Supporting Information

Matrix Infrared Spectra and Density Functional Calculations for New *iso*-halomethanes: $CHCl_2$-Cl, CHFCl-Cl, $CFCl_2$-Cl, $CHBr_2$-Br and CBr_3-Br in Solid Argon

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Table S1: Observed and Calculated Fundamental Frequencies of CCl_3-Br Isotopomers in the Ground ^{1}A' Electronic State[a]

Approximate Description	CCl_3-Br					$^{13}CCl_3$-Br			
	Obs	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
A' as CCl_3 str.	under	1032.7	120	983.5	118	999.3	109	951.5	108
A" as CCl_2 str.	925	914.4	198	887.0	203	884.2	184	857.7	189
A' s CCl_3 str.	492,488	506.8	54	492.0	44	506.6	54	491.9	45
A' CCl_3 deform	356	396.9	32	383.9	30	383.0	30	370.6	28
A" CCl_3 bend		314.4	0	304.5	0	313.8	0	303.8	0
A' CCl_3 bend		293.1	11	284.9	11	292.1	11	283.9	11
A' Cl-Br str.		186.4	38	182.7	29	186.3	38	182.5	29
A" CClBr bend		70.3	1	70.8	0	70.3	1	70.8	0
A' CClBr bend		60.9	5	60.8	4	60.9	5	60.7	4

[a] Frequencies observed in radiolysis experiments, ref. 6b. Carbon-13 sample not available. Harmonic frequencies (cm^{-1}) and intensities (km/mol) were computed with 6-311++G(3df, 3pd).

[b] Computed with B3LYP. [c] Computed with BPW91. CCl_3-Br has a C_s structure.

Table S2: Observed and Calculated Fundamental Frequencies of $CBrCl_2$-Cl Isotopomers in the Ground ^{1}A Electronic State[a]

Approximate Description	$CBrCl_2$-Cl					$^{13}CBrCl_2$-Cl			
	Obs	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
as $CBrCl_2$ str.	under	1032.4	97	981.0	97	999.5	87	949.5	88
as $CBrCl_2$ str.	870	857.4	194	830.4	201	828.4	180	802.4	187
s $CBrCl_2$ str.	430	446.5	49	433.7	44	445.1	49	432.4	44
$CBrCl_2$ deform		387.7	19	373.9	20	373.9	17	360.6	18
CCl_2Br bend		276.2	8	268.6	10	275.9	8	268.3	9
CCl_2Br bend	251	256.1	50	251.8	44	255.5	52	251.3	45
Cl-Cl str.	225	219.9	32	215.9	19	219.7	31	215.7	18
CClCl bend		77.6	4	77.7	3	77.5	4	77.6	3
CClCl bend		62.3	6	61.7	5	62.2	6	61.7	5

[a] Frequencies observed in radiolysis experiments, ref. 6b. Harmonic frequencies (cm^{-1}) and intensities (km/mol)

were computed with 6-311++G(3df, 3pd). [b] Computed with B3LYP. [c] Computed with BPW91.

Table S3: Calculated Fundamental Frequencies of $CClBr_2$-Br Isotopomers in the Ground ^1A Electronic State[a]

Approximate Description	$CClBr_2$-Br					$^{13}CClBr_2$-Br			
	Obs	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
as $CClBr_2$ str.		873.2	182	840.4	186	843.9	171	812.6	174
as $CClBr_2$ str.		803.6	162	768.7	163	774.8	149	740.8	150
$CClBr_2$ deform		367.6	10	369.3	18	358.6	3	356.7	13
s $CClBr_2$ str.		349.4	39	335.1	27	344.5	43	333.6	30
$CClBr_2$ bend		222.5	3	214.6	4	222.3	3	214.4	4
$CClBr_2$ bend		195.7	14	189.6	16	195.2	14	189.2	16
Br-Br str.		155.0	31	155.6	19	154.9	31	155.5	19
oop CBrBr bend		59.2	1	58.7	1	59.2	1	58.7	1
ip CBrBr bend		37.2	4	36.5	3	37.2	4	36.5	3

[a] These frequencies were not observed in radiolysis experiments with CBr_3Cl, ref. 6b, but CBr_3-Br was observed.

Harmonic frequencies (cm^{-1}) and intensities (km/mol) were computed with 6-311++G(3df,3pd).

[b] Computed with B3LYP. [c] Computed with BPW91.

Table S4: Calculated Fundamental Frequencies of CBr_3-Cl Isotopomers in the Ground ^{1}A' Electronic State[a]

Approximate Description	CBr_3-Cl				$^{13}CBr_3$-Cl			
	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
A' as CBr_3 str.	814.6	114	771.5	110	785.1	105	743.5	101
A" as CBr_2 str.	761.5	186	737.9	202	733.8	173	711.0	187
A' CBr_3 deform	364.8	7	369.7	8	352.0	6	356.5	7
A' s CBr_3 str.	282.6	33	270.9	37	282.3	33	270.8	37
A' Br-Cl str.	221.1	87	224.5	64	220.8	87	224.2	65
A" CBr_3 bend	186.2	0	180.5	0	186.0	0	180.3	0
A' CBr_3 bend	163.3	0	156.8	0	163.1	0	156.7	0
A" CBrCl bend	62.8	2	61.5	1	62.8	2	61.5	1
A' CBrCl bend	43.2	8	41.6	6	43.2	8	41.6	6

[a] These frequencies were not observed in radiolysis experiments with CBr_3Cl, ref. 6b, but CBr_3-Br was observed. Harmonic frequencies (cm^{-1}) and intensities (km/mol) were computed with 6-311++G(3df, 3pd). [b] Computed with B3LYP. [c] Computed with BPW91.

Cartesian Coordinates calculated using B3LYP

CCl_3-Cl

	Coordinates (Angstroms) X	Y	Z
C	.849313	.000002	.257734
Cl	1.587183	-1.447262	-.239185
Cl	1.587006	1.447367	-.239115
Cl	-.666606	-.000097	.826459
Cl	-2.807341	-.000009	-.439124

$CHCl_2$-Cl

C	1.091917	0.556844	0.489665
H	1.240411	0.891806	1.505670
Cl	2.213639	-0.564125	-0.096384
Cl	-0.314473	0.837982	-0.232114
Cl	-2.357514	-0.522849	0.067107

CHFCl-Cl

C	1.566683	0.136567	0.426563
H	1.829340	0.244585	1.470410
F	2.241527	-0.781992	-0.221123
Cl	0.191643	0.691598	-0.168713
Cl	-2.038889	-0.340190	0.048732

$CFCl_2$-Cl

C	-1.029845	.412627	.128529
F	-1.388177	1.462058	-.566775
Cl	-2.025563	-.932850	-.095366
Cl	.486125	.325259	.690795
Cl	2.637830	-.312072	-.340734

$CHBr_2$-Br

C	-1.283025	0.652456	0.631590
H	-1.382549	0.854065	1.688044
Br	-2.543232	-0.524272	-0.061956
Br	0.297728	0.964141	-0.129060
Br	2.504952	-0.576121	0.034513

CBr_3-Br

C	1.021454	-0.000045	0.339904
Br	1.838947	-1.591436	-0.220891
Br	1.838919	1.591443	-0.220901
Br	-0.736594	0.000016	0.818606
Br	-3.116379	-0.000016	-0.435084

CCl_3-Br

C	1.155621	-0.963470	0.000000
Cl	1.155621	-1.849661	1.448504
Cl	1.155621	-1.849661	-1.448504
Cl	0.746445	0.610762	0.000000
Br	-1.683268	1.665324	0.000000

$CBrCl_2$-Cl

C	0.399537	0.475935	0.308451
Br	1.599299	-0.899315	-0.102249
Cl	0.769969	2.023745	-0.284355
Cl	-1.088415	0.136196	0.845959
Cl	-3.115241	-0.476386	-0.459956

$CClBr_2$-Br

C	1.243680	0.478159	0.216539
Br	2.305531	-1.024933	-0.153396
Cl	1.740411	1.934569	-0.505460
Br	-0.491981	0.266885	0.745283
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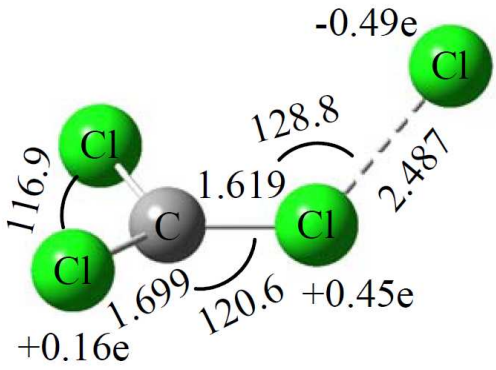
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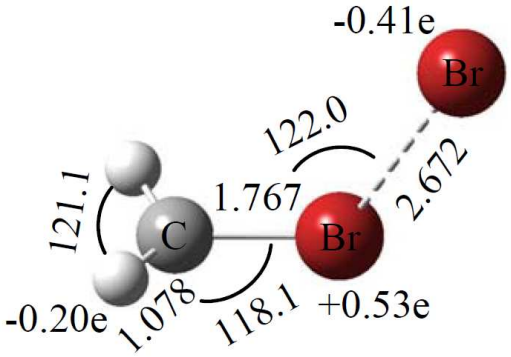
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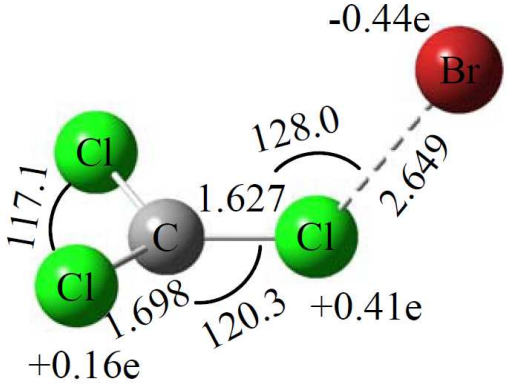
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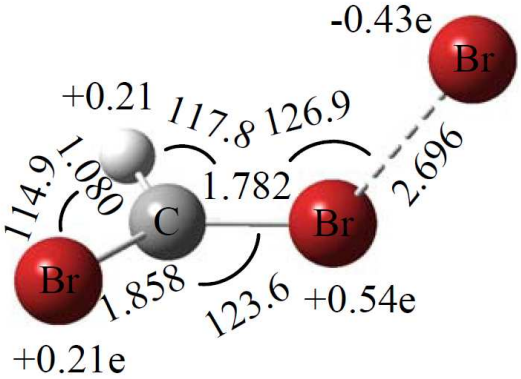
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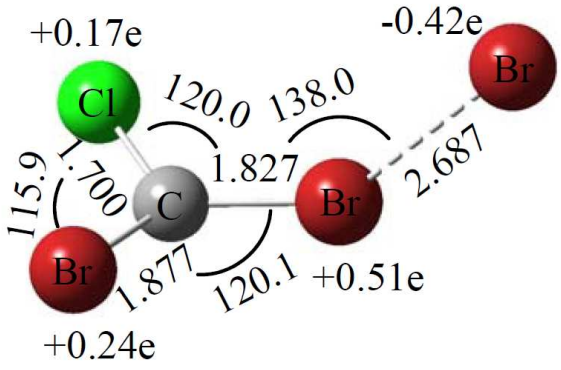
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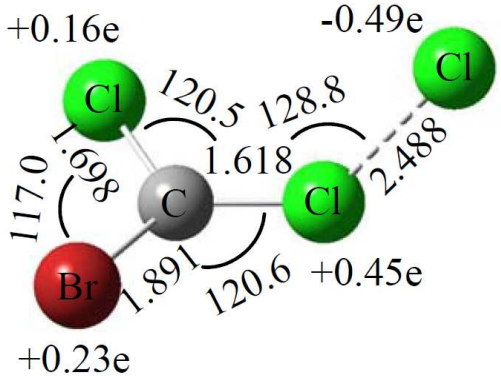
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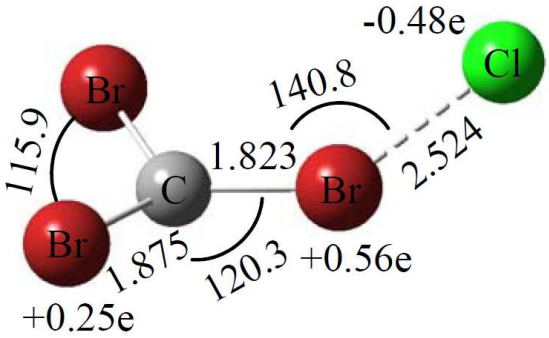
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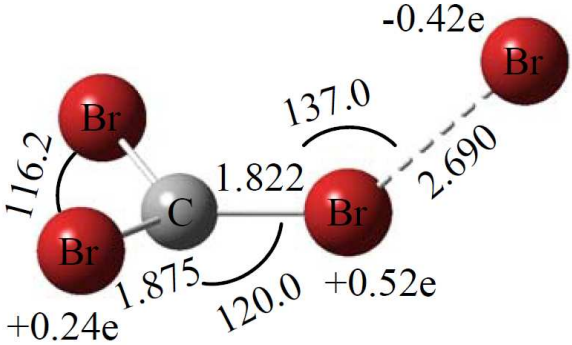
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