

## Electronic Supplementary Information for “Solvation dependence of valence electronic states of water diluted in organic solvents probed by soft X-ray spectroscopy”

### Comparison of XES spectra using liquid flow cell and liquid microjet for acetonitrile-D<sub>2</sub>O mixture.

Fig.S1 shows a comparison of XES spectra using the liquid flow cell and previously reported spectrum using liquid microjet (Ref. 21 in main text) for acetonitrile-D<sub>2</sub>O mixture. For XES spectra using liquid flow cell, XES spectra at several concentrations including  $X_{D_2O}=0.17$ , which is the spectra used in main text, are plotted. XES spectra using liquid microjet shows similarity to XES spectra using liquid flow cell for concentration around  $X_{D_2O}=0.33$  and 0.5. Therefore, presented XES spectra of D<sub>2</sub>O/AN mixture using the liquid flow cell is consistent with previously reported XES spectra using liquid microjet by taking differences of sample condition, such as pressure and temperature, into account.

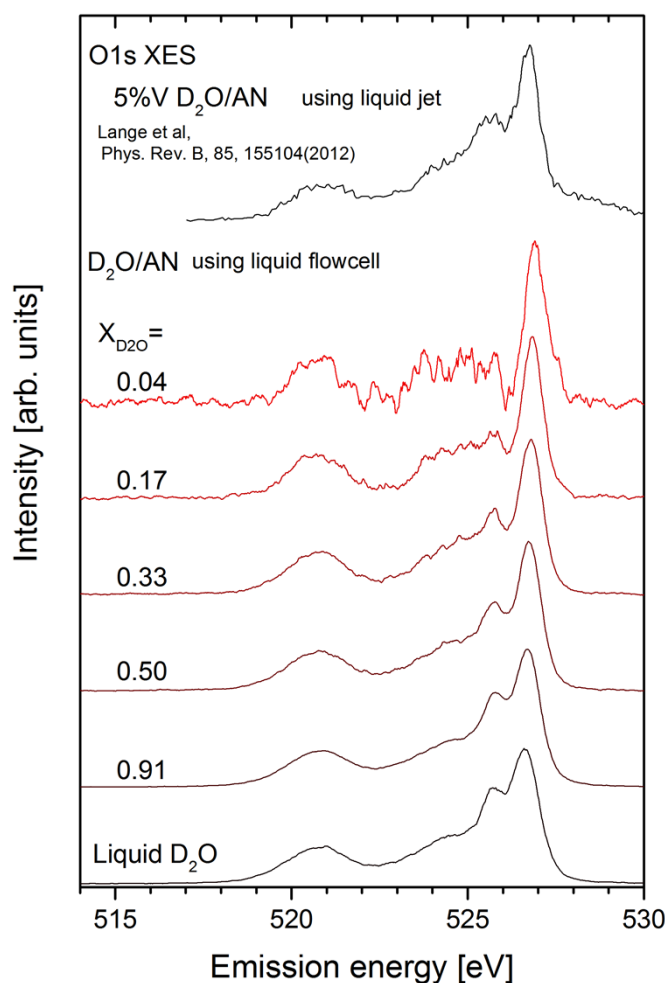


Fig. S1

## Optimized geometries of complexes used in XAS calculations in XYZ format

### Water-AN 1:1 complex

C	0.083440000	-0.393119000	-1.327786000
H	-0.742951000	-0.837059000	-1.876084000
H	1.008590000	-0.883044000	-1.618796000
H	0.144715000	0.668367000	-1.553496000
C	-0.130733000	-0.541648000	0.104651000
N	-0.301473000	-0.611763000	1.259726000
O	-0.038440000	2.414972000	0.296921000
H	-0.109760000	3.282307000	0.699431000
H	-0.169553000	1.802566000	1.027537000

### Water-AN 1:2 complex

C	-1.395896000	-0.638114000	-0.742013000
H	-1.741305000	0.104363000	-1.456261000
H	-2.172861000	-1.384204000	-0.599550000
H	-0.494391000	-1.115136000	-1.118493000
C	-1.075749000	0.000012000	0.526734000
N	-0.771394000	0.497186000	1.540995000
O	1.819325000	-0.905572000	0.261707000
H	2.489518000	-0.305488000	-0.082421000
H	1.357738000	-0.383320000	0.926432000
C	4.831329000	-2.274248000	0.946078000
H	5.333270000	-2.165893000	1.903701000
H	5.327770000	-3.049653000	0.369096000
H	3.791374000	-2.546831000	1.107838000
C	4.862161000	-1.012664000	0.220210000
N	4.836957000	0.001705000	-0.362037000

### Water-3MP 1:1 complex

C	0.059600000	-0.012054000	-0.026599000
C	0.033803000	-0.105348000	1.361713000
C	1.238077000	-0.111381000	2.054977000
C	2.437978000	-0.024400000	1.346928000
C	2.350953000	0.066714000	-0.042422000
N	1.197524000	0.073553000	-0.726489000
H	1.249211000	-0.184290000	3.135419000
H	-0.857946000	-0.006681000	-0.600534000
H	-0.910513000	-0.172688000	1.882867000
H	3.248734000	0.132017000	-0.646423000
O	2.474472000	0.210509000	-3.297739000
H	1.854017000	0.128383000	-2.553437000
H	2.444360000	1.146502000	-3.504185000
C	3.767157000	-0.028384000	2.041991000
H	3.897817000	-0.939947000	2.623829000
H	4.581585000	0.035387000	1.323957000
H	3.849988000	0.815127000	2.726378000