Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

A Spectroscopic and *ab initio* Study of the Hydrogen Peroxide–Formic Acid Complex: Hindering of a Large Amplitude Motion

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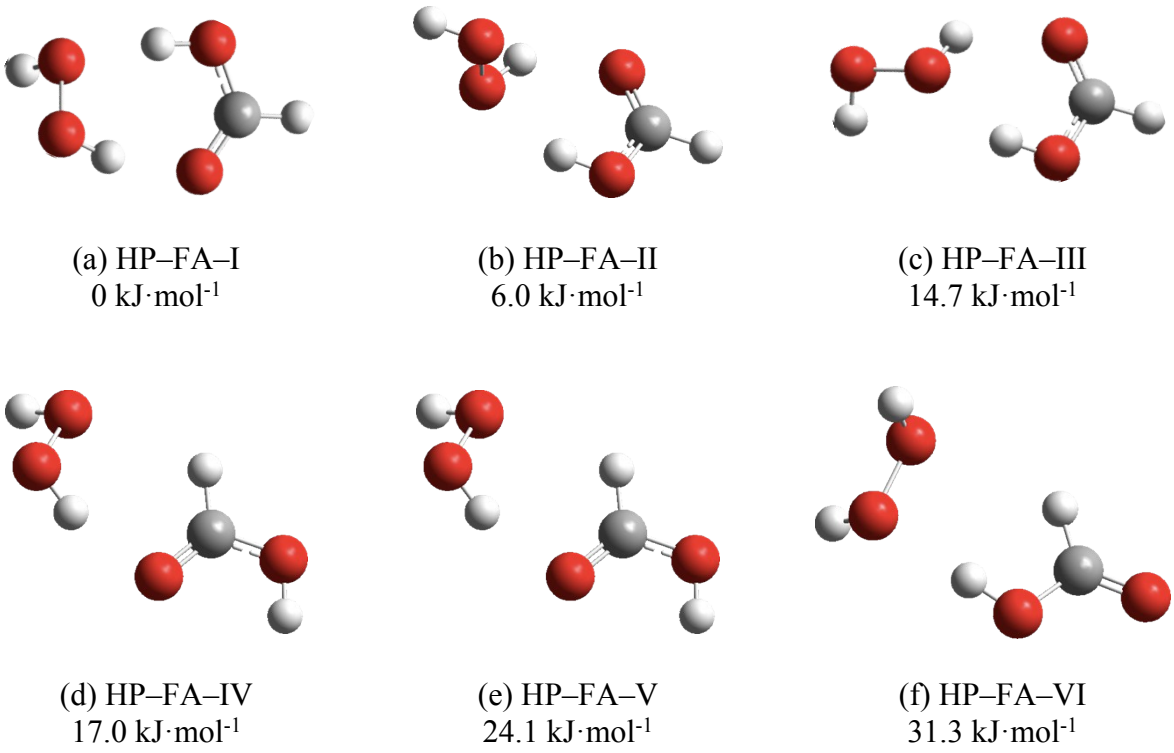

(a) HP–FA–I
0 kJ·mol^{-1}

(b) HP–FA–II
6.0 kJ·mol^{-1}

(c) HP–FA–III
14.7 kJ·mol^{-1}

(d) HP–FA–IV
17.0 kJ·mol^{-1}

(e) HP–FA–V
24.1 kJ·mol^{-1}

(f) HP–FA–VI
31.3 kJ·mol^{-1}

Fig. S1 Six optimized structures of the HP–FA complex and their relative energies. All structures and energies were calculated at the MP2/6-311++G(2d,p) level of theory.

Table S2 Experimental intrastate (*a*-/*b*-type) transition frequencies (in MHz) and quantum number assignments

$J'(K_a', K_c') \leftarrow J''(K_a'', K_c'')$	0^+	0^-
1(0,1) – 0(0,0)	5106.851	5107.584
1(1,1) – 0(0,0)	10457.728	10457.831
1(1,0) – 1(0,1)	6075.883	6075.166
2(0,2) – 1(0,1)	10144.812	10147.023
2(1,1) – 1(1,0)	10937.631	10939.417
2(1,2) – 1(0,1)	14839.246	14839.902
2(0,2) – 1(1,1)	4793.935	4796.776
2(1,2) – 1(1,1)	9488.369	9489.655
2(1,1) – 2(0,2)	6868.702	6867.560
3(0,3) – 2(0,2)	15049.022	15044.800
3(1,2) – 2(1,1)	16368.463	16363.714
3(0,3) – 2(1,2)	10354.588	10351.921
3(1,3) – 2(1,2)		14193.477
3(1,2) – 3(0,3)	8188.143	8186.474

Table S3 Experimental interstate (*c*-type) transition frequencies (in MHz)

$J'(K_a', K_c') \leftarrow J''(K_a'', K_c'')$	$0^+ \leftarrow 0^-$	$0^- \leftarrow 0^+$
1(1,1) – 1(0,1)	13019.529	
2(1,1) – 1(0,1)		9344.232
2(0,2) – 1(1,0)	11740.422	
2(1,2) – 2(0,2)	12364.372	
3(1,2) – 2(0,2)		15565.672
3(0,3) – 2(1,1)	15847.591	
3(1,3) – 3(0,3)	11508.827	