# Electronic Supplementary Information:
# Electronic Structure of Aqueous Nitrite and Nitrate Ions from Resonant Inelastic X-ray Scattering

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## POTENTIAL ENERGY SCANS ALONG NORMAL COORDINATES

Fig. S1 present the core-excited state potentials of nitrite at the in the nitrogen and oxygen 1s→ $\pi^*$ states along the dimensionless normal coordinates. The nitrogen 1s excitation, modeled in Fig. S1 (left), induces exclusively dynamics along the symmetric bending and stretch coordinate. Excitation at the oxygen edge activates both, symmetric, as well as anti-symmetric distortions, characterized by the Jahn-Teller split potentials for excitation at the 1s levels at the individual oxygen sites.

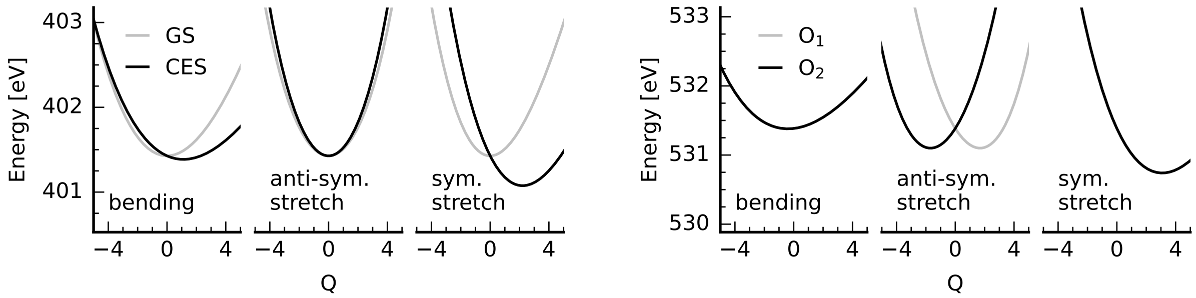

Figure S1: Core-excited state dynamics of nitrite at the different edges. Left: Nitrogen 1s→ $\pi^*$ Z+1 equivalent core-excited state (CES) potential in comparison to the ground-state (GS) potential along the normal coordinates. Right: Oxygen 1s→ $\pi^*$ Z+1 equivalent core-excited state potentials for excitation at the individual oxygen sites.

For nitrate, the nitrogen 1s excitation induces dynamics along the symmetric stretch mode. As can be seen from the potentials in Fig. S2, the umbrella mode is also activated due to the double well shape of the corresponding core-excited state potential. As expected the nitrogen 1s excitation does not induce dynamics which would break the equivalence of the bonds towards the three oxygen atoms. Contrarily, oxygen 1s excitation activates dynamics along all modes. The individual symmetry reduction is reflected in the overlap of the potentials for excitation at the individual oxygen sites.

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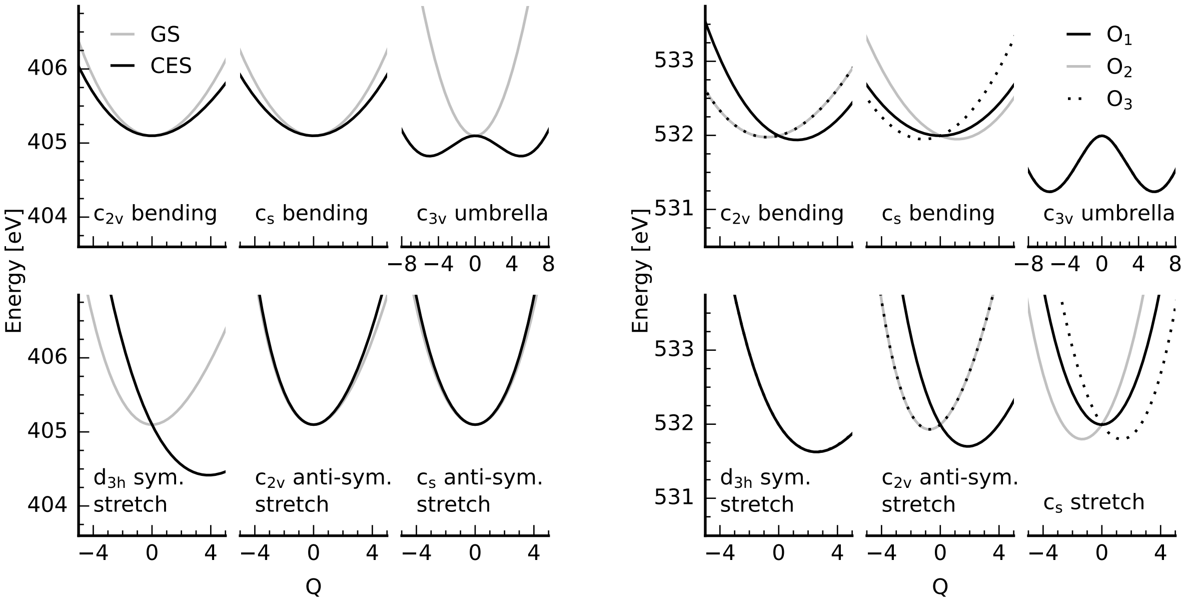

Figure S2: Core-excited state dynamics of nitrate at the different edges. Left: Nitrogen 1s→ $\pi^*$ Z+1 equivalent core-excited state (CES) potential in comparison to the ground-state (GS) potential along the normal coordinates. Right: Oxygen 1s→ $\pi^*$ Z+1 equivalent core-excited state potentials for excitation at the individual oxygen sites.

## COMPARISON BETWEEN Z+1 APPROXIMATION AND EXPLICIT CORE-HOLE TREATMENT

Tabs. SI and SII contain the internal coordinates of nitrite and nitrate obtained from optimized geometries calculated with the equivalent core (Z+1) approximation as well as for a determinant including the 1s→ $\pi^*$ excitation explicitly, using the ΔSCF scheme in Orca Version 6.0.1. The geometric distortions resulting from the two schemes modeling the core-excited state are in good agreement, exhibiting only small quantitative differences. For the nitrogen K-edge simulations of nitrate starting from the symmetric ground state geometry, the optimizations converge to a saddle point instead of the minimum. Hence, we started the geometry optimization also from an asymmetric structure exhibiting a 0.1Å out of plane displacement of the nitrogen atom. These results show that the Z+1 approximation works well for 1s→ $\pi^*$ excitations at both the nitrogen K-edge and oxygen K-edge of nitrite and nitrate.

Table SI: Optimized coordinates of nitrite in the electronic ground state (GS) and in the nitrogen and oxygen 1s→ $\pi^*$ core-excited states in the ΔSCF and equivalent core (Z+1) approximation. Bond lengths R are given in Ångström and angles in degree.

| | | N K-edge | | O K-edge ($O_1$) | |
|---|---|---|---|---|---|
| | GS | ΔSCF | Z+1 | ΔSCF | Z+1 |
| R(N-$O_1$) | 1.248 | 1.318 | 1.334 | 2.449 | 2.162 |
| R(N-$O_2$) | 1.248 | 1.318 | 1.334 | 1.146 | 1.157 |
| ∠ $O_1NO_2$ | 116.1 | 115.5 | 114.6 | 103.8 | 106.3 |

Table SII: Optimized coordinates of nitrate in the electronic ground state (GS) and in the nitrogen and oxygen 1s→ $\pi^*$ core-excited states in the ΔSCF and equivalent core (Z+1) approximation. Bond lengths R are given in Ångström and angles in degree. As convergence to a saddle point is observed at the nitrogen K-edge, an asymmetric starting geometry has been considered.

| | | asym. starting geometry | | | | sym. starting geometry | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | N K-edge | | O K-edge ($O_1$) | | N K-edge | | O K-edge ($O_1$) | |
| | GS | ΔSCF | Z+1 | ΔSCF | Z+1 | ΔSCF | Z+1 | ΔSCF | Z+1 |
| R(N-$O_1$) | 1.246 | 1.331 | 1.348 | 2.605 | 2.135 | 1.328 | 1.343 | 2.575 | 2.132 |
| R(N-$O_2$) | 1.246 | 1.331 | 1.348 | 1.185 | 1.196 | 1.328 | 1.343 | 1.185 | 1.196 |
| R(N-$O_3$) | 1.246 | 1.331 | 1.348 | 1.185 | 1.196 | 1.328 | 1.343 | 1.185 | 1.196 |
| $\angle$ $O_1NO_2$ | 120.0 | 116.3 | 117.8 | 100.4 | 107.0 | 120.0 | 120.0 | 100.3 | 107.0 |
| $\angle$ $O_1NO_3$ | 120.0 | 116.3 | 117.8 | 100.4 | 107.0 | 120.0 | 120.0 | 100.3 | 107.0 |
| dihedral | 180.0 | 217.4 | 208.9 | 221.5 | 217.6 | 180.0 | 180.0 | 221.7 | 217.6 |

## CUTOFF DISTANCES FOR EXPLICIT SOLVATION

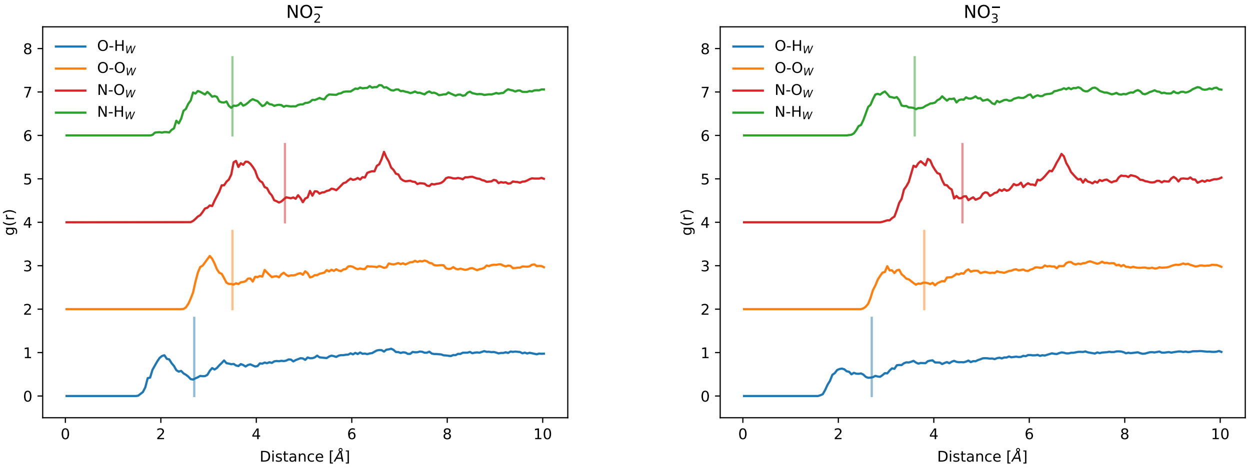

Figure S3: Pair wise radial distribution functions for nitrite (left) and nitrate (right) and the water solvent molecules. Vertical lines indicate the thresholds defining the maximum distance for the selection of water molecules from first solvation shell, considered in the simulations of explicitly solvated structures.

## NITRATE OXYGEN K-EDGE RIXS SPECTRUM BACKGROUND

We assess the maximal contribution of the solvent background to the experimental RIXS spectra of nitrate based on the experimental data presented in Fig. 4. Measurements of the 1M sodium-nitrate solution and the solvent water jet under the same excitation conditions are normalized to the total intensity in an energy loss range between 9 eV and 10.5 eV. Mainly weak emission features with energy losses above ∼7 eV are affected by the solvent background. The emission line between 11 eV and 12 eV loss, exhibiting a strong detuning dependence, clearly exceeds the solvent background. This emission line can thus be assigned to final state characterized by excitations from the $3b_1$ and $7a_1$ orbitals, which are strongly quenched by interference effects at detuned excitation conditions (see main text).

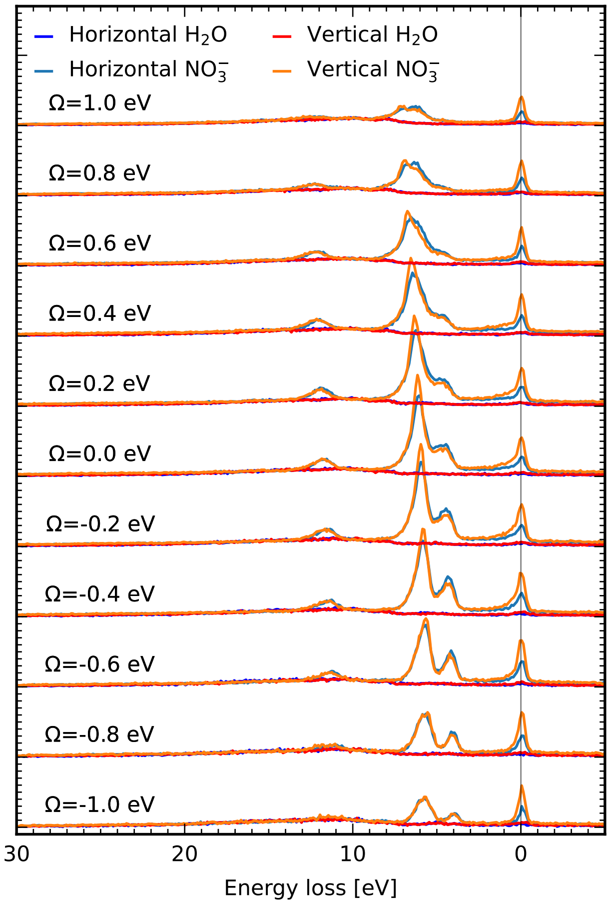

Figure S4: Oxygen 1s→ $\pi^*$ RIXS of nitrate in comparison to measurements of a water jet. The spectra are normalized to the total intensity detected in the energy loss interval between 9 eV and 10.5 eV.