Supporting Information for

Auger electron spectroscopy of fulminic acid: An experimental and theoretical study

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S1 X-Ray photoelectron spectra

To determine the 1s ionization energies, X-ray photoelectron spectra (XPES) were recorded at all three edges (S1, S2 and S3). In those spectra the binding energy of the electrons were determined by subtracting the experimentally determined kinetic energy from the photon energy.



Fig. S1 : C 1s photoelectron spectrum of HCNO. An ionisation energy of 292.9 eV is determined. Contaminations from CO_2 and HNCO are visible at 297.8¹ and 295.9 eV.²



Fig. S2 N 1s photelectron spectrum of HCNO. An ionisation energy of 410.5 eV is determined. Contaminations due to HCN from the synthesis are visible at 406.9 eV. 3



Fig. S3 O 1s photelectron spectrum of HCNO. An ionisation energy of 539.6 eV is determined. Contaminations from CO_2 and O_2 are visible at 541.2 and 543.4 eV.⁴

S2 Comparison of HCNO Auger electron spectra to those of HNCO, CO_2 and N_2

In this section, we compare our normal Auger electron spectra (AES) to known spectra of HNCO, N_2 and CO_2 . The spectra of CO_2 and N_2 were recorded for calibration purposes during the beamtime. The spectra of Isocyanic acid were taken from Holzmeier *et al.*.²

S2.1 Normal Auger electron spectra

Note that the electron kinetic energy is chosen for comparison.



Fig. S4 Comparison of normal Auger electron spectra (AES) at the carbon K-edge of HCNO (black), HNCO (red), ² and CO₂ (blue). The spectra show that a contamination from HNCO or CO₂ can be ruled out.



Fig. S5 Comparison of AES at the nitrogen K-edge of HCNO (black), HNCO (red),² and N₂ (blue). Again, a contamination can be ruled out.



Fig. S6 Comparison of AES at the oxygen K-edge of HCNO (black), HNCO (red), ² and CO₂ (blue). The spectra show that a contamination from CO_2 can be ruled out.

S3 Additional resonant Auger electron spectra

Figure S7 shows the resonant Auger electron spectra (RAES) at the C 1s edge upon all excitation energies indicated in the NEXAFS spectra (Fig. 3a in the main paper). The top trace shows the off-resonant photoelectron spectrum obtained at 284.1 eV. The additional peak at 8 eV is created by the second harmonic of the synchrotron light ionizing the C1s electron. The next five traces show the RAES recorded on the $3\pi^* \leftarrow 1s$ band. The spectra have a similar appearance, demonstrating the absence of vibrational effects. The weak bands at 288.8 eV and 289.6 eV show only small resonance enhancement. The bottom three spectra show the RAES obtained upon exciting the band that shows a vibrational progression in the NEXAFS spectrum, presumably a Rydberg state. They exhibit a massive enhancement of participator states at binding energies between 24 eV and 34 eV, but only a weak enhancement of the low energy



Fig. S7 Resonant Auger electron spectra (RAES) at the carbon edge. The top trace shows the off-resonant spectrum. The additional peak at 8 eV is due to the second harmonic of the synchrotron light ionizing the C1s electron. The other traces show the RAES recorded on the various absorption bands.

spectator states. However, the RAES recorded on the various vibrational bands are very similar.

Figure S8 shows the RAES at the N 1s edge upon all excitation energies indicated in the NEXAFS spectra (Fig. 3b in the main paper). The top trace shows the off-resonant photoelectron spectrum. The RAES recorded on the $3\pi^*$ excitation show small, but recognisable differences. With increasing energy the resonant enhancement of the 7σ signal at 18 eV binding energy decreases, compared to the 1π signal (see Table 3 in the main paper for detailed description of the states). The weak Rydberg states at 407.1 eV and 408.6 eV show a strong enhancement of spectator states at high binding energies.

Finally, figure S9 shows the RAES at the O 1s edge upon all excitation energies indicated in the NEXAFS spectra (Fig. 3c in the main paper). The spectra recorded on the $3\pi^*$ band between 532.6 eV and 534.6 eV are very similar. Like in the C 1s and N 1s case, excitation of Rydberg states leads to strong enhancement of high binding energy spectator states. At an excitation energy of 535.62 eV (possibly excitation to a 3s Rydberg state) an intense band appears at a binding energy of around 21 eV, most likely due to a spectator state. As the computed RAES are based on the $3\pi^*$ excitation, it is difficult to draw reasonable conclusions on the character of the state.



Fig. S8 Resonant Auger electron spectra (RAES) at the nitrogen edge. The top trace shows the off-resonant excitation at 389.1 eV, the traces below show RAES recorded at the excitation energies marked in Figure 3 b) in the main paper.



Fig. S9 Resonant Auger electron spectra at the oxygen 1s edge with the off-resonant spectrum at 528.2 eV in the top trace. The traces below show RAES recorded at the excitation energies marked in Figure 3 c) in the main paper.

S4 References

References

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