Supporting Information for

Alkali Metal Cation Interactions with 15-Crown-5 in the Gas Phase: Revisited

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Table S1. Structures and Relative Energies (kJ/mol) at 0 K of M⁺(15C5) Conformations ^a

Metal	Conformer	Sequences about CC, CO, OC dihedral angles	B3LYP/ def2-TZVPPD	MP2/ 6-31+G(d) ^b
Na	1(O5)	−00 / +00 / − −0 / −00 / +00 ^b −00 / +00 / −0− / −00 / +00	0.0	0.0
	2(O5)	−0− / −0− / −00 / ++0 / +00 ^b −0− / −00 / ++0 / ++0 / +00	9.3	10.5
	4(O5)	++0 / +00 / ++0 / +00 / ++0	27.5	34.1
	O4	−00 / +− − / +0− / −00 / +00	66.5	
	O2	−00 / +− − / 0− − / 0− − / +00	202.6	
K	2(O5)	−0− / −0− / −00 / ++0 / +00	0.0	0.0
	1(O5)	−00 / +00 / − −0 / −00 / +00	5.3	6.4
	4(C ₅)	++0 / ++0 / ++0 / ++0 / ++0	8.0	9.7
	O4	−00 / +− − / +0− / −00 / +00	62.1	
	O3	−00 / +− − / 0− − / ++0 / +00	117.4	

Table S1. Continued.

Metal	Conformer	Sequences about CC, CO, OC	B3LYP/	MP2/
		dihedral angles	def2-TZVPPD	6-31+G(d) ^b
Rb	2(O5)	−0− / −0− / −00 / ++0 / +00	0.0	0.0
	4(C ₅)	++0 / ++0 / ++0 / ++0 / ++0	4.4	5.6
	1(O5)	−00 / +00 / − −0 / −00 / +00	7.9	10.3
	O4	−00 / +− − / +0− / −00 / +00	61.1	
	O3	−00 / +− − / 0− − / ++0 / +00	111.0	
Cs	2(O5)	−0− / −0− / −00 / ++0 / +00	0.0	0.0
	4(C ₅)	++0 / ++0 / ++0 / ++0 / ++0	3.8	3.2
	1(O5)	−00 / +00 / − −0 / −00 / +00	9.1	12.4
	O4	−00 / +− − / 0+− / −00 / +00	62.4	
	O3	−00 / +− − / 0− − / ++0 / +00	105.5	

^a Calculated at the B3LYP/def2-TZVPPD level here. ^b Hill and Feller.⁷⁷

Table S2. B3LYP/def2-TZVPPD Cartesian Coordinates of 15C5 (0)

C	3.29248800	-1.21518000	0.05004600
H	3.43477400	-1.34141800	-1.02865000
H	4.16317600	-1.64237400	0.55386700
O	2.18495600	0.87432900	-0.34111400
O	2.16088200	-1.93544200	0.49856800
C	1.94917400	2.22734900	-0.00615300
H	2.73981300	2.86779700	-0.42089200
H	1.94186700	2.35814000	1.08257000
C	1.09689400	-2.06675200	-0.44034000
H	1.19229100	-3.01581000	-0.98025900
H	1.11266400	-1.25093700	-1.16280400
C	-0.21475000	-2.02651700	0.32006100
H	-0.23297700	-2.81072500	1.08699000
H	-0.32613200	-1.05777600	0.80808200
C	3.22679300	0.26164100	0.39355900
H	3.04530400	0.37568900	1.46949700
H	4.19529600	0.72896500	0.15914600
O	-1.25277900	-2.24701300	-0.63084700
O	-0.41793500	2.09734400	0.23199200
C	-2.57187300	-2.09008900	-0.14461600
H	-3.20522200	-2.73286700	-0.76072400
H	-2.65041900	-2.43222700	0.89374100
C	-3.09420200	-0.66892200	-0.25551900
H	-4.18856400	-0.67424100	-0.14254300
H	-2.85884000	-0.28839400	-1.25563700
C	-1.70723000	2.19195900	-0.33365100
H	-1.72181400	1.71626200	-1.32308200
H	-1.99793400	3.24458300	-0.46947200
C	-2.70572300	1.53185700	0.60133700
H	-3.72294500	1.74613300	0.24855500
H	-2.59466200	1.96390300	1.59668500
C	0.61014500	2.65058400	-0.56486300
H	0.54381000	3.74757800	-0.56819800
H	0.52445400	2.30286100	-1.60190200
O	-2.51065200	0.13819100	0.75338300

Table S3. B3LYP/def2-TZVPPD Cartesian Coordinates of Na⁺(15C5) **1(O5)**

Na	0.01653000	-0.00240500	-0.50733000
O	-0.01041100	-2.16834000	0.35217100
C	1.16263600	-2.86884900	-0.05976200
C	-1.24779700	-2.83273600	0.09837400
C	2.36439500	-2.02227600	0.29907300
C	-2.36814900	-1.85130900	0.36540600
H	1.12531000	-3.05585400	-1.13882800
H	1.23860300	-3.83283400	0.45259800
H	-1.35638100	-3.70402200	0.75130300
H	-1.28564500	-3.17042000	-0.94263800
O	2.24325000	-0.74889700	-0.33782100
O	-2.20977900	-0.75400700	-0.53681700
H	3.27805300	-2.53028500	-0.02420800
H	2.40899100	-1.88359200	1.38381000
H	-2.32776700	-1.50748700	1.40409700
H	-3.33053900	-2.34357800	0.19861500
C	3.15454400	0.24208600	0.14202200
C	-3.15380900	0.31697600	-0.42795700
C	2.66431900	1.60812300	-0.28860200
C	-2.61114200	1.47037500	0.39828200
H	4.15842900	0.06697500	-0.25606100
H	3.20014600	0.19659500	1.23434900
H	-3.34708900	0.65491700	-1.44607000
H	-4.09514200	-0.03533000	-0.00046400
O	-1.36629200	1.86901200	-0.17418000
O	1.34692000	1.77483100	0.23092000
H	3.33910500	2.37348000	0.10683900
H	2.65229400	1.69411500	-1.38133000
H	-3.32930500	2.29677400	0.37879200
H	-2.45895000	1.17818400	1.44398700
C	-0.70003300	2.93943500	0.49654100
C	0.71327600	3.02388400	-0.03880000
H	-0.67930300	2.74721800	1.57423900
H	-1.22106400	3.88529300	0.32136400
H	1.24511200	3.84239300	0.45558600
H	0.70436200	3.21885400	-1.11698200

Table S4. B3LYP/def2-TZVPPD Cartesian coordinates of $K^+(15C5) 2(O5)$

K	-0.00457000	0.01783500	-1.55921500
O	0.54688600	1.90945400	0.41336700
C	-0.45143900	2.92329400	0.41956700
C	1.88441400	2.36957300	0.25811000
C	-1.78091300	2.26997200	0.71418400
C	2.81087100	1.19627700	0.47798500
H	-0.48203200	3.43916400	-0.54771300
H	-0.23909500	3.66765300	1.19438900
H	2.11384600	3.14736900	0.99420100
H	2.02907700	2.79752800	-0.74143100
O	-2.10096300	1.36512600	-0.34157500
O	2.54221100	0.19676100	-0.50486200
H	-2.55593000	3.03894500	0.79632700
H	-1.71718900	1.73935100	1.66901000
H	2.65008900	0.79861300	1.48360400
H	3.85110100	1.52844800	0.39986000
C	-3.20055800	0.49235100	-0.07280800
C	3.03875700	-1.10546200	-0.19190600
C	-2.76529600	-0.80852500	0.57501700
C	2.11209800	-1.88480600	0.72280900
H	-3.66833600	0.28079000	-1.03462800
H	-3.94099500	0.98889700	0.56002700
H	3.14073000	-1.62679500	-1.14409300
H	4.03209200	-1.04309300	0.26180700
O	0.85381800	-2.05080000	0.07595600
O	-1.92830000	-1.50820900	-0.34383200
H	-2.23381500	-0.61616400	1.51309400
H	-3.65220000	-1.40915500	0.80520600
H	2.56167500	-2.86062700	0.93916100
H	1.97025600	-1.36398800	1.67633800
C	-0.14100700	-2.65087500	0.89998000
C	-1.42978800	-2.76766700	0.10845500
H	-0.28230700	-2.04969100	1.80573500
H	0.17308600	-3.65383800	1.21110100
H	-2.18167300	-3.28478200	0.71147300
H	-1.25358800	-3.36092900	-0.78917900

Table S5. B3LYP/def2-TZVPPD Cartesian coordinates of $\text{Rb}^+(15\text{C}5) \mathbf{2}(\text{O}5)$

Rb	0.00355500	0.02169300	1.62375600
O	-0.55413400	1.89099000	-0.64857000
C	0.44146300	2.90538800	-0.67825000
C	-1.89130100	2.35322600	-0.50901800
C	1.76999700	2.25478200	-0.98287100
C	-2.82074500	1.18403800	-0.73874000
H	0.48352600	3.43473900	0.28177300
H	0.21826300	3.64074300	-1.45902400
H	-2.11137700	3.13109500	-1.24831300
H	-2.04797300	2.78424000	0.48791100
O	2.12371400	1.37971200	0.08613200
O	-2.58185300	0.18857800	0.25455800
H	2.53623000	3.02811100	-1.10229800
H	1.68882100	1.70093000	-1.92297900
H	-2.64124500	0.78028300	-1.73853300
H	-3.86020900	1.52430100	-0.68547100
C	3.21227600	0.49982100	-0.19753200
C	-3.05122100	-1.11798600	-0.07679200
C	2.76473800	-0.80359400	-0.83211500
C	-2.10016400	-1.88193300	-0.97932800
H	3.69703400	0.29157500	0.75673700
H	3.94460700	0.98944900	-0.84570000
H	-3.16603700	-1.64723800	0.86978100
H	-4.03669500	-1.06748400	-0.54962100
O	-0.85465300	-2.05932300	-0.31259100
O	1.95520300	-1.50973300	0.10492500
H	2.21015900	-0.61303500	-1.75684000
H	3.64886500	-1.39956100	-1.08570000
H	-2.54504200	-2.85441000	-1.22085300
H	-1.93981800	-1.34674500	-1.92190500
C	0.15125000	-2.63489500	-1.13939500
C	1.43997800	-2.76064200	-0.34922200
H	0.29261700	-2.01606200	-2.03306500
H	-0.15306300	-3.63431500	-1.47220200
H	2.18491600	-3.28464000	-0.95568500
H	1.26103600	-3.35562700	0.54695800

Table S6. B3LYP/def2-TZVPPD Cartesian coordinates of $\text{Cs}^+(15\text{C5})$ **2(O5)**

Cs	0.00762100	0.02880800	1.64628500
O	-0.56835600	1.87266800	-0.90326200
C	0.42201900	2.89042400	-0.94589200
C	-1.90501900	2.33299200	-0.76405300
C	1.75205100	2.24610200	-1.25587900
C	-2.83425100	1.16383500	-0.99282500
H	0.46870800	3.42721700	0.01007200
H	0.19005700	3.62012800	-1.72970800
H	-2.12632200	3.11014400	-1.50408600
H	-2.06298300	2.76579700	0.23217400
O	2.12755200	1.39160500	-0.17847400
O	-2.60351000	0.17233100	0.00571500
H	2.51021500	3.02391900	-1.39727900
H	1.66356700	1.67736700	-2.18634500
H	-2.64916000	0.75616500	-1.98989400
H	-3.87376900	1.50558200	-0.94769200
C	3.21362300	0.51144100	-0.46701000
C	-3.05419100	-1.13800300	-0.33348000
C	2.76412900	-0.79745800	-1.08848100
C	-2.08726100	-1.89067500	-1.22810600
H	3.70914000	0.31067200	0.48343100
H	3.93900800	0.99781500	-1.12571400
H	-3.17475900	-1.67137400	0.61013100
H	-4.03516100	-1.09701200	-0.81697400
O	-0.84858800	-2.06843600	-0.54996500
O	1.97470200	-1.50624200	-0.13727800
H	2.19430500	-0.61369400	-2.00499700
H	3.64830800	-1.38852500	-1.35402700
H	-2.52530200	-2.86333100	-1.48219000
H	-1.91890300	-1.34817400	-2.16511700
C	0.16425000	-2.63247100	-1.37521800
C	1.45288500	-2.75597500	-0.58500200
H	0.30413200	-2.00886600	-2.26573100
H	-0.13249000	-3.63232600	-1.71430300
H	2.19542800	-3.28599400	-1.18960300
H	1.27300000	-3.34666200	0.31394200