

Table II. Geometries of formate anion, formic acid and its protonated form by different methods.

HCOO ⁻								
Variable ^a	RHF/6d ^b	RHF/+6d ^c	MP2/6d	MP2/+6d ^d	DMol	DG/L	DN/L	DN/N
C1-O2	1.236	1.236	1.266	1.267	1.261	1.261	1.260	1.273
C1-O3	1.236	1.236	1.266	1.267	1.261	1.261	1.261	1.273
C1-H4	1.122	1.119	1.130	1.125	1.155	1.154	1.154	1.152
H4-C1-O3	114.639	114.821	114.674	114.979	114.770	114.842	114.934	114.954
H4-C1-O2	114.641	114.821	114.674	114.979	114.768	114.726	114.699	114.609
O3-C1-O2	130.720	130.358	130.651	130.042	130.461	130.432	130.367	130.437

HCOOH									
Variable ^a	RHF/6d ^b	RHF/+6d ^c	MP2/6d	MP2/+6d ^d	DMol	DG/L	DN/L	DN/N	Exp. ^e
C1-O2	1.323	1.322	1.352	1.352	1.343	1.342	1.342	1.365	1.340
C1-O3	1.184	1.184	1.215	1.214	1.211	1.212	1.211	1.219	1.202
C1-H4	1.086	1.086	1.094	1.094	1.111	1.114	1.113	1.109	1.091
O2-H5	0.950	0.950	0.972	0.973	0.998	0.987	0.988	0.985	0.969
H4-C1-O3	124.604	124.478	125.561	125.292	125.001	125.694	125.585	125.721	123.26
H4-C1-O2	110.475	110.750	109.232	109.749	109.981	109.451	109.613	109.187	111.94
O3-C1-O2	124.921	124.772	125.206	124.959	125.018	124.856	124.801	125.092	124.80
H5-O2-C1	109.202	109.224	106.531	106.460	105.555	106.416	106.140	106.160	106.61
H4-C1-O2-H5	-179.949	-179.94	180.000	180.000	180.000	180.000	180.000	180.000	<i>planar</i>
O3-C1-O2-H5	0.033	0.033	0.000	0.000	0.000	0.000	0.000	0.000	

HCOOH ₂ ⁺							
Variable ^a	RHF/6d	MP2/6d	DMol	DG/L	DN/L	DN/N	
C1-O2	1.247	1.270	1.268	1.267	1.267	1.280	
C1-O3	1.256	1.280	1.277	1.277	1.276	1.290	
C1-H4	1.080	1.088	1.104	1.107	1.106	1.101	
O2-H5	0.960	0.982	1.009	0.997	0.997	0.994	
O3-H6	0.956	0.977	1.003	0.991	0.991	0.988	
H4-C1-O3	122.640	123.296	123.163	123.284	123.484	123.300	
H4-C1-O2	116.612	116.132	116.324	116.511	116.176	116.019	
O3-C1-O2	120.748	120.572	120.513	120.205	120.340	120.681	
H5-O2-C1	115.909	113.633	113.677	114.148	114.629	114.209	
H6-O3-C1	116.255	113.867	113.664	114.716	115.010	113.847	
H4-C1-O2-H5	180.000	180.000	180.000	179.816	180.000	180.000	
O3-C1-O2-H5	0.000	0.000	0.000	-0.095	0.000	-0.018	
H4-C1-O3-H6	0.000	0.000	0.000	0.168	0.000	-0.015	
O2-C1-O3-H6	180.000	180.000	180.000	-179.927	180.000	180.000	

^aAtom numbering in Fig 1.^bMethods as in Table I or otherwise noted.^cRHF geometry optimization with DH6D⁽⁺⁾ basis set.^dMP2 geometry optimization with DH6D⁽⁺⁾ basis set.^eFormic acid gas phase geometry taken from ref. 39.