Supplementary electronic material

The CCSD(T)/aug-cc-pVQZ potential energy surface (PES) for HCO_2^- is given by the expression

$$V = \sum_{i,j,k,l,m,n} C_{ijklmn} \varrho_1^i \, \varrho_2^j \, \varrho_3^k \, \Delta\beta_1^l \, \Delta\beta_2^m \, \cos(n\tau), \tag{1}$$

with the constraint that

$$C_{ijklmn} = C_{ikjmln}. \tag{2}$$

In eqn. (1), the stretching coordinates ϱ_i are defined as

$$\varrho_i = \frac{1}{a_i}\{1 - \exp[-a_i(R_i/R_i^e - 1)]\}, \qquad (i = 1, 2, 3). \tag{3}$$

The displacement coordinates $\Delta\beta_i = \beta_i(\mathrm{HCO}) - \beta_e$ (i = 1,2) and the torsional angle τ are employed to describe the angular dependence of the PES.
The non-linear parameters a_1 - a_3 and the linear parameters C_{ijklmn} were determined by means of least-squares fitting techniques. The latter are collected in Table 1, while the former have values of $a_1 = 0.9047$ and $a_2 = a_3 = 0.8455$.

Table 1: Linear parameters of the analytical CCSD(T)/avqz potential energy surface for HCO_2^- (all coefficients in atomic units).

ijklmn	coefficient	ijklmn	coefficient	ijklmn	coefficient
200000	0.60411735	022000	0.17371784	011020	0.50699093
300000	-0.92903060	010100	-0.25005765	012001	-0.69521692
400000	0.60798143	010200	-0.41782498	012010	-0.82126819
500000	-0.32558919	010300	-0.08173401	012100	-0.84954812
600000	0.29303321	020100	0.05671403	100110	-0.07751958
700000	-0.15468989	020200	-0.09688389	100120	0.07231911
020000	1.86944908	020300	0.21745529	101001	-0.11965152
030000	-3.43006023	030100	-0.07467478	101010	-0.36239916
040000	3.80766338	030200	0.23877952	101100	-0.19629833
050000	-2.93800745	010010	-0.60402448	101110	0.29376874
060000	1.46768403	010020	-0.25621337	101200	0.09807025
000100	0.36825295	010030	-0.11039726	102010	0.37152867
000200	0.26461450	020010	0.10395274	102100	0.15540445
000300	0.10657421	020020	0.22362982	200110	-0.10380086

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Table 1 continued

ijklmn	coefficient	ijklmn	coefficient	ijklmn	coefficient
000400	0.07209887	020030	0.15385217	201001	-0.04706539
000500	0.03260729	030010	0.02622335	201010	-0.21974640
000001	-0.21504143	010001	0.25754803	201100	-0.07289553
000002	-0.42412138	010002	0.42516820	001130	-0.16468244
000003	-0.31673596	010003	0.20559179	001202	0.01854882
000004	-0.13993328	010004	0.03797096	001220	-0.24378070
000005	-0.03681967	020001	0.10374180	001301	0.05231784
000006	-0.00454386	030001	0.09490720	001310	-0.15490938
110000	0.06616818	000110	0.34149723	002120	0.28400823
120000	-0.32402580	000120	0.20480511	002201	0.27706003
130000	0.15608035	000130	0.22411878	002210	0.25683026
210000	0.08035471	000140	0.13570605	011030	0.68699040
220000	-0.12876314	000220	0.30157110	022010	0.71487810
230000	-0.31408452	000230	0.29929593	100130	-0.07374925
310000	-0.12836874	000101	0.46216655	100220	-0.05609019
320000	0.23932424	000102	0.10972238	101021	-0.33706014
410000	-0.19020814	000103	0.01580873	101030	-0.25345716
100100	0.08883353	000201	0.04281523	101120	-0.30744575
100200	-0.07511848	000202	0.02606821	101210	-0.18602800
100300	0.05638057	000301	0.08529859	101300	-0.11319956
200100	0.08854630	111000	-0.07841360	102002	-0.02940705
200200	-0.08337456	211000	0.25638035	102020	-0.35052311
200300	0.09215879	001011	-0.24740082	102200	0.06428430
300100	-0.04296715	001101	-0.52809782	103010	0.25308530
400100	-0.08547400	001102	-0.07434050	103100	0.38850388
100001	-0.01566040	001110	-0.49311362	200120	0.10906059
100002	-0.02066568	001120	-0.52736014	201020	0.09986366
100003	-0.00500544	001210	-0.54273868	201110	-0.16492925
200001	0.02396423	002101	-0.09043350	201200	-0.09024760
300001	-0.06677819	002110	-0.18196382	202010	-0.21888750
011000	2.07054392	011001	1.90586642	202100	-0.36577884
012000	-1.12789054	011002	0.34012550	300110	0.13369673
013000	0.21528270	011010	0.61160972	301010	0.24506449
301100	0.23569490				

Table 2: Dissociation reaction $HCO_2^- \longrightarrow H^- + CO_2$. Points on minimum energy path.

r(CH)/$\mathring{A}$	$R_{opt}/\mathring{A}$	$\alpha_{opt}/^o$	E_{opt}/cm^{-1}
∞	1.1631	180	19872
5.0	1.1632	178.1	19218
4.5	1.1633	177.6	18979
4.0	1.1635	177.0	18641
3.75	1.1638	176.5	18425
3.5	1.1640	175.9	18175
3.375	1.1642	175.5	18036
3.25	1.1645	175.0	17890
3.125	1.1648	174.3	17737
3.0	1.1653	173.5	17577
2.875	1.1660	172.5	17412
2.75	1.1669	171.0	17239
2.625	1.1684	169.1	17052
2.5	1.1708	166.4	16831
2.375	1.1751	162.5	16528
2.25	1.1819	157.5	16050
2.125	1.1907	152.1	15279
2.0	1.1995	147.6	14156
1.875	1.2075	144.0	12675
1.75	1.2152	141.0	10835
1.625	1.2227	138.3	8635
1.5	1.2305	135.9	6115
1.375	1.2385	133.7	3446
1.25	1.2464	131.8	1080
1.12936	1.25351	130.18	0
1.0	1.2602	128.8	2170
0.9	1.2644	128.1	8679
0.8	1.2676	127.5	23061