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On the Dissociation and Reactivity of Hydrogen at Low-Coordination Transition-Metal Sites

by

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The electronic structure of "coordinatively unsaturated" transition-metal complexes, in conjunction with the concept of orbital electronegativity, suggests how such complexes, along with low-coordination sites on transition-metal clusters and surfaces, can act as centers for the dissociation and reactivity of H_2.

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It is well known that certain "coordinatively unsaturated" transition-metal complexes in solution can homogeneously catalyze chemical reactions,[1] while it has long been suspected that low-coordination sites on transition-metal surfaces and supported transition-metal clusters are centers of heterogeneous reactivity.[2,3] In this communication, we wish to show that the electronic structure of such complexes, in conjunction with the concept of orbital electronegativity,[4,5] is consistent with their reactivity and is suggestive of how low-coordination sites on transition-metal surfaces can act as centers of reactivity. The dissociation and reactivity of H_2 is considered as an illustrative example.

As our working model, we have chosen a Group-VIII transition-metal atom (M) dihedrally coordinated by ligands (L), yielding the coordinatively unsaturated L_2M complex illustrated at the top of Fig. 1. This model has the advantage that it can realistically represent transition-metal complexes of the type (e.g., M = Pt, Ir, Rh; L = Ph_3P = triphenylphosphine) which dissociatively bind and homogeneously catalyze reactions of H_2,[1] and it can simulate low-coordination sites (e.g., "corner atoms") of faceted transition-metal clusters or stepped transition-metal surfaces which dissociatively chemisorb and heterogeneously catalyze reactions of H_2.[2,3] In the latter systems, the ligand (L) is also a metal atom, either of the same species as the transition metal (M), or of a different species in the case of an alloy surface or bimetallic cluster.

Molecular-orbital calculations have been carried out for L_2M and L_2MH_2 complexes by the self-consistent-field X-alpha (SCF-Xα) method[6] as a function of metal species (M = Pt, Ir), ligand species (L = phosphine, Pt), and molecular geometry. The resulting orbital energies for M = Pt, L = phosphine, and geometry characteristic of the platinum-phosphine complexes described in

Ref. 1 are shown in Fig. 1. Also shown, for comparison, are the SCF-Xα orbital energies for the isolated metal, ligand, and hydrogen molecule at the free-molecule internuclear distance 1.4 Å (H_2) and internuclear distance 2.8 Å (H_2*) characteristic of the partially dissociated ("dihydride") configuration of H_2 in the L_2MH_2 complex.

The SCF-Xα orbital energy eigenvalues shown in Fig. 1 can be rigorously identified with "orbital electronegativities" which are a measure of the relative average electron donor-acceptor character of the individual orbitals.[4,5] Thus the fact that the isolated ligand energy level, which corresponds to a phosphine "lone-pair" orbital, nearly coincides with the d-orbital energy level of the isolated Pt atom (neglecting relativistic shifts) implies a predominantly covalent L-Pt(5d) interaction similar to that expected for a direct Pt(5d)-Pt(5d) interaction. In this respect, the effect of coordinatively unsaturated phosphine ligands on the electronic structure of a platinum atom is expected to be similar to that of embedding a Pt atom in a low-coordination Pt environment, such as that provided by a surface or cluster.

The ligand-metal interaction in the L_2M complex leads to the bonding orbital energies labeled L-M(d_{yz}) and L-M(d_{z^2}) in Fig. 1, and to the antibonding orbital energies labeled M(d_{z^2})-L*, M(d_{yz})-L*, and M(s)-L*, of which M(d_{yz})-L* is the highest occupied energy level in the ground state of the complex. A simple interpretation of the position of the latter energy level is that the strong ligand-field repulsion of the metal d-orbital pointed on the ligand directions (the d_{yz} orbital for the chosen coordinate system) raises the energy level of this orbital, reduces the corresponding orbital electronegativity, and mixes in significant antibonding ligand character. The d_{z^2} orbital is also subject to some antibonding ligand-field repulsion, whereas the $d_{x^2-y^2}$, d_{xz}, and d_{xy} orbitals remain essentially nonbonding. When platinum atoms are substituted for the phosphine ligands, the electronic structure reduces to the manifold of bonding, nonbonding, and antibonding d-orbital energy levels (the "d-band") characteristic of a small platinum cluster.[7] In this case, the $M(d_{yz})$-L* (L = M) antibonding orbital may be interpreted as the analogue of a localized "surface state" which is split off from the top of the d-band.

The most important result of the strong ligand-metal antibonding component is to bring the $M(d_{yz})$-L* orbital, the highest occupied orbital, closer in energy and electronegativity (as compared with the isolated Pt atom) to the empty antibonding σ_u orbital of the H_2 molecule. This facilitates overlap and electron flow between the $M(d_{yz})$-L* and σ_u orbitals, which are symmetry conserving,[8] thereby promoting dissociation of H_2. The partially dissociated molecule (H_2*), characterized by σ_g and σ_u orbital energies approaching the SCF-Xα 1s orbital energy of a free hydrogen atom (see Fig. 1),[9] can bind or "chemisorb" in a dihydride configuration to the coordinatively unsaturated metal site. This is revealed by the L_2MH_2 molecular-orbital energies shown in Fig. 1 and the corresponding orbital wavefunction contour maps shown in Fig. 2. The $2b_2$ orbital, for example, results from overlap and electron flow between the $M(d_{yz})$-L* orbital and the H_2 σ_u orbital. The dihydride configuration is further stabilized by the "butterfly-like" $1a_1$ and $2a_1$ orbitals shown in Fig. 2, formed from the overlap of the equatorial parts of the L-$M(d_{z^2})$ and $M(d_{z^2})$-L* orbitals with the H(1s) (or H_2* σ_g) orbitals. Note that the $M(d_{z^2})$ lobe pointed along the z-direction acts as a repulsive barrier which helps to keep the H atoms apart. These dihydride bonding orbitals are offset somewhat by the $4a_1$ and $3a_1$ orbitals resulting respectively from the antibonding interaction of the L-$M(d_{z^2})$ and $M(d_{x^2-y^2})$ orbitals with the H_2* σ_g orbital, as is evident in the $4a_1$ orbital contour map shown in Fig. 2. There is negligible contribution of the M(s) orbital component in the binding of hydrogen to these platinum and iridium complexes. This is consistent with the finding, based on SCF-Xα cluster calculations[10] and photoemission studies[11] that the metal d-orbitals are almost exclusively responsible for the chemisorption of hydrogen on second- and third-row transition metals such as palladium and platinum, whereas significant metal s,d-hybridization (with the s-orbital component dominant) is involved in hydrogen chemisorption on first-row transition metals such as nickel. Since the deuterium molecule (D_2) is chemically identical to the hydrogen molecule (H_2), all the results described above for the dissociation of H_2 at a low-coordination transition-metal site apply equally well for the dissociation of D_2 at such a site.

The above described electronic structure of the L_2MH_2 (or L_2MD_2) coordination complex leads to possible explanations of the observed homogeneous and heterogeneous catalytic reactivity of H_2 (or D_2). For example, the near cancellation of the contributions of the bonding ($1a_1$, $2a_1$) orbitals and antibonding ($3a_1$, $4a_1$) orbitals to metal-hydrogen bond strength, leaving the dissociative $2b_2$ bonding orbital dominant, explains the relatively weak, reversible binding of H_2 (or D_2) to such complexes and their ability to activate H_2-D_2 exchange.[1] Since such a complex is also a good model for H_2 (or D_2) dissociation at the corner atoms of a platinum surface step, the results suggest why atomic steps on platinum surfaces are essential in dissociating H_2 and D_2 and in activating H_2-D_2 exchange.[2]

The electronic structure of the L_2MH_2 complex also suggests a possible reaction path for the hydrogenation of unsaturated hydrocarbons at low-coordination transition-metal sites. The $4a_1$ orbital, which defines the Fermi energy of the site, is closely matched in symmetry, energy, and electronegativity to the π orbitals of hydrocarbons such as acetylene (C_2H_2) and ethylene (C_2H_4). When the $4a_1$ orbital, which is an antibonding mixture of L-M(d_{z^2}) and H_2^* σ_g orbital character, is only partially occupied (as is the case for M = Ir, Rh), it offers a pathway for electron flow from a C_2H_2 (or C_2H_4) π orbital to the dissociatively "chemisorbed" hydrogen. Electron flow directly between C_2H_2 (or C_2H_4) and H_2 in the gas phase via the filled π and σ_g orbitals is forbidden by the Pauli exclusion principle, whereas electron flow directly between the π orbital and empty σ_u orbital is forbidden by orbital symmetry.[8] Because the $4a_1$ orbital of L_2MH_2 is antibonding between the L_2M site and H_2, while bonding between H_2 and C_2H_2 (or C_2H_4), the net result of electron flow between a π orbital and the $4a_1$ orbital is the breaking of a C-C π bond, the formation of two new C-H bonds, and the expulsion of the hydrogenated species C_2H_4 (or C_2H_6), as suggested by the reaction path shown in Fig. 3. Also shown is a contour map for the $4a_1$ orbital of the $L_2MH_2C_2H_2$ reaction intermediate (the third step of the proposed reaction path) formed as a result of the interaction of acetylene with the L_2MH_2 complex. The incipient formation of C-H bonds via the overlap of the C-C π orbital with the antibonding metal-dihydride orbital and the resulting ethylene-like configuration are clearly visible in this map. It is important to note that the concerted reaction path indicated in Fig. 3 is not the conventional one for hydrogenation on ideal transition-metal surfaces, where it is usually assumed that chemisorption of acetylene or ethylene on one or two metal sites is the precursor to combining with hydrogen chemisorbed on neighboring sites. Nonconcerted reaction paths in which both reactants are coordinated to the same metal site are also possible and indeed have been argued to be favored kinetically in certain homogeneous reactions.[12] Alternative reaction paths at low-coordination transition-metal sites are currently under investigation in conjunction with theoretical studies of the reactivity of $IrCl(CO)(Ph_3P)_2$ (Vaska's complex).[13]

In conclusion, we have attempted to show that a detailed theoretical study of the electronic structure of well characterized coordinatively unsaturated transition-metal complexes and their interactions with H_2 can not only lead to an understanding of their homogeneous reactivity but can also serve as a model for the dissociative chemisorption and heterogeneous reactivity of H_2 on low-coordination transition-metal surface sites, where definitive structural information is lacking. There are many useful analogies to be made between molecular transition-metal coordination complexes and surface-adsorbate interactions.[14,15] Such analogies are probably not fortuitous. They should be sought after and the common basis of understanding elucidated.

References

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1. R. Ugo, Catal. Rev. Sci. Eng. 11, 225 (1975); R. Ugo, G. La Monica, F. Cariati, S. Cenini, and F. Conti, Inorg. Chim. Acta 4, 390 (1970).
2. G. A. Somorjai, in The Physical Basis for Heterogeneous Catalysis, edited by E. Drauglis and R. I. Jaffee (Plenum, New York, 1975), p. 395.
3. J. R. Anderson, The Structure of Metallic Catalysis (Academic, New York, 1975), p. 244.
4. J. Hinze, M. A. Whitehead, and H. H. Jaffe, J. Am. Chem. Soc. 85, 148 (1963).
5. K. H. Johnson (manuscript in preparation).
6. J. C. Slater and K. H. Johnson, Phys. Rev. B5, 844 (1972); K. H. Johnson, in Advances in Quantum Chemistry, edited by P.-O. Löwdin (Academic, New York, 1973), Vol. 7, p. 143; J. C. Slater, The Self Consistent Field for Molecules and Solids, Vol. 4 of Quantum Theory of Molecules and Solids (McGraw-Hill, New York, 1974); K. H. Johnson, in Annual Review of Physical Chemistry, edited by H. Eyring, C. J. Christensen, and H. S. Johnston (Annual Reviews, Palo Alto, California, 1975), Vol. 26, p. 39.
7. R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, Phys. Rev. B13, 1396 (1976).
8. R. G. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry (Academic, New York, 1969).

9. In the SCF-Xα method, the 1s orbital energy of the hydrogen atom corresponds approximately to the electronegativity $\frac{1}{2}$ (I + A), where I is the ionization potential and A is the electron affinity. The transition-state procedure (see Ref. 6) leads to relaxed orbital energies corresponding to I and A separately.

10. R. P. Messmer, D. R. Salahub, K. H. Johnson, and C. Y. Yang, Chem. Phys. Lett. (submitted for publication).

11. J. E. Demuth, to be published.

12. J. Halpern, in Proceedings of the 14th International Conference on Coordination Chemistry, Toronto (1972), p. 698.

13. G. G. Eberhart and L. Vaska, J. Catal. 8, 183 (1967).

14. J. C. Slater and K. H. Johnson, Physics Today 27, 34 (1974).

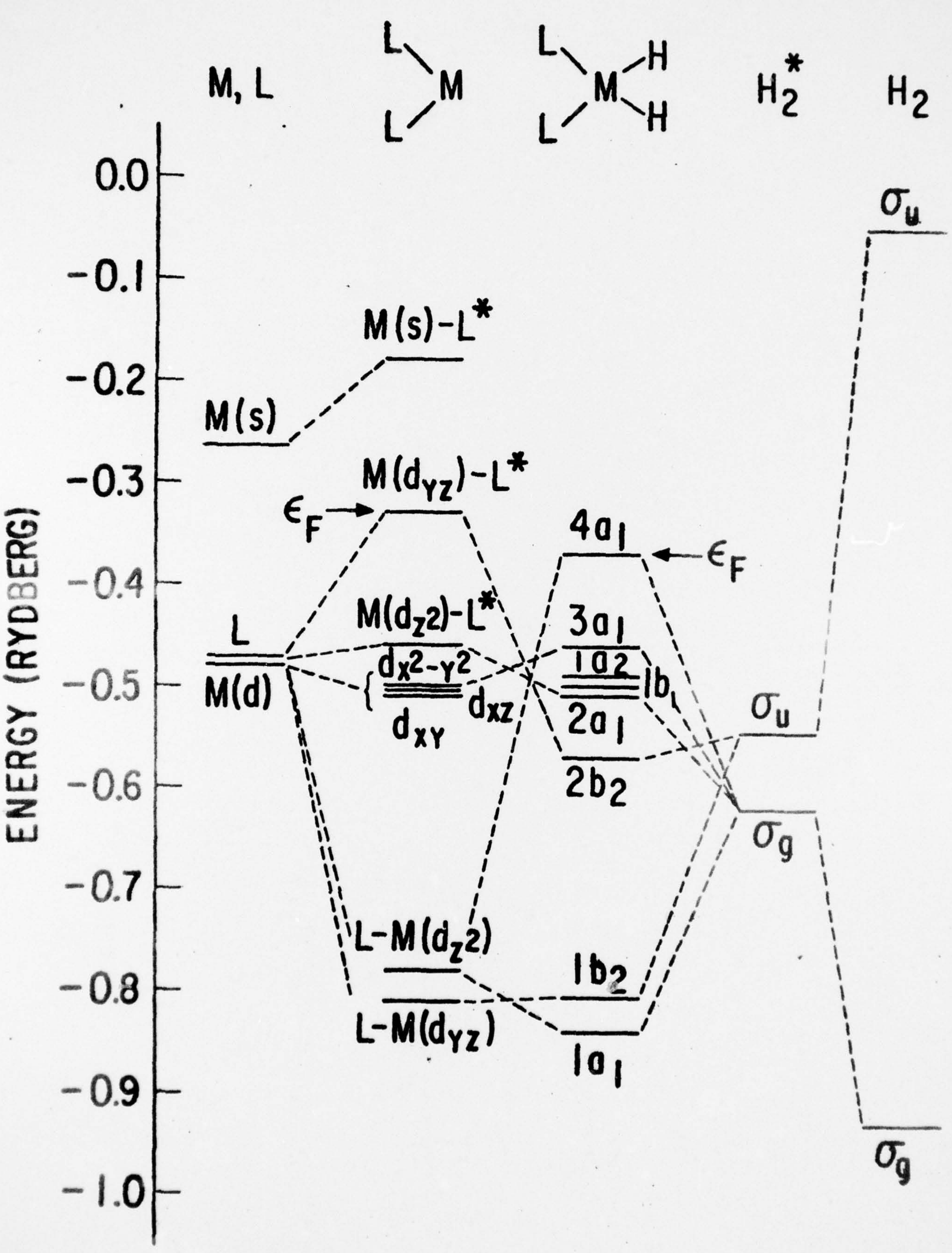
15. R. P. Messmer, in The Physical Basis for Heterogeneous Catalysis, edited by E. Drauglis and R. I. Jaffee (Plenum, New York, 1975), p. 261.

Figure Captions

Fig. 1. The SCF-Xα orbital energies for coordinatively unsaturated transition-metal complexes representing low-coordination transition-metal sites and dissociative hydrogen chemisorption thereon. The L_2M energy levels are labeled according to their principal orbital character, whereas the L_2MH_2 levels are labeled according to the irreducible representations of the C_{2v} symmetry group. The highest occupied orbital is indicated by the "Fermi level" ε_F. The results shown are for M = platinum and L = phosphine, although they are qualitatively similar for other Group-VIII transition metals such as iridium. Also shown are the SCF-Xα orbital energies for the isolated metal atom, ligand, and hydrogen molecule at the free-molecule internuclear distance 1.4 Å (H_2) and internuclear distance 2.8 Å (H_2*) characteristic of the dihydride configuration in the L_2MH_2 complex. The unimportant nonbonding phosphine ligand orbitals are not shown.

Fig. 2. Contour maps of the principal bonding and antibonding molecular-orbital wavefunctions corresponding to the orbital energies of the L_2MH_2 complex shown in Fig. 1. Regions of differing sign are separated by nodes. The high-density contours and inner nodes corresponding to the atomic core electrons are not shown.

Fig. 3. Possible reaction path for the hydrogenation of acetylene at a coordinatively unsaturated transition-metal site. Also shown is a contour map for the $4a_1$ orbital wavefunction of the $L_2MH_2C_2H_2$ reaction intermediate (the third step of the reaction path) formed as a result of the interaction of acetylene with the L_2MH_2 complex. The results shown are for M = iridium and L = phosphine.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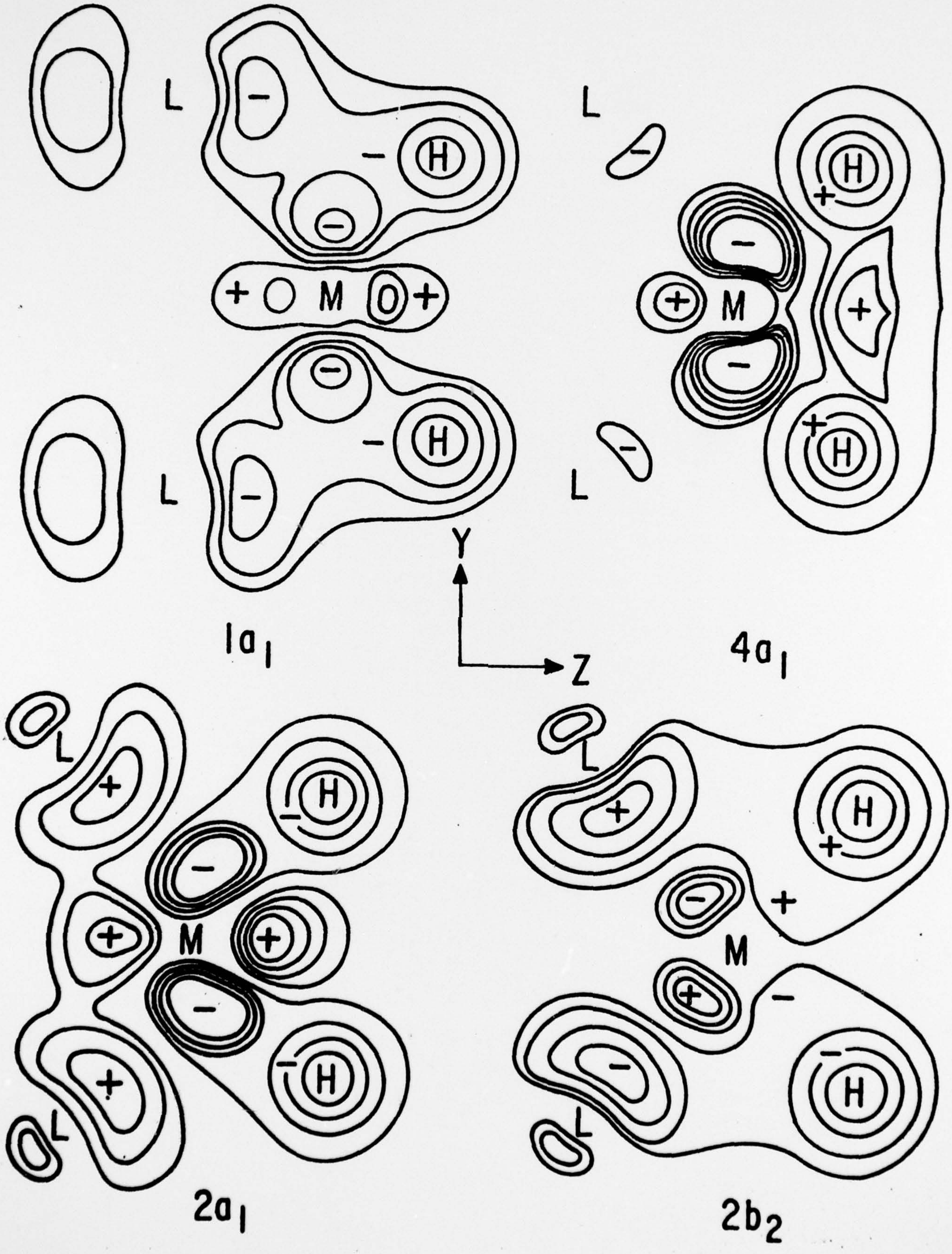
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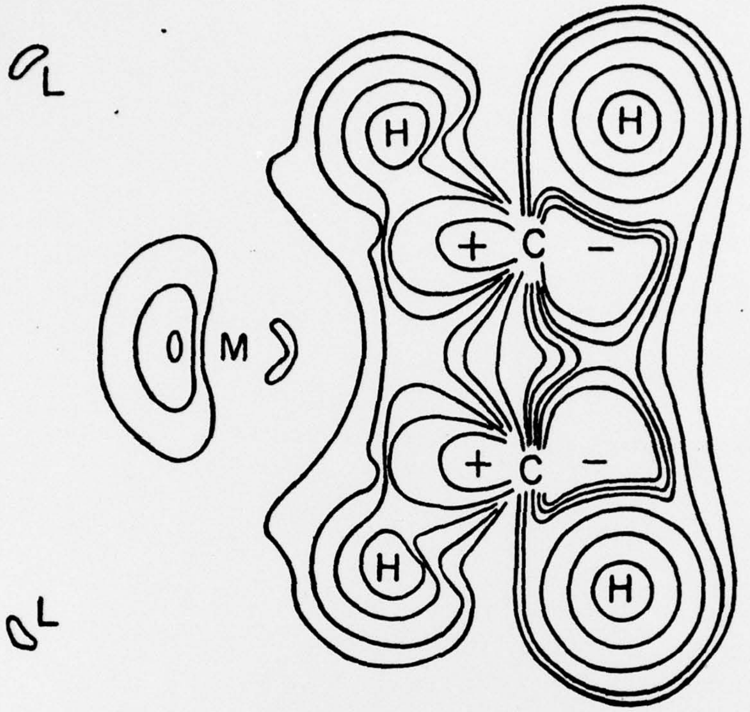
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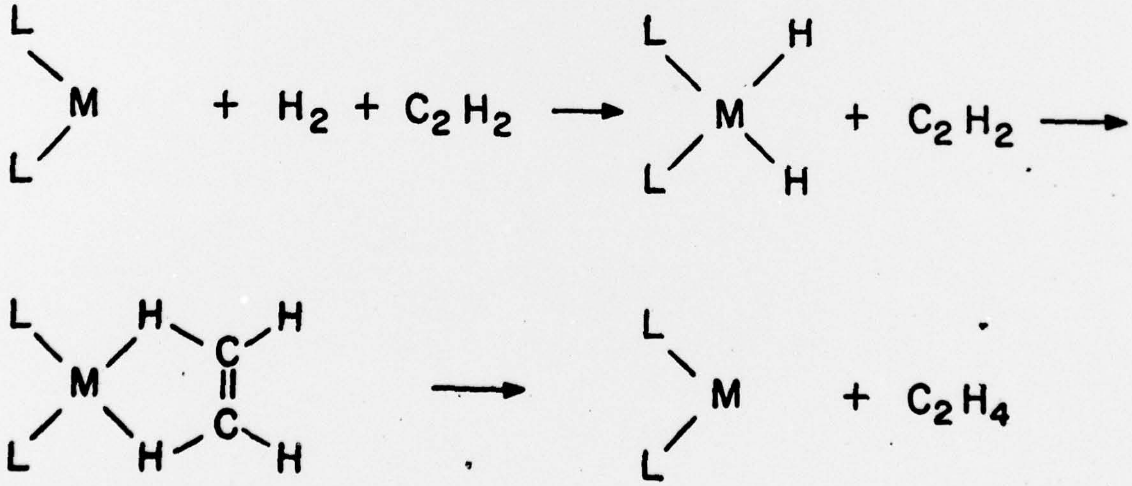
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