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

Supplementary Information

An infrared study of CO_2 activation by Holmium ions, Ho^+ and HoO^+

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KEYWORDS: Carbon dioxide, molecular activation, ion-molecular complexes, action spectroscopy

Contents

1 Computational Structures (UB3P86/Def2-TZVP)

Given below are the coordinates of the main structural isomers observed for Ho^+ and HoO^+ reacting with CO_2 calculated with the Gaussian suite of programs at the UB3P86/Def2-TZVP level of theory. Hirshfeld charges are given for atoms within each isomer.

1.1 $Ho(CO_2)_n^+$

1.1.1 $Ho(CO_2)^+$

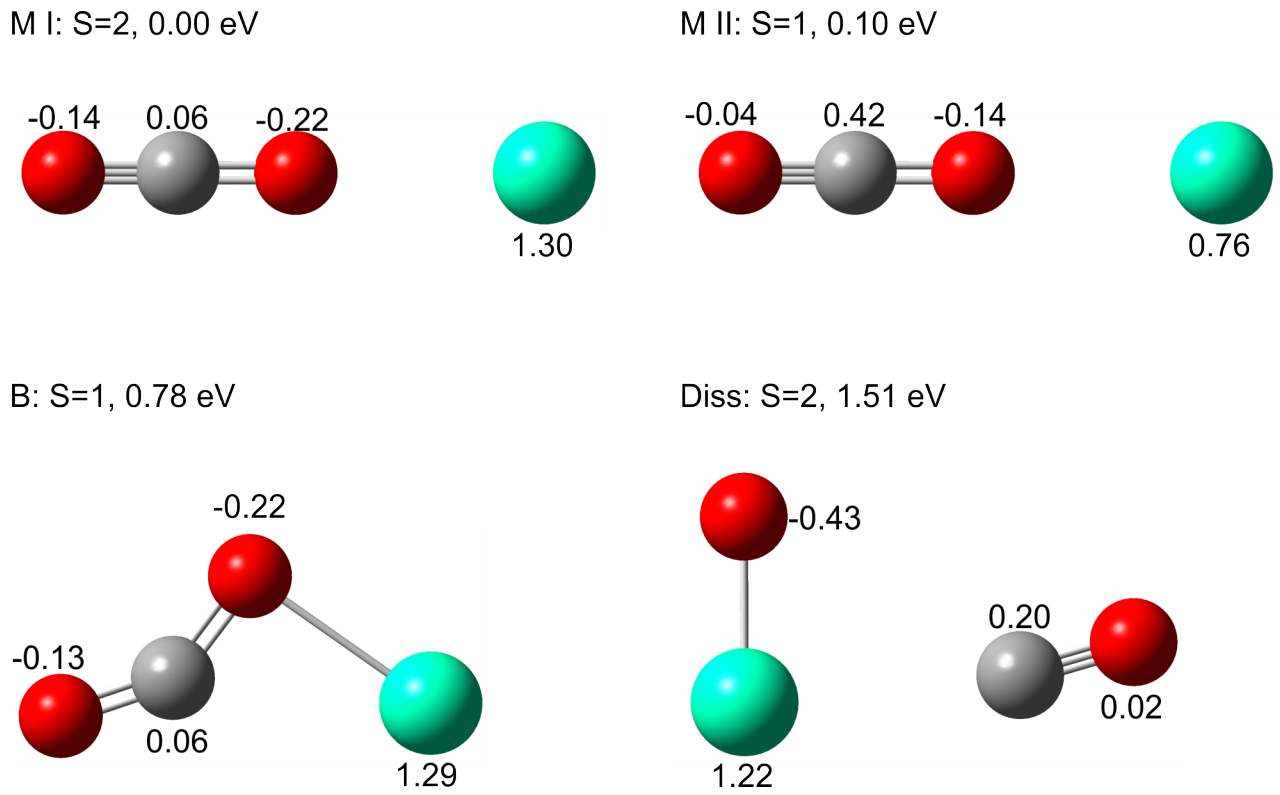

Figure S1: Structures and Hirshfeld charges of the molecularly bound isomers (M) and dissociative isomers (Diss) of $HoO(CO_2)^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.899	0.000	0.000
C	6	-2.750	-0.001	0.000
O	8	-3.891	0.001	0.000
O	8	-1.575	-0.002	0.000

(a) M: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.899	0.000	0.000
C	6	-2.749	0.000	0.000
O	8	-3.890	0.001	0.000
O	8	-1.574	-0.001	0.000

(b) M: S=1, 0.10 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.672	0.000
C	6	-0.203	-1.880	0.000
O	8	-0.767	-2.903	0.000
O	8	0.919	-1.311	0.000

(c) B: S=1, 0.78 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.524	-0.174	0.000
C	6	2.088	-0.178	0.000
O	8	3.184	0.024	0.000
O	8	-0.358	1.565	0.000

(d) Diss: S=2, 1.51 eV

Table S1: Cartesian coordinates of $Ho(CO_2)^+$ isomers.

1.1.2 $Ho(CO_2)_2^+$

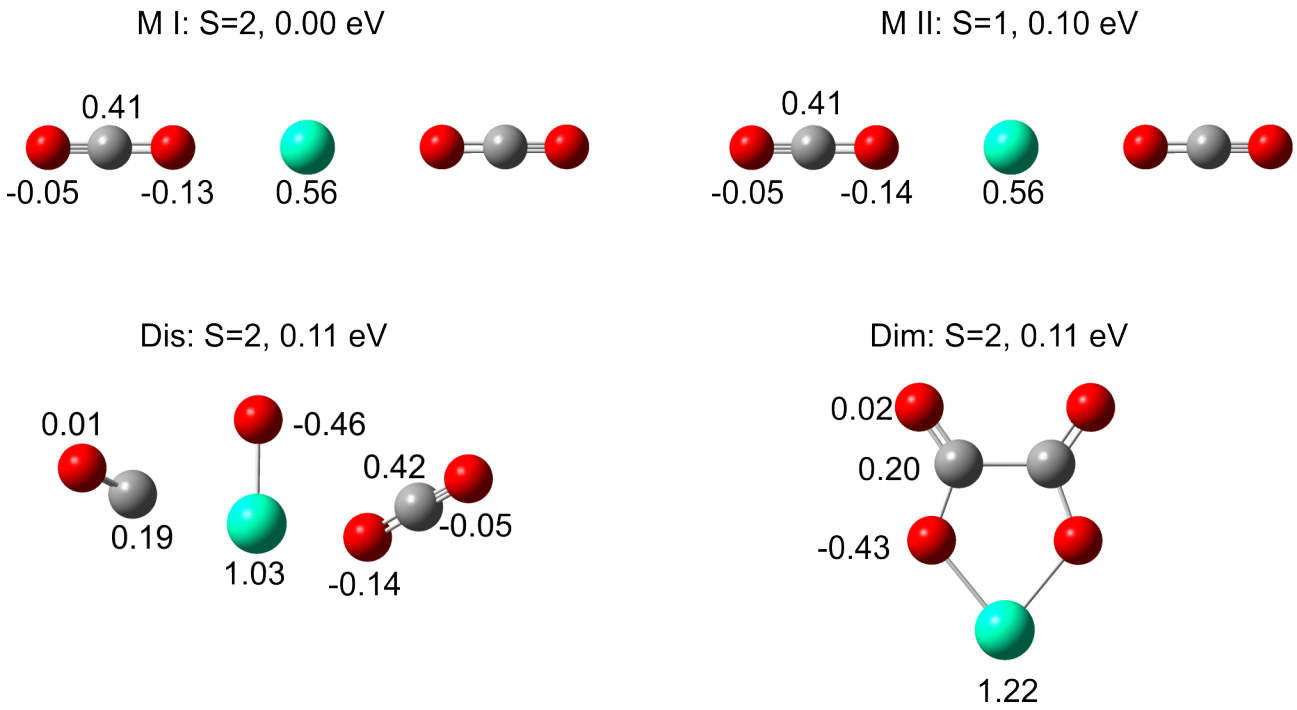

Figure S2: Structures and Hirshfeld charges of the molecularly bound isomers (M), dissociative isomers (Diss) and dimerised isomers (Dim) of $Ho(CO_2)_2^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.000	0.000
C	6	0.000	0.000	-3.669
O	8	0.000	0.000	-2.496
O	8	0.000	0.000	-4.811
C	6	0.000	0.000	3.669
O	8	0.000	0.000	2.496
O	8	0.000	0.000	4.811

(a) M I: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.000	0.000
C	6	0.000	0.000	-3.670
O	8	0.000	0.000	-2.496
O	8	0.000	0.000	-4.811
C	6	0.000	0.000	3.670
O	8	0.000	0.000	2.496
O	8	0.000	0.000	4.811

(b) M II: S=1, 0.10 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.371	-0.592	0.115
C	6	-2.031	1.369	0.254
O	8	-2.716	2.231	0.076
O	8	-0.425	-0.170	-1.602
C	6	2.835	0.687	0.123
O	8	1.848	0.198	0.538
O	8	3.797	1.160	-0.260

(c) Dis: S=2, 0.11 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.368	-0.590	-0.115
C	6	-2.046	1.356	-0.255
O	8	-2.739	2.212	-0.078
O	8	-0.424	-0.164	1.602
C	6	2.838	0.689	-0.123
O	8	1.851	0.199	-0.537
O	8	3.801	1.162	0.258

(d) Dim: S=2, 0.11 eV

Table S2: Cartesian coordinates of $Ho(CO_2)_2^+$ isomers.

1.1.3 $Ho(CO_2)_3^+$

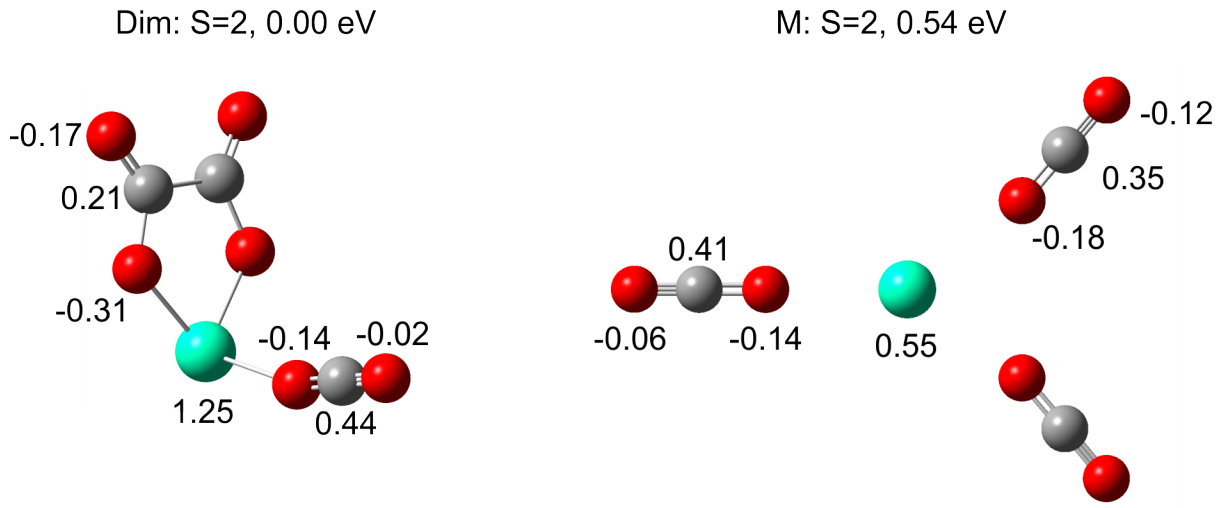

Figure S3: Structures and Hirshfeld charges of the molecularly bound isomers (M), dissociative isomers (Diss) and dimerised isomers (Dim) of $Ho(CO_2)_3^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.276	-0.921	0.000
C	6	1.967	0.796	-0.783
O	8	0.947	0.012	-1.251
O	8	2.732	1.391	-1.450
C	6	1.967	0.795	0.783
O	8	0.948	0.011	1.251
O	8	2.732	1.391	1.450
C	6	-2.915	1.365	0.000
O	8	-3.623	2.253	0.001
O	8	-2.189	0.435	0.000

(a) Dim: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.310	-0.077	-0.027
C	6	-3.974	-0.033	0.036
O	8	-2.802	-0.028	0.021
O	8	-5.116	-0.039	0.050
C	6	2.635	-2.302	0.027
O	8	1.818	-1.463	0.020
O	8	3.434	-3.121	0.034
C	6	2.288	2.569	0.021
O	8	1.585	1.632	0.009
O	8	2.969	3.488	0.032

(b) M: S=2, 0.54 eV

Table S3: Cartesian coordinates of $Ho(CO_2)_3^+$ isomers.

1.2 $HoO(CO_2)_n^+$

1.2.1 $HoO(CO_2)^+$

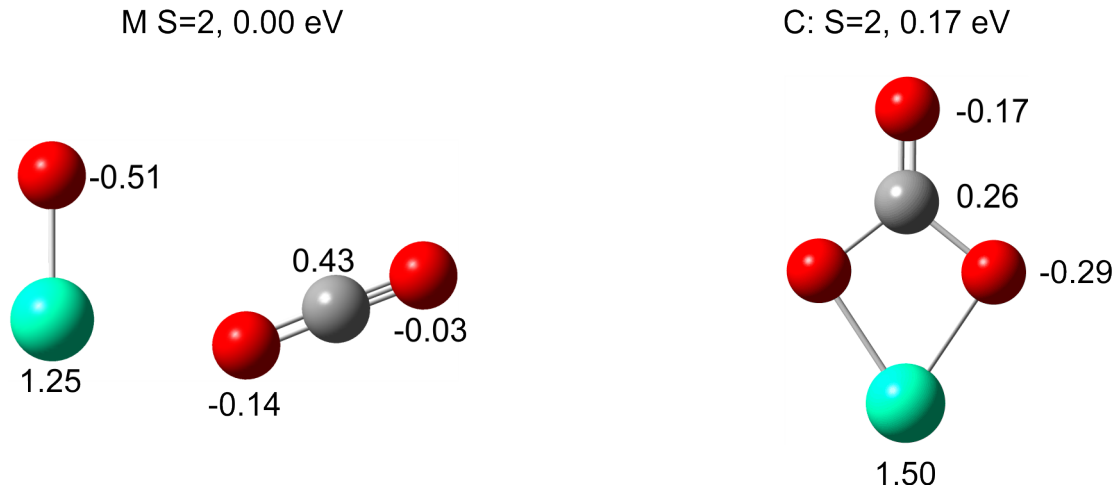

Figure S4: Structures and Hirshfeld charges of the molecularly bound isomers (M) and quasi-carbonate isomers (C) of $HoO(CO_2)^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.782	-0.158	0.000
O	8	-0.761	1.593	0.001
C	6	2.671	-0.085	0.000
O	8	1.572	-0.511	0.002
O	8	3.739	0.307	-0.002

(a) M: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.728	0.000	0.000
O	8	0.922	-1.098	0.000
C	6	1.759	0.000	0.000
O	8	0.922	1.099	0.000
O	8	2.931	0.000	0.000

(b) C: S=2, 0.17 eV

Table S4: Cartesian coordinates of $HoO(CO_2)^+$ isomers

1.2.2 $HoO(CO_2)_2^+$

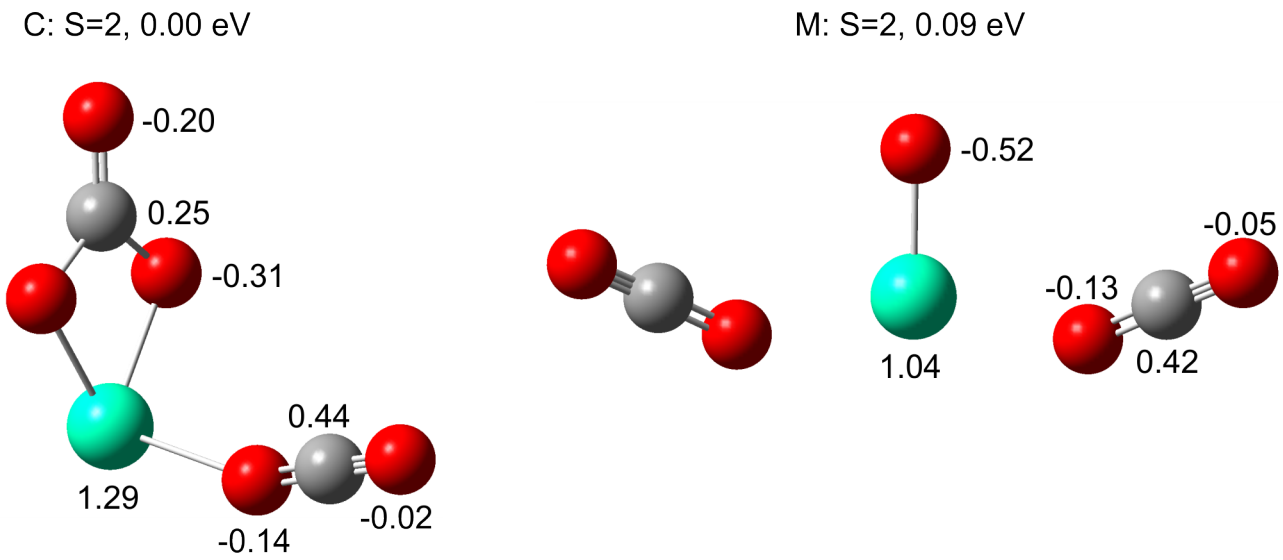

Figure S5: Structures and Hirshfeld charges of the molecularly bound isomers (M) and quasi-carbonate isomers (C) of $HoO(CO_2)_2^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.298	-0.782	0.000
O	8	1.099	0.680	1.101
C	6	1.486	1.410	-0.000
O	8	1.099	0.680	-1.101
O	8	2.030	2.452	-0.000
C	6	-2.859	0.625	-0.000
O	8	-1.940	-0.115	-0.000
O	8	-3.754	1.325	-0.001

(a) C: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	-0.647	-0.101
O	8	-0.001	-0.393	1.646
C	6	-3.000	1.063	-0.134
O	8	-2.074	0.477	-0.561
O	8	-3.905	1.632	0.260
C	6	3.000	1.063	-0.133
O	8	3.905	1.631	0.261
O	8	2.074	0.478	-0.561

(b) M: S=2, 0.09 eV

Table S5: Cartesian coordinates of $HoO(CO_2)_2^+$ isomers.

1.2.3 $HoO(CO_2)_3^+$

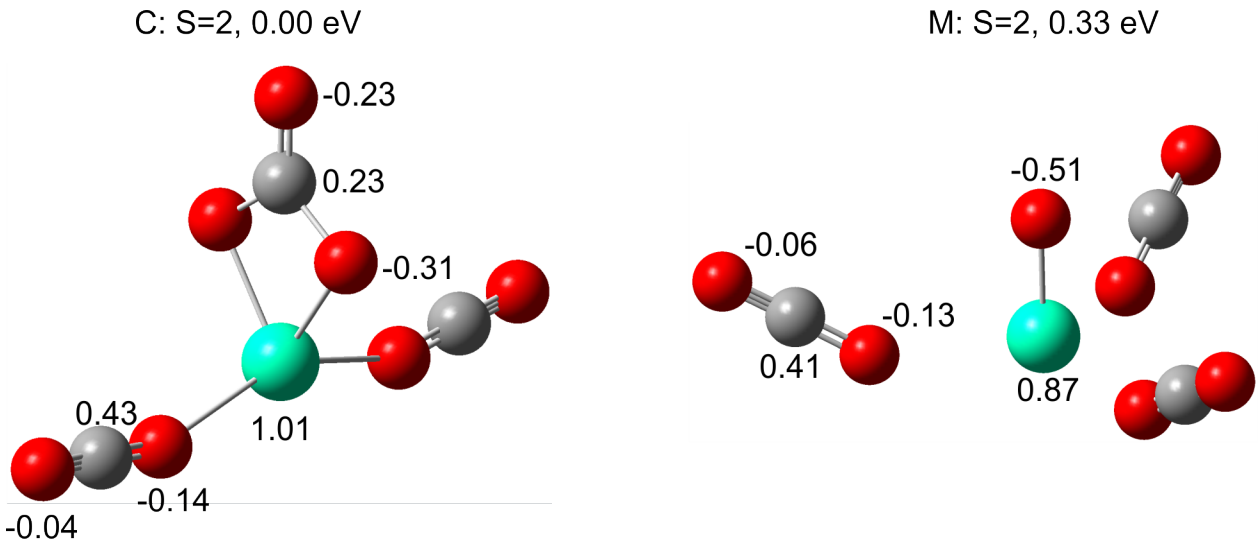

Figure S6: Structures and Hirshfeld charges of the molecularly bound isomers (M) and quasi-carbonate isomers (C) of $HoO(CO_2)_3^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	-0.378	0.000
O	8	-0.000	1.301	1.106
C	6	-3.473	-0.778	0.000
O	8	-2.306	-0.940	0.000
O	8	-4.601	-0.637	-0.000
C	6	3.473	-0.778	-0.000
O	8	2.306	-0.940	-0.000
O	8	4.601	-0.637	-0.001
C	6	-0.000	2.115	-0.000
O	8	-0.000	1.301	-1.106
O	8	-0.000	3.295	-0.000

(a) C: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.000	-0.046	-0.259
O	8	0.000	-0.037	1.520
C	6	-3.047	-1.607	0.098
O	8	-2.147	-1.143	-0.498
O	8	-3.931	-2.061	0.657
C	6	3.042	-1.616	0.098
O	8	2.143	-1.150	-0.499
O	8	3.924	-2.072	0.657
C	6	0.006	3.377	0.080
O	8	0.007	4.373	0.635
O	8	0.004	2.362	-0.513

(b) M: S=2, 0.33 eV

Table S6: Cartesian coordinates of $HoO(CO_2)_3^+$ isomers

1.2.4 $HoO(CO_2)_4^+$

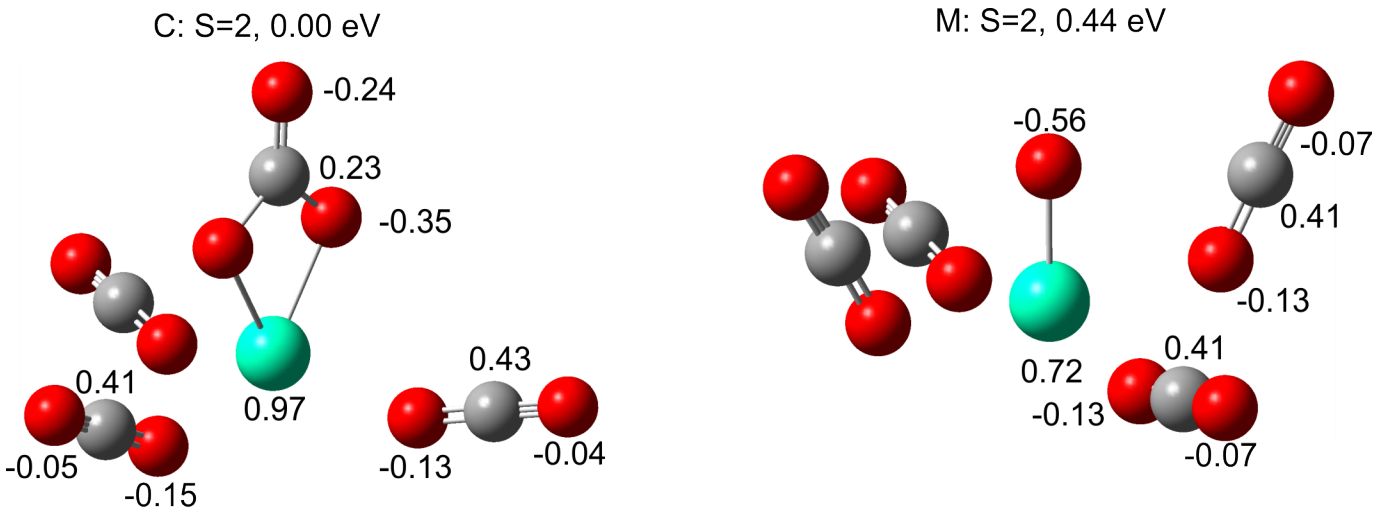

Figure S7: Structures and Hirshfeld charges of the molecularly bound isomers (M) and quasi-carbonate isomers (C) of $HoO(CO_2)_4^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	-0.166	-0.384
O	8	0.001	-1.663	0.988
C	6	-3.402	-0.828	-0.767
O	8	-2.302	-0.449	-0.951
O	8	-4.469	-1.187	-0.605
C	6	3.403	-0.824	-0.766
O	8	2.303	-0.447	-0.950
O	8	4.471	-1.182	-0.604
C	6	-0.003	3.207	0.090
O	8	-0.004	4.128	0.760
O	8	-0.002	2.272	-0.626
C	6	0.001	-0.807	2.053
O	8	0.000	0.466	1.551
O	8	0.001	-1.107	3.197

(a) C: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	-0.000	-0.339
O	8	-0.001	-0.000	1.456
C	6	-3.554	0.002	-0.544
O	8	-2.409	0.001	-0.793
O	8	-4.673	0.003	-0.315
C	6	-0.001	-3.017	0.821
O	8	-0.001	-2.446	-0.208
O	8	-0.002	-3.608	1.797
C	6	3.555	0.001	-0.543
O	8	2.409	0.000	-0.791
O	8	4.674	0.001	-0.315
C	6	0.000	3.016	0.822
O	8	0.000	3.606	1.798
O	8	0.001	2.445	-0.208

(b) M: S=2, 0.44 eV

Table S7: Cartesian coordinates of $HoO(CO_2)_4^+$ isomers.

1.2.5 $HoO(CO_2)_5^+$

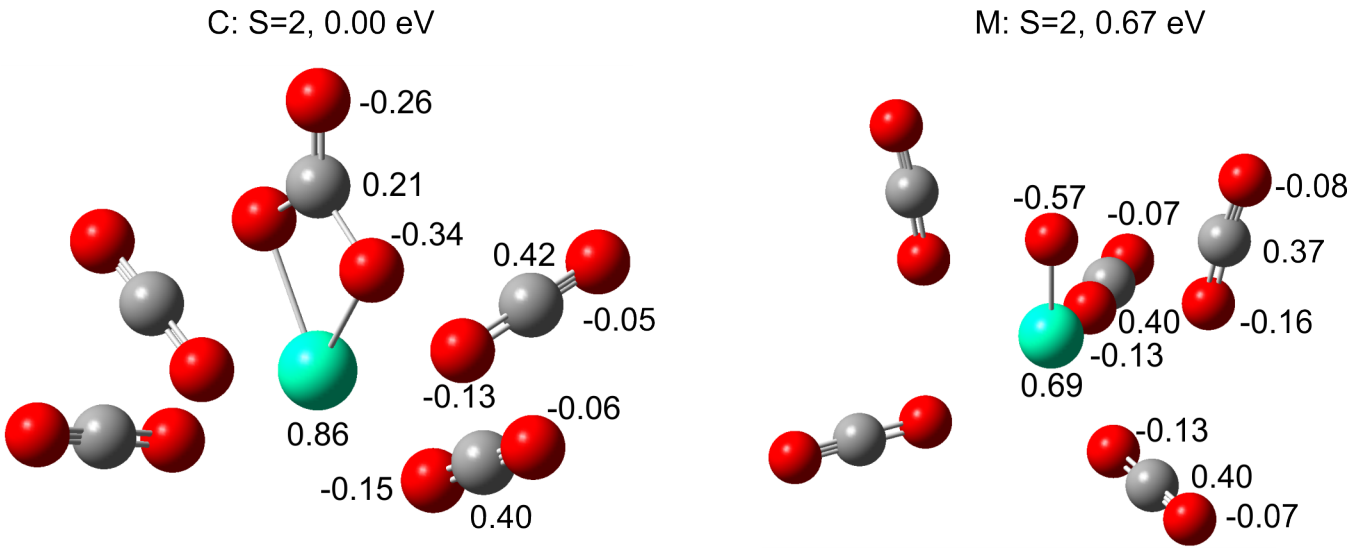

Figure S8: Structures and Hirshfeld charges of the molecularly bound isomers (M) and quasi-carbonate isomers (C) of $HoO(CO_2)_5^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.000	-0.000	-0.346
O	8	-0.001	1.094	1.395
C	6	-0.003	3.381	-0.520
O	8	-0.002	2.358	-1.102
O	8	-0.003	4.387	0.016
C	6	-3.507	-0.003	-0.351
O	8	-2.382	-0.002	-0.691
O	8	-4.603	-0.003	-0.040
C	6	0.000	0.000	2.206
O	8	0.001	-1.094	1.395
O	8	0.000	0.000	3.391
C	6	3.507	0.003	-0.352
O	8	4.603	0.003	-0.041
O	8	2.382	0.002	-0.691
C	6	0.003	-3.381	-0.520
O	8	0.003	-4.387	0.017
O	8	0.002	-2.358	-1.101

(a) C: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.027	0.000	-0.151
O	8	0.168	0.000	1.646
C	6	-2.751	-2.361	-0.496
O	8	-1.952	-1.516	-0.626
O	8	-3.536	-3.184	-0.379
C	6	1.123	-2.520	1.339
O	8	0.894	-2.297	0.205
O	8	1.373	-2.813	2.414
C	6	1.123	2.520	1.339
O	8	0.894	2.298	0.204
O	8	1.373	2.813	2.414
C	6	-2.752	2.361	-0.496
O	8	-3.537	3.183	-0.379
O	8	-1.952	1.516	-0.626
C	6	3.262	0.000	-1.775
O	8	2.164	0.000	-1.371
O	8	4.333	-0.000	-2.175

(b) M: S=2, 0.67 eV

Table S8: Cartesian coordinates of $HoO(CO_2)_6^+$ isomers.

1.2.6 $HoO(CO_2)_8^+$

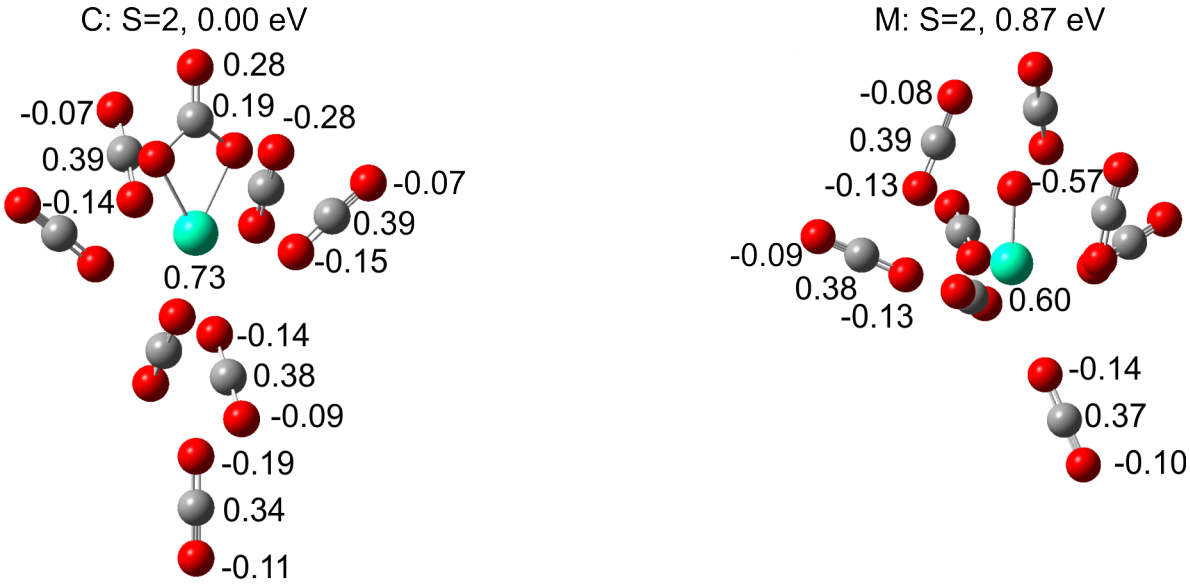

Figure S9: Structures and Hirshfeld charges of the molecularly bound isomers (M) and quasi-carbonate isomers (C) of $HoO(CO_2)_8^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.495	-0.000	-0.000
O	8	2.272	-0.022	1.100
C	6	0.692	-0.729	-3.252
O	8	-0.065	-0.571	-2.365
O	8	1.389	-0.892	-4.140
C	6	-2.476	2.136	-0.644
O	8	-1.605	1.376	-0.472
O	8	-3.323	2.886	-0.817
C	6	-2.475	-2.139	0.635
O	8	-1.605	-1.379	0.464
O	8	-3.322	-2.890	0.806
C	6	1.913	-3.131	0.296
O	8	2.814	-3.802	0.500
O	8	0.967	-2.468	0.085
C	6	3.072	0.001	0.005
O	8	4.262	0.002	0.008
O	8	2.277	0.023	-1.093
C	6	0.678	0.730	3.252
O	8	-0.075	0.572	2.362
O	8	1.372	0.895	4.143
C	6	1.911	3.132	-0.294
O	8	2.812	3.803	-0.495
O	8	0.965	2.468	-0.085
C	6	-5.740	-0.000	0.001
O	8	-6.890	-0.000	0.002
O	8	-4.575	-0.001	-0.000

(a) C: S=2, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.028	0.430	-0.177
O	8	0.091	-1.155	0.721
C	6	-3.406	0.699	0.944
O	8	-2.405	1.013	0.427
O	8	-4.393	0.421	1.451
C	6	-2.239	-1.008	-2.595
O	8	-1.508	-0.245	-2.093
O	8	-2.951	-1.738	-3.112
C	6	3.373	1.182	0.647
O	8	2.287	1.326	0.237
O	8	4.439	1.070	1.048
C	6	0.101	0.304	2.967
O	8	0.180	-0.513	3.763
O	8	0.018	1.212	2.221
C	6	2.541	-2.584	0.741
O	8	2.164	-3.460	1.383
O	8	2.973	-1.719	0.088
C	6	-2.135	-2.907	0.722
O	8	-2.703	-2.081	0.125
O	8	-1.620	-3.752	1.307
C	6	2.138	-0.946	-2.643
O	8	1.409	-0.178	-2.145
O	8	2.844	-1.684	-3.159
C	6	-0.316	4.307	-0.498
O	8	-0.232	3.142	-0.512
O	8	-0.397	5.450	-0.486

(b) M: S=2, 0.87 eV

Table S9: Cartesian coordinates of $HoO(CO_2)_8^+$ isomers.

2 Computational and Experimental Spectral Comparisons (UB3P86/Def2-TZVP)

Comparisons between theoretical spectra (from the UB3P86/Def2-TZVP level of theory) of and the experimental spectra of $Ho(CO_2)_n^+$ and $HoO(CO_2)_n^+$. The vertical dashed line indicates the vibrational frequency of the asymmetric stretch (υ_3) of free CO_2 at 2349 cm^{-1}.

2.1 $Ho(CO_2)_n^+$

2.1.1 $Ho(CO_2)^+$

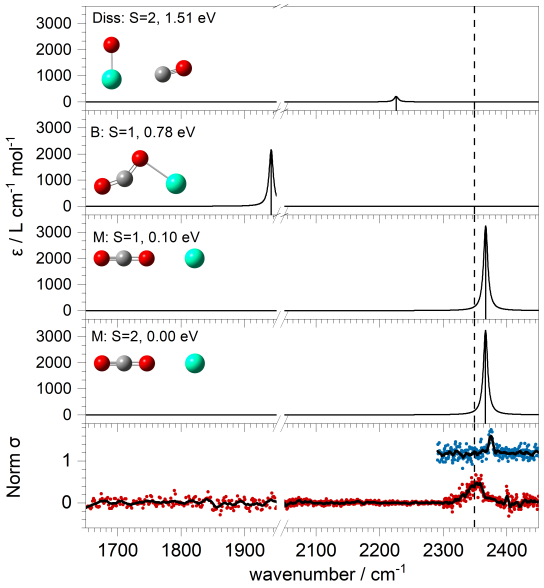

Figure S10: $Ho(CO_2)^+$ experimental and theoretical spectrum comparison.

2.1.2 $Ho(CO_2)_2^+$

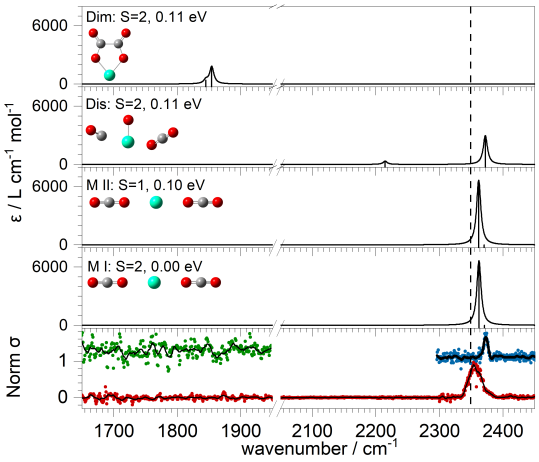

Figure S11: $Ho(CO_2)_2^+$ experimental and theoretical spectrum comparison.

2.1.3 $Ho(CO_2)_3^+$

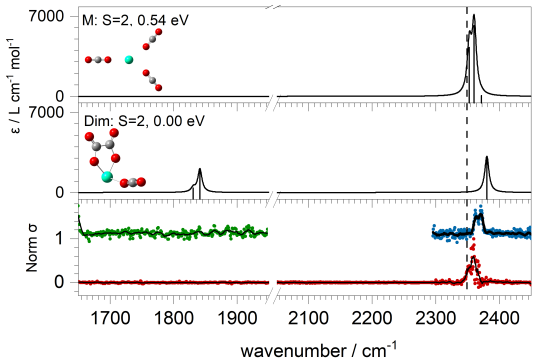

Figure S12: $Ho(CO_2)_3^+$ experimental and theoretical spectrum comparison.

2.2 $HoO(CO_2)_n^+$

2.2.1 $HoO(CO_2)^+$

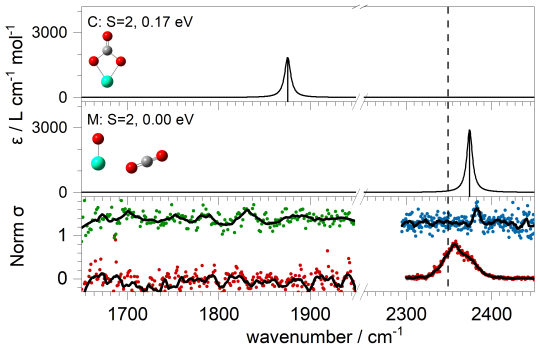

Figure S13: $HoO(CO_2)^+$ experimental and theoretical spectrum comparison.

2.2.2 $HoO(CO_2)_2^+$

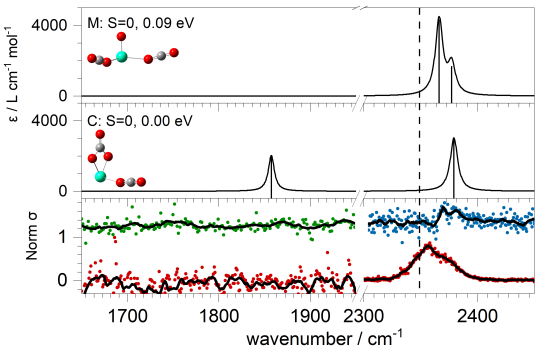

Figure S14: $HoO(CO_2)_2^+$ experimental and theoretical spectrum comparison.

2.2.3 $HoO(CO_2)_3^+$

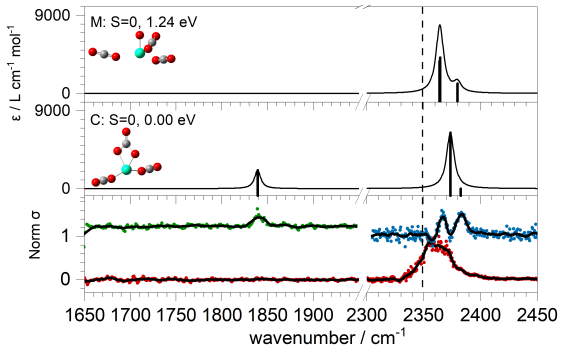

Figure S15: $HoO(CO_2)_3^+$ experimental and theoretical spectrum comparison.

2.2.4 $HoO(CO_2)_4^+$

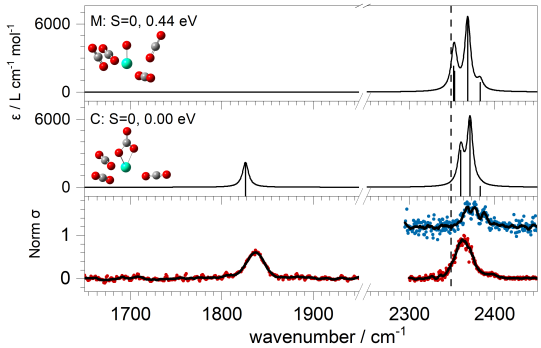

Figure S16: $HoO(CO_2)_4^+$ experimental and theoretical spectrum comparison.

2.2.5 $HoO(CO_2)_5^+$

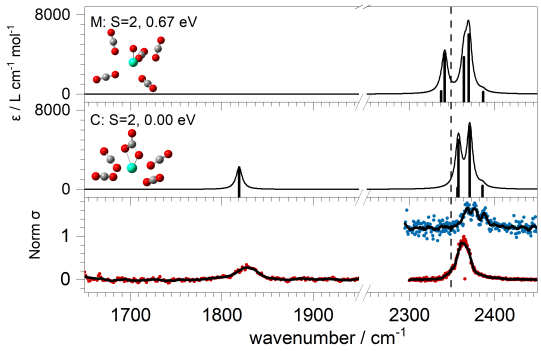

Figure S17: $HoO(CO_2)_5^+$ experimental and theoretical spectrum comparison.

2.2.6 $HoO(CO_2)_8^+$

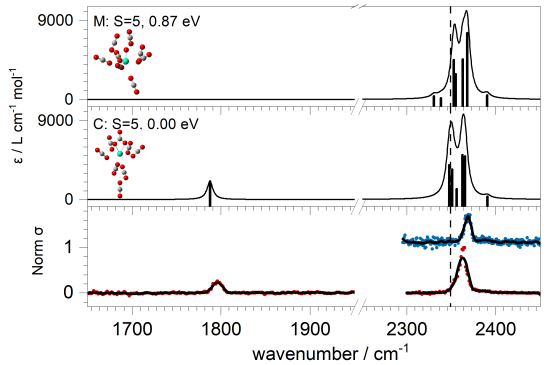

Figure S18: $HoO(CO_2)_8^+$ experimental and theoretical spectrum comparison.

2.3 Ar Tagged Spectra

2.3.1 $HoO(CO_2)_3Ar^+$

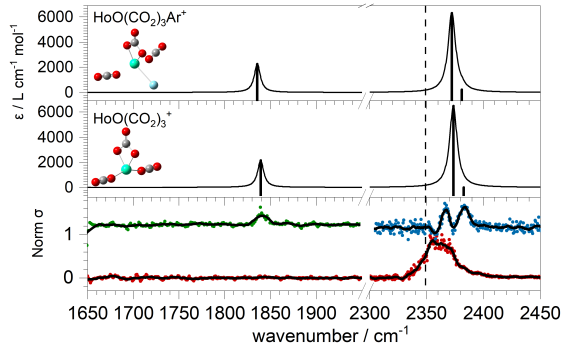

Figure S19: $HoO(CO_2)_3Ar^+$ experimental and theoretical spectrum comparison.

3 Computational Structures (UB3P86/SDD)

The initial potential energy surface search was carried out with an SDD basis set which were then re-optimised with a the larger Def2-TZVP basis set as shown in the previous sections. The structures and coordinates of the main structural isomers observed for Ho^+ and HoO^+ reacting with CO_2 calculated with the Gaussian suite of programs at the UB3P86/SDD level of theory are given below for completeness.

3.1 $Ho(CO_2)_n^+$

3.1.1 $Ho(CO_2)^+$

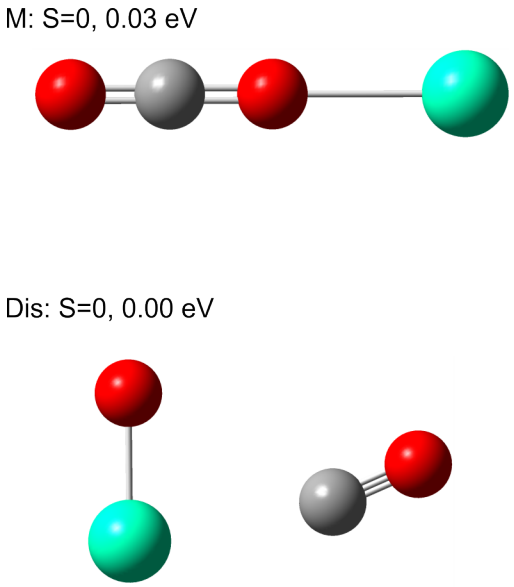

Figure S20: Structures and Mulliken charges of the molecularly bound isomers (M) and dissociative isomers (Diss) of $Ho(CO_2)^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.537	-0.164	0.000
C	6	2.006	-0.256	0.001
O	8	3.135	-0.039	0.000
O	8	-0.144	1.609	0.000

(a) M: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.000	-0.855
C	6	0.000	0.000	2.620
O	8	0.000	0.000	1.412
O	8	0.000	0.000	3.785

(b) Dis: S=0, 0.03 eV

Table S20: Cartesian Coordinates of $Ho(CO_2)^+$ isomers.

3.1.2 $Ho(CO_2)_2^+$

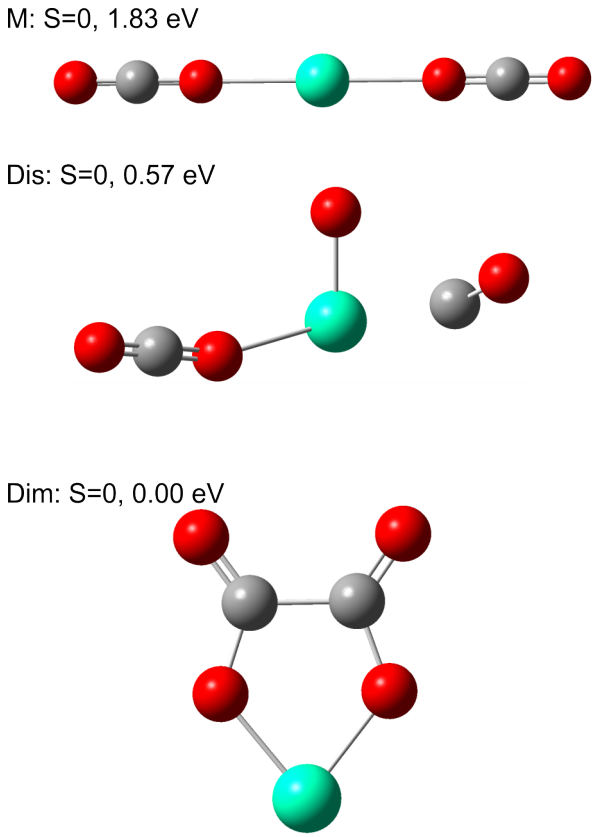

Figure S21: Structures of the molecularly bound isomer (M), dissociative isomer (Diss) and dimerised isomer (Dim) of $Ho(CO_2)_2^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	1.099	0.000	0.000
C	6	-1.802	0.792	0.000
O	8	-0.465	1.246	0.000
O	8	-2.786	1.491	0.000
C	6	-1.802	-0.792	0.000
O	8	-0.465	-1.246	0.000
O	8	-2.786	-1.491	0.000

(a) Dim: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.385	0.596	-0.119
C	6	1.960	-1.365	-0.331
O	8	2.648	-2.265	-0.127
O	8	0.649	0.032	1.606
C	6	-2.915	-0.638	-0.076
O	8	-1.844	-0.150	-0.326
O	8	-3.961	-1.109	0.152

(b) Dis S=0, 0.57 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.000	0.000
C	6	-2.816	1.646	-1.290
O	8	-1.850	1.081	-0.848
O	8	-3.755	2.193	-1.719
C	6	2.817	-1.644	1.291
O	8	1.850	-1.081	0.848
O	8	3.755	-2.192	1.720

(c) M: S=0, 1.83 eV

Table S21: Cartesian Coordinates of $Ho(CO_2)_2^+$ isomers.

3.1.3 $Ho(CO_2)_3^+$

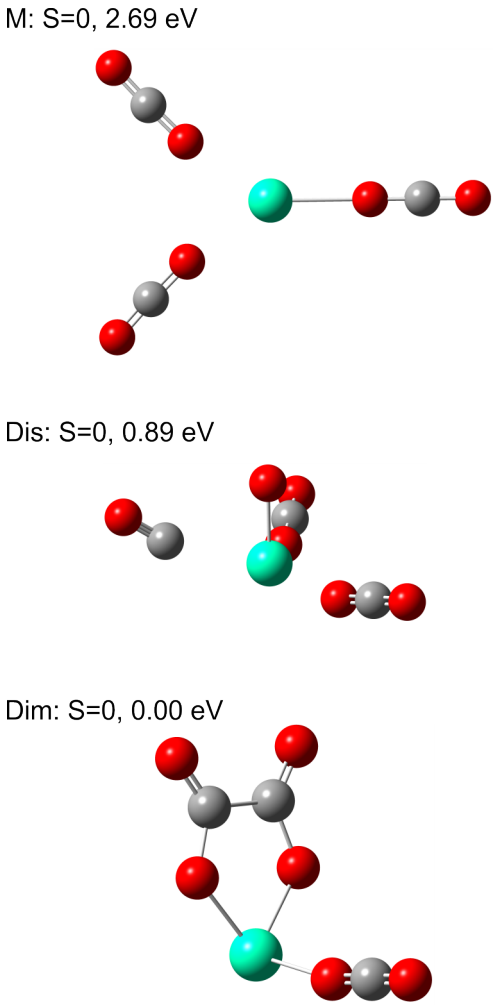

Figure S22: Structures of the molecularly bound isomer (M), dissociative isomer (Diss) and dimerised isomer (Dim) of $Ho(CO_2)_3^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.312	-0.940	-0.001
C	6	2.019	0.794	-0.792
O	8	0.959	0.001	-1.253
O	8	2.810	1.394	-1.484
C	6	2.020	0.792	0.793
O	8	0.961	-0.003	1.253
O	8	2.812	1.390	1.485
C	6	-2.900	1.433	0.001
O	8	-3.656	2.321	0.002
O	8	-2.126	0.508	0.001

(a) Dim: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.101	-0.245
C	6	-3.242	-1.296	0.090
O	8	-2.163	-0.905	-0.267
O	8	-4.296	-1.683	0.425
C	6	3.242	-1.297	0.090
O	8	2.163	-0.905	-0.266
O	8	4.296	-1.683	0.425
C	6	0.001	2.609	-0.168
O	8	-0.001	0.613	1.533
O	8	0.001	3.705	0.194

(b) Dis: S=0, 0.89 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.337	0.000	-0.001
C	6	3.841	0.000	0.001
O	8	2.640	0.000	0.000
O	8	5.011	0.000	0.002
C	6	-2.448	-2.237	0.001
O	8	-1.602	-1.384	0.000
O	8	-3.238	-3.106	0.001
C	6	-2.449	2.237	0.001
O	8	-3.238	3.105	0.001
O	8	-1.602	1.384	0.000

(c) M: S=0, 2.69 eV

Table S22: Cartesian Coordinates of $Ho(CO_2)_3^+$ isomers.

3.2 $HoO(CO_2)_n^+$

3.2.1 $HoO(CO_2)^+$

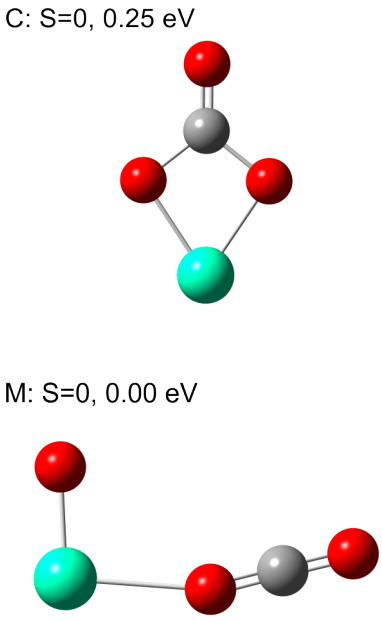

Figure S23: Structures of the molecularly bound isomer (M) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.787	-0.177	0.000
O	8	-0.868	1.632	0.000
C	6	2.723	-0.046	0.000
O	8	1.557	-0.347	0.001
O	8	3.859	0.230	0.000

(a) M: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.752	0.000	0.000
O	8	0.942	-1.121	0.000
C	6	1.838	0.001	0.000
O	8	0.944	1.121	0.000
O	8	3.036	-0.001	0.000

(b) C: S=0, 0.25 eV

Table S23: Cartesian Coordinates of $HoO(CO_2)^+$ isomers.

3.2.2 $HoO(CO_2)_2^+$

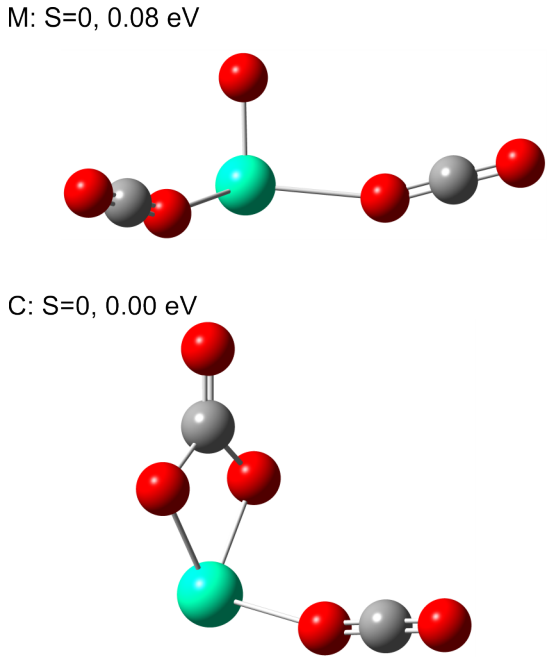

Figure S24: Structures of the molecularly bound isomer (M) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_2^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.256	-0.805	0.000
O	8	1.156	0.653	1.124
C	6	1.611	1.405	0.000
O	8	1.158	0.652	-1.124
O	8	2.226	2.439	0.000
C	6	-2.878	0.721	0.000
O	8	-1.897	0.018	0.000
O	8	-3.834	1.388	0.000

(a) C: S=0, E_{rel}=0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	-0.652	-0.158
O	8	0.004	-0.699	1.665
C	6	-3.045	1.123	-0.053
O	8	-2.038	0.545	-0.366
O	8	-4.028	1.688	0.235
C	6	3.043	1.125	-0.055
O	8	4.026	1.688	0.237
O	8	2.036	0.548	-0.370

(b) M: S=0, E_{rel}=0.08 eV

Table S24: Cartesian Coordinates of $HoO(CO_2)_2^+$ isomers.

3.2.3 $HoO(CO_2)_3^+$

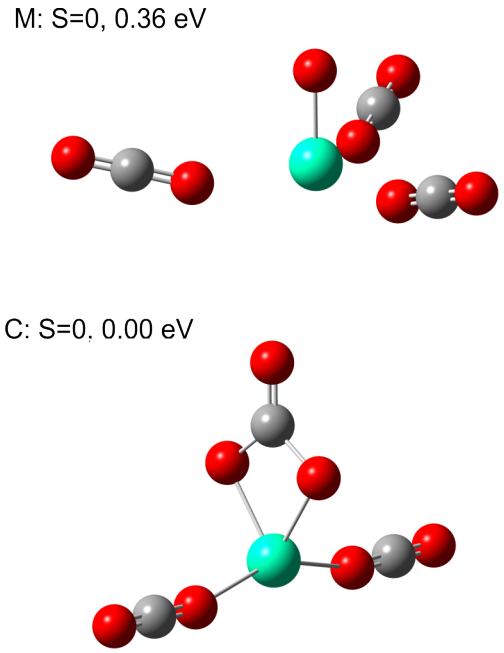

Figure S25: Structures of the molecularly bound isomer (M) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_3^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.001	-0.366	0.001
O	8	0.001	1.363	-1.127
C	6	3.492	-0.865	-0.001
O	8	2.287	-0.887	0.000
O	8	4.659	-0.855	-0.002
C	6	-3.493	-0.862	0.000
O	8	-2.289	-0.884	0.001
O	8	-4.661	-0.852	-0.002
C	6	0.003	2.230	0.000
O	8	0.002	1.364	1.127
O	8	0.004	3.438	-0.001

(a) C: S=0, E_{rel}=0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.002	-0.001	-0.152
O	8	0.000	0.000	1.684
C	6	1.399	3.247	-0.042
O	8	0.941	2.188	-0.376
O	8	1.846	4.284	0.268
C	6	2.121	-2.830	-0.041
O	8	1.427	-1.907	-0.375
O	8	2.800	-3.732	0.268
C	6	-3.515	-0.415	-0.041
O	8	-4.637	-0.548	0.268
O	8	-2.368	-0.280	-0.374

(b) M: S=0, E_{rel}=0.36 eV

Table S25: Cartesian Coordinates of $HoO(CO_2)_3^+$ isomers

3.2.4 $HoO(CO_2)_4^+$

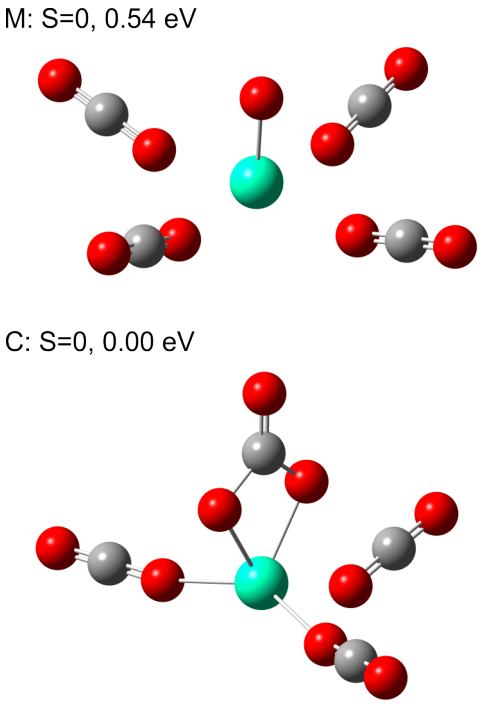

Figure S26: Structures of the molecularly bound isomer (M) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_4^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.002	-0.247	-0.338
O	8	0.002	-1.450	1.361
C	6	-3.436	-0.956	-0.779
O	8	-2.273	-0.654	-0.839
O	8	-4.567	-1.246	-0.733
C	6	3.428	-0.959	-0.792
O	8	2.265	-0.656	-0.847
O	8	4.560	-1.250	-0.751
C	6	0.000	3.177	-0.308
O	8	0.006	4.237	0.187
O	8	-0.005	2.100	-0.853
C	6	0.011	-0.383	2.290
O	8	0.008	0.785	1.496
O	8	0.020	-0.456	3.498

(a) C: S=0, E_{rel}=0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.002	0.002	-0.149
O	8	0.003	0.000	1.696
C	6	-3.567	-0.081	-0.048
O	8	-2.415	-0.054	-0.379
O	8	-4.699	-0.108	0.262
C	6	0.072	-3.563	-0.019
O	8	0.049	-2.417	-0.369
O	8	0.095	-4.689	0.309
C	6	3.570	0.073	-0.048
O	8	2.419	0.050	-0.380
O	8	4.702	0.095	0.262
C	6	-0.082	3.567	-0.018
O	8	-0.108	4.694	0.308
O	8	-0.055	2.420	-0.366

(b) M: S=0, E_{rel}=0.54 eV

Table S26: Cartesian Coordinates of $HoO(CO_2)_4^+$ isomers.

3.2.5 $HoO(CO_2)_5^+$

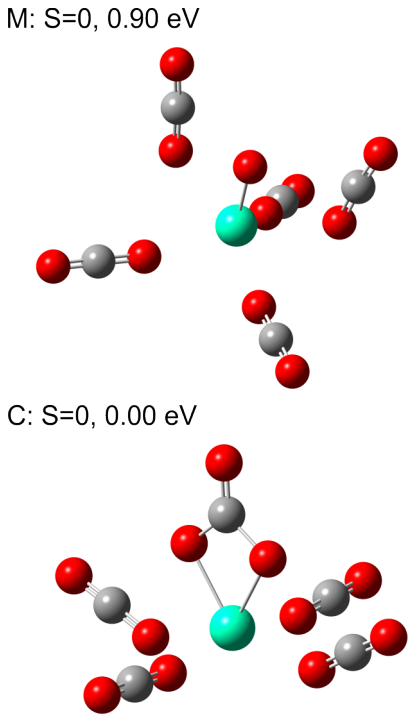

Figure S27: Structures of the molecularly bound isomer (M) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_5^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	-0.001	0.327
O	8	0.007	1.116	-1.470
C	6	0.018	3.414	0.349
O	8	0.012	2.353	0.924
O	8	0.024	4.461	-0.172
C	6	3.541	-0.017	0.625
O	8	2.343	-0.012	0.714
O	8	4.709	-0.021	0.551
C	6	0.001	0.001	-2.330
O	8	-0.006	-1.115	-1.472
O	8	0.002	0.001	-3.543
C	6	-3.541	0.020	0.624
O	8	-4.709	0.027	0.549
O	8	-2.344	0.012	0.713
C	6	-0.018	-3.416	0.348
O	8	-0.023	-4.464	-0.172
O	8	-0.013	-2.355	0.923

(a) C: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.049	0.000	0.166
O	8	0.123	-0.001	-1.700
C	6	-2.734	2.404	0.488
O	8	-1.894	1.553	0.552
O	8	-3.561	3.236	0.435
C	6	1.213	2.445	-1.462
O	8	0.998	2.218	-0.292
O	8	1.462	2.759	-2.564
C	6	1.213	-2.446	-1.461
O	8	0.998	-2.219	-0.291
O	8	1.462	-2.762	-2.562
C	6	-2.734	-2.404	0.489
O	8	-3.560	-3.236	0.435
O	8	-1.894	-1.552	0.553
C	6	3.121	0.001	2.001
O	8	2.039	0.000	1.486
O	8	4.177	0.001	2.513

(b) M: S=0, 0.90 eV

Table S27: Cartesian Coordinates of $HoO(CO_2)_5^+$ isomers.

3.2.6 $HoO(CO_2)_6^+$

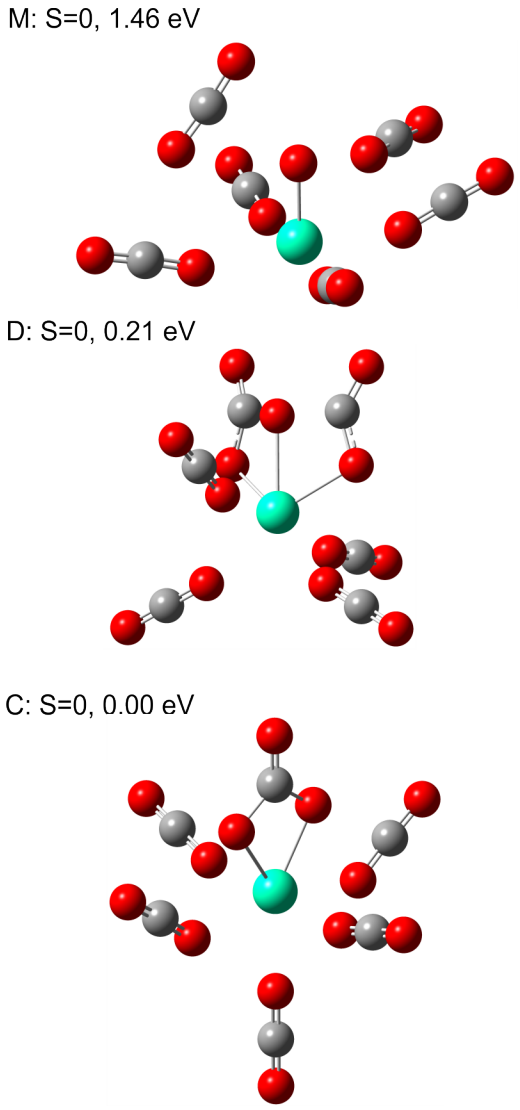

Figure S28: Structures of the molecularly bound isomer (M), $\{(CO_2)O(CO_2)\}$ type isomer (D) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_6^+$.

Table S28: Cartesian Coordinates of $HoO(CO_2)_4^+$ isomers.

Atom	Atomic Number	X	Y	Z
Ho	67	0.001	-0.098	0.000
C	6	-0.007	0.217	3.340
O	8	-0.013	0.907	4.286
O	8	0.000	-0.552	2.409
O	8	-0.009	1.733	-1.107
C	6	-0.017	2.581	0.012
O	8	-0.014	1.724	1.123
O	8	-0.024	3.797	0.017
C	6	3.527	0.200	0.004
O	8	2.387	-0.176	0.002
O	8	4.644	0.551	0.006
C	6	0.023	-3.795	-0.014
O	8	0.016	-2.596	-0.010
O	8	0.031	-4.969	-0.018
C	6	-3.529	0.158	-0.007
O	8	-4.650	0.495	-0.009
O	8	-2.385	-0.205	-0.006
C	6	0.005	0.245	-3.338
O	8	0.002	0.943	-4.278
O	8	0.008	-0.531	-2.412

(a) C: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	0.064	-0.102	0.000
C	6	1.603	-1.788	-2.782
O	8	1.991	-2.148	-3.827
O	8	1.213	-1.428	-1.705
O	8	-1.865	1.117	0.003
C	6	-2.676	-2.297	-0.004
O	8	-1.567	-1.833	-0.003
O	8	-3.747	-2.767	-0.005
C	6	1.606	-1.804	2.771
O	8	1.215	-1.437	1.697
O	8	1.994	-2.171	3.814
C	6	2.810	2.146	0.004
O	8	2.060	1.209	0.002
O	8	3.554	3.050	0.007
C	6	-1.575	1.763	-1.383
O	8	-2.270	2.630	-1.838
O	8	-0.497	1.091	-1.769
C	6	-1.573	1.758	1.391
O	8	-2.268	2.623	1.851
O	8	-0.495	1.084	1.774

(b) D: S=0, 0.21 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.095	0.426	-0.697
O	8	0.137	-0.197	1.039
C	6	-3.347	-0.947	-0.749
O	8	-2.327	-0.381	-1.035
O	8	-4.364	-1.484	-0.527
C	6	1.086	-2.787	-1.624
O	8	0.727	-1.641	-1.636
O	8	1.432	-3.907	-1.648
C	6	3.089	1.878	-0.178
O	8	2.063	1.507	-0.681
O	8	4.094	2.273	0.276
C	6	-1.519	3.531	0.412
O	8	-1.962	4.463	0.969
O	8	-1.067	2.584	-0.168
C	6	2.468	-1.331	1.437
O	8	2.037	-2.410	1.176
O	8	3.004	-0.288	1.644
C	6	-1.541	-1.560	2.515
O	8	-2.346	-1.509	1.631
O	8	-0.813	-1.662	3.441

(c) M: S=0, 1.46 eV

3.2.7 $HoO(CO_2)_7^+$

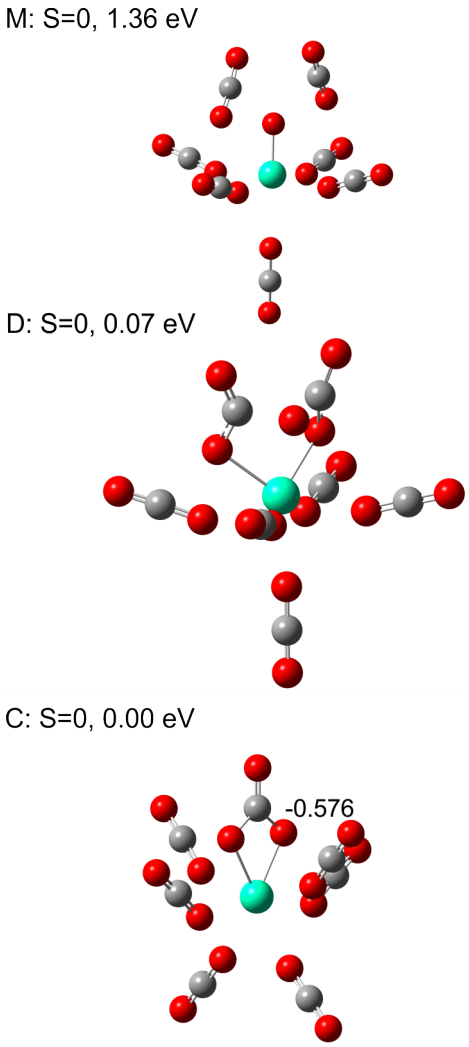

Figure S29: Structures of the molecularly bound isomer (M), $\{(CO_2)O(CO_2)\}$ type isomer (D) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_7^+$.

Atom	Atomic Number	X	Y	Z
Ho	67	-0.124	0.000	0.000
O	8	1.723	-0.001	-1.120
C	6	0.255	0.001	3.327
O	8	-0.536	0.000	2.414
O	8	0.965	0.001	4.258
C	6	-3.008	-2.292	0.002
O	8	-2.168	-1.440	0.002
O	8	-3.837	-3.125	0.002
C	6	-3.011	2.288	0.009
O	8	-2.170	1.437	0.006
O	8	-3.842	3.118	0.011
C	6	1.324	3.218	-0.003
O	8	2.174	4.026	-0.004
O	8	0.432	2.413	-0.002
C	6	2.570	0.000	-0.007
O	8	3.790	0.000	-0.010
O	8	1.729	0.002	1.111
C	6	0.237	0.002	-3.329
O	8	-0.548	0.001	-2.412
O	8	0.942	0.003	-4.264
C	6	1.328	-3.216	0.001
O	8	2.179	-4.023	-0.001
O	8	0.434	-2.413	0.004

(a) C: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.153	-0.051	0.052
C	6	-3.299	-0.639	-1.702
O	8	-4.363	-0.822	-2.161
O	8	-2.211	-0.452	-1.238
O	8	2.181	0.363	0.185
C	6	0.435	2.635	-2.245
O	8	0.015	1.670	-1.669
O	8	0.832	3.576	-2.821
C	6	-1.974	2.109	1.994
O	8	-1.923	1.207	1.197
O	8	-2.071	2.983	2.768
C	6	-1.054	-2.690	2.035
O	8	-1.342	-1.764	1.319
O	8	-0.820	-3.597	2.737
C	6	2.445	-0.997	0.866
O	8	3.560	-1.354	1.147
O	8	1.233	-1.529	0.957
C	6	1.974	1.563	1.129
O	8	2.902	2.210	1.541
O	8	0.653	1.626	1.253
C	6	1.372	-1.888	-2.621
O	8	0.628	-1.249	-1.929
O	8	2.084	-2.511	-3.312

(b) D: S=0, 0.21 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.382	0.001	-0.001
O	8	1.495	-0.004	0.001
C	6	-0.360	-3.405	-0.953
O	8	-0.709	-2.291	-0.670
O	8	-0.089	-4.507	-1.245
C	6	-0.194	0.963	-3.435
O	8	-0.569	0.658	-2.339
O	8	0.158	1.264	-4.513
C	6	-0.347	3.408	0.951
O	8	-0.700	2.295	0.667
O	8	-0.071	4.508	1.244
C	6	-0.200	-0.960	3.432
O	8	0.153	-1.262	4.510
O	8	-0.576	-0.653	2.336
C	6	3.033	2.121	-0.032
O	8	4.029	1.556	-0.326
O	8	2.086	2.798	0.253
C	6	3.024	-2.135	0.037
O	8	2.074	-2.808	-0.249
O	8	4.021	-1.574	0.333
C	6	-4.305	0.005	0.003
O	8	-3.107	0.004	0.001
O	8	-5.482	0.007	0.005

(c) M S=0, 1.36 eV

Table S29: Cartesian Coordinates of $HoO(CO_2)_7^+$ isomers.

3.2.8 $HoO(CO_2)_8^+$

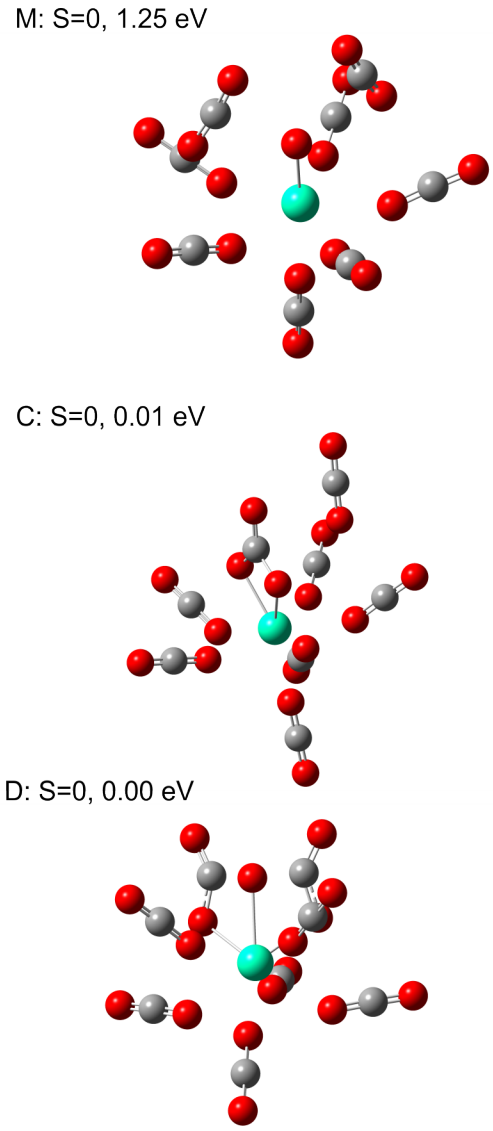

Figure S30: Structures of the molecularly bound isomer (M), $\{(CO_2)O(CO_2)\}$ type isomer (D) and $\{CO_3\}$ type isomer (C) of $HoO(CO_2)_8^+$.

Table S30: Cartesian Coordinates of $HoO(CO_2)_8^+$ isomers

Atom	Atomic Number	X	Y	Z
Ho	67	0.000	0.016	0.180
C	6	-0.002	2.175	3.143
O	8	-0.002	2.793	4.142
O	8	-0.001	1.551	2.124
O	8	-0.002	-0.075	-2.187
C	6	2.169	2.549	-1.198
O	8	1.451	1.911	-0.482
O	8	2.873	3.190	-1.884
C	6	3.122	-0.863	1.430
O	8	2.061	-0.318	1.582
O	8	4.167	-1.386	1.322
C	6	0.005	-3.477	0.884
O	8	0.004	-2.293	1.073
O	8	0.007	-4.639	0.721
C	6	-1.313	-0.887	-2.234
O	8	-1.808	-1.221	-3.282
O	8	-1.639	-1.009	-0.957
C	6	1.312	-0.883	-2.236
O	8	1.806	-1.216	-3.285
O	8	1.640	-1.005	-0.959
C	6	-3.118	-0.872	1.433
O	8	-4.161	-1.397	1.324
O	8	-2.058	-0.323	1.584
C	6	-2.176	2.544	-1.196
O	8	-2.883	3.183	-1.882
O	8	-1.456	1.907	-0.480

(a) D: S=0, 0.00 eV

Atom	Atomic Number	X	Y	Z
Ho	67	-0.504	0.000	-0.155
C	6	1.928	-2.043	-1.684
O	8	2.896	-2.696	-1.803
O	8	0.922	-1.396	-1.595
O	8	0.605	-1.120	1.318
C	6	1.215	-0.004	1.886
O	8	0.599	1.114	1.327
O	8	2.160	-0.005	2.664
C	6	-2.974	0.001	2.435
O	8	-2.393	-0.001	1.387
O	8	-3.558	0.004	3.452
C	6	-2.938	0.005	-2.916
O	8	-2.141	0.004	-2.023
O	8	-3.719	0.005	-3.792
C	6	-1.060	-3.262	0.683
O	8	-0.790	-4.194	1.343
O	8	-1.375	-2.337	-0.020
C	6	-1.052	3.259	0.696
O	8	-0.778	4.187	1.360
O	8	-1.371	2.339	-0.012
C	6	4.199	0.002	0.586
O	8	3.311	0.005	-0.225
O	8	5.100	-0.001	1.345
C	6	1.928	2.041	-1.695
O	8	0.921	1.398	-1.592
O	8	2.896	2.691	-1.828

(b) C: S=0, 0.01 eV

Table S30: Cartesian Coordinates of $HoO(CO_2)_8^+$ isomers II

Atom	Atomic Number	X	Y	Z
Ho	67	-0.002	0.414	0.066
O	8	0.008	-1.452	0.347
C	6	-3.459	0.483	0.995
O	8	-2.334	0.834	0.775
O	8	-4.570	0.181	1.226
C	6	-2.174	-0.491	-2.600
O	8	-1.466	0.199	-1.923
O	8	-2.863	-1.141	-3.296
C	6	3.454	0.518	0.999
O	8	2.326	0.857	0.778
O	8	4.568	0.227	1.232
C	6	-0.006	0.812	3.672
O	8	-0.007	0.667	4.839
O	8	-0.005	0.970	2.487
C	6	2.132	-2.850	0.196
O	8	1.669	-3.865	0.581
O	8	2.737	-1.890	-0.207
C	6	-2.101	-2.871	0.199
O	8	-2.716	-1.919	-0.206
O	8	-1.628	-3.881	0.586
C	6	2.184	-0.463	-2.599
O	8	1.467	0.216	-1.922
O	8	2.882	-1.103	-3.295
C	6	-0.029	4.107	-1.167
O	8	-0.019	2.982	-0.758
O	8	-0.038	5.213	-1.570

(a) M: S=0, 1.25 eV

4 Computational and Experimental Spectral Comparisons (UB3P86/SDD)

The initial potential energy surface search was carried out with an SDD basis set which were then re-optimised with a the larger Def2-TZVP basis set as shown in the previous sections. Comparisons between theoretical spectra (from the UB3P86/SDD level of theory) and the experimental spectra of $Ho(CO_2)_n^+$ and $HoO(CO_2)_n^+$ isomers are given below for completeness. The vertical dashed line indicates the vibrational frequency of the asymmetric stretch (v_3) of free CO_2 at 2349 cm^{-1}.

4.1 $Ho(CO_2)_n^+$

4.1.1 $Ho(CO_2)^+$

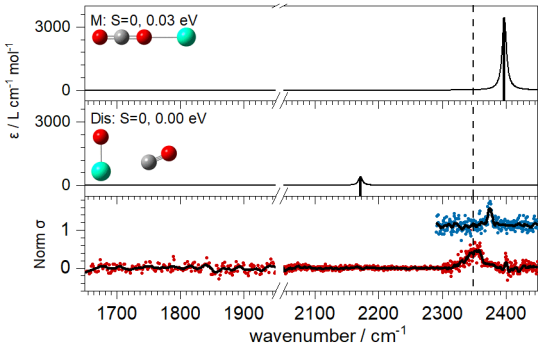

Figure S31: $Ho(CO_2)^+$ experimental and theoretical spectrum comparison.

4.1.2 $Ho(CO_2)_2^+$

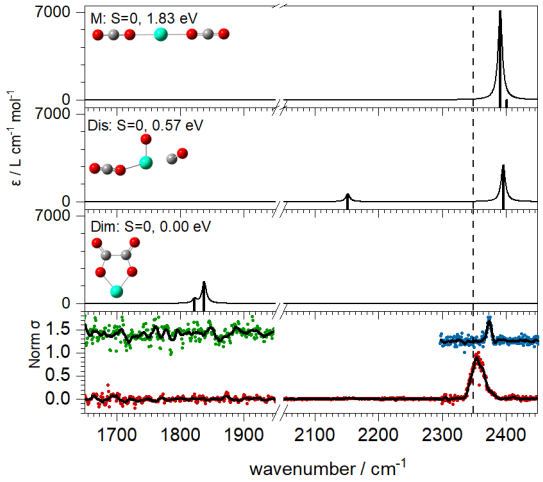

Figure S32: $Ho(CO_2)_2^+$ experimental and theoretical spectrum comparison.

4.1.3 $Ho(CO_2)_3^+$

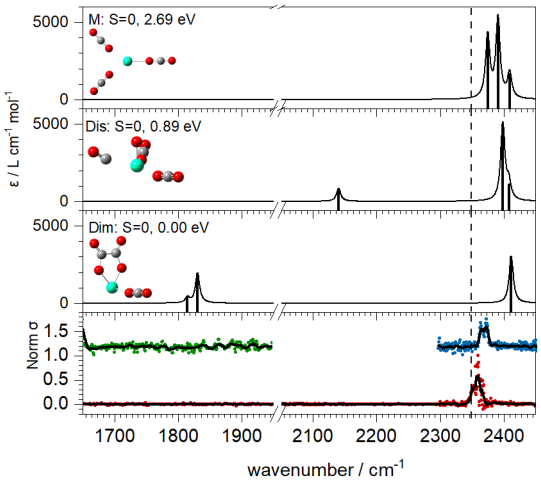

Figure S33: $Ho(CO_2)_3^+$ experimental and theoretical spectrum comparison.

4.2 $HoO(CO_2)_n^+$

4.2.1 $HoO(CO_2)^+$

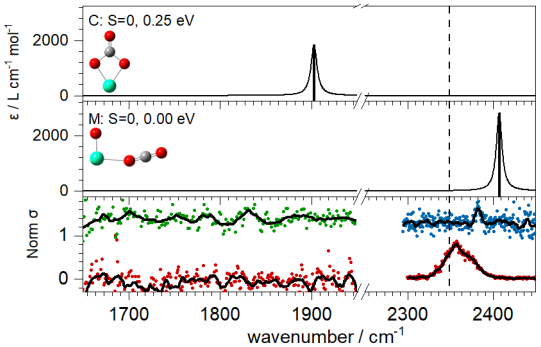

Figure S34: $HoO(CO_2)^+$ experimental and theoretical spectrum comparison.

4.2.2 $HoO(CO_2)_2^+$

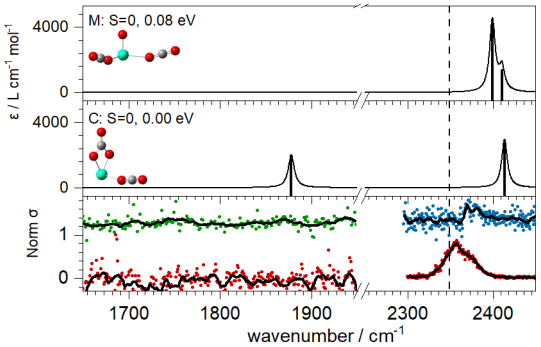

Figure S35: $HoO(CO_2)_2^+$ experimental and theoretical spectrum comparison.

4.2.3 $HoO(CO_2)_3^+$

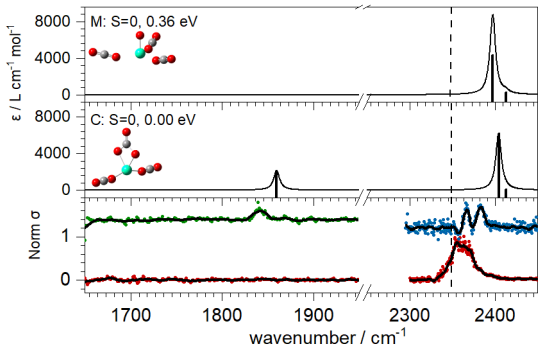

Figure S36: $HoO(CO_2)_3^+$ experimental and theoretical spectrum comparison.

4.2.4 $HoO(CO_2)_4^+$

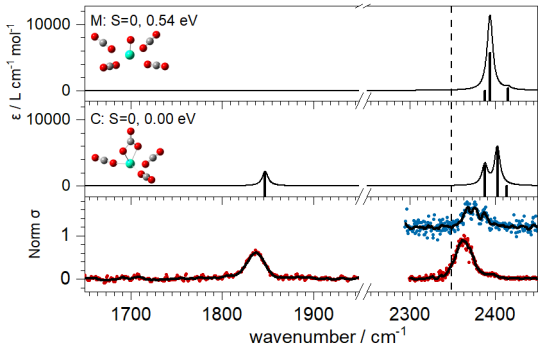

Figure S37: $HoO(CO_2)_4^+$ experimental and theoretical spectrum comparison.

4.2.5 $HoO(CO_2)_5^+$

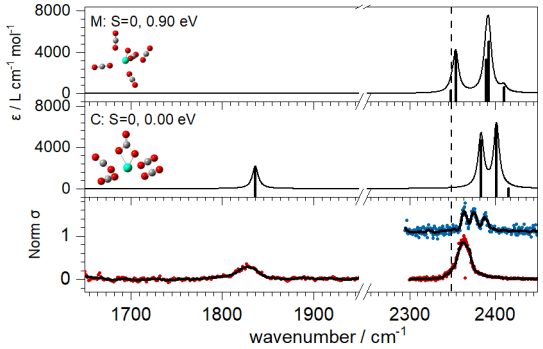

Figure S38: $HoO(CO_2)_5^+$ experimental and theoretical spectrum comparison.

4.2.6 $HoO(CO_2)_6^+$

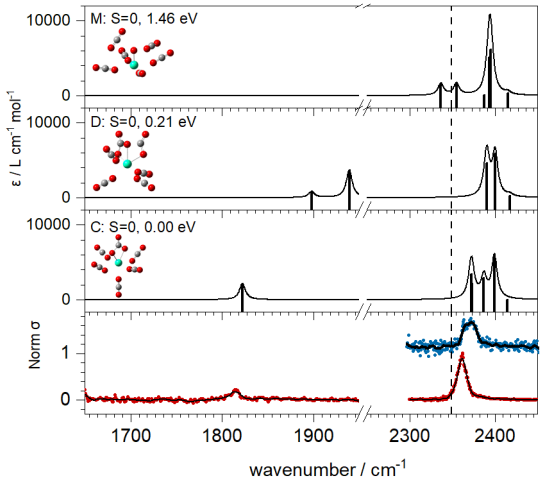

Figure S39: $HoO(CO_2)_6^+$ experimental and theoretical spectrum comparison.

4.2.7 $HoO(CO_2)_7^+$

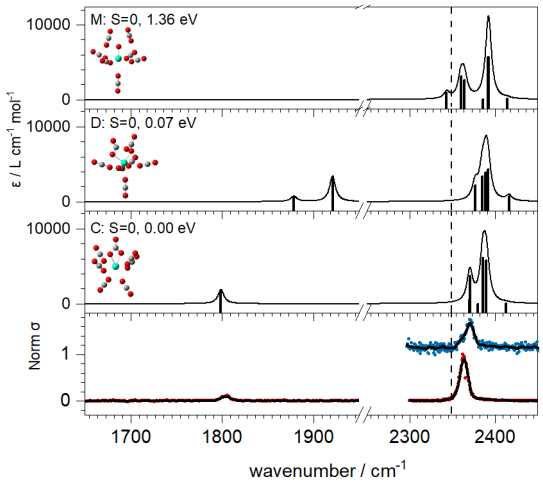

Figure S40: $HoO(CO_2)_7^+$ experimental and theoretical spectrum comparison.

4.2.8 $HoO(CO_2)_8^+$

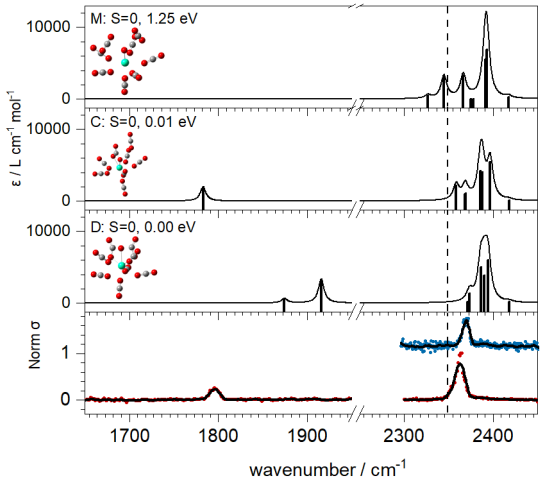

Figure S41: $HoO(CO_2)_8^+$ experimental and theoretical spectrum comparison.

5 Potential Energy Surfaces (UB3P86/SDD)

Potential energy surfaces for both $Ho(CO_2)^+$ and $Ho(CO_2)_2^+$ calcualted at the UB3P86/SDD level of theory are shown in Figures S43 and S43 for completeness. In both cases the possible route for the formation of HoO^+ ions are illustrated. For $Ho(CO_2)_2^+$ (Figure S43), the route and transition state for formation of the dimerised form is illustrated.

5.1 $Ho(CO_2)^+$

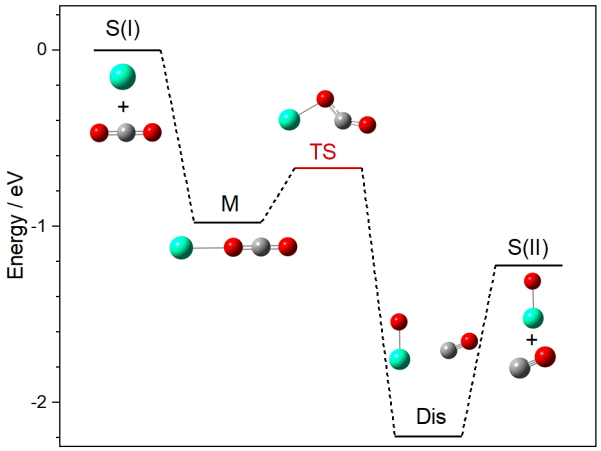

Figure S42: Potential energy surface for $Ho(CO_2)^+$ generated at the UB3P86/SDD + WBPS level of theory showing the relative energies of $HoO(CO)^+$ and $Ho(CO_2)^+$ structure. The surfaces show the transformation between species.

5.2 $Ho(CO_2)_2^+$

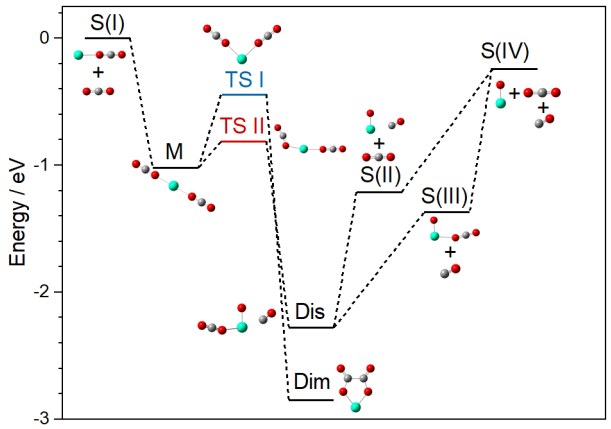

Figure S43: Potential energy surface for $Ho(CO_2)_2^+$ generated at the UB3P86/SDD + WBPS level of theory showing the relative energies of $HoO(CO)(CO_2)^+$, $Ho(CO_2)_2^+$ and $HoO(CO_2)^+$ structures. The surfaces show the transformation between species.