

Nuclear Size and Shape Effects in Chemical Reactions. Isotope Chemistry of the Heavy Elements

Jacob Bigeleisen

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

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Abstract: The theory of the isotopic enrichment factor is extended to include hyperfine splitting and the nuclear field shift. It is shown that hyperfine splitting is an order of magnitude too small to explain the anomaly in the $^{238}\text{U}/^{235}\text{U}$ separation in the U(III)–U(VI) exchange reaction. The “anomalous mass effect” in this reaction and the related U(IV)–U(VI) exchange reactions are shown to be related to the nuclear field shift of the electron energy levels. Calculations of the effects of these shifts exactly reproduce the odd–even staggering in the U(IV)–U(VI) exchange reaction and the separation factors for the even–even nuclei. In the U(IV)–U(VI) exchange reactions the nuclear field effect is three times as large as the absolute value and of opposite sign to the vibrational energy term. It is the nuclear field shift which leads to a preference of the U(IV) for the heavy isotope in each of these exchange reactions. A revision of the reduced partition function ratios of uranium ions in solution, which takes into account the nuclear field shift, is presented.

Background

Isotope shifts in the electronic spectra of atoms and molecules are well-known.^{1,2} There are two types of shifts: (1) the mass shift, which results from the coupling of the motion of the nuclei and the electrons, and (2) the field shift, which results from the difference in nuclear sizes and shapes of isotopes. Only the implications of the mass shift on isotope chemistry have been considered to this date. Conventional wisdom has been that the mass shift is either small or does not differ significantly from one chemical species to another. Within this appraisal the mass shift has been largely neglected in isotope chemistry. A major exception has been the work of Wolfsberg et al.,^{3–5} who have evaluated the mass shift in the quantum mechanical approximation for diatomic hydrides and water. Generally they find that the correction to H–D fractionation factors is of the order of 1%; larger effects are found in diatomic hydrides with large electronic angular momenta. It thus requires experiments of high accuracy and a detailed knowledge of the usual vibrational factors that contribute to isotope fractionation to detect the isotope mass shift, K_{BOELE} .³ The mass shift scales with $\delta M/M^2$ and thus becomes negligible for the isotope chemistry of elements with $Z > 40$.

Isotope shifts up to 1 cm^{-1} have been found in the atomic spectra of the heavy elements.¹ A shift of this magnitude to the ground state of an atom or molecule adds (subtracts) 5×10^{-3} to the logarithm of the isotopic reduced partition function ratio at 300 K. Recall that the typical values for the logarithm of the isotopic partition function ratio at 300 K are 0.01 for $^{80}\text{Se}/^{78}\text{Se}$ and 0.002 for $^{238}\text{U}/^{235}\text{U}$.^{6,7} The difference in the

logarithms of the reduced partition function ratios of two chemical species is just the logarithm of the isotope fractionation factor. The field shifts do not scale with $\delta M/M^2$. Since vibrational isotope effects in the heavy elements scale with $\delta M/M^2$, an anomalous mass effect in isotope chemistry may be a signature of the effect of field shifts on isotope chemistry. When the quantum effects related to molecular vibrations are not small, i.e. $E(\text{vib}) \geq kT$, one may encounter anomalous mass effects. The conditions when such anomalous mass effects may occur have been studied in detail⁸ and need not concern us in this work.

Specific enhancement of ^{235}U over and above a linear δM dependence has been found in the chemical exchange reaction of uranium between different oxidation states, cf. Table 1. Fujii et al.^{9,10} and Takeda et al.¹¹ have found the $^{238}\text{U}/^{235}\text{U}$ isotope fractionation factor in the U(IV)–U(VI) exchange reaction to be 1.9×10^{-4} larger than a linear interpolation between the $^{238}\text{U}/^{236}\text{U}$ and $^{238}\text{U}/^{234}\text{U}$ separation factors at 300 K, cf. Figure 1. The reaction studied is the exchange of U(IV)_{aq} vs U(VI) on an anion exchange resin. The ^{238}U concentrates in the U(IV) species. The $^{238}\text{U}/^{235}\text{U}$ separation factor is 13×10^{-4} at 300 K. Similar but less detailed studies have been reported by Dujardin et al.¹² in the U(III)–U(IV) exchange. Here the excess separation factor is 5×10^{-4} , which is 22% of the $^{238}\text{U}/^{235}\text{U}$ separation factor. This anomalous mass effect has been attributed to the nuclear spin of ^{235}U .⁹

(7) Bigeleisen, J. *Bulletin Research Laboratory for Nuclear Reactors*; Fujii, Y., Ishida, T., Takeuchi, K., Eds.; Special Issue No. 1, Tokyo, 1992; p 24, ISSN 0387-6144.

(8) Kotaka, M.; Okamoto, M.; Bigeleisen, J. *J. Am. Chem. Soc.* **1992**, *114*, 6436.

(9) Fujii, Y.; Nomura, M.; Okamoto, M.; Onitsuka, H.; Kawakami, F.; Takeda, K. *Z. Naturforsch.* **1989**, *44a*, 395.

(10) Fujii, Y.; Nomura, M.; Okamoto, M.; Onitsuka, H.; Nakanishi, T. *Bulletin Research Laboratory for Nuclear Reactors*; Fujii, Y., Ishida, T., Takeuchi, K., Eds.; Special Issue No. 1; Tokyo, 1992; p 214, ISSN 0387-6144.

(11) Takeda, K.; Obanawa, H.; Kawakami, F. *Bulletin Research Laboratory for Nuclear Reactors*; Fujii, Y., Ishida, T., Takeuchi, K., Eds.; Special Issue No. 1, Tokyo, 1992; p 192, ISSN 0387-6144.

(12) Dujardin, T.; Lonchampt, G. *Bulletin Research Laboratory for Nuclear Reactors*; Fujii, Y., Ishida, T., Takeuchi, K., Eds.; Special Issue No. 1, Tokyo, 1992; p 161, ISSN 0387-6144.

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(1) King, W. H. *Isotope Shifts in Atomic Spectra*; Plenum Press: New York, 1984.

(2) Van Vleck, J. H. *J. Chem. Phys.* **1936**, *4*, 327.

(3) Kleinman, L.; Wolfsberg, M. *J. Chem. Phys.* **1973**, *59*, 2043; **1974**, *60*, 4740, 4749.

(4) Wolfsberg, M. *Isotopes and Chemical Principles*; Rock, P., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1975; Vol. 11, p 64.

(5) Bardo, R.; Wolfsberg, M. *J. Phys. Chem.* **1976**, *80*, 1068.

(6) Bigeleisen, J. *Isotopes and Chemical Principles*; Rock, P., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1975; Vol. 11, p 2.

Table 1. Enhanced ^{235}U Isotope Separation Factors in Uranium Chemical Exchange Reactions

exchange reaction	$\epsilon(235-238)$	$\epsilon(235-238) - 1.5\epsilon(236-238)$
U(III)–U(IV) ^a	23.0×10^{-4}	5×10^{-4}
U(IV)–U(VI) ^b	13.0×10^{-4}	1.9×10^{-4}

^a Reference 12. ^b References 9–11.

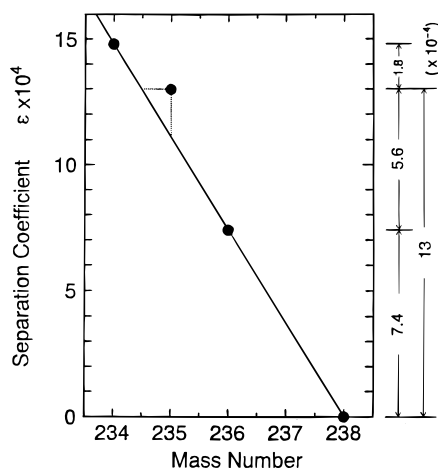
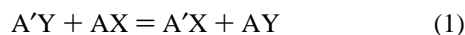


Figure 1. Plot of the logarithms of the ^{234}U , ^{235}U , and ^{236}U isotope separation factors vs ^{238}U , $\epsilon = \ln[(^{238}\text{U}/\text{U})_{(\text{IV})\text{aq}}/(^{238}\text{U}/\text{U})_{(\text{VI})\text{resin}}]$, as a function of the isotope mass, m , as reduced to 308 K.^{9–11} See, however, Tables 4 and 5 and the text.

In this paper I report calculations of the nuclear spin effect in uranium exchange reactions. I show that it is a negligible effect. Then I consider evidence for the field shift, particularly with respect to uranium isotope exchange, where there are the most extensive data available on isotope chemistry and spectral shifts for a heavy element. The implications for the general isotope chemistry of the heavy elements follow.

General Considerations

Consider the isotopic exchange reaction



where A and A' are the heavy and light isotope of the element A, and X and Y represent polyatomic groups. The logarithm of the complete isotope fractionation factor, $\alpha = (\text{A}/\text{A}')_{\text{AY}}/(\text{A}/\text{A}')_{\text{AX}}$, for this reaction is

$$\ln \alpha = \ln \alpha_0 + \ln K_{\text{anh}} + \ln K_{\text{BOELE}} + \ln K_{\text{hf}} + \ln K_{\text{fs}} \quad (2)$$

where

$$\ln \alpha_0 = \ln (s/s')f(\text{AY}/\text{A}'\text{Y}) - \ln (s/s')f(\text{AX}/\text{A}'\text{X}) \quad (3)$$

is the Bigeleisen–Mayer¹³ approximation to the logarithm of the separation factor and $(s/s')f$ is the reduced partition function ratio. The correction terms are the anharmonic vibration correction (K_{anh}), the correction to the Born–Oppenheimer approximation, the isotope mass shift (K_{BOELE}), the nuclear spin effect (K_{hf}), and the nuclear field shift effect (K_{fs}). The anharmonic correction¹⁴ and the correction to the Born–Oppenheimer approximation^{3–5} have been treated both analytically and numerically by Wolfsberg and co-workers. The correct calculation of $\ln K_{\text{anh}}$ leads to corrections to $\ln \alpha_0$ of the order of 1% for D/H exchange reactions. The magnitude of the anharmonic correction depends on the vibrational

(13) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261.

(14) Wolfsberg, M. *Advances in Chemistry*; Spindel, W., Ed.; American Chemical Society: Washington, DC, 1969; Vol. 89, p 185.

Table 2. Hyperfine Splitting in $^{235}\text{U}^{3+}$ ^{16,17}

F^a	M_F	g	$10^2\Delta E$ (cm ⁻¹)
4	4	2	3.754
4	3	2	2.661
4	2	2	1.727
4	1	2	1.025
4	0	1	0.738
3	0	1	-1.590
3	1	2	-1.678
3	2	2	-2.140
3	3	2	-2.523

^a F is a state label, but not a quantum number.¹⁷

amplitude and its change with isotopic substitution. It is a smaller correction for isotope effects in the heavy elements and cannot be a significant factor in the enhanced ^{235}U separation in redox reactions. The nuclear mass shift is estimated to give a correction of 1×10^{-5} to $\ln (s/s')f$ at 300 K for a shift of three mass units to a hydrogen like atom of mass 250. Thus the correction from $\ln K_{\text{BOELE}}$ to $\ln \alpha_0$ for uranium isotope chemistry is negligible.

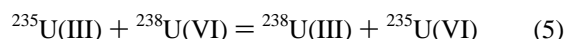
Nuclear Spin Effect

In the absence of any hyperfine splitting or a symmetric splitting of a degenerate ground electronic energy of a polyatomic molecule, the nuclear spin introduces a multiplicative factor Q_{ns} to the molecular partition function. Within this approximation

$$Q_{\text{ns}} = \prod_j (2i_j + 1) \quad (4)$$

where i_j is the spin of the j th nucleus in the molecule. Since nuclear spins are conserved in chemical reactions, the contribution of $\ln K_{\text{hf}}$ to $\ln \alpha$ is identically zero in the absence of hyperfine splitting or in the case of symmetric splitting.¹⁵

It is not possible to calculate $\ln K_{\text{hf}}$ for either the U(III)–U(IV) or the U(IV)–U(VI) exchange reactions. As an illustration of the magnitude of the nuclear spin effect we can calculate $\ln K_{\text{hf}}$ for the hypothetical U(III)–U(VI) exchange and compare the result with the sum of the excess fractionation factors given in Table 1.



For reaction 5 we have

$$K_{\text{hf}} = \frac{[^{238}(Q_{\text{ns}}g_e)^{235}(Q_{\text{ns}}g_e)]\text{U}(\text{III})/[^{238}(Q_{\text{ns}}g_e)^{235}(Q_{\text{ns}}g_e)]\text{U}(\text{VI})}{\quad} \quad (6)$$

In eq 6 the product Q_{ns} is replaced by the quantum sum, $\sum_{gM_F} \exp(-\Delta E_{M_F}/kT)$, where there is hyperfine splitting. In the absence of hyperfine splitting, U(VI), Q_{ns} is given by eq 4.

The hyperfine splitting in $^{235}\text{U}^{3+}$ has been determined by Hutchison et al.^{16,17} From their analysis of the EPR spectrum of a dilute solution of $^{235}\text{UCl}_3$ in a single crystal of LaCl_3 the hyperfine levels of the ground electronic state, $^4I_{9/2}$, compared with that of ^{238}U taken as zero, are given in Table 2. The electron spin of U^{3+} is $1/2$; the ^{235}U nuclear spin is $7/2$; the nuclear spin of ^{238}U is 0. The ground electronic state of $^{235}\text{U}^{3+}$ is split into 7 doublets with quantum numbers $M_F = \pm 1, \pm 2, \pm 3, \pm 4$ and two singlets with quantum numbers $M_F = 0, 0$. K_{hf} can be

(15) Gibson, G. E.; Heitler, W. Z. *Phys.* **1928**, *49*, 465.

(16) Hutchison, C. A., Jr.; Llewellyn, P. M.; Wong, E.; Dorain, P. *Phys. Rev.* **1956**, *102*, 292.

(17) Bleaney, B.; Hutchison, C. A., Jr.; Llewellyn, P. M.; Pope, D. F. D. *Proc. Phys. Soc. B* **1956**, *69*, 1167.

Table 3. Nuclear Spin Effect in a Uranium Isotope Exchange Reaction

$^{235}\text{U(III)} + ^{238}\text{U(VI)} = ^{238}\text{U(III)} + ^{235}\text{U(VI)}$			
$K_{\text{hf}} = \frac{[^{238}\text{U(III)}]_{\text{eq}} [^{235}\text{U(VI)}]_{\text{eq}}}{[^{235}\text{U(III)}]_{\text{eq}} [^{238}\text{U(VI)}]_{\text{eq}}}$			
$^{238}\text{U(III)}$	$Q_{\text{ns}} = 1; g_e = 2$	$^{235}\text{U(III)}$	$Q_{\text{ns}} g_e = \sum g_{M_f} e - \Delta E/kT$
$^{238}\text{U(VI)}$	$Q_{\text{ns}} = 1; g_e = 1$	$^{235}\text{U(VI)}$	$Q_{\text{ns}} = 8; g_e = 1$
$\ln K_{\text{hf}}(300\text{K}) = 1.4 \times 10^{-5}$			

calculated from the levels given in Table 2 and the degeneracies given in Table 3. We find for reaction 5 $\ln K_{\text{hf}} = 1.4 \times 10^{-5}$ at 300 K. We can compare this value with the value of $[\epsilon - (235-238) - \frac{3}{2}\epsilon(236-238)]$, which is equal to 7×10^{-4} (cf. Table 1). Rigorously an experimental value for the U(III)–U(VI) exchange is not simply the sum of the U(III)–U(IV) and the U(IV)–U(VI) values, since the U(IV) solutions are not the same in the U(III)–U(IV) and U(IV)–U(VI) experiments. However, numerous experiments have shown that different complexing agents, pH, and other variables do not change the U(IV)–U(VI) separation factors by more than 2×10^{-4} .^{18,19} The calculated value of $\ln K_{\text{hf}} = 1.4 \times 10^{-5}$ is at least an order of magnitude smaller than $\epsilon(235-238) - \frac{3}{2}\epsilon(236-238)$. Since ^{236}U has no nuclear spin, $\ln K_{\text{hf}}$ should be equal to $\epsilon(235-238) - \frac{3}{2}\epsilon(236-238)$, if there are no contributions other than nuclear spin to $\ln \alpha - \ln \alpha_0$.

Nuclear Field Shifts

We review first some qualitative features of the nuclear field shift and show their relevance to the anomalous mass effects in the isotope chemistry of uranium. The nuclear field shift is a displacement of the ground electronic energy of an atom or molecule due to the differences in nuclear sizes and shapes of isotopes.^{1,20–22} The shift caused by an odd (neutron number) nucleus is generally not midway between those of the even isotopes of next higher and lower atomic mass. The odd neutron isotope level is displaced toward the next lower even nucleus (odd–even staggering). Contrary to zero-point energy effects, e.g. vibrational zero-point energy and the nuclear mass effect, the electronic energy of a light isotope lies lower than that of a heavier isotope. This is a consequence of the smaller size and larger surface charge density of the light isotope compared with that of a heavier isotope. The magnitude of the shift is a product of two factors: (1) the electron density at the nucleus and (2) the charge, size, and shape of the nucleus and the change of the latter two between isotopes.

Isotope shifts have been measured in the atomic spectra of $^{233}\text{U I}$,²³ $^{234}\text{U I}$,²⁴ $^{235}\text{U I}$,²⁵ and $^{236}\text{U I}$ ²³ compared with $^{238}\text{U I}$ ²⁶ vapor. There are extensive data on $^{235}\text{U I}$.²⁷ The shifts for $^{235}\text{U I}$ are in the range of 0–0.9 cm^{-1} . It has been estimated that

(18) Oi, T.; Kakihana, H. *Z. Naturforsch.* **1989**, *44a*, 399.(19) Kakihana, H.; Oi, T. *Bulletin Research Laboratory for Nuclear Reactors*; Fujii, Y., Ishida, T., Takeuchi, K., Eds.; Special Issue No. 1, Tokyo, 1992; p 18, ISSN 0387-6144.(20) Breit, G. *Phys. Rev.* **1931**, *37*, 51.(21) Breit, G. *Rev. Mod. Phys.* **1958**, *30*, 507.(22) Kopfermann, H.; Schneider, E. E. *Nuclear Moments*; Academic Press: New York, 1958.(23) Gagne, J. M.; Saint-Dizier, J. P.; Pianarosa, P. *Opt. Commun.* **1978**, *26*, 348.(24) Gagne, J. M.; Nguyen Van, S.; Saint-Dizier, J. P.; Pianarosa, P. *J. Opt. Soc. Am.* **1976**, *66*, 1415.(25) Gagne, J. M.; Saint-Dizier, J. P.; Pianarosa, P. *Opt. Commun.* **1977**, *20*, 269.(26) We use the conventional spectroscopic notation, U I, to refer to neutral atomic uranium vapor. Symbols with a Roman numeral in parentheses following a chemical symbol, e.g. U(VI), refer to uranium ion in oxidation level +6, i.e. UO_2^{2+} hydrated, complexed.(27) Blaise, J.; Radziemski, L. J., Jr. *J. Opt. Soc. Am.* **1976**, *66*, 644.**Table 4.** Comparison of Relative U(IV)–U(VI) Fractionation Factors at 433 K with Relative Field Shifts in the 5027 Å Line in U I

isotope pair	field shift ^a	$\epsilon_f/\epsilon_{235}$		
		433 K exp ^{b,c}	433 K ^d theor	308 K ^d theor
236–238	0.599	0.568 ± 6	0.576	0.562
235–238	1	1	1	1
234–238	1.194	1.142 ± 4	(1.142)	1.109
233–238	1.561	1.519 ± 6	1.519	1.492

^a King, W. H. *Isotope Shifts in Atomic Spectra*; Plenum Press: New York, 1984; p 159. ^b Fujii, Y.; et al. *Z. Naturforsch.* **1989**, *44a*, 395. ^c Nomura, M.; Higuchi, N.; Fujii, Y. In press. ^d See Table 5 in this paper. ^e Values in parentheses in this and succeeding tables have been used as input parameters in the calculations. The absolute field shift $^{238}\text{U} - ^{235}\text{U}$ is 0.4098 cm^{-1} .

the ground state of $^{235}\text{U I}$ is 1.2 cm^{-1} lower than that of $^{238}\text{U I}$.²⁸ Rajnak and Fred²⁹ have calculated the electron densities at the nuclei of the transuranic elements. They show a one-to-one correlation between the electron density and the field shift. The largest shifts are found when the number of valence s electrons decreases in the transition. There is a smaller effect of opposite sign associated with a decrease in the number of f electrons. This is due to the screening effect of the inner-shell f electrons on the valence s electrons.

For the exchange reaction 1, $\ln K_{\text{fs}}$ is equal to

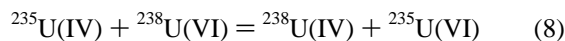
$$\ln K_{\text{fs}} = (kT)^{-1} \{ [E^\circ(\text{AX}) - E^\circ(\text{A}'\text{X})] - [E^\circ(\text{AY}) - E^\circ(\text{A}'\text{Y})] \} \quad (7)$$

E° is the minimum in the ground electronic state potential energy. Since the ground level of the light isotope lies lower than that of the heavy isotope, each term in eq 7 is positive. **The field shift will lead to a preference of the heavy isotope for the chemical species with the smallest number of s electrons in the bonding or valence orbital.** The valence state wave function of the free UO_2^{2+} ion is a 24-electron problem. The molecular orbitals are built from the atomic configurations U^{2+} ($5f^3 6s^2 6p^6 6d^1$) and $2 \text{O}(2s^2 2p^4)$.³⁰ A population analysis of the lowest valence molecular orbitals has 5.8 of the six atomic s orbitals involved in bonding orbitals.³¹ The electron density of the hydrated and complexed uranyl ion, U(VI), at the uranium nucleus is larger than can be expected for the hydrated or complexed U(IV) ion. Thus the field shift will lead to a preference of ^{238}U for the U(IV) species, in agreement with experiment. The odd–even staggering found in the atomic spectra of U I is mirrored in the isotope separation factors for the various uranium isotopomers. Field shifts in the 5027-Å line of atomic uranium are given in Table 4 for the isotopes ^{233}U , ^{234}U , ^{235}U , and ^{236}U with reference to ^{238}U . There is a one-to-one correlation of the U(IV)–U(VI) fractionation factors with the field shifts. Shifts in the range 0.25–0.50 cm^{-1} were found in many of the absorption lines in $\text{Cs}_2^{235}\text{UO}_2\text{Cl}_4$ compared with $\text{Cs}_2^{238}\text{UO}_2\text{Cl}_4$, apart from those associated with the molecular vibrations of the UO_2^{2+} ion.³² This is of the order of magnitude which will account for the enhanced isotope separation factors observed for the odd isotopes ^{233}U and ^{235}U .

For a quantitative calculation of the field shift effect on a chemical exchange equilibrium, we require data on the zero-point energy shifts of the two chemical species. Although these

(28) Diringer, M. *Ann. Phys.* **1966**, *10*, 89.(29) Rajnak, K.; Fred, M. *J. Opt. Soc. Am.* **1977**, *67*, 1314.(30) Boring, M.; Wood, J. H.; Moskowitz, J. W. *J. Chem. Phys.* **1975**, *63*, 638.(31) Walch, P. F.; Ellis, D. E. *J. Chem. Phys.* **1976**, *65*, 2387.(32) Dieke, G. H.; Duncan, A. B. F. *Spectroscopic Properties of Uranium Compounds*; NNS III-2, McGraw-Hill Book Co., Inc.: New York, 1949; Appendix I, Table 4 (see also p 78).

are not known individually, there are enough spectroscopic data and fractionation experiments to permit quantitative calculations of the separation factors for the U(IV)–U(VI) exchange. For this exchange reaction



$$\ln \alpha \approx \ln \alpha_0 + (kT)^{-1} \{ (^{238}E^\circ - ^{235}E^\circ)\text{U(VI)} - (^{238}E^\circ - ^{235}E^\circ)\text{U(IV)} \} \quad (9)$$

if one neglects anharmonic and nuclear spin effects.

$$\ln \alpha_0 = \ln (s/s')f \text{U(IV)} - \ln (s/s')f \text{U(VI)} \quad (10)$$

WINIMAX¹ is an excellent approximation to $\ln \alpha_0$.^{33,34}

$$\ln \alpha_0 = (1/24)(\hbar/kT)^2 \frac{\delta m_i}{m_i 238} \times (W_1(\text{IV})\langle \nabla^2 \text{U} \rangle_{\text{U(IV)}} - W_1(\text{VI})\langle \nabla^2 \text{U} \rangle_{\text{U(VI)}}) \quad (11)$$

where m_i is the mass of the i th uranium isotope and $\delta m_i = (m_{238} - m_i)$. $\langle \nabla^2 \text{U} \rangle_{\text{U(IV)}}$ and $\langle \nabla^2 \text{U} \rangle_{\text{U(VI)}}$ are the mean values of the Laplacians of the potential energies of the U(IV) and U(VI) species, respectively. $W_1(\text{IV})$ and $W_1(\text{VI})$ are finite polynomial modulating coefficients.^{33,34} In the harmonic oscillator approximation $\langle \nabla^2 \text{U} \rangle$ is just the force constant in Cartesian coordinates. The quantities W_1 and $\nabla^2 \text{U}$ are isotope independent. The term $\ln \alpha_0$ scales as $\delta m_i/(m_i m_{238} T^2)$. We now show that the terms $(E^\circ - E^\circ')$ scale as the field shift for the respective isotopes in any spectrum of the element. The field shift in any level is^{20–22}

$$\delta T \approx |\psi(0)|^2 C \quad (12)$$

where $|\psi(0)|^2$ is the electron density at the nucleus and is isotope independent within the Born–Oppenheimer approximation. C is a nuclear property, constant for all energy levels of an atom and for all molecular species of the element. C is a property of the reference isotope and one of its isotopes. Each isotope has its value of C . The difference in field shifts of the ground states of U(VI) and U(IV) is

$$\delta E^\circ \text{U(VI)} - \delta E^\circ \text{U(IV)} = \delta T(\text{U I}) \frac{\{ |\psi(0)|^2 \text{U(VI)} - |\psi(0)|^2 \text{U(IV)} \}}{|\psi(0)|^2 (\text{U I})} \quad (13)$$

$\delta T(\text{U I})$ is the field shift in a selected line in atomic uranium referred to ²³⁸U, e.g. the 5027-Å line. Equation 9 can, therefore, be written

$$\ln \alpha_i = (hc/kT)fs_i a + (1/24)(\hbar/kT)^2 \frac{\delta m_i}{m_i 238} b \quad (14)$$

fs_i is the field shift of the 5027-Å line for the i th isotopomer with respect to ²³⁸U and a is the field shift scaling factor; b is the difference in the weighted Laplacians of the potential energies of U(IV) and U(VI), cf. eq 11.

We have evaluated the parameters a and b in eq 14 from the field shifts given in Table 4, the experimental ratio $\epsilon_{234}/\epsilon_{235} = 1.142$ at 433 K, and the absolute value of ϵ_{235} at 308 K = 13.0×10^{-4} .³⁵ This procedure assumes that the temperature dependence of ϵ_{235} is given by eq 14. With this assumption

(33) Bigeleisen, J.; Ishida, T. *J. Chem. Phys.* **1968**, *48*, 1311.

(34) Lee, M. W.; Bigeleisen, J. *J. Chem. Phys.* **1978**, *68*, 3496.

(35) Florence, T. M.; Batley, G. E.; Ekstrom, A.; Fardy, J. J.; Farrar, Y. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1961.

Table 5. Contributions of Vibrational Effects ($\ln \alpha_0$) and Field Shifts ($\ln K_{fs}$) to the U(IV)–U(VI) Isotope Separation Factors at 308 and 433 K

isotope pair	308 K			433 K		
	$\ln \alpha_0$ $\times 10^4$	$\ln K_{fs}$ $\times 10^4$	$\ln \alpha$ $\times 10^4$	$\ln \alpha_0$ $\times 10^4$	$\ln K_{fs}$ $\times 10^4$	$\ln \alpha$ $\times 10^4$
236–238	–5.02	12.32	7.30	–2.54	8.76	6.22
235–238	–7.56	20.56	(13.00)	–3.82	14.62	10.80
234–238	–10.12	24.54	14.42	–5.12	17.46	12.34
233–238	–12.70	32.09	19.39	–6.43	22.83	16.40

and the experimental data cited above we derive the values $a = 1.075$ and $(1/24)(\hbar/k)^2(b/238) = (-5.615 \times 10^3)K^2$. With these parameters we have calculated the ratios of $\epsilon_i/\epsilon_{235}$ and the absolute values of ϵ_i at both 308 and 433 K. The ratios $\epsilon_i/\epsilon_{235}$ at 433 K are compared with the experimental values in Table 4. Inasmuch as our calculated ratios are in quantitative agreement with the 433 K experimental values, we could have obtained the identical values of the parameters a and b by combining the experimental $\epsilon_{234}/\epsilon_{235}$ ratio with another ratio at 433 K. In that case we would have arrived at the parameters a and b without any assumption of the temperature coefficients of the ratios and would have obtained the exact literature value for ϵ_{235} at 308 K.

The ratios $\epsilon_i/\epsilon_{235}$ at 308 K differ from those at 433 K by 3% or less. The present values of the 308 K ratios are to be preferred to earlier values which assumed them to be the same as the 433 K values. Thus, the absolute values of the separation factors given previously, which were derived from the 433 K ratios and the 308 K ratios,^{10,11} and the values shown in Figure 1 of this paper are to be replaced by the values given in Table 5 for the absolute values of the isotopic separation factors at 308 K.

In Table 5 we also give a breakdown of the total fractionation factor, $\ln \alpha$, into the vibrational term, $\ln \alpha_0$, and the field shift effect. For each of the isotopes, not just those of odd mass, the field shift effect, $\ln K_{fs}$, is approximately three times that of the vibrational effect, $\ln \alpha_0$. For the U(IV)–U(VI) exchange the field shift and vibrational effects are opposite in sign. The positive sign for $\ln K_{fs}$ is in accord with the larger number of s electrons and smaller number of f electrons in the valence shell of the uranyl ion, U(VI), compared with the hydrated-complexed U(IV) ion. The negative sign for $\ln \alpha_0$ shows that the bonding of the uranium atom in the uranyl ion, with a triple bond to each of the two oxygen atoms, is stronger than the hydration and complexing of the U(IV). This is contrary to conclusions arrived at in the past which neglected the field shift effect.^{7,18} The greater stability of the uranyl ion (aqueous) compared with the hydrated uranous ion,³⁶ while not necessarily a direct measure of bond strength, also favors a larger value of the mean force constant for the uranyl ion.

In Table 6 we show the failure of either a simple mass or field shift scaling as compared with eq 14 to reproduce the experimental data.

Equation 14 along with the parameters used in Tables 4 and 5 does not reproduce the temperature dependence reported for ²³⁸U/²³⁵U in the U(IV)–U(VI) exchange.³⁷ The calculated temperature dependence with temperature independent force constants is smaller than that reported. Recent experimental data indicate that revisions of the older data in this direction are in order.³⁸

(36) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *Chemistry of the Actinide Elements*; Chapman and Hall: London, New York, 1986; Vol. 2, p 1315.

(37) Fukuda, J.; Fujii, Y.; Okamoto, M. *Z. Naturforsch.* **1983**, *38a*, 1072.

(38) Fujii, Y.; Haruno, Y.; Niguchi, N. Private communication.

Table 6. Comparison of U(IV)–U(VI) Isotope Fractionation Factors, $\epsilon = \ln \alpha$, at 433 K Calculated on Different Bases

isotope pair	$10^4\epsilon$			this paper ^b
	exp	mass effect ^a	field shift ^a	
236–238	6.2	6.1	6.2	6.2
235–238	10.8	9.2	10.3	10.8
234–238	(12.3)	(12.3)	(12.3)	(12.3)
233–238	16.4	15.5	16.1	16.4

^a Calculated from the 234–238 separation factor and the ratios of $\epsilon_i/\epsilon_{234}$. ^b Calculated from the experimental ratio $\epsilon_{234}/\epsilon_{235}$ at 433 K and the experimental value of ϵ_{235} at 308 K.

Table 7. Reduced Partition Function Ratios, $10^4(\ln (s/s')f)$, of Uranium Compounds at 300 K

species	Table 9 in ref <i>a</i>	present
UO ₂ ²⁺ crown complex	10	
UO ₂ ²⁺ crystal	11 ^b	11
UO ₂ ²⁺ aqueous	12 ^c	12
U(IV) aqueous	33–34	12.4 ^d
UO ₂ ²⁺ (H ₂ O) _{5–n} L _n	18–20 ^e	18–20
UO ₂ ²⁺ (H ₂ O) ₅	20 ^c	20
UF ₆ (g)	20 ^b	20
NOUF ₆ (soln)	36	
U(III) aqueous	53	

^a Bigeleisen, J. *Bulletin Research Laboratory for Nuclear Reactors*; Tokyo Institute of Technology, Special Issue 1, Tokyo, 1992; p 24.

^b Bigeleisen, J. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2505. ^c Oi, T.; Kakihana, H. *J. Nucl. Sci. Technol.* **1989**, *26*, 298. ^d $\ln (s/s')f$ (UO₂²⁺(H₂O)₅) – $\ln \alpha_0$. ^e Oi, T.; Kakihana, H. *Z. Naturforsch.* **1989**, *44a*, 399.

Reduced Partition Function Ratios

All compilations up to the present one of reduced partition function ratios, RPFs, start with calculations from spectroscopic data.¹³ When such data are not available, the separation factor of a species with another species with known RPF has been used to give the RPF of the unknown RPF. We have previously cautioned against this procedure,⁷ since it assumes that $\ln \alpha$ is given by eq 3, which relates $\ln \alpha_0$ to the RPFs. The proper procedure is to use eq 2 combined with eq 3 to obtain the unknown RPF. This requires a knowledge of the correction terms. For the heavy elements the principal correction is $\ln K_{fs}$, the field shift effect. In Table 7 we correct a previous compilation⁷ of RPFs of uranium compounds, which explicitly had a caveat that those RPFs were valid in the absence of the nuclear effects discussed here. The only revised entry is for U(IV) aqueous, based on the value of $\ln (s/s')f$ for

UO₂²⁺(H₂O)₅³⁹ and $\ln \alpha_0$ given in Table 5. There are no values for $\ln K_{fs}$ for reactions which involve UO₂²⁺(crown complex), NOUF₆, and U(III) aqueous and therefore it is not possible to give $\ln (s/s')f$ values for these compounds.

Summary

It is shown that the nuclear spin effect is an order of magnitude too small to account for the “anomalous mass effect” in the 235–238 U(III)–U(VI) exchange reaction. By comparison of the general features of the known nuclear field shift with the anomalous features of the U(IV)–U(VI) and U(III)–U(IV) exchange reactions it is shown that nuclear field shifts must be considered in the isotopic chemistry of the heavy elements.

As a consequence of the nuclear field shift, a nucleus with an odd number of neutrons will behave in chemical exchange reactions as though it has a smaller atomic mass. The nuclear field shift leads to a concentration of a heavy isotope into the chemical species with the smallest electron density at the nucleus.

From the experimental ratio of the 234–238 U to 235–238 U separation factor at 433 K and the absolute value of the 235–238 U separation factor at 308 K in the U(IV)–U(VI) exchange reaction we have derived the ratios of the 236–235 and 233–235 separation factors at 433 K in quantitative agreement with experiment. The separation factor consists of two terms: (1) the conventional zero-point energy effect and (2) the nuclear field shift. The nuclear field shift term is opposite in sign from the vibrational term in the U(IV)–U(VI) exchange and approximately three times as large as the absolute value of the latter. It is the nuclear field shift that is responsible for the concentration of the ²³⁸U in the U(IV) species in this exchange reaction.

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(39) Oi, T.; Kakihana, H. *J. Nucl. Sci. Technol.* **1989**, *26*, 298.