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# A Quantum Chemical Investigation of the C−O Bond Length and Stretching Mode of the Phenolate Anion

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The structure and vibrational spectrum of the phenolate anion have been calculated with various quantum chemical methods. Correlated methods predict a C−O bond length between 1.28 and 1.29 Å, which is significantly shorter than an earlier suggested value of 1.40 Å. This indicates a partial double bond character for the C−O bond in the phenolate anion, which is explained in terms of resonance structures. IR frequencies determined with pure density functional methods agree well with FTIR data in the case of the modes $\nu_4$ and $\nu_5$ while the frequency of the C−O mode is significantly overestimated in all calculations. The calculations of the isolated phenolate anion do thus poorly agree with experimental data. We demonstrate that upon complexation of the phenolate anion with a positively charged counterion the C−O bond is elongated and has considerable single bond character. The intermolecular interaction also causes a downshift of ∼30 $cm^{-1}$ of the C−O stretching mode and thus reveals a better agreement with experimental data.

## Introduction

The C−O bond length and stretching vibration of the phenolate anion are 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 the 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 $cm^{-1}$. 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]

On the other hand, DFT calculations of the *p*-benzosemiquinone radical anion revealed C−O frequencies that are in reasonable agreement with experimental data.[5,6] In addition, other DFT calculations of anions such as $SiF_{(n)}$ ($n = 1-5$)[7−9] or the anions of triazole and tetrazole[10] exist which are in reasonable agreement with experimental data.

We have, therefore, decided to carry out an additional computational study of the structure and vibrational spectrum of the phenolate anion by applying different quantum chemical methods and by focusing on the C−O bond length and stretching vibration. Our strategy is as follows: we first check for possible basis set effects in pure DFT calculations by using basis sets of different quality. Besides DFT methods, we also apply ab initio methods and take correlation effects into account by means of perturbation theory (MP2) or configuration interaction (at the SRCI or MRCI level) as well as by using ACPF and AQCC methods.

## Methods of Calculation

Hartree−Fock, density functional, MP2, and QCISD calculations have been performed with the Gaussian94 program.[11] As standard AO basis set, we have chosen the 6-31+G* basis of Pople and co-workers.[12−15] Larger basis sets (6-31++G**, aug-cc-pVDZ, and aug-cc-pVTZ[16,17]) have been employed in DFT calculations in order to check for possible basis set effects. In all DFT calculations the BLYP[18,19] and B3LYP[20] functionals were used.

In all geometry minimizations $C_{2v}$ symmetry has been applied. Applying this symmetry restriction, one imaginary frequency has been found in the case of the MP2 and QCISD calculations. For MP2 we have carried out a complete minimization without any restrictions. The resulting structure is slightly nonplanar. The deviations from planarity are smaller than 5°. Within the given accuracy, the bond lengths of bonds R1, R2, R3, and R7 exactly correspond to those of the planar structure. Moreover, the vibrational frequencies of the modes $\nu_4$, $\nu_5$, and $\nu_6$ agree with those of the planar structure within 2 $cm^{-1}$. Since all properties of interest are essentially correctly predicted upon applying symmetry restrictions, we have decided to use $C_{2v}$ symmetry throughout this investigation.

The quantum chemically derived Cartesian force constant matrix was then read into the program GAMESS,[21] which was employed to compute normal modes, force constants of internal

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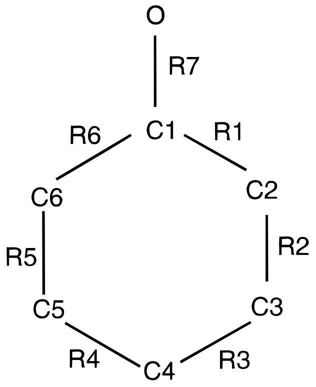

**Figure 1.** Atom labeling of phenolate anion and phenoxyl radical.

coordinates, total energy distributions in order to assign the normal vibrations,[22,23] and frequencies of isotopically labeled compounds.

Geometry optimizations have also been carried out at the SRCI, MRCI, ACPF,[24] and AQCC[25] levels of theory. ACPF (averaged coupled pair functional) and AQCC (averaged quadratic coupled cluster) were designed like the original CPF[26,27] and MCPF[28] to correct approximatively for the size consistency not met by the CI approaches. A throughout discussion of the theory and performance of the various methods can be found in the excellent article by Szalay and Bartlett.[29] The computational procedures for ACPF and AQCC are similar to CI and can be used for the same CI spaces as MR-SDCI. In all correlated methods the 1s orbitals of carbon and oxygen atoms were kept frozen. All these calculations have been carried out with the COLUMBUS[30,31] program system. The 6-31+G* basis set has been applied in all these calculations. As noted above, $C_{2v}$ symmetry has been applied in all geometry minimizations. The threshold for numerical minimization was 0.001 bohr and 0.01°. The COLUMBUS suite of programs allows the calculation of analytical gradients[32,33] for CI as well as for ACPF and AQCC.

We have additionally determined the harmonic force field at the ACPF level of theory. The Cartesian force constant matrix was calculated by numerical differentiation of the gradients according to

$$\frac{\partial^2 E}{\partial q_i\,\partial q_j} \cong \left[\frac{\partial}{\partial q_i}E(q_j+\Delta) - \frac{\partial}{\partial q_i}E(q_j)\right]/\Delta$$

where the two terms represent the analytic derivatives at the equilibrium geometry and at a geometry with coordinate $q_j$ displaced by a distance $\Delta = 0.01$ au. As in the MP2 and QCISD calculations, the ACPF harmonic force field predicts one small imaginary frequency.

Atom labeling and definition of CC and CO bonds of the phenolate anion are shown in Figure 1.

## Results and Discussion

**Effect of Basis Set and Level of Theory.** Bond lengths as calculated with the BLYP functional are listed in Table 1. We can note that the C−O bond length strongly depends on whether a set of diffuse functions is added to the basis set or not. The BLYP/6-31G** basis set predicts a short C−O bond length of 1.278 Å while all calculations using basis sets that have been augmented with diffuse functions predict C−O bond lengths between 1.28 and 1.29 Å, which agree with the bond length of 1.283 Å as determined in ref 3 by using the BLYP functional. The choice of basis sets we have applied in our calculations makes us confident that the found disagreement between calculated and experimental C−O bond length and stretching vibration is most likely not a problem of the quality of the basis sets.

**TABLE 1: Optimized Geometrical Parameters of the Phenolate Anion Determined with the BLYP Functional and Different Basis Sets**

| parameter | 6-31+G* | 6-31G** | 6-31++ G** | 6-31++ G**(f) | aug-cc-pVDZ | aug-cc-pVTZ |
|---|---|---|---|---|---|---|
| R7 | 1.290 | 1.278 | 1.289 | 1.288 | 1.288 | 1.282 |
| R1 | 1.461 | 1.465 | 1.461 | 1.460 | 1.462 | 1.454 |
| R2 | 1.403 | 1.399 | 1.402 | 1.401 | 1.403 | 1.394 |
| R3 | 1.419 | 1.415 | 1.417 | 1.417 | 1.418 | 1.410 |

**TABLE 2: Optimized Geometrical Parameters of the Phenolate Anion Determined with HF, B3LYP, and Various Correlated ab Initio Methods Using the 6-31+G* Basis Set**

| parameter | HF | B3LYP | MP2 | CISD | ACPF | AQCC | QCISD | MRCI |
|---|---|---|---|---|---|---|---|---|
| R7 | 1.252 | 1.276 | 1.288 | 1.266 | 1.287 | 1.284 | 1.284 | 1.277 |
| R1 | 1.439 | 1.449 | 1.442 | 1.439 | 1.446 | 1.443 | 1.445 | 1.441 |
| R2 | 1.379 | 1.392 | 1.396 | 1.382 | 1.397 | 1.392 | 1.394 | 1.394 |
| R3 | 1.397 | 1.407 | 1.405 | 1.397 | 1.410 | 1.405 | 1.407 | 1.405 |

To check whether the finding of a short C−O bond might be caused by a failure of DFT methods as suggested in ref 3, we have also carried out geometry optimizations using various correlated ab initio methods. Inspection of the results of a standard single reference SDCI calculations makes clear that four configurations have coefficients larger than 0.1 in the CI expansion: the ground-state configuration $(13a_1)^2(8b_1)^2(3b_2)^2(1a_2)^2$ and the excited configurations $(13a_1)^2(8b_1)^2(3b_2)^2(1a_2)^1(2a_2)^1$, $(13a_1)^2(8b_1)^2(3b_2)^1(4b_2)^1(1a_2)^2$, and $(13a_1)^2(8b_1)^2(3b_2)^1(4b_2)^1(1a_2)^1(2a_2)^1$. A description of the system by means of a simple single reference SDCI method is thus inadequate. Taking all four configurations as reference configurations into account elongates the C−O bond length from 1.266 Å (SDCI) to 1.277 Å (MRCI); i.e., multireference effects tend to elongate the C−O bond (see Table 2).

We have also carried out geometry optimizations at the MP2, SR-ACPF, SR-AQCC, and QCISD levels of theory applying the standard 6-31+G* basis set. Optimized bond lengths are listed in Table 2. The largest predicted C−O bond lengths are 1.290 Å in the series of DFT calculations and 1.288 Å in the "conventional" ab initio calculations by the MP2 method. As expected, the optimized geometries of the ACPF, AQCC, and QCISD calculations are nearly identical. In previous calculations on *p*-benzoquinone[34] we made the observation that BP86 and BLYP methods tend to predict bond lengths that are up to about 0.01 Å longer than those predicted in MP2 calculations. In the present investigation a similar behavior is found. We have furthermore carried out a geometry optimization at the MP2 level using the larger 6-31++G(d,p) basis set. This calculation resulted in a C−O bond length of 1.287 Å. As in the case of the DFT calculations, enlargement of the basis set does not result in a longer C−O bond. All applied quantum chemical methods predict a C−O bond that exhibits considerable double bond character.

None of the applied methods could confirm a C−O bond length of 1.4 Å as was applied by Mukherjee et al.[1] in their normal coordinate analysis of the phenolate anion. This bond length of 1.4 Å was taken from force field calculations of Harada and Takeuchi[35] on *p*-xylene, para-substituted phenol, and para-substituted phenolate anion. A justification for a C−O single bond in the phenolate anion had also been drawn from its isoelectronicity with fluorobenzene which exhibits a C−F single bond. We have calculated a C−F bond length of 1.381 Å

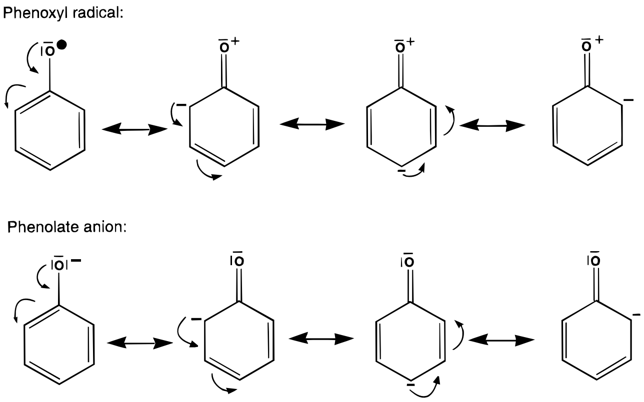

**Figure 2.** Resonance structures of phenolate anion and phenoxyl radical.

(BLYP/6-31+G*) for fluorobenzene, which agrees well with the C−O bond length calculated for phenol using the same method (1.389 Å) but is clearly longer than the C−O bonds calculated for the phenolate anion. Mesomeric structures as depicted in Figure 2 are commonly used for explaining the reaction selectivity of the phenolate anion[36] and the acidity of phenol.[37] This simple model suggests that both the phenoxyl radical and the phenolate anion should exhibit similar resonance effects which lead to a partial double bond character of the C−O bond in both molecules. Such a resonance model is in line with electrostatic potential derived atomic partial charges listed in Table 6. In phenol, the COH angle is calculated to be 108.9° (BLYP/6-31+G*). The oxygen atom corresponds thus to a nearly pure sp$^3$ hybrid and is not involved in resonance phenomena with the aromatic ring. According to our calculations, the radical shows a slightly shorter C−O bond than the anion (1.273 Å vs 1.290 Å at the BLYP/6-31+G* level of theory). The different bond lengths can be explained with different electrostatic interactions between the negatively charged oxygen atom and the ring system which has a positive net charge in the case of the radical and a negative net charge in the case of the anion. Concerning the C−O$^-$ bond, a certain similarity between the phenolate anion and the enolate anion ($CH_2$−CHO$^-$) can be expected. Applying the 6-31+G* basis set, we indeed find C−O bond lengths of 1.251, 1.274, 1.271, 1.285, and 1.284 Å in HF, B3LYP, CISD, MP2, and QCISD calculations, respectively. All these bond lengths are in perfect agreement with the results of the corresponding calculation of the phenolate anion.

Vibrational frequencies and $^{18}$O, $^{13}$C, and d$_5$ isotope shifts have been determined at different levels of theory. Frequencies and percentage of C−O stretching character of the a$_1$ modes $\nu_4$, $\nu_5$, and $\nu_6$ are listed in Table 3. In all calculations, modes containing considerable C−O stretching character are predicted above about 1340 cm$^{-1}$ and, thus, at least 70 cm$^{-1}$ higher in energy than the mode found in the FTIR spectrum.[2] For $\nu_4$ and $\nu_5$ we find a good agreement with FTIR data in all DFT calculations that use basis sets with added diffuse functions. The large deviations in the case of $\nu_6$ are surprising as in calculations on the phenoxyl radical[3] or on the benzosemiquinone radical anion[5,6] density functional methods gave good predictions of CC and CO stretching vibrations. The results of correlated ab initio methods such as MP2 or QCISD, however, deviate even more from experimental data. Various scale factors for MP2 frequencies had been proposed in the past. For triazole and tetrazole anions, optimal scale factors between 0.928 and 0.975 have been found for force constants determined by means of MP2/6-31++G** calculations.[10] A frequency scaling factor of 0.9427 for MP2/6-31G* frequencies was determined by Pople and co-workers.[38] If we apply the latter scaling factor for the scaling of our MP2/6-31+G* frequencies, we obtain modes at 1560, 1463, and 1324 cm$^{-1}$. This procedure underestimates the frequencies of modes $\nu_4$ and $\nu_5$ by ~20 cm$^{-1}$ but still overestimates $\nu_6$ by ~50 cm$^{-1}$. Adapting the force constant scaling factor of 0.928 to our frequency scaling, i.e., using a scaling factor of $\sqrt{0.928}$ for vibrational frequencies, results in vibrational modes at 1594, 1495, and 1353 cm$^{-1}$. This procedure thus leads to a good agreement with experimental data in the case of modes $\nu_4$ and $\nu_5$ but overestimates mode $\nu_6$ by 80 cm$^{-1}$.

All calculations agree in their prediction of the IR intensities of modes $\nu_4$, $\nu_5$, and $\nu_6$. According to the calculations, $\nu_4$ should be clearly stronger than the modes $\nu_5$ and $\nu_6$. This disagrees with the FTIR spectrum which exhibits strong absorptions at 1483 and 1273 cm$^{-1}$. Normal-mode analysis furthermore predicts a delocalization of the C−O stretching vibration among the modes $\nu_4$ and $\nu_5$. Calculated $^{18}$O, $^{13}$C, and d$_5$ isotope shifts are listed in Table 4. For $\nu_6$, $^{18}$O shifts between 11 and 17 cm$^{-1}$ are predicted. In the BLYP/6-31+G*, BLYP/6-31++G**, BLYP/aug-cc-pVTZ, MP2, and QCISD calculations, an acceptable agreement with the experimentally found $^{18}$O shift of 17 cm$^{-1}$ is achieved.[39] Due to the delocalization of the CO mode, the predicted $^{18}$O shifts of $\nu_5$ are too large in all calculations. For the $^{13}$C and d$_5$ shifts, large deviations from experimental data are found for most modes.

We have so far shown that DFT methods and all applied ab initio methods agree in their prediction of a CO bond with considerable double bond character. This clearly contradicts the experimental findings. We have shown that the disagreement between calculation and experiment cannot be simply attributed to a failure of DFT methods as stated previously.[3] The deviation from experiment can, however, most likely not be ascribed to multireference effects, either. These are expected to be relatively small as may be seen from the elongation of the CO bond of only ~0.01 Å upon going from SRCI to MRCI. Upon such a correction, none of the methods would predict a CO bond length longer than 1.3 Å. Also, DFT methods normally correct for multireference effects.[40] The QCISD

**TABLE 3: Selected Frequencies of a$_1$ Symmetry (in cm$^{-1}$) of the Phenolate Anion Determined with the BLYP Functional and Different Basis Sets and with the B3LYP, MP2, QCISD, and ACPF Methods Using the 6-31+G* Basis Set and Percentage of C−O Stretching Character**

| | | BLYP/ | | | | | | | | | | | | B3LYP/ | | MP2/ | | QCISD/ | | ACPF/ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | exp | 6-31+G* | | 6-31G** | | 6-31++G** | | 6-31++G**(f) | | aug-cc-pVDZ | | aug-cc-pVTZ | | 6-31+G* | | 6-31+G* | | 6-31+G* | | 6-31+G* | |
| mode | cm$^{-1}$ | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % | cm$^{-1}$ | % |
| $\nu_4$ | 1585,[a] 1592 or 1564[b] | 1564 | 9 | 1601 | 27 | 1561 | 9 | 1552 | 9 | 1578 | 16 | 1550 | 7 | 1629 | 11 | 1655 | 12 | 1654 | 5 | 1634 | 4 |
| $\nu_5$ | 1534,[a] 1483[b] | 1485 | 37 | 1525 | 36 | 1480 | 39 | 1473 | 39 | 1490 | 41 | 1472 | 38 | 1548 | 42 | 1552 | 33 | 1556 | 37 | 1539 | 33 |
| $\nu_6$ | 1264,[a] 1273[b] | 1357 | 40 | 1375 | 23 | 1351 | 37 | 1345 | 36 | 1343 | 28 | 1349 | 40 | 1409 | 33 | 1404 | 39 | 1411 | 41 | 1395 | 44 |

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

**TABLE 4: Selected Isotope Shifts of $a_1$ Modes (in $cm^{-1}$) of the Phenolate Anion Determined with the BLYP Functional and Different Basis Sets and with the B3LYP, MP2, QCISD, and ACPF Methods Using the 6-31+G* Basis Set**

| | exp | | | BLYP/ | | | | | | | | | | | | | | | | | B3LYP/6-31+G* | | | MP2/6-31+G* | | | QCISD/6-31+G* | | | ACPF/6-31+G* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 6-31+G* | | | 6-31+G** | | | 6-31++G** | | | 6-31++G**(f) | | | aug-cc-pVDZ | | | aug-cc-pVTZ | | | | | | | | | | | | | |
| mode | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ |
| $\nu_4$ | | 51[c] | 35,[a] 39 or 33[b] | 2 | 53 | 32 | 6 | 52 | 22 | 2 | 46 | 30 | 2 | 47 | 29 | 3 | 55 | 24 | 1 | 47 | 32 | 2 | 56 | 32 | 2 | 57 | 28 | 1 | 57 | 36 | 1 | 55 | 37 |
| $\nu_5$ | 2[c] | 47[a] | 131,[a] 100[b] | 10 | 37 | 45 | 12 | 41 | 40 | 10 | 37 | 42 | 10 | 37 | 40 | 12 | 40 | 37 | 10 | 36 | 43 | 12 | 39 | 40 | 9 | 40 | 48 | 10 | 39 | 46 | 8 | 38 | 51 |
| $\nu_6$ | 17[c] | 36[a] | 58,[a] 71[b] | 15 | 27 | 130 | 11 | 25 | 140 | 15 | 26 | 130 | 14 | 25 | 129 | 12 | 26 | 122 | 15 | 26 | 128 | 14 | 27 | 137 | 15 | 27 | 127 | 17 | 28 | 126 | 17 | 29 | 119 |

[a] Reference 1. [b] Reference 2. [c] Reference 39.

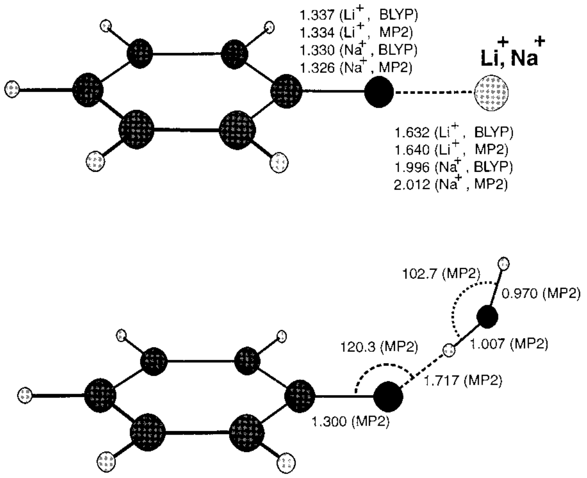

**Figure 3.** Structures of the optimized complexes. Bond lengths are given in angstroms and bond angles in degrees.

method, although being a single-reference method, can at least improve MP2 results in the case of multireference effects as had been shown for the $b_2$ mode of ozone.[41] To get an idea about the effect of the static correlation in the phenolate anion, some CASSCF and MCSCF calculations with the same 6-31+G* AO basis set were performed. The results of all these calculation are between the HF and the MP2 results. They do, therefore, not show an improvement over the MP2 result, what one would expect if strong static correlation effects would be present. A CASSCF(10,10) calculation resulting in nearly 16 000 determinants, for example, reveals a CO bond length of 1.285 Å and a $\nu_6$ of 1450 $cm^{-1}$. Since a general failure of ab initio methods in the case of the phenolate anion seems rather unlikely, we suggest that the experimentally determined spectroscopic properties correspond to the properties of a complex of the phenolate anion with either solvent molecules or with a counterion. Intermolecular interactions would thus weaken the CO bond and induce a downshift of the corresponding stretching mode.

**Effects of Intermolecular Interactions.** Resonance Raman experiments had been carried out in 0.1 M NaOH solutions. The vibrational spectrum of the phenolate anion can thus be expected to be perturbed due to intermolecular interactions. We have optimized structures of a phenolate−water, a phenolate−$Li^+$, and a phenolate−$Na^+$ complex. Structures of these complexes are depicted in Figure 3. At the MP2/6-31+G* level of theory, the complexation with water reveals modes with significant C−O stretching character at 1391 and 1546 $cm^{-1}$. Compared to the free molecule with modes exhibiting C−O stretching character at 1404 and 1552 $cm^{-1}$, only a weak perturbation due to the complexation is found. The C−O bond length is only slightly elongated by 0.012 Å to 1.300 Å.

MP2/6-31+G* calculations predict a lengthening of the C−O bond of 0.046 or 0.038 Å upon complexation with $Li^+$ or $Na^+$, respectively. The CO bond length becomes 1.334 Å ($Li^+$) or 1.326 Å ($Na^+$) and has thus significant single bond character. The vibrational frequencies of the modes $\nu_4$, $\nu_5$, and $\nu_6$ of the phenolate−$Li^+$ complex are predicted at 1665, 1548, and 1372 $cm^{-1}$, respectively. This corresponds to a downshift of mode $\nu_6$ of 32 $cm^{-1}$ due to the interaction with the positively charged counterion. $\nu_6$ is now a predominant C−O stretching mode (64%) which is downshifted by 22 $cm^{-1}$ upon $^{18}O$ labeling. In the case of the phenolate−$Na^+$ complex, we calculate frequencies of 1662, 1544, and 1365 $cm^{-1}$ for the three modes. We find an even larger downshift of $\nu_6$ of 39 $cm^{-1}$ upon complex-

**TABLE 5: Selected Isotope Shifts of $a_1$ Modes (in $cm^{-1}$) of the Phenolate Anion Complexed with a Counterion Determined at the BLYP/6-31+G* and MP2/6-31+G* Levels of Theory**

| | | | | phenolate−$Li^+$ complex | | | | | | phenolate−$Li^+$ complex | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | exp | | | BLYP | | | MP2 | | | exp | | | BLYP | | | MP2 | | |
| mode | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ | $^{18}O$ | $^{13}C$ | $d_5$ |
| $\nu_4$ | | 51[c] | 35,[a] 39 or 33[b] | 0 | 54 | 34 | 1 | 59 | 31 | | 51[a] | 35,[a] 39 or 33[b] | 0 | 54 | 33 | 1 | 58 | 31 |
| $\nu_5$ | 2[c] | 47[a] | 131,[a] 100[b] | 3 | 34 | 79 | 3 | 37 | 77 | 2[c] | 47[a] | 131,[a] 100[b] | 3 | 34 | 78 | 3 | 37 | 76 |
| $\nu_6$ | 17[c] | 36[a] | 58,[a] 71[b] | 23 | 25 | 84 | 22 | 26 | 89 | 17[c] | 36[a] | 58,[a] 71[b] | 19 | 25 | 86 | 18 | 25 | 90 |

**TABLE 6: Electrostatic Potential Derived Atomic Partial Charges of Phenoxyl Radical and Phenolate Anion (BLYP/6-31+G* Level)**

| | phenoxyl radical | | | phenolate anion | | |
|---|---|---|---|---|---|---|
| atom | MK | CHELP | CHELPG | MK | CHELP | CHELPG |
| O | −0.52 | −0.51 | −0.52 | −0.82 | −0.78 | −0.84 |
| C1 | 0.59 | 0.57 | 0.55 | 0.68 | 0.57 | 0.66 |
| C2 | −0.21 | −0.16 | −0.15 | −0.38 | −0.28 | −0.33 |
| C3 | −0.12 | −0.02 | −0.08 | −0.10 | 0.10 | −0.01 |
| C4 | −0.06 | −0.03 | −0.06 | −0.31 | −0.33 | −0.31 |

ation with $Na^+$. $\nu_6$ is now predicted to be the strongest infrared absorption in this spectral region. Applying the previously discussed scaling procedures results in vibrational frequencies of the phenolate−$Na^+$ complex for the modes $\nu_4$, $\nu_5$, and $\nu_6$ of 1576, 1456, and 1287 $cm^{-1}$, respectively, for a scaling factor of 0.9427[38] and of 1601, 1487, and 1315 $cm^{-1}$, respectively, for a scaling factor of $\sqrt{0.928}$.[10] Both procedures lead to an acceptable agreement with the FTIR data.

Similar results are also predicted by the BLYP/6-31+G* calculations. The C−O bond lengths of the $Li^+$ and $Na^+$ complexes are elongated by 0.047 and 0.040 Å, respectively, and become 1.337 and 1.330 Å, respectively. For the phenolate anion−$Li^+$ complex, the frequencies of the modes $\nu_4$, $\nu_5$, and $\nu_6$ are calculated at 1579, 1485, and 1323 $cm^{-1}$, respectively. Complexation with $Na^+$ reveals modes at 1574, 1481, and 1318 $cm^{-1}$. In agreement with the MP2 calculation, complexation with $Na^+$ induces a larger downshift of $\nu_6$ than complexation with $Li^+$. In both complexes, $\nu_6$ is a C−O stretching mode with more than 60% CO character, and it is the most intense infrared absorption. Due to its predominant C−O stretching mode character, the $^{18}O$ shift of $\nu_6$ is larger than in the free phenolate anion and amounts to 23 $cm^{-1}$ ($Li^+$) and 19 $cm^{-1}$ ($Na^+$). These shifts are in perfect agreement with the available FTIR data. Due to the loss of CO contribution in $\nu_5$, the corresponding $^{18}O$ shift is considerably smaller than in the free phenolate anion. It is calculated to be 3 $cm^{-1}$ at both levels of theory and independent of the nature of the counterion and agrees well with the corresponding shift of 2 $cm^{-1}$ found in the FTIR investigation. A summary of calculated isotope shifts of these complexes is given in Table 5. We can also note that $d_5$ shifts of $\nu_5$ and $\nu_6$ are considerably affected through the interaction with a counterion and that they shift closer to the experimental values. In contrast, $^{13}C$ shifts stay nearly unaffected and do still deviate considerably from experimental data.

Although our modeled phenolate anion−$Li^+$ and phenolate anion−$Na^+$ complexes reveal results that agree better with experimental data than those of the free phenolate anion, the deviation of the CO stretching mode frequency and of some of the $^{13}C$ and $d_5$ isotope shifts are still relatively large. This lets us suspect that the model of a phenolate anion−counterion complex is basically correct but that dimers or tetramers of such complexes are formed in solution. Indeed, both types of complexes have been found experimentally for lithium enolates[42] and lithium phenolates.[43] Calculations of such systems are currently in progress and show some very promising first results.[44]

## Conclusion

We have applied various quantum chemical methods for investigating the structure and vibrational spectrum of the phenolate anion. A reasonable agreement of predicted C−O bond lengths among correlated methods is obtained contrary to the supposition that DFT should fail for anions. The C−O bond length is predicted to be around 1.28−1.29 Å and is thus significantly shorter than the previously assumed 1.40 Å. The calculations predict thus a partial double bond character for the C−O bond of an isolated phenolate anion which is in disagreement with experimental data. A similar bond length has also been determined for the enolate anion. These findings can also be expected when mesomeric structures of the molecule are analyzed. Such resonance structures agree with electrostatic potential derived atomic partial charges.

Calculated IR frequencies agree well with recently reported FTIR results in the case of $\nu_4$ and $\nu_5$ but are considerably overestimated in the case of $\nu_6$, which was experimentally detected at 1273 $cm^{-1}$ but is predicted above 1350 $cm^{-1}$ by all applied methods. While some of the calculations predict $^{18}O$ shifts of $\nu_6$ that are close to the shift of 17 $cm^{-1}$ found in the FTIR investigation, the $^{18}O$ shifts of mode $\nu_5$ are significantly overestimated. The predicted distribution of the CO stretching vibration over at least two normal modes is therefore most likely not correctly predicted by these calculations.

Calculations of phenolate anion−$Li^+$ and phenolate anion−$Na^+$ complexes result in an elongated C−O bond and in a downshifted mode $\nu_6$ which becomes a predominant C−O stretching mode and is more intense than $\nu_4$ and $\nu_5$. The C−O bond thus loses some double bond character upon complexation with a counterion. Such a weakening of the C−O bond is necessary in order to achieve agreement with experimental data. Complexation also results in very good $^{18}O$ shifts of $\nu_5$ and $\nu_6$ and shifts the $d_5$ isotope shifts of these two modes closer to the experimental values.

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