Supplementary Information

A Theoretical Study of the Potential Energy Surface of the $HBr^+ + CO_2 \rightarrow HOCO^+ + Br\cdot$ Reaction

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Table S1. The harmonic vibrational frequencies (calculated with UMP2/cc-pVDZ/lanl08d) of the intermediates and transition state of the $HBr^+ + CO_2 \rightarrow HOCO^+ + Br$ reaction.[a,b,c]

	Vib. Index	Vib. Freq. (cm^{-1})	Vib. Motion
IM	1	81.391	ip O-C-H bending
	2	255.043	Br--H streching
	3	582.663	ip O-C-O bending
	4	585.779	op O-C-O bending
	5	745.404	op O-H-Br bending
	6	975.826	ip O-H-Br bending
	7	1255.075	sym O-C-O stretching
	8	1340.41	asym O-H-Br stretching
	9	2438.795	asym O-C-O stretching
v-IM	1	49.237	O-C-O rocking
	2	56.256	op O--H-Br bending
	3	178.87	O--Br stretching
	4	360.576	O--H stretching
	5	622.790	op O-C-O bending
	6	638.566	ip O-C-O bending
	7	1319.503	sym O-C-O stretching
	8	2430.764	asym O-C-O stretching
	9	2580.362	H-Br stretching
TS	1	-216.271	asym H--O--Br stretching
	2	57.208	op O-H-Br bending
	3	63.214	O-C-O rocking
	4	175.509	sym H--O--Br stretching
	5	634.706	op O-C-O bending
	6	640.541	ip O-C-O bending
	7	1333.188	sym O-C-O stretching
	8	2453.762	asym O-C-O stretching
	9	2535.096	H-Br stretching

a. The optimized geometries of IM, v-IM, and TS are planar (C_s symmetry).
b. Definitions of acronyms: sym, symmetric; asym, asymmetric; ip, in-plane (σ_h plane); op, out-of-plane (σ_h plane).
c. The motion is named to best describe the major component of the vibration. For sym and asym stretching of X-Y-Z, Y is the central atom; for ip and op bending X-Y-Z, Y is the central atom. Double hyphen indicts the distance between two atoms is larger than 1.5 angstroms.

Figure S1. Snapshots of an ab initio molecular dynamics (UMP2/cc-pVDZ/lanl08d) trajectory in which the IM is formed (0.9 ps).

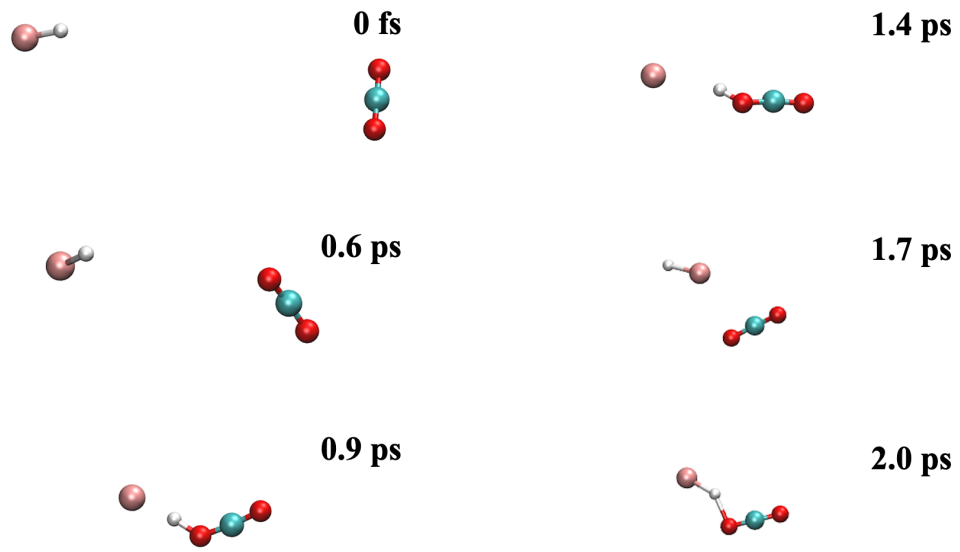
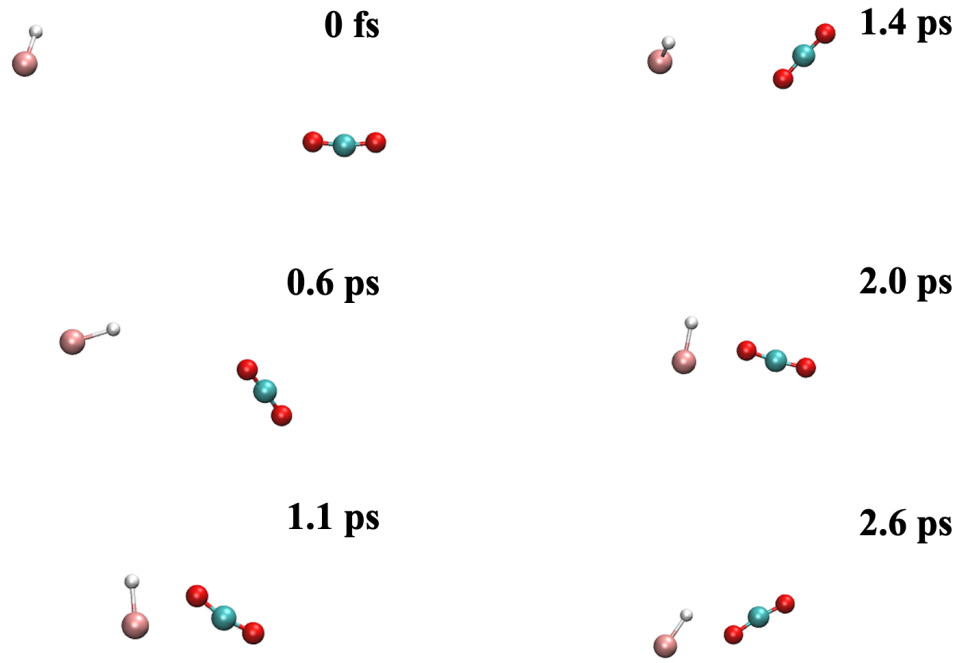
Figure S2. Snapshots of an ab initio molecular dynamics (UMP2/cc-pVDZ/lanl08d) trajectory in which the v-IM is formed (1.1 and 2.0 ps).