Electronic Structure and Chemical Dynamics

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The connection between the measurable properties of isolated molecules and the course, mechanisms, and rates of reactions is a central problem in chemistry. While an enormous number and variety of empirical, semiempirical, and fundamental approaches to this problem have and are being explored, the successes of orbital and state symmetry and correlation methods have been outstanding and widespread. Also, the importance of intersections and avoided intersections of potential-energy surfaces in a variety of thermal as well as photochemical reactions has become increasingly evident.[1]

To provide a firm basis for the understanding of the behavior of complex chemical systems, it is valuable to determine the degree to which one can rationalize or predict detailed dynamical behavior in systems comprised of a small number of atoms, but which have several low-lying, strongly interacting potential energy surfaces. The area of gaseous ion–molecule reactions provides a particularly effective vehicle for this type of study, since even in systems with very few electrons the surfaces corresponding to the different charge exchange states of reactants and products generally lie close to each other, and often interact strongly. Moreover, detailed information on the reaction dynamics of many of these systems is available from ion-beam scattering experiments.

In this Account, I shall describe how, by using the known electronic properties of reactants, products, and intermediates, much of the dynamical behavior of these simple systems can be understood. In particular, electronic state correlation diagrams will be used to deduce the qualitative nature of the potential surfaces which control the reaction dynamics. Molecular *orbital* correlation diagrams have, of course, been applied extensively and successfully[2] to problems of this type, but much less use has been made of electronic state correlations.[3,4] One of the major purposes of this paper is to demonstrate the value of making electronic state correlations and illuminating them by orbital correlations.

Noble Gas–Hydrogen Systems

The reactions of the noble gas ions and atoms with respectively the hydrogen molecule and molecule ion together constitute an intriguing example of the relation between reactivity and electronic configuration. Despite the simplicity of these systems, there are several possible product channels. Letting A stand for any noble gas atom, we have

$$H_2^+ + A \longrightarrow AH^+ + H$$
$$A^+ + H_2 \longrightarrow AH^+ + H$$
$$A^+ + H_2 \longrightarrow A + H_2^+$$
$$A^+ + H_2 \longrightarrow A + H^+ + H$$

These processes, in addition to simple collisional dissociation without charge transfer, constitute the possible results of low-energy collisions. The relative importance of the different channels varies rather spectacularly in the noble gas family.

The reaction

$$H_2^+ + He \longrightarrow HeH^+ + H \qquad \Delta H = +0.8 \text{ eV}$$

is endoergic, but proceeds readily if the necessary energy is supplied either as relative translational energy of the reactants or as vibrational energy of H_2^+. Indeed, the photoionization experiments of Chupka[5,6] have shown that vibrational energy is particularly effective in promoting reaction. In contrast, the reaction

$$He^+ + H_2 \longrightarrow HeH^+ + H \qquad \Delta H = -8.3 \text{ eV}$$

has never been observed, and has a rate constant that is four orders of magnitude[7] smaller than that expected for an exoergic ion–molecule reaction.

The explanation of these results and a rationalization of what does happen when He^+ collides with H_2 can be gleaned from Figure 1, in which are plotted the potential energy curves that correspond to cuts through the potential energy surfaces in the asymptotic reactant and product regions. The separated atoms with lowest total energy are He + H^+ + H. Bringing together H^+ and H on the lowest surface merely generates the $^2\Sigma_g{}^+$ potential energy curve of H_2^+, if He is far away. Bringing together He and H^+ generates the lowest $^1\Sigma^+$ potential energy curve of HeH^+, and this constitutes a cut through the lowest surface for the system in the product region. Because the reactants H_2^+ + He and the products HeH^+ + H both correlate adiabatically to He + H^+ + H, we can expect that the system can pass adiabatically

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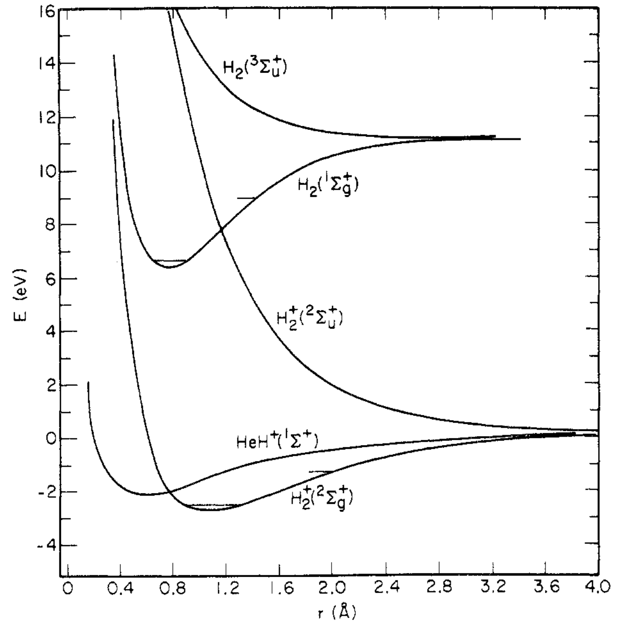

Figure 1. Potential energy curves for the diatoms in the asymptotic reactant and product regions of the $(He\text{-}H_2)^+$ system. Note the crossing of the curves for $H_2(^1\Sigma_g{}^+)$ and $H_2{}^+(^2\Sigma_u{}^+)$ which occurs in the reactant region of $He^+ + H_2$, but which becomes avoided when all three atoms are close to each other.

(*i.e.*, on one Born-Oppenheimer surface) from reactants to products.

The same conclusion can be reached for the other of the first four noble gas-hydrogen systems, as was pointed out by Kuntz and Roach.[8] Indeed, reaction with $H_2{}^+$ to form the protonated noble gas molecular ion is observed experimentally in all these cases. The lowest potential energy surface for the $H_2{}^+$-He system has been calculated by Brown and Hayes[9] for collinear conformations and appears to have the qualitative features expected to be consistent with the observed[5,6] effectiveness of vibrational energy in increasing the reaction cross section.

Consider now the higher energy atomic state $He^+ + H + H$. Bringing together the two hydrogen atoms with paired spins generates the $^1\Sigma_g{}^+$ ground-state potential-energy curve, which is accordingly a cut in the reactant region through the surface on which $He^+ + H_2$ collisions occur. The apparent peculiarity of having the ground state of H_2 lie above the states of $H_2{}^+$ is of course a result of our (proper) inclusion of the energies of He and He^+ in the diagram. To generate a cut through the product region of this upper surface, we bring together He^+ and H. There are calculations[10] that demonstrate that the resulting excited $^1\Sigma$ state of HeH^+ is totally repulsive, and the corresponding $^3\Sigma$ state is at best very weakly bound. Consequently, we have the first indication of the difficulty of forming a stable HeH^+ molecule from He^+ and H_2.

Figure 1 shows that, in the asymptotic reactant region, the potential-energy curve for H_2 crosses the repulsive $^2\Sigma_u{}^+$ state of $H_2{}^+$ at approximately 1 Å, and may intersect the repulsive wall of the $^2\Sigma_g{}^+$ ground state of $H_2{}^+$ at a smaller distance. These potential surface crossings do occur when helium is far away, and not interacting with the hydrogen moiety. In effect, the crossings occur because there is no electron readily available to convert $H_2{}^+$ to H_2. However, since all the surfaces involved are of $^2\Sigma$-^2A symmetry, these intersections become avoided when the helium-hydrogen separation decreases. As a result, the surface which has asymptotically the character of $He^+ + H_2$ may upon contraction of the H-H distance *adiabatically* acquire the characteristic of $He + H_2{}^+$ $(^2\Sigma_g{}^+)$, and upon expansion of the H-H distance assume the characteristics of $He + H_2{}^+$ $(^2\Sigma_u{}^+)$. In the latter instance, the surface leads directly to dissociation to $H^+ + H + He$. In the former case, the shape of the potential surface is affected, but the system remains bound with respect to $H^+ + H$.

There are two important questions to be considered. First, is the interaction between the primitive crossing states in fact strong enough to produce substantial mixing and avoided crossings, and thereby form an adiabatic path from $He^+ + H_2$ to $He + H^+ + H$? Second, are the avoided intersections reached in the course of a significant number of collision trajectories? For the He^+-H_2 system, these questions can only be answered by detailed calculation of the potential-energy surfaces and exact trajectories on them. However, we can say that if these avoided intersections are accessible, the result of He^+ colliding with H_2 should be to produce dissociative charge transfer to $H^+ + H + He$. It is unlikely that significant amounts of either $H_2{}^+$ or HeH^+ can be formed. This argument is consistent with recent experimental findings[7] which show that the cross section for disappearance of He^+ in H_2 is very small and that the product is predominantly and perhaps exclusively $He + H + H^+$.

A diagram which is very similar to Figure 1 can be drawn for the $(Ne\text{-}H_2)^+$ system, with the major difference being that the reactant states which dissociate to $Ne^+ + H + H$ are 3 eV lower than the corresponding curves in Figure 1. The conclusions to be reached are the same: $Ne + H_2{}^+$ will react to produce NeH^+; $Ne^+ + H_2$ should be largely unreactive and produce no NeH^+ or $H_2{}^+$. If anything, dissociative charge transfer to $H^+ + H$ should occur, but with small cross section. These conclusions are consistent with the experimental facts that are known.[11,12]

Qualitatively different chemical behavior is observed in the $(Ar\text{-}H_2)^+$ system, and can also be rationalized by a similar analysis of the asymptotic potential energy surfaces displayed in Figure 2. Again, since the reactants $H_2{}^+ + Ar$ and the products $ArH^+ + H$ dissociate to $H^+ + H + Ar$, it is not surprising that there is an adiabatic surface which leads to reaction.

In the lowest approximation, one would not expect that there is a surface which permits reaction of Ar^+ with H_2 to produce ArH^+ in its ground state. However, because of the near coincidence of the ionization energies of Ar and H_2 (15.76 and 15.43 eV, respectively), the potential curve for $H_2{}^+$ (and Ar) intersects that for H_2 (and Ar^+) very near the equilib-

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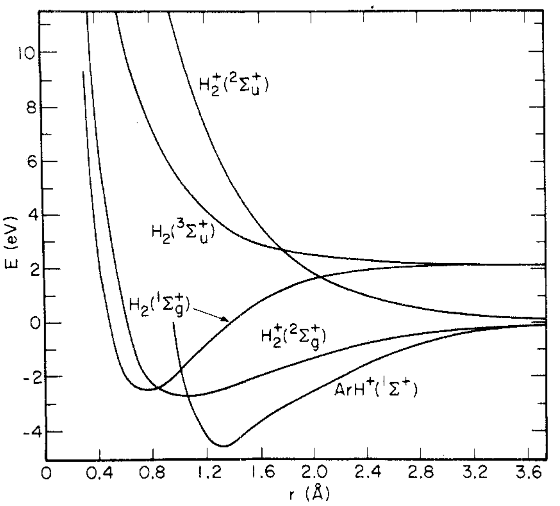

Figure 2. Potential energy curves for the diatomic reactants and products of the $(Ar\text{-}H_2)^+$ system. Note that the crossing of the curves for $H_2(^1\Sigma_g^+)$ and $H_2^+(^2\Sigma_g^+)$ occurs very near the minimum energy of the former state. This crossing becomes avoided when all three atoms are close to each other, and permits formation of ArH^+ from $H_2 + Ar^+$, as well as from $H_2^+ + Ar$.

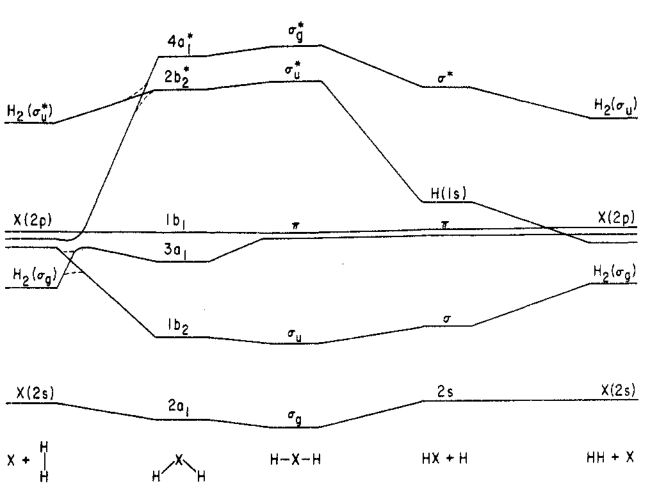

Figure 3. A molecular orbital correlation diagram for the approach of a second-row atom or ion to hydrogen. At the left, the correlations are made assuming C_{2v} conformations, whereas at the far right, a collinear approach is assumed. The mixing of a_1 and b_2 orbitals which occurs when the system is distorted to C_s symmetry is indicated by dashed lines.

rium internuclear distance of H_2. As the argon–hydrogen distance decreases in a collision, this intersection becomes avoided, and lower and upper adiabatic noncrossing surfaces are generated.[8,13]

The lower adiabatic surface has the character of $Ar^+ + H_2$ at small H-H separation, and of $Ar + H_2^+$ at larger H-H separations. Thus, during a collision of Ar^+ and H_2, the system can pass adiabatically to regions closely related to $Ar + H_2^+$ by expansion of the H-H distance. If the collision is of a grazing nature, the argon and hydrogen may separate in this electronic condition, and thereby produce the simple charge exchange products $Ar + H_2^+$. It is also easy to imagine that if the collision is of a more intimate nature, production of ArH^+ and H can occur. Both these processes have been observed experimentally. Moreover, an exact classical trajectory analysis of $Ar^+\text{-}H_2$ collisions by Chapman and Preston[13] shows very clearly that grazing collisions lead principally to electron transfer, while more intimate collisions lead to atom transfer.

The foregoing analyses show how knowledge of the asymptotic properties of reactants and products can be used to rationalize or predict the chemical behavior of systems that can lead to more than one set of reaction products. It is seen that the central points of the analysis are delineation of the adiabatic correlations between reactants and products and recognition of surface intersections and of avoided surface crossings. An important lesson to be learned is that these avoided surface intersections can lead to products whose electronic orbital configurations do not correlate in lowest order with those of the reactants. This type of analysis can also be applied to rationalize the qualitative nature of the detailed reaction dynamics, as the following examples show.

The $C^+\text{-}H_2$ and $N^+\text{-}H_2$ Systems

The reaction of C^+ with H_2 provides a particularly instructive example of the correlation of electronic structure and reaction dynamics. Ion-beam scattering experiments[14] show that the velocity vector distribution of the CH^+ product has considerable symmetry about the ±90° axis in the center-of-mass coordinate system. As has been extensively discussed,[14,15] this is consistent with, but does not necessarily indicate, the occurrence of a CH_2^+ collision intermediate whose lifetime is greater than a molecular rotational period. Superficially, such a "long-lived" collision complex might be expected from the fact, known from appearance potential measurements, that the $^2A_1$ ground state of CH_2^+ lies approximately 4.3 eV below the minimum energy of the reactants $C^+ + H_2$, and 4.7 eV below the products $CH^+(^1\Sigma)$ and H. Such a potential energy well can produce the long-lived collision complex that is suggested by the experimental data. However, the question which should be answered is whether or not the potential-energy well is accessible to reactants by a low-energy adiabatic path. In other words, does C^+ readily insert into H_2 to form the symmetric CH_2^+?

A first attempt to answer this question can be made by using a molecular orbital correlation diagram to determine how the various possible electron configurations of the reactants evolve to those of the intermediate CH_2^+. An orbital correlation diagram suitable for this analysis is shown in Figure 3.

We consider the part of the diagram in which C^+ approaches H_2 along the perpendicular bisector of the bond, so that the system remains in the C_{2v} point group. From Figure 3, which shows only the valence-shell orbitals, it is clear that, in the $^2A_1$ ground state of CH_2^+, the C-H bonding $2a_1$ and $1b_2$ orbitals are doubly occupied, and the largely nonbonding $3a_1$ orbital is singly occupied. For $C^+(^2P)$ approaching H_2 in the C_{2v} (isoceles triangle) conformation, we have two electrons in the carbon $2s(a_1)$ orbital, two more in the hydrogen $\sigma_g(a_1)$ orbital, and one electron in the carbon 2p orbital, which may be of b_1, b_2, or a_1 symmetry, depending on whether the symmetry axis of the orbital is perpendicular to the nuclear plane, or in-plane parallel or perpendicular

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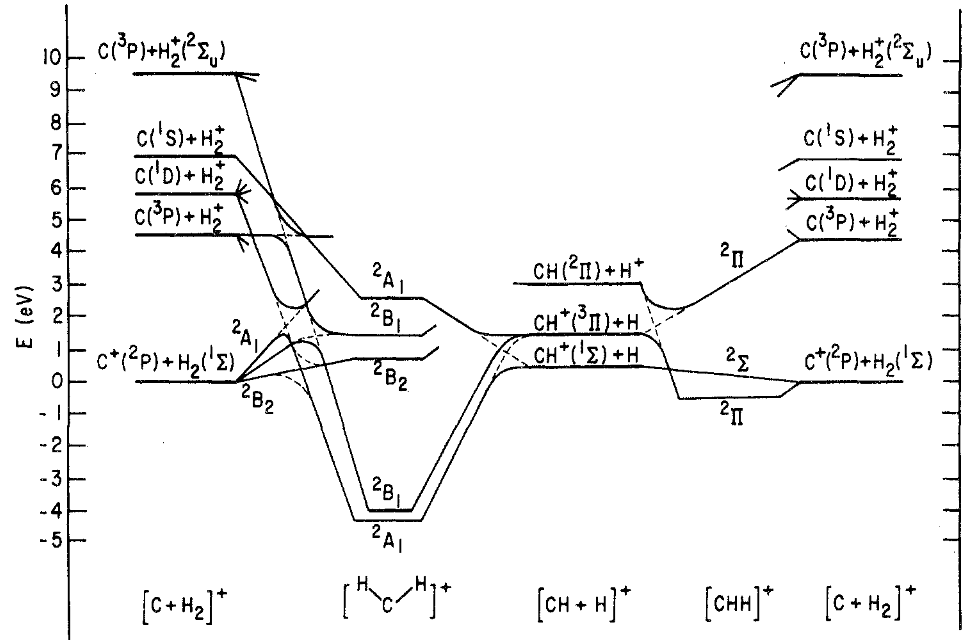

Figure 4. A correlation diagram linking the electronic states of reactants, intermediates, and products of the $(C{-}H_2)^+$ system. On the left of the diagram, states which arise for isosceles triangular conformations (C_{2v}) are indicated, while on the right, correlations for collinear unsymmetrical conformations are shown. The crossing of the $^2B_2$ and $^2A_1$ states which occurs for strict C_{2v} symmetry is avoided in C_s symmetry, as is indicated by the dashed curves.

to the internuclear axis of H_2. The latter choice generates a $^2A_1$ potential surface, since all electrons are in orbitals of a_1 symmetry. Thus, this $^2A_1$ surface which has lowest energy in the reactant region does not have the same orbital occupancy as does the $^2A_1$ electronic ground state of CH_2^+ near its most stable equilibrium geometry. In fact, as Figure 3 shows, the orbital occupancy of the reactants corresponds to the configuration $(2a_1)^2(3a_1)^2(4a_1^*)^1$, in which the bonding $1b_2$ orbital is unoccupied, and the antibonding $4a_1^*$ orbital possesses one electron.

Consideration of the electron configuration leads to the conclusion that, as C^+ approaches H_2 on the $^2A_1$ surface, the potential energy must rise. Eventually this "reaction" surface must attempt to cross the $^2A_1$ surface which has the ground-state electronic configuration and which dissociates in the lowest or diabatic approximation to $C(^1D)$ and $H_2^+(^2\Sigma_g^+)$. The result is the behavior indicated on the electronic state correlation diagram, Figure 4. While a correlation diagram can only represent the true potential-energy surface in a very limited and almost entirely qualitative manner, certain features can be displayed with considerable assurance. In Figure 4, we see that the $^2A_1$ ground state of CH_2^+ is accessible to the reactants $C^+(^2P)$ and H_2, but only if the system passes over what must be a considerable potential-energy barrier.

It is important to note how both state and orbital correlations contribute to this conclusion. Since states of the same symmetry do not cross, the lowest $^2A_1$ state of reactants must correlate adiabatically to the lowest $^2A_1$ state of the intermediate. However, this forces the electron orbital occupancy to change as the system evolves from reactants to the intermediate. Consideration of the orbitals occupied in the reactants leads to the conclusion that they are separated from the intermediate by a potential energy barrier.

Much the same argument can be constructed for the $^2B_1$ surface of Figure 4. On this surface, reactants have an electronic configuration which according to Figure 3 correlates to the highly excited $(2a_1)^2(3a_1)^2(1b_1)^1$ configuration of CH_2^+. The configuration of the lowest $^2B_1$ state of CH_2^+ near its equilibrium conformation is $(2a_1)^2(1b_2)^2(1b_1)^1$, which corresponds to the highly excited reactants $C(^3P)$ and $H_2^+(^2\Sigma_u^+)$. Thus the $^2B_1$ surface must have a potential energy barrier between the reactants and the potential energy well, as is indicated in Figure 4. Again, access of reactants with low kinetic energy to the strongly bound regions of CH_2^+ is blocked.

The behavior of the $^2B_2$ surface is qualitatively different from that of the two previous situations. The electronic configuration of the reactants on the $^2B_2$ surface corresponds to $(2a_1)^2(1b_2)^1(3a_1)^2$, the expected configuration of the lowest $^2B_2$ state of CH_2^+. Because there are three bonding electrons and no antibonding electrons present, the surface might be expected to be flat or slightly attractive at large $C^+{-}H_2$ distances. In fact, *ab initio* calculations[16] show that the surface is rather flat initially, but rises at small $C^+{-}H_2$ separations. The $^2B_2$ surface therefore crosses the lowest $^2A_1$ and $^2B_1$ surfaces in the region where they are rapidly dropping in energy. These crossings are allowed in strict C_{2v} nuclear conformations because of the different symmetries of the states. It therefore appears that, in C_{2v} conformations, reactants with low kinetic energy do not have access to the deep potential-energy wells associated with the $^2B_1$ and $^2A_1$ states of CH_2^+. In the light of these considerations alone, it would be hard to understand the occurrence of a long-lived collision complex in the $C^+(H_2,H)CH^+$ reaction at low kinetic energies.

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A significant new feature appears when scalene triangular geometries for CH_2^+ are considered. In the C_s point group, the $^2B_1$ state of CH_2^+ becomes $^2A''$, but both the $^2A_1$ and $^2B_2$ states become $^2A'$. Thus the crossing of the $^2B_2$ and $^2A_1$ surfaces, allowed in C_{2v} symmetry, becomes avoided in C_s symmetry. Accordingly, reactants on the $^2B_2$-$^2A'$ surface can pass adiabatically by a low-energy path to the $^2A'$-$^2A_1$ ground state of CH_2^+. The deep potential-energy well of CH_2^+ is therefore accessible to the reactants even when they have low kinetic energy, and the occurrence of a long-lived collision complex in the $C^+(H_2,H)CH^+$ reaction is quite reasonable.

There is a rather pictorial description of the mixing of the $^2A_1$ and $^2B_2$ states that occurs when the C^+-H_2 collision complex is distorted from C_{2v} to C_s geometry. The carbon 2p orbitals which lie in the (yz) plane defined by the nuclei together produce in the isolated atomic ion an electron distribution which is cylindrically symmetric, and appears to be a doughnut in the yz plane. As C^+ approaches H_2, the doughnut-like electron distribution is distorted. If the nuclear conformation has C_{2v} symmetry, these in-plane orbitals can be resolved and expressed in terms of either the conventional $2p_z(a_1)$ or $2p_y(b_2)$ orbitals of carbon, which point respectively perpendicular and parallel to the axis of H_2. Occupation of one of these orbitals produces either the $^2A_1$ or $^2B_2$ surface.

When the nuclear conformation departs from C_{2v} symmetry, *both* these surfaces contain contributions from what have been designated as the a_1 and b_2 2p orbitals, both mixed with the $\sigma(a')$ orbital of H_2. The lower of the two $^2A'$ surfaces generated in this manner has the lowest lying a' orbitals occupied to the maximum extent possible. Its close relation to the $^2A_1$ ground state of CH_2^+ is displayed by writing the electron configuration as $(2a_1\text{-}2a')^2(1b_2\text{-}3a')^2(3a_1\text{-}4a')^1$, which shows the association of the orbitals in C_{2v} and C_s symmetry explicitly. In brief: on the lowest energy surface available to $C^+ + H_2$, all electrons have a' symmetry for C_s nuclear conformations. This surface evolves adiabatically to the ground state of CH_2^+, which has its minimum energy in the symmetric C_{2v} conformation, and is then designated $^2A_1$.

The foregoing arguments were constructed in anticipation and as rationalizations of the experimental results[14] on the reactive scattering of C^+ by H_2. Subsequent to the completion of that work and construction of the arguments based on the correlation diagram, Liskow, Bender, and Schaefer[16] performed extensive SCF-CI calculations to determine certain profiles of the C^+-H_2 potential-energy surfaces. Some of the results of these calculations are shown in Figure 5. The barrier on the $^2A_1$ surface between reactants and the complex anticipated from the correlation diagram is nicely confirmed by the calculations. The barrier on the $^2B_1$ surface, which was not anticipated in the original work, is also clearly demonstrated. As required by experiment, the calculations show that for C_s geometries the $^2B_2$ and $^2A_1$ states interact to form a $^2A'$ surface which provides a low-energy path from reactants to the $CH_2^+(^2A_1)$ potential-energy well. Thus the major qualitative features of the potential surface deduced from experiments, correlation diagrams, and the asymptotic properties of reactant, product, and intermediate states are substantially confirmed by the *ab initio* calculation.

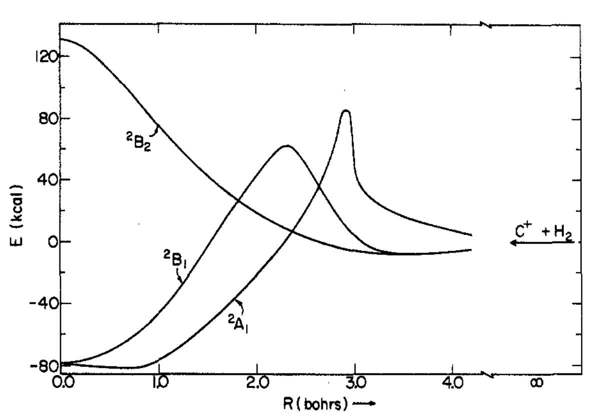

Figure 5. Calculations by Liskow, Bender, and Schaefer of the minimum energies on the lowest $^2A_1$, $^2B_1$, and $^2B_2$ states of CH_2^+. The coordinate R is the distance between the center of mass of H_2 and the carbon nucleus. Note the barriers between reactants and the CH_2^+ complex on the $^2A_1$ and $^2B_2$ surfaces. The crossing of the $^2A_1$ and $^2B_2$ surfaces shown here becomes avoided when the system is distorted to C_s symmetry.

Can the lessons learned from this analysis be profitably applied elsewhere? The reaction of $N^+(^3P)$ with H_2 to give NH^+ provides a test. This reaction is thermoneutral or slightly exoergic, and it is known that the potential energy of symmetric NH_2^+ in its $^3B_1$ ground state lies approximately 6 eV below that of reactants and products. If this state is accessible to low-energy reactants, a long-lived collision complex should be observed.

Construction of the correlation diagram for the N^+-H_2 reaction is greatly aided by our knowledge of the C^+-H_2 system. As $N^+(^3P)$ approaches H_2 in the C_{2v} conformation, $^3B_1$, $^3B_2$, and $^3A_2$ states are generated. The $^3B_1$ state is very closely related to the $^2A_1$ state of the C^+-H_2 system, since it can be generated by adding a nonbonding $1b_1$ electron to the C^+-H_2 system and appropriately increasing the nuclear charge. The $^3B_1$ surface should therefore be repulsive at large N^+-H_2 distances, and then drop abruptly to the deep ground-state potential energy well of symmetrical NH_2^+. This behavior is indicated in Figure 6.

Similarly, the $^3B_2$ state of N^+-H_2 is generated from the repulsive $^2A_1$ state of C^+-H_2 by addition of a bonding $1b_2$ electron. This surface should also be repulsive, but not as much as the $^3B_1$ state. As Figure 6 shows, the $^3B_2$ surface does not provide access to the deep potential wells of NH_2^+. The $^3A_2$ state of N^+-H_2 can be obtained from the $^2B_2$ state of C^+-H_2, again by addition of a nonbonding $1b_1$ electron. Accordingly, the $^3A_2$ surface of the N^+-H_2 system is indicated to be rather flat in Figure 6.

The surfaces appropriate for strict C_{2v} symmetry offer no access to the deep potential-energy well of NH_2^+ by a low-energy path. However, in C_s symmetry, the $^3A_2$ and $^3B_1$ surfaces both assume $^3A''$ character. Thus the crossing of the $^3A_2$ and $^3B_1$ surfaces indicated in Figure 6 is actually avoided when the system is distorted from C_{2v} symmetry. The reactants do in fact have a low-energy adiabatic path to

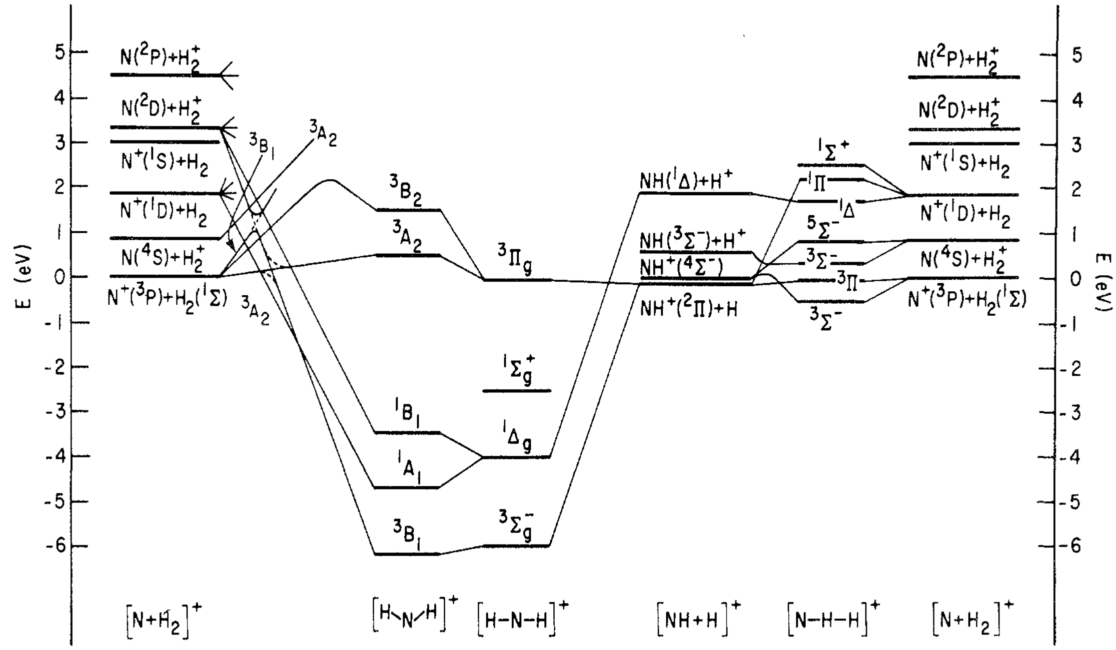

Figure 6. A correlation diagram linking the relevant electronic states of reactants, products, and intermediates of the $(N-H_2)^+$ system. The arrangement of the diagram is as in Figure 4, with C_{2v} correlations on the left, and $C_{\infty v}$ correlations on the right. Note the close resemblance to the correlation diagram for the $(C-H_2)^+$ system, particularly the crossing of the $^3A_2$ and $^3B_1$ states, which is avoided in C_s symmetry.

the potential energy well, and from there to the products $NH^+ + H$. Do the experimental measurements of the product distribution indicate the occurrence of a long-lived collision complex, as might be expected from this analysis? The velocity vector distributions of NH^+ measured at reactant energies of 2 eV and above[17] indicate that the reaction proceeds by a direct, short-lived interaction, not a long-lived complex. Only when the initial relative energy is reduced to the vicinity of 1 eV and below[18] does any indication of a long-lived complex appear.

This result is superficially surprising, since the NH_2^+ well is very deep, and might be expected to produce a long-lived collision complex at energies as high as 3 eV. However, an explanation is available. In order to reach the $^3B_1$–$^3A''$ well of NH_2^+, the reactants on the lower $^3A''$ surface must travel *adiabatically* past the region where the $^3B_1$ and $^3A_2$ surfaces intersect. In the limit of vanishing relative velocity, systems on the lower $^3A''$ surface will remain on this surface as it evolves to the $^3B_1$–$^3A''$ ground-state well of NH_2^+. However, when the relative velocity is finite, the system may exhibit *diabatic* behavior, and make a transition to the upper $^3A''$ surface. At small N^+–H_2 separations this surface is related to the excited $^3A_2$ state of NH_2^+, which has no deep potential energy well. As Figure 6 shows, the system can then evolve to the products $NH^+ + H$.

Motion on the diabatic $^3A''$–$^3A_2$ surface should lead to product formation by a direct, short-lived interaction. The velocity vector distribution of NH^+ should therefore be asymmetric at the higher relative energies, as is observed experimentally. At low relative energies, the system should behave adiabatically, and remain on the lower $^3A''$–$^3B_1$ surface, visit the deep potential-energy well, and form product by a long-lived interaction. The greater the splitting between the upper and lower $^3A''$ surfaces and the smaller the initial relative translational energy, the more pronounced will be this adiabatic behavior. Thus it is the separation between the two $^3A''$ surfaces rather than the depth of the potential-energy well which controls formation of a long-lived complex in this system.

The foregoing argument provides an adequate explanation of the behavior of the N^+–H_2 system. However, its validity probably can only be established by an elaborate calculation of the exact potential-energy surfaces in the region of the $^3A_2$–$^3B_1$ intersection. While this example illustrates the limitations of the predictions that can be made from asymptotic state properties and correlation diagrams, it also shows how these techniques can lead to recognition of at least the possibility of certain types of otherwise unexpected behavior.

In his paper which first outlined the electronic state correlation technique, Shuler[3] emphasized the importance of correlating reactants and products through the least symmetric intermediate complex. The formation of long-lived intermediates in the C^+–H_2 and N^+–H_2 systems illustrates this point, since it is only the scalene triangular conformations that provide low-energy adiabatic paths from reactants to the deep potential well of the intermediate. On the other hand, it is important to realize that, if only C_s conformations had been considered, an important aspect of the N^+–H_2 problem would have been overlooked.

In highly symmetric nuclear conformations, the electronic states each belong to one of a variety of symmetry species. Some of these states of different symmetry may cross each other. In less symmetric conformations, fewer symmetry species are available, and some of the states which crossed in symmetric conformations may belong to the same symmetry

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species of the less symmetric conformation. Thus their crossings become avoided as the intermediate is distorted. However, because these states cross in symmetric conformations, they will approach each other closely even in less symmetric conformations, thereby facilitating diabatic behavior, or electronic transitions in the course of reaction. In short, making correlation diagrams for symmetric conformations is a good way to discover the possibility of diabatic behavior.

A brief comment on the dynamics of the $O^+(H_2,H)OH^+$ reaction[19,20] is in order because of its obviously close relation to the C^+–H_2 and N^+–H_2 systems. The $^2B_1$ ground state of H_2O^+ lies approximately 5 eV below the ground states of the reactants and products, and again one can entertain the possibility that a long-lived complex reaction mechanism will be followed. However, the correlation diagram[17] for this system shows that the reactants $O^+(^4S)$ + $H_2(^1\Sigma_g{}^+)$ move initially on a $^4A_2$–$^4A''$–$^4\Sigma$ surface which leads adiabatically to products, and has no deep wells that can produce a long-lived collision complex. This $^4A_2$ surface does cross the $^2B_1$ surface that leads to the ground state of H_2O^+. Because electron spin is for the most part conserved in systems of low atomic number, systems on the $^4A_2$–$^4A''$–$^4\Sigma$ surface cannot reach the deep $^2B_1$ well with any appreciable probability. Consequently, it is not surprising that this reaction proceeds by a direct, short-lived interaction mechanism even at the lowest energies.[21]

Summary

Analysis of the behavior of a number of triatomic ion–molecule systems shows that certain properties of the reactants, products, and intermediates can be used to deduce the feasibility, course, and detailed dynamic mechanism of a reaction. Correlation of the electronic *states* of reactants and products is important for, in the course of a reaction, the principal contributing electronic orbital configuration may change substantially.

In constructing these correlation diagrams, information from one system may be used to ascertain the qualitative nature of some of the potential-energy surfaces in other systems. Surface crossings and avoided crossings are important. To ascertain the existence of these features, it is necessary not only to correlate states corresponding to highly symmetric nuclear conformations but to consider the effects of distortions to lower symmetry. Also, the effect of variation of coordinates other than what appears to be the reaction coordinate should be assessed. Both adiabatic and diabatic behavior near avoided crossings is possible and has been observed to affect the reaction dynamics profoundly.

It is to be hoped that there will be continued development of methods which permit facile quantitative assessment of the nature of avoided crossings of potential-energy surfaces without extensive computational effort.

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