The Whole Story of the Two-Electron Bond, with the δ Bond as a Paradigm

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ABSTRACT

It is shown that the δ bond, as found particularly in the Re₆δ⁺ and Mo₄δ⁺ cores of hundreds of compounds, provides a paradigm for the behavior of two-electron bonds of all types. By control of the angle of twist around the M–M axis, the strength of the bond can be systematically varied. By means of conventional electronic spectroscopy, nuclear magnetic resonance spectroscopy, and two-photon excitation spectroscopy, the entire picture of the manifold of four states for two electrons bonding two atoms, as first described by Coulson and Fischer in 1949, has been confirmed.

Introduction

It can be said without fear of contradiction that the two-electron bond is the single most important stereoelectronic feature of chemistry. This does not exclude multiple bonds since they are commonly, if not exactly rigorously, regarded as composed of two, three, or four, two-electron components.

The concept of a two-electron bond was first introduced by G. N. Lewis in 1916.² It was not possible at the time to describe it in any more detail than he did, namely, that a single bond is formed by a pair of shared electrons. Nor was it possible to represent it in any more detail than he did, namely, a pair of dots placed between the symbols for two atoms, much as a line had been (and still is) used for the same purpose:

```
  O          O
  \         /  
   \       /   
    \  /    
     \/
  H—H
```

These simple representations of bonds are all a chemist needs in much of the usual discussion of chemical formulas, reactions, and other phenomena. Moreover, when the explicit recognition that “—” means “·” is coupled with the octet concept, a significant improvement occurs because this leads to better appreciation of the dependence of charge distribution (at least formally) and stereochemistry on electronic structure.³

With the advent of quantum mechanics, theoreticians acquired the tools to explore the nature of the two-electron bond in a much more profound way. From the start, the bond in the hydrogen molecule was taken as prototypical, for example by Heitler and London (1927) in their development of valence bond theory.⁴ In 1933, James and Coolidge very laboriously showed⁵ that a quantum mechanical calculation, when carried to a sufficient level of accuracy via the variation principle, could provide very accurate values for the length and energy of this bond. This validated both Lewis’s proposal and the correctness of the quantum theory of chemical bonding.

Given that the application of the wave equation to the electronic structures of molecules was feasible and desirable, the question of how best to construct the appropriate wave functions came to the fore. A proposal made by Linus Pauling in 1928⁶ and again by Lennard-Jones in 1929⁷ gained support. This proposal was to construct orbitals for an entire molecule as superpositions of orbitals on the individual atoms. The method, which is now known as the LCAO (linear combination of atomic orbitals) approach, was first fully implemented in 1949 by Coulson and Fischer for the H₂ molecule.⁸

The work of Coulson and Fischer was seminal because it dealt with the bonding problem in all its aspects:

1. It described the entire manifold of four electronic states that arise when there are two atoms, two orbitals, and two electrons.
2. It described the electronic structure over the entire range of internuclear distances, from those shorter than the equilibrium distance for the ground state to the dissociation limit.
3. It explicitly included, and drew attention to, the important role played by configuration interaction, i.e., the interaction of states of the same symmetry derived from different electron configurations.

In short, Coulson and Fischer gave us a complete picture of the two-electron bond as obtained by the LCAO–MO method of constructing wave functions. The results of

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their treatment are represented in Figure 1, which is taken from their paper.

There is no reason to suspect that these results might be in any way incorrect, so long as it is agreed that wave mechanics itself, at this level of approximation at least, is correct. So what else is left to say? Perhaps only this: it is central to the concept of scientific research that all theoretical results, however little reason there might be to doubt their correctness, ought to be tested experimentally. Another way to put this is the following: to be fully scientific we should not only answer theoretical questions but question theoretical answers. But has the picture in Figure 1 ever been fully checked experimentally, namely, by showing experimentally how all four states behave as a function of bond strength (which is, in turn, determined by internuclear distance)? Clearly not, because except for a few aspects, this overall picture cannot be evaluated experimentally for the H–H bond, nor for any other bond. We cannot examine the evolution of all four states as we gradually and systematically stretch the molecule. Molecular tweezers are yet to be invented.

Here is where the δ bond enters the arena. The δ bond has the useful property that there are two ways to reduce its strength: (1) as for any bond, by increasing the internuclear distance, and (2) by changing the internal angle, χ, as defined in Figure 2, from 0° where the δ–δ overlap is maximal, to 45° where the overlap becomes zero and the δ bond is abolished. It may not be immediately obvious why the δ bond should necessarily offer any advantage over a σ bond because the aforementioned lack of molecular tweezers would appear to imply that we can no more twist a molecule at will than we can stretch it at will. But, by chemical means, we can, as will now be explained.

**A Brief Chemical Background**

Some background concerning the chemistry of compounds that contain a δ bond will first be necessary before we describe the work that has been done using the δ bond. While there was earlier mention of δ bonding, the concept became an indisputable reality only with the first report of the quadruple bond in Re₂Cl₈²⁻, which was soon followed by reports of quadruple bonds in other species.

The quadruple bond consists of a σ bond, two equivalent π bonds, and the δ bond. A simplified energy level diagram is shown in Figure 3. Several important points that underlie the main theme can be made by referring to this diagram. First, the σ and two π bonds account for nearly all of the bonding between the metal atoms. This means that even with the loss of all the δ bonding (as in the case where one δ electron is promoted to the δ* orbital), the bond length changes little (typically 3%). Second, the bonding that arises from the σ²π⁴ configuration is independent of the internal twist angle. This means that a quadruply bonded M₂ unit together with the σ and...
In some molecules of type twist angles, depending on the identities of R and X and ions (Figure 4). The chemistry of the Mo$_2$Cl$_8^{4-}$ based on the eclipsed rotational conformation of these angles exceeds $45^\circ$. The upper curve is for compounds in which $X = Cl$ and the lower one for $X = Br$. (Taken from ref 16).

The most important result of these studies in the Whole Story of the Two-Electron Bond

A Brief Theoretical Background

Before explaining what has been done experimentally, we shall briefly review the LCAO method as it applies to any two-electron bond. It is important to do this because what might be done for a $\sigma$ bond is, mutatis mutandis, applicable to $\pi$ bonds as well. [Note: In principle, $\pi$ bonds can also be weakened by twisting as well as by stretching, but they do not lend themselves as well as $\sigma$ bonds to full-range characterization because, to abolish a $\pi$ bond, a 90° twist is required. In fact, the largest twist that has been reported for a ground-state structure is only 40° (Leuf, W.; Reese, R. Top. Stereochem. 1991, 20, 231), and because $\pi$ bond strength varies as $cos \chi$, a 40° twist covers less than a quarter of the total $\pi$ bond strength range.]

\begin{align*}
\text{Mo}_2\text{Cl}_8^{4-} + 4\text{PR}_3 & \rightarrow \text{Mo}_2\text{Cl}_4(\text{PR}_3)_4 + 4\text{Cl}^- \\
\text{Mo}_2\text{Cl}_8^{4-} + 2\text{P} = \text{P} & \rightarrow \text{Mo}_2\text{Cl}_4(\text{P} = \text{P})_2 + 4\text{Cl}^- 
\end{align*}

\[
\delta - \delta^* \text{transition energy at } \chi = 45^\circ \text{ (cos } 2\chi = 1) \text{ is not zero even though the } \delta - \delta \text{ overlap is zero. How can this be? Because, as already shown by Coulson and Fischer for a stretched } H_2 \text{ molecule, the energies of the four electronic states that exist for the molecule in its normal bonded state converge, pairwise, to two energies, and these are separated by an energy } 2K, \text{ where } K \text{ is a quantity in electronic structure theory called the exchange energy. What the data in Figure 6 enable us to do is to measure, approximately, but directly from experiment, the value of } K \text{ for a chemical bond. This had never been done before. Even more interesting was the idea that by making further measurements on actual molecules that have twist angles between 0° and 45°, it might be possible to trace the behavior of all four states of the } \delta \text{ bond manifold as a function of } \delta - \delta \text{ overlap and see if they follow the pattern implied by the work of Coulson and Fischer for any two-electron bond.}

As shown in Figure 5, the main structural results were that (a) the Mo$_2X_4$(PR$_3)_4$ species always had a structure of type a, in which the internal torsion (twist) angle is zero, (b) the Mo$_2X_4$(R$_2$P(CH$_2$)$_n$PR$_2$) molecules always have a structure of type b, wherein the twist angle is again zero, and (c) compounds of the type Mo$_2X_4$(R$_2$P(CH$_2$)$_n$PR$_2$) ($n = 2, 3, \text{ or } 4$) have a structure of type c but with a range of twist angles, depending on the identities of R and X and the number of methylene subunits in the ligand backbone. In some molecules of type c the P-Mo-Mo-P torsion angle exceeds 45°. In view of the symmetry of the $\delta$ orbitals, however, $\chi$ angles $0^\circ - 45^\circ$ and $45^\circ - 90^\circ$ are equivalent insofar as the $d_{\sigma}/d_{\sigma}$ overlap is concerned.

The most important result of these studies in the present context was that there is a relationship between the twist angle and the energy of the $\delta - \delta^*$ absorption band, as shown in Figure 6. We see here that the extrapolated $\delta - \delta^*$ transition energy at $\chi = 45^\circ$ (cos $2\chi = 1$) is not zero even though the $\delta - \delta$ overlap is zero. How can this be? Because, as already shown by Coulson and Fischer for a stretched $H_2$ molecule, the energies of the four electronic states that exist for the molecule in its normal bonded state converge, pairwise, to two energies, and these are separated by an energy $2K$, where $K$ is a quantity in electronic structure theory called the exchange energy. What the data in Figure 6 enable us to do is to measure, approximately, but directly from experiment, the value of $K$ for a chemical bond. This had never been done before. Even more interesting was the idea that by making further measurements on actual molecules that have twist angles between $0^\circ$ and $45^\circ$, it might be possible to trace the behavior of all four states of the $\delta$ bond manifold as a function of $\delta - \delta$ overlap and see if they follow the pattern implied by the work of Coulson and Fischer for any two-electron bond.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{M$_2$Cl$_8^{n-}$ ions, with $M = Re$, $n = 2$ and $M = Mo$, $n = 4$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Three types of structures arising when four Cl$^-$ ions are substituted by four PR$_3$ or two diphosphines.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Energies of the $\delta(\delta \rightarrow \delta^*)$ transition for a series of Mo$_2X_4L_4$ and Mo$_2X_4(P = P)_2$ compounds, where L and $P = P$ are mono- and diphosphine ligands, plotted against the internal twist angle $\chi$.}
\end{figure}
For any two-center, homonuclear bond, whether \( \alpha, \pi, \) or \( \delta, \) an LCAO–MO treatment begins with the following four steps:

1. Let the atomic orbitals on atoms 1 and 2 be designated \( \gamma_1 \) and \( \gamma_2. \)
2. The bonding, \( \phi, \) and antibonding, \( \chi, \) LCAO–MOs (neglecting overlap) are
   \[
   \phi = \frac{1}{\sqrt{2}}(\gamma_1 + \gamma_2)
   \]
   \[
   \chi = \frac{1}{\sqrt{2}}(\gamma_1 - \gamma_2)
   \]
3. The energies of these MOs are
   \[
   E_\phi = \langle \phi | H | \phi \rangle = \int \gamma_1 \gamma_1^* \, dx + \int \gamma_2 \gamma_2^* \, dx \quad \text{where} \quad i = 1 \text{ or } 2
   \]
   \[
   E_\chi = E_\gamma - W
   \]
   Since \( E_\gamma \) is the energy of one electron in the atomic orbital \( \gamma_1 \) or \( \gamma_2, \) we may take this as the zero of energy and write
   \[
   E_\phi = W \quad \text{and} \quad E_\chi = -W
   \]
   If there is only one electron to occupy these MOs, we have a very simple (and very familiar) picture, as shown in Figure 7. There are only two states, \( \phi \) and \( \chi, \) and only one electronic transition, namely, that from the ground state to the excited state, whose energy is exactly \( 2W. \) But what happens when there are two electrons?
4. We must now write determinantal wave functions for the four states that can arise. If both electrons occupy the \( \phi \) MO, to give a full bond, we have
   \[
   \psi_1 = \begin{vmatrix}
   \phi \\
   \phi
   \end{vmatrix}
   = \frac{1}{\sqrt{2}} \begin{pmatrix}
   \phi(1) \\
   \phi(2)
   \end{pmatrix}
   \]
   \[
   = -\frac{1}{\sqrt{2}} \left[ \phi(1) \phi(2) - \phi(1) \phi(2) \right]
   \]
   After separating orbital and spin functions, using \( \alpha \) (\( = \frac{1}{\sqrt{2}} \)) and \( \beta \) (\( = -\frac{1}{\sqrt{2}} \)) for the latter, we obtain
   \[
   \psi_1 = \frac{1}{\sqrt{2}} \phi(1) \phi(2) [\alpha \beta - \beta \alpha]
   \]
   where the antisymmetrization required by the Pauli principle is accomplished by the spin function. We could also place both electrons in the \( \chi \) MO and get an analogous expression,
   \[
   \psi_1 = \frac{1}{\sqrt{2}} \chi(1) \chi(2) [\alpha \beta - \beta \alpha]
   \]
   Both of these represent spin singlet states.

Because the Pauli principle no longer restricts us to antisymmetrizing the wave function by way of the spins, we have two possibilities when we develop the corresponding expressions for the states arising from placing one electron in \( \phi \) and the other in \( \chi. \) Spin-paired electrons give a singlet state, but antisymmetrization can also be done if both electrons have the same spin by way of an antisymmetric orbital (i.e., spatial) function, giving a triplet state. Altogether, we have the following four states in what is called the bond manifold:

- \( \psi_1 = \frac{1}{\sqrt{2}} \phi(1) \phi(2) [\alpha \beta - \beta \alpha] \]
- \( \psi_2 = \frac{1}{\sqrt{2}} [\phi(1) \chi(2) - \phi(2) \chi(1)] [\alpha \beta + \beta \alpha] \]
- \( \psi_3 = \frac{1}{2} [\phi(1) \chi(2) + \phi(2) \chi(1)] [\alpha \beta - \beta \alpha] \]
- \( \psi_4 = \frac{1}{2} \chi(1) \chi(2) [\alpha \beta - \beta \alpha] \)

The two-term orbital factors in \( \psi_2 \) and \( \psi_3 \) arise because of the indistinguishability of electrons; we cannot assert that electron 1 is in \( \phi \) and electron 2 in \( \chi \) rather than the reverse, so we must give both assignments equal weight.

These four steps set up our problem. We now have to determine the energies of the four states. Before actually doing so, we pause to note that most chemists would “intuitively” (whatever that means exactly) expect the following order of increasing energy,

\( \psi_1 < \psi_2 \approx \psi_3 < \psi_4 \)

on the grounds that \( \psi_1 \) represents a net bond, \( \psi_2 \) and \( \psi_3 \) involve the promotion of one electron and represent no net bond, and \( \psi_4 \) involves a two-electron promotion and is completely antibonding.

This, however, is not the case; to find out why, we must first derive expressions for the state energies and also look more closely at the wave functions. There are several computational approaches that can be used, including a generalized valence bond (GVB) method. Since this is, perhaps, not as transparent to most chemists as the
Accordingly, we shall henceforth assign to the four states apart, to convert $X$ half the energy required, for two atoms, $X$, infinitely far between the charge clouds of two electrons that are either inherently positive, and represent the repulsive interaction of the manifold are not to the valence bond approach later. We shall, however, return to the $\theta$ manifold altogether since they are not really wave functions and substitute in the LCAO expressions for $\phi$ and $\chi$, we obtain the following results:

\[
\psi_1 = [\gamma_1(1\sigma_1) + \gamma_2(1\sigma_2)] + [\gamma_1(1\sigma_2) + \gamma_2(1\sigma_1)] \\
\psi_2 = [\gamma_1(1\sigma_2) + \gamma_2(1\sigma_1)] \\
\psi_3 = [\gamma_1(1\sigma_1) + \gamma_2(1\sigma_2)] \\
\psi_4 = [\gamma_1(1\sigma_1) + \gamma_2(1\sigma_2)] - [\gamma_1(1\sigma_2) + \gamma_2(1\sigma_1)]
\]

States 1–4 here correspond to those numbered 1, 2, 3, and 4 in Figure 1. We see that $\psi_2$ and $\psi_3$ which are the actual wave functions (so long as we treat the $\theta$ manifold alone) are, respectively, purely covalent and purely ionic. On the other hand, $\psi_1$ and $\psi_4$ both have half covalent and half ionic character. These are not credible wave functions as they stand. It is not, for example, believable that in the $1\Delta_{1g}$ state there are two electrons on one atom half the time. The ionic distribution must be of much higher energy than the covalent one and, accordingly, should contribute mainly to the $1\Delta_{1g}$ state, while the $1\Delta_{1g}$ ground state should be mainly covalent. This is, in fact, exactly what occurs. The wave functions $\psi_1$ and $\psi_4$ are not really the orbital wave functions for the $1\Delta_{1g}$ and $1\Delta_{1g}^*$ states; through the off-diagonal element, these two orbital wave functions are mixed (configuration interaction) and the true orbital wave functions for these two states are given by

\[
\psi(1\Delta_{1g}) = \psi_1 - \lambda \psi_4 \\
\psi(1\Delta_{1g}^*) = \psi_4 + \lambda \psi_1
\]

If we examine the expressions for $\psi_1$ and $\psi_4$ given above we see that as $\lambda$ increases, $\psi(1\Delta_{1g})$ becomes more covalent and $\psi(1\Delta_{1g}^*)$ becomes more ionic. This mixing contributes to the stability of the $1\Delta_{1g}$ ground state and raises the energy of the $1\Delta_{1g}^*$ state.

**Energy Measurements of the $\theta$ Bond Manifold**

We can show the essence of what has just been done in a very simple diagram of the four states, and how their energies would be expected to evolve as the $\delta$ bond proceeds from its maximum when the molecule is eclipsed ($\chi = 0^\circ$, $\cos 2\chi = 1$) through intermediate angles to the situation in the perfectly staggered molecule ($\chi = 45^\circ$, $\cos 2\chi = 0$). Such a diagram is presented in Figure 8. It will be noted that here the relative energies of the four states follow the pattern $E_1 < E_2 < E_3 < E_4$, rather than the “intuitive” pattern mentioned earlier. This happens because $2K \gg W$ for $\delta$ bonds as a result of the weak overlap resulting from the parallel disposition of the $\delta$ orbitals. For example, in Mo$_2$Cl$_8^{4-}$, $2K/W \approx 4$.

Let us now return to the wave functions previously written for the four states and see what they tell us about the electron distribution in each state. If we take the state wave functions and substitute in the LCAO expressions for $\phi$ and $\chi$, we obtain the following results:

**Ionic**
\[
\psi_1 = [\gamma_1(1\sigma_1) + \gamma_2(1\sigma_2)] + [\gamma_1(1\sigma_2) + \gamma_2(1\sigma_1)] \\
\psi_2 = [\gamma_1(1\sigma_2) + \gamma_2(1\sigma_1)] \\
\psi_3 = [\gamma_1(1\sigma_1) + \gamma_2(1\sigma_2)] \\
\psi_4 = [\gamma_1(1\sigma_1) + \gamma_2(1\sigma_2)] - [\gamma_1(1\sigma_2) + \gamma_2(1\sigma_1)]
\]

**Covalent**
\[
\psi(1\Delta_{1g}) = \psi_1 - \lambda \psi_4 \\
\psi(1\Delta_{1g}^*) = \psi_4 + \lambda \psi_1
\]
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9a, where the four states are represented by broken lines, meant to represent everything that was, initially, predicted but not yet experimentally verified. This diagram is basically the same as what is shown in Figure 1 by the curves 2, 3, 5, and 6, which are the Coulson and Fischer results that take account of configuration interaction.

If we now refer back to the experimental results presented in Figure 6, it is easily seen that they can be used to transform Figure 9a to Figure 9b. That is, we can change two of the theoretical lines (broken) to experimental lines (solid). The $^1A_{1g}$ → $^1A_{2u}$ transition, commonly referred to as the $\delta$ → $\delta^*$ transition, does indeed start at a high value, 15 000–16 000 cm$^{-1}$ at $\chi$ = 0 and asymptotically approach a much lower value, ca. 12 000 cm$^{-1}$, as $\chi$ → 45°. The question remaining is, “How much further can we go in demonstrating experimentally that the entire picture in Figure 9a is correct?”

To convert all of the theoretical picture to experimental fact, it is necessary to measure two more independent energy separations. There are four choices: $^1A_{1g}$−$^3A_{2u}$, $^1A_{1g}$−$^3A_{1g}^*$, $^3A_{2u}$−$^1A_{2u}$, and $^3A_{2u}$−$^1A_{1g}$*. At first sight, none of these measurements appears easily feasible, but the last two look really hopeless. The difficulty with each of the first two is that the corresponding spectroscopic transitions are forbidden. The first is spin-forbidden and the second is forbidden because it is a two-electron transition. When the spin-forbiddenness of the $^1A_{1g}$ → $^3A_{2u}$ transition is added to the fact that even the spin-allowed $^3A_{2u}$ → $^1A_{2u}$ transition is weak, one cannot be too surprised that it has never been observed directly in any molecule. However, both of these forbiddenness problems have been overcome.

The first problem that was solved was the measurement of the $^1A_{1g}$−$^3A_{2u}$ energy difference. The method employed depends on the fact that the $^1A_{1g}$−$^3A_{2u}$ energy gap is small, especially as the bond is twisted and the $\delta$−$\delta$ overlap is lessened. When the torsion angle is in the range of 20°–40° (or, equivalently, 50°–70°), the gap is of the order of kT at and below room temperature. Therefore, there is enough thermal population of the $^3A_{2u}$ state, following a Boltzmann distribution, to cause a measurable change in the chemical shift of the $^{31}P$ resonance, without making the line too broad for accurate measurement. This NMR method was used for several of the Mo$_2$Cl$_4$(P−P) compounds to afford $^1A_{1g}$−$^3A_{2u}$ energy gaps for six compounds of the Mo$_2$Cl$_4$(P−P) type, with $\chi$ values of 24.7°, 41.4°, 50.0°, 59.5°, 64.5°, and 69.4°. These data define a line that is parallel, within experimental error, to the line for the $^1A_{2u}$ state. The $^1A_{2u}$−$^3A_{2u}$ separations are in the range 10 190–10 780 cm$^{-1}$, average 10 440 ± 180 cm$^{-1}$. Thus, we can add another solid line to Figure 9b so as to obtain Figure 9c.

We now have the problem of getting from Figure 9c to Figure 9d, that is, relating the energy of the $^1A_{1g}$* state to the energies of the other three states by experimental measurements. That task was addressed in the following way. We first observe that, although forbidden by one-photon selection rules, the $^1A_{1g}$ → $^1A_{1g}$* transition is allowed in the two-photon absorption spectrum. Here, two $\delta$ electrons are promoted to the $\delta^*$ level by the simultaneous absorption of two photons whose energies sum to the energy required for the transition. Because we can estimate the $^1A_{1g}$ → $^1A_{2u}$ transition energy from our knowledge of $^1A_{1g}$−$^1A_{2u}$, we recognize that the two exciting photons must be in the near-infrared frequency range. Moreover, the simultaneous absorption of two photons is an unlikely event, the probability of which increases with the square of the intensity of the absorbing light, so the flux of the exciting photons must be intense. These demanding conditions of intense and tunable near-infrared photons can be satisfied with the output from optical parametric oscillators. But providing the necessary laser excitation source constitutes only one half of the experimental problem. There is also the question of how one knows when $^1A_{1g}$ → $^1A_{1g}$* is occurring? The most obvious approach would be to measure the transmittance, but this is impractical for a two-photon experiment and especially so when the spin-allowed transitions are weak, as is the case within the $\delta$ manifold.

A more promising strategy is to monitor a fluorescence intensity that is dependent on the population of the $^1A_{1g}$* state. Although $^1A_{1g}$* is sure to be photon-silent, its neighboring $^3A_{2u}$ excited state may be emissive for selected quadruple bond metal complexes. Because the $^1A_{1g}$* → $^1A_{2u}$ conversion is fully allowed, $^1A_{1g}$* may internally convert to $^3A_{2u}$ on a much faster time scale than that associated with emissive decay from the $^3A_{2u}$ state. Therefore, as the two-photon laser excitation frequency is tuned into the $^1A_{1g}$* excited state, emission from $^3A_{2u}$ can be observed. Conversely, no $^3A_{2u}$-based luminescence will be generated when the two near-infrared photons are off resonance from the $^1A_{1g}$ → $^1A_{1g}$* transition. In this manner, the absorption profile of the $^1A_{1g}$* state can be mapped out (at twice the excitation frequency) by monitoring the laser-induced fluorescence (LIF) from the $^3A_{2u}$ excited state as the near-infrared spectral region is scanned.

On the basis of these considerations, the first experiment undertaken employed the LIF technique in a case.
where the response function of conventional detectors is
nescence should occur further into the near-infrared

Et2P(CH2)2PEt2, respectively) emit at sufficiently high

where the 1A1g excited state was found to lie 4800
cm⁻¹ above the 1A2u excited state. It will be noted immedi-
ately that this result agrees well with the energy gap

The reason for this is that steric factors lock in the
geometry so that, even though the δ bond is abolished in
the 1A2u state, the two states have essentially the same
structure. By monitoring the two-photon LIF from Mo2-
Cl4(PMe3)4, the 1A1g excited state was found to lie 4800

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FIGURE 10. Actual experimental state energies vs cos 2χ for the
M₃O₄X₄(P–P)₂ molecules. Data from refs 16, 19, 20, and 22.
The reason for this is that steric factors lock in the
geometry so that, even though the δ bond is abolished in
the 1A2u state, the two states have essentially the same
structure. By monitoring the two-photon LIF from Mo2-
Cl4(PMe3)4, the 1A1g excited state was found to lie 4800

as though they are completely isolated from all other electronic states in the
molecule. This is a reasonable but obviously imperfect approximation.23 We have also ignored the possible dif-
fferences between the two configurations with χ = 0°, namely that with the PR₃ groups eclipsed and that in
which they are staggered. Finally, we have not taken
account of small vibrational energy differences. For in-
stance, the NMR measurements of the 1A1g–3A2u energy
gaps involve molecules that are thermally equilibrated in
each state and thus provide true 0,0 transitions. On the
other hand, the method of measuring the 1A1g–1A1g gaps
provides vertical transition energies, where the 1A1g
molecules must be, to some extent, vibrationally excited.

Despite such caveats, of which we are well aware, a
beautiful picture, directly from experiment, of the manifold
of states as a function of bond strength for a two-electron
bond has been obtained for the first time. As stated at
the outset, the relationships inherent in the Coulson–
Fischer treatment of the hydrogen molecule were not in
any sense suspect, but for science to be science, theoreti-
cal predictions must be confirmed experimentally. What
has now been accomplished is to find a situation in which
the necessary experimental evidence is obtainable and to
obtain it, in full.

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5, 157. This excellent article deals in greater detail with several
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question of what happens when χ = 45° (exactly).

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