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Ab Initio Calculation of Conformation and Vibrational Spectrum for the Pyrosulfate Ion

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Theoretical calculations have been performed and applied to determine the most likely geometry for the pyrosulfate ion. The main question was to determine as to whether the system has C_2 or C_{2v} conformation. The present study favors C_2 symmetry. Bond lengths and angles have been calculated for the isolated ion, and the results compare well with experimental results for the ion in solid-state salts. Also, the vibrational spectrum of the $S_2O_7^{2-}$ ion has been calculated and compared with experimental results, obtained by extrapolation from Raman spectra of salt melts of $M_2S_2O_7$, M = Na, K, Rb, and Cs.

Introduction

The pyrosulfate ion, $S_2O_7^{2-}$, appears in many catalyst models for the oxidation of SO_2 to SO_3, which is a very important step in the production of sulfuric acid. The ion has been the target of many spectroscopic investigations, but there has been some controversy about its conformation. The only reported single-crystal structure determination is for $K_2S_2O_7$, published in 1960.[1] This shows a mere C_2 symmetry for the ion placed in a monoclinic crystal (spacegroup *C*2/*c*, No. 15). A powder diffraction analysis on the same compound[2] also gave C_2 conformation, but that study further involved $Na_2S_2O_7$ and $NaKS_2O_7$ salts, for which crystal structures no symmetry element at all was found for the pyrosulfate part. However, the $S_2O_7^{2-}$ ion in these three salts adopts a conformation which is very near the eclipsed C_{2v} symmetry.

There have been various IR and Raman investigations, and of these some have suggested C_2 symmetry[3,4] and some C_{2v}[5,6] to be the equilibrium symmetry of the ion. Walrafen et al.[3] did a systematic analysis of the spectral expectations of the five different conformations, and we will take the same approach in the present theoretical investigation. The conformations will be labeled C_2, C_s^a, C_s^b, C_{2v}^a, and C_{2v}^b. The various conformations may be difficult to visualize and have therefore been presented with symmetry elements in Figure 1 (apart from the trivial C_1, with no symmetry elements). Described in words: In the C_2 symmetry a 2-fold axis is present through the bridging oxygen, C_s^a has a symmetry plane containing the S−O−S atoms, and in C_s^b a symmetry plane perpendicular to this plane exists. In the C_{2v} conformations both of these planes act as symmetry planes, but in C_{2v}^a one oxygen atom is on the low-angle side of the S−O−S bridge from each SO_3 group, and in C_{2v}^b two oxygen atoms are on the same side.

The aim of the investigation has been to determine the most likely geometry for the isolated pyrosulfate ion by means of ab initio calculations and to find bond lengths, bond angles, and vibrational frequencies. To have the most reliable experimental vibrational data to compare with the calculations, we have redetermined spectra of four alkali metal pyrosulfate salts. By comparing these spectra carefully, the risk of weak bonds not being detected or near-degeneracies not being resolved is reduced as much as possible.

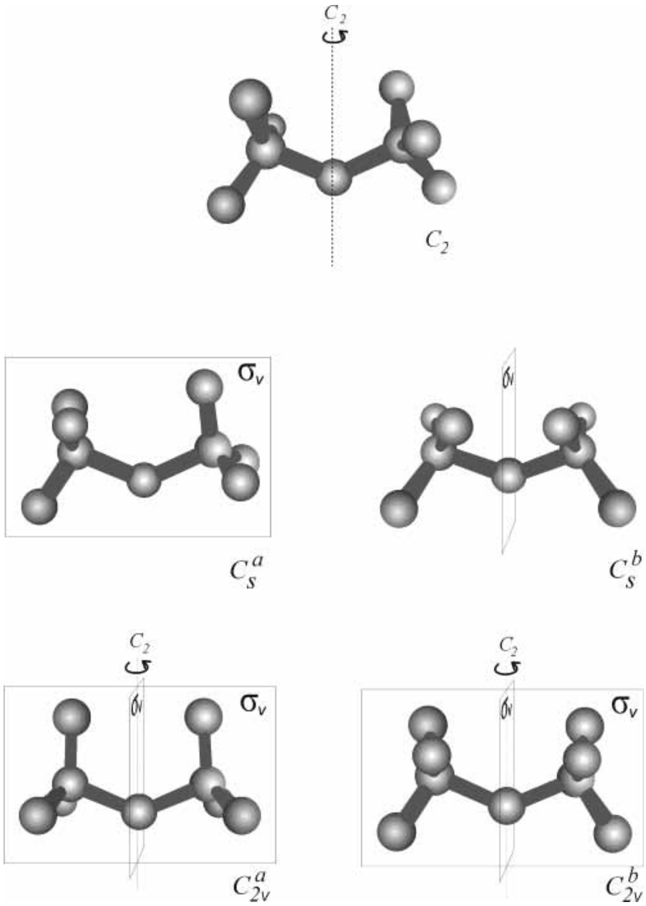

Figure 1. Notation used for the different conformations of the $S_2O_7^{2-}$ ion.

Methods of Calculation

Calculations have been performed at the restricted Hartree−Fock (RHF) and at the multiconfiguration self-consistent-field (MCSCF) levels of approximation. The program systems applied are Spartan[7] and MOLCAS.[8]

The basis set chosen for the calculations with Spartan, basis set I, is of the segmented form 6-31G**, having split valence

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TABLE 1: Bond Lengths (pm) and Angles (deg) for the Pyrosulfate Ion

	C_2 RHF I	C_2 RHF II	C_2 MCSCF	C_{2v}[b] MCSCF	exptl[a]
S_1–O_1	164.0	161.8	162.7	162.1	164.5
S_1–O_2	144.1	142.9	145.1	143.2	144.7
S_1–O_3	144.4	143.2	143.4	143.2	143.8
S_1–O_4	144.8	143.6	143.7	144.7	142.8
S_1–O_1–S_1'	130.3	131.1	130.2	132.7	124.2
O_2–S_1–O_1–S_1'	38.9	38.2	37.8	61.0	58.3
O_3–S_1–O_1–S_1'	83.4	84.1	84.7	61.0	61.7
O_4–S_1–O_1–S_1'	158.4	157.8	157.1	180.0	177.3

[a] Reference 1.

functions as well as polarization functions on both oxygen and sulfur.[9] For the MOLCAS calculations the general contraction scheme was chosen, with a primitive 10s6p3d set for oxygen and a 13s10p4d set for sulfur, contracted as 4s3p1d and 5s4p2d, respectively.[10] This is denoted basis set II.

The MCSCF calculations were of the complete-active-space (CAS) type[11] and based on basis set II. A distribution of 22 electrons in 15 space orbitals was used to generate the configurations. This resulted in about 5×10^5 determinants for the C_{2v} symmetries and twice as many for the C_2 conformation. The C_s conformers were not calculated by the MCSCF method, since we have been mostly concerned with the question of the C_{2v} versus the C_2 conformations.

Experimental Section

a. Chemicals. Pure anhydrous salts $M_2S_2O_7$ (M = Na, K, Rb, and Cs) were made in a stream of dry N_2 by thermal decomposition (250 °C for 3 h) of dry $M_2S_2O_8$ salts, which were bought or synthesized as described earlier.[5,12] All salt manipulations were performed in a glovebox with a H_2O content less than 20 ppm by volume. The salts were contained in sampling ampules (made from fused quartz tubes of inner Ø = 6.0 mm) which were sealed and subsequently heated until equilibrium was reached in a home designed furnace which had four windows and a temperature regulation better than 1 °C. Minute amounts of sulfate (M_2SO_4) were obviously present (bands near 960−980 cm^{-1} due to the strong $\nu_1(A_1)$ sulfate S−O symmetrical stretching). The origins of the contaminants were either due to $MHSO_4$ in the $M_2S_2O_8$ salts or, less likely, due to decomposition of $S_2O_7{}^{2-}$ ion into $SO_4{}^{2-}$ and SO_3.

b. Raman Spectroscopy. Raman spectra were measured with a DILOR XY spectrometer using the macroscopic sample entrance. Spectra were excited with an Ar$^+$ ion laser of about 500 mW power at 514.5 nm wavelength, with vertical polarization (V) and with the Argon plasma lines filtered off with an interference filter. The Rayleigh line was filtered off by using a double fore-monochromator or a Kaiser holographic Super-Notch-Plus filter (approximately 200 cm^{-1} cutoff), giving spectra looking identical. The Raman light was dispersed by use of an 1800 lines/mm grating in an 800-mm focal length single spectrograph and focused onto a CCD detector, cooled by liquid nitrogen to 140 K. The slits were set to 200 μm corresponding to a spectral resolution of about 5 cm^{-1}. A sheet polaroid analyzer, which permitted vertically (V) or horizontally (H) polarized light to pass, followed by a quarterwave depolarizer, was used to obtain polarization data. Calibration of the wavenumber scale was achieved with cyclohexane Raman and neon emission lines superimposed on the spectra, and the

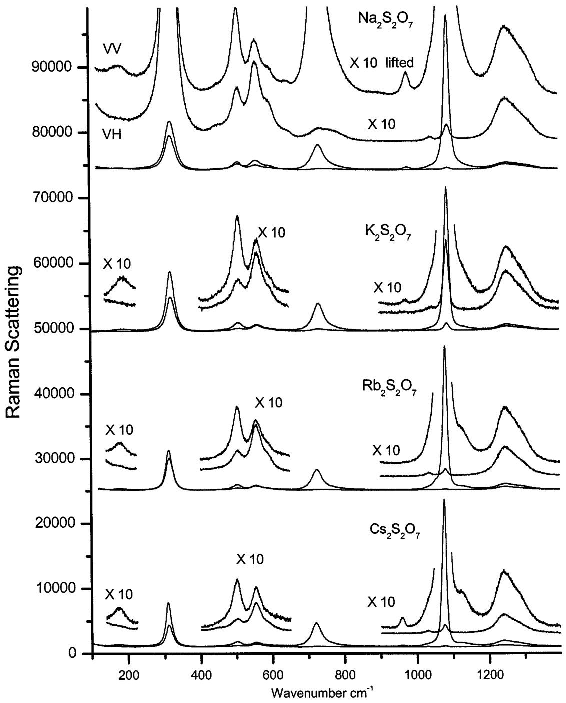
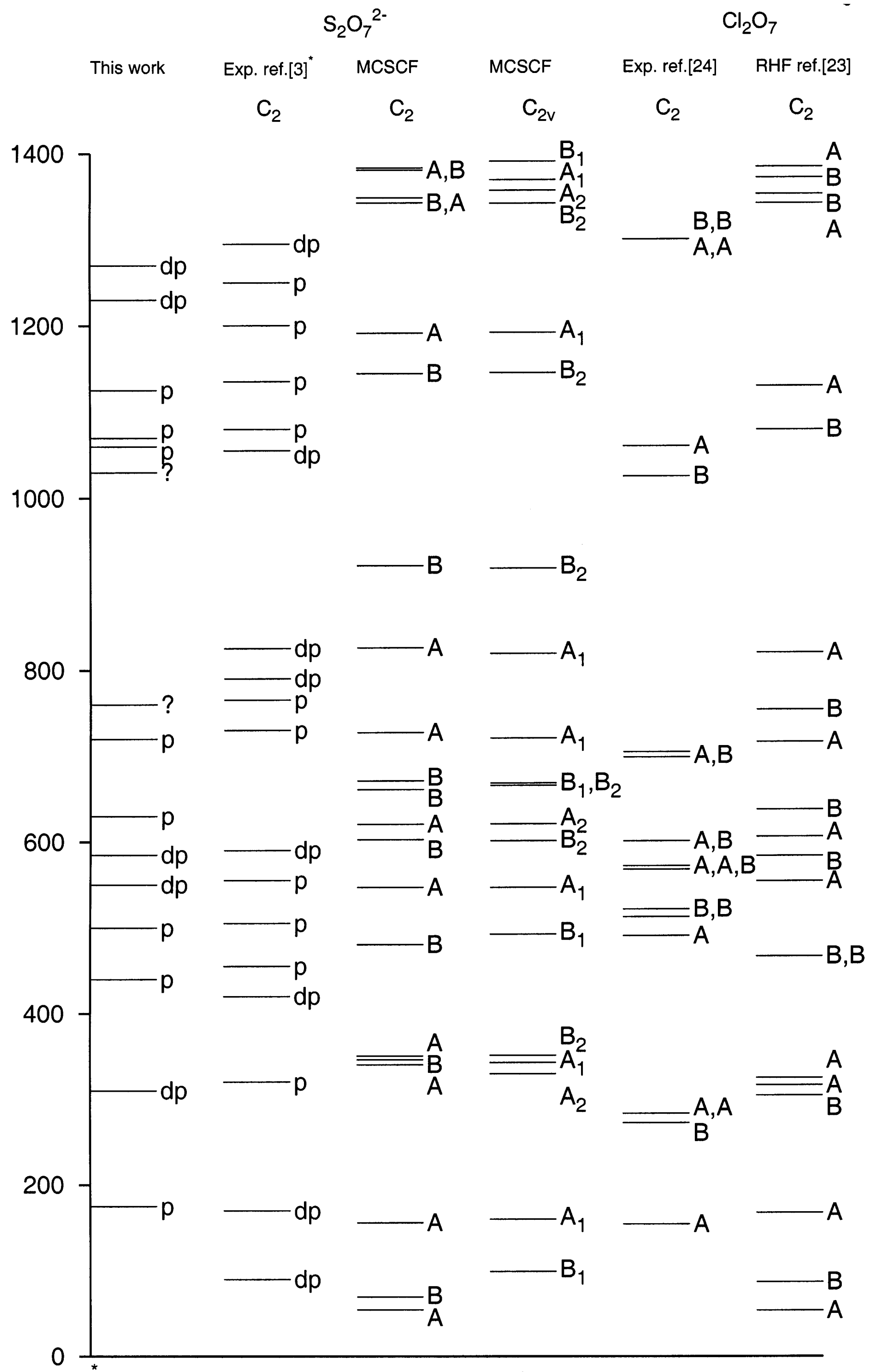


Figure 2. Raman spectra of melts $Na_2S_2O_7$, $K_2S_2O_7$, $Rb_2S_2O_7$, and $Cs_2S_2O_7$ at 480 °C. Polarized (VV) and depolarized (VH) spectra are shown. Selected ranges are also shown (magnified ×10, appropriately lifted).

TABLE 2: Raman Spectra[a] of Melts at 480 °C

$Na_2S_2O_7$	$K_2S_2O_7$	$Rb_2S_2O_7$	$Cs_2S_2O_7$	$S_2O_7{}^{2-}$ (estimated)[b]
1306 w,br,dp	1304 w,br,dp	1297 w,br,dp	1278 w,br,dp	1270 dp
1256 w,br,dp	1252 w,br,dp	1248 w,br,dp	1240 w,br,dp	1230 dp
	1137 vw,br,p	1128 w,br,p	1128 w,br,p	1125 p
1092 vs,p	1084 vs,p	1083 vs,p	1078 vs,p	1070 p
		1054.9 w,p	1072.0 m,p	1060 p
1045 w,dp	1045 vs,p	1036 w,p	1032 w,dp	1030 ?
(981 w,p)[c]	(973 w,p)[c]		(961.6 w,p)[c]	
782 w,p	775 w,br,dp	769 w,br,p	761 w,br,p or dp	760 ?
742 m,p	729 m,p	727 m,p	723 m,p	720 p
650 vw,p	639 vw,?	636 vw,?		630 p
601 w,dp	599 w,dp	592 w,dp?	590 vw,?	585 dp
562 w,dp	560 w,dp	559 w,dp	555 w,dp	550 dp
512 w,p	510 w,p	507 w,p	503 w,p	500 p
451 vw,p[d]	450 vw,?[d]	448 vw,?[d]	447 vw,p[d]	440 p
324 m,dp	323 m,dp	316 s,dp	314 s,dp	310 dp
185 w,p	191 w,p	180.6 w,p	178 w,p	175 p

[a] Band positions are given in cm^{-1}. Abbreviations: s = strong, m = medium, w = weak, v = very, br = broad, p = polarized, dp = depolarized, ? = polarization not determined. [b] Qualitative estimation of values for the free ion. [c] Band due to $\nu_1(A_1)$ from presence of trace amounts of $SO_4{}^{2-}$. [d] Cannot be due to $\nu_2(E)$ of $SO_4{}^{2-}$ because the band is also seen in the pure $Rb_2S_2O_7$.



* Possibly contaminated by $KHSO_4$, Ref.[5].

Figure 3. Calculated and experimentally determined vibrational levels for $S_2O_7^{2-}$ and Cl_2O_7. *p* = polarized, *dp* = depolarized.

wavenumbers reported are accurate to about 0.5 cm^{-1} for sharp bands. Other technical details are given in the figures or have been given previously.[13]

Results and Discussion

a. Geometry. The present calculations on both the RHF and the MCSCF level of approximation all resulted in the C_2 conformation having the lowest energy. This is also the only conformation that does not show imaginary frequencies in the vibration analysis. Therefore the only conformation located in a real minimum when constraints are lifted seems to be the C_2. In all our calculations $C_s{}^b$ turned out to collapse into the higher $C_{2v}{}^b$ symmetry.

The total energy for the C_2 conformation was calculated to: −1318.922 84 (RHF I), −1319.216 17 (RHF II), and −1319.324 23 (MCSCF) all in atomic units (1 au = 2.625 501 05 $\times 10^3$ kJ mol^{-1}). Energies relative to the C_2 calculation in the RHF II approximation are, in kJ mol^{-1}, $C_s{}^a$, 1.52; $C_s{}^b$, 12.23; $C_{2v}{}^a$, 16.59; and $C_{2v}{}^b$, 12.23. It appears that the $C_s{}^a$ conformation is within what could be reached by thermal activation (kT is ~ 1.2 kJ mol^{-1} at room temperature and about 3.6 kJ mol^{-1} at 500 °C). The $C_s{}^a$ has a lower energy than the C_{2v} conformations.

On the MCSCF level $C_{2v}{}^b$ is found 22.55 kJ mol^{-1} above C_2, but due to the lack of comparability in configuration space, the MCSCF results are of more interest in connection with the geometrical parameters.

Bond lengths and angles for the pyrosulfate ion in the C_2 and $C_{2v}{}^b$ conformations are shown in Table 1. The results for the C_2 conformation compare well with the experiment.[1] The results are fairly consistent; distances between sulfur and oxygen in the SO_3 groups are close to 144 pm, the O−S−O angles are around 114°, and the distance between sulfur and a bridging oxygen is about 163 pm. The only major difference between calculations and the experiment is the angle for the S−O−S bridge. This is calculated close to 130°, which is about 6° too open. There may be several reasons for this, but the most important one is probably that the calculations treat a free ion in the gas phase, and the structure determinations relate to the solid state with surrounding cations. Further, calculations on relatively small systems with more than one negative charge have always been troublesome.[14] With no surroundings to counteract the charges, it seems natural for the angle to open up.

The calculations on the other conformers show, mutatis mutandis, very similar numbers, and they will therefore not be presented here. Even the S−O−S bridging angle was very stable; we obtained the following results: C_2, 131.1°; $C_s{}^a$, 132.0°; $C_s{}^b$, 132.6°; $C_{2v}{}^a$, 138.9°; and $C_{2v}{}^b$, 132.6°, all at the RHF basis set II level of approximation.

b. Vibrational Structure. There have been many Raman[3−5,15,16] and IR studies[3,5,6,17] of pyrosulfate systems. The experimental results differ substantially in both the measured frequencies and their interpretations. The most remarkable differences are generally due to the difficulty with which moisture-free salts are prepared;[5] when the method of peroxodisulfate decomposition is used, the bands due to the HSO_4^- ion disappear. We have previously been able to obtain consistent results.[18−22] A summary of the results are given in Table 2 and in Figure 2. The wavenumber scale was reproducible within ± 1 cm^{-1}.

Figure 3 displays an overview of experimental results together with the theoretical calculations for C_2 and $C_{2v}{}^b$, the two conformations primarily considered in the spectroscopic investigations. In the figure we also show, for comparison, the calculated[23] and experimental[24] results for chlorine heptoxide, Cl_2O_7. The figure has been organized in a way to make pair wise comparison easy. The calculated levels have been designated according to the irreducible representations of the point group in question, and the experimental levels for $S_2O_7{}^{2-}$ with *p* and *dp* corresponding to polarized and depolarized behavior of the bands, respectively. *p* should correlate with a totally symmetric representation (A or A_1) and *dp* with the remaining symmetry species of the particular point group. In this work, a counting of the polarized bands, depolarized bands, and bands of questionable polarization gives 8, 5, and 2 bands, respectively. According to the selection rules,[3,5,22] no more than seven polarized bands should be seen for an ion of C_{2v} symmetry. Hence, if no extra bands (e.g., due to Fermi resonance, overtones, combinations, etc.) are present in the spectra, a C_{2v} conformation cannot account for the observations. We therefore, conclude from spectroscopy that the pyrosulfate ion in the melt probably has a C_2 or lower symmetry.

The first column in Figure 3 shows the spectrum for the pyrosulfate ion estimated in the present study. The second column is the result of an experiment[3] which was interpreted in favor of C_2 symmetry. The third and fourth columns show the vibrational spectra obtained from our ab initio calculations for the symmetries C_{2v} and C_2, respectively. Finally, experimental[24] and calculated[23] results for the Cl_2O_7 molecule are shown for comparison in the last two columns.

Agreements between comparable columns are fair, but there is no reason to promote the $C_{2v}{}^b$ conformation as a better candidate for the geometry than C_2.

The neutral system Cl_2O_7 does not have a necessity for strongly charged surroundings, and there the calculated and experimental results are more in accord. Cl_2O_7 has also been calculated in our study and by Parthiban et al.[23] with essentially similar results, but the presentation by Parthiban et al.[23] suffices for the present arguments. Their work may be consulted with respect to an analysis of coordinates for the vibration frequencies. The Cl_2O_7 levels are very similar to those found in the $S_2O_7{}^{2-}$ calculations (Figure 3), and they presumably have a very parallel interpretation. Part of the discrepancies experiment/experiment and experiment/calculation may, therefore, be due to effects from the local surroundings.

Conclusions

The present investigation, i.e., both calculations and spectroscopic data, supports the view that the most stable conformation of the pyrosulfate ion has C_2 symmetry. Such a geometry was found in X-ray structure analyses, both for the single crystal and for powder. The geometry was, however, very close to C_{2v}. From an energetic point of view, even a C_s conformation was found by our calculations to have an energy below $C_{2v}{}^b$, a structure favored in some of the spectroscopic investigations seen in the literature. The bond lengths and angles agree within the expected accuracy for calculations of the present types. The reproduction and interpretation of the Raman spectra is less convincing, but the results seem reasonable, considering the scatter in experimental lines and comparing with the isoelectronic Cl_2O_7. The local surroundings probably play a major role.

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References and Notes

(1) Lynton, H.; Truter, M. R. *J. Chem. Soc.* **1960**, 5112.

(2) Rasmussen, S. B.; Eriksen, K. M.; Hatem, G.; Silva, F. da; Ståhl, K.; Fehrmann, R. *J. Phys. Chem. B* **2001**, *105*, 2737.

(3) Walrafen, G. E.; Irish, D. E.; Young, T. F. *J. Chem. Phys.* **1962**, *37*, 662.

(4) Walrafen, G. E. *J. Chem. Phys.* **1964**, *40*, 2326.

(5) Fehrmann, R.; Hansen, N. H.; Bjerrum, N. J. *Inorg. Chem.* **1983**, *22*, 4009.

(6) Simon, A.; Wagner, H. *Z. Anorg. Allg. Chem.* **1961**, *311*, 102.

(7) SPARTAN IBM Version 5.0.1, 18401 Von Karmen Ave, Suite 370, Irvine, CA 92612.

(8) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadley, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *Molcas Version 4.1.*, Department of Theoretical Chemistry, Chemisry Center, University of Lund, S-22100 Lund, Sweden, 1997.

(9) Frand, 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.

(10) Pierloot, K.; Dumez, B.; Widmark, P.-O.; Roos, B. O. *Theor. Chim. Acta* **1995**, *90*, 87.

(11) Roos, B. O. In *Advances in Chemical Physics; Ab initio Methods in Quantum Chemistry − II.*; Lawley, K. P., Ed.; John Wiley & Sons: Chichester, England, **1987**, p 399 and references therein.

(12) Folkmann, G. E.; Eriksen, K. M.; Fehrmann, R.; Gaune-Escard, M.; Hatem, G.; Lapina, O. B.; Terskikh, V. V. *J. Phys. Chem. B* **1998**, *102*, 24.

(13) Folkmann, G. E.; Hatem, G.; Fehrmann, R.; Gaune-Escard, M.; Bjerrum, N. J. *Inorg. Chem.* **1991**, *30*, 4057.

(14) Johansen, H. *Theor. Chim. Acta (Berlin)* **1974**, *32*, 273.

(15) Berg, R. W.; Petrushina, I. M. In *Progress in Molten Salt Chemistry 1*; Berg, R. W., Hjuler, H. A., Eds.; Elsevier: Paris; 2000; p 95.

(16) Cleaver, K. D.; Davies, J. E. D. *J. Raman Spectrosc.* **1980**, *9*, 376.

(17) Brown, R. G.; Ross, S. D. *Spectrochim. Acta* **1972**, *28A*, 1263.

(18) Boghosian, S.; Borup, F.; Berg, R. W. *in Proceedings Eleventh International Symposium on Molten Salts*, Volume 98−11, Edited by Trulove, P. C., DeLong, H. C., Stafford, R. G., Deki, S. The Electrochemical Society: Pennington, NJ, 1998; p 536.

(19) Rasmussen, S. B.; Berg, R. W.; Fehrmann, R. In *Progress in Molten Salt Chemistry 1*; Berg, R. W., Hjuler, H. A., Eds.; Elsevier: 2000, p 449.

(20) Boghosian, S.; Berg, R. W. *Appl. Spectrosc.* **1999**, *53*, 565.

(21) Noerbygaard, T.; Berg, R. W.; Nielsen, K. In *Proceedings Eleventh International Symposium on Molten Salts*; Trulove, P. C., DeLong, H. C., Stafford, G. R., Deki, S., Eds.; The Electrochemical Society: Pennington, NJ, 1998; Vol. 98-11, p 553.

(22) Berg, R. W.; Borup, F.; Bjerrum, N. J. *Molten Salt Forum* **1993**, *1−2*, 69.

(23) Parthiban, S.; Raghunandan, B. N.; Sumathi, R. *Spectrochim. Acta* **1995**, *51A*, 2453.

(24) Witt, J. D.; Hammaker, R. M. *J. Chem. Phys.* **1973**, *38*, 303.