**Supporting Information**

First-Principles Study of Adsorption of $CH_4$ on a Fluorinated Model $NiF_2$ Surface

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# List of Figures



# List of Tables

On the following pages numerical results belonging to the paper "First-Principles Study of Adsorption of $CH_4$ on a Fluorinated Model $NiF_2$ Surface" are collected. For the adsorption of $CH_4$ the methane molecule was placed on the surface at six different higher symmetry positions and three different distances (1.5, 1.7 and 2.0 Å, respectively) which is indicated in the tables. For the study of co-adsorption of $CH_4$ and HF only one distance from the surface was considered. All possible combinations of methane and HF on the 6 higher symmetry positions were considered. Furthermore, three different orientations of the HF molecule were considered, namely flat, F down and F up (with respect to the surface). The starting orientations are indicated in the tables.

All the presented results are the calculations done in VASP within the framework of spin unrestricted PBE+U D3(BJ) approach, with the kinetic cut-off energy of 700 eV and the K-point mesh of 8×8×1. More detailed model details and computational settings are described in the main text.

The following data are presented in the tables:

- #: numbering of the structure in each group
- Distance: distance of the adsorbates from the surface in the starting structure
- Position: position of the adsorbates on the surface; in case of co-adsorption the first number indicates position of $CH_4$ and the second the position of HF
- Orientation: u - up, d - down, f - flat; regarding the orientation of co-adsorbed HF as explained in the main text
- $E_{ads}$: adsorption energy as defined in the main text, in eV
- d($X_1X_2$): bond length between element $X_1$ and $X_2$, where X is the element symbol; in Å
- magnetic moments are in the units of $\mu_B$
- charge transfer, as defined in the main text, in the units of e
- vibrational frequencies are in the units of $cm^{-1}$

A careful reader might notice the presence of some low imaginary frequencies for some of the structures. These mostly occur for weakly physisorbed cases where many possible rotations of adsorbates with low energy barriers are possible. It is important to note that these specific structures do not represent the energetically most favourable configurations. Consequently, the substantial computational cost required to refine these structures and eliminate the imaginary frequencies was considered disproportionate to the potential gain in scientific understanding and thus, deemed not justifiable.

# 1 Adsorption of $CH_4$

Table S1: Adsorption energies and structural parameters for the adsorption of $CH_4$. N.B.: d(NiF/HF) may represent the Ni−F or H−F distance and should be interpreted together with the figure of the appropriate structure; the same holds true for d(CF/HF).

| # | Distance | Position | $E_{ads}$ | d(NiF) | d(NiF/HF) | d(CH) | d(CH) | d(CH) | d(CF/HF) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.7 | 0 | -10.2826 | 2.067 | 2.156 | 1.091 | 1.094 | 1.096 | 1.433 |
| 2 | 1.7 | 3 | -10.2822 | 2.067 | 2.156 | 1.092 | 1.093 | 1.096 | 1.433 |
| 3 | 1.7 | 5 | -10.2518 | 2.054 | 2.206 | 1.092 | 1.093 | 1.096 | 1.436 |
| 4 | 1.7 | 2 | -9.2965 | 2.275 | 0.984 | 1.088 | 1.089 | 1.093 | 1.456 |
| 5 | 1.5 | 5 | -8.5881 | 1.828 | 1.030 | 1.094 | 1.094 | 1.095 | 1.467 |
| 6 | 2.0 | 5 | -8.5864 | 1.833 | 1.027 | 1.094 | 1.095 | 1.096 | 1.468 |
| 7 | 2.0 | 1 | -8.5859 | 1.826 | 1.030 | 1.094 | 1.094 | 1.095 | 1.467 |
| 8 | 1.7 | 4 | -8.5826 | 1.835 | 1.025 | 1.093 | 1.095 | 1.096 | 1.468 |
| 9 | 1.7 | 1 | -8.4467 | 1.825 | 1.026 | 1.094 | 1.094 | 1.097 | 1.457 |
| 10 | 2.0 | 2 | -8.4459 | 1.826 | 1.025 | 1.094 | 1.094 | 1.097 | 1.456 |
| 11 | 1.5 | 3 | -0.2111 | 1.879 | 1.880 | 1.096 | 1.096 | 1.096 | 1.097 |
| 12 | 2.0 | 3 | -0.2035 | 1.876 | 1.883 | 1.095 | 1.096 | 1.096 | 1.097 |
| 13 | 1.5 | 4 | -0.1765 | 1.877 | 1.883 | 1.095 | 1.096 | 1.096 | 1.097 |
| 14 | 2.0 | 0 | -0.1736 | 1.872 | 1.889 | 1.096 | 1.096 | 1.096 | 1.097 |
| 15 | 1.5 | 0 | -0.1722 | 1.867 | 1.893 | 1.096 | 1.096 | 1.096 | 1.097 |
| 16 | 2.0 | 4 | -0.1703 | 1.878 | 1.882 | 1.096 | 1.096 | 1.097 | 1.097 |

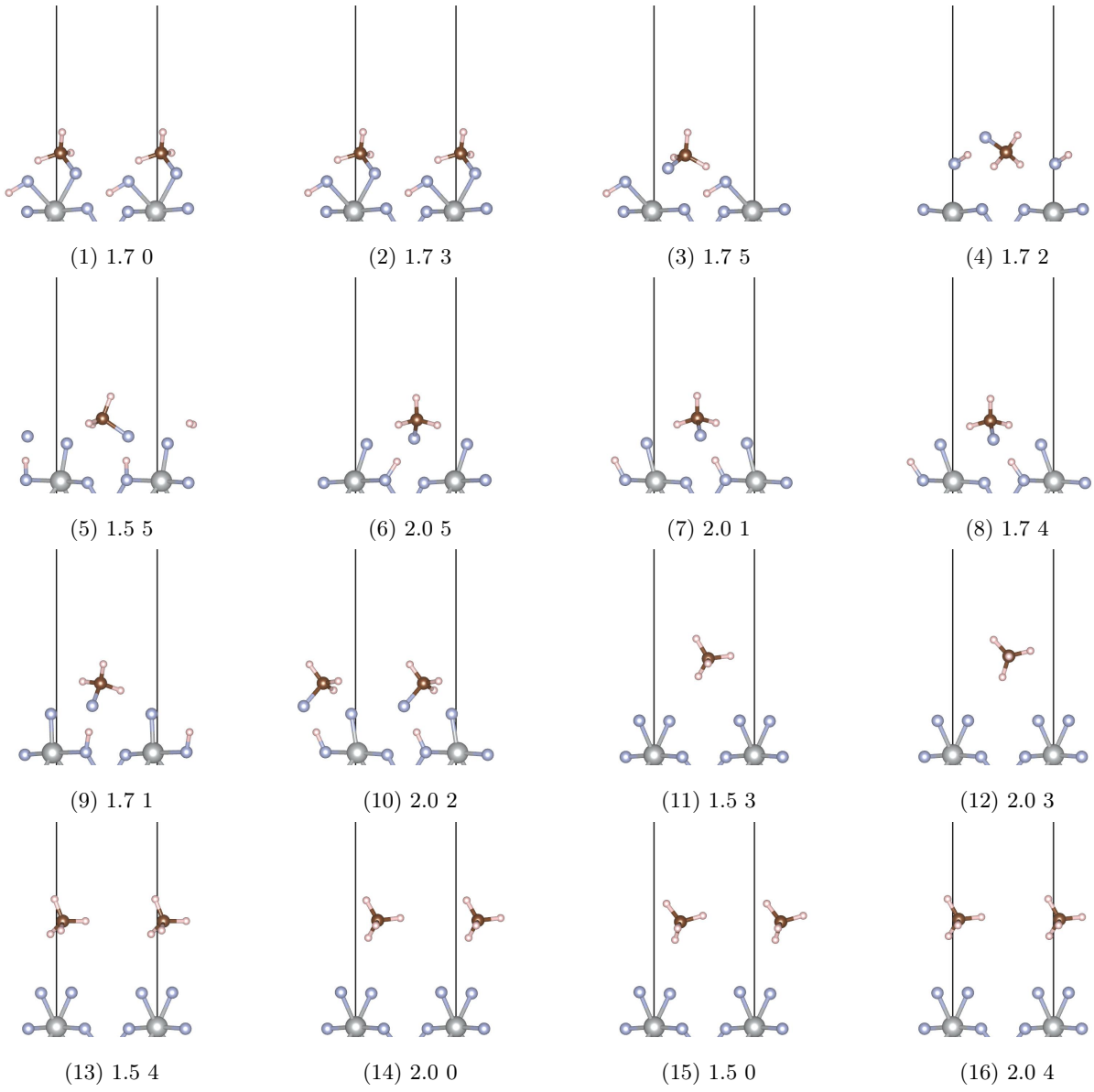


Figure S1: Adsorbed structures for the adsorption of $CH_4$.

Table S2: Magnetic moments on the surface nickel, fluorine and the adsorbate.

| # | Distance | Position | Ni | F | F | C | H | H | H | H |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.7 | 0 | -1.827 | -0.014 | -0.022 | -0.0 | -0.0 | -0.0 | -0.0 | -0.0 |
| 2 | 1.7 | 3 | -1.827 | -0.014 | -0.022 | -0.0 | -0.0 | -0.0 | -0.0 | -0.0 |
| 3 | 1.7 | 5 | -1.828 | -0.01 | -0.023 | -0.001 | -0.0 | -0.0 | 0.0 | -0.0 |
| 4 | 1.7 | 2 | -1.819 | -0.008 | -0.0 | -0.0 | -0.0 | -0.0 | -0.0 | -0.0 |
| 5 | 1.5 | 5 | -1.818 | -0.06 | -0.0 | -0.0 | -0.0 | 0.0 | 0.0 | 0.0 |
| 6 | 2.0 | 5 | -1.819 | -0.057 | -0.0 | -0.0 | -0.0 | 0.0 | 0.0 | 0.0 |
| 7 | 2.0 | 1 | -1.818 | -0.0 | -0.06 | -0.0 | 0.0 | -0.0 | 0.0 | 0.0 |
| 8 | 1.7 | 4 | -1.819 | -0.001 | -0.056 | -0.0 | 0.0 | -0.0 | 0.0 | 0.0 |
| 9 | 1.7 | 1 | -1.819 | 0.0 | -0.062 | -0.0 | -0.0 | -0.0 | -0.0 | 0.0 |
| 10 | 2.0 | 2 | -1.819 | 0.0 | -0.062 | -0.0 | -0.0 | -0.0 | -0.0 | 0.0 |
| 11 | 1.5 | 3 | -2.218 | -0.582 | -0.59 | -0.002 | -0.002 | -0.001 | -0.001 | -0.001 |
| 12 | 2.0 | 3 | -2.218 | -0.585 | -0.588 | -0.002 | -0.001 | -0.001 | -0.001 | -0.001 |
| 13 | 1.5 | 4 | -2.219 | -0.587 | -0.587 | -0.0 | -0.0 | -0.0 | -0.0 | -0.0 |
| 14 | 2.0 | 0 | -2.218 | -0.585 | -0.589 | -0.001 | -0.0 | -0.0 | -0.0 | -0.001 |
| 15 | 1.5 | 0 | -2.218 | -0.582 | -0.59 | -0.001 | -0.0 | -0.0 | -0.0 | -0.001 |
| 16 | 2.0 | 4 | -2.219 | -0.587 | -0.586 | -0.0 | -0.0 | -0.0 | -0.0 | -0.0 |

Table S3: Charge transfer on the surface nickel, fluorine and the adsorbate for adsorbed $CH_4$.

| # | Distance | Position | Ni | F | F | C | H | H | H | H |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.7 | 0 | 0.279 | 0.349 | 0.494 | -0.534 | -0.009 | -0.044 | -0.081 | -0.708 |
| 2 | 1.7 | 3 | 0.285 | 0.346 | 0.493 | -0.487 | -0.032 | -0.052 | -0.095 | -0.706 |
| 3 | 1.7 | 5 | 0.281 | 0.362 | 0.493 | -0.475 | -0.033 | -0.105 | -0.063 | -0.712 |
| 4 | 1.7 | 2 | 0.294 | 0.491 | 0.378 | -0.496 | -0.077 | -0.066 | -0.044 | -0.727 |
| 5 | 1.5 | 5 | 0.314 | 0.449 | 0.371 | -0.370 | -0.142 | -0.017 | -0.151 | -0.725 |
| 6 | 2.0 | 5 | 0.314 | 0.450 | 0.368 | -0.411 | -0.118 | -0.122 | -0.025 | -0.735 |
| 7 | 2.0 | 1 | 0.314 | 0.349 | 0.467 | -0.393 | -0.036 | -0.125 | -0.123 | -0.732 |
| 8 | 1.7 | 4 | 0.311 | 0.349 | 0.470 | -0.424 | -0.009 | -0.117 | -0.126 | -0.730 |
| 9 | 1.7 | 1 | 0.315 | 0.340 | 0.467 | -0.420 | -0.020 | -0.158 | -0.072 | -0.730 |
| 10 | 2.0 | 2 | 0.316 | 0.340 | 0.467 | -0.431 | -0.087 | -0.126 | -0.027 | -0.731 |
| 11 | 1.5 | 3 | 0.000 | 0.010 | 0.014 | -0.040 | -0.008 | -0.008 | 0.025 | 0.006 |
| 12 | 2.0 | 3 | 0.000 | -0.004 | 0.026 | -0.068 | 0.029 | 0.013 | 0.009 | -0.005 |
| 13 | 1.5 | 4 | -0.002 | 0.002 | 0.019 | -0.032 | 0.011 | -0.010 | 0.002 | 0.011 |
| 14 | 2.0 | 0 | -0.002 | 0.009 | 0.013 | -0.013 | -0.007 | -0.003 | 0.007 | -0.004 |
| 15 | 1.5 | 0 | 0.003 | 0.006 | 0.015 | -0.018 | -0.013 | 0.014 | -0.006 | 0.001 |
| 16 | 2.0 | 4 | -0.001 | 0.007 | 0.013 | -0.044 | 0.007 | 0.013 | 0.017 | -0.011 |

Table S4: Calculated frequencies for the adsorption of $CH_4$ .

| 0 | 3 | 5 | 2 | 5 | 5 | 1 | 4 |
|---|---|---|---|---|---|---|---|
| 1.7 | 1.7 | 1.7 | 1.7 | 1.5 | 2.0 | 2.0 | 1.7 |
| 3142.13 | 3140.05 | 3141.49 | 3181.78 | 3121.76 | 3120.42 | 3119.13 | 3121.7 |
| 3106.18 | 3107.07 | 3109.12 | 3159.0 | 3098.35 | 3094.3 | 3098.06 | 3095.03 |
| 3009.25 | 3009.0 | 3011.44 | 3074.77 | 2994.24 | 2990.57 | 2993.23 | 2991.35 |
| 2133.2 | 2137.64 | 2212.01 | 3042.55 | 2416.4 | 2435.79 | 2411.11 | 2452.02 |
| 1434.77 | 1434.09 | 1457.19 | 1428.68 | 1474.6 | 1471.88 | 1472.73 | 1472.82 |
| 1425.44 | 1423.3 | 1429.97 | 1427.59 | 1438.15 | 1438.58 | 1437.37 | 1438.15 |
| 1419.14 | 1418.48 | 1418.39 | 1392.71 | 1428.85 | 1428.11 | 1429.39 | 1427.63 |
| 1206.73 | 1205.92 | 1194.89 | 1139.79 | 1173.44 | 1171.91 | 1172.45 | 1171.17 |
| 1157.15 | 1156.71 | 1152.52 | 1117.09 | 1150.47 | 1150.86 | 1149.16 | 1150.22 |
| 1145.88 | 1144.96 | 1148.25 | 943.8 | 1036.59 | 1032.92 | 1040.08 | 1028.49 |
| 1028.76 | 1027.23 | 1027.75 | 852.37 | 975.35 | 972.75 | 972.38 | 969.39 |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 938.59 | 939.07 | 923.67 | 825.15 | 850.26 | 847.92 | 849.51 | 845.23 |
| 369.83 | 369.29 | 369.19 | 444.79 | 472.86 | 467.7 | 477.04 | 467.08 |
| 252.48 | 253.12 | 248.99 | 277.4 | 285.55 | 286.34 | 282.71 | 278.68 |
| 203.17 | 202.52 | 200.43 | 148.87 | 201.53 | 203.48 | 199.0 | 203.19 |
| 180.15 | 179.67 | 171.01 | 140.8 | 180.89 | 185.59 | 181.73 | 189.0 |
| 143.23 | 141.78 | 163.55 | 98.19 | 160.77 | 151.99 | 158.01 | 150.42 |
| 111.58 | 108.98 | 129.29 | 62.01 | 119.82 | 121.52 | 118.59 | 125.93 |
| 97.28 | 95.9 | 111.39 | 20.15 | 96.51 | 96.93 | 92.64 | 92.01 |
| 84.84 | 73.77 | 82.56 | 27.5i | 75.67 | 87.97 | 75.73 | 84.59 |
| 57.15 | 43.77 | 62.7 | 107.07i | 31.09 | 29.84 | 34.29 | 35.04i |
| 1 | 2 | 3 | 3 | 4 | 0 | 0 | 4 |
| 1.7 | 2.0 | 1.5 | 2.0 | 1.5 | 2.0 | 1.5 | 2.0 |
| 3124.23 | 3120.67 | 3071.65 | 3057.0 | 3079.85 | 3074.63 | 3070.38 | 3073.4 |
| 3097.68 | 3094.84 | 3046.05 | 3047.09 | 3047.02 | 3046.45 | 3042.9 | 3050.06 |
| 2990.78 | 2988.06 | 2998.96 | 2993.96 | 3002.9 | 3002.1 | 2996.92 | 2989.45 |
| 2461.51 | 2466.79 | 2963.79 | 2963.43 | 2966.3 | 2966.85 | 2965.24 | 2965.74 |
| 1469.44 | 1468.7 | 1351.47 | 1327.9 | 1391.09 | 1390.78 | 1399.52 | 1395.48 |
| 1433.29 | 1432.37 | 1298.71 | 1281.8 | 1297.42 | 1304.12 | 1277.27 | 1280.47 |
| 1403.67 | 1403.81 | 1232.45 | 1218.08 | 1248.62 | 1243.79 | 1243.2 | 1236.94 |
| 1177.69 | 1178.25 | 1185.74 | 1188.4 | 1193.43 | 1197.24 | 1197.08 | 1187.52 |
| 1153.22 | 1153.54 | 1094.76 | 1099.13 | 1080.55 | 1093.4 | 1096.12 | 1061.13 |
| 1076.58 | 1075.29 | 469.6 | 469.78 | 469.15 | 467.96 | 468.49 | 468.66 |
| 916.44 | 910.44 | 244.75 | 244.64 | 243.67 | 250.06 | 256.29 | 242.16 |
| 882.56 | 886.79 | 230.16 | 231.72 | 235.24 | 232.21 | 233.02 | 234.43 |
| 472.49 | 470.72 | 137.5 | 140.02 | 139.38 | 143.52 | 144.77 | 141.71 |
| 279.75 | 275.88 | 131.75 | 136.05 | 137.05 | 142.1 | 136.56 | 136.71 |
| 183.42 | 186.57 | 70.32 | 73.61 | 81.46 | 77.45 | 83.03 | 70.09 |
| 162.68 | 158.87 | 64.96 | 65.72 | 72.19 | 66.33 | 62.7 | 65.71 |
| 149.81 | 143.26 | 61.71 | 33.24 | 53.57 | 28.89 | 19.81 | 23.71 |
| 126.39 | 129.04 | 34.98 | 8.17i | 8.78 | 15.94 | 8.14i | 32.26i |
| 82.9 | 78.84 | 13.07 | 48.41i | 25.85i | 25.2i | 42.96i | 43.22i |
| 64.53 | 57.59 | 23.83i | 56.84i | 49.1i | 44.02i | 53.88i | 66.65i |
| 32.86 | 41.97 | 60.72i | 83.49i | 66.38i | 63.78i | 71.89i | 76.49i |

# 2 Co-adsorption of $CH_4$ and HF

## 2.1 Group I

Table S5: Adsorption energies and bond distances for the adsorbed structures in group I.

| # | Orientation | Position | $E_{ads}$ | d(CH) | d(CH) | d(CH) | d(CF) | d(NiF) | d(NiF) | d(HF) | d(HF) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | d | 5_1 | -11.5292 | 1.096 | 1.097 | 1.097 | 1.413 | 2.030 | 2.033 | 1.013 | 1.013 |
| 2 | u | 2_5 | -11.5231 | 1.097 | 1.097 | 1.098 | 1.416 | 2.034 | 2.038 | 1.011 | 1.011 |
| 3 | f | 4_1 | -11.4700 | 1.097 | 1.097 | 1.097 | 1.414 | 2.034 | 2.038 | 1.010 | 1.011 |
| 4 | u | 0_4 | -11.4406 | 1.097 | 1.097 | 1.097 | 1.415 | 2.033 | 2.039 | 1.010 | 1.012 |

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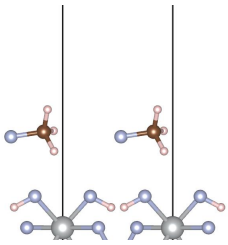
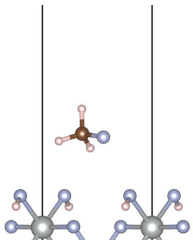
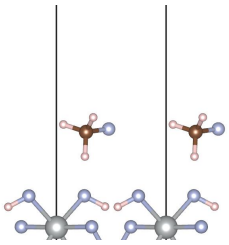
| # | Orientation | Position | $E_{ads}$ | d(CH) | d(CH) | d(CH) | d(CF) | d(NiF) | d(NiF) | d(HF) | d(HF) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | d | 4_0 | -11.2778 | 1.092 | 1.092 | 1.093 | 1.452 | 2.068 | 2.110 | 1.118 | 0.965 |
| 6 | u | 4_2 | -11.2673 | 1.091 | 1.093 | 1.093 | 1.453 | 2.089 | 2.106 | 1.104 | 0.961 |
| 7 | f | 4_2 | -11.2670 | 1.091 | 1.093 | 1.093 | 1.453 | 2.088 | 2.107 | 1.104 | 0.961 |
| 8 | u | 4_0 | -11.2132 | 1.097 | 1.098 | 1.098 | 1.414 | 2.040 | 2.044 | 0.991 | 0.988 |
| 9 | u | 0_5 | -11.1536 | 1.092 | 1.093 | 1.094 | 1.452 | 2.212 | 2.246 | 1.088 | 0.961 |
| 10 | f | 3_5 | -11.1535 | 1.092 | 1.093 | 1.094 | 1.452 | 2.215 | 2.244 | 1.087 | 0.961 |
| 11 | d | 4_1 | -11.1425 | 1.092 | 1.093 | 1.094 | 1.442 | 2.082 | 2.105 | 1.063 | 0.968 |
| 12 | f | 0_1 | -11.1355 | 1.092 | 1.092 | 1.093 | 1.449 | 2.203 | 2.249 | 1.090 | 0.963 |
| 13 | f | 4_5 | -11.1253 | 1.093 | 1.094 | 1.095 | 1.441 | 2.086 | 2.106 | 1.058 | 0.968 |
| 14 | f | 1_3 | -11.1235 | 1.092 | 1.093 | 1.095 | 1.441 | 2.087 | 2.107 | 1.060 | 0.968 |
| 15 | f | 4_3 | -11.1234 | 1.092 | 1.093 | 1.095 | 1.441 | 2.088 | 2.106 | 1.059 | 0.968 |
| 16 | u | 0_1 | -11.1219 | 1.092 | 1.093 | 1.095 | 1.441 | 2.088 | 2.104 | 1.060 | 0.968 |
| 17 | u | 4_3 | -11.1167 | 1.092 | 1.093 | 1.094 | 1.442 | 2.089 | 2.102 | 1.060 | 0.968 |
| 18 | u | 5_1 | -11.0900 | 1.091 | 1.093 | 1.095 | 1.440 | 2.061 | 2.146 | 1.057 | 0.966 |
| 19 | u | 2_1 | -11.0536 | 1.096 | 1.097 | 1.098 | 1.416 | 2.079 | 2.119 | 1.067 | 0.967 |
| 20 | f | 4_0 | -11.0093 | 1.096 | 1.097 | 1.098 | 1.417 | 2.085 | 2.122 | 1.065 | 0.967 |
| 21 | f | 2_4 | -11.0076 | 1.093 | 1.095 | 1.096 | 1.436 | 2.072 | 2.126 | 1.047 | 0.962 |
| 22 | d | 0_1 | -10.9160 | 1.097 | 1.097 | 1.097 | 1.416 | 2.219 | 2.220 | 1.088 | 0.978 |
| 23 | f | 3_1 | -10.8636 | 1.091 | 1.094 | 1.095 | 1.441 | 2.150 | 2.349 | 1.048 | 0.963 |
| 24 | f | 1_0 | -10.8488 | 1.093 | 1.094 | 1.094 | 1.442 | 2.200 | 2.303 | 1.052 | 0.964 |
| 25 | u | 1_5 | -10.8109 | 1.092 | 1.096 | 1.096 | 1.430 | 2.164 | 2.304 | 1.040 | 0.960 |
| 26 | u | 4_1 | -10.2132 | 1.092 | 1.095 | 1.095 | 1.443 | 2.079 | 2.156 | 1.055 | 0.965 |
| 27 | f | 0_5 | -10.1197 | 1.097 | 1.097 | 1.097 | 1.415 | 2.034 | 2.045 | 1.011 | 1.012 |
| 28 | d | 0_4 | -10.0996 | 1.089 | 1.090 | 1.092 | 1.490 | 1.873 | 2.455 | 1.011 | 0.996 |
| 29 | u | 3_4 | -10.0384 | 1.089 | 1.090 | 1.092 | 1.490 | 1.874 | 2.495 | 0.996 | 1.017 |
| 30 | u | 3_2 | -10.0369 | 1.089 | 1.089 | 1.091 | 1.490 | 1.876 | 2.466 | 0.997 | 1.015 |
| 31 | f | 0_3 | -10.0356 | 1.088 | 1.093 | 1.093 | 1.472 | 2.282 | - | 0.990 | 0.990 |
| 32 | f | 5_1 | -10.0353 | 1.087 | 1.093 | 1.093 | 1.472 | 2.280 | - | 0.990 | 0.990 |
| 33 | d | 5_4 | -10.0081 | 1.090 | 1.091 | 1.092 | 1.481 | 1.860 | - | 0.990 | 1.043 |
| 34 | d | 5_0 | -10.0074 | 1.091 | 1.091 | 1.092 | 1.481 | 1.861 | - | 0.990 | 1.044 |
| 35 | d | 2_0 | -10.0041 | 1.089 | 1.091 | 1.092 | 1.489 | 1.863 | - | 0.987 | 1.035 |
| 36 | d | 2_4 | -10.0040 | 1.090 | 1.091 | 1.092 | 1.480 | 1.859 | - | 0.988 | 1.047 |
| 37 | u | 3_0 | -9.9971 | 1.087 | 1.093 | 1.093 | 1.475 | 2.161 | - | 0.993 | 1.000 |
| 38 | u | 5_0 | -9.9965 | 1.087 | 1.093 | 1.093 | 1.475 | 2.158 | - | 0.992 | 1.000 |
| 39 | u | 5_3 | -9.9962 | 1.088 | 1.093 | 1.093 | 1.475 | 2.166 | - | 0.993 | 1.000 |
| 40 | u | 2_0 | -9.9467 | 1.089 | 1.091 | 1.091 | 1.488 | 1.864 | - | 0.986 | 1.043 |
| 41 | u | 2_4 | -9.9467 | 1.089 | 1.091 | 1.091 | 1.488 | 1.864 | - | 0.986 | 1.043 |
| 42 | f | 0_4 | -9.9464 | 1.089 | 1.091 | 1.091 | 1.491 | 1.868 | - | 0.988 | 1.037 |
| 43 | u | 1_0 | -9.9128 | 1.086 | 1.087 | 1.094 | 1.475 | 2.139 | - | 0.996 | 1.000 |
| 44 | f | 3_0 | -9.9115 | 1.089 | 1.091 | 1.091 | 1.491 | 1.868 | - | 0.988 | 1.038 |
| 45 | u | 3_1 | -9.8759 | 1.089 | 1.089 | 1.090 | 1.491 | 1.868 | - | 0.981 | 1.041 |
| 46 | f | 2_1 | -9.6577 | 1.091 | 1.093 | 1.094 | 1.478 | 2.287 | - | 0.949 | 0.973 |
| 47 | f | 2_5 | -9.4962 | 1.097 | 1.097 | 1.097 | 1.417 | 2.221 | - | 0.974 | 1.073 |
| 48 | f | 2_0 | -9.2559 | 1.089 | 1.090 | 1.092 | 1.488 | 1.864 | - | 0.987 | 1.042 |
| 49 | f | 3_4 | -9.0016 | 1.091 | 1.092 | 1.093 | 1.449 | 2.189 | - | 1.087 | 0.960 |
| 50 | u | 2_3 | -8.6131 | 1.087 | 1.093 | 1.093 | 1.475 | 2.159 | - | 0.993 | 1.000 |



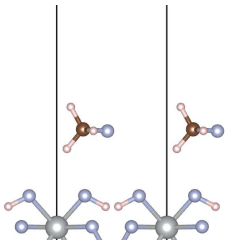
(1) d 5_1



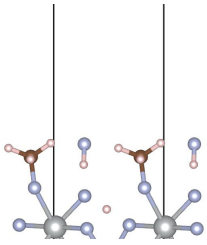
(2) u 2_5



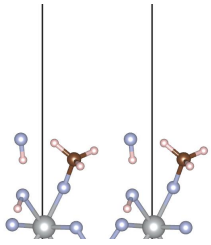
(3) f 4_1



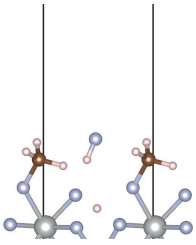
(4) u 0_4



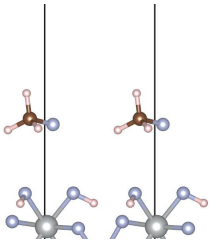
(5) d 4_0



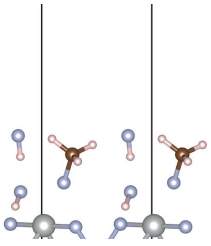
(6) u 4_2



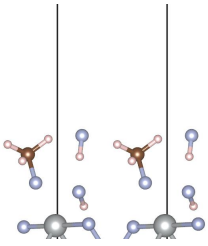
(7) f 4_2



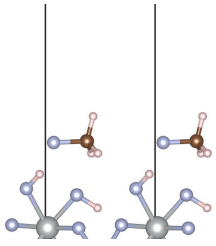
(8) u 4_0



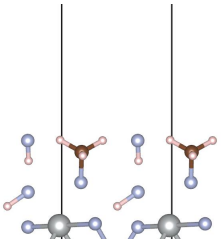
(9) u 0_5



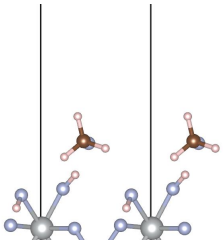
(10) f 3_5



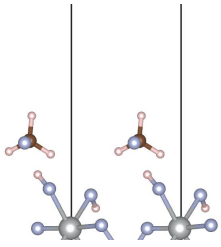
(11) d 4_1



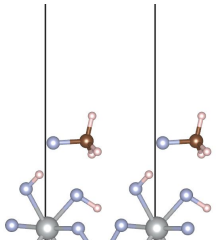
(12) f 0_1



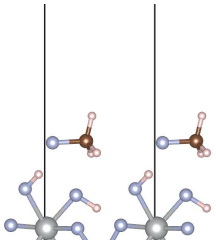
(13) f 4_5



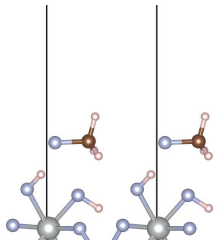
(14) f 1_3



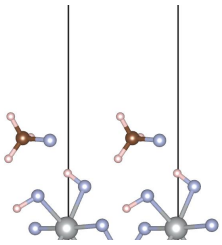
(15) f 4_3



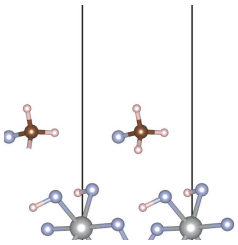
(16) u 0_1



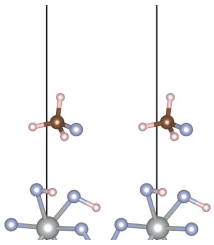
(17) u 4_3



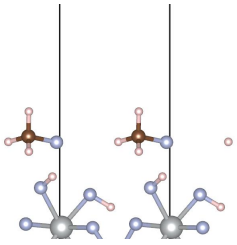
(18) u 5_1



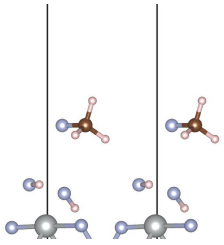
(19) u 2_1



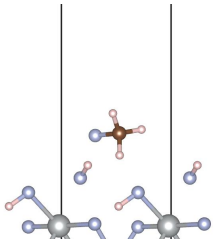
(20) f 4_0



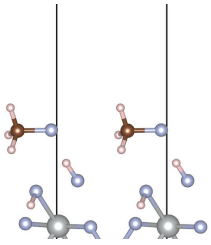
(21) f 2_4



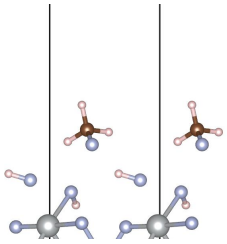
(22) d 0_1



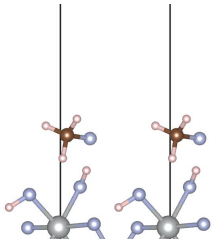
(23) f 3_1



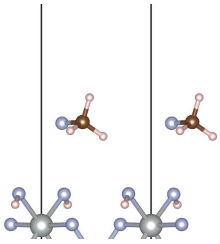
(24) f 1_0



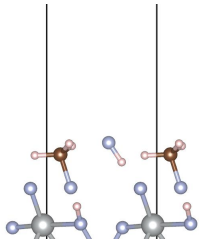
(25) u 1_5



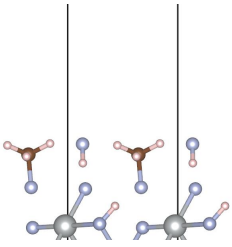
(26) u 4_1



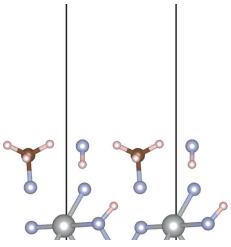
(27) f 0_5



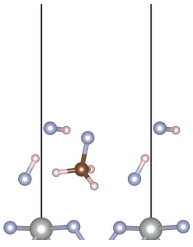
(28) d 0_4



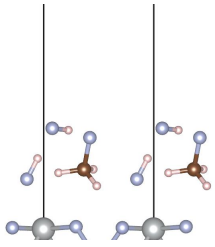
(29) u 3_4



(30) u 3_2



(31) f 0_3



(32) f 5_1

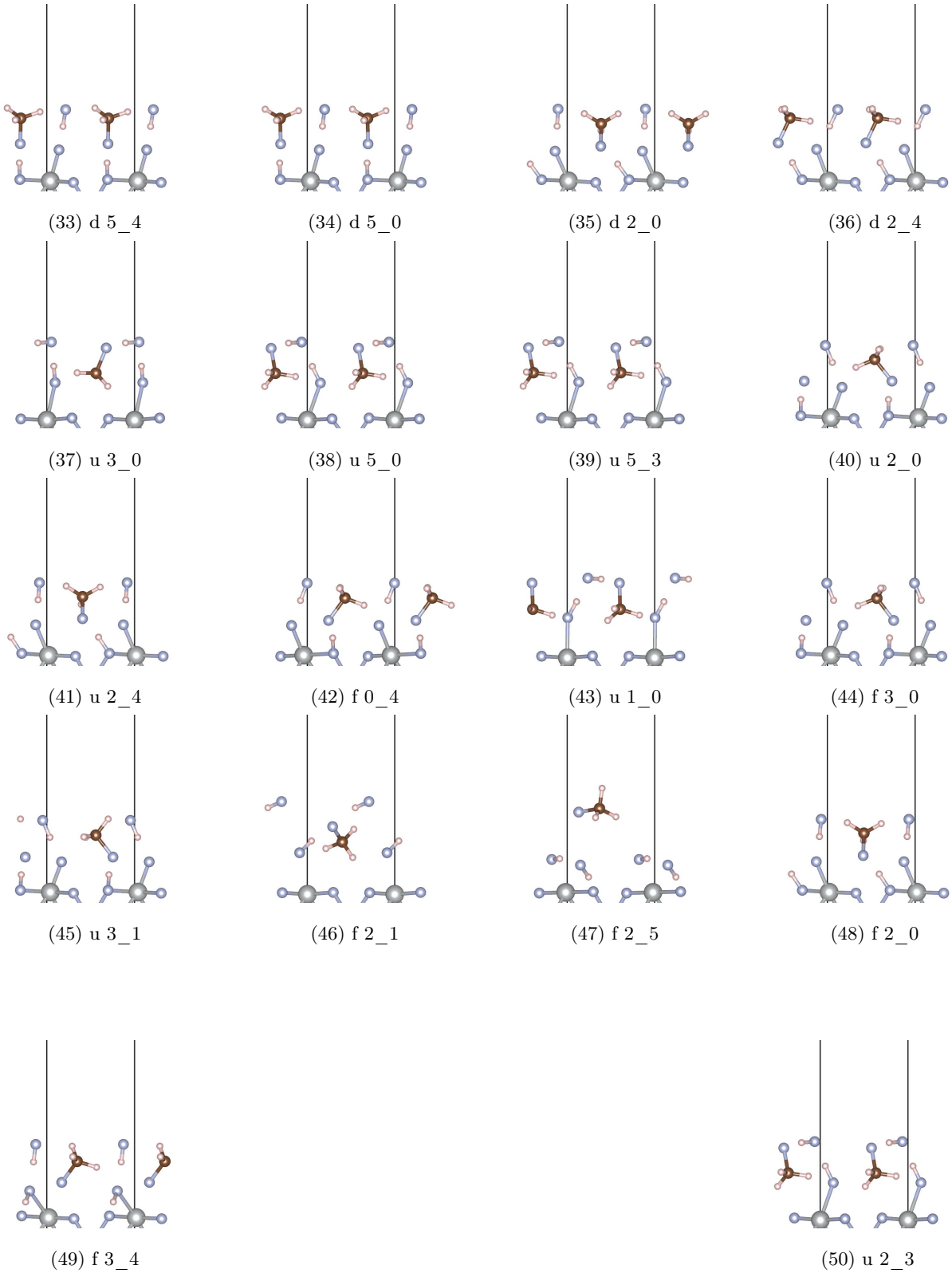



Figure S2: Adsorbed structures belonging to group I.

Table S6: Magnetic moments on the surface nickel, fluorine and on the adsorbates for group I.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | H | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | d | 5_1 | -1.837 | -0.023 | -0.022 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 2 | u | 2_5 | -1.837 | -0.022 | -0.022 | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.000 | -0.000 |
| 3 | f | 4_1 | -1.837 | -0.022 | -0.022 | -0.000 | -0.000 | 0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 4 | u | 0_4 | -1.837 | -0.022 | -0.022 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 5 | d | 4_0 | -1.830 | -0.020 | -0.014 | -0.001 | -0.000 | -0.000 | -0.001 | -0.000 | -0.000 | -0.001 |
| 6 | u | 4_2 | -1.830 | -0.016 | -0.019 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 | -0.000 |
| 7 | f | 4_2 | -1.830 | -0.019 | -0.016 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 8 | u | 4_0 | -1.831 | -0.022 | -0.022 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 9 | u | 0_5 | -1.833 | -0.013 | -0.016 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 | -0.000 |
| 10 | f | 3_5 | -1.833 | -0.016 | -0.013 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 11 | d | 4_1 | -1.830 | -0.021 | -0.014 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 12 | f | 0_1 | -1.834 | -0.012 | -0.016 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 13 | f | 4_5 | -1.830 | -0.014 | -0.021 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 14 | f | 1_3 | -1.830 | -0.000 | -0.014 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.021 |
| 15 | f | 4_3 | -1.830 | -0.021 | -0.014 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 16 | u | 0_1 | -1.830 | -0.021 | -0.014 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 17 | u | 4_3 | -1.830 | -0.021 | -0.014 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 18 | u | 5_1 | -1.829 | -0.013 | -0.022 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 19 | u | 2_1 | -1.830 | -0.017 | -0.021 | -0.000 | -0.000 | 0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 20 | f | 4_0 | -1.830 | -0.000 | -0.017 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.021 |
| 21 | f | 2_4 | -1.829 | -0.022 | -0.013 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 22 | d | 0_1 | -1.834 | -0.017 | -0.013 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 23 | f | 3_1 | -1.832 | -0.008 | -0.020 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 24 | f | 1_0 | -1.832 | -0.009 | -0.018 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 25 | u | 1_5 | -1.833 | -0.019 | -0.009 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 26 | u | 4_1 | -1.829 | -0.012 | -0.021 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 27 | f | 0_5 | -1.839 | -0.023 | -0.023 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 28 | d | 0_4 | -1.830 | -0.008 | -0.037 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.001 |
| 29 | u | 3_4 | -1.829 | -0.038 | -0.007 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.001 | -0.000 |
| 30 | u | 3_2 | -1.829 | -0.038 | -0.007 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.001 | -0.000 |
| 31 | f | 0_3 | -1.817 | -0.000 | -0.006 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 | -0.000 |
| 32 | f | 5_1 | -1.817 | -0.000 | -0.006 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 | -0.000 |
| 33 | d | 5_4 | -1.826 | -0.040 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.002 |
| 34 | d | 5_0 | -1.827 | -0.040 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.002 |
| 35 | d | 2_0 | -1.826 | -0.002 | -0.038 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.001 | -0.002 |
| 36 | d | 2_4 | -1.826 | -0.000 | -0.041 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.000 | -0.002 |
| 37 | u | 3_0 | -1.816 | -0.008 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 38 | u | 5_0 | -1.816 | -0.008 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 39 | u | 5_3 | -1.816 | -0.008 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 40 | u | 2_0 | -1.825 | -0.039 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.002 | -0.001 |
| 41 | u | 2_4 | -1.825 | -0.001 | -0.039 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.002 | -0.001 |
| 42 | f | 0_4 | -1.826 | -0.002 | -0.038 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.001 | -0.002 |
| 43 | u | 1_0 | -1.818 | -0.009 | -0.000 | -0.000 | -0.000 | 0.000 | 0.000 | -0.000 | -0.000 | -0.001 |
| 44 | f | 3_0 | -1.826 | -0.038 | -0.002 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.001 | -0.002 |
| 45 | u | 3_1 | -1.826 | -0.038 | -0.002 | -0.000 | -0.000 | -0.001 | 0.000 | 0.000 | -0.002 | 0.000 |
| 46 | f | 2_1 | -1.817 | -0.000 | -0.006 | 0.000 | -0.000 | 0.000 | -0.000 | -0.000 | -0.001 | -0.000 |
| 47 | f | 2_5 | -1.833 | -0.015 | -0.013 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 48 | f | 2_0 | -1.826 | -0.001 | -0.039 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.001 | -0.002 |
| 49 | f | 3_4 | -1.839 | -0.011 | -0.017 | -0.001 | -0.000 | -0.000 | -0.001 | 0.000 | -0.000 | -0.000 |
| 50 | u | 2_3 | -1.816 | -0.008 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |

Table S7: Charge transfer for the surface nickel, fluorine and the adsorbates for group I.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | d | 5_1 | 0.273 | 0.448 | 0.465 | -0.548 | -0.028 | -0.044 | -0.032 | -0.705 | -0.141 | 0.047 |
| 2 | u | 2_5 | 0.269 | 0.458 | 0.478 | -0.552 | -0.053 | -0.032 | -0.011 | -0.714 | -0.144 | 0.035 |
| 3 | f | 4_1 | 0.269 | 0.459 | 0.472 | -0.559 | -0.011 | -0.049 | -0.038 | -0.716 | -0.136 | 0.041 |
| 4 | u | 0_4 | 0.270 | 0.460 | 0.481 | -0.552 | -0.043 | -0.044 | -0.016 | -0.716 | -0.137 | 0.031 |

Continued on next page

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | d | 4_0 | 0.269 | 0.467 | 0.365 | -0.445 | -0.721 | -0.097 | -0.085 | -0.703 | 0.000 | 0.701 |
| 6 | u | 4_2 | 0.271 | 0.350 | 0.485 | -0.465 | -0.064 | -0.080 | -0.075 | -0.701 | -0.020 | 0.051 |
| 7 | f | 4_2 | 0.271 | 0.466 | 0.369 | -0.492 | -0.066 | -0.052 | -0.073 | -0.708 | -0.013 | 0.051 |
| 8 | u | 4_0 | 0.280 | 0.452 | 0.466 | -0.543 | -0.034 | -0.055 | -0.016 | -0.712 | -0.144 | 0.034 |
| 9 | u | 0_5 | 0.270 | 0.351 | 0.493 | -0.463 | -0.744 | -0.073 | -0.059 | -0.083 | 0.022 | 0.048 |
| 10 | f | 3_5 | 0.265 | 0.476 | 0.373 | -0.465 | -0.092 | -0.072 | -0.052 | -0.721 | 0.000 | 0.046 |
| 11 | d | 4_1 | 0.276 | 0.478 | 0.472 | -0.490 | -0.085 | -0.026 | -0.711 | -0.087 | -0.132 | 0.047 |
| 12 | f | 0_1 | 0.267 | 0.351 | 0.493 | -0.472 | -0.044 | -0.079 | -0.081 | -0.719 | -0.004 | 0.048 |
| 13 | f | 4_5 | 0.283 | 0.471 | 0.495 | -0.493 | -0.089 | -0.038 | -0.730 | -0.067 | -0.132 | 0.048 |
| 14 | f | 1_3 | 0.284 | 0.366 | 0.492 | -0.477 | -0.733 | -0.094 | -0.039 | -0.071 | -0.026 | 0.048 |
| 15 | f | 4_3 | 0.283 | 0.477 | 0.493 | -0.492 | -0.051 | -0.091 | -0.043 | -0.733 | -0.141 | 0.047 |
| 16 | u | 0_1 | 0.285 | 0.478 | 0.485 | -0.465 | -0.076 | -0.096 | -0.041 | -0.724 | -0.141 | 0.047 |
| 17 | u | 4_3 | 0.285 | 0.479 | 0.491 | -0.470 | -0.099 | -0.076 | -0.043 | -0.731 | -0.131 | 0.046 |
| 18 | u | 5_1 | 0.284 | 0.469 | 0.495 | -0.512 | -0.060 | -0.010 | -0.092 | -0.707 | -0.140 | 0.022 |
| 19 | u | 2_1 | 0.282 | 0.462 | 0.484 | -0.544 | -0.045 | -0.735 | -0.019 | -0.041 | -0.142 | 0.043 |
| 20 | f | 4_0 | 0.282 | 0.362 | 0.479 | -0.562 | -0.022 | -0.017 | -0.048 | -0.736 | -0.036 | 0.043 |
| 21 | f | 2_4 | 0.286 | 0.482 | 0.488 | -0.508 | -0.003 | -0.094 | -0.060 | -0.712 | -0.148 | 0.019 |
| 22 | d | 0_1 | 0.266 | 0.462 | 0.495 | -0.549 | -0.040 | -0.031 | -0.733 | -0.030 | -0.142 | 0.056 |
| 23 | f | 3_1 | 0.268 | 0.484 | 0.496 | -0.477 | -0.060 | -0.734 | -0.034 | -0.103 | -0.140 | 0.048 |
| 24 | f | 1_0 | 0.272 | 0.474 | 0.502 | -0.507 | -0.095 | -0.706 | -0.029 | -0.043 | -0.142 | 0.029 |
| 25 | u | 1_5 | 0.265 | 0.477 | 0.522 | -0.532 | 0.005 | -0.042 | -0.091 | -0.755 | -0.152 | 0.045 |
| 26 | u | 4_1 | 0.285 | 0.466 | 0.498 | -0.504 | -0.125 | -0.010 | -0.037 | -0.723 | -0.140 | 0.046 |
| 27 | f | 0_5 | 0.274 | 0.449 | 0.476 | -0.558 | -0.043 | -0.019 | -0.709 | -0.032 | -0.139 | 0.038 |
| 28 | d | 0_4 | 0.284 | 0.357 | 0.478 | -0.419 | -0.097 | -0.101 | -0.083 | -0.737 | 0.012 | 0.037 |
| 29 | u | 3_4 | 0.286 | 0.459 | 0.375 | -0.394 | -0.115 | -0.126 | -0.065 | -0.735 | 0.011 | 0.039 |
| 30 | u | 3_2 | 0.285 | 0.457 | 0.375 | -0.402 | -0.105 | -0.082 | -0.112 | -0.731 | -0.000 | 0.052 |
| 31 | f | 0_3 | 0.290 | 0.345 | 0.522 | -0.437 | -0.719 | -0.080 | -0.027 | -0.126 | -0.031 | 0.024 |
| 32 | f | 5_1 | 0.290 | 0.346 | 0.521 | -0.422 | -0.081 | -0.140 | -0.028 | -0.716 | -0.034 | 0.025 |
| 33 | d | 5_4 | 0.292 | 0.452 | 0.371 | -0.437 | -0.070 | -0.078 | -0.111 | -0.731 | 0.014 | 0.033 |
| 34 | d | 5_0 | 0.294 | 0.453 | 0.370 | -0.414 | -0.083 | -0.097 | -0.103 | -0.723 | 0.004 | 0.043 |
| 35 | d | 2_0 | 0.293 | 0.359 | 0.474 | -0.402 | -0.084 | -0.093 | -0.129 | -0.723 | 0.003 | 0.042 |
| 36 | d | 2_4 | 0.294 | 0.350 | 0.470 | -0.426 | -0.100 | -0.061 | -0.112 | -0.717 | 0.006 | 0.040 |
| 37 | u | 3_0 | 0.291 | 0.487 | 0.364 | -0.413 | -0.079 | -0.721 | -0.056 | -0.123 | -0.028 | 0.035 |
| 38 | u | 5_0 | 0.291 | 0.489 | 0.363 | -0.421 | -0.031 | -0.713 | -0.080 | -0.138 | -0.036 | 0.033 |
| 39 | u | 5_3 | 0.294 | 0.495 | 0.365 | -0.440 | -0.017 | -0.722 | -0.089 | -0.127 | -0.026 | 0.027 |
| 40 | u | 2_0 | 0.297 | 0.455 | 0.375 | -0.388 | -0.102 | -0.121 | -0.094 | -0.720 | 0.006 | 0.039 |
| 41 | u | 2_4 | 0.297 | 0.358 | 0.473 | -0.445 | -0.080 | -0.068 | -0.114 | -0.722 | -0.007 | 0.053 |
| 42 | f | 0_4 | 0.296 | 0.361 | 0.474 | -0.399 | -0.117 | -0.071 | -0.119 | -0.727 | 0.008 | 0.038 |
| 43 | u | 1_0 | 0.276 | 0.504 | 0.370 | -0.426 | -0.112 | -0.090 | -0.051 | -0.719 | -0.031 | 0.029 |
| 44 | f | 3_0 | 0.296 | 0.455 | 0.381 | -0.404 | -0.092 | -0.120 | -0.092 | -0.727 | 0.005 | 0.041 |
| 45 | u | 3_1 | 0.295 | 0.459 | 0.376 | -0.398 | -0.093 | -0.707 | -0.117 | -0.100 | 0.002 | 0.027 |
| 46 | f | 2_1 | 0.295 | 0.358 | 0.505 | -0.405 | -0.068 | -0.709 | -0.077 | -0.134 | -0.029 | 0.024 |
| 47 | f | 2_5 | 0.266 | 0.468 | 0.488 | -0.560 | -0.048 | -0.032 | -0.012 | -0.729 | -0.139 | 0.050 |
| 48 | f | 2_0 | 0.297 | 0.359 | 0.473 | -0.396 | -0.116 | -0.082 | -0.114 | -0.721 | 0.011 | 0.035 |
| 49 | f | 3_4 | 0.265 | 0.363 | 0.494 | -0.502 | -0.696 | -0.059 | -0.093 | -0.034 | -0.026 | 0.045 |
| 50 | u | 2_3 | 0.291 | 0.490 | 0.363 | -0.425 | -0.031 | -0.715 | -0.079 | -0.135 | -0.034 | 0.032 |

Table S8: Calculated frequencies for group I.

| 5_1 | 2_5 | 4_1 | 0_4 | 4_0 | 4_2 | 4_2 | 4_0 | 0_5 | 3_5 |
|---|---|---|---|---|---|---|---|---|---|
| d | u | f | u | d | u | f | u | u | f |
| 3089.73 | 3081.22 | 3077.65 | 3080.85 | 3461.13 | 3528.24 | 3532.31 | 3073.98 | 3531.43 | 3523.9 |
| 3073.32 | 3072.65 | 3076.32 | 3074.14 | 3142.96 | 3151.08 | 3152.18 | 3067.07 | 3144.37 | 3145.03 |
| 2986.91 | 2984.12 | 2985.43 | 2984.23 | 3139.72 | 3130.35 | 3131.97 | 3062.1 | 3129.33 | 3129.57 |
| 2587.98 | 2618.35 | 2627.06 | 2632.45 | 3027.53 | 3024.26 | 3025.96 | 2978.88 | 3022.39 | 3022.93 |
| 2570.81 | 2601.52 | 2613.08 | 2598.5 | 1614.71 | 1683.56 | 1686.79 | 2861.36 | 1796.87 | 1804.49 |
| 1442.52 | 1448.9 | 1444.29 | 1443.77 | 1456.99 | 1455.24 | 1452.67 | 1448.33 | 1455.89 | 1456.48 |

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| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1437.12 | 1442.98 | 1439.98 | 1440.14 | 1425.75 | 1437.8 | 1436.27 | 1441.81 | 1433.89 | 1434.79 |
| 1424.84 | 1427.97 | 1430.01 | 1432.3 | 1421.7 | 1410.74 | 1410.59 | 1431.12 | 1412.93 | 1413.69 |
| 1141.56 | 1151.39 | 1151.53 | 1150.49 | 1271.45 | 1293.37 | 1292.14 | 1156.36 | 1278.34 | 1277.01 |
| 1136.39 | 1144.41 | 1140.02 | 1146.09 | 1150.92 | 1154.78 | 1153.54 | 1146.5 | 1156.46 | 1157.24 |
| 1131.53 | 1128.3 | 1133.16 | 1134.15 | 1141.23 | 1135.35 | 1135.02 | 1100.89 | 1135.63 | 1135.94 |
| 1075.45 | 1069.75 | 1064.36 | 1066.39 | 1098.87 | 1078.15 | 1078.45 | 970.87 | 1059.83 | 1059.18 |
| 1024.66 | 1020.52 | 1025.84 | 1021.89 | 897.38 | 893.94 | 894.45 | 960.86 | 922.95 | 923.52 |
| 976.49 | 966.65 | 972.01 | 969.41 | 782.8 | 749.07 | 748.6 | 822.52 | 747.73 | 751.16 |
| 876.57 | 866.87 | 865.9 | 866.72 | 679.23 | 663.99 | 665.38 | 733.24 | 662.88 | 668.43 |
| 328.08 | 326.01 | 322.79 | 322.99 | 446.45 | 426.12 | 427.11 | 328.06 | 647.46 | 645.81 |
| 306.51 | 303.74 | 301.04 | 301.01 | 332.0 | 320.43 | 321.36 | 288.01 | 412.62 | 410.63 |
| 248.05 | 241.28 | 241.59 | 241.57 | 221.75 | 224.66 | 223.7 | 237.08 | 228.54 | 228.74 |
| 243.71 | 237.92 | 238.22 | 237.73 | 178.03 | 197.16 | 195.35 | 198.26 | 184.07 | 187.31 |
| 166.43 | 170.58 | 173.6 | 170.05 | 165.92 | 167.51 | 161.71 | 146.55 | 147.83 | 150.08 |
| 148.7 | 150.92 | 155.79 | 151.91 | 153.78 | 151.58 | 143.82 | 138.26 | 144.12 | 146.42 |
| 85.5 | 94.98 | 95.12 | 86.02 | 141.04 | 132.95 | 133.62 | 120.66 | 125.43 | 124.62 |
| 57.2 | 75.16 | 66.47 | 51.7 | 117.57 | 117.27 | 116.2 | 83.71 | 108.68 | 114.3 |
| 30.26 | 71.52 | 61.1 | 36.33 | 106.33 | 102.14 | 103.53 | 48.02 | 93.52 | 96.13 |
| 17.8 | 50.34 | 31.69 | 8.83 | 99.06 | 99.91 | 98.16 | 27.84i | 92.09 | 89.1 |
| 33.35i | 33.02 | 15.19 | 16.33i | 49.18 | 56.58 | 63.69 | 42.83i | 45.25 | 44.9 |
| 53.58i | 29.45i | 35.85i | 65.41i | 37.03 | 35.89 | 49.94 | 50.5i | 40.5 | 43.09 |
| 4_1 | 0_1 | 4_5 | 1_3 | 4_3 | 0_1 | 4_3 | 5_1 | 2_1 | 4_0 |
| d | f | f | f | f | u | u | u | u | f |
| 3391.67 | 3486.39 | 3388.38 | 3392.74 | 3391.02 | 3388.9 | 3395.01 | 3449.64 | 3428.95 | 3444.21 |
| 3137.25 | 3142.97 | 3131.38 | 3133.82 | 3135.03 | 3137.31 | 3140.03 | 3146.17 | 3082.03 | 3084.25 |
| 3122.5 | 3135.93 | 3116.49 | 3119.58 | 3121.75 | 3122.04 | 3124.03 | 3111.75 | 3069.23 | 3070.18 |
| 3016.36 | 3026.87 | 3011.08 | 3013.8 | 3015.79 | 3016.2 | 3018.27 | 3012.13 | 2982.54 | 2983.38 |
| 1961.57 | 1780.29 | 2014.40 | 1999.8 | 2008.45 | 1998.13 | 1991.19 | 2025.79 | 1882.29 | 1904.96 |
| 1452.62 | 1457.36 | 1453.93 | 1455.17 | 1454.55 | 1454.99 | 1452.85 | 1444.9 | 1448.56 | 1448.94 |
| 1436.43 | 1426.07 | 1442.39 | 1438.36 | 1437.61 | 1436.47 | 1432.13 | 1427.62 | 1442.02 | 1438.22 |
| 1415.96 | 1420.41 | 1417.26 | 1417.07 | 1416.34 | 1415.73 | 1416.22 | 1425.45 | 1425.7 | 1428.45 |
| 1237.47 | 1259.07 | 1229.53 | 1232.59 | 1231.11 | 1233.05 | 1233.96 | 1221.9 | 1191.13 | 1196.48 |
| 1161.73 | 1151.91 | 1164.73 | 1162.27 | 1161.45 | 1160.55 | 1157.08 | 1149.03 | 1149.8 | 1153.96 |
| 1140.98 | 1141.46 | 1138.89 | 1140.36 | 1139.94 | 1139.97 | 1143.71 | 1146.12 | 1144.86 | 1145.04 |
| 1054.74 | 1082.55 | 1047.49 | 1049.69 | 1047.35 | 1049.2 | 1049.54 | 1047.31 | 1099.01 | 1089.72 |
| 911.25 | 928.67 | 912.24 | 912.71 | 912.52 | 912.58 | 911.72 | 911.99 | 968.77 | 966.98 |
| 861.17 | 761.85 | 859.04 | 857.28 | 858.89 | 862.42 | 862.12 | 797.6 | 759.98 | 740.26 |
| 605.08 | 670.06 | 599.74 | 601.14 | 601.03 | 604.9 | 606.24 | 616.43 | 618.26 | 608.47 |
| 382.25 | 650.43 | 371.97 | 372.69 | 371.72 | 371.33 | 372.18 | 378.37 | 363.58 | 366.16 |
| 312.0 | 422.63 | 309.29 | 309.43 | 308.74 | 312.85 | 315.55 | 272.43 | 249.73 | 239.82 |
| 262.85 | 227.09 | 250.49 | 252.69 | 251.06 | 252.49 | 253.38 | 265.48 | 231.33 | 225.99 |
| 223.52 | 183.13 | 217.45 | 216.76 | 217.58 | 217.72 | 221.45 | 214.88 | 173.43 | 167.74 |
| 167.44 | 168.81 | 160.05 | 159.24 | 160.14 | 160.49 | 160.32 | 153.98 | 160.63 | 157.71 |
| 133.14 | 150.35 | 138.87 | 144.65 | 137.44 | 138.91 | 145.19 | 147.44 | 127.84 | 131.9 |
| 102.78 | 125.38 | 102.74 | 106.41 | 103.32 | 107.61 | 116.34 | 138.4 | 124.0 | 112.73 |
| 98.18 | 111.71 | 99.62 | 99.46 | 96.06 | 96.89 | 104.92 | 101.65 | 73.61 | 94.55 |
| 70.72 | 106.23 | 88.51 | 89.72 | 82.36 | 89.86 | 90.02 | 91.11 | 61.54 | 53.82 |

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|---|---|---|---|---|---|---|---|---|---|
| 62.45 | 91.07 | 63.12 | 75.53 | 70.83 | 71.41 | 73.7 | 65.92 | 50.94 | 43.73 |
| 54.93 | 54.18 | 47.57 | 53.36 | 50.89 | 54.17 | 58.07 | 28.34 | 11.76i | 22.48 |
| 19.32i | 48.59 | 36.80 | 37.03 | 32.64 | 10.7 | 35.82 | 20.9 | 17.7i | 13.26i |
| 2_4 | 0_1 | 3_1 | 1_0 | 1_5 | 4_1 | 0_5 | 0_4 | 3_4 | 3_2 |
| f | d | f | f | u | u | f | d | u | u |
| 3520.59 | 3200.51 | 3485.21 | 3471.29 | 3566.13 | 3462.73 | 3075.6 | 3185.38 | 3183.89 | 3186.33 |
| 3127.49 | 3081.46 | 3144.79 | 3126.14 | 3125.97 | 3138.16 | 3072.16 | 3161.63 | 3162.55 | 3172.11 |
| 3103.8 | 3078.21 | 3108.36 | 3114.69 | 3088.08 | 3103.99 | 2982.3 | 3046.03 | 3045.42 | 3051.71 |
| 3006.94 | 2986.92 | 3010.85 | 3008.76 | 2998.98 | 3006.6 | 2608.66 | 2896.88 | 2886.41 | 2871.84 |
| 2123.33 | 1806.95 | 2140.16 | 2084.23 | 2229.21 | 2042.25 | 2597.68 | 2594.06 | 2513.93 | 2546.5 |
| 1454.77 | 1440.05 | 1442.61 | 1456.16 | 1445.0 | 1443.86 | 1442.18 | 1452.51 | 1451.89 | 1450.2 |
| 1433.01 | 1436.82 | 1430.06 | 1430.8 | 1430.04 | 1431.57 | 1440.65 | 1423.94 | 1420.37 | 1416.94 |
| 1423.52 | 1426.77 | 1424.63 | 1419.62 | 1422.81 | 1428.49 | 1429.38 | 1407.51 | 1405.43 | 1405.15 |
| 1215.51 | 1281.66 | 1227.52 | 1210.14 | 1191.03 | 1230.83 | 1150.13 | 1158.73 | 1160.07 | 1155.53 |
| 1151.69 | 1148.08 | 1148.92 | 1151.34 | 1154.07 | 1153.46 | 1143.55 | 1128.07 | 1127.23 | 1127.39 |
| 1140.34 | 1141.24 | 1139.18 | 1148.48 | 1142.59 | 1144.75 | 1134.36 | 1058.55 | 1072.29 | 1060.15 |
| 1021.34 | 1124.35 | 1015.51 | 1018.31 | 1005.58 | 1022.75 | 1071.08 | 961.35 | 959.1 | 960.75 |
| 923.31 | 965.38 | 902.38 | 906.45 | 944.34 | 901.15 | 1023.12 | 944.21 | 947.99 | 953.38 |
| 707.54 | 896.31 | 793.68 | 847.54 | 677.69 | 848.59 | 970.09 | 822.68 | 832.31 | 828.55 |
| 555.07 | 704.43 | 632.93 | 650.97 | 630.61 | 578.88 | 868.97 | 788.33 | 790.49 | 785.31 |
| 357.14 | 628.63 | 593.83 | 607.77 | 541.8 | 371.73 | 321.81 | 522.59 | 520.7 | 523.14 |
| 278.54 | 384.28 | 345.18 | 360.47 | 348.25 | 272.62 | 298.83 | 301.38 | 298.72 | 304.03 |
| 246.52 | 245.09 | 234.15 | 261.01 | 253.94 | 246.26 | 243.96 | 267.17 | 273.64 | 273.03 |
| 188.94 | 181.37 | 198.37 | 173.13 | 162.41 | 204.77 | 233.08 | 202.04 | 204.53 | 207.0 |
| 156.89 | 130.19 | 156.21 | 152.7 | 147.07 | 160.91 | 171.23 | 177.67 | 166.56 | 181.62 |
| 133.02 | 100.59 | 145.2 | 136.95 | 130.88 | 136.49 | 154.95 | 156.56 | 157.36 | 163.41 |
| 107.75 | 92.3 | 128.09 | 115.68 | 100.31 | 126.79 | 87.71 | 151.08 | 152.34 | 157.56 |
| 79.48 | 52.9 | 106.37 | 102.18 | 95.89 | 87.24 | 54.48 | 130.76 | 128.78 | 132.93 |
| 71.77 | 46.21 | 85.87 | 85.55 | 58.74 | 76.96 | 46.41 | 122.16 | 116.73 | 121.81 |
| 68.49 | 21.17i | 68.16 | 44.78 | 41.42 | 45.25 | 22.45 | 110.65 | 108.19 | 112.56 |
| 43.96 | 24.5i | 27.01 | 37.55 | 35.37 | 6.35 | 21.73 | 59.83 | 70.29 | 54.63 |
| 30.45i | 64.6i | 25.33 | 34.76i | 47.45i | 36.9i | 31.43i | 41.38 | 32.81 | 12.56 |
| 0_3 | 5_1 | 5_4 | 5_0 | 2_0 | 2_4 | 3_0 | 5_0 | 5_3 | 2_0 |
| f | f | d | d | d | d | u | u | u | u |
| 3185.08 | 3186.67 | 3174.36 | 3169.59 | 3183.81 | 3171.02 | 3188.72 | 3189.9 | 3184.98 | 3184.96 |
| 3140.92 | 3141.66 | 3159.51 | 3157.83 | 3158.62 | 3160.34 | 3141.84 | 3142.69 | 3143.31 | 3162.93 |
| 3100.34 | 3097.6 | 3044.69 | 3041.71 | 3058.59 | 3048.75 | 3059.68 | 3067.27 | 3059.66 | 3067.5 |
| 3027.22 | 3027.89 | 3009.41 | 3001.66 | 3037.07 | 3027.5 | 3024.33 | 3026.3 | 3024.45 | 3042.57 |
| 2757.4 | 2749.28 | 2242.75 | 2239.05 | 2317.39 | 2210.46 | 2704.57 | 2712.48 | 2705.57 | 2235.11 |
| 1458.11 | 1457.96 | 1450.59 | 1454.05 | 1454.49 | 1453.63 | 1456.49 | 1457.31 | 1456.42 | 1452.93 |
| 1432.2 | 1432.1 | 1418.83 | 1418.89 | 1406.61 | 1414.06 | 1434.72 | 1434.24 | 1434.66 | 1405.91 |
| 1395.33 | 1394.48 | 1407.77 | 1406.71 | 1402.51 | 1405.5 | 1393.01 | 1392.32 | 1395.72 | 1400.38 |
| 1183.47 | 1185.07 | 1191.53 | 1191.28 | 1159.06 | 1195.31 | 1197.19 | 1196.27 | 1195.13 | 1161.72 |
| 1137.76 | 1136.73 | 1138.43 | 1140.94 | 1129.68 | 1140.22 | 1133.92 | 1134.77 | 1135.59 | 1128.54 |
| 1113.61 | 1113.17 | 1125.11 | 1125.66 | 1074.67 | 1125.16 | 1111.38 | 1110.55 | 1111.48 | 1081.86 |
| 887.41 | 888.86 | 942.07 | 943.44 | 983.89 | 932.5 | 902.69 | 902.98 | 900.23 | 1006.0 |
| 850.37 | 850.93 | 914.29 | 917.59 | 940.5 | 923.76 | 857.4 | 852.83 | 856.5 | 933.5 |

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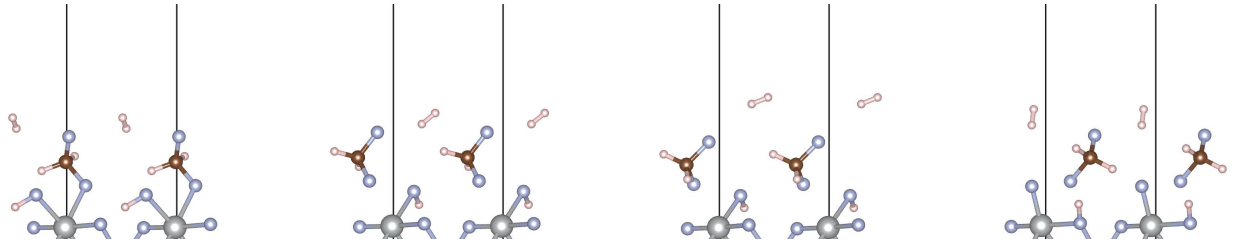
|---|---|---|---|---|---|---|---|---|---|
| 832.72 | 834.81 | 908.9 | 909.78 | 898.73 | 909.58 | 837.21 | 834.09 | 836.11 | 893.47 |
| 802.45 | 803.36 | 824.37 | 824.22 | 793.98 | 824.23 | 801.26 | 799.87 | 798.44 | 796.19 |
| 478.86 | 482.46 | 497.1 | 496.77 | 492.96 | 491.26 | 433.09 | 431.09 | 428.69 | 494.01 |
| 371.11 | 373.46 | 308.88 | 309.16 | 310.83 | 313.9 | 329.74 | 327.55 | 324.79 | 302.76 |
| 272.21 | 274.85 | 294.58 | 294.51 | 288.53 | 298.55 | 241.43 | 239.55 | 240.74 | 290.89 |
| 221.95 | 221.82 | 171.24 | 169.06 | 166.08 | 168.24 | 205.51 | 204.09 | 197.24 | 169.96 |
| 174.87 | 173.01 | 144.94 | 141.9 | 138.21 | 142.59 | 158.61 | 158.32 | 152.85 | 141.98 |
| 143.29 | 139.84 | 134.43 | 133.49 | 125.09 | 135.14 | 149.35 | 146.12 | 149.94 | 122.04 |
| 117.57 | 118.09 | 115.1 | 110.84 | 114.06 | 112.8 | 123.46 | 120.48 | 115.18 | 112.38 |
| 99.97 | 98.13 | 96.21 | 100.32 | 100.43 | 89.56 | 107.23 | 101.48 | 99.25 | 102.16 |
| 79.65 | 83.24 | 82.45 | 81.08 | 96.79 | 83.21 | 83.34 | 83.3 | 77.49 | 88.93 |
| 59.97 | 57.59 | 62.72 | 69.05 | 79.04 | 73.83 | 60.03 | 56.78 | 60.38 | 79.75 |
| 42.14 | 41.18 | 41.75 | 32.19 | 45.31 | 48.27 | 42.71 | 41.36 | 17.84 | 46.38 |
| 27.58 | 18.55 | 15.03i | 13.56 | 27.2 | 27.7 | 33.2 | 22.69 | 23.79i | 34.73 |
| 2_4 | 0_4 | 1_0 | 3_0 | 3_1 | 2_1 | 2_5 | 2_0 | 3_4 | 2_3 |

| u | f | u | f | u | f | f | f | f | u |
|---|---|---|---|---|---|---|---|---|---|
| 3184.57 | 3185.65 | 3204.34 | 3186.61 | 3195.5 | 3754.14 | 3283.45 | 3185.49 | 3554.09 | 3187.22 |
| 3161.93 | 3161.59 | 3168.14 | 3161.42 | 3185.64 | 3289.09 | 3084.86 | 3162.37 | 3149.42 | 3140.8 |
| 3065.76 | 3049.32 | 3042.63 | 3050.64 | 3143.29 | 3150.62 | 3075.37 | 3064.57 | 3140.76 | 3067.3 |
| 3041.76 | 3026.85 | 3007.01 | 3029.34 | 3059.36 | 3132.33 | 2986.6 | 3041.98 | 3031.48 | 3024.32 |
| 2239.49 | 2295.64 | 2638.24 | 2287.97 | 2252.54 | 3015.59 | 1924.03 | 2242.91 | 1788.21 | 2712.82 |
| 1453.16 | 1455.11 | 1439.52 | 1453.38 | 1439.3 | 1461.47 | 1445.22 | 1453.9 | 1440.97 | 1456.79 |
| 1406.29 | 1404.03 | 1429.13 | 1404.04 | 1410.98 | 1453.91 | 1438.72 | 1407.24 | 1432.93 | 1433.35 |
| 1401.55 | 1403.14 | 1393.75 | 1401.36 | 1395.34 | 1412.38 | 1427.48 | 1399.86 | 1409.77 | 1392.76 |
| 1161.38 | 1160.65 | 1195.33 | 1162.25 | 1154.55 | 1154.43 | 1267.55 | 1162.34 | 1270.45 | 1195.81 |
| 1127.67 | 1126.39 | 1120.18 | 1125.72 | 1129.18 | 1111.35 | 1151.59 | 1129.86 | 1147.76 | 1135.45 |
| 1081.45 | 1079.88 | 1116.84 | 1080.71 | 1089.07 | 844.8 | 1143.6 | 1084.55 | 1133.03 | 1111.29 |
| 1003.79 | 986.39 | 865.12 | 989.98 | 998.13 | 815.59 | 1107.18 | 999.75 | 1059.92 | 902.28 |
| 935.4 | 948.86 | 855.7 | 945.9 | 925.09 | 725.15 | 966.18 | 934.64 | 935.58 | 851.49 |
| 894.75 | 907.0 | 844.98 | 905.61 | 865.76 | 574.03 | 869.45 | 896.58 | 742.37 | 832.8 |
| 796.42 | 790.95 | 810.23 | 789.12 | 787.87 | 523.84 | 665.65 | 797.24 | 666.77 | 798.49 |
| 493.77 | 493.51 | 459.7 | 493.09 | 487.23 | 422.4 | 569.15 | 494.96 | 631.36 | 431.5 |
| 300.54 | 307.05 | 341.68 | 305.35 | 304.7 | 253.96 | 368.36 | 301.76 | 422.16 | 327.48 |
| 287.41 | 288.7 | 235.31 | 290.68 | 294.25 | 193.13 | 223.14 | 288.99 | 224.41 | 238.14 |
| 164.2 | 164.13 | 204.41 | 164.39 | 163.84 | 174.23 | 180.56 | 166.23 | 172.3 | 203.34 |
| 139.55 | 144.08 | 147.09 | 148.92 | 151.94 | 141.55 | 129.2 | 141.09 | 139.5 | 157.42 |
| 124.42 | 129.87 | 132.22 | 131.0 | 123.78 | 115.93 | 104.16 | 119.96 | 132.29 | 144.35 |
| 120.63 | 114.33 | 124.45 | 109.11 | 106.21 | 98.47 | 97.48 | 109.22 | 120.07 | 120.15 |
| 98.53 | 104.03 | 92.96 | 96.52 | 96.54 | 83.51 | 62.04 | 100.16 | 102.3 | 103.2 |
| 87.69 | 94.5 | 60.34 | 86.21 | 77.64 | 74.27 | 54.48 | 85.29 | 91.62 | 82.09 |
| 73.77 | 74.87 | 44.92 | 71.01 | 41.17 | 47.65 | 49.36 | 76.49 | 58.77 | 53.45 |
| 28.91 | 43.15 | 34.4 | 52.8 | 31.77 | 26.72 | 33.91 | 46.5 | 37.14 | 38.52 |
| 15.79 | 22.75 | 33.58i | 27.76 | 137.59i | 7.37i | 32.03i | 21.37 | 34.24i | 21.94 |

## 2.2 Group 2

Table S9: Adsorption energies and bond distances for the adsorbed structures in group II.

| # | Orientation | Position | $E_{ads}$ | d(CH) | d(CH) | d(CF) | d(CF) | d(NiF) | d(NiF) | d(HF) | d(HH) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | u | 1_4 | -9.1177 | 1.092 | 1.094 | 1.369 | 1.421 | 2.063 | 2.194 | 1.047 | 0.752 |
| 2 | u | 0_3 | -9.0037 | 1.094 | 1.095 | 1.370 | 1.416 | 2.176 | 2.355 | 1.039 | 0.752 |
| 3 | d | 2_1 | -8.9944 | 1.093 | 1.096 | 1.370 | 1.417 | 2.043 | 2.222 | 1.041 | 0.751 |
| 4 | f | 1_5 | -7.0577 | 1.095 | 1.095 | 1.357 | 1.452 | 1.830 | 2.860 | 1.010 | 0.752 |



(1) u 1_4 (2) u 0_3 (3) d 2_1 (4) f 1_5

Figure S3: Adsorbed structures belonging to group II.

Table S10: Magnetic moments on the surface nickel, fluorine and on the adsorbates for group II.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | u | 1_4 | -1.827 | -0.012 | -0.022 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 |
| 2 | u | 0_3 | -1.830 | -0.000 | -0.009 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.019 | -0.000 |
| 3 | d | 2_1 | -1.829 | -0.023 | -0.009 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.001 |
| 4 | f | 1_5 | -1.816 | -0.002 | -0.059 | 0.000 | 0.000 | 0.000 | 0.000 | -0.000 | -0.000 | -0.000 |

Table S11: Charge transfer for the surface nickel, fluorine and the adsorbates for group II.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | u | 1_4 | 0.282 | 0.343 | 0.494 | -1.099 | -0.071 | 0.022 | 0.007 | -0.113 | -0.157 | 0.041 |
| 2 | u | 0_3 | 0.274 | 0.348 | 0.362 | -1.056 | -0.715 | 0.011 | 0.018 | -0.108 | -0.020 | 0.638 |
| 3 | d | 2_1 | 0.274 | 0.464 | 0.372 | -1.063 | -0.005 | -0.086 | 0.036 | -0.140 | -0.152 | 0.044 |
| 4 | f | 1_5 | 0.319 | 0.347 | 0.465 | -1.031 | -0.726 | -0.167 | -0.104 | -0.002 | -0.148 | 0.783 |

Table S12: Calculated frequencies for group II

| 1_4 | 0_3 | 2_1 | 1_5 |
|---|---|---|---|
| u | u | d | f |
| 4270.63 | 4273.81 | 4302.96 | 4264.3 |
| 3151.92 | 3139.79 | 3140.79 | 3137.66 |
| 3052.38 | 3042.85 | 3038.53 | 3033.42 |
| 2131.67 | 2238.94 | 2210.16 | 2714.56 |
| 1451.06 | 1452.43 | 1470.87 | 1473.6 |
| 1383.83 | 1388.61 | 1387.76 | 1388.07 |
| 1212.99 | 1216.33 | 1215.0 | 1216.32 |

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| | | | |
|---|---|---|---|
| 1194.47 | 1180.37 | 1194.0 | 1115.41 |
| 1125.26 | 1127.56 | 1135.43 | 1099.02 |
| 1073.81 | 1069.66 | 1066.55 | 927.25 |
| 1032.24 | 1012.73 | 1031.55 | 874.22 |
| 919.97 | 938.65 | 920.71 | 813.03 |
| 495.82 | 625.8 | 491.26 | 484.92 |
| 363.82 | 473.96 | 359.08 | 463.12 |
| 253.95 | 326.19 | 259.11 | 321.7 |
| 241.48 | 232.99 | 223.12 | 257.34 |
| 224.24 | 197.63 | 183.91 | 240.91 |
| 215.33 | 189.68 | 171.91 | 179.29 |
| 169.7 | 157.01 | 162.35 | 171.52 |
| 153.67 | 143.45 | 155.13 | 130.42 |
| 146.55 | 138.2 | 132.18 | 112.89 |
| 116.38 | 91.74 | 108.57 | 104.52 |
| 95.77 | 75.79 | 93.5 | 77.13 |
| 84.91 | 66.75 | 85.48 | 65.25 |
| 74.97 | 59.15 | 62.41 | 41.9 |
| 60.02 | 28.38 | 51.6 | 10.56 |
| 42.83 | 17.01i | 37.84 | 19.9i |

## 2.3 Group 3

Table S13: Adsorption energies and bond distances for the adsorbed structures in group III.

| # | Orientation | Position | $E_{ads}$ | d(CH) | d(CH) | d(CH) | d(NiF) | d(NiF) | d(HF) | d(HF) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | u | 5_4 | -3.2646 | 1.089 | 1.089 | 1.092 | 1.775 | 2.063 | 0.976 | 0.994 |
| 2 | f | 5_0 | -3.2623 | 1.089 | 1.089 | 1.091 | 1.774 | 2.061 | 0.976 | 0.995 |
| 3 | f | 5_4 | -3.2569 | 1.089 | 1.089 | 1.092 | 1.774 | 2.060 | 0.975 | 0.992 |
| 4 | f | 1_4 | -2.5749 | 1.089 | 1.089 | 1.092 | 1.774 | 2.062 | 0.976 | 0.995 |
| 5 | u | 3_5 | -2.3095 | 1.089 | 1.090 | 1.093 | 1.777 | 2.066 | 0.975 | 1.013 |

Table S14: Magnetic moments on the surface nickel, fluorine and on the adsorbates for group III.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | u | 5_4 | -2.227 | -0.039 | -0.237 | 0.264 | 0.027 | -0.004 | -0.004 | -0.005 | 0.070 | -0.000 |
| 2 | f | 5_0 | -2.227 | -0.039 | -0.237 | 0.263 | 0.027 | -0.004 | -0.004 | -0.004 | -0.000 | 0.072 |
| 3 | f | 5_4 | -2.230 | -0.245 | -0.040 | -0.268 | 0.004 | -0.026 | 0.004 | 0.005 | -0.000 | -0.072 |
| 4 | f | 1_4 | -2.227 | -0.236 | -0.039 | 0.263 | -0.004 | 0.027 | -0.004 | -0.005 | -0.000 | 0.071 |
| 5 | u | 3_5 | -2.223 | -0.039 | -0.238 | -0.005 | -0.000 | 0.000 | -0.000 | -0.001 | -0.002 | -0.000 |

Table S15: Charge transfer for the surface nickel, fluorine and the adsorbates for group III.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | u | 5_4 | 0.002 | 0.439 | 0.323 | 0.153 | -0.641 | -0.078 | -0.033 | -0.165 | -0.046 | 0.032 |

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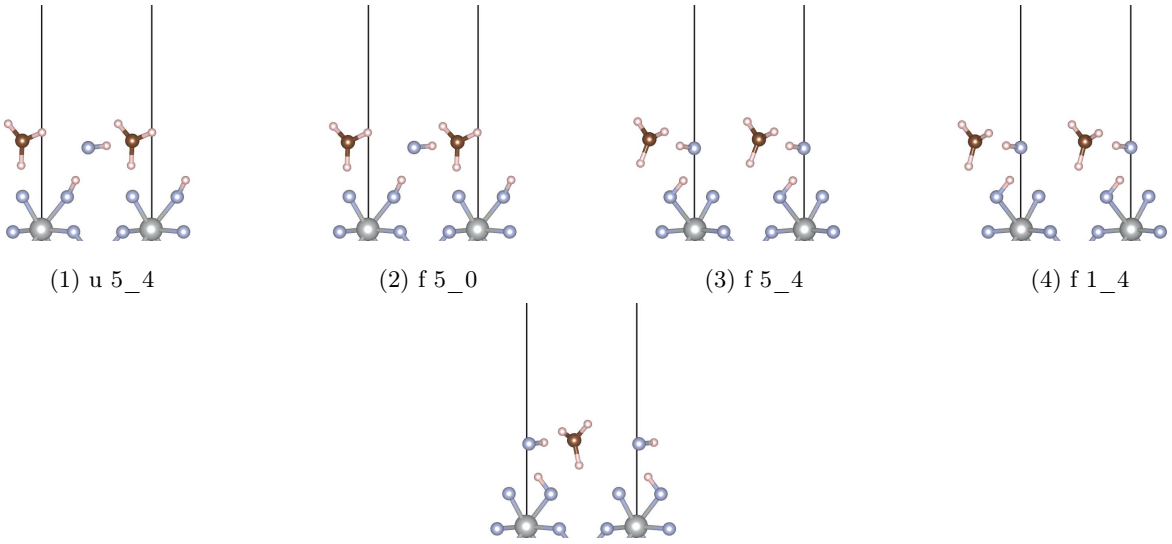
| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | f | 5_0 | 0.002 | 0.453 | 0.323 | 0.151 | -0.622 | -0.067 | -0.051 | -0.159 | -0.063 | 0.019 |
| 3 | f | 5_4 | -0.000 | 0.304 | 0.469 | 0.116 | -0.045 | -0.627 | -0.044 | -0.143 | -0.062 | 0.021 |
| 4 | f | 1_4 | 0.002 | 0.305 | 0.470 | 0.141 | -0.069 | -0.625 | -0.051 | -0.146 | -0.060 | 0.020 |
| 5 | u | 3_5 | 0.004 | 0.452 | 0.323 | 0.116 | -0.576 | -0.050 | -0.071 | -0.146 | -0.088 | 0.022 |

Table S16: Calculated frequencies for group III

| 5_4 | 5_0 | 5_4 | 1_4 | 3_5 |
|---|---|---|---|---|
| u | f | f | f | u |
| 3276.97 | 3271.02 | 3284.45 | 3277.16 | 3258.19 |
| 3204.32 | 3206.17 | 3202.34 | 3204.76 | 3204.36 |
| 3189.74 | 3195.09 | 3188.03 | 3191.48 | 3183.48 |
| 3017.98 | 3022.37 | 3017.04 | 3019.4 | 3007.71 |
| 2830.64 | 2805.98 | 2856.17 | 2813.42 | 2465.13 |
| 1369.46 | 1368.04 | 1372.91 | 1369.91 | 1367.38 |
| 1357.21 | 1357.41 | 1354.8 | 1356.85 | 1357.61 |
| 1000.55 | 1009.57 | 996.72 | 1006.71 | 992.86 |
| 839.86 | 842.76 | 832.14 | 840.47 | 901.01 |
| 771.59 | 774.57 | 774.66 | 772.67 | 754.87 |
| 648.19 | 658.83 | 638.79 | 655.96 | 678.62 |
| 582.51 | 585.1 | 577.22 | 583.72 | 602.88 |
| 495.49 | 496.65 | 498.7 | 495.93 | 480.24 |
| 337.59 | 338.06 | 339.13 | 337.8 | 380.35 |
| 315.4 | 316.93 | 308.61 | 314.84 | 333.22 |
| 259.51 | 268.36 | 264.1 | 265.46 | 270.35 |
| 246.91 | 250.34 | 252.24 | 250.78 | 238.99 |
| 240.45 | 241.89 | 239.56 | 242.48 | 219.14 |
| 175.04 | 177.56 | 179.38 | 176.54 | 177.41 |
| 172.26 | 171.49 | 177.39 | 171.67 | 161.06 |
| 143.75 | 141.14 | 148.53 | 142.46 | 140.88 |
| 137.77 | 139.91 | 138.71 | 137.68 | 131.28 |
| 115.57 | 117.39 | 115.43 | 117.3 | 108.93 |
| 93.12 | 93.78 | 102.06 | 96.17 | 98.88 |
| 75.36 | 76.26 | 92.44 | 77.79 | 57.79 |
| 43.68 | 50.79 | 55.54 | 50.04 | 40.99 |
| 24.43 | 42.36 | 27.29 | 39.03 | 4.48 |



(1) u 5_4 (2) f 5_0 (3) f 5_4 (4) f 1_4

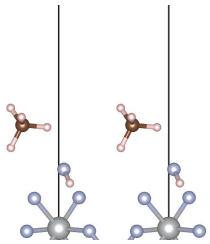
(5) u 3_5

Figure S4: Adsorbed structures belonging to group III.

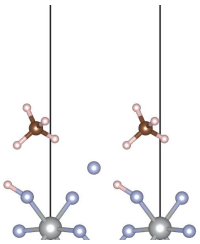
## 2.4 Group 4

Table S17: Adsorption energies and bond distances for the adsorbed structures in group IV.

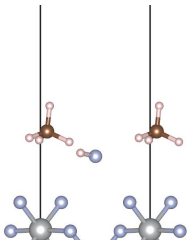
| # | Orientation | Position | $E_{ads}$ | d(CH) | d(CH) | d(CH) | d(CH) | d(NiF) | d(NiF) | d(HF) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | d | 1_5 | -1.4193 | 1.096 | 1.096 | 1.096 | 1.097 | 1.837 | 1.930 | 1.076 |
| 2 | f | 5_3 | -1.3821 | 1.096 | 1.096 | 1.097 | 1.097 | 1.836 | 1.945 | 1.058 |
| 3 | u | 0_2 | -0.9983 | 1.095 | 1.096 | 1.099 | 1.099 | 1.705 | 1.710 | 0.950 |
| 4 | f | 3_2 | -0.8739 | 1.095 | 1.095 | 1.096 | 1.111 | 1.779 | 1.926 | 0.977 |
| 5 | d | 2_5 | -0.7621 | 1.095 | 1.095 | 1.096 | 1.110 | 1.839 | 1.843 | 0.972 |
| 6 | d | 1_2 | -0.7281 | 1.095 | 1.096 | 1.099 | 1.099 | 1.866 | 1.896 | 0.949 |
| 7 | f | 5_2 | -0.7279 | 1.095 | 1.096 | 1.099 | 1.099 | 1.870 | 1.892 | 0.948 |
| 8 | d | 5_2 | -0.7272 | 1.095 | 1.096 | 1.099 | 1.099 | 1.876 | 1.885 | 0.949 |
| 9 | d | 4_2 | -0.7155 | 1.095 | 1.096 | 1.099 | 1.099 | 1.874 | 1.889 | 0.948 |
| 10 | d | 0_2 | -0.7058 | 1.095 | 1.096 | 1.099 | 1.099 | 1.875 | 1.887 | 0.948 |
| 11 | d | 1_3 | -0.7049 | 1.095 | 1.096 | 1.098 | 1.099 | 1.872 | 1.889 | 0.948 |
| 12 | d | 2_3 | -0.7027 | 1.096 | 1.098 | 1.098 | 1.100 | 1.874 | 1.881 | 0.949 |
| 13 | d | 5_3 | -0.6988 | 1.096 | 1.096 | 1.100 | 1.100 | 1.866 | 1.889 | 0.949 |
| 14 | f | 2_3 | -0.6937 | 1.096 | 1.096 | 1.099 | 1.099 | 1.866 | 1.889 | 0.949 |
| 15 | d | 1_4 | -0.6909 | 1.094 | 1.096 | 1.100 | 1.100 | 1.868 | 1.887 | 0.949 |
| 16 | d | 4_3 | -0.6859 | 1.095 | 1.096 | 1.099 | 1.099 | 1.875 | 1.888 | 0.948 |
| 17 | d | 3_2 | -0.6856 | 1.095 | 1.096 | 1.098 | 1.098 | 1.834 | 1.941 | 0.948 |
| 18 | d | 3_5 | -0.6842 | 1.096 | 1.096 | 1.099 | 1.100 | 1.863 | 1.894 | 0.949 |
| 19 | d | 3_4 | -0.6829 | 1.096 | 1.098 | 1.098 | 1.100 | 1.876 | 1.881 | 0.949 |
| 20 | u | 4_5 | -0.6797 | 1.095 | 1.096 | 1.098 | 1.099 | 1.866 | 1.899 | 0.947 |
| 21 | d | 0_3 | -0.6742 | 1.095 | 1.096 | 1.099 | 1.099 | 1.879 | 1.883 | 0.948 |
| 22 | d | 3_0 | -0.6705 | 1.095 | 1.098 | 1.099 | 1.100 | 1.874 | 1.882 | 0.949 |
| 23 | d | 1_0 | -0.6703 | 1.096 | 1.096 | 1.099 | 1.100 | 1.867 | 1.889 | 0.949 |
| 24 | u | 1_2 | -0.5754 | 1.095 | 1.096 | 1.099 | 1.100 | 1.814 | 1.919 | 0.951 |
| 25 | f | 1_2 | -0.5744 | 1.095 | 1.096 | 1.099 | 1.099 | 1.815 | 1.920 | 0.950 |
| 26 | u | 5_2 | -0.1752 | 1.095 | 1.096 | 1.099 | 1.100 | 1.781 | 1.994 | 0.950 |



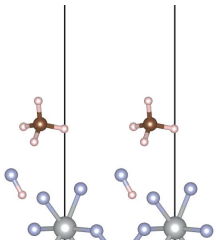
(1) d 1_5



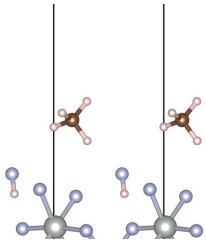
(2) f 5_3



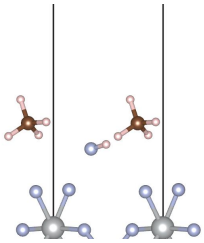
(3) u 0_2



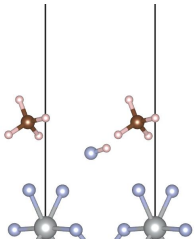
(4) f 3_2



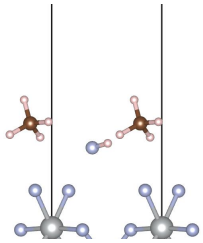
(5) d 2_5



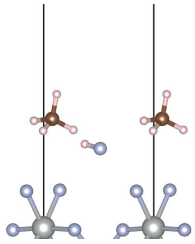
(6) d 1_2



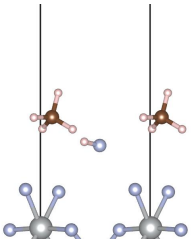
(7) f 5_2



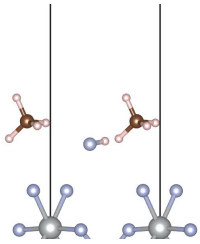
(8) d 5_2



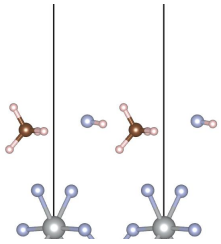
(9) d 4_2



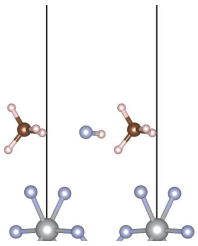
(10) d 0_2



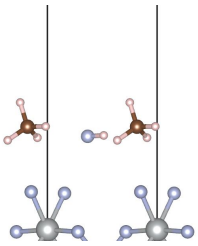
(11) d 1_3



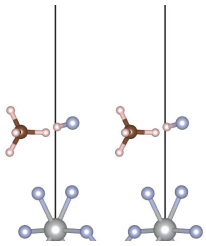
(12) d 2_3



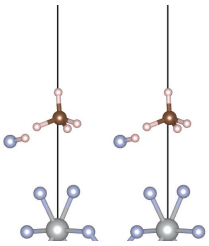
(13) d 5_3



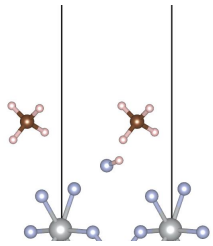
(14) f 2_3



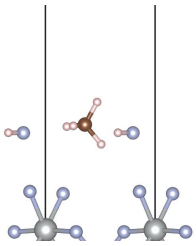
(15) d 1_4



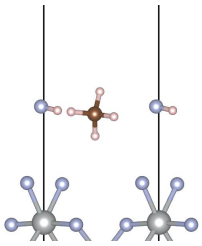
(16) d 4_3



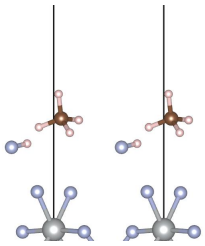
(17) d 3_2



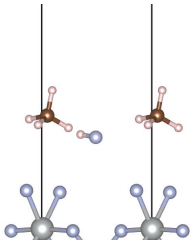
(18) d 3_5



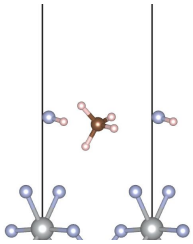
(19) d 3_4



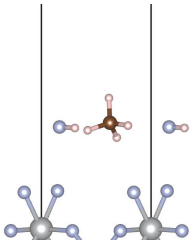
(20) u 4_5



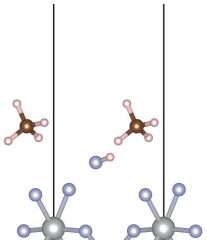
(21) d 0_3



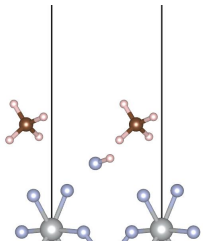
(22) d 3_0



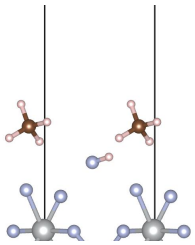
(23) d 1_0



(24) u 1_2



(25) f 1_2



(26) u 5_2

Figure S5: Adsorbed structures belonging to group IV.

Table S18: Magnetic moments on the surface nickel, fluorine and on the adsorbates for group IV.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | H | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | d | 1_5 | -2.240 | -0.147 | -0.581 | -0.003 | -0.001 | -0.002 | -0.000 | -0.001 | 0.002 | -0.397 |
| 2 | f | 5_3 | -2.224 | 0.181 | -0.065 | 0.003 | 0.002 | 0.001 | 0.000 | 0.003 | -0.004 | 0.512 |
| 3 | u | 0_2 | 0.106 | -0.020 | -0.017 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.006 | 0.000 |
| 4 | f | 3_2 | -2.212 | -0.540 | -0.425 | -0.026 | -0.003 | -0.003 | -0.002 | -0.029 | 0.002 | -0.226 |
| 5 | d | 2_5 | -2.222 | -0.448 | -0.522 | -0.024 | 0.002 | -0.003 | -0.002 | -0.029 | -0.003 | -0.204 |
| 6 | d | 1_2 | -2.219 | -0.586 | -0.577 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.025 |
| 7 | f | 5_2 | -2.220 | -0.575 | -0.582 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.033 |
| 8 | d | 5_2 | -2.220 | -0.582 | -0.585 | -0.001 | -0.000 | 0.000 | -0.000 | -0.000 | 0.000 | -0.020 |
| 9 | d | 4_2 | -2.219 | -0.585 | -0.579 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.026 |
| 10 | d | 0_2 | -2.220 | -0.571 | -0.598 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | -0.017 |
| 11 | d | 1_3 | -2.220 | -0.586 | -0.582 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.013 |
| 12 | d | 2_3 | -2.221 | -0.575 | -0.574 | -0.002 | -0.000 | -0.001 | -0.001 | -0.002 | 0.000 | -0.002 |
| 13 | d | 5_3 | -2.221 | -0.571 | -0.575 | -0.002 | -0.001 | -0.000 | -0.000 | -0.001 | 0.000 | -0.005 |
| 14 | f | 2_3 | -2.220 | -0.581 | -0.578 | -0.001 | -0.000 | -0.001 | -0.000 | -0.001 | 0.000 | -0.006 |
| 15 | d | 1_4 | -2.222 | -0.571 | -0.566 | -0.004 | -0.001 | -0.001 | -0.000 | -0.003 | 0.000 | -0.006 |
| 16 | d | 4_3 | -2.219 | -0.592 | -0.580 | -0.001 | -0.000 | -0.000 | -0.001 | -0.000 | 0.000 | -0.012 |
| 17 | d | 3_2 | -2.216 | -0.575 | -0.538 | -0.001 | -0.000 | -0.000 | -0.000 | -0.001 | 0.001 | -0.085 |
| 18 | d | 3_5 | -2.219 | -0.578 | -0.581 | -0.001 | -0.000 | -0.000 | -0.001 | -0.001 | 0.000 | -0.004 |
| 19 | d | 3_4 | -2.221 | -0.570 | -0.574 | -0.001 | -0.000 | -0.001 | -0.001 | -0.001 | 0.000 | -0.002 |
| 20 | u | 4_5 | -2.219 | -0.586 | -0.577 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | -0.021 | 0.000 |
| 21 | d | 0_3 | -2.219 | -0.580 | -0.595 | -0.000 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.011 |
| 22 | d | 3_0 | -2.221 | -0.566 | -0.572 | -0.002 | -0.000 | -0.001 | -0.001 | -0.001 | 0.000 | -0.004 |
| 23 | d | 1_0 | -2.220 | -0.577 | -0.578 | -0.001 | -0.000 | -0.000 | -0.000 | -0.000 | 0.000 | -0.004 |
| 24 | u | 1_2 | -2.228 | 0.394 | 0.156 | 0.000 | 0.000 | 0.000 | -0.000 | 0.000 | 0.088 | -0.001 |
| 25 | f | 1_2 | -2.229 | 0.395 | 0.159 | 0.000 | 0.000 | 0.000 | -0.000 | 0.000 | -0.001 | 0.086 |
| 26 | u | 5_2 | -0.908 | -0.305 | -0.601 | -0.001 | -0.000 | -0.000 | 0.000 | -0.000 | -0.067 | 0.001 |

Table S19: Charge transfer for the surface nickel, fluorine and the adsorbates for group IV.

| # | Orientation | Position | Ni | F | F | C | H | H | H | H | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | d | 1_5 | -0.015 | 0.353 | 0.030 | -0.002 | -0.013 | -0.012 | 0.009 | -0.001 | -0.356 | 0.042 |
| 2 | f | 5_3 | -0.011 | 0.067 | 0.433 | -0.008 | -0.015 | 0.007 | -0.001 | -0.008 | -0.467 | 0.044 |
| 3 | u | 0_2 | 0.079 | 0.111 | 0.118 | -0.003 | -0.033 | -0.009 | 0.013 | -0.007 | -0.058 | 0.045 |
| 4 | f | 3_2 | 0.018 | 0.051 | 0.162 | -0.015 | 0.007 | -0.030 | -0.006 | -0.065 | -0.208 | 0.026 |
| 5 | d | 2_5 | 0.002 | 0.130 | 0.075 | -0.033 | -0.725 | -0.014 | 0.013 | -0.074 | -0.193 | 0.753 |
| 6 | d | 1_2 | 0.001 | 0.006 | 0.030 | 0.025 | -0.016 | -0.021 | -0.009 | -0.014 | -0.050 | 0.054 |
| 7 | f | 5_2 | 0.001 | 0.015 | 0.028 | 0.020 | -0.027 | -0.024 | 0.006 | -0.008 | -0.063 | 0.057 |
| 8 | d | 5_2 | -0.002 | 0.004 | 0.026 | 0.028 | -0.033 | 0.014 | -0.020 | -0.025 | -0.054 | 0.063 |
| 9 | d | 4_2 | 0.003 | 0.004 | 0.032 | -0.011 | -0.007 | -0.004 | 0.012 | -0.023 | -0.055 | 0.055 |
| 10 | d | 0_2 | 0.001 | 0.020 | 0.008 | 0.016 | -0.033 | -0.023 | 0.014 | -0.007 | -0.040 | 0.049 |
| 11 | d | 1_3 | 0.002 | 0.006 | 0.022 | 0.034 | -0.009 | -0.044 | -0.004 | -0.012 | -0.039 | 0.051 |
| 12 | d | 2_3 | -0.002 | 0.016 | 0.032 | 0.035 | -0.041 | -0.025 | -0.005 | -0.020 | -0.050 | 0.060 |
| 13 | d | 5_3 | -0.002 | 0.016 | 0.035 | 0.009 | -0.020 | -0.046 | -0.015 | 0.017 | -0.050 | 0.058 |
| 14 | f | 2_3 | 0.001 | 0.008 | 0.028 | 0.007 | -0.029 | -0.025 | 0.008 | -0.008 | -0.039 | 0.052 |
| 15 | d | 1_4 | -0.002 | 0.020 | 0.040 | -0.014 | 0.001 | -0.010 | -0.023 | -0.018 | -0.054 | 0.061 |
| 16 | d | 4_3 | -0.001 | -0.004 | 0.032 | -0.012 | -0.017 | 0.031 | -0.014 | -0.022 | -0.038 | 0.052 |
| 17 | d | 3_2 | 0.001 | 0.027 | 0.070 | 0.007 | -0.012 | 0.006 | 0.003 | -0.031 | -0.107 | 0.042 |
| 18 | d | 3_5 | 0.001 | 0.012 | 0.025 | 0.027 | -0.034 | -0.000 | -0.018 | -0.023 | -0.045 | 0.059 |
| 19 | d | 3_4 | 0.000 | 0.016 | 0.033 | 0.037 | -0.056 | -0.013 | -0.026 | 0.002 | -0.048 | 0.053 |
| 20 | u | 4_5 | 0.003 | -0.004 | 0.037 | -0.007 | 0.011 | -0.020 | -0.011 | -0.004 | -0.046 | 0.050 |
| 21 | d | 0_3 | 0.003 | 0.008 | 0.013 | -0.019 | -0.014 | -0.001 | 0.012 | -0.014 | -0.033 | 0.048 |
| 22 | d | 3_0 | -0.001 | 0.020 | 0.036 | 0.068 | -0.049 | -0.056 | -0.015 | -0.007 | -0.051 | 0.055 |
| 23 | d | 1_0 | -0.001 | 0.014 | 0.027 | 0.058 | -0.052 | -0.014 | -0.029 | -0.012 | -0.036 | 0.047 |
| 24 | u | 1_2 | -0.007 | 0.035 | 0.095 | 0.002 | -0.007 | -0.016 | 0.003 | -0.017 | -0.110 | 0.043 |
| 25 | f | 1_2 | -0.007 | 0.033 | 0.095 | 0.010 | -0.014 | -0.014 | 0.001 | -0.015 | -0.105 | 0.036 |
| 26 | u | 5_2 | 0.130 | 0.031 | 0.022 | -0.031 | -0.004 | -0.019 | 0.021 | -0.001 | -0.087 | 0.042 |

Table S20: Calculated frequencies for group IV

| 1_5 | 5_3 | 0_2 | 3_2 | 2_5 | 1_2 | 5_2 | 5_2 | 4_2 |
|---|---|---|---|---|---|---|---|---|
| d | f | u | f | d | d | f | d | d |
| 3090.69 | 3090.42 | 3746.3 | 3175.63 | 3259.51 | 3755.63 | 3771.93 | 3756.69 | 3783.77 |
| 3087.94 | 3077.81 | 3102.66 | 3096.41 | 3089.96 | 3099.73 | 3098.14 | 3097.84 | 3105.72 |
| 3072.56 | 3069.25 | 3071.0 | 3091.79 | 3086.13 | 3071.06 | 3070.82 | 3072.42 | 3072.68 |
| 2973.01 | 2970.44 | 3064.95 | 3011.41 | 3008.88 | 3063.3 | 3062.73 | 3064.2 | 3063.94 |
| 1646.8 | 1827.24 | 2960.68 | 2831.56 | 2843.62 | 2957.05 | 2956.98 | 2957.25 | 2959.92 |
| 1484.59 | 1492.51 | 1515.05 | 1397.12 | 1386.17 | 1527.53 | 1527.28 | 1528.78 | 1519.79 |
| 1477.87 | 1470.65 | 1512.71 | 1370.06 | 1363.46 | 1518.85 | 1521.11 | 1518.81 | 1519.31 |
| 1279.13 | 1276.87 | 1320.06 | 1209.18 | 1197.12 | 1304.97 | 1301.1 | 1304.09 | 1311.24 |
| 1272.47 | 1265.33 | 1299.18 | 1151.12 | 1126.97 | 1294.07 | 1292.1 | 1293.82 | 1296.58 |
| 1268.23 | 1260.79 | 1253.69 | 1144.58 | 1097.36 | 1271.89 | 1274.88 | 1273.45 | 1265.0 |
| 1115.06 | 1119.92 | 571.5 | 750.64 | 698.88 | 469.68 | 468.68 | 469.0 | 471.79 |
| 935.26 | 963.47 | 552.56 | 637.59 | 606.07 | 433.93 | 417.08 | 427.9 | 411.45 |
| 497.38 | 495.63 | 406.0 | 502.05 | 476.95 | 341.01 | 325.7 | 339.88 | 345.99 |
| 382.51 | 430.11 | 366.23 | 306.98 | 257.07 | 260.27 | 259.42 | 255.65 | 263.56 |
| 349.81 | 330.53 | 251.14 | 259.92 | 225.07 | 240.37 | 228.28 | 233.46 | 233.09 |
| 288.88 | 247.05 | 249.5 | 204.18 | 196.48 | 219.02 | 207.35 | 215.42 | 220.73 |
| 178.14 | 176.83 | 214.53 | 167.94 | 158.76 | 170.1 | 161.02 | 170.07 | 148.09 |
| 165.01 | 142.9 | 208.51 | 160.92 | 145.97 | 148.54 | 149.27 | 146.11 | 147.16 |
| 137.27 | 131.98 | 162.5 | 152.92 | 138.85 | 142.1 | 143.52 | 140.31 | 141.4 |
| 120.59 | 113.23 | 146.86 | 135.55 | 123.16 | 117.52 | 114.39 | 122.47 | 112.27 |
| 103.66 | 92.36 | 107.97 | 116.18 | 101.77 | 106.88 | 107.27 | 111.42 | 97.27 |
| 75.18 | 70.83 | 92.49 | 103.31 | 98.23 | 91.21 | 95.26 | 89.93 | 92.87 |
| 60.66 | 62.23 | 85.54 | 87.03 | 79.11 | 84.44 | 74.67 | 78.94 | 83.81 |
| 39.12 | 37.24 | 73.55 | 75.45 | 64.75 | 73.79 | 60.17 | 74.44 | 68.84 |
| 18.78 | 32.85 | 66.78 | 46.96 | 45.07 | 34.95 | 16.03 | 37.23 | 41.67 |
| 26.76i | 23.71i | 38.84 | 41.29 | 24.25i | 20.5 | 7.86i | 22.25 | 23.31 |
| 54.07i | 64.79i | 9.83 | 14.15 | 55.57i | 13.38 | 16.84i | 15.15i | 22.33i |
| 0_2 | 1_3 | 2_3 | 5_3 | 2_3 | 1_4 | 4_3 | 3_2 | 3_5 |
| d | d | d | d | f | d | d | d | d |
| 3781.87 | 3773.24 | 3749.67 | 3743.34 | 3742.17 | 3730.72 | 3782.88 | 3804.87 | 3739.4 |
| 3100.41 | 3101.11 | 3086.99 | 3094.64 | 3093.01 | 3104.93 | 3103.59 | 3092.82 | 3094.54 |
| 3071.63 | 3073.69 | 3060.83 | 3069.17 | 3071.46 | 3036.03 | 3071.83 | 3075.11 | 3071.12 |
| 3064.89 | 3065.02 | 3042.03 | 3038.43 | 3052.13 | 3034.34 | 3066.6 | 3070.69 | 3050.1 |
| 2959.64 | 2959.6 | 2946.86 | 2945.19 | 2949.32 | 2943.96 | 2959.71 | 2963.29 | 2949.12 |
| 1526.64 | 1519.76 | 1479.89 | 1489.69 | 1500.94 | 1484.35 | 1516.12 | 1526.49 | 1501.83 |
| 1517.01 | 1508.93 | 1464.64 | 1462.07 | 1497.39 | 1409.28 | 1513.21 | 1520.03 | 1489.24 |
| 1310.48 | 1305.65 | 1271.25 | 1277.65 | 1281.98 | 1279.59 | 1314.88 | 1292.93 | 1283.84 |
| 1296.54 | 1288.98 | 1262.6 | 1265.82 | 1278.1 | 1264.67 | 1295.03 | 1284.59 | 1272.61 |
| 1267.88 | 1267.08 | 1256.72 | 1260.41 | 1266.27 | 1224.77 | 1261.36 | 1281.35 | 1271.15 |
| 471.55 | 466.76 | 465.04 | 464.85 | 467.7 | 465.29 | 473.34 | 474.06 | 470.95 |
| 388.32 | 399.78 | 385.45 | 385.24 | 399.17 | 415.98 | 395.36 | 369.2 | 410.25 |
| 346.31 | 339.96 | 333.51 | 323.03 | 331.17 | 382.96 | 359.55 | 274.4 | 336.17 |
| 258.15 | 241.05 | 241.4 | 244.85 | 247.49 | 253.75 | 255.22 | 255.11 | 256.97 |

Continued on next page

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 235.91 | 231.29 | 217.39 | 214.93 | 218.57 | 237.5 | 240.4 | 247.24 | 226.69 |
| 227.5 | 221.87 | 171.01 | 184.9 | 184.72 | 219.32 | 230.62 | 173.59 | 197.0 |
| 148.74 | 143.6 | 151.62 | 167.69 | 171.44 | 150.04 | 147.55 | 151.46 | 171.34 |
| 145.16 | 141.02 | 140.05 | 142.39 | 141.12 | 140.69 | 144.74 | 148.81 | 144.45 |
| 137.28 | 139.08 | 138.26 | 139.8 | 139.15 | 138.08 | 136.77 | 136.04 | 141.13 |
| 115.25 | 113.55 | 114.8 | 128.23 | 124.92 | 116.72 | 108.55 | 119.66 | 116.27 |
| 102.05 | 97.51 | 106.12 | 117.15 | 115.62 | 104.63 | 94.03 | 105.97 | 112.17 |
| 87.78 | 81.2 | 72.14 | 95.2 | 70.15 | 79.6 | 87.49 | 74.65 | 79.32 |
| 82.19 | 78.61 | 62.4 | 78.61 | 60.37 | 74.43 | 79.22 | 68.9 | 70.49 |
| 67.0 | 61.62 | 41.69 | 64.23 | 44.28 | 51.75 | 57.05 | 50.78 | 48.07 |
| 30.7 | 43.28 | 36.11 | 56.43 | 33.04 | 24.66 | 32.01 | 42.89 | 38.72 |
| 13.01 | 16.02 | 19.97 | 26.86 | 10.25i | 19.7 | 22.48 | 11.46 | 23.0 |
| 21.27i | 27.99i | 16.88i | 13.07i | 35.93i | 31.87i | 5.0i | 17.89i | 12.3i |
| 3_4 | 4_5 | 0_3 | 3_0 | 1_0 | 1_2 | 1_2 | 5_2 | |

| d | u | d | d | d | u | f | u | |
|---|---|---|---|---|---|---|---|---|
| 3753.95 | 3796.08 | 3765.82 | 3741.11 | 3736.96 | 3718.06 | 3750.34 | 3746.41 | |
| 3082.25 | 3102.67 | 3102.71 | 3085.87 | 3097.63 | 3101.65 | 3097.21 | 3101.25 | |
| 3063.61 | 3074.62 | 3072.19 | 3063.02 | 3073.02 | 3070.29 | 3071.23 | 3072.7 | |
| 3044.73 | 3067.89 | 3066.78 | 3044.95 | 3048.39 | 3059.08 | 3061.83 | 3061.05 | |
| 2943.41 | 2963.02 | 2958.94 | 2944.8 | 2950.27 | 2955.85 | 2957.7 | 2957.55 | |
| 1483.49 | 1523.42 | 1520.53 | 1490.41 | 1501.85 | 1524.65 | 1526.42 | 1525.82 | |
| 1459.26 | 1515.93 | 1513.91 | 1449.15 | 1480.08 | 1520.21 | 1522.09 | 1522.05 | |
| 1274.03 | 1310.97 | 1312.32 | 1282.79 | 1277.73 | 1304.38 | 1297.43 | 1302.49 | |
| 1268.29 | 1295.71 | 1292.04 | 1260.97 | 1275.11 | 1295.12 | 1292.72 | 1294.68 | |
| 1253.26 | 1266.22 | 1265.15 | 1244.43 | 1267.13 | 1266.63 | 1272.74 | 1271.42 | |
| 466.77 | 468.69 | 474.78 | 464.99 | 468.58 | 471.75 | 471.32 | 474.05 | |
| 355.45 | 378.24 | 406.27 | 364.63 | 395.52 | 428.12 | 401.89 | 428.28 | |
| 335.32 | 338.15 | 360.3 | 354.95 | 340.01 | 344.55 | 318.6 | 338.44 | |
| 243.47 | 257.16 | 248.74 | 245.05 | 251.2 | 308.89 | 303.15 | 289.35 | |
| 222.1 | 234.86 | 241.6 | 217.8 | 223.05 | 233.26 | 206.47 | 238.32 | |
| 163.17 | 217.29 | 230.79 | 166.86 | 198.54 | 206.11 | 203.52 | 227.79 | |
| 148.28 | 146.86 | 150.75 | 142.36 | 173.23 | 166.34 | 161.8 | 194.34 | |
| 141.54 | 140.52 | 143.66 | 140.33 | 140.25 | 164.14 | 148.62 | 171.37 | |
| 140.37 | 131.16 | 132.36 | 139.7 | 138.42 | 149.91 | 143.91 | 143.07 | |
| 109.64 | 108.82 | 113.14 | 135.55 | 118.76 | 139.94 | 134.06 | 134.0 | |
| 94.86 | 97.4 | 88.02 | 121.77 | 106.03 | 110.02 | 107.59 | 118.48 | |
| 78.86 | 83.23 | 83.31 | 76.66 | 75.1 | 104.8 | 97.33 | 111.6 | |
| 58.38 | 75.09 | 71.65 | 65.43 | 46.49 | 83.6 | 69.54 | 77.6 | |
| 45.2 | 49.33 | 48.97 | 40.6 | 30.37 | 58.52 | 54.99 | 69.75 | |
| 36.03 | 26.29 | 37.9 | 22.77 | 16.48i | 43.38 | 27.97 | 50.7 | |
| 17.79i | 20.3 | 18.7 | 27.29i | 23.54i | 22.09 | 3.95i | 44.06 | |
| 32.18i | 21.31i | 31.56i | 39.49i | 46.68i | 32.73i | 26.25i | 23.81 | |

## 3 Stability of the $NiF_2(F_2)$ (001) surface

Figure S6 shows the surface energy of different surface cuts of $NiF_2$ versus the potential calculated via the computational hydrogen electrode. The surface model under investigation in this work is denoted by orange dashed line. A detailed explanation of how the surface energies are calculated and detailed discussion of other surface cuts can be found in reference [22]. Potentials at which the Ni(III) and Ni(IV) surfaces are stabilised are marked with arrows.

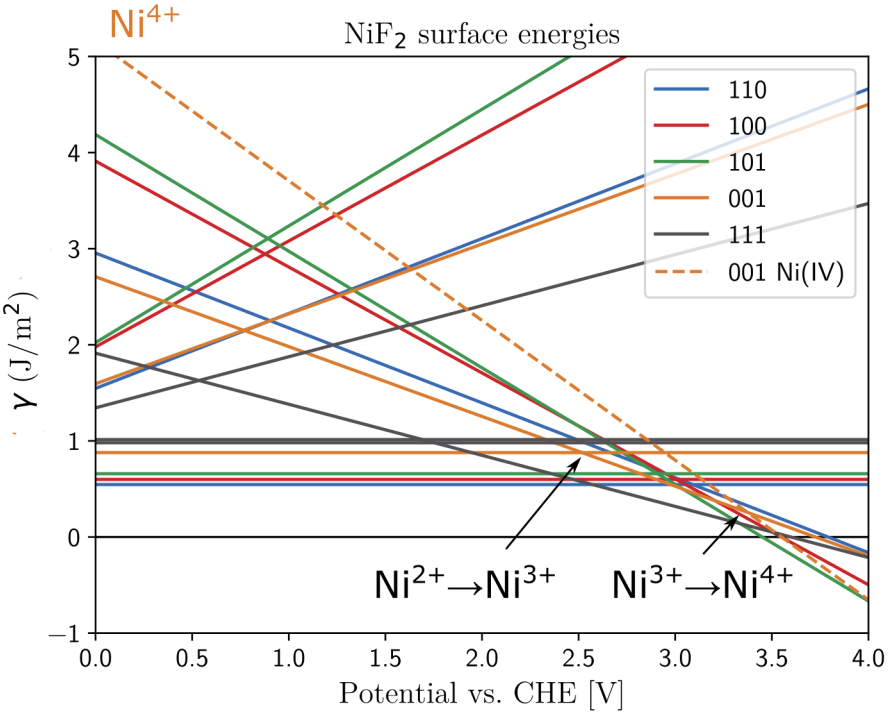



Figure S6: Surface energies of different cuts of $NiF_2$ surface versus the potential calculated via the computational hydrogen electrode. The surface energies of the $Ni^{2+}$ to $Ni^{3+}$ transition are taken from reference [22]. The same methodology as in this reference was applied to calculate the surface energy of $NiF_2(F_2)$ (001) surface, shown with dashed line.

## 4 Plot of imaginary vibrational mode from NEB

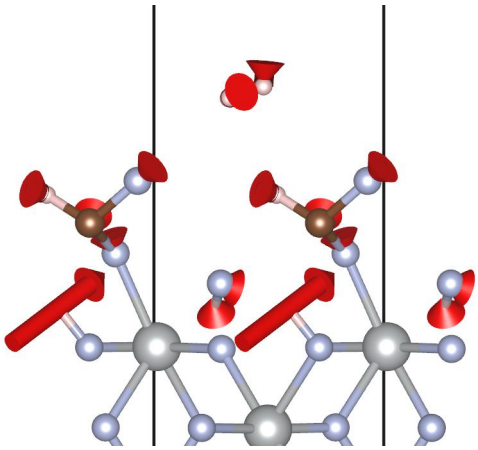


Figure S7: Imaginary vibrational mode displacements of the calculated transition state (image 4 in Figure 7 in the manuscript), with movement of atoms depicted by red arrows.