The Electronic Structure of $V(CO)_6$. Why It Is Black

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Abstract: The stable free radical vanadium hexacarbonyl does not absorb appreciably below 25 000 cm^{-1} in dilute solution or when isolated in N_2 matrices at 15 K. In the solid state, however, $V(CO)_6$ appears black due to a broad weak electronic absorption centered at 580 nm (17 250 cm^{-1}). Nonempirical SCF-Xα-DV calculations predict an orbital energy scheme for $V(CO)_6$ that is very similar to the 18e systems $V(CO)_6^-$ and $Cr(CO)_6$. These calculations satisfactorily account for the ionization spectrum of $V(CO)_6$ and its electronic absorption spectrum in dilute solution. Furthermore, the electron-density distribution calculated for the highest occupied molecular orbital [$d^5(t_{2g}{}^5)$] agrees well with that deduced in a previous EPR study. The t_{2g} electrons reside on vanadium about 55% of the time and are about 45% delocalized onto the CO ligands. These data indicate extensive metal–CO π bonding. Single-molecule properties cannot explain the color of solid $V(CO)_6$. A model based on the solid-state excitation process $V(CO)_6V(CO)_6\ (+h\nu) \rightarrow [V(CO)_6{}^+][V(CO)_6{}^-]$ is energetically reasonable on the basis of SCF-Xα-DV calculations. To test this conclusion, electronic spectra of $V(CO)_6/M(CO)_6$ [M = Cr, Mo, W] mixed crystals were measured. In these systems the $M(CO)_6V(CO)_6\ (+h\nu) \rightarrow [M(CO)_6{}^+][V(CO)_6{}^-]$ excitation should occur at higher energy due to the greater ionization potentials of the $M(CO)_6$ complexes compared to $V(CO)_6$. In fact, the doped crystals are pale orange colored and absorb maximally at 475 nm.

Since its synthesis in 1959,[1] the electronic structure of $V(CO)_6$ has remained an enigma. Vanadium hexacarbonyl is the only homoleptic metal carbonyl that exists as a stable free radical. Magnetic susceptibility measurements show the d^5 complex to possess one unpaired electron,[1-3] as expected for the $d^5(t_{2g}{}^5)$ configuration. Below 66 K weak antiferromagnetic coupling ($J = -50$ cm^{-1}) has been observed[3] in the solid state. Infrared,[4,5] EPR,[6,7] and MCD[8] spectral studies all point to a dynamic Jahn–Teller perturbation of the $^2T_{2g}$ ground state at moderate temperatures. Both gas-phase electron diffraction data[9] and an X-ray crystal structure[10] (at −28 °C) indicate approximate octahedral symmetry near room temperature. At low (<100 K) temperatures, a small static distortion appears to lead to a $^2B_{2g}$ ground term; however, there is not yet a consensus as to the exact nature of the distortion.[7a-c] Perhaps more intriguing than the Jahn–Teller distortion, and certainly more puzzling, is the origin of the color of $V(CO)_6$. Vanadium hexacarbonyl has been reported to be yellow in solution;[2,5,7,11] however, it appears black to blue black as solid crystals.

The most detailed study of the electronic spectrum of $V(CO)_6$ is that of the matrix isolated species reported by Barton et al.[8] The UV region consists of very broad bands with a number of overlapping peaks and shoulders, beginning at 25 650 cm^{-1}. In addition, a solid-state spectrum recorded at 77 K by Rubinson[7a] reports other very weak absorption bands extending through the visible and into the near-IR region. Solution spectral studies have been hampered by the broadness of the UV absorptions and the poor solubility and stability of $V(CO)_6$.[12] Electronic spectra of 18e $M(CO)_6$ compounds usually exhibit two intense transitions in the ultraviolet, but do not absorb appreciably at visible wavelengths either in solution or in the solid state.[13] The unusual optical properties of $V(CO)_6$ prompted us to investigate its electronic absorption spectrum in the solid state and in nitrogen matrices at several concentrations.

Electronic structural aspects of the 18e metal hexacarbonyls have not been without controversy. Early extended Hückel calculations[13] found the highest occupied MO to be of t_{2g} symmetry and metal d character and the lowest unoccupied MO to be the metal centered e_g orbital. Other calculations[14-19] also predict that the HOMO is of t_{2g} type, but the nature of the LUMO has not been agreed upon. From crystal field theory, the LUMO is expected to be of e_g symmetry, but semiempirical refined Hückel theory[14] and more recent Xα-MSW[18] and Xα-DV[19] calculations place the e_g orbital above the CO(π^*) levels. One attractive aspect of $V(CO)_6$ is that we can compare the calculated t_{2g} orbital wave function with that experimentally deduced from the EPR hyperfine splittings. Such a test of theory has not been possible for the diamagnetic $M(CO)_6$ systems [M = Cr, Mo, W, V(−I)], where the exact extent of CO–metal π bonding continues to be controversial.[20]

Since no theoretical studies of $V(CO)_6$ have been reported, and in view of the current interest in the properties of organometallic radicals, we examined its electronic structure with the discrete variational (DV) Xα method,[21] which has proved to be capable of spectroscopic accuracy in other calculations of transition-metal complexes.[19,22] The electronic structure of the 18e $V(CO)_6^-$

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Table I. Orbitals, Eigenvalues, and Atomic Orbital Character for Ground-State V(CO)$_6$

orbital	energy, eV	IP, Xα-DV[a]	IP (exptl)[b]	% V 3d	% V 4p	% C 2s	% C 2p	% O 2s(3s)	% O 2p
$4e_g$	0.52			51		25	11	<1 (7)	4
$3t_{2g}$	0.14			48			33		19
$2t_{1g}$	0.06						63		36
$2t_{2u}$	−0.93						60		38
$6t_{1u}$	−1.40				<1	5	58	<1	33
$2t_{2g}$	−4.57	7.37	7.5, 7.8	54			25		20
$5t_{1u}$	−9.21	11.99			4	36	33	<1	28
$3e_g$	−9.98	12.79		16		33	30	1	18
$1t_{1g}$	−10.93	13.66					19		80
$1t_{2u}$	−11.06	13.79					22		77
$4t_{1u}$	−11.29	14.01	12.2–17.5		1	1	19	1	65
$3a_{1g}$	−11.35	14.14				18	30	14	32
$1t_{2g}$	−11.42	14.13		<1			33		65
$2e_g$	−13.08	15.77		1		20	<1	24	54
$3t_{1u}$	−13.10	15.78			1	20	<1	24	54
$2a_{1g}$	−13.79	16.48				46	5	26	23

[a] Based on transition-state calculations for the $2t_{2g}$ and $5t_{1u}$ orbitals. [b] Reference 29.

complex has also been computed for comparison with neutral V(CO)$_6$ and with the literature calculations of closed-shell metal hexacarbonyls. Our spectroscopic data and theoretical estimates suggest the presence of novel charge-separated excited states in solid V(CO)$_6$.

Experimental Section

Vanadium hexacarbonyl anion, as the diglyme-stabilized sodium salt, and the metal hexacarbonyls (Cr, Mo, W) were purchased from Strem Chemicals. Neutral V(CO)$_6$ was synthesized in good yield by oxidation of the anion with orthophosphoric acid (MCB).[23] Mixed crystals of V(CO)$_6$ in Cr(CO)$_6$ were prepared by two different routes. A mixture of vanadium hexacarbonyl and chromium hexacarbonyl crystals ~1:1000 were cooled to 77 K, evacuated to 10^{-4} torr, and then stored for 10 days at 20 °C, resulting in small, rust-orange colored crystals. In the second method, a sublimator was charged with a ~1:100 (V(CO)$_6$:Cr(CO)$_6$) mixture in a drybox, then evacuated to 10^{-4} torr, and left overnight at 35 °C; large crystals identical in color with the first method deposited rapidly upon a cold finger (5 °C) in the flask. The vanadium content of doped crystals used in spectroscopic studies was determined by atomic absorption spectroscopy (Hitachi 180-70 polarized Zeeman atomic absorption spectrophotometer), using $[N(C_2H_5)_4][V(CO)_6]$ as a standard (in acetonitrile solvent). The mixed crystals appeared to be moderately air stable at room temperature. As an added precaution, KBr pellets for electronic and infrared spectra were prepared in a Vacuum Atmospheres drybox under nitrogen. Mixed V(CO)$_6$/Mo(CO)$_6$ and V(CO)$_6$/W(CO)$_6$ samples were prepared and analyzed in a similar fashion. Solutions for optical spectra were prepared by using dry, triply freeze–pump–thaw degassed hexane or cyclohexane that was vacuum distilled onto the sample.

Low-temperature spectra utilized a modified closed-cycle helium refrigerator described previously.[24] For both the optical and infrared studies the sample substrate was sapphire and the vacuum shroud windows were made of CaF$_2$. Electronic spectra were measured on either a Cary 17D or Perkin-Elmer 320 spectrophotometer; infrared spectra were recorded on a Nicolet 7199 Fourier transform infrared spectrophotometer. Nitrogen (Airco 99.999%) matrices were prepared by using the pulsed deposition technique.[25] The sample bulb was equipped with a freeze-out tip as described by Rochkind[25a] (necessitated due to the high volatility of V(CO)$_6$). Solid films of V(CO)$_6$ were generated on the cold window with a sample bulb containing only solid complex (no matrix gas) and with a system pressure below 10^{-5} torr. Over protracted periods of time (>4 h) at room temperature, the vanadium hexacarbonyl in the sample bulb gradually decomposed, coating the inside of the bulb with a pyrophoric vanadium mirror, and yielding gaseous CO (by IR analysis). Solid microcrystalline films of about 1:200 V(CO)$_6$/Cr(CO)$_6$ mixed crystals were prepared by sublimation (at 50 °C) onto a cooled (−77 °C) sapphire window. Electronic spectra (15 K) of KBr pellets of other more dilute mixed crystals (V(CO)$_6$:Cr(CO)$_6$ = 1:700 by atomic absorption) proved to be identical with spectra of the more concentrated microcrystalline films, except for some diminished resolution from scattering. Diffuse reflectance spectra of doped crystals were also recorded on the Cary 17 with the Model 1411 reflectance attachment. Powered samples dispersed in BaSO$_4$ were mounted on Scotch-brand tape and measured at room temperature. Pure BaSO$_4$ powder was used to establish a base line.

Electronic structure calculations of V(CO)$_6$ and V(CO)$_6^-$ were performed on a Harris 800 minicomputer and employed the discrete variational Xα[21] method. Numerical atomic orbitals were used as basis functions. For vanadium, all orbitals through 4d were included; for C and O, orbitals through 3p were used. Orbitals 1s, 2s, 2p, 3s on vanadium and 1s on both carbon and oxygen were treated as part of a frozen core in the molecular calculations. Valence orbitals were explicity orthogonalized against the numerical atomic core wave functions. Atomic orbital populations were computed using the Mulliken scheme.[26] The molecular Coulomb potential was calculated by utilizing a least-squares fit of the model electron density to the true density (eq 1),[21e] evaluated over the

$$\langle(\rho^{\text{true}} - \rho^{\text{model}})^2\rangle = \text{minimum} \qquad (1)$$

same point grid used in the variational (SCF) solution of the Schrödinger equation. Here the "true" charge density, ρ^{true}, is given by

$$\rho^{\text{true}}(\bar{r}) = \sum_j f_j|\phi_j(\bar{r})|^2 \qquad (2)$$

and the model charge density is expressed as an s-wave expansion with overlapping spherical functions on each center,

$$\rho^{\text{model}}(\bar{r}) = \sum_{\nu\text{nl}} g_{\text{nl}}{}^{\nu}|R_{\text{nl}}(r_\nu)|^2 \qquad (3)$$

where R_{nl} are the radial atomic basis functions and $g_{\text{nl}}{}^{\nu}$ the coefficients that best satisfy eq 1. Spin-restricted and spin-polarized transition-state[27] calculations provided energies for optical transitions and for ionization processes. Valence ionization potentials for V(CO)$_6$ were computed by assuming similar relaxation to the $2t_{2g}$ IP case as was found valid (±0.1 eV) for Mo(CO)$_6$.[19b] Bond distances for V(CO)$_6$ and V(CO)$_6^-$ were taken from published structures[10,28] and idealized to octahedral symmetry.

Results and Discussion

Electronic Structure Calculations and the Isolated Molecule. Although V(CO)$_6$ has the distinction of being the only isolable 17-electron hexacarbonyl, its electronic structure does not differ greatly from that of the 18-electron hexacarbonyls. Our computational results for V(CO)$_6$ and its reduced form, V(CO)$_6^-$, are very similar. The ensuing discussion summarizes the findings for neutral V(CO)$_6$; those for the anion may be made by analogy, except where specifically noted.

Previous calculations from these laboratories employed the SCC-Xα-DV[19,22] (self-consistent charge) approach, whereby the coefficients $g_{\text{nl}}{}^{\nu}$ to the radial atomic functions $R_{\text{nl}}(r_\nu)$ (see eq 3) in the model density were taken directly from atomic Mulliken populations. This led to calculations that reproduced relative orbital energies very well, but frequently the calculated ionization

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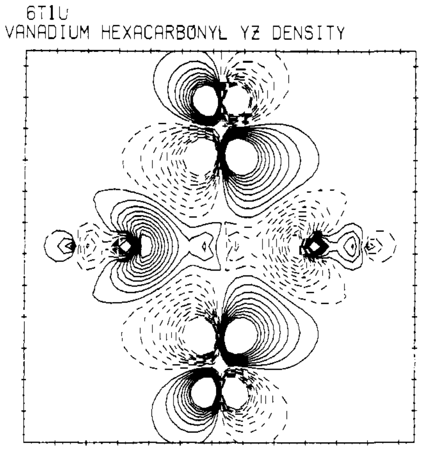

Figure 1. Contour plot of the $6t_{1u}$ orbital of $V(CO)_6$ in a $V(CO)_4$ plane. Contributions from four carbon monoxides dominate since vanadium d orbitals do not transform as t_{1u}. The interval between successive contours is 0.0675 e/Å³.

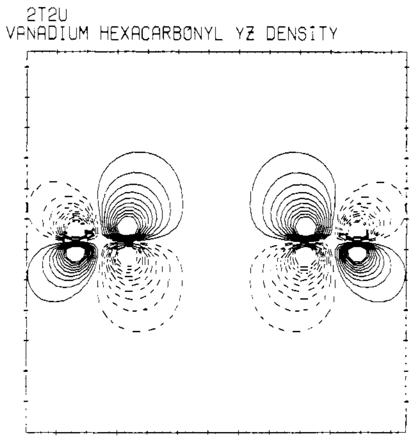

Figure 2. Contour plot of the $2t_{2u}$ orbital of $V(CO)_6$ in a $V(CO)_4$ plane. Only contribution from two CO ligands is evident because this section is a nodal plane for the other two CO's. The interval between successive contours is 0.1012 e/Å³.

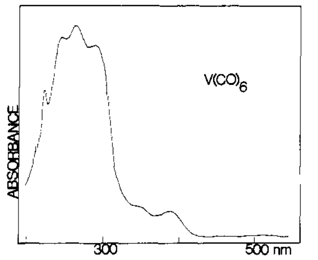

Figure 3. Electronic absorption spectrum of a thin film of $V(CO)_6$ at 15 K. The periodic ripples in the base line arise from interference fringes due to the thin film.

potentials were too tightly bound. Similar results were obtained in preliminary SCC-Xα-DV calculations on $V(CO)_6$. The least-squares approach (hereafter abbreviated SCF-Xα-DV) we then adopted (eq 1) substantially refines the calculation of the Coulomb contribution to the potential. This improves the relative energies, compared to the SCC results, and leads to calculated ionization potentials that agree well with experimental energies.

Results of SCF-Xα-DV calculations for $V(CO)_6$ (Table I) closely resemble those found experimentally in photoelectron,[29,30] optical,[8,13] and EPR[7] spectroscopic studies. The highest occupied molecular orbital is of t_{2g} symmetry, with a calculated ionization energy of 7.4 eV, compared to the experimentally observed 7.5/7.8 eV doublet. In agreement with the UV PES studies,[29] we expect the next ionization band to be very broad, extending from 12 to 17 eV. While the HOMO consists of 54% vanadium 3d and approximately 45% carbon and oxygen 2p atomic character, the more tightly bound, broad band of ionizations is composed of chiefly ligand-based orbitals. At higher ionization energy than 16.5 eV, there is about an 11-eV gap calculated before core ionizations are reached.

Our calculations account for the optical properties of isolated $V(CO)_6$. Two dipole-allowed electronic excitations, $2t_{2g} \rightarrow 6t_{1u}$ and $2t_{2g} \rightarrow 2t_{2u}$, are placed at 3.32 eV (26780 cm^{-1}) and 3.84 eV (30980 cm^{-1}), respectively, by spin-restricted transition-state calculations. The $6t_{1u}$ and $2t_{2u}$ orbitals are largely CO-based π^* orbitals (Figures 1 and 2). In fact, the onset of intense absorption in both matrix-isolated and solid $V(CO)_6$ (Figure 3) occurs at 400 nm (25000 cm^{-1}, 3.1 eV) and continues throughout the ultraviolet spectral regime. The spectral complexity is not unexpected since the two one-electron transitions actually give rise to a collection of states. For example, $2t_{2g}{}^4 6t_{1u}$ yields ${}^2A_{1u}$, ${}^2A_{2u}$, 2 ${}^2E_u$, 4 ${}^2T_{1u}$, 3 ${}^2T_{2u}$, ${}^4A_{1u}$, ${}^4E_u$, ${}^4T_{1u}$, and ${}^4T_{2u}$, while $2t_{2g}{}^4 2t_{2u}$ produces ${}^2A_{1u}$, ${}^2A_{2u}$, 2 ${}^2E_u$, 3 ${}^2T_{1u}$, 4 ${}^2T_{2u}$, ${}^4A_{2u}$, ${}^4E_u$, ${}^4T_{1u}$, and ${}^4T_{2u}$. Transitions from ${}^2T_{2g}$ to ${}^2A_{2u}$, ${}^2E_u$, ${}^2T_{1u}$, and ${}^2T_{2u}$ excited states are spin and electric dipole allowed. Therefore, the two one-electron transitions should generate 20 dipole-allowed transitions in the ultraviolet absorption spectrum! Furthermore, LMCT transitions such as $5t_{1u} \rightarrow 2t_{2g}$ are calculated to begin to occur at 4.74 eV (38200 cm^{-1}). We will not attempt a more detailed assignment of the complex UV spectrum.

In closed-shell $V(CO)_6^-$ the situation is simpler. We calculate $2t_{2g} \rightarrow 6t_{1u}$ (${}^1A_{1g} \rightarrow {}^1T_{1u}$) and $2t_{2g} \rightarrow 2t_{2u}$ (${}^1A_{1g} \rightarrow {}^1T_{2u}$) at 3.34 eV and 3.85 eV. Experimentally it is known [13,31] that these absorption bands occur at 3.52 eV and 4.66 eV in $[(C_2H_5)N][V(CO)_6]$. A previous spectroscopic study[19] demonstrated a significantly distorted (0.15 Å) metal–carbon bond length in the $2t_{2g} \rightarrow 6t_{1u}$ (${}^1T_{1u}$) excited states of 18e $M(CO)_6$ complexes. The contribution from the CO sp-hybrid σ orbital shown in Figure 1 does suggest that metal–carbon σ as well as π bonding should be affected by the "MLCT" process.

While the highest occupied molecular orbital is generally agreed to be t_{2g}, the symmetry assignment of the lowest energy unoccupied orbital (LUMO) of the metal hexacarbonyls has been a matter of debate. Crystal field theory predicts the LUMO for an octahedral transition-metal complex to be of e_g symmetry and of predominantly metal d character. Beach and Gray,[13] using an extended Hückel MO approach, calculated the LUMO to transform as e_g for $Cr(CO)_6$. On the basis of these calculations, a weak band slightly lower in energy than the intense MLCT transitions has been assigned as a ligand field $2t_{2g} \rightarrow 4e_g$ transition. The uncommonly high intensity ($\epsilon \sim 2000$)[13] of this low-energy shoulder may cast some doubt on its assignment as a symmetry-forbidden d–d type ligand field transition. An alternative assignment (but not any better on intensity grounds) is possible if one considers the shoulder to be the low-energy triplet component of the $2t_{2g} \rightarrow 6t_{1u}$ excitation, a ${}^3T_{1u}$ state. Spin triplet character has, in fact, been observed in emission spectra for $M(CO)_6$ complexes[32] subsequent to excitation into the lowest energy absorption band. One other assignment for the transition would be a dipole-forbidden MLCT excitation (e.g., one of the dipole-forbidden singlet states derived from $2t_{2g} \rightarrow 6t_{1u}$).

The possibility that the LUMO is not of e_g symmetry has been guardedly advanced in the past.[14,18] At present we know of no definitive experimental evidence for either viewpoint, but note that several different Xα calculations do not predict the LUMO to

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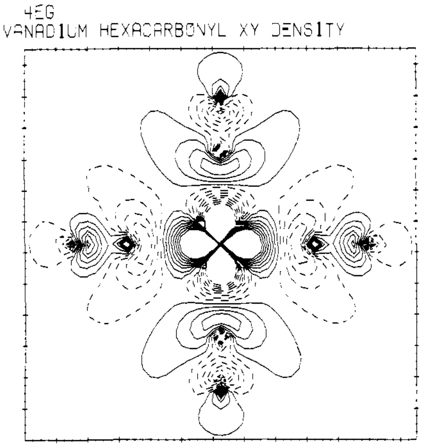

Figure 4. Contour plot of the $4e_g$ orbital of $V(CO)_6$ in a $V(CO)_4$ plane. Note the metal–ligand σ^* character. The interval between successive contours is 0.1350e/Å^3.

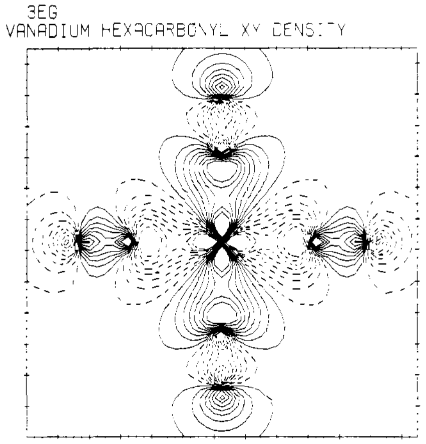

Figure 5. Contour plot of the $3e_g$ orbital of $V(CO)_6$ in a $V(CO)_4$ plane. Note the covalent metal–ligand σ bonding between $d_{x^2-y^2}$ and the CO "lone pair" σ-donor orbital. The interval between successive contours is 0.1350 e/Å^3.

be e_g. Using the SCF-Xα-DV approach, we find the LUMO to be of t_{1u} symmetry, with the "metal-based" (Figure 4) e_g orbitals at significantly higher energy. Localized "d–d" excitations may be subject to large relaxation energy shifts and exchange splittings. This could alter predictions based on orbital energies. Therefore, we have employed spin-polarized transition-state calculations to explicitly estimate the energies of the $^1A_{1g} \rightarrow {}^3E_g$ and $^1A_{1g} \rightarrow {}^1E_g$ excitations derived from the one-electron $2t_{2g} \rightarrow 4e_g$ promotion in $V(CO)_6^-$. These energies were found to be 5.07 and 5.42 eV, respectively. We realize that our calculations neglect configuration interaction and employ a limited basis set. Serious errors may therefore occur in computed excitation energies. Nonetheless a discrepancy exists between the Xα and Hückel calculations as to the placement of the d–d transition in simple metal hexacarbonyls. For the M–L σ^* (e_g) orbital to be destabilized so much with respect to the highest occupied M–L π (t_{2g}) MO, the σ- and π-bonding interactions between the metal and the six carbonyls must be very strong. Figures 4 and 5 illustrate the pronounced σ^*- and σ-bonding nature, respectively, of the $4e_g$ and $3e_g$ orbitals.

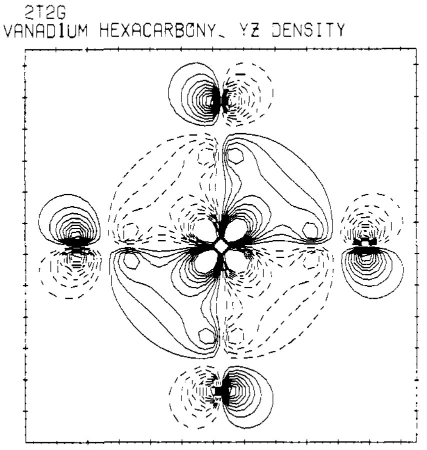

Figure 6. Contour plot of the $2t_{2g}$ orbital of $V(CO)_6$ in a $V(CO)_4$ plane. Note the covalent π bonding between the d_{yz} orbital and the CO(π^*) orbitals. The interval between successive contours is 0.1350 e/Å^3.

Table II. Atomic Orbital Populations for Ground-State $V(CO)_6$

V	C	O
3p 6.00	2s 1.54	2s 1.78
3d 3.62	2p 2.43	2p 4.37
4s 0.17	3s 0.01	3s 0.01
4p −0.08	3p 0.09	3p 0.00
4d −0.19		
$Q^a = +1.48$	$Q_C = -0.08$	$Q_O = -0.16$
$\int_{chg}{}^b = 1.57$	$\int = -0.09$	$\int = -0.17$

[a] Q denotes the atomic charge from a Mulliken population analysis. [b] $\int_{chg}$ denotes the charge calculated by volume integration about each atom

Table III. Atomic-Orbital Populations for Ground-State $V(CO)_6^-$

V	C	O
3p 6.01	2s 1.57	2s 1.76
3d 3.77	2p 2.50	2p 4.47
4s 0.02	3s 0.02	3s 0.01
4p −0.15	3p 0.09	3p −0.01
4d −0.12		
$\int_{chg}{}^a = +1.42$	$\int = -0.09$	$\int = -0.32$

[a] $\int_{chg}$ denotes the charge calculated by volume integration about each atom.

Mulliken atomic charge analyses of the molecular eigenvectors (see Table I) and the orbital contour plot (Figure 6) reveal that the vanadium–carbonyl $2t_{2g}$ π linkage is covalent in character; i.e., the π-bonding electrons are very much delocalized over all atoms in the molecule. The differences between atomic charges in $V(CO)_6$ and $V(CO)_6^-$ (note the small difference in vanadium charges in Tables II and III) further illustrate this point. In a recent low-temperature EPR study, Bratt et al.[7b] took advantage of the hyperfine splittings in the EPR spectrum of $V(CO)_6$ to show that the unpaired electron resides in an orbtial composed of approximately 57% metal 3d, 8.5% metal 4s,[33a] and 35% CO character. For the first time we can compare the calculated t_{2g} orbital wave function (Table I) with these values. The agreement between experiment and theory suggests that our Xα calculations not only reproduce ionization energies well but also provide reasonable models of orbital densities.

Covalent π bonding in the metal hexacarbonyls has been a controversial subject.[13,14–20] Recent Xα calculations differ as to how significant this may be in $Cr(CO)_6$.[17–20] Projection of the SCF-Xα-SW charge distribution onto an LCAO basis led to a composition of 74% Cr 3d and 25% CO π character for the t_{2g} orbital wave function.[20a] This was said to constitute significant π back-bonding. Our calculations and the EPR data suggest that metal–ligand π bonding may be somewhat more extensive in $V(CO)_6$. Delocalization of the t_{2g} electrons would be expected to quench the orbital angular momentum of the $^2T_{2g}$ ground state.[33b] This helps to account for the small Jahn–Teller splitting and the near free-electron g value ($g_{iso} = 2.035$)[7b] seen for $V(CO)_6$.

Electronic Absorption Spectra of Solid $V(CO)_6$. The electronic absorption spectrum of a sublimed solid film of vanadium hexacarbonyl at 15 K is presented in Figure 7. This spectrum closely resembles the matrix isolation results in the ultraviolet region;

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(33) (a) Bratt et al.[7b] assumed that a small static Jahn–Teller distortion led to mixing of the a_{1g}(4s) orbital with the t_{2g}(3d) orbital. (b) Figgis, B. N. "Introduction of Ligand Fields"; Interscience: New York, 1966; p 275.

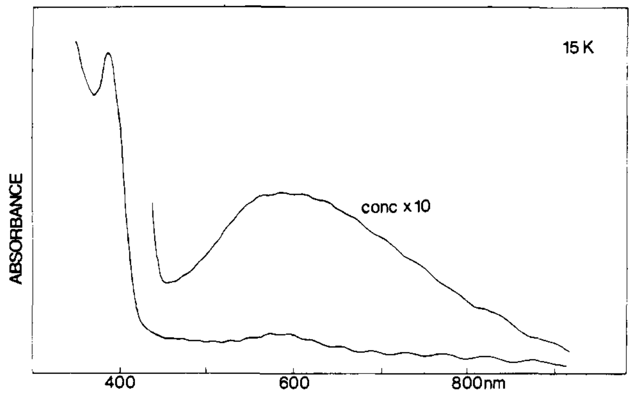

Figure 7. Expanded views of the low-energy region of the electronic absorption spectrum of solid $V(CO)_6$ at 15 K.

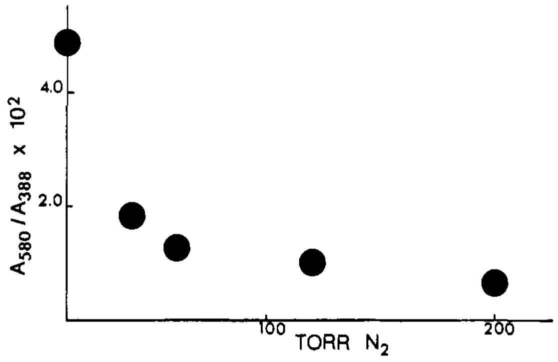

Figure 8. Plot of the ratio of visible to UV absorption in $V(CO)_6$ as a function of relative dilution in a nitrogen matrix at 15 K. Increasing the pressure of N_2 at constant temperature corresponds to more dilute matrices.

however, we find an additional weak, broad transition centered at 580 nm. Although the absorption responsible for the blue-black color of the solid is not especially intense, it is very broad and therefore absorbs at nearly all visible wavelengths. Varying the concentration of $V(CO)_6$ from pure substrate (solid film) to approximately 1:300 in a nitrogen matrix provided a qualitatively identical ultraviolet spectrum. The intensity of the visible absorption (580 nm) was found to be strongly dependent on the concentration of $V(CO)_6$ and vanished in dilute matrices.

Since the intensities of the UV bands appeared to be independent of substrate concentration, they were chosen to serve as internal standards for a closer examination of the visible spectral region. In particular, the 388-nm absorption was adopted as a standard. The ϵ for this transition is about 2000 M^{-1} cm^{-1} in hexane solution.[34] Assuming a similar intensity in the solid provides an estimate of 100 M^{-1} cm^{-1} for the 580-nm absorption in solid $V(CO)_6$. When the 388-nm standard is used, the relative concentration of $V(CO)_6$ could be varied in a N_2 matrix while keeping the total amount of complex constant. A plot of the absorbance at 580 nm (relative to the 388-nm absorbance) vs. the matrix concentration appears in Figure 8. This dilution dependence strongly suggests that the visible band is due to aggregates of vanadium hexacarbonyl and not to individual molecules.

There are several possible explanations for the origin of the low-energy absorption. Initially, we considered Davydov or factor group effects. A photon incident on one of two symmetry-equivalent absorbing sites produces an excited state capable of interacting with the other site. Two degenerate electronic transitions (for isolated molecules) would then split into one high- and one low-energy component.[35] Hence a Davydov splitting of a UV transition could generate a new component at lower energy. If the 580-nm band were indeed the low-energy component of this exciton-split absorption, one would expect a similar substrate-concentration-dependent band in the ultraviolet. However, no change in the UV spectrum of $V(CO)_6$ was observed with variation of concentration from a dilute matrix to a solid film. Furthermore, the UV bands in the d^6 metal hexacarbonyls might also be expected to show similar solid-state behavior [$V(CO)_6$ and $M(CO)_6$, M = Cr, Mo, W, are essentially isomorphous in the solid state[10,36]] if the exciton hypothesis were true. The d^6 hexacarbonyls do not possess such a low-energy absorption. Similarly, both the concentration dependence and the energy (17 250 cm^{-1}) of the visible band argue against a d → d transition among sublevels of the Jahn–Teller split $^2T_{2g}$ ground state. Estimates of the Jahn–Teller splitting range from 400 to 1400 cm^{-1}.[6-10]

A magnetic susceptibility study by Bernier and Kahn[3] found vanadium hexacarbonyl to behave in a typically paramagnetic fashion from 66 to 300 K. At 66 K there is a sharp break in the susceptibility curve as it becomes more antiferromagnetic in shape; a phase transition at that temperature was suggested. It seems unlikely that the dark color of solid $V(CO)_6$ is due to direct V–V overlap since the exchange coupling is weak ($J = -50$ cm^{-1} below 66 K), and the color persists, with an approximately (±20%) temperature-independent intensity, from 300 K down to 15 K; any interaction responsible for the visible absorption would need to appear at all temperatures. The unit cell of $V(CO)_6$ (Figure 9) does not provide evidence for direct intermolecular interactions. There are no metal–metal distances shorter than 6.397 Å, and the closest V–O contacts are about 4.07 Å. A previous band-structure calculation[37a] based on weak chain interactions along the crystallographic *c* axis (Figure 9) could not account for the color of the solid. Ozin and co-workers[37b] have demonstrated the reluctance of $V(CO)_6$ to form dimers; the unstable $V_2(CO)_{12}$ complex could only be prepared by condensing V_2 and CO vapors at 15 K. The possibility of pair transitions[38] can also be eliminated since the isolated molecule does not possess an absorption at half the frequency of the 580-nm (17 200 cm^{-1}) band.

An electronic excitation from the second highest occupied orbital into the partly occupied $2t_{2g}$ orbital may also be ruled out. Our transition-state Xα calculations estimate the electric dipole allowed $5t_{1u}{}^6 2t_{2g}{}^5 \rightarrow 5t_{1u}{}^5 2t_{2g}{}^6$ excitation energy to be 4.74 eV (38 200 cm^{-1}), much higher than the energy of concern here. The large $5t_{1u}$–$2t_{2g}$ splitting is experimentally confirmed by the photoelectron spectroscopic studies.[29]

Shortcomings of the above possible assignments and the known stability of the vanadium hexacarbonyl anion[39] lead us to propose the assignment depicted by eq 4 for the transition unique to the

$$2V(CO)_6 \xrightarrow{h\nu} \underset{16e}{[V(CO)_6{}^+]}\ \underset{18e}{[V(CO)_6{}^-]} \quad (4)$$

solid state. According to this mechanism, absorption of one photon of light by $V(CO)_6$ leads to a resonance-stablized ionic excited state.[40,41] A theoretical estimate suggests that excitation to the ionic excited state is energetically feasible. The energy of the transition is approximated[42] by eq 5, where $h\nu$ is the transition

$$h\nu = IP[V(CO)_6] - EA[V(CO)_6] - e^2/r_{V-V} \quad (5)$$

energy, IP and EA stand for the ionization potential and electron affinity, respectively, and r_{V-V} is the vanadium–vanadium separation in the crystal. Using $r_{V-V} = 6.40$ Å and the calculated IP

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[34] Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032–4034.

[35] Craig, D. P.; Walmsley, S. H. "Excitons in Molecular Crystals: Theory and Applications"; W. A. Benjamin: New York, 1968.

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[37] (a) Bullett, D. W.; Woolley, R. G. calculation cited in ref 10. (b) Ford, T. A.; Huber, H.; Klotzbucher, W.; Moskovits, M.; Ozin, G. A. *Inorg. Chem.* **1976**, *15*, 1666–1669.

[38] Varsaynl, F.; Dieke, G. H. *Phys. Rev. Lett.* **1961**, *7*, 442–443.

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[40] Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600–608; **1952**, *74*, 811–814.

[41] (a) Schramm, C.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 4554–4558. (b) Webb, J. D.; Bernstein, E. R. *Ibid.* **1978**, *100*, 483–485.

[42] An analogous equation was used to estimate the energy of the "anomalous" low-energy band in alkali halides (Hilsch, R.; Pohl, R. W. *Z. Phys.* **1929**, *57*, 145–153).

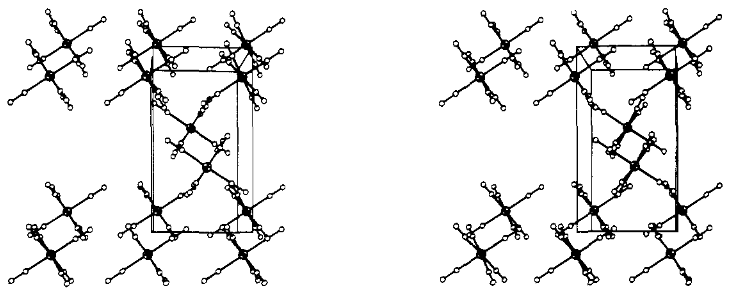

Figure 9. Stereoscopic plot of the unit cell of $V(CO)_6$ at 244.7 K (using coordinates of ref 10). The vertical axis is *a* and the horizontal axis is *c*.

and EA yields a value for $h\nu$ of 3.05 eV. The estimate compares fairly well with the energy (2.15 eV) of the 580-nm absorption and establishes the plausibility of such an excitation process. Although we have to rely on the accuracy of the SCF-Xα-DV calculated EA, this seems justified in view of the accuracy of the calculated IP. This approach also suggests why the 580-nm absorption is so broad. Several values of r_{V-V} are possible, and the excited state is derived by coupling single-site wave functions such as t_{2g}^4 and t_{2g}^6. Several components of the t_{2g}^4 configuration (in addition to possible Jahn–Teller effects) can lead to splittings of the 580-nm absorption. Furthermore, in the solid state it may be more appropriate to view the process as a charge-transfer exciton.[43] Such delocalization will also tend to increase the electronic bandwidth.

The alternative possibility, that there may exist an equlibrium amount of $[V(CO)_6]^+$ and $[V(CO)_6]^-$ pairs,[44] was investigated by examining the Fourier-transform infrared spectrum of both matrix-isolated and solid films of vanadium hexacarbonyl. The C–O stretching frequency of the anionic species is known to be $\sim$1860 cm^{-1}; the ν_{CO} for the neutral is 1970 cm^{-1}; the cationic hexacarbonyl would be anticipated to have ν_{CO} $\sim$2050 cm^{-1}.[45] The FT–IR spectrum of a solid film of $V(CO)_6$ showed no evidence of any metal carbonyl based absorption band other than that of neutral $V(CO)_6$. Photolysis with λ $\sim$600 nm for periods of up to 1.5 h gave no change in this spectrum; UV photolysis appeared to only lead to slow decomposition of the hexacarbonyl to the metal. These experiments rule out the presence of spectroscopically detectable quantities of $[V(CO)_6]^+[V(CO)_6]^-$ in the solid state at equilibrium or after photolysis. An intervalence transition from such an impurity is therefore an unlikely possiblity. The ionic excited state of eq 4 must relax to the ground state on time scales short compared to our experiments. If the ion pair corresponds to an electronic excited state that rapidly relaxes to the ground state after excitation, then the appropriate antisymmetric wave function[46] (vide infra) for the charge-separated state must be constructed.

To further test the hypothesis of an intermolecular ionic excited state, $V(CO)_6$ was doped 1:700 and 1:200 into the isostructural[36] chromium hexacarbonyl host. Since the EA calculated could well be in error, we used the visible absorption energy (2.15 eV) in solid vanadium hexacarbonyl and the experimental IP for $V(CO)_6$ to obtain an empirical electron affinity for $V(CO)_6$ of 3.11 eV (as opposed to that of 2.10 eV calculated from Xα-DV theory), which fits the experimental electronic absorption energy of 2.15 eV. This EA was used, along with the experimental IP of $Cr(CO)_6$ (Table IV), to predict the position of the charge-separated excited state for $V(CO)_6$ doped $Cr(CO)_6$ according to eq 6. The higher

$$\begin{gathered} Cr(CO)_6V(CO)_6 \xrightarrow{h\nu} [Cr(CO)_6{}^+][V(CO)_6{}^-] \\ h\nu = IP[Cr(CO)_6] - EA[V(CO)_6] - e^2/r_{Cr-V} \end{gathered} \tag{6}$$

first IP of $Cr(CO)_6$ compared to $V(CO)_6$ should blue-shift the transition energy to 3.02 eV from 2.15 eV (Table IV). In fact, the mixture of blue-black $V(CO)_6$ microcrystals and white $Cr(CO)_6$ yielded intensely colored rust-orange crystals upon cosublimation. Composition of the rust-orange solid as consisting of only $Cr(CO)_6$ and $V(CO)_6$ molecular units was confirmed by solid-state infrared measurements and by dissolving a crystal in hexane and recording its absorption spectrum (which lacked the "orange" solid-state absorption). Figure 10 gives the electronic spectrum of the doped ($\sim$1:200) crystals as a polycrystalline film at 15 K. A similar spectrum was obtained for more dilute, 1:700, mixed crystals dispersed in a KBr pellet. As expected, the absorption band lies to higher energy than in pure $V(CO)_6$. In addition, the visible band for the doped species appears to be sharper and possibly more intense than in solid $V(CO)_6$.

Table IV. Parameters Used in the Calculation of Absorption Band Energies for the Ionic Excited State

M	IP $M(CO)_6$, eV	r_{V-M}, Å	e^2/r_{V-M}, eV	E_{vis}^{calcd}, eV	E_{vis}^{exptl}, eV
V	7.5[a]	6.40[c]	2.25	3.05[e]	2.15
V	7.5	6.40	2.25	2.15[f]	2.15
Cr	8.40[b]	6.33[d]	2.27	3.02[f]	2.58
Mo	8.45[b]	6.48[d]	2.22	3.17[f]	2.6–2.7
W	8.30/8.59[b]	6.42[d]	2.24	2.95[f]	2.6–2.7

[a] From ref 29. [b] From ref 30. [c] From ref 10. [d] From ref 36. [e] Using EA^{calcd} $[V(CO)_6]$ = 2.10 eV from DV-Xα transition-state calculations. [f] Using $EA^{effective}$ $[V(CO)_6]$ = 3.11 eV, which is derived to "fit" the electronic absorption spectrum of solid $V(CO)_6$.

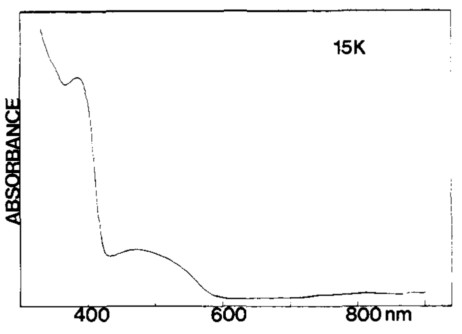

Figure 10. Electronic absorption spectrum at 15 K of $V(CO)_6$ doped ca. 1:200 into $Cr(CO)_6$.

Diffuse reflectance spectra of $Cr(CO)_6/V(CO)_6$ mixed crystals also exhibit the 2.58-eV absorption. When $V(CO)_6$ was doped into $Mo(CO)_6$ and $W(CO)_6$, a solid-state absorption was found at about 2.6–2.7 eV. Due to the broadness of the band and the nearby UV absorption, it was not possible to accurately determine band positions. On the basis of the ionization potentials of $Mo(CO)_6$ and $W(CO)_6$ and the structural data (Table IV and eq 6), we would still predict a transition in this spectral region.

Nature of the Transition. We have provided evidence for ionic excited states in $V(CO)_6$ and in $V(CO)_6/M(CO)_6$ [M = Cr, Mo, W] mixed crystals. It is appropriate to compare these transitions with those found in mixed-valence compounds and in donor–acceptor (charge-transfer) complexes. The ionic excited state does not resemble the intervalence charge-transfer state common to mixed-valence systems. In the latter case the energy of excitation arises from vibrational (Franck–Condon) reorganization, and there

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(43) Gutman, F.; Lyons, L. E. "Organic Semiconductors"; Wiley: New York, 1967. Abbi, S. C.; Hanson, D. M. *J. Chem. Phys.* **1974**, *60*, 319–320.

(44) First suggested to us by Prof. Calderazzo.

(45) Breeze, P. A.; Burdett, J. K.; Turner, J. J. *Inorg. Chem.* **1981**, *20*, 3369–3378.

(46) Trogler, W. C. *Inorg. Chem.* **1980**, *19*, 697–700; **1982**, *21*, 2118.

is little difference between the amount of charge separation in the ground and excited states.[47] Better analogues of the optical transitions in $V(CO)_6$ are the charge-transfer transitions found in donor–acceptor complexes.[48] In these cases the excitation energy may also be correlated with ionization potentials and electron affinities; however, such systems usually evidence appreciable ground-state interaction. Ground-state effects must be extremely weak in the $V(CO)_6$ systems we studied. For example, hexane solutions of $V(CO)_6$ do not exhibit detectable absorption due to aggregate formation. The proximity of the molecular centers dictated by the solid state is necessary to observe the transition. Consequently, the $V(CO)_6$ systems could be considered donor–acceptor complexes approaching the limit of zero-ground-state interaction.

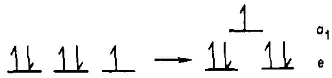
In the coupled chromophore model[49] the ionic transition in $V(CO)_6$ can be represented as

$$V(CO)_6V(CO)_6 \rightarrow V(CO)_6^{\mp}V(CO)_6^{\pm}$$

$$a_{t_{2g}}{}^5b_{t_{2g}}{}^5 \rightarrow a_{t_{2g}}{}^4b_{t_{2g}}{}^6 \text{ or } a_{t_{2g}}{}^6b_{t_{2g}}{}^4$$

The single-center electronic states for $t_{2g}{}^4$ are ${}^1A_{1g}$, ${}^1E_g$, ${}^1T_{2g}$, ${}^3T_{1g}$; for $t_{2g}{}^5$, ${}^2T_{2g}$; and for $t_{2g}{}^6$, ${}^1A_{1g}$. Spin selection rules dictate that a singlet-coupled $a_{t_{2g}}{}^5b_{t_{2g}}{}^5$ ground state may only be excited to an $a_{t_{2g}}{}^4b_{t_{2g}}{}^6$ state derived from the singlet components of $a_{t_{2g}}{}^4$. A similar argument can be made for the triplet case. This shows that our proposed transition does not violate spin selection rules.

Next the orbital nature of dimer states will be explored. Assume that a small trigonal perturbation[50] (e.g., solid state along *c*) splits the $t_{2g}{}^5$ configuration as follows:



Two unpaired electrons on two vanadium centers (using a and b for the two centers, the electrons no. 1 and 2 are in parentheses) can couple to yield the weak coupling wave functions[46] (neglecting normalization constants):

$$\Psi_g = a_{a_1}(1)b_{a_1}(2) + a_{a_1}(2)b_{a_1}(1) \quad (7)$$

$$\Psi_T = a_{a_1}(1)b_{a_1}(2) - a_{a_1}(2)b_{a_1}(1) \quad (8)$$

$$\Psi_{ionic} = a_{a_1}(1)a_{a_1}(2) + b_{a_1}(1)b_{a_1}(2) \quad (9)$$

$$\Psi'_{ionic} = a_{a_1}(1)a_{a_1}(2) - b_{a_1}(1)b_{a_1}(2) \quad (10)$$

Application of the Pauli principle demands that Ψ_g correspond to the singlet coupled ground state; Ψ_T correspond to the low lying triplet; Ψ_{ionic} and Ψ'_{ionic} correspond to two singlet ionic excited states. Only the transition $\Psi_g \rightarrow \Psi_{ionic}$ is both spin and dipole allowed; however, it will possess very weak intensity due to low orbital overlap. In view of the large V–V separation, it is somewhat surprising that there is appreciable oscillator strength for the ionic excited state in solid $V(CO)_6$.

We do not fully understand the intensity-giving mechanism; however, there is precedent for such behavior. Outer-sphere charge-transfer transitions between coordinately saturated metal complexes are known in systems where the direct overlap between two metal centers must be small.[51] Rare gases and some metal hexafluorides exhibit rare gas to metal complex charge-transfer bands in condensed phases even though ground-state overlap is extremely weak.[41b] "Stacked" donor–acceptor crystals exhibit optical charge-transfer bands even in cases where there is poor overlap between donor and acceptor orbitals.[52] Finally, we note the existence of intervalence charge-transfer absorptions between metals as far as 11 Å apart even when they are bridged by saturated ligands.[53]

Conclusions

The orbital energy scheme for the 17e $V(CO)_6$ radical does not differ greatly from that of related 18e species such as $Cr(CO)_6$. Consequently, their photoelectron and optical absorption spectra display many similarities. One difference is the large electron affinity of the $V(CO)_6$ radical.[54] This unique aspect of its electronic structure explains the low-energy intermolecular ionic excited states observed in condensed phases. One other distinguishing feature of $V(CO)_6$ is its kinetic lability. Recent work[34] has shown $V(CO)_6$ to be 10^{10} times more reactive than $Cr(CO)_6$ toward nucleophiles as a consequence of a low-energy associative pathway. Again, the high electron affinity of $V(CO)_6$ compared to $Cr(CO)_6$ (which does not possess a suitable acceptor orbital) may stabilize the buildup of excess electron density in the transition state of expanded coordination number. Studies are currently under way to explore this latter hypothesis. A final point of note is the greater ease of oxidation of $V(CO)_6$ (IP = 7.5 eV) as compared to $Cr(CO)_6$ (IP = 8.4 eV).

Acknowledgment. Support of the Chemistry Department's minicomputer facility by the National Science Foundation (CHE-8108990) is gratefully acknowledged. This work was supported in part by the National Science Foundation, Grants DMR79-25379 and CHE81-05069. We thank Professors F. Calderazzo and M. Ratner for helpful discussions and Dr. Frank Kutzler for assistance with computational and plotting details.

Registry No. $V(CO)_6$, 14024-00-1; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $[V(CO)_6^+][V(CO)_6^-]$, 84911-05-7.

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(50) This assumption merely simplifies the explicit wave functions for the dimer but is not required.

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