

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1974, by the American Chemical Society

VOLUME 96, NUMBER 1

JANUARY 9, 1974

The Generalized Valence Bond Description of Titanium Carbonyl^{1a}

A. P. Mortola^{1b} and W. A. Goddard III^{*1c}

Contribution No. 4714 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91109.

Received June 15, 1973

Abstract: *Ab initio* calculations using the generalized valence bond (GVB) method are reported for a number of electronic states of TiCO⁺ and TiCO. The nature of the bonding in these compounds is discussed in terms of the GVB orbitals, and the implications for the bonding in other carbonyls are discussed. These results indicate that the TiC bond can be accurately described as a CO nonbonding pair that is slightly shifted onto (donated to) the Ti. In return, the Ti(3d π) orbitals shift back somewhat onto the CO (into the π^* orbital); one might refer to this as π back bonding.

Transition metal carbonyls have been of immense interest to chemists ever since the discovery of nickel tetracarbonyl in 1890 by Mond, Langer, and Quincke.² Since that time a great deal of progress has been made both in synthesizing new compounds and in understanding the nature of the bonding between the carbon and the metal atom. One of the principal successes of molecular orbital theory for inorganic molecules was its application by Beach and Gray^{3a} to the metal hexacarbonyls resulting in a lucid interpretation of their spectra. The method used in their calculation was the "extended Wolfsberg-Helmholtz method" as outlined by Basch, Viste, and Gray in 1966.^{3b} In recent years, theoretical and calculational methods have been developed to the point that it is now possible to carry out *ab initio* calculations on transition metal carbonyls. Such methods have demonstrated that the doubly occupied molecular orbitals of Hartree-Fock wave functions do not generally lead to consistent descriptions of the ground and excited states of molecules. In many cases, it is necessary to include some configuration interaction to obtain the proper consistency. One particularly useful method of including such correlation effects, while retaining a simple orbital interpretation, is the generalized valence bond

(GVB) method.^{4,5} In this method the wave function is taken to have the form of a valence bond (VB) wave function, but the orbitals are solved for self-consistently rather than taken as (hybridized) atomic orbitals as in the VB method.

In this paper we consider the very simple carbonyls TiCO⁺ and TiCO and report results from both HF and GVB calculations. The bonding in the various states of these compounds is interpreted in terms of the GVB orbitals and this interpretation is in turn applied to other carbonyls such as Cr(CO)₆.

I. Methods of Calculation

The GVB method has been described in detail elsewhere⁴ so it will suffice to give only a brief outline of it here. The principal facet of this approach is the replacing of doubly occupied orbitals φ_i in the Hartree-Fock (HF) wave function

$$\psi_{\text{HF}} = \mathcal{R}[\varphi_{1\alpha}\varphi_{1\beta}\varphi_{2\alpha}\varphi_{2\beta}\dots\varphi_{n\alpha}\varphi_{n\beta}] \quad (1)$$

by singlet-coupled pairs of singly occupied orbitals.⁵

$$\psi_{\text{GVB}} = \mathcal{R}[(\varphi_{1a}\varphi_{1b} + \varphi_{1b}\varphi_{1a})\alpha\beta(\varphi_{2a}\varphi_{2b} + \varphi_{2b}\varphi_{2a})\alpha\beta\dots(\varphi_{na}\varphi_{nb} + \varphi_{nb}\varphi_{na})\alpha\beta] \quad (2)$$

(4) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972).

(5) The GVB calculations carried out here and discussed in ref 4 are often referred to as GVB perfect pairing or GVB(PP) calculations to indicate that only the simple VB spin coupling of (2) is allowed and that the orbitals of different pairs are taken as orthogonal. The more general approach in which the restrictions are not made [R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.*, **51**, 1073 (1969); W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971)] is usually referred to as GVB. In this paper we discuss only GVB(PP) but for simplicity the PP is deleted.

(1) (a) Partially based on a Ph.D. thesis submitted by A. P. Mortola, May 1972, California Institute of Technology; (b) National Science Foundation Predoctoral Fellow; Department of Chemistry, the Cooper Union, New York, N. Y. 10003; (c) partially supported by a grant (GP-15423) from the National Science Foundation.

(2) L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, **57**, 749 (1890).

(3) (a) N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968); (b) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).

If the orbitals are taken to be atomic orbitals, (2) becomes the valence bond wave function of Pauling and Slater.⁶ However, in the GVB method the orbitals are solved for variationally (a procedure analogous to that in the HF method).

Since each electron is allowed to be in a different orbital, one obtains a proper description of bond dissociation, avoiding one of the major difficulties in the HF method. Since each orbital is solved for variationally, one obtains quantitatively good results near the equilibrium geometry R_e , leading to better energies than either the HF or VB wave functions. An additional bonus is that the resulting orbitals in the molecule lead to simple interpretations of the bonding in terms of such common concepts as hybridization, ionic vs. covalent character, bond-bond interactions, etc.⁷

The method of solving for the variationally optimum GVB orbitals in (2) is to expand each pair function in terms of two natural orbitals^{4,8}

$$[\varphi_{1a}(1)\varphi_{1b}(2) + \varphi_{1b}(2)\varphi_{1a}(1)] = C_{1i}\varphi_{1i}(1)\varphi_{1i}(2) - C_{2i}\varphi_{2i}(1)\varphi_{2i}(2) \quad (3)$$

where C_{1i} and C_{2i} are related to the overlap of φ_{1a} and φ_{1b} . If the orbitals of *different* pairs are taken as orthogonal (strong orthogonality), then the resulting variational equations for φ_{1i} and φ_{2i} involve just Coulomb and exchange operators comparable to those in the HF equations, leading to rapid computational procedures.^{4,5}

In terms of the natural orbitals the GVB wave function has the form of a multiconfiguration wave function in which the first configuration corresponds to the Hartree-Fock configuration with each subsequent configuration having a doubly occupied pair of orbitals replaced by a new doubly occupied pair. Thus, from a multiconfiguration SCF (MCSCF) wave function of this form, we can obtain the GVB orbitals by using (3). For the calculations reported herein, we used the general MCSCF program written by Hinze⁹ with the configurations chosen to match the requirements of the GVB wave function.

The basis set consists of a minimum basis set of Slater orbitals from the calculation by Clementi and Raimondi¹⁰ except for the addition of a set of Ti(4p) orbitals and the change of the carbon 2p exponents from 1.5679 to 1.75.^{11,12} The CO bond length was taken to be 2.17 a_0 (1.15 Å) and the Ti-C distance as 3.70 a_0 (1.96 Å). This latter distance was based on the known metal-carbon distances of 1.84 Å in $\text{Fe}(\text{CO})_6$

(6) L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367 (1931); J. C. Slater, *Phys. Rev.*, **37**, 481 (1931); **38**, 1109 (1931).

(7) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 8293 (1972).

(8) A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **220**, 446 (1953).

(9) J. Hinze, private communication; see also J. Hinze and C. C. J. Roothaan, *Progr. Theor. Phys. Suppl.*, **40**, 37 (1967).

(10) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(11) The basis set consisted of the following Slater orbitals (orbital exponents in parentheses): on the Ti, 1s (21.44), 2s (7.69), 2p (9.03), 3s (3.68), 3p (3.37), 3d (2.71), 4s (1.20), 4p (1.12); on the C, 1s (5.6727), 2s (1.6083), 2p (1.75); on the O, 1s (7.6579), 2s (2.2458), 2p (2.2266).

(12) On the basis of previous optimizations of orbital exponents¹³ only the C(2p) and C(2s) exponents change significantly for the molecular system. We should have used a C(2s) exponent of 1.75.

(13) (a) R. M. Pitzer, *J. Chem. Phys.*, **46**, 4871 (1967); R. M. Pitzer and D. P. Merrifield, *J. Chem. Phys.*, **52**, 4782 (1970); (b) E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **51**, 5229 (1969); (c) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

and 1.92 Å in $\text{Cr}(\text{CO})_6$ ¹⁴ but probably should have been a bit larger.

For molecules such as CO_2 and O_3 it has been found that minimal basis sets and extended basis sets give very nearly the same vertical excitation energies (using the ground state geometry) if GVB or CI wave functions are used.^{15,16} In addition studies of a number of first row compounds (*e.g.*, BH, CH, C_2H_4 , CO, CF, CO_2 , and O_3) indicate no special change in the descriptions of bonding as one changes from minimal to extended bases. It is our judgment that the same will prove true for TiCO. However, one should be aware of a significant difference between Ti and the first row atoms. For the first row atoms the changes between the atom and the molecule involve primarily mixing of the 2s and 2p atomic orbitals (hybridization) and contraction of these orbitals about each nucleus. In Ti the relevant valence orbitals are the 3d, 4s, and 4p orbitals. The 3d atomic orbital is concentrated much closer to the nucleus than the 4s and 4p orbitals; hence, conditions are not favorable for hybridization and we find none. It is possible that use of a more extended basis would have allowed the sizes of the 4s, 4p, and 3d orbitals to adjust sufficiently for hybridization effects to become more important. We believe that the qualitative GVB descriptions of the bonding would not be affected by such extension of the basis.

II. Results

Before proceeding to the states of TiCO and TiCO^+ , we will discuss the Ti, Ti^+ , and CO wave functions.

A. Ti and Ti^+ . In addition to the Ar core

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6 \quad (4)$$

(which changes little upon bond formation) the Ti atom has four valence electrons. For the ground state the configuration of valence orbitals is

$$(4s)^2(3d)^2 \quad {}^3F \quad (5)$$

however, the first excited state with configuration

$$(4s)(3d)^3 \quad {}^5F \quad (6)$$

is only 0.8 eV higher.¹⁷

In applying the GVB method to Ti we allow only the valence orbitals to be split as in (3), since changes in the core orbitals occur in the same way for both the atom and the molecule. For the ground state (5) the 4s pair leads to a GVB pair of the form

$$(4s)^2 - \lambda(4p)^2 \quad (7)$$

quite analogous to the results for Be, B, and C where the (2s)² pair becomes^{7,18,19}

$$(2s)^2 - \lambda(2p)^2 \quad (8)$$

(14) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 724.

(15) N. W. Winter, W. A. Goddard III, and C. F. Bender, submitted for publication, see also *Chem. Phys. Lett.*, **20**, 489 (1973).

(16) P. J. Hay, T. H. Dunning, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, in press; see also P. J. Hay and W. A. Goddard III, *ibid.*, **14**, 46 (1972).

(17) C. E. Moore, "Atomic Energy Levels," Vol. I, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949, p 274 ff.

(18) W. A. Goddard III and R. J. Blint, *Chem. Phys. Lett.*, **14**, 616 (1972).

(19) In (8) one should use a ¹S combination of p_x , p_y , and p_z orbitals: $p_x^2 + p_y^2 + p_z^2$. We have used instead the ¹Σ combination $p_x^2 + p_y^2$ to be consistent with the description of this pair in various states of TiCO^+ and TiCO.

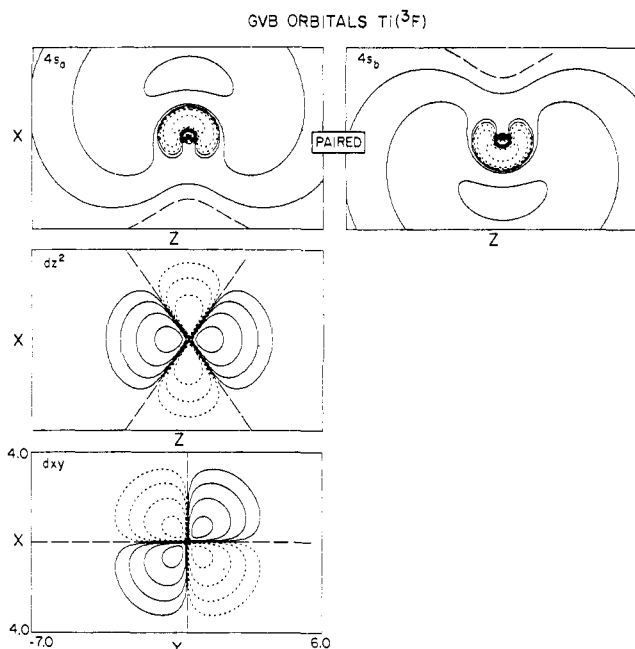


Figure 1. Amplitudes of the GVB orbitals for the $(3s)^2(3d)^2$ (3F) state of Ti. See Figure 3 for the scale. The lines with long dashes indicate the nodal lines. Positive contours are solid (contour values = 0.005, 0.02, 0.08, 0.32) and negative contours are dotted. The same conventions are used for all plots.

Table I. Energies for HF and GVB Wave Functions of Ti and Ti^+ (all Energies in Hartrees)^a

State	Con-figuration ^b	Method	Energy	—GVB pairs—	
				Pair	Energy lowering
$Ti(^3F)$	$(4s)^2(3d)^2$	HF	-846.84032		
		GVB	-846.86325	(4s, 4p)	0.0229
$Ti^+(^4F)$	$(4s)^1(3d)^2$	HF	-846.64363		
$Ti^+(^2D)$	$(4s)^2(3d)^1$	HF	-846.58020		
		GVB	-846.60081	(4s, 4p)	0.0206

^a 1 hartree = 27.2117 eV = 627.53 kcal/mol. ^b In each case the 18 electron argon core $[(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6]$ is present and solved for self-consistently.

As shown in Table I this splitting leads to a drop of 0.0229 hartree = 0.623 eV in the energy. Recoupling the natural orbitals of (7) into the GVB orbitals from (3) leads to the orbitals in Figure 1. Thus, in addition to the usual two d orbitals of ground state Ti, say, $3d_{z^2}$ and $3d_{xy}$, we find that the 4s pair becomes described in terms of a pair of lobe functions, say

$$\phi_{4sa} = \phi_{4s} + \mu\phi_{4pz}$$

$$\phi_{4sb} = \phi_{4s} - \mu\phi_{4pz}$$

The ground state of Ti^+ is

$$(4s)^1(3d)^2 \quad ^4F \quad (9)$$

but the first excited state

$$(3d)^3 \quad ^4F \quad (10)$$

is only 0.1 eV higher. The lowest state with an s^2d configuration is

$$(4s)^2(3d)^1 \quad ^2D \quad (11)$$

which is about 3 eV above the ground state.¹⁷

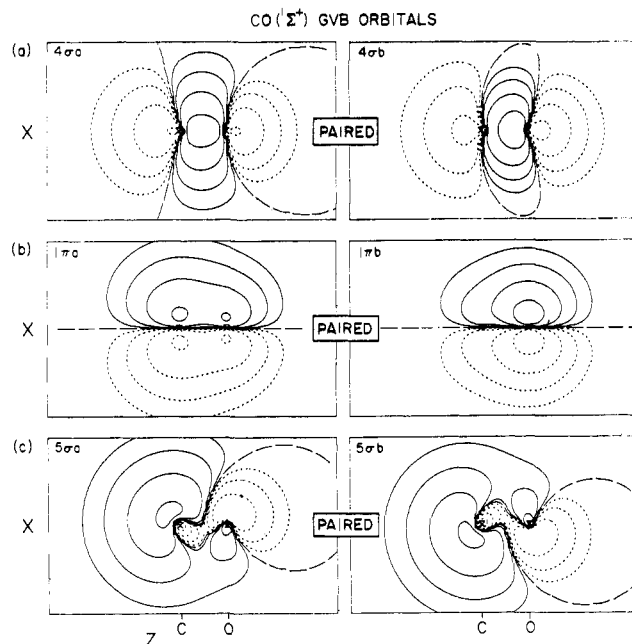


Figure 2. The GVB orbitals of the ground state ($^1\Sigma^+$) of CO. See Figure 3 for the scale.

Of these states of Ti^+ only the 2D state (eq 11) involves a paired orbital to be split in GVB. The GVB orbitals of this state resemble those for the $Ti(^3F)$ state (see Figure 1) and are not shown.

B. CO Molecule. In the HF method CO is described as

$$\mathcal{Q}\{(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2\chi\} \quad (12)$$

The 1σ and 2σ orbitals correspond to O(1s) and C(1s) orbitals, respectively, and the 1π orbitals are involved in the π bonds. On the basis of orbital correlation diagrams (Mulliken diagrams), one expects the 5σ orbital to arise from a bonding combination of the C($2p\sigma$) and O($2p\sigma$) orbitals and the 3σ and 4σ orbitals to be nonbonding orbitals arising from the C(2s) and O(2s) orbitals. However, as is well known, the HF wave function of CO dissociates to the wrong states as the bond is broken and hence the interpretation based on the orbital correlation diagram may not be appropriate.

We find that for the GVB wave function there are four important pairs to be split in the CO wave function in eq 12. This leads to the wave function

$$\mathcal{Q}\{[(1\sigma)^2(2\sigma)^2(3\sigma)^2[(4\sigma)^2 - \lambda(6\sigma)^2][(1\pi)^4 - \lambda'(1\pi)^2(2\pi)^2][(5\sigma)^2 - \lambda''(2\pi)^2]\chi\} \quad (13)$$

where the term for the π orbitals represents three configurations

$$(1\pi_x)^2(1\pi_y)^2 - \lambda'[(1\pi_x)^2(2\pi_y)^2 + (1\pi_y)^2(2\pi_x)^2] \quad (14)$$

Combining the split pairs of (13) into GVB orbitals by (3) leads to the orbitals in Figure 2 where the natural orbitals and GVB orbitals correspond as follows

$$\begin{aligned} (4\sigma, 6\sigma) &\longrightarrow (4\sigma_a, 4\sigma_b) \\ (5\sigma, 2\pi) &\longrightarrow (5\sigma_a, 5\sigma_b) \\ (1\pi, 2\pi) &\longrightarrow [1\pi_a, 1\pi_b] \end{aligned} \quad (15)$$

Here we see that the pair $(4\sigma_a, 4\sigma_b)$ corresponds to a

somewhat ionic CO(σ) bond (more on the O than on the C), and each ($1\pi a$, $1\pi b$) pair corresponds to a somewhat ionic CO(π) bond. The other pair ($5\sigma a$, $5\sigma b$) corresponds to a nonbonding pair on the C pointing away from the molecule. These latter orbitals consist of two lobe functions at about 90° to each other. The energies for various GVB calculations on CO are listed in Table II. Note that the pair splitting energies are approximately additive.

Table II. Energies for HF and GVB Wave Functions of CO($^1\Sigma^+$) (all Energies in Hartrees)

Method	Pairs split ^a	Energy	$E_{\text{HF}} - E_{\text{GVB}}$
HF		-112.34842	0
GVB	(5σ , 2π)	-112.36374	0.0153
GVB	(1π , 2π)	-112.37864	0.0302
GVB	(5σ , 2π)	-112.39133	0.0429
	(1π , 2π)		
GVB	(5σ , 2π)	-112.37202	0.0236
	(4σ , 6σ)		
GVB	(5σ , 2π)	-112.39906	0.0506
	(4σ , 6σ)		
	(1π , 2π)		

^a The basic configuration is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4$.

Although we have numbered the orbitals in (13) the same as those in (12), one should *not* assume that the first natural orbital of each pair in (13) corresponds to one of the HF orbitals. This is *not* the case as can be seen from Table III which compares the 3σ , 4σ , and

ionization potentials.²¹ However, in interpreting the bonding in the ground state of a system, the canonical HF orbitals are far too delocalized.²⁰ For example, in ethylene the five bonding orbitals all have large contributions in each of the four CH bond regions.⁷ For this reason many workers have investigated ways of localizing the HF orbitals in order to obtain orbitals more consistent with the usual chemical ideas of bonding.²⁰ All these procedures involve a degree of arbitrariness since the transformations lead to no change in the energy or any other property. Thus, one uses any of several *ad hoc* criteria which have been found to lead to localized orbitals.

On the other hand, there is no such arbitrariness in the GVB orbitals.^{4,5} The GVB wave function does change when orbitals are recombined as can be seen from (13). Recombining the 4σ and 5σ orbitals *would*

$$4\sigma' = 4\sigma \cos \alpha + 5\sigma \sin \alpha$$

$$5\sigma' = 5\sigma \cos \alpha - 4\sigma \sin \alpha$$

change the energy of the wave function in (13) although it would *not* change the energy of (12). Thus, one might hope that since the GVB orbitals are unique they might lead to chemically useful nonarbitrary interpretations. As shown elsewhere,^{4,5,7,18,22} this does prove to be the case for a number of systems.

For CO we see that the GVB first natural orbitals do correspond to the expected description. Orbital 3σ is primarily an O(2s) orbital hybridized a little (25%) so as to point away from the C. Orbital 4σ is essentially a bonding combination of C(2p) and O(2p)

Table III. Comparison of the HF Valence Orbitals and the First Natural Orbital of Each GVB Pair

Orbital	Orbital energy, hartrees	Orbital coefficients ^a						
		C(1s)	C(2s)	C(2p σ)	O(1s)	O(2s)	O(2p σ)	
HF	3σ	-1.4864	-0.1129	0.2210	0.1664	-0.2121	0.7731	-0.2254
	4σ	-0.7167	+0.1468	-0.5393	-0.0695	-0.1220	0.6493	+0.6336
	5σ	-0.4831	-0.1390	+0.7789	-0.5459	+0.0029	+0.0065	+0.4398
GVB	3σ	-1.1614	-0.0638	0.1813	-0.1045	-0.2262	0.9348	0.3107
	4σ	-0.9482	-0.0734	-0.0274	+0.4472	-0.0678	+0.1359	-0.7357
	5σ	-0.6080	-0.1931	+0.9630	-0.3272	+0.0620	-0.3641	-0.1195

^a Slater orbitals, see ref 11.

5σ HF orbitals with the 3σ , 4σ , and 5σ GVB first natural orbitals. However, it is the case that the GVB first natural orbitals are very nearly just linear combinations of the HF occupied orbitals.

A well-known problem with interpreting HF orbitals is their nonuniqueness.²⁰ For a closed shell wave function as in (12), we can take any (nonsingular) combination of orbitals with each other and not change the energy or any other physical property of the system (this results from the Slater determinant form of the wave function).²⁰ Thus, we must decide which combination (if any) is the proper one to use. In interpreting ionization potentials of systems it seems clear that the canonical HF orbitals (*i.e.*, the solutions of the HF self-consistent field equations) are the proper ones

$$H^{\text{HF}}\phi_i = \epsilon_i\phi_i$$

because their energies correspond well to the observed

(20) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

orbitals but ionic toward the O. Orbital 5σ is mainly a C(2s) orbital hybridized so as to point away from the O.

Of the HF orbitals (see Table III or ref 23) 3σ is mainly on the O but it is hybridized *toward* the C, not away as expected for a nonbonding orbital, and in addition it has a somewhat significant component on the C, hybridized toward the O and combined in a symmetric (bonding) way. Thus, this orbital shows all the attributes of a bonding MO except that the bond seems to involve the O(2s) orbital rather than O(2p) as expected. Orbital 4σ has large components on both atoms with approximately equal parts of C(2s), O(2s), and O(2p σ) character. These are combined so that the O part is hybridized *away* from the O and the C(2s) pair is combined in an antibonding way. Thus, 4σ appears to be an oxygen nonbonding orbital.

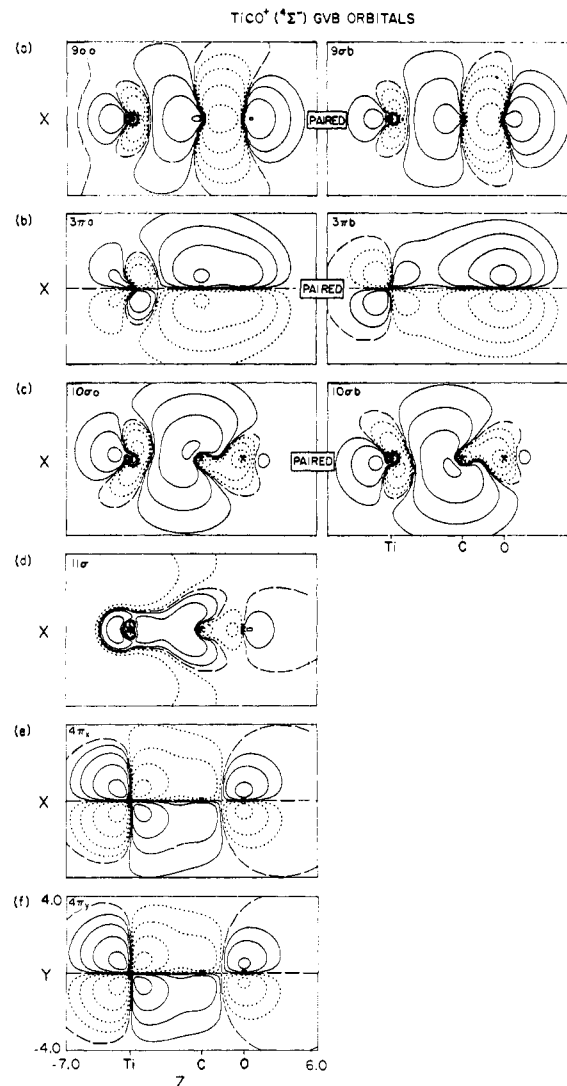
(21) See, for example, P. E. Best, *J. Chem. Phys.*, **44**, 3248 (1966); Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).

(22) W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 793 (1972).

(23) W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965).

Table IV. Orbital Energies^a for Various States of Ti, CO, and TiCO

Orbital	Character	CO(⁴ Σ ⁻)		Ti(³ F)		TiCO(⁶ Δ)		TiCO(⁴ Σ ⁻)	
		HF	GVB	HF	GVB	HF	GVB	HF	GVB
1σ	Ti(1s)	-183.267	-183.268	-183.599	-183.684	-183.687	-183.528	-183.557	-183.528
2σ	Ti(2s)	-21.1407	-21.1423	-21.4782	-21.5640	-21.5656	-21.4328	-21.4328	-21.4038
3σ	O(1s)	-20.7388	-20.7604	-20.7884	-20.8117	-20.8122	-21.0467	-21.0467	-21.0849
4σ	Ti(2p)	-17.6621	-17.6634	-18.0003	-18.0886	-18.0914	-17.9416	-17.9416	-17.9124
1π	Ti(2p)	-17.6557	-17.6570	-17.9930	-18.0775	-18.0802	-17.9540	-17.9540	-17.9251
5σ	C(1s)	-11.3146	-11.2907	-11.3320	-11.3828	-11.3813	-11.5851	-11.5851	-11.5715
6σ	Ti(3s)	-2.74888	-2.75202	-3.00912	-3.07847	-3.07664	-3.04186	-3.04186	-3.01251
7σ	Ti(3p)	-1.72720	-1.72965	-1.98117	-2.05124	-2.05296	-2.00632	-2.00632	-1.98333
2π	Ti(3p)	-1.72090	-1.72299	-1.96500	-2.03200	-2.03391	-2.01212	-2.01212	-1.99022
8σ	O(2s)	-1.48638	-1.16138	-1.49885	-1.51887	-1.19443	-1.72796	-1.72796	-1.41908
9σ	CO bond	-0.71666	-0.94818 ^c	-0.77735	-0.79798	-1.01377 ^c	-0.98389	-0.98389	-1.21354 ^c
10σ	CO lobes	-0.48313	-0.60800 ^c	-0.62888	-0.65461	-0.77791	-0.82755	-0.82755	-0.96511 ^c
3π	CO bond	-0.57294	-0.58981 ^c	-0.60654	-0.62520	-0.62565	-0.82221	-0.82221	-0.85024 ^c
1δ	Ti(3d _{xy})	-0.26921 ^b	-0.27092 ^b	-0.46381 ^b	-0.51270 ^b	-0.51416 ^b	-0.56167 ^b	-0.56167 ^b	-0.40417 ^b
11σ	Ti(4s)	-0.20138	-0.22263 ^c	-0.23020	-0.31977 ^b	-0.31923 ^b	-0.44042 ^b	-0.44042 ^b	-0.51711 ^d
4π	Ti(3d _{xy} + Co π*)	-0.26857 ^b	-0.27094 ^b	-0.21467 ^b	-0.21943 ^d	-0.21995 ^d	-0.56104 ^b	-0.56104 ^b	-0.50768 ^d

^a All energies in hartrees (1 hartree = 27.2117 eV).^b Singly occupied orbitals.^c First natural orbital of a GVB pair.^d Each π orbital is singly occupied.Figure 3. The GVB orbitals of the ground state (⁴Σ⁻) of TiCO⁺.

Orbital 5σ is mainly on the C and is hybridized away from the O. It has a significant O(2p) component which is combined in an antibonding way; thus, this appears to be a C nonbonding pair.

Overall the GVB orbitals for CO correspond well to the expected chemical intuition whereas the canonical HF orbitals do not.

C. TiCO and TiCO⁺. In describing the various states of TiCO and TiCO⁺, we will find that the orbitals have basically the same shapes as in Ti and CO. For this reason we will use the same names (for example, 8σ, 3π, etc.), to describe corresponding orbitals of each system, as indicated in Table IV. Thus, from Table IV we see that the Ar core of the Ti is

$$(1\sigma)^2(2\sigma)^2(4\sigma)^2(1\pi)^4(6\sigma)^2(7\sigma)^2(2\pi)^4 \quad (16)$$

and the (1σ)²(2σ)²(3σ)² core of the CO [see (13)] becomes

$$(3\sigma)^2(5\sigma)^2(8\sigma)^2 \quad (17)$$

From Table IV we see that the orbital energies of the core orbitals in (16) and (17) are relatively unchanged as the Ti and CO are bonded, and hence we will ignore these orbitals in the following discussions.

(1) TiCO⁺(⁴Σ⁻). The ground state of TiCO⁺ was found to be ⁴Σ⁻ with the configuration

$$(9\sigma)^2(10\sigma)^2(3\pi)^4(11\sigma)^1(4\pi)^2 \quad (18)$$

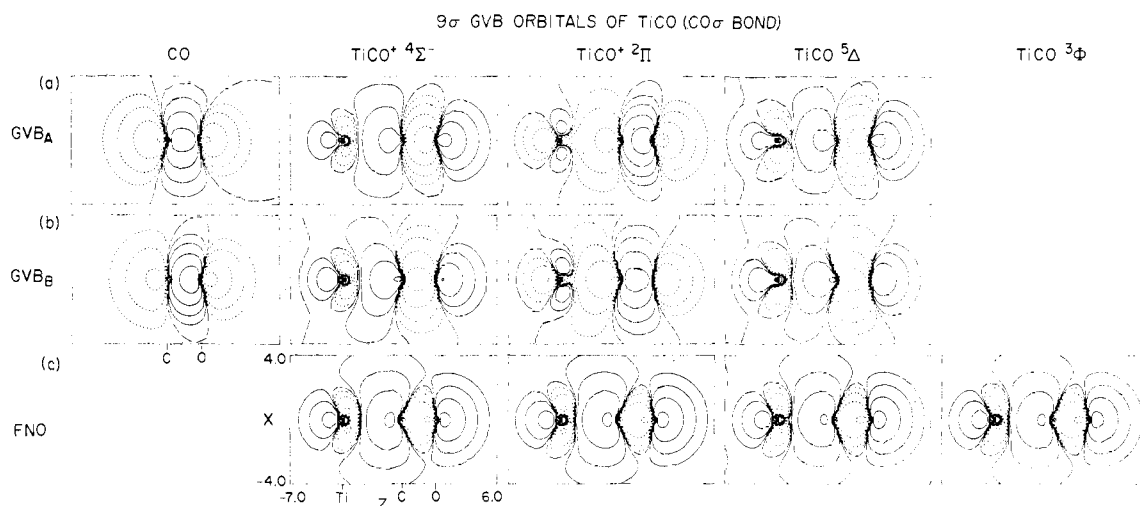


Figure 4. The 9σ orbitals of TiCO^+ and TiCO (this corresponds to the $\text{CO}(\sigma)$ bonding pair). FNO indicates the first natural orbital; it is a (normalized) sum of the GVB_a and GVB_b orbitals.

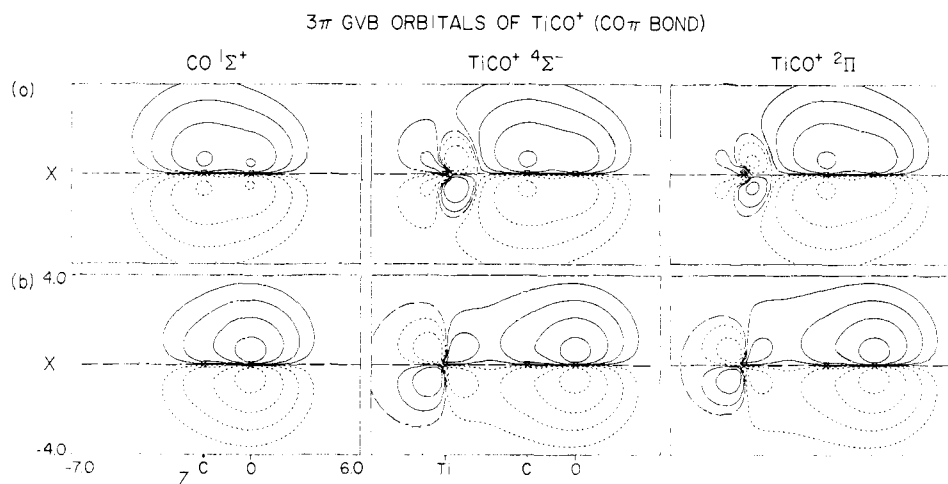


Figure 5. The 3π orbitals of TiCO^+ (this corresponds to a $\text{CO}(\pi)$ bonding pair).

Splitting the paired orbitals 9σ , 10σ , and 3π leads to the GVB orbitals in Figure 3. Comparing parts a–c of Figure 3 with a–c of Figure 2 we see that the TiCO^+ orbitals retain the character of the CO orbitals. The other orbitals (11σ)(4π) correspond to Ti^+ orbitals. Of these 11σ is much like one of the $4s$ – $4p$ lobes of Ti (see Figure 1a), and the 4π orbitals (each singly occupied) correspond to d_{xz} and d_{yz} orbitals.

The only change in the $\text{CO}(\sigma)$ bonding orbitals ($9\sigma_{ab}$ of TiCO^+ and $4\sigma_{ab}$ of CO) is that they must become orthogonal to the Ar core of the Ti, and as a result the part of these orbitals to the left of the C takes on the character of a $d\sigma$ orbital. This may be easier to see in Figure 4 which also shows the 9σ orbitals for other states of TiCO^+ and TiCO . Similarly the $\text{CO}(\pi)$ bonding orbitals ($3\pi_{ab}$ of TiCO^+ and $1\pi_{ab}$ of CO) must also become orthogonal to the Ar core and as a result take on the character of $d\pi$ orbitals in the region of the Ti. This may be easier to see in Figure 5 which also shows the 3π orbitals for other states of TiCO^+ . The result of these changes in the $\text{CO}(\sigma)$ and $-(\pi)$ bonding orbitals should be to decrease the bond strength slightly since the orbitals are forced to become somewhat distorted.

On the other hand, the $10\sigma_{ab}$ orbitals are nonbonding

in CO but become TiC bonding orbitals in TiCO . These orbitals are compared in Figure 6. In TiCO^+ these orbitals are primarily a combination of the CO nonbonding orbitals plus the $\text{Ti}(d\sigma)$ orbital. Note that this CO nonbonding orbital has a significant amount of π antibonding character in CO but that this character disappears in TiCO . The origin of this antibonding character is that the nonbonding orbitals in CO need to build in $p\pi$ character to allow the paired orbitals to move farther apart, but yet as they build in $\text{C}(p\pi)$ character these orbitals would overlap the $\text{CO}(\pi)$ bonding orbitals (1π in Figure 2). Because of Pauli's principle this is not allowed²⁴ and hence $\text{CO}(\pi^*)$ character rather than simple $\text{C}(p\pi)$ character must be used in splitting the CO nonbonding orbitals. However, as we form a bond to the Ti, it is important for the $10\sigma_{ab}$ orbitals to concentrate in the region of the new Ti–C bond. To retain orthogonality between the $10\sigma_{ab}$ and $3\pi_{ab}$ pairs, it is necessary to distort both the $10\sigma_{ab}$ and $3\pi_{ab}$ orbitals, from what would have been the

(24) One can write a wave function in which the orbitals are not orthogonal. However, when the wave function is antisymmetrized (to satisfy Pauli's principle), the parts of the wave function involving overlapping orbitals get projected out. Thus, the Pauli principle effectively eliminates part of the Hilbert space that otherwise would have been accessible.

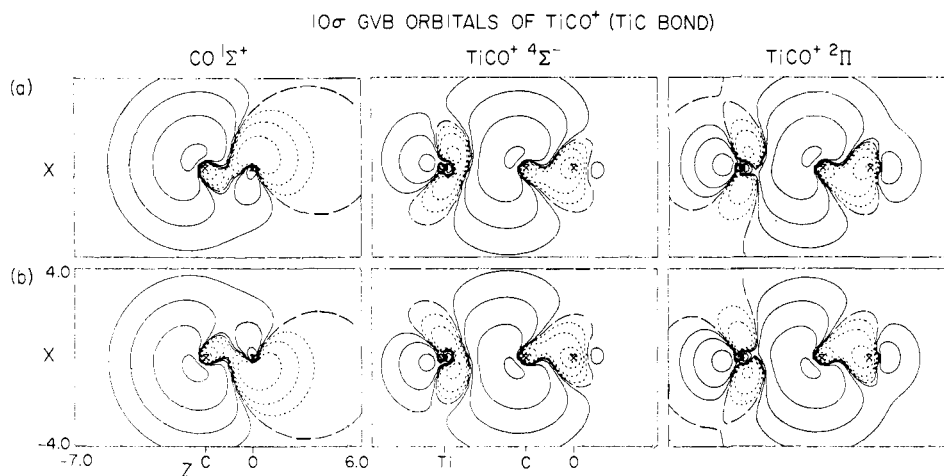


Figure 6. The 10σ orbitals of TiCO^+ (this corresponds to the TiC bonding pairs).

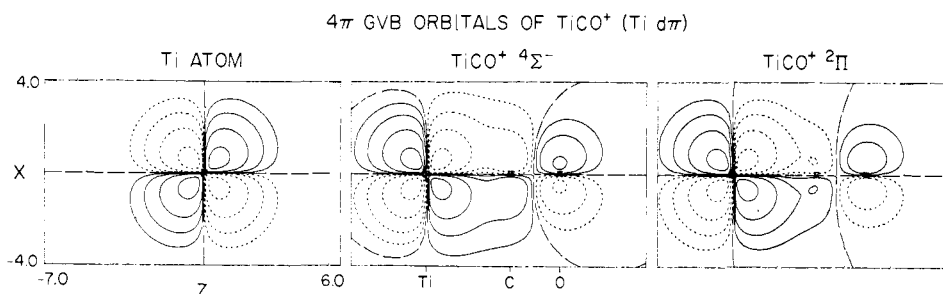


Figure 7. The 4π orbitals of Ti and TiCO^+ (this corresponds to the Ti($d\pi$) orbital).

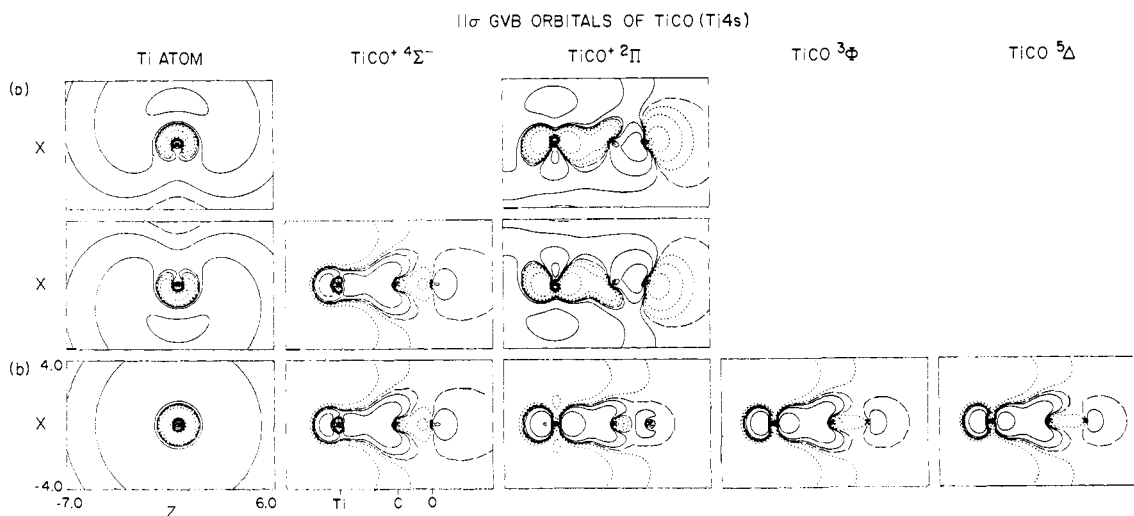


Figure 8. The 11σ orbitals of TiCO^+ and TiCO (this corresponds to the Ti(4s) orbital).

optimum shapes. In CO primarily the $10\sigma_{ab}$ pair ($5\sigma_{ab}$ in CO) suffered since the $3\pi_{ab}$ orbitals (1π in CO) were involved in a bond. However, for TiCO^+ both the $10\sigma_{ab}$ and $3\pi_{ab}$ pairs are involved in bonds and both suffer somewhat from the orthogonality conditions (in addition both must readjust so as to stay orthogonal to the Ar core of Ti). As a result the $\text{CO}(\pi)$ bond is somewhat weakened as the CO is bonded to the Ti. Overall, the changes in these orbitals lead to a net transfer of electrons to the left (toward the Ti).

As the Ti-CO bond is formed, the Ti($d\pi$) orbitals delocalize onto the CO by building in some $\text{CO}(\pi^*)$ character (see Figure 7). This character can be referred

to as π back bonding and has long been presumed to play a part in the stability of certain transition metal complexes.²⁵

The other orbital, 11σ , started out as a 4s orbital of Ti^+ and for TiCO^+ has the form of a $4s-4p$ lobe function, as found in the GVB wave function of Ti (see Figure 1).

(2) $\text{TiCO}^+(\text{}^2\Pi)$. We also examined the GVB wave functions of the $\text{}^2\Pi$ excited state of TiCO^+ . This state results from bonding CO to the

$$(4s)^2(3d) \quad (19)$$

(25) See, for example, ref 14, p 628, and references therein.

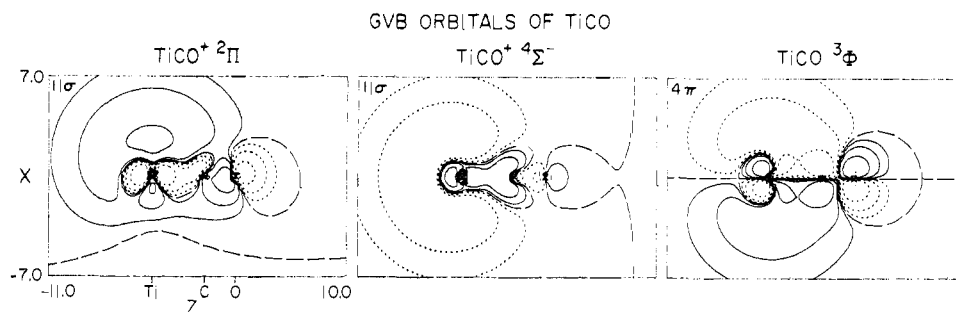


Figure 9. Some GVB orbitals of TiCO and TiCO⁺ (an enlargement of some of the orbitals of Figures 8 and 10).

Table V. GVB and HF Results for TiCO⁺ (all Energies in Hartrees)

	⁴ Σ ⁻	² Δ	² Π	⁴ Φ
Configuration	(11σ) ² (4π) ²	(11σ) ² (1δ) ¹	(11σ) ² (4π) ¹	(11σ) ¹ (4π) ¹ (1δ) ¹
HF energy ^a	-8.97985	-8.95978	-8.94992	-8.93744
GVB energy ^a	-9.02392		-9.01907	
Energy lowering	0.0441		0.0691	

^a Energies relative to -950.0 hartrees.

state of Ti⁺ and could be considered as the excited state obtained by exciting an electron from the dπ orbital to the 11σ orbital of ⁴Σ⁻.

As shown in Figures 4-7, the 9σ, 3π, 10σ, and 4π orbitals are quite similar to those of the ⁴Σ⁻ state. The 3π orbitals of ²Π seem to have somewhat less antibonding character on the Ti and the 4π orbital is less delocalized (less back bonding?) onto the CO.

The configuration in (19) has the 4s orbital paired and we expect the corresponding GVB orbitals to be as much as for the ³F state of Ti(5), as shown in Figure 1. This is the case as shown in Figure 8 where comparison is also made with the corresponding orbitals of other states. An enlargement of some of these orbitals is given in Figure 9.

The energies of the ⁴Σ⁻, ²Δ, ²Π, and ⁴Φ states are given in Table V and the GVB energy lowerings are presented in Table VI. GVB calculations were carried

Table VI. GVB Energies for TiCO⁺ (all Energies in Hartrees)

State	Split pairs	Energy ^a	Energy lowering
² Π	(10σ, 5π)	-8.95991	0.0100
	(10σ, 5π)	-8.97985	0.0299
	(11σ, 6π)	-8.98437	0.0344
	(10σ, 5π)		
	(11σ, 6π)		
	(9σ, 12σ)		
	(10σ, 5π)	-9.01907	0.0691
	(11σ, 6π)		
	(9σ, 12σ)		
	(3π, 5π)		
⁴ Σ ⁻	(10σ, 5π)	-9.02392	0.0441
	(9σ, 12σ)		
	(3π, 5π)		

^a Energies relative to -950.0 hartrees.

out only for the ⁴Σ⁻ and ²Π states, but the changes for the ⁴Φ and ²Δ states should be comparable. The GVB energy lowering is greater for the ²Π state since there is one more orbital paired in this state, but the ⁴Σ⁻ state is the lowest state of TiCO⁺ in both the HF and GVB descriptions.

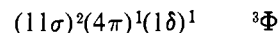
(3) TiCO. Hartree-Fock wave functions were obtained for a number of states of TiCO as indicated in Table VII. From these calculations the lowest state of

Table VII. Hartree-Fock Results for TiCO

Configuration ^a	State	Energy, ^a hartrees		Ti atomic limits
(11σ) ² (4π) ¹ (1δ) ¹	³ Φ	-9.15524	s ² d ²	³ F _A
	³ Π	-9.15162		³ F _A + ³ P
	¹ Φ	-9.14539		¹ G
	¹ Π			¹ G + ¹ D
(11σ) ¹ (4π) ² (1δ) ^{1b}	⁵ Δ	-9.14531	sd ³	⁵ F
	³ Γ	-9.08585		³ G
	² Δ _A	-9.06911		³ F _B
	² Σ _A ⁻	-9.13530	s ² d ²	³ F _A + ³ P
(11σ) ² (4π) ²	¹ Δ	-9.09119		¹ D + ¹ G
	¹ Σ ⁺	-9.05503		¹ D + ¹ G + ¹ S
	³ Δ _C	-9.12844	s ² d ²	³ F _A
(11σ) ² (1δ) ²	¹ Δ _C		s ² pd	
	³ Σ _B ⁻	-9.05577	s ² d ²	³ F _A + ³ P
(11σ) ¹ (4π) ³	³ Π _B	-9.03070	sd ³	³ G
	¹ Π _B			
(4π) ⁴	¹ Σ _B ⁺	-8.89027	d ⁴	

^a Energy relative to -950.0 hartrees. ^b Not all states from this configuration are listed. ^c The orbitals 1σ through 10σ and 1π through 3π are completely filled.

TiCO is expected to be the ³Φ state



GVB calculations were carried out on only a couple of states²⁶ (see Table VIII) and should also lead to a ³Φ ground state.

Table VIII. GVB Results for TiCO (all Energies in Hartrees)

State	Split pairs	Energy ^a	Energy lowering
⁵ Δ	(10σ, 12σ)	-9.15389	0.0086
³ Σ ⁻	(3π, 4π)	-9.13651	0.0012
	(3π, 5π)	-9.14172	0.0064

^a Energy relative to -950 hartrees.

(26) We were unable to obtain converged GVB wave functions for the ³Φ state using the Hinze MCSCF program.

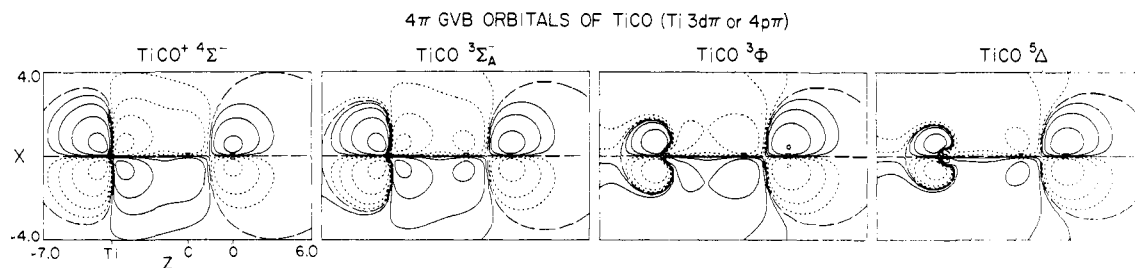


Figure 10. The 4π orbitals of TiCO^+ and TiCO (this corresponds to either $\text{Ti}(3d\pi)$ or $\text{Ti}(4p\pi)$ character).

Table IX. Expansion Coefficients for the 3π and 4π HF Orbitals of Several States of TiCO

State	Orbital	Expansion coefficients ^a					
		Ti(2p)	Ti(3p)	Ti(3d)	Ti(4p)	C(2p)	O(2p)
$^3\Phi$	3π	0.0085	-0.0290	0.0337	0.0493	0.4831	0.7581
	4π	-0.0486	0.1650	-0.3082	-0.6817	-0.4534	0.4984
$^5\Delta$	3π	0.0076	-0.0261	0.0339	0.0416	0.4845	0.7584
	4π	-0.0569	0.1938	-0.1624	-0.9009	-0.2202	0.3414
$^3\Sigma_A^-$	3π	0.0079	-0.0269	0.0196	0.0298	0.4680	0.7737
	4π	-0.0213	0.0716	-0.9056	-0.2252	-0.2319	0.2564

^a Slater orbitals, see ref 10.

The most unusual feature of the TiCO states is that when a δ orbital is occupied, as in the $^3\Phi$ and $^5\Delta$ states, the 4π orbital is mainly $4p\pi$ in character (see Figures 9 and 10 and Table IX) rather than $3d\pi$ like as in the states of TiCO^+ . On the other hand, for the $^3\Sigma^-$ state of TiCO (with no δ orbitals), the 4π orbital is $3d\pi$ like just as for TiCO^+ (see Figure 10 and Table IX). Thus, it would appear that for neutral TiCO the maximum population of d orbitals on the Ti is just under two.

As one proceeds from Ti^{3+} to Ti the relative energy of the 4p orbital relative to the 3d orbital becomes smaller and smaller as indicated in Table X. On this

Table X. Comparison of $3d \rightarrow 4p$ Excitation Energies for Various Ti Ions

Ion	Configuration		3d \rightarrow 4p excitation energy, cm^{-1} ^a
	Low	High	
Ti^{3+}	$3d(^2D_{3/2})$	$4p(^2P_{1/2})$	127913
Ti^{2+}	$3d(^3F_2)$	$3d4p(^1D_2)$	75197
Ti^+	$3d^24s(^4F_{3/2})$	$3d4s4p(^4D_{1/2})$	52330
Ti^0	$(3d)^3(^4F_{3/2})$	$(3d)^24p(^4G_{3/2})$	28636
Ti	$(3d)^3(4s)(^5F_1)$	$(3d)^2(4s)(4p)(^5G_2)$	9320

^a From Moore, ref 17.

basis we might expect Ti^- to prefer a configuration such as $(3d)^2(4s)^2(4p)$. Comparing with the ground state configuration of Ti, $(3d)^2(4s)^2$, this could indicate that donation of electrons to the Ti would favor increased 4p character in the valence orbitals. In TiCO the CO nonbonding orbital is partially donated to the Ti, and the part of these orbitals on the Ti has $d\sigma$ character. Thus, we might expect that the total population of d character in the other valence electrons on the Ti would be less than two, as observed.

This tendency to induce 4p character into the valence orbitals should be greater for Sc than for Ti and should decrease rapidly as one proceeds to V and beyond. On the other hand, ionizing an electron to obtain TiCO^+ also greatly decreases the tendency to build in 4p char-

acter. Thus, the bonding in TiCO^+ should be closer to the bonding in the Cr, Fe, and Ni carbonyls than it is to the bonding in TiCO . It was for this reason that we emphasized the case of TiCO^+ in this paper.

III. Discussion

From the results of these calculations, one obtains some understanding of the nature of the bonding between a metal and a carbonyl. Both σ and π bonding occur, but not to an extent significant enough to cause a drastic change in orbitals of the separated Ti and CO. Because the GVB approach leads to naturally localized orbitals and because the wave function is treated consistently in the united (TiCO) and separated molecule ($\text{Ti} + \text{CO}$) limits, one is able to examine exactly how the orbitals came together to form the bond and how others changed because of the bond. The σ bond forms through the acquisition of $\text{Ti}(3d_{z^2})$ character by the CO nonbonding orbitals. In other words, this is the classical σ donating effect of the ligand; the electrons coming exclusively from the carbonyl are given to the empty $3d_{z^2}$ orbital. Concomitantly, the occupied d orbitals of Ti delocalize slightly onto the C (acquiring $\text{CO}(\pi^*)$ character), thereby leading to the formation of a weak π bond.

This π accepting capability of the ligand balances its σ donating activity thereby allowing the metal to stay relatively neutral despite the σ donation. The π bonding orbitals of CO have an unfavorable interaction with the back bonding π orbitals of Ti leading to a somewhat weaker CO bond in TiCO .²⁵ In addition, the orbitals in the $\text{CO}(\sigma)$ bond shift slightly toward the Ti. The nonbonding electrons of Ti position themselves in the 4s (or $4s-\lambda dp$) orbital(s) on the side opposite to the CO so as to minimize electronic repulsion.

Thus, one can confidently say that carbonyl is a σ -donating, π -accepting ligand which retains much of its character as CO while bonded to the metal. This last fact seems to indicate that the presence of the metal is just a minor perturbation on the bonding in CO. However, for the metal, the CO causes more than a slight perturbation as crystal field theory would imply, with 3d

orbitals being involved in covalent bonding and 4s orbital(s) not involved.

Consider now what would happen if a second CO is bonded to the Ti. With a linear geometry, we must promote the 4s electrons to get them out of the way of the lobe pairs on the second CO. Hence the four valence electrons of Ti must be either in π orbitals or δ orbitals. With one valence electron in a π orbital, it will delocalize onto both carbonyl groups giving rise to π bonding on both of them. With two electrons in, for example, a π_x orbital, the orbitals would split in GVB fashion leading to one orbital more π bonding to, say, the left CO and one more to the right one. The π_y electrons would follow suit resulting in two π electrons donated to each carbonyl and two σ electrons received from each carbonyl. One expects all the valence electrons to be involved in bonding so that the Ti does not feel a negative charge. Hence this compound should be linear with the configuration $(15\sigma)^2(5\pi)^4$ (a ${}^1\Sigma_g^+$ state). However, it is not clear from these considerations whether the bonding interactions with the second CO will be sufficiently strong to overcome the promotion energy.

One can extend these bonding concepts to other carbonyl systems. In $\text{Cr}(\text{CO})_6$, there are six valence electrons provided by the chromium. One expects each carbonyl to donate two electrons toward the formation of a Cr-CO σ bond and each of the six valence electrons to enter into a π back bond. The π orbitals in an octahedral system are the d_{xy} , d_{xz} , and d_{yz} orbitals, and if the GVB description is applied, these orbitals split somewhat as indicated above for $\text{Ti}(\text{CO})_2$.

Based on the GVB results for TiCO and TiCO^+ , we expect each σ bonding orbital to have primarily the character of the CO nonbonding pair but with the character of a d_{z^2} orbital (in the direction of the σ bond) in the region near the Cr. This differs greatly from the usual valence bond picture in which the Cr orbitals are assumed to be d^2sp^3 hybrids.²⁷ This difference arises because in the VB model a covalent bond involves one singly occupied orbital from each atom and the orbitals on the atom must be orthogonal. In the GVB model we allow the orbitals to have whatever shape they want. As a result the components on a particular center, say a Cr, need not all be orthogonal. Hence it is acceptable for each σ bond to make use of d_{z^2} (or d_{x^2} or d_{y^2}) character on the Cr even though there are six σ bonding pairs and only two linearly independent such Cr orbitals.

The remaining six electrons are in t_{2g} orbitals. There are in addition two much higher e_g orbitals which have the character of d_{z^2} and $d_{x^2-y^2}$ orbitals on the Cr but

(27) As discussed in section I, our use of a minimal basis would tend to bias our calculations against large hybridization effects, since the atomic 3d and 4s orbitals are so greatly different in size. However, the VB description is based on the use of atomic orbitals and hence our results do argue against the use of d^2sp^3 hybrids in the analysis of transition metal complexes.

with large antibonding components of CO lobe orbital character.

Thus, ignoring the σ bonding orbitals, the GVB description is $(t_{2g})^6(e_g)^0$ just as would be used in a crystal field model. The low spin character results partly from the high overlap of d_{z^2} and CO lobe orbitals leading to a low lying occupied bonding pair and a high lying empty antibonding orbital (e_g). In addition the π back bonding character of the t_{2g} orbital may decrease its energy a bit. The result is a large $t_{2g} - e_g$ splitting and consequently a low spin complex.

From this description of $\text{Cr}(\text{CO})_6$ we see that there is no more room for more electrons. Thus, we would not expect $\text{Fe}(\text{CO})_6$ to be bound. On the other hand, removing a CO should allow accommodation of an additional electron pair so that one would expect $\text{Fe}(\text{CO})_5$ to be stable. Similarly, to obtain a stable Ni compound, it would be necessary to remove another carbonyl, yielding $\text{Ni}(\text{CO})_4$. At this point we would analyze the requirements of CO(σ) bonding orbitals to predict the geometries of the Fe and Ni carbonyls. Then we should examine the forms of the various d orbitals on the Fe and Ni and predict how effective they are for back bonding. The adequacy of the model would be judged in terms of whether it leads to a trigonal bipyramid for $\text{Fe}(\text{CO})_5$ and a tetrahedral structure for $\text{Ni}(\text{CO})_4$ and whether it would successfully predict, for example, that the reaction



goes by axial attack (X is halogen). However, our understanding of the form of the GVB orbitals for transition metal complexes is not yet sufficient to make reliable predictions on the shapes and interactions of the orbitals in cases like $\text{Fe}(\text{CO})_5$ where antibonding orbitals may be occupied. As a result we cannot at the moment add anything new to the usual arguments for rationalizing the structures and reactivity of Fe and Ni carbonyls. What we can say from this calculation is that both the σ and π interactions are important in the bonding of transition metal carbonyls.

IV. Summary

The calculations of several states of TiCO^+ and TiCO have indicated some of the characteristic features of a metal carbonyl. As expected, carbonyls bind through a σ -donating, π -accepting interaction. It was found that the π back bonding was considerably weaker in TiCO than in TiCO^+ and that this leads to instability of that compound with respect to TiCO^+ . We believe that these ideas will be useful in describing the bonding of other transition metal carbonyls.

Acknowledgment. We thank Professor H. B. Gray for discussions and helpful comments. Professor J. Hinze and Dr. B. Liu are thanked for the use of their MCSCF programs and Dr. T. H. Dunning is thanked for aid in the use of these programs.