Supplementary information for
## "Pronounced polarization anisotropy in resonant X-ray emission from acetic acid molecules in solution"

Yuka Horikawa, Takashi Tokushima, Atsunari Hiraya and Shik Shin

Intensity normalization

As shown in Figure S1, the spectrometer has wide energy range of measurement which covers N1s and O1s emission simultaneously. To normalize spectra accurately, the intensity of N 1s emission was used to evaluate intensity of incident X-rays.

XES spectra in N 1s region consist of signals from nitrogen atoms in Si_3N_4 window and solvent acetonitrile. As shown in Fig. S2, N1s XES spectra of sample solution using X-ray at 532.2 eV show no polarization dependence. Since excitation energy for O 1s emission is far above the N 1s ionization threshold, there is no polarization dependence in N 1s emission, i.e. intensity of N 1s emission is proportional to the incident light intensity for any polarization of the incident light. Hence, in this study, all the spectra have been normalized by the emission intensity in N 1s region.
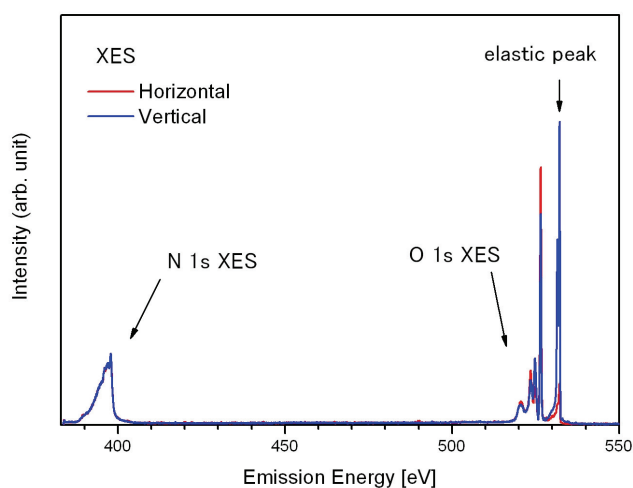
Figure S1. Full-spectra of measured XES for acetic acid in acetonitrile.
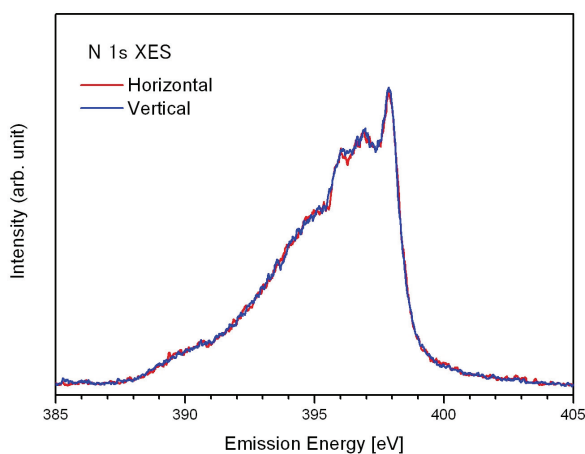
Figure S2. N 1s region spectra of Fig. S1.

Theoretical prediction of polarization dependence using actual degree linear polarization

Assuming 100% linear polarization for the incident light and no polarization sensitivity on the detection efficiency, emission intensity can be written as

$$I(\theta) = I_0 \left[1 + R \left(\frac{3}{2} \sin^2 \theta - 1 \right) \right] \qquad (1),$$

where θ is the angle between the polarization vector of the incident light and the direction of the emitted light, I_0 is the total intensity, and R is the anisotropy parameter. In our experimental setup, θ is 0° for horizontal polarization and 90° for vertical polarization. The anisotropy parameter R is 2/5 when the emission comes from an orbital with the same symmetry as the initially excited orbital. For the emission coming from an orbital with different symmetry, R becomes $-1/5$ [1]. Because the initially excited orbital is out-of-plane π^* orbital, the emission from out-of-plane valence orbital represents a transition between orbitals with same symmetry, and the emission from the in-plane valence orbital represents a transition between orbitals with different symmetry. Hereinafter, the suffixes "s" and "d" indicate the same symmetry and different symmetry respectively compared to the initially excited orbital π^*.

Using defined value of R, emission intensity for horizontal polarization (θ=0°) and vertical polarization (θ=90°) are written as

$$I_s(0) = \frac{3}{5} I_0, \quad I_s(90) = \frac{6}{5} I_0 \qquad (2),$$

$$I_d(0) = \frac{6}{5} I_0, \quad I_d(90) = \frac{9}{10} I_0 \qquad (3).$$

Anisotropy ratios of the emission for out-of-plane orbitals (A_s) and in-plane orbitals (A_d) are written in the same way of Forsberg et al. [2] as

$$A_s = \frac{I_s(90) - I_s(0)}{I_s(90) + I_s(0)} = 0.33, \quad A_d = \frac{I_d(90) - I_d(0)}{I_d(90) + I_d(0)} = -0.14 \qquad (4).$$

These values are obtained so far for 100 % linear polarization. Actually, linear polarization is not perfect and the expected degree of linear polarization of the incident light at around 550 eV is 0.9 for horizontal polarization and -0.84 for vertical polarization [3].

Degree of linear polarization is defined as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}, \quad \frac{I_{\perp}}{I_{\parallel}} = \frac{1 - P}{1 + P} \qquad (5),$$

using horizontal ($I_{\parallel}$) and vertical ($I_{\perp}$) components of light intensity.

And $I_{\perp} / I_{\parallel} = 1/19$ for P=0.9, and $I_{\perp} / I_{\parallel} = 23/2$ for P=-0.84.

Taking into account the actual polarization, anisotropy ratios becomes as follows;

$$A_s = \frac{\left(I_s(90) \times \frac{23}{25} + I_s(0) \times \frac{2}{25} \right) - \left(I_s(0) \times \frac{19}{20} + I_s(90) \times \frac{1}{20} \right)}{\left(I_s(90) \times \frac{23}{25} + I_s(0) \times \frac{2}{25} \right) + \left(I_s(0) \times \frac{19}{20} + I_s(90) \times \frac{1}{20} \right)} = 0.29 ,$$

$$A_d = \frac{\left(I_d(90) \times \frac{23}{25} + I_d(0) \times \frac{2}{25} \right) - \left(I_d(0) \times \frac{19}{20} + I_d(90) \times \frac{1}{20} \right)}{\left(I_d(90) \times \frac{23}{25} + I_d(0) \times \frac{2}{25} \right) + \left(I_d(0) \times \frac{19}{20} + I_d(90) \times \frac{1}{20} \right)} = -0.12 \qquad (6)$$

Experimental value of anisotropy ratio

Figure S3 shows the fitting results of measured XES spectra for acetic acid in acetonitrile excited by horizontally or vertically polarized X-rays. Fitting analysis has been done with Gaussian functions, and the details of parameters for Gaussian peaks are summarized in Table S1.

The definition of anisotropy ratio is

$$A = \frac{I_V - I_H}{I_V + I_H} \tag{7},$$

where I_V and I_H indicate emission intensity for horizontally and vertically polarized X-rays. Hence, using area intensity of Gaussian peaks, experimental values of anisotropy are obtained as summarized in Table S2.

Fitting errors in experimental anisotropy ratio are evaluated by considering propagation of errors written as follows,

$$\Delta A^2 = \left(\frac{dA}{dI_V}\right)^2 \Delta I_V^2 + \left(\frac{dA}{dI_H}\right)^2 \Delta I_H^2 = \left\{\frac{2I_H}{(I_V + I_H)^2}\right\}^2 \Delta I_V^2 + \left\{\frac{-2I_V}{(I_V + I_H)^2}\right\}^2 \Delta I_H^2 \tag{8}.$$

The values of fitting error in anisotropy ratio evaluated using equations (7) and (8) are also summarized in Table S2.
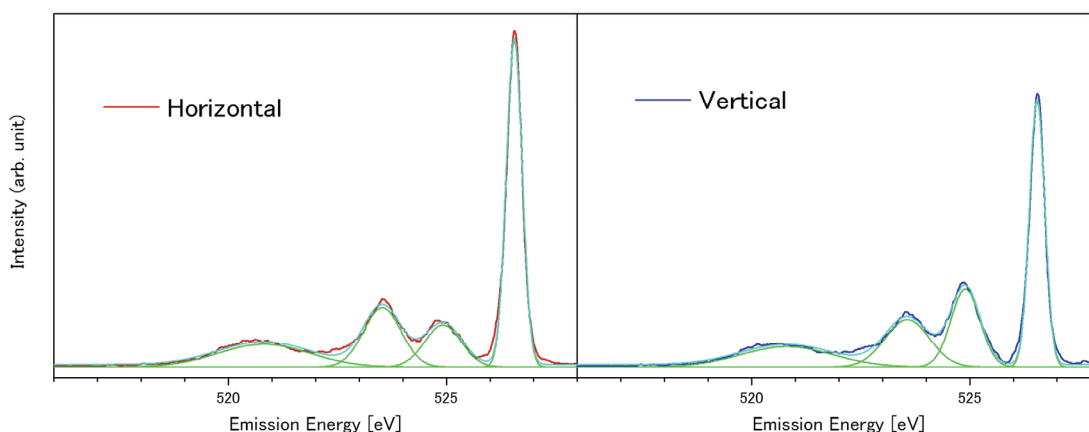
Figure S3. Fitting results of XES spectra for horizontally and vertically polarized X-rays for acetic acid in acetonitrile

Table S1 Fitting results of XES spectra for horizontally and vertically polarized X-rays using four Gaussian peaks.

Peak label	Horizontal				Vertical			
	Peak position (eV)	Area	Width σ (eV)	Std. Error for Area	Peak position (eV)	Area	Width σ (eV)	Std. Error for Area
A	526.6	2368.57	0.18	11.51	526.5	1854.48	0.18	9.76
B	524.9	706.81	0.42	7.87	524.9	1040.38	0.33	7.36
C	523.5	1027.97	0.43	7.70	523.6	698.35	0.51	6.07
D	520.8	957.62	1.05	5.23	520.8	857.50	1.05	4.35

Table S2 Experimental anisotoropy ratio of XES spectra using fitting results. Correspondence between XES peaks and calculated MOs are also shown in the table.

Peak label	MO Calculation			Fitting results
	MO number	Symmetry	Bonding type	Anisotropy ratio
A	1	In	Non-bonding	-0.122 (± 0.0034)
B	2	Out	Non-bonding	0.191 (± 0.016)
C	3	In *	σ (C=O)	-0.028 (± 0.015)
	4	Out	π (C=O)	
	5	In	σ (C=O)	
D	6	In *	σ (C=O)	-0.055 (± 0.023)
	7	In	σ (C=O)	
	8	Out	π (C=O)	

References

1   Y. Luo, H. Ågren and F. Gel'mukhanov, *Phys. Rev. A*, 1996, **53**, 1340.

2   J. Forsberg, J. Grasjo, B. Brena, J. Nordgren, L. C. Duda and J. E. Rubensson, *Phys. Rev. B*, 2009, **79**, 132203.

3   M. Oura, T. Nakamura, T. Takeuchi, Y. Senba, H. Ohashi, K. Shirasawa, T. Tanaka, M. Takeuchi, Y. Furukawa, T. Hirono, T. Ohata, H. Kitamura and S. Shin, *J. Synchrotron Rad.*, 2007, **14**, 483-486.