Chemical Effects on Photo-electron Spectra—Hopes, Deceptions and Surprises 1971–74*

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Summary

The chemical shift on the ionization energy *I* of inner shells depends to a great extent on interatomic relaxation (in particular in metallic samples and in salts of Pearson-soft anions) and not only on fractional atomic charges and the Madelung potential. The limited, rather specific use for semi-quantitative analysis and the consequences of the Copenhagen principle of final states are discussed, with emphasis on thulium and its compounds.

Seen from the point of view of the chemist, the most amazing aspect of the ionization energy *I* of a given inner shell *nl* is that it frequently changes 5 eV (= 115 kcal/mole) from one compound to another of the same element, slightly more than the strongest single bond dissociation energies. However, the total electronic energy of an atom is the sum of the *consecutive* ionization energies, which is larger than the sum of one-shot *I* for each electron because the interelectronic repulsion has been counted twice in the latter case. It can be shown[1] that a variation of the outer shells (or the adjunction of an external Madelung potential) to the first approximation changes *I* of all the inner shells to the same extent, but these chemical shifts do not contribute to the total energy.

Since the removal of an outer electron with $\langle r^{-1} \rangle$ measured in reciprocal bohr units to a good approximation[2] increases *I* of all inner shells (slightly less than) 27.2 eV times $\langle r^{-1} \rangle$ the oldest interpretation of chemical shifts is a variation with the *oxidation state*[3] though it was already pointed out[4] in 1968 that the Madelung potential makes a significant contribution. This V_{Mad} is positive (for electrons) on cation sites and negative (increasing *I*) on anion sites and varies in the alkaline halides[5, 6] from 12.5 eV in LiF to 6.4 eV in CsI. The numerical value is 15.3 eV in CaF_2 if this compound is fully ionic. However, electrovalent halides are somewhat atypical in this respect, and it was soon suggested[7] that the chemical shift is determined by the *fractional atomic charges* combined with the Madelung (interatomic Coulomb) potential. The influence of the ligating neighbour atoms modifying an exclusive dependence on the oxidation states is particularly clear-cut in gaseous molecules (free of the problems of charging effects on non-conducting solid samples). Thus, *I*(S2p) in gaseous[7, 91] sulphur compounds is in eV

$$SF_6\ 180.4;\ SF_4\ 177.6;\ SO_2F_2\ 177.5;\ SO_3\ 176.5;\ SOF_2\ 176.2;\ SO_2\ 174.8;\ SCO\ 170.6;\ H_2S\ 170.2;\ CS_2\ 169.8;\ S(CH_3)_2\ 168.9 \tag{1}$$

It is clear that sulphur (VI) fluoride has a considerably higher *I* than solid sulphates distributed between 175 and 173 eV after correction for charging effects[8] to be compared with sulphides between 167 and 168 eV. The chemical shift between fluoro and oxo complexes of the same oxidation state z (which is close[9] to z eV except for smaller values in cadmium and mercury) is also exemplified for sulphur (IV) in eq. (1). An impressive effect of the ligands is observed[10] on *I*(B1*s*) in gaseous boron compounds:

$$BF_3\ 202.8;\ BCl_3\ 199.8;\ BBr_3\ 199.0;\ BI_3\ 197.8\ B(OCH_3)_3\ 197.8;\ B(OC_2H_5)_3\ 197.6;\ B(C_2H_5)_3\ 195.5\ B_2H_6\ 196.5;\ H_3BN(C_2H_5)_3\ 193.2 \tag{2}$$

Inversions of *I* values as a function of z are known[5, 8] from Tl_2O_3 having lower *I* than all thallium (I) and PbO_2 lower *I* than all lead (II) compounds measured. Most cobalt (III) complexes also have lower *I* than cobalt (II). These observations would be compatible with estimates of fractional atomic charges obtained, for instance, from the nephelauxetic effect (the decrease of the parameters of interelectronic repulsion in compounds containing a partly filled shell relative to the corresponding gaseous ion) where values between +1 and +2 usually are obtained[3, 11, 12] for d group complexes. However, it is now established that the chemical shift cannot be completely explained by a variation of a generalized Hartree potential (the sum of the central field $U(r)$ and V_{Mad}).

The strongest experimental evidence for such discrepancies is the behaviour of neon, argon, krypton and xenon atoms incorporated in metallic copper, silver and gold by ion bombardment.[13, 14] In all cases, *I* are decreased between 2.2 and 4.0 eV relative to the noble gases. This decrease seems to be more a function of the atomic volume than of the electric polarizability since it is larger for neon than for xenon, and it can hardly be argued that the atoms acquire a negative fractional charge in the coinage metals. Rather, *I* is decreased because the conduction electrons screen the positive charge of the neon or xenon atom (lacking an electron in an inner shell) to some extent. This effect of metallic

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bonding has been confirmed for gaseous mercury atoms[15] having $I(\mathrm{Hg}\,4f_{7/2})$ = 107.1 eV to be compared with I^* (relative to the Fermi level) of metallic mercury reported[16] to be 99.2 eV and found in Geneva (for mercury adsorbed on electrically connected gold surfaces) to be close to 99.4 eV whereas less than monolayers of mercury atoms on gold[17] have I^* = 99.6 eV for Hg and 83.7 eV for Au. Though the Fermi level is not quite easy to estimate, I of the metal is probably close to 104 eV corresponding to a chemical shift − 3 eV by the condensation of the atoms.

In isolated atoms, the *intra-atomic relaxation energy* is the decrease of I relative to the behaviour of the Hartree-Fock functions (the other orbitals remaining "frozen" during the ionization process) described by Koopmans. This decrease can be ascribed, in the first approximation, to the adaptation (in a single atom: contraction of the radial functions) of the electronic density, though a small, opposite contribution to the relaxation energy comes from the correlation energy[1] normally slightly less negative in the ionized system than in the neutral groundstate. It is an empirical fact[18] that for inner shells with I between 100 and 2000 eV the intra-atomic relaxation energy is close to 0.8 eV times the *square-root* of I in eV, hence increasing from 8 to 36 eV in the interval given. A major question when predicting chemical shifts is the *interatomic* relaxation energy, discussed by Shirley.[19] Detailed "frozen" and "relaxed" M.O. calculations[20] on di- to penta-atomic molecules show relaxation energies varying from 11.7 to 15.2 eV for carbon 1s, 16.7 to 19.2 eV for nitrogen 1s, and between 19.3 and 22.3 eV for oxygen 1s. The somewhat erratic variation (probably between 2 and 5 eV) of the interatomic relaxation energy constitutes a significant and rather unpredictable contribution to the chemical shift. It is not probable that the condensation of such molecules to solids introduces additional relaxation energy exceeding 1 eV. An argument is the weak variation[21] of $I(\mathrm{C}\,1s)$ from methane 290.8, ethylene 290.7, ethane 290.6 to larger (gaseous) hydrocarbon molecules such as benzene 290.4 and cyclo-hexane 290.3 eV. We argue[5, 8, 22] that solid hydrocarbons have I close to 290 eV.

A rather pure case of chemical shifts consisting of interatomic relaxation energy is $I(\mathrm{K}\,2p_{3/2})$ measured[8] of some 60 potassium (I) salts. It is astonishing to what extent the I values not corrected for charging effects[23] show the same order as the anions arranged according to hard and soft character in the classification by Pearson[24, 25, 26] with the notable exception of iodide. It is true that for the 28 potassium salts[8] for which a reliable correction for charging effects can be performed, the correlation is less impressive, but the nine compounds having I' above 298.5 eV (KBF_4, KPF_6, K_3RhF_6, K_2SiF_6, K_2GeF_6, K_4BiI_7, K_2BeF_4, K_2NbF_7 and K_2HfF_6) all contain fluoro-complexes with one exception. I' for KBr, KF, KI and KCl are scattered between 298.3 and 297.8 eV, and KSeCN has 296.5 eV. This variation of almost 3 eV in I' can hardly be ascribed to fractional atomic charges well below + 1, and it most definitely cannot be ascribed to variations of V_{Mad} which should produce the highest I for the large anions though $K_2Pt(SeCN)_6$ has I' = 297.7 eV. It may also be noted that I = 298.4 eV for $KB(C_6H_5)_4$ is a lower limit to I' but probably quite close. The physical mechanisms of chemical softness have recently been discussed[27]. A major contribution may come from continuum effects[28] but is not directly connected with the electric polarizabilities as known[29] from the approximately additive contributions of the atomic constituents to the molar refractivities. However, it may be noted that Berggren[30] recently has revived the Herzfeld description of metals as materials having the molar refractivity (cm^3/mole) equal to the molar volume. It is characteristic[27, 28] for soft central atoms to deviate (fluxionally or statically) from the highest symmetry conceivable, as known from linear mercury (II), non-centrosymmetric lead (II) and not exactly quadratic copper (II), palladium (II), tellurium (IV) and gold (III) complexes with pronounced *trans*-influence of soft ligands (including hydride and carbanions).

The realization that chemical shifts are determined by interatomic relaxation energies comparable to the variation of the Hartree potential [with exception of 4*f* group compounds[4, 8, 31] showing large shifts above 10 eV going from Eu(II) to Eu(III) or from Tb(III) to Tb(IV)] makes the determination of I values somewhat unproductive for chemical purposes, however much they may be interesting as quantum-mechanical data. Nevertheless, the I difference between highly non-equivalent atoms of the same element remains interesting, and is not affected by corrections for charging effects. The classical example of the two S2*p* signals separated by 6.0 eV in thiosulphate is modified[8] to 5.5 eV in the sodium salt (of which the crystal structure has been determined[32]) and to 5.3 eV in the $Co(NH_3)_6^{+3}$ salt of the gold (I) complex $Au(S_2O_3)_2^{-3}$ to be compared with 4.3 eV in the tetrathionate $K_2O_3SSSSO_3$ showing that the influence of the S—S bond is thrice as strong as of the Au—S bond. Comparable studies of non-equivalent nitrogen atoms[33, 34, 35] and of $SbCl_6^{-3}$ and $SbCl_6^-$ in[36] dark blue $Cs_4(SbCl_6)_2$ show related effects. It is interesting to note that the one-sided half-width δ of the photo-electron signals is not much larger in many non-conducting samples than in metals showing that dispersion of charging effects and the occurrence of mildly non-equivalent atoms usually is of minor practical importance in spite of V_{Mad} expected to differ strongly in the outermost atomic layers. The combined line-width and instrumental resolution contributions to δ is close to 0.6 eV in good photo-electron spectrometers operating under favourable conditions, unless a monochromatic device is included, as is true for the Hewlett-Packard instrument and for a home-made apparatus in Uppsala[15] where δ down to 0.3 eV can be obtained. If the ionized state has a short half-life, Lorentzian signals are observed[8, 37] with $\delta = 2.3$ eV divided with the half-life in the unit 10^{-16} sec. However, it should not be argued that all signals with δ in the range 1 to 1.5 eV are broadened because of this consequence of Heisenberg's uncertainty principle. Another, major contribution to δ comes from the coexcitation of a vibrational continuum according to Franck and Condon, since the internuclear distances are not modified from their groundstate distribution during the exceedingly rapid ionization process. Franck-Condon vibronic broadening has recently been recognized by several authors.[38, 39, 40] Under high resolution, vibrational structure with three equidistant components separated by the C—H stretching frequency 0.43 eV can be detected[40] in the C 1s signal of methane. This additional source of structure would make it difficult to determine the slightly lower I(C 1s) of the central atom than of the four terminal atoms in neopentane $C(CH_3)_4$ though a comparison of rather different quantum-mechanical models shows a common trend of charge separation in aliphatic hydrocarbons (excluding cyclopropane) which can be determined in a very simplified hypothesis[41]. When it is argued[42] that the chemical shift from neopentane to methane is only 0.4 eV but 1.3 eV for M=Si and Ge between $M(CH_3)_4$ and MH_4 because of covalent bonding involving silicon 3d or germanium 4d orbitals, an attractive alternative[18] is stronger interatomic relaxation in the methyl derivatives. For comparison, it may be noted that the chemical shift[42] from MH_4 to gaseous MF_4 is 10.4 eV for M=C but only 4.4 eV for M=Si and Ge.

It is interesting that certain photo-electron signals due to inner shells in d-group metals are slightly asymmetric[43, 44] with a tail toward higher I, though by no means as pronounced as for the d-like valence band[45, 46] with I below 12 eV. It was once suggested[31] that an instantaneous picture of elements such as iron, cobalt or rhodium might contain various concentrations of well-defined conditional oxidation states[3] M[0], M[I] and M[II] characterized by their number of d-like electrons on an individual atom. Though this description is appropriate for metallic lanthanide compounds discussed below, it is more probable that the asymmetry[44] is determined by the density of electrons having energies just below the Fermi level.

The major conclusion of extended studies of *charging effects* is that thin spots of metals (such as Au, Pd, Tl_2O_3, CuS) readily are isolated by non-conducting samples (and increase their I values by the positive potential V between 1 and 5 volt acquired[8] as a quasi-stationary property of the insulator) but that no reliable technique is available for connecting typical non-conducting samples to the metallic parts of the photo-electron spectrometer. Ginnard and Riggs[47] studied the effect of differing coverage of polymerized CH_2 and CF_2 by evaporated gold. Whereas many organic or other heat-unstable compounds obviously may decompose by this treatment, another difficulty[48] is the possible reaction between the gold and constituents such as cyanide or copper (II) phthalocyanine in the sample. The debate whether oil or gold is the better standard (for I values) also involves the important question whether I(C 1s) of solid hydrocarbons and $I(\mathrm{Au}4f_{7/2})$ of metallic gold always have the same difference found close[22] to 200.8 eV or between[47] 200.3 and 200.0 eV. Though the accuracy of I values of non-conductors relative to *vacuo* may not[8, 22] be better than 1 eV, the I' values obtained by correction for charge effects using the hydrocarbon from one-sided Scotch tape are indeed reproducible with an average deviation 0.2 eV.

The use of photo-electron signal intensities for *semi-quantitative analysis* is somewhat restricted in practice. Wagner[49] determined the intensity of the strongest signal of 43 elements relative to fluorine 1 s (induced by 1486.6 eV photons from an aluminium anti-cathode). This study was extended[50] to 72 elements including many weak signals, frequently 100 to 1000 times weaker than the strongest signal of a given element, and it was shown that the intensity is roughly proportional to the product of the number of electrons in the shell and its value of $\langle r^{-2} \rangle$ in the Hartree-Fock wave-functions kindly supplied by Dr. Watson. The intensities of 264 shells in 77 elements[51] using 1253.6 eV photons from a magnesium anti-cathode usually do not differ from the previous values[50] outside a factor of 1.5. It is true that the outermost 30 Å of 2 cm^2 sample under typical conditions weigh 10^{-6} g but it is difficult to detect less than one, and in less intense cases, 10 percent of a given element. This lack of sensitivity is not due to low counting rates but to the high and mildly undulating background of inelastically scattered electrons emerging from the solid. It seems that the precision is 15 percent with the high-intensity magnesium X-ray source[51] in our Varian IEE-15 apparatus, whereas it was not better than a-quarter of the relative concentrations with the aluminium source previously used.[50] The need for substantial concentrations can be circumvented by an ingenious technique invented by Hercules et al.[52] where a glass fiber disk is treated to form a superficial silicone-dithiocarbamate extracting Hg(II) and Pb(II) in extremely low concentration from aqueous solution. By the same token[53] heavy metals can be electrolyzed on the surface of a carbon electrode, and we already mentioned the adsorption of mercury vapour on gold[17]. The adsorption of NH_4^+, Rb^+ and Cs^+ on $Zr(HPO_4)_2$ can be studied[54] and this work is now continued by Mr. Simona on alkaline and alkaline-earth ions on hafnium phosphate, and Mr. Pitton investigates oxygen and fluorine on aluminium surfaces. It is obvious that these measurements are far less sensitive and somewhat less precise than X-ray fluorescence of heavier elements; but the latter technique is not normally performed at a resolution where highly non-equivalent atoms of the same element can be distinguished, as is true for photo-electron spectra.

Far more important than the narrow and specific analytical applications, photo-electron spectra of solids have a considerable impact on *quantum chemistry*. The *Copenhagen principle of final states*[55] has been confirmed for monatomic and oligo-atomic systems in spite of the doubts one may express[56] about systems which are so large that they cannot be reproduced as indiscernably identical entities. The final states formed by the ionization process are eigen-functions of the *new* Hamiltonian after the ejected electron has left. This statement is already related to the highly varying intensities for differing shells.[50, 51] If quantum mechanics is taken seriously, the system is like a honest gambling machine where each outcome of putting in a slug (a photon) has a definite proability though the result of an individual process has no sufficient cause in Medieval sense. Hence, the intra- and interatomic relaxation[18] takes place in the main photo-electron signals though weaker shake-up and shake-off satellites sometimes are observed[7] as alternative final states of the ionization process.

However, a more striking example of the principle of final states is the distribution of final states belonging to the configuration $4f^{q-1}$ obtained by ionizing the groundstate of the partly filled shell $4f^{q}$ in lanthanides. The corresponding photo-electron spectra are relatively simple for q at most 7 where the total spin quantum number S only is allowed to decrease half a unit, but when q is between 8 and 13, S can change by ± ½ and many different states are obtained. Cox[57, 58] demonstrated that these states are formed with a probability proportional to the square of the cœfficient of fractional parentage. It is more informative to study this problem on metallic samples with better resolved signals. It is very difficult to avoid superficial oxidation of metallic lanthanides; such work was started by Hagström[59] and continued by Baer[57, 60] now using an instrument with intrinsic half-width δ below 0.3 eV. It is possible[57, 61] to compare the distribution of $4f^{9-1}$ levels with the isoelectronic M(III) fluorides and aqua ions[1, 62] of the preceeding element M. A comparison between the photo-electron spectrum of metallic terbium with the ultraviolet absorption spectrum of gadolinium(III) compounds show that the term distances in $4f^7$ from ^8S to ^6I, ^6G and ^6H are increased 12 percent to 5.1, 7.0 and 8.0 eV from 4.5, 6.2 and 7.3 eV. The same comparison of metallic thulium with erbium (III) shows an increase of term distances in $4f^{11}$ of only 6 percent. Thus, the first and last sharp signals are separated by 5.5 eV to be compared with 5.2 eV between $^4I_{15/2}$ and $^2L_{17/2}$ in Er(III). Since gaseous Tm^{+4} is expected[3, 11] to have term distances 20 percent larger than Er^{+3} which is about 1 percent higher than Er(III) compounds, the *nephelauxetic ratio* β derived from the photo-electron spectrum of metallic thulium is $1.06/(1.20 \cdot 1.01) = 0.88$. This is not entirely unexpected because the final states having the conditional oxidation state[3] Tm[IV] are isoelectronic with thulium(IV) which is too oxidizing[63] to form any known compounds.

Campagna and Wertheim[64] have found that the metallic cubic (NaCl-type) thulium telluride TmTe has two distinct regions in the photo-electron spectrum due to the ionization of Tm[II] to $4f^{12}$ and another to Tm[III] having $4f^{11}$ final states. This can be interpreted as comparable amounts of Tm[II] and Tm[III] co-existing on an *instantaneous picture*[28] in agreement with the magnetic susceptibility intermediate between the values expected for $^2F_{7/2}$ of $4f^{13}$ and $^3H_6$ of $4f^{12}$. It is not known how much slower the hopping of an electron from $4f^{13}$ sites to $4f^{12}$ is than the time-scale of the primary photo-electron ionization process (close[8] to 10^{-17} sec.) but it is not slow enough to induce static collective distortions of the cubic symmetry of the time-average picture found by crystallography. Perhaps the most fascinating aspect of TmTe is that Tm[III] has $\beta = 0.91$ since the distance from $^4I_{15/2}$ to $^2L_{17/2}$ is 5.7 eV like it is in the isotypic antimonide TmSb (the semi-conducting MSb have a weak signal at $I^* = 2$ eV due to Sb $5p$ followed[65] by the $4f^{q-1}$ structure at I^* values 1 eV higher than in the metallic elements) whereas the term distances in the Tm[II] region, such as 4.3 eV from $^3H_6$ to $^1I_6$ belonging to $4f^{12}$ are at most 1 percent below those in the thulium(III) aqua ion[62, 66]. Hence, the nephelauxetic ratio β is at least 0.98 for the Tm[II] sites, again confirming the principle of final states. The authors at Bell[67] also studied the NaCl-type semi-conducting SmS showing a straightforward $4f^6 \rightarrow 4f^5$ samarium(II) photo-electron spectrum at low I^* values. However, when gadolinium or thorium are substituted to form $Sm_{0.82}Gd_{0.18}S$ and $Sm_{0.85}Th_{0.15}S$, the crystal structure remains cubic but the samples are metallic, and the photo-electron spectrum shows comparable concentrations of Sm[II] and Sm[III] on an instantaneous picture. One of the conclusions of such measurements is the direct evaluation of the difference between the ionization energy and electron affinity of the partly filled $4f$ shell in the *same* crystal, 7.4 eV in TmTe and 5 eV in Sm(II,III) sulphides. The theoretical estimate[68, 69] of this difference is 7 eV, somewhat smaller than $I^* = 8.0$ eV in metallic gadolinium[57] (which is a lower limit to the difference, since the conduction electrons do not invade the half-filled $4f$ shell) and 9 eV obtained[8, 70] from the difference 16 eV between $I(4f)$ of terbium (IV) and terbium(III) in Tb_4O_7 of which 7 eV is due to spin-pairing energy.

The measurements of $4f$ photo-electron signals are strongly favoured by the intensity conditions.[50] By the same token, d-like contributions in the valence region are conspicuous, as pointed out[71] for metallic ReO_3 (having a cubic structure consisting of perovskite with vacant 12-coordinated positions) and in blue[72], reduced MoO_3. The $3d^q \rightarrow 3d^{q-1}$ ionization of $3d$ group compounds[73] is influenced by ligand field effects, the final states not imitating spherical symmetry as in the $4f$ group. Sakisaka, Ishii and Sagawa[74] have used a synchrotron as a source of a continous spectrum determining the absorption spectrum between 3 and 15 eV of $3d$ group anhydrous halides, and comparing with the photo-electron spectra induced by soft X-rays.

We do not here discuss the well-resolved photo-electron spectra of gaseous molecules using 21.2 or 40.8 eV photons, as developed in the groups of Turner and Orchard; Heilbronner; and Bock[75]. As far goes closed-shell d^{10} systems, the gaseous mercury (II) compounds[76] disperse $I(\mathrm{Hg}5d)$ between 15 and 19 eV and evidence is presented for π-back-bonding in NCHgCN. It is a considerable problem for ligand field theory[70, 77] that several $3d$ and nearly all $4f$ group compounds have I of the partly filled shell higher than of the loosest bound M.O. mainly consisting of ligand electronic density, though the question of determining L.C.A.O. eigenvectors may have a satisfactory solution.[18, 61] On the other hand, the hybridization model[78, 79, 80] has been brought in considerable difficulty by the photo-electron spectra. It must be added in all fairness that the ionization of an inner shell produces a strong contribution to the local Hartree potential, and we do not strictly speaking obtain information about the groundstate, because of the principle of final states. This is particularly true for *Auger transitions.* Though ligand field effects distinguish the Auger spectra of uniaxial and cubic fluorides[81] where final $1s^2 2s^2 2p^4$ states are formed by ejection of an electron from an initially ionized state $1s 2s^2 2p^6$, the Auger spectra of metallic copper[82, 83] have final [Ar] $3d^8$ states very similar to the spherical symmetry in krypton atoms[7] (though showing a nephelauxetic effect[81] relative to gaseous Cu^{+3}) in spite of the asymmetric photo-electron signal in the valence region[45, 46] of metallic copper. Said in other words, the copper atom initially ionized in the $2p$ shell constitutes a positively charged «impurity» having its own localized $3d$ orbitals. It is interesting to speculate about how much of the dielectric screening of the metal (perfect on a long time-scale) has the time to operate in the Manne-Åberg version of final states. In this connection, it may be noted that the [Ar] $3d^8$ final states formed by an Auger transition in a gaseous zinc atom[84, 85] not less than 19 eV energy above (lower kinetic energy of the ejected electron) the corresponding states in metallic zinc. Dr. Berthou also finds larger chemical shifts of many Auger transitions in copper and silver compounds than of the I-values.

It is obvious that very little structural information about the disposition of neighbour atoms can be expected from photo-electron spectra. With exception of extreme cases such as diamond[86, 87] and graphite, there is hardly any difference observed between allomorphic modifications. There is no perceptible shift[88] of the photo-electron spectrum of V_2O_3 below and above the Mott transition temperature from semi-conducting to metallic behaviour. Solid-state physicists appreciate sputtering with rapid argon ions as a technique of cleaning surfaces, but here, metallic palladium seems to be modified[89]. Actually, one of the advantages of photo-electron spectra is that the signal intensity does not vanish in vitreous and amorphous materials compared with single crystals, though minor shifts and broadening may occur.

During the last four years, the theoretical interpretation of photo-electron spectra has gone through much of the same pattern of evolution as the theory of excited levels of transition group complexes[28] containing partly filled shells went through between 1950 and 1965. In the latter case, the experimental rapid expansion started with the availability of a convenient, reliable and fool-proofed visible and ultra-violet spectrophotometer such as Beckman DU, and the theory started from scratch, impressing uncorrupted and slightly credulous chemists with exceedingly naïve, but mathematically scaffolded explanations. Actually, there is little doubt that one frequently can extrapolate from the modifications which happened to the one-electron description in each step of "ligand field" theory[28] to the step-wise inclusion of fractional atomic charges and of relaxation effects[18] where chemists have to accept that the variation of I, the multiplet separation in intermediate coupling, and the satellites constitute interesting subjects for study by their own right. However, it is important for chemists that the penultimate M.O. now can be detected in the valence region (say I below 40 eV) and it is surprising that a linear relation[5, 55] can be established with the optical electronegativities originally derived from electron transfer spectra[1, 90] of complexes of oxidizing central atoms with reducing ligands.

Note Added in Proof. Jolly and Perry[91] recently compiled 220 I-values for inner shells of 144 gaseous compounds, with the main purpose of comparison with the model of fractional atomic charges and Madelung potentials. The variation of $I(\mathrm{W}\,4f_{7/2})$ from 37.60 eV in $W(CO)_6$ to 46.67 eV in WF_6 is impressive, though not as large as I' being 25 eV in terbium (IV) and 9 eV in Tb (III) oxides. The $I(\mathrm{F}\,1s) = 693.36$ eV in WF_6, 693.8 eV in HF, 694.04 eV in ClF, 695.2 eV in CF_4 and 696.2 eV in F_2 are 1 to 4 eV higher than the highest known I' of solid fluorides. The new $I(\mathrm{Cl}\,2p) = 206.68$ eV in ICl, 206.84 eV in CCl_4, 207.22 eV in HCl, 207.64 eV in Cl_2 and 208.21 eV in ClF show the combined effect of low ionicity and minimum relaxation in gaseous hydrogen chloride. The much lower I values of methyl, silyl and germanyl compounds are probably influenced by extensive relaxation. It is also instructive to compare the $I(\mathrm{Br}\,3d)$ in eV:

GeH_3Br: 75.65 IBr: 76.0 CH_3Br: 76.08
SiH_3Br: 76.13 $GeBr_4$: 76.24 $SiBr_4$: 76.47
CBr_4: 76.57 HBr: 77.06 Br_2: 77.10
BrF_5: 84.5 (3)

with I' situated between 73.4 and 74.2 eV for solid CsBr, RbBr, NaBr and KBr, 74.9 eV $\mathrm{Cs_2PtBr_6}$ and 79.8 eV for $\mathrm{KBrO_3}$. Both $[\mathrm{N(CH_3)_4}]\mathrm{Br}$ and $[\mathrm{Fe\,dip_3}]\mathrm{Br_2}$ have $I = 72.7$ eV. If it was meaningful to correct I' for the alkaline metal bromides with the full Madelung potential, isolated $\mathrm{Br^-}$ would be close to 66 eV. The isoelectronic krypton atom has $I = 93.80$ eV, and selenium $3d$ in $\mathrm{BaSeO_4}$ $I' = 65.6$ eV.

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