

# From synchrotrons for XFELs: the soft x-ray near-edge spectrum of the ESCA molecule — Supplementary Material

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Figure 1 in the supplementary material is the unshifted version of Figure 3 in the main text. The original EOM-CCSD(T)(a)\* energies were used here. In figure 3 of the main text, the lines are red-shifted by 0.5 eV to align the computed COO  $1s \rightarrow \pi^*$  transition with the peak at 288.3 eV.

Figure 2, 3, and 4 in the supplementary material are EOM-CCSD spectrum obtained using cc-pVTZ+2spd, cc-pVTZ+3spd, and cc-pVTZ+4spd basis for targeted atoms. The purpose is to show the convergence of the description for Rydberg states to the effects due to diffuse functions. The cc-pVTZ+2spd has correct description for local excitations and the first set of Rydberg states, but overestimate energies and intensities for higher Rydberg transitions, with transitions around 298 eV as prominent examples.

Table 1 in the supplementary material summarizes the raw data for figure 3 in the main text.

Table 2 in the supplementary material presents the raw data for figure 2 in the main text.

Table 3 in the supplementary material presents a comparison of computational results for the ESCA molecule in the  $C_s$  geometry with those in  $C_1$  geometry.

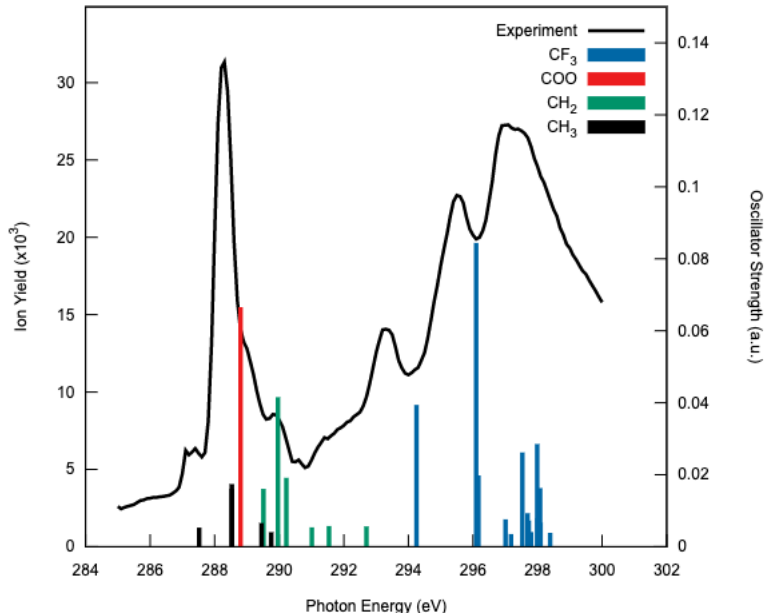


Figure 1: Experimental and computed NEXAFS spectra for the carbon edges of the ethyl trifluoroacetate molecule. The black solid line shows the variation of measured ion yield with respect to photon energies. Blue, red, green, and black sticks represent computed absorption lines for the CF<sub>3</sub>, COO, CH<sub>2</sub>, and CH<sub>3</sub> carbon edges, respectively, with the height being the computed oscillator strengths. Energy level positions were computed using the SFX2C-1e EOM-CCSD(T)(a)\* method, while transition dipole moments were obtained from EOM-CCSD calculations.

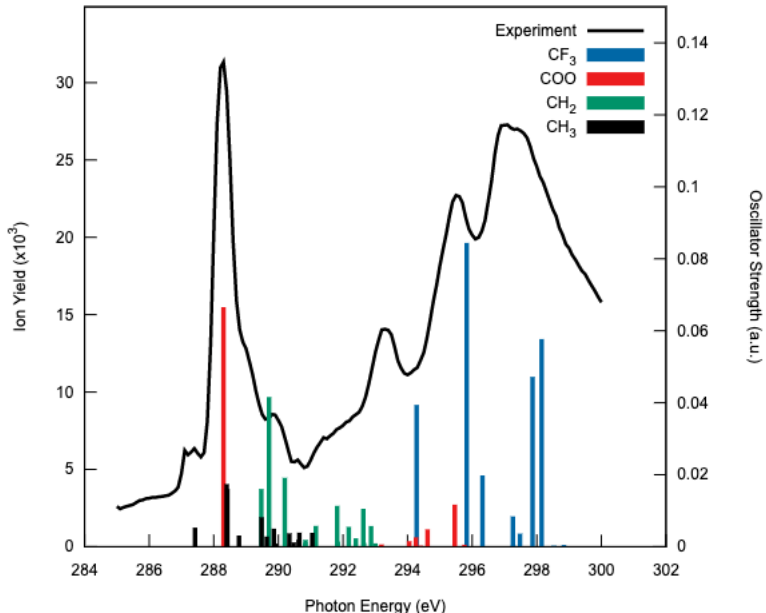


Figure 2: Experimental and computed NEXAFS spectra for the carbon edges of the ethyl trifluoroacetate molecule. The black solid line shows the variation of measured ion yield with respect to photon energies. Blue, red, green, and black sticks represent computed absorption lines for the CF<sub>3</sub>, COO, CH<sub>2</sub>, and CH<sub>3</sub> carbon edges, respectively, with the height being the computed oscillator strengths. Energy levels and transition dipole moments were obtained from EOM-CCSD calculations. The computed spectrum has been red-shifted by 0.81 eV to align the computed  $1s \rightarrow \pi^*$  transition with the experiment. The cc-pVTZ basis set augmented with two sets of additional diffuse s-, p-, and d-type functions for the targeted carbon and cc-pVTZ basis set for the other atoms have been used in all calculation.

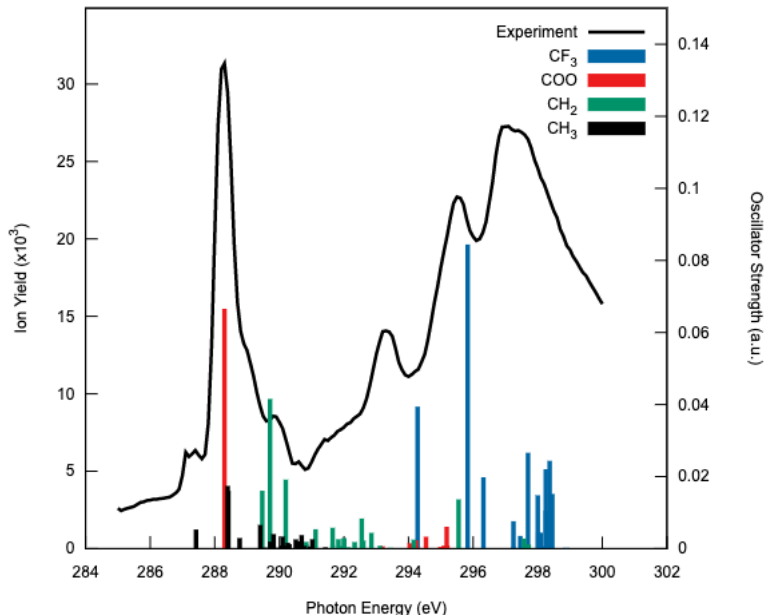


Figure 3: Experimental and computed NEXAFS spectra for the carbon edges of the ethyl trifluoroacetate molecule. The black solid line shows the variation of measured ion yield with respect to photon energies. Blue, red, green, and black sticks represent computed absorption lines for the  $\text{CF}_3$ ,  $\text{COO}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  carbon edges, respectively, with the height being the computed oscillator strengths. Energy levels and transition dipole moments were obtained from EOM-CCSD calculations. The computed spectrum has been red-shifted by 0.81 eV to align the computed  $1s \rightarrow \pi^*$  transition with the experiment. The cc-pVTZ basis set augmented with three sets of additional diffuse s-, p-, and d-type functions for the targeted carbon and cc-pVTZ basis set for the other atoms have been used in all calculation.

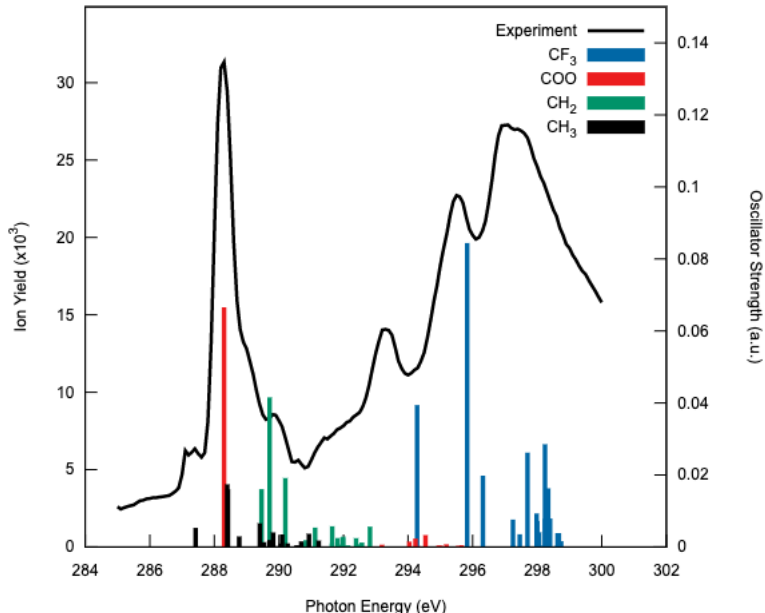


Figure 4: Experimental and computed NEXAFS spectra for the carbon edges of the ethyl trifluoroacetate molecule. The black solid line shows the variation of measured ion yield with respect to photon energies. Blue, red, green, and black sticks represent computed absorption lines for the CF<sub>3</sub>, COO, CH<sub>2</sub>, and CH<sub>3</sub> carbon edges, respectively, with the height being the computed oscillator strengths. Energy levels and transition dipole moments were obtained from EOM-CCSD calculations. The computed spectrum has been red-shifted by 0.81 eV to align the computed 1s → π\* transition with the experiment. The cc-pVTZ basis set augmented with four sets of additional diffuse s-, p-, and d-type functions for the targeted carbon and cc-pVTZ basis set for the other atoms have been used in all calculation.

Table 1: Computed transition energies (in eV) and oscillator strength (in a.u.) for  $\text{CF}_3$ ,  $\text{COO}$ ,  $\text{CH}_2$  and  $\text{CH}_3$  C edges of the ESCA molecule used in Figure 3. Energy level positions were computed using the EOM-CCSD(T)(a)\* method, while transition dipole moments were obtained from EOM-CCSD calculations. Transitions with the higher intensities were specified. The cc-pVTZ basis set augmented with four sets of additional diffuse s-, p-, and d-type functions for the targeted carbon atom and cc-pVTZ basis set for the other atoms have been used in all calculation.

	Transition	Transition energy		Oscillator strength
		(original)	(shifted)	
<b><math>\text{CF}_3</math></b>	$1s \rightarrow \pi$	294.25	293.75	0.03923
	$1s \rightarrow \text{C-F}\sigma^*$	296.10	295.60	0.08421
	$1s \rightarrow 3p$	296.17	295.67	0.01962
		297.01	296.51	0.00740
		297.18	296.68	0.00332
	$1s \rightarrow 3p$	297.53	297.03	0.02601
		297.69	297.19	0.00913
		297.73	297.23	0.00704
		297.80	297.30	0.00389
	$1s \rightarrow 3p + \pi^*$	297.99	297.49	0.02834
		298.00	297.50	0.00758
		298.08	297.58	0.01609
		298.09	297.59	0.00648
298.39		297.89	0.00366	
<b><math>\text{COO}</math></b>	$1s \rightarrow \pi^*$	288.80	288.30	0.06639
<b><math>\text{CH}_2</math></b>	$1s \rightarrow \text{C-H}\sigma^*$	289.51	289.01	0.01588
	$1s \rightarrow \text{C-O}\sigma^*$	289.96	289.46	0.04136
	$1s \rightarrow 3p$	290.22	289.72	0.01896
		291.01	290.51	0.00520
		291.54	291.04	0.00557
	292.70	292.20	0.00547	
<b><math>\text{CH}_3</math></b>	$1s \rightarrow \text{C-C}\sigma^*$	287.52	287.02	0.00513
	$1s \rightarrow 3p$	288.53	288.03	0.01721
	$1s \rightarrow 3p$	288.53	288.03	0.01581
		289.45	288.95	0.00638
		289.75	289.25	0.00386

Table 2: EOM-CCSD values for transition energies (in eV) for the nitrogen edge of ammonia used in Figure 2. Oscillator strengths (in a.u.) are enclosed in the parentheses. The transition energies have been red-shifted by 1.3 eV in last column.

Transition	cc-pVTZ	cc-pVTZ				
		+spd	2spd	+3spd	+4spd	+4spd(shifted)
1s $\rightarrow$ $\sigma^*$	402.20 (0.00680)	402.02 (0.00672)	401.85 (0.00564)	401.84 (0.00565)	401.84 (0.00565)	400.54 (0.00565)
1s $\rightarrow$ 3p( <i>e</i> )	404.07 (0.03525)	403.97 (0.02908)	403.51 (0.01916)	403.50 (0.01902)	403.50 (0.01903)	402.20 (0.01903)
1s $\rightarrow$ 3p( <i>a</i> <sub>1</sub> )	/	405.03 (0.01267)	404.15 (0.00640)	404.13 (0.00608)	404.13 (0.00608)	402.83 (0.00608)
1s $\rightarrow$ 4p( <i>e</i> )	/	405.72 (0.00676)	405.04 (0.00762)	404.83 (0.00382)	404.82 (0.00372)	403.52 (0.00372)
1s $\rightarrow$ 4p( <i>a</i> <sub>1</sub> )	/	/	406.09 (0.00112)	405.54 (0.00212)	405.49 (0.00172)	404.19 (0.00172)
1s $\rightarrow$ 5p( <i>e</i> )	/	/	405.98 (0.00121)	405.40 (0.00222)	405.34 (0.00273)	404.04 (0.00273)
1s $\rightarrow$ 6p( <i>e</i> )	/	/	406.68 (0.00560)	406.07 (0.00704)	405.70 (0.00111)	404.40 (0.00111)



Table 3: EOM-CCSD values for transition energies (in eV) and oscillator strengths for the  $C_s$  and  $C_1$  conformers for the pre-methyl carbon edge. Note that the separation between COO  $1s \rightarrow \pi^*$  and CH<sub>2</sub>  $1s \rightarrow \sigma^*$  transitions (the first and third lines) is 1.41 eV for the  $C_s$  conformer and 1.37 eV for the  $C_1$  conformer. The cc-pVTZ basis set augmented with two sets of additional diffuse s-, p-, and d-type functions for the targeted carbon atom and cc-pVTZ basis set for the other atoms have been used in all calculation.

Transition energies		Oscillator strength	
$C_s$	$C_1$	$C_s$	$C_1$
289.11	289.12	0.66400	0.06464
290.28	290.28	0.01254	0.01734
290.52	290.49	0.03833	0.03376
291.01	291.14	0.01895	0.01983
291.64	291.44	0.00090	0.00096
288.23	288.24	0.00391	0.00404
289.21	289.15	0.01219	0.01014
289.23	289.31	0.01579	0.01011
289.59	289.69	0.00235	0.00518
/	290.29	/	0.00437
290.29	290.33	0.00796	0.00882
290.45	290.5	0.00262	0.00075
290.67	290.63	0.00385	0.00211
/	290.82	/	0.00218