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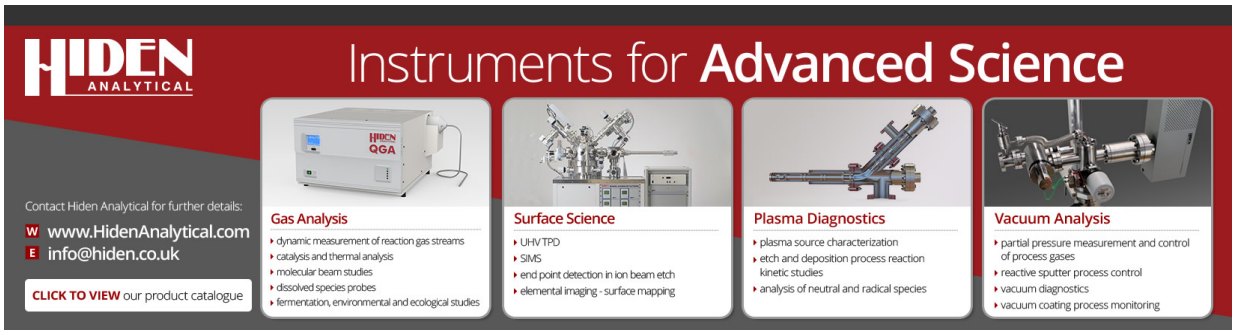

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PERSPECTIVE

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ABSTRACT

We present a perspective on the use of XPS relative peak intensities for determining composition in homogeneous bulk materials. Nonhomogenous effects, such as composition variation with depth or severe topography effects (e.g., in nanoparticles), are not discussed. We consider only the use of conventional laboratory-based instruments with x-ray sources, Alk$_\alpha$ or Mgk$_\alpha$. We address accuracy (not precision, which is much more straightforward) using relative sensitivity factors, RSFs, obtained either empirically from standards (e-RSF) or from the use of theoretical cross sections, σ, (t-RSF). Issues involved are (1) the uncertainty of background subtraction of inelastically scattered electrons, (2) the accuracy of the RSFs, and (3) the role of XPS peak satellite structure, which affects both (1) and (2) above. The XPS of materials tends to fall into two broad classes: where the signals being used for quantification are "main" peaks, which are narrower and more symmetric, followed by a relatively low background with only weak satellite structure and where the "main" peaks are broader and often asymmetric, followed by backgrounds that are higher and have a stronger satellite structure. The former generally will yield better accuracy, more easily, than the latter. The latter comprises all compounds containing elements with open valence shell electrons. These are mostly the 3d, 4d, and 5d transition metals, the lanthanides, and the actinides. Compounds involving only the first row elements, Li to F, where the 1s binding energy is used for quantitation, are those where the best accuracy is potentially achievable. We specifically address the issue of long-claimed serious discrepancies between e-RSFs and t-RSFs, which were interpreted as indicating calculated σs, used as a parameter in t-RSFs, were seriously in error. We conclude this claim to be untrue and that, if done correctly, there is no disagreement between the two approaches within the limits of accuracy claimed. Finally, we suggest protocols for rapid element composition analysis by obtaining relative XPS signal intensities using only low energy resolution.

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I. INTRODUCTION

Following the discovery, more than 50 years ago, of Chemical Shifts in the core-level BE's of atoms, thereby allowing distinction between different bonding situations for a given element atom, it was initially hoped that XPS would become a general chemical analysis technique for solids, hence the original acronym, ESCA, electron spectroscopy for chemical analysis, coined by Siegbahn *et al.*[1] However, it is already understood[1] that XPS probed somewhat close to the surface; initially, the probing depth was greatly overestimated.

It soon became clear that, using the laboratory sources of AlK$_\alpha$ and MgK$_\alpha$ soft x rays, the technique probed *mostly* only down into the top 10–100 Å of the material in an exponentially decreasing manner (dependent on the material, the kinetic energy (KE) of the photoelectrons being measured, and the detection angle with respect to the surface). In fact, for emitted electrons of similar kinetic energies, there is little difference in probing depth between electron impact Auger spectroscopy and XPS.[2] Given that the top 10 A or so for most classes of air exposed materials are often unlikely to be representative of the bulk solid, it became clear that XPS was not going to provide, *nondestructively*, a

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straightforward bulk general chemical analysis, and for the next 30 years, the emphasis was on playing to its strength in studying, often under UHV conditions, clean surfaces, ambient reaction at surfaces, and controlled adsorption and reaction on clean surfaces, ranging from submonolayer through to situations that went deeper, such as the early stages of oxidation and corrosion.

Information beyond the natural probing depth was obtained by combining XPS with sputter depth profiling using rare gas ions (usually Ar or Xe). This, of course, is a *destructive* analysis, which often introduced serious artifacts, such as the preferential sputtering of elements, induced chemistry changes, knock-on intermixing, and surface roughening. The one general class of materials where the nondestructive approach could (and did) provide relatively straightforward chemistry information on the bulk was for those organic polymers which (1) have the same surface composition as the bulk and (2) are inert enough not to suffer significantly from surface contamination or ambient reaction.[3] Such material samples could be measured "as received" and/or scrapped or cut before insertion into the instrument vacuum chamber. For most other materials, cleaving/fracturing/scribing/grinding in the UHV vacuum of the instrument, or at least preparing this way in an attached glove box or high vacuum entry loadlock, was necessary to provide bulk composition analysis without the compromising effects of the surface contamination or reaction.[4]

Over the last 25 years, however, several developments have led both to rapidly increase the use of XPS and also a change in the mix of usage and of users. One is the general trend in many types of technology to thinner and thinner layers so that the total thickness of a layer to be analyzed is often in the ballpark of the natural probing depth of XPS. Another is the great improvement in depth profiling, particularly the development of a variety of cluster ion beams, for which, for specific classes of materials, sputtering conditions can be found (cluster size, energy, sample temperature, impact angle), where the depth profiling artifacts mentioned above can be eliminated, or greatly reduced, making more accurate analysis possible.[5] The third is simply the vast improvement in instrumentation, automation, and turnkey data analysis. The final factor, which is based on the third, is the encouragement by instrument vendors for XPS users, the majority of whom are no longer experts, to now think of XPS as a straightforward, easy, and *quantitative* technique generally applicable for elemental and chemical state analysis of solid materials. Institutions often go along with this and do not invest in experts to run both XPS instruments and interpret data, as opposed to, say, more expensive, nonturnkey SIMS instrumentation.

The items above then beg the questions "how quantitative," "how generally applicable," and "how easy," which leads us to a discussion of how to turn the relative intensities of XPS signals (absolute XPS intensities are rarely used in XPS) from different elements, or different chemical states of a given element, in a solid sample, into a compositional analysis, or, if you like, a *stoichiometry*. This is the subject of this Perspective.

Our general opinion is that, even for "perfect samples" (flat, homogenous in depth and laterally), accurate quantification is often not easy and is strongly material dependent. At one extreme, it is much easier for polymers containing only first row elements, where better than ±4% accuracy has been demonstrated,[3] than at the other extreme of oxides (and other compounds) of the transition, lanthanide and actinide elements, where, in cases involving complex spectra with strong satellite structure, it may be problematical to achieve better than ±15% routinely. This paper and our perspective consider the fundamental issues involved concerning accuracy but only goes as far as considering flat bulk, homogeneous material. Other situations, such as a varying composition with depth, or samples with strongly structured surfaces (e.g., nanoparticles) present additional complications that are not discussed in this paper.

We should stress that this Perspective does not at all address precision of XPS measurements. It is well established that high precision can be achieved in XPS peak intensity measurements, allowing, for instance, determination of very small fractional changes in both thickness and composition of homogeneous films which have a thickness compatible with the probing depth of the technique. In industrial applications, particularly in quality control, this is often more important than knowing accurately the true thickness or composition. Basically, it allows a materials processing tolerance control.

II. PHOTOEMISSION INTENSITIES AND SAMPLE COMPOSITION

There are two fundamental factors limiting the accuracy in converting photoemission intensities from *solid samples* into atomic concentrations. These are

(1) Subtraction of the *extrinsic* background. *Extrinsic* is defined as the intensity that has been lost from the generated photoelectron signal, into the background at lower KE, by inelastic electron scattering as the photoelectrons pass through the solid, escape the surface, and are detected.
(2) Knowledge of the spectral distribution of the *intrinsic* photoelectron signal concerned. *Intrinsic* is defined as that part of the observed spectrum resulting from the initial photoemission process ejecting an electron, which escapes the solid *without* having undergone inelastic scattering. For quantitation, using XPS peak relative intensities, it is the intrinsic component we use.

A. Photoionization process and quantitation

Figure 1(a) is the hypothetical schematic spectrum of gas phase LiF, using the simplest approximation of the photoemission process—that is, if an individual x-ray photon interacts with an individual LiF molecule in an ensemble of molecules, it *may*, with some probability, cause the ejection of an electron (the photoelectron) from one of the LiF quantum energy levels (molecular orbitals) in that molecule, according to the Einstein photoelectric equation,

$$\mathrm{KE} = \mathrm{h}\nu - \mathrm{BE}, \tag{1}$$

where hν is the x-ray energy, BE is the binding energy of the electron in the orbital concerned (the energy required to remove it to infinity), and KE is the resulting kinetic energy of the ejected photoelectron. In the simplest approximation, it is also

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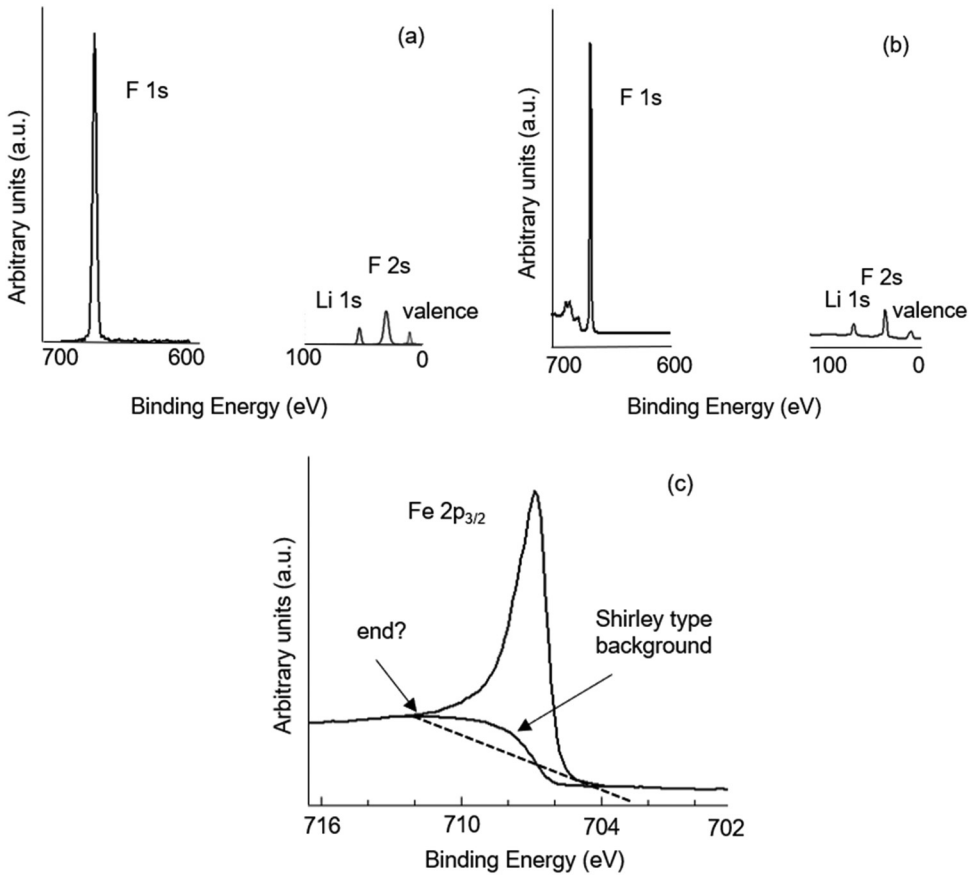

FIG. 1. (a) Schematic hypothetical XPS spectrum expected for gas phase LiF. (b) Schematic XPS spectrum for solid LiF. (c) $2p_{3/2}$ XPS spectrum for Fe metal.

assumed that when the particular core-level electron concerned is ejected other electrons in other molecular orbitals do not respond in any way (the *frozen orbital approximation*). Knowing hν and measuring KE thus allow determination of BE. If the orbital concerned is a core-electron, meaning deep enough to not be involved directly in the bonding between different atoms (in this case Li and F atoms), then the BE measured is unique to the element concerned. This is the basis of XPS atomic identification. So-called chemical shifts[1] are slight changes in a core-level BE that are due to major changes in the valence levels caused by bonding between atoms—i.e., chemistry. Though this is the primary basis of chemical state identification by XPS, it is only one of several effects that can, and should be, exploited for bonding information.[6]

The Li atom has a full 1s atomic core level (two electrons) and one valence electron in the 2s orbital. Atomic F has full 1s and 2s orbitals and five electrons in its 2p valence orbitals. In the XPS of an ensemble of LiF molecules, the spectrum should then consist of a Li1s signal, an F2s signal, an F1s signal, plus a signal from the valence region consisting of the six valence electrons involved in the bonding between Li and F, approximated in chemistry parlance as an ionic bond, Li^+F^-, where the Li2s electron has been transferred to the F2p orbital.

The relative photoelectron peak intensities are controlled by the *relative probability* for each orbital level to undergo photoionization at the hν value being used (either Alk_α at 1486.6 eV or Mgk_α at 1254.4 eV for standard laboratory-based XPS instrumentation). These probabilities, which are known as *partial photoionization cross sections, σ*, can be very different for different orbitals of a given atom and from atom to atom. They depend on the overlap between the x-ray wave function and the orbital wave function. Fortunately, we do know the calculated theoretical relative values. The XPS signal intensities in Fig. 1(a) are drawn assuming these theoretical σ values[7] to be appropriate. If we knew the values *exactly* and if we assume that *all* the intensity resulting from photoionizing a 1s electron of Li and a 1s electron from F, goes into the peaks as drawn in Fig. 1(a) (the frozen orbital approximation), plus there is no background and no instrument artifacts (such as a transmission function, T, varying with the electron KE), then it would be straightforward to turn the measured intensities (the areas under the peaks) into relative atomic concentrations by normalizing (dividing) each peak intensity by its σ value.

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1. Extrinsic background subtraction

Figure 1(b) is the equivalent hypothetical XPS for *solid LiF*. The obvious difference from the free molecule spectrum is that there is now a background. There is a step increase in intensity of that background on the low KE side of each peak. The step is drawn (realistically for this case) as about 5% of the peak height for F1s. It is barely observable for the other core-levels in this figure but is still there. The intensity of this background step is intimately related to the surface sensitivity of the technique, as described below.

The peaks originate from photoelectrons which have exited the solid without any energy loss caused by *inelastic scattering* on passing through the LiF matrix on the way out. They are, therefore, *intrinsic* electrons. Because the *average* distance an electron, of these energies, can travel without being scattered (the inelastic mean free path length or λ), is very small,[8] most, but not all (because we are talking average distances) of the electrons in the peaks must, therefore, have originated from very close to the surface. The background step, on the other hand, is the inverse of this. It is made up of those photoelectrons which have suffered inelastic collisions and lost energy on the way out (the *extrinsic photoelectrons*), so have been removed from the intrinsic peak. They may be scattered once, twice, or many times, losing more and more energy, and so the background step extends 100s eV to lower KE. Most (but not all) must, therefore, come from deeper in the solid. It is also worth noting that since the x rays going in penetrate many 100s of times deeper than the average inelastic scattering distance of the photoelectrons coming out, *the total intensity in the extrinsic background step is actually far larger than that in the intrinsic peak*. This may be annoying from an analysis point of view but is a direct consequence of the surface sensitivity of the technique.

The devil is always in the details, of course, so a reader unfamiliar with XPS should be asking what exactly is meant above by "most" and "very near the surface." Figure 2 is instructive. It shows,[9] for a collection angle normal to the surface, the fraction of the intrinsic XPS signal escaping the surface, as a function of the distance traveled (which for collection normal to the surface is the depth of origination). The decaying exponential functional form is derived from the well-known Beer's law for attenuation of light by absorption through a medium. Inelastic scattering of electrons can be treated similarly. Beer's law states that the absorption (scattering) goes as the inverse exponential function, $e^{-d/\lambda}$, where d is the light (electron) path length and λ is the mean absorption (inelastic scattering) length. So, for a path length of $d = \lambda$, the fraction of the total detected intrinsic signal (measured normal to the surface) that originates from a depth $d = \lambda$ is $1 - 1/e$ or 63.8%. For $d = 2\lambda$, the amount is $1 - 1/e^2$ or 86.5%, $d = 3\lambda$, it is $1 - 1/e^3$ or 95.02%, and so on and it will never quite reach exactly 100%. 3λ is often referred to as the analysis depth or information depth defined as the depth from which, for normal emission measurement, 95.02% of the detected intrinsic signal originates. The values of λ have been determined experimentally in many cases but have also been calculated quite accurately.[8] Over most of the KE range for which we are concerned in XPS (~1480 eV down to about 300 eV when using an AlK_α laboratory x-ray source), λ varies as KE^x, where x varies between 0.6 and 0.75 and also with the nature of the material. The TPP-2M calculations probably provide a greater accuracy.[8] λ can range from a few angstroms for some metals to ~50 Å for some organics (the material variability depends on density, among other things). Readers should refer to the article by Powell for further discussion of the effects of inelastic scattering and also the modifying effects of elastic scattering on XPS measurements.[8]

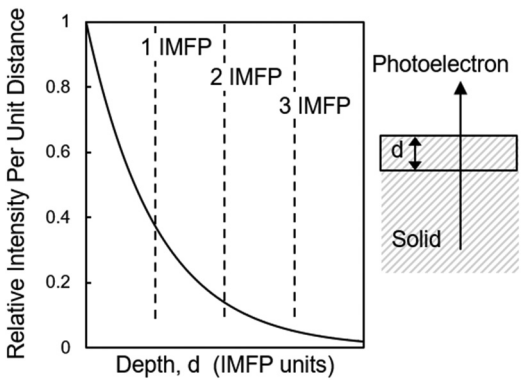

FIG. 2. Relative intensity of an XPS signal, per unit depth, emerging normal to the surface at its unscattered original KE.

Note that in Fig. 1(b) the step is drawn with a gap between it and the peak it follows. This is because our example, solid LiF is an insulator and has essentially no scattering mechanisms for energies smaller than the bandgap. If the solid had been a conductor, say a metal, the spectrum would look very different, as drawn schematically in Fig. 1(c) for the $2p_{3/2}$ XPS peak of Fe metal. There is no longer a gap because scattering involving levels close to the Fermi level leads to small incremental energy losses. Also, there may be discrete extrinsic structure on the step because specific scattering processes of given energies may have high probability, such as plasmonlike excitation (a plasmon is a collective oscillation of conduction electrons in a free electron metal). The photoelectron peak itself may be asymmetric on the high BE side, as drawn in Fig. 1(c), resulting from a cascade of small, unresolved, energy losses.

The point of all this, as related to our subject matter, accuracy of stoichiometry quantitation in XPS is that if one adopts even the simplest (and often quite poor) assumption that *all* the XPS intrinsic intensity is in one "main peak" (the frozen orbital approximation), as implied in Fig. 1, the ability to separate the intrinsic photoelectron peak from the onset of the extrinsic background following it is limited and can be very different for different XPS signals. In our example in Fig. 1(b), it is easy and reliable for the insulating LiF but less so for the conductive metal case, Fig. 1(c).

Two approaches to subtracting a background have been extensively used in XPS when trying to establish stoichiometry from relative intensities, both empirical. The first is simply drawing a straight line from where you think the peak starts to where you think it finishes. In Fig. 1(b), this is an easy task as the background before the peak and after is almost the same. The area under the peak is almost unaffected by small variations in where one picks the start and end. For Fig. 1(c), however, it is not obvious exactly where the peak ends and small variations in choice make a more significant difference.

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The second method is the so-called Shirley background subtraction,[10] which again requires picking start and finish points and then calculating the scattered background between them assuming the intensity of the scattered background at any BE is proportional to the integrated total signal intensity up to that BE. The end point, by definition, assumes the signal at that point is now totally from the background (i.e., the intrinsic signal has finished). For Fig. 1(b), there is no significant difference between the two approaches because start and end points have (nearly) identical intensities. In Fig. 1(c), the two approaches *are* significantly different, even if identical start and end points are picked. In reality, things are often much more complex than even Fig. 1(c), because all of the XPS intensity *may not go into one well-defined main peak*, as discussed in Sec. II A 2.

There is a third method for removing a background, the Tougaard background approach.[11] Unlike the straight line and Shirley background approaches, it is not entirely empirical but attempts to calculate the actual inelastic scattering events using parameters derived from other experiments. Using those parameters often results in a much-reduced background removal compared to Shirley[12,13] because the end point, which is not picked by the operator but comes from the calculation, is shifted much further to lower KE (several 10s eV in the original two-parameter formalism). It can be arbitrarily forced to coincide with a defined end point by changing the parameters to unrealistic ones, in which case it becomes more similar, but not identical to Shirley. Currently, it is our opinion that it is not known whether Shirley or Tougaard is more correct and this may vary with the spectrum being analyzed. In general, in our experience and opinion, Shirley tends to remove too much intensity when complex spectra with satellite structure are involved, so underestimating the intrinsic signal, whereas Tougaard removes too little. What is important for quantitative analysis is that the same method, covering appropriate energy ranges (start to end points) be used for the XPS signals being ratioed. This is discussed in more detail later.

2. Spectral distribution of the intrinsic photoelectron signal

The idea that photoemission is a one electron process is a first order assumption (the frozen orbital assumption), and often not a very good one, as we will see. There are (at least) two *final state* effects that are important here. A final state effect means it is specific to the final state of the atom resulting from the photoionization, which is a positively charged ion with an electron missing from a specific core-level. The two effects are known as "*shake structure*," and "*multiplet splitting*." Both "steal" intensity from an XPS "main line" and distribute it at lower KE, as described below.

Figure 3(a) is the XPS of an ensemble of Ne atoms acquired in the gas phase.[1,14] The "main peak" at ~818 eV BE (~618 eV KE) is the one which corresponds most closely to the description of a one electron photoionization process, in that it represents that fraction of the atoms in the ensemble where removal of a 1s electron occurs without any other electrons changing orbitals. At higher *apparent BE*, spread over *at least* 100 eV are peaks from those Ne atoms which have undergone 1s electron removal, *plus a "shake-up" process*, meaning that in addition to the 1s electron removal, another electron, or even two electrons, in the valence levels of the atom, have been excited to a higher unoccupied quantum energy level, using up an extra amount of the available x-ray photon energy, hν, and so result in a peak at lower KE than the main peak.

The relative intensity of all the shake-up process peaks in Fig. 3(a) is ~12% of the main peak. In addition, "*shake-off*" processes occur, where in addition to 1s removal, another electron is also removed. This gives intensity in the form of an *intrinsic step*, starting at about 43 eV below the main peak in this case. The fractional intensity going into shake off is estimated as ~16%. So, in terms of fractions of the total photoemission from the 1s level, 78% of the atoms undergo a one electron transition, the Ne1s removal only (the main peak), 9% undergo 1s removal plus shake up, and 13% involve 1s plus shake off. All the shake processes for Ne atoms are, of necessity, *intra-atomic*, meaning they all occur within the Ne atom. For *molecules*, there are greater opportunities for shake structure because neighboring atom valence electrons can be involved. In solids, there will be even greater opportunities owing to increased coordination of atoms in a lattice.

Why does this matter for quantitation? In compounds, the fraction of a photoelectron signal originating from a given orbital (e.g., the 1s of Ne used as the example here) that goes into the main peak *can, and does, vary with the chemical state of the atom concerned,* and also may vary from core level to core level for a given atom in a given chemical state.[15] The classic solid-state example of this, well known for over 45 years,[6] is the difference between the Cu2p XPS of Cu^{2+} compounds and Cu^{+} compounds. Owing to the strong difference in the valence level electronic structure in these two oxidation states (Cu^{2+} is $3d^9$; Cu^{+} has a closed shell, $3d^{10}$), much greater intensity is transferred from the "main" peaks into shake-up structure for Cu^{2+} than in Cu^{+}, as shown in Figs. 3(b) and 3(c), for the $2p_{3/2,1/2}$ spectra from CuO and Cu_2O.[6,16] These are the peaks normally used for quantitation, because they are the strongest and narrowest peaks in the Cu XPS. The Cu^{2+} species has ~ 50% of its total intrinsic intensity in the *observed* shake satellites, whereas there is very little (but *not* zero) for Cu^{+}. So, if one tried to use the intensity of the "main" $Cu2p_{3/2}$ peaks ratioed to that of the O1s peak intensity to determine the stoichiometry difference between CuO and Cu_2O, one would obviously be seriously wrong. In this case of Cu^{2+} and Cu^{+}, this problem of varying spectral distribution with chemistry is very obvious and cannot easily be ignored by analysts, and so the Cu^{2+} shake intensity *is* usually included in the total. In general, though, separation of any intrinsic spectral intensity of shake satellites from the extrinsic background can be more complex and difficult than in the Cu^{2+} and Cu^{+} case used as an example here. This presents a very real limitation to the accuracy of quantification in many cases.

The second final state effect which steals XPS signal intensity from a "main" peak is multiplet splitting. It is most easily explained by looking at the N1s spectrum of the NO gaseous molecule, Fig. 4(a), which was first reported in 1969.[17] Even though there is only a single N atom, there are two peaks separated by about 1.8 eV. NO is a paramagnetic molecule, having a single electron with unpaired spin in its valence levels. N1s photoionization results in an unpaired electron left in that orbital, which can couple either parallel (high spin state) or antiparallel (low spin state) with the unpaired valence electron. These two

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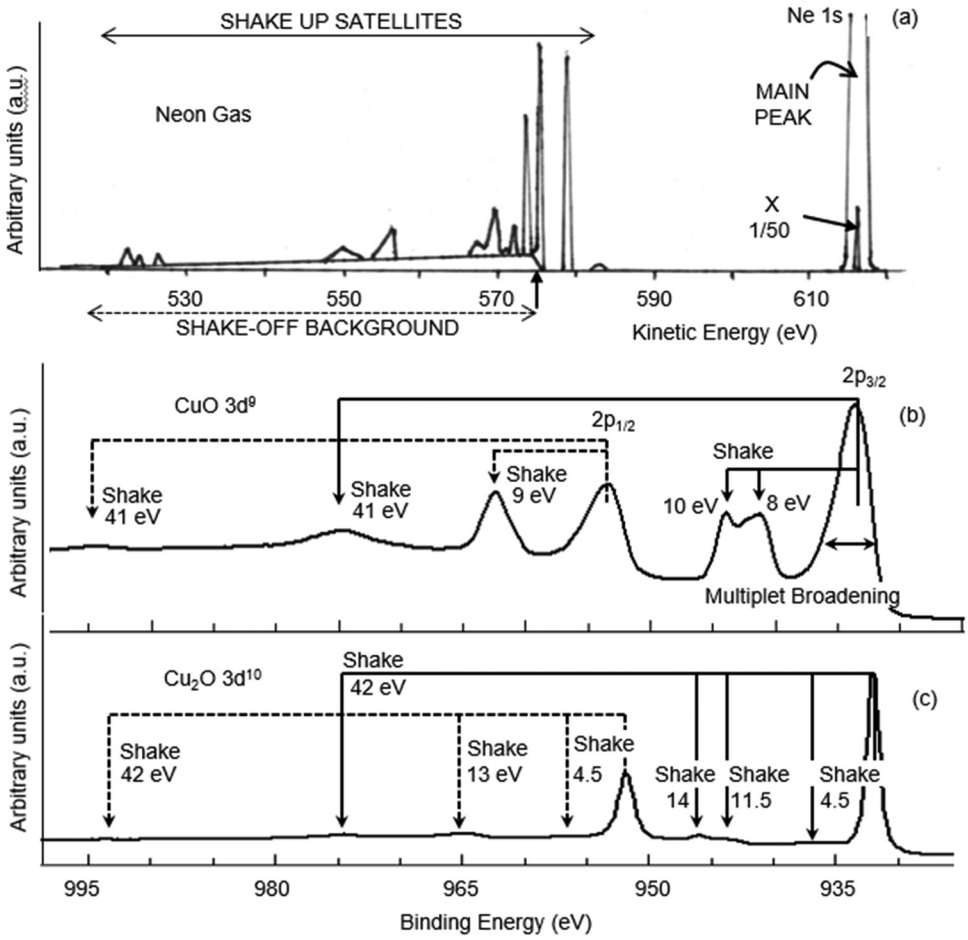

FIG. 3. (a) XPS of the Ne atom showing shake-up and shake-off contributions spreading over 100 eV KE (schematic) (Ref. 14). (b) XPS 2p spectrum of CuO. (c) XPS 2p spectrum of Cu_2O.

final states are separated by ~1.8 eV energy (high spin states are always lower in energy than low spin states), explaining the spectrum. The O1s XPS is similarly split, but the magnitude of the splitting is less.

In more complex situations, such as the 3d transition element compounds, where there can be up to five unpaired valence d electrons, the coupling can be very complex (owing to more possible coupling arrangements). For the 2p and 3p XPS spectra, there is also the angular momentum leading to spin–orbit splitting, S-O, resulting in the $2p_{3/2}$ and $2p_{1/2}$ components in the 2p XPS structure of CuO in Fig. 3(b). The multiplet splitting broadening of Cu^{2+} is superimposed on top of this and is *not identical* for the two spin–orbit components. The Cu^{+} 2p spectra of Cu_2O, on the other hand, has no multiplet splitting, because there are no unpaired valence d electrons, and so the main peaks are much narrower than in CuO. When valence f electrons are involved (lanthanides and actinides), the situation can be even more complex because there can be up to seven unpaired electrons.

Another example of multiplet splitting is shown in Fig. 4(b), the 2p spectrum of solid Fe_2O_3.[16] The expected positions and intensities of the multiplet components, calculated, *ab initio*, using an FeO_6 cluster model with Fe in the Fe^{3+} oxidation state, are also shown in Fig. 4(c).[18] Those features not explained by the multiplet splitting components in the cluster calculation are shake features, which are not included in these calculations. Altogether, the intrinsic spectrum is very complex and sits on a large extrinsic background. Just as shake features are chemistry dependent, so are multiplet spittings, strongly on the oxidation state for the transition metals (since this controls the number of d electrons present) and less so on the ligand (connected to the degree of covalency involved).

III. CONVERTING XPS INTENSITIES INTO STOICHIOMETRIES

Two methods have been extensively used for over 40 years to turn relative XPS intensities into stoichiometries. One is based on

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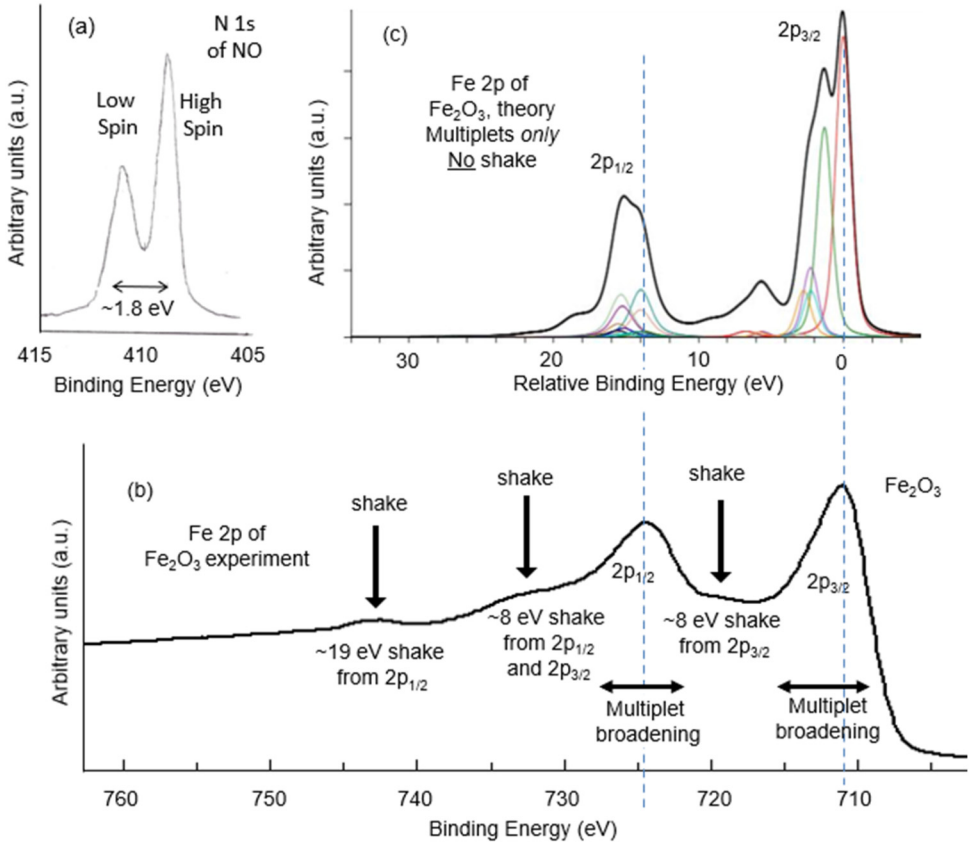

FIG. 4. (a) N1s spectrum of the NO free molecule showing the multiplet split components. (b) XPS 2p spectrum of single crystal hematite, Fe_2O_3, showing multiplet broadening of the main $2p_{3/2}$ and $2p_{1/2}$ peaks, plus shake-up features. (c) Representation of the calculated multiplet splittings of the 2p spectrum of Fe_2O_3, assuming realistic line widths. The envelope is the sum of all components (Ref. 18).

using the theoretically calculated σ values to normalize intensities and derive a *theoretical RSF, t-RSF*. The other establishes *empirical RSFs, e-RSF*, valid for a given instrument, using reference standard materials of known composition measured on that instrument. How each works in practice is discussed below.

A. Theoretical cross section, σ, based RSFs, t-RSF

In 1972, Scofield[7] published tabulated calculated σ values for all orbitals of most elements in the periodic table, at photon energies of 1487 eV (Al K_α radiation) and 1254 eV (Mg K_α radiation), *normalized against C1s as unity*. For a short while this was the second most referenced paper in the physical sciences. This was not because of originality or sophistication of the calculations. They were standard atomic quantum physics calculations. Some had been published by Scofield earlier, while others (notably Nefedov's group in Russia[19]) performed similar calculations. They were cited so often because the *relative* σ values allowed, in principle, a simple approach for converting XPS relative intensities into material stoichiometries.

If one plots Scofield calculated σ values against Z, it is clear that there is a smooth variation with Z so that one can interpolate any missing values. The problem, however, is that a calculated σ value for a given orbital is for the *total photoemission intensity originating from that orbital*, i.e., in the Ne case of Fig. 3(a), *it is the total of the "main" peak and all shake-up and shake-off satellites*. If only the "main" peak intensity was included, it would represent only 78% of the σ value. In the case of Fe_2O_3 [Fig. 4(b)], to use the calculated σ value for Fe2p, or Fe3p to normalize the XPS Fe signal intensities to the O1s XPS signal *requires inclusion of all the multiplet splitting components and all shake components and separation of these from the extrinsic background.*[12]

The full equation for photoemission intensity generation in a solid[20] is given by

$$I = nF\sigma\phi yT\lambda, \tag{2}$$

where I is the number of photoelectrons detected per second from the orbital concerned, going into the measured XPS peak, n is the concentration of the atom concerned (atoms/cm^3), F is the x-ray

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flux (photons/cm^2), σ is the partial ionization cross section for the orbital concerned, y is the fraction of σ retained in the measured peak [i.e., it would be 0.78 for Ne atoms if only the main peak intensity at 618 eV KE in Fig. 3(a) was measured], ϕ is an angular distribution term (see below), T is the efficiency of detection of the spectrometer (the transmission function, a function of KE), and λ is the IMFP (a function of KE, as already discussed, though the use of the experimental attenuation length, which includes the modifying effect of elastic scattering is more accurate.[8]

For atoms a and b, then, in a given spectrum, where F drops out, the stoichiometry is derived from

$$\frac{n_a}{n_b} = \frac{I_a}{\sigma_a \phi_a y_a T_a \lambda_a} \div \frac{I_b}{\sigma_b \phi_b y_b T_b \lambda_b}. \tag{3}$$

So, since an RSF is defined as the factor a measured XPS signal intensity must be normalized by to obtain relative atom intensities, *σϕyTλ is the full t-RSF* of the atom concerned.

The behavior of ϕ for free atoms is well understood.[14] It is a function of the angle between incoming x rays and outgoing photoelectrons and also depends on the angular momentum quantum number of the orbital concerned (s, p, d, and f) and the atomic number, Z. For all s orbitals, the angular behavior is the same so ϕ_a/ϕ_b becomes unity if ratioing s level intensities. In addition, there is a "magic angle," 54.7°, for which ϕ_a/ϕ_b is unity for all orbitals, so if measurement is made at this angle, ϕ_a/ϕ_b drops out of the equation. Unfortunately, it is not at all clear for solids whether any significant angular effect has ever been observed (it must at least be reduced by elastic scattering, which changes the direction of the emitted electrons), and the assumption is usually made that there is none (φ_a/φ_b becomes unity), or that the effect is smaller than other errors, so is ignored.

The behavior of T, which is a function of KE, is usually well characterized in modern commercial instruments. It is corrected for by "removal at source" in some instrument software (i.e., the spectrum you see has already been corrected for T). If not, then it should be corrected for after acquisition. In older instruments, and publications, T might not have been very well known and not have been corrected properly, if at all.

The behavior of λ as a function of KE has already been addressed above.[8] It goes as ~KE^x, where x is between 0.6 and 0.75 for most compounds. Note it is not important, for RSF's, what the actual λ values are, only what the value for x is. At low KE, the behavior of λ can become anomalous and may not follow this simple relationship, so we do not recommend using XPS peaks below ~300 eV when attempting quantification.[8]

Making the usual assumption that the T effect has been corrected for, and that φ_a/φ_b is unity, we now have

$$\frac{n_a}{n_b} = \frac{I_a}{\sigma_a y_a \lambda_a} \div \frac{I_b}{\sigma_b y_b \lambda_b} = \frac{I_a}{I_b} \times \frac{\sigma_b y_b \lambda_b}{\sigma_a y_a \lambda_a} = \frac{I_a}{I_b} \times \frac{\sigma_b y_b}{\sigma_a y_a} \times \left(\frac{KE_b}{KE_a}\right)^x. \tag{4}$$

Assuming the measured peaks capture all the signal (i.e., including all satellite intensity), then y = 1. Alternatively, if y is not 1, but is the same for both a and b, then it still drops out and we have for either case,

$$\frac{n_a}{n_b} = \frac{I_a}{I_b} \times \frac{\sigma_b}{\sigma_a} \times \left(\frac{KE_b}{KE_a}\right)^x \tag{5}$$

or generically,

$$I \; \alpha \; n\sigma KE^x. \tag{6}$$

This is the usually used default theory equation for converting a relative intensity, I_a/I_b, into a stoichiometry, n_a/n_b and so *σKE^x is the reduced version of t-RSF*, ignoring the possibility of any noncancelling ϕ, noncancelling y, and incorrectly characterized T. It simply corrects the proportionality of intensity to σ by the escape depth effect.

Assuming, then, that ϕ, y, and T present no issues, the potential accuracy of a determined stoichiometry, based on σ values, obviously is limited by the accuracy of the theory for σ. Scofield[7] reviewed agreement of his calculations with experimentally derived information available at that time from x-ray absorption data (*not* XPS). He concluded general agreement within 5% except for high Z elements for his calculated *total cross sections* (i.e., the sum of all the partial values). For H to Ne, the 1s partial photoionization cross section dominates the total, so one may expect ~5% accuracy for the XPS 1s values.

B. Standard based e-RSFs

In Sec. III A, it was shown that t-RSFs are given by σϕyTλ, but in practice are usually reduced to σKE^x, with the assumption that T has been accounted for by the instrument software, or corrected for after measurement, and that ϕ and y are unity, or are at least the same for all the photoelectron peaks used to establish the RSFs.

For RSFs, based on a standard containing atoms A and B, with composition $A_{na}B_{nb}$,

$$\frac{e\text{-}RSF_A}{e\text{-}RSF_B} = \frac{I_A}{n_a} \times \frac{n_b}{I_b}, \tag{7}$$

where I_A and I_B are the XPS intensities experimentally measured for the standard on a given instrument. Thus, e-RSF$_A$/e-RSF$_B$ for a given instrument, under given acquisition conditions, is determined directly from I_A/I_B. *No knowledge of σ, ϕ, T, or λ is required, but it must be stressed that the e-RSF values obtained are for that instrument with its particular characteristics.*

Unless the experimental intensity measurement includes both the "main peak" and all satellite intensities, which is often hard to know, it is, however, still an assumption that y *does not change for the given element in different compounds; that is the fraction of the total intensity captured in the measured peak(s) remains constant.* If it does change, then the e-RSF determined is strictly valid only for the specific chemical state of the atom in that standard. In addition, of course, the values are only valid for the instrument on which the standards were run. They will not be valid for measurements on other instruments having different geometries and analyzer transmission functions.

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IV. RECONCILING APPARENT DISCREPANCIES BETWEEN HISTORICAL E-RSFS AND T-RSFS

Though Scofield's work is so old his values are still used, as is, by many analysts today to provide material composition, sometimes with the appropriate λ corrections [Eq. (6)], sometimes not. His tabulated values, relative to C1s as 1.00, are given to three significant figures, unfortunately allowing an analyst, applying them to analysis of solid material, to quote composition to three figures, which is clearly totally unjustified given the other experimental uncertainties.

Other authors calculated σ values to a similarly expected level of accuracy as Scofield (i.e., a similar level of physics was included). A check of Scofield against Yeh and Lindau,[21] indicates agreement at an hν of 1486 eV to within 6% across the periodic table with the Scofield values being consistently slightly higher. For $Z < 20$, the calculated values are remarkably close, except for Li1s, where the Lindau and Yeh value is ∼2% higher.

In 1982, Wagner *et al.*[20] put together, from 135 standards, a database of *relative peak intensities* for XPS peaks of 62 elements in the periodic table. The data included new measurements (primarily fluorides) and previous values already published by Wagner and by others. The values were normalized to F1s as unity, either directly or through secondary standards. Two early commercial instruments (Varian and PHI) were used, and, on the basis of not finding any consistent trends in differences between instruments, it was *assumed* that instrument characteristics were similar, values transferable, and there were no angular effects. The database included, for some elements, multiple measurements on multiple samples on both instruments and at the other extreme, only a single measurement (Be1s derived from BeF_2).

There was a large uncertainty in the values obtained, normalized to F1s as unity (the values unfortunately were quoted to two or even three significant figures, however). For example, for four measurements on LiF, Li1s varied by ∼35%; Na1s by a factor of two for eight measurements; and Zn2p by 35% over three measurements. No significant trends in the variations were found from instrument to instrument or lab to lab.

Wagner *et al.* took these values and plotted them against the KE of the XPS peak on a log-log scale, separating them into 1s, 2p, 3d, and 4f curves. He then fitted the results to straight-line segments and generated a second table of e-RSF values, *derived from these straight-line segment fits* (note: decidedly *not* from the average of the actual data points for a given element). Despite the obvious limitations of this approach, which essentially is introducing interpolation between elements, even when the experimental data disagreed with this, these e-RSF values were reported to two significant figures (though some were bracketed to indicate "rough"). 1s XPS peak relative intensities of Wagner *et al.* for Li to F, and his straight-line fit to yield their e-RSF values, are plotted in Fig. 5(a).

These "Wagner" e-RSF values for the 62 elements concerned have persisted in XPS quantification for 38 years, sometimes being adjusted in a highly questionable manner for differing T and ϕ characteristics of other instruments, sometimes not, and sometimes being quoted to three significant figures! This is not the fault of the original authors, who clearly understood the issues, and whose goals were to establish, empirically, the *trends* and to compare to the σ derived results for t-RSF. However, in addition to later misrepresentations of their data, there are two serious issues concerning the original measurements:

(1) Wagner's paper does not provide information on whether the bulk known composition of the standards is maintained in the XPS analysis depth. The authors took what care they could to minimize air exposure and poor vacuum effects, but today we would consider these methods inadequate to guarantee unreacted surfaces.
(2) The most frustrating issue, and the one most relevant to today's concerns about "irreproducible data," is that *no actual spectra were reported*. Only derived peak intensities were given, without adequate information on background subtraction, or what part of the spectral distribution was and was not included. In general, it seems that in most instances, but not all, only main line intensity was included (i.e., excluding satellites). If the actual full spectra had been reported, then we would be able to establish whether samples were degraded, or contaminated, and how backgrounds were drawn.

In addition, though it was clearly appreciated that y was not unity for paramagnetic compounds because of multiplet splitting, the general importance of shake intensities, which is not limited to paramagnetic materials, was not considered. Neither was it appreciated (or at least not discussed) that y may vary substantially with the chemical state of an atom [e.g., Cu^{2+} versus Cu^{+}, Figs. 3(b) and 3(c)]. In such cases, e-RSF based on "main peak only" intensity would be strictly valid only for the atom in that particular chemical state.

Wagner *et al.*[20] then compared the e-RSF values, which were specific for the Varian and PHI instruments of that era, to σ based (Scofield values) t-RSF values. This comparison could have been done in one of two ways.

(1) By either removing the effects of λ, T, y, and ϕ from the empirical measurements, leaving only the σ dependence or
(2) by adding in the λ, T, y, and ϕ corrections to the σ values to give a t-RSF for the instruments concerned.

They chose to do the latter and presented sets of comparison plots of e-RSF versus t-RSF for 1s, 2p, 3d, and 4f levels for the 62 elements in the study. In this comparison, the λ correction used, with λ being proportional to $KE^{0.66}$, is appropriate and small variations are insignificant compared to other inaccuracies, but the validity of T as proportional to KE^{-1} is less certain. ϕ was assumed to be unity on the basis that there was no evidence for any difference in results between the Varian and PHI instruments, which had differing geometries that would be expected to produce different results if ϕ correction was significant. Y was set at unity for all the comparisons because, though it was appreciated that it was less than unity in some cases, there was no information on what the values might be. The general conclusion of Wagner *et al.*, across the periodic table, was that the relative Scofield calculated σ values, normalized against F1s as unity, were "*significantly in error—as much as 40% in some cases for strong lines and far more than that for some of the secondary lines.*"

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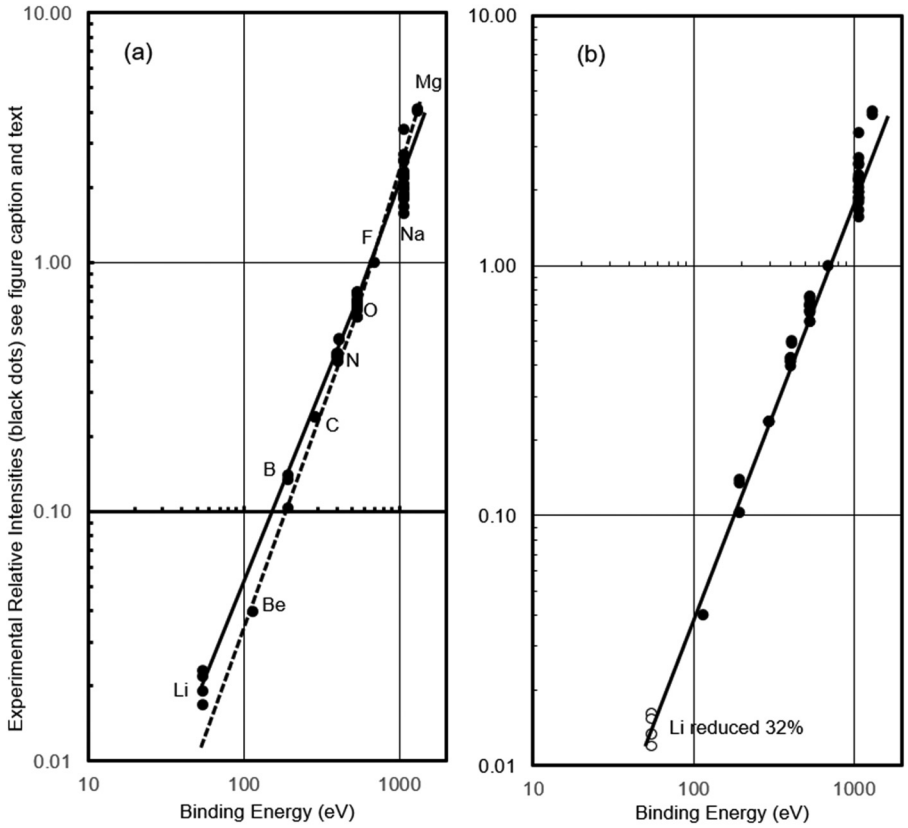

FIG. 5. (a) XPS experimental relative intensities (black dots) for the 1s levels of Li through to Mg using specific early XPS instrumentation (Ref. 20). The solid curve approximates the fit to the data proposed in Ref. 20. e-RSFs quoted in Ref. 20 were taken directly from this curve. t-RSFs (dotted line) were calculated using Scofield σ values and assuming $\lambda \propto KE^{0.66}$ and $T \propto KE^{-1}$. (b) Proposed correction to the e-RSF curve of Fig. 5(a) due to a 35% correction in the Li/F ratio (see the text). Changing the assumed T dependence on KE from KE^{-1} to $KE^{-0.5}$ brings the t-RSF curve into coincidence with the e-RSF curve (see the text).

A. 1s BEs: Elements Li to F

Though a large error in Scofield values might not have been too surprising for high z elements (more electrons; d and f states), it was, and still is, very surprising for the much simpler situation of the 1s only levels in the first row elements, especially as the Scofield claim of 5% accuracy for this set was supported by other experimental evidence. In addition, there can be no differential ϕ behavior as a function of Z for 1s orbitals, so no concern in setting it as unity. In Fig. 5(a), where the e-RSF curve (solid line) and t-RSF (dotted line) curve have been replotted, it is the Li1s t-RSF value (based on the Scofield Li1s σ value) which appears to be "40% or more in error" (actually more like a factor of 2!), but the interpolated Be value of the empirical curve is also considerably different from theory (note, however, that the single experimental measurement involved here, on BeF_2, is actually closer to t-RSF and far from the value assigned for e-RSF by the curve drawn).

There are four factors that could contribute to the discrepancy between the authors' e-RSFs and t-RSFs in Fig. 5(a).

(1) The calculated σ values could be seriously in error, as claimed by the authors.[20]
(2) The assumption that $y = 0$ for these elements in the compounds measured is incorrect and it is neither zero nor the same for each element.
(3) The transmission function assumed, proportional to KE^{-1}, is incorrect, which is possible based on a report,[20] where Seah suggested, it should be $KE^{-0.5}$ for at least part of the KE range involved.
(4) The effect of hydrocarbon contamination, which was considered, is far greater than the authors thought.

For (2) above, it is instructive to reexamine, in a modern instrument, the spectrum of LiF, which was the compound used to establish the Li1s e-RSF value. Figure 6 shows a modern XPS survey spectrum (corrected at source for T), with good statistics, for a LiF crystal.[16] Higher resolution expanded regions are shown as insets for the F1s and the F2p/F2s/Li1s regions, respectively. *It is important to note that the BE range acquired for these high-resolution spectra is far wider than is normally used in XPS analysis (20–30 eV is usual), in order to capture all observable satellites.* The F1s spectrum clearly shows the position of the start of the expected extrinsic background as a step at ~13 eV. Superimposed on this background is a series of peaks, labeled 1–10, spreading out over the full 100 eV of the scan. They constitute about 25% of the total F1s intensity. This is quite consistent with the expected shake contribution, judged from the atomic spectrum of the next element in the periodic table, Ne, in Fig. 3(a). So, we estimate that a "main line" only measurement of F1s in LIF may *underestimate* the total F1s intensity by ~25%.

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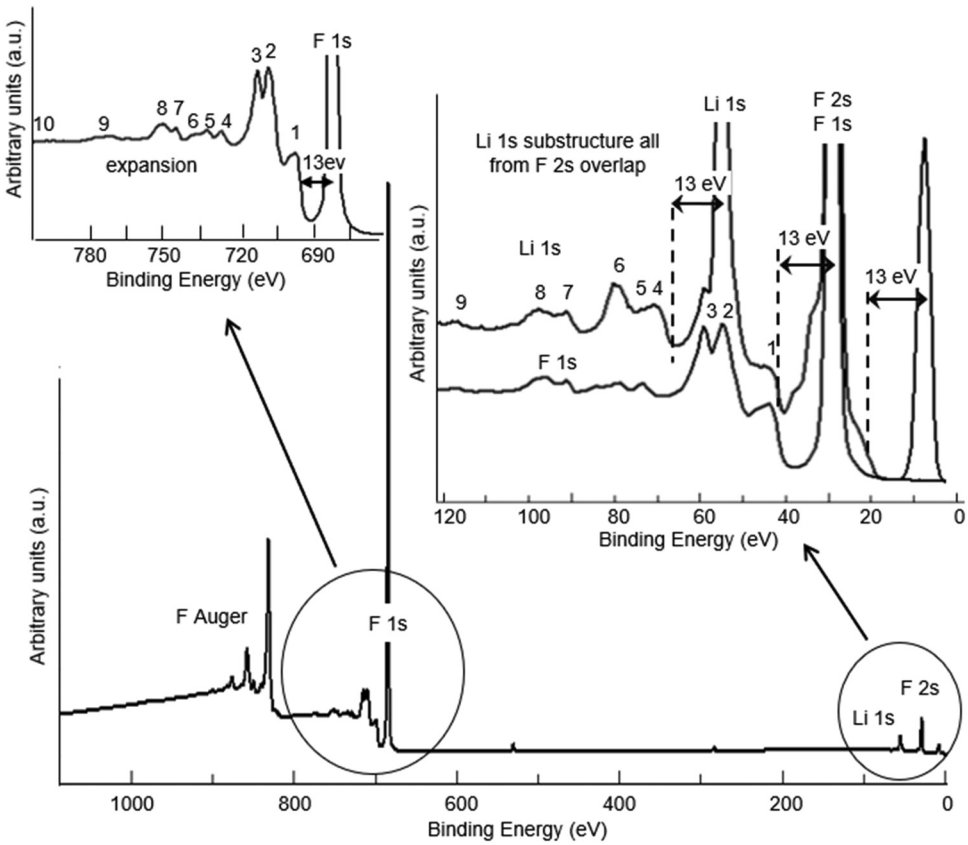

FIG. 6. Survey spectrum of LiF single crystal. The inset (left) shows a high-resolution spectrum of the F1s region with ten identifiable satellite features. The inset (right) shows a high-resolution spectrum of the F2s and Li1s region (upper) and an overlay of the F1s spectrum (lower), demonstrating the overlap interference of the F2s satellites with the Li1s spectrum.

Looking at the F2s, F2p, and Li1s high-resolution spectrum, in Fig. 6, one can identify the same step initiation of the extrinsic background at ~13 eV after each main line. One also sees that exactly the same series of shake satellites found for F1s is present on the F2s spectrum. The overlay comparison, where F1s and F2s main lines are aligned, makes it clear that the shake-up positions are identical in F2s and F1s. Note that satellites 2 and 3 from F2s lie right under Li1s, causing the experimental intensity of the Li1s line to be *overestimated* by between 10% and 30%, depending on how the background is drawn and the peaks are curve fit. As far as we can tell, there is *little discernable satellite intensity* actually associated with Li1s. The structure after Li1s comes mainly from the overlapping satellites of F2s. The lack of significant shake structure for Li1s is actually expected from simple argument, as Li^+ has *no valence electrons to be excited into higher lying orbitals*. Full *ab initio* theory supports these arguments, calculating a 1.4% loss to satellites for Li^+, but 22.7% for F^-.[22] In solid LiF, both losses would be expected to increase slightly because of the availability of screening electrons from the surrounding lattice.

Thus, the corrections necessary to the experimentally determined F1s and Li1s intensities to compare to theory require an *increase* of ~25% for F1s (i.e., y is not unity, but is 0.75) and a *reduction* to the Li1s intensity of ~10%–30% due to the overlapping F2s structure. A total correction of ~35%, renormalized to F1s as unity, to the e-RSF value for Li1s is marked in Fig. 5(b) and a corrected e-RSF curve drawn based on a straight-line fit to the data.

We initially expected that the losses of intensity to satellites from the main 1s line to gradually increase on moving from ~0 for Li1s (y = 1.0) through Be, B, C, N, and O to the ~25% value for F1s (y = 0.75), simply on the basis that there is a smoothly increasing number of valence electrons available for shake up. Work by the present authors on BeF_2 and $(CF_2)_n$ does not support this, however. Both the F1s and the Be1s in BeF_2 spectrum have backgrounds with some superimposed structure, but they seem to be of roughly similar intensities. F1s and C1s in $(CF_2)_n$ behave similarly. This may be because these compounds have much greater percentage covalent bonding, with only LiF being fully ionic, leading to the completely different satellite behavior for the F1s and the Li1s.

Considering item (3) above, changing the KE dependence of T significantly will make a large difference in the Wagner t-RSF curve plotted in Fig. 5(a). The normalization to F1s of course dictates that the t-RSF and e-RSF are identical at F1s, so the two curves

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must meet and cross there if they have different slopes, as they do in Fig. 5(a). Changing the KE dependence from KE^{-1} to $KE^{-0.5}$ for the t-RSF plot *makes it indistinguishable from the corrected e-RSF plot in* Fig. 5(b).

Hydrocarbon contamination, item (4) above, was considered by Wagner. They showed that even assuming significant amounts (~8 Å) were present on their standards, corrections of less than 10% relative to F1s would occur by including the effect on the t-RSF curve. For freshly prepared samples, it is not likely that more contamination is present and it would take much more to significantly alter their plot.

Summarizing, it appears likely that the uniqueness of Li^+ (no, or very little, satellite losses for Li1s), plus the large satellite losses for F1s, and plus an incorrect T behavior as function of KE *account entirely for the apparent discrepancy between the e-RSF and t-RSF curves in* Fig. 5(a), especially when considering the actual wide spread in these old atom relative intensity measurements. We also note that recent experimental values of σ, determined, by removing the T and λ effects, using modern instruments with hugely increased sensitivities and well-characterized T functions, do not find significant disagreement with the Scofield calculated σ values for the first row elements. There is typically a ±7% scatter around the theoretical values,[23] which might be improved upon with detailed information on which satellite intensities were included.

What does all this mean in practical terms for XPS quantification for first row elements? First, it supports the extensive work on polymers involving C, N, O, and F, over many years, where reasonable agreement with known bulk composition has been obtained using Scofield σ values such that if all observable satellites are included better than 4% accuracy has been demonstrated.[3] Second for the whole first row, if one wants to use standards based on main line intensities only, this will work provided the losses are the same for the elements in the analysis (i.e., y is identical but not necessarily 1.0). However, using this method, which is the preferred one by practical analysts because it is much faster than looking for genuine satellite intensity spread over large energy ranges, accuracy will, of course, degrade with any variation of y between the elements being compared (such as in LiF).

B. 2p BEs: Mg (Z = 12) through As (Z = 33), excluding the transition elements Sc (Z = 21) to Zn (Z = 30)

The 2p BEs are the XPS lines usually used for analysis in this section of the periodic table because they are the strongest. Figure 7(a) replots the Wagner experimental relative intensity data for these elements, in a like manner to Fig. 5(a). Again, there is a large spread in the data, and their fit to the data (solid curve), from which the Wagner e-RSF values were derived, comes nowhere near the actual data for Mg. The t-RSF curve (dotted line), using Scofield σ values and the T and λ parameters suggested by Wagner, is also plotted. The slopes of the two curves differ substantially, just as in the 1s plots of Fig. 5 so that by K and Ca the difference of e-RSF from t-RSF is reduced from about a factor of 2 to only about 40%, and by Ge and As the curves have crossed and e-RSF is apparently smaller than t-RSF. The transition elements, Sc to Zn deviate strongly from a straight-line fit, as expected because of the strong satellite structure not included in the intensities measured. They are discussed separately in Sec. IV C.

The crossing point of the Wagner e-RSF and t-RSF curves is at ~700 eV, which is exactly what is expected if the difference in slopes is due to an incorrect T dependence on KE, normalized to the F1s BE energy at 685 eV. As in the 1s plot in Fig. 5, changing the T dependence used in deriving t-RSF from KE^{-1} to $KE^{-0.5}$ would bring the two curves essentially into agreement. Just as for the 1s BEs, modern experimental values of σ, extracted from e-RSF by removing the T and λ dependence, do not at all agree with the Wagner conclusions. Extracted values, using main line intensity only, indicates a 5%–25% discrepancy with the Scofield calculated σ values, with no particular trend,[23] and this may be reduced if satellite intensities are included. We conclude again that the apparent very large errors in Scofield calculated σ values claimed by Wagner *et al.* for 2p are incorrect and caused by an incorrect assumed T dependence on KE.

There is one aspect where there does appear to be major errors in the calculated σ values, however, and that concerns the 2p/2s ratios. Since the BEs of 2p and 2s are close together, neither T nor λ effects can make any significant difference to these ratios, so measured peak area ratios are directly comparable to the theoretical σ ratios. For Al, Si, and P, the measured ratios are close to the Scofield σ ratios, but they deviate substantially for S, Cl, K, and Ca. An example is shown in Fig. 8 for the Cl2p and 2s regions of NaCl.[16] The ratio of the 2p/2s peak intensities is 1.3 times greater than the Scofield σ ratios. This does not change significantly if the satellite intensity at ~20 eV loss is included, since it is roughly the same, relative to its parent line, for both 2p and 2s. We have no explanation for the discrepancy, which was actually suspected by Scofield[7] from the fragmentary XPS experimental data existing at that time, but note that it is unlikely to be caused by a differing angular term, ϕ, between 2p and 2s, because the current measurement was made fairly close to the magic angle of 54.7° (centered at 60° with an angular spread of ±8°).

C. 2p BEs of the transition elements Sc (21) to Zn (30)

The 2p levels are, again, the usual ones used for study and quantification of compounds of these transition metal elements. Many of these elements can exist in two or more different oxidation states, so the number of unpaired electrons in the valence 3d levels varies. The presence of unpaired electrons means there will be multiplet splitting of XPS peaks, which may be resolved (and in some cases spread over 20 eV in energy range), or simply broaden the "main" line. Variation in the number of unpaired electrons leads to variation in the multiplet splittings, both in positions and intensities. Though not directly related to this, variation in the number of unpaired valence electrons also results in variation in losses from "main" peaks to shake structure. Finally, since the spin–orbit split components, $2p_{3/2}$ and $2p_{1/2}$ are resolved but not separated by large energies, the multiplet components and satellites originating from one spin–orbit component can actually spread enough to overlap the other.

Cu^{2+} versus Cu^+ is the classic extreme example of variation in multiplet splitting and shakes with oxidation state, as shown in Fig. 3. Cu^{2+} has an open shell $3d^9$ configuration, leading to

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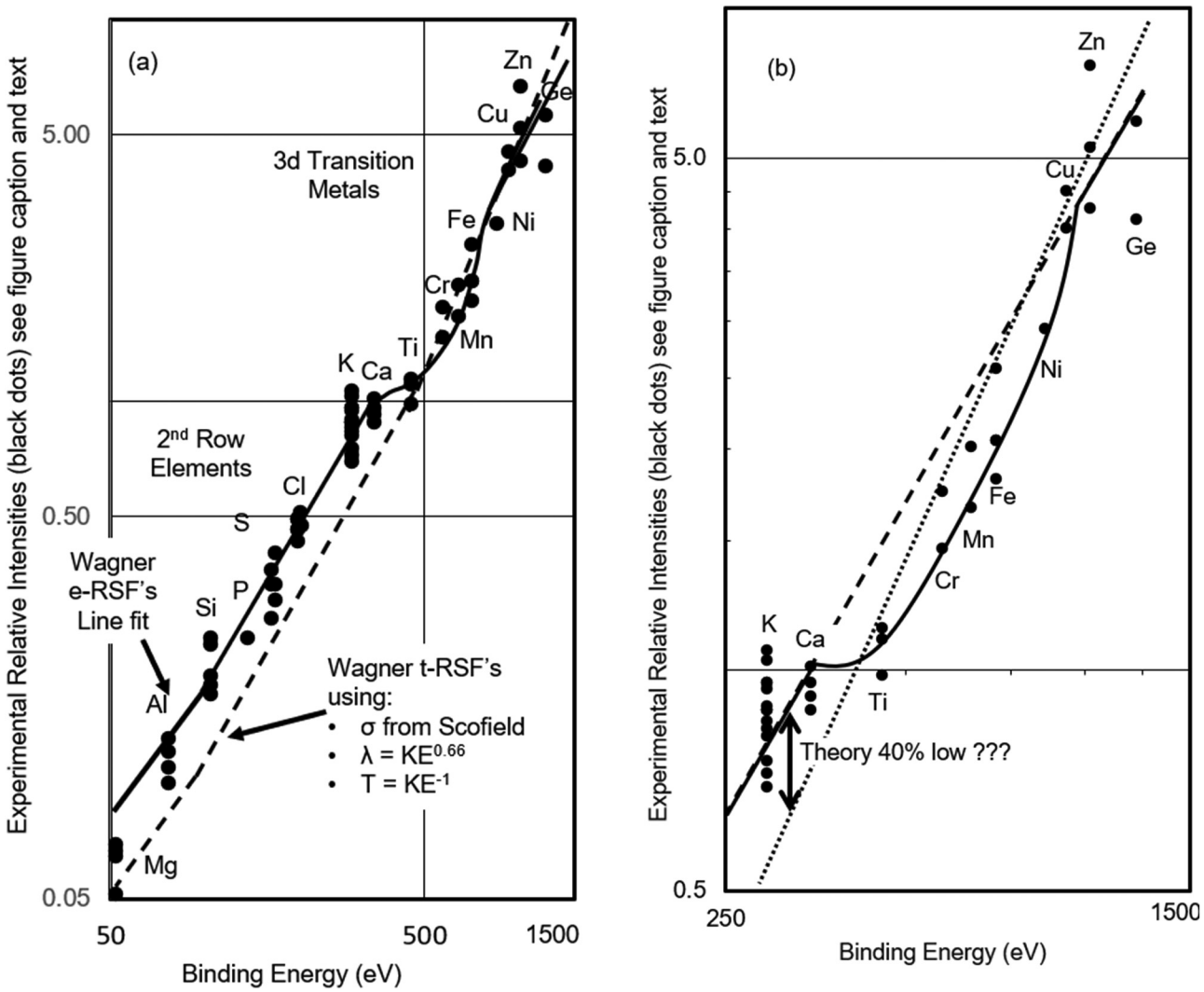

FIG. 7. (a) XPS experimental relative intensities (black dots) for the 2p levels of Mg through Ge using specific early XPS instrumentation (Ref. 20). The solid curve approximates the fit proposed in Ref. 20. e-RSFs quoted in Ref. 20 were taken directly from such a curve. t-RSFs (dotted line) were calculated using Scofield σ values and assuming $\lambda \propto KE^{0.66}$ and $T \propto KE^{-1}$. (b) Showing the transition element region of Fig. 7(a) in more detail. Some Nefedov values for the transition metals (Ref. 19) lie roughly on the dotted straight line joining the e-RSFs of Ca and Cu (see the text for discussion).

multiplet splitting effects, which, though not resolved, broaden the XPS "main" 2p lines, and also an unusually strong and *apparently* well-resolved shake satellite structure, as shown in Fig. 3(b) for CuO. Cu^+, on the other hand, has a closed $3d^{10}$ structure, meaning multiplet splitting is impossible so there is no broadening of the "main" lines, and very much weaker and differently positioned shake structure, as in Cu_2O [Fig. 3(c)]. Cu^{2+} and Cu^+ with different ligands (e.g., OH, F, etc.) will behave similarly *but not necessarily identically*.

Because in this particular 3d element case (Cu^{2+} and Cu^+) the shake structure *appears* to be well-separated from the main lines, a materials composition analyst might make one of two choices for quantification of Cu compounds in use of e-RSF values:

(1) Establish separate e-RSFs for Cu^{2+} and for Cu^+ using standard samples (maybe CuO and Cu_2O) using only the "main" $2p_{3/2}$ line only and then apply this to other Cu^{2+} and Cu^+ compounds.
(2) Establish an e-RSF by integrating the areas over the whole $Cu2p_{3/2,1/2}$ region, out as far as satellite structure is observed, and apply this to determine composition of other Cu compounds.

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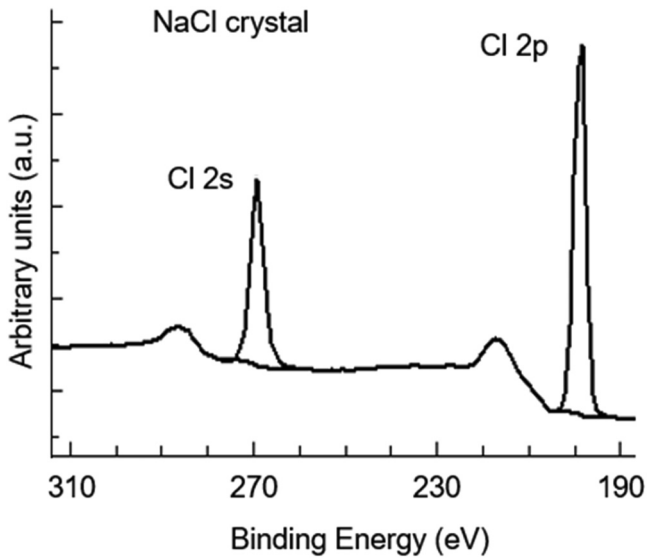

FIG. 8. Cl2s and 2p region of a single crystal of NaCl with Shirley type backgrounds drawn for the main peaks. Scofield σ normalized intensities give a ratio of 1.3 instead of the expected 1.0 (see the text).

The second approach is, in principle, going to be the more accurate, because it takes into account any changes in multiplet splitting and shake structure with change in ligand, and also because it is likely that the shake structure and main lines are *not really* completely separated (i.e., there is some genuine intrinsic intensity between them). It requires, however, taking data over a much larger energy range, which takes longer.

If, instead of using e-RSF values, one relies on the accuracy of the Scofield 2p σ value for Cu (which is not oxidation state dependent); for t-RSF, the analyst really has no choice but to integrate the Cu2p intensity over the whole region.

The large dip from a straight line for the e-RSF in the Wagner plot for the elements Ti to Ni in Fig. 7(b) is a direct consequence of excluding satellite intensity. The authors knew this but seemed to ascribe it to only multiplet splitting effects in paramagnetic materials. In reality, it is due to both multiplet and shake with shake effects being dominant in some cases. Because the S-O splitting is fairly small, ranging from ~6 eV for Ti to ~17 eV for Ni, and the shake and multiplet effects spread over this or greater range, it is generally not realistic, unlike the Cu examples, to try and separate out "main" line only intensities to establish e-RSFs and integration over the whole 2p region must be used for best accuracy.

Nefedov *et al.*[19] also reported results (but not actual spectra) for these transition elements. Though they did not state which compounds were used, they did claim to have taken into account satellite intensities in deriving their values of experimental σ. Their values fall roughly on the dotted line between Ca and Cu in Fig. 7(b), as would be expected if satellite intensity were included.

An example of the futility of trying to separate just the $2p_{3/2}$ "main" peak intensity in some cases is given for the well-studied case of Fe_2O_3,[12,24–27] for which a partial survey scan is shown in Fig. 9(a), and a higher resolution Fe2p spectrum in Fig. 4(b), for a single crystal sample of hematite.[16] Clearly, as pointed out by Bravo-Sanchez *et al*,[12] trying to fit any type of background to just the $2p_{3/2}$ region will result in the removal of a significant amount of genuine intrinsic signal, making nonsense of any stoichiometry determination. With the background (Shirley type) subtracted in the manner shown in Fig. 9(a), and with the specific start end points shown, an experimental σ value of ~14.5 for Fe2p can be extracted from e-RSF determined by ratioing the total Fe2p intensity to that of O1s (backgrounds as drawn). This is ~12% lower than the Scofield σ value of 16.4. However, the necessity of integrating over the large energy range for Fe2p, with structure throughout it, exacerbates the problem of appropriate background subtraction. The end point is somewhat arbitrary. Here, and in some publications, it is chosen to be where we have placed it in Fig. 9(a), because there is a small peak at ~743 eV, which is considered to be a shake component, and we want to include that. In other studies, authors have picked the end point to be ~728 eV,[27] excluding this peak. This, of course, makes a difference, and the degree of difference actually depends a lot on what version of Shirley background (traditional, iterated, "active") is used. A traditional, noniterated, Shirley background *cannot be extended beyond the point where the total signal starts to decline without assuming a component of genuine intrinsic signal exists in the declining region.* An iterated Shirley background[10] requires a few points of flat background at the end point to correctly finish, which is why ~728 eV is sometimes chosen as the signal there passes through a brief flat region. The "active" approach[12] involves, among other things, the possibility of adding a downward sloping background at some point. This is, however, also arbitrary and in essence is saying "*I know it is all background from here on, with no intrinsic signal.*" This might be correct but is an arbitrary assumption. The current authors believe, but cannot prove, that there *may be* intrinsic signal contribution beyond 743 eV in Fig. 9(a), based on the fact that the downward slope of the signal is much larger than would be expected for just extrinsic background (e.g., compare to after the O1s peak). Also, in the spectrum of Fe metal, there is a slight, but clear, break in the slope at ~760 eV in the MgK_α recorded spectrum,[28] which may indicate the true end of the Fe2p signal. This region is masked using an AlK_α x-ray source because of the start of the overlapping Fe Auger signal.

There is yet an additional catch if wanting to use Scofield cross sections for the analysis. A careful examination of the O1s signal at high resolution, [Fig. 9(b)], reveals there is considerable intensity in structure spreading over a 70 eV range beyond the main peak (though most of the intensity is within 30 eV). In the compositional analysis, one is comparing intensities of Fe2p to O1s. If one uses Scofield σ values for quantification and includes shake intensity for Fe2p, then the shake intensity for O1s should surely be included also. The fractional intensity in the structure after the main O1s is about 35% of the total, as determined by an iterated Shirley Background fit.[29] If all this is shake, excluding it, while including the satellite structure in the Fe2p (unavoidable), would result in a 35% error in stoichiometry determination! Of course, we do not know how much of this structure represents genuine shake structure. The peaks are broad and flat and some of it may well be extrinsic structure. Given this complication, a

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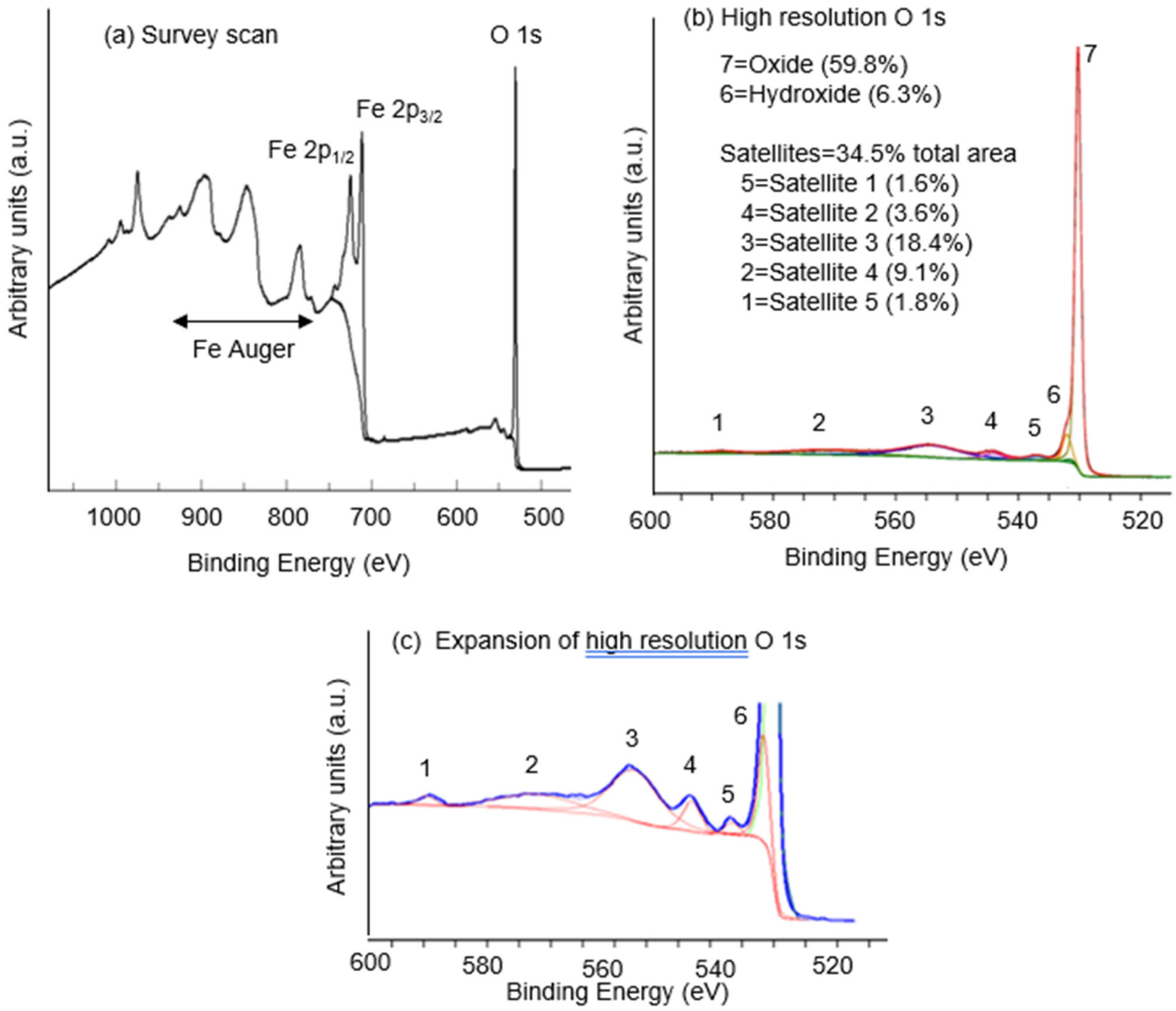

FIG. 9. (a) Survey spectrum of single crystal hematite, Fe_2O_3. Shirley backgrounds with start and end points as shown. (b) High-resolution spectrum of O1s of the hematite sample with fully iterated Shirley background (Ref. 29) extended to cover all observable satellites. (c) Vertical expansion of Fig. 9(b).

claimed accuracy for a Fe_2O_3 analysis of $Fe_{2.00+/-0.05}O_3$ done by including all Fe2p satellite structure, but without including any O1s satellite structure, is surprising.[12]

D. Rest of the periodic table

The discussion above, concerning the spectral distribution of intrinsic signal for the 3d transition metal elements, is valid also for the elements Y(39) to Pd(46) (4d valence electrons) and La(57) to Pt (78) (5d valence electrons). The Lanthanides, Ce(58) to Lu(71), and Th(90) and U(92) are even more complex because of the potential involvement of 4f and 5f open valence shells. An extreme example, the 3d spectrum of Ce^{4+} in CeO_2, is given in Fig. 10.[16] The assignment of the peaks, as marked, to the 3d spin–orbit components and related shake satellites,[25] has not been verified by any theory but is very plausible. The percentage of intensity in shake structure is much more intense than that in the "main" peaks. From a theory point of view, this means that the one electron picture of photoemission has *completely broken down*. So far it has not been possible to come very close to describing the spectrum from *ab initio* cluster calculations, even when including significant many body interaction terms by configuration interaction in the final state,[30] but they do agree with experiment in that there is far more intensity lost to satellite structure than there is in the "main" lines. From a quantitative analysis point

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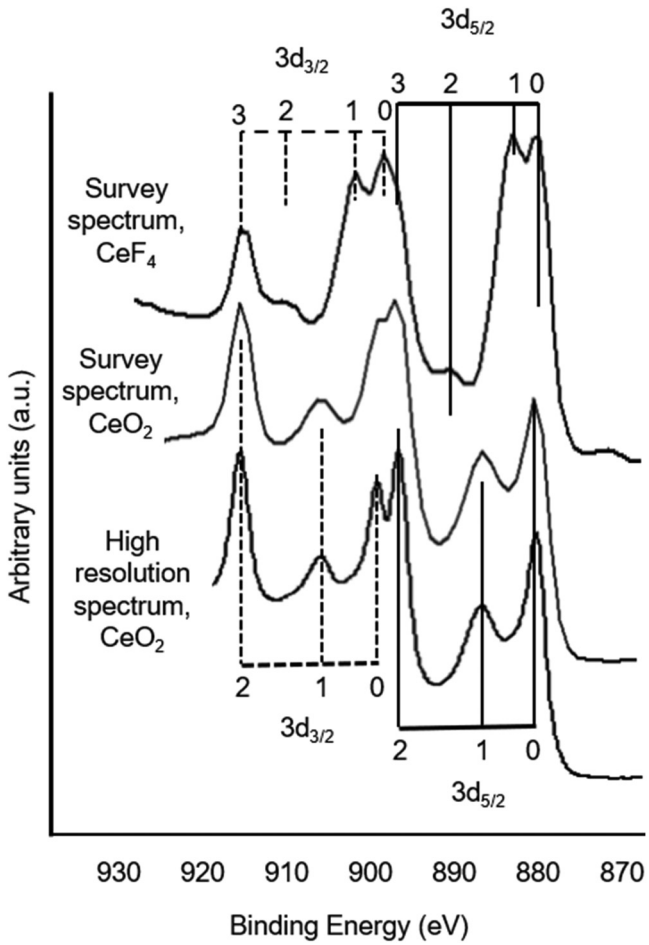

FIG. 10. Ce3d XPS spectrum of CeO_2 and CeF_4. Spin–orbit and satellite assignments as proposed in (Ref. 25).

of view, the intensity over the whole Ce3d spectrum *must be used*. Though, from just looking at CeO_2 in Fig. 10, it might seem feasible to just use the leading peak to provide an e-RSF, we know this is not the case, because changing the ligand from O to F, (CeF_4), results in large changes in relative intensities throughout the whole spectrum, as can be seen in Fig. 10.

Of course, there is much of the periodic table that we have not discussed at all: the heavier elements in groups IA and IIA and the heavier elements in groups IIIA–VIIA. These all have closed valence shell structures, so there are no multiplet splitting effects. The problem of potentially significant shake intensity remains, however, and it is also likely that the Scofield σ values are less accurate than for the lighter elements.

V. SUMMARY

We have reviewed two approaches, e-RSF and t-RSF, used for quantification in XPS using relative peak intensities. The original goal of one of the authors (C.R.B) was simply to try and establish whether there was justification to the Wagner *et al.* claim[20] that Scofield's calculated σ values[7] were seriously in error. Our conclusion is that for the first row elements they are not and the reason for the reported discrepancy was a combination of not including satellite intensities when necessary in e-RSF, and a wrong transmission function, T, value when deriving σ from t-RSF, plus in the specific case of Li in LiF the necessity of removing overlapping F2s satellite intensity from the Li1s spectrum. We believe the calculated Scofield σ values for the 1s level of the first row elements are accurate to ±5% as claimed by Scofield. So, if an analyst's work involves only these elements (e.g., much polymer and biomaterials work, and a few ceramics) using Scofield σ values will not cause greater errors than this 5%. Background subtraction and satellite structure are not major issues either for such material except for the unique case of LiF. However, if structure identifiable as shake is present, it improves accuracy by including it (e.g., the well-known π to π* shake of C1s for aromatic compounds[3].

For nontransition elements. where the 2p BEs peaks are usually used for quantification (Na to As), there is also no evidence of huge discrepancies in σ, but for some of the elements, P to Ca, it seems certain that the calculated 2p/2s ratio *is* in significant error, with 2p being perhaps up to 15% high and 2s up to 15% low, suggesting some mechanism that transfers intensity from 2s to 2p, or large differences in satellite intensity that are lost in the scattered electron background.

For the elements later in the periodic table with d or f valence shells, quantification accuracy is likely to be much poorer in situations where d or f valence shells are open, leading to large multiplet splitting and shake effects. These effects can vary considerably with oxidation state (variation of the number of unpaired valence electrons) and also significantly with ligand (variation of covalency), but there is no strong evidence that Scofield values are hugely in error. Owing to the variation in multiplet and shake intensities and positions, accuracy in quantification is severely limited if attempts are made to use only the "main" line part of the spectrum and a generic e-RSF for that element. Intensity generally spreads over the whole 2p region and well beyond and it is necessary to integrate intensity over the whole region to improve accuracy. This, however, increases the effect, on measured intensities, of variability in background subtraction using different procedures.

For elements where open f shells are involved (lanthanides and actinides), the one electron approximation of photoemission becomes untenable in some cases (e.g., Ce). Shake effects can become so large that the "main" line is no longer that—satellite intensity swamps it, and also can vary a lot with change in ligand. Quantification requires integration across the whole spectral region. There is not enough data available to evaluate Scofield cross-sectional inaccuracies, but it is reasonable to suspect they are significantly worse than for the first row elements.

VI. SUGGESTED PROTOCOLS FOR RAPID XPS ANALYSIS AIMED AT QUANTIFYING ELEMENTAL COMPOSITION

Finally, some brief comments concerning the practical analyst's dilemma to quantitation—"*do I have time to do the job*

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thoroughly or can I get the desired level of accuracy in a fraction of the time by a restricted default approach that uses RSF's." We certainly do not advocate making "perfect" the enemy of "good enough," but, of course, "good enough" should be defined and agreed upon by analyst and customer before the measurement is made. In the experience of one of the authors (C.R.B.), it is not unusual for a customer to ask for accuracy well beyond what he/she can justify needing, but at least that is a better starting point than just "please analyze this."

The goal of the other author (B.V.C.) is to provide an analysis procedure which a typical "in the trenches" analyst can live with and still generate reliable quantitation. Given that the effects of background subtraction, and the uncertainties of changing multiplet and shake structure with chemistry, are not generically well documented across the periodic table, even a close to perfect job in collecting the data, involving much individual input per analysis, is not going to guarantee a high level of accuracy in stoichiometry, except for the first row compounds (where it might be ±5% or better). For compounds where open d or f shells are involved, there is probably *no advantage in going beyond a properly set up low energy resolution survey spectrum* (enough points per eV; enough S/N statistics) for a stoichiometry analysis of the bulk of a homogeneous material. In any case, a survey spectrum should always be the default first step (and repeated as the last to see if anything has changed during the analysis). This will require defining the start and end points of the background fits to the peaks being used for quantitation in the survey and being consistent in this for the XPS level being considered. Of course, if detailed information relating to chemistry is required, that is entirely another matter and high energy resolution scans are required over whatever energy range encompasses the main signal and satellites that may carry chemical state information on that element.

If the analyst chooses not to go beyond the survey spectrum for quantitation by measuring key XPS peaks at higher energy resolution, then *the spectral range actually used to integrate peak intensities should not be limited to the conventional 20 or 30 eV for each element, but rather should be great enough to capture any significant satellite structure.* This range will vary, but could be as much as 80 eV, as in Fig. 9(b), for O1s. The survey spectrum in Fig. 9(a) was acquired using a 200 eV pass energy, with only 1 point per eV, and took <3 min. *Acquiring just high energy resolution scans of Fe2p and O1s, generating the same S/N statistics, over the 80 eV wide range needed, takes ∼10 times longer, and does not significantly change the ratio determined Fe/O stoichiometry.*

Changing the end point of the background subtraction and/or the method of subtraction (Shirley, Tougaard, or modifications of either) may produce more significant variation in determined composition. Again, it is important to be consistent in the approach to background subtraction for the peaks being ratioed.

For a sample of *unknown* Fe/O composition and chemistry using this default survey spectrum approach, combined e-RSFs measured the same way on appropriate pure standards (e.g., Fe_2O_3, hematite crystal) is recommended. Using e-RSFs established for different oxidation state standards (in this case, Fe^0, Fe^{2+} and Fe^{3+}) will improve accuracy if differing fractions of the total photoemission are captured in the defined energy range, which, generally is going to be hard to know *a priori*. If standards are not available and t-RSFs based on Scofield σ values are used, then all significant satellites should be included in the measured intensities.

In the supplementary material, we provide a suggested protocol for establishing a procedure of measurement that will return a correct stoichiometry, using Scofield σ values, for chemical compounds (standards) of known composition, but remember, this is somewhat arbitrary in nature, relying on adjustment of start- and endpoints and the method of background subtraction. Once these have been established for the standard, the protocol can then be used for the unknown containing the same element. We are currently testing this approach for robustness for transition metal compounds.[31]

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REFERENCES

[1]K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, and T. Bergmark, *Nova Acta Regiae Societatis Scientiarum Upsaliensis, Series IV* (Almqvist and Wiksells, Stockholm, 1967), Vol. 20.
[2]C. R. Brundle, J. Vac. Sci. Technol. **11**, 212 (1974).
[3]B. D. Ratner and D. G. Castner, *Electron Spectroscopy for Chemical Analysis, Surface Analysis—The Principal Techniques*, 2nd ed., edited by J. C. Vickerman and I. Gilmore (Wiley, Chichester, 2009), pp. 47–112.
[4]T. J. Chuang, C. R. Brundle, and D. W. Rice, Surf. Sci. **59**, 413 (1976).
[5]T. Nagatomi and T. Kazuhiro, "Status of depth profiling in XPS" (unpublished); D. Eaton, C. Kinnear, S. L. McArthur, and T. R. Gengenbach, J. Vac. Sci. Technol. A **38**, 023207 (2020).
[6]C. R. Brundle, "X-ray photoelectron spectroscopy," in *Encyclopedia of Materials Characterization*, edited by C. R. Brundle, C. A. Evans, and S. Wilson (Butterworth-Heineman, Boston, 1992); R. F. Roberts, *J. Electron Spectrosc. Relat. Phenom.* 4, 273 (1974).
[7]J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8**, 129 (1976).
[8]C. J. Powell, J. Vac. Sci. Technol. A **38**, 023209 (2020).
[9]J. F. Watts and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES* (Wiley, New York, 2003).
[10]D. Shirley, Phys. Rev. B. **5**, 4709 (1972); A. Proctor and P. Sherwood, Anal. Chem. **54**, 13, (1982).
[11]S. Tougaard, Surf. Interface Anal. **25**, 137 (1997).
[12]M. Bravo-Sanchez, J. A. Huerta-Ruelas, D. Cabrera-Germana, and A. Herrera-Gomez, Surf. Interface Anal. **49**, 253 (2017).
[13]C. J. Powell and J. M. Conny, Surf. Interface Anal. **41**, 269 (2009).
[14]C. S. Fadley, *Electron Spectroscopy, Theory, Techniques, and Applications*, edited by C. R. Brundle and A. D. Baker (Academic, London, 1978), Vol. 2.
[15]P. S. Bagus, E. S. Ilton, and C. J. Nelin, Surf. Sci. Rep. **68**, 273 (2013).
[16]B. V. Crist, see https://xpsdata.com (accessed 16 December 2019).
[17]K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* (North Holland, Amsterdam, 1969).
[18]P. S. Bagus, C. J. Nelin, C. R. Brundle, N. Lahiri, E. S. Ilton, and K. M. Rosso, J. Chem. Phys. **152**, 014704 (2020).
[19]V. I. Nefedov, N. P. Serguishin, I. M. Band, and Trzhaskovskaya, J. Electron Spectrosc. Relat. Phenom. **2**, 383 (1973); V. I. Nefedov, N. P. Serguishin,

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Y. V. Salyn, I. M. Band, and M. B. Trzhaskovskaya, J. Electron Spectrosc. Relat. Phenom. **7**, 175 (1975).
[20]C. D. Wagner, L. E. Davis, M. V. Zeller, A. J. Taylor, R. H. Raymond, and L. H. Gayle, Surf. Interface Anal. **3**, 211 (1981).
[21]J. J. Yeh and I. Lindau, Atom. Data Nucl. Data Tables **32**, 1 (1985).
[22]P. S. Bagus, private communication (August 15, 2019).
[23]B. V. Crist, "σ Values, Website," see https://xpslibrary.com/crist-empirical-rsfs-scofield-base/https://xpsdata.com; accessed 16 December 2019; "Thermo σ Values," see https://xpslibrary.com/crist-empirical-rsfs-scofield-base/https://xpsdata.com; accessed 16 December 2019.
[24]C. R. Brundle, T. J. Chuang, and K. Wandelt, Surf. Sci. **68**, 459 (1978).
[25]N. Pauly, F. Yubero, J. P. Espinos, and S. Tougaard, Surf. Interface Anal. **51**, 353 (2019).
[26]M. Aronniemi, J. Sainio, and J. Lahtinen, Surf. Sci. **578**, 108 (2005).
[27]T. Doubray and S. A. Chambers, Phys. Rev. B **64**, 205414 (2001).
[28]J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Physical Electronics, Eden Prairie, 1992).
[29]Peter Sherwood, private communication (October 14, 2019).
[30]C. J. Nelin, P. S. Bagus, E. S. Ilton, S. A. Chambers, H. Kuhlenbeck, and H. J. Freund, Int. J. Quant. Chem. **110**, 2752 (2010).
[31]See the supplementary material at http://dx.doi.org/10.1116/1.5143897 for the above mentioned protocol.

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