

Supplementary information for

“Identification of valence electronic states of aqueous acetic acid in acid-base equilibrium using site-selective x-ray emission spectroscopy”

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Comparison between measured and calculated XES spectra

Figure S1 shows simulated XES spectra using DFT calculations for both forms of the molecule. As we noted in the main text, we have performed calculations for an isolated molecule as an approximate approach. The calculated energy levels for the XES spectra of neutral and anionic acetic acid are shown along with the measured spectra in Fig. S1 a and S1 b, respectively. Since calculation was performed for an isolated molecule as an approximate approach, it is difficult to determine absolute energy of XES emission lines. Therefore, in this study, the both calculated spectra were shifted by -1.2eV to fit the experimental peak feature with highest intensity. The bar graph indicates the calculated XES emission lines and intensity. Pictures of the MO shape corresponding to pronounced emission lines are also depicted in figure. Peak positions of XES spectra and calculated emission lines are summarized in Tables S1 and S2. As noted in the main text, all peak structures in the experiment are well reproduced in the calculation, with small differences in their energy positions.

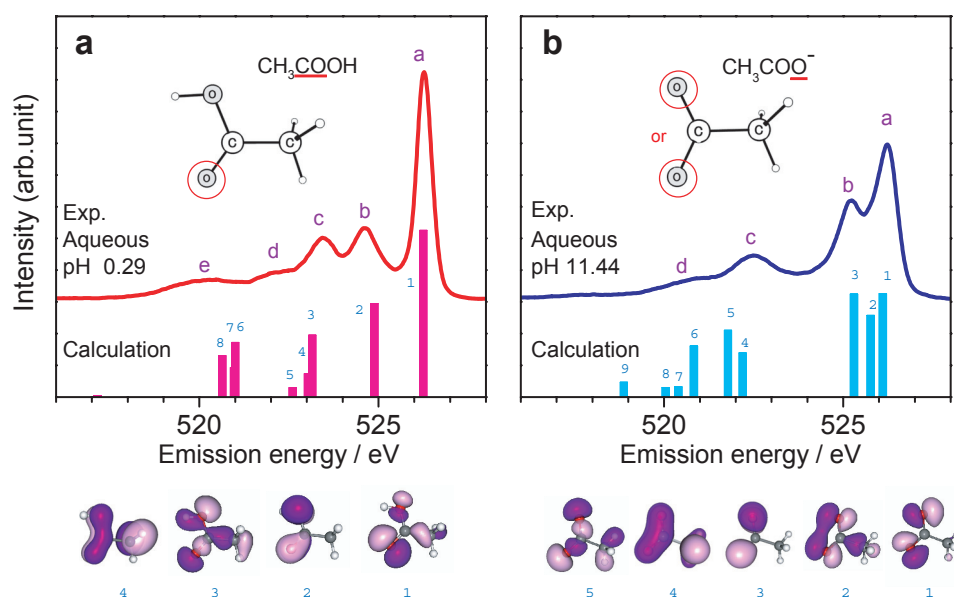


Figure S1. Calculation (bar graph) and measured (line) O 1s XES spectra of acetic acid in neutral form (a) and anionic form (b).

MOs can be categorized into in-plane and out-of-plane orbitals from their shapes. In Figure S1, MO1, 3 of neutral form (a), MO1, 2, 5 of anionic form (b) are in-plane orbitals and MO2, 4 of neutral form (a), M3, 4 of anionic form (b) are out-of-plane orbitals. The MOs for the anionic form has a symmetry which is lost in the neutral form through the presence of the extra H. Although its orbital symmetry is changed, we can easily find a clear connection between MOs of neutral and anionic form because of the small effect of symmetry changes on out-of-plane orbitals; the out-of-plane orbitals, MO2 and MO4 of the neutral form correspond to MO3 and MO4 of anionic form, respectively.

Table S1. measured and calculated emission lines of XES spectra for acetic acid in neutral form

Calculation		Experiment	
Index	Energy [eV]	Index	Energy [eV]
1	526.251	a	526.3
2	524.885	b	524.8
3	523.153	c	523.6
4	523.030		
5	522.601	d	~522
6	521.002	e	~520
7	520.966		
8	520.644		

Table S2. measured and calculated emission lines of XES spectra for acetic acid in anionic form

Calculation		Experiment	
Index	Energy [eV]	Index	Energy [eV]
1	526.105	a	526.3
2	525.764		
3	525.302	b	525.3
4	522.192	c	522.7
5	521.782		
6	520.832	d	~520.7
7	520.399		
8	520.045		
9	518.875		

Component ratio analysis

As mentioned in the main text, the obtained XES spectra of intermediate pH values can be nicely reproduced using a sum of two components, i.e. anionic form and neutral form. The optimized ratios that gives the minimum residual error in the fittings are summarized in Table S3. Figure S2 show the experimental XES spectra on which is superimposed the reproduced XES spectra (black lines) obtained by summing the spectra of two components: spectrum A (pH 11.44, strongly basic, anionic form) and spectrum I (pH 0.29, strongly acidic, neutral form) in Figure 2 in the main text. Two components of the spectra are indicated by blue lines (spectrum A) and red lines (spectrum I).

The relative emission efficiency, P , for anionic and neutral forms is obtained from the analysis of intensity changes of XES spectra as a function of pH. Figure S3 shows areal intensity of O1s emission in the XES spectra before area normalization. Clearly, the areal intensity is almost a constant value and is independent to the pH values. Since concentration of all samples were prepared as 2mol/l, this results indicate that efficiencies of whole emission process including absorption process are nearly equivalent for anionic form and neutral form of acetic acid. Finally, we can obtain the relative emission efficiency, P , is 1.0+/-0.05 from measured spectra.

Table S3. component ratio of each sample

Sample	Ratio of spectrum A	Ratio of spectrum I
B: pH 3.28	0.95	0.05
C: pH 3.73	0.92	0.08
D: pH 4.30	0.72	0.28
E: pH 4.73	0.52	0.48
F: pH 5.20	0.28	0.72
G: pH 5.71	0.12	0.88
H: pH 6.30	0.04	0.96

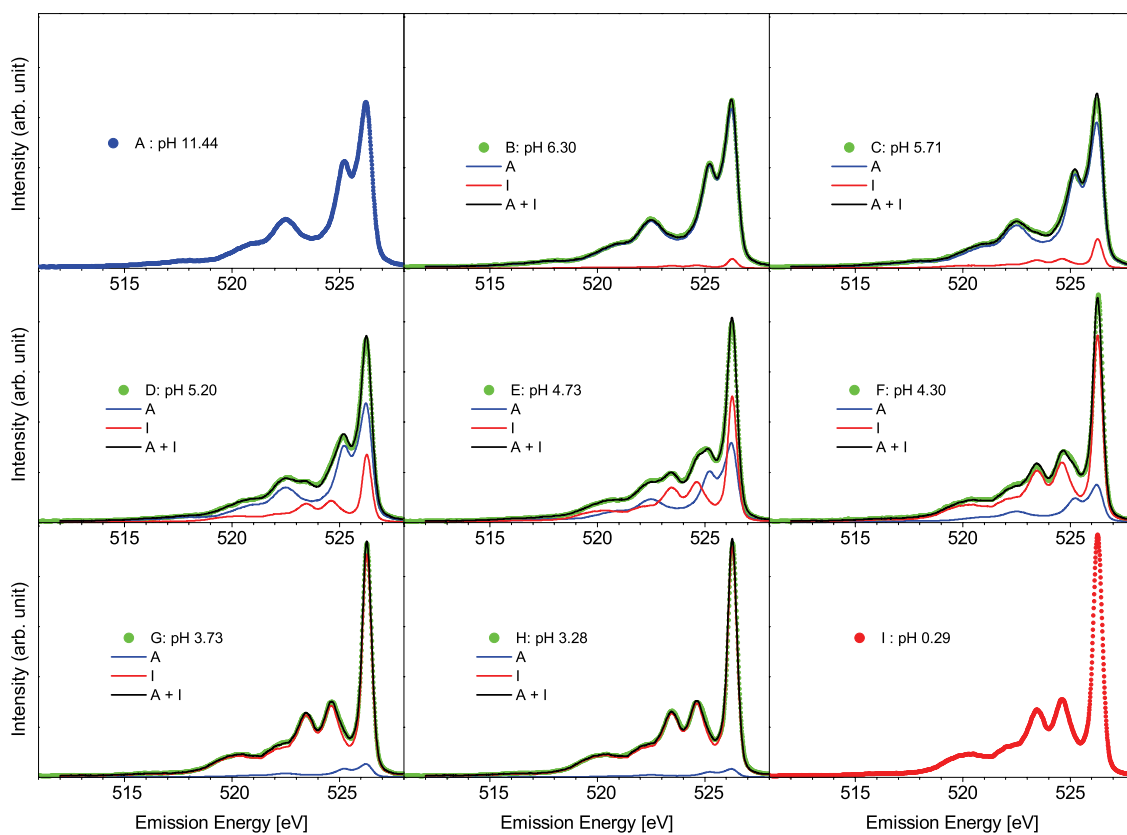


Figure S2. The experimental XES spectra (blue, green and red dots) and the reproduced XES spectra (black lines) obtained by summing the spectra of two components; spectrum A (pH 11.44, strongly basic, anionic form) and spectrum I (pH 0.29, strongly acidic, neutral form) in Figure 2 in the main text. Two components of the spectra are indicated by blue lines (spectrum A) and red lines (spectrum I).

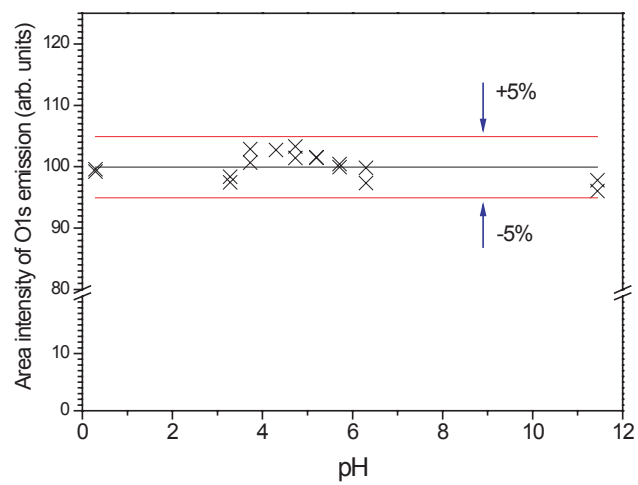


Figure S3. Areal intensity of O1s emission in the XES spectra without area normalization. Cross marks indicate individual data points of XES measurement. Exposure time of each measurements was the same (30min).