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Experimental and Theoretical Study of the Vibrational Spectra of Free 12-Crown-4

A. A. El-Azhary* and A. A. Al-Kahtani

Chemistry Department, Faculty of Science, King Saud University, P.O. Box 2455,
Riyadh 11451, Kingdom of Saudi Arabia

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The Raman and IR spectra of free 12-crown-4 (12c4) were measured in the solid, liquid, and solution phases. In the three phases, IR active modes were Raman inactive and IR inactive modes were Raman active. According to the exclusion rule, this is consistent with a conformation with a center of inversion. This indicates that 12c4 in the above-mentioned three phases exists in the C_i conformation. Harmonic force fields were calculated for five of the lowest energy conformations of 12c4 of C_i, S_4, C_4, C_2, and C_s symmetries at the corresponding optimized geometries at the B3LYP/6-31+G* level. The five force fields were scaled using a six-scale-factor scaling scheme. The scale factors were varied to minimize the difference between the calculated and experimental fundamental frequencies, except that corresponding to the C−H stretching mode that was held fixed. The root-mean-square (rms) deviation of the experimental to the calculated vibrational frequencies was 6.2, 12.0, 10.8, 13.2, and 13.5 cm^{-1}, for C_i, S_4, C_4, C_2, and C_s conformations, respectively. This supports the above conclusion that 12c4 in the solid, liquid, and considered solution phases exists in the C_i conformation.

Introduction

Although crown ethers were first discovered by Pedersen at DuPont in 1967,[1,2] cyclic polyethers were known long before[3−5] and Pedersen was only the first to indicate their outstanding binding properties. Much of the interest in crown ethers is due to their unique and high specific binding properties to metal cations and various solubility capabilities and therefore different cation binding properties. Since the discovery of crown ethers, there has been an increasing interest in their chemistry and applications. For example, a new field in chemistry called molecular design[6,7] was opened with a large variety of molecules, e.g., cavitands, cryptands, cyclidenes, cryptophanes, etc.

Our main goal is the conformational study of some of the important crown ethers as 12c4, 15-crown-5 (15c5), and 18-crown-6 (18c6) and some of their metal cation complexes. In addition, to do vibrational study of these molecules and their metal cations in an effort to aid in the determination of which conformation or conformations these molecules exists in. In a recent publication, conformational analysis of one of the smallest crown ethers, 12c4, was presented.[8] In that report, the S_4 conformation was predicted to be the lowest energy conformation of free 12c4. This is in agreement with the previous conformational analysis results.[9−11] This result is similar to the new finding for free 18c6 that, interestingly, a similar S_6 conformation, and not the experimentally known C_i conformation, is the lowest energy conformation of free 18c6.[12] The conformational search of free 12c4 and 18c6 was performed at the MM3 level and the energy order of the predicted conformations was determined at the HF/6-31+G*, MP2/6-31+G*//HF/6-31+G*, B3LYP/6-31+G*, and MP2/6-31+G*//BLYP/6-31+G* levels. Energy order of the predicted conformations of 12c4 was also determined at the MP2/6-31+G* level for the 20 lowest energy conformations, according to the MP2/6-31+G*//BLYP/6-31+G* energy order. For 18c6, due to its large size, energy order at the MP2/6-31+G* level was determined for only three of the high-symmetry low energy, according to the MP2/6-31+G*//BLYP/6-31+G* energy order, conformations. These are the S_6, C_i, and D_{3d} conformations. A comparison between the structure of the S_6 and C_i conformations of 18c6 and the S_4 and C_i conformations of 12c4 was performed.[12]

It is surprising with this much interest in the chemistry of crown ethers, no detailed vibrational spectra of free, or rather uncomplexed, 12c4 was reported. In addition, modern methods of accurate force field computations, e.g., the B3LYP[13] method, and vibrational analysis were not applied to 12c4, although already applied to a large number of molecules. This delay in the study of the vibrational spectra of 12c4 is partially due to its large size and the focus of these studies on the vibrational spectra of the more important 18c6.[14] The study of the vibrational spectra of 12c4 has been set as one of the goals of the current research report. A second goal is to determination of which conformation or conformations 12c4 exists in. This is to support and take advantage of the recently reported conformational analysis of 12c4,[8] through the comparison between the experimental and calculated vibrational spectra and using accurately predicted vibrational frequencies calculated by scaling the B3LYP force field.[13,15,16] A third important goal of this report, is to use the results concluded in this work in the study of the larger 18c6 which has a more complex, and consequently, harder to study vibrational spectra.

The number of studies of the vibrational spectra of 12c4 is quite limited with only a small number of vibrational bands assigned.[17−22] These studies were concerned mainly with the changes due complexation with different metal cations. Fukushima et al.[18] reported a Raman study of the vibrational spectra of 12c4 and some of its alkali metal and alkaline earth metal as well as NH_4^+ complexes. Using empirical force fields of the C_{4v}, C_{2v}, D_{2d}, and C_s conformations, the study concluded that the Li^+, Na^+, K^+, NH_4^+, and Mg^+ complexes have an approximate D_{2d} structure and the Ca^{2+}, Sr^{2+}, and Ba^{2+} complexes have an approximate C_{2v} structure. Li et al.[21] also

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* Corresponding author. Telephone: (9661) 467 4367. Fax: (9661) 467 5992.

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reported the IR and Raman spectra of 12c4 and its manganese(II) halides. Comparison between these data and the results obtained in this report will be performed in the discussion section.

Experimentally, X-ray study by Groth[23] has shown that 12c4 in the free state at −150 °C exists in the C_i conformation. A later NMR study by Borgen et al.[24] at low temperature could not determine which conformation or conformations free 12c4 exists in but the authors suggested a rapid interconversion between different conformations especially the C_i and C_4 conformations. X-ray reports of 12c4 metal cations has shown that the complex exists in the C_4,[25−28] C_i,[29] and C_s[30] conformations.

Experimental Details

12c4 purchased from Aldrich was used without further purification. The IR spectra were measured using Thermo Nicolet Nexus 870 FT-IR instrument equipped with a KBr beam splitter and an InGaAs detector. Liquid and solution samples were measured using a KBr cell and a resolution of 1 cm^{-1}. Typically, between 128 and 516 scans were averaged.

The Raman spectra were measured using Thermo Nicolet FT-Raman Nexus module attached to the FT-IR spectrometer. The instrument uses an air-cooled Nd: YVO4 laser source, which emits continuous-wave laser energy at a wavelength of 1064 nm. The instrument uses a XT-KBr beam splitter, a 180° sample configuration, and an InGaAs detector. Between 1028 and 2048 scans were averaged at a resolution of 4 cm^{-1}. A laser power of 0.7 W was used in all measurements except for the solid sample, where, to avoid heating the sample, a power of 0.5 W was used.

Computational Details

Cartesian coordinate force fields were calculated at the B3LYP/6-31+G* level[13] at the corresponding optimized geometries for five of the important conformations of 12c4 or its cation metal complexes. These are conformations 1, 2, 19, 41, and 53 in ref 8 of S_4, C_i, C_s, C_2, and C_4 symmetries, respectively, and relative energies from the S_4 lowest energy conformation of 0.0, 2.61, 4.65, 4.05, and 8.22 kcal/mol, at the MP2/6-31+G* level, respectively.

The computations were done using the Gaussian 98[31] and Gaussian 03[32] programs. The Gaussian program default parameters were used in all computations. The diffuse function in the 6-31+G* basis set was used, as was used in the conformational analysis of free 12c4 reported in ref 8, for possible future comparison with the results of the 12c4 metal cations where the diffuse function is known to be necessary for the accurate prediction of properties of the metal cations complexes. The force fields and dipole moment derivative tensors were calculated analytically and the Raman polarizability derivatives were calculated numerically since analytical polarizability derivatives are not available in the current version of the Gaussian program.

Cartesian coordinate force fields were transferred to internal coordinate[33,34] force fields using the scale2[35] program. The program has the advantage of generating the natural internal coordinates that might not be a simple to generate for a molecule as large as 12c4. To account for the overestimation of the ab initio force fields and for the accurate prediction of the calculated vibrational frequencies, scaling of the internal coordinate force field was done according to the equation[36,37]

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

TABLE 1: Geometry of the C_i Conformation of 12c4 at the B3LYP/6-31+G* Level[a]

coordinate		coordinate		coordinate	
O_1-C_2	1.423	$C_{12}O_1C_2$	114.5	$O_1C_2H_{13}$	109.7
C_2-C_3	1.521	$O_1C_2C_3$	110.1	$C_3C_2H_{13}$	109.7
C_3-O_4	1.421	$C_2C_3O_4$	112.1	$O_1C_2H_{14}$	111.0
O_4-C_5	1.425	$C_{12}O_1C_2$	116.3	$C_3C_2H_{14}$	108.1
C_5-C_6	1.524	$O_1C_2C_3$	108.1	$C_2C_3H_{15}$	108.5
C_6-O_7	1.425	$C_2C_3O_4$	112.7	$O_4C_3H_{15}$	106.6
C_2-H_{13}	1.104	$C_{11}C_{12}O_1C_2$	90.0	$C_2C_3H_{16}$	110.2
C_2-H_{14}	1.110	$C_{12}O_1C_2C_3$	−153.7	$O_4C_3H_{16}$	111.2
C_3-H_{15}	1.098	$O_1C_2C_3O_4$	75.3	$O_4C_5H_{17}$	109.6
C_3-H_{16}	1.110	$C_2C_3O_4C_5$	−97.2	$C_6C_5H_{17}$	109.4
C_5-H_{17}	1.104	$C_3O_4C_5C_6$	159.6	$O_4C_5H_{18}$	110.7
C_5-H_{18}	1.097	$O_4C_5C_6O_7$	−76.2	$C_6C_5H_{18}$	110.3
C_6-H_{19}	1.095			$C_5C_6H_{19}$	109.1
C_6-H_{20}	1.101			$O_7C_6H_{19}$	106.6
				$C_5C_7H_{20}$	109.8
				$O_7C_7H_{20}$	110.4

[a] Bond lengths in Å and angles in degrees.

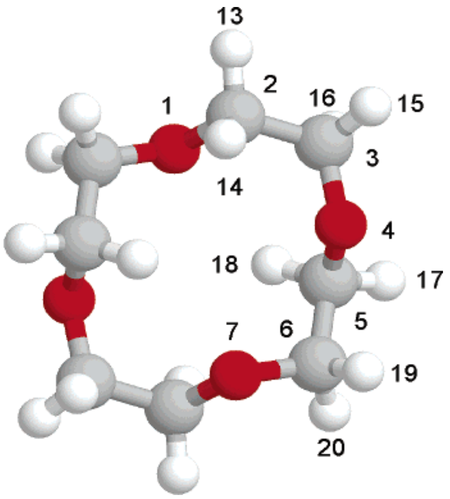

Figure 1. Structure and atom numbering of the C_i conformation of 12c4.

where c_i and c_j are scale factors of internal coordinates i and j, respectively. A fixed scale factor of 1.00 was used first to reproduce the vibrational frequencies calculated by the Gaussian program. The calculated vibrational frequencies were assigned to the experimental vibrational frequencies and the scale factors were varied to minimize the difference between the calculated and experimental vibrational frequencies.

Results

The geometry of the C_i conformation of 12c4 at the B3LYP/6-31+G* level is given in Table 1. The atom numbering is shown in Figure 1. The definition of the nonredundant natural internal coordinates used in the conversion of the Cartesian coordinate force fields to internal coordinate force fields is given in Table 2. Figure 2 shows the experimental FT-IR and FT-Raman spectra of free 12c4 in the liquid phase. Table 3 depicts the experimental Raman frequencies and intensities of the solid, liquid and CS_2 and methanol solution phases of 12c4 and the IR frequencies and intensities of the liquid and CS_2 and methanol solution phases. The results of the vibrational assignment of the fundamental vibrations of free 12c4 based on the Raman spectrum reported in ref 18 and that based on the Raman and IR spectra in ref 21 are included to Table 3. The assignment of the experimental fundamental vibrational frequencies to the calculated vibrational frequencies of the C_i conformation is given

TABLE 2: Natural Internal Coordinate Scale Factors

			final						
coordinate	description	initial	C_i	S_4	C_4	C_2	C_s	ref 15	ref 41
R_1-R_4	C—C stretching	0.930	1.0032	0. 9702	1.1000	1. 0519	1.0320	0.922[b]	0.9337[b]
R_5-R_{12}	C—O stretching	0.920	0.9363	0. 9452	0.9081	0. 9467	0. 9070	0.922[b]	0.9337[b]
$r_{13}-r_{28}$	C—H stretching	0.920	0.9200[a]	0.9200[a]	0.9200[a]	0.9200[a]	0.9200[a]	0.920	0.9122
$\alpha_1-\alpha_{32}$	CH_2 bending	0.980	0.9428	0. 9423	0. 9385	0. 9404	0.9412	0.915	
$\zeta_1-\zeta_9$	ring bending	0.975	1.0425	1.0710	0. 9997	1.0966	1.0453	0.990	0.9880
$\tau_1-\tau_9$	ring Torsion	0.913	1.0715	1.1216	1.0273	0. 8838	0.9907	0.935	0.9619
rms			6.2	12.0	10.8	13.2	13.5		

[a] Fixed. See text. [b] Same scale factor was used for C—C and C—O stretching modes.

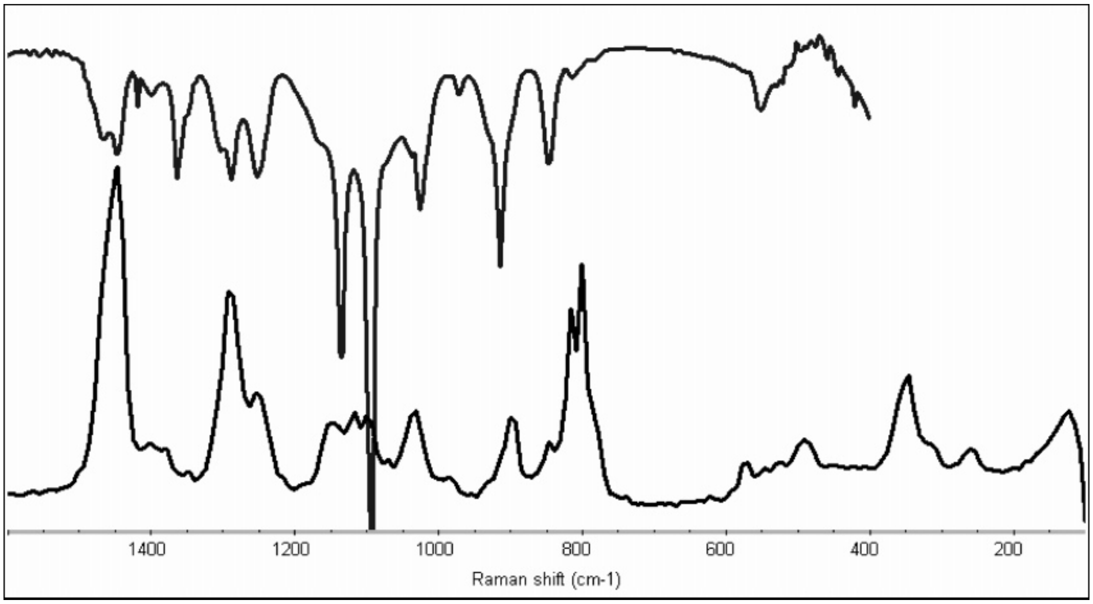

Figure 2. FT-IR (top) and FT-Raman (bottom) spectra of liquid 12c4. The Raman spectra were measured using a air-cooled Nd:YVO4 laser source which emits a continuous-wave laser energy at a wavelength of 1064 nm. A laser power of 0.7 W was used in the measurement.

in Table 4. The calculated IR and Raman intensities are also included in Table 4.

12c4 has 28 atoms and consequently 78 fundamental vibrations. Table 5 shows the possible irreducible representations for each of the C_i, S_4, C_4, C_2, and C_s point groups, the number of vibrations of 12c4 belonging to each representation and the corresponding Raman and IR activities. For the initial scaling of the force fields and to aid in the assignment of the experimental fundamental vibrational frequencies to the calculated ones, the force fields were scaled using a six-scale-factors scaling scheme. Scale factors of 0.930, 0.920, 0.920, 0.980, 0.975, and 0.913 were used for the C—C stretching, C—O stretching, C—H stretching, CH_2 bending, ring bending, and ring torsion coordinates, respectively. These scale factors were selected after comparison between the values of the scale factors optimized for different molecules.[15,16,38−41] The experimental fundamental vibrations were assigned to the calculated ones first according to symmetry, whenever appropriate, then in frequency order. The initial scale factors were varied to minimize the difference between the experimental and calculated vibrational frequencies. Scaling of the force fields started using only few bands of the experimental vibrations that were strong features and their assignment was certain. Additional experimental vibrations were added subsequently. Table 2 lists the starting and final scale factors used in the scaling of the force fields for the five, C_i, S_4, C_4, C_2, and C_s, conformations. The value of the C—H stretching scale factor was selected as that reported in ref 15 as an average scale factor for the C—H stretching mode for 20 organic molecules and was held fixed in the present scaling of the force fields of free 12c4.

Discussion

Experimental Vibrational Spectra. An important observation that can be made from the vibrational spectra in Figure 2 and the data in Table 3 is that the IR active modes are Raman inactive and the IR inactive modes are Raman inactive. This is shown in more detail in Figure 3 in the 750−1000 cm^{-1} region. For example, υ_{66} and υ_{67} observed at 928 and 914 cm^{-1} are quite intense in the IR spectra and almost absent in the Raman spectra. Also, υ_{29} and υ_{30} observed at 816 and 800 cm^{-1} are quite intense in the Raman spectra and quite weak in the IR spectra. According to the exclusion rule, it is then concluded that the conformation assumed by 12c4 must possess a center of inversion, Table 5. From ref 8, where a full conformational search of 12c4 was performed, the only conformation of 12c4 that possesses a center of inversion is the C_i conformation, conformation 2 in ref 8. Since the vibrational spectra of free 12c4 in the three, solid, liquid, and solution phases, are quite similar, except for small shifts in bands position and intensity differences, it is reasonable to assume that the spectra of the three phases correspond to the same conformation. This leads to the conclusion that 12c4 in the free, or rather uncomplexed, form in the three, solid, liquid and considered solution, phases exists in the C_i conformation. The results of the force field scaling step, as will be detailed shortly, for the C_i, S_4, C_4, C_2, and C_s conformations, also support this conclusion, as C_i conformation has the lowest rms deviation of the calculated frequencies from the experimental frequencies.

The conclusion that 12c4 in the above-mentioned phases exists in the C_i conformation was probably not reached before,

TABLE 3: FT-Raman and FT-IR Frequencies (cm^{-1}) and Intensities and Assignment of 12c4[a]

Raman								IR									
solid		liquid		CS$_2$		methanol		liquid		CS$_2$		methanol		ref 18[b]	ref 21		
freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	Raman	Raman	IR	assn
182	vw	179	vw														ν_{37}
253	vw	257	m	258	w	260	m							255	259		ν_{36}
269	w	264	m			268	sh							263			ν_{35}
295	vw	296	vw			299	sh							296			
310	vw	313	sh	316	vw	314	w							323			(ν_{74})
339	vw																
355	s	347	s	348	s	350	s							358	352		ν_{34}
		359	sh	359	sh	359	sh										(ν_{73})
501	s	489	w	492	w	491	m							504	483		ν_{32}
								528	sh	530	w			525		520	ν_{71}
								551	m	539	vw			550[c]			ν_{70}
563	m	573	m	573	w	575	m							579[c]			ν_{31}
															602		
		782	sh	784	sh	783	sh	785	vw	776	vw						ν_{69}
800	vs	800	vs	800	vs	801	vs	800	vw	803	sh			800			ν_{30}
821	vs	816	vs	816	vs	816	vs	815	w	815	vw			814	812		ν_{29}
845	vw	844	vw	844	vw	844	m	847	s	844	s	849	s	845	843	845	ν_{68}
901	s	897	s	897	s	899	s	896	sh	898	sh			900	899		ν_{28}
						911	sh	913	vs	914	s	916	vs			915	ν_{67}
926	vw	926	sh														(ν_{27})
								930	sh	928	sh						ν_{66}
972	vw	978	vw	972	vw			972	w	972	w			965[c]	969	965	
														985[c]	989		
		1020	sh					1024	m	1021	m					1020	ν_{65}
1031	s	1032	s					1030	sh	1029	sh			1030[c]	1033		ν_{26}
1043	s	1040	sh	1037	m									1037[c]			ν_{25}
								1042	vw	1041	vw						(ν_{64})
		1068	vw	1072	vw	1072	vw	1072	vw	1072	s			1075[c]		1073	ν_{63}
						1088	sh										
1086	s	1092	sh	1091	sh	1097	vw										ν_{24}
1098	m	1101	m	1101	m	1103	m										ν_{23}
									vvs	1101	s					1099	ν_{62}
1119	s	1119	m	1119	m	1119	m			1118	sh			1109[c]			ν_{22}
									vvs	1133	vs			1124[c]		1133	ν_{61}
1149	m	1149	m	1147	m	1145	m							1154[c]	1152		ν_{21}
						1162	sh	1164	sh	1162	sh	1167	vw				ν_{60}
		1237	sh	1238	sh	1240	sh			1237	sh	1236	sh				ν_{20}
1245	m	1247	w					1250	m	1247	m	1250	m		1250	1250	ν_{59}
								1256	sh	1255	sh	1264	sh				ν_{58}
1261	m	1254	w	1252	w	1257	m							1261[c]			ν_{19}
		1275	sh	1276	sh	1279	sh										(ν_{18})
										1283	sh						
								1288	s	1292	w	1290	m		1292		ν_{57}
1296	vs	1290	vs	1290	s	1291	vs							1297[c]		1292	ν_{17}
		1306	sh	1306	s	1309	sh	1303	m	1305	m	1305	w			1306	ν_{56}
1350	vw	1346	vw	1347	vw	1349	w	1347	sh	1348	sh						ν_{16}
								1360	s	1362	s					1362	ν_{55}
1360	vw	1363	vw	1364	vw			1362	sh	1363	sh						ν_{54}
1379	m	1380	vw	1380	w	1380	vw										ν_{15}
1396	m	1401	vw	1400	w	1400	vw										ν_{14}
								1403	vw	1398	vw						ν_{53}
1408	m	1407	vw	1407	vw												ν_{13}
1442	vs	1448	vs	1447	vs										1450		ν_{12}
								1447	m							1448	ν_{51}
1449	s	1460	sh	1460	sh												ν_{11}
1463	vs	1470	sh	1468	sh									1465[c]		1462	ν_{10}
								1471	m								ν_{49}
								1487	w								ν_{48}
2835	sh							2831	sh								
2862	vs	2862	vs	2860	vs	2866	vs								2860		
								2865	s	2853	s					2850	
								2897	m	2897	m					2905	
2900	sh	2903	vs	2900	vs												
2920	vs																
								2924	m	2925	m					2941	
2927	s	2935	vs	2937	vs												
2945	vs														2946		
								2947	m	2948	m						
2955	sh																
															2990		

[a] Freq and int are the vibrational frequency and intensity. Assn is the fundamental band assignment. For bands in parentheses, their assignment as fundamentals was not certain, and they were not considered in the scaling of the force field. Key: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, and sh = shoulder. [b] Solution in methanol. [c] Liquid phase.

TABLE 4: Experimental and Calculated Vibrational Frequencies (cm^{-1}) and Raman and IR Intensities ($(4\pi\epsilon_o)^2$ $Å^4$ amu^{-1}) of the C_i Conformation of 12c4[a]

			calcd						calcd	
no.	sym.	expt	freq.	Raman int	depol	no.	sym	expt	IR freq	int
1	A_g		2978	129.0	0.41	40	A_u		2978	70.0
2			2953	167.9	0.57	41			2954	93.4
3			2950	194.7	0.30	42			2949	8.8
4			2921	85.5	0.74	43			2921	116.4
5			2904	486.7	0.03	44			2902	98.5
6			2891	246.8	0.26	45			2891	204.2
7			2855	266.9	0.12	46			2854	91.8
8			2854	223.3	0.62	47			2854	156.3
9			1476	16.0	0.72	48		1487	1480	16.5
10		1468	1474	12.0	0.73	49		1471	1472	5.7
11		1460	1464	15.5	0.74	50			1462	5.5
12		1447	1460	21.3	0.75	51		1447	1461	5.0
13		1407	1408	4.7	0.24	52			1406	5.1
14		1400	1395	2.5	0.65	53		1398	1402	8.3
15		1380	1379	4.4	0.72	54		1363	1366	44.2
16		1348	1347	2.3	0.74	55		1362	1361	54.5
17		1290	1293	19.6	0.63	56		1305	1306	78.5
18		(1276)	1291	16.9	0.72	57		1288	1273	3.0
19		1252	1250	16.6	0.75	58		1255	1244	11.1
20		1238	1238	5.7	0.54	59		1247	1240	33.8
21		1147	1150	6.9	0.59	60		1162	1164	36.6
22		1119	1128	6.4	0.15	61		1133	1133	235.7
23		1101	1096	3.5	0.65	62		1101	1124	187.4
24		1091	1087	4.0	0.59	63		1072	1068	131.9
25		1040	1037	6.4	0.72	64		(1041)	1045	50.3
26		1032	1036	5.2	0.75	65		1021	1009	40.5
27		(926)	929	1.3	0.69	66		928	931	60.3
28		897	899	12.1	0.75	67		914	911	57.3
29		816	813	10.6	0.74	68		844	834	42.6
30		800	792	9.3	0.10	69		776	773	2.9
31		573	571	2.7	0.08	70		539	546	11.0
32		492	500	3.8	0.74	71		530	527	13.6
33			406	0.2	0.58	72			388	7.0
34		348	350	4.1	0.03	73		(359)	355	7.4
35		264	266	0.5	0.45	74		(316)	305	4.6
36		258	252	0.7	0.11	75			232	5.5
37		179	175	0.9	0.27	76			156	14.3
38			107	1.1	0.74	77			106	7.0
39			53	0.3	0.71	78			56	6.2

[a] Bands in parentheses, their assignment as fundamentals was not certain and were not considered in the scaling of the force field. See text.

TABLE 5: Number of Modes Belonging to Each of the Irreducible Representations for the C_i, S_4, C_4, C_2, and C_s Conformations for the 78 Fundamental Vibrational Modes of 12c4 and the Corresponding Raman and IR Activities

point group	irreducible representation	Raman activity	IR activity
C_i	39 A_g	active	inactive
	39 A_u	inactive	active
S_4	20 A	active	inactive
	20 B	active	active
	38 E	active	active
C_4	19 A	active	active
	21 B	active	inactive
	19 E	active	active
C_2	40 A	active	active
	38 B	active	active
C_s	40 A′	active	active
	38 A″	active	active

according to the best of our knowledge, since a detailed vibrational analysis of free 12c4 did not receive a suitable attention.[17−24] This conclusion is in agreement with the previous X-ray study of solid 12c4 at −150 °C,[23] but contradicts with the NMR study which could not indicate what conformation, or conformations, 12c4 exists in.[24] This was attributed to the rapid interconversion of 12c4 between different conformations. Interestingly, the existence of 12c4 in the C_i conformation agrees with the known existence of 18c6 in the C_i conformation in the solid phase, both by X-ray[42,43] and vibrational study.[14,44−46] In the aqueous solutions, 18c6 may exist in more than one conformation including the D_{3d} conformation.[44,45,47] A more detailed study of the vibrational spectra of free 18c6 in the different phases is being planed in our laboratory.[48]

On the other hand, previous conformational analysis results[8] indicate, according to the MP2/6-31+G* energy order, that the three lowest energy conformations of 12c4 are of S_4, C_1 and C_i symmetries. The C_1 and C_i conformations have relative energies, from the lowest energy S_4 conformation, of 2.48 and 2.61 kcal/mol, respectively, at the MP2/6-31+G* level. The S_4 conformation is not observed experimentally in the three, solid, liquid and solution phases may be attributed to the fact that computations correspond to the gas-phase isolated molecule at 0 K. On the other hand, it can be concluded that the interaction between the 12c4 molecules in the solid and liquid phases and with the solvent molecules in the solution phase leads to the stabilization of the C_i conformation over the S_4 conformation. This is similar to the rationalization by Schaefer et al.[9] that the S_4 conformation of 12c4 is not observed experimentally due to the crystal packing forces.

All reported fundamental vibrations in ref 18 are observed in the current work. There is a small difference between the position of some bands as high as 10 cm^{-1}. Surprisingly, vibrational modes ν_{61}, ν_{70}, and ν_{71} reported in ref 18 in the Raman spectrum are observed only in the IR spectra in the current work but not in the Raman spectra. Also the band reported in ref 18 at 985 cm^{-1} is not observed in the current work. The Raman and IR spectra reported in ref 21 is also consistent with that in the present report but it is clear that those reported in ref 21 are basically for the strong features in the Raman and IR spectra only. This is with the exception of the Raman bands at 602 and 2990 cm^{-1}, which are not observed in the spectra reported in the current work.

Scaling of the Force Fields. The values of the experimental frequencies used in the scaling of the force fields are mainly those of the CS_2 solution; otherwise, they are those of the liquid phase. Bands their assignment as fundamentals was not certain, were not used in the scaling of the force fields and are included between parentheses in Tables 4. These are five bands. The first two are observed at 316 and 359 cm^{-1} and were excluded since both correspond to IR active modes and are observed only in the Raman spectra as very weak features. The next two bands are the Raman active mode at 926 cm^{-1} and the IR active mode at 1041 cm^{-1}. Both bands were excluded since they are very weak bands. The fifth band is at 1276 cm^{-1} and was excluded since it is observed as a shoulder in the liquid and solution spectra but not in the solid-phase spectra, and has a large deviation from the corresponding calculated value.

Thus, in the scaling step, 46 fundamental vibrations were used to vary five scale factors. This ensures the accuracy of the calculated scale factors and scaled frequencies. The scale factor corresponding to the C−H stretching mode was held fixed at a value of 0.920. The calculated scale factors and the corresponding rms deviations of the calculated frequencies from the experimental frequencies for the five the C_i, S_4, C_4, C_2, and C_s conformations are given in Table 2. The obtained rms deviations for the C_i, S_4, C_4, C_2, and C_s conformations are 6.2, 12.0, 10.8, 13.2, and 13.5 cm^{-1}, respectively. These values support the above conclusion that 12c4 in the solid, liquid, and solution phases exists in the C_i conformation. The values of the scaling

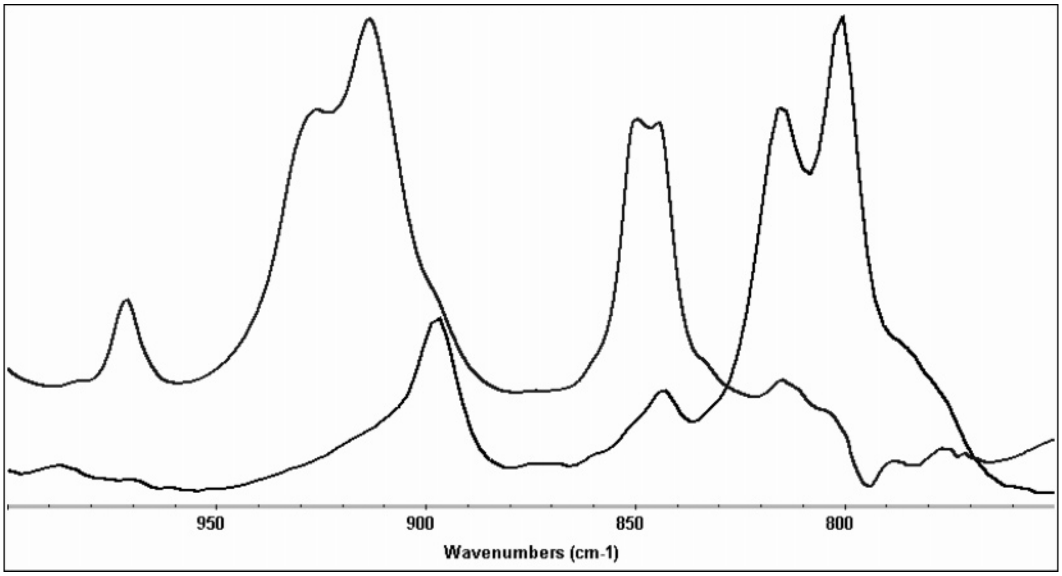

Figure 3. Raman active (top right) and IR active (top left) modes of the CS_2 solution of 12c4.

factors obtained in the current work for 12c4 are quite important since they can be used in the scaling of the force fields of similar crown ethers as 12c4−alkali metal cation complexes[49] which are known to exist mainly in the C_4[25−28] conformation and 18c6,[48] which has a larger number of vibrations and consequently more complex vibrational spectra. As was mentioned above, such study is underway in our laboratory.[48]

The data in Table 4 show a good agreement between the calculated and experimental frequencies for four of the five excluded bands from the scaling of the force fields. These are the observed bands at 316, 359, 926, and 1041 cm^{-1}, with a difference of not more than 8 cm^{-1} from the corresponding calculated value. These four bands were still not considered in the scaling of the force fields, as they may not correspond to fundamental bands as was explained above. The difference between the experimental and calculated frequencies for the fifth band observed at 1276 cm^{-1} is larger than the other four bands, 15 cm^{-1}.

In the scaling of the C_i force field, adding four of the excluded bands at 316, 359, 926, and 1041 cm^{-1}, whose assignment as fundamental is not certain, the rms deviation remained almost unchanged at 6.1 cm^{-1}, and the values of scale factors of the C−C stretching, C−O stretching, CH_2 bending, ring bending, and ring torsion modes were 0.997, 0.936, 0.943, 1.043, and 1.104, respectively. Similarly, adding the band at 1276 cm^{-1}, in addition to the above-mentioned four bands, in the scaling step, the value of the rms deviation remained the same, 6.2 cm^{-1}, and the value of the scale factors became 0.998, 0.936, 0.942, 1.043, and 1.104, for the above-mentioned five vibrational modes, respectively. It is apparent that adding these five bands had a minor effect on the value of the calculated rms deviation and scale factors. It was then preferred to leave these five bands unassigned as an indication that any of them may not correspond to a fundamental vibration.

A quite interesting observation, which was also noticed for free 18c6,[49] is that the fundamental vibrational bands exist in groups of four bands. For example, the four bands predicted to be at 232, 252, 266, and 305 cm^{-1}, followed by the four bands at 350, 355, 388, and 406 cm^{-1}. This significantly facilitated the assignment of the experimental bands to the calculated ones in the 100−1000 cm^{-1} region. In the 1000−1500 cm^{-1} region, most bands, even with the same symmetry, are too close to each other making it difficult to assign. The number of fundamental vibrations in the 50−1000 cm^{-1} region is 26 bands whereas the 1000−1500 cm^{-1} region is crowded with 26 bands. The calculated potential energy distribution of a given group of the four bands does not reflect that the vibrational modes of these four bands are necessarily related.

Finally, it is worth mentioning that most of the values of the scale factors considered in this work, Table 2, excluding the C−H stretching scale factor which was held fixed, for the five C_i, S_4, C_4, C_2, and C_s force fields, are larger than those reported for the similar more firm large ring porphine[41] molecule. In addition, the values of the scale factors determined for both molecules, 12c4 and porphine, are larger than those optimized for a set of 20 organic molecules reported in ref 15. The values of the scale factor showed a significant dependence on the symmetry or conformation of 12c4. For example, the C−C stretching mode had a value of 1.0032 for the C_i conformation, 1.1000 for the C_4 conformation, and 1.0320 for the C_s conformation. This is with the exception of the value of the scale factor corresponding to the CH_2 bending mode that had a value of about 0.94 for all conformations.

Conclusion

It is concluded by studying the vibrational spectra of free 12c4 in the solid, liquid and methanol, CCl_4 and CS_2 solution phases that 12c4 in these phases exists in the C_i conformation. This is further supported by the force field calculations as the C_i conformation had the lowest rms deviation of the experimental to the calculated frequencies of only 6.2 cm^{-1}. This conclusion was not reached before, according to the best of our knowledge, since in the present report a detailed vibrational study of the vibrational spectra of free 12c4 was carried out. In addition, the experimental vibrational assignment was supported by a force field calculated at the B3LYP level of theory, known of its high accuracy.[13,15,16] The values of the scale factors calculated in this work are larger than those reported as average scale factors of a set of 20 molecules[15] and than those reported for the large ring, more rigid, porphine.[41] These scale factors can be used for the scaling of force fields of similar crown ethers and their metal complexes.

The method used in this report, which combines the study of the vibrational spectra and force field calculations, has proven to be successful in the determination of which conformation, or conformations, a molecule may exist in and qualifies to be used for similar molecules. As an example are 18c6[48] and the metal complexes of 12c4[49] and 18c6. Such study is underway in the current laboratory.

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