Electronic Supplementary Information
Iron L₃-edge energy shifts for the full range of possible 3d occupations within the same oxidation state of iron halides

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1 Sample preparation

1.1 Electrospray ionisation source

Commercially available salts (see table S1) are dissolved in methanol or water as solvents to obtain solutions with a concentration of \(\approx 1\) mmol/L. The solution is is sprayed at a flowrate of 0.25 ml/h.

| Salt            | purity  | CAS          |
|-----------------|---------|--------------|
| Fe(II)I\(_2\) (anhydrous) | min 97% | 7783-86-0    |
| Fe(II)Br\(_2\) (anhydrous)   | min 98% | 7789-46-0    |
| Fe(II)Cl\(_2\) (anhydrous)   | min 99.5% | 7758-94-3   |
| Fe(III)F\(_3\) (anhydrous)   | min 97%  | 7783-50-8    |

Table S1: Compilation of chemicals used in sample preparation. All samples were purchased from Alfa Aesar.

1.2 Magnetron sputter source

Fe\(^+\) cations also used as a precursor for FeCl\(^+\) production are generated by argon sputtering of an iron target. For FeCl\(^+\) production, iron ions are exposed to CH\(_2\)Cl\(_2\) gas in a collision cell at a pressure of \(\approx 10^{-4}\) mbar. FeCl\(^+\) is subsequently isolated using a quadrupole mass filter.

2 Data treatment

All data sets were acquired at the UE52PGM Ion Trap setup \([\text{1}]\) with a bandwidth of 80 meV (step size 0.03 eV) for the high resolution spectra and 200 meV (step size 0.08 eV) for the overview spectra.

For consistency across different samples only partial ion yield of Fe\(^{2+}\) product ions are considered. We, however, also checked the partial ion yield of all other photo ions to be proportional to Fe\(^{2+}\). Hence, the presented data is proportional to the total ion yield and therefore also to the X-ray absorption.

2.1 Energy calibration

In order to account for photon energy drift over time, the energy in all scans was sequentially referenced after acquisition to one FeCl\(^+\) scan of high signal-to-noise ratio. The latter was acquired right after energy calibration during commissioning of the beamline.

2.2 Averaging procedure and error estimation

To improve the signal-to-noise ratio, multiple scans of the same sample were averaged after single scan referencing for energy calibration, using linear interpolation. The total uncertainty \(\Delta E_{\text{total}}\) was obtained through error propagation taking into account the uncertainties of beamline \((\Delta E_1)\), sample \((\Delta E_2)\) and reference \((\Delta E_3)\) scan reproducibility, and of the sequential referencing during analysis \((\Delta E_4)\).
3 Charge transfer multiplet calculations

The calculated spectra were shifted to fit the energy position of the experimental data by the amounts shown in table S5.

| System | $\Delta E_1/eV$ | $\Delta E_2/eV$ | $\Delta E_3/eV$ | $\Delta E_4/eV$ | $\Delta E_{\text{total}}/eV$ |
|--------|----------------|----------------|----------------|----------------|-----------------|
| FeF$^+$ | ±0.014         | ±0.018         | ±0.003         | ±0.030         | ±0.037          |
| FeCl$^+$ | ±0.014         | ±0.019         | ±0.011         | ±0.030         | ±0.040          |
| FeBr$^+$ | ±0.014         | ±0.025         | ±0.006         | ±0.030         | ±0.042          |
| FeI$^+$  | ±0.014         | ±0.027         | ±0.011         | ±0.030         | ±0.044          |

Table S4: Table of error contributions of the measured samples and the resulting total error.

4 Turbomole density functional theory (DFT)

The Turbomole DFT calculation were done with the B3LYP functional and the def2-TZVP basis set, with the iron 3d orbital population derived by natural population analysis, after a geometry optimization was performed.

| System | Fe 3d(tot.)/e |
|--------|----------------|
| FeF$^+$ | 6.34           |
| FeCl$^+$ | 6.53           |
| FeBr$^+$ | 6.57           |
| FeI$^+$  | 6.73           |

Table 4: Natural populations of iron 3d derived from Turbomole DFT calculations.

5 Electronegativities

All electronegativities $\chi$ were determined from ionization energies (IE) and electron affinities (EA) according to Mulliken.
### Table S6: Compilation of first ionization energies and electron affinities for all halogens. Electronegativities are determined according to Mulliken [4].

| Element | IE/eV | EA/eV | χ/eV |
|---------|-------|-------|------|
| F       | 17.42282 | 3.448 | 10.43541 |
| Cl      | 12.967633 | 3.613 | 8.2903165 |
| Br      | 11.81381  | 3.363 | 7.588405 |
| I       | 10.451260 | 3.063 | 6.75713 |

### 6 Overview spectra

In addition to the high resolution spectra of the iron L$_3$-edge, we also measured overview spectra of the iron L$_{2,3}$-edge (see figure S1).

![Overview spectra](image)

**Figure S1:** Overview spectra FeX$^+$ Iron L$_{2,3}$-edge measured with a bandwidth of 200 meV and step size of 0.08 eV.
References

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