

RESEARCH ARTICLE

Measurement of the surface excitation parameter of Kapton, polyethylene (PE), polymethyl methacrylate (PMMA), polystyrene (PS) and polytetrafluoroethylene (PTFE)

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Reflection electron energy loss spectra (REELS) were measured for five insulating organic compounds: Kapton, polyethylene (PE), poly(methyl methacrylate) (PMMA), polystyrene (PS) and polytetrafluoroethylene (PTFE), as well as for Ni and Si, in the energy range between 200 and 1600 eV. The average number of surface excitations for a single surface crossing were determined from the experimental data and were found to be considerably smaller than for earlier studied materials, which mainly consisted of elemental metals [Surf. Sci. 486(2001)L461]. The surface excitation parameter, a material parameter used to quantify the relative intensity of surface losses in (photo)electron spectroscopy, was extracted from the data and compared with values found in the literature. The results indicate that surface excitations only have a minor influence on quantification of XPS spectra of polymers. On the other hand, a correction for surface excitations turns out to be essential for measurements of the electron inelastic mean free path of polymers when a metal is used as reference material.

KEYWORDS

Kapton, Ni, organic polymers, polyethylene, polymethylmetacrylate, polystyrene, polytetrafluoroethylene, reflection electron energy loss spectroscopy, Si, surface excitation parameter, surface plasmon

1 | INTRODUCTION

The modern field of plasmonics¹ essentially goes back to the theoretical prediction by Ritchie² that oscillations of the weakly bound solid state electrons can propagate along boundaries of media with different dielectric constant. Powell and Swan^{3,4} observed surface excitations in the loss spectra of aluminium and magnesium in addition to the bulk excitations that had been observed previously. The corresponding quasiparticles are nowadays commonly referred to as surface plasmons and bulk plasmons, respectively.

Surface excitations are also distinctly important for surface analysis with electron spectroscopy. Obtaining optical constants from

reflection electron energy loss spectroscopy requires a diligent treatment of surface excitations.⁵⁻⁷ A sound understanding of surface excitations is also important for accurate quantitative interpretation of electron spectra⁸ and for measurement of the electron inelastic mean free path (IMFP) in solids using the absolute intensity of the elastic peak, so-called elastic peak electron spectroscopy (EPES).^{9,10} Furthermore, it was found^{11,12} that surface excitations induced while the primary electron is in vacuum contribute significantly to the secondary electron yield. Finally, Werner et al.¹³ explicitly demonstrated the in vacuo-excitation of inelastic processes for electron reflection.

A substantial number of theoretical studies of this phenomenon can be found in the literature.¹⁴⁻²² Experimental results on the

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surface excitation probability for non-nearly free electron (NFE) materials are still rare. While comprehensive data sets have been measured for metals,²³ for polymers only a few data are available.^{24,25} In the present work, experimental results for the surface excitation probability (SEP), extracted from reflection electron loss spectra (REELS) for energies between 200 and 1600 eV, are presented for selected organic polymers: Kapton, polyethylene (PE), poly(methyl methacrylate) (PMMA), polystyrene (PS) and polytetrafluoroethylene (PTFE). Measurements were also performed on a Ni and a Si sample for comparison with earlier results. The surface excitation parameter, a material parameter used to quantify the relative intensity of surface losses in (photo-) electron spectroscopy, is extracted from the data and compared with values found in the literature.

2 | THEORETICAL

A measured reflection energy loss spectrum contains groups of electrons that have participated in n_b bulk and n_s surface excitations. The energy loss distribution $L_{n_b, n_s}(\Delta E)$ of each group is given by a multiple convolution of the (normalised) differential probability for an energy loss ΔE in an individual bulk, $w_b(\Delta E)$, and surface, $w_s(\Delta E)$, excitation.^{26,27} The latter quantities are known as the normalised differential inverse inelastic mean free path (DIIMFP) and differential surface excitation probability (DSEP), respectively. Convoluting with the source energy distribution $f(E)$ and weighting each group with the number of electrons within each group, the so-called partial intensities C_{n_b, n_s} , one obtains the following expression for the measured loss spectrum:

$$Y(E) = \sum_{n_b=0}^{\infty} \sum_{n_s=0}^{\infty} C_{n_b, n_s} L_{n_b, n_s}(\Delta E) \otimes f(E + \Delta E), \quad (1)$$

where the symbol \otimes denotes an energy convolution and the term with $n_b = 0, n_s = 0$ corresponds to the elastic peak. Consequently, the zero order partial intensity $C_{n_b=0, n_s=0}$ represents the elastic peak intensity. The measured spectra are commonly transformed to an energy loss scale and divided by the elastic peak area, to obtain the (reduced) loss spectrum (in *absolute* units of reciprocal eV). After elimination of the elastic peak the reduced loss spectrum assumes the form:

$$y(\Delta E) = \sum_{n_b=1}^N \sum_{n_s=1}^N \gamma_{n_b, n_s} L_{n_b, n_s}(\Delta E), \quad (2)$$

where the maximum collision order considered is denoted by N ($N = 2 - 3$ in the present work; see Figure 1 below), and the *reduced* partial intensities are now given by

$$\gamma_{n_b, n_s} = \frac{C_{n_b, n_s}}{C_{n_b=0, n_s=0}}. \quad (3)$$

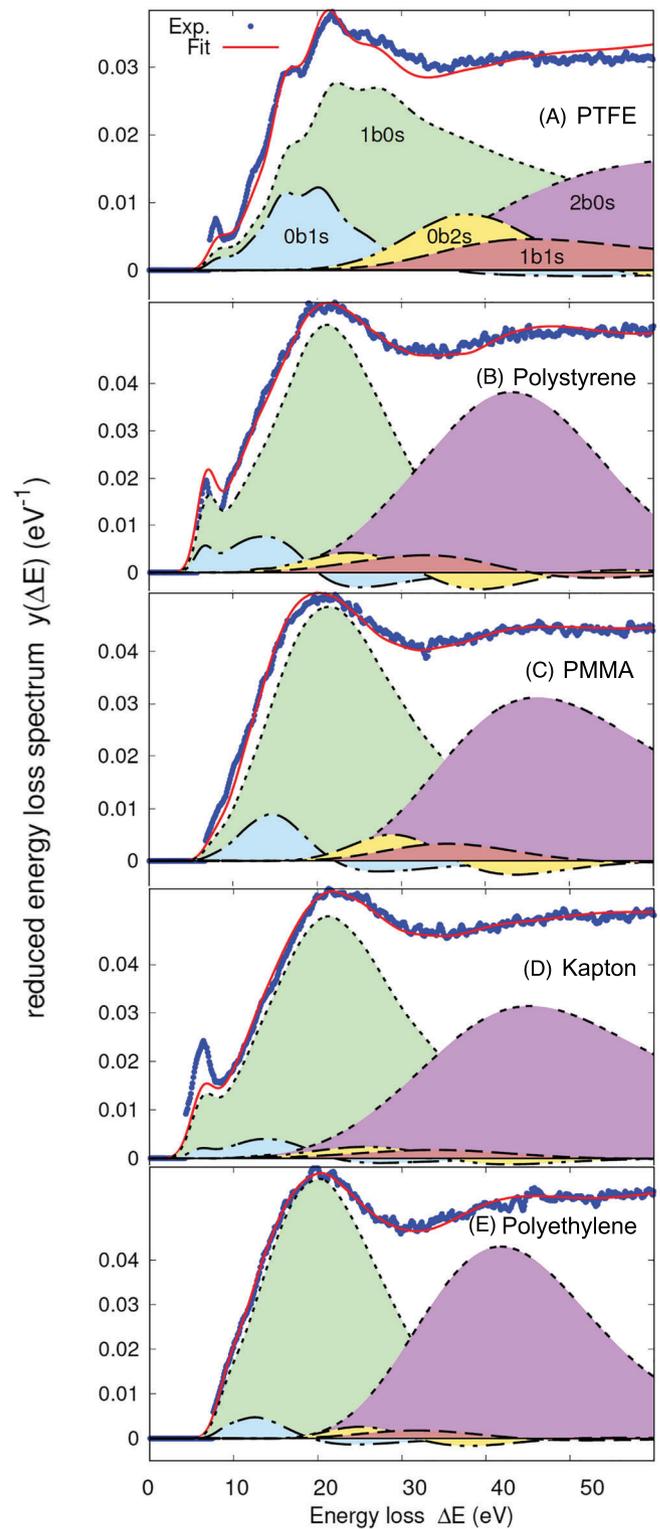


FIGURE 1 Experimental reduced energy loss spectra for PTFE (A), polystyrene (B), PMMA (C), Kapton (D) and PE (E) for a primary energy of $E_0 = 1200$ eV (blue datapoints). The red curves represent a fit to Equation (2) using $\langle \mu_s^{tot} \rangle$ as a free parameter. The filled curves indicate the contributions to the spectrum of electrons which have experienced, respectively, one bulk excitation (curve labelled “1b0s,” green), one surface excitation (curve labelled “0b1s,” light blue), one bulk and one surface excitation (curve labelled “1b1s,” brown), etc

Because the partial loss distributions are normalised to unity area, the reduced partial intensities represent the relative number of electrons in the group of any given collision order (n_b , n_s).

The depth range ($\langle z_{ss} \rangle$) (at either side of the solid-vacuum interface) in which surface excitations occur is small compared with the transport mean free path. Therefore, the trajectories of electrons in the surface scattering zone are rectilinear to a good approximation. This has two important consequences²⁸: First of all, it implies that the partial intensities for surface and bulk scattering are uncorrelated:

$$C_{n_b, n_s} = C_{n_b} \times C_{n_s}. \quad (4)$$

Second, because the partial intensities are related to the distribution of pathlengths $Q(s)$ travelled by the signal electrons via

$$C_n = \int_0^\infty Q(s) P_n(s) ds, \quad (5)$$

where $P_n(s)$ is the Poisson stochastic process, it follows that for a pathlength distribution of the form $\delta(s - \langle z_{ss} \rangle)$, the number of electrons having experienced multiple surface excitations $C_{n_s}(\theta, E)$ is described by

$$C_{n_s}(\theta, E) = \langle \mu_s(\theta, E) \rangle^{n_s} \frac{\exp(-\langle \mu_s(\theta, E) \rangle)}{n_s!}. \quad (6)$$

In this expression, $\langle \mu_s(\theta, E) \rangle$ is the average number of surface excitations for an electron with kinetic energy E , for a single surface crossing under an angle θ relative to the surface normal. Taking into account the above, it is seen that in the reduced loss spectrum, the contribution of electrons that have suffered n_s surface excitations is given by

$$\gamma_{n_s} = \frac{\langle \mu_s \rangle^{n_s}}{n_s!}. \quad (7)$$

In particular, the contribution of single surface scattering to the reduced yield, $\gamma_{n_s=1}$, exactly equals the average number of surface excitations for the considered geometry $\langle \mu_s^{tot} \rangle = \langle \mu_s^{in} \rangle + \langle \mu_s^{out} \rangle$

A convenient formula describing the dependence of the average number of surface excitations on the energy and surface crossing direction in terms of a single material parameter, a_s , the so-called surface excitation parameter, has been given earlier by Oswald^{20,23}:

$$\langle \mu_s(\theta, E) \rangle = \frac{1}{a_s \sqrt{E} \cos \theta + 1}. \quad (8)$$

An alternative to Equation (8) has been proposed by Chen²⁹ and is also in common use.

3 | EXPERIMENTAL

The following organic compounds were investigated in this study: (1) a sample of Kapton foil ($[\text{C}_{22}\text{N}_2\text{O}_5\text{H}_{10}]_n$), (2) a roughly 1.5 mm thick sample of low-density polyethylene (PE, $[\text{C}_2\text{H}_4]_n$), (3) a film of poly(methyl methacrylate) (PMMA, $[\text{C}_5\text{O}_2\text{H}_8]_n$) spin cast on a piece of a Si-wafer, (4) a fragment of a polystyrene cuvette (PS, $[\text{C}_8\text{H}_8]_n$) and (5) a piece of polytetrafluoroethylene foil (PTFE, $[\text{C}_2\text{F}_4]_n$). In addition, a piece of an n -doped silicon-wafer and a thin (≈ 50 nm) Ni-film sputtered on a Si-wafer were measured to check consistency with earlier work.²³

The samples of Kapton, PE, PS, PTFE, Ni and Si were cleaned by ultrasonication in p.a. grade ethanol immediately prior to introduction into the vacuum. The PMMA sample was blown clean with helium and otherwise measured as received. The Si and Ni samples were sputter cleaned with 4-keV Ar⁺ ions until the Auger spectra were void of oxygen and carbon contamination. During sputtering, the samples were continuously rotated to minimise roughening of the surface.

The REELS spectra were acquired under UHV conditions in a modified VG ESCALAB MkII spectrometer equipped with a hemispherical mirror analyser with five channeltrons operated at a pass energy of 20 eV. For each of the channeltrons, the deadtime was measured to be about 250 ns. A Kimball Physics ELG-2 electron gun was used as a primary electron source. The electron current was measured with the Faraday cup built on to the electron source to be about 0.7 nA for all energies. Count rates during the experiments were below 2×10^6 Hz. The angles of incidence and emission amounted to 60° , relative to the surface normal. The sample height was carefully adjusted for each sample individually by maximising the elastic peak intensity in the measurement position. The pressure in the analysis chamber during the measurement did not exceed 2×10^{-10} mbar. REELS spectra were measured for energies of 200, 300, 500, 700, 1000, 1200, 1500 and 1600 eV. For mitigation of charging, the procedure in Ridzel et al³⁰ was followed.

4 | DATA ANALYSIS

The experimental REELS were converted to energy loss spectra by fitting the elastic peak to a Gaussian, converting to energy loss scale and dividing the spectrum by the area of the elastic peak, giving the loss spectrum in absolute units of reciprocal eV. The experimental spectra were then fitted to Equation (2). The only free parameter in the optimisation procedure is the average number of surface excitations corresponding to the experimental geometry, $\langle \mu_s^{tot} \rangle = \langle \mu_s^{in} \rangle + \langle \mu_s^{out} \rangle$. The fitting was performed by calculating the surface and bulk single scattering distributions as described in Werner et al²³ and Ridzel et al³⁰ using sets of Drude-oscillators for the dielectric function, which were recently published.³⁰ These

oscillators do not always perfectly describe the sharpness of certain peaks (such as the π -plasmon peak at ≈ 6 eV), leading to minor discrepancies between the fit and the data shown in Figure 1 below. The reduced bulk partial intensities γ_{nb}^{MC} were established by means of Monte Carlo calculations.³¹ The input parameters for the calculation of these quantities are the differential cross section for elastic scattering, calculated using the ELSEPA software,³² and the electron inelastic mean free path (IMFP), which was obtained from the TPP-2M formula.³³ While the absolute partial intensities are very sensitive to the value of the IMFP, the *reduced* partial intensities are only marginally affected by a variation of the IMFP since the pathlength distribution for electron reflection is much broader than the IMFP.⁵ To account for a minor statistical error in the elastic peak area determination of the experimental spectra, the value of the reduced bulk partial intensities was allowed to vary within $\pm 5\%$ to improve the quality of the fit. For energies of 200 and 300 eV and for any material, the measured reduced loss spectrum did not agree with Equation (2) within this error margin, while for higher energies, Equation (2) predicts the correct absolute intensity to within the 5%-error margin. This indicates that the simple model for REELS is only qualitatively correct for energies below 500 eV, while for higher energies, quantitative agreement is observed. The reason for the discrepancies below 500 eV is not clear at present. The measurements at lower energies are therefore disregarded in the following.

An example of the above procedure is shown in Figure 1 for the spectra of PTFE, Kapton and PE taken at 1200 eV. Note that this kinetic energy approximately corresponds to the C1s-peak in Al-K α -excited photoelectron spectra. The blue datapoints represent the experimental data after conversion of the REELS into the absolute loss spectrum, the red curves are the resulting fit. The curves labelled “1b0s; and “0b1s” represent the contribution of single scattering in a bulk or surface excitation, the higher order partial loss distributions are given by the curves labelled accordingly. Their shape is given by the corresponding (multiple) self- and cross-convolutions of the DIIMFP and DSEP.^{23,31} The slightly negative values of the surface excitation contributions are a consequence of the coupling of the bulk and surface modes, a well-known effect commonly referred to as “*Begrenzungs*”-effect.³⁴ Note again that by dividing the spectrum by the elastic peak intensity, the area under individual curves is equal to the corresponding *reduced* partial intensity $\gamma_{nb,n_s} = C_{nb,n_s}/C_{nb=0,n_s=0}$. Therefore, the area under the curve labelled “0b1s” is equal to $\langle \mu_s^{tot} \rangle$ (see Equations 2 and 7).

Comparison of the experimental spectra (blue datapoints) with the contribution of single bulk scattering (“1b0s,” green area) immediately makes it clear that the contribution of surface excitations (“0b1s,” blue) is small compared with the contribution of single volume scattering. This is in contrast to the case of metals where the contribution of the first order volume and surface excitations are of the same order of magnitude and the contribution of surface excitations is visible with the bare eye in the raw experimental REELS (see, e.g., Werner et al.^{5,23}).

5 | RESULTS AND DISCUSSION

The result of the procedure outlined in the previous section is summarised for PTFE, PMMA and Kapton as well as for Ni and Si in Figure 2, which displays the value of $\langle \mu_s^{tot} \rangle$ as a function of the energy (data points). The solid curves are a least square fit of these data to Equation (8) for $\theta_{in} = \theta_{out} = 60^\circ$ using a_s as a free parameter. For comparison, the earlier results²³ for Si and Ni are given in the figure as dashed curves. Good agreement with the earlier values is obtained in spite of the fact that these were obtained about 20 years ago on different samples and measured on a different instrument with a different scattering geometry.

The resulting values of a_s for the investigated materials are given in Table 1. The average number of surface excitations for the

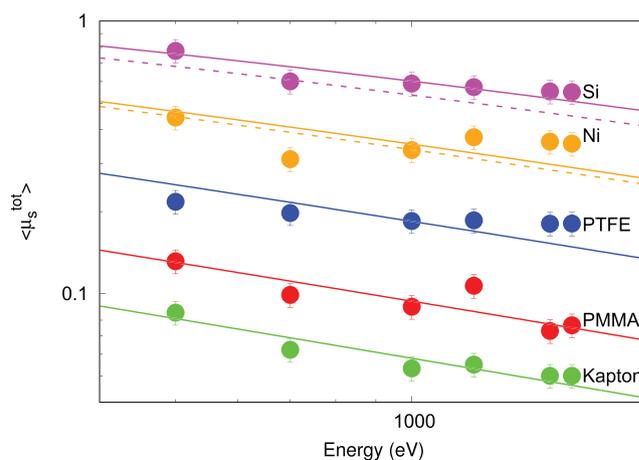


FIGURE 2 Average number of surface excitations $\langle \mu_s^{tot} \rangle = \langle \mu_s^{in} \rangle + \langle \mu_s^{out} \rangle$ as a function of the energy for PTFE (blue data points), PMMA (red), Kapton (green), Si (magenta) and Ni (orange) displayed together with a fit to Oswald's formula Equation (8). For comparison, the results for Si and Ni found in an earlier work²³ are also shown as dashed curves

TABLE 1 Material parameters used in the present work: average atomic number Z_{av} , mass densities ρ , atomic densities N_a , valence electron densities N_v were taken from the literature, while the surface excitation parameter a_s established in the present work is presented in units of $a_{NFE} = 0.173 \text{ eV}^{-1/2}$

	Z_{av}	ρ g/cm^3	N_a \AA^{-3}	N_v \AA^{-3}	a_s/a_{NFE}	a_s/a_{NFE} literature
PE	2.7	0.94	0.121	0.242	13.4(0.8)	1.25 ²⁴
Kapton	5.0	1.42	0.087	0.309	12.2(0.4)	-
PMMA	3.6	1.18	0.106	0.284	7.4(0.4)	-
PS	3.5	1.05	0.097	0.242	5.9(0.4)	-
PTFE	8.0	2.17	0.078	0.470	3.6(0.3)	-
Ni	28	8.9	0.09	0.9	1.7(0.2)	1.8(0.2) ²³
Si	14	2.33	0.05	0.2	0.9(0.1)	1.0(0.1) ²³

Note: Available literature values are given in the rightmost column.

polymers is seen to be significantly smaller than those measured earlier for metals and semiconductors, giving rise to a significantly larger value of a_s (see Table 1). The present values for a_s are compared with those from Werner et al²³ in Figure 3, where they are plotted against the generalised plasmon energy $\hbar\Omega_p = \sqrt{4\pi N_v e^2 / m_e}$ where N_v is the valence electron density and e^2 and m_e represent the elementary charge squared and the electron mass respectively. The grey area indicates the range of values for a_s found by Gergely et al^{24,25} for a series of selected polymers. There is a distinct difference in the range of the present values and the earlier ones, which has significant implications, in particular for the determination of the inelastic mean free path via elastic peak electron spectroscopy measurements.

In EPES for IMFP determination, the elastic reflection coefficient, i.e. the elastic peak intensity or, equivalently, the *absolute* zero order partial intensity, is evaluated theoretically using Monte Carlo (MC) calculations. The absolute partial intensities depend sensitively on the value of the inelastic mean free path (see Equation 5). Therefore, the pathlength distribution $Q^{MC}(s)$ is calculated via MC calculations. The only input parameter of this procedure is the differential elastic scattering cross section,³² which is known to a much better accuracy than IMFP values.³⁵ Then, for any value of the IMFP, λ , the elastic reflection coefficient $\eta_e = C_{n_b=0, n_s=0}$ follows from Equation (5) as

$$\eta_e(\lambda) = C_{n_b=0, n_s=0}(\lambda) = e^{-\langle\mu_s^{tot}\rangle} \int_0^\infty Q^{MC}(s) e^{-s/\lambda} ds = e^{-\langle\mu_s^{tot}\rangle} C_0^{MC}(\lambda), \quad (9)$$

where the zero order bulk partial intensity $C_{n_b=0}$ calculated using the MC approach is designated as C_0^{MC} . Equation (9) can be interpreted as a calibration curve and the value of the IMFP follows by comparing the experimental reflection coefficient with the calculated one. Since it is very difficult to perform absolute measurements of the reflection coefficient, a reference material, for which the energy dependent IMFP (λ_{ref}) is assumed to be known, is often used:

$$\left(\frac{\eta_e}{\eta_{ref}}\right)_{Exp.} = e^{-(\langle\mu_s^{tot}\rangle - \langle\mu_{s,ref}^{tot}\rangle)} \frac{C_0^{MC}(\lambda)}{C_{0,ref}^{MC}(\lambda_{ref})} \quad (10)$$

When the surface excitation parameters for the unknown sample and the reference material are known, that value of the unknown IMFP, λ , which minimises the difference between the right and left side of Equation (10) is taken to be the value of the IMFP for the unknown sample consistent with experiment. If the IMFP of both, the reference and the unknown sample are known, along with the surface excitation probability of the reference, Equation (10) can be used to quantify $\langle\mu_s^{tot}\rangle$ of the unknown sample.

The huge difference between the present results and those of Gergely et al^{24,25} is striking. For PE, the resulting value of a_s differs by a factor more than 10(!). It is believed that the present method, which uses an essentially different approach, is more reliable. First of all, the present method seems advantageous from the point of view of error propagation. While in Gergely et al,^{24,25} the *elastic* peak intensity was used to determine $\langle\mu_s^{tot}\rangle$, it is essentially the first order reduced partial intensity for surface excitations $\gamma_{n_b=0, n_s=1}$ in the present work. As already mentioned above, in the reduced loss spectrum the first order reduced surface partial intensity is given by the area under the curve labelled “0b1s” (see Figure 1). According to Equation (7), this is just $\gamma_{n_b=0, n_s=1} = \langle\mu_s\rangle$. Therefore, the relative error in $\langle\mu_s\rangle$ is equal to the relative error in the area under the curve labelled “0b1s”.

In contrast to this, if the elastic peak ($n_b=0, n_s=0$) is used to measure the surface excitation probability the essential relationship between the measured elastic peak intensity I and the quantity of interest $\langle\mu_s\rangle$, according to Equation (10) is given by

$$I = Const. \exp(-\langle\mu_s\rangle). \quad (11)$$

Applying the rules of error propagation to the above equation one finds that the *absolute* error in $\langle\mu_s\rangle$ is equal to the *relative* error in the intensity measurement:

$$\Delta\langle\mu_s\rangle = \left(\frac{\Delta I}{I}\right). \quad (12)$$

For typical values of $\langle\mu_s\rangle \approx 0.1$ and assuming that the error in the elastic peak intensity measurement is about 5%, it follows that the relative error in $\langle\mu_s\rangle$ is of the order of 50%. For even smaller values of $\langle\mu_s\rangle$, such as those found in the present work, the relative error may exceed several 100%(!).

Secondly, for the method of Gergely et al^{24,25} which uses the intensity of the elastic peak to quantify surface excitations, a realistic value of the IMFP is needed to calculate the *absolute* zero order bulk partial intensity. It seems that in Gergely et al,^{24,25} the derived value of the surface excitation parameter was varied to match the experimental reflection coefficient consistent with the expected literature value of the IMFP. Finally, the present method benefits from the advantage that visual inspection of the raw data immediately allows a rough estimate of the magnitude of surface excitations to be made by comparison of raw energy loss spectra with the corresponding

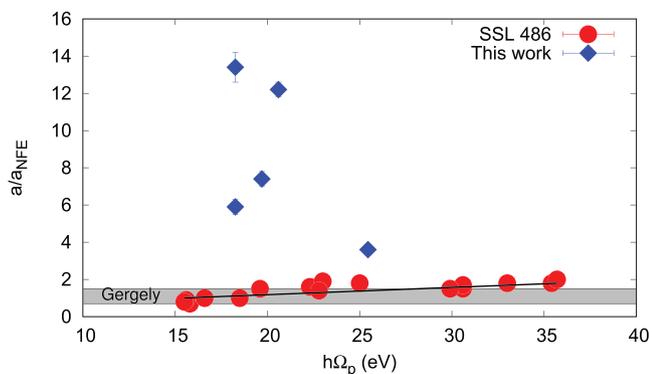


FIGURE 3 Comparison of the surface excitation parameter a_s/a_{NFE} found in the present work for organic polymers (blue diamonds) with earlier results for metals and semiconductors²³ (red circles). The empirical predictive formula proposed in Werner et al²³ is indicated by the black line. The grey area indicates the range of values a_s for a several conducting polymers reported by Gergely et al.^{24,25}

DIIMFP (see Figure 1 and compare with, e.g., the data in Werner et al.^{5,23}). Nonetheless, the magnitude of the discrepancy between the present results and those in Werner et al.^{24,25} seems to be too substantial to be attributable to any of the above and is not understood presently.

Concerning the physical explanation of the weak influence of surface excitations in the investigated polymers it is difficult to make a definitive statement. According to the momentum exciton model, proposed by Ferrell and Quinn,³⁶ the plasmon is a coherent superposition of a few (of the order of ten or less) electron-hole pairs occurring at the resonance energy $\hbar\omega_b$ corresponding to the zero crossing of the real part of the dielectric function $\epsilon(\omega)$. Likewise, the surface plasmon resonance energy $\hbar\omega_s$ is given by the poles due to $\epsilon(\omega) + 1$. Horie³⁷ has compared plasmon resonances in conductors and insulators on a theoretical model and arrived at the conclusion that the character of the excitation is either more excitonic or more plasmonic in the true sense, depending on the extent to which the wave functions of the solid state electrons are extended (plasmonic character) or more localised (excitonic character). For the investigated materials which are all veritable insulators, one may expect the excitonic character to dominate. This could make it kinematically more difficult to excite surface plasmons.

6 | CONCLUSIONS

Reflection electron energy loss spectra (REELS) were measured for five insulating organic compounds: Kapton, polyethylene (PE), poly(methyl methacrylate) (PMMA), polystyrene (PS) and polytetrafluoroethylene (PTFE), as well as for Ni and Si. The average number of surface excitations for a single surface crossing was determined from the experimental data by fitting the reduced energy loss spectra to theory. The contribution of surface excitations to the loss spectra was found to be considerably smaller than for elemental metals.²³ The surface excitation parameter, a material parameter used to quantify the relative intensity of surface losses in (photo-)electron spectroscopy, was extracted from the data by fitting the average number of surface excitations in a single surface crossing to the semiempirical relationship given by Equation (8). In this way, the influence of surface excitations on electron spectra of the investigated polymers can be quantified for any given application and, moreover, the results should provide at least a rough guideline for other organic materials. As a rule, the influence of surface excitations for quantification of XPS spectra of polymers is expected to be negligible. On the other hand, it is essential for the determination of the electron inelastic mean free path of polymers employing elastic peak electron spectroscopy if a metallic sample is used as a reference material (see Equation 10).

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DATA AVAILABILITY STATEMENT

Data will be made available upon reasonable request.

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