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CHARGING AND ROTATIONAL DEPENDENCE OF LINE POSITION

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ABSTRACT

For a charged sample the measured binding energies depend on the location of the sample within the sample chamber[1, 2] If it is only the angle between the sample surface and the analyser which is varied then the line position depends, in a characteristic way, on the rotation angle This dependence can be used to prove whether or not a sample is charged In addition, the amount of rotational dependence of line positions gives an indication of the magnitude of charging

Charging effects have gained increasing interest in XPS during recent years Especially in connection with the chemical application of XPS, charging turned out to be one of the limiting factors Samples of chemical interest are mainly insulators and are often available only as powders For these types of samples shifts in binding energies caused by charging usually extend from a few tenths of an eV to a few eV Unfortunately, the shifts arising from variations in the chemical environment which one wants to measure are of the same order of magnitude This leads to great difficulties, especially if the binding energies of different samples have to be compared Several methods to establish internal standards have therefore been proposed The most important of these methods are (a) reference to carbon contamination[3–5], (b) evaporation of small amounts of gold on the sample surface[6], (c) mixing of the sample with graphite[4], and (d) mixing of the sample with LiF (ref 7) Methods (c) and (d) are applicable to powders only

The applicability of these four methods depends on the following factors (1) the standard is chemically stable and does not react with the sample under the conditions of an XPS experiment, (2) the surface region investigated has a nearly uniform potential, and in this region electrical equilibrium between sample and reference material is established

The second condition is often fulfilled This is confirmed by some experiments

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in which the sample is biased[2, 8, 9] or exposed to a flood-gun[10, 11], and also by the fact that line-broadening, owing to differential charging, is usually small There are examples, however, in which substantial line-broadening can be observed[11] Other experiments have given rise to doubts about the method of internal standards as a whole, especially in connection with the first of the two statements given above[4, 17, 18] It is therefore very important to know whether a sample is charged or not before one bothers with the problem of relying on a standard Such evidence is of increasing interest since it has been recognised that, by preparation of thin films of the non-conducting material on a conducting background, charging can generally be kept rather small[3, 4, 6, 15]

The following methods of detecting sample-charging have been described
(a) It has been shown[9] that the dependence of the charging shift Δ_{ch} on the X-ray tube current is adequately described by the expression

$$\Delta_{ch} = A \frac{B\,i}{1 + B\,i}$$

where A and B are constants

A measurement of line position as a function of X-ray intensity should not only give an indication of the appearance of charging, but also yield the possibility of detecting its absolute value The experimental data have shown, however, that saturation is reached far below the intensities required in the usual XPS experiments
(b) If the sample holder is biased by a few volts then the observed line-shift does not correspond with the applied potential in the case of a charged sample
(c) If a charged sample is exposed to a flood-gun the line positions depend on the current applied to the flood-gun

To apply the methods (b) and (c) some additional equipment has to be present within the instrument In the following we shall describe a much simpler method of detecting whether or not a sample is charged This method is based upon the observation that the amount of charging depends on the location of the sample within the sample chamber The effect relies upon the electron currents, which condition the surface potential of the insulated sample, being distributed anisotropically within the recipient Therefore, only in samples of which the surfaces are not in electrical equilibrium with the sample holder does variation in sample position lead to changes in the surface potential and thereby to a displacement of the line

A variation of measured binding energies with sample location has been noticed by one of us in connection with investigations on organic mercury compounds[1] Independently, Ascarelli and Missoni[2] observed a position-dependent variation of the charging potential measured directly on a metal sample which was mounted with insulation on the sample holder

To prove whether there is really a clear connection between sample charging and sample location, we investigated one or two characteristic binding energies, for different types of samples, as a function of the angle θ defined in Fig 1, θ can be

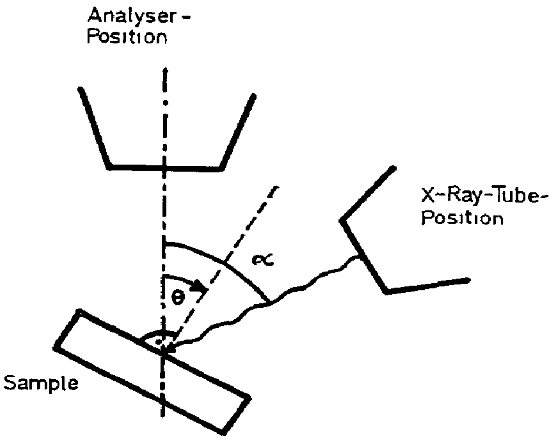


Figure 1 Schematical drawing of the experimental set-up and definition of the rotation angle θ

altered simply by rotating the sample rod which is present in most of the commercially available ESCA instruments, and the measured effect we refei to as "rotational dependence of line position" (RDOLP) Our measurements were made with a Leybold–Heraeus LHS 10 spectrometer In this instrument the angle between X-ray source and analyser (see Fig 1) is 60° With the available set-up, the angle θ could be fixed to a precision of $\pm$ 1 5°

Three types of samples have been investigated First, we looked at model samples consisting of a piece of metal insulated from the sample holder with Teflon To avoid possible photoconduction the set-up was arranged in such a way that the insulating material was hidden from X-ray illumination up to at least $\theta = -25°$

Figure 2 shows a typical result obtained from a copper sample Pronounced shifts of the Cu $2p_{3/2}$ line, which reach 9 2 eV for $\theta = +10°$ compared with the non-insulated sample, can be observed The shifts correspond to positive charging The most drastic change of the charging potential appears at angles θ between $-10°$ and $-25°$ At $\theta = -30°$ the line position for the insulated sample is identical with that of the non-insulated one Presumably the insulating material was not protected from irradiation at this angle

In Fig 3 the rotational dependence of the position of characteristic ESCA lines is shown for four different samples Three of them are model samples as defined above For these probes the line positions of the non-insulated samples are marked by ⊕ Curve A corresponds to the copper sample of Fig 2 Curve B is from a gold sample (Au $4f_{7/2}$) of almost equal size to the copper sample (13 × 20 mm) It can be seen that the shape of B is similar to that of A, however the magnitude of charging is somewhat higher in the case of gold This corresponds to the fact that gold has a larger cross-section for emission of secondary electrons

If the size of the sample is reduced (curve C, gold sample 10 × 13 mm) the RDOLP is less pronounced than for larger samples The magnitude of the charging is reduced and the rotational dependence somewhat flattened

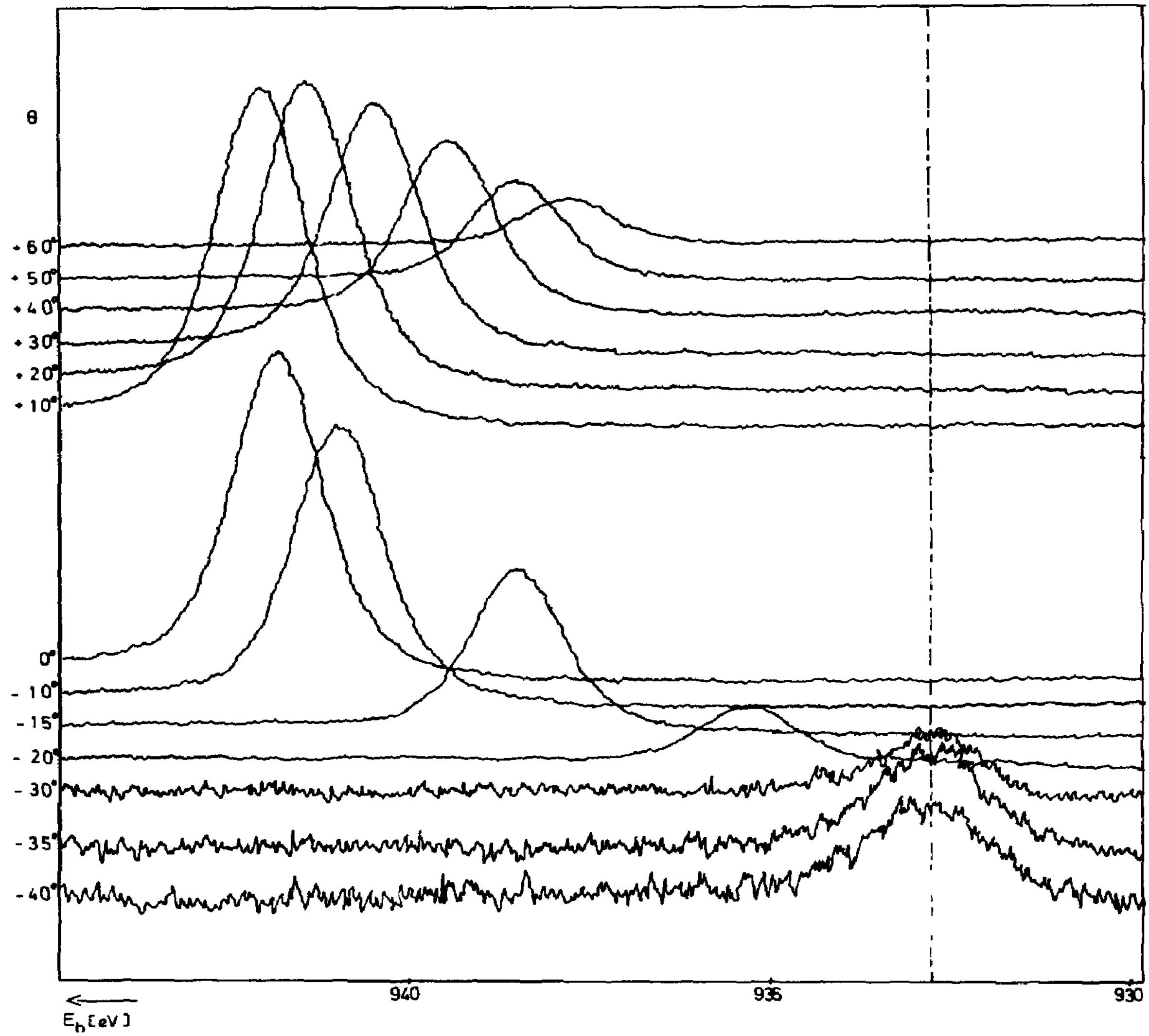


Figure 2 Line position as a function of the angle θ Spectra of a Cu sample mounted with insulation to the sample holder Measured line Cu $2p_{3/2}$ Reference Au $4f_{7/2}$ For $\theta = -30°$ to $\theta = -40°$ amplification was raised by a factor of 10 The broken line indicates the line position of a non-insulated sample

The experimental error is indicated by symbols at some characteristic points of the curve The width of the symbol corresponds to the uncertainty of the angle θ The height of the symbols indicates the uncertainty of the measured energy, which is in part (± 0 1 eV) owing to the accuracy of the analyser voltage, measured directly at the analyser with a 6 1/2 digit digital voltmeter, and in part (± 0 1 to ± 0 3 eV) owing to the accuracy to which the band maximum could be located by analysis with a DuPont curve resolver

To investigate the RDOLP on real samples, especially in connection with sample thickness, two methods of sample preparation have been used In the prepara-

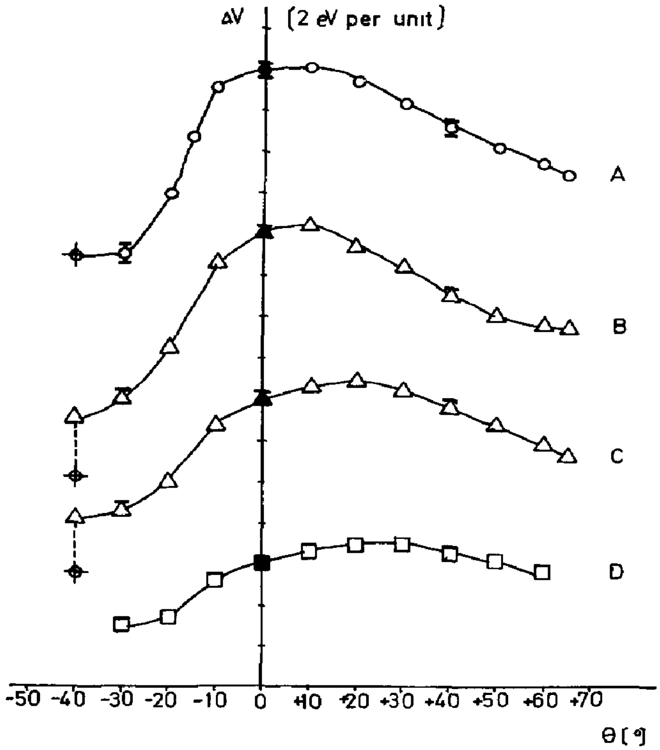


Figure 3 Plot of θ versus change in line position referred to line position at $\theta = 0$ (A) Cu sample Measured line $2p_{3/2}$ (see Fig 2) (B) Gold sample Measured line $4f_{7/2}$ (C) Gold sample (smaller than case A) Measured line $4f_{7/2}$ (D) MgO sample Measured line Mg 2s (⊕) Indicates line position of the non-insulated sample

tion of "thick" samples the material was compacted into a depression in a metallic sample holder, of ca 1 mm depth and 10 mm diameter, and lightly pressed To obtain "thin" samples the material was deposited on a flat metallic sample holder by sublimation or by evaporation from a drop of solution

Curve D in Fig 3 shows the RDOLP of a "thick" sample of MgO Again a strong rotational dependence is observed with a maximum line-shift of 3 9 eV The shape of the curve is similar to that of the small gold sample As for curve C, the strongest line-shift is observed for angles θ around $-15°$

In consequence of the claim[4] that the largest charging effects are observed with alkali halides, we used these materials to investigate the influence of sample thickness In Fig 4 results for LiF and LiCl are shown In each case, the RDOLP of both a thick and a thin sample is compared The thick samples exhibit a strong RDOLP as well The maximum of the charging shift appears at somewhat larger positive angles θ than for the samples of Fig 3 Within the limits of experimental error, the rotational dependence is the same for Li 1s and the halogen line in both cases This is to be expected when charging is sufficiently homogenous

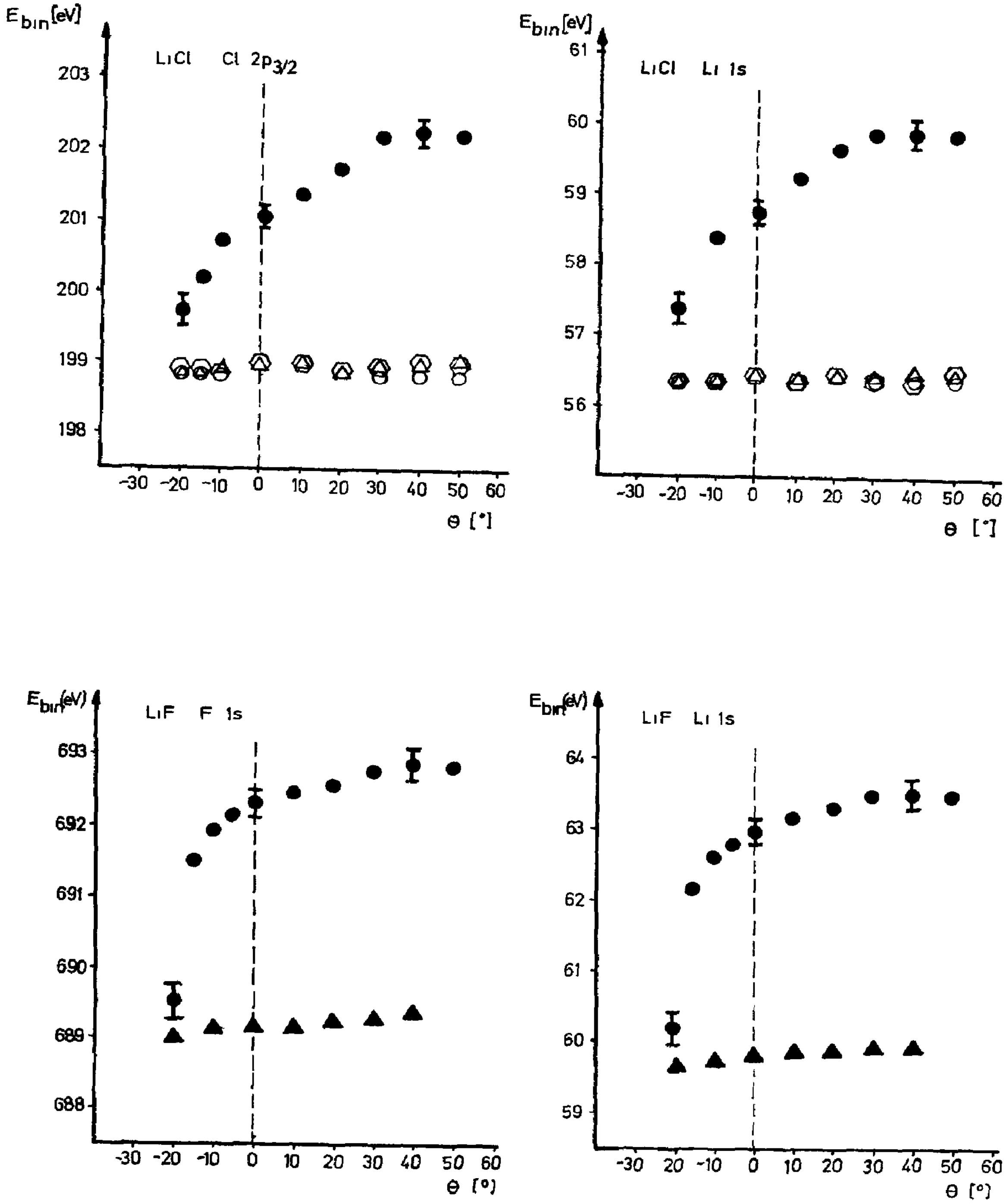


Figure 4 RDOLP for LiCl and LiF All binding energies refer to Au $4f_{7/2}$ (•) Thick samples. (▲, △, ⬡) Thin samples (○) Line position of the signal from a thin film measured simultaneously with the thick sample of LiCl

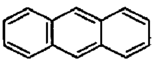
Thin samples of LiF and LiCl have been investigated In the case of LiCl, the measured energies are identical for different samples and independent of θ within the experimental limits In connection with the preparation of the thick LiCl sample, part of the sample holder was covered with a very thin layer of material which was illuminated by X-rays at some positions only The ensuing signal showed no θ dependence and its energy was within the experimental error range of the energy of the other two samples This shows that even for materials such as alkali halides it is possible to prepare samples of which the charging is less than ± 0 2 eV In the case of LiF we found equivalent results, but it was not easy to obtain layers which were thin enough to reveal absolutely no RDOLP

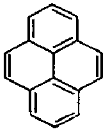
For the substances tested, LiF and LiCl, these results show the following absolute binding energies (in eV), with Au $4f_{7/2}$ as the standard

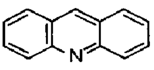
	LiF	LiCl
Li	59 6	56 4
F	689 0	—
Cl	—	198 9

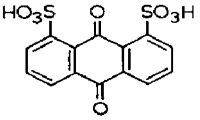
Combining the measurements of thin and thick samples, the absolute amount of charging of the latter can be estimated With regard to LiCl, for example, at $\theta = 0$ we determined a value of 2 6 ± 0 3 eV

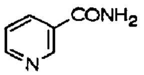
We also investigated a representative variety of organic compounds, as for example

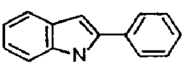


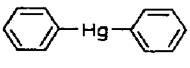












Most of these compounds were measured as thick and as thin samples, but in all cases the line positions did not vary systematically from θ within a range of ± 0 2 eV Of particular note is the fact that there was no pronounced dependence of line positions around $\theta = -15°$, as had been observed for all charged samples

The same observation of θ independent line positions has been made with a thick sample of sulphur (S_8), although sulphur is known to be a very good insulator

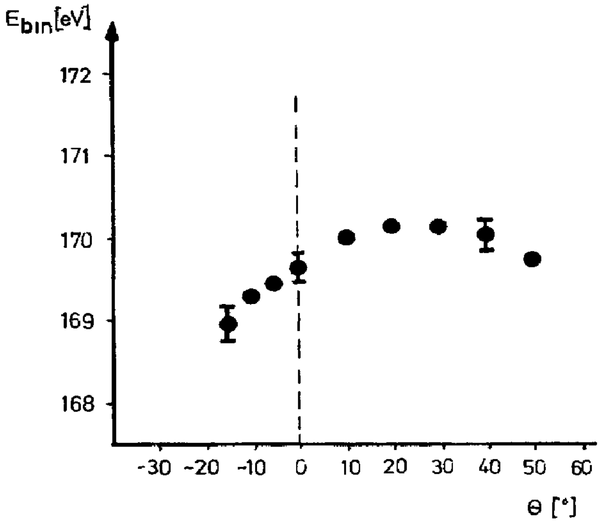


Figure 5 RDOLP for a thick sample of 1,8-anthraquinonedisulphonic acid Binding energies refer to Au $4f_{7/2}$

In order to obtain a charged sample of organic material at all, we had to cover the whole sample holder with a thick layer of the material As an example, Fig 5 shows the results obtained for such a sample of 1,8-anthraquinonedisulphonic acid An RDOLP is clearly detectable in this case, but charging is still smaller than for compounds such as LiCl or MgO

Our observations show clearly that, under the conditions of an ESCA experiment, sufficient sample conductivity is induced in most organic, and also in many inorganic materials, so charging of more than one or two tenths of an eV can be avoided This is true for our instrument at least, but it seems to hold for most of the other commercially available ESCA spectrometers as well

There is one more important question concerning sample conductivity under ESCA conditions which has still to be discussed is it mainly bulk or mainly surface conductivity which is responsible for the lack of charging? The experience we gained from the type of samples used to obtain the results of Fig 5, together with some specially designed experiments, strongly supports the assumption that for thick samples the main contribution results from conduction induced in the illuminated part of the sample surface These findings will be reported in detail in a further paper[14]

Before turning to some applications, we want to give at least a slight indication of the theoretical explanation of RDOLP As mentioned above, the surface potential of a given sample is mainly determined by the interference of three different currents, usually labelled I_1, I_2 and I_3 (see, for example, ref 9) I_1 is due to photoelectrons leaving the sample surface, I_2 results mainly from secondary electrons coming to the sample surface from different sources and I_3 represents a possible flow of charge between sample surface and sample holder Each of these currents is a function of X-ray conditions, surface potential and geometry of sample and spectrometer

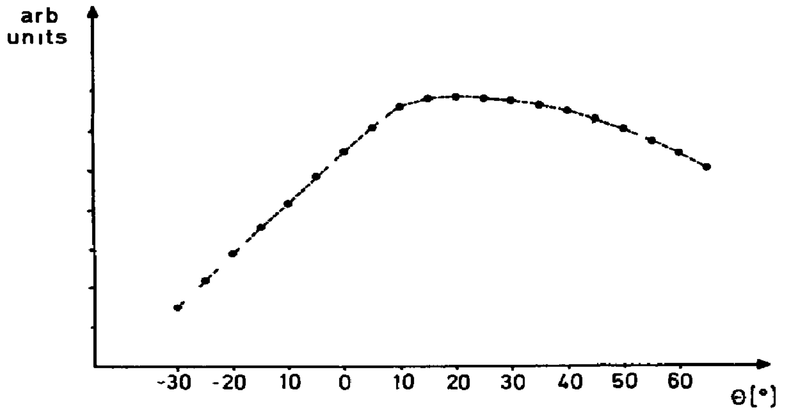


Figure 6 Calculated θ dependence of I_1 for fixed surface potential

For a fixed surface potential I_1 should be proportional to the effective illuminated sample surface Making use of this proportionality, the variation of I_1 with θ can be calculated if the geometrical conditions of the spectrometer are known In Fig 6 the relative dependence of I_1 on θ derived for the LHS 10 spectrometer is plotted After a relative steep ascent, I_1 reaches a maximum at about $\theta = 20°$ and then descends smoothly with increasing θ This curvature explains qualitatively the θ dependence found for the experimentally observed line-shifts This type of consideration also explains the dependence of RDOLP on sample dimensions (compare Fig 3)[19]

The deviations between experimental results and those of this crude model which only includes the θ dependence of I_1 for a fixed surface potential are due to the influence of I_2 and I_3 The interactions of the different currents which are responsible for the setting of the surface potential will be discussed in detail in a subsequent paper[13]

TWO APPLICATIONS

In order to demonstrate the usefulness of the RDOLP in detecting charging, we shall, in the following, describe two minor applications

As was shown in Fig 4 the energy of the Cl 2*p* line of a well prepared film of LiCl is independent of the angle θ If such a sample is sputtered (ion current, 10 μA) with argon ions for ca 2 min, the 2*p* line is shifted by 1 eV to higher binding energies The investigation of the θ dependence shows the sputtered sample to be uncharged Therefore, the observed line-shift must be attributed to alterations within the surface layers Heating the sample up to 150 °C for 10 min removes the shift completely[16]

The second application relates to the determination of the binding energies of elements whose states either possess particularly small cross-sections, or are present in the sample in the minutest concentration In such cases problems of intensity can arise during the measuring of thin samples, as a result of which a determining of charging on the line to be examined itself would be difficult Where appropriate, one can then examine the most intensive line of the system and can correct all other lines accordingly

CONCLUSIONS

If a sample is charged in an ESCA experiment then the measured binding energies depend on the location of the sample within the sample chamber A simple way of making use of this effect consists of observing binding energies as a function of the angle θ, defined in Fig 1 Characteristic variations for charged samples are observed, which sometimes reach up to a few eV A comparison of the magnitude of the RDOLP in the region $-20° \leqslant \theta \leqslant 50°$ of samples of varying thickness allows a rough estimate of the charging for samples for which it is not possible to obtain uncharged samples through the preparation of very thin films In the Leybold–Heraeus LHS 10 spectrometer the greatest variations of binding energies appear around $\theta = -15°$, so in the LHS 10 this is the best region for testing whether or not a sample is charged

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