SUPPORTING INFORMATION

"Guanine Tautomerism in Ionic Complexes with Ag^+ Investigated by IRMPD Spectroscopy and Mass Spectrometry"

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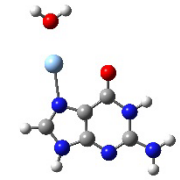
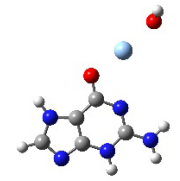
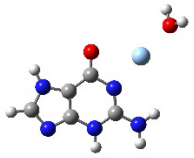
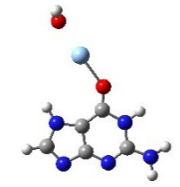
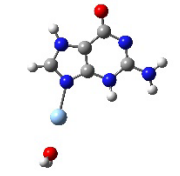
Table SI 1. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GKA(1,7)Ag\text{-}H_2O]^+$ and $[GKA(1,9)Ag\text{-}H_2O]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GKA(1,9)N7Ag{-}H_2O]^+$	0	0	1	0	0	1
 $[GKA(1,7)N9Ag{-}H_2O]^+$	4.3	4.0	$1x10^{-3}$	0.2	0.3	0.6
 $[GKA(1,7)N3Ag{-}H_2O]^+$	8.3	7.9	$2x10^{-6}$	2.6	2.4	$2x10^{-2}$
 $[GKA(1,7)OAg{-}H_2O]^+$	19.9	18.9	$2x10^{-14}$	9.5	8.6	$5x10^{-7}$
 $[GKA(1,9)N3Ag{-}H_2O]^+$	23.5	23.3	$8x10^{-18}$	4.1	3.9	$1x10^{-3}$

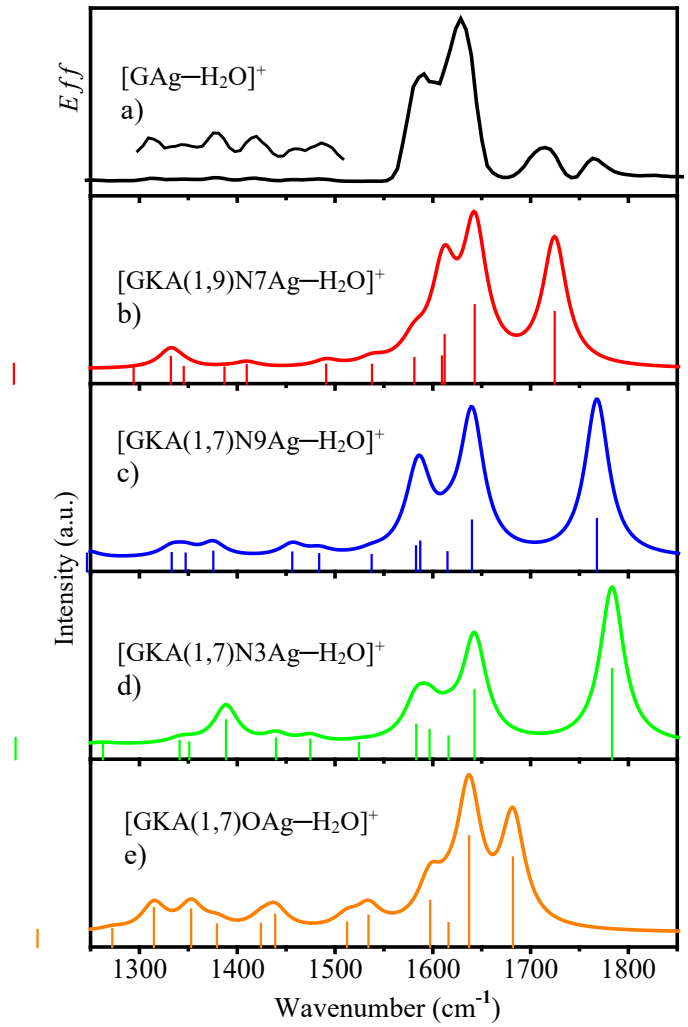
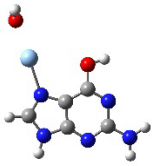
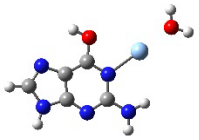
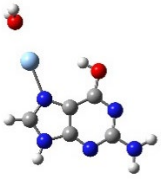
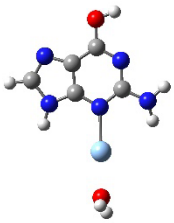
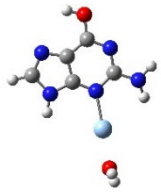
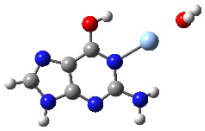


Figure SI 1. a) Experimental IRMPD spectrum of $[GAg–H_2O]^+$ complex recorded in the spectral range 1250–1850 cm^{-1} and calculated spectra of the four lowest energy isomers calculated at the B3LYP/6-311G++(d,p) and SDD level for Ag^+: b) $[GKA(1,9)N7Ag–H_2O]^+$, c) $[GKA(1,7)N9Ag–H_2O]^+$, d) $[GKA(1,7)N3Ag–H_2O]^+$ and e) $[GKA(1,7)OAg–H_2O]^+$. The vibrational frequencies were corrected with a factor of 0.983.

Table SI 2. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GEA(9)Ag\text{-}H_2O]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GEA(9)_{anti}N7Ag{-}H_2O]^+$	7.0	6.7	$1x10^{-5}$	7.3	6.9	$9x10^{-5}$
 $[GEA(9)_{syn}N1Ag{-}H_2O]^+$	11.8	12.4	$8x10^{-10}$	11.1	11.4	$4x10^{-9}$
 $[GEA(9)_{syn}N7Ag{-}H_2O]^+$	18.2	17.9	$8x10^{-14}$	10.4	10.4	$2x10^{-8}$
 $[GEA(9)_{anti}N3Ag{-}H_2O]^+$	19.3	19.5	$5x10^{-15}$	9.5	9.9	$6x10^{-8}$

	19.8	20.0	$2x10^{-15}$	10.5	9.6	$9x10^{-8}$
$[GEA(9)_{syn}N3Ag{-}H_2O]^+$						
	21.8	21.8	$1x10^{-16}$	12.8	13.2	$2x10^{-1}$
$[GEA(9)_{anti}N1Ag{-}H_2O]^+$						

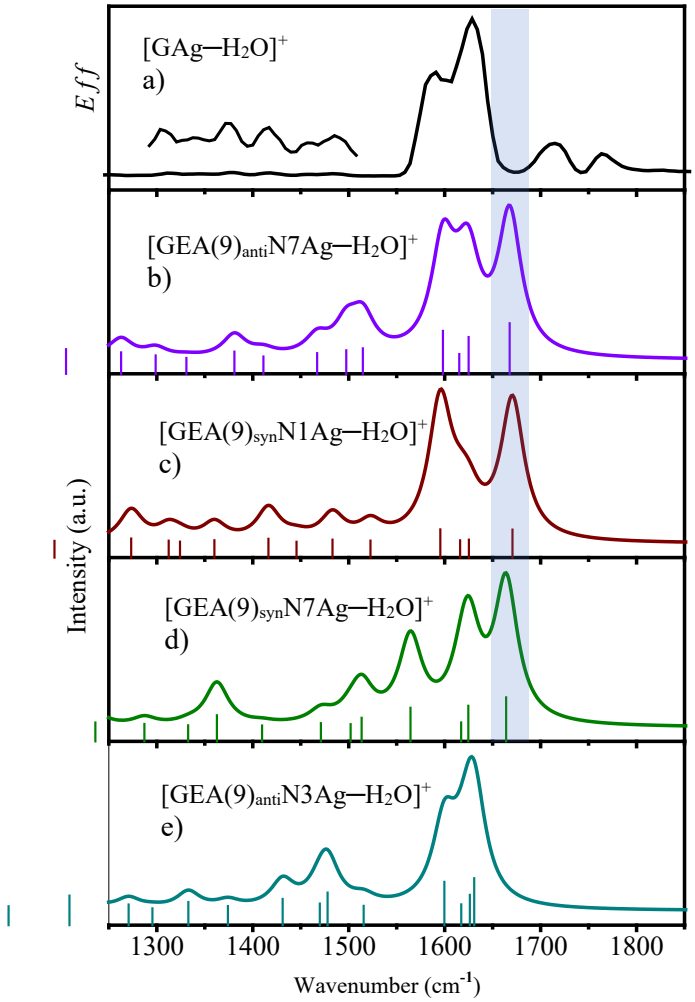
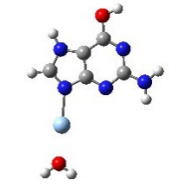
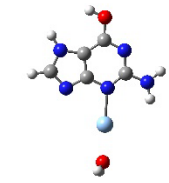
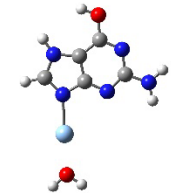
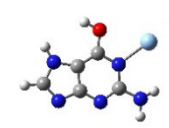
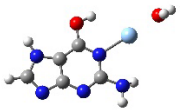


Figure SI 2. a) Experimental IRMPD spectrum of $[GAg{-}H_2O]^+$ complex recorded in the spectral range 1250─1850 cm^{-1} and calculated spectra of the four lowest energy isomers calculated at the B3LYP/6-311G++(d,p) and SDD level for Ag^+: b) $[GEA(9)_{anti}N7Ag{-}H_2O]^+$, c) $[GEA(9)_{syn}N1Ag{-}H_2O]^+$, d) $[GEA(9)_{syn}N7Ag{-}H_2O]^+$ and e) $[GEA(9)_{anti}N3Ag{-}H_2O]^+$. The vibrational frequencies were corrected with a factor of 0.983. The vertical bar indicates the diagnostic bands of the three most stable isomers of $[GEA(9)Ag{-}H_2O]^+$, which are absent in the IRMPD spectrum.

Table SI 3. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GEA(7)Ag\text{-}H_2O]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GEA(7)_{anti}N9Ag{-}H_2O]^+$	7.3	8.2	$1x10^{-6}$	8.3	8.3	$8x10^{-7}$
 $[GEA(7)_{anti}N3Ag{-}H_2O]^+$	8.0	7.8	$2x10^{-6}$	9.2	9.2	$2x10^{-7}$
 $[GEA(7)_{syn}N3Ag{-}H_2O]^+$	16.1	15.4	$5x10^{-12}$	12.4	12.5	$7x10^{-10}$
 $[GEA(7)_{syn}N9Ag{-}H_2O]^+$	16.3	16.9	$4x10^{-13}$	11.5	11.8	$2x10^{-9}$
 $[GEA(7)_{syn}N1Ag{-}H_2O]^+$	23.3	23.1	$1x10^{-17}$	15.2	15.2	$7x10^{-12}$

	25.1	25.0	$5x10^{-19}$	14.6	14.5	$2x10^{-11}$
$[GEA(7)_{anti}N1Ag{-}H_2O]^+$						

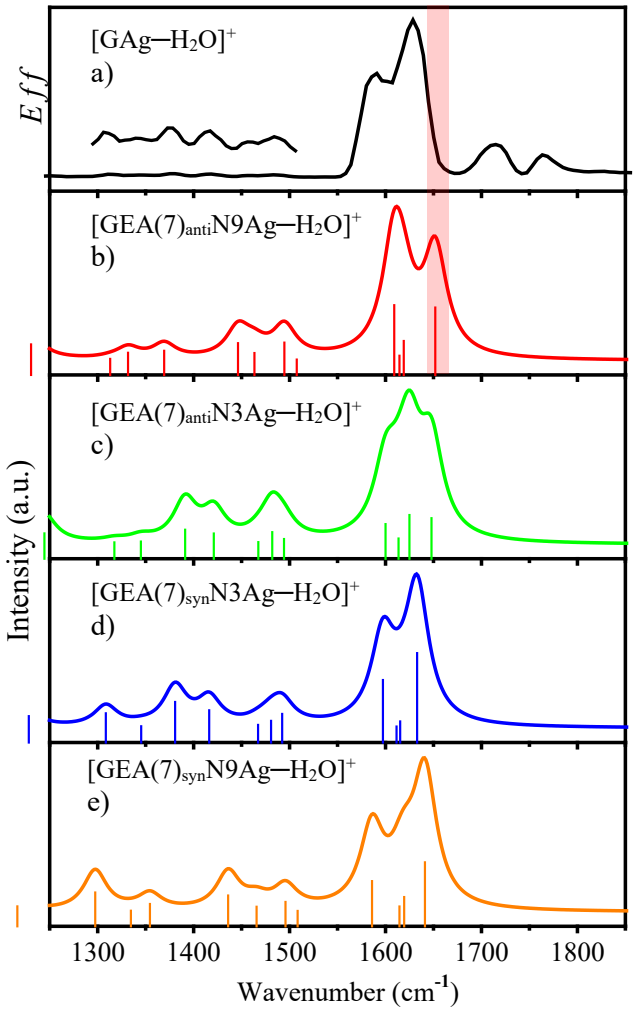
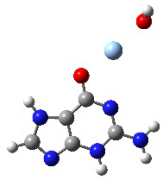
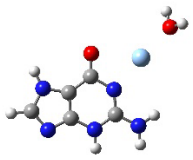
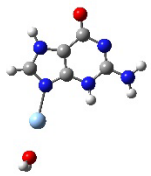


Figure SI 3. a) Experimental IRMPD spectrum of $[GAg{-}H_2O]^+$ complex recorded in the spectral range 1250─1850 cm^{-1} and calculated spectra of the four lowest energy isomers calculated at the B3LYP/6-311G++(d,p) and SDD level for Ag^+: b) $[GEA(7)_{anti}N9Ag{-}H_2O]^+$, c) $[GEA(7)_{anti}N3Ag{-}H_2O]^+$, d) $[GEA(7)_{syn}N3Ag{-}H_2O]^+$ and e) $[GEA(7)_{syn}N9Ag{-}H_2O]^+$. The vibrational frequencies were corrected with a factor of 0.983. The vertical bar indicates the diagnostic band of the most stable isomer of $[GEA(7)Ag{-}H_2O]^+$, which is absent in the IRMPD spectrum.

Table SI 4. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GKA(3,7)Ag\text{-}H_2O]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GKA(3,7)O/N1Ag{-}H_2O]^+$	8.8	7.0	$7x10^{-6}$	8.8	7.4	$4x10^{-6}$
 $[GKA(3,7)N1Ag{-}H_2O]^+$	9.4	8.4	$7x10^{-7}$	5.4	4.8	$3x10^{-4}$
 $[GKA(3,7)N9Ag{-}H_2O]^+$	24.2	23.7	$4x10^{-18}$	6.8	6.1	$3x10^{-5}$

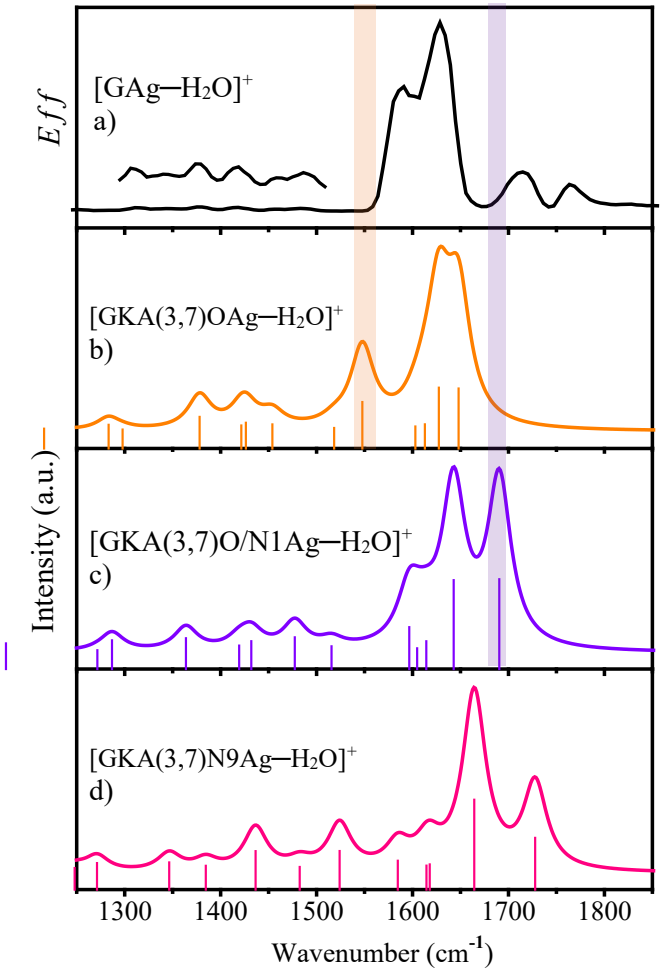
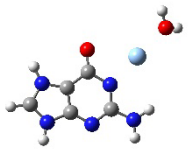
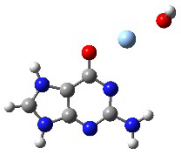
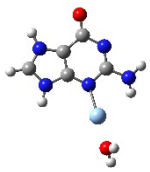


Figure SI 4. a) Experimental IRMPD spectrum of $[GAg{-}H_2O]^+$ complex recorded in the spectral range 1250─1850 cm^{-1} and calculated spectra of the four lowest energy isomers calculated at the B3LYP/6-311G++(d,p) and SDD level for Ag^+: b) $[GKA(3,7)OAg{-}H_2O]^+$, c) $[GKA(3,7)O/N1Ag{-}H_2O]^+$ and d) $[GKA(3,7)N9Ag{-}H_2O]^+$. The vibrational frequencies were corrected with a factor of 0.983. The vertical bars indicate the diagnostic bands of the two most stable isomers of $[GKA(3,7)Ag{-}H_2O]^+$, which are absent in the IRMPD spectrum.

Table SI 5. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GKA(7,9)Ag\text{-}H_2O]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GKA(7,9)N1Ag{-}H_2O]^+$	11.4	10.7	$1x10^{-8}$	8.5	8.2	$1x10^{-6}$
 $[GKA(7,9)OAg{-}H_2O]^+$	13.4	12.1	$1x10^{-9}$	12.9	12.7	$5x10^{-10}$
 $[GKA(7,9)N3Ag{-}H_2O]^+$	33.0	32.8	$9.x10^{-25}$	13.0	12.5	$7x10^{-10}$

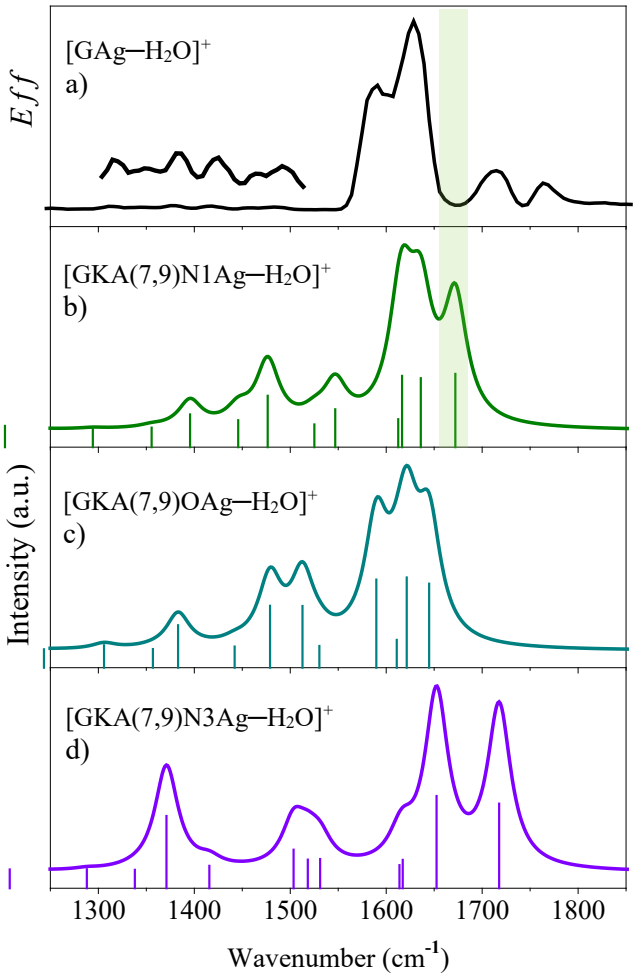
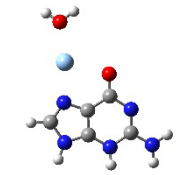
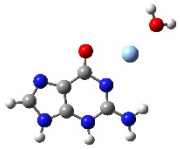


Figure SI 5. a) Experimental IRMPD spectrum of $[GAg─H_2O]^+$ complex recorded in the spectral range 1250─1850 cm^{-1} and calculated spectra of the four lowest energy isomers calculated at the B3LYP/6-311G++(d,p) and SDD level for Ag^+: b) $[GKA(7,9)N71Ag─H_2O]^+$, c) $[GKA(7,9)OAg─H_2O]^+$ and d) $[GKA(7,9)N3Ag─H_2O]^+$. The vibrational frequencies were corrected with a factor of 0.983. The vertical bar indicates the diagnostic band of the most stable isomer of $[GKA(7,9)Ag─H_2O]^+$, which is absent in the IRMPD spectrum.

Table SI 6. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GKA(3,9)Ag\text{-}H_2O]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GKA(3,9)N7/OAg{-}H_2O]^+$	15.6	14.8	$2x10^{-11}$	9.3	8.6	$5x10^{-7}$
 $[GKA(3,9)N1Ag{-}H_2O]^+$	20.3	19.1	$1x10^{-14}$	9.3	8.8	$4x10^{-7}$

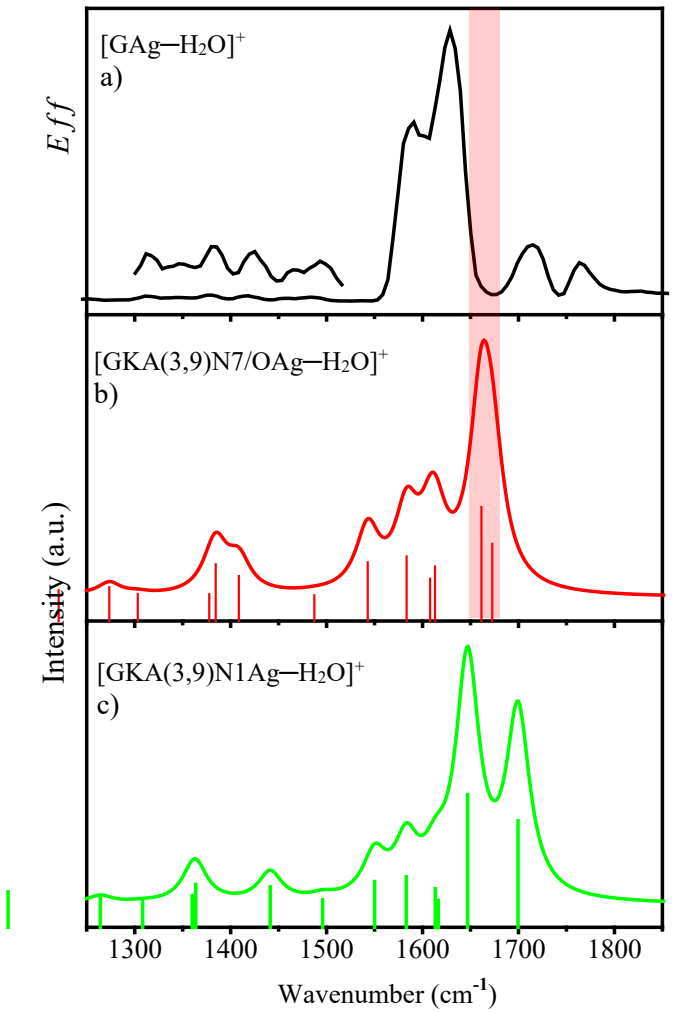


Figure SI 6. a) Experimental IRMPD spectrum of $[GAg─H_2O]^+$ complex recorded in the spectral range 1250─1850 cm^{-1} and calculated spectra of the four lowest energy isomers calculated at the B3LYP/6-311G++(d,p) and SDD level for Ag^+: b) $[GKA(3,9)N7/OAg─H_2O]^+$ and c) $[GKA(3,9)N1Ag─H_2O]^+$. The vibrational frequencies were corrected with a factor of 0.983. The vertical bar indicates the diagnostic band of the most stable isomer of $[GKA(3,9)Ag─H_2O]^+$, which is absent in the IRMPD spectrum.

Table SI 7. Relative standard Gibbs energies calculated at 298K (ΔG°) for the monohydrated isomers of $[GKA(1,9)N7Ag]^+$. Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

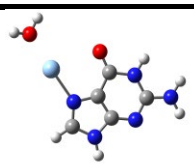
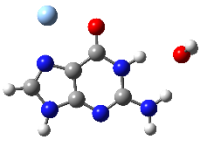
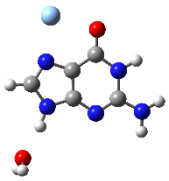
Structure	Gas phase	
	$\Delta G°_{298K}$ (kcal/mol)	R.P. 298 K
 $[GKA(1,9)N7Ag{-}H_2O]^+$	0	1
 $[GKA(1,9)N7Ag{-}H_2O]^+$-1	8.6	$5x10^{-7}$
 $[GKA(1,9)N7Ag{-}H_2O]^+$ -2	9.7	$7.8x10^{-8}$
 $[GKA(1,9)N7Ag{-}H_2O]^+$-3	10.1	$4x10^{-8}$
 $[GKA(1,9)N7Ag{-}H_2O]^+$-4	12.3	$9.6x10^{-10}$

Table SI 8. Relative standard Gibbs energies calculated at 298K (ΔG°) for the monohydrated isomers of $[GKA(1,7)N9Ag]^+$. Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

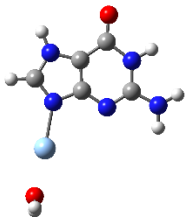
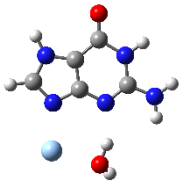
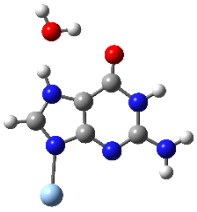
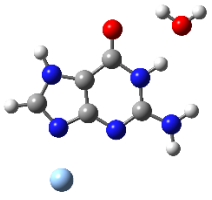
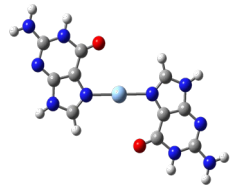
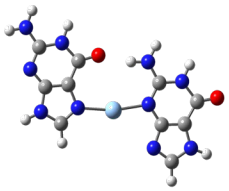
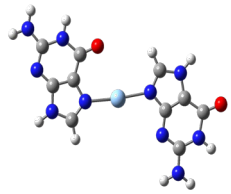
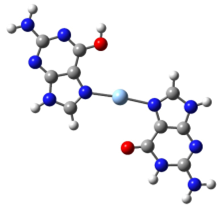
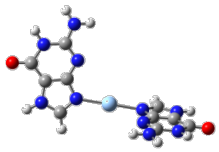
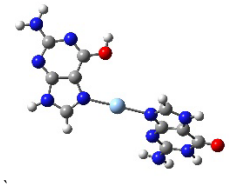
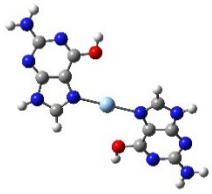
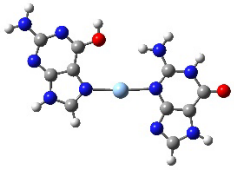
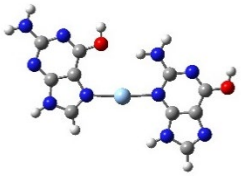
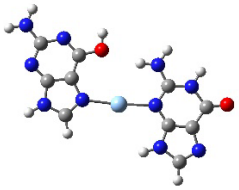
Structure	Gas phase	
	$\Delta G°_{298K}$ (kcal/mol)	R.P. 298 K
 $[GKA(1,7)N9Ag{-}H_2O]^+$	0	1
 $[GKA(1,7)N9Ag{-}H_2O]^+$-1	9	$2.5x10^{-7}$
 $[GKA(1,7)N9Ag{-}H_2O]^+$ -2	11.7	$2.7x10^{-9}$
 $[GKA(1,7)N9Ag{-}H_2O]^+$-3	14.3	$3.3x10^{-11}$

Table SI 9. Relative energies including zero point energy corrections (EE+ZPE) and relative standard Gibbs energies calculated at 298K (ΔG°) for the isomers of $[GAgG]^+$ complex and the correction of relative energies considering the effect of the solvent (PCM). Relative populations (R.P.) were calculated assuming a Boltzmann distribution at 298 K.

Structure	Gas phase			PCM (water)		
	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.	EE+ZPE (kcal/mol)	$\Delta G°_{298K}$ (kcal/mol)	R.P.
 $[GKA(1,9)N7\text{-}Ag\text{-}N7GKA(1,9)]^+$	0	0	1	0	0	1
 $[GKA(1,9)N7\text{-}Ag\text{-}N3GKA(1,7)]^+$	2.2	2.7	$1x10^{-2}$	0.5	2.2	$2x10^{-2}$
 $[GKA(1,9)N7\text{-}Ag\text{-}N9GKA(1,7)]^+$	2.9	2.8	$9x10^{-3}$	0.5	1.2	0.1
 $[GEA(9)_{anti}N7\text{-}Ag\text{-}N7GKA(1,9)]^+$	5.2	5.0	$2x10^{-4}$	7.7	8.2	$1x10^{-6}$
 $[GKA(1,7)N9\text{-}Ag\text{-}N9GKA(1,7)]^+$	6.3	5.8	$6x10^{-5}$	1.2	2.4	$2x10^{-2}$

	8.7	8.3	$8x10^{-7}$	8.1	8.8	$4x10^{-7}$
$[GEA(9)_{anti}N7\text{-}Ag\text{-}N9GKA(1,7)]^+$						
	11.2	10.4	$2x10^{-8}$	6.3	6.4	$2x10^{-5}$
$[GEA(9)_{anti}N7\text{-}Ag\text{-}N7GEA(9)_{anti}]^+$						
	11.8	11.8	$2x10^{-9}$	9.9	10.9	$1x10^{-8}$
$[GEA(9)_{anti}N7\text{-}Ag\text{-}N3GKA(1,7)]^+$						
	20.7	22.9	$2x10^{-17}$	16.7	17.9	$8x10^{-14}$
$[GEA(9)_{anti}N7\text{-}Ag\text{-}N3GEA(9)_{anti}]^+$						
	23.8	26.2	$6x10^{-20}$	10.8	12.2	$1x10^{-9}$
$[GEA(9)_{anti}N7\text{-}Ag\text{-}N3GKA(1, 9)]^+$						