

## The delta bond—an old story with a new twist

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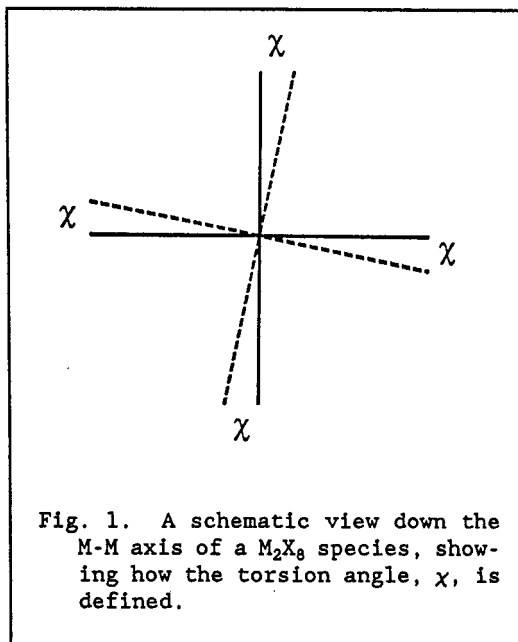
**Abstract.** The nature of the two electron  $\delta$ -bond is examined in detail, with attention to the four states that constitute the  $\delta$ -manifold, viz.,  $^1A_{1g}$  (ground state),  $^3A_{2u}$ ,  $^1A_{2u}$  and  $^1A_{1g}^*$ , in a species,  $M_2X_8^{n-}$ , with  $D_{4h}$  symmetry. The effects of increasing the M-M distance, twisting from  $D_{4h}$  through  $D_4$  to  $D_{4d}$ , and configuration interaction are then discussed. Experimental measurements of the  $^1A_{1g} - ^3A_{2u}$  separations in  $Mo_2Cl_4(P-P)_2$  complexes with twist angles between 17 and  $40^\circ$  as well as CASSCF calculations for the model system,  $Mo_2Cl_4(PH_3)_4$  are discussed. It is concluded that the  $\delta$ -bond energy is 12 (Exp.) - 17 (theor.) kcal mol $^{-1}$  and the rotational barrier is 24.5 kcal mol $^{-1}$ .

### INTRODUCTION

With the discovery of the quadruple bond in 1964 (ref. 1) the delta ( $\delta$ ) bond became for the first time a subject not only worthy of detailed theoretical attention but, more important, available for thorough and exacting experimental investigation.

Even in the abstract the concept of a delta bond is not old. Bonds between a pair of metal atoms can be classified according to the number of nodal planes that contain the internuclear axis:  $\sigma$  (no plane),  $\pi$  (one plane),  $\delta$  (two planes), and so on. The first two are so well known that even students in introductory chemistry courses are made aware of them. On the other hand, prior to 1964 references to  $\delta$  bonds were rare indeed. The earliest reference (so far as I have found) occurred in a paper by Craig, Maccoll, Nyholm, Orgel and Sutton (ref. 2), who stated as one of their main conclusions that " $\delta$ -bonding, between two atomic  $d_{xy}$ -orbitals, is unlikely to be of importance."

Not too long after this, Figgis and Martin (ref. 3) explicitly suggested that a very weak  $\delta$  interaction was likely to be responsible for the "anomalous" magnetic behavior (antiferromagnetic coupling) between the two copper(II) atoms in dicopper tetracetate. In 1965, Hansen and Ballhausen (ref. 4) included it in their treatment of the over-all electronic properties (spectrum and magnetism) of dicopper tetracetate. The Hansen and Ballhausen paper addressed for the first time in detail many of the essential features of the problem of  $\delta$  bonding as we have encountered it in our studies of quadruple bonds, even though they were dealing with what is, in certain respects, a quite different situation. The  $\delta$  interaction in  $Cu_2(O_2CCH_3)_4$ , with a metal-metal distance of ca. 2.6 Å is so weak that the lowest singlet and triplet states are

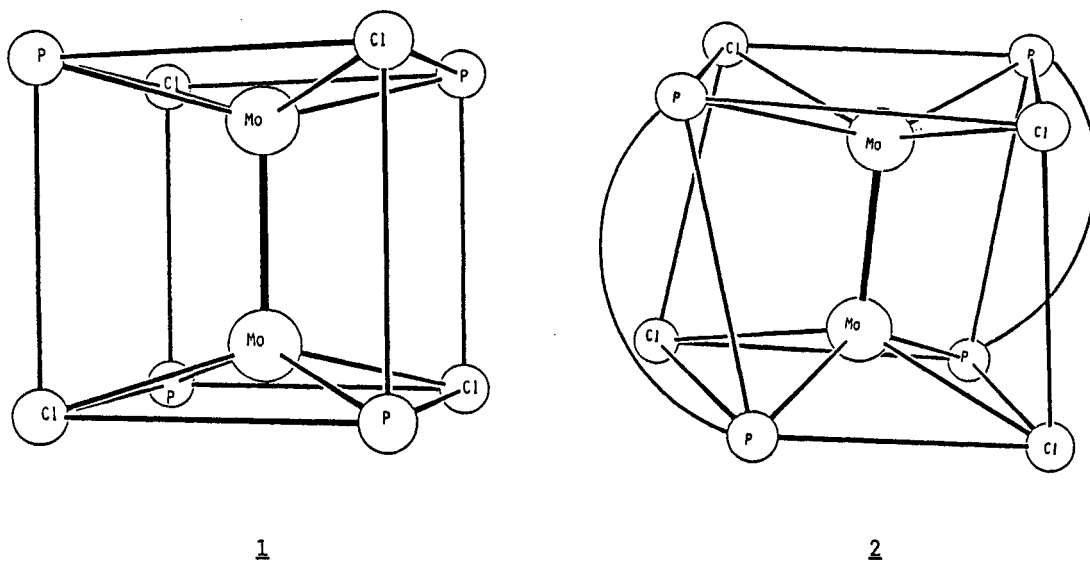


separated by only a few hundred wave numbers. In the quadruple bonds the  $\delta$  interaction is much stronger, though still, compared to most other bonds, weak.

Because, even at their strongest  $\delta$  bonds are still relatively weak, they cannot be easily understood by concepts usually employed for ordinary, strong electron pair bonds of the  $\sigma$  (or even  $\pi$ ) type. There is, however, an advantageous side of this weakness, namely, that it enables us to observe, in isolable molecules of permanent stability, the limiting behavior characteristic of other bonds only under the ephemeral conditions where they have been stretched close to their dissociative limits. This is attributable to another special feature of  $\delta$  bonds, namely, their angle-sensitivity and our ability to control the angle. This affords us another opportunity, by a means other than dissociation, to see how a bond behaves as it approaches extinction. This type of opportunity is in principle possible for a  $\pi$  bond, but practical means for "angle-tuning" such bonds over a wide range have not yet been found. (Note a)

The first subject of the remainder of this article will be a detailed description of the manifold of states arising from interaction of two atomic  $d\delta$  orbitals as a function of the angle of rotation of one relative to the other. The theoretical aspects will then be further examined and finally we shall make a comparison of theory with experimental data. The theoretical problem has been specifically addressed before, first by a treatment of the  $\delta$  bond in eclipsed  $[\text{Re}_2\text{Cl}_8]^{2-}$  in a pioneering study by Hay (ref. 5), and then in a calculation of the electronic states of this ion as a function of rotation angle by Smith and Goddard (ref. 6). Unfortunately, it is not for this system that experimental data on twisted molecules are available.

The compounds in which angle tuning of the  $\delta$  interaction has been studied experimentally are those of types 1 and 2, where P and P-P represent  $\text{PR}_3$  and



$\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ , and Br or I may be present in place of Cl. In 1 the torsion angle, that is, the angle defined in Fig. 1 is zero, while there are compounds of type 2 in which this angle varies from  $-0$  to ca.  $40^\circ$ . The following discussion is based primarily on several theoretical treatments (ref. 7, 8) and on experimental data published elsewhere (ref. 9, 10).

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Note a: It must be noted that  $\delta$  bonds decrease in strength proportionally to  $\cos 2\chi$  (See Fig. 1) whereas  $\pi$  bonds follow  $\cos \chi$ . Thus even a  $40^\circ$  twist in a  $\pi$  bond ( $\cos 40^\circ = 0.766$ ) covers less than a quarter of the total bond strength range. It appears that there is but one example of a twist as large as  $40^\circ$  in an olefin and that most of the "large twists" are only in the  $20$ - $30^\circ$  range. Cf. W. Leuf and R. Keese, Top. Stereochem. 20, 231 (1991).

## THE FULLY ECLIPSED DELTA BOND

For any two-center, homonuclear bond, whether  $\sigma$ ,  $\pi$  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 are

$$\begin{aligned}\phi &= 2^{-\frac{1}{2}}(\gamma_1 + \gamma_2) \\ \chi &= 2^{-\frac{1}{2}}(\gamma_1 - \gamma_2)\end{aligned}$$

3. The energies of these MOs are

$$\begin{aligned}E_\phi &= \frac{1}{2}\langle\phi|H_0|\phi\rangle = \int\gamma_1H\gamma_1dr + \int\gamma_2H\gamma_2dr \\ &\quad i = 1 \text{ or } 2 \\ &= E_\gamma + W \quad (W < 0)\end{aligned}$$

$$E_\chi = E_\gamma - W$$

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

$$E_\phi = W \text{ and } E_\chi = -W.$$

If there is only one electron to occupy these MOs, we have a very simple (and very familiar) picture, as shown in Fig. 2. There are only two states,  ${}^2A_g(\phi)$  and  ${}^2A_u(\chi)$ , and only one electronic transition, namely, that from the  ${}^2A_g$  ground state to the  ${}^2A_u$  excited state, whose energy is exactly  $2W$ .

There are, in fact, a number of real compounds that have only one  $\delta$  electron (or what is formally equivalent, three  $\delta$  electrons) and for these one can observe a spin-allowed  $\delta \rightarrow \delta^*$  transition, the energy of which provides a direct experimental measurement of the  $\delta$  bond energy. Examples are  $[\text{Mo}_2(\text{SO}_4)_4]^{3-}$ ,  $[\text{Tc}_2\text{Cl}_8]^{3-}$  and  $\text{Re}_2\text{Cl}_5(\text{PET}_3)_3$ . But let us return to the theoretical development and see what happens when there are two  $\delta$  electrons.

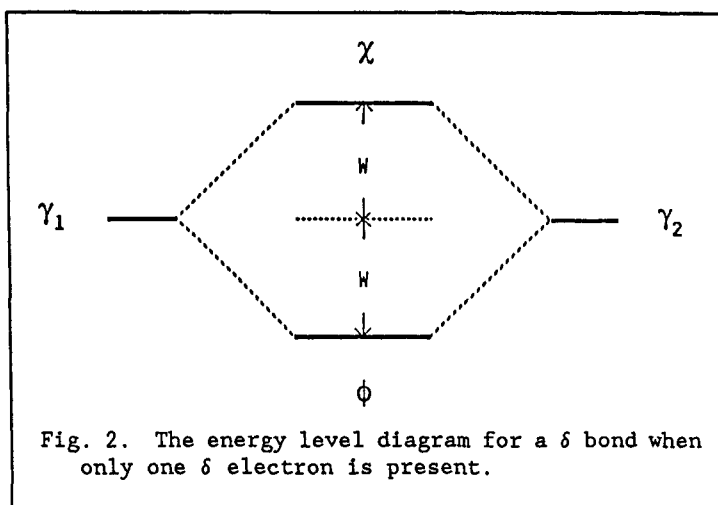


Fig. 2. The energy level diagram for a  $\delta$  bond when only one  $\delta$  electron is present.

4. We must now write determinantal wave functions for the four states that can arise (ref. 11). If both electrons occupy the  $\phi$  MO, to give a full  $\delta$  bond, we have (where this and other symmetry designations are for  $D_{4h}$ ):

$$\begin{aligned}\psi_1({}^1A_{1g}) &= |\bar{\phi}\bar{\phi}| = |\bar{\phi}(1)\bar{\phi}(1)| \\ &\quad |\bar{\phi}(2)\bar{\phi}(2)| \\ &= \bar{\phi}(1)\bar{\phi}(2) - \bar{\phi}(1)\bar{\phi}(2)\end{aligned}$$

After separating orbital and spin functions, using  $\alpha (= \frac{1}{2})$  and  $\beta (= -\frac{1}{2})$  for the latter, we obtain:

$$\psi_1({}^1A_{1g}) = \phi(1)\phi(2)[\alpha\beta - \beta\alpha]$$

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,  $\chi(1)\chi(2)[\alpha\beta - \beta\alpha]$ .

When we develop the corresponding expressions for the states arising from placing one electron in  $\phi$  and the other in  $\chi$ , we have two possibilities, because the Pauli

principle no longer restricts us to antisymmetrizing the wave function by way of the spins. That can be done, giving a singlet state,  ${}^1A_{2u}$ , 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  ${}^3A_{2u}$  state. Altogether, we have the following four states in what is called the  $\delta$  manifold:

$$\begin{aligned}\psi_1({}^1A_{1g}) &= \phi(1)\phi(2) [\alpha\beta - \beta\alpha] \\ \psi_2({}^3A_{2u}) &= 1/\sqrt{2} [\phi(1)\chi(2) - \phi(2)\chi(1)] \begin{cases} [\alpha\alpha] \\ [\beta\beta] \\ [\alpha\beta + \beta\alpha] \end{cases} \\ \psi_3({}^1A_{2u}) &= 1/\sqrt{2} [\phi(1)\chi(2) + \phi(2)\chi(1)] [\alpha\beta - \beta\alpha] \\ \psi_4({}^1A_{1g}^*) &= \chi(1)\chi(2) [\alpha\beta - \beta\alpha]\end{aligned}$$

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 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 may pause to note that most chemists would "intuitively" (whatever that means exactly) expect the following order of increasing energy

$$\psi_1 \ll \psi_2 \approx \psi_3 \ll \psi_4$$

on the grounds that  $\psi_1$  represents a net bond,  $\psi_2$  and  $\psi_3$  represent no net bond, and  $\psi_4$  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 many computational approaches that can be used. We have already alluded to calculations (refs. 5, 6) on  $[\text{Re}_2\text{Cl}_8]^{2-}$  by generalized valence bond (GVB) methods. Since these are, perhaps, not so transparent to most chemists as the LCAO-MO method we shall continue to develop our arguments by the latter method.

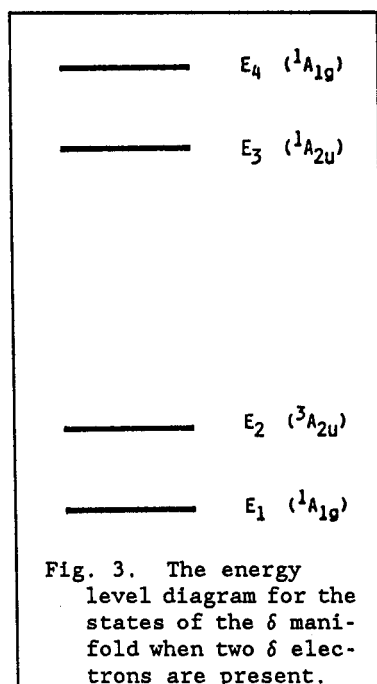
By methods that are explained in full algebraic detail in introductory texts (ref. 11) we may obtain the energies and it is convenient to express them in a way previously adopted by Hopkins, Gray and Miskowski (ref. 12)

For  $E_1$  and  $E_4$  we must obtain the roots of a quadratic equation, because  $\psi_1$  and  $\psi_4$  have the same symmetry and the true wave functions for the highest and lowest states of the  $\delta$  manifold are not  $\psi_1$  and  $\psi_4$  but, as we shall see in detail shortly, mixtures of both. For  $E_2$  and  $E_3$  we have simple, independent expressions. The entire set of results is:

$$\begin{aligned}\begin{vmatrix} W = J_{\phi\phi} - E_1 & K \\ K & -W + J_{\chi\chi} - E_4 \end{vmatrix} &= 0 \\ E_2 &= J_{\phi\chi} - K \\ E_3 &= J_{\phi\chi} + K\end{aligned}$$

In these equations  $\pm W$  has the same meaning as before, namely, it is the energy by which  $\phi$  or  $\chi$ , as a one-electron orbital, is lowered or raised, respectively, from their average value.  $J_{\phi\phi}$ ,  $J_{\chi\chi}$  and  $J_{\phi\chi}$  are Coulomb integrals, inherently positive, and representing the repulsive interaction between the charge clouds of two electrons that are either in the same orbital ( $J_{\phi\phi}$ ,  $J_{\chi\chi}$ ) or different orbitals ( $J_{\phi\chi}$ ). Finally we have  $K$ , the exchange integral, which is simply the energy required, for two atoms,  $X$ , infinitely far apart, to convert  $X^+ + X^-$  to  $X^- + X^+$ . When the atoms get closer together the value of  $K$  decreases somewhat because of repulsion between the electrons.

Simple though they are, these equations are still a little bit awkward, and it has been suggested (ref. 12) that since the overlap between two  $d\delta$  orbitals is always small, one may assume it to be zero, thus making  $J_{\phi\phi} = J_{\chi\chi} = J_{\phi\chi}$ . This, then allows us to omit the  $J$ 's altogether since they change each energy additively in the same direction. We can now draw the energy level diagram shown in Fig. 3.



It will be noted that here the relative energies of the four states follow the pattern  $E_1 < E_2 \ll E_3 < E_4$ , rather than the "intuitive" pattern mentioned earlier. This happens because  $2K \gg W$  for  $\delta$  bonds. For example, in  $\text{Mo}_2\text{Cl}_8^{4-}$ ,  $2K/W \approx 4$ .

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 (ref. 13). If we take the state wave functions and substitute in the LCAO expressions for  $\phi$  and  $\chi$ , we obtain the following results:

	Ionic	Covalent
$\psi_1 = [\gamma_1(1)\gamma_1(2) + \gamma_2(1)\gamma_2(2)] + [\gamma_1(1)\gamma_2(2) + \gamma_2(1)\gamma_1(2)]$		
$\psi_2 = [\gamma_1(1)\gamma_2(2) - \gamma_2(1)\gamma_1(2)]$		
$\psi_3 = [\gamma_1(1)\gamma_1(2) - \gamma_2(1)\gamma_2(2)]$		
$\psi_4 = [\gamma_1(1)\gamma_1(2) + \gamma_2(1)\gamma_2(2)] - [\gamma_1(1)\gamma_2(2) + \gamma_2(1)\gamma_1(2)]$		

We see that  $\psi_2$  and  $\psi_3$  which are the actual wave functions (so long as we treat the  $\delta$  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  ${}^1A_{1g}$  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  ${}^1A_{1g}^*$  state, while the  ${}^1A_{1g}$  ground state should be mainly covalent. This is, in fact, exactly what occurs, and the wave functions  $\psi_1$  and  $\psi_4$  are not really the orbital wave functions for the  ${}^1A_{1g}$  and  ${}^1A_{1g}^*$  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

$$\begin{aligned}\psi({}^1A_{1g}) &= \psi_1 + \lambda\psi_4 \\ \psi({}^1A_{1g}^*) &= \psi_4 + \lambda\psi_1\end{aligned}$$

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

### STRETCHING THE $\delta$ BOND

Like any other bond, the  $\delta$  bond will weaken if stretched and eventually cease to exist if stretched far enough. The  $\delta$  bond is, as we have already noted, already rather weak, even at its best, but nonetheless, its behavior on stretching should not be (and is not) different from that of any other bond. The general problem, as embodied by the particular case of the bond in  $\text{H}_2$ , was solved by Coulson and Fischer (ref. 14) a long time ago. The exchange integral  $K$  will change its value somewhat, but it does not vanish, while the  $J_{\phi\phi}$ ,  $J_{\chi\chi}$  and  $J_{\phi\chi}$  integrals become truly (not as an approximation) equal, as the internuclear distance goes to infinity. Therefore, the energy expressions become

$$\begin{aligned}E_1 = E_2 &= -K \\ E_3 = E_4 &= +K\end{aligned}$$

A diagram expressing these results is shown in Fig. 4 adapted from one by Hopkins, Gray

and Miskowski (ref. 12). It is simply a different way of drawing Fig. 3 of Coulson and Fischer's paper which pertained to the dissociating  $H_2$  molecule. It will be recalled that the  $^3A_{2u}$  state was previously shown to be a totally covalent state and the  $^1A_{1g}$  now also, in the limit, becomes totally covalent. Conversely, the two upper states become equi-energetic and totally ionic.

It should be noted that the limiting behavior of the  $\delta$  bond as it is stretched has exceptional simplicity. All the approximations that have been made cease to trouble us when we reach the dissociation limit. At the limit, the picture in Fig. 4 is completely correct, because it deals with a very simple system - two non-interacting atoms! Along the way, however, we do not have a completely correct picture. The mirror symmetry of the upper and lower parts of Fig. 4 is an idealization, not reality. We have already confessed to one approximation, that of setting all Coulomb integrals equal. They must differ and this alone will destroy the symmetry of the diagram. In addition, we are treating the  $\delta$  manifold as an isolated system. In dealing with real quadruple bonds, we must also take into account the effects of configuration interaction involving all states of the molecule, not just the two  $A_{1g}$  states in the  $\delta$  manifold. At a minimum, we should at least consider the  $\delta$  manifold as it is embedded in the entire manifold of states arising from all of the orbitals and electrons that make up the entire quadruple bond.

There are published results that enable us to see how important these additional configuration interactions may be. For the  $Mo_2(O_2CH)_4$  molecule (ref. 15) the ground state is made up of 67%  $\sigma^2\pi^4\delta^2$  and 15%  $\sigma^2\pi^4\delta^{*2}$ . Of the missing 18%, half comes from  $\sigma^2\pi^2\delta^2\pi^{*2}$  (6%) and  $\pi^4\delta^2\sigma^{*2}$  (3%), but then a large number of configurations altogether provide the remaining 9%. In the case of  $[Re_2Cl_8]^{2-}$ , the following results were obtained (ref. 5) for each of the four states in the  $\delta$  manifold.

State	Leading Conf. and %	% of Other Configurations		
		$\delta$ Manif.	d Manif.	Other
$^1A_{1g}$	$\sigma^2\pi^4\delta^2$ , 62	21	3	14
$^3A_{2u}$	$\sigma^2\pi^4\delta\delta^*$ , 85	--	3	12
$^1A_{2u}$	$\sigma^2\pi^4\delta\delta^*$ , 72	--	19	8
$^1A_{1g}^*$	$\sigma^2\pi^4\delta^{*2}$ , 50	20	17	13

These two sets of results give a general idea of how far we can trust various levels of approximation relating to calculations on the  $\delta$  bond. Those that deal only with the  $\delta$  manifold are capturing only 70-85% of the picture and even those that treat the  $\delta$  bond within the entire d manifold (that is, all components of the quadruple bond) miss 8-14% of the complete picture. At however high a level of approximation we employ, a picture of how the  $\delta$  bond behaves on being stretched to extinction suffers from being divorced from reality. We cannot experimentally measure the properties of a  $\delta$  manifold as the internuclear distances increases toward the dissociation limit. We therefore

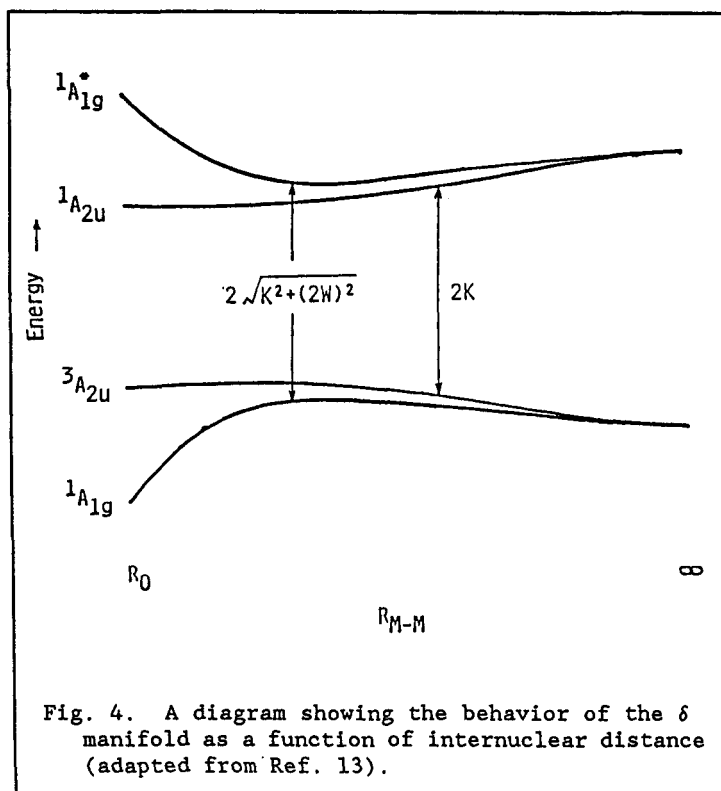


Fig. 4. A diagram showing the behavior of the  $\delta$  manifold as a function of internuclear distance (adapted from Ref. 13).

began looking, several years ago, for some realistic way to really manipulate or tune the strength of the  $\delta$  bond.

### TWISTING THE $\delta$ BOND

It has been found (ref. 10) that we can, by doing chemistry, create a series of compounds in which the torsional angle (Fig. 1) is changed in fairly small increments between eclipsed and staggered while practically nothing else is changed. Actually, we can adjust the angle to be in the range  $45^\circ < \chi \leq 90^\circ$  as well, a point of particular interest with respect to the optical rotatory dispersion (ref. 16) of the  ${}^1A_{1g} \rightarrow {}^1A_{2u}$  transition, but a subject we shall not deal with here.

We may reasonably expect that to some appreciable degree, the changes in the four states of the  $\delta$  manifold as the  $\delta$  bond is weakened by twisting will resemble those that result when it is weakened by stretching, but it is also evident that there will be some differences. A very obvious difference is that while it is rigorously true that when the  $\delta$  bond is annihilated by stretching it, the two lower and the two upper states will converge as shown in Fig. 4, this need not be - and is unlikely a priori to be - the case when the bond is annihilated by twisting it. Therefore, rather than simply assuming (as has been done (ref. 12)) that the latter situation can serve as a reasonable model for the former, let us look explicitly at what should happen when the bond is twisted.

### CHARACTERISTICS OF THE $\delta$ BOND

Three qualitative characteristics of quadruple bonds that have been well established for a long time (ref. 13) are:

- (1) There is an inherent barrier to rotation that arises from the  $\delta$  component and favors the eclipsed conformation ( $\chi = 0$ ).
- (2) The contribution of the  $\delta$  component of the quadruple bond to its overall strength (ca. 350 kJ mol<sup>-1</sup>) is a minor one, probably about 10%.
- (3) The overlap between the two  $d\delta$  orbitals and hence the strength of the  $\delta$  bond will be a function of  $\cos 2\chi$ . Thus from a maximum at  $\chi = 0$ , the strength will decrease, slowly at first, until it become zero at  $\chi = 45^\circ$ .

There is no doubt that point (1) is correct, but practical questions arise concerning the relationship of the total (or net) barrier to rotation in any given case to the contribution made by the electronic properties of the  $\delta$  bond, and as to how either one, or both, of these quantities can be measured experimentally.

With regard to points (1) and (2) jointly, there is some lack of precision in the literature as to what the relationship is between the electronic component of the rotation barrier and the  $\delta$  bond strength. Are they the same thing? If not, how do they differ?

As an  $M_2X_8^{n-}$  species is twisted from the eclipsed configuration ( $\chi = 0$ ) the symmetry changes from  $D_{4h}$  to  $D_4$  and then becomes  $D_{4d}$ . Throughout the range of intermediate configurations, the two  $d\delta$  atomic orbitals continue to interact to form bonding and antibonding MOs, but at the  $45^\circ$  limit their overlap becomes zero and they become rigorously degenerate, forming a basis for the  $E_2$  representation of the  $D_{4d}$  point group. Nevertheless, straightforward analysis shows that the  $e_2^2$  configuration gives rise to four separate states,  ${}^1B_1$  and  ${}^3A_2$  that are covalent and  ${}^1A_1$  and  ${}^1B_2$  that are ionic. These may be correlated with the intermediate ( $D_4$ ) states, which in turn correlate to the  $D_{4h}$  states, as shown in Fig. 5.

A formal analysis (refs. 7, 8) of the behavior of the four states of the  $\delta$  manifold, along the same lines as those used above for the untwisted ( $D_{4h}$ ) case, leads, as shown in Fig. 5, to the conclusion that the triplet state will be below the singlet state at  $45^\circ$  ( $D_{4d}$ ). From this it would be concluded that internal rotation about the M-M bond in an  $M_2X_8^{n-}$  species from one  $D_{4h}$  minimum to another, would require passage through an intermediate range of angles, surrounding  $45^\circ$ , where the species is in a triplet state. As we shall see later, this is incorrect.

The actual compounds employed for measurements of the relative energies of the three

lowest states as a function of  $\chi$  are of lower symmetry. As a result of four X ligands being substituted by  $\text{PR}_3$  ligands, the symmetries corresponding to  $D_{4h}$ ,  $D_4$  and  $D_{4d}$  are, respectively,  $D_{2h}$ ,  $D_2$  and  $D_{2d}$ . This does not affect any essential feature of the analysis and the final result (ref. 8) is still the same: the ground state at  $45^\circ$  is predicted to be a triplet state when the behavior of the  $\delta$  manifold is considered in isolation.

### DEFINITIONS OF $\delta$ -BOND ENERGY, $\delta$ -BARRIER AND ROTATIONAL BARRIER

Before numerical values for pertinent parameters can be considered and compared, the parameters must be defined. Let us begin with Fig. 6, where  $\delta$ -bond energy and  $\delta$ -barrier are defined. The definition of the  $\delta$ -bond energy seems obvious: it is the least costly way to annul the  $\delta$ -bond within the fixed molecular geometry. The  $\delta$ -barrier corresponds to the least rise in energy that is sufficient to allow transit from one minimum to the next, assuming that the energy of the triplet state is constant. If we focus only on the  $\delta$ -manifold, this should be true.

The  $\delta$ -bond energy could, perhaps, have been taken as equal to the  $\delta$ -barrier, and some authors have explicitly (or, apparently, implicitly) done this. We prefer, however, to do as Smith and Goddard (ref. 6) have done, and call the  ${}^1A_{1g} - {}^3A_{2u}$  energy difference at  $\chi = 0$  the  $\delta$ -bond energy. This seems justified since it is the rise in energy when we simply change from the spin-paired ground state to the nearest state in which the spins are parallel.

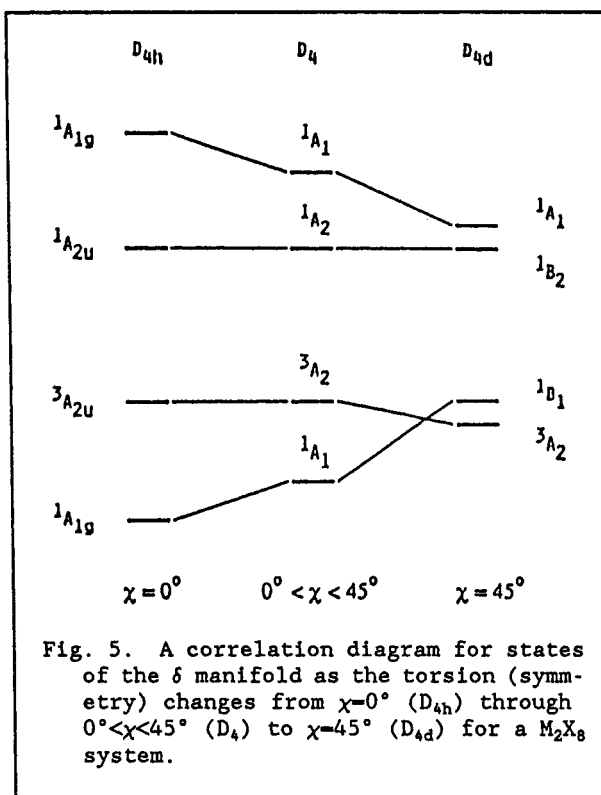


Fig. 5. A correlation diagram for states of the  $\delta$  manifold as the torsion (symmetry) changes from  $\chi = 0^\circ$  ( $D_{4h}$ ) through  $0^\circ < \chi < 45^\circ$  ( $D_4$ ) to  $\chi = 45^\circ$  ( $D_{4d}$ ) for a  $M_2X_8$  system.

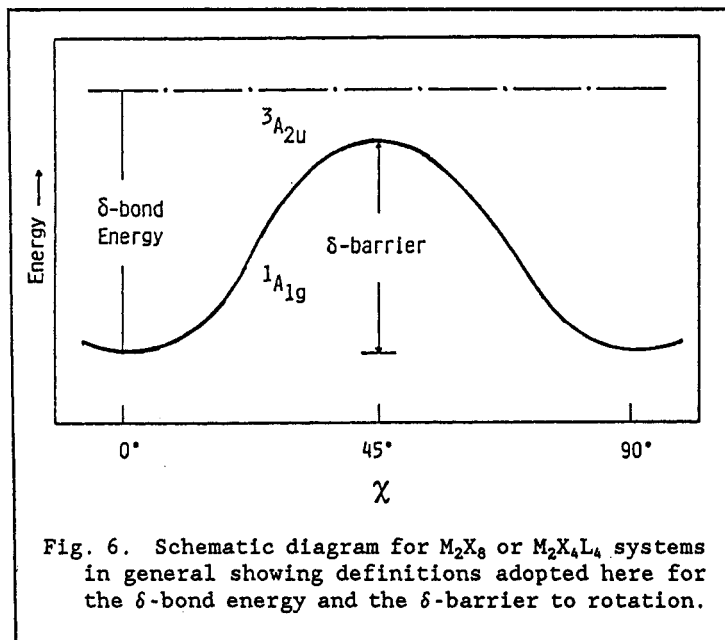


Fig. 6. Schematic diagram for  $M_2X_8$  or  $M_2X_4L_4$  systems in general showing definitions adopted here for the  $\delta$ -bond energy and the  $\delta$ -barrier to rotation.

The  $\delta$ -barrier is not, of course, the barrier for the actual, physical process of internal rotation, which we shall call the rotational barrier. The actual rotational barrier must include the  $\delta$ -barrier, but other contributions, for example interactions between non-bonded atoms, will also contribute. Whether the rotational barrier will be higher or lower than the  $\delta$ -barrier depends on specific factors in each case and no generalization would be justified. There is only one type of molecule for which experimental measurement of rotational barriers has been carried out, namely, the (porph)MM(porph) molecules (ref. 17) with  $M = \text{Mo, W}$ , and porphyrins substituted so as



to allow NMR measurements of the rotational process.  $\Delta G$  values of 11-13 kcal mol<sup>-1</sup> were obtained.

### THEORETICAL ESTIMATION OF $\delta$ -BOND STRENGTH AND $\delta$ -BARRIER IN REAL MOLECULES

One approach to determining the  $\delta$  contributions to bond strength and to the rotational barrier (which we shall henceforth simply call the  $\delta$ -barrier) is to calculate them. Two attempts have been made to do this. The first calculation, by Smith and Goddard (ref. 6) was done for  $[\text{Re}_2\text{Cl}_8]^{2-}$ . Their results, (Fig. 7) show several features of special interest. First, in contrast to the bond stretching process, rotation to 45° does not cause the  $^1A_{1g}$  and  $^3A_{2u}$  states to become degenerate, and in contrast to the

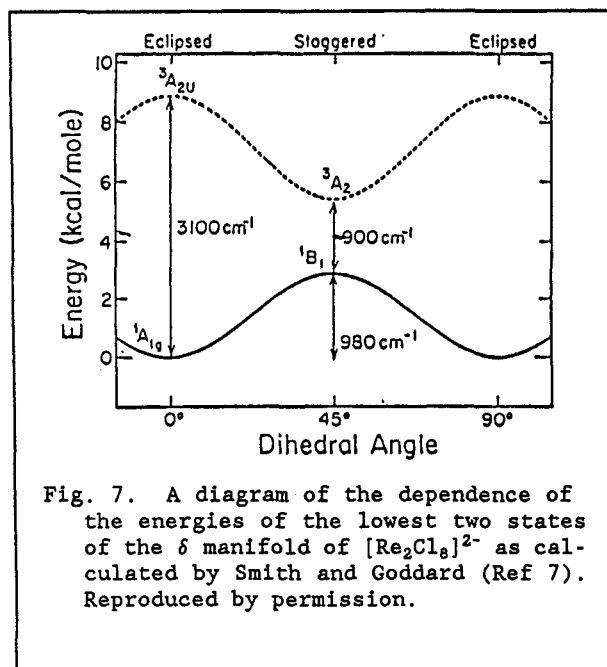


Fig. 7. A diagram of the dependence of the energies of the lowest two states of the  $\delta$  manifold of  $[\text{Re}_2\text{Cl}_8]^{2-}$  as calculated by Smith and Goddard (Ref 7). Reproduced by permission.

prediction from the isolated  $\delta$  manifold analysis, the lowest triplet state never becomes the ground state. Instead, a 900 cm<sup>-1</sup> gap remains. Thus, it is clear that the molecule can undergo internal rotation without passing into a triplet state. Second, the rotational barrier, as indicated by Fig. 7, is 980 cm<sup>-1</sup> or 2.8 kcal mol<sup>-1</sup>. This low value is the result of having a rather high  $\delta$ -barrier, 3100-900 = 2200 cm<sup>-1</sup>, about 6.3 kcal mol<sup>-1</sup> partially offset by a loss of repulsive energy, 3100-980-900 = 1,220 cm<sup>-1</sup> (ca. 3.5 kcal mol<sup>-1</sup>) between the two sets of four chlorine atoms, which repel each other less in the staggered than in the eclipsed confirmation. Unfortunately, there has been no experimental test of these results, nor is it evident how such a test could be carried out. There is, in principle a possibility of checking the calculated  $^1A_{1g}$ - $^3A_{2u}$  separation in the eclipsed ion by observing this spin-forbidden transition, but no one has as yet succeeded in doing this for  $\text{Re}_2\text{Cl}_8^{2-}$  or for any analogous case.

There is no apparent way to obtain such information at any other angle of rotation.

There is one other ambiguity about the calculations on  $[\text{Re}_2\text{Cl}_8]^{2-}$  or any other system from the third transition series, namely, the effect of spin-orbit coupling. This must give rise to a zero-field splitting of the  $^3A_{2u}$  state into a non-magnetic state ( $m_s = 0$ ) and a Kramers doublet ( $m_s = \pm 1$ ). With the large magnitude of the spin-orbit coupling that is expected for the rhenium atom, or any other atom from the third transition series, this splitting could be  $\geq 1000$  cm<sup>-1</sup>. Since the magnitude of this splitting is as large or larger than the calculated  $^1A_{1g}$  -  $^3A_{2u}$  separation, it is not clear what the true picture at  $\chi = 45^\circ$  would really be.

Because it is for  $\text{Mo}_2\text{X}_4\text{P}_4$  and  $\text{Mo}_2\text{X}_4(\text{P-P})_2$  type molecules that the experimental data to be discussed in the next section are available, it is desirable to have theoretical results specifically for them. These molybdenum systems are also attractive subjects because spin-orbit splitting of the  $^3A_{2u}$  state should be relatively small (perhaps 200-300 cm<sup>-1</sup>). Calculations have been made (ref. 8) (Note b) for a  $\text{Mo}_2\text{Cl}_4(\text{PH}_3)_4$  model system, at both  $\chi = 0^\circ$  and  $\chi = 45^\circ$ , by employing an *ab initio* method (CASSCF) that includes as "active configuration space" the full quadruple bond manifold. This gave about 500 configurations for each state.

This calculation gives a totally symmetric, singlet ground state at both ends of the

Note b: The eclipsed molecule for which the calculation was done was the one with  $D_{2d}$  symmetry (type 1). There is no reason to believe the energies of states within the  $\delta$  manifold will be significantly different for this eclipsed molecule as compared to the one with  $D_{2h}$  symmetry.

range of  $\chi$  (i.e.,  $\chi = 0^\circ$  and  $\chi = 45^\circ$ ) with  ${}^1A_{1g} - {}^3A_{2u}$  separations of  $5890\text{ cm}^{-1}$  at  $0^\circ$  and  $1650\text{ cm}^{-1}$  at  $45^\circ$ . There is very pleasing qualitative and even semiquantitative similarity to the results summarized above for  $[\text{Re}_2\text{Cl}_8]^{2-}$ . The results of this calculation, shown on the left side of Fig. 8, allow us to predict the  $\delta$ -bond strength ( $5890\text{ cm}^{-1} = 16.8\text{ kcal mol}^{-1}$ ), the  $\delta$ -barrier ( $5890 - 1650 = 4240\text{ cm}^{-1} = 12.1\text{ kcal mol}^{-1}$ ), and the rotation barrier. The latter is the difference between the calculated energies of the  $D_{2d}$  eclipsed state with which we begin at the left and the energy of the molecule with  $\chi = 45^\circ$ . For a molecule of the type we are dealing with, this diagram will not have the mirror symmetry expected for the  $M_2X_8$  type molecule. Instead, on the  $D_{2h}$  side (which has not yet been calculated) we expect the energies of the two lowest states,  ${}^1A_g$  and  ${}^3B_{1u}$ , to be higher than on the  $D_{2d}$  side, because the  $D_{2h}$  isomer is the less stable one. What we do expect however, (and experimental measurements of singlet-triplet energy separations described below confirm this) is that the  ${}^1A_g - {}^3B_{1u}$  energy difference will be about the same in both eclipsed isomers. To put it another way, the  $\text{Mo}_2\text{X}_4\text{P}_4$  and  $\text{Mo}_2\text{X}_4(\text{P-P})_2$  molecules will give a virtually symmetrical diagram of the type shown in Fig. 6, even though the two minima do not correspond to identical structures.

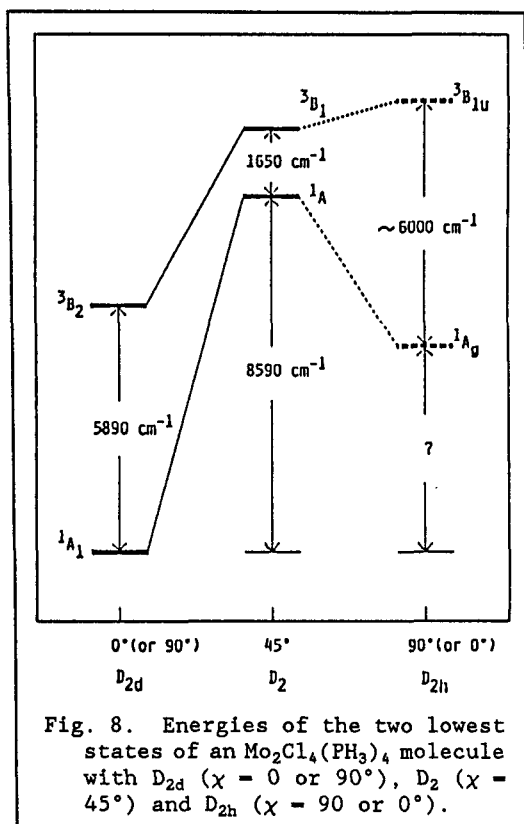


Fig. 8. Energies of the two lowest states of an  $\text{Mo}_2\text{Cl}_4(\text{PH}_3)_4$  molecule with  $D_{2d}$  ( $\chi = 0$  or  $90^\circ$ ),  $D_2$  ( $\chi = 45^\circ$ ) and  $D_{2h}$  ( $\chi = 90$  or  $0^\circ$ ).

#### EXPERIMENTAL DATA DEFINING THE $\delta$ -MANIFOLD AS A FUNCTION OF TWIST ANGLE $\chi$

Three energy separations are required to define the relative energies of the four states in the  $\delta$ -manifold. One of these is readily measurable, namely, the  ${}^1A_{1g} - {}^1A_{2u}$  separation. This corresponds to the energy of the allowed " $\delta \rightarrow \delta^*$ " transition that is characteristically observed in the visible or near infrared spectra of quadruply-bonded species. More precisely it corresponds to the energy of the  $\nu = 0$  to  $\nu' = 0$  vibrational component of that transition.

Another of these energy differences has never been measured for any quadruply bonded species and may never be, namely, the  ${}^1A_{1g} - {}^1A_{1g}^*$  separation.

This two-electron transition, which should occur several thousand wave numbers higher than the  ${}^1A_{1g} \rightarrow {}^1A_{2u}$  transition should be so weak that it will not be detectable, especially in the presence of other, stronger transitions that are expected in the same spectral region. There is no evident non-spectroscopic method that could provide an experimental measurement of this energy.

Finally, we have the  ${}^1A_{1g} - {}^3A_{2u}$  energy separation. The orbitally allowed but spin-forbidden  ${}^1A_{1g} \rightarrow {}^3A_{2u}$  transition might in some cases at least, be barely observable, but in fact, there is not yet any credible observation of this kind. However, there is another experimental avenue to evaluate this energy difference, at least in those cases where it is comparable to  $kT$ . The paramagnetism of the  ${}^3A_{2u}$  state will contribute to the magnetic susceptibility, and if the latter is measured over a temperature range, the energy difference that governs the Boltzmann population of the  ${}^3A_{2u}$  state can be determined. There is, however, only one reported case where this has actually been undertaken, and only a crude result was obtained (ref. 18)

There is another way to measure the  ${}^1A_{2g} - {}^3A_{2u}$  separation and that is by means of NMR measurements. Again, this is applicable only when the energy is comparable to  $kT$ . By measuring the temperature dependence of the chemical shift of some type of atom in one of the ligands attached to the quadruply-bonded  $M_2^{n+}$  unit, and fitting the results with the pertinent equation containing the  ${}^1A_{1g} - {}^3A_{2u}$  energy difference parametrically, the value of this energy difference can be obtained - with considerable accuracy in favorable cases (ref. 9). This type of study using the  ${}^{31}\text{P}$  signal has been carried out for a group of five  $\text{Mo}_2\text{Cl}_4(\text{P-P})_2$  compounds with torsion angles ranging from  $17^\circ$  to  $40^\circ$ .

Previously, the energies of the  ${}^1A_{1g} \rightarrow {}^1A_{2u}$  transitions had been measured for the same (as well as several other) compounds (ref. 10). These two sets of results may be combined to produce the diagram shown in Fig. 9. Here we see behavior that is very much what theory, for both  $[\text{Re}_2\text{Cl}_8]^{2-}$  and the  $\text{Mo}_2\text{X}_4\text{P}_4$  systems themselves, had led us to expect. In fact, the numerical values given by the *ab initio* calculations for the molybdenum system are in remarkably good agreement with the experimental values.

By applying the previously given definitions for  $\delta$ -bond energy,  $\delta$ -barrier and rotational barrier, we obtain the following values for these quantities:

$\delta$ -bond energy:  $4200 \text{ cm}^{-1} = 12.0 \text{ kcal mol}^{-1}$  (theor.,  $16.8 \text{ kcal mol}^{-1}$ )

$\delta$ -barrier:  $3470 \text{ cm}^{-1} = 9.9 \text{ kcal mol}^{-1}$  (theor.,  $12.1 \text{ kcal mol}^{-1}$ )

Rotation barrier:  $8590 \text{ cm}^{-1} = 24.5 \text{ kcal mol}^{-1}$

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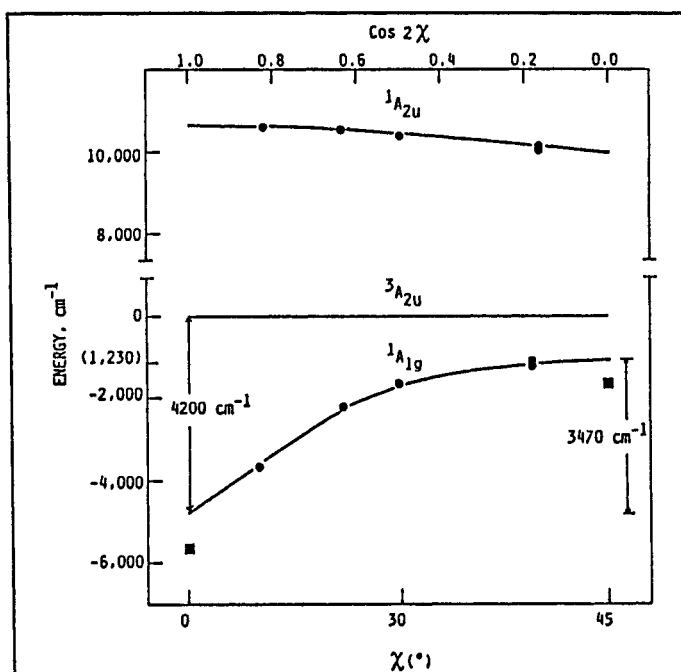


Fig. 9. The experimental results (●) for the relative energies of the lower three states of the  $\delta$  manifold in a series of  $\text{Mo}_2\text{Cl}_4(\text{P-P})_2$  type compounds with different torsion angles. Shown also (■) are the points calculated by the *ab initio* CASSCF method for  $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$  type complexes.