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Alkali Metal Cation Binding Affinities of Cytosine in the Gas Phase: Revisited

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Table S1. Vibrational frequencies and average vibrational energies of low-energy neutral cytosine tautomers, ground-state M^+(cytosine) complexes, and transition states for tautomerization.[a]

System	E_{int}, eV[b]	Frequencies
C_1	0.16 (0.02)	109, 135, 200, 351, 401, 522, 530, 536, 569, 624, 716, 754, 764, 780,905, 960, 970, 1066, 1106, 1193, 1233, 1414, 1534, 1600, 1652, 1728, 3135, 3160, 3535, 3548, 3667
C_2	0.15 (0.02)	185, 216, 251, 337, 447, 489, 503, 551, 553, 591, 711, 781, 785, 814, 972, 983, 987, 1077, 1108, 1218, 1268, 1320, 1375, 1437, 1494, 1573, 1602, 1621, 3099, 3141, 3533, 3657, 3710
C_3	0.15 (0.02)	185, 219, 278, 336, 444, 477, 500, 540, 550, 597, 710, 782, 786, 813, 972, 985, 989, 1074, 1107, 1210, 1271, 1332, 1376, 1424, 1491, 1585, 1696, 1618, 3096, 3141, 3532, 3654, 3717
C_4	0.14 (0.01)	136, 157, 371, 386, 511, 521, 527, 557, 653, 695, 749, 755, 762, 821, 947, 953, 978, 1069, 1122, 1194, 1274, 1372, 1391, 1410, 1470, 1622, 1676, 1755, 3143, 3170, 3449, 3531, 3576
C_5	0.14 (0.01)	136, 155, 370, 388, 511, 518, 529, 552, 599, 690, 749, 760, 788, 818, 951, 955, 975, 1055, 1123, 1185, 1252, 1375, 1393, 1403, 1462, 1635, 1680, 1751, 3140, 3186, 3406, 3535, 3576
C_6	0.15 (0.02)	135, 195, 307, 336, 405, 438, 511, 532, 587, 621, 692, 749, 783, 787, 911, 989, 1010, 1056, 1068, 1125, 1290, 1344, 1400, 1463, 1573, 1614, 1635, 1730, 3064, 3159, 3517, 3523, 3630
$Na^+(C_1)$	0.19 (0.02)	79, 113, 171, 201, 268, 358, 379, 424, 534, 543, 559, 585, 653, 726, 778, 786, 801, 943, 979, 982, 1101, 1118, 1212, 1268, 1358, 1432, 1495, 1528, 1624, 1651, 1669, 3157, 3172, 3530, 3534, 3650
$K^+(C_1)$	0.20 (0.02)	58, 67, 163, 197, 209, 319, 369, 419, 530, 541, 550, 579, 652, 726, 775, 785, 798, 936, 976, 979, 1095, 1115, 1209, 1260, 1354, 1426, 1488, 1529, 1619, 1652, 1671, 3155, 3172, 3533, 3537, 3656
$Rb^+(C_1)$	0.20 (0.02)	47, 50, 153, 161, 208, 305, 367, 418, 528, 540, 546, 579, 650, 725, 775, 784, 796, 934, 975, 979, 1093, 1115, 1208, 1258, 1352, 1424, 1486, 1530, 1618, 1652, 1673, 3154, 3171, 3535, 3538, 3658
$Cs^+(C_1)$	0.21 (0.02)	23, 45, 135, 160, 207, 304, 362, 418, 534, 540, 544, 579, 649, 725, 775, 784, 796, 934, 974, 978, 1092, 1113, 1207, 1264, 1352, 1421, 1486, 1529, 1615, 1653, 1668, 3153, 3171, 3535, 3538, 3657
$Na^+(C)\_TS_{12}$	0.19 (0.02)	**-1841**, 74, 107, 196, 206, 246, 349, 381, 429, 523, 559, 572, 646, 682, 763, 812, 825, 977, 988, 991, 1049, 1095, 1143, 1282, 1310, 1400, 1468, 1510, 1559, 1607, 1637, 2054, 3151, 3165, 3533, 3651
$K^+(C)\_TS_{12}$	0.19 (0.02)	**-1832**, 57, 65, 181, 190, 206, 317, 377, 428, 520, 558, 565, 645, 687, 764, 809, 826, 973, 987, 990, 1060, 1092, 1142, 1274, 1310, 1397, 1458, 1513, 1557, 1607, 1633, 2069, 3149, 3164, 3537, 3656
$Rb^+(C)\_TS_{12}$	0.20 (0.02)	**-1831**, 46, 47, 138, 186, 205, 302, 374, 427, 517, 557, 562, 643, 687, 763, 807, 826, 971, 987, 988, 1059, 1093, 1141, 1271, 1309, 1395, 1456, 1514, 1555, 1608, 1630, 2073, 3148, 3164, 3538, 3658
$Cs^+(C)\_TS_{12}$	0.20 (0.02)	**-1829**, 31, 42, 123, 185, 204, 297, 372, 426, 520, 557, 561, 644, 687, 763, 806, 826, 970, 987, 987, 1059, 1092, 1140, 1271, 1308, 1395, 1453, 1514, 1554, 1609, 1629, 2075, 3147, 3163, 3538, 3658

[a] Determined at the B3LYP/def2-TZVPPD level of theory with frequencies scaled by 0.9804. [b] Uncertainties are listed in parentheses.

Table S2. Rotational constants of ground-state M^+(cytosine) complexes and PSL TSs for CID determined at the B3LYP/ def2-TZVPPD level of theory.

System	Energized Molecule		Transition State	
	1D[a]	2D[b]	1D[c]	2D[c]
Na^+(cytosine)	0.077	0.036	0.130	0.055
			0.078	*0.036*
K^+(cytosine)	0.075	0.025	0.130	0.055
			0.075	*0.025*
Rb^+(cytosine)	0.075	0.016	0.130	0.055
			0.074	*0.016*
Cs^+(cytosine)	0.075	0.012	0.130	0.055
			0.075	*0.012*

[a]Active external. [b]Inactive external. [c]Rotational constants of the TS treated as free internal rotors.

Table S3. Enthalpies and free energies of M^+ binding to cytosine at 0 and 298 K in kJ/mol[a]

M^+	ΔH_0	ΔH_0[b]	$\Delta H_{298} - \Delta H_0$[b]	ΔH_{298}	ΔH_{298}[b]	$T\Delta S_{298}$[b]	ΔG_{298}	ΔG_{298}[b]
Na^+	209.5 (5.0)	214.1	2.7 (0.7)	212.2 (5.0)	216.8	34.9 (3.4)	177.3 (6.1)	181.9
K^+	161.5 (4.5)	159.9	1.8 (1.1)	163.3(4.6)	161.7	32.3 (4.1)	131.0 (6.2)	129.4
Rb^+	148.0 (3.6)	143.1	1.4 (0.4)	149.4 (3.6)	144.5	29.1 (3.5)	120.2 (5.0)	115.3
Cs^+	137.2 (4.3)	131.7	1.1 (0.3)	138.3 (4.3)	132.8	28.8 (3.5)	109.5 (5.6)	104.0

[a] Present results, uncertainties are listed in parentheses. [b] Density functional theory calculations at the B3LYP/def2-TZVPPD level of theory.

Figure Captions

Figure S1. Cross sections for collision-induced dissociation of the M^+(cytosine) complexes, where $M^+ = Na^+$, Rb^+, and Cs^+, with Xe as a function of collision energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis), parts a–c, respectively. Figure S1a also shows comparison of dc discharge-flow tube ion source (DC/FT) data from reference 28 with the present ESI data. The DC/FT data have been scaled up by a factor of three. Zero-pressure-extrapolated cross sections for collision-induced dissociation of the M^+(cytosine) complexes, where $M^+ = Na^+$, Rb^+, and Cs^+, with Xe in the threshold region as a function of kinetic energy in the center-of-mass frame (lower *x*-axis) and the laboratory frame (upper *x*-axis), parts d–f, respectively. The solid lines show the best fits to the data using the model of eqn (1) convoluted over the neutral and ion kinetic and internal energy distributions. The dotted lines show the model cross sections in the absence of experimental kinetic energy broadening for the M^+(cytosine) complexes with an internal temperature of 0 K. The data and models are shown expanded by a factor of 10 and offset from zero in the insets.

Figure S2. B3LYP/def2-TZVPPD potential energy surfaces for dissociation of the ground-state M^+(cytosine) complexes, where $M^+ = Na^+$, K^+, Rb^+, and Cs^+, (parts a-d, respectively) to produce ground-state $M^+ + C_1$ products and excited $M^+ + C_2$ products. Energies for all structures along the PESs include ZPE corrections, whereas the dissociation asymptotes also include BSSE corrections.

Figure S3. MP2(full)/6-311+G(2d,2p)_HW* potential energy surfaces for dissociation of the ground-state M^+(cytosine) complexes, where $M^+ = Na^+$, K^+, Rb^+, and Cs^+, (parts a-d, respectively) to produce ground-state $M^+ + C_2$ products and excited $M^+ + C_1$ products. Energies for all structures along the PESs include ZPE corrections, whereas the dissociation asymptotes also include BSSE corrections.

Figure S1.

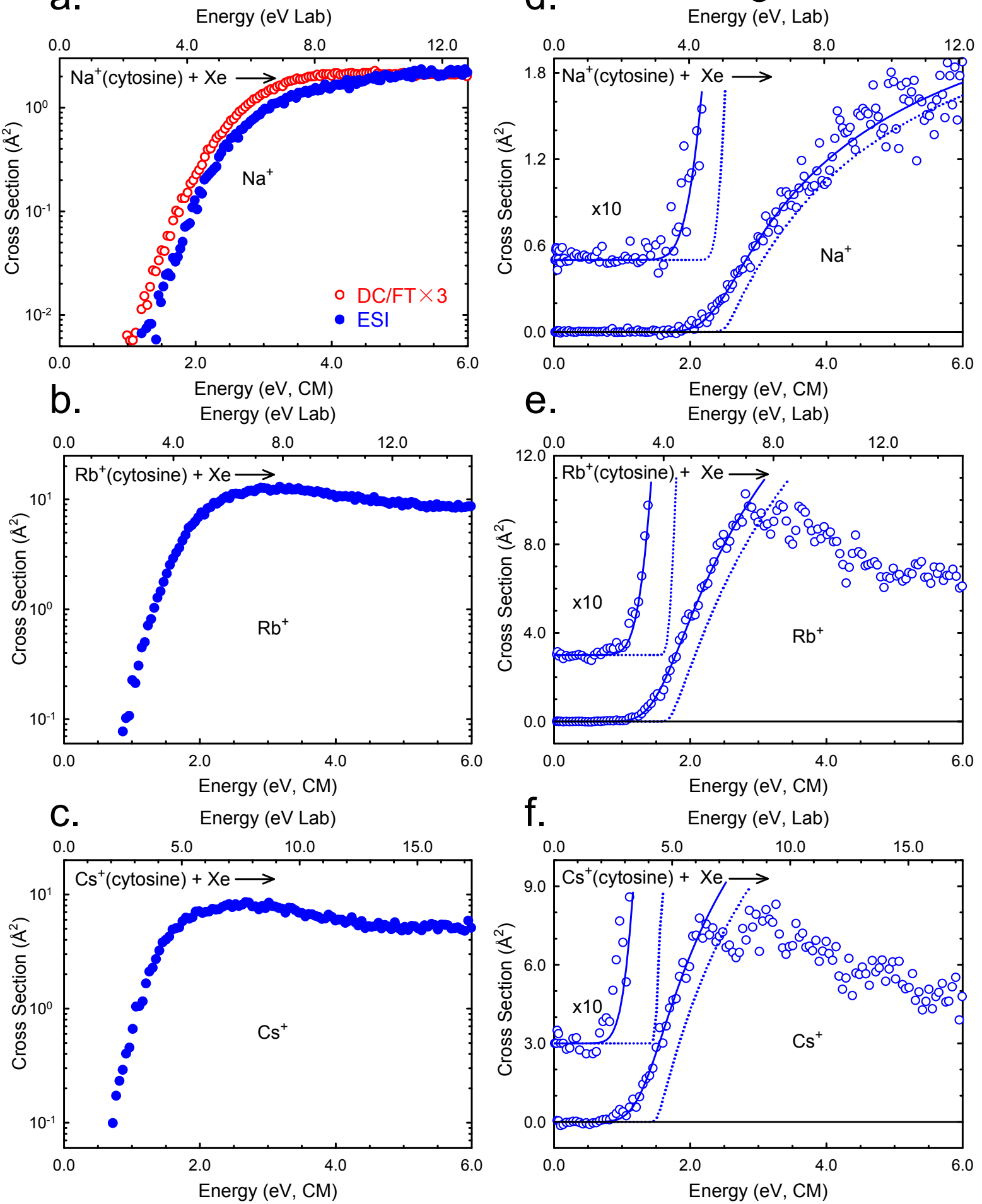

a.
Energy (eV Lab)
0.0
4.0
8.0
12.0
Na+(cytosine) + Xe
Cross Section (Å2)
10^0
10^-1
10^-2
Na+
DC/FT×3
ESI
0.0
2.0
4.0
6.0
Energy (eV, CM)
d.
Energy (eV, Lab)
1.8
1.2
0.6
0.0
x10
b.
Rb+(cytosine) + Xe
10^1
10^0
10^-1
Rb+
e.
12.0
8.0
4.0
c.
Cs+(cytosine) + Xe
Cs+
f.
9.0
6.0
3.0

Figure S2.

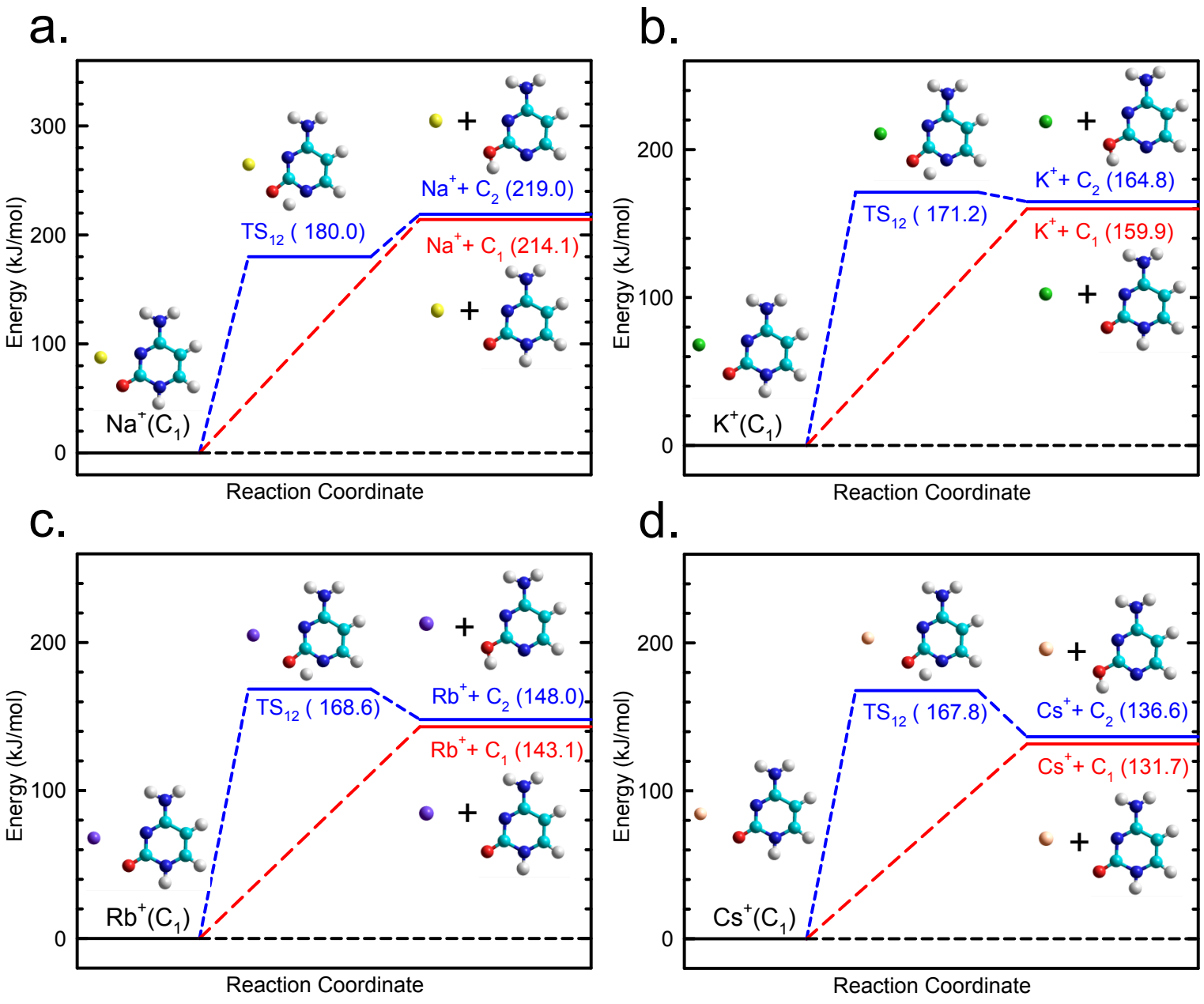
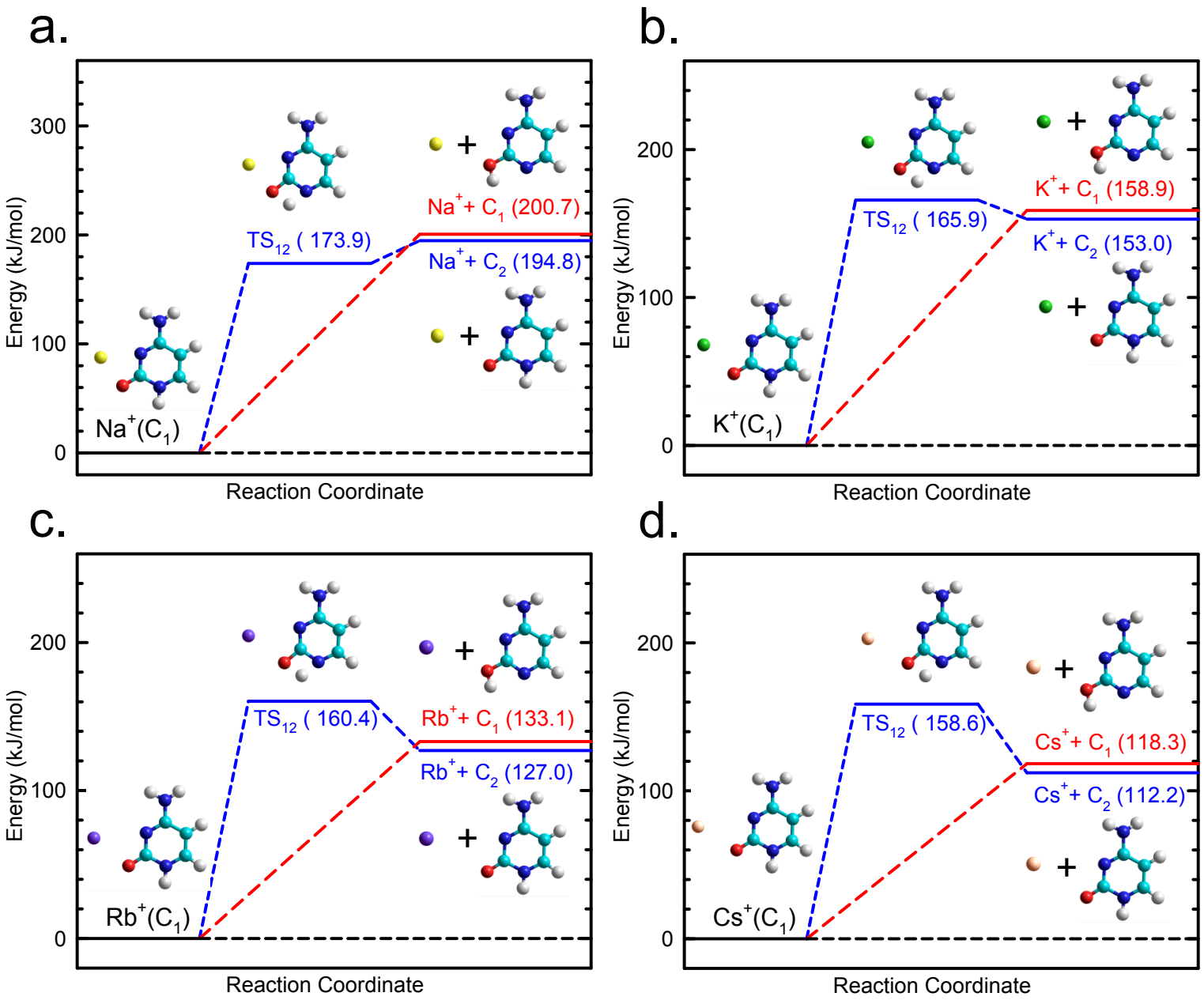

a.
Energy (kJ/mol)
300
200
100
0
Na+(C1)
TS12 (180.0)
Na+ + C2 (219.0)
Na+ + C1 (214.1)
Reaction Coordinate
b.
Energy (kJ/mol)
200
100
0
K+(C1)
TS12 (171.2)
K+ + C2 (164.8)
K+ + C1 (159.9)
Reaction Coordinate
c.
Energy (kJ/mol)
200
100
0
Rb+(C1)
TS12 (168.6)
Rb+ + C2 (148.0)
Rb+ + C1 (143.1)
Reaction Coordinate
d.
Energy (kJ/mol)
200
100
0
Cs+(C1)
TS12 (167.8)
Cs+ + C2 (136.6)
Cs+ + C1 (131.7)
Reaction Coordinate

Figure S3.


a.
Energy (kJ/mol)
300
200
100
0
Na+(C1)
TS12 (173.9)
Na+ + C1 (200.7)
Na+ + C2 (194.8)
Reaction Coordinate
b.
Energy (kJ/mol)
200
100
0
K+(C1)
TS12 (165.9)
K+ + C1 (158.9)
K+ + C2 (153.0)
Reaction Coordinate
c.
Energy (kJ/mol)
200
100
0
Rb+(C1)
TS12 (160.4)
Rb+ + C1 (133.1)
Rb+ + C2 (127.0)
Reaction Coordinate
d.
Energy (kJ/mol)
200
100
0
Cs+(C1)
TS12 (158.6)
Cs+ + C1 (118.3)
Cs+ + C2 (112.2)
Reaction Coordinate