proximation are similar to those obtained recently[26] from the "ZH" integral equation.

5. Conclusions

The effects brought about by the inclusion of the approximate bridge functions in the HNC theory of asymmetric electrolytes are significant. The accuracy of all three correlation functions, as judged by comparison with our recent simulation results, is improved. The counterion–counterion correlation function, which may play an important role in studies of the polyelectrolyte effect on the reaction rate in electrolyte solutions, is in excellent agreement with the simulation results. This is also true for the polyion–polyion correlation function. There is some correction to the partial structure factor $S_{pp}(k)$, which is the experimental observable.

For highly charged colloids the corrections are expected to be larger. A useful first test for situations where (i) solutions to the HNC equation exist and (ii) computer simulations are difficult, expensive, or unavailable is to calculate a "first-order" estimate to the corrections to the HNC equation from eq 5. Although it is impossible to give a definite conclusion on the basis of this example alone, it is expected that the HNC+B theory will yield a more realistic analysis of the experimental neutron and light-scattering experiments.

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Electronegativity and Lewis Acid Strength

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Abstract: For main group elements in their highest oxidation state we show that a scale of Lewis acid strength derived from observed structures correlates with a scale of electronegativity derived from electron energies in the free atom. If the bonding geometry is also explicitly taken into account the same correlation holds for the same atoms in their next lower oxidation state. Although the two scales are conceptually quite distinct they correlate because both have a similar dependence on the screened nuclear charge and the ionic radius.

1. Introduction

Approaches to the definition of electronegativity range from empirical to fundamental and from theoretical to experimental, yet all the scales agree in the essential ordering of the elements in the Periodic Table. The reason for this agreement is that, in spite of their different origins, each of the scales samples the properties of the atom's outermost electrons, the ones most directly involved in chemical bonding. This paper explores two recently proposed scales based on quite different physical models: Allen's[1] free atom spectroscopic electronegativity and Brown's[2] scale of Lewis acid strength derived from the coordination numbers observed in solids. In spite of the different physical models underlying them, the two scales correlate well because both depend in a similar way on the screened nuclear charge and the ionic radius.

2. The Correlation between Spectroscopic Electronegativity and Lewis Acid Strength

In Allen's[1] scale, the free-atom spectroscopic electronegativity (χ) of main group elements is defined as the average energy of the valence shell s and p electrons (eq 1), where n_s and n_p are the

$$\chi = (n_s e_s + n_p e_p)/(n_s + n_p) \qquad (1)$$

numbers and e_s and e_p are the spectroscopic energies of the valence s and p electrons, respectively. Allen points out that the spectroscopic electronegativity is a property of the free atom and that different values are expected once the atom is placed in a solid. When suitably scaled, his electronegativity scale is similar to other traditional scales such as those given by Pauling[3] and Allred and Rochow.[4]

Table I. Free-Atom Spectroscopic Electronegativities (χ, Taken from Allen,[1] Table III) and Intrinsic Lewis Acid Strengths (Sa, Taken from Brown,[2] Table II) for Main Group Elements in Their Highest Oxidation State

element	χ, Ry	Sa, vu	element	χ, Ry	Sa, vu
Li	0.40	0.20	Ge	0.87	0.89
Na	0.38	0.16	Sn	0.79	0.68
K	0.32	0.13	N	1.33	1.67
Rb	0.31	0.12	P	0.98	1.25
Be	0.69	0.50	As	0.96	1.13
Mg	0.56	0.33	Sb	0.86	0.83
Ca	0.45	0.27	O	1.57	
Sr	0.42	0.23	S	1.13	1.5
B	0.89	0.87	Se	1.05	1.5
Al	0.70	0.57	Te	0.94	1.0
Ga	0.76	0.65	F	1.82	
In	0.72	0.50	Cl	1.25	1.75
C	1.11	1.35	Br	1.17	
Si	0.83	1.00	I	1.03	1.2

Brown's scale of Lewis acid strength (Sa),[5] here called "average Lewis acid strength", is defined for a given cation by eq 2, where

$$\mathrm{Sa} = V/N_t \qquad (2)$$

V is the oxidation state of the cation and N_t is the average of the coordination numbers to oxygen observed in a large sample of

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(1) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003–9014.

(2) Brown, I. D. *Acta Crystallogr.* **1988**, *B44*, 545–553.

(3) Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960.

(4) Allred, A. L.; Rochow, E. G. *J. Nucl. Inorg. Chem.* **1958**, *5*, 264–268.

(5) The term "Lewis acid strength" was used in ref 2 to describe the quantity Sa defined by eq 2 because Sa allows one to predict which Lewis acids will bond to which Lewis bases (their numerical strengths must be equal). The scale, however, is derived entirely from the oxidation state and the coordination numbers observed in crystals and does not depend in any direct way on electron energies or free atom properties. If the term "Lewis acid strength" is read with this definition in mind the remarkable nature of the correlation will become more apparent.

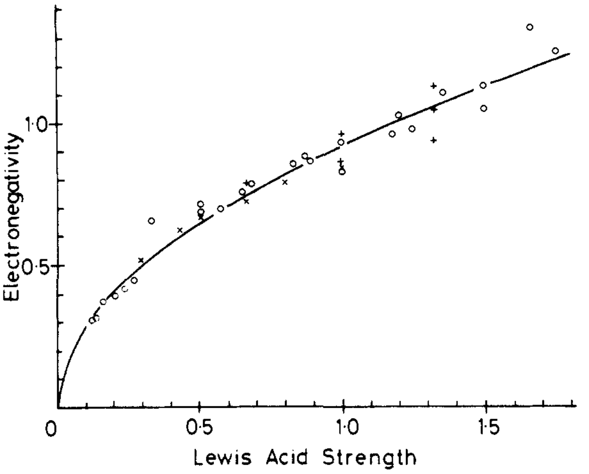

Figure 1. Spectroscopic electronegativity in Rydbergs versus Lewis acid strength in valence units for main group elements. Circles represent cations in their highest oxidation state: (+) cations with stereoactive lone pairs and (x) cations with nonstereoactive lone pairs. Data taken from Tables I and II. The curve represents eq 3.

compounds.[2] The average Lewis acid strength is thus the Pauling bond strength averaged over all the compounds in which the cation appears. It represents the best a priori estimate of the valence (or strength) of the bonds that the cation forms.

Values of χ and Sa are given in Table I and are shown as circles in Figure 1 for main group elements in their highest oxidation state. The line shown in Figure 1 represents eq 3, where χ is given in Rydbergs and Sa in valence units (vu).

$$\mathrm{Sa} = 1.18\chi^2 \qquad (3)$$

Using the values of χ given in Table III of Allen's paper[1] and of Sa given in Table II of Brown's paper,[2] eq 3 holds only for cations of the main group elements in their highest oxidation state. Transition metals, for which only tentative values of χ could be assigned, give rise to points (not shown) that lie significantly below the line, while main group elements in their lower oxidation states, having values of Sa that are generally smaller than those for the highest oxidation state, give rise to points (also not shown) that tend to lie above the line. We can improve the correlation for the main group elements in their lower oxidation state by choosing values of χ and Sa that reflect the actual chemical context in which the atoms find themselves.

To do this we note that the Lewis acid strength of a cation depends not only on its oxidation state but also on its coordination number which, for cations with valence-shell lone electron pairs, can vary widely. Tl(I), for example, is known with all coordination numbers between 3 and 12. To explore this variation it is convenient to define an "actual Lewis acid strength", Sa′, according to eq 4, where N_a is the actual coordination number found at a

$$\mathrm{Sa}' = V/N_a \qquad (4)$$

given site in a given compound. Sa′ will be similar to, though in general different from, Sa since it reflects the actual chemical environment in which the cation finds itself. The value of 0.15 vu given by Brown[2] for the Sa of Tl(I) is an average of values that range from 0.08 (=1/12) to 0.33 (=1/3). The actual Lewis acid strength that Tl(I) displays in a particular compound depends on the Lewis base strength (Sb, defined by the analogue of eq 2) of the counterion[2] since the acid strength of the cation and the base strength of the anion are both estimates of the valence of the bond between them (the Valence Matching Principle[6]). Strong bases lead to Tl displaying a large value of Sa′ (coordination numbers of 3 with the lone pair occupying the fourth coordination position of a tetrahedron) but weak bases favor a low Sa′ (coordination numbers of 10–12 with a symmetrical coordination sphere and no stereoactive lone pair).[2]

Table II. Spectroscopic Electronegativities (χ) and Actual Lewis Acid Strengths (Sa′) for Cations with a Single Nonbonding Electron Pair[a]

element	state	χ, Ry	Sa′, vu
Tl(I)	A		0.33
	B		0.08
Sn(II)	A	0.79	0.67
	B	0.52	0.29
Pb(II)	A		0.67
	B		0.25
As(III)	A	0.96	1.00
	B	0.67	0.50
Sb(III)	A	0.86	1.00
	B	0.62	0.43
Bi(III)	A		1.00
	B		0.38
S(IV)	A	1.13	1.33
	B	0.85	1.0
Se(IV)	A	1.05	1.33
	B	0.79	0.8
Te(IV)	A	0.94	1.33
	B	0.72	0.67

[a] See text for definitions. A = electron pair stereoactive; B = electron pair inactive.

Consider first the case of symmetrical coordination where the nonbonding electron pair occupies a pure s state, a state that can be considered as part of the core. Since only the p electrons are involved in the valence shell the appropriate spectroscopic electronegativity depends only on the p electron energy, i.e. n_s in eq 1 will be 0. Table II shows that the pure p state electronegativities (the lines labeled B in Table II), calculated from values given by Allen,[1] are considerably smaller than the corresponding sp electronegativities of the free atom.

By contrast, when the nonbonding electron pair occupies one of the four equivalent sp^3 orbitals it is fully part of the valence shell. In this case the spectroscopic electronegativity must be calculated by using both the s and p electrons and will be the same as the free-atom electronegativity (Table II, lines labeled A).

To match these electronegativities we need to calculate the corresponding values of Sa′ from the coordination numbers found in the two extreme cases. Unfortunately these extremes are observed for only Tl(I) and Pb(II) for which Allen does not give electronegativities. Most of the other cations of the series do not show symmetric coordination with oxygen. In order to predict Sa′ for cations when the lone pair is fully suppressed, we assume that coordination number will be limited only by anion–anion repulsions. These coordination numbers are the predicted coordination numbers (the PCN's given in Table I of Brown[2]) calculated from the bonding radius ratios.

When the lone pair is fully stereoactive we assume a tetrahedral arrangement of one nonbonding and three bonding electron pairs giving a coordination number of three. Both sets of coordination numbers are used to calculate the values of Sa′ given in Table II. The correlation between the actual Lewis acid strength and the corresponding spectroscopic electronegativity is shown in Figure 1 both for the case where the lone pair is stereoactive (shown by +) and where it is inactive (shown by x). The agreement with eq 3 is good in both cases, confirming that this relation also applies to the actual Lewis acid strengths of lone pair cations and the corresponding spectroscopic electronegativities.

3. Discussion

Because the spectroscopic electronegativity and the Lewis acid strengths are related to two quite different models of chemical activity, it is interesting to examine their underlying concepts in order to see why χ and Sa should correlate so well.

Electronegativity is a concept, recently reviewed by Mullay,[7] that has a history going back at least to Pauling's[3] early work. Most authors concur that it is related to the energy of the valence

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electrons and is measured in units of energy. When a bond is formed between two neutral atoms the valence electrons move from the atom with the smaller electronegativity (the cation) toward the atom with the larger electronegativity (the anion). The difference in the free-atom electronegativities of the atoms entering into the bond thus indicates the direction and extent of the electron transfer and gives a measure of the ionicity of the resulting bond.

The concept of the Lewis acid strength as defined by eq 4 can also be traced back to Pauling.[3] It is an estimate of the valence of a typical bond formed by a cation and is given in valence units (electron pairs per bond). As suggested by its name, it is, in contrast to the electronegativity, intrinsically an ionic property since eq 4 (or eq 2) has no meaning for a free atom. Furthermore, again in contrast to the electronegativity, it can only be defined in terms of the strengths of bonds to a reference anion, here chosen to be O^{2-} because of the large amount of information available on the coordination of cations by O. In this model the species that enter into a bond are the ions rather than the free atoms, and during bond formation the electrons move from the anion to the cation, i.e. in the opposite direction to that implied by the free atom model. The extent of the transfer is given by Sa and Sb which are both estimates of the strength of the resulting bond.

The models underlying electronegativity and Lewis acid strength are therefore quite different, but the scales correlate because both depend on the nuclear charge screened by the core electrons (approximately equal to the formal oxidation state (V)) and the radius of the valence shell (approximately equal to the radius of the core electrons that form the surface of the cation (*r*)).

The Lewis acid strength and the spectroscopic electronegativity are conceptually quite distinct properties that correlate only because both reflect the properties of the surface of the electron core of an atom. While correlations like that given by eq 3 may be useful, one should not confuse two scales that derive from fundamentally different concepts. To avoid confusion, the term electronegativity should be reserved for those scales that are directly measured in units of energy. Others scales, like that of Boyd and Edgecombe,[8] constructed from surface properties other than energy, should be considered as scales that measure different properties but that correlate with the electronegativity for the reasons given above. Since the chemical properties of an atom are the properties of its surface, correlation between chemically useful scales that depend on these properties is not unexpected.

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Chiroptical Properties of the Diazirine Chromophore

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Abstract: Chiroptical properties of the diazirine chromophore are investigated experimentally and by ab initio molecular orbital calculations. Measurement of the CD spectra of (αS)-3-*sec*-butyldiazirine (**1**), (5*S*)-5-methyl-1,2-diazaspiro[2.5]oct-1-ene (**2**), (4*R*,7*R*)-4-isopropyl-7-methyl-1,2-diazaspiro[2.5]oct-1-ene (**3**), 3-azi-5α-cholestane (**4**), and 3-azi-5α-androstan-17β-yl benzoate (**5**) and computations on *gauche*-3-ethyldiazirine (**6**) suggest that the Cotton effect of the long wavelength (350-370 nm) absorption obeys an octant rule. The signs of the octants are the same as observed for the analogous carbonyl compounds. The octant nature of the sector rule is consistent with the nodal properties of the molecular orbitals in the description of the lowest excited state, $n_-\pi_{NN}^*$. It is anticipated that the octant rule for diazirines will prove applicable and useful in compounds containing other chromophores and in compounds containing a less strained cis-azo group.

The introduction of chromophore groups into a strained three-membered ring raises their stereochemical rigidity and, at the same time, practically has no effect on the nature of the lower electronic transitions. This, for example, was demonstrated in studying the halogenamino chromophore in a series of aziridines, diaziridines,[2] and oxaziridines.[3] The compounds containing stereochemically rigid chromophore groups are most suitable for developing the regional rules that correlate the Cotton effect (CE) sign with the stereochemistry of the chromophore environment. Therefore it is interesting to consider the diazirine chromophore as a rigid model of the cis-azo chromophore. The latter has been quite thoroughly investigated by CD and ORD methods.[4-6] However, the general regional rule for this chromophore has not been developed yet. The Snatzke empirical rule known so far[4] is applicable only to α-carbonyl-substituted pyrazolines.

The diazirine ring itself can be considered a prospective chromophore for studying the stereochemistry of chiral molecules by chiroptical methods since, in our opinion, this chromophore exhibits the following advantages: (i) high C_{2v} symmetry similar to the carbonyl chromophore; (ii) long-wavelength UV absorption (350-370 nm);[7,8] (iii) ready availability.[9,10] However, there are no studies of the chiroptical properties of this class of three-

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