CHIMIA Vol. 25 Fasc. 7-1971 Pag. 213–260

Photo-Electron Spectrometry of Inorganic Solids*

By CHRISTIAN KLIXBÜLL JØRGENSEN
Département de Chimie Physique, Université de Genève, 1211 Geneva 4

Summary

The highly different probability of ionization of each shell of a given element by X-ray photons is discussed. The chemical shift of ionization energies I indicates differing HARTREE potential. The multiple I of an inner shell in systems having positive spin quantum number S are studied in 11 high-spin nickel(II) compounds. The choice of scotch tape as internal standard and the MADELUNG potential in almost ionic compounds are treated, as well as the relation between optical electronegativities and I of valence electrons.

Relative Ionization Probabilities of Different Shells of Different Elements

When the kinetic energy of electrons ejected from the sample by high-energy photons is measured, the ionization energies I of inner shells and penultimate orbitals can be evaluated from the peaks of the probability distribution as a function of kinetic energy. The peak maxima occur at the difference between the photon energy and the I-value.

In actual practice, photo-electron spectrometry (also called ESCA = electron spectroscopy for chemical analysis, or IEE = induced electron emission) is performed with two rather distinct techniques, either using the helium resonance line at 584 Å corresponding to 21.2 eV (or the $2p \rightarrow 1s$ transition of He^+ at 304 Å or 40.8 eV) on gaseous samples (as first done on a large scale by DAVID TURNER[1]) or otherwise using soft X-rays in the 10 Å region, such as the $2p \rightarrow 1s$ transitions of metallic magnesium (1253.6 eV) or aluminium (1486.6 eV) where the surfaces of solid samples can be studied. The obvious advantage of the former technique is the good resolution, frequently 0.01 eV, allowing vibrational structure to be resolved. The results for diatomic and triatomic molecules have been most interesting and confirm previous M.O. calculations on such systems. Polyatomic molecules frequently show excessive vibrational structure, like ultra-violet absorption spectra, though HEILBRONNER[2] obtains instructive information about organic molecules. It is possible that vapours of inorganic compounds would be investigated in the future, though one may have to combine the apparatus with a mass spectrometer studying the composition of the vapour. The disadvantages are that only I values below 21 (or 40) eV can be measured, and that a gaseous sample is needed. On the other hand, the soft X-ray technique only allows a resolution of about 1 eV, but I-values at least up to 1400 eV can be measured. The reason why intermediate photon energies have not been used is that the $2p$ shell of the elements lithium to fluorine is involved in chemical bonding and exhibits a broad interval of energy, whereas neon and sodium are too volatile to be used as anti-cathode. On the other hand, elements heavier than aluminium have their life-time of the excited states lacking a $1s$ electron so short that HEISENBERG's uncertainty principle make them broader than 1 eV. Actually, a radiative half-life of 10^{-15} sec corresponds to an uncertainty of energy 1 eV; 10^{-16} sec to 10 eV and so on. The chemist might wish that monochromatic photon sources somewhere between 100 and 200 eV might be found, not only because of a possible narrower line width but also because of the variation of the ionization probabilities of different shells to be discussed below. However, at present, the output of counted photo-electrons is so low that one cannot accept the low luminosity of a monochromator based on engraved or crystalline gratings, and only an almost monochromatic source obtained by filtering alone is useful.

Both the original instrument in Uppsala[3] and the home-made instrument in Berkeley[4] use magnetic deflection like a β-ray spectrograph. On the other hand, most of the commercial instruments available use electrostatic fields alone, allowing a more compact and robust set-up. Varian delivered a V-IEE-15 instrument to our laboratory in January 1971, and after several starting difficulties mainly originating in the titanium pump and its power supply, we have measured 160 compounds (containing 63 elements) in February, March and April 1971. Typically, two or three inner shells of each element is measured, with exception of elements from lithium to fluorine mainly seen as the $1s$ signal. In pure compounds, the strongest signals are clearly seen after 100 seconds of measurement, whereas weak signals may demand 2000 seconds or more. Un-

* Partly based on lecture given at I.SAT, Lausanne, 8 May 1971.
1 D.W. TURNER, C. BAKER, A.D. BAKER and C.R. BRUNDLE, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London 1970.
2 E. HEILBRONNER, K.A. MUSZKAT and J. SCHÄUBLIN, *Helv. Chim. Acta 54* (1971) 58.
3 K. SIEGBAHN, C. NORDLING, G. JOHANSSON, J. HEDMAN, P.F. HEDÉN, K. HAMRIN, U. GELIUS, T. BERGMARK, L.O. WERME, R. MANNE and Y. BAER, ESCA *Applied to Free Molecules*, North-Holland, Amsterdam 1969.
4 J.M. HOLLANDER and W.L. JOLLY, *Accounts Chem. Res. 3* (1970) 193.

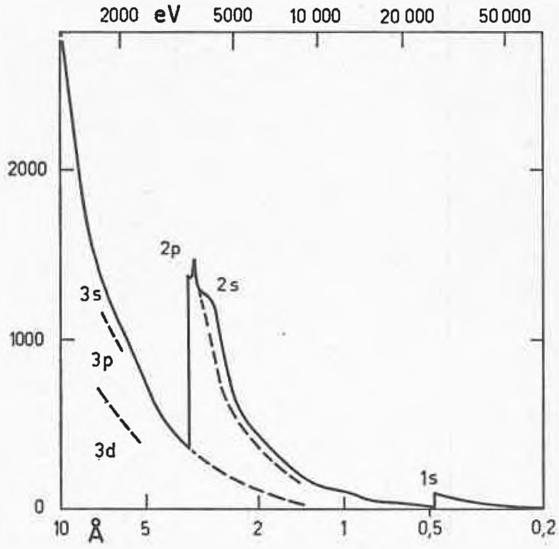

Fig. 1. Absorption spectrum of metallic silver for photons between 1240 and 61975 eV. The variable x is defined in the text

fortunately for the chemist, the so-called valence region with I below 50 eV with peaks corresponding to delocalized M.O. usually is very weak and may take hours in the worst case. Said in other words, the probability of ejecting an electron with almost as high a kinetic energy as the photon energy is very low. This restriction does not apply to post-transition group elements having closed d-shells with I below 100 eV, nor to the very strong signal of $4f$ having I increasing[5] from 16 eV for Lu_2O_3 ($Z = 71$) to 387 and 398 eV for UO_2 ($Z = 92$) and well-known from the demonstration of gold surfaces (having the additional advantage of no superficial oxide coverage). We now attempt to explain this pronounced variation of the intensity.

Fig. 1 shows the absorption spectrum of metallic silver in the region from 10 to 0.2 Å based on data in the handbook of HODGMAN. The variable given is x in the expression $(I/I^0) = \exp(-xld)$ with the path l in cm and d the density (10.5 for silver). Since the molar concentration of silver is 97, the molar extinction coefficient is $\varepsilon = (107.9 \cdot \log_{10} e/1000)x = 0.0466x$. The penetration of soft X-rays in the region at 10 Å of interest to us is about 3000 Å, about half the wave-length of visible light. Hence, if we want to study X-ray absorption spectra in this region, we need homogeneous films of this thickness[6]. It is remembered that a large part of the oscillator strength 47 per silver atom, about 36 units, is concentrated[7,8] between 1000 Å and 3.67 Å (the edge for $2p$ absorption) and only about 10 units below 3.67 Å. It should not be argued that the photo-electrons originate uniformly in the outermost 3000 Å of a silver sample bombarded with 10 Å radiation. Actually, experiments in Uppsala with superposed monomolecular layers of iodostearic acid and with chromium-plated gold show that the photo-electrons originate in a layer with half-width between 20 and 50 Å though this value, of course, depends on the density and the chemical constitution of the sample. The larger number of electrons liberated in the sample in a depth between 100 and 3000 Å are scattered inelastically, many are absorbed by the sample, and the rest form a background of all possible kinetic energies below their original energy. As a matter of fact, the peaks have maxima frequently less than 10 percent higher than the background, even for undiluted compounds, and only in exceptional cases, their intensity is comparable to the background.

Whereas EINSTEIN's principle for photo-emission prevents that electrons are ionized from shells having a higher I than the photon energy, it is seen from Fig. 1 that for photon energies higher than a given set of I-values, the shells each contribute a decreasing probability as a function of increasing photon energy. Neglecting the aspect that electrons with high kinetic energy (corresponding to low I) arrive from a deeper layer of the samples, the relative intensity of the signals belonging to different inner shells is determined by the ratios between these ionization probabilities for the photon energy utilized. Fig. 2 shows a qualitative representation of the absorption spectrum of metallic gold on a logarithmic energy scale from 50 to 4000 eV indicating the relative ionization probabilities for 1486 eV radiation, which are large for the $4p$ and $4d$ shells and even larger for the $4f$ shell. The lower curve indicates, in a qualitative way, how the yield of $4f$ ionization varies as a function of the photon energy[9,10]. The large extension toward

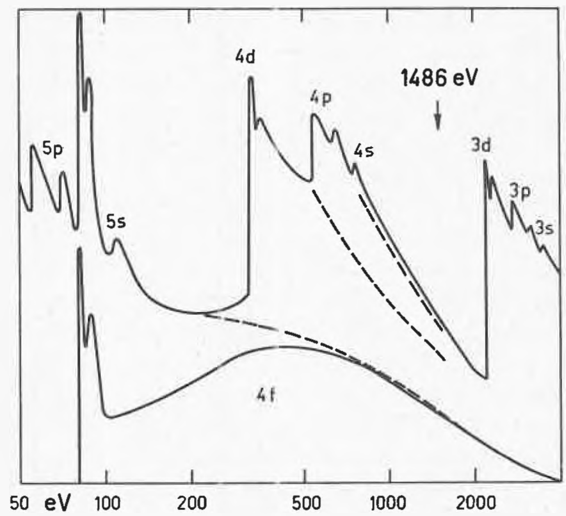

Fig. 2. Qualitative representation of the absorption spectrum of metallic gold for photons between 50 and 4000 eV. The contribution to the ionization probability from each inner shell is indicated by dashed lines, with exception of the unusual $4f$ shell

[5] C.K. JØRGENSEN, *Theoret. Chim. Acta*, in press.
[6] C. BONNELLE, *Ann. Physique 1* (1966) 439.
[7] J.J. SALZMANN and C.K. JØRGENSEN, *Helv. Chim. Acta 51* (1968) 1276.
[8] C.K. JØRGENSEN, *Rev. Chim. Minérale* (Paris) *6* (1969) 183.
[9] S.T. MANSON and J.W. COOPER, *Physic. Rev. 165* (1968) 126.
[10] U. FANO and J.W. COOPER, *Rev. Mod. Physics 40* (1968) 441.

higher energies is connected with the fact that the angular part $l(l+1)\langle r^{-2}\rangle/2$ of the kinetic energy is much larger than I for f electrons having $l=3$.

In a compound containing different atoms, or in a mixture of compounds, the yield of ionization from each shell is proportional to the concentration of the atom considered and inversely proportional to the penetration depth in the undiluted element. However, these two statements are restricted by a normalization to what is essentially the reciprocal value of the sum of x values from Fig. 1. In a sample containing heavy atoms, most of the soft X-ray photons are absorbed by heavy atoms with large x. It is typical that examples suggested for high sensitivity of photo-electron spectrometric methods involves a single heavier atom, such as cobalt in vitamin B_{12} surrounded by about a hundred carbon and nitrogen atoms, or traces of lead or uranium in mixtures. The opposite example of searching Be in the beryllium phthalocyanine would be almost hopeless. Though the lower limit depends on the time of exposure, it is definitely above 1 percent for most elements in typical situations, and the apparatus is not a serious competitor to a X-ray fluorescence instrument for detection of all elements though it can be used that way. On the other hand, high concentrations of elements in tiny samples (say 10^{-5} g) which can be smeared out on 2 cm^2 are good candidates. Thus, the «anomalous water» which attracted so much attention recently, turned out to be an anhydrous mixture[11] of silicates formed from the quartz capillaries, sodium sulphate and lactate (originating in transpiration). Obviously, many uses are conceivable in geology, biology and in the field of heterogeneous catalysts and metallic surfaces.

The Chemical Shifts and Multiple Ionization Energies

For the academic purpose of obtaining information about chemical bonding, the two main effects observed is the variation dI of I for a given inner shell of a given element from one compound to another, and the occurrence of multiple I values when the groundstate of the compound considered has a partly filled shell and a positive total spin quantum number S. The simplest such effect is a lower I for the ionized system $(S+½)$ than I going to $(S-½)$ and was discovered in Uppsala[3] for the gaseous molecules O_2 and NO having $S=1$ and ½ respectively. Similar effects[12] occur for the $3s$ orbital of manganese (II) and iron (III) ($S={}^5/_2$) and manganese (IV) ($S={}^3/_2$) fluorides and oxides, whereas the behaviour of the $3p$ orbitals is slightly more complicated because the two partly filled shells $3p^5 3d^3$ or $3p^5 3d^5$ have several energy levels as previously discussed[13] in the case of $2p^5 3d^9$ studied in X-ray spectra of nickel-(II) oxide.

The chemical shift dI is mainly an expression[14] for the variation of the HARTREE potential $U(x,y,z)$ in the atomic core considered. This variation is almost the same[15] for all the inner shells of a given atom and is not a direct measure of the oxidation state, as was first thought[4]. Rather, dI is proportional to the fractional atomic charge δ which is known[16,17] to be between $+1$ and $+2$ for most central atoms of d-group complexes. However, dI is smaller than it would be for a corresponding gaseous ion carrying an integral charge $\delta=2$ because dI is compensated[14] by the MADELUNG potential produced by the adjacent atoms having opposite charge. Thus, dI shows a variation with the oxidation state and the ligands rather similar to the nephelauxetic effect[17,18] which is the variation of parameters of interelectronic repulsion in compounds containing one partly filled d- or f-shell. Fig. 3 shows the shift of three among twenty nickel-containing samples given in Table 1. Whereas the shift from the fluoride to the ethylenediamine complex on Fig. 3 is 4.5 eV, the total variation of paramagnetic ($S=1$) nickel(II)complexes in Table is 4.8 eV, well above the effect of changing the oxidation number by one unit in many elements. The low-spin ($S=0$) nickel(II) complexes have, on the whole, lower

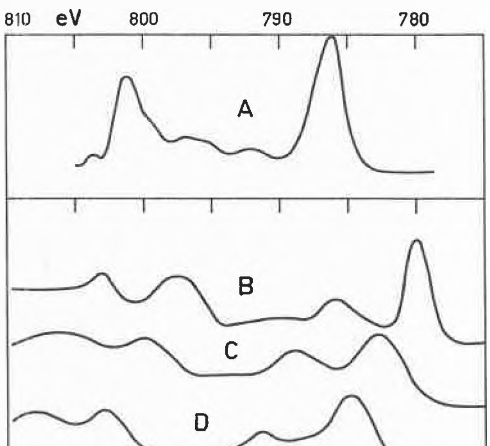

Fig. 3. Photo-electron spectra in the cobalt or nickel $2p$ region of:
A: $[Co(NH_3)_6]Cl_3$
B: $[Ni(NH_2CH_2CH_2NH_2)_3]SO_4$
C: NiO
D: $NiF_2, 4H_2O$

[11] R. E. DAVIS, D. L. ROUSSEAU and R. D. BOARD, *Science 171* (1971) 167.
[12] C. S. FADLEY, D. A. SHIRLEY, A. J. FREEMAN, P. S. BAGUS and J. V. MALLOW, *Physic. Rev. Letters 23* (1969) 1397.
[13] C. BONNELLE and C. K. JØRGENSEN, *J. Chim. Physique 61* (1964) 826.
[14] C. K. JØRGENSEN, *Modern Aspects of Ligand Field Theory*, North-Holland, Amsterdam 1971.
[15] C. K. JØRGENSEN, *Orbitals in Atoms and Molecules*, Academic Press, London 1962.
[16] C. K. JØRGENSEN, *Helv. Chim. Acta* (Fasc. extraord. ALFRED WERNER) *1967*, 131.
[17] C. K. JØRGENSEN, *Oxidation Numbers and Oxidation States*, Verlag Springer, Berlin 1969.
[18] C. K. JØRGENSEN, *Progr. Inorg. Chem. 4* (1962) 73.

Table 1. Ionization energies I relative to vacuo of the $2p$ shell of nickel compounds obtained by correction with C_{st} using the carbon $1s$ signal of scotch tape as internal standard, as described in the text. The unit is 1 eV = 8067 cm^{-1}

	C_{st}	I-values			
$NiF_2, 4H_2O$	4.7	887.8	882.5	870.5	864.4
$KNiF_3$	3.6	–	882.25	869.9	864.0
NiO	4.8	886.8	879.9	868.6	862.4
$NiC_2O_4, 2H_2O$	4.3	885.7	879.9	867.9	862.1
$[Ni(H_2O)_6]SO_4$	4.1	885.2	879.3	867	861.9
$Ni(NH_2CH_2CO_2)_2(H_2O)_2$	3.8	883	877.8	865.6	860.4
Nitren $(NCS)_2$	4.6	883	878.2	867	860.3
[Ni(tren)phen] $(ClO_4)_2$	4.5	882	877.8	866	860.2
[Ni $phen_3$] $(ClO_4)_2$	5.0	884	877.6	867	860.0
[Ni en_3] SO_4	3.8	883.2	877.5	866.0	859.9
Ni $dptp_2$ phen	5.2	–	877	865	859.6
[Ni en_2] $(ClO_4)_2$	4.6	–	877.6	–	860.5
[Ni $tetrac_2$] $(ClO_4)_2$	4.7	–	877.5	–	860.1
[Ni $aminin_2$] $(NO_3)_2$	4.6	–	877.2	–	860.1
[Ni $(aminin)_2$Br] Br	4.5	–	876.9	–	859.8
Ni dimethylglyoximate	4.9	–	876.6	–	859.6
Ni $dptp_2$	5.1	–	876.7	–	859.2
Ni $[S_2CN(C_2H_5)_2]_2$	4.7	–	875.8	–	858.7
Ni_2O_3	4.5	884.8	878.0	866.3	860.3
Ni	5.3	878.2	876	860.5	857.8

The ligands are abbreviated:

tren: tris(2-aminoethyl)amine; *cf.* L. RASMUSSEN and C. K. JØRGENSEN, *Inorg. Chim. Acta* (Padova) *3* (1969) 547.
phen: 1,10-phenanthroline.
en: ethylenediamine; *cf.* M. E. FARAGO, J. M. JAMES and V. C. G. TREW, *J. Chem. Soc. A*, *1967*, 728.
dptp: di(*i*-propyl)dithiophosphate $(C_3H_7O)_2PS_2^-$.
tetrac: condensation product of ethylenediamine and acetone; *cf.* N. F. CURTIS, *J. Chem. Soc. 1960*, 4409.
aminin: 1-amino-1-aminomethyl-cyclohexane, kindly supplied by Professor F. HEIN; *cf.* C. K. JØRGENSEN, *Z. anorg. Chem. 316* (1962) 12.

I values in Table 1, but the major difference is that they have only two peaks corresponding to the ionization of the two relativistic (spin-orbit coupling) components $2p_{1/2}$ and $2p_{3/2}$, the former corresponding to I 17.2 eV higher. On the other hand, the high-spin complexes show four signals, two for each relativistic component. The separation between the first and the third peak is close to 17.7 eV, and the separations 1–2 and 3–4 are about 6 eV. It cannot be simply argued that the peak at higher I is due to ($S = 1/2$) of the ionized system and the lower I to ($S = 3/2$). In RUSSELL-SAUNDERS coupling, the energy difference[17] between the two sets of states would be $3K_{av}(2p,nl)$ like it is $2K_{av}(2p,ns)$ in a $2p^5(ns)^1$ system. However, we have the opposite case, where the latter system shows the splitting $4K_{av}/3$ for $2p_{3/2}$ ionization and $2K_{av}/3$. JOHN GRIFFITH was so kind as to point out that if only the groundstate $^3A_{2g}$ of the $3d^8$ shell is considered, the $2p_{3/2}$ region should show three signals separated, to the first approximation, by $(5K_{av}/18)$ and by $(K_{av}/6)$ whereas the two signals in the $2p_{1/2}$ region would be separated also by $(K_{av}/6)$. This description does not apply to our case, because it is known[13] from WATSON's calculations that $K_{av}(2p, 3d) = 2G_1 + 21G_3$ would be about 1.7 eV, somewhat larger[17] than $K_{av}(3d, 3d) =$ 0.65 eV in NiO. On the other hand, the effects of interelectronic repulsion separating the 60 states of $2p^5 3d^9$ or the 270 states of $2p^5 3d^8$ away from the average energy for a given S have the order of magnitude[13] 5.0 and 2.1 eV in the excited levels of the X-ray absorption spectrum of NiO. As a matter of fact, the $3d^9$ system $CuSO_4, 5H_2O$ has shoulders at 961.7 and 941.4 eV on the major peaks of the photo-electron spectrum at 958.6 and 938.7 eV. The conclusion is that whereas the distribution of ionization probability is a matter of $^3A_{2g}$ fractional parentage, they are distributed energy-wise in two regions each about 6 eV wide in the nickel(II) compounds. It is also important to note that whereas the (double-sided) half-width of narrow signals under our standard conditions (100 eV analyzer energy) invariably is 1.9 to 2.0 eV, the half-widths around 2.3 eV in high-spin Ni(II) indicate a superposition of adjacent signals. The «ligand field» effects are rather negligible energy-wise; the sub-shell energy difference Δ varies between 0.9 and 1.5 eV in our compounds.

On Fig. 3, we have also included the $2p$ ionization of the diamagnetic ($S = 0$) cobalt(III) complex $[Co(NH_3)_6]Cl_3$ producing $I = 785.2$ eV for $2p_{3/2}$ and 800.3 eV for $2p_{1/2}$. This system, like the closed-shell ZnO having $I = 1026.7$ and 1049.8 eV, does not show structure due to effects of interelectronic repulsion. However, weak additional signals are seen in the luteo salt at 10 eV higher energy. Since the lower $3d$ sub-shell has this order of magnitude of I, it is probable that the higher-energy satellites are due to primary ionization of both the $2p$ and the $3d$ shell by the same photon. However, an alternative phenomenon is the AUGER effect, that the ionized systems eject loosely bound electrons as a secondary process. If such electrons do not undergo inelastic scattering with the sample, they have characteristic kinetic energies and might show up as sharp peaks in the photo-electron spectrum. However, we have not seen much evidence for such "superfluous" signals.

It is not easy to know why Ni_2O_3 also shows four peaks at lower I-values than NiO itself. It is not contrary to the analogy with the nephelauxetic effect[16,17] to assume slightly lower I of Ni(III) than of Ni(II), and as a matter of fact, the $4f_{5/2}$ and $4f_{7/2}$ ionization energies occur at lower values for Tl(III) than for Tl(I) and lower for Pb(IV) than for Pb(II):

Tl_2SO_4	129.3,	124.85
Tl_2CO_3	129.1,	124.65
TlBr	128.75,	124.3
Tl_2O_3	127.35,	123.0
PbF_2	150.75,	145.9
$Pb(NO_3)_2$	150.2,	145.35
PbS	149.9,	145.05
PbI_2	149.6,	144.7
PbO	149.0,	144.15
$PbCO_3$	148.8,	144.0
$PbCrO_4$	148.6,	143.75
PbO_2	147.2,	142.4

Correspondingly, Pb_3O_4 known to contain two Pb(II) and one Pb(IV) only showed one set (of slightly broadened) peaks at 148.8 and 143.9 eV. However, this sample might conceivably be covered with $PbCO_3$.

In Table 1 are also included our measurements on metallic nickel. It is, of course, quite conceivable that our sample is partly oxidized. However, the spectrum produced does not look like that of NiO. The two strongest peaks occur at 857.8 and 876 eV, about 4 eV below those of NiO. If the four peaks originate in the same species, the effects of interelectronic repulsion are only about half of the 6 eV found for paramagnetic nickel (II) compounds. This may be a genuine effect of expanded 3*d* orbitals in the metal, whereas we do not believe in the suggestion[19] that the 6 eV separation is due to simultaneous presence of NiO and the metal. This would not be conceivable in several of the complexes included in Table 1.

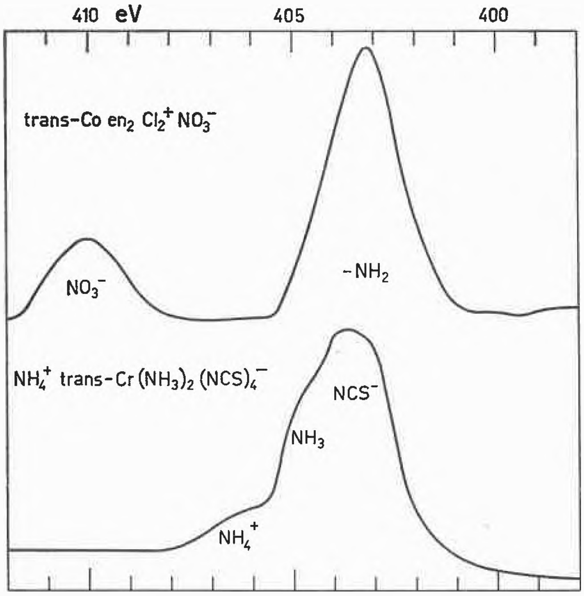

Fig. 4. Photo-electron spectra in the nitrogen 1*s* region of two complexes containing highly non-equivalent nitrogen atoms

As an example of non-equivalent atoms of the same element, Fig. 4 shows the nitrogen 1*s* signals from the cobalt (III) ethylenediamine complex *trans*-$Co\,en_2Cl_2^+NO_3^-$ having the nitrate signal at 409.7 and the four times stronger signal of the amine at 403.2 eV. Such effects were well established by HENDRICKSON, HOLLANDER and JOLLY[20] and Fig. 4 also illustrates REINECKE's salt having one NH_4^+, two NH_3 bound to Cr (III) and four NCS^- bound by the nitrogen end to the central atom. Technically, these complexes contain mixed oxidation states of nitrogen, but we have not been particularly fortunate, until now, with cases of two oxidation states of a given metallic element, such as[21] Sb (III, V) or Pb (II, IV) though the MÖSSBAUER effect is excellent[22, 23] for detecting non-equivalent antimony atoms. However, a sample of the dark blue Cs_2SbCl_6 kindly supplied by PETER DAY[21] shows Sb $3d_{3/2}$ ionization at 548.9 and 547.1 eV, whereas the stronger signal of $3d_{5/2}$ at 537.9 eV is partly obscured by the rather ubiquitous oxygen 1*s* peak due to adsorbed water and hydroxo groups. $CsSbCl_6$ shows peaks at 548.7 and 539.1 eV, whereas $[Co(NH_3)_6]SbCl_6$ has $I = 545.4$ and 536.1 eV, suggesting I for $SbCl_6^-$ higher than for $SbCl_6^{-3}$. However, for comparison, it may be mentioned that $KSb(OH)_6$ has the $3d_{3/2}$ signal at 545.4 eV too.

Scotch Tape as Internal Standard and the Madelung Potential of Ionic Salts

Metallic conducting samples brought in contact with the spectrometer obtain the same potential as the copper metal utilized. Assuming the work function to be 4.6 volt, the kinetic energy of the electrons ejected by 1486.6 eV photons is $(1486.6 - I) = (1482.0 - I^*)$ where the recorded result I^* is the ionization energy relative to the FERMI level. When non-conducting samples are measured a quasi-stationary equilibrium is established, where the positive charge left behind due to the removal of photo-electrons is slowly neutralized by electrons diffusing in from the surroundings. Correspondingly, I^* recorded by the apparatus is between 3 and 5.5 eV lower than I relative to vacuo. Fortunately enough, I^* does not vary perceptibly during a measurement taking an hour or two, so the signals are not broadened for this reason. However, the variation between two different samples has the same order of magnitude as typical chemical shifts dI and has to be evaluated if significant dI values are desired. One might imagine various devices, such as spraying a thin layer of graphite with the help of an aerosol, but it seems difficult to obtain a sufficiently intimate electric contact to avoid the very small charges producing a potential difference of a volt or two. Until now, the main solution to this problem has been an internal standard of I. It is also advantageous that the unknown correction is the same for different atoms in the same compound, and as seen below, there is some reason to believe in regularities in the small dI values for alkali-metal ions in salts which can serve as internal standards. A more general technique is to distribute the powdered sample on scotch tape and use the carbon 1*s* signal from the tape. We cover the aluminium cylinder with 15 mm broad scotch tape (no. 600 P from the company 3 M) and roll it about 300° in the powder on a hard Bristol paper, like Babylonians signing a contract with a sigillum, leaving 60° as a pure tape surface. We have to use uni-

[19] W. N. DALGASS, T. R. HUGHES and C. S. FADLEY, *Catalysis Rev. 4* (1970) 179.
[20] D. N. HENDRICKSON, J. M. HOLLANDER and W. L. JOLLY, *Inorg. Chem. 8* (1969) 2642.
[21] L. ATKINSON and P. DAY, *J. Chem. Soc. A 1969*, 2423.
[22] T. BIRCHALL and B. DELLA VALLE, *Chem. Comm.* (London) *1970*, 675.
[23] L. H. BOWEN, P. E. GARROU and G. G. LONG, *J. Inorg. Nucl. Chem. 33* (1971) 953.

Table 2. Observed ionization energies of the loosest bound shell of cations and anions in fairly ionic compounds, and I calculated from the MADELUNG potential for full ionicity. C_{st} is given as in Table 1

	C_{st}		I_{obs}	I_{calc}		I_{obs}	I_{calc}
LiF	4.2	Li 1*s*	63.5	75.62 − 12.5 = 63.1	F 2*p*	15.6	3.45 + 12.5 = 15.95
KF	4.15	K 3*p*	24.15	31.81 − 9.42 = 22.4		13.6	3.45 + 9.42 = 12.9
KCl	4.8		23.9	31.81 − 8.0 = 23.8	Cl 3*p*	11.9	3.61 + 8.0 = 11.6
KBr	4.6		23.3	31.81 − 7.64 = 24.2	Br 4*p*	10.7	3.36 + 7.64 = 11.0
KI	4.7		24.8	31.81 − 7.11 = 24.7	I 5*p*	11.0	3.06 + 7.11 = 10.2
CsF	4.1	Cs 5*p*	16.3	25.1 − 8.35 = 16.75	F 2*p*	14	3.45 + 8.35 = 11.8
CsCl	5.2		19.6	25.1 − 7.1 = 18.0	Cl 3*p*	13.4	3.61 + 7.1 = 10.7
CsBr	4.9		18.3	25.1 − 6.83 = 18.3	Br 4*p*	12.0	3.36 + 6.83 = 10.2
CsI	5.15		18.75	25.1 − 6.41 = 18.7	I 5*p*	11.85	3.06 + 6.41 = 9.5
CaF_2	4.55	Ca 3*p*	33.4	51.21 − 15.35 = 35.85	F 2*p*	16.15	3.45 + 15.35 = 18.8
SrF_2	5.5	Sr 4*p*	28.6	(43.5) − 14.3 = (29.2)		17.0	3.45 + 14.3 = 17.75
BaF_2	4.7	Ba 5*p*	23.6	(41.5) − 13.5 = (28)		16.3	3.45 + 13.53 = 17.0
CdF_2	4.75	Cd 4*d*	19.15	37.47 − 15.5 = 22.0		13.65	3.45 + 15.5 = 18.95
MgO	4.4	Mg 2*p*	56.4	80.12 − 23.9 = 56.2			
ZnO	4.9	Zn 3*d*	15.65	39.7 − (23) = (16.7)			
ZnS	2.7		15.7	39.7 − 20.0 = 19.7			
CdO	4.9	Cd 4*d*	19.4	37.47 − 21.44 = 16.0			
CdS	4.7		18.3	37.47 − 18.7 = 16.8			

lateral tape for this purpose, though it needs to be glued 120° at first and then turned in counter-clockwise direction some 500° in order to expose the adhesive surface to the powder. When we try double-sided scotch tape (which would be more convenient) it shows a second carbon signal at higher I due to C—O—C bridges in a poly-ether (like cellosolve) or carbonyl groups, and what is more serious, an oxygen signal even stronger than the carbon signal.

We recommend to assume $I = 290.0$ eV for carbon 1*s* in one-sided scotch tape (which must be essentially a hydrocarbon $\sim CH_2$). Among the arguments for this choice is the well-known fact[24] that the carbon I varies as a linear function of x in gaseous CH_xF_{4-x} between 290.8 eV for CH_4 and 301.8 eV for CF_4. By the way, the fluorine 1*s* also varies linearly from 692.4 eV in CH_3F to 695.0 eV in CF_4. We are writing a paper[25] on fluorides. When teflon (PTFE) tape (consisting of polymerized CF_2) is measured, the two carbon signals are separated by 10.2 eV. This supports the general opinion that the bonding of a carbon atom to hydrogen atoms have the same effect as bonding to other carbon atoms, and that catenated hydrocarbons such as scotch tape should not be very different from CH_4. If 290.0 eV is accepted for scotch tape, the CF_2 polymer has $I = 300.2$ eV for C 1*s* and 696.7 eV for F 1*s*. In this connection, it is worth noting[3,26] that I for N 1*s* in gaseous ONF_3 is 417.0 eV, N_2 409.9, NH_3 405.6 and the central atom in NNO 412.5 whereas the terminal nitrogen atom has 408.6 eV. These values may be compared with 409.7 for NO_3^-, 403.2 coordinated ethylenediamine, 406.3 for NH_4^+ and 404.9 eV for coordinated ammonia on Fig. 4. It must be realized that almost all I-values in the literature are relative to the supposed work function, and hence some 4 eV lower than our values. The scotch tape correction C_{st} in Tables 1 and 2 is the difference between 290 eV and the read-out of the instrument for the lowest I carbon signal observed. In literature, it is frequently suggested to use pump oil (which is also essentially CH_2) as internal standard. We believe that it is more convenient (for comparison with M.O. calculations, with atomic spectroscopy and with photo-electron spectra of gaseous samples[1]) to estimate I relative to the empty space rather than relative to the work-function, at least in the case of non-metallic solids.

Perhaps the best argument available for I being 290 ± 1 eV for carbon 1*s* in scotch tape is the agreement with the theory of MADELUNG potentials[14,17] for typically ionic salts if this value is accepted. Table 2 shows the observed ionization energy of the outermost orbitals of the cation and the anion, and the theoretical value obtained by adding V to the ionization energy of the halide anion known from spectroscopic studies of BERRY and REIMANN[27] and subtracting V from the ionization energy of the cation known from CHARLOTTE MOORE's tables[28]. It is seen in Table 2 that the agreement is good for the alkali-metal halides and slightly worse for the compounds of the divalent metals. With exception of the wurtzite ZnO, all the crystals in Table 2 are cubic, and V can be found explicitly from the expression (α^*/a) where a is the unit cell parameter in Å and the reduced MADELUNG constant α^*

50.2 eV for NaCl type
29.3 eV for CsCl type
83.6 eV for CaF_2 type
54.4 eV for CuCl type

[24] C.R. BRUNDLE, M.B. ROBIN and H. BASCH, *J. Chem. Physics 53* (1970) 2196.
[25] C.K. JØRGENSEN, H. BERTHOU and L. BALSENC, *J. Fluorine Chem.*, under preparation.
[26] P. FINN, R.K. PEARSON, J.M. HOLLANDER and W.L. JOLLY, *Inorg. Chem. 10* (1971) 378.
[27] R.S. BERRY and C.W. REIMANN, *J. Chem. Physics 38* (1963) 1540.
[28] C.E. MOORE, *Atomic Energy Levels*, Nat. Bur. Stand. Circular No. 467, Vol. I, II and III, Washington (D.C.) 1949, 1952 and 1958.

When the oxidation numbers are twice as large as in the typical compound (MgO rather than NaCl; ThO_2 rather than CaF_2; CdS rather than CuCl) these figures have to be multiplied by two. In cubic crystals, the three *p*-like orbitals remain degenerate, and the valence regions consist of atomic orbitals with well-defined *l* to a larger extent[14] than in crystals of lower symmetry.

It is seen from Table 2 that if $I = 288$ eV was accepted for scotch tape C 1*s*, all *I*-values would be 2 eV lower, and the agreement with the MADELUNG potential would not be as good. In the first ESCA book from Uppsala (this bibliophilic rarity will soon be re-edited by North-Holland, Amsterdam) it was suggested that the outermost halogen *p* orbitals have $I = 8.4$ eV in KCl, 7.7 eV in KBr and 6.3 eV in KI, whereas the potassium 2*p* orbitals have = 20.5, 20.6 and 20.1 eV in the three compounds. These values, about 3 eV below ours, are based on the position of the conduction band deduced from absorption spectra in the ultra-violet[29] and the assumption that the lower limit for EINSTEIN photo-emission has almost the same energy. However, the maximum of ionization probability may very well occur 2 eV above this limit, and there may be other minor uncertainties neglected in this hypothesis.

It is by no means evident whether weak covalent bonding produces positive or negative deviations from the simple MADELUNG theory[17] and the success of the latter description does not, by itself, prove exclusive electrostatic bonding in a given crystal. In Table 2, the *I*-values of highly polarizable crystals (such as the caesium salts) are unexpectedly high, and it is possible that such a correction occurs to the MADELUNG approximation. This might perhaps also explain the unexpected high *I* of Pb 4*f* in the iodide and the sulphide. On the other hand, there is no doubt that compounds occur for which the MADELUNG potential for full ionicity is not appropriate. Thus, BeO (with $C_{st} = 4.7$ eV) has $I = 121.6$ eV for Be 1*s* though gaseous Be^{+2} has $I = 153.85$ eV. It is interesting to compare with K_2BeF_4 having[25] $I = 122.4$ eV. The theory seems to work for MgO. In Table 2, the *I*-values 43.5 eV for Sr^{+2} and 41.5 eV for Ba^{+2} have been obtained by parabolic extrapolation in the iso-electronic series; the value observed for BaF_2 might suggest about 38 eV for Ba^{+2}, and it would not be inconsistent with the trends in Table 2 if *I* for Cs^+ were 24 eV only.

Optical Electronegativities and Penultimate Molecular Orbitals

Rather than the opinion prevailing around 1925, considering the bonding in most inorganic compounds as almost electrostatic, it is also possible to argue that closed-shell constituents have characteristic *I* values. When considering gaseous molecules[1] it is striking that most fluorides have their lowest *I* values around 16 eV, chlorides 12, bromides 11 and iodides 10 eV. Actually, the neutral halogen atoms have $I = 17.42$, 13.01, 11.84 and 10.45 eV, respectively. It might be argued that the values in Table 2 are slightly below *I* for neutral atoms, and when a sufficiently strong MADELUNG potential *V* is superposed, making *I* predicted above the values for neutral atoms, the development branches off and leave an almost constant *I* for a given halogen. This is the other aspect of the obvious fact that even fluorides of high oxidation states cannot be described by *V*. Thus, C 1*s* has $I = 301.8$ eV in CF_4 but 391.9 eV in gaseous C^{+4} and the calculated *V* for full ionicity is 43 eV on the carbon atom.

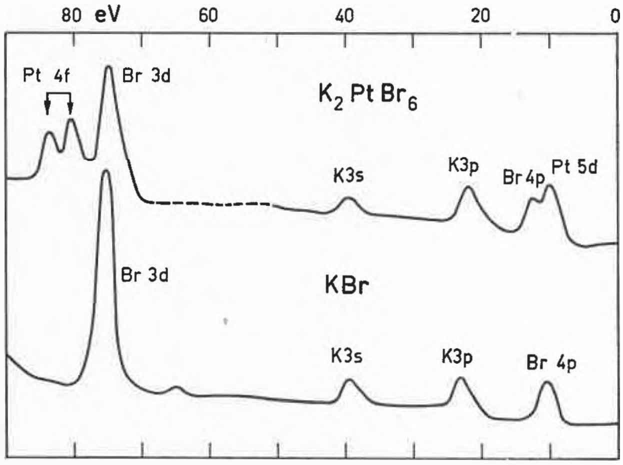

Fig. 5. Photo-electron spectra of KBr and K_2PtBr_6 showing the signals corresponding to ionization of the loosest bound shells. The zero-point of ionization energy has been fixed using the scotch tape internal standard described in the text

It has previously been pointed out[17] that *I* for gaseous HX is close to $(1 + 3.7x_{opt})$ eV where x_{opt} is the optical electronegativity introduced with the purpose of classifying the electron transfer spectra[15, 30]. The constant 3.7 eV is simply the 30000 cm^{-1} used in the description of visible and ultra-violet spectra. It is by no means evident that a general connection of this kind exists with x_{opt} of central atoms. Unfortunately, the signals in the valence region are very weak (with exception of 4*f*) and it is not completely easy to be certain that the *d*-electrons of transition group compounds have not been skipped in the broad background and noise close to $I = 0$. Fig. 5 shows the photo-electron spectra of KBr and K_2PtBr_6. The platinum (IV) complex has undoubted maxima at $I = 12.4$ and 9.8 eV, the latter rather sharp. In octahedral $PtBr_6^{-2}$, the eighteen Br 4*p* orbitals separate, to the first approximation, in six σ and twelve π orbitals (quantized with respect to the Pt–Br axis[14]) and then in seven sets of degenerate M.O. adapted to octahedral symmetry (taking Pt–Br and

[29] C.K. JØRGENSEN, *Halogen Chemistry 1* (1967) 265, Academic Press, London.

[30] C.K. JØRGENSEN, *Progr. Inorg. Chem. 12* (1970) 101.

Br—Br chemical interactions into account) and finally into twelve distinct I-values for relativistic reasons[29, 30]. It would be conceivable that the two maxima correspond to σ and π orbitals, but the indisputable observation of d ionization in post-transition group compounds [such as zinc(II) and cadmium(II)] makes it far more probable that the narrow peak at 9.8 eV is due to ionization from the lower sub-shell of Pt $5d$ containing six electrons. This opinion is supported by $(NH_4)_2PtCl_6$ having a broad peak at 13.1 and a sharp peak at 9.6 eV. Comparable structures have been observed (shoulders in parenthesis):

$[Co(NH_3)_6]Cl_3$	9
$[Ru(NH_3)_6]Cl_3$	8.9
$[Ru(NH_3)_5NCS](ClO_4)_2$	8.8
$[N(CH_3)_4]_3[Ru(NCS)_6]$	8.9
K_2ReCl_6	12.1, 9.7, ~ 7.7
K_2OsCl_6	12.1, 10,6, (8,6)
$[Ir(NH_3)_5Cl]Cl_2$	9.2
K_2IrBr_6	11.9, (10.5), 8.7

Surprisingly enough, the lowest I value is rather on the low side of the formula applied to halides, since

	x_{opt}	I_{calc}
Co (III)	2.4	10.0
Ru (III)	2.1	8.9
Re (IV)	2.1	8.9
Os (IV)	2.2	9.2
Ir (III)	2.25	9.4
Ir (IV)	2.4	10.0
Pt (IV)	2.6	10.6

though considerations of charge separation effects[15, 30] rather suggest that the difference between I of the ligand and of the central atom should be *smaller* than 3.7 eV times the difference of their optical electronegativities. The latter argument is clearly backed up by $4f$ group compounds (*cf.* also treatment by far-ultra-violet induced photo-electron spectra[31] and X-ray emission and absorption spectra[32] both of oxides and of metallic elements) where we find strong peaks close to 15 eV in Dy_2O_3, Er_2O_3, Yb_2O_3 and Lu_2O_3. It is clear from the electron transfer spectra[33] that the difference in x_{opt} is some 1.3 unit (5 eV) in Yb_2O_3 and larger in the earlier oxides whereas we rather find a negative difference of I values between O $2p$ and M $4f$. Said in other words, the ionized states M(IV) produced in M_2O_3 by removing a $4f$ electron are almost degenerate with the ionized states produced by removing an electron from oxide. It is not recommended to say that the excited state has strong covalent bonding because of this degeneracy, but it is still fascinating. On the other hand, the states of M_2O_3 studied by visible spectra show a very moderate nephelauxetic effect[17, 33] indicating that the partly filled $4f$ shell is only very slightly expanded and delocalized by covalent bonding.

The most favourable case for study of $3d$ ionization in iron group compounds would be a fluoride. $KNiF_3$ has a broad signal at 15.6 eV undoubtedly connected with F $2p$ and an asymmetric peak at 12.6 eV slowly fading away toward lower I and still perceptible at 10.6 eV. This is a somewhat ackward position for Ni $3d$ which should be easier to ionize (it may be noted that K $3p$ has the unusually high $I = 24.8$ eV which may be compared with 24.1 in $KClO_4$ and 22.4 in K_2ReCl_6) but the two sub-shells in the octahedral chromophore $Ni(II)F_6$ containing six and two electrons may be responsible for the asymmetric signal. This kind of problem of utmost importance to the understanding of chemical bonding merits much further study. The best analogy in gaseous compounds[1] is the sharp V $3d$ peak of VCl_4 at 9.41 eV having additional (mainly Cl $3p$) delocalized M.O. between 11.75 and 14 eV exactly like $TiCl_4$ without a $3d$-like electron[34]. The first electron transfer band[29] of VCl_4 at 24800 cm^{-1} indicates $x_{opt} = 2.1$ for vanadium(IV) after correction for spin-pairing energy, in reasonable agreement with $I = 8.9$ eV calculated above. It may be that charge separation effects are more important in $KNiF_3$ than in the chlorides discussed here. Other gaseous $3d$ group compounds such as tetrahedral $Ni(CO)_4$ having $I = 8.8$ and 9.7 eV for the two sub-shells or $Ni(PF_3)_4$ having $I = 9.55$ and 10.58 eV[35] cannot so readily be brought in relation to electron transfer spectra[30] neither $M(CO)_6$ (M = Cr, Mo, W) having $I = 8.5$ eV for their six d-electrons[1]. The lowest I known for a gaseous molecule[1] is 5,75 eV for $Co(C_5H_5)_2$ having the two sets of bonding d-like orbitals at 7.3 (and 9 ?) eV. The latter occur at 6.9 and 7.2 eV in $Fe(C_5H_5)_2$.

The potassium and bromine signals on Fig. 5, as well as signals at higher I, are almost the same in the two compounds

	KBr	K_2PtBr_6
K $2p_{1/2}$	302.4	301.45
K $2p_{3/2}$	299.8	298.8
Br $3p_{1/2}$	195.4	194.8
Br $3p_{3/2}$	188.7	188.25
Br $3d$	75.6	75.2
K $3s$	39.3	39.4
K $3p$	23.3	23.1
Br $4p$	10.7	12.4

For comparison, it may be mentioned that the K $2p$ signals occur at 301.6 and 299.0 eV in $KBrO_3$ whereas the Br $3d$ signal is seen at 81.6 eV. Hence, Br(V) has I increased 6.0 eV in bromate relative to the value for Br(−I). The weak peak seen on Fig 5 at 65 eV is due to

31 P. O. Hedén, H. Löfgren and S. B. M. Hagström, *Physic. Rev. Letters 26* (1971) 432.
32 R. C. Karnatak, Thèse, Université de Paris, 1971.
33 C. K. Jørgensen, R. Pappalardo and E. Rittershaus, *Z. Naturforsch. 20a* (1965) 54.
34 P. A. Cox, S. Evans, A. Hamnett and A. F. Orchard, *Chem. Physics Letters 7* (1970) 414.
35 J. C. Green, D. I. King and J. H. D. Eland, *Chem. Comm.* (London) *1970*, 1121.

the lack of absolute monochromacy of the photons employed. The so-called aluminium $K\alpha_3$ line (due to the transition $1s\ 2s^2\ 2p^5 \rightarrow 1s^2\ 2s^2\ 2p^4$ in an atom lacking two electrons in inner shells) occurs at 1496.4 eV, at 9.8 eV higher energy than the main line. Hence, it cannot be avoided that weak signals occur at apparent I values 9.8 eV lower than the main peaks. The continuous background in the exciting spectrum only contributes to the undifferentiated background in our measurements.

It is difficult to tell all about the future from the experience gained in three months. However, we firmly believe that chemical shifts and multiple I in systems having positive S are the most interesting results, together with the delicate and difficult problems of studying the valence region. We have not had great luck with mixed oxidation states (though excellent work[36] has been reported on Prussian blue) but we cooperate with DAY and with LUDI, planning work on cyanides of two d-group elements together. A most important question has recently been resolved by MANNE and ÅBERG[37]. When I for $1s$ electrons of methane or neon is measured, they are 15 to 20 eV lower than the first-order HARTREE-FOCK values obtained with «frozen» outer orbitals (such as $2p$) whereas they are in excellent agreement with the energy difference between the HARTREE-FOCK wave-functions of the ionized state lacking a $1s$ electron (with adapted, contracted, outer orbitals feeling an additional potential $1/r$) and of the groundstate. It might at first seem paradoxical that the other nine electrons have the time during the excitation by the X-ray photon to contract their orbitals, but the truth is more subtle[37]. The primary peak of ionization discussed here is followed, at higher energy, by a long series of weak peaks corresponding to the simultaneous ionization of two or three electrons. It turns out that the average energy of all this structure including the primary peak occurs at the KOOPMANS value obtained in the approximation of "frozen" orbitals, constituting an electronic analogy to the vibronic effects governed by FRANCK and CONDON's principle. This has very important bearings on the time-scale of the primary process of photo-electron spectra, which must be well below 10^{-15} sec. For the study of solid samples, it is rather an advantage that the rest of the structure is broadened out beyond recognition in the weakly oscillating background, whereas it and the related AUGER electrons are of interest in gaseous samples[3]. Actually, the weak satellites shown on Fig. 3 in the case of $[Co(NH_3)_6]Cl_3$ are rather the exception and seems to be a rather specific effect of co-ejection of d electrons.

The chemical effects and other features of photo-electron spectra clearly show that the concept of «inner shell energies» of a given element is not as sharply defined as sometimes believed by X-ray spectroscopists[38]. As pointed out many years ago by CAUCHOIS, the effects of interelectronic repulsion modify the simple identification of emission line wave-numbers with differences between orbital energies. The usual treatment tends to concentrate the concomitant uncertainties on the loosest bound orbitals, and it is hence highly useful that I can be directly determined from photo-electron spectra. This is also why the problems related to internal standards, such as the 290 eV definition, are so important for the general understanding of energy levels high up in the continuum beginning with the lowest I.

Our instrument operates at pressures below $3 \cdot 10^{-5}$ mm though ten times lower pressures frequently are obtained. Hence, volatile substances should not be introduced without appropriate cooling. Sufficiently volatile materials make no troubles, they evaporate by the pumping, which anyhow has to be done for 10 to 20 minutes after each new sample. It is far more inconvenient that some materials may maintain a low pressure (preventing the measurements) for a long time. We have only had this experience twice. $Mo(CO)_6$ (which would have been nice to have for comparison with the well-resolved measurements below 21 eV of the vapour[1]) entertained a constant pressure of $13 \cdot 10^{-3}$ mm, like in a text-book of thermodynamics, and had to be pumped on a night before it was removed from the system. A gold sample covered with mercury maintained $1.2 \cdot 10^{-3}$ mm and was removed after unsuccessful pumping for three hours. In this connection, it is interesting that TOVBORG JENSEN[39] pointed out that most salt hydrates only establish their equilibria with water vapour very slowly if the crystals are hard in the mineralogical sense. There is no reason to believe that a hydrate establishing equilibrium with a moderate water vapour pressure only within many days would dehydrate much more rapidly at extremely low pressure. As a matter of fact, we have succeeded in measuring photo-electron spectra of several hydrates without difficulty.

One should always have the eyes open for the possibility of samples decomposing during the measurement, and it may be advisable to repeat one or more characteristic regions. Thus, the Au $4f$ signals of $KAuBr_4$ consisted in the beginning of a shoulder at 97.6 and two maxima at 95.1 and 91.8 eV, already suggesting some decomposition ($KAuCl_4$ shows maxima at 97.4 and 93.85 eV). After an hour, the two peaks occur at 93.6 and 90.0 eV, probably due to a gold(I) compound such as $KAuBr_2$ since metallic gold has the peaks at 91.7 and 88.05 eV on our scale. This is not necessarily a photo-chemical decomposition by the X-rays but may a simple dissociation of elemental bromine. Actually, 1 cm^2 of the typical surface layer producing the counted photo-electrons contains about 10^{16} atoms, and it is not clear whether, say, 10^{14} photons pass with a photo-chemical quantum

[36] D. LEIBFRITZ and W. BREMSER, *Chemiker-Z.* (Heidelberg) *94* (1970) 882.

[37] R. MANNE and T. ÅBERG, *Chem. Physics Letters* 7 (1970) 282.

[38] J. A. BEARDEN and A. F. BURR, *Rev. Mod. Physics 39* (1967) 78 and 125.

[39] A. TOVBORG JENSEN, *Ark. Kemi* (Stockholm) *30* (1968) 165.

yield of 10 in a typical measurement. The number of counts is seven orders of magnitude lower. However, KCl and CsCl turned blue due to formation of "F" colour centers. On the other hand, one litre of air diluted to the pressure 10^{-3} mm contains 10^{16} oxygen molecules, showing how difficult it is to prevent oxidation of immediately reacting surfaces. We have found carbonate on the surface of a remarkable variety of samples.

Acknowledgements. The Swiss National Science Foundation has granted the funds necessary for purchase of the instrument. I am grateful to my collaborators, Mr. HERVÉ BERTHOU and Dr. LUCETTE BALSENC for their careful and helpful assistance with the measurements. I would also like to thank the engineers E. HALBEISEN and A. BODMER, Varian, Zug for their patient and competent help, as well as Dr. W. BREMSER and Mr. F. LINNEMANN from the Varian Laboratory in Darmstadt and Dr. J. C. HELMER, Dr. W. PROCTOR and Dr. L. A. WILSON in Palo Alto, Cf.