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XPS Insight Note: Carbon Sp^2–Sp^3 Ratios Derived From the Carbon Auger Signal and Its Accuracy

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ABSTRACT

Understanding the surface chemistry of carbon materials is typically explored using x-ray photoelectron spectroscopy (XPS). Researchers typically focus on the C(1s) core-level to deduce chemistry, often overlooking complementary spectral information. This insight note summarizes the use of the x-ray excited Auger peak for carbon, deriving the D-parameter to aid in the measurement of sp^2—sp^3 ratios.

1 | Introduction

Carbon materials are highly important in technological fields such as energy storage, sensor technology, composite materials and catalysis [1, 2]; hence, understanding the surface chemistry of the carbonaceous materials is important if we wish to tailor their properties. X-ray photoelectron spectroscopy (XPS) is inherently surface sensitive and therefore ideally suited to the study of carbon surfaces.

Through analysis of the C(1s) core-level, together with analysis of spectral regions for other atoms present in the material (e.g., O(1s), Cl(2p), etc.), an idea of the surface functionalities may be derived. However, a detailed analysis typically requires a robust fitting routine with constraints, such as peak position and FWHM. For graphitic materials, the asymmetric nature of the sp^2 carbon is often overlooked, as is the relationship between the amount of sp^2 and sp^3 carbon, which can inform the fitting of the C(1s) peak [3].

Understanding the degree of hybridisation in carbon materials is important as it allows for the tuning of their fundamental properties, including electrical, optical and mechanical characteristics. To obtain hybridisation information, researchers have previously studied the C(1s) loss-structure via the ESCALOSS method [4, 5], electron energy loss spectroscopy (EELS) and photoelectron loss spectroscopy (PELS) [6, 7] and UPS [7, 8]. However, these can be time-consuming, sensitive to surface contamination (e.g., UPS), or potentially damaging (e.g., EELS).

Building on the work of Mizokawa et al. [9], Lascovitch and coworkers highlighted the use of the carbon x-ray excited Auger (XAES) peak in XPS experiments to derive hybridisation information, yielding an informed view of a sample [6, 10–12]. Coining the term the D-Parameter for the numerical separation (D) between peak maximum and minimum points of the differential measurement, the method has found use in the derivation of block co-polymers [13], the study of carbon allotropes and nanomaterials [14–16] and in XPS imaging of textured samples [17].

In this insight note, we discuss the measurement of the carbon Auger signal for the determination of the D-parameter value, comment on its accuracy and care that should be taken in its application.

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2 | The Carbon Auger: Nomenclature and Energy Dependence

The carbon Auger peak, commonly referred to as the C (KLL) peak, where KLL is x-ray notation and refers to:

- K: Formation of the core hole in the K-shell created by the photoemission event
- L: Electron transition from the L-shell to the K-shell, filling the core hole
- L: Ejection of an electron (Auger electron) from the L-shell through transfer of the excess energy from the L- to K-shell transition

The C (KLL) peak may also be termed C (KVV), where V refers to valence electrons (which are those in the L-shell for carbon) and indicates both final state holes are in the valence band (VB). Using a one-electron model, the carbon Auger has been shown to reflect the VB, giving a good description of the VB density of states (DOS) and therefore may be used to probe the ground state DOS [18–20].

It is important to note, given the kinetic energy difference of ca. 1000 eV between C(1s) and C (KLL) photoelectrons, there will be a difference in the information depth (ID). Using the QUASES-TPP-2M software, which utilizes the Tanuma, Powell and Penn formula [21], the inelastic mean free path (IMFP, λ) of a C(1s) core-electron with a kinetic energy of 1202 eV (binding energy 285 eV) is 3.3 nm, whilst a C (KLL) Auger electron with a kinetic energy of 270 eV (binding energy 1217 eV) is 1.2 nm, hence assuming the ID is 3λ [22], then for normal emission, the ID is 9.9 and 3.6 nm for the respective carbon signals using Al radiation and slightly less for Mg radiation with its lower photon energy. Consequently, there is an enhancement in the surface chemistry for the Auger versus the C(1s) core level.

3 | Measuring the D-Parameter

The C (KLL) Auger peak is typically acquired at a pass energy of 100 eV and a step size of 0.5 eV over a binding energy range of ca. 1190–1250 eV. The number of sweeps is generally around 50–100 scans to ensure good signal-to-noise levels. The D-parameter is then derived by taking the first differential of the C (KLL) Auger spectrum and measuring the difference between the highest and lowest points of the differential, as shown in Figure 1 for highly oriented pyrolytic graphite (HOPG), where the differential reveals a value of 23 eV and is representative of 100% sp^2 carbon.

The corresponding value is a measure of the percentage of sp^2 present based on a linear plot between the extreme values of 14 for pure sp^3 (diamond) and 23 for pure sp^2 (HOPG) [10].

The derived value of the D-parameter will be affected by factors such as data quality (signal-to-noise) and the method used to perform the differentiation [3], with some methods leading to unexpected values, especially with noisy data, as discussed by Fairley et al. [23]. It should also be noted that values for the D-parameter have been reported between 11 and 13 eV for highly sp^3-like materials and 21–23 eV for highly sp^2–like materials [24] and could potentially differ because of surface contamination

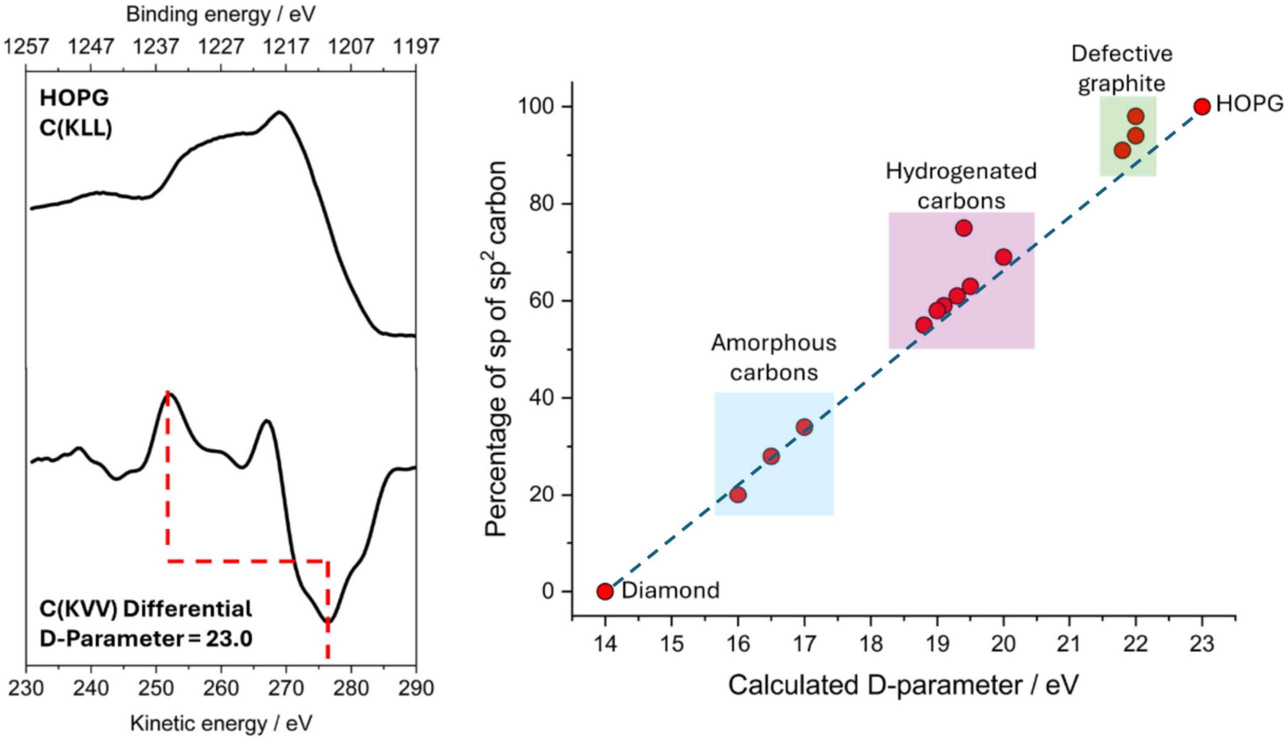

FIGURE 1 | The C (KLL) spectrum for HOPG and its differential spectrum (left) and a plot of the data from Lascovitch et al. [6, 10] used to calculate the amount of sp^2 carbon (right).

TABLE 1 | D-parameter values for a freshly cleaved HOPG sample calculated from data acquired under different analysis conditions.

Scan parameters		Calculated D-parameter (eV) for specified pass energy			
Step Size (eV)	No. of scans	150 eV	100 eV	80 eV	40 eV
1.0	100	22.0	22.0	22.0	22.0
0.5		23.5	23.5	23.5	23.5
0.1		23.5	23.6	23.7	23.5
1.0	20	20.0	24.0	23.0	21.0
0.5		23.6	23.0	24.0	20.5
0.1		23.4	23.6	23.5	23.5

or charging effects if a flood-source is required, as noted by Kaciulis [14].

To consider accuracy, we present the calculated D-parameter for different pass energies, step sizes and number of scans (Table 1). Here, the D-parameters have been calculated using the standard methodology used within our laboratories, as detailed below:

1. A smooth synthetic approximation of the C (KLL) signal is made using the poly regression (PR) background function in CasaXPS. The fist parameter in the cross-section field is taken to be a value of 32, which is the degree of the polynomial used to fit the data.
2. The synthetic data envelope is differentiated using the *Diff. Synthetic Env.* function under the ‘Test Data’ tab under the ‘Spectrum Processing’ options in CasaXPS.
3. The D-parameter is calculated from the resulting spectrum using the *SP2SP3* (SP) background type, which measures the numerical distance (D) between the maximum and minimum points of the spectrum, reporting the D-parameter in both area and FWHM fields.

We note here that software from instrument manufactures (e.g., Thermo Scientific's Avantage) and open-source offerings (e.g., Khervefitting [25]) have built-in routines, which generally apply a smoothing function (e.g., Savitzky–Golay) prior to differentiation. The effect of this is comparable to the effect of the PR function applied in CasaXPS, and can generate similar results [3].

From Table 1, it is evident that sufficiently accurate data can be obtained whilst using a high pass energy (80 eV or above) and a step size not exceeding 0.5 eV, yielding results with a variation corresponding to around a 5% uncertainty based on the plot shown in Figure 1, whilst poor parameter selection means this uncertainty could be as high as ca. 15%. Furthermore, using our processing methodology, this can be achieved also with a lower number of scans, although it should be recalled that the data used in Table 1 is for a bulk carbon sample, and consequently lower carbon concentrations may require a larger number of scans.

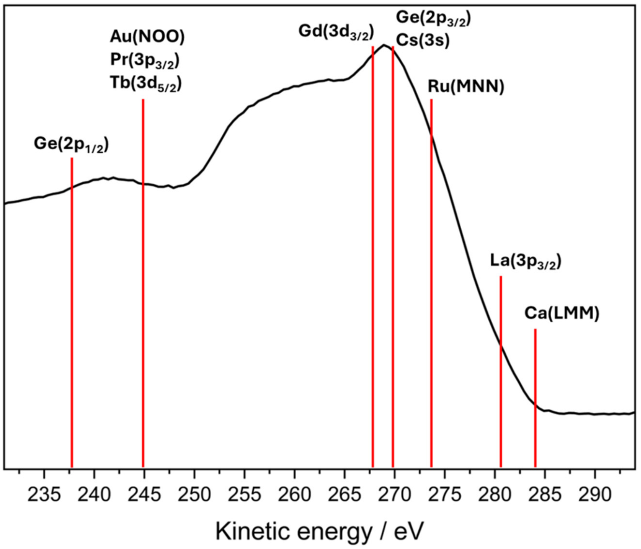

FIGURE 2 | C (KLL) spectrum for HOPG with approximate positions of different core-level and Auger signals which may interfere with derivation of the D-Parameter.

Derivation of the D-parameter must be made with care, and an appreciation of potentially overlapping core-levels or Auger signals may lead to an erroneous analysis. Some examples of these overlaps are shown in Figure 2, where the lines highlight approximate positions. In some of these cases, it may be useful to use an alternative x-ray source for analysis.

Additionally, as discussed earlier, given the difference in information depth for the C(1s) and C (KLL) signals, should a surface have a significant sp^3-containing overlayer, then this will bias the sp^2–sp^3 ratio; examples of this have been discussed by Zemek et al. in relation to carbon films modified by argon ions [26].

4 | Application of the D-Parameter

To exemplify the use of the D-parameter, Figure 3 shows the derivative C (KLL) spectrum and the corresponding C(1s) core-level for an oxidised few-layered graphene sample. A D-parameter of 21.5 eV corresponds to ca. 82% sp^2 character, meaning that ca. 18% of the C(1s) signal should be attributable to carbon in a sp^3 environment.

Fitting of the C(1s) spectrum (Figure 3(b)) using a peak model based on a clean graphite sample and the inclusion of peaks for carbonyl and ether/alcohol containing functionalities as confirmed by the O(1s) spectrum (not shown), we find the sp^3 carbon peak to be 17% in excellent agreement with that expected from the plot in Figure 1 and the noted accuracy. Any significant derivation from the expected relative percentage of sp^3 carbon would likely mean a poor fitting model has been applied to the spectrum, and the analyst should reanalyse the data in accordance with the methodology discussed in reference [3].

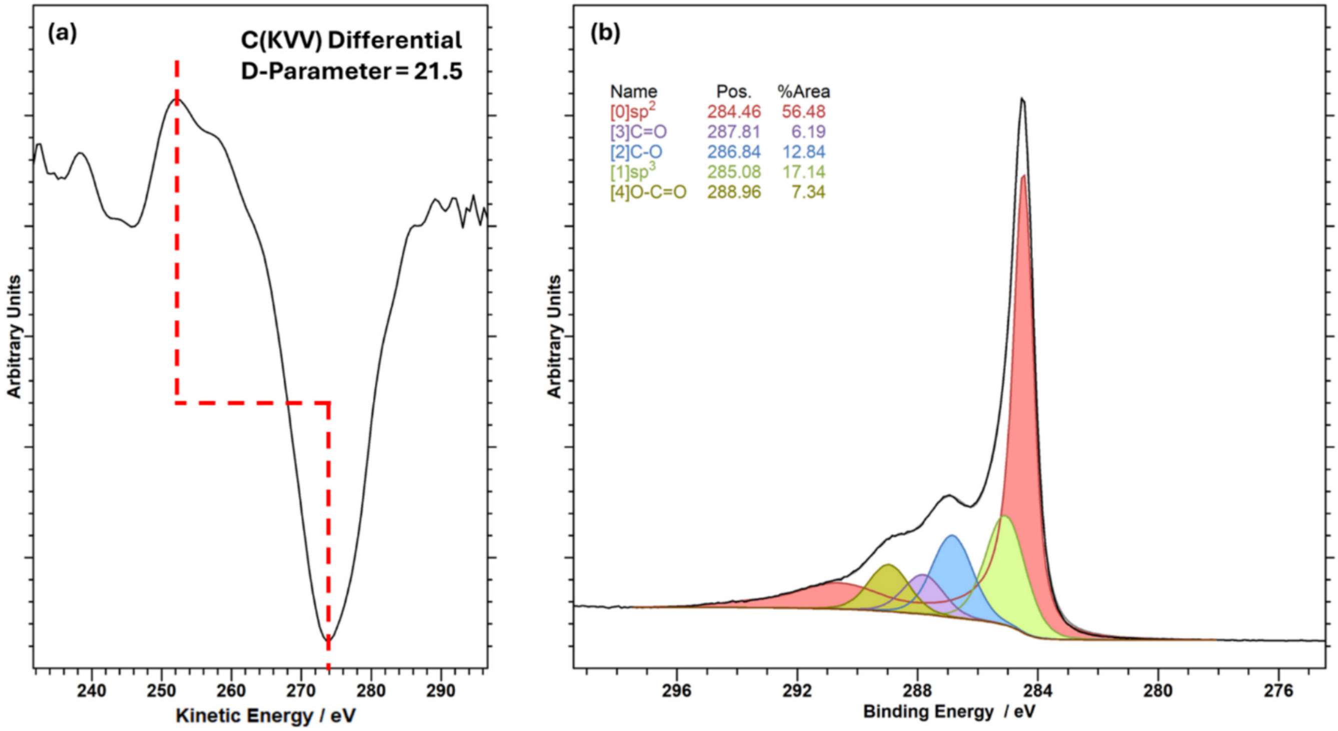

FIGURE 3 | (a) derivative of the C (KLL) spectrum for an oxidised few-layer graphene sample and (b) the corresponding fitted C(1s) core-level spectrum. The C(1s) spectrum is colour coded for each carbon function and hybridisation.

5 | Summary

We have highlighted the application of the D-parameter, derived from the C (KLL) Auger signal to aid elucidation of the sp^2–sp^3 ratios in carbon materials. With suitable pass energies and step sizes, together with sufficient signal-to-noise, accuracies better than 5% can be achieved. Generally not addressed in other papers, we have noted typical overlapping photoelectron and Auger signals which may complicate analysis without care and further data processing.

It is hoped this insight note will guide and aid experimentalists in their analysis of carbon materials, leading to a more informed understanding of their surface chemistry and hybridisation.

Author Contributions

D.J. Morgan–Conceptualisation, writing original draft, original data collection, data curation and formal analysis. M. A. Isaacs–review and editing of original draft; A. Graf–review and editing of original draft.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing not applicable to this article as no new datasets were generated or analysed during the current study.

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