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

Supporting Information

for

Carbon Monoxide Protonation in Condensed Phases and Bonding to Surface Superacidic Brønsted Centers

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1. Supplemental Figures

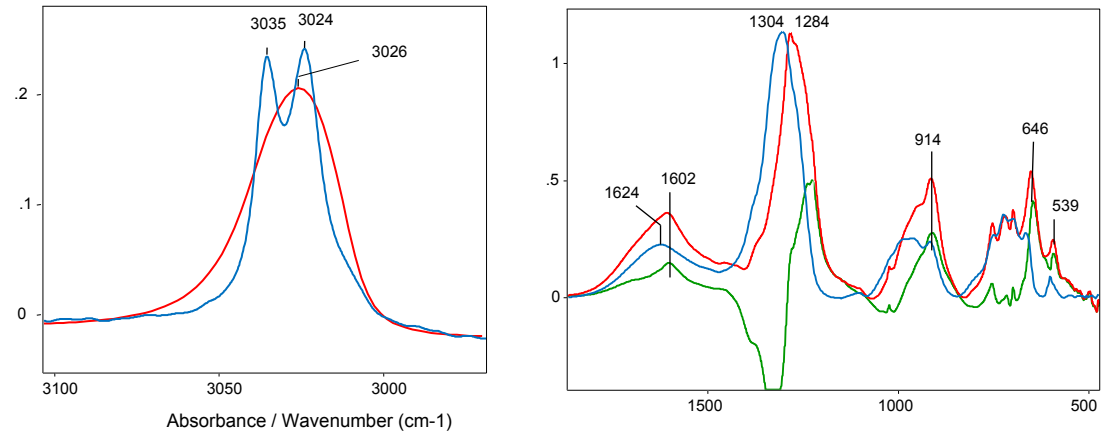

Figure S1. IR spectra of the H{F_{11}} acid: a powder precipitated from liquid HCl with mostly crystalline structure (red) and the sublimed film, mostly amorphous (blue). Their difference (green) shows that the bands at 1624/1602, 914 and 646 cm^{-1} corresponding to bridged hydrogen vibrations differ substantially. νCH frequencies of the {F_{11}^-} anion (left) at 3000–3500 cm^{-1} also differ, pointing to their differences in bonding with a proton. The B–B and B–F stretches of the {F_{11}^-} anion are ~1280–1300 cm^{-1}.

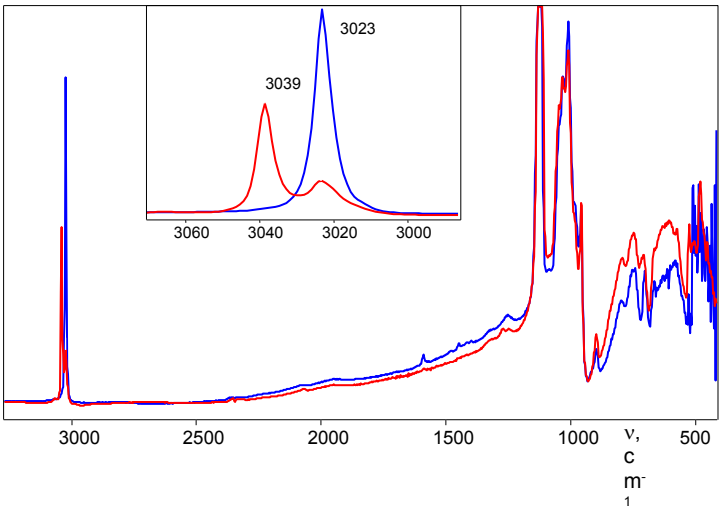

Figure S2. IR spectra of the H{Cl_{11}} acid: red is the powder precipitated from liquid HCl and mostly crystalline, studied by X-ray analysis; blue is sublimed film. νCH frequencies of the {Cl_{11}}$^-$ anion are shown in the inset; (b) the B–B and B–Cl stretches of the {Cl_{11}}$^-$ anion are in the range 1125–960 cm^{-1}, and strong broad adsorption corresponding to H atom vibrations is at 1250–400 cm^{-1}.

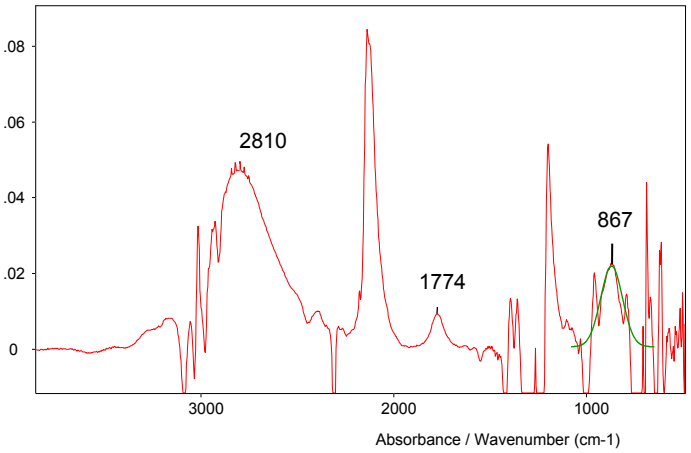

Figure S3. An IR spectrum of the equilibrium mixture of IIb ↔ OIIb, which was consumed within the first minute of the reaction with CH_3Cl. The spectrum was obtained as a difference of the spectra of compounds II and OII before and 1 min after injection of gaseous CH_3Cl. Subtraction was carried out with full compensation of the absorption of the $\{F_{11}^-\}$ anion and methyl chloride. Negative absorption corresponds to the formed CH_3CO^+.

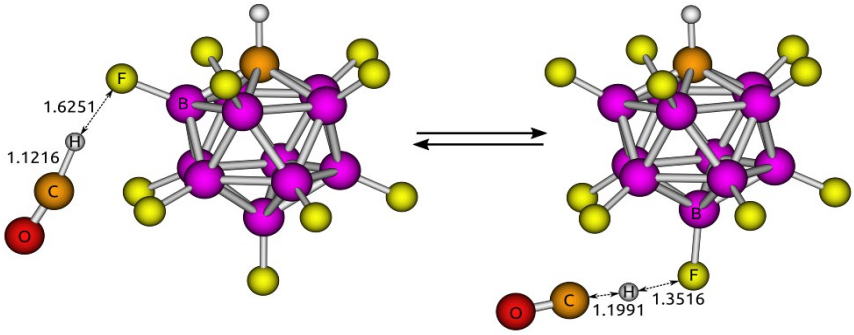

Figure S4. Optimized structures of OC·H$\{F_{11}\}$ isomers “a” (left) and “c” (right) at the B3LYP/6-311g(df,p) level of theory.

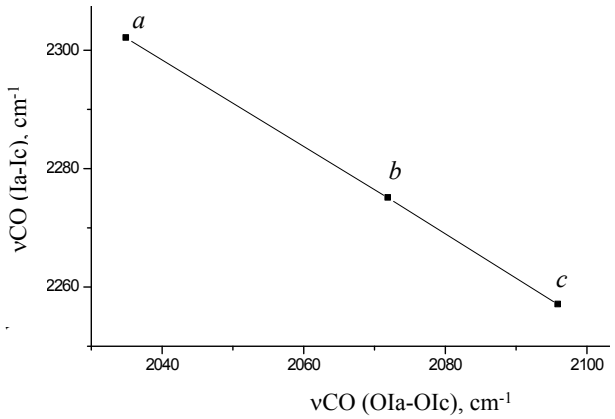

Figure S5. Correlation between νCO of compounds Ia, Ib, and Ic and that of the corresponding OIa, OIb, and OIc compounds.

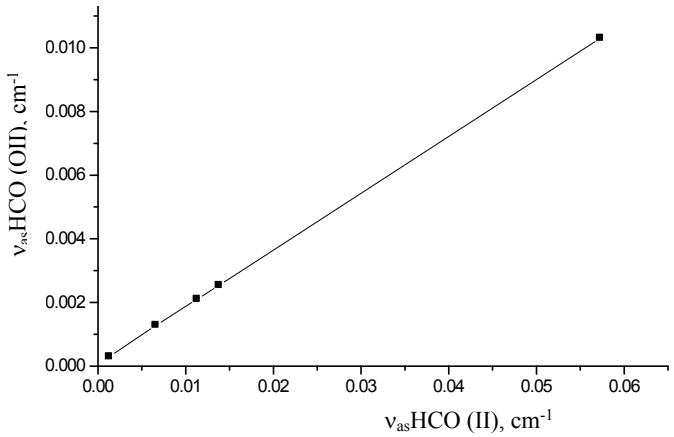

Figure S6 Dependence of the intensity of the band ν_{as}HCO at 1774 cm^{-1} of the type OII cation COH^+ on intensity of ν_{as}HCO absorption at 2810 cm^{-1} of the type II cation.

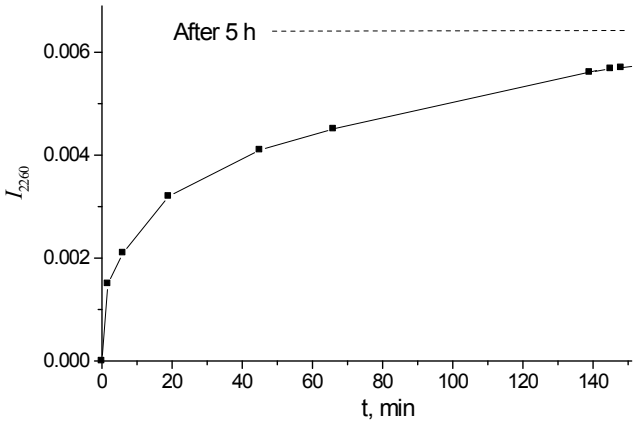

Figure S7. The kinetics of formation of the Ic compound (dependence of the intensity of its νCO band at 2260 cm^{-1} on the duration of absorption of CO by the surface of H{Cl_{11}}).

2. Supplemental Tables

Table S1. Calculated IR frequencies, intrinsic frequencies and C–O/C–H distances for optimized (by the B3LYP/cc-pVQZ level of theory) structures of $COH^+\cdots L$ cations, analogs of the II type compounds (frequencies in cm^{-1} are rounded to integer values).

Cation	ν_{as}HCO/νCH	νOHL Bridged H	ν_sHCO/νCO	ν_iCH	ν_iCO	$R_{C\cdots O,}$ Å	$R_{C\cdots H,}$ Å
OCH^+	3206.6	-	2266.5	3103	2407	1.1004	1.0950
$OCH^+\cdots He$	3162	-	2259	3056	2406	1.1005	1.0981
$OCH^+\cdots Ne$	3108	-	2249	2998	2404	1.1007	1.1021
$OCH^+\cdots Ar$	2874	-	2178	2738	2396	1.1017	1.1214
$OCH^+\cdots\{F_{11}^-\}_{(a)}$	2786	-	2120			1.1102	1.1216
$OCH^+\text{---}\{F_{11}^-\}_{(b)}$	-	1864	2515			1.1094	1.1640
$OCH^+\text{---}\{F_{11}^-\}_{(c)}$	-	1587	2441			1.1094	1.1991

Table S2. Calculated CO stretches and C–O distances for optimized (by the B3LYP/cc-pVQZ level of theory) structures of $LH^+\cdots(CO)$ compounds, analogs of I/OI-type compounds (frequencies in cm^{-1} are rounded to the integer values).

Compound	νCO	$R_{C\cdots O,}$ Å	Notes
CO_{gas}	2214	1.12375	Reference
$H_2OH^+\cdots CO$	2321	1.1125	I type
$SO_2H^+\cdots CO$	2325	1.1123	
$C_2H_3^+\cdots CO$	2297	1.1146	
$H_2OH^+\cdots OC$	2131	1.1341	OI type
$HFH^+\cdots OC$	2102	1.1406	

Table S3. Calculated IR frequencies, intrinsic frequencies (ν_i), and C–O/C–H distances for optimized (by the B3LYP/cc-pVQZ level of theory) structures of $COH^+\cdots$ L cations, analogs of OII-type compounds (frequencies in cm^{-1} are rounded to the integer values).

Cation	νCH	νOHL Bridged H	νCO	ν_iCH	ν_iCO	$R_{C\cdots O,}$ Å	$R_{O\cdots H,}$ Å
COH^+	3407		1965	3103	2407	1.1529	0.9948
$COH^+\cdots He$	3070		1978	3956	2406	1.1510	1.0122
$COH^+\cdots Ne$	2919		1984	2998	2404	1.1502	1.0216
$CO\text{-}H^+\text{-}Ar$		1758	2198	2738	2396	1.1466	1.0968
$CO\text{-}H^+\text{-}FH$		1612	2102			1.1406	1.2692

3. Calculations

3.1. Estimation of the energy of L–H^+CO and COH^+–L compounds and barrier for proton transfer from the Bronsted acid to the CO molecule.

To make the accurate estimation of the energy of H^+CO/COH^+ cations binding with basic molecules, the CBS-QB3 quantum-chemical method was applied. It is a Complete Basis Set (CBS) developed by George Peterson and coworkers [J.A. Montgomery, M.J. Frisch, J.W. Ochterski, and G.A. Petersson, J. Chem. Phys. 110 (1999) 2822-2827]. The several single-point energies were extrapolated in order to get the best estimate of the total energy. It is hard to compute due to an incomplete electron correlation energy account and finite size of the basis set. The CBS-QB3 calculations were performed with the Gaussian 09 software [Gaussian 09, Revision D.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian, Inc., Wallingford CT, 2009]. The results are shown in Table 1.

Table S4. Calculated enthalpies (in kJ/mol) of the H^+CO/H^+OC binding with various ligands, L (basicity of Ar and $\{F_{11}^-\}$ is very close).

	He	Ne	Ar	HF	C_2H_2	SO_2	H_2O
L–H^+CO	-1.8	-6.0	-19.7	-67.4	-84.4	-103.2	-157.1
L–H^+OC	-7.3	-15.3	-51.2	-135.9	-229.6	-234.2	-292.2

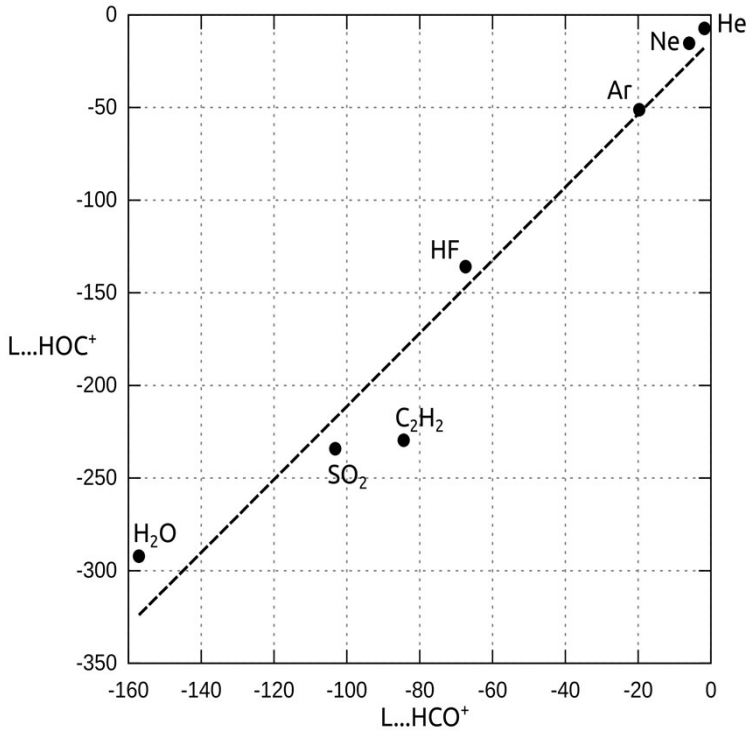

Figure S7. Correlation between binding enthalpies of HCO^+ and HOC^+ (kJ/mol).

According to CBS-QB3 calculation, the ArH^+ interaction with CO with the formation of $Ar..H^+CO$, is highly exothermic – 234.4 kJ/mol. It is expected that the barrier of proton transfer should be very low, because of perfect energy compensation between the breaking of the Ar-H bond and formation of the C-H bond. In fact, the scan of Potential Energy Surface (PES) along Ar-H distance shows no energetic barrier. The ArH^+ acid is the best model to describe the interaction of $\{F_{11}^-\}H^+$ acid with CO molecules, because of comparable basicity of Ar and $\{F_{11}^-\}$ anion. Therefore, it can be expected that in case of a real $\{F_{11}^-\}H^+$ acid the noticeable barrier to CO protonation also does not exist.

3.2. Scan of the potential energy surface when CO approaching to ArH^+ via C atom

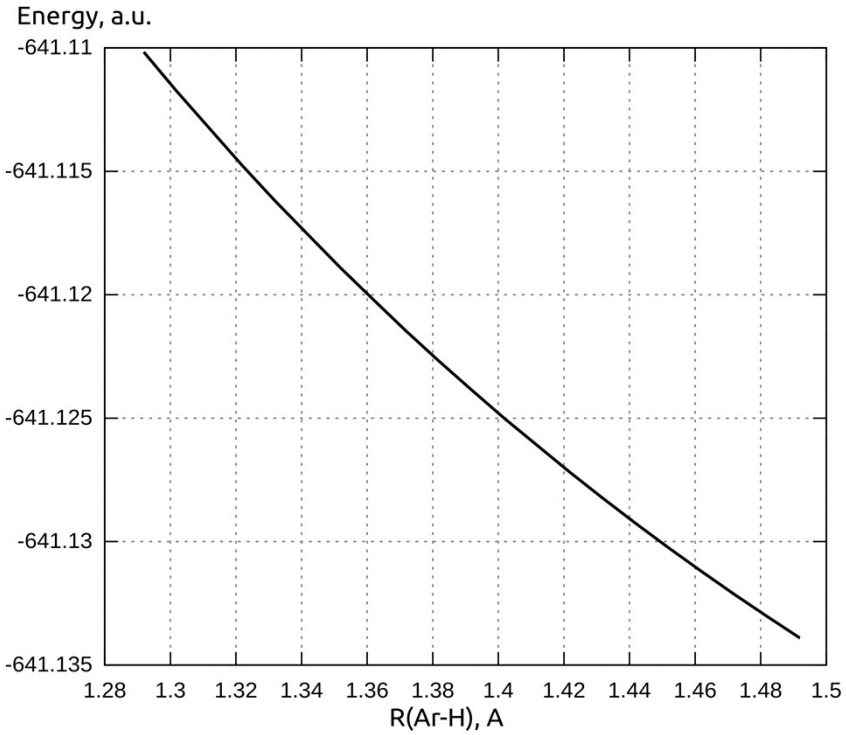

Figure S8. Relaxed molecule PES scan along the Ar-H distance as CO molecule approaching to the ArH^+ cation.

3.3. Evaluation of the different functional effect, such as B3LYP, M06, PW91, on the vibration frequencies of H^+CO and COH^+ cations

Table S5. IR frequencies of H^+CO calculated with various DFT functionals.

	SVWN	PW91	B3PW91	B3LYP	B2PLYP	M06L	M06	M06-2X
νCH	3111.37	3144.35	3216.77	3224.97	3217.49	3206.77	3141.75	3261.86
νCO	2223.52	2188.84	2273.37	2265.78	2204.68	2254.12	2279.68	2337.55
δHCO	819.49	830.79	867.62	867.21	858.30	894.56	901.96	887.14

Table S6. IR frequencies of COH^+ calculated with various DFT functionals.

	SVWN	PW91	B3PW91	B3LYP	B2PLYP	M06L	M06	M06-2X
νOH	3282.61	3316.13	3436.24	3401.31	3425.90	3456.46	3464.87	3449.34
νCO	1942.93	1891.89	1970.51	1965.08	1948.20	1982.48	2001.28	2009.54
δHCO	284.98	215.26	200.93	184.48	160.77	256.91	259.65	280.86

3.4. Others

Example of the GAMESS US input for DFT calculation for Ar...H^+CO cation. It shows all parameters required to reproduce results in the present Manuscript. Note that DFTTYP=B3LYPV1R selected for the convenience if one wants to reproduce results using Gaussian 09 software.

```
 $SYSTEM TIMLIM=1000 MWORDS=50 MEMDDI=30 $END
 $CONTRL SCFTYP=RHF
  RUNTYP=OPTIMIZE EXETYP=RUN
  MULT=1 ICHARG=1 ISPHER=1
  DFTTYP=B3LYPV1R
  COORD=UNIQUE NZVAR=5
 $END
 $DFT SWOFF=0.0 JANS=2 $END
 $GUESS GUESS=HUCKEL $END
 $SCF DIIS=.TRUE. SHIFT=.T. ETHRSH=0.1 SWDIIS=0.0 $END
 $FORCE RDHESS=.F. DECOMP=.T. PURIFY=.T. $END
 $ZMAT IZMAT(1)=1,1,2, 1,2,3, 1,3,4, 5,1,2,3, 5,2,3,4 $END
 $LIBE APTS(1)=1.0,0.0,0.0, 1.0,0.0,0.0 $END
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 $BASIS GBASIS=CCQ $END
 $DATA
 COH+
 CNV 4

 O           8.0   0.0000000000   0.0000000000  -1.0958457359
 C           6.0  -0.0000000000   0.0000000000   0.0057741388
 H           1.0  -0.0000000000   0.0000000000   1.1281379068
 AR         18.0   0.0000000000   0.0000000000   3.2020894711
 $END
```

Optimized geometries at B3LYP/cc-VQZ level (Cartesian coordinates, A) and total energies (a.u.) for the L+HOC and L+HCO cations are listed below.

```
COH            E = -113.5393377
C               0.0000000000   0.0000000000  -0.0367682523
O               0.0000000000   0.0000000000   1.1161509183
H               0.0000000000   0.0000000000   2.1109823723

COH+He         E = -116.4592564
C               0.0000000000   0.0000000000  -0.0384038391
O              -0.0000000000   0.0000000000  -1.1894442666
H              -0.0000000000   0.0000000000  -2.2016418937
HE              0.0000000000   0.0000000000  -3.5924505611

COH+Ne         E = -242.5234473
C              -0.0000000000   0.0000000000  -0.1285337571
O               0.0000000000   0.0000000000  -1.2787285725
```

H	0.0000000000	0.0000000000	-2.3003608789
NE	-0.0000000000	0.0000000000	-3.8294097712

COH+Ar E = -641.1232020

C	0.0000000000	0.0000000000	-0.0619742336
O	-0.0000000000	0.0000000000	-1.2085427880
H	-0.0000000000	0.0000000000	-2.3053465642
AR	0.0000000000	0.0000000000	-3.9885226262

$COH+H_2O$ E = -190.1267176

O	-0.0212294787	0.7968781004	0.0000000000
C	0.0077769515	1.9306478553	0.0000000000
H	0.0090125104	-0.8434817059	0.0000000000
H	-0.2729072033	-2.2612213575	-0.8091732915
H	-0.2729072033	-2.2612213575	0.8091732915
O	0.0796852741	-1.8462793182	0.0000000000

HCO+ E = -113.6011750

O	0.0000000000	0.0000000000	-1.1004597675
C	0.0000000000	0.0000000000	-0.0000946106
H	0.0000000000	0.0000000000	1.0948615508

HCO+He E = -116.5176347

O	-0.0000000000	0.0000000000	-1.0993978890
C	0.0000000000	0.0000000000	0.0011503476
H	0.0000000000	0.0000000000	1.0992557025
HE	-0.0000000000	0.0000000000	2.9421918768

HCO+Ne E = -242.5802384

O	-0.0000000000	0.0000000000	-1.0098347701
C	0.0000000000	0.0000000000	0.0908763478
H	0.0000000000	0.0000000000	1.1929382361
NE	-0.0000000000	0.0000000000	3.0746151215

HCO+Ar E = -641.1728738

O	-0.0000000000	0.0000000000	-1.1005394329
C	0.0000000000	0.0000000000	0.0011891801
H	0.0000000000	0.0000000000	1.1226302885
AR	-0.0000000000	0.0000000000	3.2054850223

$HCO+H_2O$ E = -190.1375961

O	-0.0010585400	1.9437527500	0.0000000000
C	-0.0118407900	0.8313043600	0.0000000000
H	-0.0025100200	-0.8365989200	0.0000000000
H	-0.2662259700	-2.3126785600	-0.8041740000
H	-0.2662259700	-2.3126785600	0.8041740000
O	0.0768093800	-1.8844865100	0.0000000000

HF+HCO E = -214.1273977

C	-0.0025580098	0.0000000000	0.0140681992
O	0.1219238751	0.0000000000	1.1099683223
H	-0.1308327208	0.0000000000	-1.1303756439
F	-0.0536820083	0.0000000000	-2.6221831488
H	-0.6931900424	0.0000000000	-3.3041734339

HF+HOC E = -214.0917791

F	1.6996367067	0.1443539641	0.0000000000
H	0.6066700438	0.0117149434	0.0000000000
C	-1.8018790406	0.0043091366	0.0000000000
O	-0.6617943413	-0.0311890454	0.0000000000
H	2.2312641214	-0.6425369888	0.0000000000

C_2H_2+HCO E = -191.0041173

O	0.0000000000	0.0000000000	2.3590460700
C	0.0000000000	0.0000000000	1.2444060700
H	0.0000000000	0.0000000000	-0.6142419300
C	-0.0000000000	-0.6050090000	-1.8358099300
C	0.0000000000	0.6050090000	-1.8358099300
H	0.0000000000	1.6784520000	-1.8474219300
H	0.0000000000	-1.6784520000	-1.8474219300

SO_2+HCO E = -662.3779061

H	-0.8820010220	0.4007781519	0.0000000000
C	-2.3551063004	-0.2604923360	0.0000000000
O	-3.3789863610	-0.6951370061	0.0000000000
O	0.0381513015	0.9615931113	0.0000000000
O	1.5181420520	-1.0279289334	0.0000000000
S	1.4355280800	0.3899908924	0.0000000000

Optimized geometry at B3LYP/6-311g(3df,3pd) level (Cartesian coordinates, A) and total energy (a.u.) for the $(CHB_{11}F_{11})^-HCO^+$ complex.

CHB11F11+HCO E = -1525.4422023

B	-0.0001712309	-0.0013674010	0.0039823555
B	0.0021690122	-0.0021263760	2.9008807604
B	1.6951324703	-0.0020973114	2.3796604345
B	0.4914841355	0.9681909574	1.4762649348
B	1.6932835653	-0.0205132047	0.5862041852
B	-0.8137961220	-1.5444646458	0.5573807948
B	0.4006891757	-2.4938918349	1.4684052411
B	-0.7823539204	-1.5123276764	2.3485965472
B	0.8938378599	-1.5155815717	2.8746013917
B	-1.0614992814	0.0181412090	1.4582594235
B	0.8986681019	-1.5501425582	0.0268150866
C	1.8170456170	-1.4898198177	1.4927348219
H	2.7786929060	-1.9852136577	1.4813458854
F	2.7488555666	0.4454486772	3.0873888100

F	2.7680934323	0.4347897327	-0.0774438507
F	1.2177945009	-2.1284658121	4.0903289948
F	0.5263654305	-3.8328296934	1.5228122178
F	1.4028098329	-2.1933718949	-1.0385688189
F	-0.4080725523	0.4406665510	4.1610381505
F	-1.7037298222	-2.0534648666	3.2489283494
F	-1.7985618813	-2.1309647874	-0.1556592746
F	-0.3521018128	0.6033563405	-1.1496935117
F	0.5125428747	2.3178961230	1.4712997587
F	-2.2659867928	0.6327660241	1.4885714967
H	-0.0895616988	-1.7782940978	4.9899041219
C	-1.0693617164	-1.4198916004	5.4016770098
O	-1.9840910143	-1.1530903030	5.9714967466