On the relation between X-ray Photoelectron Spectroscopy and XAFS

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Abstract. XAFS and X-ray Photoelectron Spectroscopy (XPS) are element specific techniques used in a great variety of research fields. The near edge regime of XAFS provides information on the unoccupied electronic states of a system. For the detailed interpretation of the XAFS results, input from XPS is crucial. The combination of the two techniques is also the basis for the so called core-hole clock technique. One of the important aspects of photoelectron spectroscopy is its chemical sensitivity and that one can obtain detailed information about the composition of a sample. We have for a series of carbon based model molecules carefully investigated the relationship between core level photoelectron intensities and stoichiometry. We find strong EXAFS-like modulations of the core ionization cross sections as function of photon energy and that the intensities at high photon energies converge towards values that do not correspond to the stoichiometric ratios. The photoelectron intensities are dependent on the local molecular structure around the ionized atoms. These effects are well described by molecular calculations using multiple scattering theory and by considering the effects due to monopole shake-up and shake-off as well as to intramolecular inelastic scattering processes.

1. Introduction

X-ray Absorption Spectroscopy (XAS) or X-ray Absorption Fine Structure (XAFS) measurements and core-level X-ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) are two powerful spectroscopic techniques. Both techniques involve the excitation of a core electron. This makes the techniques atom specific and furthermore they provide information about the local structure and electronic structure around individual atomic sites in a system. In XAFS the absorption of a monochromatic X-ray beam is probed as function of the X-ray energy. This is done either by recording the degree of attenuation of the X-ray beam or by monitoring a secondary signal due to the decay of the excited state, such as electrons or fluorescent light, which is considered to be proportional to the absorption. In XPS one is analyzing the kinetic energy of the photoelectrons that are emitted due to the excitation by X-rays of well-defined energy.
XAS or XAFS provides unique information on the structure as well as on the electronic structure of a system [1, 2, 3]. The near-edge regime can be used to study the unoccupied electronic states of a system. The technique can also be used to study the orientation of various molecular species, e.g., adsorbed molecules. Due to the dipole selection rules the XAS intensities will depend strongly on the orientation of the molecule relative to the E-vector of the incident X-rays. In the case of Extended XAFS (EXAFS) the absorption is recorded over an extended energy range above a core level edge. EXAFS gives detailed information on the local arrangement of atoms in terms of bond distances and coordination numbers around the absorbing atomic species. By recording the EXAFS spectra using electron yield measurements, the technique can also be made very surface sensitive. In that case the technique is called Surface EXAFS or SEXAFS.

XPS has unique capabilities for studying the properties of solids and surfaces [4]. Through the chemical shift one can distinguish different chemical species of the same element. The chemical shift also provides information on properties such as charge distribution, oxidation state, ionicity, etc. Much XPS work today is performed using synchrotron radiation. The high brilliance of the synchrotron radiation allows much improved monochromatization of the beam and much higher spectral resolution can be achieved than with a conventional Al K\(\alpha\) X-ray source. The tunability of the excitation source furthermore opens up many more possibilities. By varying the photon energy the cross section of different processes can be modified relative to each other. In certain cases specific transitions can be much enhanced due to resonant photoemission. The tunability also makes it possible to vary the information depth of the probe. The mean free path of the photoelectrons is strongly energy dependent with a minimum, typically at kinetic energies of about 50 eV, corresponding to only a couple of atomic layers [4].

The basis for much of the quantitative use of XPS is that the cross section is considered to be a purely atomic property, whereby the core line intensities can be used as a direct measure of the relative amounts of different atomic species. However, we have recently shown that there are large variations in the cross sections that may extend several hundred eV above the ionization thresholds [5]. It is also well-known that the intensities are affected by elastic scattering and diffraction. This provides a method for obtaining detailed structural information [6, 7] also from photoelectron spectroscopy measurements. This requires that the spectra are recorded with angular resolution. One interesting aspect of this structural technique is that one can separately investigate the diffraction for electrons originating from different chemically shifted species in the system. For electron kinetic energies above several hundred eV the results can often be treated considering only single scattering. In the low kinetic energy regime the scattering angles are larger and multiple scattering becomes important.

In this contribution we discuss some important links between XAFS and XPS. At first we discuss the importance of having access to XPS data for the detailed study of unoccupied electronic states using XAFS. After that we briefly discuss the core-hole clock technique where one can study the time evolution of different core excited states. A combination of XAFS and XPS is often needed in these studies. We then focus on our recent results where we have found strongly non-stoichiometric intensity ratios for the core ionization cross sections in a set of molecular model systems [5]. The connections to EXAFS as well as the implications for the quantitative use of XPS are discussed.

2. X-ray Photoelectron Spectroscopy and the near-edge regime of XAFS

One of the important aspects of the near-edge regime in XAFS is that it probes the unoccupied valence electron states in a system. A core electron at a specific site is excited to an initially unoccupied valence level. Usually the transitions can be accurately interpreted in terms of dipole selection rules. This implies that one obtains a symmetry projected view of the unoccupied electronic structure. For an s core level one reaches p-symmetry states, for a p core level one
Figure 1. X-ray Absorption Spectra (XAS) and X-ray Photoelectron Spectra (XPS) plotted on common energy scales for three different situations. In the XA spectra the photon energy is given while the XP spectra are plotted on a binding energy scale relative to the Fermi level. (a): The 2p to 3d XA and the 2p XP spectra from Ni metal [8]. (b): The N1s to 1\pi_g XA and N1s XP spectra for one monolayer of N_2 physisorbed on graphite [9]. (c): The Ar 2p to 4s XA and 2p XP spectra of Ar physisorbed on Pt(111) [10].

becomes sensitive to the s- and d-symmetry states of that atomic species, etc. By combining results from different core levels one can in this way get very detailed information on the unoccupied density of states of a system.

When interpreting the XAFS results in terms of unoccupied valence electron states it is necessary to account for the effects of the core hole. This requires that the results are combined with information obtained from XPS core-level spectra. First of all one needs to partition the XA energy into two parts, one related to the excitation of a core electron to the Fermi level and one related to the excitation of an electron from the Fermi level to the initially unoccupied valence state. Furthermore, in many cases the core hole may influence the unoccupied states by the additional attractive potential. In order to identify these effects and to be able to account for them it is usually necessary to have access to information from XPS.

In Fig. 1, X-ray Absorption Spectra (XAS) are compared to X-ray Photoelectron Spectra (XPS) for three drastically different situations. Ni(100) [8] represents a metallic system. Nitrogen on graphite [9] and argon on Pt(111) [10] are both weakly adsorbed (physisorbed) systems. In all cases the comparison is made by plotting the spectra on common energy scales. For the XA spectra the photon energy scale is used. For the XP spectra the binding energy is plotted relative to the Fermi level. We immediately note that there are pronounced differences in terms of energy alignment of the XAS and XPS features for the different systems.

In the case of the Ni 2p spectra the two spectra are essentially identical [8]. Ni has an unfilled but nearly filled 3d band. The 2p X-ray absorption process creates a state with a fully occupied 3d-band for this particular system. This implies that the energy of the final state is well-defined which is manifested by a very narrow XA spectrum. The fact that the main peak in XPS occurs at the same energy implies that the same state is created through the screening process. Through the complete screening of the core hole state, the XPS final state corresponds to the lowest core excited state and thus it provides the energy onset for the XA spectrum. This is generally the case for metallic systems. For the empty valence electron states the XPS energy
can thus be viewed as providing the Fermi level position.

Turning to N\textsubscript{2} physisorbed on graphite we note that the XAS absorption feature lies 3 eV below the XPS peak position [9]. The XAS final state is a neutral core excited state. The higher energy of the XPS peak implies that the neutral final state is not reached through screening, although this state is energetically more favorable. The required charge transfer from the substrate is too slow to occur with any significant probability. XPS can therefore not be used to locate the Fermi level in this situation. This energy is instead given by the onset of the XA spectrum.

For Ar physisorbed on Pt(111) we observe the reverse situation. The XAS final state occurs at 3.9 eV higher energy than the XPS feature [10]. The energy difference is again a signature of a very weak coupling between the adsorbate and the substrate. However, in this case the XPS line position corresponds to the lowest core excited state and can therefore be used to locate the position of the Fermi level for the valence electron states as seen in XAS. This energy onset cannot be accurately identified from the XA spectrum. Even if there is some intensity at lower energies than the main resonance, there is no sign of a sharp edge. One interesting aspect of the XAS results for adsorbed Ar is that they can be used to obtain information on the properties of adsorbed potassium atoms. The reason is that a core ionized argon atom is isoelectronic to a potassium atom (equivalent core approximation). From experimental Ar XAS data, combined with calculated corrections for the equivalent core error, one can derive unique information relevant to the properties of potassium adsorbed on a number of different surfaces [11, 12].

3. The core-hole clock technique

One interesting consequence of the fact that different states are reached in the XAS and XPS processes, as shown in Figs. 1b and c, is that characteristically different core-hole decay spectra are obtained for the two processes. In certain cases this provides a way to study the time evolution of the different excited states. Even if the screening for the weakly bonded systems in Figs. 1b and c is slow it occurs on a time-scale, comparable to the time scale of the core-hole decay. These processes will lead to characteristic features in the decay spectra that can be studied in different situations. This is the basis for the so called core-hole clock technique [9, 13, 14].

In the case of N\textsubscript{2} physisorbed on graphite, the Auger decay spectra after an N1s core ionization contains additional features characteristic of the decay from a neutral excited state. As seen from Fig. 1b, XPS produces only the ionic state. This implies that the neutralized state has been reached through a charge transfer process from the substrate to the molecule that occurs during the life-time of the core-hole. By measuring the intensity ratio between the two types of decay features, originating from neutral or ionic initial states, respectively, and by knowing the core hole decay rate, the charge transfer rate can be determined. For Ar/Pt(111), as seen in Fig. 1c, a related behavior is observed. In this case the neutral 2p\textsuperscript{-1}4s core excited state may become ionized through electron hopping to the substrate before the Auger decay process. Again, signatures characteristic of neutral and ionic adsorbate states are observed in parallel and the hopping rates from the adsorbate to the substrate can be determined from the observed intensity ratios between the two types of decay spectra.

The core-hole clock technique can provide information on different processes, which are difficult to study in other ways. The lifetimes of many frequently used core levels are in the low fs time regime, which opens up the technique for various ultrafast phenomena. It has for instance been used to determine the charge transfer rate for one of the fundamental subprocesses in a model system for a dye sensitized solar cell [15]. By using more short-lived core hole states, the technique has also been used to study processes in the attosecond regime [16].
4. Electron scattering effects in Photoelectron Spectroscopy

XAFS and XPS are related also in another important way. In both techniques the elastic scattering of the excited electrons plays an important role. In EXAFS the X-ray absorption is measured as function of photon energy. The absorption occurs at a specific site where a core electron is excited to the continuum. The photoelectron wave may then be backscattered against the neighboring sites in the lattice. This leads to interference effects which manifest themselves as modulations of the absorption cross section as the photon energy is varied. This provides important information about the local structure around individual sites in the system. One of the important aspects of this technique is that it does not require any type of long range order of the system.

In the case of Photoelectron Diffraction (PhD) one is analyzing the emitted photoelectrons in an angular resolved way [6, 7]. The interference between the directly emitted and the various scattered waves creates a characteristic angular pattern from which structural information can be deduced. One advantage with this technique is that one can separately obtain structural data from chemically shifted components for the same element. PhD measurements can be performed in two different ways. One possibility is to measure the photoemission intensity as function of emission angle at a fixed energy. Another possibility is to perform the measurements at a fixed angle but by varying the photon energy. The photoelectron diffraction technique requires short-range order, although not necessarily long-range order. For disordered systems it is generally assumed that all diffraction effects cancel and that they do not need to be considered. This assumption lies behind much of the use of photoelectron spectroscopy for detailed quantitative analysis.

However, when measuring angle integrated photoelectron spectra from solids, Rothberg et al. observed pronounced photon energy dependent intensity modulations [17]. The results were compared to EXAFS data for the same system and it was concluded that the photon energy dependent variations could be interpreted in the same way as EXAFS. This was proposed to provide an alternative way to record EXAFS spectra and the acronym Photoelectron EXAFS or PEXAFS was introduced. This technique has then the additional advantage that one can use the chemical sensitivity provided by photoelectron spectroscopy to separately study different chemical species of the same element. PEXAFS has been used in a number of structural studies, e.g. for semiconductor surfaces [18, 19, 20] where the results have been interpreted using EXAFS codes.

The proposal that the PEXAFS measurements create results identical to EXAFS has, however, been questioned. First of all, from theoretical considerations it has been concluded that even a $2\pi$ integration of the photoemission signal is insufficient in order to yield the EXAFS spectrum [21, 22]. The foundations for PEXAFS has also been investigated experimentally. Scanned energy PhD spectra were recorded by Toomes et al. for a large range of angles for a disordered surface of oxygen adsorbed on Cu(111) [23]. They found that very similar spectra were obtained at all investigated angles. From this they concluded that these spectra also represent the angle integrated results. These spectra were then compared to results obtained by SEXAFS for the same surface. They found first of all that the intensity modulations in PEXAFS were much more pronounced than in SEXAFS. Furthermore, when analyzing the PEXAFS results using EXAFS theory, quite different results were obtained in terms of bond distances and coordination numbers as compared to SEXAFS. The conclusion from this investigation was therefore that the angle integrated photoelectron spectroscopy results obtained in this way are still much affected by PhD effects.

In order to investigate the photon energy dependence of the photoemission intensity in more detail we have performed measurements for a series of molecular model systems in the gas phase. This choice of systems has several advantages. The gas phase molecules are by nature randomly oriented. In this way we can perform measurements that correspond to a complete
Figure 2. Experimental spectra of CH$_3$CCl$_3$, CH$_3$CHCl$_2$ and CH$_3$CH$_2$Cl. All spectra used to determine intensity ratios in the present investigation have been recorded at the magic angle. The spectrum of CH$_3$CH$_2$Cl shown in this figure, however, was recorded at an angle of 0° between the polarization vector and the direction of the escaping photoelectrons in order to maximize intensity and reduce statistical errors. The right-hand panels show for each molecule the measured C1s intensity ratio between the Cl substituted and non-substituted carbon atoms as function of photon energy. The solid lines are the calculated ratios using the FEFF code, see text.

$4\pi$ integration of the photoemission intensities. We have furthermore chosen molecules that contain the same element in different chemical environments. In this way one can measure intensity ratios between chemically shifted peaks in the same spectra instead of monitoring absolute intensities originating from individual atomic species, whereby all normalization issues are avoided. Furthermore, the concentration ratios are exactly known. All measurements used in the cross section determinations have been performed at the magic angle of 54.7° between the polarization direction of the ionizing x-rays and the propagation direction of the escaping photoelectron to avoid any angular dependent effects.

In one series of measurements we have recorded the C1s core level intensities for CH$_3$CCl$_3$, CH$_3$CHCl$_2$, and CH$_3$CH$_2$Cl over a wide photon energy range [5]. Examples of high resolution C1s photoelectron spectra for the three molecules are shown in the left hand panels of Fig. 2. The spectra in Fig. 2 have been fitted using a number of vibrational components. The parameters derived from these fits have then been used to fit all the spectra recorded at different photon energies in order to derive accurate intensity ratios.

The experimental intensity ratios for the three molecules are shown in the right hand panels of Fig. 2. In all cases we note large oscillations of the intensity ratios as function of photon energy. The oscillations extend several hundred eV above the C1s ionization threshold. In Fig. 3 we compare the experimental intensity ratios for the three molecules. We immediately
Figure 3. Comparison of the photon energy dependent C1s intensity ratio between the Cl substituted and non-substituted carbon atoms for CH$_3$CCl$_3$, CH$_3$CHCl$_2$ and CH$_3$CH$_2$Cl. The experimental lines are connected by dotted lines in order to help separating the three curves.

We see that the oscillatory pattern is very similar for the three molecules and that the amplitude of the oscillations increases with the number of Cl atoms in the molecule. The oscillations are damped with energy and the intensity ratios approach asymptotic values at high photon energies, significantly different from the stoichiometric ratio of one. The asymptotic intensities are lower for the chlorine substituted carbon atoms and they decrease as the number of chlorine substituents increases.

We interpret the oscillations as due to an EXAFS-like modulation of the photoionization cross section, dominated by backscattering from the chlorine atoms. In order to test this assumption we have performed theoretical multiple-scattering calculations using the latest FEFF codes [3, 24]. The calculations include Debye-Waller factors, chemical shifts, and estimates of inelastic losses. The calculated intensity ratios are compared to the experimental results in Fig. 2. We have in this figure normalized the FEFF calculated ratios to match the experimental values at our highest photon energies. It is immediately clear that the theoretical (FEFF) results describe the observed intensity variations very well. We therefore conclude that the observed intensity oscillations are entirely due to the variations in the absorption cross section. Furthermore, we find that they can be handled to a good approximation by present theoretical tools. These findings are consistent with the predicted equivalence between angular integrated photoemission spectra and x-ray absorption spectra (XAS), provided that a full 4$\pi$ integration can be performed [22].

We have also performed measurements for a number of other molecules that support the present picture. We have for instance investigated molecules where the different carbon atoms have very different types of atomic coordination, such as ethyl trifluoroacetate (CF$_3$-CO-O-C$_2$H$_5$), a molecule that has been frequently used as a showcase of chemical effects in photoelectron spectroscopy (see e.g. Ref.[25]). This leads to characteristically different oscillatory patterns for the different carbon atoms. Again the results are well reproduced by the FEFF calculations. These results will be presented in forthcoming publications.

We also need to consider the fact that the measured intensity ratios approach values that are different from the stoichiometric ones at higher photon energies. This is due in part to shake-up...
and shake-off processes, which transfer intensity from the main line to a satellite spectrum. This has also to be accounted for when photoelectron spectroscopy is used quantitatively. According to the Manne - Åberg theorem [26] the shake probability is linked to the relaxation energy and hence to the core level shifts. The chemical shifts are due to the combined effect of ground state effects, which can often be discussed in terms of charge transfer, and relaxation effects. From Fig. 2 we see that each electronegative chlorine substituent causes a C1s shift to higher binding energies. This is consistent with the expectations from a simple ground state model since the chlorine substituents make the carbon atoms more positive. However, a detailed treatment of core-level shifts requires much more elaborate considerations. Especially one needs to take the relaxation effects into account. From our calculations we see that the relaxation energy increases with the number of polarizable chlorine substituents. According to the Manne - Åberg theorem [26] this is consistent with a larger shake probability and hence to a reduced main line intensity for the chlorine substituted carbon atoms, as seen in Fig. 2.

The sum of the intensity of the monopole shake-up and shake-off processes can be calculated from the square of the overlap integral, $S_0^2$, between the initial-state wave function with the active core electron annihilated and the relaxed final state wave function. This value is typically around 0.75 for the present C1s ionizations. However, the detailed value depends on the atomic coordination and it gets consistently lower as the number of chlorine substituents increases. We have also considered one additional process, which is usually not accounted for in free molecules. We denote this process intramolecular inelastic scattering. This is a loss due to the propagation by the photoelectron through the ionized molecule. This effect can be estimated semiclassically [27], in terms of the density-dependent mean-free path of the photoelectron, and it yields further energy dependent reductions. The calculated ratios originating from these two processes range from 0.85 - 0.91 for CH$_3$CCl$_3$, 0.90 - 0.95 for CH$_3$CHCl$_2$ and 0.94 - 0.97 for CH$_3$CH$_2$Cl, over the photon energy range from 400 - 800 eV. These values vary roughly linearly with the number of Cl atoms in agreement with experiment and they are comparable to, although somewhat higher than the experimental values of 0.79, 0.88, and 0.96. The discrepancies are likely due to the approximations used in the calculations. Correlation effects are for instance not included in the calculation of the factors $S_0^2$. Furthermore, we do not know if the experimental ratios have fully converged at the highest photon energies used in the present experiment.

Our results are important in connection with the use of photoelectron spectroscopy for detailed analytical purposes. This technique is normally considered to be quantitative in a very accurate way. Most often it is assumed that the cross section is an atomic property, largely independent of the surroundings. It is furthermore assumed that elastic scattering effects can be neglected for disordered systems. It is, however, clear that one has to go beyond this approximation. The core ionization cross section is a property of the absorbing atom as well as of its surrounding atomic shells. This is in particular the case for relatively low photoelectron kinetic energies. This energy regime is often of special interest since it optimizes the surface sensitivity of the probe. When performing surface sensitive measurements it may also be of interest to vary the information depth. Within certain limits this can be made in two different ways. One possibility is to change the effective information depth by varying the angle of emission for the photoelectrons. This requires a relatively well-defined surface. For complex samples, for instance liquid samples, depth-profiling must be made in a different way. In that case one can achieve different information depths by recording spectra at different photon energies, leading to different kinetic energies of the photoelectrons. This, however, requires that one can distinguish the intensity variations caused by different probing depths and different relative abundancies of the probed species from those variations that are due to photon energy dependent cross section variations [5, 17, 23, 28, 29].

For the present molecular system, studied in the gas phase, the necessary corrections can be accurately obtained by applying the FEFF code to account for the scattering effects and
by calculating the $S_2^0$ factors and the effects of intramolecular inelastic scattering in order to estimate the intensity reduction due to shake-up and shake-off. For condensed systems the same type of calculations can provide a first approximation for the necessary cross section corrections. However, more experimental and theoretical work is needed in order to determine what additional corrections have to be made when studying solid samples, considering the fact that a $4\pi$ integration is no longer possible to achieve. The results by Toomes et al. [23] indicate that also for a disordered solid system there remain strong PhD effects. However, the adsorbate system that was used in their study cannot be considered to be a completely random system and further studies are needed in order to develop a strategy for handling the necessary corrections for condensed samples. Studies of a liquid system could provide additional information on the cross section variations for a truly disordered system.

5. Summary
There are important links between XAFS and XPS. When using XAFS to study the unoccupied electronic structure, the XPS core level spectra are needed for instance in order to determine the Fermi level position for the unoccupied electronic states. By comparing the results from the two techniques one can also derive important information on the character of the chemical bonds in a system. The comparison between XAFS and XPS is also important when investigating the dynamics of various excited states and for the use of the so-called core-hole clock technique. For a molecular model system we have furthermore shown that the core level photoionization cross sections show strong modulations as function of photon energy, which for these molecular systems can be directly related to EXAFS. The observed intensities are also affected by shake-up and shake-off processes, the magnitude of which are depending on the chemical surroundings of the ionized atoms. These effects lead to strongly non-stoichiometric core level intensities. This has important consequences when using XPS for quantitative purposes. We show that the present molecular results can be accurately reproduced by FEFF calculations for the intensity modulations, by calculating the monopole shake-up and shake-off intensities by standard quantum chemical methods and by considering losses due to intramolecular inelastic scattering in terms of the density-dependent mean-free path of the photoelectrons.

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Appendix A. Experiment
The measurements were performed at the PLEIADES beamline at the SOLEIL national synchrotron radiation facility, France. The beamline uses two quasi-periodic undulators with 256 mm and 80 mm period to cover the 7-400 eV and 35-1000 eV energy ranges, respectively, with any kind of polarization available from 55 eV. The plane grating beamline operates without entrance slit and it is equipped with four varied line spacing gratings. The gratings have varied groove depths in the direction perpendicular to the beam propagation axis allowing optimization of the grating efficiencies throughout the whole energy range. An ultimate resolving power of approximately $10^5$ is achievable at 50 eV. In this study we especially made use of the high photon flux available at relatively high photon energies [30]. Some of the characteristics of the beamline can e.g. be found in Refs. [31, 32, 33].
The measurements were performed using a wide-angle lens VG-Sciento R4000 electron spectrometer installed at a fixed position, with the electron detection axis perpendicular to the storage-ring plane. The polarization vector of the X-ray light has been set at the magic angle of 54.7° with respect to the electron detection axis. The analyzer was also mounted perpendicular to the propagation direction of the ionizing radiation i.e. in the so-called dipole plane in order to minimize non-dipole effects. The degree of linear polarization of the photon beam was better than 98%.

The samples were used to fill a differentially pumped gas cell equipped with a series of electrodes allowing to compensate the local potentials (so called plasma potentials) associated with the ion density gradient created along the beam propagation axis within the gas cell.

The total instrumental broadening was less than 250 meV for all the spectra. The spectra were fitted with PCI profiles [34] with calculated asymmetry parameters using IgorPro with the SPANCF curve fitting package [35]. The fits were used to derive accurate total peak intensities. For some photon energies additional peaks, such as chlorine derived Auger transitions had to be added. The Gaussian line width parameters were constrained to be the same for all of the components in a spectrum, and the Lorentzian line width parameters had to be the same for all of the components within a given peak.

Appendix B. Theory

The XAS calculations were carried out using the real-space multiple-scattering code FEFF9 [24]. Muffin-tin scattering potentials and phase shifts were calculated self-consistently for configurations including a core-hole. The spectral intensities were calculated as \( \mu_i = Z_i \mu_{0i}(1 + X_i) \), where \( \mu_{0i} \) is the atomic background cross-section in the one-electron approximation, \( X_i \) is the extended fine structure for the carbon atom \( C_i \), and \( Z_i = S^2_{0i} A_i \) is an amplitude reduction factor that accounts for intrinsic and intramolecular scattering losses. The quantity \( S^2_{0i} \) corresponds to the fraction of photoelectrons emitted without shake-up or shake-off. The X-ray absorption was calculated for each carbon site using the multiple-scattering path expansion in FEFF from 300 - 1000 eV, with about 300 paths. Ab initio Debye-Waller factors at 300K were included, obtained using the Lanczos algorithm in Ref. [36] with a dynamical matrix calculated using Gaussian03. The atomic background absorption \( \mu_{0i} \) was calculated in the dipole approximation. Since the embedded atomic potentials are nearly identical for the substituted (C\(_{Cl}\)) and non-substituted (C\(_{H}\)) carbon atoms, these factors cancel in the calculated ratios \( R = \mu_{C_{Cl}}/\mu_{C_{H}} \). The observed oscillatory structure is approximately given by the difference \( X_R \approx X_{C_{Cl}} - X_{C_{H}} \). This fine structure is dominated by the scattering from the Cl atoms in the C-Cl bonds, since the C-C scattering cancels to leading order in the ratios, and C-H-scattering is negligible.

Estimates of \( S^2_{0i} \) were calculated from \( S^2 = |\langle 0 | 0' \rangle| \) overlap integrals between single determinant, restricted Hartree-Fock wave functions from the Gaussian03 code. The results show that the overlap integrals are dominated by atomic relaxation and that they are quite similar for both C atoms. For CH\(_3\)CCl\(_3\), for example, we obtain 0.708 for the CCl hole and 0.755 for the CH hole, yielding an intrinsic ratio of 0.937. Moreover there are substantial contributions from intramolecular inelastic scattering. These have been estimated semi-classically in terms of the energy dependent mean free path of the photoelectron, averaged over solid angle. This quantity is strongly energy dependent, and yields ratios varying from about 0.90 to 0.96 between photoelectron energies 100 and 400 eV above threshold (photo energies between about 400 to 700 eV). Consequently the net ratio is a combination of monopole shake-up and shake-off and intramolecular scattering losses.
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