Supplementary Material For Dalton Trans. Manuscript (Version: 13 March 2008)

"Gas Phase Synthesis, Structure and Unimolecular Reactivity of Silver Iodide Cluster Cations, $Ag_nI_m^+$ (n=2-5, 0<m<n)." by George N. Khairallah and Richard A. J. O'Hair*, School of Chemistry and Bio21 Institute of Molecular Science and Biotechnology, The University of Melbourne, Victoria 3010, AUSTRALIA

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List of Supplementary Material:

(A) Cartesian Coordinates for structures shown in Figures 3 and 4 (pages S1-S33)(The point groups of the output geometries (using GaussView with tolerance 0.01) are listed in brackets);
(B) Supplementary Figures S1 and S2 (pages S34-S36);
(C) Supplementary Tables S1, S2, and S3 (pages S37-S44).

Coordinates for $Ag_xI_y^{0/+}$ (SDD basis set, all energies are in Hartrees; where there are several isomers, relative energies are in kcal mol^{-1}):

AgI neutral: (Used in Figure 3a)

E(B3LYP) =-158.4732823; Zero-point correction = 0.000436

Ag	0.000000	0.000000	-1.393829
I	0.000000	0.000000	1.236037

Ag_2 neutral:

E(B3LYP) = -294.0430056; Zero-point correction = 0.000406

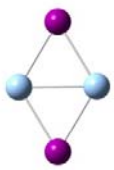
Ag	0.000000	0.000000	1.298211
Ag	0.000000	0.000000	-1.298211

Ag_2I^+ (C_{2v}):
Unique isomer (Used in Figure 4a)

E(B3LYP) = -305.25137; Zero-point correction = 0.000816

Ag	2.158825	-0.595263	0.000000
Ag	-2.158825	-0.595265	0.000000
I	0.000000	1.055751	0.000000

Ag_2I_2 neutral (D_{2h}): (Used in Figure 3b)

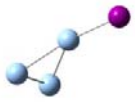


E(B3LYP) = -317.0025911; Zero-point correction = 0.001390

Ag	0.000000	1.430794	0.000000
Ag	0.000000	-1.430794	0.000000
I	0.000000	0.000000	2.438866
I	0.000000	0.000000	-2.438866

Ag_3I^+:

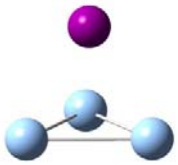
a) Unique isomer (Used in Figure 4b)



E(B3LYP) = -452.262528; Zero-point correction = 0.001215

Ag	1.948597	-1.351896	-0.109717
Ag	1.948559	1.351920	-0.109707
Ag	-0.408997	-0.000026	0.412142
I	-3.093273	0.000002	-0.170901

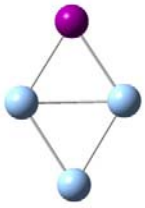
b) In and Out (C_{3v}):



E(B3LYP) = -452.2770734; Zero-point correction = 0.001158

Ag	0.000000	1.648187	-0.670612
Ag	1.427372	-0.824093	-0.670612
Ag	-1.427372	-0.824093	-0.670612
I	0.000000	0.000000	1.784082

c) In and Out (C_{2v}):



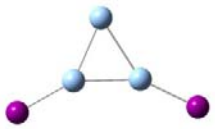
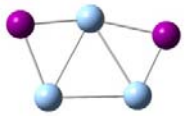
E(B3LYP) = -452.2805541; Zero-point correction = 0.001250

Ag	0.00000000	-0.00000000	2.46753230
Ag	0.00000000	-1.48552515	0.05113636
Ag	-0.00000000	1.48552515	0.05113636
I	0.00000000	-0.00000000	-2.27888370

$Ag_3I_2^+$ (C_{2h}):

a) Isomer 1 (C_{2h}) (Used in Figure 4c)

The following two different input guesses

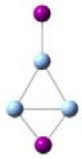
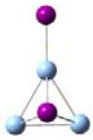
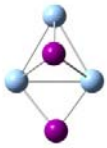
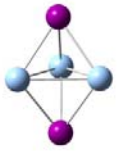



Converged to the same structure:

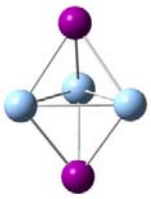
E(B3LYP) = -463.7818205; Zero-point correction = 0.001758
Relative energy = 0 kcal mol^{-1}

Ag	4.118484	0.832083	0.088397
Ag	-0.000002	-0.000033	-0.049426
Ag	-4.118511	-0.832042	0.088414
I	-2.421270	1.255075	-0.056505
I	2.421296	-1.255083	-0.056459

b) **Isomer 2 (D_{3h}): The following four different input guesses**

Converged to the same structure:



E(B3LYP) = -463.7798878; Zero-point correction = 0.001768
Relative energy = 1.2 kcal mol^{-1}

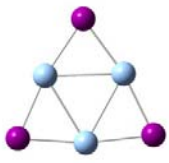
Ag	0.000000	1.797790	0.000000
Ag	-1.556932	-0.898895	0.000000
Ag	1.556932	-0.898895	0.000000
I	0.000000	0.000000	2.279405
I	0.000000	0.000000	-2.279405

c) **Isomer 3:** has 1 small imaginary frequency -7.3473 cm^{-1}

E(B3LYP) = -463.7793828 ; Zero-point correction = 0.001744
Relative energy = 1.5 kcal mol^{-1}

I	2.718192	0.996524	0.000000
Ag	0.000000	0.717177	0.000000
I	-2.718203	0.996487	0.000000
Ag	-3.759736	-1.482330	0.000000
Ag	3.759748	-1.482284	0.000000

Ag_3I_3 neutral:
a) **Isomer 1 (D_{3h}) (Used in Figure 3c)**

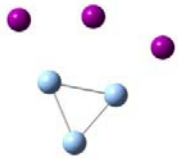


E(B3LYP) = -475.552877; Zero-point correction = 0.002637
Relative energy = 0 kcal mol^{-1}

Ag	0.000000	1.817581	0.000000

Ag	1.574072	-0.908791	0.000000
Ag	-1.574072	-0.908791	0.000000
I	0.000000	-3.146658	0.000000
I	2.725086	1.573329	0.000000
I	-2.725086	1.573329	0.000000

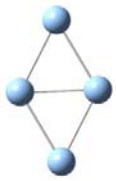
b) **Isomer 2 (C_{2v})**



E(B3LYP) = -475.429427; Zero-point correction = 0.002286
Relative energy = 77.2 kcal mol^{-1}

Ag	0.000000	0.000000	-3.293988
Ag	0.000000	1.418989	-1.001714
Ag	0.000000	-1.418989	-1.001714
I	0.000000	0.000000	2.043908
I	0.000000	3.070964	1.326900
I	0.000000	-3.070964	1.326900

Ag_4^+ (D_{2h}):

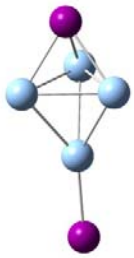


E(B3LYP) = -587.8724978; Zero-point correction = 0.001283

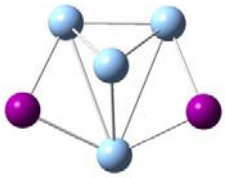
Ag	0.000000	1.350967	0.000000
Ag	0.000000	-1.350967	0.000000
Ag	0.000000	0.000000	2.462614
Ag	0.000000	0.000000	-2.462614

Ag_4I^+ : four isomers have been previously reported in: Khairallah, G.N.; O'Hair, R. A. J., "Activation of the C-I and C-OH Bonds of 2-Iodoethanol by Gas Phase Silver Cluster Cations Yields Subvalent Silver-Iodide and -Hydroxide Cluster Cations.", *Dalton Trans*., 2007, 3149 - 3157. **The structure shown in Figure 4e is taken from this paper.**

$Ag_4I_2^+$:
a) **Isomer 1 (C_s) (Used in Figure 4e):**
The following input guess



Converged to:

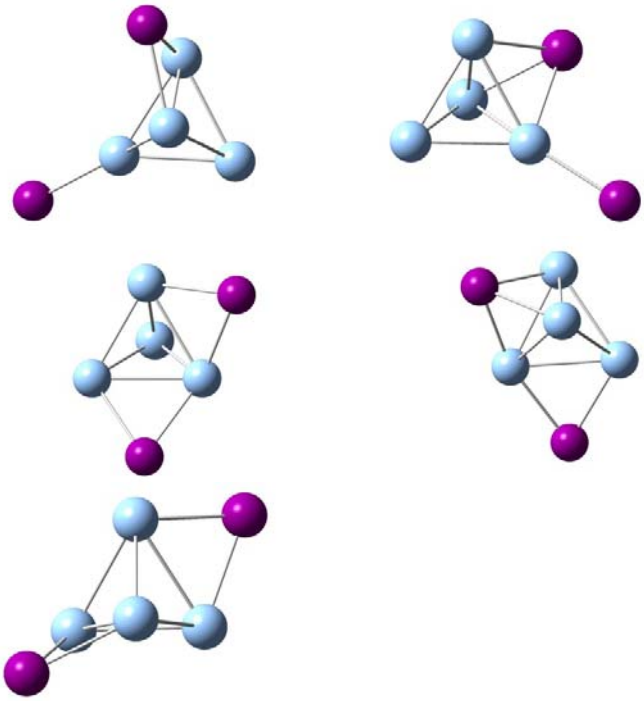


E(B3LYP) = -610.8151529; Zero-point correction = 0.002226

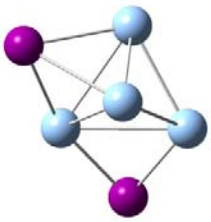
Relative energy = 0 kcal mol^{-1}

I	-2.494500	-0.834081	0.101026
Ag	-1.406880	1.820034	-0.400834
Ag	1.408128	1.819757	-0.400329
Ag	0.000026	0.059964	1.433184
Ag	-0.000620	-1.817211	-0.859580
I	2.493920	-0.835345	0.100771

b) **Isomer 2 (C_s) : The following five different input guesses**



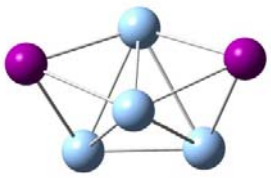
Converged to the same structure:



E(B3LYP) = -610.813766; Zero-point correction = 0.002325
Relative energy = 0.9 kcal mol^{-1}

I	2.934328	-0.808843	-0.000841
Ag	0.273600	-1.406917	-0.001328
Ag	-1.070287	1.028614	1.407446
Ag	1.399990	1.510970	-0.000251
Ag	-1.073757	1.033479	-1.403997
I	-2.517133	-1.112080	-0.000817

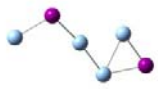
c) **Isomer 3:** has 1 small imaginary frequency -21.2 cm^{-1}



E(B3LYP) = -610.8135422; Zero-point correction = 0.002130
Relative energy = 1.0 kcal mol^{-1}

I	2.515394	-0.922171	0.003282
Ag	1.385517	1.729986	-0.007721
Ag	-1.391184	1.727205	-0.006344
Ag	0.001050	-0.698839	-1.448860
Ag	0.001286	-0.674340	1.456125
I	-2.512440	-0.925915	0.002749

d) **Isomer 4:** has 1 small imaginary frequency -4.9034 cm^{-1}



E(B3LYP) = -610.8000989; Zero-point correction = 0.002088
Relative energy = 9.4 kcal mol^{-1}

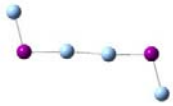
Ag	1.541014	-1.849522	0.000000
Ag	-1.291008	-2.036170	0.000000
Ag	0.000000	0.509479	0.000000
I	-1.192879	3.033989	0.000000
Ag	0.791190	4.853811	0.000000
I	0.269554	-4.344311	0.000000

e) **Isomer 5:** has 1 small imaginary frequency -1.3667 cm^{-1}

E(B3LYP) = -610.7983978; Zero-point correction = 0.002197
Relative energy = 10.5 kcal mol^{-1}

Ag	-1.084803	-0.625709	-1.269039
Ag	1.088624	-1.261557	0.640860
Ag	1.094728	1.274003	-0.621291
Ag	-1.098221	0.636323	1.266317
I	-3.502468	-0.010063	-0.007030
I	3.502178	-0.010386	-0.007910

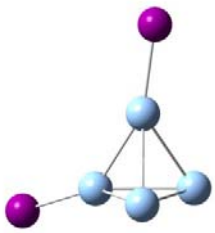
f) **Isomer 6 (C_{2h}):** has 1 small imaginary frequency -5.9439 cm^{-1}



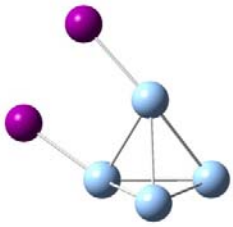
E(B3LYP) = -610.7959515; Zero-point correction = 0.001937
Relative energy = 11.9 kcal mol^{-1}

Ag	-2.317912	5.010329	0.000000
Ag	0.000000	1.372156	0.000000
Ag	0.000008	-1.372176	0.000000
Ag	2.317913	-5.010308	0.000000
I	0.228699	4.163068	0.000000
I	-0.228707	-4.163069	0.000000

g) **Isomer 7 (C_{2v}): The following input guess**



Converged to:

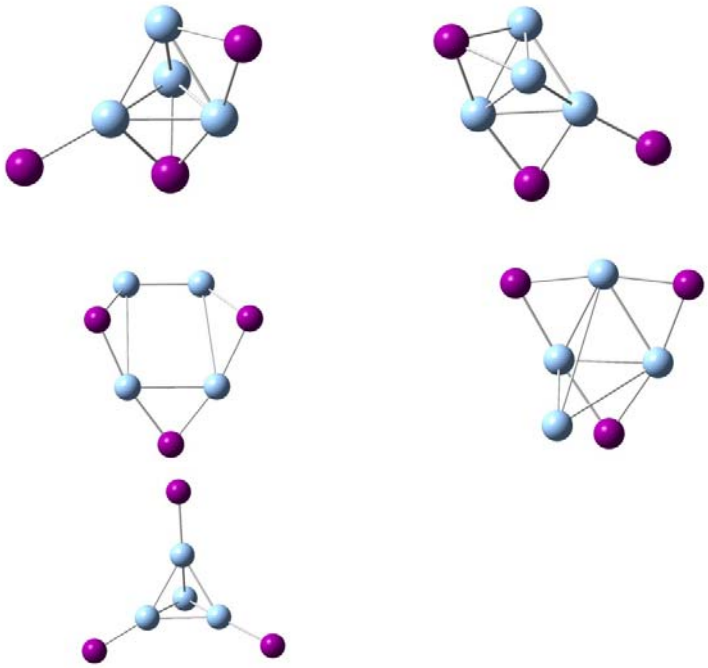


E(B3LYP) = -610.7862828; Zero-point correction = 0.002424
Relative energy = 18.2 kcal mol^{-1}

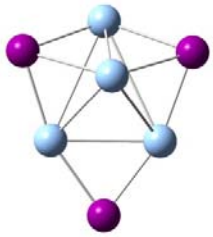
I	-2.383612	-1.762679	0.000035
Ag	0.302651	-1.413319	-0.000193
Ag	2.385233	-0.000168	1.357355
Ag	2.385223	0.000123	-1.357343
Ag	0.302661	1.413367	0.000165
I	-2.383577	1.762676	-0.000022

$Ag_4I_3^+$:

a) **Isomer 1 (C_s): (Used in Figure 4f)**
The following four different input guesses



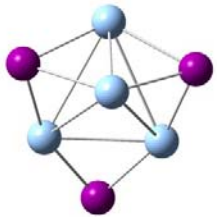
Converged to the same structure:



E(B3LYP) = -622.3239667; Zero-point correction = 0.002983
Relative energy = 0 kcal mol^{-1}

I	1.424303	2.485671	0.068635
Ag	0.851292	0.000009	1.475822
Ag	2.191163	0.000777	-1.153800
Ag	-1.210871	-1.602753	-0.130863
Ag	-1.212576	1.602371	-0.130134
I	1.426190	-2.484849	0.068868
I	-3.399425	-0.001180	-0.191620

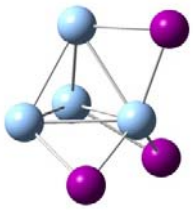
b) **Isomer 2:** has 1 small imaginary frequency -15.7800 cm^{-1}

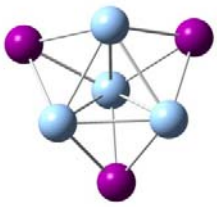


E(B3LYP) = -622.3232744; Zero-point correction = 0.002837
Relative energy = 0.3 kcal mol^{-1}

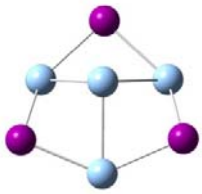
Ag	-1.960030	0.292998	0.000000
Ag	0.765457	1.827772	0.000000
Ag	0.765457	-1.359093	1.478959
Ag	0.765457	-1.359093	-1.478959
I	-1.466305	-2.445954	0.000000
I	2.851720	-0.013552	0.000000
I	-1.683678	2.989290	0.000000

c) **Isomer 3:** has 1 small imaginary frequency -16.3 cm^{-1}
The following two different input guesses





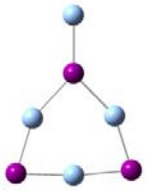
Converged to the same structure:



E(B3LYP) = -622.320497; Zero-point correction = 0.002781
Relative energy = 2.1 kcal mol^{-1}

I	0.853784	2.830987	0.130433
Ag	-1.612335	1.686108	-0.524555
Ag	0.029306	0.027091	1.199633
Ag	-0.676335	-2.214092	-0.491741
Ag	2.290731	0.529968	-0.565444
I	2.040750	-2.167990	0.114894
I	-2.922351	-0.688780	0.093523

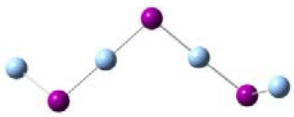
d) **Isomer 4:** has 1 small imaginary frequency -26.7 cm^{-1}

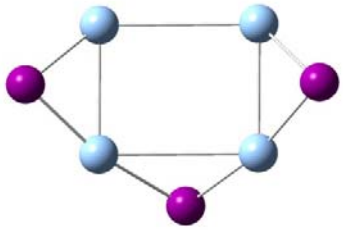


E(B3LYP) = -622.306748; Zero-point correction = 0.002701
Relative energy = 10.6 kcal mol^{-1}

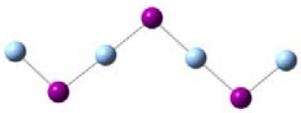
Ag	0.000000	1.940896	0.184783
Ag	0.000000	-1.940896	0.184783
Ag	0.000000	0.000000	-2.551873
I	0.000000	0.000000	2.270360
Ag	0.000000	0.000000	5.007237
I	0.000000	2.728701	-2.387744
I	0.000000	-2.728701	-2.387744

e) **Isomer 5 (C_{2v}): The following four different input guesses**





Converged to the same structure:

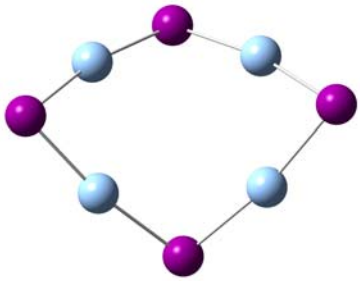


E(B3LYP) = -622.3064865; Zero-point correction = 0.002688
Relative energy = 10.8 kcal mol^{-1}

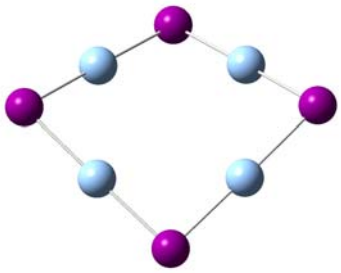
Ag	6.175719	0.283422	0.002481
Ag	2.054454	0.258854	-0.001190
Ag	-2.054500	0.258803	0.000872
Ag	-6.175602	0.283496	-0.001617
I	4.158337	-1.491250	-0.002365
I	-4.158356	-1.491335	0.002128
I	-0.000044	2.020792	-0.000247

Ag_4I_4 neutral:

a) Isomer **(D_{2d}):** (used in figure 3d):
The following input guess:



Converged to:

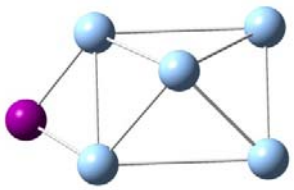


E(B3LYP) = -634.0762313; Zero-point correction = 0.003608

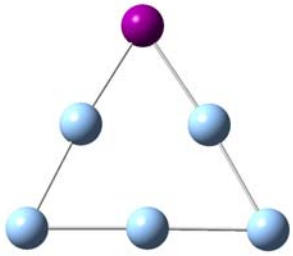
Ag	1.885402	1.885383	-0.000126
Ag	-1.885402	1.885383	-0.000126
Ag	-1.885402	-1.885383	-0.000126
Ag	1.885402	-1.885383	-0.000126
I	0.000000	3.742718	0.599787
I	0.000000	-3.742718	0.599787
I	-3.742900	0.000000	-0.599563
I	3.742900	0.000000	-0.599563

Ag_5I^+:

a) **Isomer 1 (C_{2v}): (Used in Figure 4g)**
The following input guess:



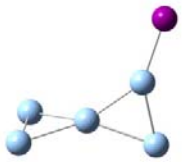
Converged to:

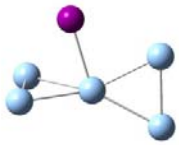


E(B3LYP) = -746.39529; Zero-point correction = 0.002320
Relative energy = 0 kcal mol^{-1}

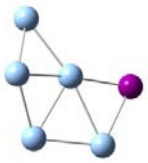
Ag	0.774539	-1.481713	-0.000595
Ag	0.776809	1.480450	0.000732
Ag	-1.687099	2.783356	-0.000360
Ag	-1.691491	-2.780837	0.000347
Ag	-1.670850	0.001351	-0.000053
I	3.102082	-0.002312	-0.000062

b) **Isomer 2 (C_1): The following two different input guesses**





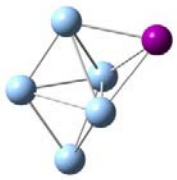
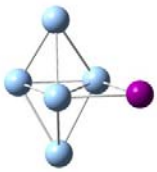
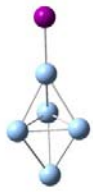
Converged to the same structure:



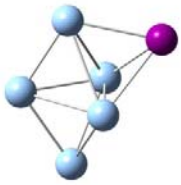
E(B3LYP) = -746.3933769; Zero-point correction = 0.002315
Relative energy = 1.2 kcal mol^{-1}

Ag	2.603761	-1.699923	-0.341211
Ag	0.123510	2.236835	-0.472330
Ag	0.067878	-0.563589	0.090673
Ag	-2.405241	1.067504	0.114369
Ag	2.379428	0.868555	0.560481
I	-2.455827	-1.693227	0.042582

c) **Isomer 3 (C_s): The following three different input guesses**

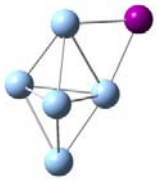
Converged to the same structure:



E(B3LYP) = -746.392747; Zero-point correction = 0.002308
Relative energy = 1.6 kcal mol^{-1}

Ag	1.419429	1.705540	-0.000234
Ag	-1.374498	1.616720	-0.000621
Ag	-0.116729	-0.591510	1.385330
Ag	-0.116991	-0.593041	-1.385008
Ag	-2.569089	-0.975318	0.000429
I	2.445666	-1.030800	0.000092

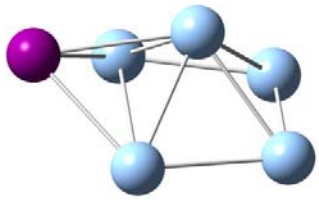
d) **Isomer 4 (C_s):**



E(B3LYP) = -746.3920387; Zero-point correction = 0.002357
Relative energy = 2.1 kcal mol^{-1}

Ag	-2.597154	-1.149806	-0.002055
Ag	0.163136	-1.301660	-0.003819
Ag	-1.100347	0.946007	1.356976
Ag	-1.102357	0.957112	-1.351228
Ag	1.390147	1.515608	0.000987
I	2.879037	-0.857760	-0.000763

e) **Isomer 5 (C_s):**



E(B3LYP) = -746.3919542; Zero-point correction = 0.002309
Relative energy = 2.1 kcal mol^{-1}

Ag	-2.076107	1.448649	-0.111450
Ag	0.652143	1.957052	-0.620993
Ag	0.651718	-1.957074	-0.621015
Ag	-2.076334	-1.448419	-0.111421
Ag	-0.133136	0.000043	1.269724
I	2.644164	-0.000222	0.173061

f) **Isomer 6 (C_s)**

E(B3LYP) = -746.3833394; Zero-point correction = 0.002201
Relative energy = 7.4 kcal mol^{-1}

Ag	2.518168	-0.172410	0.000000
Ag	2.574902	-2.885130	0.000000
Ag	0.074831	-1.430981	0.000000
Ag	0.000000	1.360293	0.000000
Ag	-2.487728	-0.012918	0.000000
I	-2.376757	2.785544	0.000000

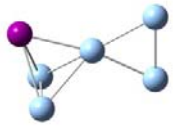
g) **Isomer 7 (C_{2v})**

E(B3LYP) = -746.3830176; Zero-point correction = 0.002171
Relative energy = 7.6 kcal mol^{-1}

Ag	0.000387	3.367379	1.337450
Ag	0.000387	3.367379	-1.337450

Ag	-0.000645	0.909850	0.000000
Ag	1.407316	-1.572597	0.000000
Ag	-1.407883	-1.573353	0.000000
I	0.000387	-3.989376	0.000000

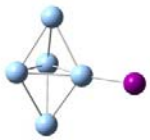
h) **Isomer 8 (C_s):**



E(B3LYP) = -746.3814152; Zero-point correction = 0.002095
Relative energy = 8.6 kcal mol^{-1}

Ag	3.070293	1.212201	-0.000038
Ag	-1.851517	-0.952750	1.394412
Ag	0.431860	0.334212	-0.005582
Ag	-1.800122	-1.043232	-1.363690
Ag	2.527017	-1.415255	0.016519
I	-2.108376	1.653712	-0.036909

i) **Isomer 9 (C2v):** has 1 small imaginary frequency -15.3 cm^{-1}

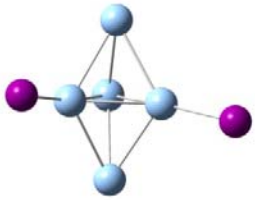
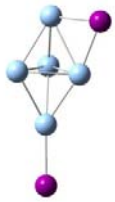
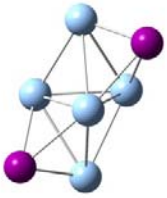
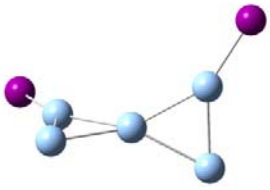
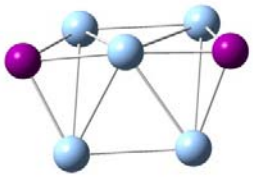


E(B3LYP) = -746.3732857; Zero-point correction = 0.002339
Relative energy = 13.8 kcal mol^{-1}

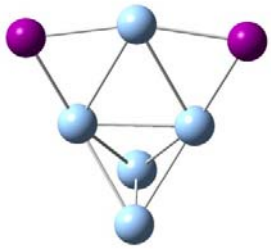
Ag	0.006082	0.844008	0.000000
Ag	-1.376506	-1.601919	0.000000
Ag	1.369357	-1.613087	0.000000
Ag	0.000341	-0.757793	2.380600
Ag	0.000341	-0.757793	-2.380600
I	0.000341	3.446594	0.000000

$Ag_5I_2^+$:

a) **Isomer 1 (C2v): (Used in Figure 4h)**
The following five different input guesses

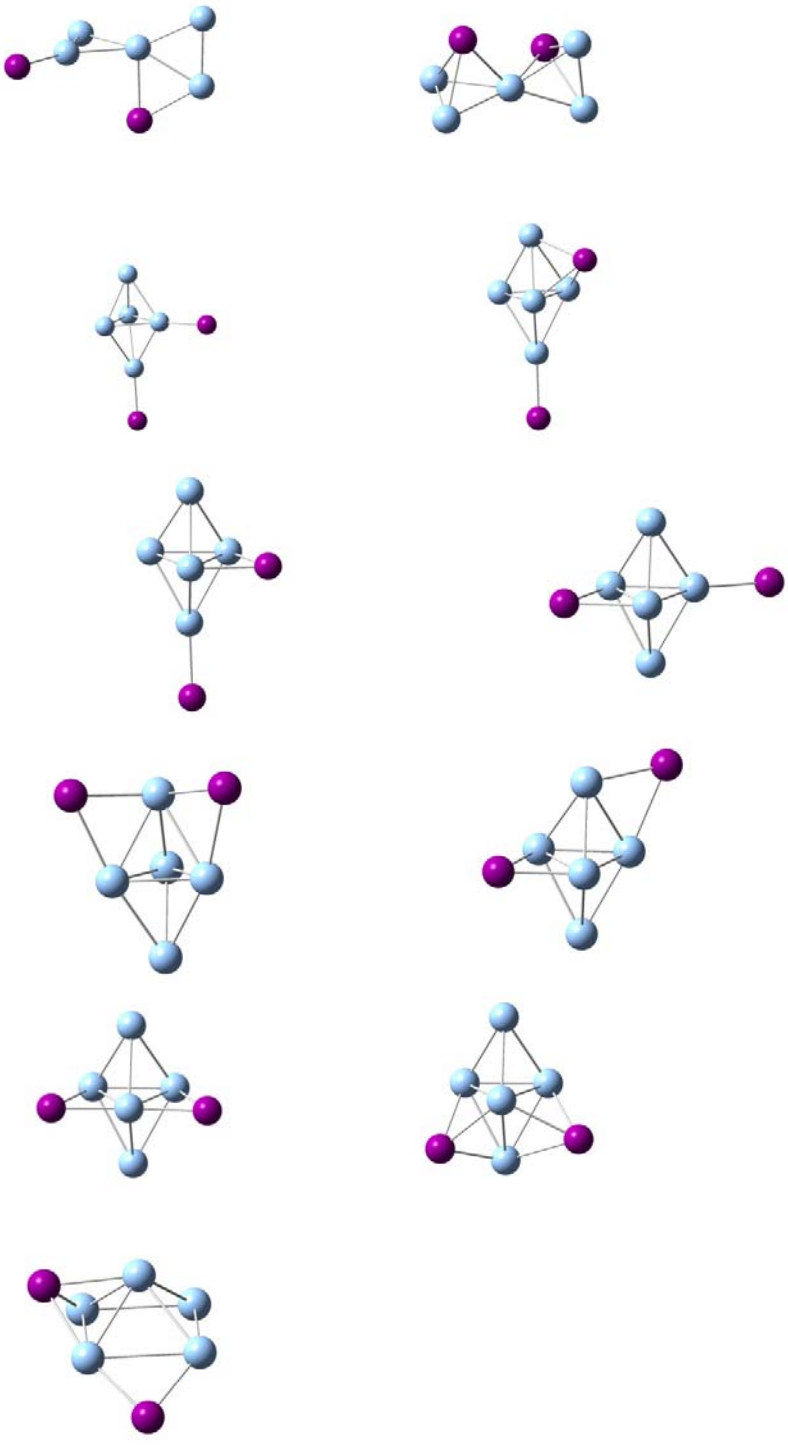
Converged to the same structure:



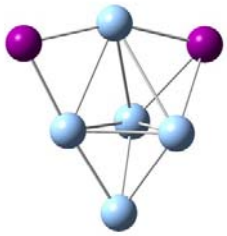
E(B3LYP) = -757.9026117; Zero-point correction = 0.003149
Relative energy = 0 kcal mol^{-1}

Ag	0.000000	1.433869	-0.569957
Ag	-1.360364	0.000000	-2.611312
Ag	0.000000	-1.433869	-0.569957
Ag	0.000000	0.000000	2.247853
Ag	1.360364	0.000000	-2.611312
I	0.000000	2.710702	1.824435
I	0.000000	-2.710702	1.824435

b) **Isomer 2 (C_s): The following 11 different input guesses**



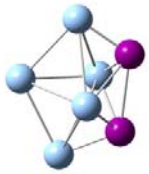
Converged to the same structure:

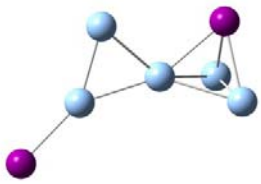


E(B3LYP) = -757.9014567; Zero-point correction = 0.003061
Relative energy = 0.7 kcal mol^{-1}

Ag	1.303386	0.109268	-1.382361
Ag	-1.509946	1.398550	-0.000029
Ag	1.304234	0.109229	1.382410
Ag	-0.609189	-1.593252	0.000055
Ag	2.068576	-2.246300	-0.000229
I	0.945011	2.696660	-0.000058
I	-3.212593	-0.725759	0.000196

c) **Isomer 3 (C_s): The following two different input guesses**



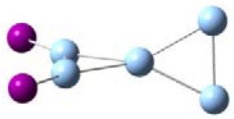


Converged to the same structure:

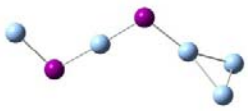
E(B3LYP) = -757.8980473; Zero-point correction = 0.002933
Relative energy = 2.7 kcal mol^{-1}

Ag	-1.262274	-1.398514	-0.189996
Ag	2.195098	0.000116	-1.085611
Ag	0.782616	-0.000026	1.492984
Ag	-3.584530	-0.001518	-0.157318
Ag	-1.264834	1.399694	-0.186221
I	1.389401	2.485242	0.055021
I	1.389739	-2.485022	0.056858

d) **Isomer 4 (C_1): The input guess:**



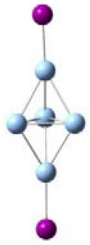
Converged to:

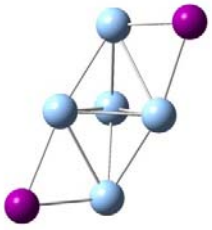


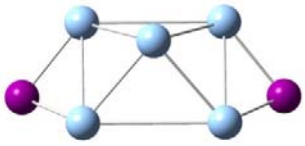
E(B3LYP) = -757.8864396; Zero-point correction = 0.002720
Relative energy = 9.9 kcal mol^{-1}

Ag	-4.632255	-0.547244	1.360182
Ag	-4.486515	-0.967404	-1.269665
Ag	-2.497927	0.492683	-0.040637
I	-0.246845	2.064355	-0.131081
Ag	1.744097	0.241151	-0.024350
I	3.812451	-1.549186	0.089910
Ag	5.851811	0.199879	0.020895

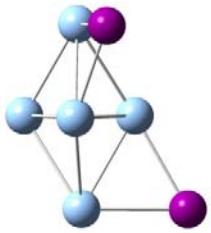
e) **Isomer 5 (C_2): The following three different input guesses**







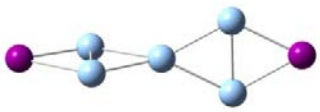
Converged to the same structure:

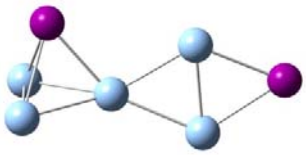


E(B3LYP) = -757.8726038; Zero-point correction = 0.002949
Relative energy = 18.7 kcal mol^{-1}

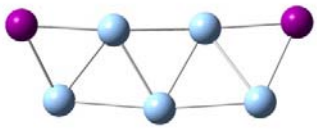
Ag	-0.000134	2.308170	-0.000240
Ag	0.751106	-0.155069	1.234315
Ag	-0.750625	-0.155402	-1.233697
Ag	2.100213	0.630867	-1.148207
Ag	-2.100729	0.630785	1.148069
I	-3.080942	-1.445260	-0.427543
I	3.081092	-1.445108	0.427330

f) **Isomer 6 (C_2): The following two different input guesses**





Converged to the same structure:

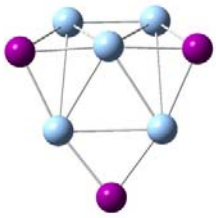


E(B3LYP) = -757.865901; Zero-point correction = 0.002794
Relative energy = 22.8 kcal mol^{-1}

Ag	-1.372893	-0.866587	-0.314169
Ag	1.372818	-0.866737	0.313874
Ag	0.000303	1.498717	-0.000717
Ag	3.015432	1.283038	-0.642325
Ag	-3.015682	1.282887	0.643206
I	4.140984	-1.033743	0.322824
I	-4.140965	-1.033652	-0.322708

$Ag_5I_3^+$:

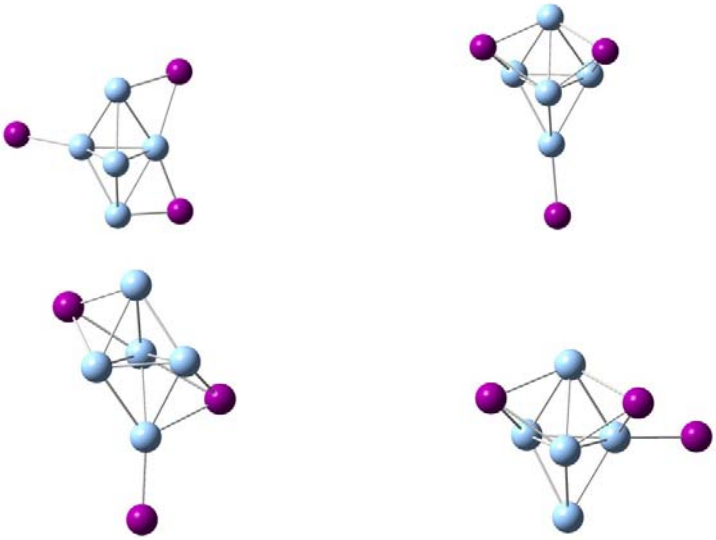
a) **Isomer 1 (C_s) (Used in Figure 4i)**

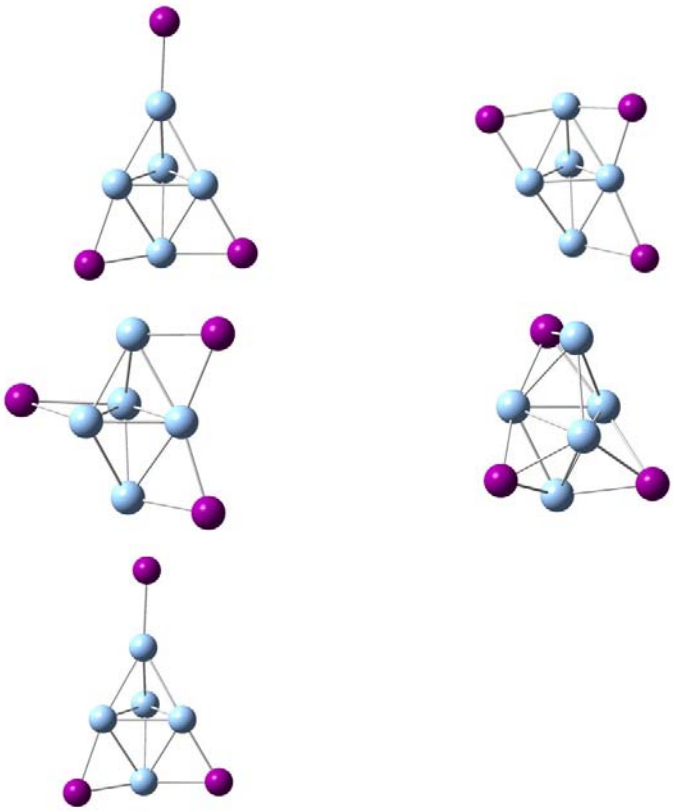


E(B3LYP) = -769.3593624; Zero-point correction = 0.003411
Relative energy = 0 kcal mol^{-1}

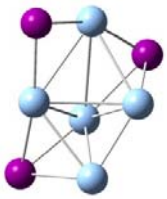
Ag	1.617557	1.653932	-0.020155
Ag	-0.840609	0.000019	-1.027211
Ag	1.617405	-1.653992	-0.020129
I	-0.760649	-2.822589	-0.874008
I	-0.760469	2.822627	-0.873989
I	3.626307	-0.000118	0.729898
Ag	-2.384185	-1.388942	1.107786
Ag	-2.384104	1.389073	1.107779

b) **Isomer 2 (C_1) :** has 1 small imaginary frequency -4.8 cm^{-1}
The following nine different input guesses:





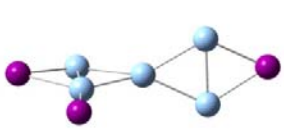
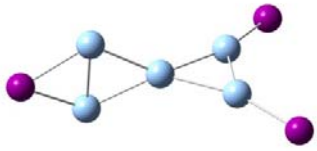
Converged to the same structure:



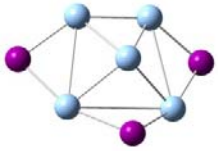
E(B3LYP) = -769.3569614; Zero-point correction = 0.003313
Relative energy = 1.4 kcal mol^{-1}

Ag	-0.502687	1.584238	-0.287645
Ag	0.367512	-0.829574	1.705836
Ag	-0.786849	-1.472991	-0.976984
Ag	2.332111	0.080239	-0.396141
Ag	-2.229314	0.119929	1.685771
I	1.672975	-2.625507	-0.301788
I	-2.907525	0.336337	-1.172644
I	1.961035	2.748670	-0.060461

c) **Isomer 3 (C_s) : The following two different input guesses**

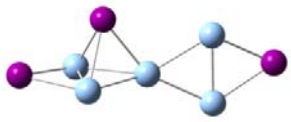
Converged to the same structure:



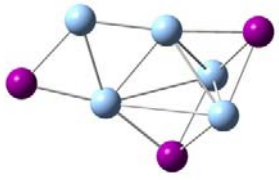
E(B3LYP) = -769.3535597; Zero-point correction = 0.003495
Relative energy = 3.7 kcal mol^{-1}

Ag	1.431974	-2.107064	0.440369
Ag	2.084979	1.334595	-0.459761
Ag	0.000003	0.188091	1.255309
Ag	-1.432279	-2.107003	0.440775
Ag	-2.084839	1.334728	-0.459889
I	0.000101	2.986521	0.403091
I	3.614408	-0.891819	-0.741010
I	-3.614364	-0.891633	-0.741133

d) **Isomer 4 (C_s) :** has 1 small imaginary frequency -5.8 cm^{-1}
The following input guess



Converged to the structure:



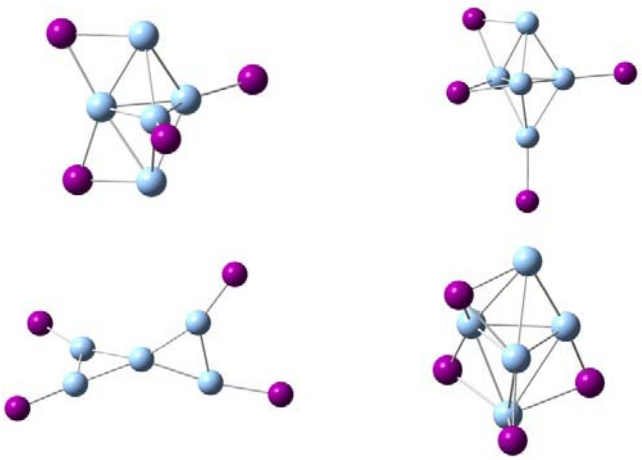
E(B3LYP) = -769.3402865; Zero-point correction = 0.003128
Relative energy = 11.8 kcal mol^{-1}

Ag	2.040945	0.545514	-1.480894
Ag	-1.470620	0.910009	0.000451

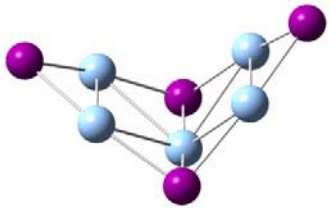
Ag	0.231673	-1.609973	-0.003531
Ag	-2.509387	-1.867823	0.003429
Ag	2.026465	0.532350	1.484811
I	0.771552	2.645320	0.005026
I	-4.174201	0.341825	-0.006104
I	3.119694	-1.665893	-0.002704

$Ag_5I_4^+$:

a) **Isomer 1 (C_{2v}) (Used in Figure 4j):**
The following four different input guesses



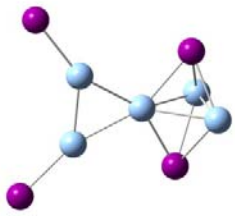
Converged to the same structure:



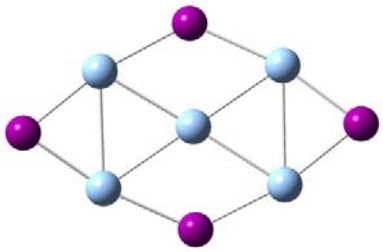
E(B3LYP) = -780.8694168; Zero-point correction = 0.004152
Relative energy = 0 kcal mol^{-1}

I	3.698147	-0.000003	1.568482
Ag	2.008541	1.645983	0.241181
Ag	2.008543	-1.645982	0.241170
Ag	0.000649	0.000004	-1.511226
I	0.000253	2.800018	-1.324810
I	0.000255	-2.800011	-1.324825
Ag	-2.008862	1.646217	0.240399
I	-3.698667	-0.000005	1.567187
Ag	-2.008857	-1.646220	0.240396

b) **Isomer 2:** has 1 small imaginary frequency -18.0 cm^{-1}
The following input guess



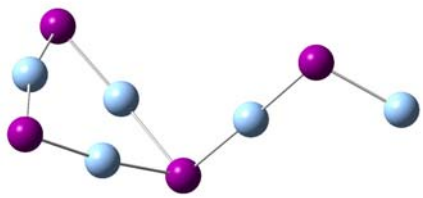
Converged to the structure:



E(B3LYP) = -780.8593291; Zero-point correction = 0.004037
Relative energy = 6.3 kcal mol^{-1}

Ag	2.503838	-1.620965	0.031879
Ag	-2.489666	-1.647160	-0.126438
Ag	-0.020528	0.014287	0.050426
Ag	-2.526190	1.637435	0.068854
Ag	2.504802	1.624981	-0.058083
I	4.657480	-0.006570	-0.247028
I	0.010412	-2.851027	0.283413
I	-4.646991	-0.015321	-0.232621
I	0.003703	2.865311	0.225821

c) **Isomer 3 (C_s):**

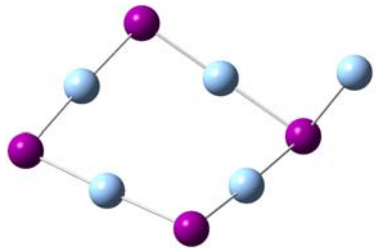


E(B3LYP) = -780.8469822; Zero-point correction = 0.003870
Relative energy = 13.9 kcal mol^{-1}

Ag	-1.505191	-1.569466	0.796859
Ag	-1.453134	1.572792	0.791851

Ag	-3.648340	0.037181	-0.913038
I	-3.341917	2.750588	-0.736705
I	0.369841	-0.026245	2.220781
I	-3.433685	-2.684336	-0.729222
Ag	2.377140	-0.068468	0.341394
I	4.321772	-0.124602	-1.560830
Ag	6.579556	0.123355	-0.108199

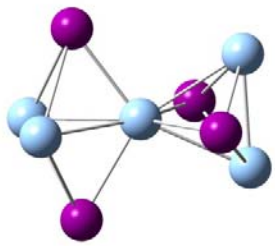
d) **Isomer 4 (C_1):**



E(B3LYP) = -780.837153; Zero-point correction = 0.003906
Relative energy = 20.1 kcal mol^{-1}

Ag	2.496500	-1.920990	0.126636
Ag	-1.345153	-1.971224	-0.442124
Ag	-1.345152	1.971224	-0.442124
Ag	2.496501	1.920990	0.126636
I	0.499229	-3.788657	0.210219
I	-3.260115	0.000000	-1.037749
I	0.499230	3.788657	0.210219
I	4.394615	0.000000	0.036472
Ag	-4.707947	0.000000	1.285965

e) **Isomer 5 (D_{2d}):**

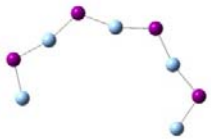


E(B3LYP) = -780.81918; Zero-point correction = 0.003379
Relative energy = 31.0 kcal mol^{-1}

Ag	2.649139	0.604181	-1.418768
Ag	-2.642461	1.421641	0.605400
Ag	-0.000105	-0.004088	-0.003724
Ag	-2.652629	-1.417981	-0.602571
Ag	2.645213	-0.603376	1.420424

I	2.042680	-2.142698	-0.911650
I	-2.042498	0.911450	-2.142111
I	-2.039283	-0.911812	2.142276
I	2.039848	2.142727	0.910810

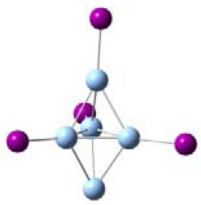
f) **Isomer 6:** has 2 small imaginary frequencies -12.5676 and -4.5454cm^{-1}



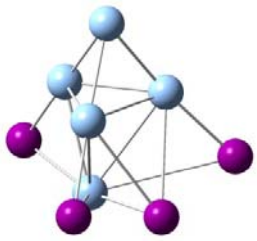
E(B3LYP) = -780.8177435; Zero-point correction = 0.003538
Relative energy = 32.0 kcal mol^{-1}

Ag	0.000000	0.000000	2.325176
Ag	0.000000	4.283974	0.595595
Ag	0.000000	-4.283974	0.595595
Ag	0.000000	5.338836	-3.592776
Ag	0.000000	-5.338836	-3.592776
I	0.000000	2.685225	2.769012
I	0.000000	-2.685225	2.769012
I	0.000000	6.414264	-1.142109
I	0.000000	-6.414264	-1.142109

g) **Isomer 7 (C_s): The following input guess**



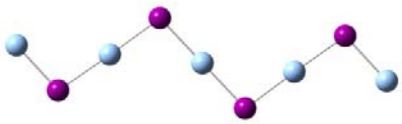
Converged to the structure:



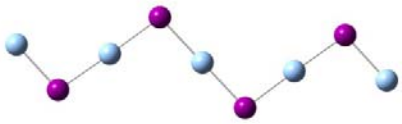
E(B3LYP) = -780.7555356; Zero-point correction = 0.003977
Relative energy = 71.4 kcal mol^{-1}

Ag	0.029808	-1.478786	1.289360
Ag	2.218561	-0.001233	0.181229
Ag	0.030735	1.473635	1.294759
Ag	1.743024	-0.006180	2.912979
Ag	-0.018078	0.004253	-2.025153
I	2.647882	0.004353	-2.525108
I	-1.861781	-3.067887	-0.041940
I	-1.859757	3.069040	-0.030578
I	-2.477106	0.001865	-0.641981

g) **Isomer 8 (C_2): The following input guess**



Converged to the structure:



E(B3LYP) = -780.8288073; Zero-point correction = 0.003623
Relative energy = 18.9 kcal mol^{-1}

Ag	-4.043527	0.260958	0.014768
Ag	-0.000006	0.000074	0.170078
Ag	4.043537	-0.260920	0.014860
Ag	8.110437	-0.548146	-0.129258
I	-1.920792	1.921141	0.174893
I	6.237033	1.373621	-0.148916
I	1.920732	-1.921033	0.175047
I	-6.236952	-1.373679	-0.149037
Ag	-8.110464	0.547979	-0.129070

Neutrals used in calculations for reactions of cluster cations with allyl iodide:

Allyl iodide (C_3H_5I):

C	3.135366	-0.468335	-0.252017
C	2.149599	0.068822	0.473956
C	1.084754	0.920323	-0.100124
I	-0.935226	-0.086954	-0.008734
H	3.921634	-1.059910	0.207677

H 3.191902 -0.332539 -1.329837
H 2.113063 -0.094337 1.549618
H 1.221064 1.136324 -1.158379
H 0.901009 1.834171 0.462946
E(B3LYP) = -128.7198675; Zero-point correction = 0.070932

Allyl Radical (C_3H_5):
C 1.230252 0.196157 0.000011
C 0.000044 -0.443164 -0.000070
C -1.230271 0.196066 0.000017
H 2.161085 -0.361223 0.000234
H 1.299657 1.280844 -0.000110
H 0.000135 -1.533677 -0.000021
H -2.161253 -0.361072 0.000135
H -1.299774 1.280778 0.000017
E(B3LYP) = -117.2579397; Zero-point correction = 0.066578

Propene (C_3H_6):
C -1.283184 0.220545 -0.000067
C -0.133803 -0.455933 -0.000186
C 1.235076 0.163011 0.000037
H -2.245583 -0.284386 0.000620
H -1.305021 1.308841 0.000029
H -0.163952 -1.546669 0.000243
H 1.811694 -0.148618 0.881676
H 1.181011 1.256961 -0.001949
H 1.813318 -0.151868 -0.879324
E(B3LYP) = -117.90521; Zero-point correction = 0.080097

1,5-hexadiene, $(C_3H_6)_2$:
C -0.572990 -0.297257 -0.520358
C -1.934984 -0.338121 0.117232
C -2.873995 0.600181 -0.012816
H 0.448335 -1.172903 1.176072
H -0.483599 0.589179 -1.160256
H -2.140627 -1.210375 0.741202
H -2.713406 1.487796 -0.622006
H -3.839819 0.517423 0.478733
C 2.874002 0.600175 0.012798
C 1.934981 -0.338121 -0.117221
C 0.572985 -0.297223 0.520364
H 3.839828 0.517386 -0.478742
H 2.713421 1.487813 0.621956
H 2.140617 -1.210399 -0.741159
H 0.483590 0.589252 1.160209
H -0.448336 -1.172979 -1.176010

E(B3LYP) = -234.6071736; Zero-point correction = 0.14252

Fig S1: Ion-molecule reactions of CH_3I with: (a) Ag_2H^+, (b) Ag_3^+, (c) Ag_4H^+ and (d) Ag_5^+

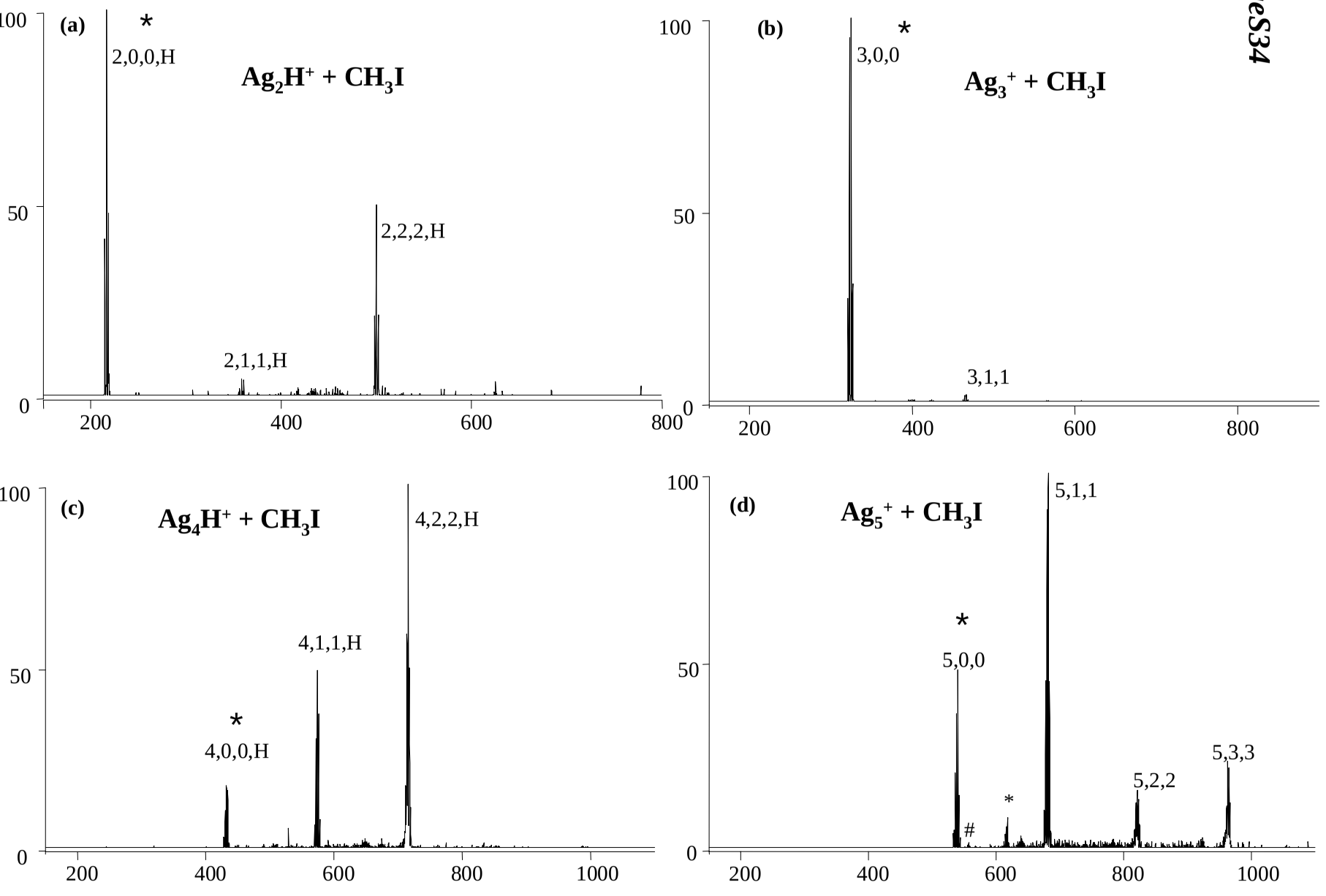
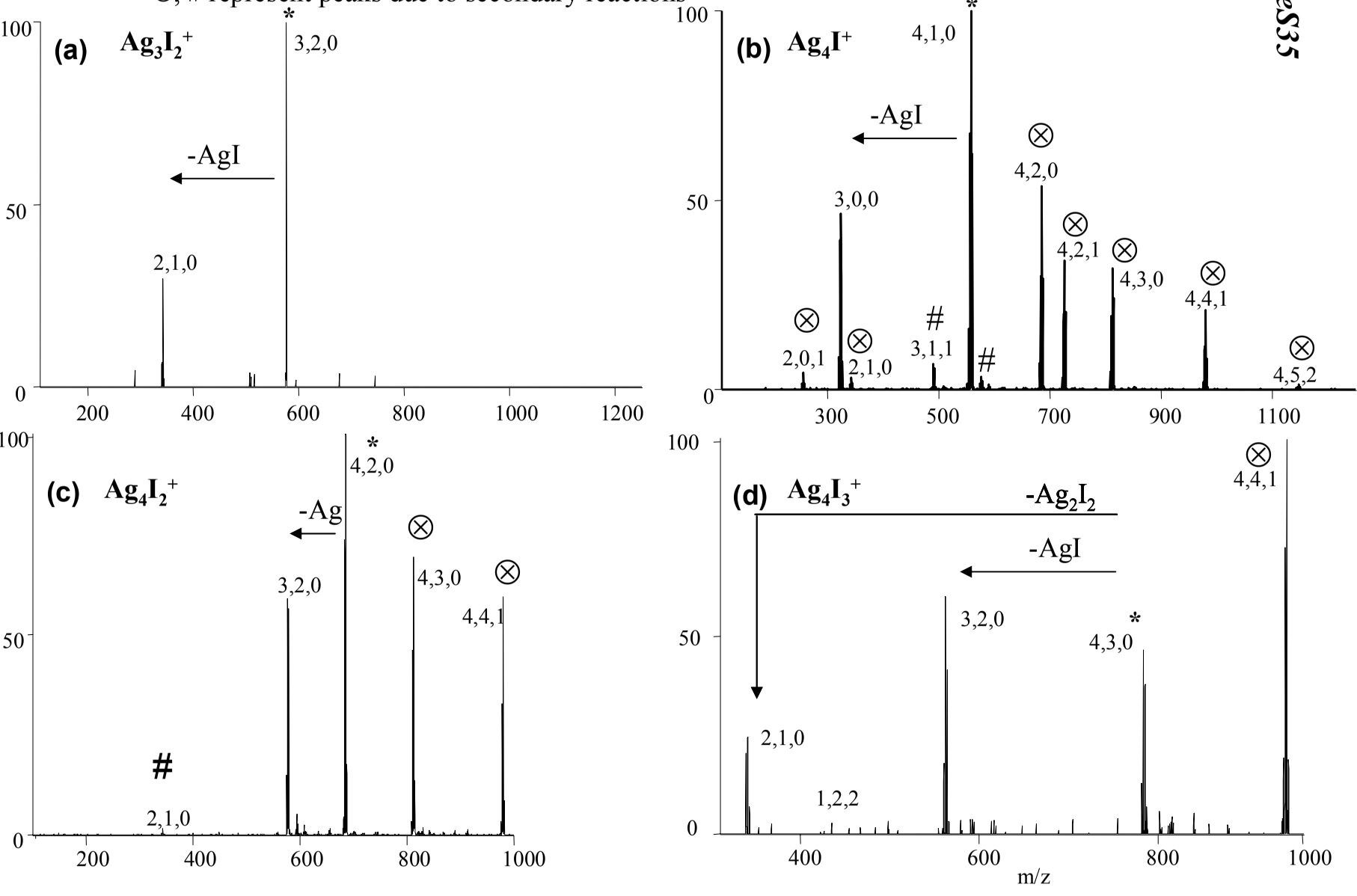
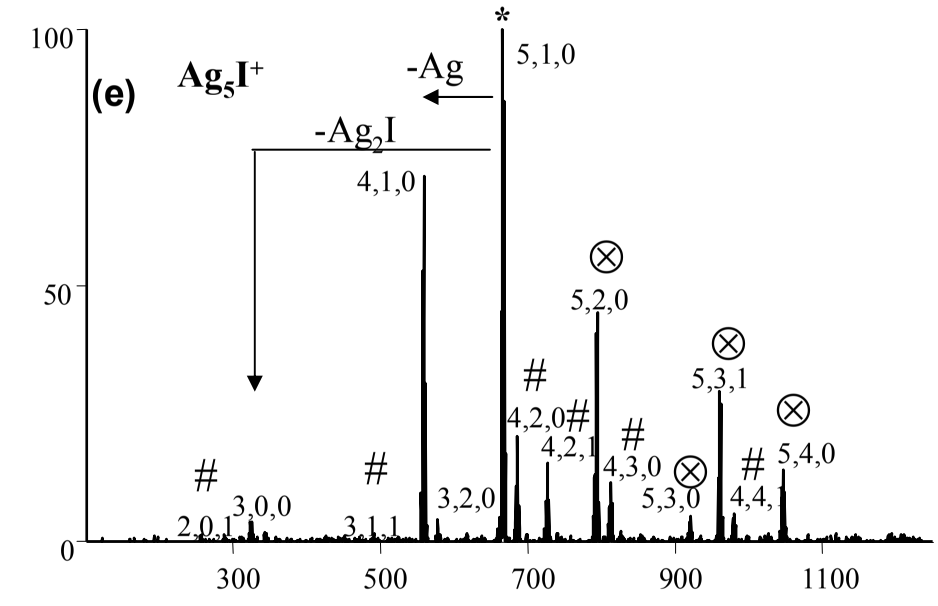
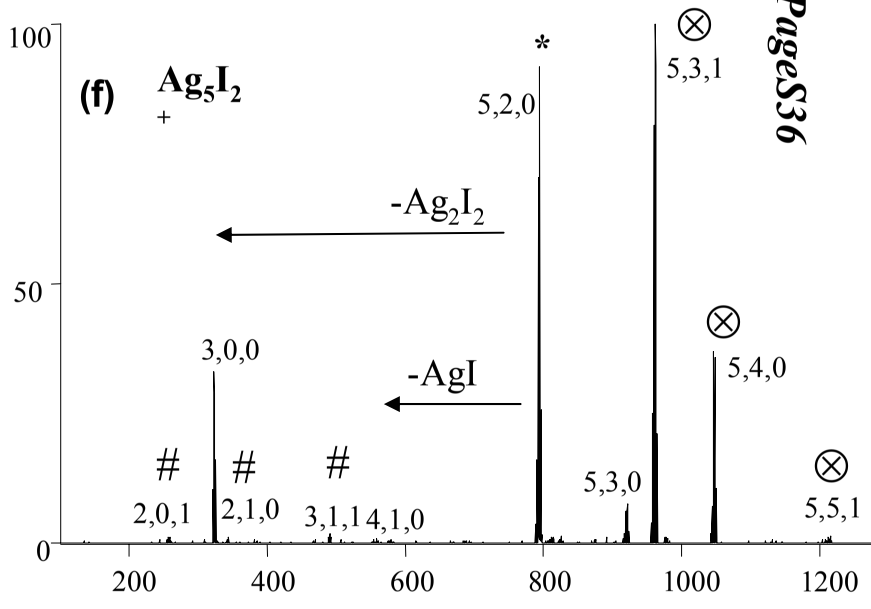


Fig S2: CID spectra of the observed $Ag_nI_m^+$. The * represent the selected peak for CID ⊗, # represent peaks due to secondary reactions




(e)
Ag_5I^+
-Ag
-Ag_2I
5,1,0
4,1,0
5,2,0
5,3,1
4,2,0
4,2,1
4,3,0
5,4,0
5,3,0
3,2,0
3,0,0
2,0,1
3,1,1
100
50
0
300
500
700
900
1100


(f)
$Ag_5I_2^+$
5,2,0
5,3,1
-Ag_2I_2
3,0,0
-AgI
5,4,0
5,3,0
2,0,1
2,1,0
3,1,1
4,1,0
5,5,1
100
50
0
200
400
600
800
1000
1200

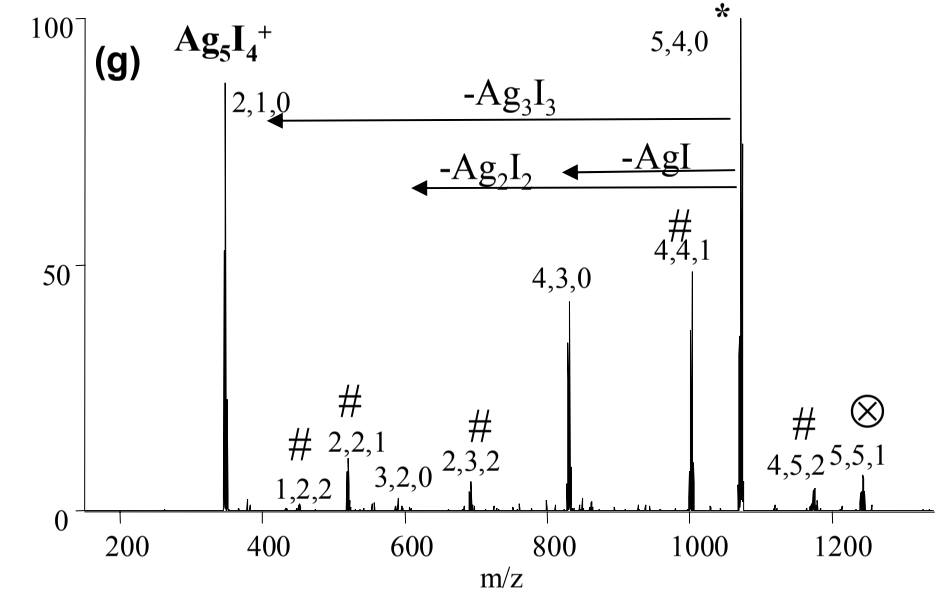

(g)
$Ag_5I_4^+$
5,4,0
2,1,0
-Ag_3I_3
-Ag_2I_2
-AgI
4,4,1
4,3,0
2,2,1
2,3,2
1,2,2
3,2,0
4,5,2
5,5,1
100
50
0
200
400
600
800
1000
1200
m/z

Table S1: DFT calculated energies for ground state structures relevant to the silver clusters used in the thermochemistry calculations. The scaling factor used is 0.9806 and the basis sets were LanL2DZ for Ag and I, and 6-31G* for C, N and H.

Species	Isomer[a]	Comments[b]	E[c]	ZPE[d]	ZPE corr[e]	E+ZPEcorr[f]	Rel E (kcal mol^{-1})[g]
Ag^+			-146.70064			-146.70064	
Ag_2H^+		from DT	-294.36431	0.005742	0.00563061	-294.35868	
Ag_2I^+		Figure 4a	-305.25137	0.000816	0.00080017	-305.25057	
Ag_3^+		from DT	-440.84253	0.000896	0.00087862	-440.84165	
Ag_3I^+	Isomer 1		-452.26253	0.001215	0.00119143	-452.26134	11.28977024
	Isomer 2		-452.27707	0.001158	0.00113553	-452.27594	2.127563117
	Isomer 3	Figure 4b	-452.28055	0.00125	0.00122575	-452.27933	0
$Ag_3I_2^+$	Isomer 1	Figure 4c	-463.78182	0.001758	0.00172389	-463.7801	0
	Isomer 2		-463.77989	0.001768	0.0017337	-463.77815	1.21894194
	Isomer 3		-463.77938	0.001744	0.00171017	-463.77767	1.521066419
$Ag_4^{+(h)}$			-587.872498	0.001283	0.00125811	-587.87124	
Ag_4H^+		from DT	-588.475	0.007106	0.00696814	-588.46803	
Ag_4I^+		from DT	-599.36216	0.00179	0.00175527	-599.3604	
$Ag_4I_2^+$	Isomer 1	Figure 4e	-610.81515	0.002226	0.00218282	-610.81297	0
	Isomer 2		-610.81377	0.002325	0.0022799	-610.81149	0.931211913

Species	Isomer[a]	Comments[b]	E[c]	ZPE[d]	ZPE corr[e]	E+ZPEcorr[f]	Rel E (kcal mol^{-1})[g]
	Isomer 3	ifreq -21.2 cm^{-1}	-610.81354	0.00213	0.00208868	-610.81145	0.951658072
	Isomer 4	ifreq -4.9 cm^{-2}	-610.8001	0.002088	0.00204749	-610.79805	9.36161913
	Isomer 5	ifreq -1.4 cm^{-3}	-610.7984	0.002197	0.00215438	-610.79624	10.49614805
	Isomer 6	ifreq -5.9 cm^{-3}	-610.79595	0.001937	0.00189942	-610.79405	11.87123832
	Isomer 7		-610.78628	0.002424	0.00237697	-610.78391	18.23811304
$Ag_4I_3^+$	**Isomer 1**	**Figure 4f**	-622.32397	0.002983	0.00292513	-622.32104	0
	Isomer 2	ifreq -15.8 cm^{-1}	-622.32327	0.002837	0.00278196	-622.32049	0.344586072
	Isomer 3	ifreq -16.3 cm^{-2}	-622.3205	0.002781	0.00272705	-622.31777	2.052973513
	Isomer 4	ifreq -26.7 cm^{-3}	-622.30675	0.002701	0.0026486	-622.3041	10.6313816
	Isomer 5		-622.30649	0.002688	0.00263585	-622.30385	10.78747609
Ag_5I^+	**Isomer 1**	**Figure 4g**	-746.39529	0.00232	0.00227499	-746.39302	0
	Isomer 2		-746.39338	0.002315	0.00227009	-746.39111	1.197412699
	Isomer 3		-746.39275	0.002308	0.00226322	-746.39048	1.588373894
	Isomer 4		-746.39204	0.002357	0.00231127	-746.38973	2.062990706
	Isomer 5		-746.39195	0.002309	0.00226421	-746.38969	2.086479159
	Isomer 6		-746.38334	0.002201	0.0021583	-746.38118	7.425895986

Species	Isomer[a]	Comments[b]	E[c]	ZPE[d]	ZPE corr[e]	E+ZPEcorr[f]	Rel E (kcal mol^{-1})[g]
	Isomer 7		-746.38302	0.002171	0.00212888	-746.38089	7.609368614
	Isomer 8		-746.3814	0.002061	0.00202102	-746.37938	8.555926034
	Isomer 9	ifreq -15.3 cm^{-3}	-746.37329	0.002339	0.00229362	-746.37099	13.81960968
$Ag_5I_2^+$	Isomer 1	Figure 4h	-757.90261	0.003149	0.00308791	-757.89952	0
	Isomer 2		-757.90146	0.003061	0.00300162	-757.89846	0.670624455
	Isomer 3		-757.89805	0.002933	0.0028761	-757.89517	2.731294002
	Isomer 4		-757.88644	0.00272	0.00266723	-757.88377	9.884175196
	Isomer 5		-757.8726	0.002949	0.00289179	-757.86971	18.70719007
	Isomer 6		-757.8659	0.002794	0.0027398	-757.86316	22.81788697
$Ag_5I_3^+$	Isomer 1	Figure 4i	-769.35936	0.003411	0.00334483	-769.35602	0
	Isomer 2	ifreq -4.8 cm^{-3}	-769.35696	0.003313	0.00324873	-769.35371	1.446348552
	Isomer 3		-769.35356	0.003495	0.0034272	-769.35013	3.692940527
	Isomer 4	ifreq -5.8 cm^{-3}	-769.34029	0.003128	0.00306732	-769.33722	11.79617783
$Ag_5I_4^+$	Isomer 1	Figure 4j	-780.86942	0.004152	0.00407145	-780.86535	0
	Isomer 2	ifreq -18.0 cm^{-3}	-780.85933	0.004037	0.00395868	-780.85537	6.259368952
	Isomer 3		-780.84698	0.00387	0.00379492	-780.84319	13.90441101

Species	Isomer[a]	Comments[b]	E[c]	ZPE[d]	ZPE corr[e]	E+ZPEcorr[f]	Rel E (kcal mol^{-1})[g]
	Isomer 4		-780.83715	0.003906	0.00383022	-780.83332	20.09448441
	Isomer 5		-780.81918	0.003379	0.00331345	-780.81586	31.05013368
	Isomer 6	2 x ifreq -12.6, -4.5 cm^{-3}	-780.81774	0.003538	0.00346936	-780.81427	32.04769599
	Isomer 7		-780.75554	0.003977	0.00389985	-780.75164	71.35390796
	Isomer8		-780.82881	0.003623	0.00355271	-780.82525	18.89798549
$I^{\cdot}$			-11.394691			-11.394691	
$CH_2=CHCH_2^{\cdot}$			-117.25794	0.066578	0.06528639	-117.19265	
$CH_2=CHCH_2I$			-128.71987	0.070932	0.06955592	-128.65031	
$CH_2=CHCH_3$			-117.90521	0.080097	0.07854312	-117.82667	
$(CH_2=CHCH_2)_2$			-234.60717	0.142525	0.13976002	-234.46741	
$Ag^{\cdot}$			-146.9936			-146.9936	
AgI		Figure 3a	-158.47328	0.000436	0.00042754	-158.47285	
Ag_2I_2		Figure 3b	-317.00259	0.00139	0.00136303	-317.00123	
Ag_3I_3	Isomer 1	Figure 3c	-475.55288	0.002637	0.00258584	-475.55029	0
	Isomer 2		-475.42943	0.002286	0.00224165	-475.42719	77.25012646
Ag_2			-294.04301	0.000406	0.00039812	-294.04261	

(a) The isomer number as it appears in the supplementary material part A.
(b) The figure where the relevant structure is shown.
(c) The converged geometries B3LYP/SDD energies.
(d) Zero point energy.
(e) ZPE x 0.9806.
(f) The sum of the B3LYP/SDD energy and ZPE scaled.
(g) The relative energy to the most stable isomer in each case.
(h) This structure has been previously calculated; e.g.; P. Weis, T. Bierweiler, S. Gilb, M. M. Kappes, *Chem. Phys. Lett.*, 2002, **355**, 355

Table S2: Calculated energetics for the ion-molecule reactions.

Reaction		**Reaction ΔH in kcal.mol^{-1}** [b]
Benchmark BDE of allyliodide	**Experimental value**	
$CH_2=CHCH_2I \rightarrow I^{\bullet} + CH_2=CHCH_2^{\bullet}$	+45.6 ± 0.9 [c]	+39.5
Ion-molecule reactions with allyliodide	**Relevant eq. in text (reactants, products)** [a]	
$Ag_2H^+ + CH_2=CHCH_2I \rightarrow Ag_2I^+ + CH_2=CHCH_3$	(6)	-42.8
$Ag_3^+ + CH_2=CHCH_2I \rightarrow Ag_3I^+ + CH_2=CHCH_2^{\bullet}$	does not occur	+12.5
$Ag_3^+ + 2CH_2=CHCH_2I \rightarrow Ag_3I_2^+ + (CH_2=CHCH_2)_2$	(7) and (8)	-66.0
$Ag_4H^+ + CH_2=CHCH_2I \rightarrow Ag_4I^+ + CH_2=CHCH_3$	(9)	-43.1
$Ag_4I^+ + CH_2=CHCH_2I \rightarrow Ag_4I_2^+ + CH_2=CHCH_2^{\bullet}$	(10a)	+3.2
$Ag_4I_2^+ + CH_2=CHCH_2I \rightarrow Ag_4I_3^+ + CH_2=CHCH_2^{\bullet}$	(11)	-31.6
$Ag_4I^+ + 2CH_2=CHCH_2I \rightarrow Ag_4I_3^+ + (CH_2=CHCH_2)_2$	(10b) and (12)	-79.9
$Ag_5^+ + CH_2=CHCH_2I \rightarrow Ag_5I^+ + CH_2=CHCH_2^{\bullet}$	(13b)	+2.3
$Ag_5^+ + 2\ CH_2=CHCH_2I \rightarrow Ag_4I^+ + AgI + (CH_2=CHCH_2)_2$		-38.2
$Ag_5I^+ + CH_2=CHCH_2I \rightarrow Ag_5I_2^+ + CH_2=CHCH_2^{\bullet}$	(14)	-30.7
$Ag_5I_2^+ + 2CH_2=CHCH_2I \rightarrow Ag_5I_4^+ + (CH_2=CHCH_2)_2$	(16b) and (17)	-83.2

$Ag_5I_2^+ + CH_2{=}CHCH_2I \rightarrow Ag_5I_3^+ + CH_2{=}CHCH_2^{\bullet}$	(16a)	+0.7
$Ag_5I_3^+ + CH_2{=}CHCH_2I \rightarrow Ag_5I_4^+ + CH_2{=}CHCH_2^{\bullet}$	(18)	-32.4

Table S3: Calculated reaction energetics for CID reactions

Reactions (eq. number in text)	**SDD Reaction ΔH in kcal.mol^{-1} [b]**
$Ag_2I^+ \rightarrow Ag^+ + AgI$ (eq. 24c)	+48.4
$Ag_3I_2^+ \rightarrow Ag_2I^+ + AgI$ (eq. 24c)	+35.6
$Ag_3I_2^+ \rightarrow Ag^+ + Ag_2I_2$ (eq. 24d)	+49.1
$Ag_4I^+ \rightarrow Ag_3^+ + AgI$ (eq. 24c)	+28.8
$Ag_4I^+ \rightarrow Ag_2I^+ + Ag_2$ (eq. 24b)	+42.2
$Ag_4I_2^+ \rightarrow Ag_3I_2^+ + Ag$ (eq. 24a)	+24.6
$Ag_4I_2^+ \rightarrow Ag_3I^+ + AgI$ (eq. 24c)	+38.1
$Ag_4I_3^+ \rightarrow Ag_3I_2^+ + AgI$ (eq. 24c)	+42.7
$Ag_4I_3^+ \rightarrow Ag_2I^+ + Ag_2I_2$ (eq. 24d)	+43.5
$Ag_4I_3^+ \rightarrow Ag^+ + Ag_3I_3$ (eq. 24e)	+43.9
$Ag_5I^+ \rightarrow Ag_4I^+ + Ag$ (eq. 24a)	+24.5
$Ag_5I^+ \rightarrow Ag_3I^+ + Ag_2$ (eq. 24b)	+44.6

$Ag_5I^+ \rightarrow Ag_4^+ + AgI$ (eq. 24c)	+30.7
$Ag_5I_2^+ \rightarrow Ag_4I^+ + AgI$ (eq. 24c)	+41.6
$Ag_5I_2^+ \rightarrow Ag_3I_2^+ + Ag_2$ (eq. 24b)	+48.2
$Ag_5I_2^+ \rightarrow Ag_3^+ + Ag_2I_2$ (eq. 24d)	+35.6
$Ag_5I_4^+ \rightarrow Ag_4I_3^+ + AgI$ (eq. 24c)	+44.8
$Ag_5I_4^+ \rightarrow Ag_3I_2^+ + Ag_2I_2$ (eq. 24d)	+52.7
$Ag_5I_4^+ \rightarrow Ag_2I^+ + Ag_3I_3$ (eq. 24e)	+40.5

(a) The numbers refer to those equation numbers used in the text and figures.
(b) The reaction enthalpy is calculated using the (B3LYP/SDD + ZPE) values
(c) Experimental bond enthalpy value from Blanksby S. J.; Ellison G. B., *Acc. Chem. Res.* **2003**, 36, 255