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

Supporting Information

Cryogenic Ion Spectroscopy of Adenine Complexes Containing Alkali Metal Cations

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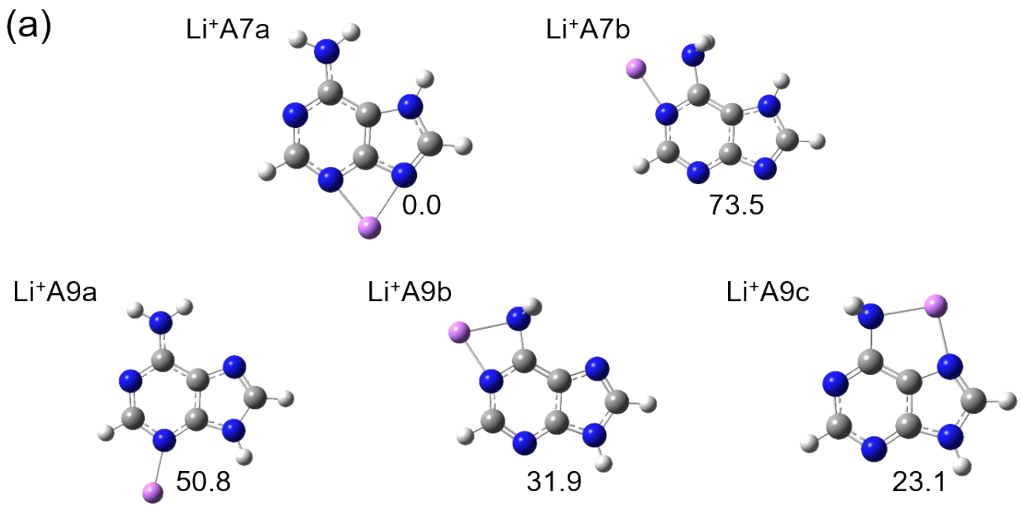
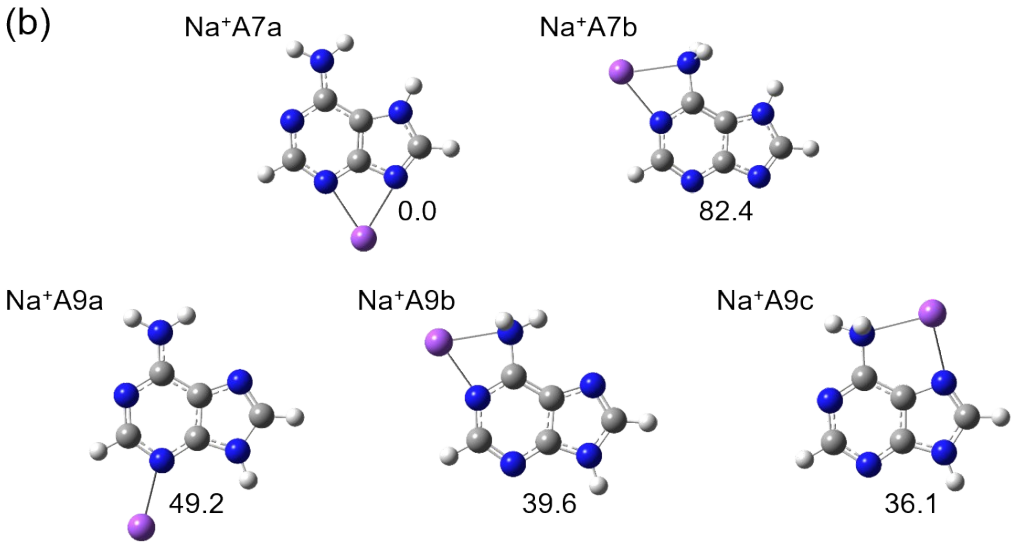
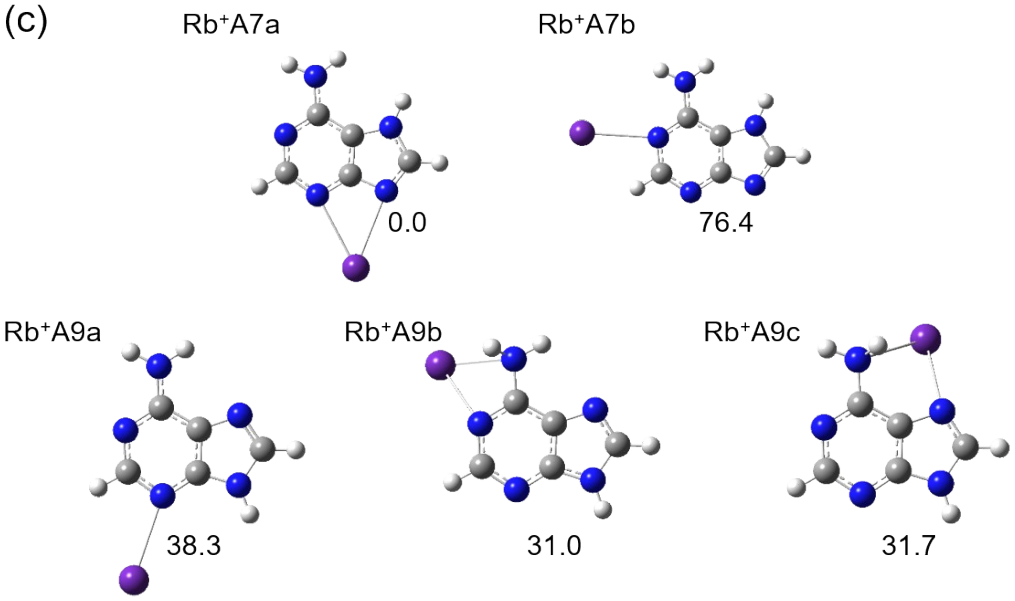
Figure S1. Optimized structures of low-lying isomers of (a) Li^+A, (b) Na^+A, (c) Rb^+A, and (d) Cs^+A predicted at the M06-2X/6-311++G(d,p) level. The numbers represent the relative energies in kJ/mol with zero-point energy corrections.





(c)


Rb⁺A7a
Rb⁺A7b
0.0
76.4
Rb⁺A9a
Rb⁺A9b
Rb⁺A9c
38.3
31.0
31.7

(d)

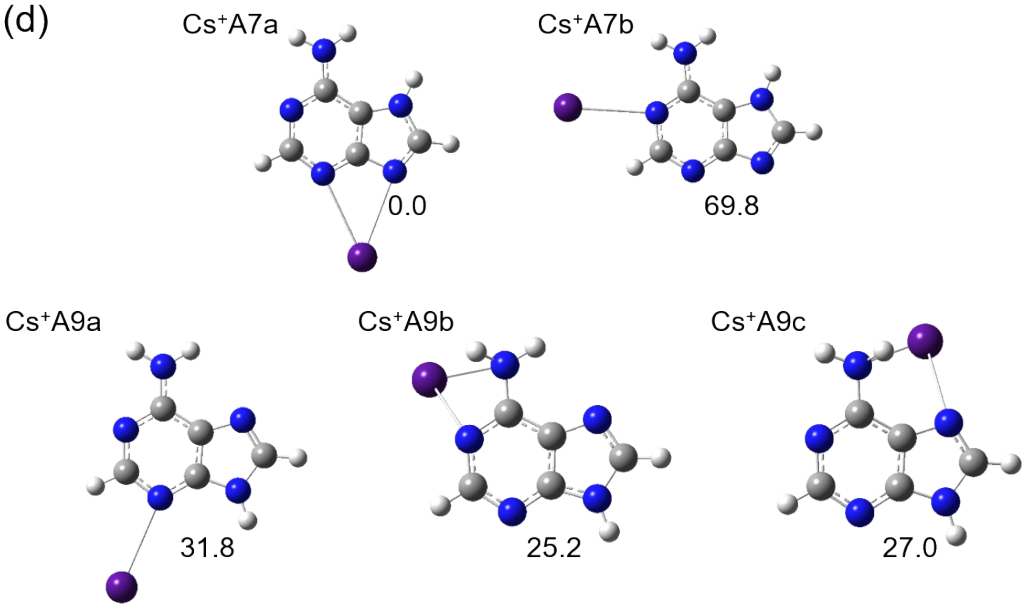

Cs⁺A7a
Cs⁺A7b
0.0
69.8
Cs⁺A9a
Cs⁺A9b
Cs⁺A9c
31.8
25.2
27.0

Figure S2. Theoretical IR spectra of low-lying isomers of (a) Li^+A, (b) Na^+A, (c) Rb^+A, and (d) Cs^+A predicted at the CAM-B3LYP/6-311++G(d,p) level with the scaling factor of 0.95. The IR ion-dip spectra of M^+A are shown at the top for comparison.

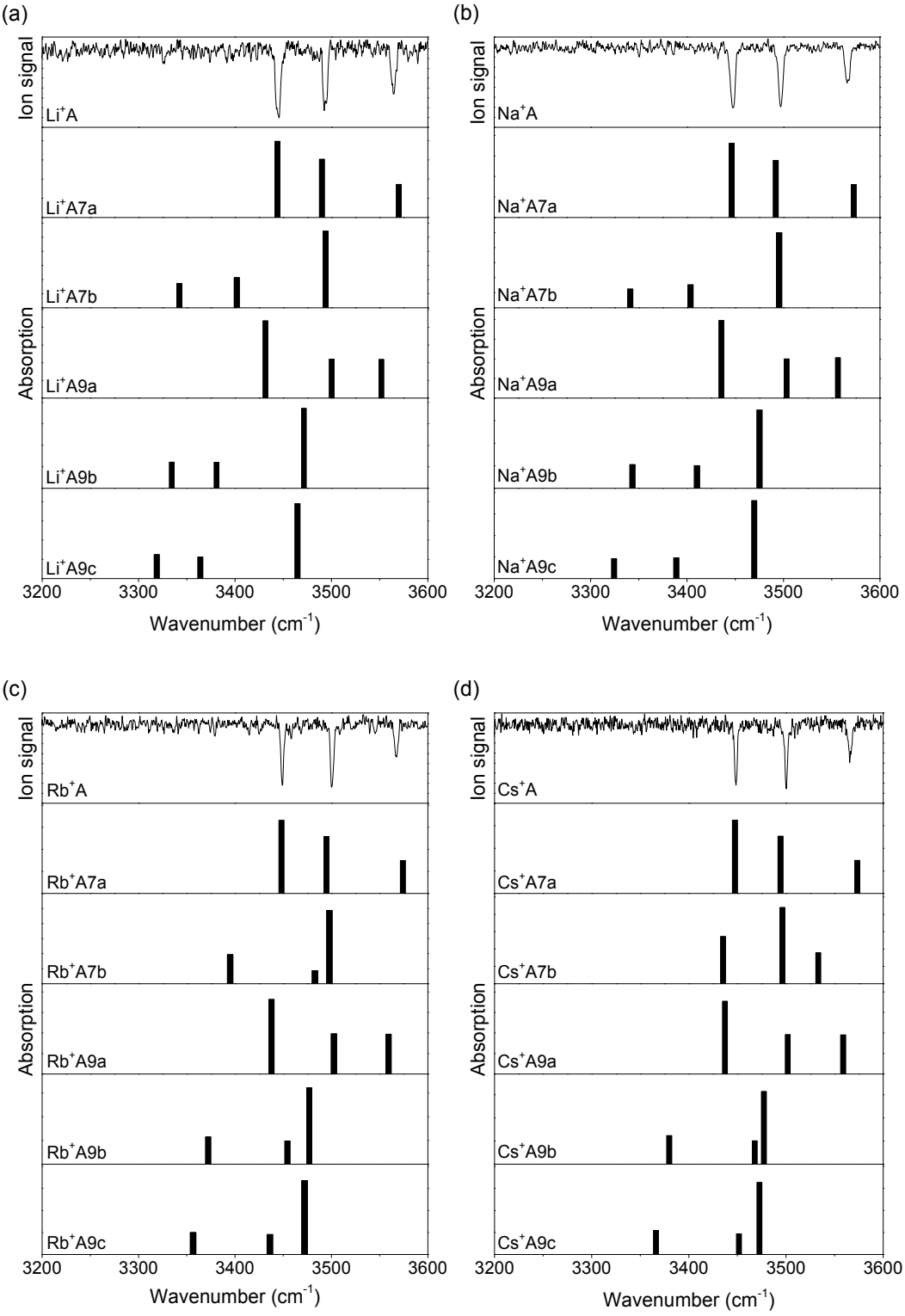
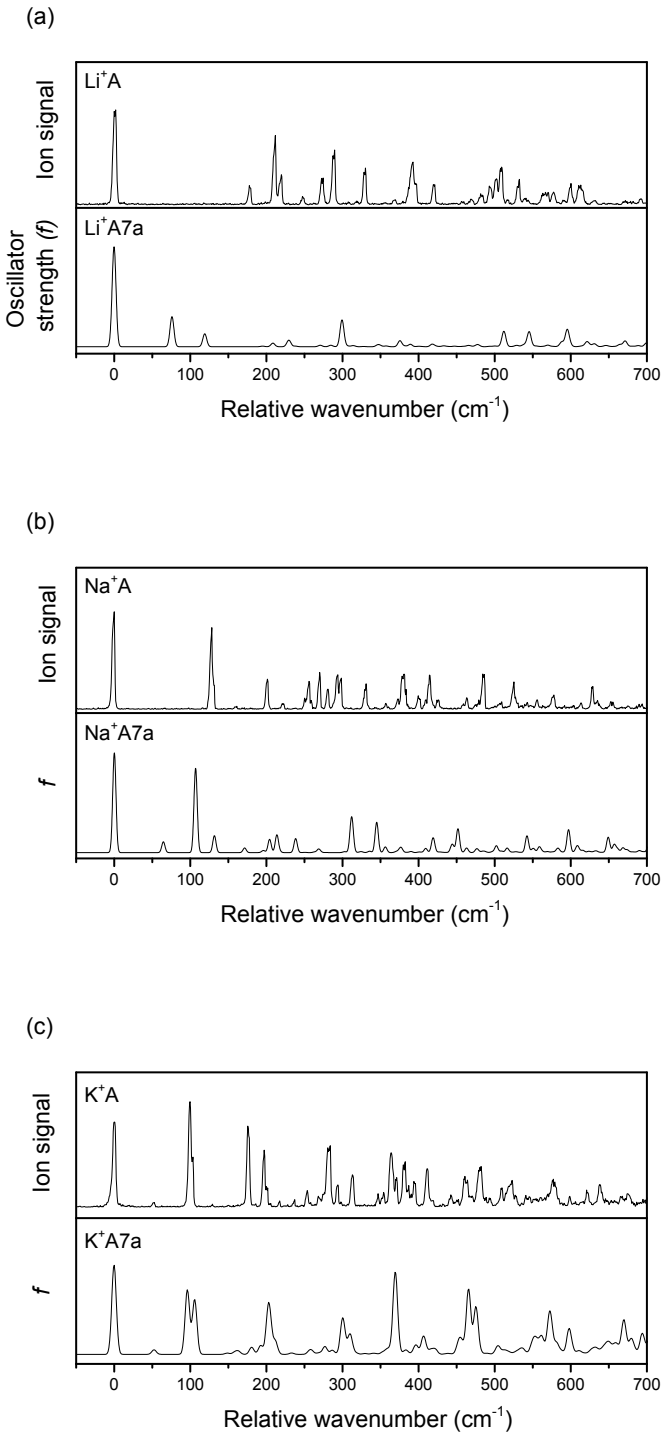


Figure S3. Electronic spectra of (a) Li^+A7a, (b) Na^+A7a, (c) K^+A7a, and (d) Rb^+A7a simulated using TDDFT at the M06-2X/6-311++G(d,p) level in consideration of Franck-Condon factors. The UVPD spectra of M^+A ions are shown at the top for comparison. The simulated electronic spectra of M^+A9a were not able to be obtained due to the dissociative nature of N3-M^+ bonds at the S_1 state. The electronic spectrum of Cs^+A7a was not able to be simulated, possibly due to an error associated with the core potential basis set for Cs atom.



(d)

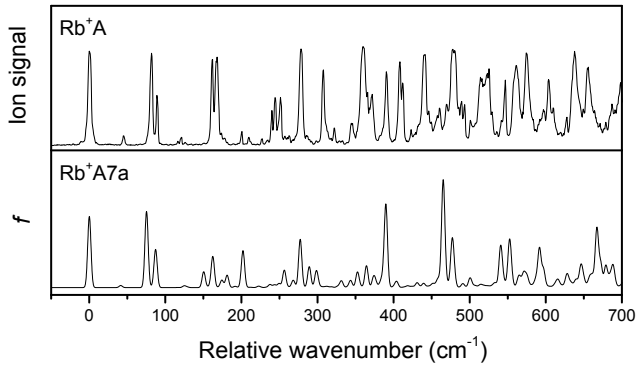

Rb+A
Rb+A7a
Ion signal
f
0
100
200
300
400
500
600
700
Relative wavenumber (cm-1)

Figure S4. ESI mass spectrum of K^+A ions.