

Lawrence Berkeley National Laboratory

LBL Publications

Title

PROTON MAGNETIC RESONANCE SHIFTS IN BIS(CYCLOOCTATE-TRIAENYL)URANIUM(IV)

Permalink

<https://escholarship.org/uc/item/1pg2f3f7>

Authors

Edelstein, H.

LaMar, G.N.

Mares, F.

et al.

Publication Date

1970-12-01

PROTON MAGNETIC RESONANCE SHIFTS IN
BIS(CYCLOOCTATETRAENYL)URANIUM(IV)

N. Edelstein, G. N. LaMar, F. Mares, and A. Streitwieser, Jr.

December 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

PROTON MAGNETIC RESONANCE SHIFTS IN BIS(CYCLOOCTATETRAENYL)URANIUM(IV)[†]

N. Edelstein

Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

G. N. LaMar

Shell Development Company
Emeryville, California 94608

and

F. Mares and A. Streitwieser, Jr.

Chemistry Department
University of California
Berkeley, California 94720

December 1970

The measured proton resonance shifts of $U(COT)_2$ are analyzed on the basis of a crystalline field model and magnetic susceptibility data. It is pointed out that in $U(COT)_2$ the orbital and spin angular momenta are coupled antiparallel for the ground state, so that a positive hyperfine coupling constant due to the Fermi contact term will result in an upfield proton resonance shift. The hyperfine coupling constant arising from the Fermi contact term is found to be $A_F = +0.90 \text{ Mhz} \pm 25\%$.

[†]Part of this work was performed under the auspices of the U. S. Atomic Energy Commission; the work in the Chemistry Department, University of California, was supported in part by NSF Grant No. 13369.

I. Introduction

The question of the extent of participation of the f orbitals in the metal-ligand covalency of organometallic actinide complexes has received renewed attention recently [1-4], with the emphasis on interpreting the Fermi contact contribution to the observed proton nmr shift of such paramagnetic complexes [1]. In complexes with magnetic anisotropy [2,3], both the contact and dipolar interactions [5,6] contribute to the isotropic shift, and before any interpretation of the contact shift can be put forth, an estimate of the dipolar shift must be made. The lack of reliable structural or magnetic data has prevented detailed and unambiguous analyses for most systems. We wish to present here solution proton nmr data for bis (cyclooctatetraenyl)uranium(IV), $U(COT)_2$ [7], also called "uranocene", for which both the structural [8] and magnetic [9] data are available, and interpret the shifts in terms of a crystalline field model [9]. From our analysis, we determine that part of the isotropic shift arises from the Fermi contact term, and reach some qualitative conclusions as to its electronic origin in relation to the metal-ligand bonding.

II. Experimental

Samples of uranocene prepared according to the method of Streitwieser and Müller-Westerhoff [7] were dissolved in hot THF-d₈ or deuterated toluene and sealed under argon. The proton magnetic resonance shifts were measured on a Varian HR-100 spectrometer modified for variable frequency modulation. The temperature was controlled by a precalibrated Varian V-4343 unit. The shifts measured are plotted in fig. 1 and tabulated in Table I. All shifts are referenced to the proton resonance in COT²⁺ which was taken as -5.9 ppm with respect to TMS. The actual data were measured with respect to the trace amounts of protons in the deuterated solvents and were later corrected to the proton resonance of COT²⁺. The shifts in both solvents agreed within experimental error. The lines widths appeared to be temperature independent and of the order of 10 Hz.

III. Discussion

The magnetic susceptibility data on polycrystalline $U(COT)_2$ of Karraker, et al. [9], followed the Curie-Weiss law in the temperature range $4.2^\circ K - 45^\circ K$ with an effective moment of 2.4 BM. Measurements of the magnetic susceptibility of $U(COT)_2$ in the temperature range $10^\circ K - 300^\circ K$ have been performed by Dr. D. K. Fujita of the Lawrence Radiation Laboratory who found Curie-Weiss behaviour with an effective moment of 2.6 BM. The above magnetic data were interpreted on the basis of a crystalline field model with covalency parameterized by use of the orbital reduction factor [9]. We shall use the same model to interpret the proton magnetic resonance shifts.

We make the following assumptions: 1) only the ground crystalline field state is populated in the temperature range of interest; that is, $E_1 \gg kT$ where E_1 is the energy of the first excited crystalline field state, 2) the crystalline field does not mix different J states; 3) the effects of intermediate coupling are negligible.

For U^{4+} (Ac core, $5f^2$) the ground term is a 3H_4 . In a crystalline field of D_{8h} symmetry this ninefold degenerate level will split into four doublets ($J_z = \pm 4, \pm 3, \pm 2, \pm 1$) and 1 singlet ($J_z = 0$). It was shown previously that the magnetic susceptibility data were consistent with the $J_z = \pm 4$ doublet lying lowest if an orbital reduction factor of $k \approx .8$ was introduced [9]. We have calculated the dipolar shift using the equation [10]

$$\left\langle \frac{\Delta H_D}{H_0} \right\rangle = (3R^3)^{-1} [\chi_{\parallel} - \chi_{\perp}] [3 \cos^2 \Omega - 1]$$

which is applicable when $T_1 \ll \tau_c$; where T_1 is the electronic relaxation time, τ_c is correlation time of complex, χ_{\parallel} is the magnetic susceptibility along the

C_8 axis, and χ_{\perp} is the magnetic susceptibility in the plane perpendicular to the C_8 axis and is zero according to our model. The angle Ω is the angle between the C_8 symmetry axis and the vector of length R connecting the U nucleus with a proton nucleus. This angle can be calculated from the previously determined crystallographic structure [8]. Because the quantity $(3 \cos^2 \Omega - 1)$ is close to zero, it is very sensitive to the uncertainty in the structure. We have used in our calculations the two extreme values and the average value for the angle and a C-H distance of 1.09 Å, the results for the dipolar shift at 302°K are shown in Table II. The last column in Table II shows the possible range of the Fermi contact shift at 302°K due to the uncertainty of the angle Ω .

The Hamiltonian for the Fermi contact term may be written in the effective operator formalism as

$$\mathcal{H}_F = A_F \vec{I} \cdot \vec{S} ,$$

where A_F is hyperfine coupling constant for this type of interaction.

In the $SLJJ_z$ representation it is straightforward to evaluate matrix elements of the type [11]

$$\langle SLJJ_z | \vec{O} | SLJJ_z \rangle$$

for a 3H_4 state with $J_z = \pm 4$ and \vec{O} being \vec{S} or $kL + 2\vec{S}$. The matrix elements needed are tabulated in Table III. The off-diagonal components (S_x , etc.) are zero since we assumed only the $J_z = \pm 4$ states were populated.

It is important to note that in a magnetic field the $J_z = -4$ state is lowest in energy and for this state $S_z = +4/5$. Thus the ground crystalline field state of $U(COT)_2$ has S_z parallel to the magnetic field. This is opposite to the direction found, for example, in 3d transition metal complexes where the orbital angular momentum is quenched so the spin angular momentum will be anti-parallel to the magnetic field. Thus for the same type of spin delocalization mechanism in iso-structural 3d and 5f complexes, assuming Hund's rules are valid for the ground state, the contact shifts in the two complexes will be of opposite sign if the f shell is less than half filled, and of the same sign if the f shell is more than half filled [12].

The thermal average of $\langle S_z \rangle$ is

$$\langle S_z \rangle = \frac{4/5 \exp \left(+ \frac{4g_J' \beta H_0}{kT} \right) - 4/5 \exp \left(- \frac{4g_J' \beta H_0}{kT} \right)}{\exp \left(+ \frac{4g_J' \beta H_0}{kT} \right) + \exp \left(- \frac{4g_J' \beta H_0}{kT} \right)}$$

If we assume for the temperatures and magnetic fields of interest

$$4g_J' \beta H_0 \ll kT$$

so

$$\langle S_z \rangle = \frac{16}{5} \frac{g_J' \beta H_0}{kT}$$

and therefore in the limit $T_1 \ll \tau_c$

$$\langle S_z \rangle_{\text{Ave.}} = \frac{1}{3} \left(\frac{16}{5} \frac{g_J' \beta H_0}{kT} \right)$$

Then if we use frequency units

$$\delta = \frac{1}{3} A_F \left(\frac{16}{5} \frac{g_J' \beta H_0}{kT} \right)$$

where δ is the Fermi contact shift, A_F is the hyperfine coupling constant of the protons and the units are Mhz. From our data assuming $k = .85$ and therefore $g_J = .6$, we obtain

$$A_F = +0.90 \text{ Mhz} \pm 25\%.$$

It should be emphasized that because of the assumptions in our calculations and the uncertainty in the dipolar contribution we place this large error on the value of A_F .

Extrapolation of the experimental shifts of fig. 1 to $1/T = 0$ yields ~ -6 ppm for the intercept. The proton magnetic resonance spectrum of a similar diamagnetic compound has not been obtained so our reference could be off by -2 to -3 ppm. If we consider the $J_z = \pm 3$ level to be at $\sim 400-600 \text{ cm}^{-1}$, an extrapolated shift of ~ -3 ppm can be explained. A crystalline field level around this energy would be consistent with the accuracy of the magnetic susceptibility experiments.

If only pi bonding were present in this complex we would expect much smaller Fermi contact shifts and the opposite sign. Therefore, sigma bonding is certainly important if not dominant, although as yet we do not have enough information to be more quantitative. Furthermore, even the sigma spin delocalization need not be directly related to 5f covalency, since exchange polarization between the 5f and 6s or 6p electrons or other mechanisms cannot be ruled out [12-14]. Further investigations, some of which are currently in progress in our laboratories are required to elucidate the bonding in this complex.

We wish to thank Dr. D. K. Fujita for allowing us to quote his unpublished measurements, Dr. A. Zalkin and Prof. K. Raymond for helpful discussions, and Mr. K. Hodgson for experimental assistance.

References

1. R. V. Ammon, B. Kanellakopoulos, and R. D. Fischer, Chem. Phys. Letters 2 (1968) 513.
2. R. V. Ammon, B. Kanellakopoulos, R. D. Fischer, and P. Lauberau, Inorg. Nucl. Chem. Letters 5 (1969) 219, 315; R. V. Ammon, B. Kanellakopoulos, and R. D. Fischer, Radiochim. Acta. 11 (1969) 162.
3. R. V. Ammon, B. Kanellakopoulos, and R. D. Fischer, Chem. Phys. Letters 4 (1970) 553.
4. N. Paladino, G. Lugli, U. Pedretti, M. Brunelli, and G. Giacometti, Chem. Phys. Letters 5 (1970) 15.
5. D. R. Eaton and W. D. Phillips, Advances in Magnetic Resonance 1 (1965) 103.
6. R. J. Kurland and B. R. McGarvey, J. Magnetic Res. 2 (1970) 286.
7. A. Streitwieser, Jr. and V. Müller-Westerhoff, J. Amer. Chem. Soc. 90 (1968) 7364.
8. A. Zalkin and K. N. Raymond, J. Amer. Chem. Soc. 91 (1969) 5667.
9. D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, J. Amer. Chem. Soc. 92 (1970) 4841.
10. B. R. McGarvey, J. Chem. Phys. 53 (1970) 86.
11. B. R. Judd, "Operator Techniques in Atomic Spectroscopy", McGraw-Hill, New York, 1963.
12. W. B. Lewis, J. A. Jackson, J. F. Lemons, and H. Taube, J. Chem. Phys. 36 (1962) 694.
13. R. E. Watson and A. J. Freeman, Phys. Rev. 156 (1967) 251.
14. R. E. Watson and A. J. Freeman, Phys. Rev. Letters 6 (1961) 277.

Table I. Proton resonance shifts of $U(COT)_2$ as a function temperature (referenced with respect to $COT^=$).

Temperature $^{\circ}K$	Measured Shift (ppm)
353 ± 2	+ 34.9
328 ± 2	+ 37.6
302 ± 1	+ 41.9
273 ± 2	+ 47.0
248 ± 2	+ 52.0
223 ± 3	+ 58.4
198 ± 3	+ 67.7

Table II. Contributions to the measured proton shifts at 302°K from the dipolar and Fermi contact terms for various values of the angle Ω .

R (Å)	$(3\cos^2\Omega-1)$	$\left\langle \frac{\Delta H_D}{H} \right\rangle$ at 302°K (ppm)	$\left\langle \frac{\Delta H_F}{H} \right\rangle$ at 302°K (ppm)
3.481	-0.092	+ 8.6	+33.3
3.498	-0.152	+14.0	+27.9
3.515	-0.210	+19.2	+22.7

Table III. Values of the matrix elements for various operators for the ground state of $U(COT)_2$.

Operator	J_z	Value of Matrix Element
$kL_z + 2S_z$	-4	$-4g_j^1$
$kL_z + 2S_z$	4	$4g_j^1$
S_z	-4	+4/5
S_z	4	-4/5

Figure Caption

Fig. 1. Proton resonance shifts as a function of $1/T$ for $U(COT)_2$ (referenced with respect to COT^{\ominus}).

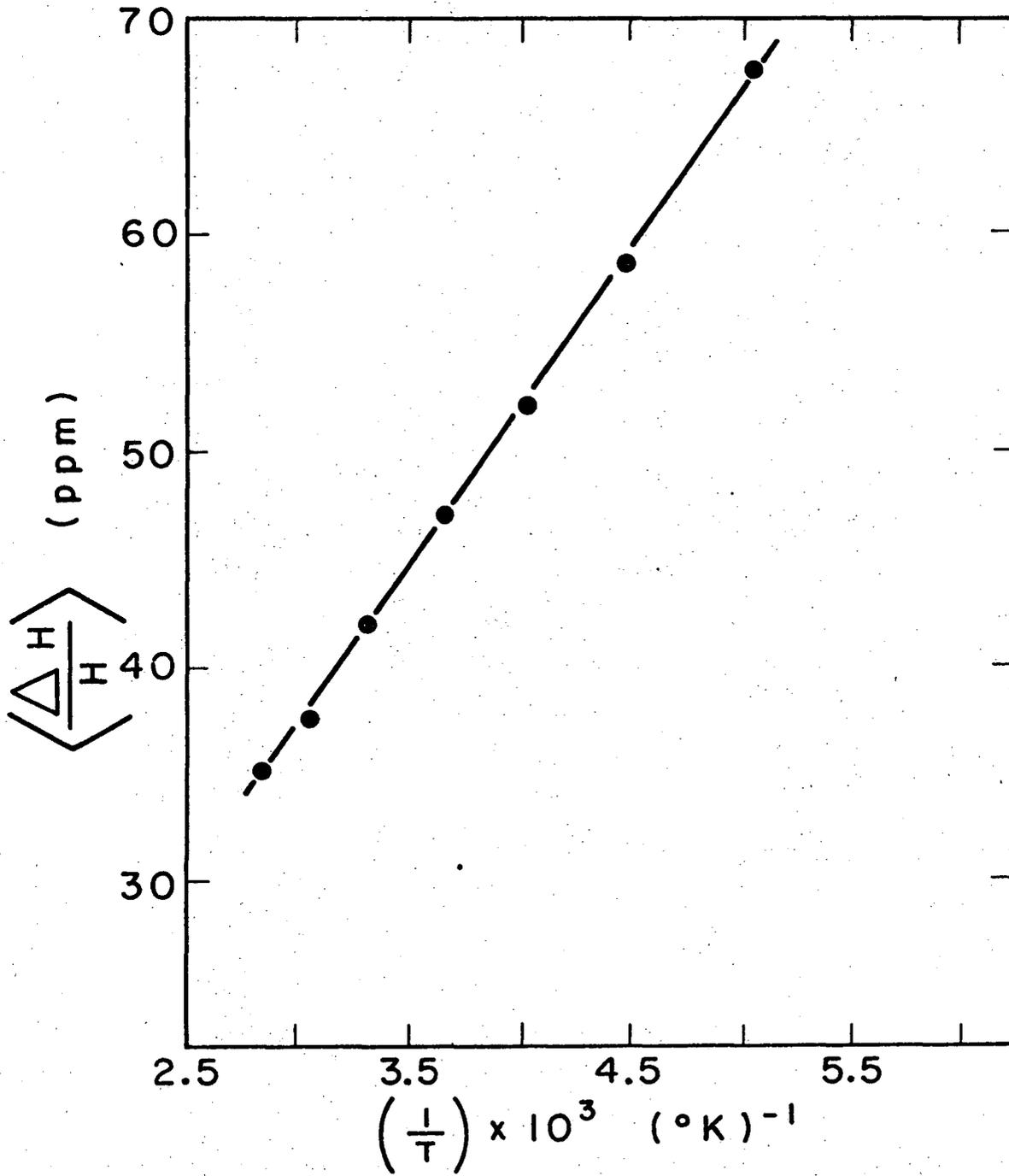


Fig. 1

XBL7012 - 4170

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720