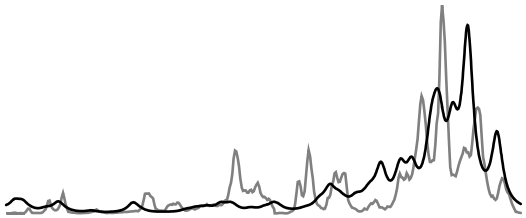
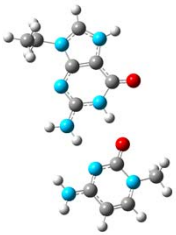
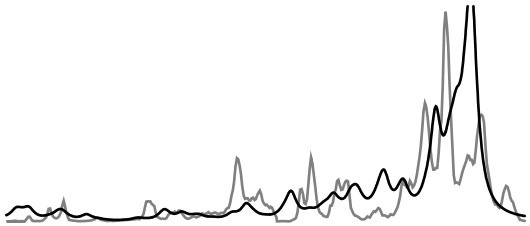
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Figure S1

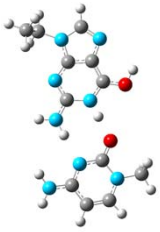


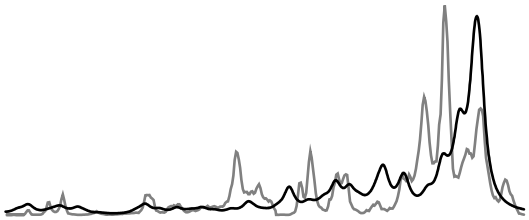
(9eG:1mC)H$^+$_N7(G)
$\Delta_{rel}H$ = 46.9
$\Delta_{rel}G$ = *40.8*



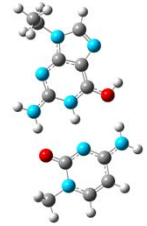


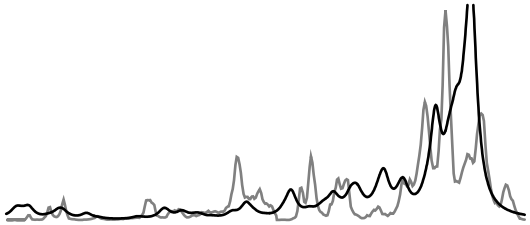
(9eG:1mC)H$^+$_O6(G)
$\Delta_{rel}H$ = 52.2
$\Delta_{rel}G$ = *45.9*



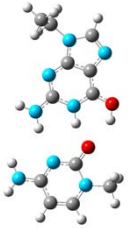


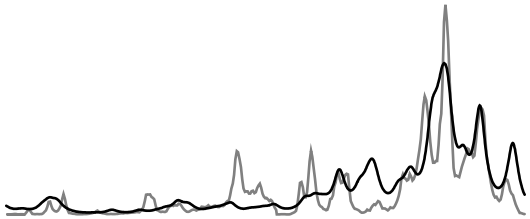
(9eG:1mC)H$^+$_ O6(G)_2
$\Delta_{rel}H$ = 49.4
$\Delta_{rel}G$ = *47.1*





(9eG:1mC)H$^+$_O6(G)_3
$\Delta_{rel}H$ = 63.1
$\Delta_{rel}G$ = *53.2*

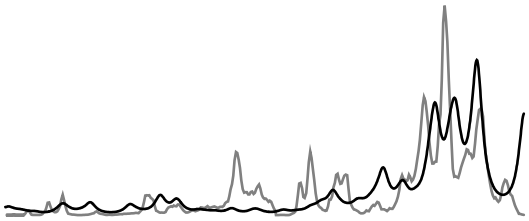




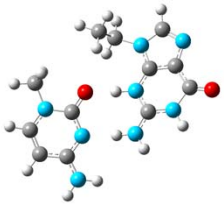
(9eG:1mC)H$^+$_N7(G)_2
$\Delta_{rel}H$ = 57.5
$\Delta_{rel}G$ = *55.1*

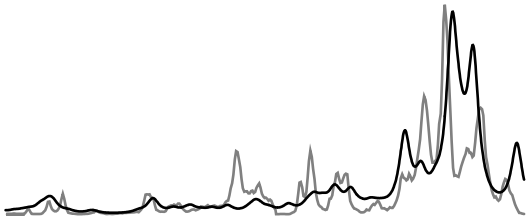
Some other higher energy structures of **(9eG:1mC)H$^+$** along with their enthalpies and 298 K Gibbs energies relative to Hoo-N3(1mC)H$^+$ and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are based on their protonation sites. All energies are presented in kJ mol^{-1}

Figure S2

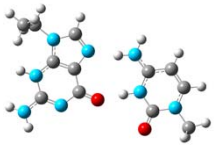


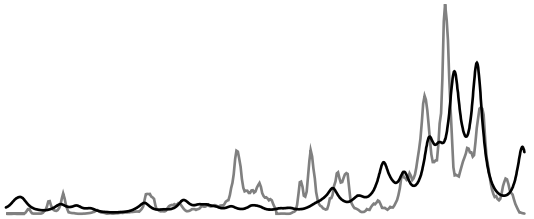
(9eG:1mC)H$^+$_N3(G)
$\Delta_{rel}H$ = 73.2
$\Delta_{rel}G$ = *71.2*



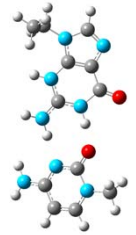


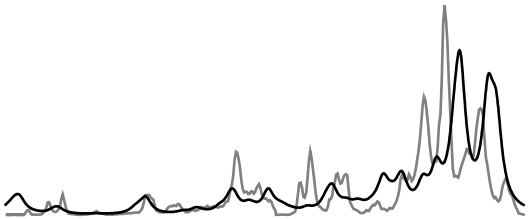
(9eG:1mC)H$^+$_N3(G)_2
$\Delta_{rel}H$ = 86.2
$\Delta_{rel}G$ = *79.7*



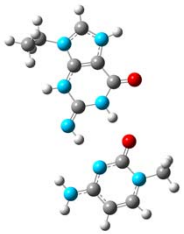


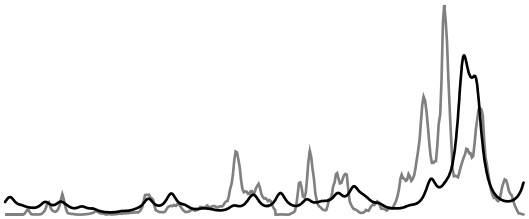
(9eG:1mC)H$^+$_N3(G)_3
$\Delta_{rel}H$ = 102.8
$\Delta_{rel}G$ = *96.3*



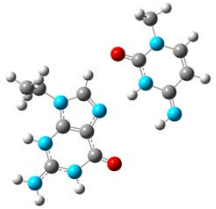


(9eG:1mC)H$^+$_N7(G)_3
$\Delta_{rel}H$ = 151.1
$\Delta_{rel}G$ = *143.8*



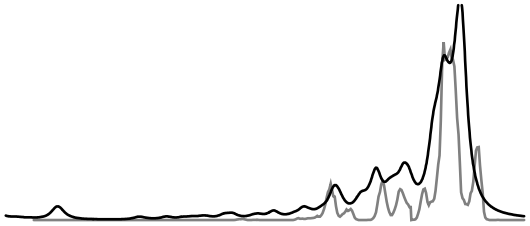


(9eG:1mC)H$^+$ _N3(G)_4
$\Delta_{rel}H$ = 228.9
$\Delta_{rel}G$ = *212.7*



Some other higher energy structures of **(9eG:1mC)H$^+$** along with their enthalpies and 298 K Gibbs energies relative to Hoo-N3(1mC)H$^+$ and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are based on their protonation sites. All energies are presented in kJ mol^{-1}

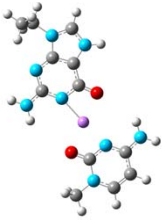
Figure S3

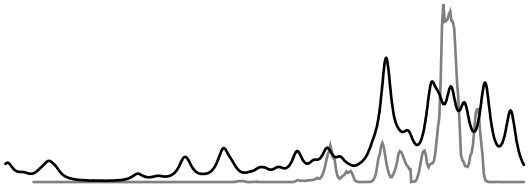


Li_N1O6-O2N3_1

$\Delta_{rel}H$ = 48.8

$\Delta_{rel}G$ = *41.0*

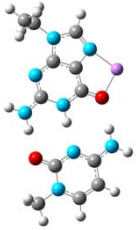


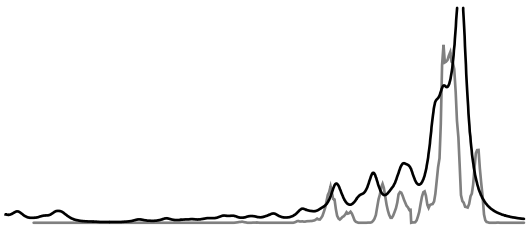


Li_O6N7

$\Delta_{rel}H$ = 33.5

$\Delta_{rel}G$ = *41.4*

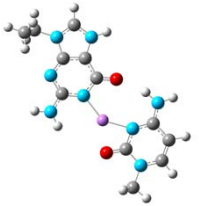


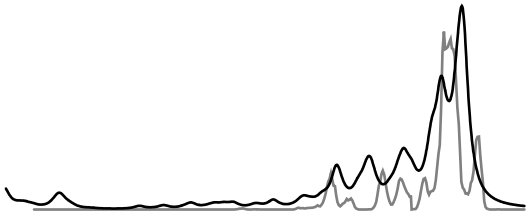


Li_N1-O2N3

$\Delta_{rel}H$ = 49.6

$\Delta_{rel}G$ = *46.5*

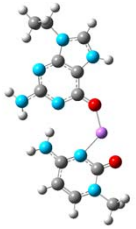


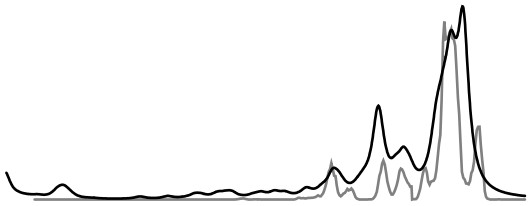


Li_O6-O2N3_1

$\Delta_{rel}H$ = 43.9

$\Delta_{rel}G$ = *46.8*





Li_N1O6-O2_1

$\Delta_{rel}H$ = 48.5

$\Delta_{rel}G$ = *50.9*

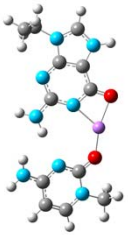


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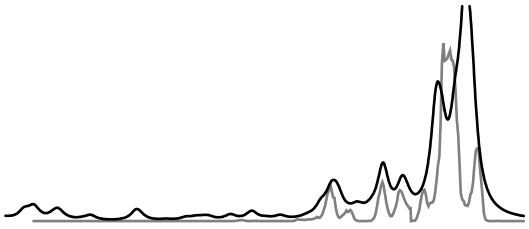
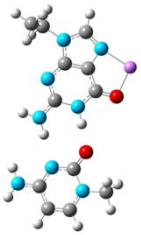
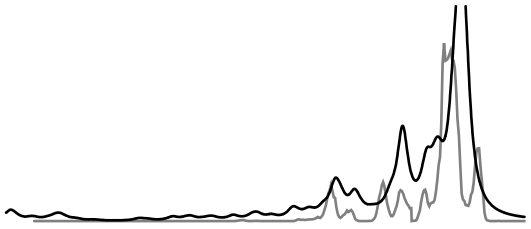
Figure S4

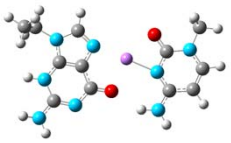


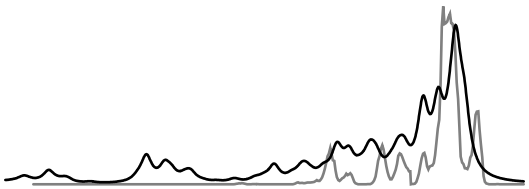
Li_O6N7_2
$\Delta_{rel}H$ = 55.4
$\Delta_{rel}G$ = *53.8*



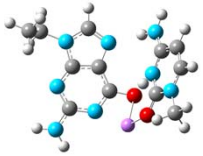


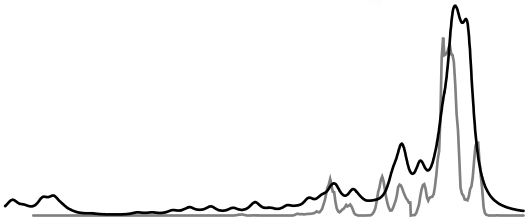
Li_O6N7-O2N3_3
$\Delta_{rel}H$ = 61.3
$\Delta_{rel}G$ = *55.4*



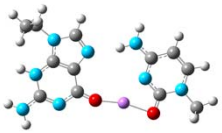


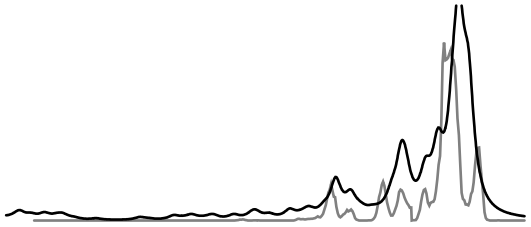
Li_N1O6-O2_2
$\Delta_{rel}H$ = 46.6
$\Delta_{rel}G$ = *57.0*



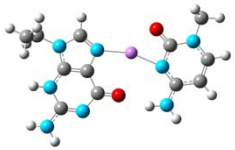


Li_N1-O2N3_2
$\Delta_{rel}H$ = 58.2
$\Delta_{rel}G$ = *57.5*



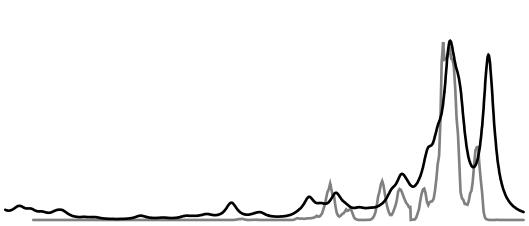


Li_N7-O2N3_2
$\Delta_{rel}H$ = 62.1
$\Delta_{rel}G$ = *58.7*

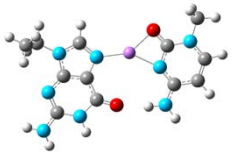


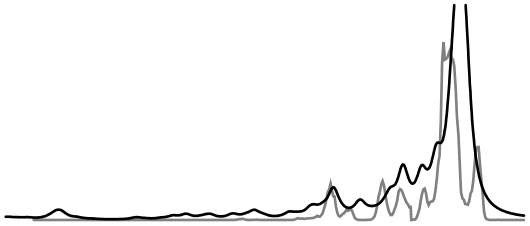
Some other higher energy structures of **(9eG:1mC)Li**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Li_O6-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S5

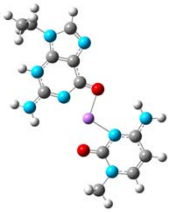


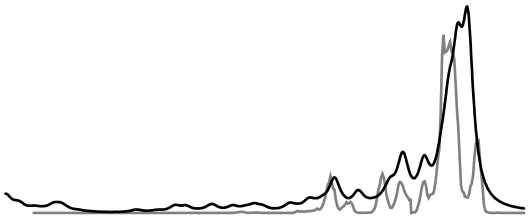
Li_N7-O2N3_3
$\Delta_{rel}H$ = 62.6
$\Delta_{rel}G$ = *62.8*



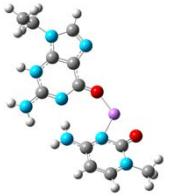


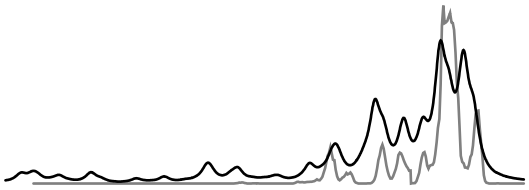
Li_N1O6-O2N3_2
$\Delta_{rel}H$ = 73.6
$\Delta_{rel}G$ = *65.0*



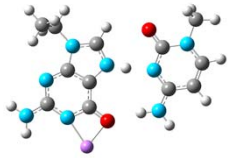


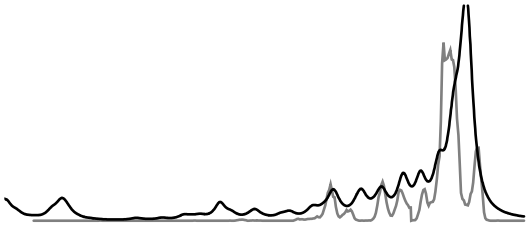
Li_O6-O2N3_2
$\Delta_{rel}H$ = 78.8
$\Delta_{rel}G$ = *76.5*





Li_N1O6
$\Delta_{rel}H$ = 74.2
$\Delta_{rel}G$ = *78.8*





Li_N1O6-O2_3
$\Delta_{rel}H$ = 79.0
$\Delta_{rel}G$ = *81.0*

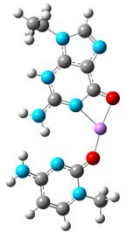


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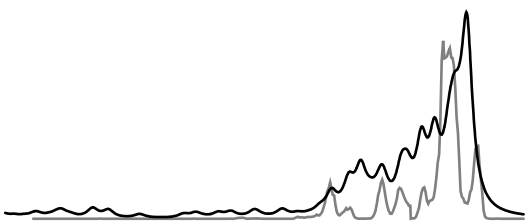
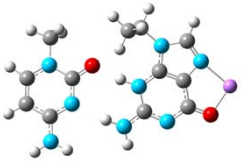
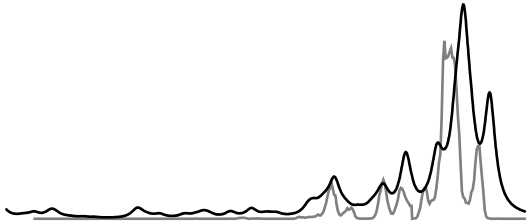
Figure S6

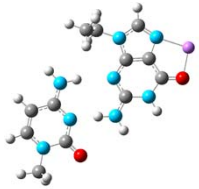


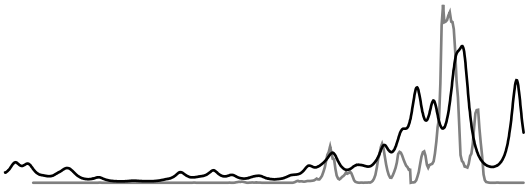
Li-O6N7_3
$\Delta_{rel}H$ = 85.0
$\Delta_{rel}G$ = *86.4*



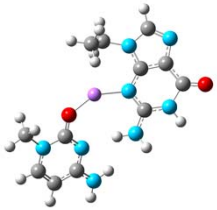


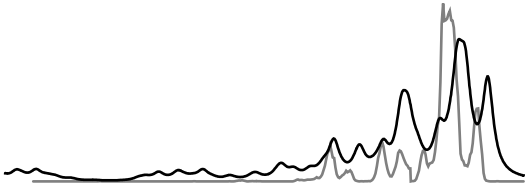
Li_O6N7_4
$\Delta_{rel}H$ = 93.6
$\Delta_{rel}G$ = *94.3*



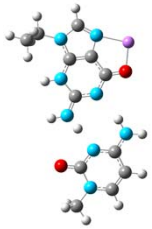


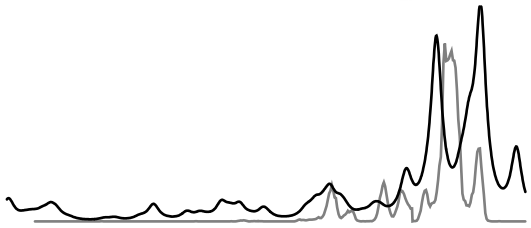
Li_N3-O2
$\Delta_{rel}H$ = 104.6
$\Delta_{rel}G$ = *104.7*



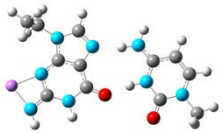


Li_O6N7_5
$\Delta_{rel}H$ = 128.7
$\Delta_{rel}G$ = *129.9*



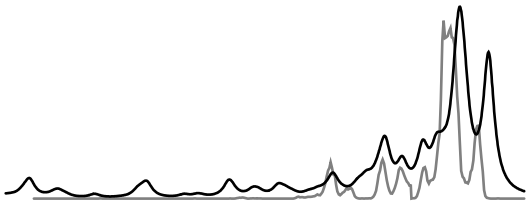


Li_N2N3_1
$\Delta_{rel}H$ = 130.1
$\Delta_{rel}G$ = *133.4*



Some other higher energy structures of **(9eG:1mC)Li**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Li_O6-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

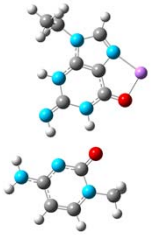
Figure S7

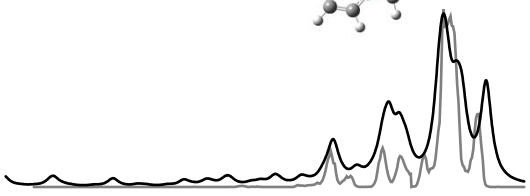


Li_O6N7_6

$\Delta_{rel}H$ = 139.8

$\Delta_{rel}G$ = *138.8*

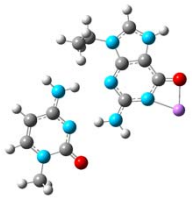


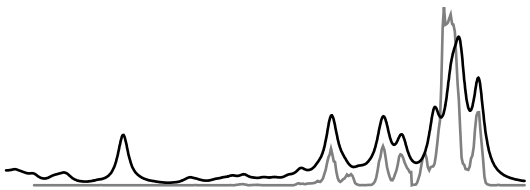


Li_N1O6_2

$\Delta_{rel}H$ = 148.9

$\Delta_{rel}G$ = *148.6*

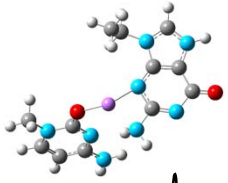


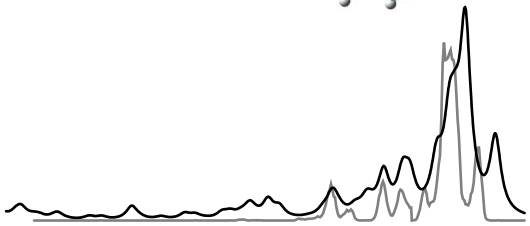


Li_N3-O2_2

$\Delta_{rel}H$ = 137.4

$\Delta_{rel}G$ = *141.3*

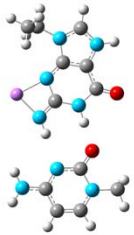


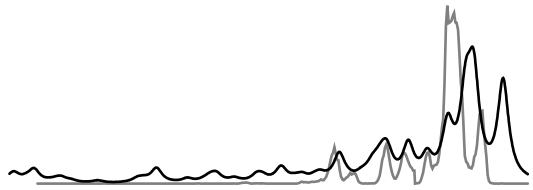


Li_N2N3_2

$\Delta_{rel}H$ = 181.8

$\Delta_{rel}G$ = *178.0*

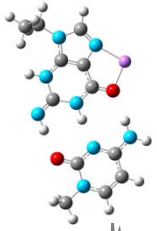


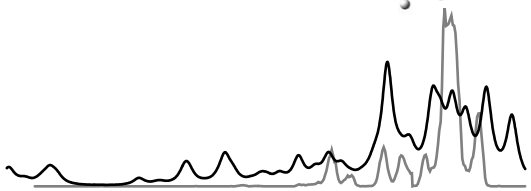


Li_O6N7_7

$\Delta_{rel}H$ = 137.4

$\Delta_{rel}G$ = *141.3*





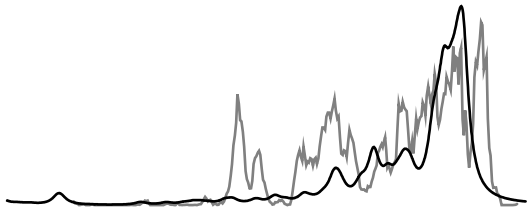
Li_N2N3_3

$\Delta_{rel}H$ = 191.6

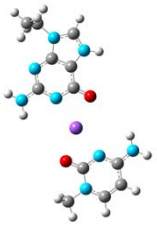
$\Delta_{rel}G$ = *194.5*

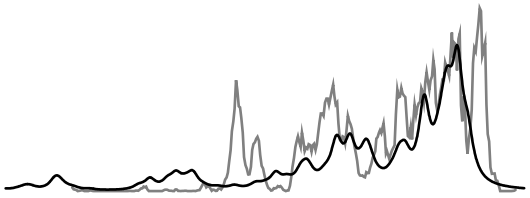
Some other higher energy structures of **(9eG:1mC)Li**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Li_O6-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S8

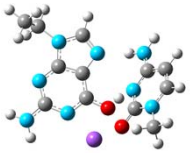


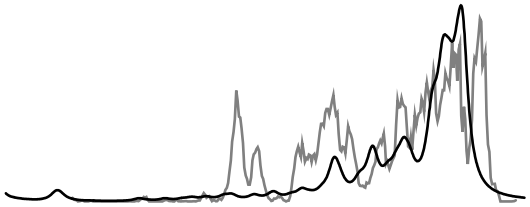
Na_N1O6-O2N3_1
$\Delta_{rel}H$ = 53.4
$\Delta_{rel}G$ = *45.3*



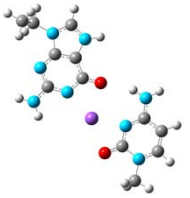


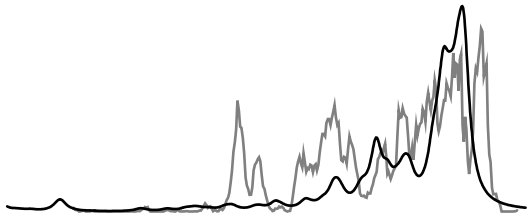
Na_N1O6-O2_1
$\Delta_{rel}H$ = 34.7
$\Delta_{rel}G$ = *46.2*



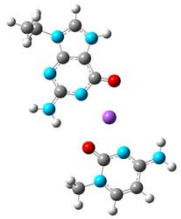


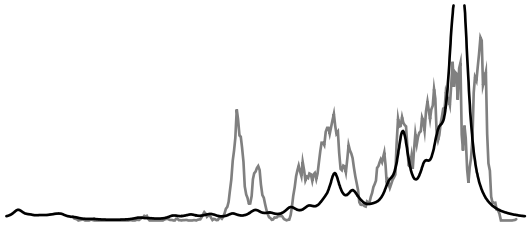
Na_N1O6-O2N3_2
$\Delta_{rel}H$ = 51.9
$\Delta_{rel}G$ = *47.9*



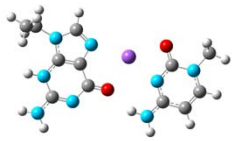


Na_N1O6-O2N3_3
$\Delta_{rel}H$ = 54.8
$\Delta_{rel}G$ = *48.2*



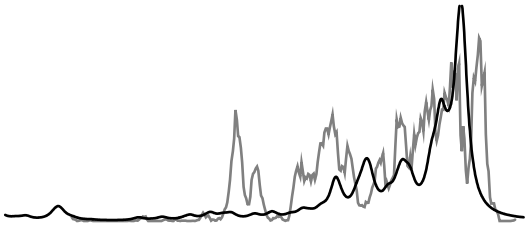


Na_O6N7-O2N3_1
$\Delta_{rel}H$ = 53.8
$\Delta_{rel}G$ = *53.4*

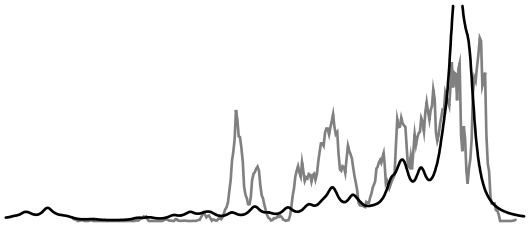


Some other higher energy structures of **(9eG:1mC)Na**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Na_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

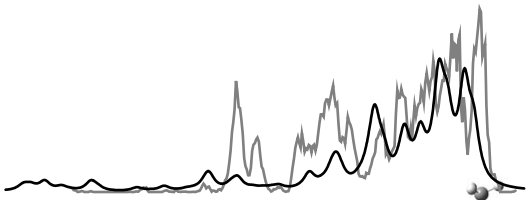
Figure S9

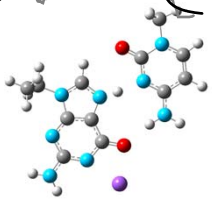


Na_O6-O2N3_2
$\Delta_{rel}H$ = 52.3
$\Delta_{rel}G$ = *56.7*

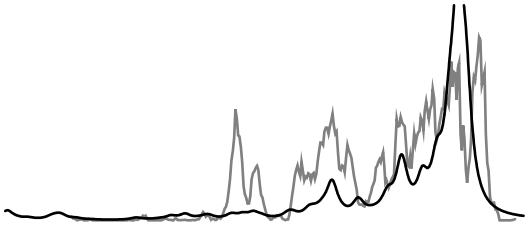


Na_O6-O2N3_3
$\Delta_{rel}H$ = 67.4
$\Delta_{rel}G$ = *66.9*

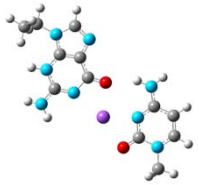


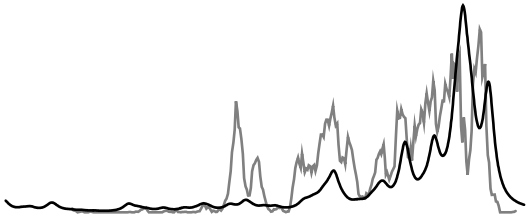


Na_N1O6
$\Delta_{rel}H$ = 61.7
$\Delta_{rel}G$ = *69.5*



Na_N1O6-O2N3_4
$\Delta_{rel}H$ = 75.5
$\Delta_{rel}G$ = *71.8*





Na_O6N7_2
$\Delta_{rel}H$ = 71.5
$\Delta_{rel}G$ = *74.9*

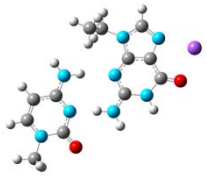


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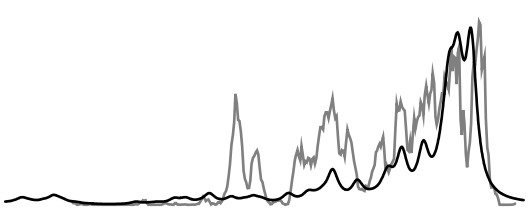
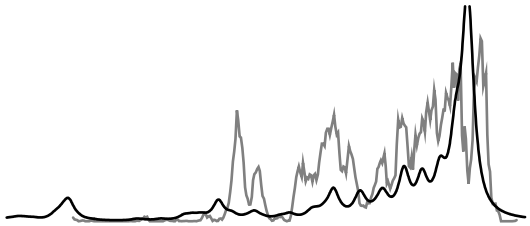
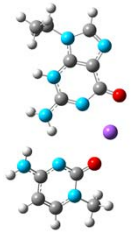
Figure S10

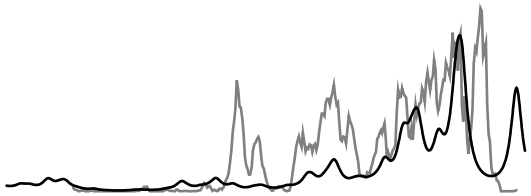


Na_O6-O2N3_4
$\Delta_{rel}H$ = 83.0
$\Delta_{rel}G$ = *81.6*

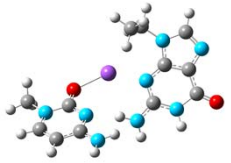


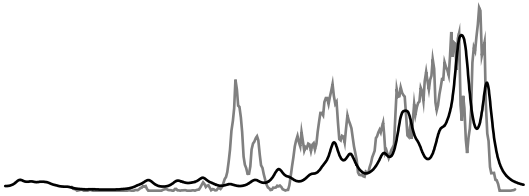
Na_N1O6-O2
$\Delta_{rel}H$ = 85.4
$\Delta_{rel}G$ = *88.3*



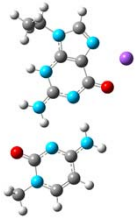


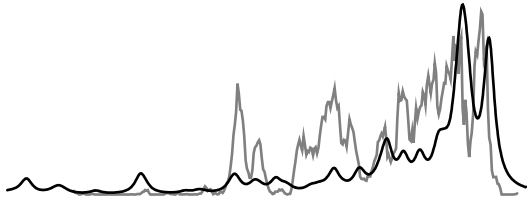
Na_N3-O2
$\Delta_{rel}H$ = 111.7
$\Delta_{rel}G$ = *112.3*





Na_O6N7_3
$\Delta_{rel}H$ = 113.6
$\Delta_{rel}G$ = *116.1*





Na_O6N7_4
$\Delta_{rel}H$ = 123.9
$\Delta_{rel}G$ = *124.7*

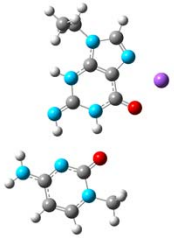


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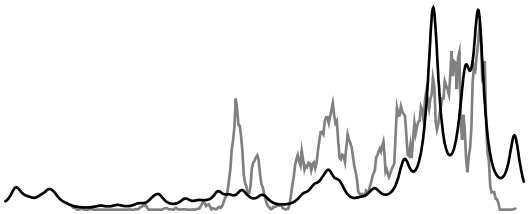
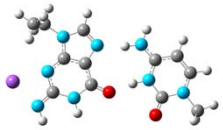
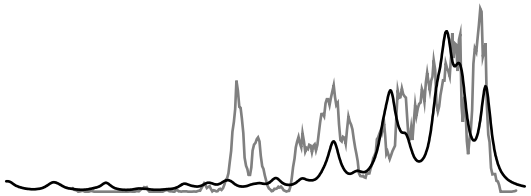
Figure S11

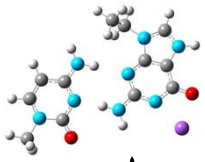


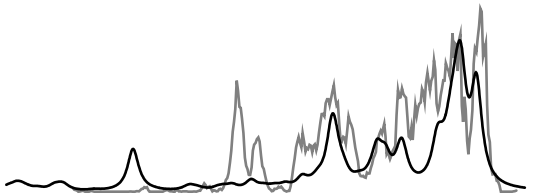
Na_N2N3
$\Delta_{rel}H$ = 120.4
$\Delta_{rel}G$ = *126.6*



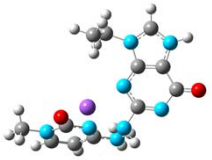


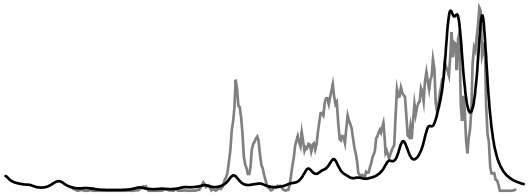
Na_N1O6_2
$\Delta_{rel}H$ = 131.3
$\Delta_{rel}G$ = *133.7*



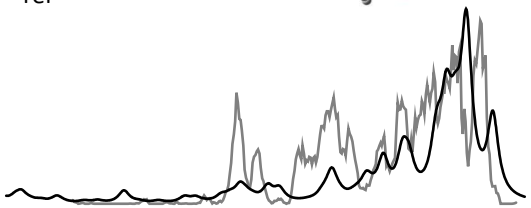


Na_N3-O2_2
$\Delta_{rel}H$ = 145.2
$\Delta_{rel}G$ = *147.8*

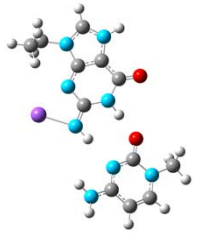


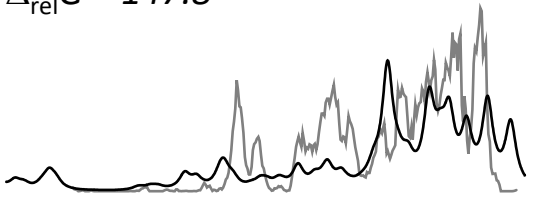


Na_N7-N2O3_2
$\Delta_{rel}H$ = 176.5
$\Delta_{rel}G$ = *176.9*

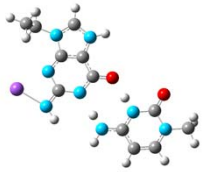


Na_N2N3_2
$\Delta_{rel}H$ = 178.0
$\Delta_{rel}G$ = *176.9*



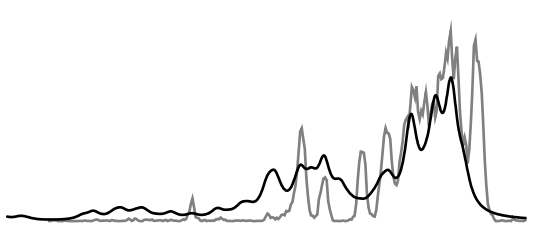


Na_N2N3_3
$\Delta_{rel}H$ = 189.2
$\Delta_{rel}G$ = *193.9*

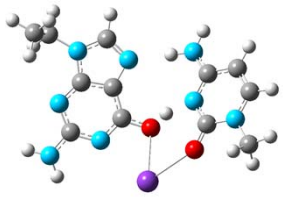


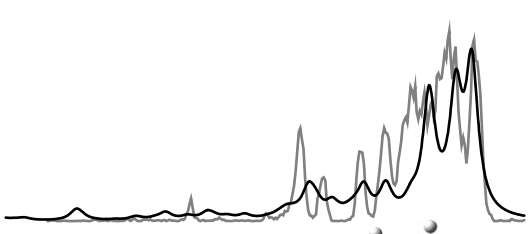
Some other higher energy structures of **(9eG:1mC)Na**$^+$ along with their energies and 298 K Gibbs energies relative to **Na_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S12

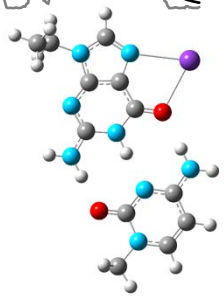


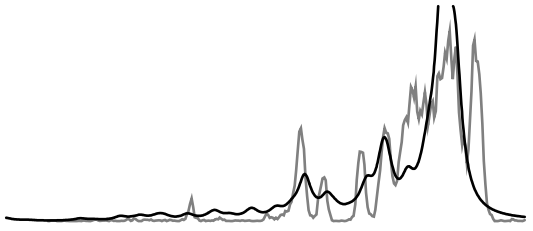
K_N1O6-O2_2
$\Delta_{rel}H$ = 18.4
$\Delta_{rel}G$ = *28.5*



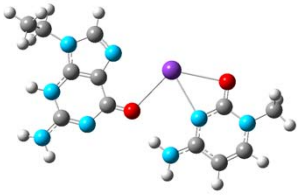


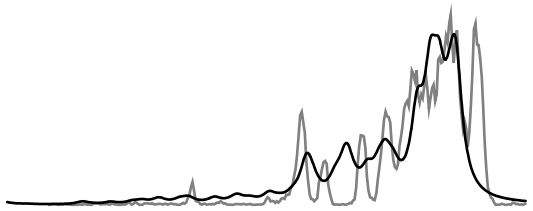
K_O6N7_3
$\Delta_{rel}H$ = 47.5
$\Delta_{rel}G$ = *50.5*



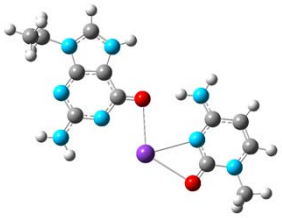


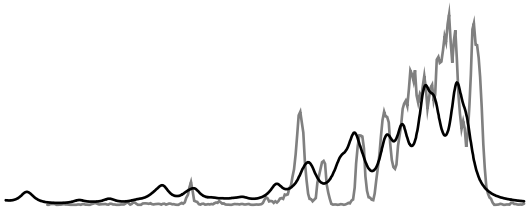
K_O6N7-O2N3
$\Delta_{rel}H$ = 52.6
$\Delta_{rel}G$ = *53.0*



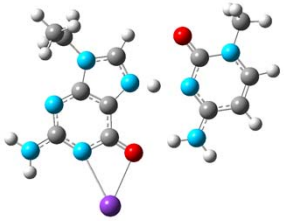


K_N1O6-O2N3
$\Delta_{rel}H$ = 55.8
$\Delta_{rel}G$ = *53.5*



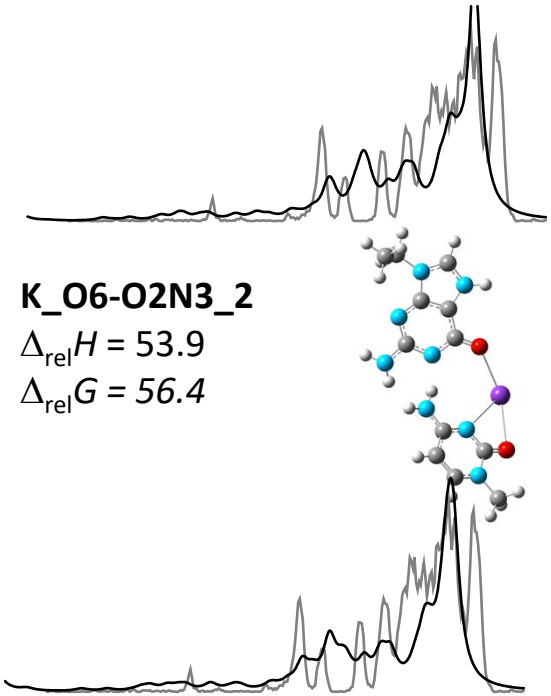


K_N1O6
$\Delta_{rel}H$ = 46.2
$\Delta_{rel}G$ = *54.1*

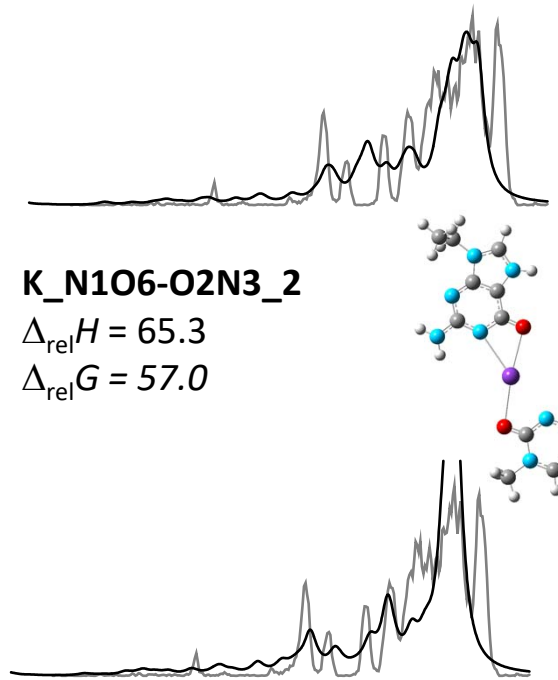


Some other higher energy structures of **(9eG:1mC)K**$^{+}$ along with their energies and 298 K Gibbs energies relative to **K_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

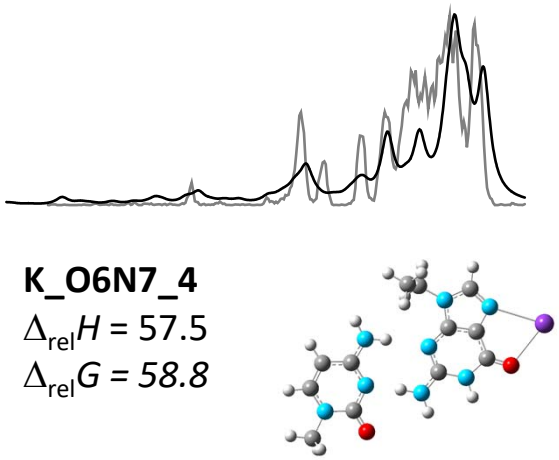
Figure S13



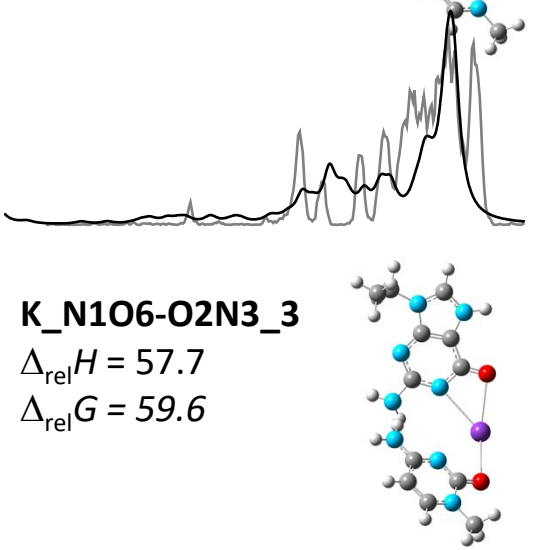
K_O6-O2N3_2
$\Delta_{rel}H$ = 53.9
$\Delta_{rel}G$ = *56.4*



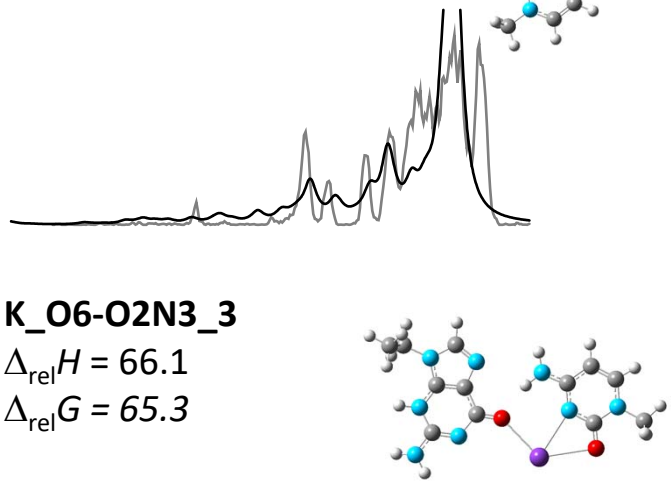
K_N1O6-O2N3_2
$\Delta_{rel}H$ = 65.3
$\Delta_{rel}G$ = *57.0*



K_O6N7_4
$\Delta_{rel}H$ = 57.5
$\Delta_{rel}G$ = *58.8*



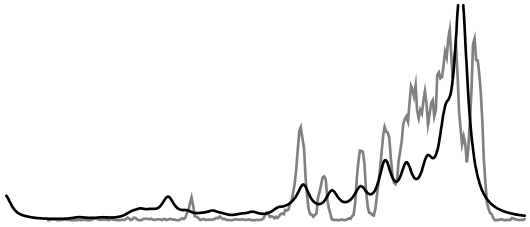
K_N1O6-O2N3_3
$\Delta_{rel}H$ = 57.7
$\Delta_{rel}G$ = *59.6*



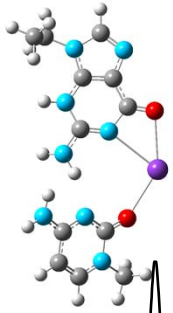
K_O6-O2N3_3
$\Delta_{rel}H$ = 66.1
$\Delta_{rel}G$ = *65.3*

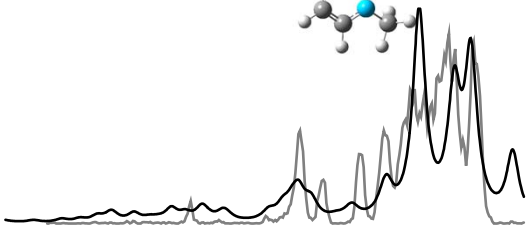
Some other higher energy structures of **(9eG:1mC)K**$^+$ along with their energies and 298 K Gibbs energies relative to **K_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S14

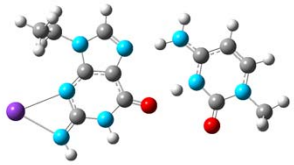


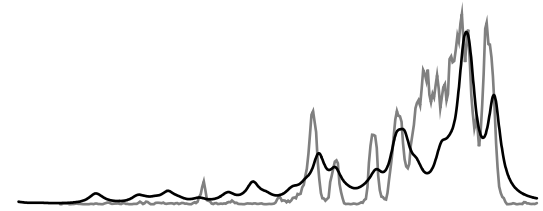
K_N1O6-O2_3
$\Delta_{rel}H$ = 86.1
$\Delta_{rel}G$ = *87.0*



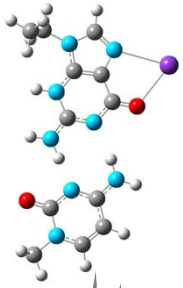


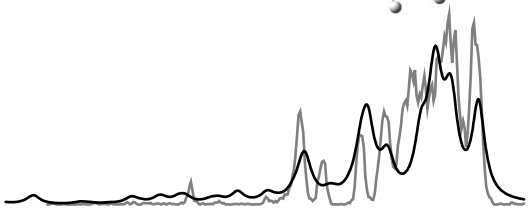
K_N2N3
$\Delta_{rel}H$ = 108.2
$\Delta_{rel}G$ = *114.4*



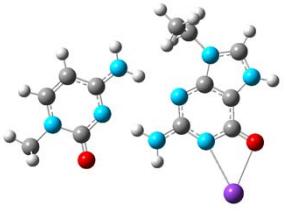


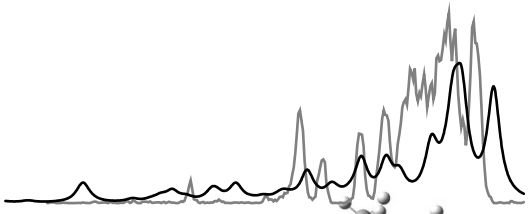
K_O6N7_5
$\Delta_{rel}H$ = 93.7
$\Delta_{rel}G$ = *94.9*



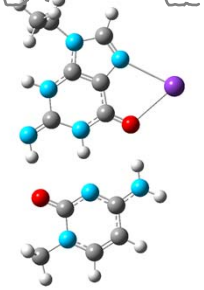


K_N1O6_2
$\Delta_{rel}H$ = 113.0
$\Delta_{rel}G$ = *114.8*



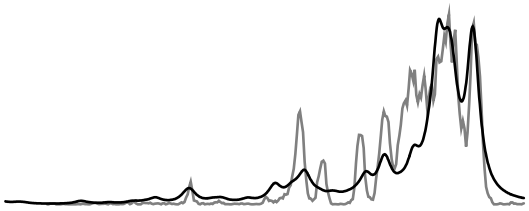


K_O6N7_6
$\Delta_{rel}H$ = 99.9
$\Delta_{rel}G$ = *104.3*

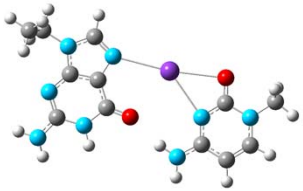


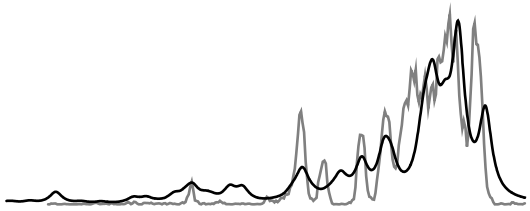
Some other higher energy structures of **(9eG:1mC)K**$^{+}$ along with their energies and 298 K Gibbs energies relative to **K_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S15

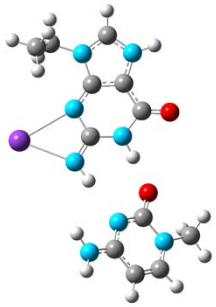


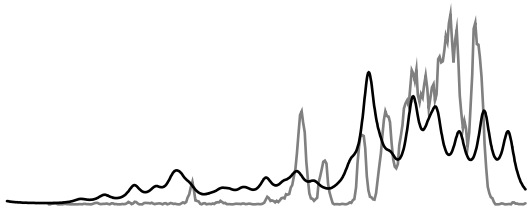
K_N7-O2N3_2
$\Delta_{rel}H$ = 159.6
$\Delta_{rel}G$ = *158.4*



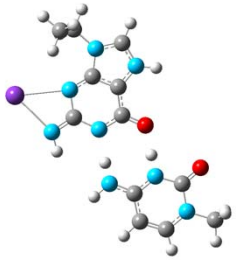


K_N2N3_2
$\Delta_{rel}H$ = 169.1
$\Delta_{rel}G$ = *166.6*



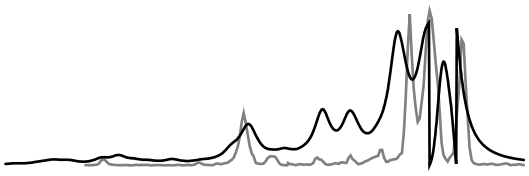


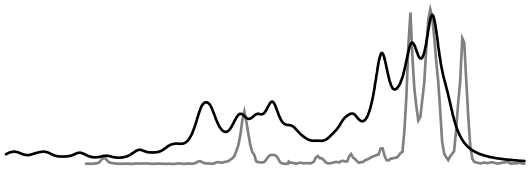
K_N2N3_3
$\Delta_{rel}H$ = 181.6
$\Delta_{rel}G$ = *186.2*

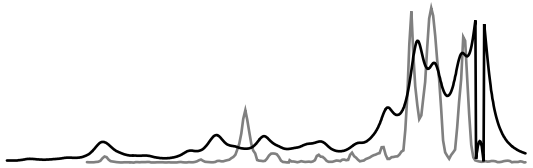


Some other higher energy structures of **(9eG:1mC)K$^+$** along with their energies and 298 K Gibbs energies relative to **K_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

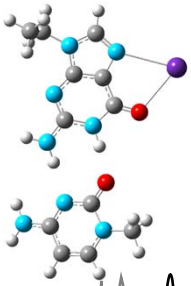
Figure S16



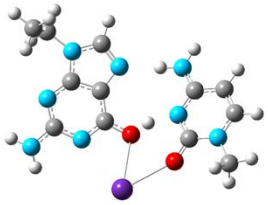




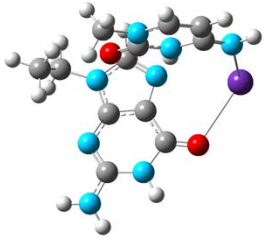
Rb_O6N7_2
$\Delta_{rel}H$ = 14.8
$\Delta_{rel}G$ = *17.2*

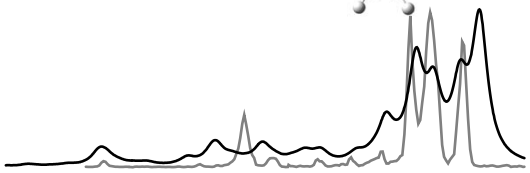


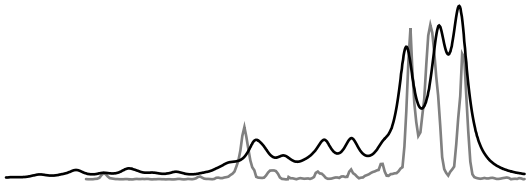
Rb_N1O6
$\Delta_{rel}H$ = 12.0
$\Delta_{rel}G$ = *24.3*



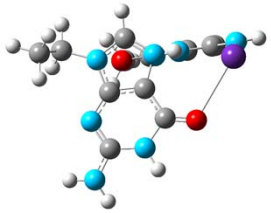
Rb_O6N7-N4_2
$\Delta_{rel}H$ = 38.7
$\Delta_{rel}G$ = *41.2*



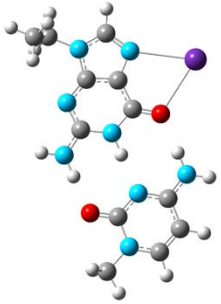




Rb_O6N7-N4
$\Delta_{rel}H$ = 40.5
$\Delta_{rel}G$ = *44.0*

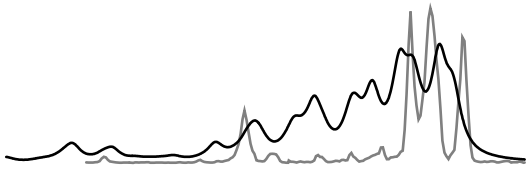


Rb-O6N7_2
$\Delta_{rel}H$ = 39.2
$\Delta_{rel}G$ = *45.4*

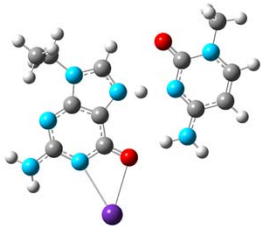


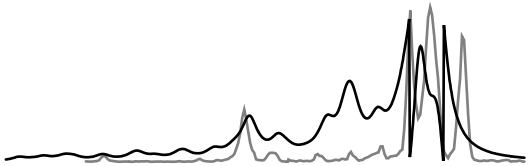
Some other higher energy structures of **(9eG:1mC)Rb**$^+$ along with their energies and 298 K Gibbs energies relative to **Rb_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S17

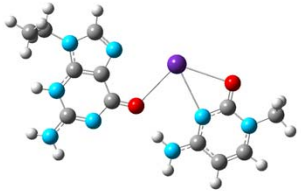


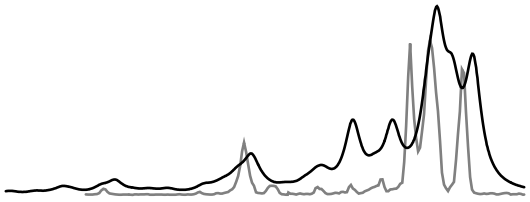
Rb_N1O6_2
$\Delta_{rel}H$ = 39.3
$\Delta_{rel}G$ = *50.0*



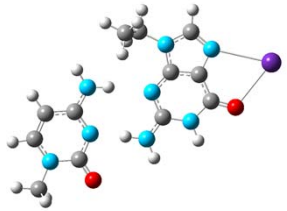


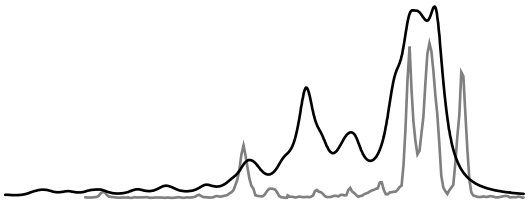
Rb_N7-O2N3_2
$\Delta_{rel}H$ = 51.9
$\Delta_{rel}G$ = *53.2*



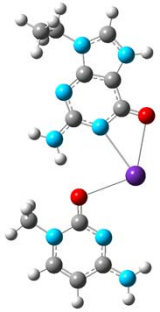


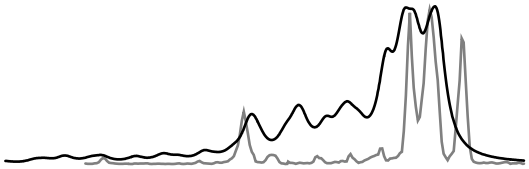
Rb_O6N7_3
$\Delta_{rel}H$ = 51.4
$\Delta_{rel}G$ = *54.1*



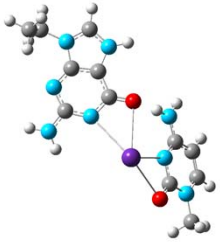


Rb_N1O6-O2
$\Delta_{rel}H$ = 59.9
$\Delta_{rel}G$ = *56.9*



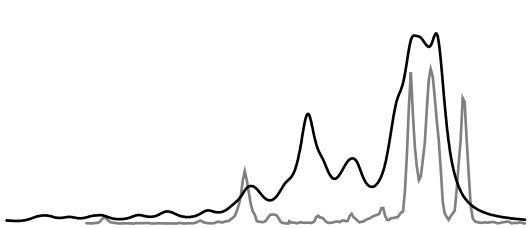


Rb_N1O6-O2N3_1
$\Delta_{rel}H$ = 54.6
$\Delta_{rel}G$ = *56.6*

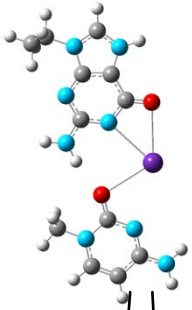


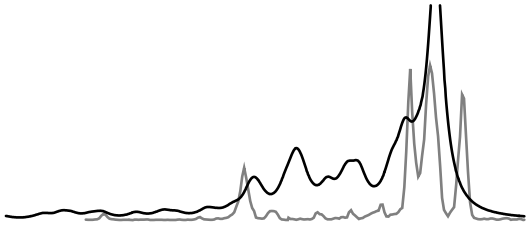
Some other higher energy structures of **(9eG:1mC)Rb**$^+$ along with their energies and 298 K Gibbs energies relative to **Rb_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S18

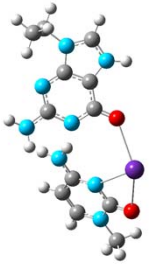


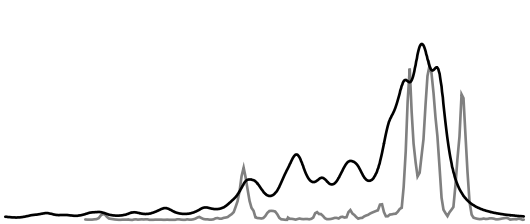
Rb_N1O6-O2N3_2
$\Delta_{rel}H$ = 60.0
$\Delta_{rel}G$ = *57.6*



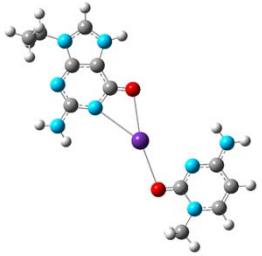


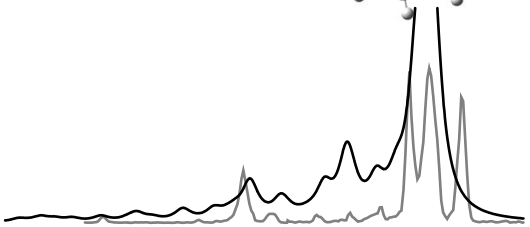
Rb_O6-O2N3_2
$\Delta_{rel}H$ = 53.7
$\Delta_{rel}G$ = *59.1*



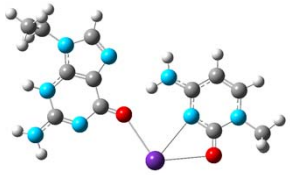


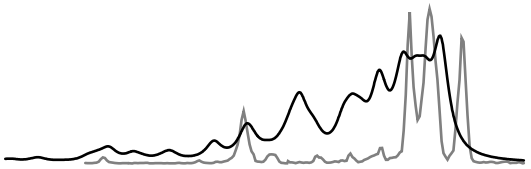
Rb_N1O6-O2N3_2
$\Delta_{rel}H$ = 69.3
$\Delta_{rel}G$ = *60.1*



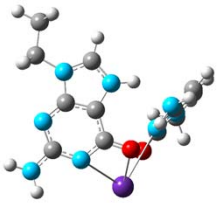


Rb_O6-O2N3_3
$\Delta_{rel}H$ = 63.2
$\Delta_{rel}G$ = *65.2*



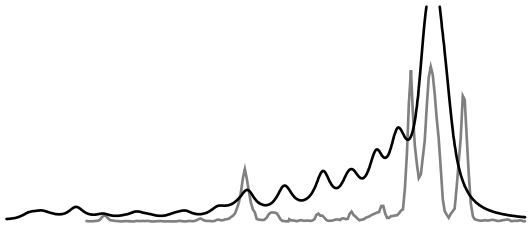


Rb_N1O6-O2N3_3
$\Delta_{rel}H$ = 62.7
$\Delta_{rel}G$ = *73.1*

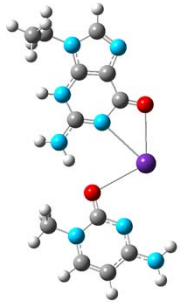


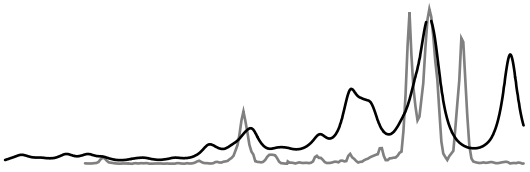
Some other higher energy structures of **(9eG:1mC)Rb$^+$** along with their energies and 298 K Gibbs energies relative to **Rb_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S19

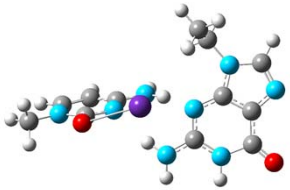


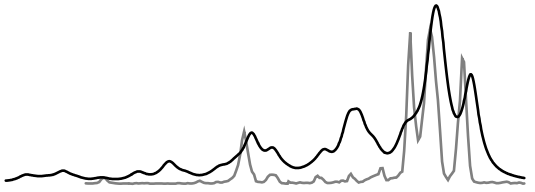
Rb_N1O6-O2N3_4
$\Delta_{rel}H$ = 83.8
$\Delta_{rel}G$ = *77.0*



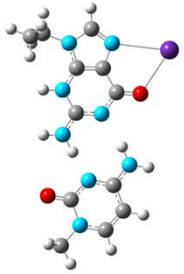


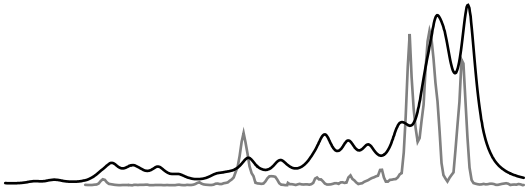
Rb_N3-O2_1
$\Delta_{rel}H$ = 84.3
$\Delta_{rel}G$ = *88.5*



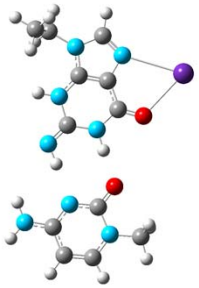


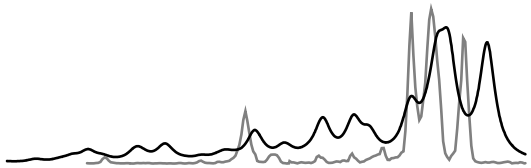
Rb_O6N7_4
$\Delta_{rel}H$ = 86.4
$\Delta_{rel}G$ = *90.8*



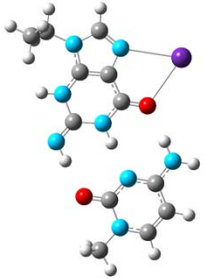


Rb_O6N7_5
$\Delta_{rel}H$ = 96.5
$\Delta_{rel}G$ = *99.3*



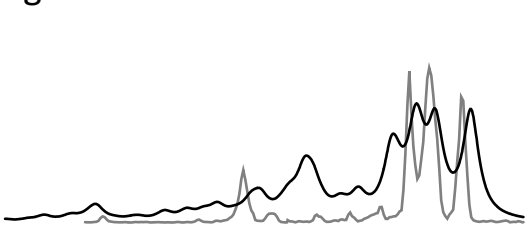


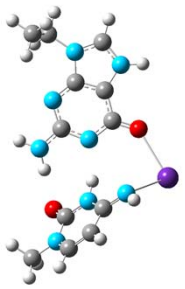
Rb_O6N7_6
$\Delta_{rel}H$ = 92.6
$\Delta_{rel}G$ = *100.7*



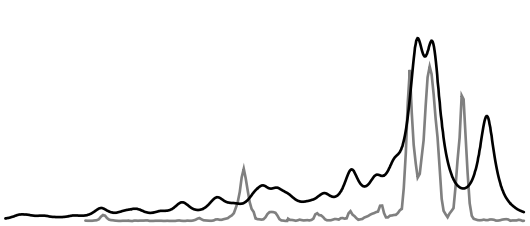
Some other higher energy structures of **(9eG:1mC)Rb$^+$** along with their energies and 298 K Gibbs energies relative to **Rb_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

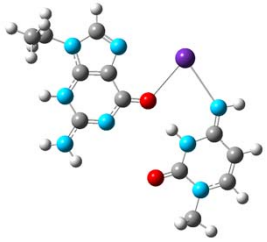
Figure S20



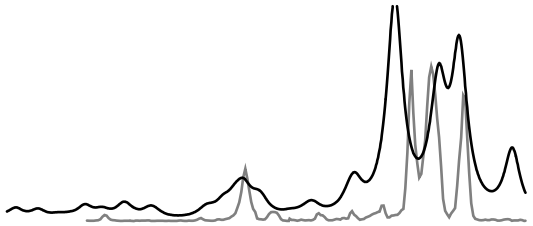


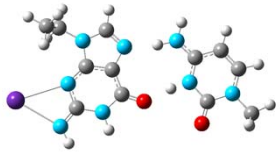
Rb_O6-N4
$\Delta_{rel}H$ = 96.9
$\Delta_{rel}G$ = *104.5*



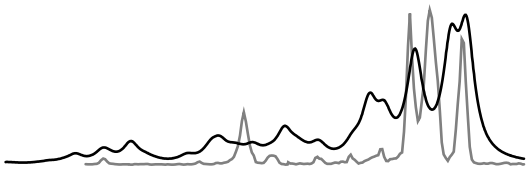


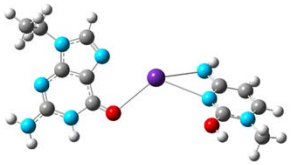
Rb_O6N7-N4_2
$\Delta_{rel}H$ = 106.3
$\Delta_{rel}G$ = *105.4*



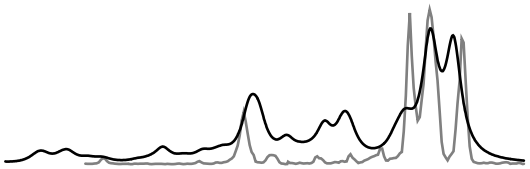


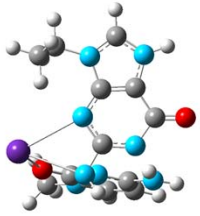
Rb_N2N3
$\Delta_{rel}H$ = 102.4
$\Delta_{rel}G$ = *111.3*





Rb_O6N7-N3N4_1
$\Delta_{rel}H$ = 134.9
$\Delta_{rel}G$ = *122.2*

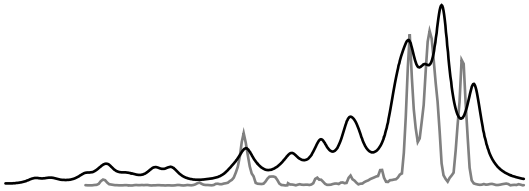




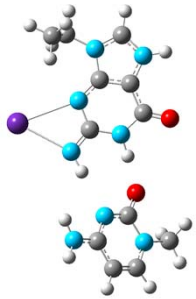
Rb_N3-O2_2
$\Delta_{rel}H$ = 126.4
$\Delta_{rel}G$ = *136.5*

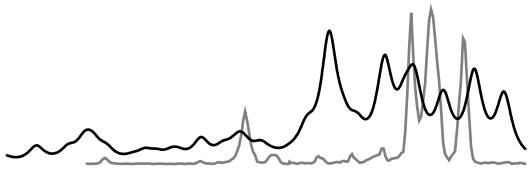
Some other higher energy structures of **(9eG:1mC)Rb**$^+$ along with their energies and 298 K Gibbs energies relative to **Rb_N7-O2N3** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S21



Rb_N2N3_2
$\Delta_{rel}H$ = 163.8
$\Delta_{rel}G$ = *165.2*





Rb_N2N3_3
$\Delta_{rel}H$ = 176.7
$\Delta_{rel}G$ = *184.4*

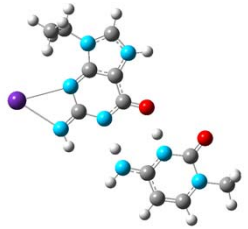


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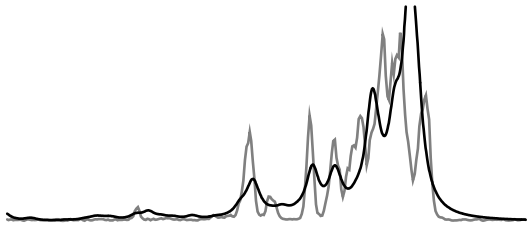
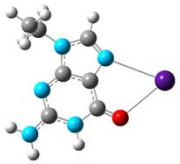
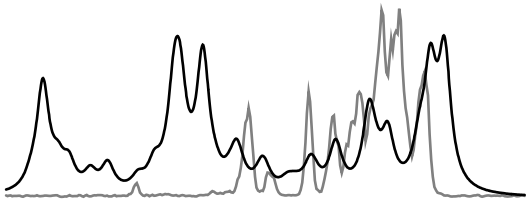
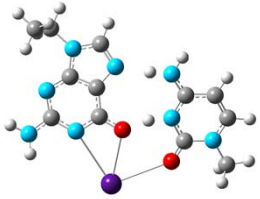
Figure S22



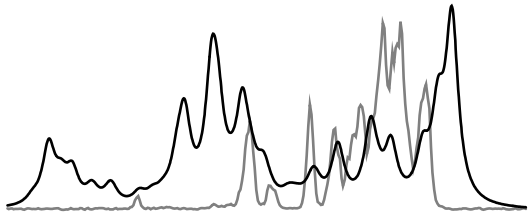


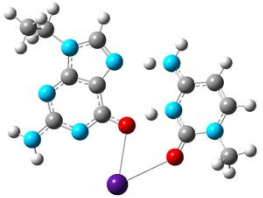
Cs_O6N7_2
$\Delta_{rel}H$ = 24.2
$\Delta_{rel}G$ = *15.4*



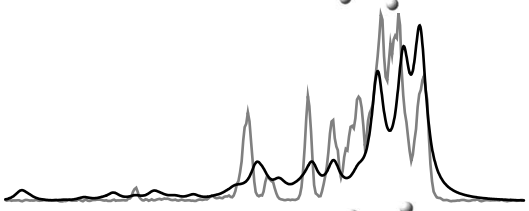


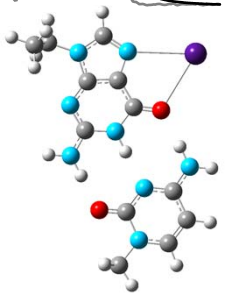
Cs_N1O6-O2_1
$\Delta_{rel}H$ = 29.6
$\Delta_{rel}G$ = *29.4*



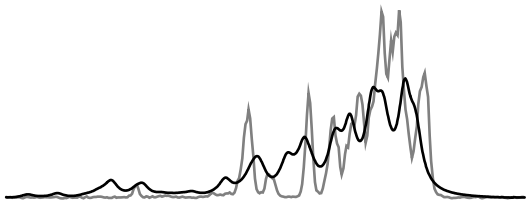


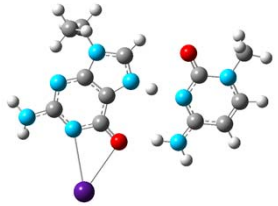
Cs_N1O6-O2_2
$\Delta_{rel}H$ = 29.9
$\Delta_{rel}G$ = *30.4*





Cs_O6N7_3
$\Delta_{rel}H$ = 47.3
$\Delta_{rel}G$ = *42.4*

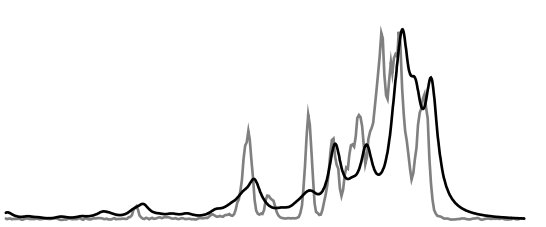




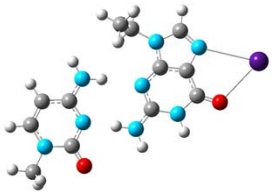
Cs_N1O6_1
$\Delta_{rel}H$ = 49.4
$\Delta_{rel}G$ = *49.1*

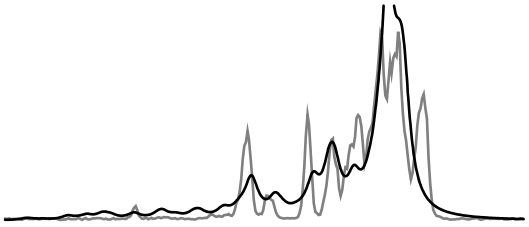
Some other higher energy structures of **(9eG:1mC)Cs**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Cs_O6N7** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S23

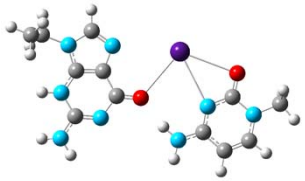


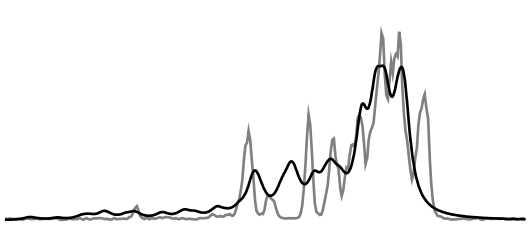
Cs_O6N7_4
$\Delta_{rel}H$ = 61.0
$\Delta_{rel}G$ = *54.2*



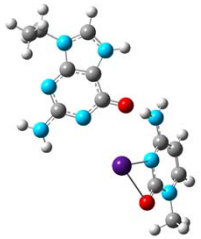


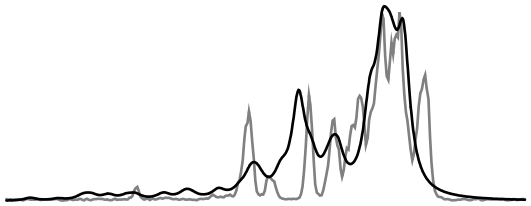
Cs_O6N7-O2N3_3
$\Delta_{rel}H$ = 68.3
$\Delta_{rel}G$ = *58.6*



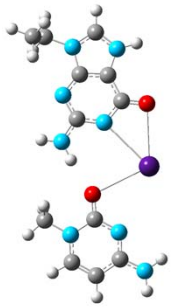


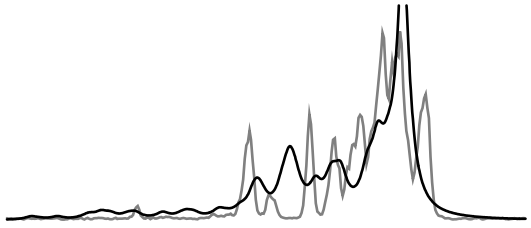
Cs_N1O6-O2N3
$\Delta_{rel}H$ = 71.0
$\Delta_{rel}G$ = *61.7*



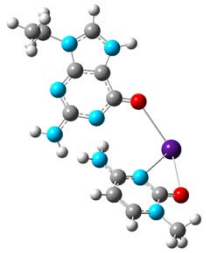


Cs_N1O6-O2_3
$\Delta_{rel}H$ = 76.4
$\Delta_{rel}G$ = *63.2*



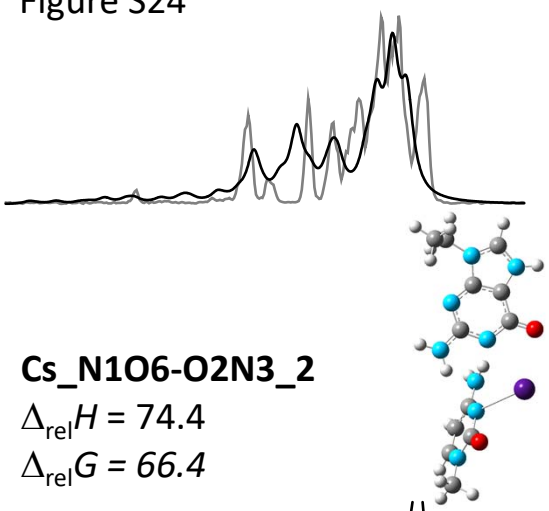


Cs_O6-O2N3_2
$\Delta_{rel}H$ = 70.2
$\Delta_{rel}G$ = *63.2*

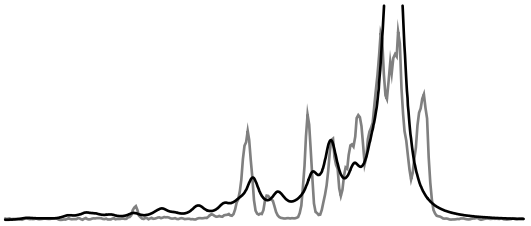


Some other higher energy structures of **(9eG:1mC)Cs**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Cs_O6N7** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

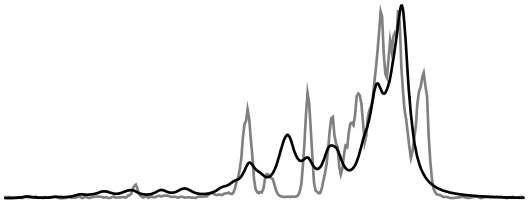
Figure S24



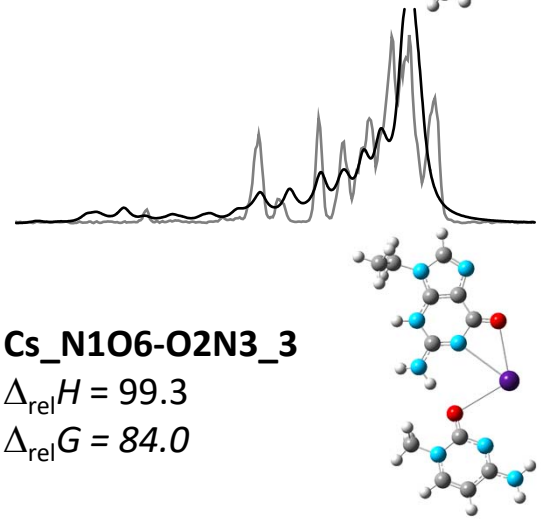
Cs_N1O6-O2N3_2
$\Delta_{rel}H$ = 74.4
$\Delta_{rel}G$ = *66.4*



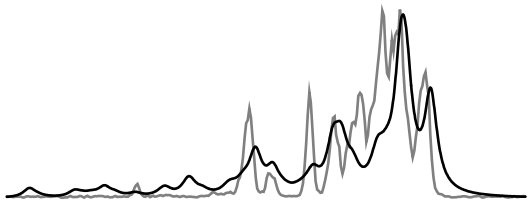
Cs_O6-O2N3_3
$\Delta_{rel}H$ = 77.3
$\Delta_{rel}G$ = *68.8*



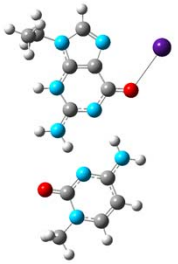
Cs_O6-O2N3_4
$\Delta_{rel}H$ = 84.0
$\Delta_{rel}G$ = *80.6*



Cs_N1O6-O2N3_3
$\Delta_{rel}H$ = 99.3
$\Delta_{rel}G$ = *84.0*

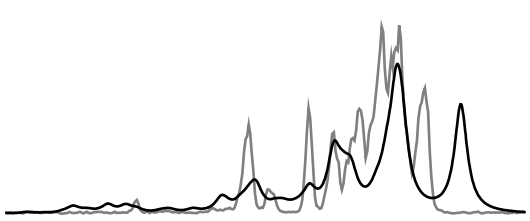


Cs_O6N7_5
$\Delta_{rel}H$ = 95.5
$\Delta_{rel}G$ = *88.1*

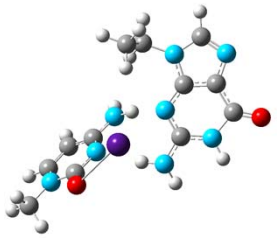


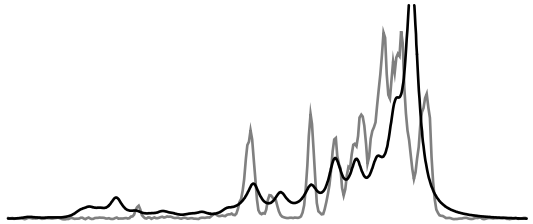
Some other higher energy structures of **(9eG:1mC)Cs**$^+$ along with their energies and 298 K Gibbs energies relative to **Cs_O6N7** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

Figure S25

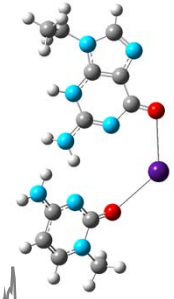


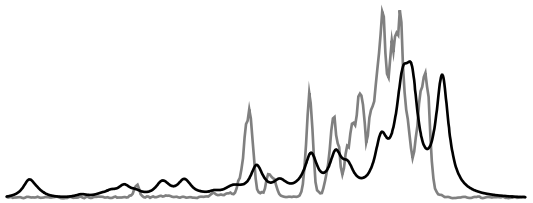
Cs_N3-O2N3_1
$\Delta_{rel}H$ = 89.0
$\Delta_{rel}G$ = *92.4*



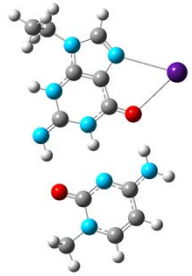


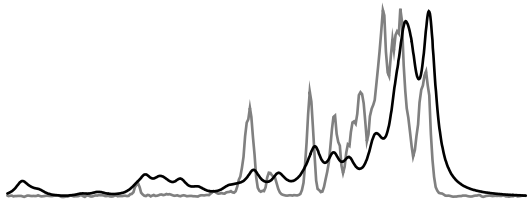
Cs_N1O6-O2_4
$\Delta_{rel}H$ = 100.8
$\Delta_{rel}G$ = *92.6*



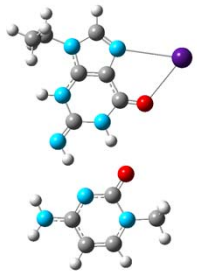


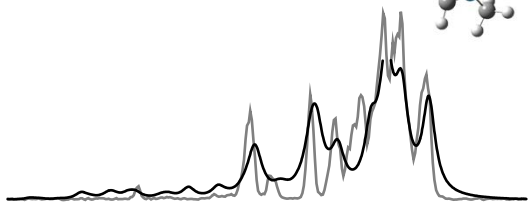
Cs_O6N7_5
$\Delta_{rel}H$ = 101.4
$\Delta_{rel}G$ = *97.4*



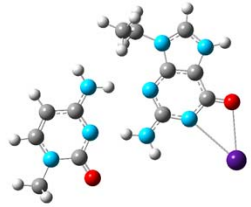


Cs_O6N7_6
$\Delta_{rel}H$ = 105.4
$\Delta_{rel}G$ = *98.0*



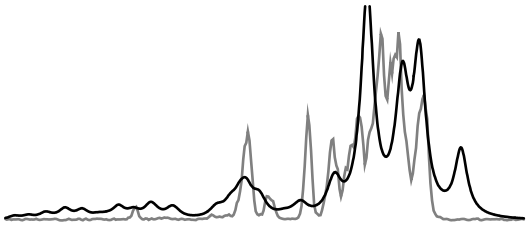


Cs_N1O6_2
$\Delta_{rel}H$ = 115.2
$\Delta_{rel}G$ = *108.7*



Some other higher energy structures of **(9eG:1mC)Cs**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Cs_O6N7** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

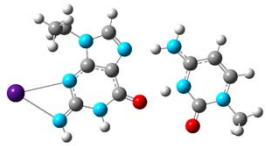
Figure S26

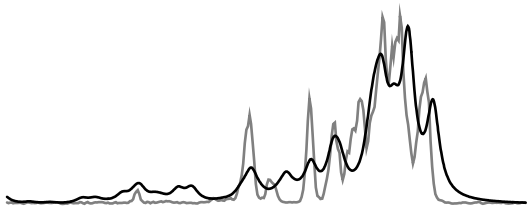


Cs_N2N3_1

$\Delta_{rel}H$ = 113.0

$\Delta_{rel}G$ = *111.3*

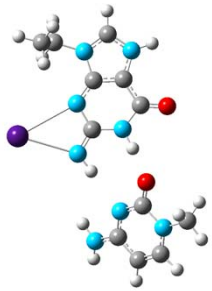


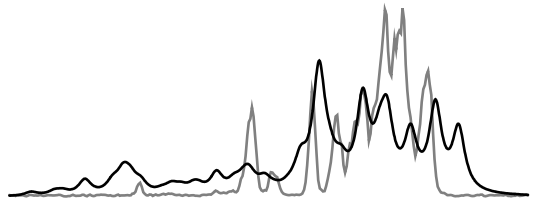


Cs_N2N3_2

$\Delta_{rel}H$ = 174.6

$\Delta_{rel}G$ = *164.1*

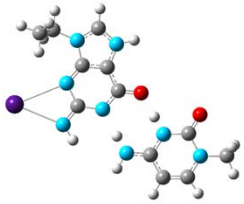




Cs_N2N3_3

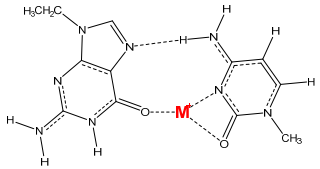
$\Delta_{rel}H$ = 188.0

$\Delta_{rel}G$ = *184.4*

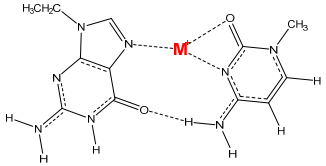


Some other higher energy structures of **(9eG:1mC)Cs**$^{+}$ along with their energies and 298 K Gibbs energies relative to **Cs_O6N7** and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace). The nomenclature of these isomers are same as the isomers presented in paper. All energies are presented in kJ mol^{-1}

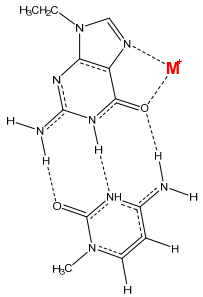
Figure S27. Schematic of metal cationized O6-O2N3, N7-O2N3 and O6N7 along with the table of computed relative 298 K enthalpies and Gibbs energies (kJ mol^{-1}) of isomers for different alkali metal cationized (9eG:1mC) complexes.



M_O6-O2N3



M_N7-O2N3



M-O6N7

M	M_O6-O2N3		M_N7-O2N3		M-O6N7	
	$\Delta_{rel}H$	$\Delta_{rel}G$	$\Delta_{rel}H$	$\Delta_{rel}G$	$\Delta_{rel}H$	$\Delta_{rel}G$
Li	**0.0**	**0.0**	0.0	0.9	16.9	26.1
Na	8.0	9.0	**0.0**	**0.0**	26.1	16.9
K	10.2	7.7	**0.0**	**0.0**	-2.3	6.0
Rb	8.0	8.4	**0.0**	**0.0**	-9.4	2.0
Cs	Not located	Not located	17.2	5.4	**0.0**	**0.0**

Figure S28. OPO IRMPD spectra for (9eG:1mC)Li^+.

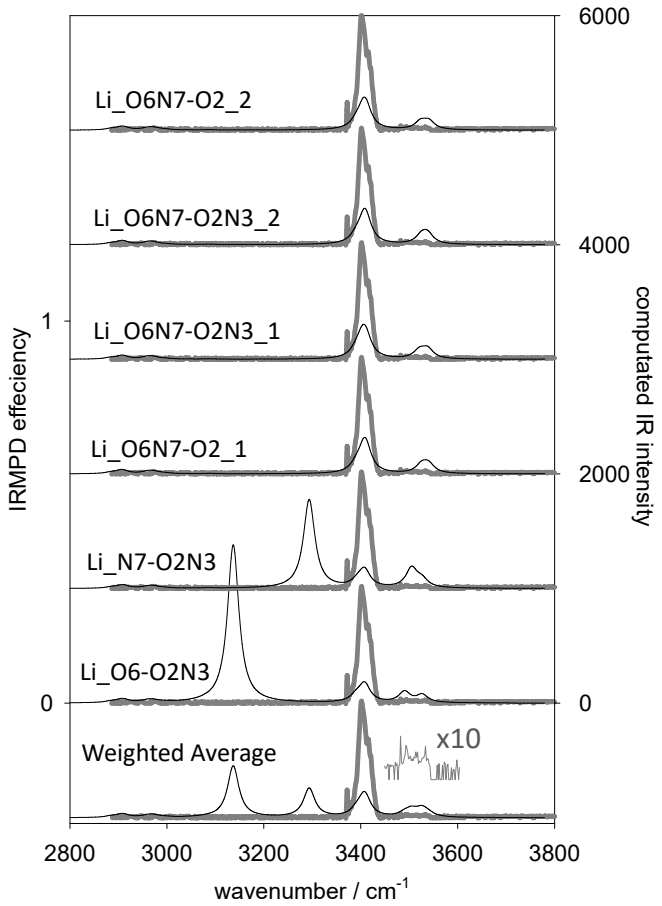


Figure S29. OPO IRMPD spectra for (9eG:1mC)Na^+.

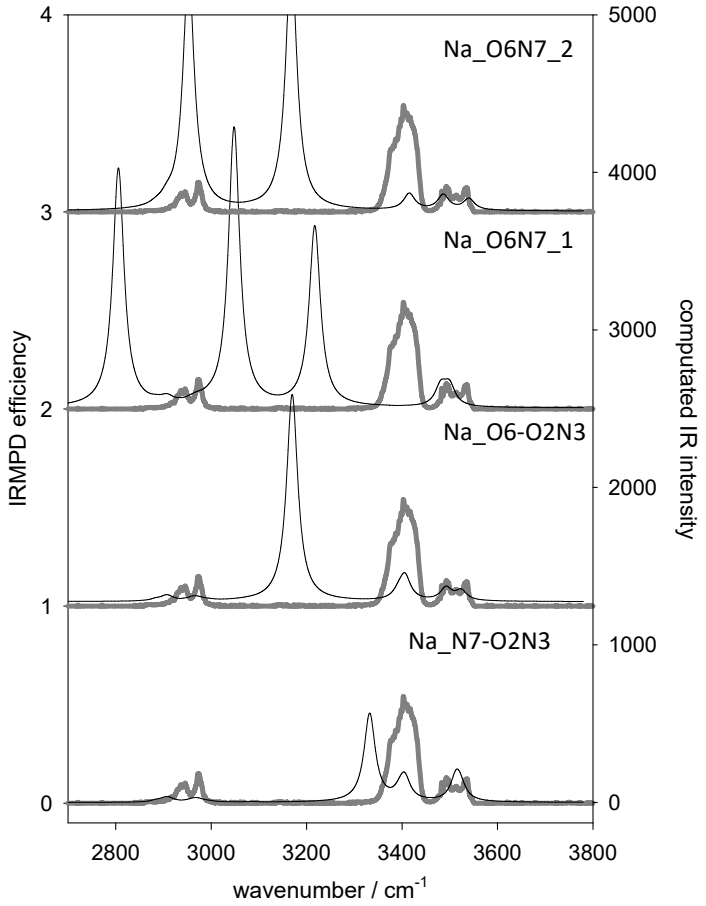


Figure S30. OPO IRMPD spectra for (9eG:1mC)K^+.

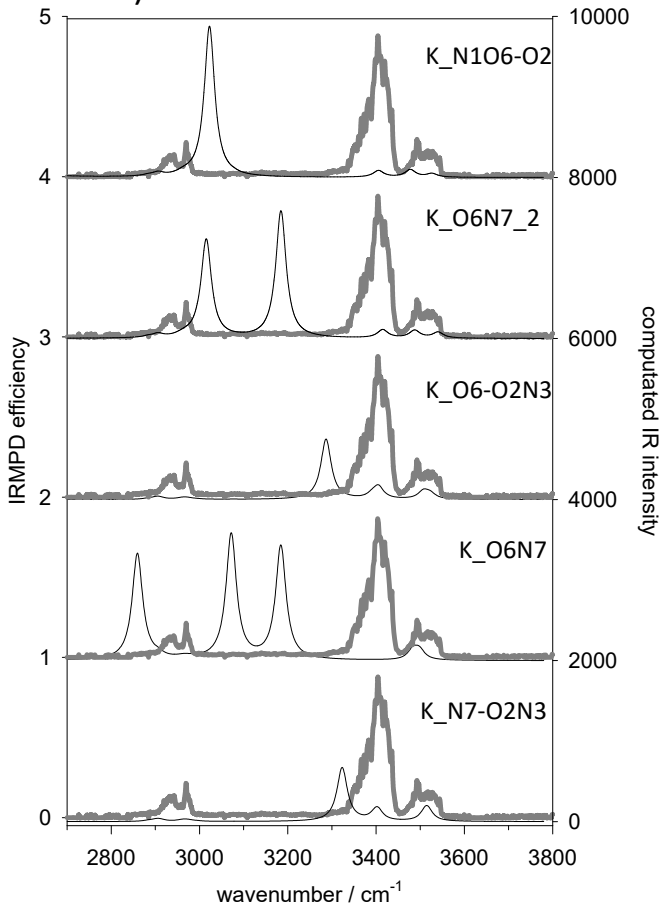


Figure S31. OPO IRMPD spectra for (9eG:1mC)Rb^+.

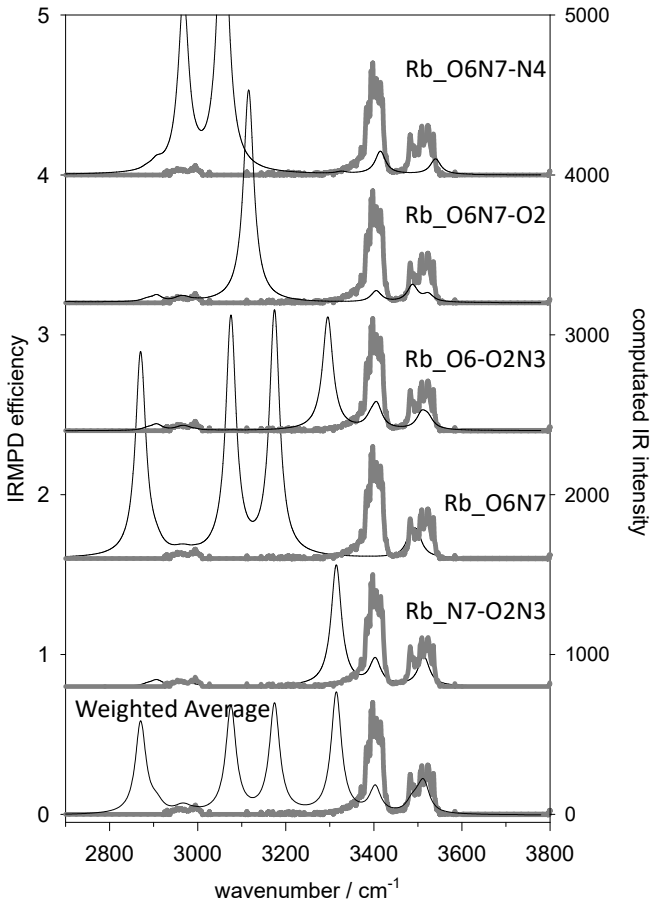


Figure S32. OPO IRMPD spectra for (9eG:1mC)Cs^+.

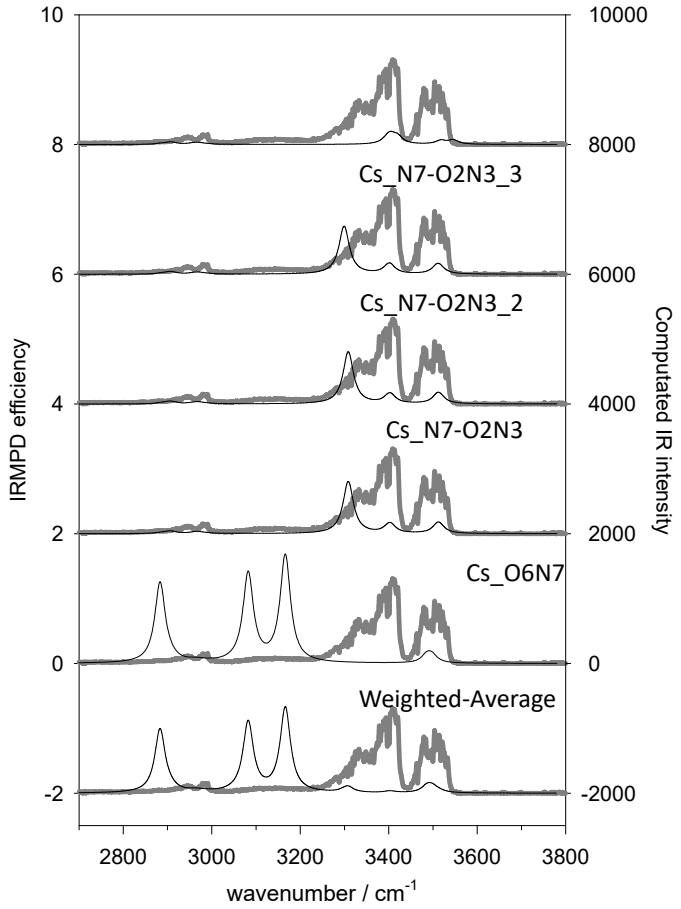


Table S2 Comparison of basis set on the 298K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of five lowest energy (9eG:1mC)H^+.

Structures	B3LYPD3/6-31+G(d,p)	B3LYPD3/6-311+G(3df,3pd)
Hoo N3(1mC)H+	0.0	0.0
	0.0	0.0
Hoo N7(9eG)H+	8.1	8.9
	7.0	7.8
R-Hoo N3(1mC)H+	18.5	16.7
	14.8	13.0
WC N7(9eG)H+	12.3	11.8
	15.7	15.3
WC O6(9eG)H+	30.0	29.8
	27.9	27.8

Table S3 Comparison of basis set on the 298K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of six lowest energy (9eG:1mC)Li^+.

Structures	B3LYPD3/6-31+G(d,p)	B3LYPD3/6-311+G(3df,3pd)
Li_O6-O2N3	0.0	0.0
	0.0	0.0
Li_N7-O2N3	0.9	1.7
	0.0	0.7
Li_O6N7-O2_1	14.6	14.0
	2.3	1.8
Li_O6N7-O2N3_1	11.2	10.0
	3.6	2.4
Li_O6N7-O2N3_2	11.2	10.0
	3.7	2.5
Li_O6N7-O2_2	14.7	14.2
	3.8	3.3

Table S4 Comparison of basis set on the 298K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of four lowest energy (9eG:1mC)Na^{+}.

Structures	B3LYPD3/6-31+G(d,p)	B3LYPD3/6-311+G(3df,3pd)
Na_N7-O2N3	0.0	0.0
	0.0	0.0
Na_O6-O2N3	8.0	7.7
	9.0	8.6
Na_O6N7_1	16.9	18.3
	26.1	27.6
Na_O6N7_2	39.8	39.4
	41.6	41.2

Table S5 Comparison of basis set on the 298K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of five lowest energy (9eG:1mC)K^{+}.

Structures	B3LYPD3/6-31+G(d,p)	B3LYPD3/6-311+G(3df,3pd)
K_N7-O2N3	0.0	0.0
	0.0	0.0
K_O6N7	-2.3	-1.3
	6.0	7.1
K_O6-O2N3	10.2	8.7
	7.7	6.2
K_O6N7_2	21.5	20.2
	22.0	20.8
K_N1O6-O2	18.3	20.9
	27.9	30.5

Table S6 Comparison of basis set on the 298K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of five lowest energy (9eG:1mC)Rb^{+}.

Structures	B3LYP-D3/6-31 +G(d,p) 0.0	B3LYP-D3/6-311 +G(3df,3pd) 0.0
Rb_N7-O2N3	0.0	0.0
	-9.4	-7.1
Rb_O6N7	2.0	4.3
	8.0	7.7
Rb_O6-O2N3	8.4	8.1
	4.7	9.4
Rb_O6N7-O2	15.1	19.8
	10.7	11.9
Rb_O6N7-N4	15.2	16.4

Table S7 Comparison of basis set on the 298K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of five lowest energy (9eG:1mC)Cs^{+}.

Structures	B3LYP-D3/6-31 +G(d,p) 0.0	B3LYP-D3/6-311 +G(3df,3pd) 0.0
Cs_O6N7	0.0	0.0
	17.2	14.9
Cs_N7-O2N3	5.4	3.1
	17.2	15.5
Cs_N7-O2N3_2	6.0	4.3
	17.0	14.8
Cs_N7-O2N3_3	7.5	5.3
	31.2	29.0
Cs_N7-O2N3_4	9.3	7.1