Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for "Tautomerization in the Formation and Collision-Induced Dissociation of Alkali Metal Ion-Cytosine Complexes" by Zhibo Yang and M. T. Rodgers*

Table 1S. Vibrational Frequencies and Average Vibrational Energies of Cytosine and M^+(cytosine)[a]

Species	E_{int}, eV	Vibrational Frequencies[a], cm^{-1}
C_1	0.14 (0.01)	**-508**, **-51**, 125, 246, 301, 364, 470, 493, 527, 553, 616, 646, 709, 765, 822, 893, 957, 1049, 1097, 1180, 1283, 1340, 1413, 1510, 1587, 1640, 1751, 1847, 3280, 3313, 3658, 3689, 3800
C_2	0.14 (0.01)	**-376**, 179, 212, 329, 430, 481, 483, 543, 545, 581, 650, 725, 750, 771, 916, 965, 979, 1071, 1111, 1237, 1296, 1331, 1394, 1456, 1509, 1595, 1610, 1651, 3110, 3146, 3519, 3585, 3654
C_3	0.14 (0.01)	**-389**, 178, 215, 328, 432, 467, 483, 529, 539, 588, 646, 724, 750, 771, 924, 963, 982, 1068, 1109, 1229, 1301, 1342, 1393, 1445, 1506, 1603, 1608, 1649, 3107, 3146, 3522, 3590, 3655
C_4	0.15 (0.01)	106, 136, 341, 361, 494, 496, 519, 550, 610, 642, 686, 712, 752, 815, 868, 953, 965, 1078, 1135, 1204, 1299, 1375, 1386, 1421, 1484, 1623, 1701, 1797, 3145, 3166, 3388, 3489, 3535
C_5	0.15 (0.01)	110, 134, 346, 359, 490, 496, 517, 542, 567, 623, 692, 734, 758, 823, 871, 959, 961, 1061, 1134, 1193, 1280, 1376, 1392, 1413, 1475, 1634, 1703, 1794, 3153, 3187, 3343, 3486, 3536
C_6	0.14 (0.02)	**-424**, 129, 186, 326, 330, 425, 497, 524, 577, 582, 637, 692, 734, 775, 907, 948, 1004, 1051, 1071, 1144, 1306, 1363, 1398, 1491, 1602, 1630, 1663, 1770, 3080, 3166, 3474, 3526, 3648
$Li^+(C_1)$	0.17 (0.02)	126, 175, 203, 236, 339, 373, 398, 472, 531, 543, 567, 596, 644, 682, 730, 749, 778, 906, 949, 976, 1105, 1122, 1223, 1320, 1372, 1437, 1526, 1550, 1636, 1678, 1690, 3164, 3177, 3474, 3489, 3612
$Li^+(C_2)$	0.19 (0.02)	91, 164, 195, 238, 264, 381, 425, 443, 448, 477, 515, 547, 592, 644, 722, 762, 788, 942, 976, 977, 1069, 1119, 1208, 1282, 1340, 1409, 1432, 1524, 1590, 1633, 1680, 3146, 3161, 3500, 3571, 3622
$Li^+(C_3)$	0.19 (0.02)	111, 192, 227, 260, 311, 360, 420, 430, 435, 499, 538, 572, 589, 656, 726, 774, 787, 927, 971, 984, 1067, 1126, 1201, 1291, 1334, 1404, 1466, 1541, 1575, 1637, 1677, 3148, 3162, 3486, 3581, 3613
$Li^+(C_4)$	0.19 (0.02)	73, 144, 147, 182, 372, 381, 462, 512, 553, 599, 604, 612, 649, 696, 713, 757, 779, 913, 964, 984, 1105, 1215, 1224, 1294, 1369, 1392, 1462, 1537, 1610, 1683, 1824, 3159, 3176, 3392, 3484, 3492
$Li^+(C_5)$	0.19 (0.02)	81, 95, 120, 188, 352, 370, 463, 500, 513, 521, 602, 635, 651, 689, 756, 784, 838, 889, 962, 996, 1045, 1114, 1204, 1272, 1373, 1392, 1442, 1509, 1641, 1702, 1716, 3174, 3189, 3371, 3475, 3517
$Li^+(C_6)$	0.18 (0.02)	128, 182, 210, 250, 253, 358, 415, 436, 461, 523, 571, 603, 627, 675, 728, 754, 790, 951, 955, 1003, 1056, 1134, 1235, 1326, 1350, 1405, 1530, 1597, 1625, 1685, 1689, 3135, 3175, 3443, 3485, 3601

Table 1S (continued). Vibrational Frequencies and Average Vibrational Energies of Cytosine and M^+(cytosine)[a]

Species	E_{int}, eV	Vibrational Frequencies[a], cm^{-1}
$Na^+(C_1)$	0.20 (0.02)	74, 125, 160, 197, 263, 271, 373, 394, 518, 535, 546, 573, 641, 680, 727, 742, 775, 905, 941, 975, 1101, 1120, 1222, 1300, 1367, 1434, 1519, 1554, 1633, 1682, 1696, 3162, 3177, 3483, 3498, 3622
$Na^+(C_2)$	0.20 (0.02)	59, 147, 187, 194, 236, 243, 360, 431, 480, 506, 511, 542, 584, 682, 762, 764, 804, 966, 968, 972, 1060, 1104, 1202, 1263, 1311, 1384, 1406, 1497, 1557, 1610, 1641, 3106, 3125, 3486, 3570, 3595
$Na^+(C_3)$	0.20 (0.02)	65, 145, 184, 213, 237, 241, 348, 428, 476, 498, 525, 552, 585, 647, 714, 771, 775, 916, 973, 978, 1068, 1122, 1218, 1291, 1336, 1407, 1455, 1532, 1579, 1628, 1670, 3138, 3159, 3492, 3575, 3620
$Na^+(C_4)$	0.20 (0.02)	48, 81, 148, 179, 242, 391, 395, 510, 547, 551, 582, 600, 691, 706, 726, 760, 778, 944, 949, 968, 1086, 1184, 1199, 1265, 1356, 1375, 1441, 1498, 1585, 1643, 1807, 3128, 3143, 3364, 3482, 3488
$Na^+(C_5)$	0.20 (0.02)	54, 59, 120, 177, 249, 358, 368, 499, 507, 515, 574, 594, 632, 694, 754, 769, 836, 887, 958, 988, 1048, 1115, 1202, 1277, 1373, 1394, 1444, 1486, 1642, 1711, 1720, 3172, 3189, 3366, 3482, 3525
$Na^+(C_6)$	0.20 (0.02)	76, 145, 167, 177, 203, 243, 361, 416, 424, 517, 546, 596, 624, 672, 724, 748, 787, 943, 952, 1006, 1057, 1126, 1211, 1325, 1351, 1403, 1523, 1603, 1623, 1681, 1700, 3125, 3175, 3450, 3492, 3609
$K^+(C_1)$	0.21 (0.02)	50, 86, 154, 173, 200, 222, 367, 390, 511, 534, 537, 568, 642, 682, 726, 740, 773, 903, 936, 973, 1096, 1119, 1220, 1289, 1363, 1431, 1513, 1558, 1630, 1681, 1712, 3160, 3175, 3488, 3504, 3629
$K^+(C_2)$	0.19 (0.02)	**-51**, 8, 171, 191, 225, 353, 430, 472, 503, 542, 546, 581, 685, 765, 766, 801, 963, 966, 970, 1060, 1104, 1211, 1265, 1310, 1381, 1412, 1494, 1558, 1607, 1636, 3101, 3122, 3490, 3566, 3601
$K^+(C_3)$	0.21 (0.02)	50, 112, 148, 164, 186, 225, 345, 430, 496, 509, 521, 548, 585, 647, 717, 769, 772, 919, 974, 976, 1069, 1119, 1229, 1291, 1338, 1407, 1446, 1528, 1583, 1624, 1667, 3130, 3158, 3497, 3574, 3626
$K^+(C_4)$	0.20 (0.02)	47(2), 115, 175, 175, 362, 363, 500, 503, 520, 570, 625, 662, 698, 737, 763, 840, 880, 965, 980, 1063, 1123, 1211, 1311, 1374, 1396, 1451, 1479, 1630, 1707, 1738, 3160, 3175, 3406, 3481, 3531
$K^+(C_5)$	0.21 (0.02)	47, 51, 120, 171, 173, 359, 366, 499(2), 517, 563, 588, 631, 701, 753, 766, 835, 886, 958, 983, 1050, 1117, 1201, 1279, 1374, 1396, 1445, 1472, 1641, 1711, 1732, 3169, 3188, 3360, 3484, 3530
$K^+(C_6)$	0.22 (0.02)	34, 64, 108, 166, 180, 197, 353, 409, 422, 512, 540, 592, 621, 670, 721, 745, 786, 937, 954, 1008, 1057, 1118, 1193, 1323, 1353, 1401, 1518, 1609, 1622, 1678, 1715, 3115, 3174, 3454, 3497, 3615

[a]Obtained from vibrational analyses of the optimized geometries as described in the text and scaled by 0.9646. The imaginary frequencies (indicated in boldface) correspond to the out-of-plane vibration(s) of the amino group.

Table 2S. Vibrational Frequencies (in cm^{-1}) of the Transition States for the Unimolecular Tautomerization of M^+(Cytosine) [a]

Species	E_{int}, eV	Vibrational Frequencies[a], cm^{-1}
Li^+(C)-$TS_{1,2}$	0.18 (0.02)	**-1832**, 108, 191, 194, 205, 323, 374, 408, 454, 513, 552, 571, 631, 642, 694, 763, 810, 924, 978, 982, 999, 1098, 1151, 1308, 1330, 1414, 1486, 1530, 1586, 1627, 1670, 1980, 3158, 3170, 3488, 3611
Li^+(C)-$TS_{2,3}$	0.17 (0.02)	**-137**, 85, 178, 223, 318, 323, 434, 450, 520, 534, 541, 557, 591, 660, 727, 756, 800, 938, 965, 970, 1063, 1112, 1225, 1248, 1323, 1379, 1450, 1524, 1557, 1619, 1667, 3143, 3158, 3487, 3541, 3614
Li^+(C)-$TS_{3,6}$	0.18 (0.02)	**-1827**, 110, 200, 212, 218, 348, 350, 418, 431, 516, 545, 602, 622, 645, 688, 762, 778, 932, 976, 988, 988, 1131, 1151, 1282, 1349, 1419, 1483, 1536, 1601, 1621, 1684, 1986, 3149, 3164, 3481, 3603
Li^+(C)-$TS_{1,4}$	0.18 (0.02)	**-1853**, 80, 87, 132, 204, 378, 382, 468, 547, 564, 583, 615, 643, 662, 698, 751, 816, 902, 971, 1026, 1071, 1076, 1132, 1226, 1373, 1376, 1439, 1470, 1604, 1691, 1702, 1986, 3163, 3184, 3482, 3501
Li^+(C)-$TS_{4,5}$	0.16 (0.02)	**-993**, 114, 130, 156, 251, 393, 444, 501, 549, 557, 692, 703, 730, 767, 802, 811, 930, 955, 1017, 1063, 1071, 1145, 1212, 1319, 1472, 1486, 1533, 1572, 1768, 1796, 1979, 3299, 3322, 3646, 3677, 3902
Na^+(C)-$TS_{1,2}$	0.17 (0.02)	**-1826**, 76, 101, 211, 222, 259, 397, 405, 453, 571, 588, 610, 688, 726, 824, 865, 869, 1047, 1054, 1097, 1126, 1178, 1216, 1336, 1397, 1501, 1582, 1638, 1691, 1745, 1769, 2168, 3297, 3314, 3701, 3819
Na^+(C)-$TS_{2,3}$	0.18 (0.02)	**-83**, 54, 173, 202, 290, 331, 356, 435, 468, 518, 540, 544, 590, 662, 735, 762, 796, 938, 968, 974, 1071, 1115, 1229, 1265, 1325, 1386, 1446, 1519, 1565, 1618, 1664, 3139, 3156, 3484, 3554, 3609
Na^+(C)-$TS_{3,6}$	0.19 (0.02)	**-1820**, 68, 132, 194, 201, 230, 297, 351, 420, 505, 537, 597, 623, 645, 689, 757, 777, 930, 974, 987, 1005, 1127, 1153, 1282, 1346, 1403, 1488, 1530, 1610, 1617, 1681, 2010, 3142, 3164, 3488, 3610
Na^+(C)-$TS_{1,4}$	0.19 (0.02)	**-1857**, 44, 57, 129, 195, 264, 374, 386, 524, 555, 566, 582, 633, 642, 698, 745, 784, 902, 968, 1023, 1063, 1079, 1130, 1224, 1374, 1379, 1421, 1470, 1605, 1686, 1715, 1991, 3160, 3184, 3485, 3506
Na^+(C)-$TS_{4,5}$	0.18 (0.02)	**-1011**, 74(2), 158, 237, 299, 399, 445, 545, 555, 619, 677, 691, 761, 782, 797, 927, 951, 1001, 1058, 1076, 1145, 1211, 1319, 1477, 1484, 1524, 1560, 1780, 1794, 1971, 3294, 3320, 3655, 3686, 3915
K^+(C)-$TS_{1,2}$	0.20 (0.02)	**-1821**, 47, 80, 164, 184, 188, 214, 373, 405, 496, 548, 554, 636, 642, 699, 755, 816, 923, 971, 981, 1030, 1094, 1150, 1297, 1326, 1401, 1486, 1532, 1587, 1628, 1658, 2021, 3155, 3168, 3503, 3628
K^+(C)-$TS_{2,3}$	0.18 (0.02)	**-51**, 53, 167, 178, 237, 331, 384, 435, 469, 512, 527, 543, 590, 659, 730, 765, 791, 934, 970, 979, 1077, 1117, 1234, 1276, 1326, 1391, 1447, 1516, 1571, 1618, 1661, 3133, 3155, 3482, 3568, 3606
K^+(C)-$TS_{3,6}$	0.20 (0.02)	**-1814**, 53, 104, 169, 188, 197, 248, 347, 423, 497, 534, 591, 623, 647, 691, 753, 777, 934, 971, 987, 1018, 1124, 1153, 1281, 1341, 1392, 1494, 1527, 1612, 1621, 1679, 2026, 3134, 3163, 3492, 3616
K^+(C)-$TS_{1,4}$	0.20 (0.02)	**-1861**, 35, 49, 127, 188, 189, 370, 386, 520, 538, 562, 579, 631, 641, 702, 740, 778, 902, 967, 1022, 1057, 1081, 1128, 1222, 1373, 1381, 1408, 1473, 1605, 1683, 1729, 1994, 3157, 3184, 3487, 3509

Table 2S. (continued) Vibrational Frequencies (in cm^{-1}) of the Transition States for the Unimolecular Tautomerization of M^+(Cytosine) [a]

Species	E_{int}, eV	Vibrational Frequencies[a], cm^{-1}
K^+(C)-$TS_{4,5}$	0.18 (0.02)	**-1029**, 58(2), 159, 177, 228, 399, 444, 546, 554, 597, 662, 681, 754, 779, 794, 924, 947, 997, 1053, 1081, 1143, 1212, 1317, 1476, 1482, 1515, 1556, 1790, 1797, 1964, 3291, 3321, 3661, 3692, 3923

[a]Obtained from a vibrational analysis of the MP2(full)/6-31G* geometry optimized structures and scaled by 0.9646. The imaginary frequencies (indicated in boldface) correspond to the reaction coordinate for the tautomerization.

Table 3S. Rotational Constants of M^+(cytosine) in cm^{-1}

Reactant	Energized Molecule		Transition State		
	1-D[a]	2-D[b]	1-D[a]	2-D[c]	2-D[b,d]
$Li^+(C_1)$	0.097	0.049	0.131	0.055	0.060
$Li^+(C_2)$	0.097	0.050	0.131	0.054	0.060
$Li^+(C_3)$	0.128	0.044	0.129	0.055	0.064
$Li^+(C_4)$	0.114	0.041	0.128	0.054	0.068
$Li^+(C_5)$	0.117	0.040	0.129	0.054	
$Li^+(C_6)$	0.130	0.044	0.130	0.054	
$Na^+(C_1)$	0.077	0.036	0.131	0.055	0.0070
$Na^+(C_2)$	0.075	0.037	0.131	0.054	0.0063
$Na^+(C_3)$	0.124	0.029	0.129	0.055	0.0085
$Na^+(C_4)$	0.106	0.024	0.128	0.054	0.010
$Na^+(C_5)$	0.111	0.024	0.129	0.054	
$Na^+(C_6)$	0.111	0.024	0.130	0.054	
$K^+(C_1)$	0.074	0.025	0.131	0.055	0.0036
$K^+(C_2)$	0.071	0.026	0.131	0.054	0.0036
$K^+(C_3)$	0.123	0.021	0.129	0.055	0.0043
$K^+(C_4)$	0.104	0.017	0.128	0.054	0.0054
$K^+(C_5)$	0.109	0.016	0.129	0.054	
$K^+(C_6)$	0.127	0.021	0.130	0.054	

[a]Active external. [b]Inactive external. [c]Rotational constants of the transition state treated as free internal rotors. [d]Two-dimensional rotational constant of the transition state at the threshold energy for dissociation, treated variationally and statistically.

Table 4S. Rotational Constants for Unimolecular Tautomerization of M^+(cytosine) Complexes in cm^{-1}

Process	Energized Molecule		Transition State	
	1-D[a]	2-D[b]	1-D[a]	2-D[b]
$Li^+(C_2) \rightarrow Li^+(C_3)$	0.097	0.050	0.128	0.044
$Na^+(C_2) \rightarrow Na^+(C_3)$	0.075	0.036	0.085	0.035
$K^+(C_2) \rightarrow K^+(C_3)$	0.072	0.026	0.073	0.027
$Li^+(C_2) \rightarrow Li^+(C_1)$	0.097	0.050	0.097	0.049
$Na^+(C_2) \rightarrow Na^+(C_1)$	0.075	0.036	0.077	0.036

[a]Active external. [b]Inactive external.

Table 5S. MP2(full)/6-31G* Optimized Geometries of cytosine and M^+(cytosine)[a]

	C_1		C_2		C_3
	x, y, z		x, y, z		x, y, z
N	0.082054, -1.025299, -0.000345	N	0.048633, -1.005303, -0.000279	N	-0.006719, -0.977298, -0.000008
C	-1.190120, -0.521040, 0.000025	C	-1.104881, -0.335882, -0.000697	C	1.134373, -0.274980, -0.000019
N	-1.277603, 0.891306, -0.000460	N	-1.303504, 0.986104, -0.000173	N	1.296524, 1.047206, -0.000004
C	-0.188685, 1.696894, -0.000143	C	-0.170585, 1.718193, 0.000109	C	0.138854, 1.736292, 0.000004
C	1.0452331, 0.180541, 0.000522	C	1.093093, 1.162525, 0.000110	C	-1.113217, 1.148959, 0.000003
C	1.129889, -0.260218, -0.000021	C	1.156166, -0.246405, 0.000058	C	-1.141633, -0.257701, 0.000001
H	-2.202156, 1.268127, -0.000665	H	-0.304054, 2.798396, 0.000241	H	0.237684, 2.820567, 0.000008
H	-0.369506, 2.751702, 0.000072	H	1.985912, 1.778956, 0.000220	H	-2.021554, 1.742414, 0.000006
H	1.917553, 1.794551, 0.001168	N	2.337432, -0.919227, 0.000104	N	-2.302873, -0.966464, 0.000002
N	2.339955, -0.844685, 0.000257	H	2.313351, -1.928373, 0.000029	H	-2.254876, -1.974322, 0.000000
H	2.371902, -1.841570, -0.000010	H	3.224787, -0.442785, 0.000229	H	-3.202718, -0.513797, 0.000006
H	3.188205, -0.325928, 0.000677	O	-2.210038, -1.117123, 0.000427	O	2.278575, -0.997758, 0.000012
O	-2.211843, -1.171650, 0.000488	H	-2.960380, -0.490815, 0.000823	H	1.994079, -1.932313, 0.000020

	C_4		C_5		C_6
	x, y, z		x, y, z		x, y, z
N	-0.034986, -0.975596, -0.000141	N	0.049275, -0.973002, -0.000031	N	-0.026097, -0.907268, -0.000011
C	1.226164, -0.421340, -0.000603	C	-1.224301, -0.424771, -0.000099	C	1.296613, -0.374482, -0.000032
N	1.206793, 0.970524, -0.000020	N	-1.220193, 0.959335, -0.000007	N	1.394982, 1.001886, -0.000001
C	0.047526, 1.716155, 0.000072	C	-0.064325, 1.721278, 0.000014	C	0.274888, 1.700144, 0.000005
C	-1.169647, 1.130575, -0.000038	C	1.156100, 1.148088, -0.000008	C	-1.037662, 1.197243, 0.000000
C	-1.277214, -0.322145, 0.000054	C	1.287848, -0.300037, -0.000003	C	-1.169163, -0.176820, -0.000001
H	0.182326, 2.793052, 0.000290	H	-0.212950, 2.795847, 0.000060	H	0.406878, 2.783088, 0.000017
H	-2.070072, 1.733359, 0.000043	H	2.063656, 1.737178, 0.000014	H	-1.901424, 1.850022, 0.000008
H	-2.327367, -1.070700, 0.000110	N	2.447266, -0.862960, 0.000026	N	-2.351598, -0.847266, 0.000007
N	-3.164983, -0.483227, 0.000032	H	2.364426, -1.885957, 0.000030	H	-2.397503, -1.854435, -0.000001
O	2.266388, -1.068915, 0.000335	O	-2.249031, -1.097352, 0.000061	H	-3.220606, -0.336626, 0.000011
H	2.118441, 1.410524, 0.000265	H	-2.136336, 1.389770, 0.000050	O	2.231706, -1.165828, 0.000023
H	-0.068873, -1.991447, 0.000142	H	0.047087, -1.988974, 0.000011	H	-0.050049, -1.923405, -0.000008

	$Li^+(C_1)$		$Li^+(C_2)$		$Li^+(C_3)$
	x, y, z		x, y, z		x, y, z
N	-0.050600, -0.907629, 0.000013	N	-0.058955, -0.866651, -0.00012	N	-0.250167, -1.023062, -0.00009
C	-1.169617, -0.123258, 0.000035	C	-1.069276, 0.019086, 0.000013	C	0.906143, -0.404814, -0.000103
N	-1.028158, 1.241203, 0.000007	N	-1.059954, 1.322168, 0.000141	N	1.194166, 0.896039, 0.000002
C	0.198377, 1.840496, 0.000011	C	0.194859, 1.852331, 0.000159	C	0.100135, 1.704816, 0.000076
C	1.323954, 1.082327, 0.000005	C	1.331564, 1.081216, 0.000050	C	-1.177165, 1.202732, 0.000068
C	1.163108, -0.339838, -0.000004	C	1.181370, -0.326677, -0.000114	C	-1.333014, -0.206867, -0.00001
H	-1.886724, 1.787610, -0.000011	H	0.249752, 2.936880, 0.000310	H	0.290345, 2.773492, 0.000087
H	0.208147, 2.924807, 0.000001	H	2.316005, 1.535828, 0.000141	H	-2.034767, 1.866167, 0.000088
H	2.304153, 1.542867, -0.000002	N	2.235857, -1.156941, -0.000061	N	-2.529812, -0.802414, -0.00004
N	2.233894, -1.138382, -0.000019	H	2.110368, -2.159614, -0.000575	H	-2.581158, -1.813706, -0.00009
H	2.122066, -2.144231, -0.000027	H	3.181883, -0.800773, -0.000224	H	-3.391739, -0.274235, -0.00006
H	3.174249, -0.766001, -0.000032	O	-2.279020, -0.648141, -0.00045	O	2.062603, -1.156066, 0.000191
O	-2.306329, -0.659162, -0.00006	H	-3.009338, 0.005490, -0.000419	H	1.842012, -2.110094, 0.000290
Li	-1.550713, -2.398823, 0.000092	Li	-1.422086, -2.392815, 0.001362	Li	3.166193, 0.512585, -0.000395

[a]Standard Orientation, Å.

Table 5S (continued). MP2(full)/6-31G* Optimized Geometries of Cytosine and M^+(cytosine)[a]

	$Li^+(C_1)$		$Li^+(C_2)$		$Li^+(C_3)$
	x, y, z		x, y, z		x, y, z
N	-0.050600, -0.907629, 0.000013	N	-0.058955, -0.866651, -0.00012	N	-0.250167, -1.023062, -0.00009
C	-1.169617, -0.123258, 0.000035	C	-1.069276, 0.019086, 0.000013	C	0.906143, -0.404814, -0.000103
N	-1.028158, 1.241203, 0.000007	N	-1.059954, 1.322168, 0.000141	N	1.194166, 0.896039, 0.000002
C	0.198377, 1.840496, 0.000011	C	0.194859, 1.852331, 0.000159	C	0.100135, 1.704816, 0.000076
C	1.323954, 1.082327, 0.000005	C	1.331564, 1.081216, 0.000050	C	-1.177165, 1.202732, 0.000068
C	1.163108, -0.339838, -0.000004	C	1.181370, -0.326677, -0.000114	C	-1.333014, -0.206867, -0.00001
H	-1.886724, 1.787610, -0.000011	H	0.249752, 2.936880, 0.000310	H	0.290345, 2.773492, 0.000087
H	0.208147, 2.924807, 0.000001	H	2.316005, 1.535828, 0.000141	H	-2.034767, 1.866167, 0.000088
H	2.304153, 1.542867, -0.000002	N	2.235857, -1.156941, -0.000061	N	-2.529812, -0.802414, -0.00004
N	2.233894, -1.138382, -0.000019	H	2.110368, -2.159614, -0.000575	H	-2.581158, -1.813706, -0.00009
H	2.122066, -2.144231, -0.000027	H	3.181883, -0.800773, -0.000224	H	-3.391739, -0.274235, -0.00006
H	3.174249, -0.766001, -0.000032	O	-2.279020, -0.648141, -0.00045	O	2.062603, -1.156066, 0.000191
O	-2.306329, -0.659162, -0.00006	H	-3.009338, 0.005490, -0.000419	H	1.842012, -2.110094, 0.000290
Li	-1.550713, -2.398823, 0.000092	Li	-1.422086, -2.392815, 0.001362	Li	3.166193, 0.512585, -0.000395

	$Li^+(C_4)$		$Li^+(C_5)$		$Li^+(C_6)$
	x, y, z		x, y, z		x, y, z
N	-0.015283, -0.886334, -0.00002	N	-0.002646, -0.900579, -0.00004	N	0.229790, -0.948051, -0.000554
C	-1.053343, -0.036154, -0.00009	C	1.052658, -0.056956, -0.000011	C	-1.065009, -0.449860, -0.00156
N	-0.743820, 1.283093, -0.000002	N	0.766821, 1.260451, -0.000001	C	1.339211, -0.158669, 0.000060
C	0.572331, 1.741917, 0.000003	C	-0.545119, 1.747481, 0.000001	H	0.299618, -1.965466, -0.000559
C	1.607135, 0.880814, 0.000004	C	-1.589545, 0.902229, -0.000004	N	-1.250669, 0.894427, -0.000879
C	1.369532, -0.554792, 0.000004	C	-1.388562, -0.536711, -0.00001	C	1.135290, 1.226709, 0.000652
H	-1.519758, 1.935616, -0.000006	H	1.553645, 1.899958, 0.000015	N	2.541523, -0.743473, -0.000025
H	0.688306, 2.819301, 0.000005	H	-0.638845, 2.826534, 0.000006	O	-2.043209, -1.237040, 0.000683
H	2.625070, 1.252133, 0.000006	H	-2.610268, 1.262928, -0.000002	C	-0.167395, 1.686765, -0.000036
N	2.166140, -1.554796, 0.000000	N	-2.368722, -1.356114, 0.000003	H	1.975085, 1.910130, 0.001329
H	3.142904, -1.252019, -0.000008	H	-2.084146, -2.340634, 0.000005	H	2.664108, -1.748303, -0.000154
O	-2.255712, -0.427423, -0.00006	O	2.244998, -0.480377, 0.000016	H	3.381169, -0.178369, 0.000099
H	-0.212968, -1.885427, -0.00003	H	0.231568, -1.890335, 0.000009	H	-0.362740, 2.756077, -0.000201
Li	-3.833687, -1.178224, 0.000023	Li	3.881103, -1.092666, -0.000019	Li	-3.236217, 0.290752, 0.000370

	$Na^+(C_1)$		$Na^+(C_2)$		$Na^+(C_3)$
	x, y, z		x, y, z		x, y, z
N	-0.259786, 0.540524, 0.000081	N	0.243011, 0.502429, -0.000008	N	-0.775696, -1.024459, -0.00003
C	-0.609842, -0.784103, -0.00002	C	0.491375, -0.813755, -0.000061	C	0.443314, -0.519508, -0.000027
N	0.397692, -1.728696, -0.000048	N	-0.337467, -1.828210, -0.00003	N	0.846330, 0.751044, 0.000010
C	1.718009, -1.395257, -0.000104	C	-1.645647, -1.475376, 0.000009	C	-0.175836, 1.650094, 0.000035
C	2.083684, -0.088652, -0.000071	C	-2.067857, -0.165009, 0.000000	C	-1.497717, 1.272622, 0.000019
C	0.033676, 0.883071, 0.000050	C	-1.070868, 0.842031, 0.000018	C	-1.779810, -0.116428, -0.00001
H	0.097299, -2.700170, -0.000011	H	-2.359402, -2.294227, -0.00002	H	0.108551, 2.698554, 0.000048
H	2.427466, -2.215437, -0.000151	H	-3.120791, 0.091424, -0.000013	H	-2.289750, 2.013623, 0.000024
H	3.127464, 0.199481, -0.000112	N	-1.385700, 2.151727, 0.000019	N	-3.029752, -0.603444, -0.00002
N	1.338028, 2.188040, 0.000065	H	-0.667870, 2.860316, 0.000011	H	-3.170451, -1.605732, -0.00004
H	0.602606, 2.881751, 0.000226	H	-2.347664, 2.456543, 0.000007	H	-3.839861, 0.000452, -0.000012
H	2.295837, 2.510582, 0.000099	O	1.835033, -1.092374, 0.000060	O	1.494998, -1.408648, 0.000069
O	-1.804871, -1.150411, 0.000277	H	1.935826, -2.062805, 0.000100	H	1.121832, -2.314490, 0.000104
Na	-2.708764, 0.894332, -0.000188	Na	0.545337, 1.052616, -0.000022	Na	3.171256, 0.263101, -0.000046

Table 5S (continued). MP2(full)/6-31G* Optimized Geometries of Cytosine and M^+(cytosine)[a]

	$Na^+(C_4)$		$Na^+(C_5)$		$Na^+(C_6)$
	x, y, z		x, y, z		x, y, z
N	0.333700, -0.800135, -0.000024	N	-0.372955, -0.827594, 0.000022	N	-0.718857, -0.947240, 0.000727
C	-0.530924, 0.236966, -0.000005	C	0.534743, 0.182332, 0.000033	C	0.613825, -0.533374, -0.008496
N	0.044054, 1.473337, -0.000001	N	0.015740, 1.433894, 0.000011	N	0.869771, 0.805147, -0.008111
C	1.423927, 1.662927, 0.000005	C	-1.358267, 1.686051, -0.000018	C	-0.173372, 1.646412, -0.005102
C	2.271789, 0.614893, -0.000002	C	-2.243726, 0.675211, -0.000029	C	-1.504194, 1.266877, -0.001123
C	1.754025, -0.746430, 0.000005	C	-1.796307, -0.706702, -0.00007	C	-1.783511, -0.101946, 0.002247
H	-0.587021, 2.266127, 0.000026	H	0.679333, 2.199467, 0.000032	H	0.077175, 2.704797, -0.005791
H	1.750873, 2.696557, 0.000002	H	-1.637884, 2.732651, -0.000031	H	-2.301921, 1.998755, 0.000370
H	3.343074, 0.778661, -0.000005	H	-3.311023, 0.855287, -0.000052	N	-3.017549, -0.623860, 0.007966
N	2.344974, -1.883595, 0.000014	N	-2.623217, -1.682753, -0.00002	H	-3.191242, -1.620480, 0.009341
H	3.361273, -1.768112, 0.000010	H	-2.168027, -2.601178, 0.000003	H	-3.825729, -0.015696, 0.009771
O	-1.779232, 0.088987, -0.000001	O	1.773188, -0.030046, 0.000071	O	1.515854, -1.396842, -0.011464
H	-0.055559, -1.740417, -0.00002	H	0.025697, -1.762587, 0.000049	H	-0.846231, -1.958383, 0.001534
Na	-3.831889, -0.462009, 0.000006	Na	3.842797, -0.424496, -0.000052	Na	3.191916, 0.159964, 0.013386

	$K^+(C_1)$		$K^+(C_2)$		$K^+(C_3)$
	x, y, z		x, y, z		x, y, z
N	0.033315, 0.429114, 0.000139	N	-0.027527, 0.363210, -0.000039	N	1.234418, -1.015598, -0.000068
C	-0.056088, -0.939275, -0.00099	C	-0.120877, -0.970604, 0.000035	C	-0.006001, -0.553732, -0.00007
N	1.124124, -1.668894, -0.000101	N	-1.188315, -1.740573, 0.000026	N	-0.449863, 0.702916, 0.000038
C	2.354553, -1.089499, -0.000204	C	-2.361395, -1.068989, -0.00004	C	0.546193, 1.628792, 0.000091
C	2.459575, 0.263239, -0.000164	C	-2.436431, 0.306499, 0.000020	C	1.881946, 1.299689, 0.000045
C	1.237298, 1.007045, 0.000069	C	-1.213424, 1.019889, -0.000043	C	2.207940, -0.077804, -0.000026
H	1.016386, -2.679504, -0.000014	H	-3.260335, -1.679292, 0.000107	H	0.230806, 2.668958, 0.000124
H	3.209160, -1.757280, -0.000277	H	-3.388762, 0.823973, 0.000121	H	2.648388, 2.066997, 0.000052
H	3.426693, 0.750289, -0.000228	N	-1.185054, 2.370036, 0.000005	N	3.475274, -0.525566, -0.000065
N	1.286805, 2.349692, 0.000180	H	-0.309468, 2.869468, -0.000042	H	3.647019, -1.522437, -0.000126
H	0.430926, 2.886541, 0.000355	H	-2.037177, 2.909720, 0.000046	H	4.264952, 0.103939, -0.000068
H	2.164252, 2.850143, 0.000122	O	1.091975, -1.605116, -0.000029	O	-1.010427, -1.490409, 0.000187
O	-1.145065, -1.543116, 0.000566	H	0.899508, -2.561683, -0.000023	H	-0.574763, -2.367327, 0.000245
K	-2.850981, 0.372437, -0.000191	K	2.787341, 0.411014, 0.000014	K	-3.143803, 0.161010, -0.000068

	$K^+(C_4)$		$K^+(C_5)$		$K^+(C_6)$
	x, y, z		x, y, z		x, y, z
N	-0.773647, -0.774165, -0.00003	N	0.826830, -0.808417, -0.000062	N	1.168808, -0.940686, -0.000064
C	0.036611, 0.310697, 0.000004	C	-0.039121, 0.244337, -0.000111	C	-0.179363, -0.557080, 0.000337
N	-0.617993, 1.511324, 0.000002	N	0.549663, 1.470615, -0.000028	N	-0.459370, 0.779258, 0.000557
C	-2.003234, 1.616991, -0.000001	C	1.932643, 1.652381, 0.000046	C	0.571766, 1.631786, 0.000384
C	-2.787908, 0.522299, -0.000003	C	2.768098, 0.599420, 0.000061	C	1.913407, 1.282465, 0.000018
C	-2.190049, -0.803782, -0.00001	C	2.251486, -0.757849, 0.000015	C	2.217860, -0.078519, -0.000190
H	-0.036258, 2.340253, 0.000004	H	-0.073809, 2.268639, -0.000029	H	0.305339, 2.687024, 0.000504
H	-2.392787, 2.628610, 0.000002	H	2.265618, 2.683458, 0.000094	H	2.695200, 2.031293, -0.000091
H	-3.866633, 0.622428, 0.000003	H	3.842931, 0.726477, 0.000120	N	3.462871, -0.580469, -0.000521
N	-2.717520, -1.971527, 0.000004	N	3.030226, -1.774541, 0.000044	H	3.651767, -1.573786, -0.000613
H	-3.738074, -1.910120, 0.000023	H	2.525735, -2.667308, 0.000007	H	4.260073, 0.041156, -0.000618
O	1.283735, 0.234282, 0.000004	O	-1.280368, 0.093351, -0.000119	O	-1.048291, -1.447389, 0.000849
H	-0.330678, -1.689559, -0.00004	H	0.383539, -1.722753, -0.000087	H	1.314055, -1.948917, -0.000083
K	3.711903, -0.268554, -0.000001	K	-3.738250, -0.246245, 0.000058	K	-3.167804, 0.098090, -0.000473

Table 6S. MP2(full)/6-31G* Optimized Geometries of Transition States for Unimolecular Tautomerization of Cytosine and M^+(cytosine) Complexes.[a]

C-$TS_{1,2}$	C-$TS_{2,3}$	C-$TS_{3,6}$
x, y, z	x, y, z	x, y, z
N -0.136188, 1.088360, 0.000176	N -0.830699, -0.048605, -0.519890	N 0.004375, -0.901962, 0.002031
C 1.075642, -0.521443, -0.001252	C -0.822213, -0.096984, 0.814539	C -1.230879, -0.285446, 0.001416
N 1.308951, 0.830533, 0.000823	N 0.232684, -0.043552, 1.625709	N -1.414997, 1.039964, 0.006518
C 0.281816, 1.691596, 0.002443	C 1.419976, 0.069063, 0.998712	C -0.260860, 1.730463, 0.003176
C -1.001645, 1.192915, -0.001383	C 1.552285, 0.126590, -0.375101	C 1.021431, 1.192347, -0.004276
C -1.157334, -0.218644, -0.001445	C 0.364093, 0.064861, -1.119681	C 1.144351, -0.205033, -0.001621
H 0.506617, 2.754187, 0.004309	H 2.295254, 0.113988, 1.643806	H -0.373867, 2.813642, 0.006226
H -1.859362, 1.855058, -0.013141	H 2.523448, 0.223203, -0.849720	H 1.896671, 1.831412, -0.013474
N -2.402038, -0.772658, -0.056609	N 0.346786, 0.181017, -2.489314	N 2.332488, -0.875019, -0.064882
H -2.441306, -1.766883, 0.131094	H -0.524313, -0.115487, -2.913993	H 2.313416, -1.852729, 0.196524
H -3.197690, -0.225444, 0.239386	H 1.178441, -0.108320, -2.987463	H 3.159131, -0.371975, 0.228659
O 2.240969, -1.070330, 0.003961	O -2.044651, -0.287200, 1.411022	O -2.083329, -1.248985, 0.001438
H 2.478051, 0.292569, 0.005763	H -2.441870, 0.581016, 1.592843	H -0.826044, -1.863341, -0.004269

C-$TS_{1,4}$	C-$TS_{4,5}$	Li^+(C)-$TS_{1,2}$
x, y, z	x, y, z	x, y, z
N 0.000000, 0.974535, 0.000000	N -0.057780, -0.963843, 0.034987	N 0.018503 -0.962177 -0.001065
C 1.221963, 0.372137, 0.000000	C 1.222130, -0.453978, 0.002282	C -1.037092 -0.157415 -0.000644
N 1.116360, -1.047007, 0.000000	N 1.246723, 0.934183, -0.005550	N -1.094865 1.171880 -0.000464
C -0.054195, -1.740483, 0.000000	C 0.112180, 1.715479, 0.000767	C 0.083405 1.841342 0.000323
C -1.260206, -1.109707, 0.000000	C -1.124838, 1.176102, 0.011698	C 1.256471 1.124035 0.000620
C -1.199293, 0.317924, 0.000000	C -1.313910, -0.276176, 0.011294	C 1.208049 -0.299618 -0.000079
H 2.007437, -1.530867, 0.000000	H 0.285282, 2.786872, -0.000875	H 0.052496 2.925815 0.000774
H 0.036205, -2.822718, 0.000000	H -2.007239, 1.802765, 0.012168	H 2.210802 1.638028 0.001348
N -2.191603, -1.660139, 0.000000	N -2.391390, -0.894868, -0.064860	N 2.321672 -1.037960 -0.000040
H -2.075054, 1.299335, 0.000000	H -3.224465, -1.376122, 0.178634	H 2.265908 -2.048383 -0.000942
H -3.080234, 1.157654, 0.000000	O 2.241752, -1.134749, -0.011813	H 3.239611 -0.613021 0.000412
O 2.323242, 0.905477, 0.000000	H 2.171126, 1.345713, -0.026382	O -2.288902 -0.588002 -0.000047
H -0.896501, 1.984985, 0.000000	H -0.114956, -1.978102, 0.022684	H -2.388858 0.743288 0.000556
		Li -1.616971 -2.397993 0.002632

Li^+(C)-$TS_{2,3}$	Li^+(C)-$TS_{3,6}$	Li^+(C)-$TS_{1,4}$
x, y, z	x, y, z	x, y, z
N -0.090713, -0.969603, -0.129432	N 0.198203, -0.946660, -0.000296	N 0.044173, -0.862863, 0.000000
C 0.963292, -0.179770, -0.200109	C -0.997038, -0.330181, -0.000332	C 1.046324, 0.009312, 0.000000
C -1.272389, -0.318032, -0.000693	N -1.271730, 0.959748, -0.000571	C -1.301700, -0.512727, 0.000000
N 1.083355, 1.131407, -0.086448	C -0.141463, 1.732800, -0.000028	N 0.676004, 1.338234, 0.000001
C -1.313069, 1.097131, 0.053615	C 1.132310, 1.214981, 0.000205	C -1.665078, 0.870264, 0.000000
N -2.371141, -1.083108, 0.089931	C 1.319087, -0.197600, 0.000014	N -1.893377, -1.672798, 0.000000
O 2.192184, -0.876689, -0.299451	H -0.300739, 2.806697, 0.000028	O 2.276975, -0.285581, -0.000001
Li 2.556146, -0.714601, 1.546281	H 1.989858, 1.878185, 0.000536	C -0.635062, 1.755267, 0.000000
C -0.114543, 1.771378, 0.025313	N 2.511305, -0.791197, 0.000187	H 1.431215, 2.016843, 0.000001
H -2.252077, 1.633205, 0.140432	H 2.587197, -1.801356, 0.000025	H -2.695056, 1.202999, -0.000001
H -2.284356, -2.080778, -0.060626	H 3.366708, -0.250692, 0.000423	H -2.903839, -1.792319, 0.000001
H -3.297325, -0.678791, 0.089957	O -1.899598, -1.291422, 0.000021	Li 3.605565, -1.427573, 0.000002
H 2.768366, -0.345884, -0.891482	H -0.704311, -1.934079, 0.000218	H -0.783171, 2.829670, 0.000000
H -0.070772, 2.854458, 0.091366	Li -3.227917, 0.186460, 0.001399	H -0.536157, -2.040526, 0.000000

Table 6S (continued). MP2(full)/6-31G* Optimized Geometries of Transition States for Unimolecular Tautomerization of Cytosine and M^+(cytosine) Complexes.

Na^+(C)-$TS_{4,5}$	Na^+(C)-$TS_{1,2}$	Na^+(C)-$TS_{2,3}$
x, y, z	x, y, z	x, y, z
N 0.002373, -0.887470, 0.000000	N -0.188781, 0.646303, 0.000014	N -0.354906, -0.881098, -0.422653
C -1.063507, -0.072173, 0.000000	C -0.577325, -0.625343, 0.000021	C 0.597701, 0.021997, -0.589343
N -0.795784, 1.255096, 0.000000	N 0.182119, -1.729258, 0.000007	N 0.618174, 1.314245, -0.293134
C 0.503943, 1.756599, 0.000000	C 1.523941, -1.577347, -0.000026	C -0.580271, 1.793147, 0.139750
C 1.573841, 0.939469, 0.000000	C 2.048139, -0.306069, -0.000030	C -1.687356, 0.991838, 0.295018
C 1.430213, -0.517962, 0.000000	C 1.161895, 0.805799, 0.000002	C -1.533115, -0.389560, 0.026004
H 0.579870, 2.837735, 0.000000	H 2.137820, -2.471990, -0.000049	H -0.615975, 2.856525, 0.358897
H 2.577599, 1.345531, 0.000000	H 3.121159, -0.154016, -0.000053	H -2.631641, 1.401350, 0.637521
N 2.300773, -1.383880, 0.000000	N 1.626245, 2.062699, 0.000018	N -2.517065, -1.284508, 0.227078
H 2.992163, -2.099851, 0.000000	H 0.983365, 2.842923, 0.000074	H -2.385435, -2.227071, -0.119348
O -2.258889, -0.495552, 0.000000	H 2.617195, 2.262095, 0.000042	H -3.461762, -0.984103, 0.425661
H -1.591207, 1.883222, 0.000000	O -1.824712, -1.050298, 0.000045	O 1.810705, -0.507198, -1.032487
H -0.179485, -1.888689, 0.000000	H -1.086205, -2.167863, 0.000021	H 2.250353, 0.207948, -1.539339
Li -3.842102, -1.211785, 0.000000	Na -2.677511, 1.040981, -0.000042	Na 2.486695, -0.522007, 1.153536

Na^+(C)-$TS_{3,6}$	Na^+(C)-$TS_{1,4}$	Na^+(C)-$TS_{4,5}$
x, y, z	x, y, z	x, y, z
N 0.666527, -0.941756, 0.000072	N 0.354111, -0.802479, 0.000008	N 0.666527, -0.941756, 0.000072
C -0.565839, -0.381890, 0.000294	C -0.546962, 0.201438, -0.000007	C -0.565839, -0.381890, 0.000294
N -0.875868, 0.903473, 0.000310	N -0.016821, 1.454639, 0.000000	N -0.875868, 0.903473, 0.000310
C 0.229725, 1.707758, 0.000181	C 1.353470, 1.693517, 0.000004	C 0.229725, 1.707758, 0.000181
C 1.524739, 1.243791, 0.000005	C 2.245614, 0.685192, 0.000008	C 1.524739, 1.243791, 0.000005
C 1.759307, -0.158429, -0.000101	C 1.817885, -0.715663, 0.000003	C 1.759307, -0.158429, -0.000101
H 0.034336, 2.776139, 0.000263	H 1.638815, 2.739283, 0.000006	H 0.034336, 2.776139, 0.000263
H 2.355969, 1.939452, -0.000032	H 3.309077, 0.888035, 0.000008	H 2.355969, 1.939452, -0.000032
N 2.973205, -0.713476, -0.000614	N 2.506159, -1.735174, -0.000008	N 2.973205, -0.713476, -0.000614
H 3.081590, -1.719988, 0.000438	H 3.062616, -2.559431, 0.000017	H 3.081590, -1.719988, 0.000438
H 3.809305, -0.144721, 0.000566	O -1.792286, 0.015954, -0.000025	H 3.809305, -0.144721, 0.000566
O -1.403442, -1.394156, 0.000427	H -0.674434, 2.224941, -0.000012	O -1.403442, -1.394156, 0.000427
Na -3.174648, 0.096466, -0.000501	H -0.014902, -1.750009, -0.000011	Na -3.174648, 0.096466, -0.000501
H -0.167180, -1.963829, 0.000208	Na -3.827915, -0.479660, 0.000013	H -0.167180, -1.963829, 0.000208

K^+(C)$TS_{1,2}$	K^+(C)-$TS_{2,3}$	K^+(C)-$TS_{3,6}$
x, y, z	x, y, z	x, y, z
N 0.064443, 0.524155, 0.000174	N 0.737177, -0.828333, 0.591401	N -0.914455, -0.004447, -1.112178
C -0.039050, -0.802828, 0.000089	C -0.167225, 0.106201, 0.844053	C -0.383273, -0.000088, 0.122321
N 0.959664, -1.706125, -0.000129	N -0.224144, 1.367935, 0.428811	N 0.880299, 0.001965, 0.440935
C 2.232360, -1.263935, -0.000132	C 0.877831, 1.771510, -0.257188	C 1.691019, -0.000816, -0.642604
C 2.462074, 0.092018, -0.000024	C 1.928704, 0.929727, -0.541005	C 1.269943, -0.005255, -1.939068
C 1.346851, 0.971905, 0.000053	C 1.813200, -0.413215, -0.111601	C -0.130630, -0.007164, -2.183276
H 3.028412, -2.001336, -0.000206	H 0.884311, 2.809651, -0.578481	H 2.744150, 0.000701, -0.431165
H 3.473718, 0.480562, -0.000073	H 2.797134, 1.280075, -1.088440	H 1.967904, -0.007253, -2.752266
N 1.521635, 2.303494, -0.000027	N 2.733916, -1.353270, -0.408328	N -0.663633, -0.011383, -3.393907
H 0.720394, 2.918877, 0.000182	H 2.666989, -2.243357, 0.070564	H -1.652030, -0.012573, -3.515370
H 2.442912, 2.718109, 0.000085	H 3.640863, -1.087685, -0.768030	H -0.091750, -0.013465, -4.207943
O -1.147041, -1.509509, 0.000235	O -1.263281, -0.338178, 1.558307	O -1.400006, 0.001585, 0.900987
K -2.850740, 0.449937, -0.000101	H -1.596468, 0.439816, 2.050853	K 0.019192, 0.010506, 3.174813
H -0.158656, -2.422578, 0.000015	K -2.512120, -0.376986, -0.844298	H -1.930715, -0.002708, -0.310782

Table 6S. (continued) MP2(full)/6-31G* Optimized Geometries of Transition States for Unimolecular Tautomerization of Cytosine and M^+(cytosine) Complexes.

K^+(C)-$TS_{1,4}$	K^+(C)-$TS_{4,5}$
x, y, z	x, y, z
N 0.639681, 0.714270, 0.000000	N -0.799842, -0.779466, 0.000000
C -0.024477, -0.451169, 0.000000	C 0.051206, 0.274551, 0.000000
N 0.799556, -1.574538, 0.000000	N -0.558754, 1.496637, 0.000000
C 2.169840, -1.518089, 0.000000	C -1.939164, 1.654203, 0.000000
C 2.836708, -0.334461, 0.000000	C -2.771728, 0.596169, 0.000000
C 2.018019, 0.836859, 0.000000	C -2.260835, -0.776491, 0.000000
H 0.323540, -2.470414, 0.000000	H -2.286280, 2.681282, 0.000000
H 2.678435, -2.476424, 0.000000	H -3.845218, 0.735533, 0.000000
H 3.918077, -0.293285, 0.000000	N -2.896272, -1.831659, 0.000000
N 2.190798, 2.131302, 0.000000	H -3.390776, -2.693876, 0.000001
H 3.103502, 2.579418, 0.000000	H 1.298561, 0.159468, 0.000000
O -1.266310, -0.589652, -0.000001	O 0.051974, 2.303989, 0.000000
H 0.802483, 2.026843, 0.000000	H -0.377022, -1.703617, 0.000000
K -3.584544, 0.276579, 0.000000	K 3.724529, -0.278328, 0.000000

Table 7S. Enthalpies and Free Energies of Alkali Metal Ion Binding to Cytosine at 298 K in kJ/mol[a]

System	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]
$Li^+(C_1)$	296.4 (6.6)	269.4	4.7 (0.3)	301.1 (6.6)	274.1	40.0 (0.6)	261.1 (6.6)	234.1
$Li^+(C_2)$	284.7 (6.7)	209.8	3.7 (0.4)	288.4 (6.7)	213.5	38.7 (0.5)	249.7 (6.7)	174.8
$Li^+(C_3)$	281.6 (6.9)	230.1	4.2 (0.4)	285.8 (6.9)	234.3	39.7 (0.5)	246.1 (6.9)	194.6
$Li^+(C_4)$	270.2 (7.3)	199.7	3.9 (0.3)	274.1 (7.3)	203.6	36.6 (0.5)	237.5 (7.3)	167.0
$Li^+(C_5)$		187.8	3.8 (0.3)		191.6	36.6 (0.5)		155.0
$Li^+(C_6)$		279.7	4.2 (0.5)		283.9	39.7 (0.5)		244.2
$Na^+(C_1)$	179.3 (4.5)	200.7	1.7 (0.2)	181.0 (4.5)	202.4	34.7 (0.6)	146.3 (4.5)	167.7
$Na^+(C_2)$	175.4 (4.8)	150.2	1.1 (0.3)	176.5 (4.8)	151.3	33.7 (0.7)	142.8 (4.8)	117.6
$Na^+(C_3)$	178.9 (6.2)	170.9	1.1 (0.3)	180.0 (6.2)	172.0	34.0 (0.7)	146.0 (6.2)	138.0
$Na^+(C_4)$	170.9 (4.8)	135.8	1.0 (0.1)	171.9 (4.8)	136.8	27.4 (0.5)	144.5 (4.8)	109.4
$Na^+(C_5)$		128.2	1.1 (0.2)		129.3	27.8 (0.5)		101.5
$Na^+(C_6)$		213.1	2.0 (0.2)		215.1	32.2 (0.6)		182.9
$K^+(C_1)$	138.2 (3.4)	158.9	1.9 (0.3)	140.1 (3.4)	160.8	37.7 (0.7)	102.4 (3.5)	123.1
$K^+(C_2)$	133.1 (3.5)	115.1	1.0 (0.1)	134.1 (3.5)	116.1	30.2 (0.5)	103.9 (3.5)	85.9
$K^+(C_3)$	136.0 (3.5)	133.7	0.3 (0.1)	133.4 (3.5)	134.0	32.5 (0.8)	101.5 (3.6)	101.5
$K^+(C_4)$	131.5 (3.8)	103.8	0.7 (0.2)	132.2 (3.8)	104.5	27.1 (0.6)	105.1 (3.8)	77.4
$K^+(C_5)$		96.5	0.6 (0.1)		97.1	27.2 (0.6)		69.9
$K^+(C_6)$		171.8	0.4 (0.2)		172.2	30.8 (0.7)		141.4

[a]Uncertainties are listed in the parentheses. [b]Values from calculations as described in text with frequencies scaled by 0.9646. Uncertainties in the enthalpic and entropic corrections are determined by 10% variation in the molecular constants.

Figure Captions

Fig. 1S. Cross sections for the collision-induced dissociation of M^+(cytosine) complexes, where $M^+ = Li^+$ and K^+ parts a and b respectively, with Xe as a function of collision energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). Data for the M^+ product channel are shown for a Xe pressure of 0.2 mTorr (●) and extrapolated to zero (○).

Fig. 2S. Zero-pressure-extrapolated cross sections for collision-induced dissociation of M^+(cytosine) complexes, where $M^+ = Li^+$ and K^+ parts a and b respectively, with Xe in the threshold region as a function of kinetic energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). The solid lines show the best fits to the data using eq 1 convoluted over the neutral and ion kinetic and internal energy distributions. The dashed lines show the model cross sections in the absence of experimental kinetic energy broadening for reactants with an internal energy corresponding to 0 K.

Fig. 3S. RRKM rate constants for the unimolecular tautomerization, $M^+(C_x) \rightarrow M^+(C_y)$, where (x,y) = (1,2), (3,6), (4,1), (3,2), (6,3), (1,4), (5,4), and (4,5), parts a through h, respectively. The internal energy is provided by the association of M^+ with C_x, and taken from theoretical calculations at the MP2(full)/6-311+G(2d,2p)//MP2(full)/6-31G* level of theory including ZPE and BSSE corrections.

(41) Gaussian 98, Revision A.11, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery Jr, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D.K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov. B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc Pittsburgh, PA, 2001.

Figure 1S.

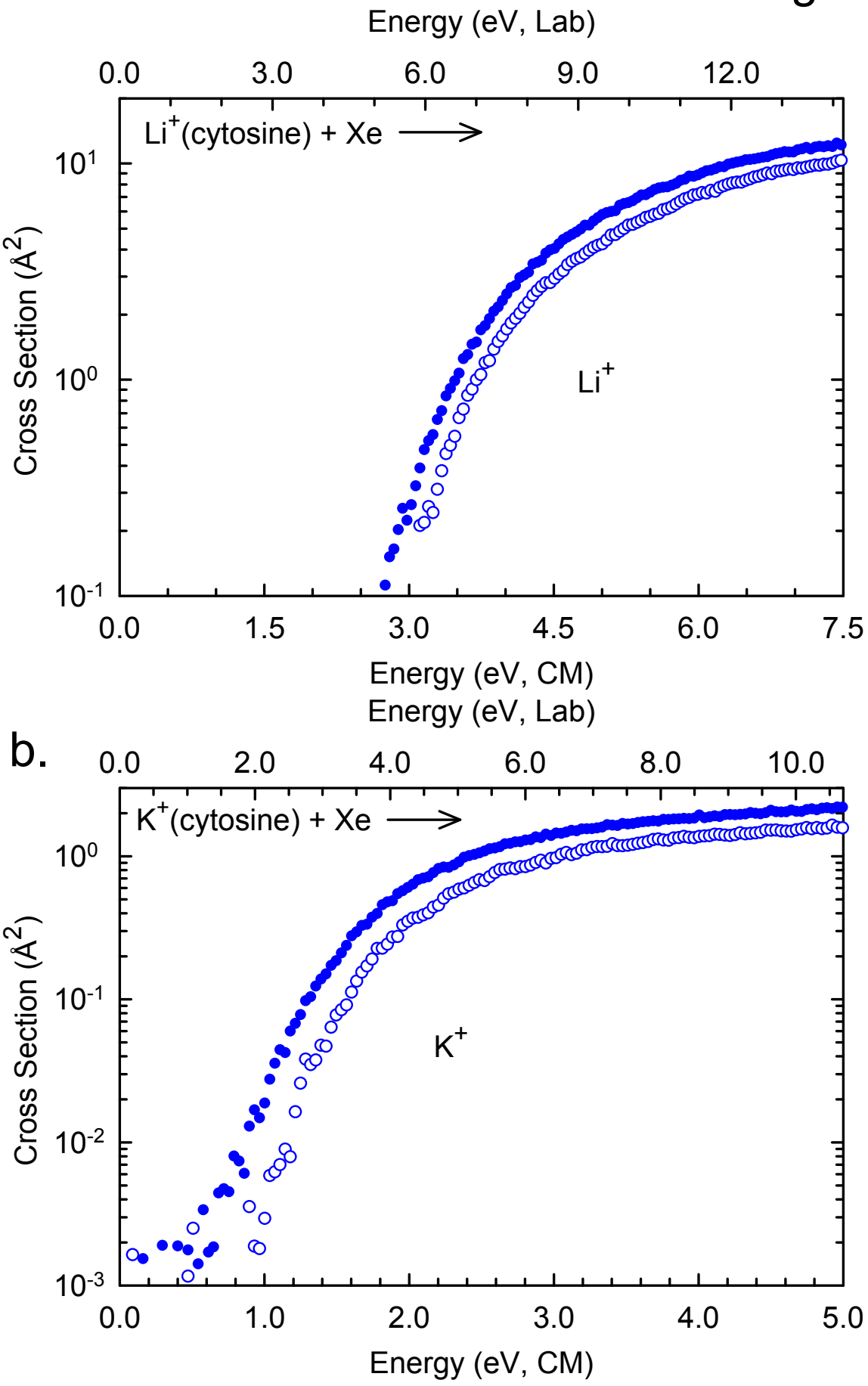


Figure 2S.

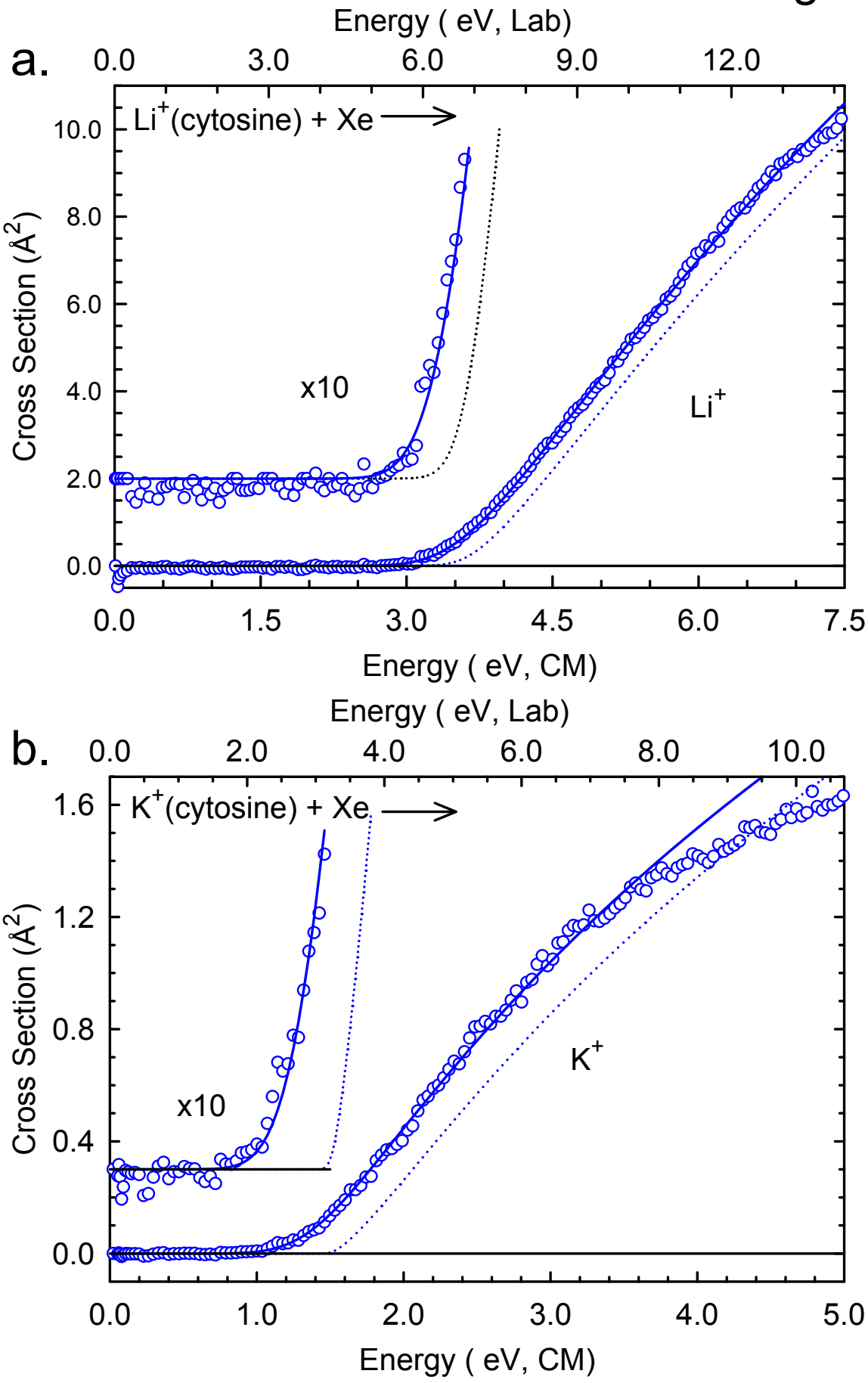


Figure 3S.

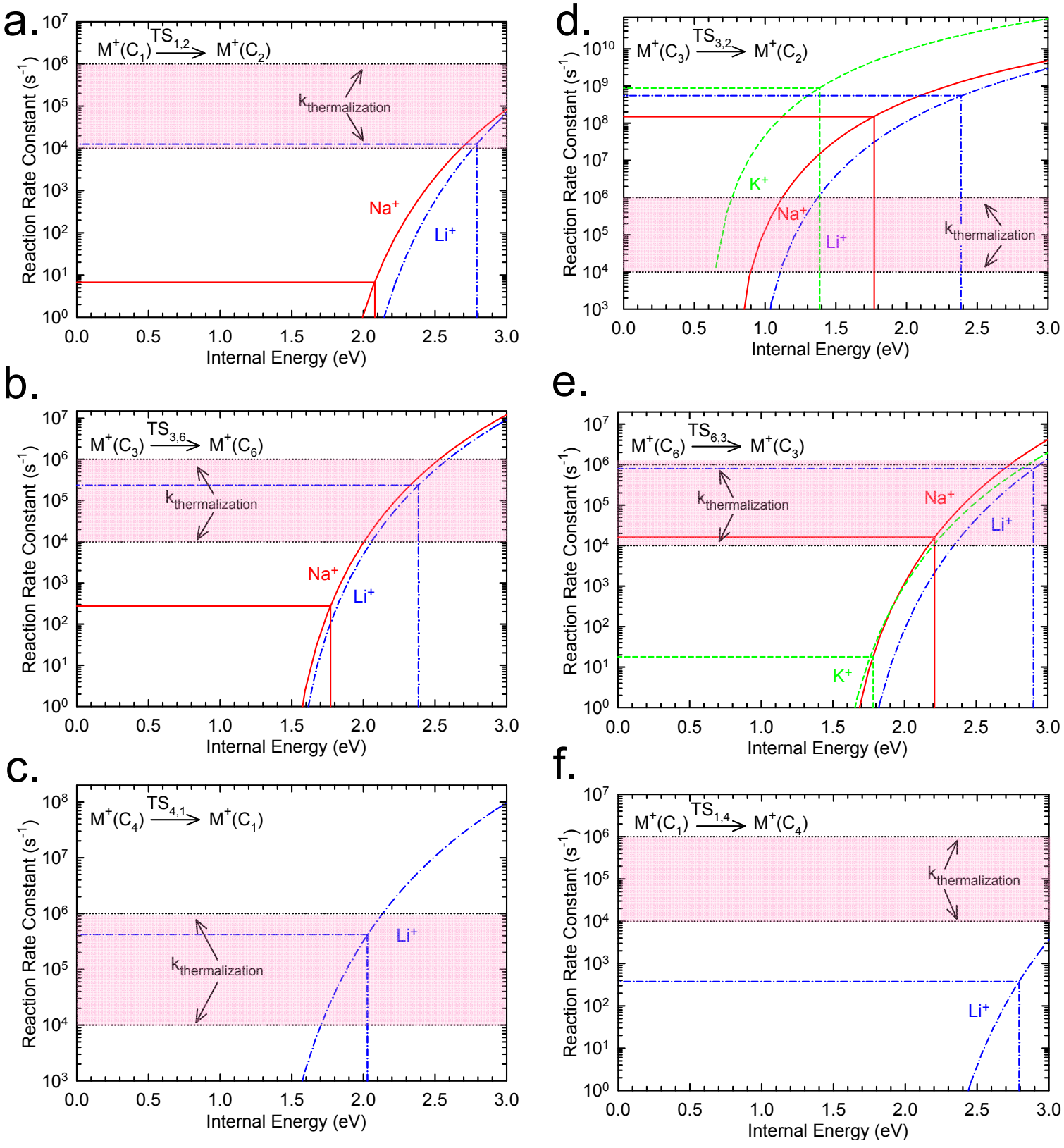
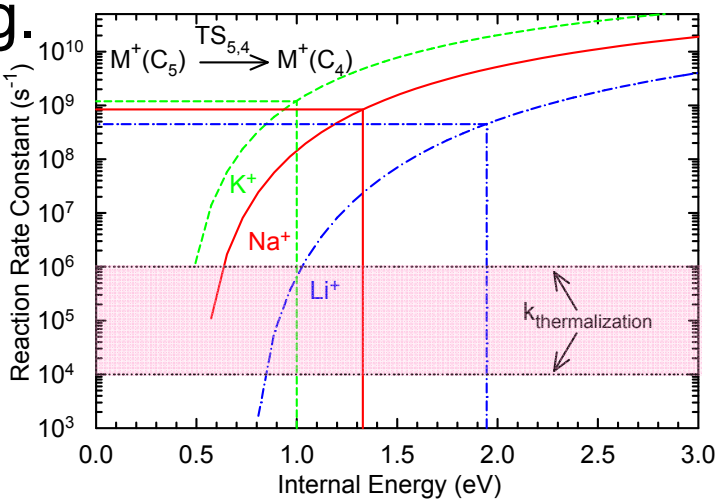
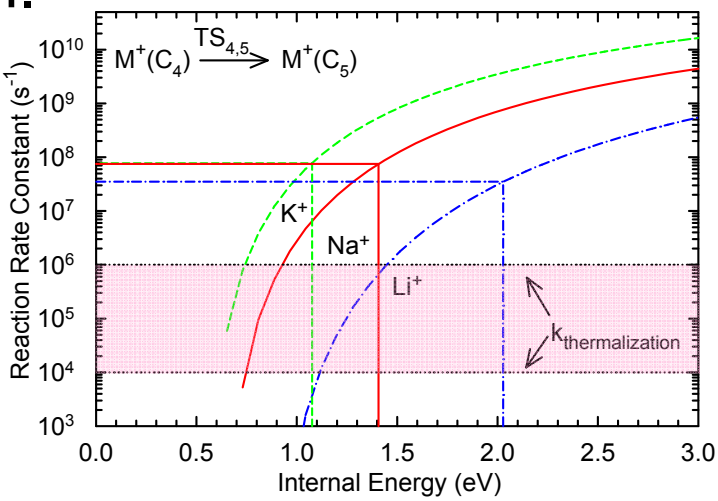

a.
M+(C1) TS1,2 M+(C2)
kthermalization
Na+
Li+
b.
M+(C3) TS3,6 M+(C6)
kthermalization
Na+
Li+
c.
M+(C4) TS4,1 M+(C1)
kthermalization
Li+
d.
M+(C3) TS3,2 M+(C2)
K+
Na+
Li+
kthermalization
e.
M+(C6) TS6,3 M+(C3)
kthermalization
Na+
Li+
K+
f.
M+(C1) TS1,4 M+(C4)
kthermalization
Li+
Reaction Rate Constant (s-1)
Internal Energy (eV)

Figure 3S.

g.


TS5,4
M+(C5) → M+(C4)
K+
Na+
Li+
kthermalization
Reaction Rate Constant (s-1)
Internal Energy (eV)

h.


TS4,5
M+(C4) → M+(C5)
K+
Na+
Li+
kthermalization
Reaction Rate Constant (s-1)
Internal Energy (eV)