



# Ab initio quantum chemical and experimental study of structure, harmonic vibrational frequencies and internal Ph–SO<sub>3</sub> torsion of benzenesulfonate anion

L. Pejov\*, M. Ristova, Z. Zdravkovski, B. Šoptrajanov

*Institut za hemija, PMF, Univerzitet "Sv. Kiril i Metodij", P.O. Box 162, 91001 Skopje, Macedonia*

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## Abstract

A combined quantum chemical and experimental study of the structure, harmonic vibrational frequencies, charge distribution and internal torsional motion of benzenesulfonate anion was performed. The geometry of the anion was optimized at the HF/3-21+G(d) and HF/6-31+G(d) levels of theory, followed by numerical harmonic vibrational analysis. Furthermore, the FT-IR spectra of several metal benzenesulfonate salts were recorded. The computed structural parameters of the anion at both levels of theory are in very good agreement with the X-ray data. Regarding the vibrational analysis, the HF/6-31+G(d) force field is significantly superior over the HF/3-21+G(d). On the basis of the HF/6-31+G(d) vibrational analysis, several important reassignments of the IR bands owing to the benzenesulfonate anion are suggested. The larger basis set methodology gives the correct order of conformational stabilities (staggered vs. eclipsed anion conformation), while the lower basis reproduces the experimental data only upon inclusion of the zero-point energy corrections. On the basis of ab initio HF/6-31+G(d) energetics, the torsional energy levels of the Ph–SO<sub>3</sub> rotor were computed within a one-dimensional approach, diagonalizing the torsion Hamiltonian in the free-rotor basis. Both the Mulliken and the NPA charge-partitioning schemes predict a strong delocalization of the anionic charge over the phenyl ring, while the electrostatic potential based schemes (CHelp, CHelpG and MK) predict only a slight delocalization. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Benzenesulfonate anion; Ab initio force field; Internal torsion; Ab initio charge distribution; FT-IR spectroscopy

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## 1. Introduction

In recent years, there has been an increased interest in mixed inorganic–organic compounds with layered structures. This is primarily because of their potential application as ion exchange and intercalation materials, as well as hosts for size and shape selective catalysts [1]. The structures of the investigated series

of isostructural metal benzenesulfonates ( $M \in \{Co, Ni, Mn, Cu\}$ ) hexahydrates [2–4] have been shown to contain alternating layers of benzenesulfonate and  $[M(H_2O)_6]^{2+}$  ions, making them interesting from a purely structural viewpoint. On the other hand, the previous vibrational spectroscopic studies of hydrates of metal salts containing the benzenesulfonate anion [5] have been mainly devoted to the vibrational spectra of the water molecules. A complete vibrational assignment does not seem to have been done for the benzenesulfonate anion, except the normal coordinate treatment study reported by Uno

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\* Corresponding author. Tel.: +389-91-117-055; fax: +389-91-117-865.

*E-mail address:* ljupcop@iunona.pmf.ukim.edu.mk (L. Pejov).

Table 1

Ab initio HF/3-21+G(d) and HF/6-31+G(d) bond lengths, along with the crystallographic data for copper benzenesulfonate hexahydrate [2]

Bond	Distances (Å)		
	HF/6-31+G(d)	HF/3-21+G(d)	Experimental
C <sup>1</sup> –C <sup>2</sup>	1.388	1.386	1.377
C <sup>1</sup> –C <sup>6</sup>	1.388	1.386	1.389
C <sup>5</sup> –C <sup>6</sup>	1.389	1.387	1.397
C <sup>2</sup> –C <sup>3</sup>	1.389	1.387	1.388
C <sup>3</sup> –C <sup>4</sup>	1.389	1.388	1.372
C <sup>4</sup> –C <sup>5</sup>	1.389	1.388	1.365
C <sup>1</sup> –S	1.799	1.783	1.764
S–O <sup>1</sup>	1.453	1.467	1.457
S–O <sup>2</sup>	1.453	1.467	1.454
S–O <sup>3</sup>	1.453	1.467	1.463
C <sup>2</sup> –H	1.074	1.072	–
C <sup>3</sup> –H	1.077	1.074	–
C <sup>6</sup> –H	1.074	1.072	–
C <sup>5</sup> –H	1.077	1.074	–
C <sup>4</sup> –H	1.077	1.075	–

et al. [6]. However, owing to the well-known deficiencies of the classical NCT methods, a more rigorous vibrational analysis of these anionic species is obviously required.

In this paper, we report an ab initio HF/3-21+G(d) and HF/6-31+G(d) study of the structure, harmonic

Table 2

Ab initio HF/3-21+G(d) and HF/6-31+G(d) bond angles, along with the crystallographic data for copper benzenesulfonate hexahydrate [2]

Bond angles	Angles (°)		
	HF/6-31+G(d)	HF/3-21+G(d)	Experimental
C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup>	119.6	119.9	120.8
C <sup>3</sup> –C <sup>2</sup> –C <sup>1</sup>	120.2	120.1	119.6
C <sup>4</sup> –C <sup>3</sup> –C <sup>2</sup>	120.2	120.1	119.8
C <sup>5</sup> –C <sup>4</sup> –C <sup>3</sup>	119.7	119.7	121.0
C <sup>6</sup> –C <sup>5</sup> –C <sup>4</sup>	120.2	120.1	120.1
C <sup>1</sup> –C <sup>6</sup> –C <sup>5</sup>	120.2	120.1	118.6
C <sup>1</sup> –S–O <sup>1</sup>	104.4	104.7	106.8
C <sup>1</sup> –S–O <sup>2</sup>	104.4	104.7	106.3
C <sup>1</sup> –S–O <sup>3</sup>	104.4	104.7	106.6
O <sup>1</sup> –S–O <sup>2</sup>	114.0	113.8	112.5
O <sup>1</sup> –S–O <sup>3</sup>	114.0	113.8	112.0
O <sup>2</sup> –S–O <sup>3</sup>	114.0	113.8	112.1
C <sup>2</sup> –C <sup>1</sup> –S	120.1	120.0	119.5
C <sup>6</sup> –C <sup>1</sup> –S	120.1	120.0	119.6

vibrational frequencies, charge distribution and internal Ph–SO<sub>3</sub> torsional motion of benzenesulfonate anion, along with an experimental FT-IR study of several metal(II) benzenesulfonates hexahydrates. Closely related to the present study is our previous paper on the ab initio HF SCF vibrational analysis of the 4-methylbenzenesulfonate anion [7].

## 2. Experimental

The Cu(II), Co(II) and Ni(II) benzenesulfonate hexahydrates were prepared as reported in the literature [2]. Room (RT) and low-temperature (LT, ~100 K) FT-IR spectra of the mentioned compounds (KBr pellets) were recorded on a Perkin–Elmer System 2000 FT-IR interferometer. A Graseby Specac variable temperature cell was used for the low-temperature measurements.

## 3. Computational details

The computational study of benzenesulfonate anion was performed using the restricted (closed-shell) Hartree–Fock Self-Consistent Field (RHF SCF) formalism [8], with the 3-21+G(d) and 6-31+G(d) basis sets [9–19]. These basis sets are supplemented with diffuse functions [20], for a better description of the anionic wavefunction. The smaller basis contains polarization functions on only the sulfur atom, while the larger one includes them on all the heavy atoms. Full geometry optimizations of the anion were performed in redundant internal coordinates, with Berny's optimization algorithm [21] (computing the energy derivatives analytically) at the mentioned levels of theory, without any symmetry restrictions. The stationary points found on the molecular potential energy hypersurfaces were characterized with standard harmonic vibrational analysis, accounting for a number of imaginary frequencies, as well as a number of negative eigenvalues of the Hessian matrix. Harmonic vibrational analyses were performed by numerically computing the second energy derivatives with respect to nuclear coordinates. No scaling in the ab initio force field has been done. All computations were performed using the GAUSSIAN 94 series of programs [22].

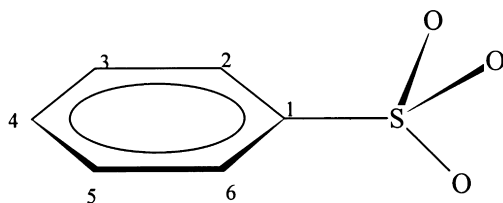


Fig. 1. The HF/6-31+G(d) minimum on the potential energy hypersurface of benzenesulfonate anion, together with the atomic numbering.

## 4. Results and discussion

### 4.1. Structure and conformational stability

The optimized structural parameters of the anion (for the more stable conformation, see the text below) at both levels of theory are given in Tables 1 and 2, along with the corresponding crystallographic data [2,23]. The HF/6-31+G(d) minimum on the potential energy hypersurface of benzenesulfonate anion together with the atomic numbering is shown in Fig. 1. As can be seen, in comparison to the 4-methylbenzenesulfonate (*p*-toluenesulfonate) anion [7], the S–O bonds in the present case are slightly shorter, while the C–S bond is somewhat longer.

The agreement between the theoretically calculated and the experimentally obtained structural parameters of benzenesulfonate anion is very good. The discrepancies between the theoretical predictions and the experimental data are mainly due to the following reasons. First, the theoretical calculations refer to a free (isolated) anion, while experimental data were obtained by single crystal X-ray crystallography. Further, the Hartree–Fock (HF) (single-determinant) theory does not include the dynamical electron correlation effects explicitly [24]. However, as stated by Boese et al. [25], on the basis of *ab initio* MO calculations one may rationalize and even verify the X-ray crystallographically determined structures. Comparisons between theoretical and X-ray experimental geometries are therefore of significant value, especially when a vibrational analysis is in question.

The higher basis level (6-31+G(d)) predicts that the staggered conformation (one of the S–O bonds lies in the plane perpendicular to the phenyl group plane) is more stable than the eclipsed conformation (one of the S–O bonds lies within the phenyl group

plane). This prediction is in agreement with the crystallographic data. The rotation barrier calculated at this level is  $214.6 \text{ J mol}^{-1}$  without, and  $28.2 \text{ J mol}^{-1}$  with an inclusion of the zero-point energy (ZPE) corrections. Such a low barrier is somewhat expected owing to the large C–S distance (see Section 4.3). The 3-21+G(d) level fails to explain the details of the potential energy hypersurface correctly. Only after inclusion of the ZPE corrections the correct trend is obtained, with a rotational barrier of  $7.7 \text{ J mol}^{-1}$ . In order to estimate at least qualitatively the effect of electron correlation on the rotation barrier in this system, and to get further evidence of the energy difference between the conformers, single-point energy calculations on the HF/6-31+G(d) optimized geometries were performed with larger basis sets using both the HF and the density functional theory (DFT) approach. The higher level HF study, using the rather large triple-zeta quality 6-311++G(d,p) basis set, yields the rotational barrier of  $292.9 \text{ J mol}^{-1}$ . Within the DFT, Becke's three-parameter hybrid method [26] with the Lee–Yang–Parr [27,28] correlation functional (B3LYP) was applied within the 6-31+G(d) and the 6-311++G(d,p) basis sets. The DFT level of theory again predicts the same order of stability of the conformers as the HF/6-31+G(d) level. The rotational barriers are (of course, without a ZPE correction)  $62.4$  and  $234.8 \text{ J mol}^{-1}$ , respectively. One should, at least intuitively, expect that the B3LYP/6-31+G(d) full geometry optimizations would lead to an even lower rotational barrier, since the inclusion of electron correlation should predict longer bond lengths compared to those obtained within the HF theory. However, a detailed density functional study of the structure, vibrational analysis and conformational stability of this system, using both BLYP (gradient corrected method based on the Becke exchange [29] with LYP correlation functional) and B3LYP combination of the exchange and correlation functionals is near completion [30].

The total energy of the benzenesulfonate anion (the more stable conformation), calculated at the HF/3-21+G(d) level without inclusion of the ZPE correction is  $-847.971565$  hartrees, while when this correction is included the value reduces to  $-847.859379$  hartrees. The higher basis yields the value of  $-852.225921$  hartrees without, and  $-852.114585$  hartrees with the inclusion of the ZPE

Table 3

Ab initio HF/6-31+G(d) and 3-21+G(d) harmonic vibrational frequencies (scaled by a constant factor of 0.9), IR intensities and approximate description of normal modes

HF/6-31+G(d)			HF/3-21+G(d)		
$\nu$ (cm <sup>-1</sup> )	$I$ (km mol <sup>-1</sup> )	Approximate description	$\nu$ (cm <sup>-1</sup> )	$I$ (km mol <sup>-1</sup> )	Approximate description
3061.8	3.3	$\nu_{\text{PhH}}$	3054.3	4.5	$\nu_{\text{PhH}}$
3060.9	10.0	$\nu_{\text{PhH}}$	3038.0	8.7	$\nu_{\text{PhH}}$
3024.6	62.5	$\nu_{\text{PhH}}$	3017.2	44.7	$\nu_{\text{PhH}}$
3010.5	49.4	$\nu_{\text{PhH}}$	3003.6	36.7	$\nu_{\text{PhH}}$
2996.2	0.8	$\nu_{\text{PhH}}$	2988.8	1.4	$\nu_{\text{PhH}}$
1609.2	1.2	$\nu_{\text{CC}}$	1579.8	0.3	$\nu_{\text{CC}}, \delta_{\text{PhH}}$
1593.8	1.9	$\nu_{\text{CC}}$	1561.9	1.6	$\nu_{\text{CC}}, \delta_{\text{PhH}}$
1485.4	4.6	$\delta_{\text{PhH}}$	1487.0	6.9	$\delta_{\text{PhH}}, \nu_{\text{CC}}$
1437.1	12.3	$\delta_{\text{PhH}}$	1440.3	16.6	$\delta_{\text{PhH}}, \nu_{\text{CC}}$
1311.2	0.2	$\delta_{\text{PhH}}$	1339.0	2.8	$\delta_{\text{PhH}}$
1206.4	93.9	$\nu_{\text{CC}}, \delta_{\text{PhH}}, \nu_{\text{SO}_3}^{\text{as}}$	1211.0	4.9	$\nu_{\text{CC}}, \delta_{\text{PhH}}$
1188.2	247.9	$\delta_{\text{PhH}}, \nu_{\text{SO}_3}^{\text{as}}$	1187.6	4.6	$\delta_{\text{PhH}}$
1186.6	397.8	$\nu_{\text{SO}_3}^{\text{as}}$	1156.7	325.4	$\nu_{\text{SO}_3}^{\text{as}}, \delta_{\text{PhH}}$
1161.3	3.9	$\delta_{\text{PhH}}$	1148.3	412.4	$\nu_{\text{SO}_3}^{\text{as}}$
1112.0	89.3	$\nu_{\text{CS}}, \delta_{\text{PhH}}$	1128.4	27.1	$\nu_{\text{CC}}, \delta_{\text{PhH}}$
1094.9	5.1	$\nu_{\text{CC}}, \delta_{\text{PhH}}$	1114.6	63.2	$\delta_{\text{CCC}}, \delta_{\text{PhH}}$
1052.7	5.4	$\nu_{\text{CC}}, \delta_{\text{PhH}}$	1076.6	0.9	$\gamma_{\text{PhH}}$
1013.5	20.4	$\delta_{\text{CCC}}, \nu_{\text{SO}_3}^{\text{s}}$	1057.0	1.0	$\gamma_{\text{PhH}}$
1000.7	0.1	$\gamma_{\text{PhH}}$	1055.8	11.8	$\delta_{\text{CCC}}, \delta_{\text{PhH}}$
999.5	0.2	$\gamma_{\text{PhH}}$	1023.7	2.6	$\delta_{\text{CCC}}, \delta_{\text{PhH}}$
992.3	187.5	$\nu_{\text{SO}_3}^{\text{as}}, \nu_{\text{CC}}$	1000.7	2.3	$\gamma_{\text{PhH}}$
975.5	8.3	$\nu_{\text{CC}}$	981.2	1.3	$\nu_{\text{CC}}(\text{breathe})$
940.1	1.3	$\gamma_{\text{PhH}}$	954.6	252.6	$\nu_{\text{SO}_3}^{\text{s}}, \delta_{\text{CCC}}$
858.2	0.1	$\gamma_{\text{PhH}}$	898.9	0.5	$\gamma_{\text{PhH}}$
760.0	41.1	$\gamma_{\text{PhH}}$	813.9	29.3	$\gamma_{\text{PhH}}$
715.5	106.5	$\delta_{\text{SO}_3}^{\text{s}}, \delta_{\text{CCC}}$	729.5	99.9	$\gamma_{\text{PhH}}$
690.3	59.0	$\gamma_{\text{PhH}}$	723.1	67.0	$\delta_{\text{CCC}}, \delta_{\text{SO}_3}^{\text{s}}$
608.3	0.4	$\delta_{\text{CCC}}$	635.5	0.4	$\delta_{\text{CCC}}$
607.3	176.4	$\delta_{\text{CCC}}, \delta_{\text{SO}_3}^{\text{s}}$	609.4	219.1	$\delta_{\text{SO}_3}^{\text{s}}, \delta_{\text{CCC}}$
558.1	53.0	$\tau_{\text{CCCC}}, \gamma_{\text{PhH}}, \delta_{\text{SO}_3}^{\text{as}}$	569.1	54.7	$\tau_{\text{CCCC}}, \gamma_{\text{PhH}}$
533.8	24.5	$\delta_{\text{SO}_3}$	524.2	27.8	$\delta_{\text{SO}_3}^{\text{as}}$
472.7	2.7	$\delta_{\text{SO}_3}^{\text{as}}$	481.1	9.8	$\tau_{\text{CCCC}}, \delta_{\text{SO}_3}^{\text{as}}$
408.1	0.0	$\tau_{\text{CCCC}}$	425.5	0.1	$\tau_{\text{CCCC}}$
355.1	1.8	$\delta_{\text{SO}_3}, \delta_{\text{CCC}}$	360.5	2.2	$\delta_{\text{Scc}}, \delta_{\text{SO}_3}^{\text{as}}$
298.6	2.1	$\delta_{\text{SO}_3}, \delta_{\text{CCC}}$	300.0	8.7	$\nu_{\text{CS}}$
288.7	4.3	$\tau_{\text{CCCC}}$	298.8	0.1	$\delta_{\text{SO}_3}, \tau_{\text{CCCC}}$
178.6	0.9	$\delta_{\text{CCC}}$	181.5	6.8	$\delta_{\text{Scc}}, \delta_{\text{SO}_3}$
123.3	0.4	$\tau_{\text{Sccc}}$	138.1	0.5	$\tau_{\text{CCCC}}$
12.2	0.0	$\tau_{\text{SO}_3}$	24.9	0.1	$\tau_{\text{SO}_3}$

correction. Thus, according to the energy-based criterion, the improvement of the results with the usage of higher basis is significant.

#### 4.2. Vibrational analysis

Both conventional single-determinant based HF

SCF ab initio methodologies, and the ones including dynamical electron correlation effects (based on the many-body perturbation theory-such as MP2, or on the DFT) are very useful for vibrational analysis of polyatomic species [31]. Although the correlation methods are superior in many aspects over the HF, the scaled HF values are often in better agreement

Table 4

Solid state FT-IR data for Co, Ni and Cu benzenesulfonates hexahydrates and Na benzenesulfonate along with the HF/6-31+G(d) calculated harmonic vibrational frequencies (scaled by a constant factor of 0.9) and approximate description of normal modes

Experimental data					HF/6-31+G(d) force field
Co	Ni	Cu	Na	$\nu$ (cm <sup>-1</sup> )	Approximate description
3065	3066	3063	3060	3061.8	$\nu_{\text{PhH}}$
			3050	3060.9	$\nu_{\text{PhH}}$
3019		3020		3024.6	$\nu_{\text{PhH}}$
		2990		3010.5	$\nu_{\text{PhH}}$
		2950	2920	2996.2	$\nu_{\text{PhH}}$
1595	1600			1609.2	$\nu_{\text{CC}}$
		1588		1593.8	$\nu_{\text{CC}}$
1480	1481	1483	1485	1485.4	$\delta_{\text{PhH}}$
1448	1448	1446	1442	1437.1	$\delta_{\text{PhH}}$
1310	1314	1314	1315	1311.2	$\delta_{\text{PhH}}$
1297		1221	1200	1206.4	$\delta_{\text{PhH}}, \nu_{\text{SO}_3}^{\text{as}}$
1190	1189	1185		1188.2	$\delta_{\text{PhH}}, \nu_{\text{SO}_3}^{\text{as}}$
1155			1170	1186.6	$\nu_{\text{SO}_3}^{\text{as}}$
		1160	1140	1161.3	$\delta_{\text{PhH}}$
1132	1132	1131	1130	1112.0	$\nu_{\text{CS}}, \delta_{\text{PhH}}$
1108	1101	1075	1070	1094.9	$\nu_{\text{CC}}, \delta_{\text{PhH}}$
1074	1075	1041	1050	1052.7	$\nu_{\text{CC}}, \delta_{\text{PhH}}$
		1020	1025	1013.5	$\delta_{\text{CCC}}, \nu_{\text{SO}_3}^{\text{s}}$
1041	1040		1020	1000.7	$\gamma_{\text{PhH}}$
1020	1020	998		999.5	$\gamma_{\text{PhH}}$
997	997		990	992.3	$\nu_{\text{SO}_3}^{\text{as}}, \nu_{\text{CC}}$
977		977	980	975.5	$\nu_{\text{CC}}$
		925	925	940.1	$\gamma_{\text{PhH}}$
858	857	828	845	858.2	$\gamma_{\text{PhH}}$
766	820	762	755	760.0	$\gamma_{\text{PhH}}$
730	763	733	740	715.5	$\delta_{\text{SO}_3}^{\text{s}}, \delta_{\text{CCC}}$
710	731	689	690	690.3	$\gamma_{\text{PhH}}$
689	689			608.3	$\delta_{\text{CCC}}$
611	610	609	575	607.3	$\delta_{\text{CCC}}, \delta_{\text{SO}_3}^{\text{s}}$
572	579	581	560	558.1	$\gamma_{\text{PhH}}, \delta_{\text{SO}_3}^{\text{as}}, \tau_{\text{CCCC}}$
557		538		533.8	$\delta_{\text{SO}_3}^{\text{s}}$
490	485	482	485	472.7	$\delta_{\text{SO}_3}^{\text{as}}$
409		429	394	408.1	$\tau_{\text{CCCC}}$
386		380		355.1	$\delta_{\text{SO}_3}, \delta_{\text{CCC}}$
				298.6	$\delta_{\text{SO}_3}, \delta_{\text{CCC}}$
				288.7	$\tau_{\text{CCCC}}$
				178.6	$\delta_{\text{CCC}}$
				123.3	$\tau_{\text{SCCC}}$
				12.2	$\tau_{\text{SO}_3}$

with the experimental results when predicting the harmonic vibrational frequencies. It thus seems that the scaled HF force fields will not lose in actuality possibly until more exact functionals are constructed for the DFT approaches. In order to account for the dynamical electron correlation effects, as well as for the basis set truncation errors, in the present study the

obtained HF harmonic vibrational frequencies were scaled with a single constant factor (0.9). Theoretical results, along with the experimental ones for the studied metal benzenesulfonate salts are summarized in Tables 3 and 4.

It has been recognized that for molecules with more than 12 atoms the frequencies based on the HF/3-21G

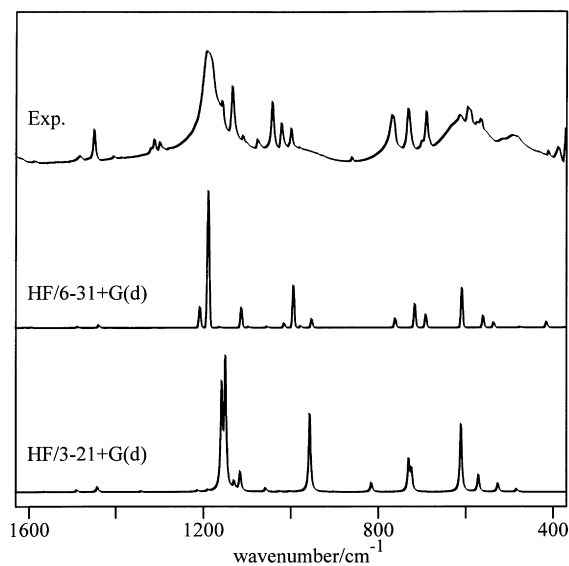


Fig. 2. Experimental IR spectrum of Co benzenesulfonate hexahydrate, together with those of theoretical HF/6-31+G(d) and HF/3-21+G(d).

(or HF/3-21G(d)) force fields are very valuable [32], and that even for particular cases, very little is gained [33–35] by the usage of a larger basis set (such as 6-31G and 6-31G(d)). In the present study, we compared the performances of the two basis sets

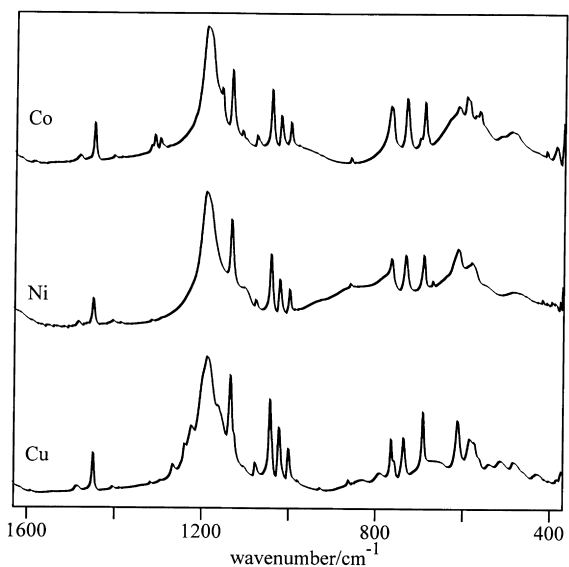


Fig. 3. Experimental IR spectra of Co, Ni and Cu benzenesulfonates hexahydrates.

(supplemented with diffuse functions for a better description of the anionic wavefunction). The theoretical 3-21+G(d) and 6-31+G(d) spectra, along with the experimental one (for cobalt(II) benzenesulfonate hexahydrate) are shown in Fig. 2. The experimental FT-IR spectra of the hexahydrates of Co, Ni and Cu benzenesulfonates are shown in Fig. 3. It is obvious, from both Fig. 2 and Tables 3 and 4, that for the present case the 6-31+G(d) results are significantly superior over the 3-21+G(d). This may arise both from a more flexible description of the core and valence electrons with the larger basis, as well as from the inclusion of polarization functions on all heavy atoms (the 3-21+G(d) basis contains d functions only on the sulfur atom).

On the basis of the ab initio force field calculations, several important reassignments of vibrational bands are proposed in this work. The band appearing at about  $1200\text{ cm}^{-1}$  in the IR spectra of metal benzenesulfonate salts was previously attributed to the antisymmetric  $\text{SO}_3$  stretching, while the one at about  $1190\text{ cm}^{-1}$  was left unassigned. The HF/6-31+G(d) results suggest that both bands should be attributed to complex modes which include ring CH bendings, although the antisymmetric  $\text{SO}_3$  stretching coordinate contributes significantly to these modes as well (see Tables 3 and 4 for more detailed descriptions). The band appearing at about  $1180\text{ cm}^{-1}$  according to the HF/6-31+G(d) force field may be described as a pure antisymmetric  $\text{SO}_3$  stretching mode. On the other hand, the band at  $\sim 1130\text{ cm}^{-1}$ , previously assigned to the symmetric  $\text{SO}_3$  stretch, is now attributed predominantly to the C–S stretching mode. The band appearing at  $\sim 1015\text{ cm}^{-1}$ , in previous works assigned as due (predominantly) to a C–C ring stretching mode is now attributed to a ring bending mode, with significant contribution of the symmetric  $\text{SO}_3$  stretching coordinate. The intensive band at  $\sim 990\text{ cm}^{-1}$  is attributed to the symmetric  $\text{SO}_3$  stretching mode. Contrary to the results presented previously [6], both the antisymmetric and symmetric  $\text{SO}_3$  stretching modes in the case of benzenesulfonate salts appear at somewhat higher frequencies compared to those of *p*-toluenesulfonate. Since the bands at  $\sim 1200$ ,  $1190$  and  $1180\text{ cm}^{-1}$  are the strongest ones in the IR spectra, these reassignments are in line with the intuitive expectations. An even more important conclusion based on quantum

chemical calculations concerns the order of appearance of bands due to the  $\text{SO}_3$  bending modes. According to the normal coordinate analysis (on which previous assignments were mainly based), the antisymmetric  $\text{SO}_3$  bending should appear at higher frequencies than the symmetric one. Contrary to this statement, according to the ab initio results for the benzenesulfonate anion, the band at  $\sim 730 \text{ cm}^{-1}$  is assigned to the symmetric  $\text{SO}_3$  bending, and that at  $\sim 470 \text{ cm}^{-1}$  to the antisymmetric  $\text{SO}_3$  bending mode. The last coordinate contributes significantly to the band appearing at  $\sim 560 \text{ cm}^{-1}$ , while that of  $\delta_{\text{SO}_3}^s$  contributes to the band appearing at  $\sim 610 \text{ cm}^{-1}$ . Such an order of the bands due to the  $\text{SO}_3$  bending modes is in agreement with recent calculations [36,37] for several molecular and ionic systems which include the  $\text{SO}_3$  group in their structures.

Thus, we believe that all these reassignments are legitimate despite the fact that they are based on theoretical results for an idealized “free” ion, whereas the experimental frequencies are for a solid-state sample where the intermolecular interactions certainly play an important role.

Regarding the phenyl ring, it is particularly interesting to study the performances of the uncorrelated HF methodology in predicting the frequencies that are reminiscent of  $\nu_4$  and  $\nu_{14}$  modes in benzene (according to Wilson’s notation) [38]. The  $\nu_4$  ( $\text{B}_{2g}$ ) mode is the so-called ring puckering vibration i.e. it corresponds to a ring torsional motion, while  $\nu_{14}$  ( $\text{B}_{2u}$ ) is the “Kekule” type vibration [39,40], recognized in the language of electronic structure theory as a multi-configurational problem [41–43]. In the case of benzene and some of its monosubstituted derivatives, the mentioned modes have been shown to be particularly sensitive to electron correlation effects as well as to the basis set size [38,41,42]. Even the MP2 methodology using the standard 6-31G(d,p) basis fails to describe them correctly [38]. It has been shown that rather large basis sets of the TZ2P + f quality are required for successful treatment of this problem [38]. On the other hand, the density functional BLYP methodology has been shown to be capable of handling both vibrations with sufficient accuracy even with a DZP quality basis set [41], implying a correct description of the correlated density provided by this gradient-corrected DFT method. In the case of benzenesulfonate anion, the HF/6-31+G(d)

methodology predicts a value of  $1206.4 \text{ cm}^{-1}$  for the harmonic vibrational frequency of the multireference  $\nu_{14}$  ring mode, which is some  $100 \text{ cm}^{-1}$  lower than the value measured for benzene. Since the frequency of this mode is not expected to be such significantly affected upon monosubstitution [39,42], one is lead to a conclusion that the HF/6-31+G(d) force field does not allow an accurate description of this vibration for the present case. It is unfortunately not possible to make an unambiguous assignment of this mode in the vibrational spectra of the studied compounds, however, it seems that the predicted frequency is significantly lower than expected. The predicted HF/3-21+G(d) frequency of the  $\nu_{14}$  mode is  $1211.0 \text{ cm}^{-1}$ , rather close to the higher level value. On the other hand, the HF/6-31+G(d) and HF/3-21+G(d) frequencies of the  $\nu_4$  ring puckering mode for benzenesulfonate anion are, correspondingly,  $558.1$  and  $569.1 \text{ cm}^{-1}$ . These values are about  $150 \text{ cm}^{-1}$  lower than the measured frequency for benzene. Since this mode is also expected to be only slightly sensitive to substituent effects [39,42], the predicted frequencies seem to have large discrepancies when compared with the experimentally expected ones. It is also a rather difficult task to precisely assign this mode in the IR spectra of the studied compounds, since other, significantly more intensive bands appear in the same spectral region. However, the general conclusion on the inadequacy of the single-determinant HF theory in prediction of the harmonic vibrational frequencies for such multireference modes is supported by presented results.

#### 4.3. Analysis of the internal torsional motion

Since the rigid  $\text{C}_6\text{H}_5$  frame is characterized by  $C_{2v}$  symmetry, the lowest term in a Fourier expansion of the  $\text{SO}_3$  torsional potential has six-fold symmetry [44,45]. The Schrödinger equation for the internal hindered rotation of the  $\text{SO}_3$  group within the one-dimensional rigid rotor approximation is thus of the form [46]:

$$\hat{H}\Psi(\varphi) = E\Psi(\varphi) \quad (1)$$

where [47–49]:

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{d^2}{d\varphi^2} + \frac{V_6}{2} [1 - \cos(6\varphi)]. \quad (2)$$

Table 5  
Ab initio HF/6-31+G(d) SO<sub>3</sub> torsional states for the free benzene-sulfonate anion

State	$E$ (cm <sup>-1</sup> )
0a <sub>1</sub> '	0.00
1e''	0.11
2e'	0.46
3a <sub>2</sub> ''	7.38
3a <sub>1</sub> ''	17.94
4e'	18.18
5e''	18.90

The sign of  $V_6$  “fixes” the most stable conformer (staggered if  $V_6 < 0$ , and eclipsed if  $V_6 > 0$ ). In the previous equation,  $I$  is the reduced moment of inertia of the rotor, while  $\varphi$  is the torsional angle. The Schrödinger equation (1) may be in principle solved analytically, as it reduces to a Mathieu equation [50]. However, it is much more convenient to obtain the torsional energy levels by standard diagonalization procedures [44–49], using the free rotor basis functions of the form [51]:

$$\psi_m(\varphi) = \frac{1}{\sqrt{2\pi}} \exp(im\varphi). \quad (3)$$

Although, rigorously speaking,  $m$  is not a good

quantum number for the present problem, it is still useful [52]. The internal rotation energy levels are usually denoted by a combination of the rotational quantum number  $m$  (characterizing the free rotor wavefunction) and the symmetry species of the permutation inversion group ( $G_{12}$  for the present case). The six-fold perturbation leaves the degeneracy of the  $m = \pm 1, \pm 2, \pm 4$  and  $\pm 5$  states, while the degeneracy is lifted for the  $m = \pm 3$  and  $\pm 6$  pairs. In order of increasing the energy, the states are: 0a<sub>1</sub>', 1e'', 2e', 3a<sub>2</sub>'', 3a<sub>1</sub>'', 4e', 5e'', 6a<sub>2</sub>', 6a<sub>1</sub>' etc [52].

Based on the previously mentioned energy data (at HF/6-31+G(d) level) for the staggered and eclipsed conformers, the value of  $-1.63 \times 10^{-4}$  hartrees ( $-35.88$  cm<sup>-1</sup>) was obtained for the  $V_6$  parameter. The torsional energy levels were obtained by diagonalization of the Hamiltonian matrix in the basis (3) (11 basis functions were considered enough for the present purposes). The calculated torsional potential and the corresponding energy levels are presented in Table 5 and Fig. 4. The (small) rotational barriers as well as the phases of the six-fold potentials in molecular/ionic systems with local six-fold symmetry may be attributed solely to steric interactions (or other subtle effects) [52]. The resonance modulation effects [52] cannot be considered as dominant in six-fold

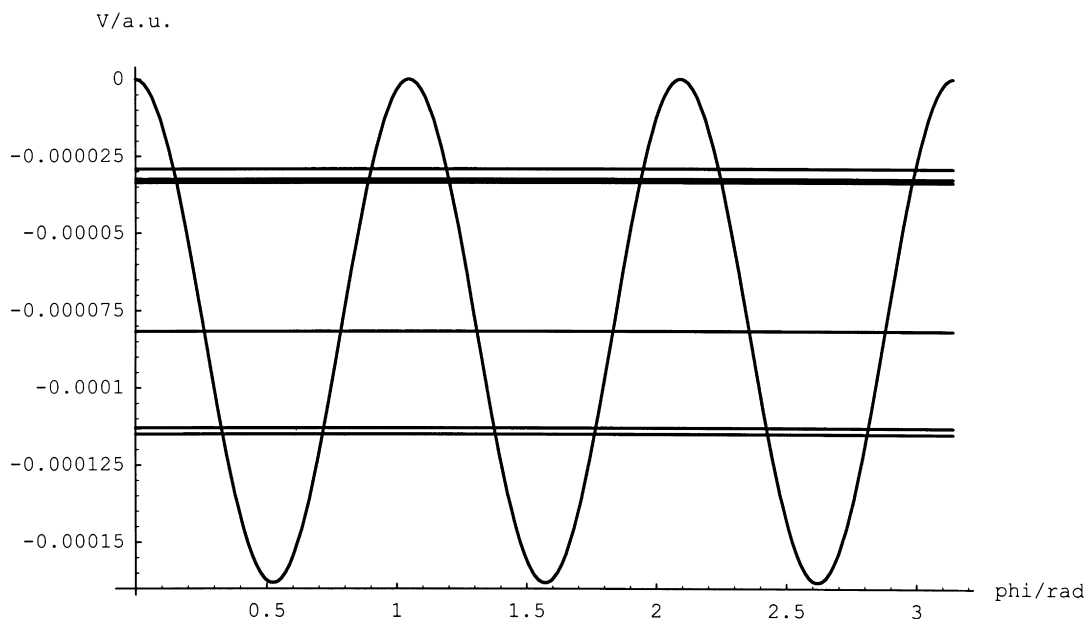


Fig. 4. The HF/6-31+G(d) torsional potential of the Ph-SO<sub>3</sub> rotor and the corresponding energy states.



Table 6  
Ab initio computed fragmental charges from the HF/6-31+G(d) density, using various charge-assignment algorithms

Fragment	$Q/e$ (HF/6-31+G(d))				
	Mulliken	NPA	CHelp	CHelpG	MK
Phenyl	-0.48	-0.32	-0.16	-0.16	-0.13
SO <sub>3</sub>	-0.52	-0.68	-0.84	-0.84	-0.87

ground state cases, since these effects favor the eclipsed conformer as energetically more stable, which is contrary to most experimental data for such systems. However, it should be noted that the SO<sub>3</sub> torsional potential could be significantly modified in the solid state, especially because of the hydrogen bonding interactions. In a solid matrix, the internal rotation modes are in fact a part of a collective crystal dynamics, exhibiting effects such as dispersion and coupling with other modes of the same symmetry.

#### 4.4. Charge distribution

The total (net,  $\sigma + \pi$ ) charge distribution in molecular/ionic species is a very important parameter on the basis of which several important properties may be discussed, such as: hydrogen bond proton acceptor ability [53,54], basicity, character (dipolar vs. zwitterionic) of the studied species [40]. It is most common and close to classical chemical intuition to describe the total (continuous) charge distributions via the discrete sets of values assigned to atomic centers in the molecular system. However, it is well known that since the *atomic charges* are not quantum-mechanical observables (i.e. there is no quantum-mechanical operator corresponding to this physical property), no unique method based on the first-principles may be established for their calculation [55]. Several algorithms have been proposed for partitioning the total ab initio charge distribution into atomic charges [56–61]. The first, and probably the most commonly used one is the Mulliken partitioning scheme [56]. Although the Mulliken algorithm has several well-known and well-documented weaknesses [61], it is shown to be very useful for comparative purposes [55]. On the contrary, the natural population analysis (NPA) [55] as well as the electrostatic potential (ESP) based schemes (CHelp [59], CHelpG [60] and MK

[57,58]) have a deeper physical background. Still, no single one of them may be regarded as a priori more suitable than the other schemes.

In this work, we have studied the anionic charge distribution over the phenyl ring and the SO<sub>3</sub> group of the benzenesulfonate anion. All of the previously mentioned charge-assignment schemes were employed. Note that, in fact, the CHelp, CHelpG and MK algorithms are based on fitting of the point charges to the molecular electrostatic potential computed from the ab initio electron density. They differ only in the point-selection algorithm [57–60].

The computed charges of both phenyl and SO<sub>3</sub> fragments from the HF/6-31+G(d) density are presented in Table 6. As can be seen, the Mulliken scheme leads to approximately equalized charge distribution over both of these fragments (strong charge delocalization). Contrary to this, the ESP-based algorithms suggest that the negative charge is essentially localized in the SO<sub>3</sub> group. The latest conclusion seems to be more in line both with intuitive chemical expectations, and with the observed hydrogen bonding in solid-state samples containing benzenesulfonate(–) species [5]. The NPA results are, on the other hand, between those of Mulliken and ESP.

## 5. Conclusions

On the basis of ab initio HF SCF 3-21+G(d) and 6-31+G(d) calculations and experimental FT-IR spectra, the structural and vibrational properties of the benzenesulfonate anion were studied. The staggered conformer is found to be more stable at HF/6-31+G(d) level, in agreement with the experimental data, while the lower level of theory fails to predict the order of conformational stability. Although both levels of theory agree well with the X-ray crystallographic data, the 6-31+G(d) force field was found to be superior for the vibrational analysis. Several reassignments (compared to the NCT ones) of the vibrational bands are suggested on the basis of the HF vibrational analysis. The torsional states of benzenesulfonate anion were computed at the HF/6-31+G(d) level within the one-dimensional rigid-rotor approximation. These data should be useful in interpreting the far-IR spectrum of these species. While the Mulliken population analysis predicts strong delocalization of the anionic charge over the phenyl

ring, the electrostatic-potential derived schemes seem to be more in line with the experimental observations, suggesting only a slight delocalization.

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