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Calibration of computationally predicted N *1s* binding energies by comparison with X-ray photoelectron spectroscopy measurements

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ABSTRACT

Density functional theory (DFT) predictions of the N *1s* binding energies based on Koopmans' theorem are calibrated and compared with experimental X-ray photoelectron spectroscopy (XPS) measurements of gas phase molecules and surface adducts. A convenient and effective method for comparing these predicted energies to experimental measurements, using para-nitroaniline (p-$NO_2C_6H_4NH_2$) as a spectroscopic "ruler", is presented. The experimental difference between the N *1s* binding energies of the nitrogen atoms from the $-NH_2$ and $-NO_2$ groups of para-nitroaniline is compared to the difference predicted by DFT, using the B3LYP functional with multiple basis sets. Gas phase and molecularly intact condensed multilayer experimental spectra of para-nitroaniline are used to calibrate the predicted binding energies to gas phase and condensed phase (surface adducts) measurements, respectively. A method for improving the agreement with experiment by using the predicted partial charge of nitrogen is also presented.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful analytical spectroscopic technique often used to understand composition and chemical nature of molecules and fragments in the gas phase, in condensed phases, and of species chemisorbed on surfaces. A growing amount of work has used computational predictions to interpret XPS spectra. These predictions mostly focus on the differences between chemical species, environments, and the core-level shifts, rather than the absolute binding energies measured with XPS. This publication details a convenient and simple calibration procedure to compare the results of density functional theory (DFT) investigations with the binding energies measured by XPS. This work also uses the relationship between the partial charge of the element of interest and the binding energy of this element, as an additional correction to these predictions.

There are many methods which employ computational predictions of the XPS core-level shifts. Some of these methods use the partial charge of the element of interest, while other methods use the eigenvalues corresponding to the core-level of interest to predict core-level shifts.

A linear relationship is the most common between the binding energy and the partial charge. This approach has been used for a number of elements [1–15] including nitrogen [9]. This correlation may be improved further when computationally predicting the partial charge by including the effect of the neighboring charges in a so-called potential model [16].

One of the commonly used methods to obtain the binding energy of an electron computationally is to utilize Koopmans' theorem, which approximates the binding energy as the eigenvalue of the core-level of the optimized ground state. It should be noted that formally Koopmans' theorem is directly applicable for the eigenvalues obtained using Hartree Fock method. However, a Koopmans' theorem-like approach can also be used with the Kohn–Sham eigenvalues of DFT predictions which includes electron–electron correlation and may produce a better prediction of the orbital energy level. A more detailed discussion of the difference between Koopmans' theorem and Koopmans' theorem-like predictions [17] and other methods [18] can be found elsewhere. Despite the formal definition, we will refer to using the Kohn–Sham eigenvalues of the core-level to predict the binding energy as Koopmans' theorem in this work. Despite some limitations of Koopmans' theorem with modeling orbital relaxation that can occur during ionization, the so-called "final state effect", these predictions have shown nice agreement with experimental valence-level binding energies [17] and core-level shifts [19].

In principle, to account for orbital relaxation during ionization, the Slater–Janak transition-state model [20,21] and the generalized transition-state model can be used to obtain binding energies based on Janak's theorem, which states that the Kohn–Sham eigenvalue is equal to the derivative of the total-energy functional with respect to the electron occupation number [22]. These methods require calculations where one electron or partial electron density is removed from the core-level. The Slater–Janak transition-

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state model predicts the binding energy from the Kohn–Sham eigenvalue of the core-level when it has half the electron density of one electron removed. The generalized transition-state model predicts the binding energy as the sum of one fourth the Kohn–Sham eigenvalue of the full core-level and three quarters the Kohn–Sham eigenvalue of the same core-level with two thirds of the electron density of one electron removed [23]. The generalized transition-state model has smaller errors in estimating the difference between the final and initial states of the core-level than the Slater–Janak transition-state model. The Slater–Janak transition-state model assumes that the Kohn–Sham eigenvalue is a linear function of electron occupation number. It should be noted that the validity of this assumption was examined in a paper by Goransson et al. [24]. There it was suggested that the accuracy of the Slater–Janak transition-state model could be extended by using the Simpson approximation, which would require a total of three calculations. It should be noted that if one uses a method where electron density is removed from the core-level, such as the Slater–Janak transition-state model or the generalized transition-state model, to describe the core-level binding energy of chemisorbed molecules on metal surfaces that the electron density that is removed from the core-level should be placed in the lowest unoccupied orbital. This should be done because of “metallic screening”, where electrons from the metal substrate transfer to the molecule on the surface, which can result in the binding energy, measured by XPS, being similar to the excitation energy to the lowest unoccupied orbital, measured by X-ray absorption spectroscopy (XAS) [25].

While the Slater–Janak transition-state model and the generalized transition-state model try to approximate the difference between the “initial state” and “final state”, ΔSCF and Δ*E* calculations try to directly calculate this difference. In these methods the “initial state” is modeled as the fully occupied core and the “final state” is modeled as a core that has one electron removed. Chong [26] has reviewed the recent developments in these and other methods and showed that Δ*E*(PW86–PW91)/cc-pCVTZ yields remarkable agreement with gas phase measurements. Gas phase predictions with this method, when the experimental geometry is used, have average absolute deviations (AAD) ranging from 0.10 to 0.20 eV [27]. The AAD for the N *1s* region with this method was 0.20 eV [27]. Gas phase predictions, for the C *1s* region, show even lower deviation, AAD 0.08 eV, when compared to binding energy measurements obtained using a synchrotron source [26].

It is also possible to account for the “final state effects” without calculating the Khom–Sham eigenvalues of partially occupied core-levels by applying the equivalent core method [19,28,29]. This method models the final state as the filled core of the element with the next highest atomic number with respect to the element of interest, keeping the number of electrons constant. When using this method, the difference between the Kohn–Sham eigenvalues of the ground and final states must be related to the difference between the eigenvalues of the ground and final state of a reference compound calculated using the same method. This means that this approach calculates the core-level shift relative to the reference compound chosen.

While all of these methods have been used to predict gas phase XPS spectra with varying accuracy, the XPS experiments analyzing surface species benefit from the computational predictions in the most practical and direct way, as the analysis of the XPS spectra can help in identification of the possible surface species present. There are several difficulties in the prediction of these condensed phase measurements. The first major difficulty that must be overcome is the solid-state effect. The binding energy of an electron of a molecule in the gas phase will be markedly higher than the binding energy of an electron in the same energy level of the same molecule in the condensed phase. Folkesson and Larsson [8] empirically investigated the relation between molar polarizability and the difference between calculated solid state core-level binding energies and previously measured gas phase core-level binding energies. The solid state binding energies where calculated by previously determined relations between partial charge of noncarbon atoms and core-level binding energies [1–7,9–15]. However, the most common way to correct gas phase predictions for this effect is to predict a value to subtract from the gas phase prediction that minimizes the average absolute deviation between the gas phase predictions and the condensed phase measurements: the solid-state work function. This approach works reasonably well when the exact nature of the species present on a surface is known. However, it becomes less practical for the purposes of identification of potential surface species.

In the present work, an experimental measure of the solid-state effect is used to calibrate the gas phase predictions to condensed phase measurements. These gas phase predictions are calibrated to gas phase measurements of para-nitroaniline. The reliable measurements for this compound in gas and solid phase [30] and the presence of two nitrogen-containing functional groups with very different chemical properties make this compound a very attractive molecular “ruler” for comparison with theoretical predictions.

From the results presented in Fig. 1 it can be deduced that para-nitroaniline exhibits shake-up phenomenon; however, the peaks in the N 1s XPS spectra due to this effect can be clearly distinguished from the peaks that are not due to this effect. The shake-up phenomenon for para-nitroaniline has been examined in detail and the more pronounced effect in the condensed phase is explained

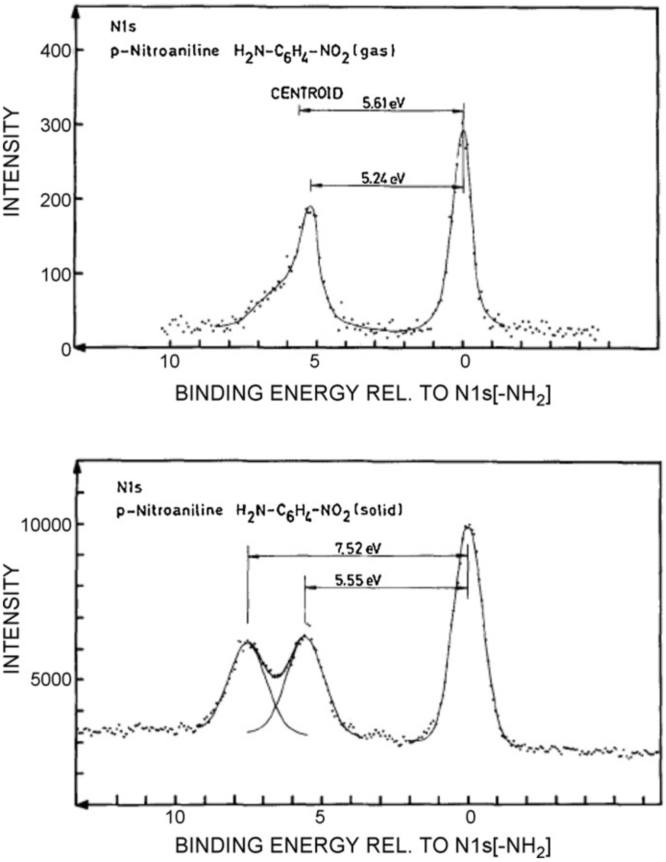

Fig. 1. Gas phase, top, and molecularly intact condensed multilayer, bottom, high resolution N *1s* XPS spectra of para-nitroaniline. Binding energy is reported, in electron volts, relative to the binding energy of the $-NH_2$ group, 406.0 eV and 399.4 eV, for the gas and condensed phase respectively. Reprinted with permission from Agren et al. [30]. Copyright 1982, American Institute of Physics.