Electronic Supplementary Information:

Spectroscopic Evidence for Intact Carbonic Acid Stabilized by Halide Anions in the Gas Phase

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Table of content

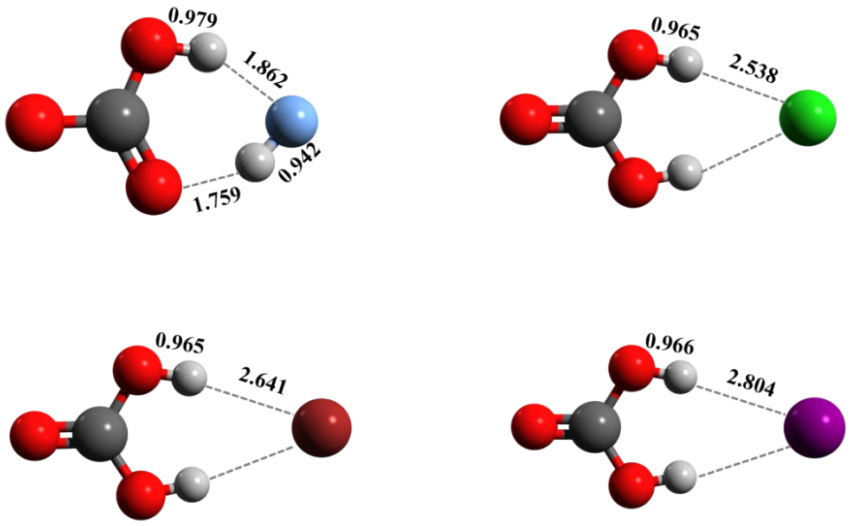


Figure S1. Optimized structures of neutral $H_2CO_3 \cdot X$ complexes (X = F, Cl, Br, and I), calculated at the CCSD(T)/aug-cc-pVTZ level of theory. The distances of the O−H and H···X bonds are noted with the unit of Å.

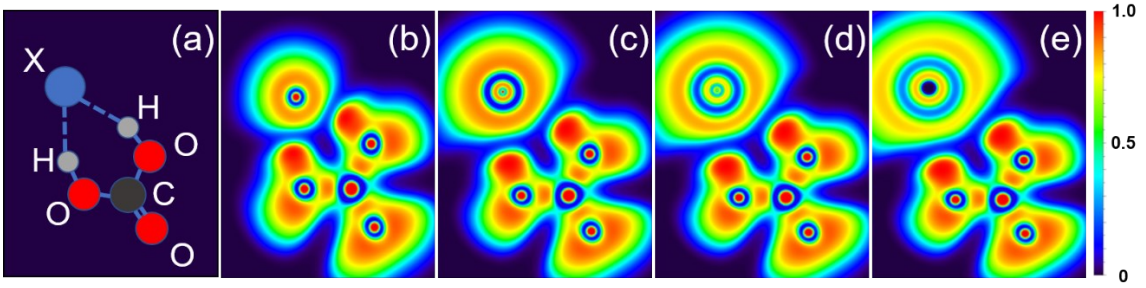


Figure S2. Electron density topological graphs of Isomer 1 of $H_2CO_3 \cdot X^-$ (X = F, Cl, Br, I), (a) location scheme of all atoms in the molecular plane, (b) $H_2CO_3 \cdot F^-$, (c) $H_2CO_3 \cdot Cl^-$, (d) $H_2CO_3 \cdot Br^-$, (e) $H_2CO_3 \cdot I^-$.

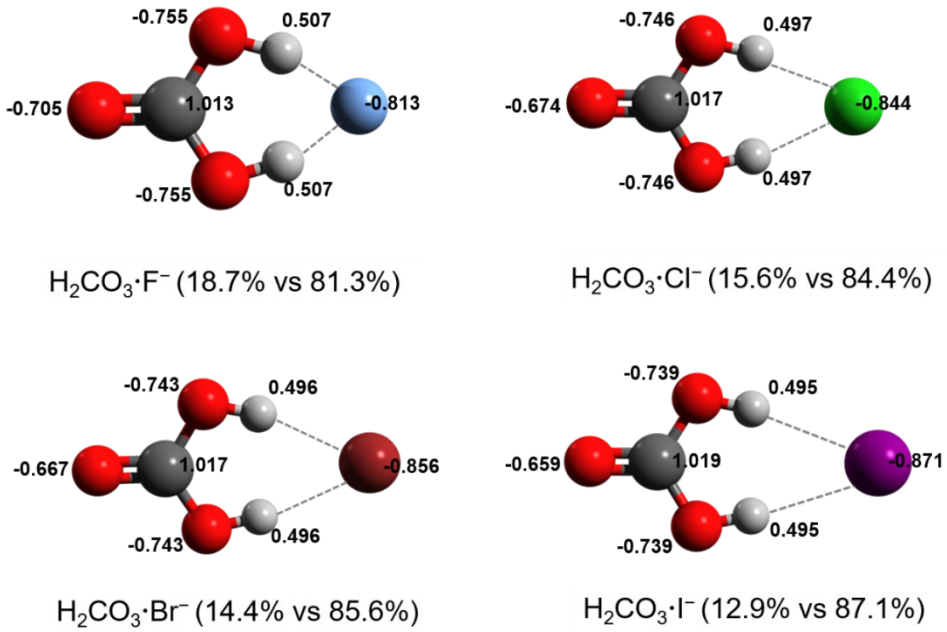


Figure S3. NPA charge distributions of the $H_2CO_3 \cdot X^-$ (X = F, Cl, Br, and I) complex anions

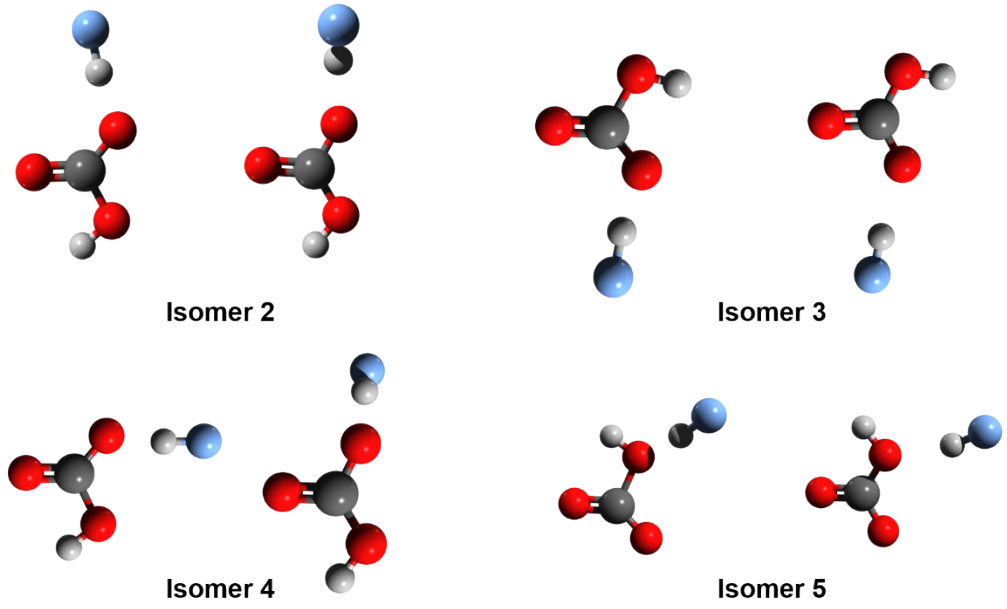
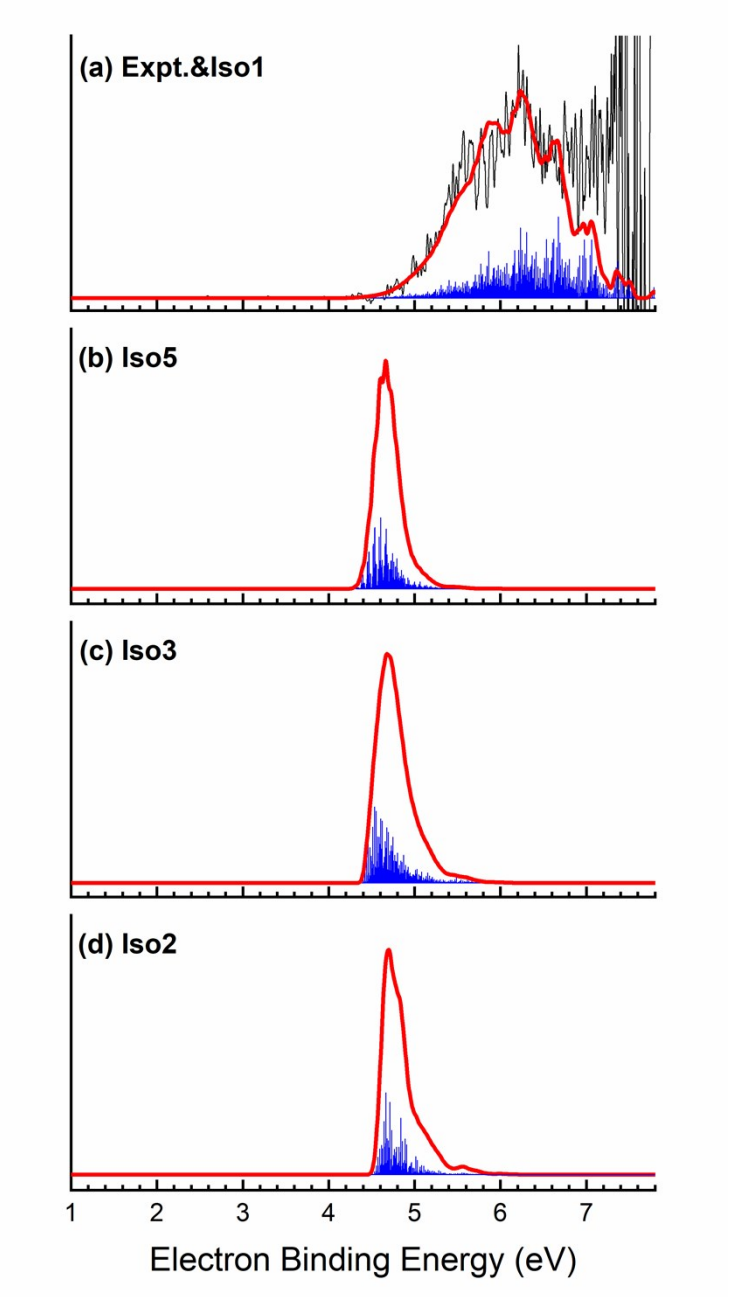


Figure S4. Schematic structures of all anion isomers of $H_2CO_3 \cdot F^-$ (left) and the corresponding neutrals (right)

In Figure S4, we listed the optimized geometries of anions and the corresponding neutrals for Isomers 2–4 of $H_2CO_3 \cdot F^-$. Notably, for the neutral complex, Isomer 2 and 4 actually are identical, which means that the HF group of Isomer 4 undergoes a large rotation along the adjacent C–O bond to form *cis-cis* conformation from the original *cis-trans* during electron detachment. Thus, the significant structural change resulted in too small FC factors for photodetachment of Isomer 4, failing to simulate its FC spectrum.



Figures S5. Franck-Condon simulated NIPE spectra (red and blue) of different $H_2CO_3 \cdot F^-$ isomers, along with the experimental spectrum (black)

Figure S5 lists the FC simulated spectra of Isomer 2, 3 and 5. The calculated spectra apparently are far different from the experimental data, indicative of no contributions from the other isomers.

Table S1. The binding energies (BEs) between carbonic acid and halides in $H_2CO_3 \cdot X^-$ (X = F, Cl, Br and I).

X	H_2CO_3	$H_2CO_3 \cdot X^-$	X^-	BE	ΔVDE
F	-264.63894000	-364.48496800	-99.74953761	2.63	2.82
Cl	-264.63894000	-724.50128500	-459.80504178	1.56	1.58
Br	-264.63894000	-680.46419700	-415.77547994	1.35	1.25
I	-264.63894000	-559.59589100	-294.91568141	1.12	1.04

The energies of H_2CO_3, $H_2CO_3 \cdot X^-$ and X^- were calculated at the CCSD(T) level of theory, including the ZPE corrections with the unit of Hartree. The binding energies (BEs) between H_2CO_3 and halide anions in $H_2CO_3 \cdot X^-$ (X = F, Cl, Br, and I) were calculated according to the equation, $BE = E(H_2CO_3) + E(X^-) - E(H_2CO_3 \cdot X^-)$. A perfect consistency is obtained between the variation trends of calculated BEs and experimental ΔVDE values.

Table S2. Topological properties at the BCPs (bond critical points, Figure S2) in $H_2CO_3 \cdot X^-$ (X = F, Cl, Br, I)

X	Bond	ρ(r)/(e·Å^{-3})	Eigenvalues of Hessian Matrix			$\nabla^2\rho(r)$	V(r)/Hartree
			λ_1	λ_2	λ_3		
F	O−H	0.3023	−1.4814	−1.5039	0.9505	−2.0348	−0.6453
	F−H	0.0705	−0.1400	−0.1385	0.4754	0.1969	−0.0805
Cl	O−H	0.3304	−1.6583	−1.6849	1.0248	−2.3185	−0.7099
	Cl−H	0.0352	−0.0451	−0.0441	0.1619	0.0728	−0.0260
Br	O−H	0.3344	−1.6790	−1.7062	1.0306	−2.3546	−0.7187
	Br−H	0.0293	−0.0332	−0.0322	0.1229	0.0575	−0.0185
I	O−H	0.3383	−1.6984	−1.7262	1.0355	−2.3891	−0.7274
	I−H	0.0239	−0.0225	−0.0216	0.0844	0.0402	−0.0124

According to the quantum theory of "atoms in molecule", the topological property of electron density distribution depends on the electron density ρ(r) and the Laplacian quantity $\nabla^2\rho(r)$ of charge density. And the bonding of two atoms may be classified into two groups: shared and closed-shell interactions, based on the distribution of ρ(r) and the associated $\nabla^2\rho(r)$ at bond critical point (BCP). The shared interaction has a large ρ(r) and a negative $\nabla^2\rho(r)$ at the BCP, whereas a small ρ(r) and a positive $\nabla^2\rho(r)$ exist for the closed-shell interaction. Thus, the topological properties of electron density at the BCPs for the complex anions are summarized in Table S2. The second derivatives of electron density in three dimensional directions consisted of Hessian matrix of electron density are included in Table S2 as well. Generally, when the three eigenvalues of Hessian matrix are one positive and two negative values, it is denoted as the key point of (3, –1), indicative of a chemical bond being formed between two atoms. Moreover, the more negative $\nabla^2\rho(r)$ implies the stronger covalent bond.

As shown in Table S2, the prominent higher ρ(r) of O−H bond was found than the X−H bond, which is also further confirmed by the calculated potential energy density V(r). Moreover, in $H_2CO_3 \cdot X^-$ (X=F, Cl, Br, and I) complex anions, all $\nabla^2\rho(r)$ values for the BCPs between oxygen and hydrogen atom are negative and less than –2. Therefore, the O−H bond remains the covalent property in the complexes like it in the isolated carbonic acid, but increases in bond strength in the F→Cl→Br→I sequence, where the X^- anions play a role of charge inducer. In addition, in contrast to $H_2CO_3 \cdot X^-$ (X = Cl, Br, and I), the significantly increased ρ(r) and $\nabla^2\rho(r)$ on the F–H bond of $H_2CO_3 \cdot F^-$ imply

stronger interaction between them. All these conclusions agree with the deduction from the optimized geometries.

Table S3. Relative energies and enthalpies of formation (in kJ/mol) of $H_2CO_3 \cdot X^-$ in Isomer 1 conformation, calculated at CCSD(T)/aug-cc-pVTZ(-PP) level of theory.

Reactions	ΔE	ΔE+ZPE	$\Delta H_{298.15}$	$\Delta G_{298.15}$
$F^-(H_2O) + CO_2 \rightarrow H_2CO_3 \cdot F^-$	-127.43	-110.94	-113.75	-69.02
$Cl^-(H_2O) + CO_2 \rightarrow H_2CO_3 \cdot Cl^-$	-77.11	-62.57	-65.77	-19.52
$Br^-(H_2O) + CO_2 \rightarrow H_2CO_3 \cdot Br^-$	-64.87	-50.66	-53.78	-7.37
$I^-(H_2O) + CO_2 \rightarrow H_2CO_3 \cdot I^-$	-50.46	-36.4	-39.54	7.03

Table S4 Cartesian Coordinates of all investigated species.

$H_2CO_3 \cdot F^-$ ISO1				$H_2CO_3 \cdot F^-$ ISO2			
C	0.000000	0.000000	1.448424	C	0.000000	-0.106868	-1.366534
O	0.000000	0.000000	3.751095	O	0.000000	-2.449007	-1.482164
O	2.130554	0.000000	0.084814	O	0.000000	1.373013	0.493889
O	-2.130554	0.000000	0.084814	O	0.000000	1.180921	-3.701029
H	1.598160	0.000000	-1.774406	H	0.000000	-0.194752	-4.896274
H	-1.598160	0.000000	-1.774406	H	0.000000	0.402451	3.093957
F	0.000000	0.000000	-4.029247	F	0.000000	-0.031820	4.908629
$H_2CO_3 \cdot F^-$ ISO3				$H_2CO_3 \cdot F^-$ ISO4			
C	0.000000	-0.184327	-1.406745	C	0.000000	0.230019	1.557293
O	0.000000	-2.499609	-1.516982	O	0.000000	0.871547	3.814106
O	0.000000	1.315907	0.478585	O	0.000000	1.564099	-0.410896
O	0.000000	1.109902	-3.736945	O	0.000000	-2.388761	1.082350
H	0.000000	2.859122	-3.225731	H	0.000000	-3.090055	2.764129
H	0.000000	0.393579	3.091701	H	0.000000	0.486647	-2.961700
F	0.000000	0.006115	4.917998	F	0.000000	-0.046784	-4.751545
$H_2CO_3 \cdot F^-$ ISO5							
C	-1.003259	0.104830	0.006046				
O	-1.857216	-0.751361	-0.249895				
O	-0.968206	1.325180	0.046546				
O	0.317405	-0.525309	0.366514				
H	0.155136	-1.466613	0.246214				
F	2.687441	0.059952	-0.178499				
H	1.741593	-0.090017	0.018679				
$H_2CO_3 \cdot Cl^-$ ISO1				$H_2CO_3 \cdot Cl^-$ ISO2			
C	0.000000	0.000000	2.532657	C	0.000000	-0.155133	2.479334
O	0.000000	0.000000	4.822614	O	0.000000	-2.449433	2.342491
O	2.149035	0.000000	1.189127	O	0.000000	1.037471	4.791140
O	-2.149035	0.000000	1.189127	H	0.000000	-0.347688	5.976283
H	1.754101	0.000000	-0.649119	O	0.000000	1.538714	0.698608
H	-1.754101	0.000000	-0.649119	H	0.000000	0.763928	-1.101135
Cl	0.000000	0.000000	-4.070764	Cl	0.000000	-0.016478	-4.513137
$H_2CO_3 \cdot Cl^-$ ISO3				$H_2CO_3 \cdot Cl^-$ ISO4			
C	0.000000	-0.230133	2.868514	C	0.000000	-0.130303	2.642753
O	0.000000	-2.498475	2.736450	O	0.000000	-0.663474	4.886842
O	0.000000	0.982439	5.151525	O	0.000000	2.326033	1.856036
H	0.000000	2.766431	4.773037	H	0.000000	3.279943	3.410092
O	0.000000	1.466629	1.020186	O	0.000000	-1.753752	0.795808
H	0.000000	0.678050	-0.706635	H	0.000000	-0.950198	-0.986647
Cl	0.000000	0.002335	-5.107541	Cl	0.000000	0.019063	-4.366323

$H_2CO_3 \cdot Br^-$ ISO1				$H_2CO_3 \cdot Br^-$ ISO2			
C	0.000000	0.000000	4.004684	C	0.000000	-0.160489	4.107516
O	0.000000	0.000000	6.291784	O	0.000000	-2.448156	3.934956
O	2.152885	0.000000	2.664080	O	0.000000	1.016663	6.418637
O	-2.152885	0.000000	2.664080	H	0.000000	-0.370812	7.601323
H	1.779929	0.000000	0.828807	O	0.000000	1.558863	2.336907
H	-1.779929	0.000000	0.828807	H	0.000000	0.791040	0.572241
Br	0.000000	0.000000	-2.949579	Br	0.000000	-0.006680	-3.261592
$H_2CO_3 \cdot Br^-$ ISO3				$H_2CO_3 \cdot Br^-$ ISO4			
C	0.000000	-0.227216	4.169208	C	0.000000	-0.119449	4.224627
O	0.000000	-2.499458	4.054773	O	0.000000	-0.635339	6.467698
O	0.000000	0.987034	6.460267	O	0.000000	2.316847	3.396146
H	0.000000	2.768771	6.072195	H	0.000000	3.306357	4.928016
O	0.000000	1.461199	2.326630	O	0.000000	-1.775288	2.393149
H	0.000000	0.685092	0.564760	H	0.000000	-0.989474	0.639056
Br	0.000000	0.000843	-3.281751	Br	0.000000	0.007507	-3.159514
$H_2CO_3 \cdot I^-$ ISO1				$H_2CO_3 \cdot I^-$ ISO2			
C	0.000000	0.000000	5.070804	C	0.000000	-0.165576	5.271652
O	0.000000	0.000000	7.354381	O	0.000000	-2.447149	5.068433
O	2.157048	0.000000	3.732542	O	0.000000	1.001271	7.579239
O	-2.157048	0.000000	3.732542	H	0.000000	-0.385248	8.763358
H	1.805844	0.000000	1.900928	O	0.000000	1.573150	3.506052
H	-1.805844	0.000000	1.900928	H	0.000000	0.804691	1.770472
I	0.000000	0.000000	-2.378465	I	0.000000	-0.003706	-2.619157
$H_2CO_3 \cdot I^-$ ISO3				$H_2CO_3 \cdot I^-$ ISO4			
C	0.230142	0.000000	5.340885	C	0.000000	-0.107786	5.351279
O	2.498512	0.000000	5.209297	O	0.000000	-0.586932	7.597303
O	-0.982909	0.000000	7.623641	O	0.000000	2.300699	4.459871
H	-2.766822	0.000000	7.244778	H	0.000000	3.340314	5.958436
O	-1.466232	0.000000	3.492200	O	0.000000	-1.809582	3.548258
H	-0.677290	0.000000	1.765545	H	0.000000	-1.048720	1.810952
I	-0.000652	0.000000	-2.635220	I	0.000000	0.004080	-2.535612
cis-trans H_2CO_3				*trans-trans* H_2CO_3			
C	0.000000	0.157623	0.160051	C	0.000000	0.000000	0.221308
O	0.000000	1.509791	1.976366	O	0.000000	0.000000	2.472719
O	0.000000	0.988096	-2.232333	O	0.000000	2.179162	-1.134823
O	0.000000	-2.406565	0.221652	O	0.000000	-2.179162	-1.134823
H	0.000000	-0.454948	-3.349743	H	0.000000	1.884537	-2.930323
H	0.000000	-2.872943	1.987206	H	0.000000	-1.884537	-2.930323

cis-cis H_2CO_3				CO_2			
C	0.000000	0.000000	0.186740	C	0.000000	0.000000	0.000000
O	0.000000	0.000000	2.467407	O	0.000000	0.000000	2.205300
O	0.000000	2.055062	-1.293795	O	0.000000	0.000000	-2.205300
O	0.000000	-2.055062	-1.293795				
H	0.000000	3.485400	-0.158783				
H	0.000000	-3.485400	-0.158783				
$F^-(H_2O)$				$Cl^-(H_2O)$			
O	-0.109391	-2.407543	0.000000	O	-0.096605	-3.928787	0.000000
H	1.667990	-2.777204	0.000000	H	1.715415	-4.053292	0.000000
H	-0.115654	-0.411305	0.000000	H	-0.318952	-2.074905	0.000000
F	0.009765	2.196662	0.000000	CL	0.003894	1.947229	0.000000
$Br^-(H_2O)$				$I^-(H_2O)$			
O	-0.091799	-5.105211	0.000000	O	-0.085699	-5.900506	0.000000
H	1.724558	-5.146577	0.000000	H	1.730864	-5.843368	0.000000
H	-0.394909	-3.273144	0.000000	H	-0.486290	-4.096784	0.000000
Br	0.001608	1.128440	0.000000	I	0.000919	0.822846	0.000000
H_2CO_3·F Neutral ISO1				H_2CO_3·Cl Neutral ISO1			
C	0.000000	-0.055417	1.325028	C	0.000000	0.000000	2.897522
O	0.000000	-0.157017	3.792506	O	0.000000	0.000000	5.151036
O	0.000000	2.247612	0.383083	O	2.174473	0.000000	1.536982
O	0.000000	-2.071966	0.184531	O	-2.174473	0.000000	1.536982
H	0.000000	2.097623	-1.460462	H	1.858018	0.000000	-0.258063
H	0.000000	-1.322471	-3.054810	H	-1.858018	0.000000	-0.258063
F	0.000000	-0.021777	-4.269996	Cl	0.000000	0.000000	-4.678785
H_2CO_3·Br Neutral ISO1				H_2CO_3·I Neutral ISO1			
C	0.000000	0.000000	4.483140	C	0.000000	0.000000	5.529362
O	0.000000	0.000000	6.737122	O	0.000000	0.000000	7.783912
O	2.174058	0.000000	3.122624	O	2.173656	0.000000	4.169103
O	-2.174058	0.000000	3.122624	O	-2.173656	0.000000	4.169103
H	1.855851	0.000000	1.326428	H	1.853997	0.000000	2.371246
H	-1.855851	0.000000	1.326428	H	-1.853997	0.000000	2.371246
Br	0.000000	0.000000	-3.306856	I	0.000000	0.000000	-2.593566