**Supplementary Material For Dalton Trans. Manuscript B700132K (Version: April 5, 2007) "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" 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:**



**Supplementary Figure Captions:**

**Figure S1.** Ion-molecule reactions of 2-iodoethanol ($ICH_2CH_2OH$) with: (a) $Ag_2H^+$ (pressure = *ca* $1.6x10^{-7}$ Torr; reaction time = 300ms); (b) $Ag_3^+$ (pressure = *ca* $1.6x10^{-7}$ Torr; reaction time = 300ms); (c) $Ag_4H^+$ (pressure = *ca* $1.6x10^{-7}$ Torr; reaction time = 300ms). The "^" denotes addition of background water and "&" addition of background MeOH. The asterisk denotes the selected peak.

**Figure S2.** Ion-molecule reactions of 2-iodoethanol ($ICH_2CH_2OH$) with: (a) $Ag_5(ICH_2CH_2OH)^+$ (pressure = *ca* $1.4x10^{-7}$ Torr; reaction time = 300ms); (b) $Ag_5HOI^+$ (pressure = *ca* $1.4x10^{-7}$ Torr; reaction time = 30ms). The "^" denotes addition of background water

and "&" addition of background MeOH, the "#" denotes a noise peak. The asterisk denotes the selected peak.

**Figure S3.** CID spectra of $Ag_5HOI^+$. The peaks at *m/z* 793, 965 and 1137 arise from competing ion-molecule reactions of $Ag_5HOI^+$ with $ICH_2CH_2OH$ (See fig. S2b): (a) short CID time (15 ms); (b) longer CID time (30 ms); (c) ion-molecule reaction of 2-iodoethanol ($ICH_2CH_2OH$) with $Ag_4OH^+$.

**Fig. S1**Ion-molecule reactions of 2-iodoethanol ($ICH_2CH_2OH$) with: (a) $Ag_2H^+$ (pressure = *ca* $1.6x10^{-7}$ Torr; reaction time = 300ms); (b) $Ag_3^+$ (pressure = *ca* $1.6x10^{-7}$ Torr; reaction time = 300ms); (c) $Ag_4H$ (pressure = *ca* $1.6x10^{-7}$ Torr; reaction time = 300ms). The "^" denotes addition of background water and "&" addition of background MeOH. The asterisk denotes the selected peak.

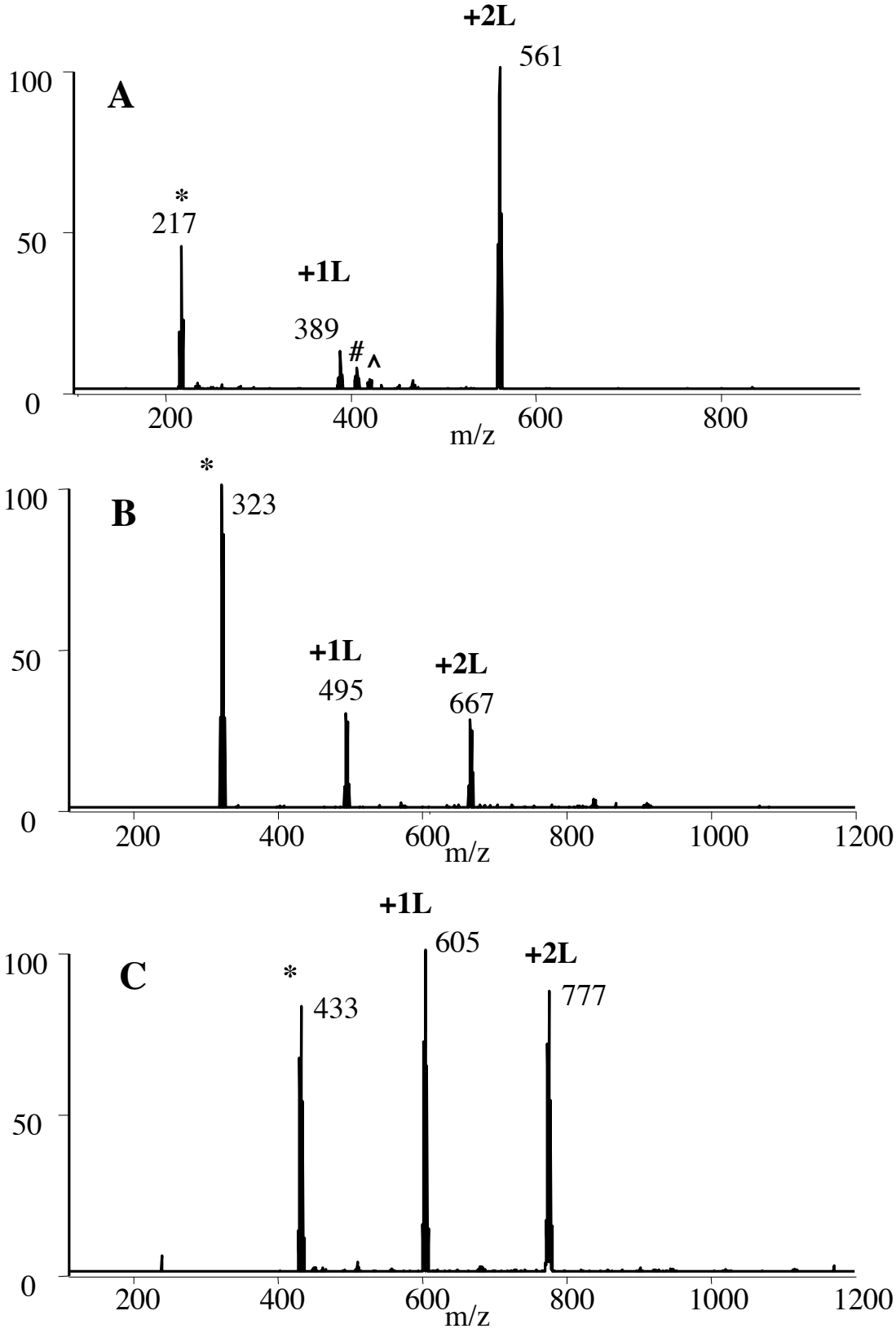


**Fig. S 2(a):** Ion-molecule reactions of 2-iodoethanol ($ICH_2CH_2OH$) with: $Ag_5(ICH_2CH_2OH)^+$ (pressure = *ca* $1.4x10^{-7}$ Torr; reaction time = 300ms)

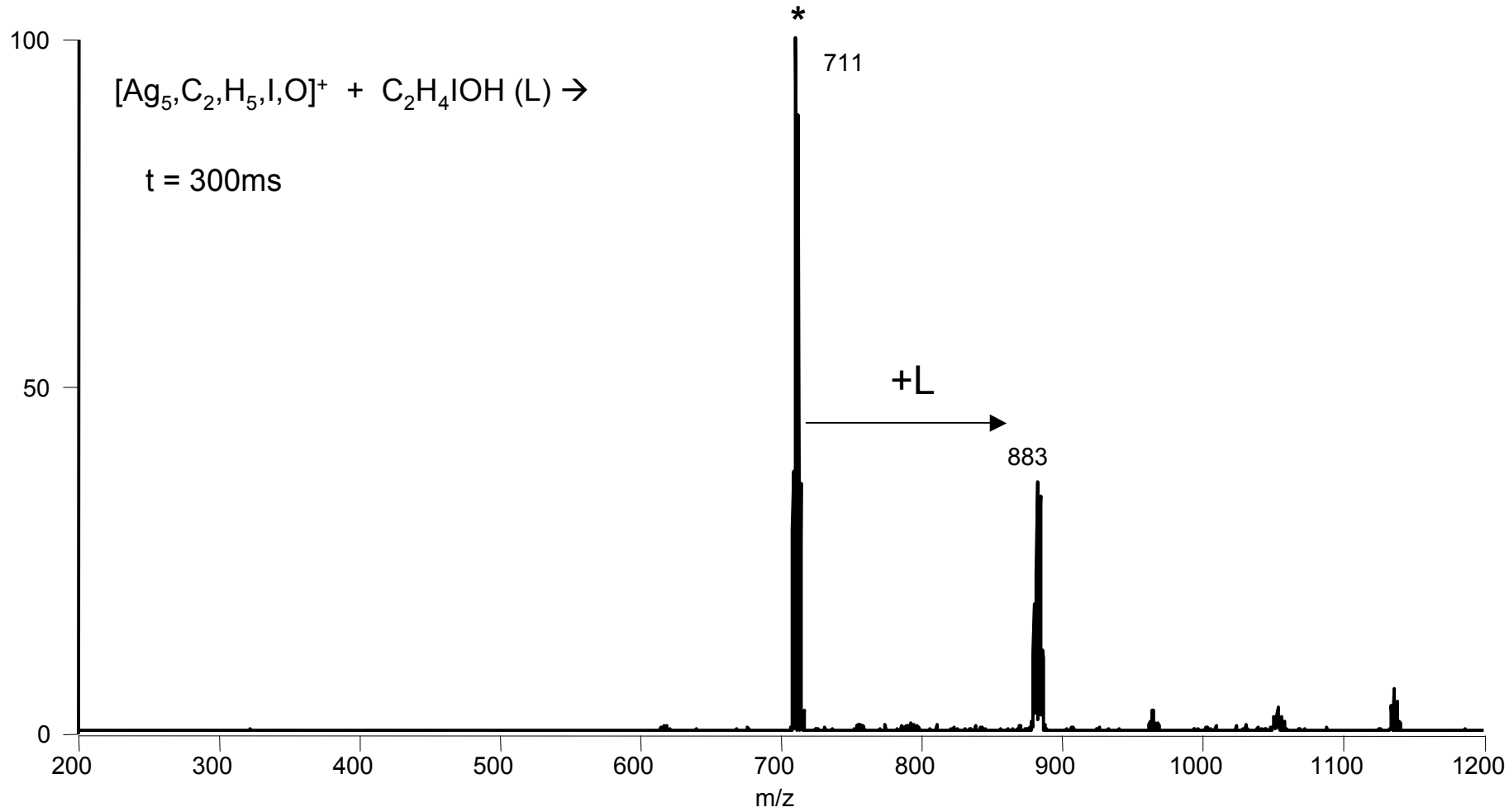


**Fig. S 2(b):** Ion-molecule reactions of 2-iodoethanol ($ICH_2CH_2OH$) with $Ag_5(I,O,H)^+$ (pressure = *ca* $1.4x10^{-7}$ Torr; reaction time = 30ms). The "^" denotes addition of background water and "&" addition of background MeOH, the "#" denotes a noise peak. The asterisk denotes the selected peak.

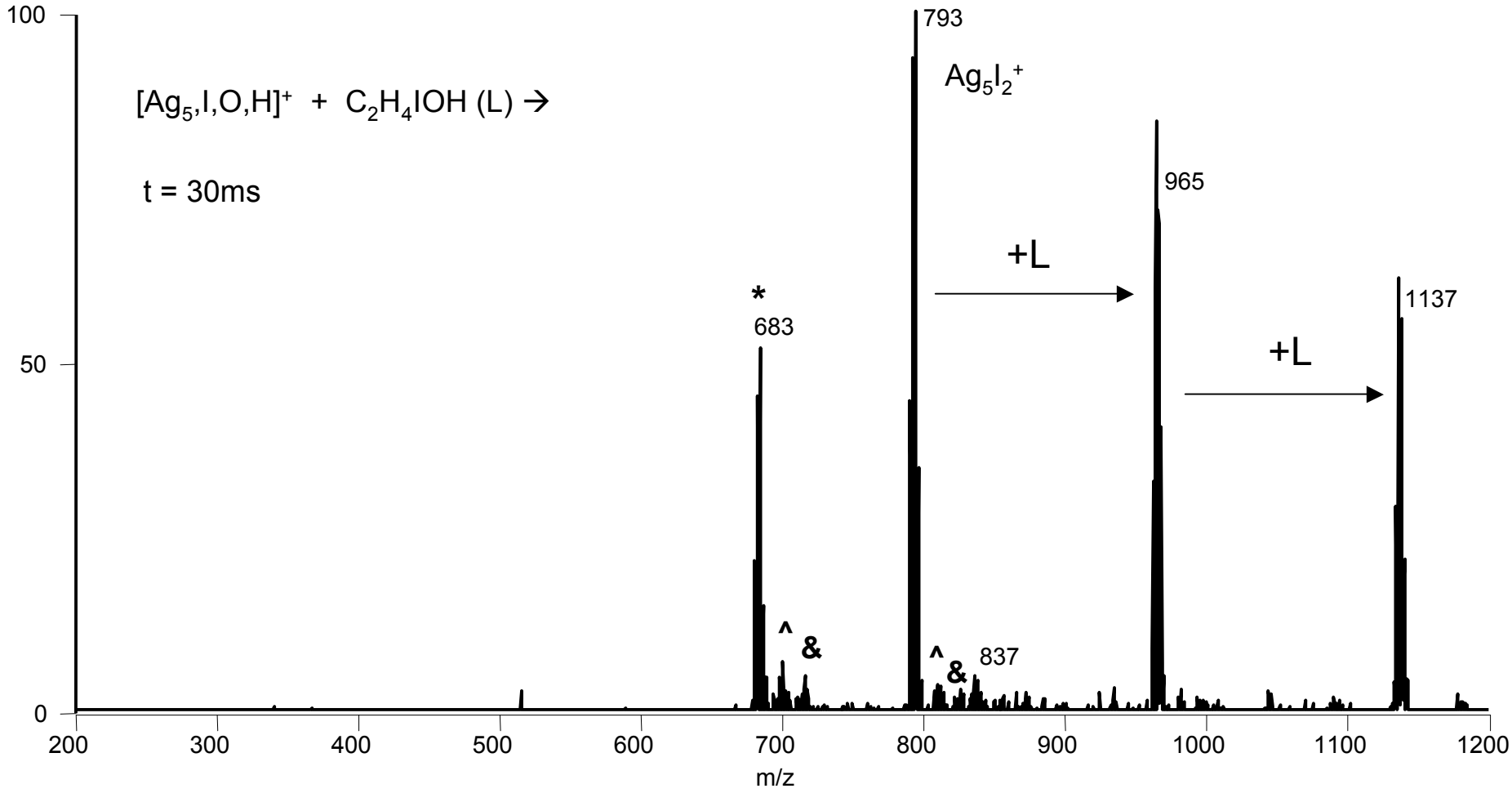


**Fig. S 3(a)**

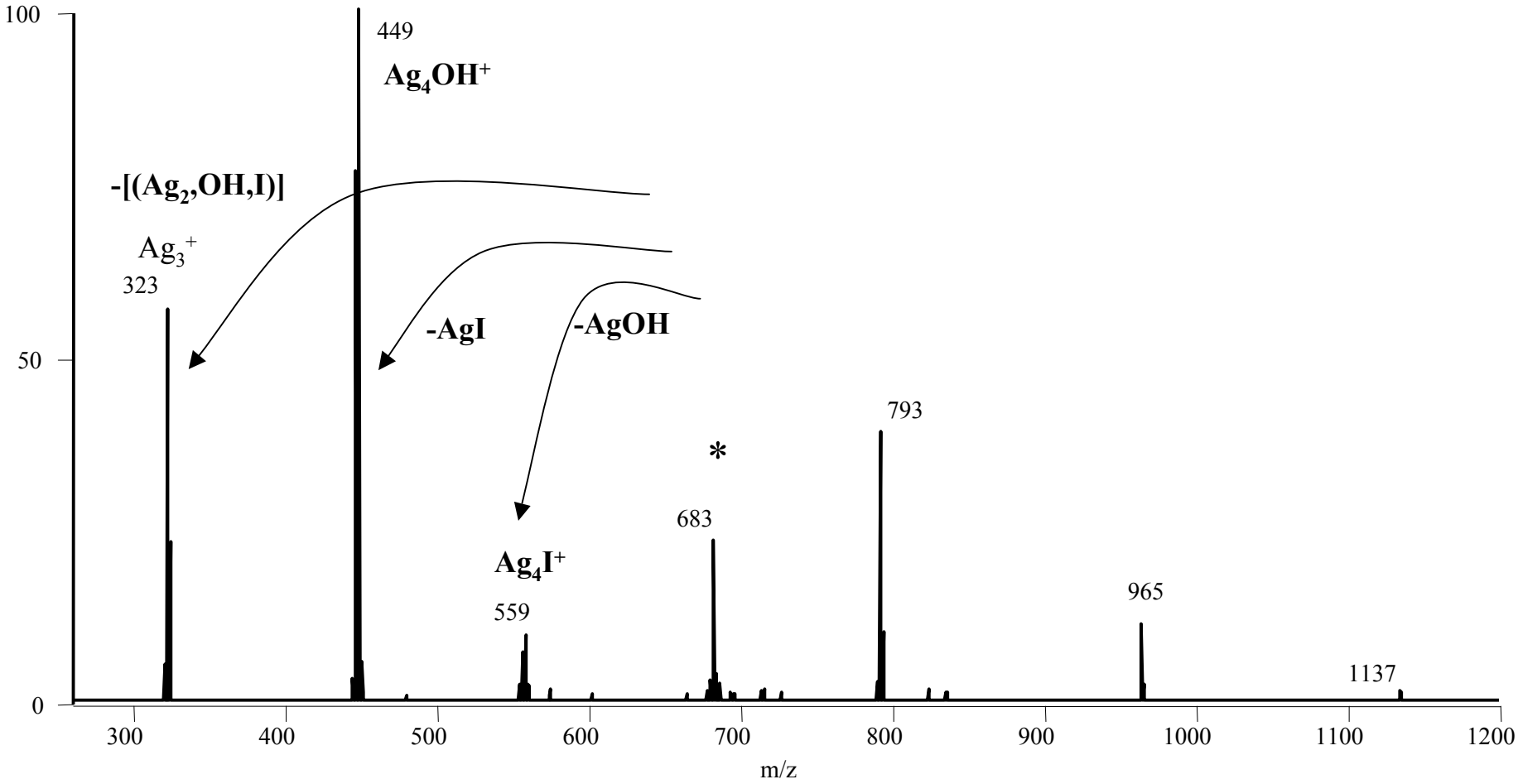

100
50
0
449
$Ag_4OH^+$
-[($Ag_2$,OH,I)]
$Ag_3^+$
323
-AgI
-AgOH
*
793
683
$Ag_4I^+$
559
965
1137
300
400
500
600
700
800
900
1000
1100
1200
m/z

**Fig. S 3(b)**

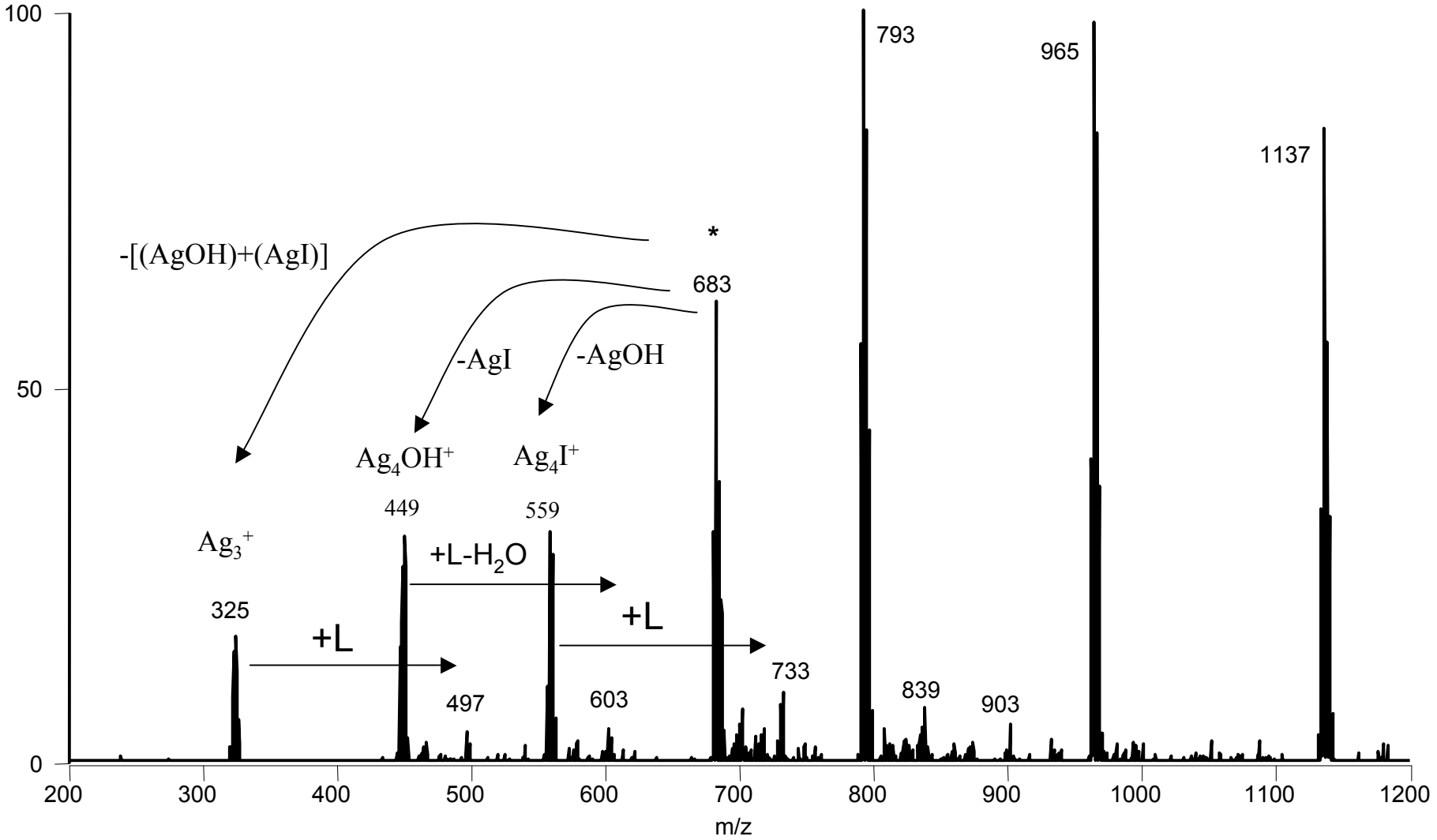
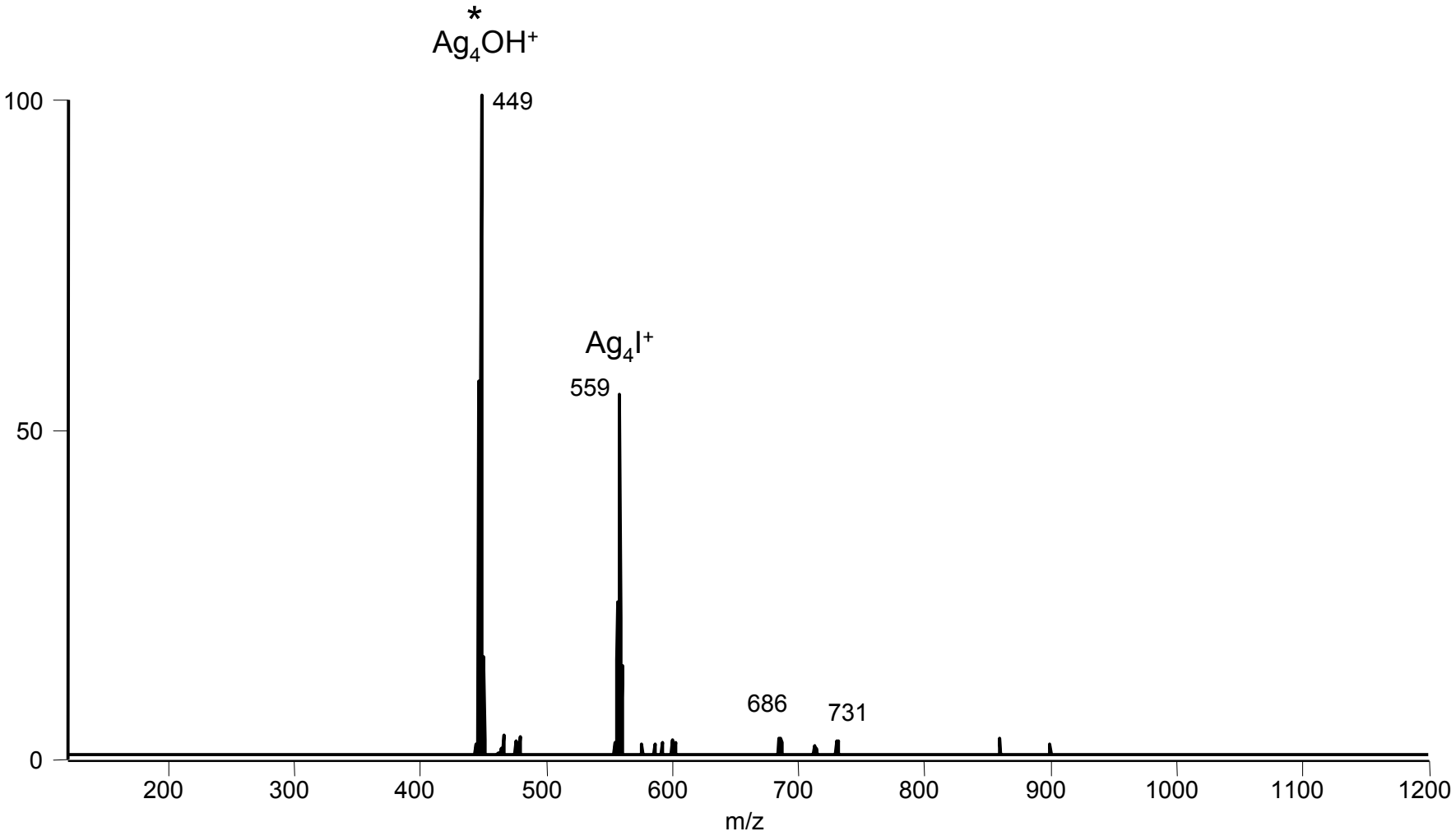

100
50
0
200
300
400
500
600
700
800
900
1000
1100
1200
m/z
793
965
1137
*
683
-[(AgOH)+(AgI)]
-AgI
-AgOH
$Ag_4OH^+$
$Ag_4I^+$
449
559
$Ag_3^+$
325
+L-$H_2O$
+L
+L
497
603
733
839
903

**Fig. S 3(c)**

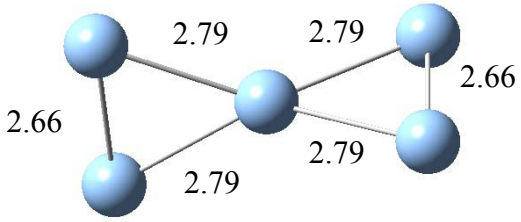

*
$Ag_4OH^+$
449
$Ag_4I^+$
559
686
731
100
50
0
200
300
400
500
600
700
800
900
1000
1100
1200
m/z

**(A) Cartesian Coordinates for structures shown in Figures 2 and 3. All calculations carried out at the B3LYP/6-31G* level of theory with the SDD ECP for Ag and I.**

**$Ag_5^+$ "bow-tie" isomer (1) (Figure 2a)**

E(B3LYP) = -734.9407527 (0 imag. Freq.), ZPC = 0.001823

| | | | |
|---|---|---|---|
| Ag | 2.459670 | -0.943020 | -0.937226 |
| Ag | 2.458700 | 0.943446 | 0.937622 |
| Ag | 0.000001 | -0.000623 | -0.000279 |
| Ag | -2.459000 | 0.943265 | -0.937549 |
| Ag | -2.459372 | -0.943068 | 0.937432 |

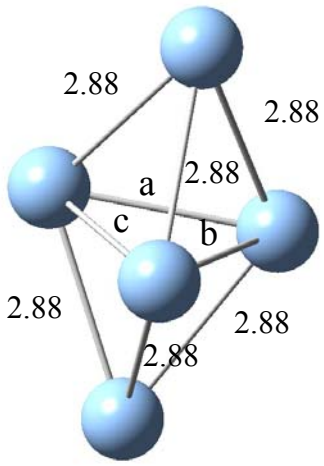



**(1)**

**$Ag_5^+$ "trigonal bipyramidal" isomer (2) (Figure 2b)**

E(B3LYP)=-734.9145446 (2 small imag. Freq.; -21.6 and -18.1) ZPC = 0.001731

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 0.000000 | 1.373613 | -0.792884 |
| 2 | 47 | 0 | 0.000000 | -1.373613 | -0.792884 |
| 3 | 47 | 0 | 0.000000 | 0.000000 | 1.586786 |
| 4 | 47 | 0 | -2.400133 | 0.000000 | -0.000509 |
| 5 | 47 | 0 | 2.400133 | 0.000000 | -0.000509 |



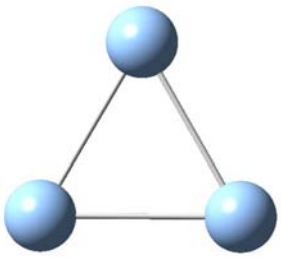

a = b = c = 2.75

**(2)**

**$Ag_3^+$**

E(B3LYP) =-440.842526, (0 imag. Freq.)  ZPC = 0.000896

| | | | |
|---|---|---|---|
| Ag | 1.365972 | -0.789317 | 0.000000 |
| Ag | 0.000000 | 1.576555 | 0.000000 |
| Ag | -1.365972 | -0.787238 | 0.000000 |



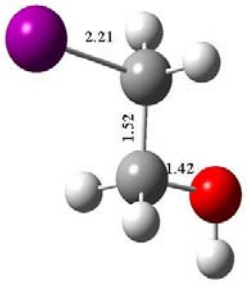
**(3)**

**$ICH_2CH_2OH$ (Figure 2c).**

E(B3LYP) = -165.842973; (0 imag. Freq.)  ZPC = 0.070610

| | | | |
|---|---|---|---|
| C | -1.047032 | 0.686404 | 0.000011 |
| I | 1.036615 | -0.036657 | -0.000020 |
| C | -2.023016 | -0.478178 | 0.000030 |

| | | | |
|---|---|---|---|
| O | -3.316744 | 0.112667 | 0.000117 |
| H | -1.146771 | 1.300299 | -0.893732 |
| H | -1.146747 | 1.300297 | 0.893759 |
| H | -1.859958 | -1.103737 | 0.889849 |
| H | -1.860048 | -1.103682 | -0.889843 |
| H | -3.972853 | -0.601048 | -0.000165 |

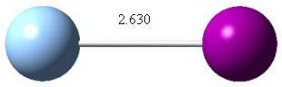



**(5)**

**AgI**

E(B3LYP) =-158.4732823, (0 imag. Freq.)  ZPC = 0.000436

| | | | |
|---|---|---|---|
| Ag | 0.000000 | 0.000000 | -1.393829 |
| I | 0.000000 | 0.000000 | 1.236037 |

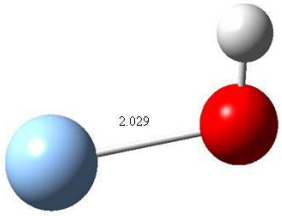



**(6)**

**AgOH**

E(B3LYP) =-222.7978503, (0 imag. Freq.)  ZPC = 0.011498

| | | | |
|---|---|---|---|
| Ag | 0.016722 | -0.330750 | 0.000000 |
| O | 0.016722 | 1.698038 | 0.000000 |
| H | -0.919732 | 1.960947 | 0.000000 |



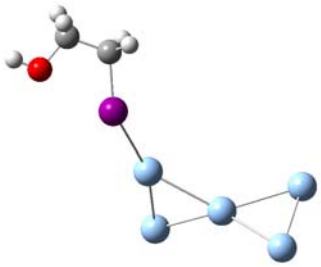

**(7)**

**$Ag_5(IC_2H_4OH)^+$ complexes.**

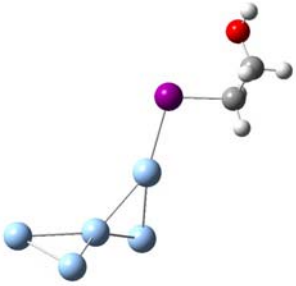
**8a-**
E(B3LYP) =-900.8167765; (0 imag. Freq.) ; ZPC = 0.073161

| | | | |
|---|---|---|---|
| Ag | -3.256732 | 0.413872 | 2.019458 |
| Ag | -3.304767 | -1.784336 | 0.542013 |
| Ag | -1.523454 | 0.254922 | -0.179628 |
| Ag | -0.471877 | 1.709442 | -2.233724 |
| Ag | 1.254289 | 0.501434 | -0.580369 |
| I | 3.670008 | -0.314914 | 0.642641 |
| C | 4.895273 | -0.930590 | -1.133086 |
| C | 5.985069 | -1.879953 | -0.700680 |
| O | 6.796133 | -1.223858 | 0.246747 |
| H | 4.187837 | -1.380457 | -1.827851 |
| H | 5.285853 | 0.015849 | -1.504102 |
| H | 6.542786 | -2.125177 | -1.623052 |
| H | 5.554450 | -2.814323 | -0.311963 |
| H | 7.487012 | -1.831997 | 0.551418 |

**IN**:



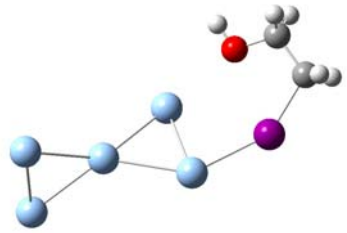
**OUT:**



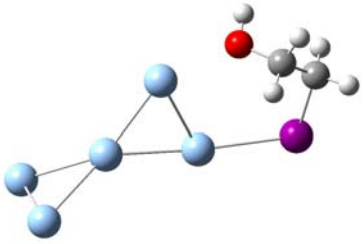
**8b-**
E(B3LYP) =-900.82169;  (0 imag. Freq.) ;  ZPC =   0.073559

| | | | |
|---|---|---|---|
| Ag | -3.763303 | -0.286047 | 1.376109 |
| Ag | -3.803429 | -0.465237 | -1.256147 |
| Ag | -1.364622 | 0.240667 | -0.019197 |
| Ag | 0.787665 | 1.934920 | -0.177892 |
| Ag | 1.256037 | -0.689151 | -0.034014 |
| I | 4.106467 | -1.389047 | -0.005934 |
| C | 5.114860 | 0.585415 | 0.238968 |
| C | 4.233727 | 1.726674 | 0.711746 |
| O | 3.278788 | 2.178079 | -0.251331 |
| H | 5.891758 | 0.365131 | 0.972030 |
| H | 5.565096 | 0.766840 | -0.737753 |
| H | 4.905171 | 2.553051 | 0.990366 |
| H | 3.662129 | 1.450543 | 1.600101 |
| H | 3.730900 | 2.634610 | -0.980217 |

**IN**:



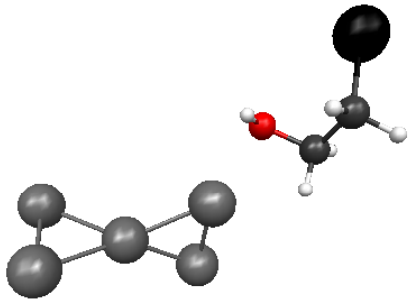
**OUT**:



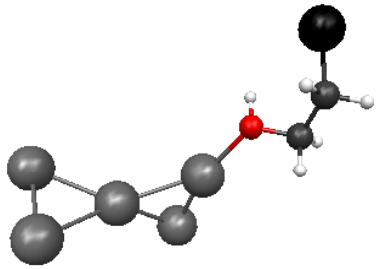
**8c-(unconverged)**

| | | | |
|---|---|---|---|
| Ag | 3.43232989 | -1.59188700 | -1.29580796 |
| Ag | 3.64298701 | -1.31798005 | 1.33183706 |
| Ag | 1.81712306 | 0.31336001 | -0.02818600 |
| Ag | 0.93053102 | 2.89176202 | -0.29030901 |
| Ag | -0.89648300 | 1.00077200 | 0.12927300 |
| O | -2.94299507 | 0.03616800 | 0.39069301 |
| C | -3.97697306 | 0.44088799 | 1.31920695 |
| C | -5.01222992 | -0.64509499 | 1.52204597 |
| I | -6.04576921 | -1.12885404 | -0.37458700 |
| H | -3.46169209 | 0.61605000 | 2.26811910 |
| H | -4.43098783 | 1.38056898 | 0.98585403 |
| H | -5.79523993 | -0.31844300 | 2.20611596 |
| H | -4.57397604 | -1.58360302 | 1.85894704 |
| H | -3.37806106 | -0.24269301 | -0.43891799 |

**IN**:



**OUT: (Unconverged)**

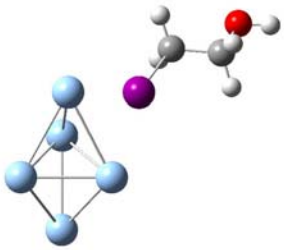


**8d-**

E(B3LYP) =-900.814274 (1 small imag. Freq. -7.29); ZPC = 0.073292

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -3.586054 | -0.945575 | -1.050223 |
| 2 | 47 | 0 | 1.393036 | 0.315112 | -0.347427 |
| 3 | 47 | 0 | -1.395765 | 0.456268 | -0.007023 |
| 4 | 47 | 0 | -3.387049 | -0.712219 | 1.580735 |
| 5 | 47 | 0 | 0.150470 | 2.686679 | -0.318788 |
| 6 | 1 | 0 | 6.950337 | 0.327902 | 2.139946 |
| 7 | 8 | 0 | 6.076035 | 0.747450 | 2.107322 |
| 8 | 6 | 0 | 5.413476 | 0.359192 | 0.921777 |
| 9 | 6 | 0 | 4.746352 | -0.987732 | 1.183528 |
| 10 | 1 | 0 | 4.660277 | 1.126403 | 0.717108 |
| 11 | 1 | 0 | 6.087258 | 0.303241 | 0.056621 |
| 12 | 53 | 0 | 3.471869 | -1.618940 | -0.547384 |
| 13 | 1 | 0 | 5.450562 | -1.814944 | 1.280903 |
| 14 | 1 | 0 | 4.067342 | -0.959611 | 2.034436 |

**IN**:



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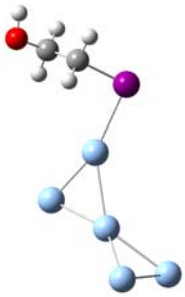
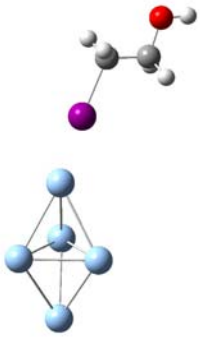


**8e-**
E(B3LYP) = -900.8141639;  (0 imag. Freq.) ;  ZPC =  0.073324

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -1.392228 | 0.438730 | 0.031620 |
| 2 | 47 | 0 | -3.641177 | -0.811628 | -1.076363 |
| 3 | 47 | 0 | 0.103838 | 2.718430 | -0.129259 |
| 4 | 47 | 0 | 1.390717 | 0.385981 | -0.386651 |
| 5 | 47 | 0 | -3.278638 | -0.979170 | 1.543616 |
| 6 | 1 | 0 | 6.631516 | -0.251994 | 2.696322 |
| 7 | 8 | 0 | 5.803630 | 0.245916 | 2.605093 |
| 8 | 6 | 0 | 4.852703 | -0.545776 | 1.923690 |
| 9 | 6 | 0 | 5.121609 | -0.411705 | 0.428083 |
| 10 | 1 | 0 | 4.875229 | -1.598917 | 2.234105 |
| 11 | 1 | 0 | 3.868507 | -0.138062 | 2.173782 |
| 12 | 53 | 0 | 3.540256 | -1.439853 | -0.781958 |
| 13 | 1 | 0 | 5.100994 | 0.623338 | 0.090333 |
| 14 | 1 | 0 | 6.037185 | -0.904741 | 0.098665 |

**IN**:



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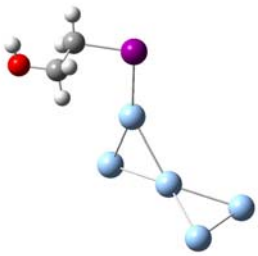
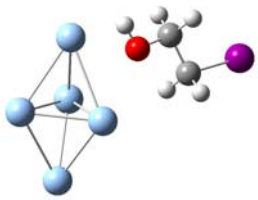


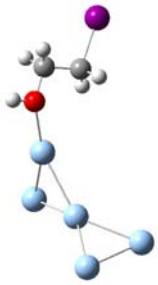
**8f-**
E(B3LYP) = -900.8174116; (0 imag. Freq.) ;  ZPC =  0.073868

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -3.011472 | -2.015761 | -0.995244 |
| 2 | 47 | 0 | 0.848583 | 1.117767 | 0.665345 |
| 3 | 47 | 0 | -1.720716 | 0.310551 | -0.113812 |
| 4 | 47 | 0 | -4.020159 | -0.737125 | 1.096859 |
| 5 | 47 | 0 | -0.578765 | 2.641606 | -0.990387 |
| 6 | 1 | 0 | 2.635776 | 0.955828 | 2.861787 |
| 7 | 8 | 0 | 2.607233 | 0.514462 | 1.996306 |
| 8 | 6 | 0 | 3.971935 | 0.216759 | 1.567950 |
| 9 | 6 | 0 | 3.879649 | -0.689284 | 0.358782 |
| 10 | 1 | 0 | 4.489872 | 1.150611 | 1.328817 |
| 11 | 1 | 0 | 4.485797 | -0.284664 | 2.392758 |
| 12 | 53 | 0 | 5.892897 | -1.191761 | -0.346675 |
| 13 | 1 | 0 | 3.392556 | -1.635111 | 0.594169 |
| 14 | 1 | 0 | 3.383914 | -0.204628 | -0.484386 |

**IN**:



**OUT**:



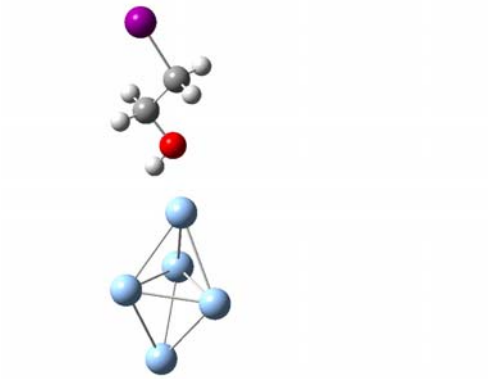
**8g-**

E(B3LYP) = -900.8174116; (0 imag. Freq.) ; ZPC = 0.073868

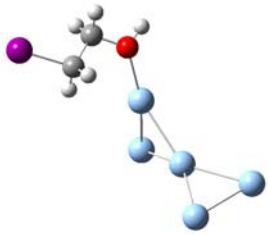
| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 1.720673 | 0.310631 | -0.113746 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 47 | 0 | 0.578947 | 2.641687 | -0.990586 |
| 3 | 47 | 0 | 3.010622 | -2.016244 | -0.994846 |
| 4 | 47 | 0 | -0.848548 | 1.118158 | 0.665343 |
| 5 | 47 | 0 | 4.020257 | -0.737247 | 1.096527 |
| 6 | 1 | 0 | -2.636067 | 0.957166 | 2.861634 |
| 7 | 8 | 0 | -2.607376 | 0.515437 | 1.996342 |
| 8 | 6 | 0 | -3.971950 | 0.216958 | 1.568147 |
| 9 | 6 | 0 | -3.879322 | -0.688463 | 0.358540 |
| 10 | 1 | 0 | -4.485276 | -0.285201 | 2.392843 |
| 11 | 1 | 0 | -4.490592 | 1.150553 | 1.329544 |
| 12 | 53 | 0 | -5.892405 | -1.192041 | -0.346608 |
| 13 | 1 | 0 | -3.384164 | -0.203056 | -0.484536 |
| 14 | 1 | 0 | -3.391503 | -1.634055 | 0.593361 |

**IN** :



**OUT**:

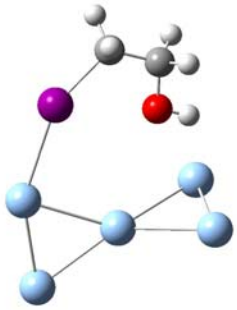


**9a-**

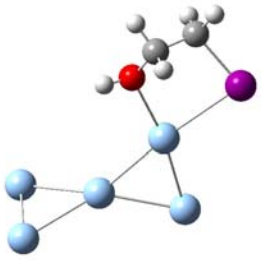
E(B3LYP) =-900.826584;  (0 imag. Freq.) ;  ZPC  =  0.073927

| | | | |
|---|---|---|---|
| Ag | -2.254808 | -3.007613 | 0.921186 |
| Ag | -2.112672 | -2.888770 | -1.717089 |
| Ag | -1.147154 | -0.698249 | -0.239333 |
| Ag | -1.352151 | 2.022026 | -0.234177 |
| Ag | 1.076981 | 0.972994 | 0.174092 |
| I | 3.211356 | 3.034526 | 0.655932 |
| C | 4.595870 | 1.398991 | 1.222460 |
| C | 4.437519 | 0.183731 | 0.342591 |
| O | 3.110050 | -0.352248 | 0.490021 |
| H | 5.589732 | 1.833890 | 1.121014 |
| H | 4.370562 | 1.190810 | 2.267816 |
| H | 5.166051 | -0.562792 | 0.688888 |
| H | 4.645186 | 0.420198 | -0.707487 |
| H | 3.066670 | -1.208573 | 0.035034 |

**IN**:



**OUT**:

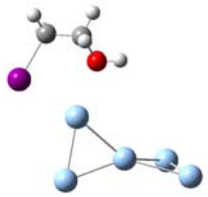


**9a'-**

E(B3LYP) = -900.8265806 (0 imag. Freq) ZPC = 0.073931

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 1.331222 | 0.304049 | -0.018883 |
| 2 | 47 | 0 | -0.407226 | 2.405091 | 0.044626 |
| 3 | 47 | 0 | -1.458157 | -0.055260 | -0.064762 |
| 4 | 47 | 0 | 3.532940 | -0.784218 | 1.348493 |

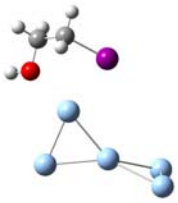
| | | | | | |
|---|---|---|---|---|---|
| 5 | 47 | 0 | 3.753105 | -0.409391 | -1.259956 |
| 6 | 6 | 0 | -3.351840 | -2.876776 | -0.692822 |
| 7 | 8 | 0 | -2.046961 | -2.419600 | -0.293411 |
| 8 | 6 | 0 | -4.398683 | -2.282214 | 0.215763 |
| 9 | 53 | 0 | -4.462736 | -0.069931 | 0.090343 |
| 10 | 1 | 0 | -3.401603 | -3.968166 | -0.572632 |
| 11 | 1 | 0 | -3.545178 | -2.627747 | -1.742719 |
| 12 | 1 | 0 | -4.211343 | -2.497891 | 1.267097 |
| 13 | 1 | 0 | -5.399844 | -2.602074 | -0.071419 |
| 14 | 1 | 0 | -1.376781 | -2.919836 | -0.786258 |



**9b-**

E(B3LYP) =-900.8283383 (0 imag. Freq) ZPC = 0.073870

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 1.124928 | 0.527687 | -0.029132 |
| 2 | 47 | 0 | -0.191976 | 2.922761 | -0.114912 |
| 3 | 47 | 0 | -1.666321 | 0.687211 | 0.001706 |
| 4 | 47 | 0 | 3.248117 | -0.710057 | 1.328114 |
| 5 | 47 | 0 | 3.064861 | -1.059091 | -1.290318 |
| 6 | 6 | 0 | -4.764620 | -1.286636 | -0.348447 |
| 7 | 53 | 0 | -2.731928 | -2.080771 | 0.075856 |
| 8 | 6 | 0 | -5.046969 | -0.011542 | 0.406313 |
| 9 | 8 | 0 | -4.113830 | 1.000885 | 0.001170 |
| 10 | 1 | 0 | -5.435869 | -2.089744 | -0.045896 |
| 11 | 1 | 0 | -4.783822 | -1.149265 | -1.429035 |
| 12 | 1 | 0 | -5.005839 | -0.170581 | 1.490356 |
| 13 | 1 | 0 | -6.065370 | 0.300839 | 0.133787 |
| 14 | 1 | 0 | -4.378340 | 1.851535 | 0.387311 |

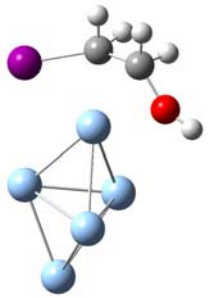


**9b'**.-

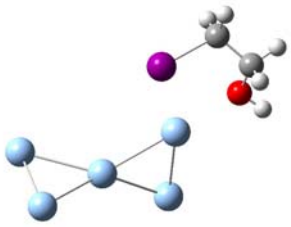
E(B3LYP) = -900.8283462 (0 imag. Freq.) ZPC = 0.073875

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -1.103129 | 0.563675 | 0.019196 |
| 2 | 47 | 0 | -3.205653 | -0.754304 | -1.300698 |
| 3 | 47 | 0 | 0.213187 | 2.964133 | 0.055796 |
| 4 | 47 | 0 | 1.685552 | 0.725988 | -0.002305 |
| 5 | 47 | 0 | -3.009692 | -1.029009 | 1.324414 |
| 6 | 6 | 0 | 4.638310 | -1.435974 | 0.456197 |
| 7 | 6 | 0 | 5.043278 | -0.161997 | -0.242617 |
| 8 | 53 | 0 | 2.604325 | -2.105637 | -0.134032 |
| 9 | 8 | 0 | 4.141493 | 0.891955 | 0.125960 |
| 10 | 1 | 0 | 4.480115 | 1.735996 | -0.213952 |
| 11 | 1 | 0 | 4.585635 | -1.323473 | 1.538555 |
| 12 | 1 | 0 | 5.287012 | -2.267633 | 0.183155 |
| 13 | 1 | 0 | 5.068192 | -0.292505 | -1.330903 |
| 14 | 1 | 0 | 6.055906 | 0.085849 | 0.106788 |

**IN**



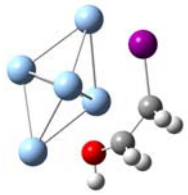
**OUT**



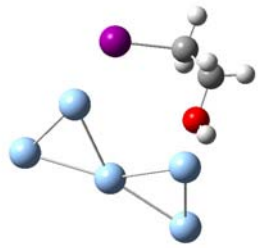
**9c-**
E(B3LYP) =-900.8335442 ( 0 imag. Freq) ZPC =  0.074137

| | | | |
|---|---|---|---|
| Ag | 0.834485 | -1.980878 | -0.277431 |
| Ag | 1.499759 | 0.706395 | 0.023872 |
| Ag | -1.220031 | 1.327253 | -0.036495 |
| Ag | 3.359362 | -1.336645 | 0.223996 |
| Ag | 0.581407 | 3.299358 | -0.052064 |
| C | -2.630339 | -2.194452 | 1.061835 |
| C | -2.307243 | -3.319869 | 0.109550 |
| I | -3.518452 | -0.425766 | 0.050723 |
| O | -1.242037 | -2.931059 | -0.778240 |
| H | -1.222380 | -3.530135 | -1.542525 |
| H | -1.753602 | -1.812033 | 1.585192 |
| H | -3.391811 | -2.496431 | 1.781136 |
| H | -3.184273 | -3.607280 | -0.478422 |
| H | -1.992323 | -4.181877 | 0.715671 |

**IN**:



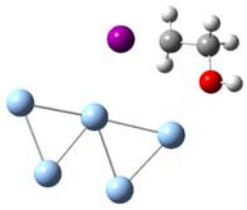
**OUT**:



**9d-**

E(B3LYP) = -900.8244831 (0 imag. Freq) ZPC = 0.073772

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -0.256136 | -0.243739 | 0.077304 |
| 2 | 47 | 0 | 1.706768 | 1.759256 | -0.265610 |
| 3 | 47 | 0 | -0.760271 | 2.496600 | 0.410078 |
| 4 | 47 | 0 | -2.326098 | -2.153843 | -0.035071 |
| 5 | 47 | 0 | -2.867027 | 0.470332 | -0.247020 |
| 6 | 6 | 0 | 3.769642 | -0.865192 | 0.867279 |
| 7 | 53 | 0 | 2.050373 | -2.052947 | 0.090854 |
| 8 | 6 | 0 | 4.578575 | -0.186452 | -0.209802 |
| 9 | 8 | 0 | 3.809578 | 0.855698 | -0.832219 |
| 10 | 1 | 0 | 4.368627 | -1.606806 | 1.396211 |
| 11 | 1 | 0 | 3.325295 | -0.165700 | 1.575667 |
| 12 | 1 | 0 | 4.916746 | -0.902773 | -0.966106 |
| 13 | 1 | 0 | 5.461590 | 0.248353 | 0.282045 |
| 14 | 1 | 0 | 4.321945 | 1.252936 | -1.555180 |



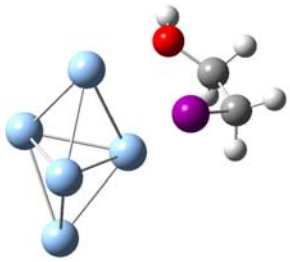
**9e-**

E(B3LYP) = -900.8325944 ( 0 imag. Freq.) ZPC = 0.074046

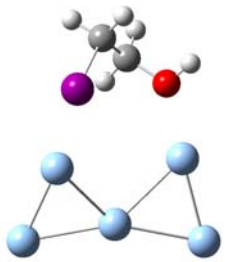
| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 1.464164 | 0.745798 | -0.018696 |
| 2 | 47 | 0 | 1.029346 | -1.998801 | 0.160321 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 47 | 0 | 0.362215 | 3.246172 | 0.337565 |
| 4 | 47 | 0 | -1.291594 | 1.194136 | -0.082630 |
| 5 | 47 | 0 | 3.481027 | -1.125172 | -0.358777 |
| 6 | 53 | 0 | -3.455943 | -0.653419 | -0.597127 |
| 7 | 6 | 0 | -3.394428 | -2.082631 | 1.100996 |
| 8 | 6 | 0 | -2.007909 | -2.327273 | 1.662302 |
| 9 | 1 | 0 | -4.051355 | -1.646624 | 1.854621 |
| 10 | 1 | 0 | -3.854527 | -2.979718 | 0.683507 |
| 11 | 8 | 0 | -1.083089 | -2.874601 | 0.712839 |
| 12 | 1 | 0 | -2.112574 | -3.006861 | 2.520339 |
| 13 | 1 | 0 | -1.554189 | -1.401248 | 2.020935 |
| 14 | 1 | 0 | -1.306032 | -3.798346 | 0.510076 |

**IN**:



**OUT**:



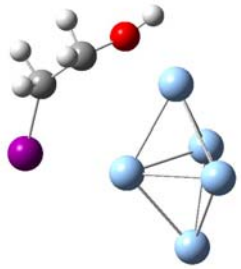
**9f-**

E(B3LYP) = -900.8314317 ( 0 imag. Freq.) ZPC = 0.074026

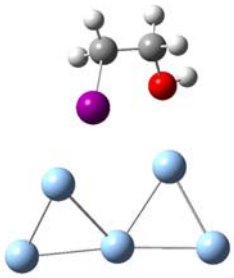
| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 2.111446 | -2.632092 | -0.490301 |
| 2 | 47 | 0 | 1.852942 | 0.072113 | -0.005467 |
| 3 | 47 | 0 | -0.450078 | 1.617740 | -0.111069 |
| 4 | 47 | 0 | -0.245758 | -1.706712 | 0.370932 |
| 5 | 47 | 0 | 1.888703 | 2.812657 | 0.381147 |
| 6 | 6 | 0 | -3.876890 | -0.217812 | 1.123999 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 6 | 0 | -3.618975 | -1.678531 | 1.399068 |
| 8 | 53 | 0 | -3.037002 | 0.479477 | -0.818318 |
| 9 | 8 | 0 | -2.223092 | -1.899345 | 1.679127 |
| 10 | 1 | 0 | -2.135039 | -2.702535 | 2.217838 |
| 11 | 1 | 0 | -3.437900 | 0.437534 | 1.875261 |
| 12 | 1 | 0 | -4.942689 | -0.019085 | 1.013397 |
| 13 | 1 | 0 | -3.950740 | -2.316570 | 0.572688 |
| 14 | 1 | 0 | -4.203587 | -1.932995 | 2.293868 |

**IN**:



**OUT** :



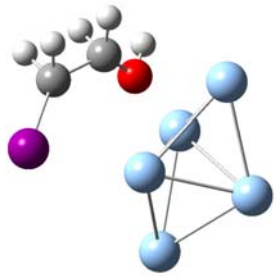
**9g-**

E(B3LYP)= -900.8325564 (0 imag. Freq.) ZPC = 0.074084

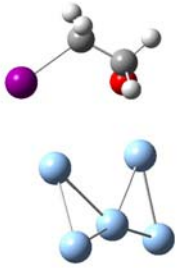
| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 1.308468 | 1.203486 | -0.084043 |
| 2 | 47 | 0 | -1.445223 | 0.744035 | -0.013751 |
| 3 | 47 | 0 | -1.058876 | -2.007100 | 0.230637 |
| 4 | 47 | 0 | -0.350024 | 3.246211 | 0.355150 |
| 5 | 47 | 0 | -3.468136 | -1.102639 | -0.419899 |
| 6 | 6 | 0 | 3.391974 | -2.071793 | 1.094482 |
| 7 | 6 | 0 | 2.014572 | -2.296862 | 1.685906 |
| 8 | 53 | 0 | 3.429319 | -0.681702 | -0.635827 |
| 9 | 8 | 0 | 1.069740 | -2.861894 | 0.766721 |
| 10 | 1 | 0 | 1.288766 | -3.789567 | 0.577939 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 1 | 0 | 3.840280 | -2.980508 | 0.689420 |
| 12 | 1 | 0 | 4.064403 | -1.622466 | 1.826308 |
| 13 | 1 | 0 | 1.571241 | -1.360818 | 2.031366 |
| 14 | 1 | 0 | 2.132378 | -2.957073 | 2.557310 |

**IN**:



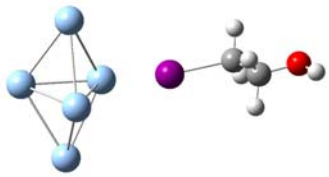
**OUT**:



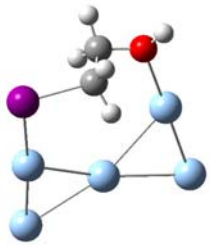
**9h-**
E(B3LYP) =-900.8303377;  (0 imag. Freq.) ;  ZPC=  0.074298

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 1.125057 | 0.741150 | -0.001763 |
| 2 | 47 | 0 | -1.672590 | 1.136961 | -0.003984 |
| 3 | 47 | 0 | 3.656939 | -0.350464 | -0.310458 |
| 4 | 47 | 0 | 1.664105 | -2.016396 | 0.189538 |
| 5 | 47 | 0 | -0.043675 | 3.230708 | 0.196368 |
| 6 | 1 | 0 | -0.186703 | -4.381225 | 0.270252 |
| 7 | 8 | 0 | -0.123581 | -3.479375 | 0.627600 |
| 8 | 6 | 0 | -1.431012 | -2.909698 | 0.836761 |
| 9 | 6 | 0 | -2.043929 | -2.507136 | -0.500760 |
| 10 | 1 | 0 | -2.066633 | -3.617678 | 1.377686 |
| 11 | 1 | 0 | -1.258973 | -2.042975 | 1.476801 |
| 12 | 53 | 0 | -3.643493 | -1.002884 | -0.212410 |
| 13 | 1 | 0 | -1.318715 | -2.014024 | -1.147663 |
| 14 | 1 | 0 | -2.527855 | -3.327356 | -1.032099 |

**IN** :



**OUT**:

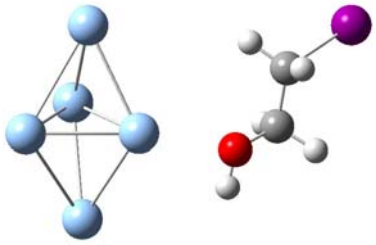


**10a-**

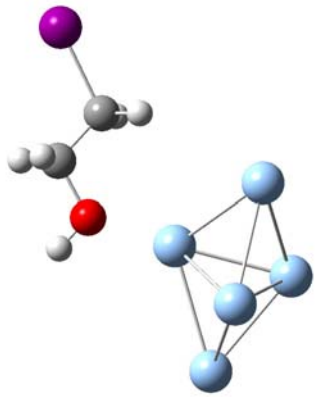
E(B3LYP)=-900.7972188 (0 imag. Freq.) ZPC = 0.073845

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -0.115497 | -0.642205 | -0.115020 |
| 2 | 47 | 0 | -2.312880 | 0.542472 | -1.297080 |
| 3 | 47 | 0 | -2.069038 | 0.566504 | 1.414862 |
| 4 | 47 | 0 | -0.304400 | 2.223112 | -0.098737 |
| 5 | 47 | 0 | -2.859168 | -1.834823 | 0.114099 |
| 6 | 1 | 0 | 1.450129 | -2.924681 | -0.624671 |
| 7 | 8 | 0 | 1.645626 | -2.039499 | -0.276189 |
| 8 | 6 | 0 | 3.046373 | -1.705532 | -0.548683 |
| 9 | 6 | 0 | 3.458362 | -0.628800 | 0.431308 |
| 10 | 1 | 0 | 3.640713 | -2.611870 | -0.406786 |
| 11 | 1 | 0 | 3.137702 | -1.366961 | -1.584897 |
| 12 | 53 | 0 | 5.535085 | -0.042742 | 0.054743 |
| 13 | 1 | 0 | 2.867105 | 0.281023 | 0.314161 |
| 14 | 1 | 0 | 3.417608 | -0.977988 | 1.462791 |

**Start**:



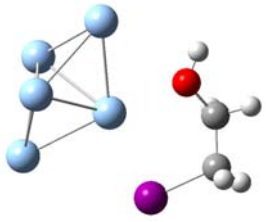
**END**:



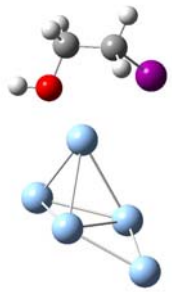
**11a-**
E(B3LYP) = -900.8177201 (0 imag Freq) ZPC = 0.074003

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -1.322347 | -0.319689 | -1.284171 |
| 2 | 47 | 0 | 1.087499 | 0.705834 | 0.036130 |
| 3 | 47 | 0 | -1.645616 | 0.342388 | 1.265992 |
| 4 | 47 | 0 | -2.830504 | -1.971970 | 0.348704 |
| 5 | 47 | 0 | -0.807616 | 2.497290 | -0.548626 |
| 6 | 53 | 0 | 3.200180 | -1.196407 | -0.678331 |
| 7 | 6 | 0 | 4.031694 | -0.981943 | 1.374337 |
| 8 | 6 | 0 | 4.015908 | 0.447729 | 1.855559 |
| 9 | 1 | 0 | 3.418693 | -1.641326 | 1.987855 |
| 10 | 1 | 0 | 5.048349 | -1.364224 | 1.289918 |
| 11 | 8 | 0 | 2.659888 | 0.916586 | 1.934171 |
| 12 | 1 | 0 | 4.615664 | 1.094957 | 1.205274 |
| 13 | 1 | 0 | 4.459661 | 0.448211 | 2.861523 |
| 14 | 1 | 0 | 2.656806 | 1.813444 | 2.306842 |

**IN**:



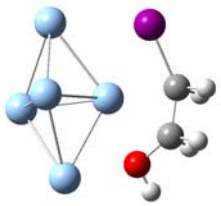
**OUT**:



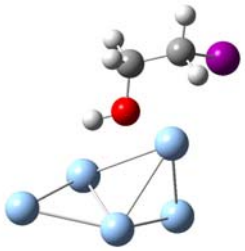
**11b-**
E(B3LYP) = -900.8161269 (0 imag. Freq.) ZPC = 0.073934

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -1.509987 | 0.178204 | 1.343740 |
| 2 | 47 | 0 | -1.603526 | 0.140549 | -1.309231 |
| 3 | 47 | 0 | 1.088791 | 0.424226 | -0.090421 |
| 4 | 47 | 0 | -3.063528 | -1.747143 | 0.112043 |
| 5 | 47 | 0 | -0.523645 | 2.562960 | -0.075006 |
| 6 | 6 | 0 | 3.514953 | -2.271542 | -0.591194 |
| 7 | 6 | 0 | 2.234813 | -2.854848 | -0.044340 |
| 8 | 53 | 0 | 3.918762 | -0.225236 | 0.185120 |
| 9 | 8 | 0 | 1.123938 | -2.038084 | -0.444826 |
| 10 | 1 | 0 | 0.290713 | -2.451376 | -0.160398 |
| 11 | 1 | 0 | 3.495083 | -2.151245 | -1.673752 |
| 12 | 1 | 0 | 4.383475 | -2.851748 | -0.281658 |
| 13 | 1 | 0 | 2.275338 | -2.951165 | 1.046932 |
| 14 | 1 | 0 | 2.129998 | -3.857394 | -0.483520 |

**IN**:



**OUT**:

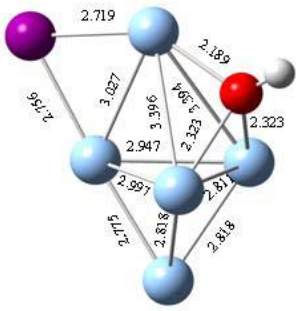


**(B) Cartesian Coordinates for structures shown in Figures 4, 5 and 6. All calculations carried out at the B3LYP/6-31G* level of theory with the SDD ECP for Ag and I.**

**$Ag_5(I,O,H)^+$**
**Type 1: I and OH on different positions of the $Ag_5^+$ structure :**

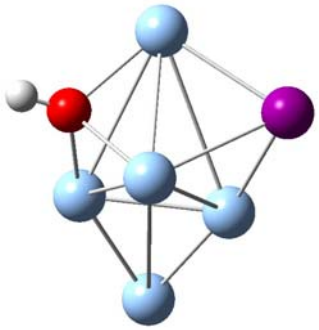
**12a-**
E(B3LYP) = -822.2471369 (0 imag freq), ZPC= 0.015809

| | | | |
|---|---|---|---|
| Ag | 1.354353 | 0.819893 | 1.405834 |
| Ag | 1.353310 | 0.821298 | -1.405146 |
| Ag | -1.672473 | 1.459959 | 0.000081 |
| Ag | 2.522735 | -1.324314 | -0.000969 |
| Ag | -0.250096 | -1.213364 | 0.000195 |
| I | -2.990549 | -0.918161 | -0.000062 |
| O | 0.324484 | 2.357040 | 0.000409 |
| H | 0.435210 | 3.323003 | 0.000220 |




**12b-**
E(B3LYP) = -822.2433511 (0 imag. Freq), ZPC= 0.015760

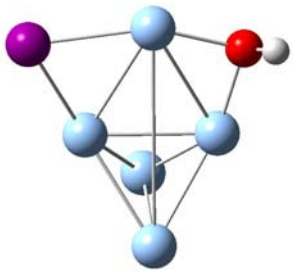
| | | | |
|---|---|---|---|
| Ag | -3.342932 | -0.529438 | -0.189314 |
| Ag | -0.719677 | -1.259063 | -0.210111 |
| Ag | 0.961878 | 0.493204 | 1.654230 |
| Ag | -1.479367 | 1.414577 | -0.073615 |
| Ag | 2.044079 | 1.142600 | -1.143282 |
| I | 2.144838 | -1.517945 | -0.072120 |
| O | 0.597991 | 2.245805 | 0.199261 |
| H | 0.732521 | 3.176210 | 0.446636 |



**12c-**
E(B3LYP) = -822.2468969 (0 imag. Freq), ZPC= 0.015882

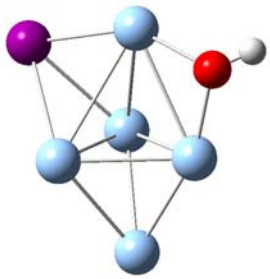
| | | | |
|---|---|---|---|
| Ag | 2.049341 | 1.387105 | 0.000374 |
| Ag | -1.061830 | 1.564759 | -0.082955 |

| | | | |
|---|---|---|---|
| Ag | 0.192984 | -1.024585 | -0.027850 |
| Ag | -2.332769 | -0.625628 | -1.308471 |
| Ag | -2.243044 | -0.523467 | 1.404989 |
| I | 2.914622 | -1.199989 | 0.003228 |
| O | 0.560084 | 2.925858 | 0.128997 |
| H | 0.624256 | 3.617954 | -0.549186 |



**12d-**
E(B3LYP) = -822.2448656 (0 imag. Freq) ZPC: 0.015755

| | | | |
|---|---|---|---|
| Ag | 1.727522 | 1.501857 | -0.005856 |
| Ag | -1.350869 | 1.553713 | -0.042163 |
| Ag | -0.188225 | -0.671559 | 1.391553 |
| Ag | -0.225181 | -0.828720 | -1.360833 |
| Ag | -2.701397 | -0.820768 | 0.038141 |
| I | 2.388375 | -1.174958 | 0.006722 |
| O | 0.232220 | 3.005582 | -0.223173 |
| H | 0.251386 | 3.705478 | 0.449617 |

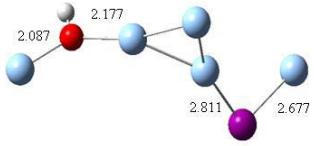


**Type 2: $Ag_3^+$ structure + AgX + AgY:**

**13a-**
E(B3LYP) = -822.220479 (0 imag. Freq.) ZPC: 0.015079

| | | | |
|---|---|---|---|
| Ag | 5.339552 | -1.599523 | 0.017499 |

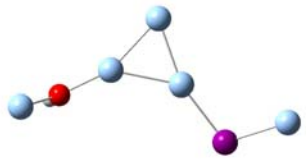
| | | | |
|---|---|---|---|
| Ag | 1.964935 | 0.497609 | 0.363971 |
| Ag | 0.653114 | 2.766007 | -0.217940 |
| Ag | -0.719636 | 0.450191 | -0.326103 |
| I | -2.869933 | -1.278462 | -0.861794 |
| O | 3.661390 | -0.748184 | 0.919466 |
| H | 3.709686 | -0.869247 | 1.881070 |
| Ag | -4.703801 | -0.526769 | 0.937855 |




**13b-**

E(B3LYP) = -822.2201773 (0 imag. Freq.) ZPC: 0.015007

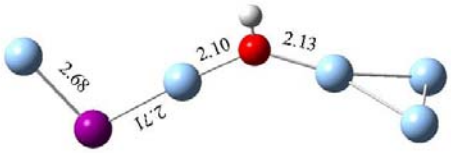
| | | | |
|---|---|---|---|
| Ag | -0.602115 | 2.736630 | 0.083724 |
| Ag | 0.733809 | 0.419890 | -0.244004 |
| Ag | -2.040479 | 0.503638 | -0.298796 |
| O | -3.798262 | -0.743324 | -0.599769 |
| Ag | -5.395871 | -1.522724 | 0.506609 |
| H | -3.972305 | -0.867648 | -1.546487 |
| I | 2.822525 | -1.426522 | -0.616066 |
| Ag | 4.852838 | -0.383819 | 0.782172 |



**13c-**

E(B3LYP) = -822.237697;  0 imag. Freq.;  ZPC: 0.015196

| | | | |
|---|---|---|---|
| Ag | 0.08875400 | 4.61915300 | 1.33459400 |
| Ag | 0.08875400 | 4.61915300 | -1.33459400 |
| Ag | 0.66399500 | 2.29611600 | 0.00000000 |
| O | 1.16309200 | 0.22240300 | 0.00000000 |
| Ag | 0.08875400 | -1.58469700 | 0.00000000 |
| I | -1.45473400 | -3.81403900 | 0.00000000 |
| Ag | 0.46708900 | -5.68828700 | 0.00000000 |
| H | 2.12094900 | 0.07724800 | 0.00000000 |



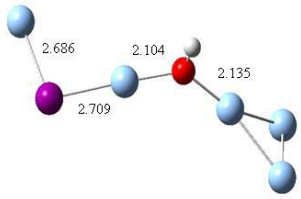

**13c'-**

E(B3LYP) =-822.2378454  (0 imag. Freq.) ZPC: 0.015396

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | 4.537468 | 1.380128 | -0.539220 |
| 2 | 47 | 0 | 4.579871 | -1.251514 | -0.094757 |
| 3 | 47 | 0 | 2.311112 | 0.166693 | 0.499452 |
| 4 | 8 | 0 | 0.303489 | 0.267775 | 1.217893 |
| 5 | 47 | 0 | -1.588580 | -0.284760 | 0.481802 |
| 6 | 47 | 0 | -5.409915 | 1.145275 | -0.016770 |
| 7 | 53 | 0 | -3.979578 | -1.072222 | -0.518101 |
| 8 | 1 | 0 | 0.281843 | 0.361947 | 2.182351 |

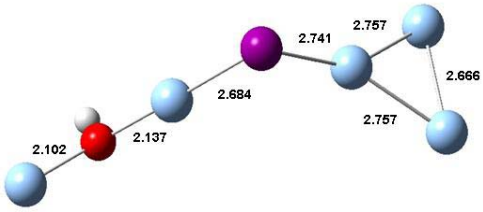
**START**

**END**




**13d-**
E(B3LYP) = - 822.2335119 (0 imag. Freq) ZPC: 0.015450

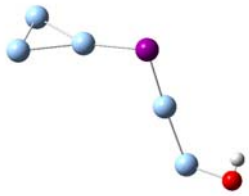
| | | | |
|---|---|---|---|
| Ag | 3.876715 | -1.096121 | -1.210812 |
| Ag | 4.052056 | -0.429427 | 1.364215 |
| Ag | 1.854681 | 0.398999 | -0.082361 |
| I | -0.431268 | 1.900274 | -0.269832 |
| Ag | -2.405277 | 0.122553 | 0.116487 |
| O | -4.073529 | -1.188548 | 0.373067 |
| Ag | -6.114596 | -0.898587 | 0.029273 |
| H | -3.942741 | -1.784713 | 1.126857 |



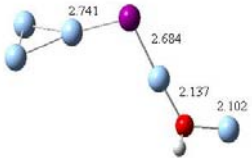

**13d'-**
E(B3LYP) =-822.2335102 (0 imag. Freq.) ZPC: 0.015394

| | | | | | |
|---|---|---|---|---|---|
| 1 | 47 | 0 | -4.003997 | -0.496833 | 1.353569 |
| 2 | 47 | 0 | -3.823582 | -1.134459 | -1.228515 |
| 3 | 47 | 0 | -1.839386 | 0.407777 | -0.095276 |
| 4 | 53 | 0 | 0.408364 | 1.962921 | -0.304608 |
| 5 | 47 | 0 | 2.398889 | 0.251635 | 0.253620 |
| 6 | 47 | 0 | 6.030338 | -1.037266 | -0.083614 |
| 7 | 8 | 0 | 4.059644 | -1.033566 | 0.648084 |
| 8 | 1 | 0 | 4.053255 | -1.336422 | 1.569646 |

**START**



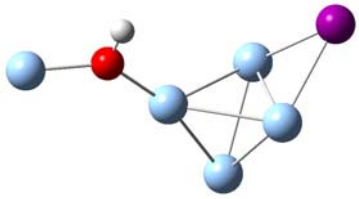
**END**




**Type 3: $Ag_4X^+$ structure + AgY:**

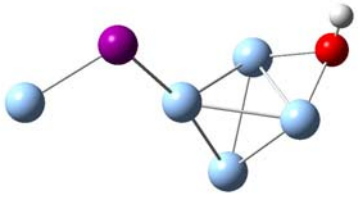
**14a-**
E(B3LYP) = -822.2250823 (0 imag. Freq) ZPC: 0.015215

| | | | |
|---|---|---|---|
| Ag | -4.977384 | -0.820716 | 0.000857 |
| Ag | -1.137375 | 0.354727 | -0.000110 |
| Ag | 0.557156 | 2.464534 | -0.000024 |
| Ag | 1.406340 | 0.118731 | -1.388934 |
| Ag | 1.405610 | 0.118801 | 1.389084 |
| I | 2.917783 | -1.807415 | 0.000386 |
| O | -2.873710 | -0.929934 | -0.006081 |
| H | -2.607084 | -1.863177 | -0.012832 |



**14b-**
E(B3LYP) = -822.2133053 (0 imag. Freq.) ZPC = 0.015025 (Hartree/Particle)

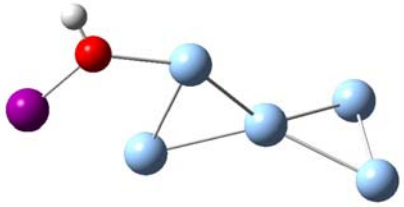
| | | | |
|---|---|---|---|
| Ag | -2.100636 | -3.341643 | -0.579487 |
| Ag | 0.103945 | 0.409729 | -0.132650 |
| Ag | -0.682943 | 2.997991 | 0.073649 |
| Ag | 1.776054 | 2.502921 | -1.306920 |
| Ag | 1.652514 | 2.237949 | 1.545156 |
| O | 3.289289 | 2.863594 | 0.232888 |
| I | 0.390656 | -2.354161 | -0.376509 |
| H | 4.122023 | 2.363933 | 0.222721 |



**Type 4: $Ag_5^+$ structure + hypoiodous acid (IOH):**

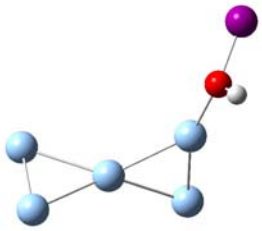
**15a-**
E(B3LYP) = -822.1536828 (0 imag. Freq.) ZPC = 0.015269 (Hartree/Particle)

| | | | |
|---|---|---|---|
| Ag | -3.633121 | 0.215439 | 1.301384 |
| Ag | -3.617699 | -0.389172 | -1.277573 |
| Ag | -1.149492 | 0.015257 | 0.003511 |
| Ag | 1.205014 | 1.445973 | -0.277016 |
| Ag | 1.363915 | -1.180968 | 0.233523 |
| I | 4.550933 | -0.353338 | 0.061754 |
| O | 3.589116 | 1.446219 | -0.319551 |
| H | 4.162583 | 2.150401 | 0.043524 |



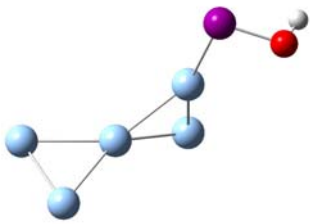
**15b-**
E(B3LYP) = -822.1610929 (0 imag. Freq.)  ZPC = 0.015660 (Hartree/Particle)

| | | | |
|---|---|---|---|
| Ag | 2.967738 | -1.462506 | -1.242124 |
| Ag | 3.476838 | -0.722833 | 1.253135 |
| Ag | 1.242143 | 0.377454 | -0.025955 |
| Ag | -0.075922 | 2.757687 | -0.422086 |
| Ag | -1.518297 | 0.654416 | 0.342554 |
| I | -4.843094 | -1.325708 | -0.108939 |
| O | -3.287148 | -0.584508 | 1.046617 |
| H | -3.672180 | -0.355006 | 1.912745 |



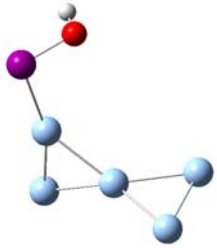
**15c-**
E(B3LYP) = -822.1521615  (0 imag. Freq)  ZPC: 0.015359

| | | | |
|---|---|---|---|
| Ag | 3.324804 | -0.733400 | -1.276351 |
| Ag | 3.105825 | -0.989182 | 1.353518 |
| Ag | 1.097199 | 0.404637 | -0.015536 |
| Ag | -0.418666 | 2.686267 | 0.058641 |
| Ag | -1.708984 | 0.351457 | -0.082387 |
| I | -3.922373 | -1.486225 | -0.195241 |
| O | -5.031519 | -0.278325 | 1.017666 |
| H | -5.670444 | 0.166933 | 0.425881 |



**15d-**
E(B3LYP) = -822.1522958 (0 imag. Freq.) ZPC: 0.015284

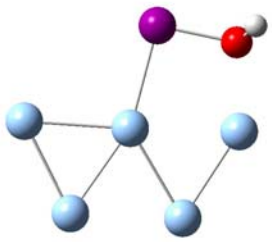
| | | | |
|---|---|---|---|
| O | -3.223143 | -2.543003 | -1.090004 |
| Ag | 1.057383 | 0.467299 | -0.044670 |
| I | -3.955985 | -1.271977 | 0.328499 |
| Ag | 2.953324 | -1.215266 | -1.233092 |
| Ag | 3.185009 | -0.694173 | 1.357847 |
| Ag | -1.751158 | 0.549241 | -0.000501 |
| H | -3.791376 | -2.407975 | -1.874219 |
| Ag | -0.354267 | 2.811341 | -0.224609 |



**15e- (The initial input guess for this structure was from adduct 9d less $C_2H_4$)**
E(B3LYP) =-822.1581668 (0 imag. Freq.) ZPC= 0.015369

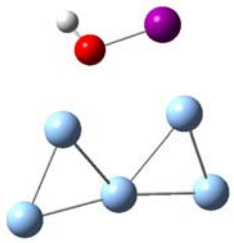
| | | | |
|---|---|---|---|
| Ag | 0.07585300 | -0.24516600 | -0.00217800 |
| Ag | -2.25265200 | 1.42813700 | 0.01865000 |
| Ag | 0.22405500 | 2.53148000 | -0.05051100 |

| | | | |
|---|---|---|---|
| Ag | 2.27779900 | -1.95994100 | -0.02050500 |
| Ag | 2.60310600 | 0.75049000 | 0.05323200 |
| I | -1.99387000 | -2.11776700 | -0.01433100 |
| O | -3.47837600 | -0.58535400 | 0.01301000 |
| H | -4.12143900 | -0.81055700 | 0.71711800 |



**15f- (The initial input guess for this structure was from adducts 9c and 9h less $C_2H_4$)**
E(B3LYP) =-822.1630131 (0 imag. Freq.) ZPC = 0.015674

| | | | |
|---|---|---|---|
| Ag | -0.58865900 | -1.88246400 | 0.07973000 |
| Ag | -1.38892100 | 0.78737100 | 0.00264200 |
| Ag | 1.36998000 | 1.06802500 | -0.00447500 |
| Ag | -3.19281800 | -1.34708400 | -0.07319500 |
| Ag | -0.14664100 | 3.26315500 | 0.02733600 |
| I | 3.21737500 | -1.22914700 | -0.07033800 |
| O | 1.63710300 | -2.55826600 | 0.16723000 |
| H | 1.89407900 | -3.17222400 | 0.88430300 |

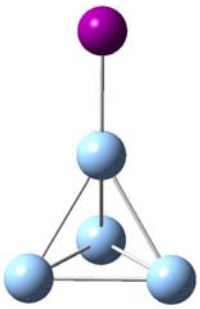


**$Ag_4I^+$**

**16a-**
E(B3LYP) =-599.334828 (2 imag. Freq. (-6.7 and -6.8)) ZPC = 0.001926

| | | | |
|---|---|---|---|
| I | 0.000000 | 0.000000 | 3.356867 |
| Ag | 0.000000 | 0.000000 | 0.770932 |
| Ag | 0.000000 | 1.618907 | -1.518778 |

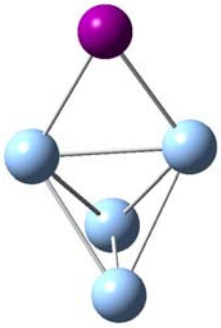
| | | | |
|---|---|---|---|
| Ag | 1.402015 | -0.809454 | -1.518778 |
| Ag | -1.402015 | -0.809454 | -1.518778 |



**16b-**

E(B3LYP) =-599.3568604, (0 imag. Freq.) ZPC = 0.001903

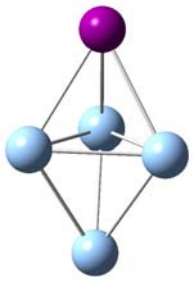
| | | | |
|---|---|---|---|
| Ag | 0.320655 | 1.403943 | -0.040603 |
| Ag | -1.853877 | 0.038977 | 1.347903 |
| Ag | -1.861103 | -0.039149 | -1.342504 |
| Ag | 0.317379 | -1.401592 | 0.034311 |
| I | 2.728612 | -0.001932 | 0.000792 |



**16c-**

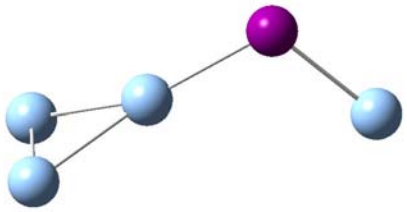
E(B3LYP) =-599.3556366, (0 imag. Freq.) ZPC = 0.001911

| | | | |
|---|---|---|---|
| Ag | -0.090269 | 1.645170 | 0.000000 |
| Ag | -2.399799 | -0.001779 | 0.000000 |
| Ag | -0.090269 | -0.822396 | 1.424832 |
| Ag | -0.090269 | -0.822396 | -1.424832 |
| I | 2.368273 | 0.001242 | 0.000000 |



**17a-**
E(B3LYP) =-599.3621601, (0 imag. Freq.) ZPC = 0.001790

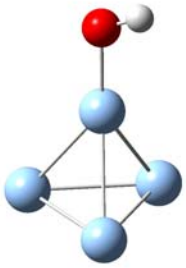
| | | | |
|---|---|---|---|
| Ag | -2.809096 | 1.367646 | -0.069729 |
| Ag | -2.836624 | -1.285517 | -0.400182 |
| Ag | -0.472120 | -0.046804 | 0.277545 |
| I | 2.169429 | -0.178840 | 1.125452 |
| Ag | 3.671463 | 0.166346 | -1.076760 |



**$Ag_4OH^+$**

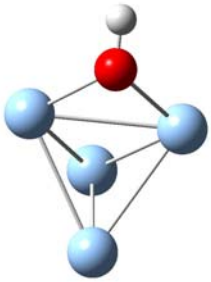
**18a-**
E(B3LYP) =-663.6686064, (1 imag. Freq. (- 68.6)) ZPC = 0.013389

| | | | |
|---|---|---|---|
| Ag | -1.525745 | -0.002766 | 0.096333 |
| Ag | 0.644915 | 1.439208 | -0.825943 |
| Ag | 0.647750 | -1.414508 | -0.861902 |
| Ag | 0.915991 | -0.016223 | 1.530225 |
| O | -3.494577 | -0.018398 | 0.358496 |
| H | -4.007611 | -0.009357 | -0.467714 |



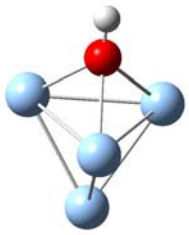
**18b-**
E(B3LYP) =-663.6960219, (0 imag. Freq.) ZPC = 0.014104

| | | | |
|---|---|---|---|
| Ag | 0.932044 | -1.486346 | -0.074395 |
| Ag | -1.240573 | -0.000241 | -1.292113 |
| Ag | -1.115477 | 0.000211 | 1.400147 |
| Ag | 0.931965 | 1.486360 | -0.074805 |
| O | 2.476874 | 0.000090 | 0.270292 |
| H | 3.310950 | 0.000042 | -0.227524 |



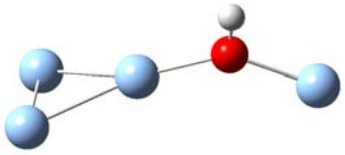
**18c-**
E(B3LYP) =-663.7019323, (0 imag. Freq.) ZPC = 0.014195

| | | | |
|---|---|---|---|
| Ag | 1.777097 | 0.185392 | 0.000000 |
| Ag | -0.639483 | 1.661861 | 0.000000 |
| Ag | -0.639483 | -0.738535 | 1.497498 |
| Ag | -0.639483 | -0.738535 | -1.497498 |
| O | 0.699144 | -1.832023 | 0.000000 |
| H | 1.050359 | -2.742384 | 0.000000 |



**19a-**
E(B3LYP) =-663.7111376, (0 imag. Freq.)  ZPC = 0.014250

| | | | |
|---|---|---|---|
| Ag | -2.216405 | 1.372458 | -0.099586 |
| Ag | -2.322347 | -1.300538 | -0.145632 |
| Ag | 0.078800 | -0.065257 | 0.316246 |
| O | 2.193081 | -0.145333 | 0.751155 |
| Ag | 4.036756 | 0.022839 | -0.235192 |
| H | 2.345559 | -0.223962 | 1.706462 |

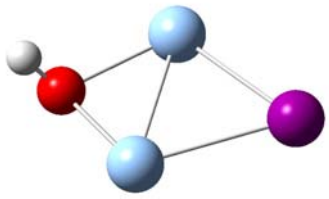


**(C) Cartesian coordinates for other structures used in thermochemical calculations**

**$Ag_2$(I,OH)**

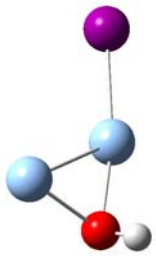
**20a-**
E(B3LYP) = -381.334069 , (0 imag. Freq.)  ZPC = 0.013801

| | | | |
|---|---|---|---|
| Ag | -0.73553997 | -1.43393898 | 0.00440200 |
| Ag | -0.73259199 | 1.43463099 | 0.00440200 |
| O | -2.41957092 | 0.00299200 | -0.12446300 |
| I | 1.72359896 | -0.00114300 | -0.00145800 |
| H | -2.99200511 | 0.00415600 | 0.65916902 |



**20b-**
E(B3LYP) = -381.3240814, (0 imag. Freq.)  ZPC = 0.014264

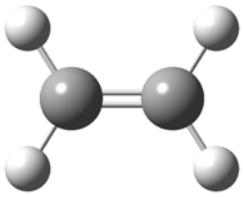
I  1.06759596  2.00652909  -0.33129799
Ag  -2.49902010  -0.13926500  0.12458700
O  -3.99553609  -1.69439304  0.36558101
Ag  -5.34554291  -0.09815100  -0.09125500
H  -4.05971479  -1.92374003  1.30823696



**$CH_2CH_2$**

E(B3LYP) = -78.585824; (0 imag. Freq.)  ZPC = 0.051256

C  -0.665608  0.000001  -0.000068
C  0.665608  -0.000003  -0.000093
H  -1.239365  0.923289  0.000015
H  -1.239371  -0.923284  0.000429
H  1.239366  -0.923290  0.000055
H  1.239370  0.923299  0.000470



**(B) Supplementary table S1; lists DFT energies, relative energies and reaction thermodynamics.**

**Table S1:** DFT calculated energies for ground state structures relevant to the formation of adducts of $Ag_5^+$ and $ICH_2CH_2OH$. The scaling factor used is 0.9806 and the basis sets were SDD for Ag and I, and 6-31G* for C,O and H.

| **calculations on $Ag_5^+$ + $ICH_2CH_2OH$** | *B3LYP/6-31G* (SDD ecp on Ag and I)* | *ZPE* | *ZPE scaled* | *E(B3LYP) corrected* | *Rel. energy kcal/mol* | *Figure#* |
|---|---|---|---|---|---|---|
| | | | | | | |
| Ag5+ **, 1** | -734.940793 | 0.001823 | 0.001787634 | -734.9390054 | 0 | 2 |
| Ag5+ **, 2** | -734.914545 | 0.001731 | 0.001697418 | -734.9128476 | 16.41428 | 2 |
| ICH2CH2OH, **3** | -165.84297 | 0.07061 | 0.069240166 | -165.7737298 | | 2 |
| | | | | | | |
| **monodentate adducts (input on bitrigonal orthogonal structure (BOS))** | | | | | | |
| | | | | | | |
| structure 8a, initial adduct on BOS | -900.816777 | 0.073161 | 0.071741677 | -900.7450353 | 9.920891935 | |
| structure 8b, initial adduct on BOS | -900.82169 | 0.073559 | 0.072131955 | -900.749558 | 7.082839155 | |
| structure 9a, initial adduct on BOS | -900.826584 | 0.073927 | 0.072492816 | -900.7540912 | 4.238248976 | 3(a) |
| structure 8c, initial adduct on BOS(unconv) | -900.82228 | 0.074237 | 0.072796802 | -900.7494832 | 7.129806271 | |
| | | | | | | |
| **monodentate adducts (input on trigonal bipyramidal structure (TBS))** | | | | | | |
| | | | | | | |
| structure 8d, initial adduct on TBS | -900.814274 | 0.073292 | 0.071870135 | -900.7424039 | 11.57215852 | |
| structure 9h, initial adduct on TBS | -900.830338 | 0.074298 | 0.072856619 | -900.7574814 | 2.110866205 | 3(d) |
| structure 8e, initial adduct on TBS | -900.814164 | 0.073324 | 0.071901514 | -900.7422625 | 11.66087538 | |
| structure 8f and 8g, initial adduct on TBS | -900.817412 | 0.073868 | 0.072434961 | -900.744977 | 9.957465854 | |
| structure 11a, initial adduct on TBS | -900.797219 | 0.073845 | 0.072412407 | -900.7248066 | 22.61462255 | 3(b) |
| | | | | | | |
| **Bidentate structures** | | | | | | |
| | | | | | | |
| structure 9b, initial adduct on BOS | -900.828338 | 0.07387 | 0.072436922 | -900.7559011 | 3.102522266 | |
| structure 9a, initial adduct on BOS | -900.826581 | 0.073931 | 0.072496739 | -900.7540843 | 4.242592851 | |
| structure 9d, initial adduct on BOS | -900.824483 | 0.073772 | 0.072340823 | -900.7521422 | 5.461270358 | 3(e) |
| structure 9b', initial adduct on TBS | -900.828346 | 0.073875 | 0.072441825 | -900.7559042 | 3.100578868 | |
| structure 10a, initial adduct on TBS | -900.81772 | 0.074003 | 0.072567342 | -900.7451527 | 9.847263175 | 3(f) |
| structure 9c, initial adduct on TBS | -900.833544 | 0.074137 | 0.072698742 | -900.7608453 | 0 | 3(c) |
| structure 9e, initial adduct on TBS | -900.832594 | 0.074046 | 0.072609508 | -900.7599845 | 0.540138896 | |
| structure 9f, initial adduct on TBS | -900.831432 | 0.074026 | 0.072589896 | -900.7588421 | 1.25699879 | |
| structure 10b, initial adduct on TBS | -900.816127 | 0.073934 | 0.07249968 | -900.7436273 | 10.8044284 | |
| structure 9g, initial adduct on TBS | -900.832556 | 0.074084 | 0.07264677 | -900.7599092 | 0.587367056 | |

**Table S2:** DFT calculated energies for ground state structures relevant to the structures used in the thermochemistry calculations. The scaling factor used is 0.9806 and the basis sets were SDD for Ag and I, and 6-31G* for C,O and H.

| | **B3LYP/6-31G* (SDD ECP on Ag and I)** | **ZPE (Scaled)** | **E(B3LYP)+ZPE** | **Rel. energy kcal/mol** | **Figure#** | | |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| Ag5+ **1** | -734.940753 | 0.001788 | -734.938965 | 0 | | | |
| Ag5+ **2** | -734.914545 | 0.001697418 | -734.9128476 | 16.41428 | | | |
| | | | | | | | |
| ICH2CH2OH, **5** | -165.84297 | 0.06924 | -165.77373 | | | | |
| C2H4 | -78.585824 | 0.050262 | -78.535562 | | | | |
| AgOH, **7** | -222.79785 | 0.011275 | -222.786575 | | | | |
| AgI, **6** | -158.47328 | 0.000428 | -158.472852 | | | | |
| | | | | | | | |
| | | | | | | **DH eq. 14 in kcal** | |
| | | | | | | | |
| Ag5(I,O,H)+ , **12a** | -822.247137 | 0.015502 | -822.231635 | 0 | | -34.20055 | |
| Ag5(I,O,H)+ **, 12b** | -822.243351 | 0.015454 | -822.227897 | 2.34500487 | | -31.854917 | |
| Ag5(I,O,H)+ **, 12c** | -822.246897 | 0.015574 | -822.231323 | 0.19641063 | | -34.0047669 | |
| Ag5(I,O,H)+ **, 12d** | -822.244866 | 0.015449 | -822.229417 | 1.39118967 | | -32.80873 | |
| Ag5(I,O,H)+ ,**13d** | -822.233512 | 0.01515 | -822.218362 | 8.32454766 | | -25.87161 | |
| Ag5(I,O,H)+ **,13c** | -822.237697 | 0.014901 | -822.222796 | 5.53903077 | | -28.65399 | |
| Ag5(I,O,H)+ **, 13a** | -822.220479 | 0.014786 | -822.205693 | 16.278864 | | -17.92168 | |
| Ag5(I,O,H)+ **, 13b** | -822.220177 | 0.0147159 | -822.207054 | 15.42474 | | -18.77573 | |
| Ag5(I,O,H)+ **, 14a** | -822.225082 | 0.01492 | -822.210162 | 13.46699211 | | -20.726028 | |
| Ag5(I,O,H)+ **, 14b** | -822.213305 | 0.014734 | -822.198571 | 20.73795048 | | -13.452559 | |
| Ag5(I,O,H)+ **, 15a** | -822.153683 | 0.014973 | -822.13871 | 58.30446414 | removing CH2=CH2 from adduct#2 | 24.110817 | |
| Ag5(I,O,H)+ **, 15b** | -822.161093 | 0.015356 | -822.145737 | 53.89997145 | removing CH2=CH2 from adduct#3 | 19.701304 | |
| Ag5(I,O,H)+ **, 15c** | -822.152162 | 0.015061 | -822.137101 | 59.31538275 | | 25.12048 | |
| Ag5(I,O,H)+ **, 15d** | -822.152296 | 0.014988 | -822.137308 | 59.18486067 | | 24.990586 | |
| Ag5(I,O,H)+ **, 15e** | -822.158167 | 0.015071 | -822.173238 | 36.6447 | | 2.444151 | |
| Ag5(I,O,H)+ **15f** | -822.163012 | 0.015386 | -822.147626 | 52.71648 | | 18.515938 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| Ag4I+ ,**16a** | -599.3348297 | 0.001877 | -599.3329527 | 17.22791054 | | 2 imag freq: -6.7, -6.8 | |
| Ag4I+ ,**16b** | -599.3568604 | 0.001866 | -599.3549944 | 3.396523377 | Figure 5a | | |
| Ag4I+ ,**16c** | -599.3556366 | 0.001874 | -599.3537626 | 4.169490195 | Figure 5b | | |
| Ag4I+ **, 17** | -599.3621601 | 0.001755 | -599.3604051 | 0 | Figure 5c | | |
| | | | | | | | |
| Ag4OH+ **, 18a** | -663.6686064 | 0.013129 | -663.6554774 | 26.1484672 | | 1 imag freq.: -68.6 | |
| Ag4OH+ **, 18b** | -663.6960219 | 0.01383 | -663.6821919 | 9.393636447 | Figure 6a | | |
| Ag4OH+ **,18c** | -663.7019323 | 0.01392 | -663.6880123 | 5.741904753 | Figure 6b | | |
| Ag4OH+ **, 19** | -663.7111376 | 0.013974 | -663.6971636 | 0 | Figure 6c | | |
| | | | | | | | |
| Ag2,I,OH neutral **, 20a** | -381.334069 | 0.013533 | -381.320536 | 0 | | | |
| Ag2,I,OH neutral **, 20b** | -381.3240814 | 0.013987 | -381.3100944 | 6.557856006 | | | |
| | | | | | | | |
| Ag3+**, 3** | -440.842526 | 0.000879 | -440.841647 | | | | |
| | | | | | | | |
| | | | | | | | |
| **Competing patways for** | **Eqs. 19 a -f** | DHr (Hartrees) | DHr (kcal.mol-1) | | | | |
| | | | | | | | |
| CID ofAg5HIO+ --> | Ag4I+ + AgOH **(19a)** | 0.0846059 | 53.09104831 | | | | |
| | Ag4OH+ + AgI **(19b)** | 0.0615964 | **38.65235696** | | | | |
| | Ag3+ + AgI + AgOH **(19d)** | 0.130502 | 81.89131002 | | | | |
| | Ag3+ + [Ag2,I,OH] **(19c)** | 0.06943 | **43.5680193** | | | | |
| | Ag2I+ + Ag3OH **(19e)** | 0.10024 | 62.901602 | | | | |
| | Ag2OH + + Ag3I **(19f)** | 0.08903 | 55.867215 | | | | |
| | | | | | | | |
| **Other reactions** | | | | | | | |
| | | | | | | | |
| Ag5+ (1) + ICH2CH2OH --> | Ag5ICH2CH2OH + (9c) | -0.0481503 | -30.21479475 | | | | |
| | | | | | | | |
| Ag5+ (1) + ICH2CH2OH --> | Ag5ICH2CH2OH + (11a) | -0.0324577 | -20.36753133 | | | | |
| | | | | | | | |
| Ag5+ (2) + ICH2CH2OH --> | Ag5ICH2CH2OH + (11a) | -0.0585697 | -36.75307245 | | | | |

**Table S3:** Assignments of the peaks observed in Figs. 7a and 7b for the reactions of $Ag_6H^+$ with $ICH_2CH_2OH$ (L). These assignments were also compared to single isotope experiments. A * denotes a weak peak, assignment is tentative.

| *m/z* | Assignment |
|---|---|
| | |
| 323 | $Ag_3^+$ |
| 649 | $Ag_6H^+$ |
| 775 | $Ag_6I^+$ |
| 793 | $Ag_6I^+.H_2O$ |
| 821 | $Ag_6H^+.L$ |
| 902 | $Ag_6I_2^+$ |
| 919 | $[Ag_6I,I,OH]^+$ |
| 947 | $Ag_6I^+.L$ |
| 993* | $Ag_6H^+.2L$ |
| 1029 | $Ag_6I_3^+$ |
| 1074 | $Ag_6I_2^+.L$ |
| 1119 | $Ag_6I^+.2L$ |
| 1201 | $Ag_6I_3^+.L$ |
| 1246* | $Ag_6I_2^+.2L$ |