J. Phys. Chem. A **1999,** *103,* 7867−7871

Formation of Phenolate Anion−Counterion Complexes Can Explain the Vibrational Properties of the Phenolate Anion in Solution

Marco Nonella*

Biochemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Hans Ulrich Suter

Physikalisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received: April 29, 1999; In Final Form: July 29, 1999

Structures of enolate−counterion complexes and structures and vibrational spectra of phenolate anion−counterion complexes have been calculated by means of MP2 and density functional methods. Compared to corresponding monomeric complexes, higher complexes reveal longer C−O bond lengths which causes a downshift of the C−O stretching mode. In the case of phenolate we find C−O stretching frequencies and isotope shifts upon ^{18}O and d_2 labeling which are in good agreement with recent IR data of phenolate generated in solution. The C−O stretching frequency, for example, is predicted to be around 1270 cm^{-1} compared to an experimental value of 1273 cm^{-1} and the ^{18}O shift of this mode is calculated to be 18 cm^{-1} compared to an experimental shift of 17 cm^{-1}. For a free phenolate anion, our calculations predict a C−O stretching frequency of ~1350 cm^{-1}. The vibrational spectrum of phenolate anions in solution can thus be explained in terms of higher phenolate anion-counterion complexes in agreement with recent NMR experiments of Jackman and Smith (Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 3829).

Introduction

The C−O bond length and stretching vibration of the phenolate anion was the topic of recent experimental and computational investigations. A resonance Raman investigation revealed a band at 1264 cm^{-1}.[1] This mode was assigned as a predominant C−O stretching mode after carrying out a normal coordinate analysis. For this analysis, the C−O bond was assumed to correspond to a pure single bond, and bond length and force constant had been chosen accordingly. An FTIR investigation of UV irradiated phenol revealed a strong band at 1273 cm^{-1} [2] which, due to its 17 cm^{-1} downshift upon ^{18}O labeling, had been assigned to the C−O stretching mode of the phenolate anion.

Density functional (DFT) calculations of the structures and vibrational spectra of the phenoxyl radical and the phenolate anion have been recently presented.[3] The most surprising results revealed by this study are a short C−O bond length in the phenolate anion which is similar to that determined for the phenoxyl radical and, as a consequence, a C−O stretching frequency which is overestimated by about 100 cm^{-1} compared to the experimental data. The authors had concluded that the large deviation between calculated and observed C−O stretching frequency corroborates earlier statements that DFT might be inappropriate for calculations of negative molecular ions.[4] Although this statement can be justified theoretically, it is incompatible with many successful calculations of anions.[5−10] We have shown in a recent contribution[11] that high-level ab initio methods such as MP2, CISD, ACPF, AQCC, QCISD, and MRCI predict a C−O bond length for the free phenolate anion which agrees with the bond length obtained from various DFT calculations.

Experimental investigations on enolates and phenolates made clear that a formation of higher anion (phenolate or enolate)−counterion (Li$^+$ or Na$^+$) complexes is favored in solution. Dimers of Li−enolates were proposed to account for the diastereoselectivity of enolate dimerization.[12] X-ray structures of Li−enolates have been first reported by Amstutz et al.[13] and revealed dimeric, tetrameric, and hexameric complexes of Li−enolate monomers. For Li−phenolates, Jackman and Smith[14] reported NMR data which agreed with the existence of monomers, dimers, tetramers, and hexamers of phenolate anion−counterion complexes.

Guided by these findings we have modeled simple phenolate anion−counterion complexes.[11] Upon such complexations we have found an elongation of the C−O bond length which causes a downshift of the C−O stretching frequency. The weaker C−O bond causes a decoupling of CO and CC stretching modes and reveals a better agreement of the calculated ^{18}O isotope shifts with infrared spectroscopic data. Since the CO stretching mode of such monomeric complexes is still about 50 cm^{-1} too high in energy and since some of the d_5 and ^{13}C isotope shifts still deviated considerably from the shifts determined with resonance Raman spectroscopy, we concluded that our assumption, a formation of phenolate anion−counterion complexes could be responsible for the recently reported IR and resonance Raman data of the phenolate anion,[1,2,15] is basically correct but has to be extended to the formation of higher complexes.

In this contribution we present results of density functional calculations on dimers and tetramers of enolate anion−counterion and phenolate anion−counterion complexes. In the case of the enolate complexes we have compared structural parameters with X-ray crystal structures of similar compounds. In the case of the phenolate complexes we demonstrate that a dimeric structure reveals a very good agreement with infrared

---

* Corresponding author. Present address: Institut für Medizinische Optik, Ludwig-Maximilians Universität, Oettingenstr. 67, D-80538 München.

10.1021/jp9914267 CCC: $18.00

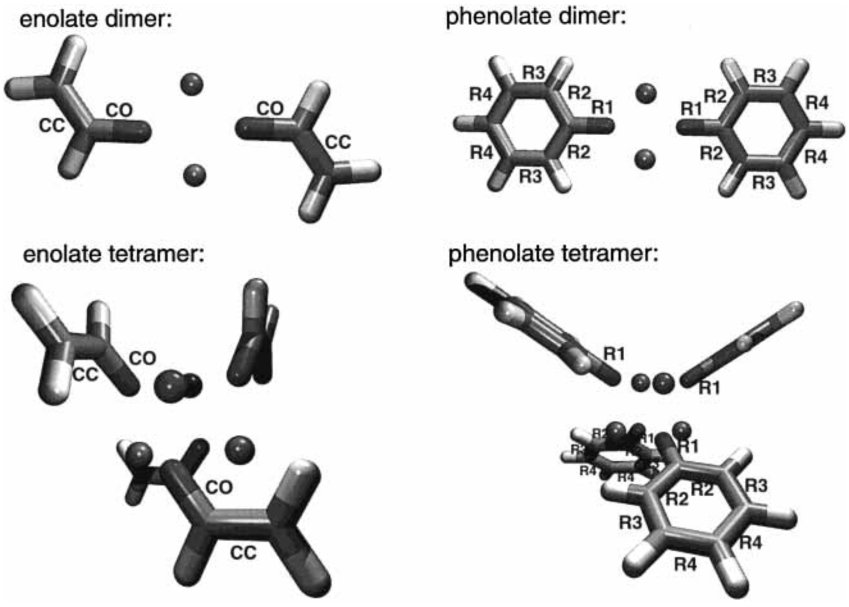

Figure 1. Structures of dimers and tetramers of complexes of enolate and phenolate with a counterion.

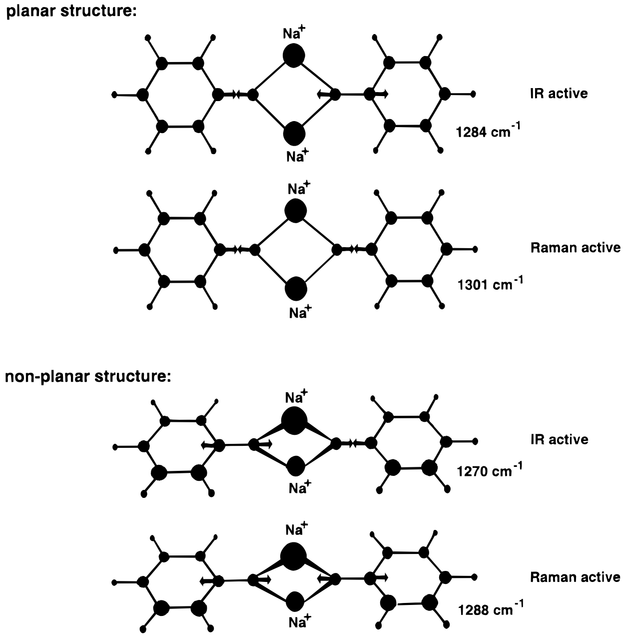

Figure 2. Displacement vectors of the anti-symmetric and symmetric C−O stretching modes of the two phenolate anion−Na^+ dimeric complexes.

data for the frequency and ^{18}O isotope shift of the CO stretching mode. Furthermore, d_5 isotope shifts of the dimer agree considerably better with experimental infrared data than those of the monomer. The agreement of the calculated deuterium and ^{13}C shifts with resonance Raman data, however, is still modest. On the basis of the symmetry of the optimized complexes, we postulate a possible explanation for these findings and for the generally found deviation between infrared and resonance Raman data.

Methods of Calculation

Density functional and MP2 calculations have been performed with the GAUSSIAN94 program.[16] The BLYP[17,18] functional was applied in all DFT calculations. As standard AO basis set the 6-31+G* basis of Pople and co-workers[19,22] was chosen. Planar and nonplanar dimers of phenolate anion−counterion complexes have been optimized under application of D_{2h} symmetry restriction. In the case of enolate dimers, symmetry restrictions resulted in small imaginary frequencies. Tetrameric complexes were optimized in S_4 symmetry. The A_1 C−C and C−O stretching modes of the free phenolate anion correspond to B_{1u} and B_{3u} modes in the planar and nonplanar dimeric complex, respectively. In the tetrameric complex, the C−O and C−C modes in question belong to the irreducible representations A, B, and E.

The quantum chemically derived Cartesian force constant matrix was then read into the program GAMESS[23] which was employed to compute normal modes, force constants of internal coordinates, total energy distributions in order to assign the normal vibrations,[24,25] and frequencies of isotopically labeled compounds.

The definitions of the CC and CO bonds of the dimeric and tetrameric phenolate and enolate complexes are shown in Figure 1. Molecular structures contained in this figure have been visualized using VMD.[26] The graphical representation of the molecular structures and normal modes shown in Figure 2 have been prepared with the program MacMolPlot.[27]

Results and Discussion

Structures. Structural parameters of optimized complexes of enolate anion−counterion and phenolate anion−counterion complexes are given in Tables 1 and 2, respectively. For the dimers of the enolate anion−counterion complexes, stable structures are nearly planar, showing only very little deviation from planarity. Placing the counterions perpendicular to the molecular plane results in two imaginary frequencies. Upon complete minimization, such a structure relaxes toward the nearly planar structure. The BLYP/6-31+G* calculations reveal bond distances of the Li−O, O−C, and C−C bonds of 1.813, 1.348, and 1.359 Å, respectively, with lithium as counterion, and 2.178, 1.335, and 1.366 Å, respectively, with sodium as counterion. For the tetrameric complex with lithium as counterion, the corresponding bond lengths are 1.913, 1.343, and 1.368 Å, respectively. Experimentally, O−Li, O−C, and C−C distances of 1.851, 1.342, and 1.330 Å had been found in a hexameric complex with lithium as counterions.[28] The corresponding bond lengths for a tetrameric complex with sodium

TABLE 1: Selected Bond Lengths (in angstroms) of the Enolate Anion and Enolate Anion−Counterion Complexes[a]

	Li-dimer		Na-dimer		Li-tetramer		Li-monomer		Na-monomer		free anion	
	BLYP	MP2	BLYP	MP2	BLYP	exp ref 13	BLYP	MP2	BLYP	MP2	BLYP	MP2
O−Li (Na)	1.813	1.821	2.178	2.200	1.913	1.94	1.633	1.639	2.097	2.013		
R_{C-O}	1.348	1.343	1.335	1.331	1.343	1.35	1.335	1.331	1.318	1.323	1.287	1.285
R_{C-C}	1.359	1.350	1.366	1.357	1.368	1.34	1.362	1.352	1.381	1.358	1.399	1.387

[a] In all calculations the 6-31+G* basis set has been applied. Only the shortest of the Li−O distances of the tetramer is given.

TABLE 2: Optimized Geometrical Parameters (in angstroms) of the Phenolate Anion−Counterion Complexes Determined with the BLYP Functional and the 6-31+G* Basis Sets[a]

	Li-dimer		Na-dimer			monomers		
	planar	out of plane	planar	out of plane	Li-tetramer	Li	Na	free anion[b]
O−Li(Na)	1.811	1.801	2.177	2.164	1.916	1.632	1.996	
R1	1.352	1.357	1.340	1.347	1.363	1.337	1.330	1.290
R2	1.423	1.421	1.429	1.428	1.421	1.426	1.431	1.461
R3	1.406	1.407	1.405	1.406	1.407	1.406	1.406	1.403
R4	1.409	1.409	1.409	1.410	1.409	1.410	1.412	1.419

[a] Also included are the structural parameters of the corresponding monomers. [b] Reference 11.

as counterions are 2.241, 1.308, and 1.358 Å, respectively.[28] In a butyllithium−lithium−butoxide tetrameric complex, O−Li distances of 1.85 Å had been found.[29] A larger O−Li distance of ∼1.94 Å had been found by Amstutz et al.[13] Here, the C−O and C−C bond lengths are given as 1.35 and 1.34 Å, respectively.

Compared to experimental data we find the largest deviation for the Li−O bond length. According to our calculations, this bond length gradually increases with increasing size of the complex. In contrast, the available X-ray data report O−Li distances of 1.94 Å in a tetrameric[13] and 1.85 Å in a hexameric complex.[28] Experimental data and calculation agree in that they find three different O−Li distances whereof we have only discussed the shortest one.

For the dimers of phenolate anion−counterion complexes the counterions can either be placed in the molecular plane or perpendicular to this plane. Both structures correspond to proper energy minima, i.e., no imaginary frequencies have been found. The planar structures are slightly more stable than the structures having the counterions out of the molecular plane. The energy differences are however very small: for the lithium complexes, the energy difference among the two conformers is only 0.04 kJ/mol and for the sodium complexes the planar structure is 1.28 kJ/mol lower in energy than the nonplanar one.

Upon dimerization, the C−O bond R1 and the adjacent C−C bond R2 are most prominently affected. Compared to the free phenolate anion, R1 is elongated by up to 0.07 Å and R2 is shortened by up to 0.04 Å. The O−counterion distance is also strongly affected through the dimerization. In the monomer these bond lengths are 1.632 (lithium) and 1.996 Å (sodium). In the planar dimeric complex, these distances are 1.811 (lithium) and 2.177 Å (sodium). The C−O bond length has values of 1.347 (Na^+, out-of-plane), 1.340 (Na^+, planar), 1.357 (Li^+, out-of-plane), and 1.352 Å (Li^+, planar). Dimerization thus leads to an additional weakening of the C−O bond which will show up in a further downshift of the C−O stretching frequency. Bonds R3 and R4 are not altered by more than 0.01 Å. All other bond lengths are not significantly affected and agree with those found in the nonplanar dimeric lithium complex. The structural parameters of the dimeric complexes can be compared with structural data of crystals of lithium and sodium 2,6-di-*tert*-butylphenoxides.[30] Li−O bonds of 1.849 and 1.867 Å had been found in this investigation.

Compared to the nonplanar dimer with lithium as counterion, we find in the tetrameric phenolate anion−Li^+ complex a small additional elongation of the C−O bond length to 1.364 Å. All other bond lengths are not significantly affected. Probably due to sterical repulsion, the planarity found in the phenolate anion−Li^+ dimers cannot be retained in the tetramer and the phenol rings are pushed out of the O−Li^+−O−Li^+ plane. This distortion might destabilize higher complexes.

TABLE 3: Estimated Binding Energies per Phenolate Anion−Counterion Unit (in kJ/mol)[a]

	Li-dimer	Li-tetramer
HF	101	168
BLYP	109	152
MP2	109	169

[a] The 6-31+G* basis set has been used in all calculations.

An accurate computational prediction of binding energies for such a molecular system is not straightforward due to several reasons. The size of the dimeric and tetrameric complexes prohibits the use of high quality basis sets and quantum chemical methods. Furthermore, solvation effects can be expected to affect stabilization energies considerably. As a crude estimation of the stabilization energy per phenolate anion−counterion unit, we have additionally to our BLYP/6-31+G* calculations also carried out MP2/6-31+G* single point calculations at the BLYP/6-31+G* optimized geometries. Calculated estimates for such binding energies are listed in Table 3 and predict a preferred formation of tetrameric complexes. The Coulomb contribution to the binding energy is thus large enough to over compensate the sterical repulsion and to favor the formation of a tetrameric complex. While higher complexes had been detected by NMR spectroscopy,[14] in a crystal structure of 2,6-di-*tert*-butylphenolate only dimeric substructures have been found.[30] These findings can most likely be attributed to the larger sterical interactions in the latter case.

Vibrational Frequencies of Phenolate−Counterion Complexes. In the free anion as well as in the monomeric complex, the modes ν_4, ν_5, and ν_6 belong to the symmetry group A_g. In the planar and nonplanar dimeric complexes, the corresponding modes belong to symmetry groups B_{1u} and B_{3u}, respectively. For simplicity, we will continue to refer to these three modes in question as modes ν_4, ν_5, and ν_6.

Vibrational frequencies of the three modes are listed in Table 4. We find that these modes only weakly depend on the nature of the counterion. The largest differences are found for mode ν_6. This mode is found about 10 cm^{-1} higher in energy when sodium instead of lithium is chosen as counterion. Also, ν_6 is

TABLE 4: Experimental and Calculated Infrared Active modes of Phenolate Anion−Counterion Complexes (in cm^{-1})[a]

		Li-complex dimer		Na-complex dimer			monomer complex[c]		
mode	exptl	planar	out of plane	planar	out of plane	Li-complex tetramer	Li$^+$	Na$^+$	free anion[d]
ν_4	1585,[b] 1592 or 1564[c]	1579	1577	1576	1574	1579	1579	1574	1564
ν_5	1534,[b] 1483[c]	1480	1478	1475	1474	1479	1485	1481	1485
ν_6	1264,[b] 1273[c]	1273	1261	1284	1270	1247	1323	1318	1357

[a] In all calculations the BLYP functional and the 6-31+G* basis set had been applied. [b] Reference 1. [c] Reference 2. [d] Reference 11.

TABLE 5: Selected Isotope Shifts (in cm^{-1}) of Phenolate Anion−Counterion Complexes Determined with the BLYP Functional and the 6-31+G* Basis Set

				Li-complex dimer						Na-complex dimer								
	exptl			planar			out of plane			planar			out of plane			Li-complex tetramer		
mode	^{18}O	^{13}C	d_5	^{18}O	^{13}C	d_5	^{18}O	^{13}C	d_5	^{18}O	^{13}C	d_5	^{18}O	^{13}C	d_5	^{18}O	^{13}C	d_5
ν_4		51[a]	35,[a] 39 or 33[b]	0	54	33	0	54	35	0	55	34	1	55	36	0	55	35
ν_5	2[c]	47[a]	131,[a] 100[b]	1	33	102	1	32	105	1	33	96	2	33	102	1	33	111
ν_6	17[c]	36[a]	58,[a] 71[b]	18	30	67	17	30	62	18	30	72	17	30	66	16	31	60

[a] Reference 1. [b] Reference 2. [c] Reference 15.

predicted to be found about 10 cm^{-1} lower in energy in the nonplanar than in the planar complex. The calculated frequencies of the dimeric complexes are in good agreement with the set of experimental frequencies of ref 2. Compared to modes ν_4 and ν_5 the C−O mode is clearly more sensitive with respect to intermolecular interaction. Formation of a monomeric phenolate anion−Na$^+$ caused a downshift of this mode of ~40 cm^{-1}.[11] We find in the present investigation that dimerization of such a monomeric complex results in a further downshift of 30−40 cm^{-1} of ν_6, while the frequencies of modes ν_4 and ν_5 stay nearly unaffected. In the free phenolate anion, ν_4 contains about 60% CC stretching character and 9% CO stretching character. Modes ν_5 and ν_6 are mixed modes and contain about 40% CO stretching mode character and about 40% CH bending character. Formation of a monomeric phenolate anion−Na$^+$ complex changes the mode decomposition of the modes ν_5 and ν_6. In such a complex, ν_5 has 53% CH bending character and only 16% CO stretching character and ν_6 has 64% CO stretching character and corresponds thus to a predominant CO stretching mode. In the dimeric complex, we find a symmetric and anti-symmetric combination of C−O stretching vibrations. The infrared active anti-symmetric mode of the planar phenolate anion−Na$^+$ complex at 1284 cm^{-1} contains 31% of each C−O bond stretching, i.e., the mode decomposition corresponds closely to that found in the monomer. The symmetric infrared inactive C−O combination mode of this complex is found at 1301 cm^{-1} and contains 30% of each C−O bond stretching. Displacement vectors of the CO stretching modes of both Na$^+$ dimers are shown in Figure 2.

Calculated isotope shifts of modes ν_4, ν_5, and ν_6 upon ^{18}O, ^{13}C, and d_5 labeling are listed in Table 5. A good agreement with the FTIR data was found in the case of the ^{18}O (ref 15) and d_5 (ref 2) shifts. While the dimerization seems not to affect the ^{18}O shifts of modes ν_5 and ν_6, the d_5 shifts of these two modes are significantly changed and agree considerably better with the experimental data of ref 2 than with those of the monomeric complex.

In the tetrameric complex the additional lengthening of the C−O bond compared to the dimeric complexes results in a further downshift of the intensive C−O stretching mode to 1247 cm^{-1}. The agreement between experiment and calculation is thus better for a dimeric complex. The frequencies of the modes corresponding to the modes ν_4 and ν_5 of the free phenolate anion agree well with those calculated for the dimeric complexes and are found at 1579 and 1479 cm^{-1}. As previously stated only the C−O stretching mode seems to be affected significantly through intermolecular interactions. For the infrared active modes ν_4, ν_5, and ν_6, the calculation predicts ^{18}O isotope shifts of 0, 1, and 16 cm^{-1}, respectively, and ^{13}C shifts of 55, 33, and 31 cm^{-1}, respectively. The corresponding deuterium shifts are 35, 111, and 60 cm^{-1}, respectively. Deuterium and ^{18}O shifts are in acceptable agreement with the FTIR data. Large deviations are again found between our calculated ^{13}C and deuterium isotope shifts and those determined with resonance Raman spectroscopy.

The discussion above makes clear that we find generally a good agreement between our calculated infrared active frequencies and their isotope shifts with the available FTIR data of refs 2 and 15. Since the agreement between the two experimental sets of frequencies and isotope shifts is not very satisfactory, we find therefore unexpected large deviations from some of the frequencies and isotope shifts obtained from the resonance Raman experiment of ref 1. We propose that this discrepancy could be a consequence of the formation of higher phenolate anion−counterion complexes. In contrast to the free phenolate anion or to a monomeric phenolate anion−counterion complex, the dimeric complex has D_{2h} symmetry and, thus, a center of symmetry. The exclusion rule is therefore valid and vibrational modes are either IR or Raman active. The different spectroscopic methods that had been applied in the two experimental investigations should thus detect different vibrational modes. For the planar Na$^+$ dimer, we find Raman active modes at 1581 (A_g), 1543 (B_{3g}), and 1269 cm^{-1} (B_{3g}) which could correspond to the experimental frequencies at 1585, 1534, and 1264 cm^{-1} found in ref 1. The corresponding calculated ^{13}C shifts are 55, 52, and 37 cm^{-1} which agree well with the experimental shifts of 51, 47, and 36 cm^{-1}. For the deuterium shifts we only find a good agreement in the case of the mode at 1581 cm^{-1} (32 cm^{-1} compared to the experimental value of 35 cm^{-1}). For the modes at 1543 and 1269 cm^{-1} we calculate on the basis of the corresponding potential energy distribution deuterium shifts of 39 and 299 cm^{-1}, respectively, which are far away from the experimental shifts of 131 and 58 cm^{-1}. The Raman active, symmetric C−O stretching mode however is predicted at 1301 cm^{-1} and does most likely not correspond to the Raman frequency at 1264 cm^{-1}. Isotope shifts of 19 cm^{-1} (^{18}O), 29 cm^{-1} (^{13}C), and 81 cm^{-1} (deuterium) are predicted for this mode. For the Li$^+$ dimer, Raman active frequencies of the three modes in question have been calculated at 1585 (A_g), 1553 (B_{3g}), and 1282 cm^{-1} (B_{3g}). The frequency of the symmetric C−O stretching mode has been calculated at 1297 cm^{-1}. All these modes seem to depend only weakly on the nature of the counterion.

The tetrameric complex has been calculated in S_4 symmetry. Because of the size of this system, we have only used lithium as a counterion. The vibrational analysis revealed no imaginary frequency, i.e., the optimized structure corresponds to a proper energy minimum. In S_4 symmetry, the nondegenerate symmetries A and B are either Raman or IR active while the degenerate modes of symmetry E are Raman and IR active. We find Raman active modes for the tetramer at 1588 (A) and 1579 (E), 1555 (A) and 1479 (E), and 1282 (A) and 1247 (E) cm^{-1}. The bands of A symmetry at 1588, 1555, and 1282 nearly exactly correspond to the Raman active modes of the dimer and agree with the available Raman data. The ^{13}C shifts of these three modes are 55, 53, and 39 cm^{-1}, respectively. They are very similar to the shifts we have calculated for the dimer and show again a satisfactory agreement with the experimental data. Upon deuteration, we calculate shifts for the three modes of 33, 165, and 64 cm^{-1}, respectively. For the mode at 1555 cm^{-1} we still find a large deviation between experimental and calculated deuterium shift. The bands of E symmetry, however, could possibly not be detected in the experiment. Our analysis of the vibrational spectrum and the isotope shifts of the dimeric and tetrameric complexes of phenolate anion−counterion units lets us suspect that under experimental conditions as used in the Raman and FTIR experiments, predominantly phenolate anion−counterion dimers are most likely formed.

Conclusion

In this contribution we have shown by means of DFT calculations that IR active modes of the phenolate anion in the 1200−1600 cm^{-1} region together with their ^{18}O and deuterium shifts can be well predicted when a formation of dimers or tetramers of phenolate anion−counterion complexes is assumed. A significantly less good agreement is achieved when we compare our calculated frequencies and isotope shifts with experimental Raman data. Because of the symmetry of dimeric and tetrameric phenolate anion−counterion complexes, we suggest that the two spectroscopic methods detect different vibrational modes. In the dimeric as well as in the tetrameric complex we can assign Raman active modes which agree satisfactory with the frequencies and ^{13}C isotope shifts given in Mukherjee et al.[1] Only in the case of the deuterium shifts a large deviation is found at least for one mode. Our results suggest that higher phenolate anion−counterion complexes have been detected by means of infrared spectroscopy. Such complexes had previously been suggested on the basis of NMR spectroscopic data by Jackman and Smith.[14] The frequencies of the C−O stretching modes have shown to be very sensitive with respect to intermolecular interactions. On the basis of the slightly better agreement between experimental data and the calculated infrared active C−O stretching mode of the dimeric complex, we suggest that under the conditions chosen for recording Raman and FTIR spectra of the phenolate anion dimeric complexes might preferentially be formed.

Acknowledgment. The authors thank Catherine Berthomieu for discussions of the C−O stretching mode of the phenolate anion and for making available experimental data prior to publication. We also thank Dieter Seebach for a helpful discussion and for important hints to the recent literature. Computing time has been provided by the Rechenzentrum der Universität Zürich and by the Centro Svizzero di Calcolo Scientifico (CSCS) in Manno. Support by the Swiss National Foundation (Project 31-49630.96), the Alfred Werner Legat, and the Jubiläumsspende der Universität Zürich is gratefully acknowledged.

References and Notes

(1) Mukherjee, A.; McGlashen, M. L.; Spiro, T. G. *J. Phys. Chem.* **1995**, *99*, 4912.
(2) Berthomieu, C.; Boussac, A. *Biospectroscopy* **1995**, *1*, 187.
(3) Nwobi, O.; Higgins, J.; Zhou, X.; Liu, R. *Chem. Phys. Lett.* **1997**, *272*, 155.
(4) Cole, L. A.; Perdew, J. P. *Phys. Rev. A* **1982**, *25*, 1265.
(5) Nonella, M. *J. Phys. Chem. B* **1997**, *101*, 1235.
(6) Zhan, C.-G.; Chipman, D. M. *J. Phys. Chem. A* **1998**, *102*, 1230.
(7) El-Azhary, A. A.; Suter, H. U.; Kubelka, J. *J. Phys. Chem. A* **1998**, *102*, 620.
(8) King, R. A.; Galbraith, J. M.; Schaefer, H. F. *J. Phys. Chem.* **1995**, *100*, 6061.
(9) van Huis, T. J.; Galbraith, J. M.; Schaefer, H. F. *Mol. Phys.* **1996**, *89*, 607.
(10) Tschumper, G. S.; Freeman, J. T.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *104*, 3676.
(11) Suter, H. U.; Nonella, M. *J. Chem. Phys. A* **1998**, *102*, 10128.
(12) Seebach, D.; Golinsky, J. *Helv. Chim. Acta* **1981**, *64*, 1413.
(13) Amstutz, R.; Schweizer, W. B.; Seebach, D.; Dunitz, J. D. *Helv. Chim. Acta* **1981**, *64*, 2417.
(14) Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 3829.
(15) Berthomieu, C.; Boullais, C.; Neumann, J.-M.; Boussac, A. *Biochim. Biophys. Acta* **1998**, *1365*, 112.
(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian 94, Revision d.2; Gaussian, Inc.: Pittsburgh, PA, 1995.
(17) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(18) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 786.
(19) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(20) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(21) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
(22) Clark, T.; Chandraseklar, J.; Spitznagel, G. W.; v. R. Schleyer, P. *J. Comput. Chem.* **1983**, *4*, 294.
(23) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE* **1990**, *10*, 52.
(24) Pulay, P.; Török, F. *Acta Chim. Hung.* **1965**, *47*, 273.
(25) Keresztury, G.; Jalsovszky, G. *J. Mol. Spectrosc.* **1971**, *10*, 304.
(26) Humphrey, W.; Dalke, A.; Schulten. K. *J. Mol. Graphics* **1996**, *14.1*, 33.
(27) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Modell.* **1998**, *16*, 133.
(28) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462.
(29) Marsch, M.; Harms, K.; Lochmann, L.; Boche, G. *Angew. Chem.* **1990**, *102*, 334.
(30) Cetinkaya, B.; Gümürükcü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.