# LETTERS

## The "Sextuple" Bond of Cr$_2$

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Using a self-consistent 6000-configuration wave function corresponding to spin-optimized generalized valence bond (GVB) plus interpair correlations and van der Waals interactions, we find that the ground state of Cr$_2$ is best described not as a sextuple bond, but rather as an *antiferromagnetic dimer* with very low-lying electronic excited states. Our calculations predict a red shift of $0.3_0$ eV for the first strong absorption in Cr$_2$ as compared with Cr, in excellent agreement with matrix isolation studies. The ground state is calculated to have $R_e = 3.0_6$ Å and $D_e = 0.3_5$ eV. The best experimental dissociation energy is $1.0 \pm 0.3$ eV (based on our structural parameters) but may suffer from experimental difficulties.

## I. Introduction

In recent years there has been an intense effort to synthesize and characterize systems with metal–metal multiple bonds.[1] There continues to be controversy concerning the bond strengths and the description of the low-lying states.[2] We report here the results of a series of ab initio calculations on Cr$_2$, a molecule with a formal sextuple bond. Our results, which are in agreement with available experimental data, establish that the *bond does not involve multiple bonding*. Rather, the ground state is best described as two high-spin ($S = 3$) Cr atoms coupled antiferromagnetically to obtain a singlet ($S = 0$) state.

In carrying out these calculations, we have used a newly developed MC-SCF program,[3] GVB3, in which the orbitals

TABLE I:   Energies for GVB Wave Functions at $R = 5.6$ $a_0 = 2.96$ Å

| state | spin | no. of spin eigenfunctions | $J_s$,[a] cm$^{-1}$ |
|---|---|---|---|
| $^{13}\Sigma_g^+$ | 6 | 1 | $-73$ |
| $^{11}\Sigma_u^+$ | 5 | 12 | $-77$ |
| $^{9}\Sigma_g^+$ | 4 | 114 | $-74$ |
| $^{7}\Sigma_u^+$ | 3 | 580 | $-72$ |
| $^{5}\Sigma_g^+$ | 2 | 1715 | $-70$ |
| $^{3}\Sigma_u^+$ | 1 | 2712 | $-69$ |
| $^{1}\Sigma_g^+$ | 0 | 1516 | |

[a] Defined as $(E_0 - E_s)/(S^2 + S)$, where $E_s$ is the GVB energy for the $S$ spin state.

of a 6000-configuration (spin-eigenfunction) wave function were optimized in a full MC-SCF treatment.

[†] Contribution no. 6337.

(1) Cotton, F. A. *Acc. Chem. Res.* 1978, *11*, 225.
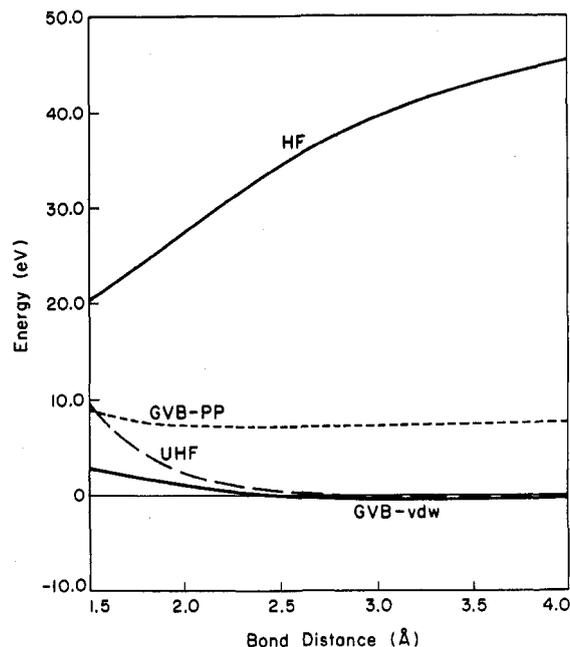(2) Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* 1978, *11*, 232.
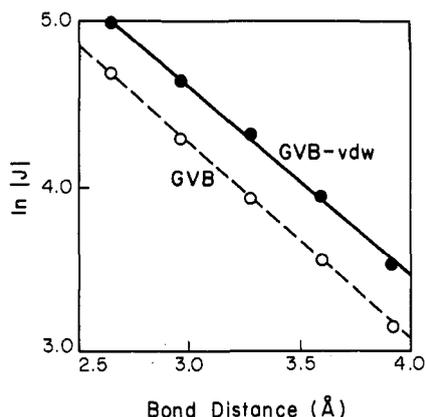
**Figure 1.** Calculated potential curves for $Cr_2$.



**Figure 2.** Dependence of $J$ upon $R$. Using $J$ in $cm^{-1}$ and $R$ in Å, we find In $|J| = a - bR$, where $a = 7.84$ and $b = 1.19$ for GVB, and $a = 8.02$ and $b = 1.14$ for GVB-vdw.

## II. Results and Discussion

Various details of the wave functions are described in section III, and the potential curves are shown in Figure 1. First we shall consider the nature of the ground state.

*A. Nature of the Ground State.* Starting with two $S = 3$ atoms and coupling the spins leads to states of total spin, $S = 0, 1, 2, 3, 4, 5, 6$, with an energy formula

$$E_S = E_0 - JS(S + 1) \tag{1}$$

where $J < 0$ for antiferromagnetic coupling ($J \to 0$ as $R \to \infty$). For finite $R$ the spin coupling may change so that each atom is no longer $S = 3$, leading to deviations from this formula; however, as shown in Table I, the energies of $Cr_2$ wave functions at the optimum ground-state geometry are accurately described by formula (1). Thus, rather than a sextuple bond, we should think of $Cr_2$ as an antiferromagnetically coupled diatomic.

The MC-SCF wave function corresponding to the GVB wave function (with and without van der Waals terms) of various total spins was calculated self-consistently at various distances. As shown in Figure 2, we find that the

(3) Yaffe, L. G.; Goddard, III, W. A. *Phys. Rev. A* **1976**, *13*, 1682. Improvements to the original program have been contributed by R. A. Bair, M. M. Goodgame, and T. H. Upton.
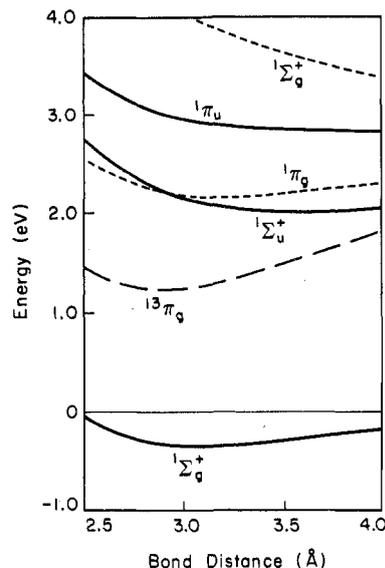


**Figure 3.** Excited 4p ← 4s states of $Cr_2$.

magnitude of $J$ in formula (1) decreases exponentially with increasing $R$.

*B. Ground State Properties.* From the GVB-vdw wave function of the ground state we obtain $R_e = 3.0_6$ Å, $\omega_e = 110$ $cm^{-1}$, and $D_e = 0.3_5$ eV. [For GVB, the corresponding quantities are $R_e = 3.2_5$ Å, $\omega_e = 70$ $cm^{-1}$, and $D_e = 0.1_3$ eV.] Knudsen effusion mass spectrometric data on $Cr_2$ were interpreted with the third-law method by using rough estimates of electronic multiplicity, $R_e$, and $\omega_e$ to yield a dissociation energy $D_0 = 1.56 \pm 0.30$ eV.[4] However, recalculating the partition function for $Cr_2$ using spectroscopic parameters from our calculations (and including contributions from all seven bound states),[5] we obtain a new experimental value of $D_0 = 1.0 \pm 0.3$ eV. This is still considerably larger than our calculated value of $0.3_5$ eV and could indicate the importance of additional electron correlation terms. However, effusion flow was not maintained during the experiments, so there is some uncertainty in the accuracy of the experimental dissociation energy.

A bond distance of 1.7 Å for $Cr_2$ has been obtained from analysis of a 460-nm band in flash-photolyzed $Cr(CO)_6$.[6] However, there is no evidence that this band is due to $Cr_2$, and, based on our studies, we conclude that the origin of this band has not been properly identified.

*C. Excited States.* Matrix isolation studies of Cr atoms in Ar matrices provide the best evidence for $Cr_2$. In these studies a 455-nm absorption band to the red of the 4p ← 4s atomic transition (427-nm gas phase; ~390-nm matrix) has been assigned to $Cr_2$.[7] We have calculated the states of $Cr_2$ corresponding to the 4p ← 4s transition of Cr, the results of which are shown in Figure 3. One dipole-allowed transition, $^1\Sigma_u^+(4p) \leftarrow {}^1\Sigma_g^+(4s)$, we find shifted by $0.3_0$ eV to the red from the atomic value, and this transition we assign to the 455-nm band. The other dipole-allowed transition, $^1\Pi_u \leftarrow {}^1\Sigma_g^+$, leads to a much larger bond length and may lead to a broad, continuous absorption to the blue of the atomic line. There are slight ambiguities in interpreting the experimental results since there is a blue matrix

(4) Kant, A.; Strauss, B. *J. Chem. Phys.* **1966**, *45*, 3161.
(5) Spectroscopic constants for each state were obtained from a cubic spline fit to the GVB-vdw results, and the partition function was calculated by approximating each of the seven bound electronic states as a Morse oscillator (using calculated $R_e$, $\omega_e$, and $D_e$).
(6) Efremov, Yu. M.; Samoilova, A. N.; Gurvich, L. V. *Opt. Spektrosk.* **1974**, *36*, 654.
(7) Kündig, E. P.; Moskovits, M.; Ozin, G. A. *Nature (London)* **1975**, *254*, 503.

shift ($\sim$0.27 eV) for the atomic line. Our results suggest a smaller matrix shift of $0.1_2$ eV for $^1\Sigma_u^+(4p) \leftarrow {}^1\Sigma_g^+(4s)$[8] (reasonable since $Cr_2$ would have fewer matrix atoms near either Cr atom).

## III. Wave Functions[9]

*The Hartree–Fock Wave Function.* The ground state of a Cr atom is the $^7S$ state arising from the $(3d)^5(4s)^1$ valence configuration. Bonding the orbitals of two Cr atoms into a sextuple bond leads to the configuration

$$(\sigma_g 4s)^2(\sigma_g 3d)^2(\pi_{ux} 3d)^2(\pi_{uy} 3d)^2(\delta_{gxy} 3d)^2(\delta_{gx^2-y^2} 3d)^2$$

However, from Figure 1 we see that the energy of this HF wave function is over 20 eV *above* the energy of two HF atoms! Other cases are also known where the HF energy of a molecule is above that of the atoms (e.g., the HF energy of $F_2$ is over 1.6 eV above that of two HF atoms);[10] however, the error for $Cr_2$ is extremely large. This difficulty with the HF wave function is usually referred to as electron-correlation error.

*Generalized Valence Bond Wave Function.* In the generalized valence bond description[11] one would describe the valence part of the wave function

$$\Psi_{\text{val}} = \mathcal{A}[\phi_{1a}(1)...\phi_{6a}(6)\phi_{1b}(7)...\phi_{6b}(12)\chi] \quad (2)$$

in terms of 12 singly-occupied orbitals ($\phi_{1a}, ...\phi_{6a}, \phi_{1b}, ...\phi_{6b}$) that are allowed to overlap and a general spin eigenfunction $\chi$ for coupling the spins of 12 electrons into a singlet. The 12 orbitals and the spin eigenfunction $\chi$ are then optimized self-consistently for each $R$. At $R = \infty$ this GVB wave function would have six orbitals ($\phi_{1a}...\phi_{6a}$) corresponding to atomic Cr orbitals at the left, six orbitals ($\phi_{1b}, ...\phi_{6b}$) corresponding to atomic Cr orbitals at the right, and an optimum spin eigenfunction $\chi$ corresponding to coupling spins 1–6 into $S = 3$, spins 7–12 into $S = 3$, and the spins 1–12 to $S = 0$ (referred to as the GF spin coupling[11]). For finite $R$, the orbitals would delocalize onto opposite centers and the optimum spin function would change.

For systems having strong multiple bonds, the GVB wave function can be written in the restricted form

$$\mathcal{A}[\phi_{1a}\phi_{1b}(\alpha\beta - \beta\alpha)][\phi_{2a}\phi_{2b}(\alpha\beta - \beta\alpha)]...[\phi_{6a}\phi_{6b}(\alpha\beta - \beta\alpha)] \quad (3)$$

in which each bond pair (e.g., $\phi_{1a}$ and $\phi_{1b}$) is singlet paired. This pairing of the orbitals is referred to as the valence bond (VB) or perfect pairing (PP) form. Defining natural orbitals $\phi_{ig}$ and $\phi_{iu}$ as

$$\phi_{ig} = (\phi_{ia} + \phi_{ib})/\eta_{ig} \qquad \phi_{iu} = (\phi_{ia} - \phi_{ib})/\eta_{iu} \quad (4)$$

(where $\eta_i$ are normalizing constants) leads to

(8) The matrix-isolated $Cr_2$ absorption is experimentally 0.18 eV less (red shift) than the gas-phase 4p $\leftarrow$ 4s atomic transition. Our calculations lead to a transition energy for gas-phase $Cr_2$ $0.3_0$ eV less than that for gas-phase Cr (red shift). Thus, comparing theory and experiment, the matrix-isolated $Cr_2$ absorption is $0.1_2$ eV greater (blue shift) than the gas-phase $Cr_2$ absorption. This compares with a 0.27-eV blue shift for the atomic transition.

(9) (a) The basis set used in these calculations is a new one[9b] involving five d primitives contracted valence double zeta and optimized for the $d^6$ state of Cr atom. This basis set is suitable for the $d^4$, $d^5$, and $d^6$ states of Cr, removing a well-known deficiency[9c] of the Wachter basis.[9d] (b) Rappé, A. K.; Goodgame, M. M.; Goddard, III, W. A. unpublished results; (c) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377; (d) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(10) Wahl, A. C. *J. Chem. Phys.* **1964**, *41*, 2600.

(11) Goddard, III, W. A.; Ladner, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 6750.

$$(\phi_{ia}\phi_{ib} + \phi_{ib}\phi_{ia}) = C_{ig}\phi_{ig}\phi_{ig} - C_{iu}\phi_{iu}\phi_{iu} \quad (5)$$

Thus, in terms of natural orbitals, the GVB-PP wave function (3) leads to $2^6 = 64$ closed-shell configurations. The optimum spin function at $R = \infty$ is of GF form, not the VB or PP form, and hence the GVB-PP wave function does not go to the correct limit as the bond is broken. Consequently, we must use the more general GVB form of the wave function.

The GVB wave function (2) can also be expanded in terms of natural orbitals (4) leading to $3^6 = 729$ spatial configurations (of which 365 can occur in a $^1\Sigma_g^+$ wave function). With up to 12 singly-occupied orbitals, each spatial configuration can have a number of spin eigenfunctions. For $^1\Sigma_g^+$, the 365 spatial configurations have a total of 1516 spin eigenfunctions (which can be expanded with 6628 determinants). The MC-SCF wave function which optimizes the unrestricted linear combination of all these spin eigenfunctions corresponds to the GVB wave function but also includes interpair correlations.[12] Solving for the orbitals of this GVB form of wave function is more complicated than for PP, and to do so we have used a new program[3] capable of describing both general MC-SCF wave functions and restricted forms such as GVB-PP.

*van der Waals Terms.* The long-range (van der Waals) interactions between atoms such as in $K_2$ involve adding terms of the form $p_{\lambda l}p_{\lambda r}$ (where $\lambda = x, y$, or $z$) to the term $s_l s_r$ in the GVB wave function. In terms of natural orbitals, this changes a two-configuration wave function to an eight-configuration wave function.

For the GVB wave function of $Cr_2$, (2), inclusion of these van der Waals terms for the 4s–4s bond leads to 1460 spatial configurations of symmetry $^1\Sigma_g^+$ (in place of 365) and to 6064 spin eigenfunctions (26512 determinants). We used the GVB3 program to solve for the optimum 18 orbitals for this 6064 spin eigenfunction wave function.

*Excited Wave Functions.* For Cr atom the first dipole-allowed transition (at 2.90 eV = 23 400 cm$^{-1}$)[13] is

$$^7P[(4p)^1(3d)^5] \leftarrow {}^7S[(4s)^1(3d)^5]$$
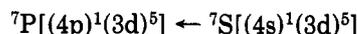
that is, excitation of 4s to 4p. For $Cr_2$ we find that the first strong transitions correspond to this same excitation. However, we may have

$$4p\sigma \leftarrow 4s \quad \text{or} \quad 4p\pi \leftarrow 4s$$
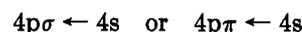
on either center, leading to four singlet states $^1\Sigma_g^+$, $^1\Sigma_u^+$, $^1\Pi_u$, $^1\Pi_g$, each of which involves a resonance combination of 4s to 4p excitations on either atom. Combining with the d orbitals leads to 3408 spin eigenfunctions (486 spatial configurations or 16776 determinants) of each symmetry for which we optimized all 14 orbitals.

*Unrestricted Hartree-Fock.* Replacing the singlet spin eigenfunction $\chi$ of (2) with

$$\chi = \alpha\alpha\alpha\alpha\alpha\beta\beta\beta\beta\beta$$

leads to a single determinant wave function that is a mixture of seven spin states.

(12) Harding, L. B.; Goddard, III, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 6293.

(13) Moore, C. E. *Natl. Bur. Stand. Circ.* **1971**, *No. 467*.