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PHOTO-ELECTRON SPECTRA INDUCED BY X-RAYS OF ABOVE 600 NON-METALLIC COMPOUNDS CONTAINING 77 ELEMENTS

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Synopsis

The chemical shift d*I* of the ionization energy *I* of the inner shells is not only dependent on the oxidation state of a given element, but also on the ligands. Even for a fixed oxidation state, d*I* has been shown to vary between 2 and 8 eV in a comparative study of all elements which are neither noble gases nor strongly radioactive. However, this conclusion is, to some extent, modified by reproducible positive potentials on non-conducting samples which have been measured between 1 and 4V in typical cases and compared with the theory for almost ionic cubic crystals and with experiments with mixtures of non-conducting powdered MgF_2, $BaSO_4$ and ThF_4 and metals such as Au, Tl_2O_3 and CuS. The widths and highly varying intensities of photo-electron signals are theoretically discussed. The d and f shells of transition and post-transition group atoms give relatively intense signals even for *I* between 8 and 30 eV since the 1486.6 eV photons most readily ionize shells with small average radii. Interesting relations can be established with electron transfer spectra and optical electronegativities.

The effects of interelectronic repulsion produce multiple signals when the groundstate has positive *S*. Special satellites occur in copper(II), lanthanum(III) and other lanthanide compounds. A systematic study is made of alkaline metal, tetra-alkylammonium, tetraphenylarsonium, methylene blue and Co $en_2Cl_2^+$ salts of several anions. The adaptation of the electronic density of the neighbour atoms in the ionized system contribute to d*I* which cannot be explained exclusively on the basis of fractional atomic charges and the Madelung potential.

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Introduction

The ionization energy I of inner shells or delocalized penultimate molecular orbitals can be determined as the difference between hν of monoenergetic photons and the kinetic energy E_{kin} of the electron ejected. Since about 1963, such measurements are performed on gaseous samples [107] using the resonance line of helium at 21.2 eV or of He^+ at 40.8 eV. This has allowed the confirmation of previous conclusions of M.O. theory, in particular for diatomic and triatomic molecules. The resolution 0.01 eV can be achieved, allowing accurate measurement of the vibrational structure, but only moderate I values can be evaluated. Photons originating in an aluminium anti-cathode have hν = 1486.6 eV (or in a magnesium anti-cathode 1253.6 eV) permitting I to be measured in a much larger interval, but the resolution obtained is not much better than 1eV. Such soft X-rays have also been used on gaseous atoms and molecules [98], but an important advantage is that also the surface of solid samples can be studied. The original instrument in Uppsala [97] and another in Berkeley [45] use magnetic deflection for determining E_{kin} whereas the commercial instruments available from at least five companies use electrostatic deflection allowing a much more compact construction. In January 1971, we received a Varian IEE-15 photo-electron spectrometer using 1486.6 eV photons. As discussed below, the values I^* recorded by the apparatus are slightly smaller (usually 2 to 5 eV) than I relative to vacuo, and under our standard conditions of 100 eV analyzer energy, I^* between 0 and 1382 eV can be measured, and the sharp peaks (not broadened for special reasons) have the sum of the half-width $\delta(-)$ toward lower I and $\delta(+)$ toward higher I between 1.9 eV and 2.0 eV. Recent reviews of X-ray induced photo-electron spectra have appeared [38, 43] and can be compared with the weak chemical effects on X-ray spectra [30].

We decided to compare a large number of non-metallic, mainly inorganic, compounds, containing all those elements which are neither noble gases nor strongly radioactive in order to facilitate future work with all kinds of related compounds. Two years ago, it was felt that one of the major applications of photo-electron spectrometry would be the distinction between non-equivalent atoms of the same element. In 1928, Stelling[100] found that the X-ray absorption edges have 8 to 11 eV higher energy in sulphur(VI) than in sulphur(– II), also in thiosulphate where the central atom has the former oxidation state and the terminal sulphur atom the latter. Actually, $S_2O_3^{-2}$ was one of the first examples of a dramatic effect of non-equivalent atoms found in Uppsala[36], and it is seen from Table 3 that the separation of the two 2p signals is 6.0 eV which is attenuated in the gold(I) thiosulphate complexes to 5.5 eV in $Na_3[Au(S_2O_3)_2]$ and 5.3 eV in $[Co(NH_3)_6][Au(S_2O_3)_2]$ having the terminal sulphur atom bound to a gold atom. The corresponding separation is 4.3 eV in tetrathionate $O_3SSSSO_3^{-2}$ having two of each kind of sulphur atoms. However, many other compounds containing mixed oxidation states[95] such as Pb_3O_4 and U_3O_8 at most show slightly broadened signals, and whereas the dark blue $Cs_4(Sb^{III}Cl_6)(Sb^{V}Cl_6)$ shows a detectable splitting 1.8 eV of the $Sb3d_{3/2}$ signal (in Table 14) this is not much compared with the range of chemical shifts 6.8 eV for antimony(V) and 3.3 eV for antimony(III) varying the ligating atoms from fluorine to sulphur. Said in other words, the chemical shift dI depends more upon the nature of the neighbour atoms than on the oxidation state of the element considered.

The main conclusion of this study of 617 samples is that a given element in the *same* oxidation state varies I of the inner shells between 2 and 8 eV (the latter, maximum interval occurs[62] for fluorine(– I), but both Mg(II), P(V), S(VI), Ni(II), Cu(II), Br(– I), Rh(III), Sb(V), La(III), Re(VII) and Pt(IV) show intervals above 5 eV). It is true that the elements able to change their oxidation state by eight units[56] such as nitrogen[41] and sulphur[77] show large ranges of dI above 10 eV. However, the separation according to oxidation state is by no means clear-cut. Thus, the perchlorates in Table 4 have their 2p signals distributed over 2.5 eV, the lower limit being 5 eV above the higher limit of the interval for chlorides which is itself 4.6 eV wide. The only exceptions to the statement of minimum interval 2 eV are Tb(III), Ho(III) and Tm(III) of which only two compounds have been studied here, and Sc(III) with three.

There was a time when it was believed that dI indicates the oxidation number though the strong influence of the Madelung potential was emphasized early[27]. This hypothesis was refuted by Kramer and Klein[70, 71] showing that I(Fe3p) of highly covalent iron(III) compounds such as $Fe(S_2CN(C_2H_5)_2)_3$ is below $Fe(CO)_5$ and salts of $Fe(H_2O)_6^{+2}$ though even larger I values are observed for the less covalent iron(III) complexes FeF_6^{-3}

and $Fe(H_2O)_6^{+3}$. One might have argued that the important variable is the fractional charge of the central atom[52], but our results show that this cannot be the whole truth. As discussed below, our 59 potassium salts cannot seriously be suspected for strong deviations from the charge + 1 of K(I), and the observed interval 4 eV of I-values varies, on the whole, in the opposite direction of the changes of the Madelung potential acting on the cation. Other conclusions of our work relate to half-widths and relative intensities of photo-electron signals and to multiple signals either due to effects of interelectronic repulsion (when the groundstate has positive total spin quantum number S) or to satellites of the kind prominent in copper(II), lanthanum(III) and the earlier lanthanides. Further on, it is of obvious interest to the chemist to obtain as much information as possible about the valence region with I below 50 eV. However, the non-conducting samples involve difficult problems of intrinsic calibration, as we shall discuss at first.

Orbital Energies Relative to the Vacuo Zero-point and Internal References

Metallic samples brought in electric contact with the apparatus do not produce serious difficulties. The instrument records the number of photo-electrons counted as a function of their kinetic energy E_{kin}, and since the work-function of the metallic copper used in the analyzer is said to be 4.6 eV, an ionization energy I^* relative to this prevailing Fermi level is indicated by the simple relation $I^* = 1482.0 \text{ eV} - E_{kin}$. Gold has a strong signal due to the eight $4f_{7/2}$ electrons (I^* has been carefully determined to be 83.8 eV in Uppsala) and is one of the few metals not showing covering oxide, hydroxide or carbonate layers. Hence, a Varian instrument like ours[113] has been used to measure the small changes from $I^* = 83.15$ eV for pure Au to 83.45 eV for the alloy $Au_{0.05}Ag_{0.95}$ and 84.5 eV in $AuAl_2$ and $AuGa_2$. All gaseous hydrocarbons (containing single, double or triple bonds, but only hydrogen and carbon bound to a given carbon atom) have I(C1s) only a few tenths eV below the value 290.8 eV for CH_4, and it was suggested[60] to use the aliphatic hydrocarbon (polymerized isoprene) on the adhesive side of one-sided scotch tape (15 mm 600 P from the 3 M company) as internal standard having $I = 290$ eV relative to vacuo and to define the scotch tape correction C_{st} as the difference between 290 eV and the lowest I^*(C1s) recorded by the instrument when a sample covers some 300° of a cylindrical surface 60° of which consists of scotch tape without sample. The purpose of this definition is to evaluate $I = I^* + C_{st}$ of all the other signals measured.

It may be noted that double-sided scotch tape (a poly-ether) or certain brands containing polyvinylchloride are not suitable, because of adjacent shoulders on the carbon signal, due to carbon atoms bound to oxygen or Cl.

Tables 1 to 19 gives the C_{st} values (without brackets) and I-values (shoulders in parentheses) for 617 compounds and other samples in order of increasing atomic number of the elements Li, Be, B, N, F, Na to Cl, K to Br, Rb to I, Cs to Nd, Sm to Bi, Th and U. For some elements, the oxidation number is given as a super-script Roman numeral for all the compounds where it is defined [56]; in some other cases, only relatively exceptional oxidation states are indicated. Table 20 gives some weak signals measured of 22 selected samples. Each sample has an identification number. Figure 1 gives typical spectra between $I = 0$ and 250 eV of compounds mainly containing elements between iodine and osmium, whereas Figure 2 gives spectra between $I = 0$ and 450 eV of compounds mainly containing elements between platinum and uranium.

There is no doubt that the I-values evaluated in this way do not correspond exactly to the ionization energies relative to vacuo. The main reason [97] is that the non-conducting sample becomes positive because it looses photoelectrons, and a quasi-stationary equilibrium is soon established where electrons come back to the sample, but in insufficient number, maintaining a potential V decreasing the kinetic energy of the ejected electrons to $E_{kin} - V$ corresponding to an apparent higher ionization energy $I = I' + V$ where I' would be the ionization energy relative to vacuo in absence of this *charging effect*. Actually, the physicists [44] at Brookhaven National Laboratory made experiments with a metallic cylinder covered with $BaSO_4$ on which thin layers of gold or palladium were evaporated. The I^* value of $Au4f_{7/2}$ of the isolated gold turned out to be 1.6 eV higher than when the gold was in electric contact with the sample holder. Further on, this difference was increased to 2.2 eV if an external potential of -1.6 V was imposed on the sample holder, whereas the difference decreased to 1.2 eV if the external potential was $+1.6$ V. It may be noted that I^* of the "connected" gold varied perfectly linearly, 82.8, 81.2 and 84.3 eV in the three cases, whereas the "isolated" gold varied less, 84.4, 83.4 and 85.5 eV in the three cases. These values are all 1eV too low in the sense that they refer to 82.8 eV derived from X-ray spectra by BEARDEN and BURR [3].

When we measured gold powder distributed in a dense way on scotch tape, two independent measurements both gave $I^* = 83.15$ eV, $C_{st} = 5.4$ eV and $I = 88.55$ eV. If the work-function of gold is 4.8 eV, $I = 88.6$ eV confirming the choice of 290.0 eV. A cylinder made from 0.2 mm thick gold plate

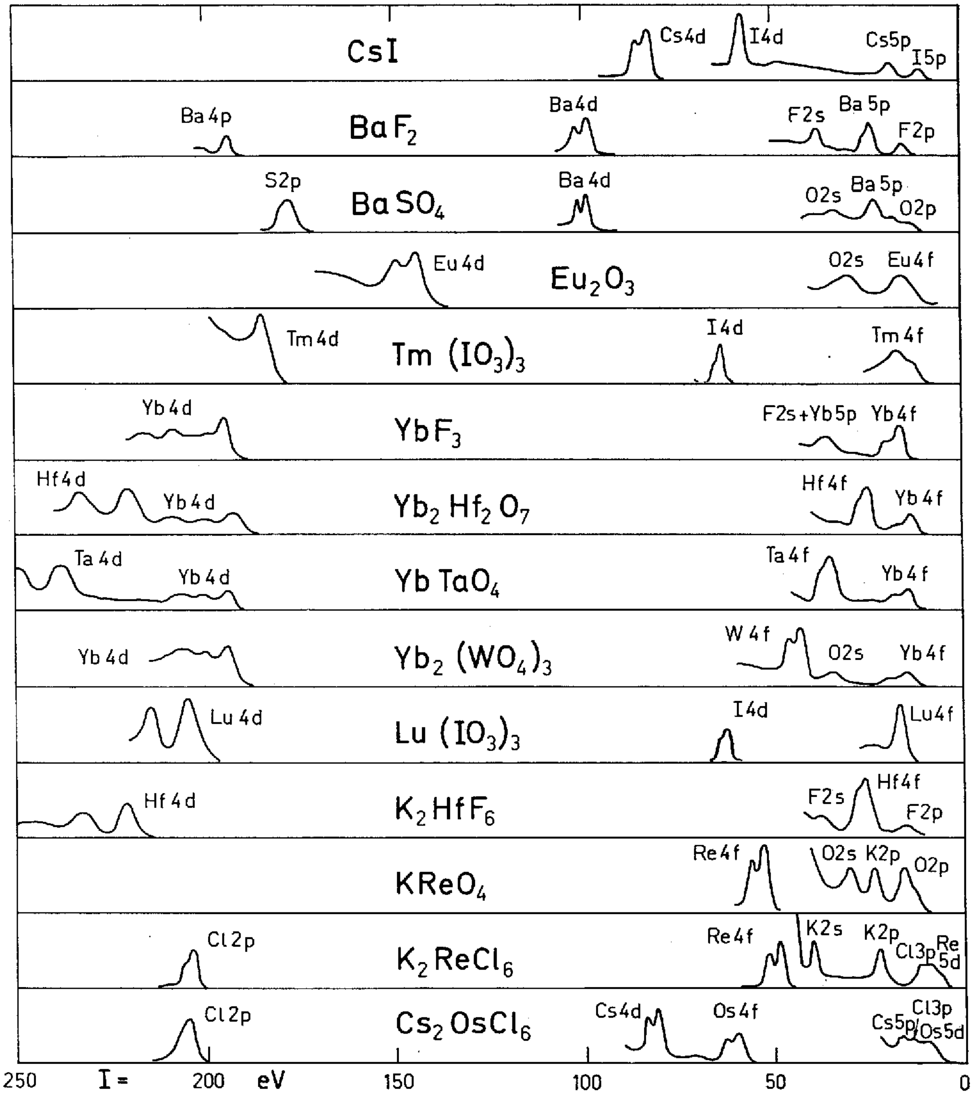

Figure 1. Photo-electron spectra of fourteen selected compounds in the region of *I* below 250 eV. The scale of intensities is not identical, and an arbitrary amount of background counts have been subtracted in each region. Elements between *Z* = 53 (iodine) and *Z* = 76 (osmium) are mainly considered.

showed $I^* = 83.75$ eV again in good agreement with the Uppsala value. A piece of scotch tape glued to this cylinder showed $I^* = 283.9$ eV but we do

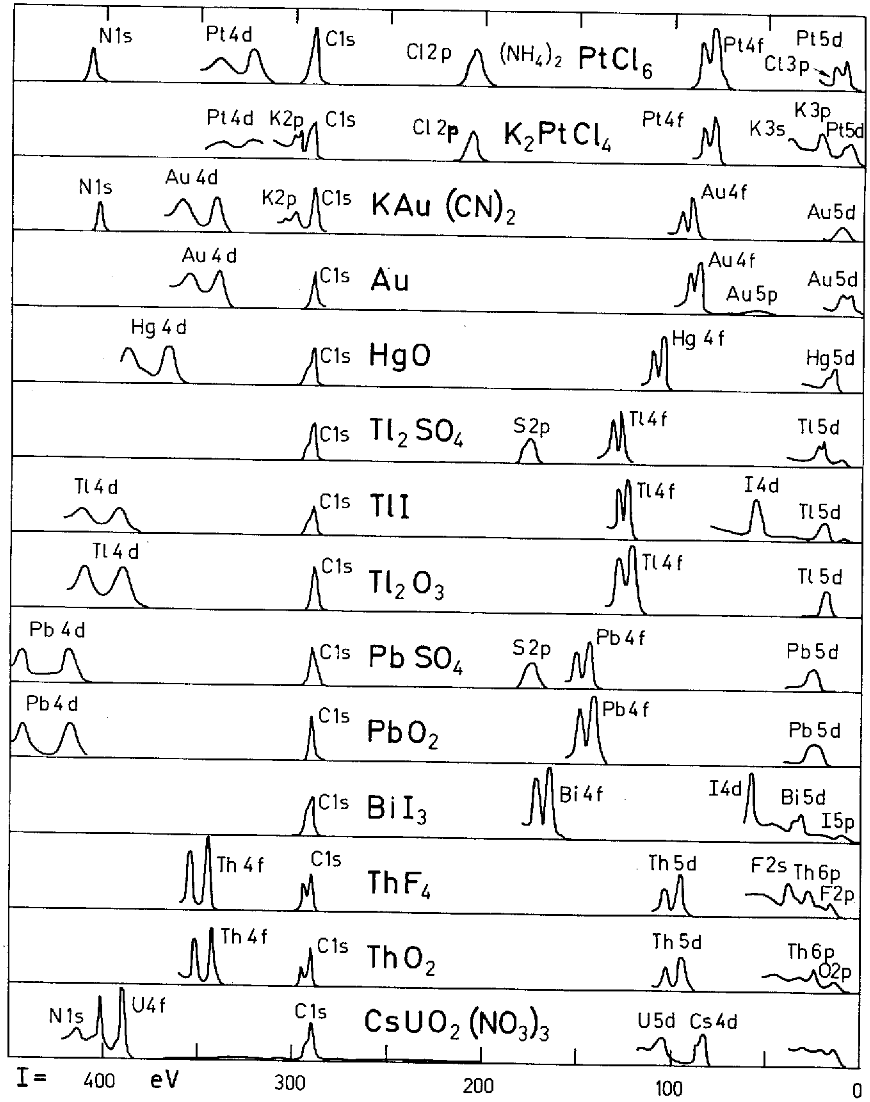

Figure 2. Photo-electron spectra of fourteen selected compounds in the region of I below 450 eV. One or two carbon 1s signals are seen, as discussed in the text. Elements between $Z = 78$ (platinum) and 92 (uranium) are mainly considered.

not ascribe physical significance to the corollary $C_{st} = 6.1$ eV. During 12 hours of continued measurements, we varied the X-ray potential from its standard value (9000 V) to 6000 V and the X-ray filament current from its standard value (70 mA) to 50 and 30 mA in various combinations in order to study the effect of varying radiation density. The number of electrons counted varied by a factor of six. The sample measured was a powdered mixture of (equimolar quantities) of 2.4 g $BaSO_4$, 3.0 g ThF_4 and 2.0 g Au on one-sided scotch tape. The two non-conducting and the metallic constituent were chosen in order to avoid mutual chemical reactions. I^*(C1s) varied from 285.25 eV at the beginning to 285.05 eV at the lowest irradiation level and back to 285.1 eV at the standard conditions. The corresponding drift of the F1s, Ba3d and Th4f signals was a decrease, at most between 0.45 and 0.75 eV, and showing a certain hysteresis in the sense that I did not return fully to the original values when the standard conditions were restored. A positive result of this experiment is that the gold powder only had a very small influence on the signals of the atoms in the isolators (it may be noted that $Th4f_{7/2}$ and $Au4d_{5/2}$ are adjacent and measured in the same region, as is also true for $Th5d_{5/2}$ and the two Au4f signals) and the I values are only marginally larger of pure $BaSO_4$ or ThF_4 on scotch tape. On the other hand, it cannot be denied that the "isolated" gold was brought in a state comparable to that described above[44], I^* varied from 86.65 to 86.25 eV during the experiment, 2.9 to 2.5 eV above the gold alone. One conclusion is that this charging effect hardly depends on the X-ray density in the interval varied here, but is induced by a much lower level of irradiation[65].

It is known from the statistical treatment of a mixture of isolating and metallic grains of comparable size that the bulk electric conductivity rather suddenly raises in a narrow interval as a function of the percentage of the metallic grains. We seem to have arrived at both sides of this interval when measuring two mixtures of magnesium(II) fluoride and thallium(III) oxide. Actually, dark brown Tl_2O_3 is a physical metal, and it was found surprising that I is some 2 to 4 eV lower than of the thallium(I) compounds (*cf.* Table 19). A mixture $6MgF_2 : 2Au : Tl_2O_3$ (having $I^*(Au4f_{7/2}) = 83.1$ eV) conserves this "metallic" situation whereas Tl_2O_3 must be isolated having I 3 eV higher in the mixture $16MgF_2 : 2Au : Tl_2O_3$ (where the gold signal has $I^* = 86.7$ eV). The effect is less dramatic on the mixture $5MgF_2 : 1CuS$ increasing I^* of the lowest copper 2p signal 2.2 eV and I 1.5 eV relative to CuS alone (*cf.* Table 8).

One might lose the hope of evaluating these charging effects increasing the apparent I-values of non-conducting samples some 2 to 4 eV relatively to "connected" metallic samples. However, there is one way out, as pointed out by BREMSER and LINNEMANN[8]. The carbon 1s signal is frequently accompanied by a shoulder or separate signal at 2 to 4 eV higher I^*. It was felt for some time that this shoulder might be due to alcohols (CH_3OH is known[98] to have I 1.9 eV higher than CH_4) either originating from residual organic solvents from the preparation of the samples, from filter paper fibers (cellulose is a poly-alcohol) or from the action of strong oxidants (such as PbO_2 or Cs_2RhCl_6) on the hydrocarbon. However, this is not too probable in *all* cases because of the variable distance of this shoulder. On the other hand, this signal is situated at I^* between 289 and 290 eV in several fluorides, at first suggesting carbonate impurities. Again, this is not plausible because an actual carbonate C1s signal has been observed at $I^* = 291.5$ eV in Li_2CO_3, 291.9 eV in the complex no. 9 discussed in the experimental section, 291.2 eV in Ag_2CO_3, 292.7 eV in $CdCO_3$, 291.9 eV in $PbCO_3$ and 292.4 eV in the salt of $Th(CO_3)_5^{-6}$. These values may be compared with $I = 297.6$ eV for[98] gaseous CO_2. As a matter of fact, the carbonates mentioned show *three* signals. A reasonable working hypothesis is that the middle signal of carbonate and the left-hand signal (highest I^*) of many other compounds are due to the adhesive hydrocarbon *on the sample* in contrast to the right-hand signal due to scotch tape without adherent sample. Correspondingly, the C_{st} columns in Tables 1–20 contain values in sharp brackets obtained as the difference between 290 eV and I^* of the left-hand signal. In the following, we call I^* plus C_{st} in sharp brackets I', and we call the difference between the two C_{st} values for ∂.

The question is now whether ∂ is a reasonable measure of the charging effects and whether I' has the physical significance of an ionization energy of an orbital in an uncharged solid relative to vacuo. One of the arguments[60] for C_{st} based on the choice of 290 eV was the good agreement with the Madelung potential V_{Mad} added to the ionization energy[4,81] of gaseous X^- and subtracted from the ionization energy[82] of gaseous M^+ or M^{+2} with exception of iodides and caesium salts having I of the loosest bound shells some 1 to 2 eV higher than excepted. Table 21 gives the new I' values. They agree definitely less well with the simple Madelung theory; thus, the 15 alkali metal halides have on the average $I'(M)$ 2.4 eV too low and $I'(X)$ 1.8 eV too low. However, MOTT and GURNEY[84] give the ionization energies 10.17 eV for NaCl, 9.49 eV for KCl and 9.00 eV for KBr in astonishing agreement with our I' values, in particular when it is realized that presently known values of the electron affinity of Cl and Br atoms are 0.15 eV lower. It may be noted that MOTT and GURNEY do not use the Madelung potential but the heats of formation of the crystal from gaseous ions (hence including a certain amount of core-core repulsion in decreased I) and they have to add contributions around 1.5 eV from electric polarizability of the groundstate.

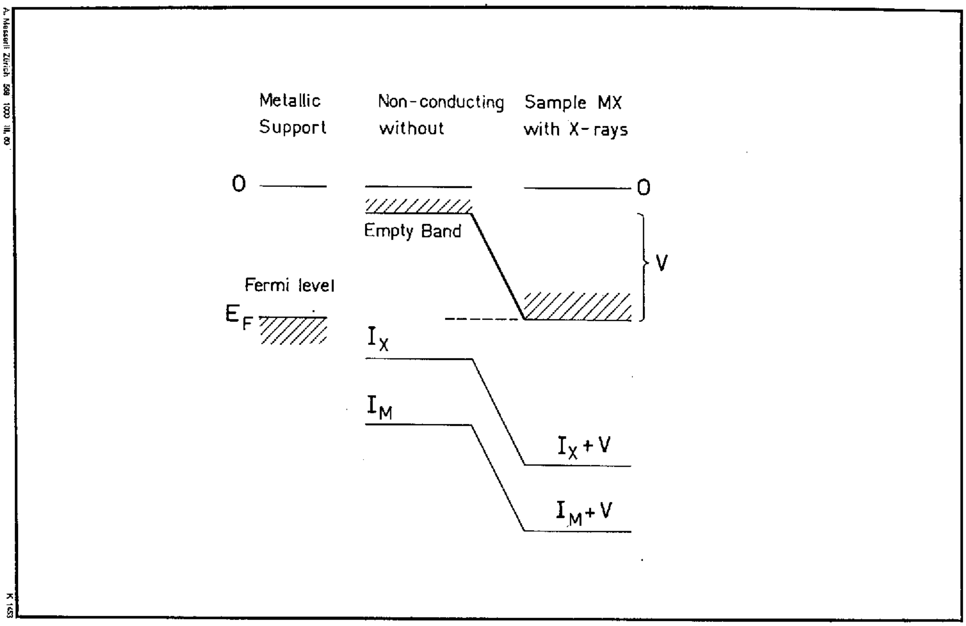

Figure 3. Explanation of almost constant positive potential V on the surface of non-metallic samples under X-ray irradiation. As discussed in the text, V can be identified with the difference ∂ between the two carbon 1s signals indicated as the difference between C_{st} and the value in sharp brackets in Tables 1–19.

One may ask the question why the charging effects remain roughly constant over a wide interval of X-ray densities, and Figure 3 suggests an explanation. All the apparent I values are the sum of the I' valid for the neutral crystal and a potential V determined by the condition that the lower limit of the empty conduction band is brought down just below the Fermi level of the adjacent metallic objects with the result that electrons can be supplied at a reasonable rate to replace the ejected photo-electrons. When identifying ∂ with V, it is easy to understand why most fluorides have large values close to 4 eV, whereas most compounds measured have V between 1 and 2 eV which are difficult to detect as distinct shoulders in the carbon 1s region. Actually, if this explanation is perfectly valid, it would be better to cover the scotch tape completely with the sample and make no attempt to observe the pure hydrocarbon. The first ten compounds measured by us (see K_2ReCl_6, K_2OsCl_6 and $KNiF_3$) were treated this way and produced low C_{st} values close to 3.7 eV. However, we doubt that this would be a very accurate technique, though it is surprising how narrow are distinct left-hand signals indicating a well-defined situation of the "isolated" hydrocarbon. Another interesting corollary is that the energy gap, the difference between the highest filled orbitals and the lower limit of the conduction band should be exactly (I – 4.8 eV) in this model. This is why the last column of Table 21 gives this quantity showing good agreement with the values obtained from absorption spectra of the crystals[54], the photo-conductivity usually setting in about 0.5 eV above the maximum of the first strong absorption band.

There is no doubt that ∂ does not represent the average energy between the top of the valence band and the bottom of the lowest conduction band, (that is half the energy gap disregarding band width) as frequently said[105] to be the Fermi level of a semi-conductor. Actually, ∂ can be larger than half the energy gap, as can be seen from the specific examples 2.7 eV for CuO, 2.4 eV for ZnS, 2.0 eV for GaS, 2.8 eV for Ag_3PO_4, 1.9 eV for AgBr, 2.6 eV for CdO, 1.5 eV for CdS and 3.4 eV for PbI_2. LANGER and VESELY[73] argue that their results (also obtained with a Varian IEE–15 spectrometer) for ZnO, ZnS, ZnSe, ZnTe, and the corresponding cadmium(II) and mercury(II) compounds are compatible with the conventional definition of the Fermi level, identifying the difference between I' and I^* with the top of the valence band plus half the energy gap[109, 110].

If we define I' by subtracting ∂ (in the cases where two carbon 1s signals have been detected) from the I-values, we reach smaller chemical shifts (roughly two-thirds as large as in Tables 1 to 20) because ∂ is particularly large for fluorides and small (and not detectable) for sulphides and many complexes of organic ligands. It is perhaps not superfluous to note that large chemical shifts are known for gaseous nitrogen compounds[31] where $I = I' =$ 417.0 eV for N1s of NOF_3, 414.2 eV NF_3, 412.5 eV for the central and 408.6 for the terminal nitrogen atom of NNO, 409.9 eV for N_2, 406.8 eV for HCN, 405.6 eV for NH_3, 405.1 eV for CH_3NH_2 and 404.7 eV for $N(CH_3)_3$. Actually, the I-values in Table 1 are 405 ± 1 eV for coordinated ammonia and ethylenediamine and 404 ± 1 eV for coordinated cyanide. These values (which do not refer to fluorides) may be rather representative and only about 1 eV above the I' values. For certain elements, the corrections with ∂ almost cancels the chemical shift. Thus, I' (Li1s) = 60.7 eV for LiF, 60.2 eV for Li_2CO_3 and 60.0 eV for Li_3PO_4 though it is probably close to 58 eV for Li_2SO_4 and $Li_3Co(CN)_6$. Again, I' (Be1s) = 120.8 eV for BeF_2, 119.6 eV for K_2BeF_4 (two independent measurements agree, like in the case of LiF), 119.3 eV for BeO, 118.5 eV for the carbonate complex no. 9 and somewhere between 117 and 118 eV for $[Be(H_2O)_4]SO_4$.

Table 22 gives I' (F1s) and I' ($K2p_{3/2}$) of 48 fluorine[62] and 29 potassium compounds. There is no doubt that the reproducibility is far better, some 0.2 eV, than the 0.7 eV we find for repeated measurements of I-values. In all fairness, it must be added that we have most frequently repeated compounds where the position of the right-hand signal of C1s was doubtful the first time, and the repetition almost always has increased the I-value. When compounds are repeated under good conditions at some months' interval, the reproducibility seems to be close to 0.4 eV. The conclusions from Table 2 and 5 are not modified strongly, essentially the same order of compounds is found, though the scale is compressed. It must be remembered that the lower I-values of potassium salts do not have known ∂ values; Table 5 probably ends with I' close to 296 eV since no metallic sample containing potassium has been measured.

It is also striking that I' of iodates varies less, and in a more regular way, than I of Table 15. Thus, I' ($I3d_{5/2}$) varies from 629.8 to 628.9 eV in the order Hf, Th, Y, In, Ni, Sm, Eu, La, Pr, Nd, Pb, UO_2, Gd, Ho, Ca, Tm, Zn, Zr, Er, Ce, Yb, Ag, Ba, Hg, Tl, K, Cu and Lu. It is also interesting to compare I' ($Th4f_{7/2}$) for eight mixed oxides (of which several are black [53] and should conduct to some extent) varying from 339.5 to 338.25 eV with the average 338.9 eV. The higher $I' = 341.8$ eV for ThF_4 and 341.0 eV for $Th(IO_3)_4$ shows that even thorium(IV) have perceptible chemical shifts. The oxidized powdered metallic thorium with $I' = 339.3$ eV and $\partial = 3.5$ eV shows that it has hardly any effect if a non-conducting sample is metallic inside. Since the 4f signals are so important for the understanding of the lanthanides, Table 23 gives I' (4f) when they can be evaluated.

Though I' undoubtedly is a better approximation to ionization energies relative to vacuo than I in the case of highly isolating samples, a few conceptual difficulties remain. For instance, it is not easy to accept the accessible hydrocarbon not covered by sample as a kind of metal, establishing its $I' = I^* + 4.8$ eV whereas the "isolated" hydrocarbon of the surface of isolating samples shows $I^* = I + \partial - 4.8$ eV. This is not an easy question to answer by experimentation in the laboratory. The propensity of establishing electric equilibrium may perhaps only develop under the X-ray irradiation. It is more difficult to understand why C_{st} in Tables 1 to 20 does not remain constant but shows systematic variations. Thus, the high C_{st} values between 5.2 and 6 eV usually develop when the sample is a metallic powder. One explanation is that the electric equilibrium is so distorted in this case that some of the photo-electrons and secondary (Auger *etc.*) electrons emitted fix on the scotch tape, much in the same way as on amber, making the surface *negative* to the extent of about 1 eV. We do not have an absolute guaranty that the parameters $C_{st} = 5.4$ eV and $I = 290.0$ eV compatible with our measurements of gold powder on scotch tape really refers to neutral hydrocarbon; it might have, for instance, $I' = 291$ eV and a potential $V = -1$ eV. On the other hand, the typical values of C_{st} around 4 eV (most frequently due to adjacent left-hand and right-hand signals) may also be explained as $V = +1$ eV on the scotch tape without coverage. It is somewhat difficult to understand why the ∂ values of caesium salts are so large in Table 21 since they are not expected to have particularly large energy gaps. As a matter of fact, the high ∂ values tend to cancel the unusually high I values of caesium salts previously discussed[60], the I' values rather being on the low side. This might be interpreted as an effect of the highly polarizable Cs^+ on the thin layer of the hydrocarbon. If this layer becomes particularly difficult to ionize, it may be that Table 21 underestimates I' of caesium salts. On the other hand, the I-values of tetraphenylarsonium and methylene blue salts of anions seem low, and of tetraphenylborates of cations. It may be that these salts have low ∂ values because the conjugated constituents readily become "metallic", that is sufficiently conducting, under the influence of X-rays. This tendency reaches its climax in copper(II) phthalocyanine combining a doubtless small ∂ with a high C_{st}.

From a practical point of view, one may ask what one can do to make I^* values measured physically more significant. We believe that this is a very difficult problem outside the cases where ∂ can be measured and where they are accepted as indicators of $I' = I^*$ plus the difference between 290 eV and I^* of the left-hand C1s signal. In mixtures, ∂ is determined by the major constituent, as seen from the values around 3 eV for gold mixed with sufficient amounts of non-conducting powders such as MgF_2, $BaSO_4$ and ThF_4. We do not believe in the beneficial effects of nets or decorations of metal attempting electric connection with non-conducting samples. An argument against this possibility is the measurement of $5MgF_2 : 1CuS$ where I^* of the lowest copper 2p signal increases 2.2 eV relative to CuS on scotch tape, I increases 1.5 eV (since C_{st} decreases from 5.5 to 4.8 eV) but ∂ is as large as 4.0 eV, a characteristic property of magnesium fluoride. It is even probable that a mixture of two non-conducting materials have their individual ∂ values, so internal standards such as admixed LiF or MgF_2 would only produce representative I values in sofar the measured compound does not have a different ∂. This attitude would bring I-values of non-conducting samples in the same systematic difficulties as activity coefficients making the mass-action law rather tautological. Thin films, say of organic compounds, on a metallic support, such as gold, probably have their I^* values changing dramatically as a function of thickness of the film. Many of these difficulties are less serious by the comparison of related compounds, but one has to worry about the extent of similar conductivity in the experiment in the sense of comparable ∂ values. The only compound found to have ∂ above 5.0 eV is LuF_3, but other closed-shell cations form fluorides lacking a positive electron affinity having high ∂ and may also increase C_{st} by pushing off electrons to the scotch tape.

The Individual Elements

A comparison of $I^*(\mathrm{Be1s})$ of BeF_2, BeO and Be is shown in the first ESCA book [97]. $I^*(\mathrm{F1s}) = 686.1$ and $I^*(\mathrm{Li1s}) = 56.9$ eV reported [39] for LiF are about 4 eV below our I' values and $I^*(\mathrm{Be1s}) = 114.2$ eV for BeO is 5 eV below. The Berkeley group [42] has made a careful study of many boron compounds showing a chemical shift 8.4 eV between $NaBF_4$ and B_4C. Certain boron compounds [9] have also been measured in connection with the use of LiF as an internal standard. We have also studied a few salts of BF_4^- and $B(C_6H_5)_4^-$ showing a chemical shift of 7 to 8 eV.

We do not here discuss carbon compounds specifically [13, 34]. Nitrogen compounds have been extensively discussed in literature [41, 97]. The spreading 3.5 eV of I-values for nitrates in Table 1 would probably be only 2 eV in I', but the order as a function of the cations would be approximately the same. It has already been noted [32] that coordinated NO shows higher I than ammonia, as seen here in the cases of $Ru(NO)Cl_5^{-2}$ and $Fe(CN)_5NO^{-2}$. A comparative study has been made (assuming $I^*(\mathrm{N1s}) = 406.9$ eV of KNO_3) of quaternary ammonium salts [47] but our measurements do not allow a clear distinction between NH_4^+ and various tetra-alkylammonium salts, and we believe that most of the spreading (above 3 eV) of I-values observed is a function of the accompanying anion. We find the lowest $I(\mathrm{N1s})$ for the nitrogen end of pseudohalogens such as CN^- and $SeCN^-$, and we do not detect any significant difference between sulphur- and nitrogen-bound thiocyanate. Coordinated azide might conceivably show three N1s signals, and actually, $Pt(N_3)_6^{-2}$ has the middle atom of each ligand producing $I = 407.7$ eV whereas the nitrogen atom bound to platinum(IV) produces a shoulder to the left of the peak at $I = 403.8$ eV due to the terminal nitrogen atom. Similar effects are observed [76] in a rhenium(II) complex of N_2, whereas rhenium(I) produces two distinct signals separated by 2.0 eV. We do not here discuss oxygen; adsorbed water and superficial hydroxo groups are a considerable problem for a significant interpretation.

Fluorine has the oxidation state F(– I) in all its compounds. It has been discussed separately[62] how the I-values of fluorides in Table 2 span 7.9 eV. The lower extreme is CsF, and its vanishing ∂ may have something to do with its highly hygroscopic nature. Quite generally, salt hydrates (frequently loosing their water very slowly even under a high vacuo[106]) and even compounds recently prepared from aqueous solution tend to show small ∂ values. Though the detectable double C1s signals only allow I'(F1s) in Table 22 to vary 4.6 eV, the inclusion of the small ∂ for RbF and assuming $\partial = 0$ in CsF extends this interval slightly, and it would be 7.2 eV when including the $I = 695.0$ eV for gaseous CF_4. The strongly hydrogen-bound ammonium salts of fluoro anions generally have lower I(and ∂) than the corresponding potassium salts.

Though the I variation of sodium(I) is 4 eV, the dependence on anions does not show a clear-cut trend except the tendency (contrary to the idea of a Madelung potential) for small anions to induce the highest I(Na1s). However, the corrected I' values do not show this trend. $I' = 1076.4$ or 1076.7 eV for NaF, 1076.8 for NaCl, 1076.9 for NaBr and 1077.4 eV for NaI (to be compared with values between 1076.8 and 1076.0 eV for the acidic selenite, stannate and antimonate) are all smaller than the minimum value 1077.5 eV for the tetraphenylborate.

We find a variation 6.5 eV of I(Mg1s) between the fluoride and the phthalocyanine. Apparently, the corresponding variation of I' values is only about 3 eV. When Mg(II) is coordinated exclusively to four, six or eight oxygen atoms[33], a variation of I can be observed which may perhaps, to the first approximation, indicate varying Mg-O distances. Photo-electron spectrometry is a *scalar* technique in the sense of the properties of a given atom not directly being influenced by the *angular* distribution of the neighbour atoms, though their electronegativity and distance have a great influence. Here, we only report two aluminium compounds, because OSCAR PITTON is working on a larger, comparative study of aluminium oxidized surfaces. The only silicate we have measured is the mineral pollucite. It is seen how I is slightly smaller than in salts of SiF_6^{-2}; I'(Si2p) is 1.8 eV lower in pollucit than in K_2SiF_6. Several silicon compounds are reported in literature[86] to have chemical shifts above 7 eV. The corresponding shift[89] between NH_4PF_6 and CrP is 8.5 eV. Most other studies of P2p signals have concentrated on phosphonium salts[102] and phosphines R_3P free[14, 83] or coordinated to platinum(II) and on R_3PO, R_3PS and R_3PSe, where the typical range of variation is 2 eV. As seen from Table 2, we find an I interval of 6.6 eV and I' cannot vary less than 5 eV. Though it can be discussed whether

PR_4^+ contains P(V), the variation $PF_6^- > PO_4^{-3} > (RO)_2PS_2^-$ occurs for the latter oxidation state.

Probably no other element has been as much studied by photo-electron spectrometry as sulphur[77, 97] Table 3 gives $I(S2p_{3/2})$ of 98 compounds. In most cases, we do not indicate the number of water molecules in sulphates in view of the fact shown by TOVBORG JENSEN[106] of slow establishment of most hydration equilibria. Thus, Madame WATELLE pointed out to us the difference between $CuSO_4$, $3H_2O$ and $CuSO_4$, $5H_2O$. Our variation 4.8 eV of the I-values of sulphates may be overestimated because of the systematically low ∂ values in hydrated crystals. Thus, I of anhydrous, almost insoluble sulphates are high, but $I'(S2p_{3/2})$ are only 173.6 eV for $SrSO_4$, 173.8 eV for $EuSO_4$ and 173.9 eV for $BaSO_4$ to be compared with $I = 180.4$ eV for gaseous SF_6 and I' between 174.1 and 174.3 eV for the hydrated sulphates of La(III), Eu(III), Gd(III) and U(IV). The lower limit of I' for sulphates seems to be close to 172 eV but is, of course, difficult to determine. Instances of highly non-equivalent sulphur atoms were discussed in the introduction. Thio-ethers R_2S fall in the wide gap between typical S(VI) and S(−II) compounds, here having I between 169.3 and 172.1 eV. Methylene blue cations contain one heterocyclic sulphur atom falling in the same category. I-values between 168.5 and 170 eV are under some suspicion for being due to superficial oxidation of the samples to elemental sulphur. Unfortunately, the charging effects prevent a reliable determination of S_8 alone. Many double sulphides and salts of tetra-thio anions were prepared by MÜLLER and DIEMANN and discussed elsewhere[85]. Both such compounds, thiocyanate complexes and [55] dithiocarbamates $R_2NCS_2^-$ and dithiophosphates $(RO)_2PS_2^-$ have their $I(S2p_{3/2})$ values in the rather narrow interval from 169 to 166.8 eV and, undoubtedly, have low (if not vanishing) ∂ values. The valence region between $I = 9$ and 30 eV of sulphate (and of related anions such as the isoelectronic perchlorate) show an interesting structure[18, 91] due to the seven sets of delocalized M.O., and we are going, separately, to discuss this aspect of our results. To the first approximation, five of these sets correspond to oxygen 2p and two sets to oxygen 2s orbitals.

There is a clear-cut gap 5 eV in Table 4 of $I(Cl2p_{3/2})$ values between perchlorates and chlorides. Like it is the case for nitrates, the total width 2.5 eV of I-values may be somewhat illusory, though ∂ for most perchlorates is small. The width 4.6 eV for chlorides must also be influenced by charging effects. Thus, $I'(2p_{3/2}) = 203.9$ eV for NaCl and 203.8 eV for $CsSbCl_6$ are larger than for RbCl(203.3) and CsCl(202.8) and there is little doubt that highly covalent chlorides such as Rb_2PtCl_6(204.3), Au_2Cl_6 and Bengal Rosa B (representing a non-volatile organic compound with C-Cl bond like the derivatives studied by Clark[13]) have even higher I'. On the other hand, ionic chlorides of large cations (such as $Ru(NH_3)_6^{+3}$) and chloro complexes with large cations have both the lowest I and I' values (the latter close to 202 eV) in agreement with the Madelung theory.

The I values of potassium are given in Table 5 and the $I'(2p_{3/2})$ in Table 22. As already discussed[62], their variation is (with the exception of the iodide) essentially a question of the hard or soft character of the anion according by Pearson. We return to this question below. We have only measured a few calcium, scandium and titanium compounds, they show familar trends. $I'(Ti2p_{3/2}) = 466.9$ eV for K_2TiF_6 and 463.5 eV for TiO_2 may be noted. Our ten vanadium compounds do not show a spectacular dependence on the oxidation state, but the sulphur-containing compound has a remarkably low set of I-values. Recently, the I values (obtained by adding 4.8 eV to I^* relative to the Fermi level of gold) of V_2O_3 have been reported as 528.8 eV for $V2p_{1/2}$, 521.3 eV for $V2p_{3/2}$, 74.8 eV for V3s, 46.7 eV for V3p and 6.0 eV for V3d, both below and above the temperature where it becomes metallic[46].

The variation of $I^*(Cr3p)$ reported by the Berkeley group[42] involved a higher limit 48.7 eV for $K_2Cr_2O_7$ and 43.5 eV for Cr_2O_3, with $Cr(CO)_6$ in the middle having $I^* = 45.8$ eV. Our results show a total width of $I(2p_{3/2})$ variation 7.3 eV and of $I(3p)$ 8.2 eV. The intervals corresponding to Cr(VI) and Cr(III) overlap slightly. With exception of the high $\partial = 3.2$ eV for $K_2[Cr(H_2O)F_5]$ these conclusions would be similar for I'. Chromium(III) is the first case of strong effects of interelectronic repulsion to be discussed in the section below.

We believe that the sets of two signals of permanganates are due to superficial reduction to Mn(IV) at lower I, and the variation of $I(Mn2p_{3/2})$ is 5.9 eV. However, the positions of signals belonging to Mn(II), Mn(III) and Mn(IV) are insufficiently different to allow safe conclusions to be drawn regarding the mixed oxides studied by Feitknecht and kindly put at our disposal. Similar comments can be made about iron(II) and iron(III) showing the overall tendency Fe(III) ($S = 5/2$) > Fe(III) ($S = 1/2$) > Fe(II) ($S = 2$) > Fe(II) ($S = 0$) but also dependent on the nature of the ligands. Kramer and Klein[70] studied the wide variation of $I^*(Fe3p)$ of iron(III) complexes, and Prussian blue (of which the idealized formula is$K[Fe(CN)_6Fe]$ containing the octahedral chromophores low-spin ($S = 0$)$Fe(II)C_6$ and high-spin ($S = 5/2$)$Fe(III)N_6$) has been studied by Leibfritz and Bremser[75] and by Wertheim and Rosencwaig[115]. Mixed cyanide complexes involving Fe, Co, Ni, Cu, Ru, Pd, Cd, Os, Ir and Pt are prepared by ANDREAS LUDI, and though some are included in the Tables here for comparison, they are going to be discussed more thoroughly by us. Other instances of mixed oxidation states are $K_{0.5}FeF_3$[10] containing equal amounts of high-spin Fe(II) and Fe(III), and the biferrocene(II, III) picrate[20] where Fe(III) has $I = 3.4$ eV higher than Fe(II). We have had difficulties of detecting individual spectra in mixed oxides. However, it is beyond doubt that Fe_3O_4 *also* contains iron(II). This is not a perfectly trivial statement, because magnetite is a physical metal at room temperature ascribed by VERWEY to rapid electron exchange between Fe(II) and Fe(III) on the octahedral sites. Our interval 5.7 eV of $I(Fe2p_{3/2})$ is only weakly affected by charging effects since ∂ of the ammonium salt no. 70 is small.

Our 42 cobalt compounds exemplify the case previously noted for Tl_2O_3 and PbO_2 compared with Tl(I) and Pb(II), *viz.* that the lower oxidation state Co(II) on the whole has *higher* I-values than Co(III). It must be admitted that $I'(2p_{3/2})$ of CoF_2 is only 787.8 eV, but only eight cobalt(III) complexes have higher I, and probably none higher I'. Thus, $Cs_3Co(CN)_6$ has $I' = 787.0$ eV, a value which might conceivably be valid for the lithium salt too, but not for the potassium and tetra-ethylammonium salts. We have precipitated many anions with the yellow $Co(NH_3)_6^{+3}$ and the green *trans*-$[Coen_2Cl_2]^+$ The interval of I-variation is 3.4 and 1.4 eV, respectively. The former interval cannot conceivably be due to charging effects alone, since ∂ is at most 1.9 eV. The acetylacetonates and the complexes of sulphur-containing ligands having strong covalent bonding according to the visible absorption spectra[55] show the lowest I-values.

It has previously been discussed[60] how high-spin ($S = 1$) nickel(II) complexes show four signals in the 2p region, whereas low-spin ($S = 0$) diamagnetic complexes show only two signals, as normally expected. We return below to this question, and here, we only consider the range of chemical shifts being 7.5 eV for the I-values of paramagnetic and 3.7 eV for $I(Ni2p_{3/2})$ of diamagnetic Ni(II). However, the former estimate is not quite realistic, since I' is known to be 862.6 eV for $KNiF_3$, 862.3 eV for NiF_2, $4H_2O$ and 860.1 eV for pale green (almost stoichiometric) NiO. Unfortunately, ∂ cannot be measured for most other nickel(II) compounds, but the lower limit of I' is below 858 eV.

The interpretation of the complicated photo-electron spectra of copper compounds is intimately connected with the satellites to be discussed below. Reliable $I'(Cu2p_{3/2})$ values are 941.1 eV for CuF_2, $2H_2O$, 938.8 eV for CuO, 938.3 eV for synthetic torbernite (no. 242), 937.8 eV for CuCN and 936.6 eV for the copper(I) iodo complex no. 60. Our seven zinc(II) compounds show a moderate variation 2.8 eV, and almost the same variation of I' occurs in view of the almost constant ∂. VESELY and LANGER[109] report a mild variation of I of all the inner shells $ZnO < ZnS \sim ZnSe > ZnTe$ within half an eV. Our five gallium compounds only vary I within 1.5 eV, including the yellow semiconductor[105] GaS having direct Ga-Ga bonds. The lowest $I'(Ga2p_{3/2}) = 1122.6$ eV for Ga_2O_3 is still 2 eV above I for metallic gallium. We may shortly note $I'(Ge2p_{3/2}) = 1226.3$ eV for K_2GeF_6 and 1225.2 eV for GeO_2. Arsenic is the last element for which an aluminium anti-cathode allows the detection of the $2p_{3/2}$ signal. Though I varies by 4.1 eV, the interval of I' is smaller since $I' = 1331.4$ eV for $LaAsO_4$, 1330.9 for $NdAsO_4$, 1331.0 for $YbAsO_4$ but 1331.6 eV for K_2HAsO_4. The ten tetraphenylarsonium salts probably have I' somewhat below 1330 eV. $I^*(As3d_{5/2})$ values between 147.6 eV for $KAsF_6$ and 140.4 eV for Zn_3As_2 have been reported[99]. These authors use $I^*(Pb4f_{7/2}) = 138.3$ eV of Pb_3O_4 as internal standard.

Selenium has attracted some interest[104] because of the close chemical analogies with sulphur. A roughly monotonic increase of I-values (to the extent of 5 eV) as a function of the oxidation state increasing from Se(−II) to Se(VI) is observed. We find also a range of I-values close to 8 eV though it must be noted that $I'(Se3p_{3/2})$ is only 171.7 eV for both measurements of $BaSeO_4$. It is expected that I of bromates are some 6 eV higher than of the corresponding bromides. Our I interval of 5 eV of 26 bromides includes, at the higher limit, caesium(I) salts (with lower I') and dibromosuccinic acid having C-Br bonds. The influence of the Madelung potential on electrovalent bromides is discussed in Table 21.

No characteristic conclusion can be drawn about the moderate variation 2.6 eV of $I(Rb3p_{3/2})$ in ten rubidium(I) salts. When the I' values are considered, it is one of the elements closest to show no chemical shifts. The same is true for strontium(II), where the observation of the $3p_{1/2}$ signal is made difficult due to the adjacent C1s signal. The I-intervals of yttrium(III) are almost 5 eV but it must be noted that $I'(Y2p_{3/2}) = 307.8$ eV for YF_3 and 307.0 eV for $Y(IO_3)_3$ probably are not much above Y_2O_3. Comparable comments can be made about zirconium(IV) and niobium(V). The actual I' intervals occurring in our compounds seem to be close to 3 eV in the three latter elements. It must be noted that the fluorides have distinctly the highest I' values.

We find a rather moderate I-variation of molybdenum(VI) compounds with the lowest values of tetrathiomolybdates[85] comparable with Mo(III). SWARTZ and HERCULES[103] report a I^* variation 1.7 eV between fifteen

Mo(VI) compounds including many heteropolymolybdates, and MoO_2aca_2 at the lower end, below $MoCl_5$ and MoO_2. These authors have succeeded in measuring I^* of freshly cleaned molybdenum, 6 eV below that of Na_2MoO_4. Comparable signal positions are found for cooled $Mo(CO)_6$.

It is rather difficult to study the 3d region of ruthenium compounds because of coincidences with the scotch tape main at $I = 290.0$ eV, with other carbon 1s signals at higher I and with the replica signal at an apparent $I = 280.2$ eV induced by the small intensity of so-called aluminium $K\alpha_3$ ($1s2s^22p^5 \rightarrow 1s^22s^22p^4$) photons (1496.4 eV) present in the X-ray source. Though the 3p signals are weaker, they are more readily identified. $I^*(3d_{5/2}) = 284.4$ eV for $BaRu^{VI}O_4$, 282.2 eV for $[Ru(NH_3)_6](BF_4)_3$, 279.8 eV for $[Ru(NH_3)_6]I_2$ and 279 eV for Ru are reported[74] in a study of the dehydrogenation product of $Ruen_3^{+2}$ forming C = N double bonds. We believe in a roughly monotonic variation with the oxidation state and accept unusually high I in the perruthenate, ascribing the shoulders at lower I to reduced species in analogy to permanganate.

K_3RhF_6 has exceptionally high I, even $I'(Rh3d_{5/2}) = 317.3$ eV is considerably larger than 314.7 eV for $Cs_2[Rh(H_2O)Cl_5]$. Probably, our dark green[48] Cs_2RhCl_6 was reduced to the latter species. Many rhodium(III) complexes of sulphur-containing ligands have I comparable to the metal, but we do not believe that they have been transformed superficially. The compound $[Rhns_3]_2\ Ni(ClO_4)_2$ supplied by WALTER SCHNEIDER has three bidentate ligands forming the chromophore *fac*-$Rh(III)N_3S_3$ but each sulphur atom forms a bridge to the central ($S = 1$) nickel atom forming octahedral $Ni(II)S_6$.

Palladium compounds have been studied[72] having $I^*(3d_{5/2}) = 340.3$ eV for K_2PdCl_6, Pd(II) varying from 339.6 eV for $Pd(CN)_2$ and 339.2 eV for $K_2Pd(CN)_4$ down to 336.6 eV for PdI_2 (the metal has 335.7 eV) stressing the dependence of I on the electronegativity of the ligating atoms though cyanide has remarkable high I as also seen in Table 13 in the case of $Pd(CN)_6^{-2}$ prepared by LUDI[79]. The range of I for Pd(II) is 2.15 eV, and metallic Pd slightly below. Our fifteen silver(I) compounds show a similar I range of 2.9 eV probably moderated to slightly above 1 eV in I'. One of the most stable silver(II) compounds, the peroxodisulphate of the tetrakis (pyridine) complex shows a lower I than Ag_2SO_4 but it seems to represent a mixture of Ag(I) and Ag(II). A weak satellite of the $Ag3d_{5/2}$ signal can be perceived, this would be an interesting analogy to Cu(II) discussed below.

The I variation 2.6 eV of cadmium(II) compounds do not follow a very clear-cut order of ligands but is compatible with the weak variation

CdO > CdS ~ CdSe reported by VESELY and LANGER[109]. Indium(III) compounds vary I to the extent 3.7 eV, the highest $I'(\mathrm{In3d_{5/2}}) = 450.8$ eV is represented by both the sulphate and the fluoro complex. Metallic indium may have been successfully measured in the sample having $I = 448.8$ eV. Among the tin(IV) compounds, Cs_2SnBr_6 has exceptionally high I but $I'(\mathrm{Sn3d_{5/2}})$ is only 492.4 and 492.6 eV in the two measurements. Metallic tin evidently was oxidized, and the lowest I is observed for tetraphenyltin, which fortunately enough was not too volatile.

The measurements of the (otherwise very strong) antimony $3d_{5/2}$ signal are sometimes difficult because of almost coinciding signals from oxygen 1s. We base our discussion on $\mathrm{Sb3d_{3/2}}$ having overlapping intervals of Sb(V) and Sb(III). The total I width of these two intervals is 6.8 eV and 3.3 eV, but as usual, ∂ of the fluoro complexes is rather large, and the I' variation of Sb(V) is between 547.7 eV for $CsSbF_6$ (still well above 545.7 eV for $CsSbCl_6$ and 545.0 eV for $NaSb(OH)_6$) and somewhat below 544 eV for Na_3SbS_4. The $I(3d_{5/2})$ range of tellurium compounds is 6.8 eV in agreement with the I^* variation between 576.8 eV for TeO_3 and 572.4 eV for Na_2Te reported by SWARTZ, WAYNE and HERCULES[104].

It was mentioned above how 28 iodates (excepting those of Co(II) and Bi(III)) vary $I'(\mathrm{I3d_{5/2}})$ within the narrow interval 629.8 to 628.9 eV. On the average, iodates have I about 4 eV and I' about 5 eV above those of the corresponding iodides. The range of I-values for iodides is rather large, 3.7 eV, including the C-I bond in Bengal Rosa B. Large cations produce low I-values (in qualitative agreement with the Madelung potential) and a low $I' = 622.0$ eV has been observed in $[N(CH_3)_4]I$. The less covalent iodides have the higher I-values, but tend, at the same time, to have larger ∂ decreasing I'. Thus, KI having $I' = 623.8$ eV and RbI 624.6 eV have a higher I' than CsI (623.3 eV) but lower than AgI (625.2 eV).

Our 34 caesium(I) salts show a spreading 4.8 eV of $I(3d_{5/2})$. Generally, the monatomic anions (and SbF_6^-) produce the high I-values, whereas the polyatomic anions (soft in the sense of PEARSON) have low I-values in analogy to potassium salts in Table 22. However, $I'(\mathrm{Cs3d_{5/2}})$ is between 728.9 and 729.1 eV for CsCl, CsBr, CsI, $CsNO_3$, $CsReO_4$ and Cs_2PtCl_6 which is a rather unexpected coincidence, whereas I' is close to 729.8 eV for $CsSbF_6$, pollucite and conceivably for the tetraphenylborate. Though $I(\mathrm{Ba3d_{5/2}})$ vary 3.5 eV in our seven barium(II) compounds, I' is close to 785 eV for the five cases where ∂ has been determined.

The 3d region of lanthanum(III) shows four signals though the closed-shell groundstate has $S = 0$. We have ascribed this unusual effect[63] to electron transfer from the neighbour atoms to the empty 4f shell of La becoming highly stabilized in the ionized system lacking a 3d electron. We return to this problem in the section on satellites. The chemical shift of I-values is 6 eV in Table 17, but the extreme values of $I'(\mathrm{La3d_{5/2}}) = 842.3$ eV for LaF_3 and 838.9 eV for La_2O_3 only differ by 3.4 eV.

Also the photo-electron spectra of cerium compounds are unexpectedly complicated. The most plausible explanation is that otherwise stable cerium(IV) compounds always contain some Ce(III) in the surface (whether due to simple reduction or to attack by the carbon dioxide of air forming carbonates) and that I of the inner shells is 16 eV higher of Ce(IV) than of Ce(III). This is a most spectacular difference from the previous elements where a change of the oxidation state by one unit do not usually produce a chemical shift above 2 eV. Actually, this shift is even larger than in the cases of europium and terbium in Table 17. The double signals of cerium(III) compounds are most probably due to effects of interelectronic repulsion, the groundstate having $S = 1/2$. However, it is not excluded that some of the signals are electron transfer satellites like in the case of La(III). Black Pr_6O_{11} should consist of a mixture of two-thirds Pr(IV) and a third Pr(III), but we observe only weak signals at approximately 15 eV higher I due to Pr(IV). As far goes Pr(III), the chemical shift are rather similar to La(III), but the 3d signals have shoulders toward *lower I*. This is a phenomenon only known from neodymium(III) compounds too, and a possible explanation has been suggested by CHRISTIANE BONNELLE that the electron transfer satellites correspond to lower energy of the ionized system than the conventional ionization process. The probability of electron transfer becomes negligible for elements heavier than Nd, the 4f shell having a much smaller average radius than the orbitals delocalized on the neighbour atoms. However, it is also conceivable that effects of interelectronic repulsion combined with strong relativistic effects (spin-orbit coupling) in the 3d shell produces an unexpected distribution of the probability of forming the many possible energy levels of $3d^94f^2$ in Pr(III) and of $3d^94f^3$ in Nd(III) (*cf.* the $4d^94f^q$ configuration treated theoretically by SUGAR [101] and compared with soft X-ray absorption spectra of 4f group metals). $I'(3d_{5/2})$ varies only slightly more than 1 eV for Nd(III). The same is true for our four samarium(III) compounds having $I' = 1088.6$ eV for SmF_3 and 1087.7 eV for Sm_2O_3.

The strong chemical shift between europium(III) and Eu(II) has been known [26, 27] since 1967. Here, our $EuSO_4$ could not be measured without some superficial Eu(III); the chemical shift is 11 eV for 3d, 9 eV for 4d and 7 eV for 4f, as discussed below. The variation of $I(3d_{5/2})$ is 2.5 eV between

EuF_3 and Eu_2O_3 and the corresponding variation of I' is 1.6 eV. The chemical shift dI is 3.6 eV between GdF_3 and Gd_2O_3 and dI' is 2.0 eV. The weakly asymmetric 3d signals of Sm(III), Eu(III) and Gd(III) can be ascribed to effects of interelectronic repulsion; there are no perceptible satellites.

Brown Tb_4O_7 should contain equal amounts of Tb(IV) and Tb(III). With exception of the 4f signal of Tb(IV), the higher oxidation state cannot be detected. Professor GEORG BRAUER was so kind as to send us a sample of fox-red TbO_2 prepared by exhaustive extraction of Tb_4O_7 with acetic acid [6]. Though the cubic unit cell parameter and chemical analysis shows a deviation from the stoichiometry TbO_2 by less than one percent, we find Tb(IV) and Tb(III) signals superposed like in the case of CeO_2. The chemical shift is 10.6 eV in the case of the 3d shell. Since we did not succeed in measuring the $3d_{5/2}$ signal of holmium, which should be on the limit of the instrument, dysprosium is the last element showing this signal. Dy_2O_3 and $DyVO_4$ differ 1.9 eV in I and 1.1 eV in I'.

Ho(III), Er(III) and Tm(III) show comparable shift in the fluoride, iodate and oxide of the very broad 4d signals[5] and of the 4f signals to be discussed below. A systematic comparison of ten ytterbium(III) compounds indicates dI of the lowest 4d signal 5.5 eV between the fluoride and the oxide and I' varies from 192.2 eV in YbF_3 to somewhere below 188 eV in Yb_2O_3. In Table 23 are given I'(Yb4f). Lutetium(III) compounds have simpler photo-electron spectra (since the closed-shell groundstate has $S = 0$). It is very important for the understanding of the 4f group that I(4d) increases 17 eV from Lu(III) to the isoelectronic Hf(IV) and I(4f) increases 9 eV. This shows that the end of the lanthanides is more a question of the oxidation state than of a definite atomic number (such as 71) and constitutes an analogy to the huge chemical shifts between Ce(III) and Ce(IV) or between Tb(III) and Tb(IV). The chemical shifts dI are 2.9 eV for $4d_{5/2}$ and 2.4 eV for $4f_{7/2}$ of hafnium(IV) compounds. As usually, the variation of I' must be somewhat smaller. The corresponding range of dI is 3.0 eV for $4d_{5/2}$ and 2.9 eV for $4f_{7/2}$ of tantalum(V) compounds. Whereas the 4f signals of the lanthanides up to Yb(III) has a structure due to the multiple levels possible of $4f^{q-1}$, the splitting of the 4f signal starting from Hf(IV) is simply due to the two j-levels $^5/_2$ and $^7/_2$ which are known to be separated 1.3 eV in ytterbium(III) compounds [50] from near infra-red spectra and 1.46 eV in gaseous Lu^{+4}.

The chemical effects on the photo-electron spectra of tungsten(VI) compounds are closely similar to those of molybdenum(VI). The I range of rhenium(VII) compounds is 6.1 eV both in the case of $4d_{5/2}$ and $4f_{7/2}$. The high I values for $CsReO_4$ and $TlReO_4$ are diminuished by $\partial = 3.1$ and 2.5 eV, respectively. As a matter of fact, the I' values of these two perrhenates are the same as of $KReO_4$ within 0.2 eV. However, even if ∂ were zero for the methylene blue and the tetraphenylarsonium perrhenates, $I'(4f)$ would be 0.5 eV lower. The four rhenium(IV) compounds studied have somewhat lower I values with $I(4f_{7/2})$ varying 1.2 eV.

It is rather difficult to study the 4d region of osmium compounds because of interference with the carbon 1s signals and their $K\alpha_3$ replica. However, we have studied $I(4f)$ of sixteen complexes, iodo-chloro-osmates (IV) kindly supplied by PREETZ and HOMBORG [61] and the double cyanides by LUDI. It is a general characteristic that ∂ is below 2 eV and cannot be measured with exception of the osmium(VIII) nitrido complex $K[OsO_3N]$. On the whole, the I increase follows the order Os(II) < Os(IV) < Os(VI) < Os(VIII) but the intervals of the oxidation states Os(II) and Os(IV) overlap strongly. Similar conclusions can be reached regarding Ir(III) and Ir(IV) where total variation of $I(4f_{7/2})$ is 3.1 eV but where the ligands (sulphurcontaining ligands < amines < Cl^- < CN^-) are of greater importance than the oxidation state. It must be added that iridium(IV) chloro and bromo complexes may loose elemental halogens in the vacuo.

Several authors have studied photo-electron spectra of platinum complexes, in particular involving bonds to carbon and to phosphorus. The Uppsala group [19] using $I^* = 285$ eV for C1s as internal standard report $I^*(Pt4f_{7/2}) = 73.4$ eV for L_2PtCl_2 and 71.7 eV for PtL_4 (where L is triphenylphosphine $P(C_6H_5)_3$) whereas the metal has 71.2 eV. CLARK, ADAMS and BRIGGS [14] study related complexes such as $I^* = 71.2$ eV for $L_2Pt(CH_3)_2$ and 72.2 eV for L_2PtCl_2 using $I^*(Au4f_{7/2}) = 84.0$ eV of gold supports as internal standard. These authors find $I^* = 284.7$ for the carbon and 71.1 eV for metallic Pt. RIGGS [94] also uses $I^* = 285$ eV as internal standard and reports $I^* = 75.9$ eV for $K_2Pt^{IV}Cl_6$, 74.0 eV for $K_2Pt^{II}(CN)_4$, 73.4 eV for $K_2Pt^{II}Cl_4$, 73.3 eV for $((C_2H_5)_3P)_2Pt^{II}Cl_2$ and 71.6 eV for Pt^0L_4 among thirteen other platinum complexes. His I^* values are about 6 eV below the I values in Table 19 suggesting charging effects of the order of magnitude 1 eV. Our I intervals for Pt(IV) 5.6 eV and for Pt(II) 1.7 eV overlap almost completely, but this is due to the hexa-iodo complexes no. 37, 114 and 358. The $I'(Pt4f_{7/2})$ are 80.4 eV for K_2PtCl_6, 80.75 eV for Rb_2PtCl_6 and 80.8 eV for Cs_2PtCl_6 suggesting a weak residual stabilization by the larger, more polarizable alkali ions, and 79.8 eV for the slightly more covalent Cs_2PtBr_6. It is probable that $I = I'$ for $(NH_4)_2PtCl_6$ and Tl_2PtCl_6 because of too little non-covered scotch tape. There is no doubt that salts of PtI_6^{-2} have lower I-values in contrast to alkaline metal iodides.

Gold is very popular because of its absence of superficial oxidation. Taken at their face value, the I-values of Table 19 suggest I of Au(III) complexes some 5.3 eV above the metal. However, because of the charging effects discussed above, the I' shift may be less than 3 eV. The salts of $AuCl_4^-$ and $AuBr_4^-$ deteriorate under the measurement perhaps more by loosing free halogen in the vacuo (and remaining as $AuCl_2^-$ and $AuBr_2^-$) than by photo-chemical decomposition. We believe the lower I values developing are due to Au(I) rather than to the metal. $K[Au(CN)_2]$ does not change its photo-electron spectrum. It is, of course, conceivable that its signals coincide with those of "isolated" metal.

Our 8 mercury(II) compounds show moderate dI within 2 eV. We were restricted in the choice by the volatility of many compounds and of the element. This may not only maintain pressures above 3.10^{-6} torr, but the vapours destroy the photomultiplier receiving the electrons. FADLEY and SHIRLEY [28] studied the valence band (I^* below 10 eV) of twelve metallic elements and also HgO, noting the separation 1. 6 eV between the two components $I^*(5d) = 13.6$ and 12.0 eV. It is not yet known whether the corresponding splitting 3.1 eV of Au also is due to spin-orbit coupling alone, or whether it is due to "ligand field" non-equivalence of two and three d-like orbitals in this cubic crystal, or finally to collective effects producing two energy bands (or at least two maxima of probability of ionization by the X-rays). The corresponding separation is far smaller in metallic silver and has not been detected in copper. The gaseous $HgCl_2$, $HgBr_2$ and HgI_2 have been studied by ELAND [25], their lowest I(5d) occurs at 16.8, 16.4 and 15.9 eV, respectively. Our I values fall in this interval, whereas the lowest I' is 14.1 eV for $Hg(IO_3)_2$ and 14.0 eV for HgO. HgF_2 behaves rather different from most fluorides and have been discussed elsewhere [67 a].

Our 21 thallium(I) compounds span an $I(4f_{7/2})$ interval of 2.8 eV. A few of the previously given values [60] have been revised when the C1s signals were better characterized. It is seen that Tl_2O_3 has I almost 3 eV *below* the average thallium(I). However, this dark brown compound (crystallizing in the cubic C-type [53] like lemon-yellow In_2O_3, white Y_2O_3 and most of the heavier rare earths) is a physical metal, and when diluted in isolating compounds such as MgF_2, it turns out to have I in the middle of the univalent compounds (like the salts containing $TlCl_6^{-3}$) though I' remains 122.9 eV (to be compared with 124.5 eV for $TlReO_4$, 123.75 eV for Tl_2MoO_4 and 123.6 eV for Tl_2CO_3). Like it is also true in the analogous case of PbO_2, the I(5d) values vary parallel to the I(4f) values. Our fifteen lead(II) compounds show an $I(4f_{7/2})$ interval of 3.9 eV, but the I' values vary less. They are, for a few selected cases, 144.1 (PbF_2), 144.0 ($PbCl_2$) 143.75 ($PbBr_2$), 143.35 (PbI_2), 144.7 ($Pb(NO_3)_2$) and 144.35 eV ($Pb(IO_3)_2$). On the whole, the lead (IV) compounds have the *lower* I-values, as previously pointed out for PbO_2. The high I-value for Cs_2PbCl_6 seems to be a common property of caesium salts (with exception of the fluoride) and actually, $I' = 144.3$ eV similar to lead (II) iodate. I' for PbO_2 is somewhat below 143 eV. We only detect slightly broadened signals of Pb_3O_4 at I slightly below PbO, and actually, minium has been suggested [99] as internal standard. It is not quite certain that bismuth (V) has been observed in our nominal Bi_2O_4 and $NaBiO_3$; if it has, the signals have almost the same positions as of Bi (III) in contrast to arsenic and antimony, but in analogy with thallium and lead. The $I(Bi4f_{7/2})$ range is 2.9 eV for our nine Bi (III) compounds; $I' = 165.7$ eV for the fluoride and 164.15 eV for the oxide show a distinct difference.

Besides 8 stoichiometric thorium (IV) compounds, we have measured six mixed oxides [53] which have also kindly been measured by PROCTOR and WILSON in the Varian laboratories in Palo Alto, Cf. and by BREMSER and LINNEMANN in Darmstadt. It was mentioned above how the I' values vary only slightly less (by 3.5 eV) than $I(4f_{7/2})$ by 3.9 eV, but I' for the oxides fall in a narrower interval. In the case of uranium compounds, it is not easy to know whether certain mixed oxides are not superficially oxidized to U (VI). Certain uranyl salts show weak satellites to the left, probably of electron transfer type to the empty 5f shell in analogy to the stronger satellites of La (III) 3d signals. As later discussed with CORNELIUS KELLER, uranium (V) in mixed oxides show strong satellites at 8 eV higher I than the $4f_{5/2}$ signal. It may seem somewhat worrying that the strong 4f signals of UO_2SO_4, $3H_2O$ and $U(SO_4)_2$, $4H_2O$ almost coincide, but the uranium (IV) compound has a pronounced structure with maxima at 5 eV higher I, probably due to effects of interelectronic repulsion. The salt of UCl_6^{-2} has the lowest I values observed, whereas K_2UF_6 occurs in the middle of the uranyl salts. This constitutes a major difference from the chemical shift about 16 eV between cerium (IV) and Ce (III) with none and one 4f electron. The I interval of U (VI) is 2.1 eV, the highest $I'(4f_{7/2}) = 388.1$ eV occurs for $CsUO_2(NO_3)_3$.

The separation between $4f_{5/2}$ and $4f_{7/2}$ signals from hafnium to uranium has previously been discussed [64]. Its variation for a given element, at most 0.1 eV, is on the limit of the experimental uncertainty.

General Trends in the Chemical Shift as a Function of Neighbour Atoms and the Manne Effect

To the first approximation, the chemical shifts dI in inner shells follow the general ideas (partly based on the nephelauxetic effect derived from excited levels of d and f shells containing from two to $4l$ electrons) of fractional atomic charges [52, 56] in transition group and post-transition group elements, the fluorides having the highest fractional charges of the central atom and ligands containing elements of low electronegativity, such as sulphur, producing the lowest fractional charges due to more pronounced covalent bonding. The same type of behaviour was also found in Uppsala [34] for gaseous and solid carbon compounds, the effect of hydrogen and carbon neighbour atoms being almost identical. It was early recognized that dI is smaller than the theoretical values obtained by interpolation between gaseous ions M^+, M^{+2}, . . . where the change of I per unit of charge is approximately $<r^{-1}>$ in atomic units of the valence shell being depopulated. This theoretical slope is between 10 and 20 eV, and hence, the typical chemical shift $dI = 5$ eV corresponds to charges between 0.25 and 0.5 which would be almost incompatible with the visible absorption spectra [59]. However, the negative charges on adjacent atoms produce a Madelung potential counteracting dI by a large amount which, in a binary molecule MX_N, is proportional to the fractional charge of M and inversely proportional to the internuclear distance M-X. In Table 21, the Madelung potential in the alkali metal halides vary between 12.52 eV in LiF and 6.41 eV in CsI. Hence, it is quite conceivable that the fractional charges are several times larger than supposed if the Madelung potential is neglected. Only in the 4f group, such as the cases Ce(III), Ce(IV); Eu(II), Eu(III) and Tb(III), Tb(IV), the observed dI are not much below the theoretical slope close to 20 eV.

The low I-values of transition and post-transition group oxides agree with the pronounced nephelauxetic effect (a common exception to both effects is NiO) [51, 56] though it is not generally believed by chemists that oxides have particularly low fractional atomic charges. What is stranger is that cyanides have unusually high I-values (this becomes even more striking when I' are considered, decreasing the fluoride values) as noted [72, 94] by several authors. This may be taken as an argument for π-back-bonding to empty orbitals of cyanide, increasing the positive charge of the central atom. It is also true that carbon monoxide complexes tend to have rather high I-values (though they lack significant Madelung potentials) but a difference is that much independent evidence suggests that the π-back-bonding becomes progressively more important when the central atom oxidation state becomes more negative in a series such $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{-2}$ whereas even palladium(IV) in $Pd(CN)_6^{-2}$ presents a rather extreme, high I-value. Several authors [15, 16, 117] have discussed metallo-organic compounds, in particular of chromium, and their fractional charges. In view of the variation of I-values of potassium, this is perhaps a difficult conclusion to draw. The opinion that iron(II) in $Fe(C_5H_5)_2$ has a negative fractional charge is based on $I^*(Fe2p_{3/2})$ being 710.8 eV to be compared with 713.0 eV in $Fe(CO)_5$. We find $I^* = 711.7$ eV for FeC_2O_4, $2H_2O$ and 707.6 eV for $[Fedip_3]Br_2$ and our conclusion would only be that the central atom in ferrocene is less positive than in iron(0) carbonyl but perhaps more positive than in the dipyridyl complex.

A less dramatic but more universal trend than the high I-values of cyanides is a general tendency for complexes of neutral ligands (water, ammonia, amines, *etc.*) to have lower I-values of the central atoms than chloro complexes, in contrast to the nephelauxetic effect and chemical consensus. It may be that crystals involving strong hydrogen bonds, as has already been mentioned in the case of ammonium salts of fluoro complexes, have intrinsically small ∂ values. However, one has to accept that the general variation of I of inner shells of d group complexes as a function of the ligands is somewhat similar, but by no means identical, with the nephelauxetic series[51, 56] .The situation is quite different in the case of cations not forming covalent bonds at all.

Extrapolating the comparison of potassium and caesium salts, we have made a systematic study of several anions with tetra-alkylammonium ions NR_4^+ (where we have concentrated on the smallest, $R = CH_3$, and $R = n-C_4H_9$ which can be obtained in a high degree of purity) and with $As(C_6H_5)_4^+$ precipitating many large anions as crystalline salts which are soluble in organic solvents. As a student with JANNIK BJERRUM, one of us started work in 1950 on the precipitation of anions (most frequently forming weakly soluble caesium salts) with the green "praseo" ion *trans*- $[Coen_2Cl_2]^+$ (a somewhat analogous anion is the raspberry-red "reineckeate" *trans*-$[Cr(NH_3)_2(NCS)_4]^-$; the salt no. 100 is extraordinary by being off-white; the complementary colours of the cation and the anion compensate almost exactly, also intensity-wise). Here, we also study salts of the univalent methylene blue cation. We bought it as the chloride (though some commercial samples are the tetrachlorozincate) and in spite of the very high $\varepsilon \sim 10^5$, many anions precipitate it so quantitatively that the supernatant solution hardly is pale blue. Thus, the blue-violet perchlorate, blue perrhenate, slightly greenish blue tetraphenylborate and blackish blue reineckeate and hexa-iodoplatinate can be prepared.

The decrease of I-values with increasing radius of the cation agrees qualitatively with the Madelung potential. There is little doubt that the total expression for the Madelung potential is a fairly good approximation, and for instance, $I(\mathrm{K2p_{3/2}})$ for gaseous K^+ is probably close to 306 eV obtained by adding 8 eV to the I' values in Table 22 though it is striking how frequently ∂ seems to cancel variations in the Madelung potential. Quite generally, the differential variation from one salt to another seems to be less well represented. In particular, in ten caesium salts (excepting the fluoride), the I values of the strongest signal of twelve elements are, on the average, 1.3 eV higher than of the analogous ten potassium salts, whereas one would have expected a *decrease* about 0.8 eV due to the Madelung potential. It is seen from Table 21 how caesium salts tend to have high ∂ values, and the six cases of I' values known do not vary (0.0 eV) on the average from caesium to potassium salts. Said in other words, the Madelung theory underestimates I' values of caesium salts some 0.8 eV and I some 2 eV. It was suggested [27] in 1968 that the highly polarizable salts are more difficult to ionize because of the groundstate polarization.

However, there is no doubt that one also encounters an effect of polarizability of opposite sign, decreasing the I^* values observed of the sharp peaks in the photo-electron spectra. In the case of the neon atom, the ionization energy of a 1s electron in the Hartree-Fock wave-function maintaining the "frozen" orbitals of the other nine electrons is calculated to be 891.7 eV in disagreement with the observed value 870.2 eV. On the other hand, if a Hartree-Fock calculation for the ionized system Ne^+ is performed [108] with the constraint that the electron configuration is $1s2s^22p^6$ but allowing the radial functions of the eight outer electrons to adapt (contract) the energy difference relative to the Hartree-Fock groundstate is 868.6 eV. When the two minor corrections of relativistic effects on the 1s energy and the correlation effect in the pair of 1s electrons in the groundstate are added, 870.6 eV is obtained. One can now ask the question whether a Franck-Condon principle is valid for the other electrons. The agreement between the experimental I and the difference between the two Hartree-Fock functions suggests that the other electrons have time to adapt during the ionization of the 1s shell. However, this adaptation is improbable for other reasons, and the problem was finally resolved by MANNE and ÅBERG [80]. In the neon photo-electron spectrum, many satellites occur between $I = 900$ and 1000 eV. Though individually, they are weaker than 4 percent of the primary signal at 870.2 eV, the integrated intensity of all these satellites (due to *shake-up* forming excited levels such as $1s2s^22p^53p$ and *shake-off* loosing two or three electrons such as $1s2s^22p^5$ or $1s2s2p^5$) is about a quarter of the intensity of the primary signal. The important point is now that the baricenter of all this structure including the primary signal occurs at 886 eV, close to the

Koopmans value assuming "frozen" orbitals. Hence, the ionization process can be described as "sudden" in the sense that the instantaneously formed $1s2s^2 2p^6$ decays to the hundreds of alternatives among which one alternative, the "adapted" $1s2s^2 2p^6$ (which would have been formed by an adiabatic process in the electron system) accounts for 80 percent of the squared amplitude. In the Copenhagen representation of quantum mechanics, it is normally said that quantum jumps do not take any time at all. However, this is a non-relativistic statement; it takes light 10^{-18} sec to cross an atom with a diameter of 3 Å, and it can hardly be argued that the primary process of photo-ionization can be more rapid. On the other hand, good arguments are available that this process is not slower than 10^{-17} sec.

We suspect that this *Manne effect* occurs also for electrons in adjacent atoms in solids and not only for outer electrons in the same atom. For relativistic reasons, there is a limit for how distant atoms have the time to be informed about the primary ionization process, and in practice, we believe the first two or three layers of neighbour atoms to be the most important. Hence, the higher I values of $K2p_{3/2}$ in salts of fluoro complexes relative to pseudohalide complexes may be connected with the larger deformability adapting to the ionized system in the latter case. In solids, we observe only the primary signal, and the numerous satellites due to shake-up and to shake-off are swamped by the intense background due to inelastically scattered electrons. Anyhow, the neon atom may perhaps be somewhat exceptional by allowing eight electrons to be stabilized 2.5 eV each by the contraction in the adapted anti-Koopmans ionized state, and it may be that the inter-atomic Manne effect in most polyatomic systems amounts to some 5 eV perhaps combined with an intra-atomic Manne effect between 15 and 30 eV. It is obvious that a differential change of 2 eV of the inter-atomic Manne effect can contribute significantly to the range of I values observed. Colloquially speaking, this effect can be considered to indicate the extent to which the ionized system has the capability to develop additional covalent bonding within a very short time.

The Widths and Radiative Half-lifes

The typical photo-electron signal, when corrected for a much intenser background, is a Gaussian error-curve. With our standard conditions of 100 V analyzer potential (not giving the best resolution, but the strongest signals) the one-sided half-width $\delta(-)$ toward lower I-values is between 0.95 and 1.0 eV. We frequently run into asymmetric and somewhat broadened signals which must be due to the superposition of two or more adjacent signals. Unfortunately, it is very difficult to calculate backwards from the observed spectrum to a unique choice of two components. In particular, one encounters the problem of great importance for visible spectra of solutions that two Gaussian curves with the *same* δ add to a curve almost looking like a new Gaussian with a slightly larger δ, if the two maxima are of comparable heights and a not too far distance, say below 1.28 δ. CLAUS SCHÄFFER has investigated this problem thoroughly explaining how many adjacent energy levels predicted in "ligand field" theory cannot conceivably be resolved. Thus, the function $\exp(-x^2/2)$ (which is frequently tabulated for the use by statisticians) has $\delta = (2 \ln 2)^{1/2} = 1.177$. When two identical Gaussians have their maxima situated at $x_1 = -\varkappa$ and at $x_2 = +\varkappa$, their sum forms an almost perfect Gaussian for small $\varkappa$ having its maximum at $x = 0$ and the half-width

$$\delta = 1.177\ (1 + 0.589\ \varkappa^2 + \ldots) \tag{1}$$

where 0.589 is half the numerical constant 1.177. The important point is the quadratic singularity in $\varkappa$; it is not possible to calculate backwards from an experimental spectrum with its usual uncertainty inherent in all such measurements to a reliable value of $\varkappa$; once $\varkappa$ is small, it might equally well be half as large or zero indicating only one Gaussian component of the signal. The sum curve has a flat maximum with vanishing second differential quotient for $\varkappa = 1$; for this value, curvature at $x = 0$ is due exclusively to the fourth and subsequent (even) differential quotients. When $\varkappa$ is larger, two maxima with a minimum in the middle develop.

There are good reasons to believe that the observed δ of our signals can be described as the square-root of the sum of squared contributions from differing sources of signal broadening. FADLEY and SHIRLEY[29] pointed out that the two 4d signals of lutetium(III) fluoride each have $2\delta = 4.23$ eV due to short radiative half-life of the ionized system $4d^9 4f^{14}$ where a 4f electron rapidly jumps down in the 4d vacancy forming the lowest configuration $4d^{10} 4f^{13}$ of Lu(IV) (which then picks up an electron from the surroundings less rapidly). According to Heisenberg's uncertainty principle, the double-sided half-width 2δ should be 0.46 eV if the radiative half-life is 10^{-15} sec and 4.6 eV for 10^{-16} sec, the product of the two quantities remaining constant. We have also found $\delta = 2.1$ eV for Lu4d signals of Lu_2O_3 and $Lu(IO_3)_3$. In the heavier elements, δ of the 4d signal remains roughly constant and is 2.0 eV in HfO_2, 2.1 eV in K_2HfF_6, 2.3 eV in powdered Au and in HgO, 2.4 eV in $PbSO_4$, 2.2 eV in BiF_3, 2.5 eV in $Th(IO_3)_4$, $UO_2(IO_3)_2$ and $Cu(UO_2)_2(PO_4)_2$.

Hence, the half-life of these states lacking a 4d electron is between 1 and 1.3 times 10^{-16} sec.

Quite generally, most of the intense signals observed by us have δ close to the standard value 1.0 eV. This is particularly true for the 4f signals of elements above tungsten [64] whereas the 4f signals of ytterbium(III) are broadened by effects of interelectronic repulsion (separating terms of $4f^{12}$) and of lutetium(III) and hafnium(IV) by spin-orbit coupling not sufficiently resolved. Since a half-life 10^{-15} sec would increase δ by 0.06 eV, this is the lower limit where Heisenberg uncertainty broadening becomes perceptible. Many of the lower l values correspond to broadened signals, and we are now going to discuss them in the order s, p, d.

Parrett [88] discussed the uncertainty width of 1s holes as a function of Z. The radiative width due to 2p → 1s X-ray fluorescence is $Z^4.1.2.10^{-6}$ eV, but the observed width in eV (0.5 for Ar, 1.5 for Cu, 3.0 for Kr, 7.5 for Ag and 54 for Au) is larger because of competing processes, such as the emission of Auger electrons. We find some 1s signals significantly broadened, such as 1.3 eV for several lithium(I) salts and 1.1 eV for beryllium(II). We do not believe that this is due to half-lifes below 10^{-15} sec for so low Z values, but rather a dependence of I on the internuclear distance producing a broadened signal according to Franck and Condon's principle, having the maximum at the "vertical" transition with unchanged distances, like the broadening (with frequent vibrational structure) one finds in the photo-electron spectra of gaseous molecules [107] when a strongly bonding (or anti-bonding) electron is removed. It is of obvious importance for the use of carbon 1s signals as internal standards to consider their δ values, in view of eq. (1), as an indicator of closely adjacent signals. As a matter of fact, the pure scotch tape hydrocarbon shows $\delta = 0.95$ eV. Many nitrogen 1s signals have $\delta = 1.0$ eV but it must be noted that in other cases, larger values may be observed though no obviously non-equivalent nitrogen atoms are involved. This may again be connected with Franck-Condon-broadening. Fluorine 1s signals vary between 1.2 and 1.4 eV. On the other hand, most sodium(I) salts have δ close to 1.05 eV. Finally, Mg(II) shows $\delta = 1.4$ eV.

δ of 2s signals is difficult to evaluate in fluorides because of the rapidly varying background, but seems to be close to 1.5 eV as it is also in Mg(II). The Al2s signal in Na_3AlF_6 has $\delta = 1.3$ eV. This value increases to 2.0 eV for CaF_2 and 2.1 eV for $Ca(IO_3)_2$ and seems to be as large as 3.5 eV for $BaCrO_4$.

δ of the 3s signal is 1.6 eV in CaF_2 and 2.4 eV in SrF_2. In the 3d group, effects of interelectronic repulsion produce two broad signals (see Table 20) when the groundstate has positive S.

δ of the 4s signal in BaF_2 is 2.0 eV. According to COHEN *et al.* [17], the intrinsic width of the lanthanide 4s signals (again split by interelectronic repulsion) corresponds to $\delta \sim 3$ eV.

δ of fluorine 2p in CaF_2, SrF_2 and BaF_2 is close to 1.5 eV but is difficult to evaluate in other compounds, partly because of adjacent I-values of delocalized M.O. The 2p signal has $\delta = 1.3$ eV in Mg(II) and 1.2 eV in Al(III) but becomes difficult to measure in the following elements because of the perceptible spin-orbit coupling. When the two j-values are sufficiently distinct again, δ is 1.0 to 1.1 eV in K(I) and Ca(II). Cr2p has $\delta = 1.1$ eV in $BaCrO_4$ but the subsequent elements have slightly broadening due to positive S of the groundstate, though diamagnetic Co(III) has $\delta = 1.05$ eV. Similar moderate $\delta \sim 1.1$ eV can be seen in Zn(II) and Ga(III).

δ of calcium 3p in CaF_2 is 1.3 eV. When not broadened by effects of interelectronic repulsion, the 3d group has δ of 3p signals close to 1.5 eV, whereas $\delta = 1.6$ for Ge(IV) and 1.4 eV for As(V). In Se, Br, Rb and Sr, δ is also close to 1.5 eV. Y(III), Zr(IV) and Ru(III) show 1.8 eV and CdF_2 1.9 eV, whereas the value finally increases to 2.9 eV in BaF_2.

δ of 4p in SrF_2 is 1.4 eV and seems to be as low as 1.0 eV in YF_3. It then increases rapidly, being about 2 eV in Rh(III), 3 eV in Pd(II), 4 eV in Ag(I) and close to 5 eV in Cd(II). This increase does not continue, $\delta = 2.7$ eV for Au and as narrow as 1.3 eV for Ba(II).

δ of the 5p signal has only been measured to 1.3 eV in BaF_2 and about 1.4 eV in Au.

δ of the 3d signal is difficult to measure as long it remains in the region with I below 20 eV. It is 1.2 eV in Ga(III), 1.1 eV in Ge(IV) and 1.3 eV in As(V). It is possible that a part of this broadening must be ascribed to beginning spin-orbit splitting. δ is 1.15 eV in bromides, 1.0 eV for Mo(VI) and Rh(III) and as low as 0.95 eV for Pd(II) and Ag(I). It then increase slightly to 1.05 eV in Cd(II), about 1.2 eV in tellurium, 1.15 eV in both iodides and iodates, 1.05 eV in Cs(I) and 1.2 eV in Ba(II). The signal at lowest I in La(III) has $\delta = 1.5$ eV whereas the broad and somewhat asymmetric signals of Sm(III), Eu(III), Gd(III) and Dy(III) all are close to 2.5 eV.

δ of the 4d signal of Ag(I) is 1.5 eV, perhaps due to "ligand field" effects of differing energy of the five 4d orbitals. δ decreases to 1.0 eV in CdF_2 and is 1.1 eV for Cs(I) and Ba(II) having a clear-cut separation between the two j-values. All the lanthanides have asymmetric (and frequently irregular) shape, δ is 1.5 eV in La(III), 3.2 eV in Nd(III), 1.7 eV in Eu(III) and 2.3 eV in Gd(III). The following elements all have δ around 2 eV. The relatively sharp signal of Yb(III) at lowest I (*cf.* Fig. 1) has $\delta = 1.9$ eV. It was discussed above how δ slowly increases from 2.1 to 2.5 eV in the elements from lutetium to uranium.

δ of the 5d signal is 1.0 eV in Pb(II), 1.1 eV in Th(IV) and 1.3 eV in U(VI).

The general conclusion is that the half-width only becomes spectacularly large (above 2 eV) for several ns-signals when Z increases, in the rather isolated case of 3p in BaF_2, for all 4p signals when Z larger than 45 and for all 3d and 4d signals for Z above 60. It is even possible to maintain that only 4p and 4d signals have a pronounced propensity toward high δ. The physical explanation may be that the half-lifes only are shorter than 2.10^{-16} sec when $n(l+1)$ electrons are present to fill the nl vacancy. If this condition for extremely short half-life is valid, 1s, 2p, 3d and 4f signals should never become exceedingly broad .The 3p signal broadens in the presence of 3d electrons, but this is not a convincing argument for the hypothesis. However, it is striking that the 4p signal broadens tremendously in the interval from Rh(III) to Cd(II) where the number of 4d electrons available increase from six to ten. In this case, δ decreases slightly in the heavier elements barium and gold, whereas δ remains almost constant of the 4d signal once the 4f shell is filled, starting with Lu(III) and Hf(IV). There are good reasons to believe that the 5d signal would broaden in transuranium elements once many 5f electrons are present.

One may ask whether δ is influenced by chemical effects. There is a distinct tendency to sharp (and as we see below, higher) peaks of alkaline metal ions compared with the broader, slightly lower peaks of the isoelectronic halides. Such an effect might be connected with Franck-Condon broadening being more important for the anions. We do not know a clear-cut case of the same element (conserving the same value of S) varying δ as a function of the neighbour atoms, with exception of the nitrogen and oxygen 1s signals mentioned above.

Relative Signal Intensities

In stoichiometric compounds, the relative intensities (expressed as the difference of counts/sec between the maximum and the interpolated background) of different elements, or for that matter, different shells of the same element, do not reproduce better than 20 percent. Hence, the instrument is not perfectly suited for quantitative analysis, though it can be of great interest to obtain information about relative concentrations (even within a

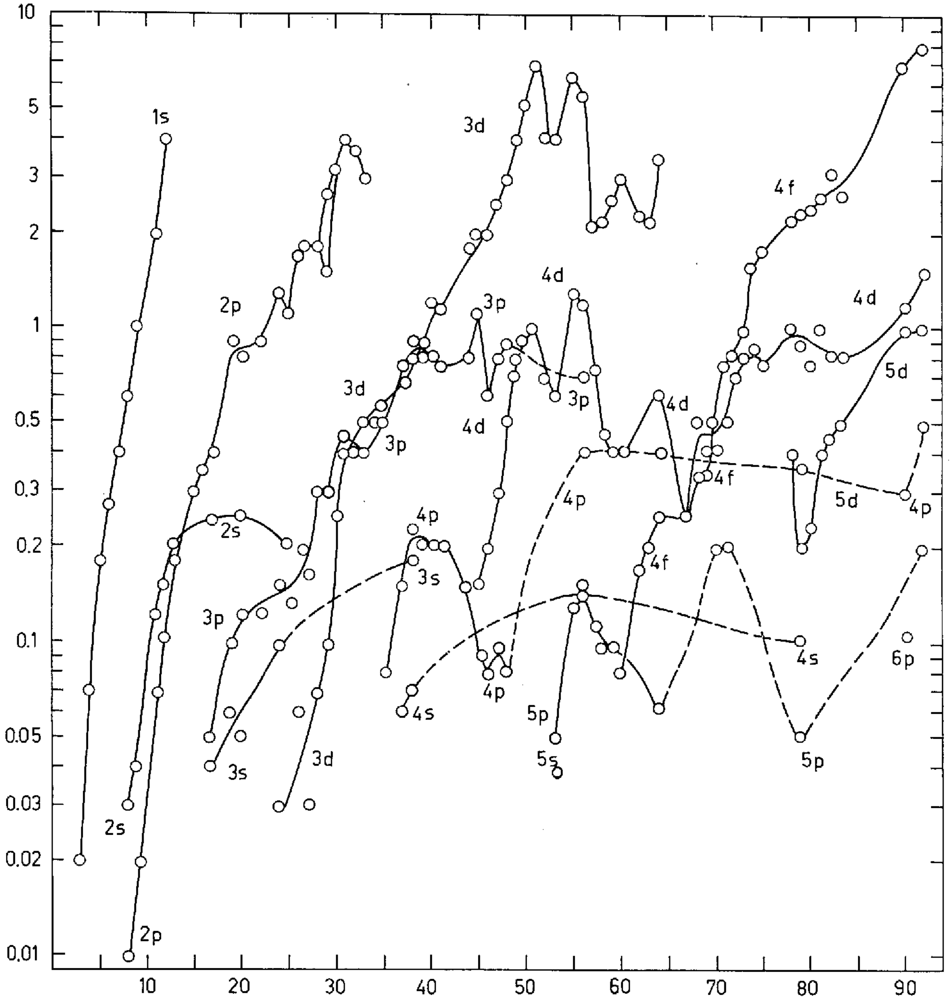

Figure 4. Intensities of photo-electron signals from the *nl* shells in different elements (as a function of *Z*) relative to fluorine 1s. As discussed in ref. [67] this is not better determined than within a factor 1.3. When two *j*-signals are seen, the maximum at lower *I* due to the higher *j* is considered; otherwise, the observed maximum is simply used.

factor 1.5) of elements in the outermost 30 Å of a solid sample. Wagner [112] studied the strongest signal (usually the highest *I* among the alternatives 1s, $2p_{3/2}$, $3d_{5/2}$ and $4f_{7/2}$) of 43 elements relative to fluorine 1s. In the following, we use the colloquial abbreviation "w" for this unit. We are also interested in the less intense signals and find a variation by a factor of 1000. Figure 4 shows the relative intensities as a function of Z. It must once more be emphasized that they may be some 30 percent wrong. In practice, we established a set of secondary standards, such as 0.4w for N1s, 2.0w for Na1s, 4.0w for I3d$_{5/2}$ and 6.5w for Cs3d$_{5/2}$. We agree with Wagner that C1s has 0.27w and that iodine (at least in iodides) represents a relative minimum of the curve between antimony and caesium. Most of our values differ less than 25 percent from those given by Wagner .It may be added that his $K_4Ni(CN)_6$ most probably is $K_2Ni(CN)_4$ dividing the nickel intensity by two.

An attractive hypothesis also suggested by Wagner[112] is that the number of photo-electrons counted in a given signal is proportional to the number of X-ray photons absorbed by a given shell (anyhow, the yield of electrons not suffering inelastic scattering is low, since the penetration depth of the soft X-rays is about 100 times deeper than the surface layer allowing photo-electrons to escape). If the typical absorption edges where the molar extinction coefficient is proportional to ν^{-3} (in agreement with an argument by Kramers based on the correspondence principle) are extrapolated to large ν, the signal intensity should be proportional to $(2j + 1)I^2$ where $(2j + 1)$ is the number of electrons producing the nlj signal. However, this argument is only valid for s- and perhaps for p- electrons. For higher l, the probability of absorption of a high-energy photon is far larger, and we have proposed that the intensity is proportional to the product of three factors, $(2j + 1)$, the average $<r^{-2}>$ of the shell being ionized, and a kind of squared effective nuclear charge. Actually, Watson was as kind as to supply $<r^{-2}>$ values for Hartree-Fock functions, and the third factor seems remarkably invariant[67].

Since small average radii favour photo-ionization by the X-rays, the d and f shells at the end of the transition groups and in the subsequent post-transition elements show rather strong signals, as also seen on Fig. 1 and 2. This is rather fortunate, because the number of valence electrons can be rather overwhelming. This number is 32 in each sulphate or perchlorate anion, 40 in acetylacetonate and 120 in tetraphenylborate, whereas the methylene blue cation presents 126 valence electrons. In particular, hydrocarbons have a virtually flat photo-electron spectrum in the region of I below 20 eV showing a vanishing probability of ionizing carbon 2p orbitals. In oxides, the 2s signal close to 30 eV has the intensity 0.02 w whereas 2p is on the limit of detection. F2s(0.04 w) and F2p(0.02 w) are quite perceptible.

On the whole, the curves on Fig. 4 are smoothly increasing as a function of Z until the limit 1382 eV of I is reached. However, there is pronounced tendency for the transition groups to have too weak signals. In view of what we said about probability for a given shell to absorb the photon, one would consider the product of the height and the width to be the important quantity, but this distinction would make little actual difference. Even the satellites to be discussed below and the multiple signals due to effects of interelectronic repulsion would not change the intensities by more than a factor of three, whereas an extrapolation of the 3d intensity on Fig. 4 would arrive at 10 to 20 w for Sm to Dy. However, we have indicated the two highly different sets of intensities for Cu(I) and Cu(II) on Fig. 4. Most of these differences can only be qualitatively understood as an increased probability of secondary processes (such as emission of electrons in broad shake-up and shake-off signals at higher I) since the probability of inelastic scattering should only depend on the kinetic energy of the electron.

Obviously, the identification of *nlj*-values for a given signal is an important problem. Usually, there is no ambiguity when comparing with literature, but one has to realize that the Uppsala tables[97] based partly on I^* measurements relative to the Fermi level and partly on the critical analysis of X-ray spectra by BEARDEN and BURR[3], besides chemical shifts, shows unexplained irregularities up to 5 eV. This can most readily be seen from the plot[66] of dI/dZ as a function of Z, especially in the lanthanides. However, we have had no serious difficulties with identifying given shells (except due to coincidences with stronger signals or their $K\alpha_3$ replica) with the exception of the 6p signals of thorium and uranium. The Uppsala tables supposed to give I^* of metallic elements relative to the Fermi level indicate $Th6p_{1/2}$ at 49 and $Th6p_{3/2}$ at 43 eV whereas the values for uranium should be 43 and 33 eV. It is obvious that this must be wrong for at least one of the two elements. We find a sharp signal with $I = 27.2$ eV and $I' = 23.6$ eV for ThF_4 and $I = 24.3$ and $I' = 20.7$ eV for ThO_2 and ascribe it to $6p_{3/2}$. When compared with $I = 10.75$ eV of the radon atom measured by EBBE RASMUSSEN, it is probable that I is close to 55 eV for Th^{+4}, and the Madelung potential would decrease this value by 30 eV in fully ionic ThO_2. It is seen in Table 21 that the difference 25 eV is expected to be slightly higher than the actual I. The spin-orbit separation is 3.8 eV in Rn^+, and it is quite conceivable that it has increased to 6 eV in thorium, but we are not able to see a signal close to 30 eV in ThO_2 because of the oxygen 2s signal having $I = 31.3$ and $I' = 27.7$ eV. We have not succeeded in identifying the 6p signals in uranium compounds; some of them have a weak signal with $I \sim 54$ eV which seems rather high. This problem needs further studies.

It is frequently argued in literature[7] that Auger electrons with the kinetic energy E_{kin} can produce signals in our type of spectrometer with the apparent $I^* = (1482 \text{ eV}) - E_{kin}$. WAGNER[111] even reports that these signals may be almost as intense as genuine photo-electron signals between 0.2 and 1 w. Usually, we did not detect Auger signals. However, they have been found in MgF_2, NaF and NaI, where they are particularly strong. The kinetic energy is 645.6 and 645.5 eV for the strongest fluorine signal, respectively, 979.3 eV and 983.2 eV for sodium, and 1169.3 eV for magnesium. It can be argued that $\partial = 3.9$, 4.3 and 3.7 eV should be added in order to correct for the positive charge of the three samples. On the other hand, graphite and many other samples have very broad Auger signals. Some low apparent I^* are in eV 381 for As(V), 191 $BaSeO_4$, 183 KSeCN, 104 Er_2O_3 and 46.6 for Tm_2O_3.

Satellites and Multiple Signals due to Interelectronic Repulsion

When the groundstate *has* positive S, the ionized system has lower energy for $(S + {}^1/_2)$ than for $(S - {}^1/_2)$, essentially because of the lower interelectronic repulsion $\langle r_{12}^{-1} \rangle$ in the former case. This effect was detected in Uppsala[97, 98] for gaseous $O_2(S = 1)$ and $NO(S = {}^1/_2)$ having their 1s signals split to the extent of about 1 eV. Also solid chromium(III) $(S = {}^3/_2)$ and manganese(II) and iron(III) $(S = {}^5/_2)$ show this effect[29]. From a theoretical point of view, the situation is the most clear-cut if one of the two partly filled shells consists of an s orbital containing one electron, such as sd^q or sf^q in which case the intensity ratio between the two signals is $(S + 1)/S$, the ratio between the degeneracy numbers, and their distance $(2S + 1)K_{av}$ where K_{av} is the average value[56] of the exchange integral of the two-electron operator between the s orbital and the five d or the seven f orbitals (the formation of an average value is not strictly necessary when one of the orbitals is spherically symmetric). This phenomenon has been observed[17] for the 4s and 5s signals of lanthanides and seen in Table 20 as the separation 3.4 eV in the Cr2s signals of $Cr(NH_3)_2(NCS)_4^-$, 4.8 eV in the Co3s signals of CoF_2 and 2.8 eV in the Ni3s signals of $NiF_2, 4H_2O$. Hence, $K_{av}(2s, 3d) = 0.85$ eV in Cr(III), $K_{av}(3s, 3d) = 1.2$ eV in Co(II) and 0.93 eV in Ni(II), all of the same order of magnitude as the spin-pairing energy parameter D (representing $7K_{av}(3d, 3d)/6$) for the partly filled 3d shell. We return in the next section to the partly filled shell itself. Between Gd(III) and Tm(III), $K_{av}(4s, 4f) = 1.1$ eV and $K_{av}(5s, 4f)$ increases from 0.4 to 0.5 eV in the series Pr(III) to Dy(III)[17].

The 2p signals in the 3d group are stronger (see Fig. 4) but the many states of the configuration $2p^5 3d^q$ may produce several signals. The splitting has the order of magnitude 2 eV in Cr(III), 4 eV in Mn(II), 8 eV in Fe(III) but only 3 eV in Fe(II) and 5 eV in Co(II). Apparently, $K_{av}(2p, 3d)$ increases in direction of the later members of the 3d group. However, the strong deviations from Russell-Saunders coupling in the 2p shell exclude the possibility of evaluating this parameter, the 120.6 = 720 states of $2p^5 3d^7$ are far wider distributed than to the extent of $4K_{av}(2p, 3d)$. We still believe that the corresponding splitting 6 eV of the two 2p signals of high-spin ($S = 1$) nickel(II) compounds are due to effects of interelectronic repulsion separating the 45.6 = 270 states of $2p^5 3d^8$. ROSENCWAIG, WERTHEIM and GUGGENHEIM[96] suggest that these multiple signals are satellites of the same kind as the copper(II) signals discussed in the next paragraph. We do not believe that the main origin of the four Ni2p signals is such satellites, in part because only two strong signals are observed in the case of diamagnetic ($S = 0$) nickel(II) complexes[60] and also because the separation is 17.2 eV in the latter case, whereas the distance between the first and third signal of paramagnetic Ni(II) is close to 17.7 eV. It is known that the chemical variation[64] of spin-orbit splitting is on the limit of experimental uncertainty, normally below 0.1 eV, and the increase from 17.2 to about 17.7 eV is what one would expect of effects of interelectronic repulsion, as first noted by HELMER comparing Cr_2O_3 with $K_2Cr_2O_7$. This does not prevent that the unusually strong left-hand components of the 2p signals of the acetylacetonate $Ni(aca)_2(H_2O)_2$ (probably dehydrating to Ni_3aca_6 in vacuo) may partly be due to electron transfer satellites of the kind discussed below in the case of La(III) in view of the strongly reducing character of acetylacetonate ligands derived from electron transfer spectra in the visible and the ultra-violet[49].

NOVAKOV[87] detected satellites 8 to 10 eV to the left of 2p signals of copper compounds. It was originally reported that also copper(I) compounds such as CuCl, CuI and Cu_2O show satellites. However, we believe that these satellites really belong to Cu(II) in superficial oxidation products. Actually, the non-oxidizable CuCN, Cu_2HgI_4 and $[Nien_2](CuI_2)_2$ show just two strong signals like the isoelectronic Zn(II) and Ga(III). At present, the origin of the copper(II) satellites is not perfectly clear. Though Cu(II) is rather oxidizing, it is not too probable that they are due to electron transfer like in La(III) because similar strong satellites are not observed in Rh(III) and Pd(II). Further on, their distance from the main signals is *smaller* in the fluoride. The numerical value 8 to 10 eV is slightly below the ionization energy of the 3d electrons suggesting shake-off (simultaneous ionization of a 2p and a 3d electron by the same photon, in contrast to consecutive emission of Auger electrons) or shake-up, the 3d electron simultaneously jumping to a low-lying empty orbital such as 4s. The former alternative seems less plausible in view of the central field becoming more negative, increasing the effective I(3d). The fundamental difficulty for both alternatives is that copper(I) has a 3d shell easier to excite than Cu(II). This might be explained away if a selection rule holds that such satellites are only conspicuous when the groundstate has positive S. Anyhow, diamagnetic Ni(II) and Pd(II) do not show satellites, though both electron transfer and d shake-up should be equally possible. One way out of this difficulty would be to connect the satellites with the presence of a strongly σ-anti-bonding ($x^2 - y^2$) electron delocalized to a large extent on the ligands[58]. The quadratic d^8 systems have the ($x^2 - y^2$) orbital empty. It must be noted that octahedral high-spin Mn(II), Fe(II), Co(II) and Ni(II) also contain two σ-anti-bonding electrons, one ($x^2 - y^2$) and one ($3z^2 - r^2$). It might then be argued that these systems show weaker satellites because the delocalization is less pronounced, and at smaller distance from the main signal because I(3d) is smaller, except of Fe(III). Outside the elements from manganese to copper, very few cases of distinctly σ-anti-bonding electrons occur in the groundstate, though they are the origin of most of the excited levels treated in "ligand field" theory[59]. We tend to believe that shoulders or residual asymmetry of the main 2p signals of Cu(II) are due to effects of interelectronic repulsion, and that the distant satellites have a rather specific origin. Quite generally, copper(II) complexes of pseudo-halides[80a] and the oxidized surface of copper-nickel alloys[12] show satellites, and it becomes an interesting question whether diamagnetic quadratic Cu(III) also shows satellites. We have precipitated the periodato complex (no. 67) and find somewhat ambiguous evidence of much weaker satellites probably belonging to a superficially reduced impurity of Cu(II). Similar results have been obtained by STEGGERDA and us for Cu(III) biguanide complexes. One might have hoped that the silver(II) complex Agpy_4^{+2} shows illustrating analogies. Actually, the 3d signals hardly have any satellites, whereas 3p shows doubtful broad satellites.

LORQUET and CADET[78] and their colleague MOMIGNY pointed out that the intensity of shake-up satellites is a quantitative measure for the extent of configuration interaction in the groundstate. Thus, the configuration $1s^2 2p^2$ contributes 0.15 of the squared amplitude of the groundstate ^1S of the beryllium atom (the preponderant configuration of which is $1s^2 2s^2$) and correspondingly, fairly strong Rydberg series in the auto-ionizing continuum above the first ionization limit ($1s^2 2s$) converge to the excited configuration $1s^2 2p$ of Be^+ The carbon 1s and oxygen 1s signals of carbon monoxide complexes of zerovalent chromium, iron, nickel and tungsten show satellites at 5.4 to 6.0 eV higher I^*. According to BARBER, CONNOR and HILLIER[2] the occurrence of these satellites indicates a poor description of the ground-state by a Hartree-Fock M.O. configuration, and they ascribe the satellites to the valence bond structure $M^+(CO)^-_N$ This is somewhat analogous, but not exactly equivalent, to our opinion of "inverted electron transfer" satellites from the d-like orbitals of the central atom to the empty orbitals of the ligands (again stabilized by the 1s hole on either the carbon or the oxygen atom). Similar satellites have been observed in other metallo-organic compounds[89a] but one has to be rather cautious regarding the possibility of superficial admixture of other compounds and of charging effects of the ∂ type discussed above.

We have already discussed the satellites in the closed-shell system La(III) due to electron transfer $\lambda^{-1}3d^94f$ where λ denotes a M.O. localized on adjacent atoms. There is little doubt that electron transfer satellites also contribute to some structure in Ce, Pr and Nd compounds, though Nd(III) may be determined by effects of interelectronic repulsion alone in $3d^94f^3$, and that $\lambda^{-1}4f^{13}5f$ occur with low intensity in uranium(VI). Nevertheless, our conclusion is that strong satellites are rather uncommon and are concentrated on a few elements in definite oxidation states such as Cu(II) and La(III).

The Valence Region and Optical Electronegativities

For the chemist, one of the most interesting problems to be studied by photo-electron spectrometry is the valence region with I below 50 eV. Somewhat exceptionally, the fluorine 2s signals[98] are split by ligand-ligand interactions[64] to the extent of 3.5 eV in CF_4 and 4.9 eV in SF_6 but usually, chemical effects of this kind are only observed for I below 40 eV. The resolution is far better in gaseous molecules than in solid samples, and with exception of d and f shells, the signals are rather weak when induced by X-rays. The *optical electronegativity* was introduced[50, 57] with the purpose of describing electron transfer spectra where an electron is transferred from one or more reducing ligands to an oxidizing central atom. The Pauling values $\varkappa_{opt} = 3.9(F^-)$, $3.0(Cl^-)$, $2.8(Br^-)$ and $2.5(I^-)$ can be obtained for the halide ligands if each unit of $\varkappa_{opt}$ corresponds to the wavenumber difference 30000 cm^{-1} or 3.7 eV. It was pointed out[54] that most gaseous halides[107] have their lowest ionization energy

$$I = (1 + 3.7\ \varkappa_{opt})\ \text{eV} \tag{2}$$

close to 15.4 eV for fluorides, 12.1 eV for chlorides, 11.3 eV for bromides and 10.2 eV for iodides. It is seen from Table 21 that the almost ionic halides have I values without corrections for charging effects close to eq. (2) whereas I' is lower. One may conclude that rather covalent halides have slightly higher ionization energies than ionic solids though normally below the values [82] for the gaseous atoms 17.42 (F), 12.97 (Cl), 11.81 (Br) and 10.45 (I) eV.

The partly filled d shell has I values between 8 and 12 eV in most cases. The variation with the ligands for a given element in the same oxidation state may, to some degree, be an illusion when I' are considered. One might have hoped for a determination of the sub-shell energy difference Δ (which is known from visible spectra [56] to be about 1 eV in these cases) from the 3d ionization energies of octahedral cobalt(II) and nickel(II) complexes, though it is by no means evident that the same Δ value would be obtained from I differences as from the excitation energies studied by "ligand field" theory. However, our present results are on the limit of the experimental uncertainty. The two sub-shells of $Fe(C_5H_5)_2$ containing four and two d-like electrons have $I = 6.9$ and 7.2 eV [107]. By the way, the chromium(II) methylcyclopentadienide $Cr(C_5H_4CH_3)_2$ has [22] $I = 5.55$ and 6.9 eV, the former value being the lowest known for any gaseous molecule (whereas solid alkali metals have I close to 2 eV). Nevertheless, the d-group molecules have not been particularly informative for our purposes; Cox, Evans, Hamnett and Orchard [21] found $I = 9.41$ eV for the single 3d electron of gaseous VCl_4. It is interesting that the loosest bound M.O. of PF_3 corresponding to the lone-pair has $I = 12.3$ eV whereas $Ni(PF_3)_4$ has $I = 9.55$ eV for six of the 3d-like electrons and 10.58 eV for the other sub-shell containing four electrons [35]. These values may be compared with $I = 8.8$ and 9.7 eV for the two similar sub-shells of $Ni(CO)_4$. Recently, the separation between halogen np and copper 3d signals has been reported [69] for solid CuCl, CuBr and CuI. What is particularly interesting is a shoulder towards lower I of the latter signal possibly representing the separation between the two sub-shells in the tetrahedral chromophore in close analogy to the isoelectronic Ni(0) complexes.

It is beyond doubt that I(3d) of zinc(II) compounds is some 5 eV higher than corresponding nickel(II) and copper(II), and I(3d) of gallium(III) some 16 eV higher than cobalt(III). This is a most striking difference from the lanthanides with comparable I(4f) of gadolinium(III) and lutetium(III) and I(4f) only increasing about 2 eV from Yb(III) to Lu(III). Actually, I(4f) is higher of TbO_2 than of HfO_2. Said in other words, there is an absolute sense in which the closed-shell character of Zn(II) and Ga(III) shows up as considerably higher I(3d) than of the partly filled shell in preceeding elements having the same oxidation state. The valence region of metallic Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt and Au have been studied both by BAER et al.[1] and by FADLEY and SHIRLEY[28]. There is no doubt that in many d group compounds, I of the partly filled shell is comparable or higher than I of the loosest bound ligand orbitals. It might be felt a somewhat paradoxical situation, but the point is that partly filled shells with small average radii have large differences between the ionization energy and the electron affinity, and the main condition for a well-defined oxidation state with an integral number of electron in the partly filled shell is that its electron affinity is significantly smaller than the ionization energy of any of the ligand orbitals.

WERTHEIM and HÜFNER[116] studied several d group oxides, concluding in almost coincidence of oxygen 2p and central atom 3d signals. It was even argued that metallic ReO_3 has a weak shoulder at $I^* \sim 1$ eV due to rhenium 5d electrons. However, the I^* values reported seem to be some 8 eV below our I values. Though it is seen from Table 21 that the Madelung theory is not perfectly valid, it is interesting to note that a change from 310°K to 500°K produced an increase of the distances between potassium K3s and K3p and chlorine (3p) signals in KCl in excellent agreement with the result 0.13 eV calculated from the change of the Madelung potential by the thermal expansion whereas the similar heating of LiF produced an increase of the distance I(Li1s) – I(F2s) two-thirds and I(Li1s) – I(F2p) half the calculated value 0.18 eV [10a].

WERTHEIM, ROSENCWAIG, COHEN and GUGGENHEIM[114] found that anhydrous fluorides MF_3 have a weak signal corresponding to I(M4f) being slightly lower than I(F2p) for M = Ce, Pr and Nd. When I(M4f) increases for M = Sm, Eu and Gd, the (now weaker) fluorine 2p signal is masked and does not contribute significantly to the observed spectrum for heavier M (*cf.* Fig. 4). However, the subsequent M = Tb, Dy, Ho, Er, Tm and Yb have two signals which can be ascribed, to the first approximation, to the lower energy of the terms of $4f^{q-1}$ having $(S + {}^1/_2)$ relative to the terms having $(S - {}^1/_2)$ decreased from the groundstate of $4f^q$. The distribution of intensities on these signals can, in principle, be calculated from the coefficients of fractional parentage[22] and the separation 3.8 eV between the two signals of the $4f^{13}$ system Yb(III) is considerably larger than the pure spin-pairing energy $2D = 1.6$ eV but agrees with the well-known distribution[50] of the energy levels of $4f^{12}$, Tm(III) being isoelectronic with Yb(IV). The authors at Bell[114] did not want to pronounce themselves about the absolute I values and the extent of the charging effects. It is seen from Table 23 that

$I'(4f) = 15.3$ eV for both GdF_3 and LuF_3. This may conceivably be slightly less than real I, but the values in Tables 17 and 18 are too large due to charging effects. HAGSTRÖM and collaborators[37, 40] measured photoelectron spectra of metallic lanthanides. When the conditional oxidation state[56] is M[II], the I^* values relative to the Fermi level are low, such as 2.0 eV for europium and 2.7 and 1.4 eV (split by spin-orbit coupling) for ytterbium. Other elements are M[III] and show the structure expected for the terms of $4f^{q-1}$. Thus, $I^* = 7.8$ eV for gadolinium. Since the work-function of this metal is said[24] to be 3.2 eV, $I(\mathrm{Gd}4f) = 11.0$ eV relative to vacuo. The chemical shift from $I' = 15.3$ eV GdF_3 and 13.6 eV in Gd_2O_3 to the metal, or from $I' = 6.9$ eV for $EuSO_4$ to I close to 4 eV for Eu are quite normal for other elements too. The adiabatic ionization energy of europium (II) aqua ions derived from $(E_0 + 4.5)$ eV where E_0 is the standard oxidation potential[59, 66] is 4.1 eV, and demonstrates a difference between "vertical" processes obeying the Franck-Condon principle and chemical equilibria. The variation of $I(4f)$ with the number of 4f electrons is in excellent agreement with the spin-pairing energy theory[59, 66] and the compounds of M(III) are close to follow eq. (2) for M(IV), as one would expect.

From a theoretical point of view, it is fascinating that $I(\mathrm{M}4f)$ is larger or comparable with the ionization energies of the loosest bound, filled orbitals of the ligands, even in fluorides, since it is evident from the visible absorption spectra[50, 53] that the nephelauxetic effect (giving a higher limit of the extent of covalent bonding in the sense of delocalization of the partly filled shell[56, 59]) is below 10 percent, and actually below 3 percent in almost all cases. It cannot be concluded in this case that comparable central atom and ligand ionization energies are a sufficient condition for strong covalent bonding. Presumably, the much smaller electron affinity E_A than ionization energy I of the 4f shell may be connected with this paradox[1], and the situation in the metallic elements is also that the 4f shell does not get invaded by the conduction electrons though I^* is positive, *i.e.* I is larger than E_F, because E_A is far smaller than the Fermi level E_F. The extent of covalent bonding in highly heteronuclear cases may be determined by I of the ligands and E_A of the partly filled shell. It may also be argued [59] that the diagonal elements of M.O. theories represent the Mulliken electronegativity $(I + E_A)/2$ rather

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[1] Taking the extreme form of $I'(4f)$ about 25 eV in Tb(IV) and about 9 eV in Tb(III) (*cf.* Table 23) with $(96\ D/13) = 6$ eV due to spin-pairing energy differences and 10 eV is the difference between one-electron ionization energy and affinity. It is noted that the ligand ionization energy is slightly larger than the electron affinity of Tb(IV) which is almost as large as the ionization energy of Tb(III) and identical if disregarding the consequences of the Franck-Condon principle.

than *I*. It should be remembered that the covalent bonding has the extent which minimizes the total energy of the whole molecule or polyatomic ion. Seen from this angle, photo-electron spectrometry determining "vertical" ionization energies complements the information derived from visible and ultra-violet spectra [57, 59] about excitations in a most helpful and unexpected way.

Experimental

The Varian IEE-15 photo-electron spectrometer has been described [7]. With exception of the samples of metallic Ni, Ga, In, Sn and Pt, we measured powdered samples covering about five-sixths of a cylinder covered with one-sided scotch tape [60] (15 mm broad, no. 600P from the Company 3M) normally using the analyzer potential 100 V.
Among the samples, we bought from:

American Potash (Lindsay Division) 455, 525, 526, 531, 533, 534, 536, 537, 539, 541, 543, 544, 545, 546, 547 and 551.

British Drug Houses the AnalaR 5, 19, 21, 22, 27, 183, 193, 262, 325, 355, 365, 419, 461, 477, 489, 572, 573, 601 and the 1, 13, 23, 28, 76, 97, 145, 171, 196, 197, 200, 201, 203, 212, 213, 217, 221, 223, 224, 229, 231, 232, 236, 249, 258, 274, 285, 293, 329, 351, 356, 363, 367, 371, 372, 379, 389, 391, 393, 394, 396, 397, 400, 407, 408, 409, 418, 444, 478, 479, 484, 487, 511, 512, 521, 564, 568, 588, 590, 591, 592, 594, 598 and 602.

Dodge Fibers 181.

Drijfhout (Amsterdam) 51, 72, 323, 328, 332, 352, 357, 362, 366, 465, 468, 483, 486, 596 and 600.

Fluka (Buchs, SG) the puriss. 15, 82, 167, 184, 190, 233, 235, 243, 255, 260, 261, 270, 290, 291, 350, 384, 403, 425, 426, 427, 472, 481, 519, 552, 560 and the 6, 8, 12, 35, 41, 43, 63, 75, 86, 144, 149, 204, 208, 215, 237, 267, 272, 275, 303, 305, 308, 319, 339, 353, 354, 411, 436, 445, 447, 449, 453, 459, 471, 473, 476, 488, 490, 491, 506, 530, 553, 556, 557, 558, 571, 593 and 607.

Heraeus 99.

Johnson and Matthey 124.

Merck pro analysii 2, 30, 269, 462, 567, 575, 577, 580, 589 and the 158, 160, 239, 273, 321, 347, 349, 361, 369, 424, 574, 579, 595 and 597.

Métaux Précieux (Neuchâtel) 470.

Riedel de Haën 374, 399 and 416.

Schuchardt (München) 38, 45, 173, 180, 186, 188, 194, 195, 198, 202, 206, 211, 214, 219, 220, 244, 268, 278, 348, 373, 422, 439, 510, 578, 603 and 605.

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3, 10, 11, 209, 240, 283, 364, 387, 388, 401, 402, 423, 561 and 576.

We are grateful for the gifts of the following samples from

LUCETTE BALSENC (Geneva) 555 and 587.
FRED BASOLO (Evanston, Ill.) 137.
OLE BOSTRUP (Nakskov) 131.
GEORG BRAUER (Freiburg-im-Breisgau) 540.
PETER DAY (Oxford) 109, 146, 309, 311, 313, 318 and 341.
MARCEL DELÉPINE (†, Paris) 39, 103 and 108.
E. DIEMANN (Dortmund) 65, 280, 286, 287, 288, 295, 297, 300, 301, 383, 437, 438, 440, 458, 460, 522, 559, 569 (*cf.* further discussion in ref. [85]).
W. FEITKNECHT (Bern) 392.
R. GUT (Zürich) 182, 192 and 610.
F. HEIN (Jena) 33 and 415.
GEORGE KAUFFMAN (Fresno, Cf.) 282.
CORNELIUS KELLER (Karlsruhe) 606.
YUKIO KONDO (Tokyo) 29, 87, 117, 150, 159 and 404.
KAREN KÜMMEL (née JENSEN) 32.
SALVATORE LOSI (Geneva) 234, 316, 566, 599 and 604.
ANTHONY LUCKEN (Geneva) 281.
ANDREAS LUDI (Bern) 4, 52, 56, 57, 58, 84, 91, 104, 107, 115, 121, 132, 134, 136, 140, 142, 143, 147, 148, 152, 153, 154, 156, 157, 161, 162, 164, 174, 175, 176, 177, 385, 398 and 463.
These compounds are later to be discussed in greater detail.
ROMANO PAPPALARDO (Waltham, Mass.) 191 and 207.
W. PREETZ (Kiel) 327, 334, 340, 345, 360, 516, 517 and 518 [ref. 61].
LENE RASMUSSEN 128 [ref. 92] and 138 [ref. 93].
R. ROULET (Lausanne) 54, 96, 279, 335, 343 and 450.
WALTER SCHNEIDER (Zürich) 106 and 155.
CLAUS SCHÄFFER (Copenhagen) 31, 69, 94 and 277.
G. WATELLE (Dijon) 256.

When one of us worked 1961–68 at the Cyanamid European Research Institute, Cologny (Republic of Geneva) DIETER GARTHOFF (now São Paulo) and HANS-HERBERT SCHMIDTKE (now Frankfurt-am-Main) prepared the following compounds: 40, 44, 46, 49, 55, 61, 68, 71, 73, 79, 90, 92, 93, 110, 111, 123, 129, 163, 165, 166, 168, 169, 170, 172, 178, 179, 185, 289 and

565, a major part of which already has been described by these two authors.

The remaining 200 compounds were prepared by ourselves. The mixed oxides [ref. 53] 386, 457, 527, 528, 529, 532, 550, 582, 585, 586 were made by calcination of the co-precipitated hydroxides from aqueous ammonia. A similar precipitation of lanthanide chlorides in ethanol and $TaCl_5$ in acetonitrile with ammonia was used for the tantalates 535, 538 and 548. The orthovanadates 376, 377, 378 and 380 were obtained by calcination of thoroughly mixed, stoichiometric quantities of the rare earths and no. 82.

Most of the other compounds were made from rather obvious metathetical precipitation in aqueous solution. Stock solutions of indium metal in nitric acid, rare earths in perchloric or hydrochloric acid, HfO_2 in 5M sulphuric acid etc. were used, for instance precipitating the iodates described in the text with 1M iodic acid. A pure sample of 405 precipitated many anions, also 9, 135 and 584 from a solution of Be(II) ,Ce(IV) and Th(IV) in strong $(NH_4)_2CO_3$ We give the literature [90] formula $[Co(NH_3)_6]$ $[Be_2(OH)_3(CO_3)_2]$ for compound no. 9 but we suspect it for being $[Co(NH_3)_6]_2$ $[OBe_4(CO_3)_6]$ in analogy to basic beryllium acetate. Freshly prepared solutions of green *trans*- $[Co\,en_2Cl_2]$ Cl were used for precipitating the salts of this cation. Solutions of $PbCl_6^{-2}$ were obtained from PbO_2 in ice-cold 12M HCl. The tetraphenylborates of many univalent cations are almost insoluble [11, 68], we precipitated them with 0.5M no. 15. The fluorides 187 and 222 were obtained by evaporating a solution of the carbonates in hydrofluoric acid in a nickel crucible. 189 and 210 were obtained by melting the dioxides with KHF_2. $EuSO_4$ was formed from 254 in 2M H_2SO_4 treated with p.a. zinc. The crystalline sulphates were generally made with sulphuric acid from oxides, and from a few carbonates. Palladium(II) chemistry has been discussed [92, 93], 80 and 81 precipitate readily by acidification of a mixture of X^- and $Pdphen(OH)_2$. The black iodides 467, 479 and 514 also precipitate by adding I^- to a solution of Rh(III), Pd(II) or Bi(III) in HCl. Synthetic torbernite 242 was co-precipitated according to MARIE CURIE.

In the tables, we use the abbreviations for the ligands and organic molecules:

aca$^-$ is deprotonated acetylacetone (or 2,4-pentanedione) coordinated to the central atom by two oxygen atoms.

aminin is 1-amino-1-aminomethylcyclohexane, coordinating with two nitrogen atoms.

Bengal Rosa B is a dyestuff $Na_2[C_{20}H_2O_5Cl_4I_4]$

curtis is the condensation product of acetone and ethylenediamine[23] coordinating with two nitrogen atoms.

daes is bis (2-aminoethyl) sulphide coordinating with two nitrogen and one sulphur atom.

den is diethylenetriamine $HN(CH_2CH_2NH_2)_2$ able to coordinate with three nitrogen atoms.

dip is 2,2′-dipyridyl (or 2,2′-bipyridine) coordinating with two nitrogen atoms.

dmg^- is deprotonated dimethylglyoxime, normally coordinating with the two three nitrogen atoms.

en is ethylenediamine (1,2-diaminoethane) $NH_2CH_2CH_2NH_2$ coordinating with two nitrogen atoms.

et_4den is N, N, N″, N″-tetra-ethyl-diethylenetriamine coordinating with nitrogen atoms.

methylene blue is the cation $^{N}_{S}\{C_6H_3N(CH_3)_2\}_2^+$

ns^- is deprotonated 2-mercaptoethylamine $NH_2CH_2CH_2S^-$ coordinating with the nitrogen and the sulphur atom.

phen is 1,10-phenanthroline coordinating with two nitrogen atoms.

phthalocyanine is a macrocyclic ligand; it is di-deprotonated in our complexes and coordinating with four nitrogen atoms.

py is pyridine C_5H_5Ncoordinating with the nitrogen atom.

tartrate is di-deprotonated tartaric acid bound by two oxygen atoms in our dimeric antimony(III) complex (tartar emetic). However, ANDEREGG kindly indicated tetra-deprotonated tartrate and no oxide ligands.

tren is tris (2-aminoethyl) amine $N(CH_2CH_2NH_2)_3$ coordinating with four nitrogen atoms.

urea is $(NH_2)_2CO$. In our complexes, it is coordinated with the oxygen atom.

In almost all our sulphur-containing ligands[55] such as dithiocarbamates $R_2NCS_2^-$ and dithiophosphates $(RO)_2PS_2^-$ both sulphur atoms are coordinated. Contrary to previous belief, many nitrate complexes have two oxygen atoms coordinated to the central atom.

Acknowledgments

We thank the many colleagues for the most interesting compounds mentioned above. The Swiss National Science Foundation provided the funds allowing the purchase of the photo-electron spectrometer.

TABLE 1. Photo-electron signals of lithium, beryllium, boron and nitrogen.

	Compound	C_{st}	I(1s)
1	LiF	[1.4],4.2	63.5
1	repeated	[0.7],4.4	64.4
2	Li_2CO_3	[3.4],4.8	61.6
3	Li_3PO_4	[3.5],5.1	61.6
4	$Li_3[Co(CN)_6]$	4.7	61.3
5	Li_2SO_4	5.2	61.0
6	BeF_2	[3],5.3	123.1
7	K_2BeF_4	[2.5],5.3	122.4
7	repeated	[2.0],5.0	122.6
8	BeO	[2.4],4.7	121.6
9	$[Co(NH_3)_6]\,[Be_2(OH)_3(CO_3)_2]$	[2.8],4.6	120.3
10	$[Be(H_2O)_4]SO_4$	4.8	120.1
10	repeated	4.7	120.8
11	NH_4BePO_4	4.5	119.5
12	$Be(OH)_2$	5.3	118.9
13	KBF_4	[3.1],4.6	202.3
14	[Co en$_2$Cl$_2$]BF$_4$	4.6	200.1
15	$Na[B(C_6H_5)_4]$	6.6	193.0
16	$K[B(C_6H_5)_4]$	5.1	192.9
17	methylene blue[B(C$_6$H$_5$)$_4$]	6.1	191.9
18	$CsUO_2(NO_3)_3$	[2.8],5.1	414.9
19	$Pb(NO_3)_2$	[2.8],5.3	414.8
20	$RbUO_2(NO_3)_3$	[2.7],4.8	414.6
21	$Ba(NO_3)_2$	[3],5.1	414.0
22	$UO_2(NO_3)_2$	4.5	414
23	$CsNO_3$	[3.2],4.8	413.5
607	$Th(NO_3)_4,5H_2O$	4.4	413.2
24	KNO_3	5.1	413.1
25	$RbNO_3$	5.1	413.1
26	$Mg_3Nd_2(NO_3)_{12},24H_2O$	4.6	413.1
27	$Sr(NO_3)_2$	4.7	413.0
28	$Cr(NO_3)_3,9H_2O$	4.6	412.6
29	[Cu en$_2$](NO$_3$)$_2$	4.6	412.4 & 405.5
30	$Fe(NO_3)_3,9H_2O$	4.8	412.2
31	[Crurea$_6$](NO$_3$)$_3$	5.3	412.1 & 405.2
32	[Co en$_2$Cl$_2$]NO$_3$	4.4	411.9 & 405.3
33	[Ni aminin$_2$](NO$_3$)$_2$	4.6	411.4 & 404.8
34	$[N(CH_3)_4]_2PtI_6$	[2],4.8	410.0
35	$Na_2[Fe(CN)_5NO]$	4.7	(409.1) & 403.8

TABLE 1. (continued).

	Compound	C_{st}	$I(1s)$
36	$[N(CH_3)_4]_2CeCl_6$	[2.7],4.5	409.0
37	$[N(C_4H_9)_4]_2PtI_6$	4.8	409.0
38	NH_4SbF_4	[3.5],5.3	408.9
39	$K_2[Ru(NO)Cl_5]$	4.8	408.7
40	$[N(CH_3)_4]SeCN$	4.6	408.6 & 404.2
41	$(NH_4)_3GaF_6$	[3.7],5.4	408.5
42	$(NH_4)_2[In(H_2O)F_5]$	[3.8],5.0	408.3
43	$[N(CH_3)_4]I$	4.9	408.2
44	$[N(C_4H_9)_4]SeCN$	4.2	408.2 & 403.4
45	$(NH_4)_2ZrF_6$	5.1	408.1
46	$[N(CH_3)_4]SCN$	5.1	407.9 & 403.1
47	$[N(CH_3)_3CH_2C_6H_5]_2PtCl_6$	4.6	407.9
48	$[N(C_2H_5)_4]_2PtBr_6$	4.6	407.8
49	$[C_{19}H_{42}N_2]_2[Pt(N_3)_6]$	5.3	407.7 & 403.8 asym.
50	$(NH_4)_3ScF_6$	5.4	407.7
289	$[N(CH_3)_4]_3[Ru(NCS)_6]$	4.3	407.7 & 403.5
51	$(NH_4)_2PtCl_6$	4.8	407.6
52	$[N(CH_3)_4]_3[Co(CN)_6]$	4.9	407.5 & 403.2
53	$[Ni\,en_2](AgI_2)_2$	[2.0],4.6	407.4
54	$[N(C_4H_9)_4][Au(CN)_2Br_2]$	5.3	407.4 & 404.3
11	NH_4BePO_4	4.5	407.3
55	$[N(C_4H_9)_4]ClO_4$	4.8	407.3
56	$(NH_4)_3[Co(CN)_6]$	4.8	407.2 & 403.6
57	$[N(C_2H_5)_4]_3[Co(CN)_6]$	5.1	407.2 & 403.1
58	$[N(C_4H_9)_4]_3[Co(CN)_6]$	5.0	407.2 & 403.4
59	*trans*-$Pd(NH_3)_2Cl_2$	4.8	407.2
60	$[Ni\,en_2](CuI_2)_2$	[2.2],4.6	407.2
61	$[N(CH_3)_4]_3[Ir(SCN)_6]$	4.4	(407.2) & 403.2 &(401.6)
62	$[Ag\,py_4]S_2O_8$	4.2	407.1
584	$[Co(NH_3)_6]_2[Th(CO_3)_5]$	[2.3],4.2	407.0
63	$[N(CH_3)_4]Br$	4.9	407.0
64	$[N(C_2H_5)_4]_2OsCl_6$	5.2	407.0

TABLE 1. (continued).

	Compound	C_{st}	$I(1s)$
65	$[\mathrm{N(CH_3)_4}]\mathrm{ReS_4}$	4.4	407
66	$[\mathrm{N(C_2H_5)_4}]_2\mathrm{MnBr_4}$	4.6	406.9
67	$[\mathrm{Co(NH_3)_6}]_7[\mathrm{Cu(IO_6)_2}]_3$	4.7	406.9
68	$[\mathrm{N(C_4H_9)_4}]_3\mathrm{IrCl_6}$	4.4	406.9
69	$\mathrm{(NH_4)_3CrF_6}$	4.8	406.8
70	$\mathrm{(NH_4)_2}[\mathrm{Fe(H_2O)F_5}]$	4.8	406.8
9	$[\mathrm{Co(NH_3)_6}][\mathrm{Be_2(OH)_3(CO_3)_2}]$	[2.8],4.6	406.8
71	$[\mathrm{Rh\ den\ I_3}]$	[2.4],4.6	406.8
72	$\mathrm{(NH_4)_2PdCl_6}$	5.0	406.8
73	$[\mathrm{N(C_4H_9)_4}]_2[\mathrm{Sn(NCS)_6}]$	5.0	406.8
			& 403.5
74	$[\mathrm{N(CH_3)_4}]_2\mathrm{IrCl_6}$	4.4	406.7
75	$[\mathrm{N(C_2H_5)_4}]\mathrm{I}$	4.5	406.6
76	$\mathrm{(NH_4)_3}[\mathrm{Cr(C_2O_4)_3}]$	5.2	406.6
77	$[\mathrm{Co\ en_2Cl_2}]\mathrm{PF_6}$	4.7	406.6
78	$[\mathrm{Co\ en_2Cl_2}]_3\mathrm{(PW_{12}O_{40})}$	4.0	406.5
79	$[\mathrm{Pd(et_4\ den)Cl}]\mathrm{ClO_4}$	[3.3],5.0	406.5
80	$[\mathrm{Pd\ phen\ Br_2}]$	4.5	406.5
81	$[\mathrm{Pd\ phen\ I_2}]$	4.9	406.5
135	$[\mathrm{Co(NH_3)_6}]_2[\mathrm{Ce(CO_3)_5}]$	4.2	406.5
82	$\mathrm{(NH_4)_3V_3O_9}$	4.6	406.4
83	$[\mathrm{Co(NH_3)_6}][\mathrm{Au(S_2O_3)_2}]$	4.4	406.4
84	$\mathrm{Cd}[\mathrm{Pd(CN)_6}]$	[2.2],4.9	406.3
85	$\mathrm{Pd\ dmg_2}$	4.4	406.3
86	$\mathrm{NH_4}[\mathrm{Cr(NH_3)_2(NCS)_4}]$	[3.7],5.2	406.2
			&(404.9)
			& 403.6
87	$[\mathrm{Co(NH_3)_6}]_2\mathrm{(SiF_6)_3}$	4.4	406.2
88	$[\mathrm{Co\ en_2Cl_2}]\mathrm{BF_4}$	4.6	406.1
89	$[\mathrm{Co\ en_2Cl_2}]\mathrm{MnO_4}$	4.7	406.0
90	$[\mathrm{Rh(NH_3)_5Cl}]\mathrm{Cl_2}$	4.6	406.0
91	$[\mathrm{Ni(CN)_2(NH_3)(C_4H_4S)}]$	5.5	405.9
92	$[\mathrm{Pd(et_4\ den)Br}]\mathrm{ClO_4}$	4.4	405.9
93	$[\mathrm{Pt\ den\ Cl_3}]\mathrm{ClO_4}$	4.5	405.9
94	$[\mathrm{Cr(NH_3)_6}][\mathrm{InCl_6}]$	5.0	405.8
95	$[\mathrm{Co\ en_2\ Cl_2}][\mathrm{B(C_6H_5)_4}]$	5.2	405.8
96	$[\mathrm{Ni(et_4\ den)Cl}]\mathrm{Cl}$	5.1	405.7
97	CuCN	[3.2],5.3	405.7
98	$\mathrm{Cu(S_2CN(C_2H_5)_2)_2}$	4.4	405.7
99	$[\mathrm{Ir(NH_3)_5Cl}]\mathrm{Cl_2}$	4.4	405.7
100	$[\mathrm{Co\ en_2Cl_2}][\mathrm{Cr(NH_3)_2(NCS)_4}]$	4.5	405.6
			&(404.0)
101	$[\mathrm{Pd\ phen\ Cl_2}]$	4.5	405.5

TABLE 1. (continued).

	Compound	C_{st}	$I(1s)$
102	[Pd phen$_2$](ClO$_4$)$_2$	5.1	405.5
103	K[Ir py Cl$_5$]	4.7	405.5
104	Cs$_3$[Co(CN)$_6$]	[2.5],4.6	405.4
105	[(NH$_3$)$_5$CoO$_2$Co(NH$_3$)$_5$](SO$_4$)$_2$HSO$_4$	5.3	405.4
106	[Rh ns$_3$]$_2$Ni(ClO$_4$)$_2$	4.6	405.4
107	Rb$_2$[Pd(CN)$_4$]	4.6	405.4
608	K[OsO$_3$N]	[2.1],4.4	405.4
108	[Ir py$_4$ Cl$_2$]Cl	4.7	405.4
109	[Co(NH$_3$)$_6$]SbCl$_6$	4.3	405.3
110	[Ru(NH$_3$)$_5$NCS](ClO$_4$)$_2$	4.7	405.3
			&(402.9)
111	[Rh den Cl$_3$]	4.8	405.3
112	[Rh py$_4$ Br$_2$]ClO$_4$	4.4	405.3
113	[Ni en$_2$](ClO$_4$)$_2$	4.6	405.2
114	(methylene blue)$_2$PtI$_6$	5.0	405.2
115	Co[Pd(CN)$_4$]	[2],4.0	405.1
116	Ni dmg$_2$	4.9	405.1
117	[Pt(NH$_3$)$_4$](PtCl$_4$)	4.0	405.05
118	Te(S$_2$CN(C$_2$H$_5$)$_2$)$_4$	4.9	405.0
119	[Pd py$_4$]SO$_4$	4.65	404.95
120	[Fe urea$_6$](ClO$_4$)$_3$	5.1	404.9
121	Cu$_3$[Ir(CN)$_6$]$_2$,11H$_2$O	4.5	404.9
122	K[Ag(CN)$_2$]	[2.7],4.5	404.9
123	[Cu den Br]Br	4.7	404.8
124	[Ru(NH$_3$)$_6$]Cl$_3$	4.7	404.75
125	methylene blue[Cr(NH$_3$)$_2$(NCS)$_4$]	5.0	404.7
			& 403.1
126	Cr(S$_2$CN(C$_4$H$_9$)$_2$)$_3$	5.9	404.7
127	Ni(S$_2$CN(C$_2$H$_5$)$_2$)$_2$	4.7	404.7
128	[Pd(NH$_3$)$_4$](CH$_3$C$_6$H$_4$SO$_3$)$_2$	4.8	404.6
128	repeated	4.6	405.2
129	K$_2$[Pt(SeCN)$_6$]	[2.7],4.8	404.6
130	[N(CH$_3$)$_4$]$_2$ReBr$_6$	4.6	404.5
131	[Fe dip$_3$]Br$_2$	5.6	404.4
132	Na$_3$[Co(CN)$_6$]	4.8	404.4
133	[Ni daes$_2$](ClO$_4$)$_2$	4.6	404.4
134	Ni$_2$[Os(CN)$_6$]	5.0	404.4
17	methylene blue[B(C$_6$H$_5$)$_4$]	6.0	404.3
136	Co$_2$[Os(CN)$_6$]	5.0	404.3
137	Ni(NH$_2$CH$_2$CO$_2$)$_2$(H$_2$O)$_2$	3.7	404.3
138	[Ni(tren)phen](ClO$_4$)$_2$	4.6	404.3
139	methylene blue(ClO$_4$)	5.1	404.2
140	H$_3$Co(CN)$_6$	4.7	404.2

TABLE 1. (continued),

	Compound	C_{st}	I(1s)
141	$Co(S_2CN(C_2H_5)_2)_3$	5.8	404.2
142	$[Ni\ en_2][Ni(CN_4]$	5.0	404.2
143	$[Pd\ en_2][Pd(CN)_4]$	4.4	404.2
144	$K[Au(CN)_2]$	4.5	404.2
145	$Na_4[Fe(CN)_6]$, $10H_2O$	4.7	404.1
146	$[Co(NH_3)_6]BiCl_6$	3.6	404.1
147	$[Ni\ en_3][Ni(CN)_4]$	4.9	404.1
148	$[Ni\ en_2][Pd(CN)_4]$	4.4	404.1
149	$K_2[Pd(CN)_4]$	5.1	404.1
150	$[Ni\ en_3]SO_4$	3.8	404.0
151	$[Ni(tren)(NCS)_2]$	4.6	404.0
152	$[Ni\ en_3][Pd(CN)_4]$	4.4	404.0
153	$Cu_3[Co(CN)_6]_2$, $11H_2O$	4.5	404.0
4	$Li_3[Co(CN)_6]$	4.7	403.9
154	$Cu_2[Fe(CN)_6]$, $11H_2O$	4.8	403.8
155	$Co(NCS)_4Hg$	4.7	403.8
156	$[Ni\ en_2][Pt(CN)_4]$	4.1	403.8
157	$[Ni\ en_3][Pt(CN)_4]$	3.9	403.8
158	methylene blue Cl	5.5	403.7
159	$[Co(NH_3)_5Cl]Cl_2$	3.9	403.7
160	$K_2[Ni(CN)_4]$	4.9	403.7
161	$Co_2[Ru(CN)_6]$	4.5	403.6
162	$Ni_2[Ru(CN)_6]$	4.5	403.6
163	$K_2[Hg(SCN)_4]$	5.0	403.6
164	$Cu_2[Os(CN)_6]$	5.0	403.5
165	$[As(C_6H_5)_4][Au(SeCN)_4]$	4.8	403.5
166	$[As(C_6H_5)_4]_3[Ir(SeCN)_6]$	4.1	403.45
167	$K_3[Cr(NCS)_6]$	4.8	403.4 asym.
168	$K_2[Pt(SCN)_6]$	4.8	403.35
169	$K_3[Rh(SCN)_6]$	4.7	403.3
170	$[As(C_6H_5)_4]_3[Os(SCN)_6]$	5.2	403.1
170	repeated	4.6	403.6
171	KSeCN	3.6	403.1
171	repeated	[3.3],5.0	403.9
609	$[As(C_6H_5)_4][OsO_3N]$	4.2	403.6
172	$[As(C_6H_5)_4]_2[Cd(NCSe)_4]$	4.5	403 asym.
173	Mg phthalocyanine	5.4	402.9
174	$Cu_2[Ru(CN)_6]$	4.4	402.8
175	$Ru_4[Fe(CN)_6]_3$	4.9	402.8
176	$Fe_4[Ru(CN)_6]_3$	4.6	402.7 asym.
177	$Fe_4[Os(CN)_6]_3$	4.6	402.7 asym.
178	$[As(C_6H_5)_4]SCN$	4.8	402.2
179	$[P(C_6H_5)_4]SCN$	5.3	401.9
180	Cu phthalocyanine	6.0	401.9

TABLE 2. Photo-electron signals of fluorine, sodium, magnesium, aluminium, silicon and phosphorus.

	Compound	C_{st}	I(1s)	I(2s)	I(2p)
181	CF_2polymer	3.8	695.7	–	–
606	LuF_3	[0.3],5.5	695.5	–	–
182	$CsSbF_6$	[1.5],5.1	695.0	39.3	–
182	repeated	[1.3],5.5	695.3	–	–
–	CF_4(ref. 97)	–	695.0	43.8,40.3	25–16.2
183	MgF_2	[0.8],5.1	695.0	39.4	18.3
183	repeated	[0.1],5.0	695.6	40.6	20
184	LaF_3	[0.0],4.7	694.8	39.1	18.1
185	K_3RhF_6	[2.0],4.7	694.8	38.9	16.4
13	KBF_4	[3.1],4.6	694.0	–	(18),16.1
13	repeated	[2.8],5.4	694.8	38.7	17.7
–	SF_6 (ref. 97)	–	694.6	44.2–39.3	27–16
186	YF_3	[1.5],5.2	694.2	39	17.5
187	TlF	[2.6],5.2	694.2 asym.	37.3	13
1	LiF	[1.4],4.2	692.8	37.4	15.6
1	repeated	[0.7],4.4	694.1	38.0	16.6
–	CHF_3(ref. 97)	–	694.1	–	–
188	CoF_2	[1.1],5.4	694.1	38.9	–
189	K_2GeF_6	[1.3],4.7	694.1	–	–
190	CeF_3	[0.5],4.8	694.1	38.4	17
191	PrF_3	[1.5],4.9	694.1	–	–
192	KPF_6	[2.7],4.5	694.0	39.0	17.3,15.7
193	NaF	[1.2],5.0	692.9	–	16
193	repeated	[0.9],5.1	693.8	(38)	16.8
194	EuF_3	[1],4.8	693.8	37.5	–
195	ErF_3	[1],4.5	693.8	–	–
196	Na_3AlF_6	[1.8],4.8	693.7	–	16.0
197	SrF_2	[1.7],5.5	693.4	37.9	17.0
197	repeated	[1.2],5.0	693.7	38.0	17.1
198	GdF_3	[0.8],4.4	693.6	37.7	–
199	ThF_4	[1.3],4.9	693.6	38.7	17.3
200	K_2SiF_6	[2.4],4.8	693.5	38.6	16.0
200	repeated	[2.4],5.0	693.5	38.8	16.7
201	CaF_2	[1.8],4.6	692.7	38.4	16.1
201	repeated	[1.3],4.5	693.5	38.6	16.3
202	ZrF_4	[1.8],4.4	693.5	37.2	–
7	K_2BeF_4	[2.0],5.0	693.4	38.0	(18),16.0
7	repeated	[2.5],5.3	692.8	–	–
203	BaF_2	[0.3],4.7	693.2	38.0	16.3
203	repeated	[0.1],4.4	693.3	37.9	16.2
77	[Co en_2Cl_2]PF_6	4.7	692.9	–	–
204	GaF_3, $3H_2O$	[2.3],5.0	692.9	38.1	17.6
205	YbF_3	[2.2],4.7	692.9	38.7	–

TABLE 2. (continued).

	Compound	C_{st}	I(1s)	I(2s)	I(2p)
206	NdF_3	[2],4.7	692.8 asym.	37.4	–
207	SmF_3	[2.0],5.0	692.8	–	–
208	K_2NbF_7	[3],5.0	692.7	37	–
209	$KNiF_3$	3.6	690.8	37.2	15.6
209	repeated	[1.3],4.5	692.6	–	–
210	K_2HfF_6	[2.7],5.0	692.6	37.0	–
211	TaF_5	5.3	692.4	–	(17.5),14.9
–	CH_3F(ref. 97)	–	692.4	–	–
212	$[Zn(H_2O)_6]SiF_6$	[2.5],4.9	692.2	38.0	13.6
6	BeF_2	[3],5.3	692.1	39.0	16.7
213	K_2TiF_6	[2.4],4.5	692.1	–	15.2
214	$CuF_2, 2H_2O$	[3.0],5.2	692.0 asym.	–	15.8
215	K_2TaF_7	[3.1],4.5	692.0	–	15
216	$K_2[Cr(H_2O)F_5]$	[1.7],4.9	691.9	36.5	14.7
217	CdF_2	[3],4.8	692.1	–	13.7
217	repeated	[2],4.3	691.9	36.4	14.5
38	NH_4SbF_4	[3.5],5.3	691.9	37.0	–
218	K_2UF_6	[2.4],4.9	691.9	–	–
14	$[Co\ en_2Cl_2]BF_4$	4.6	691.8	–	–
219	CeF_4, H_2O	4.9	691.8	36.9	15.6
219	repeated	[1.7],4.5	692.4	–	–
220	BiF_3	[3.3],5.4	691.7	–	–
221	$NiF_2, 4H_2O$	[2.6],4.7	691.5	–	–
41	$(NH_4)_3GaF_6$	[3.7],5.4	691.3	–	–
222	RbF	4.4	691.3	35.4	14
87	$[Co(NH_3)_6]_2(SiF_6)_3$	4.4	691.1	36.2	–
45	$(NH_4)_2ZrF_6$	5.1	691.0 asym.	35.5	(16)14.1
42	$(NH_4)_2[In(H_2O)F_5]$	[3.8],5.0	691.0	35.8	14.2
50	$(NH_4)_3ScF_6$	5.4	690.9	35.7	–
223	KF	[1.7],4.15	690.4	34.8	14.0
224	PbF_2	[3],4.8	690.1	36	–
610	HgF_2	[2.5],4.5	690.0	–	–
69	$(NH_4)_3CrF_6$	4.75	689.5	–	–
70	$(NH_4)_2[Fe(H_2O)F_5]$	4.8	689.45	34.6	–
225	CsF	4.1	687.8	–	14
–	Ne (ref. 97)	–	870.2	48.4	21.6
193	NaF	[1.2],5.0	1080.2	–	38
193	repeated	[0.9],5.1	1080.9	72.4	39.7
226	NaI	[2.8],5.6	1080.2	72.0	38.4
196	Na_3AlF_6	[1.8],4.8	1080.1	71.6	(37)
227	NaBr	[2.9],5.3	1079.3	71	37.7
228	NaCl	[3.0],5.2	1079.0	–	37.8
15	$Na[B(C_6H_5)_4]$	6.6	1078.8	–	37.4
230	$NaZn(UO_2)_3(CH_3CO_2)_9$	[2.5],4.6	1078.4	–	–

TABLE 2. (continued).

	Compound	C_{st}	I(1s)	I(1s)	I(2p)
231	$Na_2S_2O_6, 2H_2O$	5.3	1078.3	–	37.4
232	$NaHSeO_3$	[2.3],4.7	1078.3	70.3	–
233	Na_2WO_4	[3.4],5.6	1078,3	–	–
234	$Na_3[Au(S_2O_3)_2]$	4.8	1078.3	–	–
235	$NaIO_4$	4.7	1078.2	–	37.3
236	$Na_2SeO_4, 10H_2O$	[3],4.7	1078.0	–	37.5
237	Na_5IO_6	5.2	1078.0	–	37.6
238	$NaMg(UO_2)_3(CH_3CO_2)_9$	[3],4.4	1078.0	–	–
239	$NaBrO_3$	5.2	1077.8	–	37.4
229	$Na[Sb(OH)_6]$	[2.5],4.4	1077.7	–	–
591	Na_2TeO_3	5.0	1077.6	–	36.7
591	repeated	[2.8],4.8	1078.0	–	–
145	$Na_4[Fe(CN)_6], 10H_2O$	4.7	1077.5	69.9	37.0
132	$Na_3[Co(CN)_6]$	4.8	1077.5	–	–
592	$Na_2[Sn(OH)_6]$	[3],4.5	1077.5	–	36
593	Bengal Rosa B	4.8	1077.4	–	37
594	$NaAsO_2$	4.7	1077.4	–	37.0
595	Na_2MoO_4	5.0	1077.4	–	36.7
596	$Na_3RhCl_6, 12H_2O$	5.0	1077.4	–	36.5
597	$Na_2HAsO_4, 7H_2O$	4.3	1077.3	69.5	36.1
598	$Na_2[TeO_2(OH)_4]$	4.7	1077.3	–	–
599	$Na_3[Au(SO_3)_2]$	[2.7],5.4	1076.9	–	–
600	Na_2IrCl_6	4.6	1076.8	–	36.1
600	repeated	4.7	1077.4	–	–
35	$Na_2[Fe(CN)_5NO]$	4.7	1076.7	68.8	–
601	$Na_2S_2O_3$	5.7	1076.5	–	–
602	$Na_3VO_4, 14H_2O$	4.5	1076.4	–	35.3
603	Na_3SbS_4	4.3	1076.3	69.4	36.3
604	$Na_7H_4Mn(IO_6)_3$	4.1	1076.2	–	–
183	MgF_2	[0.8],5.1	1314.1	98.9	60.1
183	repeated	[0.1],5.0	1314.3	99.9	60.5
183	repeated	[1.1],5.0	1313.7	–	–
403	MgO	[0.4],4.0	1311.3	96.5	57.7
26	$Mg_3Nd_2(NO_3)_{12}, 24H_2O$	4.6	1310.1	95.6	56.5
238	$NaMg(UO_2)_3(CH_3CO_2)_9$	[3],4.4	1310	–	–
605	$Mg(UO_2)_2(CH_3CO_2)_6$	5.1	1309.3	–	56.1
173	Mg phthalocyanine	5.4	1307.7	–	–
196	Na_3AlF_6	[1.8],4.8	–	128.1	83.3
240	$CsAlSi_2O_6$	[2.5],4.7	–	126.4	–
241	Al, foil, + oxide	4.3	–	124.5 & 122.6	79.7 & 76.9
200	K_2SiF_6	[2.4],4.8	–	–	111.7
200	repeated	[2.4],5.0	–	163	112.0
212	$[Zn(H_2O)_6]SiF_6$	[2.6],4.9	–	162	110

TABLE 2. (continued).

	Compound	C_{st}	$I(1s)$	$I(2s)$	$I(2p)$
87	$[Co(NH_3)_6]_2(SiF_6)_3$	4.4	–	160.8	109.9
240	$CsAlSi_2O_6$	[2.5],4.7	–	160.8	109.8
192	KPF_6	[2.7],4.5	–	–	145.4
77	$[Co\ en_2Cl_2]PF_6$	4.7	–	–	143.2
242	$Cu(UO_2)_2(PO_4)_2$	[2.0],4.6	–	–	141.3
243	Ag_3PO_4	[1.9],4.7	–	–	141.1
244	$CePO_4$	[2.4],4.8	–	–	141.1
3	Li_3PO_4	[3.5],5.1	–	–	140.2
11	NH_4BePO_4	4.5	–	–	139.6
245	$Ni(S_2P(OC_3H_7)_2)_2$	5.1	–	–	139.1
246	$Ir(S_2P(OC_3H_7)_2)_3$	4.5	–	–	138.6
247	$Co(S_2P(OC_3H_7)_2)_3$	6.4	–	–	138.5
248	$[P(C_6H_5)_3H]_2UCl_6$	4.6	–	–	138.1
179	$[P(C_6H_5)_4]SCN$	5.3	–	–	137.8

TABLE 3. Photo-electron signals of sulphur (the shoulder corresponding to $2p_{1/2}$ is not given).

	Compound	C_{st}	$I(2p)$
–	SF_6(ref. 97)	–	180.4
249	$BaSO_4$	[3.2],5.9	177.7
249	repeated	[1.1],5.0	177.8
250	$La_2(SO_4)_3$	[2.6],5.0	176.6
251	$Gd_2(SO_4)_3$	[2.5],4.8	176.6
252	$U(SO_4)_2$	[2.5],4.8	176.4
253	$SrSO_4$	[2.5],4.9	176.2
254	$Eu_2(SO_4)_3$	[2.5],4.5	176.2
255	$CdSO_4, H_2O$	5.0	176.1
256	$CuSO_4, 3H_2O$	5.0	176.0
257	Cs_2SO_4	4.9	175.8
258	$BaS_2O_6, 2H_2O$	4.8	175.8
259	$EuSO_4$	[2.4],4.4	175.8
234	$Na_3[Au(S_2O_3)_2]$	[2.7],4.8	175.8 & 170.3
260	$Sc_2(SO_4)_3$	5.3	175.7
261	$Ga_2(SO_4)_3$	4.4	175.7
262	Tl_2SO_4	5.1	175.7
263	$Pr_2(SO_4)_3$	4.2	175.6
264	$PbSO_4$	4.5	175.6
231	$Na_2S_2O_6, 2H_2O$	5.3	175.5
265	$Y_2(SO_4)_3$	4.4	175.5
10	$[Be(H_2O)_4]SO_4$	4.8	175.2

TABLE 3. (continued).

	Compound	C_{st}	$I(2p)$
10	repeated	4.7	175.8
266	$Yb_2(SO_4)_3$	4.2	175.2
267	$Ce_2(SO_4)_3$	4.7	175.1
268	UO_2SO_4	5.1	175.1
269	$VOSO_4, 5H_2O$	4.8	174.8
270	$CuSO_4, 5H_2O$	5.3	174.8
271	$[Ag\,py_4]S_2O_8$	4.2	174.8
272	Ag_2SO_4	[3],4.3	174.8
5	Li_2SO_4	5.2	174.7
273	$[Ni(H_2O)_6]SO_4$	4.1	174.6
274	$PbS(+PbSO_4?)$	4.2	174.6 & 167.7
83	$[Co(NH_3)_6][Au(S_2O_3)_2]$	4.4	174.5 & 169.2
275	Rb_2SO_4	4.1	174.4
276	$Nd_2(SO_4)_3$	[2.5],4.6	174.4
277	$[Cr(NH_3)_6](SO_4)Cl$	5.3	174.2
105	$[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2HSO_4$	5.3	174.1
278	$K_2S_4O_6$	5.3	174.0 & 169.7
110	$[Ru(NH_3)_5NCS](ClO_4)_2$	4.7	173.9
601	$Na_2S_2O_3$	5.7	173.8 & 167.8
128	$[Pd(NH_3)_4](CH_3C_6H_4SO_3)_2$	4.8	173.3
128	repeated	4.6	173.5
91	$[Ni(CN)_2(NH_3)(C_4H_4S)]$	5.5	173.3
119	$[Pd\,py_4]SO_4$	4.6	173.25
599	$Na_3[Au(SO_3)_2]$	5.45	173.1
150	$[Ni\,en_3]SO_4$	3.8	173.0
279	$[PtCl_2(S(C_2H_5)_2)_2]$	5.0	172.1
–	H_2S(ref. 97)	–	170.2
280	Tl_3TaS_4	4.8	170.1
281	GaS	[3.0],5.0	169.9
–	CS_2(ref. 97)	–	169.8
282	$[Ir(S(C_2H_5)_2)_3Cl_3]$	5.2	169.6
283	ZnS	[2.2],4.6	169.4
139	methylene blue(ClO_4)	5.1	169.3
133	$[Ni\,daes_2](ClO_4)_2$	4.6	169.3
284	$Au(SCH_2CO_2H)$	3.9	169.3
17	methylene blue$[B(C_6H_5)_4]$	6.0	169.2
168	$K_2[Pt(SCN)_6]$	4.8	169.1
163	$K_2[Hg(SCN)_4]$	5.0	169.0
155	$Co(NCS)_4Hg$	4.7	168.9
285	CdS	[3.2],4.7	168.9
158	methylene blue Cl	5.5	168.7

TABLE 3. (continued).

	Compound	C_{st}	$I(2p)$
286	$\mathrm{Tl_2[MoO_2S_2]}$	4.7	168.6
287	$\mathrm{Cs_2WS_4(+S?)}$	5.2	168.6 & 165.8
288	$\mathrm{Tl_2MoS_4}$	4.4	168.5
73	$\mathrm{[N(C_4H_9)_4]_2[Sn(NCS)_6]}$	5.0	168.5
61	$\mathrm{[N(CH_3)_4]_3[Ir(SCN)_6]}$	4.4	168.5
100	$\mathrm{[Coen_2\,Cl_2][Cr(NH_3)_2(NCS)_4]}$	4.5	168.4
98	$\mathrm{Cu(S_2CN(C_2H_5)_2)_2}$	4.4	168.3
289	$\mathrm{[N(CH_3)_4]_3[Ru(NCS)_6]}$	4.3	168.3
169	$\mathrm{K_3[Rh(SCN)_6]}$	4.7	168.3
86	$\mathrm{NH_4[Cr(NH_3)_2(NCS)_4]}$	[3.7],5.2	168.2
106	$\mathrm{[Rh\,ns_3]_2Ni(ClO_4)_2}$	4.6	168.2
290	$\mathrm{AgS_2CN(C_2H_5)_2}$	[3.3],5.1	168.2
291	$\mathrm{In_2S_3}$	[3],4.7	168.1
292	$\mathrm{In_2(S_2CN(C_2H_5)_2)_3}$	[3],4.8	168.1
167	$\mathrm{K_3[Cr(NCS)_6]}$	4.8	168.0
245	$\mathrm{Ni(S_2P(OC_3H_7)_2)_2}$	5.1	168.0
46	$\mathrm{[N(CH_3)_4]SCN}$	5.1	167.9
125	methylene blue$\mathrm{[Cr(NH_3)_2(NCS)_4]}$	5.0	167.9
293	CuS	5.5	167.9
294	$\mathrm{Rh(S_2P(OC_2H_5)_2)_3}$	4.5	167.9
295	$\mathrm{Tl_2WS_4}$	4.2	167.9
170	$\mathrm{[As(C_6H_5)_4]_3[Os(SCN)_6]}$	5.2	167.9
170	repeated	4.6	168.4
296	$\mathrm{Pb(S_2CN(C_2H_5)_2)_2}$	4.2	167.9
297	$\mathrm{Tl_3VS_4}$	4.7	167.8
151	$\mathrm{[Ni\,tren(NCS)_2]}$	4.6	167.6
298	$\mathrm{As(S_2CN(C_2H_5)_2)_3}$	4.8	167.6
299	$\mathrm{Sb(S_2CN(C_2H_5)_2)_3}$	4.9	167.6
141	$\mathrm{Co(S_2CN(C_2H_5)_2)_3}$	5.8	167.5
247	$\mathrm{Co(S_2P(OC_3H_7)_2)_3}$	6.4	167.5
65	$\mathrm{[N(CH_3)_4]ReS_4}$	4.4	167.5
300	$\mathrm{(NH_4)_3VS_4}$	5.5	167.4
178	$\mathrm{[As(C_6H_5)_4]SCN}$	4.8	167.4
118	$\mathrm{Te(S_2CN(C_2H_5)_2)_4}$	4.9	167.4
126	$\mathrm{Cr(S_2CN(C_4H_9)_2)_3}$	5.9	167.2
301	$\mathrm{Cs_2MoS_4(+S?)}$	4.1	167.2 & 164.5
603	$\mathrm{Na_3SbS_4}$	4.3	167.2
302	$\mathrm{Pb(S_2P(OC_2H_5)_2)_2}$	4.8	167.0
179	$\mathrm{[P(C_6H_5)_4]SCN}$	5.3	166.9
303	$\mathrm{Ag_2S}$	4.6	166.9
127	$\mathrm{Ni(S_2CN(C_2H_5)_2)_2}$	4.7	166.8
246	$\mathrm{Ir(S_2P(OC_3H_7)_2)_3}$	4.5	166.8

TABLE 4. Photo-electron signals of chlorine (the shoulder corresponding to $2p_{1/2}$ is not given).

	Compound	C_{st}	$I(2p_{3/2})$	$I(3p)$
304	$KClO_4$	4.8	215.0	–
305	$[Co(H_2O)_6](ClO_4)_2$	4.8	214.5	–
306	$[V\ urea_6](ClO_4)_3$	5.4	214.0	–
79	$[Pd(et_4\ den)Cl]ClO_4$	[3.3],5.0	213.9	–
			& 204.2	–
110	$[Ru(NH_3)_5NCS](ClO_4)_2$	4.7	213.7	–
93	$[Pt\ den\ Cl_3]ClO_4$	4.5	213.7	–
			& 204.5	–
106	$[Rh\ ns_3]_2Ni(ClO_4)_2$	4.6	213.5	–
113	$[Ni\ en_2](ClO_4)_2$	4.6	213.3	–
133	$[Ni\ daes_2](ClO_4)_2$	4.6	213.3	–
92	$[Pd(et_4\ den)Br]ClO_4$	4.4	213.2	–
120	$[Fe\ urea_6](ClO_4)_3$	5.1	213.1	–
138	$[Ni(tren)phen](ClO_4)_2$	4.6	213.1	–
307	$[Ni\ curtis_2](ClO_4)_2$	4.7	212.8	–
102	$[Pd\ phen_2](ClO_4)_2$	5.1	212.8	–
55	$[N(C_4H_9)_4]ClO_4$	4.8	212.6	–
139	methylene blue(ClO_4)	5.1	212.6	–
112	$[Rh\ py_4\ Br_2]ClO_4$	4.4	212.5	–
308	CsCl	[0.4],5.2	207.6	13.4
308	repeated	[0.7],5.2	207.3	13.8
309	$Cs_4(InCl_6)(SbCl_6)$	[3.3],4.9	207	–
310	Cs_2PtCl_6	[1.6],4.3	206.9	15.7
311	$CsSbCl_6$	[2.0],5.0	208.8	–
312	Rb_2PtCl_6	[2.5],5.0	206.8	15.6
313	$Cs_4(SbCl_6)(TlCl_6)$	[2.3],4.6	206.7	–
314	Cs_2PbCl_6	[2.1],4.9	206.5	12.5
315	$Cs_2[Rh(H_2O)Cl_5]$	[2.0],4.9	206.3	14.0
316	Au_2Cl_6	4.4	206.2	15
228	NaCl	[3.0],5.2	206.1	12.2
593	Bengal Rosa B	4.8	206.0	–
317	LaOCl	[2],4.4	206.0	–
318	$Cs_4(Sb^{III}Cl_6)(Sb^{V}Cl_6)$	[3.1],4.9	205.9	–
319	RbCl	[2.8],5.2	205.7	11.9
59	$[Pd(NH_3)_2Cl_2]$	4.8	205.6	–
320	K_2PtCl_6	[3],4.6	205.5	14.2
321	KCl	[2.3],4.8	205.45	11.9
322	Cs_2IrCl_6	5.7	205.4	–
322	repeated	4.9	205.6	14
323	$KAuCl_4$	3.2	205.4	–
324	K_2OsCl_6	3.8	203.9	12.1
324	repeated	5.0	205.3	13.7
325	$MnCl_2,\ 4H_2O$	4.3	205.2	–

TABLE 4. (continued).

	Compound	C_{st}	$I(2p_{3/2})$	$I(3p)$
326	$\mathrm{Cs_2OsCl_6}$	4.8	205.2	–
327	$\mathrm{Cs_2[OsCl_5I]}$	4.4	205.2	–
328	$\mathrm{K_2PtCl_4}$	4.4	205.2	–
329	SbOCl	[2.5],4.7	205.1	–
330	$\mathrm{PbCl_2}$	[2.5],4.6	205.1	–
331	$\mathrm{[Co\ en_2Cl_2]_2PbCl_6}$	[3.0],5.0	205.1	11
332	$\mathrm{K_2PdCl_4}$	4.8	205.0	–
77	$\mathrm{[Co\ en_2Cl_2]PF_6}$	4.7	205.0	–
78	$\mathrm{[Co\ en_2Cl_2]_3(PW_{12}O_{40})}$	4.0	204.9	–
36	$\mathrm{[N(CH_3)_4]_2CeCl_6}$	4.2	204.9	–
64	$\mathrm{[N(C_2H_5)_4]_2OsCl_6}$	5.2	204.8	11.6
89	$\mathrm{[Co\ en_2Cl_2]MnO_4}$	4.7	204.7	–
333	$\mathrm{RhCl_3}$	4.9	204.7	–
14	$\mathrm{[Co\ en_2Cl_2]BF_4}$	4.6	204.6	–
39	$\mathrm{K_2[Ru(NO)Cl_5]}$	[1.5],4.8	204.6	–
334	$\mathrm{Rb_2[OsCl_4I_2]}$	4.6	204.6	–
335	$\mathrm{[N(C_4H_9)_4]AuCl_4}$	5.2	204.6	–
600	$\mathrm{Na_2IrCl_6}$	4.6	204.5	–
600	repeated	4.7	204.9	–
596	$\mathrm{Na_3RhCl_6, 12H_2O}$	5.0	204.4	12.4
51	$\mathrm{(NH_4)_2PtCl_6}$	3.3	204.4	13.1
51	repeated	4.8	204.6	13.6
94	$\mathrm{[Cr(NH_3)_6]InCl_6}$	5.0	204.4	–
336	$\mathrm{K_3MoCl_6}$	4.5	204.3	–
337	$\mathrm{K_2ReCl_6}$	3.7	204.2	12.1
338	$\mathrm{Tl_2PtCl_6}$	2.8	204.2	–
339	AgCl	4.8	204.1	–
99	$\mathrm{[Ir(NH_3)_5Cl]Cl_2}$	4.4	204.1	–
117	$\mathrm{[Pt(NH_3)_4](PtCl_4)}$	4.0	204.1	–
47	$\mathrm{[N(CH_3)_3CH_2C_6H_5]_2PtCl_6}$	4.6	204.1	13
95	$\mathrm{[Co\ en_2Cl_2][B(C_6H_5)_4]}$	5.2	204.0	–
90	$\mathrm{[Rh(NH_3)_5Cl]Cl_2}$	4.6	204.0	–
279	$\mathrm{[PtCl_2(S(C_2H_5)_2)_2]}$	5.0	203.9	–
159	$\mathrm{[Co(NH_3)_5Cl]Cl_2}$	3.9	203.8	–
32	$\mathrm{[Co\ en_2Cl_2]NO_3}$	4.4	203.8	–
109	$\mathrm{[Co(NH_3)_6]SbCl_6}$	4.3	203.8	–
340	$\mathrm{Cs_2[OsCl_2I_4]}$	5.0	203.8	–
72	$\mathrm{(NH_4)_2PdCl_6}$	5.0	203.75	–
248	$\mathrm{[P(C_6H_5)_3H]_2UCl_6}$	4.6	203.75	–
111	$\mathrm{[Rh\ den\ Cl_3]}$	4.8	203.7	(11)
108	$\mathrm{[Irpy_4Cl_2]Cl}$	4.7	203.7	–
103	$\mathrm{K[IrpyCl_5]}$	4.7	203.7	–
96	$\mathrm{[Ni(et_4\ den)Cl]Cl}$	5.1	203.6	–
101	$\mathrm{[Pd\ phen\ Cl_2]}$	4.5	203.6	–

TABLE 4. (continued).

	Compound	C_{st}	$I(2p_{3/2})$	$I(3p)$
341	$[Co(NH_3)_6]TlCl_6$	3.7	203.6	–
146	$[Co(NH_3)_6]BiCl_6$	3.6	203.5	–
342	$[Co\ en_2Cl_2]ReO_4$	5.0	203.5	–
343	$[N(C_4H_9)_4]_2PtCl_4$	5.3	203.5	11
282	$[Ir(S(C_2H_5)_2)_3Cl_3]$	5.2	203.4	–
344	$[As(C_6H_5)_4]_2PbCl_6$	4.8	203.4	–
345	$[N(C_4H_9)_4]_2[OsCl_4I_2]$	4.2	203.3	–
346	$[As(C_6H_5)_4]_2ReCl_6$	4.9	203.2	–
68	$[N(C_4H_9)_4]_3IrCl_6$	4.4	203.1	–
124	$[Ru(NH_3)_6]Cl_3$	4.7	202.95	–
74	$[N(CH_3)_4]_2IrCl_6$	4.4	202.85	–

TABLE 5. Photo-electron signals of potassium, calcium, scandium, titanium and vanadium.

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3s)$	$I(3p)$
–	Ar (ref. 97)	–	250.6	248.5	29.3	15.8
189	K_2GeF_6	[1.3],4.7	304.7	302.0	–	26.0
185	K_3RhF_6	[2.0],4.7	304.4	301.7	42	25.7
7	K_2BeF_4	[2.5],5.3	303.8	301.3	–	–
7	repeated	[2.0],5.0	304.2	301.5	41.6	25.4
200	K_2SiF_6	[2.4],4.8	303.7	301.2	41.0	25.2
200	repeated	[2.4],5.0	304.1	301.4	41.9	25.5
192	KPF_6	[2.7],4.5	303.8	301.05	39.0	24.75
13	KBF_4	[3.1],4.6	303.4	301.0	39.6	24.8
13	repeated	[2.8],5.4	304.4	301.8	41.4	25.7
347	KI	[1.6],4.7	303.75	301.0	40.7	24.8
209	$KNiF_3$	3.6	–	300.75	(37.8)	24.8
209	repeated	[1.3],4.5	303.7	300.9	(38)	25.2
210	K_2HfF_6	[2.7],5.0	303.5	300.8	(41)	–
348	K_4BiI_7	[3],4.9	303	300.5	–	24.2
208	K_2NbF_7	[3],5.0	303.2	300.5	40	–
349	KIO_4	[2.8],5.3	303.4	300.5	40.1	24.3
213	K_2TiF_6	[2.4],4.5	303.1	300.45	(36.9)	24.3
223	KF	[1.7],4.15	303.0	300.35	40.3	24.15
321	KCl	[2.3],4.8	303.0	300.3	40.2	23.9
216	$K_2[Cr(H_2O)F_5]$	[1.7],4.9	303.0	300.3	41	24.3
218	K_2UF_6	[2.4],4.9	302.9	300.3	–	–
350	KIO_3	[3.2],5.3	303.1	300.2	40.5	23.8
351	K_2HgI_4	[2.4],4.6	302.6	300.2	–	–
608	$K[OsO_3N]$	[2.1],4.4	303	300.0	40	24.0

TABLE 5. (continued).

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3s)$	$I(3p)$
352	$KAuBr_4$	3.4	302.65	300.0	(38.3)	22.4
320	K_2PtCl_6	[3],4.6	302.6	299.9	39.9	23.7
304	$KClO_4$	4.8	302.5	299.8	39.9	23.9
353	KBr	[3.1],4.6	302.4	299.8	39.3	23.3
129	$K_2Pt(SeCN)_6$	[2.7],4.8	303	299.8	–	23.6
354	$KSb(OH)_6$	5.1	302.3	299.7	(38)	–
355	$K_2[Sb_2O_2tartrate_2]$	[3],4.9	302.5	299.6	(39)	–
215	K_2TaF_7	[3.1],4.5	302.3	299.6	(36)	23.8
356	K_2HAsO_4	[2.8],4.5	303	299.5	40	23.5
39	$K_2[Ru(NO)Cl_5]$	[1.5],4.8	302.1	299.4	39.4	23.2
357	$KReO_4$	[2],3.7	302.1	299.4	–	23.6
358	K_2PtI_6	4.6	302.0	299.4	–	23.6
332	K_2PdCl_4	4.8	301.9	299.3	39.2	23.2
122	$K[Ag(CN)_2]$	[2.7],4.5	302.1	299.3	–	–
359	K_2ReBr_6	4.8	302.1	299.3	39.4	22.9
360	$K_2[OsCl_2I_4]$	4.1	301.8	299.2	39.4	23.0
328	K_2PtCl_4	4.4	302	299.2	–	23.4
149	$K_2[Pd(CN)_4]$	5.1	301.8	299.1	38	–
361	$KBrO_3$	[3.3],5.0	301.6	299.0	–	–
362	$K_2[OsO_2(OH)_4]$	4.8	301.7	299.0	–	–
16	$K[B(C_6H_5)_4]$	5.1	301.6	298.9	39.0	22.7
24	KNO_3	5.1	301.4	298.8	38.9	22.7
278	$K_2S_4O_6$	5.3	301.4	298.8	38.5	22.5
337	K_2ReCl_6	3.7	301.3	298.7	39.0	22.4
363	$K_2[TiO(C_2O_4)_2]$	4.9	301.6	298.8	–	–
160	$K_2[Ni(CN)_4]$	4.9	301.3	298.8	38.9	22.9
336	K_3MoCl_6	4.5	301.6	298.8	38.9	23.4
364	K_2PtBr_6	2.6	301.45	298.8	39.4	23.1
364	repeated	5.0	301.7	299.0	–	23.9
144	$K[Au(CN)_2]$	4.5	301.3	298.8	–	–
163	$K_2[Hg(SCN)_4]$	5.0	301.5	298.8	–	–
365	$K_4[Fe(CN)_6]$	5.1	301.3	298.6	39.0	22.8
366	K_2IrBr_6	4.7	301.3	298.5	39.0	23.6
167	$K_3[Cr(NCS)_6]$	4.8	301.1	298.4	38.7	22.6
367	$K_3[Cr(C_2O_4)_3]$	5.3	–	298.4	38.4	22.3
368	$KMnO_4$	5.1	301.1	298.4	38.5	22.4
324	K_2OsCl_6	3.8	301.1	298.4	38.7	22.7
324	repeated	5.0	302.4	299.7	–	–
168	$K_2[Pt(SCN)_6]$	4.8	301.0	298.3	38.5	22.5
171	KSeCN	3.6	301.0	298.1	–	–
171	repeated	[3.3],5.0	301.0	298.2	39	–
369	$K_3[Fe(CN)_6]$	5.4	300.5	297.9	38.1	21.9
103	$K[IrpyCl_5]$	4.7	301	297.9	–	–
201	CaF_2	[1.8],4.6	359.5	356.0	–	33.4
201	repeated	[1.3],4.5	359.6	356.1	52.5	33.7

TABLE 5. (continued).

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3s)$	$I(3p)$
370	$Ca(IO_3)_2$	[2.2],4.6	358.2	354.7	–	32.2
371	$CaCrO_4$	4.7	355.7	352.3	–	30.3
260	$Sc_2(SO_4)_3$	5.3	414.6	410.05	–	39.5
50	$(NH_4)_3ScF_6$	5.4	414.2	410	–	39.4
372	Sc_2O_3	5.0	413.2	408.75	–	38.3
213	K_2TiF_6	[2.4],4.5	472	469.0	–	–
373	$Bi_2Ti_2O_7$	[2.3],4.7	473	465.9	–	45
374	TiO_2	[3],4.8	471.0	465.3	–	43.6
363	$K_2[TiO(C_2O_4)_2]$	4.9	470.6	464.7	–	–
375	$Yb_2Ti_2O_7$	4.6	469.8	464.1	–	–
376	$YbVO_4$	[2.8],4.9	531	524.1	–	49.1
377	YVO_4	4.7	530	523.4	–	48.9
378	$PrVO_4$	4.8	530.6	523.0	–	49
269	$VOSO_4, 5H_2O$	4.8	530,528	522.9	–	(51),47.5
379	V_2O_5	[3],5.3	529.6	522.2	–	47.4
380	$DyVO_4$	3.4	529	522.1	–	–
380	repeated	[1.8],4.2	531	524.2	–	49.8
602	$Na_3VO_4, 14H_2O$	4.5	528	522.0	–	47.0
82	$(NH_4)_3V_3O_9$	4.6	529.5	521.6	75.8	47.6
306	$[V urea_6](ClO_4)_3$	5.4	527.6	521.3	–	48,46
300	$(NH_4)_3VS_4$	5.5	526.6	519.1	–	43.7

TABLE 6. Photo-electron signals of chromium, manganese, iron and cobalt.

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p)$	$I(3d)$
81	$BaCr^{VI}O_4$	[2.2],4.9	596.7	587.5	56.2	–
82	$Ce(Cr^{VI}O_4)_2$	[3.0],4.8	595.5	586.6	55	–
16	$K_2[Cr^{III}(H_2O)F_5]$	[1.7],4.9	(598.2),596.0	(588.2),586.1	(55),52.8	10.8
11	$Hg_2Cr^{VI}O_4$	[1.8],4.0	595.3	585.9 asym	55.2	–
71	$CaCr^{VI}O_4$	4.7	594.1	584.9	53.7	–
83	$Tl_2Cr^{VI}O_4$	4.5	594	584.9	54.6	–
84	$Ag_2Cr^{VI}O_4$	[3.1],5.1	593.9	584.7	54.3	–
85	$Cd_3[Cr^{III}(CN)_6]_2$	[2.9],4.8	(597),594.2	(586),584.3	51.5	–
69	$(NH_4)_3Cr^{III}F_6$	4.8	594.0	(586),583.8	(55),51.0	12
28	$Cr^{III}(NO_3)_3, 9H_2O$	4.6	(595),593.1	(586),583.6	(55),50.4	10.6
67	$K_3[Cr^{III}(C_2O_4)_3]$	5.3	593.2	(585),583.5	55.8,50.6	10.5
94	$[Cr^{III}(NH_3)_6]InCl_6$	5.0	593.7	(586),583.5	(52),50.4	10.5
31	$[Cr^{III}urea_6](NO_3)_3$	5.3	(595),592.9	(585),583.4	(53),49.9	10.7
77	$[Cr^{III}(NH_3)_6](SO_4)Cl$	5.3	593.1	583.3	(55),50.1	11
86	$LaCr^{III}O_3$	[2.5],4.5	(596),593.2	(586),583.1	–	12
00	$[Co\ en_2\ Cl_2][Cr^{III}(NH_3)_2(NCS)_4]$	4.5	593	(585),583.0	50 broad	–
67	$K_3[Cr^{III}(NCS)_6]$	4.8	(594),592.1	(585),582.9	(53),50	8.2

TABLE 6. (continued).

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p)$	$I(3d)$
387	$PbCr^{VI}O_4$	3.3	592.2	582.9	52.7	–
76	$(NH_4)_3[Cr^{III}(C_2O_4)_3]$	5.2	(594),592.5	(585),582.8	–	–
86	$NH_4[Cr^{III}(NH_3)_2(NCS)_4]$	[3.7],5.2	(594),592.0	582.8	50.0	–
125	methylene blue$[Cr^{III}(NH_3)_2(NCS)_4]$	5.0	592.4 asym.	(584),582.4	–	–
388	Cr_2O_3	4.2	(594),592.3	(584),582.3	(51),49.5	8.2
126	$Cr(S_2CN(C_4H_9)_2)_3$	5.9	589.6	580.4	48.0	–
389	Cr, powder, oxidized	4.5	592.7	582.8	51.3,49.6	–
390	$CsMnO_4$(shoulders Mn^{IV})	[2.7],4.7	663.4,(660)	652.3,(648.7)	61.3	–
391	$Ba(MnO_4)_2$ (“ ”)	4.4	663,660.1	651.2,648.7	60,57	–
368	$KMnO_4$ (“ ”)	5.1	663,659.7	651.2,(647.9)	60.4,55.7	–
89	$[Co\ en_2\ Cl_2]MnO_4$ (“ ”)	4.7	662.8,659.8	651.4,(648.2)	59.5,55.5	–
604	$Na_7H_4[Mn^{IV}(IO_6)_3]$	4.1	658 broad	648.4	–	–
325	$MnCl_2, 4H_2O$	4.3	664.8,659.9	651.9,648.2	(59),55.4)	–
392	α-type MnO_2	4.7	(663),659.6	(652),648.0	55.5	–
393	$Mn^{II}C_2O_4, 2H_2O$	4.7	661.3 broad	647.7 broad	(59),55.0	11.3
66	$[N(C_2H_5)_4]_2\ Mn^{II}Br_4$	4.6	663,657.8	650.6,646.4	(55),53.2	8.5
70	$(NH_4)_2[Fe^{III}(H_2O)F_5]$	4.8	(739.8),733.1	(727.8),718.9	63.6	13.6,12.1
120	$[Fe^{III}urea_6](ClO_4)_3$	5.1	(735),731.7	(726),717.8	63,62	10.2
30	$Fe^{III}(NO_3)_3, 9H_2O$	4.8	(735),731.0	(724),717.6	(64.5),62.1	10
394	$(NH_4)_3[Fe^{III}(C_2O_4)_3]$	5.0	(729)726	717.5	63,60	–
369	$K_3[Fe^{III}(CN)_6]$	5.4	728.6	717.1	60.9	12.7
395	$Fe^{III}{}_2O_3$	4.4	(739.2),730.2	724.8,716.6	(65),62.3	13.6,10.6
396	Fe_3O_4	5.0	730.5	(719.2),716.5	(68),61.5	–
35	$Na_2[Fe(CN)_5NO]$	4.7	729.2	716.3	62.8	–
397	$Fe^{II}C_2O_4, 2H_2O$	4.3	(733),729.7	(719),716.0	70,67,61.3	–
398	$Fe^{III}{}_4[Fe^{II}(CN)_6]_3$	5.1	(731),726.5	(717),713.5	61	–
154	$Cu^{II}{}_2[Fe(CN)_6], 11H_2O$	4.8	727.2	714.2	60.8	–
175	$Ru^{III}{}_4[Fe^{II}(CN)_6]_3$	4.9	727	713.6	60.2	–
176	$Fe^{III}{}_4[Ru^{II}(CN)_6]_3$	4.6	(731),726.8	717.3	–	–
177	$Fe^{III}{}_4[Os^{II}(CN)_6]_3$	4.6	(731),728	717.5,714.7	–	–
145	$Na_4[Fe^{II}(CN)_6], 10H_2O$	4.7	727.7	714.7	61.5	8.2
365	$K_4[Fe^{II}(CN)_6]$	5.1	727.2	714.3	60.7	11.5
131	$[Fe^{II}dip_3]Br_2$	5.6	726.0	713.2	60.6	–
188	$Co^{II}F_2$	[1.1],5.4	814,808.3	(798),792.1	(75),71.2	14
104	$Cs_3[Co^{III}(CN)_6]$	[2.5],4.6	804.2	789.1	71	–
115	$Co^{II}[Pd(CN)_4]$	[2],4.0	(810),804.5	(792),788.8	(72),68.5	–
9	$[Co^{III}(NH_3)_6][Be_2(OH)_3(CO_3)_2]$	[2.8],4.6	803.5	788.6	–	11
67	$[Co^{III}(NH_3)_6]_7[Cu(IO_6)_2]_3$	4.7	803.5	788.6	69.3	–
584	$[Co^{III}(NH_3)_6]_2[Th(CO_3)_5]$	[2.3],4.2	803.6	788.6	–	–
135	$[Co^{III}(NH_3)_6)]_2[Ce(CO_3)_5]$	4.2	803.3	788.3	–	–
83	$[Co^{III}(NH_3)_6][Au(S_2O_3)_2]$	4.4	803.2	788.2	69.2	–
136	$Co^{II}{}_2[Os(CN)_6]$	5.0	804	(790),788.2	(71)	–
161	$Co^{II}{}_2[Ru(CN)_6]$	4.5	804	788.0	70	–
87	$[Co^{III}(NH_3)_6]_2(SiF_6)_3$	4.4	803.0	787.9	69.1	–

TABLE 6. (continued).

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p)$	$I(3d)$
132	$Na_3[Co^{III}(CN)_6]$	4.8	802.9	787.9	69	10
05	$[Co^{II}(H_2O)_6](ClO_4)_2$	4.8	809.3,804.3	(793),787.9	73,70,68	11,9
55	$Co^{II}(NCS)_4Hg$	4.7	809.3,804.0	792.5,787.9	73,68	–
77	$[Co^{III}en_2Cl_2]PF_6$	4.7	802.9	787.9	68.8	–
40	$H_3Co^{III}(CN)_6$	4.7	802.8	787.8	68.8	10.7
31	$[Co^{III}en_2Cl_2]_2PbCl_6$	[3.0],5.0	802.8	787.7	–	–
78	$[Co^{III}en_2Cl_2]_3(PW_{12}O_{40})$	4.0	802.5	787.5	68	–
4	$Li_3[Co^{III}(CN)_6]$	4.7	802.5	787.5	68.7	9.6
99	$Co^{III}{}_2O_3$	[2.8],4.9	802.4	787.3	67.8	–
05	$[(NH_3)_5Co^{III}(O_2)Co^{III}(NH_3)_5]$ $(SO_4)_2HSO_4$	5.3	802.4	787.3	68.0	–
09	$[Co^{III}(NH_3)_6]SbCl_6$	4.3	802.3	787.3	68.5	–
89	$[Co^{III}en_2Cl_2]MnO_4$	4.7	802.4	787.3	68.7	–
50	$(NH_4)_3[Co^{III}(CN)_6]$	4.8	802.3	787.3	68.6	–
53	$Cu_3[Co^{III}(CN)_6]_2, 11H_2O$	4.5	802.5	787.3	69	–
88	$[Co^{III}en_2Cl_2]BF_4$	4.6	802.2	787.2	68.6	–
58	$[N(C_4H_9)_4]_3[Co^{III}(CN)_6]$	5.0	802.2	787.2	68.3	–
95	$[Co^{III}en_2Cl_2][B(C_6H_5)_4]$	5.2	802.2	787.1	68.1	–
52	$[N(CH_3)_4]_3[Co^{III}(CN)_6]$	4.9	802.0	787.0	68.1	–
0	$K_3[Co^{III}(CN)_6]$	4.7	802	787.0	–	13.4
1	$Co^{II}{}_4aca_8$	[3],5.0	808,802.4	(793),(791),786.9	67	9.4
57	$[N(C_2H_5)_4]_3[Co^{III}(CN)_6]$	5.0	801.8	786.8	68	–
32	$[Co^{III}en_2Cl_2]NO_3$	4.4	801.6	786.6	68	–
0	$[Co^{III}en_2Cl_2][Cr(NH_3)_2(NCS)_4]$	4.5	801.6	786.6	68.1	–
2	$Co^{II}(IO_3)_2$	3.5	802.5	786.5	–	–
2	repeated	[2.4],4.5	809,803.4	793.3,787.9	–	11,(8)
2	$[Co^{III}en_2Cl_2]ReO_4$	5.0	801.6	786.5	67.5	–
4	$Co^{III}aca_3$	4.9	801.5	786.4	67.2	9
6	$[Co^{III}(NH_3)_6]BiCl_6$	3.6	801.0	786.1	67.2	10.1
9	$[Co^{III}(NH_3)_5Cl_2]Cl$	3.9	800.4	785.4	67.5	9.2
5	$[Co^{III}(NH_3)_6]Cl_3$	3.9	800.3	785.2	67.4	10
7	$Co^{III}(S_2P(OC_3H_7)_2)_3$	6.4	799.6	784.7	–	–
1	$Co^{III}(S_2CN(C_2H_5)_2)_3$	5.2	799.2	784.1	66	–

ABLE 7. Photo-electron signals of nickel. High-spin complexes ($S = 1$) are given first, ıowing four signals (separated by effects of interelectronic repulsion) in the 2p region, llowed by low-spin complexes ($S = 0$) giving only two. In iodides, $Ni2p_{1/2}$ tends to coincide with $I3p_{3/2}$.

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p)$	$I(3d)$
9	$KNiF_3$	3.6	– ,882.2	869.9,864.0	77.4	12.6

TABLE 7. (continued).

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p)$	$I(3d)$
209	repeated	[1.3],4.5	889.8,883.7	871.7,865.8	–	12.
221	$\mathrm{NiF_2, 4H_2O}$	[2.6],4.7	887.8,882.5	870.5,864.4	(79),76.6	12
612	$\mathrm{Ni(IO_3)_2}$	[2.5],4.9	– ,(882.4)	870.5,863.9	82,77	(11)
134	$\mathrm{Ni_2[Os(CN)_6]}$	5.2	(887) ,880.6	(869) ,862.9	(78),76.2	–
406	$\mathrm{[Ni\ en_3]PtI_6}$	4.8	882	870 ,862.8	–	–
91	$\mathrm{[Ni(CN)_2(NH_3)(C_4H_4S)]}$	5.5	887 ,880.3	869.8,862.7	(78),74.9	10.
162	$\mathrm{Ni_2[Ru(CN)_6]}$	4.5	(886) ,880	(869) ,862.7	(77),75	–
407	NiO, black	[2.2],4.9	887.0,880.4	868.5,862.6	–	10.
408	NiO, pale	[2.5],4.8	886.8,879.9	868.6,862.4	(80),75.4	11
409	$\mathrm{NiC_2O_4, 2H_2O}$	4.3	886 ,879.9	868 ,862.1	(78),75.0	10.
410	$\mathrm{[Ni\ en_3]I_2}$	[2.7],4.9	885 ,881	868.2,862.1	79.2,74.7	–
273	$\mathrm{[Ni(H_2O)_6]SO_4}$	4.1	885.2,879.3	867 ,861.9	(81),74.8	11
156	$\mathrm{[Ni\ en_2][Pt(CN)_4]}$	4.1	884 ,878.5	868 ,861.0	74	–
411	$\mathrm{Ni_3acac_6}$	5.3	884 ,878.6	866 ,860.9	(77),73.6	8
142	$\mathrm{[Ni\ en_2][Ni(CN)_4]}$	5.0	(884) ,878.2	(867) ,860.9	74	–
96	$\mathrm{[Ni(et_4den)Cl]Cl}$	5.1	884.5,877.9	866.9,860.6	(76),73.9	–
148	$\mathrm{[Ni\ en_2][Pd(CN)_4]}$	4.2	(884) ,878.0	866.5,860.6	78 ,73.7	–
147	$\mathrm{[Ni\ en_3][Ni(CN)_4]}$	4.9	(885) ,877.9	(867) ,860.5	(76),74.1	–
137	$\mathrm{Ni(NH_2CH_2CO_2)_2(H_2O)_2}$	3.8	883 ,877.8	865.6,860.4	(80),74.3	9
152	$\mathrm{[Ni\ en_3][Pd(CN)_4]}$	4.4	886 ,878.3	867 ,860.4	79 ,73	–
151	$\mathrm{[Ni\ tren(NCS)_2]}$	4.6	883 ,878.2	867 ,860.3	79 ,73	–
138	$\mathrm{[Ni(tren)phen](ClO_4)_2}$	4.5	882 ,877.8	866 ,860.2	80 ,73.5	
157	$\mathrm{[Ni\ en_3][Pt(CN)_4]}$	3.9	885 ,877.7	866.5,860.0	73	–
150	$\mathrm{[Ni\ en_3]SO_4}$	3.8	883.2,877.5	866.0,859.9	(79),73.1	8
412	$\mathrm{[Ni\ phen_3](ClO_4)_2}$	5.0	884 ,877.6	867 ,859.9	–	–
133	$\mathrm{[Ni\ daes_2](ClO_4)_2}$	4.6	– ,877	866 ,859.8	74	9
413	$\mathrm{[Ni(S_2P(OC_3H_7)_2)_2\ phen]}$	5.2	– ,877	865 ,859.6	73	9
106	$\mathrm{[Rh\ ns_3]_2Ni(ClO_4)_2}$	4.6	882 ,876.7	864 ,859.4	–	–
414	$\mathrm{[Ni\ pyridinalhydrazone_3](ClO_4)_2}$	3.0	881 ,876	865 ,858.3	–	–
53	$\mathrm{[Ni\ en_2](AgI_2)_2}$	[2.0],4.6	881	862.4	76.2	–
60	$\mathrm{[Ni\ en_2](CuI_2)_2}$	[2.2],4.6	881	862.2	76	–
160	$\mathrm{K_2[Ni(CN)_4]}$	4.9	878.2	860.8	74.8	9
113	$\mathrm{[Ni\ en_2](ClO_4)_2}$	4.6	877.6	860.5	74.4	1
33	$\mathrm{[Ni\ aminin_2](NO_3)_2}$	4.6	877.2	860.1	73.8	1
307	$\mathrm{[Ni\ curtis_2](ClO_4)_2}$	4.7	877.5	860.1	73	
415	$\mathrm{[Ni\ aminin_2Br]Br}$	4.5	876.9	859.8	73.3	
116	$\mathrm{Ni\ dmg_2}$	4.9	876.6	859.6	73.6	
245	$\mathrm{Ni(S_2P(OC_3H_7)_2)_2}$	5.1	876	859.2	73.6	
127	$\mathrm{Ni(S_2CN(C_2H_5)_2)_2}$	4.7	875.8	858.7	73.0	
416	$\mathrm{Ni_2O_3}$	4.5	884.8,878.0	866.3,860.0	(75),73.2	
417	Ni, powder (oxidized?)	4.9	880.3,(877.6)	862.8,(859.5)	–	
418	Ni, foil	5.2	878.2,876	860.5,857.8	72.5,71	

TABLE 8. Photo-electron signals of copper. Satellites are observed in the 2p region in the case of copper(II) compounds.

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p)$	$I(3d)$
214	$Cu^{II}F_2, 2H_2O$	[3.0],5.2	971,963.5	950.8,943.3	86.0	13.3
256	$Cu^{II}SO_4, 3H_2O$	5.0	962.2	951,947,942.1	–	13.0
121	$Cu^{II}_3[Ir(CN)_6]_2, 11H_2O$	4.5	962.3	948,942.0	(89),86.7	–
613	$Cu^{II}(IO_3)_2$	[2.3],4.4	969,961.2	949.1,941.7	85	–
419	$Cu^{II}O$	[2.2],4.9	(963.2),961.4	950.2,941.5	(93.3),85.6	–
67	$[Co(NH_3)_6]_7[Cu^{III}(IO_6)_2]$	4.7	961.0	949 weak, 941.3	85	–
153	$Cu^{II}_3[Co(CN)_6]_2 11H_2O$	4.5	961.5	950,941.3	85	–
242	$Cu^{II}(UO_2)_2(PO_4)_2$	[2.0],4.6	961 broad	951,(943),940.9	–	–
29	$[Cu^{II}en_2](NO_3)_2$	4.6	959.9	949.0,940.1,(937.6)	82.6	10.8
97	$Cu^{I}CN$	[3.2],5.3	959.8	939.9	83.2	11.0
420	$Cu^{I}_2HgI_4$	[4.3],6.1	959.4	939.6	82.0	10
123	$[Cu^{II}denBr]Br$	4.7	(961.0),959.0	949,939.4,(936.0)	–	–
60	$[Ni\ en_2](Cu^{I}I_2)_2$	[2.2],4.6	958.8	939.0	82.4	–
98	$Cu^{II}(S_2CN(C_2H_5)_2)_2$	4.4	968.6,(960.6),959.0	948.6,(940),939.0	83.3	–
270	$Cu^{II}SO_4, 5H_2O$	5.3	958.6	(941.4),938.7	–	–
154	$Cu^{II}_2[Fe(CN)_6], 11H_2O$	4.8	(961.2),958.4	949,(941.2),938.4	83.3	–
164	$Cu^{II}_2(Os[CN)_6]$	5.0	(961),958.3	949.2,(941.2),938.4	83	–
180	Cu^{II} phthalocyanine	6.0	966,958.2	947,938.2	–	–
174	$Cu^{II}_2[Ru(CN)_6]$	4.4	(960),957.4	948,(940),937.7	83	–
293	CuS	5.5	(960),957.4	949,(939),937.3	81	–
–	$5MgF_2 : 1CuS$	[0.8],4.8	(965),958.9	951,(941.8),938.8	–	–

TABLE 9. Photo-electron signals of zinc, gallium, germanium and arsenic.

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d)$
212	$[Zn(H_2O)_6]SiF_6$	[2.5],4.9	1052.65	1029.5	(101)	97.5	18.9
421	$Zn(IO_3)_2$	[2.4],5.0	1052.4	1029.2	–	–	18.2
283	ZnS	[2.2],4.6	1052.2	1029.0	(97)	94	18.0
230	$NaZn(UO_2)_3(CH_3CO_2)_9$	4.6	1054	1029	–	–	–
422	$Zn(UO_2)_2(CH_3CO_2)_6$	[3.7],5.6	1052.0	1028.8	–	–	17.7
423	Zn aca_2	5.3	1050.5	1027.4	–	–	16.2
424	ZnO	4.9	1049.8	1026.7	(97)	94.2	15.7
204	$GaF_3, 3H_2O$	[2.3],5.0	1153.4	1126.4	118	114.8	29.5
425	Ga_2O_3	[1.8],4.9	1152.6	1125.7	117.4	114.2	28.7
281	GaS	[3.0],5.0	1151.8	1125.2	–	–	27.9
41	$(NH_4)_3GaF_6$	[3.7],5.4	1151.8	1125.0	116.7	113.1	27.6
261	$Ga_2(SO_4)_3$	4.4	1151.9	1124.9	116	113	27.6
426	Ga, coherent	4.2	–	1120.6	(112)	108.0	22.7
189	K_2GeF_6	[1.3],4.7	1260.9	1229.7	138.5	134.2	42.3
427	GeO_2	[2.1],4.7	1259.0	1227.8	136.7	132.9	41.0

TABLE 9. (continued).

	Compound	C_{st}	$I(2p_{1/2})$	$I(2p_{3/2})$	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d)$
428	$LaAsO_4$	[2.0],4.7	1370.1	1334.1	157.0	152.4	53.3
429	$NdAsO_4$	[1.9],4.5	1369.7	1333.5	157.3	152.5	53.7
356	K_2HAsO_4	[2.8],4.5	1369.3	1333.3	156.5	151.7	52.9
430	$YbAsO_4$	[2.5],4.2	1368.8	1332.7	155.4	150.9	52.2
597	$Na_2HAsO_4, 7H_2O$	4.3	1368.4	1332.4	155.4	150.5	51.6
431	$[As(C_6H_5)_4]_2PtI_6$	4.8	1368.3	1332.3	–	–	–
594	$NaAsO_2$	4.7	1367.9	1331.9	–	–	51.3
432	Ag_3AsO_4	4.7	1367.9	1331.9	154.4	149.9	50.9
172	$[As(C_6H_5)_4]_2[Cd(NCSe)_4]$	4.5	1367.5	1331.4	–	–	50.2
344	$[As(C_6H_5)_4]_2PbCl_6$	4.8	1367.5	1331.4	–	149.0	50.3
346	$[As(C_6H_5)_4]_2ReCl_6$	4.9	1367.3	1331.3	–	–	–
170	$[As(C_6H_5)_4]_2[Os(SCN)_6]$	5.2	1367.0	1331.3	–	–	–
170	repeated	4.6	1367.2	1331.3	154	149.2	50.4
178	$[As(C_6H_5)_4]SCN$	4.8	1367.1	1331.1	154	149.0	50.2
433	$[As(C_6H_5)_4]RuO_4$	4.5	1367.0	1331.0	–	–	50.1
434	$[As(C_6H_5)_4]ReO_4$	3.9	1366.7	1330.9	–	–	–
610	$[As(C_6H_5)_4][OsO_3N]$	4.2	1366.8	1330.9	155	149.3	50.7
166	$[As(C_6H_5)_4]_3[Ir(SeCN)_6]$	4.1	1366.5	1330.7	–	149.3	49.7
298	$As(S_2CN(C_2H_5)_2)_3$	4.8	1365.8	1330.0	152	147.4	48.4

TABLE 10. Photo-electron signals of selenium and bromine.

	Compound	C_{st}	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d)$	$I(4p)$
435	$BaSeO_4$	[2.2],4.8	180	174.1	–	–
435	repeated	[1.1],4.7	180.9	175.1	69.2	–
236	$Na_2SeO_4, 10H_2O$	[3],4.7	179.3	173.5	67.8	–
232	$NaHSeO_3$	[2.3],4.7	178.3	172.55	66.6	–
436	SeO_2	4.5	176.9	171.2	65.2	–
129	$K_2[Pt(SeCN)_6]$	4.8	174.0	168.3	–	–
437	Tl_3VSe_4	4.7	174	168.0	–	–
40	$[N(CH_3)_4]SeCN$	4.6	173	167.0	61.1	–
166	$[As(C_6H_5)_4]_3[Ir(SeCN)_6]$	4.1	172.7	166.8	60.4	–
171	KSeCN	3.6	172.4	166.7	60.7	–
171	repeated	[3.3],5.0	172.1	166.3	61.9	–
438	Tl_3NbSe_4	4.7	(174),173	(168),166.7	–	–
439	CdSe	[4],5.7	172.3	166.7	60.7	–
172	$[As(C_6H_5)_4]_2[Cd(NCSe)_4]$	4.5	172.5	166.6	60.6	–
440	Tl_3TaSe_4	4.3	173	166.5	–	–
44	$[N(C_4H_9)_4]SeCN$	4.2	172	166.3	60.3	–
239	$NaBrO_3$	5.2	202.3	195.6	82.4	–
361	$KBrO_3$	[3.3],5.0	–	–	81.5	–

TABLE 10. (continued).

	Compound	C_{st}	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d)$	$I(4p)$
441	Cs_2PtBr_6	[1.5],4.8	197.7	191.1	78.2	14.5
442	Cs_2SnBr_6	[2.9],5.2	–	–	76.9	12.0
442	repeated	[2.0],4.8	197.1	190.5	77.3	12.2
443	$(\text{-}CHBrCO_2H)_2$	4.8	196.7	190.0	76.6	–
444	CsBr	[1.6],4.95	196.7	189.95	76.7	12.0
352	$KAuBr_4$	3.4	196.35	189.7	74.2	(12.4)
227	NaBr	[2.9],5.3	196.1	189.5	76.3	11.4
445	RbBr	[2.7],5.1	196.1	189.4	76.0	11.3
446	$PbBr_2$	[2.7],4.9	195.8	189.2	76.0	10.7
364	K_2PtBr_6	2.6	194.8	188.2	75.2	12.4
364	repeated	5.0	195.8	189.1	76.0	13.7
353	KBr	[3.1],4.6	195.4	188.7	75.7	10.7
447	AgBr	[3.4],5.3	195.3	188.7	75.6	–
448	Cs_2OsBr_6	3.8	194.9	188.5	75.5	–
80	$[Pd\ phen\ Br_2]$	4.5	194.9	188.2	75.1	(11.8)
359	K_2ReBr_6	4.8	194.7	188.1	75.0	(11.4)
449	TlBr	4.6	194.7	188.1	75.0	10.2
450	$[N(C_4H_9)_4]AuBr_4$	5.0	194.6	188.0	74.9	–
451	Tl_2OsBr_6	6.0	194.2	187.6	74.5	–
54	$[N(C_4H_9)_4][Au(CN)_2Br_2]$	5.3	194	187.5	74.0	–
92	$[Pd(et_4den)Br]ClO_4$	4.4	194.0	187.3	74.3	–
452	$[N(C_4H_9)_4]_2OsBr_6$	5.1	193.9	187.2	74.1	10.6
112	$[Rh\ py_4\ Br_2]ClO_4$	4.4	193.7	187.1	74.1	10.4
130	$[N(CH_3)_4]_2ReBr_6$	4.6	193.6	186.95	73.8	(10.8)
66	$[N(C_2H_5)_4]_2MnBr_4$	4.6	193.7	186.9	73.8	(9.8)
63	$[N(CH_3)_4]Br$	4.9	192.5	186.0	72.7	8.3
131	$[Fe\ dip_3]Br_2$	5.6	192.2	185.9	72.7	–
48	$[N(C_2H_5)_4]_2PtBr_6$	4.6	192.6	185.9	74.9	12.1

TABLE 11. Photo-electron signals of rubidium, strontium, yttrium, zirconium, niobium and molybdenum.

	Compound	C_{st}	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4p)$
–	Kr (ref. 97)	–	222.2	214.4	94.9	93.7	14.0
445	RbBr	[2.7],5.1	254.75	245.8	(119)	117.2	20.9
312	Rb_2PtCl_6	[2.5],5.0	254.8	245.8	(119)	117.8	21.5
319	RbCl	[2.8],5.2	254.5	245.5	119.4	117.6	21.4
453	RbI	[3.1],4.8	253.9	245.0	(118)	116.7	20.5
107	$Rb_2[Pd(CN)_4]$	4.6	253.6	244.6	(118)	116.7	20.1
222	RbF	4.4	253.4	244.4	(117.6)	116.5	19.7
25	$RbNO_3$	5.0	253.0	244.1	(117.5)	116.2	19.7

TABLE 11. (continued).

	Compound	C_{st}	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4p)$
275	Rb_2SO_4	4.1	253.1	244.1	(118)	117.1	19.3
334	$Rb_2[OsCl_4I_2]$	4.6	252.9	243.9	(117.6)	116.2	19.7
20	$RbUO_2(NO_3)_3$	[2.7],4.8	252.1	243.2	–	117.3	–
197	SrF_2	[1.7],5.5	–	278.6	145.5	143.2	28.7
197	repeated	[1.2],5.0	–	278.4	(144.5)	143.0	28.8
253	$SrSO_4$	[2.5],4.9	287	277.1	(143.1)	141.4	27.1
27	$Sr(NO_3)_2$	4.7	286	275.9	(142.6)	140.6	–
186	YF_3	[1.5],5.2	323.4	311.5	(171)	168.5	35.3
454	$Y(IO_3)_3$	[2.2],4.8	321.3	309.6	(168)	166.3	33.8
265	$Y_2(SO_4)_3$	4.4	320.4	308.4	(167.2)	165.3	32.5
377	YVO_4	4.7	–	–	(165.5)	163.8	31.4
455	Y_2O_3	4.6	319.1	306.9	165.8	163.6	32
202	ZrF_4	[1.8],4.4	357.6	343.8	(195.6)	193.2	41.5
456	$Zr(IO_3)_4$	[2.1],4.6	354.5	341.1	(192.9)	190.5	39.3
45	$(NH_4)_2ZrF_6$	5.1	354.6	340.9	192.7	190.4	39.5
457	$Pr_{0.2}Zr_{0.8}O_{1.95}$	4.6	353.0	339.2	192	188.3	37
208	K_2NbF_7	[3],5.0	389.6	374.4	219	216.0	44.8
458	Tl_3NbS_4	4.8	388	371.2	216	213.4	41.8
459	Nb_2O_5	4.4	386.0	370.6	215.4	212.7	41
460	Tl_2MoO_4	[2.6],4.8	–	–	242.0	239.0	–
595	Na_2MoO_4	5.0	421.8	404.3	241.9	238.9	47.4
461	$H_3PMo_{12}O_{40}$	4.6	421.9	404.4	241.7	238.6	47
462	MoO_3	4.6	421.4	404.0	241.5	238.5	–
286	$Tl_2[MoO_2S_2]$	4.7	421	403.7	240.6	237.6	–
288	Tl_2MoS_4	4.4	419	402	239.6	236.7	45
336	K_3MoCl_6	4.5	419.8	402.3	240.0	236.5	–
301	Cs_2MoS_4	4.1	–	–	239.0	235.8	–

TABLE 12. Photo-electron signals of ruthenium and rhodium. It is often difficult to detect Ru3d because of the coincidence with C1s.

	Compound	C_{st}	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4p)$	$I(4d)$
433	$[As(C_6H_5)_4]Ru^{VII}O_4$ (shoulders Ru^{IV})	4.5	494.0,(490)	472.0,(468)	–	–	54	–
39	$K_2[Ru(NO)Cl_5]$	[1.5],4.8	492.5	470.3	–	–	53.0	–
110	$[Ru^{III}(NH_3)_5NCS](ClO_4)_2$	4.7	491.9	469.6	–	–	53	8.8
124	$[Ru^{III}(NH_3)_6]Cl_3$	4.7	491.5	469.1	–	287.8	53.7	8.9
175	$Ru^{III}{}_4[Fe(CN)_6]_3$	4.9	490.9	468.5	–	287	51	–
463	$Ru^{III}{}_4[Ru^{II}(CN)_6]_3$	4.6	490.1	468.4	–	–	52	–
464	$Ru^{IV}O_2, xH_2O$	[2],4.7	490.9	468.3	–	286	–	–
162	$Ni_2[Ru^{II}(CN)_6]$	4.5	490.4	468.0	–	–	51	–

Table 12. (continued).

	Compound	C_{st}	$I(3p_{1/2})$	$I(3p_{3/2})$	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4p)$	$I(4d)$
161	$Co_2[Ru^{II}(CN)_6]$	4.5	490.2	467.9	–	–	51	–
289	$[N(CH_3)_4]_3[Ru^{III}(NCS)_6]$	4.6	488.6	467.2	–	285.9	–	8.9
289	repeated	4.3	490.3	468.1	–	286.8	51	–
176	$Fe_4[Ru^{II}(CN)_6]_3$	4.6	489.7	467.1	–	286.1	–	–
174	$Cu_2[Ru^{II}(CN)_6]$	4.4	489.4	466.9	–	–	–	–
465	Ru, powder (oxidized?)	4.3	489.8	(469),467.2	–	–	–	–
185	K_3RhF_6	[2.0],4.7	–	507	324.8	320.0	58	11.9
466	$Cs_2Rh^{IV}Cl_6$(reduced?)	[2.3],5.0	–	–	322.5	317.7	–	11.3
315	$Cs_2[Rh^{III}(H_2O)Cl_5]$	[2.0],4.9	–	–	322.3	317.6	57	11.3
90	$[Rh(NH_3)_5Cl]Cl_2$	4.6	–	–	320.8	316.2	–	9.6
71	[Rh den I_3]	[2.4],4.6	529.6	505.0	320.9	316.2	–	10.2
596	$Na_3RhCl_6, 12H_2O$	5.0	–	–	320.5	315.8	56	9.5
333	$RhCl_3$	4.9	–	–	320.2	315.5	56	8.9
112	[Rh py$_4$ Br$_2$]ClO$_4$	4.4	528.5	504.3	320.0	315.4	–	9.0
111	[Rh den Cl_3]	4.8	–	–	320.0	315.3	56	8.5
467	RhI_3	4.5	–	–	319.7	315.1	–	10
106	[Rh ns$_3$]$_2$Ni(ClO$_4$)$_2$	4.6	528	503.6	319.3	314.7	–	–
169	$K_3[Rh(SCN)_6]$	4.7	527.8	503.1	319.0	314.3	–	9
294	$Rh(S_2P(OC_2H_5)_2)_3$	4.5	528.0	503.8	318.9	314.3	–	8
468	Rh, powder	5.2	527.9	503.5	318.9	314.2	55	–

Table 13. Photo-electron signals of palladium and silver.

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4p)$	$I(4d)$
84	$Cd[Pd^{IV}(CN)_6]$	[2.2],4.9	355.3	350.0	65.5	14
107	$Rb_2[Pd(CN)_4]$	4.6	350.9	345.65	62	10.6
115	$Co[Pd(CN)_4]$	[2],4.0	350.7	345.4	61	11.0
59	*trans*-$[Pd(NH_3)_2Cl_2]$	4.8	350.5	345.3	–	11.1
72	$(NH_4)_2Pd^{IV}Cl_6$	5.0	349.5	345.3	62	9.4
149	$K_2[Pd(CN)_4]$	5.1	350.2	344.9	61	10
332	K_2PdCl_4	4.8	350.0	344.7	60	10.2
469	PdI_2	5.1	349.9	344.6	–	11
79	[Pd(et$_4$den)Cl]ClO$_4$	[3.3],5.0	349.6	344.4	60	–
81	[Pd phen I_2]	4.9	349.6	344.3	–	–
80	[Pd phen Br_2]	4.5	349.5	344.2	–	9.9
148	[Ni en$_2$][Pd(CN)$_4$]	4.4	349.5	344.2	61	–
85	Pd dmg$_2$	4.4	349.3	344.1	–	–
152	[Ni en$_3$][Pd(CN)$_4$]	4.4	349.4	344.1	–	–
143	[Pd en$_2$][Pd(CN)$_4$]	4.4	349.4	344.1	–	–
102	[Pd phen$_2$](ClO$_4$)$_2$	5.1	349.3	344.0	–	9.9
128	$[Pd(NH_3)_4](CH_3C_6H_4SO_3)_2$	4.8	349.0	343.7	–	10

TABLE 13. (continued).

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4p)$	$I(4d)$
128	repeated	4.6	349.1	343.8	60	9.7
92	$[Pd(et_4\,den)Br]ClO_4$	4.4	348.9	343.6	60	–
101	$[Pd\,phen\,Cl_2]$	4.5	348.8	343.55	–	10.2
119	$[Pd\,py_4]SO_4$	4.65	348.8	343.5	59.5	–
470	Pd, powder	4.3	346.9	341.5	58	–
471	$AgIO_3$	[2.3],4.8	382.6	376.6	68	13.0
243	Ag_3PO_4	[1.9],4.7	382.1	376.1	–	13.3
53	$[Ni\,en_2](AgI_2)_2$	[2.0],4.6	381.7	375.7	68	–
122	$K[Ag(CN)_2]$	[2.7],4.5	381.6	375.55	–	12.8
472	AgI	[3.3],5.0	381.5	375.5	69	12.7
473	Ag_2CO_3	[2.6],4.6	381.2	375.1	66	–
474	$AgReO_4$	4.7	381.1	375.0	68	12.3
384	Ag_2CrO_4	[3.1],5.1	380.9	374.85	66	12.2
447	AgBr	[3.4],5.3	380.8	374.75	–	11.9
475	$Ag[B(C_6H_5)_4]$	5.3	380.2	374.2	–	11.5
272	Ag_2SO_4	[3],4.3	380.2	374.2	–	11.2
303	Ag_2S	4.6	380.0	374.0	66	–
290	$AgS_2CN(C_2H_5)_2$	[3.3],5.1	380.0	374.0	65	–
339	AgCl	4.8	379.9	373.9	65	10.8
432	Ag_3AsO_4	4.7	379.7	373.7	65	11.3
271	$[Ag^{II}py_4]S_2O_8$	4.2	379.6	373.6	–	11.1
476	Ag, wool	5.9	379.2	373.2	66	–

TABLE 14. Photo-electron signals of cadmium, indium, tin, antimony and tellurium. It is frequently difficult to distinguish $Sb3d_{5/2}$ from oxygen 1s.

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d)$
477	CdI_2	[2.4],4.7	420.0	413.3	19.6
84	$Cd[Pd(CN)_6]$	[2.2],4.9	419.8	413.0	19.4
217	CdF_2	[3],4.8	419.2	412.4	19.2
217	repeated	[2],4.3	419.7	412.9	19.1
478	CdO	[2.3],4.9	419.65	412.8	19.4
255	$CdSO_4, H_2O$	5.0	419.6	412.8	19.1
385	$Cd_3[Cr(CN)_6]_2$	[2.9],4.8	419.6	412.8	19.3
479	$CdCO_3$	[2.1],4.6	419.5	412.7	19.3
285	CdS	[3.2],4.7	418.75	412.0	18.3
439	CdSe	[4],5.7	418.5	411.7	17.8
172	$[As(C_6H_5)_4]_2[Cd(NCSe)_4]$	4.5	417.5	410.7	17.2
480	$In(IO_3)_3$	[2.0],4.8	460.9	453.3	26.9
481	$In_2(SO_4)_3$	[2.8],5.1	460.7	453.1	26.6
309	$Cs_4(InCl_6)(SbCl_6)$	[2.3],4.9	460.2	452.7	25.5

TABLE 14. (continued).

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d)$
42	$(NH_4)_2[In(H_2O)F_5]$	[3.8],5.0	459.5	452.0	25.6
94	$[Cr(NH_3)_6]InCl_6$	5.0	458.8	451.2	24.6
291	In_2S_3	[3],4.7	458.4	450.8	24.8
292	$In_2(S_2CN(C_2H_5)_2)_3$	[3],4.8	457.4	449.8	23.9
482	In_2O_3	5.8	457.2	449.6	23.0
483	In, coherent(oxidized?)	5.3	456.4	448.8	21.9
442	Cs_2SnBr_6	[2.9],5.2	503.2	494.7	34.7
442	repeated	[2.0],4.8	503.9	495.4	35.0
484	$Sn^{II}C_2O_4$	4.9	502.1	493.6	33.7
592	$Na_2[Sn^{IV}(OH)_6]$	[3],4.5	502	493.3	33.1
485	$Sn^{IV}{}_{1-2\chi}Sb^{III}{}_{\chi}Sb^{V}{}_{\chi}O_2$	5.4	501.0	492.6	32.6
486	Sn, foil, oxidized	5.0	500.8	492.3	31.8
73	$[N(C_4H_9)_4]_2[Sn(NCS)_6]$	5.0	500.7	492.2	32.3
487	SnO_2	5.4	500.5	492.0	32.1
488	$Sn(C_6H_5)_4$	5.1	499.7	491.2	31.0
182	$CsSb^{V}F_6$	[1.3],5.5	551.9	542.4	46.4
318	$Cs_4(Sb^{III}Cl_6)(Sb^{V}Cl_6)$	[3.1],4.9	548.9	538	42.5
			& 547.1		& 41.4
311	$CsSb^{V}Cl_6$	[2.0],5.0	548.7	539.1	44
309	$Cs_4(InCl_6)(Sb^{V}Cl_6)$	[2.3],4.9	548.7	539.1	43.7
313	$Cs_4(Sb^{V}Cl_6)(TlCl_6)$	[2.3],4.6	548.7	539	43.7
485	$Sn_{1-2\chi}Sb^{III}{}_{\chi}Sb^{V}{}_{\chi}O_2$	5.4	547.8	539	44
			& 545.7		& 41.2
38	$NH_4Sb^{III}F_4$	[3.5],5.3	547.7	538.3	43.0
354	$K[Sb^{V}(OH)_6]$	5.1	547.1	538	42.1
329	$Sb^{III}OCl$	[2.5],4.7	547.0	537.6	42.1
355	$K_2[Sb^{III}{}_2O_2tartrate_2]$	[3],4.9	546.9	538	41.8
229	$Na[Sb^{V}(OH)_6]$	[2.5],4.4	546.9	537.6	42.1
109	$[Co(NH_3)_6]Sb^{III}Cl_6$	4.3	545.4	536.1	40.8
603	$Na_3Sb^{V}S_4$	4.3	545.1	535.8	40.1
299	$Sb^{III}(S_2CN(C_2H_5)_2)_3$	4.9	544.4	535.1	39.3
489	$Te^{VI}(OH)_6$	5.0	594.4	583.9	52.7
490	$Te^{IV}O_2$	4.4	593.3	582.8	51.2
490	repeated (oxidized)	4.7	594.3	583.85	52.0
591	$Na_2Te^{IV}O_3$	5.0	592.8	582.4	50.8
591	repeated	[2.8],4.8	593.5	583.05	51.1
598	$Na_2[Te^{VI}O_2(OH)_4]$	4.7	593.7	581.45	51.7
118	$Te^{IV}(S_2CN(C_2H_5)_2)_4$	4.9	590.6	580.2	48.1
491	Al_2Te_3 (oxidized to Te?)	5.3	587.55	577.1	45.6

TABLE 15. Photo-electron signals of iodine. The shoulder on the 4d signal is not indicated.

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d)$	$I(5p)$
492	$Eu(IO_3)_3$	[1.6],4.9	644.4	632.9	63.6	–
493	$La(IO_3)_3$	[1.7],5.0	644.4	632.85	63.3	–
349	$KI^{VII}O_4$	[2.8],5.3	644.3	632.8	63.7	–
494	$UO_2(IO_3)_2$	[1.4],4.7	644.4	632.8	63.2	–
495	$Sm(IO_3)_3$	[1.5],4.6	644.3	632.75	63.2	–
496	$Gd(IO_3)_3$	[1.8],5.0	644.2	632.65	63.2	–
480	$In(IO_3)_3$	[2.0],4.8	644.0	632.5	62.8	–
497	$Nd(IO_3)_3$	[1.7],4.7	644.05	632.5	62.9	–
498	$Pr(IO_3)_3$	[1.7],4.6	643.95	632.4	63.0	–
454	$Y(IO_3)_3$	[2.2],4.8	643.85	632.3	62.5	–
499	$Th(IO_3)_4$	[2.2],4.7	643.85	632.3	62.7	–
235	$NaI^{VII}O_4$	4.75	643.75	632.25	63.35	–
500	$Hf(IO_3)_4$	[2.6],5.0	643.7	632.2	62.7	–
501	$Pb(IO_3)_2$	[1.5],4.1	643.7	632.1	62.3	–
502	$Ho(IO_3)_3$	[1.6],4.2	643.6	632.05	62.8	–
612	$Ni(IO_3)_2$	[2.5],4.9	643.6	632.05	62.7	–
503	$Ce(IO_3)_4$	[1.8],4.6	643.55	632.0	62.4	–
421	$Zn(IO_3)_2$	[2.4],5.0	643.45	631.9	62.3	–
504	$Yb(IO_3)_3$	[2],4.7	643.4	631.9	62.3	–
370	$Ca(IO_3)_2$	[2.2],4.6	643.3	631.8	61.8	–
456	$Zr(IO_3)_4$	[2.1],4.6	643.35	631.8	62.0	–
505	$Tm(IO_3)_3$	[1.9],4.3	643.3	631.75	62.4	–
614	$Ba(IO_3)_2$	[1.9],4.6	643.25	631.7	62.3	–
237	$Na_5I^{VII}O_6$	5.25	643.25	631.65	62.65	–
506	$TlIO_3$	[2.5],5.1	643.2	631.6	61.8	–
507	$Er(IO_3)_3$	[2],4.3	643.1	631.6	–	–
471	$AgIO_3$	[2.3],4.8	643.0	631.5	61.8	–
508	$Lu(IO_3)_3$	[2],4.5	642.9	631.4	62.0	–
509	$Bi(IO_3)_3$	4.1	642.8	631.3	61.4	–
67	$[Co(NH_3)_6]_7[Cu(I^{VII}O_6)_2]_3$	4.7	642.7	631.2	61.9	–
510	$Hg(IO_3)_2$	[3.5],5.6	642.6	631.1	61.5	–
350	KIO_3	[3.2],5.3	642.5	631.0	62.1	–
613	$Cu(IO_3)_2$	[2.3],4.4	642.55	631.0	61.9	–
604	$Na_7H_4[Mn(I^{VII}O_6)_3]$	4.1	640.9	629.5	60.3	–
402	$Co(IO_3)_2$	3.5	640.5	629.0	–	–
402	repeated	[2.4],4.5	642.3	630.75	61.2	–
226	NaI	[2.8],5.6	638.9	627.3	57.6	11.2
511	PbI_2	[1.7],5.1	638.7	627.15	58.0	11.8
512	CsI	[1.5],5.15	638.55	627.0	57.95	11.7
347	KI	[1.6],4.7	638.5	626.9	57.4	10.2
472	AgI	[3.3],5.0	638.4	626.9	56.5	(9.7)
477	CdI_2	[2.4],4.7	638.4	626.8	58.3	11.1
469	PdI_2	5.1	638.3	626.75	58.0	11.6

TABLE 15. (continued).

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d)$	$I(5p)$
34	$[N(CH_3)_4]_2PtI_6$	4.8	638.3	626.75	57.2	13
420	Cu_2HgI_4	[4.3],6.1	638.2	626.7	56.7	10.1
593	Bengal Rosa B	5.1	638.1	626.5	57.9	11
406	$[Ni\ en_3]PtI_6$	4.8	638.0	626.45	57.0	–
453	RbI	[3.1],4.8	637.9	626.3	55.6	10
53	$[Ni\ en_2](AgI_2)_2$	[2.0],4.6	637.9	626.3	56.9	–
60	$[Ni\ en_2](CuI_2)_2$	[2.2],4.6	637.7	626.2	57.0	–
348	K_4BiI_7	[3],4.9	637.7	626.15	56.9	10.2
351	K_2HgI_4	[2.4],4.6	637.6	626.1	57.3	10.6
37	$[N(C_4H_9)_4]_2PtI_6$	[2],4.7	637.6	626.05	56.6	12
467	RhI_3	4.5	637.55	626.0	56.5	10
513	$CsBiI_4$	[3],5.0	637.5	626.0	57.6	10.3
513	repeated	4.5	637.9	626.4	57.1	10.7
71	$[Rh\ den\ I_3]$	[2.4],4.6	637.4	625.9	56.4	(11.2)
514	BiI_3	[3],5.0	637.25	625.8	57.8	–
81	$[Pd\ phen\ I_2]$	4.9	637.2	625.7	56.2	–
75	$[N(C_2H_5)_4]I$	4.5	636.9	625.6	54.1	8
410	$[Ni\ en_3]I_2$	[2.7],4.9	636.8	625.3	55.7	–
431	$[As(C_6H_5)_4]_2PtI_6$	4.8	636.8	625.3	56.0	–
327	$Cs_2[OsCl_5I]$	4.4	636.75	625.25	56.0	–
334	$Rb_2\textit{cis}\text{-}[OsCl_4I_2]$	4.6	636.65	625.1	–	–
358	K_2PtI_6	4.6	636.5	624.9	56.3	9.6
360	$K_2\textit{cis}\text{-}[OsCl_2I_4]$	4.1	636.4	624.85	55	–
515	TlI	4.85	636.25	624.75	56.25	9.7
516	$Cs_2\textit{fac}\text{-}[OsCl_3I_3]$	3.5	636.0	624.4	56	–
114	$(\text{methylene blue})_2PtI_6$	5.0	635.8	624.3	55.2	–
517	$Cs_2\textit{trans}\text{-}[OsCl_2I_4]$	5.0	635.8	624.25	55.7	9
43	$[N(CH_3)_4]I$	[2.8],4.9	635.6	624.15	54.3	9
518	Cs_2OsI_6	5.7	635.7	624.15	56	10.5
519	$[N(C_4H_9)_4]I$	4.7	635.1	623.6	54.6	–
345	$[N(C_4H_9)_4]_2\textit{trans}\text{-}[OsCl_4I_2]$	4.2	635.1	623.55	54	–

TABLE 16. Photo-electron signals of caesium and barium.

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(5p)$
–	Xe (ref. 97)	–	689.0	676.4	69.5	67.5	13.4,12.1
182	$CsSbF_6$	[1.5],5.1	747.7	733.8	86.8	84.6	–
182	repeated	[1.3],5.5	747.9	733.9	–	–	–
308	CsCl	[0.4],5.2	747.8	733.8	86.8	84.7	19.6
308	repeated	[0.7],5.2	747.5	733.4	87.5	85.1	19.6
512	CsI	[1.5],5.15	746.85	732.75	86.0	83.7	18.75

TABLE 16. (continued).

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(5p)$
444	$CsBr$	[1.6],4.95	746.3	732.25	85.7	83.5	18.3
520	$CsReO_4$	[1.6],4.7	746.3	732.2	–	83.7	16.7
521	Cs_2CO_3	[2.5],4.9	746.0	732.0	84.9	82.7	17.7
240	$CsAlSi_2O_6$	[2.5],4.7	746.05	732.0	(85.7)	83.1	18.3
309	$Cs_4(InCl_6)(SbCl_6)$	[2.3],4.9	746.0	731.9	84.9	82.8	17.4
314	Cs_2PbCl_6	[2.1],4.9	745.8	731.9	85.4	83.1	17.9
315	$Cs_2[Rh(H_2O)Cl_5]$	[2.2],4.9	745.8	731.8	85.4	83.2	18
311	$CsSbCl_6$	[2.0],5.0	745.6	731.7	85.2	83.1	–
310	Cs_2PtCl_6	[1.6],4.3	745.7	731.7	–	–	18
513	$CsBiI_4$	[3],5.0	745.6	731.5	–	–	–
513	repeated	4.5	745.9	731.9	85.4	83.3	18.7
313	$Cs_4(SbCl_6)(TlCl_6)$	[2.4],4.6	745.5	731.5	84.8	82.6	–
18	$CsUO_2(NO_3)_3$	[2.8],5.1	(745.7)	731.5	85.3	83.1	–
104	$Cs_3[Co(CN)_6]$	[2.5],4.6	745.4	731.4	84.8	82.6	18.1
442	Cs_2SnBr_6	[2.9],5.2	745.4	731.4	85.3	83.0	–
442	repeated	[2.0],4.8	746.2	732.2	85.6	83.4	18.4
466	Cs_2RhCl_6(?)	[2.3],5.0	745.3	731.3	84.9	82.7	18
441	Cs_2PtBr_6	4.0	745.3	731.3	–	–	17.6
318	$Cs_4(Sb^{III}Cl_6)(Sb^{V}Cl_6)$	[3.1],4.9	745.0	731.1	84.6	82.4	–
522	Cs_2WSe_4	4.7	745.1	731.1	–	–	–
257	Cs_2SO_4	4.9	744.8	730.8	84.1	81.9	17.1
390	$CsMnO_4$	[2.7],4.7	744.8	730.8	84.4	82.2	17.3
287	Cs_2WS_4	5.2	744.7	730.7	84.4	82.4	–
23	$CsNO_3$	[3.2],4.8	744.55	730.5	84.2	81.9	–
523	$Cs[B(C_6H_5)_4]$	4.7	744.2	730.2	83.5	81.3	–
326	Cs_2OsCl_6	4.8	744.05	730.1	83.5	81.3	16.0
322	Cs_2IrCl_6	5.7	744.0	730.0	83.7	81.5	–
322	repeated	4.9	744.7	730.7	83.7	81.7	17
327	$Cs_2[OsCl_5I]$	4.4	743.9	729.9	83.7	81.5	–
448	Cs_2OsBr_6	3.8	743.7	729.7	83.8	81.5	–
225	CsF	4.1	743.5	729.5	83.0	80.7	16.3
340	$Cs_2[OsCl_2I_4]$	5.0	743.4	729.4	(82.7)	80.3	–
301	Cs_2MoS_4	4.1	743.25	729.3	83.3	81.0	–
518	Cs_2OsI_6	5.7	743.15	729.1	82.7	80.7	–
203	BaF_2	[0.3],4.7	804.6	789.3	101.7	99.1	23.6
203	repeated	[0.1],4.4	804.6	789.3	101.4	98.8	23.6
249	$BaSO_4$	[3.2],5.9	804.0	788.7	101.4	98.8	22.3
249	repeated	[1.1],5.0	804.3	789.0	101.3	98.7	23.3
258	$BaS_2O_6, 2H_2O$	4.8	803.0	787.7	100.2	97.5	21.8
381	$BaCrO_4$	[2.2],4.9	803.0	787.7	100.2	97.7	22.1
435	$BaSeO_4$	[2.2],4.8	802.85	787.5	100.2	97.6	–
435	repeated	[1.1],4.7	804.2	788.9	101.2	98.7	–
609	$Ba(IO_3)_2$	[1.9],4.6	802.6	787.2	99.6	97.2	21.6
21	$Ba(NO_3)_2$	[3],5.1	802.5	787.0	99.7	97.1	21.2
391	$Ba(MnO_4)_2$	4.4	801.1	785.8	98.2	95.7	20.1

TABLE 17. Photo-electron signals of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium and dysprosium.

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d)$	$I(5p)$	$I(4f)$
84	LaF_3	[0.0],4.7	(868),863.9	(851.4),847.0	117.1,114.3	29.3 asym.	–
93	$La(IO_3)_3$	[1.7],5.0	863.8,860.7	847.0,843.9	114.6,112.1	–	–
50	$La_2(SO_4)_3$	[2.6],5.0	863.6,860.4	846.6,843.4	114.6,111.7	26	–
24	$La_2(CO_3)_3$	[1.4],4.0	863.5,860.1	846.4,843.2	117.3,115.8	–	–
28	$LaAsO_4$	[2.0],4.7	863.2,859.9	846.5,843.1	114.0,111.4	–	–
17	LaOCl	[2],4.4	862.8,859.1	845.5,842.4	113.7,110.9	–	–
86	$LaCrO_3$	[2.5],4.5	862.1,858.6	845.2,841.5	112.4,109.6	24.2	–
25	La_2O_3, calcined	[2.6],4.6	861.9,857.2	844.5,840.9	–	24.6	–
19	CeF_4, H_2O: Ce^{IV} ...	4.9	–	907.9	–	–	–
	Ce^{III} ..		913.1	(902,)894.4,(890.7)	120.6 broad	28.4	–
19	repeated: Ce^{IV} ...	[1.7],4.5	926.0	907.9	(136),132.5	–	–
	Ce^{III} ..		(921),913.0	894.3,(891)	120.9,(118)	–	–
26	CeO_2: Ce^{IV} ...	[2.2],4.7	–	915.7,906.7	–	–	–
	Ce^{III} ..		909	896.8,890.7	–	25.4	–
26	repeated: Ce^{IV} ...	[2],5.0	–	914.8,905.8	–	–	–
	Ce^{III} ..		(908.4)	896.0,890.0	119.6,116.3	–	–
26	repeated: Ce^{IV} ...	[2.2],4.8	924.2	905.8	(133),129.9	–	–
	Ce^{III} ..		(908.4)	896.3,890.1	121.0,116.7	–	–
27	$Th_{0\cdot6}Ce_{0\cdot2}U_{0\cdot2}O_2$:						
	Ce^{IV} ...	5.9	–	906.4	–	–	–
	Ce^{III} ..		909	896,890.4	–	–	–
28	$Th_{0\cdot8}Ce_{0\cdot15}U_{0\cdot05}O_2$:						
	Ce^{IV} ...	[2.2],4.8	–	915.4,906.0	–	–	–
	Ce^{III} ..		908.7	896.2,890.4	–	–	–
29	$Ce_{0\cdot5}U_{0\cdot5}O_2$	6.1	908,906.1	895,889.8	–	–	–
3	$Ce^{IV}(IO_3)_4$	[1.8],4.6	912,907.3	892,887.4	123,120.6,117	–	–
32	$Ce^{IV}(CrO_4)_2$: Ce^{IV} ...	[2.7],4.8	923.8	905.4	–	–	–
	Ce^{III} ..		914.5,908.6	895.5,889.9	118.3 broad	–	–
36	$[N(CH_3)_4]_2Ce^{IV}Cl_6$	[2.7],4.5	910.6,906.2	892.5,(889.0)	118.4 broad	–	–
35	$[Co(NH_3)_6]_2Ce^{IV}(CO_3)_5$:						
	Ce^{IV} ...	4.2	923.1	904.9	128.6	–	–
	Ce^{III} ..		(913),904.9	895.2,889.4	119.5,115.5	–	–
0	$Ce^{III}F_3$	[0.5],4.8	(915.5),912.2	(897.1),893.5	(123),119.8	(31),28.5	–
4	$Ce^{III}PO_4$	[2.4],4.8	911.6,(910.3)	892.8,(890)	119,(117)	–	–
30	$Ce^{III}{}_2(CO_3)_3$	[2.6],4.8	911.6,908.2	892.8,890.0	116 broad	–	–
7	$Ce^{III}{}_2(SO_4)_3$	4.7	909.9 asym.	889.9 asym.	117.5 broad	–	–
1	PrF_3	[1.5],4.9	(968.4),962.1	943.7 broad	(130),125.3	28.5	(12.0)
8	$Pr(IO_3)_3$	[1.7],4.6	962.2,(957)	942.1,(937)	125.2	–	–
1	Pr_6O_{11}	6.5	962.3	941.6,(937.2)	–	–	–
1	repeated: Pr^{IV} ...	[1.7],4.8	979.4,(973.3)	(954)	138	(38)	–
	Pr^{III} ..		961.8	941.4,(936.4)	125.3,(122)	27.3	(11)
2	$Th_{0\cdot9}Pr^{IV}{}_{0\cdot1}O_2$	[2.0],5.5	–	941.2,(937.5)	–	–	–
3	$Pr_2(SO_4)_3$	4.2	960.8	940.2	123.7	–	(10.8)
3	$Pr_2(C_2O_4)_3$	3.7	(963.5),959.3	938.8	–	–	–

TABLE 17. (continued).

	Compound	C_{st}	$I(3d_{3/2})$	$I(3d_{5/2})$	$I(4d)$	$I(5p)$	$I(4f)$
378	$PrVO_4$	4.8	953.3	937 broad	–	–	(11)
206	NdF_3	[2],4.7	1013.2,(1005)	990.3 asym.	130.8	28.5	(17),14.9
497	$Nd(IO_3)_3$	[1.7],4.7	1013.4,(1010.3)	990.8,(988.5)	–	–	–
429	$NdAsO_4$	[1.9],4.5	1012.6,(1008)	990.0,(986)	130.5	27.9	(16.5),13.5
276	$Nd_2(SO_4)_3$	[2.5],4.6	1012.7,(1009)	990.0,(985)	130.3	28	(16),13.2
534	Nd_2O_3	[2.1],5.1	1012.4 asym.	989.8,(985)	130.3	28	(16.6),13.4
26	$Mg_3Nd_2(NO_3)_{12}, 24H_2O$	4.6	1011.3,(1005)	988.8,(984)	129.2	–	–
207	SmF_3	[2.0],5.0	(1122),1118.5	1091.6	143.2 broad	–	(15.8),14.1
495	$Sm(IO_3)_3$	[1.5],4.6	1118.6	1091.4	–	–	(14)
535	$SmTaO_4$	[1],4.1	1117.3	1090.4	144,140	–	(16),13.5
536	Sm_2O_3	[2.7],5.3	(1121),1117.6	1090.3	141.3 broad	32	(16),13.7
194	EuF_3	[1],4.8	(1177),1173.6	(1146),1143.8	151.6,146.3	30.8	17.5
492	$Eu(IO_3)_3$	[1.6],4.9	1172.6	1143.0	–	–	(17.6)
254	$Eu_2(SO_4)_3$	[2.5],4.5	1171.5	1141.8	149.8,144.4	–	16.0
537	Eu_2O_3	[1.6],4.5	1171.0	1141.3	148.8,143.6	29	14.9
259	$Eu^{II}SO_4$	[2.4],4.4	1160.6	1130.8	135	17.9?	8.9
	(and Eu^{III})		& 1171.7	& 1141.4	& 141	–	17.9?
198	GdF_3	[0.8],4.4	1229.0	1196.6	157.9,152.5	32.0	18.9
496	$Gd(IO_3)_3$	[1.8],5.0	1229	1195.3	157,151.6	–	–
538	$GdTaO_4$	[3.2],5.0	1227.7	1194.9 asym.	156.4,151.4	(31)	17.4
251	$Gd_2(SO_4)_3$	[2.5],4.8	1227.8	1194.8	156.2,150.9	–	17.5
539	Gd_2O_3	[2],4.0	1227.3	1193.0	154.6,149.3	–	15.6
540	$Tb^{IV}O_2$	[2.3],5.4	1296	1260.0	173,166.2	–	27.8
	(and Tb^{III})		& 1284.5	& 1249.4	158.4	–	18,(12)
541	Tb_4O_7: Tb^{IV}	[2.5],5.1	–	–	–	–	27.0
	Tb^{III}		1283.9	1249.1	158	–	17.2,11.1
542	$Tb(OH)_3$	[2.5],5.1	1284.0	1248.9	–	31.3	18.1,(11.5)
543	$TbCl_3$	4.5	1283.2	1248.1	–	30.8	17.7,11.0
544	Dy_2O_3	3.3	–	–	163.3 broad	36	16.8,(13.8),(1
544	repeated	[1.1],4.3	1342.5	1303.6	164.3 broad	37	17.9,14.7,(12.
380	$DyVO_4$	3.4	–	–	163.2 broad	–	–
380	repeated	[1.8],4.2	1340.2	1301.7	163,161	–	16.9,(12.0)

TABLE 18. Photo-electron signals of holmium, erbium, thulium, ytterbium and lutetium.

	Compound	C_{st}	$I(4d)$	$I(5p)$	$I(4f)$
502	$Ho(IO_3)_3$	[1.6],4.2	(172),170.4	–	17.8,(15.4),(13)
545	Ho_2O_3	[2.3],4.9	(174),169.4	32	16.9,(13)
195	ErF_3	[1],4.5	plateau + 178.8	34.4	18.7,(15.7)
507	$Er(IO_3)_3$	[2],4.3	plateau + 177.1	–	17.5,(16),(13.8)

TABLE 18. (continued).

	Compound	C_{st}	$I(4d)$	$I(5p)$	$I(4f)$
546	Er_2O_3	[1.6],4.7	plateau + 177	34	17,5,(14)
505	$Tm(IO_3)_3$	[1.9],4.3	plateau + 185.1	–	17.2,(13.8)
547	Tm_2O_3	[2.3],5.1	(187),184.5	34	17.7,(13.6)
547	repeated	[1.6],4.2	197,184.2	40.8,33.4	16.9,(13.4)
205	YbF_3	[2.2],4.7	216,209,202,194.7	35.4	20.5,16.7
504	$Yb(IO_3)_3$	[2],4.7	214,207.3,199.2,193.9	–	(20),16.0
548	$YbTaO_4$	[1.9],4.7	207,(200),193.3	–	19.4,15.7
549	$Yb_2(WO_4)_3$	[2.5],4.3	205,198,193.0	–	19.1,15.1
550	$Yb_2Hf_2O_7$	[2.2],4.7	208,200,193.1	–	18.7,15.0
266	$Yb_2(SO_4)_3$	4.2	206,(199),192.4	33	18.4,14.6
430	$YbAsO_4$	[2.5],4.2	205,199,192.4	33	(18.8),14.6
376	$YbVO_4$	[2.8],4.9	205,199,192.2	39.9,33.5	18.2,14.3
375	$Yb_2Ti_2O_7$	4.6	205,199,191.4	32.7	17.5,13.7
551	Yb_2O_3	3.8	(210),203.3,(196),189.2	33.1	(17.6),13.6
606	LuF_3	[0.3],5.5	218.6,208.7	38.5	20.5
606	repeated	[0.4],4.9	217.6,207.6	44.9,37.8	19.7
508	$Lu(IO_3)_3$	[2],4.5	214.8,204.8	–	16.8
552	Lu_2O_3	[2.7],4.8	213.9,203.9	35.0	16.0

TABLE 19. Photo-electron signals of the elements hafnium to uranium. It is often to difficult to detect $Re4d_{3/2}$ and Os4d because of coincidences with C1s.

	Compound	C_{st}	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(4f_{5/2})$	$I(4f_{7/2})$	$I(5d)$
10	K_2HfF_6	[2.7],5.0	232.9	222.4	(27.5)	26.0	–
0	$Hf(IO_3)_4$	[2.6],5.0	232.6	221.9	(27.3)	25.6	–
53	HfO_2	[2.2],4.5	231.5	220.8	–	25.0	–
50	$Yb_2Hf_2O_7$	[2.2],4.7	231.4	220.7	(26.1)	24.4	–
54	$Hf(C_6H_5CHOHCO_2)_4$	5.0	230.2	219.5	(24.9)	23.2	–
55	Hf, powder, oxidized	5.0	–	220	–	23.6	–
15	K_2TaF_7	[3.1],4.5	250.7	239.2	(37.5)	35.7	–
38	$GdTaO_4$	[3.2],5.0	250.6	239.1	(37.0)	35.4	–
11	TaF_5	5.3	250.2	238.7	(36.6)	34.8	–
18	$YbTaO_4$	[1.9],4.7	250.1	238.3	36.3	34.6	–
5	$SmTaO_4$	[1],3.9	–	–	35.6	33.8	–
6	TaC (oxidized?)	[2.8],5.1	249.2	237.6	(35.6)	33.6	–
7	Ta_2O_5	[2.8],4.9	248.8	237.4	35.1	33.3	–
0	Tl_3TaS_4	4.8	248.6	237.1	35	33.2	–
0	Tl_3TaSe_4	4.3	247.8	236.2	–	32.8	–
8	Ta, powder, oxidized	4.7	248.7	237.3	(35.3)	33.4	–
9	$Yb_2(WO_4)_3$	4.3	267.1	254.6	45.1	43.2	–
3	Na_2WO_4	[3.4],5.6	267.3	254.6	44.7	42.9	–

TABLE 19. (continued).

	Compound	C_{st}	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(4f_{5/2})$	$I(4f_{7/2})$	$I(5d)$
559	Tl_2WO_4	[2.9],4.8	266.7	254.1	44.2	42.7	–
78	$[Co\ en_2Cl_2]_3(PW_{12}O_{40})$	4.0	–	–	44.7	42.7	–
560	$H_3PW_{12}O_{40}$	4.0	265	252.8	43.0	41.1	–
287	Cs_2WS_4	5.2	265	252.6	42.7	40.9	–
295	Tl_2WS_4	4.5	264.2	251.7	41.5	39.5	–
561	W, powder, oxidized	4.5	265.6	253.1	43.2	41.3	–
520	$CsReO_4$	[1.6],4.7	287	273.7	56.5	54.3	–
562	$TlReO_4$	[2.6],5.1	286	273.2	56.1	53.9	–
474	$AgReO_4$	4.7	286	272.6	(55.5)	53.4	–
357	$KReO_4$	[2],3.7	286.2	272.5	55.1	52.9	–
563	methylene blue (ReO_4)	4.5	284	270.3	53.1	50.7	–
434	$[As(C_6H_5)_4]ReO_4$	3.9	284	272	(53.0)	50.6	–
337	K_2ReCl_6	3.7	282.9	268.7	51.5	49.1	9.7,(8)
359	K_2ReBr_6	4.8	–	269.0	51.4	49.0	8.9
65	$[N(CH_3)_4]ReS_4$	4.4	280	267.6	(50.8)	48.2	–
130	$[N(CH_3)_4]_2ReBr_6$	4.6	–	267.8	50.4	47.9	8.2
346	$[As(C_6H_5)_4]_2ReCl_6$	4.9	–	267	50.1	47.9	–
607	$K[Os^{VIII}O_3N]$	[2.1],4.4	–	–	66.2	63.7	–
608	$[As(C_6H_5)_4][Os^{VIII}O_3N]$	4.2	–	–	63.9	61.3	–
362	$K_2[Os^{VI}O_2(OH)_4]$	4.8	–	–	63.2	60.7	10
326	$Cs_2Os^{IV}Cl_6$	4.8	–	–	62.4	59.8	9
327	$Cs_2[Os^{IV}Cl_5I]$	4.4	–	286	62.2	59.2	9.6
448	$Cs_2Os^{IV}Br_6$	3.8	301.6	–	61.8	59.1	9.8
324	$K_2Os^{IV}Cl_6$	3.8	–	286.3	61.6	58.9	10.6,(8.
324	repeated	5.0	–	287	62.8	59.9	10.8,(8.
64	$[N(C_2H_5)_4]_2Os^{IV}Cl_6$	5.2	–	–	62.4	58.6	9.1,(7.
334	Rb_2*cis*-$[Os^{IV}Cl_4I_2]$	4.6	–	–	61.1	58	9.0
136	$Co_2[Os^{II}(CN)_6]$	5.0	300.4	285	60.6	57.9	–
134	$Ni_2[Os^{II}(CN)_6]$	5.2	301.0	285	60.6	57.9	–
451	$Tl_2Os^{IV}Br_6$	6.0	301	285	60.7	57.9	8.8
452	$[N(C_4H_9)_4]_2Os^{IV}Br_6$	5.1	–	–	60.3	57.5	8.5
345	$[N(C_4H_9)_4]_2$*trans*-$[Os^{IV}Cl_4I_2]$	4.2	–	–	60.0	57.5	–
170	$[As(C_6H_5)_4]_3[Os^{III}(SCN)_6]$	4.6	–	–	59.8	57.1	–
518	$Cs_2Os^{IV}I_6$	5.7	–	–	59.8	57	–
340	Cs_2*trans*-$[Os^{IV}Cl_2I_4]$	5.0	–	284.9	59.6	56.5	9,(8)
177	$Fe_4[Os^{II}(CN)_6]_3$	4.6	–	–	58.4	55.8	–
322	$Cs_2Ir^{IV}Cl_6$	4.9	321	306	73.5	70.7	10.6
121	$Cu_3[Ir^{III}(CN)_6]_2, 11H_2O$	4.5	320	305.4	72.9	70.0	–
103	$K[Ir^{IV}pyCl_5]$	4.7	319.5	303.7	71.9	68.9	–
600	$Na_2Ir^{IV}Cl_6$	4.6	–	303.7	71.2	68.6	–
600	repeated	4.7	319	304	71.6	68.9	–
99	$[Ir^{III}(NH_3)_5Cl]Cl_2$	4.4	319.5	303.7	71.5	68.65	9.2
366	$K_2Ir^{IV}Br_6$	4.7	–	–	71.1	68.6	8.7
74	$[N(CH_3)_4]_2Ir^{IV}Cl_6$	4.4	–	303.9	71.3	68.5	–

TABLE 19. (continued).

	Compnund	C_{st}	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(4f_{5/2})$	$I(4f_{7/2})$	$I(5d)$
08	$[Ir^{III}py_4Cl_2]Cl$	4.7	319.3	303.8	71.15	68.2	8.5
82	$[Ir^{III}(S(C_2H_5)_2)_3Cl_3]$	5.2	–	303	70.5	67.5	–
61	$[N(CH_3)_4]_3[Ir^{III}(SCN)_6]$ ..	4.4	318	301.4	70.3	67.4	–
68	$[N(C_4H_9)_4]_3Ir^{III}Cl_6$	4.4	–	–	69.8	67.1	–
66	$[As(C_6H_5)_4]_3[Ir^{III}(SeCN)_6]$	4.1	316	299	69.8	67.0	–
46	$Ir^{III}(S_2P(OC_3H_7)_2)_3$	4.5	318.1	302.3	69.8	66.85	–
10	Cs_2PtCl_6	[1.6],4.3	–	–	(86.3)	83.5	12.4
12	Rb_2PtCl_6	[2.5],5.0	–	–	86.5	83.25	12.1
41	Cs_2PtBr_6	[1],4.0	–	–	(85)	82.8	11.5
20	K_2PtCl_6	[3],4.6	342.0	325.0	85.25	82.0	10.9
93	$[Pt\ den\ Cl_3]ClO_4$	4.5	340.4	323.3	84.5	81.4	–
64	K_2PtBr_6	2.6	340.0	323.2	83.7	80.4	9.8
64	repeated	5.0	341.2	324.3	84.6	81.3	10.5
47	$[N(CH_3)_3CH_2C_6H_5]_2PtCl_6$	4.6	–	–	84.2	81.0	9.2
38	Tl_2PtCl_6	2.8	341.6	323.0	84.2	81.0	10.0
51	$(NH_4)_2PtCl_6$	3.3	340.9	323.7	84.15	80.9	9.6
51	repeated	4.8	340.8	324.0	84.4	81.1	10.0
34	$[N(CH_3)_4]_2PtI_6$	[2],4.8	–	323	84.1	80.8	10.4
29	$K_2[Pt(SeCN)_6]$	[2.7],4.8	340	323.4	83.9	80.6	10
6	$[Ni\ en_3]PtI_6$	4.8	–	–	83.8	80.5	–
48	$[N(C_2H_5)_4]_2PtBr_6$	4.6	–	–	83.6	80.4	9.3
8	$K_2[Pt(SCN)_6]$	4.8	339.6	322.5	83.1	80.0	10.9,(9)
1	$[As(C_6H_5)_4]_2PtI_6$	4.8	–	323	83.2	80.0	–
9	$[C_{19}H_{42}N_2]_2[Pt(N_3)_6]$	5.3	338	321	83.0	79.8	–
8	$K_2Pt^{II}Cl_4$	4.4	339.2	–	82.6	79.4	9.4
6	$[Ni\ en_2][Pt^{II}(CN)_4]$	4.1	339.5	322.1	82.4	79.3	–
9	$[Pt^{II}(S(C_2H_5)_2)_2Cl_2]$	5.0	338.6	321.6	81.9	78.7	–
7	$[N(C_4H_9)_4]_2PtI_6$	4.7	–	–	81.9	78.7	9.5
8	K_2PtI_6	4.6	338	321.5	81.2	78.4	9.6
7	$[Pt^{II}(NH_3)_4][Pt^{II}Cl_4]$	4.0	338.3	321.2	81.55	78.25	–
4	(methylene blue)$_2$(PtI_6) ..	5.0	–	–	81.1	77.9	8.2
3	$[N(C_4H_9)_4]_2Pt^{II}Cl_4$	5.3	338	320.2	80.9	77.7	8.3
4	Pt, foil	5.7	337.3	320.3	80.1	76.8	10.1
6	Au_2Cl_6	4.4	361.8	343.6	97.9	94.6,92.0	11.8
3	$KAu^{III}Cl_4$	3.2	–	344.4	97.4	93.85	–
3	$KAu^{III}Cl_4$, 1^h later	3.2	–	–	97.2	93.8,(91.2)	–
2	$KAu^{III}Br_4(+Au^I)$	3.4	–	–	(97.6),95.1	(93.5),91.8	9.8
4	$[N(CH_3)_4][Au^{III}(CN)_2Br_2]$	5.3	362	343.4	96.7	93.3	–
5	$[N(C_4H_9)_4]Au^{III}Cl_4$	5.2	360.8	342.8	96.8	93.4	–
4	$Na_3[Au^I(S_2O_3)_2]$	4.8	361.1	343.1	96.35	92.8	–
0	$[N(C_4H_9)_4]Au^{III}Br_4$	4.9	360.7	342.4	95.8	92.4(90)	–
3	$[Co(NH_3)_6][Au^I(S_2O_3)_2]$ ..	4.4	360.0	342.3	95.0	91.4	–
4	$K[Au^I(CN)_2]$	4.5	360.1	342.0	94.9	91.2	10.5
5	$[As(C_6H_5)_4][Au^{III}(SeCN)_4]$	4.8	359	342.0	94.5	90.9	–

TABLE 19. (continued).

	Compound	C_{st}	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(4f_{5/2})$	$I(4f_{7/2})$	$I(5d)$
284	$Au^{I}S_2CH_2CO_2H$	3.9	359.6	341.6	94.45	90.8	–
599	$Na_3[Au^{I}(SO_3)_2]$	5.4	359.4	341.3	94.4	90.8	10.7
566	Au, powder	5.4	358.1	339.9	92.2	88.55	10.8,8.0
–	Au, powder ($BaSO_4 + ThF_4$)	[1.7],4.8	–	342.1	95.2	91.3	–
–	6 MgF_2: 2Au: Tl_2O_3	5.6	–	–	92.6	88.8	–
–	16 MgF_2: 2Au: Tl_2O_3	[2],4.2	–	–	94.5	90.9	–
–	$2BaSO_4$: 2Au: Tl_2O_3: $2ThF_4$	[1.0],4.8	–	–	–	92.9	–
567	HgO	[3.2],5.5	386.4	367.1	112.6	108.55	–
567	repeated	[2.5],4.8	386.4	367.0	112.3	108.25	(17.7),16.3
610	HgF_2	[2.5],4.5	386.3	366.8	112.55	108.5	17.7,16.3
611	$(Hg_2)CrO_4$	[1.8],4.0	386.2	366.8	112.25	108.2	(17.9),16.5
510	$Hg(IO_3)_2$	[3.5],5.6	386.1	366.6	111.95	107.9	(17.6),16.2
351	K_2HgI_4	4.6	385	366.2	111.85	107.8	–
420	Cu_2HgI_4	[4.3],6.1	386	366.7	111.9	107.8	–
163	$K_2[Hg(SCN)_4]$	5.0	384	365.2	110.85	106.75	–
155	$Co(NCS)_4Hg$	4.7	384.4	364.9	110.6	106.55	–
187	TlF	[2.6],5.2	–	–	131.6	127.2	(24.2),22.0
562	$TlReO_4$	[2.6],5.1	414.5	393.7	131.45	127.0	23.9,21.8
506	$TlIO_3$	[2.5],5.1	–	–	131.4	126.95	23.9,21.7
262	Tl_2SO_4	5.1	–	–	131.15	126.7	23.6,21.4
313	$Cs_4(SbCl_6)(Tl^{III}Cl_6)$	[2.3],4.6	–	–	130.9	126.45	(23.6),21.4
559	Tl_2WO_4	[2.9],4.8	–	–	130.8	126.35	(23.4),21.1
460	Tl_2MoO_4	[2.6],4.8	413.3	392.0	130.4	125.95	(23.1),20.8
568	Tl_2CO_3	[2.4],4.7	413.7	392.8	130.35	125.9	(22.8),20.7
286	$Tl_2[MoO_2S_2]$	4.7	413.3	–	130.1	125.65	(23),20.4
569	$Tl_2[WO_2S_2]$	4.5	–	–	130.05	125.65	(22.7),20.5
280	Tl_3TaS_4	4.8	–	–	130.05	125.6	(22.8),20.8
383	Tl_2CrO_4	4.5	–	–	129.95	125.55	(22.8),20.4
449	TlBr	4.6	–	–	129.9	125.45	22.2,20.1
288	Tl_2MoS_4	4.4	412.5	–	129.75	125.3	(22.5),20.2
458	Tl_3NbS_4	4.8	–	–	129.7	125.25	(22.3),20.1
438	Tl_3NbSe_4	4.7	–	–	129.7	125.25	(23),20.3
295	Tl_2WS_4	4.5	–	–	129.6	125.15	21.8,19.5
570	$Tl[B(C_6H_5)_4]$	5.0	412.9	392.0	129.55	125.1	22.1,19.8
515	TlI	4.85	412.1	391.5	129.4	125.05	23.4,20.4
338	Tl_2PtCl_6	2.8	412.0	391.0	129.15	124.7	19.7
440	Tl_3TaSe_4	4.3	–	–	129.1	124.65	(22.2),19.9
341	$[Co(NH_3)_6]Tl^{III}Cl_6$	3.7	–	–	129.0	124.6	–
451	Tl_2OsBr_6	6.0	–	–	128.75	124.4	21.1,19.1
571	$Tl^{III}{}_2O_3$	4.4	–	–	127.35	123.0	–
571	repeated	5.4	410.9	390.0	127.05	122.7	20,18.0
–	$6MgF_2$: 2Au: Tl_2O_3	5.6	–	–	127.2	122.85	–
–	$16MgF_2$: 2Au: Tl_2O_3	[2],4.2	–	–	129.4	125.0	–

TABLE 19. (continued).

	Compound	C_{st}	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(4f_{5/2})$	$I(4f_{7/2})$	$I(5d)$
–	$2BaSO_4$: 2Au: Tl_2O_3: $2ThF_4$	[1.0],4.8	–	–	131.1	126.7	–
19	$Pb(NO_3)_2$	[2.8],5.3	–	422.2	152.1	147.2	30.9,28.3
314	$Cs_2Pb^{IV}Cl_6$	[2.1],4.9	–	–	151.95	147.1	30.5,27.8
501	$Pb(IO_3)_2$	[1.5],4.1	–	–	151.85	146.95	30.6,28.0
511	PbI_2	[1.7],5.1	–	–	151.7	146.75	30.4,28.0
264	$PbSO_4$	4.5	443.2	420.7	150.95	146.1	29.8,27.2
330	$PbCl_2$	[2.5],4.6	–	–	151.0	146.1	29.3,26.8
46	$PbBr_2$	[2.7],4.9	–	–	150.85	145.95	29.4,26.9
24	PbF_2	[3],4.8	–	–	150.75	145.9	29.6,27.1
72	$Pb_3(OH)_3(CH_3CO_2)_3$	5.2	–	–	150.8	145.85	– ,27.2
31	$[Co\ en_2Cl_2]_2Pb^{IV}Cl_6$	[3.0],5.0	–	–	150.7	145.85	29.4,26.7
73	$Pb(CH_3CO_2)_2, 2H_2O$	4.9	–	–	150.0	145.1	28.9,26.3
74	$PbCO_3$	3.2	–	–	149.8	145.0	–
74	PbS	4.2	–	–	149.85	145.0	28.9,26.3
44	$[As(C_6H_5)_4]_2Pb^{IV}Cl_6$	4.8	–	–	149.2	144.25	– ,25.2
75	PbO	3.3	–	–	149.0	144.15	–
96	$Pb(S_2CN(C_2H_5)_2)_2$	4.2	–	–	148.9	144.0	26.6,24.2
76	$Pb^{II}{}_2Pb^{IV}O_4$	3.6	–	–	148.8	143.9	–
87	$PbCrO_4$	3.3	–	–	148.6	143.75	27,25.0
02	$Pb(S_2P(OC_2H_5)_2)_2$	4.8	–	–	148.2	143.3	(26.5),24.3
77	PbO_2	4.4	–	–	147.2	142.4	–
77	repeated	5.0	440.6	418.4	148.0	143.1	27,24.4
20	BiF_3	[3.3],5.4	474.7	450.9	173.1	167.8	37.6,34.7
78	$Bi^{III}Bi^{V}O_4$	[2.3],4.8	474.0	450.1	172.5	167.15	37.3,34.4
09	$Bi(IO_3)_3$	4.1	–	–	172.3	166.95	36.7,33.9
73	$Bi_2Ti_2O_7$	[2.3],4.7	473	449.8	172.2	166.9	36.9,34.0
79	Bi_2O_3	[2.1],4.7	–	–	172.2	166.85	36.8,33.8
80	$NaBi^{V}O_3$	4.55	–	–	171.8	166.5	–
14	BiI_3	[3],5.0	–	–	171.8	166.5	(36.8),33.7
13	$CsBiI_4$	[3],5.0	–	–	171.6	166.3	(36.5),33.7
13	repeated	4.5	473	449.3	–	–	36.4,33.3
81	BiOI	[2],5.05	–	–	171.4	166.1	–
48	K_4BiI_7	[3],4.9	472.6	449.1	171.3	166.0	35.8,32.9
46	$[Co(NH_3)_6]BiCl_6$	3.6	–	–	170.2	164.9	35,31.9
99	ThF_4	[1.3],4.9	723.5	686.1	354.75	345.4	104.15,97.3
15	$Th(C_2O_4)_2$	[1.9],4.6	722.6	685.1	353.45	344.1	103.1,96.2
99	$Th(IO_3)_4$	[2.2],4.7	722.4	684.3	352.85	343.5	102.4,95.55
32	$Th_{0\cdot95}U_{0\cdot05}O_2$	[2.3],6.4	–	–	352.35	343.0	–
33	ThO_2	[1.0],4.6	720.6	683.4	352.0	342.65	101.5,94.5
34	$[Co(NH_3)_6]_2[Th(CO_3)_5]$	[2.3],4.2	720.7	683.0	351.8	342.45	–
27	$Th_{0\cdot6}Ce_{0\cdot2}U_{0\cdot2}O_2$	[2.8],5.9	–	–	351.4	342.1	–
32	$Th_{0\cdot9}Pr_{0\cdot1}O_2$	[2.0],5.5	–	–	351.1	341.8	–
16	$Thaca_4$	[2.3],4.3	720.0	682.5	351.1	341.75	100.8,94.0
35	$Th_{0\cdot5}Eu_{0\cdot5}O_{1\cdot75}$	[2.3],5.8	–	–	351.1	341.75	–

TABLE 19. (continued).

	Compound	C_{st}	$I(4d_{3/2})$	$I(4d_{5/2})$	$I(4f_{5/2})$	$I(4f_{7/2})$	$I(5d)$
586	$Th_{0\cdot8}Ce_{0\cdot1}U_{0\cdot1}O_2$	[2.6],4.8	–	–	351.0	341.7	–
528	$Th_{0\cdot8}Ce_{0\cdot15}U_{0\cdot05}O_2$	[2.2],4.8	720.3	682.4	351.0	341.7	100.8,93.9
607	$Th(NO_3)_4,5H_2O$	4.4	720.3	682.8	351.0	341.65	100.3,93.6
617	$Th(C_6H_5CHOHCO_2)_4$	4.3	719.7	682.4	350.85	341.5	100.4,93.5
587	Th, powder, oxidized	[2.3],5.7	–	–	352.0	342.7	–
494	$UO_2(IO_3)_2$	[1.4],4.7	791.1	748.8	401.7	(394),390.8	115.2,106.9
18	$CsUO_2(NO_3)_3$	[2.8],5.1	790.3	746	(405),401.2	(394),390.4	– ,106.6
242	$Cu(UO_2)_2(PO_4)_2$	[2.0],4.6	790.8	747.9	400.9	390.0	114.7,106.3
20	$RbUO_2(NO_3)_3$	[2.7],4.8	790.0	747.4	(404),400.6	(393),389.7	–
230	$NaZn(UO_2)_3(CH_3CO_2)_9$	[2.5],4.6	790	747.8	400.4	389.6	114.0,105.5
218	$K_2U^{IV}F_6$	[2.4],4.9	790 asym.	747.5	407.3,400.4	396.7,389.5	–
238	$NaMg(UO_2)_3(CH_3CO_2)_9$	[3],4.4	789.5	747.4	400.4	(393),389.5	114.2,105.4
422	$Zn(UO_2)_2(CH_3CO_2)_6$	[3.7],5.6	–	–	400.2	389.4	–
528	$Th_{0\cdot8}Ce_{0\cdot15}U_{0\cdot05}O_2$	[2.2],4.8	–	–	400.1	389.2	–
527	$Th_{0\cdot6}Ce_{0\cdot2}U_{0\cdot2}O_2$	[2.8],5.9	–	–	400.05	389.15	–
588	$(NH_4)_2U_2O_7$	4.7	789.0	747.1	399.9	389.05	–
529	$Ce_{0\cdot5}U_{0\cdot5}O_2$	6.1	–	–	399.5	(397),388.8	–
268	$UO_2SO_4, 3H_2O$	5.1	789.4	746.9	399.6	388.8	113.3,104.8
252	$U(SO_4)_2, 4H_2O$	[2.5],4.8	789	747.0	405,399.5	393.8,388.7	113,107,104.8
252	repeated	4.8	(795),789.7	(752.4),747.0	405.2,398.9	393.9,389.0	113.4,108,105.
22	$UO_2(NO_3)_2\,6H_2O$	4.0	790	746.8	399.5	(392),388.65	113,105.0
586	$Th_{0\cdot8}Ce_{0\cdot1}U_{0\cdot1}O_2$	[2.6],4.8	–	–	399.5	388.6	–
589	$U^{IV}O_2$	3.6	787.9	745.4	398.1	387.3	–
590	U_3O_8	4.1	(794),787.5	(750.7),745.3	398.0	387.2	–
248	$[P(C_6H_5)_3H]_2U^{IV}Cl_6$	4.6	787	746.2	396.6	386.0	–

TABLE 20. Various weak photo-electron signals from 22 selected compounds.

	Compound	C_{st}	
403	MgO	[0.4],4.0	$I(O2s) = 29.6$ $I(O2p) = 14$
388	Cr_2O_3	4.2	$I(O2s) = 28.3$ $I(O2p) = 11.5$ $I(Cr3d) = 8.2$
395	Fe_2O_3	4.4	$I(O2s) = 28.4$ $I(O2p)$, $I(Fe3d) = 13.6, 10.6$
304	$KClO_4$	4.8	$I(Cl2s) = 285.3$
321	KCl	[2.3],4.8	$I(Cl2s) = 276.7$ $I(Cl3s) = (22.1)$
320	K_2PtCl_6	[3],4.6	$I(Cl2s) = 276.4$
324	K_2OsCl_6	5.0	$I(Cl2s) = 276.2$
201	CaF_2	[1.3],4.5	$I(Ca2s) = 448.0$ $I(Ca3s) = 52.5$
370	$Ca(IO_3)_2$	[2.2],4.6	$I(Ca2s) = 446.4$
306	$[Vurea_6](ClO_4)_3$	5.4	$I(O2s) = 31.8$ $I(V3d) = 11.1$
381	$BaCrO_4$	[2.2],4.9	$I(Cr2s) = 708.5$ $I(O2s) = 30.1$
216	$K_2[Cr(H_2O)F_5]$	[1.7],4.9	$I(Cr2s) = 707.2$ broad $I(Cr3s) = 88.6, 84.3$
86	$NH_4[Cr(NH_3)_2(NCS)_4]$	[3.7],5.2	$I(Cr2s) = 706.6, 703.2$

TABLE 20. (continued).

	Compound	C_{st}	
188	CoF_2	[1.1],5.4	$I(Co3s) = 118.2, 113.4$
221	$NiF_2, 4H_2O$	[2.6],4.7	$I(Ni3s) = 120.0, 117.2$
197	SrF_2	[1.2],5.0	$I(Sr3s) = 367.0$ $I(Sr4s) = 47.2$
217	CdF_2	[2],4.3	$I(Cd3p_{3/2}) = 625.8$ $I(Cd4p) = 76.5$ broad
203	BaF_2	[0.1],4.4	$I(Ba3p_{3/2}) = 1071.6$ $I(Ba4s) = 261.8$ $I(Ba4p_{3/2}) = 187.4$
566	Au, powder	5.4	$I(Au4s) = 761.4$ $I(Au4p_{3/2}) = 751.2$ $I(Au5p_{3/2}) = 61$
199	ThF_4	[1.3],4.9	$I(Th4p_{3/2}) = 977$ broad $I(Th6p_{3/2}) = 27.2$
583	ThO_2	[1.0],4.6	$I(Th4p_{3/2}) = 979.3$ $I(O2s) = 31.3$ $I(Th6p_{3/2}) = 24.3$ $I(O2p) = 13.3$
252	$U(SO_4)_2, 4H_2O$	[2.5],4.8	$I(O2s) = 31.6$ $I(U5f) = 10.1$

TABLE 21. Comparison of I' Values (corrected for charging effects) with the calculated values I_{calc} from atomic ionization energies and Madelung potentials. ∂ is defined in the text the distance between the two carbon 1s signals.

	∂	$I'(M)$	I_{calc}	$I'(X)$	I_{calc}	$I - 4.8$
LiF	2.8,3.7	60.7	63.12	12.85	12.92	10.8,11.8
NaF	4.2	35.5	36.43	12.8	14.26	12.0
NaCl	2.2	35.6	38.37	10.0	12.53	7.4
NaBr	2.4	35.3	39.84	9.0	11.81	6.6
NaI	2.8	35.6	39.52	8.4	10.83	6.4
KF	2.4	21.7	22.20	11.5	12.82	9.2
KCl	2.5	21.4	23.63	9.4	11.60	7.1
KBr	1.5	21.8	23.98	9.2	11.00	5.9
KI	3.1	21.7	24.51	7.9	10.17	6.2
RbCl	2.4	19.0	19.64	9.5	11.25	7.1
RbBr	2.4	18.5	19.97	8.9	10.67	6.5
RbI	1.7	18.8	20.43	8.3	9.91	5.2
CsCl	4.8,4.5	15.0	18.0	9.0	10.7	8.6,9.0
CsBr	3.35	15.0	18.27	8.7	10.2	7.2
CsI	3.65	15.1	18.7	8.1	9.5	6.9
MgO	3.6	54.1	56.24	9	–	–
CaF_2	2.75,3.2	30.6	35.56	13.3	18.75	11.3,11.5
SrF_2	3.8,3.8	25.0	29.3	13.3	17.70	12.2,12.3
BaF_2	4.4,4.3	19.3	28.0	11.9	16.93	11.5,11.4
ZnS	2.4	15.6	19.72	–	–	–
CdO	2.6	16.8	16.04	–	–	–
CdS	1.5	16.8	18.78	–	–	–
AgBr	1.9	10.0	14.77	–	–	–
CdF_2	1.8	17.4	22.0	11.9	18.9	8.9
HgF_2	2.0	14.3	19.1	–	–	–

TABLE 22. I' of fluorine and potassium compounds. Sometimes, two independent determinations have been performed.

	∂	$I'(\mathrm{F1s})$		∂	$I'(\mathrm{F1s})$		∂	$I'(\mathrm{K2p_{3/2}})$
KBF_4	1.5,2.6	692.5,692.2	CoF_2	4.3	689.8	KBF_4	1.5,2.6	299.5,299.2
KPF_6	1.8	692.2	$CuF_2, 2H_2O$	2.2	689.8	KPF_6	1.8	299.2
K_3RhF_6	2.7	692.1	$[Zn(H_2O)_6]SiF_6$	2.3	689.8	K_3RhF_6	2.7	299.0
$CsSbF_6$	3.6,4.2	691.4,691.1	$(NH_4)_2[In(H_2O)F_5]$			K_2SiF_6	2.4,2.6	298.8,298.8
K_2SiF_6	2.4,2.6	691.1,690.9		1.2	689.8	K_2GeF_6	3.4	298.6
ZrF_4	2.6	690.9	CeF_3	4.3	689.8	K_4BiI_7	1.9	298.6
MgF_2	4.3,4.9	690.7,690.7	SmF_3	3.0	689.8	K_2BeF_4	3.0,2.8	298.5,298.5
Na_3AlF_6	3.0	690.7	BiF_3	2.1	689.8	K_2NbF_7	2.0	298.5
K_2GeF_6	3.4	690.7	SrF_2	3.8,3.8	689.9,689.7	K_2HfF_6	2.3	298.5
K_2NbF_7	2.0	690.7	CeF_4, H_2O	2.8	689.6	K_2TiF_6	2.1	298.4
PrF_3	3.4	690.7	CdF_2	2.3,1.7	689.6,689.3	K_2PtCl_6	1.6	298.3
K_2TaF_7	1.4	690.6	NaF	4.2,3.8	689.6,689.1	KBr	1.5	298.3
YF_3	3.7	690.5	$NiF_2, 4H_2O$	2.1	689.4	K_2TaF_7	1.4	298.2
YbF_3	2.5	690.4	$KNiF_3$	3.2	689.4	KIO_3	2.1	298.1
LiF	2.8,3.7	690.0,690.4	K_2UF_6	2.5	689.4	KIO_4	2.5	298.0
K_2BeF_4	3.0,2.8	690.4,690.0	BaF_2	4.3,4.4	689.0,688.8	K_2HgI_4	2.2	298.0
ErF_3	3.5	690.3	$K_2[Cr(H_2O)F_5]$	3.2	688.7	KF	2.4	297.9
LuF_3	5.2	690.3	PbF_2	1.7	688.4	KI	3.1	297.9
K_2HfF_6	2.3	690.3	HgF_2	2.0	688.0	KCl	2.5	297.8
$GaF_3, 3H_2O$	2.7	690.2	KF	2.4	687.9,687.6	K_2HAsO_4	1.7	297.8
LaF_3	4.7	690.1				K_2UF_6	2.5	297.8
NdF_3	2.7	690.1				$KNiF_3$	3.2	297.7
CaF_2	3.2,2.7	690.3,690.0				$K[OsO_3N]$	2.3	297.7
K_2TiF_6	2.0	690.0				$K_2Pt(SeCN)_6$	2.1	297.7
NH_4SbF_4	1.7	690.0				$KAg(CN)_2$	1.8	297.5
EuF_3	3.8	690.0				$KBrO_3$	1.7	297.3
GdF_3	3.6	690.0				$K_2[Cr(H_2O)F_5]$	3.2	297.1
ThF_4	3.6	690.0				$KSeCN$	1.7	296.5
BeF_2	2.3	689.8				$K_2[Ru(NO)Cl_5]$	3.3	296.1

TABLE 23. $I'(4f)$ of compounds of lanthanides, hafnium and tantalum.

	∂	$I'(4f)$
PrF_3	3.4	10.3,(8.6)
NdF_3	2.7	12.2
$NdAsO_4$	2.6	10.9
$Nd_2(SO_4)_3$	2.1	11.1
Nd_2O_3	3.0	10.4
SmF_3	3.0	11.1
Sm_2O_3	2.6	11
EuF_3	3.8	13.7
$Eu_2(SO_4)_3$	2.0	14
Eu_2O_3	2.9	12.0
$EuSO_4$	2.0	6.9
$GdTaO_4$	1.8	15.6
GdF_3	3.6	15.3
$Gd_2(SO_4)_3$	2.3	15.2
Gd_2O_3	2.0	13.6
TbO_2	3.1	24.7
Tb_4O_7	2.6	24.4,14.6,8.5
$Tb(OH)_3$	2.6	15.5,8.9
Dy_2O_3	3.2	14.7,11.5,(9.1)
$DyVO_4$	2.4	14.5,(9.6)
$Ho(IO_3)_3$	2.6	15.2,(12.8),(10.5)
Ho_2O_3	2.6	14.3,(10.6)
ErF_3	3.5	15.2,(12.2)
$Er(IO_3)_3$	2.3	15.2,(14),(11.5)
Er_2O_3	3.2	14.4,(11)
$Tm(IO_3)_3$	2.4	14.8,(11.4)
Tm_2O_3	2.8	14.9,(10.8)
YbF_3	2.5	18.0,14.2
$Yb(IO_3)_3$	2.7	17,13.3
$Yb_2(WO_4)_3$	1.8	17.3,13.3
$YbTaO_4$	2.8	(16.6),12.9
$YbAsO_4$	1.7	(17),12.9
$Yb_2Hf_2O_7$	2.5	(16),12.5
$YbVO_4$	2.1	16.1,12.2
LuF_3	5.2,4.5	15.3,15.2
$Lu(IO_3)_3$	2.5	14.3
Lu_2O_3	2.1	13.9
K_2HfF_6	2.3	(25.2),23.7
$Hf(IO_3)_4$	2.4	(24.9),23.2
HfO_2	2.3	22.7
$Yb_2Hf_2O_7$	2.5	(23.6),21.9
K_2TaF_7	1.4	(36),34.3
$YbTaO_4$	2.8	(33.6),31.8
Ta_2O_5	2.1	(33.0),31.2

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