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

Supporting Information for

Ambient Preparation and Reactions of Gas Phase Silver Cluster Cations and Anions

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Mechanism of Formation of Oxo-cations

The loss of ethenone from $[Ag_n(CH_3COO)_{n-1}]^+$ is possible as evidenced by the observation of $[Ag_6(CH_3COO)_3OH_2O]^+$ and $[Ag_5(CH_3COO)_2OH_2O]^+$ (1). The ethenone product can go on to dimerize (2). The heat of formation of ethenone is -47.5 kJ/mol with its dimer having a heat of formation of -190.3 kJ/mol.[1] The hydration energy of Ag_3O^+ is assumed to be close to that of Ag^+, which is -139 kJ/mol.[2, 3] The observation that multiple ions, including $Ag_5(CH_3COO)_2^+$, bind water upon isolation in the ion trap suggests this interaction is quite weak. The formation of 2 ethenone and monohydrated Ag_3O^+ is predicted to be exothermic by -234 kJ/mol, as calculated from the heat of formation and hydration energy. If the ethenone dimerizes, the reaction is even more exothermic at -329.3 kJ/mol. This is still much less favorable than the formation of acetic anhydride, and thus it is assumed to be a minor pathway.

$$Ag_n(CH_3COO)_{n-1}^+ \rightarrow [Ag_n(CH_3COO)_{n-1-2m}O_m(H_2O)_m]^+ + 2mC_2H_2O \ (m=1,2,4) \quad (1)$$

$$2\ C_2H_4O \rightarrow C_4H_8O_2 \ (2)$$

References

1. W. M. Haynes and D. R. Lide, *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data*, CRC Press, Boca Raton, Fla., 2011.
2. D. Feller, E. D. Glendening and W. A. de Jong, *The Journal of Chemical Physics*, 1999, 110, 1475-1491.
3. B. S. Fox, M. K. Beyer and V. E. Bondybey, *Journal of the American Chemical Society*, 2002, 124, 13613-13623.

Supplementary Tables

Table S1: Reaction products of Ag^+ with various reagents[a]

Reactant	Ag^+	$[AgL]^+$	$[AgL_2]^+$
Ethanol	9.7%	14%	100%
1-propanol	4.4%	6.7%	100%
Isopropyl Alcohol	24.5%	13.2%	100%
Tert-Butyl Alcohol	18.2%	3.6%	100%
Acetone	24.8%	28.5%	100%
Acetonitrile	9.4%	N.R.	100%

[a] L refers to the respective reagent

Table S2: Reaction products of Ag_3^+ with various reactants[a]

Reactant	Ag_3^+	$[Ag_3L]^+$	$[Ag_3L_2]^+$	$[Ag_3L_3]^+$
Ethanol	100%	75.4%	57.3%	N.R.
1-propanol	33.0%	48.4%	100%	N.R.
Isopropyl Alcohol	100%	44.2%	73.%	N.R.
Tert-Butyl Alcohol	38.6%	11.0%	100%	N.R.
Acetone	100%	48.5%	51.8%	N.R.
Acetonitrile	44.8%	N.R.	57.5%	100%

[a] L refers to the respective reagent

Table S3: Reaction products of Ag^+ with various methyl-substituted pyridines[a]

Reactant	Ag^+	$[AgL]^+$	$[AgL_2]^+$
Pyridine	1.0%	6.3%	100%
2-ethylpyridine	0.1%	1.4%	100%
3-ethylpyridine	0.9%	1.8%	100%
4-ethylpyridine	0.09%	0.9%	100%
3,4-Lutidine	1.8%	2.5%	100%
2,6-Lutidine	3.6%	1.2%	100%
2,5-Lutidine	2.2%	2.0%	100%
3,5-Lutidine	3.1%	1.4%	100%
2,4,6-trimethylpyridine	1.2%	10.6%	100%

[a] L refers to the respective reagent

Table S4: Reaction products of Ag_3^+ with various methyl-substituted pyridines[a]

Reactant	Ag_3^+	$[Ag_3L]^+$	$[Ag_3L_2]^+$	$[Ag_3L_3]^+$
Pyridine	28.8%	44.1%	73.8%	100%
2-ethylpyridine	N.R.	N.R.	N.R.	100%
3-ethylpyridine	N.R.	N.R.	N.R.	100%
4-ethylpyridine	N.R.	N.R.	N.R.	100%
3,4-Lutidine	N.R.	N.R.	N.R.	100%
2,6-Lutidine	N.R.	N.R.	N.R.	100%
2,5-Lutidine	N.R.	N.R.	N.R.	100%
3,5-Lutidine	N.R.	N.R.	N.R.	100%
2,4,6-trimethylpyridine	23.2%	52.5%	51.0%	100%

[a] L refers to the respective reagent

Table S5: Reaction products of Ag_3^+ with acetone, acetontrile, acetone followed by acetonitrile, and acetonitrile followed by acetone[a]

Compound $[Ag_3 + (C_3H_6O)_x + (C_2H_3N)_y]^+$	Acetone Only	Acetonitrile Only	Acetone, then Acetonitrile	Acetonitrile, then Acetone
[1,0]	✓		✓	N.R.
[2,0]	✓		✓	N.R.
[3,0]			N.R.	N.R.
[0,1]		✓	✓	✓
[0,2]		✓	✓	✓
[0,3]		✓	✓	✓
[1,1]			✓	N.R.
[2,1]			N.R.	N.R.
[1,2]			N.R.	N.R.

[a] Checkmarks indicate the presence of a species as determined by the appropriate MS/MS experiment.

Supplemenary Figures

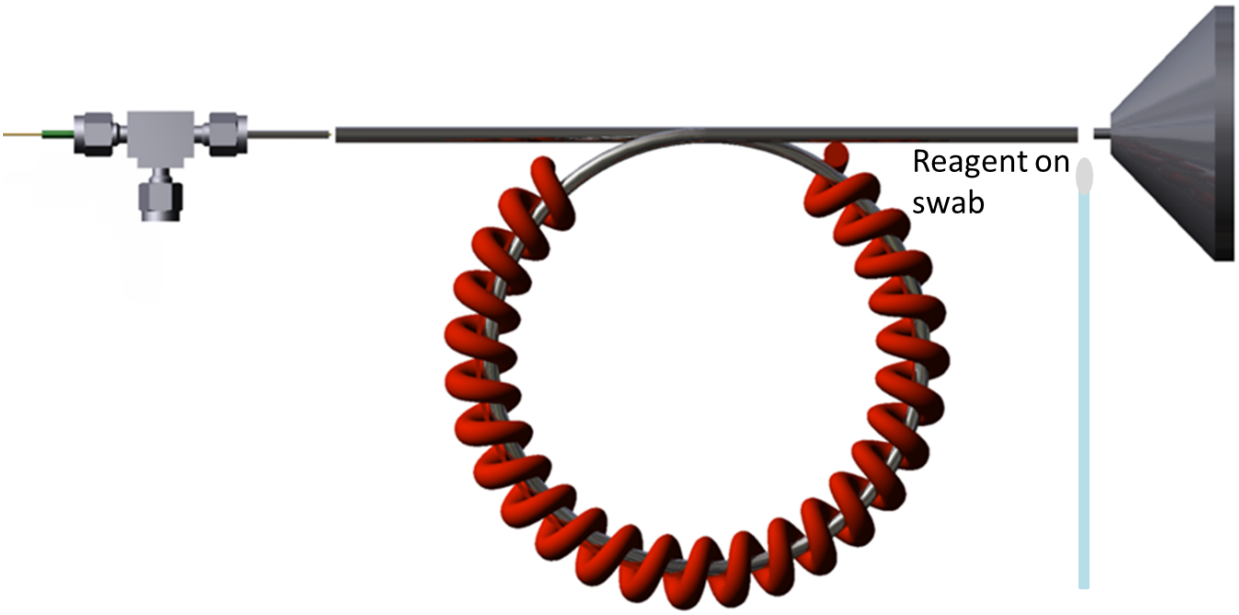

Figure S1: Apparatus for studying atmospheric pressure ion/molecule reactions of silver clusters (cations/anions) with various reagents

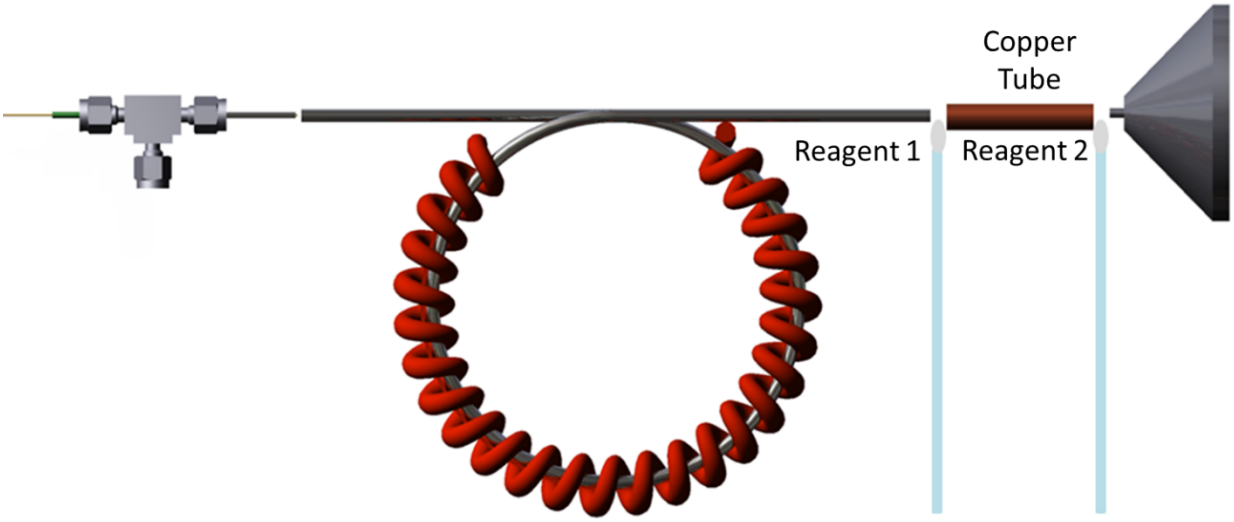

Figure S2: Apparatus for performing atmospheric pressure ion/molecule ligand exchange reactions of silver clusters with various reagents

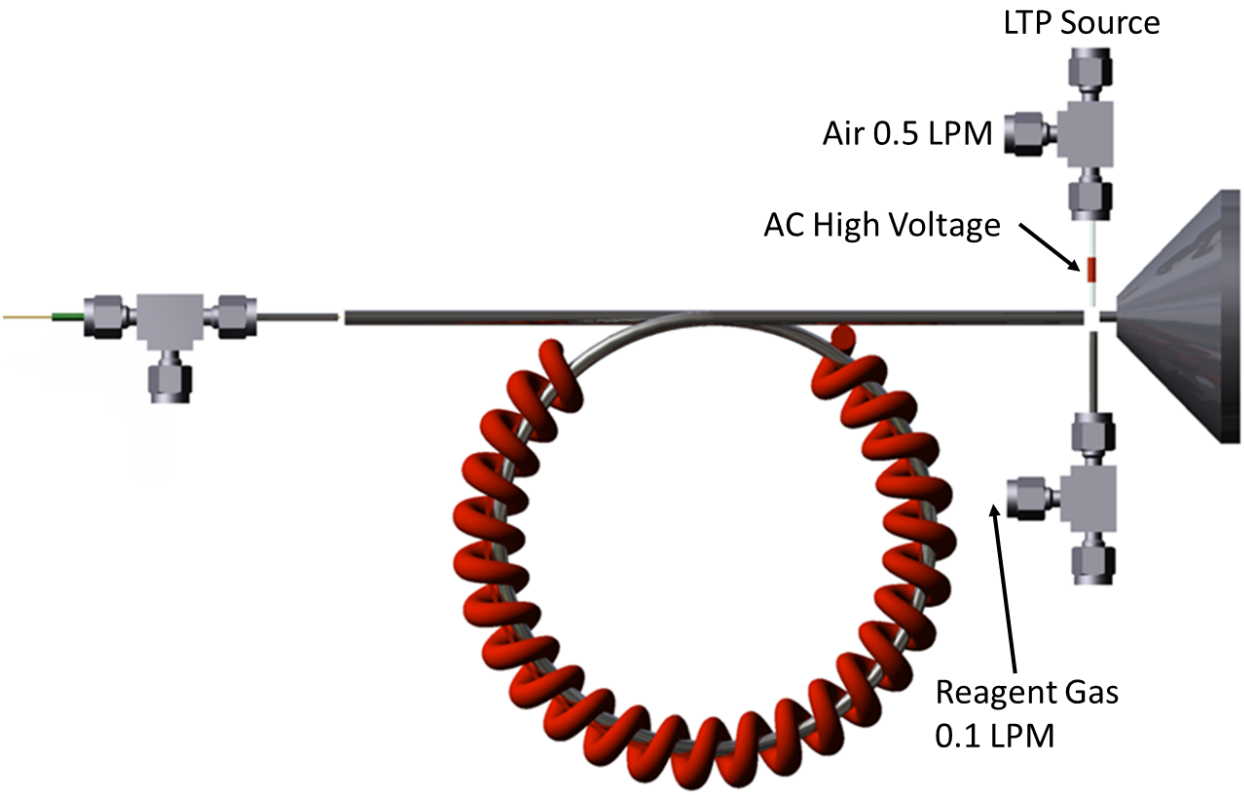

Figure S3: Apparatus for performing ion/molecule reactions using either a gas, low temperature plasma, or both. The low temperature plasma is used to generate reactive species to oxidize silver cluster cations

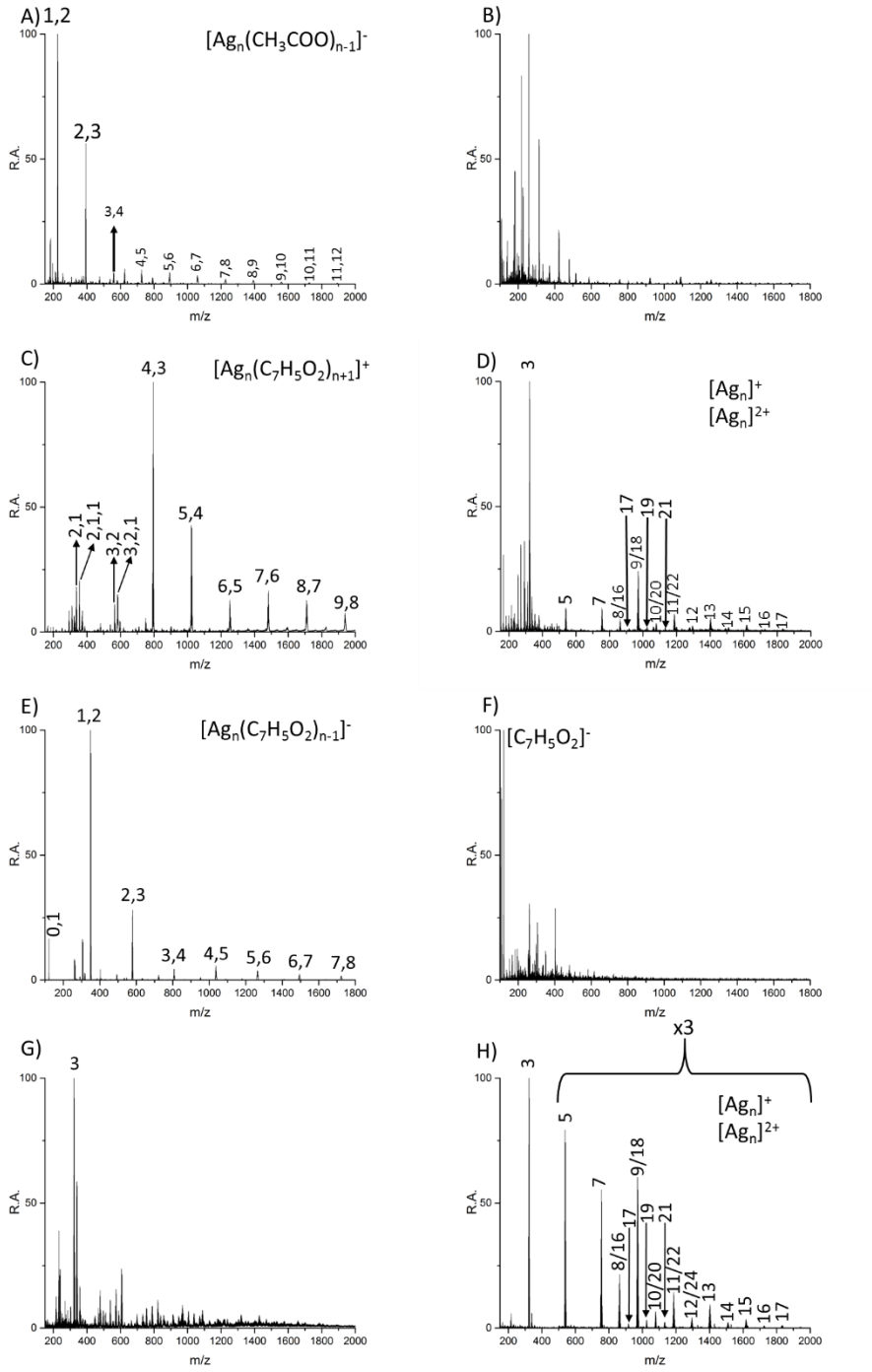

Figure S4: Negative ion mode mass spectra of A) unheated and B) heated silver acetate. Positive ion mode of C) unheated and D) heated silver benzoate. Negative ion mode mass spectra of E) unheated and F) heated silver benzoate. Positive ion mode mass spectra of G) unheated and H) heated silver fluoride. The numbers above each peak indicate the number of silver atoms, ligands, and water present, and the absence of the final number indicates zero water molecules are present

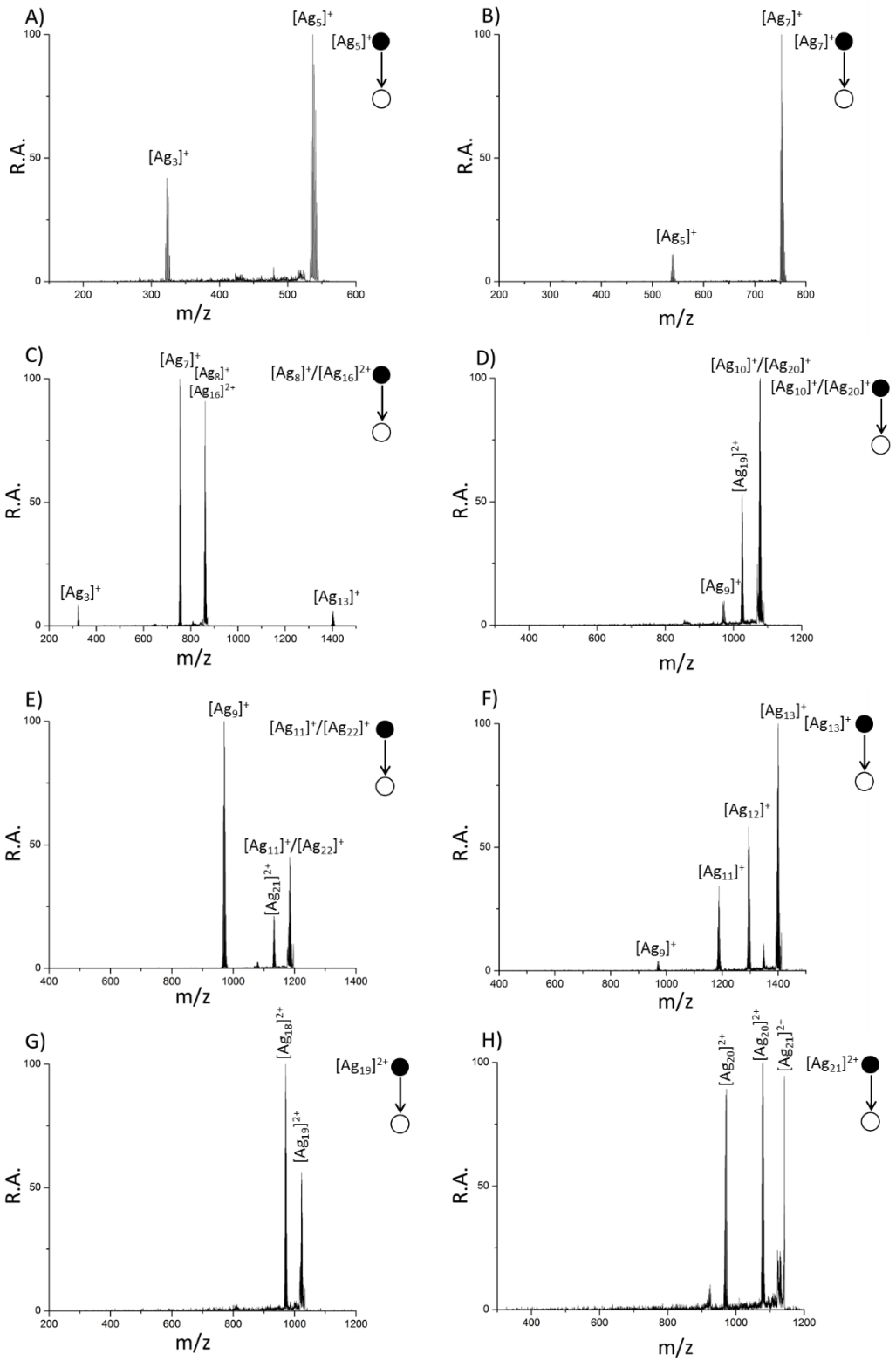

Figure S5: Tandem MS of A) Ag_5^+, B) $Ag7^+$, C) Ag_8^+/Ag_{16}^{2+}, D) Ag_{10}^+/Ag_{20}^{2+}, E) Ag_{11}^+/Ag_{22}^{2+}, F) Ag_{13}^+, G) Ag_{19}^{2+}, and H) Ag_{21}^{2+}

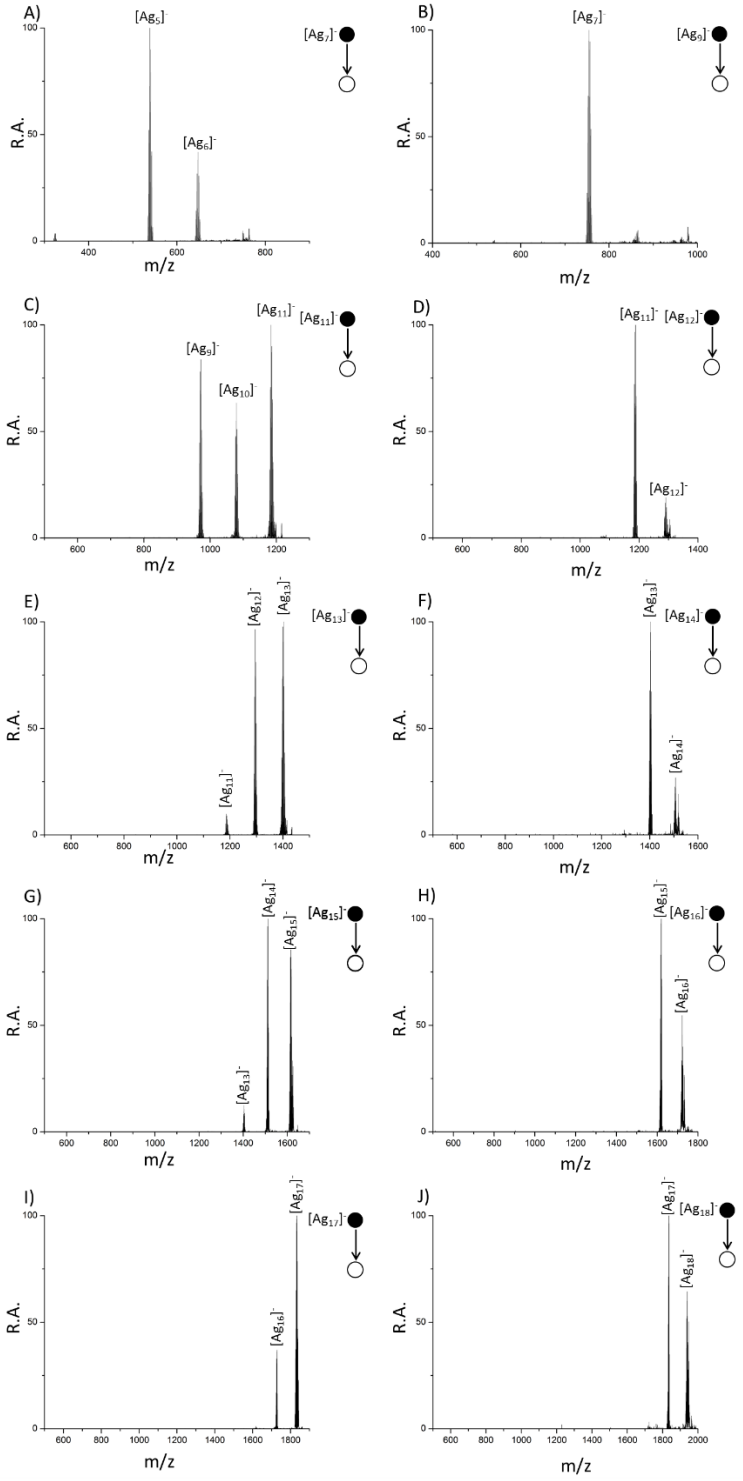

Figure S6: Tandem MS of A) Ag_7^-, B) Ag_9^-, C) Ag_{11}^-, D) Ag_{12}^-, E) Ag_{13}^-, F) Ag_{14}^-, G) Ag_{15}^-, H) Ag_{16}^-, I) Ag_{17}^-, and J) Ag_{18}^-

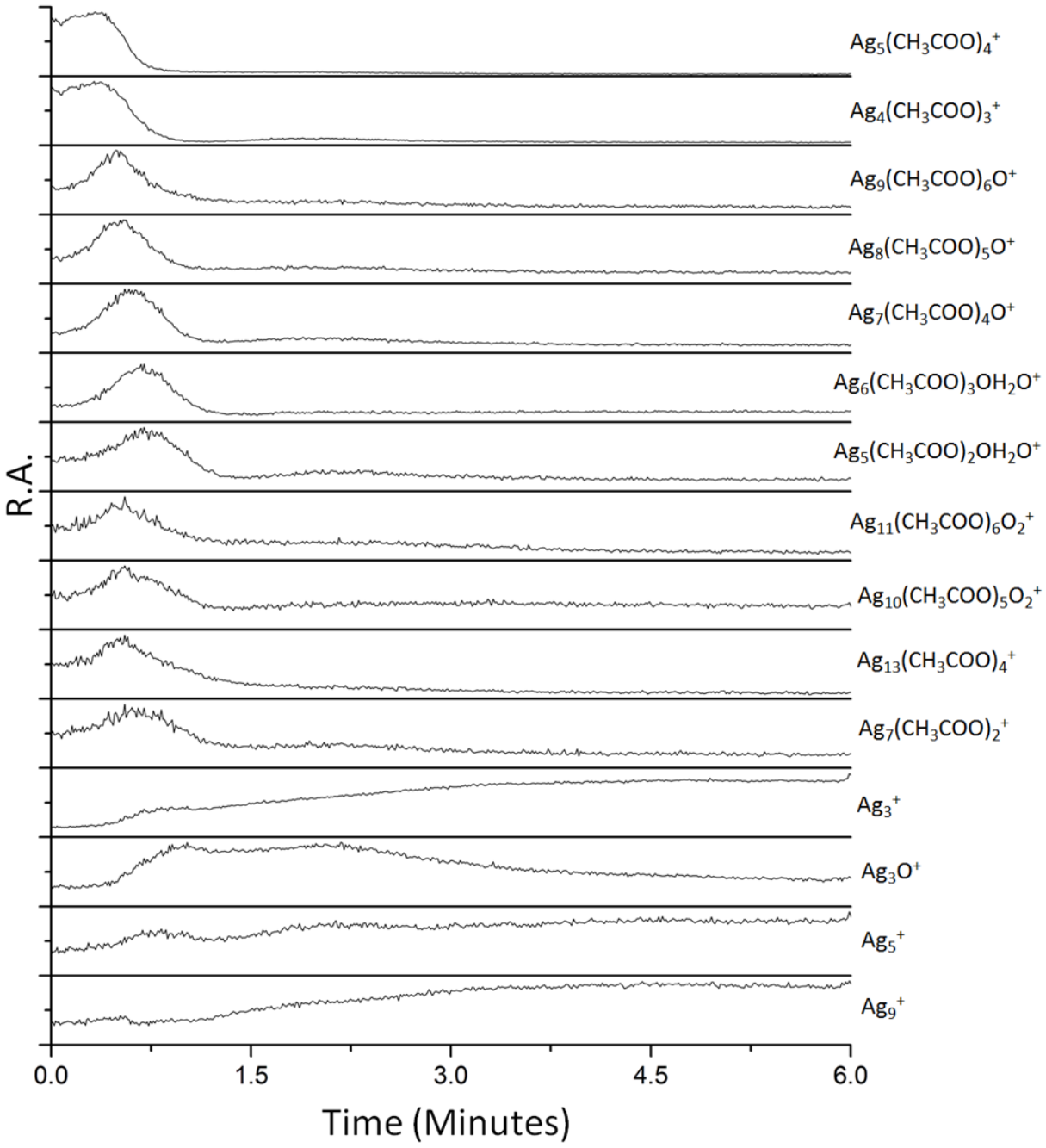

Figure S7: Selected ion chronograms for ions of interest in the formation of silver cluster cations from a silver acetate precursor. At time zero the heating is turned on and temperature slowly rises to 250 Celsisus over the course of a few minutes

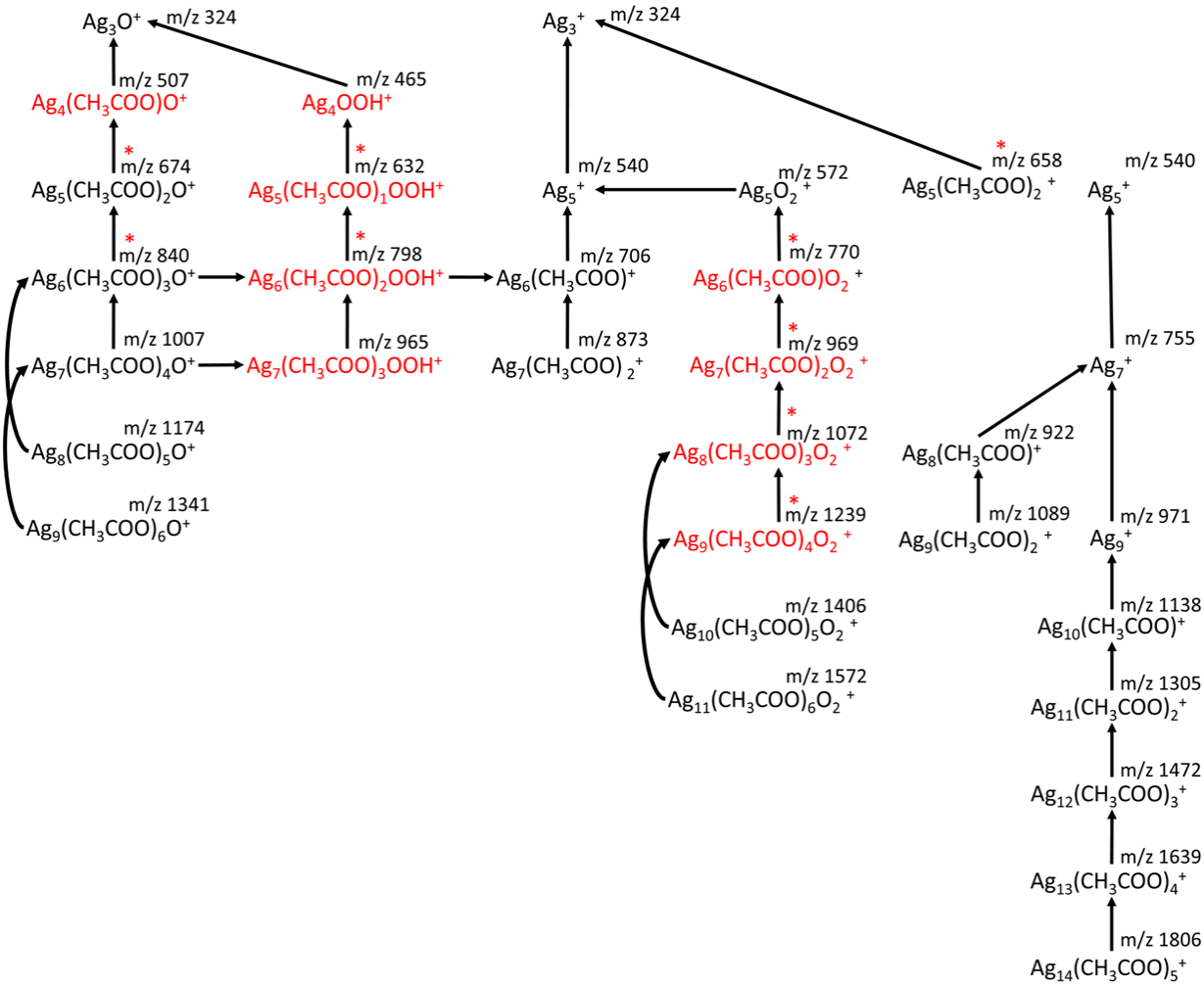

Figure S8: Tandem MS tree for ions observed when silver acetate is subjected to 100-150 C and harsh in source conditions. Species in black text are observed in the full MS, while species appearing in red are only observed by tandem MS. Red asterisks indicate ions that reversibly bind H_2O in the ion trap

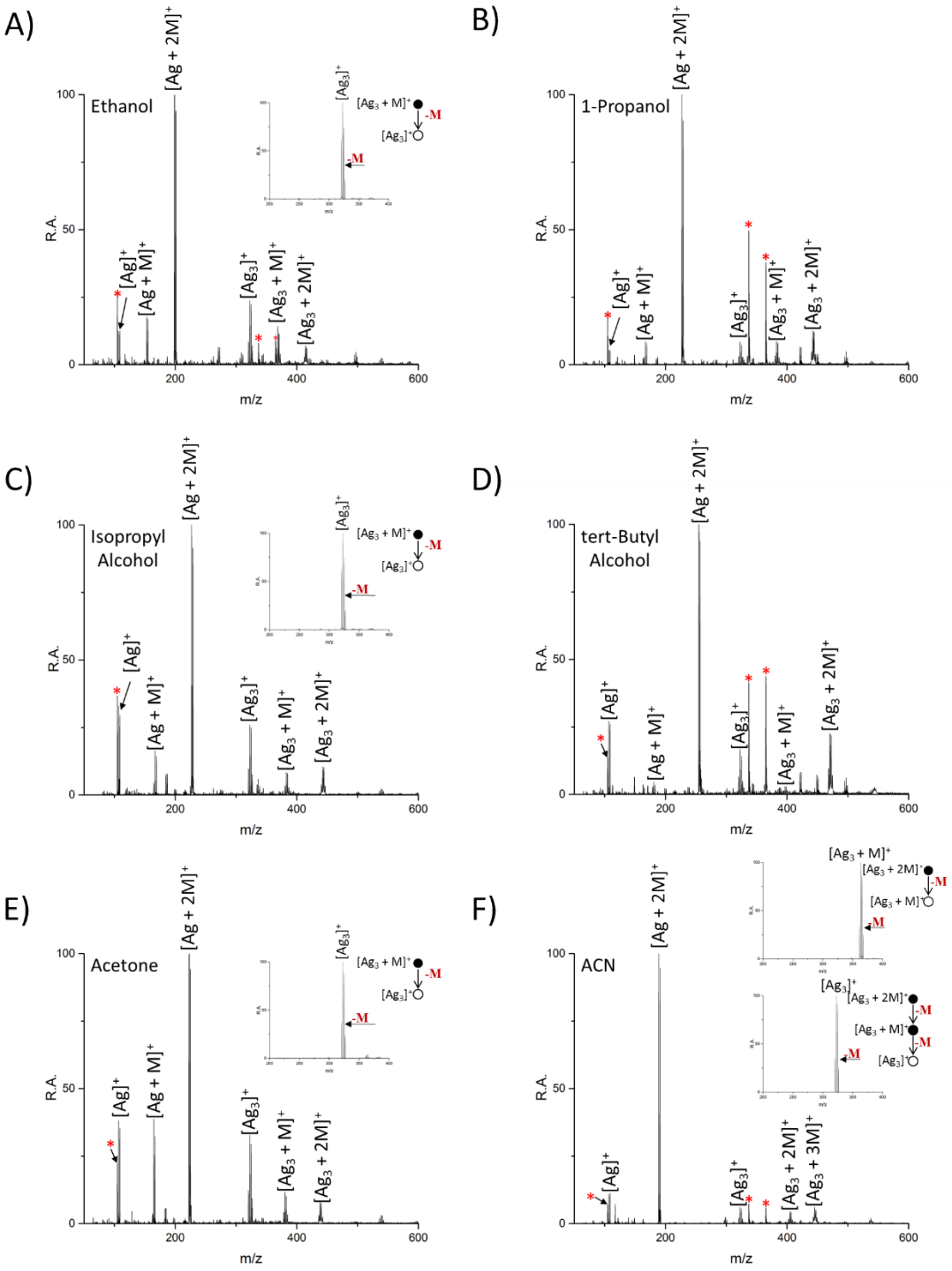

Figure S9: Reaction of silver cluster cations with A) ethanol, B) 1-propanol, C) isopropyl alcohol, D) tert-butyl alcohol, E) acetone, and F) acetonitrile. Tandem MS for selected ions are shown as insets. M stands for the reactant of interest. Peaks at m/z 105, 337, and 365 are common background ions with the first originating from the spray and the latter arising from the cotton swab

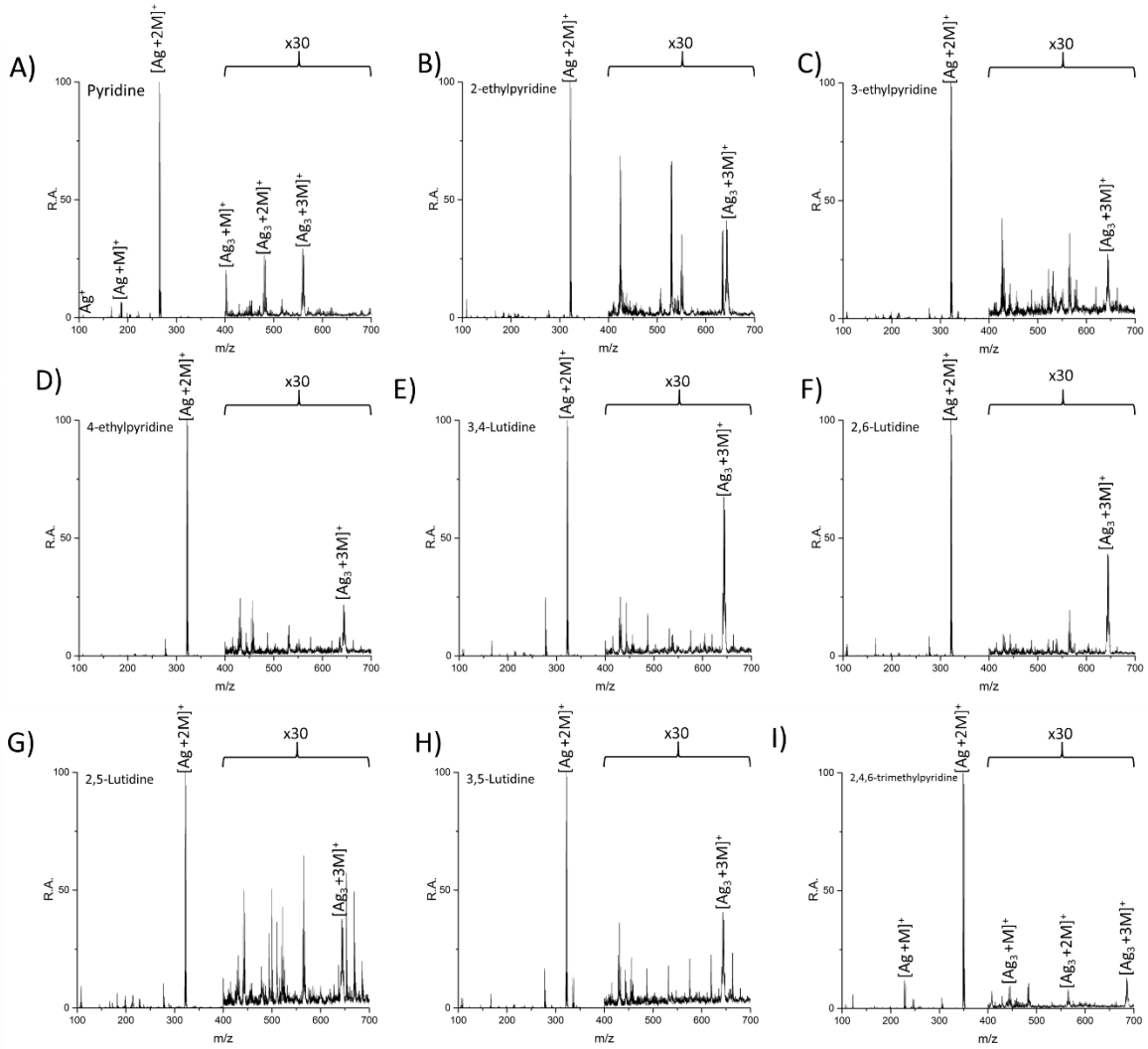

Figure S10: Reaction of silver cluster cations with A) pyridine, B) 2-ethylpyridine, C) 3-ethylpyridine, D) 4-ethylpyridine, E) 3,4-lutidine, F) 2,6-lutidine, G) 2,5-lutidine, H) 3,5-lutidine, and I) 2,4,6-trimethylpyridine. M stands for the reactant of interest

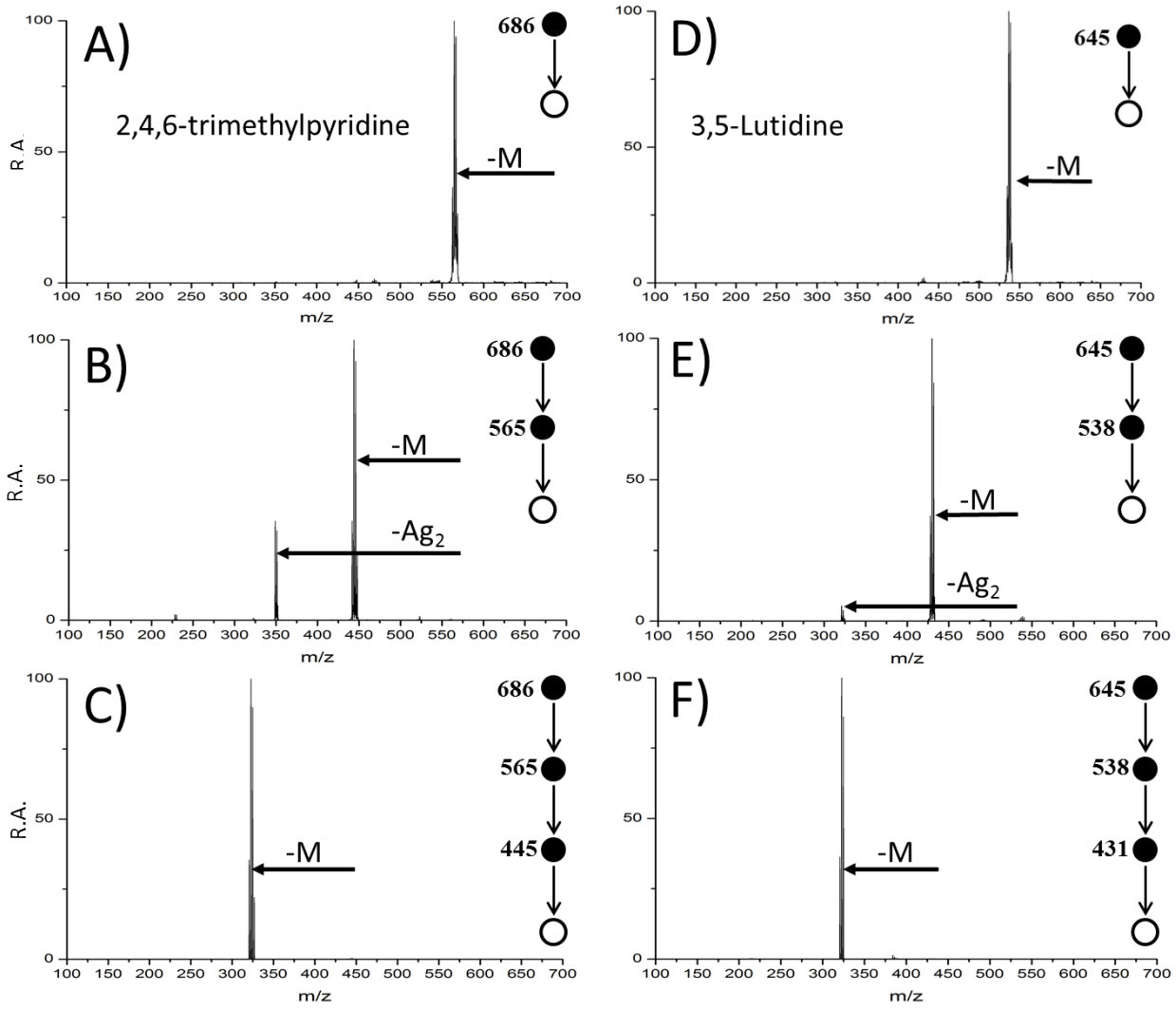

Figure S11: Tandem mass spectrometry data for $[Ag_3(C_8H_{11}N)_3]^+$ (left) and $[Ag_3(C_7H_9N)_3]^+$ (right) where 2,4,6-trimethylpyridine and 3,5-lutidine are the respective neutral reactants. A) MS^2, B) MS^3, C) MS^4 of $[Ag_3+(2,4,6\text{-trimethylpyridine})_3]^+$. D) MS^2, E) MS^3, F) MS^4 of $[Ag_3+(3,5\text{-lutidine})_3]^+$. M stands for the reactant of interest

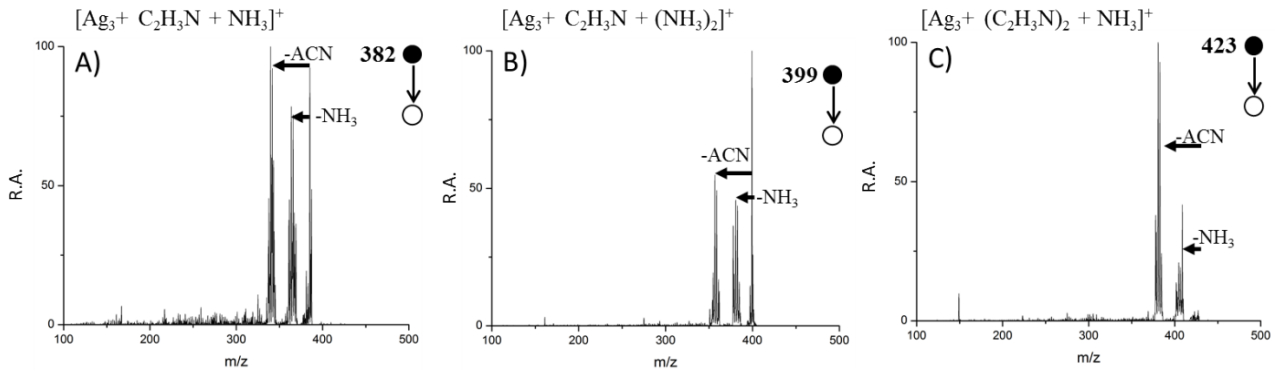

Figure S12: A) MS^2 of $[Ag_3+C_2H_3N+NH_3]^+$, B) MS^2 of $[Ag_3+C_2H_3N+(NH_3)_2]^+$, and C) MS^2 of $[Ag_3+(C_2H_3N)_2+NH_3]^+$ for the reaction of silver clusters with first ammonia (from ammonium hydroxide) then acetonitrile

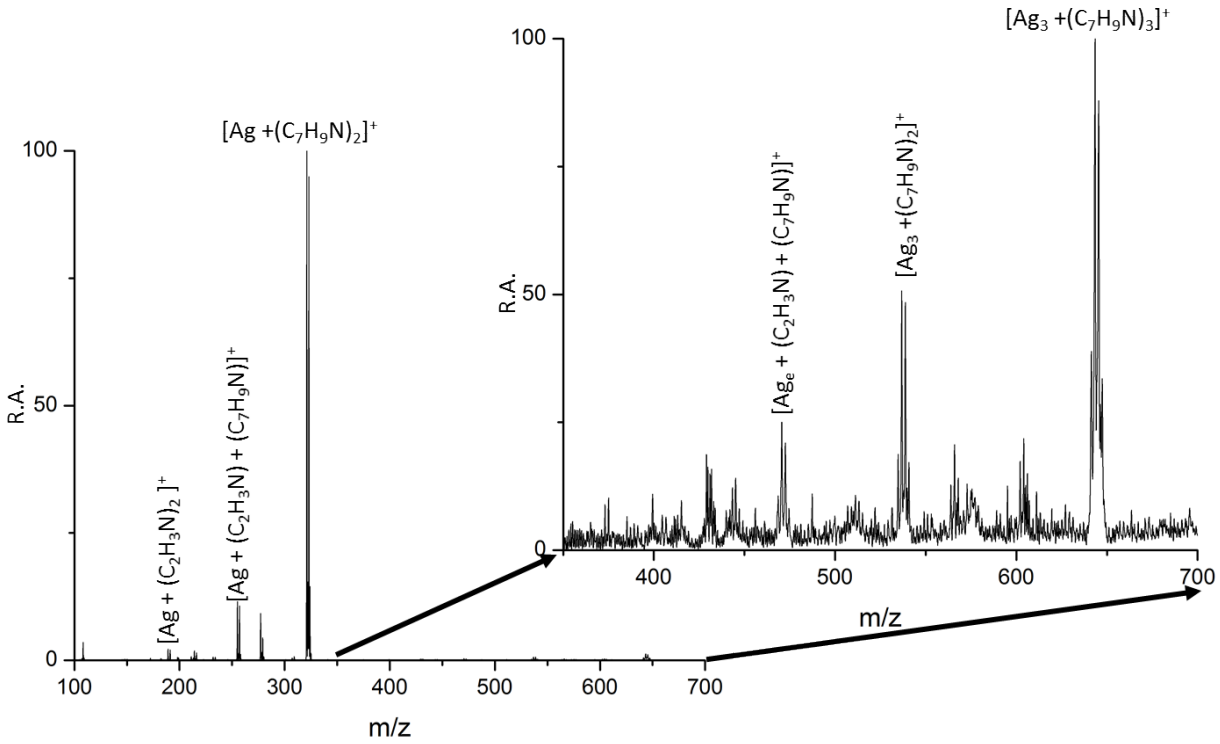

Figure S13: Full MS for the reaction of silver clusters with first 2,6-lutidine then acetonitrile. Inset: Blowup of m/z 350-700

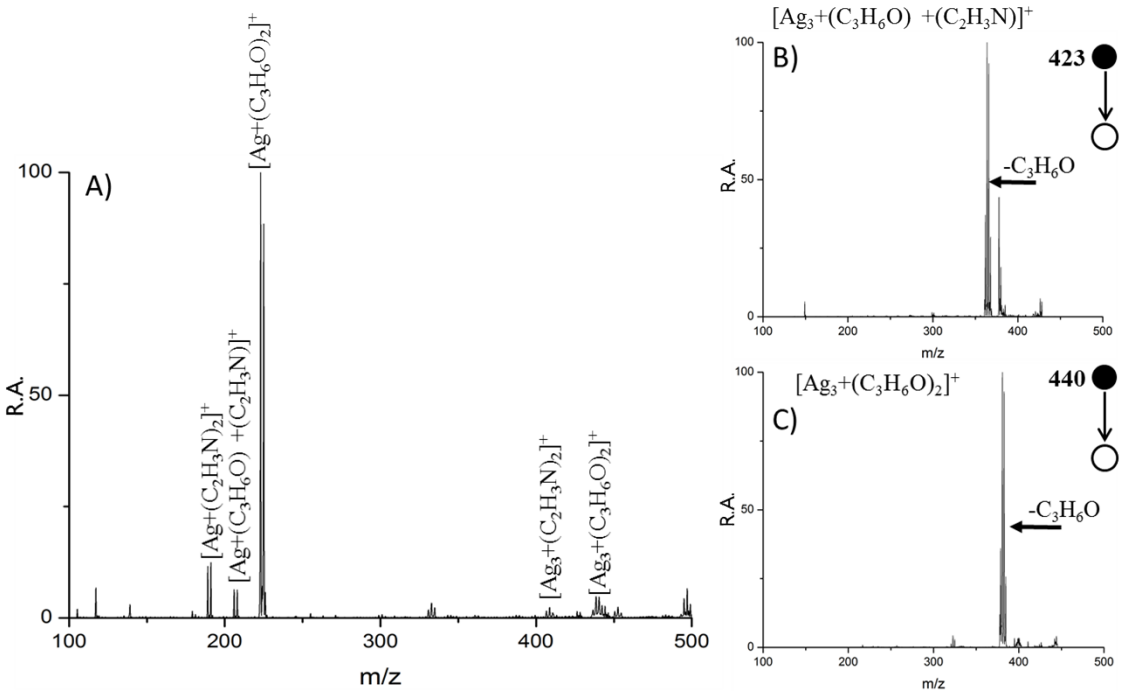

Figure S14: A) Full MS, B) MS^2 of $[Ag_3 + (C_3H_6O) + (C_2H_3N)]^+$, and C) MS^2 of $[Ag_3 + (C_3H_6O)_2]^+$ for the reaction of silver clusters with Ag_3^+ with first acetone, than acetonitrile

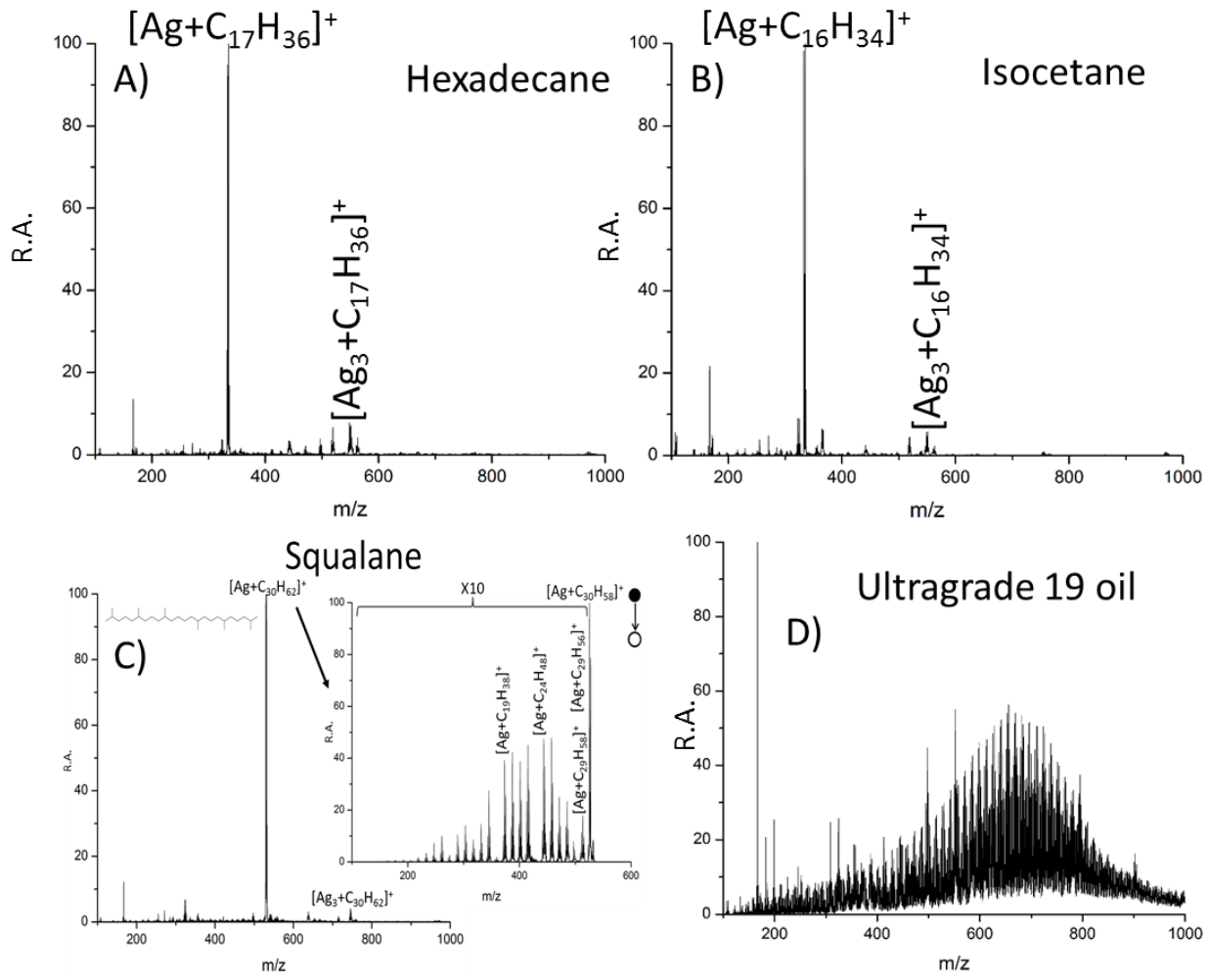

Figure S15: Analysis of A) Hexadecane, B) Isocetane, C) Squalane, and D) Ultragrade 19 oil using silver cluster spray. The inset of C) is the MS^2 of $[Ag+Squalane]^+$

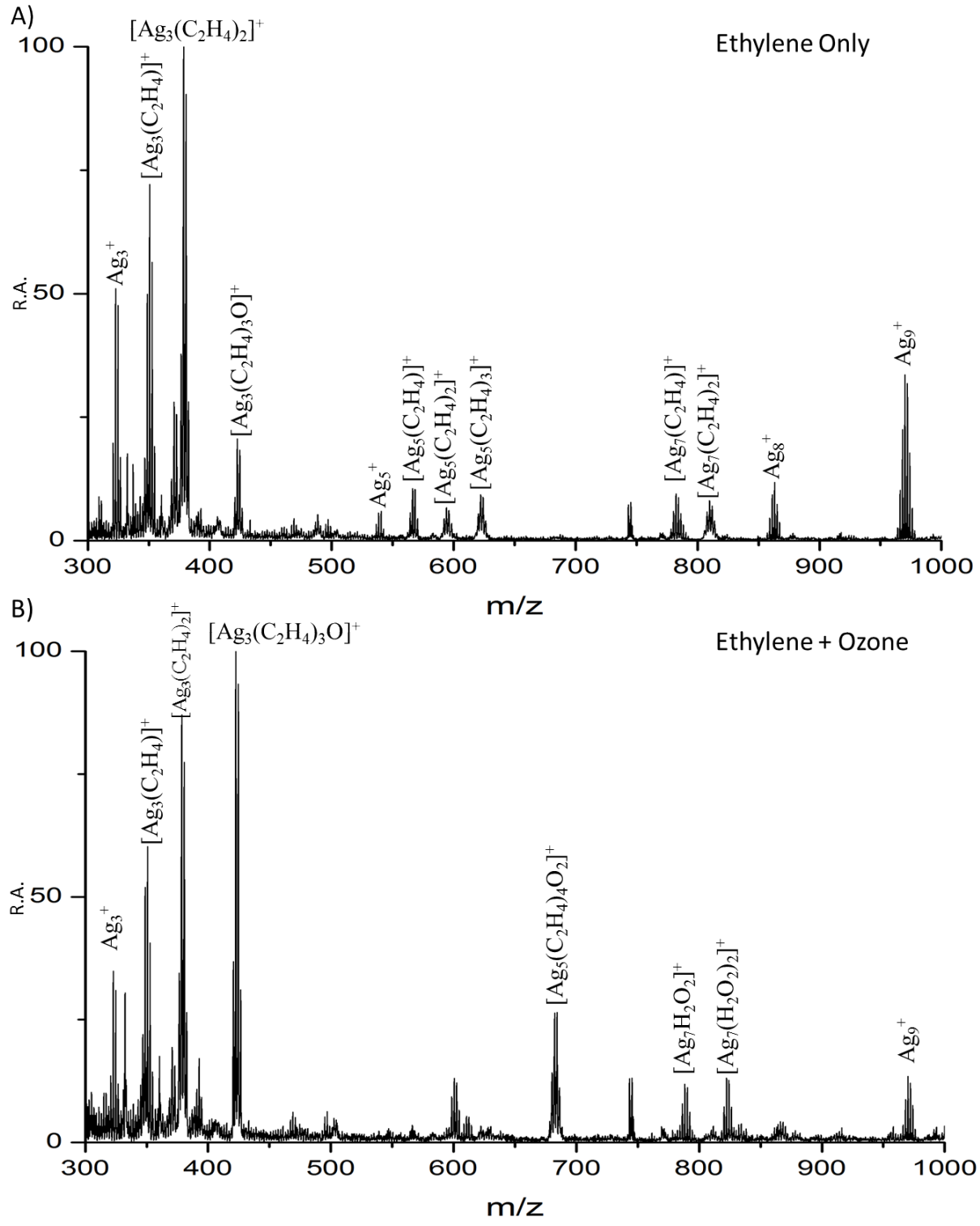

Figure S16: Reaction of silver cluster cations with A) ethylene and B) ethylene and ozone

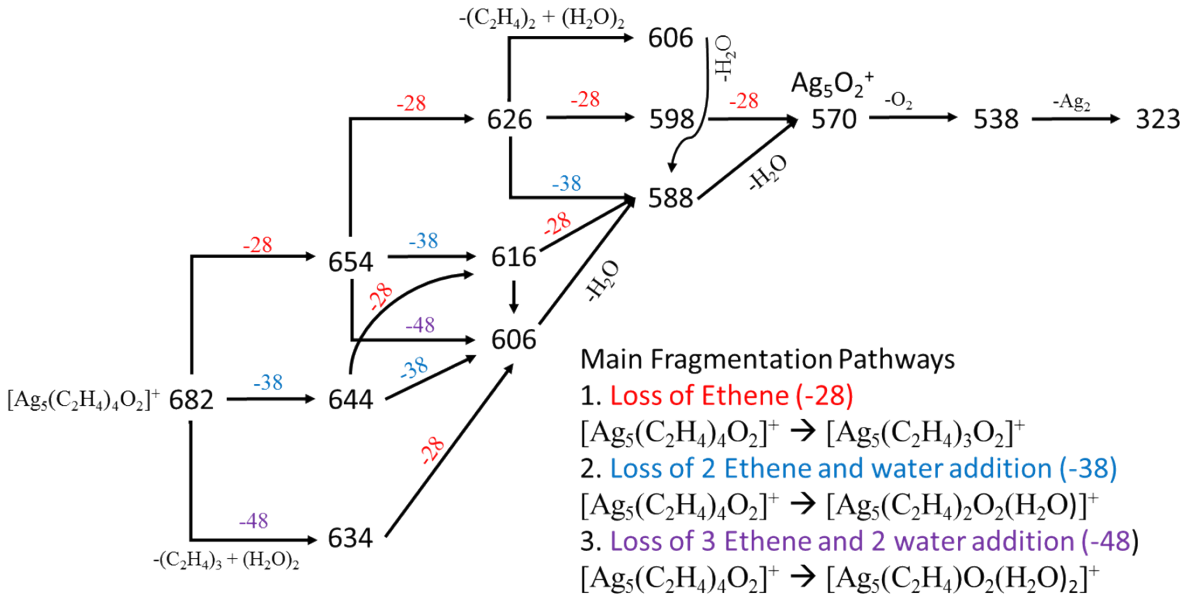

Figure S17: MS fragmentation tree for $[Ag_5(C_2H_4)O_2]^+$. Arrows indicate a single stage of CID.

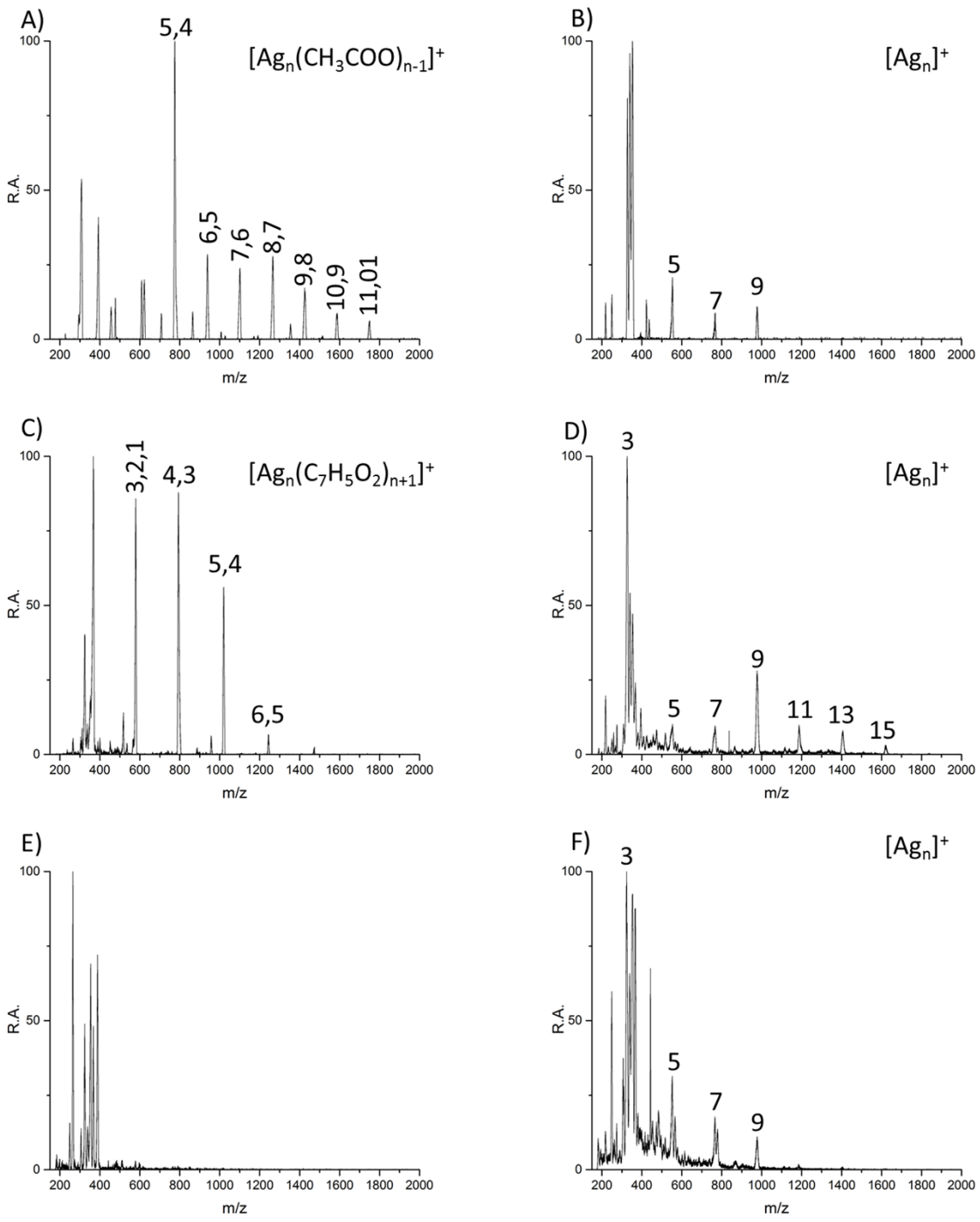

Figure S18: Positive ion mode mass spectra of A) unheated and B) heated silver acetate. Positive ion mode of C) unheated and D) heated silver benzoate. Positive ion mode mass spectra of E) unheated and F) heated silver fluoride. All these mass spectra were collected on a custom surface science instrument. The numbers above each peak indicate the number of silver atoms and ligands present