

Nonstoichiometric Intensities in Core Photoelectron Spectroscopy

J. Söderström,¹ N. Mårtensson,¹ O. Travnikova,² M. Patanen,² C. Miron,² L. J. Sæthre,³ K. J. Børve,³ J. J. Rehr,⁴ J. J. Kas,⁴ F. D. Vila,⁴ T. D. Thomas,⁵ and S. Svensson¹

¹*Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden*

²*Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France*

³*Department of Chemistry, University of Bergen, Allégaten 41, NO-5007 Bergen, Norway*

⁴*Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560, USA*

⁵*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA*

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X-ray photoemission spectroscopy is used in a great variety of research fields; one observable is the sample's stoichiometry. The stoichiometry can be deduced based on the expectation that the ionization cross sections for inner-shell orbitals are independent of the molecular composition. Here we used chlorine-substituted ethanes in the gas phase to investigate the apparent carbon stoichiometry. We observe a nonstoichiometric ratio for a wide range of photon energies, the ratio exhibits x-ray-absorption fine structure spectroscopy (EXAFS)-like oscillations and hundreds of eV above the $C1s$ ionization approaches a value far from 1. These effects can be accounted for by considering the scattering of the outgoing photoelectron, which we model by multiple-scattering EXAFS calculations, and by considering the effects of losses due to monopole shakeup and shakeoff and to intramolecular inelastic scattering processes.

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Innershell ionization of atoms in molecules is expected to be essentially an atomic process. Even though inner-shell ionization energies depend on the molecular composition, this dependence arises primarily from differences in the distribution of the valence electrons and not from differences in the inner-shell orbitals. We might, therefore, expect that the ionization cross sections for inner-shell orbitals would be independent of the molecular composition. However, experience (our own, mostly unpublished, data) indicates that this is not the case. For instance, for $C1s$ ionization of 1,1,1-trichloroethane (CH_3CCl_3) at a photon energy of 330 eV the intensity of the peak attributed to the CCl_3 carbon in the photoelectron spectrum is only about half of that for the peak attributable to the CH_3 carbon. Similarly for the $C1s$ photoelectron spectrum of 2-butyne (CH_3CCCH_3), the intensity for the two central, triply bonded carbon atoms is less than 80% of that for the two terminal, singly bonded carbon atoms. We have also observed similar behavior from several other molecules, which will be discussed in forthcoming publications. Although such anecdotal evidence has long been known, no systematic studies of the relationship between intensity and the stoichiometry of the molecule have been reported. Here we present such a study of the carbon $1s$ photoelectron spectra of three chlorinated ethanes over a wide range of photon energies.

We find (1) that the relative intensities of the peaks in the photoelectron spectra fail to reflect the molecular stoichiometry over the entire range of photon energies, (2) that the ratios of the peak intensities show an oscillatory behavior similar to what is seen in extended x-ray-absorption fine structure

(EXAFS) spectroscopy, (3) that the amplitude of the oscillations increases with the number of chlorines, and (4) that the nonstoichiometric intensities persist even at photon energies several hundred eV above threshold. These results have important consequences for any attempt to use inner-shell spectroscopy as a quantitative analytical tool or for analysis of the photoelectron spectra of complex molecules, especially where the analysis of overlapping peaks might be simplified by the assumption of stoichiometric intensity ratios.

In order to make a systematic investigation, we have studied the $C1s$ core level intensities from the series of molecules CH_3CCl_3 , CH_3CHCl_2 , and $\text{CH}_3\text{CH}_2\text{Cl}$ over a wide range of photon energies. The measurements were performed at the PLEIADES [1] beam line, which has been described in previous publications [2–4], at the SOLEIL synchrotron in France; details of the experimental procedure are described in the Methods section. Instead of monitoring the absolute intensities of the individual carbon atoms we consider the intensity ratio between two chemically shifted $C1s$ peaks recorded in the same spectrum (similar to those presented in Fig. 1). In this way all normalization issues are avoided and, furthermore, the concentration ratio is exactly known (in this case 1:1). In addition, gas-phase molecules are by nature randomly oriented, and the measurements are made 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. Thus the measurements are equivalent to a complete 4π integration of the photoemission intensities. See Supplemental Material (Ref. [5]) for the experimental details.

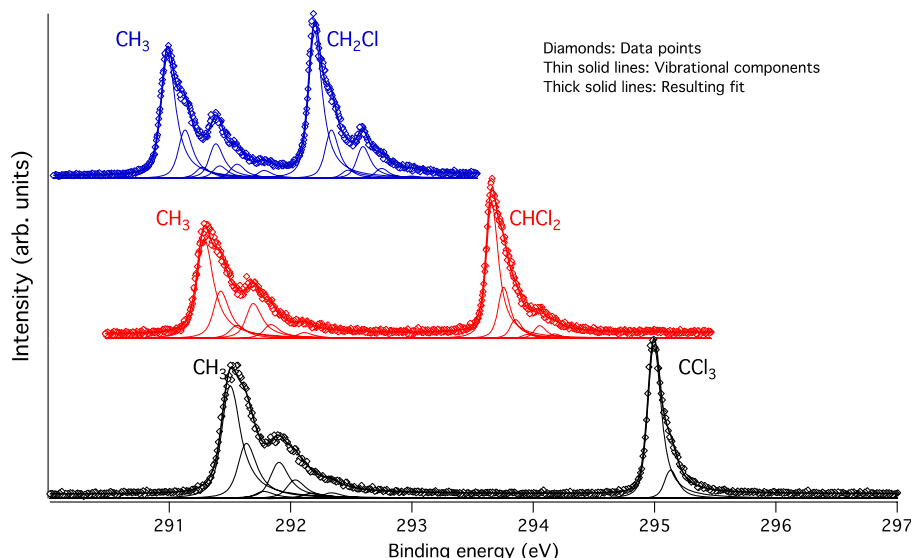


FIG. 1 (color online). High-resolution $C1s$ photoionization spectra of CH_3CCl_3 , CH_3CHCl_2 , and CH_3CH_2Cl . Fitted vibrational components (see Methods section) are included, shown in thin lines. The spectra are all recorded at a photon energy near 340 eV. The spectra of CH_3CHCl_2 and CH_3CH_2Cl are recorded at the magic angle, while the spectrum of CH_3CCl_3 is recorded at an angle of 0° between the polarization vector and the escaping photoelectrons.

As an example of the quality of our experimental data high-resolution $C1s$ photoelectron spectra of CH_3CCl_3 , CH_3CHCl_2 , and CH_3CH_2Cl are shown in Fig. 1. The spectra of CH_3CHCl_2 and CH_3CH_2Cl are recorded at the magic angle, while the spectrum of CH_3CCl_3 is 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 spectra have been fitted using a number of vibrational components as shown in the figure; details of the fitting procedure are described in the Supplemental Material [5]. The parameters derived from these fits (most importantly the lifetime widths and relative energies of the vibrational components) are then used to fit a series of spectra recorded for different photon energies, all recorded at the magic angle. The fits have been used to derive intensity ratios for all the spectra. The same procedure for determining the spectral intensities has been used for all three molecules.

In Fig. 2 the $C_{Cl}1s/C_H1s$ intensity ratios for CH_3CCl_3 , CH_3CHCl_2 , and CH_3CH_2Cl are displayed as a function of excitation energy, where C_{Cl} denotes the chlorine-substituted carbon atom and C_H the CH_3 carbon atom. The most striking observation is the large oscillations in the intensity ratios as a function of photon energy. These oscillations extend over a range of several hundred eV above the $C1s$ ionization threshold. We interpret the oscillations as arising from an EXAFS-like modulation of the photoionization cross section that is dominated by back-scattering from the chlorine atoms, and this interpretation is supported by theoretical multiple-scattering calculations using the latest FEFF codes [6,7]. In support of this view, we note that if we plot the ratio as a function of momentum the

period of the oscillations is approximately consistent with the carbon-chlorine bond length and that their amplitude increases progressively with increasing number of chlorine atoms. Furthermore, we note that the oscillatory pattern is damped with energy and approaches an asymptotic value at high photon energies. This value is below one, and decreases as the number of chlorine substituents increases. We interpret this as being due to a higher probability for inelastic losses (i.e., shakeup or shakeoff processes) for the more chlorine-substituted carbon atoms, which remove intensity from the main lines. The shakeup or shakeoff intensity is broadly distributed and mainly observed in the energy range 10–60 eV above the main lines. It is not possible to separate the shake spectrum into individual contributions corresponding to the two chemically shifted main lines. However, according to the Manne-Åberg sum rule [8] the shake probability is linked to the relaxation energy. We see from our calculations that the extra-atomic relaxation energy increases with the number of polarizable substituents, which is consistent with a larger shakeup intensity and hence to a reduced main line intensity. Note that interference effects, such as those observed in Ref. [9] are negligible in this case due to the large chemical shift of the $C1s$ orbitals in question. Furthermore these differences in ionization energies are so small that they have a negligible effect on the observed ratios, especially for photon energies far above threshold.

In order to test the assumption that the wiggles are due to EXAFS-like oscillations we have compared the experimental results to calculations including Debye-Waller factors, chemical shifts, and estimates of inelastic losses. This comparison is shown in Fig. 2, where it can be seen that the

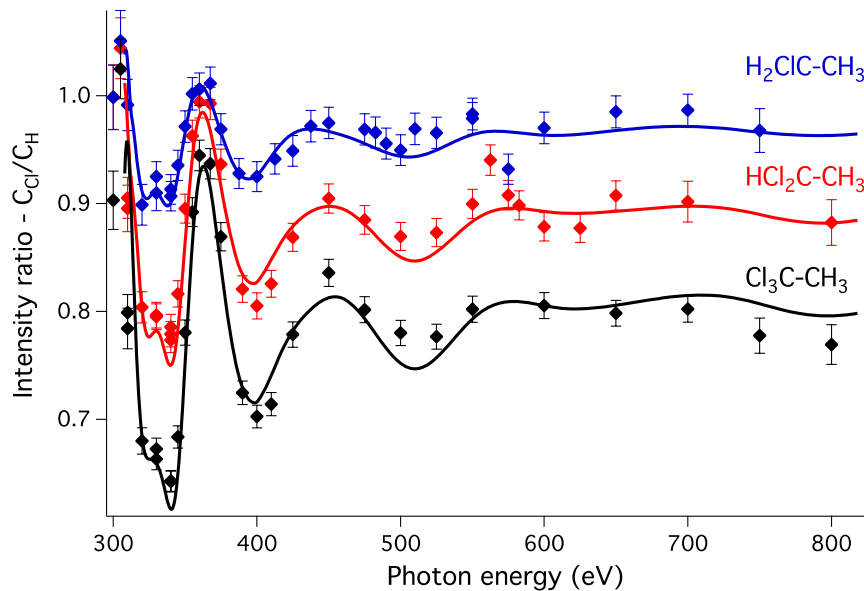


FIG. 2 (color online). The $C_{Cl}1s/C_H1s$ intensity ratios for CH_3CCl_3 , CH_3CHCl_2 , and CH_3CH_2Cl as a function of excitation energy. The diamonds are experimental data points with error bars that have been estimated from the scatter of the results obtained from duplicate experiments or from alternate approaches to analyzing the data. The theoretical results (solid lines) are based on FEFF XAS calculations including Debye-Waller factors, chemical shifts, and inelastic losses. The theoretical ratios have been normalized to agree with the experimental results at high energy, as discussed in the text.

theoretical (FEFF) results describe the observed intensity variations very well in all three cases. We therefore conclude that the oscillations in the relative intensities are due to the variations in the absorption cross section, and that they can be handled to a good approximation by present theoretical tools, consistent with the predicted equivalence between angular integrated photoemission spectra and x-ray absorption spectra (XAS) [10].

At high photon energies, the asymptotic values of the calculated ratios are 1, but the asymptotic values of the experimental ratios are, as noted, less than 1. For the comparison between experimental and FEFF results in Fig. 2 we have therefore normalized the FEFF calculated ratios to match the experimental values at our highest photon energies. As already stated, we interpret this lowering of the ratios as due to multielectron excitations, i.e., excitations due to monopole shake and intramolecular inelastic scattering losses, which remove intensity from the main $C1s$ lines. The monopole shakeup and shakeoff losses 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 reduces the strength of the signal by factors $S_0^2 \approx 0.75$ which differ by a few percent between the two carbon atoms in these molecules and are consistently lower for the C_{Cl} carbons than for the C_H carbons. In addition intramolecular inelastic scattering losses in propagation can be estimated semiclassically [11], in terms of the density-dependent mean-free path of the photoelectron $\lambda(k)$, yielding further energy dependent

reductions. Combining these results, the calculated ratios from both inelastic processes range from 0.85–0.91 for CH_3CCl_3 , 0.90–0.95 for CH_3CHCl_2 , and 0.94–0.97 for CH_3CH_2Cl , over the photon energy range from 400–800 eV. These vary roughly linearly in the number of Cl atoms in the molecule in agreement with experiment and are comparable to, although somewhat higher than the values 0.79, 0.88, and 0.96 observed in Fig. 2. The additional normalization factors used to match the theoretical results with the experimental results are 0.88, 0.94, and 1.00, respectively. See Supplemental Material [5] for a more detailed description of the theoretical framework.

Pronounced photon energy dependent intensity modulations have previously been reported in angle-integrated photoelectron spectra from solids [12]. It was proposed that the photon dependent variations could be interpreted in the same way as EXAFS, and the acronym PEXAFS (photoelectron EXAFS) was introduced. PEXAFS has later been used in a number of structural studies. See, e.g., Refs. [13–15]. This direct analogue was, however, questioned with the following arguments. From theory it was concluded that not even a full 2π integration of the photoemission signal emitted from a surface is sufficient to yield the EXAFS spectrum [10,16]. In an experimental comparison of PEXAFS and surface EXAFS (SEXAFS) for a disordered surface of oxygen adsorbed on Cu(111) [17] it was found that the intensity modulations in PEXAFS are much more pronounced, and furthermore, the two techniques yield different bond distances and coordination numbers. Hence, it was concluded that the

observed modulations in angle-integrated photoemission spectra from solids are still dominated by photoelectron diffraction [17]. An interesting theoretical discussion of the behavior of the photoionization cross sections, of interest for this study, has also recently been published in Ref. [18].

With today's experimental techniques it is possible to isolate and study the true cross section variations only with the present type of molecular model systems as discussed here. It is of utmost importance to understand these effects since relative cross sections are frequently used when studying quantitative aspects in a variety of situations. This is, for instance, the case for studies of liquids where practically no other methods are available for studies of the detailed composition of the surface.

In conclusion, we have observed an "EXAFS-like" oscillation of the intensity ratios between the two chemically shifted core photoelectron lines in a series of chlorinated ethane molecules. Our results show that the relation between stoichiometry and intensity in the core photoelectron spectra is much more complex than what has been previously assumed. We have performed theoretical calculations including the effects of inelastic losses that quantitatively describe the behavior of the cross section ratios, and we have outlined a strategy to handle the relation between core photoelectron peak ratios and stoichiometry.

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