Chemistry of Excited Electronic States

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Atomic and molecular orbitals are among the tools used by chemists to view the world. The validity of this view for reaction systems can be experimentally probed by examination of the chemistry of electronically excited states and, in particular, by comparison of the reactivities of states having different orbital occupations (electron configurations). Reactivity changes associated with electron configuration are instructive with regard to chemists' views of molecular orbital interactions, but electronic excitation can also influence the course of a chemical reaction by increasing the energy content of the system or by affecting access to different potential energy surfaces by changing spin, orbital symmetry, or spin-orbit level. These various effects are illustrated by studies of gas-phase transition metal–mediated H–H and C–H bond-activation processes.

CHEMISTS USE ATOMIC AND MOLECULAR ORBITALS TO UNderstand and predict chemical reactivity. From the organic chemist's "arrow pushing" to the Woodward-Hoffmann symmetry rules (*1*) to detailed ab initio quantum calculations, knowing where the electrons are (that is, knowing the occupancy of the orbitals and their spatial and symmetry characteristics) is a central aspect of understanding and predicting chemical phenomena. Unfortunately, such pictures for reaction systems are rarely amenable to direct experimental verification. In principle, these concepts could be probed by examination of the effect that moving an electron from one orbital to another would have on the chemistry of the system. In practice, this ideal experiment is difficult but can be performed by careful comparison of the reactivities of different electronic states.

A specific example of these ideas is illustrated by the orbital interactions shown in Fig. 1 for the activation of H–H and C–H bonds by transition metals, a topic of intense research efforts within organometallic chemistry and surface science (*2*). (In this context, the term "activation" is used to refer to a chemical interaction that weakens or cleaves a bond that is ordinarily inert.) These concepts have been used to describe the reactions of transition metal atoms (*3*) and ions (*4*), organometallic complexes (*5, 6*), and surfaces (*6, 7*) alike.

The occupied σ bonding and unoccupied σ^* antibonding orbitals of H_2 (and, by extrapolation, any covalent bond) and an acceptor and donor orbital on the metal M (represented here by atomic *s* and *d* orbitals, respectively) are shown in Fig. 1. As the H_2 approaches the metal center, the σ and *s* orbitals (which have the same symmetry) interact to form bonding and antibonding orbitals of the metal dihydride intermediate. Analogous mixing of the σ^* and *d* orbitals occurs to form a second pair of bonding and antibonding orbitals for the intermediate. Reaction of M with H_2 occurs most easily if the donor orbital on M contains two electrons and the acceptor orbital contains none, because then only the bonding orbitals of the intermediate are occupied, as shown in Fig. 1. If an electron could be moved into the metal acceptor orbital, this electron would be forced into an antibonding orbital in the intermediate (because the bonding orbital is already fully occupied), which would result in a considerable reduction in the reactivity of M toward H_2.

Chemical reactions involving excited electronic states are uncommon because condensed-phase environments generally suppress electronic excitation. For the most part, solution and solid-state chemistry occurs on ground-state potential energy surfaces. Nevertheless, many studies of electronically excited states have been done in the rarefied environment of the gas phase (*8–10*) and by generation of the excited reagent directly within the reaction mixture (for example, in organic and biochemical photochemistry). Orbital concepts are illustrated here by bimolecular chemical reactions, as opposed to unimolecular processes (such as isomerizations) or simple quenching processes (in which the electronic energy is dissipated without rearrangement of any chemical bonds). A large fraction of the gas-phase studies of excited electronic states involve species containing main group elements (*8, 9*) because these generally have states that are well separated energetically (making photolysis an efficient means of generating such species). In particular, recent experiments on the reactivity of the group 2 (such as Mg and Ca) and group 12 (such as Zn, Cd, and Hg) excited states (*11*) provide conspicuous examples of studies that give a view of orbital principles similar to the one developed here. Relatively few studies of excited electronic states have involved transition metals, but this chemistry is highlighted for its topical interest and because the energy spacing between these electronic states can be quite small, thus deemphasizing the effect of total energy content on the chemistry.

Designation of Electronic States

The most commonly used nomenclature for identifying different electronic states is the Russell-Saunders term symbol, ${}^{2S+1}L_J$, which specifies the orbital (L) and spin (S) angular momenta of all the electrons and how they couple together into the total (J) angular momentum. For atoms, the capital letters $S, P, D, F, \ldots$ are used to designate the values of $L = 0, 1, 2, 3, \ldots$ in direct analogy with the $s, p, d, f, \ldots$ names given to atomic orbitals. The value $2S + 1$ is referred to as the multiplicity of the state. When $S = 0$, $2S + 1 = 1$, and the state is a "singlet"; $S = 1/2$ is a "doublet"; $S = 1$ is a "triplet"; and so forth. For most ground-state systems, there are no unpaired electrons; hence singlet states are the rule. In general, J must be positive, and it ranges in integer steps from the sum of L and S down to $L - S$. Parallel terminology exists for molecular term symbols and is distinguished by the use of Greek letters for

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molecular orbitals (σ, π, δ, ϕ, . . .) and molecular states (Σ, Π, Δ, Φ . . .).

This nomenclature is an approximation that is most useful for light atoms (through the first transition series, that is, atomic numbers less than about 40), where the interaction between the spin and orbital angular momenta (the "spin-orbit coupling") is small. Hence, electronically excited states with large excitation energies are chiefly the result of different electron configurations and are represented by different L and S values. For heavier elements, the spin-orbit coupling is large enough that states with the same L and S quantum numbers but different J values can have excitation energies that are in excess of those for states of different electron configurations. For very heavy elements, the designation of L and S is ambiguous, and such states may be referred to by their J quantum number only (*12*).

To the degree that the L, S, and J quantum numbers are well defined, quantum mechanics requires that these quantities be conserved along the reaction path. Indeed, spin-forbidden (S changing) reactions involving light elements are generally not observed, and the Woodward-Hoffmann rules (*1*) that assume conservation of orbital symmetry are of general utility. With heavier elements, "spin-forbidden" reactions can be observed because only J need be rigorously conserved. In all of these cases, the reactions occur along electronic potential energy surfaces that are described as adiabatic, that is, for which the Born-Oppenheimer approximation is valid (*13*). This very useful approximation says that electron and nuclear motions are completely decoupled because the light electrons respond rapidly (adiabatically) to the relatively ponderous movements of the nuclei. In some circumstances, reactions that are nonadiabatic can occur by means of a jump from one adiabatic surface to another. Examples of nonadiabatic behavior include radiationless relaxation processes such as intersystem crossing and internal conversion.

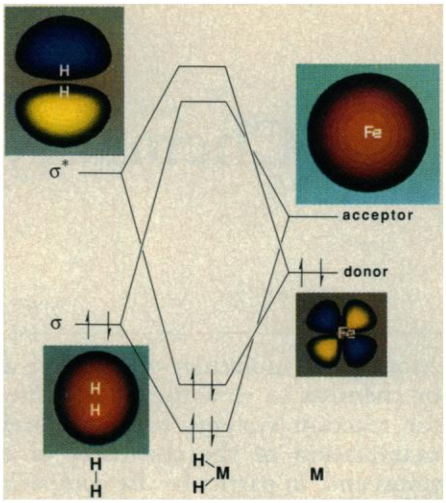
Experimental Considerations

In order to use excited-state chemistry as a probe of fundamental orbital principles, it is important to understand the various ways that electronic excitation can change the chemistry of a species. In addition to possibly changing the electron configuration, excitation can alter the total energy available for reaction, or it can change the spin or spin-orbit level of the reagent. These changes can, in turn, influence the structure of the reactant species, thereby inducing isomerization or affecting the steric requirements of a bimolecular reaction. Most studies of electronically excited states are carried out under thermal conditions, such that a change in the efficiency of the reaction of interest can be observed. In such studies it can be difficult to differentiate whether the observed change is due to a change in the total energy content or to the effects of spin, spin-orbit level, and electron configuration. This problem can be overcome by simultaneous examination of the effects that kinetic and electronic energy have on the chemistry of the reaction, thus enabling a comparison of the reactivity of different electronic states at a constant total energy. Such studies are easily accomplished by examination of the chemistry of ions, because the charge on an ion allows facile control of its kinetic energy over a very wide range (*4, 10, 14*).

Effect of Electronic Energy

The simplest effect that electronic excitation can have on a reaction is to increase the amount of total energy available to the process. The most obvious evidence for such an increase would involve a reaction that is endothermic for the ground state and therefore not observed in an experiment at thermal conditions. After electronic excitation, the reaction would become exothermic and would thus be easily observed.

Fig. 1. Molecular orbital interactions between a metal center (M) and H_2 (the prototype for any covalently bonded species). Arrows represent electrons in the orbital occupancy that is most favorable for bond activation.



Many such observations have been made, especially for main group elements. Here, the effect is illustrated by the first transition metal ion system for which electronic excitation was demonstrated: the reaction of Cr$^+$ with methane (CH_4) (*15–17*) [Fig. 2 (*18*)]. At thermal energies (the lowest energy point shown), ground-state Cr$^+$(^6S) undergoes no reactions with CH_4, but the ^4D and ^4G excited states (which lie 2.46 and 2.56 eV above the ground state, respectively) efficiently dehydrogenate CH_4, yielding $CrCH_2^+$ + H_2. This reaction does not occur for the Cr$^+$ ground state until 2.45 eV of translational energy is supplied (Fig. 2). The excitation energy of the quartet states is sufficient to overcome this endothermicity, thereby making the reaction exothermic and facile at low kinetic energies.

A simple energy content argument is sufficient to explain why electronic excitation might enhance the reactivity of many species, but it fails to explain two observations. First, there are numerous examples where electronic energy does not couple directly into the

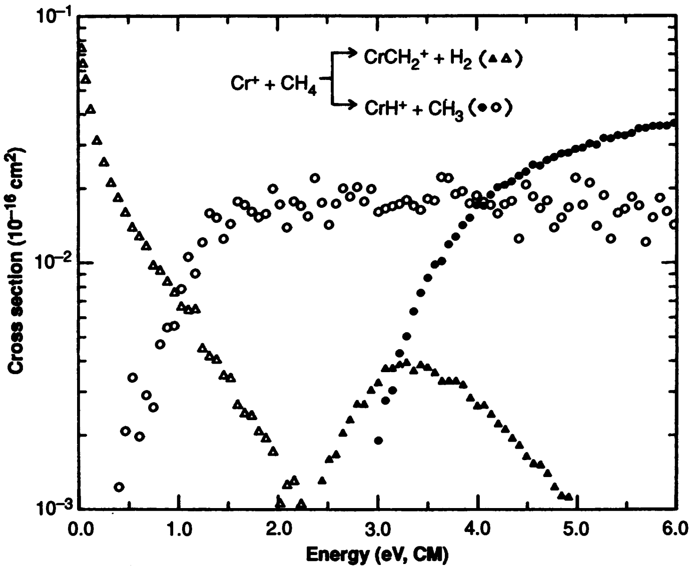


Fig. 2. State-specific cross sections for the reaction of Cr$^+$ with CH_4 as a function of relative translational energy. Results for ground-state Cr$^+$(^6S) are shown by the solid symbols, and those for Cr$^+$(^4D, ^4G) excited states scaled down by a factor of 100 are shown by open symbols. (CM, center of mass.)

reaction coordinate and thereby enhance the reactivity. For example, in the system illustrated here, the $Cr^+(^6D)$ first excited state at 1.52 eV is much less reactive than ground-state Cr^+ with CH_4 and H_2 at all kinetic energies (*17, 19*).

Second, the relative reaction efficiencies of ground and excited electronic states are often very different even after the effect of total energy has been accounted for. For example, the relative cross section for dehydrogenation by $Cr^+(^4D, ^4G)$ at 0.5 eV is more than 300 times that for $Cr^+(^6S)$ at 3.0 eV (Fig. 2). However, this ratio is energy-dependent because the effect of kinetic energy on exothermic and endothermic reactions is fundamentally different (Fig. 2). A more quantitative comparison of the energy-independent reaction efficiencies of two states can be made if their reactions are either both exothermic or both endothermic. The $Cr^+ + CH_4$ system provides such an example in the form of the $CrH^+ + CH_3$ product channel (Fig. 2). Electronic excitation has shifted the threshold for this endothermic reaction from about 3.0 eV for $Cr^+(^6S)$ to about 0.5 eV for $Cr^+(^4D, ^4G)$. (Indeed, the correspondence of this shift to the known electronic energy levels of the ^4D and ^4G states helps identify them.) After modeling the effect that lowering the threshold has on the reaction probability (that is, accounting for the change in reactivity with total energy content), the efficiency of the excited-state reaction is 30 ± 10 times that of the ground-state reaction (*17*).

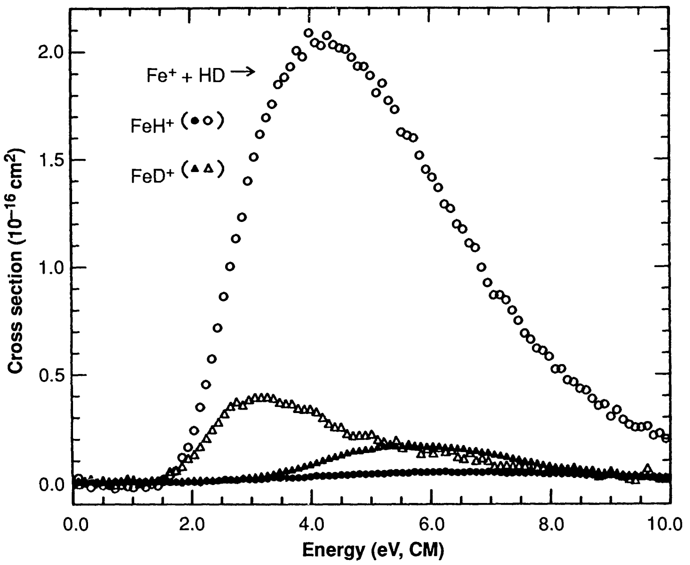


Fig. 3. State-specific cross sections for the reaction of Fe^+ with HD as a function of relative translational energy. Results for ground-state $Fe^+(^6D)$ are shown by solid symbols, and those for excited-state $Fe^+(^4F)$ are shown by open symbols.

Effect of Spin

An understanding of the origins of this change in efficiency requires a mechanism for the reaction. In agreement with the orbital interactions of Fig. 1, it is postulated that these transition metal–alkane reactions occur through an initial C–H bond-activation step (*20*). In the $Cr^+–CH_4$ system, this reaction generates the intermediate $H–Cr^+–CH_3$. Dehydrogenation of $H–Cr^+–CH_3$ leads to $CrCH_2{}^+$, whereas cleavage of the Cr–C bond yields CrH^+ (and cleavage of the Cr–H bond yields $CrCH_3{}^+ + H$, which is also observed as a minor channel) (*17*).

Chromium ions have five valence electrons. In $H–Cr^+–CH_3$, two of these are engaged in forming covalent bonds with the H and CH_3 ligands (as suggested by Fig. 1). Thus, $H–Cr^+–CH_3$ should have only three unpaired electrons (such that the maximum value of $S = 3/2$), which means that the ground state of $H–Cr^+–CH_3$ has quartet multiplicity. The reactivity of the Cr^+ excited states (which also have quartet multiplicity) is thus enhanced because the spin quantum number can be conserved in the reaction, whereas this is not possible for the ground state or the first excited state (which have sextet multiplicity). This type of selectivity is well known in organic chemistry as the explanation for the difference in reactivity of singlet and triplet carbenes and has been invoked to explain the relative reactivities of other transition metal ion reactions (*21, 22*).

One such example is Fe^+, which has a ^6D ground state and a ^4F excited state. Because the relative energy of the states is only 0.25 eV, simple energy effects are minimized and differences in reaction efficiency are much more obvious. The simplest possible reaction of this species is with H_2 to form FeH^+, a process that is endothermic by 2.36 eV (*23*). Experimental results indicate that the quartet excited state is about 70 times as reactive as the sextet ground state, after accounting for the energy difference between the states. This effect is shown for the HD isotopomer of H_2 (Fig. 3). Similar relative reactivities are observed for reactions with CH_4 and ethane (*24*). This difference in reactivities could again be rationalized in terms of spin conservation of the intermediate (which should have quartet multiplicity); however, the effect of spin cannot easily explain the striking change in the branching ratio shown in Fig. 3. The ^6D ground state produces much more FeD^+ than FeH^+ (which is nearly absent), whereas the ^4F excited state shows the opposite reactivity. These two electronic states must react with HD through different reaction mechanisms.

Effect of Electron Configuration

In order to explain this drastic change in branching ratio, the electron configurations of the two states of Fe^+ must be examined. In the $Fe^+(^6D)$ ground state, the seven valence electrons are distributed such that six of them are in 3*d* orbitals and one is in the 4*s* orbital. In the $Fe^+(^4F)$ excited state, all of the electrons are in the 3*d* orbitals; hence it has a $3d^7$ electron configuration. The reason this makes a difference follows from the orbital concepts introduced in Fig. 1.

For first-row atomic transition metals, the acceptor orbital is primarily the valence 4*s* (although contributions from other orbitals can be influential) (*25*), and the donor is the particular 3*d* orbital with the symmetry shown in Fig. 1. In essence, the $3d^7$ electron configuration has a near-optimum electron configuration for reaction since the acceptor is empty and the donor can be doubly occupied. Comparing the chemistry of the $3d^7$ configuration with that of the $4s^13d^6$ configuration is equivalent to moving an electron from a nonbonding or donating 3*d* orbital into the acceptor orbital. The experimental result is a drastic decline in the reactivity that can be rationalized on the basis of Fig. 1. Since the acceptor orbital is already occupied, it cannot accept the two H_2 σ electrons; thus one electron is forced into the antibonding molecular orbital of very high energy. This effect yields a relatively repulsive potential energy surface that drastically reduces the reactivity of the $4s^13d^6$ state and forces the reaction to proceed by an alternative mechanism (*23*) that results in a different branching ratio.

The chemistry of other transition metal ions illustrates that this effect is primarily due to the electron configuration rather than spin or energy. For instance, the reactivity of H_2 with ground-state $Mn^+(^7S,4s^13d^5)$ is similar to that of $Fe^+(^6D,4s^13d^6)$ (*26*), whereas ground-state $Co^+(^3F,3d^8)$ and $Ni^+(^2D,3d^9)$ behave similarly to $Fe^+(^4F,3d^7)$ (*27*). These concepts extend to the activation of CH_4 and other alkanes by gas-phase transition metal ions (*20, 28*). The observation that ground-state $Cr^+(^6S,3d^5)$ reacts with H_2 and CH_4 whereas the $Cr^+(^6D,4s^13d^4)$ first excited state does not (a result that cannot be attributed to energy content or spin) is easily explained by the electron configuration arguments.

The reaction of Fe^+ with propane (C_3H_8) also illustrates the role that the electron configuration can play. Two of the endothermic channels observed are formation of FeH + $C_3H_7^+$ and the directly competing channel, FeH^+ + C_3H_7 (*24*). In both cases, the quartet excited state is much more reactive than the sextet ground state; however, in the first reaction, virtually no reactivity is observed for $Fe^+(^6D)$ (the ^4F state is a factor of >75 more reactive), whereas in the second reaction the difference in reactivity is only about a factor of 5. The formation of FeH from Fe^+ + C_3H_8 is a hydride (H^-) transfer reaction in which two electrons are donated to Fe^+; therefore, $Fe^+(^4F,3d^7)$ can readily accept both electrons in its empty 4*s* orbital and thereby form a strong covalent bond, whereas the occupied 4*s* orbital of $Fe^+(^6D,4s^13d^6)$ makes formation of ground-state FeH inaccessible.

A final demonstration of the effect of electron configuration on the interactions of different electronic states comes from recent work by Kemper and Bowers (*29*). They find that the mobilities (which describe the diffusion of ions in a medium) of atomic transition metal ions in 1 to 2 torr of He show bimodal behavior that arises from different electronic states of the ions. The mobilities of different metals and different states fall into two groups that are distinguishable by the occupation of the 4*s* orbital. The results show that the interaction of the metal ions with He is more repulsive when the 4*s* orbital is occupied than when it is empty. This behavior is a straightforward result of molecular orbital interactions analogous to those shown in Fig. 1.

Effect of Spin-Orbit Level

For some electronically excited states the spin and electron configuration are identical to those of the ground state, and the only difference between the states is the *J* quantum number, that is, the spin-orbit level. It might be expected that this change is sufficiently subtle that drastic changes in the chemistry of such states would not be observed. This is a common observation, but spin-orbit effects have been observed in many chemical systems, as recently reviewed (*30*).

Although this review includes no examples of the reactivity of specific spin-orbit levels of transition metals, recent experimental advances have enabled such studies by Weisshaar and co-workers, who have shown that the reactivity of $V^+(^3F_J)$ with C_2H_6, C_3H_8, and C_2H_4 does not depend on the spin-orbit level (*22*). In contrast, the J = 5/2 level of $Fe^+(^4F_J)$ is almost twice as reactive with C_3H_8 as the slightly lower lying J = 9/2 and 7/2 levels (*31*), although it is unknown whether this is simply the result of an increase in the total energy of the system. Further experiments in this area are clearly an avenue for continued exploration.

An example where the spin-orbit level makes a significant change in the chemical reactivity concerns the reactions of $Kr^+(^2P_J)$. Here the spin-orbit splitting between the J = 3/2 ground state and the J = 1/2 excited state is large, 0.67 eV. Both spin-orbit states react with D_2 at low kinetic energies with no apparent barrier (Fig. 4) (*32*). Although neither state reacts very efficiently compared to the total collision cross section, the ground-state reaction is much more efficient than the excited-state reaction, demonstrating that total energy content cannot explain the observation. In addition, the $Kr^+(^2P_{3/2})$ cross section shows a feature at high energies that is not found in the $Kr^+(^2P_{1/2})$ cross section.

Despite the chemical simplicity of this reaction, an explanation for these observations requires consideration of four potential energy surfaces (*32*). To form the KrD^+ + D reaction products, the Kr^+ + D_2 reactants must first charge-transfer to form the Kr + D_2^+ charge state, which can then transform easily to the observed products. The charge-transfer step is the rate-limiting process in this reaction. Of the various spin-orbit components of Kr^+, only ground-state $Kr^+(^2P_{3/2})$ correlates adiabatically with the Kr + D_2^+ state; hence this state reacts more efficiently at low kinetic energies. The $Kr^+(^2P_{1/2})$ excited state can react only through a nonadiabatic transition to the $^2P_{3/2}$ ground-state surface, suppressing the reaction efficiency of this state but not resulting in any energy barrier.

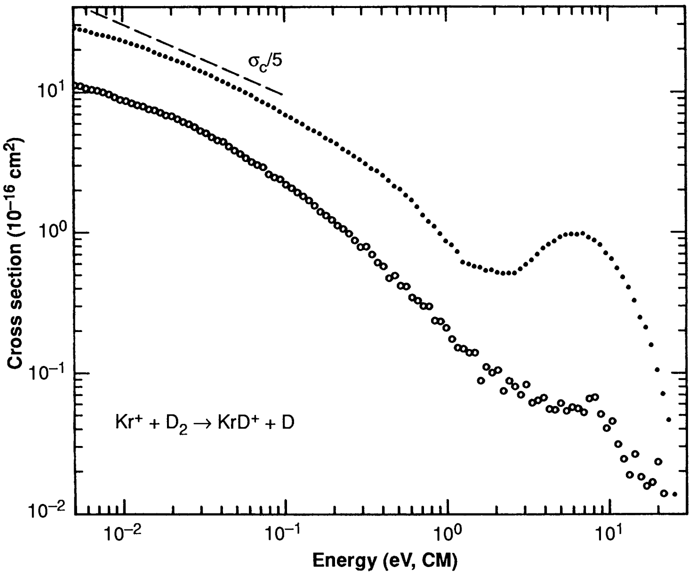


Fig. 4. Spin-orbit state-specific cross sections for the reaction of Kr^+ with D_2 as a function of relative translational energy. Results for ground-state $Kr^+(^2P_{3/2})$ are shown by solid circles, and those for excited-state $Kr^+(^2P_{1/2})$ are shown by open circles. The collision cross section (σ_c) divided by 5 is given by the broken line.

The introduction of the quantum number m_J (which can have values ranging from J to $-J$ separated by one unit) explains the origins of the high-energy feature in the $Kr^+(^2P_{3/2})$ ground-state cross section. The reactive component of $Kr^+(^2P_{3/2})$ is $m_J = \pm 1/2$, whereas the $m_J = \pm 3/2$ component is believed to be responsible for the high-energy feature. Because the $^2P_{1/2}$ state has no $m_J = \pm 3/2$ quantum numbers, there is no high-energy feature for this state. The $m_J = \pm 3/2$ component is believed to be unreactive because it has a fundamentally different symmetry than the reactive $m_J = \pm 1/2$ component in the presence of the D_2 molecule. To react, these components must interact, a process that is believed to occur through rotationally nonadiabatic (Coriolis) coupling (*33*).

Outlook

The chemistry of excited electronic states is not always a simple matter to interpret, but well-crafted experiments can be reasonably direct probes of the molecular orbital ideas ubiquitous in present-day chemistry. In particular, studies of excited electronic states of transition metal ions can help validate the molecular orbital ideas that are used routinely to understand the activation of covalent bonds by transition metals. Such studies are an ideal example of the synergistic relation between experiment and theory. One exciting implication for such research is that excited electronic states may offer a means of exercising control over the efficiency and specificity of a wide range of chemical reactions.

REFERENCES AND NOTES

1. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* (Academic Press, New York, 1970).
2. See, for example, C. L. Hill, Ed., *Activation and Functionalization of Alkanes* (Wiley, New York, 1989); J. A. Davies, P. L. Watson, J. F. Liebman, A. Greenberg, Eds., *Selective Hydrocarbon Activation* (VCH Publishers, New York, 1990).
3. A. Sevin and P. Chaquin, *Nouv. J. Chim.* 7, 353 (1983); M. E. Ruiz, J. Garcia-Prieto, O. Novaro, *J. Chem. Phys.* **80**, 1529 (1984); P. E. M. Siegbahn, M. R. A. Blomberg, C. W. Bauschlicher, *ibid.* **81**, 1373 (1984).
4. J. L. Elkind and P. B. Armentrout, *J. Phys. Chem.* **89**, 5626 (1985).
5. A. Dedieu and A. Strich, *Inorg. Chem.* **18**, 2940 (1979); P. J. Brothers, *Prog. Inorg. Chem.* **28**, 1 (1981).
6. J.-Y. Saillard and R. Hoffman, *J. Am. Chem. Soc.* **106**, 2006 (1984).
7. E. Shustorovich, R. C. Baetzold, E. L. Muetterties, *J. Phys. Chem.* **87**, 1100 (1983); P. E. M. Siegbahn, M. R. A. Blomberg, C. W. Bauschlicher, *J. Chem. Phys.* **81**, 2103 (1984).
8. D. Husain, *Ber. Bunsenges. Phys. Chem.* **81**, 168 (1977).
9. W. H. Breckenridge, in *Reactions of Small Transient Species*, A. Fontijn and M. A. A. Clyne, Eds. (Academic Press, London, 1983), pp. 157–230; T. G. Slanger, *ibid.*, pp. 231–310.
10. P. B. Armentrout, *Structure/Reactivity and Thermochemistry of Ions*, P. Ausloos and S. G. Lias, Eds. (Reidel, Dordrecht, Germany, 1987), pp. 97–164.
11. C. T. Rettner and R. N. Zare, *J. Chem. Phys.* 77, 2416 (1982); P. D. Kleiber, A. M. Lyyra, K. M. Sando, V. Zafiropulos, W. C. Stwalley, *J. Chem. Phys.* **85**, 5493 (1986); W. H. Breckenridge, *Acc. Chem. Res.* **22**, 21 (1989).
12. In such cases, the Russell-Saunders (*LS*) coupling scheme begins to be inappropriate and may be replaced by the "*j-j* coupling" scheme. G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover, New York, 1944).
13. M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)* **84**, 457 (1927).
14. K. M. Ervin and P. B. Armentrout, *J. Chem. Phys.* **83**, 166 (1985).
15. R. B. Freas and D. P. Ridge, *J. Am. Chem. Soc.* **102**, 7131 (1980). W. D. Reents, F. Strobel, R. B. Freas, J. Wronka, D. P. Ridge, *J. Phys. Chem.* **89**, 5666 (1985).
16. L. F. Halle *et al.*, *J. Am. Chem. Soc.* **103**, 962 (1981).
17. R. Georgiadis and P. B. Armentrout, *J. Phys. Chem.* **92**, 7067 (1988).
18. The state-specific cross sections shown in Fig. 2 are derived from raw data published in (*17*) by correcting for the state populations also given in this reference.
19. J. L. Elkind and P. B. Armentrout, *J. Chem. Phys.* **86**, 1868 (1987).
20. P. B. Armentrout and J. L. Beauchamp, *Acc. Chem. Res.* **22**, 315 (1989).
21. P. B. Armentrout, *Annu. Rev. Phys. Chem.* **41**, 313 (1990).
22. S. Hanton, L. Sanders, J. C. Weisshaar, *J. Phys. Chem.* **93**, 1963 (1989). L. Sanders, S. D. Hanton, J. C. Weisshaar, *J. Chem. Phys.* **92**, 3498 (1990).
23. J. L. Elkind and P. B. Armentrout, *J. Phys. Chem.* **90**, 5736 (1986).
24. R. H. Schultz, J. L. Elkind, P. B. Armentrout, *J. Am. Chem. Soc.* **110**, 411 (1988).
25. J. L. Elkind and P. B. Armentrout, *J. Phys. Chem.* **91**, 2037 (1987).
26. ———, *J. Chem. Phys.* **84**, 4862 (1986).
27. ———, *J. Phys. Chem.* **90**, 6576 (1986).
28. P. B. Armentrout, in *Gas Phase Inorganic Chemistry*, D. H. Russell, Ed. (Plenum, New York, 1989), pp. 1–42; in *Selective Hydrocarbon Activation*, J. A. Davies, P. L. Watson, J. F. Liebman, A. Greenberg, Eds. (VCH Publishers, New York, 1990), pp. 467–533.
29. P. R. Kemper and M. T. Bowers, *J. Am. Chem. Soc.* **112**, 3231 (1990).
30. P. J. Dagdigian and M. L. Campbell, *Chem. Rev.* **87**, 1 (1987).
31. S. D. Hanton, R. J. Noll, J. C. Weisshaar, *J. Phys. Chem.* **94**, 5655 (1990).
32. K. M. Ervin and P. B. Armentrout, *J. Chem. Phys.* **85**, 6380 (1986).
33. H. Laue, *ibid.* **46**, 3034 (1967).
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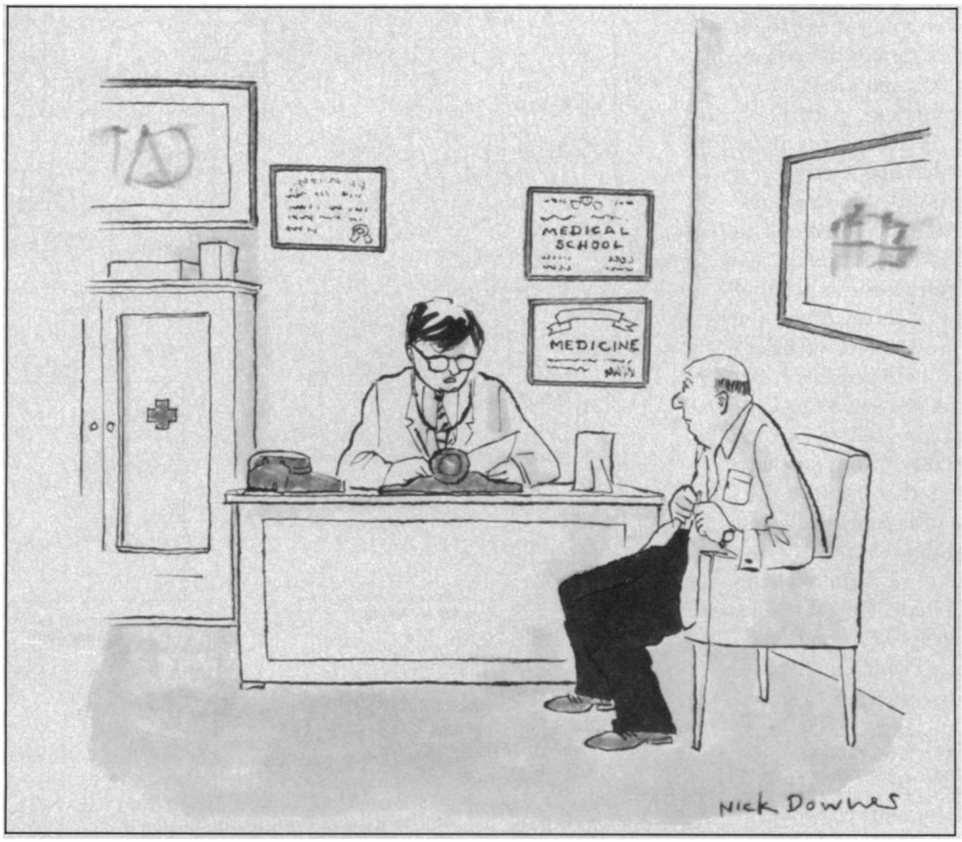

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