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Universal Calibration of Computationally Predicted N 1s Binding Energies for Interpretation of XPS Experimental Measurements

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Abstract

Computationally predicted N 1s core level energies are commonly used to interpret the experimental measurements obtained with X-ray photoelectron spectroscopy. This work compares the application of Koopmans' theorem to core electrons using the B3LYP functional with two commonly used basis sets, analyzes the factors relevant to the comparison of the computational with experimental data, and presents several correlations that allow an accurate prediction of the N 1s binding energy. The first correlation is obtained with a series of known nitrogen-containing functional groups on well-characterized organic monolayers. This approach can then be reliably extended to a number of nitrogen-containing chemical systems on silicon surfaces in which the nature of the chemical environment of nitrogen atoms had only been proposed based on a number of analytical techniques. In most of those cases, the XPS analysis is consistent with the proposed structures, but is not always sufficient for conclusive assignments. Third, it was attempted to also include N-containing systems on metals. Despite the admittedly oversimplified approach taken in this case (the metal surface is approximated by a single atom), the observed correlations are still experimentally useful, although in this case significant outliers are found. Finally, previously published correlations between experimental and theoretical C 1s data were reexamined, yielding a set of correlations that allow experimentalists to predict C 1s and N 1s XPS spectra with high accuracy.

Graphical abstract

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INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a powerful surface analytical technique commonly applied to investigate the chemical environment of a variety of functionalized surface species.^{1,2} This approach utilizes the measurements of the core electron binding energies of the target elements and then uses these data to characterize the chemical state(s) or functional groups on a surface.^{3–6} Carbon and nitrogen core level energies are commonly used to assess the chemical environment of a variety of functional groups on surfaces of organic monolayers and multilayers. Given the rapidly widening range of heterogeneous hybrid surfaces,^{7–9} multielement polymers,^{10–12} and the increasing breadth of organic and bio-organic species specifically linked to a surface,^{13,14} the analysis of the observed C 1s and N 1s binding energies becomes more and more significant, but also more complex.

In order to correlate the experimentally obtained binding energies with the proposed surface species, simulation of the core levels, especially utilizing density functional theory (DFT), is commonly used.^{15,16} This powerful combination of experiment and theory allows a precise assessment of the chemical states and chemical environments of carbon and nitrogen atoms within the organic layers. However, while the *differences* between the core level energies in species with different chemical environments (core level shifts) are typically sufficiently and reliably predicted in this way, prediction of the *absolute* binding energies has presented a number of challenges. Some of these challenges are described in a very detailed study by Löytynoja et al. of the C 1s electron binding energies in water–ethanol solutions.¹⁷ At the same time, these absolute energy comparisons are what would make the computational predictions a universal measuring stick for a wide variety of chemical systems on a wide variety of solid substrates. The work and motivations described below are building on the successful and highly practical correlation procedure offered by Zuilhof group for C 1s energies and XPS measurements for surface species in 2013¹⁸ and the exploratory correlations offered for N 1s energies and surface spectroscopy studies by the groups of Zuilhof¹⁸ and Teplyakov.¹⁹

The differences between the computationally predicted and experimentally measured values depend on a number of factors, including, for example, the work function of a sample.¹⁸ When comparing the same chemical groups on different solid surfaces, this difference should therefore be calibrated based on a specific peak observed in the XPS data. However, accounting for differences in work function typically is not sufficient for establishing an

unequivocal correlation between a core energy as obtained with a cluster calculation in DFT and the experimentally measured value for solid surfaces. Another major challenge is to discern the subtle differences in functional groups containing the same chemical element in different chemical environments, where the measurement results in unresolved features that do not allow unequivocal fitting. This case can be aided substantially by computational investigations that can allow for quantifying these differences in binding energies and reproducing the experimental spectra.

Given that the characterization of C 1s and N 1s core levels by XPS is very common, over the years, there have been a number of studies proposing the correlations between computationally predicted and experimental values for these elements. A detailed correlation of the quantum mechanical predictions for C 1s binding energies based on a variety of organic monolayers on silicon surfaces has been described by Zuilhof and co-workers.¹⁸ That study provided a highly useful correlation, with average error ~0.3 eV for both B3LYP and M11-based calculations, and largest outliers of 0.7 eV for B3LYP and 0.6 eV for M11-based calculations. That work also attempted to expand the same correlation for several chemical elements, including N 1s, but while the limited data available then suggested potential for further work, it precluded firm conclusions.¹⁸

An attempt to provide a set of specific correlations for N 1s in chemically bound species on silicon surfaces has been made by Doren and Opila,²⁰ who concluded—based on a few surface structures identified with other analytical techniques—that the simple Koopmans' theorem approach is as reliable as more sophisticated methods. Detailed investigations by Bagus, Illas, and co-workers show that, while Koopmans' theorem based on the Kohn–Sham energies of core orbitals does not yield accurate binding energies due to neglect of final state effects,²¹ relative changes are predicted rather accurately within a series of analogues.²² Relying on that principle, Leftwich and Teplyakov¹⁹ suggested a simple calibration approach based on the measurements recorded for molecular species and expanded this to several proposed surface structures containing nitrogen. The correlations found for several functionals and basis sets were satisfactory, but no definitive calibration based on well-known surface species was offered. Recently, a linear correlation between experimental and calculated N 1s binding energies was published targeting nitrogen dopants in carbonaceous materials.²³ Although useful for this set of materials, the correlation was limited to specifically distinguishing the placement of a nitrogen atom within graphene sheets, and no overall correlation with other possible surface species or nitrogen-containing surface-bound chemical groups was attempted.

In this work, we focus on simulating N 1s core level binding energies by density functional theory, based on calculations performed on small cluster models representing relevant surfaces. Here we evaluate the potential of Koopmans' theorem for analysis of these data, essentially excluding final state effects. In this we take a two-pronged approach: First, we obtain and evaluate a correlation between computational and experimental N 1s energies of well-known and well-characterized surface species. This set includes a variety of functional groups produced that are part of surface-bound organic monolayers, including amines, amides, azides, triazoles, etc. These monolayers are either classical self-assembled monolayers (for example, on gold surfaces) or organic monolayers produced on

semiconductors, where the attachment chemistry leads to the formation of a strong linker that does not easily diffuse on a surface. For consistency, all these monolayers will be referred to as self-assembled monolayers throughout this work. This initial calibration is performed using the B3LYP functional with two commonly used basis sets, LANL2DZ and 6-311+G(d,p), to thus also investigate whether the choice of a basis set makes a substantial difference in describing core levels in light elements. The LANL2DZ basis set is an effective core potential basis set which is known to be useful for simulating molecules interacting with metals and metal oxide structures. It is a very cost-effective basis set that normally allows for exploring a large number of potentially interesting structures.^{24–26} The 6-311+G(d,p) basis is a very widely applicable basis set for first-row elements, and takes explicit account of the core electrons. Compared to LANL2DZ, this basis set is considered more reliable in simulating organic molecules and organic fragments attached to surfaces.^{25,26} Second, the thus obtained correlation between experimental and theoretical N 1s energies is then used to investigate the chemical environment of nitrogen atoms in a number of less well-understood (proposed) nitrogen-containing surface species. The analysis thereof shows that the obtained correlation allows for the assignment of N 1s energies to specific functional groups based on B3LYP-calculated data, and outlines its potential for use in complex experimental situations.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

Density functional theory computational studies were carried out using the Gaussian 09 suite of programs.²⁷ Geometry optimizations and binding energy predictions were all performed using the B3LYP functional, with LANL2DZ²⁸ and 6-311G+(d,p)^{29,30} basis sets as implemented in there.²⁷ A small Si₄H₉ cluster representing the Si(111) surface was used as a model in the simulations of organic monolayers on silicon. A Si₉H₁₂ model cluster and Si₁₀H₁₅ model cluster, representing a single silicon dimer of the Si(100)-2 × 1 surface and a single surface silicon site of the unreconstructed Si(111) surface were used in the simulations of organic adducts on silicon surfaces. A single metal atom representing the metal (Cu, Ni) surface was used in the simulations of surface-bound model compounds on the surfaces of these metals. Natural bond orbital (NBO)³¹ analysis was employed to obtain the N 1s core level binding energies. NBO analysis is based on a method that transforms wave functions into one center (lone pair) and two center (bond) representations. NBO analysis provides an insight into interactions between various parts of molecules. The diagonal elements of the Fock matrix in the NBO representation represent the energies of localized bonds, lone pairs, and antibonds. Off-diagonal elements represent bond/antibond, lone pair/antibond, and antibond/antibond interactions. To aid in the correlation process, the computationally predicted energies are given to within 0.01 eV. Of course, realistic experimental measurements on surfaces are normally only accurate to within approximately 0.1 eV.

XPS measurements were collected on several instruments in the Teplyakov Lab. On a VG ESCALAB 220i-XL electron spectrometer (VG Scientific Ltd., U.K.), spectra were collected with monochromatic Al K α X-rays ($h\nu = 1486.7$) eV 15 kV and 8.9 mA with a pass energy of 20 eV. The base pressure was in the 10⁻⁹ Torr range. On a PHI-5600 instrument, spectra were collected with monochromatic Al K α X-rays ($h\nu = 1486.6$ eV) at a

base pressure of 1×10^{-9} Torr. The takeoff angle was 45° with respect to the analyzer. Several spectra were also collected on a Thermo Scientific K-Alpha⁺ instrument equipped with an Al K source ($h\nu = 1486.6$ eV) at base pressure below 5×10^{-9} Torr with a 20 eV pass energy.

XPS spectra from the Zuilhof Lab were measured on a JEOL JPS 9200 photoelectron spectrometer (JEOL, Japan). Spectra were collected using monochromatic Al K α X-rays ($h\nu = 1486.7$ eV) 12 kV and 20 mA using an analyzer pass energy of 10 eV. The base pressure in the chamber during the measurements was 3×10^{-7} Torr, and spectra were collected at room temperature. The X-ray incidence angle and the electron acceptance angle were 80° to the surface normal, respectively, as defined with a precision 1° .

RESULTS AND DISCUSSION

To obtain a widely applicable correlation of experimental and theoretical N 1s energies, the data based on the organic monolayers on several substrates were analyzed first. Figure 1 schematically shows the structures of 11 organic monolayers containing in total 20 N atoms in a variety of N-containing functional groups on silicon and gold (nitrogen atom number 20) substrates; this data set is much larger than any of the ones used before (e.g., in ref 18). Each of the nitrogen atoms in this figure is assigned a number that is used in further analysis of the data.

Simulations Using B3LYP/LANL2DZ

First, N 1s binding energies were predicted by this basis set with B3LYP functional for the well-characterized organic monolayers shown in Figure 1. The data details are provided in Table 1. Figure 2 shows the plot of the computationally predicted binding energies, as obtained from application of Koopmans' theorem, versus the experimental XPS data. To compare the effect of linearization and a simple offset, two linear fits were applied. In Figure 2a, the slope was set to 1, while Figure 2b shows the unrestricted linear fit. Both fits display a good correlation over a wide range, with $R^2 = 0.9456$ for the first case and $R^2 = 0.9471$ for the second. In this case, the mean-unsigned error of calculated data vs experimental data is 0.28 eV for the first case, and 0.27 eV for the second. In addition, the largest error is 0.76 eV for the first case (with slope set to 1) and also 0.76 eV for the second.

Simulations Using B3LYP/6-311+G (d,p)

Analogously, the N 1s binding energies were predicted by B3LYP/6-311+G(d,p) and then plotted versus the experimental XPS data (Figure 3). Similarly to the analysis described in Figure 2, the slope of the linear fit was set to be 1 in Figure 3a, while Figure 3b shows the unrestricted linear fitting plot. Again, overall a good correlation was recorded with $R^2 = 0.9615$ for the first case and $R^2 = 0.9552$ for the second. In this case, the mean-unsigned error of calculated data vs experimental data is 0.27 eV for both cases and the largest error is 0.67 eV (slope fixed to one)/0.73 eV (unrestricted linear fit).

The data allow us to conclude four things: (1) B3LYP-calculated N 1s energies correlate well with experimentally observed data over 6 eV of binding energy variations. Since the average error of <0.3 eV is very close to what can reasonably be considered to be a standard

experimental error in the studies of surface-bound species by XPS, it indicates that B3LYP-calculated N 1s data can be reliably used to analyze the N 1s spectra of organic monolayers. (2) The obtained correlation is as good as previously obtained for C 1s simulations, which have shown their value by application to a very wide range of surface studies. This suggests a similarly high potential for application of the obtained correlations for N 1s spectra of organic monolayers. (3) The mean-unsigned errors are actually smaller than in the previous study;¹⁸ however, the largest deviations are somewhat higher. This observation likely reflects the much wider set of models considered in the current study. (4) Overall, based on the statistical treatment of the data, it appears that the use of either one of the basis sets considered provides similar confidence. As the 6-311+G(d,p) basis set is actually somewhat better in describing the strained geometries such as those present in, e.g., the first and fourth monolayers (containing a cyclooctyne with attached cyclopropyl group), and also available in almost any computational chemistry package, we will continue our further studies with that basis set.

Test of the Calibration Procedure with Proposed Surface-Bound N-Containing Species

Based on the obtained correlations of experimental N 1s energies with B3LYP/6-311+G(d,p)-derived N 1s energies for well-characterized N-containing organic monolayers, we now aim to extend this approach to a series of structures of several surface species that were proposed as the main surface chemical groups in a number of previous investigations (Figure 4). Table 2 lists the exact positions of measured and predicted N 1s binding energies, Figure 5 shows the proposed correlations, and Table 3 provides the numerical characteristics of these studies.

The results summarized in Table 3 present an overview of the reliability of the proposed calibration procedure. The initial set of models (first column) involves nitrogen-containing groups that are well-defined and positioned within a SAM. The correlation is very high for any of the linearization approaches and basis sets used. As would be expected, when this calibration procedure is tested on less well-understood data set obtained for the species in Figure 4 (species a–k), the errors of prediction are increased. Nevertheless, if these models are included into the correlation fits, the mean unsigned error only increases from 0.27 to 0.39 eV. Such an error is usually sufficient to distinguish different N-containing species possibly present during a surface reaction, although the maximum error of 1.06 eV, observed for azide N atoms indicates that there is room for improvement, either by efforts to proper account of the final state, but primarily by improved computational methods (better functionals), as the charge distribution in azides seems to stretch the limits of B3LYP. Interestingly, when the proposed calibration procedure is extended to nitrogen-containing species on metal surfaces, where the computational models based on a single surface atom are evidently no more than a first-order approximation to the exact bonding configurations, this correlation can still yield reliable information for comparison with the XPS spectra. The mean unsigned error in this case is just around 0.5 eV if all the species considered in this work are included for the fit, which is still very low and is sufficient for identification of the surface functional group based on a single XPS measurement.

Finally, while the unrestricted fits, of course, give the best fit to the data, we would advocate the use of “slope-restricted” correlations (see below). For N 1s binding energies in SAMs, we would advocate $EN\ 1s\ (exp) = EN\ 1s\ (theory) + 10.03\ (\text{in eV})$, while if mixed sets on nonmetals are concerned, we would propose $EN\ 1s\ (exp) = EN\ 1s\ (theory) + 9.77\ (\text{in eV})$; all correlations based on B3LYP/6-311+G(d,p) calculations).

Revisiting C 1s Data: Physically Meaningful Correlations, and Comparison with N 1s Data

In reference 18, the SAM-on-Si data set used in there (analogous to Figure 1) was fitted with a linear fit with optimized slope. This yielded the published, and often used, correlation: $EC\ 1s\ (exp) = 0.9698\ EC\ 1s\ (theory) + 20.34\ (\text{in eV})$ (based on B3LYP/6-311G(d,p) data), which yielded a mean unsigned error of 0.29 eV and a largest outlier of 0.72 eV. Such a slope-optimized fit necessarily gives the smallest deviation from experiment, and is thus highly useful from a practical point of view. However, while an offset also makes physical sense in our Koopmans’ theorem-based approach (caused by neglect of final state effects, neglect of work function, self-interaction error in DFT, and possibly other factors), there is no sound physical basis for a nonunity slope: if the experimental data set would be large enough and of high enough accuracy, then any deviation of the slope from one reflects methodological errors in the theoretical chemistry models used. Therefore it made sense to reevaluate the C 1s data set of reference 18 with a slope = 1 linear fit, which yielded: $EC\ 1s\ (exp) = EC\ 1s\ (theory) + 11.97\ (\text{in eV})$ (based on B3LYP/6-311+G(d,p) data). In reference 18, model SAMon-Si data set (analogous to Figure 1) was fitted with a linear fit with optimized slope described in Figure 6. This fit produces an MUE (Mean-Unsigned Error) of 0.32 eV (vs 0.29 eV for the unrestricted linear fit), and a maximum outlier of 0.73 eV (vs 0.72 eV for the unrestricted linear fit). Given that the procedure to determine the peak maximum routinely yields a 0.1 eV error, we regard these differences between the unrestricted linear fit and the slope-restricted linear fit as statistically irrelevant. In addition, we would like to note the small difference (~2 eV) between the offset for N 1s and C 1s data. Given the differences in elements and thus, e.g., in final state effects, there is no reason why the two would have to have identical offsets, but it seems reasonable that highly analogous offsets are to be found for both, as is indeed the case. As a result we thus advocate the simpler and physically more reasonable slope-restricted fit for future use, and also as a benchmark for future theoretical investigations that would allow further predictive improvements.

Thus, based on this comparison, it is clear that the proposed calibration procedure provides a reliable and robust approach to correlating experimentally obtained XPS spectral features with the N 1s core-level energies predicted computationally. This approach can help in identifying and assigning the chemical nature of surface-bound functional groups containing nitrogen atoms. More importantly, the proposed correlations are applicable to different surfaces and for very simple cluster representations of the proposed models. In the simulations for silicon surfaces, small clusters (Si_9H_{12} , $Si_{10}H_{15}$) were applied to represent the Si(100) and Si(111) surfaces, which have been shown to be small but reliable models for silicon surface calculations.^{19,25,26} It should be pointed out that when the fit obtained based on correlations with the self-assembled monolayer models is applied to the very simplified models of chemical functionalities interacting with metal surfaces (where metal surfaces are

represented by single atoms), the maximum errors are still smaller than 2 eV (1.84 eV for the slope set to be 1 and 1.95 eV for the unrestricted fit), which can often be sufficient to distinguish different surface species based on comparison with simplistic computational models. This further proves the universal application of the obtained calibration curves.

CONCLUSIONS

The application of Koopmans' theorem using routine B3LYP/LANL2DZ and B3LYP/6-311+G(d,p) calculations yields highly reliable predictions for the N 1s and C 1s binding energies for a wide variety of surface-bound species. Such predictions thus easily allow for the analysis and/or prediction of C 1s and N 1s XPS spectra. For organic monolayers/SAMs we find correlations for nitrogen of $EN\ 1s\ (exp) = EN\ 1s\ (theory) + 10.03\ (in\ eV)$, while revisiting literature data for carbon we derive $EC\ 1s\ (exp) = EC\ 1s\ (theory) + 11.97\ (in\ eV)$, all based on B3LYP/6-311+G(d,p) calculations. These correlations display a mean unsigned error of <0.3 eV (i.e., less than the typical experimental error), while the biggest outliers were 0.7 eV, for both correlations. When a wider series of nitrogen-containing moieties on silicon is included, the offset for nitrogen decreases somewhat, and a general purpose correlation for N 1s energies would be $EN\ 1s\ (exp) = EN\ 1s\ (theory) + 9.77\ (in\ eV)$ (mean unsigned error: <0.4 eV). In calculations describing chemical groups bound to metal surfaces, even simpler single atom representations were used to describe Cu and Ni surfaces. Despite such a simplistic representation, given that we are only interested in the core binding energies for nitrogen atoms in the chemical groups attached to the surfaces, these computational studies provided a good set of models to compare with experimental findings. Overall, this simple use of Koopmans' theorem results in a very good universal calibration curve, which can be used to predict the XPS spectra of unknown surface species based on DFT calculations applied to the possible surface functionalities and assigning the species consistent with the XPS measurements.

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Figure 1.

SAM-based model compounds used to correlate experimental N 1s XPS spectra to DFT-calculated data. Each nitrogen atom is assigned a number shown in red to be used as a label in further studies.

Figure 2.

Correlation of the experimental XPS N 1s energies with simulated N 1s binding energies in self-assembled monolayers, as obtained with B3LYP/LANL2DZ calculations: (a) with the slope fixed to be one; (b) the unrestricted linear fit.

Figure 3.

Correlation of the experimental XPS N 1s energies with simulated N 1s binding energies in self-assembled monolayers, as obtained with B3LYP/6-311+G(d,p) calculations: (a) with the slope fixed to 1; (b) the unrestricted linear fit.

Figure 4.

Schematic representation of the surface-bound model compounds used to test the calibration based on SAMs of the experimental N 1s XPS spectra by comparison with the DFT calculations. Each nitrogen atom is designated a letter as a label in further analysis.

Figure 5.

Linear correlation of the experimental XPS N 1s energies for nitrogen-containing surface species with B3LYP/6-311+G(d,p)-simulated N 1s binding energies in self-assembled monolayers [blue solid line - slope fixed at 1; red dash line - unrestricted linear fit], and for the wider set of nitrogen-containing surface species in self-assembled monolayers, silicon and metal models [green solid line - slope fixed at 1; black dash line: unrestricted linear fit].

Figure 6. Correlation of the experimental XPS C 1s energies for surface species with simulated C 1s binding energies (for the slope fixed at 1).

Table 1
Experimental and Theoretical N 1s Energies of Nitrogen Atoms in SAM-Based Model Compounds

	Predicted Data with (eV)		E (N 1s) after calibration LANL2DZ (eV)		E (N 1s) after calibration 6-311G+(d,p) (eV)	
	Lan12dz	6-311G+(d, p)	(x + 9.56)	(0.9625x + 24.24)	(x + 10.03)	(0.9416x + 32.88)
1	390.22	389.96	399.8	399.8	400.0	400.1
2	390.4	389.7	400.0	400.0	399.7	399.8
3	390.54	390.09	400.1	400.1	400.1	400.2
4	390.54	390.20	400.1	400.1	400.2	400.3
5	390.62	390.23	400.2	400.2	400.3	400.3
6	390.66	390.31	400.2	400.3	400.3	400.4
7	390.74	390.30	400.3	400.3	400.3	400.4
8	390.68	390.25	400.2	400.3	400.3	400.3
9	390.83	390.32	400.4	400.4	400.4	400.4
10	390.94	390.53	400.5	400.5	400.6	400.6
11	391.08	390.56	400.6	400.7	400.6	400.6
12	391.13	390.64	400.7	400.7	400.7	400.7
13	391.4	390.7	401.0	401.0	400.7	400.8
14	391.51	390.87	401.1	401.1	400.9	400.9
15	391.65	390.97	401.2	401.2	401.0	401.0
16	392.2	391.9	401.8	401.7	401.9	401.9
17	392.51	391.58	402.1	402.0	401.6	401.6
18	393.22	392.79	402.8	402.7	402.8	402.7
19	394.88	394.37	404.4	404.3	404.4	404.2
20	396.3	396.2	405.9	405.7	406.2	405.9
						405.7

Table 2

Experimental and Theoretical [B3LYP/6-311G+(d,p)] N 1s Energies of Nitrogen Atoms in Various Organic Species on Silicon and Metal Surfaces

Structure	<i>E</i> (N 1s) before calibration	<i>E</i> (N 1s) after calibration by $y = x + 10.03$	<i>E</i> (N 1s) after calibration by $y = 0.9416x + 32.88$	Experimental <i>E</i> (N 1s)
Si-NH-NH-Si ³²	390.1	400.1	400.2	399.6
Si-NH ₂ ³³	389.2	399.2	399.3	398.9
Si-PhN-NH-Si ³⁴	390.7	400.7	400.8	399.7
N=N-N-Si ³⁵	391.4	401.4	401.4	400.9
N=N-N-Si ³⁵	394.5	404.5	404.3	404.0
N=N-N-Si ³⁵	390.7	400.7	400.8	399.4
Si-CH ₂ -CH=C=N-Si ³⁶	390.0	400.0	400.1	398.8
Si-PhN-O-Si ³⁷	391.1	401.1	401.1	400.3
Si-O-NCH ₃ -O-Si ²⁰	392.6	402.6	402.6	401.9
Si-NCH ₃ -O-Si ²⁰	390.6	400.6	400.7	400.1
Si-NCH ₃ -Si ²⁰	389.4	399.4	399.5	398.9
Cytosine on Cu (110) ³⁸ -N=	388.8	398.8	399.0	398.0
Cytosine on Cu (110) ³⁸ -N-Cu	389.7	399.7	399.8	400.3
Cytosine on Cu (110) ³⁸ -NH ₂ -	390.1	400.1	400.2	400.9
Thymine on Cu(110) ³⁸ -N-Cu	389.7	399.7	399.8	398.7
Thymine on Cu(110) ³⁸ -NH-	391.0	401.0	401.0	400.4
Pyridine on Ni(110) ³⁹ -N-Ni	390.9	400.9	401.0	399.7
CH ₃ -C=N-Ni ⁴⁰	389.2	399.2	399.3	397.7
Nitrosobenzene on Ni ⁴¹	391.0	401.0	401.0	400.2
Phenylnitrene on Ni ⁴¹	389.4	399.4	399.5	397.6

Table 3

Comparison of the linear fits utilizing N 1s correlation based on nitrogen-containing functional groups in SAMs with the extension of this approach to include organic species identified on silicon surfaces and on metal surfaces

	Calibration based on SAM only		SAM calibration extended to models on silicon		Calibration including all the models	
	Slope	1	Slope	1	Slope	1
LANL2DZ						
slope	1	0.9625				
offset	9.56	24.24				
R^2	0.9456	0.9471				
MU-error ^a	0.28	0.27				
Max-error ^b	0.76	0.76				
6-311+G(d,p)						
slope	1	0.9416	1	0.9770	1	1.0310
offset	10.03	32.88	9.77	18.76	9.66	-2.46
R^2	0.9615	0.9552	0.9057	0.9065	0.8603	0.8611
MU-error	0.27	0.27	0.39	0.39	0.50	0.50
Max-error	0.67	0.73	1.06	1.07	1.46	1.42

^aMU-error = mean-unsigned error of calculated data vs experimental data.

^bMax-error = biggest error found.