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The Polarized Absorption Spectra of Three Crystalline Polymorphs of VOSO$_4$·5H$_2$O

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Abstract: Single-crystal X-ray diffraction studies have confirmed the existence of a stable form and revealed the formation of at least two new, unstable modifications of VOSO$_4$·5H$_2$O. In the stable form the crystals are monoclinic, space group P2$_1$/c, with unit cell dimensions $a = 6.99 \pm 0.03$ Å, $b = 9.73 \pm 0.03$ Å, $c = 12.98 \pm 0.04$ Å, $\beta = 110° 53' \pm 20'$. The previously published structure has been revised following an analysis by three-dimensional Patterson, heavy-atom, and least-squares refinement methods using 1863 observed, independent, counter-measured X-ray diffraction data. Since the molecules crystallize as VO(H$_2$O)$_4$(SO$_4$)·H$_2$O, there are significant, but small, deviations from C$_{4v}$ symmetry in the inner coordination sphere. The V$=$O bonds of the molecules are nearly parallel. One unstable form is orthorhombic, space group Pm2$_1$n or Pmmn, with unit cell dimensions $a = 16.12 \pm 0.07$ Å, $b = 21.12 \pm 0.10$ Å, $c = 12.22 \pm 0.06$ Å; the other is also orthorhombic, space group Pmn2$_1$ or Pmnm, having a unit cell with $a = 7.23 \pm 0.05$ Å, $b = 9.33 \pm 0.07$ Å, $c = 6.18 \pm 0.05$ Å. The polarized electronic absorption spectra from single crystals of these three polymorphs have been recorded at approximately 20, 90, and 295°K. They conform to the predictions of Ballhausen and Gray. A fine structure was observed only on the spectra from some of the crystals of the unstable forms.

The question of the assignment of the absorption spectral bands produced by VOSO$_4$·5H$_2$O has been reopened by Ortolano, Selbin, and McGlynn[2] and Selbin.[3,4] In contrast to the proposals of Ballhausen and Gray,[5] it is suggested that the low-lying absorption bands represent the whole of the d–d transitions, and the possibility of a splitting, in terms of a spin–orbit coupling mechanism, is invoked. Much of the argument of Ortolano, Selbin, and McGlynn[2–4] is based upon the solution and pellet absorption spectra of pentafluorovanadyl compounds and of vanadyl bisacetylacetonate. However, for the pentahalovanadyl complexes conclusive evidence supporting the Ballhausen and Gray assignments has been obtained by Wentworth and Piper.[6] In the bisacetylacetonates the

level scheme may of course be different from that in VOSO$_4$·5H$_2$O. Nevertheless, the postulated assignments of Ballhausen and Gray have received support from the measurements of induced circular dichroism by Jones and Larsen.[7] Evidently no general agreement exists as to the assignments of the excited states. It seemed clear that before this could be achieved for any individual vanadyl compound a great deal of experimental information was needed.

The present work was undertaken, therefore, to reinvestigate experimentally the low-lying bands produced by crystals of VOSO$_4$·5H$_2$O and to see whether they developed structure at low temperatures, thereby offering a means toward the identification of the energy levels. As a preliminary to this, the following crystal-growth experiments and X-ray diffraction studies were made.

Experimental Section

It is relatively difficult to grow, in a reproducible manner, crystals of vanadyl sulfate from aqueous solution suitable for single-crystal

(1) Author to whom correspondence should be addressed.
(2) T. R. Ortolano, J. Selbin, and S. P. McGlynn, J. Chem. Phys., 41, 262 (1964).
(3) J. Selbin, Chem. Rev., 65, 153 (1965).
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(5) C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1, 111 (1962).
(6) R. A. D. Wentworth and T. S. Piper, J. Chem. Phys., 41, 3884 (1964).
(7) K. M. Jones and E. Larsen, Acta Chem. Scand., 19, 1210 (1965).

absorption spectral study. The physical requirements of the spectrophotometer and the large molar extinction coefficient of crystals of the compound necessitate the growth of very thin plates of large area. If the crystallization is performed by uncontrolled evaporation of an aqueous solution, the mother liquor becomes supersaturated, after which crystallization follows very quickly in forms critically dependent upon the external physical conditions. Several authors (Palma-Vittorelli, et al.,[8] Roch,[9] and Tudo,[10] for example) have studied this phenomenon and together report the existence of hydrated crystalline forms with 6.5, 6, 5, 4, 3, 2, and 1 molecules of water per unit of $VOSO_4$, and an anhydrous form. Dehydration of the higher hydrates to the lower species is possible. Some conflict between the various published results, and also with those of this research, throws doubt on the real identity of the various crystalline products reported. For example, Tudo[10] finds that the hexahydrate is the most stable form in normal laboratory conditions. In this work, single crystals of only the pentahydrate were stable.

Single crystals of vanadyl sulfate were obtained as the required thin plates by very slow crystallization, at room temperature, of a supersaturated aqueous solution, a few drops of which had been placed between two flat glass plates (microscope slides) which were pressed together to spread the mother liquor evenly over a wide area. Crystallization was often enhanced by the introduction, at the sides of the plates, of a small seed crystal. Some measure of control over the identity of the crystallizing plate face could be obtained by suitable orientation of this seed crystal. The thicknesses of the crystals could also be controlled by altering the distance between the glass plates. Crystals used were between 0.02 and 0.25 mm thick.

At least three distinct crystalline forms resulted. They occurred together in the same crystallization batches. Two of the three forms, which were unstable in air and in mother liquor, appeared well before the third stable modification. The unstable forms were more soluble than the stable form, and an unusual observation was that the crystals of one of these, if left in mother liquor between the glass plates, changed slowly (under the varying day-to-day conditions of the laboratory) into badly formed or small polycrystals of the stable form.

Single crystals of the stable form of vanadyl sulfate more suitable for absorption spectral study were obtained from similar experiments in which the ambient temperature was kept between 25 and 40°.

Crystal data for these three forms studied were obtained from precession, oscillation, and Weissenberg X-ray diffraction photographs of the actual crystals used in the spectral measurements. Specimens of the unstable products were preserved by coating them with a thin layer of vacuum grease. Crystal densities were measured by flotation in mixtures of bromobenzene and ethylene dibromide.

Analyses of the various forms were made volumetrically by titration against standardized potassium permanganate solution, and gravimetric determinations of the hydration states were also made, the specimens being heated to 335°, the temperature required[10] for complete dehydration. The experiments were repeated many times and in all cases gave the water content of the crystals unequivocally as five molecules per unit of $VOSO_4$. This figure has been confirmed for the stable species from an accurate single-crystal structure analysis (see analysis).

Single-crystal absorption spectra were recorded, at approximately 20, 90, and 295°K, on a Cary Model 14 spectrophotometer. The low-temperature spectra were obtained from crystals mounted in a commercially available liquid hydrogen cold finger (Air Products and Chemicals "Cryotip") and in a glass liquid nitrogen dewar apparatus designed in this laboratory. These were, in turn, mounted into the spectrophotometer sample compartment in the manner described by Ballhausen, et al.[11]

Crystal Data

(i) $VOSO_4 \cdot 5H_2O$ (Stable Form). These crystals grow as blue elongated plates or prisms. When viewed on the plate or prism faces in polarized light, they appear almost colorless when the electric vector is at

about 18° to the elongation direction. With the electric vector at right angles to this direction, the crystals are blue. With crossed Nicol prisms there is strong sharp extinction in these directions.

The crystals are monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14[12]) (determined from systematically absent X-ray diffraction spectra), and $a = 6.99 \pm 0.03$ Å, $b = 9.73 \pm 0.03$ Å, $c = 12.98 \pm 0.04$ Å, $\beta = 110°53' \pm 20'$. With four units of $VOSO_4 \cdot 5H_2O$ in the cell, the calculated density of 2.04 ± 0.01 g cm⁻³ agrees well with the observed density of 2.036 ± 0.008 g cm⁻³. This is the form studied by Palma-Vittorelli, et al.,[8] who reported the results of a single-crystal structure determination. Doubts of the correctness of these results, which were based on the analysis of a single projection which was extended to the third dimension by an extremely dubious method, led to a detailed reinvestigation of this crystal structure from 1863 nonzero, independent three-dimensional diffraction data collected on a Philips PAILRED diffractometer using monochromatized Mo Kα radiation incident on a prismatic crystal of dimensions $0.15 \times 0.12 \times 0.55$ mm³ mounted about the c axis.[13] The vanadium ion coordinates were determined from a three-dimensional unsharpened Patterson map, and these were used to compute a vanadium-phased electron density map from which the coordinates of all nonhydrogen atoms were deduced. The postulated structural parameters (atomic positions and anisotropic temperature factors and a data scale factor) were improved with six cycles of full-matrix least-squares refinement with the data weighted individually according to their standard deviations based on counting statistics. The present R factor[14] is 0.067. The final refinement awaits the detailed checking of observed data for experimental errors, the application of absorption and extinction corrections, and the inclusion of the hydrogen atomic parameters.

The analysis has shown that the atomic coordinates of Palma-Vittorelli, et al.,[8] are quite wrong. The molecules crystallize as $VO(H_2O)_4SO_4 \cdot H_2O$, each vanadium ion being surrounded by a distorted octahedron of six oxygen atoms of which the coordinated oxygen of the sulfato group is cis to the vanadyl (V=O) oxygen atom, identified by its short distance (1.591 ± 0.005 Å) from the vanadium. The fifth water molecule of each asymmetric unit exists as free water of crystallization, although it appears to be hydrogen bonded to one of the coordinated oxygen atoms (O–O distance 2.71 Å). The vanadyl (V=O) bonds of the structure are approximately parallel and are very nearly perpendicular to the ab plane (cf. Palma-Vittorelli, et al.[8]). Figure 1 and Table I show the present geometry of the inner coordination sphere, and it can be seen that the coordination of the sulfato group, the hydrogen bonding, and presumably other packing effects have caused significant deviations from C_{4v} symmetry within the volume. It has been considered, however, that the magnitudes of these deviations are such that the validity of the assumption of this symmetry in the spectral interpretation is not affected.

(8) M. B. Palma-Vittorelli, M. U. Palma, D. Palumbo, and F. Sgarlata, *Nuovo Cimento*, 3, 718 (1956).

(9) (a) J. Roch, *Compt. Rend.*, 248, 3549 (1959); (b) *ibid.*, 249, 56 (1959); (c) *ibid.*, 250, 2167 (1960).

(10) J. Tudo, *Rev. Chim. Minerale*, 2, 53 (1965).

(11) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, 4, 514 (1965).

(12) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 99.

(13) K. J. Watson, submitted for publication.

(14) Defined as usual, as $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes.
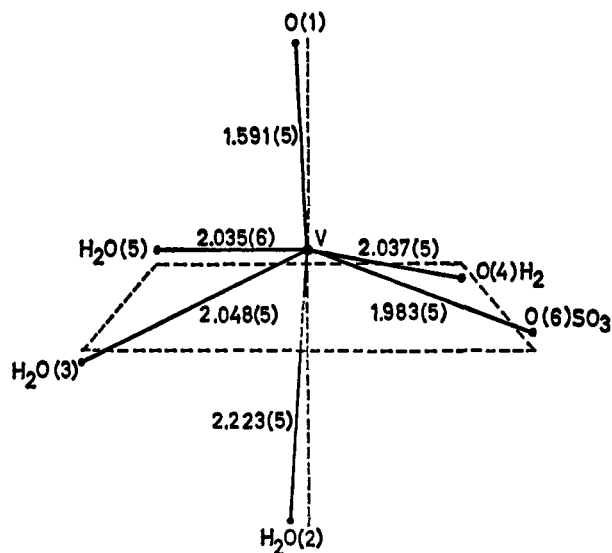
Figure 1. Interatomic distances (Å) of the inner coordination sphere of the stable form of $VOSO_4 \cdot 5H_2O$. Their estimated standard deviations ($\times 10^3$) are given in parentheses.

Figure 2. Single-crystal polarized absorption spectra of $VOSO_4 \cdot$ $5H_2O$: curves A, electric vector perpendicular to the V=O axis; curves B, electric vector parallel to the V=O axis.

The elongation directions of crystals of this stable form are parallel to the c axis, and the developed plate and prism faces are {110}. Polarized single-crystal absorption spectra were recorded with light incident on [110] and with the electric vector parallel (B spectra in Figure 2) and perpendicular (A spectra) to the direction of minimum absorption (i.e. to the V=O bond direction).

(ii) $VOSO_4 \cdot 5H_2O$ (Unstable Form I). The crystals grow as deep blue, elongated plates. They are more deeply colored than those of the stable form. When viewed on the plate face in polarized light, the crystals are blue when the electric vector is parallel to the elongation direction (cf. stable form) and either colorless or blue when the electric vector is at right angles to this. With crossed Nicol prisms there is sharp, parallel extinction.

The crystals are orthorhombic, the space group (from systematically absent X-ray diffraction spectra) being either $Pm2_1n$ (C_{2v}^7, no. 31^{12}) or $Pmmn$ (D_{2h}^{13}, no. 59^{12}), and with $a = 16.12 \pm 0.07$ Å, $b = 21.12 \pm 0.10$ Å, $c = 12.22 \pm 0.05$ Å. The observed density is 2.026 ± 0.008 g cm^{-3}. With 20 units of $VOSO_4 \cdot 5H_2O$ per unit cell, the calculated density is 2.02 ± 0.01 g cm^{-3}.

The elongated growth direction is parallel to the a axis, the strongly pleochroic developed faces are {001}, and the other, nonpleochroic plates have {010} developed. Absorption spectra with light incident on {001} were recorded.

The optical properties of the crystal suggest that the molecules are arranged with the V=O bonds all approximately parallel to the b crystallographic axis.

(iii) $VOSO_4 \cdot 5H_2O$ (Unstable Form II). These crystals grow as light blue, elongated plates. They are less pleochroic than the other forms, appearing blue in polarized light incident perpendicular to the plate face with the electric vector parallel to the elongated growth direction, and light blue with the electric vector at right angles to this. There is sharp, parallel extinction under crossed Nicols.

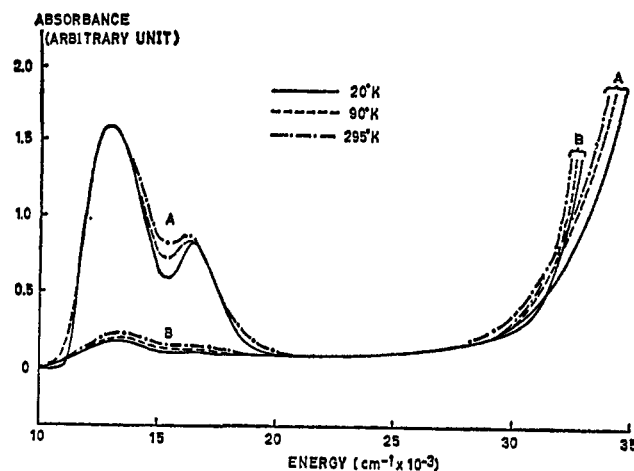This form is orthorhombic, and the systematically absent X-ray reflections show the space group to be

either $Pmn2_1$ (C_{2v}^7, no. 31^{12}) or $Pmnm$ (D_{2h}^{13}, no. 59^{12}). The unit cell dimensions are $a = 7.23 \pm 0.05$ Å, $b = 9.33 \pm 0.07$ Å, $c = 6.18 \pm 0.05$ Å. The observed density is 2.021 ± 0.008 g cm^{-3}. With two units of $VOSO_4 \cdot 5H_2O$ per unit cell, the calculated density is 2.02 ± 0.01 g cm^{-3}.

The elongated growth direction is parallel to the c axis, and spectra were recorded with the light incident on {010}, the only developed faces observed.

In either space group, the V and O atoms of the vanadyl group must occupy special positions. In Pmnm, the only allowed positions require all the V=O bonds to be parallel to the b axis, while in $Pmn2_1$ the V=O bonds are constrained only to be parallel to the b-c plane and may take any orientation therein. Only if the bonds are parallel to the b or c axes are they parallel to each other in this space group. The absence of marked pleochroic behavior and the relation between the unit cells of this and the stable form suggest strongly that the correct space group is $Pmn2_1$ and that the V=O bonds are somewhat inclined to the c axis and to each other.

Spectra of $VOSO_4 \cdot 5H_2O$. The polarized absorption spectra of the various polymorphs were recorded at room temperature and at the temperatures of liquid nitrogen and liquid hydrogen. The over-all absorbance from 10,000 to 30,000 cm^{-1} is quite similar to that given in Figure 5 of ref 5. In the perpendicularly polarized spectrum (viz. perpendicular to the V=O molecular axis), no recognizable vibrational structure appears on cooling; the first band at 13,000 cm^{-1} retains its shape and intensity with an estimated oscillator strength of 2.0 × 10^{-4}, but the second band appearing at 16,000 cm^{-1} as a weak shoulder in the room-temperature measurements becomes much more defined. The over-all intensity of this band decreases by cooling and it appears distinctly at 20°K (the f number for the shoulder is estimated to be 3.8 × 10^{-5}). Figure 2 shows the spectra from the stable form at various temperatures. Those of the other forms are similar, although small shifts of the maxima are observed. In the parallel polarization the intensities for both of the weak bands decrease with temperature, again with the result that the peaks are better resolved. The oscillator strength for the parallel band at 13,000 cm^{-1} is approximately

2.3×10^{-5}. The perpendicular and the axial crystal spectra are completely identical showing that we are dealing with electric dipole transitions.[15]

It is rather interesting that the unstable crystalline modifications of $VOSO_4 \cdot 5H_2O$ often show some fine structure on the perpendicular band at 13,000 cm^{-1} when cooled to liquid hydrogen temperature. Usually, but not always, three or four peaks can be discerned with a spacing of about 800 cm^{-1}.

The new measurements differ significantly from those reported earlier[5] since it is now found that in *both* polarizations a very intense band, beginning at 30,000 cm^{-1}, appears. At 33,000 cm^{-1} its extinction becomes too high to follow further. The old erroneous measurements were unfortunately due to bad instrumentation.

Discussion

The crystal structural data reported here show that the vanadium ion is placed above the plane defined by the four oxygen atoms 3, 4, 5, and 6 (see Figure 1). For instance, the angle O(1)–V–O(3) is experimentally found to be 99.6° (Table I). Such a situation has in-

Table I. Geometry of the Inner Coordination Sphere of the Stable Form of $VOSO_4 \cdot 5H_2O$

(a) Interatomic Angles (deg)[a]

O(1)–V–O(3)	99.6 (3)	O(3)–V–O(5)	90.5 (2)
O(1)–V–O(4)	97.9 (3)	O(3)–V–O(6)	89.6 (2)
O(1)–V–O(5)	93.8 (3)	O(4)–V–O(5)	89.1 (2)
O(1)–V–O(6)	100.7 (3)	O(4)–V–O(6)	86.4 (2)
O(2)–V–O(3)	79.8 (2)	O(1)–V–O(2)	174.2 (3)
O(2)–V–O(4)	82.9 (2)		
O(2)–V–O(5)	80.5 (2)		
O(2)–V–O(6)	85.1 (2)		

(b) Atomic Deviations from the Least-Squares Plane Calculated through the Oxygen Atoms O(3), O(4), O(5), O(6) (Å)

O(3)	0.027 Å
O(4)	0.029
O(5)	−0.027
O(6)	−0.029
V	−0.281

The angle between V–O(1) and this plane is 86.6°
The angle between V–O(2) and this plane is 87.1°

[a] Their estimated standard deviations ($\times 10$) are given in parentheses.

deed been anticipated by Vanquickenborne and McGlynn,[16] who find that the one-electron energies calculated as a function of this angle agree best with the available experimental data for just an angle of 100°.

Characterizing the system in C_{2v} symmetry, Vanquickenborne and McGlynn[16] deduce for the low-lying d states an ordering corresponding to that of Ballhausen and Gray.[5] The actual numbers differ for the two calculations, but, since both methods by necessity use crude and different approximation schemes, the possibility of this is to be expected. Without performing any elaborate calculations, then, one would expect the one unpaired electron found in the vanadyl sulfate system to be located in the nonbonding $b_2(d_{xy})$ level. The excited levels are the antibonding $e(\pi^*)$ level, being antibonding between the vanadium and the doubly bonded vanadyl oxygen atom, and the $b_1(\sigma^*)$ level, be-

(15) E. V. Sayre, K. Sancier, and S. Freed, *J. Chem. Phys.*, 23, 2060 (1955).
(16) L. G. Vanquickenborne and S. P. McGlynn, *Theor. Chim. Acta*, 9, 390 (1968).

ing antibonding between the vanadium and the four equatorial oxygen atoms. The relative placement of these antibonding orbitals is of course uncertain, but one would expect them to be of comparable energy. Much higher we expect to find the antibonding a_1 orbital, which is an antibonding combination of d_{z^2}, 4s, and all of the ligand σ orbitals.

With the ground state transforming as $^2B_2$, a transition is electric dipole allowed to ^2E with the electric vector perpendicular to the V=O axis. Parallel electric dipole transitions are not allowed to any of the excited states considered. If we turn our attention toward vibronically allowed transitions, the $^2B_2 \rightarrow {}^2E$ transition would be allowed parallel with the simultaneous excitation of an ϵ vibration and the $^2B_2 \rightarrow {}^2B_1$ should be allowed parallel with the simultaneous excitation of an α_2 vibration and perpendicular with an ϵ vibration. If we treat the system as $O-V(O)_5$ possessing C_{4v} symmetry, no vibrational coordinate of α_2 symmetry is, however, found. The transition $^2B_2 \rightarrow {}^2B_1$ should therefore only be observed as a perpendicular, "vibronic" band.

A peculiarity of vibronic bands is that, in contrast to allowed bands, their intensities decrease upon cooling. It is furthermore on the red sides of the bands that the effect is greatest, since the "hot" vibrations of the ground state are those which are frozen out.

All available calculations indicate that the lowest excited state is ^2E. The band at 13,000 cm^{-1} is therefore identified as $^2B_2 \rightarrow {}^2E(I)$. It behaves as a single electronic transition and its polarization behavior and the invariance of the intensity of the perpendicular polarized band with cooling support this assignment. The energetically most reasonable assignment for the second band at 16,000 cm^{-1} is then $^2B_2 \rightarrow {}^2B_1$; this transition is perpendicularly allowed vibronically and it shows the expected temperature dependence for vibronic bands.

The above assignments raise the question why the 13,000-cm^{-1} band $^2B_2 \rightarrow {}^2E$ in parallel polarization has a different form to the 16,000 cm^{-1} band $^2B_2 \rightarrow {}^2B_1$ in perpendicular polarization since both assigned transitions are vibronically allowed using an ϵ vibration. Notice, however, that the intensity of the parallel band seen at 13,000 cm^{-1} ($f = 2.3 \times 10^{-5}$) is found to be of the same order of magnitude as the intensity of the perpendicular band ($f = 3.8 \times 10^{-5}$) seen as a shoulder at 16,000 cm^{-1}. Although both transitions are made allowed by means of an ϵ vibration, the *potential surfaces* of the two excited states are expected to be quite different. This is easy to understand when we remember that the $^2B_2 \rightarrow {}^2E$ transition is likely to expand the V=O bond length, but that a $^2B_2 \rightarrow {}^2B_1$ transition would expand the equatorial plane of the molecule. There is therefore no reason to expect the band shapes to be identical, but only that the total intensities in each of the two bands should be comparable, which is the case.

As to the observed fine structure of the 13,000-cm^{-1} band, we feel that this probably represents some quanta of the V–O totally symmetric stretching mode superimposed upon the electronic (O–O) level. The reduction of this frequency from the 1000 cm^{-1} found in the ground state[17] can be explained as due to the transfer of the nonbonding b_2 electron to an antibonding e level.

(17) J. C. Evans, *Inorg. Chem.*, 2, 372 (1963).

Why the fine structure appears on the spectra from only some of the unstable crystals remains unexplained. That the structure should be due to a spin–orbit splitting of the $^2B_2 \rightarrow {}^2E$ transition[2] seems unlikely to us, since the number of bands and the order of magnitude to be expected for a spin–orbit splitting are not comparable to our observations.

As to the "charge-transfer spectrum" setting in for both polarizations at 30,000 cm^{-1} we must expect such bands to be due to a transfer of an electron localized on the metal to the equatorial ligands. Since the vector from the vanadium metal to an equatorial ligand is not perpendicular to the V=O bond, the transition moment will have both perpendicular and parallel components.

Such a strongly allowed transition is therefore expected to be seen in both polarizations.

In conclusion, the spectral behavior of vanadyl sulfate observed in the new measurements seems best explained on the basis of the original Ballhausen–Gray level scheme. On the other hand, we are not of course suggesting that this level scheme is valid for all vanadyl complexes.

Complete Neglect of Differential Overlap Calculations on Second-Row Molecules

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Abstract: The CNDO parameters necessary for calculations on molecules containing second-row atoms have been estimated, by comparison with reference calculations, for the atoms Si, P, S, and Cl. It was found that this method of deriving the parameters, as opposed to the method which makes some use of spectral data, is subject to certain restrictions. The parameters have been used to calculate the bond angles and dipole moments of a selection of chemically interesting molecules containing a second-row atom. Both of these properties were found to be reliably within reasonable agreement of the experimental values. Finally, the importance of 3d orbitals to the bonding in these molecules is discussed.

The simplification of Roothaan's[2] self-consistent field equations through the adoption of semiempirical schemes has permitted the calculation of properties and charge distributions of large chemically interesting molecules.[3] One of the more successful approximations to be investigated is the complete neglect of differential overlap (CNDO) method.[4,5] This method is based on the neglect of all overlap charge distributions and the empirical calculation of all one-electron matrix elements. An important feature of the method is that these matrix elements are constructed from atomic parameters which are obtained from atomic spectral data and by comparison of CNDO calculations with more detailed calculations on simple molecules. These parameters have been estimated for all first-row atoms (Li → F) and hydrogen,[5,6] and calculations based on them have proved very successful.[7]

In the case of second-row atoms (Na → Cl) the estimation of the atomic parameters, necessary for CNDO calculations, has been hampered by the paucity of detailed calculations on second-row molecules. How-

ever, CNDO calculations, based on assumed atomic parameters, have been carried out[8] for a series of second-row molecules and suggest that the CNDO method should be very useful as a means of interpreting the properties of these molecules. Although the bond angles and the general trends of the dipole moment, calculated by the CNDO method, were very good, the poor dipole moments of certain of the molecules suggested that the theory needs to be carefully parametrized. In the present paper the atomic parameters for Si, S, P, and Cl are estimated by comparison with detailed calculations (based on Gaussian orbitals) on simple molecules. As the estimation of the diagonal elements from atomic spectral data presents serious difficulties in the case of second-row atoms,[8] these too were estimated by comparison with the reference calculations.

Theory

Molecular orbital theory approximates the N-electron wave function for a molecule by an antisymmetrized product of doubly occupied molecular orbitals (one-electron functions). The molecular orbitals ϕ_i are expressed as a linear combination of atomic orbitals

$$\phi_i = \sum_{\mu} \chi_{\mu} C_{\mu i} \tag{1}$$

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(3) J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953).
(4) J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, S129 (1965).
(5) J. A. Pople and G. A. Segal, ibid., 43, S136 (1965).
(6) J. A. Pople and G. A. Segal, ibid., 44, 3289 (1966).
(7) D. Breen, M.Sc. Thesis, University of Virginia.

(8) D. P. Santry and G. A. Segal, J. Chem. Phys., 47, 158 (1967).