

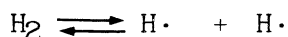
MULTI-REFERENCE CLUSTER EXPANSION THEORY AND
AN INTERACTION OF HYDROGEN MOLECULE WITH PALLADIUM

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ABSTRACT. A new multi-reference cluster expansion theory called MR-SAC theory is given. It is exact, unique, and does not include non-commutative operator algebra without imposing a completeness of the multi-reference space. From test applications, it was confirmed that the theory is a good approximation of the exact theory not only for ground states but also for quasi-degenerate states and excited states.

The interaction of hydrogen molecule with palladium is studied in the Pd-H₂ and Pd₂-H₂ systems as a model of chemisorption of hydrogen molecule on a metal surface. The SAC and SAC-CI theories are used to investigate the states involved. For the Pd-H₂ system a triangular adduct form is a stable geometry. From the study of the Pd₂-H₂ system, the equilibrium between molecular hydrogen and atomic hydrogens



is shown to occur very smoothly on the metal surface.

1. INTRODUCTION

In the Nobel Laureate Symposium on Applied Quantum Chemistry, I gave a talk which consists of two topics. One is a presentation of a new theory in the multi-reference cluster expansion approach. I called it MR-SAC (multi-reference symmetry-adapted-cluster) theory¹ because it corresponds to a generalization of the SAC theory,² which is a single-reference cluster expansion theory, and also of the SAC-CI theory³ which has been widely used for calculations of excited and ionized states.⁴ I explained the necessity of the multi-reference (MR) theory and presented the MR-SAC theory. Some results of the test

calculations⁵ were also given. The second topic I presented at the Honolulu meeting was a theoretical study on the interaction of hydrogen molecule with palladium. We studied Pd-H₂ and Pd₂-H₂ systems^{6,7} as a model of chemisorption of a hydrogen molecule on a palladium metal. Here, I briefly give an overview of these studies. The details of the studies will be published elsewhere in the literature.^{1,5,7}

2. MR-SAC THEORY

Recently, it has been generally recognized that the cluster expansion theory is a very efficient theory for calculations of accurate wave functions of molecules.⁸ However, an ordinary single reference theory breaks down when we deal with for example quasi-degenerate systems.¹⁰ It is therefore difficult to investigate molecular excited states and potential energy curves with such theories. In the CI approach, it is well known that a multi-reference formulation is appropriate for such systems.^{11,12} In the cluster expansion approach, Sinanoglu et al.,¹³ Mukherjee et al.,¹⁴ and Jeziorski and Monkhorst¹⁵ introduced multi-reference formulations. However, in contrast to the CI approach, a problem arose in the cluster expansion approach. That is an introduction of a non-commutative operator algebra, though it can be resolved by requiring a completeness to the multi-reference space.¹⁵ The occurrence of the non-commutative operator algebra or the completeness requirement on the multi-reference space is indeed difficult to stand with a practical utility of the theory.

We have recently considered a possibility to generalize the SAC theory to the multi-reference case, and found that it is possible to formulate a multi-reference version of the SAC theory without introducing a non-commutative operator algebra and therefore without imposing a completeness to the multi-reference space. We called it MR-SAC theory.¹

For simplicity we consider here the ground and excited states of a totally symmetric singlet state. The MR-SAC theory itself can be applied also to the non-degenerate open-shell states with the spin multiplicity of singlet, doublet, triplet, etc.¹ The ansatz of the MR-SAC theory is written as¹

$$\Psi^\mu = \left[\sum_{k=0} b_k^\mu M_k^\dagger \right] \exp \left(\sum_l C_l^\mu S_l^\dagger \right) |0\rangle \quad (1a)$$

$$= \exp \left(\sum_l C_l^\mu S_l^\dagger \right) \left[\sum_{k=0} b_k^\mu M_k^\dagger \right] |0\rangle. \quad (1b)$$

where $|0\rangle$ is a single determinant

$$|0\rangle = \|\varphi_1\alpha\varphi_1\beta \dots \varphi_i\alpha\varphi_i\beta \dots \varphi_N\alpha\varphi_N\beta\| \quad (2)$$

The operators M_k^\dagger and S_l^\dagger are symmetry-adapted excitation operators and are defined by the excitations from the occupied orbital $\{i\}$ to the unoccupied orbital $\{a\}$. Because of this definition, all of the operators involved are commutative. Two expressions of the MR-SAC ansatz, Eqs. (1a) and (1b), are therefore equivalent. In Eq. (1b) the part $(\sum_{K=0} b_K^\mu M_K^\dagger) |0\rangle$ corresponds to the multi-reference (MR) part and the operator $\exp(\sum_l C_l^\mu S_l^\dagger)$ represents a cluster expansion around this MR part. A merit of the present theory is that the MR part needs not to be complete, since all the operators are commutative, in contrast to the existing multi-reference cluster expansion theories.^{14,15} Between the two equivalent expressions of Eq. (1), the upper formula may be considered to correspond to a generalization of the SAC-CI formalism³ and the lower one to that of the SAC formalism.²

There are two ways of formulation starting from Eq. (1). One is to treat both of the coefficients $\{C_l^\mu\}$ and $\{b_K^\mu\}$ as unknown coefficients and determine them iteratively. There, the operators $\{S_l^\dagger\}$ and $\{M_K^\dagger\}$ should be chosen exclusively to each other in order to uniquely determine these variables. The other is to consider the MR part to be given in advance from for example a preliminary calculation. Here, the $\{S_l^\dagger\}$ operators need not to be exclusive to the $\{M_K^\dagger\}$ operators. Rather, they should have some important elements in common. In this paper, we adopt the first approach, since it formally includes the second one.

Physically, the MR part should represent well the state-specific correlations like quasi-degeneracy, first-order correlation, internal correlation in open shells, etc.¹³ These state-specific correlations usually don't require a large number of configurations but are characterized by a non-existence of a dominant configuration. The zero-th order approximation of such state is given by the MR part, $(\sum_{K=0} b_K^\mu M_K^\dagger) |0\rangle$ rather than a single determinant. The orbitals $\{\varphi_i\}$ in Eq. (2) may be the MC-SCF orbitals optimized for the MR part. The operator $\exp(\sum_l C_l^\mu S_l^\dagger)$ represents the 'collisions' of electrons occurring in such zero-th order state. Because such collisions would occur independently in different parts of the molecule, the exponential form of the operator is adequate.^{13,16} This part of correlation was called 'dynamic' correlation by Sinanoglu.¹³ It is more-or-less transferable among different states of molecules.

In the multi-reference theory, the choice of the multi-reference part is obviously very important to get accurate results. In the MR-SAC theory we can choose this part only from physical considerations because it needs not to be complete. From the consideration of the reason of the breakdown of the single reference cluster expansion theory in the quasi-degenerate case, we have found that the choice of the MR part

$$(\sum_{K=0} b_K^\mu M_K^\dagger) \rightarrow \mathcal{E}\mathcal{C}\mathcal{P}(\sum_K b_K^\mu M_K^\dagger)$$

is appropriate¹ (note that the meaning of the M_K^\dagger operators is different in the two expressions). Here, the $\mathcal{E}\mathcal{C}\mathcal{P}$ operator is defined by

$$\begin{aligned} \mathcal{E}\mathcal{X}\mathcal{P} \left(\sum_K b_K^\mu M_K^\dagger \right) &= b_0^\mu + \sum_K b_K^\mu M_K^\dagger \\ &+ \frac{1}{2!} \sum_{K,L} b_{KL}^\mu M_K^\dagger M_L^\dagger + \frac{1}{3!} \sum_{K,L,N} b_{KLN}^\mu M_K^\dagger M_L^\dagger M_N^\dagger + \dots \end{aligned} \quad (3)$$

This operator has the same product operators as those of an ordinary exponential operator, but the coefficients are free from those of the lower operators. Therefore, even if the physics of the product operators $M_K^\dagger M_L^\dagger$ is entirely *different* from a simultaneous occurrence of the 'collisions' M_K^\dagger and M_L^\dagger (*dynamic correlation*), the product operators are able to represent their own physics. We call such coupling of two operators as '*strong and synthetic coupling*'. Note that a set of the product operators may involve redundant terms. We therefore include only the linearly independent terms in the summations in Eq. (3). In this form, the MR-SAC theory is written as

$$\Psi^\mu = \exp \left(\sum_I C_I^\mu S_I^\dagger \right) \mathcal{E}\mathcal{X}\mathcal{P} \left(\sum_K b_K^\mu M_K^\dagger \right) | 0 \rangle \quad (4)$$

This form of the MR-SAC theory has another merit that it is size consistent,^{1,16} since the operator $\mathcal{E}\mathcal{X}\mathcal{P}$ is a generalization of the *exp* operator.

In the applications of the MR-SAC ansatz given by Eq. (4), we terminate the $\mathcal{E}\mathcal{X}\mathcal{P}$ operator at an appropriate level. It is physically unnecessary and also impractical to include all the higher order terms of Eq. (3). Since this is a MR part, only the state-specific correlations like quasi-degeneracy need to be adequately described. The dynamic correlations are taken care of by the operator $\exp \left(\sum_I C_I^\mu S_I^\dagger \right)$. In the present calculations, we have included up to the third term of Eq. (3). For the molecule studied here, the higher terms are not considered to be necessary. Rather, it is necessary to include all the important lower order terms. This is possible only in the present MR-SAC theory. In the other MR cluster expansion theory,^{14,15} the MR part should be complete. Otherwise, a tedious non-commutative operator algebra must be introduced. Therefore, the dimension of the MR functions soon becomes very large, much larger than that necessary in the present MR-SAC theory. Further, the completeness requirement means that even very unimportant configurations should be included as reference functions just for a mathematical reason. This is far from physical! This is also impractical because the dimension of the MR functions is directly reflected on a computation time. Further, when the system becomes large or complex, the completeness requirement is difficult to be compatible with the physical requirement.

The unknown variables in the present formulation of the MR-SAC theory are $\{C_I^\mu\}$ and $\{b_K^\mu, b_{KL}^\mu\}$. They are associated with the operators $\{S_I^\dagger\}$ and $\{M_K^\dagger, M_K^\dagger M_L^\dagger\}$. We choose these operators

exclusively to each other so that the theory is unique. The solution of the MR-SAC theory may be obtained by requiring the Schrodinger equation $(H - E_\mu)\Psi^\mu = 0$ within the space of the linked configurations. From the projection onto the S -part operators, we obtain

$$\langle 0 | H - E_\mu | \Psi^\mu \rangle = 0 \quad (5a)$$

$$\langle 0 | S_N (H - E_\mu) | \Psi^\mu \rangle = 0 \quad (5b)$$

and from the projection onto the operators in the multi-reference space, we obtain

$$\langle 0 | M_P (H - E_\mu) | \Psi^\mu \rangle = 0 \quad (5c)$$

$$\langle 0 | M_P M_Q (H - E_\mu) | \Psi^\mu \rangle = 0 \quad (5d)$$

These equations are sufficient to determine all the unknown variables in the present calculations. We note that the solution given by Eq. (5) is non-variational so that the energy obtained does not necessarily satisfy an upper bound nature.

3. APPLICATION OF THE MR-SAC THEORY TO THE CALCULATIONS OF THE LOWER FOUR $^1\Sigma^+$ STATES OF THE CO MOLECULE

When we apply the MR-SAC theory to actual systems and write down a computer program,¹⁷ some approximations need to be introduced. We expand Eq. (1) as

$$\begin{aligned} \Psi^\mu = & b_0^\mu | 0 \rangle + \sum_K b_K^\mu M_K^\dagger | 0 \rangle + b_0^\mu \sum_I C_I^\mu S_I^\dagger | 0 \rangle + \frac{1}{2} \sum_{K,L} b_{KL}^\mu M_K^\dagger M_L^\dagger | 0 \rangle \\ & + \sum_{K,I} b_{KI}^\mu C_I^\mu M_K^\dagger S_I^\dagger | 0 \rangle + \frac{1}{2} b_0^\mu \sum_{I,J} C_I^\mu C_J^\mu S_I^\dagger S_J^\dagger | 0 \rangle \\ & + \frac{1}{2} \sum_{K,L,I} b_{KL}^\mu C_I^\mu M_K^\dagger M_L^\dagger S_I^\dagger | 0 \rangle + \frac{1}{2} \sum_{K,I,J} b_{KI}^\mu C_I^\mu C_J^\mu M_K^\dagger S_I^\dagger S_J^\dagger | 0 \rangle \\ & + \frac{1}{4} \sum_{K,L,I,J} b_{KL}^\mu C_I^\mu C_J^\mu M_K^\dagger M_L^\dagger S_I^\dagger S_J^\dagger | 0 \rangle + \dots \end{aligned} \quad (6)$$

The first four terms are linked terms which have independent variables and the other five terms are unlinked terms in which the coefficients are the products of the lower order terms. In the present calculations, we have neglected the last three terms of Eq. (6).

As the linked operators $\{M_k^\dagger\}$ and $\{S_l^\dagger\}$, we have considered all the single and double excitation operators. The product operators, $\{M_k^\dagger M_L^\dagger\}$ were generated from those lower operators whose contributions in a preliminary CI are larger than a given threshold. They consist of the triple and quadruple excitations.

The unlinked terms, the fifth and sixth terms of Eq. (6) were generated automatically. As the S operators, we included only the double excitations. Since the M operators include both single and double excitations, the unlinked terms consist of the triple and quadruple excitations. Though the terms duplicate with the linked term $M_k^\dagger M_L^\dagger |0\rangle$ may occur, we have excluded such terms from the unlinked terms.

Thus, in the present approximations, the MR-SAC wave function includes all single and double excitations in the linked terms, some triple and quadruple excitations in the synthetic coupling terms and many other triple and quadruple excitations in the unlinked terms. Probably the most severe approximation in this version of the program is a neglect of the last three terms of Eq. (6). Especially, through the neglect of the seventh term, we didn't include (some important) five and six electron excited configurations which are double excitations from (relatively important) triple and quadruple excitations.

The potential energy curves of the ground and excited states of the CO molecule provide a good test for the multi-reference type theory. Figure 1 shows the main configurations in the full CI wave functions based on the Hartree-Fock orbitals. As the CO distance increases from the equilibrium one, the main configurations of the lower four $^1\Sigma^+$ states change drastically. They involve the Hartree-Fock, singly excited, doubly excited, triply excited, and quadruply excited configurations. It shows an *interesting complexity* of the system. In order to *accurately* describe these four states *simultaneously*, a balanced theory of multi-reference is essential.

For the ground state, the HF configuration is a dominant configuration near the equilibrium distance ($R = 2.132$ au), but its weight decreases monotonously as the CO distance increases and becomes zero at the dissociation limit, $C(^3P) + O(^3P)$. There the dominant configuration is the quadruply excited configuration which may be illustrated as



On the other hand, the HF configuration itself becomes a main

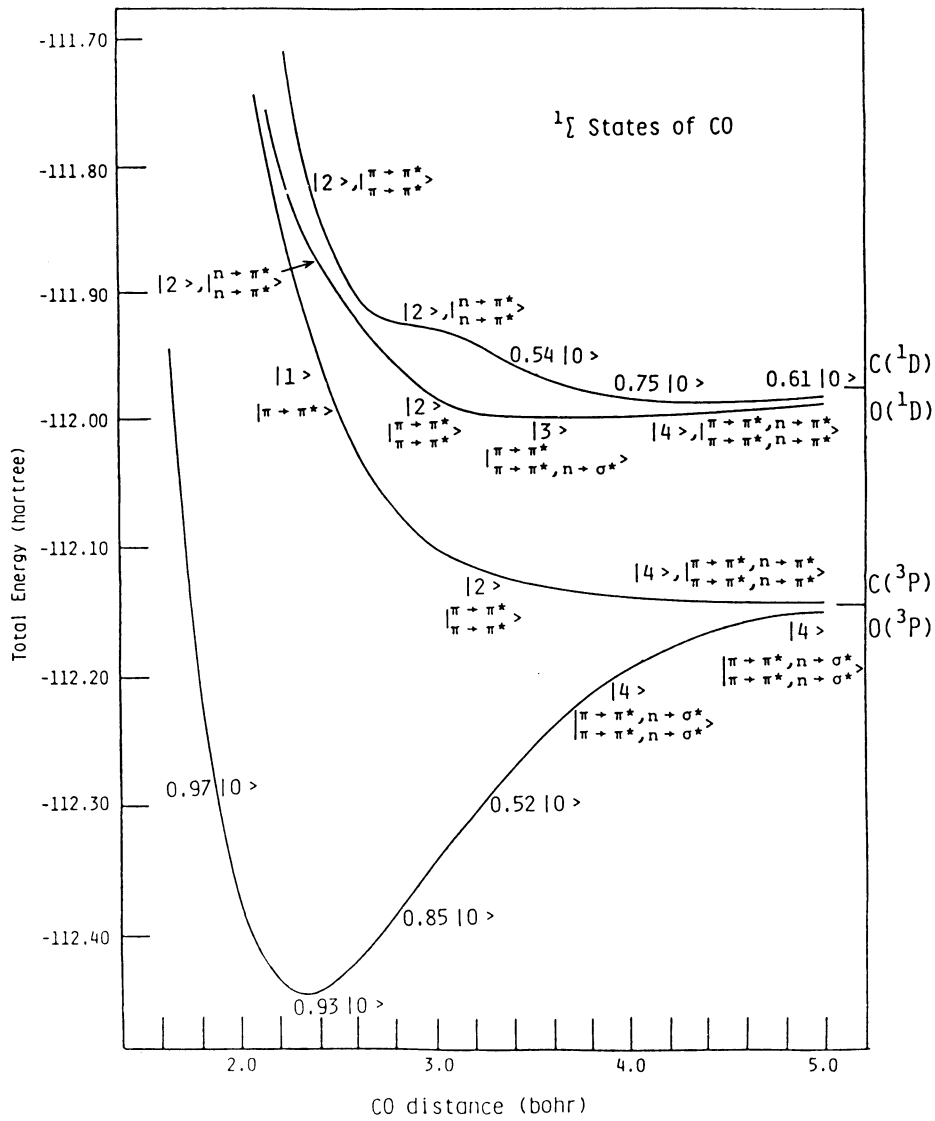
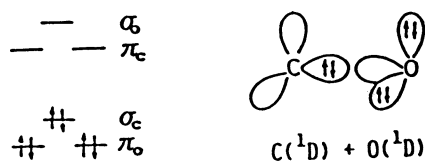


Figure 1. Main configurations of the lower four $^1\Sigma^+$ states of the CO molecule in the full-CI calculations based on the Hartree-Fock orbitals with minimal STO-6G basis.

configuration of the fourth ${}^1\Sigma^+$ state which dissociates into the $C({}^1D) + O({}^1D)$ state as illustrated by



The second ${}^1\Sigma^+$ state is the $\pi \rightarrow \pi^*$ singly excited state at shorter distances, but becomes doubly excited $\pi \rightarrow \pi^*$ state in the intermediate region, which is an electron-transferred state from oxygen to carbon, and finally the quadruply excited configuration becomes a dominant configuration. This state dissociates into $C({}^3P)$ and $O({}^3P)$ as the ground state does. The third ${}^1\Sigma^+$ state is the doubly excited state at the shorter distance. It suffers a strong avoided crossing with the fourth state. In the intermediate region the triply excited configuration becomes a main configuration and finally the quadruply excited configuration becomes a main configuration. This state dissociates into $C({}^1D)$ and $O({}^1D)$. The fourth state is a doubly excited state at shorter region but becomes the HF configuration in the longer region.

We performed the MR-SAC calculations of the potential energy curves of the lower four ${}^1\Sigma^+$ states of the CO molecule. We used the minimal STO-6G basis¹⁸ and the two 1s core MO's were fixed throughout the calculations. Since the basis set is different from that of O'Neil and Schaefer,¹⁹ we performed the full CI and SDTQ CI calculations, for comparison, with the use of the program GAMESS.²⁰ The details of the calculations were described in a separate paper.⁵

In Figure 2, we showed the potential energy curves of the first four ${}^1\Sigma^+$ states of the CO molecule calculated by the full-CI, SDTQ-CI, and the MR-SAC theories. It is seen that the MR-SAC theory reproduces well the general features of the potential energy curves. For the lower two states, the potential curves of the three theories almost overlap at the shorter and the longer regions, but in the intermediate region the MR-SAC curves are close to the SDTQ-CI curves. This is due to the present method of truncation of the wave function. Namely, we considered only up to the quadruple excitations in both linked and unlinked terms and neglected higher excitations. The differences between the SDTQ-CI and full-CI curves are due to the more-than-five electron excitations and their contributions become appreciable only in the intermediate region. For the higher two states, the behavior is similar to the lower cases except that the MR-SAC result deviates from the SDTQ-CI result in the shorter ($R < 2.5$ au) region of the third state and in the 2.6 - 3.0 au region of the fourth state.

We performed the MR-SAC calculations also for the CO molecule with a different basis set¹ and for the H_2O molecule with the equilibrium and two symmetrically elongated distances.⁵ The results of these calculations showed similar trends to those shown here. From these calculations, we conclude that the MR-SAC theory is a good approximation

of the exact theory. It gives accurate and reliable results not only for ordinary ground states but also for quasi-degenerate states and excited states.

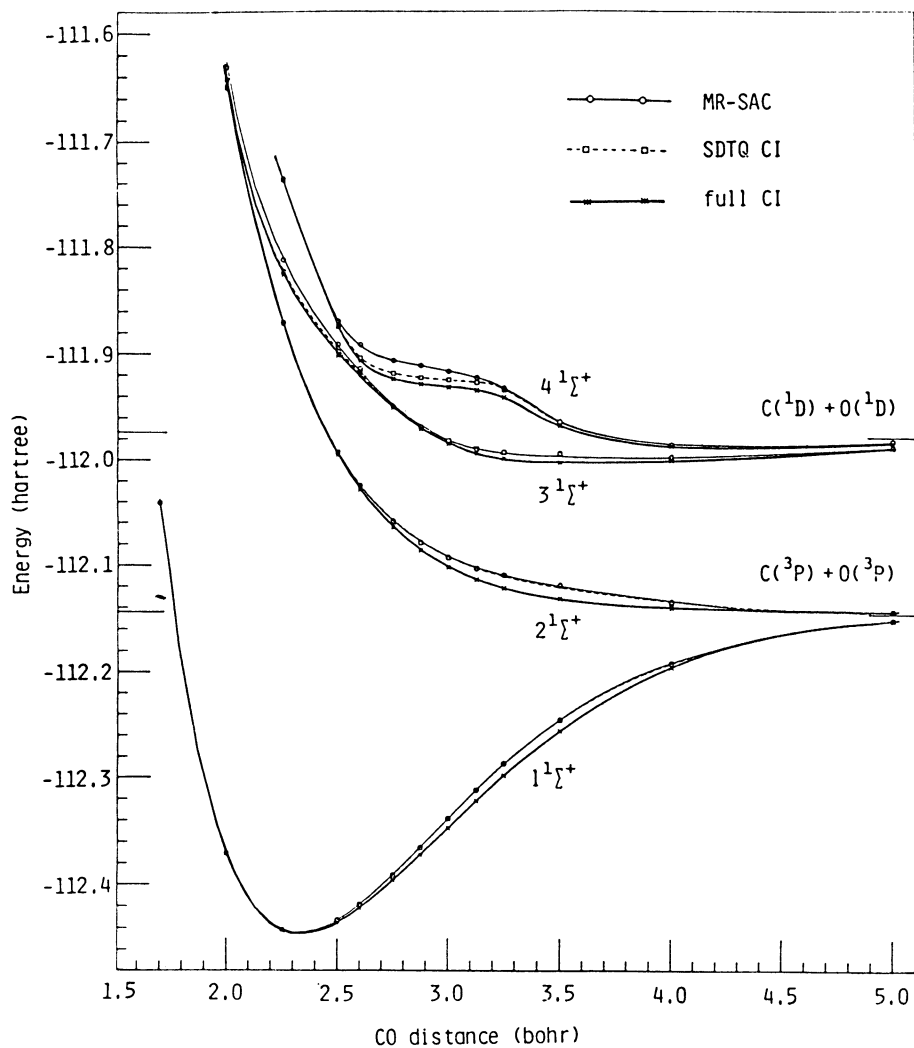


Figure 2. Potential energy curves for the lower four $1\Sigma^+$ states of the CO molecule with minimal STO-6G basis calculated by the full-CI, SDTQ-CI, and MR-SAC theories

4. INTERACTION OF HYDROGEN MOLECULE WITH PALLADIUM

Next we study an interaction of the hydrogen molecule with palladium as a model of chemisorption on a metal surface. The basic assumption here is a local nature of the interaction between hydrogen and palladium, which is supported by several previous investigations for the interactions of *atomic* hydrogen with palladium.²¹⁻²³ We want to clarify the nature of the interactions and the states involved in the chemisorptive processes.

The systems we studied are the Pd-H₂ and Pd₂-H₂ systems. The path of the approach is illustrated in Figure 3. For the Pd-H₂ system this side-on approach is a favorable path.⁶

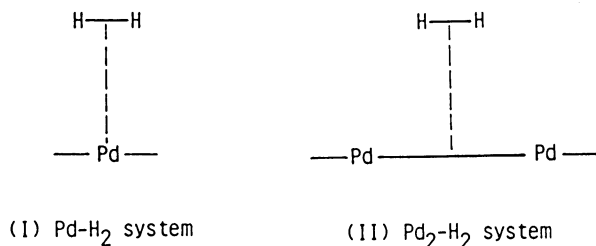


Figure 3. Interaction of the hydrogen molecule with the Pd and Pd₂ fragments

The gaussian basis set for the Pd atom is (3s3p3d)/[3s2p2d] set and the Kr core was replaced by the effective core potential.²⁴ For hydrogen, we used (4s)/[2s] set of Huzinaga-Dunning²⁵ plus p-type functions which are the first derivatives of the [2s] set. The Hellmann-Feynman theorem is then satisfied for the force acting on the hydrogen nuclei, as we showed previously.²⁶ The force acting on hydrogen is directly connected to the electron distribution of the system.⁶ The optimal path of the approach was calculated by the Hartree-Fock method for the Pd-H₂ system and by the CAS-MC-SCF method²⁷ for the Pd₂-H₂ system within 8 (lower) × 2 (upper) active orbital spaces. Both theories satisfy the Hellmann - Feynman theorem. Further we studied, along these optimal paths, the potential energy curves of the ground and excited states of the Pd-H₂ and Pd₂-H₂ systems by the SAC and SAC-CI methods. The details of the calculational methods will be explained elsewhere in the literature.⁷

4.1. Pd-H₂ SYSTEM

Figure 4 shows the optimized approach of the hydrogen molecule to the palladium atom. The most stable geometry of the system is a triangle shown there. This geometry corresponds to the molecular hydrogen attached to the metal atom. The H-H distance, 0.768 Å, is only slightly longer than the equilibrium length 0.741 Å in a free hydrogen molecule. The Pd-H distance is 1.898 Å which is much longer than the bond distance 1.529 Å of the free PdH molecule.²⁸ The stabilization energy was calculated to be only 3.7 Kcal/mol at the Hartree-Fock level. These

results are very similar to those reported recently by Brandemark et al.²⁹ Note that the linear PdH₂ molecule was calculated to be 37 Kcal/mol more unstable than the triangular geometry shown in Figure 4. Note further that when the electronegative ligands are attached to the Pd atom like PdL₂, the hydrogen molecule reacts more easily with the Pd atom (oxidative addition).^{29,30}

In Figure 5, we have shown the potential energy curves of the Pd-H₂ system. The ground state was calculated by the SAC method and the singlet and triplet excited states by the SAC-CI method. Among the states studied here, only the ground state is attractive and all the other states are repulsive. These excited states are essentially the excited states of the Pd atom. These potential curves may suggest an existence of an interesting detachment or 'desorption' processes through the excited states of the metal. We note that in the present approximation the state separations seem to be underestimated. The ³D and ¹D states of the Pd atom was calculated to be 9 and 19 kcal/mol above the ¹S ground state in comparison with the experimental values, 19 and 33 kcal/mol, respectively.³¹

From Figure 5, we see that the effect of electron correlation is large. The stabilization energy of the Pd-H₂ system was calculated to be ~ 15 Kcal/mol relative to the separated system.

The effect of electron correlation on the stabilization energy is about 11 Kcal/mol. The Pd-H₂ distance also became 1.65 Å in comparison with that at the Hartree-Fock level 1.85 Å. In the correlated level, the ground state of the Pd-H₂ system is calculated to be more stable in our calculation than in the calculation of Brandemark et al.²⁹ This is probably due to the existence of the derivative bases at the hydrogen atoms in the present calculations, though Brandemark et al. also added one polarization function on the hydrogen. Similar important effects of the extensive polarization functions on the hydrogen atom were also reported by Wang and Pitzer³² for the PtH system. The use of the effective core potential for the Pd atom may also be another reason.

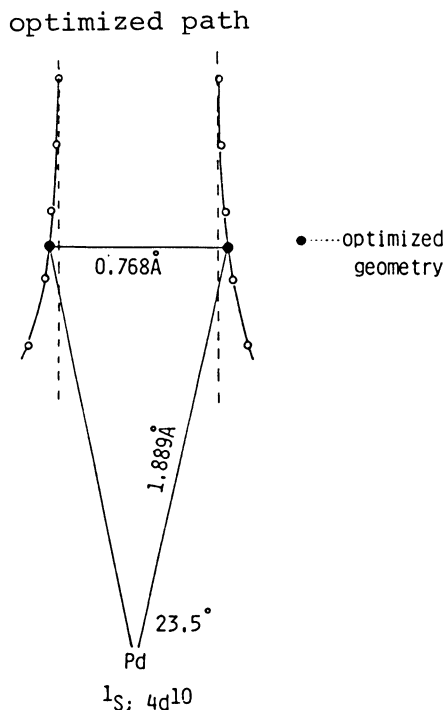


Figure 4. Optimized path of the approach of the hydrogen molecule to the Pd atom and the optimized geometry of the Pd-H₂ complex

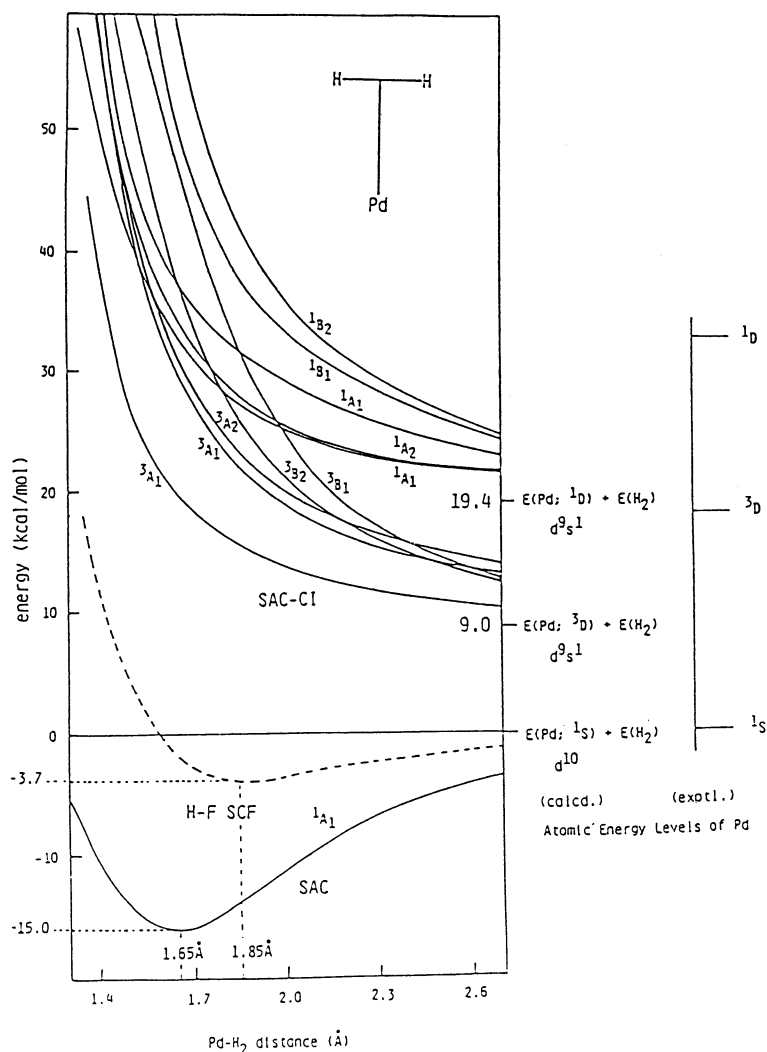


Figure 5. Potential energy curves of the ground and excited states of the Pd-H₂ system calculated by the SAC and SAC-CI methods

4.2. Pd₂-H₂ SYSTEM

Some years ago, Melius et al.^{33,34} proposed an interesting molecular complex model for the chemisorption of hydrogen molecule on a nickel surface. They reported a spin-coupling role of the d-electrons in the molecular complex and an important participation of the ³B₂ state in the dissociative process of the H₂ molecule on a nickel surface. We study here the Pd₂-H₂ system and show that this is a smallest possible model system for the study of the chemisorption of the H₂ molecule on a Pd

surface. We will also investigate a possibility of the participation of the triplet states.

The path of the approach of the H_2 molecule to the Pd_2 fragment is illustrated in Figure 3. The Pd-Pd distance was fixed to 2.7511 Å, which is an observed value for the bulk fcc crystal structure.³⁵ In Figure 6, we showed the potential curves for the H-H stretching motion at several Pd_2-H_2 separations, R . The table in Figure 6 gives the optimized H-H distances. They were calculated by the CAS-MC-SCF method. When the H_2 molecule is separated from the Pd_2 fragment by more than 2.5 Å, the potential of the H_2 molecule is essentially the same as that of the free hydrogen. When the H_2 molecule approaches Pd_2 by $R = 2.0$ Å, the H-H distance becomes longer but the potential is still very sharp. However, at $R = 1.5$ Å, the potential curve suddenly becomes very flat and the second minimum seems to appear near $R_{H-H} = 2.0$ Å other than the

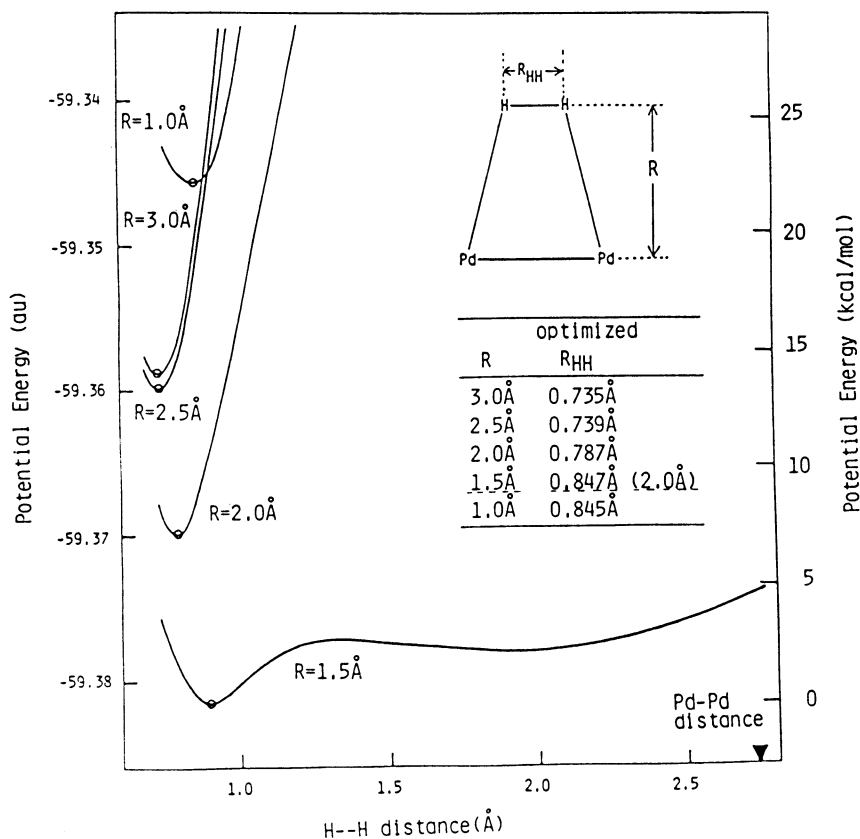
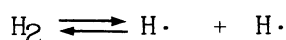


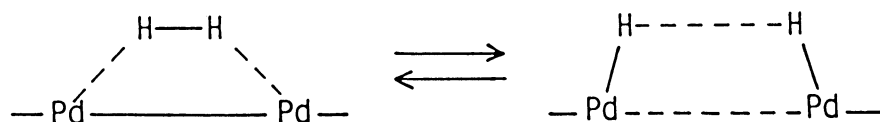
Figure 6. Potential curves for the H-H stretching of the Pd_2-H_2 system at different Pd_2-H_2 separations. (CAS-MC-SCF method)

first minimum at $R_{H-H} = 0.847 \text{ \AA}$. The system is considerably stabilized by about 14 Kcal/mol relative to the free Pd_2 and H_2 systems. However, when R becomes 1.0 \AA , the system is very much repulsive. A stable adsorption of the H_2 molecule seems to occur at about 1.5 \AA apart from the Pd surface.

In order to obtain more reliable potential curve of the H_2 molecule interacting with Pd_2 at $R = 1.5 \text{ \AA}$, we calculated the potential curve of the ground state by the SAC method. We also calculated the potential curves of the singlet and triplet excited states by the SAC-CI method. Figure 7 shows the results. From the SAC curve for the ground state, we clearly see two potential minima. The minimum at $R_{H-H} = \sim 0.89 \text{ \AA}$ corresponds to the molecular hydrogen adsorbed on the surface and the minimum at $R_{H-H} = \sim 2.1 \text{ \AA}$ corresponds to the dissociative attachment in the form of the two hydrogen radicals. This calculation suggests an existence of a smooth equilibrium between molecular hydrogen and two atomic hydrogen radicals on the metal surface, i.e.,



In the present path, i.e., the stretching motion of H_2 at 1.5 \AA apart from the metal surface, the dissociative form is more stable than the molecular form by 2.2 Kcal/mol and the barrier height is 5.6 Kcal/mol. However, since the motion along the metal surface was not energetically optimized, these values should be considered only qualitatively. We note that at $R_{H-H} = \sim 2.1 \text{ \AA}$, the Pd-H distance is $\sim 1.5 \text{ \AA}$ which is close to the experimental internuclear distance of a free PdH molecule, 1.5285 \AA .²⁸ Thus the above equilibrium reaction may be written as



From the analysis of the density map of the system, we found a reorganization of the electron density which supports the above bond alteration.⁷ Though the change in the electronic structure of the system along the above process is very very large, it occurs *with a very small* activation barrier. This certainly shows a *catalytic* ability of the Pd_2 fragment.

From Figure 7, we further see that the excited states of the $\text{Pd}_2\text{-H}_2$ system are well separated from the ground state by more than 40 Kcal/mol. There is almost no chance for the excited states to participate in the chemisorption processes. The triplet B_2 state, which was considered important in the $\text{Ni}_2\text{-H}_2$ system by Melius et al.³⁴, is also far apart from the ground state. Therefore, we conclude that the mechanism of the chemisorption of the H_2 molecule on the Pd surface would be different from that proposed for the Ni surface by Melius et al.³⁴ The mechanism in the $\text{Pd}_2\text{-H}_2$ system is a simple totally symmetric

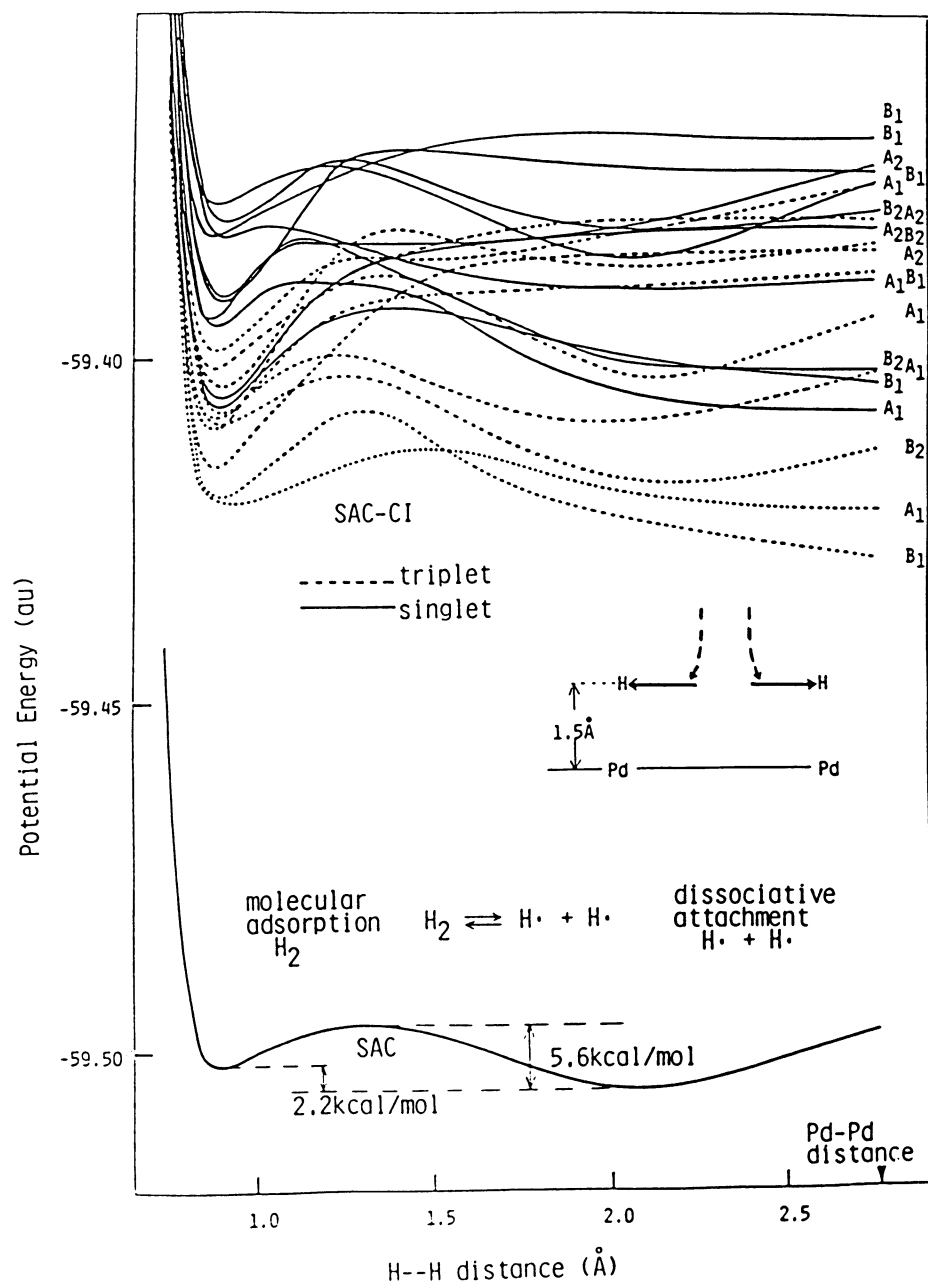


Figure 7. Potential energy curves of the ground and excited states of the Pd₂-H₂ system as a function of the H-H distance of the H₂ molecule at 1.5 Å apart from the Pd₂ fragment. (SAC and SAC-CI methods)

symmetry-allowed path, and the ground state is 1A_1 throughout the process.

From the study for the Pd-H₂ and Pd₂-H₂ systems, we conclude that the interaction of the hydrogen molecule with palladium is attractive, as experimentally observed. For the chemisorptive processes, the Pd₂-H₂ system seems to be a smallest possible model system. We found an interesting equilibrium process between the molecular hydrogen and the two dissociated hydrogen radicals of the adsorbed H₂ molecule on the Pd₂ fragment with a very low activation barrier. This process would correspond to the chemisorptive and catalytic processes of the palladium metal involving hydrogen molecule. More details of the study will be published elsewhere in the literature.⁷

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REFERENCE

1. H. Nakatsuji, J. Chem. Phys. in press.
2. H. Nakatsuji and K. Hirao, J. Chem. Phys. 68, 2053 (1978).
3. H. Nakatsuji, Chem. Phys. Lett. 59, 362 (1978); 67, 329 (1979).
4. For example, see H. Nakatsuji, J. Chem. Phys. 80, 3703 (1984) and the references cited therein.
5. H. Nakatsuji, to be published.
6. H. Nakatsuji and M. Hada, Croatica Chem. Acta, in press.
7. H. Nakatsuji, M. Hada, and T. Yonezawa, to be published.
8. J. A. Pople, R. Seeger, and R. Krishnan, Intern. J. Quantum Chem. Symp. 11, 149 (1977).
9. R. J. Bartlett, Ann. Rev. Phys. Chem. 32, 359 (1981), and the references cited therein.
10. J. Paldus, in *New Horizons of Quantum Chemistry*, ed. by P. -O. Lowdin and B. Pullman, D. Reidel Pub. Co., p.31, 1983, and the references cited therein.
11. R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. 35, 771 (1978).
12. R. J. Buenker and S. D. Peyerimhoff, in *New Horizons of Quantum Chemistry*, ed. by P. -O. Lowdin and B. Pullman, D. Reidel Pub. Co., p. 183, 1983.
13. O. Sinanoglu and I. Oksuz, Phys. Rev. Lett. 21, 507 (1968); Phys. Rev. 181, 42 (1969).
14. D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. 30, 1861 (1975); 33, 955 (1977).
15. B. Jeziorski and H. J. Monkhorst, Phys. Rev. A24, 1668 (1981).
16. H. Primas, in *Modern Quantum Chemistry, Istanbul Lectures*, ed. by O. Sinanoglu (Academic Press, New York, 1965), Part 2, p.45.

17. H. Nakatsuji, Program system for the MR-SAC calculations, to be published.
18. W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* 51, 2657 (1969).
19. S. V. O'Neil and H. F. Schaefer III, *J. Chem. Phys.* 53, 3994 (1970).
20. B. R. Brooks, P. Saxe, W. D. Laidig, and M. Dupuis, Program System GAMESS (Program Library No. 481, Computer Center of the Institute for Molecular Science, 1981).
21. R. P. Messmer, D. R. Salahub, K. H. Johnson, and C. Y. Yang, *Chem. Phys. Lett.* 51, 84 (1977).
22. S.G. Louie, *Phys. Rev. Lett.* 42, 476 (1979).
C. T. Chan and S. G. Louie, *Phys. Rev. B* 27, 3325 (1983).
W. Eberhardt, S. G. Louie, and E. W. Plummer, *Phys. Rev. B* 28, 465 (1983).
23. G. Pacchioni and J. Kouteckey, *Theoretical Investigation of the Interaction between the Hydrogen Atom and Pd Clusters*, private communication.
24. P. J. Hay, *J. Am. Chem. Soc.* 103, 1390 (1981).
25. S. Huzinaga, *J. Chem. Phys.* 42, 1293 (1965).
T. H. Dunning, Jr., *J. Chem. Phys.* 53, 2823 (1970).
26. H. Nakatsuji, K. Kanda, and T. Yonezawa, *Chem. Phys. Lett.* 75, 340 (1980).
H. Nakatsuji, T. Hayakawa, and M. Hada, *Chem. Phys. Lett.* 80, 94 (1981).
H. Nakatsuji, K. Kanda, M. Hada, and T. Yonezawa, *J. Chem. Phys.* 77, 3109 (1982).
27. B. Roos, P. Taylor, and P. Siegbahn, *Chem. Phys.* 48, 157 (1980).
P. Siegbahn, A. Heiberg, B. Roos, and B. Levy, *Phys. Scripta*, 21, 323 (1980).
28. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co., New York, 1979.
29. U. B. Brandemark, M. R. A. Blomberg, L. G. M. Pettersson, and P. E. M. Siegbahn, *J. Phys. Chem.* 88, 4617 (1984).
30. K. Tatsumi, R. Hoffmann, A. Yamamoto, and J. K. Stille, *Bull. Chem. Soc. Jpn.* 54, 1857 (1981).
K. Kitaura, S. Obara, and K. Morokuma, *J. Am. Chem. Soc.* 103, 2891 (1981).
J. O. Noell and P. J. Hay, *J. Am. Chem. Soc.* 104, 4578 (1982);
Inorg. Chem. 21, 14 (1982).
31. C. E. Moore, *Atomic Energy Levels*, National Bureau of Standard, Washington, 1971, Vol. 3.
32. S. W. Wang and K. S. Pitzer, *J. Chem. Phys.* 79, 3851 (1983).
33. C. F. Melius, *Chem. Phys. Lett.*, 39, 287 (1976).
34. C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baillie, and M. A. Ratner, *Surf. Sci.* 59, 279 (1976).
35. *Handbook of Chemistry and Physics*, 1984-1985, CRC Press, Inc., Cleveland, Ohio, F-167.