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We examine the application of molecular orbital correlation diagrams to ion-molecule collision processes. In situations where the reactant and product orbitals are few in number and well spaced in energy, the correlation diagrams give a clear picture of how the reactant electron configuration evolves to that of the products. The diagrams lead to a simple explanation of why the endothermic \( H_2^+ (He, H) HeH^+ \) and \( H_2^+ (Ne, H) NeH^+ \) reactions occur, whereas the exothermic processes \( He^+ (H_2, H) HeH^+ \) and \( Ne^+ (H_2, H) NeH^+ \) have undetectably small cross sections. Similarly, it is possible to use the diagrams to explain why the \( CO^+ (H_2, H) HCO^+ \) and \( N_2^+ (H_2, H) N_2H^+ \) reactions proceed by direct interaction mechanisms despite the substantial stability of the intermediate ions \( H_2CO^+ \) and \( N_2H^+ \). Several other applications of the diagrams are discussed.
In recent years, much experimental evidence concerning the nature of gaseous ion-molecule reactions has been obtained. While the origin of the sometimes spectacularly large cross sections of these reactions is understood, a number of other phenomena have been discovered that so far have had no clear, generally accepted explanation. For example, the reaction of $\text{H}_2^+$ with He to form $\text{HeH}^+$ and H is a well-known, slightly endothermic reaction which has a substantial cross section at kinetic energies above threshold. However, the corresponding strongly exothermic reaction between $\text{He}^+$ and $\text{H}_2$ does not occur. The analogous situation holds for the $(\text{Ne-H}_2)^+$ system. In contrast, for $(\text{Ar-H}_2)^+$ and $(\text{Kr-H}_2)^+$, formation of the rare gas hydrides occurs regardless of where the charge initially resides.

Another apparently puzzling set of phenomena is the observation that the $\text{N}_2^+(\text{H}_2,\text{H})\text{N}_2\text{H}^+$ and $\text{CO}^+(\text{H}_2,\text{H})\text{HCO}^+$ reactions proceed by direct, impulsive interactions, rather than through persistent complexes, even at low relative kinetic energies. The intermediate ions $\text{N}_2\text{H}^+$ and $\text{H}_2\text{CO}^+$ formed by electron impact are well known to be stable. Their stability makes it clear that the potential energy surfaces for these systems have the deep wells which should make the effects of persistent complexes appear in the product angular distributions. In fact, a persistent complex has been detected in the highly analogous $\text{O}_2^+(\text{H}_2,\text{H})\text{HO}_2^+$ reaction, and this makes it even less clear why the reactions of $\text{N}_2^+$ and $\text{CO}^+$ with $\text{H}_2$ proceed by an impulsive mechanism.
The answer to these questions lies, of course, in consideration of the detailed potential energy surfaces for the reactions. However, these surfaces are not yet available, and may be obtained for polyatomic systems only after the expenditure of considerable cost and effort. In the meantime, interpretation of scattering and rate data must be based on qualitative features of the potential energy surfaces discerned by approximate methods.

The most obvious feature common to the surfaces for ion-molecule reactions is the strong, long-range attraction which arises from the dipole moment induced in a polarizable molecule by the approaching ion. This ion-induced dipole interaction potential varies as $-\alpha e^2/(2r^4)$, where $\alpha$ is the molecular polarizability, $e$ is the electronic charge, and $r$ is the ion-molecule separation. This potential has been used successfully and probably correctly to rationalize the magnitude and energy dependence of the cross sections of many ion-molecule reactions in the limit of low relative kinetic energies of collision. It has also been used, however, with less obvious validity to interpret phenomena which arise from the relatively short range interactions involved in the details of atom transfers, isotope effects, and the occurrence of sticky collisions. The expression for the ion-induced dipole potential is derived in the perturbation and point dipole limits. Therefore, any accuracy it exhibits for intermolecular separation which are of the order of bond distances or for potential energies which
are appreciable fractions of typical electronic excitation energies, must be considered quite accidental. Moreover, the ion-induced dipole potential gives no information about the details of the bond making and breaking processes which are the essence of chemical reaction. It is clear that some more detailed guidance concerning the potential energy surface, even if of a qualitative nature, would be useful.

As any bimolecular reaction occurs, the molecular orbitals of the reactants interact and evolve into the orbitals of the collision complex and then into those of the product molecules. Consequently it is possible to make a correlation diagram which shows the connection between the orbitals of reactants and products. The simplest such diagrams are those which correlate atomic to diatomic molecular orbitals, and such diagrams have been a very great aid to the qualitative understanding of molecular stability. More recently, Herzberg\textsuperscript{13} has given several diagrams which correlate the molecular orbitals of polyatomic molecules with those of their atomic or molecular fragments. A few diagrams which correlated orbitals of the reactants and products of chemical reaction were given by Griffing\textsuperscript{14-16} and it is her work which is the principal basis for the present paper. Another important early paper is by Schuler\textsuperscript{17} who demonstrated how to use group theory to predict the possible electronic states of reaction products. Recently, Kaufman and Koski\textsuperscript{18} have extended and applied these methods to the \(0^+ - N_2\) reaction, and Gimarc\textsuperscript{19} has discussed the \(H_2 - D_2\) reaction in these terms. In addition, there has been a
a copious demonstration of the usefulness of correlation diagrams based on molecular orbital symmetry arguments in predicting the steric course of reactions and the geometry of molecules.

In what follows we shall construct and discuss molecular orbital correlation diagrams for several ion-molecule reaction. We confine ourselves here to reactions in which the hydrogen molecule is involved, since the most detailed dynamical information is available for these processes. The procedure to be followed is straightforward. A collision geometry, preferably with some symmetry elements, is selected, and the molecular orbitals of the reactants, intermediate complex, and, if possible, the products are resolved into species of the appropriate point group. Then, starting with those of lowest energy, reactant, intermediate, and product orbitals of the same species are connected. When no useful symmetry elements are present, the nodal structure of the orbitals serves as a guide. Mixing of orbitals of different symmetry under the influence of nontotally symmetric nuclear motions is considered. Considerable guidance concerning the order of orbital energies is available from ultraviolet and photoelectron spectroscopy, and SCF calculations. Some ambiguities can be resolved and predicted features of the potential energy surfaces can be verified by appearance potential information from mass spectrometry. The resulting diagrams are strictly qualitative, but do allow one to understand several apparently paradoxical experimental findings, and provide a more rational basis for
the discussion and prediction of reaction dynamical features than has been available in the past.

THREE ATOM SYSTEMS

First we consider the correlation diagram for a linear three atom system which would apply to the He-H_2^+ reaction. The appropriate form for the diagram has been given by Griffing and Vanderslice, and Fig. 1 is an adaptation of their diagram to the (He-H_2)^+ system. By using ionization energies to measure orbital energies, we see that for the reactants, the 1s orbital of helium lies lowest, with the energy of -24.6 eV. The \( \sigma_g \) orbital of H_2 is approximately 9 eV higher, and the \( \sigma_u^* \) orbital about 10 eV higher still. As He and H_2^+ approach, the He 1s orbital evolves into a nodeless \( \sigma \) bonding orbital of the HeHH^+ complex, and drops in energy. This orbital correlates to the nodeless 1s bonding orbital of HeH^+. The \( \sigma_g \) orbital of H_2 is raised in energy as the reactants approach, and starts to correlate with the 2s orbital of HeH^+, which is strongly antibonding. On the other hand, the \( \sigma_u^* \) orbital of H_2 initially drops in energy, and starts to correlate with the 1s orbital of the hydrogen atom. The impending crossings of the two uppermost zero-order orbitals is avoided, and their interaction produces two new orbitals. The lower of these has one node located approximately at the central H-atom, and is therefore weakly antibonding between the end atoms. The upper orbital has two nodes, one between the central atom and each end atom. Consequently, it is strongly antibonding.
If one enters the initial electron configuration for He + H₂ on the diagram, it is clear that these reactants evolve adiabatically and by a minimum energy path to HeH⁺(1σ)² and H(1s)¹. This is consistent with the reaction

\[ \text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H} \quad \Delta H = 0.80 \text{ eV} \]

which has a substantial cross section for kinetic energies above the threshold.

In contrast, the electron configuration which corresponds to He⁺ + H₂ leads to a more complicated situation. Only one electron is initially in the orbital which correlates to the 1σ bonding orbital of HeH⁺. There are two possible fates for the two electrons that are initially in H₂(σ_g). Both might end up in H(1s), giving the very high energy products HeH⁺⁺ and H⁻. Alternatively, one electron might enter H(1s), and the other the 2σ antibonding orbital of HeH⁺. The consequence of the latter disposition would be a normal hydrogen atom plus an excited, unbound HeH⁺(1σ)¹(2σ)¹ which would separate to He⁺ and H. The result of He⁺-H₂ collisions would be simply the dissociation of hydrogen, if sufficient initial relative kinetic energy were available, or the inelastic and elastic scattering of He⁺ at lower energies.

The latter prediction seems consistent with experimental observations. The cross section²¹ for atom transfer to He⁺ from H₂ is less than 10⁻¹⁸ cm², and for dissociative charge exchange,²² less than 0.6 Å².
The \( (\text{Ne-H}_2)^+ \) system behaves essentially identically\(^2,^3,^22\) to the \( (\text{He-H}_2)^+ \) system. Formation of \( \text{NeH}^+ \) from Ne and \( \text{H}_2^+ \) is well known, but no chemical products from the charge exchanged reactants have been detected. The orbital correlation diagram for \( (\text{Ne-H}_2)^+ \) is very similar to Fig. 1, since the ionization energies of \( \text{H}_2 \) (15.5 eV) and Ne (21.4 eV) are quite different, and the first excited state of \( \text{NeH}^+ \), like that of \( \text{HeH}^+ \), is very probably unbound. Thus, as was predicted for \( \text{He}^+ \), \( \text{Ne}^+ \) should be scattered elastically, inelastically, and at high energies, with dissociation of \( \text{H}_2 \). In fact, we have found experimentally\(^23\) that at high relative energies (16 eV) \( \text{Ne}^+ \) is back scattered from \( \text{D}_2 \) both elastically, and inelastically with a large relative energy loss (7 eV).

We see that correlation diagrams lead to an explanation of the apparently puzzling behavior of the \( (\text{He-H}_2)^+ \) and \( (\text{Ne-H}_2)^+ \) systems. This success or integrity of the correlations can in large measure be attributed to large difference in the ionization energies of hydrogen and the lighter rare gases, which leads to well-separated potential surfaces for the two initial charge states. Such dramatic chemical inequivalence of reactants and their charge exchanged state may well occur in other systems, for example, \( \text{F}^+ + \text{Li}_2 \) or \( \text{Mg}^+ + \text{H}_2 \). When the highest occupied orbitals of the reacting partners have nearly the same energy, however, we would expect that a pair of reactants and their charge exchanged state would produce the same chemical products.
An example of the latter situation occurs in the \((\text{Ar-H}_2)^+\) system. Both the reactions

\[
\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}
\]

\[
\text{Ar} + \text{H}_2^+ \rightarrow \text{ArH}^+ + \text{H}
\]

are known to be rapid. A correlation diagram appropriate for them is shown in Fig. 2. The ionization energy of Ar to its ground \(3\text{P}_{3/2}\) state is 15.76 eV, and can be taken as the energy of the 3p orbital of Ar. The energy of the \(\sigma_g\) orbital of \(\text{H}_2\) is rather ill-defined, however. While the adiabatic ionization energy of \(\text{H}_2\) is 15.45 eV, the vertical ionization energy is 16 eV, and the vertical recombination energy of \(\text{H}_2^+\) is 14.5 eV. Depending on which of these is chosen as the energy of the \(\sigma_g\) orbital, it is degenerate with, or lies below or above the 3p orbital of Ar. Consequently, we indicate the position of \(\text{H}_2(\sigma_g)\) by a band of approximately 2 eV amplitude in Fig. 2.

The significance of this uncertainty in the orbital energy is considerable. In constructing and interpreting the correlation diagrams, we are following the zero order rule that the valence orbital of lowest energy in the reactants correlates with the lowest energy orbital of the product. If the reactant orbitals are degenerate or nearly so, this unique association cannot be made. Consequently, the systems \(\text{Ar}^+\text{-H}_2\) and \(\text{Ar}\text{-H}_2^+\) must be considered equivalent, and both correlate to the ground state orbital occupancy of the collision complex and the reaction products.
There is another way of looking at this problem. The most appropriate value for the energy of the $\sigma_g$ orbital in $H_2$ might be the vertical ionization energy, 16 eV. Thus for the $Ar^+-H_2$ reaction, we might assume that it is the lower energy, doubly occupied $H_2(\sigma_g)$ orbital which correlates to the lowest orbital of $ArH^+$. Since this orbital is doubly occupied, the products are formed in their ground states. For the $Ar-H_2^+$ reaction, the appropriate energy for the hydrogen $\sigma_g$ orbital might be 14.5 eV, the vertical recombination energy for $H_2^+$. Thus in this case the lowest reactant orbital is the doubly occupied $Ar(3p)$, which now correlates with the product ground state. Once again, adiabatic correlation forms products in their ground states, and we conclude that both charge states of $(Ar-H_2)^+$ are equivalent. The same argument applies to $(Kr-H_2)^+$, where similar behavior is observed experimentally.

The uncertainty in orbital energies becomes even more important for polyatomic ions and molecules. In interpreting the correlation diagrams for such systems, it must be remembered that sometimes rather small distortions in the nuclear framework can bring the energies of certain molecular orbitals into near coincidence, and thereby greatly influence the correlations between reactants and products.

For the reactions of atomic ions like $C^+$, $N^+$, $O^+$, and $F^+$ with $H_2$, one may ask whether an insertion of the ion to form a bent or linear $H-X-H^+$ ion can occur. Were such ions formed from reactants in their ground states, the velocity vector distributions of the eventual reaction products $HX^+$ and $H$ might
show the symmetry associated with the occurrence of a persistent collision complex for low collision energies. To treat this problem, we assume that the atomic ion approaches along the perpendicular bisector of the \( H_2 \) bond, and the \( C_{2v} \) symmetry is maintained until valence interactions have begun. We use the resulting correlation diagram between reactant orbitals and those of the bent and linear complexes to decide whether the ground state of the complex can be reached adiabatically, and also to consider whether orbital mixing which results from distortions from \( C_{2v} \) symmetry is important.

We begin by resolving the orbitals of the ion and \( H_2 \) into the species of \( C_{2v} \). This can be done with the assistance of tables provided by Herzberg,\(^{13}\) or in this simple case, by inspection. The \( \sigma_g \) and \( \sigma_u \) orbitals of hydrogen transform as \( a_1 \) and \( b_2 \) in \( C_{2v} \), while the \( p \) orbitals of the heavy atom resolve into \( a_1, b_1, \) and \( b_2 \). The orbital energy level diagram for bent and linear \( H-X-H \) molecules has been given by Walsh,\(^{25}\) and it is a simple matter to make the appropriate correlations which result in the diagram in Fig. 3. The \( H_2 \) \( \sigma_g \) orbital is set below the \( 2p \) atomic orbitals, but the modifications which must be made when these levels are reversed are obvious.

We must expect that there will be no crossing of the \( a_1 \) orbitals which originate as \( \sigma_g \) and \( p \) of the reactants, and consequently an avoided crossing is shown. The question of whether deviation from \( C_{2v} \) symmetry mixes the \( a_1 \) and \( b_2 \) orbitals sufficiently to lead to an avoided crossing cannot be answered without detailed calculations for specific cases. For the present, we shall assume that no mixing occurs.
Now consider the two associative detachment reactions\(^{26,27}\):

\[
\begin{align*}
C^- + H_2 &\rightarrow CH_2 + e \quad \Delta H = -2 \text{ eV}, \quad k < 10^{-13} \text{ cm}^3/\text{sec} \\
O^- + H_2 &\rightarrow H_2O + e \quad \Delta H = -3.6 \text{ eV}, \quad k = 6 \times 10^{-10} \text{ cm}^3/\text{sec}
\end{align*}
\]

Since the ground state of \(C^-\) is \(4S\), we have one electron in the \(a_1\), \(b_1\), and \(b_2\) p orbitals, all with parallel spins. Thus from Fig. 3 we see that the reactants evolve to the valence electron configuration \((2a_1)^2 (1b_2)^1 (3a_1)^2 (1b_1)^1 (4a_1)^1\). If we then imagine that the highest energy 4\(a_1\) antibonding electron is detached, we are left with a substantially excited state of \(CH_2\) which has one \(1b_2\) bonding electron promoted to the 3\(a_1\) nonbonding orbital. Thus the adiabatic autodetachment reaction would not be possible in thermal energy collisions. However, if there were mixing of the 3\(a_1\) and 1\(b_2\) orbitals induced by departures from \(C_2\)\(^v\) symmetry, the ground state configuration of \(CH_2\) could be reached, and the detachment reaction would be energetically possible. Since the reaction has a rate constant\(^{26}\) which indicates that detachment occurs less frequently than one in \(10^4\) collisions, it appears that the 3\(a_1\) and 1\(b_2\) orbitals do not mix appreciably.

For the \(O^-H_2\) reaction, in at least some of the collisions the \(O^-\) will have the p-electron configuration \((a_1)^1(b_1)^2(b_2)^2\). Figure 3 shows that this configuration, with detachment of the 4\(a_1\) electron, does evolve to the ground state of the \(H_2O\) molecule. The reaction does in fact occur with large, but less than unit collision frequency.\(^{27}\) Thus the correlation diagram, interpreted in a straightforward manner, is consistent with
two experimental facts. We are unable, however, to explain on this basis why the $S^- - H_2$ associative detachment reaction does not occur.\textsuperscript{28}

Application of the correlation diagram to the reactions of ground state C\textsuperscript{+}, N\textsuperscript{+}, O\textsuperscript{+}, and F\textsuperscript{+} with H\textsubscript{2} leads to the conclusion that in the absence of a\textsubscript{1}-b\textsubscript{2} orbital interaction in no case can the ground electronic configuration of the intermediate HXH\textsuperscript{+} molecular ion be reached adiabatically from the reactants. All four reactions can give XH\textsuperscript{+} by a direct interaction through a linear XHH\textsuperscript{+} complex, and consequently we expect to observe the asymmetry characteristic of direct interactions in the product velocity vector distributions. Only the N\textsuperscript{+}-H\textsubscript{2} reaction has been studied by measurement of product angular distributions,\textsuperscript{29} and it has been found to proceed by a direct interaction mechanism at relative energies above 3.7 eV. However, before any firm conclusion concerning the accessibility of the ground state of NH\textsubscript{2}\textsuperscript{+} is reached, the reaction should be studied at lower relative energies. The C\textsuperscript{+}(H\textsubscript{2},H)CH\textsuperscript{+} reaction has been studied with a fixed tandem mass spectrometer\textsuperscript{30} but apart from the finding that there is no barrier in excess of the endothermicity, no explicit information on the dynamics of the reaction was obtained. Further investigations of this closely related series of reactions at low relative energies should be valuable.
FOUR CENTER SYSTEMS

Here we consider such reactions as

\[ \text{CO}^+ + \text{D}_2 \rightarrow \text{DCO}^+ + \text{D} \quad \Delta \text{H} = -1.0 \text{ eV} \quad (1) \]
\[ \text{N}_2^+ + \text{D}_2 \rightarrow \text{N}_2\text{D}^+ + \text{D} \quad \Delta \text{H} = -2.1 \text{ eV} \quad (2) \]
\[ \text{O}_2^+ + \text{D}_2 \rightarrow \text{DO}_2^+ + \text{D} \quad \Delta \text{H} = 2.0 \text{ eV} \quad (3) \]
\[ \text{C}_2\text{H}_2^+ + \text{D}_2 \rightarrow \text{C}_2\text{H}_2\text{D}^+ + \text{D} \quad \Delta \text{H} = 0.2 \text{ eV} \quad (4) \]

Reactions 1-3 have been studied extensively\(^5,6,8,31-33\) by product velocity vector distribution measurements over a wide range of initial energies, and details of such experiments for the acetylene-deuterium reaction will be reported subsequently.\(^34\)

There are some clear chemical similarities among these reactions, but the most important for our purposes is that in each case, the ground state potential energy surface has a substantial minimum for at least one configuration of the atoms. That is, the ions \(\text{H}_2\text{CO}^+, \text{N}_2\text{H}^+, \text{H}_2\text{O}^+,\) and \(\text{C}_2\text{H}_4^+\) are well known in mass spectrometry, and their appearance potentials show that they lie 2.5 to 3 eV below the separated reactants in reactions 1-4. Considering this common feature and the similar molecular complexities it has been quite surprising to find that reactions 1 and 2 proceed by direct interaction mechanisms even at quite low energies, while in reactions 3 and 4, persistent complexes are involved.

We consider reaction 1 as involving a collision which maintains \(C_{2v}\) symmetry until the intermediate \(\text{H}_2\text{CO}^+\) is formed. The orbitals of \(\text{CO}^+\) and \(\text{H}_2\) are resolved into the species of
and then systematically correlated with the orbitals of formaldehyde. The resulting correlation diagram is shown in Fig. 4. An approximate energy scale is provided, with the energies of the various orbitals of the reactants and intermediate located using the results of photoelectron and ultraviolet spectroscopy. The positions of the higher antibonding orbitals, the orbitals of HCO⁺, and of the crossing points are largely conjecture. While the energetics of the \( H_2\text{-CO}^+ \) system have guided construction of the diagram, no emphasis is placed on the numerical values of the energies, so the diagram should be applicable with minor modifications to any \( H_2\text{-X}_2^+ \) or \( H_2\text{-XY}^+ \) system in which the order of the orbitals is similar.

As \( H_2\text{CO}^+ \) is formed from \( H_2 \) and \( \text{CO}^+ \), we expect the oxygen 2s orbital to remain essentially unchanged, while the carbon 2s and hydrogen \( \sigma_g \) orbitals combine to form a pair of orbitals which initially correlate with an \( a_1 - a_1^* \) pair which are C-H bonding and antibonding. The \( \pi \sigma \) bonding orbital of \( \text{CO}^+ \) starts to correlate with the C-O \( \sigma \) bonding orbital of formaldehyde. As a result, there is an avoided crossing of two \( a_1 \) orbitals, and the \( \sigma_g \) orbital of \( H_2 \) appears to correlate with the C-O \( \sigma \) orbital of formaldehyde, while the \( \sigma \) orbital of \( \text{CO}^+ \) correlates with the C-H antibonding \( a_1^* \) orbital of formaldehyde. The other correlations are quite straightforward. One \( \pi \) orbital of \( \text{CO}^+ \) correlates with the \( \pi \) bonding orbital of \( H_2\text{CO}^+ \), while the other combines with the \( \sigma_u^* \) orbital of hydrogen to produce
a C-H bonding-antibonding pair. The $b_2^n$ nonbonding orbital of formaldehyde comes largely from the $b_2\pi^*$ orbital of CO$^+$. Consider now the adiabatic evolution of CO$^+$(2$\Sigma^+$) and H$_2$(1$\Sigma_g^+$) into the complex H$_2$CO$^+$. One electron is missing from the bonding $\pi\sigma$ orbital of CO$^+$, so depending on the strength of the interaction between the highest occupied $a_1$ orbitals of the reactants, either one or two electrons will occupy the $a_1^*$ C-H antibonding orbital of H$_2$CO$^+$. No electrons are found in the $b_2^h$ orbital. Thus the orbital occupation reached adiabatically in the collision is not that of the ground state of H$_2$CO$^+$, but is that of an excited configuration which has one electron in a C-H antibonding orbital, and no electrons in the nonbonding $b_2^h$ orbital. In terms of the species of C$_2\nu$, the reactants correlate to a $^2A_1$ state of the complex, whereas the ground state of the complex is $^2B_2$. If this is an accurate description of the evolution of the system in a collision, then it is not surprising that the effects of the potential well associated with the ground state of H$_2$CO$^+$ are not evident in the angular distribution of products.

It may be argued that since the highest occupied $a_1$ orbital of the reactants crosses the empty $b_2$ orbital, the system can evolve to the ground state of H$_2$CO$^+$ if the $a_1$ and $b_2$ orbitals are coupled by the antisymmetric $b_2$ bending or stretching motion of the CH$_2$ group. This interaction might be expected to be weak, however, since the two orbitals concerned are largely concentrated on opposite ends of the H$_2$CO$^+$ molecule.
Therefore, the conclusion that $H_2$ and $CO^+$ correlate only with excited states of $H_2CO^+$ seems quite secure.

There is experimental evidence which supports this conclusion. The measured appearance potential of $CO^+$ from $H_2CO$ is 4.5 volts above the value calculated from the heats of formation of $H_2$, $CO^+$, and $H_2CO$. This shows that there is indeed a potential barrier between $H_2 + CO^+$ and $H_2CO^+$ which is 4.5 eV high. Since 4.5 eV is approximately the bond dissociation energy of $H_2$, the value of the appearance potential of $CO^+$ from $H_2CO$ suggests that two hydrogen atoms, rather than $H_2$, may be formed along with $CO^+$. Thus, either there is a 4.5 eV barrier between $H_2 + CO^+$ and ground state $H_2CO^+$, or only $2H + CO^+$ can correlate with ground state $H_2CO^+$. In either case, the potential well of $H_2CO^+$ is not accessible in low energy collisions of $H_2$ and $CO^+$.

If we consider the evolution of ground state $H_2CO^+$ to $H + HCO^+$, we find from the correlation diagram no reason to expect a barrier in excess of the minimum energy necessary to form products. In confirmation of this, the appearance potential of $HCO^+$ from formaldehyde is in fairly good agreement with the value calculated from thermodynamic data (including the admittedly uncertain proton affinity of $CO^+$).

The following picture emerges from the correlation diagram and appearance potentials. As shown schematically in Fig. 5a, $H_2$ and $CO^+$ approaching in the $C_{2v}$ configuration encounter a 4.5 eV barrier before reaching the region of minimum potential energy. Systems which have enough energy to surmount this barrier are very unstable with respect to $H + HCO^+$, and thus
spend only a very short time as $\text{H}_2\text{CO}^+$. A calculation using RRKM unimolecular reaction rate theory and the energetics of Fig. 5a indicates a maximum lifetime for $\text{H}_2\text{CO}^+$ which is of the order of one or two vibrational periods. The products of such processes will have an intensity distribution which is characteristic of a direct interaction. When the reactants have less than 4.5 eV initial relative energy, the region of minimum potential energy cannot be reached, and no long-lived complexes are formed.

Since the reaction between $\text{CO}^+$ and $\text{H}_2$ has a large cross section even for relative energies below 0.1 eV, there must be a path between reactants and products which does not have a potential energy barrier. This leads us to construct the correlation diagram for collinear $\text{H}_2$-$\text{CO}^+$ configurations shown in Fig. 6. There is very little guidance from experiment available to aid the construction of this diagram, aside from the orbital energies of the reactants and those of HCN, which is isoelectronic to $\text{HCO}^+$. It is clear, however, that the $\pi$ orbitals of CO evolve in a straightforward way into those of $\text{HCO}^+$. The $\sigma$ orbitals may be correlated by recognizing that to a first approximation the $\sigma_g$ and $\sigma_u^*$ orbitals of $\text{H}_2$ and the $2s$ orbital of carbon combine in the same manner as is shown in Fig. 1 for the $\text{H}_2$-He system. This simple scheme, which would result in $2s(\text{C}), \sigma_g(\text{H}_2)$ and $\sigma_u^*(\text{H}_2)$ correlating respectively with $\sigma(\text{C-H}), 1s(\text{H})$, and $\sigma^*(\text{C-H})$ of the $\text{HCO}^*$ and $\text{H}$ products, is complicated by the crossings of these $\sigma$ orbitals with the
bonding and antibonding $\sigma$ orbitals of the CO group. These interactions lead to the avoided crossings indicated in Fig. 6.

We now introduce the 11 valence electrons of the $H_2 + CO^+$ system. The $\sigma$ orbital of $CO^+$ is occupied by only one electron, with all lower orbitals filled. It is clear that as the system evolves toward $H + HCO^+$, the ground state electron configuration is maintained, and thus there is no reason to expect any substantial potential energy barriers to occur. At qualitative assessment of the bonding character of the occupied orbitals does not suggest the occurrence of any particularly deep potential well for any linear configuration. Thus the potential seems to have the qualitative characteristics which are required to explain reaction by direct interaction at even the lowest relative energies of collision.

To summarize: A correlation diagram suggests, and appearance potential measurements confirm, that there is a 4.5 eV barrier between $H_2 + CO^+$ and the ground state of $C_2V$ $H_2CO^+$. Thus the potential well corresponding to $H_2CO^+$ is not accessible in low energy collisions of $H_2$ and $CO^+$. The correlation diagram for collinear collisions suggests that there are no high barriers or deep wells between reactants and products for these configurations. The reaction should therefore proceed by a direct interaction mechanism at all energies, as is observed experimentally.

We turn now to the $N_2^+ - H_2$ system. Here the stable intermediate which might give rise to a persistent collision complex is the di-imide ion, $HN=NH^+$. We must therefore construct a
correlation diagram for the approach of \( N_2^+ \) to \( H_2 \) which leads to one hydrogen atom on each nitrogen and which maintains \( C_{2v} \) symmetry.

The result is shown in Fig. 7. The essentially nonbonding \( 2s \) \( a_1 \) and \( b_2 \) orbitals of \( N_2 \) in combination with the \( \sigma_g \) and \( \sigma_u^* \) orbitals of \( H_2 \) produce \( a_1-a_1 \) and \( b_2-b_2^* \) \( N-H \) bonding and antibonding orbital pairs in \( N_2H_2^+ \). The \( \sigma_g-a_1 \) and \( \sigma_u-b_2^* \) bonding and antibonding orbitals of \( N_2 \) evolve into the corresponding orbitals of \( N_2H_2^+ \). One \( \pi-\pi^* \) (out of plane) orbital pair of nitrogen is essentially unchanged, while the other, in-plane, \( \pi-\pi^* \) pair of orbitals becomes the \( a_1^n \) and \( b_2^n \) nonbonding orbitals of \( N_2H_2^+ \). The correlations to the orbitals of a linear HAAH molecule are also given in Fig. 7, so that the diagram can be used to discuss formation of \( C_2H_2^+ \) from \( C_2^+ \) and \( H_2 \), for example.

Insertion of the 11 valence electrons of \( N_2^+ \) and \( H_2 \) into the lowest reactant orbitals leads to the conclusion that \( N_2H_2^+ \) would be formed adiabatically with at least one electron in the \( a_1^* \) \( N-H \) antibonding orbital. This conclusion would be consistent with the fact that ion beam experiments have produced no evidence that a persistent complex occurs in this reaction. However, if one considers the possibility of orbital mixing by electronic-vibrational interaction, the situation becomes somewhat ambiguous. Distortions of species \( B_2 \) may eliminate the crossings of the curves leading to the \( a_1^* \) and \( b_2^n \) orbitals of \( N_2H_2^+ \), and thereby allow adiabatic evolution of the reactants to the ground state of \( N_2H_2^+ \). This vibronic interaction and
mixing of the $a_1^*$ and $b_2^n$ orbitals could very easily be strong, since in contrast to the situation in the $H_2CO^+$ case, the orbitals overlap rather substantially. However, even with the occurrence of this vibronic mixing, some potential barrier between the reactants and $N_2H_2^+$ might remain, and prevent low energy reactants from reaching the regions of potential energy minima.

Unfortunately, there has been no published measurement of the appearance potential of $N_2^+$ from $N_2H_2^+$, so it is not possible to use experimental data to resolve the question of the existence or importance of this barrier, as was done for the $CO^+-H_2$ system. However, an answer to this question is not necessary in order to decide why no persistent complex is observed in the $N_2^+-H_2$ system. Figure 5b shows the relative enthalpies of $N_2^++H_2$, $N_2H_2^+$, and $N_2H^++H$ which can be calculated from tabulated data and the proton affinity of $N_2$ recently measured by Schiff and coworkers. $^{37}$ The potential well of $N_2H_2^+$ is only approximately 0.5 eV deep with respect to $N_2H^++H$, and no dissociation barrier in excess of this is expected. If we assume that there is no barrier between $N_2^++H_2$ and $N_2H_2^+$, then even complexes formed by essentially zero energy collisions between $N_2^+$ and $H_2$ would have a total energy six times the minimum necessary to decompose to products. Consequently, the lifetime of such complexes would be very small, approximately $2 \times 10^{-14}$ sec, according to an RRKM calculation. This is so short that the reaction will appear to proceed by direct interaction. If
any barrier between reactants and the complex does exist, reactants with enough energy to cross it will form "complexes" whose lifetimes would be even shorter than $2 \times 10^{-14}$ sec. Moreover, the direct interaction path through linear HHNN$^+$ is also available to the system, and will undoubtedly contribute to the scattering pattern.

To summarize, we can say that it is likely that vibronic coupling makes the N$_2$H$_2^+$ potential well accessible to N$_2^+$-H$_2$ at some fairly small collision energy. However, even if this well is accessible at the lowest energies, the lifetime of the collision complex is expected to be much shorter than a rotational period, and the reaction will appear to go by a direct interaction mechanism. This is observed experimentally.

The correlation diagram which applies to the O$_2^+$-H$_2$ system is in many respects similar to that for the N$_2^+$-H$_2$ system. Once again we assume that C$_{2v}$ symmetry is maintained as a nonlinear, planar, HOOH$^+$ molecule is formed from reactants. However, the $\sigma$ bonding orbital in O$_2^+$ lies below, rather than above, the $\pi_u$ orbitals, and the 2s orbitals of O$_2$ are lower than those in N$_2$, and participate correspondingly less in the bonding. These considerations make no substantial change in the qualitative arguments which follow, and so Fig. 7 can be applied to the (O$_2$-H$_2$)$^+$ system.

In the O$_2^+$(2$\pi_g$)-H$_2$ system, one electron occupies the $\pi_g^*$ orbital of O$_2^+$, and all lower orbitals are filled. An adiabatic evolution to H$_2$O$_2^+$ would produce a highly excited molecule with the configuration $(1a_1)^2 (1b_2)^2 (2a_1)^2 (2b_2)^1 (3a_1)^2 (1b_1)^2 (1a_2)^0 (4a^*_1)^2$. However, the crossing of the orbitals which
correlate to \( \pi^*(\text{H}_2) \) and \( \pi^*(\text{O}_2) \) may be eliminated by vibronic interaction produced by the \( B_2 \) bending and stretching modes of \( \text{H}_2\text{O}_2^+ \). In addition, coupling between the antibonding \( 4a_1^* \) orbital and the \( a_2 \) orbital might arise from the torsional motion of \( A_2 \) species, but the strength of this coupling might be small. Consequently, the initial correlation of the \( \sigma_g(\text{H}_2) \) orbital to the \( 4a_1^* \) antibonding orbital, even if modified by vibronic mixing, would seem to produce a potential energy barrier between \( \text{H}_2 + \text{O}_2^+ \) and \( \text{H}_2\text{O}_2^+ \). This supposition is confirmed by experiment,\(^3\) since the appearance potential of \( \text{O}_2^+ \) from \( \text{H}_2\text{O}_2 \) indicates that there is a \( 2.5 \pm 0.5 \) eV barrier between \( \text{H}_2 + \text{O}_2^+ \) and the potential well region of \( \text{H}_2\text{O}_2^+ \).

Dissociation of a strictly planar \( \text{H}_2\text{O}_2^+ \) to \( \text{H} + \text{HO}_2^+ \) would produce an excited configuration of \( \text{HO}_2^+ \) with one electron excited from a \( \sigma^2 \) nonbonding orbital to the \( \pi^* \) orbital. This correlation to excited products can be avoided if \( \text{H}_2\text{O}_2^+ \) is non-planar, since this situation permits interaction and mixing of the \( \pi^* \) and \( \sigma^2 \) orbitals. This may very well be the correct description of \( \text{H}_2\text{O}_2^+ \) since the appearance potential of \( \text{HO}_2^+ \) from \( \text{H}_2\text{O}_2 \) shows that the ground state is formed, and that there is no barrier between \( \text{H}_2\text{O}_2^+ \) and \( \text{H} + \text{HO}_2^+ \) in excess of the dissociation energy.

We are led, therefore, to the potential energy profile given in Fig. 5c. The reason why a long-lived \( \text{H}_2\text{O}_2^+ \) collision complex occurs even for initial relative energies as high as 5 eV is now clear. There is a deep potential well which is...
a consequence not only of the stability of \( H_2O_2^+ \), but of the potential barrier in the reactant channel. Thus in this case the tendency for the reactants to correlate in the lowest approximation to an excited state of the complex actually produces the feature which is in large measure responsible for the occurrence of a persistent complex.

We can also use Fig. 7 to analyze the reaction of metastable \( O_2^+(4\pi_g) \) with hydrogen. In \( O_2^+(4\pi_g) \), only one electron occupies the \( \sigma \) bonding orbital, while the two \( \pi_g \) orbitals each have one electron. The correlation diagram shows that this necessarily leads to an excited state of \( H_2O_2^+ \), with one 0-0 \( \sigma \)-bonding electron excited to a \( 5a_1^* \) 0-H antibonding orbital. A long-lived complex would not be expected, and indeed experiment\(^{41}\) shows that the reaction proceeds by a direct interaction mechanism.

It is also useful to construct the correlation diagram for \( H_2-O_2^+ \) collisions under the assumption that the collision occurs through a planar nonlinear or L-shaped intermediate. In this case, one of the \( \pi_u \) orbitals of \( O_2^+ \) evolves to an 0-H bonding orbital on one oxygen atom, while the corresponding \( \pi_g \) orbital becomes a nonbonding orbital on the other oxygen atom. The \( \pi_u \) and \( \pi_g^* \) orbitals perpendicular to the plane of the complex remain largely unchanged, as is also true in a first approximation for the \( \sigma_g \) and \( \sigma_u^* \) orbitals of \( O_2^+ \). The \( \sigma_g \) and \( \sigma_u^* \) orbitals of \( H_2 \) evolve in the first approximation to an 0-H antibonding orbital of \( H_2O_2^+ \) and the \( 1s \) orbital of the free
hydrogen atom. The resulting diagram, Fig. 8, has several curve crossings. Since the only useful symmetry operation of such a nonlinear planar complex is reflection in the plane of the molecule, it can be argued that there is strong mixing of all orbitals which are symmetric under this operation, and consequently all crossings of such orbitals are avoided. Figure 8 has been drawn with this point in mind.

Several conclusions are possible from Fig. 8. First, \( \text{O}_2^+(\text{v}_g^2) \) can react directly with \( \text{H}_2 \) via this nonlinear complex to give \( \text{HO}_2^+ \) and \( \text{H} \). It has been suggested that the failure of the RRKM or quasiequilibrium theory to explain the relative intensities of the reaction products \( \text{HO}_2^+ \), \( \text{OH}^+ \), and \( \text{H}_2\text{O}^+ \) can be rationalized if some of the \( \text{HO}_2^+ \) is formed by a direct interaction process. Second, the direct reaction between \( \text{O}_2^+(\text{v}_g^4) \) and \( \text{H}_2 \) can occur through a nonlinear complex, but the product appears to be an excited configuration of \( \text{HO}_2^+ \) with one electron present in the \( \pi^* \) orbital, and one electron missing from the \( \sigma \) \text{O}-\text{O} bonding orbital. Similarly, the \( \text{H}_2^+-\text{O}_2 \) reaction would produce a configuration in which an electron had been excited from the \( \sigma^0 \) orbital to the \( \pi^* \) orbital. Since the reaction of \( \text{O}_2^+(\text{v}_g^4) \) with \( \text{H}_2 \) to form ground state \( \text{HO}_2^+ \) is 2.2 eV exothermic, it is possible that a low lying electronic state of \( \text{HO}_2^+ \) might be formed. The \( \text{H}_2^+-\text{O}_2 \) reaction is only 0.6 eV exothermic, however, so it is unlikely that an excited state of \( \text{HO}_2^+ \) could be produced by the reaction at room temperature. It seems likely that either the \( \pi^* \) orbitals are mixed by deviations
from planar geometry in the nonlinear 0-0-H-H complex so that the system can evolve to ground state products, or the H₂⁺-O₂ reaction proceeds through the complex which has the hydrogen peroxide structure, and which can dissociate to ground state products.

We consider now Fig. 9, the correlation diagram for the reaction of acetylene ion with hydrogen. The reactants approach with C₂ᵥ symmetry and evolve to the D₂h symmetry of ethylene. We assign the symmetry species of the orbitals consistently under the convention that the z-axis lies in the plane and is the perpendicular bisector of the carbon-carbon bond. The more conventional symmetry designations for ethylene which assume a z-axis perpendicular to the molecular plane are given in brackets.

The σ and σ* orbitals of acetylene all evolve in a straightforward and obvious way to those of ethylene. The σ₉ orbital of hydrogen combines with the in-plane πᵤ orbital of acetylene to produce a b₂ᵤ C-H bonding-antibonding pair of orbitals in ethylene, while σ*ₓ(H₂) and one π₉(C₂H₂) give in a similar manner b₃g C-H bonding and antibonding orbitals of ethylene. Only one crossing of importance occurs, which is between the lines leading to the b₃g C-H bonding and b₁ᵤ C-H antibonding orbitals of ethylene. These two orbitals could be mixed by the two B₂u vibrations of ethylene, or by motions of species B₂ as the reactants approach with C₂ᵥ symmetry. Because the two orbitals overlap rather well and are probably both sensitive
to hydrogen motion, the vibronic coupling between them is probably large.

The acetylene ion has the configuration \( \cdots \pi^3_u \), and consequently, as \( \text{C}_2\text{H}_2^+ \) and \( \text{H}_2 \) collide with \( \text{C}_2\text{V} \) symmetry, one electron is present in the \( \pi_u - a_1 - b_2u \) orbital which is initially C-H antibonding. Because only one electron is in this orbital, and because of the vibronic coupling of \( b_{2u} \) to the C-H bonding \( \pi^* - b_2 - b_{3g} \) orbital, we do not expect a large activation barrier between the reactants and \( \text{C}_2\text{H}_4^+ \). This expectation is confirmed by the experimental observation\(^7\) that the appearance potential of \( \text{C}_2\text{H}_2^+ + \text{H}_2 \) from \( \text{C}_2\text{H}_4 \) is the same as that calculated from the relevant heats of formation. Since no potential barrier in excess of the bond energy is expected for the withdrawal of one hydrogen atom from \( \text{C}_2\text{H}_4^+ \), we expect the potential energy profile shown in Fig. 5d.

Inasmuch as the deep well corresponding to \( \text{C}_2\text{H}_4^+ \) is completely accessible in low energy collisions, we expect that the reaction between \( \text{C}_2\text{H}_2^+ \) and \( \text{H}_2 \) would show evidence of the occurrence of a persistent collision complex. We\(^3,4\) have measured the velocity spectra at zero laboratory scattering and of \( \text{C}_2\text{D}_2\text{H}^+ \) from \( \text{C}_2\text{D}_2^+ - \text{H}_2 \) collisions. At high relative energies (5.5 eV) \( \text{C}_2\text{D}_2\text{H}^+ \) has its maximum intensity near the value calculated for spectator stripping, but as the initial relative energy is lowered, this peak moves toward the center of mass. At less than 3 eV initial relative energy, the distribution is symmetric about the center of mass velocity. While this is not an entirely
conclusive proof of the occurrence of a persistent complex, it is highly suggestive that the expectations derived from the correlation diagram are correct.

As a final example, we discuss the OH$^+$(H$_2$,H)H$_2$O$^+$ reaction. Because of the great stability of H$_3$O$^+$, it would seem likely that a persistent complex might occur in this reaction. The correlation diagram is most easily constructed if it is assumed that OH$^+$($^3\pi$) and H$_2$ approach in a T-shaped configuration of C$_{2v}$ symmetry. The correlations are then very much like those in the H$_2$-CO$^+$ reaction. The resulting planar D$_{3h}$ H$_3$O$^+$ is then allowed to relax to its equilibrium C$_{3v}$ symmetry. There is, of course, no implication that the molecules rigidly follow this sequence of geometries in the reaction, but the introduction of the planar intermediate makes the correlation diagram easier to construct and also applicable to the OH$^+-$H$_2$ reaction. The result is shown in Fig. 10.

In OH$^+$($^3\pi$) two electrons with parallel spin occupy the two degenerate π* orbitals, and all orbitals of lower energy are filled. As the reactants approach, vibronic interaction may mix the $\sigma^*$ orbital of H$_2$ with the π* orbital of OH, but our analysis of the reactions of atomic ions with hydrogen seemed to be most consistent with the idea that this interaction was not important. The out of plane or umbrella motion of H$_3$O$^+$ would also tend to mix the $\sigma^*$ and π* orbitals as H$_2$ approaches OH$^+$. However, even if either or both of these interactions occurs, one electron will be found in the $\sigma^*$ 0-H
antibonding orbital of H$_3$O$^+$, if the electron spin conservation rule is obeyed. Therefore, the ground state of the H$_3$O$^+$ complex is not accessible to the reactants OH$^+$(3$\pi$) and H$_2$(1$\Sigma$), and no evidence for a persistent complex is expected. We have measured the velocity spectra of H$_2$O$^+$ from this reaction at relative energies from 5.0 to 7.6 eV and find evidence for only a direct interaction process.

CONCLUSION

We have explored the application of molecular orbital correlation diagrams to a number of ion-molecule collision processes. In situations where the reactant and product orbitals are few in number and well spaced in energy, the correlation between reactant and product electronic configurations is clear and leads to several predictions which are consistent with known experimental facts. When the orbital energies are more closely spaced so that orbital energy degeneracies occur as reactants evolve to products, the correlation diagrams can be ambiguous. However, reference to measured ion appearance potentials can sometimes remove such ambiguities and provide a qualitative picture of the potential energy surface which is sufficient to predict the major features of the dynamics of a reaction. It would appear that despite their qualitative nature, as these diagrams are modified and refined in the light of new experimental and calculational data, they will provide an increasingly useful guide to the understanding of a variety of reactive collision processes.
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References:

References (Continued)

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Fig. 1. A correlation diagram for the lowest orbitals of the linear (HeHH)⁺ system. The orbital energies are only semiquantitative, except for the atomic species. The lowest-order correlations are indicated by the dashed lines which cross.

Fig. 2. A correlation diagram for the lowest orbitals of the linear (ArHH)⁺ system. The energy of the σg orbital of H₂ is indicated by a shaded band to represent the spread between the vertical ionization energy of H₂ and the vertical recombination energy of H₂⁺.

Fig. 3. A correlation diagram for collisions of a heavy atom or ion x with H₂. During their approach, the reactants are assumed to maintain C₂ᵥ symmetry. The crossing of the a* and aᵣ curves in all probability is avoided.

Fig. 4. A correlation diagram for CO⁺-H₂ collisions. It is assumed that C₂ᵥ symmetry is maintained as the reactants approach. The circled crossings between the a₁ orbitals originating as σg(H₂) and σ(CO) and σ*(CO) probably are avoided.

Fig. 5. Schematic representations of the principal features of four potential energy surfaces. (a) Surface for the CO⁺(H₂,H)HCO⁺ reaction. The 4.5 eV barrier between reactants and products is established by the appearance potential of CO⁺ from H₂CO⁺. (b) Surface for the N₂⁺(H₂,H)N₂H⁺ reaction. The barrier suggested by the
correlation diagrams but unknown experimentally is indicated by the shaded area. (c) Surface for the $O_2^+(H_2,H)HO_2^+$ reaction. The location of the barrier and well are determined from appearance potentials. (d) Surface for the $C_2H_2^+(H_2,H)C_2H_3^+$ reaction. The barrier suggested by the lowest order orbital correlation but apparently eliminated by vibronic interaction is indicated by the shaded area.

Fig. 6. A correlation diagram for the collinear reaction of $CO^+$ with $H_2$. The circled crossings are probably avoided.

Fig. 7. A correlation diagram for the addition of $H_2$ to a $\pi$ system of a diatomic molecule to form either a bent or linear intermediate and eventually a linear triatomic product. The circled crossings are very probably avoided. It is assumed that the $\sigma_g$ orbital of $A_2$ lies above the $\pi$ orbitals, as would be the case for $N_2$, but reversal of the order of these orbitals makes no important changes in the correlations.

Fig. 8. A correlation diagram for the reaction $O_2^+(H_2,H)HO_2^+$ proceeding through a nonlinear collision complex.

Fig. 9. A correlation diagram for the addition of $H_2$ to $C_2H_2$. The molecular orbitals are labeled assuming that the $z$-axis is the perpendicular bisector of the carbon-carbon bond. The designations for the ethylene orbitals
assuming that the z axis is perpendicular to the molecular plane are given in brackets.

Fig. 10. A correlation diagram for the \( \text{OH}^+(\text{H}_2,\text{H})\text{H}_2\text{O}^+ \) reaction and other similar reactions in which the intermediate may be planar or pyramidal.
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
The diagram illustrates the electronic energy levels (E in eV) for various molecular orbitals and their interactions.

- $\sigma^*(O_2)$
- $\sigma^*(H_2)$
- $\pi^*(O_2)$
- $\sigma_n(O)$
- $\sigma(O_2)$
- $\sigma(OH)$
- $2s\sigma_u$
- $2s\sigma_g$

The reactions shown are:

- $O_2 + H_2 \rightarrow OO_H H$
- $HO_2 + H$

**Fig. 8**
Fig. 9
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