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

Halide-Propene Complexes: Validated DSD-PBEP86-D3BJ Calculations and Photoelectron Spectroscopy

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Supporting Information

The supporting information presented here comprises results of DFT calculations performed on a number of halide- and halogen-molecule gas-phase complexes. Included are structures, energies, vibrational data, and cartesian coordinates predicted with the DSD-PBEP86-D3BJ functional, with def2QZVP, aug-cc-pVTZ and aug-cc-pVQZ basis sets. The aug-cc-pVXZ PP basis sets were employed for bromine and iodine. Also attached are the peak assignments of the mass spectra of the CCl_4/CH_2Br_2/CH_3I:C_3H_6:Ar gas mixtures.

List of Figures

List of Tables

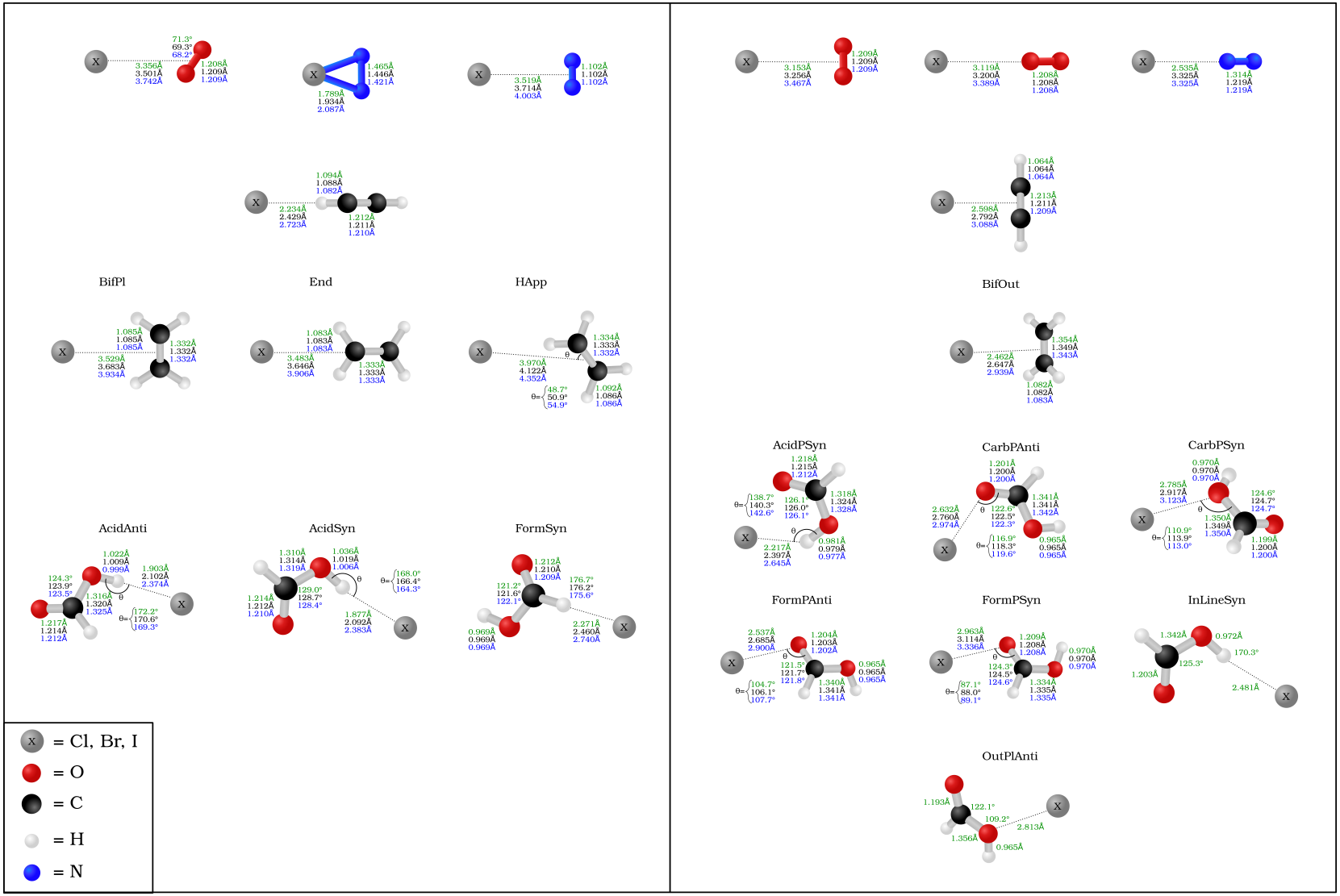

Figure S1: *Structures of halide-molecule complexes calculated from DSD-PBEP86-D3BJ functional using AVQZ basis sets. Complete data sets, including for def2QZVP and AVTZ basis sets are are provided in the following tabulated data.*

Table S1: *Gaussian format of the d-aug-cc-pV(T+d)Z basis set for chlorine. Generated using the Basis Set Exchange Python API module.[1, 2]*

Cl	0		*Continued*			*Continued*		
S	15	1	S	15	1	P	9	1
	4.561000D+05	4.929700D-05		4.561000D+05	4.185460D-06		6.633000D+02	-6.521450D-04
	6.833000D+04	3.830290D-04		6.833000D+04	3.243950D-05		1.568000D+02	-5.194450D-03
	1.555000D+04	2.008540D-03		1.555000D+04	1.711050D-04		4.998000D+01	-2.469380D-02
	4.405000D+03	8.385580D-03		4.405000D+03	7.141760D-04		1.842000D+01	-7.281670D-02
	1.439000D+03	2.947030D-02		1.439000D+03	2.567050D-03		7.240000D+00	-1.340300D-01
	5.204000D+02	8.783250D-02		5.204000D+02	7.885520D-03		2.922000D+00	-9.477420D-02
	2.031000D+02	2.114730D-01		2.031000D+02	2.108670D-02		1.022000D+00	2.622890D-01
	8.396000D+01	3.653640D-01		8.396000D+01	4.422640D-02		3.818000D-01	5.646670D-01
	3.620000D+01	3.408840D-01		3.620000D+01	6.516700D-02		1.301000D-01	3.412500D-01
	1.583000D+01	1.021330D-01		1.583000D+01	6.030120D-03	P	1	1
	6.334000D+00	3.116750D-03		6.334000D+00	-2.064950D-01		1.301000D-01	1.000000D+00
	2.694000D+00	1.057510D-03		2.694000D+00	-4.058710D-01	P	1	1
	9.768000D-01	-3.780000D-04		9.768000D-01	7.595580D-02		0.0419	1
	4.313000D-01	1.561360D-04		4.313000D-01	7.256610D-01	P	1	1
	1.625000D-01	-5.141260D-05		1.625000D-01	3.944230D-01		1.349431D-02	1
S	15	1	S	1	1	D	1	1
	4.561000D+05	-1.383040D-05		1.625000D-01	1.000000D+00		4.610000D+00	1.000000D+00
	6.833000D+04	-1.072790D-04	S	1	1	D	1	1
	1.555000D+04	-5.650830D-04		0.0591	1		1.011000D+00	1.000000D+00
	4.405000D+03	-2.361350D-03	S	1	1	D	1	1
	1.439000D+03	-8.458860D-03		2.149422D-02	1		3.390000D-01	1.000000D+00
	5.204000D+02	-2.596380D-02	P	9	1	D	1	1
	2.031000D+02	-6.863620D-02		6.633000D+02	2.404480D-03		1.300000D-01	1.000000D+00
	8.396000D+01	-1.418740D-01		1.568000D+02	1.921480D-02	D	1	1
	3.620000D+01	-1.993190D-01		4.998000D+01	8.850970D-02		4.985251D-02	1
	1.583000D+01	-1.956620D-02		1.842000D+01	2.560200D-01	F	1	1
	6.334000D+00	4.997410D-01		7.240000D+00	4.369270D-01		7.060000D-01	1
	2.694000D+00	5.637360D-01		2.922000D+00	3.503340D-01	F	1	1
	9.768000D-01	7.903250D-02		1.022000D+00	5.854950D-02		0.312	1
	4.313000D-01	-8.350910D-03		3.818000D-01	-4.584230D-03	F	1	1
	1.625000D-01	2.324560D-03		1.301000D-01	2.269700D-03		1.378810D-01	1
S	1	1	P	1	1			
	9.768000D-01	1.000000D+00		1.022000D+00	1.000000D+00			

Table S2: *DSD-PBEP86-D3BJ calculated energies for N_2, O_2, HCCH, C_2H_4, HCOOH and C_3H_6.*

		E_{DFT}
N_2	def2QZVP	-109.4134226
	AVTZ	-109.3966059
	AVQZ	-109.4146999
O_2	def2QZVP	-150.1826986
	AVTZ	-150.1591013
	AVQZ	-150.1841387
HCCH	def2QZVP	-77.2198341
	AVTZ	-77.2071669
	AVQZ	-77.2204955
C_2H_4	def2QZVP	-78.4700163
	AVTZ	-78.4564437
	AVQZ	-78.4707010
syn-HCOOH	def2QZVP	-189.5772139
	AVTZ	-189.5455173
	AVQZ	-189.5789606
anti-HCOOH	def2QZVP	-189.5704712
	AVTZ	-189.5388110
	AVQZ	-189.5722829
C_3H_6	def2QZVP	-117.7315112
	AVTZ	-117.7113490

Table S3: *Cartesian coordinates of the geometries of N_2, O_2, HCCH and C_2H_4 optimised with the DSD-PBEP86-D3BJ functional, in* Å.

		N_2		
		x	y	z
def2QZVP	N	0.000000	0.000000	0.549874
	N	0.000000	0.000000	-0.549874
AVTZ	N	0.000000	0.000000	0.551020
	N	0.000000	0.000000	-0.551020
AVQZ	N	0.000000	0.000000	0.549977
	N	0.000000	0.000000	-0.549977
		O_2		
		x	y	z
def2QZVP	O	0.000000	0.000000	0.602257
	O	0.000000	0.000000	-0.602257
AVTZ	O	0.000000	0.000000	0.551020
	O	0.000000	0.000000	-0.551020
AVQZ	O	0.000000	0.000000	0.549977
	O	0.000000	0.000000	-0.549977
		HCCH		
		x	y	z
def2QZVP	H	0.000000	0.000000	1.664640
	C	0.000000	0.000000	0.601800
	C	0.000000	0.000000	-0.601800
	H	0.000000	0.000000	-1.664640
AVTZ	H	0.000000	0.000000	1.666097
	C	0.000000	0.000000	0.602865
	C	0.000000	0.000000	-0.602865
	H	0.000000	0.000000	-1.666097
AVQZ	H	0.000000	0.000000	1.664982
	C	0.000000	0.000000	0.601954
	C	0.000000	0.000000	-0.601954
	H	0.000000	0.000000	-1.664982
		C_2H_4		
		x	y	z
def2QZVP	C	0.000000	0.000000	0.664363
	C	0.000000	0.000000	-0.664363
	H	0.000000	0.922830	1.229687
	H	0.000000	-0.922830	1.229687
	H	0.000000	0.922830	-1.229687
	H	0.000000	-0.922830	-1.229687
AVTZ	C	0.000000	0.000000	0.665374
	C	0.000000	0.000000	-0.665374
	H	0.000000	0.923801	1.231011
	H	0.000000	-0.923801	1.231011
	H	0.000000	0.923801	-1.231011
	H	0.000000	-0.923801	-1.231011
AVQZ	C	0.000000	0.000000	0.664527
	C	0.000000	0.000000	-0.664527
	H	0.000000	0.923119	1.229862
	H	0.000000	-0.923119	1.229862
	H	0.000000	0.923119	-1.229862
	H	0.000000	-0.923119	-1.229862

Table S4: *Cartesian coordinates of the geometries of HCOOH optimised with the DSD-PBEP86-D3BJ functional, in* Å.

		syn-HCOOH		
		x	y	z
	C	0.000000	0.420861	0.000000
	O	-1.029128	-0.439674	0.000000
def2QZVP	H	-0.652638	-1.330813	0.000000
	O	1.157655	0.109274	0.000000
	H	-0.375575	1.448852	0.000000
	C	0.000000	0.421667	0.000000
	O	-1.031572	-0.439849	0.000000
AVTZ	H	-0.653735	-1.332777	0.000000
	O	1.160220	0.108900	0.000000
	H	-0.375451	1.450370	0.000000
	C	0.000000	0.421103	0.000000
	O	-1.029438	-0.439440	0.000000
AVQZ	H	-0.653250	-1.331125	0.000000
	O	1.157942	0.108805	0.000000
	H	-0.374783	1.449590	0.000000
		anti-HCOOH		
		x	y	z
	C	0.000000	0.384423	0.000000
	O	-0.895847	-0.623262	0.000000
def2QZVP	H	-1.786619	-0.259457	0.000000
	O	1.176923	0.194405	0.000000
	H	-0.461992	1.383774	0.000000
	C	0.000000	0.385682	0.000000
	O	-0.897988	-0.623662	0.000000
AVTZ	H	-1.790361	-0.257933	0.000000
	O	1.179387	0.193382	0.000000
	H	-0.460834	1.386081	0.000000
	C	0.000000	0.384982	0.000000
	O	-0.896086	-0.623021	0.000000
AVQZ	H	-1.787680	-0.260102	0.000000
	O	1.177187	0.193691	0.000000
	H	-0.461123	1.384852	0.000000

Table S5: *Cartesian coordinates of the geometries of C_3H_6 optimised with the DSD-PBEP86-D3BJ functional, in* Å.

		C_3H_6		
		x	y	z
	H	0.000000	1.553187	0.000000
	C	0.081182	0.470159	0.000000
	C	1.291857	-0.081703	0.000000
	H	2.188451	0.523436	0.000000
def2QZVP	H	1.418361	-1.158049	0.000000
	C	-1.202680	-0.296420	0.000000
	H	-1.019482	-1.370853	0.000000
	H	-1.804758	-0.049943	-0.877274
	H	-1.804758	-0.049943	0.877274
	H	1.551265	0.098326	0.000000
	C	0.474521	-0.051169	0.000000
	C	0.000000	-1.296202	0.000000
	H	0.661801	-2.153115	0.000000
AVTZ	H	-1.067163	-1.490843	0.000000
	C	-0.372063	1.183073	0.000000
	H	-1.433972	0.932017	0.000000
	H	-0.163322	1.799712	-0.878462
	H	-0.163322	1.799712	0.878462

Table S6: *Calculated harmonic frequencies and mode assignments for the N_2 and O_2. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *and zero-point energies are in* $\mathrm{kJ\,mol}^{-1}$.

	N_2				O_2			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)
def2QZVP	ω_1	σ_g	2329	0	ω_1	σ_g	1590	0
		zpe	13.9			zpe	9.5	
AVTZ	ω_1	σ_g	2319	0	ω_1	σ_g	1573	0
		zpe	13.9			zpe	9.4	
AVQZ	ω_1	σ_g	2327	0	ω_1	σ_g	1591	0
		zpe	13.9			zpe	9.5	

Table S7: *Calculated harmonic frequencies and mode assignments for the HCCH. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *and zero-point energies are in* $\mathrm{kJ\,mol}^{-1}$.

	HCCH			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)
def2QZVP	ω_1	π_g	637	0
	ω_2	π_g	637	0
	ω_3	π_u	762	96.1584
	ω_4	π_u	762	96.1584
	ω_5	σ_g	2018	0
	ω_6	σ_u	3430	89.6562
	ω_7	σ_g	3521	0
		zpe	70.4	
AVTZ	ω_1	π_g	637	0
	ω_2	π_g	637	0
	ω_3	π_u	760	94.2912
	ω_4	π_u	760	94.2912
	ω_5	σ_g	2017	0
	ω_6	σ_u	3427	89.3858
	ω_7	σ_g	3519	0
		zpe	70.3	
AVQZ	ω_1	π_g	631	0
	ω_2	π_g	631	0
	ω_3	π_u	764	95.0086
	ω_4	π_u	764	95.0086
	ω_5	σ_g	2014	0
	ω_6	σ_u	3421	90.0289
	ω_7	σ_g	3524	0
		zpe	70.3	

Table S8: *Calculated harmonic frequencies and mode assignments for the C_2H_4. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

	C_2H_4			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	b_{2u}	847	0.0559
	ω_2	b_{2g}	987	0
	ω_3	b_{3u}	991	96.7265
	ω_4	a_u	1077	0
	ω_5	b_{3g}	1259	0
	ω_6	a_g	1383	0
	ω_7	b_{1u}	1490	9.2607
	ω_8	a_g	1682	0
	ω_9	b_{1u}	3134	14.3934
	ω_{10}	a_g	3148	0
	ω_{11}	b_{3g}	3211	0
	ω_{12}	b_{2u}	3238	18.2044
		zpe	134.3	
AVTZ	ω_1	b_{2u}	845	0.0112
	ω_2	b_{2g}	982	0
	ω_3	b_{3u}	990	95.605
	ω_4	a_u	1066	0
	ω_5	b_{3g}	1256	0
	ω_6	a_g	1381	0
	ω_7	b_{1u}	1488	9.121
	ω_8	a_g	1679	0
	ω_9	b_{1u}	3130	14.3582
	ω_{10}	a_g	3146	0
	ω_{11}	b_{3g}	3206	0
	ω_{12}	b_{2u}	3234	18.087
		zpe	134.0	
AVQZ	ω_1	b_{2u}	847	0.0147
	ω_2	b_{2g}	989	0
	ω_3	b_{3u}	992	95.0699
	ω_4	a_u	1076	0
	ω_5	b_{3g}	1259	0
	ω_6	a_g	1382	0
	ω_7	b_{1u}	1490	9.236
	ω_8	a_g	1681	0
	ω_9	b_{1u}	3132	14.3126
	ω_{10}	a_g	3146	0
	ω_{11}	b_{3g}	3208	0
	ω_{12}	b_{2u}	3236	17.7833
		zpe	134.2	

Table S9: *Calculated harmonic frequencies and mode assignments for the syn-HCOOH. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *and zero-point energies are in* $\mathrm{kJ\,mol}^{-1}$.

	syn-HCOOH			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)
def2QZVP	ω_1	a'	631	42.8576
	ω_2	a''	680	139.6173
	ω_3	a''	1064	2.2978
	ω_4	a'	1131	258.6051
	ω_5	a'	1311	10.7484
	ω_6	a'	1414	2.1165
	ω_7	a'	1801	349.9734
	ω_8	a'	3074	38.6537
	ω_9	a'	3752	67.9389
		zpe	88.9	
AVTZ	ω_1	a'	628	41.8438
	ω_2	a''	678	135.9755
	ω_3	a''	1061	2.5649
	ω_4	a'	1129	259.2305
	ω_5	a'	1308	10.1887
	ω_6	a'	1410	2.1837
	ω_7	a'	1793	353.6612
	ω_8	a'	3073	36.5412
	ω_9	a'	3733	67.0135
		zpe	88.6	
AVQZ	ω_1	a'	632	42.7646
	ω_2	a''	679	136.403
	ω_3	a''	1062	2.6452
	ω_4	a'	1138	260.9
	ω_5	a'	1312	13.475
	ω_6	a'	1412	2.1979
	ω_7	a'	1810	352.4324
	ω_8	a'	3097	36.1147
	ω_9	a'	3761	71.7799
		zpe	89.1	

Table S10: *Calculated harmonic frequencies and mode assignments for the anti-HCOOH. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

	anti-HCOOH			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a''	531	84.8941
	ω_2	a'	663	9.9889
	ω_3	a''	1044	0.0004
	ω_4	a'	1117	53.8717
	ω_5	a'	1281	309.5716
	ω_6	a'	1428	0.2462
	ω_7	a'	1845	286.9204
	ω_8	a'	2986	72.9278
	ω_9	a'	3819	66.3408
		zpe	88.0	
AVTZ	ω_1	a''	531	82.4527
	ω_2	a'	658	9.841
	ω_3	a''	1040	0.0276
	ω_4	a'	1114	55.7165
	ω_5	a'	1278	307.9854
	ω_6	a'	1422	0.3037
	ω_7	a'	1836	289.8965
	ω_8	a'	2986	68.5814
	ω_9	a'	3799	64.7155
		zpe	87.7	
AVQZ	ω_1	a''	532	83.8795
	ω_2	a'	663	10.0384
	ω_3	a''	1041	0.0379
	ω_4	a'	1122	51.3566
	ω_5	a'	1287	315.6214
	ω_6	a'	1424	0.2124
	ω_7	a'	1852	291.3314
	ω_8	a'	3011	67.0324
	ω_9	a'	3828	71.5515
		zpe	88.3	

Table S11: *Calculated harmonic frequencies and mode assignments for the C_3H_6. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

	C_3H_6			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a''	240	0.4944
	ω_2	a'	436	0.989
	ω_3	a''	608	12.1755
	ω_4	a'	936	3.1317
	ω_5	a''	956	45.1356
	ω_6	a'	962	2.8641
	ω_7	a''	1040	11.6772
	ω_8	a''	1085	3.188
	ω_9	a'	1203	0.2129
	ω_{10}	a'	1336	0.0264
	ω_{11}	a'	1422	1.6779
	ω_{12}	a'	1464	1.0468
	ω_{13}	a''	1495	6.4543
	ω_{14}	a'	1509	14.6895
	ω_{15}	a'	1702	13.9876
	ω_{16}	a'	3024	22.8269
	ω_{17}	a''	3077	16.5321
	ω_{18}	a'	3105	9.8699
	ω_{19}	a'	3131	18.4572
	ω_{20}	a'	3139	10.5356
	ω_{21}	a'	3222	14.9995
		zpe	209.9	
AVTZ	ω_1	a''	243	0.5103
	ω_2	a'	435	0.9905
	ω_3	a''	608	12.0366
	ω_4	a'	934	2.9633
	ω_5	a''	955	44.3972
	ω_6	a'	961	2.9805
	ω_7	a''	1038	12.3244
	ω_8	a''	1085	3.2642
	ω_9	a'	1202	0.1988
	ω_{10}	a'	1334	0.0231
	ω_{11}	a'	1421	1.5594
	ω_{12}	a'	1463	1.1066
	ω_{13}	a''	1496	6.4428
	ω_{14}	a'	1510	14.5494
	ω_{15}	a'	1698	14.3762
	ω_{16}	a'	3021	23.1078
	ω_{17}	a''	3073	16.3951
	ω_{18}	a'	3100	10.0625
	ω_{19}	a'	3127	19.4893
	ω_{20}	a'	3136	9.2531
	ω_{21}	a'	3217	15.2241
		zpe	209.7	

Table S12: *$X^-\cdots N_2$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots N}$	$R_{X\cdots\vert\vert\vert}$	$R_{N\equiv N}$	$\angle_{X\cdots\vert\vert\vert-N}$	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
$Cl^-\cdots N_2$	C_{2v} ($^1A_1$)	def2QZVP	3.550	3.507	1.100	90.0	-569.3954404	15.0	10.3	11.4
		AVTZ	3.562	3.519	1.102	90.0	-569.3697830	15.0	9.6	10.7
		AVQZ	3.567	3.524	1.100	90.0	-569.4004761	15.0	9.5	10.6
	C_{2v} ($^1A_1$)	def2QZVP	1.784	1.625	1.473	90.0	-569.0662056	11.8	-854.1	-856.2
		AVTZ	1.789	1.632	1.465	90.0	-569.044673	11.7	-844.0	-846.2
		AVQZ	1.781	1.625	1.460	90.0	-569.0754805	11.8	-843.8	-845.9
$Br^-\cdots N_2$	C_{2v} ($^1A_1$)	def2QZVP	3.751	3.710	1.100	90.0	-2682.870589	14.9	9.0	10.0
		AVTZ	3.755	3.714	1.102	90.0	-525.7036079	14.9	8.5	9.5
		AVQZ	3.753	3.712	1.100	90.0	-525.7583353	14.9	8.5	9.5
	C_{2v} ($^1A_1$)	def2QZVP	1.928	1.786	1.455	90.0	-2682.542289	11.3	-853.0	-855.6
		AVTZ	1.934	1.794	1.446	90.0	-525.3807198	11.2	-839.3	-842.0
		AVQZ	1.926	1.786	1.441	90.0	-525.4359308	11.3	-837.9	-840.6
$I^-\cdots N_2$	C_{2v} ($^1A_1$)	def2QZVP	4.053	4.015	1.100	90.0	-406.9600737	14.9	7.1	8.0
		AVTZ	4.041	4.003	1.102	90.0	-404.7504327	14.8	7.0	8.0
		AVQZ	4.048	4.010	1.100	90.0	-404.8059345	14.9	7.2	8.1
	C_{2v} ($^1A_1$)	def2QZVP	2.065	1.936	1.435	90.0	-406.6462360	11.2	-816.9	-819.7
		AVTZ	2.087	1.962	1.421	90.0	-404.4398739	11.0	-808.4	-811.2
		AVQZ	2.075	1.950	1.417	90.0	-404.4962983	11.1	-805.7	-808.6

Table S13: *$X\cdots N_2$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots N}$	$R_{X\cdots\vert\vert\vert}$	$R_{N\equiv N}$	$\angle_{X\cdots\vert\vert\vert-N}$	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
		def2QZVP	3.452	3.408	1.100	90.0	-569.2636164	14.7	1.7	2.5
	C_{2v} ($^2A_1$)	AVTZ	3.440	3.396	1.102	90.0	-569.2358274	14.7	2.0	2.8
		AVQZ	3.438	3.394	1.100	90.0	-569.2649119	14.7	1.8	2.6
		def2QZVP	3.090	3.640	1.100	180.0	-569.2645367	15.5	4.2	5.8
Cl$\cdots$N$_2$	C_∞ ($^2\Sigma$)	AVTZ	3.090	3.641	1.102	180.0	-569.2368121	15.6	4.5	6.3
		AVQZ	3.080	3.630	1.100	180.0	-569.2659032	15.6	4.4	6.0
		def2QZVP	1.826	1.710	1.284	90.0	-569.0855604	14.7	-465.7	-465.0
	C_{2v} ($^2A_2$)	AVTZ	1.832	1.715	1.286	90.0	-569.0580805	14.6	-464.7	-464.0
		AVQZ	1.826	1.709	1.284	90.0	-569.0878104	14.7	-463.2	-462.4
		def2QZVP	3.578	3.536	1.100	90.0	-2682.743574	14.7	2.0	2.7
	C_{2v} ($^2A_1$)	AVTZ	3.541	3.498	1.102	90.0	-525.5765349	14.7	2.5	3.3
		AVQZ	3.521	3.477	1.100	90.0	-525.6294864	14.7	2.5	3.2
		def2QZVP	3.213	3.763	1.100	180.0	-2682.744566	15.5	4.6	6.1
Br$\cdots$N$_2$	C_∞ ($^2\Sigma$)	AVTZ	3.178	3.729	1.102	180.0	-525.5776332	15.6	5.4	7.1
		AVQZ	3.163	3.713	1.100	180.0	-525.6306504	15.5	5.5	7.2
		def2QZVP	1.972	1.867	1.271	90.0	-2682.566674	14.1	-462.5	-462.3
	C_{2v} ($^2A_2$)	AVTZ	1.979	1.874	1.272	90.0	-525.4002369	14.0	-460.4	-460.2
		AVQZ	1.972	1.866	1.271	90.0	-525.4542589	14.1	-457.6	-457.4
		def2QZVP	3.780	3.740	1.100	90.0	-406.8394867	14.7	2.4	3.1
	C_{2v} ($^2A_1$)	AVTZ	3.754	3.713	1.102	90.0	-404.6298774	14.7	2.7	3.5
		AVQZ	3.763	3.723	1.100	90.0	-404.6833062	14.7	2.7	3.5
		def2QZVP	3.409	3.959	1.100	180.0	-406.8404464	15.5	4.9	6.4
I$\cdots$N$_2$	C_∞ ($^2\Sigma$)	AVTZ	3.403	3.954	1.102	180.0	-404.6309697	15.6	5.5	7.2
		AVQZ	3.376	3.925	1.100	180.0	-404.6844412	15.5	5.7	7.3
		def2QZVP	2.141	2.047	1.255	90.0	-406.6730168	13.8	-434.7	-434.9
	C_{2v} ($^2A_2$)	AVTZ	2.158	2.064	1.257	90.0	-404.4623282	13.7	-437.2	-437.5
		AVQZ	2.147	2.053	1.255	90.0	-404.5171476	13.8	-433.5	-433.7

Table S14: *$X^-\cdots N_2$ complex VDEs from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			E_{VDE}	$VDE_{^2P_{3/2}}$	$VDE_{^2P_{1/2}}$	$ADE_{^2P_{3/2}}$	$ADE_{^2P_{1/2}}$
			E_h	eV	eV	eV	eV
		def2QZVP	-569.2635983	3.692	3.801	3.699	3.808
$Cl^-\cdots N_2$	C_{2v} ($^1A_1$)	pVTZ	-569.2357978	3.681	3.790	3.689	3.798
		pVQZ	-569.2648817	3.683	3.792	3.690	3.799
		def2QZVP	-2682.743523	3.428	3.885	3.434	3.891
$Br^-\cdots N_2$	C_{2v} ($^1A_1$)	pVTZ	-525.5764473	3.418	3.875	3.424	3.881
		pVQZ	-525.6293851	3.419	3.876	3.425	3.882
		def2QZVP	-406.8393688	3.101	4.043	3.106	4.048
$I^-\cdots N_2$	C_{2v} ($^1A_1$)	pVTZ	-404.6297293	3.098	4.040	3.103	4.045
		pVQZ	-404.6831711	3.100	4.042	3.104	4.046

Table S15: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots N_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Cl^-\cdots N_2$ C_{2v} ($^1A_1$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	72	15.0073	Intermolecular stretch
	ω_2	b_2	108	0.0045	Intermolecular bend
	ω_3	a_1	2329	0.9975	N_2 stretch
		zpe	15		
AVTZ	ω_1	a_1	71	14.0865	Intermolecular stretch
	ω_2	b_2	116	0.002	Intermolecular bend
	ω_3	a_1	2319	1.7023	N_2 stretch
		zpe	15		
AVQZ	ω_1	a_1	70	14.0712	Intermolecular stretch
	ω_2	b_2	109	0.0012	Intermolecular bend
	ω_3	a_1	2327	1.6745	N_2 stretch
		zpe	15		
	$Cl^-\cdots N_2$ C_{2v} ($^1A_1$) Molecular Anion				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	504	1.6905	Cl−N symmetric stretch
	ω_2	b_2	559	4.8361	Cl−N asymmetric stretch
	ω_3	a_1	907	0.3536	N_2 stretch
		zpe	11.8		
AVTZ	ω_1	a_1	507	0.1693	Cl−N symmetric stretch
	ω_2	b_2	553	17.445	Cl−N asymmetric stretch
	ω_3	a_1	895	1.2473	N_2 stretch
		zpe	11.7		
AVQZ	ω_1	a_1	511	0.029	Cl−N symmetric stretch
	ω_2	b_2	559	22.1362	Cl−N asymmetric stretch
	ω_3	a_1	902	0.936	N_2 stretch
		zpe	11.8		

Table S16: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots N_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			$Br^-\cdots N_2$		
			C_{2v} ($^1A_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	57	4.0559	Intermolecular stretch
	ω_2	b_2	109	0.0877	Intermolecular bend
	ω_3	a_1	2329	0.7423	N_2 stretch
		zpe	14.9		
AVTZ	ω_1	a_1	56	3.6149	Intermolecular stretch
	ω_2	b_2	116	0.1073	Intermolecular bend
	ω_3	a_1	2319	1.4442	N_2 stretch
		zpe	14.9		
AVQZ	ω_1	a'	56	3.6124	Intermolecular stretch
	ω_2	a'	109	0.1133	Intermolecular bend
	ω_3	a'	2326	1.4457	N_2 stretch
		zpe	14.9		
			$Br^-\cdots N_2$		
			C_{2v} ($^1A_1$) Molecular Anion		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	463	1.0411	Cl−N symmetric stretch
	ω_2	b_2	513	8.9023	Cl−N asymmetric stretch
	ω_3	a_1	910	0.2415	N_2 stretch
		zpe	11.3		
AVTZ	ω_1	a_1	464	3.812	Cl−N symmetric stretch
	ω_2	b_2	509	27.7077	Cl−N asymmetric stretch
	ω_3	a_1	893	2.2495	N_2 stretch
		zpe	11.2		
AVQZ	ω_1	a_1	469	4.589	Cl−N symmetric stretch
	ω_2	b_2	516	38.4954	Cl−N asymmetric stretch
	ω_3	a_1	899	2.1305	N_2 stretch
		zpe	11.3		

Table S17: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots N_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			$I^-\cdots N_2$		
			C_{2v} ($^1A_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	46	1.6224	Intermolecular stretch
	ω_2	b_2	110	0.1865	Intermolecular bend
	ω_3	a_1	2329	0.5022	N_2 stretch
		zpe	14.9		
AVTZ	ω_1	a_1	46	1.4147	Intermolecular stretch
	ω_2	b_2	117	0.1717	Intermolecular bend
	ω_3	a_1	2319	1.0515	N_2 stretch
		zpe	14.8		
AVQZ	ω_1	a_1	46	1.4231	Intermolecular stretch
	ω_2	b_2	110	0.1744	Intermolecular bend
	ω_3	a_1	2326	1.0342	N_2 stretch
		zpe	14.9		
			$I^-\cdots N_2$		
			C_{2v} ($^1A_1$) Molecular Anion		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	454	10.9117	Cl−N symmetric stretch
	ω_2	b_2	495	24.3173	Cl−N asymmetric stretch
	ω_3	a_1	916	0.7516	N_2 stretch
		zpe	11.2		
AVTZ	ω_1	a_1	453	17.4854	Cl−N symmetric stretch
	ω_2	b_2	481	48.1854	Cl−N asymmetric stretch
	ω_3	a_1	905	0.4241	N_2 stretch
		zpe	11		
AVQZ	ω_1	a_1	456	18.5728	Cl−N symmetric stretch
	ω_2	b_2	488	65.1373	Cl−N asymmetric stretch
	ω_3	a_1	910	0.3125	N_2 stretch
		zpe	11.1		

Table S18: *Calculated harmonic frequencies and mode assignments for the Cl···N_2 complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

			Cl···N_2		
			C_{2v} ($^2A_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a_1	44	0.0637	Intermolecular stretch
	ω_2	b_2	85	0.0559	Intermolecular bend
	ω_3	a_1	2326	0.1393	N_2 stretch
		zpe	14.7		
AVTZ	ω_1	a_1	47	0.0655	Intermolecular stretch
	ω_2	b_2	97	0.0438	Intermolecular bend
	ω_3	a_1	2316	0.1371	N_2 stretch
		zpe	14.7		
AVQZ	ω_1	a_1	46	0.0673	Intermolecular stretch
	ω_2	b_2	86	0.0462	Intermolecular bend
	ω_3	a_1	2324	0.1368	N_2 stretch
		zpe	14.7		
			Cl···N_2		
			C_{∞} ($^2\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	σ	59	0.4721	Intermolecular bend
	ω_2	π	105	0.0115	Degenerate intermolecular bend
	ω_3	π	105	0.0115	Degenerate intermolecular bend
	ω_4	σ	2330	0.2437	N_2 stretch
		zpe	15.5		
AVTZ	ω_1	σ	59	0.459	Intermolecular bend
	ω_2	π	115	0.012	Degenerate intermolecular bend
	ω_3	π	115	0.012	Degenerate intermolecular bend
	ω_4	σ	2320	0.2338	N_2 stretch
		zpe	15.6		
AVQZ	ω_1	σ	60	0.4866	Intermolecular bend
	ω_2	π	107	0.0133	Degenerate intermolecular bend
	ω_3	π	107	0.0133	Degenerate intermolecular bend
	ω_4	σ	2328	0.2419	N_2 stretch
		zpe	15.6		
			Cl···N_2		
			C_{2v} ($^1A_1$) Neutral Molecule		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	496	0.3686	Cl−N asymmetric stretch
	ω_2	a_1	577	2.9976	Cl−N symmetric stretch
	ω_3	a_1	1387	1.541	N_2 stretch
		zpe	14.7		
AVTZ	ω_1	b_2	494	0.5564	Cl−N asymmetric stretch
	ω_2	a_1	575	2.6304	Cl−N symmetric stretch
	ω_3	a_1	1376	1.7213	N_2 stretch
		zpe	14.6		
AVQZ	ω_1	b_2	498	0.6094	Cl−N asymmetric stretch
	ω_2	a_1	578	2.6496	Cl−N symmetric stretch
	ω_3	a_1	1384	1.4423	N_2 stretch
		zpe	14.7		

Table S19: *Calculated harmonic frequencies and mode assignments for the $Br\cdots N_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			$Br\cdots N_2$		
			C_{2v} ($^2A_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	39	0.0543	Intermolecular stretch
	ω_2	b_2	86	0.0412	Intermolecular bend
	ω_3	a_1	2326	0.1255	N_2 stretch
		zpe	14.7		
AVTZ	ω_1	a_1	43	0.0628	Intermolecular stretch
	ω_2	b_2	97	0.0208	Intermolecular bend
	ω_3	a_1	2315	0.129	N_2 stretch
		zpe	14.7		
AVQZ	ω_1	a_1	44	0.0712	Intermolecular stretch
	ω_2	b_2	87	0.0199	Intermolecular bend
	ω_3	a_1	2323	0.1363	N_2 stretch
		zpe	14.7		
			$Br\cdots N_2$		
			C_{∞} ($^2\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	52	0.3871	Intermolecular bend
	ω_2	π	105	0.0148	Degenerate intermolecular bend
	ω_3	π	105	0.0148	Degenerate intermolecular bend
	ω_4	σ	2330	0.208	N_2 stretch
		zpe	15.5		
AVTZ	ω_1	σ	55	0.4193	Intermolecular bend
	ω_2	π	115	0.02	Degenerate intermolecular bend
	ω_3	π	115	0.02	Degenerate intermolecular bend
	ω_4	σ	2320	0.2146	N_2 stretch
		zpe	15.6		
AVQZ	ω_1	σ	58	0.449	Intermolecular bend
	ω_2	π	107	0.0219	Degenerate intermolecular bend
	ω_3	π	107	0.0219	Degenerate intermolecular bend
	ω_4	σ	2328	0.2254	N_2 stretch
		zpe	15.5		
			$Br\cdots N_2$		
			C_{2v} ($^1A_1$) Neutral Molecule		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	452	1.1287	Br−N asymmetric stretch
	ω_2	a_1	486	0.0349	Br−N symmetric stretch
	ω_3	a_1	1416	1.1292	N_2 stretch
		zpe	14.1		
AVTZ	ω_1	b_2	453	1.4864	Br−N asymmetric stretch
	ω_2	a_1	483	0.0058	Br−N symmetric stretch
	ω_3	a_1	1407	1.634	N_2 stretch
		zpe	14		
AVQZ	ω_1	b_2	459	1.5664	Br−N asymmetric stretch
	ω_2	a_1	487	0.0099	Br−N symmetric stretch
	ω_3	a_1	1413	1.2875	N_2 stretch
		zpe	14.1		

Table S20: *Calculated harmonic frequencies and mode assignments for the I···N_2 complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			I···N_2		
			C_{2v} ($^2A_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	40	0.0592	Intermolecular stretch
	ω_2	b_2	89	0.0098	Intermolecular bend
	ω_3	a_1	2326	0.111	N_2 stretch
		zpe	14.7		
AVTZ	ω_1	a_1	42	0.0636	Intermolecular stretch
	ω_2	b_2	99	0.0062	Intermolecular bend
	ω_3	a_1	2315	0.1028	N_2 stretch
		zpe	14.7		
AVQZ	ω_1	a_1	41	0.0621	Intermolecular stretch
	ω_2	b_2	89	0.0078	Intermolecular bend
	ω_3	a_1	2323	0.1006	N_2 stretch
		zpe	14.7		
			I···N_2		
			C_∞ ($^2\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	50	0.363	Intermolecular bend
	ω_2	π	104	0.0373	Degenerate intermolecular bend
	ω_3	π	104	0.0373	Degenerate intermolecular bend
	ω_4	σ	2329	0.1224	N_2 stretch
		zpe	15.5		
AVTZ	ω_1	σ	52	0.3667	Intermolecular bend
	ω_2	π	114	0.0291	Degenerate intermolecular bend
	ω_3	π	114	0.0291	Degenerate intermolecular bend
	ω_4	σ	2320	0.1219	N_2 stretch
		zpe	15.6		
AVQZ	ω_1	σ	52	0.4089	Intermolecular bend
	ω_2	π	106	0.0329	Degenerate intermolecular bend
	ω_3	π	106	0.0329	Degenerate intermolecular bend
	ω_4	σ	2327	0.1341	N_2 stretch
		zpe	15.5		
			I···N_2		
			C_{2v} ($^1A_1$) Neutral Molecule		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	407	3.6661	I–N asymmetric stretch
	ω_2	a_1	435	2.3388	I–N symmetric stretch
	ω_3	a_1	1458	0.0268	N_2 stretch
		zpe	13.8		
AVTZ	ω_1	b_2	400	3.7069	I–N asymmetric stretch
	ω_2	a_1	433	2.7182	I–N symmetric stretch
	ω_3	a_1	1452	0.0488	N_2 stretch
		zpe	13.7		
AVQZ	ω_1	b_2	407	3.8895	I–N asymmetric stretch
	ω_2	a_1	436	2.5425	I–N symmetric stretch
	ω_3	a_1	1457	0.0017	N_2 stretch
		zpe	13.8		

Table S21: *Cartesian coordinates of the geometries of halide-nitrogen complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots N_2$			$Br^-\cdots N_2$			$I^-\cdots N_2$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^1A_1$)	def2QZVP	X	0.000000	0.000000	-1.583880	0.000000	0.000000	-1.060026	0.000000	0.000000	0.839020
		N	0.000000	-0.549796	1.923282	0.000000	-0.549808	2.650065	0.000000	-0.549838	-3.176289
		N	0.000000	0.549796	1.923282	0.000000	0.549808	2.650065	0.000000	0.549838	-3.176289
	AVTZ	X	0.000000	0.000000	1.589098	0.000000	0.000000	-1.061265	0.000000	0.000000	-0.836491
		N	0.000000	0.550974	-1.929619	0.000000	-0.550989	2.653163	0.000000	-0.551001	3.166717
		N	0.000000	-0.550974	-1.929619	0.000000	0.550989	2.653163	0.000000	0.551001	3.166717
	AVQZ	X	0.000000	0.000000	1.591687	0.000000	0.000000	-1.060653	0.000000	0.000000	0.838004
		N	0.000000	0.549948	-1.932763	0.000000	-0.549963	2.651567	0.000000	-0.549974	-3.172444
		N	0.000000	-0.549948	-1.932763	0.000000	0.549963	2.651697	0.000000	0.549974	-3.172444
			x	y	z	x	y	z	x	y	z
C_{2v} ($^1A_1$)	def2QZVP	X	0.000000	0.000000	0.733734	0.000000	0.000000	0.510172	0.000000	0.000000	0.404622
		N	0.000000	-0.736692	-0.890963	0.000000	-0.727693	-1.275431	0.000000	-0.717268	-1.531782
		N	0.000000	0.736692	-0.890963	0.000000	0.727693	-1.275431	0.000000	0.717268	-1.531782
	AVTZ	X	0.000000	0.000000	0.737106	0.000000	0.000000	0.512599	0.000000	0.000000	0.410056
		N	0.000000	-0.732619	-0.895058	0.000000	0.722812	-1.281497	0.000000	-0.710523	-1.552356
		N	0.000000	0.732619	-0.895058	0.000000	-0.722812	-1.281497	0.000000	0.710523	-1.552356
	AVQZ	X	0.000000	0.000000	0.733819	0.000000	0.000000	0.510399	0.000000	0.000000	0.407469
		N	0.000000	-0.730168	-0.891066	0.000000	-0.720416	-1.275998	0.000000	-0.708427	-1.542560
		N	0.000000	0.730168	-0.891066	0.000000	0.720416	-1.275998	0.000000	0.708427	-1.542560

Table S22: *Cartesian coordinates of the geometries of halogen-nitrogen complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots N_2$			$Br\cdots N_2$			$I\cdots N_2$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^2A_1$)	def2QZVP	X	0.000000	0.000000	1.539002	0.000000	0.000000	1.010210	0.000000	0.000000	0.781461
		N	0.000000	0.550032	-1.868788	0.000000	0.550040	-2.525524	0.000000	0.550049	-2.958388
		N	0.000000	-0.550032	-1.868788	0.000000	-0.550040	-2.525524	0.000000	-0.550049	-2.958388
	AVTZ	X	0.000000	0.000000	1.533680	0.000000	0.000000	0.999523	0.000000	0.000000	0.775841
		N	0.000000	0.551182	-1.862326	0.000000	0.551202	-2.498806	0.000000	0.551201	-2.937114
		N	0.000000	-0.551182	-1.862326	0.000000	-0.551202	-2.498806	0.000000	-0.551201	-2.937114
	AVQZ	X	0.000000	0.000000	1.532795	0.000000	0.000000	0.993570	0.000000	0.000000	0.777890
		N	0.000000	0.550149	-1.861252	0.000000	0.550176	-2.483925	0.000000	0.550167	-2.944868
		N	0.000000	-0.550149	-1.861252	0.000000	-0.550176	-2.483925	0.000000	-0.550167	-2.944868
			x	y	z	x	y	z	x	y	z
C_∞ ($^2\Sigma$)	def2QZVP	X	0.000000	0.000000	1.643833	0.000000	0.000000	1.075012	0.000000	0.000000	0.827244
		N	0.000000	0.000000	-1.446279	0.000000	0.000000	-2.137722	0.000000	0.000000	-2.581886
		N	0.000000	0.000000	-2.545888	0.000000	0.000000	-3.237336	0.000000	0.000000	-3.681537
	AVTZ	X	0.000000	0.000000	1.644099	0.000000	0.000000	1.065363	0.000000	0.000000	0.826239
		N	0.000000	0.000000	-1.445472	0.000000	0.000000	-2.112473	0.000000	0.000000	-2.576955
		N	0.000000	0.000000	-2.547339	0.000000	0.000000	-3.214340	0.000000	0.000000	-3.678854
	AVQZ	X	0.000000	0.000000	1.639142	0.000000	0.000000	1.060841	0.000000	0.000000	0.820245
		N	0.000000	0.000000	-1.440475	0.000000	0.000000	-2.102192	0.000000	0.000000	-2.555285
		N	0.000000	0.000000	-2.540297	0.000000	0.000000	-3.202014	0.000000	0.000000	-3.655138
			x	y	z	x	y	z	x	y	z
C_{2v} ($^2A_2$)	def2QZVP	X	0.000000	0.000000	0.772132	0.000000	0.000000	0.533520	0.000000	0.000000	0.427634
		N	0.000000	0.641839	-0.937589	0.000000	0.635333	-1.333799	0.000000	0.627633	-1.618901
		N	0.000000	-0.641839	-0.937589	0.000000	-0.635333	-1.333799	0.000000	-0.627633	-1.618901
	AVTZ	X	0.000000	0.000000	0.774634	0.000000	0.000000	0.535362	0.000000	0.000000	0.431369
		N	0.000000	0.643051	-0.940627	0.000000	0.636249	-1.338406	0.000000	0.628272	-1.633038
		N	0.000000	-0.643051	-0.940627	0.000000	-0.636249	-1.338406	0.000000	-0.628272	-1.633038
	AVQZ	X	0.000000	0.000000	0.771904	0.000000	0.000000	0.533253	0.000000	0.000000	0.428999
		N	0.000000	0.642039	-0.937312	0.000000	-0.635355	-1.333132	0.000000	0.627461	-1.624068
		N	0.000000	-0.642039	-0.937312	0.000000	0.635355	-1.333132	0.000000	-0.627461	-1.624068

Table S23: *$X^-\cdots HCCH$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots H}$	R_{H-C}	$R_{C\equiv C}$	$\angle_{X\cdots\vert\vert\vert-C}$	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
		def2QZVP	2.227	1.095	1.210	180.0	-537.2167692	72.4	49.5	51.6
$Cl^-\cdots HCCH$	C_∞ ($^1\Sigma$)	AVTZ	2.234	1.094	1.212	180.0	-537.1947703	72.6	47.4	49.7
		AVQZ	2.238	1.094	1.210	180.0	-537.2204020	72.4	46.6	48.8
		def2QZVP	2.444	1.088	1.209	180.0	-2650.6896270	72.4	42.1	44.1
$Br^-\cdots HCCH$	C_∞ ($^1\Sigma$)	AVTZ	2.429	1.088	1.211	180.0	-493.5268837	72.8	41.9	44.3
		AVQZ	2.417	1.089	1.209	180.0	-493.5765940	72.6	41.3	43.6
		def2QZVP	2.748	1.082	1.208	180.0	-374.7762103	72.4	32.6	34.6
$I^-\cdots HCCH$	C_∞ ($^1\Sigma$)	AVTZ	2.723	1.082	1.210	180.0	-372.5712921	72.4	34.0	36.2
		AVQZ	2.726	1.082	1.208	180.0	-372.6217568	72.4	33.5	35.7

Table S24: *X···HCCH complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H}	R_{H-C}	$R_{C=C}$	$\angle_{X\cdots\vert\vert\vert-C}$	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
		def2QZVP	2.862	1.064	1.204	180.0	-537.0706373	72.1	3.3	5.0
	C_∞ ($^2\Sigma$)	AVTZ	2.808	1.064	1.206	180.0	-537.0472343	72.0	4.2	5.9
		AVQZ	2.839	1.064	1.204	180.0	-537.0714364	72.1	3.7	5.5
Cl···HCCH			$R_{X-\vert\vert}$							
		def2QZVP	2.599	1.064	1.211	90.0	-537.0784914	72.2	24.0	25.8
	C_{2v} ($^2A_1$)	AVTZ	2.598	1.064	1.213	90.0	-537.0550247	72.4	24.6	26.7
		AVQZ	2.590	1.064	1.211	90.0	-537.0796033	72.2	25.1	27.1
			R_{X-H}							
		def2QZVP	2.974	1.064	1.204	180.0	-2650.550701	72.0	3.8	5.4
	C_∞ ($^2\Sigma$)	AVTZ	2.873	1.065	1.206	180.0	-493.388187	71.9	5.4	6.9
		AVQZ	2.921	1.064	1.204	180.0	-493.4362775	71.9	5.1	6.8
Br···HCCH			$R_{X-\vert\vert}$							
		def2QZVP	2.804	1.064	1.209	90.0	-2650.557247	72.1	21.0	22.8
	C_{2v} ($^2A_1$)	AVTZ	2.792	1.064	1.211	90.0	-493.3946638	72.4	22.4	24.5
		AVQZ	2.782	1.064	1.209	90.0	-493.4432061	72.3	23.3	25.3
			R_{X-H}							
		def2QZVP	3.170	1.064	1.204	180.0	-374.6465738	71.8	4.2	5.6
	C_∞ ($^2\Sigma$)	AVTZ	3.082	1.065	1.206	180.0	-372.4416306	71.8	5.8	7.2
		AVQZ	3.101	1.065	1.204	180.0	-372.49021	71.9	5.6	7.2
I···HCCH			$R_{X-\vert\vert}$							
		def2QZVP	3.079	1.064	1.207	90.0	-374.6517729	72.1	17.8	19.5
	C_{2v} ($^2A_1$)	AVTZ	3.088	1.064	1.209	90.0	-372.4465497	72.3	18.7	20.6
		AVQZ	3.062	1.064	1.208	90.0	-372.4956211	72.2	19.8	21.8

Table S25: *$X^-\cdots$HCCH complex VDEs from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			E_{VDE}	$VDE_{^2P_{3/2}}$	$VDE_{^2P_{1/2}}$	$ADE_{^2P_{3/2}}$	$ADE_{^2P_{1/2}}$
			E_h	eV	eV	eV	eV
$Cl^-\cdots$HCCH	C_∞ ($^1\Sigma$)	def2QZVP	-537.0663205	4.177	4.286	4.088	4.197
		AVTZ	-537.0433570	4.135	4.244	4.056	4.165
		AVQZ	-537.0675151	4.133	4.242	4.054	4.163
$Br^-\cdots$HCCH	C_∞ ($^1\Sigma$)	def2QZVP	-2650.548089	3.804	4.261	3.756	4.213
		AVTZ	-493.3859097	3.775	4.232	3.733	4.190
		AVQZ	-493.4337816	3.778	4.235	3.732	4.189
$I^-\cdots$HCCH	C_∞ ($^1\Sigma$)	def2QZVP	-374.6452678	3.365	4.307	3.349	4.291
		AVTZ	-372.4404508	3.358	4.300	3.345	4.287
		AVQZ	-372.4890118	3.356	4.298	3.342	4.284

Table S26: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots HCCH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Cl^-\cdots HCCH$ C_∞ ($^1\Sigma$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	158	36.2239	Intermolecular stretch
	ω_2	π	175	0.0072	Intermolecular bend
	ω_3	π	175	0.0072	Intermolecular bend
	ω_4	π	646	40.1775	HCCH asymmetric bend
	ω_5	π	646	40.1775	HCCH asymmetric bend
	ω_6	π	951	41.1917	HCCH symmetric bend
	ω_7	π	951	41.1917	HCCH symmetric bend
	ω_8	σ	1942	200.0991	C=C stretch
	ω_9	σ	3004	1036.1935	X−HC stretch
	ω_{10}	σ	3463	3.4646	CH stretch
		zpe	72.4		
AVTZ	ω_1	σ	157	35.6147	Intermolecular stretch
	ω_2	π	180	0.0139	Intermolecular bend
	ω_3	π	180	0.0139	Intermolecular bend
	ω_4	π	647	39.3462	HCCH asymmetric bend
	ω_5	π	647	39.3462	HCCH asymmetric bend
	ω_6	π	954	34.5997	HCCH symmetric bend
	ω_7	π	954	34.5997	HCCH symmetric bend
	ω_8	σ	1939	201.5187	C=C stretch
	ω_9	σ	3021	1057.398	X−HC stretch
	ω_{10}	σ	3459	2.0068	CH stretch
		zpe	72.6		
AVQZ	ω_1	σ	155	35.494	Intermolecular stretch
	ω_2	π	174	0.0191	Intermolecular bend
	ω_3	π	174	0.0191	Intermolecular bend
	ω_4	π	648	39.084	HCCH asymmetric bend
	ω_5	π	648	39.084	HCCH asymmetric bend
	ω_6	π	944	33.1817	HCCH symmetric bend
	ω_7	π	944	33.1816	HCCH symmetric bend
	ω_8	σ	1943	198.6608	C=C stretch
	ω_9	σ	3020	1044.7302	X−HC stretch
	ω_{10}	σ	3460	3.2184	CH stretch
		zpe	72.4		

Table S27: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots HCCH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br^-\cdots HCCH$ C_∞ ($^1\Sigma$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	122	11.9635	Intermolecular stretch
	ω_2	π	165	0.0683	Intermolecular bend
	ω_3	π	165	0.0683	Intermolecular bend
	ω_4	π	650	36.2362	HCCH asymmetric bend
	ω_5	π	650	36.2362	HCCH asymmetric bend
	ω_6	π	916	42.5262	HCCH symmetric bend
	ω_7	π	916	42.5262	HCCH symmetric bend
	ω_8	σ	1956	147.0963	C=C stretch
	ω_9	σ	3095	897.1692	X−HC stretch
	ω_{10}	σ	3465	2.5913	CH stretch
		zpe	72.4		
AVTZ	ω_1	σ	126	11.6269	Intermolecular stretch
	ω_2	π	174	0.3301	Intermolecular bend
	ω_3	π	174	0.3301	Intermolecular bend
	ω_4	π	651	38.1887	HCCH asymmetric bend
	ω_5	π	651	38.1887	HCCH asymmetric bend
	ω_6	π	939	29.9404	HCCH symmetric bend
	ω_7	π	939	29.9404	HCCH symmetric bend
	ω_8	σ	1952	157.2776	C=C stretch
	ω_9	σ	3098	949.7586	X−HC stretch
	ω_{10}	σ	3462	1.4997	CH stretch
		zpe	72.8		
AVQZ	ω_1	σ	126	11.8294	Intermolecular stretch
	ω_2	π	166	0.3284	Intermolecular bend
	ω_3	π	166	0.3284	Intermolecular bend
	ω_4	π	659	38.4296	HCCH asymmetric bend
	ω_5	π	659	38.4296	HCCH asymmetric bend
	ω_6	π	929	28.5729	HCCH symmetric bend
	ω_7	π	929	28.5729	HCCH symmetric bend
	ω_8	σ	1954	161.8224	HCCH stretch
	ω_9	σ	3087	961.8901	X−HC stretch
	ω_{10}	σ	3463	2.5801	CH stretch
		zpe	72.6		

Table S28: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots HCCH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I^-\cdots HCCH$ C_∞ ($^1\Sigma$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	96	5.1021	Intermolecular stretch
	ω_2	π	155	0.2184	Intermolecular bend
	ω_3	π	155	0.2184	Intermolecular bend
	ω_4	π	654	33.2069	HCCH asymmetric bend
	ω_5	π	654	33.2069	HCCH asymmetric bend
	ω_6	π	882	37.6393	HCCH symmetric bend
	ω_7	π	882	37.6393	HCCH symmetric bend
	ω_8	σ	1970	105.0683	C=C stretch
	ω_9	σ	3183	756.1346	X−HC stretch
	ω_{10}	σ	3469	1.6545	CH stretch
		zpe	72.4		
AVTZ	ω_1	σ	101	4.9837	Intermolecular stretch
	ω_2	π	160	0.4863	Intermolecular bend
	ω_3	π	160	0.4863	Intermolecular bend
	ω_4	π	652	32.4392	HCCH asymmetric bend
	ω_5	π	652	32.4392	HCCH asymmetric bend
	ω_6	π	890	31.425	HCCH symmetric bend
	ω_7	π	890	31.425	HCCH symmetric bend
	ω_8	σ	1964	113.7152	C=C stretch
	ω_9	σ	3176	794.6119	X−HC stretch
	ω_{10}	σ	3466	0.8813	CH stretch
		zpe	72.4		
AVQZ	ω_1	σ	100	5.0038	Intermolecular stretch
	ω_2	π	155	0.4579	Intermolecular bend
	ω_3	π	155	0.4579	Intermolecular bend
	ω_4	π	658	33.4378	HCCH asymmetric bend
	ω_5	π	658	33.4378	HCCH asymmetric bend
	ω_6	π	888	29.8602	HCCH symmetric bend
	ω_7	π	888	29.8602	HCCH symmetric bend
	ω_8	σ	1968	112.3375	C=C stretch
	ω_9	σ	3176	784.8093	X−HC stretch
	ω_{10}	σ	3465	1.6412	CH stretch
		zpe	72.4		

Table S29: *Calculated harmonic frequencies and mode assignments for the Cl···HCCH complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	Cl···HCCH C_∞ ($^2\Sigma$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	57	0.1258	Intermolecular stretch
	ω_2	π	104	0.0377	Intermolecular bend
	ω_3	π	109	0.1129	Intermolecular bend
	ω_4	π	664	0.5109	HCCH asymmetric bend
	ω_5	π	666	1.2491	HCCH asymmetric bend
	ω_6	π	781	90.1171	HCCH symmetric bend
	ω_7	π	785	85.1233	HCCH symmetric bend
	ω_8	σ	2007	1.2608	C=C stretch
	ω_9	σ	3401	152.3152	X−HC stretch
	ω_{10}	σ	3494	1.867	CH stretch
		zpe	72.2		
AVTZ	ω_1	σ	64	0.1327	Intermolecular stretch
	ω_2	π	114	0.0532	Intermolecular bend
	ω_3	π	119	0.1607	Intermolecular bend
	ω_4	π	665	0.8408	HCCH asymmetric bend
	ω_5	π	666	1.9224	HCCH asymmetric bend
	ω_6	π	788	88.293	HCCH symmetric bend
	ω_7	π	792	82.0002	HCCH symmetric bend
	ω_8	σ	2002	1.4636	C=C stretch
	ω_9	σ	3396	159.283	X−HC stretch
	ω_{10}	σ	3497	3.7276	CH stretch
		zpe	72.4		
AVQZ	ω_1	σ	59	0.1266	Intermolecular stretch
	ω_2	π	105	0.0482	Intermolecular bend
	ω_3	π	111	0.1421	Intermolecular bend
	ω_4	π	667	0.6021	HCCH asymmetric bend
	ω_5	π	668	1.4777	HCCH asymmetric bend
	ω_6	π	781	87.3219	HCCH symmetric bend
	ω_7	π	785	81.6343	HCCH symmetric bend
	ω_8	σ	2006	1.3698	C=C stretch
	ω_9	σ	3398	155.8578	X−HC stretch
	ω_{10}	σ	3491	2.0886	CH stretch
		zpe	72.2		

Table S30: *Calculated harmonic frequencies and mode assignments for the Br···HCCH complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	Br···HCCH C_∞ ($^2\Sigma$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	σ	51	0.104	Intermolecular stretch
	ω_2	π	104	0.0528	Intermolecular bend
	ω_3	π	109	0.1494	Intermolecular bend
	ω_4	π	665	0.6803	HCCH asymmetric bend
	ω_5	π	666	1.5808	HCCH asymmetric bend
	ω_6	π	781	88.2055	HCCH symmetric bend
	ω_7	π	785	82.5714	HCCH symmetric bend
	ω_8	σ	2007	1.8296	C=C stretch
	ω_9	σ	3399	166.6195	X−HC stretch
	ω_{10}	σ	3492	2.0565	CH stretch
		zpe	72.1		
AVTZ	ω_1	σ	62	0.1127	Intermolecular stretch
	ω_2	π	116	0.099	Intermolecular bend
	ω_3	π	122	0.2683	Intermolecular bend
	ω_4	π	668	1.7655	HCCH asymmetric bend
	ω_5	π	669	3.4562	HCCH asymmetric bend
	ω_6	π	791	84.5822	HCCH symmetric bend
	ω_7	π	797	76.5271	HCCH symmetric bend
	ω_8	σ	2001	2.4292	C=C stretch
	ω_9	σ	3391	184.4347	X−HC stretch
	ω_{10}	σ	3493	4.0307	CH stretch
		zpe	72.4		
AVQZ	ω_1	σ	56	0.1053	Intermolecular stretch
	ω_2	π	108	0.0877	Intermolecular bend
	ω_3	π	114	0.2292	Intermolecular bend
	ω_4	π	671	1.4347	HCCH asymmetric bend
	ω_5	π	672	2.8585	HCCH asymmetric bend
	ω_6	π	784	83.9909	HCCH symmetric bend
	ω_7	π	789	76.8878	HCCH symmetric bend
	ω_8	σ	2005	2.1632	C=C stretch
	ω_9	σ	3395	176.3143	X−HC stretch
	ω_{10}	σ	3489	2.4602	CH stretch
		zpe	72.3		

Table S31: *Calculated harmonic frequencies and mode assignments for the I···HCCH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCCH C_∞ ($^2\Sigma$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	σ	50	0.0797	Intermolecular stretch
	ω_2	π	104	0.1133	Intermolecular bend
	ω_3	π	109	0.2532	Intermolecular bend
	ω_4	π	665	1.0309	HCCH asymmetric bend
	ω_5	π	666	2.1477	HCCH asymmetric bend
	ω_6	π	781	83.2566	HCCH symmetric bend
	ω_7	π	786	77.0709	HCCH symmetric bend
	ω_8	σ	2006	2.6096	C=C stretch
	ω_9	σ	3396	184.7604	X−HC stretch
	ω_{10}	σ	3491	2.2965	CH stretch
		zpe	72.1		
AVTZ	ω_1	σ	59	0.0833	Intermolecular stretch
	ω_2	π	113	0.1418	Intermolecular bend
	ω_3	π	119	0.3402	Intermolecular bend
	ω_4	π	664	1.5656	HCCH asymmetric bend
	ω_5	π	666	3.1478	HCCH asymmetric bend
	ω_6	π	788	81.0712	HCCH symmetric bend
	ω_7	π	793	73.0896	HCCH symmetric bend
	ω_8	σ	2001	3.2749	C=C stretch
	ω_9	σ	3388	201.675	X−HC stretch
	ω_{10}	σ	3491	3.7948	CH stretch
		zpe	72.3		
AVQZ	ω_1	σ	57	0.0812	Intermolecular stretch
	ω_2	π	107	0.14	Intermolecular bend
	ω_3	π	113	0.3231	Intermolecular bend
	ω_4	π	668	1.7621	HCCH asymmetric bend
	ω_5	π	670	3.3666	HCCH asymmetric bend
	ω_6	π	784	80.1203	HCCH symmetric bend
	ω_7	π	790	72.5081	HCCH symmetric bend
	ω_8	σ	2004	3.0965	C=C stretch
	ω_9	σ	3391	196.8645	X−HC stretch
	ω_{10}	σ	3487	2.7528	CH stretch
		zpe	72.2		

Table S32: *Calculated harmonic frequencies and mode assignments for the Cl···HCCH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Cl···HCCH C_{2v} ($^2A_1$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	106	0.4344	Intermolecular bend
	ω_2	a_1	190	8.2528	Intermolecular stretch
	ω_3	a_2	653	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	669	0.0155	HCCH ‖ asymmetric stretch
	ω_5	b_1	773	87.9909	HCCH ⊥ symmetric stretch
	ω_6	a_1	791	98.6903	HCCH ‖ symmetric stretch
	ω_7	a_1	1974	45.0413	C=C stretch
	ω_8	b_2	3402	133.8134	HCCH asymmetric stretch
	ω_9	a_1	3491	0.9595	HCCH symmetric stretch
		zpe	72.1		
AVTZ	ω_1	b_2	109	0.4881	Intermolecular bend
	ω_2	a_1	191	8.0043	Intermolecular stretch
	ω_3	a_2	650	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	665	0.0008	HCCH ‖ asymmetric stretch
	ω_5	b_1	776	86.3087	HCCH ⊥ symmetric stretch
	ω_6	a_1	793	98.4618	HCCH ‖ symmetric stretch
	ω_7	a_1	1970	43.9158	C=C stretch
	ω_8	b_2	3396	133.261	HCCH asymmetric stretch
	ω_9	a_1	3491	0.894	HCCH symmetric stretch
		zpe	72		
AVQZ	ω_1	b_2	106	0.4888	Intermolecular bend
	ω_2	a_1	194	7.803	Intermolecular stretch
	ω_3	a_2	656	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	670	0.0017	HCCH ‖ asymmetric stretch
	ω_5	b_1	773	85.7775	HCCH ⊥ symmetric stretch
	ω_6	a_1	791	97.5035	HCCH ‖ symmetric stretch
	ω_7	a_1	1972	43.9868	C=C stretch
	ω_8	b_2	3399	132.8153	HCCH asymmetric stretch
	ω_9	a_1	3488	0.8801	HCCH symmetric stretch
		zpe	72.1		

Table S33: *Calculated harmonic frequencies and mode assignments for the Br···HCCH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Br···HCCH C_{2v} ($^2A_1$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	129	0.3115	Intermolecular bend
	ω_2	a_1	142	7.5928	Intermolecular stretch
	ω_3	a_2	655	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	667	0.021	HCCH ‖ asymmetric stretch
	ω_5	b_1	774	87.0683	HCCH ⊥ symmetric stretch
	ω_6	a_1	790	108.6275	HCCH ‖ symmetric stretch
	ω_7	a_1	1982	38.9597	C=C stretch
	ω_8	b_2	3402	127.4093	HCCH asymmetric stretch
	ω_9	a_1	3491	0.3827	HCCH symmetric stretch
		zpe	72		
AVTZ	ω_1	b_2	133	0.3771	Intermolecular bend
	ω_2	a_1	143	7.0278	Intermolecular stretch
	ω_3	a_2	651	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	661	0.001	HCCH ‖ asymmetric stretch
	ω_5	b_1	777	84.5057	HCCH ⊥ symmetric stretch
	ω_6	a_1	792	107.8652	HCCH ‖ symmetric stretch
	ω_7	a_1	1977	35.0775	C=C stretch
	ω_8	b_2	3395	125.8284	HCCH asymmetric stretch
	ω_9	a_1	3492	0.2501	HCCH symmetric stretch
		zpe	71.9		
AVQZ	ω_1	b_2	130	0.3789	Intermolecular bend
	ω_2	a_1	146	6.9612	Intermolecular stretch
	ω_3	a_2	658	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	667	0.0018	HCCH ‖ asymmetric stretch
	ω_5	b_1	774	83.9539	HCCH ⊥ symmetric stretch
	ω_6	a_1	788	107.0564	HCCH ‖ symmetric stretch
	ω_7	a_1	1979	35.4508	C=C stretch
	ω_8	b_2	3399	125.5024	HCCH asymmetric stretch
	ω_9	a_1	3488	0.2567	HCCH symmetric stretch
		zpe	71.9		

Table S34: *Calculated harmonic frequencies and mode assignments for the I···HCCH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCCH C_{2v} ($^2A_1$) vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a_1	109	6.3793	Intermolecular stretch
	ω_2	b_2	136	0.3997	Intermolecular bend
	ω_3	a_2	656	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	664	0.0224	HCCH ‖ asymmetric stretch
	ω_5	b_1	776	82.4624	HCCH ⊥ symmetric stretch
	ω_6	a_1	789	119.8728	HCCH ‖ symmetric stretch
	ω_7	a_1	1989	25.2862	C=C stretch
	ω_8	b_2	3401	117.3399	HCCH asymmetric stretch
	ω_9	a_1	3491	0.0005	HCCH symmetric stretch
		zpe	71.8		
AVTZ	ω_1	a_1	109	6.2255	Intermolecular stretch
	ω_2	b_2	139	0.4278	Intermolecular bend
	ω_3	a_2	653	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	657	0.0453	HCCH ‖ asymmetric stretch
	ω_5	b_1	779	81.6111	HCCH ⊥ symmetric stretch
	ω_6	a_1	790	120.39	HCCH ‖ symmetric stretch
	ω_7	a_1	1985	24.072	C=C stretch
	ω_8	b_2	3395	116.3059	HCCH asymmetric stretch
	ω_9	a_1	3493	0.0031	HCCH symmetric stretch
		zpe	71.8		
AVQZ	ω_1	a_1	114	6.3293	Intermolecular stretch
	ω_2	b_2	139	0.4385	Intermolecular bend
	ω_3	a_2	659	0	HCCH ⊥ asymmetric stretch
	ω_4	b_2	665	0.0508	HCCH ‖ asymmetric stretch
	ω_5	b_1	776	80.8719	HCCH ⊥ symmetric stretch
	ω_6	a_1	788	119.0957	HCCH ‖ symmetric stretch
	ω_7	a_1	1987	24.7003	C=C stretch
	ω_8	b_2	3398	116.6343	HCCH asymmetric stretch
	ω_9	a_1	3488	0.0031	HCCH symmetric stretch
		zpe	71.9		

Table S35: *Cartesian coordinates of the geometries of halide-acetylene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots$HCCH			$Br^-\cdots$HCCH			$I^-\cdots$HCCH		
			x	y	z	x	y	z	x	y	z
C_∞ ($^1\Sigma$)	def2QZVP	X	0.000000	0.000000	1.772137	0.000000	0.000000	1.181204	0.000000	0.000000	0.926032
		H	0.000000	0.000000	-3.821020	0.000000	0.000000	-4.621083	0.000000	0.000000	-5.172717
		C	0.000000	0.000000	-2.759224	0.000000	0.000000	-3.559348	0.000000	0.000000	-4.110998
		C	0.000000	0.000000	-1.549258	0.000000	0.000000	-2.350434	0.000000	0.000000	-2.903213
		H	0.000000	0.000000	-0.454408	0.000000	0.000000	-1.262354	0.000000	0.000000	-1.821695
	AVTZ	X	0.000000	0.000000	1.775545	0.000000	0.000000	1.177498	0.000000	0.000000	0.921173
		H	0.000000	0.000000	-3.826651	0.000000	0.000000	-4.613483	0.000000	0.000000	-5.156006
		C	0.000000	0.000000	-2.764221	0.000000	0.000000	-3.551086	0.000000	0.000000	-4.093709
		C	0.000000	0.000000	-1.552292	0.000000	0.000000	-2.340092	0.000000	0.000000	-2.883738
		H	0.000000	0.000000	-0.458536	0.000000	0.000000	-1.251886	0.000000	0.000000	-1.801481
	AVQZ	X	0.000000	0.000000	1.776998	0.000000	0.000000	1.173942	0.000000	0.000000	0.921544
		H	0.000000	0.000000	-3.827124	0.000000	0.000000	-4.603369	0.000000	0.000000	-5.156171
		C	0.000000	0.000000	-2.765103	0.000000	0.000000	-3.541402	0.000000	0.000000	-4.094212
		C	0.000000	0.000000	-1.554977	0.000000	0.000000	-2.332105	0.000000	0.000000	-2.886054
		H	0.000000	0.000000	-0.461362	0.000000	0.000000	-1.243555	0.000000	0.000000	-1.804063

Table S36: *Cartesian coordinates of the geometries of halogen-acetylene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCCH			Br···HCCH			I···HCCH		
			x	y	z	x	y	z	x	y	z
C_∞ ($^2\Sigma$)	def2QZVP	X	0.000000	0.000000	2.044900	0.000000	0.000000	1.325767	0.000000	0.000000	1.010603
		H	0.000000	0.000000	-4.147965	0.000000	0.000000	-4.979329	0.000000	0.000000	-5.490805
		C	0.000000	0.000000	-3.085148	0.000000	0.000000	-3.916514	0.000000	0.000000	-4.427991
		C	0.000000	0.000000	-1.881197	0.000000	0.000000	-2.712510	0.000000	0.000000	-3.223937
		H	0.000000	0.000000	-0.817274	0.000000	0.000000	-1.648381	0.000000	0.000000	-2.159571
	AVTZ	X	0.000000	0.000000	2.020921	0.000000	0.000000	1.297396	0.000000	0.000000	0.992622
		H	0.000000	0.000000	-4.120454	0.000000	0.000000	-4.910034	0.000000	0.000000	-5.424340
		C	0.000000	0.000000	-3.057086	0.000000	0.000000	-3.846692	0.000000	0.000000	-4.361032
		C	0.000000	0.000000	-1.850997	0.000000	0.000000	-2.640504	0.000000	0.000000	-3.154784
		H	0.000000	0.000000	-0.786703	0.000000	0.000000	-1.575664	0.000000	0.000000	-2.089727
	AVQZ	X	0.000000	0.000000	2.034593	0.000000	0.000000	1.310697	0.000000	0.000000	0.996341
		H	0.000000	0.000000	-4.135819	0.000000	0.000000	-4.942038	0.000000	0.000000	-5.437207
		C	0.000000	0.000000	-3.072802	0.000000	0.000000	-3.879023	0.000000	0.000000	-4.374198
		C	0.000000	0.000000	-1.868520	0.000000	0.000000	-2.674669	0.000000	0.000000	-3.169778
		H	0.000000	0.000000	-0.804339	0.000000	0.000000	-1.610189	0.000000	0.000000	-2.105017
			x	y	z	x	y	z	x	y	z
C_{2v} ($^2A_1$)	def2QZVP	X	0.000000	0.000000	1.174600	0.000000	0.000000	0.801656	0.000000	0.000000	0.643655
		H	0.000000	1.669150	-1.440469	0.000000	1.668263	-2.016796	0.000000	1.667449	-2.447200
		C	0.000000	0.605352	-1.423938	0.000000	0.604488	-2.002032	0.000000	0.603692	-2.434943
		C	0.000000	-0.605352	-1.423938	0.000000	-0.604488	-2.002032	0.000000	-0.603692	-2.434943
		H	0.000000	-1.669150	-1.440469	0.000000	-1.668263	-2.016796	0.000000	-1.667449	-2.447200
	AVTZ	X	0.000000	0.000000	1.174505	0.000000	0.000000	0.798215	0.000000	0.000000	0.645666
		H	0.000000	1.670708	-1.439935	0.000000	1.669782	-2.008416	0.000000	1.668865	-2.454292
		C	0.000000	0.606393	-1.423893	0.000000	0.605533	-1.993390	0.000000	0.604679	-2.442645
		C	0.000000	-0.606393	-1.423893	0.000000	-0.605533	-1.993390	0.000000	-0.604679	-2.442645
		H	0.000000	-1.670708	-1.439935	0.000000	-1.669782	-2.008416	0.000000	-1.668865	-2.454292
	AVQZ	X	0.000000	0.000000	1.170925	0.000000	0.000000	0.795512	0.000000	0.000000	0.640116
		H	0.000000	1.669621	-1.435889	0.000000	1.668712	-2.001656	0.000000	1.667872	-2.433191
		C	0.000000	0.605595	-1.419495	0.000000	0.604729	-1.986634	0.000000	0.603903	-2.421646
		C	0.000000	-0.605595	-1.419495	0.000000	-0.604729	-1.986634	0.000000	-0.603903	-2.421646
		H	0.000000	-1.669621	-1.435889	0.000000	-1.668712	-2.001656	0.000000	-1.667872	-2.433191

Table S37: *$X^- \cdots O_2$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots O}$	$R_{X\cdots\|\|}$	$R_{O=O}$	$\angle_{X\cdots\|\|-O}$	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
		def2QZVP	3.376	3.519	1.204	73.3	-610.1632503	9.8	6.5	6.8
	C_s ($^3A''$)	AVTZ	3.356	3.541	1.208	71.3	-610.1309845	9.7	6.2	6.5
		AVQZ	3.456	3.513	1.204	77.4	-610.1686802	9.9	6.3	6.6
		def2QZVP	3.544	3.493	1.203	90.0	-610.1632375	9.9	6.5	6.9
$Cl^- \cdots O_2$	C_{2v} ($^3B_1$)	AVTZ	3.547	3.496	1.207	90.0	-610.1309601	9.8	6.1	6.5
		AVQZ	3.555	3.504	1.204	90.0	-610.1686792	9.9	6.3	6.6
		def2QZVP	3.413	4.017	1.209	180.0	-610.1627115	9.6	5.1	5.2
	C_∞ ($^3\Sigma$)	AVTZ	3.403	4.009	1.212	180.0	-610.1306244	9.6	5.2	5.4
		AVQZ	3.414	4.018	1.209	180.0	-610.1682058	9.7	5.0	5.2
		def2QZVP	3.535	3.719	1.205	71.9	-2723.6386170	9.7	5.7	5.9
	C_s ($^3A''$)	AVTZ	3.501	3.740	1.209	69.3	-566.4650186	9.6	5.6	5.8
		AVQZ	3.529	3.714	1.205	71.8	-566.5267298	9.7	5.8	6.0
		def2QZVP	3.732	3.684	1.203	90.0	-2723.6385920	9.8	5.6	5.9
$Br^- \cdots O_2$	C_{2v} ($^3B_1$)	AVTZ	3.734	3.685	1.207	90.0	-566.4649620	9.7	5.5	5.8
		AVQZ	3.725	3.676	1.204	90.0	-566.5267067	9.8	5.7	6.0
		def2QZVP	3.600	4.204	1.208	180.0	-2723.6381500	9.6	4.5	4.5
	C_∞ ($^3\Sigma$)	AVTZ	3.585	4.190	1.212	180.0	-566.4646799	9.5	4.8	4.8
		AVQZ	3.575	4.179	1.208	180.0	-566.5263040	9.6	4.7	4.8
		def2QZVP	3.797	3.994	1.205	72.0	-447.7284107	9.7	4.6	4.8
	C_s ($^3A''$)	AVTZ	3.742	4.019	1.209	68.2	-445.5120777	9.5	4.8	4.9
		AVQZ	3.787	3.986	1.205	71.8	-445.5745371	9.7	5.0	5.2
		def2QZVP	4.013	3.968	1.204	90.0	-447.7283860	9.8	4.6	4.8
$I^- \cdots O_2$	C_{2v} ($^3B_1$)	AVTZ	4.010	3.965	1.207	90.0	-445.5120046	9.6	4.6	4.8
		AVQZ	4.001	3.955	1.204	90.0	-445.5745118	9.8	5.0	5.2
		def2QZVP	3.881	4.485	1.207	180.0	-447.7279550	9.6	3.4	3.5
	C_∞ ($^3\Sigma$)	AVTZ	3.846	4.452	1.211	180.0	-445.5117800	9.5	4.0	4.1
		AVQZ	3.857	4.460	1.208	180.0	-445.5741556	9.6	4.0	4.1

Table S38: *$X\cdots O_2$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots O}$ Å	$R_{X\cdots\|\|}$ Å	$R_{O=O}$ Å	$\angle_{X\cdots\|\|-O}$ °	E_{DFT} E_h	zpe kJ mol^{-1}	D_e kJ mol^{-1}	D_o kJ mol^{-1}
$Cl\cdots O_2$	C_{2v} ($^4A''$)	def2QZVP	3.232	3.175	1.206	90.0	-610.0332420	9.8	2.7	3.0
		AVTZ	3.211	3.153	1.209	90.0	-609.9986846	9.7	2.9	3.2
		AVQZ	3.224	3.168	1.206	90.0	-610.0347063	9.8	2.7	3.0
	C_∞ ($^4\Sigma$)	def2QZVP	3.122	3.724	1.204	180.0	-610.0330545	9.8	2.2	2.5
		AVTZ	3.119	3.722	1.208	180.0	-609.9984977	9.7	2.4	2.7
		AVQZ	3.113	3.715	1.204	180.0	-610.0345567	9.8	2.3	2.6
$Br\cdots O_2$	C_{2v} ($^4A''$)	def2QZVP	3.352	3.298	1.206	90.0	-2723.5132140	9.8	2.9	3.2
		AVTZ	3.311	3.256	1.209	90.0	-566.3394182	9.7	3.5	3.8
		AVQZ	3.313	3.258	1.206	90.0	-566.3993241	9.8	3.5	3.8
	C_∞ ($^4\Sigma$)	def2QZVP	3.235	3.837	1.204	180.0	-2723.5130620	9.8	2.5	2.8
		AVTZ	3.200	3.804	1.208	180.0	-566.3392407	9.7	3.0	3.3
		AVQZ	3.183	3.786	1.204	180.0	-566.3992000	9.8	3.2	3.5
$I\cdots O_2$	C_{2v} ($^4A''$)	def2QZVP	3.549	3.497	1.206	90.0	-447.6091613	9.7	3.4	3.7
		AVTZ	3.520	3.467	1.209	90.0	-445.3927653	9.6	3.7	3.9
		AVQZ	3.533	3.481	1.206	90.0	-445.4531433	9.7	3.8	4.0
	C_∞ ($^4\Sigma$)	def2QZVP	3.397	3.999	1.204	180.0	-447.6090005	9.8	3.0	3.3
		AVTZ	3.389	3.993	1.208	180.0	-445.3926351	9.7	3.3	3.6
		AVQZ	3.372	3.974	1.204	180.0	-445.4530378	9.8	3.5	3.7

Table S39: *$X^-\cdots O_2$ complex VDEs from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			E_{VDE}	$VDE_{^2P_{3/2}}$	$VDE_{^2P_{1/2}}$	$ADE_{^2P_{3/2}}$	$ADE_{^2P_{1/2}}$
			E_h	eV	eV	eV	eV
		def2QZVP	-610.0330130	3.656	3.765	3.653	3.762
	C_s ($^3A''$)	AVTZ	-609.9979436	3.664	3.773	3.647	3.756
		AVQZ	-610.0344759	3.653	3.762	3.649	3.758
		def2QZVP	-610.0330359	3.654	3.763	3.651	3.766
$Cl^-\cdots O_2$	C_{2v} ($^3B_1$)	AVTZ	-609.9984333	3.650	3.759	3.646	3.760
		AVQZ	-610.0344807	3.652	3.761	3.649	3.762
		def2QZVP	-610.0328873	3.645	3.754	3.645	3.754
	C_∞ ($^3\Sigma$)	AVTZ	-609.9983254	3.644	3.753	3.644	3.753
		AVQZ	-610.0343761	3.643	3.752	3.643	3.752
		def2QZVP	-2723.5129260	3.398	3.855	3.393	3.850
	C_s ($^3A''$)	AVTZ	-566.3390289	3.394	3.851	3.387	3.844
		AVQZ	-566.3989522	3.395	3.852	3.388	3.845
		def2QZVP	-2723.5129330	3.397	3.854	3.392	3.849
$Br^-\cdots O_2$	C_{2v} ($^3B_1$)	AVTZ	-566.3390458	3.392	3.849	3.384	3.841
		AVQZ	-566.3989575	3.394	3.851	3.387	3.844
		def2QZVP	-2723.5128280	3.388	3.845	3.386	3.843
	C_∞ ($^3\Sigma$)	AVTZ	-566.3389652	3.387	3.844	3.384	3.841
		AVQZ	-566.3988855	3.385	3.842	3.381	3.838
		def2QZVP	-447.6084858	3.088	4.030	3.072	4.014
	C_s ($^3A''$)	AVTZ	-445.3919629	3.090	4.032	3.071	4.013
		AVQZ	-445.4524412	3.089	4.031	3.073	4.015
		def2QZVP	-447.6087767	3.079	4.021	3.071	4.013
$I^-\cdots O_2$	C_{2v} ($^3B_1$)	AVTZ	-445.3923135	3.078	4.020	3.068	4.010
		AVQZ	-445.4527358	3.080	4.022	3.071	4.013
		def2QZVP	-447.6086445	3.071	4.013	3.066	4.008
	C_∞ ($^3\Sigma$)	AVTZ	-445.3922748	3.073	4.015	3.068	4.010
		AVQZ	-445.4526560	3.073	4.015	3.067	4.009

Table S40: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots O_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

			$Cl^-\cdots O_2$		
			C_s ($^3A''$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	126i	2.2704	Intermolecular bend
	ω_2	a'	57	18.1061	Intermolecular stretch
	ω_3	a'	1587	8.748	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	a'	119i	1.8797	Intermolecular bend
	ω_2	a'	55	18.2687	Intermolecular stretch
	ω_3	a'	1566	12.1418	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	a'	127i	0.6456	Intermolecular bend
	ω_2	a'	58	15.6093	Intermolecular stretch
	ω_3	a'	1592	2.5507	O_2 stretch
		zpe	9.9		
			$Cl^-\cdots O_2$		
			C_{2v} ($^3B_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	131i	0.0002	Intermolecular bend
	ω_2	a_1	59	15.716	Intermolecular stretch
	ω_3	a_1	1596	0.833	O_2 stretch
		zpe	9.9		
AVTZ	ω_1	b_2	126i	0.0064	Intermolecular bend
	ω_2	a_1	58	15.0582	Intermolecular stretch
	ω_3	a_1	1577	1.1278	O_2 stretch
		zpe	9.8		
AVQZ	ω_1	b_2	129i	0.0065	Intermolecular bend
	ω_2	a_1	58	14.9281	Intermolecular stretch
	ω_3	a_1	1594	1.0538	O_2 stretch
		zpe	9.9		
			$Cl^-\cdots O_2$		
			C_∞ ($^3\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	π	133i	1.6726	Degenerate intermolecular bend
	ω_2	π	133i	1.6726	Degenerate intermolecular bend
	ω_3	σ	52	17.2142	Intermolecular stretch
	ω_4	σ	1560	15.0525	O_2 stretch
		zpe	9.6		
AVTZ	ω_1	π	126i	1.5404	Degenerate intermolecular bend
	ω_2	π	126i	1.5404	Degenerate intermolecular bend
	ω_3	σ	53	16.8356	Intermolecular stretch
	ω_4	σ	1543	14.5207	O_2 stretch
		zpe	9.6		
AVQZ	ω_1	π	130i	1.5146	Degenerate intermolecular bend
	ω_2	π	130i	1.5146	Degenerate intermolecular bend
	ω_3	σ	53	16.6934	Intermolecular stretch
	ω_4	σ	1562	13.651	O_2 stretch
		zpe	9.7		

Table S41: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots O_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

			$Br^-\cdots O_2$		
			C_s ($^3A''$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	$125i$	2.3925	Intermolecular bend
	ω_2	a'	45	5.8516	Intermolecular stretch
	ω_3	a'	1583	14.4937	O_2 stretch
		zpe	9.7		
AVTZ	ω_1	a'	$118i$	1.9085	Intermolecular bend
	ω_2	a'	43	6.0956	Intermolecular stretch
	ω_3	a'	1560	22.9537	O_2 stretch
		zpe	9.6		
AVQZ	ω_1	a'	$124i$	1.7656	Intermolecular bend
	ω_2	a'	45	5.3901	Intermolecular stretch
	ω_3	a'	1582	13.5477	O_2 stretch
		zpe	9.7		
			$Br^-\cdots O_2$		
			C_{2v} ($^3B_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	$133i$	0.146	Intermolecular bend
	ω_2	a'	45	4.347	Intermolecular stretch
	ω_3	a'	1595	0.7625	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	b_2	$128i$	0.0962	Intermolecular bend
	ω_2	a_1	44	4.0585	Intermolecular stretch
	ω_3	a_1	1576	1.1703	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	b_2	$131i$	0.0976	Intermolecular bend
	ω_2	a_1	46	4.014	Intermolecular stretch
	ω_3	a_1	1593	1.1484	O_2 stretch
		zpe	9.8		
			$Br^-\cdots O_2$		
			C_∞ ($^3\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	π	$133i$	0.7148	Degenerate intermolecular bend
	ω_2	π	$133i$	0.7148	Degenerate intermolecular bend
	ω_3	σ	42	4.9697	Intermolecular stretch
	ω_4	σ	1564	14.0934	O_2 stretch
		zpe	9.6		
AVTZ	ω_1	π	$127i$	0.6337	Degenerate intermolecular bend
	ω_2	π	$127i$	0.6337	Degenerate intermolecular bend
	ω_3	σ	42	4.7888	Intermolecular stretch
	ω_4	σ	1546	14.6204	O_2 stretch
		zpe	9.5		
AVQZ	ω_1	π	$131i$	0.6297	Degenerate intermolecular bend
	ω_2	π	$131i$	0.6297	Degenerate intermolecular bend
	ω_3	σ	43	4.7369	Intermolecular stretch
	ω_4	σ	1564	14.2596	O_2 stretch
		zpe	9.6		

Table S42: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots O_2$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

			$I^-\cdots O_2$		
			C_s ($^3A''$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	126i	2.0377	Intermolecular bend
	ω_2	a'	36	2.6365	Intermolecular stretch
	ω_3	a'	1582	15.4625	O_2 stretch
		zpe	9.7		
AVTZ	ω_1	a'	117i	1.5352	Intermolecular bend
	ω_2	a'	37	3.0812	Intermolecular stretch
	ω_3	a'	1557	32.0728	O_2 stretch
		zpe	9.5		
AVQZ	ω_1	a'	124i	1.6024	Intermolecular bend
	ω_2	a'	37	2.4528	Intermolecular stretch
	ω_3	a'	1581	15.6469	O_2 stretch
		zpe	9.7		
			$I^-\cdots O_2$		
			C_{2v} ($^3B_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	131i	0.188	Intermolecular bend
	ω_2	a'	39	1.8068	Intermolecular stretch
	ω_3	a'	1594	0.5861	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	b_2	127i	0.1321	Intermolecular bend
	ω_2	a_1	39	1.6658	Intermolecular stretch
	ω_3	a_1	1575	1.0028	O_2 stretch
		zpe	9.6		
AVQZ	ω_1	b_2	130i	0.1328	Intermolecular bend
	ω_2	a_1	40	1.6463	Intermolecular stretch
	ω_3	a_1	1592	0.9749	O_2 stretch
		zpe	9.8		
			$I^-\cdots O_2$		
			C_∞ ($^3\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	π	132i	0.4691	Degenerate intermolecular bend
	ω_2	π	132i	0.4691	Degenerate intermolecular bend
	ω_3	σ	32	2.1958	Intermolecular stretch
	ω_4	σ	1569	12.8008	O_2 stretch
		zpe	9.6		
AVTZ	ω_1	π	127i	0.393	Degenerate intermolecular bend
	ω_2	π	127i	0.393	Degenerate intermolecular bend
	ω_3	σ	34	2.0674	Intermolecular stretch
	ω_4	σ	1550	13.6736	O_2 stretch
		zpe	9.5		
AVQZ	ω_1	π	131i	0.3842	Degenerate intermolecular bend
	ω_2	π	131i	0.3842	Degenerate intermolecular bend
	ω_3	σ	34	2.0388	Intermolecular stretch
	ω_4	σ	1568	12.699	O_2 stretch
		zpe	9.6		

Table S43: *Calculated harmonic frequencies and mode assignments for the Cl···O_2 complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			$Cl\cdots O_2$		
			C_{2v} ($^4B_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	102i	0.004	Intermolecular bend
	ω_2	a_1	54	0.1462	Intermolecular stretch
	ω_3	a_1	1585	0.3425	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	b_2	95i	0.002	Intermolecular bend
	ω_2	a_1	57	0.1532	Intermolecular stretch
	ω_3	a_1	1566	0.3571	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	b_2	101i	0.0027	Intermolecular bend
	ω_2	a_1	54	0.1454	Intermolecular stretch
	ω_3	a_1	1584	0.3341	O_2 stretch
		zpe	9.8		
			$Cl\cdots O_2$		
			C_∞ ($^4\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	π	119i	0.0031	Degenerate intermolecular bend
	ω_2	π	119i	0.0031	Degenerate intermolecular bend
	ω_3	σ	46	0.0997	Intermolecular stretch
	ω_4	σ	1592	0.0039	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	σ	113i	0.004	Degenerate intermolecular bend
	ω_2	π	113i	0.004	Degenerate intermolecular bend
	ω_3	π	48	0.1014	Intermolecular stretch
	ω_4	σ	1575	0.004	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	π	118i	0.0037	Degenerate intermolecular bend
	ω_2	π	118i	0.0037	Degenerate intermolecular bend
	ω_3	σ	48	0.1052	Intermolecular stretch
	ω_4	σ	1592	0.0031	O_2 stretch
		zpe	9.8		

Table S44: *Calculated harmonic frequencies and mode assignments for the Br···O_2 complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			Br···O_2		
			C_{2v} ($^4B_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	103i	0.001	Intermolecular bend
	ω_2	a_1	49	0.1173	Intermolecular stretch
	ω_3	a_1	1584	0.2877	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	b_2	94i	0	Intermolecular bend
	ω_2	a_1	53	0.1299	Intermolecular stretch
	ω_3	a_1	1566	0.2927	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	b_2	99i	0	Intermolecular bend
	ω_2	a_1	53	0.1314	Intermolecular stretch
	ω_3	a_1	1583	0.2879	O_2 stretch
		zpe	9.8		
			Br···O_2		
			C_∞ ($^4\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	π	120i	0.005	Degenerate intermolecular bend
	ω_2	π	120i	0.005	Degenerate intermolecular bend
	ω_3	σ	43	0.0924	Intermolecular stretch
	ω_4	σ	1592	0	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	π	114i	0.0062	Degenerate intermolecular bend
	ω_2	π	114i	0.0062	Degenerate intermolecular bend
	ω_3	σ	45	0.1063	Intermolecular stretch
	ω_4	σ	1574	0.0003	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	π	117i	0.0059	Degenerate intermolecular bend
	ω_2	π	117i	0.0059	Degenerate intermolecular bend
	ω_3	σ	47	0.1147	Intermolecular stretch
	ω_4	σ	1592	0.0006	O_2 stretch
		zpe	9.8		

Table S45: *Calculated harmonic frequencies and mode assignments for the I···O_2 complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

			I···O_2		
			C_{2v} ($^4B_1$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	105i	0.0015	Intermolecular bend
	ω_2	a_1	44	0.1105	Intermolecular stretch
	ω_3	a_1	1584	0.1934	O_2 stretch
		zpe	9.7		
AVTZ	ω_1	b_2	97i	0.0029	Intermolecular bend
	ω_2	a_1	46	0.1192	Intermolecular stretch
	ω_3	a_1	1566	0.1803	O_2 stretch
		zpe	9.6		
AVQZ	ω_1	b_2	103i	0.0023	Intermolecular bend
	ω_2	a_1	45	0.1163	Intermolecular stretch
	ω_3	a_1	1583	0.1776	O_2 stretch
		zpe	9.7		
			I···O_2		
			C_∞ ($^4\Sigma$) vdW Complex		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	π	120i	0.0042	Degenerate intermolecular bend
	ω_2	π	120i	0.0042	Degenerate intermolecular bend
	ω_3	σ	43	0.119	Intermolecular stretch
	ω_4	σ	1591	0.0295	O_2 stretch
		zpe	9.8		
AVTZ	ω_1	π	114i	0.0074	Degenerate intermolecular bend
	ω_2	π	114i	0.0074	Degenerate intermolecular bend
	ω_3	σ	46	0.1222	Intermolecular stretch
	ω_4	σ	1573	0.026	O_2 stretch
		zpe	9.7		
AVQZ	ω_1	π	118i	0.0071	Degenerate intermolecular bend
	ω_2	π	118i	0.0071	Degenerate intermolecular bend
	ω_3	σ	46	0.1333	Intermolecular stretch
	ω_4	σ	1591	0.0299	O_2 stretch
		zpe	9.8		

Table S46: *Cartesian coordinates of the geometries of halide-oxygen complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots O_2$			$Br^-\cdots O_2$			$I^-\cdots O_2$		
			x	y	z	x	y	z	x	y	z
C_s ($^3A''$)	def2QZVP	X	0.000000	1.705990	0.000000	0.000000	1.166757	0.000000	0.000000	0.926068	0.000000
		O	0.570740	-1.620952	0.000000	0.557186	-2.323602	0.000000	0.553859	-2.830807	0.000000
		O	-0.570740	-2.004278	0.000000	-0.557186	-2.780960	0.000000	-0.553859	-3.304393	0.000000
	AVTZ	X	0.567587	1.620439	0.000000	0.000000	1.173312	0.000000	0.000000	0.931961	0.000000
		O	0.000000	-1.686918	0.000000	0.535460	-2.286370	0.000000	0.517259	-2.774258	0.000000
		O	-1.206123	-1.756516	0.000000	-0.535460	-2.846871	0.000000	-0.517259	-3.399986	0.000000
	AVQZ	X	0.000000	1.703108	0.000000	0.000000	1.165178	0.000000	0.000000	0.924255	0.000000
		O	0.592273	-1.702233	0.000000	0.557254	-2.319914	0.000000	0.553035	-2.822505	0.000000
		O	-0.592273	-1.916871	0.000000	-0.557254	-2.777740	0.000000	-0.553035	-3.300687	0.000000
			x	y	z	x	y	z	x	y	z
C_{2v} ($^3B_1$)	def2QZVP	X	0.000000	0.000000	-1.693497	0.000000	1.155675	0.000000	0.000000	0.919965	0.000000
		O	0.000000	-0.601593	1.799287	0.601682	-2.527918	0.000000	0.601815	-3.048000	0.000000
		O	0.000000	0.601593	1.799287	-0.601682	-2.528159	0.000000	-0.601815	-3.046768	0.000000
	AVTZ	X	0.000000	0.000000	1.694845	0.000000	1.156168	0.000000	0.000000	0.919357	0.000000
		O	0.000000	0.603420	-1.800710	0.603526	-2.529031	0.000000	0.603633	-3.045369	0.000000
		O	0.000000	-0.603420	-1.800836	-0.603526	-2.529204	0.000000	-0.603633	-3.045369	0.000000
	AVQZ	X	0.000000	0.000000	1.698689	0.000000	1.153366	0.000000	0.000000	0.917077	0.000000
		O	0.000000	0.601780	-1.804857	0.601876	-2.522989	0.000000	0.601979	-3.038406	0.000000
		O	0.000000	-0.601780	-1.804857	-0.601876	-2.522989	0.000000	-0.601979	-3.037227	0.000000
			x	y	z	x	y	z	x	y	z
C_∞ ($^3\Sigma$)	def2QZVP	X	0.000000	0.000000	1.947587	0.000000	0.000000	1.318907	0.000000	0.000000	1.040041
		O	0.000000	0.000000	-1.464987	0.000000	0.000000	-2.281055	0.000000	0.000000	-2.841417
		O	0.000000	0.000000	-2.673635	0.000000	0.000000	-3.489163	0.000000	0.000000	-4.048852
	AVTZ	X	0.000000	0.000000	1.943783	0.000000	0.000000	1.314630	0.000000	0.000000	1.032295
		O	0.000000	0.000000	-1.459225	0.000000	0.000000	-2.269952	0.000000	0.000000	-2.813969
		O	0.000000	0.000000	-2.671314	0.000000	0.000000	-3.481555	0.000000	0.000000	-4.024989
	AVQZ	X	0.000000	0.000000	1.948333	0.000000	0.000000	1.310994	0.000000	0.000000	1.034300
		O	0.000000	0.000000	-1.465801	0.000000	0.000000	-2.263699	0.000000	0.000000	-2.822335
		O	0.000000	0.000000	-2.674407	0.000000	0.000000	-3.471898	0.000000	0.000000	-4.029901

Table S47: *Cartesian coordinates of the geometries of halogen-oxygen complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots O_2$			$Br\cdots O_2$			$I\cdots O_2$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^4A''$)	def2QZVP	X	0.000000	0.000000	-1.539395	0.000000	0.000000	1.034536	0.000000	0.000000	0.810970
		O	0.000000	0.602756	1.635637	0.000000	0.602776	-2.263048	0.000000	0.602757	-2.686338
		O	0.000000	-0.602756	1.635637	0.000000	-0.602776	-2.263048	0.000000	-0.602757	-2.686338
	AVTZ	X	0.000000	0.000000	1.528942	0.000000	0.000000	1.021337	0.000000	0.000000	0.804053
		O	0.000000	0.604589	-1.624499	0.000000	0.604635	-2.234174	0.000000	0.604608	-2.663425
		O	0.000000	-0.604589	-1.624499	0.000000	-0.604635	-2.234174	0.000000	-0.604608	-2.663425
	AVQZ	X	0.000000	0.000000	1.535819	0.000000	0.000000	1.021989	0.000000	0.000000	0.807222
		O	0.000000	0.602900	-1.631807	0.000000	0.602964	-2.235602	0.000000	0.602923	-2.673924
		O	0.000000	-0.602900	-1.631807	0.000000	-0.602964	-2.235602	0.000000	-0.602923	-2.673924
			x	y	z	x	y	z	x	y	z
C_∞ ($^4\Sigma$)	def2QZVP	X	0.000000	0.000000	1.805653	0.000000	0.000000	1.203833	0.000000	0.000000	0.927252
		O	0.000000	0.000000	-1.316424	0.000000	0.000000	-2.031303	0.000000	0.000000	-2.469420
		O	0.000000	0.000000	-2.520589	0.000000	0.000000	-3.235466	0.000000	0.000000	-3.673626
	AVTZ	X	0.000000	0.000000	1.804848	0.000000	0.000000	1.193509	0.000000	0.000000	0.925979
		O	0.000000	0.000000	-1.313819	0.000000	0.000000	-2.006965	0.000000	0.000000	-2.463440
		O	0.000000	0.000000	-2.521483	0.000000	0.000000	-3.214635	0.000000	0.000000	-3.671168
	AVQZ	X	0.000000	0.000000	1.801359	0.000000	0.000000	1.187644	0.000000	0.000000	0.921444
		O	0.000000	0.000000	-1.311780	0.000000	0.000000	-1.995808	0.000000	0.000000	-2.450092
		O	0.000000	0.000000	-2.516107	0.000000	0.000000	-3.200136	0.000000	0.000000	-3.654476

Table S48: *$X^-\cdots C_2H_4$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots\|\|}$	R_{C-H}	$R_{C=C}$	$\angle_{X\cdots\|\|-C}$	Dihedral	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
$Cl^-\cdots C_2H_4$	BifOut	def2QZVP	4.055	1.082	1.327	90.0	87.9	-538.4475557	133.9	-1.4	-1.8
	C_{2v} ($^1A_1$)	AVTZ	4.088	1.083	1.329	90.0	88.0	-538.4252773	133.9	-1.8	-2.0
		AVQZ	4.147	1.082	1.328	90.0	88.0	-538.4521355	134.1	-1.9	-1.9
	BifPl	def2QZVP	3.521	1.085	1.330	90.0	0.0	-538.4570413	135.8	23.5	25.0
	C_{2v} ($^1A_1$)	AVTZ	3.529	1.085	1.332	90.0	0.0	-538.4343507	135.4	22.0	23.4
		AVQZ	3.531	1.085	1.331	90.0	0.0	-538.4611063	135.6	21.7	23.1
	End	def2QZVP	4.134	1.082	1.331	0.0	NA	-538.4555920	134.9	19.7	20.3
	C_{2v} ($^1A_1$)	AVTZ	4.149	1.083	1.333	0.0	NA	-538.4328090	134.3	17.9	18.3
		AVQZ	4.152	1.082	1.332	0.0	NA	-538.4595891	134.6	17.7	18.1
	HApp	def2QZVP	3.970	1.091	1.331	48.5	0.0	-538.4575113	135.8	24.7	26.3
	C_s ($^1A'$)	AVTZ	3.974	1.092	1.334	48.7	0.0	-538.4348550	135.5	23.3	24.8
		AVQZ	3.976	1.091	1.332	49.0	0.0	-538.4615400	135.7	22.8	24.3
$Br^-\cdots C_2H_4$	BifOut	def2QZVP	4.202	1.082	1.327	90.0	88.0	-2651.9233306	133.9	-1.2	-1.5
	C_{2v} ($^1A_1$)	AVTZ	4.192	1.083	1.329	90.0	88.1	-494.7597711	133.9	-1.2	-1.3
		AVQZ	4.195	1.082	1.328	90.0	88.1	-494.8106543	134.1	-1.1	-1.2
	BifPl	def2QZVP	3.703	1.084	1.330	90.0	0.0	-2651.9317804	135.8	21.0	22.6
	C_{2v} ($^1A_1$)	AVTZ	3.683	1.085	1.332	90.0	0.0	-494.7680598	135.4	20.6	22.0
		AVQZ	3.690	1.084	1.330	90.0	0.0	-494.8189530	135.8	20.7	22.2
	End	def2QZVP	4.319	1.083	1.331	0.0	NA	-2651.9303242	135.0	17.2	17.9
	C_{2v} ($^1A_1$)	AVTZ	4.311	1.083	1.333	0.0	NA	-494.7665089	134.3	16.5	16.8
		AVQZ	4.309	1.082	1.331	0.0	NA	-494.8174215	134.6	16.6	17.0
	HApp	def2QZVP	4.156	1.085	1.331	50.1	0.0	-2651.9318574	135.8	21.2	22.7
	C_s ($^1A'$)	AVTZ	4.122	1.086	1.333	50.9	0.0	-494.7682645	135.8	21.1	22.9
		AVQZ	4.132	1.085	1.331	50.9	0.0	-494.8189657	135.6	20.7	22.1

Table S49: *$X^{-}\cdots C_2H_4$ complex geometric parameters from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{\mathrm{X}\cdots\mid\mid}$	$R_{\mathrm{C-H}}$	$R_{\mathrm{C=C}}$	$\angle_{\mathrm{X}\cdots\mid\mid-\mathrm{C}}$	Dihedral	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
$I^{-}\cdots C_2H_4$	BifOut	def2QZVP	4.508	1.082	1.327	90.0	88.2	-376.0134851	134.3	-1.3	-1.2
	C_{2v} ($^1A_1$)	AVTZ	4.462	1.083	1.329	90.0	90.0	-373.8071514	133.9	-1.2	-1.3
		AVQZ	4.408	1.082	1.328	90.0	88.2	-373.8589989	134.2	-0.5	-0.5
	BifPl	def2QZVP	4.023	1.084	1.330	90.0	0.0	-376.0203758	135.9	16.8	18.4
	C_{2v} ($^1A_1$)	AVTZ	3.934	1.085	1.332	90.0	0.0	-373.8145314	135.4	18.2	19.6
		AVQZ	3.936	1.084	1.330	90.0	0.0	-373.8660877	135.6	18.1	19.6
	End	def2QZVP	4.594	1.082	1.331	0.0	NA	-376.0192264	135.1	13.8	14.7
	C_{2v} ($^1A_1$)	AVTZ	4.572	1.083	1.333	0.0	NA	-373.8131132	134.4	14.5	14.8
		AVQZ	4.575	1.082	1.331	0.0	NA	-373.8646966	134.6	14.5	14.9
	HApp	def2QZVP	4.424	1.085	1.330	52.6	0.0	-376.0201783	135.8	16.3	17.8
	C_s ($^1A'$)	AVTZ	4.352	1.086	1.332	54.9	0.0	-373.8143174	135.7	17.6	19.4
		AVQZ	3.936	1.085	1.330	90.0	0.0	-373.8660877	0.0	18.1	-116.1

Table S50: *$X\cdots C_2H_4$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			$R_{X\cdots\|\|}$	R_{C-H}	$R_{C=C}$	$\angle_{X\cdots\|\|-C}$	Dihedral	E_{DFT}	zpe	D_e	D_o
			Å	Å	Å	°	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
	BifOut	def2QZVP	2.467	1.081	1.352	90.0	90.0	-538.3358857	137.8	42.9	46.4
	C_{2v} ($^2A_1$)	AVTZ	2.462	1.082	1.354	90.0	90.0	-538.3116884	138.8	44.0	48.8
		AVQZ	2.459	1.081	1.352	90.0	90.0	-538.3371778	139.1	44.5	49.4
	BifPl	def2QZVP	3.807	1.082	1.329	90.0	0.0	-538.3208903	135.2	3.5	4.4
$Cl\cdots C_2H_4$	C_{2v} ($^2A_1$)	AVTZ	3.774	1.083	1.331	90.0	0.0	-538.2965380	134.9	4.3	5.1
		AVQZ	3.784	1.082	1.329	90.0	0.0	-538.3217340	134.1	3.9	3.9
	End	def2QZVP	4.496	1.082	1.329	0.0	NA	-538.3203473	134.7	2.1	2.5
	C_{2v} ($^2A_1$)	AVTZ	4.462	1.083	1.331	0.0	NA	-538.2959186	134.4	2.6	3.0
		AVQZ	4.474	1.082	1.329	0.0	NA	-538.3211460	134.6	2.4	2.8
	BifOut	def2QZVP	2.662	1.081	1.347	90.0	90.0	-2651.8129239	137.9	35.4	39.0
	C_{2v} ($^2A_1$)	AVTZ	2.647	1.082	1.349	92.6	90.0	-494.6496280	138.2	37.3	41.5
		AVQZ	2.658	1.081	1.348	91.1	90.0	-494.6991756	138.5	38.4	42.7
	BifPl	def2QZVP	3.943	1.082	1.329	91.3	0.0	-2651.8010190	135.1	4.2	5.0
$Br\cdots C_2H_4$	C_{2v} ($^2A_1$)	AVTZ	3.880	1.083	1.331	87.4	0.0	-494.6375171	134.9	5.5	6.4
		AVQZ	3.876	1.083	1.329	87.4	0.0	-494.6867041	134.4	5.7	5.9
	End	def2QZVP	4.641	1.081	1.329	0.0	NA	-2651.8003720	138.2	2.5	6.4
	C_{2v} ($^2A_1$)	AVTZ	4.592	1.082	1.331	0.0	NA	-494.6367236	142.7	3.4	12.1
		AVQZ	4.569	1.082	1.329	0.0	NA	-494.6858765	136.0	3.5	5.3
	BifOut	def2QZVP	2.932	1.082	1.342	90.0	90.0	-375.9055958	137.5	27.4	30.6
	C_{2v} ($^2A_1$)	AVTZ	2.939	1.083	1.343	90.0	90.0	-373.6995452	137.5	28.5	31.9
		AVQZ	2.954	1.082	1.342	87.2	90.0	-373.7497297	137.9	30.1	33.7
	BifPl	def2QZVP	4.146	1.082	1.329	85.4	0.0	-375.8970111	136.8	4.8	7.3
$I\cdots C_2H_4$	C_{2v} ($^2A_1$)	AVTZ	4.085	1.083	1.331	86.8	0.0	-373.6911592	137.2	6.4	9.7
		AVQZ	4.082	1.083	1.329	85.5	0.0	-373.7407626	138.7	6.5	11.0
	End	def2QZVP	4.858	1.082	1.329	0.0	NA	-375.8962746	136.7	2.9	5.3
	C_{2v} ($^2A_1$)	AVTZ	4.796	1.083	1.331	0.0	NA	-373.6902362	135.8	4.0	5.8
		AVQZ	4.788	1.083	1.329	0.0	NA	-373.7398358	135.7	4.1	5.6

Table S51: *$X^-\cdots C_2H_4$ complex VDEs from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			E_{VDE}	$VDE_{^2P_{3/2}}$	$VDE_{^2P_{1/2}}$	$ADE_{^2P_{3/2}}$	$ADE_{^2P_{1/2}}$
			E_h	eV	eV	eV	eV
$Cl^-\cdots C_2H_4$	BifOut	def2QZVP	-538.3195724				
	C_{2v} ($^1A_1$)	AVTZ	-538.2951167				
		AVQZ	-538.3203906				
	BifPl	def2QZVP	-538.3199428	3.817	3.926		
	C_{2v} ($^1A_1$)	AVTZ	-538.2957294	3.797	3.906		
		AVQZ	-538.3209223	3.796	3.905		
	End	def2QZVP	-538.3195152	3.804	3.913	3.794	3.903
	C_{2v} ($^1A_1$)	AVTZ	-538.2952249	3.781	3.890		
		AVQZ	-538.3204458	3.781	3.890		
	HApp	def2QZVP	-538.318339	3.874	3.983	3.836	3.945
	C_{2v} ($^1A'$)	AVTZ	-538.2941788	3.852	3.961	3.816	3.925
		AVQZ	-538.3193586	3.851	3.960	3.813	3.922
$Br^-\cdots C_2H_4$	BifOut	def2QZVP	-2651.8011283				
	C_{2v} ($^1A_1$)	AVTZ	-494.6374407				
		AVQZ	-494.6865335				
	BifPl	def2QZVP	-2651.8004338	3.527	3.984		
	C_{2v} ($^1A_1$)	AVTZ	-494.6370154	3.513	3.970		
		AVQZ	-494.6862272	3.510	3.967		
	End	def2QZVP	-2651.79982	3.518	3.975	3.550	4.007
	C_{2v} ($^1A_1$)	AVTZ	-494.6362658	3.504	3.961		
		AVQZ	-494.685444	3.503	3.960		
	HApp	def2QZVP	-2651.7991695	3.566	4.023	3.583	4.040
	C_{2v} ($^1A'$)	AVTZ	-494.6364836	3.528	3.985	3.619	4.076
		AVQZ	-494.6855081	3.532	3.989	3.547	4.004

Table S52: *$X^-\cdots C_2H_4$ complex VDEs from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			E_{VDE}	$VDE_{^2P_{3/2}}$	$VDE_{^2P_{1/2}}$	$ADE_{^2P_{3/2}}$	$ADE_{^2P_{1/2}}$
			E_h	eV	eV	eV	eV
$I^-\cdots C_2H_4$	BifOut	def2QZVP	-375.8955505				
	C_{2v} ($^1A_1$)	AVTZ	-373.7037521				
		AVQZ	-373.7389829				
	BifPl	def2QZVP	-375.8967397	3.165	4.107	3.193	4.135
	C_{2v} ($^1A_1$)	AVTZ	-373.6909003	3.167	4.109	3.200	4.142
		AVQZ	-373.7405152	3.165	4.107	3.211	4.153
	End	def2QZVP	-375.8960107	3.166	4.108	3.188	4.130
	C_{2v} ($^1A_1$)	AVTZ	-373.6900002	3.166	4.108		
		AVQZ	-373.7396115	3.165	4.107		
	HApp	def2QZVP	-375.8957326	3.190	4.132	3.207	4.149
	C_{2v} ($^1A'$)	AVTZ	-373.6898328	3.187	4.129	3.201	4.143
		AVQZ	-373.7405152	3.127	4.069	4.611	5.553

Table S53: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl^-\cdots C_2H_4$ C_{2v} ($^1A_1$) BifOut vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	74i	0.1327	In plane intermol. bend
	ω_2	b_1	62i	0.5869	C_2H_4 internal rotation
	ω_3	a_1	32	17.0338	Intermolecular stretch
	ω_4	b_1	847	0.0029	CH_2 symm rock
	ω_5	b_2	945	3.7835	CH_2 asymm wag
	ω_6	a_1	963	103.0111	CH_2 symm wag
	ω_7	a_2	1051	0	CH_2 twist
	ω_8	a_2	1257	0	CH_2 asymm rock
	ω_9	a_1	1384	0.5923	CH_2 symm scissor
	ω_{10}	b_2	1486	6.6909	CH_2 asymm scissor
	ω_{11}	a_1	1685	1.4123	C=C stretch
	ω_{12}	b_2	3136	21.8013	CH_2 unpair symm stretch
	ω_{13}	a_1	3151	0.0014	CH_2 pair symm stretch
	ω_{14}	a_2	3212	0	CH_2 unpair asymm stretch
	ω_{15}	b_1	3239	26.9475	CH_2 unpair asymm stretch
		zpe	133.9		
AVTZ	ω_1	b_1	156i	0.8847	C_2H_4 internal rotation
	ω_2	b_2	93i	0.2612	In plane intermol. bend
	ω_3	a_1	28	16.4421	Intermolecular stretch
	ω_4	b_1	827	0.0027	CH_2 symm rock
	ω_5	b_2	938	4.3216	CH_2 asymm wag
	ω_6	a_1	953	109.235	CH_2 symm wag
	ω_7	a_2	1033	0	CH_2 twist
	ω_8	a_2	1246	0	CH_2 asymm rock
	ω_9	a_1	1381	0.8956	CH_2 symm scissor
	ω_{10}	b_2	1476	6.6882	CH_2 asymm scissor
	ω_{11}	a_1	1688	1.6298	C=C stretch
	ω_{12}	b_2	3152	19.7149	CH_2 unpair symm stretch
	ω_{13}	a_1	3171	0.0774	CH_2 pair symm stretch
	ω_{14}	a_2	3231	0	CH_2 unpair asymm stretch
	ω_{15}	b_1	3259	24.2869	CH_2 pair asymm stretch
		zpe	133.9		
AVQZ	ω_1	b_1	154i	0.8288	C_2H_4 internal rotation
	ω_2	b_2	91i	0.2596	In plane intermol. bend
	ω_3	a_1	25	16.3506	Intermolecular stretch
	ω_4	b_1	830	0.0005	CH_2 symm rock
	ω_5	b_2	950	4.1068	CH_2 asymm wag
	ω_6	a_1	958	109.0714	CH_2 symm wag
	ω_7	a_2	1047	0	CH_2 twist
	ω_8	a_2	1250	0	CH_2 asymm rock
	ω_9	a_1	1382	0.8347	CH_2 symm scissor
	ω_{10}	b_2	1478	6.903	CH_2 asymm scissor
	ω_{11}	a_1	1689	1.54	C=C stretch
	ω_{12}	b_2	3153	19.2479	CH_2 unpair symm stretch
	ω_{13}	a_1	3171	0.0978	CH_2 pair symm stretch
	ω_{14}	a_2	3234	0	CH_2 unpair asymm stretch
	ω_{15}	b_1	3261	23.3394	CH_2 pair asymm stretch
		zpe	134.1		

Table S54: *Calculated harmonic frequencies and mode assignments for the $Cl^{-}\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl^{-}\cdots C_2H_4$				
	C_{2v} ($^1A_1$) BifPl vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	82	0.1601	In plane internal rotation
	ω_2	a_1	107	18.7355	Intermolecular stretch
	ω_3	b_1	276	0.9098	OoP internal rotation
	ω_4	a_1	853	8.8812	CH_2 symm. rock
	ω_5	a_2	959	0	CH_2 asymm. wag
	ω_6	b_1	995	75.7179	CH_2 symm. wag
	ω_7	a_2	1094	0	CH_2 twist
	ω_8	b_2	1267	0.5784	CH_2 asymm. rock
	ω_9	a_1	1371	9.7341	CH_2 symm. scissor
	ω_{10}	b_2	1448	12.6496	CH_2 asymm. scissor
	ω_{11}	a_1	1662	13.4487	C=C stretch
	ω_{12}	b_2	3089	37.5647	CH_2 unpair symm. stretch
	ω_{13}	a_1	3104	102.7836	CH_2 pair symm. stretch
	ω_{14}	b_2	3189	4.2636	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3211	0.9283	CH_2 pair asymm. stretch
		zpe	135.8		
AVTZ	ω_1	b_2	23	0.2517	In plane internal rotation
	ω_2	a_1	105	18.5563	Intermolecular stretch
	ω_3	b_1	234	1.015	OoP internal rotation
	ω_4	a_1	832	8.2187	CH_2 symm. rock
	ω_5	a_2	970	0	CH_2 asymm. wag
	ω_6	b_1	986	77.8935	CH_2 symm. wag
	ω_7	a_2	1075	0	CH_2 twist
	ω_8	b_2	1256	0.6603	CH_2 asymm. rock
	ω_9	a_1	1368	9.8751	CH_2 symm. scissor
	ω_{10}	b_2	1440	12.6795	CH_2 asymm. scissor
	ω_{11}	a_1	1665	15.3944	C=C stretch
	ω_{12}	b_2	3108	34.0231	CH_2 unpair symm. stretch
	ω_{13}	a_1	3127	92.1963	CH_2 pair symm. stretch
	ω_{14}	b_2	3210	4.7755	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3233	1.4227	CH_2 pair asymm. stretch
		zpe	135.4		
AVQZ	ω_1	b_2	28	0.2562	In plane internal rotation
	ω_2	a_1	103	18.5658	Intermolecular stretch
	ω_3	b_1	232	0.9544	OoP internal rotation
	ω_4	a_1	836	8.2506	CH_2 symm. rock
	ω_5	a_2	979	0	CH_2 asymm. wag
	ω_6	b_1	988	77.3198	CH_2 symm. wag
	ω_7	a_2	1087	0	CH_2 twist
	ω_8	b_2	1259	0.6745	CH_2 asymm. rock
	ω_9	a_1	1369	9.8461	CH_2 symm. scissor
	ω_{10}	b_2	1442	12.894	CH_2 asymm. scissor
	ω_{11}	a_1	1667	15.3793	C=C stretch
	ω_{12}	b_2	3110	33.5696	CH_2 unpair symm. stretch
	ω_{13}	a_1	3126	91.0359	CH_2 pair symm. stretch
	ω_{14}	b_2	3212	4.8726	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3235	1.471	CH_2 pair asymm. stretch
		zpe	135.6		

Table S55: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl^-\cdots C_2H_4$ C_{2v} ($^1A_1$) End vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	36	1.7546	In plane internal rotation
	ω_2	b_1	89	1.0112	OoP internal rotation
	ω_3	a_1	96	19.8357	Intermolecular stretch
	ω_4	b_2	804	0.2935	CH_2 symm. rock
	ω_5	b_1	939	49.0786	Farside CH_2 wag
	ω_6	b_1	1070	35.6888	Nearside CH_2 wag
	ω_7	a_2	1083	0	CH_2 twist
	ω_8	b_2	1228	0.9365	CH_2 asymm. rock
	ω_9	a_1	1359	35.6712	CH_2 symm. scissor
	ω_{10}	a_1	1477	28.9938	CH_2 asymm. scissor
	ω_{11}	a_1	1666	0.0673	C=C stretch
	ω_{12}	a_1	3113	28.1136	Farside CH_2 symm. stretch
	ω_{13}	a_1	3161	2.68	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3184	25.591	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3241	8.052	Nearside CH_2 asymm. stretch
		zpe	134.9		
AVTZ	ω_1	b_2	$75i$	1.6556	In plane internal rotation
	ω_2	b_1	68	0.9121	OoP internal rotation
	ω_3	a_1	92	19.0953	Intermolecular stretch
	ω_4	b_2	783	0.1411	CH_2 symm. rock
	ω_5	b_1	923	44.7553	Farside CH_2 wag
	ω_6	b_1	1048	38.0344	Nearside CH_2 wag
	ω_7	a_2	1058	0	CH_2 twist
	ω_8	b_2	1217	0.9833	CH_2 asymm. rock
	ω_9	a_1	1356	34.4686	CH_2 symm. scissor
	ω_{10}	a_1	1466	28.9295	CH_2 asymm. scissor
	ω_{11}	a_1	1670	0.0912	C=C stretch
	ω_{12}	a_1	3132	26.1584	Farside CH_2 symm. stretch
	ω_{13}	a_1	3179	2.7962	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3205	23.4361	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3260	7.7758	Nearside CH_2 asymm. stretch
		zpe	134.3		
AVQZ	ω_1	b_2	$74i$	1.6346	In plane internal rotation
	ω_2	b_1	67	0.8991	OoP internal rotation
	ω_3	a_1	91	19.1179	Intermolecular stretch
	ω_4	b_2	787	0.1583	CH_2 symm. rock
	ω_5	b_1	930	46.3071	Farside CH_2 wag
	ω_6	b_1	1052	35.797	Nearside CH_2 wag
	ω_7	a_2	1075	0	CH_2 twist
	ω_8	b_2	1221	0.9868	CH_2 asymm. rock
	ω_9	a_1	1358	34.0268	CH_2 symm. scissor
	ω_{10}	a_1	1468	29.281	CH_2 asymm. scissor
	ω_{11}	a_1	1671	0.0954	C=C stretch
	ω_{12}	a_1	3133	26.3244	Farside CH_2 symm. stretch
	ω_{13}	a_1	3179	2.5644	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3208	23.2194	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3262	7.4027	Nearside CH_2 asymm. stretch
		zpe	134.6		

Table S56: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl^-\cdots C_2H_4$				
	C_s ($^1A'$) HApp vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	83	8.8088	In plane internal rotation
	ω_2	a'	139	18.6605	Intermolecular stretch
	ω_3	a''	230	0.0272	OoP internal rotation
	ω_4	a'	861	0.0399	CH_2 symm. rock
	ω_5	a''	940	38.4126	Farside CH_2 wag
	ω_6	a''	1039	36.8613	Nearside CH_2 wag
	ω_7	a''	1111	6.2868	C=C twist
	ω_8	a'	1260	3.2527	C=C rock
	ω_9	a'	1381	3.7993	CH_2 symm. scissor
	ω_{10}	a'	1494	5.7863	CH_2 asymm. scissor
	ω_{11}	a'	1671	5.177	C=C stretch
	ω_{12}	a'	3036	238.5303	Nearside CH_2 symm. stretch
	ω_{13}	a'	3109	54.0287	Farside CH_2 symm. stretch
	ω_{14}	a'	3160	36.8221	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3198	23.3878	Farside CH_2 asymm. stretch
		zpe	135.8		
AVTZ	ω_1	a'	54	3.5908	In plane internal rotation
	ω_2	a'	128	22.9739	Intermolecular stretch
	ω_3	a''	184	0.1205	OoP internal rotation
	ω_4	a'	840	0.162	CH_2 symm. rock
	ω_5	a''	933	41.9717	Farside CH_2 wag
	ω_6	a''	1030	30.0713	Nearside CH_2 wag
	ω_7	a''	1098	7.534	C=C twist
	ω_8	a'	1249	3.0091	C=C rock
	ω_9	a'	1378	3.1008	CH_2 symm. scissor
	ω_{10}	a'	1484	5.1019	CH_2 asymm. scissor
	ω_{11}	a'	1675	6.5419	C=C stretch
	ω_{12}	a'	3063	209.5337	Nearside CH_2 symm. stretch
	ω_{13}	a'	3129	56.5787	Farside CH_2 symm. stretch
	ω_{14}	a'	3182	37.9033	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3219	20.5623	Farside CH_2 asymm. stretch
		zpe	135.5		
AVQZ	ω_1	a'	53	3.5862	In plane internal rotation
	ω_2	a'	127	22.9131	Intermolecular stretch
	ω_3	a''	182	0.1131	OoP internal rotation
	ω_4	a'	844	0.1462	CH_2 symm. rock
	ω_5	a''	941	44.5281	Farside CH_2 wag
	ω_6	a''	1037	28.4483	Nearside CH_2 wag
	ω_7	a''	1105	5.8108	C=C twist
	ω_8	a'	1252	2.8779	C=C rock
	ω_9	a'	1380	2.8677	CH_2 symm. scissor
	ω_{10}	a'	1486	4.9954	CH_2 asymm. scissor
	ω_{11}	a'	1676	6.7204	C=C stretch
	ω_{12}	a'	3064	207.144	Nearside CH_2 symm. stretch
	ω_{13}	a'	3130	53.2625	Farside CH_2 symm. stretch
	ω_{14}	a'	3185	37.9955	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3222	19.8197	Farside CH_2 asymm. stretch
		zpe	135.7		

Table S57: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

$Br^-\cdots C_2H_4$ C_{2v} ($^1A_1$) BifOut vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	68i	0.001	In plane intermol. bend
	ω_2	b_1	40i	0.3576	C_2H_4 internal rotation
	ω_3	a_1	29	5.0245	Intermolecular stretch
	ω_4	b_1	848	0.0032	CH_2 symm. rock
	ω_5	b_2	948	3.4723	CH_2 asymm. wag
	ω_6	a_1	965	107.3703	CH_2 symm. wag
	ω_7	a_2	1053	0	CH_2 twist
	ω_8	a_2	1257	0	CH_2 asymm. rock
	ω_9	a_1	1384	0.5158	CH_2 symm. scissor
	ω_{10}	b_2	1486	6.8135	CH_2 asymm. scissor
	ω_{11}	a_1	1685	1.1677	C=C stretch
	ω_{12}	b_2	3136	20.5737	CH_2 unpair symm. stretch
	ω_{13}	a_1	3151	0.0001	CH_2 pair symm. stretch
	ω_{14}	a_2	3212	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3239	25.513	CH_2 unpair asymm. stretch
		zpe	133.9		
AVTZ	ω_1	b_1	152i	0.6751	C_2H_4 internal rotation
	ω_2	b_2	90i	0.0199	In plane intermol. bend
	ω_3	a_1	27	4.7452	Intermolecular stretch
	ω_4	b_1	826	0.003	CH_2 symm. rock
	ω_5	b_2	938	4.2763	CH_2 asymm. wag
	ω_6	a_1	955	115.1935	CH_2 symm. wag
	ω_7	a_2	1033	0	CH_2 twist
	ω_8	a_2	1246	0	CH_2 asymm. rock
	ω_9	a_1	1381	0.8067	CH_2 symm. scissor
	ω_{10}	b_2	1476	6.5932	CH_2 asymm. scissor
	ω_{11}	a_1	1687	1.3847	C=C stretch
	ω_{12}	b_2	3151	18.2079	CH_2 unpair symm. stretch
	ω_{13}	a_1	3171	0.0449	CH_2 pair symm. stretch
	ω_{14}	a_2	3231	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3259	22.3355	CH_2 pair asymm. stretch
		zpe	133.9		
AVQZ	ω_1	b_1	151i	0.6418	C_2H_4 internal rotation
	ω_2	b_2	89i	0.0172	In plane intermol. bend
	ω_3	a_1	26	4.7535	Intermolecular stretch
	ω_4	b_1	830	0.0012	CH_2 symm. rock
	ω_5	b_2	950	4.2006	CH_2 asymm. wag
	ω_6	a_1	958	115.0636	CH_2 symm. wag
	ω_7	a_2	1047	0	CH_2 twist
	ω_8	a_2	1250	0	CH_2 asymm. rock
	ω_9	a_1	1382	0.7838	CH_2 symm. scissor
	ω_{10}	b_2	1478	6.7412	CH_2 asymm. scissor
	ω_{11}	a_1	1689	1.4014	C=C stretch
	ω_{12}	b_2	3153	18.0504	CH_2 unpair symm. stretch
	ω_{13}	a_1	3171	0.0612	CH_2 pair symm. stretch
	ω_{14}	a_2	3234	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3261	21.7628	CH_2 pair asymm. stretch
		zpe	134.1		

Table S58: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br^-\cdots C_2H_4$ C_{2v} ($^1A_1$) BifPl vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	87	5.418	Intermolecular stretch
	ω_2	b_2	93	0.0194	In plane internal rotation
	ω_3	b_1	264	1.316	OoP internal rotation
	ω_4	a_1	853	8.2173	CH_2 symm. rock
	ω_5	a_2	960	0	CH_2 asymm. wag
	ω_6	b_1	994	73.9266	CH_2 symm. wag
	ω_7	a_2	1092	0	CH_2 twist
	ω_8	b_2	1267	0.7501	CH_2 asymm. rock
	ω_9	a_1	1374	9.5463	CH_2 symm. scissor
	ω_{10}	b_2	1456	12.6125	CH_2 asymm. scissor
	ω_{11}	a_1	1664	13.7292	C=C stretch
	ω_{12}	b_2	3094	34.5103	CH_2 unpair symm. stretch
	ω_{13}	a_1	3108	94.0627	CH_2 pair symm. stretch
	ω_{14}	b_2	3191	3.8374	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3213	1.6328	CH_2 pair asymm. stretch
		zpe	135.8		
AVTZ	ω_1	b_2	38	0.0006	In plane internal rotation
	ω_2	a_1	86	5.2281	Intermolecular stretch
	ω_3	b_1	225	1.7926	OoP internal rotation
	ω_4	a_1	832	7.997	CH_2 symm. rock
	ω_5	a_2	968	0	CH_2 asymm. wag
	ω_6	b_1	985	73.0119	CH_2 symm. wag
	ω_7	a_2	1073	0	CH_2 twist
	ω_8	b_2	1255	0.9295	CH_2 asymm. rock
	ω_9	a_1	1369	10.5038	CH_2 symm. scissor
	ω_{10}	b_2	1444	13.2249	CH_2 asymm. scissor
	ω_{11}	a_1	1667	16.3686	C=C stretch
	ω_{12}	b_2	3112	31.9583	CH_2 unpair symm. stretch
	ω_{13}	a_1	3130	86.5713	CH_2 pair symm. stretch
	ω_{14}	b_2	3211	4.3278	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3234	2.4854	CH_2 pair asymm. stretch
		zpe	135.4		
AVQZ	ω_1	b_2	56	0.0002	In plane internal rotation
	ω_2	a_1	86	5.2135	Intermolecular stretch
	ω_3	b_1	224	1.6399	OoP internal rotation
	ω_4	a_1	836	7.9208	CH_2 symm. rock
	ω_5	a_2	982	0	CH_2 asymm. wag
	ω_6	b_1	988	72.7803	CH_2 symm. wag
	ω_7	a_2	1086	0	CH_2 twist
	ω_8	b_2	1259	0.9012	CH_2 asymm. rock
	ω_9	a_1	1371	10.2742	CH_2 symm. scissor
	ω_{10}	b_2	1449	13.3597	CH_2 asymm. scissor
	ω_{11}	a_1	1669	16.1977	C=C stretch
	ω_{12}	b_2	3114	31.4401	CH_2 unpair symm. stretch
	ω_{13}	a_1	3130	84.9194	CH_2 pair symm. stretch
	ω_{14}	b_2	3213	4.437	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3236	2.5801	CH_2 pair asymm. stretch
		zpe	135.8		

Table S59: *Calculated harmonic frequencies and mode assignments for the $Br^{-}\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Br^{-}\cdots C_2H_4$ C_{2v} ($^1A_1$) End vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	55	0.6514	In plane internal rotation
	ω_2	a_1	78	5.9383	Intermolecular stretch
	ω_3	b_1	87	0.2961	OoP internal rotation
	ω_4	b_2	810	0.3449	CH_2 symm. rock
	ω_5	b_1	943	48.3582	Farside CH_2 wag
	ω_6	b_1	1064	34.9266	Nearside CH_2 wag
	ω_7	a_2	1083	0	CH_2 twist
	ω_8	b_2	1232	1.0795	CH_2 asymm. rock
	ω_9	a_1	1362	32.4929	CH_2 symm. scissor
	ω_{10}	a_1	1479	30.3723	CH_2 asymm. scissor
	ω_{11}	a_1	1668	0.001	C=C stretch
	ω_{12}	a_1	3116	27.3057	Farside CH_2 symm. stretch
	ω_{13}	a_1	3159	1.884	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3187	22.9475	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3241	8.2374	Nearside CH_2 asymm. stretch
		zpe	135		
AVTZ	ω_1	b_2	69i	0.6378	In plane internal rotation
	ω_2	b_1	64	0.2007	OoP internal rotation
	ω_3	a_1	75	5.5455	Intermolecular stretch
	ω_4	b_2	788	0.2465	CH_2 symm. rock
	ω_5	b_1	927	43.5251	Farside CH_2 wag
	ω_6	b_1	1044	35.7651	Nearside CH_2 wag
	ω_7	a_2	1058	0	CH_2 twist
	ω_8	b_2	1220	1.3555	CH_2 asymm. rock
	ω_9	a_1	1359	32.8618	CH_2 symm. scissor
	ω_{10}	a_1	1468	30.6295	CH_2 asymm. scissor
	ω_{11}	a_1	1672	0.003	C=C stretch
	ω_{12}	a_1	3134	26.096	Farside CH_2 symm. stretch
	ω_{13}	a_1	3177	1.9546	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3208	20.9315	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3259	7.9844	Nearside CH_2 asymm. stretch
		zpe	134.3		
AVQZ	ω_1	b_2	62i	0.6245	In plane internal rotation
	ω_2	b_1	64	0.2016	OoP internal rotation
	ω_3	a_1	76	5.5292	Intermolecular stretch
	ω_4	b_2	793	0.2594	CH_2 symm. rock
	ω_5	b_1	933	44.9402	Farside CH_2 wag
	ω_6	b_1	1048	33.7885	Nearside CH_2 wag
	ω_7	a_2	1075	0	CH_2 twist
	ω_8	b_2	1224	1.3373	CH_2 asymm. rock
	ω_9	a_1	1361	32.2749	CH_2 symm. scissor
	ω_{10}	a_1	1470	31.3592	CH_2 asymm. scissor
	ω_{11}	a_1	1673	0.003	C=C stretch
	ω_{12}	a_1	3135	26.2261	Farside CH_2 symm. stretch
	ω_{13}	a_1	3176	1.7923	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3210	20.7629	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3261	7.621	Nearside CH_2 asymm. stretch
		zpe	134.6		

Table S60: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Br^-\cdots C_2H_4$				
	C_s ($^1A'$) HApp vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	69	3.5179	In plane internal rotation
	ω_2	a'	122	5.7324	Intermolecular stretch
	ω_3	a''	219	0.1357	OoP internal rotation
	ω_4	a'	858	0.0636	CH_2 symm. rock
	ω_5	a''	945	35.7507	Farside CH_2 wag
	ω_6	a''	1032	42.0203	Nearside CH_2 wag
	ω_7	a''	1101	3.9979	C=C twist
	ω_8	a'	1260	2.9353	C=C rock
	ω_9	a'	1381	2.3298	CH_2 symm. scissor
	ω_{10}	a'	1492	5.3354	CH_2 asymm. scissor
	ω_{11}	a'	1673	4.9219	C=C stretch
	ω_{12}	a'	3062	171.4185	Nearside CH_2 symm. stretch
	ω_{13}	a'	3114	52.3683	Farside CH_2 symm. stretch
	ω_{14}	a'	3169	37.5042	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3203	19.7355	Farside CH_2 asymm. stretch
		zpe	135.8		
AVTZ	ω_1	a'	71	3.1409	In plane internal rotation
	ω_2	a'	128	5.9071	Intermolecular stretch
	ω_3	a''	228	0.5296	OoP internal rotation
	ω_4	a'	856	0.2593	CH_2 symm. rock
	ω_5	a''	951	41.9635	Farside CH_2 wag
	ω_6	a''	1038	28.0875	Nearside CH_2 wag
	ω_7	a''	1101	4.3561	C=C twist
	ω_8	a'	1258	2.8507	C=C rock
	ω_9	a'	1379	2.1703	CH_2 symm. scissor
	ω_{10}	a'	1489	3.4935	CH_2 asymm. scissor
	ω_{11}	a'	1669	7.1271	C=C stretch
	ω_{12}	a'	3058	180.2937	Nearside CH_2 symm. stretch
	ω_{13}	a'	3110	54.5539	Farside CH_2 symm. stretch
	ω_{14}	a'	3165	37.6241	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3199	17.7562	Farside CH_2 asymm. stretch
		zpe	135.8		
AVQZ	ω_1	a'	41	0.9102	In plane internal rotation
	ω_2	a'	104	7.9251	Intermolecular stretch
	ω_3	a''	176	0.4621	OoP internal rotation
	ω_4	a'	841	0.2327	CH_2 symm. rock
	ω_5	a''	945	42.2846	Farside CH_2 wag
	ω_6	a''	1033	29.3688	Nearside CH_2 wag
	ω_7	a''	1097	3.4939	C=C twist
	ω_8	a'	1252	2.7135	C=C rock
	ω_9	a'	1379	1.7497	CH_2 symm. scissor
	ω_{10}	a'	1483	3.9627	CH_2 asymm. scissor
	ω_{11}	a'	1676	6.9636	C=C stretch
	ω_{12}	a'	3082	158.3062	Nearside CH_2 symm. stretch
	ω_{13}	a'	3134	51.9974	Farside CH_2 symm. stretch
	ω_{14}	a'	3192	35.9324	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3226	16.6705	Farside CH_2 asymm. stretch
		zpe	135.6		

Table S61: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$I^-\cdots C_2H_4$				
	C_{2v} ($^1A_1$) BifOut vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	51i	0.0012	In plane intermol. bend
	ω_2	a_1	24	2.2011	Intermolecular stretch
	ω_3	b_1	50	0.4082	C_2H_4 internal rotation
	ω_4	b_1	848	0.0023	CH_2 symm. rock
	ω_5	b_2	959	3.2336	CH_2 asymm. wag
	ω_6	a_1	970	117.535	CH_2 symm. wag
	ω_7	a_2	1058	0	CH_2 twist
	ω_8	a_2	1258	0	CH_2 asymm. rock
	ω_9	a_1	1384	0.3329	CH_2 symm. scissor
	ω_{10}	b_2	1487	6.8609	CH_2 asymm. scissor
	ω_{11}	a_1	1684	0.7235	C=C stretch
	ω_{12}	b_2	3136	17.9334	CH_2 unpair symm. stretch
	ω_{13}	a_1	3151	0.0008	CH_2 pair symm. stretch
	ω_{14}	a_2	3212	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3239	22.1829	CH_2 unpair asymm. stretch
		zpe	134.3		
AVTZ	ω_1	b_1	144i	0.3006	C_2H_4 internal rotation
	ω_2	b_2	83i	0.0002	In plane intermol. bend
	ω_3	a_1	23	2.0312	Intermolecular stretch
	ω_4	b_1	826	0.0008	CH_2 symm. rock
	ω_5	b_2	942	1.2288	CH_2 asymm. wag
	ω_6	a_1	957	120.4808	CH_2 symm. wag
	ω_7	a_2	1034	0	CH_2 twist
	ω_8	a_2	1246	0	CH_2 asymm. rock
	ω_9	a_1	1380	0.3621	CH_2 symm. scissor
	ω_{10}	b_2	1476	6.6515	CH_2 asymm. scissor
	ω_{11}	a_1	1687	0.9835	C=C stretch
	ω_{12}	b_2	3151	16.8237	CH_2 unpair symm. stretch
	ω_{13}	a_1	3171	0.0034	CH_2 pair symm. stretch
	ω_{14}	a_2	3231	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3259	20.6015	CH_2 pair asymm. stretch
		zpe	133.9		
AVQZ	ω_1	b_1	143i	0.6651	C_2H_4 internal rotation
	ω_2	b_2	83i	0.0078	In plane intermol. bend
	ω_3	a_1	27	2.0511	Intermolecular stretch
	ω_4	b_1	830	0.0012	CH_2 symm. rock
	ω_5	b_2	953	3.8432	CH_2 asymm. wag
	ω_6	a_1	961	122.3421	CH_2 symm. wag
	ω_7	a_2	1049	0	CH_2 twist
	ω_8	a_2	1250	0	CH_2 asymm. rock
	ω_9	a_1	1382	0.6204	CH_2 symm. scissor
	ω_{10}	b_2	1478	6.6923	CH_2 asymm. scissor
	ω_{11}	a_1	1688	1.0461	C=C stretch
	ω_{12}	b_2	3153	16.2934	CH_2 unpair symm. stretch
	ω_{13}	a_1	3170	0.0328	CH_2 pair symm. stretch
	ω_{14}	a_2	3234	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3261	19.6029	CH_2 pair asymm. stretch
		zpe	134.2		

Table S62: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$I^-\cdots C_2H_4$ C_{2v} ($^1A_1$) BifPl vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a_1	71	2.2233	Intermolecular stretch
	ω_2	b_2	94	0.0573	In plane internal rotation
	ω_3	b_1	246	1.4124	OoP internal rotation
	ω_4	a_1	852	7.4249	CH_2 symm. rock
	ω_5	a_2	971	0	CH_2 asymm. wag
	ω_6	b_1	993	69.8222	CH_2 symm. wag
	ω_7	a_2	1089	0	CH_2 twist
	ω_8	b_2	1266	1.0065	CH_2 asymm. rock
	ω_9	a_1	1376	9.4629	CH_2 symm. scissor
	ω_{10}	b_2	1464	12.5849	CH_2 asymm. scissor
	ω_{11}	a_1	1668	13.953	C=C stretch
	ω_{12}	b_2	3101	30.4278	CH_2 unpair symm. stretch
	ω_{13}	a_1	3114	81.0132	CH_2 pair symm. stretch
	ω_{14}	b_2	3194	3.4116	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3216	3.4029	CH_2 unpair asymm. stretch
		zpe	135.9		
AVTZ	ω_1	b_2	52	0.0263	In plane internal rotation
	ω_2	a_1	74	2.0329	Intermolecular stretch
	ω_3	b_1	205	2.0671	OoP internal rotation
	ω_4	a_1	831	7.05	CH_2 symm. rock
	ω_5	a_2	967	0	CH_2 asymm. wag
	ω_6	b_1	983	68.5478	CH_2 symm. wag
	ω_7	a_2	1071	0	CH_2 twist
	ω_8	b_2	1254	1.2199	CH_2 asymm. rock
	ω_9	a_1	1372	10.1875	CH_2 symm. scissor
	ω_{10}	b_2	1451	13.206	CH_2 asymm. scissor
	ω_{11}	a_1	1670	16.2979	C=C stretch
	ω_{12}	b_2	3118	28.6775	CH_2 unpair symm. stretch
	ω_{13}	a_1	3134	75.4815	CH_2 pair symm. stretch
	ω_{14}	b_2	3214	3.7439	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3236	4.5208	CH_2 pair asymm. stretch
		zpe	135.4		
AVQZ	ω_1	b_2	56	0.0216	In plane internal rotation
	ω_2	a_1	72	2.0479	Intermolecular stretch
	ω_3	b_1	203	1.9329	OoP internal rotation
	ω_4	a_1	835	7.039	CH_2 symm. rock
	ω_5	a_2	980	0	CH_2 asymm. wag
	ω_6	b_1	987	68.2653	CH_2 symm. wag
	ω_7	a_2	1083	0	CH_2 twist
	ω_8	b_2	1257	1.2025	CH_2 asymm. rock
	ω_9	a_1	1373	10.0611	CH_2 symm. scissor
	ω_{10}	b_2	1455	13.3807	CH_2 asymm. scissor
	ω_{11}	a_1	1672	16.1334	C=C stretch
	ω_{12}	b_2	3119	28.2683	CH_2 unpair symm. stretch
	ω_{13}	a_1	3134	74.4466	CH_2 pair symm. stretch
	ω_{14}	b_2	3215	3.866	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3238	4.5562	CH_2 pair asymm. stretch
		zpe	135.6		

Table S63: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I^-\cdots C_2H_4$				
	C_{2v} ($^1A_1$) End vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	66	2.5099	Intermolecular stretch
	ω_2	b_2	73	0.3937	In plane internal rotation
	ω_3	b_1	83	0.1475	OoP internal rotation
	ω_4	b_2	821	0.4136	CH_2 symm. rock
	ω_5	b_1	947	45.5989	Farside CH_2 wag
	ω_6	b_1	1051	33.5535	Nearside CH_2 wag
	ω_7	a_2	1082	0	CH_2 twist
	ω_8	b_2	1238	1.3302	CH_2 asymm. rock
	ω_9	a_1	1367	28.753	CH_2 symm. scissor
	ω_{10}	a_1	1483	32.1993	CH_2 asymm. scissor
	ω_{11}	a_1	1671	0.0731	C=C stretch
	ω_{12}	a_1	3119	26.4856	Farside CH_2 symm. stretch
	ω_{13}	a_1	3155	0.9335	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3191	19.1257	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3240	8.4423	Nearside CH_2 asymm. stretch
		zpe	135.1		
AVTZ	ω_1	b_2	49i	0.3869	In plane internal rotation
	ω_2	b_1	59	0.0591	OoP internal rotation
	ω_3	a_1	65	2.29	Intermolecular stretch
	ω_4	b_2	797	0.3232	CH_2 symm. rock
	ω_5	b_1	932	42.1444	Farside CH_2 wag
	ω_6	b_1	1036	33.5077	Nearside CH_2 wag
	ω_7	a_2	1059	0	CH_2 twist
	ω_8	b_2	1225	1.6811	CH_2 asymm. rock
	ω_9	a_1	1363	28.9663	CH_2 symm. scissor
	ω_{10}	a_1	1471	32.239	CH_2 asymm. scissor
	ω_{11}	a_1	1674	0.0512	C=C stretch
	ω_{12}	a_1	3137	25.7189	Farside CH_2 symm. stretch
	ω_{13}	a_1	3174	1.1284	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3212	17.6456	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3258	8.3119	Nearside CH_2 asymm. stretch
		zpe	134.4		
AVQZ	ω_1	b_2	47i	0.3822	In plane internal rotation
	ω_2	b_1	58	0.0639	OoP internal rotation
	ω_3	a_1	65	2.296	Intermolecular stretch
	ω_4	b_2	801	0.3347	CH_2 symm. rock
	ω_5	b_1	938	43.1679	Farside CH_2 wag
	ω_6	b_1	1039	32.1207	Nearside CH_2 wag
	ω_7	a_2	1073	0	CH_2 twist
	ω_8	b_2	1229	1.6386	CH_2 asymm. rock
	ω_9	a_1	1365	28.5159	CH_2 symm. scissor
	ω_{10}	a_1	1473	32.5609	CH_2 asymm. scissor
	ω_{11}	a_1	1675	0.0415	C=C stretch
	ω_{12}	a_1	3138	25.6702	Farside CH_2 symm. stretch
	ω_{13}	a_1	3174	0.9826	Nearside CH_2 symm. stretch
	ω_{14}	b_2	3214	17.562	Farside CH_2 asymm. stretch
	ω_{15}	b_2	3260	7.8891	Nearside CH_2 asymm. stretch
		zpe	134.6		

Table S64: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$I^-\cdots C_2H_4$				
	C_s ($^1A'$) HApp vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	57	1.858	In plane internal rotation
	ω_2	a'	108	2.4205	Intermolecular stretch
	ω_3	a''	208	0.2985	OoP internal rotation
	ω_4	a'	856	0.2733	CH_2 symm. rock
	ω_5	a''	952	33.7315	Farside CH_2 wag
	ω_6	a''	1025	41.2276	Nearside CH_2 wag
	ω_7	a''	1095	1.9982	C=C twist
	ω_8	a'	1261	2.6295	C=C rock
	ω_9	a'	1381	0.9777	CH_2 symm. scissor
	ω_{10}	a'	1489	4.1469	CH_2 asymm. scissor
	ω_{11}	a'	1674	5.3896	C=C stretch
	ω_{12}	a'	3085	105.775	Nearside CH_2 symm. stretch
	ω_{13}	a'	3119	50.6678	Farside CH_2 symm. stretch
	ω_{14}	a'	3180	32.6361	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3210	15.0241	Farside CH_2 asymm. stretch
		zpe	135.8		
AVTZ	ω_1	a'	60	1.3934	In plane internal rotation
	ω_2	a'	118	2.8155	Intermolecular stretch
	ω_3	a''	218	0.8119	OoP internal rotation
	ω_4	a'	854	0.6061	CH_2 symm. rock
	ω_5	a''	957	38.4627	Farside CH_2 wag
	ω_6	a''	1029	30.6209	Nearside CH_2 wag
	ω_7	a''	1087	1.685	C=C twist
	ω_8	a'	1259	2.362	C=C rock
	ω_9	a'	1379	0.7782	CH_2 symm. scissor
	ω_{10}	a'	1486	2.9637	CH_2 asymm. scissor
	ω_{11}	a'	1670	7.7493	C=C stretch
	ω_{12}	a'	3080	114.9046	Nearside CH_2 symm. stretch
	ω_{13}	a'	3115	53.2645	Farside CH_2 symm. stretch
	ω_{14}	a'	3175	32.7348	Nearside CH_2 asymm. stretch
	ω_{15}	a'	3206	13.1773	Farside CH_2 asymm. stretch
		zpe	135.7		
AVQZ	ω_1	b_2			
	ω_2	a_1			
	ω_3	b_1			
	ω_4	a_1			
	ω_5	a_2			
	ω_6	b_1			
	ω_7	a_2			
	ω_8	b_2			
	ω_9	a_1			
	ω_{10}	b_2			
	ω_{11}	a_1			
	ω_{12}	b_2			
	ω_{13}	a_1			
	ω_{14}	b_2			
	ω_{15}	a_1			
		zpe	0		

Table S65: *Calculated harmonic frequencies and mode assignments for the $Cl\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl\cdots C_2H_4$ C_{2v} ($^2A_1$) BifOut vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_2	20i	0.001	In plane intermol. bend
	ω_2	a_1	241	0.2475	Intermolecular stretch
	ω_3	b_1	380	0.2293	C_2H_4 internal rotation
	ω_4	b_1	852	0.3137	CH_2 symm. rock
	ω_5	a_2	988	0	CH_2 twist
	ω_6	b_2	995	0.1957	CH_2 asymm. wag
	ω_7	a_1	1016	70.3173	CH_2 symm. wag
	ω_8	a_2	1259	0	CH_2 asymm. rock
	ω_9	a_1	1355	16.6718	CH_2 symm. scissor
	ω_{10}	b_2	1491	12.5192	CH_2 asymm. scissor
	ω_{11}	a_1	1626	35.2028	C=C stretch
	ω_{12}	b_2	3157	0.3015	CH_2 unpair symm. stretch
	ω_{13}	a_1	3164	7.7897	CH_2 pair symm. stretch
	ω_{14}	a_2	3244	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3269	0.1449	CH_2 unpair asymm. stretch
		zpe	137.8		
AVTZ	ω_1	b_2	196	0.6477	In plane intermol. bend
	ω_2	a_1	234	1.4545	Intermolecular stretch
	ω_3	b_1	346	0.2278	C_2H_4 internal rotation
	ω_4	b_1	830	0.2375	CH_2 symm. rock
	ω_5	a_2	982	0	CH_2 twist
	ω_6	b_2	1000	0.3917	CH_2 asymm. wag
	ω_7	a_1	1004	75.0721	CH_2 symm. wag
	ω_8	a_2	1247	0	CH_2 asymm. rock
	ω_9	a_1	1355	15.1216	CH_2 symm. scissor
	ω_{10}	b_2	1480	11.5028	CH_2 asymm. scissor
	ω_{11}	a_1	1627	35.7212	C=C stretch
	ω_{12}	b_2	3173	0.4213	CH_2 unpair symm. stretch
	ω_{13}	a_1	3183	7.8035	CH_2 pair symm. stretch
	ω_{14}	a_2	3263	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3288	0.1973	CH_2 pair asymm. stretch
		zpe	138.8		
AVQZ	ω_1	b_2	199	0.6545	In plane intermol. bend
	ω_2	a_1	235	1.3096	Intermolecular stretch
	ω_3	b_1	347	0.2219	C_2H_4 internal rotation
	ω_4	b_1	834	0.2528	CH_2 symm. rock
	ω_5	a_2	987	0	CH_2 twist
	ω_6	a_1	1007	73.9845	CH_2 symm. wag
	ω_7	b_2	1011	0.3803	CH_2 asymm. wag
	ω_8	a_2	1250	0	CH_2 asymm. rock
	ω_9	a_1	1355	15.5924	CH_2 symm. scissor
	ω_{10}	b_2	1482	11.7476	CH_2 asymm. scissor
	ω_{11}	a_1	1627	36.7377	C=C stretch
	ω_{12}	b_2	3175	0.3614	CH_2 unpair symm. stretch
	ω_{13}	a_1	3184	7.9473	CH_2 pair symm. stretch
	ω_{14}	a_2	3266	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3290	0.1384	CH_2 pair asymm. stretch
		zpe	139.1		

Table S66: *Calculated harmonic frequencies and mode assignments for the $Cl\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl\cdots C_2H_4$ C_{2v} ($^2A_1$) BifPl vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_1	154i	2.129	OoP internal rotation
	ω_2	a_1	56	0	Intermolecular stretch
	ω_3	b_2	76	0.0007	In plane internal rotation
	ω_4	a_1	831	0.7528	CH_2 symm. rock
	ω_5	b_1	972	116.2064	CH_2 symm. wag
	ω_6	a_2	973	0.001	CH_2 asymm. wag
	ω_7	a_2	1068	0	CH_2 twist
	ω_8	b_2	1251	0.0517	CH_2 asymm. rock
	ω_9	a_1	1381	0.9117	CH_2 symm. scissor
	ω_{10}	b_2	1479	12.2049	CH_2 asymm. scissor
	ω_{11}	a_1	1686	0.5009	C=C stretch
	ω_{12}	b_2	3155	13.4547	CH_2 unpair symm. stretch
	ω_{13}	a_1	3170	0.5447	CH_2 pair symm. stretch
	ω_{14}	b_2	3238	0.0055	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3263	16.936	CH_2 pair asymm. stretch
		zpe	135.2		
AVTZ	ω_1	b_1	156i	2.4909	OoP internal rotation
	ω_2	a_1	60	0.0004	Intermolecular stretch
	ω_3	b_2	78	0.0007	In plane internal rotation
	ω_4	a_1	826	0.5865	CH_2 symm. rock
	ω_5	a_2	966	0	CH_2 asymm. wag
	ω_6	b_1	970	115.0523	CH_2 symm. wag
	ω_7	a_2	1052	0	CH_2 twist
	ω_8	b_2	1248	0.0696	CH_2 asymm. rock
	ω_9	a_1	1379	1.0149	CH_2 symm. scissor
	ω_{10}	b_2	1476	12.1268	CH_2 asymm. scissor
	ω_{11}	a_1	1683	0.5422	C=C stretch
	ω_{12}	b_2	3151	13.5789	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.6425	CH_2 pair symm. stretch
	ω_{14}	b_2	3233	0.0056	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3259	17.1256	CH_2 pair asymm. stretch
		zpe	134.9		
AVQZ	ω_1	b_1	163i	2.7718	OoP internal rotation
	ω_2	a_1	58	0.0002	Intermolecular stretch
	ω_3	b_2	79	0.0006	In plane internal rotation
	ω_4	a_1	830	0.6169	CH_2 symm. rock
	ω_5	b_1	972	115.9855	CH_2 symm. wag
	ω_6	a_2	975	0.0001	CH_2 asymm. wag
	ω_7	a_2	1066	0	CH_2 twist
	ω_8	b_2	1251	0.0673	CH_2 asymm. rock
	ω_9	a_1	1380	1.0139	CH_2 symm. scissor
	ω_{10}	b_2	1478	12.2802	CH_2 asymm. scissor
	ω_{11}	a_1	1684	0.541	C=C stretch
	ω_{12}	b_2	3152	13.4856	CH_2 unpair symm. stretch
	ω_{13}	a_1	3167	0.6058	CH_2 pair symm. stretch
	ω_{14}	b_2	3235	0.0062	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3260	16.7999	CH_2 pair asymm. stretch
		zpe	135.1		

Table S67: *Calculated harmonic frequencies and mode assignments for the $Cl\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	$Cl\cdots C_2H_4$				
	C_{2v} ($^2A_1$) End vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	b_1	56i	0.4679	OoP internal rotation
	ω_2	b_2	29	0.001	In plane internal rotation
	ω_3	a_1	45	0	Intermolecular stretch
	ω_4	b_2	829	0.1638	CH_2 symm. rock
	ω_5	b_1	948	101.8515	Nearside CH_2 wag
	ω_6	b_1	975	41.8331	Farside CH_2 wag
	ω_7	a_2	1070	0	CH_2 twist
	ω_8	b_2	1249	0.1446	CH_2 asymm. rock
	ω_9	a_1	1380	0.4777	CH_2 symm. scissor
	ω_{10}	a_1	1480	13.7231	CH_2 asymm. scissor
	ω_{11}	a_1	1687	0.1567	C=C stretch
	ω_{12}	a_1	3155	15.4025	CH_2 unpair symm. stretch
	ω_{13}	a_1	3171	0.0351	CH_2 pair symm. stretch
	ω_{14}	b_2	3236	0.1303	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3263	16.2208	CH_2 pair asymm. stretch
		zpe	134.7		
AVTZ	ω_1	b_1	58i	0.7337	OoP internal rotation
	ω_2	b_2	31	0.0013	In plane internal rotation
	ω_3	a_1	48	0.0001	Intermolecular stretch
	ω_4	b_2	825	0.0865	CH_2 symm. rock
	ω_5	b_1	941	103.5732	Nearside CH_2 wag
	ω_6	b_1	969	49.9127	Farside CH_2 wag
	ω_7	a_2	1052	0	CH_2 twist
	ω_8	b_2	1245	0.1845	CH_2 asymm. rock
	ω_9	a_1	1378	0.5352	CH_2 symm. scissor
	ω_{10}	a_1	1478	13.7718	CH_2 asymm. scissor
	ω_{11}	a_1	1684	0.1863	C=C stretch
	ω_{12}	a_1	3151	15.6816	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.0249	CH_2 pair symm. stretch
	ω_{14}	b_2	3231	0.1243	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3259	16.351	CH_2 pair asymm. stretch
		zpe	134.4		
AVQZ	ω_1	b_1	63i	0.8172	OoP internal rotation
	ω_2	b_2	31	0.0012	In plane internal rotation
	ω_3	a_1	47	0	Intermolecular stretch
	ω_4	b_2	828	0.0969	CH_2 symm. rock
	ω_5	b_1	943	123.5851	Nearside CH_2 wag
	ω_6	b_1	976	33.4506	Farside CH_2 wag
	ω_7	a_2	1068	0	CH_2 twist
	ω_8	b_2	1249	0.1764	CH_2 asymm. rock
	ω_9	a_1	1379	0.5366	CH_2 symm. scissor
	ω_{10}	a_1	1480	13.9375	CH_2 asymm. scissor
	ω_{11}	a_1	1685	0.1756	C=C stretch
	ω_{12}	a_1	3152	15.5536	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.0243	CH_2 pair symm. stretch
	ω_{14}	b_2	3233	0.1183	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3260	15.9921	CH_2 pair asymm. stretch
		zpe	134.6		

Table S68: *Calculated harmonic frequencies and mode assignments for the $Br\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br\cdots C_2H_4$ C_{2v} ($^2A_1$) BifOut vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	99	0.0038	In plane intermol. bend
	ω_2	a_1	181	2.0234	Intermolecular stretch
	ω_3	b_1	345	0.0791	C_2H_4 internal rotation
	ω_4	b_1	852	0.2568	CH_2 symm. rock
	ω_5	b_2	995	0.0247	CH_2 asymm. wag
	ω_6	a_2	1009	0	CH_2 twist
	ω_7	a_1	1013	84.5971	CH_2 symm. wag
	ω_8	a_2	1259	0	CH_2 asymm. rock
	ω_9	a_1	1361	17.9906	CH_2 symm. scissor
	ω_{10}	b_2	1492	11.9755	CH_2 asymm. scissor
	ω_{11}	a_1	1634	40.1003	C=C stretch
	ω_{12}	b_2	3152	0.6338	CH_2 unpair symm. stretch
	ω_{13}	a_1	3159	6.4686	CH_2 pair symm. stretch
	ω_{14}	a_2	3236	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3262	0.4207	CH_2 unpair asymm. stretch
		zpe	137.9		
AVTZ	ω_1	a_1	177	3.932	Intermolecular stretch
	ω_2	b_2	204	0.3356	In plane intermol. bend
	ω_3	b_1	303	0.1419	C_2H_4 internal rotation
	ω_4	b_1	829	0.1688	CH_2 symm. rock
	ω_5	b_2	992	0.4025	CH_2 asymm. wag
	ω_6	a_1	999	92.166	CH_2 symm. wag
	ω_7	a_2	1004	0	CH_2 twist
	ω_8	a_2	1247	0	CH_2 asymm. rock
	ω_9	a_1	1359	13.9983	CH_2 symm. scissor
	ω_{10}	b_2	1479	11.0344	CH_2 asymm. scissor
	ω_{11}	a_1	1635	35.9252	C=C stretch
	ω_{12}	b_2	3167	0.7735	CH_2 unpair symm. stretch
	ω_{13}	a_1	3178	5.7996	CH_2 pair symm. stretch
	ω_{14}	a_2	3255	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3281	0.5321	CH_2 pair asymm. stretch
		zpe	138.2		
AVQZ	ω_1	a_1	179	3.7578	Intermolecular stretch
	ω_2	b_2	207	0.3376	In plane intermol. bend
	ω_3	b_1	307	0.1391	C_2H_4 internal rotation
	ω_4	b_1	833	0.1854	CH_2 symm. rock
	ω_5	a_1	1003	90.9609	CH_2 symm. wag
	ω_6	b_2	1007	0.4023	CH_2 asymm. wag
	ω_7	a_2	1009	0	CH_2 twist
	ω_8	a_2	1250	0	CH_2 asymm. rock
	ω_9	a_1	1360	14.6331	CH_2 symm. scissor
	ω_{10}	b_2	1482	11.2706	CH_2 asymm. scissor
	ω_{11}	a_1	1635	36.8806	C=C stretch
	ω_{12}	b_2	3169	0.6791	CH_2 unpair symm. stretch
	ω_{13}	a_1	3179	6.0009	CH_2 pair symm. stretch
	ω_{14}	a_2	3258	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3283	0.4172	CH_2 pair asymm. stretch
		zpe	138.5		

Table S69: *Calculated harmonic frequencies and mode assignments for the $Br\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br\cdots C_2H_4$ C_{2v} ($^2A_1$) BifPl vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_1	154*i*	7.789	OoP internal rotation
	ω_2	a_1	52	0.0078	Intermolecular stretch
	ω_3	b_2	114	0.0003	In plane internal rotation
	ω_4	a_1	848	0.9923	CH_2 symm. rock
	ω_5	b_1	976	132.8236	CH_2 symm. wag
	ω_6	a_2	987	0	CH_2 asymm. wag
	ω_7	a_2	1074	0	CH_2 twist
	ω_8	b_2	1259	0.0949	CH_2 asymm. rock
	ω_9	a_1	1382	1.48	CH_2 symm. scissor
	ω_{10}	b_2	1487	12.2728	CH_2 asymm. scissor
	ω_{11}	a_1	1680	0.5921	C=C stretch
	ω_{12}	b_2	3135	14.0089	CH_2 unpair symm. stretch
	ω_{13}	a_1	3147	0.8678	CH_2 pair symm. stretch
	ω_{14}	b_2	3213	0.0185	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3238	17.6597	CH_2 pair asymm. stretch
		zpe	135.1		
AVTZ	ω_1	b_1	156*i*	7.7352	OoP internal rotation
	ω_2	a_1	58	0.0167	Intermolecular stretch
	ω_3	b_2	120	0.0005	In plane internal rotation
	ω_4	a_1	844	0.896	CH_2 symm. rock
	ω_5	b_1	978	125.178	CH_2 symm. wag
	ω_6	a_2	983	0	CH_2 asymm. wag
	ω_7	a_2	1063	0	CH_2 twist
	ω_8	b_2	1257	0.1428	CH_2 asymm. rock
	ω_9	a_1	1379	1.8212	CH_2 symm. scissor
	ω_{10}	b_2	1484	12.5285	CH_2 asymm. scissor
	ω_{11}	a_1	1675	0.6932	C=C stretch
	ω_{12}	b_2	3131	13.8815	CH_2 unpair symm. stretch
	ω_{13}	a_1	3144	1.0642	CH_2 pair symm. stretch
	ω_{14}	b_2	3208	0.0274	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3234	17.3631	CH_2 pair asymm. stretch
		zpe	134.9		
AVQZ	ω_1	b_1	132*i*	1.6527	OoP internal rotation
	ω_2	a_1	58	0.0053	Intermolecular stretch
	ω_3	b_2	89	0.0004	In plane internal rotation
	ω_4	a_1	830	0.8894	CH_2 symm. rock
	ω_5	a	976	108.607	CH_2 symm. wag
	ω_6	a	977	0.0089	CH_2 asymm. wag
	ω_7	a_2	1068	0	CH_2 twist
	ω_8	b_2	1251	0.1288	CH_2 asymm. rock
	ω_9	a_1	1380	1.6628	CH_2 symm. scissor
	ω_{10}	b_2	1478	13.0571	CH_2 asymm. scissor
	ω_{11}	a_1	1684	1.0159	C=C stretch
	ω_{12}	b_2	3152	13.3744	CH_2 unpair symm. stretch
	ω_{13}	a_1	3167	0.8095	CH_2 pair symm. stretch
	ω_{14}	b_2	3235	0.0215	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3260	17.1966	CH_2 pair asymm. stretch
		zpe	135.2		

Table S70: *Calculated harmonic frequencies and mode assignments for the $Br\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br\cdots C_2H_4$ C_{2v} ($^2A_1$) End vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	42	0.0021	Intermolecular stretch
	ω_2	b_2	87	0.0014	In plane internal rotation
	ω_3	b_1	158	24.0075	OoP internal rotation
	ω_4	b_2	846	0.1972	CH_2 symm. rock
	ω_5	b_1	988	25.3443	Farside CH_2 wag
	ω_6	a_2	1077	0	CH_2 twist
	ω_7	b_2	1257	0.2179	CH_2 asymm. rock
	ω_8	b_1	1369	807.377	Nearside CH_2 wag
	ω_9	a_1	1381	0.6557	CH_2 symm. scissor
	ω_{10}	a_1	1488	14.4114	CH_2 asymm. scissor
	ω_{11}	a_1	1681	0.3363	C=C stretch
	ω_{12}	a_1	3134	16.9899	CH_2 unpair symm. stretch
	ω_{13}	a_1	3148	0.0539	CH_2 pair symm. stretch
	ω_{14}	b_2	3211	0.2077	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3239	16.448	CH_2 pair asymm. stretch
		zpe	138.2		
AVTZ	ω_1	b_2	26	0.0022	In plane internal rotation
	ω_2	a_1	44	0.0024	Intermolecular stretch
	ω_3	b_1	189	75.2294	OoP internal rotation
	ω_4	b_2	824	0.122	CH_2 symm. rock
	ω_5	b_1	968	28.1996	Farside CH_2 wag
	ω_6	a_2	1052	0.0003	CH_2 twist
	ω_7	b_2	1245	0.3062	CH_2 asymm. rock
	ω_8	a_1	1378	0.8856	CH_2 symm. scissor
	ω_9	a_1	1478	15.0795	CH_2 asymm. scissor
	ω_{10}	a_1	1684	0.3125	C=C stretch
	ω_{11}	b_1	2155	23928.6925	Nearside CH_2 wag
	ω_{12}	a_1	3150	16.607	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.0338	CH_2 pair symm. stretch
	ω_{14}	b_2	3231	0.1443	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3258	15.9103	CH_2 pair asymm. stretch
		zpe	142.7		
AVQZ	ω_1	b_2	34	0.002	In plane internal rotation
	ω_2	a_1	47	0.0031	Intermolecular stretch
	ω_3	b_1	92	4.4027	OoP internal rotation
	ω_4	b_2	828	0.1379	CH_2 symm. rock
	ω_5	b_1	975	25.1879	Farside CH_2 wag
	ω_6	a_2	1069	0	CH_2 twist
	ω_7	b_1	1089	2.5998	Nearside CH_2 wag
	ω_8	b_2	1248	0.3097	CH_2 asymm. rock
	ω_9	a_1	1379	0.8865	CH_2 symm. scissor
	ω_{10}	a_1	1479	15.4219	CH_2 asymm. scissor
	ω_{11}	a_1	1685	0.3261	C=C stretch
	ω_{12}	a_1	3152	16.5168	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.0399	CH_2 pair symm. stretch
	ω_{14}	b_2	3233	0.1533	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3260	15.4899	CH_2 pair asymm. stretch
		zpe	136		

Table S71: *Calculated harmonic frequencies and mode assignments for the $I\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I\cdots C_2H_4$ C_{2v} ($^2A_1$) BifOut vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	b_2	121	0.0323	In plane intermol. bend
	ω_2	a_1	140	4.3782	Intermolecular stretch
	ω_3	b_1	302	0.1909	C_2H_4 internal rotation
	ω_4	b_1	850	0.152	CH_2 symm. rock
	ω_5	b_2	995	0	CH_2 asymm. wag
	ω_6	a_1	1010	107.2779	CH_2 symm. wag
	ω_7	a_2	1034	0	CH_2 twist
	ω_8	a_2	1259	0	CH_2 asymm. rock
	ω_9	a_1	1367	15.0291	CH_2 symm. scissor
	ω_{10}	b_2	1491	11.0454	CH_2 asymm. scissor
	ω_{11}	a_1	1644	36.6926	C=C stretch
	ω_{12}	b_2	3145	1.1709	CH_2 unpair symm. stretch
	ω_{13}	a_1	3153	3.9735	CH_2 pair symm. stretch
	ω_{14}	a_2	3228	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3253	0.9967	CH_2 unpair asymm. stretch
		zpe	137.5		
AVTZ	ω_1	a_1	133	6.2469	Intermolecular stretch
	ω_2	b_2	182	0.1979	In plane intermol. bend
	ω_3	b_1	247	0.2281	C_2H_4 internal rotation
	ω_4	b_1	828	0.0951	CH_2 symm. rock
	ω_5	b_2	982	0.1184	CH_2 asymm. wag
	ω_6	a_1	995	115.3464	CH_2 symm. wag
	ω_7	a_2	1028	0	CH_2 twist
	ω_8	a_2	1247	0	CH_2 asymm. rock
	ω_9	a_1	1366	11.2729	CH_2 symm. scissor
	ω_{10}	b_2	1478	10.5067	CH_2 asymm. scissor
	ω_{11}	a_1	1646	31.8218	C=C stretch
	ω_{12}	b_2	3160	1.3688	CH_2 unpair symm. stretch
	ω_{13}	a_1	3173	3.147	CH_2 pair symm. stretch
	ω_{14}	a_2	3246	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3272	1.2722	CH_2 pair asymm. stretch
		zpe	137.5		
AVQZ	ω_1	a_1	139	6.1187	Intermolecular stretch
	ω_2	b_2	188	0.2017	In plane intermol. bend
	ω_3	b_1	255	0.2243	C_2H_4 internal rotation
	ω_4	b_1	831	0.1119	CH_2 symm. rock
	ω_5	a_1	1000	113.8089	CH_2 symm. wag
	ω_6	b_2	1001	0.1259	CH_2 asymm. wag
	ω_7	a_2	1033	0	CH_2 twist
	ω_8	a_2	1250	0	CH_2 asymm. rock
	ω_9	a_1	1366	11.9326	CH_2 symm. scissor
	ω_{10}	b_2	1481	10.7248	CH_2 asymm. scissor
	ω_{11}	a_1	1646	32.9532	C=C stretch
	ω_{12}	b_2	3163	1.1891	CH_2 unpair symm. stretch
	ω_{13}	a_1	3173	3.3415	CH_2 pair symm. stretch
	ω_{14}	a_2	3250	0	CH_2 unpair asymm. stretch
	ω_{15}	b_1	3275	1.0342	CH_2 pair asymm. stretch
		zpe	137.9		

Table S72: *Calculated harmonic frequencies and mode assignments for the $I\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I\cdots C_2H_4$ C_{2v} ($^2A_1$) BifPl vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	80	0.0813	Intermolecular stretch
	ω_2	b_2	129	0.0002	In plane internal rotation
	ω_3	b_1	254	18.4733	OoP internal rotation
	ω_4	a_1	828	1.9682	CH_2 symm. rock
	ω_5	a_2	975	0	CH_2 asymm. wag
	ω_6	b_1	1011	37.7752	CH_2 symm. wag
	ω_7	a_2	1063	0	CH_2 twist
	ω_8	b_2	1248	0.2034	CH_2 asymm. rock
	ω_9	a_1	1381	3.5477	CH_2 symm. scissor
	ω_{10}	b_2	1481	14.6987	CH_2 asymm. scissor
	ω_{11}	a_1	1686	2.3242	C=C stretch
	ω_{12}	b_2	3154	12.6605	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.9148	CH_2 pair symm. stretch
	ω_{14}	b_2	3234	0.204	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3257	19.1615	CH_2 pair asymm. stretch
		zpe	136.8		
AVTZ	ω_1	a_1	56	0.0191	Intermolecular stretch
	ω_2	b_2	86	0.0002	In plane internal rotation
	ω_3	b_1	334	51.5211	OoP internal rotation
	ω_4	a_1	825	1.1428	CH_2 symm. rock
	ω_5	a_2	964	0	CH_2 asymm. wag
	ω_6	b_1	1039	4.9933	CH_2 symm. wag
	ω_7	a_2	1054	0	CH_2 twist
	ω_8	b_2	1248	0.2461	CH_2 asymm. rock
	ω_9	a_1	1378	2.5092	CH_2 symm. scissor
	ω_{10}	b_2	1474	13.5209	CH_2 asymm. scissor
	ω_{11}	a_1	1682	1.8612	C=C stretch
	ω_{12}	b_2	3149	13.3113	CH_2 unpair symm. stretch
	ω_{13}	a_1	3165	0.9261	CH_2 pair symm. stretch
	ω_{14}	b_2	3231	0.049	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3257	18.6624	CH_2 pair asymm. stretch
		zpe	137.2		
AVQZ	ω_1	a_1	55	0.0197	Intermolecular stretch
	ω_2	b_2	89	0.0001	In plane internal rotation
	ω_3	b_1	453	176.5691	OoP internal rotation
	ω_4	a_1	829	1.1581	CH_2 symm. rock
	ω_5	a_2	976	0	CH_2 asymm. wag
	ω_6	a_2	1068	0	CH_2 twist
	ω_7	b_1	1118	55.2231	CH_2 symm. wag
	ω_8	b_2	1251	0.2473	CH_2 asymm. rock
	ω_9	a_1	1379	2.4952	CH_2 symm. scissor
	ω_{10}	b_2	1477	13.667	CH_2 asymm. scissor
	ω_{11}	a_1	1683	1.8202	C=C stretch
	ω_{12}	b_2	3151	13.1979	CH_2 unpair symm. stretch
	ω_{13}	a_1	3165	0.8932	CH_2 pair symm. stretch
	ω_{14}	b_2	3234	0.0519	CH_2 unpair asymm. stretch
	ω_{15}	a_1	3258	18.3099	CH_2 pair asymm. stretch
		zpe	138.7		

Table S73: *Calculated harmonic frequencies and mode assignments for the $I\cdots C_2H_4$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I\cdots C_2H_4$ C_{2v} ($^2A_1$) End vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a_1	39	0.0076	Intermolecular stretch
	ω_2	b_2	87	0.0032	In plane internal rotation
	ω_3	b_1	122	8.0985	OoP internal rotation
	ω_4	b_2	846	0.2821	CH_2 symm. rock
	ω_5	b_1	987	25.4804	Farside CH_2 wag
	ω_6	a_2	1077	0	CH_2 twist
	ω_7	b_1	1153	51.2417	Nearside CH_2 wag
	ω_8	b_2	1256	0.44	CH_2 asymm. rock
	ω_9	a_1	1380	1.2237	CH_2 symm. scissor
	ω_{10}	a_1	1488	16.2963	CH_2 asymm. scissor
	ω_{11}	a_1	1681	0.5518	C=C stretch
	ω_{12}	a_1	3134	18.6225	CH_2 unpair symm. stretch
	ω_{13}	a_1	3147	0.0364	CH_2 pair symm. stretch
	ω_{14}	b_2	3211	0.2103	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3238	15.7592	CH_2 pair asymm. stretch
		zpe	136.7		
AVTZ	ω_1	b_2	19	0.0034	In plane internal rotation
	ω_2	a_1	41	0.0116	Intermolecular stretch
	ω_3	b_1	98	6.4172	OoP internal rotation
	ω_4	b_2	823	0.1749	CH_2 symm. rock
	ω_5	b_1	969	25.6663	Farside CH_2 wag
	ω_6	a_2	1053	0	CH_2 twist
	ω_7	b_1	1110	19.0927	Nearside CH_2 wag
	ω_8	b_2	1244	0.5078	CH_2 asymm. rock
	ω_9	a_1	1377	1.4498	CH_2 symm. scissor
	ω_{10}	a_1	1477	16.7616	CH_2 asymm. scissor
	ω_{11}	a_1	1684	0.5243	C=C stretch
	ω_{12}	a_1	3150	18.0679	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.0301	CH_2 pair symm. stretch
	ω_{14}	b_2	3230	0.1364	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3258	15.3362	CH_2 pair asymm. stretch
		zpe	135.8		
AVQZ	ω_1	b_2	23	0.0032	In plane internal rotation
	ω_2	a_1	42	0.0123	Intermolecular stretch
	ω_3	b_1	82	3.1727	OoP internal rotation
	ω_4	b_2	827	0.188	CH_2 symm. rock
	ω_5	b_1	976	25.3677	Farside CH_2 wag
	ω_6	a	1068	0	CH_2 twist
	ω_7	a	1069	0.0068	Nearside CH_2 wag
	ω_8	b_2	1247	0.4953	CH_2 asymm. rock
	ω_9	a_1	1378	1.4336	CH_2 symm. scissor
	ω_{10}	a_1	1479	17.0177	CH_2 asymm. scissor
	ω_{11}	a_1	1685	0.5205	C=C stretch
	ω_{12}	a_1	3152	17.9436	CH_2 unpair symm. stretch
	ω_{13}	a_1	3168	0.0294	CH_2 pair symm. stretch
	ω_{14}	b_2	3233	0.1506	CH_2 unpair asymm. stretch
	ω_{15}	b_2	3260	14.9554	CH_2 pair asymm. stretch
		zpe	135.7		

Table S74: *Cartesian coordinates of the geometries of halide-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots C_2H_4$			$Br^-\cdots C_2H_4$			$I^-\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^1A_1$) BifOut	def2QZVP	X	0.000000	0.000000	1.962151	0.000000	0.000000	1.315660	0.000000	0.000000	1.043715
		C	0.000000	0.663479	-2.093215	0.000000	0.663555	-2.886023	0.000000	0.663711	-3.464378
		C	0.000000	-0.663479	-2.093215	0.000000	-0.663555	-2.886023	0.000000	-0.663711	-3.464378
		H	0.922674	1.227245	-2.059496	0.922682	1.227459	-2.853953	0.922703	1.227920	-3.436094
		H	-0.922674	1.227245	-2.059496	-0.922682	1.227459	-2.853953	-0.922703	1.227920	-3.436094
		H	-0.922674	-1.227245	-2.059496	-0.922682	-1.227459	-2.853953	-0.922703	-1.227920	-3.436094
		H	0.922674	-1.227245	-2.059496	0.922682	-1.227459	-2.853953	0.922703	-1.227920	-3.436094
	AVTZ	X	0.000000	0.000000	1.978033	0.000000	0.000000	1.312829	0.000000	0.000000	1.034701
		C	0.000000	0.664606	-2.109803	0.000000	0.664668	-2.879630	0.000000	0.664728	-3.427448
		C	0.000000	-0.664606	-2.109803	0.000000	-0.664668	-2.879630	0.000000	-0.664728	-3.427448
		H	0.923658	1.228895	-2.077231	0.923670	1.229054	-2.848367	0.923738	1.229886	-3.427448
		H	-0.923658	1.228895	-2.077231	-0.923670	1.229054	-2.848367	-0.923738	1.229886	-3.427448
		H	-0.923658	-1.228895	-2.077231	-0.923670	-1.229054	-2.848367	-0.923738	-1.229886	-3.427448
		H	0.923658	-1.228895	-2.077231	0.923670	-1.229054	-2.848367	0.923738	-1.229886	-3.427448
	AVQZ	X	0.000000	0.000000	2.006689	0.000000	0.000000	1.313740	0.000000	0.000000	1.020542
		C	0.000000	0.663795	-2.140009	0.000000	0.663834	-2.881599	0.000000	0.663922	-3.387766
		C	0.000000	-0.663795	-2.140009	0.000000	-0.663834	-2.881599	0.000000	-0.663922	-3.387766
		H	0.922980	1.227833	-2.108401	0.922989	1.227915	-2.850424	0.922981	1.228206	-3.358883
		H	-0.922980	1.227833	-2.108401	-0.922989	1.227915	-2.850424	-0.922981	1.228206	-3.358883
		H	-0.922980	-1.227833	-2.108401	-0.922989	-1.227915	-2.850424	-0.922981	-1.228206	-3.358883
		H	0.922980	-1.227833	-2.108401	0.922989	-1.227915	-2.850424	0.922981	-1.228206	-3.358883

Table S75: *Cartesian coordinates of the geometries of halide-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots C_2H_4$			$Br^-\cdots C_2H_4$			$I^-\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^1A_1$) BifPl	def2QZVP	X	0.000000	0.000000	1.705514	0.000000	0.000000	1.160611	0.000000	0.000000	0.920649
		C	0.000000	0.665054	-1.815837	0.000000	0.664955	-2.542035	0.000000	0.664839	-3.052138
		C	0.000000	-0.665054	-1.815837	0.000000	-0.664955	-2.542035	0.000000	-0.664839	-3.052138
		H	0.000000	1.184404	-0.863744	0.000000	1.190801	-1.593869	0.000000	1.199267	-2.109200
		H	0.000000	1.237849	-2.738100	0.000000	1.236569	-3.464619	0.000000	1.234895	-3.975167
		H	0.000000	-1.184404	-0.863744	0.000000	-1.190801	-1.593869	0.000000	-1.199267	-2.109200
		H	0.000000	-1.237849	-2.738100	0.000000	-1.236569	-3.464619	0.000000	-1.234895	-3.975167
	AVTZ	X	0.000000	0.000000	1.709351	0.000000	0.000000	1.154560	0.000000	0.000000	0.911628
		C	0.000000	0.666127	-1.819794	0.000000	0.666036	-2.528909	0.000000	0.665915	-3.022458
		C	0.000000	-0.666127	-1.819794	0.000000	-0.666036	-2.528909	0.000000	-0.665915	-3.022458
		H	0.000000	1.187028	-0.867636	0.000000	1.191276	-1.579302	0.000000	1.198706	-2.077381
		H	0.000000	1.238975	-2.743086	0.000000	1.238540	-3.452051	0.000000	1.237027	-3.946000
		H	0.000000	-1.187028	-0.867636	0.000000	-1.191276	-1.579302	0.000000	-1.198706	-2.077381
		H	0.000000	-1.238975	-2.743086	0.000000	-1.238540	-3.452051	0.000000	-1.237027	-3.946000
	AVQZ	X	0.000000	0.000000	1.710211	0.000000	0.000000	1.156735	0.000000	0.000000	0.912070
		C	0.000000	0.665286	-1.820646	0.000000	0.665197	-2.533493	0.000000	0.665075	-3.023811
		C	0.000000	-0.665286	-1.820646	0.000000	-0.665197	-2.533493	0.000000	-0.665075	-3.023811
		H	0.000000	1.186614	-0.869489	0.000000	1.191857	-1.585473	0.000000	1.198677	-2.080001
		H	0.000000	1.237521	-2.743431	0.000000	1.236601	-3.456431	0.000000	1.235322	-3.946998
		H	0.000000	-1.186614	-0.869489	0.000000	-1.191857	-1.585473	0.000000	-1.198677	-2.080001
		H	0.000000	-1.237521	-2.743431	0.000000	-1.236601	-3.456431	0.000000	-1.235322	-3.946998

Table S76: *Cartesian coordinates of the geometries of halide-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots C_2H_4$			$Br^-\cdots C_2H_4$			$I^-\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^1A_1$) End	def2QZVP	X	0.000000	0.000000	2.002709	0.000000	0.000000	1.354963	0.000000	0.000000	1.064753
		C	0.000000	0.000000	-1.465186	0.000000	0.000000	-2.298419	0.000000	0.000000	-2.863833
		C	0.000000	0.000000	-2.796607	0.000000	0.000000	-3.629542	0.000000	0.000000	-4.194555
		H	0.000000	0.904433	-0.871620	0.000000	0.914810	-1.718961	0.000000	0.909644	-2.278065
		H	0.000000	-0.904433	-0.871620	0.000000	-0.914810	-1.718961	0.000000	-0.909644	-2.278065
		H	0.000000	0.922709	-3.366027	0.000000	0.914810	-4.209000	0.000000	0.922913	-4.762727
		H	0.000000	-0.922709	-3.366027	0.000000	-0.914810	-4.209000	0.000000	-0.922913	-4.762727
	AVTZ	X	0.000000	0.000000	2.010202	0.000000	0.000000	1.351718	0.000000	0.000000	1.059733
		C	0.000000	0.000000	-1.472031	0.000000	0.000000	-2.292970	0.000000	0.000000	-2.846259
		C	0.000000	0.000000	-2.805474	0.000000	0.000000	-3.626123	0.000000	0.000000	-4.179047
		H	0.000000	0.906137	-0.879222	0.000000	0.907852	-1.702656	0.000000	0.910331	-2.259633
		H	0.000000	-0.906137	-0.879222	0.000000	-0.907852	-1.702656	0.000000	-0.910331	-2.259633
		H	0.000000	0.923758	-3.374976	0.000000	0.923846	-4.195129	0.000000	0.923955	-4.747387
		H	0.000000	-0.923758	-3.374976	0.000000	-0.923846	-4.195129	0.000000	-0.923955	-4.747387
	AVQZ	X	0.000000	0.000000	2.011456	0.000000	0.000000	1.351146	0.000000	0.000000	1.060273
		C	0.000000	0.000000	-1.474205	0.000000	0.000000	-2.292566	0.000000	0.000000	-2.848865
		C	0.000000	0.000000	-2.805932	0.000000	0.000000	-3.624005	0.000000	0.000000	-4.179943
		H	0.000000	0.905582	-0.881840	0.000000	0.907251	-1.702611	0.000000	0.909826	-2.262802
		H	0.000000	-0.905582	-0.881840	0.000000	-0.907251	-1.702611	0.000000	-0.909826	-2.262802
		H	0.000000	0.923070	-3.375128	0.000000	0.923149	-4.192721	0.000000	0.923251	-4.748017
		H	0.000000	-0.923070	-3.375128	0.000000	-0.923149	-4.192721	0.000000	-0.923251	-4.748017

Table S77: *Cartesian coordinates of the geometries of halide-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots C_2H_4$			$Br^-\cdots C_2H_4$			$I^-\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_s ($^1A'$) HApp	def2QZVP	X	0.000000	1.020845	-1.631978	0.000000	0.000000	1.303859	0.000000	0.000000	1.025766
		C	0.000000	-0.428009	1.623340	0.000000	-0.510495	-2.425013	0.000000	-0.528200	-2.993238
		C	0.000000	-1.741167	1.843522	0.000000	0.510648	-3.278725	0.000000	0.528010	-3.802263
		H	0.000000	0.000000	0.619669	0.000000	-1.531042	-2.794194	0.000000	-1.534003	-3.399338
		H	0.000000	0.261789	2.461836	0.000000	-0.366691	-1.345678	0.000000	-0.423988	-1.911540
		H	0.000000	-2.441037	1.016429	0.000000	0.364335	-4.353607	0.000000	0.425635	-4.881832
		H	0.000000	-2.160067	2.844519	0.000000	1.532481	-2.919152	0.000000	1.533491	-3.399887
	AVTZ	X	0.000000	1.031663	-1.627639	0.000000	0.000000	1.293398	0.000000	0.000000	1.009266
		C	0.000000	-0.437344	1.625467	0.000000	-0.517366	-2.408733	0.000000	0.545439	-2.960110
		C	0.000000	-1.754748	1.832180	0.000000	0.517270	-3.249297	0.000000	-0.544755	-3.726283
		H	0.000000	0.000000	0.625336	0.000000	-1.533571	-2.792513	0.000000	1.534673	-3.407672
		H	0.000000	0.244604	2.471550	0.000000	-0.386164	-1.326705	0.000000	0.481137	-1.874093
		H	0.000000	-2.446665	0.997135	0.000000	0.385630	-4.327084	0.000000	-0.486897	-4.810191
		H	0.000000	-2.183660	2.829959	0.000000	1.534682	-2.874462	0.000000	-1.533013	-3.280803
	AVQZ	X	0.000000	1.042316	-1.621722	0.000000	0.000000	1.296327	0.000000	0.000000	0.912070
		C	0.000000	-0.448281	1.627299	0.000000	-0.516762	-2.415738	0.000000	0.665075	-3.023811
		C	0.000000	-1.766413	1.817882	0.000000	0.516662	-3.255137	0.000000	-0.665075	-3.023811
		H	0.000000	0.000000	0.632801	0.000000	-1.532357	-2.798945	0.000000	1.235321	-3.946999
		H	0.000000	0.223447	2.480517	0.000000	-0.385567	-1.334539	0.000000	1.198678	-2.080002
		H	0.000000	-2.447701	0.975135	0.000000	0.385170	-4.332155	0.000000	-1.235321	-3.946999
		H	0.000000	-2.206958	2.809742	0.000000	1.533357	-2.880568	0.000000	-1.198678	-2.080002

Table S78: *Cartesian coordinates of the geometries of halogen-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots C_2H_4$			$Br\cdots C_2H_4$			$I\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^2A_1$) BifOut	def2QZVP	X	0.000000	0.000000	1.196209	0.000000	0.000000	0.836035	0.000000	0.000000	0.680237
		C	0.000000	0.675792	-1.270972	0.000000	0.673434	-1.826412	0.000000	0.670850	-2.251371
		C	0.000000	-0.675792	-1.270972	0.000000	-0.673434	-1.826412	0.000000	-0.670850	-2.251371
		H	0.924475	1.235354	-1.270972	0.924159	1.234347	-1.836074	0.923851	1.233329	-2.259024
		H	-0.924475	1.235354	-1.270972	-0.924159	1.234347	-1.836074	-0.923851	1.233329	-2.259024
		H	-0.924475	-1.235354	-1.270972	-0.924159	-1.234347	-1.836074	-0.923851	-1.233329	-2.259024
		H	0.924475	-1.235354	-1.270972	0.924159	-1.234347	-1.836074	0.923851	-1.233329	-2.259024
	AVTZ	X	0.000000	0.000000	1.195149	0.000000	0.000000	0.831021	0.000000	0.000000	0.681829
		C	0.000000	0.676824	-1.267328	0.000000	0.674442	-1.815498	0.000000	0.671687	-2.256768
		C	0.000000	-0.676824	-1.267328	0.000000	-0.674442	-1.815498	0.000000	-0.671687	-2.256768
		H	0.925515	1.236510	-1.277401	0.925224	1.235490	-1.824938	0.924810	1.234476	-2.263931
		H	-0.925515	1.236510	-1.277401	-0.925224	1.235490	-1.824938	-0.924810	1.234476	-2.263931
		H	-0.925515	-1.236510	-1.277401	-0.925224	-1.235490	-1.824938	-0.924810	-1.234476	-2.263931
		H	0.925515	-1.236510	-1.277401	0.925224	-1.235490	-1.824938	0.924810	-1.234476	-2.263931
	AVQZ	X	0.000000	0.000000	1.193560	0.000000	0.000000	0.828732	0.000000	0.000000	0.677756
		C	0.000000	0.676209	-1.265587	0.000000	0.673861	-1.810568	0.000000	0.671132	-2.243313
		C	0.000000	-0.676209	-1.265587	0.000000	-0.673861	-1.810568	0.000000	-0.671132	-2.243313
		H	0.924796	1.235586	-1.275867	0.924511	1.234608	-1.819706	0.924072	1.233639	-2.250326
		H	-0.924796	1.235586	-1.275867	-0.924511	1.234608	-1.819706	-0.924072	1.233639	-2.250326
		H	-0.924796	-1.235586	-1.275867	-0.924511	-1.234608	-1.819706	-0.924072	-1.233639	-2.250326
		H	0.924796	-1.235586	-1.275867	0.924511	-1.234608	-1.819706	0.924072	-1.233639	-2.250326

Table S79: *Cartesian coordinates of the geometries of halogen-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots C_2H_4$			$Br\cdots C_2H_4$			$I\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^2A_1$) BifPl	def2QZVP	X	0.000000	0.000000	1.845778	0.000000	0.000000	1.227461	0.000000	0.000000	0.948962
		C	0.000000	0.664484	-1.961322	0.000000	0.664483	-2.685324	0.000000	0.664481	-3.143739
		C	0.000000	-0.664484	-1.961322	0.000000	-0.664483	-2.685324	0.000000	-0.664481	-3.143739
		H	0.000000	1.227130	-1.036912	0.000000	1.226540	-1.760486	0.000000	1.226376	-2.218611
		H	0.000000	1.229868	-2.884268	0.000000	1.230111	-3.608133	0.000000	1.230316	-4.066455
		H	0.000000	-1.227130	-1.036912	0.000000	-1.226540	-1.760486	0.000000	-1.226376	-2.218611
		H	0.000000	-1.229868	-2.884268	0.000000	-1.230111	-3.608133	0.000000	-1.230316	-4.066455
	AVTZ	X	0.000000	0.000000	1.829912	0.000000	0.000000	1.207559	0.000000	0.000000	0.934768
		C	0.000000	0.665511	-1.944512	0.000000	0.665519	-2.641913	0.000000	0.665508	-3.096860
		C	0.000000	-0.665511	-1.944512	0.000000	-0.665519	-2.641913	0.000000	-0.665508	-3.096860
		H	0.000000	1.227991	-1.018864	0.000000	1.231956	-3.565398	0.000000	1.232186	-4.020225
		H	0.000000	1.231408	-2.868313	0.000000	1.226709	-1.715400	0.000000	1.226366	-2.169966
		H	0.000000	-1.227991	-1.018864	0.000000	-1.231956	-3.565398	0.000000	-1.232186	-4.020225
		H	0.000000	-1.231408	-2.868313	0.000000	-1.226709	-1.715400	0.000000	-1.226366	-2.169966
	AVQZ	X	0.000000	0.000000	1.834417	0.000000	0.000000	1.206360	0.000000	0.000000	0.934234
		C	0.000000	0.664662	-1.949260	0.000000	0.664678	-2.639223	0.000000	0.664666	-3.095020
		C	0.000000	-0.664662	-1.949260	0.000000	-0.664678	-2.639223	0.000000	-0.664666	-3.095020
		H	0.000000	1.227248	-1.024494	0.000000	1.226161	-1.713708	0.000000	1.225843	-2.169148
		H	0.000000	1.230068	-2.872497	0.000000	1.230453	-3.562248	0.000000	1.230671	-4.017926
		H	0.000000	-1.227248	-1.024494	0.000000	-1.226161	-1.713708	0.000000	-1.225843	-2.169148
		H	0.000000	-1.230068	-2.872497	0.000000	-1.230453	-3.562248	0.000000	-1.230671	-4.017926

Table S80: *Cartesian coordinates of the geometries of halogen-ethene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots C_2H_4$			$Br\cdots C_2H_4$			$I\cdots C_2H_4$		
			x	y	z	x	y	z	x	y	z
C_{2v} ($^2A_1$) End	def2QZVP	X	0.000000	0.000000	2.179989	0.000000	0.000000	1.444670	0.000000	0.000000	1.111636
		C	0.000000	0.000000	-1.652014	0.000000	0.000000	-2.496024	0.000000	0.000000	-3.018108
		C	0.000000	0.000000	-2.980887	0.000000	0.000000	-3.824909	0.000000	0.000000	-4.347022
		H	0.000000	0.921657	-1.084823	0.000000	0.921483	-1.928520	0.000000	0.921462	-2.450445
		H	0.000000	-0.921657	-1.084823	0.000000	-0.921483	-1.928520	0.000000	-0.921462	-2.450445
		H	0.000000	0.922804	-3.546380	0.000000	0.922809	-4.390407	0.000000	0.922822	-4.912515
		H	0.000000	-0.922804	-3.546380	0.000000	-0.922809	-4.390407	0.000000	-0.922822	-4.912515
	AVTZ	X	0.000000	0.000000	2.163470	0.000000	0.000000	1.429065	0.000000	0.000000	1.097442
		C	0.000000	0.000000	-1.633466	0.000000	0.000000	-2.460912	0.000000	0.000000	-2.970169
		C	0.000000	0.000000	-2.964380	0.000000	0.000000	-3.791844	0.000000	0.000000	-4.301120
		H	0.000000	0.922545	-1.065790	0.000000	0.922276	-1.892748	0.000000	0.922025	-2.401491
		H	0.000000	-0.922545	-1.065790	0.000000	-0.922276	-1.892748	0.000000	-0.922025	-2.401491
		H	0.000000	0.923789	-3.530168	0.000000	0.923803	-4.357626	0.000000	0.923825	-4.866862
		H	0.000000	-0.923789	-3.530168	0.000000	-0.923803	-4.357626	0.000000	-0.923825	-4.866862
	AVQZ	X	0.000000	0.000000	2.169323	0.000000	0.000000	1.421832	0.000000	0.000000	1.095543
		C	0.000000	0.000000	-1.640520	0.000000	0.000000	-2.445963	0.000000	0.000000	-2.964709
		C	0.000000	0.000000	-2.969738	0.000000	0.000000	-3.775189	0.000000	0.000000	-4.293961
		H	0.000000	0.921924	-1.073233	0.000000	0.921476	-1.877911	0.000000	0.921404	-2.396433
		H	0.000000	-0.921924	-1.073233	0.000000	-0.921476	-1.877911	0.000000	-0.921404	-2.396433
		H	0.000000	0.923095	-3.535241	0.000000	0.923102	-4.340692	0.000000	0.923116	-4.859453
		H	0.000000	-0.923095	-3.535241	0.000000	-0.923102	-4.340692	0.000000	-0.923116	-4.859453

Table S81: *$X^-\cdots HCOOH$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H} Å	$\angle_{X-H-O}$ °	Dh °	R_{C-O} Å	$R_{C=O}$ Å	R_{O-H} Å	$\angle_{C-O-H}$ °	$\angle_{O-C=O}$ °
$Cl^-\cdots HCOOH$	AcidAnti	def2QZVP	1.898	172.0	0.0	1.313	1.214	1.020	107.7	124.3
	C_s ($^1A'$)	AVTZ	1.903	172.2	0.0	1.316	1.217	1.022	107.7	124.3
		AVQZ	1.905	171.9	0.0	1.313	1.214	1.019	107.8	124.3
	AcidSyn	def2QZVP	1.869	168.0	180.0	1.306	1.211	1.036	115.4	129.0
	C_s ($^1A'$)	AVTZ	1.877	168.0	180.0	1.310	1.214	1.036	115.1	129.0
		AVQZ	1.878	168.1	180.0	1.307	1.212	1.034	115.2	128.9
	FormSyn	def2QZVP	2.265	177.0	0.0	1.357	1.209	0.967	104.9	121.1
	C_s ($^1A'$)	AVTZ	2.271	176.7	0.0	1.359	1.212	0.969	104.9	121.2
		AVQZ	2.274	176.7	0.0	1.357	1.209	0.967	105.0	121.2
$Br^-\cdots HCOOH$	AcidAnti	def2QZVP	2.106	170.3	0.0	1.318	1.212	1.007	107.7	123.9
	C_s ($^1A'$)	AVTZ	2.102	170.6	0.0	1.320	1.214	1.009	107.6	123.9
		AVQZ	2.090	170.6	0.0	1.318	1.212	1.008	107.8	123.9
	AcidSyn	def2QZVP	2.094	166.2	180.0	1.311	1.209	1.018	114.5	128.8
	C_s ($^1A'$)	AVTZ	2.092	166.4	180.0	1.314	1.212	1.019	114.3	128.7
		AVQZ	2.078	166.7	180.0	1.311	1.210	1.019	114.4	128.7
	FormSyn	def2QZVP	2.474	176.4	0.0	1.355	1.208	0.967	105.1	121.5
	C_s ($^1A'$)	AVTZ	2.460	176.2	0.0	1.357	1.210	0.969	105.1	121.6
		AVQZ	2.449	176.2	0.0	1.357	1.208	0.967	105.0	121.4
$I^-\cdots HCOOH$	AcidAnti	def2QZVP	2.378	169.2	0.0	1.323	1.209	0.996	108.0	123.5
	C_s ($^1A'$)	AVTZ	2.374	169.3	0.0	1.325	1.212	0.999	107.7	123.5
		AVQZ	2.365	169.1	0.0	1.323	1.210	0.997	107.9	123.5
	AcidSyn	def2QZVP	2.387	164.1	180.0	1.316	1.207	1.003	113.5	128.4
	C_s ($^1A'$)	AVTZ	2.383	164.3	180.0	1.319	1.210	1.006	113.4	128.4
		AVQZ	2.373	164.5	180.0	1.316	1.207	1.004	113.5	128.3
	FormSyn	def2QZVP	2.767	175.6	0.0	1.352	1.206	0.967	105.3	122.1
	C_s ($^1A'$)	AVTZ	2.740	175.6	0.0	1.355	1.209	0.969	105.3	122.1
		AVQZ	2.744	175.3	0.0	1.355	1.207	0.967	105.2	121.9

Table S82: *X···HCOOH complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$	R_{C-O}	$R_{C=O}$	R_{O-H}	$\angle_{C-O-H}$	$\angle_{O-C=O}$	E_{DFT}	zpe	D_e	D_o
			Å	°	°	Å	Å	Å	°	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
Cl···HCOOH	AcidAnti	def2	2.495	171.8	0.0	1.346	1.194	0.965	109.2	122.7	-649.4234691	89.6	-8.6	-7.9
	C_s ($^2A''$)	AVTZ	2.467	173.8	0.0	1.348	1.196	0.967	109.1	122.7	-649.3811215	89.4	-7.5	-6.8
		AVQZ	2.480	172.1	0.0	1.346	1.194	0.965	109.2	122.7	-649.4254670	89.5	-7.9	-7.6
			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$									
	AcidPSyn	def2	2.218	138.4	0.0	1.315	1.216	0.978	107.2	126.1	-649.4255680	92.4	-3.1	0.5
	C_s ($^2A'$)	AVTZ	2.217	138.7	0.0	1.318	1.218	0.981	107.1	126.1	-649.3831184	92.1	-2.3	1.2
		AVQZ	2.214	138.3	0.0	1.315	1.216	0.979	107.2	126.1	-649.4313977	92.3	7.6	10.8
			R_{X-O}	$\angle_{X-O=C}$	$Dh_{X-O=C-O}$									
	CarbPAnti	def2	2.627	117.3	0.0	1.338	1.198	0.963	109.8	122.7	-649.4299518	90.2	26.1	28.3
	C_s ($^2A'$)	AVTZ	2.632	116.9	0.0	1.341	1.201	0.965	109.7	122.6	-649.3874881	89.9	26.8	28.9
		AVQZ	2.617	117.1	0.0	1.338	1.199	0.963	109.8	122.6	-649.4276632	90.1	15.4	17.2
			R_{X-O}	$\angle_{X-O-C}$	$Dh_{X-O-C=O}$									
	CarbPSyn	def2	2.796	111.5	137.7	1.347	1.197	0.968	107.3	124.6	-649.4270581	90.0	0.8	1.9
	C_1 (^2A)	AVTZ	2.785	110.9	132.9	1.350	1.199	0.970	107.2	124.6	-649.3845715	89.8	1.5	2.7
		AVQZ	2.779	111.6	136.8	1.348	1.224	0.968	107.4	122.4	-649.4318934	89.8	8.9	9.6
			R_{X-O}	$\angle_{X-O=C}$	$Dh_{X-O=C-O}$									
	FormPAnti	def2	2.531	104.9	180.0	1.337	1.201	0.963	109.6	121.6	-649.4234691	90.8	9.1	11.9
	C_s ($^2A'$)	AVTZ	2.537	104.7	180.0	1.340	1.204	0.965	109.6	121.5	-649.3845715	90.5	19.1	21.9
		AVQZ	2.523	104.9	180.0	1.337	1.201	0.963	109.7	121.5	-649.4291541	90.7	19.3	21.7
			R_{X-H}	$\angle_{X-O=C}$	$Dh_{X-H-C-O}$									
	FormPSyn	def2	2.963	86.9	180.0	1.331	1.207	0.968	107.6	124.3	-649.4333976	91.4	17.5	20.0
	C_s ($^2A'$)	AVTZ	2.963	87.1	180.0	1.334	1.209	0.970	107.5	124.3	-649.3908721	91.1	18.1	20.6
		AVQZ	2.957	86.8	180.0	1.332	1.207	0.968	107.7	124.3	-649.4354276	91.3	18.2	20.4
			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$									
	InLineSyn	def2	2.508	170.6	180.0	1.339	1.200	0.970	107.6	125.2	-649.4294543	90.4	7.1	8.6
	C_s ($^2A''$)	AVTZ	2.481	170.3	180.0	1.342	1.203	0.972	107.5	125.3	-649.3870798	90.2	8.1	9.7
		AVQZ	2.491	171.2	180.0	1.340	1.200	0.971	107.6	125.2	-649.4313977	90.3	7.6	8.7
			R_{X-O}	$\angle_{X-O-C}$	$Dh_{X-O-C=O}$									
	OutPlAnti	def2	2.819	110.1	59.5	1.354	1.190	0.963	109.8	122.2	-649.4231910	89.1	8.4	9.5
	C_1 (^2A)	AVTZ	2.813	109.2	60.1	1.356	1.193	0.965	109.7	122.1	-649.3807418	88.8	9.1	10.2
		AVQZ	2.805	110.0	58.8	1.354	1.191	0.963	109.9	122.1	-649.4251819	89.0	8.8	9.6

Table S83: *X···HCOOH complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$	R_{C-O}	$R_{C=O}$	R_{O-H}	$\angle_{C-O-H}$	$\angle_{O-C=O}$	E_{DFT}	zpe	D_e	D_o
			Å	°	°	Å	Å	Å	°	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
Br···HCOOH	AcidAnti	def2	2.611	179.8	180.0	1.344	1.194	0.966	109.2	122.8	-2762.9035135	89.4	9.5	10.9
	C_s ($^2A''$)	AVTZ	2.563	174.7	180.0	1.347	1.197	0.968	109.2	122.8	-605.7221965	88.8	11.6	12.6
		AVQZ	2.562	179.8	180.0	1.344	1.194	0.966	109.2	122.8	-605.7904078	89.5	11.2	12.5
			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$									
	AcidPSyn	def2	2.409	140.0	0.0	1.321	1.212	0.976	107.7	126.0	-2762.9164383	91.8	25.8	28.7
	C_s ($^2A'$)	AVTZ	2.397	140.3	0.0	1.324	1.215	0.979	107.5	126.0	-605.7352501	91.6	28.2	31.2
		AVQZ	2.375	140.2	0.0	1.321	1.213	0.978	107.6	126.0	-605.8038602	91.8	29.0	31.6
			R_{X-O}	$\angle_{X-O=C}$	$Dh_{X-O=C-O}$									
	CarbPAnti	def2	2.774	118.7	0.0	1.339	1.198	0.963	109.8	122.5	-2762.9057547	90.0	15.4	17.4
	C_s ($^2A'$)	AVTZ	2.760	118.3	0.0	1.341	1.200	0.965	109.8	122.5	-605.7242830	89.7	17.0	19.1
		AVQZ	2.747	118.0	0.0	1.339	1.198	0.963	109.9	122.5	-605.7927562	90.0	17.4	19.1
			R_{X-O}	$\angle_{X-O-C}$	$Dh_{X-O-C=O}$									
	CarbPSyn	def2	2.946	114.9	180.0	1.346	1.197	0.968	107.5	124.7	-2762.9100519	89.5	9.0	9.7
	C_s ($^2A'$)	AVTZ	2.917	113.9	180.0	1.349	1.200	0.970	107.5	124.7	-605.7285103	89.3	10.5	11.2
		AVQZ	2.905	113.3	180.0	1.347	1.197	0.968	107.6	124.6	-605.7969128	89.6	10.8	11.2
			R_{X-O}	$\angle_{X-O=C}$	$Dh_{X-O=C-O}$									
	FormPAnti	def2	2.691	106.4	180.0	1.338	1.200	0.963	109.6	121.7	-2762.9069348	90.5	18.5	21.0
	C_s ($^2A'$)	AVTZ	2.685	106.1	180.0	1.341	1.203	0.965	109.6	121.7	-605.7254671	90.2	20.2	22.6
		AVQZ	2.671	106.4	180.0	1.338	1.200	0.963	109.7	121.7	-605.7939753	90.5	20.6	22.8
			R_{X-H}	$\angle_{X-O=C}$	$Dh_{X-H-C-O}$									
	FormPSyn	def2	3.130	87.8	180.0	1.332	1.206	0.968	107.6	124.4	-2762.9132907	91.1	17.5	19.8
	C_s ($^2A'$)	AVTZ	3.114	88.0	180.0	1.335	1.208	0.970	107.5	124.5	-605.7317623	90.8	19.1	21.3
		AVQZ	3.109	87.7	180.0	1.332	1.206	0.968	107.6	124.4	-605.8002542	91.1	19.6	21.5

Table S84: *X···HCOOH complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$	R_{C-O}	$R_{C=O}$	R_{O-H}	$\angle_{C-O-H}$	$\angle_{O-C=O}$	E_{DFT}	zpe	D_e	D_o
			Å	°	°	Å	Å	Å	°	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
I···HCOOH	AcidAnti	def2	2.776	171.0	0.0	1.345	1.194	0.966	109.2	122.8	-487.0001124	89.4	11.8	13.1
	C_s ($^2A''$)	AVTZ	2.730	172.4	0.0	1.347	1.197	0.969	109.0	122.8	-484.7763941	89.2	14.0	15.5
		AVQZ	2.731	171.2	0.0	1.345	1.195	0.967	109.2	122.8	-484.8451626	89.4	13.9	15.0
			R_{X-H}	$\angle_{X-H-O}$	$Dh_{X-H-O-C}$									
	AcidPSyn	def2	2.657	141.9	0.0	1.326	1.209	0.975	108.3	126.1	-487.0113231	91.2	23.5	25.9
	C_s ($^2A'$)	AVTZ	2.645	142.6	0.0	1.328	1.212	0.977	108.2	126.1	-484.7875874	91.0	25.8	28.1
		AVQZ	2.628	142.0	0.0	1.325	1.210	0.976	108.3	126.0	-484.8567507	91.3	26.8	28.9
			R_{X-O}	$\angle_{X-O=C}$	$Dh_{X-O=C-O}$									
	CarbPAnti	def2	2.971	120.4	0.0	1.340	1.197	0.963	109.9	122.4	-487.0017667	89.8	16.1	17.9
	C_s ($^2A'$)	AVTZ	2.974	119.6	0.0	1.342	1.200	0.965	109.9	122.3	-484.7777178	89.5	17.5	19.3
		AVQZ	2.949	120.1	0.0	1.340	1.198	0.963	110.0	122.4	-484.8467327	89.8	18.0	19.5
			R_{X-O}	$\angle_{X-O-C}$	$Dh_{X-O-C=O}$									
	CarbPSyn	def2	3.130	115.1	180.0	1.347	1.197	0.968	107.5	124.7	-487.0059523	89.6	9.4	10.1
	C_s ($^2A'$)	AVTZ	3.123	113.0	180.0	1.350	1.200	0.970	107.4	124.7	-484.7819179	89.4	10.9	11.7
		AVQZ	3.094	113.7	180.0	1.348	1.197	0.968	107.5	124.6	-484.8508119	89.6	11.2	11.7
			R_{X-O}	$\angle_{X-O=C}$	$Dh_{X-O=C-O}$									
	FormPAnti	def2	2.891	108.4	180.0	1.339	1.199	0.963	109.7	121.8	-487.0026840	90.2	18.5	20.7
	C_s ($^2A'$)	AVTZ	2.900	107.7	180.0	1.341	1.202	0.965	109.6	121.8	-484.7786732	89.9	20.0	22.2
		AVQZ	2.876	108.1	180.0	1.339	1.200	0.963	109.7	121.8	-484.8476979	90.2	20.6	22.5
			R_{X-H}	$\angle_{X-O=C}$	$Dh_{X-H-C-O}$									
	FormPSyn	def2	3.354	88.4	180.0	1.333	1.205	0.968	107.5	124.5	-487.0090110	90.9	17.4	19.4
	C_s ($^2A'$)	AVTZ	3.336	89.1	180.0	1.335	1.208	0.970	107.5	124.6	-484.7849351	90.6	18.8	20.8
		AVQZ	3.332	88.5	180.0	1.332	1.206	0.968	107.6	124.5	-484.8539484	90.8	19.5	21.1

Table S85: *$X^-\cdots HCOOH$ complex VDEs from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			E_{DFT}	zpe	D_e	D_o	E_{VDE}	$VDE_{^2P_{3/2}}$	$VDE_{^2P_{1/2}}$	$EA_{^2P_{3/2}}$	$EA_{^2P_{1/2}}$
			E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	E_h	eV	eV	eV	eV
$Cl^-\cdots HCOOH$	AcidAnti	def2	-649.6010967	89.8	138.0	139.8	-649.4134411	5.188	5.297	4.946	5.055
	C_s ($^1A'$)	AVTZ	-649.5595544	89.5	134.5	136.3	-649.3715186	5.131	5.240	4.900	5.009
		AVQZ	-649.6053503	89.7	133.7	135.1	-649.4159030	5.127	5.236	4.897	5.006
	AcidSyn	def2	-649.5922838	87.6	97.1	95.9	-649.4169766	4.852	4.988	4.574	4.683
	C_s ($^1A'$)	AVTZ	-649.5508514	87.5	94.0	92.9	-649.3753025	4.790	4.926	4.532	4.641
		AVQZ	-649.5966401	87.6	93.3	91.7	-649.4196326	4.787	4.923	4.529	4.638
	FormSyn	def2	-649.5741821	90.5	49.6	51.2	-649.4238775	4.181	4.312	3.956	4.065
	C_s ($^1A'$)	AVTZ	-649.5333411	90.2	48.0	49.7	-649.3812581	4.161	4.292	3.933	4.042
		AVQZ	-649.5791659	90.4	47.4	48.6	-649.4257443	4.155	4.286	3.926	4.035
$Br^-\cdots HCOOH$	AcidAnti	def2	-2763.0708498	90.1	122.4	124.5	-2762.896959	4.684	5.165	4.526	4.983
	C_s ($^1A'$)	AVTZ	-605.8886553	89.8	121.0	123.0	-605.7159059	4.641	5.122	4.487	4.944
		AVQZ	-605.9588771	89.9	121.3	123.0	-605.7841899	4.646	5.128	4.501	4.958
	AcidSyn	def2	-2763.0620982	88.4	81.7	81.2	-2762.9024939	4.295	4.777	3.979	4.436
	C_s ($^1A'$)	AVTZ	-605.8800436	88.2	80.8	80.3	-605.7137311	4.465	4.948	3.944	4.401
		AVQZ	-605.9502153	88.2	81.1	80.1	-605.7818835	4.472	4.955	3.940	4.397
	FormSyn	def2	-2763.0472360	90.4	42.7	44.2	-2762.9046064	3.841	4.318	4.278	4.735
	C_s ($^1A'$)	AVTZ	-605.8655786	90.2	42.8	44.4	-605.7231863	3.822	4.299	4.249	4.706
		AVQZ	-605.9354309	90.2	42.2	43.3	-605.7913579	3.820	4.297	4.250	4.707
$I^-\cdots HCOOH$	AcidAnti	def2	-487.1537363	90.3	103.2	105.5	-486.9964798	4.080	5.045	3.998	4.799
	C_s ($^1A'$)	AVTZ	-484.9297720	90.0	104.5	106.8	-484.7729086	4.066	5.031	3.989	4.793
		AVQZ	-485.0005413	90.1	104.4	106.2	-484.8416544	4.067	5.032	3.990	4.849
	AcidSyn	def2	-487.1455824	89.0	64.1	64.2	-487.0014105	3.725	4.690	3.503	4.305
	C_s ($^1A'$)	AVTZ	-484.9216459	88.7	65.6	65.7	-484.7778709	3.711	4.676	3.495	4.299
		AVQZ	-484.9923347	88.7	65.3	64.9	-484.8464868	3.713	4.678	3.485	4.344
	FormSyn	def2	-487.1340271	90.4	33.8	35.3	-487.0020181	3.401	4.360	3.563	4.364
	C_s ($^1A'$)	AVTZ	-484.9101879	90.2	35.5	37.0	-484.7780558	3.401	4.361	3.563	4.367
		AVQZ	-484.9807582	90.2	34.9	36.0	-484.8467519	3.398	4.357	3.556	4.415

Table S86: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Cl^-\cdots HCOOH$				
	C_s ($^1A'$) AcidAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	111	9.7457	In plane internal rotation
	ω_2	a''	166	32.8234	OoP internal rotation
	ω_3	a'	255	58.5546	Intermolecular stretch
	ω_4	a'	708	11.1202	O=C−O bend
	ω_5	a''	997	33.3866	Acidic H wag
	ω_6	a''	1084	1.0789	Formyl H wag
	ω_7	a'	1246	124.0897	C−OH stretch
	ω_8	a'	1417	17.8938	Formyl H bend
	ω_9	a'	1463	158.4102	Acidic H bend
	ω_{10}	a'	1778	635.3989	C=O stretch
	ω_{11}	a'	2768	2446.6507	Acidic H stretch
	ω_{12}	a'	3020	100.8512	Formyl H stretch
		zpe	89.8		
AVTZ	ω_1	a'	110	9.434	In plane internal rotation
	ω_2	a''	166	32.4683	OoP internal rotation
	ω_3	a'	252	59.571	Intermolecular stretch
	ω_4	a'	703	11.2813	O=C−O bend
	ω_5	a''	991	28.7096	Acidic H wag
	ω_6	a''	1079	0.4862	Formyl H wag
	ω_7	a'	1242	125.2696	C−OH stretch
	ω_8	a'	1410	18.073	Formyl H bend
	ω_9	a'	1458	149.6864	Acidic H bend
	ω_{10}	a'	1769	664.2714	C=O stretch
	ω_{11}	a'	2770	2504.7336	Acidic H stretch
	ω_{12}	a'	3018	93.2322	Formyl H stretch
		zpe	89.5		
AVQZ	ω_1	a'	110	9.3829	In plane internal rotation
	ω_2	a''	166	32.3517	OoP internal rotation
	ω_3	a'	252	59.3582	Intermolecular stretch
	ω_4	a'	706	10.9735	O=C−O bend
	ω_5	a''	991	28.3726	Acidic H wag
	ω_6	a''	1082	0.5926	Formyl H wag
	ω_7	a'	1243	126.0268	C−OH stretch
	ω_8	a'	1414	18.0525	Formyl H bend
	ω_9	a'	1459	149.9385	Acidic H bend
	ω_{10}	a'	1773	660.9776	C=O stretch
	ω_{11}	a'	2782	2472.4127	Acidic H stretch
	ω_{12}	a'	3019	96.4658	Formyl H stretch
		zpe	89.7		

Table S87: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Cl^-\cdots HCOOH$				
	C_s ($^1A'$) AcidSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	107	1.6647	In plane internal rotation
	ω_2	a''	178	5.0905	OoP internal rotation
	ω_3	a'	261	98.1138	Intermolecular stretch
	ω_4	a'	698	41.2244	O=C−O bend
	ω_5	a''	1014	31.9186	Acidic H wag
	ω_6	a''	1099	16.8962	Formyl H wag
	ω_7	a'	1256	291.3672	C−OH stretch
	ω_8	a'	1369	11.4201	Acidic H bend
	ω_9	a'	1424	39.3859	Formyl H bend
	ω_{10}	a'	1759	615.3097	C=O stretch
	ω_{11}	a'	2527	3274.953	Acidic H stretch
	ω_{12}	a'	2954	103.8487	Formyl H stretch
		zpe	87.6		
AVTZ	ω_1	a'	106	1.6475	In plane internal rotation
	ω_2	a''	177	5.1081	OoP internal rotation
	ω_3	a'	257	98.067	Intermolecular stretch
	ω_4	a'	693	40.9312	O=C−O bend
	ω_5	a''	1005	27.8697	Acidic H wag
	ω_6	a''	1094	13.4791	Formyl H wag
	ω_7	a'	1252	283.7654	C−OH stretch
	ω_8	a'	1365	10.6312	Acidic H bend
	ω_9	a'	1419	40.5178	Formyl H bend
	ω_{10}	a'	1752	614.7495	C=O stretch
	ω_{11}	a'	2546	3306.6377	Acidic H stretch
	ω_{12}	a'	2957	98.2896	Formyl H stretch
		zpe	87.5		
AVQZ	ω_1	a'	106	1.6473	In plane internal rotation
	ω_2	a''	177	5.07	OoP internal rotation
	ω_3	a'	257	97.6713	Intermolecular stretch
	ω_4	a'	695	41.2376	O=C−O bend
	ω_5	a''	1007	27.7526	Acidic H wag
	ω_6	a''	1095	12.7135	Formyl H wag
	ω_7	a'	1252	286.5623	C−OH stretch
	ω_8	a'	1366	10.1394	Acidic H bend
	ω_9	a'	1422	39.1323	Formyl H bend
	ω_{10}	a'	1755	611.5292	C=O stretch
	ω_{11}	a'	2553	3290.0983	Acidic H stretch
	ω_{12}	a'	2958	96.5491	Formyl H stretch
		zpe	87.6		

Table S88: *Calculated harmonic frequencies and mode assignments for the $Cl^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Cl^-\cdots HCOOH$				
	C_s ($^1A'$) FormSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	88	3.6824	In plane internal rotation
	ω_2	a'	135	31.2161	Intermolecular stretch
	ω_3	a''	168	0.8281	OoP internal rotation
	ω_4	a'	631	67.7333	O=C−O bend
	ω_5	a''	684	122.2421	Acidic H wag
	ω_6	a'	1093	324.6937	C−OH stretch
	ω_7	a''	1152	1.5085	Formyl H wag
	ω_8	a'	1289	10.3903	Acidic H bend
	ω_9	a'	1442	20.0407	Formyl H bend
	ω_{10}	a'	1754	383.5942	C=O stretch
	ω_{11}	a'	2923	371.9731	Formyl H stretch
	ω_{12}	a'	3764	23.3295	Acidic H stretch
		zpe	90.5		
AVTZ	ω_1	a'	88	3.597	In plane internal rotation
	ω_2	a'	134	31.0247	Intermolecular stretch
	ω_3	a''	172	0.7365	OoP internal rotation
	ω_4	a'	628	66.4866	O=C−O bend
	ω_5	a''	679	117.5984	Acidic H wag
	ω_6	a'	1092	319.3971	C−OH stretch
	ω_7	a''	1150	1.4497	Formyl H wag
	ω_8	a'	1285	9.9472	Acidic H bend
	ω_9	a'	1439	20.7269	Formyl H bend
	ω_{10}	a'	1748	388.2159	C=O stretch
	ω_{11}	a'	2928	382.1225	Formyl H stretch
	ω_{12}	a'	3745	23.0205	Acidic H stretch
		zpe	90.2		
AVQZ	ω_1	a'	87	3.5485	In plane internal rotation
	ω_2	a'	134	31.0388	Intermolecular stretch
	ω_3	a''	168	0.7159	OoP internal rotation
	ω_4	a'	631	66.6196	O=C−O bend
	ω_5	a''	682	117.4516	Acidic H wag
	ω_6	a'	1094	318.5852	C−OH stretch
	ω_7	a''	1150	1.3496	Formyl H wag
	ω_8	a'	1287	10.0449	Acidic H bend
	ω_9	a'	1439	20.3944	Formyl H bend
	ω_{10}	a'	1751	387.7219	C=O stretch
	ω_{11}	a'	2929	373.904	Formyl H stretch
	ω_{12}	a'	3757	23.9349	Acidic H stretch
		zpe	90.4		

Table S89: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br^-\cdots HCOOH$				
	C_s ($^1A'$) AcidAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	95	5.0774	In plane internal rotation
	ω_2	a''	162	30.6552	OoP internal rotation
	ω_3	a'	201	23.248	Intermolecular stretch
	ω_4	a'	703	4.9974	O=C−O bend
	ω_5	a''	924	30.833	Acidic H wag
	ω_6	a''	1081	0.2409	Formyl H wag
	ω_7	a'	1230	123.0028	C−OH stretch
	ω_8	a'	1418	18.686	Formyl H bend
	ω_9	a'	1434	154.302	Acidic H bend
	ω_{10}	a'	1786	588.5718	C=O stretch
	ω_{11}	a'	2993	1706.3917	Acidic H stretch
	ω_{12}	a'	3034	520.9151	Formyl H stretch
		zpe	90.1		
AVTZ	ω_1	a'	92	4.6469	In plane internal rotation
	ω_2	a''	163	29.1791	OoP internal rotation
	ω_3	a'	201	23.4696	Intermolecular stretch
	ω_4	a'	698	5.3167	O=C−O bend
	ω_5	a''	926	21.9497	Acidic H wag
	ω_6	a''	1078	0.0703	Formyl H wag
	ω_7	a'	1227	126.3719	C−OH stretch
	ω_8	a'	1411	20.7791	Formyl H bend
	ω_9	a'	1431	136.0448	Acidic H bend
	ω_{10}	a'	1778	626.873	C=O stretch
	ω_{11}	a'	2977	1974.7653	Acidic H stretch
	ω_{12}	a'	3029	327.3794	Formyl H stretch
		zpe	89.8		
AVQZ	ω_1	a'	95	4.6024	In plane internal rotation
	ω_2	a''	163	28.9496	OoP internal rotation
	ω_3	a'	204	23.7071	Intermolecular stretch
	ω_4	a'	702	5.5658	O=C−O bend
	ω_5	a''	932	21.6441	Acidic H wag
	ω_6	a''	1080	0.109	Formyl H wag
	ω_7	a'	1230	127.9505	C−OH stretch
	ω_8	a'	1416	19.1608	Formyl H bend
	ω_9	a'	1434	138.4097	Acidic H bend
	ω_{10}	a'	1780	631.0495	C=O stretch
	ω_{11}	a'	2968	2037.2741	Acidic H stretch
	ω_{12}	a'	3028	289.7328	Formyl H stretch
		zpe	89.9		

Table S90: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br^-\cdots HCOOH$				
	C_s ($^1A'$) AcidSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	88	0.5016	In plane internal rotation
	ω_2	a''	169	5.7385	OoP internal rotation
	ω_3	a'	204	40.8374	Intermolecular stretch
	ω_4	a'	686	50.4025	O=C−O bend
	ω_5	a''	956	42.6213	Acidic H wag
	ω_6	a''	1081	5.1701	Formyl H wag
	ω_7	a'	1232	294.0572	C−OH stretch
	ω_8	a'	1358	3.8743	Acidic H bend
	ω_9	a'	1426	25.4849	Formyl H bend
	ω_{10}	a'	1773	522.388	C=O stretch
	ω_{11}	a'	2827	2945.868	Acidic H stretch
	ω_{12}	a'	2977	30.6134	Formyl H stretch
		zpe	88.4		
AVTZ	ω_1	a'	87	0.4913	In plane internal rotation
	ω_2	a''	170	6.2016	OoP internal rotation
	ω_3	a'	203	41.5445	Intermolecular stretch
	ω_4	a'	681	49.7884	O=C−O bend
	ω_5	a''	954	29.7089	Acidic H wag
	ω_6	a''	1079	4.0961	Formyl H wag
	ω_7	a'	1229	284.8898	C−OH stretch
	ω_8	a'	1353	5.7773	Acidic H bend
	ω_9	a'	1421	27.6681	Formyl H bend
	ω_{10}	a'	1765	520.0975	C=O stretch
	ω_{11}	a'	2818	3009.3767	Acidic H stretch
	ω_{12}	a'	2977	32.401	Formyl H stretch
		zpe	88.2		
AVQZ	ω_1	a'	87	0.4289	In plane internal rotation
	ω_2	a''	171	6.1581	OoP internal rotation
	ω_3	a'	207	42.457	Intermolecular stretch
	ω_4	a'	684	49.4776	O=C−O bend
	ω_5	a''	958	29.1813	Acidic H wag
	ω_6	a''	1081	3.8263	Formyl H wag
	ω_7	a'	1232	287.9472	C−OH stretch
	ω_8	a'	1355	6.1199	Acidic H bend
	ω_9	a'	1424	27.9619	Formyl H bend
	ω_{10}	a'	1766	524.6785	C=O stretch
	ω_{11}	a'	2802	3050.5817	Acidic H stretch
	ω_{12}	a'	2976	36.3755	Formyl H stretch
		zpe	88.2		

Table S91: *Calculated harmonic frequencies and mode assignments for the $Br^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$Br^-\cdots HCOOH$				
	C_s ($^1A'$) FormSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	77	3.118	In plane internal rotation
	ω_2	a'	100	8.5577	Intermolecular stretch
	ω_3	a''	150	0.3743	OoP internal rotation
	ω_4	a'	632	65.5607	O=C−O bend
	ω_5	a''	683	122.9308	Acidic H wag
	ω_6	a'	1102	312.3493	C−OH stretch
	ω_7	a''	1135	1.2747	Formyl H wag
	ω_8	a'	1292	11.7849	Acidic H bend
	ω_9	a'	1434	17.6277	Formyl H bend
	ω_{10}	a'	1761	378.0368	C=O stretch
	ω_{11}	a'	2976	258.6564	Formyl H stretch
	ω_{12}	a'	3767	27.0993	Acidic H stretch
		zpe	90.4		
AVTZ	ω_1	a'	77	2.8139	In plane internal rotation
	ω_2	a'	103	8.5561	Intermolecular stretch
	ω_3	a''	161	0.1954	OoP internal rotation
	ω_4	a'	629	65.0371	O=C−O bend
	ω_5	a''	678	116.0499	Acidic H wag
	ω_6	a'	1099	304.3194	C−OH stretch
	ω_7	a''	1139	0.897	Formyl H wag
	ω_8	a'	1289	11.1906	Acidic H bend
	ω_9	a'	1432	19.3465	Formyl H bend
	ω_{10}	a'	1755	380.6314	C=O stretch
	ω_{11}	a'	2973	279.8671	Formyl H stretch
	ω_{12}	a'	3748	26.2908	Acidic H stretch
		zpe	90.2		
AVQZ	ω_1	a'	77	2.9635	In plane internal rotation
	ω_2	a'	101	8.6109	Intermolecular stretch
	ω_3	a''	156	0.1932	OoP internal rotation
	ω_4	a'	631	65.6433	O=C−O bend
	ω_5	a''	680	115.9062	Acidic H wag
	ω_6	a'	1100	304.9475	C−OH stretch
	ω_7	a''	1139	0.8276	Formyl H wag
	ω_8	a'	1289	11.3538	Acidic H bend
	ω_9	a'	1433	19.3303	Formyl H bend
	ω_{10}	a'	1757	380.8994	C=O stretch
	ω_{11}	a'	2965	283.3538	Formyl H stretch
	ω_{12}	a'	3759	26.9693	Acidic H stretch
		zpe	90.2		

Table S92: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I^-\cdots HCOOH$				
	C_s ($^1A'$) AcidAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	84	3.4132	In plane internal rotation
	ω_2	a''	155	29.3415	OoP internal rotation
	ω_3	a'	169	12.8271	Intermolecular stretch
	ω_4	a'	698	2.3291	O=C−O bend
	ω_5	a''	852	22.7348	Acidic H wag
	ω_6	a''	1078	0.0789	Formyl H wag
	ω_7	a'	1213	120.5413	C−OH stretch
	ω_8	a'	1403	134.0451	Acidic H bend
	ω_9	a'	1421	28.0215	Formyl H bend
	ω_{10}	a'	1794	579.1053	C=O stretch
	ω_{11}	a'	3032	17.3591	Formyl H stretch
	ω_{12}	a'	3189	1928.5338	Acidic H stretch
		zpe	90.3		
AVTZ	ω_1	a'	87	3.0997	In plane internal rotation
	ω_2	a''	159	27.3138	OoP internal rotation
	ω_3	a'	178	13.1131	Intermolecular stretch
	ω_4	a'	698	2.9728	O=C−O bend
	ω_5	a''	878	15.9108	Acidic H wag
	ω_6	a''	1079	0.0445	Formyl H wag
	ω_7	a'	1216	128.5179	C−OH stretch
	ω_8	a'	1409	112.8081	Acidic H bend
	ω_9	a'	1418	36.9924	Formyl H bend
	ω_{10}	a'	1787	624.9662	C=O stretch
	ω_{11}	a'	3026	15.8306	Formyl H stretch
	ω_{12}	a'	3113	2119.2068	Acidic H stretch
		zpe	90		
AVQZ	ω_1	a'	84	3.2057	In plane internal rotation
	ω_2	a''	157	27.9742	OoP internal rotation
	ω_3	a'	171	12.9743	Intermolecular stretch
	ω_4	a'	696	2.375	O=C−O bend
	ω_5	a''	858	17.3723	Acidic H wag
	ω_6	a''	1077	0.0375	Formyl H wag
	ω_7	a'	1213	124.4764	C−OH stretch
	ω_8	a'	1404	121.7109	Acidic H bend
	ω_9	a'	1417	31.1044	Formyl H bend
	ω_{10}	a'	1789	608.541	C=O stretch
	ω_{11}	a'	3030	12.9357	Formyl H stretch
	ω_{12}	a'	3166	1982.3967	Acidic H stretch
		zpe	90.1		

Table S93: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I^-\cdots HCOOH$				
	C_s ($^1A'$) AcidSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	74	0.2282	In plane internal rotation
	ω_2	a''	158	5.5414	OoP internal rotation
	ω_3	a'	167	21.8737	Intermolecular stretch
	ω_4	a'	672	59.9135	O=C−O bend
	ω_5	a''	893	38.4546	Acidic H wag
	ω_6	a''	1075	1.938	Formyl H wag
	ω_7	a'	1209	295.0647	C−OH stretch
	ω_8	a'	1346	10.6669	Acidic H bend
	ω_9	a'	1426	20.2052	Formyl H bend
	ω_{10}	a'	1783	457.5414	C=O stretch
	ω_{11}	a'	2984	587.7832	Formyl H stretch
	ω_{12}	a'	3090	1958.9768	Acidic H stretch
		zpe	89		
AVTZ	ω_1	a'	74	0.2415	In plane internal rotation
	ω_2	a''	159	6.1607	OoP internal rotation
	ω_3	a'	169	22.285	Intermolecular stretch
	ω_4	a'	669	59.7262	O=C−O bend
	ω_5	a''	893	28.0078	Acidic H wag
	ω_6	a''	1072	1.6134	Formyl H wag
	ω_7	a'	1208	292.5372	C−OH stretch
	ω_8	a'	1343	11.2347	Acidic H bend
	ω_9	a'	1421	21.9574	Formyl H bend
	ω_{10}	a'	1775	460.2136	C=O stretch
	ω_{11}	a'	2982	722.0393	Acidic H stretch
	ω_{12}	a'	3068	1884.6705	Formyl H stretch
		zpe	88.7		
AVQZ	ω_1	a'	74	0.2383	In plane internal rotation
	ω_2	a''	157	5.9654	OoP internal rotation
	ω_3	a'	168	22.4094	Intermolecular stretch
	ω_4	a'	671	60.109	O=C−O bend
	ω_5	a''	890	28.2361	Acidic H wag
	ω_6	a''	1073	1.3279	Formyl H wag
	ω_7	a'	1208	292.7416	C−OH stretch
	ω_8	a'	1344	12.7328	Acidic H bend
	ω_9	a'	1424	21.6357	Formyl H bend
	ω_{10}	a'	1777	460.5677	C=O stretch
	ω_{11}	a'	2981	760.5757	Formyl H stretch
	ω_{12}	a'	3066	1859.2229	Acidic H stretch
		zpe	88.7		

Table S94: *Calculated harmonic frequencies and mode assignments for the $I^-\cdots HCOOH$ complex. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *respectively.*

	$I^-\cdots HCOOH$				
	C_s ($^1A'$) FormAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Description
def2QZVP	ω_1	a'	67	3.4626	In plane internal rotation
	ω_2	a'	79	2.2057	Intermolecular stretch
	ω_3	a''	133	0.1569	OoP internal rotation
	ω_4	a'	632	65.0057	O=C−O bend
	ω_5	a''	681	121.3898	Acidic H wag
	ω_6	a'	1110	291.8537	C−OH stretch
	ω_7	a''	1119	0.9322	Formyl H wag
	ω_8	a'	1296	13.4266	Acidic H bend
	ω_9	a'	1427	16.6146	Formyl H bend
	ω_{10}	a'	1770	367.3344	C=O stretch
	ω_{11}	a'	3023	147.943	Formyl H stretch
	ω_{12}	a'	3770	32.6726	Acidic H stretch
		zpe	90.4		
AVTZ	ω_1	a'	68	2.9815	In plane internal rotation
	ω_2	a'	83	2.5804	Intermolecular stretch
	ω_3	a''	140	0.0748	OoP internal rotation
	ω_4	a'	629	64.2551	O=C−O bend
	ω_5	a''	677	114.606	Acidic H wag
	ω_6	a'	1107	287.7821	C−OH stretch
	ω_7	a''	1123	0.5986	Formyl H wag
	ω_8	a'	1292	12.5284	Acidic H bend
	ω_9	a'	1426	17.8648	Formyl H bend
	ω_{10}	a'	1763	369.8949	C=O stretch
	ω_{11}	a'	3016	169.0224	Formyl H stretch
	ω_{12}	a'	3750.9663	31.4301	Acidic H stretch
		zpe	90.2		
AVQZ	ω_1	a'	67	3.142	In plane internal rotation
	ω_2	a'	80	2.4586	Intermolecular stretch
	ω_3	a''	132	0.0751	OoP internal rotation
	ω_4	a'	631	64.3507	O=C−O bend
	ω_5	a''	679	114.6748	Acidic H wag
	ω_6	a'	1109	286.7053	C−OH stretch
	ω_7	a''	1120	0.5394	Formyl H wag
	ω_8	a'	1294	12.7997	Acidic H bend
	ω_9	a'	1425	18.1632	Formyl H bend
	ω_{10}	a'	1765	370.1541	C=O stretch
	ω_{11}	a'	3015	162.5688	Formyl H stretch
	ω_{12}	a'	3762	32.6795	Acidic H stretch
		zpe	90.2		

Table S95: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Cl···HCOOH C_s ($^2A''$) AcidAnti vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	36	5.9228	In plane internal rotation
	ω_2	a''	56	47.4152	OoP internal rotation
	ω_3	a'	91	3.8251	Intermolecular stretch
	ω_4	a'	566	66.4222	Acidic H wag
	ω_5	a''	670	5.3195	O=C−O bend
	ω_6	a''	1045	0.0004	Formyl H wag
	ω_7	a'	1136	74.3592	C−OH stretch
	ω_8	a'	1307	254.8261	Acidic H bend
	ω_9	a'	1426	0.7696	Formyl H bend
	ω_{10}	a'	1851	338.6601	C=O stretch
	ω_{11}	a'	3009	68.5927	Formyl H stretch
	ω_{12}	a'	3786	275.5965	Acidic H stretch
		zpe	89.6		
AVTZ	ω_1	a'	35	5.8454	In plane internal rotation
	ω_2	a''	61	46.0425	OoP internal rotation
	ω_3	a'	95	3.4753	Intermolecular stretch
	ω_4	a'	568	63.1466	Acidic H wag
	ω_5	a''	666	5.4027	O=C−O bend
	ω_6	a''	1041	0.0278	Formyl H wag
	ω_7	a'	1134	76.8239	C−OH stretch
	ω_8	a'	1306	251.9152	Acidic H bend
	ω_9	a'	1420	0.8152	Formyl H bend
	ω_{10}	a'	1843	345.0486	C=O stretch
	ω_{11}	a'	3007	64.8542	Formyl H stretch
	ω_{12}	a'	3763	289.8399	Acidic H stretch
		zpe	89.4		
AVQZ	ω_1	a'	35	5.8051	In plane internal rotation
	ω_2	a''	58	46.538	OoP internal rotation
	ω_3	a'	93	3.7038	Intermolecular stretch
	ω_4	a'	569	63.639	Acidic H wag
	ω_5	a''	669	5.2722	O=C−O bend
	ω_6	a''	1044	0.0122	Formyl H wag
	ω_7	a'	1135	76.3206	C−OH stretch
	ω_8	a'	1307	251.6603	Acidic H bend
	ω_9	a'	1424	0.9241	Formyl H bend
	ω_{10}	a'	1847	345.5069	C=O stretch
	ω_{11}	a'	3008	65.6589	Formyl H stretch
	ω_{12}	a'	3776	280.7916	Acidic H stretch
		zpe	89.5		

Table S96: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Cl···HCOOH				
	C_s ($^2A'$) AcidPSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	156	5.0093	Intermolecular stretch
	ω_2	a''	186	2.7813	OoP internal rotation
	ω_3	a'	240	32.6209	In plane internal rotation
	ω_4	a'	677	41.735	O=C−O bend
	ω_5	a''	779	94.0598	Acidic H wag
	ω_6	a''	1064	3.2223	Formyl H wag
	ω_7	a'	1209	192.7091	C−OH stretch
	ω_8	a'	1339	11.9725	Acidic H bend
	ω_9	a'	1413	1.451	Formyl H bend
	ω_{10}	a'	1724	531.714	C=O stretch
	ω_{11}	a'	3115	25.7853	Formyl H stretch
	ω_{12}	a'	3551	87.0881	Acidic H stretch
		zpe	92.4		
AVTZ	ω_1	a'	155	5.2568	Intermolecular stretch
	ω_2	a''	185	2.8733	OoP internal rotation
	ω_3	a'	237	32.2708	In plane internal rotation
	ω_4	a'	674	40.9681	O=C−O bend
	ω_5	a''	775	89.6972	Acidic H wag
	ω_6	a''	1060	3.2367	Formyl H wag
	ω_7	a'	1207	187.7472	C−OH stretch
	ω_8	a'	1335	11.7295	Acidic H bend
	ω_9	a'	1409	1.5237	Formyl H bend
	ω_{10}	a'	1719	524.6424	C=O stretch
	ω_{11}	a'	3112	24.8862	Formyl H stretch
	ω_{12}	a'	3532	88.139	Acidic H stretch
		zpe	92.1		
AVQZ	ω_1	a'	158	4.7928	Intermolecular stretch
	ω_2	a''	187	2.8363	OoP internal rotation
	ω_3	a'	242	32.4941	In plane internal rotation
	ω_4	a'	677	41.2441	O=C−O bend
	ω_5	a''	780	89.9504	Acidic H wag
	ω_6	a''	1063	3.1291	Formyl H wag
	ω_7	a'	1209	189.4156	C−OH stretch
	ω_8	a'	1337	12.1105	Acidic H bend
	ω_9	a'	1411	1.654	Formyl H bend
	ω_{10}	a'	1720	528.5155	C=O stretch
	ω_{11}	a'	3113	24.6881	Formyl H stretch
	ω_{12}	a'	3539	88.5754	Acidic H stretch
		zpe	92.3		

Table S97: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Cl···HCOOH C_s ($^2A'$) CarbPAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	69	2.7875	Carb. intermol. stretch
	ω_2	a''	74	55.0428	OoP internal rotation
	ω_3	a'	132	26.3145	Hydroxyl intermol. stretch
	ω_4	a''	543	85.3225	Acidic H wag
	ω_5	a'	669	13.5862	O=C−O bend
	ω_6	a''	1043	0.0219	Formyl H wag
	ω_7	a'	1147	23.9396	C−OH stretch
	ω_8	a'	1289	304.4301	Acidic H bend
	ω_9	a'	1421	1.8538	Formyl H bend
	ω_{10}	a'	1825	379.2457	C=O stretch
	ω_{11}	a'	3031	68.2598	Formyl H stretch
	ω_{12}	a'	3832	96.6043	Acidic H stretch
		zpe	90.2		
AVTZ	ω_1	a'	70	2.8932	Carb. intermol. stretch
	ω_2	a''	75	53.3968	OoP internal rotation
	ω_3	a'	132	25.8338	Hydroxyl intermol. stretch
	ω_4	a''	540	83.1908	Acidic H wag
	ω_5	a'	665	13.6948	O=C−O bend
	ω_6	a''	1039	0.0892	Formyl H wag
	ω_7	a'	1144	24.2181	C−OH stretch
	ω_8	a'	1286	300.0301	Acidic H bend
	ω_9	a'	1415	1.8483	Formyl H bend
	ω_{10}	a'	1817	374.6835	C=O stretch
	ω_{11}	a'	3030	65.3763	Formyl H stretch
	ω_{12}	a'	3813	93.53	Acidic H stretch
		zpe	89.9		
AVQZ	ω_1	a'	71	2.7618	Carb. intermol. stretch
	ω_2	a''	76	53.3732	OoP internal rotation
	ω_3	a'	135	26.8564	Hydroxyl intermol. stretch
	ω_4	a''	544	83.6075	Acidic H wag
	ω_5	a'	668	13.7585	O=C−O bend
	ω_6	a''	1042	0.0526	Formyl H wag
	ω_7	a'	1146	23.9199	C−OH stretch
	ω_8	a'	1288	301.7887	Acidic H bend
	ω_9	a'	1419	1.9494	Formyl H bend
	ω_{10}	a'	1820	379.9374	C=O stretch
	ω_{11}	a'	3030	65.9606	Formyl H stretch
	ω_{12}	a'	3824	96.0506	Acidic H stretch
		zpe	90.1		

Table S98: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Cl···HCOOH C_1 (^2A) CarbPSyn vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a	21	1.8506	OoP internal rotation
	ω_2	a	51	1.2528	OoP internal rotation
	ω_3	a	93	2.6528	Intermolecular stretch
	ω_4	a	629	37.0005	O=C−O bend
	ω_5	a	670	128.633	Acidic H wag
	ω_6	a	1059	2.5611	Formyl H wag
	ω_7	a	1124	279.6576	C−OH stretch
	ω_8	a	1296	15.5884	Acidic H bend
	ω_9	a	1411	1.567	Formyl H bend
	ω_{10}	a	1819	370.6535	C=O stretch
	ω_{11}	a	3105	26.9746	Formyl H stretch
	ω_{12}	a	3761	84.8346	Acidic H stretch
		zpe	90		
AVTZ	ω_1	a	25	1.8502	OoP internal rotation
	ω_2	a	55	1.3947	OoP internal rotation
	ω_3	a	98	2.8485	Intermolecular stretch
	ω_4	a	626	35.4187	O=C−O bend
	ω_5	a	668	125.0774	Acidic H wag
	ω_6	a	1055	2.7704	Formyl H wag
	ω_7	a	1121	279.6262	C−OH stretch
	ω_8	a	1293	14.8413	Acidic H bend
	ω_9	a	1407	1.4535	Formyl H bend
	ω_{10}	a	1812	372.2372	C=O stretch
	ω_{11}	a	3103	25.0401	Formyl H stretch
	ω_{12}	a	3742	82.4455	Acidic H stretch
		zpe	89.8		
AVQZ	ω_1	a	20	1.9355	OoP internal rotation
	ω_2	a	52	1.37	OoP internal rotation
	ω_3	a	96	2.909	Intermolecular stretch
	ω_4	a	628	35.6095	O=C−O bend
	ω_5	a	669	124.9884	Acidic H wag
	ω_6	a	1057	2.646	Formyl H wag
	ω_7	a	1123	279.4402	C−OH stretch
	ω_8	a	1294	15.6921	Acidic H bend
	ω_9	a	1409	1.5428	Formyl H bend
	ω_{10}	a	1815	374.3723	C=O stretch
	ω_{11}	a	3103	25.3101	Formyl H stretch
	ω_{12}	a	3753	84.7726	Acidic H stretch
		zpe	89.8		

Table S99: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Cl···HCOOH C_s ($^2A'$) FormPAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	86	21.9815	OoP internal rotation
	ω_2	a'	103	0.5352	Intermolecular stretch
	ω_3	a'	153	51.2147	In plane internal rotation
	ω_4	a''	546	86.4284	Acidic H wag
	ω_5	a'	676	7.4704	O=C−O bend
	ω_6	a''	1054	0.0074	Formyl H wag
	ω_7	a'	1157	29.7967	C−OH stretch
	ω_8	a'	1296	408.9151	Acidic H bend
	ω_9	a'	1424	2.502	Formyl H bend
	ω_{10}	a'	1807	512.1326	C=O stretch
	ω_{11}	a'	3055	28.0099	Formyl H stretch
	ω_{12}	a'	3830	101.7744	Acidic H stretch
		zpe	90.8		
AVTZ	ω_1	a''	85	21.8941	OoP internal rotation
	ω_2	a'	102	0.6779	Intermolecular stretch
	ω_3	a'	151	50.6631	In plane internal rotation
	ω_4	a''	542	83.8545	Acidic H wag
	ω_5	a'	671	7.1582	O=C−O bend
	ω_6	a''	1050	0.0602	Formyl H wag
	ω_7	a'	1154	31.4201	C−OH stretch
	ω_8	a'	1293	408.2905	Acidic H bend
	ω_9	a'	1418	2.3332	Formyl H bend
	ω_{10}	a'	1800	508.853	C=O stretch
	ω_{11}	a'	3053	26.3129	Formyl H stretch
	ω_{12}	a'	3810	98.9885	Acidic H stretch
		zpe	90.5		
AVQZ	ω_1	a''	86	21.6715	OoP internal rotation
	ω_2	a'	104	0.6328	Intermolecular stretch
	ω_3	a'	155	51.8106	In plane internal rotation
	ω_4	a''	546	84.4962	Acidic H wag
	ω_5	a'	675	7.1322	O=C−O bend
	ω_6	a''	1053	0.0338	Formyl H wag
	ω_7	a'	1157	30.7085	C−OH stretch
	ω_8	a'	1295	412.7698	Acidic H bend
	ω_9	a'	1421	2.426	Formyl H bend
	ω_{10}	a'	1802	514.8234	C=O stretch
	ω_{11}	a'	3054	26.5121	Formyl H stretch
	ω_{12}	a'	3822	101.5189	Acidic H stretch
		zpe	90.7		

Table S100: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Cl···HCOOH C_s ($^2A'$) FormPSyn vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	76	0.1625	OoP internal rotation
	ω_2	a'	95	0.4984	Formyl H intermol.
	ω_3	a'	146	23.1884	Carb. intermol. stretch
	ω_4	a'	646	62.8433	O=C−O bend
	ω_5	a''	689	138.9582	Acidic H wag
	ω_6	a''	1073	2.9619	Formyl H wag
	ω_7	a'	1162	283.8047	C−OH stretch
	ω_8	a'	1331	19.4452	Acidic H bend
	ω_9	a'	1407	5.5815	Formyl H bend
	ω_{10}	a'	1770	604.933	C=O stretch
	ω_{11}	a'	3130	14.7994	Formyl H stretch
	ω_{12}	a'	3762	105.4534	Acidic H stretch
		zpe	91.4		
AVTZ	ω_1	a''	75	0.1349	OoP internal rotation
	ω_2	a'	95	0.3879	Formyl H intermol.
	ω_3	a'	145	23.1658	Carb. intermol. stretch
	ω_4	a'	643	61.8897	O=C−O bend
	ω_5	a''	685	135.0279	Acidic H wag
	ω_6	a''	1069	3.1229	Formyl H wag
	ω_7	a'	1160	284.3114	C−OH stretch
	ω_8	a'	1328	19.4039	Acidic H bend
	ω_9	a'	1404	5.299	Formyl H bend
	ω_{10}	a'	1764	601.9674	C=O stretch
	ω_{11}	a'	3127	14.0387	Formyl H stretch
	ω_{12}	a'	3744	103.1393	Acidic H stretch
		zpe	91.1		
AVQZ	ω_1	a''	77	0.1373	OoP internal rotation
	ω_2	a'	96	0.4373	Formyl H intermol.
	ω_3	a'	149	23.8435	Carb. intermol. stretch
	ω_4	a'	645	62.6175	O=C−O bend
	ω_5	a''	688	135.4245	Acidic H wag
	ω_6	a''	1072	3.0172	Formyl H wag
	ω_7	a'	1162	285.8117	C−OH stretch
	ω_8	a'	1330	20.0416	Acidic H bend
	ω_9	a'	1405	5.5405	Formyl H bend
	ω_{10}	a'	1765	609.1021	C=O stretch
	ω_{11}	a'	3128	14.2081	Formyl H stretch
	ω_{12}	a'	3755	105.8821	Acidic H stretch
		zpe	91.3		

Table S101: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Cl···HCOOH C_s ($^2A''$) InlineSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	35	1.076	In plane internal rotation
	ω_2	a''	75	0.9649	OoP internal rotation
	ω_3	a'	90	3.8625	Intermolecular stretch
	ω_4	a'	639	44.0283	O=C−O bend
	ω_5	a''	699	110.2289	Acidic H wag
	ω_6	a''	1065	2.0858	Formyl H wag
	ω_7	a'	1148	256.195	C−OH stretch
	ω_8	a'	1323	14.9041	Acidic H bend
	ω_9	a'	1415	4.7092	Formyl H bend
	ω_{10}	a'	1810	327.2176	C=O stretch
	ω_{11}	a'	3091	49.7707	Formyl H stretch
	ω_{12}	a'	3715	286.2537	Acidic H stretch
		zpe	90.4		
AVTZ	ω_1	a'	37	1.1422	In plane internal rotation
	ω_2	a''	82	1.2519	OoP internal rotation
	ω_3	a'	95	4.005	Intermolecular stretch
	ω_4	a'	638	43.128	O=C−O bend
	ω_5	a''	701	104.4058	Acidic H wag
	ω_6	a''	1061	2.3331	Formyl H wag
	ω_7	a'	1148	255.483	C−OH stretch
	ω_8	a'	1321	14.0352	Acidic H bend
	ω_9	a'	1412	5.0459	Formyl H bend
	ω_{10}	a'	1803	326.6872	C=O stretch
	ω_{11}	a'	3089	48.1848	Formyl H stretch
	ω_{12}	a'	3693	298.7531	Acidic H stretch
		zpe	90.2		
AVQZ	ω_1	a'	36	1.1619	In plane internal rotation
	ω_2	a''	77	1.1669	OoP internal rotation
	ω_3	a'	93	3.9829	Intermolecular stretch
	ω_4	a'	639	42.9702	O=C−O bend
	ω_5	a''	700	104.4654	Acidic H wag
	ω_6	a''	1063	2.142	Formyl H wag
	ω_7	a'	1148	254.4842	C−OH stretch
	ω_8	a'	1321	15.2885	Acidic H bend
	ω_9	a'	1414	4.9331	Formyl H bend
	ω_{10}	a'	1806	326.1244	C=O stretch
	ω_{11}	a'	3090	48.5574	Formyl H stretch
	ω_{12}	a'	3704	295.7677	Acidic H stretch
		zpe	90.3		

Table S102: *Calculated harmonic frequencies and mode assignments for the Cl···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Cl···HCOOH C_1 (^2A) OutPlAnti vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a	30	15.1853	OoP internal rotation
	ω_2	a	32	34.5365	OoP internal rotation
	ω_3	a	96	6.1625	Intermolecular stretch
	ω_4	a	530	87.8737	Acidic H wag
	ω_5	a	662	8.7064	O=C−O bend
	ω_6	a	1037	0.1877	Formyl H wag
	ω_7	a	1104	84.5059	C−OH stretch
	ω_8	a	1277	312.2931	Acidic H bend
	ω_9	a	1422	0.5587	Formyl H bend
	ω_{10}	a	1856	275.2737	C=O stretch
	ω_{11}	a	3021	61.3993	Formyl H stretch
	ω_{12}	a	3825	76.9859	Acidic H stretch
		zpe	89.1		
AVTZ	ω_1	a	31	3.6424	OoP internal rotation
	ω_2	a	38	46.1937	OoP internal rotation
	ω_3	a	100	5.9724	Intermolecular stretch
	ω_4	a	527	87.0114	Acidic H wag
	ω_5	a	658	8.2334	O=C−O bend
	ω_6	a	1033	0.3374	Formyl H wag
	ω_7	a	1101	85.46	C−OH stretch
	ω_8	a	1274	307.5189	Acidic H bend
	ω_9	a	1416	0.5869	Formyl H bend
	ω_{10}	a	1848	273.9623	C=O stretch
	ω_{11}	a	3021	57.6869	Formyl H stretch
	ω_{12}	a	3806	74.6551	Acidic H stretch
		zpe	88.8		
AVQZ	ω_1	a	30	3.4332	OoP internal rotation
	ω_2	a	35	46.1187	OoP internal rotation
	ω_3	a	99	5.8763	Intermolecular stretch
	ω_4	a	530	86.5224	Acidic H wag
	ω_5	a	661	8.2325	O=C−O bend
	ω_6	a	1036	0.2853	Formyl H wag
	ω_7	a	1103	86.2557	C−OH stretch
	ω_8	a	1276	309.9235	Acidic H bend
	ω_9	a	1419	0.6189	Formyl H bend
	ω_{10}	a	1852	274.7907	C=O stretch
	ω_{11}	a	3021	58.3979	Formyl H stretch
	ω_{12}	a	3817	76.1307	Acidic H stretch
		zpe	89		

Table S103: *Calculated harmonic frequencies and mode assignments for the Br···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Br···HCOOH C_s ($^2A''$) AcidAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	27	5.525	In plane internal rotation
	ω_2	a''	54	45.4992	OoP internal rotation
	ω_3	a'	79	3.7688	Intermolecular stretch
	ω_4	a''	569	61.1631	Acidic H wag
	ω_5	a'	671	6.2254	O=C−O bend
	ω_6	a''	1046	0	Formyl H wag
	ω_7	a'	1140	73.575	C−OH stretch
	ω_8	a'	1307	269.3644	Acidic H bend
	ω_9	a'	1427	0.7201	Formyl H bend
	ω_{10}	a'	1852	348.7487	C=O stretch
	ω_{11}	a'	3005	68.2173	Formyl H stretch
	ω_{12}	a'	3767	341.5823	Acidic H stretch
		zpe	89.4		
AVTZ	ω_1	a'	28	13.3501	In plane internal rotation
	ω_2	a'	51	0.0546	Intermolecular stretch
	ω_3	a''	57	48.9677	OoP internal rotation
	ω_4	a''	525	72.1691	Acidic H wag
	ω_5	a'	661	9.9976	O=C−O bend
	ω_6	a''	1037	0.0644	Formyl H wag
	ω_7	a'	1122	32.2641	C−OH stretch
	ω_8	a'	1285	304.3958	Acidic H bend
	ω_9	a'	1418	0.5998	Formyl H bend
	ω_{10}	a'	1852	280.8939	C=O stretch
	ω_{11}	a'	2988	74.2252	Formyl H stretch
	ω_{12}	a'	3816	65.4934	Acidic H stretch
		zpe	88.8		
AVQZ	ω_1	a'	22	6.1321	In plane internal rotation
	ω_2	a''	74	39.5867	OoP internal rotation
	ω_3	a'	82	3.4174	Intermolecular stretch
	ω_4	a''	608	52.1661	Acidic H wag
	ω_5	a'	671	5.618	O=C−O bend
	ω_6	a''	1042	0.0011	Formyl H wag
	ω_7	a'	1140	74.6021	C−OH stretch
	ω_8	a'	1301	271.4372	Acidic H bend
	ω_9	a'	1424	0.942	Formyl H bend
	ω_{10}	a'	1847	359.9749	C=O stretch
	ω_{11}	a'	3000	73.383	Formyl H stretch
	ω_{12}	a'	3748	370.1762	Acidic H stretch
		zpe	89.5		

Table S104: *Calculated harmonic frequencies and mode assignments for the Br···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	Br···HCOOH				
	C_s ($^2A'$) AcidPSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	115	2.8694	Intermolecular stretch
	ω_2	a''	159	2.6009	OoP internal rotation
	ω_3	a'	191	28.2509	In plane internal rotation
	ω_4	a'	671	35.9332	O=C−O bend
	ω_5	a''	749	91.1129	Acidic H wag
	ω_6	a''	1065	2.6379	Formyl H wag
	ω_7	a'	1195	197.4556	C−OH stretch
	ω_8	a'	1340	1.5729	Acidic H bend
	ω_9	a'	1414	2	Formyl H bend
	ω_{10}	a'	1744	467.827	C=O stretch
	ω_{11}	a'	3109	33.8148	Formyl H stretch
	ω_{12}	a'	3594	142.5592	Acidic H stretch
		zpe	91.8		
AVTZ	ω_1	a'	117	2.6831	Intermolecular stretch
	ω_2	a''	161	2.8691	OoP internal rotation
	ω_3	a'	191	27.5285	In plane internal rotation
	ω_4	a'	669	34.8096	O=C−O bend
	ω_5	a''	748	83.7786	Acidic H wag
	ω_6	a''	1062	2.6805	Formyl H wag
	ω_7	a'	1193	190.6678	C−OH stretch
	ω_8	a'	1337	1.5391	Acidic H bend
	ω_9	a'	1411	1.9804	Formyl H bend
	ω_{10}	a'	1739	450.1297	C=O stretch
	ω_{11}	a'	3108	33.3904	Formyl H stretch
	ω_{12}	a'	3570	153.5025	Acidic H stretch
		zpe	91.6		
AVQZ	ω_1	a'	121	2.7573	Intermolecular stretch
	ω_2	a''	167	3.0044	OoP internal rotation
	ω_3	a'	195	28.1126	In plane internal rotation
	ω_4	a'	673	34.9473	O=C−O bend
	ω_5	a''	758	82.9512	Acidic H wag
	ω_6	a''	1065	2.5632	Formyl H wag
	ω_7	a'	1198	190.6212	C−OH stretch
	ω_8	a'	1340	1.5502	Acidic H bend
	ω_9	a'	1413	2.0997	Formyl H bend
	ω_{10}	a'	1739	454.6428	C=O stretch
	ω_{11}	a'	3109	33.1176	Formyl H stretch
	ω_{12}	a'	3567	157.3642	Acidic H stretch
		zpe	91.8		

Table S105: *Calculated harmonic frequencies and mode assignments for the Br···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Br···HCOOH C_s ($^2A'$) CarbPAnti vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	57	2.8574	Carb. intermol. stretch
	ω_2	a''	69	55.3347	OoP internal rotation
	ω_3	a'	116	22.5435	Hydroxyl intermol. stretch
	ω_4	a''	542	85.2427	Acidic H wag
	ω_5	a'	669	13.9588	O=C−O bend
	ω_6	a''	1044	0.0215	Formyl H wag
	ω_7	a'	1145	24.1263	C−OH stretch
	ω_8	a'	1288	302.5445	Acidic H bend
	ω_9	a'	1422	1.1317	Formyl H bend
	ω_{10}	a'	1828	365.3429	C=O stretch
	ω_{11}	a'	3031	69.8987	Formyl H stretch
	ω_{12}	a'	3832	95.981	Acidic H stretch
		zpe	90		
AVTZ	ω_1	a'	59	3.0632	Carb. intermol. stretch
	ω_2	a''	72	53.0238	OoP internal rotation
	ω_3	a'	119	22.076	Hydroxyl intermol. stretch
	ω_4	a''	540	82.9637	Acidic H wag
	ω_5	a'	664	14.2844	O=C−O bend
	ω_6	a''	1040	0.09	Formyl H wag
	ω_7	a'	1142	23.5746	C−OH stretch
	ω_8	a'	1286	296.1627	Acidic H bend
	ω_9	a'	1416	1.1098	Formyl H bend
	ω_{10}	a'	1820	358.1274	C=O stretch
	ω_{11}	a'	3031	66.9842	Formyl H stretch
	ω_{12}	a'	3813	93.0631	Acidic H stretch
		zpe	89.7		
AVQZ	ω_1	a'	60	2.9394	Carb. intermol. stretch
	ω_2	a''	74	53.093	OoP internal rotation
	ω_3	a'	120	22.861	Hydroxyl intermol. stretch
	ω_4	a''	543	83.2524	Acidic H wag
	ω_5	a'	668	14.4304	O=C−O bend
	ω_6	a''	1043	0.0542	Formyl H wag
	ω_7	a'	1145	23.2275	C−OH stretch
	ω_8	a'	1288	297.3924	Acidic H bend
	ω_9	a'	1420	1.1612	Formyl H bend
	ω_{10}	a'	1823	361.3928	C=O stretch
	ω_{11}	a'	3031	67.5524	Formyl H stretch
	ω_{12}	a'	3824	95.4232	Acidic H stretch
		zpe	90		

Table S106: *Calculated harmonic frequencies and mode assignments for the Br···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Br···HCOOH C_s ($^2A'$) CarbPSyn vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	14i	1.2571	OoP internal rotation
	ω_2	a'	36	1.4203	In plane internal rotation
	ω_3	a'	74	2.0724	Intermolecular stretch
	ω_4	a'	630	37.6733	O=C−O bend
	ω_5	a''	660	134.9961	Acidic H wag
	ω_6	a''	1061	2.2813	Formyl H wag
	ω_7	a'	1128	266.217	C−OH stretch
	ω_8	a'	1296	15.1341	Acidic H bend
	ω_9	a'	1411	2.8223	Formyl H bend
	ω_{10}	a'	1819	380.2226	C=O stretch
	ω_{11}	a'	3102	28.5712	Formyl H stretch
	ω_{12}	a'	3764	86.0264	Acidic H stretch
		zpe	89.6		
AVTZ	ω_1	a''	10i	1.3328	OoP internal rotation
	ω_2	a'	39	1.5155	In plane internal rotation
	ω_3	a'	79	2.2183	Intermolecular stretch
	ω_4	a'	627	36.0542	O=C−O bend
	ω_5	a''	655	129.681	Acidic H wag
	ω_6	a''	1057	2.4109	Formyl H wag
	ω_7	a'	1126	259.9098	C−OH stretch
	ω_8	a'	1291	14.3003	Acidic H bend
	ω_9	a'	1406	3.1699	Formyl H bend
	ω_{10}	a'	1812	385.8248	C=O stretch
	ω_{11}	a'	3099	26.5862	Formyl H stretch
	ω_{12}	a'	3745	84.7072	Acidic H stretch
		zpe	89.3		
AVQZ	ω_1	a''	11	1.2921	OoP internal rotation
	ω_2	a'	43	1.4854	In plane internal rotation
	ω_3	a'	79	2.3266	Intermolecular stretch
	ω_4	a'	629	36.3123	O=C−O bend
	ω_5	a''	657	129.9958	Acidic H wag
	ω_6	a''	1060	2.2758	Formyl H wag
	ω_7	a'	1127	260.5441	C−OH stretch
	ω_8	a'	1292	14.6533	Acidic H bend
	ω_9	a'	1409	3.2873	Formyl H bend
	ω_{10}	a'	1816	386.1875	C=O stretch
	ω_{11}	a'	3100	26.793	Formyl H stretch
	ω_{12}	a'	3756	87.0447	Acidic H stretch
		zpe	89.6		

Table S107: *Calculated harmonic frequencies and mode assignments for the Br···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Br···HCOOH C_s ($^2A'$) FormPAnti vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	77	20.855	OoP internal rotation
	ω_2	a'	82	0.5399	Intermolecular stretch
	ω_3	a'	126	41.1341	In plane internal rotation
	ω_4	a''	546	86.1536	Acidic H wag
	ω_5	a'	675	7.2671	O=C−O bend
	ω_6	a''	1053	0.0032	Formyl H wag
	ω_7	a'	1154	34.8178	C−OH stretch
	ω_8	a'	1295	407.56	Acidic H bend
	ω_9	a'	1426	2.01	Formyl H bend
	ω_{10}	a'	1815	471.6004	C=O stretch
	ω_{11}	a'	3047	29.1001	Formyl H stretch
	ω_{12}	a'	3830	99.43	Acidic H stretch
		zpe	90.5		
AVTZ	ω_1	a''	77	20.7468	OoP internal rotation
	ω_2	a'	83	1.0612	Intermolecular stretch
	ω_3	a'	127	40.2059	In plane internal rotation
	ω_4	a''	543	83.3484	Acidic H wag
	ω_5	a'	670	6.8702	O=C−O bend
	ω_6	a''	1050	0.0439	Formyl H wag
	ω_7	a'	1151	36.2507	C−OH stretch
	ω_8	a'	1292	408.4421	Acidic H bend
	ω_9	a'	1420	1.8847	Formyl H bend
	ω_{10}	a'	1808	463.4947	C=O stretch
	ω_{11}	a'	3046	26.355	Formyl H stretch
	ω_{12}	a'	3811	96.9667	Acidic H stretch
		zpe	90.2		
AVQZ	ω_1	a''	84	21.0673	OoP internal rotation
	ω_2	a'	88	0.2047	Intermolecular stretch
	ω_3	a'	130	41.3818	In plane internal rotation
	ω_4	a''	549	83.3029	Acidic H wag
	ω_5	a'	674	6.8722	O=C−O bend
	ω_6	a''	1053	0.0215	Formyl H wag
	ω_7	a'	1154	34.5278	C−OH stretch
	ω_8	a'	1295	411.7962	Acidic H bend
	ω_9	a'	1424	2.1405	Formyl H bend
	ω_{10}	a'	1810	470.051	C=O stretch
	ω_{11}	a'	3046	26.4793	Formyl H stretch
	ω_{12}	a'	3822	99.1755	Acidic H stretch
		zpe	90.5		

Table S108: *Calculated harmonic frequencies and mode assignments for the Br···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

Br···HCOOH C_s ($^2A'$) FormPSyn vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	68	0.2612	OoP internal rotation
	ω_2	a'	77	0.3252	Formyl H intermol.
	ω_3	a'	121	15.597	Carb. intermol. stretch
	ω_4	a'	644	61.5119	O=C−O bend
	ω_5	a''	689	137.7132	Acidic H wag
	ω_6	a''	1072	2.7946	Formyl H wag
	ω_7	a'	1160	288.9404	C−OH stretch
	ω_8	a'	1330	20.3597	Acidic H bend
	ω_9	a'	1410	5.1924	Formyl H bend
	ω_{10}	a'	1776	568.3736	C=O stretch
	ω_{11}	a'	3124	14.8849	Formyl H stretch
	ω_{12}	a'	3763	101.9659	Acidic H stretch
		zpe	91.1		
AVTZ	ω_1	a''	68	0.2285	OoP internal rotation
	ω_2	a'	77	0.1849	Formyl H intermol.
	ω_3	a'	123	15.5321	Carb. intermol. stretch
	ω_4	a'	641	60.9539	O=C−O bend
	ω_5	a''	685	133.189	Acidic H wag
	ω_6	a''	1069	2.9289	Formyl H wag
	ω_7	a'	1158	289.8472	C−OH stretch
	ω_8	a'	1327	20.6749	Acidic H bend
	ω_9	a'	1405	5.115	Formyl H bend
	ω_{10}	a'	1770	561.3176	C=O stretch
	ω_{11}	a'	3121	13.5617	Formyl H stretch
	ω_{12}	a'	3744	99.654	Acidic H stretch
		zpe	90.8		
AVQZ	ω_1	a''	77	0.1907	OoP internal rotation
	ω_2	a'	83	0.4483	Formyl H intermol.
	ω_3	a'	125	15.5903	Carb. intermol. stretch
	ω_4	a'	644	61.3758	O=C−O bend
	ω_5	a''	690	133.8507	Acidic H wag
	ω_6	a''	1072	2.9334	Formyl H wag
	ω_7	a'	1160	288.4611	C−OH stretch
	ω_8	a'	1329	21.4504	Acidic H bend
	ω_9	a'	1408	5.5617	Formyl H bend
	ω_{10}	a'	1772	568.9655	C=O stretch
	ω_{11}	a'	3122	13.51	Formyl H stretch
	ω_{12}	a'	3755	101.1571	Acidic H stretch
		zpe	91.1		

Table S109: *Calculated harmonic frequencies and mode assignments for the I···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCOOH C_s ($^2A''$) AcidAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	37	4.1121	In plane internal rotation
	ω_2	a''	61	43.5955	OoP internal rotation
	ω_3	a'	76	5.2359	Intermolecular stretch
	ω_4	a''	573	50.3857	Acidic H wag
	ω_5	a'	671	4.248	O=C−O bend
	ω_6	a''	1046	0.0014	Formyl H wag
	ω_7	a'	1137	82.8435	C−OH stretch
	ω_8	a'	1308	221.31	Acidic H bend
	ω_9	a'	1426	1.6413	Formyl H bend
	ω_{10}	a'	1849	377.5807	C=O stretch
	ω_{11}	a'	3009	67.7259	Formyl H stretch
	ω_{12}	a'	3747	382.0774	Acidic H stretch
		zpe	89.4		
AVTZ	ω_1	a'	37	4.2267	In plane internal rotation
	ω_2	a''	69	41.7693	OoP internal rotation
	ω_3	a'	88	4.7208	Intermolecular stretch
	ω_4	a''	581	47.917	Acidic H wag
	ω_5	a'	667	4.1476	O=C−O bend
	ω_6	a''	1043	0.0096	Formyl H wag
	ω_7	a'	1136	87.499	C−OH stretch
	ω_8	a'	1309	216.6985	Acidic H bend
	ω_9	a'	1419	1.7266	Formyl H bend
	ω_{10}	a'	1841	387.7568	C=O stretch
	ω_{11}	a'	3007	63.9233	Formyl H stretch
	ω_{12}	a'	3718	421.3702	Acidic H stretch
		zpe	89.2		
AVQZ	ω_1	a'	39	4.0272	In plane internal rotation
	ω_2	a''	67	42.2856	OoP internal rotation
	ω_3	a'	88	5.0746	Intermolecular stretch
	ω_4	a''	583	48.4623	Acidic H wag
	ω_5	a'	670	4.0144	O=C−O bend
	ω_6	a''	1046	0.0011	Formyl H wag
	ω_7	a'	1138	87.4771	C−OH stretch
	ω_8	a'	1311	216.0616	Acidic H bend
	ω_9	a'	1423	1.9027	Formyl H bend
	ω_{10}	a'	1844	388.0276	C=O stretch
	ω_{11}	a'	3007	64.8598	Formyl H stretch
	ω_{12}	a'	3730	413.7455	Acidic H stretch
		zpe	89.4		

Table S110: *Calculated harmonic frequencies and mode assignments for the I···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCOOH				
	C_s ($^2A'$) AcidPSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	91	1.3372	Intermolecular stretch
	ω_2	a''	133	2.3344	OoP internal rotation
	ω_3	a'	153	26.0864	In plane internal rotation
	ω_4	a'	664	32.2055	O=C−O bend
	ω_5	a''	725	81.0642	Acidic H wag
	ω_6	a''	1067	2.0107	Formyl H wag
	ω_7	a'	1182	192.3838	C−OH stretch
	ω_8	a'	1337	9.9188	Acidic H bend
	ω_9	a'	1416	1.5096	Formyl H bend
	ω_{10}	a'	1761	400.831	C=O stretch
	ω_{11}	a'	3106	43.8416	Formyl H stretch
	ω_{12}	a'	3621	209.4583	Acidic H stretch
		zpe	91.2		
AVTZ	ω_1	a'	95	1.6379	Intermolecular stretch
	ω_2	a''	134	2.6173	OoP internal rotation
	ω_3	a'	153	25.6587	In plane internal rotation
	ω_4	a'	662	31.1101	O=C−O bend
	ω_5	a''	725	76.253	Acidic H wag
	ω_6	a''	1063	2.1764	Formyl H wag
	ω_7	a'	1181	187.4234	C−OH stretch
	ω_8	a'	1334	10.6144	Acidic H bend
	ω_9	a'	1413	1.6705	Formyl H bend
	ω_{10}	a'	1755	390.8881	C=O stretch
	ω_{11}	a'	3104	43.2326	Formyl H stretch
	ω_{12}	a'	3596	224.0859	Acidic H stretch
		zpe	91		
AVQZ	ω_1	a'	98	1.4774	Intermolecular stretch
	ω_2	a''	140	2.644	OoP internal rotation
	ω_3	a'	160	26.8066	In plane internal rotation
	ω_4	a'	666	31.2211	O=C−O bend
	ω_5	a''	731	75.9052	Acidic H wag
	ω_6	a''	1066	2.0421	Formyl H wag
	ω_7	a'	1185	188.43	C−OH stretch
	ω_8	a'	1337	9.987	Acidic H bend
	ω_9	a'	1415	1.7096	Formyl H bend
	ω_{10}	a'	1756	397.644	C=O stretch
	ω_{11}	a'	3105	42.8216	Formyl H stretch
	ω_{12}	a'	3599	225.2343	Acidic H stretch
		zpe	91.3		

Table S111: *Calculated harmonic frequencies and mode assignments for the I···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCOOH				
	C_s ($^2A'$) CarbPAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a'	50	3.2015	Carb. intermol. stretch
	ω_2	a''	60	52.7191	OoP internal rotation
	ω_3	a'	101	20.2175	Hydroxyl intermol. stretch
	ω_4	a''	541	84.3211	Acidic H wag
	ω_5	a'	669	15.3358	O=C−O bend
	ω_6	a''	1044	0.0192	Formyl H wag
	ω_7	a'	1143	23.0502	C−OH stretch
	ω_8	a'	1288	293.7607	Acidic H bend
	ω_9	a'	1423	0.5809	Formyl H bend
	ω_{10}	a'	1831	346.4641	C=O stretch
	ω_{11}	a'	3032	73.1252	Formyl H stretch
	ω_{12}	a'	3832	96.0051	Acidic H stretch
		zpe	89.8		
AVTZ	ω_1	a'	51	3.4152	Carb. intermol. stretch
	ω_2	a''	62	51.1888	OoP internal rotation
	ω_3	a'	103	19.9236	Hydroxyl intermol. stretch
	ω_4	a''	539	82.2371	Acidic H wag
	ω_5	a'	664	15.4585	O=C−O bend
	ω_6	a''	1041	0.0906	Formyl H wag
	ω_7	a'	1140	23.4235	C−OH stretch
	ω_8	a'	1285	289.2526	Acidic H bend
	ω_9	a'	1417	0.6006	Formyl H bend
	ω_{10}	a'	1823	341.5392	C=O stretch
	ω_{11}	a'	3032	70.2813	Formyl H stretch
	ω_{12}	a'	3813	92.8965	Acidic H stretch
		zpe	89.5		
AVQZ	ω_1	a'	51	3.3627	Carb. intermol. stretch
	ω_2	a''	65	51.3964	OoP internal rotation
	ω_3	a'	106	20.6933	Hydroxyl intermol. stretch
	ω_4	a''	543	82.4202	Acidic H wag
	ω_5	a'	668	15.5031	O=C−O bend
	ω_6	a''	1044	0.0542	Formyl H wag
	ω_7	a'	1143	22.7528	C−OH stretch
	ω_8	a'	1287	291.3355	Acidic H bend
	ω_9	a'	1421	0.636	Formyl H bend
	ω_{10}	a'	1826	347.7571	C=O stretch
	ω_{11}	a'	3032	70.8106	Formyl H stretch
	ω_{12}	a'	3824	95.656	Acidic H stretch
		zpe	89.8		

Table S112: *Calculated harmonic frequencies and mode assignments for the I···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCOOH				
	C_s ($^2A'$) CarbPSyn vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	10	1.3114	OoP internal rotation
	ω_2	a'	37	1.4942	In plane internal rotation
	ω_3	a'	69	2.1995	Intermolecular stretch
	ω_4	a'	630	34.9846	O=C−O bend
	ω_5	a''	662	129.2888	Acidic H wag
	ω_6	a''	1061	2.1186	Formyl H wag
	ω_7	a'	1126	261.1047	C−OH stretch
	ω_8	a'	1297	13.4842	Acidic H bend
	ω_9	a'	1411	3.4041	Formyl H bend
	ω_{10}	a'	1819	393.7706	C=O stretch
	ω_{11}	a'	3100	29.136	Formyl H stretch
	ω_{12}	a'	3762	84.9057	Acidic H stretch
		zpe	89.6		
AVTZ	ω_1	a''	20	1.2956	OoP internal rotation
	ω_2	a'	41	1.492	In plane internal rotation
	ω_3	a'	73	2.1992	Intermolecular stretch
	ω_4	a'	627	34.4773	O=C−O bend
	ω_5	a''	657	126.09	Acidic H wag
	ω_6	a''	1057	2.2016	Formyl H wag
	ω_7	a'	1124	254.3251	C−OH stretch
	ω_8	a'	1293	11.8841	Acidic H bend
	ω_9	a'	1407	4.2545	Formyl H bend
	ω_{10}	a'	1813	396.9914	C=O stretch
	ω_{11}	a'	3097	28.1038	Formyl H stretch
	ω_{12}	a'	3744	83.7604	Acidic H stretch
		zpe	89.4		
AVQZ	ω_1	a''	23	1.3469	OoP internal rotation
	ω_2	a'	42	1.5602	In plane internal rotation
	ω_3	a'	75	2.4129	Intermolecular stretch
	ω_4	a'	629	34.3885	O=C−O bend
	ω_5	a''	660	126.0804	Acidic H wag
	ω_6	a''	1060	2.1011	Formyl H wag
	ω_7	a'	1125	257.4264	C−OH stretch
	ω_8	a'	1293	13.09	Acidic H bend
	ω_9	a'	1409	4.0071	Formyl H bend
	ω_{10}	a'	1816	398.3785	C=O stretch
	ω_{11}	a'	3098	27.7344	Formyl H stretch
	ω_{12}	a'	3755	85.9334	Acidic H stretch
		zpe	89.6		

Table S113: *Calculated harmonic frequencies and mode assignments for the I···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

	I···HCOOH				
	C_s ($^2A'$) FormPAnti vdW Complex				
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	69	19.1224	OoP internal rotation
	ω_2	a'	71	1.3452	Intermolecular stretch
	ω_3	a'	108	36.2549	In plane internal rotation
	ω_4	a''	547	85.2287	Acidic H wag
	ω_5	a'	674	6.5562	O=C−O bend
	ω_6	a''	1053	0	Formyl H wag
	ω_7	a'	1152	39.705	C−OH stretch
	ω_8	a'	1295	416.1611	Acidic H bend
	ω_9	a'	1428	2.3938	Formyl H bend
	ω_{10}	a'	1821	435.5117	C=O stretch
	ω_{11}	a'	3038	29.3957	Formyl H stretch
	ω_{12}	a'	3830	98.7865	Acidic H stretch
		zpe	90.2		
AVTZ	ω_1	a''	70	19.4737	OoP internal rotation
	ω_2	a'	71	1.9358	Intermolecular stretch
	ω_3	a'	109	35.8225	In plane internal rotation
	ω_4	a''	543	82.6795	Acidic H wag
	ω_5	a'	669	6.3292	O=C−O bend
	ω_6	a''	1050	0.026	Formyl H wag
	ω_7	a'	1149	41.4678	C−OH stretch
	ω_8	a'	1292	416.3043	Acidic H bend
	ω_9	a'	1421	2.2007	Formyl H bend
	ω_{10}	a'	1814	429.9248	C=O stretch
	ω_{11}	a'	3037	27.0586	Formyl H stretch
	ω_{12}	a'	3811	96.1108	Acidic H stretch
		zpe	89.9		
AVQZ	ω_1	a''	72	19.0421	OoP internal rotation
	ω_2	a'	72	1.9666	Intermolecular stretch
	ω_3	a'	113	36.6959	In plane internal rotation
	ω_4	a''	547	83.2858	Acidic H wag
	ω_5	a'	673	6.2793	O=C−O bend
	ω_6	a''	1053	0.0085	Formyl H wag
	ω_7	a'	1151	40.3187	C−OH stretch
	ω_8	a'	1295	420.9147	Acidic H bend
	ω_9	a'	1424	2.3099	Formyl H bend
	ω_{10}	a'	1817	437.787	C=O stretch
	ω_{11}	a'	3038	27.0103	Formyl H stretch
	ω_{12}	a'	3822	98.7256	Acidic H stretch
		zpe	90.2		

Table S114: *Calculated harmonic frequencies and mode assignments for the I···HCOOH complex. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *respectively.*

I···HCOOH C_s ($^2A'$) FormPSyn vdW Complex					
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)	Description
def2QZVP	ω_1	a''	61	0.3354	OoP internal rotation
	ω_2	a'	66	0.1224	Formyl H intermol.
	ω_3	a'	104	12.7296	Carb. intermol. stretch
	ω_4	a'	642	61.9051	O=C−O bend
	ω_5	a''	690	134.1108	Acidic H wag
	ω_6	a''	1072	2.5272	Formyl H wag
	ω_7	a'	1158	298.4912	C−OH stretch
	ω_8	a'	1330	22.33	Acidic H bend
	ω_9	a'	1411	5.8648	Formyl H bend
	ω_{10}	a'	1782	539.2952	C=O stretch
	ω_{11}	a'	3117	14.8102	Formyl H stretch
	ω_{12}	a'	3763	99.7152	Acidic H stretch
		zpe	90.9		
AVTZ	ω_1	a''	61	0.2949	OoP internal rotation
	ω_2	a'	66	0.1071	Formyl H intermol.
	ω_3	a'	105	12.9465	Carb. intermol. stretch
	ω_4	a'	639	61.6232	O=C−O bend
	ω_5	a''	685	130.5905	Acidic H wag
	ω_6	a''	1069	2.6769	Formyl H wag
	ω_7	a'	1156	299.5934	C−OH stretch
	ω_8	a'	1326	22.4472	Acidic H bend
	ω_9	a'	1406	5.738	Formyl H bend
	ω_{10}	a'	1776	533.105	C=O stretch
	ω_{11}	a'	3114	13.7082	Formyl H stretch
	ω_{12}	a'	3745	97.5301	Acidic H stretch
		zpe	90.6		
AVQZ	ω_1	a''	64	0.2988	OoP internal rotation
	ω_2	a'	67	0.1081	Formyl H intermol.
	ω_3	a'	109	13.3972	Carb. intermol. stretch
	ω_4	a'	642	62.471	O=C−O bend
	ω_5	a''	688	130.9955	Acidic H wag
	ω_6	a''	1071	2.5933	Formyl H wag
	ω_7	a'	1158	300.1443	C−OH stretch
	ω_8	a'	1328	23.3888	Acidic H bend
	ω_9	a'	1408	5.8881	Formyl H bend
	ω_{10}	a'	1777	543.636	C=O stretch
	ω_{11}	a'	3116	13.712	Formyl H stretch
	ω_{12}	a'	3755	100.3768	Acidic H stretch
		zpe	90.8		

Table S115: *Cartesian coordinates of the geometries of halide-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots$HCOOH			$Br^-\cdots$HCOOH			$I^-\cdots$HCOOH		
			x	y	z	x	y	z	x	y	z
		C	-1.112923	-0.861954	0.000000	1.882446	0.951381	0.000000	-0.350468	-2.586369	0.000000
		O	-0.995783	0.445557	0.000000	0.708971	1.550756	0.000000	0.848572	-2.028292	0.000000
	def2QZVP	H	0.000000	0.668324	0.000000	0.000000	0.835871	0.000000	0.727114	-1.039660	0.000000
		O	-2.172235	-1.454656	0.000000	2.941964	1.538994	0.000000	-0.530678	-3.781974	0.000000
		H	-0.141554	-1.379670	0.000000	1.803338	-0.145721	0.000000	-1.167455	-1.850562	0.000000
		X	1.891955	0.820933	0.000000	-1.208729	-0.889041	0.000000	0.000000	1.224350	0.000000
		C	-1.115211	-0.864601	0.000000	1.884873	0.949669	0.000000	-0.350869	-2.584231	0.000000
		O	-0.997291	0.445630	0.000000	0.708425	1.548867	0.000000	0.851216	-2.026894	0.000000
C_s ($^1A'$)	AVTZ	H	0.000000	0.667315	0.000000	0.000000	0.830045	0.000000	0.727309	-1.035821	0.000000
AcidAnti		O	-2.177759	-1.457073	0.000000	2.945843	1.540398	0.000000	-0.533111	-3.782430	0.000000
		H	-0.144033	-1.383882	0.000000	1.807321	-0.148241	0.000000	-1.166926	-1.846368	0.000000
		X	1.896217	0.823277	0.000000	-1.210020	-0.888398	0.000000	0.000000	1.223814	0.000000
		C	-1.118882	-0.857701	0.000000	1.884056	0.940714	0.000000	0.350480	-2.577937	0.000000
		O	-0.995632	0.449921	0.000000	0.710072	1.539080	0.000000	-0.848811	-2.020231	0.000000
	AVQZ	H	0.000000	0.668977	0.000000	0.000000	0.823000	0.000000	-0.726864	-1.030388	0.000000
		O	-2.182096	-1.444153	0.000000	2.943483	1.529804	0.000000	0.530879	-3.774170	0.000000
		H	-0.150345	-1.380991	0.000000	1.806654	-0.156876	0.000000	1.167444	-1.841683	0.000000
		X	1.899145	0.812475	0.000000	-1.209698	-0.881757	0.000000	0.000000	1.220659	0.000000

Table S116: *Cartesian coordinates of the geometries of halide-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots$HCOOH			$Br^-\cdots$HCOOH			$I^-\cdots$HCOOH		
			x	y	z	x	y	z	x	y	z
		C	-1.704052	-0.534849	0.000000	1.488596	2.025228	0.000000	-0.084238	-3.047339	0.000000
		O	-1.031344	0.585022	0.000000	0.209175	1.738385	0.000000	-0.919161	-2.029985	0.000000
	def2QZVP	H	0.000000	0.483536	0.000000	0.000000	0.742495	0.000000	-0.462401	-1.136856	0.000000
		O	-1.290004	-1.673274	0.000000	2.433337	1.270840	0.000000	1.122357	-3.026831	0.000000
		H	-2.788006	-0.318247	0.000000	1.619511	3.121299	0.000000	-0.657739	-3.988742	0.000000
		X	1.857830	0.691166	0.000000	-0.905462	-1.145399	0.000000	0.000000	1.204984	0.000000
		C	-1.712756	-0.518504	0.000000	1.501305	2.014664	0.000000	-0.082950	-3.045260	0.000000
		O	-1.030176	0.599031	0.000000	0.216066	1.741123	0.000000	-0.924250	-2.029894	0.000000
C_s ($^1A'$)	AVTZ	H	0.000000	0.485296	0.000000	0.000000	0.744892	0.000000	-0.467964	-1.133614	0.000000
AcidSyn		O	-1.304899	-1.662074	0.000000	2.439269	1.247383	0.000000	1.126440	-3.018385	0.000000
		H	-2.795280	-0.293895	0.000000	1.644459	3.109557	0.000000	-0.651859	-3.989990	0.000000
		X	1.867789	0.671998	0.000000	-0.911285	-1.138585	0.000000	0.000000	1.203423	0.000000
		C	-1.713319	-0.513443	0.000000	1.510338	1.996513	0.000000	-0.082865	-3.036453	0.000000
		O	-1.028052	0.599858	0.000000	0.225827	1.732010	0.000000	-0.922153	-2.022491	0.000000
	AVQZ	H	0.000000	0.484785	0.000000	0.000000	0.738304	0.000000	-0.468307	-1.126364	0.000000
		O	-1.309496	-1.655926	0.000000	2.441264	1.224128	0.000000	1.124243	-3.009640	0.000000
		H	-2.794802	-0.285985	0.000000	1.661891	3.089934	0.000000	-0.651223	-3.981042	0.000000
		X	1.869123	0.666494	0.000000	-0.916018	-1.127326	0.000000	0.000000	1.199683	0.000000

Table S117: *Cartesian coordinates of the geometries of halide-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots$HCOOH			$Br^-\cdots$HCOOH			$I^-\cdots$HCOOH		
			x	y	z	x	y	z	x	y	z
		C	-1.061067	0.459065	0.000000	0.195655	1.943483	0.000000	-0.153570	-2.528224	0.000000
		O	-1.899033	-0.608625	0.000000	1.525059	2.204679	0.000000	1.115225	-2.995156	0.000000
	def2QZVP	H	-2.787428	-0.227635	0.000000	1.592149	3.168906	0.000000	1.033088	-3.958174	0.000000
		O	-1.490675	1.589019	0.000000	-0.622324	2.832070	0.000000	-1.107841	-3.266363	0.000000
		H	0.000000	0.142732	0.000000	0.000000	0.857599	0.000000	-0.170738	-1.428417	0.000000
		X	2.133617	-0.618391	0.000000	-0.285370	-1.599468	0.000000	0.000000	1.332983	0.000000
		C	-1.059466	0.469467	0.000000	0.204589	1.934917	0.000000	0.147352	-2.511024	0.000000
		O	-1.903211	-0.596335	0.000000	1.538581	2.184396	0.000000	-1.125078	-2.975631	0.000000
C_s ($^1A'$)	AVTZ	H	-2.792127	-0.210975	0.000000	1.614619	3.150188	0.000000	-1.044669	-3.941014	0.000002
FormSyn		O	-1.483213	1.604449	0.000000	-0.608022	2.832079	0.000000	1.102018	-3.253252	0.000000
		H	0.000000	0.147227	0.000000	0.000000	0.849814	0.000000	0.166605	-1.410127	-0.000001
		X	2.131783	-0.636351	0.000000	-0.293904	-1.592609	0.000000	0.003367	1.325441	0.000000
		C	-1.055326	0.481329	0.000000	0.203174	1.928865	0.000000	-0.154589	-2.512720	0.000000
		O	-1.910428	-0.572376	0.000000	1.534453	2.181092	0.000000	1.115562	-2.976655	0.000000
	AVQZ	H	-2.793502	-0.178264	0.000000	1.609123	3.145172	0.000000	1.036556	-3.940328	0.000000
		O	-1.464704	1.619102	0.000000	-0.609386	2.823055	0.000000	-1.107374	-3.253646	0.000000
		H	0.000000	0.147396	0.000000	0.000000	0.843571	0.000000	-0.174519	-1.412371	0.000000
		X	2.125089	-0.660642	0.000000	-0.292249	-1.588432	0.000000	0.000000	1.325876	0.000000

Table S118: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH			Br···HCOOH			I···HCOOH		
			x	y	z	x	y	z	x	y	z
		C	-1.604253	-0.286351	-0.000019	1.702723	1.821210	0.000000	-0.365928	-2.868667	0.000000
		O	-0.929321	0.877698	-0.000003	0.359830	1.883892	0.000000	0.847634	-2.288882	0.000000
		H	0.017809	0.694581	-0.000037	0.000000	0.987941	0.000000	0.738725	-1.328721	0.000000
	def2QZVP	O	-2.796532	-0.340906	0.000021	2.395764	2.793008	0.000000	-0.516003	-4.053192	0.000000
		H	-0.949804	-1.171999	-0.000071	2.093766	0.791403	0.000000	-1.196202	-2.145288	0.000000
		X	2.374373	-0.123459	0.000005	-0.981567	-1.432051	0.000000	0.000000	1.347596	0.000000
		C	-1.611971	-0.290487	-0.000024	1.592258	1.947071	0.000000	-0.368109	-2.856003	0.000000
		O	-0.911686	0.861317	-0.000005	0.249431	1.845834	0.000000	0.838268	-2.256446	0.000000
C_s ($^2A''$)		H	0.033474	0.656926	-0.000054	0.000000	0.910398	0.000000	0.711966	-1.295637	0.000000
AcidAnti	AVTZ	O	-2.807980	-0.319453	0.000028	2.162445	2.998993	0.000000	-0.499905	-4.045639	0.000000
		H	-0.976485	-1.190570	-0.000092	2.106998	0.972595	0.000000	-1.210223	-2.145491	0.000000
		X	2.374833	-0.121079	0.000006	-0.884444	-1.494973	0.000000	0.000000	1.339506	0.000000
		C	-1.602378	-0.287356	0.000081	1.720111	1.762883	0.000000	-0.366514	-2.842826	0.000000
		O	-0.921856	0.873749	0.000014	0.378846	1.853367	0.000000	0.844181	-2.257032	0.000000
		H	0.025123	0.686890	0.000175	0.000000	0.964284	0.000000	0.730476	-1.296482	0.000000
	AVQZ	O	-2.795433	-0.335419	-0.000091	2.433265	2.720765	0.000000	-0.510517	-4.028699	0.000000
		H	-0.952701	-1.176721	0.000309	2.090462	0.725205	0.000000	-1.200700	-2.123642	0.000000
		X	2.369421	-0.123098	-0.000021	-0.997372	-1.395996	0.000000	0.000000	1.335150	0.000000

Table S119: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH			Br···HCOOH			I···HCOOH		
			x	y	z	x	y	z	x	y	z
		C	1.171797	0.902633	0.000000	-0.199533	-2.062765	0.000000	-0.207021	-2.513855	0.000000
		O	1.635705	-0.328159	0.000000	1.105023	-1.854334	0.000000	1.104305	-2.319286	0.000000
		H	0.863030	-0.928415	0.000000	1.251848	-0.889351	0.000000	1.267695	-1.358531	0.000000
	def2QZVP	O	0.000000	1.226115	0.000000	-1.058082	-1.207528	0.000000	-1.052381	-1.649611	0.000000
		H	1.977261	1.641515	0.000000	-0.430178	-3.131609	0.000000	-0.440971	-3.582288	0.000000
		X	-1.350395	-0.783091	0.000000	0.000000	1.168355	0.000000	0.000000	0.976889	0.000000
		C	1.174031	0.904697	0.000000	-0.198683	-2.061581	0.000000	-0.204118	-2.519583	0.000000
		O	1.637274	-0.329251	0.000000	1.107756	-1.848071	0.000000	1.107961	-2.312675	0.000000
C_s ($^2A'$)		H	0.860760	-0.928176	0.000000	1.248410	-0.879636	0.000000	1.260021	-1.347486	0.000000
AcidPSyn	AVTZ	O	0.000000	1.230255	0.000000	-1.061621	-1.206878	0.000000	-1.058847	-1.660729	0.000000
		H	1.981293	1.642566	0.000000	-0.425385	-3.131892	0.000000	-0.428229	-3.590797	0.000000
		X	-1.352026	-0.785330	0.000000	0.000000	1.166303	0.000000	0.000000	0.978170	0.000000
		C	1.172027	0.899686	0.000000	-0.197302	-2.048461	0.000000	-0.204679	-2.500062	0.000000
		O	1.633740	-0.331866	0.000000	1.105552	-1.833037	0.000000	1.105041	-2.298121	0.000000
		H	0.859490	-0.931154	0.000000	1.244920	-0.865516	0.000000	1.262354	-1.335207	0.000000
	AVQZ	O	0.000000	1.225003	0.000000	-1.060108	-1.196028	0.000000	-1.055007	-1.639374	0.000000
		H	1.978120	1.638166	0.000000	-0.424665	-3.118135	0.000000	-0.434553	-3.569543	0.000000
		X	-1.349393	-0.779425	0.000000	0.000000	1.157341	0.000000	0.000000	0.969907	0.000000

Table S120: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH			Br···HCOOH			I···HCOOH		
			x	y	z	x	y	z	x	y	z
		C	1.186809	1.035349	0.000000	-0.246848	-2.194973	0.000000	-0.248214	-2.647196	0.000000
		O	1.748524	-0.179303	0.000000	1.081076	-2.023548	0.000000	1.080547	-2.476808	0.000000
		H	2.707377	-0.094434	0.000000	1.520638	-2.879916	0.000000	1.520365	-3.333074	0.000000
	def2QZVP	O	0.000000	1.198653	0.000000	-1.014872	-1.276068	0.000000	-1.013063	-1.726039	0.000000
		H	1.904358	1.868311	0.000000	-0.569184	-3.246043	0.000000	-0.570953	-3.698100	0.000000
		X	-1.512987	-0.949458	0.000000	0.000000	1.305507	0.000000	0.000000	1.066738	0.000000
		C	1.188700	1.035702	0.000000	-0.245546	-2.185079	0.000000	-0.245683	-2.644847	0.000000
		O	1.743574	-0.185051	0.000000	1.083644	-2.004213	0.000000	1.083676	-2.459020	0.000000
C_s ($^2A'$)		H	2.705071	-0.105379	0.000000	1.529364	-2.859888	0.000000	1.533420	-3.312598	0.000000
CarbPAnti	AVTZ	O	0.000000	1.205467	0.000000	-1.020393	-1.268147	0.000000	-1.021387	-1.729188	0.000000
		H	1.911247	1.865007	0.000000	-0.562103	-3.238377	0.000000	-0.557633	-3.699506	0.000000
		X	-1.511595	-0.949245	0.000000	0.000000	1.296789	0.000000	0.000000	1.063903	0.000000
		C	1.186554	1.028268	0.000000	-0.244962	-2.175340	0.000000	-0.247555	-2.630398	0.000000
		O	1.740775	-0.189969	0.000000	1.081696	-1.994538	0.000000	1.080710	-2.455843	0.000000
		H	2.700650	-0.112093	0.000000	1.528531	-2.847632	0.000000	1.524483	-3.310540	0.000000
	AVQZ	O	0.000000	1.197913	0.000000	-1.018842	-1.260433	0.000000	-1.014534	-1.710195	0.000000
		H	1.908264	1.857755	0.000000	-0.561589	-3.228182	0.000000	-0.568564	-3.681887	0.000000
		X	-1.509084	-0.939931	0.000000	0.000000	1.290504	0.000000	0.000000	1.058549	0.000000

Table S121: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH			Br···HCOOH			I···HCOOH		
			x	y	z	x	y	z	x	y	z
		C	1.437991	-0.264909	0.266506	-1.318519	-1.756581	0.000000	-0.414845	-2.639290	0.000000
		O	0.570468	0.762155	0.176974	0.000000	-1.483702	0.000000	0.657273	-1.823844	0.000000
		H	0.953434	1.411361	-0.430405	0.472408	-2.328314	0.000000	1.447182	-2.383073	0.000000
	def2QZVP	O	2.491162	-0.317148	-0.299580	-1.785574	-2.858657	0.000000	-0.360491	-3.834887	0.000000
		H	1.033008	-1.033515	0.931491	-1.888568	-0.822455	0.000000	-1.332361	-2.042654	0.000000
		X	-2.065143	-0.138144	-0.065840	0.674625	1.383689	0.000000	0.000000	1.236440	0.000000
		C	1.435045	-0.240101	0.297747	-1.327250	-1.715933	0.000000	-0.412922	-2.606769	0.000000
		O	0.566724	0.785980	0.170128	0.000000	-1.473668	0.000000	0.683692	-1.820110	0.000000
C_s ($^2A'$)		H	0.920358	1.378861	-0.511653	0.452828	-2.331421	0.000000	1.458854	-2.403217	0.000000
CarbPSyn	AVTZ	O	2.457840	-0.348555	-0.319418	-1.821135	-2.809183	0.000000	-0.392207	-3.806150	0.000000
		H	1.063135	-0.947631	1.045701	-1.874607	-0.767560	0.000000	-1.313198	-1.983214	0.000000
		X	-2.046487	-0.146472	-0.066248	0.684410	1.361640	0.000000	0.000000	1.227116	0.000000
		C	1.434091	-0.261763	0.271874	-1.328034	-1.697266	0.000000	-0.413773	-2.597010	0.000000
		O	0.562379	0.762051	0.178666	0.000000	-1.471563	0.000000	0.672617	-1.799683	0.000000
		H	0.936650	1.405062	-0.441281	0.443158	-2.332349	0.000000	1.453609	-2.371995	0.000000
	AVQZ	O	2.481938	-0.317194	-0.304491	-1.833417	-2.782660	0.000000	-0.378849	-3.793671	0.000000
		H	1.038448	-1.023894	0.950141	-1.864244	-0.743027	0.000000	-1.321111	-1.984619	0.000000
		X	-2.054952	-0.139379	-0.066677	0.687332	1.351222	0.000000	0.000000	1.220481	0.000000

Table S122: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH			Br···HCOOH			I···HCOOH		
			x	y	z	x	y	z	x	y	z
		C	1.077332	0.351405	0.000000	1.199735	1.370363	0.000000	0.266629	-2.289004	0.000000
		O	2.208994	1.063445	0.000000	1.909780	2.504443	0.000000	0.235497	-3.627225	0.000000
		H	2.965815	0.468302	0.000000	2.850017	2.297480	0.000000	1.134448	-3.971825	0.000000
	def2QZVP	O	0.000000	0.881825	0.000000	0.000000	1.376770	0.000000	-0.736705	-1.632548	0.000000
		H	1.213152	-0.737582	0.000000	1.799380	0.450383	0.000000	1.275448	-1.853383	0.000000
		X	-1.665583	-1.023606	0.000000	-0.775030	-1.200564	0.000000	0.000000	1.162970	0.000000
		C	1.078189	0.351686	0.000000	1.202422	1.359024	0.000000	0.265013	-2.286805	0.000000
		O	2.213440	1.063093	0.000000	1.922041	2.490092	0.000000	0.245765	-3.627883	0.000000
C_s ($^2A'$)		H	2.970270	0.464427	0.000000	2.862668	2.274873	0.000000	1.150131	-3.964309	0.000000
FormPAnti	AVTZ	O	0.000000	0.886432	0.000000	0.000000	1.375512	0.000000	-0.747025	-1.638813	0.000000
		H	1.211480	-0.738236	0.000000	1.794514	0.433495	0.000000	1.269872	-1.840691	0.000000
		X	-1.668142	-1.025442	0.000000	-0.778515	-1.193924	0.000000	0.000000	1.163385	0.000000
		C	1.076275	0.345747	0.000000	1.200368	1.354542	0.000000	0.266452	-2.275116	0.000000
		O	2.209331	1.055914	0.000000	1.913217	2.486963	0.000000	0.238415	-3.613419	0.000000
		H	2.966058	0.459974	0.000000	2.853569	2.278600	0.000000	1.138199	-3.956999	0.000000
	AVQZ	O	0.000000	0.879692	0.000000	0.000000	1.365421	0.000000	-0.739723	-1.621830	0.000000
		H	1.208806	-0.743788	0.000000	1.796240	0.431922	0.000000	1.273556	-1.835221	0.000000
		X	-1.665127	-1.016207	0.000000	-0.775936	-1.190196	0.000000	0.000000	1.157074	0.000000

Table S123: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH			Br···HCOOH			I···HCOOH		
			x	y	z	x	y	z	x	y	z
		C	1.102406	0.359457	0.000000	1.205166	1.400880	0.000000	-0.321466	-2.313306	0.000000
		O	2.235319	1.058974	0.000000	1.925282	2.521666	0.000000	-0.347432	-3.645641	0.000000
		H	2.000074	1.997911	0.000000	1.306763	3.266192	0.000000	0.569753	-3.954903	0.000000
	def2QZVP	O	0.000000	0.849785	0.000000	0.000000	1.364670	0.000000	0.684258	-1.649323	0.000000
		H	1.302829	-0.713965	0.000000	1.852539	0.520827	0.000000	-1.335570	-1.905432	0.000000
		X	-1.635287	-1.100633	0.000000	-0.736930	-1.236657	0.000000	0.000000	1.171696	0.000000
		C	1.102795	0.358924	0.000000	1.208223	1.388137	0.000000	-0.318864	-2.309032	0.000000
		O	2.241012	1.054704	0.000000	1.940337	2.504029	0.000000	-0.360894	-3.643467	0.000000
C_s ($^2A'$)		H	2.008136	1.996454	0.000000	1.326567	3.255263	0.000000	0.554983	-3.963150	0.000000
FormPSyn	AVTZ	O	0.000000	0.854959	0.000000	0.000000	1.363126	0.000000	0.696750	-1.655285	0.000000
		H	1.299228	-0.715975	0.000000	1.847566	0.501383	0.000000	-1.328652	-1.888754	0.000000
		X	-1.638367	-1.100666	0.000000	-0.741319	-1.229220	0.000000	0.000000	1.171625	0.000000
		C	1.101357	0.353234	0.000000	1.205992	1.383336	0.000000	-0.321394	-2.298883	0.000000
		O	2.236115	1.049896	0.000000	1.930319	2.501344	0.000000	-0.349622	-3.631073	0.000000
		H	2.003652	1.989925	0.000000	1.314660	3.248743	0.000000	0.567296	-3.942325	0.000000
	AVQZ	O	0.000000	0.847396	0.000000	0.000000	1.352670	0.000000	0.686539	-1.637084	0.000000
		H	1.297922	-0.721123	0.000000	1.848665	0.499572	0.000000	-1.334267	-1.887442	0.000000
		X	-1.635214	-1.092149	0.000000	-0.738338	-1.225155	0.000000	0.000000	1.165440	0.000000

Table S124: *Cartesian coordinates of the geometries of halogen-formic acid complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			Cl···HCOOH						Cl···HCOOH		
			x	y	z				x	y	z
		C	-1.875893	0.657476	0.000000			C	1.671331	0.164369	0.229680
		O	-0.711532	1.319419	0.000000			O	0.640775	0.879312	-0.279360
		H	0.000000	0.660146	0.000000			H	0.605730	1.745101	0.140869
	def2QZVP	O	-1.993525	-0.536451	0.000000		def2QZVP	O	1.904226	-0.949646	-0.119502
		H	-2.708399	1.368667	0.000000			H	2.255808	0.715230	0.981572
		X	2.094365	-0.719848	0.000000			X	-1.955855	-0.169639	0.040610
		C	-1.878758	0.623915	0.000000			C	1.662781	0.162179	0.234143
		O	-0.721432	1.302677	0.000000			O	0.639379	0.886915	-0.282628
C_s ($^2A''$)		H	0.000000	0.650795	0.000000	C_s (^1A)		H	0.602262	1.750526	0.146903
InLineSyn	AVTZ	O	-1.980683	-0.574320	0.000000	OutPlAnti	AVTZ	O	1.894663	-0.952515	-0.122900
		H	-2.721320	1.324211	0.000000			H	2.241376	0.704021	0.997768
		X	2.094753	-0.679138	0.000000			X	-1.946627	-0.170754	0.040865
		C	-1.876324	0.627438	0.000000			C	1.668998	-0.166400	-0.227025
		O	-0.724644	1.311503	0.000000			O	0.633318	-0.878139	0.277376
		H	0.000000	0.665816	0.000000			H	0.599572	-1.746560	-0.138527
	AVQZ	O	-1.970807	-0.569060	0.000000		AVQZ	O	1.898108	0.950091	0.118127
		H	-2.722924	1.322112	0.000000			H	2.260783	-0.721544	-0.970165
		X	2.090852	-0.687770	0.000000			X	-1.948574	0.170052	-0.040776

Table S125: *Peak positions and assignments of* 50 kPa C_3H_6*:*CCl_4*:argon gas mix.*

Position (m/z)	Assignment
34.9	$^{35}Cl^-$
36.9	$^{37}Cl^-$
77.1	$^{35}Cl^-\cdots C_3H_6$
79.0	$^{37}Cl^-\cdots C_3H_6$, $^{79}Br^-$
81.0	$^{81}Br^-$
119.4	$^{35}Cl^-\cdots (C_3H_6)_2$
121.3	$^{37}Cl^-\cdots (C_3H_6)_2$, $^{79}Br^-\cdots C_3H_6$
123.2	$^{81}Br^-\cdots C_3H_6$
126.9	I^-

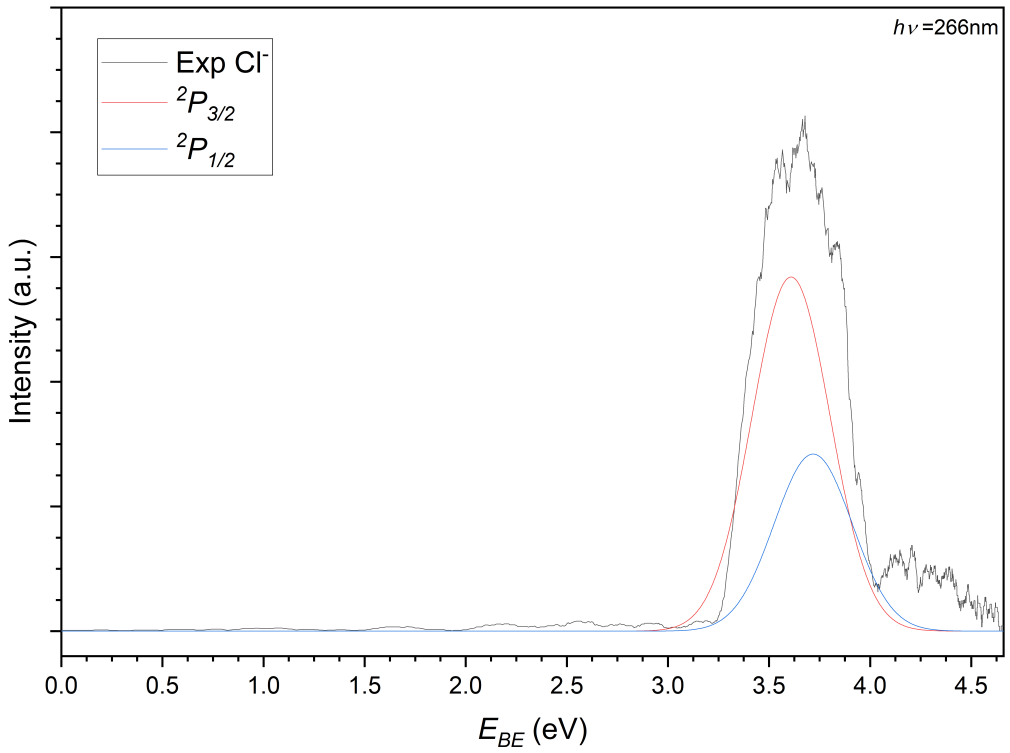

Figure S2: *An example* Cl^- *PES recorded during the halide-propene suite of experiments.*

Table S126: *Peak positions and assignments of* 50 kPa C_3H_6*:*CH_2Br_2*:argon gas mix.*

Position (m/z)	Assignment
35.1	$^{35}Cl^-$
37.0	$^{37}Cl^-$
77.1	$^{35}Cl^-\cdots C_3H_6$
79.0	$^{37}Cl^-\cdots C_3H_6$, $^{79}Br^-$
80.9	$^{81}Br^-$
118.0	$CHCl_3^-$ (^{35}Cl:^{37}Cl=3:0)
119.3	$^{35}Cl^-\cdots(C_3H_6)_2$
121.2	$^{37}Cl^-\cdots(C_3H_6)_2$, $^{79}Br^-\cdots C_3H_6$
123.2	$^{81}Br^-\cdots C_3H_6$
127.1	I^-
152.1	CCl_4^- (^{35}Cl:^{37}Cl=4:0)
153.1	$CHCl_4^-$ (^{35}Cl:^{37}Cl=4:0)
154.2	CCl_4^- (^{35}Cl:^{37}Cl=3:1)
155.2	$CHCl_4^-$ (^{35}Cl:^{37}Cl=3:1)
156.2	CCl_4^- (^{35}Cl:^{37}Cl=2:2)
160.2	CCl_4^- (^{35}Cl:^{37}Cl=1:3)
161.4	CCl_4^- (^{35}Cl:^{37}Cl=0:4)
162.2	$^{35}Cl^-\cdots(C_3H_6)_3$
163.4	$^{37}Cl^-\cdots(C_3H_6)_3$, $^{79}Br^-\cdots(C_3H_6)_2$
165.3	$^{81}Br^-\cdots(C_3H_6)_2$
169.2	$I^-\cdots C_3H_6$
172.1	$^{79}Br^-\cdots CH_2^{79}Br$
174.1	$^{79}Br^-\cdots CH_2^{81}Br$, $^{81}Br^-\cdots CH_2^{79}Br$
176.1	$^{81}Br^-\cdots CH_2^{81}Br$

Table S127: *Peak positions and assignments of* 50 kPa *C_3H_6:CH_3I:argon gas mix.*

Position (m/z)	Assignment
126.9	I^-
169.3	$I^-\cdots C_3H_6$
211.6	$I^-\cdots (C_3H_6)_2$
253.9	$I^-\cdots (C_3H_6)_3$
269.8	$I^-\cdots CH_3I$
311.9	$I^-\cdots (CH_3I)(C_3H_6)$
354.4	$I^-\cdots (CH_3I)(C_3H_6)_2$
395.0	$I^-\cdots (CH_3I)(C_3H_6)_3$
412.7	$I^-\cdots (CH_3I)_2$

Table S128: *Calibration details from the each of the bare halide PES spectra.*

Halide Source	Calibration Mass Peak	$A^\dagger$	$B^\dagger$
CH_2Br_2	$^{81}Br^-$	7.463E-12	-0.2496
CH_3I	I^-	8.053E-12	-0.3842
CCl_4	I^-	7.920E-12	-0.6378

†: $E_{BE} = h\nu + \frac{A}{TOF^2} + B$

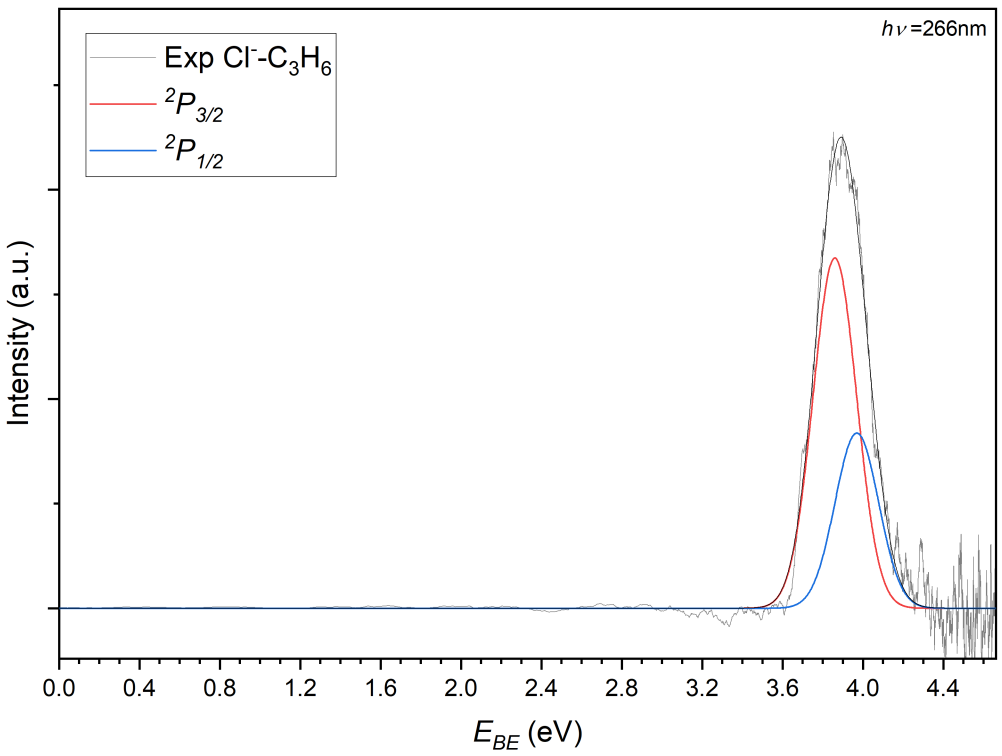

Figure S3: *Additional $Cl^{-}\cdots C_3H_6$ PES spectrum recorded. The peak has also been deconvoluted into two Gaussian functions yielding E_{BE}: $^2P_{3/2}$ =3.86 eV and $^2P_{1/2}$ =3.97 eV.*

Table S129: *$X^-\cdots C_3H_6$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H}	$\angle_{H-X-H}$	E_{DFT}	zpe	D_e	D_o	E_{VDE}	VDE $^2P_{3/2}$	VDE $^2P_{1/2}$
			Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	E_h	eV	eV
$Cl^-\cdots C_3H_6$	BiDent	def2QZVP	2.664	53.2	-577.7214109	211.1	31.0	32.2	-577.5800396	3.942	4.051
		AVTZ	2.667	53.2	-577.6919627	211.0	29.1	30.4	-577.5493893	3.906	4.018
			R_{X-H}	$\angle_{H-X-C}$							
	Bif	def2QZVP	2.659	37.6	-577.7212976	210.3	30.7	31.1	-577.5804888	3.934	4.043
		AVTZ	2.655	37.3	-577.6917547	210.1	28.6	28.9	-577.5497483	3.898	4.007
			R_{X-H}	$\angle_{X-H-C}$							
	HApp	def2QZVP	2.487	175.2	-577.7177605	210.5	21.5	22.0	-577.5799972	3.850	3.959
		AVTZ	2.494	175.0	-577.6884721	210.3	19.9	20.6	-577.5492608	3.821	3.930
			R_{X-H}	$\angle_{H-X-H}$							
$Br^-\cdots C_3H_6$	BiDent	def2QZVP	2.848	49.7	-2691.1955646	211.0	27.0	28.1	-2691.0609970	3.624	4.081
		AVTZ	2.812	50.3	-534.0253488	211.0	26.9	28.1	-533.8911496	3.601	4.058
			R_{X-H}	$\angle_{X-H-C}$							
	Bif	def2QZVP	2.865	35.9	-2691.1957939	210.2	27.6	28.0	-2691.0613613	3.627	4.084
		AVTZ	2.821	35.6	-534.0252992	210.1	26.7	27.1	-533.8914016	3.600	4.057
			R_{X-H}	$\angle_{H-X-H}$							
$I^-\cdots C_3H_6$	BiDent	def2QZVP	3.127	45.3	-415.2834016	210.9	20.9	21.8	-415.1576975	3.232	4.174
		AVTZ	3.081	46.0	-413.0711450	210.8	22.7	23.8	-412.9453864	3.230	4.172
			R_{X-H}	$\angle_{X-H-C}$							
	Bif	def2QZVP	3.158	33.5	-415.2839787	210.3	22.4	22.7	-415.1577898	3.250	4.192
		AVTZ	3.108	33.5	-413.0715007	210.1	23.6	24.0	-412.9454346	3.244	4.186

Table S130: *$X\cdots C_3H_6$ complex geometric parameters and D_0 values from DSD-PBEP86-D3BJ optimisations. zpe values are drawn from relevent harmonic frequency calculations.*

			R_{X-H}	$\angle_{H-X-H}$	E_{DFT}	zpe	D_e	D_o
			Å	°	E_h	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
$Cl\cdots C_3H_6$	BiDent	def2QZVP	3.204	45.3	-577.5821952	211.0	3.0	4.1
		AVTZ						
			R_{X-C}	$\angle_{X-C-H}$				
	MePoc	def2QZVP	3.763	66.0	-577.5818040	210.5	2.0	2.6
		AVTZ	3.724	65.7	-577.5508222	210.3	2.6	3.2
			R_{X-C}	$\angle_{X-C-C}$				
	Perp	def2QZVP	1.839	110.5	-577.6172780	213.4	95.1	98.6
		AVTZ	1.843	110.4	-577.5863091	213.2	95.8	99.3
			R_{X-H}	$\angle_{H-X-H}$				
$Br\cdots C_3H_6$	Bif	def2QZVP	3.310	38.3	-2691.0631763	210.6	5.9	6.6
		AVTZ	3.267	39.0	-533.8932934	210.3	7.8	8.4
			R_{X-C}	$\angle_{X-C-H}$				
	MePoc	def2QZVP	3.866	66.2	-2691.0618654	210.4	2.5	3.0
		AVTZ	3.816	65.1	-533.8916923	210.4	3.6	4.3
			R_{X-C}	$\angle_{X-C-C}$				
	Perp	def2QZVP	2.688	79.7	-2691.0777652	213.2	44.2	47.5
		AVTZ	2.676	79.4	-533.9079853	212.9	46.4	49.6
			R_{X-H}	$\angle_{H-X-H}$				
$I\cdots C_3H_6$	End	def2QZVP	3.688	29.2	-415.1577891	210.8	2.9	3.8
		AVTZ	3.702	29.5	-412.9452053	210.5	4.2	5.0
			R_{X-C}	$\angle_{X-C-H}$				
	MePoc	def2QZVP	4.038	66.3	-415.1577946	210.4	3.0	3.5
		AVTZ	3.987	64.4	-412.9452577	210.3	4.3	4.9
			R_{X-C}	$\angle_{X-C-C}$				
	Perp	def2QZVP	2.946	80.7	-415.1696451	212.8	34.1	36.9
		AVTZ	2.948	80.5	-412.9573379	212.5	36.0	38.9

Table S131: *Cartesian coordinates of the geometries of halide-propene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots C_3H_6$			$Br^-\cdots C_3H_6$			$I^-\cdots C_3H_6$		
			x	y	z	x	y	z	x	y	z
BiDent	def2QZVP	H	3.034471	0.523704	0.000000	-2.964427	2.458629	0.000000	-0.170655	-4.423255	0.000000
		C	1.963427	0.322903	0.000000	-2.129604	1.758758	0.000000	-0.131856	-3.335010	0.000000
		C	1.533894	-0.939035	0.000000	-2.376685	0.449130	0.000000	-1.271591	-2.644982	0.000000
		H	2.241002	-1.762154	0.000000	-3.396406	0.079232	0.000000	-2.228481	-3.154800	0.000000
		H	0.467453	-1.155886	0.000000	-1.559293	-0.267640	0.000000	-1.264852	-1.558984	0.000000
		C	1.040991	1.503570	0.000000	-0.748439	2.338372	0.000000	1.224286	-2.700323	0.000000
		H	0.000000	1.169745	0.000000	0.000000	1.542759	0.000000	1.141933	-1.612039	0.000000
		H	1.214626	2.133002	-0.878801	-0.592376	2.971899	0.878758	1.798513	-3.008831	-0.878716
		H	1.214626	2.133002	0.878801	-0.592376	2.971899	-0.878758	1.798513	-3.008831	0.878716
		X	-2.082474	-0.492120	0.000000	1.160950	-1.058124	0.000000	0.000000	1.299031	0.000000
	AVTZ	H	3.037582	0.525126	0.000000	0.178165	3.827965	0.000000	-4.391090	0.166143	0.000000
		C	1.965757	0.323381	0.000000	0.134007	2.738471	0.000000	-3.301728	0.129418	0.000000
		C	1.537328	-0.940997	0.000000	1.270666	2.038819	0.000000	-2.612860	1.272223	0.000000
		H	2.246029	-1.763975	0.000000	2.231554	2.544255	0.000000	-3.125304	2.228876	0.000000
		H	0.470478	-1.159317	0.000000	1.248848	0.950833	0.000000	-1.525744	1.265888	0.000000
		C	1.041792	1.504527	0.000000	-1.225079	2.105462	0.000000	-2.663051	-1.226462	0.000000
		H	0.000000	1.169755	0.000000	-1.137757	1.015196	0.000000	-1.573647	-1.139933	0.000000
		H	1.215585	2.134350	-0.879941	-1.799184	2.416288	-0.879975	-2.970773	-1.801677	-0.879878
		H	1.215585	2.134350	0.879941	-1.799184	2.416288	0.879975	-2.970774	-1.801678	0.879878
		X	-2.085560	-0.491868	0.000000	0.000000	-1.556210	0.000000	1.283456	0.000591	0.000000

Table S132: *Cartesian coordinates of the geometries of halide-propene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^-\cdots C_3H_6$			$Br^-\cdots C_3H_6$			$I^-\cdots C_3H_6$		
			x	y	z	x	y	z	x	y	z
Bif	def2QZVP	H	-0.802780	-0.406590	0.000000	-1.145058	0.824477	0.000096	-1.538742	1.151099	0.000000
		C	-1.125712	0.631758	0.000000	-2.058247	0.235209	0.000033	-1.417175	2.230674	0.000000
		C	-2.417746	0.963174	0.000000	-3.256978	0.819541	-0.000017	-2.481385	3.033652	0.000000
		H	-3.193873	0.207396	0.000000	-3.358744	1.897896	0.000006	-3.488373	2.635261	0.000000
		H	-2.737540	2.001215	0.000000	-4.172322	0.235279	-0.000087	-2.374923	4.114022	0.000000
		C	0.000000	1.610970	0.000000	-1.833041	-1.239681	0.000001	0.000000	2.697723	0.000000
		H	-0.357335	2.644410	0.000000	-1.231878	-1.522511	-0.865667	0.065384	3.788478	0.000000
		H	0.640882	1.434554	-0.865336	-1.232007	-1.522573	0.865740	0.526530	2.294766	-0.866906
		H	0.640882	1.434554	0.865336	-2.774934	-1.794464	-0.000084	0.526530	2.294766	0.866906
		X	1.592382	-1.561818	0.000000	1.622987	0.085471	-0.000003	0.559905	-1.208503	0.000000
	AVTZ	C	1.073749	0.715818	0.000000	-1.111717	-0.793705	0.000093	-1.688699	-0.823697	-0.000032
		C	1.949537	1.724208	0.000000	-2.042092	-0.229698	0.000034	-2.605904	-0.239467	-0.000011
		H	0.000000	0.893120	0.000000	-3.226431	-0.846519	-0.000017	-3.797512	-0.841331	0.000006
		H	1.621073	2.759056	0.000000	-3.298642	-1.928226	0.000009	-3.883284	-1.921848	-0.000003
		H	3.020190	1.543923	0.000000	-4.157836	-0.286241	-0.000089	-4.721117	-0.268865	0.000030
		C	1.452043	-0.729340	0.000000	-1.856123	1.252367	0.000000	-2.399138	1.239823	0.000000
		H	2.539644	-0.839699	0.000000	-2.813435	1.782657	-0.000134	-1.805003	1.533969	-0.868544
		H	1.023042	-1.236694	0.868104	-1.263735	1.551525	-0.867927	-3.349926	1.780978	0.000041
		H	1.023042	-1.236694	-0.868104	-1.263953	1.551597	0.868052	-1.804937	1.533946	0.868506
		X	-2.122292	-0.714537	0.000000	1.618777	-0.083843	-0.000003	1.322043	-0.052616	0.000001

Table S133: *Cartesian coordinates of the geometries of halide-propene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl^- \cdots C_3H_6$		
			x	y	z
	def2QZVP	H	-0.403974	1.802275	0.000000
		C	-1.253204	1.124407	0.000000
		C	-1.013548	-0.185150	0.000000
		H	0.000000	-0.587083	0.000000
		H	-1.845976	-0.885207	0.000000
		C	-2.615765	1.750360	0.000000
		H	-3.394624	0.985445	0.000000
		H	-2.764864	2.386074	-0.878016
		H	-2.764864	2.386074	0.878016
		X	2.380553	-1.307370	0.000000
HApp	AVTZ	H	0.417421	-1.798051	0.000000
		C	1.263808	-1.115035	0.000000
		C	1.016559	0.195012	0.000000
		H	0.000000	0.590655	0.000000
		H	1.845339	0.900819	0.000000
		C	2.630699	-1.734636	0.000000
		H	3.406492	-0.964878	0.000000
		H	2.782102	-2.370197	-0.879210
		H	2.782102	-2.370197	0.879210
		X	-2.394109	1.290577	0.000000

Table S134: *Cartesian coordinates of the geometries of halogen-propene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots C_3H_6$				$Br\cdots C_3H_6$				$I\cdots C_3H_6$		
			x	y	z		x	y	z		x	y	z
	def2QZVP	H	-3.286352	0.203741	0.000280		1.502122	1.146196	0.000000		-4.183205	1.545457	0.000255
		C	-2.201738	0.145594	0.000075		2.185647	0.302262	0.000000		-3.749861	0.549511	0.000057
		C	-1.498919	1.275687	-0.000054		3.495625	0.533837	0.000000		-2.424869	0.426578	-0.000148
		H	-1.985605	2.241870	0.000041		3.890401	1.540866	0.000000		-1.774986	1.291367	-0.000121
		H	-0.415395	1.262943	-0.000258		4.210521	-0.280678	0.000000		-1.949036	-0.547162	-0.000349
		C	-1.605472	-1.225952	-0.000041		1.566657	-1.059234	0.000000		-4.709750	-0.597142	0.000035
		H	-0.516577	-1.181639	-0.000255		0.935756	-1.202803	0.881600		-4.182562	-1.551126	-0.000171
		H	-1.927980	-1.791546	-0.877089		0.935758	-1.202803	-0.881601		-5.359630	-0.562858	-0.877145
		H	-1.927636	-1.791545	0.877135		2.326341	-1.841203	0.000000		-5.359382	-0.563099	0.877408
		X	2.464489	-0.006812	0.000016		-1.636813	0.090835	0.000000		1.662560	-0.035590	0.000009
BiDent	AVTZ	H				Bif	-1.476122	-1.149426	0.000025	End	1.427047	-4.233302	0.000000
		C					-2.156289	-0.301545	0.000008		0.464302	-3.728319	0.000000
		C					-3.469194	-0.526845	-0.000006		0.437948	-2.396007	0.000000
		H					-3.868852	-1.533032	-0.000001		1.348665	-1.810168	0.000000
		H					-4.180664	0.291995	-0.000022		-0.499110	-1.849648	0.000000
		C					-1.528994	1.057689	0.000003		-0.750101	-4.603247	0.000000
		H					-2.285034	1.844999	-0.000012		-1.663969	-4.006970	0.000000
		H					-0.897099	1.196996	-0.883205		-0.762765	-5.254208	0.878468
		H					-0.897117	1.197011	0.883220		-0.762765	-5.254208	-0.878468
		X					1.615193	-0.092124	-0.000001		0.000000	1.637244	0.000000

Table S135: *Cartesian coordinates of the geometries of halogen-propene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots C_3H_6$			$Br\cdots C_3H_6$			$I\cdots C_3H_6$		
			x	y	z	x	y	z	x	y	z
MePoc	def2QZVP	H	-2.747793	-1.458953	0.000620	-3.706591	-1.452225	-0.000006	4.313588	-1.446665	-0.000247
		C	-2.333373	-0.454990	0.000161	-3.282464	-0.452316	-0.000002	3.883716	-0.449206	-0.000066
		C	-3.167235	0.581964	0.000094	-4.106262	0.592666	-0.000001	4.701479	0.600521	-0.000039
		H	-4.240171	0.444328	0.000485	-5.180488	0.465460	-0.000005	5.776427	0.479520	-0.000195
		H	-2.796467	1.600347	-0.000356	-3.725607	1.607397	0.000004	4.314950	1.613031	0.000141
		C	-0.842330	-0.346698	-0.000354	-1.790479	-0.358378	0.000004	2.391218	-0.363785	0.000140
		H	-0.520954	0.694652	-0.000790	-1.458832	0.679747	0.000013	2.053386	0.672407	0.000321
		H	-0.413469	-0.837911	-0.876575	-1.365736	-0.853391	-0.876096	1.969095	-0.861293	0.876162
		H	-0.412896	-0.837366	0.875890	-1.365741	-0.853407	0.876097	1.968862	-0.861071	-0.875895
		X	2.893493	0.100779	0.000078	2.053664	0.048988	0.000000	-1.627449	0.031677	-0.000009
	AVTZ	H	-2.706902	-1.464045	-0.018994	-3.692644	-1.446984	0.000273	-4.304063	-1.435385	0.000000
		C	-2.305411	-0.456174	0.003213	-3.254778	-0.451916	0.000074	-3.850652	-0.447300	0.000000
		C	-3.148048	0.578894	-0.001278	-4.066036	0.605185	0.000038	-4.645197	0.622429	0.000000
		H	-4.215501	0.421065	-0.029229	-5.142810	0.491538	0.000208	-5.723631	0.525760	0.000000
		H	-2.801017	1.611167	0.029261	-3.671514	1.615701	-0.000161	-4.234705	1.626560	0.000000
		C	-0.827722	-0.337827	0.011136	-1.760309	-0.377902	-0.000154	-2.355239	-0.396523	0.000000
		H	-0.505783	0.701175	-0.024796	-1.414790	0.656988	-0.000364	-1.993323	0.632773	0.000000
		H	-0.402620	-0.843579	-0.881319	-1.342375	-0.879315	-0.877454	-1.944589	-0.904132	-0.877235
		H	-0.377563	-0.866434	0.866635	-1.342125	-0.879043	0.877184	-1.944589	-0.904132	0.877236
		X	2.864498	0.101841	-0.001175	2.031228	0.051112	0.000016	1.608518	0.033715	0.000000

Table S136: *Cartesian coordinates of the geometries of halogen-propene complexes optimised with the DSD-PBEP86-D3BJ functional, in* Å.

			$Cl\cdots C_3H_6$			$Br\cdots C_3H_6$			$I\cdots C_3H_6$		
			x	y	z	x	y	z	x	y	z
Perp	def2QZVP	C	0.145684	0.882511	0.305448	-1.099276	1.345951	-0.209853	2.029621	0.254912	0.466608
		C	-1.101663	0.533891	-0.378744	-1.574943	0.277392	0.467154	1.624305	1.344403	-0.211243
		H	-1.233685	0.881166	-1.394856	-1.515415	0.286150	1.550261	1.955877	0.263882	1.549498
		H	0.564045	1.830321	-0.017826	-0.691049	2.201877	0.307997	1.233364	2.211816	0.304072
		H	0.052878	0.859654	1.388659	-1.156189	1.390363	-1.289774	1.677612	1.384544	-1.291213
		C	-1.962278	-0.562676	0.130061	-2.212244	-0.907713	-0.169112	2.578960	-0.978224	-0.166543
		H	-1.547681	-1.541115	-0.143946	-3.261046	-0.972499	0.131287	2.009095	-1.856104	0.140789
		H	-2.969049	-0.509225	-0.282631	-1.724088	-1.825767	0.159378	2.542938	-0.902084	-1.254099
		H	-2.028673	-0.541984	1.219838	-2.159726	-0.851747	-1.255199	3.613198	-1.140921	0.139650
		X	1.451277	-0.358893	-0.065284	1.137894	-0.129204	-0.003802	-0.951498	-0.069579	-0.002295
	AVTZ	C	0.144549	0.884782	0.305662	-1.088839	1.349010	-0.209402	-1.624056	1.345655	-0.210172
		C	-1.103003	0.534183	-0.379482	-1.563710	0.277991	0.467671	-2.024211	0.250792	0.465521
		H	-1.233550	0.879024	-1.397708	-1.502543	0.285913	1.551665	-1.961514	0.261450	1.550011
		H	0.564208	1.832487	-0.019319	-0.678013	2.203852	0.310248	-1.262097	2.224331	0.307310
		H	0.052542	0.861153	1.389840	-1.146645	1.394748	-1.290201	-1.684109	1.388003	-1.291571
		C	-1.963881	-0.563834	0.130444	-2.206036	-0.906138	-0.169154	-2.587813	-0.977158	-0.167685
		H	-1.546242	-1.542954	-0.141274	-3.258033	-0.962563	0.126297	-3.628075	-1.114196	0.141605
		H	-2.970821	-0.511873	-0.285049	-1.725060	-1.827441	0.164440	-2.035641	-1.863236	0.151983
		H	-2.032285	-0.540243	1.221235	-2.147387	-0.852525	-1.256296	-2.550250	-0.915157	-1.255628
		X	1.452950	-0.359317	-0.065145	1.131691	-0.130490	-0.004024	0.953550	-0.069753	-0.002447

Table S137: *Calculated harmonic frequencies and mode assignments for the $X^-\cdots C_3H_6$ BiDent complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

		$Cl^-\cdots C_3H_6$			$Br^-\cdots C_3H_6$			$I^-\cdots C_3H_6$		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a'	90	3.3256	a'	79	6.5627	a'	65	3.7468
	ω_2	a'	105	24.6974	a'	85	2.0685	a'	73	0.04
	ω_3	a''	133	0.104	a''	121	0.004	a''	105	0.051
	ω_4	a''	224	0.4346	a''	219	0.4927	a''	214	0.4669
	ω_5	a'	446	5.1353	a'	442	3.7719	a'	437	2.7758
	ω_6	a''	595	15.9601	a''	594	15.3112	a''	592	14.6189
	ω_7	a'	937	5.925	a'	937	5.5184	a'	937	5.0114
	ω_8	a'	963	1.3491	a'	960	1.3123	a'	957	1.338
	ω_9	a''	969	17.6593	a''	967	20.279	a''	964	21.4298
	ω_{10}	a''	1051	24.382	a''	1047	21.4968	a''	1043	17.7694
	ω_{11}	a''	1082	2.1612	a''	1081	2.5494	a''	1080	3.0814
	ω_{12}	a'	1208	0.9062	a'	1207	0.5864	a'	1206	0.3122
	ω_{13}	a'	1336	0.1639	a'	1335	0.1048	a'	1334	0.1103
	ω_{14}	a'	1415	0.6794	a'	1416	0.5257	a'	1416	0.4044
	ω_{15}	a'	1455	1.9559	a'	1456	1.5657	a'	1457	1.2532
	ω_{16}	a'	1501	2.1762	a'	1502	2.9078	a''	1501	1.8897
	ω_{17}	a''	1507	2.9097	a''	1504	2.7595	a'	1502	3.9248
	ω_{18}	a'	1699	15.6093	a'	1701	14.1942	a'	1704	12.4485
	ω_{19}	a'	3003	97.8324	a'	3009	85.2186	a'	3017	69.9263
	ω_{20}	a''	3066	41.2494	a''	3071	37.5093	a''	3076	31.3927
	ω_{21}	a'	3088	7.0437	a'	3096	22.5526	a'	3105	29.6864
	ω_{22}	a'	3096	145.695	a'	3107	100.8075	a'	3119	54.0079
	ω_{23}	a'	3114	40.1046	a'	3120	42.2127	a'	3128	49.1996
	ω_{24}	a'	3206	17.3553	a'	3213	14.4542	a'	3221	11.1601
		zpe	211.1		zpe	211.0		zpe	210.9	
AVTZ	ω_1	a'	90	3.3751	a'	83	6.418	a	69	3.6386
	ω_2	a'	105	24.5551	a'	88	2.0604	a	77	0.0281
	ω_3	a''	134	0.0868	a''	131	0.0326	a	111	0.1174
	ω_4	a''	226	0.4041	a''	223	0.5105	a	217	0.5069
	ω_5	a'	443	5.3645	a'	440	4.2427	a	435	2.9781
	ω_6	a''	596	16.8573	a''	598	16.5919	a	593	15.7184
	ω_7	a'	936	5.8282	a'	936	5.5367	a	936	4.8944
	ω_8	a'	961	1.6435	a'	960	1.5335	a	956	1.5468
	ω_9	a''	978	14.9906	a''	977	15.5232	a	972	17.6738
	ω_{10}	a''	1049	24.9763	a''	1048	21.2081	a	1042	17.0956
	ω_{11}	a''	1083	2.1346	a''	1082	2.5958	a	1081	3.2452
	ω_{12}	a'	1207	0.9157	a'	1206	0.6648	a	1205	0.3379
	ω_{13}	a'	1333	0.198	a'	1332	0.1917	a	1331	0.226
	ω_{14}	a'	1415	0.4255	a'	1416	0.2645	a	1416	0.188
	ω_{15}	a'	1454	2.0865	a'	1455	1.9789	a	1456	1.443
	ω_{16}	a'	1503	2.3185	a'	1503	2.874	a	1503	0.9617
	ω_{17}	a''	1509	1.9791	a''	1506	1.3298	a	1503	3.9995
	ω_{18}	a'	1696	17.1664	a'	1697	15.6412	a	1700	13.4432
	ω_{19}	a'	3001	97.9615	a'	3006	89.8712	a	3013	73.7342
	ω_{20}	a''	3063	39.0963	a''	3067	35.4061	a	3072	30.3294
	ω_{21}	a'	3086	12.5406	a'	3091	24.3528	a	3099	30.5143
	ω_{22}	a'	3095	133.2193	a'	3103	97.3228	a	3113	51.9914
	ω_{23}	a'	3111	44.2773	a'	3115	50.3489	a	3123	56.9595
	ω_{24}	a'	3204	16.9612	a'	3209	14.347	a	3217	11.4101
		zpe	211.0		zpe	211.0		zpe	210.8	

Table S138: *Calculated harmonic frequencies and mode assignments for the $X^-\cdots C_3H_6$ Bif complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

		$Cl^-\cdots C_3H_6$			$Br^-\cdots C_3H_6$			$I^-\cdots C_3H_6$		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a''	43	1.2728	a	39	0.5398	a''	44	0.282
	ω_2	a'	64	3.0224	a	63	0.7519	a'	57	0.5467
	ω_3	a'	104	24.6244	a	81	7.6758	a'	66	3.1355
	ω_4	a''	202	0.1794	a	201	0.3111	a''	203	0.4013
	ω_5	a'	419	0.9361	a	420	1.0745	a'	421	1.1874
	ω_6	a''	608	8.228	a	606	8.2096	a''	604	7.7897
	ω_7	a''	893	50.6949	a	898	49.9987	a''	902	47.6077
	ω_8	a'	940	1.2677	a	940	1.8601	a'	940	2.8243
	ω_9	a'	951	21.4307	a	952	20.3009	a'	952	19.2858
	ω_{10}	a''	1050	2.9706	a	1049	3.5426	a''	1047	3.9063
	ω_{11}	a''	1105	8.446	a	1099	7.4151	a''	1093	5.6876
	ω_{12}	a'	1204	0.641	a	1204	0.5144	a'	1204	0.3745
	ω_{13}	a'	1306	30.5497	a	1311	26.3507	a'	1316	22.9852
	ω_{14}	a'	1405	4.0862	a	1407	4.3634	a'	1409	4.529
	ω_{15}	a'	1447	2.7751	a	1448	2.3439	a'	1449	1.6275
	ω_{16}	a''	1465	7.612	a	1467	8.3916	a''	1471	9.6868
	ω_{17}	a'	1489	33.5786	a	1490	37.3231	a'	1491	42.4944
	ω_{18}	a'	1698	21.5049	a	1699	20.637	a'	1701	19.3801
	ω_{19}	a'	3031	50.1636	a	3033	45.1303	a'	3035	37.6464
	ω_{20}	a'	3116	43.9359	a	3117	7.8204	a''	3115	7.0271
	ω_{21}	a''	3118	8.4973	a	3118	39.9743	a'	3118	39.9232
	ω_{22}	a'	3126	32.7956	a	3129	30.5254	a'	3133	28.5791
	ω_{23}	a'	3152	26.2691	a	3159	17.8014	a'	3162	9.129
	ω_{24}	a'	3215	30.5834	a	3218	29.0673	a'	3222	26.5615
		zpe	210.3		zpe	210.2		zpe	210.3	
AVTZ	ω_1	a''	52	1.0124	a	53	0.3315	a	46	0.1901
	ω_2	a'	60	3.0465	a	57	0.825	a	57	0.3549
	ω_3	a'	103	24.3815	a	81	7.3887	a	68	3.1313
	ω_4	a''	205	0.2291	a	205	0.4266	a	204	0.5304
	ω_5	a'	416	0.9681	a	417	0.9936	a	418	1.1251
	ω_6	a''	608	7.6445	a	609	7.2091	a	605	7.0751
	ω_7	a''	892	49.4245	a	898	48.2667	a	903	46.5684
	ω_8	a'	938	0.8403	a	938	1.3823	a	938	2.194
	ω_9	a'	949	22.7808	a	949	22.1513	a	949	21.0195
	ω_{10}	a''	1050	2.5651	a	1049	2.4947	a	1048	2.901
	ω_{11}	a''	1104	7.9709	a	1102	6.6347	a	1095	5.2412
	ω_{12}	a'	1202	0.5873	a	1202	0.4672	a	1202	0.3839
	ω_{13}	a'	1304	33.8674	a	1308	31.3063	a	1312	26.0076
	ω_{14}	a'	1404	3.5657	a	1406	4.016	a	1408	4.388
	ω_{15}	a'	1446	2.1845	a	1447	1.6558	a	1448	1.2094
	ω_{16}	a''	1469	8.1368	a	1471	9.0434	a	1473	10.242
	ω_{17}	a'	1491	33.3839	a	1492	36.3066	a	1493	41.9456
	ω_{18}	a'	1695	22.0115	a	1697	21.0559	a	1699	20.0712
	ω_{19}	a'	3028	49.9034	a	3029	45.2616	a	3031	38.6468
	ω_{20}	a'	3111	45.5815	a	3111	7.7554	a	3110	6.6684
	ω_{21}	a''	3112	8.1116	a	3112	44.5505	a	3113	42.8188
	ω_{22}	a'	3123	33.2938	a	3125	31.8617	a	3129	29.7519
	ω_{23}	a'	3148	28.2179	a	3151	21.621	a	3156	11.1743
	ω_{24}	a'	3211	30.0037	a	3214	28.3083	a	3218	26.2627
		zpe	210.1		zpe	210.1		zpe	210.1	

Table S139: *Calculated harmonic frequencies and mode assignments for the $X^-\cdots C_3H_6$ HApp complexes. All frequencies and intensities are in* cm^{-1} *and* $\mathrm{km\,mol}^{-1}$ *and zero-point energies are in* $\mathrm{kJ\,mol}^{-1}$.

	$Cl^-\cdots C_3H_6$			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($\mathrm{km\,mol}^{-1}$)
def2QZVP	ω_1	a'	32	4.1982
	ω_2	a''	78	0.152
	ω_3	a'	111	26.4963
	ω_4	a''	210	0.4785
	ω_5	a'	437	0.3888
	ω_6	a''	622	7.8004
	ω_7	a'	936	10.0601
	ω_8	a'	958	1.1021
	ω_9	a''	1002	46.5108
	ω_{10}	a''	1052	0.3398
	ω_{11}	a''	1073	3.8172
	ω_{12}	a'	1192	0.6881
	ω_{13}	a'	1322	0.7359
	ω_{14}	a'	1403	1.5228
	ω_{15}	a'	1472	0.3741
	ω_{16}	a''	1490	4.1846
	ω_{17}	a'	1506	8.8291
	ω_{18}	a'	1703	1.0886
	ω_{19}	a'	3021	69.8356
	ω_{20}	a'	3061	221.428
	ω_{21}	a''	3073	35.8006
	ω_{22}	a'	3106	27.2675
	ω_{23}	a'	3154	18.428
	ω_{24}	a'	3178	65.2542
		zpe	210.5	
AVTZ	ω_1	a'	31	4.0342
	ω_2	a''	78	0.1228
	ω_3	a'	110	26.0547
	ω_4	a''	209	0.4926
	ω_5	a'	434	0.4543
	ω_6	a''	622	6.872
	ω_7	a'	935	9.5394
	ω_8	a'	955	1.2702
	ω_9	a''	1003	45.0913
	ω_{10}	a''	1055	0.0986
	ω_{11}	a''	1074	3.7523
	ω_{12}	a'	1190	0.8803
	ω_{13}	a'	1319	0.5526
	ω_{14}	a'	1403	1.6437
	ω_{15}	a'	1470	0.6298
	ω_{16}	a''	1492	4.2594
	ω_{17}	a'	1508	8.3546
	ω_{18}	a'	1700	0.9019
	ω_{19}	a'	3018	70.581
	ω_{20}	a'	3063	216.8383
	ω_{21}	a''	3069	34.6115
	ω_{22}	a'	3102	27.1834
	ω_{23}	a'	3150	17.8764
	ω_{24}	a'	3176	65.1027
		zpe	210.3	

Table S140: *Calculated harmonic frequencies and mode assignments for the Cl···C_3H_6 BiDent complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

	Cl···C_3H_6			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	*a*	41	0.1128
	ω_2	*a*	44	0.0778
	ω_3	*a*	45	0.0005
	ω_4	*a*	211	0.4897
	ω_5	*a*	426	1.0148
	ω_6	*a*	595	12.8786
	ω_7	*a*	939	2.8068
	ω_8	*a*	948	40.1101
	ω_9	*a*	950	2.6525
	ω_{10}	*a*	1034	11.7839
	ω_{11}	*a*	1077	3.5817
	ω_{12}	*a*	1201	0.2079
	ω_{13}	*a*	1332	0.0015
	ω_{14}	*a*	1414	1.4506
	ω_{15}	*a*	1459	0.3585
	ω_{16}	*a*	1493	5.0208
	ω_{17}	*a*	1505	11.4552
	ω_{18}	*a*	1711	12.1385
	ω_{19}	*a*	3043	21.8158
	ω_{20}	*a*	3103	15.8139
	ω_{21}	*a*	3134	4.9312
	ω_{22}	*a*	3153	15.13
	ω_{23}	*a*	3164	13.5783
	ω_{24}	*a*	3248	12.0585
		zpe	211.0	

Table S141: *Calculated harmonic frequencies and mode assignments for the $Br\cdots C_3H_6$ Bif complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

	$Br\cdots C_3H_6$			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a	32	0.0955
	ω_2	a	37	0.0224
	ω_3	a	68	0.6047
	ω_4	a	220	0.8778
	ω_5	a	427	0.6077
	ω_6	a	590	11.7722
	ω_7	a	937	4.9739
	ω_8	a	945	2.3969
	ω_9	a	948	43.6421
	ω_{10}	a	1031	11.0996
	ω_{11}	a	1074	3.678
	ω_{12}	a	1197	0.5516
	ω_{13}	a	1331	0.1301
	ω_{14}	a	1407	3.7194
	ω_{15}	a	1459	0.3626
	ω_{16}	a	1488	6.9108
	ω_{17}	a	1505	29.6201
	ω_{18}	a	1712	11.4085
	ω_{19}	a	3030	32.9991
	ω_{20}	a	3078	19.1419
	ω_{21}	a	3125	15.1872
	ω_{22}	a	3153	15.6986
	ω_{23}	a	3164	9.2861
	ω_{24}	a	3247	12.452
		zpe	210.6	
AVTZ	ω_1	a	31	0.0852
	ω_2	a	39	0.0295
	ω_3	a	73	0.7249
	ω_4	a	215	0.987
	ω_5	a	424	0.6078
	ω_6	a	591	10.9561
	ω_7	a	936	4.6135
	ω_8	a	942	2.7319
	ω_9	a	946	42.1971
	ω_{10}	a	1029	10.8894
	ω_{11}	a	1074	3.4411
	ω_{12}	a	1195	0.6207
	ω_{13}	a	1328	0.1627
	ω_{14}	a	1406	3.7796
	ω_{15}	a	1458	0.3344
	ω_{16}	a	1490	7.4678
	ω_{17}	a	1506	30.6022
	ω_{18}	a	1710	11.5241
	ω_{19}	a	3026	34.2603
	ω_{20}	a	3072	18.2904
	ω_{21}	a	3119	15.5744
	ω_{22}	a	3149	16.3262
	ω_{23}	a	3160	8.1191
	ω_{24}	a	3243	12.6428
		zpe	210.3	

Table S142: *Calculated harmonic frequencies and mode assignments for the $I\cdots C_3H_6$ End complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

	$I\cdots C_3H_6$			
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a	20	0.0559
	ω_2	a	36	0.0374
	ω_3	a	41	0.8143
	ω_4	a	209	0.062
	ω_5	a	426	0.955
	ω_6	a	593	8.0162
	ω_7	a	938	2.8575
	ω_8	a	947	4.5714
	ω_9	a	975	11.9345
	ω_{10}	a	1032	10.9936
	ω_{11}	a	1076	2.6461
	ω_{12}	a	1199	0.4448
	ω_{13}	a	1329	0.9645
	ω_{14}	a	1413	2.0084
	ω_{15}	a	1457	2.8267
	ω_{16}	a	1491	5.4449
	ω_{17}	a	1504	18.3376
	ω_{18}	a	1710	19.4154
	ω_{19}	a	3043	23.7136
	ω_{20}	a	3104	14.9856
	ω_{21}	a	3130	8.4104
	ω_{22}	a	3153	20.9241
	ω_{23}	a	3163	11.0151
	ω_{24}	a	3247	11.4304
		zpe	210.8	
AVTZ	ω_1	a'	15	0.08
	ω_2	$?a$	39	0.0405
	ω_3	$?a$	41	0.6796
	ω_4	a''	210	0.0987
	ω_5	a'	423	0.8709
	ω_6	a''	592	9.138
	ω_7	a'	936	1.3273
	ω_8	a'	945	6.2952
	ω_9	a''	967	14.69
	ω_{10}	a''	1030	11.4866
	ω_{11}	a''	1076	2.7679
	ω_{12}	a'	1197	0.5239
	ω_{13}	a'	1326	1.2198
	ω_{14}	a'	1413	1.7253
	ω_{15}	a'	1455	3.5909
	ω_{16}	a''	1493	5.4904
	ω_{17}	a'	1506	18.2022
	ω_{18}	a'	1707	20.0401
	ω_{19}	a'	3040	24.1209
	ω_{20}	a''	3100	15.0809
	ω_{21}	a'	3126	8.436
	ω_{22}	a'	3149	23.0115
	ω_{23}	a'	3159	9.2513
	ω_{24}	a'	3242	11.6235
		zpe	210.5	

Table S143: *Calculated harmonic frequencies and mode assignments for the X···C_3H_6 MePoc complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

		Cl···C_3H_6			Br···C_3H_6			I···C_3H_6		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a	20	0.079	?a	20	0.0806	a	21	0.0831
	ω_2	a	23	0.0104	?a	22	0.0094	a	21	0.0134
	ω_3	a	40	0.0036	a'	36	0.007	a	36	0.0128
	ω_4	a	207	0.4187	a''	207	0.3943	a	207	0.3915
	ω_5	a	426	1.1582	a'	426	1.1643	a	426	1.1782
	ω_6	a	592	12.2359	a''	592	12.1579	a	592	12.1511
	ω_7	a	939	2.5281	a'	939	2.5413	a	939	2.5625
	ω_8	a	944	42.8544	a''	944	42.6101	a	944	42.0521
	ω_9	a	948	3.6776	a'	948	3.7509	a	948	3.9908
	ω_{10}	a	1032	13.857	a''	1032	13.6076	a	1031	13.4908
	ω_{11}	a	1073	1.8674	a''	1071	2.0735	a	1070	1.9694
	ω_{12}	a	1199	0.0705	a'	1199	0.064	a	1199	0.0654
	ω_{13}	a	1331	0.1392	a'	1331	0.1655	a	1331	0.2382
	ω_{14}	a	1411	3.2964	a'	1410	3.9346	a	1410	5.3478
	ω_{15}	a	1458	1.3927	a'	1458	1.59	a	1458	2.0681
	ω_{16}	a	1492	1.1432	a''	1489	0.7833	a	1487	0.4597
	ω_{17}	a	1503	12.8384	a'	1503	12.368	a	1502	11.1487
	ω_{18}	a	1712	14.15	a'	1712	14.5944	a	1711	15.6492
	ω_{19}	a	3044	27.3135	a'	3044	28.7347	a	3043	31.2958
	ω_{20}	a	3107	7.9256	a''	3107	7.5366	a	3106	6.8344
	ω_{21}	a	3132	6.7525	a'	3132	6.4031	a	3131	5.8054
	ω_{22}	a	3152	17.3752	a'	3152	17.2831	a	3152	16.8631
	ω_{23}	a	3163	11.6452	a'	3163	11.7399	a	3163	11.8019
	ω_{24}	a	3246	14.7671	a'	3246	14.8847	a	3246	15.0772
		zpe	210.5		zpe	210.4		zpe	210.4	
AVTZ	ω_1	a	20	0.0654	a	19	0.0839	a	20	0.0847
	ω_2	a	22	0.0249	a	36	0.0738	a	29	0.0088
	ω_3	a	43	0.0033	a	40	0.0208	a	40	0.0158
	ω_4	a	208	0.4197	a	209	0.1655	a	209	0.4124
	ω_5	a	424	1.1754	a	424	1.2455	a	424	1.2029
	ω_6	a	590	11.9308	a	592	11.0221	a	592	11.9221
	ω_7	a	938	1.8415	a	938	2.0286	a	938	1.9198
	ω_8	a	942	42.0289	a	942	43.1401	a	942	41.4191
	ω_9	a	946	4.3667	a	946	4.6931	a	946	4.7203
	ω_{10}	a	1030	15.0572	a	1030	12.9544	a	1029	14.0871
	ω_{11}	a	1074	1.4805	a	1075	3.519	a	1072	1.8757
	ω_{12}	a	1198	0.0465	a	1197	0.0515	a	1197	0.0263
	ω_{13}	a	1328	0.1581	a	1328	0.1846	a	1328	0.2702
	ω_{14}	a	1411	3.1695	a	1411	4.1865	a	1410	5.2323
	ω_{15}	a	1457	1.5464	a	1459	2.4296	a	1457	2.2216
	ω_{16}	a	1494	0.9726	a	1493	4.4447	a	1491	0.5444
	ω_{17}	a	1504	12.282	a	1504	13.5711	a	1503	10.8879
	ω_{18}	a	1709	14.6456	a	1709	14.9167	a	1709	16.3323
	ω_{19}	a	3040	28.4007	a	3044	38.2326	a	3040	32.2625
	ω_{20}	a	3103	7.3404	a	3099	15.541	a	3102	6.7874
	ω_{21}	a	3127	6.5937	a	3127	9.1614	a	3127	5.5378
	ω_{22}	a	3148	18.6231	a	3148	17.3731	a	3148	18.0589
	ω_{23}	a	3159	10.4608	a	3160	10.3317	a	3159	10.9123
	ω_{24}	a	3241	15.2505	a	3241	15.3822	a	3241	15.6187
		zpe	210.3		zpe	210.4		zpe	210.3	

Table S144: *Calculated harmonic frequencies and mode assignments for the X···C_3H_6 Perp complexes. All frequencies and intensities are in* cm^{-1} *and* $km\,mol^{-1}$ *and zero-point energies are in* $kJ\,mol^{-1}$.

		Cl···C_3H_6			Br···C_3H_6			I···C_3H_6		
	Mode	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)	Symmetry	Frequency (cm^{-1})	Intensity ($km\,mol^{-1}$)
def2QZVP	ω_1	a	91	1.1185	a	107	1.2351	a	94	0.2726
	ω_2	a	117	1.9072	a	153	1.7897	a	143	0.2365
	ω_3	a	286	6.644	a	198	5.3498	a	161	11.0808
	ω_4	a	405	3.0687	a	226	0.2644	a	226	0.3251
	ω_5	a	538	4.4411	a	423	0.2871	a	425	0.4774
	ω_6	a	630	86.2164	a	634	8.054	a	625	12.3364
	ω_7	a	883	4.4166	a	934	12.0901	a	934	9.0311
	ω_8	a	917	8.8271	a	952	2.4303	a	952	2.6477
	ω_9	a	1009	0.6689	a	975	47.6393	a	969	67.1585
	ω_{10}	a	1092	1.5176	a	995	10.9681	a	1011	9.1808
	ω_{11}	a	1179	4.1001	a	1069	2.9508	a	1073	6.0389
	ω_{12}	a	1235	0.4849	a	1208	0.529	a	1207	0.2467
	ω_{13}	a	1264	18.7216	a	1325	11.2881	a	1326	8.7509
	ω_{14}	a	1397	1.555	a	1410	10.0188	a	1411	9.6029
	ω_{15}	a	1427	6.8112	a	1453	14.5862	a	1455	11.0392
	ω_{16}	a	1486	5.508	a	1484	9.087	a	1486	8.7238
	ω_{17}	a	1494	11.0992	a	1500	20.2302	a	1500	21.1504
	ω_{18}	a	1504	2.2667	a	1650	126.6081	a	1664	118.6545
	ω_{19}	a	3008	9.9561	a	3049	7.2497	a	3051	8.8409
	ω_{20}	a	3083	15.6722	a	3117	3.3201	a	3124	5.6122
	ω_{21}	a	3108	12.5788	a	3149	6.7566	a	3135	7.0757
	ω_{22}	a	3135	15.027	a	3169	4.8866	a	3163	3.7763
	ω_{23}	a	3177	1.5803	a	3184	6.9539	a	3175	6.9858
	ω_{24}	a	3208	11.9783	a	3271	0.8533	a	3261	1.4483
		zpe	213.4		zpe	213.2		zpe	212.8	
AVTZ	ω_1	a	92	1.1763	a	108	1.2002	a	94	0.2335
	ω_2	a	118	1.8108	a	154	1.5493	a	147	0.7951
	ω_3	a	283	6.9152	a	200	5.0315	a	160	10.0406
	ω_4	a	403	3.0727	a	228	0.2612	a	227	0.3023
	ω_5	a	535	4.5075	a	420	0.2706	a	420	0.4652
	ω_6	a	625	87.0184	a	631	8.1829	a	622	12.8423
	ω_7	a	883	4.7567	a	933	10.5114	a	933	8.8051
	ω_8	a	917	8.5177	a	950	3.0602	a	949	3.5498
	ω_9	a	1009	0.7624	a	975	44.82	a	967	58.176
	ω_{10}	a	1092	1.4988	a	992	13.8016	a	1009	13.817
	ω_{11}	a	1178	4.3052	a	1069	2.8649	a	1073	5.4689
	ω_{12}	a	1235	0.4754	a	1206	0.4333	a	1204	0.2451
	ω_{13}	a	1263	18.5705	a	1322	9.5319	a	1324	7.9071
	ω_{14}	a	1397	1.2338	a	1411	9.3903	a	1412	8.711
	ω_{15}	a	1426	7.0627	a	1453	13.6381	a	1454	11.0283
	ω_{16}	a	1487	5.5099	a	1485	9.2658	a	1487	8.9138
	ω_{17}	a	1495	10.7199	a	1502	20.563	a	1502	21.2402
	ω_{18}	a	1506	2.3479	a	1647	114.4989	a	1661	110.0241
	ω_{19}	a	3005	10.0683	a	3046	7.8265	a	3046	9.5962
	ω_{20}	a	3079	15.7583	a	3114	3.3553	a	3112	4.8872
	ω_{21}	a	3106	12.312	a	3144	6.7619	a	3140	6.4835
	ω_{22}	a	3131	15.1623	a	3165	4.4507	a	3159	3.8524
	ω_{23}	a	3175	1.3666	a	3179	6.6381	a	3172	6.7468
	ω_{24}	a	3204	12.0851	a	3266	0.8843	a	3257	1.4496
		zpe	213.2		zpe	212.9		zpe	212.5	

Table S145: *Energies, Intensities and Franck-Condon factors calculated from ezSpectrum 3.0 for photodetachment of the $Br^-\cdots C_3H_6$ Bif complex. Notation for the transtion, 5_0^1 indicates the transition in ω_5 from $v'' = 0$ to $v' = 1$ with modes numbered according to Table S141. The band origin is the ADE from in text.*

E eV	Intensity	FCF	Assignment	E eV	Intensity	FCF	Assignment
3.5630	1.59E-01	3.98E-01	ADE	3.9870	2.73E-04	1.65E-02	18_0^2
3.6156	1.06E-04	-1.03E-02	5_0^1	3.9907	8.31E-04	-2.88E-02	$5_0^1 19_0^1$
3.6629	3.42E-04	-1.85E-02	$4_0^1 6_0^1$	4.0023	9.35E-04	-3.06E-02	$5_0^1 21_0^1$
3.6682	1.42E-04	-1.19E-02	5_0^2	4.0060	9.09E-04	3.02E-02	$5_0^1 22_0^1$
3.6790	4.61E-03	6.79E-02	7_0^1	4.0071	1.05E-04	-1.02E-02	$7_0^2 18_0^1$
3.6798	2.92E-04	-1.71E-02	8_0^1	4.0074	4.91E-04	2.21E-02	$5_0^1 23_0^1$
3.7172	7.31E-04	-2.70E-02	$4_0^1 10_0^1$	4.0171	2.11E-04	-1.45E-02	$6_0^1 20_0^1$
3.7228	2.80E-03	-5.29E-02	$4_0^1 11_0^1$	4.0550	7.76E-04	2.79E-02	$8_0^1 19_0^1$
3.7317	2.62E-03	-5.12E-02	$5_0^1 7_0^1$	4.0658	3.04E-04	1.74E-02	$7_0^1 21_0^1$
3.7324	1.27E-04	-1.13E-02	$5_0^1 8_0^1$	4.0666	2.26E-04	1.50E-02	$8_0^1 21_0^1$
3.7374	2.73E-04	1.65E-02	14_0^1	4.0695	4.10E-04	2.02E-02	$7_0^1 22_0^1$
3.7438	5.07E-04	-2.25E-02	15_0^1	4.0703	3.40E-03	5.83E-02	$8_0^1 22_0^1$
3.7497	7.88E-04	2.81E-02	17_0^1	4.0708	1.04E-03	3.22E-02	$7_0^1 23_0^1$
3.7638	3.45E-04	-1.86E-02	$5_0^1 12_0^1$	4.0811	4.52E-04	2.13E-02	$7_0^1 24_0^1$
3.7744	1.41E-03	-3.76E-02	$4_0^1 16_0^1$	4.0863	4.41E-04	2.10E-02	$12_0^1 19_0^1$
3.7750	2.99E-04	-1.73E-02	18_0^1	4.0979	6.80E-04	2.61E-02	$12_0^1 21_0^1$
3.7802	2.29E-04	-1.51E-02	$5_0^1 13_0^1$	4.1016	7.86E-04	-2.80E-02	$12_0^1 22_0^1$
3.7951	1.90E-03	4.36E-02	7_0^2	4.1180	1.09E-04	-1.04E-02	$13_0^1 22_0^1$
3.7967	2.84E-04	-1.69E-02	8_0^2	4.1194	1.08E-03	3.29E-02	$13_0^1 23_0^1$
3.8023	7.43E-04	2.73E-02	$5_0^1 17_0^1$	4.1241	7.72E-04	2.78E-02	$14_0^1 21_0^1$
3.8210	1.20E-04	1.09E-02	$6_0^1 16_0^1$	4.1286	2.07E-04	-1.44E-02	$16_0^1 20_0^1$
3.8237	1.05E-04	1.02E-02	$10_0^1 11_0^1$	4.1292	1.49E-04	-1.22E-02	$14_0^1 23_0^1$
3.8272	2.53E-04	1.59E-02	$7_0^1 12_0^1$	4.1355	1.36E-04	1.17E-02	$15_0^1 23_0^1$
3.8276	1.03E-03	-3.22E-02	$5_0^1 18_0^1$	4.1364	1.34E-04	1.16E-02	$17_0^1 21_0^1$
3.8294	3.33E-04	1.82E-02	11_0^2	4.1394	1.26E-04	-1.12E-02	$14_0^1 24_0^1$
3.8437	6.32E-04	-2.51E-02	$7_0^1 13_0^1$	4.1415	1.10E-04	-1.05E-02	$17_0^1 23_0^1$
3.8477	1.70E-04	-1.31E-02	$5_0^1 7_0^2$	4.1458	1.24E-03	3.52E-02	$15_0^1 24_0^1$
3.8665	1.36E-04	-1.16E-02	$8_0^1 17_0^1$	4.1517	2.48E-04	1.57E-02	$17_0^1 24_0^1$
3.8809	2.61E-04	1.62E-02	$11_0^1 16_0^1$	4.1617	2.03E-04	-1.43E-02	$18_0^1 21_0^1$
3.8910	1.41E-03	-3.76E-02	$7_0^1 18_0^1$	4.1668	9.26E-04	-3.04E-02	$18_0^1 23_0^1$
3.9111	1.27E-04	1.13E-02	7_0^3	4.3249	1.22E-04	1.11E-02	$19_0^1 21_0^1$
3.9396	6.98E-04	2.64E-02	$13_0^1 18_0^1$	4.3365	2.96E-04	1.72E-02	21_0^2
3.9497	4.04E-04	2.01E-02	21_0^1	4.3439	5.64E-04	2.38E-02	22_0^2
3.9534	2.13E-04	-1.46E-02	22_0^1	4.3466	4.31E-04	2.08E-02	23_0^2
3.9651	1.09E-03	3.31E-02	24_0^1	4.3671	2.36E-04	1.54E-02	24_0^2
3.9705	6.38E-04	-2.53E-02	$4_0^1 20_0^1$				

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