Electronic Supplementary Information for: "On the Choice of Reference Orbitals for Linear-Response Calculations of Solution-Phase K-Edge X-Ray Absorption Spectra"

Kevin Carter-Fenk,*and Martin Head-Gordon†
Kenneth S. Pitzer Center for Theoretical Chemistry,
Department of Chemistry, University of California, Berkeley, CA 94720, USA
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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*carter-fenk@berkeley.edu
†mhg@cchem.berkeley.edu

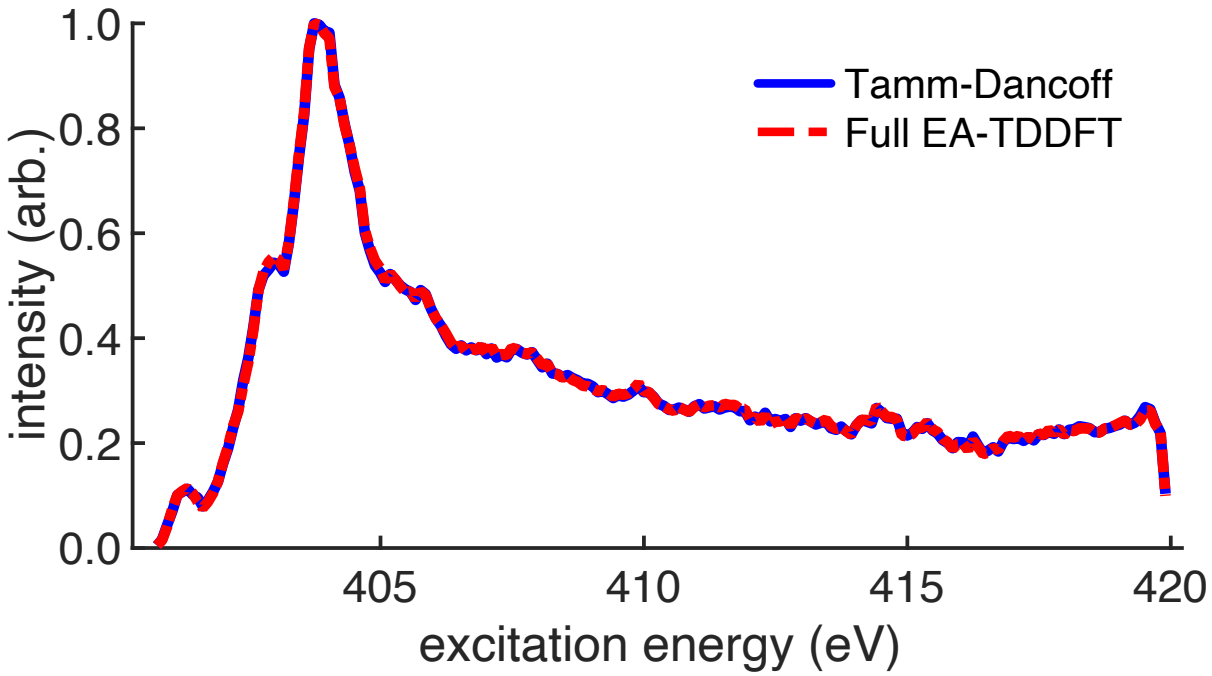

Figure S1: Spectrum of NH_3(aq) from the solution of the full EA-TDDFT equations versus the one obtained from the Tamm-Dancoff approximation. Each spectrum is plotted as a weighted histogram that summarizes 50 snapshots of molecular dynamics trajectory data. The histogram weights were taken to be the intensities, and each spectrum was binned into 200 frequency ranges.

Table S1: Linear shifts applied to computed XAS spectra.

System	Method				
	LR-TDDFT[a]	CIS	EA-TDDFT[b]	EA-CIS	CCSD[c]
H_2O	-1.8	-26.7	-2.4	-3.2	—
NH_3	-1.7	-23.8	-2.2	-3.0	-2.0
NH_4^+	-6.7	-27.0	-2.9	-4.4	-2.0

[a] SRC1-R1

[b] rCAM-B3LYP

[c] From Ref. 1

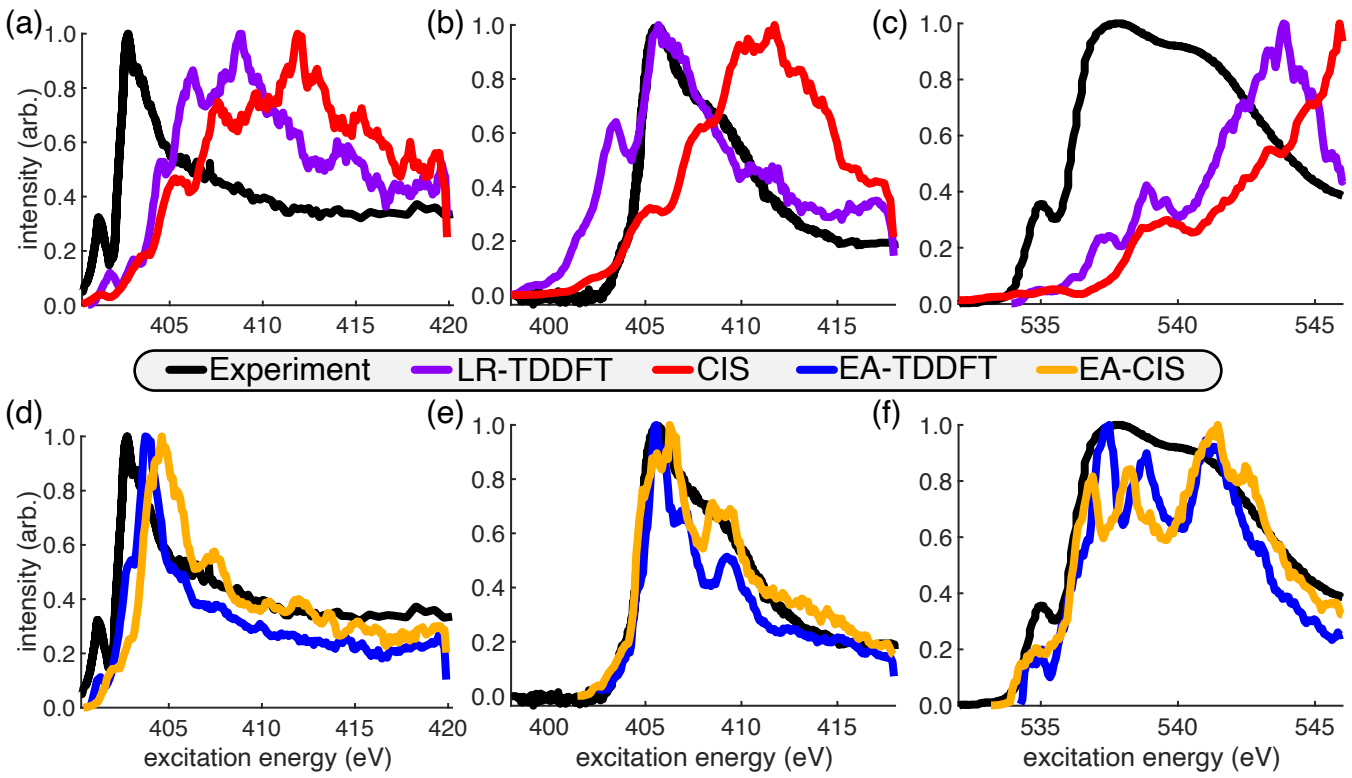

Figure S2: Calculated XAS profiles using standard linear-response methods (LR-TDDFT/CIS) for (a) NH_3(aq), (b) NH_4^+(aq) and (c) liquid water along with XAS profiles using orbital-optimized linear-response methods (EA-TDDFT/ EA-CIS) for (d) NH_3(aq), (e) NH_4^+(aq), and (f) liquid water. Each spectrum is plotted as a weighted histogram that summarizes 50 snapshots of molecular dynamics trajectory data. The histogram weights were taken to be the intensities, and each spectrum was binned into 200 frequency ranges. When possible, spectra were shifted to align the pre-edge feature with experiment (details in Tab. S1). Experimental spectra for NH_3(aq) and NH_4^+(aq) were reproduced from Ref. 2 and liquid water data are taken from Ref. 3.

References

[1] P. Reinholdt, M. L. Vidal, J. Kongsted, M. Iannuzzi, S. Coriani, and M. Odelius, Nitrogen K-Edge X-ray Absorption Spectra of Ammonium and Ammonia in Water Solution: Assessing the Performance of Polarizable Embedding Coupled Cluster Methods, *J. Phys. Chem. Lett.*, 2021, **12**, 8865–8871.

[2] M. Ekimova, W. Quevedo, Ł. Szyc, M. Iannuzzi, P. Wernet, M. Odelius, and E. T. J. Nibbering, Aqueous Solvation of Ammonia and Ammonium: Probing Hydrogen Bond Motifs with FT-IR and Soft X-ray Spectroscopy, *J. Am. Chem. Soc.*, 2017, **139**, 12773–12783.

[3] J. Meibohm, S. Schreck, and P. Wernet, Temperature dependent soft x-ray absorption spectroscopy of liquids, *Rev. Sci. Instrum.*, 2014, **85**, 103102.