atom enables a strong polar SF bond while the FN bond is predominantly covalent. Thus, the approach of the F atom toward the S end of NS is preferred, and both the NS and the SF bonds are strongly semipolar in NSF.[7] Again, this is reflected in the importance of d functions on S. Seeger et al.[6] found that without d AOs FNS and NSF have approximately the same stability and that the d population on S is very high in NSF (0.375 as compared to our value of 0.26 in NSH), but small in FNS (0.117 while we obtained 0.12 in HNS).

6. Conclusions

The main results of our study of the properties of the HNS radical can be summarized as follows:

(1) HNS and NSH are two independent isomeric species; there is no low-lying barrier that can allow for a thermal isomerization. In their respective $^1A'$ ground states HNS is 23.4 kcal/mol more stable than NSH.

(2) Though both isomers have closed-shell $^1A'$ ground states, they have to be considered as highly reactive radicals since they possess several low-lying electronically excited states. The lowest excitation energies are much lower than in the isovalent molecules HNO and (probably) NSF.

(3) The chemical bond in the ground states of the two isomers can be characterized as a conventional NS double bond in HNS and a semipolar triple bond in NSH. The latter is similar to the semipolar bonds in H_2SO, H_3PO, and NSF.

(4) Reliable results for most properties (relative stabilities, excitation energies, geometries) require good basis sets (including d AOs at least on S) and the inclusion of correlation effects.

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Multiplet Theory of Transition-Metal Ions

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For a number of ions of the 3d-transition-metal series (V, Cr, Mn, Fe, Co), the experimental excitation energies of the dd bands have been analyzed on the basis of the quantum-mechanical virial theorem and the Hellmann–Feynman theorem. It is shown that the energy sequence of the different $3d^q$ multiplets is determined predominantly by the relative value of the electron–nuclear attraction energies. This result is in agreement with an earlier Hartree–Fock study; it contrasts with the conventional multiplet theory of Slater–Condon–Shortley, where the relative energy of the different (L,S) terms is explained in terms of differences in d–d repulsion energy. Certain implications for ligand field theory are briefly discussed.

Introduction

In transition-metal ions, any nd^q configuration $(1 < q < 10)$ gives rise to a number of (L,S) multiplets, whose energy separation is described qualitatively by the well-known Slater–Condon–Shortley (SCS) theory.[1,2] This is essentially a first-order perturbation approach, starting off from a presupposed set of orbitals, which are occupied in a variety of ways. In the SCS theory, the energy difference between two multiplets stems entirely from the difference in the corresponding *open-shell repulsions*: different ways of having the nd shell occupied by q electrons correspond to different average interelectronic distances, and hence different interelectronic repulsions. If we denote the total electronic energy by E, the expectation value of the kinetic energy by T, the nuclear attraction by L, and the repulsion by C, we have

$$E = T + L + C = T + V = H + C \qquad (1)$$

and the conventional SCS theory describes the energy difference between two nd^q multiplets as

$$\Delta E = \Delta C = \Delta C_0 \qquad (2)$$

where C_0 refers to the open-shell (d–d) repulsion energy and

$$\Delta T = \Delta L = \Delta H = 0 \qquad (3)$$

If the explicit analytical expression of the radial functions (the orbital "shape") is not known explicitly, the $\Delta E = \Delta C$ values are described by means of semiempirical parameters, viz. the Slater–Condon F_k integrals or alternatively the Racah parameters B and C.

SCS theory is able to account for Hund's rules: more specifically, it predicts that the highest spin state is the ground state, because the highest spin state is calculated with the lowest interelectronic repulsion. In a similar way, the spin-pairing energy,[3,4] i.e. the energy required to turn two spins from parallel to antiparallel, can be shown to be a positive quantity:

$$E(S-1) - E(S) = 2SD \qquad (4)$$

$$D = {}^7\!/_6 K_{av} \qquad (5)$$

where $E(S)$ is the weighted mean energy of the d^q multiplets characterized by S spin quantum number and where D, the spin-pairing parameter, is positive, since it is proportional to K_{av}, the average exchange integral of the d^q system. D is a simple function of the relevant F_k integrals, and eq 4 shows in a very compact way how conventional multiplet theory ascribes spin pairing to an increased interelectronic repulsion. The spin-pairing energy is an important parameter in transition-metal chemistry, since its magnitude (with respect to $10Dq$) determines if a given complex will be of high-spin or low-spin type.[2,5]

Application of Two Quantum-Mechanical Theorems

A. The Virial Theorem. Although conventional SCS multiplet theory is both simple and successful, it obviously violates the virial

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(1) Slater, J. C. *Quantum Theory of Atomic Structure*; McGraw-Hill: New York, 1960; Vols. I, II.

(2) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962.

(3) Slater, J. C. *Phys. Rev.* **1968**, *165*, 655.

(4) Jørgensen, C. K. *Atomic Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, 1962.

(5) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

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theorem,[6] which states that for any (L,S) term of an atom or atomic ion

$$E = -T = V/2 \tag{6}$$

The validity of eq 6 for all (L,S) multiplets of a given nd^q metal ion prevents the system from satisfying eq 2 and 3 simultaneously: it is impossible to change the potential energy of a system without at the same time modifying its kinetic energy. The latter change is only possible by a change in the shape of the orbitals. If an excited multiplet is constructed from the ground-state orbitals (as in SCS theory, and thereby satisfying eq 2 and 3), the resulting system is forced to carry an undue amount of interelectronic repulsion energy; it is therefore unstable, and the d orbitals in the excited state will expand so as to reduce the repulsion and to satisfy the conditions imposed by the virial theorem. As a consequence of this expansion, both the kinetic energy and the absolute value of the electron–nuclear attraction energy will decrease. Since in all cases $T > 0$ and $L < 0$, we have $\Delta T = T^* - T < 0$ and $\Delta L = L^* - L > 0$, where the * denotes the excited state. It is tempting to assume that the opposite signs of ΔL and ΔT lead to a (partial) cancellation, so that eq 3 might be replaced by

$$\Delta H = \Delta T + \Delta L \approx 0 \tag{7}$$

maintaining the approximate validity of eq 2 and thus providing a rationalization of the success of SCS theory.

Numerical Hartree–Fock (NHF) calculations[7] do confirm the expansion ideas and the opposite signs of ΔT and ΔL. But quantitatively, the calculations fail to reproduce eq 7. At the Hartree–Fock level of approximation, the one-electron energy difference ΔH is definitely not negligible; as a matter of fact, $|\Delta H|$ turns out to be several times larger than $|\Delta C|$. Moreover, and more surprisingly, ΔE and ΔC have opposite signs. This means that the orbital shape in the excited state is modified sufficiently for the original increase in repulsion energy to beome *overcompensated* by the expansion process. The true reason that the Hartree–Fock excited multiplets are higher in energy than the ground state is no longer that they are more destabilized by a higher interelectronic repulsion but rather that they are less stabilized by a smaller electron–nuclear attraction.[7-11]

B. The Hellmann–Feynman Theorem. The Hartree–Fock wave functions are of course rather different from the exact solutions of the Schrödinger equation, and it is not inconceivable that the conclusions of the previous section would be specific for the Hartree–Fock level of approximation. If the wave functions are refined by including correlation effects, the results might again be more in line with the conventional multiplet theory—at least in principle. It is the purpose of this paper to show that this is *not* the case and that an analysis of the exact solutions only confirms the Hartree–Fock results.

Table I. Isoelectronic Series of 3d^q-Transition-Metal Ions (Ground State in Italics)

confign	corresponding states	experimentally assigned	series
3d^2	^3F, ^{3}P, ^{1}G, ^{1}D, ^{1}S	^3F, ^{3}P, ^{1}D, ^{1}G	$Ti^{2+} \rightarrow Co^{7+}$
3d^3	^4F, ^{4}P ^{2}H, ^{2}G, ^{2}F, ^{2}D$_1$, ^{2}D$_2$, ^{2}P	^4F, ^{4}P ^{2}H, ^{2}G, ^{2}D$_2$	$V^{2+} \rightarrow Ni^{7+}$
3d^4	^5D ^{3}H, ^{3}G, ^{3}F$_1$, ^{3}F$_2$, ^{3}D, ^{3}P$_1$, ^{3}P$_2$ ^{1}I, ^{1}G$_1$, ^{1}G$_2$, ^{1}F, ^{1}D$_1$, ^{1}D$_2$, ^{1}S$_1$, ^{1}S$_2$	^5D ^{3}H, ^{3}G, ^{3}F$_2$, ^{3}P$_2$	$Cr^{2+} \rightarrow Ni^{6+}$

Rather than carrying out more elaborate calculations, we will focus our attention on *experimental data*. The C, L, and T components of the total energy are not directly observable, but the derivation of their expectation values is quite straightforward, if a certain number of experimental data are available. Indeed, on the basis of the Hellmann–Feynman theorem,[6,13,14] it is easy to show that the derivative $\partial E/\partial Z$ is simply related to the expectation value of the electron–nuclear attraction energy L (as usual, Z is the atomic number). For any given (L,S) multiplet, described by the wave function Ψ, one has

$$\frac{\partial E}{\partial Z} = \left(\Psi\left|\frac{\partial\mathcal{H}}{\partial Z}\right|\Psi\right) = \left(\Psi\left|\frac{\partial\mathcal{L}}{\partial Z}\right|\Psi\right) = \left(\Psi\left|\frac{\mathcal{L}}{Z}\right|\Psi\right) = \frac{L}{Z} \tag{8}$$

where $\mathcal{L}$ is the electron–nuclear attraction operator.

If we have available the experimental energies for a series of isoelectronic ions, it is possible to obtain the experimental values of $\partial E/\partial Z$ for the corresponding multiplets. In the Sugar–Corliss tables,[12] the excitation energies of the intermultiplet transitions are listed for many different atoms and ions. Equation 8 can easily be seen to apply to excitation energies as well, and therefore

$$\frac{\partial \Delta E}{\partial Z} = \frac{\Delta L}{Z} \tag{9}$$

where ΔE is the energy of the excited state with respect to the ground state. Equation 9 allows one to obtain ΔL, the electron–nuclear attraction energy of the excited state with respect to the ground state, and since the virial theorem yields $\Delta T = -\Delta E$, the "experimental" ΔC value can also readily be obtained ($\Delta E = \Delta T + \Delta L + \Delta C$).

Analysis of the Experimental Results

The experimental excitation energies are known to a very high degree of precision,[12] providing us with an extremely good approximation to the exact solutions of the relevant wave equations. In order to simplify the picture, the effects of spin–orbit coupling have been eliminated by considering only the weighted average of the different J levels, corresponding to one given (L,S) multiplet. In this way, the experimental data can also be compared more readily with the results of the nonrelativistic numerical Hartree–Fock (NHF) calculations.[15-17]

Even for the first transition-metal series, a number of spectral data are missing; many states that are theoretically possible have not been observed or have not been identified unambiguously. Table I shows the only 3d^q isoelectronic series that were found sufficiently complete in order to carry out the present analysis. From Table I, it is clear that for none of the 3d^q systems are all the theoretically possible states available; as a consequence, it is impossible to obtain experimental values for the spin-pairing parameter (eq 4). It is possible, however, for q = 2, 3, and 4 to analyze a number of well-defined (L,S) multiplets and to obtain a breakdown of the experimental (or exact) ΔE into its individual components ΔT, ΔL, and ΔC.

If, for a given transition from the ground state to one of the excited (L,S) multiplets, the isoelectronic series of Table I contains

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(6) Levine, I. N. *Quantum Chemistry*, 2nd ed.; Allyn and Bacon: Boston, MA, 1974.

(7) Vanquickenborne, L. G.; Haspeslagh, L. *Inorg. Chem.* **1982**, *21*, 2448.

(8) Similar results have been obtained by several authors,[9-11] for the first-row atoms. For the dipositive ions however (e.g. O^{2+}) the conventional (positive) ΔC was found. In ref 7, it is shown that $\Delta C < 0$ for transition-metal ions, up to at least M^{4+}.

(9) Davidson, E. R. *J. Chem. Phys.* **1965**, *42*, 4199.

(10) Messmer, R. P.; Birss, F. W. *J. Phys. Chem.* **1969**, *73*, 2085. Kohl, A. D. *J. Chem. Phys.* **1972**, *56*, 4236. Colpa, J. P. *Mol. Phys.* **1974**, *28*, 581.

(11) Katriel, J.; Pauncz, R. *Adv. Quantum Chem.* **1977**, *10*, 143 and references therein.

(12) Moore, C. E. "Atomic Energy Levels As Derived from the Analysis of Optical Spectra", Circular 467 of the National Bureau of Standards; U.S. Government Printing Office: Washington, DC; Vol. I, 1949; Vol. II, 1952. See especially the more recent and more extensive compilation of: Sugar, J., Corliss, C. H. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supplement 2.

(13) An entirely similar procedure was used by Katriel[14] in order to separate the exact energy of the p^2-isoelectronic series ($C \rightarrow F^{3+}$) into its components.

(14) Katriel, J. *Theor. Chim. Acta* **1972**, *23*, 309.

(15) Fischer, C. H. *Comput. Phys. Commun.* **1969**, *1*, 151.

(16) Fischer, C. H. *The Hartree–Fock Methods for Atoms*; Wiley-Interscience: New York, 1977.

(17) Pyper, N. C.; Grant, I. P. *J. Phys. B* **1977**, *10*, 1803. The authors show that relativistic corrections do not significantly affect the component analysis of the total energy.

Table II. Experimental Values of the Relative Energy ($\Delta E_{\mathrm{exptl}}$) and Its Components ($\Delta L_{\mathrm{exptl}}$ and $\Delta C_{\mathrm{exptl}}$) of the different ($L,S$) Multiplets with Respect to the Ground State[a]

(a) $3d^2$ Configuration

	Z, ion					
	22, Ti^{2+}	23, V^{3+}	24, Cr^{4+}	25, Mn^{5+}	26, Fe^{6+}	27, Co^{7+}
			$\Delta E_{\mathrm{exptl}}$			
$^1D-^3F$	0.037 509	0.048 008	0.057 091	0.065 487	0.073 479	0.081 108
$^3P-^3F$	0.047 479	0.058 893	0.069 260	0.079 193	0.088 893	0.098 565
$^1G-^3F$	0.064 502	0.081 873	0.097 332	0.111 851	0.125 660	0.139 141
			$\Delta L_{\mathrm{exptl}}$			
$^1D-^3F$		0.225	0.210	0.205	0.203	
$^3P-^3F$		0.250	0.244	0.245	0.252	
$^1G-^3F$		0.378	0.360	0.354	0.355	
			$\Delta C_{\mathrm{exptl}}$			
$^1D-^3F$		−0.129	−0.096	−0.074	−0.056	
$^3P-^3F$		−0.132	−0.105	−0.087	−0.074	
$^1G-^3F$		−0.214	−0.165	−0.130	−0.104	

(b) $3d^3$ Configuration

	Z, ion					
	23, V^{2+}	24, Cr^{3+}	25, Mn^{4+}	26, Fe^{5+}	27, Co^{6+}	28, Ni^{7+}
			$\Delta E_{\mathrm{exptl}}$			
$^4P-^4F$	0.051 629	0.062 688	0.072 768	0.082 378	0.091 719	0.099 994
$^2G-^4F$	0.053 548	0.066 978	0.079 051	0.090 407	0.105 146	0.115 799
$^2H-^4F$	0.075 478	0.094 130	0.110 933	0.126 773	0.145 849	0.159 379
$^2D_2-^4F$	0.072 996	0.091 641	0.108 567	0.124 752	0.136 009	0.148 963
			$\Delta L_{\mathrm{exptl}}$			
$^4P-^4F$		0.254	0.246	0.246	0.238	
$^2G-^4F$		0.306	0.293	0.339	0.343	
$^2H-^4F$		0.425	0.408	0.454	0.440	
$^2D_2-^4F$		0.427	0.414	0.357	0.327	
			$\Delta C_{\mathrm{exptl}}$			
$^4P-^4F$		−0.129	−0.100	−0.081	−0.055	
$^2F-^4F$		−0.172	−0.135	−0.158	−0.133	
$^2H-^4F$		−0.237	−0.186	−0.200	−0.148	
$^2D_2-^4F$		−0.244	−0.197	−0.107	−0.055	

(c) $3d^4$ Configuration

	Z, ion				
	24, Cr^{2+}	25, Mn^{3+}	26, Fe^{4+}	27, Co^{5+}	28, Ni^{6+}
		$\Delta E_{\mathrm{exptl}}$			
$^3H-^5D$	0.077 757	0.095 505	0.111 536	0.126 486	0.140 664
$^3G-^5D$	0.093 507	0.114 611	0.133 917	0.152 257	0.170 040
$^3P_2-^5D$	0.079 675	0.096 818	0.113 526	0.129 202	0.144 308
$^3F_2-^5D$	0.082 824	0.101 813	0.118 892	0.134 853	0.150 051
		$\Delta L_{\mathrm{exptl}}$			
$^3H-^5D$		0.422	0.403	0.393	
$^3G-^5D$		0.505	0.489	0.488	
$^3P_2-^5D$		0.423	0.421	0.416	
$^3F_2-^5D$		0.451	0.430	0.421	
		$\Delta C_{\mathrm{exptl}}$			
$^3H-^5D$		−0.231	−0.180	−0.140	
$^3G-^5D$		−0.276	−0.221	−0.183	
$^3P_2-^5D$		−0.229	−0.194	−0.158	
$^3F_2-^5D$		−0.247	−0.192	−0.151	

[a] The data refer to the $3d^q$-isoelectronic series of Table I. All energies are in hartrees.

N members, numerical analysis of the ΔE curves as a function of Z (containing N points) yields very reliable values of the individual energy components. Indeed, the validity of this procedure has been tested numerically on the basis of the NHF results, where the ΔL value can also be calculated directly. For the ($N-2$) central points of the isoelectronic series, both procedures (direct calculation of ΔL and numerical differentiation of ΔE) yield nearly exactly the same value (maximal error 1%). For the first and the last points of the series, however, numerical differentiation becomes impossible or—at least—very unreliable, since the slope of the (ΔE, Z) curve at the two extreme points has to be extrapolated rather than interpolated; the resulting uncertainty has led us to discard the ΔL values at these two points.[18]

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(18) A plot of ΔE and its components as a function of $1/Z$, rather than as a function of Z, would have the theoretical advantage that the curves $\Delta C/\Delta L$ would converge to 1 for $1/Z = 0$ (or $Z \to \infty$); this theorem has been discussed in detail in ref 11. Still, for the limited set of experimental data, available in the present context, the curves are obviously too far from the limit to be of much significance. (For none of the cases under consideration, has $\Delta C/\Delta L$ already become positive!) Therefore, we prefer to present the data in the more natural way, as a function of Z.

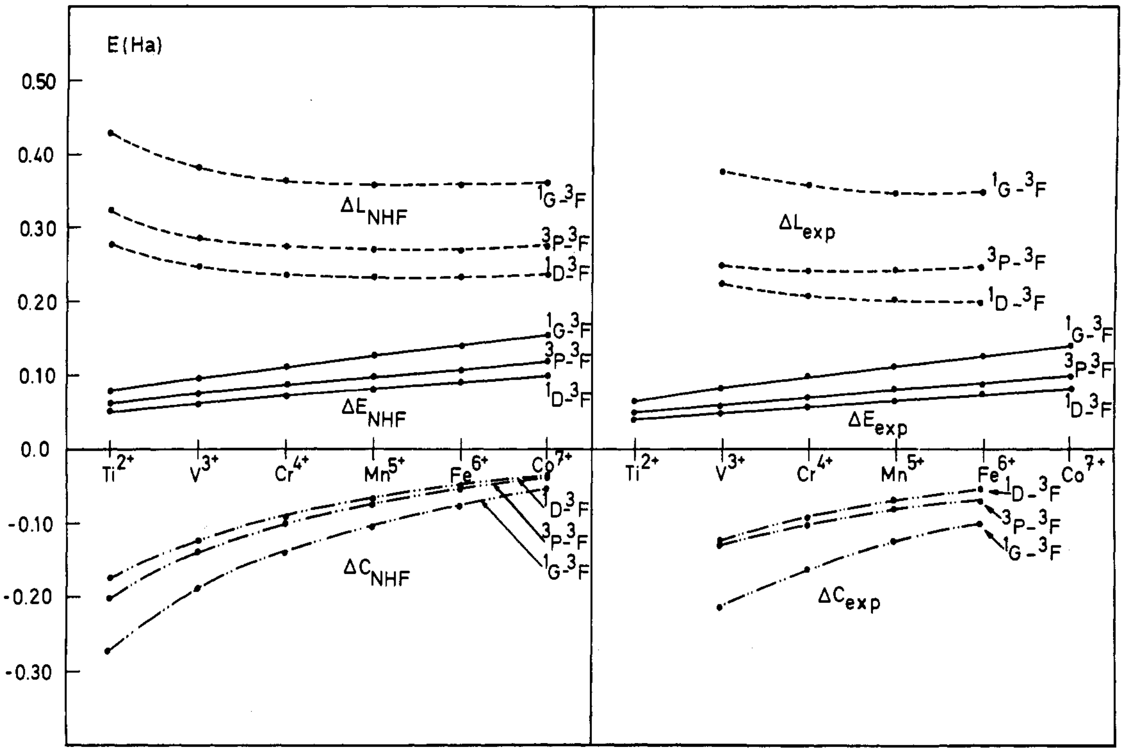

Figure 1. Relative energy ΔE and energy components ΔL and ΔC for the excited states ^1D, ^3P, and ^1G with respect to the ^3F ground state of the $3d^2$ configuration as a function Z, for the isoelectronic series Ti^{2+} ($Z = 22$) to Co^{7+} ($Z = 27$): left-hand side, numerical Hartree–Fock values ΔE_{NHF}, ΔL_{NHF}, and ΔC_{NHF}; right-hand side, experimental values ΔE_{exptl}, ΔL_{exptl} and ΔC_{exptl}.

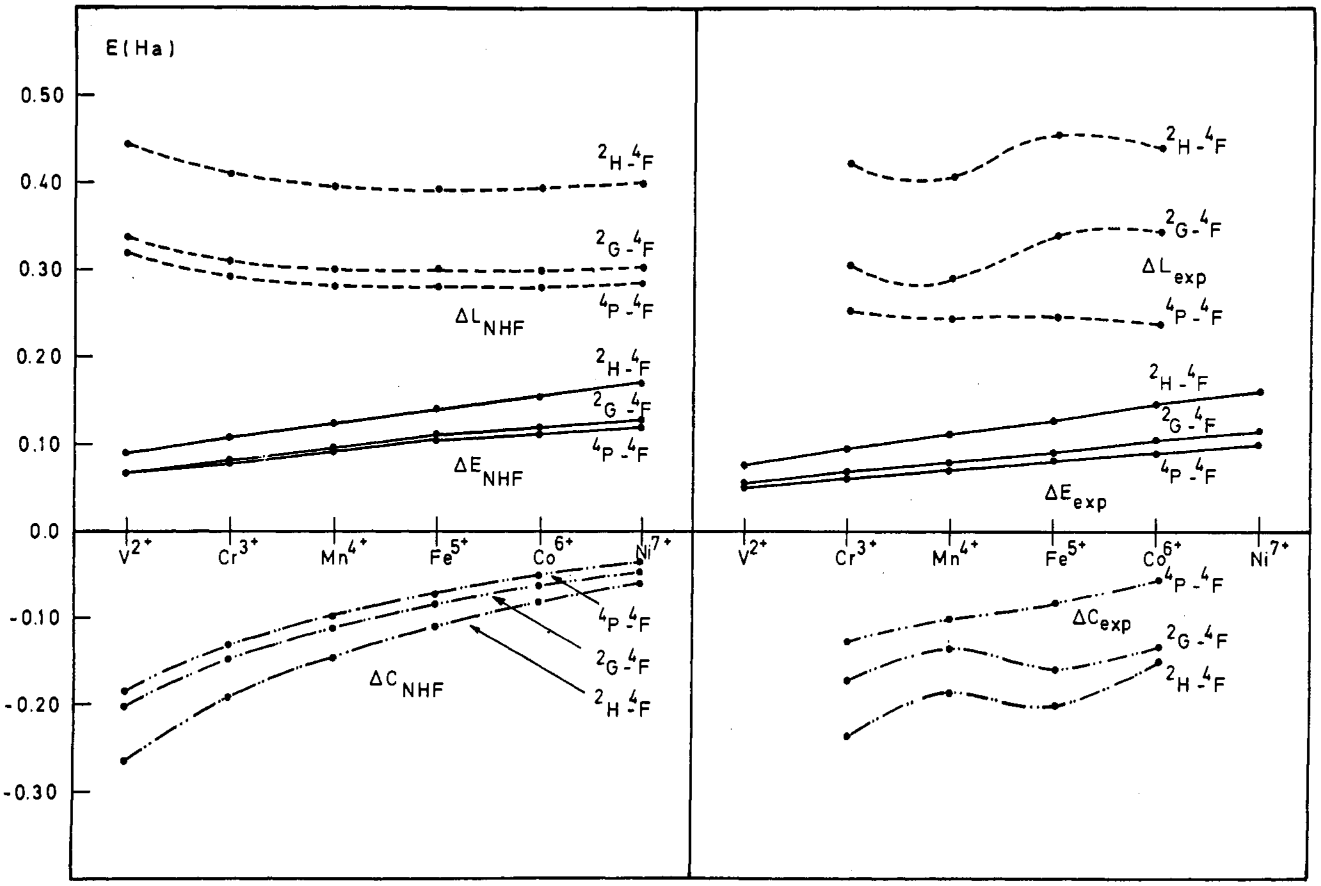

Figure 2. Relative energy ΔE and energy components ΔL and ΔC for the excited states ^4P, ^2G, and ^2H with respect to the ^4F ground state of the $3d^3$ configuration as a function Z, for the isoelectronic series V^{2+} ($Z = 23$) to Ni^{7+} ($Z = 28$): left-hand side, numerical Hartree–Fock values ΔE_{NHF}, ΔL_{NHF}, and ΔC_{NHF}; right-hand side, experimental values ΔE_{exptl}, ΔL_{exptl}, and ΔC_{exptl}.

Since the breakdown of the experimental energy into its components had not been carried out before (for the metal ions under consideration), we present the detailed numerical results of the analysis in Table II. In Figures 1–3, the values are shown for those states that have a unique (L,S) label within the d^q configuration (right-hand side) and are compared with the numerical

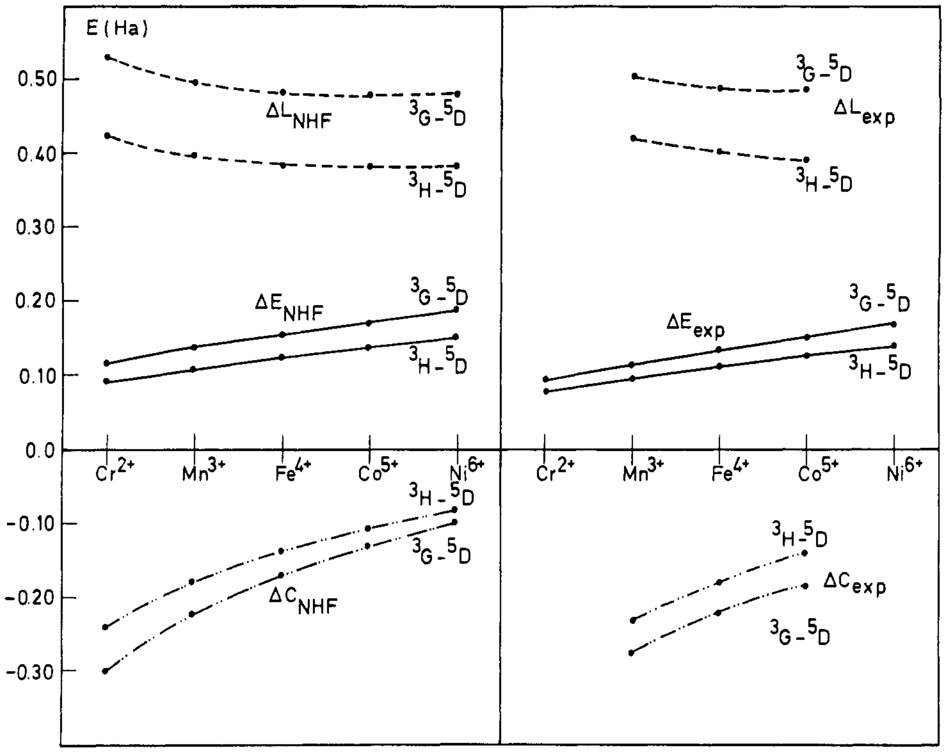

Figure 3. Relative energy ΔE and energy components ΔL and ΔC for the excited states ^3H and ^3G with respect to the ^5D ground state of the $3d^4$ configuration as a function Z, for the isoelectronic series Cr^{2+} ($Z = 24$) to Ni^{6+} ($Z = 28$): left-hand side, numerical Hartree–Fock values ΔE_{NHF}, ΔL_{NHF}, and ΔC_{NHF}; right-hand side, experimental values ΔE_{exptl}, ΔL_{exptl}, and ΔC_{exptl}.

Hartree–Fock (NHF) results (left-hand side).[19] In order to avoid undue crowding of the curves, the ΔT evolution is not shown; indeed, since the virial theorem is satisfied by both the NHF and the exact solutions, $\Delta T = -\Delta E$ in each case.

The most salient feature of Figures 1–3 is the similarity between the left-hand side and the right-hand side. Clearly the breakdown of the experimental energy into its components is qualitatively reproduced already at the Hartree–Fock level of sophistication. For all states, ΔE, ΔL, and ΔC have the same sign and even the same relative order at the left- and the right-hand sides of the three figures. In all cases, an increase of E entails an increase of L and a decrease of C. Therefore, *a d–d excitation corresponds to a decrease of the interelectronic repulsion energy.* Because of the virial theorem, an excitation also necessarily corresponds to a decrease in kinetic energy. Therefore, an excited (L,S) multiplet is higher than the ground state only because of its smaller electron–nuclear stabilization energy. Table II and the corresponding figures show that this conclusion is *not an artifact of the Hartree–Fock calculations but that it corresponds to an experimental reality.*

The difference between the left- and the right-hand sides of Figures 1–3 is due to the differential correlation energy associated with the different (L,S) multiplets. On the basis of an earlier study on first-row atoms (2p occupation), Clementi has proposed two guiding rules for the correlation energy:[20] (i) the lowest correlation is for the state of higher multiplicity; (ii) for states with the same spin multiplicity the smaller correlation is for states of highest angular momentum. From the figures, it appears that there is indeed a general tendency of the ΔE_{exptl} curves to be lower than the ΔE_{NHF} curves, indicating that the ground state has the smallest correlation error. But, otherwise, there seems to be little support to extend Clementi's rules to transition-metal ions: the correlation energies of states with different multiplicity can be very nearly identical, and when states with the same multiplicity are compared, the largest L state sometimes has the largest correlation energy.

It is also well to observe that the detailed shapes of the NHF and the experimental ΔL (or ΔC) curves are not quite identical. This may be due in part to the neglect of relativistic effects in the NHF procedure; indeed, neglecting relativistic effects is not quite equivalent to averaging over J states within each (L,S) multiplet. The difference between the left- and right-hand sides of Figures 1–3 may also be due in part to a nonmonotonous variation of the correlation energy as a function of Z.

Concluding Remarks

For any given d^n system, the Hartree–Fock equations are state-specific; that is, they depend on the (L,S) multiplet they are intended to describe. For two different multiplets, corresponding to the same d^n configuration, the only terms that make the difference are the terms describing the open-shell (d–d) repulsion. In this sense, one would be inclined to say that the open-shell repulsion is the only reason that the two multiplets have a different energy.

But if the Hartree–Fock equations are actually solved, the results are rather surprising. If the energy difference between two multiplets is written as a sum of its components

$$\begin{aligned}\Delta E &= (\Delta L_c + \Delta T_c + \Delta C_c) + (\Delta L_o + \Delta T_o + \Delta C_{oc}) + \Delta C_o \\ &= \Delta E_c + (\Delta H_{eff})_o + \Delta C_o\end{aligned} \qquad (10)$$

where c and o refer to closed and open shells, respectively, *none* of the seven components is negligible. As a matter of fact, in general ΔC_o turns out to be the *smallest* of the seven terms.[7,21] It has to be conceded, though, that ΔC_o is of the same order of magnitude as ΔE and that usually, though not always,[7] it is of the same sign as ΔE. The reason the six other components are different from zero is that different states are characterized by different orbital shapes. However, if the energy terms are taken together as shown in eq 10, the first terms almost entirely cancel each other, so that the total value of the core relaxation energy ΔE_c is negligible. Within the second three terms, the effective

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[19] Due to the existence of substantial term interaction, those states that do not have a unique (L,S) label within the d^q configuration cannot be calculated in a realistic manner with the numerical Hartree–Fock method. Therefore, those states were also omitted from the right-hand side of Figures 1–3.

[20] Clementi, E. *J. Chem. Phys.* **1963**, *38*, 2248.

[21] Vanquickenborne, L. G.; Haspeslagh, L.; Hendrickx, M.; Verhulst, J. *Inorg. Chem.* **1984**, *23*, 1677.

one-electron energy change of the screened valence electrons $(\Delta H_{\mathrm{eff}})_o$, the very large positive value of ΔL_o (for positive ΔE) is largely compensated by the negative value of ΔT_o and ΔC_{oc}. This results in a value of $(\Delta H_{\mathrm{eff}})_o$ that is of the same order of magnitude as ΔC_o. Depending on the case, one of these two energy terms will make the most important contribution to ΔE.[7,17] Sometimes, but not always,[7] it will be ΔC_o.

Whether these conclusions can be maintained beyond the Hartree–Fock level, and whether they are valid for the exact (experimental) situation, is a question that can find only a partial answer. Indeed, for the exact wave functions, the distinction between open and closed shells becomes meaningless. But the question can be discussed for the global components ΔL, ΔT, and ΔC, which—in Hartree–Fock theory—are given by

$$\begin{gathered}\Delta L = \Delta L_c + \Delta L_o \qquad \Delta T = \Delta T_c \\ \Delta C = \Delta C + \Delta C_o + \Delta C_{oc}\end{gathered} \tag{11}$$

The analysis of the experimental data presented in this paper shows that the energy sequence of the multiplets within a $3d^q$ configuration is determined by the electron–nuclear attraction L, *not* by the interelectronic repulsion C. The number of systems and states considered here is far from complete, but the present results suggest that Hartree–Fock theory is probably a reliable guide in providing a qualitatively correct picture of the excitation process.[17] Therefore, we have confidence in the Hartree–Fock predictions also for those cases where an exact analysis has not been carried out so far: examples are $4d^q$ and $5d^q$ systems,[7] f^n systems,[22] and especially molecular transition-metal complexes.[23–25]

Both conventional multiplet theory and ligand field theory are basically first-order perturbation approaches. The analysis of Table II shows that the conceptual framework underlying these classical theories is inadequate. Both theories are qualitatively very satisfactory, and they have an undeniable predictive value. But they fail (even qualitatively) in providing *the reason* that a certain energy pattern of the excited states is observed. The conventional textbook rationalization of multiplet theory, Hund's rules, and ligand field theory is basically too simplistic. One of the consequences is that phenomena such as high-spin/low-spin transitions, spin-pairing energy, the nephelauxetic effect, ligand field excitations, etc. should be reconsidered against the proper physical background.

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(22) Vanquickenborne, L. G.; Pierloot, K.; Görller-Walrand, C. *Inorg. Chim. Acta* in press.

(23) Wachters, A. H. J.; Nieuwpoort, W. C. *Phys. Rev. B: Solid State* **1972**, *5*, 4291.

(24) Vanquickenborne, L. G.; Haspeslagh, L.; Hendrickx, M. In *The Chemistry of Excited States and Reactive Intermediates*; Lever, A. B. P., Ed.; ACS Symposium Series 307; Americian Chemical Society: Washington, DC, 1986; Chapter 2.

(25) Vanquickenborne, L. G.; Hyla-Kryspin, I.; Hendrickx, M. *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; Reidel: Dordrecht, The Netherlands, 1986; pp 225–234.

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Evidence for Specific Solvent–Solute Interactions as a Major Contributor to the Franck–Condon Energy in Intervalence-Transfer Absorptions of Ruthenium Ammine Complexes

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The relationship between the electrochemically determined redox asymmetry, $\Delta E_{1/2}$, and the spectroscopic intervalence-transfer band energy, E_{IT}, over a series of asymmetric dimers of the formulation $(\mathrm{bpy})_2\mathrm{Ru}^{\mathrm{II}}(\mathrm{Cl})\mathrm{pyzRu}^{\mathrm{III}}(\mathrm{NH}_3)_4\mathrm{L}^{4+}$ has been investigated in two ways. In the first method the unique ligand L is varied synthetically so as to manipulate the potential of the ruthenium–ammine end of the dimer. In the second method the solvent is varied so as to manipulate the potential of the ruthenium–ammine end via the well-known solvent donor number effect. Comparison of these two approaches reveals that there is a solvent donor number dependent contribution to the Frank–Condon barrier of approximately 0.006 eV/DN that completely overwhelms the dielectric continuum theory derived $(1/n^2 - 1/D_s)$ solvent dependence typically observed in symmetrical dimers. Implications with respect to the potential energy surfaces governing electron transfer in these systems are discussed.

Introduction

Considerable progress has been made in recent years in both understanding and experimentally elucidating the role of the solvent in optical and thermal electron-transfer processes in fluid solution.[1–4] The roles of both solvent dielectric[1a,3–6] and solvent dynamical[1f–k,2] properties have received careful attention. One of the most notable convergences between theory and experiment has been in the application of the dielectric continuum theory of the solvent reorganizational barrier as developed by Marcus[5] and

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(1) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275. (c) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (d) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437. (e) German, E. D.; Kuzuetsov, A. M. *Electrochim. Acta* **1981**, *26*, 1595. (f) Kjaer, A. M.; Ulstrup, J. *Inorg. Chem.* **1986**, *25*, 644. (g) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387. (h) Calef, D. F.; Wolynes, P. G. *J. Chem. Phys.* **1983**, *78*, 470. (i) Van Der Swan, G.; Hynes, J. T. *Chem. Phys.* **1984**, *90*, 21. (j) Van Der Swan, G.; Hynes, J. T. *J. Chem. Phys.* **1982**, *76*, 2993. (k) Van Der Swan, G.; Hynes, J. T. *J. Chem. Phys.* **1983**, *78*, 4174.

(2) (a) Huppert, D.; Kanety, H.; Kosower, E. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 161. (b) Kosower, E. M.; Huppert, D. *Chem. Phys. Lett.* **1983**, *96*, 433. (c) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (d) Hupp, J. T.; Liu, H. Y.; Farmer, J. K.; Gennett, T.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *168*, 313. (e) Schmidt, J. A.; Siemialczuk, A.; Weedon, A. C.; Bolton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 642. (f) Pasman, P.; Mes, G.; Koper, W. W.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1985**, *107*, 5839. (g) Kakitani, T.; Mataga, N. *Chem. Phys.* **1985**, *93*, 381. (h) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 4752. (i) Kakitani, T.; Mataga, N. *Ibid.* **1985**, *90*, 993.

(3) (a) Li, L. T.; Brubaker, C. H. *J. Organomet. Chem.* **1981**, *216*, 223. (b) Li, T. T.; Weaver, M. J.; Brubaker, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 2381. (c) Chan, M.; Wahl, A. C. *J. Phys. Chem.* **1982**, *86*, 126. (d) Grampp, G.; Jaenicke, W. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1035. (e) Grampp, G.; Jaenicke, W. *Chem. Phys. Lett.* **1984**, *112*, 263. (f) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 325. (g) Russell, C.; Jaenicke, W. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *180*, 205.

(4) (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *4*, 94. (b) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Nouv. J. Chim.* **1980**, *4*, 643. (c) Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731. (d) Powers, M. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 1785. (e) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393. (f) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289. (g) Powers, M. J.; Callahan, R. W.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 1457. (h) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 752.

(5) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 906. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(6) (a) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (b) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (c) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

0020-1669/86/1325-4233$01.50/0