Supplementary Material For Dalton Trans. Manuscript (Version: 21 April 2005) "Gas Phase Synthesis and Reactivity of Ag_n^+ and $Ag_{(n-1)}H^+$ Cluster Cations." 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

* Corresponding Author: Phone +61 3 8344-2452; FAX: +613 9347-5180, EMAIL: rohair@unimelb.edu.au

List of Supplementary Material:

(A) Cartesian Coordinates for structures shown in Figures 2, 3 and 4;
(B) Supplementary Figures S1 and S2;
(C) Supplementary Tables S1 and S2.

(A) Cartesian Coordinates for structures shown in Figures 2, 3 and 4

structure 1

Ag	1.376951	-0.795392	0.000000
Ag	0.000000	1.589337	0.000000
Ag	-1.376951	-0.793946	0.000000

structure 2a

Ag	2.488199	-0.958795	-0.937246
Ag	2.486446	0.959373	0.937885
Ag	0.000134	-0.000758	-0.000338
Ag	-2.487023	0.944290	-0.952496
Ag	-2.487756	-0.944110	0.952194

structure 2b

Ag	2.538377	-1.247550	0.000000
Ag	0.360393	-2.805131	0.000000
Ag	0.000000	0.000048	0.000000
Ag	-0.360481	2.805210	0.000000
Ag	-2.538288	1.247424	0.000000

structure 3

Ag	0.824089	2.371297	0.496369
Ag	-1.051143	0.430301	0.012889
Ag	-3.043767	-0.788810	-1.603134
Ag	-3.617491	-0.329553	0.961250
Ag	1.754285	-0.195307	0.237686
Ag	3.864922	-1.592151	-1.053912
Ag	3.003804	-2.515888	1.295084

structure 4

Ag	0.000000	0.000000	2.519069

Ag	0.000000	2.395796	0.779047
Ag	0.000000	1.481190	-2.038235
Ag	0.000000	-1.481190	-2.038235
Ag	0.000000	-2.395796	0.779047
Ag	1.380987	0.000000	-0.000346
Ag	-1.380987	0.000000	-0.000346

structure 5

Ag	0.000000	-0.202575	2.803631
Ag	-2.427355	0.202790	1.402279
Ag	-2.427355	-0.202790	-1.402279
Ag	0.000000	0.202575	-2.803631
Ag	2.427355	-0.202790	-1.402279
Ag	2.427355	0.202790	1.402279
Ag	0.000000	0.000000	0.000000

structure 6

Ag	0.824089	2.371297	0.496369
Ag	-1.051143	0.430301	0.012889
Ag	-3.043767	-0.788810	-1.603134
Ag	-3.617491	-0.329553	0.961250
Ag	1.754285	-0.195307	0.237686
Ag	3.864922	-1.592151	-1.053912
Ag	3.003804	-2.515888	1.295084

structure 7

Ag	0.009807	1.503374	0.000000
Ag	0.009807	-1.503372	0.000000
H	-0.921879	-0.000090	0.000000

structure 8

Ag	-0.445931	-0.000688	0.354415
Ag	-3.442631	0.000109	-0.174330

Ag	1.966926	1.344088	-0.100538
Ag	1.967754	-1.343499	-0.100786
H	-2.167547	-0.000493	0.998236

structure 9

Ag	1.434346	1.612044	-0.002560
Ag	2.550824	-0.948088	0.001999
Ag	-2.551064	-0.947875	0.001580
Ag	-1.434318	1.611747	-0.002932
Ag	0.000698	-0.698599	-1.352700
Ag	-0.000485	-0.688458	1.354658
H	-0.000018	2.783740	-0.002097

structure 10

Ag	0.407899	-1.007382	0.000415
Ag	1.854267	1.444683	0.000382
Ag	-0.978747	1.668415	-0.000618
Ag	-2.216066	-0.573668	-1.349263
Ag	-2.216646	-0.572407	1.349412
Ag	3.138938	-1.020972	0.000112
H	0.485550	2.748577	0.000174

structure 11

Ag	0.476610	-0.000003	2.706190
Ag	0.207071	2.503227	1.195377
Ag	-0.294298	2.089080	-1.674625
Ag	-0.292945	-2.089079	-1.674863
Ag	0.205946	-2.503225	1.195578
Ag	0.011517	-0.000001	0.046555
H	-0.313902	0.000000	-1.794212

structure 12

Ag	0.822985	2.526358	-0.046732
Ag	-0.966440	0.441113	-0.010529
Ag	-3.138892	-0.815149	-1.331407
Ag	-3.175224	-0.718010	1.337402
Ag	1.869731	0.020379	0.049266
Ag	4.527950	-1.421234	-0.001196
H	2.814789	-1.572555	0.150214

structure 13a

C	4.552578	3.406767	0.030227
Ag	-0.246003	-0.238982	-0.003478
N	3.822129	2.515161	0.022206
Ag	-2.679142	0.355684	-1.332560
Ag	-2.683122	0.310738	1.337852
Ag	2.449508	0.654675	0.004950
H	5.234239	4.237216	0.038579
Ag	1.896959	-1.981773	-0.014751

structure 13b

N	-4.340908	3.471563	0.072109
Ag	0.246545	-0.298574	-0.001942
C	-3.671371	2.522861	0.040318
Ag	2.679273	0.289337	1.336527
Ag	2.658838	0.383499	-1.331556
Ag	-2.442924	0.675350	0.008252
H	-4.926492	4.288136	0.102978
Ag	-1.921709	-1.979957	-0.029358

structure 14a

N	0.359994	-0.211343	0.042169
Ag	-4.298137	-1.231387	-0.058857
C	1.518483	-0.337999	0.062430
Ag	-1.803734	-0.012361	0.007732
Ag	-4.161076	1.450176	0.022016

Ag	3.614782	-0.600796	0.094414
H	5.352162	-0.978056	0.147213
Ag	6.286824	0.489803	-0.082686

structure 14b

C	-0.354718	-0.132730	0.120373
Ag	4.290684	-1.246582	-0.183562
N	-1.516393	-0.211046	0.188915
Ag	1.786131	-0.016460	0.022800
Ag	4.188499	1.413636	0.052746
Ag	-3.613594	-0.460078	0.364049
H	-5.317418	-0.804119	0.606991
Ag	-6.267455	0.374970	-0.312451

structure 15a

H	0.157446	-0.762691	1.697064
Ag	1.550121	-0.259077	0.633832
Ag	-1.375246	-0.446972	0.972186
Ag	3.757609	-1.038050	-0.919567
Ag	3.614585	1.500735	-0.095699
N	-3.372895	-0.128073	0.243677
Ag	-6.476464	0.275693	-0.651951
C	-4.477601	0.023286	-0.087738

structure 15b

H	0.169491	-0.506988	1.751263
Ag	1.571071	-0.184250	0.660640
Ag	-1.393454	-0.325408	1.000424
Ag	3.757154	-1.134078	-0.826799
Ag	3.665848	1.467023	-0.224679
C	-3.378724	-0.130291	0.263698
Ag	-6.505865	0.207715	-0.663888
N	-4.478664	-0.024054	-0.111603

structure 15c

H	2.905008	-1.591851	0.893292
Ag	1.980868	-0.079283	0.332813
Ag	4.174915	-2.065372	-0.177155
Ag	1.303270	2.517790	-0.133758
Ag	-0.712085	0.719381	-0.004799
C	-3.893826	-0.407090	-0.027137
Ag	-5.897419	-0.997029	-0.029448
N	-2.781552	-0.064784	-0.021448

structure 15d

H	2.871315	-1.675581	0.734116
Ag	1.993492	-0.098517	0.277468
Ag	4.334279	-1.924387	-0.148791
Ag	1.247148	2.475531	-0.100767
Ag	-0.750372	0.627333	-0.012048
N	-3.896618	-0.471506	-0.035960
Ag	-5.949850	-0.959451	-0.022093
C	-2.784302	-0.114627	-0.031597

structure 15e

H	0.581404	-2.321997	-0.001076
Ag	0.246427	-0.442822	-0.001957
Ag	2.349194	-2.303973	-0.001016
Ag	2.764874	0.828236	0.004852
Ag	0.557470	2.369264	-0.002860
C	-3.146110	-0.232536	-0.002305
Ag	-5.233443	-0.341268	0.002242
N	-1.982468	-0.203760	-0.006330

structure 15f

H	0.59943	-2.31940	0.00371
Ag	0.20790	-0.45623	0.00402
Ag	2.37835	-2.22562	-0.00022
Ag	2.77091	0.78669	-0.00415

Ag	0.55917	2.33784	0.00180
N	-3.11396	-0.12813	-0.00259
Ag	-5.21668	-0.34944	-0.00204
C	-1.94754	-0.19437	0.00700

structure 16a

C	-3.042204	0.000694	0.000386
Ag	0.317497	-0.000134	0.000491
Ag	-5.136754	-0.000086	-0.000221
Ag	2.743763	-1.344894	-0.000188
Ag	2.743609	1.344964	-0.000188
N	-1.878311	0.000415	0.000380

structure 16b

C	-1.851839	-0.001640	0.063603
Ag	0.305157	-0.001011	0.041042
Ag	2.756110	1.338915	-0.017019
Ag	-5.133097	0.000710	-0.024269
Ag	2.757875	-1.337622	-0.017125
N	-3.019012	-0.005250	0.062116

structure 16c

C	-2.751526	0.377023	-0.003167
Ag	-0.911792	1.530196	-0.007584
Ag	1.301865	-0.017651	1.353604
Ag	-0.878709	-1.419160	0.004735
Ag	1.306854	-0.031537	-1.350658
Ag	-3.135292	-0.738431	0.002063

Figure S1: LCQ CID MS^n spectra of various silver cluster ions: (a) Ag_3^+; (b) Ag_2H^+; (c) Ag_5^+; (d) Ag_4H^+. A * designated the mass selected precursor cluster.

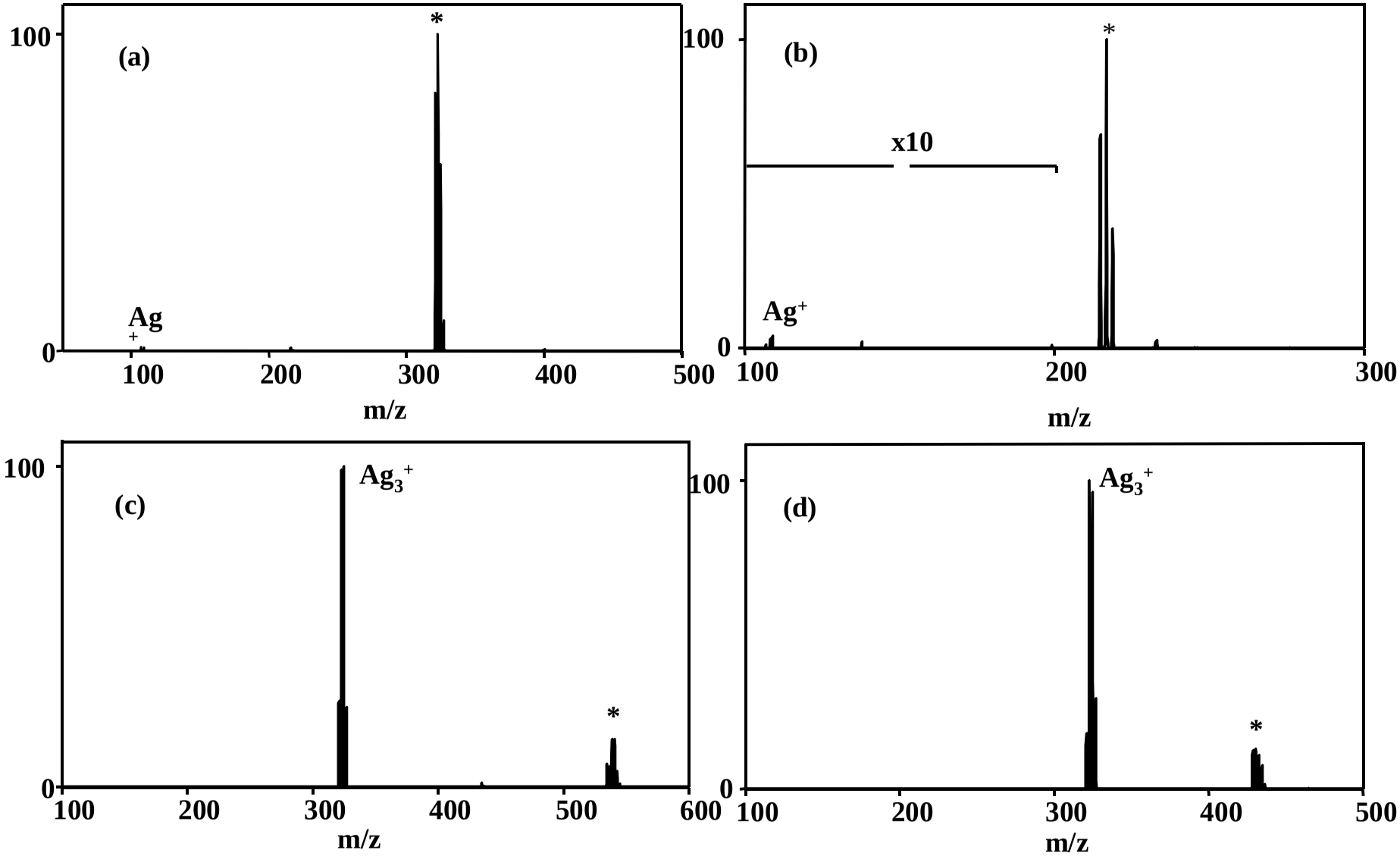

Figure S1: LCQ CID MS^n spectra of various silver cluster ions: (e) Ag_7^+; (f) Ag_6H^+; (g) $Ag_5(H,C,N)^+$; (h) Ag_4CN^+. A * designated the mass selected precursor cluster.

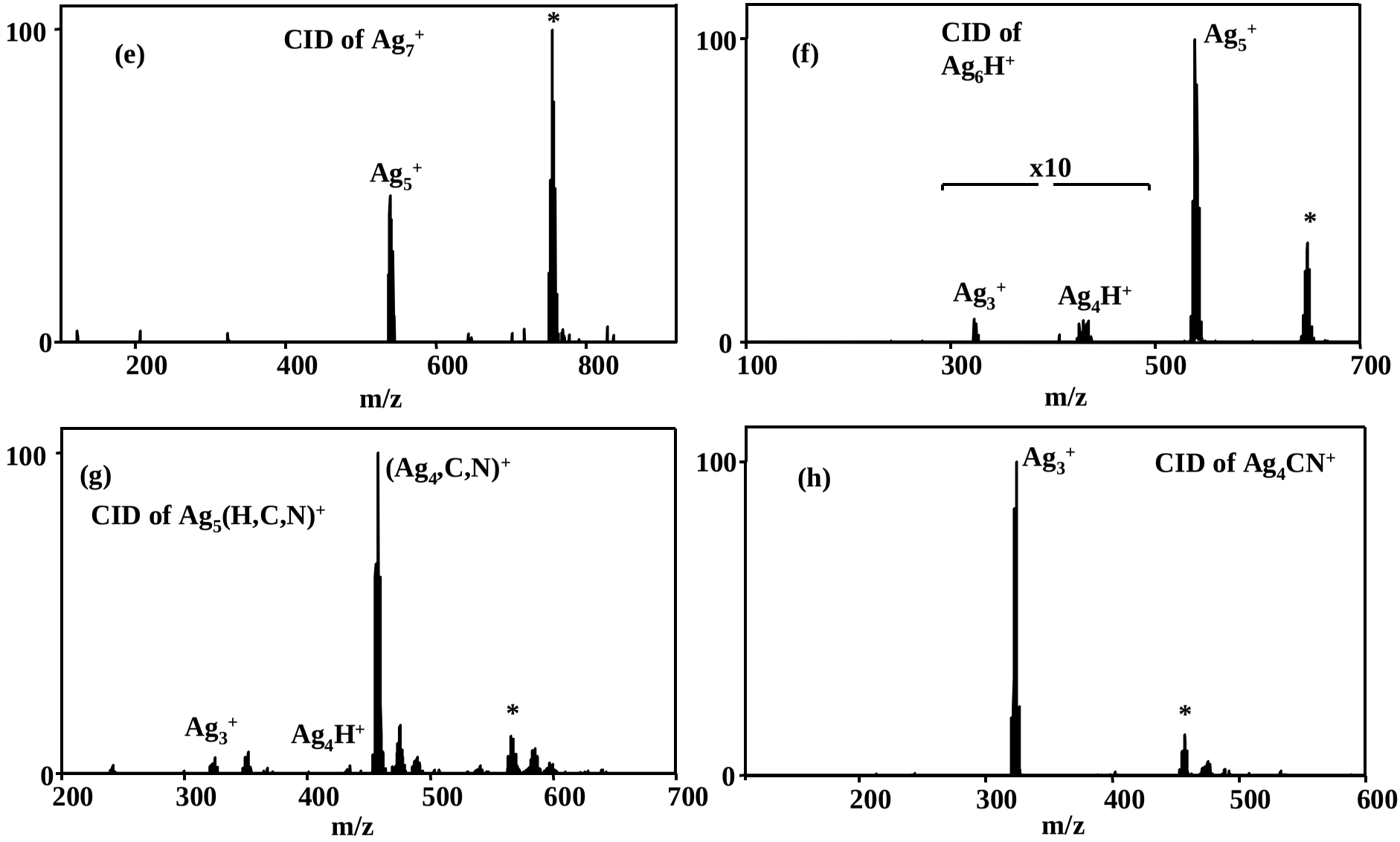

Figure S2: Ion-molecule reactions of silver cluster ions reacting with 2-propanol (L) under similar reaction conditions (pressure of 2-propanol ≈ 10^{-7} torr; reaction time = 0.3 s): (a) Ag_2H^+; (b) Ag_3^+; (c) Ag_4H^+; (d) Ag_5^+.

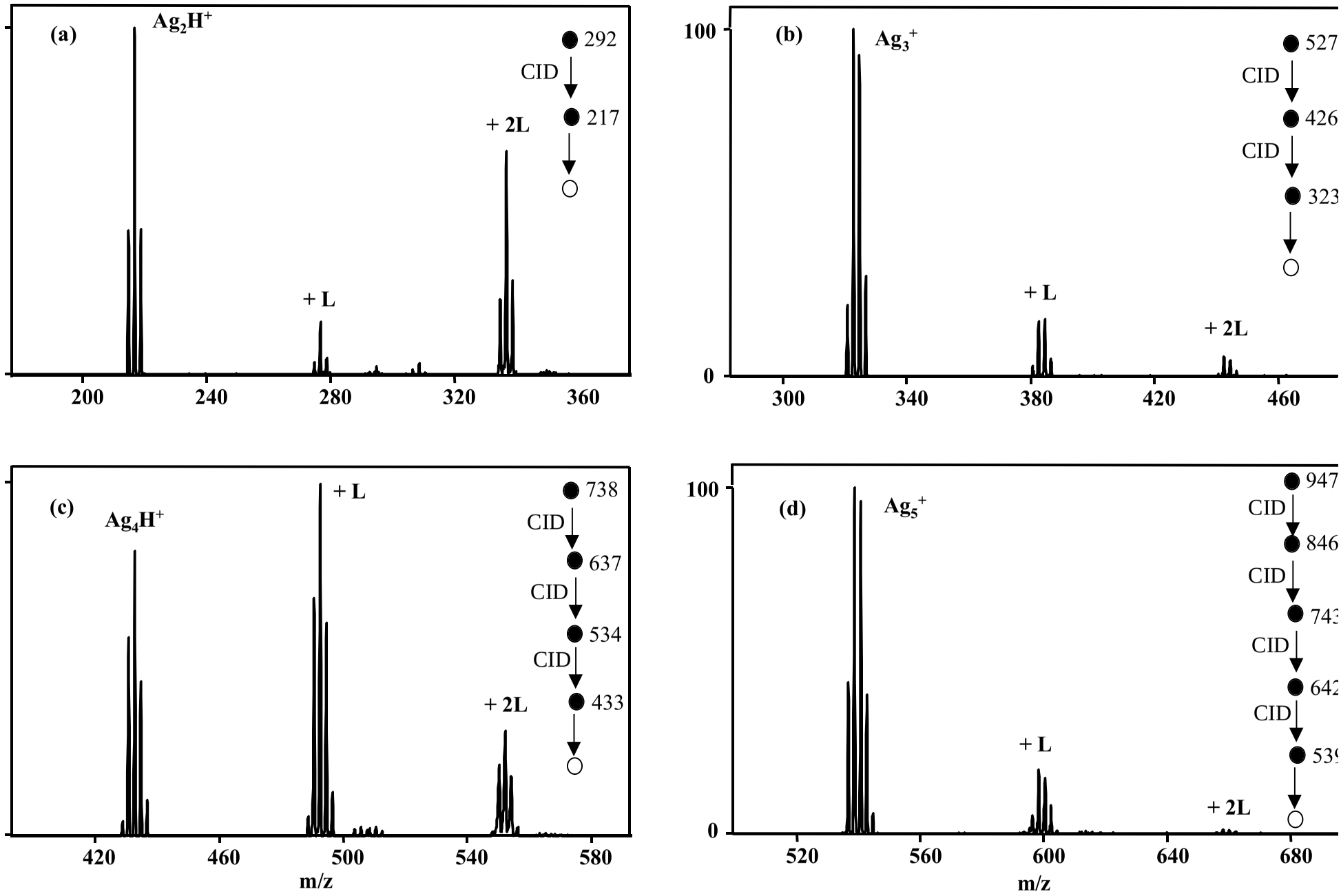

Table S1: DFT calculated energies for various structures relevant to the silver clusters used in the thermochemistry calculations. The scaling factor used is 0.9806 and the basis sets were LanL2DZ for Ag and 6-31G* for C, N and H.

Structure number in Figs. [a]	Structure shown in [b]	E(B3LYP) [c]	E (MP2) (SPE) [d]	ZPE [e]	ZPE Scaled [f]	E(B3LYP) Scaled [g]	E (MP2) Scaled [h]	Relative Energy at B3LYP [i]	Relative Energy at MP2 [j]
Ag^+		-145.47379	-144.71911				-144.71911		
Ag_2		-291.57443	-289.96641	0.000403	0.000395182	-291.57403	-289.9660148		
AgH		-146.34211	-145.516457	0.003867	0.00379198	-146.33832	-145.512665		
Ag_3H		-437.94415	-435.51844	0.005126	0.005026556	-437.93912	-435.5134134		
Ag_3^+, 1	Fig.2	-437.14447	-434.77584	0.000887	0.000869792	-437.1436	-434.7749702		
Ag_2H^+, 7	Fig.2	-291.89609	-290.3135	0.005414	0.005308968	-291.89078	-290.308191		
Ag_5^+, 2a	Fig.2	-728.77211	-724.80309	0.001796	0.001761158	-728.77035	-724.8013288	0	0
, 2b	Fig.2	-728.77094	-724.80295	0.001782	0.001747429	-728.76919	-724.8012026	0.7	0.1
Ag_4H^+, 8	Fig.2	-583.53561	-580.33745	0.006832	0.006699459	-583.52891	-580.3307505		
Ag_7^+, 5	Fig.2	-1020.40999	-1014.85657	0.002981	0.002923169	-1020.4071	-1014.853647	0	9.0
, 4	Fig.2	-1020.399	-1014.87094	0.00307	0.003010442	-1020.396	-1014.86793	6.9	0

Structure number in Figs. [a]	Structure shown in [b]	E(B3LYP) [c]	E (MP2) (SPE) [d]	ZPE [e]	ZPE Scaled [f]	E(B3LYP) Scaled [g]	E (MP2) Scaled [h]	Relative Energy at B3LYP [i]	Relative Energy at MP2 [j]
, 3	Fig.2	-1020.39975	-1014.85741	0.002962	0.002904537	-1020.3968	-1014.854505	6.4	8.4
, 6	Fig.2	-1020.38894	-1014.82227	0.002681	0.002628989	-1020.3863	-1014.819641	13.0	30.3
Ag_6H^+, 9	Fig.2	-875.161074	-870.395586	0.007906	0.007752624	-875.15332	-870.3878334	1.0	0
, 12	Fig.2	-875.15476	-870.36993	0.007593	0.007445696	-875.14731	-870.3624843	4.8	15.9
, 11	Fig.2	-875.16071	-870.38525	0.006867	0.00673378	-875.15398	-870.3785162	0.6	5.8
, 10	Fig.2	-875.16257	-870.38835	0.007767	0.00761632	-875.15495	-870.3807337	0	4.5
Ag_4CN^+, 16a	Fig.4	-675.80619	-672.39938	0.008821	0.008649873	-675.79754	-672.3907301	0	0
, 16c	Fig.4	-675.77056	-672.37414	0.00835	0.00818801	-675.76237	-672.365952	22.1	15.5
Ag_4NC^+, 16b	Fig.4	-675.79987	-672.39548	0.008757	0.008587114	-675.79128	-672.3868929	3.9	2.4
AgH		-146.34211	-145.516457	0.003867	0.00379198		-145.512665		

Structure number in Figs. [a]	Structure shown in [b]	E(B3LYP) [c]	E (MP2) (SPE)[d]	ZPE [e]	ZPE Scaled [f]	E(B3LYP) Scaled [g]	E (MP2) Scaled [h]	Relative Energy at B3LYP [i]	Relative Energy at MP2 [j]
HCN		-93.41988	-93.15355	0.016481	0.016161269		-93.1373887		
HNC		-93.39345	-93.12089	0.015643	0.015339526		-93.1055505		
AgCN		-238.59418	-237.55144	0.006981	0.006845569	-238.58733	-237.5445944		
AgNC		-238.57108	-237.52973	0.006182	0.006062069	-238.56502	-237.5236679		
$Ag_5(NCH)^+$, 13a	Fig. 3	-822.22499	-817.99044	0.019546	0.019166808	-822.20582	-817.9712732	0	0
HCN		-93.41988	-93.15355	0.016481	0.016161269	-93.403719	-93.13738873		
$Ag_5(CNH)^+$, 13b	Fig. 3	-822.21073	-817.96932	0.019638	0.019257023	-822.19147	-817.950063	9.0	13.3
HNC		-93.39345	-93.12089	0.015643	0.015339526	-93.37811	-93.10555047		
$(Ag_3)(NC)(Ag_2H)^+$, 14a	Fig. 3	-822.20791	-817.98299	0.015674	0.015369924	-822.19254	-817.9676201	8.3	2.3
$(Ag_3)(NC)(Ag)^+$,		-675.80619	-672.399344	0.00882	0.008648892	-675.79754	-672.3906951		
$(Ag_3)(CN)(Ag_2H)^+$, 14b	Fig. 3	-822.20671	-817.98145	0.015771	0.015465043	-822.19124	-817.965985	9.1	3.3
$(Ag_3)(NC)(Ag)^+$,		-675.79987	-672.39548	0.008757	0.008587114	-675.79128	-672.3868929		
$(Ag_4H)(NCAg)^+$, 15a	Fig. 3	-822.20292	-817.97903	0.01584	0.015532704	-822.18739	-817.9634973	11.6	4.9

Structure number in Figs. [a]	Structure shown in [b]	E(B3LYP) [c]	E (MP2) (SPE)[d]	ZPE [e]	ZPE Scaled [f]	E(B3LYP) Scaled [g]	E (MP2) Scaled [h]	Relative Energy at B3LYP [i]	Relative Energy at MP2 [j]
$(Ag_4H)(CNAg)^+$, 15b	Fig. 3	-822.19709	-817.976115	0.015707	0.015402284	-822.18169	-817.9607127	15.1	6.6
$(Ag_4H)(NCAg)^+$, 15c	Fig. 3	-822.18821	-817.964597	0.014682	0.014397169	-822.17381	-817.9501998	20.1	13.2
$(Ag_4H)(CNAg)^+$, 15d	Fig. 3	-822.18084	-817.959864	0.014647	0.014362848	-822.16648	-817.9455012	24.7	16.2
$(Ag_4H)(NCAg)^+$, 15e	Fig. 3	-822.1742	-817.950649	0.014713	0.014427568	-822.15977	-817.9362214	28.9	22.0
$(Ag_4H)(CNAg)^+$, 15f	Fig. 3	-822.16827	-817.947264	0.014718	0.014432471	-822.15384	-817.9328315	32.6	24.1

(a) The Structure name and number as it appears in the figures in the text.
(b) The figure where the relevant structure is shown.
(c) The converged geometries B3LYP energies.
(d) The single point energy at the MP2 level.
(e) Zero point energy.
(f) ZPE x 0.9806.
(g) The sum of the B3LYP energy and ZPE scaled.
(h) The sum of the MP2 energy and ZPE scaled.
(i) Energies (in kcal mol^{-1}) of the various isotopomers relative to the most stable one at B3LYP.
(j) Energies (in kcal mol^{-1}) of the various isotopomers relative to the most stable one at MP2.

Table S2: Calculated reaction energetics for various reactions discussed in text.

CID reaction	Relevant Structures in text (reactants, products) [a]	B3LYP Reaction ΔH in kcal mol^{-1} [b]	MP2 Reaction ΔH in $kcal.mol^{-1}$ [c]
$Ag_3^+ \rightarrow Ag^+ + Ag_2$	(1)	60.1	56.4
$Ag_2H^+ \rightarrow Ag^+ + AgH$	(7)	49.4	48.0
$Ag_3^+ + AgH \rightarrow Ag_2H^+ + Ag_2$	(1, 7)	10.7	8.4
$Ag_5^+ \rightarrow Ag_3^+ + Ag_2$	(2a, 1)	33.1	37.9
$Ag_4H^+ \rightarrow Ag_3^+ + AgH$	(8, 1)	29.5	27.1
$Ag_5^+ + AgH \rightarrow Ag_4H^+ + Ag_2$	(2a, 8)	3.6	10.8
$Ag_7^+ \rightarrow Ag_5^+ + Ag_2$	(5, 2a)	39.3	54.2
	(4, 2a)	32.4	63.1
	(3, 2a)	32.9	54.7
	(6, 2a)	26.3	32.8

CID reaction	Relevant Structures in text (reactants, products) [a]	B3LYP Reaction ΔH in kcal mol^{-1} [b]	MP2 Reaction ΔH in kcal mol^{-1} [c]
$Ag_6H^+ \rightarrow Ag_5^+ + AgH$	(9, 2a)	28.0	46.3
$\rightarrow Ag_4H^+ + Ag_2$	(9, 8)	31.6	57.1
$\rightarrow Ag_3^+ + Ag_3H$	(9, 1)	44.3	62.4
$Ag_7^+ + AgH \rightarrow Ag_6H^+ + Ag_2$	(4, 9)	4.4	16.8
$Ag_5HCN^+ \rightarrow \boldsymbol{Ag_5^+} + HCN$	(13a, 2a)	19.9	20.4
	(13b, 2a)	27.0	27.1
$Ag_5HCN \rightarrow \boldsymbol{Ag_4H^+} + AgCN$	(15a, 8)	44.6	55.3
	(15b, 8)	55.1	66.7
	(15c, 8)	36.1	47.0
	(15d, 8)	45.5	57.2
	(15e, 8)	27.3	38.2
	(15f, 8)	37.6	49.2

CID reaction	Relevant Structures in text (reactants, products) [a]	B3LYP Reaction ΔH in kcal mol^{-1} [b]	MP2 Reaction ΔH in kcal mol^{-1} [c]
$Ag_5HCN \rightarrow \mathbf{Ag_4CN^+} + AgH$	(14a, 16a)	35.6	40.3
	(14b, 16b)	38.7	41.7
	(15c, 16a)	23.8	29.4
	(15d, 16b)	23.1	28.8
	(15e, 16a)	15.0	20.6
	(15f, 16b)	15.2	20.9

(a) The numbers refer to those used in the text and figures.
(b) The reaction enthalpy is calculated using the (B3LYP + ZPE) values.
(c) The reaction enthalpy is calculated using the (MP2 + ZPE) values