

Ab Initio Calculations of Oxosulfatovanadates

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Ab initio restricted Hartree–Fock and multi-configurational self-consistent-field calculations together with second-order perturbation theory have been used to study the geometry, the electron density and the electronic spectrum of VO_2SO_4^- . A bidentate sulfate attachment to vanadium was found to be stable with an O–V–O angle of 72.5° . The calculated spectrum shows bands in reasonable agreement with an experimental spectrum which has been attributed to VO_2SO_4^- . Geometry optimizations on $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$ and $(\text{VO})_2(\text{SO}_4)_3^{2-}$, which have been proposed as intermediates in the catalytic cycle, indicate that these compounds are likely to be energetically unstable, if they occur as intermediates at all.

The vanadium-catalyzed oxidation of SO_2 to SO_3 is the main route to the technical synthesis of sulfuric acid, and it is therefore one of the most important processes in chemical industry, at least as far as volume is concerned. The catalyst is obtained in melts of, e.g., $\text{V}_2\text{O}_5/\text{K}_2\text{SO}_4$, and the temperature for industrial operation is in the range 400–600 °C.

In spite of its significance, the reaction mechanism is not very well understood. A number of models have been proposed,^{1,2} but so far only very little has been verified owing to the difficulties in performing experiments on molten systems at high temperatures. It is, however, generally acknowledged that dimeric V^{V} species must be involved in the catalytic cycle. It is thus the aim of this investigation to get a better understanding of the reaction mechanism on the molecular level using *ab initio* methods. The proposed systems and intermediates are, however, fairly large, and they are therefore also difficult to treat with accurate theoretical methods.

The main focus will be on the bonding between vanadium and oxygen in four different situations: as a link between two vanadium atoms, as a link between a vanadium atom and sulfur in an SO_4^{2-} group, as a link between a vanadium atom and sulphur in an SO_2 group, and as a free ligand on vanadium. Many of the model compounds proposed suggest that the sulfate groups have bonds to vanadium in a bidentate arrangement.^{1,2} During the course of this work, a compound with such an arrangement was actually synthesized and its structure determined using X-ray diffraction.³ There is thus a special emphasis on the connection between bidentate sulfate and vanadium. The system VO_2SO_4^- (Fig. 1a) is

taken as a model, and it is investigated in detail with respect to geometry, electron density and optical spectrum.

A system containing the unit VO_2SO_4^- is not known with certainty, but there are reasons to believe that it exists.⁴ The power of the vanadium atom in a catalytic process is its flexibility: it has coordination numbers ranging from four to six and oxidation numbers ranging from two to five, all being easily accessible. Different coordination numbers are definitely involved, but there are different opinions as to whether it is a redox process involving V^{IV} and V^{V} (Ref. 1) or a process with vanadium solely as V^{V} .²

In addition to VO_2SO_4^- the binuclear complex $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$ will be treated in two different conformations. The methods are restricted Hartree–Fock (RHF), multi-configurational self-consistent-field (MC SCF) in the complete-active-space (CASSCF) formulation⁵ and an additional second-order perturbation treatment (CASPT).⁶

Details of calculations

Two different basis sets have been used in the investigation. For the geometry optimizations a basis with segmented contraction of Gaussian-type orbitals (basis set A) was applied, and for density and spectral analyses, a larger set of Gaussian orbitals using the general contraction scheme (basis set B).

Basis set A is essentially a double-zeta basis derived from a primitive (V/14s, 9p, 5d) set⁷ which has been augmented by a diffuse d-function (exponent 0.12), and the two outer s-exponents have been increased to 0.06 and 0.23, respectively, making these functions less diffuse.

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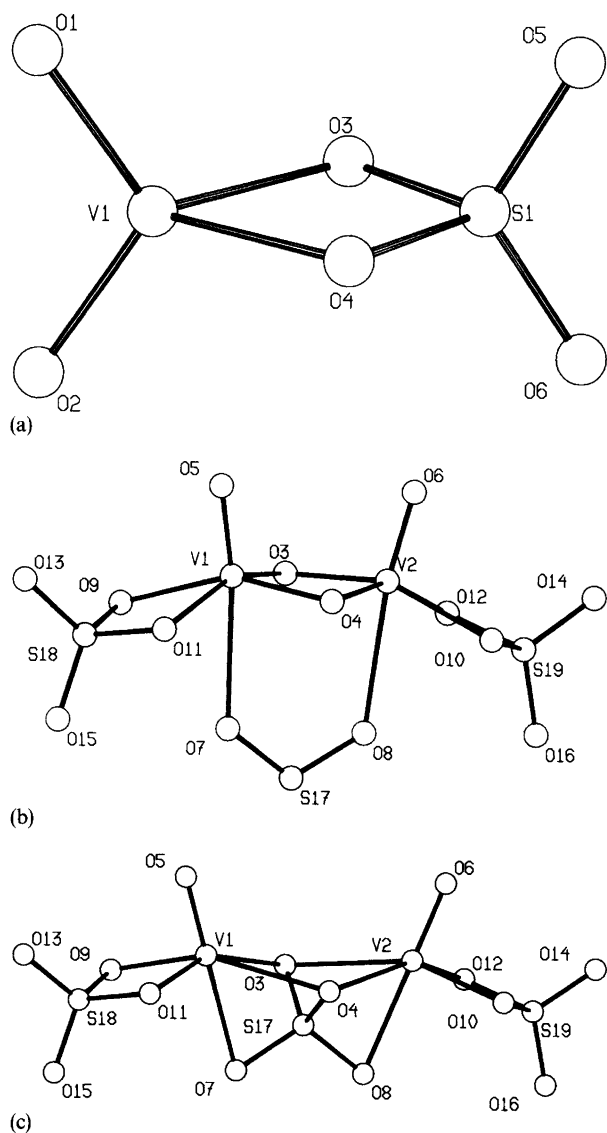


Fig. 1. Structures and atomic labeling for the calculated systems. (a) VO_2SO_4^- , (b) $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$ and (c) $(\text{VO})_2(\text{SO}_4)_3^{2-}$.

The contraction is segmented and of the form [V/8s, 4p, 3d]. For sulfur, the primitive (S/12s, 9p) set⁸ was augmented with a polarization function of d-type⁹ (exponent 0.542) and contracted as [S/6s, 4p, 1d]. For oxygen the primitive (O/9s, 5p) set was chosen in an [O/4s, 2p] contraction.¹⁰

Basis set B applies the general contraction scheme, and it is of the average density atomic natural orbital (ANO) type.¹¹ For oxygen and sulfur, basis sets constructed by Widmark *et al.*^{12,13} are used: (O/14s, 9p, 4d) contracted as [O/3s, 2p, 1d] and (S/17s, 12p, 5d, 4f) contracted as [S/4s, 3p, 2d, 1f]. The basis set for vanadium is constructed along the same lines as a part of the present investigation. It is based upon a primitive (V/16s, 11p, 8d) set¹⁴ augmented with three even-tempered f-functions, which were optimized for ⁴F using singles and doubles CI. A diffuse function was further added

for each shell, resulting in a primitive (V/17s, 12p, 9d, 4f) set, which was contracted as [V/5s, 4p, 3d, 2f].

The methods for geometry optimization have been RHF and CASPT for VO_2SO_4^- and just RHF for the larger systems. The program TURBOMOLE¹⁵ has been used in direct SCF optimizations, and the program system MOLCAS2¹⁶ for CASSCF and CASPT calculations.

Geometry optimizations

The existence of the VO_2SO_4^- ion (Fig. 1a) has not been experimentally verified, and a structure determination is, therefore, not available. Among the known structures the $\text{V}_2\text{O}_3(\text{SO}_4)_4^{4-}$ system³ comes closest, even though vanadium is here six- rather than four-coordinated. The important question to answer with the model compound VO_2SO_4^- is whether a sulfate ion bidentately connected to vanadium is a stable arrangement, and if so, which bond angles and distances will be involved, considering the strain in the system.

A complete geometry optimization for VO_2SO_4^- has been performed on the RHF level using basis set A. C_{2v} symmetry was imposed, and the resulting eigenvalues of the Hessian were all positive. Relaxation to C_1 gave no significant changes. In C_{2v} the ground state of VO_2SO_4^- is a closed-shell 1A_1 state having the electron configuration $\dots 20a_1^2 9b_1^2 12b_2^2 3a_2^2$. There are seven independent internal coordinates, which have all been optimized. The results are shown in the first column of Table 1. A partial geometry optimization has further been done at the CASPT level of approximation, as shown in the second column. Some of the geometrical parameters were here constrained to the values from the RHF calculation, and the focus was on the angles and distances in the bridge. Basis set B was used; the CASSCF calculation had eight electrons in eight active orbitals. The active space was selected to include the highest occupied and the lowest unoccupied orbital for each of the four

Table 1. Optimized bond lengths and bond angles for VO_2SO_4^- compared with experimental values for $\text{V}_2\text{O}_3(\text{SO}_4)_4^{4-}$.

	RHF	CASPT	Exp. ^a
Distances (pm)			
V-O(1)	157.4	161.9	158.1
V-O(3)	194.3	192.6	200.5
S-O(3)	156.3	(156.3) ^b	153.1
S-O(5)	144.6	(144.6)	144.2
V-S	264.7	262.6	265.4
Angles (°)			
O(1)-V-O(2)	111.44	(111.44)	— ^c
O(3)-V-O(4)	71.81	72.52	69.96
O(3)-S-O(4)	93.41	(93.41)	97.34
O(5)-S-O(6)	116.92	(116.92)	115.29

^a Ref. 3. ^b Values in parentheses have not been reoptimized.

^c No comparable angle.

symmetries in C_{2v} . The CASPT calculation correlated all 48 valence electrons. It should be mentioned that VO_2SO_4^- is found to be binding compared to $\text{VO}_2^+ + \text{SO}_4^{2-}$. As an example, the gain in energy is 0.67 au (1 au = 4.35975×10^{-18} J) using RHF and basis set B without corrections.

There are large departures from the tetrahedral angle of 109.5° . We find O–V–O and O–S–O angles of 71.8° and 93.4° , respectively, for the bridging oxygens. The strain is obvious, but the results compare favourably with the experimental values³ for $\text{V}_2\text{O}_3(\text{SO}_4)_4^{4-}$. Owing to the lower symmetry of the latter complex, average values from the structure determination have been used for some of the values in the table.

The possibility of having bidentate sulfate complexes as intermediates in the reaction chain is thus confirmed, both by the calculations and by the structure determination. The calculated system is four-coordinated and the synthesized is six-coordinated. One of the V–O bonds in the latter is, however, fairly long (241.6 pm), and it appears that coordination number four may be on the low side and six a little high, but that this range definitely is accessible.

The proposed mechanisms^{1,2} for the oxidation of SO_2 to SO_3 are mostly based upon binuclear vanadium complexes, where the vanadium atoms are connected with oxygen bridges, and each of them has a bidentate sulfate ligand. The models are fairly speculative due to the difficulties in getting reliable experimental results. The model by Fehrman¹ is therefore investigated using limited geometry optimization on two of the proposed intermediates, $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$ and $(\text{VO}_2)_2(\text{SO}_4)_3^{2-}$ (Figs. 1b and 1c).

For both complexes C_{2v} symmetry was enforced, and the lowest 1A_1 closed-shell state optimized on the RHF level of approximation using basis set A. The systems have 208 electrons, and the ground state has the electron configuration $\dots 40a_1^{23}4b_1^{21}7b_2^{21}3a_2^2$. There are 17 independent internal coordinates, and they have all been involved in the optimization. For $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$, the $(\text{VO}_2)_2(\text{SO}_4)_2^{2-}$ part finds a stable conformation with a geometry as shown in Fig. 1b. The SO_2 group was, on the other hand, still moving away when the optimization was terminated, and the proposed complex does not give rise to a stable conformation on this level of approximation. A further indication of this is given in the next section, where the electron density has been analyzed.

The complex $(\text{VO}_2)_2(\text{SO}_4)_3^{2-}$ (Fig. 1c) is isomeric with $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$, but it has a rather different conformation. A formal internal redox process leading to V^{IV} and S^{VI} is proposed to take place. It was, however, not possible to find a stable minimum in a reasonable configuration space around the proposed structure. Both intermediates, and in particular $(\text{VO}_2)_2(\text{SO}_4)_3^{2-}$, must therefore be considered as being fairly unstable conformers. But they may, of course, turn up in high energy transition states.

The charge densities

To study the various bonds, the charge distributions have been analyzed. Figure 2 depicts the charge density and the Laplacian of the density for VO_2SO_4^- in the 1A_1 ground state. The gradient paths for the charge density have been drawn on both types of display. The larger and generally contracted basis set B was applied in these calculations.

The gradient paths are used by Bader¹⁷ to define atomic regions, and the charges inside these volumes have been listed in Table 2 together with a Mulliken population analysis¹⁸ at both the RHF and the CASSCF level. The trends are the same for the two methods, but the Bader values are much more polarized and closer to the formal oxidation numbers. On the whole, the system appears as an ionic combination of a VO_2^+ part and an SO_4^{2-} part. The Laplacian of the density also confirms this, if we note that a covalent bond often leads to a relative concentration of density having a negative value for the Laplacian, whereas the opposite is the case for an ionic bond.

In Table 3 the actual numbers for the entities in the critical points are given. The lowest density is found on the bridge between vanadium and oxygen (apart, of course, from the ring critical point), the density on the S–O bridge and on the V–O bond are intermediate, and the highest value is found on the S–O bond. None of the values for the Laplacian of the density is negative in the critical points; the S–O bridge lies lowest, but it is almost on a node, as seen in Fig. 2d.

For the SO_4^{2-} part, it is interesting to note that the local charge concentration in the valence region is entirely contained in the atomic subspaces of the oxygens. Following the terminology of Bader,¹⁷ this form of interaction is called an intermediate interaction, and is characterized not only by the polarization of the local charge concentration towards the bonding region, but also by a charge transfer from the less electronegative atom (here S) to the more electronegative atom (here O) relative to neutral atoms.

To compare VO_2SO_4^- with the VO_2^+ and SO_4^{2-} fragments, a difference density has been depicted in Fig. 3. It reveals a built-up of charge on the V–O part of the bridge. An other indication of having two distinct fragments is that the active space in the CASSCF calculations, as described in the next section, almost entirely confines itself to the VO_2^+ moiety. The correlation of the remaining valence orbitals is taken care of by the CASPT calculations.

The electron density for $(\text{VO}_2)_2\text{SO}_2(\text{SO}_4)_2^{2-}$ has been calculated in the partially optimized geometry using an ANO basis of the form [V/5s, 3p, 2d], [S/4s, 3p, 1d] and [O/3s, 2p] with the same origin as basis set B. Results are listed in Table 4. The density is again fairly low between vanadium and a bridging oxygen, in particular when the bridge is to a sulfate oxygen. The value of the density in the critical point of a V–O bridging bond is roughly half of that for an unbridged bond. The Laplacian of the density is positive in all the critical

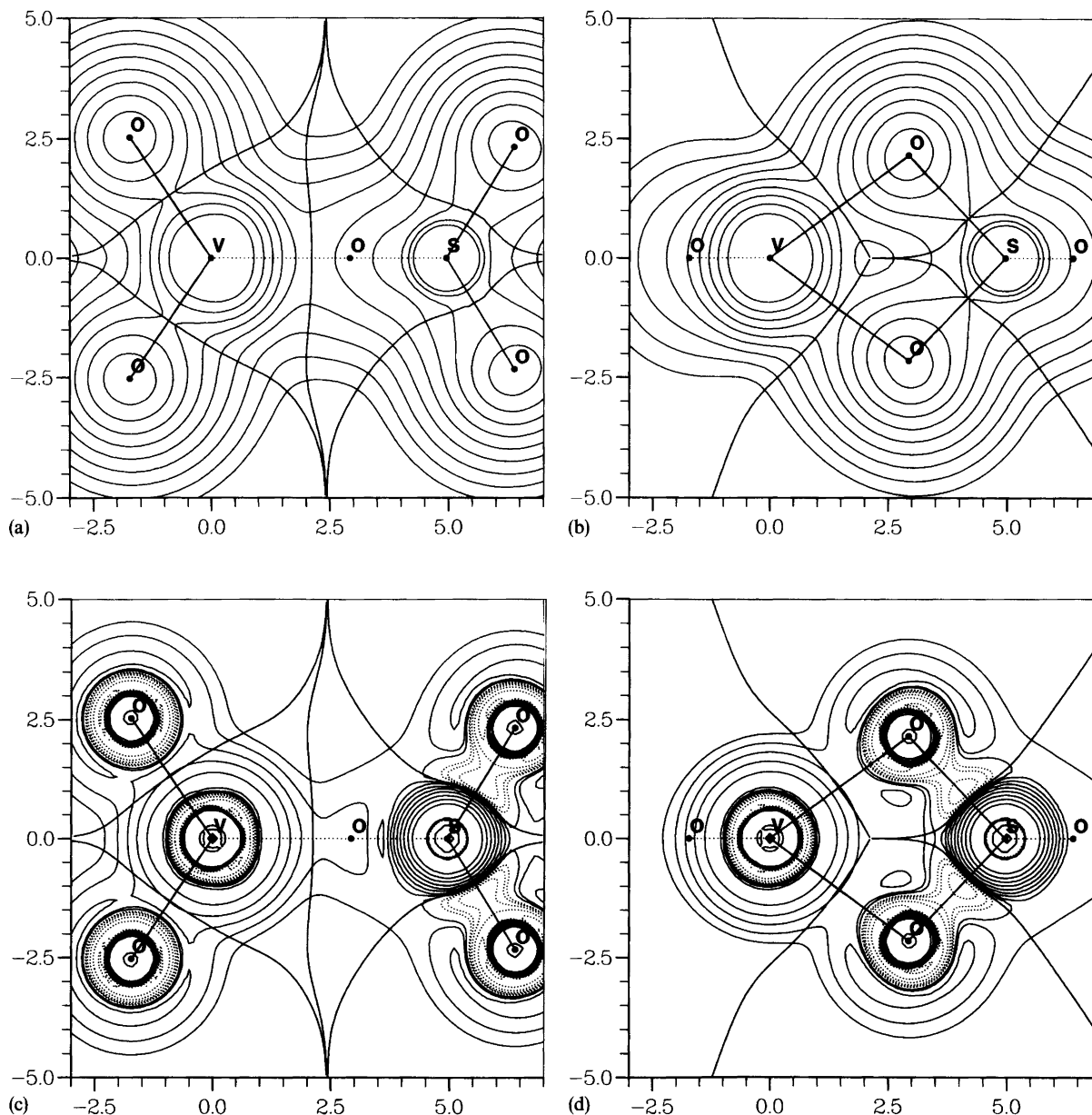


Fig. 2. The total electron density [(a) and (b)] and the Laplacian [(c) and (d)] of the density for VO_2SO_4^- . (b) and (d) depict contours in the plane containing the oxygen bridges, whereas (a) and (c) depict the perpendicular plane containing the four other oxygen atoms. CASSCF level and basis set B. Gradient paths for the density have been drawn to show the atomic subspaces. Contour levels: lowest contours 0.004 for densities and ± 0.117 for Laplacians, adjacent levels differ by a factor of two. Negative values for the Laplacian are indicated with dotted lines (atomic units).

points, apart from the S–O bridge, and the values are fairly similar to what was found for VO_2SO_4^- .

The SO_2 group is moving away from the complex, and the values are therefore only indications. All critical point densities are low. There are several ring critical points, as seen from Table 4, and a cage point in the middle. The values in the table are probably representative for the various kinds of V–O and S–O bonds in such systems.

The density of the other isomer, $(\text{VO})_2(\text{SO}_4)_3^{2-}$, was not analyzed in detail owing to the inconclusive results for the geometric parameters of the compound.

The electronic spectrum of VO_2SO_4^-

The first singlet excited state of each symmetry (2^1A_1 , 1^1B_1 , 1^1B_2 , 1^1A_2) has been calculated using the CASSCF⁵ and CASPT⁶ methods. The valence orbitals from the RHF calculation of the 1^1A_1 ground state turn out to be very delocalized. They have been used to initiate the MCSCF calculations. There are 24 filled valence orbitals with twice as many electrons. They are all included in the CASPT calculations, but the active space in the CASSCF calculations was more restricted. Three different sizes were investigated in order to ensure convergence

Table 2. Population analysis for the ground state of VO_2SO_4^- using the Mulliken¹⁸ and Bader¹⁷ methods at the RHF and CASSCF levels of approximation.

Atom/group	RHF		CASSCF	
	Mulliken	Bader	Mulliken	Bader
V	1.64	2.57	1.48	2.22
S	1.04	4.38	1.03	4.38
O(1),O(2)	-0.68	-1.00	-0.52	-0.78
O(3),O(4)	-0.69	-1.45	-0.74	-1.49
O(5),O(6)	-0.47	-1.52	-0.49	-1.54
'VO ₂ '	0.28	0.57	0.43	0.67
'SO ₄ '	-1.28	-1.57	-1.43	-1.66

Table 3. Values at the critical points of the CASSCF calculated electron density for the ground state of VO_2SO_4^- (atomic units).

Line	Critical point	Density	Laplacian of density	Energy density
V-O(1)	Bond	0.25	0.98	-0.15
V-O(3)	Bond	0.11	0.51	-0.02
S-O(3)	Bond	0.26	— ^a	-0.35
S-O(5)	Bond	0.32	— ^a	-0.44
V-S	Ring	0.05	0.29	-0.001

^a Value not listed; the location is close to a node with very rapid variations.

of the results, and these were: 8 electrons in 8 orbitals (as for the geometry optimization), 12 electrons in 11 orbitals (adding a filled orbital in a_1 and b_2 , and a virtual orbital in a_1), and 16 electrons in 13 orbitals (further adding a filled orbital in a_1 and b_2). It should be noted that the second space of these three has a size which formally corresponds to the valence orbitals of the VO_2^+ fragment, but that the objective of course is to correlate electrons in both fragments, as well as in their interaction.

The convergence in the excitation energies is very good, and only the CASSCF calculation in the smallest space for the 1B_2 state shows some deviation. The second state of A_1 symmetry has been optimized independently, and it is therefore not orthogonal to the ground state. For the intermediate size calculation the overlap is 0.05, and a two by two CI calculation¹⁹ for these states gave only very small changes, so the approximation was judged acceptable in the context.

Results using the largest active space are listed in Table 5. The CASSCF calculations involve about 10^5 configurations, and the CASPT treatment uses all these configurations as references and correlates all 48 valence electrons. The active space ends up being almost entirely confined to the VO_2^+ part, and gives thereby further support to considering VO_2SO_4^- as consisting of a VO_2^+ fragment and an SO_4^{2-} fragment.

The lowest state for each symmetry (with inclusion of the ground state) has a weight of about 82% for the respective main configurations, whereas 2^1A_1 shows no configuration with a weight above 50%.

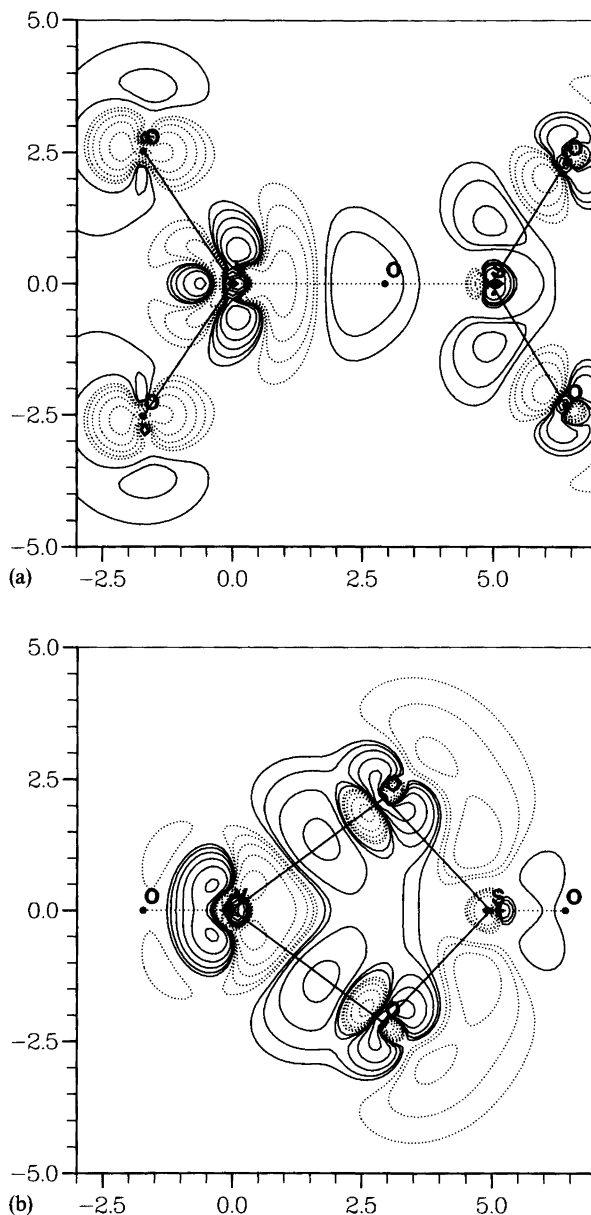


Fig. 3. Density difference between VO_2SO_4^- and the two ions VO_2^+ and SO_4^{2-} . RHF level and basis set B. Planes as in Fig. 2. Accumulation of density is shown using fully drawn lines, and regions which have lost density are indicated with dotted lines. Contour levels: lowest contours ± 0.003125 , adjacent levels differ by a factor of two (atomic units).

Hansen *et al.*⁴ have reported an electronic spectrum which they proposed was due to VO_2SO_4^- . Absorption starts at $20 \times 10^3 \text{ cm}^{-1}$ and the authors suggest a band around $29 \times 10^3 \text{ cm}^{-1}$. These values fit well with Table 5, where the 1B_2 transition is found at or a little above $20 \times 10^3 \text{ cm}^{-1}$, and the 1B_1 transition around $30 \times 10^3 \text{ cm}^{-1}$. Additional absorption starts at about $35 \times 10^3 \text{ cm}^{-1}$ and could be due to the 2^1A_1 and higher states. The 1^1A_2 state is, however, not electric dipole allowed. The calculations thus support, or at least do not contradict, the possibility that the VO_2SO_4^- moiety

Table 4. Values at the critical points of the RHF calculated electron density for the ground state of the partly geometry optimized $(VO_2)_2SO_2(SO_4)_2^{2-}$ system (atomic units). The atoms listed approximately define the appropriate line or plane involved, cf. Fig. 1b.

Line/plane	Critical point	Density	Laplacian of density	Energy density
V(1)–O(3)	Bond	0.14	0.59	–0.04
V(1)–O(5)	Bond	0.29	1.14	–0.17
V(1)–O(7)	Bond	0.02	0.11	0.00
V(1)–O(11)	Bond	0.08	0.37	–0.01
S(17)–O(7)	Bond	0.29	0.75	–0.35
S(18)–O(11)	Bond	0.25	–0.14	–0.33
S(18)–O(13)	Bond	0.30	0.27	–0.40
S(18)–O(15)	Bond	0.30	0.27	–0.40
O(7)–O(11)	Bond	0.01	0.06	0.00
V(1)–O(3)–O(4)–V(2)	Ring	0.05	0.18	–0.01
V(1)–O(9)–O(11)–S(18)	Ring	0.04	0.23	0.00
S(17)–O(3)–O(4)	Ring	0.01	0.04	0.00
O(7)–O(11)	Ring	0.01	0.06	0.00
S(17)–O(3)–O(4)	Cage	0.01	0.04	0.00

Table 5. Excitation energies relative to the ground state calculated at the same level of approximation (CASSCF: –1790.158958 au; CASPT: –1791.503996 au, 1 au = 4.359 75 × 10^{–18} J.)

State	Excitation energy/10 ³ cm ^{–1}	
	CASSCF	CASPT
1 ¹ B ₂	22.4	20.0
1 ¹ B ₁	30.2	30.9
2 ¹ A ₁	38.6	29.7
1 ¹ A ₂	42.4	40.3

could be responsible for the reported spectrum. It should though be borne in mind that the spectrum is recorded in a melt at 410–450 °C, and that the effects of the medium and the temperature may be substantial.

Conclusion

$VO_2SO_4^-$ was found to be a stable system with a bidentate sulfate arrangement having an O–V–O bond angle of 72.5° and an O–S–O angle of 94.3°. This supports the possibility of having SO_4^{2-} as a bidentate ligand in binuclear vanadium complexes, a framework which has been used for the proposal of many intermediates in the discussion of reaction pathways for the catalytic oxidation of SO_2 to SO_3 .

The electron density points towards a fairly ionic bonding in $VO_2SO_4^-$ between a VO_2^+ ion and a sulfate ion, and the differences in the various V–O and S–O bonds show up in the density as well as in the Laplacian of the density. The calculated electronic spectrum is in fair agreement with an experimental spectrum attributed to the $VO_2SO_4^-$ ion.

Geometry optimizations on $(VO_2)_2SO_2(SO_4)_2^{2-}$ and $(VO)_2(SO_4)_3^{2-}$, which have been proposed as intermediates in the catalytic cycle, indicate that these compounds are likely to be energetically unstable, if they occur as intermediates at all.

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