Supporting information for: Energy Dependent Relative Cross Sections in

Carbon 1s Photoionization. Separation of Direct Shake and Inelastic Scattering Effects in Single Molecules

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1 Subtraction of the background in C 1s electron spectra of chloroethanes at high energies ($h\nu > 2keV$)



Figure S1: Carbon 1s photoelectron spectra of tri(1,1,1)-chlroethane recorded at a photon energy of 5000 eV: (a) zoom on kinetic energy range of C 1s photoelectron lines and (b) larger kinetic energy range, showing contributions from Cl 2s photoionization. Red circles represent experimental data, black curve – fit to the experimental data, using C_{CCl₃} and C_{CH₃} C 1s contributions (thin blue and green lines, respectively) and Cl 2s shake-up contributions (purple filled curve). Cl 2s photoelectron line and corresponding shake-up contributions were modeled using Cl 1s photoelectron line (shown as dashed blue line in panel (b)) recorded at the same energy and shifted by 2551.6 eV. Dotted blue curve in (a) is a residue of the fit.

In the case of the chloroethanes we observed a strong background from Cl 2s shake contributions. Subtraction of this was made using a model taken from a Cl 1s shake spectrum.

For high-energy measurements in the case of the chloroethanes, C 1s photoelectron lines are embedded on the background from Cl 2s shake contributions. Subtraction of this was made using a model taken from a Cl 1s shake spectrum. In order to do this Cl 1s photoelectron spectra were recorded at the same time as the C 1s ones. The Cl 1s photoelectron spectrum was than shifted by about 2550 eV to match Cl 2s photoelectron lines and fitted using additional Lorenzian and Gaussian contributions to account for differences in Cl 2s/1s lifetimes and differences in Doppler broadenings due to different kinetic energies of Cl 2s/1s photoelectrons. The profiles of the convoluted Cl 1s spectra presented a very good description of the background in C 1s photoionization spectra of chloroethanes. Theoretical profiles were used to fit $C_{CH_xCl_{3-x}}$ and C_{CH_3} C 1s photoelectron lines of chloroethanes. One example of this procedure is shown in Fig. S1 for trichloroethane recorded at 5000 eV.

2 Understanding the $C=O/CF_3$ ratio for the ESCAfamily members.

Central to the results presented in Figure 4 is the understanding of the magnitude of the various effects, and how they determine the ratios as a function of photon energy. Part of this information is available from theoretical calculations. The theoretical curves are produced as products of three contributions: the XAS oscillation, the energy-dependent intramolecular inelastic scattering (IIS), and the energy-independent direct shake (DS). IIS was calculated as extrinsic amplitude reduction factors using a semi-classical expression for the electron propagator, and a local density approximation for the inelastic mean free path (IMFP). DS processes are estimated from S_0^2 , the square of the overlap integral between the initial state wave function and the relaxed final-state wavefunction with the active core electron annihilated. Figure S2 compares the effect of XAS and IIS for S-ESCA and ESCA. It is seen that below 400 eV the ratio of XAS for S-ESCA is considerably smaller than for the ESCA molecule. This is reversed for the 400-500 eV range. The reduction effect of IIS is clearly larger for S-ESCA than ESCA, making the products of the two effects more similar to each other. The third contribution to the spectrum, the DS factor, may be found from Table S1. The absolute values for CF_3 and C=O are both smaller for S-ESCA than for ESCA. In addition the $C=O/CF_3$ ratio is smaller, reducing the difference between the two curves somewhat more.

Figure S2 shows that theory overestimate the XAS component of the $C=O/CF_3$ ratio between 400–500 eV. To understand this in more detail, Figure S3 compares the XAS amplitudes of CF₃ and C=O for S-ESCA and ESCA. It is interesting to note that while the CF₃ amplitudes are almost unchanged, the variation is more pronounced for C=O, particularly below 500 eV. This is consistent with the experimental results showing that the difference in the C=O/CF₃ ratio between S-ESCA and ESCA is due to the different effect of sulfur compared to oxygen on the C=O amplitude.



Figure S2: The ratios of C 1s cross sections of $C_{C=O}$ and C_{CF_3} carbon sites, *i.e.* XAS amplitudes, (red curves); the ratios of the corresponding extrinsic amplitude reduction factors (blue curves) and their product (green curves) for (a) S-ethyl trifluoroacetate (S-ESCA) and (b) ethyl trifluorothioacetate (ESCA).

3 Direct shakes for the ESCA-family members

Table S1: Calculated direct shakes (DS) and their ratios relative to CF_3 (CX/CF₃) for ethyl trifluoroacetate (ESCA), methyl trifluoroacetate (M-ESCA). and S-ethyl trifluorothioacetate (S-ESCA).

Carbon	ESCA		M-ESCA		S-ESCA	
	DS^a	CX/CF_3	DS	CX/CF_3	DS^{a}	$\mathrm{CX}/\mathrm{CF}_3$
CF ₃	0.755	1	0.758	1	0.741	1
C=O	0.753	0.997	0.755	0.996	0.727	0.981
CH_2	0.754	0.999	_	-	0.732	0.988
CH_3	0.763	1.011	0.757	0.999	0.755	1.019

^a Average of anti-gauche and anti-anti conformers.



Figure S3: The cross sections, *i.e.* XAS amplitudes, of the (a) $C_{C=O}$ and (b) C_{CF_3} 1s states in ethyl trifluoroacetate, ESCA (red) and S-ethyl trifluorothioacetate, S-ESCA (blue).

4 Comparison of extrinsic amplitude reduction factors



for ESCA and S-ESCA

Figure S4: Comparison of calculated extrinsic amplitude reduction factors for C 1s cross sections of C_{CF_3} and $C_{C=O}$ atoms in ethyl trifluoroacetate (ESCA) and S-ethyl trifluoroth-ioacetate (S-ESCA).

5 Absolute extrinsic amplitude reduction factors



Figure S5: Calculated extrinsic amplitude reduction factors for chloroethanes: (a) monochloroethane, (b) 1,1-dichloroethane and (c) 1,1,1-trichloroethane.



Figure S6: Calculated extrinsic amplitude reduction factors for the ESCA-family members: (a) ethyl trifluoroacetate (ESCA), (b) S-ethyl trifluorothioacetate (S-ESCA) and (c) methyl trifluoroacetate (M-ESCA).

6 Calculated asymmetry parameters β



Figure S7: Calculated asymmetry parameters β for (a) 1,1,1-trichloroethane, (b) ethyl trifluoroacetate (ESCA) and (c) 2-butyne.