Experimental and Theoretical Study of the Vibrational Spectra of 12-Crown-4−Alkali Metal Cation Complexes

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The vibrational, Raman, and IR, spectra of the five 12-crown-4 (12c4) complexes with Li^+, Na^+, K^+, Rb^+, and Cs^+ alkali metal cations were measured. Except for a small shift of the position of some bands in the vibrational spectra of the Li^+ complex, the vibrational spectra of the five complexes are so similar that it is concluded that the five complexes exist in the same conformation. B3LYP/6-31+G* force fields were calculated for six of the eight predicted conformations in a previous report (*J. Phys. Chem. A* **2005**, *109*, 8041) of the 12c4−Li^+, Na^+, and K^+ complexes that are of symmetries higher than the C_1 symmetry. These six conformations, in energy order, are of C_4, C_s, C_s, C_{2v}, C_{2v}, and C_s symmetries. Comparison between the experimental and calculated vibrational frequencies assuming any of the above-mentioned six conformations shows that the five complexes exist in the C_4 conformation. This agrees with the fact that the five alkali metal cations are larger than the 12c4 ring cavity. The B3LYP/6-31+G* force fields of the C_4 conformation of the Li^+, Na^+ and K^+ complexes were scaled using a set of eight scale factors and the scale factors were varied so as to minimize the difference between the calculated and experimental vibrational frequencies. The root-mean-square (rms) deviations of the calculated frequencies from the experimental frequencies were 7.7, 5.6, and 5.1 cm^{-1} for the Li^+, Na^+, and K^+ complexes, respectively. To account for the earlier results of the Li^+ complex that the C_s conformation is more stable than the C_4 conformation by 0.16 kcal/mol at the MP2/6-31+G* level, optimized geometries of the complex were calculated for the C_4 and C_s conformations at the MP2/6-311++G** level. The C_4 conformation was calculated to be more stable than the C_s conformation by 0.13 kcal/mol.

Introduction

Recently there has been a wide interest shown in the chemistry of crown ethers. This interest is due to the ability of crown ethers to form strong complexes with ionic species, especially alkali metal cations, with high selectivity. Consequently, crown ethers have found a large number of industrial and medical applications. Crown ethers are used in nuclear waste disposal,[1−5] membrane transport,[6−8] anion activation,[9,10] formation of soluble and insoluble polymers,[11−14] and macrocyclic liquid crystals.[15]

Because of the importance of the applications of crown ethers, our objective was set to study this class of molecules to determine in which conformation, or conformations, these large ring flexible molecules exist in. The methodology we use to achieve this goal is through the conformational analysis and vibrational study of free crown ethers and some of their complexes. Although our attention was attracted first to the most important crown ether, 18-crown-6 (18c6), due to its large size, our effort was turned to the smaller and easier to study 12c4.

In a previous report,[16] a full conformational search of the possible conformations of free 12c4 was performed at the MM3 level. The search was performed using an efficient method of conformational search of cyclic molecules, the CONFLEX method.[17−20] The method, as implemented in the CAChe program,[21] has the advantage of being fully programmed. This minimizes the human interference and consequently minimizes human error. This is compared to other conformational search methods that can be termed as half programmed−half manual. The conformational search of 12c4 resulted in the prediction of 180 conformations. Energy order of the predicted conformations was calculated at levels of theory as high as the MP2/6-31+G* level. Similar to previous reports,[22−24] the study predicted that the S_4 conformation is the lowest energy conformation of 12c4. At the MP2/6-31+G* level, the S_4 conformation is more stable than the C_i conformation by 2.61 kcal/mol. In a following vibrational study of free, or rather uncomplexed, 12c4, it was shown for the first time that 12c4 in the solid, liquid, and considered solution phases exists in the C_i conformation.[25] The case is similar for the larger 18c6. It is known experimentally, using the vibrational spectra[26,27] and X-ray,[28,29] that 18c6 exists in the C_i conformation. A similar conformational search, as that performed for 12c4, predicted for the first time that the lowest energy conformation of free 18c6 is a S_6 conformation. At the MP2/6-31+G* level, the S_6 conformation is more stable than the experimentally known C_i conformation by 1.84 kcal/mol.[30] It was shown that the stability of the lowest energy S_4 conformation of 12c4 and the lowest energy S_6 conformation of 18c6 is due to a combination of both more number of oxygen atoms participating in hydrogen bonding and at distances shorter than that of any of the other conformations.[16,30]

In a continuing study, conformational analysis of 12c4−alkali metal cation complexes was performed.[31] The study predicted eight possible conformations of these complexes. It was

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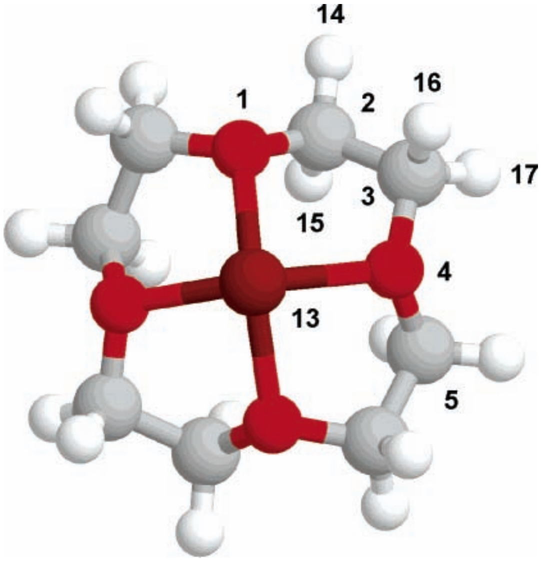

Figure 1. Structure and atom numbering of the C_4 conformation of the 12c4−alkali metal cation complexes.

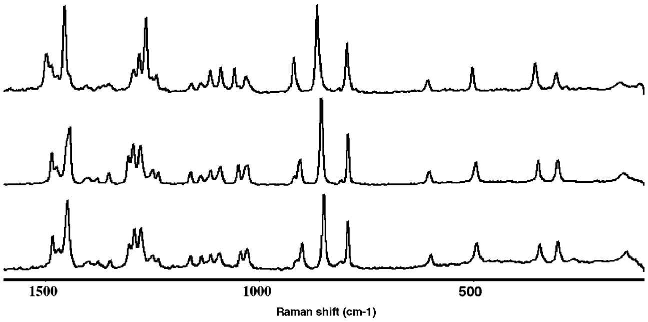

Figure 2. Raman spectra of the solid phase of the three 12c4-Li^+ (top), Na^+ (middle) and K^+ (bottom) complexes.

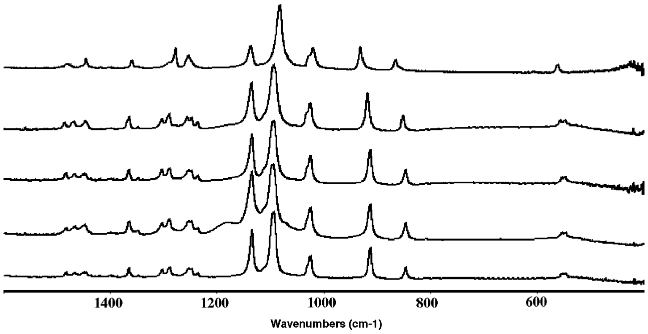

Figure 3. IR spectra of the solid phase of the 12c4−Li^+ (top), Na^+ (second from the top), K^+ (third from the top), Rb^+ (fourth from the top) and Cs+ (bottom) complexes.

TABLE 1: Geometry of the 12c4−Alkali Metal Cation Complexes at the B3LYP/6-31+G* and MP2/6-31+G* Levels[a]

coordinate	Li^+	Na^+	K^+	Rb^+	Cs^+
O_1-C_2	1.437	1.434	1.431	1.429	1.428
	1.440	1.437	1.433	1.432	1.431
C_2-C_3	1.524	1.525	1.524	1.525	1.525
	1.516	1.517	1.516	1.516	1.516
C_1-O_4	1.440	1.437	1.433	1.431	1.430
	1.444	1.441	1.437	1.435	1.434
$M-O$	2.120	2.334	2.747	2.986	3.226
	2.018	2.394	2.708	2.930	3.144
C_2-H_{14}	1.098	1.099	1.100	1.100	1.101
	1.097	1.099	1.099	1.100	1.100
C_2-H_{15}	1.099	1.098	1.098	1.098	1.098
	1.099	1.097	1.097	1.097	1.097
C_3-H_{16}	1.093	1.094	1.095	1.095	1.095
	1.093	1.093	1.094	1.094	1.094
C_3-H_{17}	1.096	1.097	1.098	1.099	1.099
	1.096	1.098	1.098	1.099	1.099
$O_1C_2C_3$	106.0	107.8	108.5	108.8	108.9
	105.3	107.1	107.3	107.5	107.5
$C_2C_3O_4$	109.0	111.8	112.6	112.9	113.1
	109.4	111.2	111.5	111.8	112.0
$C_3O_4C_5$	116.7	115.9	115.4	115.3	115.3
	115.2	114.4	114.0	113.9	113.9
MO_4C_3	109.4	109.2	109.9	110.2	110.4
	109.5	110.0	110.8	111.0	111.2
MO_4C_5	109.1	113.2	118.6	120.8	122.7
	109.2	115.1	119.7	121.9	123.7
$O_1C_2H_{14}$	110.2	110.0	110.0	110.0	110.1
	110.1	109.9	110.1	110.2	110.2
$C_3C_2H_{14}$	110.5	109.7	109.4	109.2	109.2
	111.0	110.2	110.0	109.8	109.8
$O_1C_2H_{15}$	110.2	110.3	110.4	110.4	110.5
	110.2	110.3	110.4	110.5	110.5
$O_3C_2H_{15}$	111.4	111.0	110.7	110.6	110.5
	111.5	111.1	110.9	110.8	110.8
$C_2C_3H_{16}$	110.3	110.1	109.9	109.9	109.8
	110.3	110.1	110.0	109.8	109.8
$O_4C_3H_{16}$	105.7	105.6	105.7	105.7	105.7
	105.6	105.6	105.7	105.7	105.7
$C_2C_3H_{17}$	111.1	110.2	109.8	109.6	109.5
	111.6	110.7	110.5	110.3	110.3
$O_4C_3H_{17}$	111.0	110.7	110.7	110.7	110.8
	110.7	110.5	110.7	110.7	110.7
$O_1C_2C_3O_4$	−50.9	−56.1	−58.4	−58.9	−59.4
	−52.8	−56.9	−57.9	−58.5	−58.9
$C_2C_3O_4C_5$	−91.5	−84.0	−81.0	−80.2	−79.7
	−88.8	−83.0	−81.6	−80.8	−80.4
$C_3O_4C_5C_6$	168.1	164.7	163.5	162.9	162.7
	168.7	165.6	165.0	164.6	164.4
$MO_1C_2C_3$	43.5	37.5	29.9	26.3	23.2
	45.1	36.7	30.5	27.1	24.0

[a] See Figure 1 for atom numbering. Bond lengths in Å and angles in degrees. For each coordinate, the first line corresponds to the B3LYP/6-31+G* level and the second line corresponds to the MP2/6-31+G* level. M refers to alkali metal cation.

concluded that the C_4 conformation is the lowest energy conformation of the 12c4−Na^+, K^+, Rb^+ and Cs^+ complexes. For the 12c4−Li^+ complex, a C_s conformation is the lowest energy conformation, although, at the MP2/6-31+G* level, the C_4 conformation is less stable than this C_s conformation by only 0.16 kcal/mol. The best agreement between the experimental and calculated binding energies is obtained assuming the C_4 or C_s conformation of the 12c4−Li^+ and Na^+ complexes and the C_4 conformation of the 12c4−K^+ complex. For the 12c4−Rb^+ and −Cs^+ complexes, poor agreement is obtained between the experimental and calculated binding energies assuming C_4 conformations of both complexes. Instead, the best agreement is obtained assuming a C_{2v} structure of both complexes. Since this disagrees with the energy order mentioned above, Feller and co-workers argued that spectral measurement of the binding energy of the 12c4−Rb^+ and −Cs^+ complexes samples both complexes in this high energy C_{2v} conformation rather than the lowest energy C_4 conformation.[32−37]

Surprisingly, as the number of studies of the vibrational spectra of free 12c4 is quite limited,[38−44] the number of studies of the vibrational spectra of its alkali metal cation complexes, to the best of our knowledge, is very scarce.[38,40] The most detailed study of the vibrational spectra of 12c4−alkali metal cation complexes was reported by Fukushima and Tamaki in 1987.[40] The authors reported the Raman spectra of the 12c4−Li^+, −Na^+, −K^+, −NH_4^+, −Mg^{2+}, −Ca^{2+}, −Sr^{2+}, −Ba^{2+}, and −Pb^{2+} complexes in the region below 1000 cm^{-1}. The assignment of the fundamental vibrations was aided by frequencies calculated using an empirical force field. The study predicted a D_{2d} structure of the 12c4−Li^+, −Na^+, −K^+, −NH_4^+, and −Mg^{2+} complexes and a C_{2v} structure of the 12c4−Ca^{2+}, −Sr^{2+}, and −Ba^{2+} complexes. This result contradicts an earlier

TABLE 2: FT-Raman and FT-IR Frequencies (cm^{-1}) and Assignment of the 12c4−Li$^+$ Complex[a]

Raman				IR		
MeOH^b			H_2O^c	MeOH^b		
solid	MeOH	H_2O	H_2O	solid	ref 40	assgnt
155	158					(ν_{39})
167	167	164				(ν_{61})
176	182	185				
	199	201				(ν_{20})
	214					
229		221				(ν_{38})
250					252	
266					262	
282	285		292			ν_{60}
305	305	300	307		302	ν_{19}
	311	313	310		312	
324	328		324			ν_{18}
	341	338	340			ν_{59}
355	351	352	348		355	ν_{17}
		374	374			
	400	401	399			(ν_{37})
	415	415		422		ν_{58}
501	500	499	499		504	ν_{36}
				562		ν_{57}
					579	
603	603		604	607		ν_{16}
795	786	788	785		792	ν_{35}
	802	803	800		805	ν_{56}
815	816	816	818		818	
					848	
865	862	862	860	865	865	ν_{15}
912	907	908	900		902	ν_{14}
920	917	916	917			ν_{34}
929	928	925	926	931		ν_{55}
		944	939			
1024		1022	1022	1020		ν_{13}
1033		1029	1029	1027		ν_{54}
1048		1049	1049	1046		
1059		1059	1060			
1078	1084	1085	1085	1083		
1090	1090	1092	1092			
	1102	1102	1102			
	1113	1113	1111	1111		ν_{11}
1116	1120			1117		ν_{32}
	1128		1126			
1138	1137	1138	1137	1137		ν_{52}
1159	1161	1161	1158			ν_{31}
1242	1241	1244	1243	1246		ν_{10}
1253	1252		1254	1253		
1266	1261	1260	1262			ν_{30}
		1269	1269			
1281	1277	1286	1280	1278		
1296	1288	1294	1288	1289		
	1296	1296	1298			
1349	1350	1352	1350	1348		ν_8
1367	1366	1361	1361	1360		ν_{49}
1376	1381	1369	1372			
1397	1392	1396	1388			
1405	1400		1400			
1410	1411	1307	1407			
1446	1442	1442		1446		ν_{47}
1457	1454	1454	1455	^{d}		ν_{26}
		1464		^{d}		
1472	1479	1475	1473	^{d}		ν_{25}
1487	1486		1488	^{d}		ν_{46}
1499				^{d}		ν_5
2876		2875		2875		
2886		2885	2885	2882		
2902						
2923		2919		2920		
2942		2945				
2970		2974	2974	2966		
2991				2990		
3002		3003	3001			

[a] MeOH stands for methanol. assgnt is the fundamental band assignment. For bands in parentheses, their assignment as fundamentals was not certain, and they were not used in the scaling of the force field. [b] The 12c4−alkali metal cation complex synthesized using methanol as a solvent. [c] The 12c4−alkali metal cation complex synthesized using H_2O as a solvent. [d] There is one broad band in this region.

IR and NMR study of free 12c4 and its Li$^+$ complex that both species adopt a square C_4 conformation.[38]

TABLE 3: FT-Raman and FT-IR Frequencies (cm^{-1}) and Assignment of 12c4−Na$^+$ Complex[a]

Raman					IR				
MeOH^b			H_2O^c		MeOH^b	H_2O^c			
solid	MeOH	H_2O	solid	MeOH	solid	solid	MeOH	ref 40	assgnt
	131	138	129	124					(ν_{40})
153	148		148						ν_{39}
171	171		173						
183	181		180	188					ν_{61}
193	196	193	198						ν_{20}
209	204	202	210	204					ν_{38}
215	215			212					ν_{60}
	248	240	246	243					ν_{19}
254		257	260						
260		264	268						
280	285		276	273					ν_{59}
304	302	303	302	301				303	ν_{18}
347	348	350	347	346				349	ν_{17}
355				352					
366	368	363		369					ν_{58}
421	414	416	415						(ν_{37})
494	494	496	494	493				495	ν_{36}
					553	553			ν_{57}
602	601	598	603	599				601	ν_{16}
796	794	795	792	794				796	ν_{35}
	802	803	808		808				ν_{56}
815	814	815	810	815					
821			825	823	823	825	825		
833	827	829	833	830	830	831	830	828	
855	856	853	855	855	852	853	852	858	ν_{15}
879	881	875		875					
896	895	896		898	899	897			ν_{14}
903	906	904	905	905				907	ν_{34}
918	920	916	919	918	918	918	919		ν_{55}
		1028	1028		1025	1026			ν_{13}
1029		1033	1031		1032	1030			ν_{54}
1049		1041	1049						ν_{33}
					1055				
1068		1064	1072						ν_{12}
1093	1098	1095	1092	1097	1093	1093	1098		ν_{53}
	1106	1111		1103					
1115	1115	1115	1115	1110	1113	1113			ν_{11}
1126		1124	1124	1123					ν_{32}
1140	1141	1140	1138	1139	1135	1135	1138		ν_{52}
1162	1160	1165	1162	1158					ν_{31}
1238	1236	1239	1237	1241	1236	1237	1237		ν_{10}
1251	1249	1251	1250	1254	1248	1248	1248		ν_{51}
					1256	1256	1255		ν_{30}
1273	1268	1269	1279	1266					ν_{29}
					1289	1289	1290		
1293	1291	1293	1296	1291	1293	1293	1293		ν_{50}
1307	1305	1307	1307	1306	1304	1304	1305		ν_9
						1348			
1351	1354	1353	1353	1353		1355			ν_8
						1362			
	1367	1363	1364	1366	1365	1365	1365		ν_{49}
					1368	1367			
1371		1371	1371		1375	1375			
1380	1383	1386	1380	1379	1380	1379			ν_{28}
					1387	1387			
1396	1396	1396	1396		1395	1395			(ν_7)
1400			1402	1402	1399	1399			(ν_{27})
1408	1410	1410	1408	1413	1405	1405			ν_{48}
1446			1444						ν_{26}
					1447	1447			ν_{47}
		1453	1452						ν_6
			1470						ν_{25}
1473			1476		1469	1469			ν_{46}
1493		1486	1487		1485	1485			ν_5
					2964	2965			
2871			2870		2875	2875			
		2881	2887		2878				
			2894		2891				
		2907	2910		2907	2910			
2922			2925		2922	2921			
2930		2933	2943		2936	2936			
2950		2954	2956		2957	2957			
					2966	2969			
			2975		2975				

[a,b,c] See corresponding footnotes in Table 2.

There are two reports of X-ray studies of the structure of 12c4−Na$^+$ complex.[45,46] Both studies show that the complex in the solid phase has a C_4 structure. Using X-ray, C_s,[47] C_i,[48] and C_4[49] conformations have been reported for the 12c4−Cu^{2+}, −Mg^{2+}, and −Ca^{2+} complexes, respectively.

In view of these conflicting results about the conformation, or conformations, assumed by 12c4−alkali metal cation complexes and the absence of a detailed vibrational study of these complexes, it was felt that such a study would be necessary. This would be also in line with our previous studies of the conformational and vibrational analysis of crown ethers. The aim of the present report is then to measure the vibrational, Raman, and IR spectra of the five 12c4−alkali metal cation complexes. In addition, to compare between the experimental and calculated vibrational spectra of these complexes assuming any of the possible conformations of the complexes. This is in an effort to determine in which conformation these complexes exist in. Finally, aided by accurately calculated scale quantum mechanical (SQM) B3LYP force field, the fundamental vibrational frequencies of the complex are assigned.

Experimental Details

12c4−alkali metal cation complexes were synthesized by heating for 2 h, under reflex in methanol or in aqueous solution, a slight excess of an equimolar amount of the alkali metal chloride salts and 12c4.[26] The solvent was allowed to evaporate by placing the mixture in a closed desiccator under vacuum whereby crystals of the complex were formed. Some of the complexes were obtained in an emulsified form that did not form a precipitate. To these complexes, ether was added. Upon evaporation of the ether, crystals of the complexes were obtained.

FT-IR spectra were measured using a Thermo Nicolet Nexus 870 FT-IR instrument. The instrument uses a KBr beamsplitter and an InGaAs detector. Typically, between 128 or 256 scans were collected with a resolution of 1 cm^{-1}. Solid samples were measured as KBr pellets. Solution samples, in methanol, were measured using a fixed path length cell equipped with KBr windows. The path length of the cell was varied using Teflon spacers of different thicknesses.

The FT-Raman spectra were measured using a Thermo Nicolet Nexus FT-Raman spectrometer. The instrument uses an air-cooled Nd:YVO4 laser source which emits continuous-wave laser energy at a wavelength of 1064 nm, a XT-KBr beamsplitter, a 180° sample configuration and an InGaAs detector. Between 1024 and 4096 scans at a resolution of 4 cm^{-1} were collected. To maximize the signal-to-noise ratio and due to the weak scattered light from the complex samples, a laser power of up to 1.0 W was used.

Computational Details

Conformational analysis of the five 12c4−alkali metal cation complexes, to predict the possible conformations of the complexes, was reported in a previous publication.[31] Cartesian coordinate force fields were calculated, at the corresponding optimized geometries, for six of the eight predicted conformations. The other two conformations have C_1 symmetry and were not considered. The six conformations considered have symmetries of, in energy order, C_4, C_s, C_s, C_{2v}, C_{2v}, and C_s, as detailed in ref 31. Notice that for the Li^+ complex in all levels considered in ref 31, except at the HF/3-21G level, the energy order of the first C_4 and second C_s conformations is reversed and the third C_s conformation collapses to the second C_s conformation. The force fields were calculated at the B3LYP level due to its known excellent accuracy to CPU time ratio.[50] As was detailed in ref 31, the 6-31+G* basis set was used for all atoms except for the K, Rb, and Cs atoms.[31,51−56] For these, the Hay and Wadt's 10-valence-electron effective core potential (ECP) with a (5s4p)/[3s2p] valence basis set was used.[57] The basis set has an additional six-term *d*-type polarization functions with exponents of $\alpha_d = 0.48$ for K, $\alpha_d = 0.24$ for Rb, and $\alpha_d = 0.19$ for Cs. For simplicity, this basis set will be termed the 6-31+G* basis set. The additional diffuse function in the 6-31+G* basis set was used to minimize the basis set superposition error and for its known necessity for accurate computation of the properties of the metal cation complexes. The basis set used for the K, Rb, and Cs atoms is the same as that used by Feller el al. for similar computations of 12c4− and 18c6−alkali metal cation complexes.[33,37,38,61]

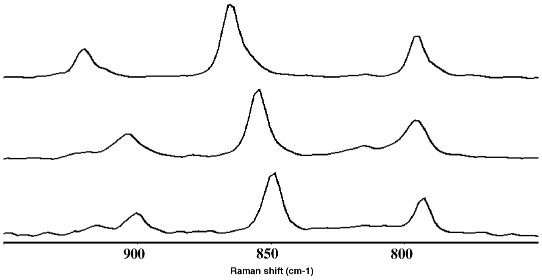

Figure 4. Raman spectra of the solid phase of the three 12c4−Li^+-(top), Na^+ (middle) and K^+ (bottom) complexes in the 950−750 cm−1 region. The Figure shows a shift of the position of some bands of the 12c4−Li^+ complex compared to the corresponding bands of the Na^+ and K^+ complexes.

All ab initio computations were performed using the Gaussian 98W[62] and Gaussian 03W[63] programs. The Gaussian program default parameters of geometry optimization and force field calculations were used. The force fields and dipole derivative tensors were calculated analytically. Since analytical polarizability derivatives are not available in the current version of the Gaussian program, these were calculated numerically.

The selection of the internal coordinates,[64−66] conversion of the Cartesian coordinate force fields to internal coordinate force fields,[65,67] scaling of the internal coordinate force fields[65,68,69] and refinement of the scale factors were done using the SCALE2 program[70] and were performed as was detailed elsewhere.[25] They are mentioned here for completeness. The SCALE2 program has the advantage of minimizing human interference and consequent error. In the first step of the program, from the frequency job archive of the Gaussian program output file, the program generates four files of the molecule Cartesian coordinates, Cartesian coordinate force field, dipole derivative tensors and polarizability derivatives. In the second step, the program generates the internal coordinates that are used to convert the Cartesian coordinate force field, dipole derivative tensors and polarizability derivatives to their internal coordinate counterparts. In the third step of the program, the internal coordinate force field is scaled according to the equation

$$F_{ij}^{\text{scaled}} = F_{ij}^{\text{theo}}(c_i\, c_j)^{1/2}$$

where c_i and c_j are the scale factors of the internal coordinates *i* and *j*, respectively. The reproducibility of the frequencies calculated by the Gaussian program is checked using a scale factor of 1.0. To aid in the initial assignment of the fundamental vibrations from the experimental spectra, the internal coordinate force fields are scaled with an initial scale factor of 0.963.[71−73] The experimental fundamental vibrations were then assigned to the calculated frequencies in frequency order taking into consideration the IR and Raman intensities. As the number of assigned bands increased, the number of scale factors was increased and the scale factors were varied, to minimize the

TABLE 4: FT-Raman and FT-IR Frequencies (cm^{-1}) and Assignment of 12c4−K^+ Complex[a]

Raman			IR		
MeOH[b]		H_2O[c]	MeOH[b]		
solid	MeOH	solid	MeOH	solid	assgnt
140	136	141			ν_{39}
191	189	188			ν_{60}
	202				
208	217	212			(ν_{38})
231	239	234			ν_{19}
269	264	265			ν_{59}
301	304	301			ν_{18}
343	349	344			ν_{17}
356	359	360			ν_{58}
375	376	376			
397	398				ν_{37}
429	425	413		419	
492	497	492			ν_{36}
				549	ν_{57}
599	597	600			ν_{16}
793	795	793		791	ν_{35}
808	804	810		808	ν_{56}
814	816				
849	848	849	848	846	ν_{15}
900	902	901			ν_{34}
915	910	914	916	913	ν_{55}
				1025	ν_{13}
1032		1030		1031	ν_{54}
1045		1045			ν_{33}
1059		1055			ν_{12}
1097	1097	1094		1094	ν_{53}
1116	1112	1115		1111	ν_{11}
1136	1138	1136		1134	ν_{52}
1162	1163	1162			ν_{31}
1238	1243	1237		1237	ν_{10}
			1250	1248	ν_{51}
1253	1256	1250			ν_{29}
				1254	ν_{30}
1267		1258		1259	
1278	1277	1278		1278	
1291	1292	1294	1291	1289	ν_{50}
1304	1304	1305	1306	1303	ν_{9}
1349	1353	1350		1348	ν_{8}
1368	1368	1371		1365	ν_{49}
1379	1377	1379		1378	ν_{28}
1392	1386	1391		1388	ν_{7}
1401	1400	1401		1399	ν_{48}
1410	1407	1410		1405	ν_{27}
				1449	ν_{47}
1450		1450			ν_{26}
				1467	ν_{46}
1471		1471		1472	ν_{6}
1485		1485		1483	ν_{5}
2871		2871		2865	
2886		2886		2882	
2906		2906		2908	
2929		2928		2926	
2938		2939		2934	
				2949	
				2956	

[a,b,c] See corresponding footnotes in Table 2.

difference between the calculated and experimental vibrational frequencies, as indicated by the rms deviation of the difference between the calculated and assigned experimental vibrational frequencies.

Results and Discussion

Structure of the 12c4—Alkali Metal Cation Complexes. Figure 1 shows the structure and atom numbering of the C_4 conformation of the 12c4−alkali metal cation complex. Table 1 shows the geometry of this conformation at the B3LYP and MP2 levels using the 6-31+G* basis set. The details of the MP2 computations are as given in ref 31. It can be noticed from the data in Table 1 that there is an increase of the displacement of the metal cation out of the ring plane, M−O bond length, where M refers to alkali metal cation, by the increase of the metal cation size. While the C−C bond length is unchanged for the five complexes, the C−O bond length of the Cs^+ complex is shorter by 0.01 Å than that of the Li^+ complex. Also, the two CCO bond angles increased by about 4 degrees. There is a large increase of the MO_4C_5 bond angle by about 14 degrees, although the other MO_4C_3 bond angle increased by less than 2 degrees. In addition, there is a large decrease of the $MO_1C_2C_3$ dihedral angle by about 20 degrees, as the large Cs^+ cation is displaced out of the ring plane compared to that of the smaller Li^+ cation. These previous differences are monotonic in going from the smallest Li^+ cation to the largest Cs^+ cation.

While the C−O bond lengths calculated at the MP2 and B3LYP levels are close to each other within 0.003 Å, the C−C bond lengths calculated at the B3LYP level are too short by not more than 0.01 Å, compared to those calculated at the MP2 level. The M−O bond length of the Li^+ complex is calculated to be equal at the MP2 and B3LYP levels, while for the Na^+ complex it is calculated to be too long by about 0.06 Å at the MP2 level compared to that at the B3LYP level. Using the effective core potential basis set for the K^+, Rb^+, and Cs^+ cations for the corresponding 12c4 complexes, the M−O lengths are calculated to be too short by about 0.06 Å at the B3LYP level compared to that at the MP2 level. There are two reports of the X-ray experimental geometry, to the best of our knowledge, of only the Na^+ complex.[45,46] The calculated geometries at the B3LYP and MP2 levels in Table 1 are in good agreement with these X-ray experimental geometries.

Experimental Vibrational Spectra of the 12c4—Alkali Metal Cation Complexes. The Raman spectra in the 100−1600 cm^{-1} region of the Li^+, Na^+, and K^+ complexes in the solid phase and the IR spectra in the 400−1600 cm^{-1} region of the five 12c4−alkali metal cation complexes of the solid phase are shown in Figures 2 and 3, respectively. No reasonable Raman spectra could be obtained for the Rb^+ and Cs^+ complexes, even using samples synthesized using either methanol or water as a solvent, as will be detailed shortly. Tables 2−4 list the Raman vibrational frequencies of the solid and methanol solution phases of the Li^+, Na^+, and K^+ complexes, in addition to the Raman frequencies of the water solution phase of the Li^+ and Na^+ complexes. The IR vibrational frequencies of the three Li^+, Na^+, and K^+ complexes of the solid phase are also added in Table 3. The assignment of the fundamental vibrations is included in Tables 2−4. The Raman vibrational frequencies of the methanol solution reported in ref 40 are added in Tables 2 and 3 for the Li^+ and Na^+ complexes, respectively.

It has been reported that the solvent used in the synthesis of the crown ether−metal complexes affects the stability of the formed complexes.[26] In the current study, the complexes were synthesized using methanol as a solvent. To study the effect of the solvent used in the synthesis of the complexes, the Li^+, Na^+, and K^+ complexes were also synthesized using water as a solvent. The Raman vibrational frequencies of the aqueous phase of the Li^+ complex, the solid and aqueous phase of the Na^+ complex and the solid phase of the K^+ complex are included in Table 2. In addition, the IR vibrational frequencies of the solid and methanol solution phases of the Na^+ complex are added to Table 3. In the IR spectra of the Na^+ complex of the solid phase, Table 3, the difference between the frequencies of the corresponding bands, when methanol and water were used as solvents in the synthesis of the complex, is about 1 or 2 cm^{-1}, but it can be as large as 6 cm^{-1} for very weak bands. For the Raman spectra of the solid phase, the difference is also 1 or 2 cm^{-1}, but for some bands, the difference is as large as 6 cm^{-1}, such as for ν_{29}. These small band position differences in the

TABLE 5: Vibrational Frequencies (cm^{-1}), in Energy Order, of the C_4, C_s, C_s, C_{2v}, C_{2v} and C_s Conformations of the 12c4−K$^+$ Complex. The Vibrational Frequencies Are Scaled with a Frequency Scale Factor of 0.963[71]

		C_4		C_s		C_s		C_{2v}		C_{2v}		C_s	
no.	exp	sym	freq	sym	freq	sym	freq	sym	freq	sym	freq	sym	freq
1		B	54	A''	56	A''	66	A_2	47	A_2	63	A''	−26
2		B	112	A'	103	A'	94	B_2	88	A_1	105	A'	57
3		E	122	A'	116	A'	109	A_1	114	B_2	106	A''	106
4				A''	129	A'	131	A_2	139	B_1	130	A'	111
5	140	B	135	A''	149	A''	140	A_1	142	B_2	131	A''	131
6		A	149	A'	156	A''	145	B_2	154	A_1	141	A'	136
7	189	E	184	A'	168	A'	149	B_1	162	A_2	153	A'	162
8				A'	187	A'	180	B_2	191	A_1	153	A'	175
9	(217)	B	195	A''	208	A'	213	A_1	194	A_1	201	A''	198
10	239	A	234	A'	249	A''	235	B_1	222	B_2	206	A'	204
11	269	E	259	A''	250	A''	249	A_1	242	B_1	219	A''	243
12				A'	266	A'	254	A_2	248	B_1	268	A'	266
13	304	A	282	A''	267	A'	304	B_2	289	A_2	292	A''	274
14	349	A	331	A'	320	A''	306	B_1	299	A_1	302	A'	331
15	356	E	346	A''	342	A'	321	A_1	337	B_2	316	A''	340
16				A'	361	A'	386	B_1	411	A_1	380	A'	354
17	398	B	391	A'	440	A''	394	A_1	422	B_1	396	A'	442
18	497	B	472	A''	482	A'	505	B_2	500	B_1	506	A''	484
19	549	E	528	A'	498	A''	507	A_2	507	B_2	509	A'	499
20				A'	567	A'	541	A_1	549	A_1	515	A''	543
21	597	A	570	A''	575	A''	544	B_1	570	A_2	534	A'	551
22	795	B	763	A'	757	A'	781	B_1	753	B_2	791	A'	759
23	808	E	782	A''	780	A''	785	A_1	757	A_1	796	A''	792
24				A'	786	A'	796	B_2	801	B_1	802	A'	796
25	848	A	825	A'	832	A'	822	A_1	833	A_1	811	A'	817
26	902	B	879	A''	873	A''	866	A_2	866	A_2	873	A''	866
27		A	882	A''	879	A''	888	A_2	879	B_1	891	A''	888
28	915	E	893	A''	891	A'	897	B_1	887	A_2	899	A'	899
29				A'	893	A''	901	B_2	889	B_2	906	A''	901
30	1024	A	998	A'	994	A''	984	B_1	985	B_1	986	A''	993
31	1030	E	1002	A''	1002	A'	1001	A_1	1002	A_1	1002	A'	999
32				A'	1014	A'	1030	B_2	1025	B_2	1021	A'	1014
33	1045	B	1019	A'	1019	A'	1031	A_1	1032	A_1	1030	A'	1023
34	1059	A	1029	A''	1037	A''	1036	A_2	1033	A_2	1050	A''	1037
35	1095	E	1072	A''	1081	A'	1067	B_2	1078	B_2	1069	A'	1071
36				A'	1086	A''	1085	A_2	1089	A_2	1086	A''	1085
37	1116	A	1092	A''	1095	A''	1093	B_1	1095	B_1	1109	A''	1089
38		B	1100	A''	1112	A''	1112	B_1	1112	B_2	1117	A'	1108
39	1135	E	1114	A'	1114	A'	1121	A_2	1115	B_1	1127	A''	1110
40				A''	1118	A''	1123	B_2	1125	A_2	1128	A''	1134
41	1162	B	1136	A'	1142	A'	1143	A_1	1148	A_1	1133	A'	1143
42	1237	A	1218	A''	1223	A''	1211	A_2	1227	A_2	1201	A''	1215
43	1250	E	1229	A'	1228	A'	1224	B_1	1227	B_2	1212	A'	1226
44				A''	1234	A''	1232	B_2	1243	B_1	1218	A''	1235
45	1250	B	1240	A'	1242	A'	1250	A_1	1244	A_1	1227	A'	1237
46	1254	B	1249	A''	1246	A''	1251	A_2	1247	A_2	1245	A''	1251
47	1291	E	1272	A'	1267	A'	1264	B_2	1265	B_1	1254	A'	1266
48				A''	1273	A''	1266	B_1	1295	B_2	1257	A''	1269
49	1306	A	1286	A'	1301	A'	1277	A_1	1303	A_1	1268	A'	1353
50	1348	A	1338	A''	1337	A''	1330	A_2	1334	A_2	1324	A''	1334
51	1365	E	1354	A''	1355	A''	1347	B_1	1351	B_1	1338	A''	1348
52				A'	1359	A'	1356	B_2	1360	B_2	1351	A'	1355
53	1377	B	1369	A''	1369	A''	1370	A_2	1372	A_2	1355	A''	1369
54	1386	A	1380	A'	1375	A'	1374	B_1	1378	A_1	1377	A'	1378
55	1400	E	1386	A'	1387	A''	1379	A_1	1379	B_2	1386	A'	1390
56				A''	1388	A'	1400	B_2	1403	B_1	1395	A''	1398
57	1407	B	1389	A''	1402	A'	1411	A_1	1406	A_1	1405	A'	1402
58	1450	B	1453	A''	1443	A''	1452	A_2	1447	B_2	1453	A''	1440
59	1449	E	1454	A'	1455	A''	1458	B_2	1447	A_2	1453	A'	1453
60				A''	1459	A'	1458	A_2	1456	B_1	1471	A''	1456
61	1471	A	1455	A'	1459	A'	1463	B_1	1456	A_2	1473	A''	1464
62		B	1459	A''	1467	A''	1469	A_1	1456	A_1	1477	A'	1464
63	1467	E	1468	A''	1471	A''	1473	B_2	1474	B_1	1479	A''	1473
64				A'	1482	A'	1479	B_1	1474	B_2	1488	A'	1476
65	1485	A	1482	A'	1491	A'	1487	A_1	1492	A_1	1491	A'	1490
66		B	2913	A''	2909	A''	2873	A_2	2905	A_2	2849	A''	2844
67		E	2919	A'	2914	A'	2878	B_1	2910	B_1	2849	A'	2853
68				A''	2915	A''	2912	B_2	2911	B_2	2855	A''	2916
69		A	2922	A'	2919	A'	2918	A_1	2915	A_1	2856	A'	2918
70		B	2938	A''	2931	A'	2933	A_2	2934	B_2	2931	A'	2930
71		E	2941	A'	2932	A''	2935	B_2	2934	A_1	2932	A''	2931
72				A''	2940	A'	2939	B_1	2936	A_2	2932	A''	2939
73		A	2944	A'	2943	A''	2939	A_1	2937	B_1	2934	A'	2941
74		B	2953	A'	2948	A''	2949	B_2	2941	B_2	2942	A''	2954
75		E	2957	A''	2949	A'	2949	A_2	2944	A_2	2943	A'	2955
76				A''	2958	A'	2954	B_1	2954	B_1	2946	A''	2970
77		A	2964	A'	2967	A''	2956	A_1	2955	A_1	2947	A'	2978
78		B	3004	A''	2996	A'	2993	A_2	2997	B_2	2992	A''	2998
79		E	3005	A'	2996	A''	2993	B_2	2997	A_2	2992	A'	3000
80				A''	3000	A''	2998	B_1	3000	B_1	2993	A''	3001
81		A	3006	A'	3002	A'	2998	A_1	3000	A_1	2994	A'	3002

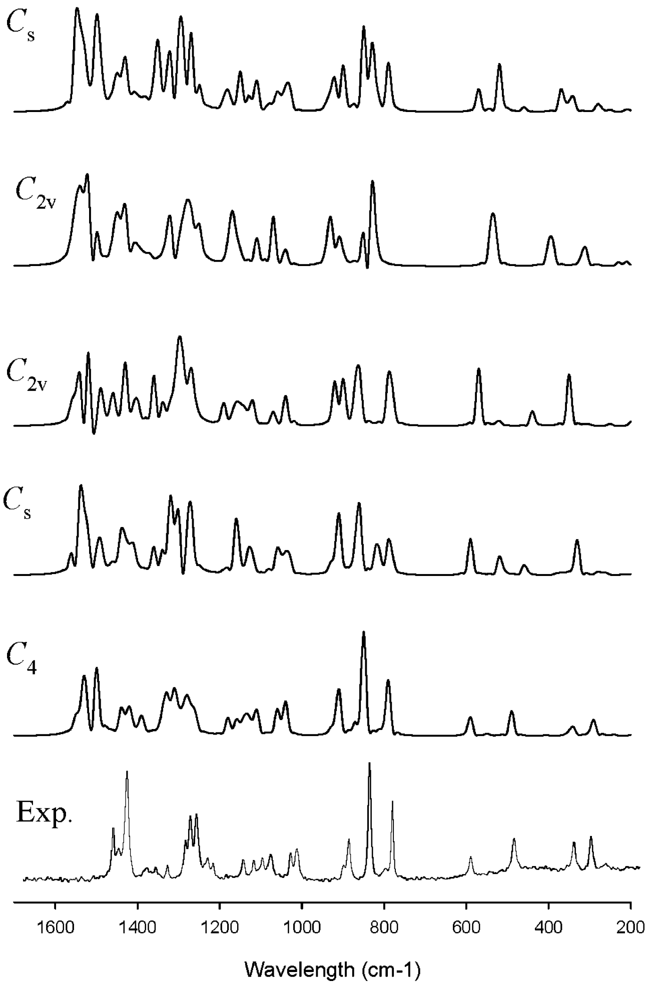

Figure 5. Experimental and calculated Raman spectra of the 12c4−K$^+$ complex using unscaled frequencies. The Raman intensity of the third lowest energy C_s conformation was not calculated. See text.

solid phase spectra are most probably due the crystal structure and orientation. In addition, these small band position differences are not associated with intensity differences and exist only in the Raman spectra and not in the IR spectra. Consequently, it is reasonable to assume that these small position differences in the Raman spectra are only due spectral reasons rather than being due to conformational change. The case is similar for the Li$^+$ and K$^+$ complexes. It can be concluded, for the 12c4−alkali metal cation complexes, that the solvent used in the synthesis of the complexes has no effect on the conformational stability of the formed complexes. It is probable that this effect might be significant for the larger 18c6−alkali metal cation complexes with a larger and more flexible ring and consequently less energy gap between the possible conformations.[26,30,73]

All bands reported in ref 40 of the Raman spectrum of the Na$^+$ complex in the methanol solution phase, Table 3, are observed in the current study, also in the Raman spectrum for the same methanol solution phase, and at a position difference of not more than 2 cm^{-1}. This is also observed for the Li$^+$ complex, Table 2, except for bands at 252, 262, and 579 cm^{-1} that are not observed in the current study. Instead, the 252 and 262 cm^{-1} bands are observed only in the Raman spectrum of the solid phase, while the 579 cm^{-1} band is not observed in any of the measured spectra in the current study. Unlike the case of the Na$^+$ complex, the position difference between the bands observed in the current study and that in ref 40 of the Li$^+$ complex is about 4 cm^{-1} and as large as 6 cm^{-1}, for the Raman spectrum measured in same methanol solvent.

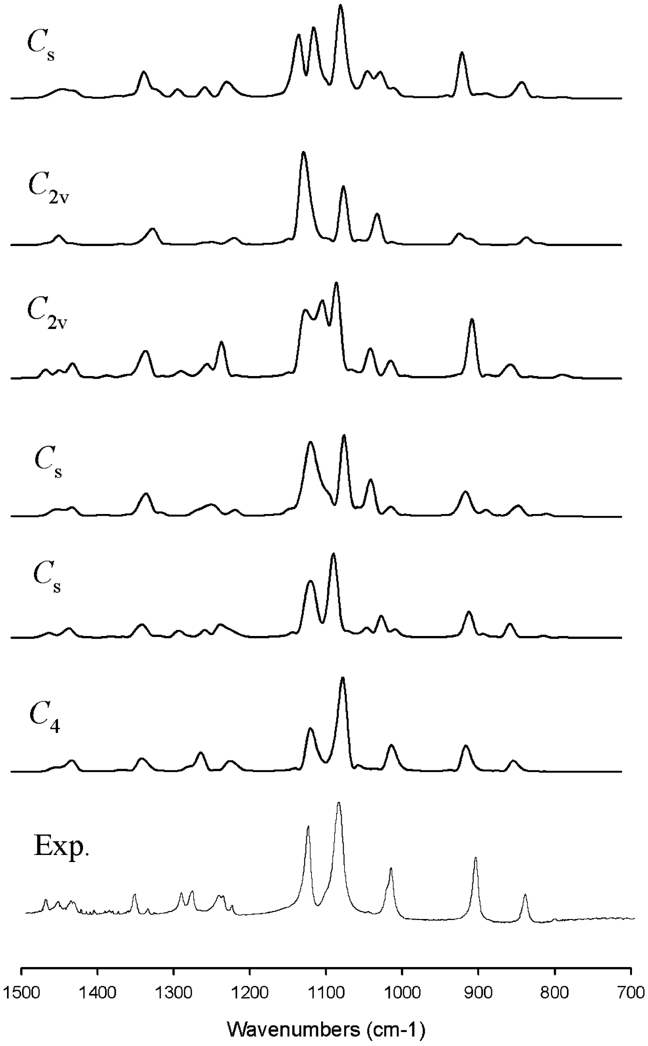

Figure 6. Experimental and calculated IR spectra of the 12c4−K$^+$ complex using unscaled frequencies.

It is clear from Figures 2 and 3 that the vibrational spectra of the five 12c4−alkali metal cation complexes are so similar that it is reasonable to conclude that the five complexes exist in the same conformation. As will be seen shortly, it is concluded that the five complexes exist in the C_4 conformation. There is a shift of the position of some bands of the Li$^+$ complex, compared to those of the other four complexes. Figure 4 compares between the Raman spectra of the solid phase of the 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes in the region of 950−750 cm^{-1}. For example, υ_{55} of the 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes is at 931, 918, and 915 cm^{-1}, respectively, while υ_{56} of the same complexes is at 802, 802, and 808 cm^{-1}, respectively. The shift of the position of some bands of the Li$^+$ complex is not necessarily toward higher energy. For example, υ_{53} of the 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes is at 1082, 1098, and 1095 cm^{-1}, respectively.

The similarity between the vibrational spectra of the five 12c4−alkali metal cation complexes, as presented by the data in Figures 2 and 3 and Tables 2−4, suggests that the five alkali metal cation complexes exist in the same conformation. Comparison was made between the experimental and calculated vibrational frequencies for six of the eight predicted conformations reported in ref 31 of the 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes that are of symmetries higher than the C_1 symmetry. These six conformations, in energy order, are of C_4, C_s, C_s, C_{2v}, C_{2v}, and C_s symmetries. Because of the doubly degenerate E representation of the C_4 point group, the comparison concludes that the three complexes exist in the C_4 conformation. Table 5 shows such comparison for the 12c4−K$^+$ complex. The vibrational frequencies are scaled with a one frequency scale factor of 0.963.[71] Although no Raman spectra could be obtained for the Rb$^+$ and Cs$^+$ complexes, the similarity between the IR spectra of the five complexes clearly shows that the five complexes exist in the same conformation. The existence of the five complexes in the C_4 conformation is a reflection of the fact that the five alkali metal cations are larger than the ring cavity of 12c4. Scaling of the force field was then conducted using the B3LYP/6-31+G* force field of the C_4 conformation. The conclusion that the Na$^+$ complex has a C_4 structure is in agreement with X-ray result that this complex exists in the C_4 conformation.[45,46] This is the only complex of the 12c4−alkali metal cation complexes for which, to the best of our knowledge, an X-ray result has been reported. Figures 5 and 6 compare between the experimental and calculated Raman and IR, respectively, spectra of the 12c4−K$^+$ complex. Because of an unsolved problem in the computations, no Raman intensities were calculated for the third lowest C_s conformation. Both figures, Figures 5 and 6, show a better agreement between the experimental and calculated Raman and IR spectra assuming a C_4 conformation of the complex.

Table 6 compares between the calculated, unscaled, vibrational frequencies of the five 12c4−alkali metal cation complexes of the C_4 conformation. The data in Table 6 reflect the similarity between the calculated vibration spectra of the five complexes as observed experimentally, Figures 2 and 3 and Tables 2−4. This is only with the exception of the region below 400 cm^{-1}. This region is characterized by the vibrational modes involving the alkali metal cation, where the difference between the calculated geometries of the five alkali metal cations, described before, is reflected by the difference between the calculated spectra in this region. For example, for the 12c4−K$^+$ complex, the calculated TED shows a large contribution of the K$^+$−O stretching mode for the υ_{18}, υ_{20}, υ_{38}, υ_{39}, υ_{59}, and υ_{61} vibrational modes. Notice also that these bands, compared to the other intense bands, are of modest intensity to have a significant influence on the measured experimental vibrational spectra.

Scaling of the Force Fields of the C_4 Conformation. 12c4−alkali metal cation complexes are large ring molecules with 81 normal modes of vibration. While free 12c4 has no redundant internal coordinates,[25] due to symmetry and the additional alkali metal cation, 12c4−alkali metal cation complexes have 90 redundant internal coordinates that were generated by the SCALE2 program. This set of 90 internal coordinates was reduced to 81 nonredundant internal coordinates. The nine vibrations corresponding to the redundant coordinates were calculated to be zero. A set of eight scale factors were used in the scaling of the force fields. The values of the scale factors were estimated after comparison between those determined for free 12c4[25] and those determined by Rauhut and Pulay as average scale factors of a set of 20 molecules.[71] Using this initial set of scale factors, without varying the scale factors, the rms deviations of the difference between the calculated and experimental vibrational frequencies for the Li$^+$, Na$^+$, and K$^+$ complexes were 11.0, 6.4, and 5.9 cm^{-1}, respectively.

The definition of the internal coordinates, used in the conversion of the internal coordinate force fields to the Cartesian coordinate force fields, the initial and final values of the eight scale factors of the force fields of the three 12c4−Li$^+$, −Na$^+$, and −K$^+$ cation complexes, and the corresponding rms devia-

TABLE 6: Comparison between the Calculated, Unscaled, Vibrational Frequencies (cm^{-1}) and IR and Raman Intensities for the Five 12c4−Alkali Metal Cation Complexes of the C_4 Conformation[a]

		Li^+			Na^+			K^+			Rb^+			Cs^+	
no.	sym.	freq	IR	Ra	freq	IR	Ra	freq	IR	Ra	freq	IR	Ra	freq	IR
1	*A*	3141	24	38	3129	37	46	3120	58	48	3116	69	49	3112	79
2		3087	0	308	3079	5	91	3077	13	50	3075	16	59	3072	18
3		3079	6	313	3067	15	539	3056	24	637	3051	29	651	3045	35
4		3037	82	226	3039	68	199	3034	54	148	3030	50	129	3024	48
5		1542	12	9	1539	11	11	1539	9	13	1540	8	13	1540	7
6		1512	1	9	1511	2	11	1510	3	12	1510	3	13	1509	3
7		1432	0	1	1434	0	1	1432	1	1	1434	2	1	1434	2
8		1385	2	2	1388	2	2	1389	2	2	1390	2	2	1391	2
9		1327	18	4	1333	20	4	1335	21	5	1337	20	5	1339	21
10		1256	6	5	1263	4	4	1264	4	4	1266	5	4	1267	5
11		1136	5	3	1133	0	1	1141	0	2	1144	0	2	1148	0
12		1057	5	0	1060	0	4	1057	0	4	1057	0	4	1058	0
13		1026	63	1	1032	72	1	1036	76	1	1038	77	1	1039	79
14		920	0	0	915	0	7	912	0	8	910	0	8	910	0
15		871	33	20	861	38	17	857	43	15	854	44	14	854	46
16		603	2	3	596	1	3	592	1	3	593	1	3	593	0
17		384	44	5	354	9	4	344	8	2	340	7	1	337	0
18		322	31	1	310	1	2	292	0	3	289	0	3	287	7
19		311	0	0	244	6	1	243	2	0	247	1	0	247	1
20		205	0	1	195	22	0	155	21	0	110	10	0	88	7
21	*B*	3140	0	40	3128	0	39	3119	0	39	3115	0	39	3110	0
22		3086	0	66	3074	0	56	3066	0	42	3062	0	35	3057	0
23		3076	0	115	3062	0	97	3050	0	86	3046	0	81	3039	0
24		3024	0	28	3026	0	50	3024	0	82	3023	0	96	3018	0
25		1525	0	2	1517	0	2	1515	0	1	1513	0	2	1513	0
26		1511	0	27	1509	0	27	1509	0	27	1508	0	26	1507	0
27		1436	0	1	1440	0	0	1442	0	0	1444	0	0	1445	0
28		1418	0	2	1420	0	3	1422	0	4	1422	0	4	1423	0
29		1287	0	10	1293	0	26	1297	0	33	1300	0	34	1301	0
30		1275	0	19	1286	0	6	1287	0	2	1289	0	1	1289	0
31		1173	0	2	1177	0	2	1180	0	2	1181	0	2	1181	0
32		1128	0	1	1132	0	3	1133	0	3	1135	0	3	1137	0
33		1064	0	3	1062	0	0	1068	0	0	1071	0	0	1073	0
34		928	0	7	915	0	0	916	0	0	915	0	1	916	0
35		782	0	8	786	0	9	792	0	9	793	0	9	795	0
36		496	0	4	493	0	4	490	0	4	488	0	3	487	0
37		403	0	0	409	0	0	406	0	0	406	0	0	406	0
38		234	0	0	216	0	0	202	0	0	198	0	0	194	0
39		171	0	0	159	0	0	140	0	0	136	0	0	136	0
40		108	0	0	124	0	0	117	0	0	112	0	0	103	0
41		63	0	0	69	0	1	56	0	1	47	0	1	45	0
42	*E*	3140	5	93	3129	8	91	3119	14	88	3115	17	86	3111	19
43		3086	63	20	3075	65	44	3069	57	61	3067	51	63	3062	46
44		3077	13	23	3064	31	30	3053	61	33	3048	79	37	3042	94
45		3030	2	4	3033	3	2	3030	5	4	3027	6	7	3021	7
46		1532	12	6	1525	12	4	1524	11	4	1523	11	4	1524	11
47		1511	14	1	1510	14	1	1509	14	1	1509	13	1	1508	12
48		1436	1	1	1438	2	1	1438	2	1	1440	3	2	1441	3
49		1402	27	0	1405	29	0	1406	31	1	1407	32	1	1408	33
50		1314	30	7	1320	28	6	1321	27	7	1323	25	7	1324	25
51		1263	24	1	1273	24	1	1276	24	2	1279	24	2	1280	24
52		1154	55	1	1154	69	1	1156	88	1	1157	98	2	1159	108
53		1102	245	4	1108	215	3	1113	187	2	1116	175	2	1118	162
54		1037	21	3	1039	16	2	1041	14	2	1042	13	2	1043	12
55		943	43	0	930	50	0	927	49	0	925	50	0	925	48
56		810	1	0	810	0	0	812	0	0	812	0	0	814	0
57		559	18	0	551	13	0	548	12	0	549	12	0	549	12
58		439	78	0	409	0	0	406	0	0	406	0	0	406	0
59		351	6	0	290	14	0	269	5	0	264	4	0	260	3
60		286	3	0	214	20	0	191	18	0	193	16	0	192	16
61		176	9	0	183	1	0	127	9	0	94	5	0	75	4

[a] IR and Ra are the IR and Raman intensities, respectively. No Raman intensity was calculated for the Cs^+ complex.

tions are given in Table 7. Since none of the vibrations corresponding to the C−H stretching mode and most of the vibrations involving the Na butterfly mode were not assigned, the scale factors corresponding to the C−H stretching and Na butterfly modes were held fixed. The total number of the experimental frequencies used in the determination of the final scale factors are 50, 60, and 56 vibrational frequencies for the 12c4−Li^+, −Na^+, and −K^+ complexes, respectively.

The experimental vibrational frequencies used in the scaling of the force fields and the corresponding calculated vibrational frequencies and Raman and IR intensities of the C_4 conformation of three 12c4−Li^+, −Na^+, and −K^+ cation complexes are given

TABLE 7: Natural Internal Coordinate Scale Factors[a]

			final		
coordinate	description	initial	Li$^+$	Na$^+$	K$^+$
R_1-R_4	C−C stretching	0.970	0.9858	0.9977	0.9785
R_5-R_{12}	C−O stretching	1.022	1.0013	1.0106	1.0092
R_{13}	M−O stretching	0.940	0.8927	0.8477	1.0900
$r_{13}-r_{28}$	C−H stretching[b]	0.920	0.9200	0.9200	0.9200
$\alpha_1-\alpha_{32}$	CH$_2$ bending	0.940	0.9454	0.9417	0.9391
$\zeta_1-\zeta_9$	ring bending[c]	1.040	1.0426	1.0130	1.0494
$\tau_1-\tau_9$	ring Torsion	1.030	0.8968	1.0634	0.9784
τ_{10}	MO buterfly[b]	0.940	0.9400	0.9400	0.9400
rms			7.7	5.6	5.1

[a] Nonredundant internal coordinates. M refers to alkali metal cation. [b] Fixed. See text. [c] Including those which contain the M metal cation.

in Tables 8−10. Bands for which their assignments as fundamental was not certain, and were consequently not used in the scaling of the force fields, are included between parentheses in Tables 8−10. In the scaling of the force fields, the experimental vibrational frequencies of the methanol solution, whenever available, were used, in most of the cases. Since the vibrational spectra of the three 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes are quite similar, Figures 2 and 3, the assignment of the experimental to the calculated vibrational frequencies was revised so that the same strong features in the spectra of the three complexes would correspond to the same mode in the calculated spectra.

A few remarks should be mentioned about the assignment of the experimental to the calculated vibrational frequencies for the three 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes. Except for υ_{17} and υ_{19} of the Li$^+$ complex and υ_{17} and υ_{18} of the Na$^+$ and K$^+$ complexes, which are observed as strong bands in the Raman spectra at about 350 and 305 cm^{-1}, respectively, most of the other vibrational bands in the 150−400 cm^{-1} region are very weak and difficult to assign. In addition, only Raman spectral data are available in this region. Bands in the 100−150 cm^{-1} region are also broad and due to the overlap of bands in this region are not possible to assign. In the vibrational spectra of the 12c4−Na$^+$ complex, three bands are observed in the 790−820 cm^{-1} region, although, using the scaled force field, two bands are predicted to be in this region. The band observed at 794 cm^{-1} was selected as a fundamental since it is observed and predicted as intense band in the Raman spectra. Two other bands are observed at 802 and 814 cm^{-1}. The 802 cm^{-1} band was selected, rather than the 814 cm^{-1} band, as a fundamental in agreement with the scaled B3LYP vibrational frequency, at 800 cm^{-1}. The 1340−1500 cm^{-1} region is the most difficult region to assign. It can be divided into two regions, the first is at 1340−1410 cm^{-1} and the second is at 1440−1500 cm^{-1}. Either region has six bands, two of which are of *E* symmetry. It was easier to assign the second 1440−1500 cm^{-1} region, but the difference between the calculated, using the scaled B3LYP force field, and experimental frequencies in this region was as high as 21 cm^{-1}. On the other hand, it was not simple to assign the first 1340−1410 cm^{-1} region, especially since some bands were weak. Consequently, two calculated bands were preferred to be left unassigned in this region.

For the three 12c4−Li$^+$, −Na$^+$, and −K$^+$ complexes, the values of the scale factors corresponding to the C−C stretching, C−O stretching, and CH$_2$ bending modes, Table 7, are close to each other, within 0.02 at the highest, and those of the ring bending mode are close to each other, within 0.04. For the M−O stretching mode, the values of the scale factors for the three complexes are different, within 0.24, although this can be rationalized in large part due to the three different M alkali metal cations, Li$^+$, Na$^+$, and K$^+$. The values of the scale factors corresponding to the ring torsion mode are also different, within 0.17. Notice that in the vibrational analysis of free 12c4, for most of the conformations considered in that study, a value of about 1.05 was obtained for the scale factor corresponding to the same ring torsion internal coordinate.[25] This value of 1.05 is the closest to that of the Na$^+$ complex, in the current study,

TABLE 8: Experimental and Calculated Vibrational Frequencies (cm^{-1}) and Raman and IR Intensities ($((4\pi\epsilon_0)^2$ Å^4 amu^{-1}) of the C_4 Conformation of the 12c4−Li$^+$ Complex[a]

			calcd			
		exptl		IR	Raman	
no.	sym	freq	freq	int	int	depo
1	*A*		3016	23.9	37.9	0.07
2			2964	0.4	307.0	0.15
3			2957	6.2	314.2	0.01
4			2916	82.5	225.6	0.00
5		1499	1499	11.8	8.7	0.75
6			1470	1.3	8.7	0.64
7			1400	0.0	1.3	0.04
8		1350	1345	2.1	2.2	0.32
9		1289	1292	18.7	3.9	0.27
10		1241	1222	6.7	5.2	0.36
11		1113	1112	7.8	3.1	0.00
12		1048	1048	1.3	0.2	0.75
13		1020	1020	64.5	1.3	0.00
14		907	908	1.2	0.4	0.18
15		862	865	27.7	20.1	0.07
16		603	605	1.3	2.2	0.10
17		351	362	45.5	5.0	0.00
18		324	320	32.0	1.4	0.08
19		305	298	0.2	0.2	0.26
20		(199)	199	0.1	0.7	0.08
21	*B*		3015	0.0	40.5	0.75
22			2963	0.0	66.1	0.75
23			2954	0.0	114.6	0.75
24			2903	0.0	28.2	0.75
25		1479	1482	0.0	2.3	0.75
26		1454	1468	0.0	26.9	0.75
27			1400	0.0	1.3	0.75
28			1378	0.0	1.9	0.75
29			1255	0.0	10.1	0.75
30		1261	1241	0.0	18.5	0.75
31		1159	1146	0.0	3.6	0.75
32		1120	1123	0.0	1.0	0.75
33		1059	1057	0.0	2.7	0.75
34		917	918	0.0	7.7	0.75
35		786	771	0.0	7.6	0.75
36		500	501	0.0	4.3	0.75
37		(400)	393	0.0	0.1	0.75
38		(229)	232	0.0	0.3	0.75
39		(158)	164	0.0	0.3	0.75
40			104	0.0	0.2	0.75
41			60	0.0	0.5	0.75
42	*E*		3015	5.2	93.2	0.75
43			2963	63.1	19.6	0.75
44			2955	13.3	22.8	0.75
45			2909	2.1	4.4	0.75
46		1487	1489	11.8	5.8	0.75
47		1446	1469	13.7	1.3	0.75
48			1398	1.1	1.0	0.75
49		1360	1362	26.6	0.2	0.75
50		1277	1281	34.2	6.6	0.75
51		1252	1229	29.5	1.3	0.75
52		1137	1131	119.1	2.0	0.75
53		1083	1092	175.3	2.7	0.75
54		1027	1030	21.1	2.7	0.75
55		931	934	41.1	0.3	0.75
56		802	799	0.2	0.0	0.75
57		562	563	20.3	0.1	0.75
58		415	413	73.4	0.2	0.75
59		341	345	4.3	0.0	0.75
60		282	281	4.8	0.1	0.75
61		(167)	170	9.5	0.1	0.75

[a] Here, sym, exptl, calcd, freq, int, and depo stand for symmetry, experimental, calculated, frequency, intensity and depolarization ratio, respectively. For the bands in parentheses, their assignment as fundamentals was not certain, and they were not used in the scaling of the force field.

TABLE 9: Experimental and Calculated Vibrational Frequencies (cm^{-1}) and Raman and IR Intensities ($((4\pi\epsilon_{\text{å}})^2$ $Å^4$ amu^{-1}) of the C_4 Conformation of the 12c4−Na^+ Complex[a]

			calcd			
					Raman	
no.	sym	exptl freq	freq	IR int	int	depo
1	*A*		3005	37.3	46.1	0.03
2			2956	4.8	91.0	0.47
3			2945	14.9	540.4	0.00
4			2918	67.6	197.5	0.01
5		1486	1494	11.0	11.2	0.75
6		1453	1467	2.0	10.5	0.66
7		(1396)	1396	0.2	1.1	0.05
8		1354	1348	3.1	2.2	0.39
9		1305	1297	21.2	3.9	0.35
10		1237	1227	5.3	4.3	0.35
11		1115	1118	8.7	3.0	0.00
12		1064	1057	0.7	0.2	0.32
13		1028	1028	70.7	1.63	0.01
14		895	899	0.2	0.3	0.71
15		852	861	34.2	16.1	0.07
16		601	594	1.2	3.1	0.08
17		347	352	9.9	2.9	0.00
18		302	300	0.3	3.1	0.04
19		248	248	7.6	0.5	0.01
20		196	191	20.4	0.1	0.64
21	*B*		3004	0.0	38.7	0.75
22			2952	0.0	55.7	0.75
23			2940	0.0	97.1	0.75
24			2905	0.0	50.0	0.75
25		1470	1473	0.0	1.7	0.75
26		1444	1465	0.0	26.7	0.75
27		(1400)	1399	0.0	0.3	0.75
28		1380	1378	0.0	2.7	0.75
29		1268	1258	0.0	27.5	0.75
30		1256	1251	0.0	3.5	0.75
31		1160	1158	0.0	3.5	0.75
32		1124	1133	0.0	1.1	0.75
33		1049	1051	0.0	3.4	0.75
34		906	907	0.0	7.8	0.75
35		794	777	0.0	8.5	0.75
36		494	494	0.0	3.6	0.75
37		(414)	410	0.0	0.1	0.75
38		204	210	0.0	0.2	0.75
39		148	155	0.0	0.5	0.75
40		(131)	121	0.0	0.1	0.75
41			71	0.0	0.8	0.75
42	*E*		3004	8.4	91.5	0.75
43			2953	64.8	43.4	0.75
44			2942	31.4	29.8	0.75
45			2912	3.1	2.0	0.75
46		1476	1480	11.7	4.2	0.75
47		1447	1466	13.4	1.0	0.75
48		1410	1399	2.2	1.2	0.75
49		1365	1363	27.5	0.4	0.75
50		1290	1284	35.1	5.9	0.75
51		1248	1239	31.6	1.4	0.75
52		1138	1140	145.9	2.4	0.75
53		1098	1100	132.8	1.8	0.75
54		1033	1033	14.3	2.3	0.75
55		918	920	45.0	0.3	0.75
56		802	800	0.1	0.2	0.75
57		553	552	12.9	0.1	0.75
58		368	364	6.6	0.1	0.75
59		285	282	10.8	0.0	0.75
60		215	215	25.9	0.2	0.75
61		181	182	0.1	0.0	0.75

[a] See corresponding footnote in Table 6.

TABLE 10: Experimental and Calculated Vibrational Frequencies (cm^{-1}) and Raman and IR Intensities ($((4\pi\epsilon_{\text{å}})^2$ $Å^4$ amu^{-1}) of the C_4 Conformation of the 12c4−K^+ Complex[a]

			calcd			
					Raman	
no.	sym	exptl freq	freq	IR int	int	depo
1	*A*		2996	58.1	47.7	0.02
2			2954	13.1	50.3	0.61
3			2934	23.8	637.0	0.01
4			2913	53.9	148.2	0.03
5		1485	1491	8.4	13.3	0.75
6		1471	1464	2.9	11.8	0.67
7		1386	1392	1.1	1.4	0.04
8		1348	1347	3.8	2.8	0.38
9		1306	1297	22.5	4.4	0.36
10		1237	1226	5.1	4.3	0.31
11		1116	1118	7.9	2.7	0.00
12		1059	1056	1.8	0.4	0.05
13		1024	1029	76.0	1.7	0.02
14			902	0.0	0.4	0.72
15		848	852	36.9	14.3	0.07
16		597	592	0.7	2.9	0.09
17		349	344	7.9	2.6	0.00
18		304	297	0.4	2.2	0.07
19		239	240	2.0	0.5	0.02
20			159	20.9	0.1	0.51
21	*B*		2995	0.0	39.3	0.75
22			2944	0.0	42.3	0.75
23			2929	0.0	86.2	0.75
24			2903	0.0	81.7	0.75
25			1468	0.0	1.8	0.75
26		1450	1463	0.0	26.3	0.75
27		1407	1398	0.0	0.3	0.75
28		1377	1378	0.0	3.6	0.75
29		1254	1259	0.0	34.2	0.75
30		1250	1251	0.0	0.7	0.75
31		1162	1158	0.0	3.4	0.75
32			1138	0.0	1.7	0.75
33		1045	1048	0.0	3.6	0.75
34		902	898	0.0	8.1	0.75
35		795	782	0.0	8.8	0.75
36		497	497	0.0	3.5	0.75
37		398	403	0.0	0.2	0.75
38		(217)	208	0.0	0.1	0.75
39		140	141	0.0	0.4	0.75
40			115	0.0	0.1	0.75
41			56	0.0	1.0	0.75
42	*E*		2995	13.6	88.1	0.75
43			2947	57.0	60.6	0.75
44			2931	61.7	32.8	0.75
45			2909	4.6	3.8	0.75
46		1467	1477	11.0	3.8	0.75
47		1449	1463	12.8	0.9	0.75
48		1400	1397	2.4	1.3	0.75
49		1365	1362	29.2	0.6	0.75
50		1291	1284	35.6	6.3	0.75
51		1250	1239	33.1	2.0	0.75
52		1134	1141	177.2	2.9	0.75
53		1094	1100	88.2	1.1	0.75
54		1030	1033	14.9	2.3	0.75
55		913	914	43.7	0.3	0.75
56		808	803	0.2	0.2	0.75
57		549	551	11.1	0.2	0.75
58		359	360	6.5	0.1	0.75
59		269	272	6.0	0.1	0.75
60		189	188	17.0	0.0	0.75
61			130	8.8	0.2	0.75

[a] See corresponding footnote in Table 6.

which has the largest number of bands corresponding to the ring torsion mode assigned. This value of 1.05 is most different from that of the Li^+ complex. In a different calculation the scale factors of the Li^+ complex were varied after all of the low energy vibrational bands whose assignment as fundamentals were not certain, and thus are included between parentheses in Table 9, were included in the refinement of the scale factors. The rms deviation became better, 6.8 cm^{-1}, but the values of the scale factors were close to those in Table 7, within 0.004. It is reasonable then to assume that the values of the scale factor corresponding to the ring torsion mode of the Li^+ complex are not in error. In addition, this difference in the values of the scale factor, between that of the Li^+ and Na^+ complexes, is most probably too large to be attributable to a wrong assignment.

The rms deviation, of the difference between the experimental and calculated vibrational frequencies, of the Li^+ complex is higher than that of the other two Na^+ and K^+ complexes, Table 7. This larger rms deviation of the Li^+ complex is attributed mainly to seven bands, out of the 50 bands assigned for this complex. In a different calculation, these seven bands were excluded from the assignment. The rms deviation became 4.1 cm^{-1} and the values of the scale factors were almost unchanged, within 0.009, including that of the ring torsion mode. Since the assignment of these seven bands was reliable, they were included in the final calculations, as presented in Table 8.

Relative Energies of the C_4 and C_s Conformations of the Li^+ Complex. The vibrational study preformed in this report predicts a C_4 structure of the 12c4−Li^+ complex, as well as for the other four alkali metal cation complexes. As was mentioned above, in the previous conformational analysis report of the 12c4−alkali metal cation complexes,[31] the C_4 conformation was predicted to be the most stable conformation for the four 12c4−Na^+, −K^+, −Rb^+, and −Cs^+ complexes. For the 12c4−Li^+ complex, a C_s conformation was calculated to be more stable than the C_4 conformation by 0.16 kcal/mol at the MP2/6-31+G* level. The calculated binding energy predict a C_4 or C_s conformation of the 12c4−Li^+ complex but could not differentiate whether the complex exists in the C_4 or C_s conformation. This is because the calculated binding energies of the C_4 and C_s conformations are too close to each other, −93.0 and −89.9 kcal/mol, at the MP2/6-31+G* level, respectively. This is accompanied by a large uncertainty of the experimental binding energy, -90 ± 12 kcal/mol. To further clarify whether the C_4 or C_s conformation is the more stable conformation of the 12c4−Li^+ complex, optimized geometry of the complex was calculated for the C_4 and C_s conformations at the MP2/6-311++G** level. The MP2 computations were performed with the fixed core option. The C_4 conformation was calculated to be more stable by 0.13 kcal/mol than the C_s conformation. This is compared to an energy difference of 0.16 kcal/mol at the MP2/6-31+G* level, with the C_s conformation being more stable than the C_4 conformation. These energy differences, at either the MP2/6-31+G* or MP2/6-311++G** level, are too small compared to the forces which are experienced in the solid or the solution phase. It is then concluded that other forces in the solid or the solution phase are the stabilizing force of the C_4 conformation over the C_s conformation for the Li^+ complex.

Conclusion

This is the first time, to the best of our knowledge, that a full and detailed vibrational analysis of the spectra of any of the five 12c4−alkali metal cation complexes is reported. The similarity between the measured vibrational spectra of the five complexes indicates that the five 12c4−alkali metal cation complexes exist in the same conformation. Comparison between the experimental and calculated vibrational frequencies of the possible conformations of the 12c4−alkali metal cation complexes, predicted in a previous conformational analysis study,[31] indicates that the five 12c4−alkali metal cation complexes exist in the C_4 conformation. This conclusion is in agreement with the previous conformational analysis study that the C_4 conformation is the lowest energy conformation of the 12c4−Na^+, −K^+, −Rb^+, and −Cs^+ complexes. For the Li^+ complex, the C_s conformation was calculated to be more stable than the C_4 conformation by only 0.16 kcal/mol, at the MP2/6-31+G* level.[31,61] To further investigate this point, optimized geometries were calculated, in the present work, for the C_s and C_4 conformations of the Li^+ complex at the MP2/6-311++G** level. The C_4 conformation was calculated to be more stable than the C_s conformation by 0.13 kcal/mol.

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