Spectral Studies of Selected Oxovanadium(iv) Complexes.

Gerald John Maus

Louisiana State University and Agricultural & Mechanical College

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SPECTRAL STUDIES OF SELECTED OXOVANADIIUM(IV) COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemistry

by

Gerald John Maus
B.S., Louisiana State University in New Orleans, 1962
May 1967
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acac - acetylacetone
hfa - hexafluoroacetylacetone
dpm - dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanediode)
en - ethylenediamine
dbm - dibenzoylmethane
bza - 1-phenyl-1,3-butanediode
kK - 1000 cm$^{-1}$
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ABSTRACT

A great deal of interest has been generated in oxovanadium(IV) chemistry in the last several years. There are several reasons for the interest in this species. Oxovanadium(IV) possesses great stability, is capable of existing in solid, liquid and in vapor phases without destruction of the $\text{VO}^{2+}$ entity, and it is a central molecule-ion and may therefore be studied by methods not applicable to the usual central atom-ions. Another reason for the interest in this species is that oxovanadium(IV) usually has square base pyramid geometry in complexes with bidentate ligands. This geometry is quite rare among the first row transition elements. Perhaps the main reason for the recent interest in oxovanadium(IV) is that it is a $d^1$ electronic species and should lend itself to an easy theoretical interpretation. Much of the recent work, in fact, has been to elucidate a theoretical scheme to account for the observed electronic transitions.

Electronic spectra were obtained mainly for the $\beta$-ketoenolate complexes $\text{VO(dpm)}_2$ and $\text{VO(hfa)}_2 \cdot \text{H}_2\text{O}$. These spectra were obtained in various solvents, in the vapor phase, in reflectance and at liquid nitrogen temperatures, in alkali halide pellets, nujol mulls, and frozen organic glasses. The vapor spectra were the first obtained for any oxovanadium(IV) complex.

Perhaps the most significant new aspect noted from the studies of these various spectra is the firm establishment of a very weak
intensity band at 10-12kK. This band had either been ignored or unnoticed probably because it is usually covered or partly covered by a slightly more intense band in the 12-15kK region. Besides these two bands a third and fourth low energy band is also observed in these 6-diketone complexes. These two bands appear in the 15-18kK and 20-25kK range, respectively. The movement of these four bands to higher or lower energies with changing solvent was closely studied. The splittings (if any) and positions of these bands were also studied in the vapor phase and at liquid nitrogen temperatures.

With the results of these various spectra, the following empirical energy assignments are proposed to account for the observed electronic transitions in these oxovanadium(IV) complexes:

<table>
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<tr>
<th>Energy Range (kK)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-12</td>
<td>xy-(x^2y^2)</td>
</tr>
<tr>
<td>12-16</td>
<td>xy-(xz,yz)</td>
</tr>
<tr>
<td>15-18</td>
<td>xy-(z^2)</td>
</tr>
<tr>
<td>20-25</td>
<td>C.T. and T-S_o(ligand)?</td>
</tr>
</tbody>
</table>
A. INTRODUCTION

A great deal of interest has been generated in oxovanadium(IV) chemistry in recent years. Much of the work on oxovanadium(IV) has involved simply the preparation and characterization of new complexes. (See references 1 and 2). Recently quite a bit of work has been done with the purpose of assigning the observed electronic bands in VO$^{2+}$ complexes according to some suitable theoretical model.

There are many reasons why the oxovanadium(IV) species is so often studied. One of the best reasons for the popularity of the oxovanadium(IV) species is its great stability. Oxovanadium(IV) forms quite a variety of stable anionic, cationic and neutral complexes. It is also capable of existing in solid, liquid and, quite unexpectedly, in the vapor phase without destruction of the VO$^{2+}$ entity. It is also usually quite stable in both aqueous and non-aqueous solutions.

The oxovanadium(IV) species is also a central "molecule-ion" and may be studied by methods not applicable to compounds of central atom-ions. Oxovanadium(IV) is also of great value to those concerned with e.s.r. for several reasons besides its stability. Naturally occurring vanadium 51 has high isotopic purity and it also has a high nuclear spin ($\frac{7}{2}$). Furthermore, and perhaps most significant of all, oxovanadium(IV) is a $d^1$ electronic system and thus should lend itself to an easy theoretical and experimental interpretation.
The presence of a single d-electron outside of a closed shell in the oxovanadium(IV) species should also make the interpretation of the optical spectrum of this species a simple matter. However, this has not proven to be the case for reasons to be elaborated later.

Another reason for the increasing interest in oxovanadium(IV) is the geometry of its complexes. The predominant geometry for most of the transition metal complexes is octahedral, distorted octahedral (tetragonal) or square planar. Other geometries are quite rare, especially for the first row transition metals. Oxovanadium(IV) however gives a geometry quite unique in the first row transition elements. In the complexes of general formula \((X)_3\text{VOL}_5(L = F^-,\text{CN}^-)\), the symmetry is a strongly distorted octahedron. In complexes of general formula \(\text{VO(AA)}_2\) (AA = various bidentate ligands) the geometry is usually a slightly distorted square base pyramid, where the O-V-A angle is always greater than ninety degrees. This is a quite unusual configuration for the first row transition metals. This geometry presents an "open" sixth position trans to the vanadyl oxygen. A solvent effect study on a compound which has this open sixth position, \(\text{VO(acac)}_2\), has been the subject of one investigation. The relative shifting of the optical bands in the 10.0 - 25.0kK range along with the results of a few liquid nitrogen temperature spectra, led to postulation of the so-called clustered level scheme. The scheme, to be discussed later, received affirmation from some workers but was
questioned by others. It was in an effort to determine if the clustered level scheme was valid or not, and if not to attempt another assignment of the electronic bands for oxovanadium(IV), that this study was undertaken.

One principal task was to attempt to obtain a vapor spectrum of one or more oxovanadium(IV) complexes. Vapor spectra of this species had never been obtained before and it was hoped that they would be helpful in the assignment of the electronic bands. With this purpose in mind, the complexes VO(hfa)$_2$·H$_2$O and VO(dpm)$_2$ were prepared. They are both very volatile, subliming at 50-75°C at 10$^{-4}$ mm Hg pressure and it was hoped that vapor spectra of both could be obtained. The spectra of these two compounds were also obtained in a variety of solvents and in reflectance to see how they supported the earlier solvent effect results obtained by Ortolano on VO(acac)$_2$, a related compound. It was during these studies that a previously unreported very low intensity band was discovered in the 11.0 - 12.0kK region. Prior to this, only three bands were usually observed in the 10.0 - 25.0kK region for oxovanadium(IV) complexes, band "I" at 12.0 - 15.0kK, band "II" at 14.0 - 18.0kK and band "III" at 20.0 - 28.0kK. This weak new band made a total of four bands below 25.0kK at room temperature. The spectra of these complexes were also run at liquid nitrogen temperature to see what if any splitting would occur and what effect this would have on the assignment of the bands to a particular theoretical model.

A low temperature spectrum was also obtained for the interesting
complex \((\text{NH}_4)_2 \text{VO(tartrate)} \cdot \text{H}_2\text{O}\). This complex shows four moderately intense bands in the 10.0 - 25.0kK region at room temperature. It was hoped that a liquid nitrogen temperature spectrum of this low symmetry complex would yield splitting which would be of value in the elucidation of a theoretical model to explain the optical spectra of oxovanadium(IV) complexes.

With the results of the above mentioned experiments an empirically derived model is proposed to account for the optical spectra of oxovanadium(IV) complexes.
Though much optical and e.s.r. data have been obtained on a variety of vanadyl complexes, there is still no thoroughly satisfactory and unambiguous assignment for the observed electronic bands.

The history of the vanadyl species and its compounds has been adequately discussed elsewhere. The following discussion will therefore be primarily concerned with the spectral properties of the vanadyl ion in the visible near-infrared and near-ultraviolet region (8.0 - 30.0kK).

Several authors have tried to fit the observed electronic bands of vanadyl complexes to theoretical models. One of the first was Jorgensen who interpreted the VO(H₂O)²⁺ ion using a simple crystal field model. By assuming a tetragonal distortion of the energy levels of an exact cubic symmetry, O₅, he was able to qualitatively obtain a scheme which accounted for the crystal field spectrum of VO(H₂O)²⁺. When one axis possesses a stronger ligand field than the other two, as for example, VO(edta)²⁻, the tetragonal splitting is decreased and the two observed bands are split further apart. Copper complexes with a pronounced tetragonality give only one optical band (d¹ positive hole system).

However, since a simple crystal field model could not consider π-bonding, it could not begin to account for all of the observed optical and magnetic data. The crystal field splitting for O₅ and C₄ᵥ symmetries is shown in Figure 1.
Figure 1: Diagrammatic representation of d orbital splittings in $O_h$ and $C_{4v}$ symmetry.
Ds and Dt are parameters which specify the degree of
tetragonality in the crystal field. Magnetic data indicate an
orbitally non-degenerate ground state for VO$^{2+}$ complexes. Thus,
the $b_2$ orbital must lie below the $e^*_\pi$ orbital. If the tetragonal
perturbation results in axial compression, as is the case for
VO(H$_2$O)$_5^{2+}$, then the $1a^*_1$ orbital is less stable than the $b^*_1$ orbital.
The $d$-$d$ transitions predicted by simple crystal field theory for
the $C_{4v}$ species are therefore $b_2 \rightarrow e^*_\pi (-3Dq + 5Dt)$, $b_2 \rightarrow b^*_1 (10Dq)$
and $b_2 \rightarrow a^*_1 (10Dq - 4Ds - 5Dt)$. The solution spectrum of VO(H$_2$O)$_5^{2+}$
reveals broad bands at 13,000 cm$^{-1}$ and 16,000 cm$^{-1}$ which were
assigned as the transitions $b_2 \rightarrow e^*_\pi$ and $b_2 \rightarrow b^*_1$. The $b_2 \rightarrow a^*_1$
band is presumed to be covered by an intense charge transfer
band at 40,000 cm$^{-1}$. $Dq$ was calculated directly from the transition
$b_2 \rightarrow b^*_1$, giving it a value of 1600 cm$^{-1}$. By assuming the $b_2 \rightarrow a^*_1$
transition to be at approximately 35,000 cm$^{-1}$, $Ds$ and $Dt$ were
calculated to be -4570 cm$^{-1}$ and -143 cm$^{-1}$, respectively. These
values may be compared with $Ds = -117$ cm$^{-1}$ and $Dt = -33$ cm$^{-1}$ for
tetragonally distorted cobaltous oxide. The relatively small
$Dq$ value and large $Ds$ and $Dt$ values calculated for VO(H$_2$O)$_5^{2+}$
indicate the presence of a very large tetragonal distortion and
points out the inadequacy of the simple crystal field model.

In 1962, Ballhausen and Gray elaborated a molecular orbital
description of the 'vanadyl ion, [VO(H$_2$O)$_5^{2+}$], using a modified
Wolfsberg-Helmholz procedure. The 3$d$, 4$s$ and 4$p$ vanadium orbitals,
along with the 2$s$, 2$p_z$ ($\sigma$-bonding), and 2$p_y$, 2$p_x$ ($\pi$-bonding).
orbitals of the oxide oxygen and the sp\(\sigma\) hybrid orbitals of the water oxygens were used. Since the vanadium to water-oxygen bonds are known to be longer than the vanadium to oxide-oxygen bond, (2.3\(^\circ\) and 1.67\(^\circ\), respectively)\(^9,10\) \(\pi\)-bonding involving the water oxygens was ignored.

Ballhausen and Gray deduced the following transformation scheme numbering the equatorial ligands 1, 2, 3, and 4, the oxide-oxygen number 5 and the axial ligand number 6.

<table>
<thead>
<tr>
<th>Symmetry Representation in (C_{4v})</th>
<th>Vanadium Orbitals</th>
<th>Ligand Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>(3d_{z^2} + 4s)</td>
<td>(\sigma_5)</td>
</tr>
<tr>
<td></td>
<td>(4s - 3d_{z^2})</td>
<td>(\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4))</td>
</tr>
<tr>
<td></td>
<td>(4p_z)</td>
<td>(\sigma_6)</td>
</tr>
<tr>
<td>(e_{\pi})</td>
<td>(3d_{xz}, 3d_{yz})</td>
<td>(\pi_5(2p_x, 2p_y))</td>
</tr>
<tr>
<td></td>
<td>(4p_x - 4p_y)</td>
<td>(2^{-\frac{1}{2}}(\sigma_1 - \sigma_3), 2^{-\frac{1}{2}}(\sigma_2 - \sigma_4))</td>
</tr>
<tr>
<td>(b_1)</td>
<td>(3d_{x^2-y^2})</td>
<td>(\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4))</td>
</tr>
<tr>
<td>(b_2)</td>
<td>(3d_{xy})</td>
<td>----</td>
</tr>
</tbody>
</table>

Using the usual criterion that bond strengths are proportional to overlap, they deduced the molecular orbital scheme shown in Figure 2, with the arrow representing the lone d electron beyond the filled argon core in vanadium(IV). All bonding orbitals are filled.
Figure 2: Molecular Orbital Scheme for VO(H₂O)²⁺ as calculated by Ballhausen and Gray.⁸
with electrons from the ligands and all antibonding (starred) orbitals are empty in the ground state.

The ordering of the energy levels for the "d-d" transitions is the same as was predicted by the crystal field model. The author's calculations gave the following energy predictions (in units of kK = 1000 cm⁻¹):

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy (kK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_2 \rightarrow e^*$</td>
<td>12.50</td>
</tr>
<tr>
<td>$b_2 \rightarrow b_1^*$</td>
<td>18.79</td>
</tr>
<tr>
<td>$b_2 \rightarrow t_{2g}^*$</td>
<td>44.76</td>
</tr>
<tr>
<td>$e^*_\pi \rightarrow b_2$</td>
<td>38.80</td>
</tr>
</tbody>
</table>

The experimental values for VO(H₂O)²⁺ are 13.06kK, 16.00kK and 41.70kK. These were assigned to the transitions $b_2 \rightarrow e^*$, $b_2 \rightarrow b_1^*$ and $e^*_\pi \rightarrow b_2$ with the $b_2 \rightarrow t_{2g}^*$ transition believed to be covered by the charge transfer band.

Selbin, Holmes and McGlynn, using the same atomic orbitals as did Ballhausen and Gray, but considering additionally equatorial $\pi$-bonding, obtained an energy level scheme showing a reversal of ordering of the antibonding $e^*$ and $b^*$ levels. The possible crossing of these two levels will be noted again later.

In all further discussion the band at 11 - 12kK will be referred to as the "weak" band. The bands in the regions 13.0 - 16.0kK, 15.0 - 19.0kK and 20.0 - 25.0kK will be referred to as the first band, second band and third band, respectively.

Horner, Tyree and Venesky prepared and obtained the optical spectra of the compounds VOCl₂ · 4(C₆H₅)₃AsO, VOCl₂ · 3(CH₃)₂SO,
VOCl₂ · 2(C₆H₅)₃PO and VO(C₂O₄)₂ · 5(C₆H₅)NO in methylene chloride. They interpreted the optical spectra according to the Ballhausen-Gray molecular orbital scheme. They noted that in some cases the 

\[ b_2 \rightarrow e^* \] transition (\( \approx 4.00 \text{kK} \)) completely covered the 

\[ b_2 \rightarrow b_1^* \] transition (\( \approx 5-16 \text{kK} \)).

Selbin and Ortolano measured the effects of thirteen solvents on the absorption spectrum of VO(acac)₂. They noted that the first band (\( \approx 4 \)kK) red-shifted and the second band (\( \approx 7 \)kK) blue-shifted slightly as the ligational strength of the solvent increased. They assigned the three low intensity bands, using the Ballhausen-Gray energy level scheme, to the transitions 

\[ b_2 \rightarrow e^*, b_2 \rightarrow b_1^* \text{ and } b_2 \rightarrow a_1^* \], respectively. They defined a new empirical quantity \( D_{II-I} \), the difference between the first and second band maxima, as a new parameter, more sensitive for ranking solvent ligand strength than Dq itself. With the strongest ligand, water, a difference of 5.49kK was observed between the first two bands. Benzene, the weakest ligand, only gave a difference of 1.07kK. This represents a range of (5.59 - 1.07) or 4.42kK, as compared to a difference of 1.3kK for 10Dq, 0.6kK for Ds and 0.3kK for Dt. Using this parameter they were able to rank the solvents as follows: 

\[ \text{H}_2\text{O} > \text{MeOH} > \text{pyridine} > \text{n-propylamine} > \text{EtOH} > \text{DMSO} > \text{DMF} > \text{CH}_3\text{CN} > \text{CH}_3\text{NO}_2 > \text{CHCl}_3 > \text{CS}_2 > \text{C}_6\text{H}_6 > \text{CCl}_4. \]

Bernal and Rieger investigated the optical and e.s.r. spectrum of vanadyl acetylacetone in six solvents. They also noticed a red shift in band I and a blue shift in band II with increasing solvent ligand strength. Band III shows little tendency
to shift in any solvent. This was assigned as the $b_2 \rightarrow a_1^*$ transition, according to the Ballhausen-Gray scheme and this transition which is to an energy level made up of (Figure 2) the $3d_{z^2}$ metal orbital and the $2p_z$ of oxygen would be expected to show a large shift when a solvent molecule enters the open sixth position. The authors noted that there was no explanation for the fact that the band did not shift markedly.

Among the first to cast doubt on the validity of the Ballhausen-Gray energy level scheme were Selbin, Ortolano and Smith, who noted that the first band of VO(acac)$_2$, at 14.00kK, split into three components at liquid nitrogen temperature. They proposed that these three bands were all electronic in origin and belonged to the $b_2 \rightarrow e_\pi^*$ transition (split in $C_{2v}$ symmetry) and the $b_2 \rightarrow b_1^*$ transition. The band at 18,000 cm$^{-1}$, which showed no splitting, was assigned by them as the $b_2 \rightarrow Ia_1^*$ transition and the 25.00kK band was assigned as a charge-transfer band. This assignment placed all four "d-d" transitions below 20.0kK.

Ortolano, Selbin and McGlynn proposed a "clustered level" scheme to explain the liquid nitrogen temperature splitting of the optical bands of VO(acac)$_2$. The authors proposed that band I (14.00kK) contains the degenerate $e_\pi^*$ (split in $C_{2v}$ symmetry) transition and the $b_1^*$ transition. The 17.00kK band was assigned as the $b_2 \rightarrow Ia_1^*$ transition. The 25.00kK band was then tentatively
assigned as a charge transfer band. Support for this scheme was the disappearance of the bands at 13.60kK and 17.10kK upon oxidation by elemental oxygen of vanadium(IV) to vanadium(V). The 25.00kK band did not disappear on oxidation, but red-shifted as oxidation occurred. This red shift was expected since the first charge transfer transition is from a ligand filled bonding orbital to a half-filled metal orbital and thus was expected to involve a repulsion energy. This repulsion energy is surely absent in vanadium(V). An apparent discrepancy in the "clustered level" scheme was found in the compound (NH₄)₃(VOF)₅, in which the first band also splits into three components at liquid nitrogen temperature. Since this compound should have C₄ᵥ symmetry, the e* level should remain degenerate and only two components should be observed in band I. Rather than abandon the "clustered level" scheme, the authors postulated a spin-orbit coupling mechanism for splitting the e* representation in C₄ᵥ symmetry. However, the authors did not completely rule out vibronic splitting as an explanation for the three components of the 14.00kK at liquid nitrogen temperatures.

Selbin and Morpurgo¹⁵ studied the aqueous solution spectra of the vanadyl ion with the ligands tartrate, citrate, lactate, mandelate and malate. In basic solution four bands are observed for each "complex" in the 10,000 - 30,000 cm⁻¹ range. Using the "clustered level" scheme of Ortolano, Selbin and McGlynn, these bands were interpreted as the four d-d bands, with the e* level split by the low symmetry of these complexes. The Ballhausen-Gray
scheme cannot easily account for four bands at such low energy. Recently however, Tapscott and Belford\textsuperscript{16} cited experiments of molecular weight determination, e.s.r. spectra, titration data and optical spectra to prove the structure of vanadyl tartrate complexes. They deduced that these tartrate complexes were bridged dimers and that two species were possible, depending on whether d, L, or d-L racemic mixture of tartaric acid was used in the preparation. The only x-ray crystallographic work on a vanadyl complex with cis-trans isomerization possible\textsuperscript{17}, vanadyl bis (benzoylacetylacetonate), has shown that only the cis isomer is obtained as the compound is normally prepared. The racemic dimer was the more stable of the tartrate complexes however. This prompted the authors to postulate a cis arrangement about the vanadium for the d-L dimer. This compound, which is red-brown, shows three bands in the 10-25kK region in alkaline solution. The d-d dimer, for which the authors postulate a trans arrangement, is violet in alkaline solution and shows four bands in the 10-25kK region. The x-ray work on ammonium vanadyl(+)tartrate has been done by Forrest and Prout\textsuperscript{18}.

Shortly after the work of Selbin, Ortolano and McGlynn was published, there appeared an interesting paper by Basu, Yeranos and Belford\textsuperscript{19}. They ran a low temperature thin-crystal spectrum of VO(acac)_2 and obtained some significant splittings. The first band at 14,00kK was split into three components, much the same
as Selbin, Ortolano and Smith had observed earlier. The separation of these components was about 0.7 kK and the authors interpreted this as the beginning of a vibrational progression (possibly the vanadyl stretching frequency which occurs at about 0.99 kK in the ground state of the molecule). The authors, however, stated that from the shape of the curve in the 10-12 kK regions, they could not definitely rule out more than one electronic band. Indeed, on close inspection of their spectrum, there appears to be a low intensity band at about 11.5 kK not pointed out by them. The second band at 17.00 kK showed no splitting whatever. The so-called "third band" at 25.00 kK was split into at least 5 components with a separation of ≈ 7 kK. They considered this splitting a vibrational progression and assigned the whole band as either a charge-transfer band or a vanadyl internal transition rather than a transition within the acetylacetone ligand system itself. A new feature in the spectrum of VO(acac)\textsubscript{2}, excluding the three previously mentioned bands, were two fairly sharp bands at approximately 23 kK, split by about 0.35 kK. The authors offered several explanations for these two bands. First, they could be components of a spin-allowed vanadyl band. They did not endorse this explanation because these bands were much sharper than those usually observed for vanadyl. Secondly, these two bands could be spin-forbidden acetylacetone-to-vanadyl charge-transfer transitions. These bands, however, are at a lower frequency than is usually expected for such acetylacetonate transitions. And
finally they proposed that these two bands could be internal ligand bands (probably spin-forbidden $\pi \rightarrow \pi^*$ transitions).

Wentworth and Piper\textsuperscript{20} obtained a low temperature polarized spectrum of VOCl\textsuperscript{5+} in various diluent crystals. Only in the case of the diluent crystal, K\textsubscript{3}TiCl\textsubscript{6} \cdot 2H\textsubscript{2}O, were they able to get alignment of the VOCl\textsuperscript{5+} ion with the unique axis of the tetragonal unit cell. From the authors own definition of $D_s$ and $D_t$, they concluded that these two quantities must be negative. They then proposed that all d-d transitions could not possibly lie below 20kK, since this would require a positive $D_t$. From their polarization spectra they assign the first band, at 15.50kK, as the $b_2 \rightarrow e^*$ transition since it is independent of temperature. The parallel polarization gives a temperature dependent band at 16.20kK which is assigned as the $b_2 \rightarrow b^*_1$ transition. The $b_2 \rightarrow a^*_1$ transition was assigned at about 50.00kK.

Some support for the Ballhausen-Gray scheme was found in the conclusions of Jones and Larsen\textsuperscript{21} from their work on circular dichroism of dissymmetric vanadyl complexes. The reason for carrying out the circular dichroism studies was the fact that two components could be observed even if the splitting was as small as 100 cm\textsuperscript{-1}. They ran a solution of vanadyl sulfate and L-lactic acid at pH of 3. They concluded that there were three bands in the 10-20kK region due to the degenerate $b_2 \rightarrow e^*$ transition and the $b_2 \rightarrow b^*_1$ transition. A band at 28kK was assigned by the authors as the $b_2 \rightarrow a^*_1$ transition. However, some of their conclusions
are almost surely invalidated by the recent discoveries concerning
the molecular structures of tartrate (and presumably related)
complexes mentioned earlier (see page 11).

Sacconi and Campigli$^{22}$ prepared a variety of vanadyl complexes
with chelates made from salicylaldehyde and N, N'-disubstituted
ethylenediamines, and they obtained their spectra in CHCl$_3$, reflectance
and in pyridine. In general, the complexes in CHCl$_3$ or by reflectance
exhibit three bands below 20kK. The approximate positions of these
bands are 11.5-12kK, 16.65-16.95kK and 18.20-19.05kK. There is a
noticeable change in the spectra of these compounds in pyridine
solution. The two higher energy bands are relatively unaffected
but the low energy band shifts to about 13.7kK. Also noticeable
with this shift is the appearance of a fourth band as a shoulder
on the 13.7kK band at about 11.5kK. This could be attributed to
a splitting of the e* representation. This then gives four bands
below 20kK, at room temperature. The authors stated that this
could be interpreted by the "clustered level" scheme of Ortolano,
Selbin and McGlynn$^4$.

Garvey and Ragsdale$^{23}$ prepared various complexes of vanadyl
with substituted pyridine N-oxides. They obtained complexes of
general formula VOL$_2^{2+}$ or VOL$_5^{2+}$ for ring-activating substituents
and complexes of general formula VOL$_2X_2 \cdot H_2O$, (X = Br, Cl), for
ring-deactivating substituents. The higher coordination was
obtained in all cases where perchlorate was the anion. The authors
noted that solution spectra of these species were solvent dependent and chose primarily to run nujol mull spectra. They usually observed two bands, one at about 12.5kK - 13.5kK and the second at around 16.0kK - 17.5kK. In some cases they noted only one band at approximately 15.5-16.5kK. The authors did not make any band assignments or do any low temperature work.

Kuska and Rogers concluded from e.s.r. and polarization data, that the 16kK band in VO(SO₄) • 5H₂O is the $b_2(d_{xy}) \rightarrow a^+(d_{3z^2})$ transition. The authors obtained a spectrum of VOSO₄ in warm DMF which could be resolved into three peaks at 12.6kK, 15.2kK and 18.0kK, which they assigned to the transitions $xy \rightarrow (xz, yz)$, $xy \rightarrow (x^2 - y^2)$, and $xy \rightarrow z^2$, respectively. They assumed that they still had the VO(H₂O)₂⁺ species in solution. From their data they could not completely rule out the possibility that the 18.0kK band is due to a charge-transfer transition with characteristics similar to the $d_{xy} \rightarrow d_{3z^2}$ transition.

Kilty and Nicholls prepared and ran the electronic reflectance spectra of several oxochlorovanadyl complexes. The compounds were of the general types $M_2VOCI_{4} \cdot xH_2O$, ($M = pyH^+, \text{quin H}^+$, isoquin $H^+$, NH₄⁺, K⁺ or Cs⁺ and $x = 0, 1$ or 2), and $MVOCl_3 \cdot xH_2O$ ($M = Me_4N^+, \text{Et}_4N^+, \text{quin H}^+; x = 0, 1.5, 2, \text{or 3}$). The reflectance spectra of these complexes each give a peak at about 13.8kK, which has a low energy shoulder at around 12.0kK, and another peak at 24.0kK. Using the reversal of energy order of the $e^*$ and $b^*$
orbitals, as predicted by Selbin, Holmes and McGlynn, they assigned the 13.8kK band as $b_2 \rightarrow e^\pi$ and the 12.0kK shoulder as $b_2 \rightarrow b_1^*$. The band at 24.0kK was assigned as the $b_2 \rightarrow a_1^*$ transition. The authors assigned the 13.8kK band as the $b_2 \rightarrow e^\pi$ transition since it is orbitally allowed and should be most intense. In a few cases where $M$ was $K^+$ or $Cs^+$, the authors noted a reversal in the intensity of these first two bands. In these cases they assumed that the first two transitions were $b_2 \rightarrow e^\pi$ and $b_2 \rightarrow b_1^*$, which is the same as the Ballhausen-Gray scheme.

Zerner and Gouterman did extended Hückel calculations on vanadyl porphyrin. They performed calculations with (I) vanadium sitting in the porphyrin plane, (II) the vanadium .492Å above the plane (similar to ferric porphyrins) and (III) with the vanadium .74Å above the plane (obtained from the known geometry of VO(acac)$_2$). The calculation for the third case gives the following transitions;

- $2b_{2g} \rightarrow 2e^\pi$ at about 11.0kK,
- $2b_{2g} \rightarrow 2a_1^*$ at about 18.3kK and
- $2b_{2g} \rightarrow 2b_1^*$ between 33.2kK for case I to 19.5kK for case III.

The calculations in all three cases predict that the $2a_{1g}$ level should lie below the $2b_{1g}$ level. This, of course, is quite different from the Ballhausen-Gray or the Ortolano-Selbin-McGlynn schemes. They then recalculated case III with a water molecule 2.0Å below the plane in the sixth position, and obtained the same energy level scheme. Since the $2b_1^*$ ($d_{x^2-y^2}$) level is strongly ligand dependent, the authors postulated that the porphyrin ligand (four nitrogens) causes stronger perturbations than the waters (four
oxygen(s) upon which Ballhausen and Gray based their calculations. This they say is what has raised the $^2b_{1g}$ orbital in energy.

Recently, Yeranos\textsuperscript{27}, from temperature dependent polarization spectra on VO(acac)$_2$, proposed the following assignments for the three observed transitions; (I) $d_{xy} \rightarrow d_{xz} (12.1kK)$, (II) $d_{xy} \rightarrow d_{yz} (14.3kK)$ and (III) $d_{xy} \rightarrow d_{z^2} (17.3kK)$. He assigned the $d_{xy} \rightarrow d_{x^2-y^2}$ transition to be somewhere between 14.3kK and 17.3kK. The author denies that structure in the 14.3kK band is electronic, since this would give five d-d bands in the 12 to 17kK region, which, of course, is not possible.

Bontchev and Nikolov\textsuperscript{28} ran the spectra of the vanadium activator complexes which they were working on. They were attempting to elucidate the behavior of some activators in homogenous catalysis by means of Molecular Orbital Theory and the electronic spectra of the complexes formed between the catalyst and the activator. The activators were oxalate, citrate and sulphosalicylate. They assumed the activator complexes were $C_{2v}$ symmetry with formula VO(L)$_2$ ($L =$ oxalate, citrate or sulphosalicylate). They concluded that if ligands which form strong $\pi$-bonds are used, that the $b_2$ level is no longer non-bonding, but forms $\pi$-bonds with the molecular orbital of the activator. They then postulated that the ground state for complexes with these various activators employed would be $e_{\pi}$. 
C. EXPERIMENTAL

1. Preparation of Complexes

a. VO(hfa)$_2$ • H$_2$O. Syrupy vanadyl chloride was made by heating 20 grams of V$_2$O$_5$ in a mixture of 110 ml. of concentrated HCl and 100 ml. of 95% ethanol. The resultant mixture was boiled to a small volume, yielding a thick blue syrup. Attempts to boil this material to dryness resulted in oxidation of the vanadyl chloride. Solutions of the vanadyl chloride are fairly acidic and a base was used to raise the pH to approximately five. The bases tried were ammonium hydroxide, sodium carbonate or sodium acetate. Ammonium hydroxide and sodium carbonate gave very poor or no yields at all of the desired complex and so sodium acetate was used. During several preparations a white material was obtained which turned out to be the hydrolysis product of hexafluoroacetylacetone. After the pH was adjusted, a slight excess (>2:1 mole ratio) of liquid hexafluoroacetylacetone was added. This formed a layer on the bottom which turned green and solidified to a green powder after several minutes of stirring. The solid was filtered, washed with water and purified by vacuum sublimation, yielding a light green microcrystalline powder. (Calc. for VO(C$_5$H$_7$O$_7$F)$_2$ • H$_2$O

% C 24.06, % H 0.83, % F 45.68; Found % C 24.40, % H 1.36, % F 45.38).

The analysis agrees well for one water molecule. The infrared spectrum of the sublimed product reveals an O-H stretch due to a water molecule, and the N.M.R. spectrum shows a proton shift.
indicative of a bound water molecule.

b. VO(dpm)$_2$. This compound was prepared by the same general procedure as outlined above for the VO(hfa)$_2$ · H$_2$O. It was also purified by vacuum sublimation yielding nicely formed green crystals. Both the analysis and the infrared spectrum indicate that this compound is anhydrous. (Calc. for VO(C$_{11}$H$_{19}$O$_2$)$_2$ %C 60.85, %H 8.84; Found %C 60.52, %H 8.79).

c. (NH$_4$)$_2$VO(tart) · H$_2$O. This compound was prepared by the method of Conn.$^{29}$

d. All other vanadyl complexes used in this study were prepared by the methods of Holmes.$^{30}$

2. Spectral Measurements

Infrared spectra were recorded using either a Beckman IR-7 or a Perkin-Elmer Model 21 employing NaCl optics. The spectra were run as Nujol mulls, between NaCl plates.

Most solvents used for room temperature solution spectra or for frozen (77°K) glasses were either of a chromatographic or spectroscopic grade from Matheson, Coleman and Bell. The n-butanol used was fluorometric grade from Harleco. The absolute ethanol used was reagent grade quality from United States Industrial Chemicals Co. All other inorganic reagents used were reagent grade quality or better.

All electronic spectra were recorded on a Cary 14 Recording Spectrophotometer, except for the reflectance spectra, which were
obtained on a Beckman D.U. manual spectrophotometer which was fitted with a standard reflectance attachment.

Liquid nitrogen temperature spectra were obtained in three media: Nujol mulls, alkali halide pellets and frozen organic solvent mixture glasses. The mull, pellet or glass mixture was mounted on a brass plate which was tailored to fit an optical quartz dewar. The dewar in turn was fitted to the Cary 14 sample compartment. The usual procedure was first to run the sample at room temperature. Then liquid nitrogen was added to the Dewar and, after allowing several minutes for thermal equilibrium, the sample spectrum was then run at 77°K. The Nujol mulls were run on filter paper against a blank of Nujol on filter paper. The appropriate alkali halide pellets were used as blanks for the pellet spectra. In some instances where the absorption was too great, one or more inert screens also had to be inserted in the reference beam to bring the spectrum on scale.

Several attempts were made to obtain a vapor spectrum. The first attempts were made using a one meter pathlength cell. The first big drawback to this meter cell was that some unknown compound had been absorbed into the mirror of the cell. Therefore, the cell itself gave a "spectrum" in the region of interest. Repeated attempts to wash out the impurity were unsuccessful. Assuming that the baseline of the cell could be subtracted from the final spectrum, further attempts were made to obtain vapor spectra.
The second big problem which arose was inability to maintain a vacuum in the cell. After disassembling the cell many times, the culprit was found to be a faulty O-ring. The third big hurdle was the inability to heat the cell uniformly or to control the heating unit. The latter problem was solved but the former problem was too difficult to overcome. The cell had a side arm which had to be heated with a heating tape while the main body of the cell was heated by a thermostat. If the temperature in the body was much greater than the side arm, the compound would not vaporize into the cell. On the other hand, if the side arm temperature was greater than the body temperature, the compound would crystallize onto the mirrors and lens. Due to the above problems, some of which were never satisfactorily solved, attempts to obtain a vapor spectrum with the meter cell were abandoned. The next attempt to obtain a vapor spectrum was by sealing the samples under reduced pressures in a 10 cm. quartz cell and heating the cell in a heating unit designed for the Cary 14. The VO(hfa)$_2$·H$_2$O was sealed at 10$^{-4}$ mm Hg and the VO(dpm)$_2$ at 10$^{-5}$ mm Hg. Spectra were obtained in 5-10 degree intervals up to 160°C. This method suffered one big drawback; crystals formed on the cell faces which were the coolest parts of the cell. To circumvent this difficulty a new apparatus was designed which would heat the cell uniformly.

The new apparatus consisted of an outer glass shell to fit around the cell. This shell had two halves with a ground glass
joint in the middle. After joining these halves around the cell and wiring them together, a clear oil was added through an orifice at the top until the cell was completely immersed. This assured a uniform heating of the cell and no compound was observed to crystallize on the windows. The cell was wrapped with a heating tape which was plugged into a Variac. The temperature was determined by inserting a thermometer through the same orifice through which the oil was added. After thermal equilibrium was obtained, the spectrum was run. The Variac was then turned up and a spectrum obtained at another higher temperature by the same procedure. By this method spectra were obtained up to about 130°C.
D. RESULTS AND DISCUSSION

I. Solution Spectra

The data obtained from solution spectra of VO(dpm)$_2$ and VO(hfa)$_2$ at room temperature are tabulated in Tables 1 and 2. Two bands, one between 12.5 and 15.5kK and the other around 16.5kK, are always observed in solution spectra of VO(dpm)$_2$. In addition to these bands, another band of low intensity is sometimes observed as a red shoulder on the 12.5-15.5kK band. It may be noticed that in all cases except piperidine, this band is only observed when the "first" band is blue-shifted to energies of about 15kK. Figure 3 gives a comparison of the spectrum of VO(dpm)$_2$ in a strong and weak ligating solvent. In addition to these three bands, a fourth band is usually observed around 25.0kK. In several solvents this band was not observed and was presumably covered by the intense ultraviolet absorption band which sets in near 25.0kK. This band is somewhat more intense than the other three and appears to be affected little by solvent changes.

The last column in Table 1 is $D_{II-I}$, the frequency, literally, the wave number difference between the maxima of bands "I" and "II". This is the empirical parameter that Ortolano$^{31}$ used to rank solvents according to ligand strength. Table 3 presents a comparison of this parameter, $D_{II-I}$, for VO(acac)$_2$, VO(dpm)$_2$ and VO(hfa)$_2$·H$_2$O.

It can be seen from this table that the solvent ranking for VO(dpm)$_2$ is essentially the same as for VO(acac)$_2$, with a few
Figure 3: VO(dpm)$_2$ in heptane and DMF.
TABLE 1

SOLUTION DATA FOR VO(dpm)$_2^-$ BAND MAXIMA IN kK

<table>
<thead>
<tr>
<th>Solvent Medium</th>
<th>Red Shoulder on &quot;I&quot;</th>
<th>&quot;I&quot;</th>
<th>&quot;II&quot;</th>
<th>&quot;III&quot;</th>
<th>D$_{II-I}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylformamide</td>
<td>---</td>
<td>12.86</td>
<td>16.67</td>
<td>24.10</td>
<td>3.81</td>
</tr>
<tr>
<td>Pyridine</td>
<td>---</td>
<td>12.91</td>
<td>17.34</td>
<td>---</td>
<td>4.43</td>
</tr>
<tr>
<td>Piperidine</td>
<td>&gt;12.10 small sh</td>
<td>13.10</td>
<td>17.20</td>
<td>23.05</td>
<td>4.10</td>
</tr>
<tr>
<td>Glacial acetic</td>
<td>---</td>
<td>13.60</td>
<td>16.00</td>
<td>---</td>
<td>2.40</td>
</tr>
<tr>
<td>T.H.F.$^a$</td>
<td>10.00</td>
<td>14.20</td>
<td>16.72</td>
<td>---</td>
<td>2.52</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>&gt;12.00</td>
<td>14.54</td>
<td>16.55</td>
<td>---</td>
<td>2.01</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>&gt;12.00</td>
<td>14.68</td>
<td>16.58</td>
<td>24.81</td>
<td>1.90</td>
</tr>
<tr>
<td>Chloroform</td>
<td>---</td>
<td>14.90</td>
<td>16.42</td>
<td>25.00sh</td>
<td>1.52</td>
</tr>
<tr>
<td>Benzene</td>
<td>&gt;11.80</td>
<td>15.15</td>
<td>16.67</td>
<td>25.00</td>
<td>1.52</td>
</tr>
<tr>
<td>Toluene</td>
<td>&gt;12.00</td>
<td>15.15</td>
<td>16.67</td>
<td>25.00</td>
<td>1.52</td>
</tr>
<tr>
<td>Heptane</td>
<td>&gt;12.10</td>
<td>15.29</td>
<td>16.70</td>
<td>25.00</td>
<td>1.41</td>
</tr>
<tr>
<td>Ethyl Ether$^b$</td>
<td></td>
<td>15.38</td>
<td>16.75</td>
<td>---</td>
<td>1.37</td>
</tr>
<tr>
<td>Methanol$^c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropanol$^d$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtOH(deoxygenated)$^e$</td>
<td></td>
<td>13.30</td>
<td>16.63</td>
<td>---</td>
<td>3.33</td>
</tr>
</tbody>
</table>

a) Goes from light green on solution to maroon to dark green.
b) Green-black solution.
c) Yellow on solution indicating oxidation.
d) Red quickly fading to yellow on solution.
e) Reliability doubtful since the solution turns yellow after 10-15 minutes.
TABLE 2

SOLUTION DATA FOR VO(hfa)₂ · H₂O, BAND MAXIMA, IN kK

<table>
<thead>
<tr>
<th>Medium</th>
<th>Red Shoulder on &quot;I&quot;</th>
<th>&quot;I&quot;</th>
<th>&quot;II&quot;</th>
<th>&quot;III&quot;</th>
<th>D_{II-I}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylsulfoxide</td>
<td>≈11.50</td>
<td>12.40</td>
<td>15.37</td>
<td>20.10</td>
<td>2.97</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td></td>
<td>13.00</td>
<td>16.12</td>
<td>20.60</td>
<td>21.50sh</td>
</tr>
<tr>
<td>50% DMF-50%CHCl₃</td>
<td>sh</td>
<td>13.50</td>
<td>16.20</td>
<td>20.70</td>
<td>21.30sh</td>
</tr>
<tr>
<td>Glacial Acetic</td>
<td></td>
<td>13.75</td>
<td>15.88</td>
<td>20.90</td>
<td>sh</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td>13.80sh</td>
<td>17.25sh</td>
<td>20.80</td>
<td></td>
</tr>
<tr>
<td>6:1 isopentane/n-butanol</td>
<td></td>
<td>13.87</td>
<td>16.10</td>
<td>20.78</td>
<td>bl.sh.</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td></td>
<td>13.90</td>
<td>16.20</td>
<td>20.70</td>
<td>bl.sh.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.90</td>
<td>14.15</td>
<td>16.34</td>
<td>20.60</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>≈12.00</td>
<td>14.20</td>
<td>16.30</td>
<td>20.75</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td></td>
<td>13.89</td>
<td>16.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Brownish color on dissolution.
b) Gives a red solution with an intense band at 20.5kK.
c) Gives a yellow solution.
<table>
<thead>
<tr>
<th>Medium</th>
<th>acac</th>
<th>dpm</th>
<th>hfa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>4.39</td>
<td>4.43</td>
<td>turns red</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.26</td>
<td>3.33&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.19</td>
</tr>
<tr>
<td>Piperidine</td>
<td>4.02</td>
<td>4.10</td>
<td>---</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>3.94</td>
<td>3.81</td>
<td>3.12</td>
</tr>
<tr>
<td>Glacial Acetic</td>
<td>3.69</td>
<td>2.40</td>
<td>2.13</td>
</tr>
<tr>
<td>T.H.F.</td>
<td>3.15</td>
<td>2.52&lt;sup&gt;b&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>2.60</td>
<td>1.90</td>
<td>2.30</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>2.26</td>
<td>2.01</td>
<td>2.60</td>
</tr>
<tr>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.94</td>
<td>1.52</td>
<td>2.51</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.58</td>
<td>1.52</td>
<td>2.10</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.55</td>
<td>1.52</td>
<td>2.10</td>
</tr>
<tr>
<td>Reflectance</td>
<td>1.70</td>
<td>1.60</td>
<td>3.42</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reliability questionable since it turns yellow in 10-15 minutes.

<sup>b</sup> Solution is green-black.
exceptions. One minor exception is the reversal of acetonitrile and nitromethane. The two major exceptions, THF and ethanol, plus some solvents not listed in Table 3, merit special discussion. THF dissolves the complex $\text{VO(dpm)}_2$, to give a maroon solution which fades to "green-black" in several minutes. The spectrum was run while the solution was maroon and no bands were observed in the 10-20kK region. There was, however, a strong absorption at 22-24kK. Several minutes later it was noted that the sample had turned green-black. The spectrum was rerun, giving the results tabulated in Table 1. Ethyl ether gave a similar green-black solution. Alcohols also give curious results. Methanol dissolves the complex to produce an immediate yellow solution. A spectrum of this solution gives a band at about 14.0kK with a shoulder around 13.0kK. The intensity of these bands is roughly two-thirds the intensity these bands have in other solvents at the same concentration. The 16-17kK band, if present, is covered by the tail of a high intensity absorption band which starts around 16kK and peaks somewhere beyond 25.0kK. Isopropanol yields a red solution that fades to yellow in less than a minute. The spectrum of this solution gives only one band ($\varepsilon \approx 100$) at 22.7kK. 6:1 isopentane-butanol, the mixture used most often for low temperature glasses, also gives an immediate yellow solution. Isopentane alone gives a green solution. Ethanol, unlike the other alcohols mentioned, gives a green solution which does not fade to yellow for about five minutes. These yellow solutions which formed were believed
to be evidence of oxidation of vanadyl(IV) to vanadium(V).

One explanation for this apparent oxidation could be dissolved oxygen, since alcohols do absorb and retain oxygen readily. To test this hypothesis, ethanol and n-butanol were deoxygenated by bubbling dry nitrogen through them for several hours. In the case of ethanol, the VO(dpm)_2 solution remained green for 20-30 minutes before any yellowing could be detected with the eye. Fifteen minutes later the solution was completely yellow. N-butanol on the other hand, while not giving an immediate yellow solution after deoxygenation, did turn yellow in only two or three minutes. Since these two solvents were a good grade to begin with, it seems that deoxygenation for several hours should have eliminated all dissolved oxygen. Dissolved oxygen cannot be eliminated as the oxidizing agent, however, since the minute amounts of O_2 in the nitrogen could effect the oxidation.

A second explanation for these occurrences could be the presence of peroxides in the solvent which could attach to the open sixth position in VO(dpm)_2 and effect oxidation.

Work is currently in progress by others in the Laboratory to determine what is occurring in these solvents.

It can be seen from Figure 3 that the intensity of these two bands for VO(dpm)_2 increases in a weak solvent. Some of this increase is due to the overlap of these bands as they move together in a weak solvent.
In many of the weaker solvents, a low intensity band is observed as a shoulder on the 14kK band. This band is not usually observed in strong solvents, probably because it is covered by the 15.0kK band which is red-shifted to 12.5-13.0kK in these solvents. The 14kK band blue shifts in weak solvents and appears to "leave behind" this weak band. This band can probably be seen most clearly in Figure 6 which shows the reflectance spectrum. The difference in bands I and II in the reflectance spectrum is only 1.60kK which is about the difference observed in benzene and toluene, two of the weakest ligating solvents. This indicates that the sixth position is most probably "open" in the solid. The room temperature mull gives a $D_{II-I}$ of 1.89kK which indicates some weak sixth position interaction in this medium. It is somewhat surprising that a KBr pellet gives a $D_{II-I}$ value of only 1.74kK. It would seem that in such a pellet, a bromide ion would surely be in the vicinity of the sixth position and act as a strong enough ligand to split these two bands further apart, but, on the other hand, bromide ion is known to be a very poor ligand for VO$^{2+}$.

Besides these three bands, a fourth is sometimes observed at about 25.0kK. This band does not change much with solvents or in reflectance, mulls or pellets. The intensity of this band is two or three times the intensity of the 14kK and 16kK bands.

$\text{VO(hfa)}_2 \cdot \text{H}_2\text{O}$ solution spectra are similar to those of $\text{VO(dpm)}_2$. Bands "I" and "II" are observed but the low intensity band at 11-12kK is not easily located. The fourth band is shifted
from about 25kK in VO(dpm)₂ to 20.5kK in VO(hfa)₂ • H₂O.

On inspection of Table 3 for the VO(hfa)₂ • H₂O compound, it may be noted that D_{II-I} does not show much of a change from solvent to solvent. This can be seen clearly in Figures 4 and 5. The largest D_{II-I} is observed in the reflectance spectrum (Figure 7). However, VO(hfa)₂ • H₂O would not be expected to show much of a solvent effect since the water molecule presumably occupies the sixth position, thus filling the first coordination sphere. Only a secondary solvent effect should be observed, and the data bears this out and suggest that this is but a small effect.

The presence of this water molecule has been confirmed by various experimental data. First, the analysis fits very well for one water molecule. Secondly, the infrared spectrum shows a band at 2450 cm⁻¹ which is in the range of the O-H stretch for coordinated water. Thirdly, the N. M. R. spectrum gives a peak indicative of a bound water molecule. The fact that this compound sublimes with a water molecule was not so surprising since Morris, Moshier and Sievers had noted this occurrence for many hexafluoroacetylacetone complexes. They prepared hexafluoroacetylacetone complexes of various metals. For oxidation states of three and four they obtained complexes of general formula X(hfa)₃ and X(hfa)₄ (X = Al, Fe(III), Rh(III), Th(IV), etc.). For oxidation states of two, complexes of general formula X(hfa)₂ • 2H₂O obtained (X = Co(II), Ni(II), Fe(II), Zn(II, Mn(II)). The authors attempted to dehydrate these compounds by sublimation but the compounds sublimed as the dihydrates.
Figure 4: VO(hfa)$_2$ · H$_2$O in CH$_3$CN and EtOH.
$\text{VO(hfa)}_2 \cdot \text{H}_2\text{O}$

<table>
<thead>
<tr>
<th></th>
<th>CH$_2$CN</th>
<th>EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.90</td>
<td>16.20</td>
</tr>
<tr>
<td>2</td>
<td>14.15</td>
<td>16.45</td>
</tr>
<tr>
<td></td>
<td>$\sim 12.5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.70</td>
<td>20.60</td>
</tr>
</tbody>
</table>
Figure 5: VO(hfa)$_2$ $\cdot$ H$_2$O in Benzene.
Figure 6: Reflectance Spectrum of VO(dpm)$_2$. 
Figure 7: Reflectance Spectrum of VO(hfa)$_2$·$\text{H}_2\text{O}$
VO(4f)_2\cdot H_2O

Ref. 10.6
13.25
16.67
21.3

frequency, kHz

0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
From the $D_{II-I}$ observed for VO(hfa)$_2$ \cdot $H_2$O in the various solvents (Table 3) it appears that this water molecule must remain attached to the sixth position in solution. Only in the case of dimethylformamide does it appear that any displacement of the water molecule takes place. This is not surprising since this is the strongest ligating solvent used with the exception of pyridine and ethanol.

The VO(hfa)$_2$ \cdot $H_2$O gives a red solution in pyridine. A spectrum of this solution shows an intense peak at 20.45$kK$ with a red shoulder, indicating that perhaps some of the 14.0$kK$ and 16.0$kK$ bands still remain. This 20.4$kK$ band coincides with the 20.5$kK$ band observed in other solvents where the other three bands are observed. The decrease in intensity of these three bands and the increase in intensity of the 20.5$kK$ band seems to indicate that the latter is not a d-d transition. Evaporation of this pyridine solution gave a gummy green material. This substance was practically insoluble in solvents which readily dissolve VO(hfa)$_2$ \cdot $H_2$O but it readily dissolves in pyridine, regenerating a red solution. It is possible that this gummy green material could be anhydrous VO(hfa)$_2$, which could exhibit some polymerization via V-O-V bonding. Formation of a thick green oil occurs when VO(hfa)$_2$ \cdot $H_2$O is heated under vacuum, which could also be an indication of dehydration followed by polymerization of VO(hfa)$_2$ \cdot $H_2$O. It is also possible that pyridine replaces the water molecule forming a strong adduct.
This should be investigated further.

Methanol gives a green solution but the bands at 13.80kK and 17.25kK appear only as shoulders on the 20.8kK band. Ethanol does not appear to displace the water molecule as the $D_{\text{II-I}}$ for VO(hfa)$_2$·H$_2$O in ethanol is much the same as in other solvents.

The largest $D_{\text{II-I}}$ observed for VO(hfa)$_2$·H$_2$O was in the reflectance spectrum (Figure 7) and the mull spectrum (Figure 11) whereas for VO(dpm)$_2$ the reflectance, mull and weak solvent spectra all gave approximately the same value for $D_{\text{II-I}}$. Solid VO(hfa)$_2$·H$_2$O, however, has a coordinated water molecule which is probably drawn or forced in toward the vanadium in the close-packed solid state and thus acts as a stronger ligand. In the greater freedom afforded in solution, this water molecule can move further away from the vanadium, especially if the solvent in question has any affinity at all for water molecules.

The weak band at about 12kK is more difficult to find with VO(hfa)$_2$·H$_2$O than with VO(dpm)$_2$. It is only observed in two solvents, in reflectance and in Nujol mull. In many solvents, however, a long "tail" is observed on the low energy side of the 14.0kK band, giving a strong indication that this band is present although not clearly resolvable. The position of this weak intensity band does seem to be relatively independent of the medium. This band is most clearly observed in the reflectance spectrum of this
compound (Figure 7). It was the clarity with which this low intensity band was observed that prompted a very careful check for a similar band in VO(acac)$_2$. The reflectance spectrum of VO(acac)$_2$ (Figure 8) does indeed show this band.

The fourth band observed in this region for VO(hfa)$_2$ • H$_2$O is at 20.5kK and also appears to be independent of the medium. This band is 4-5kK lower than the corresponding band in VO(dpm)$_2$ and VO(acac)$_2$. The significance of this will be discussed later.

2. **Low Temperature Vanadyl Spectra**

Low temperature spectra were run on various vanadyl complexes to determine if any splitting, such as was observed in VO(acac)$_2$ and (NH$_4$)$_3$(VOF)$_5$, could be observed and if the weak band at 12kK could be more clearly discerned. The results are tabulated in Table 4.

The best observation of the low energy, low intensity band is for the VO(hfa)$_2$ • H$_2$O in a Nujol mull. Room temperature and liquid nitrogen temperature spectra of this compound are shown in Figure 11. What appears as a broad band at room temperature resolves into two bands, one at 11.50kK and a second, somewhat more intense band at 13.80kK, with both a red and a blue shoulder at liquid N$_2$ temperature. The band at 17kK, as usual, shows no splitting while the band at 21kK definitely shows two maxima. Though many attempts were made to obtain a low temperature KBr pellet spectrum of this compound,
Figure 8: Reflectance Spectrum of VO(acac)$_2$. 
### TABLE 4

**LOW TEMPERATURE AND REFLECTANCE DATA FOR VO(hfa)$_2$·H$_2$O AND VO(dpm)$_2$**

**VO(hfa)$_2$·H$_2$O**

<table>
<thead>
<tr>
<th>Medium</th>
<th>Reflectance</th>
<th>11.70</th>
<th>15.10</th>
<th>16.70</th>
<th>25.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nujol mull</td>
<td>298°K</td>
<td></td>
<td>13.20</td>
<td>17.00</td>
<td>21.00(sh)</td>
</tr>
<tr>
<td>Nujol mull</td>
<td>77°K</td>
<td>11.50</td>
<td>13.60</td>
<td>17.30</td>
<td>20.87(sh)</td>
</tr>
<tr>
<td>6:1 isopentane n-butanol</td>
<td>298°K</td>
<td>≈12.2</td>
<td>14.10</td>
<td>16.24</td>
<td></td>
</tr>
<tr>
<td>6:1 isopentane n-butanol</td>
<td>77°K</td>
<td></td>
<td>13.74</td>
<td>16.24</td>
<td></td>
</tr>
<tr>
<td>Reflectance</td>
<td></td>
<td>12.00</td>
<td>13.24</td>
<td>16.67</td>
<td>21.28</td>
</tr>
</tbody>
</table>

a) 13.60 band has a shoulder on each side at about 13.30 and 14.50kK.

**VO(dpm)$_2$**

<table>
<thead>
<tr>
<th>Medium</th>
<th>Reflectance</th>
<th>11.70</th>
<th>15.10</th>
<th>16.70</th>
<th>25.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>298°K</td>
<td></td>
<td>15.10</td>
<td>16.84</td>
<td>25.00</td>
</tr>
<tr>
<td>KBr</td>
<td>77°K</td>
<td></td>
<td>14.40sh, 15.0, 15.90sh</td>
<td>17.04</td>
<td>---</td>
</tr>
<tr>
<td>Nujol mull</td>
<td>298°K</td>
<td>≈12.3sh</td>
<td>14.93</td>
<td>16.80</td>
<td>25.00</td>
</tr>
<tr>
<td>Nujol mull</td>
<td>77°K</td>
<td>≈2.1sh 14.20sh, 14.86,15.87sh</td>
<td>17.00</td>
<td>23.60,25.30</td>
<td></td>
</tr>
</tbody>
</table>
none were successful, perhaps due to destruction of the complex during pellet preparation. A frozen glass spectrum was obtained, but did not show good band resolution. At room temperature, the frozen glass mixture, 6:1 isopentane-butanol, gave peaks at 14.10kK and 16.24kK with a hint of a band at approximately 12kK. The 21kK band was not observed in this medium. At liquid nitrogen temperature only peaks at 13.74kK and 16.24kK were observable.

Nujol mull and KBr pellet spectra of VO(dpm)$_2$ at low temperature both yielded a weak low energy band. (See Figures 9 and 10). The former has this band appearing at <10kK while in the latter it is around 12kK. It can be seen that the band at 13-14kK shows some splitting in both media while the 16-17kK band again does not split.

A KBr spectrum of VO(DMSO)$_5$(C$_2$O$_4$)$_2$ at room temperature gave a small band at 10.8kK, a band at 12.85kK with a possible red shoulder and a band at 15.8kK with no splitting. Yeranos$^{27}$ from low temperature polarization spectral data for VO(acac)$_2$ proposed that the degenerate e* level was split in the C$_{2v}$ symmetry and assigned the 12kK band as $d_{xy} \rightarrow d_{xz}$ and the 14kK band as $d_{xy} \rightarrow d_{yz}$. The above dimethylsulfoxide complex is of C$_{4v}$ symmetry and should not split the degenerate e* level. This indicates that the 10-12kK band cannot be the $d_{xy} \rightarrow d_{xz}$ transition as proposed by Yeranos, since the $d_{yz}$ and $d_{xy}$ should remain degenerate in this symmetry.
Figure 9: Room and Liquid Nitrogen Temperature Spectra of VO(dpm)$_2$ in KBr Pellet.
VO(dpm)$_2$ in KBr at 298°-1

FREQUENCY, KK

0.1  0.2  0.3  0.4  0.5

1.0  0.9  0.8  0.7  0.6

26.0 24.0 22.0 20.0 18.0 16.0 14.0 12.0 10.0 8.0
Figure 10: Room and Liquid Nitrogen Temperature Spectra of VO(dpm)$_2$ in Nujol Mull.
VO(14dpm)₂

IN NUJOL MULL

1 - 298°
2 - 77°
Figure 11: Room and Liquid Nitrogen Temperature Spectra of \( \text{VO(hfa)}_2 \cdot \text{H}_2\text{O} \) in Nujol Mull.
The room temperature and low temperature spectra of \((\text{NH}_4)_2 \text{VO(tart)} \cdot \text{H}_2\text{O}\) in KBr are shown in Figure 12. There is no noticeable splitting in any of the four observed bands in going from room temperature to 77°K. This is not surprising since Tapscott and Belford\(^{16}\) obtained good magnetic and e.s.r. evidence indicating this compound is a dimer with two different compounds resulting, depending on whether d-tartaric acid or a racemic tartaric acid mixture is used. Quite recently, Forrest and Prout\(^{18}\) carried out the x-ray diffraction determination of the structure of the ammonium vanadyl(+) tartrate. It is indeed a dimer. The coordination of the vanadium atom is a distorted trigonal bipyramid with the vanadyl oxygen in the equatorial plane.

Each tartrate molecule coordinates to two vanadium atoms, with the carboxyl oxygens coordinating at the apices and the hydroxyl oxygens coordinating in the equatorial plane. The water molecules and ammonium ions bind the dimeric vanadium units into a three-dimensional network by hydrogen bonding.

The presence of a single species in the crystal rules out the possibility that the four observed transitions in vanadyl tartrate are due to the presence of more than one complex as suggested by Dunlop\(^{33}\). Also the fact that the distance between vanadium atoms is 4.35\(\text{Å}\) makes it unlikely that any interaction among the vanadium atoms would result in much of a modification in the optical bands.
Figure 12: Spectrum of $(\text{NH}_4)_2\text{VO(tart)}$ in KBr Pellet at Liquid Nitrogen Temperatures.
(NH₄)₂ VO(tart)·H₂O in KBr pellet

(1) Room Temp.
(2) Lig. N₂ Temp.
3. Vapor Spectra

The chief reason for working with VO(hfa)$_2$·H$_2$O and VO(dpm)$_2$ was their volatility. They both sublime under vacuum at 50-70°C. The great volatility of dipivaloylmethane complexes has in fact been used to separate the rare earths by vacuum sublimation of their dpm complexes. It was in the hopes of obtaining a vapor spectrum that these compounds were initially prepared and studied. The data obtained from these vapor spectra is tabulated in Table 5, along with the most probable assignment of these bands (see Figures 13 and 14).

It is assumed that the splitting in the xy→xz, yz and xy→z$^2$ transitions are vibrational in origin and this will be considered again later.
<table>
<thead>
<tr>
<th></th>
<th>xy-(x^2-y^2)</th>
<th>xy-(xz, yz)</th>
<th>xy-(z^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{VO(dpm)}_2) (138°C)</td>
<td>11.8</td>
<td>13.7sh</td>
<td>14.5sh</td>
</tr>
<tr>
<td>(\text{VO(hfa)}_2 \cdot \text{H}_2\text{O}) (112°C)</td>
<td>13.2br</td>
<td>15.4</td>
<td>16.3sh</td>
</tr>
</tbody>
</table>
Figure 13: VO(dpm)₂ Vapor Spectrum
Figure 14: VO(hfa)$_2$ · H$_2$O Vapor Spectrum.
E. CONCLUSIONS

Before attempting to assign the electronic transitions for vanadyl complexes, a brief summary of some important points will be given.

The most important new aspect for assignment of these electronic transitions is the appearance and firm establishment of a weak intensity ($\varepsilon \sim 1-5$) band at 10-12kK. This band was either unnoticed or ignored until quite recently$^{19,22,27}$. In $\beta$-diketone complexes, this band is usually either clearly observed or strongly indicated when solutions containing weak coordinating solvents are run. The weak solvents blue-shift the first big band at 13-14kK and allow better observation of this weak red band. It is difficult to determine any movement of this weak band in various solvents since it is only a shoulder to a more intense band.

The red-shifting of the 13-14kK band with better coordinating solvents has already been mentioned. The 16-18kK band shows only a slight blue shift as the ligating ability of the solvent increases. The variation in position of this band for VO(dpm)$_2$, VO(hfa)$_2 \cdot H_2O$ and several other $\beta$-diketones presently under study, is never more than 0.5kK in going from weak to strong coordinating solvents.

Intraligand spin-forbidden, $\pi \rightarrow \pi^*$, transitions ($T \rightarrow S_0$) have been reported for three $\beta$-ketoenolate ions$^{34,35}$. The results, along with the position of the fourth band in the corresponding
vanadyl $\beta$-diketone is given below:

<table>
<thead>
<tr>
<th></th>
<th>$T - S_o$</th>
<th>$[T - S_o + C.T.(?)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acac$^-$</td>
<td>25.8kK</td>
<td>VO(acac)$_2$ 25.2kK</td>
</tr>
<tr>
<td>dbm$^-$</td>
<td>20.1kK</td>
<td>VO(dbm)$_2$ 20.7kK</td>
</tr>
<tr>
<td>bza$^-$</td>
<td>21.7kK</td>
<td>VO(bza)$_2$ 22.0kK</td>
</tr>
</tbody>
</table>

Thus it is possible that the fourth band in the complexes is due entirely, or at least in part, to this intraligand spin-forbidden transition which has somehow gained some intensity through the coordination.

The interpretation of the splitting of the 13-14kK band as three electronic components$^4,14$ would place all four d-d transitions below 15kK. This would mean that the weak band was the $d_{xy} \rightarrow d_{x^2-y^2}$ transition and that the first band contained the $d_{xy} \rightarrow d_{yz}$, $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{z^2}$ transitions. Before discussing this, another point must be emphasized. All other theoretical models for vanadyl complex spectra usually consider the vanadium atom to lie in the same plane as the four equatorial ligands. It is actually out of this plane so that the O-V$_2$L angle is always greater than 90°. (See Table 6). This makes it possible for the $d_{xz}$ and $d_{yz}$ orbitals to participate in $\pi$-bonding with the equatorial ligands to some degree. This would raise the $d_{yz}$, $d_{xz}$ orbitals in energy and make it more reasonable that they may lie higher than the $d_{x^2-y^2}$ level.
**TABLE 6**

**PERTINENT X-RAY DIFFRACTION DATA FOR VO$^{2+}$ COMPOUNDS**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(aca)$_2$</td>
<td>1.57</td>
<td>1.97</td>
<td>---</td>
<td>106</td>
<td>36,37</td>
</tr>
<tr>
<td>VO(bza)$_2$</td>
<td>1.605</td>
<td>1.95, 1.98</td>
<td>---</td>
<td>106</td>
<td>38</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>1.58</td>
<td>1.77, 1.88, 2.02</td>
<td>2.81</td>
<td>105</td>
<td>39</td>
</tr>
<tr>
<td>VOMoO$_4$</td>
<td>1.68</td>
<td>1.97</td>
<td>2.59</td>
<td>102</td>
<td>40</td>
</tr>
<tr>
<td>VOSO$_4$·5H$_2$O</td>
<td>1.67</td>
<td>2.3</td>
<td>2.4</td>
<td>a</td>
<td>41</td>
</tr>
<tr>
<td>VOSO$_4$</td>
<td>1.59</td>
<td>2.01, 2.05</td>
<td>2.28</td>
<td>100</td>
<td>42,43</td>
</tr>
<tr>
<td>[VO(NCS)$_4$H$_2$O]$_2^-$</td>
<td>1.62</td>
<td>2.04(N)</td>
<td>2.22(O)</td>
<td>97</td>
<td>44</td>
</tr>
<tr>
<td>V$_2$O$_4$</td>
<td>1.76</td>
<td>1.86, 2.02</td>
<td>2.05</td>
<td>93$^b$</td>
<td>45</td>
</tr>
</tbody>
</table>

a) Not reported in reference 24, but assumed by Ballhausen and Gray to be 90°, almost certainly not possible.

b) Other O=V-X angles are 99° and 95°.
In $C_{4v}$ symmetry only the $xy \rightarrow xz, yz$ transition is allowed, the $xy \rightarrow z^2$ and $xy \rightarrow x^2-y^2$ being formally forbidden. The first-mentioned transition should therefore be the most intense.

Let us consider the effect on the various $d$ orbitals of bringing a ligand along the $z$-axis into the open sixth position. This would cause the equatorial ligands to move upward toward the plane which includes the vanadium so that the $O-V-L$ angle is lowered. It should also weaken the $V=O$ bond, causing this oxygen to move further away from the vanadium and the equatorial ligands to move closer-in. The sixth ligand moving toward the vanadium should have the opposite effect and cause the equatorial ligands to move out from the vanadium. The movement of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition with solvent would probably depend on which of the effects is dominant. These opposing effects may result in very little change in energy and hence the band may move very little. The band at 11-12kK is very weak and appears to be little affected by solvent although, as stated earlier, it is difficult to chart exactly where this shoulder is. This leads to the assignment of this band as $d_{xy} \rightarrow d_{x^2-y^2}$.

A sixth ligand would be expected to decrease the energy of the $d_{xy} \rightarrow (d_{xz}, d_{yz})$ transition. The weakening of the $V-O$ $\sigma$-bond would cause the oxygen to move out from the vanadium and also weaken the $\pi$-bonds, which involve primarily the $d_{xy}$ and $d_{yz}$ orbitals. The equatorial ligands moving upward (decreasing
O-V-L angle) would also decrease any \( \pi \)-bonding between the equatorial ligands and the \( d_{xz}, d_{yz} \) orbitals. The stronger ligating solvents would be expected to cause both of these effects and thus shift the \( d_{xy} \rightarrow (d_{xz}, d_{yz}) \) transition to lower energies. Since the band at 12-15kK shows exactly this effect, and since it is the most intense, this band is assigned as the degenerate \( d_{xy} \rightarrow (d_{xz}, d_{yz}) \) transition.

There remains only the assignment of the \( d_{xy} \rightarrow d_{z^2} \) transition. The effect of a sixth ligand on this transition is a little difficult to discern. On the one hand, it causes a weakening of the V-O \( \sigma \)-bond which tends to lower the energy of this transition since the \( d_{z^2} \) orbital is primarily involved in the V-O \( \sigma \)-bond. On the other hand, a weak \( \sigma \)-bond is formed with the sixth ligand. This effect tends to raise the energy of the \( d_{xy} \rightarrow d_{z^2} \) transition.

If the weakening of the vanadium-oxygen sigma bond is the dominating effect, the \( d_{z^2} \) transition would be expected to red shift as the strength of the sixth ligand increases. This closely parallels the action of the \( (d_{yz}, d_{xz}) \) orbitals. It would then be possible that the \( (d_{xz}, d_{yz}) \) and \( d_{z^2} \) are all under the 12-15kK band and that the splitting of this band into three components at liquid nitrogen temperatures is in fact due to \( d_{xy} \rightarrow d_{yz}, d_{xy} \rightarrow d_{xz} \) and \( d_{xy} \rightarrow d_{z^2} \). This would mean that the bands at 16-17kK were charge transfer bands and/or intraligand bands.
It is also possible, however, that the effects mentioned for the $d_{z^2}$ orbital oppose each other to the extent that there is little movement of this band with increasing solvent strength. This is the behavior noted in the band at 16-17kK. The intensity of this band is less than the 12-15kK band, which is expected of the $d_{xy} \rightarrow d_{z^2}$ transition. The assignment of this band as the $d_{z^2}$ transition means that the splitting of this 12-15kK band at liquid nitrogen temperatures must be due to a vibrational progression. The splitting of these bands is 600-700 cm$^{-1}$. This could be due to the ground state V=0 stretching frequency which is around 1000 cm$^{-1}$, but which is undoubtedly lowered by a few hundred cm$^{-1}$ in the electronic excited state.

The latter interpretation appears to be the better one since it is reasonably unlikely that the $d_{z^2}$ transition would parallel the $(d_{xz}, d_{yz})$ transition so closely that they would never be observed to split. It is more likely that the $d_{z^2}$ orbital level would show relatively little solvent effect as described in the latter interpretation.

The foregoing discussion thus leads us to the following ordering of the d orbitals in vanadyl-$\beta$-diketones:

\[
\begin{align*}
&b_2 \rightarrow b_{1g}^* & &d_{xy} \rightarrow d_{x^2-y^2} & &10-12kK \\
&b_2 \rightarrow e_{2g}^* & &d_{xy} \rightarrow (d_{xz}, d_{yz}) & &12-15kK \\
&b_2 \rightarrow a_{1g}^* & &d_{xy} \rightarrow d_{z^2} & &16-18kK
\end{align*}
\]
The band at 20-25kK is tentatively assigned as the $\beta$-ketoenolate ($T - S_0$) transition with some possibility of a charge transfer transition not excluded. The position of this band in several vanadyl $\beta$-diketone complexes investigated corresponds to the assigned $T - S_0$ transitions in the $\beta$-ketoenolate ions. In alcoholic solvents, where apparently there is oxidation or a species change as evidenced by a change of color on solution, the bands at 12-15kK and 16-18kK diminish in intensity or completely disappear. The band at 20-25kK, however, seems to increase somewhat in intensity. If this were a d-d band, it should disappear on oxidation of V(IV) to V(V). This is best seen in VO(hfa)$_2$·H$_2$O. In this complex, this "fourth" band is at about 21kK and some 2-4kK away from the much more intense ultra-violet bands. In the other $\beta$-diketone complexes this band is usually further toward the blue and usually only a shoulder. In pyridine, VO(hfa)$_2$·H$_2$O gives a red solution which shows only one band ($e \approx 100$) at 20.7kK with a slight red shoulder around 17kK. This band also is usually 2-3 times the intensity of the 12-15kK and 16-18kK bands. Work is current in progress in these Laboratories to determine the exact nature of this band and all of the ultra-violet bands. The transitions for these vanadyl $\beta$-diketones deduced from the above work is shown in Table 7. The transitions are given in d-orbitals, $C_{4v}$ crystal field and by the Ballhausen-Gray scheme.
TABLE 7

BAND ASSIGNMENTS FOR OXOVANADIUM(IV) IN d ORBITALS, C\text{4v}

CRYSTAL FIELD AND BY THE BALLHAUSEN-GRAY SCHEME

<table>
<thead>
<tr>
<th>Energy Range (kK)</th>
<th>B.G.M.O. Assignments</th>
<th>Transitions in C\text{4v} Field</th>
<th>Transitions in d orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-12</td>
<td>$^2B_2 \rightarrow ^2B_1$</td>
<td>$b_2 \rightarrow b_1^*$</td>
<td>$xy \rightarrow x^2 - y^2$</td>
</tr>
<tr>
<td>12-15</td>
<td>$^2B_2 \rightarrow ^2E(I)$</td>
<td>$b_2 \rightarrow e_\pi^*$</td>
<td>$xy \rightarrow (xz, yz)$</td>
</tr>
<tr>
<td>15-17</td>
<td>$^2B_2 \rightarrow ^2A_1$</td>
<td>$b_2 \rightarrow a_1^*$</td>
<td>$xy \rightarrow z^2$</td>
</tr>
<tr>
<td>20-25</td>
<td>?</td>
<td>?</td>
<td>----</td>
</tr>
</tbody>
</table>
F. SUGGESTIONS FOR FURTHER WORK

Although there appears to be good evidence that all four d-d transitions occur below 20kK for these vanadyl β-diketones, there is still some work which could be done to put this hypothesis on firmer ground.

Perhaps the best experiment which would help clarify band assignments for vanadyl complexes would be liquid helium temperature or liquid hydrogen temperature spectra. This should give very sharp bands and permit a more definite assignment of these bands. The splitting, if any, of the band in the 12-15kK range, which shows three components at liquid nitrogen temperature, should be of great value in the assignment of the d-d transitions. One problem in trying to work at such low temperatures is finding an appropriate medium in which to obtain a spectrum. It may be hard to find a material which would dissolve these vanadyl complexes and also form a glass at these low temperatures. Perhaps an alkali halide pellet or a single crystal may be a good medium for obtaining a spectrum at liquid helium or liquid hydrogen temperatures.

A careful investigation of the ultra-violet region, both in solution and at low temperature, should also be carried out for these vanadyl complexes. Assignment of these ultra-violet bands would certainly be helpful in the assignment of the d-d transitions. Investigation of the ultra-violet region may also help explain the
anomalous behavior of these vanadyl \(\beta\)-diketones in certain solvents. A time-dependent study of the spectra for these complexes in the solvents that give abnormal results may also be of value in the elucidation of a scheme to explain the spectra in other solvents.

It may well be that one scheme may not explain the observed transitions for all vanadyl complexes. Zerner and Gouterman did find a reversal of the \(b^*\) and \(a^*\) levels from their usual order in their calculations on vanadyl porphyrins. Investigation of other vanadyl complexes with nitrogen-donor ligands at low temperature may yield information to confirm or refute these calculations.

Some improvement could be made in the vapor spectrum apparatus. The present apparatus, while giving results, could use some refinements. The present cell is awkward to handle and perhaps a new cell may have to be designed. Along this line, a longer path length cell would certainly be useful for obtaining a clearer vapor spectrum.

Further investigation is warranted of the red solutions obtained when vanadyl complexes are dissolved in certain solvents, particularly pyridine. Characterization of the green gummy product obtained by evaporation of a pyridine solution of \(\text{VO(hfa)}_2 \cdot \text{H}_2\text{O}\) should be most interesting.
REFERENCES


VITA

Gerald John Maus was born January 21, 1941 in New Orleans, Louisiana. He graduated from Fortier High School, New Orleans in June of 1958. In September of 1958, he entered the newly opened Louisiana State University in New Orleans, from which he received his B.S. in chemistry as a member of the first graduating class in June, 1962. In September, 1962, he entered the Graduate School of Louisiana State University in Baton Rouge where he is a candidate for the degree of Doctor of Philosophy.
EXAMINATION AND THESIS REPORT

Candidate: Gerald John Maus

Major Field: Chemistry

Title of Thesis: Spectral Studies of Selected Oxovanadium(IV) Complexes

Approved:

[Signatures of Major Professor and Chairman, Dean of the Graduate School, and Examining Committee members]

Date of Examination:

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