Quantum-Mechanical Studies Of Vanadium Oxides

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Abstract

A variety of V-O systems were examined in order to model the catalytic site for VPO-catalyzed conversion of butane to maleic anhydride. All V-O systems examined could be described as a V-O triple bond, with a covalent σ-bond and two π-bonds, and a bond length of approximately 1.56-1.60 Å. The nature of the π-bonds varied. In $VOCl_4^{3-}$ and $VOCl_2^{-}$, the π-bonds were both described as donor-acceptors. All other systems displayed one covalent bond and one donor-acceptor bond. Resonance between the two π-bonds was displayed for four-chloride C_{4v} $VOCl_4^{2-/-}$. Optimized C_{2v} geometries for $VOCl_4^{2-/-}$ appear to be the result of this resonance, in which the wavefunction and geometry represent one resonance state of the overall C_{4v} system, in which one π-bond is highly covalent, and the other highly donor-acceptor. The C_{4v} system is lower in energy than the C_{2v} system at all levels of theory (HF, CASSCF, MRCI) except GVB(3/6)-PP. $VOCl_2^{0/+}$ calculations show strong similarities to C_{2v} $VOCl_4^{2-/-}$ in both V-O bond description and geometry, suggesting that these systems can be described as C_{2v} $VOCl_4^{2-/-}$ systems without the axial chlorides. VO^+ and $VOCl_3$ results, for which experimental data exists, support the descriptions of geometry and bonding given. V(V) systems display a strong degree of covalent character to the chlorides (as does VO_3 to the bound oxygen molecule), but this effect decreases significantly as the V(3dδ)-orbitals are occupied. Snap bond calculations indicate that the V(V)-O bond is approximately 28 kcal/mol weaker than the V(IV)-O bond - this may be due to the increased V-Cl interaction in the products of the V(V) bond-breaking.

I. Introduction

The purpose of this work has been to lay the groundwork for the study of VPO-catalyzed oxidation of butane to maleic anhydride (MA). Approximately 1.3 billion tons of MA and its derivatives are produced annually.[1] These compounds are used in production of unsaturated polyester resins, agricultural chemicals, food additives, lubricating oil additives, and pharmaceuticals. The need for MA is expected to grow due to new potential uses for the molecule - for example, hydrogenation of MA to form butanediol. VPO ($(VO)_2P_2O_7$) has been found to be highly structure-specific, as well as highly selective, for this conversion.[2] All industrial catalysts for this reaction are VPO-based systems.[3] This method has the additional advantage of giving a clean product stream - MA, H_2O and CO_2. The problem with this method has been the low selectivity to MA at high conversion. Also, the feed concentrations of butane must be kept low to avoid stream flammability. These concentrations may range from two to four molar percent.

The reaction is a fourteen-electron oxidation (Figure Ia). Eight hydrogen atoms are abstracted, and three oxygen atoms are inserted. It is the most complex of all industrially practiced hydrocarbon selective oxidation reactions. It is also the only industrially practiced selective oxidation involving alkane activation[4] (Table Ia).

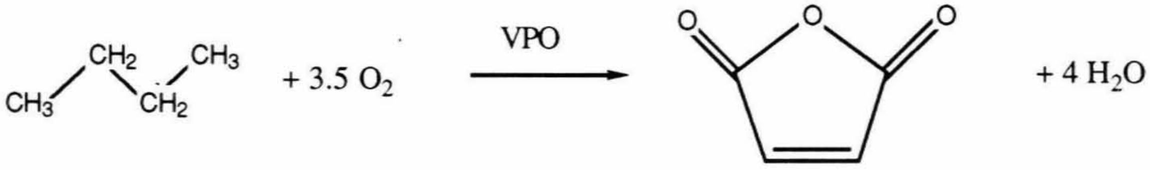

Figure Ia: Conversion of butane to maleic anhydride (MA).

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[1] Malow, M. *Hydrocarbon Process.* **1980**, *11*, 149.

[2] Centi, G.; Trifiró, F.; Ebner, J.R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55.

[3] Varma, R.A.; Saraf, D. N. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*,7.

[4] (a) Grasselli, R.K. In *Surface Properties and Catalysts by Non-Metals*; Bonnelle, J.P., Delmon, B., Deroune, E., Eds.; NATO ASI Series C.105; Reidel: Dordrecht, The Netherlands, 1982; pp. 273, 289. (b) Dadyburjor, D.B.; Jewar, S.S.; Ruckenstein, R. *Catal. Rev. - Sci. Eng.* **1979**, **19**, 293. (c) Haber, J. In *Proceedings, 8th International Congress on Catalysts*, (Berlin, 1984); Dechema, Frankfurt am Main, 1984, Vol. I, p. 85. (d) Centi, G.; Trifiró, F. *Appl. Catal.* **1984**, *12*, 1. (e) Kung, H.H. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 171. (f) Grasselli, R.K.; Burrington, J. D.; Brazdil, J.F. *Farraday Discuss. Chem. Soc.* **1981**, *72*, 203. (g) Grasselli, R.K.; Burrington, J. D.; Bradzil, J. F. *Adv. Catal.* **1981**, *30*, 133.

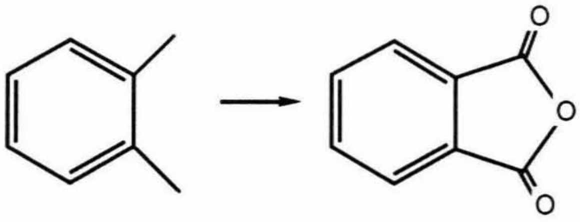
Reaction		Number of Electrons	Moles Oxygen
	+ H_2O	2	0.5
	+ H_2O	4	1
	+ H_2O	4	1
	+ 3 H_2O	12	3
	+ 4 H_2O	14	3.5

Table Ia: Principal Reactions of Industrial Interest in Selective Oxidation (Reference 1)

The structure of the surface is given in Figure Ib, taken from X-ray diffraction studies.[5] Each individual site is composed of two V-O centers, surrounded by a frame of phosphate groups. It is believed that these groups sterically isolate the active sites of the surface to these two vanadium centers, thus limiting butane oxidation by limiting the available surface oxygens. The surface involves V(IV) at the active site, with a small excess of V(V). Overoxidation occurs if too much V(V) is present.[6] Phosphorus serves to stabilize the V(IV), the optimum ratio of P/V=1.0.[7]

The reaction appears to occur as follows. The surface is pre-equilibrated with

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[5] Thompson, M. R.; Ebner, J. R. in *Studies in Surface Science and Catalysts*, 1991, Vol. 57

[6] Mori, K.; Miyamoto, A., Murakami, Y. *J. Phys. Chem.* **1985**, *89*, 4265.

[7] Centi, G.; Trifiró, G.; Busca, G.; Ebner, J.; Gleaves, J. *Farraday Discuss. Chem. Soc.* **1989**, *87*, 215.

O_2, followed by binding of butane to the surface. The abstraction of hydrogen to form $(C_4H_6)_{ads}$ is carried out by either V(IV)-O or V(IV)-O-P. This step is controlled by the rate of conversion of V(IV) to V(III). Surface V(V)-O is responsible for insertion of oxygen to the adsorbed species to form furan.[8] The chemisorbed oxygen leads to the formation of MA from furan. There are in fact three forms of oxygen which play a role in catalysis - the surface lattice oxygen which inserts into $(C_4H_6)_{ads}$ to form furan, and two forms of chemisorbed oxygen. The first is long-lived, and selective for MA formation. The second, a short-lived species, will oxidize the hydrocarbon to CO_2. The process is given schematically in Figure Ic.

Much of this work is based upon the VO^+ ion.[9] This molecule was predicted to have a triplet ground state, with R(V-O) = 1.56 Å. The bond character was found to be a triple bond, with the dominant configuration being one σ-bond, one π-bond, and one donor/acceptor π-bond. Thus there are two resonance states, depending upon which π-bond is described as being the donor/acceptor. This particular moiety has been found to be unreactive in the chemistry in which it has been studied.[10] We wish to examine if and how this character changes when bound to other atoms, as in the catalytic surface. It may also be that the system plays a role analogous to that of a "spectator oxo" , as has been studied in Mo and W systems.[11]

The aim of this work is three-fold: (1) to examine the electronic structure of the V-O bond in various systems, since this bond must play a key role in catalysis, (2) to examine how changes in oxidation state effect the V-O bond, and (3) to optimize geometries to allow for the generation of hessians for several of these systems from optimized structures. This will allow the fitting of force-field parameters for the system, and subsequent molecular dynamics studies of the catalytic surface.

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[8] Centi,G; Trifiró, F. J. Mol. Catal. **1986**, *35*, 255.

[9] Carter, E. A.; Goddard, W. A. III *J. Phys. Chem.* **1988**, *92*, 133.

[10] Jackson, T. C.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1252.

[11] (a) Rappé, A. K.; Goddard, W. A. III *Nature* **1980**, *285*, 311. (b) Rappé, A. K.; Goddard, W. A. III *J. Am. Chem. Soc.* **1980**, *102*, 5114. (c) Rappé, A.K.; Goddard, W. A. III *J. Am. Chem. Soc.* **1982**, *104*, 448.

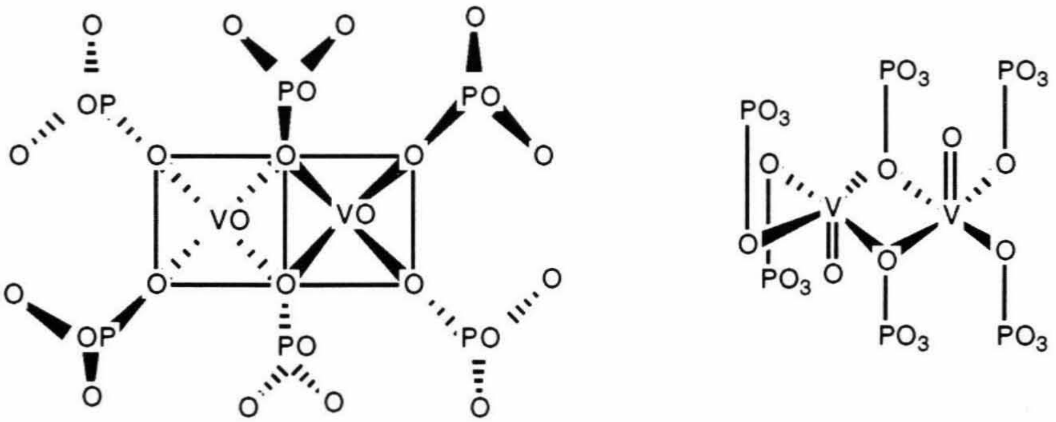

Figure Ib: A portion of the vanadium oxide surface - top and side views. The structure is an idealized model.

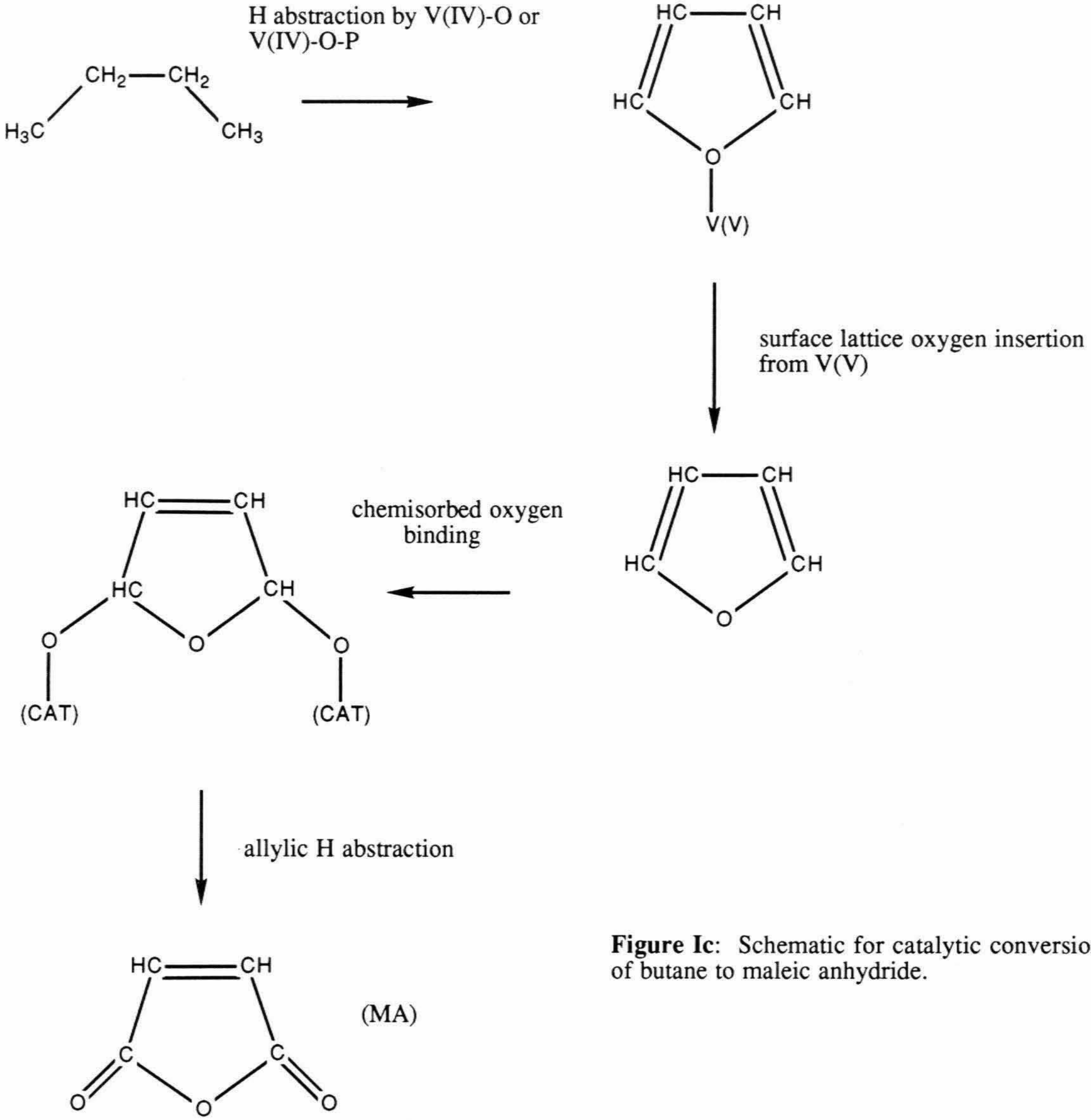

Figure Ic: Schematic for catalytic conversion of butane to maleic anhydride.

II. Methods of Calculation

(a) HF (Hartree-Fock)

Calculations were initiated at the HF level. HF provides a reasonable qualitative picture of bonding, and also provides a starting guess for including electron correlation. The HF wavefunction fails at dissociation limits, often incorrectly dissociating to an ionic limit.[12] The difficulty lies in the description of the electrons of a bond as one doubly-occupied orbital, which can never describe the separated-atom limit. In addition, since the spin-orbitals describing each electron are required to be orthogonal, the wavefunction cannot describe a molecular bond - thus the limits are described by HF, but the restrictions eliminate the possibility of a smooth description.

(b) GVB - PP (Generalized Valence Bond - Perfect Paring Restriction)

The primary goal of this study is to understand the nature of the V-O bond. This bond can be qualitatively described in terms of six orbitals and six electrons - the bonding and antibonding σ and π-orbitals of the bond. These orbitals have been described by an *ab initio* generalized valence bond wavefunction, with the perfect (singlet) pairing restriction (GVB-PP), which allows each correlated bond to be described in terms of two orbitals.[13] In this description, electrons outside the GVB space are treated at the HF level, with the spin orbitals orthogonal to one another (the strong orthogonality restriction). The orbitals of the GVB pair are described as:

$$\Psi_{GVB} = (2(1+S^2))^{-1/2}[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)](\alpha\beta-\beta\alpha) \qquad (1)$$

Here, ϕ_a and ϕ_b are variationally optimized one-electron GVB orbitals, and S is the overlap $<\phi_a|\phi_b>$. Note that (1) the GVB pair is described in terms of two orbitals, and (2) the net overlap is non-zero, thus allowing for a smooth description of molecular dissociation. This description can couple any number of GVB pairs. For example, two such pairs are described as products of equation (1). Restricting the spin function to the form $(\alpha\beta-\beta\alpha)$ for each pair is the perfect-paring restriction.

It is more computationally efficient to perform the calculations in terms of orthogonal orbitals, as the number of overlapping terms for N overlapping orbitals increases as N!.[14] To this end, GVB pairs are written in the natural orbital representation:

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[12] Goddard, W. A. III *Phys. Rev.* **1967**, *157*, 81.

[13] Bobrowicz, F. W.; Goddard, W. A. III in *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed; Plenum: New York, 1977; pp 79-127.

[14] Ladner, R. C.; Goddard, W. A. III J. Chem. Phys. **1969**, *51*, 1073.

$$\Psi_{NO} = [C_g\phi_g^2 + C_u\phi_u^2](\alpha\beta-\beta\alpha) \qquad (2)$$

where ϕ_g and ϕ_u are the bonding and antibonding natural orbitals of the GVB pair, which are now chosen to be orthogonal ($<\phi_g|\phi_u> = 0$). The overall GVB-PP wavefunction, with m-1 closed shell (HF) spin-orbitals, n GVB pairs, and N-(m+n-1) unpaired electrons, is thus described as:

$$\Psi = A[\phi_1\phi_1\alpha\beta\phi_2\phi_2\alpha\beta \ldots \Psi_{NO(m)}\Psi_{NO(m+1)} \ldots \phi_{m+n}\alpha \ldots \phi_N\alpha] \qquad (3)$$

(Where A is the determinant operator (antisymmetrizer) which makes the wavefunction satisfy the Pauli principle.)

GVB-PP will allow a qualitatively correct description of the orbitals, while including some of the electron correlation for the region of interest in each system. In addition, the GVB wavefunction provides the correct functional form to describe the dissociation products. This calculation is denoted as GVB(3/6)-PP, where three pairs are described by six orbitals. This level of calculation is the foundation on which virtually all the calculations in this work are based. In terms of a configuration interaction (CI) expansion, the correlation due to all double excitations within each GVB pair is included for a total of 8 electron configurations (configuration state functions or CSF's). (In general, given n GVB pairs, 2^n electron configurations are generated.)

(c) GVB-RCI (Restricted Configuration Interaction)

Only one of the possible spin functions are included (the perfect pairing coupling) in a GVB-PP calculation. Note from equation (3) that there is more than one way to describe the product of the n GVB pair spin functions correctly - the GVB-PP restriction is only one. A GVB-RCI calculation, starting from a GVB-PP wavefunction, eliminates this restriction by including all single excitations within each pair - for a total of 3^n configurations. Thus all spin-couplings are allowed (for a (3/6) calculation, six). In addition, GVB-RCI includes correlation between GVB pairs. This is important in bonding schemes which can be described by more than one valence bond resonance structure.

(d) GVBCI

At the next level, GVBCI, all configurations within the orbitals of the GVB pairs are allowed. Here, all electrons of the GVB pairs can be excited to any of the orbitals of the GVB space (within the symmetry restrictions of the wavefunction) - CI configurations corresponding to excitations of electrons to other pairs is included. In essence, a full CI is performed on this limited space. Starting with a GVB(3/6)-PP wavefunction, six electrons are being excited among six orbitals, the maximum excitations being sextuples.

(e) CASSCF (complete active space self-consistent field)

CASSCF or GVBCI-SCF wavefunctions include the same excitations as the GVBCI calculation, but optimizes the orbitals self-consistently, i.e. in the GVBCI wavefunction, the CI coefficients are optimized, given a set of orbitals, while in the CASSCF calculation, the orbitals are also optimized. This wavefunction may be described as an extension of a HF wavefunction, except the most important correlation effects are included in the optimization of the orbitals. The CI is carried out on those orbitals which made up the GVB pairs, as well as any open-shell orbitals. This set of orbitals and electrons is referred to as the active space. For the case of the V-O bond, the active space for these calculations was defined to be the same orbitals forming the three GVB pairs of the V-O bond, as well as any singly-occupied orbitals. Ignoring unpaired electrons, this is thus described as a 6-in-6 CASSCF wavefunction, in which all singlet-spin configurations are included by distributing the six active electrons among the six active molecular orbitals (MO's). This description maintains the smooth, continuous description of the system upon dissociation.

(f) MRCI (multireference configuration-interaction)

The CASSCF wavefunctions were used as the reference for a series of MRCI calculations.[15] The CASSCF includes the most important reference configurations for the MRCI. Two reference spaces were chosen, each with a maximum of two excitations. The first was chosen to be the states defined by 0-2 double excitations within the GVB pairs, i.e. the HF state and the states corresponding to one double excitations from the bonding to the antibonding orbital of the GVB pair - for three pairs, this leads to four references. (Equation (3)) This is the GVB reference space.

$$202020\ (\mathrm{HF}),\ 022020,\ 200220,\ 202002 \qquad (3)$$

The second is the RCI reference space. Here, all the GVB references are included, as well as all single excitations within each pair, as well as two single excitations within two separate pairs. For the GVB(3/6) case, this leads to a total of ten references in the RCI reference space. (Equation (4))

$$\mathrm{GVB} + 112020,\ 201120,\ 202011,\ 201111,\ 112011,\ 111120 \qquad (4)$$

Three types of MRCI calculations were carried out. The smallest, CCCI

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[15] (a) Bauschlicher, C. W. Jr.; Langhoff, S. R. *Science* **1991**, *254*, 394. (b) Bauschlicher, C. W. Jr.; Langhoff, S. R.; Taylor, P. R. *Adv. Chem. Phys.* **1990**, *77*, 103.

(correlation-consistent CI)[16] involves all single and double excitations within the CASSCF active space, as well as single excitations of the valence electrons. Calculations were performed using both the GVB and RCI reference spaces. These excitations are described as GVB*(SD_{bond} + S_{val}) and RCI*(SD_{bond} + S_{val}). The use of the CASSCF wavefunction allows for the correct description of dissociation products. The single excitations from the valence electrons to allow for shape changes in the orbitals in bond-breaking, in order to compensate for not re-computing the orbitals self-consistently.[17] This CI concentrates on a limited number of bonds (in this case, the V-O bond). Both the GVB-CCCI and RCI-CCCI will dissociate to high-spin HF-CCCI wavefunctions.

The next step, DCCI (dissociation-consistent CI)[18] involves all the excitations of the CCCI, as well as simultaneous single excitations from the bond and the valence electrons, effectively including correlation from the coupling of the valence electrons and the bond(s). These calculations were carried out using the RCI reference space, and the excitations are denoted as RCI*(SD_{bond} + S_{val}*S_{bond} + S_{val}). This wavefunction dissociates to HF-DCCI.

(Note that these calculations are NOT CCCI and DCCI in the strictest sense. In true CCCI, S_{bond}*S_{bond} excitations are not included. In a true DCCI, higher excitations (triples through sextuples) within the V-O triple bond are required. In the case of the former, the S_{bond}*S_{bond} excitations are included to account for interbond correlation. For the latter, the higher excitations are not expected to change the energy significantly, but will dramatically increase the number of CSF's, making the calculation extremely expensive.)

Finally, GVB*SD includes all single and double-excitations from all valence electrons (including the bonds) into the virtual space. This is the highest level of correlation for the systems under study, and is used to calibrate the smaller CI calculations. The dissociation products are high-spin HF*SD.

(g) R-GVB (Resonance - GVB)

In the event of resonance between two states, there is an additional approach. There are numerous cases in which two equivalent GVB-PP wavefunctions ψ_a and ψ_b can be used to describe a system (for example, the two resonance states of benzene, or the Perry-Ohanessian $Co(CH_3)_2^+$ system[19]). This problem arises due to the localization of specific bonds by the GVB-PP wavefunction. The wavefunction converges to a specific resonance form, instead of the proper description, in which all resonance configurations contribute. For a system composed of two resonance states, the total electronic energy for the system is thus described by:

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[16] Carter, E. A.; Goddard, W. A. III *J. Chem. Phys.* **1988**, *88*, 3132.

[17] Shin, S. K.; Goddard, W. A. III; Beachamp, J. L. *J. Chem. Phys.* **1990**, *93*, 299.

[18] Shin, S. K.; Goddard, W. A. III; Beachamp, J. L. *J. Phys. Chem.* **1990**, *94*, 6963.

[19] Perry, J. K.; Goddard, W. A. III; Ohanessian, G. to be submitted for publication.

$$E = \langle\psi_a+\psi_b|H|\psi_a+\psi_b\rangle/\langle\psi_a+\psi_b|\psi_a+\psi_b\rangle \qquad (5)$$

In order to compute E, the integrals $\langle\psi_a|H|\psi_b\rangle$ and $\langle\psi_a|\psi_b\rangle$ must be computed. This is done via an R-GVB calculation, which performs a two-by-two CI for $C_a\psi_a+C_b\psi_b$. In this case, the energy due to the two resonance states (the resonance energy) is computed, and the proper symmetry of the wavefunction restored.

(h) Basis Sets

The following basis sets were used. Vanadium was described using the Hay-Wadt valence double-ζ (vdz) basis set with effective core potential (ECP).[20] Oxygen was described using the Dunning vdz contraction[21] of the Huzinaga (9s5p) primitive basis set.[22] In addition, one set of 3d polarization functions ($\zeta^d = 0.95$)[23] was used. Chlorine, which was chosen to act as a charge-withdrawing system, was described using the vdz shape and Hamiltonian consistent (SHC) ECP basis set of Rappé, Smedley, and Goddard.[24] Polarization on the chlorines was described (when indicated) using one set of d polarization functions.[25]

(i) Computer and Program Details

Computations were performed on an Alliant FX/80 and the Floating Point Systems FPS-500 of the Goddard group (Caltech), using the GVB suite of programs. These routines are described as follows:

(1) GVB2P5: Program designed to solve for the optimum orbitals of Hartree-Fock (HF) and GVB wavefunctions.[26]

(2) GRADGVB: analytic gradients with respect to nuclear displacements for general GVB-PP wavefunctions - used for geometry optimization.[27]

(3) GRADLOOP: optimizes geometries using GRADGVB and HF or GVB wavefunctions from GVB2P5.[28]

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[20] Hay, P.J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[21] Dunning, T.H. *J. Chem. Phys.* **1970**, *53*, 2823.

[22] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

[23] The oxygen d exponent was optimized for H_2O by: Bair, R. A.; Goddard, W. A., III, unpublished results.

[24] Rappé, A. K.; Smedley, T. A.; Goddard, W. A. III *J. Phys. Chem.* **1981**, *85*, 1662.

[25] $\zeta^d = 0.60$.

[26] GVB164 was written by Bair, R.A. (1982) - a vectorized version of GVB2p5. GVB2p5 was written by Bair, R. A. (1977) - an extensive revision of GVBTWO. GVBTWO was written by Bobrowicz, F. W. and Wadt, W. R. (1973).

[27] Rappé, A. K., unpublished.

[28] Bierwagen, E. P., unpublished.

(4) RESGVB: Performs R-GVB calculations for two resonance states by computing the Hamiltonian matrix element $H_{ab} = <\Psi_a|H|\Psi_b>$ and the wavefunction overlap Sab = $<\Psi_a|\Psi_b>$ between two HF or GVB wavefunctions.[29]

(5) CIGEN, CI4P0: perform GVB-RCI and GVBCI calculations.[30]

In addition, SCF, CASSCF, and all MRCI calculations were carried out using the electronic structure program MOLECULE SWEDEN by Almlöf, et. al.[31]

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[29] Voter, A., unpublished.

[30] Olafson, B. D.; Goddard, W. A. III, unpublished.

[31] MOLECULE SWEDEN, Almlöf, J., Bauschlicher, C. W., Blomberg, M. R., Chong, D.P., Heiberg, A., Langhoff, S. R., Malmquist, P.-Å., Rendell, A. P., Roos, B. O., Siegbahn, P. E. M., Taylor, P. R.

III. Overview and Summary of Calculations and Results

The underlying goal of this study is to specifically examine several V-O systems to examine the change in the system as the oxidation state of V changes - with an emphasis on determining a qualitative description of the V-O bond, in an attempt to discover what role the oxidation state plays in the catalytic cycle. V(III), V(IV), and V(V) systems were all examined with varying numbers of ligands. Chlorine atoms were chosen in these systems to replace the oxygen of the catalyst, in order to (1) serve as a charge-withdrawing ligand, and (2) terminate the system such that a finite portion of the catalytic surface could be examined. The chlorides were added systematically - first two chlorides, then four chlorides were added to the VO-moiety. $VOCl_3$ was also examined since experimental data is available. VO_3 was studied early in our investigation to examine a V(IV) system with all V-O bonds. The molecules under study are listed in Table IIIa. By testing various states, it can be determined if it is reasonable to transfer the description for the V-O bond from system to system - in particular, if this description can be applied to the V-O bonds of the catalytic surface.

V(III)	V(IV)	V(V)
VO^+	VO^{2+}	VO^{3+}
$VOCl_2^-$	$VOCl_2$	$VOCl_2^+$
$VOCl_4^{3-}$	$VOCl_4^{2-}$	$VOCl_4^-$
	VO_3	$VOCl_3$

Table IIIa: VO-systems

The overall results can be summarized as follows. All V-O systems examined could be described as a V-O triple bond, with a covalent σ-bond and two π-bonds, and a bond length of approximately 1.56-1.60 Å. The nature of the π-bonds varied. In $VOCl_4^{3-}$ and $VOCl_2^-$, the π-bonds were both described as donor-acceptors. All other systems displayed one covalent bond and one donor-acceptor bond. Resonance between the two π-bonds was displayed for four-chloride C_{4v} $VOCl_4^{2-/-}$. Optimized C_{2v} geometries for $VOCl_4^{2-/-}$ appear to be the result of this resonance, in which the wavefunction and geometry represent one resonance state of the overall C_{4v} system, in which one π-bond is highly covalent, and the other highly donor-acceptor. The C_{4v} system is lower in energy than the C_{2v} system at all levels of theory (HF, CASSCF, MRCI) except GVB(3/6)-PP. $VOCl_2^{0/+}$ calculations show strong similarities to C_{2v} $VOCl_4^{2-/-}$ in both V-O bond description and geometry, suggesting that these systems can be described as C_{2v} $VOCl_4^{2-/-}$ systems without the axial chlorides. VO^+ and $VOCl_3$ results, for which experimental data exists, support the descriptions of geometry and bonding given. V(V) systems display a strong degree of covalent character to the chlorides (as does VO_3 to the bound oxygen molecule), but this effect decreases significantly as the V(3dδ)-orbitals are occupied. Snap bond calculations indicate that the V(V)-O bond is approximately 28 kcal/mol weaker than the V(IV)-O bond - this may be due to the increased V-Cl interaction in the products of the V(V) bond-breaking.

IV. $VOCl_4$ Systems

In order to examine the nature of a single axial V-O bond site on the catalytic surface, square pyramidal $VOCl_4$ was chosen with oxidation states of III, IV, and V, thus $VOCl_4^{3-}$, $VOCl_4^{2-}$, and $VOCl_4^{-}$ were studied. These oxidation states are those which are exhibited in the catalytic cycle of VPO. The chlorides were chosen as substitutes for the oxygen to withdraw charge from the vanadium center, as well as provide a convenient termination of the model.

The zeroth-order description of these systems is a V-O triple bond, with four chloride ligands donating into empty vanadium orbitals. Thus these systems can be considered to be a VO moiety bound to four chlorides. The initial focus of this study is the examination of the V-O triple bond, as in carbon monoxide. In valence bond (VB) terms, this bond consists of three resonance structures in which two covalent and one donor bond make up the bond. A schematic representation is given in Figure IVa. Here, the electrons are localized within the valence σ- and π-orbitals of the vanadium and oxygen atoms. The VO fragment has a charge of +1, +2, and +3 for these systems. The ground states for the corresponding V^{n+} ion is $d^{(5-n)}$, where $n=1,2,3$ = the charge on the VO fragment. In all cases, the ground state of the metal ion is high-spin, with all d-electrons unpaired. Formation of the triple bond will use two 3d-electrons to form the covalent V-O bonds, singly occupying two 3d-orbitals, while the remaining electrons will singly occupy the dδ-orbitals. The remaining d-orbital will be unoccupied, to allow for donation from the oxygen to vanadium, forming the third bond in the system. Thus the V^+ center of VO^+ is described in the zeroth-order approximation as $(d\sigma)^1(d\pi)^1(d\pi')^0(d\delta)^1(d\delta')^1$ (^5P). Subsequent ionization to VO^{2+} and VO^{3+} involve removal of the dδ-electrons (^4F, ^3P). (Note: The ground states for the V^{n+} metal centers are ^5D, ^4F, and ^3F.) Since these three systems differ only in the number of unpaired, nonbonding dδ-electrons, it would be expected that the description of the V-O bond should not be strongly affected by the change in oxidation state.

The geometry of the system was optimized from a GVB(3/6)-PP wavefunction (71 basis functions). Here, the three pairs are chosen to be the three V-O bonds, each described in terms of their respective bonding and antibonding orbitals. When optimizing the geometries, it was found that not only was a C_{4v} square pyramid (sp) observed, but also a C_{2v} trigonal bipyramid (tbp) with an equatorial oxygen. In the course of the optimization, the complex could break C_{4v} symmetry to form the tbp complex. For V(IV) and V(V), both sp and tbp geometries were optimized. Preliminary calculations to optimize a C_{3v} geometry (tbp with an axial oxygen) were unsuccessful, the geometry converging instead to C_{2v}. For V(III), only the sp geometry was optimized (tbp dissociated to $VOCl_2^-$ and two Cl^- ions). The geometries are given in Table IVa and Figure IVb. There are no experimental values for any of these systems. However, data exists for $WOCl_4$, which is isoelectronic to $VOCl_4^-$

(neglecting the core electrons). A comparison of experimental data[32] of $WOCl_4$ and optimized $VOCl_4^-$ data (Table IVb) are in reasonable agreement with one another. In addition, Dyke, et. al.[33] give an experimental value of the V-O bond length in VO^+ as 1.54 Å. Additional experimental data for $VOCl_3$ (Section VII) give credence to these geometries as being reasonable.

Initial geometry optimizations led to confusion over how best to describe these systems. While the C_{4v} sp geometries maintain C_{4v} symmetry in the GVB wavefunction, the C_{2v} systems show dramatic deviations from C_{4v} for the V-O bond. The GVB pair energies are given in Table IVc. There is a significant difference in the character of the two GVB pairs corresponding to the V-O π-bonds (differing by 58.7 and 53.6 kcal/mol), which are identical in the C_{4v} systems. The π-bond in the plane of the axial chlorides demonstrate a great deal more covalency than the π-bond in the plane of the equatorial chlorides. Orbital diagrams are given in Figures IVc-p. The GVB Mulliken populations also demonstrate this effect (Tables IVd-h). For $VOCl_4^-$, the C_{2v} geometry gives π-bonds which are 34.4% and 95.0% covalent, as opposed to 77.0% covalent for the C_{4v} system. For $VOCl_4^{2-}$, these values are 24.8% and 97.0% versus 47.5%. (Table IVi) (HF populations show a smaller effect.) $VOCl_4^{3-}$, which displays no C_{2v} structure, can be described as a σ-bond and two equivalent donor-accpetor π-bonds (Figures IVq-r).

In addition, for two systems in which the tbp system was optimized, the tbp system was lower in energy than sp by -3.89 and -1.75 kcal/mol for $VOCl_4^{2-}$ and $VOCl_4^-$, respectively. This contrasts with HF, which gives sp as the more stable geometry by 14.79 and 5.86 kcal/mol (See Table IVj). It might be argued that the C_{2v} system is actually a resonance structure, the average of which represents a C_{4v} system. In this case, the V-O bond would be described by a σ-bond and two resonance states corresponding to resonance between a covalent π-bond and a donor-acceptor π-bond. This effect might also be due to the localization of the bonds by GVB. The perfect-pairing restriction does not allow for high-spin coupling among the GVB pairs. Therefore it is important to examine the systems in such a way that coupling among the pairs is accounted for. In fact, it may be that the de-coupling of the pairs is what allows the C_{4v} geometry to converge to one of the two resonance states - which in turn favors a C_{2v} geometry.

To this end, CASSCF calculations were performed on these systems, with the active space composed of the orbitals comprising the GVB pairs, as well as any unpaired electrons (6-in-6, 7-in-7, and 8-in-8 CASSCF wavefunctions for $VOCl_4^{-/2-/3-}$). All excitations within the active space are included, including high-spin coupling of the electrons within the bond. Potential resonance between the valence-bond resonance states of the V-O bond are also considered. This should give some indication of what is occurring in these systems, as well as explain what is going on at the GVB-PP level.

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[32] Iijima, K.; Shibata, S. *Bull. Chem. Soc. Japan* **1974**, *47*, 1393.

[33] Dyke, J. M.; Gravenor, B. W. J.; Hastings, M. P.; Morris, A. *J. Phys. Chem.* **1985**, *89*, 4613.

The energies for the CASSCF results are given in Table IVj. Unlike the GVB-PP case, the C_{4v} sp geometry is now more stable than the C_{2v} tbp by 3.85 and 3.51 kcal/mol for $VOCl_4^{2-}$ and $VOCl_4^-$. In addition, the Mulliken populations (Tables IVe-h) are almost identical for the two π-bonds, although there is still a slight difference in the populations. There is a dramatic change in percent covalency from GVB-PP to CASSCF. ($VOCl_4^{2-}$: 24.8, 97.0 to 53.9, 59.9; $VOCl_4^-$: 34.4, 95.0 to 63.2, 69.1) In fact, a comparison with the CASSCF results for the C_{4v} systems suggests that the distortion from C_{4v} symmetry provided by the chlorides can be considered as a small perturbation at the CASSCF level - the π-bond in the plane of the axial chlorides being only slightly more covalent than the other π-bond, in each case by about 6 %. Note that the overall populations of the V and O change only slightly as one progresses from GVB-PP to CASSCF, although the change is larger for sp than tbp. For sp $VOCl_4^{3-/2-/-}$, the overall percent covalence of the V-O bond changes by 4.4, 2.2, and 4.3%, as opposed to only 0.6 and 0.3 for tbp $VOCl_4^{2-/-}$.

These results may be rationalized in the following way. GVB-PP does not allow for the high-spin coupling among among the GVB pairs in the bond. Assuming that this effect is important, GVB-PP will not describe metal state splittings correctly. As a result, GVB-PP may overestimate charge transfer to all the ligands, oxygen and chlorine, and thus reduce the d-character of the system. The charge transfer and d-character of these systems is given in Tables IVk and IVl. If this is the case, then the GVB results can be rationalized in two ways. If all the ligands are considered to be charged, then the C_{2v} tbp better minimizes ligand-ligand repulsion. (Using the average values for the C_{2v} chlorides, the chlorides are further from the oxygen in the C_{2v} than C_{4v}.) This effect will tend to be more important if charge transfer is overestimated. Alternatively, the systems may be described in terms of orbital hybridization. While a trigonal bipyramid is sp^3d, square pyramid is sp^2d^2-hybridized. The total "occupancy" of the bonding orbitals, including the two π-bonding d-orbitals, is sp^3d^3 (trigonal bipyramid) and sp^2d^4 (square pyramid). (Atomic V is s^2d^3.) The greater d-character of the C_{4v} geometry make it less favorable than C_{2v} at the GVB-PP level.

The simplest explanation, however, that the geometry optimization to the C_{2v} state is a result of resonance. If there is mixing of two resonance states, and the bonds are decoupled, as in GVB-PP, it is possible for the system to converge to a single resonance state. If, in the course of the geometry optimization, the optimization of the wavefunction should tend toward one of the resonance states, the geometry could also optimize so as to favor a single resonance state - in this case, a single resonance state for these systems would favor a C_{2v} geometry, while the overall system is in fact C_{4v}. This would explain also the behavior of $VOCl_4^{3-}$, which displays no C_{2v} geometry, since both V-O π-bonds are equivalent donor-accpetor bonds - there should be no resonance.

(To examine this, R-GVB calculations performed on the C_{4v} $VOCl_4^{2-/-}$ systems were performed by computing the resonance between two GVB(2/4) states, and also by freezing these orbitals and optimizing a third GVB pair. These results indicate that these systems do in fact display resonance.)

The CASSCF results do include high-spin coupling on the metal, and thus will predict state splittings more accurately. This will lead to reduced charge transfer and greater d-character of the system, thus giving greater weight to the square pyramid. In terms of the resonance explanation given, this means that this method should not converge to a single reference state, but prefer the average state. In fact, this is the trend which is observed. For the systems under examination, there is a slight increase in d-character, as well as as a slight net ligand charge decrease, in the CASSCF results when compared to the GVB results. Note that this is not the case for $VOCl_4^-$ (C_{4v}), but that the absolute changes in d-character and ligand charge are about five times smaller than for $VOCl_4^-$ (C_{2v}). In both cases in which C_{2v} and C_{4v} were examined, these changes are larger for the C_{2v} system.

To examine these trends further, MRCI (GVB-CCCI and RCI-CCCI) calculations were carried out. In both cases, the C_{4v} system was lower in energy than the C_{2v}. The difference is approximately 3-4 kcal/mol at the both GVB-CCCI and RCI-CCCI levels (excluding the Davidson correction). In these cases, there is again a decrease in charger transfer from the GVB-PP level, as well as an increase in d-character, but it is less pronounced than in the CASSCF.

The comparison of GVB-CCCI and RCI-CCCI allow a comparison of the two reference spaces used. The energy difference between the RCI and GVB reference spaces ranges from 20-25 kcal/mol. This large change is a change in the *absolute* bond energy from GVB-CCCI to RCI-CCCI, as both dissociate to the same product (high spin HF-CCCI). GVB-CCCI results also indicate that the important CSF's outside the GVB reference space are the references of the RCI space. It thus appears that the RCI reference space is critically important to correctly describing the V-O bonding in these systems.

Snap bond energies were computed at the RCI-CCCI level for the C_{4v} systems, with a reference values computed for $VOCl_4^{2-}$ at the RCI-DCCI and GVB*SD levels. The fragments were dissociated to high-spin HF-CCCI, HF-DCCI, and HF*SD, respectively, where the oxygen fragment was considered to be neutral.[34] (Due to the rapid increase in the size of the problem, higher calculations were not carried out for the other systems.) These calculations were performed to determine how the differences in the oxidation state affects V-O bond strength, with the hope that a large difference in the values might be extrapolated to help explain the significance of the different oxidation states in the VPO catalyst. Note that the system is not allowed to relax upon bond breaking, so any geometric or electronic changes in the system (outside the decoupling of the bonding electrons and the moving apart of the two fragments) are unaccounted for. The results are given in Table IVm. The results indicate a steady decrease in V-O

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[34] The calculations for the "fragments" were carried out by using the optimized geometry, except moving the oxygen atom 100 Å from the vanadium center, along the axis of the V-O bond. The resulting unpaired electrons were made high-spin.

snap bond strength as oxidation state increases. Of particular interest is that the V(V)-O bond is much weaker than the V(IV)-O bond (by 28.3 kcal/mol). This effect displays itself in the catalytic system, where it is believed that the V(V)-O bond contributes the oxygen in converting $(C_4H_6)_{ads}$ to furan. These results are consistent with the DCCI reference, but high by approximately 10 kcal/mol at the GVB*SD level. This should not affect the relative bond strengths of the three systems, assuming that the effects of including the additional excitations of GVB*SD are roughly consistent. The V(III)-O snap bond energy seems too high. This is probably due to dissociation to neutral oxygen. Since $VOCl_4^{3-}$ displays a high degree of charge transfer to the oxygen, it is likely that the correct dissociation products are VCl_4^{2-} and O^-, instead of VCl_4^{3-} and O.

In addition to providing correction terms for the snap bond energy, calculations were carried out at the RCI-DCCI and GVB*SD levels for $VOCl_4^-$ (C_{4v}) in order to appropriately evaluate the CCCI calculations. DCCI includes excitations which couple the V-O bond and the chlorides, while GVB*SD includes all single and double excitations out of the valence space. Comparison to CCCI values should give some indication of the importance of what is left out of the CCCI calculations. The energy difference between GVB*SD and GVB-CCCI is 142 kcal/mol. This value is an indication of the importance if including the chlorides in determining the minimum energy - this result is not surprising, since these calculations have, to this point, essentially treated the chlorines as pure chlorides. In addition, the difference in RCI-DCCI and RCI-CCCI energies is 26 kcal/mol. This value is a measure of how important the coupling of the V-O bond and the chlorides is - this result suggests a strong degree of interaction of the chlorides with the V-O bond. (This value is larger for $VOCl_4^{2-}$ (C_{4v}) - the energy difference being 34 kcal/mol.) One might hypothesize that the chlorides may be competing for vanadium orbitals with the oxygen.

The role of the chlorides is now briefly examined further. HF and GVB calculations on both of the C_{2v} systems demonstrated a degree of chloride interaction with the remaining "empty" vanadium $3d_{x^2-y^2}$ orbital. (See Figures IVs-t.) In addition, the CI results examined previously indicate that the chlorides cannot be ignored entirely. Motivated by the results of the examination of the $VOCl_2^{+/0/-}$ systems (see Section V), GVB calculations were carried out with additional GVB pairs in order to couple the remaining vanadium orbitals to the chlorides. Initial GVB examinations were carried out on $VOCl_4^-$ and $VOCl_4^{2-}$. These preliminary calculations indicate a V(3dδ) bond to the chlorides for $VOCl_4^-$, but not for the other systems. (VCl_4 results indicate that there is a strong degree of covalent character in that system.[35]) In addition, RCI-DCCI and GVB*SD listed the valence excitation from a chloride lone pair to V(3dδ) as the lone important CSF outside the RCI reference space. This CSF did not appear in the CCCI calculations. Thus neglecting the coupling of the V-O space with the valence space leaves out an important state.

These results raise a key issue - can these systems be fully described by

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[35] Voter, A., unpublished.

ignoring the chlorides? It appears that they cannot. The C_{4v} geometry has been computed to be more stable than C_{2v}, but most of correlation included in these calculations was for the V-O pair. Preliminary calculations indicate that there is one covalent V-Cl bond. To represent this system correctly, this additional interaction must be included in GVB/CASSCF/CI calculations. Hypothetically, it may be that the C_{2v} geometry is favored when this interaction is included, as it lowers the energy of this state. However, this is purely speculative.

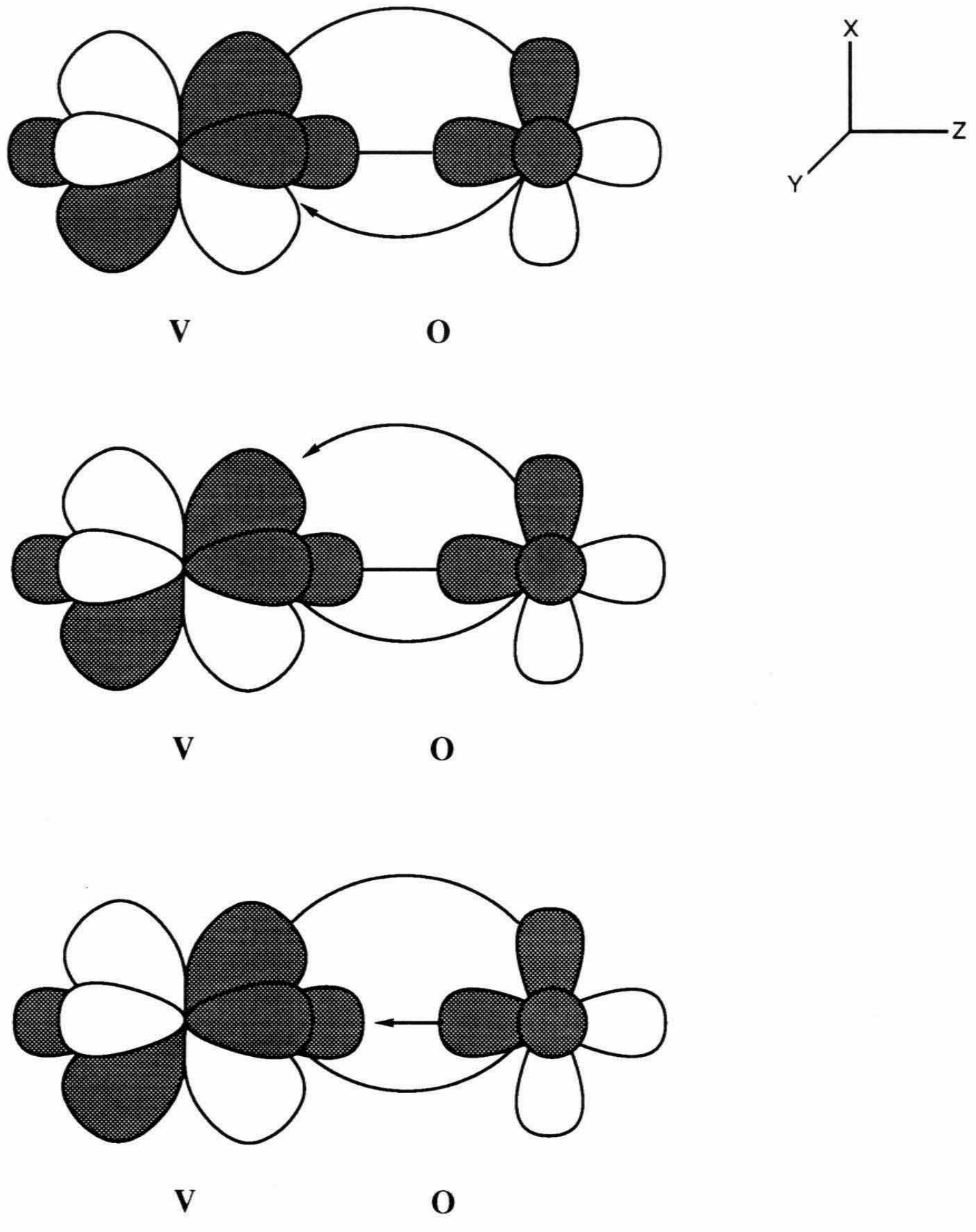


Figure IVa: The three potential resonance states of the V-O triple bond system, assuming two covalent bonds and one donor-acceptor. Note that only the first two are equivalent.

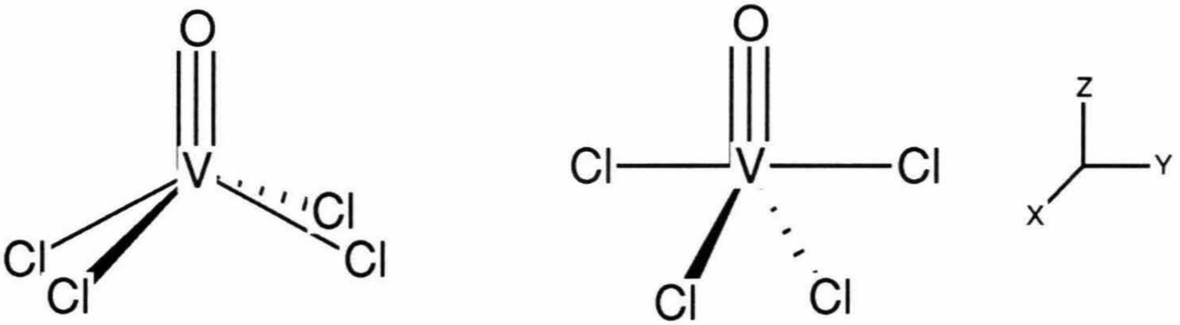


Figure IVb: The square pyramid (C_{4v}) and trigonal bipyramidal (c_{2v}) geometries of the $VOCl_4$ systems under examination.

Figures IVc - p: orbital diagram comparison of the V-O GVB pairs and singly-occupied orbitals of C_{4v} (square pyramid) and C_{2v} (trigonal bipyramid) geometries of $VOCl_4^{2-}$. The plots are given as follows:

IVc,d: VO σ (C_{4v})

IVe,f: VO π_x (C_{4v})

IVg,h: VO π_y (C_{4v})

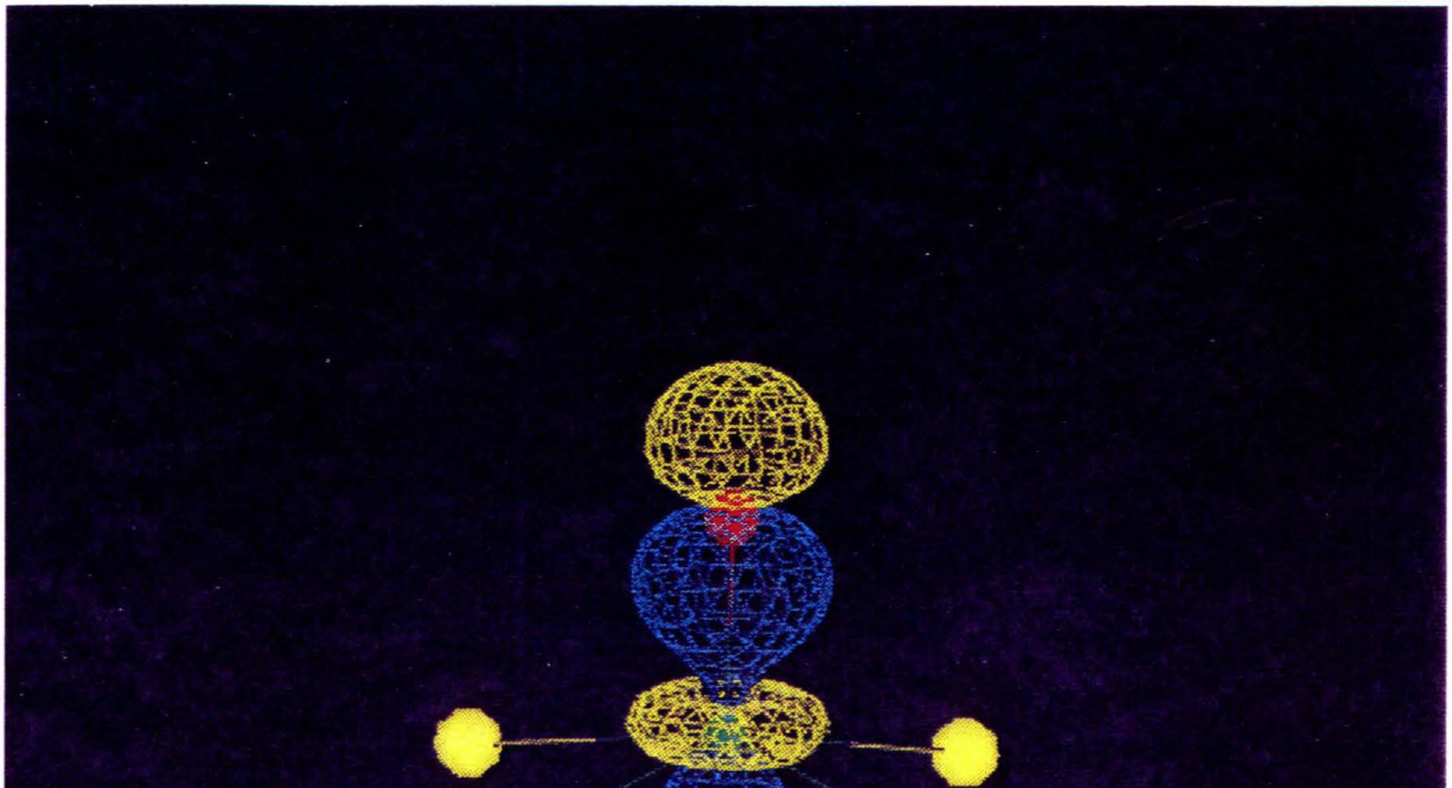
IVi: V($3d_{xy}$) (singly-occupied) (C_{4v})

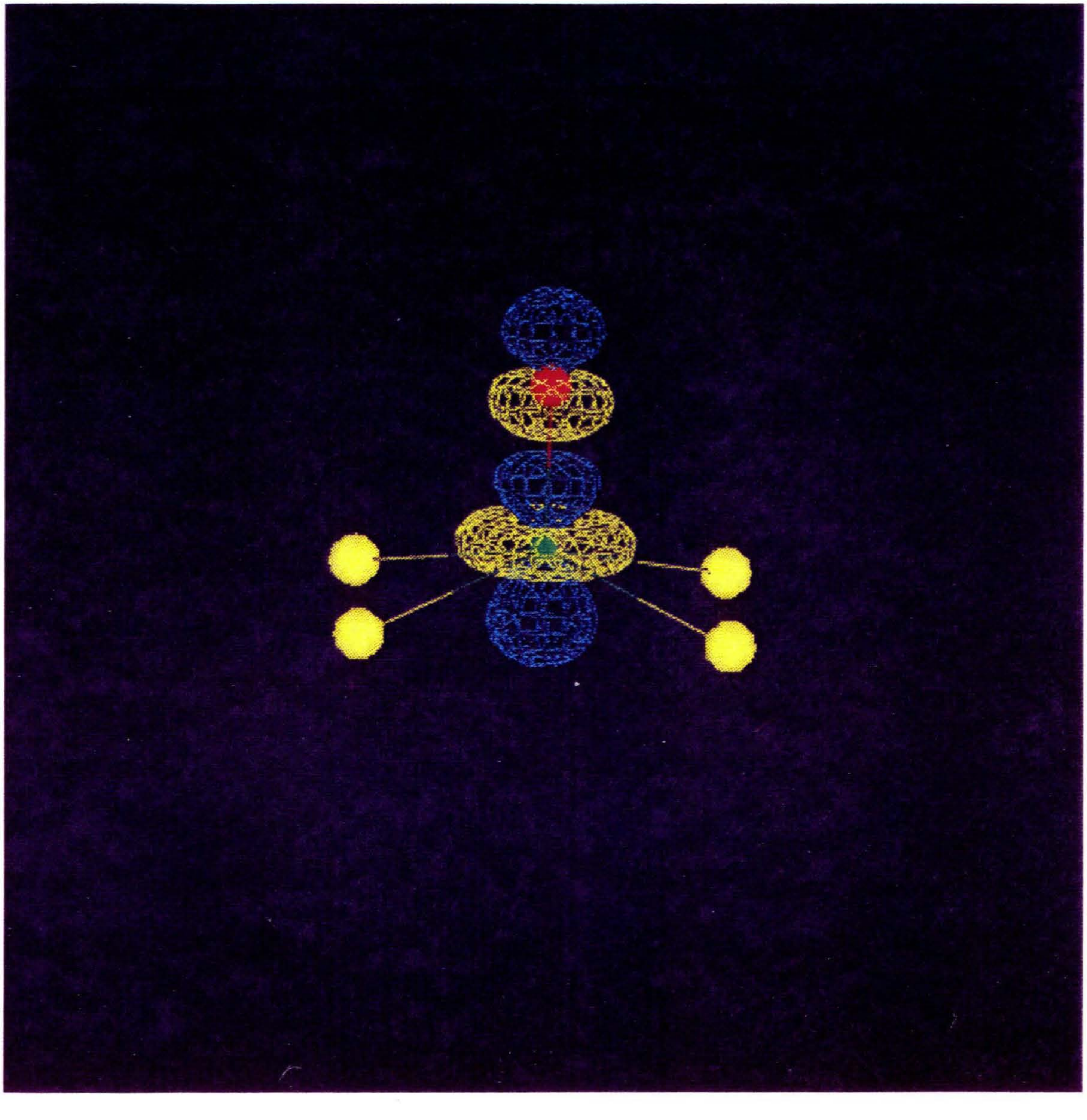
IVj,k: VO σ (C_{2v})

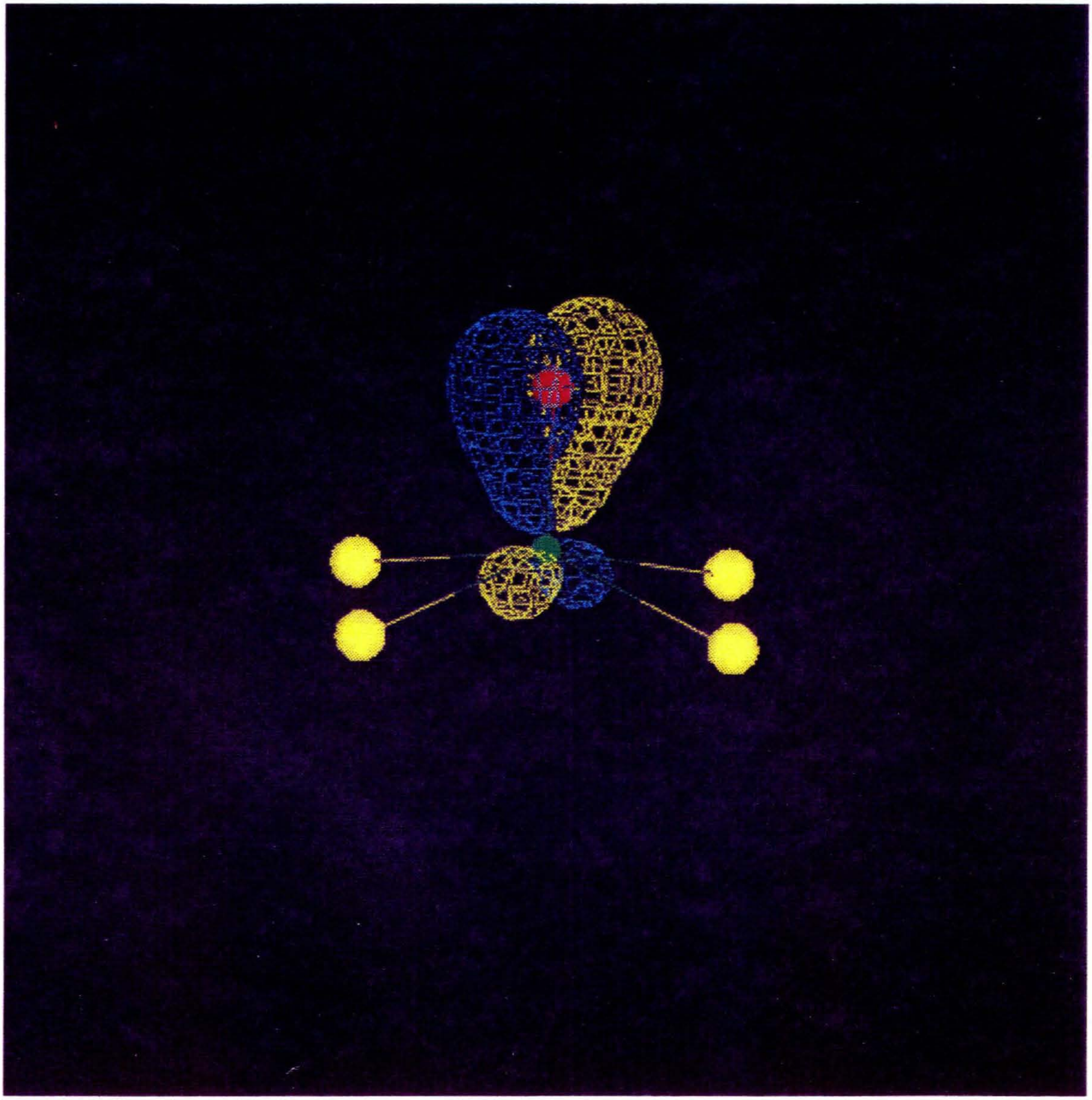
IVl,m: VO π_x (C_{2v})

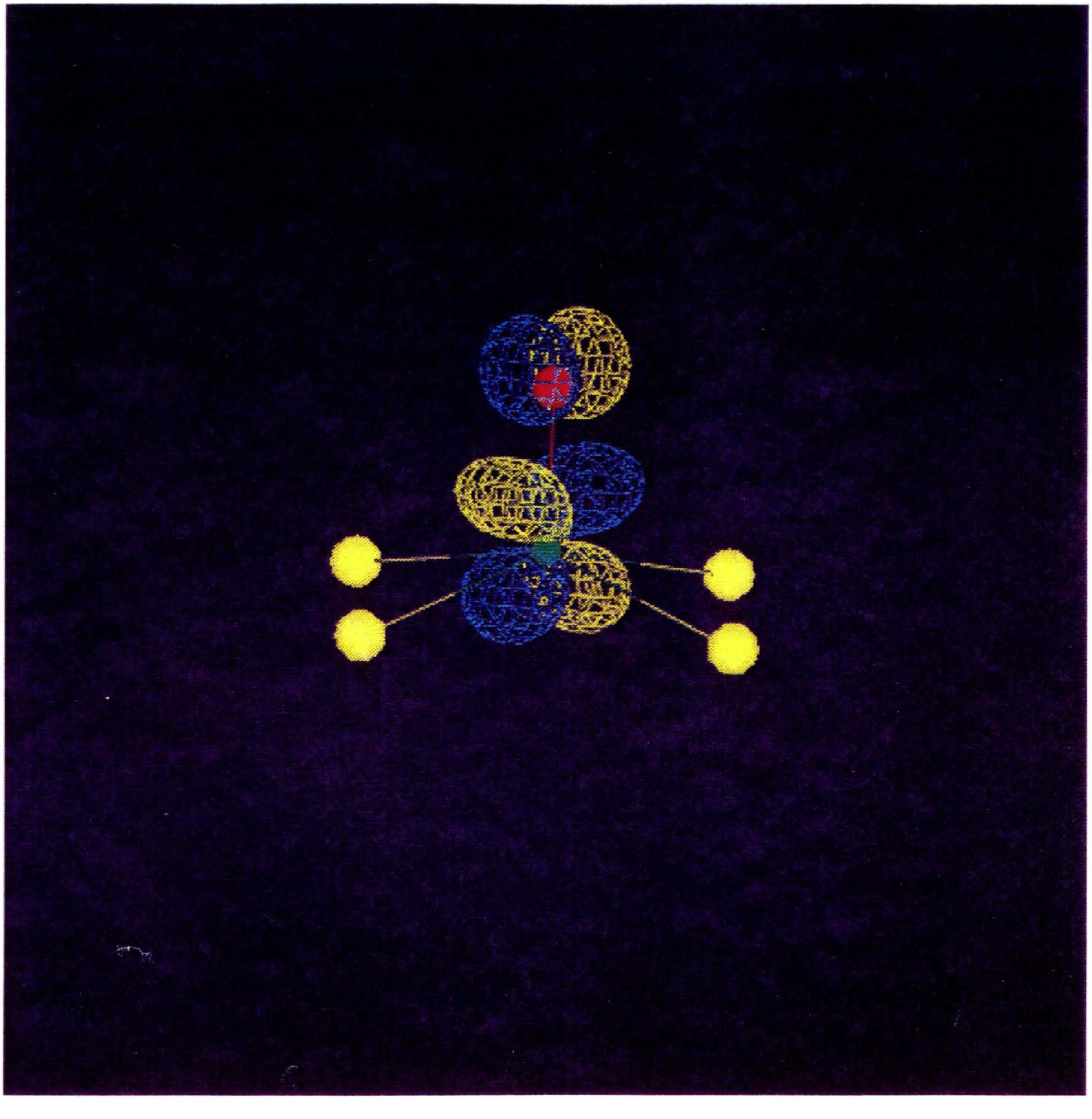
IVn,o: VO π_y (C_{2v})

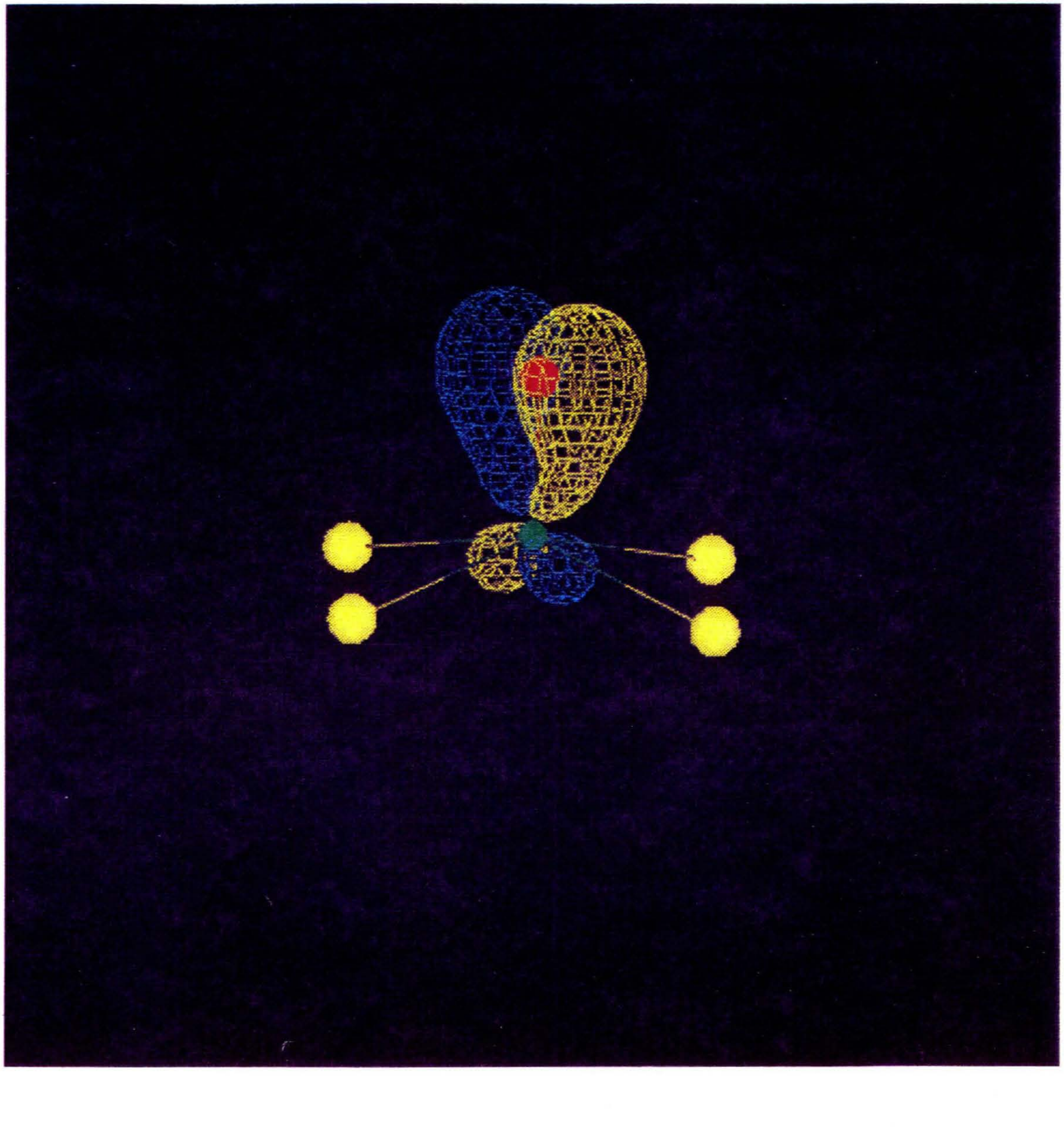
IVp: V($3d_{xy}$) (singly-occupied) (C_{2v})

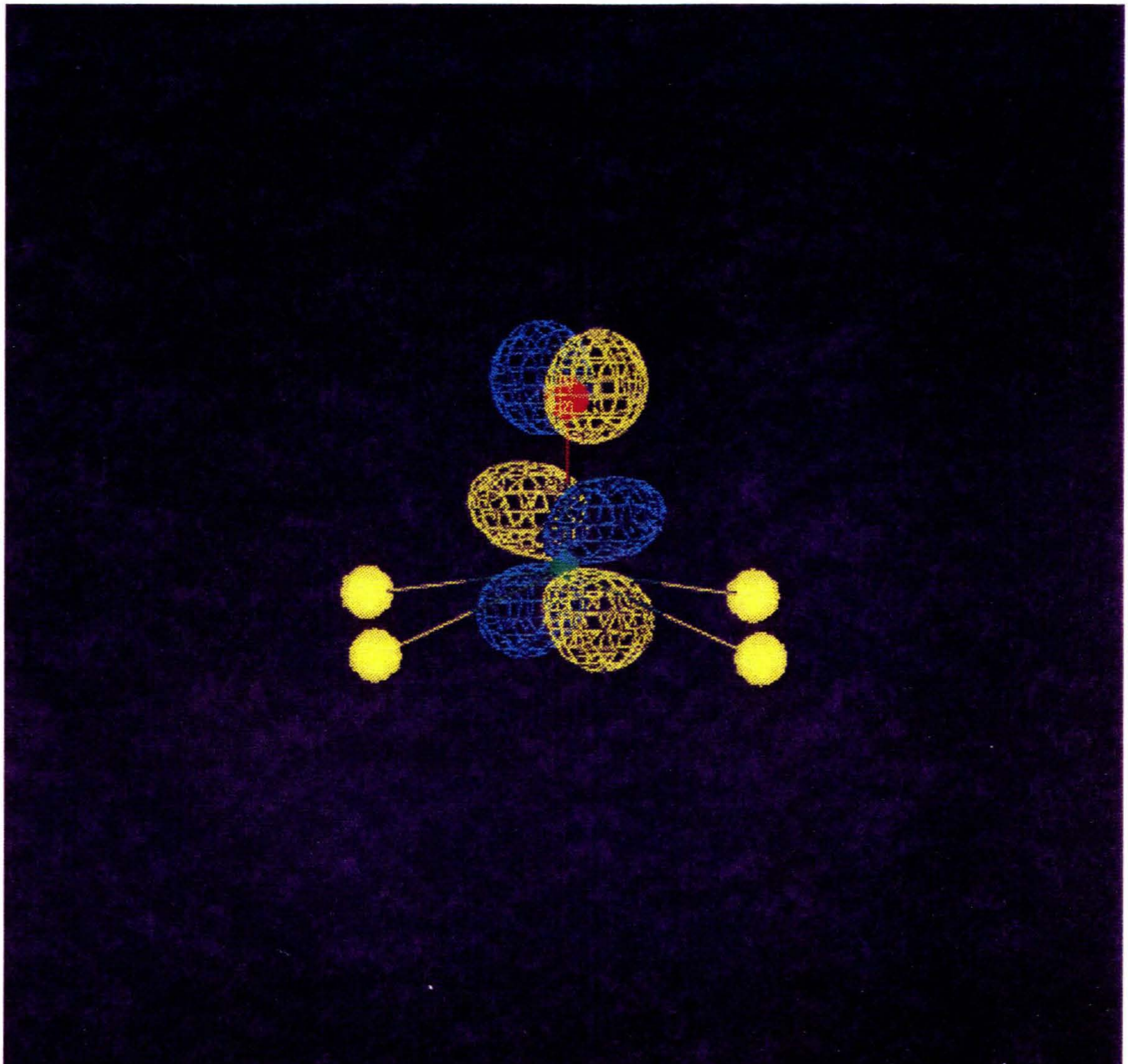


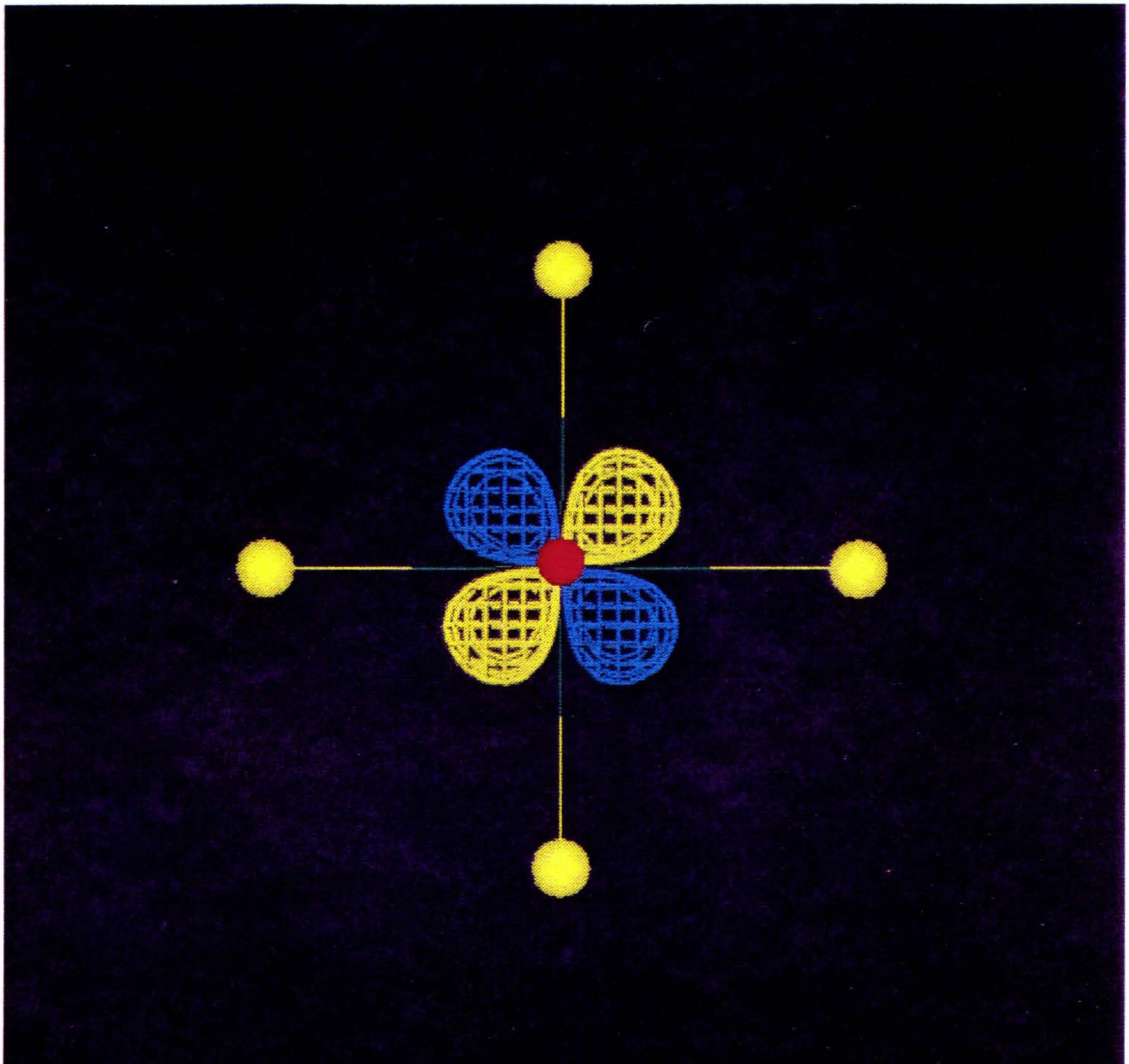


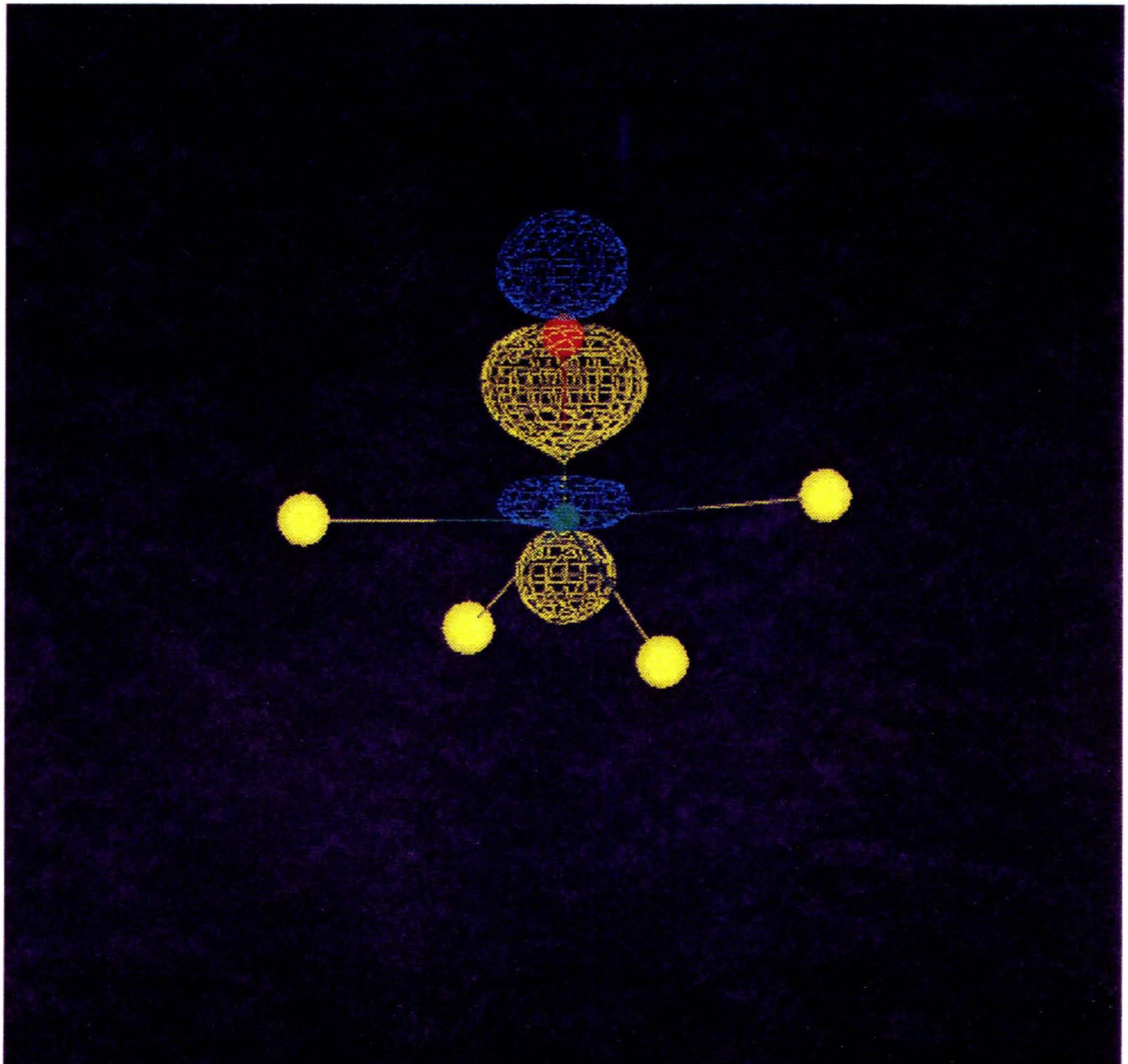


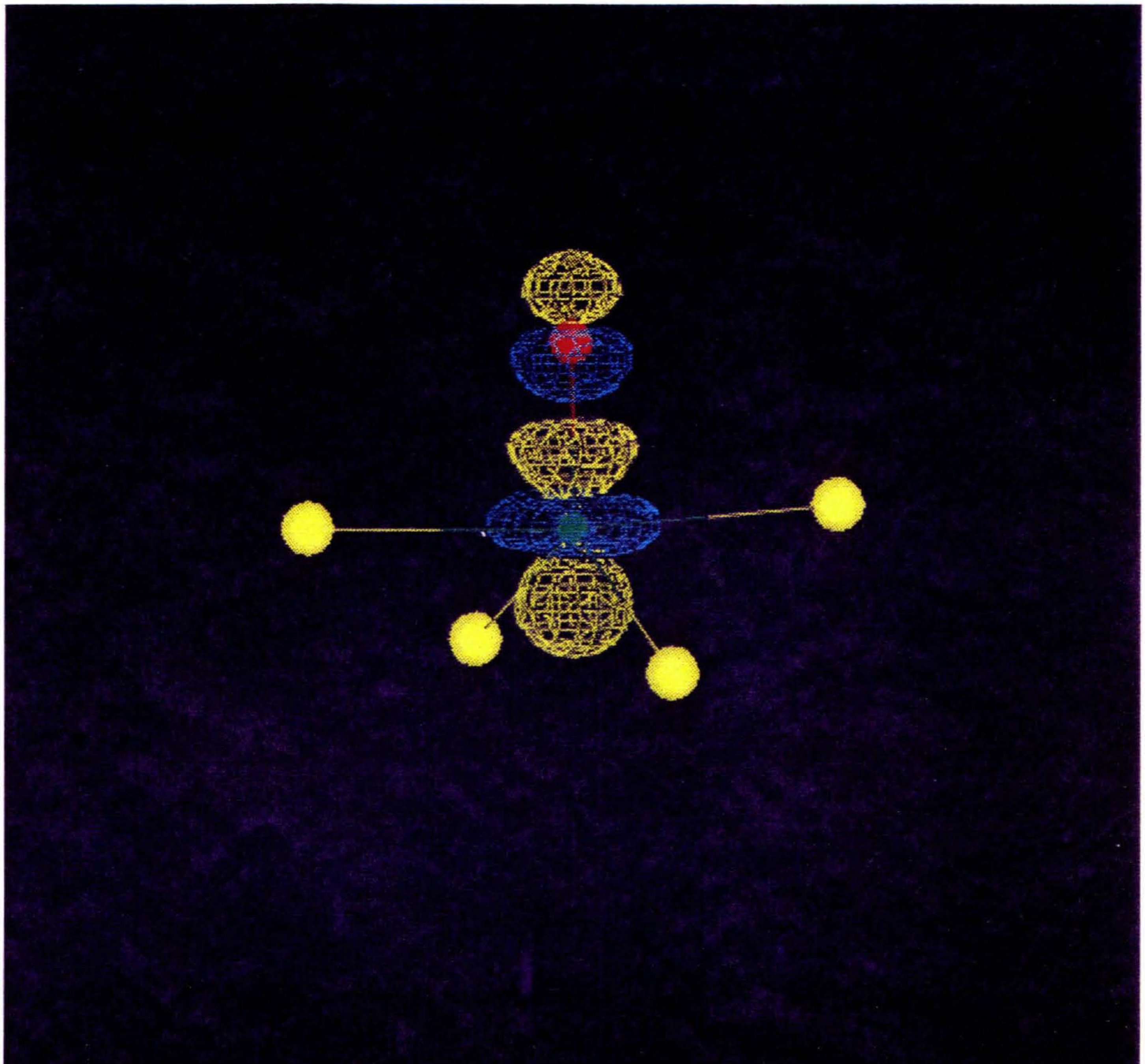


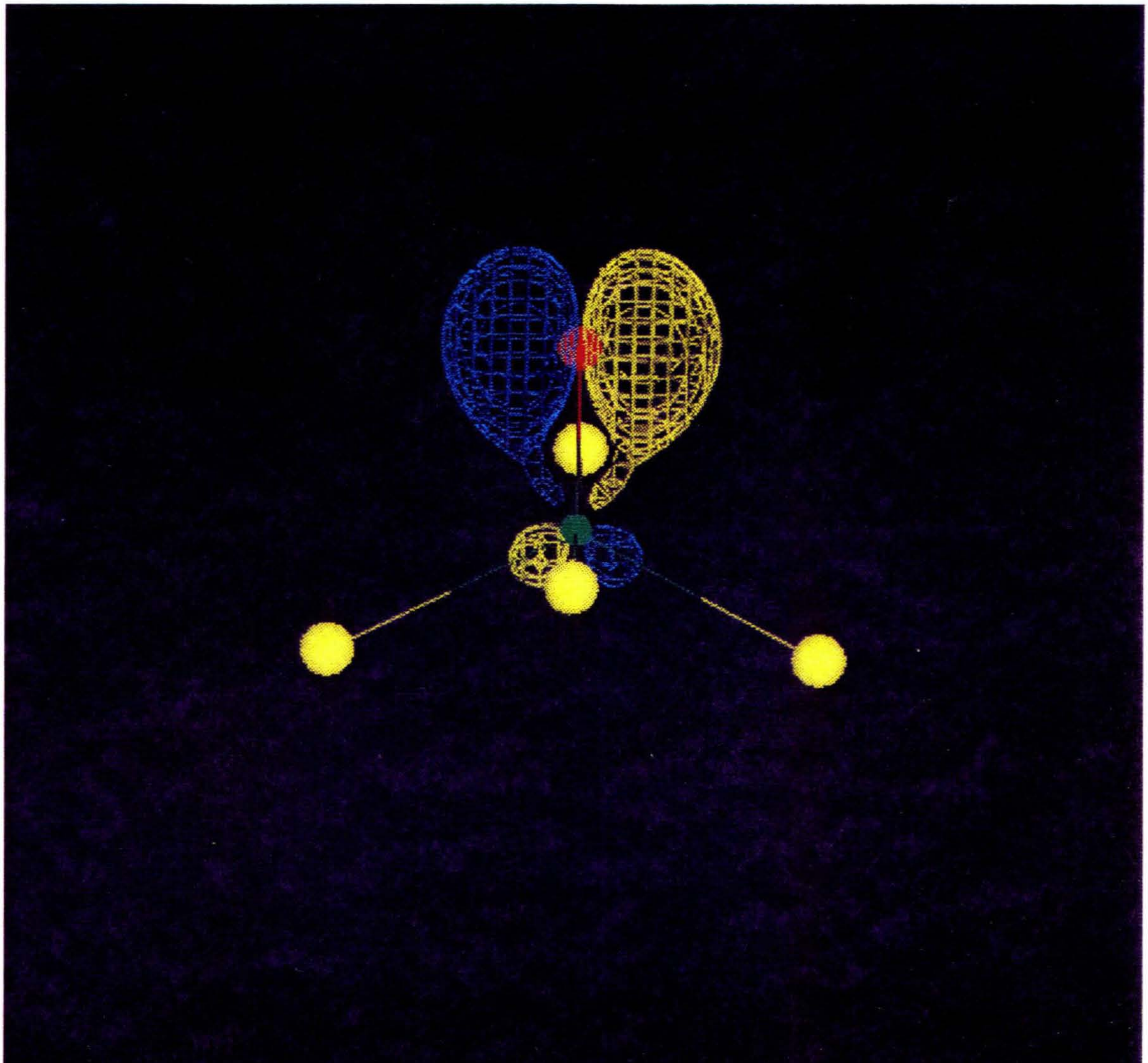


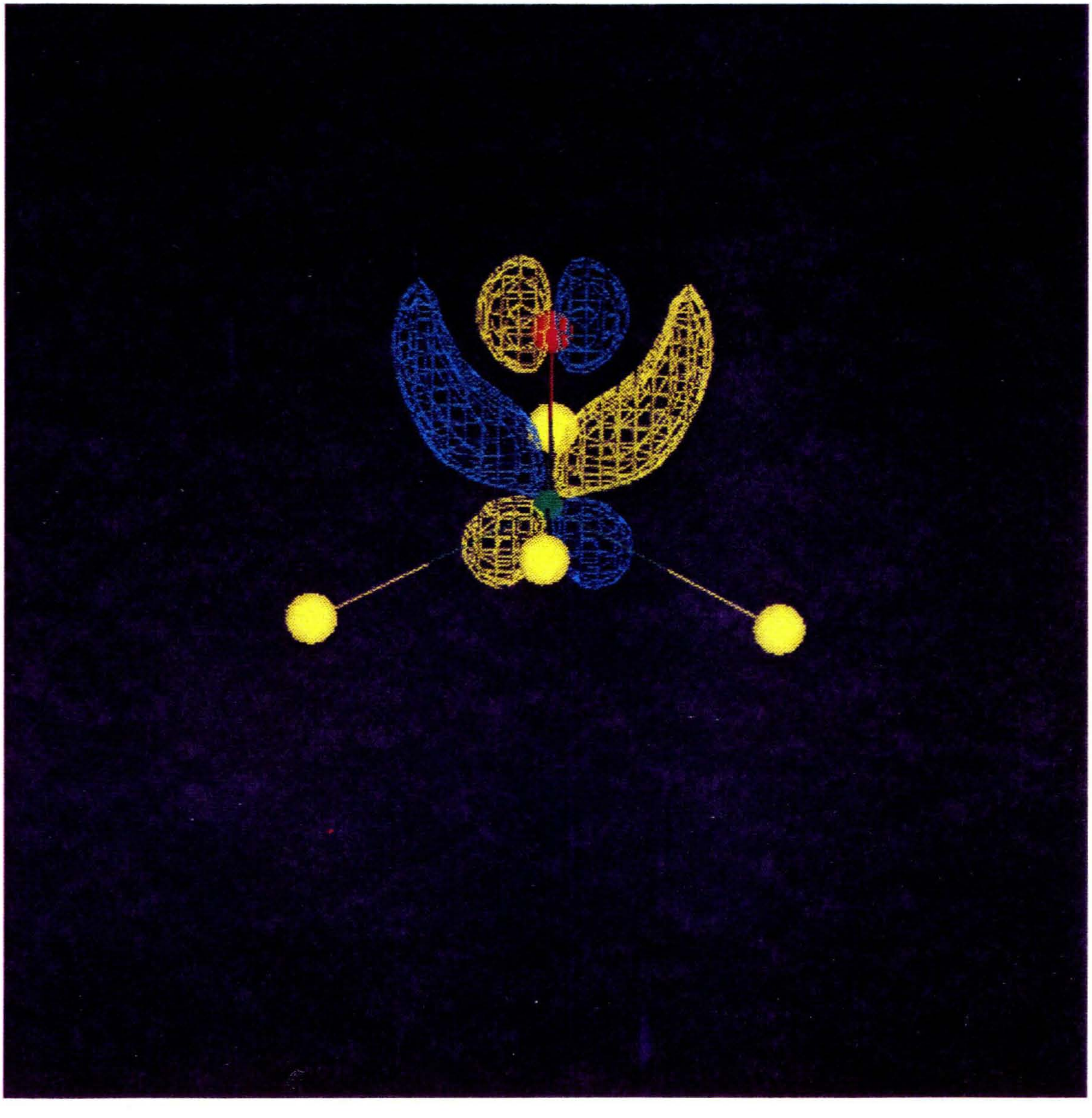


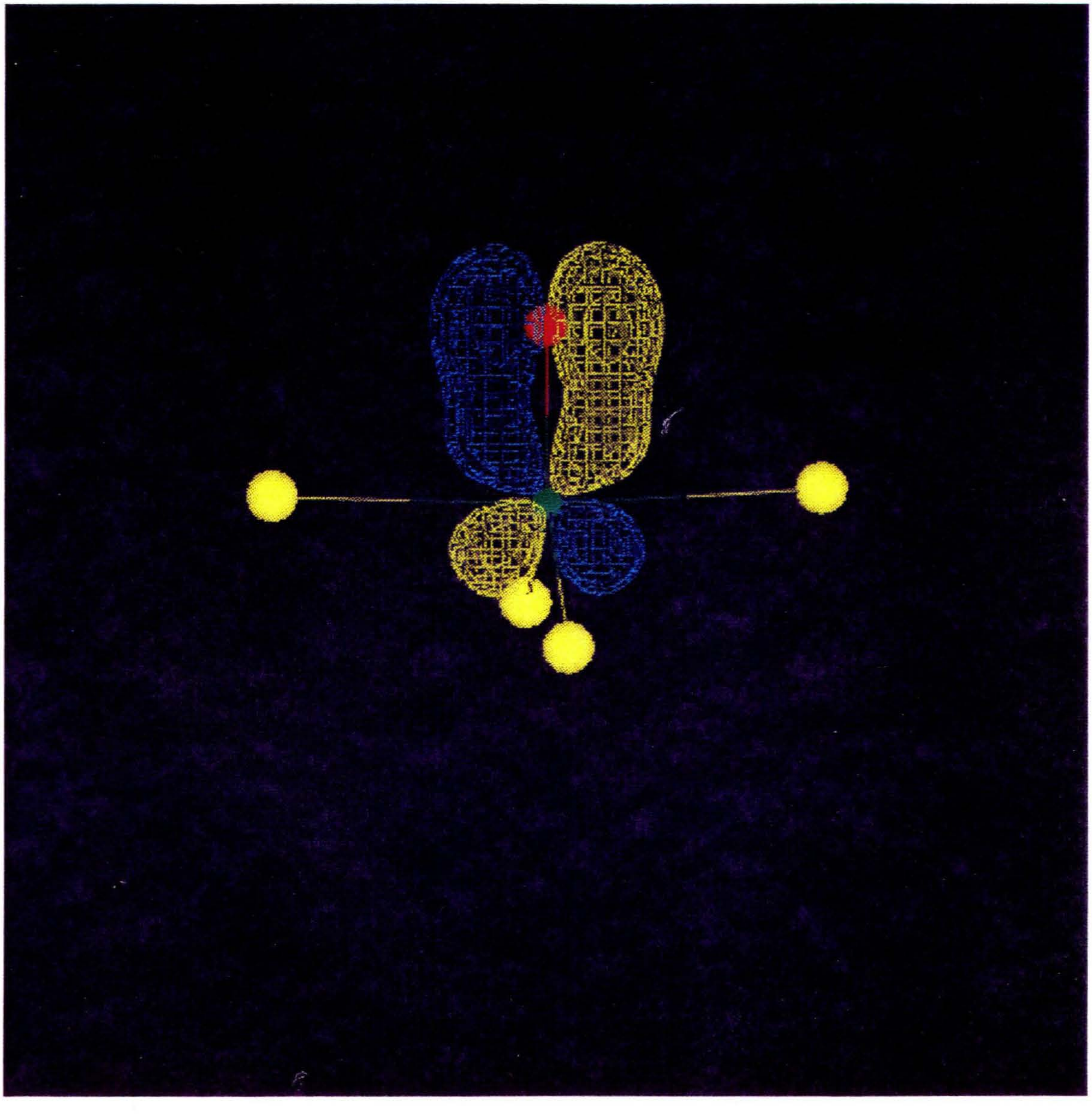


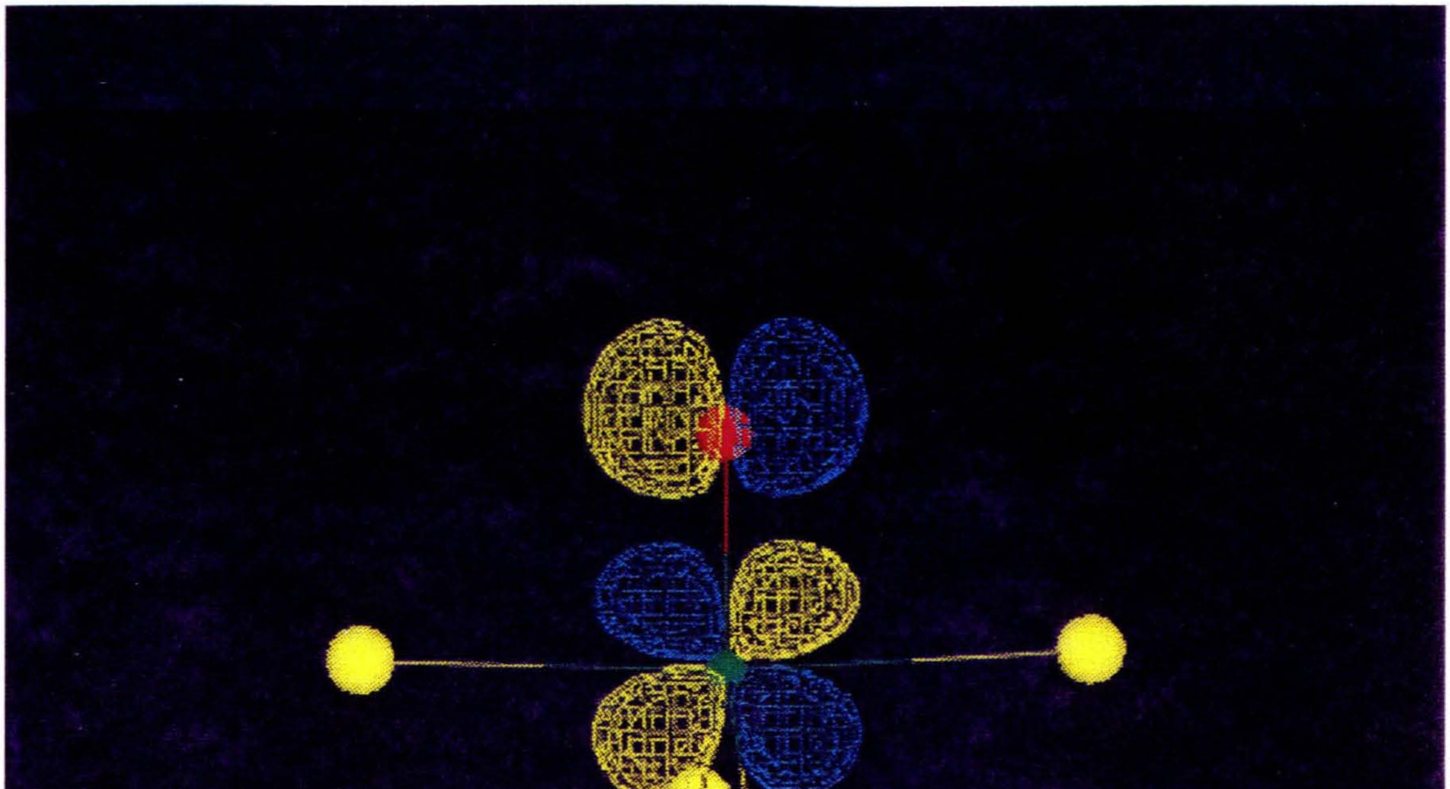


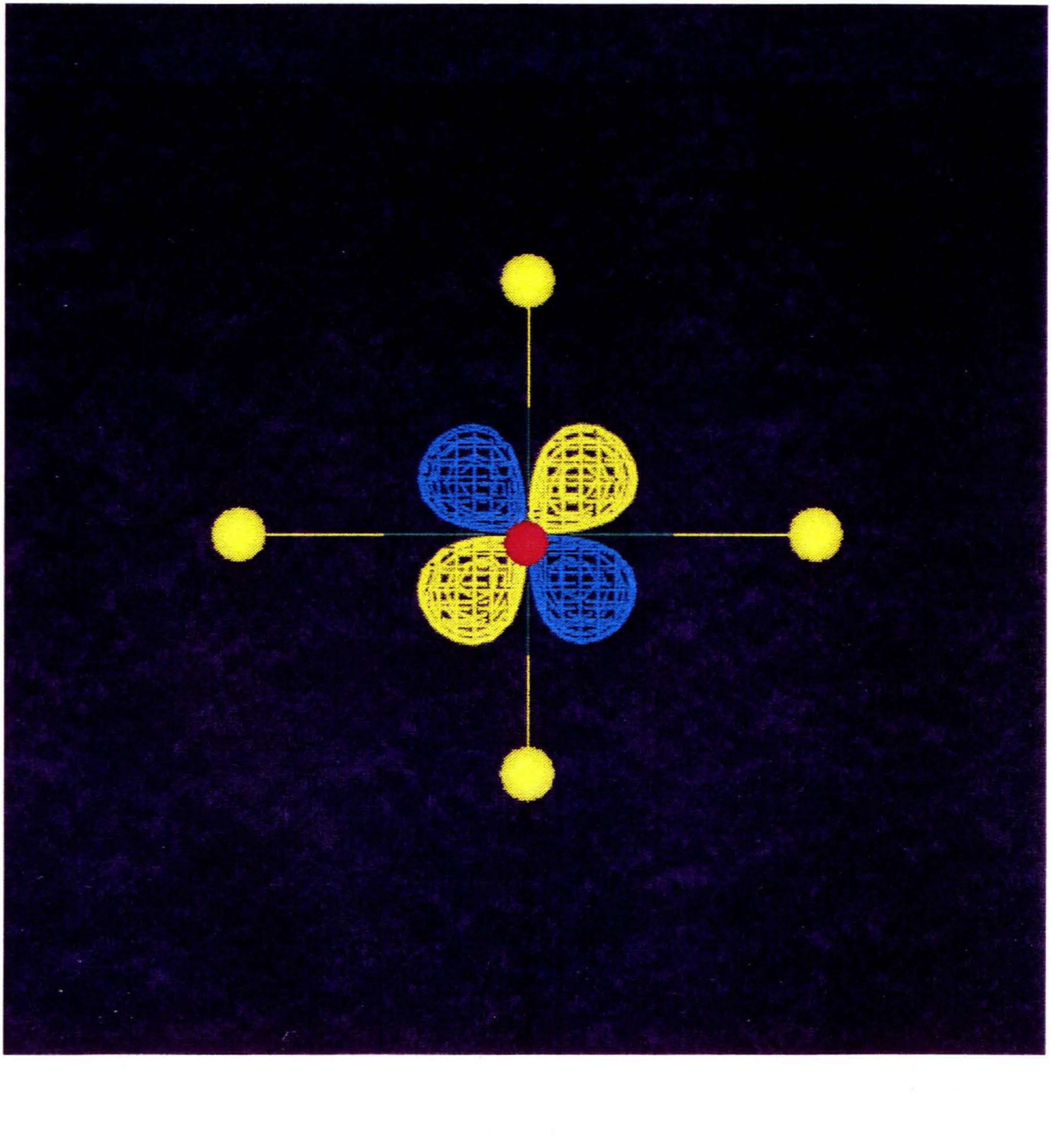




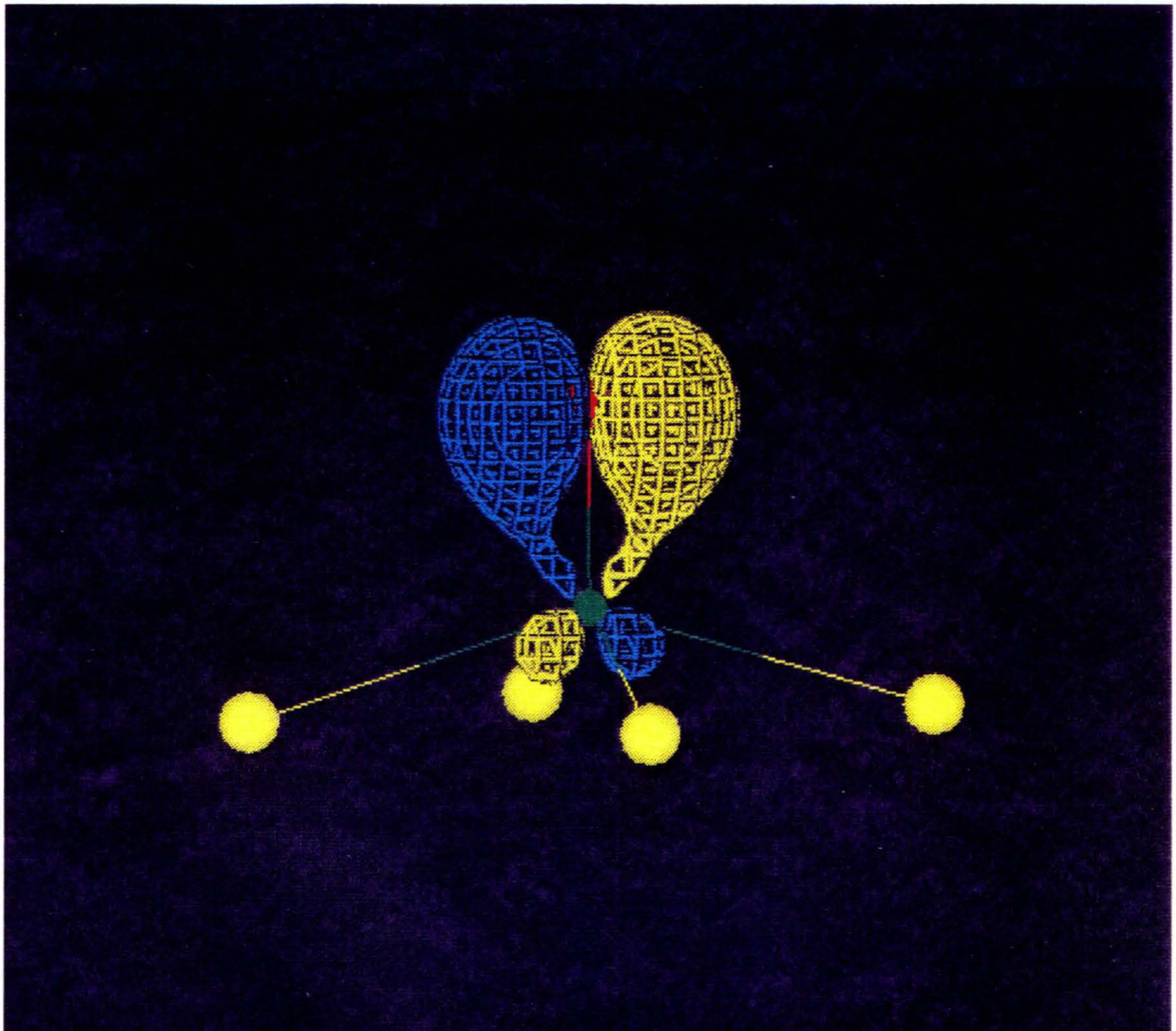


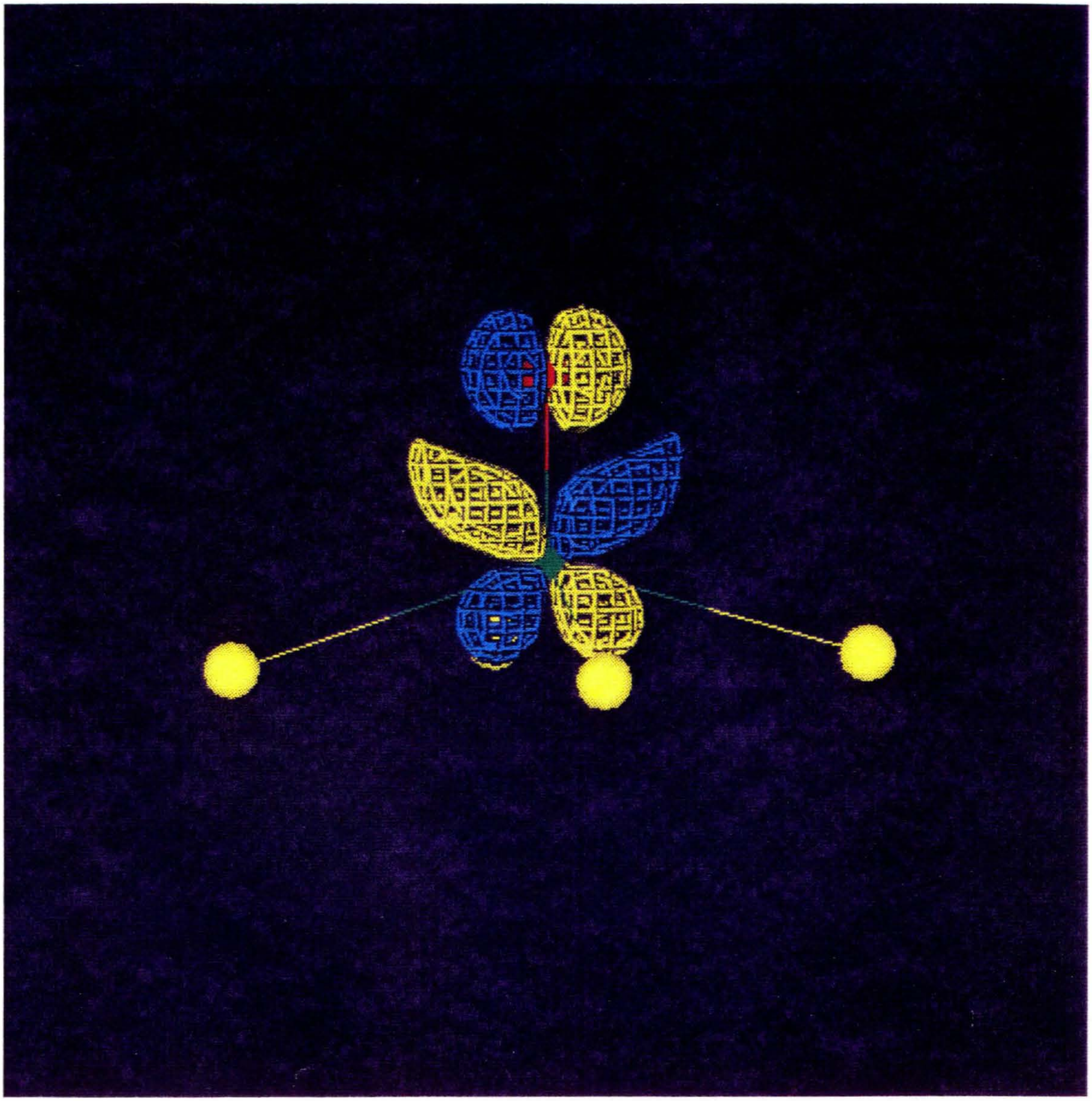




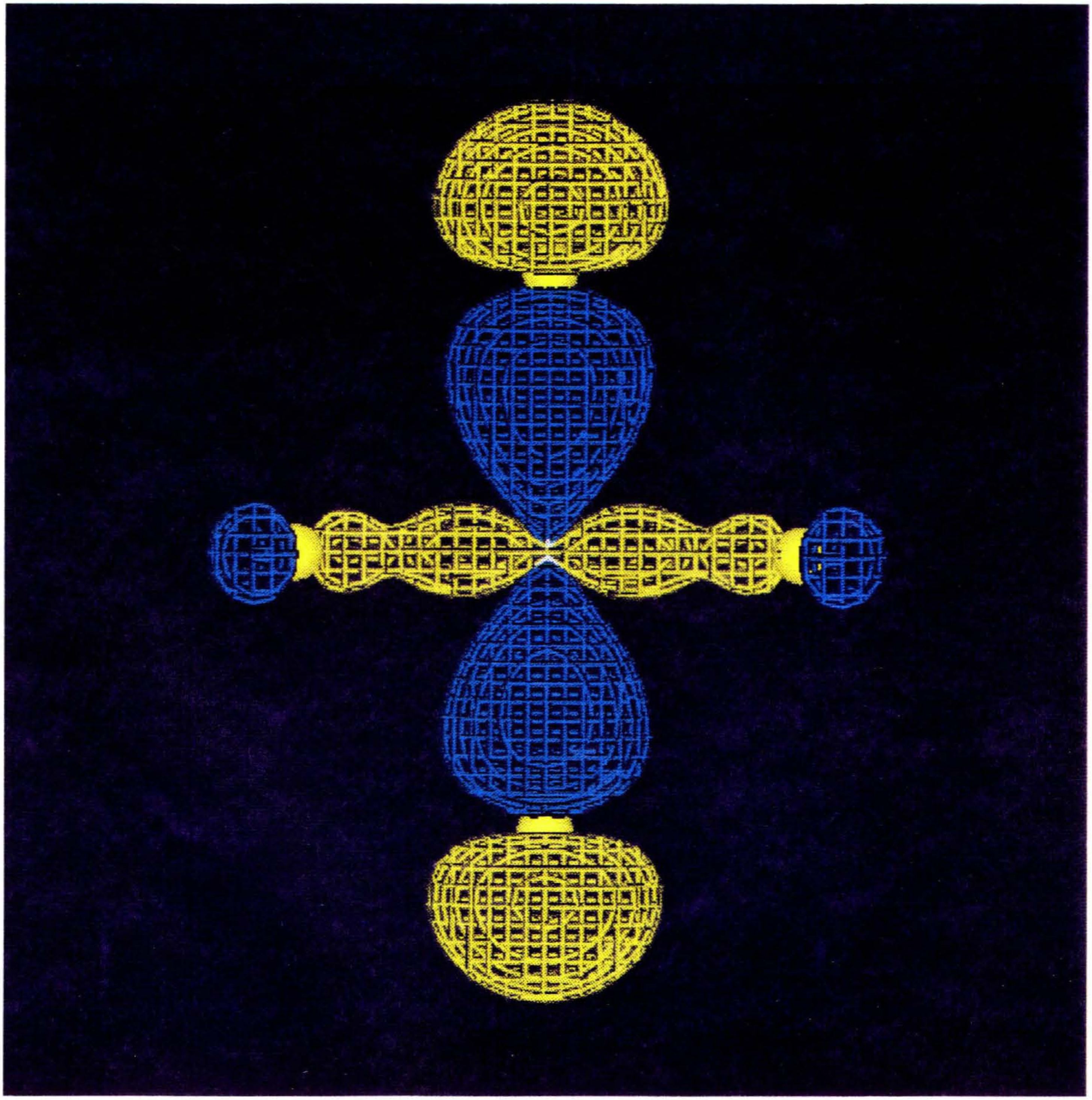


Figures IVq -r: Orbital diagrams of one of the two equivalent $VOCl_4^{3-}$ GVB pair π-bonds.





Figures IVs -t: Orbital diagrams for C_{2v} and C_{4v} $VOCl_4^-$ V-Cl MO.



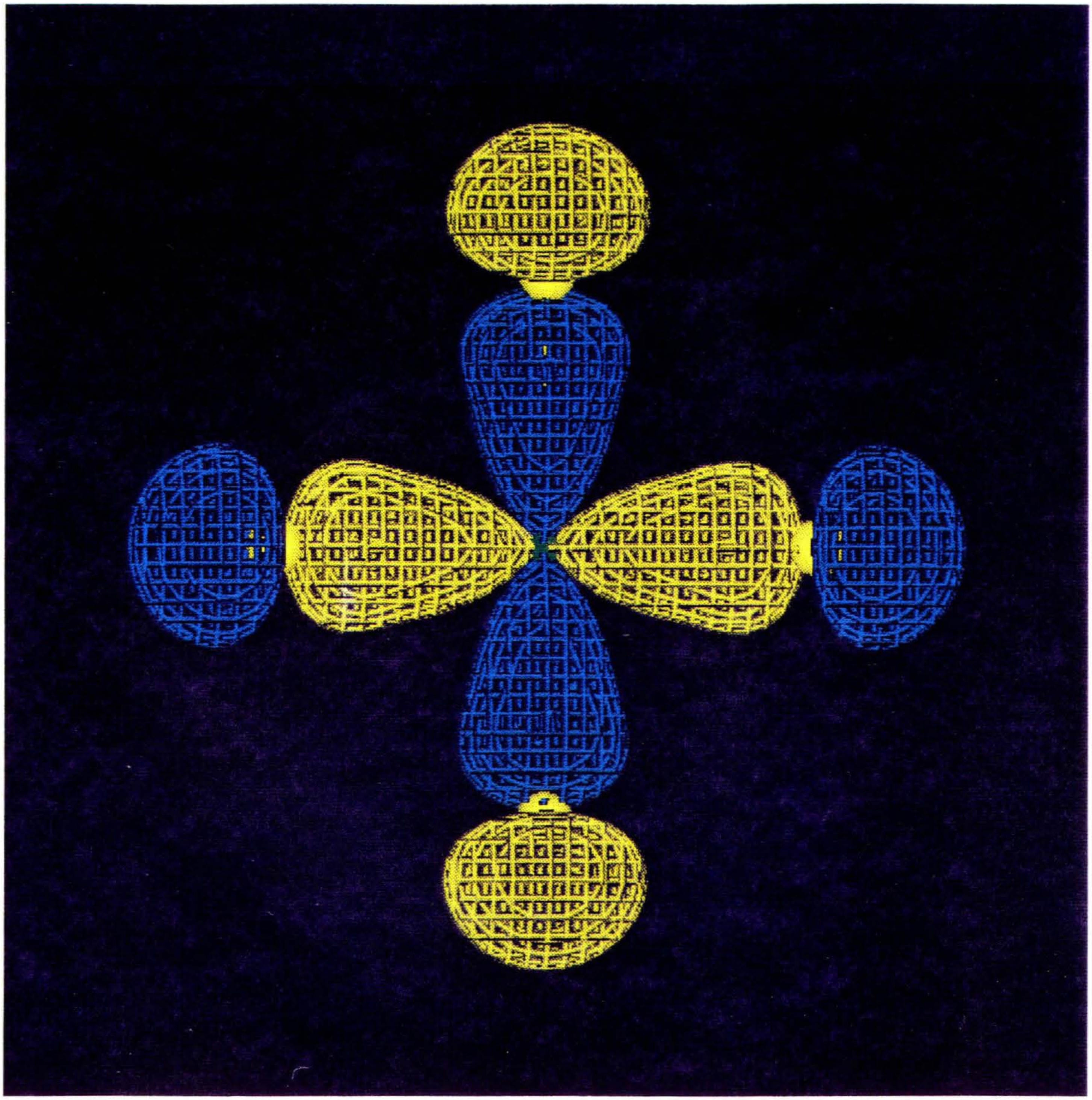


Table IVa: $VOCl_4^{3-/2-/-}$ geometries. These values were optimized at the GVB(3/6) level. Values are in angstroms and degrees. The two R(VCl) and <(OVCl) values for C_{2v} systems correspond to the values of the axial and equatorial chlorines.

System	R(VO)	R(VCl)	<(OVCl)
$VOCl_4^{3-}$ (C_{4v})	1.62	2.91	106.7
$VOCl_4^{2-}$ (C_{4v})	1.55	2.53	101.9
$VOCl_4^{2-}$ (C_{2v})	1.66	2.59/2.47	87.6/117.3
$VOCl_4^{-}$ (C_{4v})	1.57	2.34	98.9
$VOCl_4^{-}$ (C_{2v})	1.60	2.39/2.32	91.1/109.6

Table IVb: Geometry comparison - $WOCl_4$ vs. VOCl4- (C_{4v}). M = W or V.

	$WOCl_4$ (exp.)	$VOCl_4^{-}$ (calc.)
R(MO)	1.69 Å	1.55 Å
R(MCl)	2.28 Å	2.34 Å
<(OMCl)	102.4 degrees	98.9 degrees

Table IVc: GVB pair energies (kcal/mol). Key values are in boldface.

System	σ	π_x	π_y
$VOCl_4^{3-}$ (C_{4v})	23.1	11.5	11.5
$VOCl_4^{2-}$ (C_{4v})	24.9	**18.2**	**18.2**
$VOCl_4^{2-}$ (C_{2v})	15.1	**9.9**	**68.6**
$VOCl_4^{-}$ (C_{4v})	15.4	**41.2**	**41.2**
$VOCl_4^{-}$ (C_{2v})	22.2	**12.4**	**66.0**

Table IVd: Mulliken populations of $VOCl_4^{3-}$. The values were computed by summing over all V/O basis functions for the bonding (and antibonding) orbitals of the bond. The total is the sum of the populations for the three bonds.

		σ	π_x	π_y	total
HF	V	0.43912	0.30577	0.30577	1.05066
	O	1.55452	1.63984	1.63984	4.83420
GVB(3/6)	V	0.66565	0.29786	0.29786	1.26786
	O	1.33347	1.70023	1.70023	4.73393
CASSCF	V	0.57286	0.40991	0.40991	1.39268
	O	1.42655	1.58754	1.58754	4.60158
GVB-CCCI	V	0.56794	0.41194	0.41194	1.39182
	O	1.42120	1.57652	1.57652	4.57424
RCI-CCCI	V	0.55582	0.40716	0.40716	1.37014
	O	1.43209	1.58079	1.58079	4.59367

Table IVe: Mulliken populations of $VOCl_4^{2-}$ (C_{4v}).

		σ	π_x	π_y	total
HF	V	0.61676	0.40069	0.40069	1.41814
	O	1.36672	1.55048	1.55048	4.46768
GVB(3/6)	V	0.73623	0.47278	0.47279	1.68180
	O	1.26000	1.51860	1.51860	4.29720
CASSCF	V	0.66543	0.54196	0.54196	1.74935
	O	1.33114	1.45114	1.45114	4.23342
GVB-CCCI	V	0.66124	0.53494	0.53494	1.73112
	O	1.32684	1.44720	1.44720	4.22124
RCI-CCCI	V	0.64755	0.52566	0.52566	1.69887
	O	1.33939	1.45475	1.45475	4.24889

Table IVf: Mulliken populations of $VOCl_4^{2-}$ (C_{2v}).

		σ	π_x	π_y	total
HF	V	0.64618	0.45400	0.34422	1.44440
	O	1.32541	1.42740	1.46426	4.21707
GVB(3/6)	V	0.52442	0.24731	0.92399	1.69572
	O	1.46679	1.74722	0.98203	4.19604
CASSCF	V	0.61008	0.53545	0.59592	1.74145
	O	1.38354	1.45959	1.39483	4.23796
GVB-CCCI	V	0.60202	0.52358	0.58383	1.39182
	O	1.38192	1.46065	1.39343	4.57424
RCI-CCCI	V	0.59167	0.51585	0.56711	1.67463
	O	1.39074	1.46611	1.40820	4.26505

Table IVg: Mulliken populations of $VOCl_4^-$ (C_{4v}).

		σ	π_x	π_y	total
HF	V	0.68537	0.50468	0.50468	1.69471
	O	1.27131	1.40445	1.40445	4.08021
GVB(3/6)	V	0.58528	0.76080	0.76080	2.10688
	O	1.39999	1.21494	1.21494	3.82987
CASSCF	V	0.68374	0.65324	0.65324	1.99022
	O	1.30887	1.33526	1.33526	3.97939
GVB-CCCI	V	0.68390	0.63859	0.63859	1.96108
	O	1.30160	1.34046	1.34046	3.98252
RCI-CCCI	V	0.67456	0.62556	0.62556	1.91298
	O	1.30525	1.35259	0.35259	4.01043

Table IVh: Mulliken populations of $VOCl_4^-$ (C_{2v}).

		σ	π_x	π_y	total
HF	V	0.71092	0.55636	0.46048	1.72776
	O	1.23879	1.33403	1.38616	4.95898
GVB(3/6)	V	0.67444	0.34271	0.93604	1.95319
	O	1.34271	1.64450	1.03364	3.99184
CASSCF	V	0.66988	0.62550	0.68617	1.98155
	O	1.32198	1.36377	1.30050	3.98625
GVB-CCCI	V	0.66923	0.60966	0.67004	1.94843
	O	1.31530	1.37103	1.30554	3.99187
RCI-CCCI	V	0.66038	0.59933	0.65327	1.91298
	O	1.32406	1.38019	1.32152	4.02577

Table IVi: Percent covalence of V-O bonds for $VOCl_4^{3-/2-/1-}$ systems. This value is computed from the following relation:

(% covalence) = 2(1-(O population/(V+O population))

Key values are listed in boldface.

	HF	GVB(3/6)	CASSCF	GVB-CCCI	RCI-CCCI
$VOCl_4^{3-}$					
σ	44.1	66.6	57.3	57.1	55.9
π_x	31.4	**29.8**	**41.0**	41.4	41.0
π_y	31.4	**29.8**	**41.0**	41.4	41.0
total	35.7	42.1	46.5	46.7	45.9
$VOCl_4^{2-}$ (C_{4v})					
σ	62.2	73.8	66.7	66.5	65.2
π_x	41.1	**47.5**	**54.4**	54.0	53.1
π_y	41.1	**47.5**	**54.4**	54.0	53.1
total	48.2	56.3	58.5	58.2	57.1
$VOCl_4^{2-}$ (C_{2v})					
σ	65.5	52.7	61.2	60.7	59.7
π_x	48.3	**24.8**	**53.9**	52.8	52.1
π_y	38.1	**97.0**	**59.9**	59.1	57.4
total	51.0	57.6	58.2	57.5	56.4
$VOCl_4^{-}$ (C_{4v})					
σ	70.1	59.0	68.6	68.9	68.1
π_x	52.9	**77.0**	**65.7**	64.5	63.2
π_y	52.9	**77.0**	**65.7**	64.5	63.2
total	58.7	71.0	66.7	66.0	64.9
$VOCl_4^{-}$ (C_{2v})					
σ	72.9	67.8	67.3	67.4	66.6
π_x	58.9	**34.4**	**63.2**	67.8	66.2
π_y	49.9	**95.0**	**69.1**	65.6	64.4
total	60.8	67.1	66.8	61.6	60.6

Table IVj: Total energies for $VOCl_4^{3-/2-/-}$. CI results are presented with and without the Davidson correction.

System	HF	GVB(3/6)-PP	CASSCF
$VOCl_4^{3-}$ (C_{4v})	-1983.433651	-1983.502397	-1983.583011
$VOCl_4^{2-}$ (C_{4v})	-1983.600496	-1983.693443	-1983.795664
$VOCl_4^{2-}$ (C_{2v})	-1983.576921	-1983.699638	-1983.789524
$VOCl_4^{-}$ (C_{4v})	-1983.487373	-1983.616088	-1983.721187
$VOCl_4^{-}$ (C_{2v})	-1983.478029	-1983.618874	-1983.715594

System	GVB-CCCI	RCI-CCCI	RCI-DCCI	GVB*SD
$VOCl_4^{3-}$ (C_{4v})	-1983.653304	-1983.687600	-	-
(ECI + DVD)	-1983.668438	-1983.694544	-	-
$VOCl_4^{2-}$ (C_{4v})	-1983.848513	-1983.882942	-1983.924822	-1984.075478
(ECI + DVD)	-1983.863334	-1983.887876	-1983.934730	-1984.130119
$VOCl_4^{2-}$ (C_{2v})	-1983.841773	-1983.877057	-	-1984.065731
(ECI + DVD)	-1983.860977	-1983.883230	-	-1984.124449
$VOCl_4^{-}$ (C_{4v})	-1983.760998	-1983.800989	-1983.855360	-
(ECI + DVD)	-1983.774996	-1983.806225	-1983.867827	-
$VOCl_4^{-}$ (C_{2v})	-1983.755091	-1983.795333	-	-
(ECI + DVD)	-1983.769574	-1983.800889	-	-

Table IVk: net charge for $VOCl_4^{3-/2-/1-}$. Cl(ax.) and Cl(eq.) refer to the axial and equatorial chlorines, respectively, of the trigonal bipyramidal C_{2v} systems.

	HF	GVB(3/6)	CASSCF	GVB-CCCI	RCI-CCCI
$VOCl_4^{3-}$					
V	+1.04414	+0.94520	+0.86514	+0.86835	+0.88285
O	-0.84447	-0.71757	-0.61344	-0.61915	-0.63505
Cl	-0.79992	-0.80691	-0.81292	-0.81230	-0.81195
$VOCl_4^{2-}$ (C_{4v})					
V	+1.02769	+0.92996	+0.90198	+0.91782	+0.93481
O	-0.54243	-0.36610	-0.28640	-0.30474	-0.32966
Cl	-0.62132	-0.64096	-0.65390	-0.65327	-0.65129
$VOCl_4^{2-}$ (C_{2v})					
V	+1.04349	+1.02713	+0.91742	+0.94443	+0.96331
O	-0.58979	-0.33213	-0.28864	-0.31878	-0.34728
Cl(ax.)	-0.63415	-0.68550	-0.67929	-0.67838	-0.67665
Cl(eq.)	-0.59271	-0.66200	-0.63511	-0.63445	-0.63137
$VOCl_4^{-}$ (C_{4v})					
V	+0.86271	+0.74343	+0.76822	+0.79694	+0.81185
O	-0.38266	-0.05403	-0.07685	-0.10237	-0.13475
Cl	-0.37001	-0.42235	-0.42284	-0.42364	-0.41928
$VOCl_4^{-}$ (C_{2v})					
V	+0.87727	+0.85261	+0.78825	+0.81931	+0.83310
O	-0.40345	-0.13257	-0.08441	-0.11251	-0.14567
Cl(ax.)	-0.35813	-0.43965	-0.41154	-0.43803	-0.40641
Cl(eq.)	-0.37878	-0.42037	-0.44039	-0.44035	-0.43730

Table IVl: Total ligand charge and V(3d) character for VOCl43-/2-/-. The V(3d) character is defined as the total population of the V(3d) orbitals.

charge	HF	GVB(3/6)	CASSCF	GVB-CCCI	RCI-CCCI
$VOCl_4^{3-}$	-4.04414	-3.94520	-3.86514	-3.86835	-3.88285
$VOCl_4^{2-}$ (C_{4v})	-3.02769	-2.92996	-2.90198	-2.91782	-2.93481
$VOCl_4^{2-}$ (C_{2v})	-3.04349	-3.02713	-2.91742	-2.94443	-2.96331
$VOCl_4^{-}$ (C_{4v})	-1.86271	-1.74343	-1.76822	-1.79694	-1.81185
$VOCl_4^{-}$ (C_{2v})	-1.87727	-1.85261	-1.78825	-1.81931	-1.83310

3d-character	HF	GVB(3/6)	CASSCF	GVB-CCCI	RCI-CCCI
$VOCl_4^{3-}$	3.13595	3.25888	3.36746	3.36279	3.34755
$VOCl_4^{2-}$ (C_{4v})	3.12680	3.23729	3.28030	3.26426	3.24700
$VOCl_4^{2-}$ (C_{2v})	3.09334	3.17112	3.25636	3.22878	3.20973
$VOCl_4^{-}$ (C_{4v})	3.32916	3.43358	3.41564	3.38648	3.37172
$VOCl_4^{-}$ (C_{2v})	3.32331	3.35641	3.40427	3.37273	3.35907

Table IVm: V-O snap bond strengths (kcal/mol) for $VOCl_4^{3-/2-/-}$ (C_{4v}), computed from various CI calculations. The fragments were computed by performing high-spin HF calculations with the neutral oxygen "stretched" 100 Å from the vanadium center.

System	Calculation	Snap bond strength
$VOCl_4^{3-}$	RCI-CCCI	211.3
$VOCl_4^{2-}$	RCI-CCCI	109.8
	RCI-DCCI	108.1
	GVB*SD	97.3
$VOCl_4^{-}$	RCI-CCCI	81.5

V. $VOCl_2$ - Systems

These systems were examined with the zeroth-order approximation of two chlorides bound to a V-O unit (Figure Va). Again, the geometry was optimized at the GVB(3/6)-PP level (55 basis functions). The results are given in Table Va. In addition, GVB-RCI calculations were performed to test the importance of the RCI space, as was demonstrated in the $VOCl_4$ - systems. The results indicate that this is again the case (Table Vb).

Table Vc gives the resulting GVB(3/6) pair energies for these systems. $VOCl_2^-$ exhibits the same characteristics as $VOCl_4^{3-}$ (C_{4v}). This system is a triplet ($^3A_2$). Singlet states (in both cases) were found to be higher in energy by 31 kcal/mol. The geometry of the system is almost exactly trigonal planar, with O-V-Cl bond angles of 122.9 degrees. The systems both form two equivalent π-bonds, and the pair energies are virtually identical. In addition, Mulliken population information for the two systems is virtually the same. (See Table Vd.) In both cases, the π-bonds are only weakly covalent, while the σ-bond has greater covalent character. The Mulliken populations for both place approximately five (4.7) of the six V-O electrons on the oxygen. While addition of the two chlorides to form $VOCl_4^{3-}$ does create a net increase of charge on the chlorides (approximately 0.2), the description of the V-O bond appears unaffected. The additional degree of charge transfer to the oxygen in these systems suggest a smooth transition to a system, to zeroth-order, of one covalent V-O σ-bond, and two donor-acceptor V-O π-bonds.

Examination of $VOCl_2^+$ gave a dramatically different picture. This system displayed the V-O bonding character of C_{2v} $VOCl_4^-$. A comparison of Mulliken populations and GVB pair energy data of these two systems reveals essentially the same V-O bond description - a σ-bond and two different π-bonds, one highly covalent, the other donor-acceptor in nature. This is consistent with the optimized geometry of the system, in which the O-V-Cl (equatorial) bond angles of the respective systems differ by only two degrees. This system might therefore be described as the precursor to C_{2v} $VOCl_4^-$, except without the two axial chlorides.

In addition, the unoccupied $V(3d_{xy})$ orbital appears to form a covalent δ-bond to the chlorides! (It was this discovery which led to the re-examination of the four-chloride systems.) This system was thus re-examined in two ways.

In the first, a GVB(6/12) calculation was performed in which, in addition to the three V-O pairs, three potential V-Cl bonding orbitals were selected. The pairs A_1, A_2, and B_2 correspond to the symmetry of the vanadium orbital(s) with which the chlorines may interact - $4s/3d_{x^2-y^2}$, $3d_{xy}$, and $3d_{yz}$, respectively. The results of this calculation are given in Table Ve. These results indicate a strongly covalent A_2 bond, while the other V-Cl pairs exhibit considerably less GVB energy lowering. B_2 appears non-bonding, while A_1, despite having a very low GVB energy lowering, has considerable V(3d)-character. This bond appears relatively ionic. Including these pairs improves the energy of the system by 15 kcal/mol, with the chief contribution being from A_2. From these six pairs, a 12-in-12 CASSCF was carried out, with the important configurations given in Table Vf. Six of the thirteen excited states given involve the V-Cl pairs, including two of the three most important configurations. The most important contribution to V-Cl bonding again appears to be A_2, with some A_1 character. B_2 again appears to be essentially non-bonding.

Table Vg provides a different approach. Since there appears to be only one covalent bond to the chlorides, a GVB(6/12) calculation was carried out in which the symmetry of the wavefunction was broken (from C_{2v} to C_s). By mixing the A_1 and B_2 symmetries, a covalent bond to each chlorine could be formed. In this case, however, the system converges to two non-equivalent V-Cl bonds, and one chlorine lone pair. One V-Cl bond consists of $V(3d_{xy})+Cl(2p_x)$, which is strongly covalent. The weaker of the two corresponds to $V(3d_{x^2-y^2})+Cl(2p_y)$. Since this approach converges to a result which essentially includes two pairs on one chlorine, and one on the other, the calculation was repeated at the GVB(5/10) level, neglecting the additional chloride lone pair. The overall description of the system, however, remained unchanged. Note that this additional covalency does not change the character of the V-O bond. Calculations in which the donor-acceptor V-O pair was not correlated gave little change in the description of that orbital. Orbital diagrams for the V-Cl GVB pairs are displayed in Figures Vb-k. R-GVB calculations, which re-establish the C_{2v} symmetry of the wavefunction by including both resonance states, gives a resonance energy of 10.85 kcal/mol..

These results give a very different description of the bonding in C_{2v} $VOCl_4^-$ and $VOCl_2^+$, as compared to $VOCl_4^{3-}$ and $VOCl_2^-$. In the case of $VOCl_4^-/VOCl_2^+$, in addition to the V-O description given above (σ-bond and two different π-bonds, one highly covalent, the other donor-acceptor), there is resonance to form a single covalent bond to the chlorines. This is quite different than $VOCl_4^{3-}/VOCl_2^-$, in which the two chlorine system forms a precursor for a C_{4v} system, and no C_{2v} system exists for $VOCl_4^{3-}$. In contrast, the V(V) two chloride system forms a precursor for a C_{2v} system, which is more stable (at the GVB level) than the C_{4v} geometry.

These cases both can be used to explain the behavior of $VOCl_2$ - the intermediate between the previous cases. GVB(3/6) calculations (Table Vc) indicate the same V-O bonding scheme as $VOCl_2^+$. This is further borne out by a population analysis. This oxidation state of vanadium (IV) also demonstrates both C_{2v} and C_{4v} structures for four-chloride systems. In addition, the O-V-Cl bond angle differs by only two degrees in $VOCl_2$ and C_{2v} $VOCl_4^{2-}$, as with the previous system. However, the V-Cl interaction appeared weaker at the HF and GVB(3/6) levels. GVB calculations were thus performed in which additional pairs were examined - for both $^2A_2$ and $^2A_1$ states, in order to examine the effect of the additional δ-electron. These results are given in Tables Vh and Vi. The pairs chosen are analogous to those in Table Ve for $VOCl_2^+$. These results show virtually no covalency in the V-Cl bonds. In particular, The V-Cl A_2 pair gives a GVB pair energy lowering of less than one kcal/mol, as opposed to 55.7

kcal/mol in VOCl2+. Additional GVB(4/8) calculations, in which the C_{2v} symmetry of the wavefunction was broken, gave similar results.

Given this information, it is possible to further hypothesize on the behavior of the two- and four-chloride systems. In V(V) $VOCl_2^+$, the geometry optimized not only to optimize the V-O interaction, but also the V-Cl interaction. This system is analogous in both geometry and bonding scheme to the four-chloride V(V) C_{2v} system, only without the axial chlorides. For C_{2v} $VOCl_4^-$, it can thus be extrapolated that considerable vanadium covalency to the chlorine ligands is favored by the C_{2v} geometry. Although this interaction appears to be more favorable in the C_{2v} geometry, it is also present in C_{4v}. This effect favors the breaking of C_{4v} symmetry in geometry optimization in the four-chloride systems to form the C_{2v} geometry. The V-O bond in $VOCl_2^+$ and the C_{2v} state is a σ-bond and two π-bonds, one covalent, the other donor-acceptor. In the symmetric C_{4v}, this description becomes a resonance description between the two π-bonds, which now experience identical electronic environments.

Adding a δ-electron (V(IV) - $VOCl_2$ and $VOCl_4^{2-}$) reduces the covalent interaction between vanadium and the chlorines, but the effect is apparently still significant enough to give the V(IV) systems the same V-O bond properties as V(V), since the C_{2v} structure still plays an important role in examining both the C_{2v} and C_{4v} systems.

Adding a second δ-electron (V(III) - $VOCl_2^-$ and $VOCl_4^{3-}$) effectively eliminates the V-Cl covalent interaction - there are no longer 3dδ-orbitals available. The high barrier to the singlet states further precludes the likelihood of such covalency. Here, the C_{2v} state plays no role in understanding the system. Here, the V-O π-bonds are equivalent. In fact, it appears that charge transfer to oxygen is sufficient to consider both π-bonds to be donor-acceptor in character.

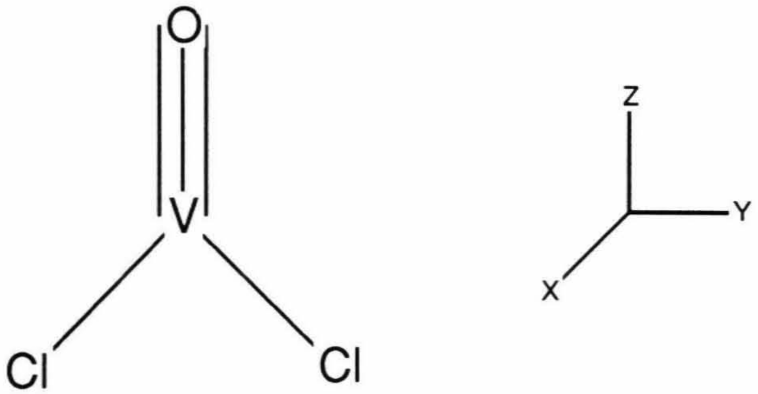


Figure Va: Geometry of $VOCl_2^{+/0/-}$ systems.

Figures Vb-k: Orbital diagrams for V-O and V-Cl GVB pairs for $VOCl_2^+$. The distortion in the V-O bond is due to the inequivalent treatment of the two chlorides in the C_s wavefunction. The plots are given as follows:

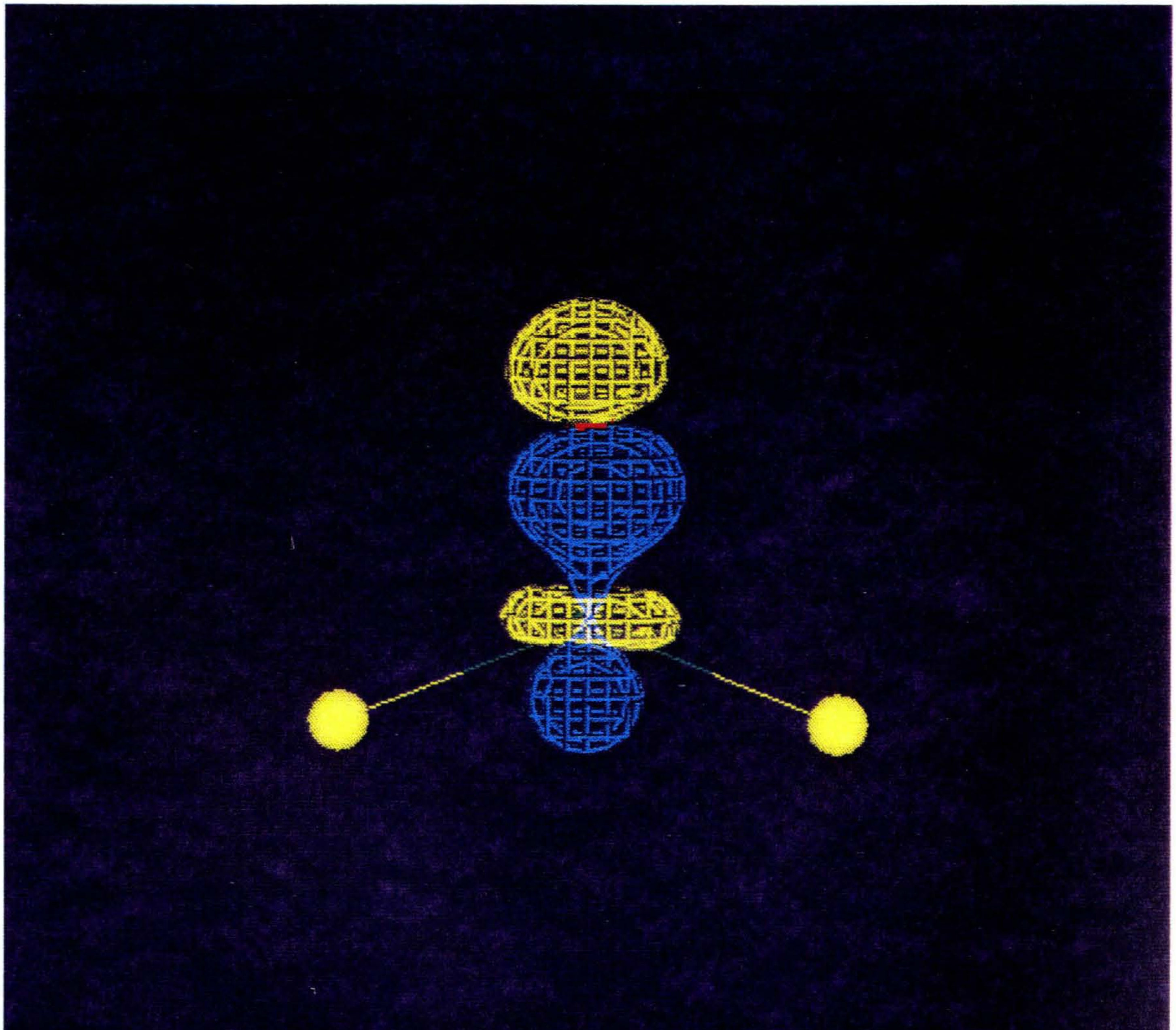
Vb,c: VO σ

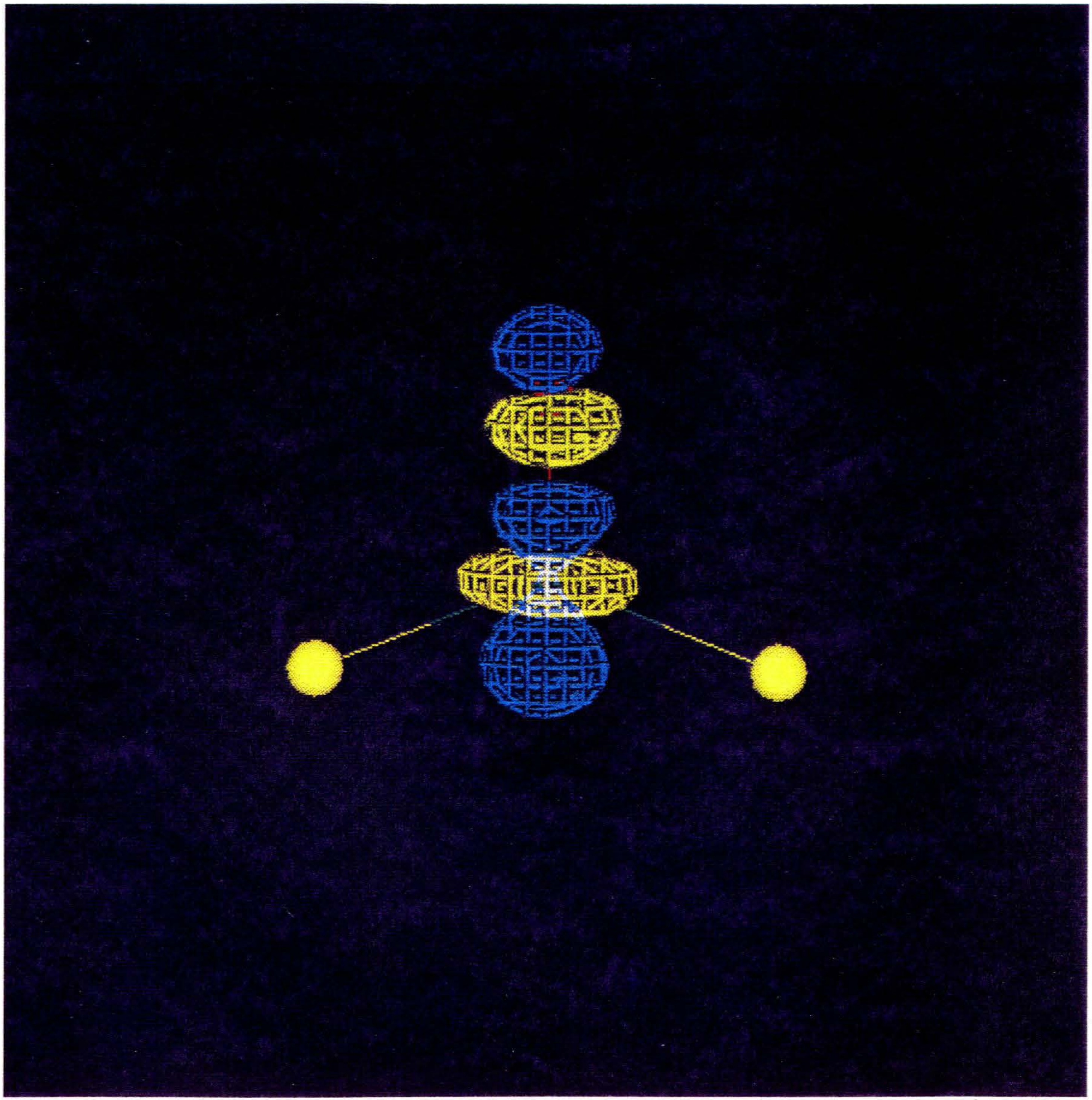
Vd,e: VO π_x

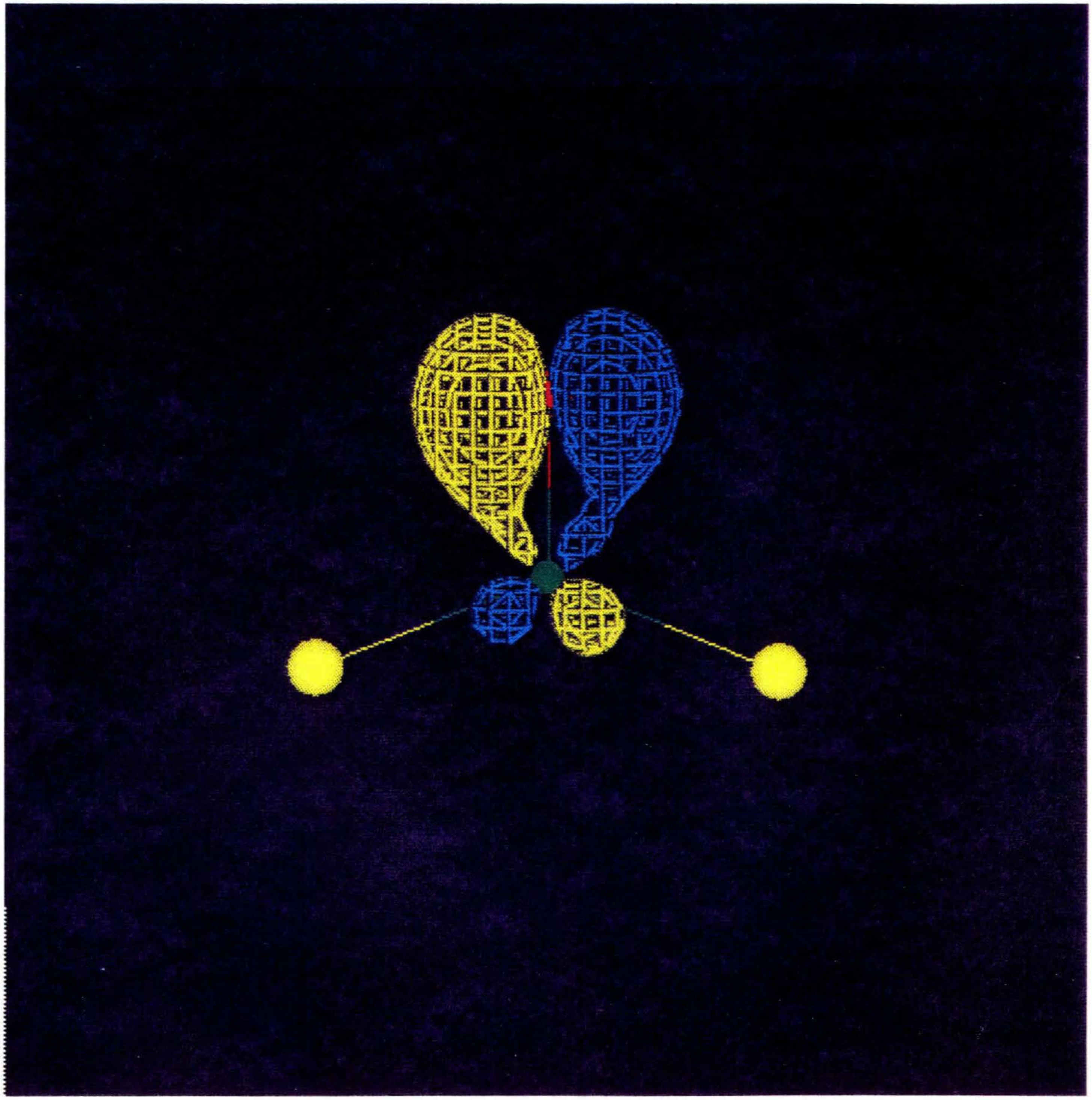
Vf,g: VO π_y

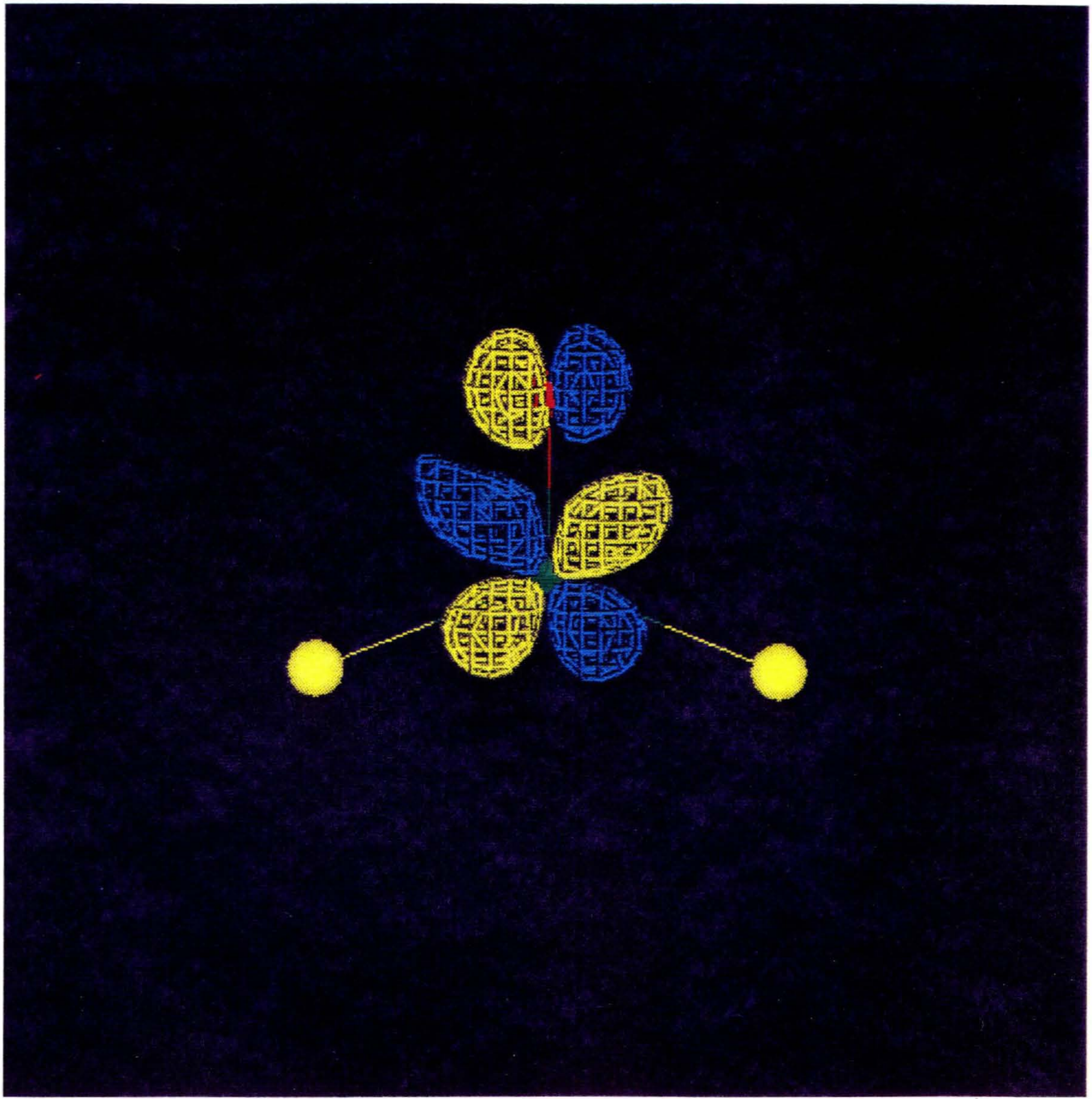
Vh,i: VCl σ

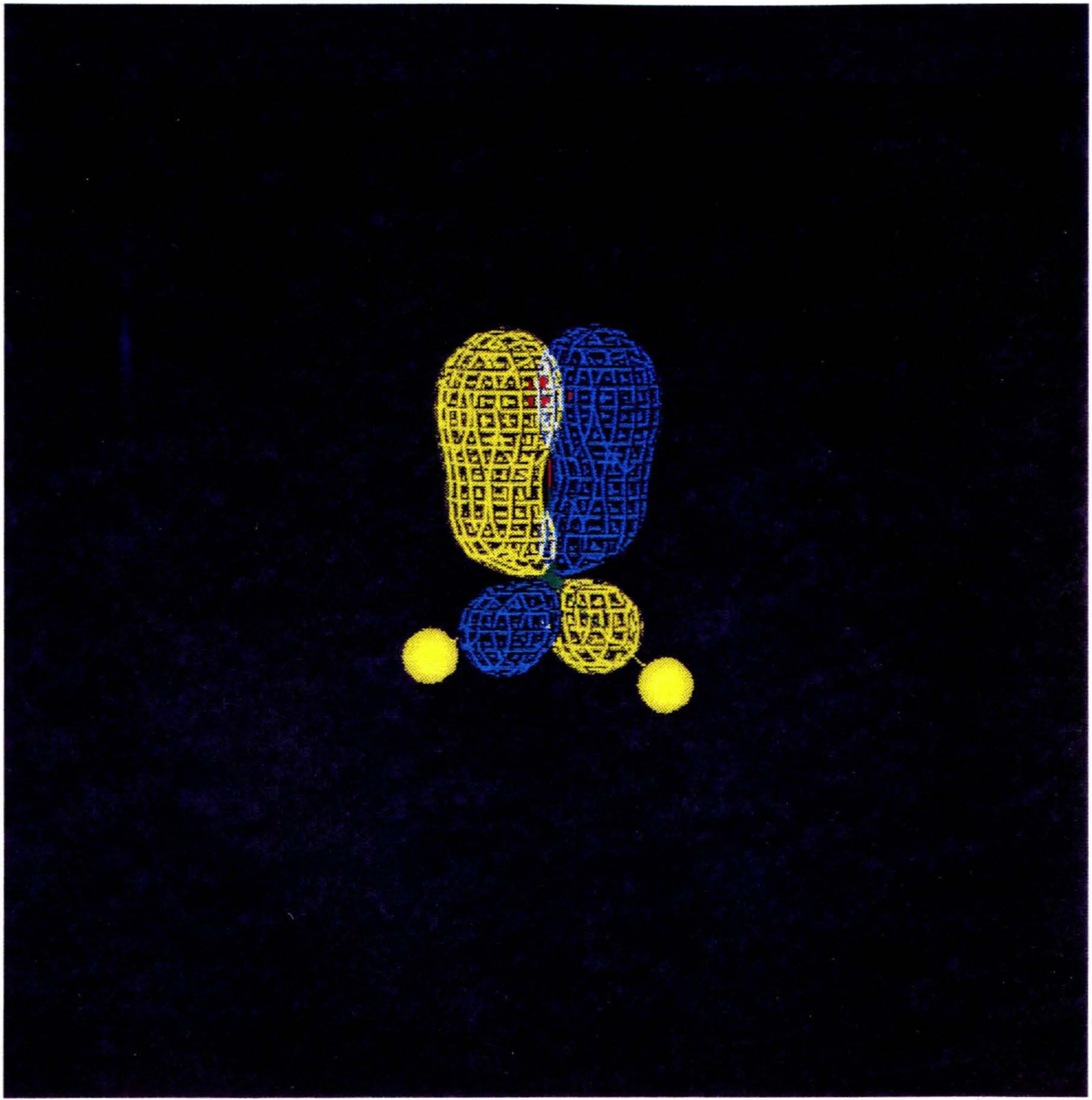
Vj,k: VCl π

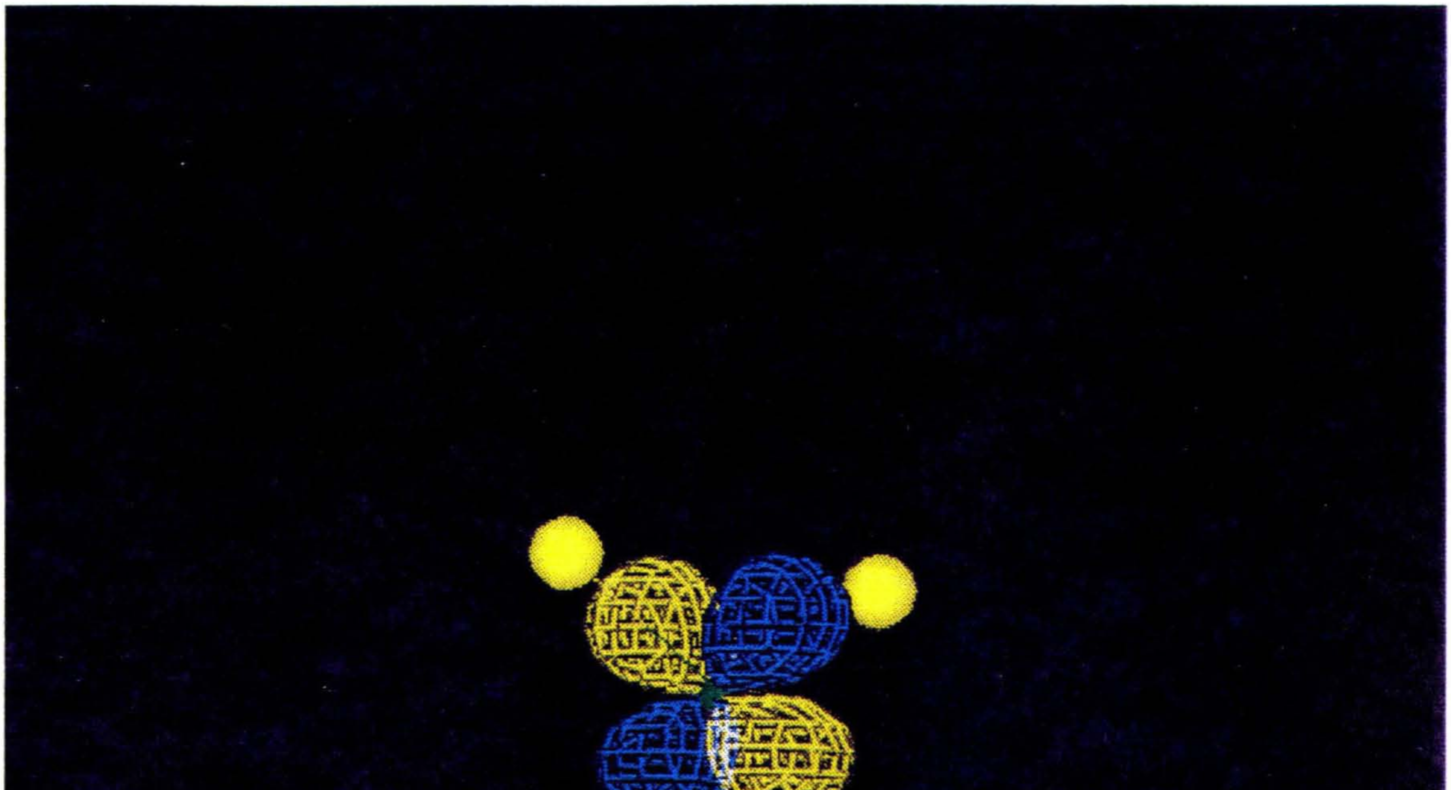


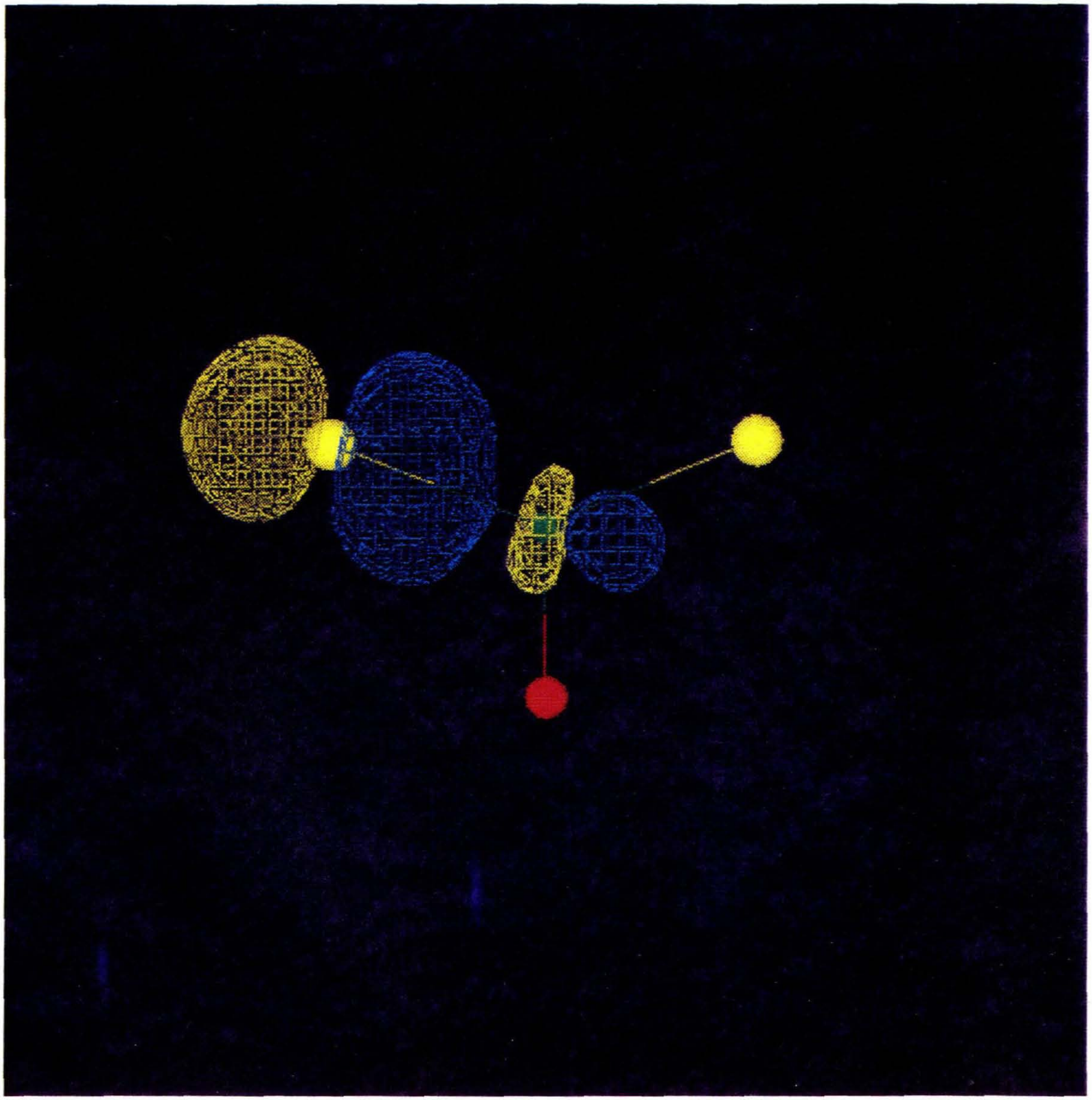


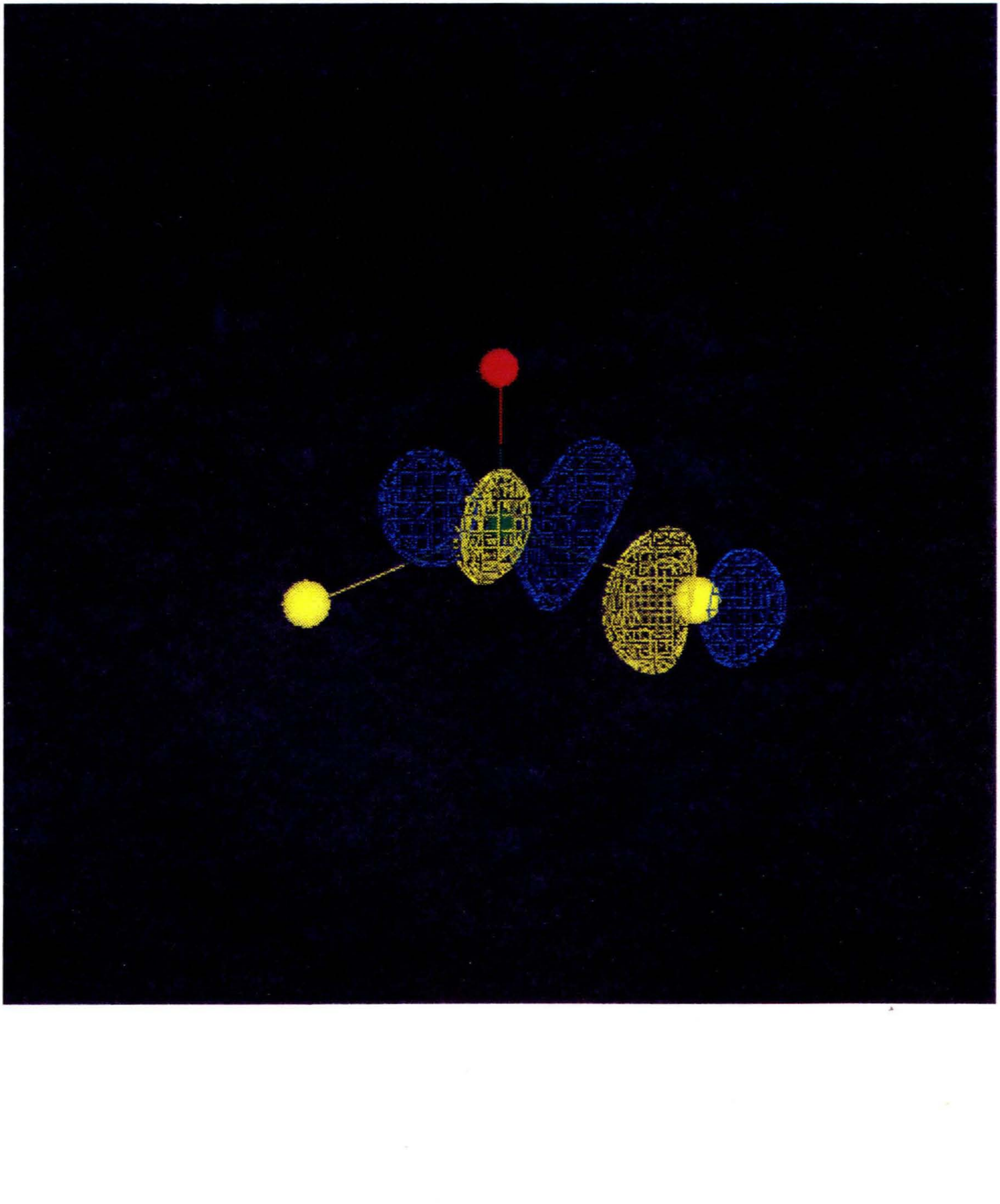


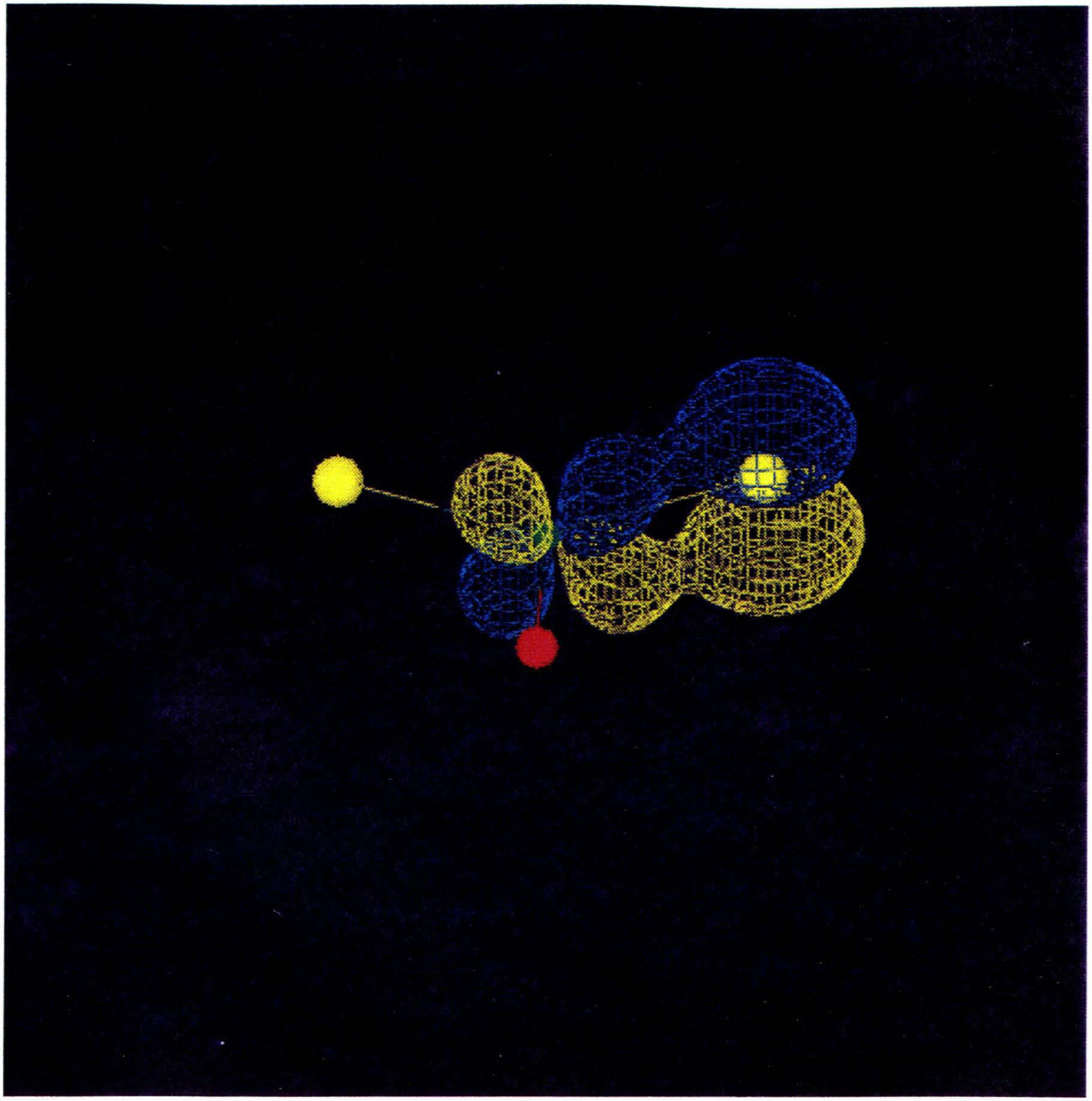












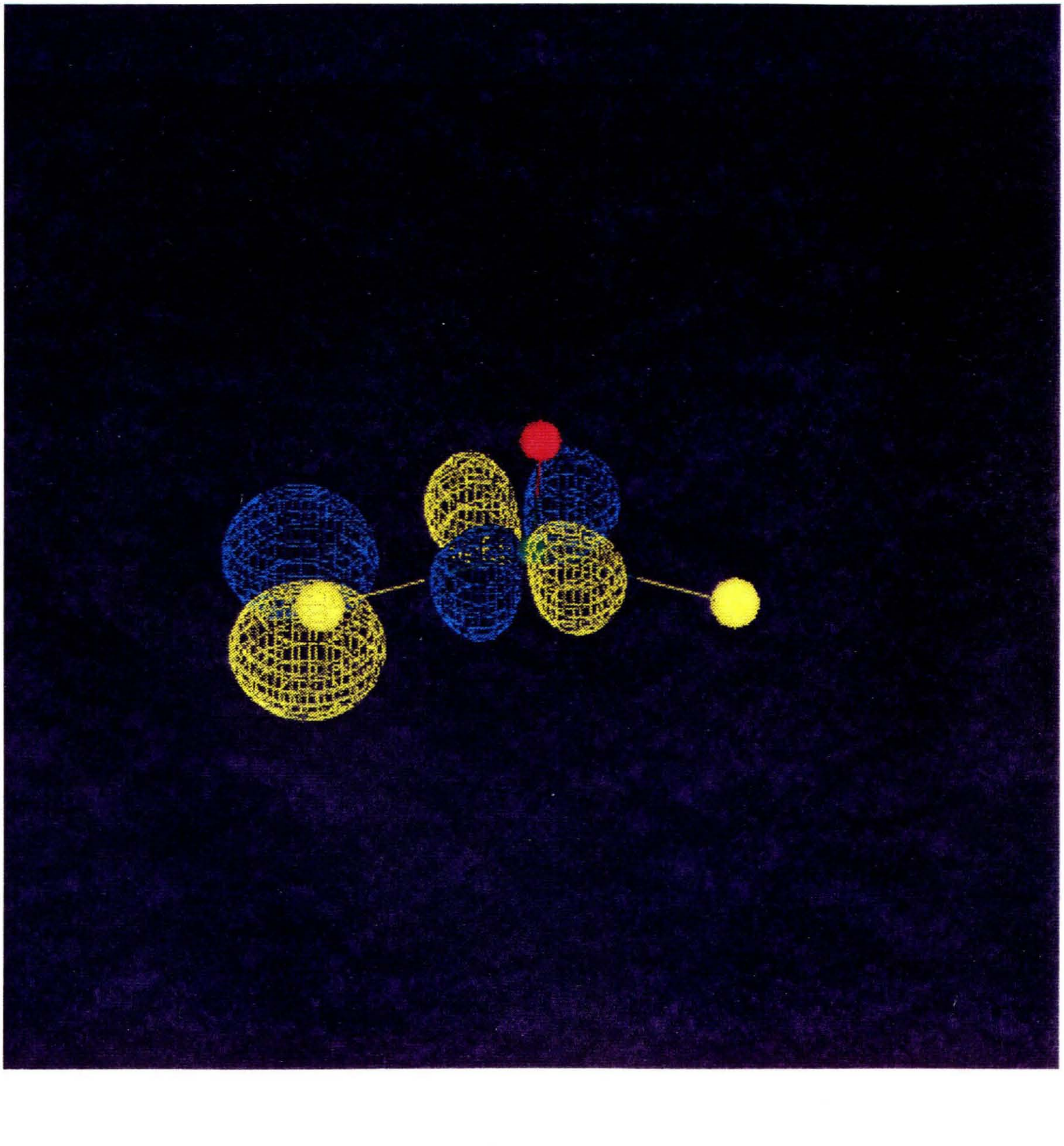


Table Va: Optimized Geometries (GVB(3/6)-PP). Bond lengths are in angstroms, and angles in degrees.

	$VOCl_2^-$	$VOCl_2$	$VOCl_2^+$
R(VO)	1.61	1.61	1.59
R(VCl)	2.46	2.29	2.15
<(OVCl)	122.9	115.3	111.5
<(ClVCl)	114.2	129.5	137.0

Table Vb: Total energy for $VOCl_2$ systems (in hartrees).

$VOCl_2^-$	$(d_{xy})^1(d_{x^2-y^2})^1$	$(d_{xy})^2$	$(d_{x^2-y^2})^2$
HF	-1064.691106	-1064.642097	-1064.642620
GVB(3/6)-PP	-1064.761359	-1064.713873	-1064.715358
GVB(3/6)-RCI	-1064.834002	-1064.781749	-1064.783964

$VOCl_2$	$(d_{xy})^1$	$(d_{x^2-y^2})^1$
HF	-1064.494621	-1064.493137
GVB(3/6)-PP	-1064.611023	-1064.608119
GVB(3/6)-RCI	-1064.683291	-1064.682217

	$VOCl_2^+$
HF	-1064.002904
GVB(3/6)-PP	-1064.154115
GVB(3/6)-RCI	-1064.232451

Table Vc: GVB(3/6) pair energies (kcal/mol) - key values are given in boldface.

Pair	$VOCl_2^-$ triplet	$VOCl_2^-$ $(d_{xy})^2$	$VOCl_2^-$ $(d_{x^2-y^2})^2$	$VOCl_2$ $(d_{xy})^1$	$VOCl_2$ $(d_{x^2-y^2})^1$	$VOCl_2^+$
σ	22.40	24.72	25.23	18.26	18.64	26.67
π_{xz}	**12.49**	12.30	11.86	**55.10**	**54.41**	**61.81**
π_{yz}	**12.49**	11.48	9.52	**10.60**	**11.04**	**13.18**

Table Vd: $VOCl_2^-$ GVB(3/6) population analysis. ("unpaired" refers to the two electrons in the V(3dδ) orbitals.) Key values are given in boldface.

	V	O	Cl
core	8.76677	3.99412	7.61956
unpaired	1.98203	0.00532	0.00632
VO σ	**0.66089**	**1.33869**	0.00021
VO π_x	**0.34810**	**1.65174**	0.00008
VO π_y	**0.34426**	**1.65261**	0.00156
----	______	______	______
total	12.10206	8.64241	7.62773
charge	+0.89794	-0.64248	-0.62773

Table Ve: GVB pair energy and population analysis of $VOCl_2^+$ (GVB(6/12)-PP). (E refers to the GVB pair energy.) Key values are given in boldface.

Total Energy (hartrees) = -1064.188218

GVB pair	E (kcal/mol)	V	O	Cl
VO σ	**23.2**	**0.67282**	**1.32784**	-0.00033
VCl (A_1)	1.7	0.50530	0.01894	0.73788
VCl (A_2)	**35.2**	**0.97459**	0.00019	**0.51261**
VO π_x	**55.9**	**0.92538**	**1.07191**	0.00136
VO π_y	12.2	0.33254	1.65341	0.00702
VCl (B_2)	0.7	0.25155	0.00986	0.86929
(core)	-	8.24270	4.02899	4.86416
____	___	______	______	______
total	-	11.90489	8.11114	6.99199
charge	-	+1.09511	-0.11114	+0.00801

Table Vf: Configurations with CI coefficients greater than 0.05 magnitude for the 12-in-12 CASSCF for $VOCl_2^+$. "HF" refers to the Hartree-Fock ground state. "GVB" and "RCI" refer to any configuration which is part of the GVB/RCI reference space - excitations within the $A_1(\sigma)$, $B_1(\pi_x)$, and $B_2(\pi_y)$ V-O bonds. "Valence" refers to the excitations within the V-Cl bonds (A_1, A_2 and B_2). "Single" and "double" refer to the excitation. (All configurations are singlet states.)

Coefficient	Weight	Description
0.869048	0.7552	HF
-0.152278	0.0232	GVB(B_1, double)
-0.145337	0.0211	valence(A_1, single; A_2, single)
-0.138584	0.0192	valence(A_2, double)
-0.131937	0.0174	RCI(A_1, single; B_1, single)
0.128514	0.0165	RCI(B_1, single; B_2, single)
0.123322	0.0152	RCI(A_1, single; B_2, single)
-0.109632	0.0120	GVB(B_2, double)
-0.101734	0.0104	GVB(A_1, double)
-0.094503	0.0089	valence(A_2, single; V-Cl(B_2) -> V-O*(B_2), single)*
0.060570	0.0037	valence(A_1, single; A_2, single)
-0.059124	0.0035	valence(A_1, double)
-0.057126	0.0033	RCI(B_1, single; B_2, single)
0.051326	0.0026	valence(A_1, single; A_2, double)

(*Note: this configuration refers to a single excitation within the A_2 V-Cl bond pair, and a single excitation from the bonding V-Cl(B_2) orbital to the antibonding V-O(B_2) orbital.)

Table Vg: Energy, GVB(5/10) pair energies and Mulliken Populations of $VOCl_2^+$. The wavefunction has C_s symmetry. Key values are given in boldface.

Total Energy (hartrees) = -1064.204585

GVB pair	E (kcal/mol)	V	O	Cl1	Cl2
VO π_y	**11.7**	**0.31974**	**1.66257**	0.00480	0.01289
VO σ	**21.6**	**0.65634**	**1.34570**	-0.00129	-0.00076
VCl (A')	**5.1**	**0.46094**	0.01642	-0.00757	**1.53021**
VO π_x	**54.2**	**0.91802**	**1.07949**	0.00021	0.00228
VCl (A")	**62.4**	**0.96377**	0.00090	**1.02184**	0.01349
(core)	-	8.61131	4.04061	5.73692	5.61116
----	---	-------	-------	-------	-------
total	-	11.93012	8.14570	6.75491	7.16927
charge	-	+1.06988	-0.14570	+0.24509	-0.16927

Table Vh: GVB(6/12) Population analysis of $VOCl_2$ ($V(d_{x^2-y^2})^1$). Key values are given in boldface. (NOTE: B_2 denotes a $V(3p_y)$, which optimized instead of VCl (B_2) (the initial guess).)

Total Energy (hartrees) = -1064.613520

GVB pair	E (kcal/mol)	V	O	Cl
VO σ	**19.4**	**0.62119**	**1.37521**	0.00180
VCl (A_1)	1.1	0.39209	0.02902	0.78944
VCl (A2)	0.9	0.19571	0.00003	0.90213
VO π_x	**55.0**	**0.91481**	**1.08333**	0.00093
VO π_y	**9.9**	**0.25432**	**1.72857**	0.00856
B_2	1.8	1.91404	0.00239	0.04178
(core)	-	6.58836	4.04440	5.68362
$V(d_{x^2-y^2})^1$	-	0.97318	0.00151	0.01266
total	-	11.85370	8.26445	7.44092
charge	-	+1.14630	-0.26445	-0.44092

Table Vi: GVB(5/10) Population analysis of $VOCl_2$ ($V(d_{xy})^1$). Key values are given in boldface.

Total Energy (hartrees) = -1064.616047

GVB pair	E (kcal/mol)	V	O	Cl
VO σ	**18.7**	**0.61052**	**1.38841**	0.00054
VCl (A_1)	1.7	0.40554	0.02417	0.78515
VO π_x	**55.7**	**0.92393**	**1.07425**	0.00091
VO π_y	**9.6**	**0.22222**	**1.74808**	0.01485
VCl (B_2)	1.9	0.22011	-0.00213	0.89101
(core)	-	8.52871	4.03077	5.72026
$V(d_{xy})^1$	-	0.96535	0.00017	0.01724
total	-	11.87637	8.26372	7.42995
charge	-	+1.12363	-0.26372	-0.42995

VI. VO Systems

VO^+ was examined previously by Carter and Goddard (CG), and was examined to ensure that the V-O bond is described identically by the different basis sets used for V in the two calculations - the key difference being the use of the effective core potential on the vanadium, as opposed to the full basis set used by CG. In addition, VO^+ was used as a reference from which to interpret the results of other calculations. The results indicate that that this is the case. 39 basis functions were used to describe this system. The bond length was optimized at the GVB(3/6)-PP level, and RCI calculations were performed upon the GVB wavefunction, including all single and double excitations within the GVB pairs. The optimized bond length was 1.56 Å, in agreement with CG. The energetics and GVB pair energies for these calculations are given in Table VIa. The ground state description is in agreement with (CG) - a triplet state with two singly-occupied dδ-orbitals ($^3\Sigma^-$). Additional calculations were performed on singlet states in which one of the dδ-orbitals was doubly-occupied. These states were computed to be 31 kcal/mol higher in energy at the GVB(3/6)-RCI level.

The V-O bond is described by CG as a triple bond, with a covalent σ-bond and resonance between a covalent π-bond and a donor-acceptor π-bond. The calculations performed here also demonstrate this behavior - the Mulliken populations give O a net -0.41 charge, with a charge in the oxygen σ- and π-systems of -1.2 and -3.2, respectively. (The Mulliken populations of the two O(2pπ)-orbitals were equivalent.) The GVB pair energies also indicate a covalent σ-bond and two equivalent π-bonds with low pairing energies - in good agreement with the pair energies of CG (obtained by exactly reproducing the CG results). A comparison of a population analysis of the CG results with these calculations is given in Table VIb, indicating that the choice of basis will reproduce earlier calculations, and that this is a valid description of the system.

Further calculations were carried out by optimizing the triplet state using a CASSCF wavefunction. Here, the bond length optimized to 1.58 Å, with Mulliken populations on the oxygen of 1.31(σ) and 1.45(π_x, π_y), and a net -0.28 charge. Again, this description is consistent with that of CG, with the decrease in charge transfer to be expected from the CASSCF calculation.

Note that the addition of chlorides to the system smoothly changes the zeroth-order bond description. In adding two or more chlorides to this system, enough charge is transferred to the oxygen to consider the resulting V-O bond to consist of two, rather than one, donor-acceptor bond. Note that even these results indicate a degree of charge already transferred to the oxygen. Additional charge transfer should thus change the simple description of the bond.

VO^{2+} is a doublet state with a singly occupied dδ-orbital. While no bound state was found at the GVB(3/6)-PP level, 7-in-7 CASSCF determined an equilibrium bond length of 1.56 Å (Table VIc). A comparison with C_{4v} $VOCl_4^{2-}$ values shows a similar charge distribution within the bond.

It was hoped that additional information could be found in an examination of VO^{3+}. However, studies at the GVB(3/6) and 6-in-6 CASSCF level were unable to locate a bound state within the range R(VO)= 1.4 to 1.9 Å, for which the system was examined.

Table VIa: VO+ energies (hartrees), GVB pair energies (kcal/mol), and CASSCF results. The GVB results were computed at R(VO)=1.56 Å, while CASSCF values were computed at R(VO)= 1.58 Å.

Calculation	$(d_{xy})^1(d_{x^2-y^2})^1$	$(d_{xy})^2$	$(d_{x^2-y^2})^2$
HF	-145.251254	-145.204076	-145.204076
GVB(3/6)-PP	-145.342275	-145.296422	-145.296422
GVB(3/6)-RCI	-145.423784	-145.373239	-145.373239

Pair	$(d_{xy})^1(d_{x^2-y^2})^1$	$(d_{xy})^2$	$(d_{x^2-y^2})^2$
σ	33.57 (32.51)	34.14	34.14
π_{xz}	13.43 (14.24)	13.62	13.62
π_{yz}	13.43 (14.24)	13.62	13.62

$(d_{xy})^1(d_{x^2-y^2})^1$	E(hartrees)
HF	-145.248657
CASSCF	-145.440376

Table VIb: Comparison of the Mulliken populations of CG and these results (RJR).

	CG		RJR	
bond	V	O	V	O
σ	0.79406	1.20594	0.81639	1.18361
π_x	0.40087	1.59113	0.38511	1.61489
π_y	0.40087	1.59113	0.38511	1.61489
total	1.61180	4.38820	1.58661	4.41339

Table VIc: 7-in-7 CASSCF results for VO^{2+}. The equilibrium bond length is 1.56 Å. Total energies are in hartrees. The population analysis is from the CASSCF wavefunction.

Calculation	Energy(hartrees)
HF	-144.604389
CASSCF	-144.874590

Population Analysis:

bond	V	O
σ	0.64	1.25
π_x	0.58	1.28
π_y	0.58	1.28

VII. $VOCl_3$

$VOCl_3$ was chosen as a means of comparison to other systems. Unlike most of the systems under study, experimental data exists for this system.[36] This system serves to both calibrate these results (in particular, the optimized geometries) and as a system for which force field parameters can be generated via the hessian. The geometry under study was taken from experiment, and is given in Figure VIIa. Calculations were performed on this system at the GVB(3/6)-PP level using the standard vdz on vanadium, and vdzp basis sets on oxygen and chlorine (81 basis functions). In addition, HF and CASSCF calculations were performed using a similar description as above, but including polarization functions on oxygen only (63 basis functions). The results of these calculations are given in Tables VId(1-3). The system exhibits the same V-O bonding scheme as seen in previous V(V) systems, as demonstrated in the GVB pair energies. Mulliken population data from the CASSCF calculation show a symmetric distribution of electrons in the π-system, with the overall charge distribution of O(2pσ) and O(2pπ) - 1.3 and 2.7 - being very similar to that for C_{2v} and C_{4v} $VOCl_4^-$ (1.3 and 2.7, respectively). In addition, V-O bond length was optimized at the CASSCF level to obtain a value of 1.56 Å, in excellent agreement with experiment.

It should be noted that examination of this system involved only the examination of the V-O bond. The effects of the chlorides were not considered. Given the results of examining the other V(V) systems ($VOCl_4^-$ and $VOCl_2^+$), it is very possible that taking the chlorides into greater consideration will result in a greater degree of V-Cl covalency. In fact, HF results demonstrate varying degrees of chloride interaction with all the available V(3d) and V(4s) orbitals.

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[36] (a) CRC Handbook of Chemistry and Physics, Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press Inc., Boca Raton, FL, 1987. (b) Karikida, K.; Kuchitsu, K. *Inorg. Chim. Acta* **1975**, *13*, 133.

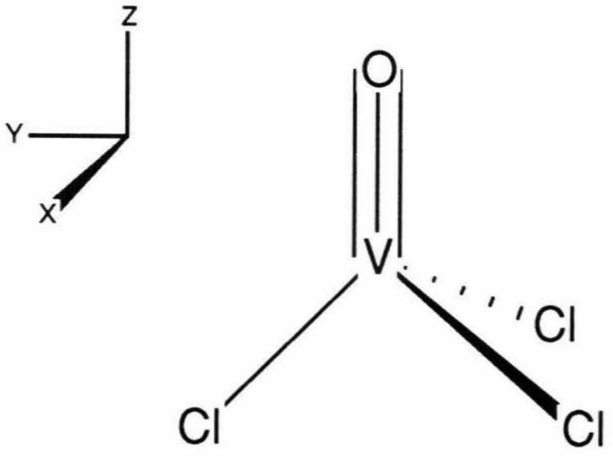

Figure VIIa: The geometry of $VOCl_3$.

Table VIIa: $VOCl_3$ data. The experimental geometry (in angstroms and degrees) (top). The total energy (middle), as well as the GVB pair energies (kcal/mol) and 6-in-6 CASSCF Mulliken populations for the bond pair (bottom).

	Exp.
R(VO)	1.56
R(VCl)	2.12
<(OVCl)	108.2

Calculation	Energy (hartrees)
HF (63 basis functions)	-1523.883188
CASSCF (63 basis functions)	-1524.101632
GVB(3/6) (81 basis functions)	-1524.056790

bond pair	GVB Pair Energy	V(3d)	O(2p)
σ	21.6	0.66	1.30
π_{xz}	43.6	0.62	1.35
π_{yz}	15.5	0.62	1.35

VIII. VO_3

Some intuition into the effects of the chlorides on the V-O moiety was gained from prior calculations carried out on VO_3. It is included since it displays many of the characteristics of $VOCl_2^+$, in particular covalent bonding to a ligand other than the triply-bonded oxygen. The geometry for the system is given in Figure VIIIa, and was taken from experimental data of several other systems.[37] This system can be considered to be a VO fragment bound to an oxygen molecule. The geometry was not optimized. Polarization functions were used on all oxygens, for a total of 69 basis functions. The system is a doublet.

Initial examinations with configurations involving unpaired electrons on the oxygen failed to converge. Two configurations were examined with a single unpaired electron on the vanadium - analogous to the prior work (Figures VIIIb and VIIIc). In each case, the configuration was generated from an initial guess at the Hartree-Fock level. The resulting total energies and correlation energies are given in Tables VIIIa and VIIIb. In retrospect, it appears that both $VOCl_2^+$ and VO_3 are composites of these two configurations.

In configuration I, a GVB(4/8) calculation was carried out by pairing the V-O σ-bond, the strongly covalent V-O π-bond, the O-O σ-bond, and one of the remaining V-O bonds to the O_2 fragment. The unpaired electron may occupy either of the 3dδ-orbitals ($3d_{x^2-y^2}$ or $3d_{xy}$). Note that the donor-acceptor V-O π-bond was not paired. Initial calculations correlating two single V-O σ-bonds led to asymmetric convergence. By biasing the initial guess to one resonance configuration or the other, the two equivalent states were generated. The correlation was most important for the π-bond and the resonating V-O σ-bond. As with $VOCl_2^+$, an asymmetric wavefunction was generated. An R-GVB calculation was then performed to account for resonance, and the proper symmetry of the wavefunction restored. These calculations were duplicated for singly-occupying the $3d_{x^2-y^2}$ or $3d_{xy}$-orbital. Note that (1) there is little difference energetically in occupying either of the 3dδ-orbitals, and (2) the resonance energy for the system is 0.015 hartrees, or 9.65 kcal/mol. This number is reasonable when compared to benzene (resonance energy approximately 8 kcal/mol).[38] Note also that no GVB(3/6) calculation was carried out on the V-O bond alone - the third pair was not correlated to allow comparison with configuration II, i.e. both calculations were made at the GVB(4/8) level. Higher correlation including the remaining V-O pπ-pair lead to an additional V-O donor-acceptor bond. There was little change in the bonding orbital with the addition of this fifth pair, as was the case with $VOCl_2^+$, thus this system appears to maintain the V-O triple bond description.

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[37] Colman, J.P.; Hegedus, L.S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley CA, 1987.

[38] Goddard, W. A. III, unpublished.

Configuration II can be described as VO+ binding to O_2^- via a δ-bond from the $O(2p_x)$-$O(2p_x)$ orbital and the vanadium $3d_{xy}$-orbital, as per $VOCl_2^+$. The remaining oxygen is triple-bonded to the vanadium. Here, the vanadium $3d_{x^2-y^2}$-orbital is singly occupied. All bonds are correlated except the O-O σ-bond. The main energy lowering from the correlation comes from the δ-bond - the contribution from the π-bonds is significantly lower than in configuration I.

Note that neither $VOCl_2^-$ nor $VOCl_2$ display this behavior, although the oxidation state of $VOCl_2$ is the same as VO3. Attempts were made to correlate δ-bonds and asymmetric V-Cl bonds in these systems. GVB pair energies for these pairs were minimal, however - only 1 to 4 kcal/mol, suggesting that there is no such bonding taking place. If we consider, in the case of VO_3 versus $VOCl_2$, both V(IV) systems , then forming either the δ-bond or the asymmetric bond to vanadium requires the donation of one electron to vanadium - more likely for O_2^- than for Cl_2^-. In this case, adding an additional electron to the vanadium center ($VOCl_2^-$) reduces the chance of electron donation further.

The steps taken here are essentially those taken for $VOCl_2^+$, except a composite of the two configurations was not formed, i.e. both of the V-O bonds to the O_2 were not simultaneously correlated. It would be reasonable to assume that given the similarity between these two systems, the qualitative description of the bonding in these two systems is the same.

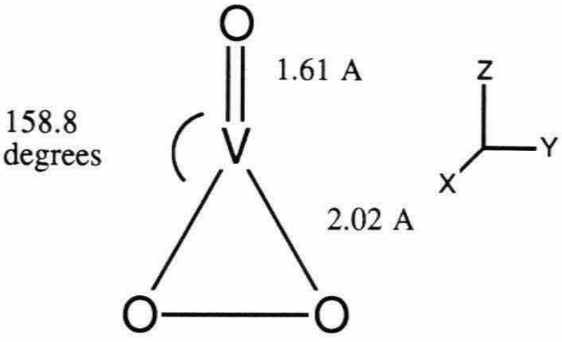

Figure VIIIa: VO_3 geometry

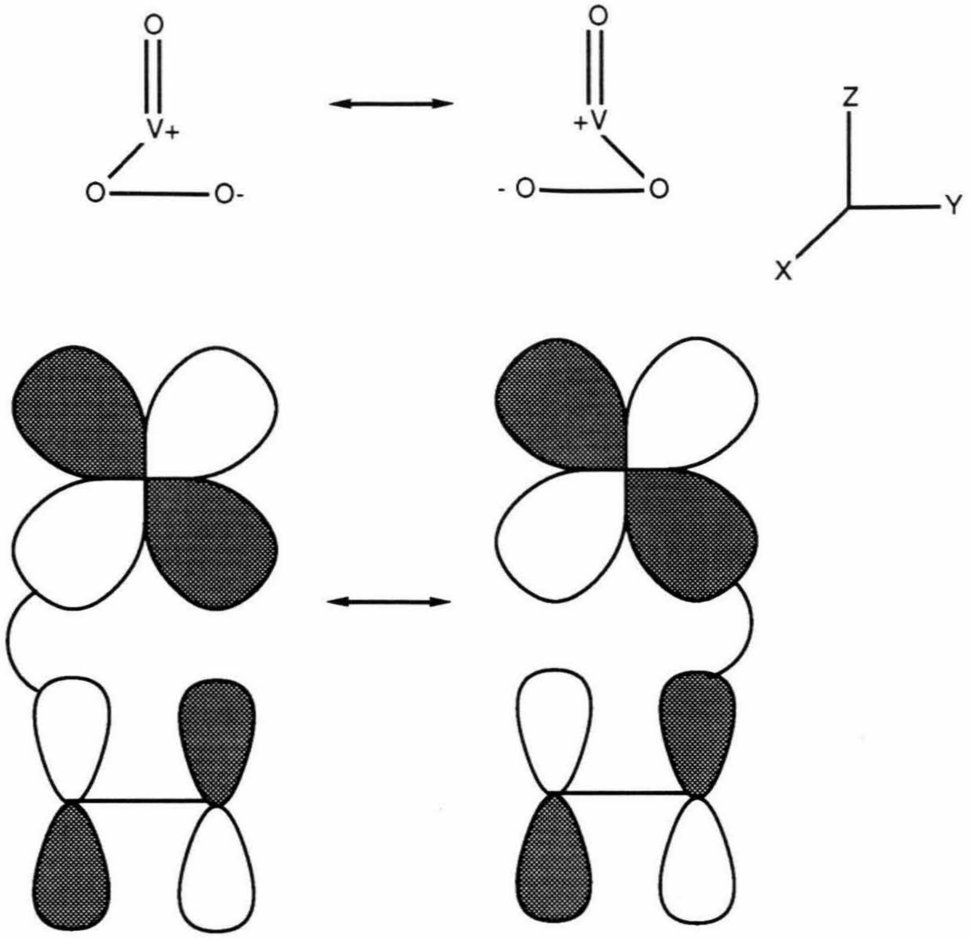

Figure VIIIb: configuration I - resonance between two GVB configurations. The d-orbital is singly occupied, the p+p orbital is doubly occupied, and the p-p orbital is singly occupied.

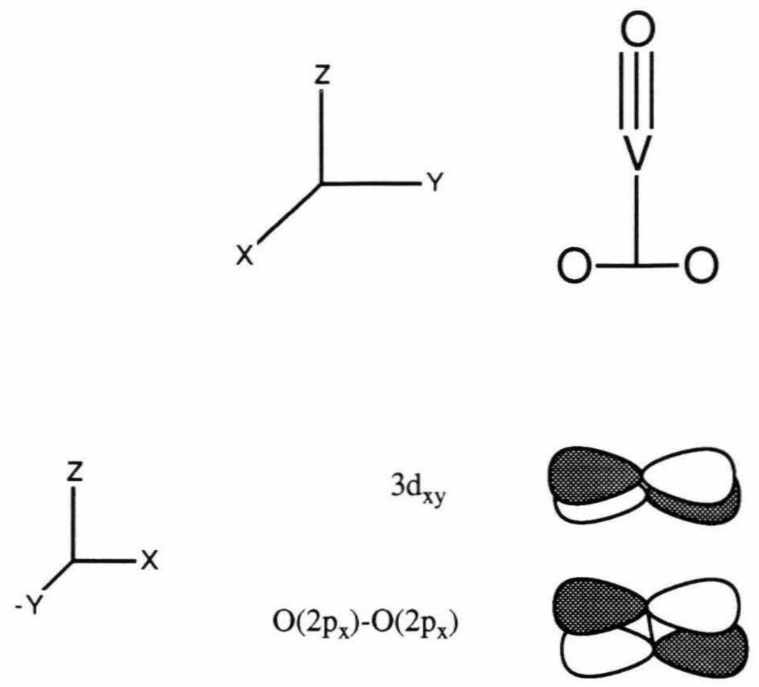

Figure VIIIc: configuration II - V-(O_2) delta bond.

Table VIIIa: Total energy for VO_3 configurations.

Configuration I

Singly-Occupied Orbital	$3d_{xy}$	$3d_{x^2-y^2}$
Method of Calculation	Energy (hartrees)	Energy (hartrees)
Hartree-Fock	-295.092197	-295.096524
GVB(4/8)	-295.260373	-295.262342
RESGVB	-295.275751	-295.275432

Configuration II	(Singly-occupied $3d_{x^2-y^2}$)
GVB(4/8)	-295.255977

Energy Differences	Energy (hartrees)	Energy (kcal/mol)
Conf. II - Conf. I	0.028402	17.80
$I(3d_{xy}) - I(3d_{x^2-y^2})$	0.000325	0.20

Table VIIIb: GVB pair energies for VO_3. Key values are given in boldface.

Configuration I (Note: Energy in kcal/mol)

pair	3dxy	3dx2-y2
V-O σ	12.5	12.5
V-O π	**40.3**	**40.7**
V-O σ (resonance)	**43.9**	**41.7**
O-O σ	29.1	29.2

Configuration II

pair	$3d_{xy}$
V-O σ	26.7
V-O π(xz)	12.9
V-O π(yz)	11.4
V-O_2 δ	**90.0**

IX. Discussion, Conclusions, and Future Work

There are still a great deal of work to be done in fully understanding the behavior of these systems. The examination of the V-O bond does reveal it to be a triple bond, but the role the additional ligands play in perturbing the precise description of the V-O bond requires further examination. There appears to be a degree of competition for vanadium orbitals among the ligands - these calculations have shown that the V-O triple bond tends to take much of this character, with the remaining V-Cl (or V-O in VO_3) bonding described at least in part by at least two resonance states. This competition for orbitals is very likely the cause of the dramatic change in V-O bond description at the GVB(3/6)-PP level for $VOCl_4^{2-/-}$ C_{4v} and C_{2v} systems, with higher V-Cl covalent character more important to the C_{2v} geometry. Several factors support this hypothesis. There is a strong degree of similarity in both bonding and the geometry of the $VOCl_2^+$/$VOCl_4^-$ (C_{2v}) and $VOCl_2$/$VOCl_4^{2-}$ (C_{2v}) pairs, each of which differ by only two chlorides. In these systems, the V-O bond is described by a σ-bond, a strongly covalent π-bond, and a donor-acceptor π-bond. The analogous four-chloride C_{4v} systems show a σ-bond and two equivalent π-bonds, in which can be described as resonance between two valence bond states (C_{2v}) in which one π-bond is covalent, the other donor-acceptor. In $VOCl_2^+$/$VOCl_4^-$ (C_{2v}), there is a significant degree of V-Cl covalent character, which decreases significantly in $VOCl_2$/$VOCl_4^{2-}$ (C_{2v}). (The chlorides of $VOCl_3$ were not thoroughly examined, but it appears at the HF level that this system may also demonstrate a strong degree of V-Cl covalent character.) The geometries of $VOCl_2^{0/+}$ suggest that they are simply C_{2v} systems in which the axial ligands have been removed. The overlap between the vanadium and chlorine bonding orbitals appear to favor bonding at the larger O-V-Cl angle of the trigonal bipyramid, and be less important for the square pyramid geometry. Neither $VOCl_2^-$ nor $VOCl_4^{3-}$, which are both triplet states in which both δ-orbitals are occupied, display the bonding scheme of the C_{2v} systems. Instead, both display equivalent π-bonds, analogous to the C_{4v} systems. In other words, $VOCl_2^-$ displays a very different character than $VOCl_2^{0/+}$. In addition, $VOCl_4^{3-}$ displays no trigonal bipyramid. Since both δ-bonds are occupied, this suggests that (1) these orbitals play a key role in V-Cl bonding, (2) this effect is favored by the trigonal bipyramid (C_{2v}) geometry, and (3) occupation of the δ-bonds decreases the importance of this effect.

The V-O bond description remains roughly consistent throughout the calculations. The bond is a triple bond of approximately 1.55 - 1.60 Å, with (using the valence bond description) two covalent bonds and one donor-acceptor bond. Population analysis tends to place a total of 3.9 to 4.7 electrons on the oxygen within these bonding orbitals. The degree of covalency does vary, however, decreasing as the charge of the system increases. ($VOCl_2^-$ and $VOCl_4^{3-}$ appear to be sufficiently charged to describe V-O bonding as one covalent bond and two donor-acceptors.) In addition, ligand effects tend to change the character of the bond from resonance between two equivalent bonds (covalent and donor-acceptor) to a well-defined covalent bond and a well-defined donor-acceptor. The ligands do not, however, appear to change the character of the bond to that of a double bond, i.e. in competition for identical vanadium orbitals, more d-character is acquired by the oxygen. Snap bond calculations indicate that the V(IV) bond is significantly stronger than the V(V) bond, which is in accordance with two properties of the catalyst: (1) the contribution of the ring-closing oxygen from V(V)-O, and (2) the tendency of the system toward total oxidation of the hydrocarbon as the percent V(V) on the surface increases. One might speculate that since there appears to be a strong degree of interaction between the chlorides and vanadium in the V(V) systems, this effect may stabilize the V(V) fragment relative to the V(IV) fragment, thus decreasing the bond strength of the V(V) system relative to V(IV).

While the results of the CI calculations demonstrate C_{4v} as the more stable system, it is important to remember that these calculations were by and large performed on the assumption that the most important correlation was present in the V-O bond, and that the rest of the system could be treated less rigorously. The GVB pairs, CASSCF active space, and the CI reference spaces virtually all include only the V-O bond. Polarization functions were included on the oxygen, but not the chlorines. This may be too strong a bias toward the V-O system, as appears that there may be a larger degree of correlation in the rest of the system than previously anticipated, particularly in the V(V) systems. It would be valuable to repeat these calculations including a single bonding/antibonding V-Cl pair in the correlation effects, to see how large an effect this has on the trends of these systems. It would appear that for V(III), this effect would be small. V(IV) appears to describe some intermediate between V(III), which suggests little V-Cl covalency, and V(V), where this covalency is strong. A precise, simple description of where these systems stand in relation to the V(V)/V(III) limits has not yet been firmly determined. Although the two-chlorine system demonstrates the same geometry and V-O bond properties of the analogous V(V) system, V-Cl covalency is weak, as in V(III). The four-chloride case demonstrates both C_{2v} and C_{4v} states, but again, little V-Cl covalency. As with V(V), the C_{4v} system is more stable at all but the GVB(3/6) levels.

It appears that the C_{2v} geometry is a result of resonance between two resonance states of the C_{4v} geometry. If the wavefunction tends toward one of the two reference states, then the geometry will optimize to that favored by that reference state. The single donor-acceptor bond allows stronger V-Cl coupling with the "accepting" V(3dπ)-orbital, stabilizing the system further. Calculations on two-chloride systems, as well as the C_{2v} systems, indicate that the C_{2v} state optimizes both the single reference state and the extra V-Cl coupling. Calculations beyond the GVB-PP level (CASSCF, CI) suggest that these interactions are averaged out, and that the C_{4v} geometry is the more stable.

One factor which has not yet been examined at the quantum-mechanical level is the role played by two coupled vanadium centers. Since each active site is centered upon such a system, it would be useful to examine such a system. To this end, $(VO)_2O_2Cl_4$ might be a useful system to study (Figure IXa). This system is analogous to those previously studied, but with two V-O units. Performing HF and GVB calculations with a vdz basis (including polarization on axial oxygens) of 134 basis functions is a feasible task. It is likely that the coupling of these centers is required to understand the catalytic mechanism.

In addition, it will also be useful to take the next step in these calculations - developing force field parameters for molecular dynamics calculations on the entire surface. To this end, hessians can be generated from the optimized geometries by systematically using the gradients taken from small displacements of the optimum geometry. This method, in which the energy is expanded about two coordinates of the system, can be shown to give third-order error.[39] The method is described as follows.

Expanding the energy about two coordinates (x,y) gives:

$$E(\delta_x,\delta_y) = E_o + \frac{\partial E_o}{\partial x}\delta_x + \frac{\partial E_o}{\partial x}\delta_y + \frac{1}{2}\frac{\partial E_o}{\partial x^2}\delta_x^2 + \frac{1}{2}\frac{\partial E_o}{\partial y^2}\delta_y^2 + \frac{\partial E_o}{\partial x \partial y}\delta_x\delta_y + O(\delta^3) \tag{6}$$

where E_o is the equilibrium energy. The second and third terms (the first derivatives of the equilibrium energy with respect to x and y) go to zero. Taking the derivative of the overall expression with respect to x and y gives (neglecting higher-order terms):

$$F_x(\delta_x,\delta_y) = \frac{\partial E}{\partial x} = \delta_x\frac{\partial E_o^2}{\partial x^2} + \delta_y\frac{\partial E_o^2}{\partial x \partial y} \tag{7}$$

$$F_y(\delta_x,\delta_y) = \frac{\partial E}{\partial y} = \delta_y\frac{\partial E_o^2}{\partial y^2} + \delta_x\frac{\partial E_o^2}{\partial x \partial y}$$

Solving (7) gives

$$\frac{\partial E_o^2}{\partial x \partial y} = \frac{F_x(0,\delta_y) - F_x(0,-\delta_y)}{4\delta_x} + \frac{F_y(\delta_x,0) - F_y(-\delta_x,0)}{4\delta_y} \tag{8}$$

Given a quality hessian, force-field parameters can be fitted which will allow for the further examination of the overall system at the molecular dynamics level.

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[39] Goddard, W. A. III, unpublished.

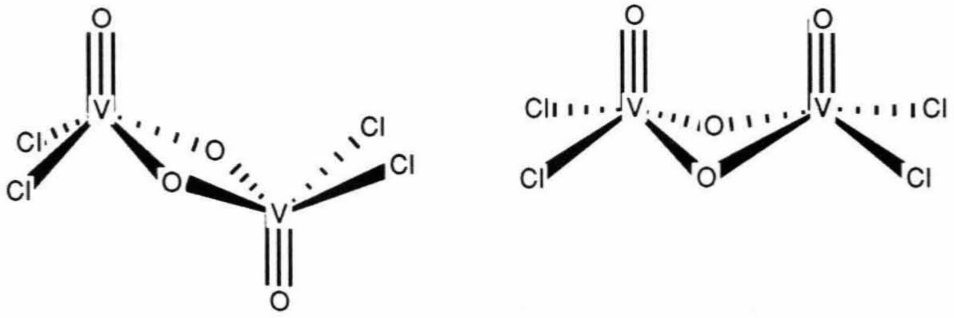

Figure IXa: Two potential $(VO)_2O_2Cl_4$ geometries. Each of these two fragments may represent an active site of the surface.