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# Supporting information

# Insight into the general rule for the activation of the X-H bonds (X=C, N, O, S) induced by the chemisorbed oxygen atom

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**Table captions**



## Figure caption:

**Table S1**

| | clean | | | | | oxygen pre-adsorbed | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Surface** | **$NH_3$** | **$H_2O$** | **$CH_3OH$** | **$H_2S$** | **$C_2H_4$** | **$NH_3$** | **$H_2O$** | **$CH_3OH$** | **$H_2S$** | **$C_2H_4$** |
| Cu | -0.40 | -0.23 | -0.12 (-0.52) | -0.32 | -0.30 | -0.96 | -0.33 | -0.31 | -0.24 | -0.11 (-0.61) |
| Ag | -0.31 | -0.11 (-0.36) | -0.06 (-0.42) | -0.10 (-0.46) | 0.06 (-0.32) | -0.81 | -0.34 | -0.28 | -0.23 | -0.11 (-0.50) |
| Au | -0.28 | -0.10 (-0.31) | -0.08 (-0.41) | -0.14 | -0.02 (-0.39) | -0.67 | -0.18 | -0.13 (-0.40) | -0.17 | 0.02 (-036) |
| Ni | -0.54 | -0.10 (-0.30) | -0.19 | -0.55 | -0.51 | -0.92 | -0.43 | -0.17 | -0.62 | 0.37 (-0.34) |
| Pd | -0.59 | -0.32 | -0.24 | -0.79 | -0.82 | -0.77 | -0.16 | -0.17 | -0.24 | 0.11 (-0.20) |
| Pt | -0.77 | -0.19 (-0.39) | -0.15 | -0.63 | -1.05 | -0.88 | -0.09 | -0.10 (-0.41) | -0.74 | -0.59 |
| Rh | -0.76 (-0.90) | -0.33 | -0.31 | -0.78 | -0.90 | -1.14 | -0.22 | -0.20 | -0.43 | -0.27 |
| Ru | -0.84 | -0.40 | -0.34 | -0.68 | -0.70 | -1.08 | -0.12 (-0.36) | -0.18 | -0.26 | -0.25 |
| Os | -0.93 | -0.43 | -0.35 | -0.57 | -0.53 | -1.13 | -0.50 | -0.11 (-0.44) | 0.00 (-0.43) | -0.41 |
| Ir | -0.80 | -0.24 | -0.22 | -0.62 | -0.85 | -1.06 | -0.15 | -0.19 | -0.11 (-0.59) | -0.56 |

Note: The data is parenthesis related to the dispersion effect correction based on the PBE functional.

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**Table S2**

| | | | clean | | |
|---|---|---|---|---|---|
| **Surfaces** | **$NH_2$+H** | **OH+H** | **$CH_3O$+H** | **SH+H** | **$C_2H_3$+H** |
| Cu | -4.76 | -5.63 | -4.89 | -5.20 | -4.65 |
| Ag | -3.76 | -4.84 | -2.95 | -4.38 | -3.50 |
| Au | -3.54 | -4.07 | -3.22 | -4.13 | -3.71 |
| Ni | -5.54 | -6.05 | -4.80 | -5.81 | -5.44 |
| Pd | -5.12 | -5.70 | -4.87 | -6.03 | -5.65 |
| Pt | -5.09 | -5.03 | -4.27 | -5.33 | -5.73 |
| Rh | -5.64 | -5.82 | -4.99 | -5.63 | -5.68 |
| Ru | -5.92 | -6.17 | -5.47 | -5.77 | -5.94 |
| Os | -5.69 | -5.39 | -4.79 | -5.72 | -5.62 |
| Ir | -5.22 | -5.39 | -4.36 | -5.55 | -5.76 |
| | | | **oxygen pre-adsorbed** | | |
| | **$NH_2$+H** | **OH+H** | **$CH_3O$+H** | **SH+H** | **$C_2H_3$+H** |
| Cu | -5.05 | -6.15 | -4.68 | -5.03 | -4.52 |
| Ag | -5.63 | -6.03 | -5.12 | -5.61 | -4.96 |
| Au | -5.32 | -5.67 | -4.64 | -5.49 | -4.88 |
| Ni | -4.67 | -5.53 | -3.80 | -4.69 | -4.30 |
| Pd | -5.12 | -5.54 | -4.12 | -4.88 | -4.80 |
| Pt | -5.51 | -5.63 | -4.71 | -5.23 | -5.27 |
| Rh | -5.25 | -5.25 | -4.44 | -5.08 | -4.78 |
| Ru | -4.79 | -5.17 | -4.27 | -4.83 | -4.67 |
| Os | -5.44 | -5.73 | -3.67 | -4.78 | -4.80 |
| Ir | -5.53 | -5.71 | -4.43 | -4.09 | -5.16 |

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**Table S3**

| Surfaces | Adsorption Site | Adsorption energy /eV |
|---|---|---|
| Cu(111) | Fcc | -5.17 |
| Ag(111) | Fcc | -3.92 |
| Au(111) | Fcc | -3.47 |
| Ni(111) | Fcc | -5.95 |
| Pd(111) | Fcc | -4.87 |
| Pt(111) | Fcc | -4.75 |
| Rh(111) | Fcc | -5.52 |
| Ru(0001) | Hcp | -6.35 |
| Os(0001) | Hcp | -6.16 |
| Ir(111) | Fcc | -5.21 |

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**Table S4**

| | Clean surface | | | O/M surface | | | |
|---|---|---|---|---|---|---|---|
| **Surfaces** | $E_a$(eV) | ΔH(eV) | N-H(Å) | $E_a$(eV) | ΔH(eV) | N-H(Å) | O-H(Å) |
| Cu(111) | 1.53 | 0.62 | 1.45 | 1.05 | 0.91 | 1.64 | 1.04 |
| Ag(111) | 2.19 | 1.55 | 1.78 | 0.54 | 0.18 | 1.78 | 1.02 |
| Au(111) | 2.12 | 1.75 | 1.88 | 0.71 | 0.36 | 1.81 | 1.02 |
| Ni(111) | 1.21 | 0.01 | 1.47 | 1.42 | 1.26 | 1.66 | 1.03 |
| Pd(111) | 1.52 | 0.48 | 1.54 | 1.00 | 0.66 | 1.74 | 1.03 |
| Pt(111) | 1.23 | 0.69 | 2.02 | 1.09 | 0.39 | 1.73 | 1.04 |
| Rh(111) | 1.48 | 0.13 | 1.47 | 1.21 | 0.90 | 1.74 | 1.03 |
| Ru(0001) | 1.43 | -0.07 | 1.47 | 1.29 | 1.25 | 1.88 | 1.01 |
| Os(0001) | 1.47 | 0.25 | 1.46 | 1.41 | 0.69 | 1.75 | 1.03 |
| Ir(111) | 1.71 | 0.58 | 1.58 | 1.22 | 0.54 | 1.93 | 1.01 |

**Table S5**

| | Clean surface | | | O/M surface | | | |
|---|---|---|---|---|---|---|---|
| **Surfaces** | $E_a$(eV) | ΔH(eV) | O-H(Å) | $E_a$(eV) | ΔH(eV) | O-H[a](Å) | O-H[b](Å) |
| Cu(111) | 1.17 | 0.24 | 1.55 | 0.33 | -0.18 | 1.29 | 1.16 |
| Ag(111) | 1.78 | 0.91 | 1.82 | 0.14 | -0.06 | 1.26 | 1.19 |
| Au(111) | 1.76 | 1.66 | 1.90 | 0.14 | -0.40 | 1.53 | 1.04 |
| Ni(111) | 0.91 | -0.32 | 1.55 | 0.66 | 0.54 | 1.54 | 1.05 |
| Pd(111) | 1.01 | 0.25 | 1.70 | 0.50 | 0.26 | 1.84 | 1.00 |
| Pt(111) | 0.86 | 0.78 | 1.76 | 0.30 | 0.10 | 1.75 | 1.00 |
| Rh(111) | 0.88 | 0.14 | 1.91 | 0.65 | 0.61 | 1.24 | 1.20 |
| Ru(0001) | 0.89 | -0.12 | 1.49 | 0.62 | 0.58 | 1.81 | 1.00 |
| Os(0001) | 0.89 | 0.46 | 1.50 | 0.47 | 0.41 | 1.21 | 1.23 |
| Ir(111) | 0.75 | 0.48 | 1.52 | 0.34 | 0.08 | 1.00 | 1.73 |

[a],[b]means the distance between dissociated hydrogen atom to difference oxygen atoms

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**Table S6**

| | Clean surface | | | O/M surface | | | |
|---|---|---|---|---|---|---|---|
| **Surfaces** | $E_a$(eV) | ΔH(eV) | O-H(Å) | $E_a$(eV) | ΔH(eV) | O-H[a](Å) | O-H[b](Å) |
| Cu(111) | 1.12 | -0.04 | 1.87 | 0.37 | 0.35 | 1.65 | 1.01 |
| Ag(111) | 1.40 | 0.83 | 1.84 | 0.17 | -0.12 | 1.75 | 1.01 |
| Au(111) | 1.75 | 1.58 | 1.55 | 0.32 | 0.22 | 1.17 | 1.28 |
| Ni(111) | 0.83 | -0.41 | 1.49 | 1.24 | 0.59 | 1.70 | 1.01 |
| Pd(111) | 0.95 | 0.09 | 1.63 | 0.51(0.43) | 0.30(0.16) | 1.55 | 1.04 |
| Pt(111) | 0.80 | 0.61 | 1.63 | 0.23 | 0.13 | 1.10 | 1.36 |
| Rh(111) | 0.86 | 0.04 | 1.56 | 0.69 | 0.49 | 1.51 | 1.07 |
| Ru(0001) | 0.73 | -0.40 | 1.47 | 0.76 | 0.65 | 1.76 | 1.01 |
| Os(0001) | 0.70 | 0.29 | 1.68 | 1.20(1.13) | 1.18(1.09) | 1.49 | 1.06 |
| Ir(111) | 0.73 | 0.60 | 1.57 | 0.69 | 0.48 | 1.66 | 1.00 |

[a][b]means the distance between dissociated hydrogen atom to difference oxygen atoms

Note: The data is parenthesis related to the dispersion effect correction based on the PBE functional.

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**Table S7**

| | Clean surface | | | O/M surface | | | |
|---|---|---|---|---|---|---|---|
| **Surfaces** | $E_a$(eV) | ΔH(eV) | S-H(Å) | $E_a$(eV) | ΔH(eV) | S-H(Å) | O-H(Å) |
| Cu(111) | 0.36(0.31) | -0.65(-0.78) | 1.81 | 0.03 | -0.56 | 1.50 | 1.42 |
| Ag(111) | 0.83(0.76) | -0.05(-0.17) | 2.04 | 0.01 | -1.16 | 1.44 | 1.62 |
| Au(111) | 0.80(0.72) | 0.24(0.11) | 2.17 | 0.08 | -1.09 | 1.48 | 1.52 |
| Ni(111) | 0.17 | -1.03 | 1.68 | 0.21 | 0.16 | 1.60 | 1.27 |
| Pd(111) | 0.28 | -1.01 | 1.85 | 0.17 | -0.42 | 1.50 | 1.43 |
| Pt(111) | 0.47 | -0.47 | 1.67 | 0.18 | -0.26 | 1.50 | 1.43 |
| Rh(111) | 0.26 | -0.62 | 1.66 | 0.21 | -0.58 | 1.55 | 1.38 |
| Ru(0001) | 0.25 | -0.86 | 1.50 | 0.18 | -0.34 | 1.52 | 1.36 |
| Os(0001) | 0.40(0.37) | -0.92(-1.03) | 1.67 | 0.32(0.29) | -0.55(-0.65) | 1.67 | 1.17 |
| Ir(111) | 0.42 | -0.71 | 1.68 | 0.26 | 0.24 | 1.57 | 1.30 |

Note: The data is parenthesis related to the dispersion effect correction based on the PBE functional.

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**Table S8**

| | Clean surface | | | O/M surface | | | |
|---|---|---|---|---|---|---|---|
| **Surfaces** | $E_a$(eV) | ΔH(eV) | C-H(Å) | $E_a$(eV) | ΔH(eV) | C-H(Å) | O-H(Å) |
| Cu(111) | 1.36 | 0.65 | 1.72 | 1.07 | 0.59 | 1.42 | 1.23 |
| Ag(111) | 1.93 | 1.44 | 1.90 | 1.25 | 0.15 | 1.38 | 1.45 |
| Au(111) | 1.61 | 1.30 | 1.76 | 0.62 | 0.10 | 1.83 | 1.02 |
| Ni(111) | 0.57 | 0.07 | 1.73 | 1.05 | 0.33 | 1.43 | 1.20 |
| Pd(111) | 0.98 | 0.17 | 1.67 | 1.01 | 0.09 | 1.40 | 1.26 |
| Pt(111) | 0.96 | 0.33 | 1.59 | 1.77 | 0.32 | 1.44 | 1.22 |
| Rh(111) | 0.54 | 0.21 | 1.62 | 1.13 | 0.49 | 2.00 | 0.99 |
| Ru(0001) | 0.24 | -0.24 | 1.85 | 1.11 | 0.58 | 1.58 | 1.18 |
| Os(0001) | 0.30 | -0.09 | 1.66 | 1.14 | 0.61 | 1.54 | 1.25 |
| Ir(111) | 0.43 | 0.10 | 1.35 | 1.29 | 0.40 | 1.36 | 1.45 |

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**Table S9**

| | Surface | $\Delta E_{XH_x}^{IS}$ | $\Delta E_{XH_{x-1}}^{TS}$ | $\Delta E_{H}^{TS}$ | $\Delta \sum E^{TS}$ | $\Delta E_{\text{int}}$ | $\Delta E_{a}$ |
|---|---|---|---|---|---|---|---|
| | Cu(111) | -0.61 | 0.79 | -0.87 | -0.08 | -1.01 | -0.48 |
| $NH_3$ | Au(111) | -0.43 | 0.10 | 0.21 | 0.31 | -2.15 | -1.41 |
| | Ru(0001) | -0.25 | 0.23 | -0.58 | -0.35 | -0.04 | -0.14 |
| | Cu(111) | -0.56 | 0.86 | 0.12 | 1.01 | -2.41 | -0.84 |
| $H_2O$ | Au(111) | -0.12 | 0.47 | -1.52 | -1.05 | -0.78 | -1.71 |
| | Ru(0001) | 0.22 | 0.27 | 0.31 | 0.58 | -0.63 | -0.27 |
| | Cu(111) | -0.16 | 0.28 | -0.38 | -0.10 | -0.81 | -0.75 |
| $CH_3OH$ | Au(111) | -0.06 | 0.32 | -0.39 | -0.07 | -1.42 | -1.43 |
| | Ru(0001) | 0.18 | 0.28 | 0.26 | 0.54 | -0.33 | 0.03 |
| | Cu(111) | 0.12 | 1.11 | 1.38 | 2.49 | -2.70 | -0.33 |
| $H_2S$ | Au(111) | -0.04 | 0.66 | 1.10 | 1.76 | -2.52 | -0.72 |
| | Ru(0001) | 0.23 | 0.89 | 1.80 | 2.68 | -2.82 | -0.37 |
| | Cu(111) | 0.17 | 0.89 | 0.67 | 1.56 | -1.68 | -0.29 |
| $C_2H_4$ | Au(111) | 0.06 | 0.86 | -1.55 | -0.68 | -0.24 | -0.99 |
| | Ru(0001) | 0.41 | 0.75 | 0.91 | 1.66 | -0.35 | 0.90 |

**Table S10**

| | | O/M surface | | | |
|---|---|---|---|---|---|
| **Surfaces** | **Oxygen coverage** | $E_a$(eV) | ΔH(eV) | O-H(Å) | O-H(Å) |
| Cu(111) | 1/9 | 0.25 | -0.32 | 1.25 | 1.18 |
| | 2/9 | 0.27 | -0.28 | 1.24 | 1.20 |
| | 3/9 | 0.16 | -0.52 | 1.27 | 1.19 |
| | 4/9 | 0.33 | 0.29 | 1.26 | 1.20 |
| | 5/9 | 0.47 | 0.25 | 1.29 | 1.20 |
| Au(111) | 1/9 | 0.61 | 0.12 | 1.29 | 1.16 |
| | 2/9 | 0.90 | 0.32 | 1.70 | 1.03 |
| | 3/9 | 0.75 | 0.41 | 1.58 | 1.04 |
| | 4/9 | 1.17 | 0.53 | 1.46 | 1.09 |
| | 5/9 | 1.20 | 0.21 | 1..45 | 1.07 |
| Ru(0001) | 1/9 | 0.58 | 0.28 | 1.77 | 1.01 |
| | 2/9 | 0.60 | 0.27 | 1.50 | 1.07 |
| | 3/9 | 0.40 | 0.35 | 1.59 | 1.03 |
| | 4/9 | 0.47 | 0.31 | 1.27 | 1.18 |
| | 5/9 | 0.75 | 0.29 | 1.68 | 1.03 |

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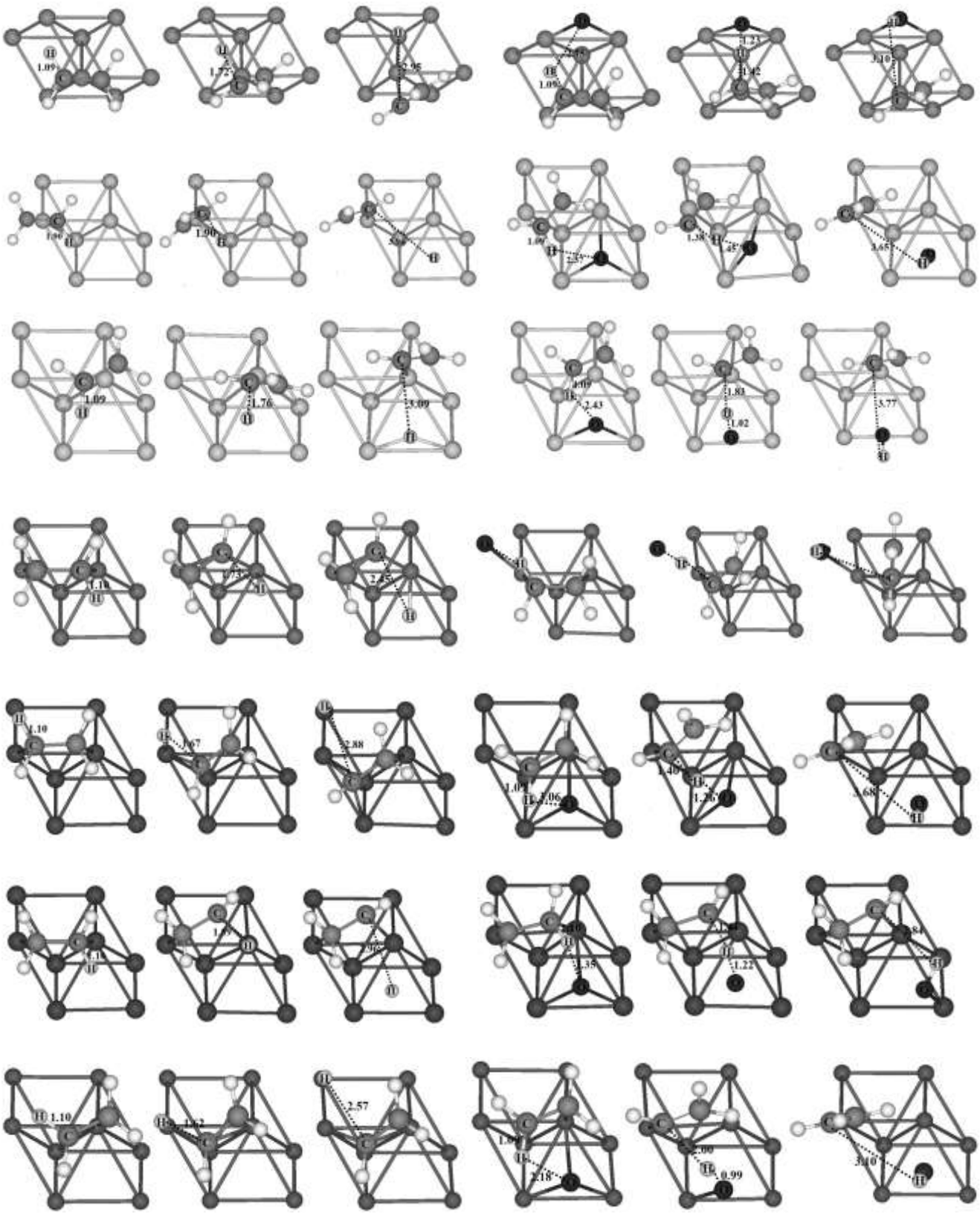
**Figure S1**



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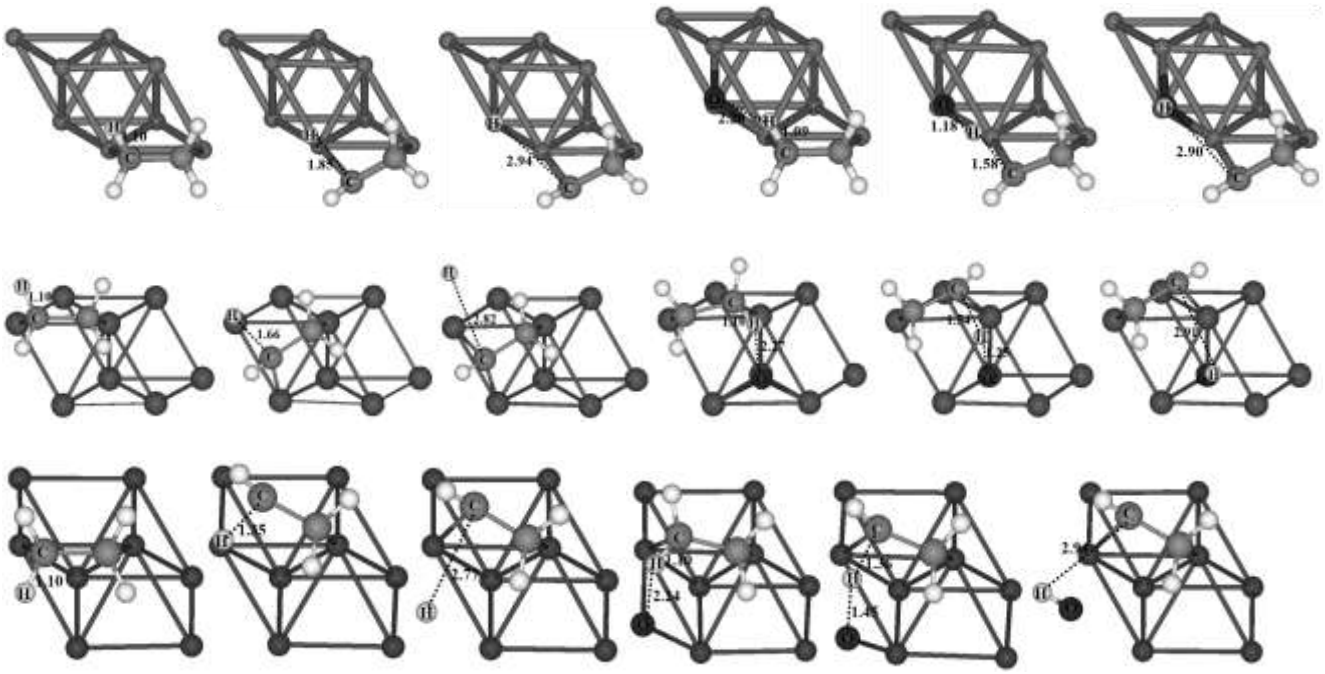

$C_2H_4$ TS $C_2H_3$+H $C_2H_4$+O TS $C_2H_3$+OH

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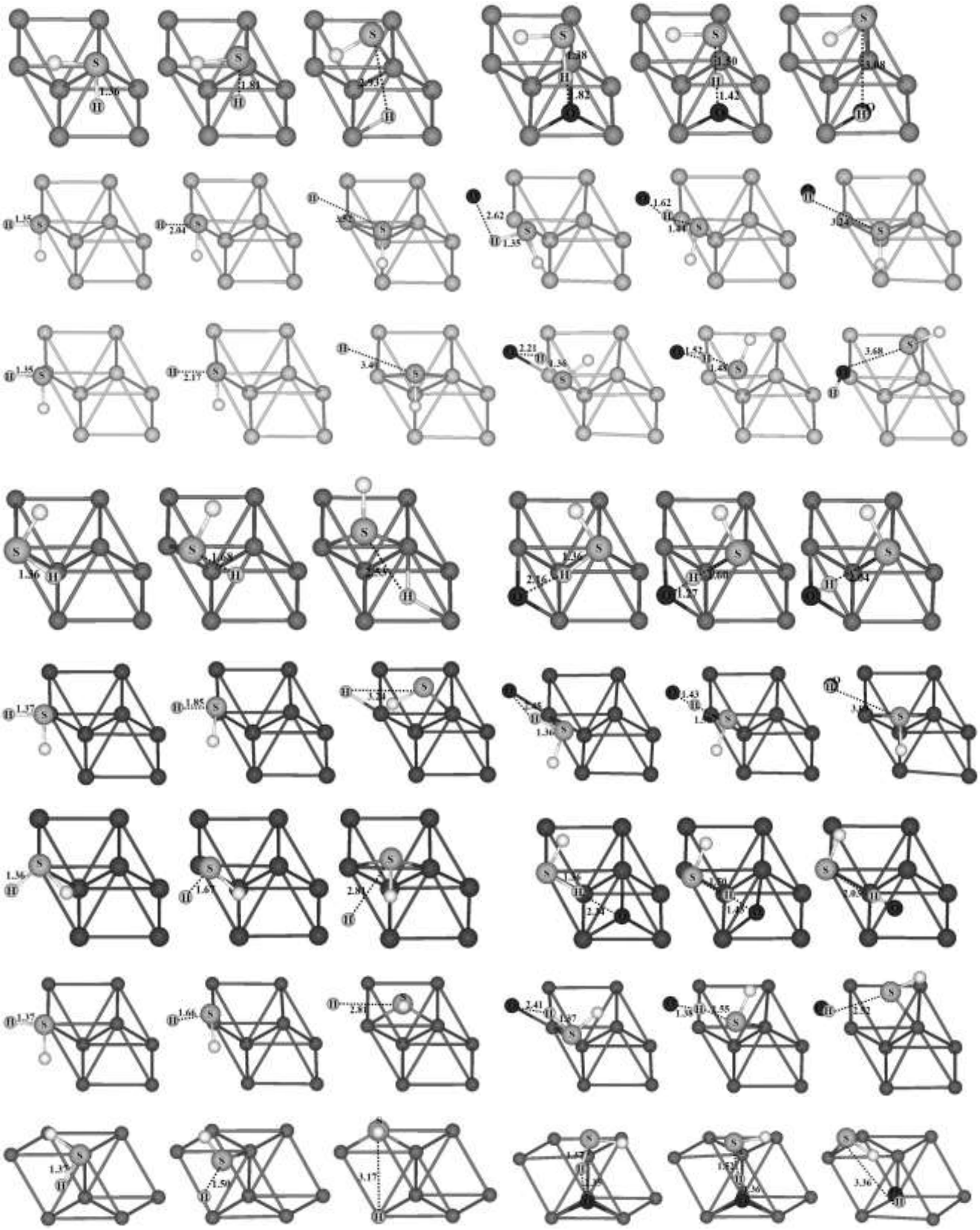
**Figure S2**



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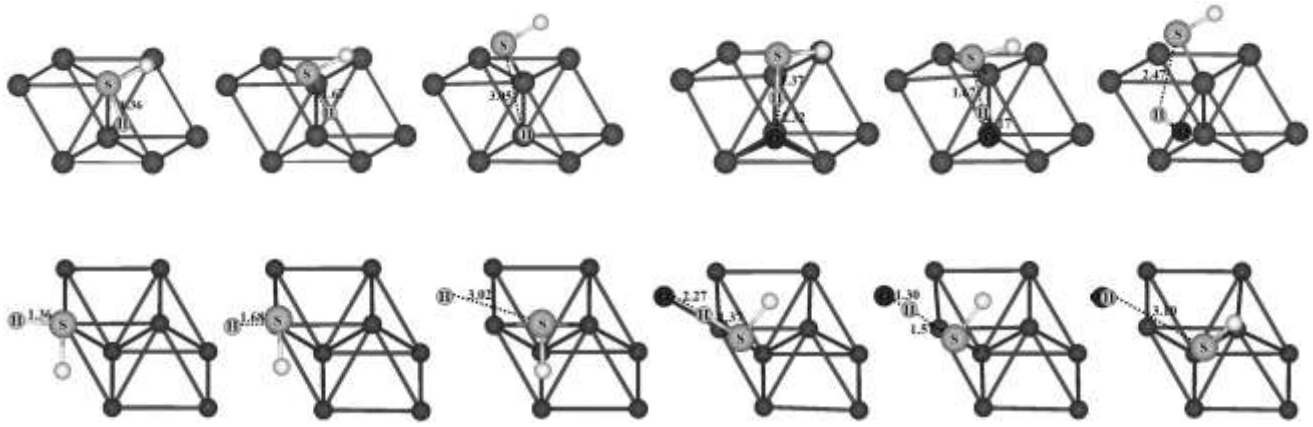

$H_2S$ TS HS+H $H_2S$+O TS HS+OH

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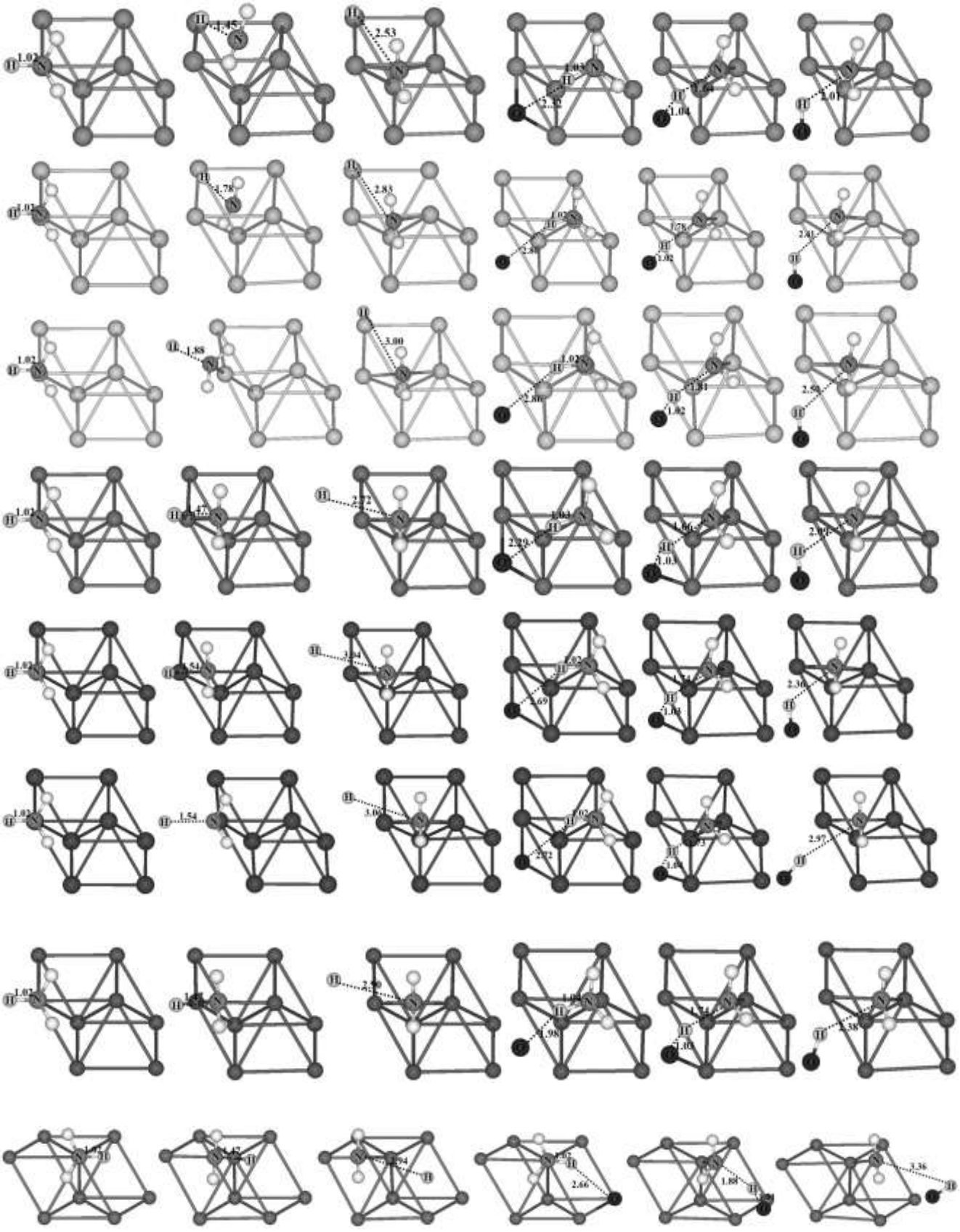
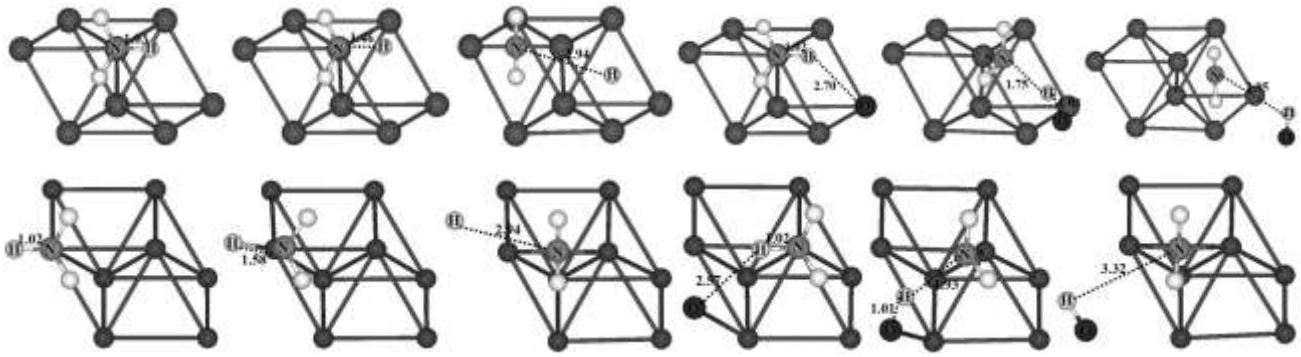
**Figure S3**





$NH_3$ TS $NH_2$+H $NH_3$+o TS $NH_2$+OH

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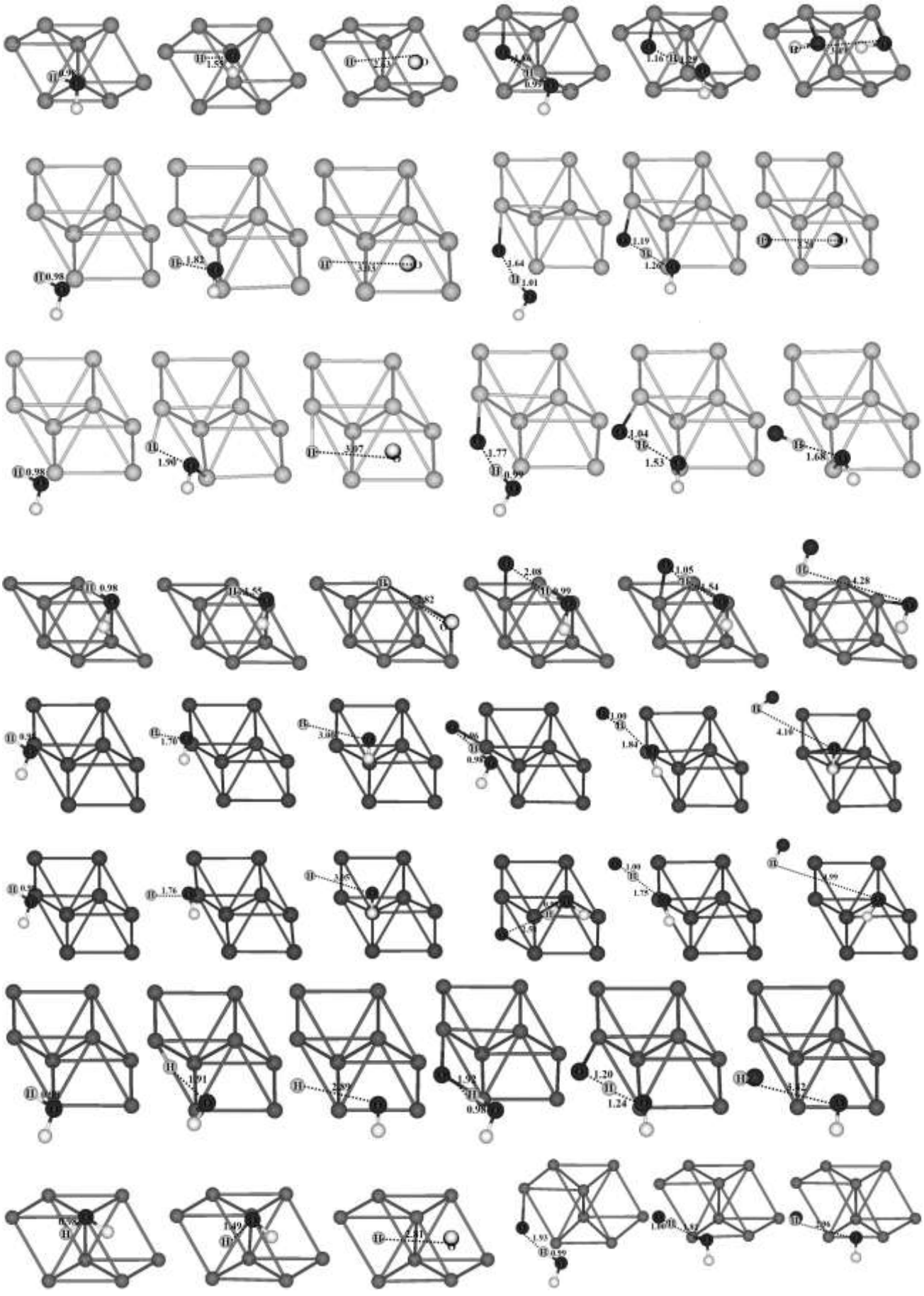
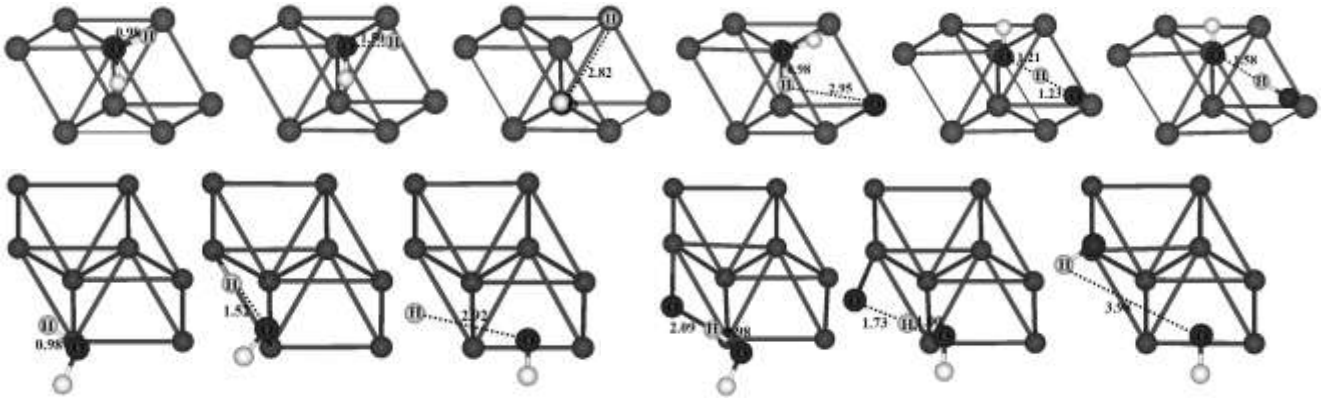
**Figure S4**





$H_2O$ TS HO+H $H_2O$+O TS HO+OH

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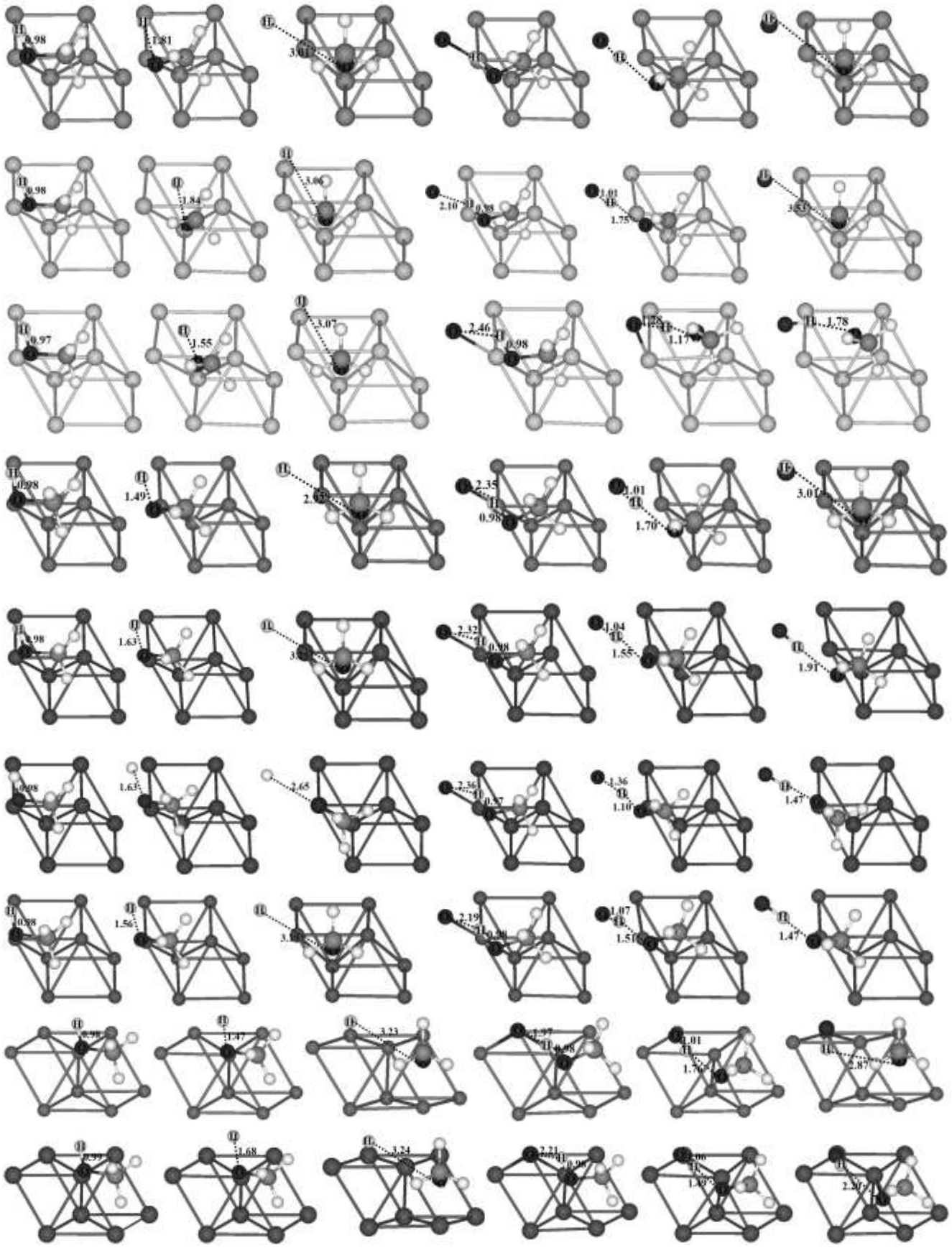
**Figure S5**



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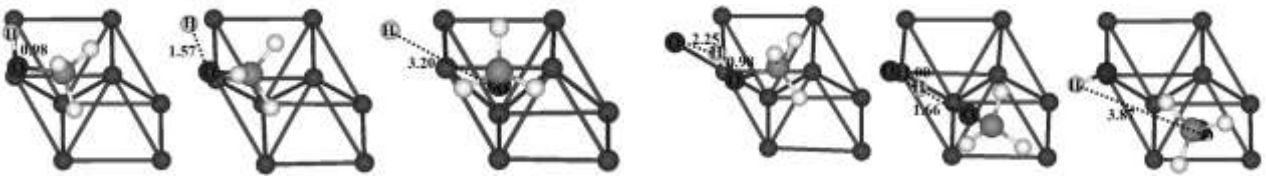

$CH_3OH$ TS $CH_3O+H$ $CH_3OH+O$ TS $CH_3O+OH$

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**Figure S6**