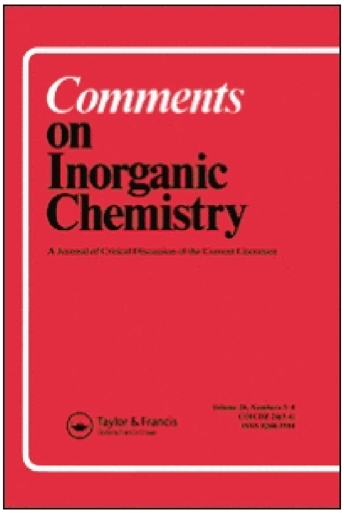
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Chemical Ionization Energies—Talking Points between Atomic Spectroscopists and Thermodynamicists

Christian K. Jorgensen[a]
[a] Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, Geneva, Switzerland

To cite this Article Jorgensen, Christian K.(1981) 'Chemical Ionization Energies—Talking Points between Atomic Spectroscopists and Thermodynamicists', Comments on Inorganic Chemistry, 1: 2, 123 — 140

To link to this Article: DOI: 10.1080/02603598108078085

URL: http://dx.doi.org/10.1080/02603598108078085

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Chemical Ionization Energies — Talking Points between Atomic Spectroscopists and Thermodynamicists

The rapidly increasing ionization energies of monatomic entities with charges increasing from -1 to $+Z$ are confronted with the conditions for stability of oxidation states. The reasons for adding 4.5 eV to standard E^0 values, the evidence from photoelectron spectra, the hydration energies of gaseous ions, optical electronegativities, and the Kossel isoelectronic series are discussed.

Monatomic Entities — Series Limits and Parabolic Extrapolations

A gaseous monatomic M^{+z} contains $K=Z-z$ electrons where the charge z can be positive, zero, or -1. When atomic spectroscopists speak about *the* ionization energy I_n they mean the energy difference between the ground state of $z=n$ and the ground state of $z=n-1$. With this definition, the electron affinity of the neutral atom is I_0. Seen from a strictly quantum mechanical point of view, the "first" ionization energy I_1 constitutes the sharp border between discrete, stationary states situated below I_1 (if the ground state of the gaseous atom is taken as the zero point of energy) and an overall dense continuum of states above, including the stationary states of positive ions (accompanied by one or more electrons at very large distance). Fortunately, it is frequently possible to describe experimental situations involving perceptible singularities in the continuum which act for all practical purposes as effectively stationary states.

The major objective of atomic spectroscopists[1] is to measure wave numbers of spectral lines, and to connect the photon energies via the Ritz combination principle, E_2-E_1, down to the ground state of the monatomic entity. At one time,[2,3] there was a pragmatic distinction between *series spectra* with long series of energy levels clearly converging toward a series limit and *multiplet spectra* showing many more spectral lines, frequently arranged in closely adjacent groups, i.e. "multiplets". The series spectra are common in elements outside the transition groups, whereas the presence of a partly filled

Comments Inorg. Chem.
1981, Vol. 1, No. 2, pp. 123–140
0260-3594/81/0102-0123$06.50/0

3d,4d,4f,5d or 5f shell enhances the propensity toward multiplet specta. The noble gases (except helium) have a filled 2p,3p,4p,5p or 6p shell in the ground state, and all the excited levels (characterized by the quantum number J and by even or odd parity, and each containing $2J+1$ states in the sense of mutually orthogonal wave functions corresponding to the same energy) can be *classified* as one of the np electrons being lifted to an empty nl orbital. The corresponding spectra combine several of the "series" and "multiplet" characteristics. In 1895, Rydberg proposed writing the energy levels of M^{+z} having $K=3,11,19,37,55$, and 87 (and hence containing one electron more that the noble gases) using modern notations:

$$E_{nl}=I_{z+1}-\frac{(z+1)^2 ry}{(n-\delta_l)^2} \tag{1}$$

where 1 $ry=1/2$ Hartree $=109737.32\,\mathrm{cm}^{-1}=13.6058$ eV (1 eV $=8065.48\,\mathrm{cm}^{-1}$ $=23.06$ kcal mol^{-1} $=96.484$ kJ mol^{-1}) and where the Rydberg defect δ_l is hardly dependent on n, but is large for ns ($l=0$), smaller for np ($l=1$), and rapidly vanishes for the higher l values d,f,g,h,... unless d or f shells are already occupied in the preceding noble gas. Because of the theoretical interest in the binding of the most weakly bound electron, it became customary to indicate "term values" relative to the series limit, but the great compilations of the National Bureau of Standards[4,5] use energies relative to the ground state of M^{+z}, as one had to do in multiplet spectra anyhow. The relativistic effect "spin-orbit coupling" has been neglected in Eq. (1). One (nl) electron with positive l has two adjacent J levels, $J=l-1/2$ usually at lower energy, $J=l+1/2$ at higher values. For the same reason, noble gases present two series limits; for the remaining $(n\mathrm{p})^5$ configuration $J=3/2$ lies at lower energy than $J=1/2$ which constitutes the first excited state of M^+.

The *precision*[4-6] of the *ionization energies* I_n is far better in some species, where Eq. (1) gives uncertainties less than 0.1 cm^{-1} (like the sharp spectral lines) and can be quite low in multiplet spectra, amounting to 5 or 10%. Within one year, I_6 of Ta^{+5} was devaluated[7] from 97.34 to 94.01 eV. Many high charges (already starting at $z=3$) have not had their I_n evaluated from line spectra, and quite a lot of interesting data (for comparison with chemistry) are still lacking. It has been known for a long time that I_n in an isoelectronic series with definite K (and conserving the same electron configuration of the ground state) varies as a parabolic function of z having its minimum close to $z=0$. Also the same element has I_n values approximately proportional to $3n+n^2$ as long as a closed nl shell is not opened up by the consecutive ionization. Whereas the extrapolation toward higher z is quite satisfactory, the parabolic variation is less reliable going to I_0. About one quarter of the elements have vanishing electron affinity of their gaseous atom (this quantity can only be negative if an electron configuration is imposed in a confined volume) and the highest I_0 is 3.61 eV for chlorine (but only 3.40 eV for fluorine) to be compared with I_1 varying from 3.894 eV for caesium to 24.587 eV for helium. The only other atoms having I_1 higher than hydrogen are: nitrogen, 14.534; oxygen, 13.618 (a close hit); fluorine, 17.422; neon, 21.564; argon, 15.759; and krypton, 13.999 eV. Whereas I_1 is only 12.967 eV for chlorine, 12.130 for xenon, 10.437 for mercury, and 10.748 for radon.

The parabolic variation can be analyzed[8,9] in terms of the SCS (Slater–Condon–Shortley[1]) *parameters of interelectronic repulsion*. It is important to realize that the parametrized expressions do not predestine a given electron configuration to contain the ground state. For K greater than 18, many isoelectronic series have different ground configurations for the low charges $z = -1, 0, +1$, whereas the situation is more clear-cut for M^{+2} (except where M = La, Gd, Lu, Ac, and Th) and all cases of $z = 3$–6 where the shells invariably are filled in the order:

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < \ldots \tag{2}$$

where the double inequality signs indicate $K = 2$, 10, 18, 36, 54, and 86 (isoelectronic with the noble gases). The exceptions in neutral atoms are mainly connected with the presence of one or two 4s,5s,6s, or 7s electrons. Re^{+8} and subsequent members[10] of $K = 67$ have their ground state belonging to a configuration containing $5p^5 4f^{14}$ rather than $5p^6 4f^{13}$ predicted by Eq. (2). Calculations[11] for several lanthanides with z of at least +7 also show depletion of the 5p shell rather than of the 4f shell. It is noted that these exceptions occur at the first deviation of Eq. (2) from hydrogenic order (according to increasing n).

The parabolic variations as a function of z can be justified by a direct theoretical argument of Linderberg and Shull[12,13] about the series expansions of nonrelativistic eigenvalues, but these coefficients may be divergent for Z above, perhaps, 10. The *phenomenological barycenter polynomial*[9] for higher Z values is more related to Hookes' law that most potential minima have a sufficiently large second differential quotient (compared with subsequent derivatives) so that the variation close to the minimum is approximately parabolic.

Monatomic entities frequently have a configuration containing a^1b^1 at lower energy than *both* a^2 and b^2. A typical case if Sc^+ having all four J levels (including the ground state) belong to [18]3d4s at very low energy, whereas the barycentre of the 45 states forming the nine J levels belong to $[18]3d^2$ occurs 1.14 eV above the ground state and the unique state of $[18]4s^2$ 1.41 eV above the ground state. Such behavior can easily be rationalized[9,14] by the interelectronic repulsion J(a,b) [in the example J(3d,4s)] being smaller than the arithmetic average of J(a,a) and J(b,b). This is always the case when one of the two orbitals (here 3d) has a much smaller average radius than the other. This case of parabolic variation is in contrast to the feelings of a chemist expecting roughly additive one-electron energies, at least to the extent of a^1b^1 being situated between a^2 and b^2.

Another important consequence is that there is no unambiguous answer to the question of whether 3d or 4s is the most stable shell in scandium. The 4s orbital is filled with first priority in the neutral atom, having its ground state belonging to $[18]3d4s^2$, but the 4s electrons are the first to be removed by ionization, leaving Sc^+ with [18]3d4s and Sc^{+2} with [18]3d in agreement with Eq. (2). By the same token, 11 of the neutral lanthanide atoms[5] have their ground state belonging to $[54]4f^q6s^2$ (and La, Ce, Gd, and Lu to $[54]4f^{q-1}5d6s^2$) whereas all the M^{+3} and all M^{+2} (except La^{+2} [54]5d, $Gd^{+2}[54]4f^7 5d$, and Lu^{+2} $[54]4f^{14}6s$) ions have ground states belonging to $[54]4f^q$. Because of the large J(4f,4f) there is an optimum number of 4f electrons close to $z-56$ or $z-57$.

The Chemical Ionization Energy of the Hydrogen Electrode

Because of the almost incredibly exact electroneutrality of macroscopic objects, textbooks of physical chemistry[15] insist that only neutral sets of cations and anions have well-defined properties. The corollary[16] is that if the product Cz of an *arbitrary* constant C and the (positive or negative) ionic charge z is added to a property of a given ion, it has no experimentally observable result. A good example is the approximately additive molar electric polarizabilities (derived from refractive indices for visible light) for ionic salts[16,17] in aqueous solution and as crystalline solids. Here the Cz problem can be circumvented by noting that the cations Li(I), Be(II), Mg(II), and Al(III) have polarizabilities below 0.2 $Å^3$ (the typical experimental uncertainty) and can be neglected. By the same token, ionic (rather than molar) electric conductivities in aqueous solution can be evaluated, following reference to Stokes' law of motion of a sphere with radius R in a viscous fluid, where an ion with large radius, such as $N(C_{18}H_{37})_4^+$ or $B(C_6H_5)_4^-$ has a low ionic conductivity (proportional to $1/R$) which cannot be negative. *Standard oxidation potentials* E^0 are nowadays given relative to the hydrogen electrode at standard conditions (i.e. 1 atm. H_2 pressure, pH$=0$ or 1 M H_{aq}^+) and the question is now whether the process

$$\frac{1}{2}\,H_2(\text{gas}) = H^+(\text{aq}) + e^-(\text{vacuum}) \qquad (3)$$

TABLE I

Reaction	E_0, V	I_{chem}, eV
$Fe(OH_2)_6^{+2} = Fe(OH_2)_6^{+3} + e^-$	+0.75	5.2
$V(OH_2)_6^{+2} = V(OH_2)_6^{+3} + e^-$	−0.25	4.2
$Eu_{aq}^{+2} = Eu_{aq}^{+3} + e^-$	−0.4	4.1
$Co(NH_3)_6^{+2} = Co(NH_3)_6^{+3} + e^-$	+0.1	4.6
$Fe(CN)_6^{-4} = Fe(CN)_6^{-3} + e^-$	+0.5	5.0
$Fe(C_5H_5)_2 = Fe(C_5H_5)_2^+ + e^-$	+0.4	4.9
$RuO_4^{-2} = RuO_4^- + e^-$	+0.6	5.1
$RuO_4^- = RuO_4 + e^-$	+1.0	5.5
$IrCl_6^{-3} = IrCl_6^{-2} + e^-$	+1.0	5.5

has a well-defined ionization energy. There is an almost Victorian pudency involved in not asking such a question in public. If this inhibition is removed, a closer analysis shows that the *hydration energy* of H^+ would suffice to determine Eq. (3) by introducing the dissociation energy of H_2 and I_1 of the hydrogen atom. Rosseinsky[18] discussed how to circumvent the *Cz* problem by comparing the hydration energies of many cations and anions. Similar results had previously been given by Latimer[19] with less attention focused on Eq. (3). By the way, vibrational (infrared and Raman) spectra provide strong evidence[20] that H_{aq}^+ is indeed monomeric H_3O^+ (like NH_4^+ in liquid ammonia) but its half-life at 25°C is only 2×10^{-12} sec explaining the many effects of highly mobile protons in water. The hydrogen bonding in $OH_3^+(OH_2)_3$ is asymmetric, like in ice, and does not warrant a description as $H_9O_4^+$. The species having $pK = 3$ in hydrofluoric acid is not diatomic HF but the strongly bound[21] ion-pair $OH_3^+F^-$. The conclusion of Rosseinsky[18] is that ΔH for hydration of gaseous H^+ is -260.5 kcal mol^{-1}, allowing the introduction[9,16] of the *chemical ionization energy*:

$$I_{\text{chem}} = E^0 + 4.5 \text{ eV} \tag{4}$$

The major problem for classical physical chemistry[15] is the distinction between enthalpy and free energy, and it is not perfectly certain[18] that ΔG and the concomitant ΔS are sharply defined for Eq. (3) though the constant of Eq. (4) in the latter case may be closer to 4.4 eV. The main component of the reluctance to add a constant to E^0 in Eq. (4) is the familiarity with electrode potentials, where the reduced form is a metal or a solid stoichiometric compound. In the two latter cases the activity is invariant with quantity of reasonably large chunks, and E^0 is used to measure the activity of aqua ions in solution and depends on the logarithm of the concentration if the activity coefficient remains constant. But we have other E^0 values where only the ratio between activities (concentrations) of the reduced and the oxidized species counts, such as in Table I. The various examples in Table I are mostly situated in the interval between $I_1 = 5.392$ eV for the lithium atom and 4.177 eV for the rubidium atom, and they are all lower than $I_1 = 7.87$ eV for iron and 5.67 eV for europium atoms. Seen from the point of view of an atomic spectroscopist, chemical oxidation processes are all confined in quite a narrow interval of I_{chem}.

It may be worthwhile noting that E^0 is a potential, given in volts in Table I, and that I_{chem} is an energy (in eV). There was a time when the term "ionization potential" prevailed in atomic spectroscopy, but the Franck experiment has only served to confirm, in a much less accurate way, the energy differences known from series limits in Eq. (1). However, Eq. (4) is only directly applicable for the removal of *one* electron. When $E^0 = +1.25$ V for oxidation of Tl(I) to Tl(III) aqua ions, we find the sum of the two I_{chem} to be 11.5 eV.

Hydration Energy Differences

There is no evident connection between the consecutive ionization energies I_n of monatomic entities (dramatically increasing as a function of increasing z) and the stability of oxidation states in compounds. As far as electrovalent compounds are concerned, Rabinowitch and Thilo[22] elaborated the idea of Berzelius that the electrostatic attraction between separated electric charges (under equal circumstances proportional to z^2, and inversely proportional to a scaling factor applied to all the internuclear distances called the Madelung potential) can, indeed, explain why all the alkaline metals form M(I), the alkaline-earths form M(II), while the only aluminum compounds known are Al(III). However, there is not even a clear-cut correlation between I_n and E^0 going from aqua ions of oxidation state $n-1$ to n. Thus it is much easier to oxidize titanium(III) than cerium(III) aqua ions in acid solution (say pH = 0) in spite of $I_4 = 43.27$ eV for Ti^{+3} but only 36.76 eV for Ce^{+3}. It is true that the two reported E^0 values of $+0.06$ V and $+1.44$ V corresponding to $I_{\text{chem}} = 4.4$ and 5.9 eV, respectively, do not represent oxidation to the unknown Ti(IV) and Ce(IV) aqua ions, but rather represent formation of an ill-defined mixture of (partly oligomeric) hydroxo complexes. However, it still remains valid that the difference between I_4 values for titanium and cerium is 7 to 8 eV larger than between the I_{chem} values.

In 1969, the writer[23] analyzed the I_{chem} for 3d and 4f group aqua ions of the type given by the first three lines of Table I. It turned out that a constant κ can be introduced for each transition group, such that

$$I_z - I_{\text{chem}} = (2z-1)\kappa \tag{5}$$

with $\kappa = 5.3$ eV for the 3d group, 4.3 eV for the 4f group, and 3.9 eV for the 5f group. Lower limits of $\kappa = 5.3$ eV can be obtained for beryllium and aluminum. If the parameter κ of *hydration energy difference* of Eq. (5) does not depend on the oxidation state, a corollary of Eq. (5) is that the *hydration energy* studied by Latimer[19] and Rosseinsky[18] of ions M^{+z} in a given group is equal to $-\kappa z^2$. The apparent lack of dependence on the ionic radius reminds one of Latimer's[19] finding that the hydration energy of halid anions is very close to the expression -14.3 eV$/2r_{\text{ion}}$ for the stabilization of an ion with the Goldschmidt ionic radius r_{ion} (in Å) by a perfect dielectric (vanishing reciprocal value of the dielectric constant) whereas cations have their ionic radii increased by 0.82 Å for some reason. Since cations shrink very little going on from $+z$ to $+z+1$, the Latimer correction may help to accept an almost invariant κ. By the way[16], κ is 5.4 eV for F^- (perhaps related to the strong hydrogen bonding to water), 3.7 eV for Cl^-, and 3.2 eV for I^-. Ahrland[24] has proposed that the *soft character* of cations as antibases (Lewis acids) as introduced by Pearson[25,26] can be described by the parameter $\sigma_A = I_{\text{chem}}/z$ for the reaction analogous to Eq. (3) where a gaseous metal atom forms the M^{+z} aqua ion and the z electrons are removed *in vacuo*. It has been further discussed[16] in what sense σ_A can be approximated by the (classical) E^0 for the metal electrode to which 4.5 eV is added, and the heat of atomization of the metal (divided by z) is subtracted. The latter quantity does not involve the hydration energy of the gaseous ion explicitly.

The physical significance of hydration energy differences has been further elaborated in the 3d-group aqua ions[9,27,28] because of interest in "ligand-field" stabilization, and in the 4f group[29] where the variation of I_3 and I_4 as a function of the number q of f electrons and perceptible effects on E^0 of M(II) and M(III) aqua ions, the photoelectron spectra of metallic elements and compounds, the $4f^{q-1}5d$ excited states of M(II), and the electron transfer spectra of M(III) and M(IV), involve related parameters. Similar arguments apply in the 5f group.[30] If Eq. (5) is applied to E^0 of europium(II) and ytterbium(II) aqua ions, it seems that $\kappa = 4.01$ and 4.33 eV increases slightly as a function of decreasing ionic radii. If the hydration energies [16,29] are equated with $-\kappa z^2$ such a variation of κ (in eV) is much more conspicuous:

$$\begin{array}{ccccc} Mg^{+2}4.98 & Ca^{+2}4.12 & Mn^{+2}4.78 & Zn^{+2}5.30 & Sr^{+2}3.75 \\ Al^{+3}5.37 & Sc^{+3}4.51 & Fe^{+3}5.04 & Ga^{+3}5.39 & Y^{+3}4.17 \end{array} \tag{6}$$

and $\kappa = 3.78$ eV for La^{+3} suggest quite a strong influence of r_{ion}. However, this cannot be the whole truth. The κ values (in eV) of 4.75 for Hg^{+2}, 4.82 for Tl^{+3}, and 3.82 for Pb^{+2} are then too large for the ionic size, and larger than 4.68 for Cd^{+2}, 4.73 for In^{+3}, and 3.37 for Ba^{+2}.

Though an uncertainty of 0.1 eV in a free energy corresponds to an equilibrium constant $K_{eq} = 50$ (in the sense $RT\ ln\ K_{eq}$) it should not be argued that I_{chem} is a sloppy concept, even if the constant 4.5 eV of Eq. (4) and other relevant quantities *cannot* be defined better than 0.1 or 0.2 eV (which is quite negligible compared with I_n of monatomic entities). It is instructive to have an overall qualitative view of relations with atomic spectra, such as Eq. (6), and any experimental quantity always has some decimal, be it the second or the sixth, where it becomes uncertain.

Photoelectron Spectra of Gaseous Molecules

The threshold of photoconductivity of dilute gases and vapors as a function of the wave number of ultraviolet photons can be used[31] for determining the first ionization energy of molecules. Around 1962, Turner[32,33] started to use *photoelectron spectra*, which are the probability distributions of electrons (as a function of their kinetic energy E_{kin}) ejected from a sample by monochromatic photons $h\nu$ (the strong helium line at 21.2 eV, the 2p→1s transition in He^+ at 40.8 eV, or the corresponding X-rays 1253.6 eV and 1486.6 eV originating in magnesium or aluminum anticathodes). The *ionization energies I* are *defined* from Einstein's equation

$$I = h\nu - E_{kin} \tag{7}$$

for the sharp maxima (*signals*) on the probability distribution curve. In simpler gaseous molecules, the vibrational (and in the case of H_2 the rotational) structure of the ionized states can be resolved using 21.2 eV photons. This technique has been very successful in verifying *penultimate MO* (molecular orbitals) for which it had been very difficult to determine I previously.

A diatomic molecule has only one internuclear distance R, and nonbonding MO give sharp signals,[32,34] whereas ionized systems, preferring a longer (or a shorter) R, coexcite vibrations (like an optical transition) following the principle of Franck and Condon. When the molecule contains N nuclei ($N \geqslant 3$), the Born-Oppenheimer factorization leaves $3N-6$ mutually independent R values, and the energy of an electronic state is a hypersurface in a $3N-5$ dimensional space. The *adiabatic I* is the energy difference between the lowest vibrational state of such a hypersurface and the vibrational ground state of the unionized system. The lowest adiabatic I value is normally accessible by Watanabe's technique.[31] The *vertical I* (this metaphor is taken from the two-dimensional potential curves of diatomic molecules) is the centre of gravity of the Franck–Condon process, conserving the relative probability of R values of the ground state. In practice the vertical I can always be determined from the signals in Eq. (7) unless there are doubts about two or more signals being superposed, whereas it can be very difficult to detect weak adiabatic origins. Thus CH_4^+ has three differing ways of distorting from a regular tetrahedron,[33] and though comparison with CD_4^+ has allowed the vibrational structure to be analyzed, it is still doubtful whether the adiabatic I is 12.51 or 12.62 eV (an additional problem is that H_2O has a very sharp and strong signal at 12.61 eV) whereas the vertical I is close to 14 eV. The other, normally behaved, signal at 23.0 eV corresponds to the penultimate MO closely similar to neon 2s having $I=48.47$ eV, whereas the broad signal (due to three degenerate, loosest bound MO) corresponds to $I=21.59$ eV for the three neon 2p orbitals. As first shown by Price, it is interesting[35] that 2s-like signals also occur at 27.7 eV in NH_3, 32.6 eV in H_2O, and 39.6 eV in HF, and even more surprising that ethane(H_3CCH_3) has two such signals at 20.3 and 23.8 eV, hydrazine(H_2NNH_2) also has signals at 24.5 and 30.0 eV, and neopentane[$C(CH_3)_4$] three signals (due to $1+3+1$ MO as demanded by group theory) at 18, 22 and 25 eV. The fascinating aspect of these MO is that both antibonding and bonding combinations are occupied. The molecules CF_4 and C_6H_6 both contain 42 electrons. Together with SF_6 they are among the rare cases where the C 1s and F 1s orbitals, as well as the 16 and 15 MO, have been full identified by symmetry types (for group theoretical reasons, there are seven different I values between 16.23 and 43.8 eV in CF_4, and ten different I values between 9.24 and 28.8 eV in benzene).

The interval spanned by the lowest vertical I of all neutral molecules studied is narrower than between cesium and helium atoms. The two nonbonding MO of HF give a sharp signal at 16.05 eV and the three loosest bound MO of SiF_4 at 16.46 eV. The π-antibonding MO of F_2 have[33] $I=15.7$ eV. On the other hand, the lowest $I=5.01$ eV occurs for the twelve-coordinate chromium(0) complex of mesitylene[$Cr(C_6H_3(CH_3)_3)_2$] and $I=5.4$ eV for the benzene complex $Cr(C_6H_6)_2$. In aqueous solution, the E^0 for oxidation to the chromium(I) complex $Cr(C_6H_6)_2^+$ is about -0.54 V and hence $I_{chem}=3.9$ eV, the cation being stabilized 1.5 eV more by hydration than the neutral molecule; this is about half the hydration energy of the iodide ion. By the same token, the lowest I of gaseous iron(II) cyclopentadienide (the ten-coordinate "ferrocene") is 6.88 eV, compared with $I_{chem}=4.9$ eV in Table I. The ligands can have a strong influence on the I values, as reviewed[36] for the octahedral chromium(0) complexes $Cr(CO)_6$ ($I=8.40$ eV) and $Cr(PF_3)_6$ ($I=9.3$ eV). There have been intense efforts of measuring and interpreting photoelectron spectra of gaseous 3d and 4d group[37-39] and 4f and 5f group[39] compounds. In agreement with Eq. (2), the d-like MO form $3d^6$ in Cr(0), $3d^8$ in Fe(0), and $3d^{10}$ in Ni(0) organometallic and PF_3 complexes. This striking contrast to the gaseous atoms may be connected[28] with 4s-like electrons being σ-antibonding on all conceivable constellations of ligating atoms.

Following pioneer work in Uppsala, commercial photoelectron spectrometers using soft X-rays from 2p→1s transitions in metallic magnesium and aluminum became available around 1970. They have been used on a large number of samples. In 1972, Berthou and the author[40] published results for 600 compounds containing 77 elements, and further work by other authors and by us has been reviewed.[35,36,41] Many physicists[42,43] have concentrated on metallic elements and alloys, and they tend to give I^* values relative to the Fermi level. Whereas the Fermi level is below -3 eV in most metals, reaching -5 eV in gold, the alkaline metals[44] have Fermi levels of around -2 eV, and hence they have about half the I_1 values of the gaseous atoms. In nonmetallic samples, it is far more interesting to know I values relative to *vacuo*, and though conceptual difficulties amount to a few tenths of an eV may be inevitable, a technique[40,41,45] has been elaborated for *charge — compensation* (the isolating samples acquiring potentials of up to $+5$ V) and the corrected values I' should be comparable to I values of gaseous molecules measured relative to *vacuo* (as for monatomic entities).

The first thought[40,46] was that the very low I_0 values of gaseous halide anions X^- would be increased[22] by the Madelung potential V_{Mad} (which can be evaluated[9,28] for spherical nonoverlapping ions as if their charges were concentrated on points at their centre), and the I_2 values of the loosest bound *n*p orbitals of alkaline M^+ would be decreased by the same V_{Mad}. This quantity can be directly calculated from the unit cell size and varies between 12.5 eV in LiF and 6.4 eV in CsI, among the alkaline-metal halides. The observed I' values[36,40] are typically 1–2 eV lower than $I_0 + V_{\mathrm{Mad}}$ for the halide, and 2–3 eV lower than $I_2 - V_{\mathrm{Mad}}$ for the cation. These systematic decreases of I' seem to be due to interatomic relaxation effects,[47] the photoelectron spectrum giving the eigenvalue of the *new* Hamiltonian valid for the ionized system. It must be noted that the Madelung description does not work for certain crystals. Thus, I' of the F 2p signals of CaF_2 occurs at 13.3 eV (close to the value in most solid electrovalent fluorides) but is calculated to be $3.4 + 15.3 = 18.7$ eV, and I' of the Ca 3p signal occurs at 30.6 eV to be compared with $50.9 - 15.3 = 35.6$ eV in a Madelung description.

The d-like orbitals in nonmetallic transition group compounds have I' values[36,40] comparable to I of gaseous molecules. Obviously, many more solid than volatile compounds can be studied, but one has to accept that the resolution is not nearly as good, and one can only detect vertical I'. Fortunately, the ionization probability[41] is much higher for d-like and f orbitals bombarded with soft X-rays, compared with 21.2 eV photons; in fact it seems impossible[39] to detect 4f signals in gaseous lanthanide compounds. One of the more unexpected results of photoelectron spectra is the "third revolution in ligand-field theory" that 3d-like orbitals of iron(III) and copper(II)[36,48,49] can have *higher I* values than the loosest bound MO mainly localized on the ligands. This creates the paradox[50] that antibonding MO apparently can show higher I than their bonding counterparts with the same symmetry type.

This unexpected behavior is the rule rather than the exception in the *lanthanides*. The origin is the very large J(4f,4f) providing a huge difference between the ionization energy and the electron affinity of the partly filled 4f shell. This characteristic is also responsible[8,9,29] for the almost invariant oxidation state M(III) of the 4f group. Said in other words, $I_4 - I_3$ is much larger than the 2κ of Eq. (5). In the metallic trivalent lanthanides,[51] the I^* of the lowest 4f signal is situated between 2.3 eV (in terbium; it is 1.9 eV in one of the modifications[52] of cerium) and 8.0 eV (in gadolinium; higher than 7.1 eV in lutetium). All of these values would be about 3 eV higher relative to *vacuo*. However, the very fact that the I^* are all positive shows that the conduction electrons do not invade the 4f shell, and $I^* = 8$ eV in gadolinium is a lower limit for the difference between ionization energy and electron affinity of the 4f shell. In the antimonides[53] MSb, all the I^*(4f) are 1 eV higher than in the metallic elements, but I^* (Sb 5p) is only 1.9–2.0 eV, having the result that the partly filled 4f shell *always* has a higher I than the filled Sb 5p shell. In oxides M_2O_3 and fluorides MF_3, I'(M 4f) and I' (X 2p) almost coincide[40] in M = Sm, Eu, Tm, and Yb, and I'(M 4f) is distinctly higher in M = Gd or Lu. It is also worthwhile to note[48] that terbium(IV) in TbO_2 and in the mixed oxide Tb_4O_7 has I'(Tb 4f) = 24 eV, higher than in HfO_2 and the highest value known for any partly filled shell. However, the most detailed result for the 4f shell is that the ionization of the ground state of $4f^q$ produces several alternative J levels of the ionized $4f^{q-1}$ giving a well-resolved structure, especially for $q = 8$–14. Cox[51,54] has calculated the probability of forming a given J level from the squared coefficients of the fractional percentage of $4f^{q-1}$ in the ground J level of $4f^q$ and finds excellent agreement with experimental intensities. The four strongest signals of $4f^7$ formed by ionization of terbium(III) allows comparison with the absorption spectrum of the isoelectronic gadolinium(III) aqua ions[55,56] or the five strongest signals of $4f^{11}$ formed by ionization of thulium(III) compared with the erbium(III) aqua ions can be used[50] for evaluating the *nephelauxetic effect* (the decrease of the parameters of interelectronic repulsion[9,29]) in the ionized state, and evidence is found for an only moderate expansion (partly by covalent bonding, decreased fractional atomic charge, etc.) of the 4f radial function compared with extrapolated SCS parameters for gaseous Tb^{+4} and Tm^{+4}. This phenomenon is particularly striking in TmSe and TmTe containing comparable amounts of $4f^{12}$ Tm(III) (accompanied by conduction electrons) and $4f^{13}$ Tm(II). The $4f^{12}$ states formed by ionization of $4f^{13}$ has the nephelauxetic ratio β as high as 0.99 whereas the $4f^{11}$ obtained from $4f^{12}$ has β

$=0.90$ suggesting a moderate radial expansion like in TmSb and in metallic thulium. Quite generally, the visible and ultraviolet absorption spectra of lanthanide compounds[56] show many of the features characterizing J levels in monatomic entities, and in particular, the nephelauxetic ratio β varies only from 0.96 for PrF_3 to 0.94 for $PrBr_3$ (relative to Pr^{+3}) to be compared with 0.94 for MnF_2 and 0.87 for $MnBr_2$ (and 0.78 for $Zn_{1-x}Mn_xSe$) relative to Mn^{+2}. Under equal circumstances, Mn(II) shows the largest β among the d-group central atoms, to be compared[9] with $\beta=0.56$ in the manganese(IV) complex MnF_6^{-2}.

Electron Transfer Spectra and Optical Electronegativities

It was already established by Fromherz before 1930 that a central atom containing an empty or partly filled shell, and being sufficiently oxidizing (i.e. high electron affinity) may provide excited states in which one (or several) reducing ligand (collectively) has lost an electron. Since the transitions may have quite high oscillator strengths (e.g. purple MnO_4^-, brown $IrCl_6^{-2}$, blue $IrBr_6^{-2}$, ...) the colors can be quite intense. We do not here discuss at length *inverted electron transfer bands*[9,57] where a reducing central atom looses an electron to a low-lying MO on the surrounding ligands. This is only known to happen with conjugated organic ligands such as bipyridine, phenanthroline, acetylacetonate (having both kinds[57] of electron transfer bands), croconate ($C_5O_5^{-2}$), etc. and has certain recent applications in utilizing solar energy.[58] Returning to conventional electron transfer bands,[59] it turned out in 1961 that one may introduce *optical electronegativities* x_{opt} and write the photon energy corresponding to the first allowed transition (with a mean deviation of 3000 cm^{-1}):

$$h\nu = 30{,}000\ \mathrm{cm}^{-1}\ [x_{opt}(X) - x_{uncorr}(M)] \tag{8}$$

The value for the central atom is uncorrected for effects of spin-pairing energy and other SCS parameters, and for the antibonding character of the d-like orbitals accepting the electron from the reducing X. With Eq. (8) it is possible to obtain Pauling values x_{opt} of 3.9 for F^-, 3.0 for Cl^-, 2.8 for Br^-, and 2.5 for I^-. When sufficient spectra are correlated, it is possible to obtain x_{opt} for other ligands, such as 3.5 for H_2O, 3.2 for SO_4^{-2}, 2.8 for N_3^-, 2.7 for acetylacetonate, and 2.6 for many RS^-. It is clear that x_{uncorr} increases with the oxidation state of the central atom, such as 2.3 for Ir(IV) and 2.7 for Ir(VI) known in IrF_6. The x_{opt} of the ligands are ionization energies (but attenuated by, colloquially speaking, the attraction[14] between the displaced electron and the hole formed in the electronic density of the ligands) whereas x_{uncorr} are much more in the

TABLE II

Ionization energies (eV)	F	Cl	Br	I
I_0	3.40	3.61	3.36	3.06
I_1	17.42	12.97	11.81	10.45
$3.7x_{\mathrm{opt}}$	14.4	11.1	10.3	9.2

nature of electron affinities, and hence related to (a vertical) I_{chem} of the central atom in an oxidation state one unit lower.

The optical electronegativities were exclusively introduced for classifying transitions in the visible and ultraviolet regions. However, using the constant 3.7 eV (=30,000 cm^{-1}) one obtains the values in eV compared with I_0 and I_1 of the halogens (see Table II). It now becomes an unexpected fact that I of the np shell of solid halides tends to be about 1 eV below $3.7x_{\mathrm{opt}}$ (though it is obvious that Eq. (8) was not intended to have a definite zero point) whereas gaseous halides tend to run about 1 eV above $3.7x_{\mathrm{opt}}$. It is noted that the Mulliken electronegativity $x_M = (I_0 + I_1)/2$ only changes by 3.8 eV from fluorine to iodine, which would demand a constant 2.7 eV rather than 3.7 eV. However, it is quite impractical to use x_M for positive species such as Na^+ or N^+ occuring in $N(CH_3)_4^+$ and the x_M of 7.17 eV for hydrogen is 0.42 eV *above* the value for iodine, in contrast to general chemical consensus. The quantum chemistry[9] behind Table II seems rather to be that iodides are rather closer to behaving as neutral iodine atoms, whereas fluorides are further removed from neutral behavior, for two complementary reasons: either the fluoride carries a considerable negative charge but I is increased by Madelung potentials, or it is more covalent but not sufficient to acquire I_1 of the fluorine atom.

Besides the numerous examples of electron transfer from reducing ligands to an oxidising central atom, other strong electron transfer bands correspond to transfer between two (more distant) atoms of metallic elements[59] or are due to an easily ionized organic molecule[60,61] (in a solvent) loosing an electron to tetracyanoethylene, I_2, $TiCl_4$, $OVCl_3$, WCl_6,... having low-lying empty MO. It has even been feasible to evaluate the trend of the variation of the (adiabatic) I from the wave number of the absorption band, which was later confirmed by photoelectron spectra of gaseous molecules. A particularly fascinating case[62] is a mixture of xenon with the yellow gas IrF_6 condensing by strong cooling to a deep purple liquid or solid. The excited state $Xe^+IrF_6^-$ corresponds to $x_{\mathrm{opt}} = 3.4$ for Xe, which is not unreasonable. By the way, $I_1/3.7$ eV for xenon is 3.3. As pointed out by Webb and Bernstein,[62] it is intriguing to look for the adiabatic origins of such electron transfer bands. When discussing the Franck–Condon principle in mixed oxides, it is customary[63] to restrict attention to the breathing mode of scaling R, but the $3N-6$ spatial variables of chromophores containing N nuclei may reserve surprises.

TABLE III

K	Orbital to be ionized	$(I_n - I_{\text{compound}})/z$
2	1s	$11.0 + 3.3z$
10	2p	$10.7 + 1.0z$
18	3p	$7.5 + 1.5z$
28	3d	$10.0 + 1.0z$
36	4p	$7.8 + 0.8z$
68	4f	$7.7 + 0.9z$

Kossel Isoelectronic Series and Inner-Shell Ionization Energies

The unperturbed character of X-ray spectra of a given element in different compounds is only a relative truth; the chemical variations in $I(nlj)$ of an inner shell (with given j value) are 8–12 eV in many elements, comparable or larger than the dissociation energies of chemical bonds. The chemical shifts of $I(nlj)$ have become far more accessible with photoelectron spectra of solids[40] and of gaseous molecules, where Jolly and Perry[64] studied 144 compounds of C, N, O, F, Si, P, S, Cl, Ge, Br, Sn, Xe, and W. Originally it was thought that the chemical shift was the sum of a linear function of the fractional atomic charge and the Madelung potential due to electric charges on the other atoms. However there is no doubt[36,47] that interatomic relaxation effects contribute a comparable amount to chemical shifts, as can most clearly be seen from the decreased I resulting from the implantation of noble gas atoms in metals, or the 3 eV decrease of I for all the inner shells by condensation of mercury atoms to the metal.

When I_n for long isoelectronic series also became available[4,6] the author[13,65] asked the question what is the difference between I_n and I of compounds having an oxidation state corresponding to the same K. Though the latter I values typically scatter some 2–5 eV between various solid and gaseous compounds, it is a conspicuous trend that this difference (in eV) *divided by the ionic charge or oxidation state* z in many cases is close to a straight line (see Table III). Other isoelectronic series, such as $K = 46$, 48, 78, and 80 (providing good candidates[16,29] for Pearson soft cations) have almost invariant $(I_n - I_{\text{compound}})/z$ values, usually close to 10 eV, and frequently a shallow function having a slightly *higher* value for $z = 1$ than for 2. Actually, the new values[66] of $I_6 = 98.6$ eV for Sb^{+5} and $I_7 = 124.0$ eV for Te^{+6} (revised from 108 and 137 eV) remove two of the major discrepancies, the new parameters being 11.4 and 12.3 eV as a smoother continuation of $K = 46$, starting with 11.2 eV for Ag(I) and going through a minimum at 10.0 eV for Cd(II) and In(III).

One way of explaining the linear functions in Table III would be the Madelung potential, but this explanation works too well[13] in the sense that the

I_6 for N^{+5} of 552.1 eV is predicted to be 5(11.0 + 5 × 3.3) = 137.5 eV higher than I(N 1s) = 417.0 eV in gaseous ONF_3 and I' = 412–412.5 eV in solid nitrates. Hence the relatively external non-1s electrons in nitrogen(V) compounds imitate the Madelung effects. Actually, gaseous N_2 shows I(N 1s) value of 409.9 eV. Because of the smaller relaxation, an isolated nitrogen atom is likely to have I(N 1s) value a few eV higher.

Conditions for Stability of Oxidation States

The elements with Z from 21 to 100 are known[9,13] to exhibit some 250–260 well-defined oxidation states in nonmetallic compounds (we do not consider catenation of closely adjacent atoms of the same element). As first pointed out by Kossel in 1916, some of the closed-shell K values such as 10, 18, 28, 36, and 46 have from 11–13 consecutive oxidation states known in chemistry, e.g. C(−IV) to Cl(VII). Though nearly all $K = 19$–100 are known in monomeric chromophores, it is rare that a K value not included in Eq. (2) corresponds to more than four or five consecutive z values.

The Madelung potential[9,22,28] and the hydration energy difference Eq. (5) were the first attempts in linking I_n of monatomic entities with the capability of a given element to occur in a definite oxidation state. More recently the photoelectron spectra have provided several other types of evidence, and it is remarkable to what extent chemistry is based on induction from facts (rather than deductions from axioms) as already seen from the periodic table.[67] The major problem is that the reducing ligands are the same ones that form strong covalent bonds and, sometimes, but not always, succeed in stabilizing high oxidation states. An extreme case is that the two best characterized iridium(V) complexes are IrF_6^- and $H_5Ir[P(C_6H_5)_3]_2$.

Though the theory of hydration energy has been applied[28,68,69] to predict the stability of oxidation states of many elements with Z above 100, a problem remains with aqua ions that they are able to deprotonate to hydroxo and oxo complexes. It cannot be construed that I_{chem} in Table I for tetroxo complexes of Ru(VI) and Ru(VII) have much to do with I_7 and I_8 of ruthenium. Actually, each type of ligand, such as O^{-2}, F^-, H_2O, CN^-, CO, and PF_3 has its own interval of oxidation states, as can be seen clearly from the chemistry of manganese or nickel. An excellent review of the complementary, and to a certain extent superficially contradictory, descriptions of chemical bonding is given by Williams.[70]

However, there is another subtle relation between monatomic entities and chemistry.[71] Organic chemists believe in diamagnetic (S zero) behavior as normal, and they call species with positive S "free radicals" in spite of O_2 having a triplet ($S = 1$) ground state. On the other hand, in agreement with the rules of Hund,[3] partly filled shells are frequently most stable with the *highest possible* S value. Like gaseous Mn^{+2} and Fe^{+3} having ground states belonging to $[18]3d^5$, *most* Mn(II) and Fe(III) compounds have $S = 5/2$ and *all* europium(II), gadolinium(III), and terbium(IV) compounds[29,56] have $S = 7/2$. Whereas L(and J) only remain reasonably good quantum numbers in the 4f group, but not usually in the d groups,[28] it is not generally recognized that Russell–Saunders coupling is a good approximation to the ground state of almost every compound admitting a definite S. This brings us to the general question[72] of whether *total symmetry* (including S zero) is an advantage or not for the stability of a many fermion system. The situation is already ambiguous in monatomic entities[13] where the closed shells of Eq. (2) do have vanishing S, but where even ^1S states are among the highest levels of a partly filled *nl* shell containing an even number of electrons. The trivial argument that if a configuration comprises several energy levels, then the lowest has lower energy than the barycentre[9] has verifiable consequences in the 4f group.[29] Nuclei "containing" simultaneously an even number of protons (even Z) and an even number of neutrons have totally symmetric ground states, and when predicting the chemical properties[72] of systems containing *unsaturated quarks*, it is interesting to note that the scarcity (if not the nonexistence) of such systems illustrates an increasing tendency toward ground states of total symmetry in the deeper stratifications of matter.

CHRISTIAN K. JORGENSEN
Département de Chimie Minérale, Analytique et Appliquée,
Université de Genève
CH1211, Geneva 4, Switzerland

References

1. E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra*, 2nd edn. (Cambridge University Press, Cambridge, 1953).
2. A. Fowler, *Report on Series in Line Spectra* (Fleetway Press, London, 1922).
3. F. Hund, *Linienspektren und Periodisches System der Elemente* (Julius Springer, Berlin, 1927).
4. C. E. Moore, *Atomic Energy Levels*, Nat. Bur. Stand. Circular No. 467, **1** (1949); *ibid.*, **2** (1952); *ibid.*, **3** (1958).
5. W. C. Martin, R. Zalubas and L. Hagan, *Atomic Energy Levels — The Rare-Earth Elements*, NSRDS-NBS **60** (1978).
6. C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra*, NSRDS-NBS **34** (1970).
7. V. Kaufman and J. Sugar, J. Opt. Soc. Am. **66**, 1019 (1976).
8. C. K. Jørgensen, Angew. Chem. Int. Ed. **12**, 12 (1973); Angew. Chem. German Ed. **85**, 1 (1973).
9. C. K. Jørgensen, *Oxidation Numbers and Oxidation States* (Springer Verlag, Berlin, 1969).
10. J. Sugar and V. Kaufman, Phys. Rev. A **12**, 994 (1975).

11. R. D. Cowan, Nucl. Instrum. Methods **110**, 173 (1973).
12. J. Linderberg, Phys. Rev. **121**, 816 (1961).
13. C. K. Jørgensen, Adv. Quant. Chem. **11**, 51 (1978).
14. C. K. Jørgensen, *Orbitals in Atoms and Molecules* (Academic Press, London, 1962).
15. A. W. Adamson, *Textbook of Physical Chemistry* (Academic Press, New York, 1973).
16. C. K. Jørgensen, Top. Curr. Chem. **56**, 1 (1975).
17. J. J. Salzmann and C. K. Jørgensen, Helv. Chim. Acta **51**, 1276 (1968).
18. D. R. Rosseinsky, Chem. Rev. **65**, 467 (1965).
19. W. M. Latimer, J. Chem. Phys. **23**, 90 (1955).
20. P. A. Giguère, J. Chem. Educ. **56**, 571 (1979).
21. P. A. Giguère, Chem. Phys. Lett. **41**, 598 (1976).
22. E. Rabinowitch and E. Thilo, *Periodisches System, Geschichte und Theorie* (Ferdinand Enke, Stuttgart, 1930).
23. C. K. Jørgensen, Chimia (Zürich) **23**, 292 (1969).
24. S. Ahrland, Struct. Bond. **5**, 118 (1968); *ibid.* **15**, 167 (1973).
25. R. G. Pearson, J. Am. Chem. Soc. **85**, 3533 (1963).
26. R. G. Pearson, J. Chem. Educ. **45**, 581; *ibid.* 643 (1968).
27. C. K. Jørgensen, Acta Chem. Scand. **10**, 1505 (1956).
28. C. K. Jørgensen, *Modern Aspects of Ligand Field Theory*, (North-Holland Publishing Co., Amsterdam, 1971).
29. C. K. Jørgensen, *Handbook on the Physics and Chemistry of Rare Earths*, ed. by K. A. Gschneidner and L. Eyring, Vol. 3, North-Holland Publishing Co., Amsterdam, 1979) p. 111.
30. L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, J. Phys. Chem. **77**, 1528 (1973).
31. K. Watanabe, J. Chem. Phys. **26**, 542 (1957).
32. D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley–Interscience, London, 1970).
33. J. W. Rabalais, *Principles of Ultraviolet Photoelectron Spectroscopy* (Wiley–Interscience, New York, 1977).
34. H. Bock, Angew. Chem. Int. Ed. **16**, 613 (1977); *ibid.* Angew Chem., German Ed. **89**, 631 (1977).
35. C. K. Jørgensen, Struct. Bond. **30**, 141 (1976).
36. C. K. Jørgensen, Struct. Bond. **24**, 1 (1975).
37. C. Furlani and C. Cauletti, Struct. Bond. **35**, 119 (1978).
38. A. H. Cowley, Prog. Inorg. Chem. **26**, 46 (1979).
39. J. C. Green, Struct. Bond. **43**, 37 (1981).
40. C. K. Jørgensen and H. Berthou, Mat. fys. Medd. Dan. Vid. Selskab **38**, no. 15 (1972).
41. C. K. Jørgensen, Fresenius Z. analyt. Chem. **288**, 161 (1977).
42. R. E. Watson and M. L. Perlman, Struct. Bond. **24**, 83 (1975).
43. J. C. Fuggle and N. Mårtensson, J. Electron Spectr. **21**, 275 (1980).
44. R. T. Poole, Chem. Phys. Lett. **42**, 151 (1976).
45. C. K. Jørgensen and H. Berthou, Chem. Phys. Lett. **31**, 416 (1975).
46. P. H. Citrin and T. D. Thomas, J. Chem. Phys. **57**, 4446 (1972).
47. C. K. Jørgensen, Adv. Quant. Chem. **8**, 137 (1974).
48. C. K. Jørgensen, Chimia (Zürich) **27**, 203 (1973); *ibid.* **28**, 6 (1974); *ibid.* **29**, 53 (1975).
49. R. Ferreira, Struct. Bond. **31**, 1 (1976).
50. C. K. Jørgensen, Struct. Bond. **22**, 49 (1975).
51. P. A. Cox, Y. Baer and C. K. Jørgensen, Chem. Phys. Lett. **22**, 433 (1973).
52. A. Platau and S. E. Karlsson, Phys. Rev. **B18**, 3820 (1978).
53. M. Campagna, G. K. Wertheim and E. Bucher, Struct. Bond. **30**, 99 (1976).
54. P. A. Cox, Struct. Bond. **24**, 59 (1975).
55. W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4412 (1968); *ibid.* **49**, 4424 (1968); *ibid.* **49**, 4443; *ibid.* **49**, 4447; *ibid.* **49**, 4450 (1968).
56. R. Reisfeld and C. K. Jørgensen, *Lasers and Excited States of Rare Earths* (Springer Verlag, Berlin, 1977).
57. C. K. Jørgensen, Acta Chem. Scand. **16**, 2406 (1962).

58. J. Kiwi, K. Kalyanasundaram and M. Grätzel, Struct. Bond., in press.
59. C. K. Jørgensen, Prog. Inorg. Chem. **12**, 101 (1970).
60. L. E. Orgel, Quart. Rev. **8**, 422 (1954).
61. H. H. Perkampus, *Wechselwirkung von π-Elektronensystemen mit Metallhalogeniden* (Springer Verlag, Berlin, 1973).
62. J. D. Webb and E. R. Bernstein, J. Am. Chem. Soc. **100**, 483 (1978).
63. G. Blasse, Struct. Bond. **26**, 43 (1976); *ibid.* **42**, 1 (1980).
64. W. L. Jolly and W. B. Perry, Inorg. Chem. **13**, 2686 (1974).
65. C. K. Jørgensen, Chimia (Zürich) **30**, 490 (1976).
66. T. A. M. van Kleef and Y. N. Joshi, J. Opt. Soc. Am. **69**, 132 (1979).
67. C. K. Jørgensen, J. chim. physique **76**, 630 (1979).
68. R. A. Penneman and J. B. Mann, *Proceedings of the Moscow Symposium on the Chemistry of Transition Elements, 1972*, ed. by V. I. Spitsyn and J. J. Katz (Pergamon Press, Oxford, 1976) p. 257.
69. C. K. Jørgensen, *Lanthanides and Elements from Thorium to 184* (Academic Press, London), in preparation.
70. A. F. Williams, *A. Theoretical Approach to Inorganic Chemistry* (Springer Verlag, Berlin, 1979).
71. C. K. Jørgensen, Israel J. Chem. **19**, 174 (1980).
72. C. K. Jørgensen, Struct. Bond. **34**, 19 (1978); *ibid.* **43**, 1 (1981).