Supplementary information

Methanol formation from CO_2 Catalyzed by Fe_3S_4{111}: Formate versus Hydrocarboxyl Pathways

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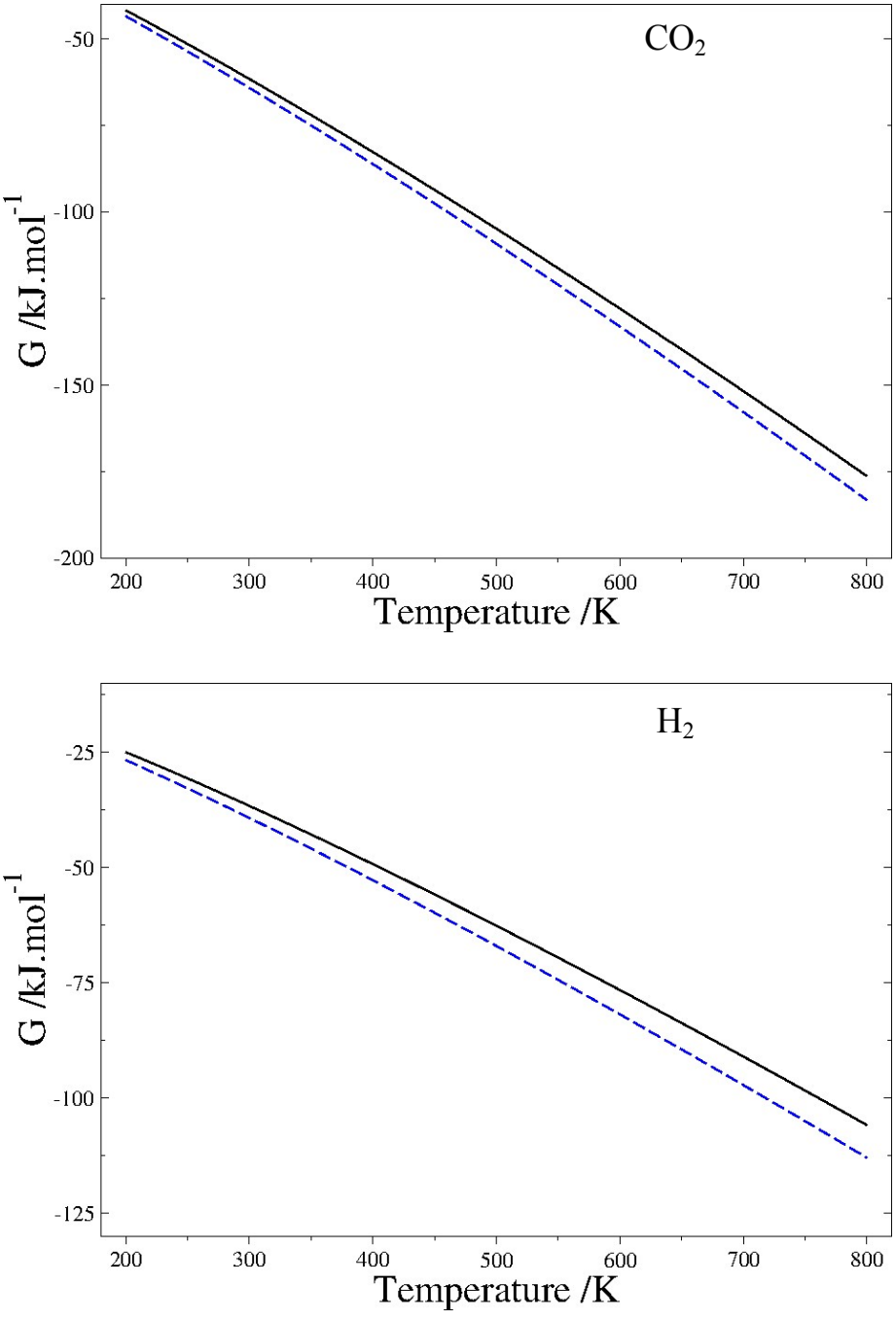
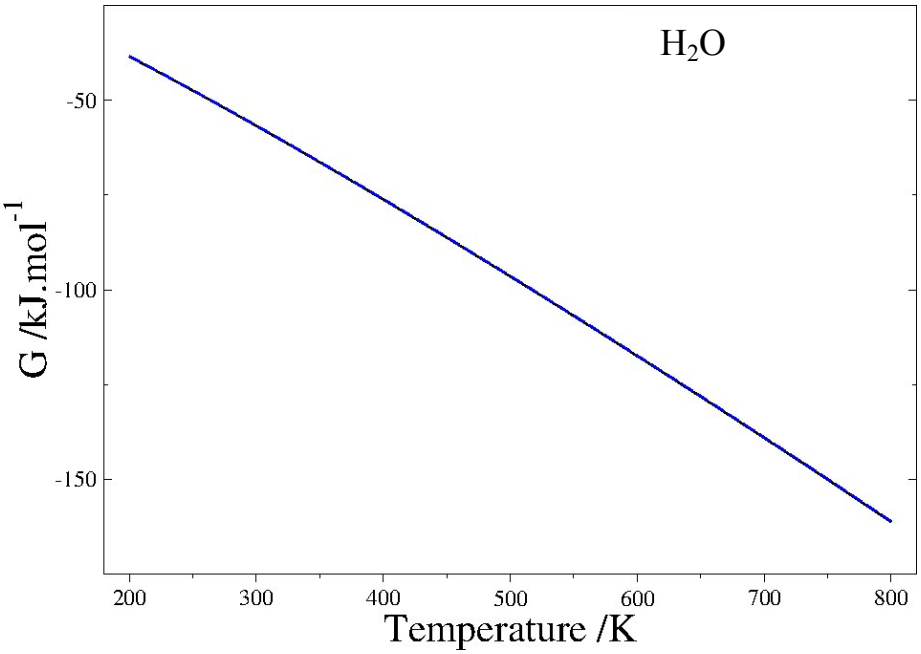
Contents

1. Gas phase molecules

For the microkinetic model, we included ZPE corrections, temperature-dependent heat capacity at constant pressure corrections and entropy contributions, all derived from DFT. Frequencies are calculated using the harmonic oscillator assumption by diagonalization of the mass-weighted Hessian matrix in internal coordinates obtained with a displacement of 0.05 Å. Translational and rotational modes for a gas phase species were defined using its center of mass and principle moments of inertia.

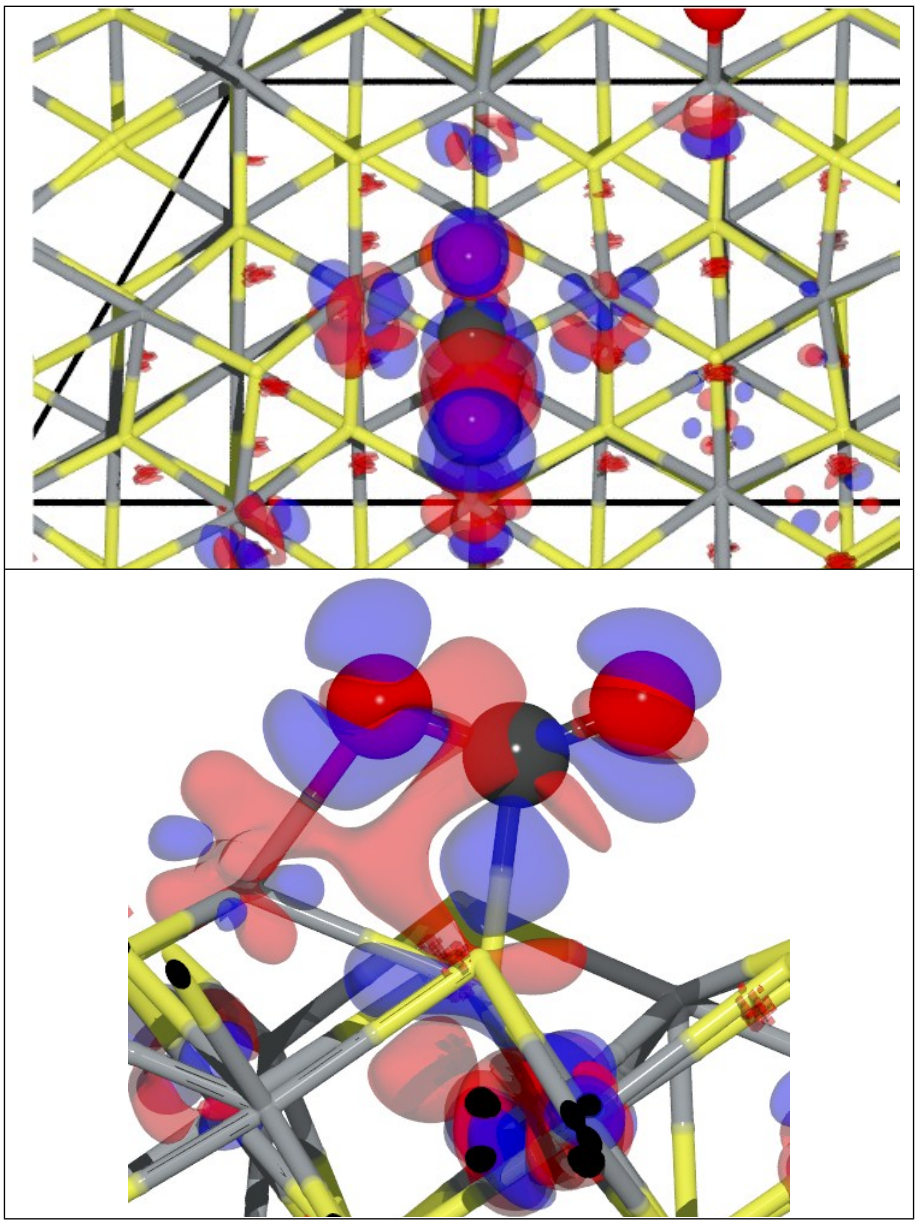
Fig S1. CO_2, H_2 and H_2O molecular free energy (G) as a function of the temperature. Solid black line indicates our calculated values and the blue-dashed line indicates the experimental extrapolation from Shomate equations.[1]




H2O
-50
-100
-150
G /kJ.mol-1
200
300
400
500
600
700
800
Temperature /K

2. CO_2 Adsorption and Activation

Fig S2. Top (a) and side (b) schematic representation of activated CO_2 on Fe_3S_4{111} surface. The isosurface has a value of 0.02 eV/Å^2, red indicate electron density depletion while blue indicates gain. Light grey and yellow sticks represents Fe and S; red and dark grey balls represent O and C.

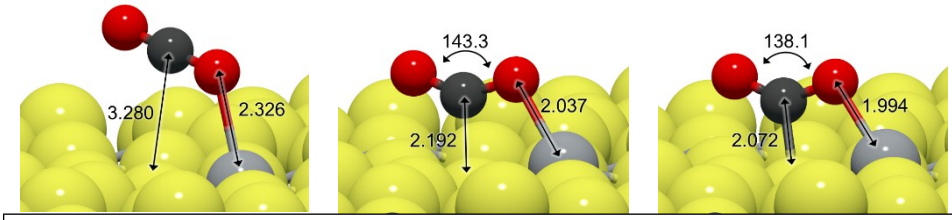


3. Reaction Intermediates

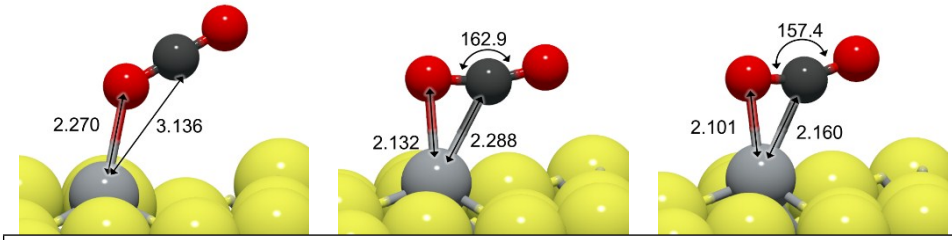
Fig S3. Schematic representation of CO_2 and intermediates hydrogenation process. Left column indicates reactants, center column indicate transition states and right column shows the products. All distances are given in Å and all the structures, on Fe_A or Fe_B, were represented with practically the same orientation. Light grey and yellow sticks represents Fe and S; red and dark grey balls represent O and C.

3.1. Illustrations related with structures in **Table 2**.

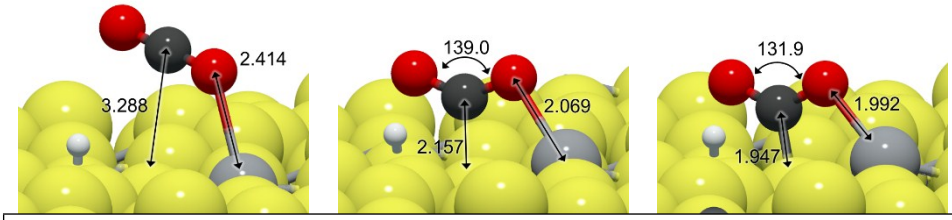
2a	$CO_2^* \leftrightarrow CO_2^{\#}$



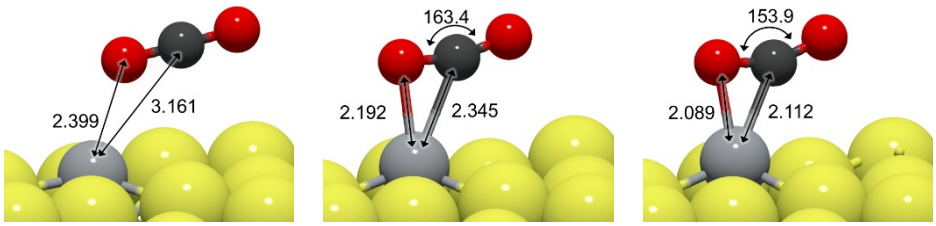
2b	$CO_2^* \leftrightarrow CO_2^{\#}$



2c	$CO_2^* + 2H^* \leftrightarrow CO_2^{\#} + 2H^*$

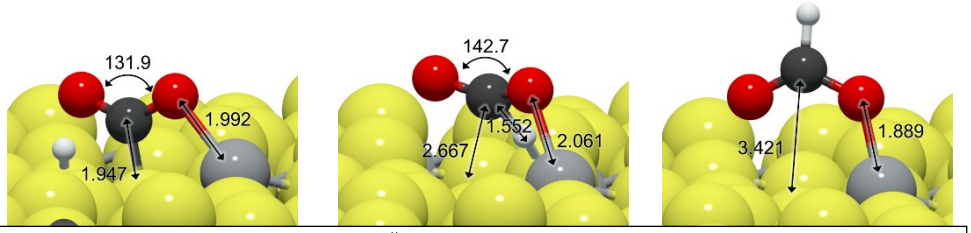


2d	$CO_2^* + 2H^* \leftrightarrow CO_2^{\#} + 2H^*$

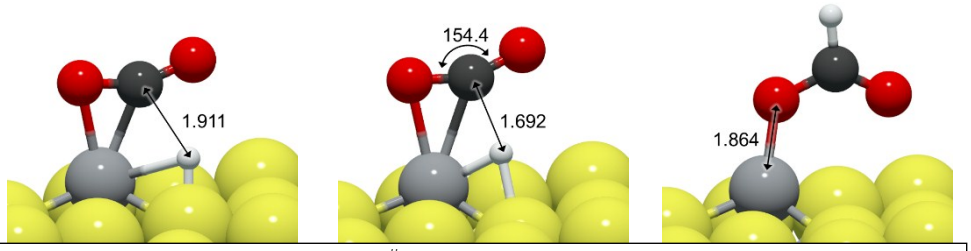


3.2. Illustrations related with structures in **Table 3**.

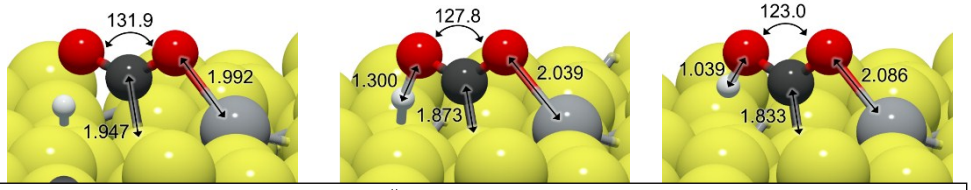
3a	$CO_2^{\#} + 2H^* \leftrightarrow HCOO^* + H^*$



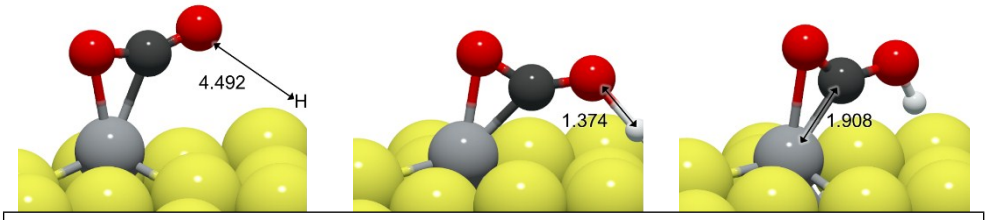
3b	$CO_2^{\#} + 2H^* \leftrightarrow HCOO^* + H^*$



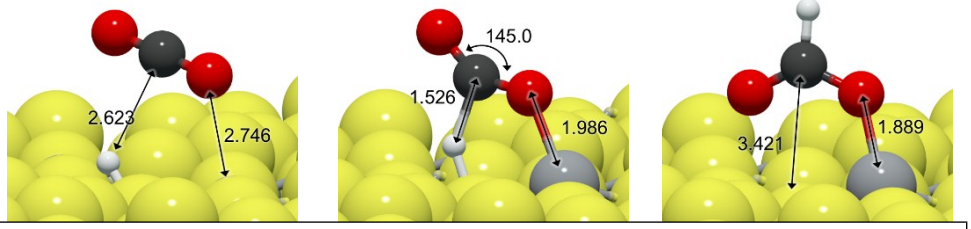
3c	$CO_2^{\#} + 2H^* \leftrightarrow COOH^* + H^*$



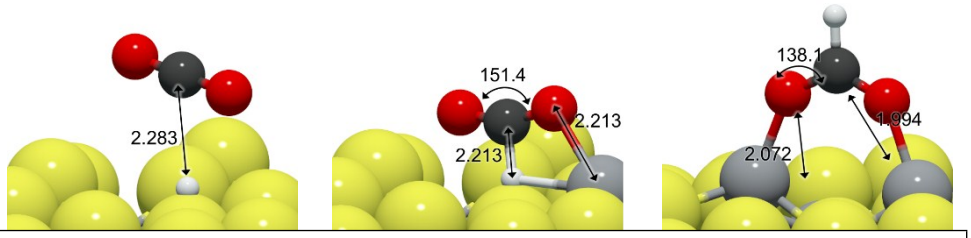
3d	$CO_2^{\#} + 2H^* \leftrightarrow COOH^* + H^*$



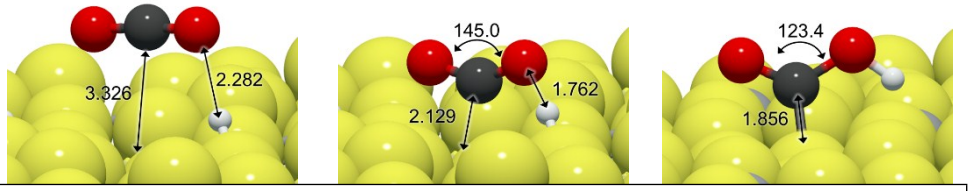
3e	$CO_2 + 2H^* \leftrightarrow HCOO^* + H^*$



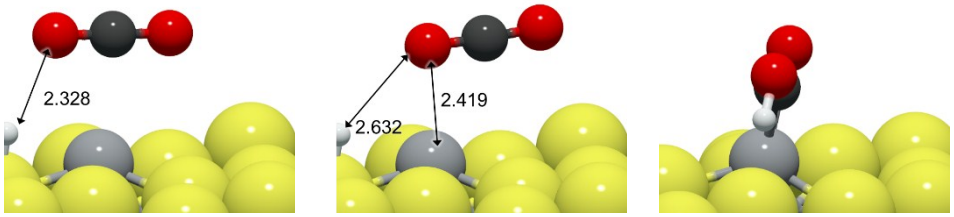
3f	$CO_2 + 2H^* \leftrightarrow HCOO^* + H^*$



3g	$CO_2 + 2H^* \leftrightarrow COOH^* + H^*$

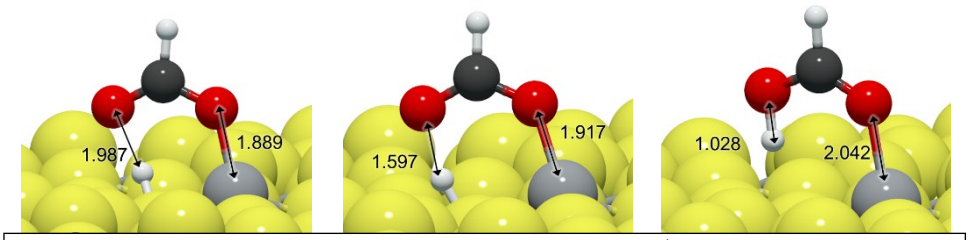


3h	$CO_2 + 2H^* \leftrightarrow COOH^* + H^*$

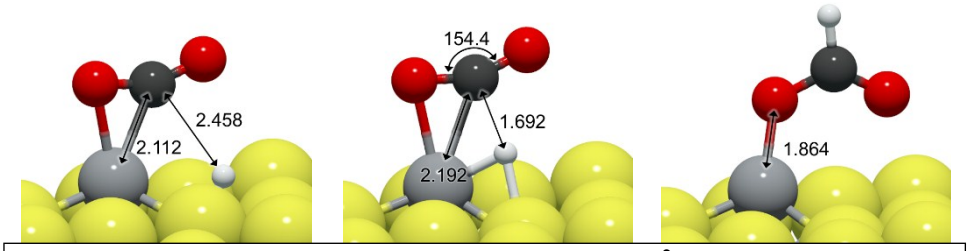


3.3. Illustrations related with structures in **Table 4**.

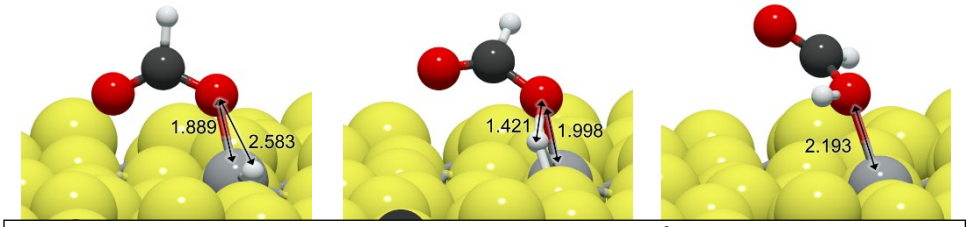
4a	HCOO* + H* ↔ HCOO^{1}H



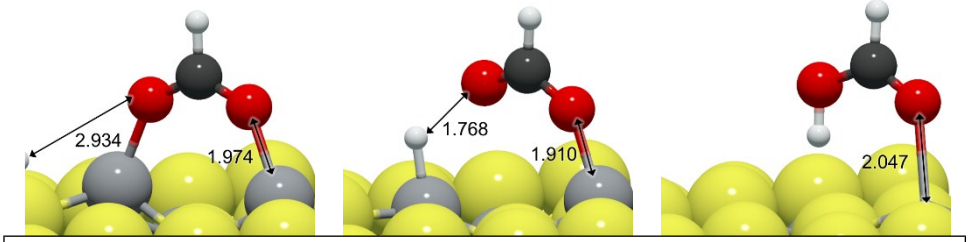
4b	HCOO* + H* ↔ HCOO^{1}H



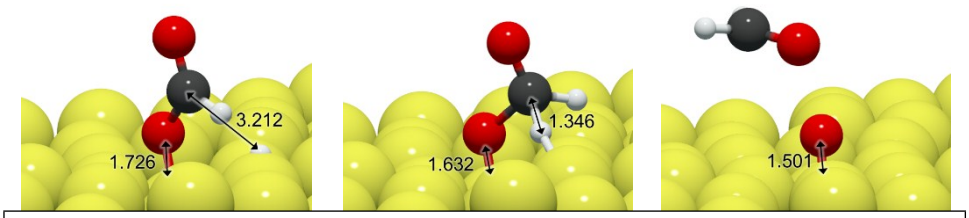
4c	HCOO* + H* ↔ HCOO^{2}H



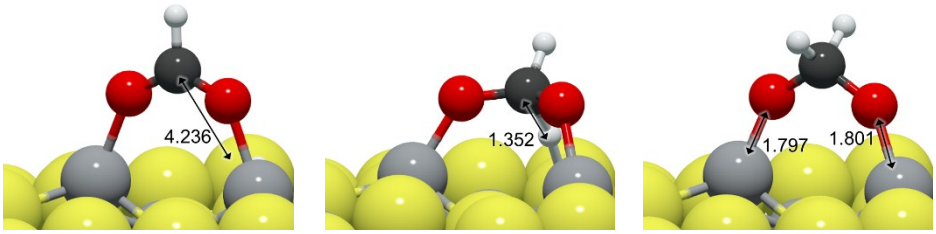
4d	HCOO* + H* ↔ HCOO^{2}H*



4e	HCOO* + H* ↔ H_2CO + O*

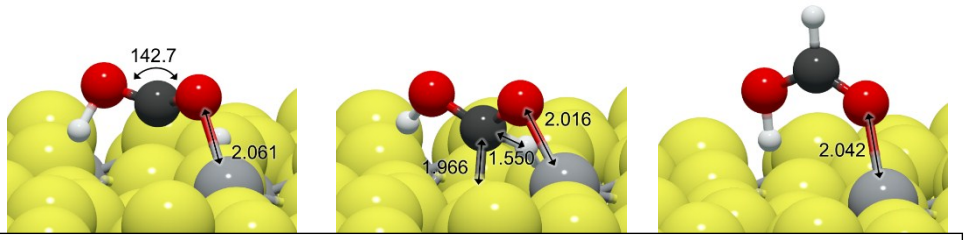


4f	HCOO* + H* ↔ H_2COO*

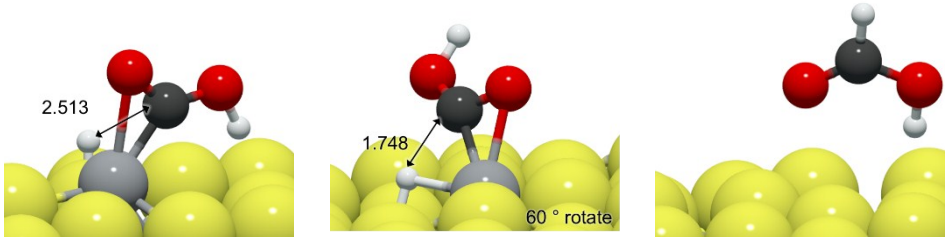

4.236
1.352
1.797
1.801

3.4. Illustrations related with structures in **Table 5**.

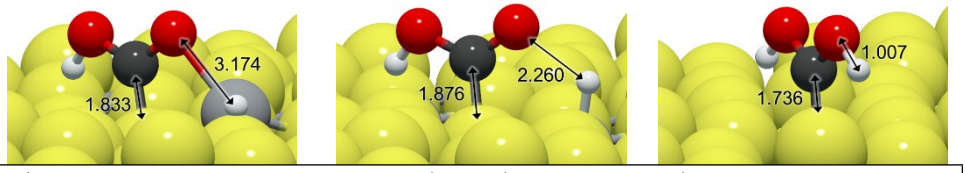
5a	COOH* + H* ↔ HCOOH*



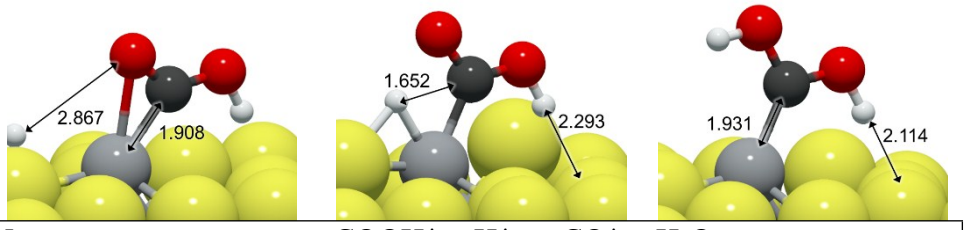
5b	COOH* + H* ↔ HCOOH*



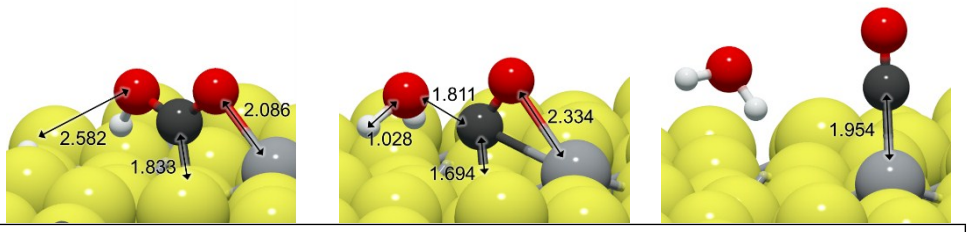
5c	COOH* + H* ↔ HOCOH*



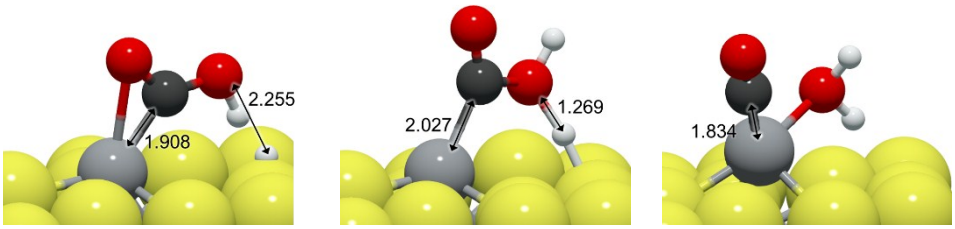
5d	COOH* + H* ↔ HOCOH*



5e	COOH* + H* ↔ CO* + H_2O

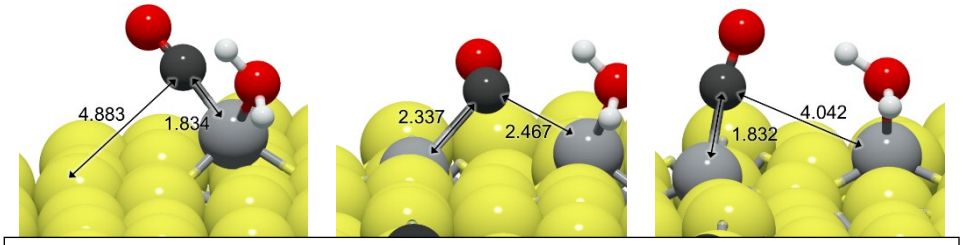


5f	COOH* + H* ↔ CO* + H_2O*

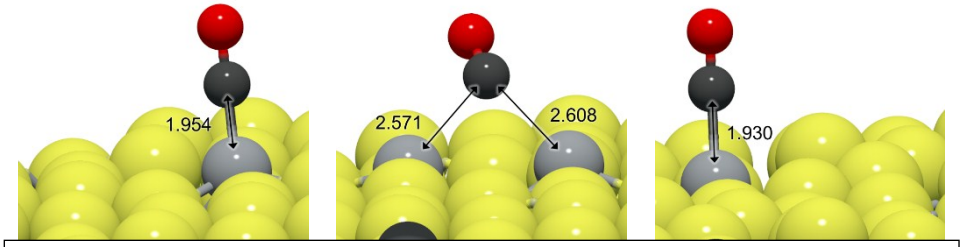


3.5. Illustrations related with structures in **Table 6**.

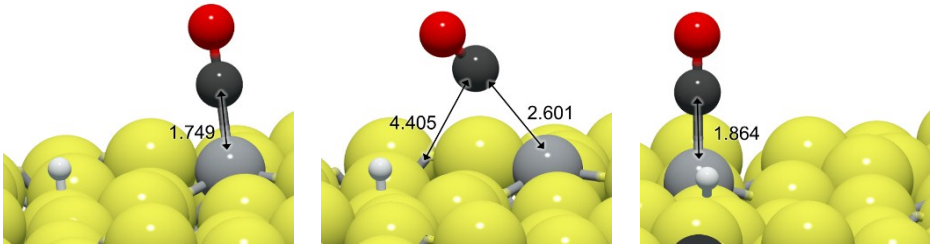
6a	$_{(B)}CO^* + {}_{(B)}H_2O^* \leftrightarrow {}_{(A)}CO^* + {}_{(B)}H_2O^*$



6b	$_{(B)}CO^* \leftrightarrow {}_{(A)}CO^*$

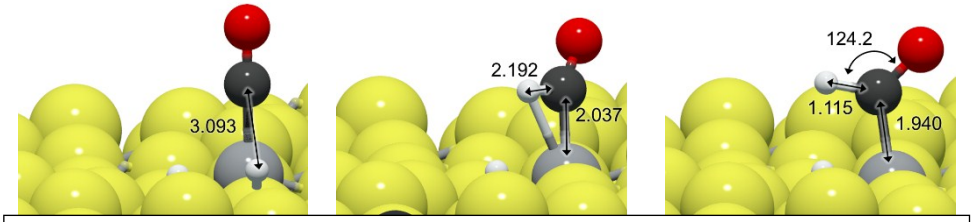


6c	$_{(B)}CO^* + 2H^* \leftrightarrow {}_{(A)}CO^* + 2H^*$

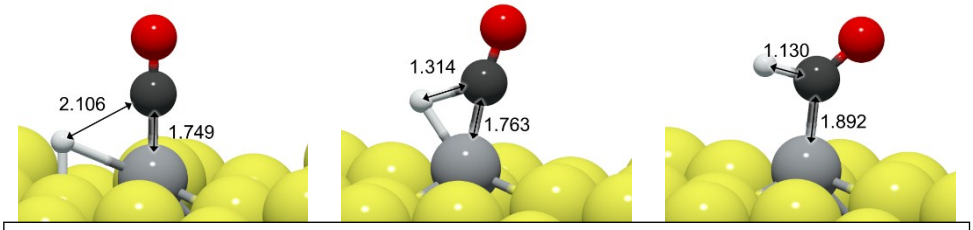


3.6. Illustrations related with structures in **Table 7**.

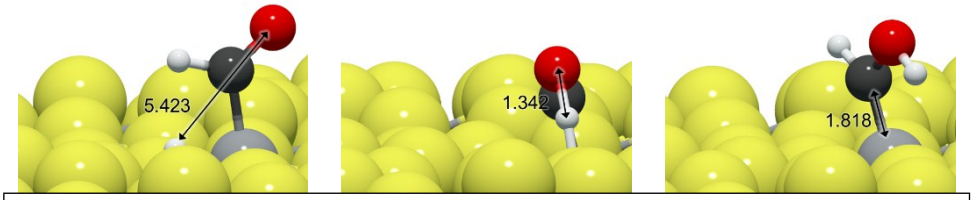
7a	CO* +2 H* ↔ HCO* + H*



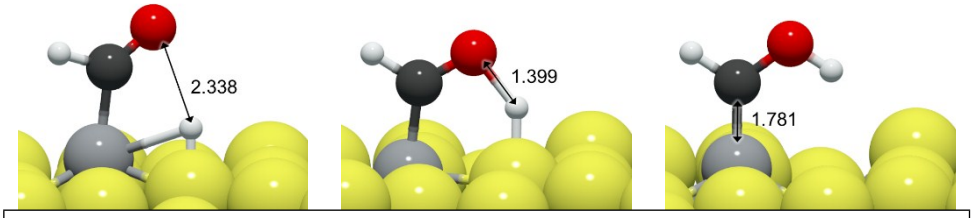
7b	CO* +2 H* ↔ HCO* + H*



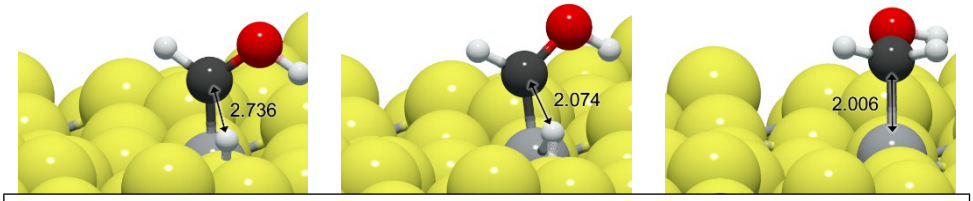
7c	HCO* + H* ↔ HCOH*



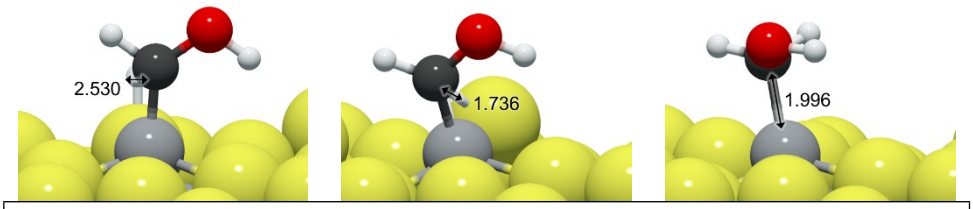
7d	HCO* + H* ↔ HCOH*



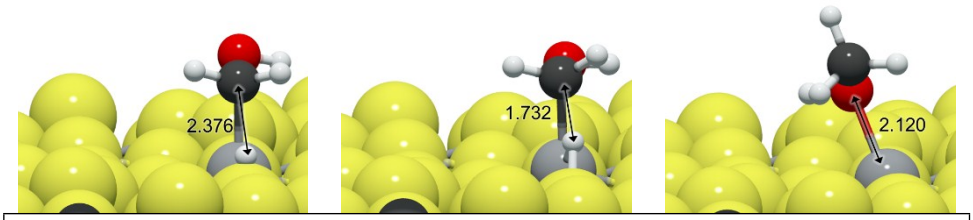
7e	HCOH* + 2 H* ↔ H_2COH^* + H*



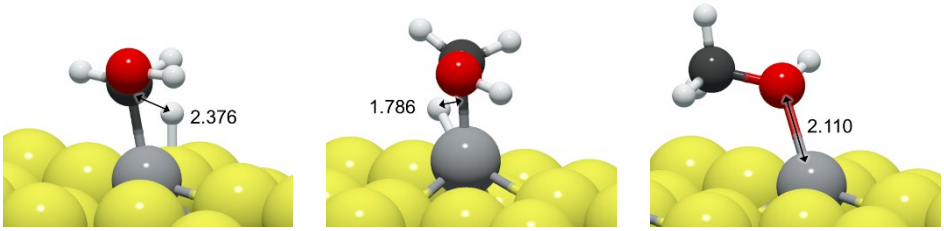
7f	HCOH* + 2 H* ↔ H_2COH^* + H*



7g	$H_2COH^* + H^* \leftrightarrow H_3COH^*$

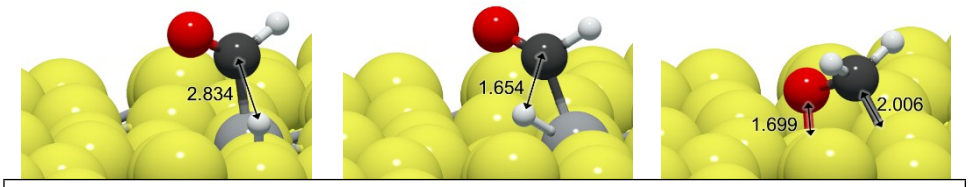


7h	$H_2COH^* + H^* \leftrightarrow H_3COH$

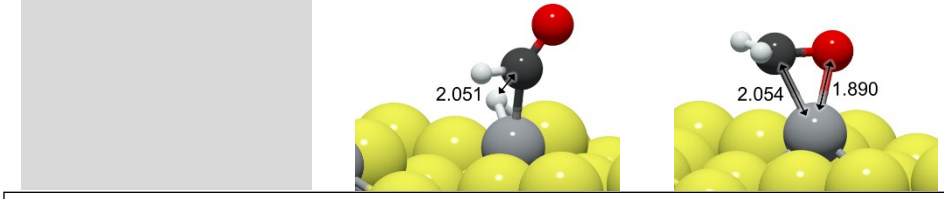


3.7. Illustrations related with structures in **Table 8**.

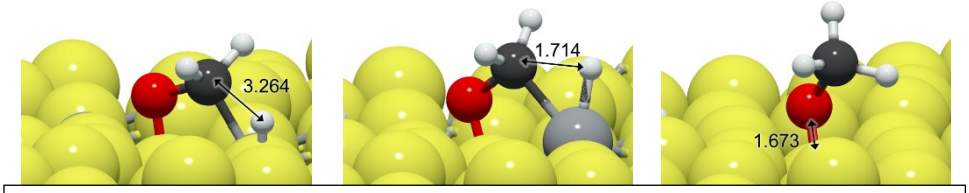
8a	$HCO^* + H^* \leftrightarrow H_2CO^*$



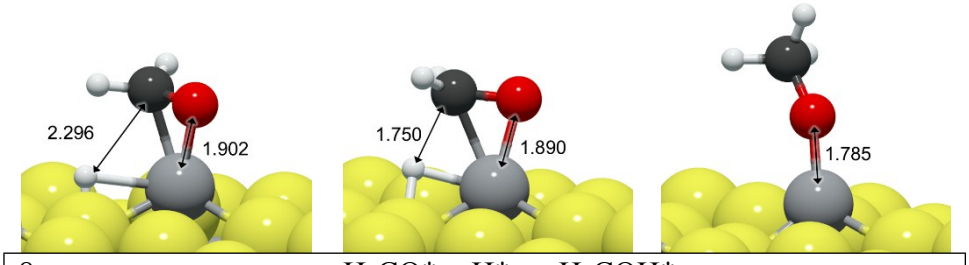
8b	$HCO^* + H^* \leftrightarrow H_2CO^*$



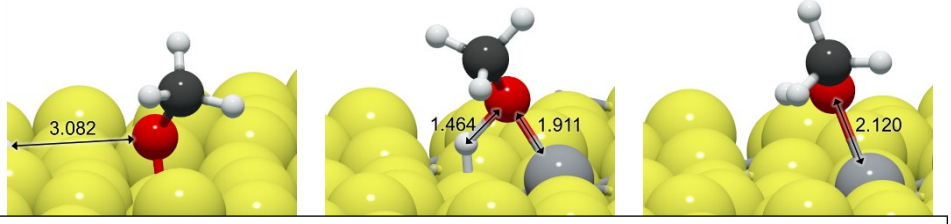
8c	$H_2CO^* + 2\ H^* \leftrightarrow H_3CO^* + H^*$



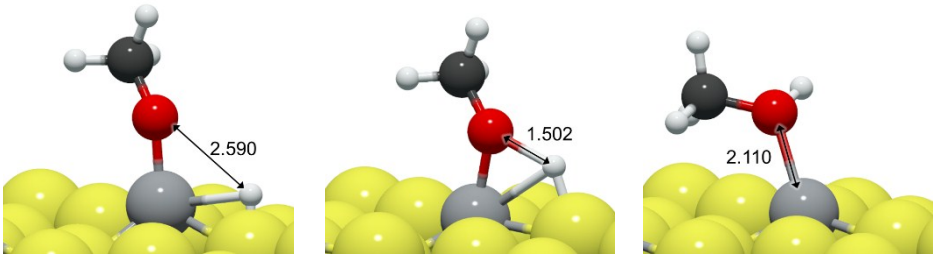
8d	$H_2CO^* + 2\ H^* \leftrightarrow H_3CO^* + H^*$



8e	$H_3CO^* + H^* \leftrightarrow H_3COH^*$

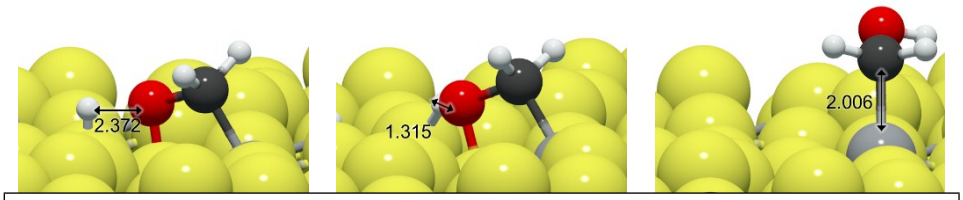


8f	$H_3CO^* + H^* \leftrightarrow H_3COH^*$

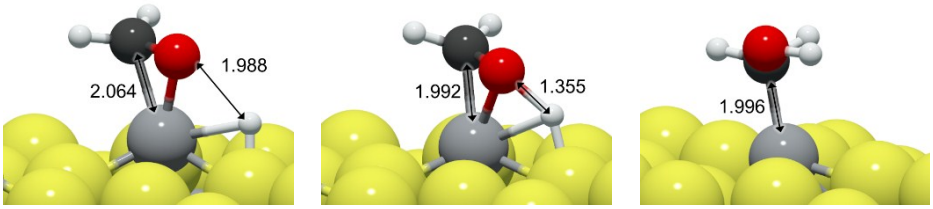


3.8. Illustrations related with structures in **Table 9**.

9a	$H_2CO^* + 2\ H^* \leftrightarrow H_2COH^* + H^*$



9b	$H_2CO^* + 2\ H^* \leftrightarrow H_2COH^* + H^*$



Reaction constants

Table S1. Calculate logarithm of the reaction constants (at 300 K) for the processes involved in the conversion of CO_2 to formic acid and methanol on Fe_3S_4{111} as represented by **Fig S3**.

Label	Reaction	Log (K_{+1}) (300 K)	Log(K_{-1}) (300 K)
2a	$CO_2^* \rightarrow CO_2^{\#}$	3.2106	13.3049
2b	$CO_2^* \rightarrow CO_2^{\#}$	7.5593	12.7960
2c	$CO_2^* + 2H^* \rightarrow CO_2^{\#} + 2H^*$	0.9264	4.4452
2d	$CO_2^* + 2H^* \rightarrow CO_2^{\#} + 2H^*$	3.6979	12.1503
3a	$CO_2^{\#} + 2H^* \rightarrow HCOO^* + H^*$	-4.8043	-10.6819
3b	$CO_2^{\#} + 2H^* \rightarrow HCOO^* + H^*$	-4.4578	-23.2762
3c	$CO_2^{\#} + 2H^* \rightarrow COOH^* + H^*$	11.8018	13.1250
3d	$CO_2^{\#} + 2H^* \rightarrow COOH^* + H^*$	1.6144	0.4859
3e	$CO_2 + 2H^* \rightarrow HCOO^* + H^*$	109.9839	-1.0155
3f	$CO_2 + 2H^* \rightarrow HCOO^* + H^*$	98.1797	-27.2257
3g	$CO_2 + 2H^* \rightarrow COOH^* + H^*$	105.3524	-7.6882
3h	$CO_2 + 2H^* \rightarrow COOH^* + H^*$	106.1252	-1.5902
4a	$HCOO^* + H^* \rightarrow HCOO^1H^*$	10.5809	5.0763
4b	$HCOO^* + H^* \rightarrow HCOO^1H^*$	5.0707	9.6004
4c	$HCOO^* + H^* \rightarrow HCOO^2H^*$	-7.2924	16.4102
4d	$HCOO^* + H^* \rightarrow HCOO^2H^*$	-19.7188	-10.5991
4e	$HCOO^* + H^* \rightarrow H_2CO + O^*$	-31.0980	-5.5480
4f	$HCOO^* + H^* \rightarrow H_2COO^*$	-22.3785	0.9419
5a	$COOH^* + H^* \rightarrow HCOOH^*$	-6.2426	-18.9481
5b	$COOH^* + H^* \rightarrow HCOOH^*$	-4.6885	-17.8488
5c	$COOH^* + H^* \rightarrow HOCOH^*$	-3.8012	4.0858
5d	$COOH^* + H^* \rightarrow HOCOH^*$	-12.6188	-10.6097
5e	$COOH^* + H^* \rightarrow CO^* + H_2O$	-16255	-35.2787
5f	$COOH^* + H^* \rightarrow CO^* + H_2O^*$	2.6518	-7.0686
6a	$_{(B)}CO^* + {}_{(B)}H_2O^* \rightarrow {}_{(A)}CO^* + {}_{(B)}H_2O^*$	-12.9935	-2.4939
6b	$_{(B)}CO^* \rightarrow {}_{(A)}CO^*$	-15.8680	-10.5651
6c	$_{(B)}CO^* + 2H^* \rightarrow {}_{(A)}CO^* + 2H^*$	1.3596	-0.7642
7a	$CO^* + 2\ H^* \rightarrow HCO^* + H^*$	0.8347	11.5185
7b	$CO^* + 2\ H^* \rightarrow HCO^* + H^*$	8.3668	9.8491
7c	$HCO^* + H^* \rightarrow HCOH^*$	3.4790	8.6764
7d	$HCO^* + H^* \rightarrow HCOH^*$	-6.4768	0.6995
7e	$HCOH^* + 2\ H^* \rightarrow H_2COH^* + H^*$	1.4573	12.3300
7f	$HCOH^* + 2\ H^* \rightarrow H_2COH^* + H^*$	-2.5535	-12.6344

7g	$H_2COH^* + H^* \rightarrow H_3COH^*$	-4.1966	-15.8381
7h	$H_2COH^* + H^* \rightarrow H_3COH^*$	-2.3381	-15.9892
8a	$HCO^* + H^* \rightarrow H_2CO^*$	-3.5936	11.9885
8b	$HCO^* + H^* \rightarrow H_2CO^*$	-5.1309	-12.0627
8c	$H_2CO^* + 2\ H^* \rightarrow H_3CO^* + H^*$	8.1947	-19.3724
8d	$H_2CO^* + 2\ H^* \rightarrow H_3CO^* + H^*$	-2.2016	-12.4416
8e	$H_3CO^* + H^* \rightarrow H_3COH^*$	7.1761	-2.8491
8f	$H_3CO^* + H^* \rightarrow H_3COH^*$	-7.4880	-9.8552
9a	$H_2CO^* + 2\ H^* \rightarrow H_2COH^* + H^*$	7.2383	-18.7125
9b	$H_2CO^* + 2\ H^* \rightarrow H_2COH^* + H^*$	-4.6774	-3.6336

References

1. M. W. J. Chase, 1998, 1951 pages.