
Supporting Info

Supercooled nitrate solution on ice at 232 K: Enhanced HONO yields

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Solid and aqueous sodium nitrate above eutectic

Figure S1 shows the sodium K-edge NEXAFS spectrum of NaNO_3 salt, acquired with different measurement settings. Sodium K-edge NEXAFS spectra of aqueous NaNO_3 in the presence of ice at different temperatures above the eutectic point are shown in Figure S2. All spectra of the solid NaNO_3 salt in Figure S1 show a more prominent absorption feature at 1080 eV photon energy, and a slightly less prominent second feature around 1084 eV with changing intensity depending on the measurement settings. Here, a differentiation between a “fresh” and a “burned” spot and between “long” and “short” acquisition time is made depending on if and how long the sample spot was exposed to photon energy around 1000 eV. This differentiation is made due to changes to the spectrum of the solid salt phase the longer it was exposed to irradiation around 1000 eV either through XPS or NEXAFS measurements. In this work, a sample spot is classified as “fresh” if at this spot either no XPS and NEXAFS measurements were acquired yet, or at maximum a survey spectrum with one iteration only and/ or a N K-edge NEXAFS spectrum (with photon energy ranging from 385 eV to 430 eV only). Sample spots were classified as “burned”, if at this spot XPS measurements at 1000 eV in the region of O1s, C1s, N1s and Na2s with multiple iterations, and/ or if Na K-edge NEXAFS measurements (between 1068 eV and 1110 eV) were performed already. Depending on the measurement settings, the acquisition time for a Na K-edge NEXAFS spectrum ranged from 6 minutes (“short acquisition” in Figure S1) to 30-50 minutes (“long acquisition”). In Figure S1 the absorption feature at 1084 eV of the spectrum acquired on a fresh spot and for a short time (blue) lost slightly in intensity when moving to a fresh spot but measured with a long acquisition time (red). This feature did not change as we stayed on the same spot, but reduced the incoming photon flux by narrowing the entrance and exit slits of the beam (yellow). When moving to a spectrum acquired on a burned spot and with a long acquisition time (blue), even a dip in the intensity between 1082 eV and 1085 eV is visible. One possible reason for the change in intensity of this absorption feature around 1084 eV in Figure S1 is the increase of the beam induced decay of nitrate, altering the local environment of sodium reflected in the spectrum. The decay of nitrate was observed in the loss of the signal intensity of the nitrate peak in the N1s region of the XPS measurements over time.

The spectrum acquired on ice at 8 K above the eutectic in Figure S2 shows an additional feature between 1093 eV and 1096 eV, which is not present in all the other spectra. This feature is probably due to fluorine contamination, which was observed in the XPS survey spectrum and occurred specifically in this one sample.

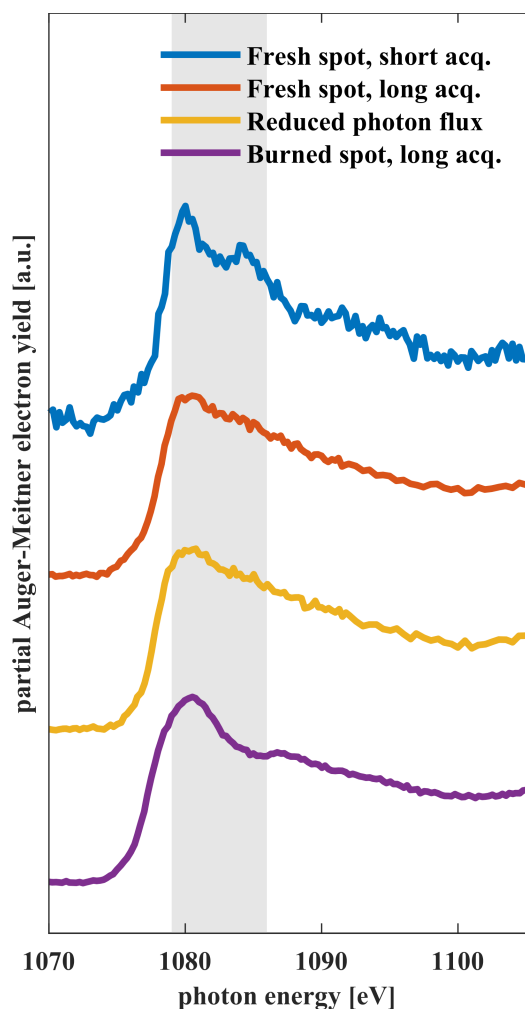


Figure S1 - Sodium K-edge NEXAFS spectrum of solid NaNO_3 salt, with photon energy on the x-axis and the normalized counts of Auger-Meitner electrons on the y-axis. The spectra were measured with either long or short acquisition (acq.) times and with the following conditions: partial water vapor pressures of 1.59 mbar (red, blue) and 1.1 mbar (purple, yellow), and sample temperatures of 20.0°C (red, blue) and 25.0°C (purple, yellow). The spectra consist of different number of repetitions; the blue curve consists of 6 repetitions, the red one of two, the yellow one of one, and the purple one of three.

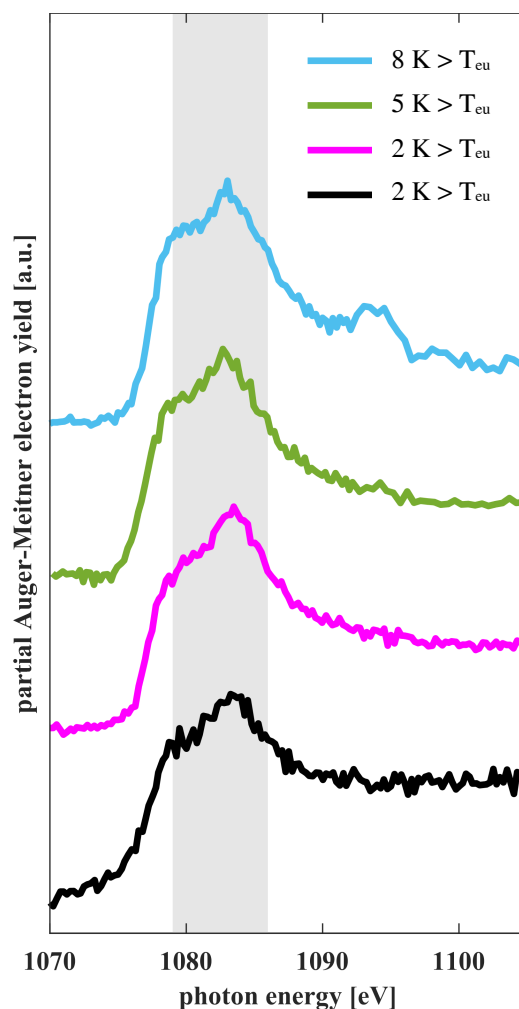


Figure S2 – Sodium K-edge NEXAFS spectrum of NaNO_3 solution (brine) in ice, acquired at different temperatures above the eutectic temperature of NaNO_3 indicated in the inset box.