Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for "TD-DFT Simulations of K-edge Resonant Inelastic X-ray Scattering within the Restricted Subspace Approximation"

Vinícius Vaz da Cruz,[1,*] Sebastian Eckert,[1] and Alexander Föhlisch[1,2]

[1] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH,*
Institute for Methods and Instrumentation for
Synchrotron Radiation Research, 12489 Berlin, Germany.

[2] *Universität Potsdam, Institut für Physik und Astronomie, 14476 Potsdam, Germany.*

EXPLICIT SOLVATION OF 2TP AND 2TP$^-$

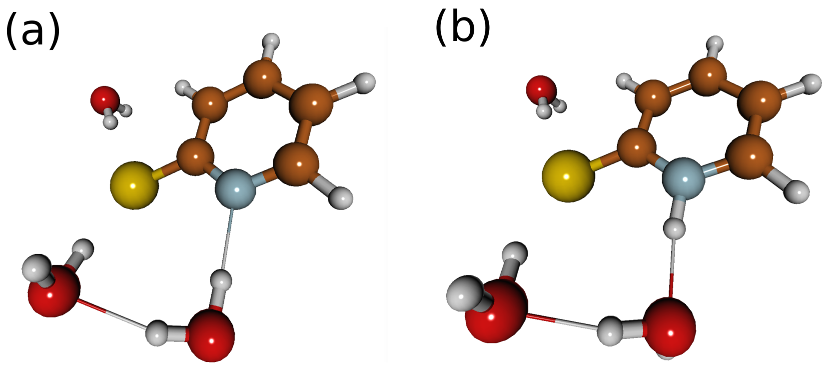

FIG. 1: Ball and stick model of the explicitly solvated structures used in the main text for (a) 2-thiopyridone and (b) its conjugated base.

TABLE I: Cartesian coordinates of the explicitly solvated structures used in the main text for 2-thiopyridone and its conjugated base

2TP				2TP$^-$			
atom	x [Å]	y [Å]	z [Å]	atom	x [Å]	y [Å]	z [Å]
C	0.26666	-1.86574	0.10092	C	0.30410	-1.87170	0.16610
C	1.38083	-1.04612	0.33047	C	1.40249	-1.04894	0.40708
C	-0.87757	-1.26685	-0.33995	C	-0.82863	-1.27488	-0.35105
C	1.30681	0.30668	0.11614	C	1.31470	0.29700	0.12542
N	-0.92773	0.06033	-0.54636	N	-0.92437	0.02279	-0.63171
H	0.29863	-2.93194	0.26381	H	0.32650	-2.93218	0.37352
H	-1.78862	-1.80935	-0.54596	H	-1.71377	-1.86851	-0.55497
H	2.30729	-1.48127	0.68129	H	2.31874	-1.45836	0.81421
C	0.11162	0.90223	-0.33974	C	0.12197	0.83061	-0.40469
S	-0.05013	2.57102	-0.63766	S	-0.00461	2.52027	-0.78259
H	-1.83987	0.44352	-0.89259	H	-2.59968	0.59581	-1.29287
H	2.16080	0.94295	0.29844	H	2.15261	0.95473	0.31294
O	-3.24116	3.29197	-0.21539	O	-3.04719	3.34858	-0.03312
H	-2.27017	3.23729	-0.24182	H	-2.11364	3.13641	-0.23148
H	-3.46206	3.21013	0.71767	H	-3.16251	3.06702	0.87868
O	-3.37408	0.85501	-1.38296	O	-3.49924	0.90143	-1.51760
H	-3.34101	1.01152	-2.33188	H	-3.54770	1.75509	-1.06418
H	-3.47327	1.74756	-0.98092	O	2.98053	3.49043	0.10408
O	3.08296	3.39846	0.09673	H	3.46625	3.23293	-0.68308
H	3.49666	3.17328	-0.74018	H	2.06000	3.24744	-0.10535
H	2.13827	3.25298	-0.06648				

EXAMPLE INPUTS

The framework described can be easily utilized by combining Orca [1] and Multiwfn [2]. In a first step we obtain the reference ground state Kohn-Sham orbitals, let us call this file ”2mp_keto3w_orbitals.inp”

```
! rks def2-TZVP pbe0 grid6 rijcosx def2/J gridx7 verytightscf cpcm(water)


* xyzfile 0 1 2mp_keto_3w_opt.xyz
```

Then these orbitals can be used in a second step to solve the TD-DFT equations within the restricted subspaces by rotating the core-orbitals of interest just below the occupied orbitals relevant for describing the RIXS process.

```
! rks def2-TZVP pbe0 grid6 rijcosx def2/J gridx7 cpcm(water)

%moinp "2mp_keto_orbitals.gbw"

%scf
MaxIter=0
rotate
{4,13,90,0,0}
end
end

%tddft
nroots 620
orbwin[0]=13,43,44,63
TPrint 0.0001
maxdim 10
nguessmat 620
maxiter 70
ETol 1e-6
RTol 1e-6
MaxCore 5000
end
```

The resulting output file can then be read by Multiwfn, using option ”18 Electron excitation analysis”, to generate all transition dipole moments between the computed states, which are then used to compute the RIXS cross-section according to the orientationally averaged Kramers-Heisenberg amplitudes shown in the Eq. (7) of the main text.

VIBRONIC XAS PROFILE AND EXCITATION ENERGY USED IN THE VIBRATIONAL RIXS SPECTRA

In this section the vibronic XAS are shown for the cases discussed in the nuclear dynamics section of the main text for H_2O, O_2 and acetone. All spectra are plotted as function of the detuning from the vertical exciatation point defined as $\Omega_{vert} = \omega - V_{vert} + \epsilon_0$, where ω is the incoming photon energy, V_{vert} is the vertical transition energy difference between the core-excited state and the ground state and ϵ_0 is the initial state vibrational enenrgy.

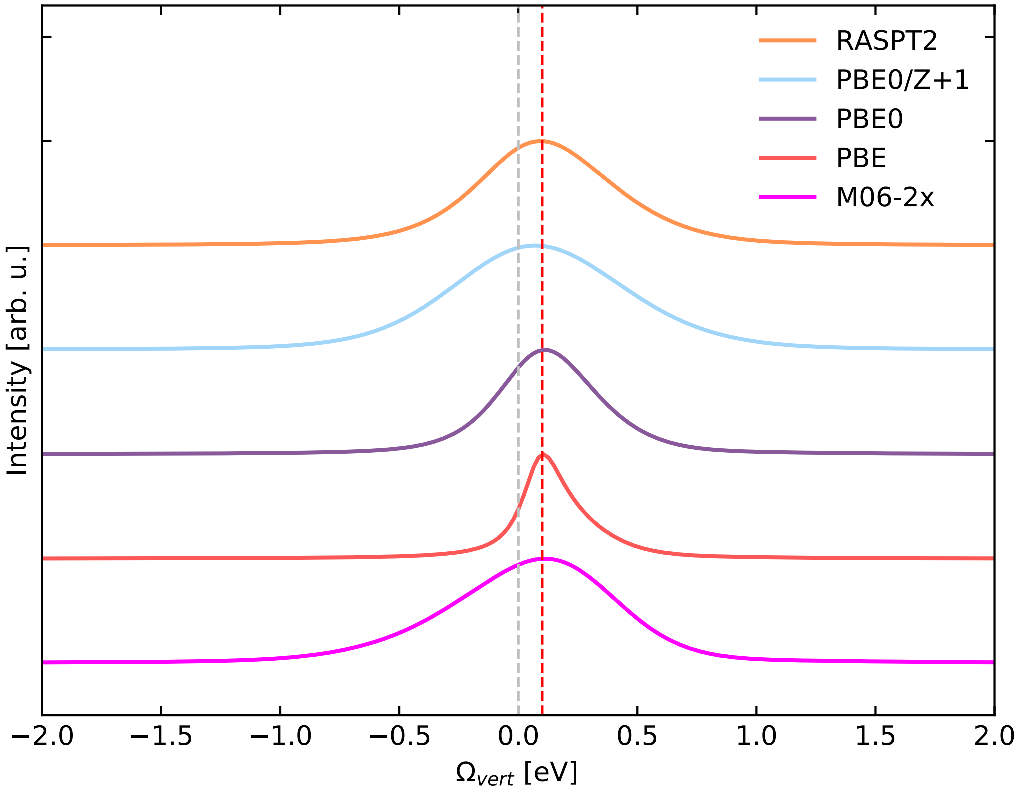

FIG. 2: Vibronic XAS computed for the $|O1s^{-1}4a_1^1\rangle$ core-excited state of water. The dashed red line displays the excitation energy used for the RIXS spectrum in the main text.

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[*] Electronic address: `vinicius.vaz_da_cruz@helmholtz-berlin.de`

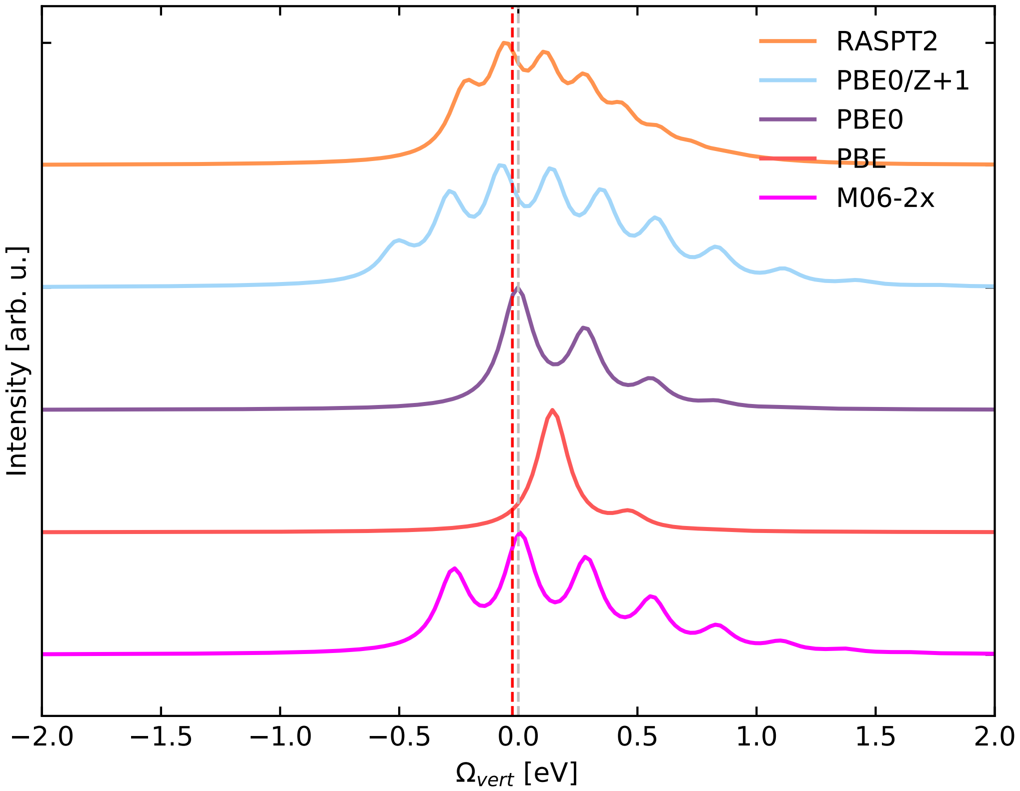

FIG. 3: Vibronic XAS computed for the $|O1s^{-1}2b_2^1\rangle$ core-excited state of water. The dashed red line displays the excitation energy used for the RIXS spectrum in the main text.

[1] F. Neese, Wiley Interdisciplinary Reviews: Computational Molecular Science **2**, 73 (2012), ISSN 1759-0884, URL `http://dx.doi.org/10.1002/wcms.81`.

[2] T. Lu and F. Chen, Journal of Computational Chemistry **33**, 580 (2012).

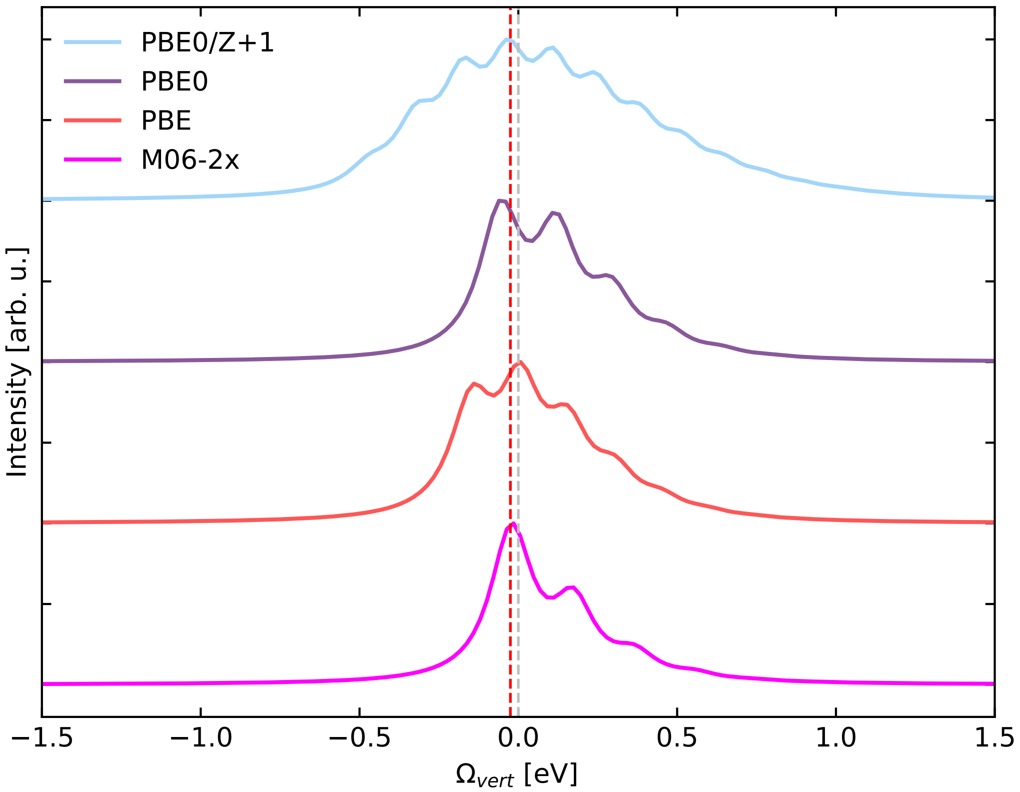

FIG. 4: Vibronic XAS computed for the $|1\sigma_u^{-1}1\pi_g^{+1}\rangle$ core-excited state of O_2. The dashed red line displays the excitation energy used for the RIXS spectrum in the main text.

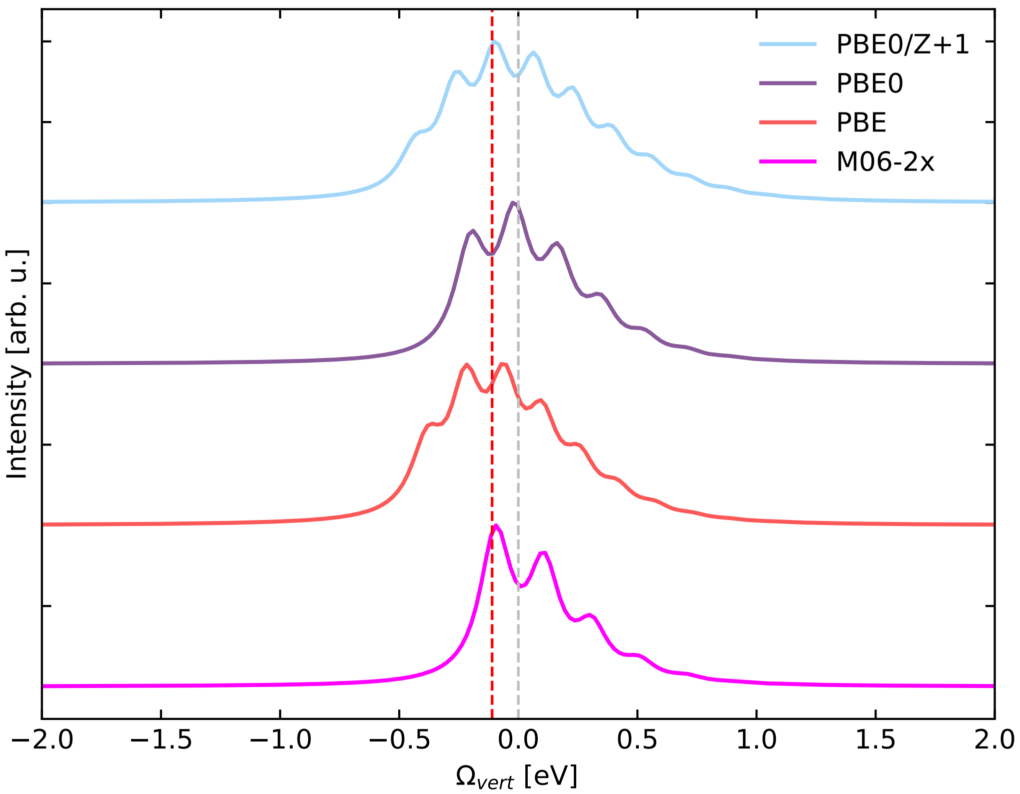

FIG. 5: Vibronic XAS computed for the $|O1s^{-1}\pi^{*1}\rangle$ core-excited state of acetone. The dashed red line displays the excitation energy used for the RIXS spectrum in the main text.