**Supporting Information**

# Bridging-hydride influence on the electronic structure of an [FeFe] hydrogenase active-site model complex revealed by XAES-DFT

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## *(1) Crystallographic coordinates of 1 and [1Hy]$^+$.*

**Table S1:** Atomic coordinates from X-ray crystallography.[a]

| **1** | | | | | | | | **[1Hy]$^+$** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | -14.708 | 12.027 | 8.875 | C | -14.738 | 10.358 | 9.410 | H | 13.810 | 12.784 | 4.237 | C | 12.521 | 8.724 | 2.736 |
| C | -13.225 | 12.519 | 9.689 | O | -14.734 | 9.249 | 9.750 | H | 11.981 | 10.647 | 4.292 | C | 15.709 | 12.289 | 0.354 |
| O | -12.265 | 12.815 | 10.257 | C | -16.115 | 14.304 | 11.002 | H | 11.775 | 12.015 | 5.022 | C | 13.951 | 13.774 | 1.574 |
| Fe | -17.152 | 12.506 | 8.303 | C | -15.075 | 15.189 | 10.257 | H | 15.483 | 8.195 | 3.821 | O | 12.250 | 8.261 | -0.717 |
| C | -18.513 | 13.626 | 8.318 | P | -13.750 | 11.295 | 6.993 | H | 15.061 | 7.361 | -0.510 | O | 11.928 | 8.077 | 3.465 |
| O | -19.394 | 14.370 | 8.285 | C | -14.348 | 9.713 | 6.348 | H | 14.379 | 6.445 | 0.562 | O | 16.768 | 12.414 | -0.064 |
| S | -15.423 | 13.857 | 7.778 | H | -13.872 | 9.495 | 5.543 | H | 17.451 | 8.515 | 1.289 | O | 13.907 | 14.828 | 2.015 |
| C | -15.356 | 15.369 | 8.819 | H | -15.286 | 9.780 | 6.156 | H | 16.881 | 9.883 | 1.801 | P | 15.163 | 8.362 | 1.554 |
| S | -16.293 | 12.584 | 10.381 | H | -14.204 | 9.025 | 7.001 | H | 16.733 | 9.488 | 0.291 | P | 13.210 | 12.756 | -1.063 |
| C | -17.289 | 11.977 | 6.637 | C | -11.987 | 10.906 | 7.193 | H | 10.472 | 11.960 | 3.131 | C | 11.420 | 12.136 | 3.017 |
| O | -17.405 | 11.617 | 5.541 | H | -11.885 | 10.221 | 7.857 | H | 11.536 | 13.098 | 2.994 | C | 12.148 | 11.599 | 4.230 |
| P | -18.305 | 10.677 | 8.867 | H | -11.517 | 11.695 | 7.470 | H | 11.580 | 11.160 | -1.404 | C | 13.649 | 11.827 | 4.232 |
| C | -20.085 | 10.826 | 8.543 | H | -11.632 | 10.597 | 6.357 | H | 11.886 | 11.903 | -2.749 | C | 12.276 | 11.509 | -1.966 |
| H | -20.526 | 10.013 | 8.803 | C | -13.820 | 12.309 | 5.491 | H | 14.994 | 12.585 | -2.529 | C | 14.415 | 13.316 | -2.292 |
| H | -20.440 | 11.559 | 9.049 | H | -13.364 | 11.856 | 4.777 | H | 14.939 | 14.031 | -1.924 | C | 12.051 | 14.143 | -0.949 |
| H | -20.228 | 10.982 | 7.607 | H | -14.736 | 12.455 | 5.245 | H | 13.955 | 13.626 | -3.075 | C | 15.134 | 7.010 | 0.379 |
| C | -18.207 | 10.035 | 10.561 | H | -13.395 | 13.154 | 5.656 | H | 11.627 | 14.278 | -1.800 | C | 15.416 | 7.540 | 3.124 |
| C | -17.940 | 9.174 | 7.926 | H | -16.310 | 15.888 | 8.697 | H | 11.384 | 13.949 | -0.287 | C | 16.741 | 9.155 | 1.192 |
| H | -17.296 | 9.809 | 10.766 | H | -14.577 | 16.007 | 8.393 | H | 12.528 | 14.939 | -0.700 | H | 12.864 | 10.795 | -2.226 |
| H | -18.516 | 10.704 | 11.175 | H | -15.820 | 14.241 | 12.053 | Fe | 13.371 | 9.724 | 1.551 | H | 15.944 | 6.499 | 0.458 |
| H | -18.756 | 9.251 | 10.639 | H | -17.096 | 14.782 | 10.953 | Fe | 14.035 | 12.136 | 0.922 | H | 14.673 | 6.958 | 3.304 |
| H | -18.488 | 8.454 | 8.248 | H | -15.081 | 16.173 | 10.735 | S | 11.930 | 11.467 | 1.405 | H | 16.224 | 7.023 | 3.089 |
| H | -17.015 | 8.945 | 8.034 | H | -14.079 | 14.774 | 10.398 | S | 14.594 | 11.108 | 2.858 | H | 14.151 | 10.592 | 0.325 |
| H | -18.125 | 9.325 | 6.996 | | | | | C | 12.668 | 8.837 | 0.171 | H | 14.006 | 11.473 | 5.061 |

[a]data are displayed in xyz-file format; coordinates for **[1Hy]$^+$** refer to the $BF_4^-$ salt of the complex.

*(2) Kβ emission spectra of iron reference compounds for resonant excitation.*

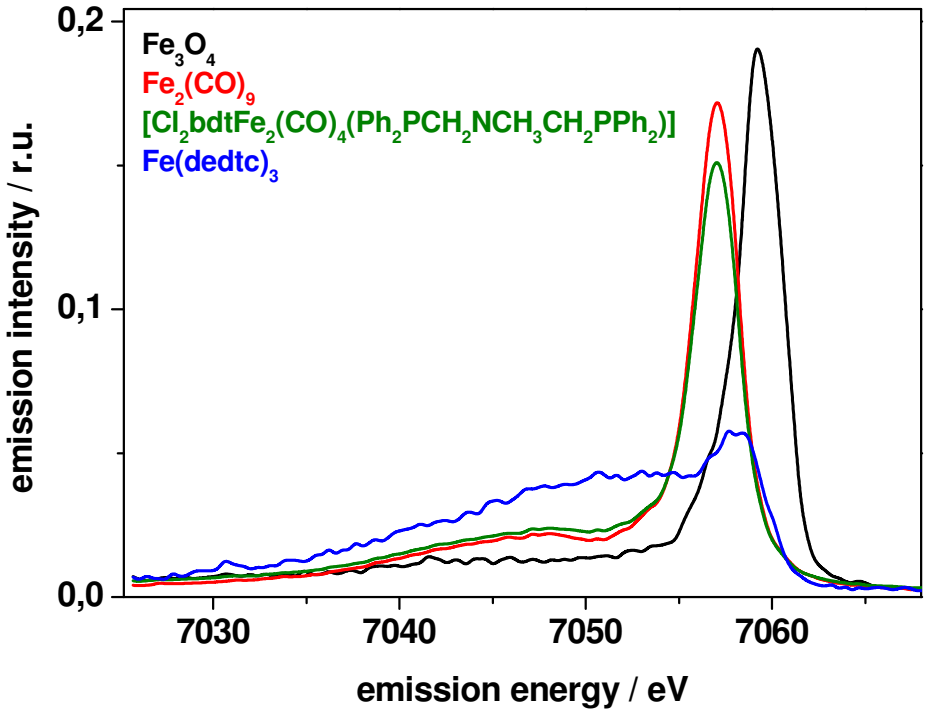


**Figure S1:** Kß emission spectra for resonant excitation into the first pre-edge peak of the Fe K-edge spectra. For further details see the legend of Fig. 4. Spectra were normalized to unity area.

*(3) Kβ CIE spectra for excitation at 7115.8 eV.*

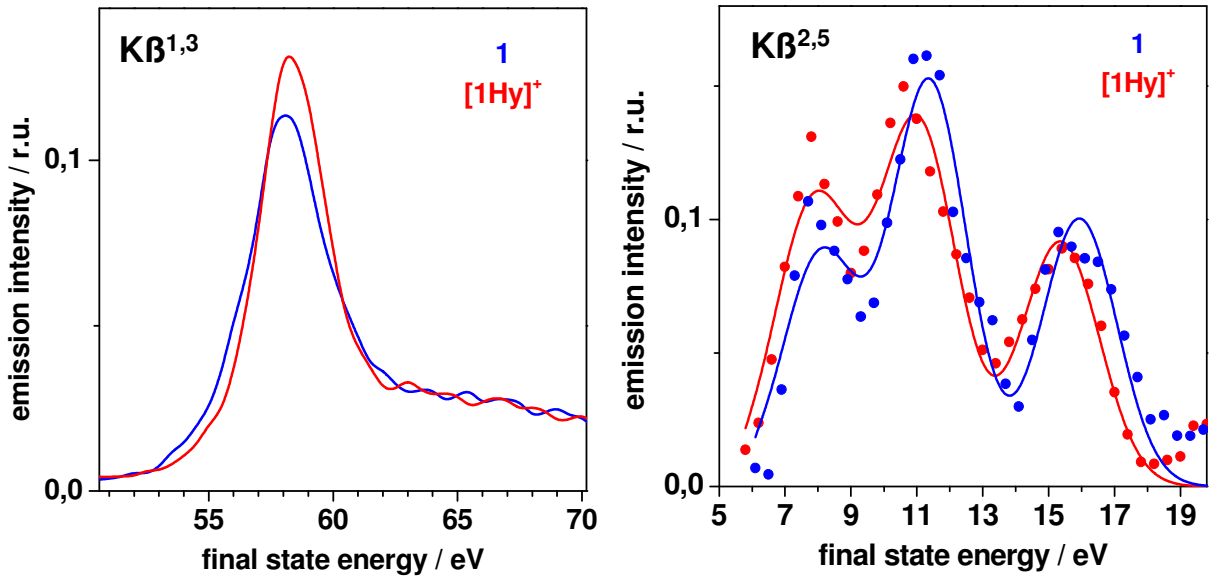


**Figure S2:** CIE line plots from Kß RIXS data for resonant excitation at 7115.8 eV. For respective RIXS plane plots see Fig. 8. Left, transects through the Kß$^{1,3}$ and Kß´ spectral regions; right, transects through the Kß$^{2,5}$ spectral region (dots, experimental data; lines, fit curves with parameters given in Table 4).