dependences of ^{11}B and ^{13}C shifts are found to depart significantly from that predicted by the polarization theory with the largest deviations shown by the ^{11}B shifts. It is shown how those deviations can be accounted for by postulating a second spin delocalization through direct covalency involving molecular orbitals formed from the uranium 5f orbitals and ligand s and p orbitals.

Introduction

The spectroscopy of f-block tetraborohydrides is of great interest because of the high molecular symmetry of the $M(BH_3\text{-}R)_4$ unit (M = Hf, Zr, Th, Pa, U, Np, Pu; R = H, CH_3).[1] Only pure solid Th, Pa and $U(BH_4)_4$ are of lower than cubic symmetry, having a polymeric structure. All the other compounds contain molecular units of T_d symmetry with each of the four tetrahedrally coordinated borohydride ligands bound to the metal via three hydrogen bridges with the fourth hydrogen or the methyl group pointing out along the three-fold axis of the complex.

The optical spectrum,[2] paramagnetic susceptibility, and EPR spectra of U and Np tetraborohydride have recently been analyzed in terms of a parametrized Hamiltonian, using the full $5f^2(5f^3)$ basis.[3] Within this basis, optical and magnetic properties could not be satisfactorily explained by the same set of Hamiltonian parameters without the introduction of orbital reduction factors. Furthermore it was shown that J-mixing by the crystal field in these compounds cannot be neglected.

Paramagnetic shifts in the NMR-spectrum of the coordinated ligands can be a powerful tool to examine interactions between the metal f electrons and the ligands.[4] Here again, a high molecular symmetry is important in that pseudocontact (dipolar) shifts which are sometimes hard to separate from the spin delocalization shifts are zero in T_d symmetry.

The only NMR spectra of U(IV) compounds with cubic molecular symmetry reported to date are those of $U(cp)_4$ (cp = cyclopentadienide),[5] $U(NCS)_8$[6] and $U(BH_4)_4$.[7] Although the latter is a polymer in the solid

state, tetrahedral molecular units were found in solution with rapid exchange on the ^{1}H NMR time scale between terminal and bridging hydrogens. Replacement of the terminal hydrogen by a methyl group prevents this exchange and at the same time increases the delocalization range for the spin density originating at the central ion.

In this paper we report paramagnetic shifts from ^{1}H, ^{11}B, and ^{13}C NMR of $U(BH_3CH_3)_4$ and interpret them in terms of spin delocalization from the central ion onto the ligands.

Theory of the Paramagnetic Shift

The theoretical parts of papers on paramagnetic NMR shifts contain a confusing variety of definitions and sign conventions.[4,6-10] We will therefore give a short survey of the necessary equations which were used in the interpretation of the paramagnetic shifts presented in this paper.

The paramagnetic shift, $\Delta H/H$, of the signal under consideration is measured relative to a diamagnetic reference of similar structure (in the present case $Th(BH_3CH_3)_4$). The shift is given in ppm and we define shifts to higher field as positive (the opposite direction has been used in the past, especially in ^{1}H and ^{13}C NMR). Kurland and McGarvey[10] have shown that the paramagnetic shift can be calculated from the following equation:

$$(\Delta H/H_i) = (kTq)^{-1} \sum_{\Gamma n,\Gamma m} e^{-\varepsilon_\Gamma/kT} \langle \Gamma n|\mu_i|\Gamma m\rangle\langle \Gamma m|A_{Ni}/g_N\beta_N|\Gamma n\rangle$$

$$-q^{-1} \sum_{\Gamma n,\Gamma' m(\Gamma'\neq\Gamma)} Q_{\Gamma\Gamma'}\langle \Gamma n|\mu_i|\Gamma' m\rangle\langle \Gamma' m|A_{Ni}/g_N\beta_N|\Gamma n\rangle \quad [1]$$

in which

$$q = \sum_{\Gamma n} e^{-\varepsilon_\Gamma/kT} \quad [2]$$

$$Q_{\Gamma\Gamma'} = (e^{-\varepsilon_\Gamma/kT} - e^{-\varepsilon_{\Gamma'}/kT})/(\varepsilon_\Gamma - \varepsilon_{\Gamma'}) \quad [3]$$

$$\mu_i = -\beta_e(L_i + g_e S_i) \quad [4]$$

$$(A_{Ni}/g_N\beta_N) = (8\pi/3)g_e\beta_e \sum_j \delta(r_j)(s_i)_j + g_e\beta_e \sum_j [3(\vec{s}_j\cdot\vec{r}_j)(r_i)_j$$

$$- r_j^2(s_i)_j] + 2\beta_e \sum_j r_j^{-3}(\ell_i)_j. \quad [5]$$

In the above equation the Γ, Γ' indices label energy levels of the system in the absence of an applied magnetic field and n, m label particular degenerate states within a given energy level ε_Γ. For the $U(BH_3CH_3)_4$ system Γ designates a particular SLJ state while n, m designate the J_z components of that state. Eq. (1) was derived for a rigid system and the subscript i refers to the direction of the magnetic field in the molecular coordinate system j. The solution shift is found by calculating the shift along the three principal axes of the molecular

coordinate system and then averaging. S_i is the total electron spin operator, $(s_i)_j$ is the single electron spin operator for electron j, L_i is the total orbital angular momentum operator, $(\ell_i)_j$ is the orbital angular momentum operator for operation j, β_e, β_N are the Bohr and nuclear magneton, respectively, g_e is the free electron g value (2.0023), g_N is the nuclear g value, $(r_i)_j$ is the i component of the $\vec{r}_j$ vector between the nucleus and the j th electron, and $\delta(r_j)$ is Dirac's delta function. T is temperature in Kelvin and k is Boltzmann's constant.

If we approximate the $|\Gamma m\rangle$ functions by purely f orbital functions, Eq. (1) reduces to the familiar dipolar shift equations[10] which predict the average shift to be proportional to the magnetic susceptibility anisotropy. The molecular unit of $U(BH_3CH_3)_4$, dissolved in toluene, has T_d symmetry and has no such anisotropy. Therefore, the dipolar shift (pseudo contact shift) should be zero and the observed paramagnetic shift is solely due to mechanisms that transfer electron spin into the ligand orbitals. In this paper we shall refer to this shift as the delocalized spin shift. Most of the literature calls this shift the contact (Fermi) shift, but this is incorrect and misleading when dealing with the paramagnetic shifts of lanthanide and actinide complexes, as it implies that the shift comes only from electron spin delocalized into ligand s orbitals. While this is generally (but not always) true for transition metal complexes (for which the term was invented), the following discussion will show that it is not the case for systems in which the orbital angular momentum is not quenched.

Two spin transfer mechanisms have been proposed to explain NMR, ESR and ENDOR results from lanthanide and actinide systems. Lewis et al.[11] and Reuben and Fiat[12] concluded from ^{17}O NMR shift studies on hydrated lanthanide ions that the shifts were primarily Fermi contact in origin with a negative contact term. Lewis et al. attributed the negative term to a polarization mechanism in which 4f electrons polarized the bonding electrons in a bond formed by the ligand atom donating electrons from its 2s and 2p orbitals into the empty 6s orbital of the lanthanide ion. Watson and Freeman[13] proposed that a negative spin density in the outer 5s and 5p electrons of the lanthanide ion is produced by a polarization interaction with the unpaired 4f electrons and that this negative spin density is transferred to adjacent ligand atoms by covalent and overlap interactions between these 5s and 5p orbitals and the 2s and 2p orbitals of the ligand.

The exact distinction between overlap and covalent transfer of spin has been discussed by McGarvey.[14] Basically this polarization mechanism transfers spin from the outer metal s and p orbitals to the ligand orbitals and this spin results from a polarization mechanism which favors spin of opposite sign to that in the inner f shell. It was further assumed that effects of spin in ligand p orbitals would average out in solution (ignoring the coupling of electron spin and electron orbital angular momentum) leaving only the isotropic contribution of electron spin in ligand s orbitals. Most of the chemical literature on NMR shifts in lanthanides and actinide complexes has assumed the above explanation to be correct, and has therefore, referred to all isotropic

shifts (obtained after subtraction of the dipolar shift) as "contact shifts".

Baker[15] has shown that although the polarization mechanism would explain ^{19}F ENDOR results for Eu^{2+} and Gd^{3+} (f^7 configuration) in CaF_2, it could not account for the results obtained for Tm^{2+} or Yb^{3+} (f^{13} configuration) in which the isotropic component of the hyperfine interaction was positive rather than negative. He showed that the results for Tm^{2+} and Yb^{3+} could be explained by a direct covalent transfer of the 2s and 2p electrons of the fluoride ion into the 4f shell. McGarvey[14,15] extended the covalent calculations to Yb^{3+} in octahedral sites and in distorted cubic sites.

The ^{19}F NMR shift at room temperature was measured for crystals of CdF_2[17] and CaF_2[18] containing Yb^{3+} and the isotropic shift was found to be upfield in the same direction found for ^{17}O NMR shifts[11] in solution which had been interpreted to mean a negative isotropic hyperfine interaction. Thus ENDOR and NMR studies in the same system appeared to arrive at contradictory results. McGarvey[19] has shown that the same covalent mechanism used to explain the hyperfine interaction measured by ENDOR could also explain the upfield shift measured by NMR using Eq. (1-5). It was found that the largest term came from the second part of Eq. (1) and the third term in Eq. (5). In other words, the sign of the NMR shift in this case was not determined by the Fermi contact term (which in this case did predict a downfield shift) but rather by the interaction between the nuclear spin and the unquenched orbital angular momentum of electrons in ligand p orbitals. Further the shift was not determined by a hyperfine matrix element for any ground or excited state

(that could be measured by ESR or ENDOR) but rather by a hyperfine matrix element between different crystal field states of the system. ^{19}F NMR shift studies on a series of elpasolites[20] has shown that the polarization mechanism is dominant in the first half of the lanthanide series but both the covalent and polarization mechanisms must be invoked to explain results for the second half of the series.

About the only satisfactory way to do a theoretical calculation for the polarization mechanism is to do an unrestricted Hartree-Fock calculation on the complete complex to obtain the $|\Gamma m\rangle$ functions. Baker[15] has suggested that the effect should be proportional to the spin in the f orbitals and therefore one could estimate the matrix elements $\langle\Gamma' m|A_{N_i}/g_N\beta_N|\Gamma n\rangle$ in Eq. (1) from the spin matrix elements $\langle\Gamma' m|S_i|\Gamma n\rangle$ which are readily calculated from the $|SLJJ_z\rangle$ functions. That is

$$\langle\Gamma'_m|A_{Ni}/g_N\beta_N|\Gamma_n\rangle = (K/g_N\beta_N)\langle\Gamma'_m|S_i|\Gamma_n\rangle \qquad [6]$$

with the proportionality constant K being independent of the SLJ quantum numbers. The constant K has a negative value for the polarization mechanism and units of energy. Baker found in the case of Eu^{2+} and Gd^{3+} in CaF_2, that different K values were required for the directions parallel and perpendicular to the vector connecting the fluoride ion and the rare earth ion. He found $K_{||} = -3.60$ MHz, $K_{\perp} = -0.93$ MHz for Gd^{3+} and $K_{||} = -3.49$ MHz, $K_{\perp} = -1.60$ MHz for Eu^{2+}.

For the isotropic shift we can assume an average value for K and calculate the shift for the z direction. Putting Eq. (6) into Eq. (1) we obtain

$$\Delta H/H = (K/g_N\beta_N)\langle S_z\rangle/H \qquad [7]$$

where $\langle S_z \rangle$ (the average total electronic spin) is found from the equation

$$\langle S_z \rangle / H = -(\beta_e / kTq) \sum_{\Gamma n, \Gamma m} e^{-\varepsilon_\Gamma / kT} \langle \Gamma n | (L_z + g_e S_z) | \Gamma m \rangle \langle \Gamma m | S_z | \Gamma n \rangle$$

$$- (\beta_e / q) \sum_{\Gamma n, \Gamma' m} Q_{\Gamma\Gamma'} \langle \Gamma n | (L_z + g_e S_z) | \Gamma' m \rangle \langle \Gamma' m | S_z | \Gamma n \rangle \qquad [8]$$

Eq. (7) is the usual equation put forward as the contact shift equation[4] except the parameter K is replaced by A which is assumed to be the isotropic hyperfine constant.

Lewis et al.[11] have pointed out that since the lowest energy states belong to the same J manifold (assuming no J mixing by the crystal field), the operators in Eq. (8) can be replaced by equivalent J operators. That is $(L_z + g_e S_z) = g_J J_z$ and $S_z = (g_J - 1) J_z$ where g_J is the Lande g factor. In this case the sign of the shift is determined by the sign of $g_J(1-g_J)K$. For ions with less than seven f electrons g_J is less than one and therefore a negative K will give a negative or downfield shift. Ions with more than seven f electrons have g_J greater than one and therefore Eq. (8) will predict a positive or upfield shift.

If the crystal field states have energies of the same magnitude as kT or larger than kT, Eq. (7,8) will not predict a simple T^{-1} (Curie law) behavior for $\Delta H/H$. It will approach such behavior only for temperatures in which $kT \gg \varepsilon_\Gamma$ of the crystal field states. The behavior at very low temperatures depends on the nature of the ground state. If the ground state matrix elements $\langle 0m | S_z | 0n \rangle$ are not zero, the

temperature dependence becomes T^{-1} at low temperatures and $\Delta H/H$ becomes very large at low temperatures. If $\langle 0m|S_z|0n\rangle = 0$ for the ground state but corresponding matrix elements between the ground state and excited state are not zero, the $\Delta H/H$ approaches a constant value at low temperatures. This is the situation for $U(BH_3CH_3)_4$. Finally if all matrix elements involving the ground state are zero, $\Delta H/H$ approaches zero at very low temperatures.

In actinide compounds, especially at the beginning of the series, spin-orbit coupling and crystal field energies are of the same magnitude and extensive f-mixing takes place so that calculations within the ground state multiplet alone can no longer explain finer effects. It has been shown, also, that orbital reduction factors are necessary to explain experimental results satisfactorily.[3,9,21] For this reason an empirical reduction factor k_z has been introduced in which the operator L_z has been replaced by k_zL_z in any calculation. The wave functions $|\Gamma n\rangle$ are linear combinations within the familiar $|\gamma SLJJ_z\rangle$ basis.[22] The computational effort grows exceedingly if all free ion terms of the f^n configuration are included in the calculation. We give, therefore, easily programmable equations for all necessary matrix elements in the Appendix.

The problem is more complex for the covalent mechanism and no simple rules can be formulated that will predict the sign of the shift. In most of the literature it has been argued that a covalent transfer leads to a positive Fermi contact term and therefore to a shift opposite in sign to that predicted by the polarization mechanism. This argument was based on two false assumptions; (1) the electrons in ligand p

orbitals will not contribute to isotropic solution shifts because this is a dipolar interaction that averages to zero and (2) the s electrons that interact through the Fermi contact term give an isotropic and positive interaction. While both assumptions are correct for systems in which the orbital angular momentum is quenched to first order, they are not true when angular momentum is not quenched (as in the case for all rare earth ions except the ^8S state of the f^7 configuration). The p electrons contribute to the shift through the second and third terms in Eq. (5). For spin only systems, the second term gives a traceless shift matrix which will average to zero in solution and the third term is zero. For complexes with orbital angular momentum the third term is neither zero or traceless and therefore contributes to the isotropic shift. Even the second term gives a non-traceless shift matrix in some ground states. Thus the first assumption is incorrect and it is wrong to call the isotropic shift a contact shift in such systems.

The second assumption is sometimes also wrong. McGarvey[14,16] has shown that the Fermi contact term leads to a positive and isotropic hyperfine interaction for the Γ_7 ground state of Yb^{3+} in cubic symmetry in CaF_2, but the ^{19}F hyperfine parameter for the Γ_6 ground state of Yb^{3+} in the octahedral symmetry of $KMgF_3$ is highly anisotropic and gives a negative value for the average hyperfine interaction. The calculation of the NMR shift[19] for ^{19}F of Yb^{3+} in CaF_2 gave an anisotropic shift for the Fermi contact contribution even though the ground state itself had an isotropic Fermi term. Thus the second assumption can also be wrong.

We have used the same methods[19] used to calculate the ^{19}F NMR shift of Yb^{3+} in CaF_2 to estimate the covalent contribution to the

paramagnetic shift in $U(BH_3CH_3)_4$. To keep the calculation simple we have assumed a pure $^3H_4$ state for the $5f^2$ configuration with no J-mixing. Rajnak et al.[3] gives the ground state for $U(BH_4)_4$ as E with the excited states in ascending energy as being T_1, T_2, and A_1. We have also left out the A_1 state from the calculation as it is much higher in energy than the T_1 and T_2 states and has no matrix elements connecting it to the E ground state. The calculation was done only for ligand atoms along a C_3 axis of the tetrahedron and is therefore applicable only to the B and C atoms of $U(BH_3CH_3)_4$. The resulting equation is

$$\Delta H/H = [g_J\beta_e/27kTqg_N\beta_N]x$$

$$\{e^{-\Delta_1/kT}[1.13939a_\sigma^2A_{2s}+(-5.24848b_\sigma^2-2.01818b_\pi^2+15.45405b_\sigma b_\pi)A_{2p}]$$

$$+e^{-\Delta_2/kT}[5.88745a_\sigma^2A_{2s}+(1.25108b_\sigma^2+19.84416b_\pi^2+62.43548b_\sigma b_\pi)A_{2p}]$$

$$+Q_{01}[24.84040a_\sigma^2A_{2s}+(-0.50101b_\sigma^2-29.44242b_\pi^2+208.16209b_\sigma b_\pi)A_{2p}]$$

$$+Q_{02}[6.21299a_\sigma^2A_{2s}+(-9.13593b_\sigma^2-9.53824b_\pi^2+111.31923b_\sigma b_\pi)A_{2p}]$$

$$-Q_{12}[2.90505a_\sigma^2A_{2s}+(16.61010b_\sigma^2+41.50909b_\pi^2-64.50323b_\sigma b_\pi)A_{2p}]\} \quad [9]$$

where

$$Q_{01} = (1-e^{-\Delta_1/kT})kT/\Delta_1 \quad [10]$$

$$Q_{02} = (1-e^{-\Delta_2/kT})kT/\Delta_2 \qquad [11]$$

$$Q_{12} = (e^{-\Delta_1/kT} - e^{-\Delta_2/kT})kT/(\Delta_1-\Delta_2) \qquad [12]$$

$$q = 2 + 3e^{-\Delta_1/kT} + 3e^{-\Delta_2/kT} + e^{-\Delta_3/kT} \qquad [13]$$

$$\Delta_1 = \varepsilon(T_1) - \varepsilon(E) \qquad [14]$$

$$\Delta_2 = \varepsilon(T_2) - \varepsilon(E) \qquad [15]$$

$$\Delta_3 = \varepsilon(A_1) - \varepsilon(E) \qquad [16]$$

$$A_{2s} = (8\pi/3)(g_e\beta_e g_N\beta_N)|2s(0)|^2 \qquad [17]$$

$$A_{2p} = (2/5)(g_e\beta_e g_N\beta_N)\langle r^{-3}\rangle_{2p} \qquad [18]$$

The a_σ term is the molecular orbital coefficient for the ligand 2s orbital mixing with the $5f_0$ metal orbital, b_σ is for $2p_\sigma$ with $5f_0$ and b_π is for $2p_{\pm1}$ with $5f_{\pm1}$, Baker[15] and McGarvey[14] found for F^- that $b_\sigma \approx b_\pi$ as was found earlier for transition metal fluorides.[23] If we assume this to be the case for B and C in $U(BH_3CH_3)_4$, the above equation predicts an upfield shift for the energies reported by Rajnak[3] et al.

Results and Discussion

The T_d molecular symmetry of the $U(BH_3CH_3)_4$ unit is shown in Fig. 1. Each ligand is bound to the metal center via three bridging hydrogens. The boron atoms lie at the tetrahedral corners and the methyl groups attached to them point out of the complex along the threefold axes of the molecular T_d unit. This leads to only four magnetically non-equivalent nuclei: bridging hydrogens (H_b), terminal hydrogens (H_t), boron and carbon. Their paramagnetic shifts (referenced to the isostructural, but diamagnetic $Th(BH_3CH_3)_4$[1] are shown in Fig. 2 as a function of T^{-1}.

No splittings from spin-spin coupling (^1H-^{11}B or ^1H-^{13}C) have been observed due to the rather large linewidths. There is no indication of low symmetry components in solution, e.g. solvent adducts (which have a markedly different NMR spectrum)[24] or dimerization. The shifts can therefore be considered as having no dipolar (pseudo contact) shift. All shifts are to low fields, and this indicates that the polarization mechanism is dominant in each case. The T^{-1} dependence shows significant curvatures and nonzero extrapolated intercepts for $T^{-1} = 0$, indicating that a first order treatment as well as the assumption that the splitting of the free ion ground term ($^3H_4$) by the crystal field is smaller than kT are not correct in the present case.

This is confirmed by the optical and magnetic analysis which have shown that it is possible to explain the optical spectrum of $U(BH_4)_4/Hf(BH_4)_4$ and the susceptibility of $U(BH_3CH_3)_4$ with the same set of parameters only if the full basis set of the f^2 configuration is used and a orbital reduction factor included.[3a] Table 1 shows the lowest levels and the main components of the corresponding eigenvectors in the $|SLJJ_z\rangle$ basis from the analysis. The lowest T_1 state has been calculated to be at 370 cm^{-1} in the optical

analysis of $U(BD_4)_4$ diluted in $Hf(BD_4)_4$. However, the analysis of the susceptibility of $U(BH_3CH_3)_4$ is especially sensitive to the position of the thermally populated lower levels and allowed a more reliable determination of the T_1 energy at 215 cm^{-1}. The discrepancy is also plausible in view of the slightly different optical spectra in solution of $U(BH_3CH_3)_4$ and $U(BH_4)_4$ where shifts of up to 250 cm^{-1} occur. The introduction of an isotropic orbital reduction factor k = 0.85 has also been necessary to explain the susceptibility and account for the reduction of about 10% of the free ion spin orbit coupling parameter ζ in the complex.

Since the polarization mechanism appears to be dominant, we will first analyze the results in terms of Eq. (7,8). $\langle S_z \rangle/H$ was calculated from all energies and complete eigenvectors as given in reference 3a up to 16,000 cm^{-1} using k_z = 1.00 and using both 370 cm^{-1} and 215 cm^{-1} for the lowest T_1 state. The calculation was repeated for k_z = 0.85 and the T_1 state at 215 cm^{-1}. For comparison purposes, the calculation was also done assuming a pure $^3H_4$ state with no J-mixing and ignoring other excited states. In this case k_z was taken to be unity. The results are plotted in Fig. 3 vs. T^{-1}. The non-Curie behavior is quite apparent as well as the pronounced dependence on the energy chosen for the lowest T_1 state. The effect of changing k_z is mainly to change the magnitude of $\langle S_z \rangle/H$ rather than the functional dependence on temperature. Using just the pure $^3H_4$ functions gives larger values of $\langle S_z \rangle/H$ but the temperature dependence is similar to that of the complete calculation.

For each $\langle S_z \rangle/H$ function a best fit between theory and experiment was obtained by varying the value of the parameter K in Eq. (7). The best fit values of K and the standard deviation for each case are given in Table 2.

Excellent fits were obtained for both the bridging protons (H_b) and terminal protons (H_t) for 215 cm^{-1} using the full basis set and k_z = 0.85 or 1.00. The solid lines in Fig. 2 are plots of fitted curves for k_z = 0.85. The fit for the ^{13}C shifts is less satisfactory and for the ^{11}B shifts is very poor.

The good fit between Eq. (7) and the experimental ^{1}H shifts using the same eigenvectors and energies that have been used to fit the optical spectra of $U(BH_4)_4$ and magnetic susceptibility of $U(BH_3CH_3)_4$ is strong support for the polarization mechanism being the only important spin transfer mechanism for both ^{1}H nuclei. The very poor fit for ^{11}B means either that another mechanism for spin transfer is also important for boron or that the chemical shift for ^{11}B is not the same in both $U(BH_3CH_3)_4$ and $Th(BH_3CH_3)_4$ since an improved fit could be attained by not forcing the data to extrapolate to zero when T becomes infinite.

The polarization mechanism predicts the same functional dependence on temperature for all nuclei with only the K parameter being different. If this were true, we could write the following equation for each of our four shifts

$$(\Delta H/H)_j = K_j f(T) + A_j \qquad [19]$$

where subscript j denotes a particular nuclear shift, f(T) is the common temperature dependence function, and A_j is chemical shift in absence of the paramagnetic shift. All A_j's = 0 if our assumption about $U(BH_3CH_3)_4$ and $Th(BH_3CH_3)_4$ having same chemical shift is valid. Plotting shift 1 versus 2 would yield a straight line whose equation is

$$(\Delta H/H)_1 = (K_1/K_2)(\Delta H/H)_2 + [A_1 - (K_1/K_2)A]. \qquad [20]$$

In Fig. 4 the H_t, C and B shifts are plotted versus the H_b shifts. For C and B the appropriate H_b shifts were interpolated or extrapolated from the

H_b versus T^{-1} plot. The data were fitted by a least-squares procedure against a straight line. The fitted slopes and intercepts are given in Table 3 and the fitted straight lines are shown in Fig. 4 as solid lines. In each case the fit is good, but it is difficult to detect curvature over the small temperature interval of the measurements and it is the intercept that is more informative. The intercept near zero for the H_t versus H_b plot is a clear indication that functional temperature dependence is nearly the same for both ^1H shifts. It is difficult to attribute the large intercepts for both ^{11}B and ^{13}C shifts as due to differences in chemical shifts and, therefore, we take these large shifts as evidence that an additional spin transfer mechanism is present for these two nuclei which has a different functional dependence on temperature.

To see if inclusion of the covalent mechanism for spin transfer might better explain the temperature behavior of the ^{11}B shift we have fitted the experimental shifts to a sum of Eq. (7) and Eq. (9) assuming $b_\sigma = b_\pi = b$. Since the covalent equations assumed pure $^3H_4$ functions we have used the equivalent calculations for the polarization shift. The fitted equation is plotted in Fig. 2 as a dashed curve. The standard deviation is 0.62 ppm. The fitted parameters were $K = -2.76$ MHz, $a_\sigma{}^2A_{2s} = 0$, and $b^2A_{2p} = 1.26$ MHz. Taking $A_{2p} = 53.1$ MHz[25] for ^{11}B, the value of the molecular orbital coefficient is $b^2 = 0.024$ which would mean a 2% covalent transfer to the boron p orbitals or an 8% reduction in the f orbitals. This is a reasonable number considering the 15% reduction in k_z. It would appear reasonable to ascribe the different temperature dependence in ^{11}B and ^{13}C to the presence of a covalent contribution (of sign opposite to that for the polarization shift) to the paramagnetic shift.

The fitted values of K and b^2 given above cannot be taken as reliable due to the assumption in the calculation of pure $^3H_4$ functions. The data in Table 2 show that these functions gave poorer agreement for the ^1H shifts. It is clear, however, that the actual K values for both ^{11}B and ^{13}C are larger than the fitted values of Table 2. Also the actual value of b^2 is probably of the same order of magnitude as found above.

It is of interest to compare our values of K to those reported by Baker[15] for ^{19}F - Gd^{3+}, Eu^{2+}. Scaled to ^1H his average values would be -1.93 MHz for Gd^{3+} and -2.23 MHz for Eu^{2+}. Our values for the bridging proton are only about twice as large in magnitude. Scaled down to ^{11}B the K values become -0.62 MHz for Gd^{3+} and -0.81 MHz for Eu^{2+}. Our computations show that K in our system is about three to four times larger in magnitude.

The contact shifts of H_b of approximately -150 ppm at room temperature are the largest reported to date in U(IV) compounds except for $U(BH_4)_4$, where they are approximately the same.[7] Reports of ^{11}B shifts are rare. In $(C_5H_5)_3UBH_4$, the delocalization shift contribution for ^{11}B has been estimated to be -240 ppm and that of the bridging protons to be -61 ppm.[26] It is not possible to explain this inversion in magnitudes without some information about the ground and excited states of the molecule. A different ground state will have a pronounced effect on both $\langle S_z \rangle/H$ and on the covalent shift. A different ground state could have a much smaller covalency contribution for ^{11}B making the measured shift more negative than is found in $U(BH_3CH_3)_4$. Comparison with other similar σ-bonding ligands is difficult due to lack of experimental results. In $(C_5H_5)_3UBH_3CH_2CH_3$ the ^1H delocalization shifts are -55.3 ± 8 ppm for the bridging protons and -7.3 ± 1.2 ppm for the methylene protons.[27] Both of these shifts are about one third, in magnitude, of the

shifts found here for corresponding protons in $U(BH_3CH_3)_4$. The bridging proton shift is, however, nearly the same as that found for the related $(C_5H_5)_3UBH_4$ indicating that both have the same ground state. A shift of -90 ppm has been reported[6] for ^{13}C in $U(NCS)_8^{4-}$ which is not much different from the -70 ppm reported here.

Conclusions

The observed contact shifts of the bridging hydrogens are the largest reported to date in U(IV)-compounds. The temperature dependence and sign of the ^1H shifts (both bridging and terminal) agree very well with what is predicted by a polarization model in which spin is transferred by an overlap between outer 6s and 6p electrons of uranium with ligand orbitals. This spin has been negatively polarized to that of the inner 5f electrons by an interaction between the 5f and 6s, 6p electrons. The agreement between the experimental and theoretical temperature dependence is best when the eigenvectors and energies for the entire f^2 set used are those that best fit the optical and magnetic data for the system.

The negative shift for both ^{13}C and ^{11}B indicate the polarization contribution is the largest, but the sizable divergences between predicted and experimental temperature dependencies is strong evidence for a large contribution from a covalent mechanism directly involving the 5f orbitals of the uranium atom.

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Appendix

It is obvious that for a calculation utilizing the entire f^n-basis set and not just one term of the free ion, computer programs must be used. In the following we give formulas which are easily programmable and allow separation of the L and S parts so that orbital reduction factors can be introduced.

The wave function Ψ in the matrix element $\langle\Psi|\hat{O}|\Psi\rangle$ consists of a number of components

$$|\Psi_i\rangle = \sum_j c_j^i |\gamma_j S_j L_j J_j J_z\rangle \tag{A1}$$

and the problem reduces to the calculation of matrix elements of the form[22,28]

$$\langle\gamma SLJJ_z|k_z L_z + g_e S_z|\gamma' S' L' J' J_z'\rangle \tag{A2}$$

(where $g_e = 2.0023$) which can be expressed as follows:

$$\langle\gamma SLJJ_z|k_z L_z + g_e S_z|\gamma' S' L' J' J_z'\rangle$$

$$= (-1)^{J-J_z} \begin{pmatrix} J & 1 & J' \\ -J_z & 0 & J_z \end{pmatrix} \langle\gamma SLJ|k_z L_z + g_e S_z|\gamma' S' L' J'\rangle \tag{A3}$$

where the quantity in $\begin{pmatrix} \quad \end{pmatrix}$ is a 3-j symbol. The above 3j symbol is not zero only if $J_z = J_z'$ and $|J-J'| \geq 1$. The reduced matrix element can now be separated into an orbital and a spin part:

$$\langle \gamma SLJ | k_z L_z + g_e S_z | \gamma' S' L' J' \rangle$$
$$= k_z \cdot (-1)^{S+L+J'+1} \begin{Bmatrix} J & 1 & J' \\ L' & S & L \end{Bmatrix} [(2J+1)(2J'+1)L(L+1)(2L+1)]^{1/2}$$
$$+ g_e \cdot (-1)^{S'+L'+J+1} \begin{Bmatrix} J & 1 & J' \\ S' & L & S \end{Bmatrix} [(2J+1)(2J'+1)S(S+1)(2S+1)]^{1/2} \qquad \text{(A4)}$$

where the quantities in $\{\ \}$ are 6-j symbols. It can easily be shown that the reduced matrix element is not zero only for $\gamma = \gamma'$, $S = S'$ and $L = L'$. Equation (A4) can also be used to calculate matrix elements of S_z alone by simply setting k_z to zero and dividing the result by g_e. The necessary 3j and 6j symbols are obtained from easily programmable equations.[29]

Table 1. Lowest calculated energy levels (cm^{-1}) from the optical analysis of $U(BD_4)_4/Hf(BD_4)_4$ and corresponding eigenvectors.[3a]

State	E_{calc}	Eigenvector[a]
E	0	$94\ ^3H_4 + 3\ ^1G_4$
T_1	215[b]	$76\ ^3H_4 + 11\ ^3H_5 + 7\ ^1G_4$
T_2	531	$78\ ^3H_4 + 11\ ^1G_4 + 6\ ^3F_3$
A_1	2036	$63\ ^3H_4 + 27\ ^1G_4$
E	2750	$57\ ^3F_2 + 31\ ^3H_4\ 9\ ^1D_2$
T_2	3562	$58\ ^3F_2 + 20\ ^3H_5 + 10\ ^1D_2$

[a]Percent of SLJ state. Enough components are given, at least 2, to include 90% of the state.

[b]From analysis of the susceptibility.

Table 2. Best fit values of hyperfine parameter K.

	H_b	H_t	B	C
$k_z = 1.00$, $\Delta_1 = 215\ cm^{-1}$, complete calculation				
K(MHz) =	-4.069	-0.4245	-0.788	-0.451
Std. Dev. (ppm) =	0.44	0.21	9.55	2.06
$k_z = 0.85$, $\Delta_1 = 215\ cm^{-1}$, complete calculation				
K(MHz) =	-5.640	-0.588	-1.093	-0.625
Std. Dev. (ppm) =	0.43	0.18	9.76	2.21
$k_z = 1.00$, $\Delta_1 = 370\ cm^{-1}$, complete calculation				
K(MHz) =	-4.526	-0.472	-0.856	-0.498
Std. Dev. (ppm) =	6.97	0.91	5.84	1.13
$k_z = 1.00$, $\Delta_1 = 215\ cm^{-1}$, $^3H_4$ functions only				
K(MHz) =	-3.520	-0.367	-0.673	-0.389
Std. Dev. (ppm) =	3.40	0.54	7.38	0.52
$k_z = 1.00$, $\Delta_1 = 370\ cm^{-1}$, $^3H_4$ functions only				
K(MHz) =	-3.915	-0.408	-0.732	-0.430
Std. Dev. (ppm) =	9.83	1.21	3.88	2.56

Table 3. Slope and intercept for shifts plotted versus bridging proton shifts.

Nucleus	Slope	Intercept (ppm)	Correlation factor
B	0.205 ± 0.008	68.2 ± 1.4	0.9994
C	0.360 ± 0.010	14.8 ± 3.7	0.9988
H_t	0.113 ± 0.006	-1.6 ± 0.1	0.9999

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Figure Captions

Figure 1. Molecular symmetry of the tetrahedral $U(BH_3CH_3)_4$ unit. The view is along a S_4 axis.

Figure 2. T^{-1} dependence of the paramagnetic shifts in $U(BH_3CH_3)_4$ referred to $Th(BH_3CH_3)_4$. All shifts are to lower field and given in ppm. The solid lines were calculated from Eq. (7,8) in paper using $k_z = 0.85$, $\Delta_1 = 215\ cm^{-1}$, K values given in Table 2, and crystal field energies and eigenvectors of the optical analysis.[3a] The dashed line for B is a combined polarization plus covalent shift theoretical curve.

Figure 3. Temperature dependence of the total average spin $\langle S_z \rangle / H$ from Eq. (8)

a: $k_z = 1.00$, $\Delta_1 = 215\ cm^{-1}$, complete set of eigenvalues and eigenvectors from reference 3a.

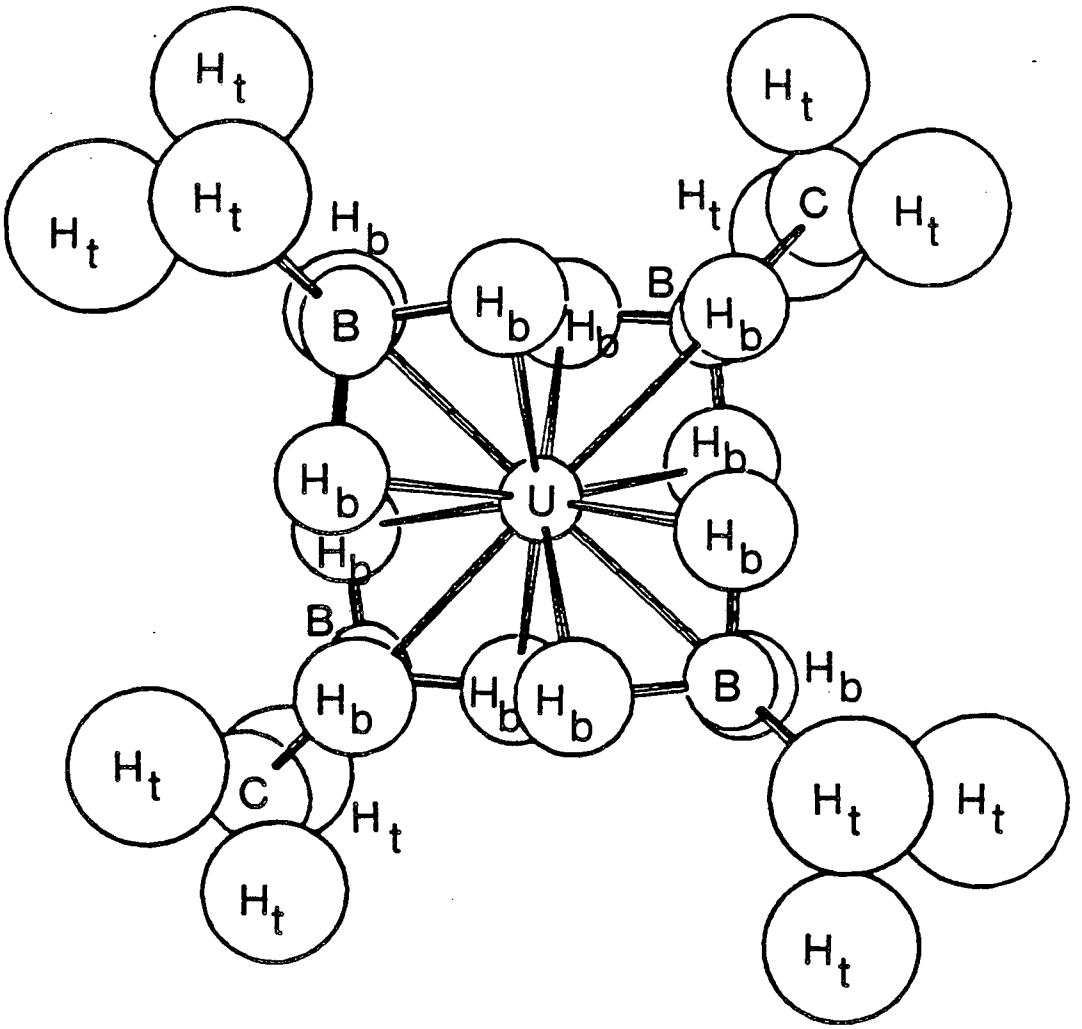
b: $k_z = 1.00$, $\Delta_1 = 370\ cm^{-1}$, complete set of eigenvalues and eigen vectors from reference 3a.

c: $k_z = 0.85$, $\Delta_1 = 215\ cm^{-1}$, complete set of eigenvalues and eigenvectors from reference 3a.

d: $k_z = 1.00$, $\Delta_1 = 215\ cm^{-1}$, pure $^3H_4$ functions only.

e: $k_z = 1.00$, $\Delta_1 = 370\ cm^{-1}$, pure $^3H_4$ functions only.

Figure 4. $\Delta H/H$ for C, B and H_t plotted as a function of $\Delta H/H$ for H_b. The solid lines are least-square fitted lines whose slopes and intercepts are given in Table 3.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B
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Figure 1

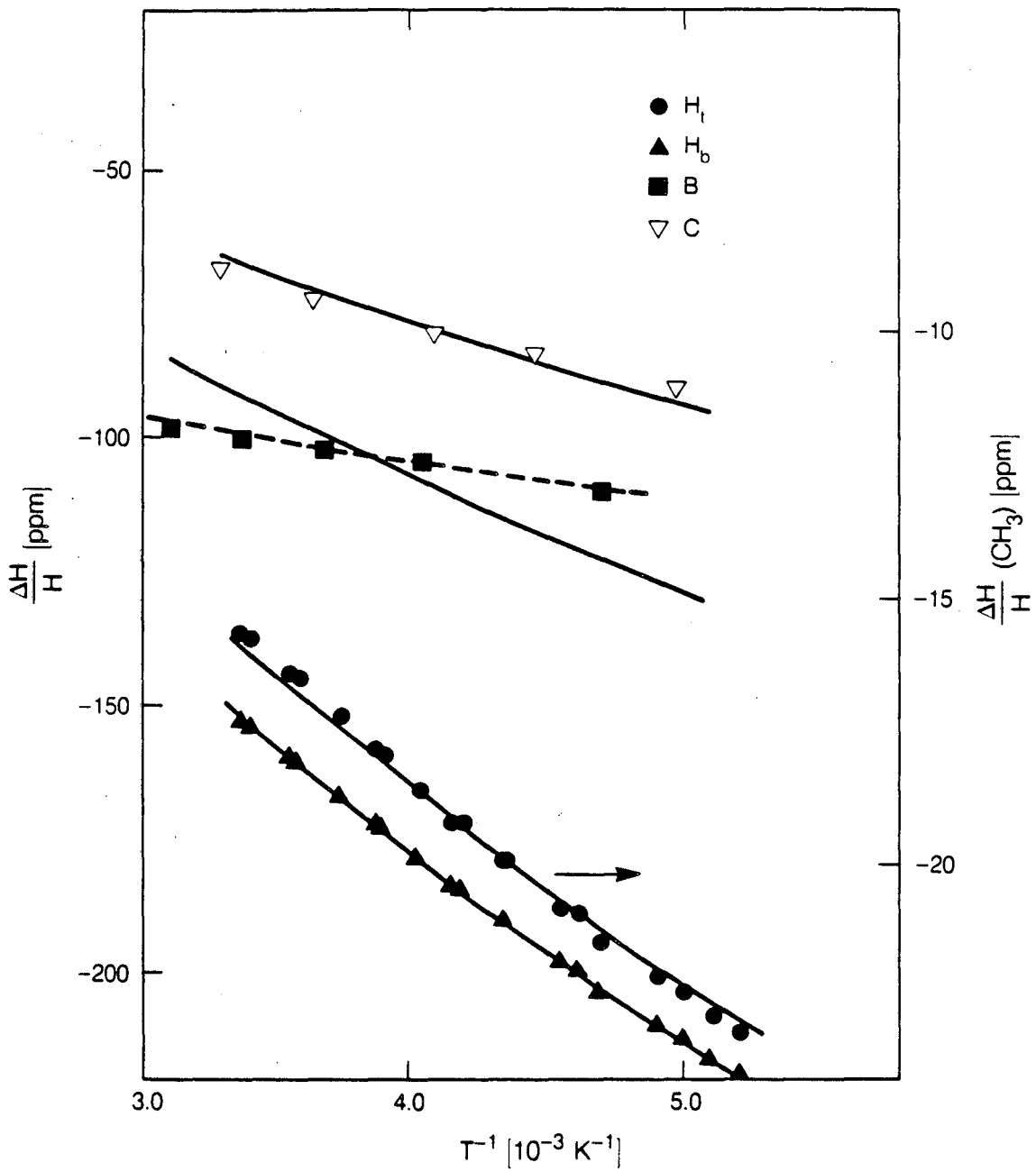

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Figure 2

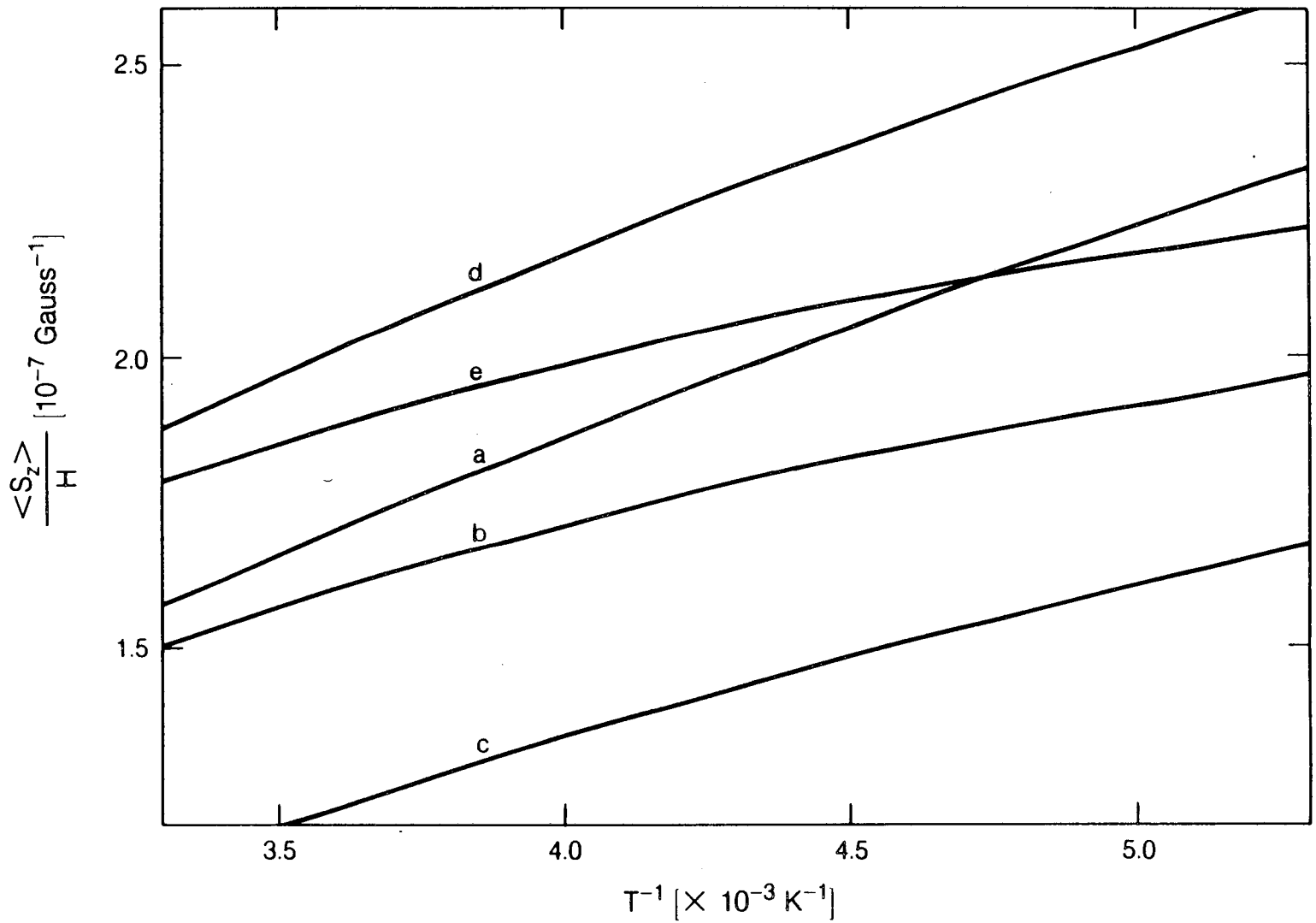

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Figure 3

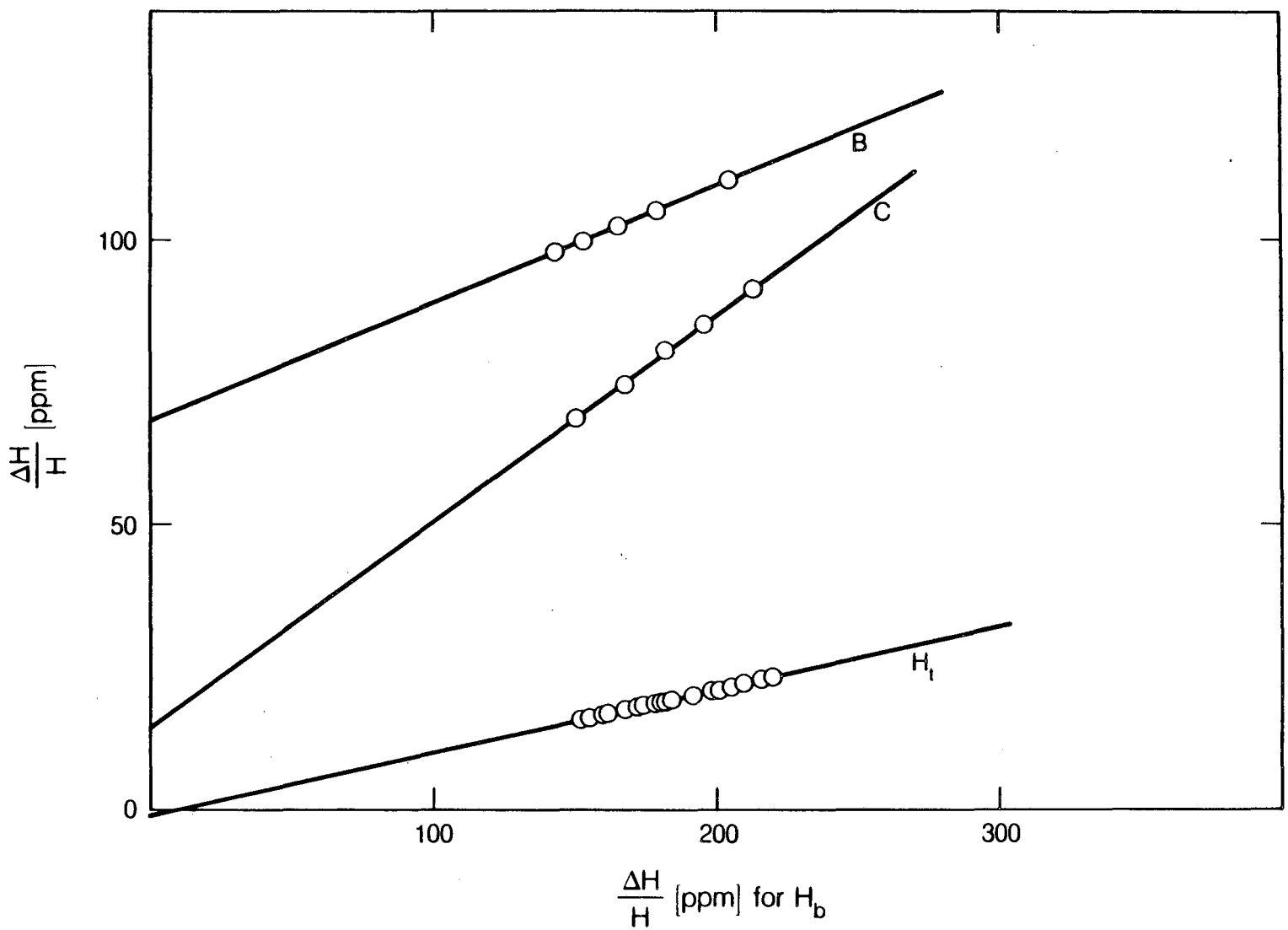

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Figure 4

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