

CORRELATIONS BETWEEN THE VISIBLE SPECTRA OF VO(AA)<sub>2</sub> IN  
DIFFERENT SOLVENTS AND THE TAFT-KAMLET SOLVENT PARAMETERS

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THE VISIBLE SPECTRA OF ACETYLACETONATE COMPLEX OF VO<sup>2+</sup>, VO(AA)<sub>2</sub>, WERE MEASURED IN THIRTY ORGANIC SOLVENTS. THE CORRELATIONS, BETWEEN THE SPECTRAL AND STRUCTURAL CHARACTERISTICS AND THE TAFT-KAMLET SOLVENT PARAMETERS,  $\pi^*$ ,  $\alpha$  AND  $\beta$ , ARE DISCUSSED.

*Introduction*

The ion VO<sup>2+</sup> with the electronic structure 3d<sup>1</sup> forms coordination compounds with coordination numbers 5 and 6. The complex VO(AA)<sub>2</sub> (AA: acetylacetonate) can be easily prepared [1]; the compound is monomeric in benzene solution<sup>1</sup> [2a] and paramagnetic (16.044 10<sup>-24</sup> A m<sup>2</sup> [3]), with a dipole moment 14.341 10<sup>-30</sup> C m [4]. A strong  $\sigma$ -bond forms between the (2p<sub>z</sub> + 2s) hybrid of the oxygen and the (3d<sub>z<sup>2</sup></sub> + 4s) hybrid of the V<sup>4+</sup>, while the 2p<sub>x</sub> and 2p<sub>y</sub> orbitals on the oxygen  $\pi$ -bond with the 3d<sub>xz</sub>, 3d<sub>yz</sub> orbitals on the metal ion, so that the high stability of VO<sup>2+</sup> is obvious. The (3d<sub>z<sup>2</sup></sub> + 4s) hybrid and the orbitals 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and 4p<sub>x</sub>, 4p<sub>y</sub>, 4p<sub>z</sub> are capable of five  $\sigma$ -bonds [5] directed in a tetragonal pyramid (the overall molecular symmetry is C<sub>2v</sub>);

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<sup>1</sup> KAWATE et al. [2b] have demonstrated the formation of a dimer of VO(AA)<sub>2</sub> in toluene-benzene solution at 77 K.

the  $V^{4+}$  is located at the centre of gravity of the five oxygen atoms [6].

BALLHAUSEN and GRAY [3] have pointed out that in vanadyl complexes the ground orbital, the  $b_2$  level, is an almost pure vanadium  $3d_{xy}$  orbital, and that in their spectra, as in that of  $VO(AA)_2$ , three crystal field bands are obtained, due to the transitions  $e_{\pi}^* \leftarrow b_2$  ( $-3Ds + 5Dt$ ):  $\nu_1$ ,  $b_1^* \leftarrow b_2$  ( $10Dq$ ):  $\nu_2$  and  $a_1^* \leftarrow b_2$  ( $10Dq - 4Ds - 5Dt$ ):  $\nu_3$ . The sixth position, *trans* to the vanadyl oxygen, is open and may be coordinated by ligand or solvent molecules, producing a roughly octahedral structure. Thus, changes in the solvent may be expected to perturb the axially oriented MO's, which is manifested in the magnetic, optical and other behaviour [4,7].

We have examined the visible spectra of  $VO(AA)_2$  in 30 pure solvents; the maximum data and the calculated parameters are listed in Table I. This permits a discussion of the correlations between the band position and the TAFT-KAMLET [8] solvent parameters  $\pi^*$ ,  $\alpha$  and  $\beta$ .

### Experimental

The complexes were prepared according to a literature procedure [1]. The spectra were measured on a SPECORD M-40 instrument in spectroscopically pure solvents, in 1.0 and 0.1 cm quartz cells.

### Conclusions

From the data in Table I, the following conclusions can be drawn.

1.) The frequency of  $\nu_1$  reflects the difference between the in-plane and axial ligand(solvent)-to-vanadium bonding. A strong axial perturbation reduces the V-O interaction, thereby lowering the  $e_{\pi}^*$  level with respect to  $b_2$ ;  $\nu_1$  shifts to bathochromically approximately  $4000\text{ cm}^{-1}$  on change of the solvent from  $Cl_2CCCl_2$  to water. A

plot of  $\nu_1$  vs.  $\pi^*$  results in two separate linear correlations (Fig. 1A); for non-alcoholic solvents:

$$\nu_1/\text{cm}^{-1} = 18296 - 5422 \pi^* \quad (r = 0.982)$$

The alcohols cause a smaller change in the band position:

$$\nu_1/\text{cm}^{-1} = 14449 - 2431 \pi^* \quad (r = 0.807)$$

$\nu_1$  is also linearly correlated with  $\alpha$  (hydrogen donor ability of solvent molecules):

$$\nu_1/\text{cm}^{-1} = 15200 - 2611 \alpha \quad (r = 0.978)$$

These relations reveal that, the higher the polarizability and hydrogen-bond-forming ability of the solvent, the larger is the bathochromic shift of  $\nu_1$ .

2.) The value of 10Dq is obtained directly from the transition  $b_1^* \leftarrow b_2$ . The position of this band should be dependent on both the  $\sigma$ -donor and  $\pi$ -donor strength of the in-plane ligands. The latter quantity does not vary to a large extent, so  $\nu_2$  should be directly related to the in-plane field strength.  $\nu_2$  varies in only a very narrow interval; it is not sensitive to change in the solvent. A more sensitive parameter is  $\nu_{2-1}$  [9] (changes from 1000 to 5500  $\text{cm}^{-1}$ ) which shows a spread nearly four times as large that of 10Dq in the series studied. The plots of  $\nu_{2-1}$  vs.  $\pi^*$  (Fig. 1B) results in linear correlations for non-alcohols:

$$\nu_{2-1}/\text{cm}^{-1} = -2650 + 7247 \pi^* \quad (r = 0.989)$$

and for alcohols:

$$\nu_{2-1}/\text{cm}^{-1} = 2115 + 4062 \pi^* \quad (r = 0.937)$$

The plot of  $\nu_{2-1}$  vs.  $\alpha$ :

$$\nu_{2-1}/\text{cm}^{-1} = 1211 - 3852 \alpha \quad (r = 0.946)$$

result in linear correlations with positive slopes, while the correlation between  $\nu_{2-1}$  and  $\beta$  is also linear, but has a negative slope:

$$\nu_{2-1}/\text{cm}^{-1} = 5793 - 1822 \beta \quad (r = 0.964)$$

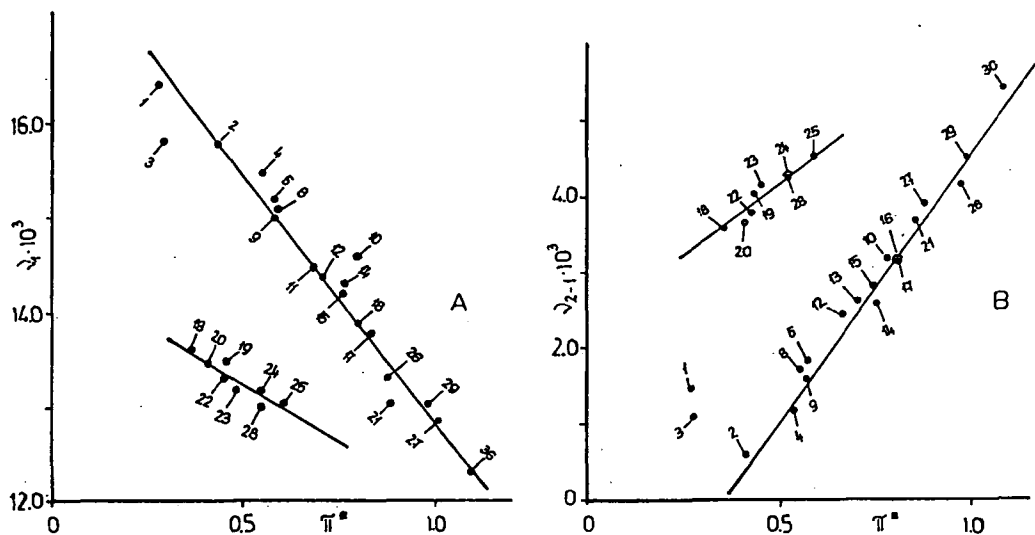


Figure 1: A) Plot of  $\nu_1/\text{cm}^{-1}$  vs.  $\pi^*$ ; B) plot of  $\nu_{2-1}/\text{cm}^{-1}$  vs.  $\pi^*$

3.)  $D_s$  [ $=(\nu_1 + \nu_3 - \nu_2)/7$ ] and  $D_t$  [ $=(\nu_1 - 3D_s)/5$ ] are measures of the tetragonal distortion of the molecule [3]. Both parameters are relatively large, indicating a very considerable distortion. The plots of  $D_s$  vs.  $\pi^*$  (Fig. 2) for non-alcohols:

$$-D_s/\text{cm}^{-1} = -3967 + 993 \pi^* \quad (r = 0.942)$$

and for alcohols:

$$-D_s/\text{cm}^{-1} = -3430 + 782 \pi^* \quad (r = 0.936)$$

show that an increase in the polarizability of the solvent results in a decrease in the distortion; in other words [9] the stronger the sixth ligand (solvent), the weaker is the total axial perturbation due to both the vanadyl oxygen and the sixth ligand. Similar high  $D_s$  and  $D_t$  are obtained for other vanadyl complexes; for example, for  $\text{VO}(\text{H}_2\text{O})_6^{2+}$ ,  $D_s = -4570$  and  $D_t = 143 \text{ cm}^{-1}$  [3].

4.) The parameter  $\rho$   $[=(1-7Dt)/4Dq]$ , the ratio of the effective axial charge and the effective equatorial charge, can be calculated on the basis of ligand field theory in the knowledge of all three band positions [9]. The increase in  $\rho$  on going from  $\text{VO}(\text{SO}_4)$  (-0.440) to  $\text{VO}(\text{AA})_2$  (+0.041) is consistent with the decrease in the  $V = 0$  double bond distance [5]. Also, the increase observed in  $\rho$  when  $\text{VO}(\text{AA})_2$  is dissolved in a more polar solvent is what one might expect from the consideration that there is an empty axial position which can be occupied by coordinating solvent [10]. Unfortunately, the exact location of  $\nu_3$  is problematic because the band appears very close to the intraligand spin-forbidden  $\pi^* \leftarrow \pi$  band; thus the calculated  $\rho$  values are uncertain. In spite of this uncertainty, the values in Table I show a similar trend to that of  $\pi^*$ .

5.) The ESR  $g$  values  $\{g_{\perp} = 2[1-(c_1^* \lambda)/\nu_1]; g_{\parallel} = 2[1-(c_1^* \lambda)/\nu_2]$  should be calculated from the optical absorption data ( $\lambda = 135 \text{ cm}^{-1}$ , while  $c_1^*$  is 0.907 and 0.946 for the first and second transitions, respectively [11]). The calculated isotropic  $\langle g \rangle$  values (Table I) agree well with the published data [12]. It is obvious that the average values of  $g$  are close to the free electron ( $g_e = 2.0023$ ) value. The  $\langle g \rangle$  values reported for the vanadyl complexes in the literature are approximately the same for measurements on crystals, powder and solution [3]. Within experimental error, the published  $\langle g \rangle$  values do not vary; the small trend in our data is due to the simplified formulae used for the calculations.

6.) It has been observed [13] that, if there is a ligand- $\text{VO}^{2+}$  interaction in the axial direction, the differences ( $g - \langle g \rangle$ ) and ( $g_e - \langle g \rangle$ ) vary approximately inversely to  $\nu_1$  and  $\nu_2$ , respectively. We did not obtain a similar correlation. Our calculated differences are very small (0.0135 - 0.0121 and 0.0300 - 0.0330, respectively), indicating that the solvent- $\text{VO}^{2+}$  interaction is weaker than the ligand- $\text{VO}^{2+}$  interaction;

Table I  
The measured spectral data and calculated parameters on VO(AA)<sub>2</sub>

No	Solvent	* $\nu_1$	* $\nu_2$	* $\nu_3$	* $\nu_{2-1}$	-Ds *	+Dt *	$\rho$	<g>	<g> **	$\alpha^2$
1	Cl <sub>2</sub> CCl <sub>2</sub>	16420	17850	26250	1430	3546	1156	-0.13	1.9730		0.45
2	p-Xylene	15800	16400	26400	600	3686	948	-0.012	1.9710		0.44
3	CCl <sub>4</sub>	15790	16860	25970	1070	3557	1024	-0.063	1.9715		0.44
4	Dioxane	15540	16650	25750	1110	3520	996	-0.047	1.9711		0.45
5	Benzene	15220	17000	25500	1780	3389	1011	-0.041	1.9713	1.970	0.45
6	c-Hexanone	15150	17500	25580	2350	3319	1039	0.039	1.9718		0.46
7	CS <sub>2</sub>	15080	16660	?	?	?	?	?	1.9709	1.968	0.45
8	CHCl <sub>3</sub>	15080	16820	25800	1740	3437	954	0.007	1.9710	1.970	0.45
9	THF	15000	16600	25800	1600	3457	926	0.024	1.9707	1.969	0.45
10	CH <sub>3</sub> NO <sub>2</sub>	14570	17770	25370	3200	3167	1014	0.001	1.9717		0.47
11	Reflectance	14500	16700	24500	2200	3186	988	-0.035	1.9705		0.46
12	Acetone	14450	16900	25000	2450	3221	957	+0.009	1.9707	1.968	0.46
13	Cl-Benzene	14400	17000	25800	2600	3314	892	0.082	1.9708		0.46
14	c-Hexane	14300	16900	25050	2600	3207	936	0.031	1.9706		0.46
15	CH <sub>3</sub> CN	14200	17000	25800	2800	3286	868	0.106	1.9706	1.969	0.46
16	o-Cl <sub>2</sub> -Benzene	13900	17100	25500	3200	3186	868	0.112	1.9705		0.47
17	CH <sub>2</sub> Cl <sub>2</sub>	13800	16900	25900	3100	3257	806	0.165	1.9702		0.47
18	Octylalc.	13600	17150	25600	3550	3150	830	0.153	1.9703		0.47
19	c-Hexanol	13520	17550	25660	4030	3090	850	0.152	1.9707		0.48
20	Hexylalc.	13480	17180	25500	3700	3114	828	0.157	1.9702		0.47
21	Pyridine	13340	17040	24800	3700	3014	860	0.117	1.9700	1.970	0.47
22	Amylalc.	13320	17080	25200	3760	3063	826	0.154	1.9700		0.47
23	Butylalc.	13220	17360	25400	4140	3037	822	0.171	1.9702		0.48
24	Propylalc.	13200	17450	25620	4250	3053	808	0.190	1.9703		0.48
25	Methanol	13040	17620	25200	4580	2946	840	0.166	1.9704	1.968	0.48
26	Benzylalc.	13030	17250	24950	4220	2961	829	0.159	1.9700		0.48
27	DMFA	13030	16970	25120	3940	3026	790	0.185	1.9700	1.968	0.47
28	Ethanol	13000	17280	25300	4280	3003	798	0.192	1.9700		0.48
29	DMSO	12850	17350	24990	4500	2927	814	0.179	1.9699		0.48
30	Water	12330	17820	25500	5490	2859	751	0.262	1.9699		0.50

\* in cm<sup>-1</sup>; \*\* [13] p. 111.

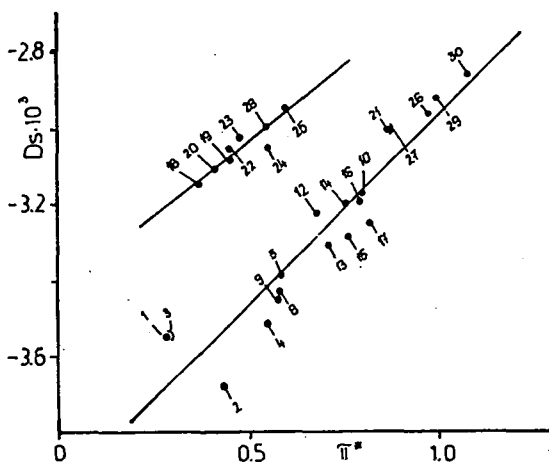


Figure 2. Dependence of  $D_s/\text{cm}^{-1}$  on  $\pi^*$

consequently, the field strength does not vary considerably either in-plane axially.

7.) The method of evaluation of the mixing coefficient  $\alpha^2 = \{[\nu_2(2-\langle g \rangle)]/8\lambda\}$  [11,14] depends on the fact that the orbital magnetic moment of an unpaired electron is reduced if the magnetic electron is spread in a MO over the entire molecule.  $\alpha^2 = 1$  for pure ionic binding and  $\alpha^2 = 0.5$  for pure covalent binding. In our case,  $\alpha^2$  varies between 0.46 and 0.50, indicating an almost pure covalent character of the bonds; the somewhat lower values are due to the uncertainty in the optical data.

8.) Several authors have modified the TAFT-KAMLET parameter  $\pi^*$ . For non-associating solvents, ABE [15] has introduced two polarity parameters,  $\pi_1^*$ ,  $\pi_2^*$ , using the optical data on non-polar and weakly polarized molecules such as naphthalene, chlorobenzene and  $\beta$ -carotene. On the other hand, BEKÁREK [16] has found that the modified TAFT-KAMLET parameter,  $\pi_n^* = \pi^*/(n^2-1)/(2n^2+1)$  gives a better fit to the experimental optical data than the original parameter. The correlations between these new parameters and our data are very poor; the original

$\pi^*$  [8], bases on the spectral data on the strongly polar N,N-diethyl-4-nitroaniline, etc., is more useful in our case.

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