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Hydronium Ion Complex of 18-Crown-6: Theory Confirms Three “Normal” Linear Hydrogen Bonds

Michael Bühl,* Ralf Ludwig,[†] Rachel Schurhammer,[‡] and Georges Wipff*[,‡,§]

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany, Universität Rostock, Abteilung Physikalische Chemie, Dr. Lorenz-Weg 1, D-18055 Rostock, Germany, and UMR 7551 CNRS, Laboratoire MSM, Institut de Chimie, 4 rue Blaise Pascal, 67000 Strasbourg, France

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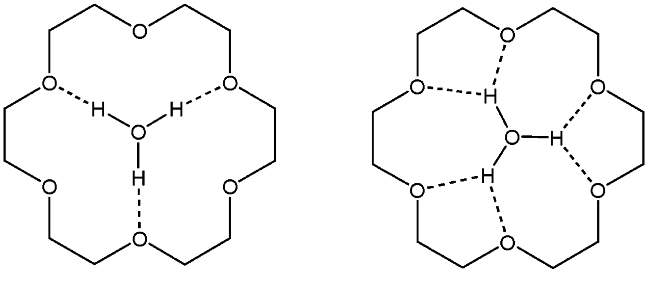
The harmonic vibrational frequencies of the complex of H_3O^+ with 18-crown-6 are reported at a variety of ab initio (Hartree−Fock and MP2) and density functional levels (gradient-corrected and hybrid functionals). At all levels, two ν_{as}(COC) vibrations with large IR intensities are obtained, which are in very good agreement, in terms of both position and relative height, with the bands observed experimentally. Effects of solvation and remote counterions on the appearance of these IR bands are indicated to be small. These results do not support the recent interpretation of the IR spectra in terms of an equivalence of all six O atoms of the crown ether, as well as the resulting claim of a “new type of low-barrier H-bonding involving rotational mobility of H_3O^+” (Stoyanov, E. S.; Reed, C. A. *J. Phys. Chem. A* **2004**, *108*, 907). A simple reassignment of one of the observed bands brings theory and experiment in concert and confirms theoretical predictions that the H_3O^+/18-crown-6 complex adopts a structure with three normal, linear hydrogen bonds.

Introduction

The observation that cyclic crown ethers can bind cations with high affinity and selectivity has had a tremendous impact in chemistry.[1] The complex (**1**) between 18-crown-6 (18c6) and the hydronium ion, H_3O^+, is a prototypical representative of this important host−guest paradigm and has been the subject of numerous experimental[2−4] and theoretical studies.[5,6] The computational evidence presented so far has favored a structure with three linear O−H···O hydrogen bridges as the lowest, stable minimum (**1a**, Chart 1), whereas a bifurcated arrangement (**1b**) has turned out to be a transition state for H_3O^+ rotation 4−5 kcal/mol higher in energy.[6]

In a recent IR study of crown ether complexes with hydronium ions,[4] Stoyanov and Reed (SR) challenged these theoretical predictions for **1.** They reported the occurrence of only *one* band for the C−O−C asymmetric stretching vibration in the IR spectrum of a solution of **1**, which would be incompatible with structure **1a**, as it would suggest the equivalence of all six oxygen atoms of the 18c6 backbone.[4] According to SR, this would imply either (a) that the ion complex adopts a different minimum structure with bifurcated hydrogen bonds (**1b**), which would render all six O atoms of the crown ether equivalent, or (b) that the nuclear dynamics of the H atoms is governed by their quantum nature, which would lead to “indeterminate positions between the O atoms”, that is, to a delocalization of the nuclear wave function between all six $O(H_3O^+)\cdots O$(18c6) axes. SR conclude that the ab initio and density functional predictions for **1**, while compatible with structural and IR data in the solid, are in error concerning the IR spectra in solution, and the authors prefer explanation b to reconcile the apparent discrepancy between theory and experiment. According to SR, “the precise nature of the motion that leads to COC bond equivalency provides a new challenge for theory”. [4]

CHART 1



1a **1b**

We now wish to emphasize that there is in fact no such discrepancy and that the IR data can be reinterpreted such that they are in accord with the theoretical predictions. To this end, we present additional computational data that support our earlier results and IR assignments, calling special attention to possible effects of solvation and ion pairing, which had been neglected in the calculations so far.

Computational Details

Geometries and harmonic vibrational frequencies have been computed using the 6-31G*(*) basis, that is, the 6-31G* or 6-31G** basis[7] on the 18c6 or H_3O^+ moiety, respectively, at the Hartree−Fock, MP2, and a variety of density functional theory (DFT) levels, the latter denoted as BLYP,[8a,9] BP86,[8a,10] and B3LYP.[8b,9] Additional elements were described with the following basis sets: K, all-electron Wachters basis;[11] Sb, Stuttgart−Dresden effective core potential together with the polarized 2s 2p 1d valence basis; Cl in $SbCl_6^-$, 6-31+G*.[12] Bulk solvent effects were estimated from the self-consistent

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* Max-Planck-Institut für Kohlenforschung. E-mail: buehl@mpi-muelheim.mpg.de.

[†] Universität Rostock.

[‡] UMR 7551 CNRS, Laboratoire MSM.

[§] E-mail: wipff@chimie.u-strasbg.fr.

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TABLE 1: Computed Harmonic Vibrational Frequencies and IR and Raman Intensities of 1a (BLYP/6-31G*$^{(*)}$ Level),[a] Together with Experimental IR Data

no.	ν (cm^{-1})	assignment	Raman act.	IR int (rel)	experiment
35	**762**	E H_3O^+ rock	0	104 **(0.3)**	
37	803	E H_3O^+ rock + CH_2 bend	6	4	
39	**810**	A_1 CH_2 bend	3	27 **(0.1)**	**805**[b]
40	**828**	E H_3O^+ rock + CH_2 bend	1	17 **(0.05)**	**830**[b]
42	860	A_1 CH_2 bend + δ(COC)	22	2	
43	907	A_2 ν_{as}(CC)	0	0	
44	926	A_2 CH_2 bend	0	0	
45	**930**	E CH_2 bend + ν_{as}(CC)	1	48 **(0.1)**	**930**[b]
47	**965**	E ν_{as}(CC) + δ(COC)	1	87 **(0.2)**	**960**[b]
49	**986**	A_1 δ_{inv}(H_3O^+)	1	170 **(0.5)**	
50	1022	E ν_{as}(CC) + ν_{as}(COC)	0	0	
52	1028	A_2 ν_{as}(COC)	0	0	
53	1039	A_1 ν_s(CC) + δ_{inv}(H_3O^+)	8	2	
54	**1054**	E ν_{as}(COC) + ν_{as}(CC)	4	356 **(1.0)**	**1095 (1.0)**[c]
56	1065	E CH_2 bend	2	11 (0.03)	
58	1085	A_2 CH_2 bend	0	0	
59	1098	A_1 CH_2 bend	0	13 (0.04)	
60	1099	E CH_2 bend	2	4	
62	1113	A_2 ν_{as}(COC)	0	0	
63	**1113**	E ν_{as}(COC)	6	144 **(0.4)**	**1143 (0.3)**[c]
65	1125	E CH_2 bend	0	1	
67	1138	A_1 CH_2 bend	8	0	
68	1220	A_2 CH_2 rock	0	0	
69	1226	E CH_2 rock	3	4	
71	1235	E CH_2 rock	19	1	
73	1239	A_1 CH_2 rock	1	43 (0.1)	
75	1269	E CH_2 rock	47	1	

[a] Symmetry labels from largest Abelian subgroup of C_{3v} (C_s); Raman activities in Å^4/AMU, IR intensities in KM/mol; intense IR vibrations printed in boldface. [b] Nujol, $(Zn,Mn)Cl_4^{2-}$ counterions, from ref 17. [c] 1,2-Dichloroethane solution, cobalt bis(dicarbollide) counterion, from ref 4.

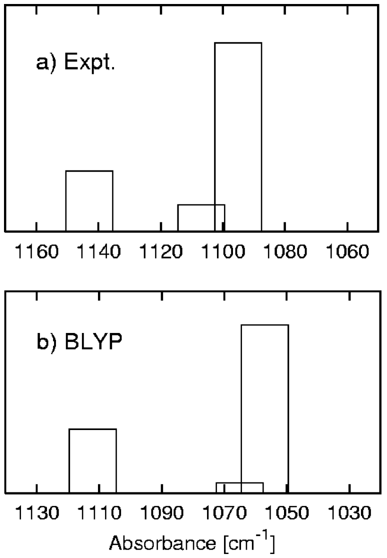

Figure 1. Schematic sketches of the ν_{as}(COC) bands in the IR spectra of **1**: (a) experimental data from ref 4 (1,2-dichlorethane solution, cobalt bis(dicarbollide) counterion); (b) theoretical data for **1a** at the BLYP/6-31G*$^{(*)}$ level.

reaction field in a polarizable continuum model (denoted PCM),[13] where the cavity is built from interlocking spheres around non-hydrogen atoms. Due to convergence problems, a somewhat larger radius of these spheres than usual was used (scaling factor 1.38 instead of 1.2), and the contributions from the cavity to the gradients were ignored. All computations were carried out with the Gaussian 98[14] and Gaussian 03[15] program packages.

Results and Discussion

In the IR spectrum in solution, two broad signals are observed in the C−O−C stretching region. The larger one at 1095 cm^{-1} is assigned to the asymmetric C−O−C stretch, whereas the smaller one at ~1145 cm^{-1} has been attributed by SR to a CH_2 bending mode of the 18c6 backbone, based on the occurrence of a similar band in the free crown ether.[4] In the following, we thus mainly focus on this region of the IR spectrum. We first describe the results of the BLYP/6-31G*$^{(*)}$ calculations, which will be confirmed at other computational levels in the gas phase. It will then be shown that the effect of "solvent" or counterions is not sufficient to affect the interpretation of the IR spectrum of the hydronium complex. For the purpose of comparison, the vibrations of **1a** will be compared with those of uncomplexed 18c6 and with those of the K^+ complex of 18c6. Finally, we investigate the effect of isotopic substitution on the salient IR pattern of the hydronium complex.

Vibrations of the Hydronium Complex 1a from BLYP/6-31G*$^{(*)}$ Calculations. The relevant parts of the vibrational spectra of **1a** predicted at the BLYP/6-31G*$^{(*)}$ level[16] are detailed in Table 1. The computed IR spectrum also shows two strong absorptions in that region, at 1054 and 1113 cm^{-1}. While the absolute frequencies do not fit perfectly to experiment, the overall pattern is reproduced remarkably well, in terms of both the separation of the two signals and their relative intensity (see the schematic sketches in Figure 1).

Both computed vibrations are in fact asymmetric C−O−C stretching modes; the one with lower energy is localized at the set of crown-ether O atoms that are involved in hydrogen-bonding to H_3O^+, and the other one is localized at the remaining three O atoms. CH_2 bending vibrations are also predicted to occur in the same region, between 1065 and 1138 cm^{-1} (Table 1), *but all with zero or near-zero intensities*! For free 18c6 and other symmetric complexes, in contrast, CH_2 bending modes can occur close to that of the (single) asymmetric C−O−C (see below). Thus, according to the computations, the intensity of particular vibrations can change dramatically on going from the neutral crown ether to the cationic complex. One should be very careful when making assignments for one species based on results for the other.

We note in passing that the presence of two C−O−C stretching modes in **1a**, indicative of the inequivalence of the crown-ether oxygen atoms, is fully consistent with observations from other IR studies in a lower frequency domain: For instance, it has been noted that the two singlets observed for symmetric $M^+ \cdot$18c6 metal complexes in the 800−1000 cm^{-1} region are split into two doublets in the hydronium complex **1** due to the lowering of the symmetry of the crown ether.[17] Again, this observed IR pattern is faithfully represented at the BLYP level (top of Table 1). Were all crown-ether oxygen atoms equivalent, as suggested by SR, no such splittings should be observed.

Vibrations of the Hydronium Complex 1a: Comparison of Different Computational Levels. To make sure that the results presented in Table 1 are not artifacts of that particular theoretical method, we have computed the harmonic frequencies of **1a** at several other levels of ab initio and density functional theory. No qualitative changes in terms of the computed IR pattern are found,[18] as is apparent from the results for the most intense IR bands (those that have been highlighted in boldface in Table 1), which are summarized in Table 2. Specifically, the positions and relative intensities of the two asymmetric C−O−C stretching bands (in boldface in Table 2) are very similar at all levels. The good accord between the BLYP and (scaled) MP2

TABLE 2: Computed Harmonic IR Frequencies of 1a (in cm^{-1}, Relative Intensities in Parentheses, 6-31G*$^{(*)}$ Basis), Together with Experimental IR Data[a]

no.[b]	BLYP	BP86	B3LYP	HF[c]	MP2[c]	expt
35	762 (0.3)	781 (0.4)	781 (0.2)	686 (0.1)	770 (0.3)	
39	810 (0.1)	818 (0.1)	849 (0.1)	827 (0.1)	827 (0.1)	805[d]
40	828 (0.05)	835 (0.03)	863 (0.05)	835 (0.1)	837 (0.04)	830[d]
45	930 (0.1)	939 (0.1)	970 (0.1)	931 (0.02)	948 (0.1)	930[d]
47	965 (0.2)	969 (0.2)	1001 (0.2)	961 (0.2)	970 (0.2)	960[d]
49	986 (0.5)	989 (0.6)	980 (0.5)	929 (0.6)	1015 (0.6)	
54	**1054 (1.0)**	**1082 (1.0)**[e]	**1127 (1.0)**	**1118 (1.0)**	**1101 (1.0)**	**1095 (1.0)**[f]
59	1098 (0.04)	1108 (0.05)	1147 (0.06)	1124 (0.07)	1107 (0.04)	
63	**1113 (0.4)**	**1141 (0.5)**	**1184 (0.4)**	**1161 (0.3)**	**1145 (0.3)**	**1143 (0.3)**[f]

[a] ν_{as}(COC) bands printed in boldface. [b] Numbering of BLYP frequencies (cf. Table 1); in some cases, the exact sequence of the respective bands is different at the other levels. [c] HF and MP2 frequencies scaled by 0.89 and 0.95, respectively; see ref 20. [d] Nujol, (Zn,Mn)Cl_4^{2-} counterions, from ref 17. [e] Another intense ν_{as}(COC) band present at 1072 cm^{-1} (rel intensity 0.4). [f] 1,2-Dichloroethane solution, cobalt bis(dicarbollide) counterion, from ref 4.

data is noteworthy. Even though the interaction energy between the hydronium ion and the crown ether is larger at MP2 than at DFT levels and is indicated to be overestimated at MP2,[6,19] the harmonic frequencies are little affected. The reliability of the MP2 level for predicting IR spectra has been amply demonstrated.[20] Thus, these results strongly support the interpretation that both bands observed at 1095 and 1143 cm^{-1} are in fact C−O−C vibrations, corresponding to hydrogen-bonded and free ether bridges, respectively.

Solvent and Counterion Effects on the Calculated Vibrations. What could compromise the reliability of these theoretical data obtained for isolated species is the neglect of solvation effects. We have adopted two approaches to estimate such effects, namely that of microsolvated clusters containing solvent molecules explicitly and that of a polarizable continuum. First, we have optimized an adduct of **1a** with one molecule of the actual solvent, 1,2-dichloroethane (DCE);[4] see top of Figure 2. While the ν_{as}(COC) band at lower energy is split into two bands with a very narrow spread of 5 cm^{-1}, that at higher energy is split into three bands covering 8 cm^{-1}. The two most intense peaks are closely bracketing the corresponding band in free **1a** (compare the first and second columns of Table 3). Thus, direct interaction with discrete solvent molecules should not alter the IR spectrum of **1a** in the region of interest.[21]

Since the DCE used experimentally was saturated with water,[4] which is a much better donor than DCE, we have − in a next step − optimized an adduct of **1a** with one molecule of H_2O. Starting from an arrangement in which the extra water molecule formed a linear hydrogen bond to the hydronium oxygen atom, this water molecule moved to the rim of the crown ether during optimization and ended up hydrogen-bonded to one of the O atoms not involved in H-bonding to H_3O^+ (middle of Figure 2). Three ν_{as}(COC) bands associated with this set of crown-ether oxygen atoms are found between 1112 and 1097 cm^{-1} (Table 3). The latter value corresponds to the COC stretch involving the O atom H-bonded to the extra water molecule. The shift from the corresponding vibration in free **1a**, $\Delta\nu = -16$ cm^{-1} (compare the first and third columns in Table 3), is the largest computed change of the IR bands due to specific interactions with a solvent molecule. The ν_{as}(COC) band of the other set of crown-ether oxygen atoms, that is, those involved in H-bonding with H_3O^+ (occurring at 1054 cm^{-1} in free **1a**), is hardly affected by water addition and is just split by 2 cm^{-1}. As with the DCE adduct discussed above, the overall IR patterns of **1a** and **1a**·H_2O are computed to be qualitatively very similar. These results are consistent with the finding that only minor shifts in frequencies occur for free 18c6 upon switching from anhydrous to water-saturated DCE.[4]

Arguably, the particular adducts of **1a** with DCE and water that have been considered here are just singular examples out of a plethora of possible conformers and positional isomers. There is little reason, however, to doubt that these examples are representative or to assume that other adducts would display completely different IR characteristics.

In a second approach, we have estimated bulk solvation effects using a popular continuum model. To obtain an upper limit for such effects, we employed the characteristics of water as solvent. Upon immersion of **1a** into such a continuum, the COC stretching vibrations are red-shifted by 4 cm^{-1} but are otherwise unaltered (compare the first and fourth columns in Table 3). This result reinforces the conclusion from the supramolecular approaches discussed above, namely that solvation should not alter the qualitative appearance of the IR spectrum of **1a** siginificantly.

Finally, we have addressed the possible effect of ion pairing on the relevant parts of the IR spectrum. The counterion used by SR, a bulky chlorinated cobalt bis(dicarbollide) ion, $[Co(C_2B_9H_8Cl_3)_2]^-$ (CCD$^-$), is typically only weakly coordinating. Electrostatic effects can be quite far-reaching, however, and may be important also for larger cation−anion separations. As a model for **1a**·CCD$^-$, which would be computationally quite demanding, we have chosen a complex between **1a** and $SbCl_6^-$. Starting from the arrangement found in the crystal of the corresponding salt, in which this anion resides on a 3-fold axis passing through the hydronium oxygen atom,[22] the C_3-symmetric minimum displayed on the bottom of Figure 2 was obtained.[23] This ion complex is fairly tight, displaying close Cl···H contacts between anion and crown ether (smallest BLYP value 2.89 Å; slightly smaller than the sum of the van der Waals radii[24] of Cl and H, 2.95 Å). The closest Cl···O distance between anion and crown ether is 3.86 Å. Even though this is somewhat longer than the corresponding van der Waals sum, 3.27 Å, the anion should be close enough to affect the IR pattern noticeably if the latter were sensitive to such electrostatic effects. However, as with the coordinated solvent molecules discussed above, only minor changes in the IR positions and intensities are found upon ion pairing, with a maximum shift of $\Delta\nu = 9$ cm^{-1} (compare the first and last columns in Table 3). The influence of the actual counterion, CCD$^-$, should be even less pronounced.

To summarize this part, we have found no computational evidence for a notable sensitivity of the salient parts of the IR spectrum of **1a** to the presence of a surrounding solvent or weakly coordinating counterions. Thus, we are confident that our results for free **1a** collected in Table 2 are not artifacts of the gas-phase conditions adopted in those computations. These

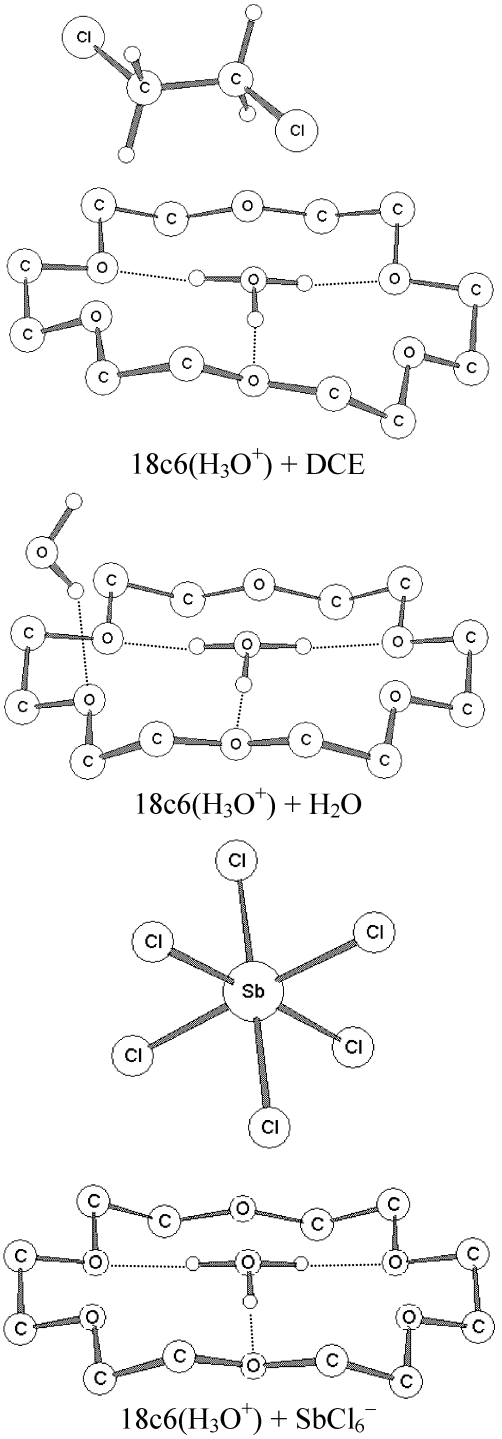

Figure 2. Optimized structures of **1a** complexed with one molecule of DCE (top), one molecule of water (middle), and one $SbCl_6^-$ counterion (bottom). Hydrogen atoms of 18c6 are omitted for clarity.

data should be directly comparable to the solution experiments and can be used for the assignments of the latter.

TABLE 3: Computed Harmonic COC Stretching Frequencies of 1a (in cm^{-1}, Relative IR Intensities in Parentheses, BLYP/6-31G*$^{(*)}$ Level) and Various Adducts Thereof

1a	**1a**·DCE	**1a**·H_2O	**1a**/PCM(H_2O)	**1a**·$SbCl_6^-$
1054 (1.0)	1150 (0.8) 1155 (1.0)	1052 (1.0) 1054 (0.9)	1050 (1.0)	1054 (1.0)
1113 (0.4)	1106 (0.1) 1111 (0.3) 1114 (0.3)	1097 (0.2) 1111 (0.1) 1112 (0.4)	1109 (0.4)	1122 (0.5)

Comparison with the Calculated Vibrations of the Free 18c6 Crown. For free 18c6, comparison between computed and observed properties is hampered by the conformational flexibility of this floppy molecule. The two most important isomers, D_{3d} and C_i, are quite close in energy,[19] and their relative population can depend sensitively on the environment. For instance, the C_i form is found in the solid,[25] whereas the D_{3d} crown becomes more dominant in solvents of increasing polarity and prevails in water.[26] According to molecular dynamics simulations, there are 14 different conformers of 18c6 at less than 2.0 kcal/mol above the lowest energy C_i form in the gas phase[26b] and three conformers at less than 2.0 kcal/mol from the minimum in water.[26c] The IR spectrum observed in DCE solution may thus arise from a complex mixture of these two — and perhaps additional — conformers. In DCE solution, a broad band is observed at ~1118 cm^{-1}, together with a shoulder at ~1134 cm^{-1}, attributed to the single asymmetric COC stretch and CH_2 bend, respectively.[4] For the D_{3d} crown the corresponding BLYP values are 1105 and 1095 cm^{-1} (Table 4), that is, reversed in order. For the C_i form, a larger number of IR-active COC and CH_2 vibrations is predicted in this region, and the latter appear up to 1147 cm^{-1}. We note at this point that, in the whole region between 800 and 1200 cm^{-1}, the computed IR frequencies of this form are in good agreement with those observed in the solid,[27] which are included in Table 4. The same has been found previously at the B3LYP level.[28] It turns out that the intensities of these CH_2 vibrations (not so much their relative positions) can depend somewhat on the theoretical level; for instance, they are more prominent at the BP86 and MP2 levels. Note that this is not the case for **1a**, where the CH_2 bends are very weak at all levels considered (see, for instance, entry 59 in Table 2).

Comparison with the K$^+$ Complex of 18C6. Since the free crown ether is so conformationally flexible, a symmetrical complex with a metal ion in the center appears to be a better reference to gauge the bonding in **1a**. We have chosen the potassium complex for this purpose and included the BLYP data for $K^+ \cdot$18c6 in Table 4. On going from this species to **1a**, the single ν_{as}(COC) band is split into two bands, with computed $\Delta\nu$ values of +41 and −14 cm^{-1} (BLYP values). A very similar pattern is observed experimentally, with $\Delta\nu$ values of +41 and −7 cm^{-1},[29] provided the band observed for **1a** at 1143 cm^{-1} is also assigned to a COC stretch. This assignment is thus further supported by the results of the K$^+$ complex.

Effect of Isotopic Substitution. When assignments of vibrations are unclear, isotopic substitution may be useful. Salient harmonic frequencies in the COC stretching region of some deuterated isotopomers are collected in Table 5. Replacing H_3O^+ by D_3O^+ is straightforward but, as expected, leaves the appearance of the COC stretching region almost unchanged. Fourier self-deconvolution of the experimental spectra reveals a small shoulder at ~1107 cm^{-1}, that is, blue-shifted by 12 cm^{-1} relative to the principal ν_{as}(COC) band. This shoulder increases slightly in intensity upon going from H_3O^+ to D_3O^+.[4] Indeed, a very weak CH_2 bend is computed near the most intense COC band, blue-shifted by 11 cm^{-1} (entry no. 56 in Table 1). A second one with similar intensity is predicted between both COC bands, however (entry no. 59 in Table 1), and it is the latter that becomes more prominent upon switching from H_3O^+ to D_3O^+ (Table 5). The computed intensities of such weak bands may thus not be quantitatively accurate (otherwise, another shoulder should be observed in the sample containing D_3O^+). It is noteworthy, however, that the relative intensity of the strong ν_{as}(COC) bands can change profoundly opon deuteration of the crown ether: For the fully deuterated form, essentially equal

TABLE 4: Computed Harmonic CH_2 Bending and COC Stretching Frequencies of 18c6 and Various Adducts Thereof (in cm^{-1}, Relative IR Intensities in Parentheses, BLYP/6-31G$^{*(*)}$ Level)

18c6			K^+·18c6		**1a**	
D_{3d}	C_i	expt[a]	D_{3d}	expt[b]	C_{3v}	expt[c]
	810 (0.04)					
814 (0.1)	822 (0.02)	*828*	814 (0.06)		810 (0.1)	*805*
826 (0.04)	845 (0.1)	*835*[d]				
835 (0.1)	868 (0.02)	*861*	822 (0.04)	*835 (s)*	828 (0.05)	*830*
949 (0.2)	932 (0.2)	*887*			930 (0.1)	*930*
	963 (0.1)	*945*	947 (0.3)	*961 (vs)*	965 (0.2)	*960*
	1011 (0.1)	*992*				
	1030 (0.1)	*1043*				
	1062 (0.1)	*1058*				
1095 (0.04)	1092 (0.2)	*1076*				
1105 (1.0)	1103 (1.0)	*1108*[d,e]	1071 (1.0)	*1102 (vs)*[f]	1054 (1.0)	*1095 (1.0)*
	1110 (0.8)	*1132*		*1130 (sh)*		
	1114 (0.2)	*1139*[d,e]	1096 (0.05)	*1150 (sh)*[f]	1098 (0.04)	
	1134 (0.02)	*1146*			1113 (0.4)	*1143 (0.3)*
	1147 (0.02)	*1159*				

[a] Solid, from ref 27; unfortunately, no intensities were given there. [b] Solid, Br^- counterion, from: Fouassier, M.; Lassegues, J.-C. *J. Chim. Phys.* **1978**, *75*, 865−874. [c] See footnotes *b* and *c* in Table 1. [d] Also found in D_{3d} form. [e] DCE solution: 1118 (1.0) and 1134 (0.3), from ref 4. [f] 1108 and 1148 cm^{-1}, as given in ref 4.

TABLE 5: Computed Harmonic CH_2 Bending and COC Stretching Frequencies of 1a and Its Isotopomers (in cm^{-1}, Relative IR Intensities in Parentheses, BLYP/6-31G$^{*(*)}$ Level)

no.[a]	H_3O^+·18c6	D_3O^+·18c6	H_3O^+·18c6-d_{24}	D_3O^+·18c6-d_{24}
49	986 (0.5)	725 (0.3)	979 (0.8)	723 (0.3)
53	1039 (0.0)	1038 (0.0)	1017 (0.0)	1012 (0.2)
54	**1054 (1.0)**	**1052 (1.0)**	**1086 (1.0)**	**1083 (1.0)**
56	1065 (0.03)	1064 (0.03)	1094 (0.3)	1096 (0.2)
59	1098 (0.04)	1096 (0.1)	1096 (0.1)	1094 (0.1)
63	**1113 (0.4)**	**1112 (0.5)**	**1129 (0.5)**	**1128 (1.0)**

[a] Numbering of frequencies as in Table 1; the bands are reordered upon isotopic substitution.

intensities of both bands are predicted (entries in boldface in the last column in Table 5). The deuterated variant of 18c6 has already been prepared.[30] The IR characteristics of such a D_3O^+·18c6-d_{24} complex should thus be accessible and could serve as an additional test for the reliability of the computations and the assignments based on them.

Discussion and Conclusions

On the basis of extensive computational evidence, we assign both resonances at 1095 and 1145 cm^{-1} observed for **1** in solution to ν_{as}(COC) vibrations, rather than to one COC stretch and one CH_2 bend, as put forward by SR. The important implication is that the structure of the hydronium complex involves three hydrogen-bonded and three "free" oxygens of the crown. We note in passing that, if indeed only one asymmetric C−O−C stretch were observed, there would be another possible explanation, namely that the C_{3v}-symmetric minimum is correct but that H_3O^+ rotates very rapidly between the two sets of O atoms, causing them to scramble on the IR time scale. Such dynamical effects (coalescence) have been observed IR spectroscopically for some very fast processes.[31] However, judging from the noticeable classical barrier computed for this process (>4 kcal/mol) and from Car−Parrinello molecular dynamics simulations (just two rotational jumps during a period of 12 ps),[6] H_3O^+ rotation should not be fast enough to cause coalescence in the IR spectra or to make the inclusion of nuclear quantum effects mandatory, as speculated by SR. The importance of such effects should ultimately be addressed by quantum Monte Carlo or path-integral molecular dynamics simulations.

The assignment of the resonances at 1095 and 1145 cm^{-1} to ν_{as}(COC) vibrations is supported at several levels of ab initio and density functional theory and is not affected when effects of solvent or weakly coordinating counterions are taken into account. The resulting reinterpretation of the IR data finds theory and experiment in concert. In particular, while the "new type of low-barrier H-bond" proposed by SR may be interesting, it does not have to be invoked for the interpretation of the observed IR spectrum of **1**. In the spirit of Occam's razor, this proposal should be deferred until it is backed by further theoretical or experimental findings. With our new assignment, the observed spectrum is compatible with a static structure such as **1a**, possessing three linear OH···O hydrogen bonds.

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Supporting Information Available: BLYP/6-31G$^{*(*)}$ geometry and frequencies of **1a** in the form of a Gaussian output, for visualization of the frequency modes with suitable software. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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