



Computational Chemistry Workshops
West Ridge Research Building-UAF Campus
9:00am-4:00pm, Room 009

Electronic Structure - July 19-21, 2016
Molecular Dynamics - July 26-28, 2016

UV-Visible Spectra of Aquavanadium Complexes

Ligand Field Theory

Ligand Field Theory (Reference 5) has been a central theme of inorganic chemistry for many years. Interpretation of $d \rightarrow d$ transitions in transition metal complexes is discussed in advanced inorganic chemistry textbooks, with the emphasis frequently placed on extraction of values for the ligand field splitting, Δ_0 and the Racah B parameter, the electron repulsion energy between electronic states, from experimental spectra (References 1 and 2). The colors of transition metal complexes result from absorption of a small portion of the visible spectrum with transmission of the unabsorbed frequencies.

For example, the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex has a d^1 electron configuration,

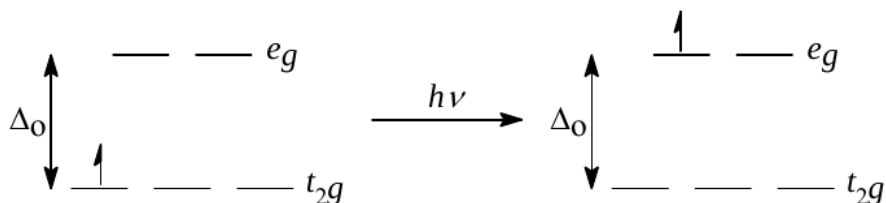


Figure 1: Splitting of d Orbitals for d^1 in O_h Symmetry.

and appears purple (i.e. red + blue), because it absorbs green light at $\sim 500 \text{ nm} = \sim 20,000 \text{ cm}^{-1}$. In the Ligand Field Theory (LFT) model, absorption causes electrons from lower lying d orbitals to be promoted to higher levels.

For the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex (d^1), the absorption causes the configuration to change from $t_{2g}^1 e_g^0$ to $t_{2g}^0 e_g^1$.

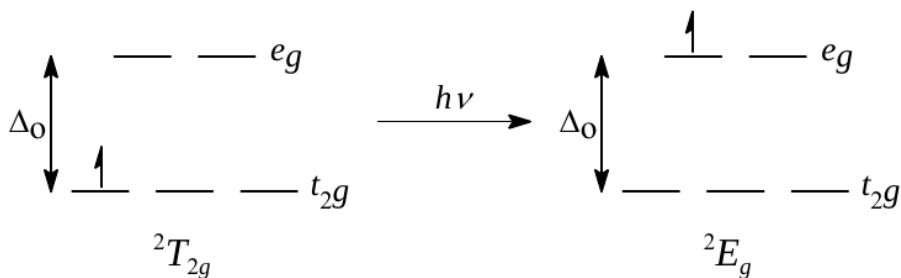


Figure 2: Term Splitting of d Orbitals for d^1 in O_h Symmetry.

Vanadium Oxidation States

Vanadium displays variable oxidation states of varying colours including the **blue** oxovanadium(IV) ion, usually written more simply as VO^{2+} but will have water molecules attached to it as well - $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, the **green** hexaaquavanadium(III) ion - $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, and the **purple-violet** hexaaquavanadium(II) ion - $[\text{V}(\text{H}_2\text{O})_6]^{2+}$.

Excited-State Calculations and Electron Density Shifts

This exercise explores calculations of the UV-Visible spectra of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ (d^3), $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (d^2), and $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (d^1) complexes shown in **Figure 3** and are also compared to experimental results (Reference 4).

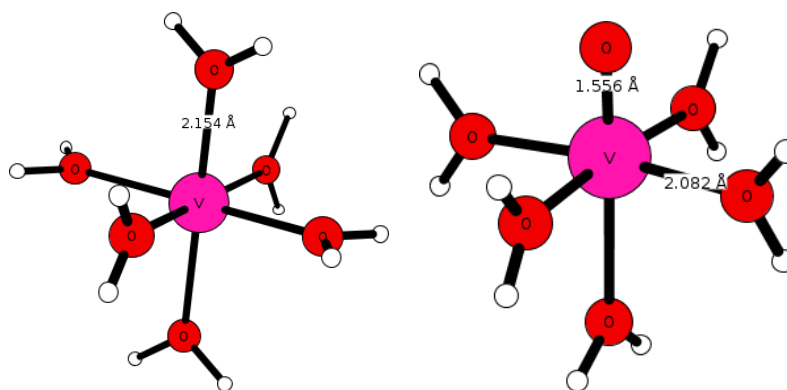


Figure 3: The $[\text{V}(\text{H}_2\text{O})_6]^{2+/3+}$ and $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ Complexes

Along with these calculations, ways in which electron density differences can be used to interpret the results of calculations will also be explored.

Geometry Optimization

Calculations are carried out to optimize the geometries of these complexes and to calculate the energies and intensities of the low-lying electronic transitions. Electron density difference plots are used to assign the nature of the transitions. Features such as Jahn-Teller distortions and charge-transfer bands, as well as $d \rightarrow d$ transitions are apparent from the calculations.

In preparation for the calculations, a starting geometry must be constructed for each of the complexes. It is important to have reasonable bond distances in the initial structure or convergence problems can occur in the SCF procedure. The geometry of each complex is then optimized.

Calculations of Excited States

Following the calculation of optimized structures, time-dependent perturbation theory (TDDFT) is used to calculate the energies and intensities of the first 20 excited states of each complex at the optimized geometry of the ground state.

In addition, charges on each atom are computed for the ground state and each excited state.

Calculations of Electron Density

Finally, cube files of the electron density are calculated for the ground state and excited states. A cube file of the electron density difference between each excited state and the ground state is then computed. Visualization of the electron density differences is carried out with GaussView.

Results

$[\text{V}(\text{H}_2\text{O})_6]^{3+}$ - d^2 Configuration

Jahn-Teller Distortions

Because of the presence of two electrons in the t_{2g} orbitals of this pseudo-octahedral complex, the calculated VO_6 local geometry is expected to show a Jahn-Teller distortion. All the calculated V-O bond distances may not be equal. As expected, the bond distances in the V(III) system are somewhat shorter than for the corresponding V(II) complex. Thus, the calculated charge on the metal is slightly more positive than for $[\text{V}(\text{H}_2\text{O})_6]^{2+}$.

Although constraints can be applied, such that the V-O bond distances are all equal, the Jahn-Teller effect is still reflected in the calculated electronic spectrum.

Excited States

The Tanabe-Sugano splitting diagram for the d^2 configuration, shown in [Figure 4](#), indicates that a d^2 octahedral complex should exhibit three $d \rightarrow d$ excitations: ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, and ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}$.

The visible/ultraviolet spectrum for $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ is shown in [Figure 5](#)

The ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}$ transition, which simultaneously promotes two electrons, is unlikely, and its band is often weak or unobserved. ν_1 (${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}$) at $17,200\text{ cm}^{-1}$ and ν_2 (${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$) at $25,000\text{ cm}^{-1}$ are shown, but the ν_3 (${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}$) at $38,000\text{ cm}^{-1}$ falls in the UV, and is not shown. Calculated lower-energy transitions most likely occur under the experimental band envelope at about $17,000\text{ cm}^{-1}$, while an allowed ligand molecular orbital (localized on O atoms of H_2O) \rightarrow Vanadium charge transfer (CT) transition is calculated at approximately $35,000\text{ cm}^{-1}$.

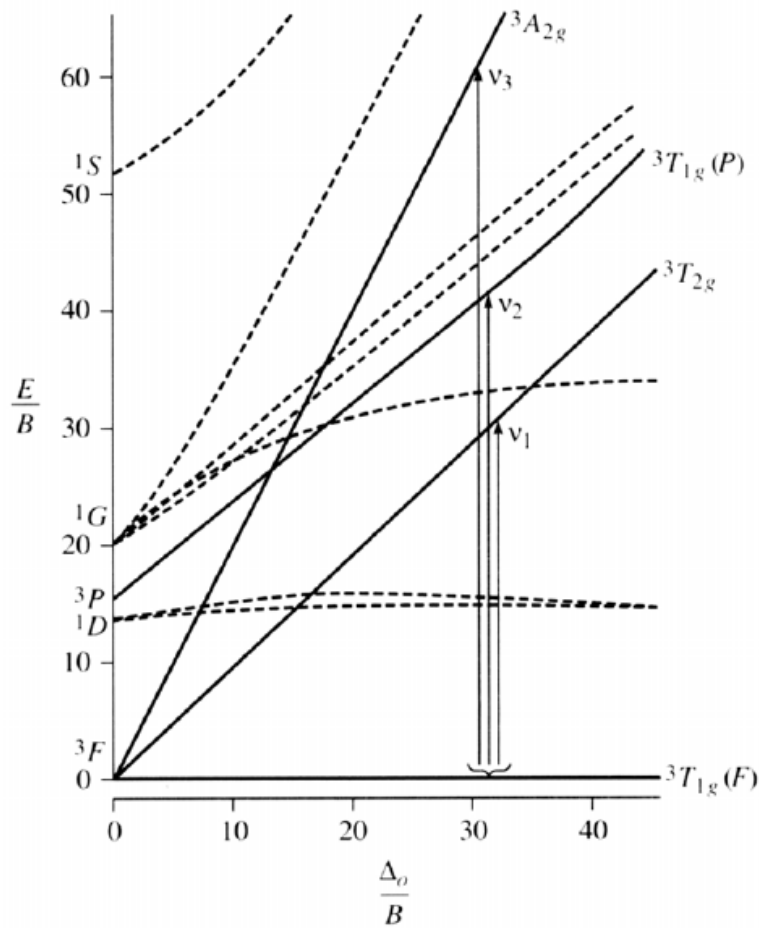


Figure 4: Tanabe-Sugano Diagram for Spin-Allowed Electronic Transitions of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$.

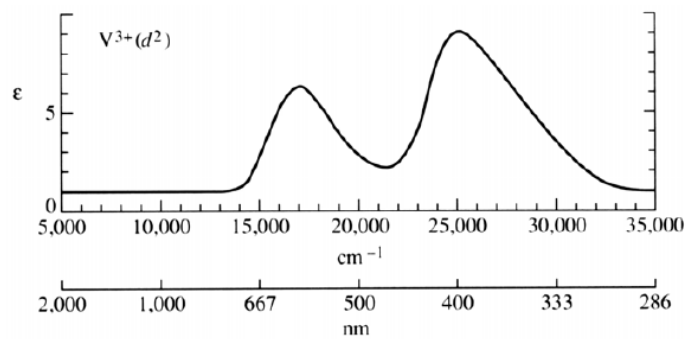


Figure 5: The Visible/Ultraviolet Spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$.

In addition to the three possible spin-allowed transitions, there are seven singlet states that suggest there could be as many as seven multiplicity (spin) forbidden transitions. Transitions from the $^3T_{1g}$ ground state to any of the singlet states would have extremely low ε values and are seldom observed in routine work. Some singlet states (e.g., $^1A_{1g}$, 1E_g) are so high in energy that transitions to them would fall in the UV, where they would likely be obscured by the intense CT band.

$[V(H_2O)_6]^{2+}$ - d^3 Configuration

Although the hydrogen atoms lower the symmetry somewhat, the local symmetry of the VO_6 framework is approximately O_h . Thus, the metal d orbitals are split energetically into a lower energy set of approximate t_{2g} symmetry and higher energy set of approximately e_g symmetry. The three d electrons on vanadium fill the t_{2g} orbitals, and no Jahn-Teller distortion occurs. Although the formal oxidation state of the vanadium is V(II), the charge on the vanadium is smaller as a result of electron donation from the ligands to the metal, and is common for transition metal complexes.

Excited States

Important bands of the calculated electronic spectrum of $[V(H_2O)_6]^{2+}$ should be compared to the experimental spectrum. Based on a Tanabe-Sugano Diagram (Reference 7) shown in [Figure 6](#), a d^3 octahedral system should exhibit three $d \rightarrow d$ excitations: $^4A_{2g} \rightarrow ^4T_{2g}(F)$; $^4A_{2g} \rightarrow ^4T_{1g}$, and $^4A_{2g} \rightarrow ^4T_{1g}(P)$.

Since the last transition involves a double excitation, it will not be observed in the singles only calculated spectrum. The first two low-energy bands with non-zero intensity involve triply degenerate excited states, and so both sets of calculated transitions are degenerate. Although the calculated energies for the bands are higher than the experimental values, the trend is sufficient to assign the bands in the experimental spectrum. One would not expect quantitative agreement even at a higher level of theory because of the lack of inclusion of the solvent in the calculated spectrum.

Charges and Electron Density

Electron density difference plots should be obtained for the lowest electronic transitions the calculated electronic spectrum. A darker color will indicate the region from which electron density was removed, while a lighter color indicates the region in which the electron density is enhanced. Since both the dark and the light electron density difference isosurfaces are located close to the metal, the $d \rightarrow d$ character of these excitations can be readily ascertained. In contrast, the lowest energy transitions with non-zero calculated intensity, can be characterized as vanadium to oxygen charge transfer from the electron density difference plot.

The trend in charges should confirm these assignments. The charge on vanadium should be only slightly higher in the lower excited states than in the ground state as expected for

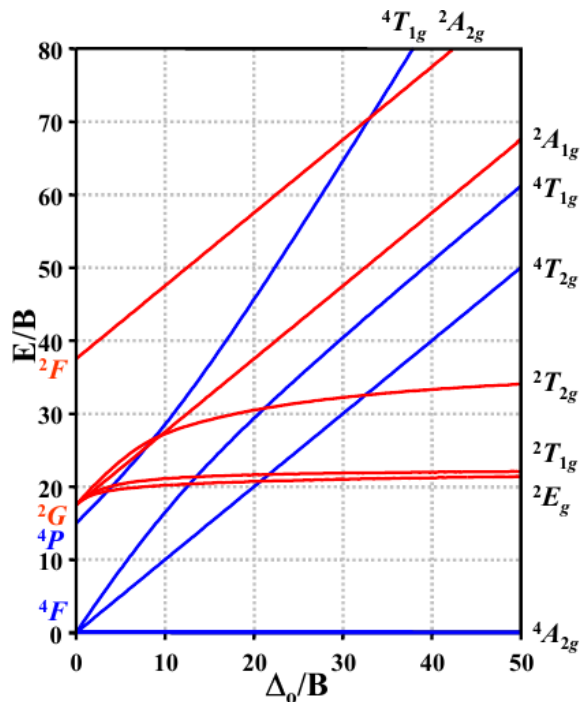


Figure 6: Tanabe-Sugano Diagram for Spin-Allowed Electronic Transitions of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$.

$d \rightarrow d$ transitions. The vanadium charge in the higher excited state, however, is much more positive than in the ground state, and is consistent with a metal to ligand charge transfer.

$[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ - d^1 Configuration

Square Pyramid Geometry and Jahn-Teller Distortion

The $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ complex forms an approximate square pyramid with the oxo-group in the apical position and four H_2O molecules in basal positions. The vanadium-oxo bond is considerably shorter than the vanadium-water bonds, as expected, and the water molecules that are in the basal positions are bent away from the oxo group by approximately 5° . If the complex were C_{4v} symmetry, the four basal V-O (H_2O) bonds should be equivalent, but local symmetry of the V-O (H_2O) linkages is reduced to C_{2v} because of a Jahn-Teller distortion. This will remove the degeneracy of the d_{xz} and d_{yz} orbitals on vanadium slightly.

Charges and Electron Density

Because of π -donation from the oxo ($=\text{O}$) group to the V atom, its charge is considerably less negative than on the water oxygen atoms.

Excited States

For a d^1 complex, the electronic states have the same symmetry as the corresponding metal d orbitals that contain the unpaired electron. The ligand field diagram for a C_{4v} complex is given in [Figure 7](#) (Reference 4).

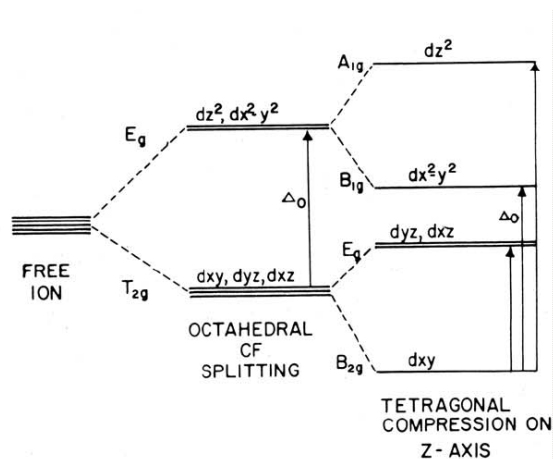


Figure 7: Ligand Field Diagram for the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ C_{4v} Complex.

Therefore, one expects 3 $d \rightarrow d$ transitions for $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$: ${}^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz,yz})$, ${}^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$, and ${}^2B_2(d_{xy}) \rightarrow {}^2A_1(d_{z^2})$. Reduction in symmetry to C_{2v} removes the degeneracy of the first transition.

As expected, the first two bands involve an electron transfer from the vanadium d_{xy} orbital to the vanadium d_{xz} and d_{yz} orbitals. The electron density on the π system of the oxo group is enhanced as well because of the covalency that occurs between the oxo group and the vanadium d_{xz} and d_{yz} orbitals. The third band is predicted to be a $d \rightarrow d$ transition ($d_{xy} \rightarrow d_{x^2-y^2}$) in Reference 4, but the calculated transition seems to point clearly to an oxo \rightarrow V charge transfer.

The remaining $d \rightarrow d$ transition ($d_{xy} \rightarrow d_{z^2}$) in the calculated spectrum occurs outside the wavelength range of the observed spectrum. Although it is possible that use of a higher level of theory and/or inclusion of the solvent in the calculation might reverse the assignment, the current model suggests that the band observed at approximately $28,600 \text{ cm}^{-1}$ in the experimental spectrum is probably a charge transfer band and not a $d \rightarrow d$ transition.

The excited state charges on the V=O fragment are consistent with the assignment of the 4th transition as a ligand (=O) orbital \rightarrow V charge transfer band.

References

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Exercises

1. Build the complexes using GaussView.

Here are some hints on building the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ complex ion. You may follow these or try using your own procedure:

- a. Place a six-coordinated vanadium atom at the center of the screen.
- b. Place oxygen atoms at each of the six coordinated positions. Be sure to select single O atom types, and not =O or -O- atom types.
- c. Now, picking five of the oxygen atoms and using the add valence button, create two additional valences at each O atom. Hydrogens should appear as this step is performed.
- d. Finally, complete the structure by setting the V=O bond length of the O atom without H atoms to 1.5 Å, and the five V-O (H_2O) distances to 2.0 Å.

This is a reasonable starting point for the optimization. Do not clean the structure with the clean button.

2. Optimize the geometry of each of the complexes, using the B3LYP functional and LANL2DZ basis for V, which replaces the core electrons with a pseudopotential, and the 6-31g(d) basis for the ligand atoms.

This combines Density Functional Theory, which can be very efficient for transition-metal complexes with a basis set that reduces the integral calculation time.

Compare the calculated structures to any experimental data which can be found. Crystallographic data may exist for these or similar complexes.

3. Now using the optimized geometries found in Step 2 above, create new Gaussian files for each excited state which solves for twenty excited states.

Compare the calculated spectra to those obtained experimentally.

Which of the excited states are seen in the optical excitation spectra? Which are not? How well do the vertical excitation energies compare?

Use GaussView to view the calculated spectra which can assist in performing a comparison between calculated and experimental results and on properly assigning the peaks in the spectrum.

4. Electronic transitions occur as electrons are shifted from one place to another within a molecule, which can be seen by examining electron density changes. The following is to be performed for each transition metal complex:

- a. Create a Gaussian electron density cube file containing the ground state electron density for the complex.
- b. Create a Gaussian electron density cube file for each of the excited states that were experimentally observable in the spectrum.

- c. Create a Gaussian **electron density difference cube** file for each of the excited states that were experimentally observable in the spectrum.
5. Now, visualize the difference densities (ground to excited state) to discover the nature of the transitions by reading the **electron-density difference cube** file into GaussView. Which color corresponds to areas where electrons are leaving? Which color corresponds to areas where electrons are going?
- To answer this, recall the dipole moment changes. How would you describe the transitions qualitatively?
- In the literature, terms such as $d \rightarrow d$, MLCT (metal-ligand charge transfer), LMCT (ligand-metal charge transfer), CT (charge transfer), etc. are used. A schematic diagram showing the various types of transitions is given in **Figure 8**.

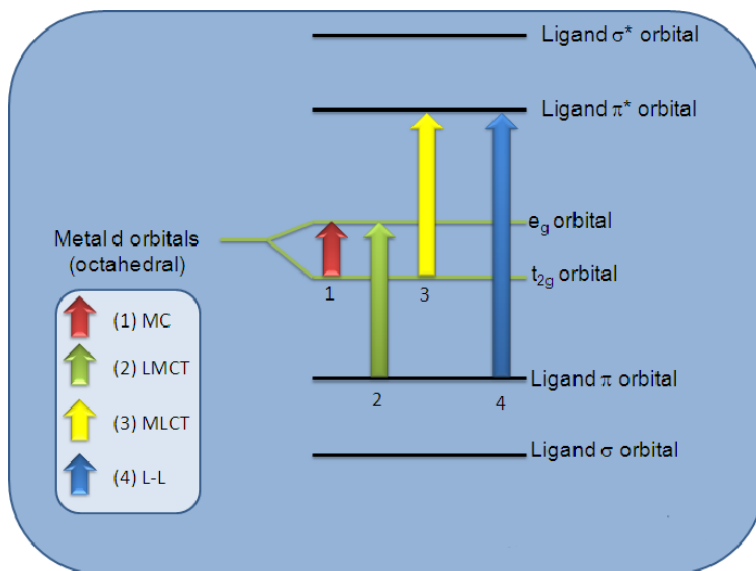


Figure 8: Schematic Diagram Showing Possible Types of Electronic Transitions in Transition Metal Complexes

6. Compare the atomic charges for the ground and excited states. What significant changes occur?
- What does this indicate about the direction of electron flow for those transitions?

Appendix

Generating Cube Files

- The first step is to create a formatted checkpoint file from an unformatted checkpoint file, resulting from a Gaussian calculation. A formatted checkpoint file will be needed for the ground state and each excited state.

Use the Gaussian **formchk** utility:

formchk ground.chk (This will create a formatted checkpoint file, ground.fck, for the ground state.)

formchk excited1.chk (This will create a formatted checkpoint file, excited1.fck, for the first excited state.)

- Next, use the **cubegen** utility to extract cube files from the formatted checkpoint files of interest:

cubegen 0 density=SCF ground.fck ground.cube 0 h (For the ground state)

cubegen 0 density=CI excited1.fck excited1.cube 0 h (First excited state, the same as specified as root=N in the TD section of the Gaussian input file)

Creating Difference Density Cube Files with Gaussian Utilities

Use the Gaussian **cubman** utility:

- **cubman**

- Enter **su** for subtract at the initial prompt

This operation subtracts two cube files to produce a new cube file.

- For the first input file type the name of the excited state cube file (example: excited1.cube)

Is the file formatted? Answer **y** for yes.

- For the second input file type the name of the ground state cube file (example: ground.cube)

Is the file formatted? Answer **y** for yes.

For the output file type in the name desired for the difference density output file (example: excited-ground.cube)

Should it be formatted? Answer **y** for yes.

- Follow the above procedure for each of the excited-state difference densities to be visualized in GaussView.

Visualizing Difference Densities in GaussView

GaussView can be used to read an electron density cube file, and create an isosurface rendering of the result.

- Select **File** → **Open**, and select the formatted checkpoint file for the excited state that you want to visualize the difference density for in GaussView. Select **OK**.
- Select **Results** → **Surfaces**, and a **Surfaces and Cubes** window will appear.
- Select the **Cube Actions** drop down menu. Select **Load Cube**.

Find the cube file that represents the difference density calculated with **cubman**. Select **OK**.

A line of data will appear in the **Cubes Available** box.

Select an appropriate isosurface value, such as 0.004.

Adjust the isosurface value until you obtain a visualization of the difference densities that is acceptable.

This will generate a graphical window with the molecule and difference density for the selected excited state.

The blue represents where the electrons are coming from, and the purple represents where the electrons are going.

- If the visualization is not ideal: Select the **Surface Actions** drop down menu; Select **Remove Surface**; Change the isosurface value.

Select the **Surface Actions** drop down menu; Select **New Surface**.

Repeat these steps until the visualization for the difference density is acceptable.

Synthesis and Spectra of Vanadium Complexes

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Although sometimes overlooked, vanadium complexes provide good examples that illustrate the use of Orgel diagrams for the interpretation of electronic transition-metal spectra. Three readily obtainable oxidation states of vanadium illustrate the electronic spectra produced by d^1 , d^2 , and d^3 electron configurations. The following experiment, which can be used in an advanced undergraduate inorganic laboratory, illustrates a variety of principles including simple synthetic techniques, redox principles in synthesis reactions, interpretation of visible spectra using Orgel diagrams, and the spectrochemical series.

The visible spectra of transition metal complexes result from $d-d$ electron transition that occur as a result of crystal field splitting and other distortions from ideal molecular geometry. Observed spectral absorptions are assigned to particular electronic transitions using the appropriate Orgel diagram as determined by the electron configuration and the geometry of the complex. Standard texts contain full explanations of electronic spectra and Orgel diagrams (1–3).

Synthesis Procedures¹

Procedure 1: Synthesis of $(\text{NH}_4)_2[\text{VO}(\text{tart})]\cdot\text{H}_2\text{O}$ (Ref. (4))

In a 600-ml beaker, mix 36 ml glacial acetic acid with 64 ml H_2O and 2 ml 85% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and heat to 65°C . To the warm solution add 11.7 g NH_4VO_3 and another 100 ml H_2O . Continue heating and stirring the solution until the NH_4VO_3 dissolves, nitrogen evolution ceases, and the solution is a deep blue color.

Cool the solution to room temperature, and then in order add, with stirring 15 g tartaric acid and 45 ml conc. NH_4OH . The now purple solution should be cooled in an ice bath. Finally, slowly (10–30 ml at a time) add 300 ml acetone to precipitate out the flocculent purple-pink $(\text{NH}_4)_2[\text{VO}(\text{tart})]\cdot\text{H}_2\text{O}$ product. Filter, wash with acetone, and air dry the product.

Procedure 2: Synthesis of $\text{VO}(\text{Acac})_2$ Ref. (5)

Use a steam bath or hot plate to reflux a mixture of 3 g V_2O_5 , 8 ml H_2O , 6 ml 18 M H_2SO_4 , and 15 ml ethanol for 1 h with occasional stirring. The alcohol causes the reduction of vanadium(V) to the dark blue vanadium(IV). Filter the solution to remove any unreacted V_2O_5 and then add 8 ml acetylacetone (Acac) or 2,4-pentanedione to the filtrate and thoroughly mix. Neutralize the acidic solution by slowly adding a solution of 13 g anhydrous Na_2CO_3 dissolved in 80 ml H_2O . The blue-green $[\text{VO}(\text{Acac})_2]$ begins to precipitate at pH 3.5. Finally, filter the solution, and air dry the product.

Solution Preparations for Spectra

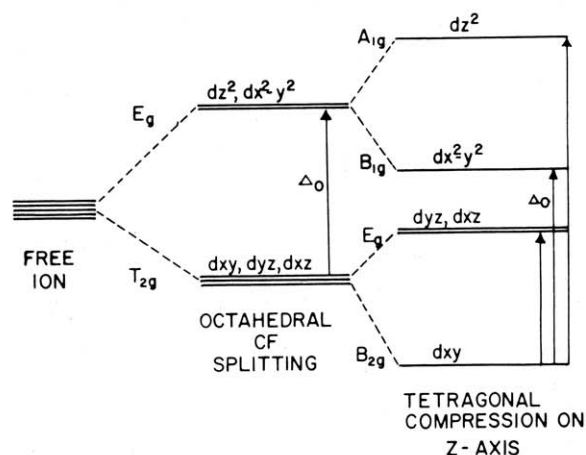
Stock Solutions

NH_4VO_3 : Dissolve 4 g NH_4VO_3 in a 250-ml water to which 2 ml 6 M NaOH have been added. Slight heating may be required to dissolve all NH_4VO_3 crystals.

Zn/Hg amalgam: Swirl 40 g of granular zinc with 50 ml 1 M HCl to clean the zinc surface. Decant the acid and swirl the zinc for 1–2 min with 150 ml 0.1 M HgCl_2 . Decant the HgCl_2 , rinse the Zn/Hg amalgam three times with 50 ml freshly boiled distilled water, and store it after the last rinse in a 250-ml flask until ready for use.

Procedure 1: Preparation of $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$

Place a 250-ml beaker in the hood and mix 50 ml stock NH_4VO_3 ,



VO_2^+ crystal field splitting diagram.

10 ml 3 M H_2SO_4 , and 4 g Na_2SO_3 . Swirl the solution for several minutes until a blue color is obtained.

Procedure 2: Preparation of $[\text{V}(\text{H}_2\text{O})_6]^{2+}$

First prepare the VO_2^+ ion in a 250-ml beaker by mixing 50 ml stock NH_4VO_3 with 10 ml 3 M H_2SO_4 . Pour the water out of the 250-ml flask containing the Zn/Hg amalgam and then pour the solution containing the VO_2^+ ion into this flask. Purge the solution for 2–3 min with nitrogen to remove oxygen. Finally, stopper the flask and swirl intermittently for 5–10 min or until the solution turns a violet-blue color.

Procedure 3: Preparation of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$

In a 100-ml beaker mix 10 ml $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ (Procedure 1) with 10 ml $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (Procedure 2) to obtain a brown solution which should turn green within 3 min.

Procedure 4: Preparation of $[\text{VO}(\text{tart})]^{2-}$

Dissolve 1 g $(\text{NH}_4)_2[\text{VO}(\text{tart})]\cdot\text{H}_2\text{O}$ in 300 ml H_2O and add 8 ml 6 M NH_4OH .

Procedure 5: Preparation of $[\text{VO}(\text{Acac})_2]$

Dissolve 0.1 g $[\text{VO}(\text{Acac})_2]$ in 20 ml methanol.

The spectra were obtained on a Coleman-Hitachi EPS-3R Recording Spectrophotometer. The wavelength of the peak or "shoulder" of maximum absorbance for the complexes are recorded in Table 1 and agree well with literature values.

Results

Prior to making the spectral interpretation, the students are expected to complete the following activities:

Balance equations for both synthesis and spectral preparation reactions.

Determine the name, oxidation state, d -electron configuration, structure, and color for VO_3^- (basic solution), VO_2^+ (acidic solution), $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{H}_2\text{O})_6]^{2+}$, $[\text{VO}(\text{Acac})_2]$, and $[\text{VO}(\text{tart})]^{2-}$.

Convert the maximum wavelength absorptions into wave numbers.

In the actual experiment, the students are asked to make all of the electron transition assignments for the spectral absorptions and develop a spectrochemical series for VO_2^+ .

¹ The student handout for this experiment may be obtained from one of the authors (CEO) for \$1.00 if a self-addressed, stamped (40¢) envelope is enclosed.

Table 1. Vanadium Complex Dilutions and Maximum Absorbances

Complex	Dilution	300–700 nm		Dilution	600–2600 nm
		λ_3	λ_2		λ_1
$V(H_2O)_6^{2+}$	none	360 s ^a	566	none	850
$V(H_2O)_6^{3+}$	2 ml/10 ml	270 ^b	420 s	2 ml/10 ml	620
$VO(H_2O)_5^{2+}$	none	350 s	630	5 ml/10 ml	770
$VOtar^{2-}$	none	396	540	none	910
$VOtar(H_2O)_2$	add 10 ml 6 M HCl/100	350 s	640	add 10 ml 6 M HCl/100	760
$VO(Acac)_2$	none	390	580	none	780

^a s = shoulder.

^b Calculated value (6).

Spectral Interpretation of V(II) and V(III)

The electron transitions for $[V(H_2O)_6]^{2+}$, a d^3 ion, are assigned by using an Orgel diagram. Since wave numbers are directly related to energy, the lowest energy transition (11,765 cm^{-1}) corresponds to the $A_{2g} \rightarrow T_{2g}$ transition which is also the crystal field splitting energy, Δ_0 . The other transitions are assigned similarly and shown in Table 2.

Electron transitions for $[V(H_2O)_6]^{3+}$, a d^2 ion, are assigned in a similar fashion. The lowest energy transition at 16,129 cm^{-1} is assigned $T_{1g}(F) \rightarrow T_{2g}$.

Spectral Interpretation of VO^{2+}

Under optimal conditions three absorptions may be observed in the spectra of VO^{2+} with various ligands. This is an unexpected result since only one absorption is predicted for a d^1 ion using the Orgel diagram. The multiple V=O bond causes a tetragonal compression type distortion from true octahedral geometry. As a result of a short V=O bond (1.62 Å) compared to a V—O (water) bond (2.3 Å), the octahedron is compressed along the Z-axis and results in a further splitting of previously equivalent d -orbitals as illustrated in the figure (7). The electron transitions for $[VO(H_2O)_5]^{2+}$ are assigned using the figure as shown in Table 3.

In the case of the VO^{2+} ions the crystal field splitting energy, Δ_0 is the second transition which is $B_{2g} \rightarrow B_{1g}$. Absorption assignment for the acetylacetonate and tartrate complexes are made in a similar fashion.

The VO tartrate in basic solution probably most clearly shows the three (possibly four) transitions predicted by the tetragonal distortion splitting diagram. In fact, the fourth transition as represented by a shoulder (about 590 nm) on the peak at 540 nm, may represent the removal of the last degeneracy in the E_g energy level.

Table 2. Vanadium(II) Aqueous Spectral Data

λ nm	$\bar{\nu}$ cm^{-1}	Electronic Transition
850	11,765	$A_{2g} \rightarrow T_{2g}$
566	17,668	$A_{2g} \rightarrow T_{1g}(F)$
360	27,778	$A_{2g} \rightarrow T_{1g}(P)$

Table 3. Spectral Data for $[VO(H_2O)_5]^{2+}$

λ nm	$\bar{\nu}$ cm^{-1}	Electronic Transition
770	12,987	$B_{2g} \rightarrow E_g$
630	15,873	$B_{2g} \rightarrow B_{1g}$
350	28,571	$B_{2g} \rightarrow A_{1g}$

There is an interesting difference in the spectra and the corresponding structures of the VO tartrate complex depending upon whether it is in ammoniacal solution or in an acidic solution. The explanation offered by Jorgensen (8) is that the tartrate is quadridentate in basic solution but only bidentate in acid solution. Coordination of the tartrate to the vanadium(IV) in basic solution is through the two carbonyl groups and two alcohol groups which have been converted into alcoxide ions giving an overall charge of -2 . In acidic solution the alcoxide groups are protonated leaving only the coordinated carboxyl groups as a bidentate ligand. The spectra of the VO tartrate complex in acidic solution resembles that of the VO^{2+} ion with oxalate or succinate which have no alcohol groups and only carboxyl groups.

Finally, a spectrochemical series can be constructed using the four ligands complexed with the VO^{2+} ion. Using the second energy transition ($B_{2g} \rightarrow B_{1g}$) as the crystal field splitting energy, Δ_0 , the following series is obtained: tart(basic) > Acac > H_2O > tart(acidic).

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