The Magnetic Circular-dichroism Spectrum of Matrix-isolated Vanadium Hexacarbonyl

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The m.c.d. spectrum of [V(CO)$_6$] in inert gas matrices has been recorded. The results indicate that a large static Jahn–Teller distortion is present.

SINCE the first synthesis of vanadium hexacarbonyl[1] there has been considerable controversy: initially, over whether it existed as a monomer or a dimer,[2-4] and more recently over the nature of its electronic structure.[5-8] It is now generally accepted that, in both the solid state and solution, vanadium hexacarbonyl exists as the monomer [V(CO)$_6$]. A recent paper by Ford *et al.*[9] has provided some evidence for the existence of [V$_2$(CO)$_{12}$] in CO matrices at high concentration of vanadium atoms.

Early magnetic-susceptibility measurements[4] showed that [V(CO)$_6$] has one unpaired electron with a value for $\mu_{eff.}$ close to the spin-only value. Thus the ground state of this d^5 compound was suggested to be $^2T_{2g}$. Such a ground state should undergo a Jahn–Teller distortion and evidence for this was provided by the i.r. and visible spectral study of Haas and Sheline.[5] An e.s.r. investigation by Pratt and Myers[6] suggested that, at liquid-helium temperatures, either a tetragonal or trigonal distortion was present, and that the ground state was $^2B_{2g}$. A more recent e.s.r. experiment[8] has essentially confirmed this conclusion. A study of the magnetic susceptibility[7] of solid [V(CO)$_6$] indicated that between 300 and 66 K the compound has an approximately octahedral geometry but that a dynamic Jahn–Teller effect is present. This study suggested that in the solid at <60 K there is antiferromagnetic exchange. In order to clarify the electronic structure of [V(CO)$_6$] we have measured the magnetic circular-dichroism (m.c.d.) spectra[10-12] in nitrogen and argon matrices.

EXPERIMENTAL

Samples of [V(CO)$_6$] were kindly provided by Dr. K. A. Rubinson. The matrix m.c.d. spectra were recorded with a new version of the apparatus previously described.[13,14] This new liquid-helium superconducting magnet cryostat has a much improved temperature-control system. The original cryostat cooled the matrix window by thermal contact to the helium reservoir can, which gave a minimum window-block temperature of *ca.* 20 K; the new apparatus cools the window block with a flow of liquid helium, controlled by a needle valve on the exhaust end of the helium flow-through system. This enables a block temperature of 4.2 K to be achieved; however, the matrix temperature may be a few degrees higher. From the insert in Figure 2 it can be seen that the plot of the m.c.d. strength against magnetic field for [V(CO)$_6$] is linear, indicating the absence of any saturation at the lowest block temperature of 4.2 K. If one accepts a value of $g = 2$ for [V(CO)$_6$] one would expect to see saturation effects below 8 K; thus the lowest matrix temperature appears to be 8 K or slightly above. The new matrix-isolation apparatus has a larger isolation window (1 cm diameter) and the maximum magnetic field has been increased from 4.8 to 7.0 T. The mixture of [V(CO)$_6$] and isolating gas (nitrogen or argon) was obtained by flowing the gas over the [V(CO)$_6$]. The ratio of [V(CO)$_6$] to isolating gas could be varied by adjusting the gas flow rate and controlling the temperature of the [V(CO)$_6$]. Matrices of good optical quality with low scattering and depolarisation were obtained. The more concentrated matrices for study of the visible region were pale yellow and the more dilute matrices for the u.v. region were colourless. The m.c.d. spectra were recorded on a Cary 61 dichrograph and the absorption spectra on a Cary 14 spectrophotometer fitted with an extended cell compartment.

RESULTS AND DISCUSSION

The m.c.d. and absorption spectra of vanadium hexacarbonyl in a nitrogen matrix at 5 K are shown in Figure 1. The corresponding spectra in argon matrices are identical. The absolute value for the ratio of isolating gas to material M : R is unknown, but in the course of several experiments with matrices of equal thickness (*i.e.* identical amounts of isolating gas sprayed on under the same experimental conditions), from the intensity of the m.c.d. and absorption spectra, it is estimated that the M : R ratio was varied by at least a factor of 20 without alteration of any spectral features. This provides good evidence that the spectra in Figure 1 are those of the isolated [V(CO)$_6$] molecule and not due to aggregates.

The absorption spectrum in Figure 1 is consistent with the earlier results.[5,8] Table 1 shows the positions of all the bands in the present matrix study together with the previous results. The data for the solution study were

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[12] P. J. Stephens, *Adv. Chem. Phys.*, 1976, **35**, 197.

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based on a curve-resolving procedure which utilised the band positions from our preliminary m.c.d. experiments, and thus do not represent completely independent results. The matrix absorption spectra exhibit more detail than any previously reported spectra.

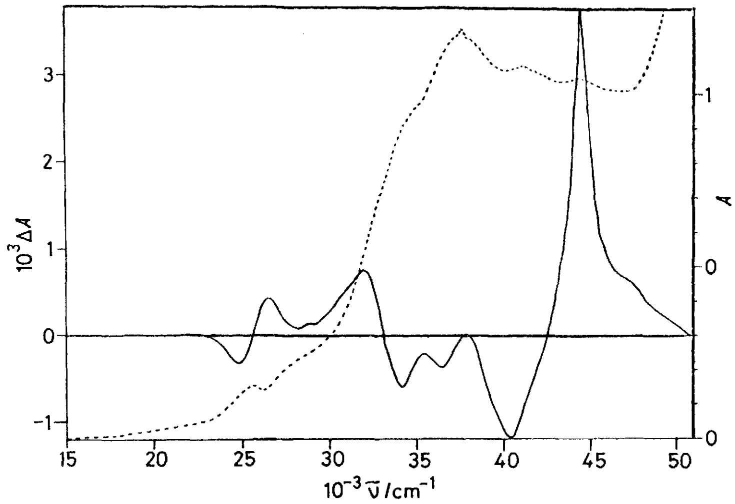

FIGURE 1 The m.c.d. (——) and absorption (— — —) spectra of $[V(CO)_6]$ in a nitrogen matrix at 5 K; $B = 7$ T

The entire m.c.d. spectrum shown in Figure 1 is strongly temperature dependent (not illustrated) as would be expected for a paramagnetic molecule.[10-12] This is further evidence that the isolated species is $[V(CO)_6]$, since the dimer $[V_2(CO)_{12}]$ is predicted to be diamagnetic. Thus all the bands in the m.c.d. spectra are C terms with variable amounts of B-term contribution.

TABLE 1

The positions of the matrix m.c.d. and absorption bands and previously published absorption spectra (in cm^{-1})

Sign of m.c.d.	Matrix m.c.d. band positions	Band no.	Matrix absorption band positions	Solution study [8]	Gas-phase study [5]
−	24 800	1			
			25 650	25 400	25 500
+	26 550	2			
+	29 150	3	29 000 (sh)		28 200
+	30 900 (sh?)	4			
+	31 950	5			
−	34 200	6	34 400 (sh)	33 200	
−	36 500	7	37 600	37 400	37 000
−	40 300	8	41 000	41 800	42 500
+	44 400	9	44 400	45 400	44 400 (sh)
+	47 300	10			

The only hexacarbonyl absorption spectra to be assigned are those of $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$.[15] The absorption spectra of these d^6 diamagnetic hexacarbonyls were all very similar, having a weak band at *ca.* 31 500 cm^{-1} and two intense bands at *ca.* 35 000 and 44 000 cm^{-1}. The band at 31 500 cm^{-1} was assigned as the *d–d* transition $^1A_{1g} \rightarrow {}^1T_{1g}$ although its absorption coefficient was rather high for a pure *d–d* band (*ca.* 500 dm^3 mol^{-1} cm^{-1}); another *d–d* band was suggested at *ca.* 37 000 cm^{-1} for $[Mo(CO)_6]$ and $[W(CO)_6]$. The two intense bands were assigned as metal-to-ligand charge transfer $t_{2g} \rightarrow t_{1u}$ and $t_{2g} \rightarrow t_{2u}$, being in both cases allowed $^1A_{1g} \rightarrow {}^1T_{1u}$ transitions. It was estimated that any ligand-to-metal charge-transfer bands would lie above 60 000 cm^{-1}.

Since $[V(CO)_6]$ has an open-shell d^5 configuration, the single-electron transitions $t_{2u} \rightarrow t_{1u}$ and $t_{2g} \rightarrow t_{2u}$ give rise to a very large number of states; in the case of the configuration $t_{2g}{}^4t_{1u}$ they are $^2A_{1u}$, $^2A_{2u}$, $2 \times {}^2E_u$, $3 \times {}^2T_{2u}$, and $4 \times {}^2T_{1u}$ as well as some quartet states. Hence the comparative simplicity of the $[V(CO)_6]$ spectrum is very remarkable. It should be noted that the m.c.d. spectrum appears to be comprised of sets of three bands, one of one sign followed by two of the opposite sign: *i.e.* 1—2,3; 5—6,7; and 8—9,10 (see Table 1). As will be shown later, this is the expected pattern for transitions to $^2T_{1u}$ or $^2T_{2u}$ states.

The absorption coefficients [8] of the bands at 25 650 and 29 000 cm^{-1} appear to be *ca.* 2 000 dm^3 mol^{-1} cm^{-1}. However, much of this intensity is probably caused by the low-energy tail from the intense u.v. bands and hence the actual value of ε is undoubtedly lower. The weakness of these bands shows that they must be forbidden transitions and it seems reasonable to assign them as *d–d* bands with some ligand character. The three low-energy m.c.d. bands together with the absorption spectrum are shown in Figure 2; the temperature and magnetic-field dependence are also illustrated.

From Griffith [16] (table A30 of the interelectron-repulsion matrix elements) it can be seen that the lowest-energy states of the $t_{2g}{}^4e_g$ configuration are $^2A_{2g}$ and $^2T_{1g}$ with $^2T_{2g}$ and ^2E_g a few thousand cm^{-1} higher in energy. This is in agreement with Tanabe and Sugano diagrams.[17] Figure 3 shows the energy-level scheme for the $^2T_{2g}$

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[15] H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, 1963, **85**, 2922.

[16] J. S. Griffith, 'The Theory of Transition-metal Ions,' Cambridge University Press, Cambridge, 1961.

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ground state and the $^2T_{1g}$ excited state in the presence of a tetragonal distortion and first-order spin–orbit coupling. Previous studies [5-9] on $[V(CO)_6]$ have suggested that the $^2T_{2g}$ ground state under tetragonal distortion has the $^2B_{2g}$ level lowest. We shall assume this.

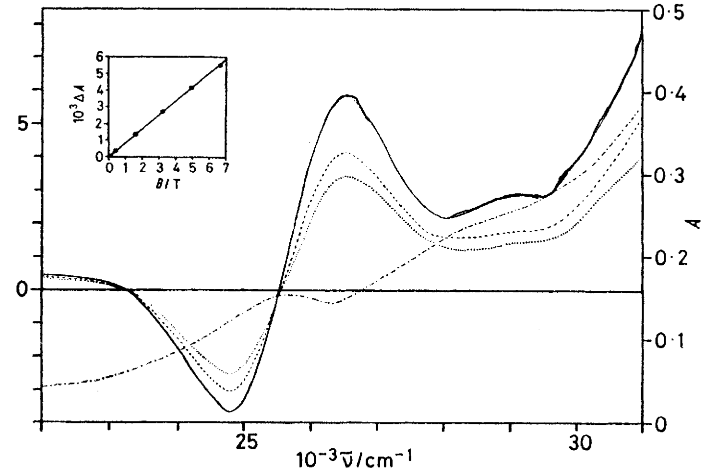

FIGURE 2 The absorption (— · — · —) and m.c.d. spectra [at 5 (——), 15 (— — —), and 25 K (· · ·)] in a nitrogen matrix; $B = 7$ T

A full analysis of the C term for the $^2T_{2g}\rightarrow{}^2T_{1g}$ transition would be very complex and thus a simple approach has been adopted. The sign of a C term for any transition $A\rightarrow J$ can be determined from symmetry arguments.[10-12] (It is thus necessary to find which transitions are m_+ or m_- allowed, but to discover this one must go down to the single-electron matrix elements.)

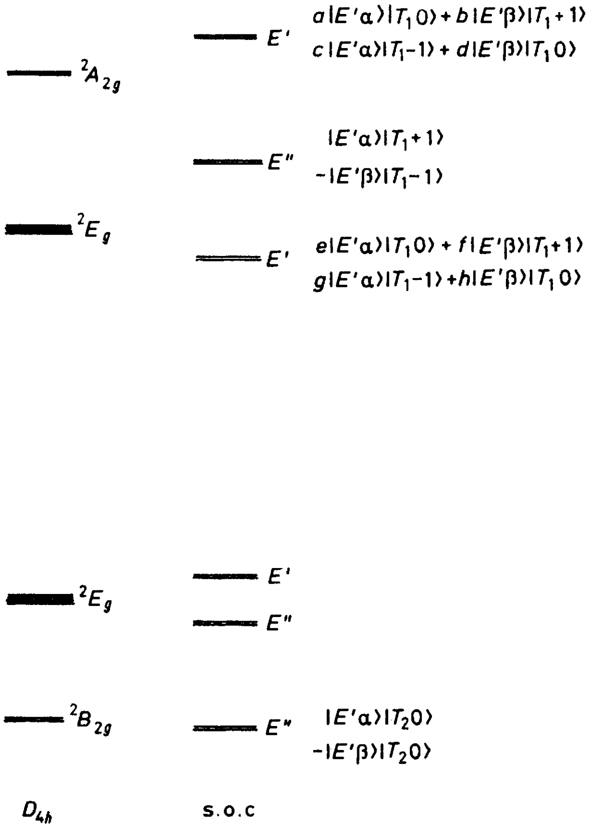

FIGURE 3 The energy states and wavefunctions for the $^2T_{2g}$ ground state and $^2T_{1g}$ excited state of $[V(CO)_6]$ in the presence of a tetragonal distortion and first-order spin–orbit coupling (s.o.c.)

In O_h symmetry the configuration $t_{2g}{}^4e_g$ gives rise to two $^2T_{1g}$ states. From Griffith (table A30) it can be shown that the lower-energy $^2T_{1g}$ arises from the coupling of $^2E(e_g{}^1)$ with $^3T_2(t_{2g}{}^4)$. Using table A20 of Griffith, the coefficients of the ^2E and $^3T_1$, considering the $+1$ component of $^2T_1$, are as in equation (1). This may be

$$|^2T_1 + 1\rangle = -\tfrac{1}{2}|^2E\theta\rangle|^3T_1 + 1\rangle - \frac{3^{\frac{1}{2}}}{2}|^2E\varepsilon\rangle|^3T_1 - 1\rangle \quad (1)$$

expressed in terms of single-electron wavefunctions by use of table A24 of Griffith,[16] and thus we obtain equation (2). Now considering the transition from the lowest

$$|^2T_1{}^{\pm} + 1\rangle = \tfrac{1}{2}|\theta^{\mp}1^{\pm} - 1^2\zeta_1{}^{\pm}\rangle + \frac{3^{\frac{1}{2}}}{2}|\varepsilon \mp 1^2 - 1^{\pm}\zeta_1{}^{\pm}\rangle \quad (2)$$

energy E'' level of the $^2T_{2g}$ ground state to $|^2T_1 + 1\rangle$ we have (3), and in D_{4h} symmetry we obtain (4). Table

$$\langle E'\alpha|\langle T_2 0|m|^2T_1 + 1\rangle|E'\alpha\rangle = \langle A|m|J\rangle = -\tfrac{1}{2}\langle 1|m|\theta\rangle - \frac{3^{\frac{1}{2}}}{2}\langle -1|m|\varepsilon\rangle \quad (3)$$

$$\langle A|m|J\rangle = -\tfrac{1}{2}\langle E + 1|m|A_1\rangle - \frac{3^{\frac{1}{2}}}{2}\langle E - 1|m|B_1\rangle \quad (4)$$

D32 of Griffith [18] may be used to express $\langle A|m|J\rangle$ in terms of reduced matrix elements and V coefficients [equation (5)]. In this way we can determine whether

$$\langle E + 1|m_+|A_1\rangle = \langle E||m||A\rangle V\begin{pmatrix} E & A_1 & E \\ -1 & & +1 \end{pmatrix} = \tfrac{1}{2}\langle E||m||A_1\rangle \quad (5)$$

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[18] J. S. Griffith, ' The Irreducible Tensor Method for Molecular Symmetry Groups,' Prentice–Hall, London, 1962.

$A \rightarrow J$ is m_+ or m_- allowed. The results of this calculation for E'' and both E' states of $^2T_{1g}$ are given in Table 2.

TABLE 2

The sign of ΔA for the various components of the $^2T_{2g} \rightarrow {}^2T_{1g}$ transition

Transition	Electric dipole allowed by	Sign of ΔA
$\lvert E\alpha\rangle \lvert E''0\rangle \rightarrow \lvert E\alpha\rangle \lvert E'\rangle^1$	m_-	$-$
$\lvert E\beta\rangle \lvert E''0\rangle \rightarrow \lvert E\beta\rangle \lvert E'\rangle^1$	m_-	
$\lvert E\alpha\rangle \lvert E''0\rangle \rightarrow \lvert E\alpha\rangle \lvert E''\rangle$	m_+	$+$
$\lvert E\beta\rangle \lvert E''0\rangle \rightarrow \lvert E\beta\rangle \lvert E''\rangle$	m_+	
$\lvert E\alpha\rangle \lvert E''0\rangle \rightarrow \lvert E\alpha\rangle \lvert E'\rangle^2$	m_-	$-$
$\lvert E\beta\rangle \lvert E''0\rangle \rightarrow \lvert E\beta\rangle \lvert E'\rangle^2$	m_+	

From Table 2 it can be seen that one would expect ΔA to be positive for the transition to E'' and negative for the two transitions to E' states. This is the opposite to the experimental results for the lowest-energy m.c.d. bands. However, the treatment employed above ignored the fact that the transition is forbidden since it is a $g \rightarrow g$ type; if a vibronic mechanism is operating which mixes in some *ungerade* states then the sign of the m.c.d. C terms will be determined by the symmetry of the mixing vibration.[19] In this particular case it means that the most important vibrational modes would be a_2 and b_2, assuming D_{4h} symmetry for $[V(CO)_6]$.

The C term at 24 800 cm^{-1} is thus assigned to the transition $E' \rightarrow E''$ where E' is the lowest-energy ground state (*i.e.* $^2B_{2g}$, in D_{4h}, no spin–orbit coupling) and the C terms at 26 500 and 29 150 cm^{-1} to $E' \rightarrow E'$ transitions. The overall size of the $^2T_{1g}$ splitting is therefore 4 350 cm^{-1} which is somewhat larger than that suggested for the $^2T_{1g}$ ground state, *i.e.* 1 350 cm^{-1}.[8] Since the spin–orbit coupling parameter is less than 100 cm^{-1},[5,6,8] it would not be expected to give rise to a splitting of the $^2T_{1g}$ state of more than a few hundred wavenumbers. Hence the m.c.d. results provide evidence for a very large static Jahn–Teller distortion. It is not possible to conclude from our experiments whether this distortion is trigonal or tetragonal.

The next highest-energy group of three C terms (5,6,7 in Table 1) have the opposite sign to the $^2T_{2g} \rightarrow {}^2T_{1g}$ transition. In view of the high value for the absorption coefficient for the corresponding absorption bands it seems probable that these bands are due to $^2T_{2g} \rightarrow {}^2T_{1u}$ or $^2T_{2g} \rightarrow {}^2T_{2u}$ transitions. Assignment of these bands unambiguously is not possible in view of the large number of excited states arising from the various charge-transfer configurations which can arise in this molecule.

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[7/1861 *Received, 24th October,* 1977]

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[19] T. J. Barton, unpublished work.