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Louisiana State University, Ph.D., 1964
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SPECTRAL STUDIES ON VANADYL COMPLEXES

A Dissertation

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

in

The Department of Chemistry

by

Thomas Russell Ortolano
B.S., Loyola University of the South, 1960
August, 1964

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SELECTED LIST OF SYMBOLS AND ABBREVIATIONS

acac	The acetylacetonate ion
DMSO	Dimethyl sulfoxide
DMF	Dimethyl formamide
THF	Tetrahydrofuran
ESR	Electron spin resonance
G.O.	Group orbital
$D_{II,I}$	Frequency difference (in cm^{-1}) between first and second visible absorption bands of vanadyl bis-(acetylacetonate) at room temperature
D_q	Octahedral crystal field parameter
D_s, D_t	Tetragonal crystal field parameters
q_a	Effective axial charge
q_e	Effective equatorial charge
α	Constant of proportionality needed to express q_a and q_e in terms of crystal field parameters. Specifically: $\alpha q_a = (20D_q - 35D_t)$ and $\alpha q_e = 20D_q$
ρ	Ratio of q_a to q_e
d_e	Symbol for the group of three d orbitals consisting of d_{xy} , d_{xz} , d_{yz}
d_γ	Symbol for the pair of d orbitals consisting of $d_{x^2-y^2}$ and d_{z^2}

- " μ_V " Total dipole moment for a solvent mixture defined as " μ_V " = $\sum_i (f_V)_i \mu_i$, where $(f_V)_i$ and μ_i are the volume fraction and dipole moment of solvent i , respectively
- $\bar{\nu}$ Frequency in wavenumbers (cm^{-1})
- $b_2, b_1, e, a_1, \text{etc.}$ Mulliken notational representations. [Refer to: Mulliken, R. S., Phys. Rev., 43, 279 (1933).]
- Γ Bethe notational representation, usually subscripted. [Refer to: Bethe, H. A., Ann. Physik [5], 3, 133 (1929).]

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ABSTRACT

The effects of twenty pure solvents on the optical absorption spectrum of vanadyl bis-(acetylacetonate), $\text{VO}(\text{acac})_2$, have been observed in the 12,000 to 30,000 cm^{-1} region. Three low intensity bands allow the calculation of the three crystal field parameters D_q , D_s , and D_t . As a solvent molecule adds to the open axial position on the vanadium, it alters slightly the strong axial perturbation of the vanadyl oxygen. This effect is most sensitively recorded in a new parameter $D_{II,I}$, the difference between the first and second bands, since the first band is red-shifted and the second band is blue-shifted. The twenty solvents are ranked as follows by this parameter: $\text{H}_2\text{O} \gg \text{MeOH} > \text{pyridine} > \text{n-propylamine} > \text{EtOH} > \text{DMSO} > \text{p-dioxane} \sim \text{piperidine} > \text{DMF} > \text{acetic acid} > \text{formic acid} > \text{THF} > \text{CH}_3\text{CN} > \text{CH}_3\text{NO}_2 > \text{CHCl}_3 > \text{CS}_2 \sim \text{C}_6\text{H}_6 > \text{toluene} > \text{m-xylene} > \text{CCl}_4$. Correlations of the empirical effects of sixth-position ligation with theory are included.

The observation at low temperature of four low intensity absorption bands below 20,000 cm^{-1} for the C_{2v} molecule

vanadyl bis-(acetylacetonate) is reported. In addition, four such bands are reported for two C_{4v} vanadyl species. The likelihood of these four bands representing the whole of the d-d series and the plausibility of understanding the splitting of the crystal field levels in the C_{4v} molecules in terms of a spin-orbit coupling mechanism is discussed. The time course of the oxidation of V(IV) to V(V) has been followed spectrally; the results appear to identify the d-d series of transitions and suggest that the transition at $\sim 25,000\text{ cm}^{-1}$ is charge transfer in nature. This is supported by the spectrum of a derivative of $VO(acac)_2$ which shows this latter band to be doublet in nature at room temperature, a fact totally inconsistent with its assignment as a crystal field transition. The included discussions serve as a critique of two alternative energy level schemes of the vanadyl ion, that scheme which is proposed herein being heavily favored by the arguments presented.

A discussion of electronic-vibronic correlations is presented; and the results of a preliminary investigation of mass effects on the vibrational frequencies of oxocation metal-oxygen bonds is included as an appendix.

GENERAL INTRODUCTION

Complex oxocations of the types MOq^+ and MO_2^{q+} have recently been of considerable interest with regard to their spectral and magnetic properties.¹ In addition to their relatively great stability, these cations form many complexes which serve as convenient subjects for observing the effects of trigonal and tetragonal fields on the energy levels of the central metal ions involved.

A particularly popular oxocation of the above type is the vanadyl ion, VO^{2+} . We shall not here digress into the complete history of this species. Such material is felt to have been outlined quite extensively in other manuscripts in this area.* For our purpose we shall be mainly interested in the spectral aspects of the vanadyl ion so that only these shall be here given discussion. From the start, therefore, it shall be assumed that the vanadyl ion is an integral

*The summary of L. H. Holmes, Jr. (Dissertation, Louisiana State University, 1961) and a comprehensive review "The Chemistry of Oxovanadium (IV)," Chem. Revs., in press, by J. Selbin are particularly recommended.

monomeric species, which retains this integral nature both in the solid state and in solution, and which is always found coordinated to either four or five other groups.

In the decade or so preceding 1962, the electronic absorption spectra of various vanadyl complexes were reported by several authors.²⁻¹⁶ Some of these attempted to assign some of the observed bands to theoretically predicted transitions.^{9-11,14} Most notable of these were the independent interpretations of Jørgensen¹⁰ and Furlani,¹¹ both of whom employed a simple crystal field model. Jørgensen considered the vanadyl ion in aqueous solution, $\text{VO}(\text{H}_2\text{O})_5^{2+}$, as a strongly tetragonally distorted octahedron and obtained a scheme which qualitatively accounts for the crystal field part of the spectrum. Furlani's treatment was conceptually somewhat less satisfying since he considered only the $C_{\infty v}$ symmetry of VO^{2+} , thus ignoring quadrate perturbations which certainly are significant.

Then in 1962 there appeared the treatment of the electronic structure of the vanadyl ion by Ballhausen and Gray.¹⁷ This treatise, in addition to amply summarizing many previous findings on the vanadyl ion, succeeded in setting the format for virtually all subsequent discussions of observed spectral, E S R, and magnetic properties of vanadyl

complexes. A brief discussion of this treatise follows.

The vanadyl ion in aqueous solution has associated with it five water molecules. Four of these are situated in a plane perpendicular to the V-O axis while the fifth--trans to the vanadyl oxygen--completes the tetragonal structure. According to an electrostatic crystal field model, then, the resultant species may be regarded as a vanadium (IV) ion situated in a field of one oxide ion and five water dipoles. As a result, Ballhausen and Gray¹⁷ propose the existence of four crystal field levels of increasing energy:

$$b_2 (d_{xy}) : - 4D_q + 2D_s - D_t$$

$$e (d_{xz}, d_{yz}) : - 4D_q - D_s + 4D_t$$

$$b_1 (d_{x^2 - y^2}) : 6D_q + 2D_s - D_t$$

$$a_1 (d_{z^2}) : 6D_q - 2D_s - 6D_t$$

The lone d-electron is then placed in the b_2 ground state and the transitions predicted are $b_2 \longrightarrow e (-3D_s + 5D_t)$, $b_2 \longrightarrow b_1 (10D_q)$, and $b_2 \longrightarrow a_1 (10D_q - 4D_s - 5D_t)$. Experimentally only two bands are observed, one at $\sim 13,000 \text{ cm}^{-1}$ and another at $\sim 16,000 \text{ cm}^{-1}$, while the third ($b_2 \longrightarrow a_1$) is presumed to be at higher energies and covered by an intense charge transfer band having a maximum at about $42,000 \text{ cm}^{-1}$.

In the usual way, and with the assumption of the position of the $b_2 \longrightarrow a_1$ transition to be about $35,000 \text{ cm}^{-1}$,

Ballhausen and Gray calculate the values of the three crystal field parameters to be: $D_q = 1600 \text{ cm}^{-1}$, $D_s = -4570 \text{ cm}^{-1}$, and $D_t = -143 \text{ cm}^{-1}$. From the values of these (i.e., D_q small, and D_s and D_t large) it is apparent that a somewhat large tetragonal distortion is present in the ion, $\text{VO}(\text{H}_2\text{O})_5^{2+}$, and the inadequacy of a pure crystal field model is thereby indicated. A modified Wolfsberg-Helmholtz self-consistent molecular orbital description was then employed so that provisions for σ and π bonding might be included.

Since the crystalline molecular structure of $\text{VO}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}$ is known, it was particularly convenient for Ballhausen and Gray to use $\text{VO}(\text{H}_2\text{O})_5^{2+}$ for their molecular orbital considerations. Assuming all bond lengths in the latter species to be approximately the same as those in the former, it was only necessary to replace the axial sulfate group in $\text{VO}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}$ by a fifth water oxygen. Numbering the four equatorial water ligands 1 through 4, the vanadyl oxygen as 5, and the axial water ligand as 6, and considering the relative bond strengths to be $5 \gg 1 = 2 = 3 = 4 > 6$, they then proceeded to deduce the following C_{4v} orbital transformation scheme:

<u>Symmetry Representation</u>	<u>M-orbitals</u>	<u>L-orbitals</u>
a_1	$3d_{z^2} + 4s$	σ_5
	$4s - 3d_{z^2}$	$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
	$4p_z$	σ_6
e	$3d_{xz}, 3d_{yz}$	$\pi_5(2p_x, 2p_y)$
	$4p_x, 4p_y$	$(\frac{1}{2})^{\frac{1}{2}}(\sigma_1 - \sigma_3),$ $(\frac{1}{2})^{\frac{1}{2}}(\sigma_2 - \sigma_4)$
b_1	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
b_2	$3d_{xy}$	

Perhaps the most obvious and significant assumption involved in these assignments is that π bonding is considered significant only in the vanadyl V-O bond itself. This approximation is based upon the short bond length therein (1.67 Å) as compared to those involving the water molecules (2.3 Å and 2.4 Å).¹² As a result of this, the b_2 (d_{xy}) orbital is taken as essentially non-bonding.

In an analogous, but less rigorous, ligand field treatment of the general species $VO\text{L}_4^{n+}$, Selbin, Holmes, and

McGlynn,¹⁸ on the other hand, placed a greater emphasis upon equatorial π -bonding with the result that the relative ordering of the b_1 and e levels is made dependent on the nature of the ligands. These workers used the same atomic orbitals for the vanadium atom and for the vanadyl oxygen as did Ballhausen and Gray, but instead of employing merely the σ G.O.'s of the equatorial ligand atoms, they considered also their $\pi_{||}$ and π_{\perp} G.O.'s. The relative importance of these was estimated by them as approximately 8:2:1, respectively, the first and third of these having the effect of raising b_1 and the second of raising ($\sim 0.1\text{eV}$) b_2 . The variance of these two approaches will become pertinent when the conclusions of this present work are discussed.

The results of the molecular orbital calculation of Ballhausen and Gray were the following energy predictions:

<u>Transition</u>	<u>Predicted Energy (cm^{-1})</u>
$b_2 \longrightarrow e_{\pi}^*$	12,502
$b_2 \longrightarrow b_1^*$	18,794
$b_2 \longrightarrow 1a_1^*$	44,766
$e_{\pi}^b \longrightarrow b_2$	38,800 [#]
$e_{\pi}^b \longrightarrow e_{\pi}^*$	44,000

[#]Since the terminal level for this transition, $b_2(d_{xy})$, contains an electron, the predicted energy includes a repulsion energy assumed¹⁷ to be $11,700 \text{ cm}^{-1}$.

These are compared to the experimentally observed transitions at 13,060, 16,000, 41,700, and 50,000 wave-numbers. These are assigned to $b_2 \rightarrow e_\pi^*$, $b_2 \rightarrow b_1^*$, $e_\pi^b \rightarrow b_2$, and $e_\pi^b \rightarrow e_\pi^*$, respectively, the $b_2 \rightarrow Ia_1^*$ transition assumed covered in the region of the charge transfer bands.

Since the publication of this foregoing detailed treatment it has become somewhat conventional procedure to interpret spectral, ESR, and magnetic observations on vanadyl accordingly. For example, Horner, Tyree, and Venesky¹⁹ reported the visible absorption bands of $VOCl_2 \cdot 4(C_6H_5)_3AsO$, $VOCl_2 \cdot 3(CH_3)_2SO$, $VOCl_2 \cdot 2(C_6H_5)_3PO$, $VO(ClO_4)_2 \cdot 5C_5H_5NO$ in methylene chloride, their assignments being based directly on the molecular orbital model of Ballhausen and Gray.¹⁷

Bernal and Rieger²⁰ used the same ideas for the assignment of the spectral bands of $VO(acac)_2$ in their discussion of solvent effects on its optical and electron spin resonance spectra. Six solvents were used (methanol, pyridine, acetone, acetonitrile, nitrobenzene, and benzene) and the authors observed that with generally increasing solvent strength, the optical band at $\sim 14,000 \text{ cm}^{-1}$ red-shifted appreciably, the band at $\sim 17,000 \text{ cm}^{-1}$ remained virtually unchanged except for a slight blue-shifting tendency, and the band at $\sim 25,000 \text{ cm}^{-1}$

showed a small blue-shift. These trends were interpreted by Bernal and Rieger to be in general accord with the ideas of Ballhausen and Gray.

Selbin and Ortolano²¹ likewise discussed solvent effects on the absorption spectrum of $\text{VO}(\text{acac})_2$ in the same light. These authors measured the effects of thirteen pure solvents and arrived at the conclusion that there was essentially no consistent trend apparent in the band at $\sim 25,000 \text{ cm}^{-1}$, but that the separation between the first two bands increased with increasing solvent ligand strength and that this separation, $D_{\text{II},\text{I}}$, could be used as a somewhat sensitive empirical parameter for the ordering of solvents.

Finally, even the spectra of non-vanadyl species have been interpreted by employment of the Ballhausen and Gray vanadyl scheme as a sufficient approximation. Gray and Hare,²² for example, used it for the interpretation of their spectral results on the ions CrOCl_5^{2-} and MoOCl_5^{2-} .

In actuality, the molecular orbital treatment of Ballhausen and Gray predicts an overlap of the crystal field and charge transfer series of bands for the vanadyl species which they treat. This, of course, would not necessarily be expected to be the general case, since greater or less σ and π bonding between the vanadium atom and its ligands should

understandably be capable of increasing, decreasing, or even eliminating this overlap. In the case of overlap or proximity of the two series of transitions one at least expects the last d-d band ($b_2 \rightarrow Ia_1^*$) to be possibly obscured by the relatively intense charge transfer bands. In cases, then, when only two low intensity optical bands are observed, the third is assumed at higher energy. Such appears certainly to be the case for $VO(H_2O)_5^{2+}$.

For many vanadyl complexes, however, a third low intensity band is observed as a shoulder in the neighborhood of 25,000 to 30,000 cm^{-1} on the low energy tail of the first intense ultraviolet band. Bernal and Rieger,²⁰ and Selbin and Ortolano²¹ have observed this to be the case for $VO(acac)_2$ in various solvents and they, accordingly, assigned the three low intensity peaks as comprising the whole of the d-d series--the first assumed to encompass both $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$ transitions which should be split in this case by the low symmetry (C_{2v}) of the molecule.

At low temperatures, however, Selbin, Ortolano, and Smith²³ have subsequently observed that the first low intensity band for $VO(acac)_2$ ($\sim 14,000\text{ }cm^{-1}$) resolves clearly into three. If these components are truly electronic, and not due to vibronic coupling, then one counts four bands before the

shoulder at $\sim 25,000 \text{ cm}^{-1}$ and may therefore be led to assign that band as the first charge transfer band, despite its low intensity. This assignment has been, in fact, proposed by the last mentioned authors.

In a subsequent paper from the same laboratory, Ortolano, Selbin, and McGlynn²⁴ present further data which verifies the existence of four bands below $20,000 \text{ cm}^{-1}$ for $\text{VO}(\text{acac})_2$. In addition, however, four such bands are reported for two C_{4v} species, which are only expected to exhibit three since the d_{xz} and d_{yz} orbitals are expected to remain degenerate in a C_{4v} field. Instead of abandoning the idea of "clustered d-d transitions" in favor of vibronic coupling in the first room temperature band--seemingly supported by their C_{4v} observations--the authors chose instead to propose spin-orbit coupling as a mechanism in the C_{4v} cases (at least).

It shall be the primary purpose of this dissertation to summarize and discuss the data and conclusions which have already served as the material for the author's three above-mentioned publications.^{21,23,24} This shall be done in the environment of other unpublished and less conclusive results which it is hoped shall prove to be of significance. In addition, discussions shall be included which attempt to

correlate some results of these investigations with the
vanadyl infrared studies from these laboratories by Selbin,
Holmes, McGlynn, Manning, and Cessac.^{18,25}

EXPERIMENTAL

$\text{VO}(\text{acac})_2$ was prepared by the method of Rowe and Jones;²⁶ $(\text{NH}_4)_3 [\text{VOF}_5]$ was prepared by the method of Muet-terties;²⁷ and $(\text{Et}_4\text{N})_3 [\text{VO}(\text{NCS})_5]$ was prepared by the method of Selbin and Holmes.²⁸

Vanadyl bis-(hexafluoroacetylacetonate) was prepared by adding commercial grade hexafluoroacetylacetone (from Chemicals Procurement Laboratories, Inc.) to an aqueous solution of commercial grade vanadyl sulfate (from K. and K. Laboratories, Inc.). A dark oil immediately formed which crystallized, with shaking, to a light green powder which was subsequently filtered and then purified by sublimation. The analyzed product had a carbon content of 24.9 per cent (calc. = 24.9 per cent). (Hydrogen analysis gave high results possibly because of the volatility of the complex and/or slight instability and/or its high fluorine content.) It has the same general solubility properties as $\text{VO}(\text{acac})_2$ and has V-O multiple bond stretching frequencies of 972 and 990 cm^{-1} , as compared to 996 cm^{-1} for $\text{VO}(\text{acac})_2$.

All solvents used were of reagent grade or spectro-

scopic quality (except isopentane, of practical grade) and were used without further purification.

Solvent effects were studied with a Cary Model 14 Spectrophotometer, solution concentrations being in the range 0.01 - 0.001 M $\text{VO}(\text{acac})_2$. The results of these absorption measurements are given in Table IV.

Low temperature solution (glass matrix) spectra, reported in Table VII, were measured with a Beckman DK recording spectrophotometer, using a low temperature double beam absorption cell²⁹ and liquid nitrogen as the coolant. (Two of these spectra are shown in Figure 3.) Low temperature KBr-pellet spectra (Table VII and Figure 4) were obtained with a Cary Model 14 Spectrophotometer. This KBr apparatus³⁰ consisted of a pellet-mounting brass plate tailored to fit a quartz Dewar flask and to make contact with liquid nitrogen. Spectra were run when the samples had been mounted and covered and when thermal equilibrium had been achieved. A pure KBr pellet was placed in the reference beam to compensate for light scattering in the sample; proper balance of the recording pen was further aided by use of an appropriate inert screen.

The data for the oxidation of $\text{VO}(\text{acac})_2$ with time (see Figure 5) were obtained in 2:1:1 ether : toluene :

ethanol solution at room temperature with the Beckman DK.

Vanadyl bis-(hexafluoroacetylacetonate) solution spectra (Table VIII) were obtained with the Cary Model 14 Spectrophotometer. The exploratory vapor spectrum of this complex was obtained at 30°C and atmospheric pressure with the Beckman DK with vapor cell (5 cm. path length) attachment.

The thin multi-crystalline film of $\text{VO}(\text{acac})_2$ was prepared by slow sublimation (~60 hours) and condensation onto a quartz disk which was held to a cold finger by high-vacuum silicone grease. Its absorption spectrum was obtained with the Cary Model 14 Spectrophotometer.

Diffuse reflectance spectra were obtained with the Beckman DU manual spectrophotometer with reflectance attachment, using magnesium carbonate as a reference.

RESULTS AND DISCUSSIONS

I. SOLVENT EFFECTS ON THE ELECTRONIC ABSORPTION SPECTRUM OF VANADYL BIS-(ACETYLACETONATE): A NEW SENSITIVE PARAMETER FOR RANKING LIGANDS

A. Introduction

Vanadyl bis-(acetylacetonate), $\text{VO}(\text{acac})_2$, has been shown by X-ray studies³¹ to be a rectangular pyramidal molecule in which the four acetylacetonate oxygen atoms lie in a plane and at the corners of a nearly perfect square. The vanadium atom, as might be expected, lies above this plane and approximately at the center of gravity of the molecule. The vanadyl oxygen is unique, being only 1.56 \AA from the vanadium atom as compared to the four equatorial oxygens which are found at $1.97 \pm 0.01 \text{ \AA}$.

Since this molecule has available an open sixth position which has been shown to be chemically accessible^{9,25,32-35} it was wondered what effects sixth-position interactions might have on its electronic spectrum. It was hoped that if such interactions with various ligands were to show any consistent spectral trends, then it might be possible

that: (1) relative ligand strengths might be determinable and (2) some knowledge of the electronic structure of the vanadyl ion itself might be obtained.

B. Results and Empirical Considerations

Preliminary investigations were undertaken to obtain a solvent which could be used as a constant medium for all spectra of the anticipated general species $\text{VO}(\text{acac})_2 \cdot \text{L}$, where L would be a dissolved ligand. At the outset, visual differences of solutions of the complex in various pure solvents were apparent. Spectral measurements soon showed these differences to be due primarily to variations in band positions rather than to differences in relative band intensities.

In general, the visible solution spectrum of $\text{VO}(\text{acac})_2$ consists of three low intensity bands ($\epsilon < 100$): one in the 12,000 to 16,000 cm^{-1} region, a second in the 16,000 to 18,000 cm^{-1} region, and a third at approximately 25,000 cm^{-1} . It soon became apparent by comparing solvents of known relative ligation ability that the first visible band generally appeared at lower energy and the second band generally at higher energy for the stronger ligating solvent. No consistent trend was apparent in the third band which was sometimes unobservable because of its precarious position as

a shoulder on the first strong ultraviolet absorption band. Theoretical considerations of these trends will be discussed in Section I-C.

It was first thought, since both bands I and II showed generally consistent trends with increasing solvent strength, that each of them independently might be capable of ranking solvents. As can be seen from Table I, these independent rankings are quite different. At best, it can be said that a very crude parallelism exists. In addition, neither seems to be completely satisfactory, though the ranking according to band I might seem better because of its giving such expectations as: $\text{CHCl}_3 > \text{CCl}_4$ and $\text{CS}_2 > \text{CCl}_4$. On the other hand, band II seems to give a more logical ranking for water and its "derivatives," i.e., $\text{HOH} > \text{HOCH}_3 > \text{HOC}_2\text{H}_5$.

In searching for a better empirical correlation of these band positions with solvent strength, it was thought possible that some region-determining factor might be present to cause the non-parallelism between the orderings of $\bar{\nu}_I$ and $\bar{\nu}_{II}$. If, for example, in addition to the absolute energy changes occurring for the first and second excited states there occurred simultaneously some small change in the absolute energy of the ground state, then these anomalies might be explained. In such a case, then,

TABLE I

ORDERINGS OF SOLVENTS OBTAINED BY OPTICAL
BANDS I AND II OF $\text{VO}(\text{acac})_2$ INDEPENDENTLY

$\bar{\nu}_I$	$\bar{\nu}_{II}$
water (12,300)	p-dioxane (17,850)
dimethyl sulfoxide (12,850)	water (17,820)
ethanol (12,980)	n-propylamine (17,480)
pyridine (13,000)	acetic acid (17,480)
methanol (13,030)	methanol (17,450)
dimethyl formamide (13,030)	pyridine (17,390)
n-propylamine (13,170)	piperidine (17,300)
piperidine (13,280)	ethanol (17,240)
formic acid (13,280)	dimethyl sulfoxide (17,030)
tetrahydrofuran (13,660)	dimethyl formamide (16,970)
acetic acid (13,790)	benzene (16,890)
p-dioxane (13,830)	carbon tetrachloride (16,860)
acetonitrile (14,200)	toluene (16,860)
nitromethane (14,570)	chloroform (16,860)
chloroform (14,920)	nitromethane (16,830)
carbon disulfide (15,080)	acetonitrile (16,800)
m-xylene (15,220)	tetrahydrofuran (16,800)
benzene (15,310)	m-xylene (16,720)
toluene (15,310)	carbon disulfide (16,660)
carbon tetrachloride (15,790)	formic acid (16,520)

consideration of the energy difference between $\bar{\nu}_I$ and $\bar{\nu}_{II}$, it was felt, might give a parameter which not only depends directly upon the red-shift of $\bar{\nu}_I$ and the blue-shift of $\bar{\nu}_{II}$, but also is independent of any changes occurring in the ground state. This energy difference, $D_{II,I}$, is tabulated in Table II for the twenty solvents investigated.

The order given by the parameter conforms in many respects to general expectations, though it is difficult to make any declarations as to its absolute validity. (Certainly solvent strength and ligand strength are not easy terms to define in a completely general way.) In general, one might say that a solvent molecule might possess some degree of ligand character if:

1. It possesses a Lewis base pair of electrons.
2. It is polar.
3. It possesses a π -electron cloud.

Consider the solvents listed in Table II. Those possessing Lewis base potential are seen to be concentrated near the top of the hierarchy. Oxygen and nitrogen donors such as water, methanol, pyridine, n-propylamine, etc., which possess considerable base strength, are seen to rank higher than acetic acid, formic acid, acetonitrile, nitromethane, etc., which are weak sigma pair donors. Chloroform, benzene,

TABLE II

ORDERING OF SOLVENTS ACCORDING TO THE DIFFERENCE BETWEEN
THE FIRST TWO OPTICAL BAND MAXIMA OF $\text{VO}(\text{acac})_2$, $D_{\text{II},\text{I}}$

Solvent	$D_{\text{II},\text{I}}$ (cm^{-1})
water	5,490
methanol	4,420
pyridine	4,390
n-propylamine	4,310
ethanol	4,260
dimethyl sulfoxide	4,180
p-dioxane	4,030
piperidine	4,020
dimethyl formamide	3,940
acetic acid	3,690
formic acid	3,250
tetrahydrofuran	3,150
acetonitrile	2,600
nitromethane	2,260
chloroform	1,940
carbon disulfide	1,580
benzene	1,580
toluene	1,550
m-xylene	1,500
carbon tetrachloride	1,070

carbon tetrachloride, and toluene accordingly rank very low, having no recognized Lewis base character.

Although there seems to be some parallelism to solvent polarity in the hierarchy of Table II, Lewis base strength apparently overshadows it in most cases. Non-polar molecules such as carbon disulfide, benzene, and carbon tetrachloride do stand conspicuously near the bottom, but the non-polar molecule p-dioxane stands relatively high being an oxygen donor. Dimethylformamide, acetonitrile, and nitromethane which have quite large dipole moments (3.82, 3.84, and 3.50 Debye, respectively) lie relatively low, being rather weak bases.

It is interesting to compare similar compounds and discuss their relative strengths in terms of the above ideas. In general, such molecules rank close together and still retain their logical order. For example, for water and its "derivatives" we get: HOH ($D_{\text{II},\text{I}} = 5,490 \text{ cm}^{-1}$) $>$ CH_3OH (4,420) $>$ $\text{CH}_3\text{CH}_2\text{OH}$ (4,260). This differentiation is not possible on the basis of polarity alone since methanol and ethanol both have dipole moments of 1.70 Debye; it is, however, parallel to decreasing Lewis base strength. For the two organic acids studied the order is CH_3COOH (3,690) $>$ HCOOH (3,250). This is the order of decreasing polarities

(1.74 D. and 1.52 D., respectively) and is also the Lewis order expected from hyperconjugation considerations. Pyridine (4,390) is seen to be stronger than piperidine (4,020), having not only greater polarity and the presence of a π -electron cloud in its favor but also being a stronger Lewis base because of the electron repelling effect of its aromatic nucleophilic ring. Finally, there are some interesting comparisons involving carbon tetrachloride which, it should be noticed, has none of the three favorable factors mentioned above. These are: CHCl_3 (1,940) > CCl_4 (1,070), the former being polar; CS_2 (1,580) > CCl_4 , both being non-polar but the former having slight base character due to its two sulfur atoms; and C_6H_6 (1,580) > CCl_4 , both being non-polar but benzene having a π cloud.

The empirical correlation of $D_{\text{II},\text{I}}$ with solvent strength is complimented by the spectrum of $\text{VO}(\text{acac})_2$ in the solid state. Diffuse reflectance spectra obtained in these laboratories show absorption bands in the visible at 14,700 cm^{-1} and 16,400 cm^{-1} , with indication of a third band forming in the region of 25,000 cm^{-1} . In addition, a more reliable spectrum was obtained through a thin multi-crystalline film of the complex (prepared via sublimation) on a quartz plate. These results showed bands at 14,700 cm^{-1} , 16,850 cm^{-1} , and

25,900 cm^{-1} . $D_{\text{II},\text{I}}$ for these sets of data are 1,700 cm^{-1} and 2,150 cm^{-1} , respectively. Thus, the general expectation of a small value of $D_{\text{II},\text{I}}$ is satisfied.

It is noteworthy, though, that even smaller values of $D_{\text{II},\text{I}}$ were obtained for the weakest solvents in Table II, indicating that stronger interactions exist in the solid state. This is not so surprising, however, in view of the large dipole moment of $\text{VO}(\text{acac})_2$.* It may well be that at high concentrations in weak solvents (having low dielectric constants) there exists a concentration factor in the positions of $\bar{\nu}_{\text{I}}$ and $\bar{\nu}_{\text{II}}$.

This parameter $D_{\text{II},\text{I}}$ is a sensitive one to the presence of different ligands in the sixth position. For the twenty solvents studied it varies over a range approaching 5,000 cm^{-1} . $10D_{\text{q}}$ ($\bar{\nu}_{\text{II}}$ according to the Ballhausen and Gray scheme), on the other hand, varies not more than about 1,200 cm^{-1} . As a result, some ligands which were barely distinguishable on the basis of $10 D_{\text{q}}$ are readily distinguishable

*The experimental dipole moment of $\text{VO}(\text{acac})_2$ may be dependent upon solvent. This is a consequence of $\text{VO}(\text{acac})_2$ having an open sixth position to which a solvent molecule can add. J. A. Hodgeson (unpublished results from these laboratories) has measured the dipole moment of $\text{VO}(\text{acac})_2$ to be 4.2 ± 0.3 D. in p-dioxane, while F. Orlandi and R. J. Mitchell (unpublished results from these laboratories) have obtained 4.02 D. in benzene.

using $D_{II,I}$. For example, the 10 D_Q values for chloroform, carbon tetrachloride, nitromethane, and acetonitrile are so similar that one can put little faith in the predicted order --especially since it puts the first two above the latter two. Also, it does not distinguish between chloroform and carbon tetrachloride which should be different.

It was hoped during these investigations to study the spectra of $VO(acac)_2$ in mixed solvents in order to track the movements of $\bar{\nu}_I$ and $\bar{\nu}_{II}$ with changing relative concentrations of the solvent components. As it turned out, data were obtained only for the solvent mixture ethanol-water. These results are listed in Table III and the variation of $D_{II,I}$ is shown in Figure 1. While the results are not very enlightening, several observations and comments are worth mentioning:

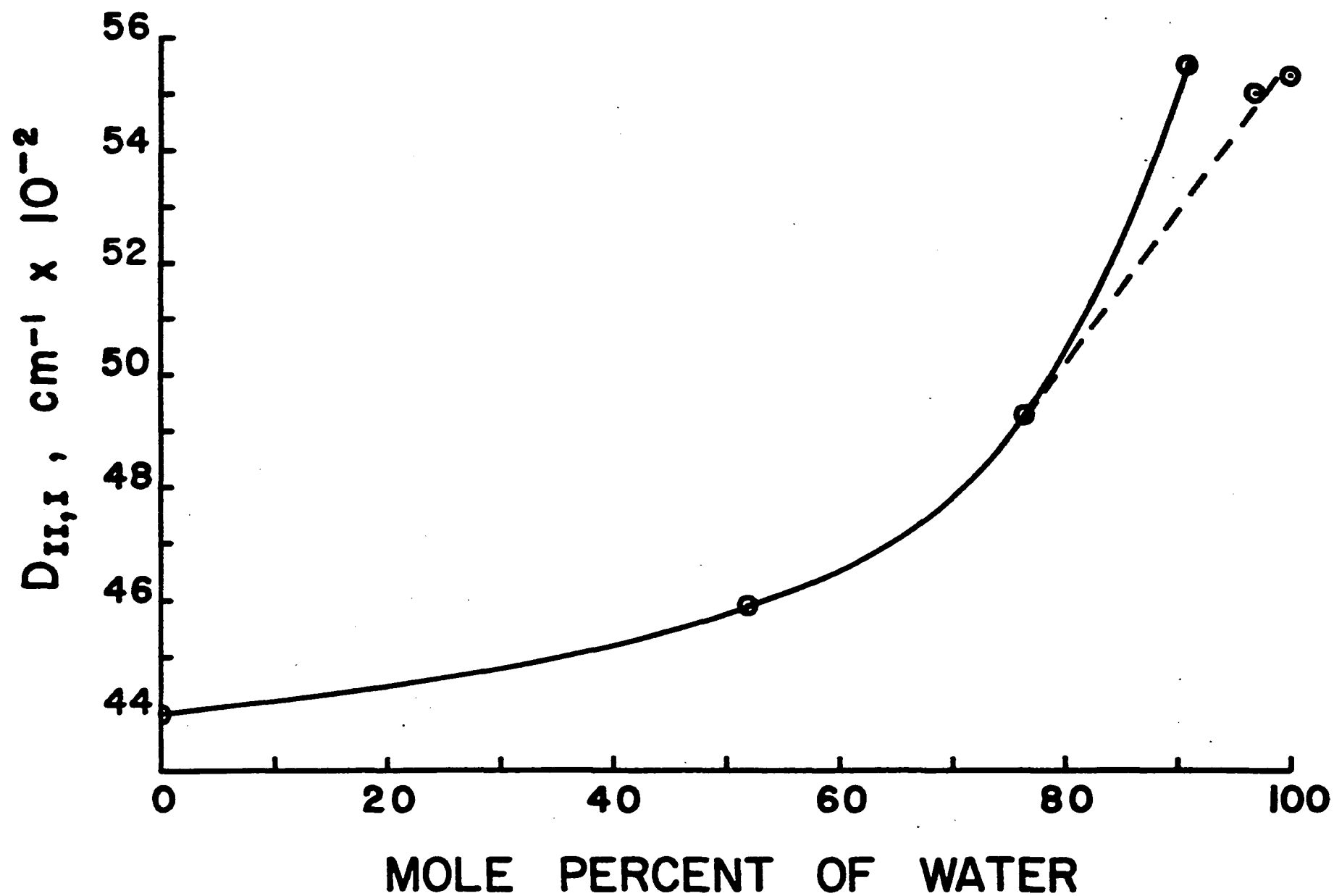
1. Table III shows how $\bar{\nu}_I$ and $\bar{\nu}_{II}$ shift with increasing mole per cent of water, the stronger solvent according to Table II. Band I is seen to generally red-shift while Band II blue-shifts, though to a lesser extent. This implies the proper behavior of $D_{II,I}$ (Figure 1) according to our previous observations on pure solvents.

2. There exists a distinct discontinuity in the band positions at very high concentrations of water (> 90 mole per

TABLE III
BAND MAXIMA AND $D_{II,I}$ for $VO(acac)_2$ IN
VARIOUS ETHANOL-WATER MIXTURES

Volume Per Cent H_2O	Mole Per Cent H_2O	$\bar{\nu}_I$	$\bar{\nu}_{II}$	$D_{II,I}$
0	0	13,000	17,400	4,400
25	51.9	12,850	17,440	4,590
50	76.4	12,770	17,700	4,930
75	90.8	12,650	18,200	5,550
90	96.7	12,200	17,700	5,500
100	100	12,340	17,870	5,530

FIGURE 1: Plot of $D_{II,I}$ Against Mole Per Cent of Water
for $VO(acac)_2$ in Various Ethanol-Water
Mixtures



cent). The last three values of $D_{II,I}$, however, may indicate a constancy at such high concentrations, since they differ within the range of experimental error. Also, it is possible that the fourth value is in error and that the dotted curve in Figure 1 is more appropriate.

3. None of the spectra showed any fine structure that might indicate the simultaneous existence of $VO(acac)_2 \cdot H_2O$ and $VO(acac)_2 \cdot EtOH$. This does not, however, rule out the possibility of such a situation existing since the widths of the bands might not allow the observation of the individual bands.

4. On the other hand, this lack of fine structure could cast some doubt on the assumption that sixth-position ligation is responsible for the shifts of $\bar{\nu}_I$ and $\bar{\nu}_{II}$. The possibility of a sort of average environmental secondary-sphere perturbation could well be worthy of consideration for there is no reason--except perhaps a steric one--to rule out the possibility of non-negligible solvent interactions with the d_e orbitals of the vanadium atom.

5. It is quite possible that the failure of $D_{II,I}$ to vary linearly--there is no apparent reason why it necessarily should--could be due to steric reasons. The less bulky water molecule would be expected to coordinate more strongly

because of its ability to approach the available positions more closely (either the sixth position of d_γ character or the secondary d_ϵ positions). This could well explain the steep rise of the $D_{II,I}$ curve at high water concentrations.

C. Theory

In the introductory part of this dissertation a brief outline of the pertinent ideas of the Ballhausen and Gray treatment of the vanadyl ion¹⁷ was presented. It was also mentioned that Selbin, Ortolano, and Smith²³ and Ortolano, Selbin, and McGlynn²⁴ had subsequently proposed and supported by various arguments an alternative interpretation based on the finer resolution they had obtained at low temperature. It is the purpose of this section to discuss the theory behind the empirical results just presented. This will be done here using mainly the ideas of Ballhausen and Gray since the room temperature data of Tables I and II do not lend themselves very well to an adequate discussion in terms of the more recent interpretation with its more rigorous experimental requirements. This is considered appropriate in view of the unsettled status of the question as it now stands. The ideas of Selbin, Ortolano, Smith, and McGlynn will be treated in Section II, at which time any possible new implications concerning the parameter $D_{II,I}$ shall be made.

The vanadyl ion is a d^1 system of symmetry $C_{\infty V}$. The hypothetical energy level scheme for this species would be expected to consist of three energy levels of decreasing energy: d_{z^2} , $d_{xz} = d_{yz}$, $d_{x^2-y^2} = d_{xy}$. This ordering is based upon the fact that the oxygen to vanadium (IV) σ bond is taken to be along the z-axis and to have superimposed on it π bonding involving equally the d_{xz} and d_{yz} metal orbitals. The $d_{x^2-y^2}$ and d_{xy} metal orbitals are lowest and are equivalent since they are not involved in the bonding and are symmetrically disposed around the z-axis.

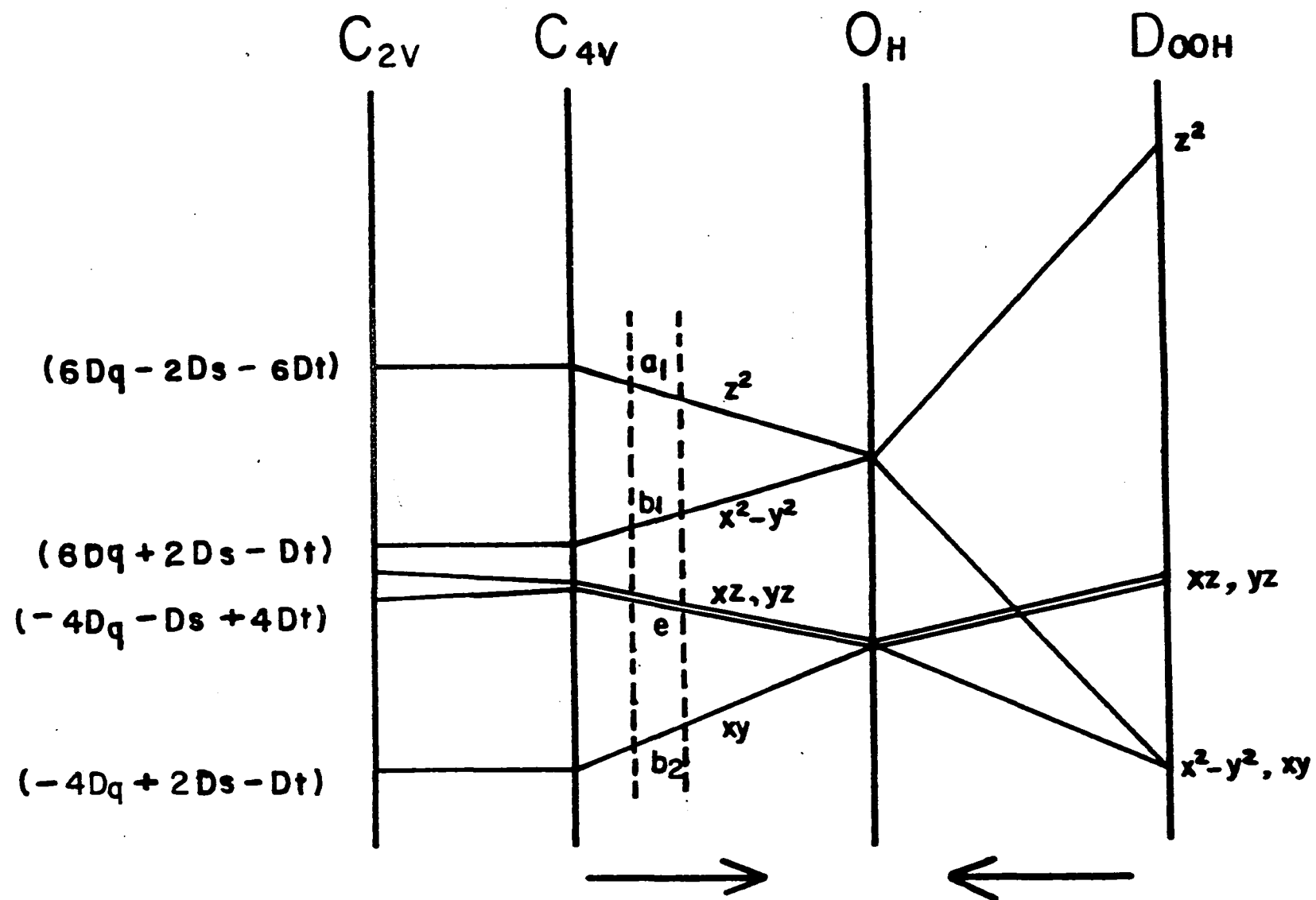
If four equivalent ligands are now brought in along the x and y axes one obtains a C_{4V} species in which the degeneracy of the ground state is removed, the $d_{x^2-y^2}$ orbital being raised in energy. The resulting ordering of the four levels now depends upon the relative axial and equatorial (both σ and π) bond strengths. That the a_1 (d_{z^2}) orbital lies highest and the b_2 (d_{xy}) orbital lowest is not questioned. The ordering of the b_1 ($d_{x^2-y^2}$) and e (d_{xz} , d_{yz}) levels, however, deserves some consideration for it depends mainly upon the relative extent of axial (vanadyl) π bonding as compared to equatorial σ bonding. Ballhausen and Gray¹⁷ conclude that $b_1 > e$ while Selbin, Holmes, and McGlynn¹⁸ favor this order only for cases of strong equatorial σ

bonding. Here we shall regard $\text{VO}(\text{acac})_2$ (assumed for convenience here as a C_{4v} molecule) as having sufficient equatorial bonding so as to satisfy both views. These qualitative derivations are summarized in Figure 2, where also is shown the C_{2v} scheme which more accurately describes $\text{VO}(\text{acac})_2$.

This ordering may be visualized in another way if one employs purely electrostatic considerations in conjunction with the detailed structure of $\text{VO}(\text{acac})_2$ as given by X-ray diffraction.³¹ This complex has four oxygen atoms in a plane perpendicular to the z axis. These, however, though primarily located in the vicinities of the four lobes of the $d_{x^2-y^2}$ orbital, are actually displaced down toward the "lower lobes" of the d_{xz} and d_{yz} orbitals by 16° , or approximately one-third of the 45° angle. The presence of the four planar oxygen atoms should therefore have as its main effects not only a significant increase in the energy of $d_{x^2-y^2}$ but also a less, but still significant, increase in the energy of d_{xz} and d_{yz} relative to the ground state. In other words, the lowest degenerate level in $\text{C}_{\infty v}$ splits and does so considerably.

Of the four energy levels, the d_{xy} orbital must be lowest since of the d_e orbitals it is farthest removed from any of the five ligand atoms. It is 90° from the axial

FIGURE 2: Diagrammatic Representation of d-orbital Splittings in Fields of Varying Symmetry. (The dotted lines bracket the approximate region observed in this work.)



oxygen and greater than 45° from the equatorial oxygens. d_{xz} and d_{yz} must be next since each one has two lobes only 29° from the equatorial oxygens and two lobes 45° from the axial oxygen. Next in energy should be the $d_{x^2-y^2}$ orbital since it is only 16° from the equatorial bonds. And finally, highest in energy should be d_{z^2} since it points directly at the very tightly bound axial oxygen.

Because of the existence of four d levels--derived by either of the two above approaches--there results the prediction of three d-d type transitions. In the crystal field approach, which Ballhausen and Gray¹⁷ have found to give the same qualitative results as a molecular orbital calculation, it will therefore be necessary to employ three parameters rather than the single parameter, D_q , sufficient for an octahedral configuration. These are D_q , D_s , and D_t , where the latter two are used to specify the degree of tetragonality present in the field. In terms of these three parameters, the energies of the four d levels are:

$$b_2 (d_{xy}): -4D_q + 2D_s - D_t$$

$$e (d_{xz}, d_{yz}): -4D_q - D_s + 4D_t$$

$$b_1 (d_{x^2-y^2}): 6D_q + 2D_s - D_t$$

$$a_1 (d_{z^2}): 6D_q - 2D_s + 6D_t.$$

The increasing energies of the three transitions are then

$$\bar{\nu}_{\text{I}} (b_2 \longrightarrow e) = (-3D_s + 5D_t),$$

$$\bar{\nu}_{\text{II}} (b_2 \longrightarrow b_1) = (10D_q),$$

$$\bar{\nu}_{\text{III}} (b_2 \longrightarrow a_1) = (10D_q - 4D_s - 5D_t).$$

If, in accord with the attitudes of Ballhausen and Gray, one now equates the three low intensity transitions of $\text{VO}(\text{acac})_2$ in the 12,000 to 26,000 cm^{-1} region to these expressions, a solution is possible which will give D_q , D_s , and D_t . The results of such calculations for all the solvent systems used in Tables I and II are tabulated in Table IV, where also are included for convenience the three experimental band positions and the parameter $D_{\text{II,I}}$. For some solvents, values of D_s and D_t were not calculable because of $\bar{\nu}_{\text{III}}$ being unobservable in those cases.

It is significant that both D_s and D_t generally approach zero as the ligand strength of the solvent increases, for it indicates the approach of the hexacoordinated molecules toward an octahedral configuration. This is quite in accord with expectations, for one can conceptually visualize that the addition of a sixth group should for electrostatic reasons, at least, cause the following spatial alterations:

1. The four planar equatorial donors will be repelled

TABLE IV

SUMMARY OF EXPERIMENTAL BAND MAXIMA FOR $\text{VO}(\text{acac})_2$ IN VARIOUS
PURE SOLVENTS AND CERTAIN DERIVED PARAMETERS

Solvent	$\bar{\nu}_I$	$\bar{\nu}_{II}$	$\bar{\nu}_{III}$	D_s	D_t	$D_{II,I}$
water	12,330	17,820	(26,100) ^a	(-2,940) ^b	(699) ^b	5,490
methanol	13,030	17,450	(26,630)	(-3,030)	(788)	4,420
pyridine	13,000	17,390	--	--	--	4,390
n-propylamine	13,170	17,480	--	--	--	4,310
ethanol	12,980	17,240	(25,700)	(-3,060)	(759)	4,260
dimethyl sulfoxide	12,850	17,030	24,990	-2,970	786	4,180
p-dioxane	13,827	17,852	--	--	--	4,025
piperidine	13,277	17,296	--	--	--	4,019
dimethyl formamide	13,030	16,970	25,120	-3,030	792	3,940
acetic acid	13,789	17,478	--	--	--	3,689
formic acid	13,277	16,524	--	--	--	3,247
tetrahydrofuran	13,657	16,803	--	--	--	3,145
acetonitrile	14,200	16,800	25,800	-3,310	851	2,600
nitromethane	14,570	16,830	(25,370)	(-3,340)	(911)	2,260
chloroform	14,920	16,860	25,970	-3,430	925	1,940
benzene	15,310	16,890	25,700	-3,450	994	1,580
carbon disulfide	15,080	16,660	--	--	--	1,580
toluene	15,310	16,859	--	--	--	1,549
m-xylene	15,217	16,718	25,309	-3,401	1,003	1,501
carbon tetrachloride	15,790	16,860	25,970	-3,560	1,024	1,070

^aValues of $\bar{\nu}_{III}$ in parentheses are only approximate as these were obtained from shoulders to an intense charge transfer band.

^bValues of D_s and D_t in parentheses are only approximate due to the uncertainty of $\bar{\nu}_{III}$.

toward the xy plane passing through the vanadium atom. This is equivalent to saying that the center of gravity of the molecule, and therefore presumably the central ion, will be shifted toward coplanarity with the acetylacetonate oxygens.

2. All of the five previously existing bonds will be lengthened, the effect being greatest for the vanadyl VO bond which owes its shortness undoubtedly to its pronounced π character. This lengthening should occur because the increased charge density around the vanadium atom, as a result of sixth-position donation, will tend to decrease its capacity to accept electrons from the previously bonded atoms. Evidence for this occurring in the case of the vanadyl VO bond is the fact that the infrared stretching frequency of this bond has been shown to decrease with sixth-position ligation.^{25,35}

Both of these effects result in a "more octahedral" structure for the solvated molecule--the stronger the solvation, the more symmetric the molecule and, consequently, the smaller the numerical values for the two tetragonality parameters.

These latter observations can be shown to have considerable relevance to the observation that the parameter $D_{II,I}$ appears to increase with solvent strength. Since $D_{II,I}$ is defined as the energy separation between $\bar{\nu}_I$ and $\bar{\nu}_{II}$, its

value in terms of the three parameters is readily seen as $(10D_q + 3D_s - 5D_t)$. Thus as D_s becomes less negative and D_t becomes less positive, this quantity will increase numerically. Also, it is gratifying that this expression for $D_{II,I}$ contains $10D_q$.

As has already been pointed out, the use of any one of the three parameters D_q , D_s , or D_t independently gives solvent orderings which are inconsistent with each other. In addition, none of them seems to give satisfactory results over the whole range of solvents investigated. This, however, should not be surprising since the very fact that they are all affected by sixth-position ligation indicates that they are intimately associated with each other. Therefore, any attempt to use any one of them alone would be an oversimplification. $D_{II,I}$, on the other hand, is a weighted combination of all three and intuitively, at least, should stand a better chance of being a more satisfactory measure of relative ligation ability.

An astute and obviously interested referee for the published article on these results²¹ pointed out, quite correctly, that the empirical parameter $D_{II,I}$ has no profound theoretical significance, whereas the parameter ρ , the ratio of the effective axial charge q_a to the effective equatorial

charge, q_e , has both a theoretical and an experimental basis. Thus q_a and q_e are proportional to $(20D_q - 35D_t)$ and $20D_q$, respectively, and the constant of proportionality in each case may be written as $\frac{1}{\alpha}$, where

$$\alpha = \frac{10e^2}{3} \langle r^4/R^5 \rangle$$

--e being the electronic charge and $\langle r^4/R^5 \rangle$ being the usual sort of fourth power radial average arising in ligand field theory. Then we may write

$$\alpha q_a = 20D_q - 35D_t$$

and

$$\alpha q_e = 20D_q$$

so that

$$\rho = q_a/q_e = 1 - (7D_t/4D_q)$$

In terms of the three transition energies $\bar{\nu}_I$, $\bar{\nu}_{II}$, and $\bar{\nu}_{III}$, this is equal to

$$\rho = [(3 \bar{\nu}_{III} - 4 \bar{\nu}_I)/2 \bar{\nu}_{II}] - \frac{1}{2}$$

Using this last equation, ρ has been calculated for those solvents in which all three transitions were observable. These are tabulated in Table V, along with αq_a and αq_e . As can be seen, the ordering obtained by ρ is unchanged except for ethanol, which moves up between water and

TABLE V
TABULATION OF αq_a , αq_e , AND ρ FOR
 $\text{VO}(\text{acac})_2$ IN VARIOUS SOLVENTS*

Solvent ($D_{\text{II},\text{I}}$)	αq_a	αq_e	ρ
water (5,490)	11,160	35,640	0.313
methanol (4,420)	7,320	34,900	0.210
pyridine (4,390)	--	34,780	--
n-propylamine (4,310)	--	34,960	--
ethanol (4,260)	7,940	34,480	0.230
dimethyl sulfoxide (4,180)	6,540	34,060	0.193
p-dioxane (4,030)	--	35,704	--
piperidine (4,020)	--	34,592	--
dimethyl formamide (3,940)	6,270	33,940	0.186
acetic acid (3,690)	--	34,956	--
formic acid (3,250)	--	33,048	--
tetrahydrofuran (3,150)	--	33,604	--
acetonitrile (2,600)	3,800	33,600	0.114
nitromethane (2,260)	1,000	33,660	0.030
chloroform (1,940)	1,370	33,720	0.041
carbon disulfide (1,580)	--	33,320	--
benzene (1,580)	-1,030	33,780	-0.030
toluene (1,550)	--	33,718	--
m-xylene (1,500)	-1,672	33,436	-0.050
carbon tetrachloride (1,070)	-2,110	33,720	-0.062

*The three parameters were calculated using expressions in which they are functions of experimental band positions only, the use of D_g and D_t being avoided. Some values of αq_a and ρ are indeterminable because of $\bar{\nu}_{\text{III}}$ being unobserved.

methanol, and chloroform, which moves up between acetonitrile and nitromethane. In fact the agreement of the two parameters is quite satisfactory when the dependence of ρ upon the exact location of $\bar{\nu}_{\text{III}}$ is considered. It is precisely on this point that most fault is found with the more theoretically acceptable parameter ρ . Not only is the precise location of the third band difficult to ascertain because of its appearance as a shoulder, but also this band is often completely hidden by the leading tail of the first intense ultraviolet band. Thus ρ is inherently somewhat less practical than $D_{\text{II},\text{I}}$.

From this more sophisticated parameter, however, there are at least a few understandings which may be derived. First, it is evident from Table V that αq_a varies considerably more than does αq_e over the range of solvents studied. This is in accord with our previous ideas, namely that ligation in the sixth position causes a retreat of the vanadyl oxygen which is greater than the retreat of the equatorial oxygens. This is the effect which results in some finite approach toward an octahedron. That both αq_a and αq_e increase with increasing ligand strength--and not just αq_a --is furthermore indicative that this ligation results in a charge contribution which is partially shared by the

plane containing the acetylacetonate oxygens--an interesting concept, at least.

Since $\alpha q_e = 20D_q$ and $\alpha q_a = 20D_q - 35D_t$, it seems that D_t can be regarded as a measure of the dissymmetry of the molecule. Since αq_e and αq_a differ only by $35D_t$, the larger the value of D_t the greater the deviation of the molecule from an octahedron, for if the deviation were zero the parameter ρ would be unity. This is indeed the trend observable in Table IV: as ligand strength (or $D_{II,I}$) increases, D_t decreases and ρ approaches unity thereby indicating the various bond adjustments discussed above.

The expression for ρ in terms of the three d-d transition energies we have already seen to be

$$\rho = \frac{3\bar{\nu}_{III} - 4\bar{\nu}_I}{2\bar{\nu}_{II}} - \frac{1}{2}$$

This becomes unity for an octahedral field since in such a case both the d_e orbitals and the d_γ orbitals are degenerate and therefore $\bar{\nu}_I = 0$ and $\bar{\nu}_{II} = \bar{\nu}_{III}$. In a tetragonal field the d_e splitting is measured by $\bar{\nu}(e) - \bar{\nu}(b_2) = \bar{\nu}_I$ and the d_γ splitting is measured by $\bar{\nu}(a_1) - \bar{\nu}(b_1) = \bar{\nu}_{III} - \bar{\nu}_{II} = D_{III,II}$. The greater these two quantities, the greater is the departure from octahedral symmetry or, in

other words, the greater the tetragonality. Table VI shows how these vary over the range of solvents investigated. It is quite in accord with our previous discussions that these quantities both show general decreasing tendencies with increasing solvent strength. It may be a source of wonder, though, that the consistency of these trends is not better in view of the quite fundamental nature of the expectation.

We are now--with the introduction of these above ideas--conveniently led into a consideration of the qualitative and semi-quantitative effects which sixth-position ligation might be expected to have on the individual d levels. We shall consider each level separately.

b_2 (d_{xy}): This level is the ground state for the lone d electron. Ballhausen and Gray¹⁷ regard it as non-bonding since they neglect all π bonding except that involving d_{xz} and d_{yz} from the vanadyl oxygen. Selbin, Holmes, and McGlynn,¹⁸ on the other hand, attribute to this b_2 level a slight anti-bonding character as a result of its participation in π bonding to the equatorial ligands. If according to our previous ideas we regard the equatorial ligands as undergoing a finite retreat as a result of ligation in the sixth position, then this level would be expected to be stabilized somewhat because of the decrease in π

TABLE VI
 d_e AND d_γ SPLITTINGS FOR $\text{VO}(\text{acac})_2$
 IN VARIOUS SOLVENTS

Solvent	$\Delta d_e (e-b_2)$	$\Delta d_\gamma (a_1-b_1)$
water	12,330	(8,280)*
methanol	13,030	(8,180)
pyridine	13,000	--
n-propylamine	13,170	--
ethanol	12,980	(8,460)
dimethyl sulfoxide	12,850	7,960
p-dioxane	13,827	--
piperidine	13,277	--
dimethyl formamide	13,030	8,150
acetic acid	13,789	--
formic acid	13,277	--
tetrahydrofuran	13,657	--
acetonitrile	14,200	9,000
nitromethane	14,570	(8,540)
chloroform	14,920	9,110
carbon disulfide	15,080	--
benzene	15,310	8,810
toluene	15,310	--
m-xylene	15,217	8,591
carbon tetrachloride	15,790	9,110

*Values of Δd_γ in parentheses are only approximate due to the uncertainty of $\bar{\nu}_{\text{III}}$ in those cases.

overlap. This effect, however, should not be large. On the other hand, the first of the above-mentioned spatial alterations (i.e., angle changes) should for electrostatic reasons result in a slight increase of this same level. Since these two effects are opposite, and neither one is large, it would seem that this level could reasonably be approximated to remain constant upon ligation in the sixth position.

$e (d_{xz}, d_{yz})$: This set of d orbitals is intimately involved in π bonding with the p_x and p_y orbitals of the vanadyl oxygen. As the V-O multiple bond lengthens upon the approach of a sixth ligand, this π overlap should decrease and the e level should be lowered in energy. Other factors being less significant, an energy decrease, then, should be the net effect. This prediction conforms, thus, to the general energy decrease of $\bar{\nu}_I$ with increasing solvent strength.

$b_1 (d_{x^2-y^2})$: Considerations and conclusions for this level should parallel very closely those given for $b_2(d_{xy})$, σ bonding being involved herein. In fact, $\bar{\nu}_{II}$ shows a general, but small, increase with solvent strength.

$a_1 (d_{z^2})$: It is difficult to make confident predictions concerning this level. Because of the relatively large

increase in αq_a and the consequent lengthening of the vanadyl VO bond, a decrease in vanadyl σ bonding is expected. Thus, the a_1 level should be lowered. When one considers, however, that the sixth-position interaction is axially directed one then expects that a de-stabilizing factor also exists. Table IV indicates that $\bar{\nu}_{III}$ generally decreases, provided one is not distracted by the values in parentheses which are at best only approximate. This shift is not large over the range of solvents studied, being of the same general magnitude as the opposite shift observed for $\bar{\nu}_{II}$. (In Section II, the question shall be raised concerning whether or not $\bar{\nu}_{III}$ should be assigned as a d-d band. If it is charge transfer in nature, as is believed now by the author, then the discussions of this paragraph pertain to $\bar{\nu}_{II}$ which increases with solvent strength.)

As a conclusion to these latter considerations, it might be commented that one qualitative correspondence appears to stand out most clearly. The greatest effect is expected to be that felt by the e (d_{xz} , d_{yz}) level and this is observed to be the case; $\bar{\nu}_I$ shows the greatest change (i.e., decreasing with solvent strength), varying almost $3,500 \text{ cm}^{-1}$ going from carbon tetrachloride to water. For $\bar{\nu}_{II}$ and $\bar{\nu}_{III}$, smaller shifts are expected and these are observed.

II. ELECTRONIC SPECTRA OF VANADYL COMPLEXES AT LOW TEMPERATURES

A. Introduction

In all previous discussions of solvent effects on the absorption spectrum of $\text{VO}(\text{acac})_2$, it was assumed for the sake of simplicity that the symmetry of the complex was C_{4v} . In actual fact, though, this molecule is more correctly characterized by C_{2v} , so that the degeneracy of the e-level is theoretically removed. This expectation finds support in the broadness observed in the first visible band at $\sim 14,000 \text{ cm}^{-1}$.

In attempting to resolve this first band at low temperature (77°K), however, three components were actually observed instead of the anticipated two. Thus, four bands could be counted in the $12,000$ to $18,000 \text{ cm}^{-1}$ region and it was proposed²³ that these might possibly be the expected four d-d transitions, and that the band usually found in the $24,500$ to $26,000 \text{ cm}^{-1}$ region might then be considered the first charge transfer band, rather than the last d-d transition as was conventionally thought. Further evidence was presented (published in a subsequent paper²⁴) in favor of the above assertions. It shall be the purpose of this section to present and discuss this evidence together with subsequent findings which supplement it.

Beginning with the quantum chemical treatment of the electronic structure and spectrum of the vanadyl ion by Ballhausen and Gray,¹⁷ there followed a number of papers which proceeded to explain their observations in the same spirit as outlined therein.¹⁹⁻²² Consideration of low temperature fine structure²³ as well as some observations by other authors^{36,37} make it imperative to consider an alternative interpretation to that of Ballhausen and Gray. According to these last authors the four room temperature crystal field bands for the C_{2v} compound $VO(acac)_2$, for example, would be expected to be contained in an unresolved pair of bands in the region 12,000 to 14,000 cm^{-1} , the band at $\sim 17,000$ to 18,000 cm^{-1} , and a final one at $\sim 24,500$ to 26,000 cm^{-1} --the exact positions being somewhat dependent upon the particular solvent used. On the other hand, low temperature (glass) spectra clearly show that the first broad band resolves consistently into three peaks with separations ranging from 440 to 1100 cm^{-1} . Delaying for the moment any discussion of such possibilities as vibronic coupling, it seems altogether possible that the band at $\sim 17,000$ cm^{-1} be the last of the four d-d transitions and that the band in the 25,000 cm^{-1} region be the first of the expected charge transfer bands.

It seemed that good low temperature data on vanadyl complexes of higher symmetry than C_{2V} , e.g., the C_{4V} species VOX_5^{3-} , should enable one to prove or disprove the above attitudes. Because of the low solubility of these C_{4V} species (which are ionic) in the solvent mixtures known suitable for the formation of good low temperature glasses, spectra were obtained instead using a low temperature KBr-pellet technique. The spectra unambiguously showed, as in C_{2V} , four peaks in the 12,000 to 20,000 cm^{-1} region while C_{4V} symmetry should ostensibly only generate three, the d_{xz} and d_{yz} orbitals being expected to remain degenerate. Reruns showed identical results and after the elimination of a few possible but unlikely factors (e.g., pressure distortions, ion substitution, and lattice perturbation) it seemed possible that the proper combination of critical conditions might exist for the observation of spin-orbit splitting in $3d^n$ complexes.

B. The Assignment of Four Crystal Field Transitions Below 20,000 cm^{-1}

In Table VII are listed the band maxima of the low temperature absorption spectra of the C_{2V} species $VO(acac)_2$ and the two C_{4V} species VOF_5^{3-} and $VO(NCS)_5^{3-}$. Spectra of $VO(acac)_2$ in two solvent systems are shown in Figure 3 while the KBr-pellet spectra of the two C_{4V} species are shown in

TABLE VII

EXPERIMENTAL BAND MAXIMA FOR SOME VANADYL COMPOUNDS AT $T=296^{\circ}\text{K}$ AND $T=77^{\circ}\text{K}$

Compound	Symmetry	Medium ^a	$\bar{\nu}_{\text{max}}, \text{cm}^{-1}$	$\bar{\nu}_{\text{max}}, \text{cm}^{-1}$	Separations $T = 77^{\circ}\text{K}$
			$T = 296^{\circ}\text{K}$	$T = 77^{\circ}\text{K}$	
$\text{VO}(\text{acac})_2^b$	C_{2v}	Solution (2:5:5 ethanol: isopentane: ether)	13,790 17,000	12,980 ^b	
				13,580	600
				14,180 ^b	600
				17,920	3,740
$\text{VO}(\text{acac})_2^b$	C_{2v}	Solution (3:7 isop. alcohol: isopentane)	13,380 16,940	12,040 ^b	
				12,980	940
				13,600	620
				18,050	4,450
$\text{VO}(\text{acac})_2$	C_{2v}	Solution (3:1:3 triethyl- amine: isopentane: ether)	13,500 17,250	11,440 ^b	
				12,550 ^b	1,100
				13,000	450
				17,500	4,500
$\text{VO}(\text{acac})_2$	C_{2v}	Solution (2:1:1 ether: toluene: ethanol)	13,580 16,880	13,000 ^b	
				13,520	520
				14,070 ^b	550
				17,790	3,720

TABLE VII (CONTINUED)

Compound	Symmetry	Medium ^a	$\bar{\nu}_{\max}, \text{cm}^{-1}$	$\bar{\nu}_{\max}, \text{cm}^{-1}$	Separations T = 77°K
			T = 296°K	T = 77°K	
VO(acac) ₂	C _{2v}	KBr-pellet	14,800	13,950 ^b	
				14,500	550
				15,100 ^b	600
				17,330	2,230
(NH ₄) ₃ VOF ₅	C _{4v}	KBr-pellet		13,160 ^b	
				13,660	500
				14,100 ^b	440
				18,200	4,100
(Et ₄ N) ₃ VO(NCS) ₅	C _{4v}	KBr-pellet		13,430 ^b	
				14,000	570
				14,500 ^b	500
				19,230	4,730

^aAll solvent component ratios are by volume.

^bThese values represent shoulder estimates ($\pm 100\text{cm}^{-1}$).

FIGURE 3: The Optical Absorption Spectra of $\text{VO}(\text{acac})_2$
Dissolved in: A, 3:7 Isopropyl Alcohol :
Isopentane; B, 2:5:5 Ethanol : Isopentane :
Ether; at 296°K and at 77°K .

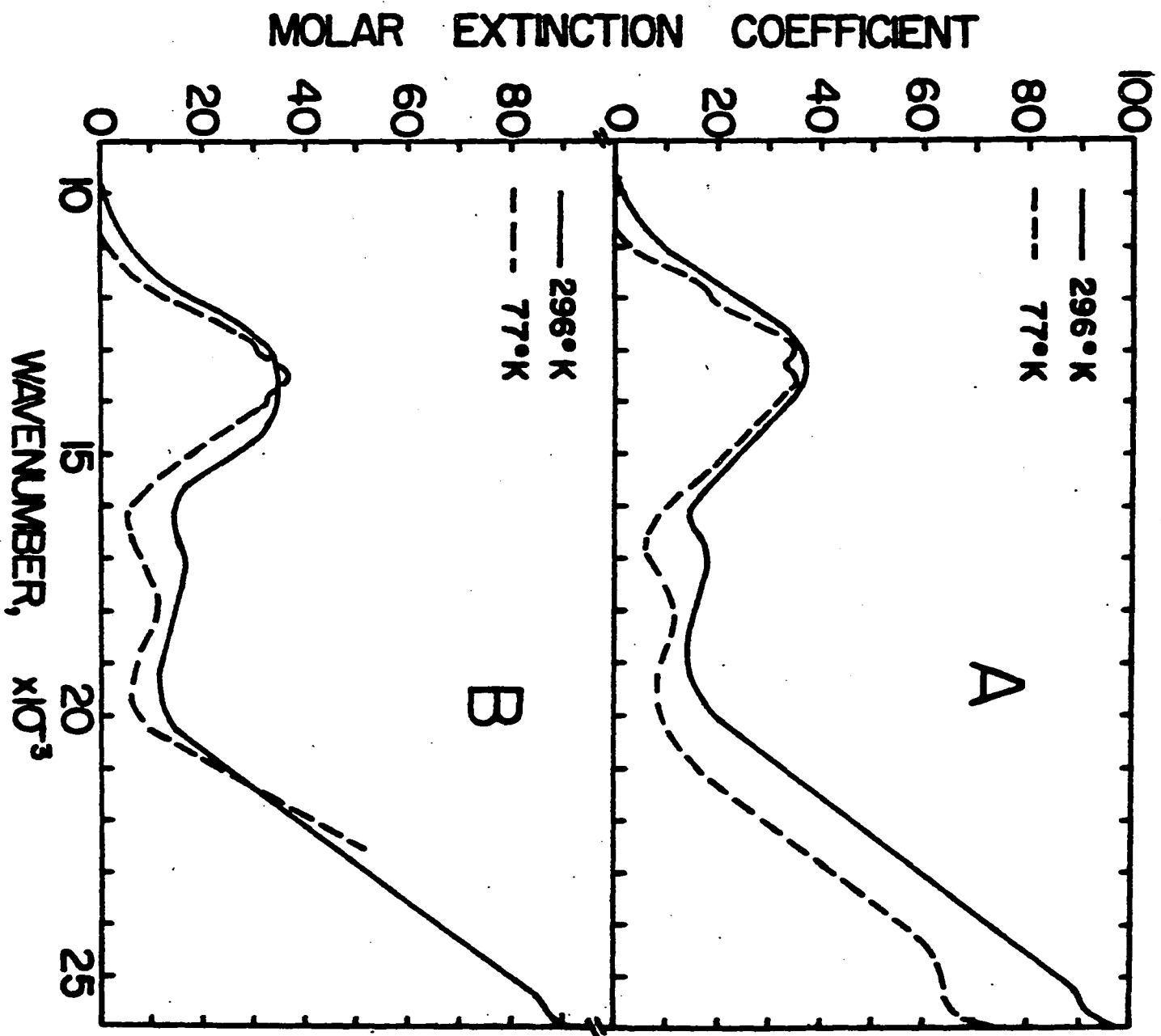


Figure 4. It should be noted that one of the five spectra on $\text{VO}(\text{acac})_2$ was also run in a KBr pellet, and it is felt that the good correspondence obtained serves as a respectable cross-check on the two general absorption methods used. It must be concluded from Table VII that the existence of four observable bands below $20,000 \text{ cm}^{-1}$ is soundly established. Before considering the possible explanation of the four d-d type transitions which occur in C_{4v} species, it is first necessary to consider the reasonableness of asserting that all d-d transitions (in either symmetry type) might occur so closely grouped and at energies less than $20,000 \text{ cm}^{-1}$, for indeed this is not presently the convention.

1. The Oxidation of $\text{VO}(\text{acac})_2$: Probably one of the more indicative types of support for the above assignment is that shown in Figure 5. When $\text{VO}(\text{acac})_2$ was dissolved in 2:1:1 ether : toluene : ethanol and allowed to stand for a number of hours, the solution color gradually changed from blue to green to yellow to orange. This was strongly suggestive of an oxidation to a vanadium (V) species and when the aged solution was analyzed, vanadium (V) was indeed found. The oxidant was soon realized to be nothing more than dissolved oxygen. Figure 6 shows quite clearly what happens spectrally (as one might be inclined to guess from the visual

FIGURE 4: KBr-pellet Optical Absorption Spectra of C_{4v} Salts at 77°K ; A, $(NH_4)_3 VOF_5$; B, $(Et_4N)_3 VO(NCS)_5$.

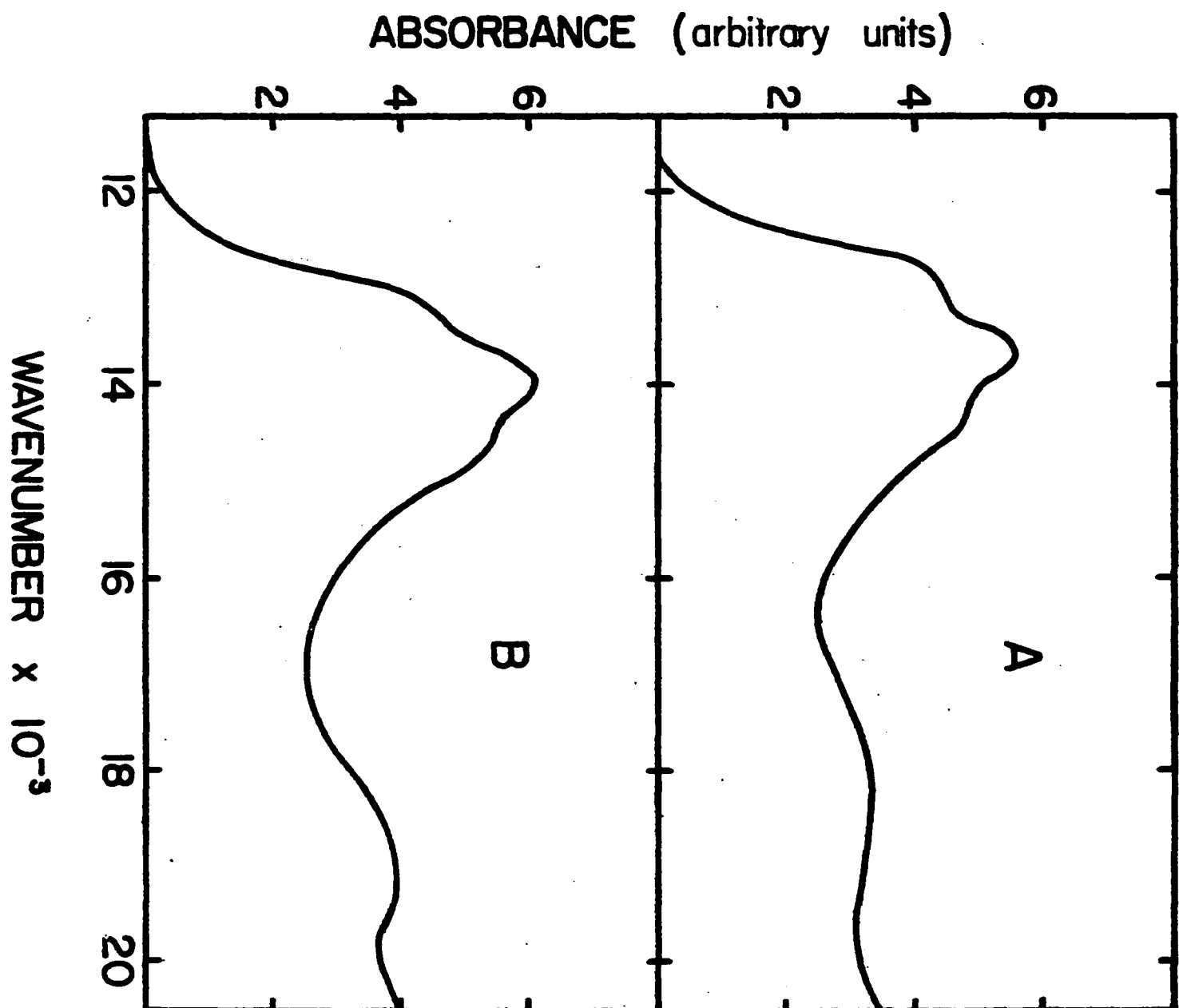
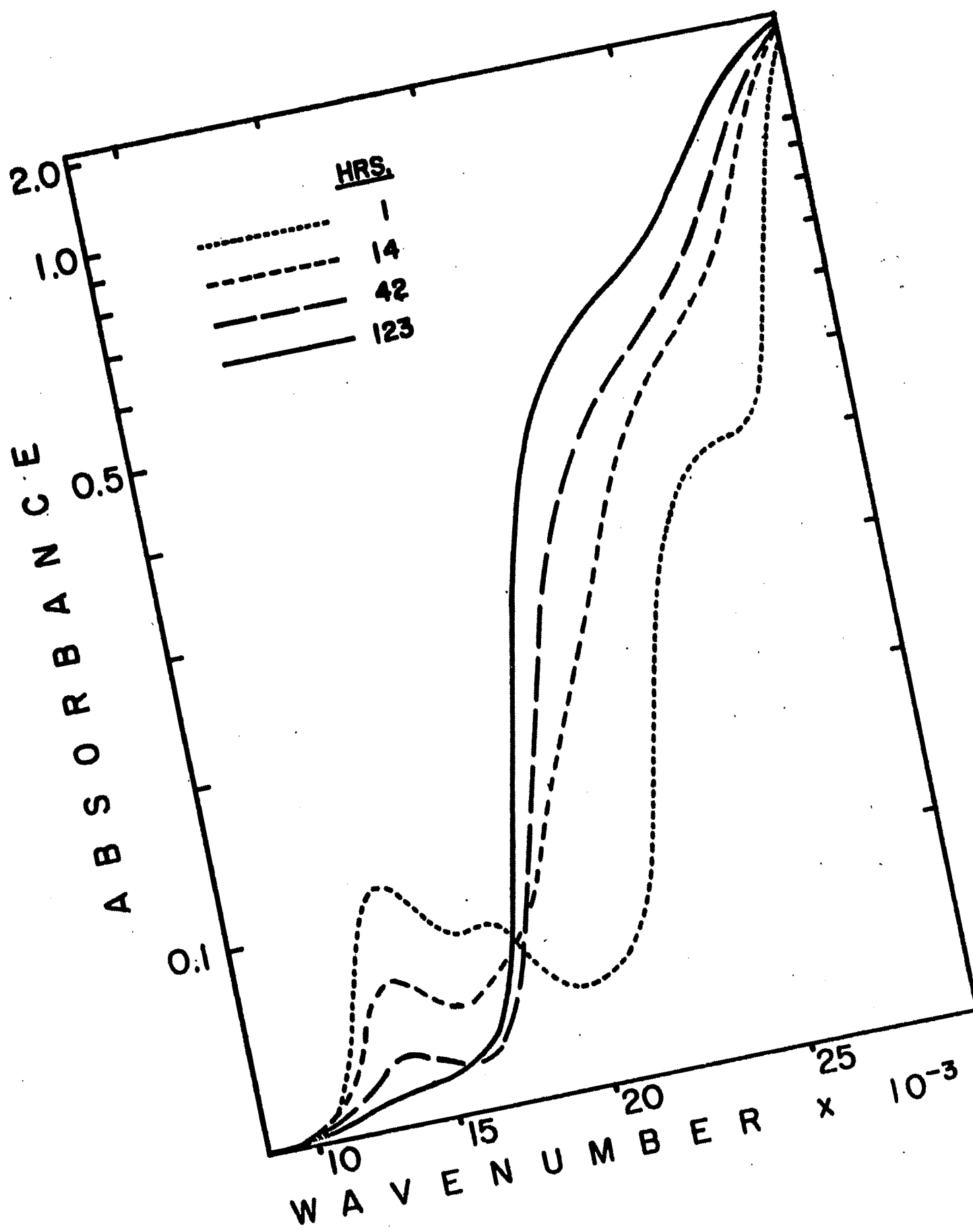


FIGURE 5: Room Temperature Absorption Spectra at Various Times During the Course of the Oxidation of $\text{VO}(\text{acac})_2$ in 2:1:1 Ether : Toluene : Ethanol Solution.



change itself). The room temperature bands at $13,600\text{ cm}^{-1}$ and $17,100\text{ cm}^{-1}$ decrease in intensity and show promise of eventual disappearance while the one at $26,000\text{ cm}^{-1}$ seems to remain. Since it is the d-d bands which are expected to disappear upon removing the lone d-electron, the $26,000\text{ cm}^{-1}$ band remaining is strong evidence of its being charge transfer in nature. Quite reasonably then one might look at lower energies to assign the series of d-d transitions in vanadyl (IV) species.

In addition, the $26,000\text{ cm}^{-1}$ band can be seen to show a distinct red shift with time. This is quite in accord with expectations for the first charge transfer band since the transition involved is one to a half-filled orbital of the V (IV) species and consequently involves a repulsion energy. This repulsion energy should be absent in the V (V) d^0 species. The magnitude of this shift is difficult to ascertain from the spectra but its value seems to be approximately $3,000$ to $5,000\text{ cm}^{-1}$; and therein, it is felt, may be a weakness in the interpretation of these results since one would generally expect a larger repulsion energy. It is possible, though, that the interpretation is correct and the small repulsion energy merely indicates a considerable delocalization of the d electron onto the ligands.

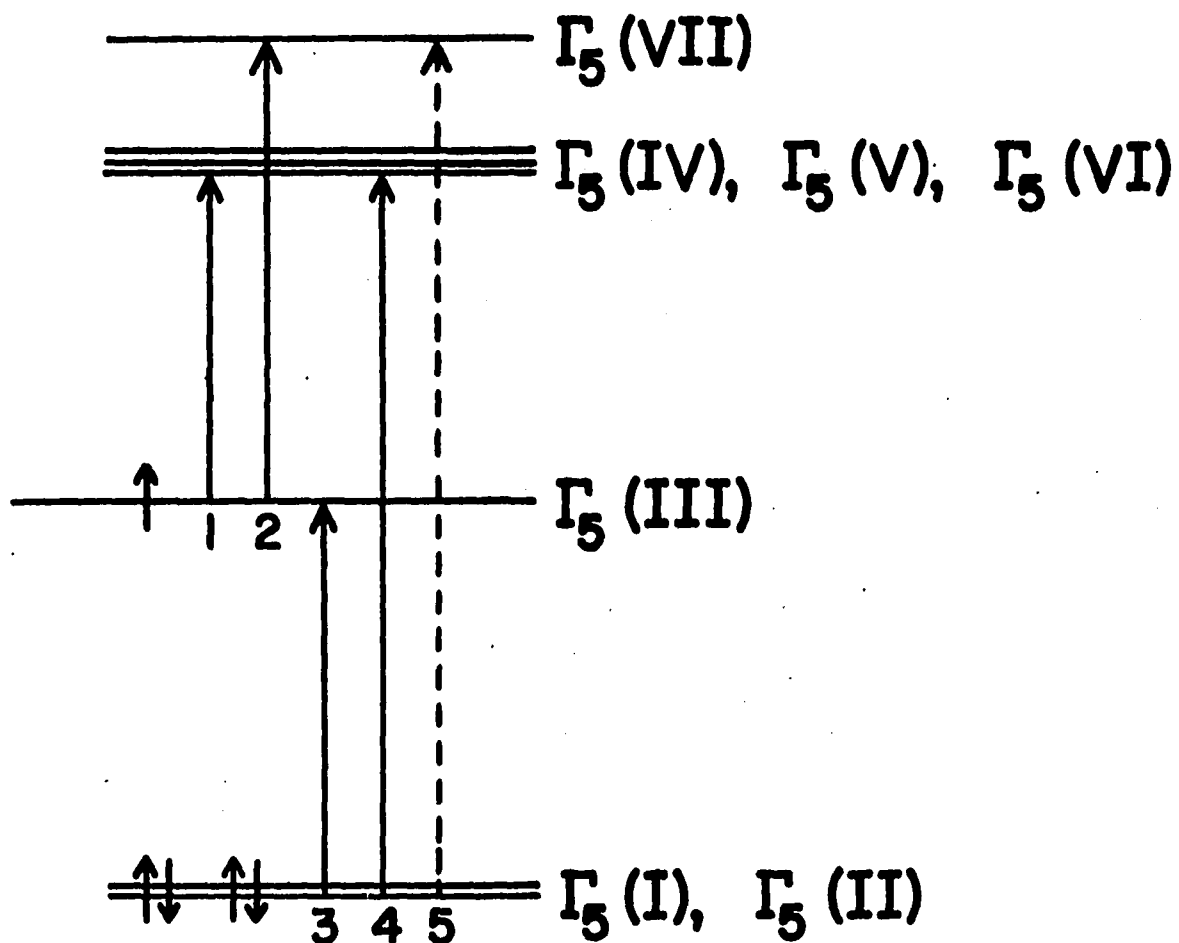
2. The Visible and Ultraviolet Spectra of $\text{VO}(\text{acac})_2$

in Ethanol Solution: $\text{VO}(\text{acac})_2$ in ethanol at room temperature shows transitions at $12,980\text{ cm}^{-1}$, $17,240\text{ cm}^{-1}$, $25,700\text{ cm}^{-1}$, and $33,000\text{ cm}^{-1}$. The band at $12,980\text{ cm}^{-1}$, according to our proposition, consists of the first three d-d transitions unresolved. The second, at $17,240\text{ cm}^{-1}$, would then be the last of that series, and the third should be the first charge transfer transition. If, in general accord with the preceding section, one assigns the repulsion energy associated with the latter transition to be $5,680\text{ cm}^{-1}$ then the transition of $33,000\text{ cm}^{-1}$ (which does not involve this repulsion energy) is shown in Figure 6 to correlate very well as the second charge transfer band.

Another band which is found at $37,000\text{ cm}^{-1}$ (dotted into Figure 6) would also correlate well as the third charge transfer band since it is of precisely the expected energy. Considerable hesitation is involved in directly assigning it as such, however, for the following reasons:

a. A band due to the ligands (acac) is expected in approximately the same position. The correlating band, however, may be hidden under the ligand band (or vice versa).

FIGURE 6: Correlation of Room Temperature Band Maxima for $\text{VO}(\text{acac})_2$ in Ethanol Solution (Not to Scale).
An Electron Repulsion Energy (\neq) of $5,680 \text{ cm}^{-1}$ is Assigned to the First Charge Transfer Band.



ENERGY, CM^{-1}

1.	12,980	
2.	17,240	
3.	25,700	(20,020 + 5,680 [‡])
4.	33,000	(12,980 + 20,020)
5.	37,000	(17,240 + 20,020 = 37,260)

b. In a private communication with Dr. Selbin* it was learned that he has personally found that the intensity of the band at $37,000\text{ cm}^{-1}$ increases with time in an oxidizing medium, and does so as the $33,000\text{ cm}^{-1}$ band decreases. This would seem to indicate that the $33,000$ and $37,000\text{ cm}^{-1}$ bands belong to vanadium (IV) and vanadium (V) species, respectively. This point has not been further investigated by the author.

3. Temperature and Solvent Effects: It is observed that the band in the $17,000$ to $19,000\text{ cm}^{-1}$ region is blue-shifted in going from room temperature to liquid nitrogen temperature, while none of the other bands seems appreciably affected. (See Table VII.) ($\text{VO}(\text{acac})_2$ in 3:1:3 Et_3N : isopentane : ether is anomalous in this respect as the first room temperature band is located to the blue of any of its low temperature components; in addition, the band in the $17,000\text{ cm}^{-1}$ region is only slightly blue-shifted.) The magnitude of this shift is seen to be in the neighborhood of 900 to 1300 cm^{-1} . In the light of our proposal that this

*Presently on Sabbatical Leave. Present address: Istituto di Chimica, Generale e Inorganica, Universita di Roma, Roma, Italia.

band is the last d-d type transition, and is therefore to an orbital of d_z^2 character,* this phenomenon seems readily understood in terms of a "freezing-on" mechanism. In a rigid medium at low temperature it should be expected that the weak, and possibly dynamic, sixth-position ligation will become more stable and that the energy of the d_z^2 orbital will thereby be increased. On the other hand, this blue shift is not easy to understand if the conventional interpretation¹⁷ of a terminal $d_{x^2-y^2}$ orbital for the 17,000 to 19,000 cm^{-1} transition is accepted.

This "freezing on" mechanism seems to be supported by the fact that there exists a correlation for the 17,000 to 19,000 cm^{-1} low temperature bands of $\text{VO}(\text{acac})_2$ which does not hold for the corresponding room temperature bands. (Again, the amine system is inconsistent.) This correlation is

*I. Bernal and P. H. Rieger, Inorg. Chem. 2, 256 (1963), have observed that the hyperfine splitting constant, $\langle A \rangle$, for $\text{VO}(\text{acac})_2$ varies with solvent to an extent they find difficult to explain by designating the 25,000 cm^{-1} band as the last d-d transition. This difficulty occurs because the 25,000 cm^{-1} band is the lowest energy d-d band conventionally supposed to possess considerable s-character (d_z^2+s) and the energy separation from the ground state of ~ 3 eV is too large. It is suggested that this difficulty might disappear at least partially if the band at $\sim 17,000$ cm^{-1} were designated as the last crystal field band.

obtained in an interesting, if not awkward, way by constructing for each solvent mixture a sort of total dipole moment, " μ_M " which is defined as

$$"\mu_M" = \sum_i (f_M)_i \mu_i,$$

where $(f_M)_i$ and μ_i are the mole fraction and dipole moment of solvent i , respectively. If " μ_M " is then plotted against the low temperature band positions, a nearly straight line is obtained for the first, second, and fourth entries in Table VII. In addition, this correlation is improved if one considers only the solvent components which have explicit Lewis base character (i.e., oxygen donors) and is not weakened if one employs the simpler parameter " μ_V " defined as

$$"\mu_V" = \sum_i (f_V)_i \mu_i,$$

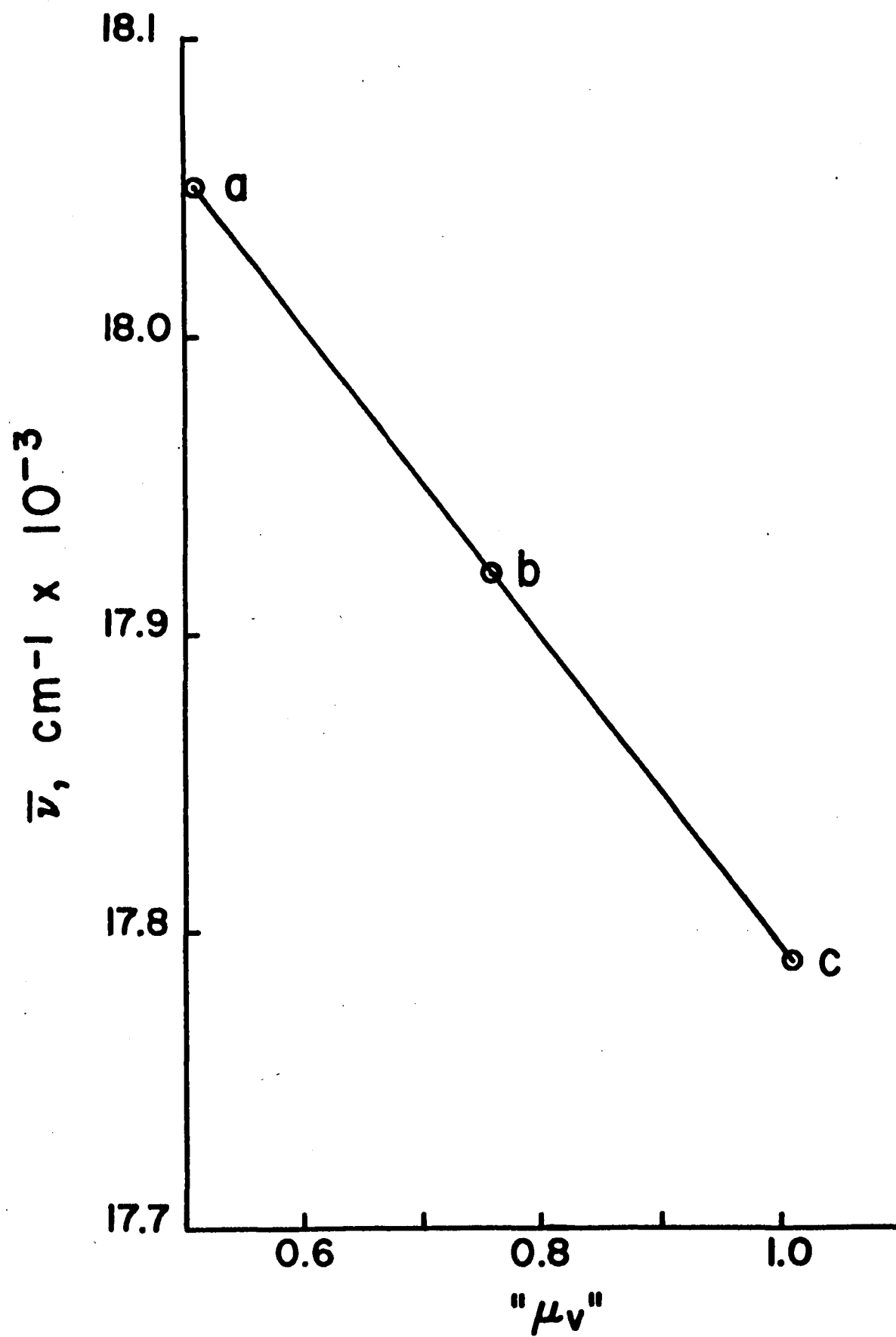
where $(f_V)_i$ is the volume fraction of solvent i . For the three above systems the pertinent data (considering only the Lewis-base components--underlined) is:

Solvent Mixture	$\bar{\nu}$ (cm ⁻¹)	" μ_M "	" μ_V "
3:7 <u>isopr. al.</u> : isopent.	18,050	0.67	0.51
2:5:5 <u>EtOH</u> :isopent.: <u>ether</u>	17,920	0.91	0.76
2:1:1 <u>ether</u> :toluene: <u>EtOH</u>	17,790	1.12	1.01

Figure 7 shows a plot of $\bar{\nu}$ against " μ_V ". It should be

FIGURE 7: Plot of $\sim 18,000 \text{ cm}^{-1}$ Band Maxima Against " μ_v " for $\text{VO}(\text{acac})_2$ in Three Solvent Mixtures at 77°K :

- a) 3:7 isopr. al. : isopent.
- b) 2:5:5 EtOH : isopent. : ether
- c) 2:1:1 ether : toluene : EtOH



noticed that therein $\bar{\nu}$ is shown to red-shift as the system polarity increases, a trend which is opposite to our previous general observations on pure solvents at room temperature. This latter point is not understood.

4. Magnetic Correlations: Expressions relating the spin-orbit coupling constant ξ , g-factors, and spectroscopic energies may be used to check the assignment of spectral bands when the first two quantities are believed known. In general, though, considerable caution should be used in doing so, especially in solution where only $\langle g \rangle$, the average g-value, is measurable. In any case, all such expressions are dependent upon the value of ξ , a quantity which is a difficult one to determine in molecules. In this present instance where two alternative assignments of the d-d bands in vanadyl complexes are being considered, it is found that the use of solution g-factors does not provide a unique means of deciding between the two assignments; indeed substitution of the assigned bands from either set of energy designations gives equally good agreement, though they are opposite in deviation. Furthermore, perfect agreement may be obtained with either set of assignments by proper adjustment of ξ well within the reasonable range of values it could possess. Even if ξ were known exactly, one might still be unable

to definitely rule out either of the alternative energy schemata by this means because of the inexact nature of the expressions which relate these schemata to ξ and $\langle g \rangle$. In sum, the assignments proposed here correlate just as well with known $\langle g \rangle$ values as do those of Ballhausen and Gray.¹⁷

5. The Visible and Ultraviolet Spectra of Vanadyl bis-(hexafluoroacetylacetonate): The original purpose for which this compound was prepared was to attempt to obtain its vapor spectrum. Such was desirable for the light it might shed on the two schemata presently being considered. Although vanadyl bis-(acetylacetonate) had already proved to be insufficiently volatile for this purpose, it was believed that this very similar derivative of the parent acetylacetonate complex might be sufficiently more volatile and provide the same information. At the time of this writing, one vapor band had been obtained at $37,500 \text{ cm}^{-1}$ on the Beckman DK (path length = 5 cm^{-1}) at $\sim 30^\circ\text{C}$ and atmospheric pressure. No structure was obvious, though slight indication of a shoulder was present. This investigation has been discontinued by the author but will be pursued further by another member of this research group.

In the solution spectra of this complex, however, results have been obtained which are believed to be of

significance. In the 10,000 to 50,000 cm^{-1} region, four distinct peaks and a number of shoulders were observed for all three of the solvents: ethanol, dimethylformamide, and chloroform. These results are tabulated in Table VIII. The following characteristics of the spectrum of this compound are deemed quite pertinent to the question of the validity of the "clustered transition" idea:

a. $\bar{\nu}_I$ and $\bar{\nu}_{II}$ appear to be solvent dependent; this is in general accord with our observations on $\text{VO}(\text{acac})_2$, though the ordering given by $D_{II,I}$ here ($\text{DMF} > \text{CHCl}_3 > \text{EtOH}$) is not. In addition, the indication of a shoulder on this band is in accord with the low temperature splitting of $\bar{\nu}_I$ for $\text{VO}(\text{acac})_2$. (Table VII.)

b. $\bar{\nu}_{III}$ for this complex is distinct and completely separated from the region of the first ultraviolet band, lying approximately 5,000 cm^{-1} to the red of this region. Thus, in contrast to all spectra on $\text{VO}(\text{acac})_2$, the intensity and exact shape and position of this band are readily and directly observable. Therefore, it can be seen that the band is quite insensitive to solvent and is four to eight times as intense as $\bar{\nu}_I$ and $\bar{\nu}_{II}$ --both facts being in general accord with the hypothesis of its being charge transfer in nature. In addition, and most importantly, it is seen

TABLE VIII
BAND MAXIMA FOR VANADYL BIS-(HEXAFLUOROACETYLACETONATE)
IN THREE SOLVENTS

Solvent	$\bar{\nu}_I$	$\bar{\nu}_{II}$	$\bar{\nu}_{III}$	$\bar{\nu}_{IV}$
ethanol	14,090 ^a	16,450	20,610 ^b	32,800 ^c
dimethylformamide	13,080 ^a	16,080	20,500 ^b	32,800 ^c
chloroform	13,890 ^a	16,400	20,600 ^b	31,300 ^c

^aRed shoulder indicated.

^bDefinite blue shoulder present.

^cOne or two definite shoulders present.

that this band has a definite blue shoulder. Not only is this fact in accord with expectations for the first charge transfer band (see Figure 6, transition number 3), but also it is in complete discord with anyone's predictions for the last d-d band, $b_2 (d_{xy}) \longrightarrow a_1 (d_{z^2})$, since that band can only be singlet in character. In this regard, it is somewhat pertinent that $\bar{\nu}_{II}$ is the only band having this observed characteristic.

c. Lastly, the complex nature of $\bar{\nu}_{IV}$ is in excellent accord with its being the second charge transfer band (transition number 4 of Figure 6). Note that no band at $\sim 33,000 \text{ cm}^{-1}$ was found in the vapor spectrum. The vapor band at $37,500 \text{ cm}^{-1}$ is probably the solution band at $33,000 \text{ cm}^{-1}$, shifted in the absence of solvent (or crystalline) perturbations.

C. The Splitting of the E-Representation in C_{4v}

1. Spin-Orbit Coupling: We now turn to consideration of the four observed transitions in the C_{4v} compounds (see Table VII and Figure 4). As mentioned previously, symmetry considerations predict only three d-d bands in C_{4v} , the E representation remaining orbitally doubly degenerate. To understand the possibility of a C_{4v} compound giving a C_{2v} -type spectrum, it is necessary then that a reasonable

mechanism be available to split E into two singly degenerate representations. The most obvious of such mechanisms are a molecular distortion to an effective C_{2v} symmetry and Jahn-Teller splitting effects in the excited state.* In addition, however, there also exists the possibility of a significant spin-orbit splitting effect. In many inorganic complexes this is indeed predictable, but seldom is it actually observed in $3d^n$ complexes with low n because of the small magnitude of its effects in relation to band widths. Usually, therefore, spin-orbit coupling seems to be a negligible factor in the interpretation of $3d^n$ experimental results and orbitally degenerate bands susceptible to its effects are assumed to remain degenerate. So prevalent, even, is this

*F. A. Cotton and M. D. Meyers³⁸ observed two bands in the spectra of $[CoF_6]^{3-}$ and $[Fe(H_2O)_6]^{2+}$ where only one was expected in an octahedral environment. The separations ranged from 1600-3400 cm^{-1} and spin-orbit coupling was ruled out on the basis of the spin-orbit coupling constant being only about -100 cm^{-1} . Static distortions of the ground state were also ruled out on the basis of structural data, and a dynamic Jahn-Teller effect was proposed as being of the proper order of magnitude. In this data, the magnitude of the splittings are about twice that expected from strict theoretical considerations and it is not felt that spin-orbit coupling is here so readily discarded. In general (though not in the case of Cotton and Meyer's data) it is felt that the various Jahn-Teller effects might possibly be too often blamed for observed splittings and that spin-orbit coupling should be given more serious consideration.

spirit of simplification that rarely are special techniques employed to attempt to find such splittings.

In the case of at least some vanadyl complexes it is suspected that there may very well exist non-insignificant spin-orbit effects. Ballhausen and Gray¹⁷ take the spin-orbit coupling constant ξ to be about 135 cm^{-1} for $\text{VO}(\text{H}_2\text{O})_5^{2+}$ by using the tabulations of Dunn³⁹ and presuming the existence of an approximate charge on the vanadium atom of +1. Other environments for V^{4+} can give ξ values in the neighborhood of 150 cm^{-1} ⁴⁰ and it is expected that larger or smaller values exist depending on the nature of the bonding and its strength in particular species, the ultimate factor being the amount of electronic shielding between the nucleus and the d-electron.

According to conventional theory, for example that of Liehr,⁴¹ the spin-orbit splitting of the E levels in question should amount to about $3/2 \xi$ in the first order. Consequently that for our case would be in the region of $200\text{--}225 \text{ cm}^{-1}$ if we rigidly adhere to the representative values of ξ quoted previously. This predicted splitting is about $1/2$ of the closest spacing observed in the components of the first band (Table VII), but the favorable order of magnitude is encouraging in the light of such things as the difficulty of measuring shoulder positions, the approximate nature of

the theory of unsymmetrical systems, the use of a crystal field model, the uncertainty of molecular spin-orbit coupling constants, and the possible importance of other more indirect effects which have been neglected.

In order to illustrate the spin-orbit splitting effects in C_{4v} , it is necessary that double groups be used since we are dealing with a d^1 system. The double groups which shall be employed here are $C'_{4v}(D'_4)$ and O' , the character tables for which are taken from Cotton.⁴²

The 2D free ion term is split in O_h into E_g and T_{2g} . In turn a distortion to C_{4v} will give $A_1 + B_1$ for E_g , and $B_2 + E$ for T_{2g} . These correspond to the Bethe⁴³ notational representations Γ_1 , Γ_3 , Γ_4 , and Γ_5 , respectively in C'_{4v} , the representation for which the spin angular momentum forms a bases is $\Gamma_{\frac{1}{2}} = \Gamma_6$, and the spin-orbit coupling should have the effect of generating the five Kramers doublets $\Gamma_6 = \Gamma_1 \times \Gamma_6$, $\Gamma_7 = \Gamma_3 \times \Gamma_6$, $\Gamma_7 = \Gamma_4 \times \Gamma_6$, and $\Gamma_6 + \Gamma_7 = \Gamma_5 \times \Gamma_6$. Thus the doubly degenerate level Γ_5 in C'_{4v} splits into Γ_6 and Γ_7 upon inclusion of spin. In C'_{2v} , degeneracy is not affected by inclusion of spin since five orbital representations-- $2\Gamma_1$, Γ_2 , Γ_3 , and Γ_4 --exist beforehand; inclusion of spin merely gives $5\Gamma_5$.

In a strong cubic field without spin-orbit coupling

the orbital energies are the usual $-4D_q$ and $6D_q$, $\Gamma_7(T_{2g})$ and $\Gamma_8(T_{2g})$ remaining degenerate. With spin-orbit coupling the energies are in first order, $E[\Gamma_7(T_{2g})] = \xi - 4D_q$, $E[\Gamma_8(T_{2g})] = -\frac{\xi}{2} - 4D_q$, and $E[\Gamma_8(E_g)] = 6D_q$. Thus it can be seen that $\Gamma_7(T_{2g})$ and $\Gamma_8(T_{2g})$ split by an amount $\frac{3}{2}\xi$ upon inclusion of spin-orbit interactions. These represent the levels shown* in Figure 8 in the column " $\Gamma_{\frac{1}{2}} \times O'$ ".

In going to a strong quadrate field the determinantal equations are:

$$\begin{vmatrix} \Gamma_6 [\Gamma_8(T_{2g})]** & \Gamma_6 [\Gamma_8(E_g)] \\ -\frac{\xi}{2} - 4D_q - D_s + 4D_t - E & \frac{3}{2}\xi \\ \frac{3}{2}\xi & 6D_q - 2D_s - 6D_t - E \end{vmatrix} = 0$$

and

*Figure 8 is constructed from the experimental data for $(NH_4)_3VOF_5$ as a basis, but is generally representative of all of the systems listed in Table VII. The levels in the column " $\Gamma_{\frac{1}{2}} \times C_{4v}'$ " are experimental, the assignment of levels 8, 9 and 10 possibly being of a different order than that indicated. All others are hypothetically to scale based on the crystal field energy expressions listed in Table IX. There is, of course, considerable simplification involved because of the high degree of π bonding in vanadyl molecules. However, the primary purpose of Figure 8 is merely to show graphically, and roughly to scale, how one might picture the actual system as having evolved from the free ion V^{4+} . This is done in two different ways.

**That is, Γ_6 , quadrate, derived from $\Gamma_8(T_{2g})$, cubic.

FIGURE 8: Experimental Crystal Field Energy Level Diagram for $(\text{NH}_4)_3 \text{VOF}_5$, Derived in Two Ways From $2D$ Free Ion Term:

- a) Via Cubic Field to Which Spin-Orbit Coupling is Applied and Subsequently Distorted to Quadrate Field.
- b) Via Cubic Field Distorted to Quadrate Field to Which Spin-Orbit Coupling is Subsequently Applied.

RELATIVE ENERGY, $\text{CM}^{-1} \times 10^{-3}$

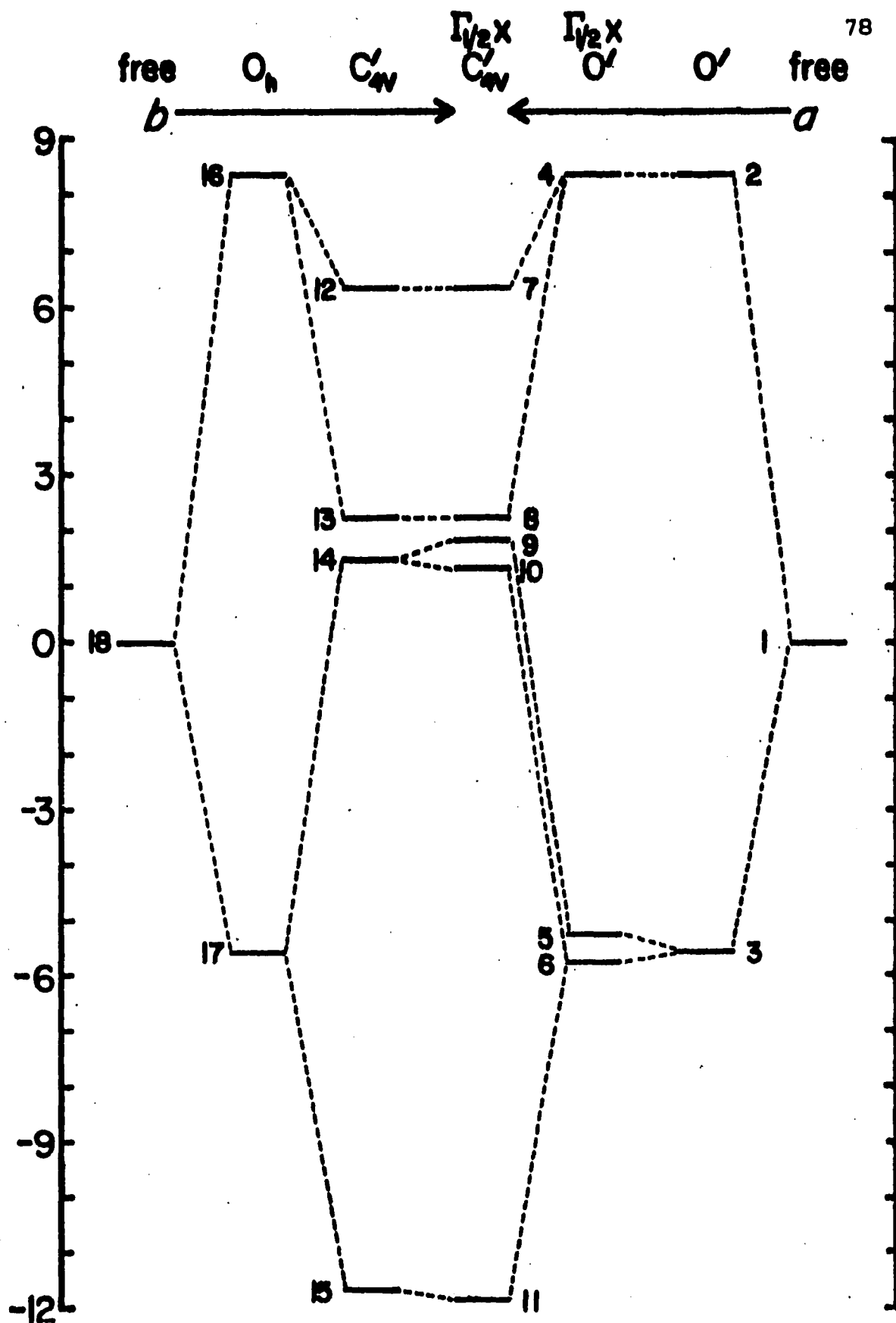


TABLE IX

ENERGIES AND ENERGY EXPRESSIONS USED IN CONSTRUCTING FIGURE 8

Level ^a	Level Designation(s)	Energy (cm ⁻¹) Relative to Free Ion	Energy Expression, 1st Order ^b
1)	2D	0	--
2)	$\Gamma_3(E'_1)$	+8,358	6D _q
3)	$\Gamma_5(T'_2)$	-5,572	-4D _q
4)	$\Gamma_8(G')$	+8,358	6D _q
5)	$\Gamma_7(E'_3)$	-5,239	$\xi' - 4D_q$
6)	$\Gamma_8(G')$	-5,739	$-\frac{\xi'}{2} - 4D_q$
7)	$\Gamma_6(E'_2)$	+6,372	6D _q - 2D _s - 6D _t
8)	$\Gamma_7(E'_3)$	+2,273	6D _q + 2D _s - D _t
9)	$\Gamma_7(E'_3)$	+1,839	$\xi' - 4D_q - D_s + 4D_t$
10)	$\Gamma_6(E'_2)$	+1,339	$-\frac{\xi'}{2} - 4D_q - D_s + 4D_t$
11)	$\Gamma_7(E'_3)$	-11,824	$-\frac{\xi'}{2} - 4D_q + 2D_s - D_t$
12)	$\Gamma_1(A'_1)$	+6,372	6D _q - 2D _s - D _t
13)	$\Gamma_3(B'_1)$	+2,273	6D _q + 2D _s - D _t
14)	$\Gamma_3(E'_1)$	+1,506	-4D _q - D _s + 4D _t
15)	$\Gamma_4(B'_2)$	-11,657	-4D _q + 2D _s - D _t

TABLE IX

ENERGIES AND ENERGY EXPRESSIONS USED IN CONSTRUCTING FIGURE 8

Level ^a	Level Designation(s)	Energy (cm ⁻¹) Relative to Free Ion	Energy Expression, 1st Order ^b
1)	2 _D	0	--
2)	$\Gamma_3(E'_1)$	+8,358	6D _q
3)	$\Gamma_5(T'_2)$	-5,572	-4D _q
4)	$\Gamma_8(G')$	+8,358	6D _q
5)	$\Gamma_7(E'_3)$	-5,239	$\xi' - 4D_q$
6)	$\Gamma_8(G')$	-5,739	$-\frac{\xi'}{2} - 4D_q$
7)	$\Gamma_6(E'_2)$	+6,372	6D _q - 2D _s - 6D _t
8)	$\Gamma_7(E'_3)$	+2,273	6D _q + 2D _s - D _t
9)	$\Gamma_7(E'_3)$	+1,839	$\xi' - 4D_q - D_s + 4D_t$
10)	$\Gamma_6(E'_2)$	+1,339	$-\frac{\xi'}{2} - 4D_q - D_s + 4D_t$
11)	$\Gamma_7(E'_3)$	-11,824	$-\frac{\xi'}{2} - 4D_q + 2D_s - D_t$
12)	$\Gamma_1(A'_1)$	+6,372	6D _q - 2D _s - D _t
13)	$\Gamma_3(B'_1)$	+2,273	6D _q + 2D _s - D _t
14)	$\Gamma_5(E'_1)$	+1,506	-4D _q - D _s + 4D _t
15)	$\Gamma_4(B'_2)$	-11,657	-4D _q + 2D _s - D _t

TABLE IX (CONTINUED)

Level ^a	Level Designation(s)	Energy (cm ⁻¹) Relative to Free Ion	Energy Expression, 1st Order ^b
16)	E _g	+8,358	6D _q
17)	T _{2g}	-5,572	-4D _q
18)	2D	0	--

^aNumbers correspond to those in Figure 8.

^b $\xi' = 333\text{cm}^{-1}$, $D_q = 1393$, $D_s = -2466$, $D_t = 1153$

$$\begin{array}{ccc}
 \Gamma_7[\Gamma_7(T_{2g})] & \Gamma_7[\Gamma_8(T_{2g})] & \Gamma_7[\Gamma_8(E_g)] \\
 \left| \begin{array}{ccc}
 \xi - 4D_q + (7/3)D_t - E & (2/9)^{1/2}(3D_s - 5D_t) & 0 \\
 (2/9)^{1/2}(3D_s - 5D_t) & -(\xi/2) - 4D_q + D_s + (2/3)D_t - E & (3/2)^{1/2}\xi \\
 0 & (3/2)^{1/2}\xi & 6D_q + 2D_s - D_t - E
 \end{array} \right| & = & 0
 \end{array}$$

These represent the levels* shown in Figure 8 in the column " $\Gamma_{1/2} \times C_{4v}$." The roots become in the first order:

$$E \{ \Gamma_6[\Gamma_8(T_{2g})] \} = -\frac{\xi}{2} - 4D_q - D_s + 4D_t$$

$$E \{ \Gamma_6[\Gamma_8(E_g)] \} = 6D_q - 2D_s - 6D_t$$

$$E \{ \Gamma_7[\Gamma_7(T_{2g})] \} = \xi - 4D_q - D_s + 4D_t$$

$$E \{ \Gamma_7[\Gamma_8(T_{2g})] \} = -\frac{\xi}{2} - 4D_q + 2D_s - D_t$$

$$E \{ \Gamma_7[\Gamma_8(E_g)] \} = 6D_q + 2D_s - D_t$$

*It might, perhaps, be disturbing to some that the uppermost level in C_{4v} is lower than the E_g level in O_h . This, however, can be understood from crystal field theory as being a natural consequence of having a system in which the ratio of the tetragonal distortion to $10D_q$ is large. Such a situation, we believe, does indeed exist in the vanadyl species with which we are dealing--and might even be a common characteristic of all vanadyl species--if our present hypothesis is correct.

In first order, then, $\Gamma_6[\Gamma_8(T_{2g})]$ and $\Gamma_7[\Gamma_8(T_{2g})]$ are lowered by $\xi/2$ while $\Gamma_7[\Gamma_7(T_{2g})]$ is raised by ξ , the splitting between the E levels in C_{4v} being theoretically $\frac{3}{2} \xi$ in first order. In second order, as may be deduced by exact solution of the above determinants, this factor of $\frac{3}{2} \xi$ will increase somewhat.

Referring back to Table IX, we find a quantity $\xi' = 333 \text{ cm}^{-1}$. This quantity is not meant to be a proposed value for ξ , the spin-orbit coupling constant itself, but rather a hypothetical coupling constant required to account for the spacings observed for a particular system if first order effects alone are considered. Higher order effects should not be large. The high value of ξ' could be interpreted to imply that spin-orbit coupling alone is insufficient and that the splitting is actually exaggerated by some slight molecular distortion and/or by Jahn-Teller splitting effects in the excited state.

2. Vibrational Coupling: It is possible that the three components of the $13,000 \text{ cm}^{-1}$ band are of vibrational origin. Admittedly, this possibility has not been refuted here in any positive way. However, it is felt that significant indirect arguments against a vibrational origin have been furnished by the data in favor of the clustered

transition idea, spin-orbit coupling being a proposed mechanism for at least the C_{4v} species. For sure, a proof (either experimental or theoretical) for or against a vibrational origin is a difficult one to realize. It is wished, then, only to add a few further comments concerning this possibility:

- a. If the splitting is vibronic, why does such splitting not also occur in the $17,000\text{ cm}^{-1}$ band?
- b. Why are only three bands consistently observed in different vanadyl complexes?
- c. In two of the spectra (i.e., the second and third entries in Table VII) the fine structure was confined to the red side of the bulk band, leaving the blue side structureless. This is inconsistent with a vibrational origin.
- d. The vibration to be suspected is the vanadyl V-O stretch which is never very far from $950\text{--}1000\text{ cm}^{-1}$. This is somewhat larger than most of the splittings observed* and

*In a recent private communication with G. Maus of this research group, it has been learned that he has apparently been successful in obtaining a better-resolved spectrum of the species VOF_5^{3-} than in this work. It appears from his results that the splittings are somewhat larger than those stated in Table VII, being 650 and 790 cm^{-1} respectively. This would better favor coupling with the vanadyl V-O stretch. On the other hand, the better resolution in his spectrum also places considerably greater reliability on the measured spacings which would be expected to be more

it does not seem possible that a sufficient increase in the electron density of the central atom, as a result of the electronic transition involved, could occur so as to account for a decrease of the V-O stretching frequency down to the magnitude of the observed splittings. The data on C_{4v} compounds, particularly, reveal splittings which are too small to be interpreted in this fashion.

e. The coupled vibrations might be intra-ligand vibrations. However, no intra-ligand vibrations exist in the pentafluoride complex and yet a splitting is observed. This thesis then becomes untenable.

f. Inspection of Table VII indicates a considerable influence of medium on the splittings which are observed for the $VO(acac)_2$ species. It is difficult, if not impossible, to understand these changes if the splittings be considered to be of vibronic origin; however, sixth-position ligation as well as second-coordination sphere effects cause one to expect such variations as are observed if the splittings be presumed to originate in ligand-field spin-orbit coupling

alike than his spectrum indicates, if their origin is vibronic. The difference, however, may still be within the realm of experimental error. In any case, it is felt that these recent findings do not necessarily vitiate the proposals of this section (II).

effects. Also, such variations are expected if the splittings are a result of molecular distortions.

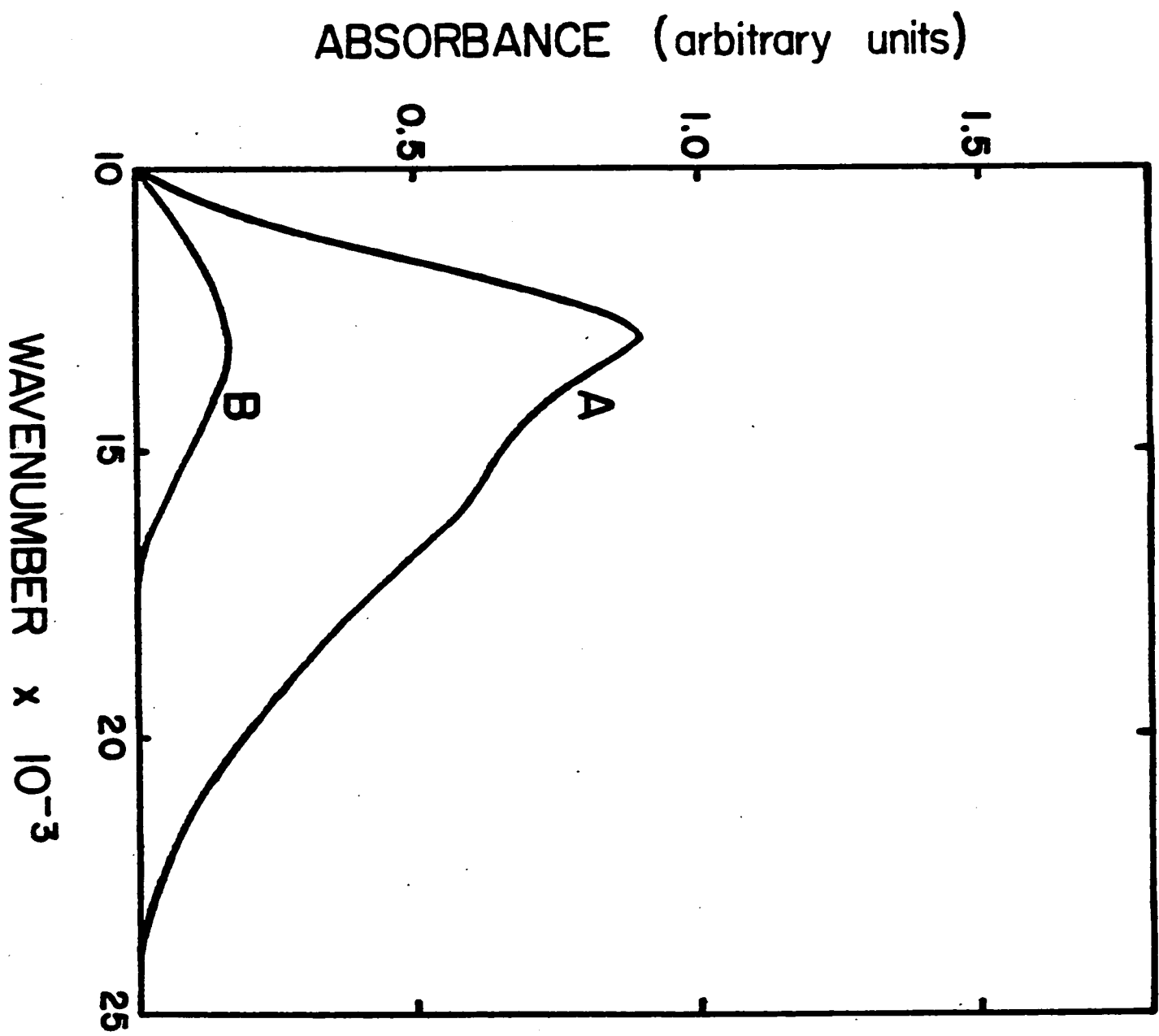
3. Polarization: Of the four possible transitions in " $\Gamma_{\frac{1}{2}} \times C'_{4V}$ ", two are of the $\Gamma_7 \rightarrow \Gamma_7$ type and two are of the $\Gamma_7 \rightarrow \Gamma_6$ type. In C'_{4V} , x and y transform as Γ_5 , while z transforms as Γ_1 . In the usual way it is found that $\Gamma_7 \rightarrow \Gamma_7 (\perp)$, $\Gamma_7 \rightarrow \Gamma_7 (\parallel)$, and $\Gamma_7 \rightarrow \Gamma_6 (\perp)$ are allowed electronically while only $\Gamma_7 \rightarrow \Gamma_6 (\parallel)$ is not. Thus, of the four d-d type transitions, the predictions for polarized absorption are:

$\Gamma_7 [\Gamma_8(T_{2g})] \longrightarrow$	\perp	\parallel
$\Gamma_6 [\Gamma_8(T_{2g})]$	a	f
$\Gamma_7 [\Gamma_7(T_{2g})]$	a	a
$\Gamma_7 [\Gamma_8(E_g)]$	a	a
$\Gamma_6 [\Gamma_8(E_g)]$	a	f

where the order of levels in Figure 8 has been assumed. Thus at room temperature the second visible band and one component of the first are forbidden for light polarized parallel to the z-axis. This prediction can be seen to agree with the polarized absorption results of Ballhausen and Gray¹⁷ (Figure 9) on a single crystal of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ which show both a $13,060 \text{ cm}^{-1}$ band and a $16,000 \text{ cm}^{-1}$ band for \perp polarization

FIGURE 9: Visible Absorption Spectra of a Single Crystal of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, Taken from C. J. Ballhausen and H. B. Gray [Inorg. Chem., 1, 111 (1962)]:

Curve A, Light Polarized \perp to the V-O Axis;
Curve B, Light Polarized \parallel to the V-O Axis.



while for \parallel polarization only a single less intense band remains in the $13,000\text{ cm}^{-1}$ region. This latter band, it is suspected, might even possibly show a small blue shift from the corresponding \perp band in the same region, though we cannot be sure from the published figure. If this is so it would seem to indicate a plurality of components in the first visible band. For C_{2v}' all transitions are of the $\Gamma_5 \rightarrow \Gamma_5$ type and all are allowed both \perp and \parallel . Again, available polarization data does not provide any choice between the energy scheme of Ballhausen and Gray and that suggested here.

D. Conclusions

Two possible interpretations of the spectra of the vanadyl ion have been discussed. The evidence indicates quite strongly that the interpretation of Ballhausen and Gray¹⁷ may be in error. This same evidence confirms and supports the "clustered transition" interpretation previously suggested.^{23,24} The most serious weakness of the present thesis is the absence of definitive proof that the observed structure in the $14,000\text{ cm}^{-1}$ region is not vibronic. Other defects are: (1) $5,680\text{ cm}^{-1}$ seems to be too small a value for electron-electron repulsion in the b_2 orbital; (2) the experimental resolution is somewhat inadequate for the demands placed on it; and (3) the $20,000$

cm^{-1} band of V (V) might correspond to the $33,000 \text{ cm}^{-1}$ band of V (IV).

III. ELECTRONIC-VIBRONIC CORRELATIONS

It has been demonstrated experimentally^{18,25,35,44-46} that the magnitude of the metal-oxygen stretching frequency in metal oxocations such as UO_2^{2+} and VO^{2+} is dependent upon the ligands attached to the oxometal entity. In all cases it was observed that decreasing $\bar{\nu}_{\text{MO}}$ is roughly parallel to increasing ligand strength, so that as a result it was possible to establish a ligand series similar to the "spectrochemical ligand series."

This frequency decrease is easily rationalized if one realizes that these metal-oxygen oxocation bands are multiple in nature and that this multiplicity is a result of $\text{L} \rightarrow \text{M}$ (i.e., ligand to metal) π bonding. The impetus for such delocalization is the high electron density of the small oxygen atom relative to that of the metal which has available empty d orbitals. The bond order, therefore, is a function of both the ability of the oxygen to donate electrons and the capacity of the metal to accept them--the greater the bond order, the higher the frequency of the vibration. Since, by its very nature, stronger (or further)

ligation (in the other five positions of the octahedral sphere) results in greater charge density on the metal, then it is to be expected that the affinity of the metal for π electrons from the oxide ion shall decrease so that the bond order and stretching frequency of the M-O multiple bond will be lowered. Thus, $\bar{\nu}_{MO}$ is a convenient measure of ligand strength when the oxocation entity is kept constant.*

In view of the fact that, for vanadyl complexes, we are now in possession of two parameters, $D_{II,I}$ and $\bar{\nu}_{VO}$, which are both evidently indicative of ligand strength, it is appropriate that at least two things be done:

1. We should compare the results (i.e., solvent rankings) they give.
2. We should attempt a correlation of the separate phenomena which they represent.

For these undertakings we shall employ, in addition to the author's, the data of Selbin, Holmes, and McGlynn^{14,18} and Selbin, Manning, and Cessac.²⁵

In Table X are tabulated the values for $D_{II,I}$ and $\bar{\nu}_{VO}$

*In addition to electronic effects, another factor which contributes to changes in $\bar{\nu}_{MO}$ is the mass change which accompanies a change of ligand. This factor is neglected in the comparisons and discussions of this section. A somewhat detailed consideration of its significance is included as an appendix to this dissertation.

TABLE X

COMPARISON OF $D_{II,I}$ AND $\bar{\nu}_{VO}$ FOR $VO(acac)_2$
WITH TWELVE LIGANDS

Ligand	$D_{II,I}$ (cm^{-1})	$\bar{\nu}_{VO}$ (cm^{-1})
pyridine	4,390	957
n-propylamine	4,310	959
dimethyl sulfoxide	4,180	969
p-dioxane	4,025	985
piperidine	4,020	958
dimethyl formamide	3,940	972
tetrahydrofuran	3,145	985
acetonitrile	2,600	1002
nitromethane	2,260	1007
chloroform	1,940	1004
carbon disulfide	1,580	1007
benzene	1,580	1008

for the twelve ligands common to the visible and infrared investigations, and these are also plotted in Figure 10. As can be seen, quite good agreement is obtained so that the validity of the use of the less theoretical parameter $D_{II,I}$ is given strong support by the better understood infrared phenomenon.

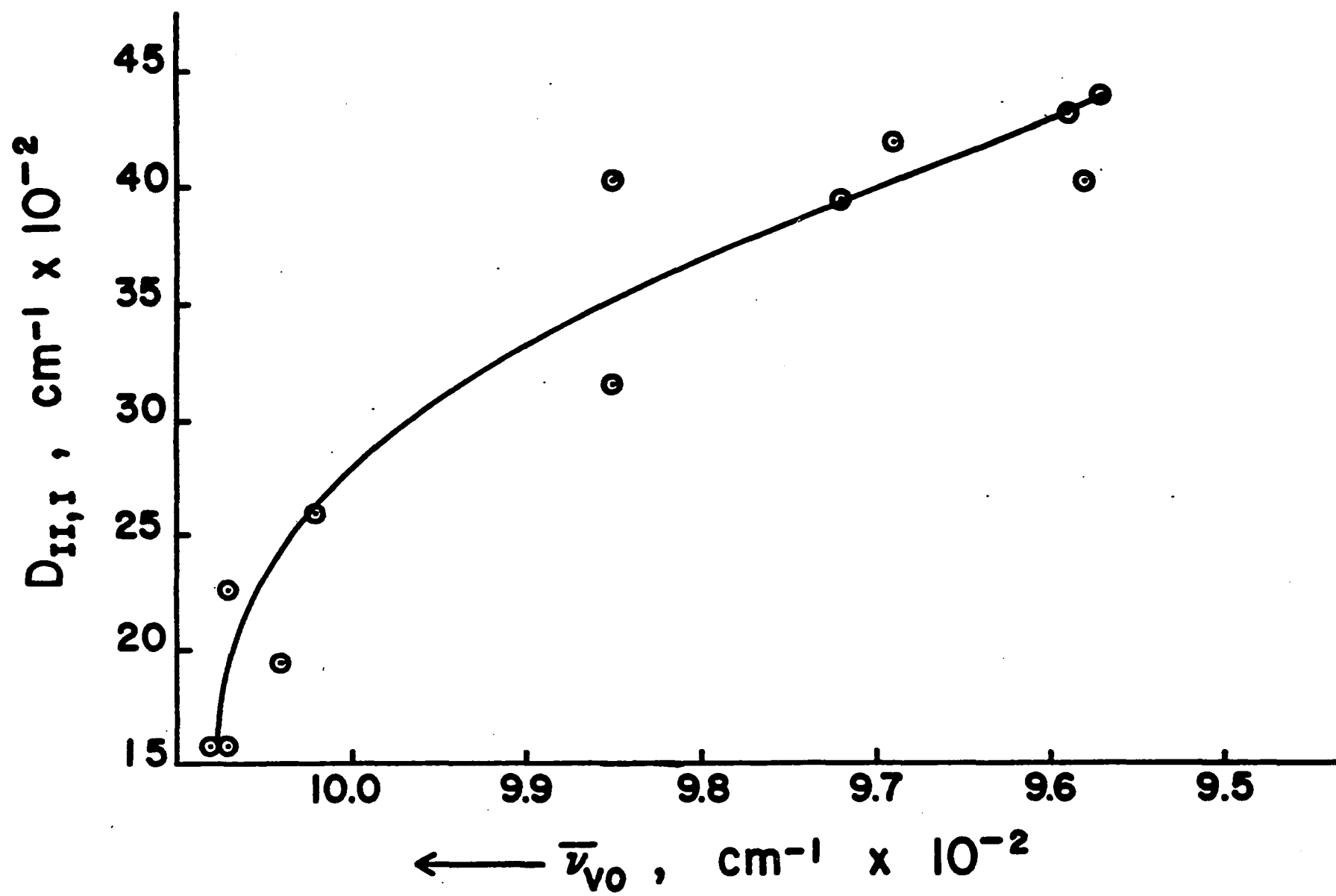
For our second above-mentioned purpose, we shall employ the data for the following eleven vanadyl compounds which were investigated by Selbin, Holmes, and McGlynn:^{14,18} $VO(acac)_2$, $VO(o\text{-phen})_2(ClO_4)_2$, $VO(o\text{-phen})_2Cl_2$, $VO(o\text{-phen})_2Br_2 \cdot H_2O$, $VO(o\text{-phen})_2SO_4$, $VO(dipy)_2(ClO_4)_2$, $VO(dipy)_2Cl_2$, $VO(dipy)_2Br_2 \cdot H_2O$, $VO(DMSO)_5Br_2$, $(Me_4N)_3VO(NCS)_5$, and $(Et_4N)_3VO(NCS)_5$. Others were excluded from these considerations because of ambiguity in either the vibrational, the electronic, or the structural data which was available.

It was initially hoped that some general correlation of all vibrational and electronic band positions for all these compounds might be possible. When this was attempted, however, it became evident that such was not feasible.

Reasons for this are possibly:

1. Variation of symmetry, some being C_{4v} while others are C_{2v} or lower.
2. Simultaneous variation, throughout the series of

FIGURE 10: Plot of $\bar{\nu}_{VO}$ Against $D_{II,I}$ for $VO(acac)_2$ with
Twelve Ligands.



compounds, of both axial and equatorial ligands.

3. The presence of ligand absorptions in most compounds which make quite ambiguous the identity of electronic bands in the ultraviolet region above $\sim 30,000 \text{ cm}^{-1}$.

4. An inconsistency in the number of low energy visible bands caused possibly by the clustering of d-d transitions, as indicated previously by low temperature measurements, and/or by the failure of some bands to appear because of a lack of sufficient intensity often characteristic of crystal field transitions.

It has been found, however, that some sub-correlations are indeed possible whenever the number of variables are minimized so that small groups of similar compounds are individually considered. One band of particular interest in these considerations is the one corresponding to the $\sim 26,000 \text{ cm}^{-1}$ band in $\text{VO}(\text{acac})_2$. Not only does this band lend itself readily to relatively unambiguous comparisons (recall the reasons above for non-feasibility of general correlation) but also it is the one whose assignment (d-d or charge transfer) is made difficult by the variance of the alternative interpretations of the electronic structure of the vanadyl ion.^{17,23,24}

The criteria for choosing this band in each case were

that it lie in the general region 25,000 to 32,000 cm^{-1} , that it either have an intermediate intensity or be the last low or first high intensity band in that region. The bands (cm^{-1}) chosen for the respective compounds are: $\text{VO}(\text{acac})_2$ --25,800; $\text{VO}(\text{o-phen})_2(\text{ClO}_4)_2$ --28,900; $\text{VO}(\text{o-phen})_2\text{Cl}_2$ --25,300; $\text{VO}(\text{o-phen})_2\text{Br}_2 \cdot \text{H}_2\text{O}$ --25,300; $\text{VO}(\text{o-phen})_2\text{SO}_4$ --23,600; $\text{VO}(\text{dipy})_2(\text{ClO}_4)_2$ --31,600; $\text{VO}(\text{dipy})_2\text{Cl}_2$ --26,800; $\text{VO}(\text{dipy})_2\text{Br}_2 \cdot \text{H}_2\text{O}$ --27,000; $\text{VO}(\text{DMSO})_5\text{Br}_2$ --25,700; $(\text{Me}_4\text{N})_3\text{VO}(\text{NCS})_5$ --23,900; and $(\text{Et}_4\text{N})_3\text{VO}(\text{NCS})_5$ --23,700.

Consider the group of four compounds in which the equatorial ligand is o-phenanthroline. All of these are identical except for the axial ligand which in each case is the anion, except for $\text{VO}(\text{o-phen})_2(\text{ClO}_4)_2$ in which the axial ligand is most probably a solvent molecule (i.e., acetonitrile). Using decreasing $\bar{\nu}_{\text{VO}}$ as a measure of relative sixth-position ligation, it is seen that stronger axial ligation is parallel to decreasing energy of the "first charge transfer band" as follows:

<u>Compound</u>	<u>$\bar{\nu}_{\text{VO}}$</u>	<u>$\bar{\nu}_{\text{CT}}$</u>
$\text{VO}(\text{o-phen})_2(\text{ClO}_4)_2$	987	28,900
$\text{VO}(\text{o-phen})_2\text{Cl}_2$	982	25,300
$\text{VO}(\text{o-phen})_2\text{Br}_2 \cdot \text{H}_2\text{O}$	981	25,300
$\text{VO}(\text{o-phen})_2\text{SO}_4$	978	23,600

A plot of this data will give very nearly a straight line.

This same conclusion can be made by considering similarly the group of α, α' -dipyridyl compounds. Thus:

<u>Compound</u>	<u>$\bar{\nu}_{VO}$</u>	<u>$\bar{\nu}_{CT}$</u>
$VO(dipy)_2(ClO_4)_2$	979	31,600
$VO(dipy)_2Cl_2$	965	26,800
$VO(dipy)_2Br_2 \cdot H_2O$	958	27,000

The correlation here is not so satisfactory as for the o-phenanthroline species, but it is still not contradictory of the general conclusion that $\bar{\nu}_{CT} \propto \bar{\nu}_{VO}$.

If on the other hand we vary the equatorial ligand, keeping the axial group constant, we see that a different result is obtained. Consider the following groups of compounds:

<u>Compound</u>	<u>$\bar{\nu}_{VO}$</u>	<u>$\bar{\nu}_{CT}$</u>
$VO(o\text{-phen})_2Cl_2$	982	25,300
$VO(dipy)_2Cl_2$	965	26,800
$VO(o\text{-phen})_2Br_2 \cdot H_2O$	981	25,300
$VO(dipy)_2Br_2 \cdot H_2O$	958	27,000
$VO(acac)_2^*$	996	25,800
$VO(o\text{-phen})_2(ClO_4)_2^*$	987	28,900
$VO(dipy)_2(ClO_4)_2^*$	979	31,600

*These three compounds are compared because in each case the sixth-position ligand is assumed to be a solvent molecule (acetonitrile). This assumption is supported by the linearity obtained.

--where the latter set is particularly impressive because of the perfect linearity which is obtained when these are plotted. Thus, it appears that increasing equatorial ligand strength (i.e., decreasing $\bar{\nu}_{VO}$ results in an increase in $\bar{\nu}_{CT}$; and since this is the opposite result obtained by varying the axial ligand strength, it is appropriate that we consider any possible reasons or implications involved. In particular, it is desirable to consider whether the above results favor the 23,000 to 32,000 cm^{-1} transition as being $b_2 \longrightarrow Ia_1^*$ (d-d) or $e_{\pi}^b \longrightarrow b_2$ (C.T.).

Efforts along these lines have proved to be quite difficult. The reasons for this are deeply imbedded in the uncertainties connected with the movements of the various levels--particularly Ia_1^* . These uncertainties are the result of the relative importance one is "free" to put on competing factors, especially when indirect effects are involved. As a result, it is the opinion of the author that it would be quite dangerous for one to draw "unambiguous" conclusions (concerning the identity of the band in question) from the above observations. Consequently, the discussions below are offered only in the nature of a critique of the various possibilities which are seen to exist. Since the question involves only e_{π}^b , b_2 , and Ia_1^* , only these levels need be discussed.

e_{π}^b : This is the π bonding level involving the $3d_{xz}$ and $3d_{yz}$ orbitals of the vanadium and the $2p_x$ and $2p_y$ orbitals of the vanadyl oxygen. There is quite general agreement that both axial and equatorial ligation should directly result in a decrease in this $L \rightarrow M$ bonding and therefore raise the e_{π}^b level. There are also arguments, however, that both types of ligation, if strong enough, are capable of involving this level in π bonding so that a lowering factor may also be present. The former effect, nevertheless, should predominate.

b_2 : Ballhausen and Gray¹⁷ assume this level to be a pure d_{xy} non-bonding orbital of the vanadium. They would therefore regard this level to be inert to the effects of both axial and equatorial ligation. Selbin, Holmes, and McGlynn,¹⁸ on the other hand, admit a small overlap with the b_2 ligand group orbital of $\pi_{||}$ type (i.e., parallel to the equatorial plane) and therefore consider it slightly antibonding. This level should therefore be directly but slightly raised by increased equatorial ligation, while it should remain unchanged by axial ligation. If, however, ligation in the sixth position results in lengthening of equatorial bonds, then a slight indirect destabilization would result--if this were not off-set by accompanying angular changes due to a shift in the "center of gravity."

Ia_1^* : This level is regarded by Ballhausen and Gray¹⁷ as a hybrid of $(3d_z^2 + 4s)$, which is involved in σ bonding with the vanadyl oxygen. The same arguments which lead to a decrease in vanadyl π bonding should also predict a decrease in the energy of this level for both types of ligation. On the other hand, since sixth-position ligation is axially directed (i.e., in direction of d_z^2) there may well be in this case a corresponding destabilization so that this level may be somewhat insensitive or actually increase. (There is even some bases for regarding the σ and π bonding along the V-O axis as complimentary so that decreased π bonding could, at one and the same time, result in an increase in e_π^b and an increase in Ia_1^* .)

From the above, the difficult problem of rationalizing our experimental observations should be apparent. Although the data seems to clearly indicate that " $\bar{\nu}_{CT}$ " is decreased by axial ligation and increased by equatorial ligation, its implications remain obscure.

There is, however, one general correlation between the infrared and visible phenomena which is worth noting here. The variation of $\bar{\nu}_{VO}$ is a direct consequence of changes in the degree of π bonding in the vanadyl V-O bond. This π bonding involves the d_{xz} and d_{yz} orbitals of the metal and

it is these same orbitals which pertain to the terminal level of $\bar{\nu}_I^\#$, which we have already seen to be the most sensitive visible band and therefore the main cause of the sensitivity of $D_{II,I}$. Thus, $\bar{\nu}_{VO}$ and $D_{II,I}$ are not without a quite direct correlation. It is indeed fitting that both $\bar{\nu}_{VO}$ and $\bar{\nu}_I$ should decrease with ligand strength.

#In the scheme of Ballhausen and Gray¹⁷ the terminal level of $\bar{\nu}_I$ is identified with e_π^* , while in the "clustered transition" interpretation^{23,24} the terminal level of this transition is composed of both $b_1^*(d_{x^2-y^2})$ and e_π^* . Thus, the choice of scheme is irrelevant in this discussion.

APPENDIX

A PRELIMINARY INVESTIGATION OF MASS EFFECTS ON THE VIBRATIONAL FREQUENCIES OF OXOCATION METAL-OXYGEN BONDS

It has been observed^{18,25,35,44-46} that strong and/or additional ligation of transition metal oxocations shifts their M-O stretching frequencies toward lower values. (Some details of this phenomenon have already been discussed in Section III.) This phenomenon is often, if not usually, implied to be solely an electronic effect of some sort. Since, however, the mass of any vibrator always plays a significant role in determining its vibrational frequency, it seems desirable to investigate what mass effects might be involved in the above-mentioned frequency shifts.

Whereas before, the entire observed frequency shift has been used to estimate relative ligand strengths, it shall be the purpose of this study to learn whether consideration of mass effects might make any appreciable differences in such predictions. Also, it is hoped that whereas previously certain ligand strengths had been predicted to be equivalent, this refinement might differentiate between them. For these

purposes, a rather simplified approach shall be used in lieu of a rigorous treatment, the complexity of which, it is felt, is not warranted.

Assuming that the oscillations involved in the oxocation metal-oxygen stretch are simple harmonic ones, the vibrational energies may be given by

$$\epsilon_v = (v + \frac{1}{2}) h\nu. \quad (1)$$

The frequency ν in this expression is given by

$$\nu = c\bar{\nu} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \quad (2)$$

where k is the force constant and μ is the reduced mass.

If now we confine ourselves to the vanadyl stretching frequency and consider the vanadyl complex to be diatomic about the V-O bond, then μ in Equation 2 can be given by $m_O m_V / A(m_O + m_V)$, where m_O refers to the atomic weight of oxygen, m_V to the "atomic" weight of the rest of the (covalent) molecule, and A to Avogadro's number. In other words, we are regarding one of the vibrators as oxygen and the other as vanadium with all its other covalent "attachments" or ligands. This is, of course, a considerable approximation since it involves assuming that the vanadium end of the oscillator is a rigid mass.

Even with the above simplifications, there still remains the question of what to do with the force constant (in Equation 2) which we know must somehow vary from compound to compound in the series being considered. To handle this problem, we will take as a standard compound vanadyl acetylacetonate (with its experimental VO stretch of 996 cm^{-1}); calculate its force constant, and assume this value to hold throughout the whole series of vanadyl species. Thus, since from (2)

$$\bar{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \quad (3)$$

then

$$k = (2\pi c \bar{\nu})^2 \mu \quad (4)$$

The value of μ for $\text{VO}(\text{acac})_2$ is 2.5×10^{-23} gm. Therefore, its force constant is calculated from (4) to be 8.80×10^5 gm/ sec^2 .

With this assumed-constant value of k we can now calculate a theoretical value of $\bar{\nu}$ for the vanadyl ion, VO^{2+} , using (3), and take this as a zero point from which we can shift the frequency by the addition of masses to the naked vanadyl ion. These theoretical shifts, based on mass changes alone, when compared to the respective experimental values, should give us some idea of the relative magnitudes of other

effects--which for the sake of simplicity, and perhaps quite accurately, might be considered totally electronic ones.

These electronic values should then be a more accurate indicator of what we usually call "ligand strength" than we previously had when we simply considered the entire experimental shifts.

Proceeding thus, we first calculate $\bar{\nu}$ for VO^{2+} from

$$\bar{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

Inserting $k = 8.80 \times 10^5 \text{ gm/sec}^2$ and $\mu = 2.02 \times 10^{-25} \text{ gm}$ into this expression and solving we obtain $\bar{\nu} = 1110 \text{ cm}^{-1}$.

This value for $\bar{\nu}$ is the zero point from which all our vanadyl compounds will shift as we increase the mass of the vanadium end of the V-O bond. Using Equation 3, as we did for VO^{2+} , one can calculate the value of $\bar{\nu}$ expected for heavier vanadyl compounds, changing in each case only the reduced mass. The results for this procedure are given in Table XI, while the " $\bar{\nu}$ -shift due to mass increase" (which is the difference between $\bar{\nu}_{\text{cal}}$ for VO^{2+} and $\bar{\nu}_{\text{cal}}$ for the respective compounds) and "other" (i.e., ~ electronic factor) are given in Table XII.

To begin, we might observe that the relative magnitudes

TABLE XI*

TABULATION OF DATA USED FOR THE CONSTRUCTION OF TABLE XII

Species	$\bar{\nu}$, exper	$m_v \times A$	μ	$\bar{\nu}$, cal
VO^{2+}	--	50.95	2.02×10^{-23}	1110
$VO(acac)_2$	996	249.17	2.50×10^{-23}	996
$VO(oxine)_2$	980	339.25	2.54×10^{-23}	988
$VO(TPP)$	1001	665.73	2.60×10^{-23}	977
$VO(phthal)$	1004	563.48	2.59×10^{-23}	980
$VO(p-Cl-TPP)$	1002	803.56	2.60×10^{-23}	977
$VO(p-OCH_3-TPP)$	1015	785.77	2.60×10^{-23}	977
$[VO(o-phen)_2] (ClO_4)_2$	987	411	2.56×10^{-23}	985
$[VO(dipy)_2] (ClO_4)_2$	979	363	2.55×10^{-23}	987

*Abbreviations used:

m_v	Mass of vanadium end of molecule
acac	Acetylacetonate ion
TPP	Tetraphenylporphine ion
phthal	Phthalocyanine ion
o-phen	o-Phenanthroline
dipy	α, α' -dipyridyl

TABLE XII

MASS AND ELECTRONIC CONTRIBUTIONS TO THE VANADYL
STRETCHING FREQUENCIES OF EIGHT
VANADYL COMPOUNDS

Species	$\bar{\nu}$ -shift Due to Mass Increase	Other (Electronic)
1. $[\text{VO}(\text{dipy})_2] (\text{ClO}_4)_2$	123 cm^{-1}	8
2. $\text{VO}(\text{oxine})_2$	122	8
3. $\text{VO}(\text{acac})_2$	114	0
4. $[\text{VO}(\text{o-phen})_2] (\text{ClO}_4)_2$	125	-2
5. $\text{VO}(\text{phthal})$	130	-24
6. $\text{VO}(\text{TPP})$	133	-24
7. $\text{VO}(\text{p-Cl-TPP})$	133	-25
8. $\text{VO}(\text{p-OCH}_3\text{-TPP})$	133	-38

of these values do show that fairly large differences in m_V (Table XI) are required to significantly affect them. For example, if we compare VO(oxine)_2 , $m_V = 339.25/A$, with VO(p-Cl-TPP) , $m_V = 803.56/A$, we can realize only an 11 cm^{-1} difference in the mass effect. Also, comparing VO(p-Cl-TPP) with $\text{VO(p-OCH}_3\text{-TPP)}$ we get (by slide rule) the same shift of 133 cm^{-1} , even though their values of m_V differ by eighteen atomic weight units. This we can understand as due to small variations in reduced mass in cases where one of the atoms of a diatomic molecule is considerably heavier than the other. Thus, this method can be visualized as probably being more valuable in cases where, instead of oxygen, we would have a more massive atom or group of atoms, more comparable in size to the other end of the molecule which is being altered.

Finally, and more importantly, are listed in the column headed "other" a group of values which we hope we may now look upon as a relative scale of electronic effects or ligand strengths. (The plus and minus signs mean stronger and weaker than the acetylacetonate ion, respectively.) Mathematically they are merely the difference between $\bar{\nu}_{\text{cal.}}$ and $\bar{\nu}_{\text{exper.}}$ in Table XI.

These results are not surprising. In general, they

tell us little more of the ligand hierarchy than we would have predicted from the conventional approach in which we disregard mass effects. However, certain finepoints of the results seem worthy of mention. Consider compounds 3 and 4 of Table XII. If we ignore mass effects, o-phenanthroline would be clearly considered a stronger ligand than the acetylacetonate ion by the significant margin of 9 cm^{-1} . If we subtract mass contributions, however, these two ligands are indicated to be of approximately the same strength--with, in fact, the order being reversed and showing the acetylacetonate ion to be the "better" ligand by 2 cm^{-1} , if one would consider such a difference to be significant. Secondly, the consideration of mass effects makes TPP, phthal., and p-Cl-TPP more the same strengths as we would expect by their close similarities of structure. On the other hand, the conventional view would usually tend to consider the 3 cm^{-1} difference between phthal. and TPP as possibly significant. However, it is not so satisfying that mass considerations do nothing towards equalizing $\text{VO}(\text{p-Cl-TPP})$ and $\text{VO}(\text{p-OCH}_3\text{-TPP})$ which differ only by the presence of quite remote substituents.

These latter-mentioned finepoints may or may not be significant. We will not attempt to decide here, since it

is felt that a more rigorous approach and a larger number of compounds would be needed. However, lest we begin to conclude that this whole investigation has little or no value, there are two points worth mentioning. Whereas before, a certain number was attributed to ligand strength, we now attribute a much smaller number to it. Secondly, it seems that absolute mass effects are appreciably larger than absolute electronic effects.

In all cases thus far we have varied only the equatorial groups around the vanadium. It is also desirable to consider the variation of groups in the axial (sixth) position. For this purpose, $\text{VO}(\text{acac})_2$ was used as the basic compound because of the availability of data for it. Proceeding as before, we obtain the results given in Tables XIII and XIV. Note that now in Table XIV, the " $\bar{\nu}$ -shift due to mass increase" is from 996 cm^{-1} , the vibrational stretching frequency of $\text{VO}(\text{acac})_2$. These results show that, for the ligands considered, the differences in mass effects are nil (within slide rule accuracy) and therefore do nothing to alter the relative scale of ligand strengths obtained conventionally. Consideration of the comparable sizes of the ligands, the bulkiness of $\text{V}(\text{acac})_2^{2+}$, and the consequently small variance in the reduced mass makes this understandable.

TABLE XIII*

TABULATION OF DATA USED FOR THE CONSTRUCTION OF TABLE XIV

Species	$\bar{\nu}$, exp	$m_L \times A$	$m_{VL} \times A$	μ	$\bar{\nu}$, cal
pyridine	957	79.10	328.27	2.53×10^{-23}	990
isobutylamine	958	73.14	322.31	2.53×10^{-23}	990
n-propylamine	959	59.11	308.28	2.53×10^{-23}	990
piperidine	958	85.15	334.22	2.53×10^{-23}	990
ethylenediamine	956	60.10	309.27	2.53×10^{-23}	990
dimethyl sulfoxide	969	78.08	327.25	2.53×10^{-23}	990
tetrahydrofuran	985	72.04	321.21	2.53×10^{-23}	990
p-dioxane	985	88.14	337.21	2.54×10^{-23}	990
aniline	976	93.06	342.23	2.54×10^{-23}	990
phenol	993	94.06	343.23	2.54×10^{-23}	990

*Abbreviations used:

 m_L Mass of sixth-position group m_{VL} Mass of entire vanadium end of molecule after sixth position is occupied.

TABLE XIV

MASS AND ELECTRONIC CONTRIBUTIONS TO THE VANADYL
STRETCHING FREQUENCY OF $\text{VO}(\text{acac})_2$
COORDINATED TO TEN LIGANDS

$\text{VO}(\text{acac})_2$ Species	$\bar{\nu}$ -shift Due to Mass Increase -from 996 for $\text{VO}(\text{acac})_2$	Other
pyridine	6 cm^{-1}	33
isobutylamine	6	32
n-propylamine	6	31
piperidine	6	32
ethylenediamine	6	34
dimethyl sulfoxide	6	21
tetrahydrofuran	6	5
p-dioxane	6	5
aniline	6	14
phenol	6	-3

SUGGESTIONS FOR FURTHER WORK

The reader should certainly be of the opinion--as is the author--that there still remains considerable work within the scope of these investigations. The following suggestions are those offered by the author as being potentially valuable efforts toward the verification and extension of these studies:

1. In the area of solvent effects and relative ligand strengths, additional complexes--of both the vanadyl ion and of the other oxocations--should be investigated to compare their electronic spectral trends with those of $\text{VO}(\text{acac})_2$. It is quite possible that new and more sensitive parameters than $D_{\text{II},\text{I}}$ might be found and that these might yield a better understanding of the electronic phenomena they represent.

2. Along these same lines, a wider range of solvent ligands should be investigated. It would be particularly interesting to test the role of polarity by studying a number of non-Lewis-base, saturated molecules.

3. Other mixed solvent systems (than the ethanol-water system studied above) should be studied. It is

particularly desirable that "extreme" components, such as methanol and carbon tetrachloride, be investigated so that the possibility of simultaneous existence of different species (e.g., $\text{VO}(\text{acac})_2\text{S}$ and $\text{VO}(\text{acac})_2\text{S}'$) be checked.

4. The visible spectra of vanadyl complexes without an open sixth position should be run in several solvents to determine the role, if any, of secondary interactions. Stable species³² such as $\text{VO}(\text{acac})_2\cdot\text{pyridine}$ and $\text{VO}(\text{acac})_2\cdot\text{piperidine}$ are suggested for this purpose.

5. There is a definite need that more work be done in the ultraviolet region:

- a. To determine the effects of solvents therein;
- b. To correlate charge transfer and crystal field band positions; and
- c. To investigate the indications that the $\sim 33,000\text{ cm}^{-1}$ and $\sim 37,000\text{ cm}^{-1}$ bands in ethanol belong to V (IV) and V (V) species, respectively.

6. Low temperature spectra of some d^0 and of other d^1 systems should be obtained for the support they might give to the ideas derived from vanadyl studies. Some suggested species are $\text{TiO}(\text{acac})_2--d^0--$ and $\text{MoOCl}_5^{2-}--d^1$.

7. A detailed study of the complex vanadyl bis-(hexafluoroacetylacetonate) should be undertaken. This compound

gives great promise of being a suitable subject for visible-U.V. vapor spectra. In addition, it is desirable that the effects of solvents on its spectra be compared with results on $\text{VO}(\text{acac})_2$, and that spectra of its oxidation product be obtained since its third room temperature band is in a most suitable position for more unambiguous conclusions than were possible in the case of $\text{VO}(\text{acac})_2$.

8. For the sake of determining the origin of the low temperature fine structure in the first visible room temperature band of vanadyl complexes, there are at least two types of experiments, the results of which may be conclusive: (Recall that the question is whether the three observed components are vibronic or electronic in origin.)

a. Either a thin single crystal of $\text{VO}(\text{acac})_2$ or a dilute mixed crystal of it (e.g., with $\text{TiO}(\text{acac})_2$ which does not absorb in the region of interest) could be run (in absorption) at low temperature using various orientations of polarized light. A comparison of such results with theoretical predictions could well be of a conclusive nature; and

b. The possibility of some vanadyl species emitting should be investigated. This suggestion is prompted by the observation of negative absorption in the near infrared region of the spectra of some vanadyl complexes and by the

success of McGlynn and Smith⁴⁴ in using emission for the elucidation of the electronic structure of the uranyl ion, UO_2^{2+} .

9. A rigorous mass effect calculation on at least a couple of vanadyl complexes would be desirable to test the reliability of the simplified approach used by the author. (See Appendix.) In addition to possibly making "operational" a convenient and practical tool for refining metal-oxygen stretching frequencies, this would also allow the evaluation of the types of approximations used therein.

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VITA

Thomas Russell Ortolano was born April 6, 1938, in New Orleans, Louisiana. He graduated from Jesuit High School, New Orleans, in June of 1956, and began six months of military service that same month. In February, 1957, he entered Loyola University of the South from which he received his B.S. in chemistry in June, 1960. In September, 1960, he entered the Graduate School of Louisiana State University where he is presently a candidate for the degree of Doctor of Philosophy.

He is married to the former June Ann Stauffer and has two children, Eloise Elizabeth and Thomas Russell, II.

EXAMINATION AND THESIS REPORT

Candidate: Thomas Russell Ortolano

Major Field: Chemistry

Title of Thesis: Spectral Studies On Vanadyl Complexes

Approved:

S. P. McGlynn
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

J. Selvin (per SPM)
Robert V. Nauman
Paul E. Smith
Richard C. Keen

Date of Examination:

July 27, 1964