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Nuclear Shielding in the Alkali Metal Anions

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Abstract: The nuclear shielding differences between gaseous metal anions and neutral atoms for the alkali series lithium through caesium have been calculated by combining Hartree–Fock predictions with electron–electron correlation corrections derived from experimental ionization potentials. From a comparison of these calculations with experimental data for $^{23}Na^-$ in solution, we conclude that the sodium anion in solution exists as an essentially "gas-like" moiety in which both the 2p core and 3s valence electrons interact very weakly, if at all, with their surroundings. In contrast, a comparison of the experimental data for $^{87}Rb^-$ and $^{133}Cs^-$ in solution and our calculated nuclear shielding differences for these anions reveals substantial interactions of these heavy ions with their environment. The potassium anion, $^{39}K^-$, has only recently been identified by NMR. The available data suggest that the potassium anion in solution is intermediate in character; that is, K^- is more gas-like than Rb^- in most systems but the $4s^2$ configuration does suffer a certain degree of perturbation on its gas-phase electronic structure.

It is now a decade since the first observation, by Ceraso and Dye,[1] of the nuclear magnetic resonance (NMR) of the sodide ion $^{23}Na^-$, in solutions of sodium in ethylamine containing the complexing agent 2,2,2 cryptand (C_{222}). Since that time, high-resolution multinuclear NMR has been used extensively to identify the metal anions $^{23}Na^-$, $^{87}Rb^-$, and $^{133}Cs^-$ in a variety of metal-solution systems.[2-9] In addition, $^{39}K^-$ has very recently been identified by NMR.[10,11]

The NMR data for the sodide ion, in particular, provide strong evidence that $^{23}Na^-$ in solution is a "genuine" anion with two spin-paired electrons in a 3s orbital which shield the inner 2p electrons from the influence of the solvent.[2] The strength of this suggestion is based upon two factors:

(i) The narrowness of the Na^- NMR in this paramagnetic solution indicates that the nucleus experiences a spherically symmetric environment and is only weakly coupled to its surroundings.[1,3,4]

(ii) The chemical shift difference ($\Delta\sigma^{(-)}(M)$) between the metal anion in solution and the isolated metal atom, deduced from experiment[2] neglecting bulk susceptibility corrections, agrees with the value calculated from atomic Hartree–Fock wave functions for the isolated systems.[12,13] As is well-known, Hartree–Fock calculations neglect the effects of electron–electron correlations.[14]

The situation for the heavier alkali metal anions is perhaps less clear. The NMR data for $^{39}K^-$ in various crown solvents[10,11] suggest that the species is reasonably well described as a genuine potassium anion with two electrons in the $4s^2$ orbital that shield the 3p electrons, to a considerable degree, from interactions with the surroundings. Any interpretation of the $^{87}Rb^-$ and $^{133}Cs^-$ results suffers from the fact that accurate and reliable calculations of the nuclear shielding constants for the gaseous atoms and anions have not been available hitherto.[2-4,15]

In this paper we report accurate computations of the difference, $\Delta\sigma_g^{(-)}(M)$, between the shielding, $\sigma(M^-)_g$, of all the gaseous alkali metal anions and that, $\sigma(M)_g$, of the gaseous metal atoms. Furthermore, the (electron–electron) correlation contribution to these nuclear shielding differences is derived reliably from experimental measurements of ionization potentials and electron affinities.[16]

We are therefore able to formulate the first complete and reliable set of gas-phase shielding constant differences, $\Delta\sigma_g^{(-)}(M)$, for the entire alkali metal anion series. A comparison is made with published chemical shift data for $^{23}Na^-$, $^{87}Rb^-$, and $^{133}Cs^-$ ions in solution, and we conclude that while $^{23}Na^-$ is indeed a "genuine" gas-like anion in solution, this is clearly not the case for the rubidide and caseside ions. For these heavier anions, solvation effects may become increasingly important.

Nuclear Shielding Calculations

Experimental Data. Optical pumping,[17,18] atomic beam,[19] and NMR techniques[20-23] have estabilished the shielding constants, $\sigma(M^+)_s$, of the aqueous cations $^{23}Na_s^+$, $^{87}Rb_s^+$, and $^{133}Cs_s^+$ relative to those of the corresponding gaseous metal atoms, $\sigma(M)_g$, with an accuracy of around 2%. We note in passing that, as far as we can ascertain, NMR shielding constants for M_s^+ are uncorrected for bulk susceptibility effects. All the alkali cation resonances are paramgnetically shifted from those of the respective gaseous atoms; for example, values range from 60.5 (±1) ppm for $^{23}Na_s^+$ to 344 (±5.8) ppm for $^{133}Cs_s^+$.

The above shielding differences are important in the present context since the aqueous solutions provide a convenient standard relative to which the shielding of the metal anion in solution is usually measured.[1,2,9] Hence, the shielding of the anion in solution (uncorrected for solution bulk susceptibility), relative to that of the gaseous metal atom, can be measured experimentally. This shielding difference is more readily interpreted theoretically than the corresponding shielding of the anion relative to that of the solvated cation.

Thus, the nature of the metal anion in solution can only be deduced if reliable values are known for the nuclear shielding difference ($\Delta\sigma_g^{(-)}(M)$) between the shielding for the gas-phase anion ($\sigma(M^-)_g$) and that ($\sigma(M)_g$) of the neutral alkali metal atom. The shielding ($\sigma(M^-)_g$) for the closed-shell species M^- is defined to be positive as implied by expression 2 provided by the Ramsey theory of nuclear shielding,[24] so that

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$$\Delta\sigma_g^{(-)}(\mathrm{M}) = \sigma(\mathrm{M}^-)_g - \sigma(\mathrm{M})_g \qquad (1)$$

However, these shielding differences can be accurately calculated by adding the predictions computed from nonrelativistic atomic Hartree–Fock wave functions to the (much smaller, but nonzero) contribution from electron–electron correlations, which can reliably be derived from experimental data.[16]

Method

In the Ramsey theory[24] the total shielding of a nucleus is the sum of a diamagnetic and paramagnetic part. The paramagnetic contribution to the shielding of any isolated atomic S state vanishes[25] if the gauge origin is chosen at the nucleus. The total shielding $\sigma(\mathrm{S})$ of species S equals the diamagnetic contribution given in the point charge point dipole description of the nucleus in nonrelativistic theory by

$$\sigma(\mathrm{S}) = \frac{1}{3c^2}\,\langle\Psi_\mathrm{S}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)|\sum_{i=1}^{N} r_i^{-1}|\Psi_\mathrm{S}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\rangle \qquad (2)$$

Here $|\Psi_\mathrm{S}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\rangle$ is the exact wave function for the N-electron system (S) and c is the velocity of light in atomic units (≈ 137).

Since the exact wave function cannot presently be accurately computed for atoms containing more than an extremely small number of electrons, it is useful to define the Hartree–Fock contribution ($\sigma_\mathrm{HF}(\mathrm{S})$) to the shielding as that predicted by replacing the exact by the Hartree–Fock wave function in (2). This wave function can be simply and exactly computed for all atoms with use of a numerical Hartree–Fock program.[26,27] The difference between the exact and Hartree–Fock shielding defines the correlation contribution ($\sigma_\mathrm{corr}(\mathrm{S})$) through

$$\sigma(\mathrm{S}) = \sigma_\mathrm{HF}(\mathrm{S}) + \sigma_\mathrm{corr}(\mathrm{S}) \qquad (3)$$

This separation is useful not only because $\sigma_\mathrm{corr}(\mathrm{S})$ is only a small fraction of $\sigma(\mathrm{S})$ but also because $\sigma_\mathrm{corr}(\mathrm{S})$ can be related[16,28,29] by using the Hellmann-Feynman theorem to the nuclear charge dependence of the correlation energy, thus,

$$\sigma_\mathrm{corr}(\mathrm{S}) = -\frac{1}{3c^2}\left(\frac{\mathrm{d}E_\mathrm{corr}(Z)}{\mathrm{d}Z}\right)_{Z=Z_\mathrm{S}} \qquad (4)$$

where the correlation energy ($E_\mathrm{corr}(Z)$) of the system having nuclear charge Z and isoelectronic with S is the exact nonrelativistic energy minus that predicted in the nonrelativistic Hartree–Fock approximation. In (4) Z_S is the nuclear charge of the system S.

An expression for the difference ($\Delta\sigma(\mathrm{S})$ between the shielding of S and that ($\sigma(\mathrm{S}_1)$) of the system (S_1) obtained by ionization of one electron from (S) is derived[16] by subtracting the results (3) and (4) for the total shieldings. The result is

$$\Delta\sigma(\mathrm{S}) = \sigma(\mathrm{S}) - \sigma(\mathrm{S}_1) = \Delta\sigma_\mathrm{HF}(\mathrm{S}) + \Delta\sigma_\mathrm{corr}(\mathrm{S}) \qquad (5)$$

$$= \Delta\sigma_\mathrm{HF}(\mathrm{S}) + \frac{1}{3c^2}\left(\frac{\mathrm{d}I_\mathrm{corr}(Z)}{\mathrm{d}Z}\right)_{Z=Z_\mathrm{S}} \qquad (6)$$

where $I_\mathrm{corr}(Z)$ is the contribution, arising from electron correlation, to the ionization potential for the removal of an electron from the system of nuclear charge Z and isoelectronic with S to yield a system isoelectronic with S_1. The result (6) is useful because the quantities $I_\mathrm{corr}(Z)$ can be evaluated by subtracting from the experimental ionization potential ($I_\mathrm{exptl}(Z)$) the sum of the Hartree–Fock prediction ($I_\mathrm{HF}(Z)$) of the ionization potential plus the corrections arising from relativity ($I_\mathrm{rel}(Z)$) and nuclear motion.

$$I_\mathrm{corr}(Z) = I_\mathrm{exptl}(Z) - I_\mathrm{HF}(Z) - I_\mathrm{rel}(Z) + I_\mathrm{exptl}(Z)/M_\mathrm{n} \qquad (7)$$

Table I. Nuclear Shielding Differences, $\Delta\sigma_g^{(+)}(\mathrm{M})$ and $\Delta\sigma_g^{(-)}(\mathrm{M})$, for the Alkali Metal Series[a,b]

metal (M)	$\Delta\sigma_g^{(\pm)}(\mathrm{M})$[c] $\Delta\sigma_g^{(+)}(\mathrm{M})$	$\Delta\sigma_g^{(-)}(\mathrm{M})$
Li	6.07 (6.046)	3.14 (2.743)
Na	5.18 (5.089)	2.88 (2.583)
K	4.08 (3.933)	2.38 (2.122)
Rb	3.77 (3.593)	2.27 (1.995)
Cs	3.31 (3.169)	2.08 (1.801)

[a] Values (in ppm) are nonrelativistic but including correlation. [b] Values in parentheses denote computed nonrelativistic Hartree–Fock shielding differences. Total error estimates (±0.03 ppm) are discussed in the text. [c] $\Delta\sigma_g^{(-)}(\mathrm{M}) = \sigma(\mathrm{M}^-)_g - \sigma(\mathrm{M})_g$. $\Delta\sigma_g^{(+)}(\mathrm{M}) = \sigma(\mathrm{M})_g - \sigma(\mathrm{M}^+)_g$.

The last term is the leading correction from nuclear motion with M_n the nuclear mass while the computation of the relativistic correction is described in the Appendix. The derivatives of $I_\mathrm{corr}(Z)$ with respect to Z were evaluated numerically (see Appendix) from the four isoelectronic ionization processes in the alkali metals, the alkaline earths and the group IIIA and group IVA elements.

The dominant source of error in the $\Delta\sigma_\mathrm{corr}(\mathrm{S})$ values arises from uncertainties in these numerical procedures and has been discussed in detail elsewhere.[16] These errors can be estimated to be approximately 0.03 ppm by comparing the results of different numerical procedures presented in the Appendix.

The experimental ionization potentials, relativistic corrections, and correlation contributions ($I_\mathrm{corr}(Z)$) are presented in the Appendix.

The Hartree–Fock contributions ($\Delta\sigma_\mathrm{HF}(\mathrm{S})$) to the shielding differences ($\Delta\sigma(\mathrm{S})$) were calculated as the difference between the total shieldings $\sigma_\mathrm{HF}(\mathrm{S})$ and $\sigma_\mathrm{HF}(\mathrm{S}_1)$ of S and S_1 computed by using the Hartree–Fock approximation to (2)

$$\Delta\sigma_\mathrm{HF}(\mathrm{S}) = \sigma_\mathrm{HF}(\mathrm{S}) - \sigma_\mathrm{HF}(\mathrm{S}_1) \qquad (8)$$

For the case where S is an alkali metal anion (i.e., $\mathrm{S} = \mathrm{M}^-$) so that $\mathrm{S}_1 = \mathrm{M}$ (the neutral alkali atom), the shielding difference $\Delta\sigma(\mathrm{M}^-)$ defined by (5) is $\Delta\sigma_g^{(-)}(\mathrm{M})$ defined by eq 1. For the case $\mathrm{S} = \mathrm{M}$, and $\mathrm{S}_1 = \mathrm{M}^+$, $\Delta\sigma(\mathrm{M})$ defined by (5) becomes $\Delta\sigma_g^{(+)}(\mathrm{M})$. Since the numerical errors in Hartree–Fock values ($\Delta\sigma_\mathrm{HF}(\mathrm{M})$) will be 10^{-5} ppm at most, the accuracy of the calculated values of $\Delta\sigma_g^{(\pm)}(\mathrm{M})$ is determined by the errors (±0.03 ppm) in the correlation contribution.

Results

The total shielding differences $\Delta\sigma_g^{(+)}(\mathrm{M})$ and $\Delta\sigma_g^{(-)}(\mathrm{M})$ for the alkali metal series Li to Cs are presented in Table I. These results show that the contribution from electron–electron correlations, i.e., the differences between exact results and the Hartree–Fock values (reported in parentheses), is small *but not negligible.*

The present status of the comparison between the theoretical $\Delta\sigma_g^{(+)}(\mathrm{M})$ results of Table I and reported experimental values is fully discussed elsewhere.[16]

Two points emerge concerning $\Delta\sigma_g^{(-)}(\mathrm{M})$:

(i) The total shielding constants $\sigma(\mathrm{M})_g$ and $\sigma(\mathrm{M}^-)_g$, of which the numbers in Table I are differences are themselves very large, e.g., $\sigma(\mathrm{Cs})_g = 5780.2$ ppm. However, the overwhelming contribution in both cases arises from the core electrons, which make very similar contributions in M^+, M, and M^-. These core contributions do not cancel exactly, however, the core of the neutral being slightly contracted relative to that of the anion thus causing the core shielding difference to contribute minutely but negatively to $\Delta\sigma_g^{(-)}(\mathrm{M})$ to the extent of less than 0.004 ppm.

(ii) The values decrease smoothly as one proceeds down the group IA elements solely because the valence orbital, whose occupation varies from 0 to 2 as one goes from cation to neutral to anion, becomes more diffuse.

The Hartree–Fock results for ^{7}Li, ^{23}Na, and ^{39}K (Table I) agree, as expected, with the earlier calculations of Dickinson[12] and Malli and Fraga.[13] However, it should be noted that the smooth variation in $\Delta\sigma_g^{(-)}(\mathrm{M})$ down the series (Table I) contrasts markedly

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Table II. Nuclear Shielding in the Alkali Metal Anions $^{23}Na^-$, $^{39}K^-$, $^{87}Rb^-$, and $^{133}Cs^-$

ion	system	temp, K	$\Delta\sigma^{(-)}(M)^a$	ref
$^{23}Na^-$	gas (calcd)		2.88 ± 0.3^b	this work
	Na/HMPA	263	1.5^c	6
	Na/DEA	203	1.9	7
	Na/DPA	213	1.9	8
	Na/DMP	231	1.5	8
	Na/12C4		1.3	9
	Na/C_{222}/MA	258	1.4	2
	Na/C_{222}/EA	256	1.6	2
	Na/C_{222}/THF	269	2.3	2
$^{39}K^-$	gas (calcd)		2.38 ± 0.3	this work
	KCs/12C4	250	−6.9	11
	K/15C5	220	0	10
$^{87}Rb^-$	gas (calcd)		2.27^b	this work
	Rb/12C4		-20.6^c	9
	Rb/C_{222}/EA	233	−26.6	2
	Rb/C_{222}/THF	227	−14.4	2
$^{133}Cs^-$	gas (calcd)		2.08^b	this work
	Cs/C_{222}/THF	202	-52.3^c	2

[a] $\Delta\sigma^{(-)}(M) = \sigma(M^-) - \sigma(M)_g$. [b] Error arising from correlation contribution estimated from the results of Table IV. [c] All ^{23}Na experimental results ±1 ppm, ^{87}Rb experimental results ±1.2 ppm, and ^{133}Cs experimental results ±5.8 ppm, arising from errors in $(\sigma(M)_g - \sigma(M^+)_{aq(\infty)})$, as discussed in the text.

with the values ($\Delta\sigma_g^{(-)}(Rb) = 54.7$ ppm; $\Delta\sigma_g^{(-)}(Cs) = 232.1$ ppm) that would be deduced by taking the difference between the total shieldings estimated from a simple analytic function[13] constructed to reproduce the known Hartree–Fock shieldings in much lighter systems. The inappropriateness of using these estimates to calculate the small shielding differences of interest here has been fully discussed elsewhere.[16]

The Nature of Alkali Metal Anions in Solution

The NMR of $^{23}Na^-$, $^{87}Rb^-$, and $^{133}Cs^-$ have been studied in a variety of solvent systems. The chemical shift data from Edwards et al.[6-9] were derived from the reported shielding differences $(\sigma(M^-) - \sigma(M^+)_{aq(\infty)})$ by subtracting the known[19] shielding differences $(\sigma(M)_g - \sigma(M^+)_{aq(\infty)})$, where $\sigma(M^+)_{aq(\infty)}$ is the shielding of the aqueous cation extrapolated to infinite dilution. The data taken from Dye and co-workers[1-5] must again have been calculated by the same procedure, although in the original measurements $(\sigma(M^-) - \sigma(M^+)_{aq(\infty)})$ values are not reported explicitly. For $^{23}Na^+$, $^{87}Rb^+$, and $^{133}Cs^+$, the reported values[19] of $(\sigma(M)_g - \sigma(M^+)_{aq(\infty)})$ are 60.5 ± 1, 211.6 ± 1.2, and 344.3 ± 5.8 ppm (respectively), so that these errors are necessarily propagated into the results assembled in Table II. We also include in this table the recent data for $^{39}K^-$ in solution.[10,11]

It should also be noted that the experimental numbers in Table II are uncorrected for the bulk susceptibilities of the respective solutions. For solutions of sodium in hexamethylphosphoramide (Table II), the volume susceptibility was measured[30] to be -0.5×10^{-6} cgs units and incorporation of this appropriate correction[31] yields a "true" experimental value of $\Delta\sigma^{(-)}(Na)$ of 2.5 ppm, a correction of some 1 ppm to the measured nuclear shielding difference.

Clearly, for the sodide ion, the observed nuclear shielding differences ($\Delta\sigma^{(-)}(Na)$) in the various metal solutions are, within experimental error (±1 ppm, see preceding comments), identical with that (2.88 ppm) calculated for the species $^{23}Na^-$ in the gas phase.

This, coupled with the remarkable insensitivity of $\Delta\sigma^{(-)}(Na)$ to the nature of the solvent in all systems examined,[1-9] shows that the 2p orbitals are well screened from interactions with surrounding solvent or solute molecules by the presence of the filled 3s valence orbital which itself is unaffected by its environment. In addition, the relative narrowness of NMR line widths in these paramagnetic systems[1-2] also provides strong evidence that $^{23}Na^-$ interacts only very weakly with its surroundings.[32]

Table III. Correlation Contributions to Ionization Potentials for the Process Core $s^2 \rightarrow$ Core s in au

		−correction to ionization potential			
	Dirac–Fock IP ($I_{DF}(Z)$)	Breit ($-I_{Br}(Z)$)	$-I_{LS}(Z)$	exptl IP	$I_{corr}(Z)$
Li^-	−0.004495	0.000 001	0.0	0.022 785	0.027 283
Na^-	−0.003789	0.0	−0.000 001	0.020 139	0.023 927
K^-	−0.002872	0.0	0.0	0.018 419	0.021 291
Rb^-	−0.002548	−0.000 001	−0.000 001	0.017 860	0.020 406
Cs^-	−0.002203	−0.000 001	−0.000 003	0.017 272	0.019 474
Be	0.295677	0.000 012	0.000 004	0.342 601	0.046 961
Mg	0.243196	0.000 019	0.000 024	0.280 985	0.037 838
Ca	0.188917	0.000 017	0.000 040	0.224 649	0.035 792
Si	0.174578	0.000 023	0.000 102	0.209 252	0.034 800
Ba	0.157316	0.000 025	0.000 155	0.191 514	0.034 379
B^+	0.861835	0.000 048	0.000 021	0.924 414	0.062 694
Al^+	0.645111	0.000 061	0.000 071	0.691 927	0.046 962
Sc^+	0.483279	0.000 053	0.000 104	0.533 281	0.050 165
Y^+	0.436819	0.000 073	0.000 243	0.483 840	0.047 340
La^+	0.387783	0.000 082	0.000 357	0.434 658	0.047 316
C^{2+}	1.683190	0.000 114	0.000 060	1.759 473	0.076 537
Si^{2+}	1.176880	0.000 128	0.000 142	1.229 940	0.053 354

In contrast, the NMR of $^{87}Rb^-$ and $^{133}Cs^-$ in solution are very significantly deshielded relative to the gaseous atom, as shown by the negative values of $\Delta\sigma^{(-)}(M)$, reported in Table II. The combination of these results[2,9] with our reliable calculated values of $\Delta\sigma_g^{(-)}(M)$ shows that the rubidide and caeside ions in solution are *deshielded* relative to the gaseous anions, although their deshielding with respect to the *gaseous atoms* is even more significant. In addition, the observed $\Delta\sigma^{(-)}(Rb)$ values show a solvent dependence in both the two-[9] and three-component solutions.[2] It is interesting to note, however, the similarity in shifts for $^{87}Rb^-$ solutions of Rb in THF with added C_{222} (3-component metal solution) and solutions of Rb in the liquid crown solvent, 1,4,7,10-tetraoxacyclododecane, 12C4 (a 2-component system), both polycyclic ether solvents. The negative experimental values of $\Delta\sigma^{(-)}(Rb)$ suggest a considerable solvent involvement in the ground-state wave function of the $^{87}Rb^-$ ion. The deshielding of $^{87}Rb^-$ is presumably caused by the introduction of orbital angular momentum via the interaction of solvent (lone-pair) electron density with the filled outer 5p orbital.[33] The recent NMR data[10,11] for $^{39}K^-$ in solution suggest that this metal anion is considerably more gas-like than the rubidium anion—certainly in the liquid crown systems. However, the $^{39}K^-$ ion does clearly suffer certain small perturbations on its gas-phase electronic structure. This can be gauged from the chemical shift data in Table II which indicate a small degree of deshielding of $^{39}K^-$ as compared to the gas-phase anion.

There is only limited experimental data for $^{133}Cs^-$ in condensed phases.[2,5] The large, and negative, values of $\Delta\sigma^{(-)}(Cs)$ observed in all systems so far studied again suggest a very substantial interaction of the $^{133}Cs^-$ ion with its environment.

Concluding Remarks

The nuclear shielding differences between alkali anions and neutral atoms have been calculated reliably by combining Hartree–Fock predictions with electron–electron correlation corrections derived from experimental ionization potentials. The close similarity between the calculated values and those measured in experiments on $^{23}Na^-$ suggests that the species exists in solution as an essentially gas-like anion only weakly coupled to its environment. The large and negative experimental values for $\Delta\sigma^{(-)}(Rb)$

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Table IV. Comparison of Different Fitting Methods in the Derivation of $\Delta\sigma_{corr}^{(-)}(M)$

M^-	$\Delta\sigma_{corr}^{(-)}(M)$; fit type linear	 quadratic	 cubic
Li^-	0.349	0.384	0.396
Na^-	0.247	0.289	0.302
K^-	0.257	0.259	
Rb^-	0.255	0.272	
Cs^-	0.265	0.282	

and $\Delta\sigma(^-)(Cs)$ in solution suggest that these species are significantly modified upon passing from the gaseous to the condensed phase.

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Appendix: Calculation of the Correlation Contribution to Ionization Processes Core $s^2 \rightarrow$ Core s

The experimental ionization potentials for the processes core $s^2 \rightarrow$ core s reported in Table III for group IIA, IIIA, and IVA elements are taken from Moore[34-37] except that for La^+.[38] Since the ground configurations of Sc^+ and La^+ are core sd and core d^2, respectively, while those of Sc^{2+}, Y^{2+}, and La^{2+} are core d, the ionization potentials reported for those systems in Table III were calculated from the literature ground-state values[33-37] by incorporation of the appropriate atomic excitation energies.[34-38] The experimental alkali metal values of Table III are electron affinities measured by photodetachment.[39]

The relativistic contribution to the ionization potential ($I_{rel}(Z)$) is given by

$$I_{rel}(Z) = I_{DF}(Z) - I_{HF}(Z) + I_{Br}(Z) + I_{LS}(Z) \qquad (A1)$$

Here $I_{DF}(Z)$ is the relativistic Dirac–Fock prediction of the ionization potential calculated as the difference between the total energy of the single configuration wave function for the core s configuration and the energy of the core s^2 configuration. The quantity $I_{HF}(Z)$ is the corresponding prediction of nonrelativistic Hartree–Fock theory, the orbitals of both the relativistic and nonrelativistic calculations being taking to satisfy the usual symmetry and equivalence restrictions.[40,41] The difference $I_{DF}(Z) - I_{HF}(Z)$ constitutes the major portion of the relativistic correction to the ionization potential, only the contribution ($I_{Br}(Z)$) from the Breit interaction,[41,42] that ($I_{LS}(Z)$) from the Lamb shift, and the small relativistic correlation correction not being included. The Breit contributions ($I_{Br}(Z)$) of Table III were computed exactly as the difference between the total Breit energies of the Dirac–Fock wave functions core s and core s^2. The Lamb shift contributions ($I_{LS}(Z)$) were calculated as the estimated Lamb shift energy of the valence electron in the configuration core s minus twice that estimated for one valence electron in the configuration core s^2. The methods used to estimate the Lamb shift of one valence electron are described fully elsewhere.[16]

Linear, quadratic, and cubic approximations to $(dI_{corr}(Z)/dZ)_{Z=Z_1}/3c^2$ for the alkali anions of nuclear charge Z_1 are presented in Table IV. The linear approximation is calculated as the difference ($I_{corr}(Z_1 + 1) - I_{corr}(Z_1)$) between the correlation contribution ($I_{corr}(Z_I + 1)$) to the first ionization potential of the alkaline earth of nuclear charge ($Z_1 + 1$) and that ($I_{corr}(Z_I)$) to the alkali metal electron affinity. The quadratic results (Table IV) are calculated by fitting a quadratic to the three quantities $I_{corr}(Z_1)$, $I_{corr}(Z_1 + 1)$, and $I_{corr}(Z_1 + 2)$ and therefore require the correlation contributions ($I_{corr}(Z_1 + 2)$) to the ionization process core $s^2 \rightarrow$ core s in the group IIIA elements. The cubic approximation used for Li^- and Na^- also requires the correlation contributions ($I_{corr}(Z_1 + 3)$) to the ionization process core $s^2 \rightarrow$ core s to enable a cubic to be fitted to $I_{corr}(Z_I)$, $I_{corr}(Z_I + 1)$, $I_{corr}(Z_1 + 2)$, and $I_{corr}(Z_1 + 3)$. The experimental data for the group IVA elements needed to derive cubic approximations for the heavier alkali anions do not appear to be available. The correlation contributions (Table IV) to the alkali anion–neutral alkali shielding differences predicted from quadratic and cubic approximations to $(dI_{corr}/dZ)_{Z=Z_1}$ agree well. Even the values predicted from the linear approximation agree with those from the quadratic one to within 16%. The data required to calculate the contribution to the shielding difference between a neutral alkali atom and its monovalent cation have been reported elsewhere.[16]

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Molecular Organoosmium Chemistry and Catalysis on the Basic Magnesium Oxide Surface

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Abstract: The complex $[H_2Os(CO)_4]$ is deprotonated upon adsorption on the basic surface of magnesia. The resulting $[HOs(CO)_4]^-$ is held strongly to the surface by a localized carbonyl–Mg^{2+} interaction analogous to the contact anion ion pairing observed for $[Na][HOs(CO)_4]$ in THF. The surface-bound complex is the precursor of surface species that are catalytically active for CO hydrogenation to give methane and higher hydrocarbons at 275 °C and 10 atm. During catalysis, the mononuclear anion is transformed into the stable $[H_3Os_4(CO)_{12}]^-$ and $[Os_{10}C(CO)_{24}]^{2-}$, which become the only surface species detected by infrared spectroscopy and by extraction of surface-bound anions. The chemistry of the molecular condensation reactions of osmium carbonyls on the basic magnesia surface closely parallels that of osmium carbonyls in basic solution. The tetranuclear osmium cluster is suggested to be involved in the CO hydrogenation catalysis.

Supported metal catalysts used in large-scale processes consist of metal crystallites of various sizes and shapes on high-surface-area metal-oxide supports.[1] Understanding of the chemistry of these catalysts is severely hindered by their nonuniformity;

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