SUPPL MATERIAL FOR ONLINE VERSION

Electronic supplementary information (ESI) for the 'Effect of internal excitations of reagent diatom on initial state-selected dynamics of C + OH reaction on its second excited ($1^4A''$) electronic state'

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†Dedicated to professor Debashis Mukherjee on the occassion of his 70th birthday.

Table S1. Structure, normal-mode frequencies and relative energies of the two minima on the electronic ground ($X^2 A'$) PES of C + OH collisional system, (Reproduced from Ref. 1).

Parameter description	Parameter value
HCO Minimum	
Energy relative to reagent asymptote (C + OH)	-7.26 eV
R_{CH}	2.10 a_0
R_{CO}	2.24 a_0
$\angle HCO$	126°
ω_1 (CH stretch)	2767 cm^{-1}
ω_2 (CO stretch)	1885 cm^{-1}
ω_3 (HCO bend)	1142 cm^{-1}
R/r/θ	2.03 a_0/3.87 a_0/151°
COH Minimum	
Energy relative to reagent asymptote (C + OH)	-5.50 eV
R_{OH}	1.85 a_0
R_{CO}	2.44 a_0
$\angle COH$	111°
ω_1 (OH stretch)	3495 cm^{-1}
ω_2 (CO stretch)	1387 cm^{-1}
ω_3 (COH bend)	1157 cm^{-1}
R/r/θ	2.48 a_0/1.85 a_0/67°

Table S2. Structure and relative energies of the saddle points on the electronic ground ($X^2A^{'}$) PES of C + OH collisional system, (Reproduced from Ref. 1).

Parameter description	Parameter value
Saddle point - I (H-CO saddle point)	
Energy relative to reagent asymptote (C + OH)	-6.34 eV
R_{CH}	3.46 a_0
R_{CO}	2.15 a_0
$\angle HCO$	115°
R/r/θ	1.95 a_0/4.79 a_0/134°
Saddle point - II (HCO inversion saddle point)	
Energy relative to reagent asymptote (C + OH)	-6.18 eV
R_{CH}	2.01 a_0
R_{CO}	2.30 a_0
$\angle HCO$	180°
R/r/θ	2.04 a_0/4.31 a_0/180°
Saddle point - III (CO-H saddle point)	
Energy relative to reagent asymptote (C + OH)	-5.03 eV
R_{OH}	2.32 a_0
R_{CO}	2.26 a_0
$\angle COH$	120°
R/r/θ	2.33 a_0/2.32 a_0/57°
Saddle point - IV (COH inversion saddle point)	
Energy relative to reagent asymptote (C + OH)	-4.23 eV
R_{OH}	1.95 a_0
R_{CO}	2.46 a_0
$\angle COH$	180°
R/r/θ	2.58 a_0/1.95 a_0/0 ^{o}
Saddle point - V (isomerisation saddle point)	
Energy relative to reagent asymptote (C + OH)	-4.44 eV
R_{CH}	2.48 a_0
R_{CO}	2.40 a_0
$\angle HCO$	52.8^o
R/r/θ	2.35 a_0/2.17 a_0/ 112°

Table S3. Geometrical structure and relative energies of the two minima on the first excited ($1^2A''$) PES of C + OH collisional system, (Reproduced from Ref. 2).

Parameter description	Parameter value
HCO Minimum	
Energy relative to reagent asymptote (C + OH)	-6.16 eV
R_{CH}	2.01 a_0
R_{CO}	2.25 a_0
$\angle HCO$	180°
R/r/θ	2.00 a_0/4.26 a_0/180°
COH Minimum	
Energy relative to reagent asymptote (C + OH)	-4.63 eV
R_{OH}	1.82 a_0
R_{CO}	2.49 a_0
$\angle COH$	116°
R/r/θ	2.54 a_0/1.82 a_0/61°

Table S4. Geometrical structure and relative energies of the saddle points on the first excited ($1^2A''$) PES of C + OH collisional system, (Reproduced from Ref. 2).

Parameter description	Parameter value
Saddle point - I (isomerisation saddle point)	
Energy relative to reagent asymptote (C + OH)	-3.11 eV
R_{CH}	2.34 a_0
R_{CO}	2.37 a_0
$\angle HCO$	68°
R/r/θ	2.82 a_0/2.64 a_0/121°
Saddle point - II (COH inversion saddle point)	
Energy relative to reagent asymptote (C + OH)	-4.34 eV
R_{OH}	1.79 a_0
R_{CO}	2.41 a_0
$\angle COH$	180°
R/r/θ	2.52 a_0/1.79 a_0/0°

Table S5. Geometrical structure and relative energies of the two minima on the second excited $(1^4A'')$ PES of C + OH collisional system, (Reproduced from Ref. 2).

Parameter description	Parameter value
HCO Minimum	
Energy relative to reagent asymptote (C + OH)	-2.25 eV
R_{CH}	2.05 a_0
R_{CO}	2.66 a_0
$\angle HCO$	118°
R/r/θ	2.38 a_0/4.06 a_0/151°
COH Minimum	
Energy relative to reagent asymptote (C + OH)	-1.85 eV
R_{OH}	1.83 a_0
R_{CO}	2.63 a_0
$\angle COH$	106°
R/r/θ	2.66 a_0/1.83 a_0/72°

Table S6. Geometrical structure and relative energies of the saddle points on the second excited ($1^4A''$) PES of C + OH collisional system, (Reproduced from Ref. 2).

Parameter description	Parameter value

Saddle point - I (isomerisation saddle point)

Energy relative to reagent asymptote (C + OH)	-0.33 eV
R_{CH}	2.39 a_0
R_{CO}	2.65 a_0
$\angle HCO$	55°
R/r/θ	2.58 a_0/2.34 a_0/121°

Saddle point - II (COH inversion saddle point)

Energy relative to reagent asymptote (C + OH)	-0.41 eV
R_{OH}	1.77 a_0
R_{CO}	2.57 a_0
$\angle COH$	180°
R/r/θ	2.68 a_0/1.77 a_0/0°

Saddle point - III (HCO inversion saddle point)

Energy relative to reagent asymptote (C + OH)	-1.05 eV
R_{OH}	2.01 a_0
R_{CO}	2.66 a_0
$\angle COH$	180°
R/r/θ	2.39 a_0/4.67 a_0/180°

Saddle point - IV (CO-H saddle point)

Energy relative to reagent asymptote (C + OH)	0.03 eV
R_{OH}	2.86 a_0
R_{CO}	2.34 a_0
$\angle COH$	121°
R/r/θ	2.43 a_0/2.86 a_0/56°

Saddle point - V (H-CO saddle point)

Energy relative to reagent asymptote (C + OH)	-0.11 eV
R_{OH}	3.40 a_0
R_{CO}	2.34 a_0
$\angle COH$	93°
R/r/θ	2.20 a_0/4.24 a_0/121°

In all the tables presented here, R/r/θ collectively represent Jacobi coordinates relative to C + OH.

References

[1] A. Zanchet, B. Bussery-Honvault, and P. Honvault, J. Phys. Chem. A **110**, 12017 (2006).

[2] A. Zanchet, B. Bussery-Honvault, M. Jorfi, and P. Honvault, Phys. Chem. Chem. Phys. **11**, 6182 (2009).