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Reaction of Sc^+ (^1D , ^3D) with H_2O , NH_3 , and CH_4 : A Density Functional Study

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Received February 23, 2000. Revised Manuscript Received July 27, 2000

Abstract: Density Functional Theory has been used to explore quantitative details of the potential energy hypersurface for the insertion reaction of scandium ion into the O–H, N–H, and C–H bond of water, ammonia, and methane molecules leading to H_2 elimination. Both singlet and triplet state channels have been considered. On the basis of the obtained results, it is possible to conclude that for the molecules considered the reaction is a spin-forbidden process. Indeed, it starts in the triplet ground state and ends in the singlet state, the change of the spin state probably occurring immediately after the formation of the electrostatic complex intermediate.

1. Introduction

The importance of transition metal centers as catalysts for selective transformations of small molecules into useful chemical species has prompted extensive studies in the gas phase. Gas-phase chemistry gives the opportunity of obtaining quantitative information regarding the dynamics, kinetics, and thermochemistry of elementary reactions in a controlled environment without disturbing factors.

Over the two past decades, considerable research, from both a theoretical and experimental point of view, has been focused on understanding the ability in the gas phase of bare transition metal cations to activate bonds in small molecules.^{1–36} Such studies provide thermochemical detail as well as insight into

the reaction mechanism. Experimentally it has been shown that the reaction of the scandium cation with water, ammonia, and methane leads to H_2 elimination at low energies.^{5,8,14,17} The reactions have been studied by guided ion beam mass spectrometry and have been proposed to proceed via oxidative addition, i.e., insertion of Sc^+ in the H–X (X = O, N, C) bond, to form an insertion intermediate that lies lower in energy than the reactants. Comparison between the cited reactions shows that, while the mechanisms are similar, the energetics are significantly different. The observed similarities have been explained as a result of the fact that water, ammonia, and methane are isoelectronic in the sense that the central heavy atom has the same number of valence electrons with the same sp^3 hybridization.³⁷ The differences in energetics have been attributed to the different numbers of lone pairs: that is, two on the oxygen atom of water, one on the nitrogen atom of ammonia, but absent on the carbon atom of methane.

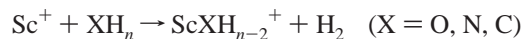
Another topic of interest in these reactions is the influence of the electronic state of the metal cation upon the reactivity and reaction path. The hypothesis of a crossing between triplet and singlet surfaces, probably occurring in the region of the ion–molecule complex, Sc^+-XH_n (X = O, N, C), has been

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proposed^{5,8,14,17} to explain the nature of the final product with respect to the reactants and the efficiency of the reaction.

In this paper we report a Density Functional (DF) study of the potential energy hypersurfaces for the reactions:



The full reaction mechanism, geometries, and energetics for both the high- and low-spin states, considering the possible transition states, are reported. We summarize briefly previous theoretical and experimental work in the literature on the dehydrogenation reaction of water, methane, and ammonia by Sc^+ . It is worth noting that a theoretically systematic study of the titled reactions at the same level of theory is not reported in the literature. Experimentally, the studies of the reaction of scandium ion with water performed by Clemmer et al.³⁷ and Kang and Beauchamp³ by ion beam tandem mass spectrometry are pertinent to this work. The same technique was used by Armentrout et al. to study the reaction of Sc^+ with D_2O ¹⁷ and the inverse reaction.¹⁶ The exothermic interaction of Sc^+ with ammonia was studied by Buckner et al.⁶ using Fourier transform ion cyclotron resonance and successively by Clemmer et al.¹⁴ extending a previous study of the reaction with methane.⁸ The activation of the carbon–hydrogen bond in methane was also studied by Tolbert and Beauchamp² by means of an ion-beam apparatus. Theoretically, Tilson and Harrison²⁰ have studied the characteristics of some of the products of the scandium ion–water reaction by Multiconfiguration Self-Consistent Field (MCSCF) and Configuration Interaction (MCSCF+1+2) methods. More recently, a MP4(SDTQ)**//MP2/6-31G**²⁴ study and a B3LYP/DZVP²⁸ density functional study of the dehydrogenation reaction of water by Sc^+ have appeared in the literature. Song theoretically investigated also the reaction with ammonia by ab initio MO methods.²¹ Finally, the mechanism of the reaction of Sc^+ with methane was studied with CASSCF and MR-SDCI methods.²³ Ugalde et al. have extensively studied the interaction between first-row transition metal ions with water,^{27–30,39} comparing the profiles of PES's as a function of the involved transition metal cation. In this context it is of interest to carry out an investigation of the influence of different small ligands on the reactivity of the same metal center and of the tool (functional and basis set) used to perform calculations extending the work previously carried out on this subject.

2. Methods

The computational method used for geometry optimization and frequency calculations was density functional theory in its B3LYP^{40,41} formulation with the DZVP for scandium and TZVP sets for the other atoms given by Goudbot et al.⁴² The choice of the B3LYP DF method is motivated by its reliability as a practical tool in transition metal chemistry.^{43–45} Moreover, previous work on this subject^{24,27–30,46} well underlines the reliability of DF methods, in their B3LYP formulation,

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Table 1. Relative Energies, in kcal/mol, of the Sc^+ Singlet ^1D (s^1d^1) State with Respect to the Triplet ^3D (s^1d^1) Ground State (ΔE)

method	ΔE	method	ΔE
B3LYP/TZVP	3.8	BPW91/DZVP	4.3
B3LYP/DZVP	4.6	BP91/LanL2DZ	5.1
B3LYP/LanL2DZ	6.8	B3PW91/TZVP	3.2
BP86/TZVP	3.6	B3P91/DZVP	3.8
BP86/DZVP	3.0	B3P91/LanL2DZ	4.9
BP86/LanL2DZ	5.2	PWP86/DZVP2	6.1
BPW91/TZVP	5.6	exp ^a	7.4

^a Reference 58.

to describe PES's for reactions involving transition metal containing systems. Geometries have been reoptimized at the B3LYP level by using the LanL2DZ effective core potential for scandium and TZVP sets for O, N, C, and H atoms to study the influence of the effective core model potential approach on geometries and energetics and in view of further applications to larger systems.

For comparison purposes computations using the Perdew and Wang exchange⁴⁷ and Perdew correlation⁴⁸ potentials (PWP86) have been performed employing the DZVP2⁴² basis set for the scandium atom, the TZVP set for O, N, and C, and the DZVP set for H atoms. For the evaluation of the gap between the ground and the first excited state of the scandium ion, test calculations have also been performed with use of the Becke exchange⁴⁹ and Perdew correlation⁴⁸ (BP86), the Becke exchange⁴⁸ and Perdew and Wang correlation^{50–52} (BPW91), and the Becke exchange⁴⁰ and Perdew and Wang correlation^{50–52} (B3PW91).

All the calculations reported here have been carried out with the GAUSSIAN94/DFT⁵³ suite of programs, except PWP86 calculations for which was used a modified version of the deMon program,⁵⁴ which includes the possibility of transition states search through the Abashkin-Russo algorithm.⁵⁵

3. Results and Discussion

Since the excitation energy of transition metal atoms and ions is notoriously difficult to compute accurately using DF approaches,^{56,57} we performed the calculation of the singlet–triplet (^1D – ^3D) energy gap of the scandium ion using several combinations of exchange and correlation potentials. In Table 1, the energy differences (ΔE) between the ground state (^3D) and the first excited electronic configuration (^1D) of Sc^+ are reported. The results are compared with experimental data.⁵⁸

The electronic ground-state configuration is found to be (d^1s^1) ^3D , as is known. All the calculated energy differences relative to the ^3D ground state are close to the experimental value, though slightly underestimated. The best value is obtained at the B3LYP level in conjunction with the LanL2DZ effective core potential

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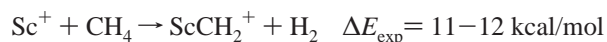
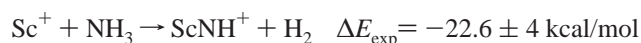
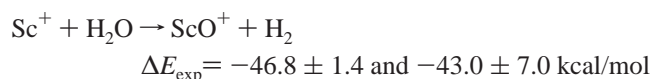
Table 2. Overall Energy for the Reactions $\text{Sc}^+(\text{}^3\text{D}) + \text{XH}_n \rightarrow \text{ScH}^+(\text{}^1\Sigma) + \text{XH}_{n-1}$ and $\text{Sc}^+(\text{}^3\text{D}) + \text{XH}_n \rightarrow \text{ScXH}_{n-1}^+ + \text{H}^a$

method	ΔE	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5
B3LYP/DZVP ^b	67.7	-3.9	59.0	22.4	56.8(52.2)	52.1(47.5)
B3LYP/LanL2DZ ^b	58.8	-6.5	54.1	18.9	52.3(45.5)	49.0(42.2)
PWP86/DZVP2 ^b	63.7	-1.9	58.2	24.2	53.1(47.0)	52.8(46.7)
exp.	63.2 ± 2.1^c	0.9 ± 2.1^c	51.1 ± 2.1^d	23.2 ± 1.6^d	47.7 ± 2.1^e	45.9 ± 3^e

^a ΔE and ΔE_1 are for X = O, ΔE_2 and ΔE_3 are for X = N, and ΔE_4 and ΔE_5 are for X = C. In parentheses are reported also the values with respect to singlet state of reactants for the reaction with methane. All the reported values are in kcal/mol. ^b The basis sets are referred to the scandium atom. ^c Reference 17. ^d Reference 14. ^e Reference 8.

for scandium and TZVP sets for the other atoms. The B3LYP/DZVP value is in error by about 3 kcal/mol. This error is small enough for a reliable assignment of the ionic states of the scandium ion and a correct understanding of the PES's. To check the influence of the basis set size, computations have been redone using the TZVP basis set for scandium used by Ugalde et al.²⁸ Results confirm that the DZVP basis set can be confidentially used, being convergence was almost reached (4.6 kcal/mol at the DZVP level versus 3.8 kcal/mol at the TZVP one).

According to experimental observations^{8,14,17} the formation of dehydrogenation products has been examined as the only exothermic process in the reaction of $\text{Sc}^+(\text{}^3\text{D}, \text{}^1\text{D})$ with water and ammonia and as the energetically most favorable in the case of methane.

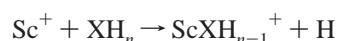
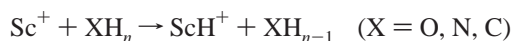


There are two reasonable mechanisms for the interaction of Sc^+ with XH_n (X = O, N, C): Sc^+ insertion into an H-X bond to form an $\text{H}-\text{Sc}^+-\text{XH}_{n-1}$ intermediate or direct abstraction of one H atom from XH_n . The first process is thermodynamically more favorable since the broken H-X bond energy is replaced by the energy of the $\text{Sc}^+-\text{XH}_{n-1}$ bond. The formation of dehydrogenation products, then, can occur by a concerted four-center elimination of H_2 .

An alternative mechanism involves the formation of the insertion intermediate followed by α -H migration to Sc^+ to form $\text{H}_2-\text{Sc}^+-\text{XH}_{n-2}$ and reductive elimination of H_2 . This path is thermodynamically unreasonable for this divalent metal ion that cannot support three covalent bonds, although the formation of the ion-molecule (H_2)- $\text{Sc}^+-\text{XH}_{n-2}$ complex is not excluded in the exit channel of the molecular hydrogen.

Another suggested pathway is the 1,1-dehydrogenation from the initial ion-molecule complex Sc^+-XH_n . This possibility also has been examined in the reaction with water, but the presence of a high barrier indicates that this mechanism may be excluded.

The energies of formation of the other experimentally observed ionic products, formed in reactions



have been calculated and reported in Table 2.

The obtained results hold well with experimental results. The reactions of formation of ScH^+ and ScXH_{n-1}^+ species correspond to a direct mechanism of bond cleavage from the

hydrido intermediate (II) and are all endothermic. In the case of water, the reaction leading to the formation of ScOH^+ product would be exothermic from a theoretical point of view and endothermic from an experimental one, but only very slightly. Then, the error is yet quite small. For the reaction with methane the energies of formation with respect to the singlet state of reactants are reported also because of the hypothesis, discussed later, that the singlet dominates the observed reactivity.

3.1. Sc^+ Insertion into the O-H Bond. The reaction of metal ions with water has received much attention in large part due to the exhaustive experimental studies of Armentrout and co-workers^{16,17} which pointed out that early transition metal cations are more reactive than their oxides, while the contrary is true with late metals. These results have been confirmed by the theoretical investigations of the reactivity of first-row transition metal cations with water.²⁷⁻³⁰ Even more interesting is that the primary product of the reverse reaction is the cation in an excited low-spin state that conserves spin with the reactants.¹⁶ We investigated the potential energy surfaces for both the singlet and triplet states of the scandium ion reaction with water.

The fully optimized geometrical structures of stationary points along the reaction path are displayed in Figure 1a,b for singlet and triplet states, respectively. In Figure 2 the PES's for the titled reaction are depicted.

As previously pointed out, in the case of water two possible pathways have been considered corresponding to the 1,2-dehydrogenation (1) from the insertion intermediate $\text{H}-\text{Sc}^+-\text{OH}$ and 1,1-dehydrogenation from the ion-molecule complex Sc^+-OH_2 (2). Along both low- and high-spin surfaces and for both (1) and (2) mechanisms the first step is the ion-molecule complex formation. Then, for pathway (1), through the transition state TS1, one hydrogen migrates from the oxygen atom to the scandium to form the insertion intermediate, HScOH^+ (II), whose existence was surmised by experimentalists. For pathway (2) the final products are obtained directly from the intermediate complex (I), see Figure 1a,b, by a 1,1- H_2 loss from the oxygen atom, through the transition state TS3. The common electrostatic complex (I), obtained from the interaction between the lone pair on oxygen and the empty 4s orbital of scandium ion has C_{2v} symmetry and is more stable in its triplet state. The experimental value for this energy difference is only estimated¹⁶ and is about 11 kcal/mol. From an inspection of the data reported in Table 3 it can be seen that this estimation is in reasonable agreement with theoretical values that are in the range of 8.6–20.3 kcal/mol.

From this intermediate complex the reaction proceeds, pathway (1), to give the transition state TS1 for the migration of a hydrogen atom from the O atom to scandium. Despite the numerous strategies pursued to find the structure of the triplet transition state, the search was unsuccessful at all the considered levels of theory. Also by using the force constant matrix relative to the same transition state found at MP2 level, the search does not converge to a saddle point of order one.

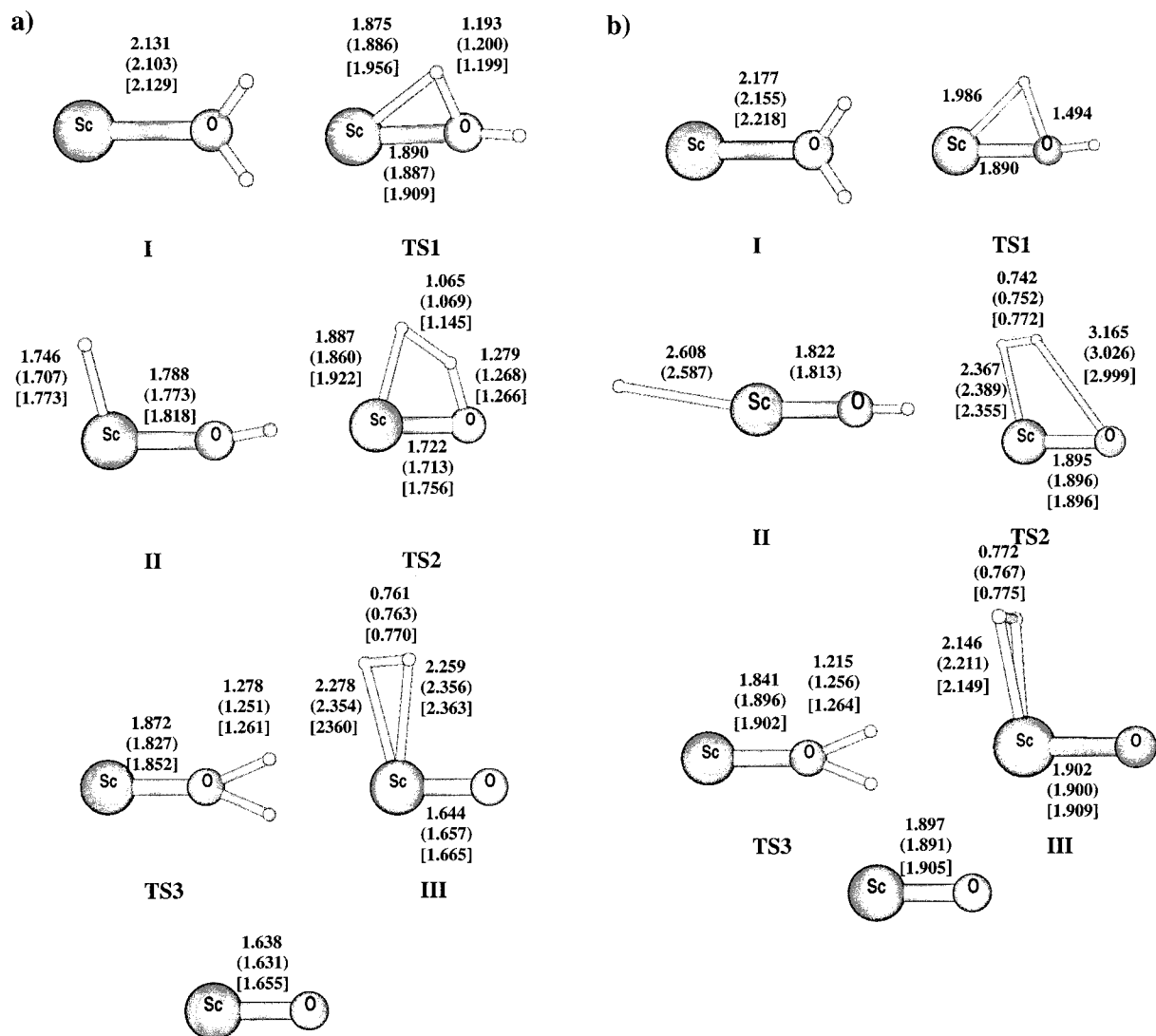


Figure 1. Geometrical parameters of minima and transition states on the B3LYP/DZVP singlet (a) and triplet (b) potential energy surfaces for the reaction of Sc^+ with H_2O . B3LYP/LanL2 and PWP86/DZVP2 data are reported in () and [], respectively. Bond lengths are in angstroms.

The insertion intermediate HScOH^+ , formed by the coupling of the unpaired electrons on the H and OH ligands with the two valence electrons on oxygen, has a singlet spin ground state, the intermediate along the triplet path being an excited state. Indeed, the high-spin state has a very long Sc–H bond at the B3LYP level, while no stable structure was found with use of the PWP86 functional.

The second oxygen to scandium hydrogen migration takes place through the four-center transition state TS2, previously hypothesized by experimentalists, shown in Figure 1a,b. For the low-spin transition state structure the distance H–H is still quite long, while the triplet structure shows an almost fully formed H–H bond and very long Sc–H and O–H distances. It is worth noting that while in the previous DF theoretical high-spin TS2 structure²⁸ the distance from scandium is longer than that from oxygen, the contrary occurs in the present study. The difference with respect to geometrical parameters of the MP2 triplet TS2 structure²⁴ is obvious because it corresponds to the abstraction of a hydrogen atom from the $\text{Sc}^+ \text{--} \text{OH}$ species.

After passing through the transition state TS2 the reaction leads to the last intermediate found along this path: the molecular hydrogen complex (III). For this complex, different geometries have been found. The most stable conformation of the complex along the singlet PES appears to be a planar one

with an Sc–O bond length only slightly longer than that found in the separate products. The difference in the triplet state structure, which is nonplanar, is due to a small interaction of the singly occupied d orbital that does not exist in the singlet (H_2) ScO^+ system.

From Figure 2 it is evident that, along pathway (2), the transition state TS3 that corresponds to 1,1- H_2 loss directly from the oxygen atom of the intermediate complex (I) is very high in energy. The value of the energy barrier, larger than 70 kcal/mol for both singlet and triplet states and at all the employed levels of theory, suggests clearly that the reaction does not occur with this less favorable mechanism. Since from an experimental point of view^{8,14,17} it was found that the data for the reaction of scandium ion with water, ammonia, and methane are very similar, corresponding to similar reaction mechanisms, pathway (2) was not taken into account along the PES's for the analogous reactions analyzed in the next sections.

The last system studied was the ScO^+ ion in its $^3\Delta$ and $^1\Sigma$ states as the product of the dehydrogenation reaction. The values of the energy separation between the above-mentioned systems are listed in Table 3 together with the predicted experimentally^{17,59,60} and previously calculated theoretic overall energies of reaction.

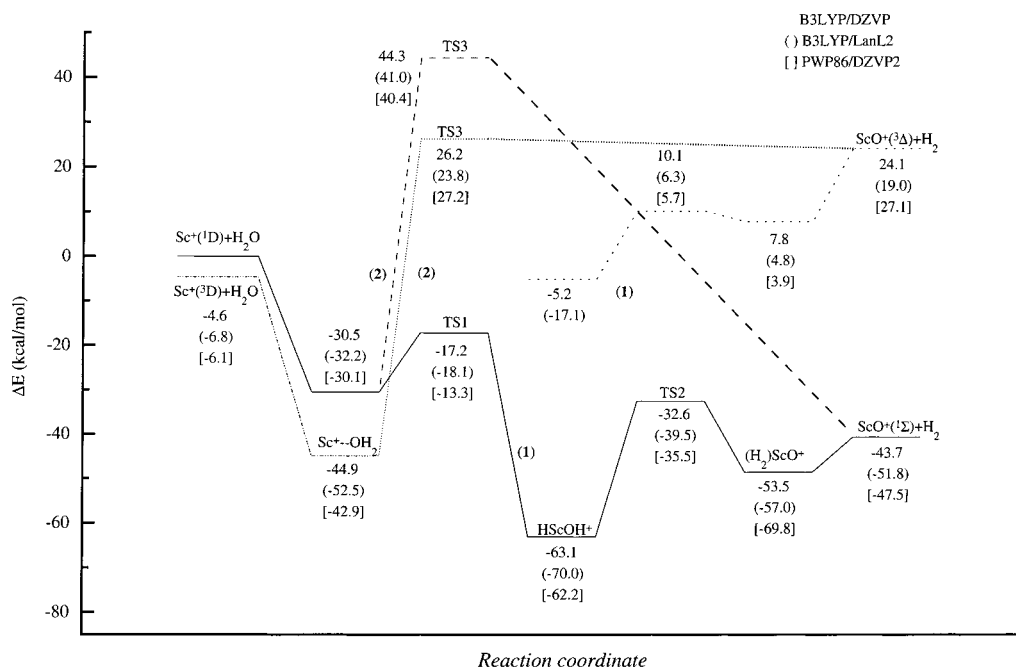


Figure 2. B3LYP/DZVP singlet and triplet potential energy surfaces for the reaction of Sc^+ with H_2O . B3LYP/LanL2 and PWP86/DZVP2 energetical parameters are reported in () and [], respectively. Energies are in kcal/mol and relative to the excited-state reactants (^1D) $\text{Sc}^+ + \text{H}_2\text{O}$. The absolute energies, in hartree, of the reactants are -836.728968 , B3LYP/DZVP; -122.537473 , B3LYP/LanL2; and -837.027739 , PWP86/DZVP2.

Table 3. Relative Energies of $\text{Sc}^+ - \text{OH}_2$ ($^1\text{A}_1$) with Respect to the $\text{Sc}^+ - \text{OH}_2$ ($^3\text{A}_2$) State (ΔE), $\text{ScO}^+ (^1\Sigma)$ with Respect to the $\text{ScO}^+ (^3\Delta)$ State (ΔE_1) and the Overall Energy for the Reaction $\text{Sc}^+ (^3\text{D}) + \text{H}_2\text{O} \rightarrow \text{ScO}^+ (^1\Sigma) + \text{H}_2$ (ΔE_2). All in kcal/mol.

method	ΔE	ΔE_1	ΔE_2
B3LYP/DZVP ^a	14.4	-67.8	-39.1
B3LYP/LanL2DZ ^a	20.3	-70.8	-45.0
PWP86/DZVP2 ^a	12.8	-74.6	-41.4
theor.	16.1, ^b 8.6, ^b 12.5 ^c	-73.6, ^b -80.6, ^b -79.6 ^c	-44.7, ^b -45.1 ^b
exp.			-46.8 \pm 1.4 ^d -43.0 \pm 7.0 ^e

^a The basis sets are referred to the scandium atom. ^b Reference 28.

^c Reference 21. ^d Reference 17. ^e References 59 and 60, estimated.

The low-spin moiety is the ground state and lies more than 60 kcal/mol below the excited high-spin triplet. The calculated energy of reaction corresponds to the exothermic process of formation of the $\text{ScO}^+ + \text{H}_2$ species in their low-spin state from the triplet ground state of Sc^+ reacting with water. The agreement with experimental results is good and the worst value is obtained at the B3LYP/DZVP level of theory. Therefore, the energetically most favorable reaction mechanism of the triplet ground state of the scandium ion would at first yield the triplet ion molecule complex $\text{Sc}(\text{OH}_2)^+ (^3\text{A}_2)$, then make an intersystem crossing to the singlet state and go over the singlet TS1 to reach the singlet insertion intermediate $\text{HScOH} (^1\text{A}_1)$. Because of the spin-forbidden crossing, this process may not be efficient but is still energetically accessible at low temperatures. Indeed, experimentally it was observed that this reaction is only 0.7 \pm 0.2% efficient at thermal energies.¹⁷

3.2. Sc^+ Insertion into the N—H Bond. On the basis of experimental observations¹⁴ and the results obtained in the case of reaction of Sc^+ with water, the only reaction pathway we consider for the exothermic dehydrogenation of ammonia (and methane) is that occurring via oxidation addition of the N—H

(and C—H) bond, for both singlet and triplet potential energy surfaces. Geometrical parameters of stationary points are reported in Figure 3a,3b and their corresponding potential energy profiles are shown in Figure 4.

The only data comparable with previous theoretical²¹ and experimental¹⁴ results are reported in Table 4.

The first step of the reaction is, also in this case, the exothermic formation of the ion—molecule complex (I), along both singlet and triplet PES's, with C_s rather than C_{3v} symmetry, due to the Jahn—Teller effect. As seen in Figure 3, the stabilization energy, with respect to the reactants, of the (I) complex is -39.2 and -47.4 kcal/mol at the B3LYP/DZVP level of theory for the $^1\text{A}_1$ and $^3\text{A}_2$ states, respectively.

The next step of the reaction is the insertion of Sc^+ into the N—H bond of ammonia through the formation of a transition state TS1, whose search, in this case, was successful at all the employed levels of theory along both singlet and triplet paths. This transition state corresponds to the shift of a hydrogen atom from N to Sc, distances from the scandium atom being very similar in both low- and high-spin structures. The active O—H bond length, on the other hand, changes significantly in going from the singlet to the triplet structure, becoming longer by about 1 Å. From the $\text{HScNH}_2^+ (\text{II})$ insertion intermediate the reaction proceeds to yield the molecular hydrogen complex $(\text{H}_2)\text{ScNH}^+ (\text{III})$ after overcoming the TS2 four-center transition state. Finally, the dehydrogenation products are formed directly from (III) without an energy barrier. As in the case of water, the potential energy behavior from $\text{Sc}(\text{NH}_3)^+$ to product formation is very different, as can be seen in Figure 4, between triplet and singlet states. Indeed, along the triplet state reaction path, except for the intermediate (II) at the PWP86 level of the theory, the formation of all the species is endothermic with respect to the reactants. In particular, because of the very small difference in energy between the insertion product and the transition state leading to it, the existence of this species cannot be established. Thus, this process is not likely to take place under normal conditions. On the other hand, for the singlet state the scandium ion inserts into the N—H bond with a relatively small barrier at

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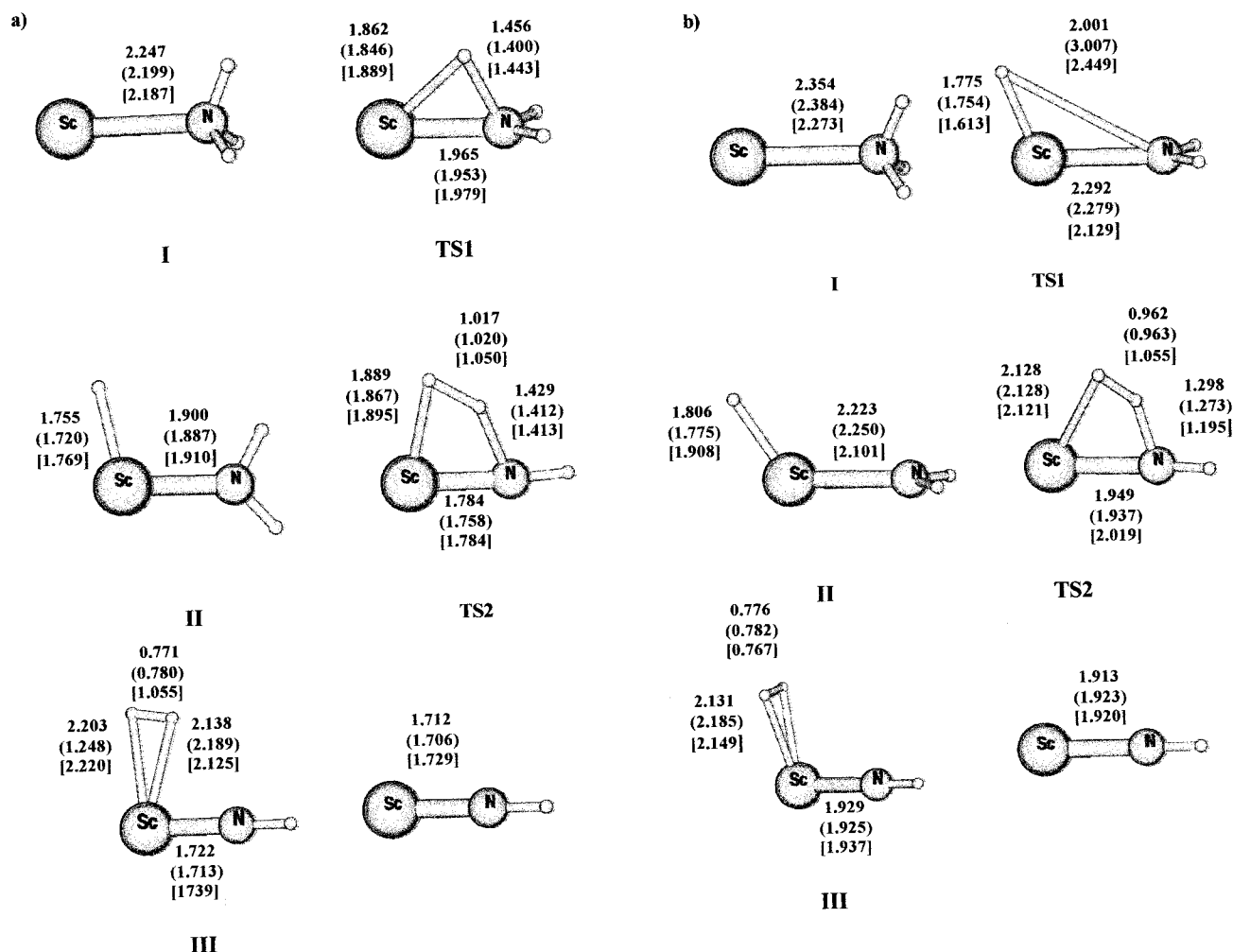


Figure 3. Geometrical parameters of minima and transition states on the B3LYP/DZVP singlet (a) and triplet (b) potential energy surfaces for the reaction of Sc^+ with NH_3 . B3LYP/LanL2 and PWP86/DZVP2 data are reported in () and [], respectively. Bond lengths are in Å.

TS1 relative to the intermediate (I) and leads to the insertion product (II) that is, except at the B3LYP/DZVP level, slightly more stable than $\text{Sc}(\text{NH}_3)^+$. Since, as seen in Figure 4, the PES's of reaction for singlet and triplet states cross in the vicinity of the collision complex (II), the obvious conclusion, in disagreement with that proposed by Song,²¹ is that the reaction is a spin-forbidden reaction that starts with Sc^+ in its triplet state and finishes with ScNH^+ in the singlet one. The need to undergo an intersystem crossing can be invoked again to explain the inefficiency of the process dominated by high-spin ions. Moreover, we note that there is a very large difference between the values of the reaction energy for the formation of the insertion intermediate (II) (ΔE_2) and the products (ΔE_3) from the reactants. For the previous ab initio MO investigation the reactants include scandium in its singlet state, while in the present study we refer to scandium in its triplet ground state, but the discrepancy is too large to be ascribed to this difference in the reference state.

3.3. Sc^+ Insertion into the C-H Bond. The experimental studies⁸ of the reaction of Sc^+ with methane suggest again that the mechanism of oxidative addition is operative to form the intermediate HScCH_3^+ that is estimated to lie 10.8 kcal/mol below the ground-state reactants. From this intermediate the dehydrogenation reaction, with an estimated endothermicity of 9.7 ± 2.6 kcal/mol, is predicted to be the most energetically favorable. In Table 5 our results together with available theoretical²³ and experimental energetical parameters are listed.

Figure 5a,b shows the structures of stationary points found along the singlet and triplet PES's (Figure 6).

The envisioned mechanism includes formation in the entrance channel of the long-lived ion-induced-dipole complex (I), which subsequently yields the insertion intermediate (II) by migration of a hydrogen atom corresponding to the transition state TS1. The methane complex (I) has the tridentate structure shown in Figures 5a,b, with C_{3v} symmetry, both in the singlet and triplet state. The corresponding C_{2v} bidentate structures result in transition states in nature. Along the path another ion-induced-dipole complex (III) is found in the exit channel for the H_2 elimination. This species is obtained from (II) through the tight four-center transition state TS2. All the mentioned species exist along the potential energy surfaces of the singlet and triplet states, but for the triplet, after the formation of the stable collision complex (I) the reaction proceeds with a large barrier to give the insertion intermediate that is more stable than the transition state by only 1 kcal. On the contrary, for the singlet, Sc^+ inserts into the C-H bond with a relatively small barrier, relative to the ScCH_4^+ complex, and leads to the insertion product, which is higher in energy by only a few kilocalories. Thus, the reactivity along the singlet path is expected to be much larger than that along the triplet one.

As shown by experimental studies,⁸ in the reaction of Sc^+ with methane there is a bottleneck that may be because most of the produced ions are in the triplet state while the reaction mechanism is dominated by the formation of intermediate

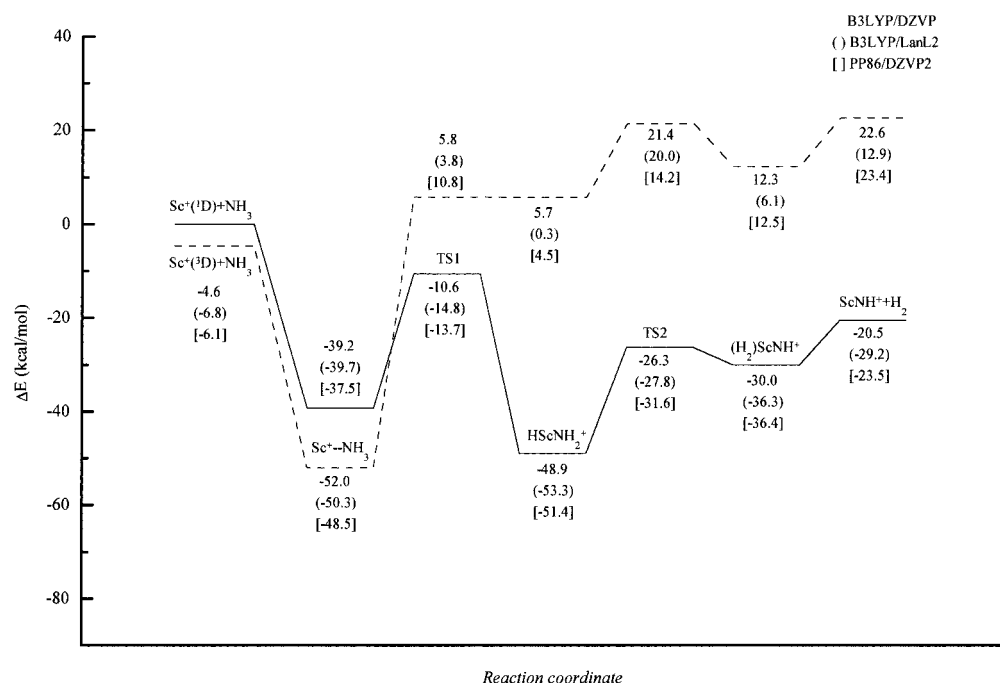


Figure 4. B3LYP/DZVP singlet and triplet potential energy surfaces for the reaction of Sc^+ with NH_3 . B3LYP/LanL2 and PWP86/DZVP2 energetical parameters are reported in () and [], respectively. Energies are in kcal/mol and relative to the excited-state reactants (^1D) $\text{Sc}^+ + \text{NH}_3$. The absolute energies, in hartree, of the reactants are -816.860541 , B3LYP/DZVP; -102.674700 , B3LYP/LanL2; and -817.162566 , PWP86/DZVP2.

Table 4. Relative Energy of Sc^+-NH_3 ($^1\text{A}_1$) with Respect to the Sc^+-NH_3 ($^3\text{A}_2$) State (ΔE), HScNH_2^+ ($^1\text{A}_1$) with Respect to the HScNH_2^+ ($^3\text{A}_2$) State (ΔE_1), HScNH_2^+ ($^1\text{A}_1$) with Respect to Ground State Reactants (ΔE_2) and the Overall Energy for the Reaction $\text{Sc}^+(\text{D})+\text{NH}_3 \rightarrow \text{ScNH}^+(\Sigma) + \text{H}_2$ (ΔE_3). All in kcal/mol.

method	ΔE	ΔE_1	ΔE_2	ΔE_3
B3LYP/DZVP ^a	12.8	-54.6	-44.3	-15.9
B3LYP/LanL2DZ ^a	10.6	-53.6	-46.5	-17.1
PWP86/DZVP2 ^a	11.0	-55.9	-45.3	-17.4
theor ^b		-53.3	-95.9 ^c	-105.4 ^c
exp ^d			~ -34.6	-22.6 ± 2.3

^a The basis sets are referred to the scandium atom. ^b Reference 21.

^c These values are calculated with respect to the singlet excited state of reactants. ^d Reference 14.

HScCH_3^+ in its singlet state. Again a singlet–triplet curve crossing can explain the low reactivity of the scandium ion with respect to other studied metal ions. The intersystem crossing is clearly evident in Figure 6.

From a comparison of data reported in Table 5 it can be seen that notwithstanding a general agreement with experiment, the endothermicity of the reaction is not well reproduced whatever the level of theory used. Musaev and Morokuma²³ have attributed this disagreement to the bad description of the Sc^+-CH_2 bond for this species in its singlet ground state. In fact, the difference between the theoretically “best estimated”⁶¹ bonding energy, 85 ± 3 kcal/mol (we obtain 85.4 kcal/mol at B3LYP/DZVP level), and the experimental one,⁸ 96.9 ± 5.3 kcal/mol, corresponds to an underestimation by about 10 ± 5 kcal/mol of the endothermicity of the reaction. We should note that Armentrout⁶² has suggested that the experimental value of the bonding energy could be about 10 kcal/mol too large due to the contribution from reaction with the excited state of Sc^+ . Adding this contribution to the experimental value of the

reaction energy (9.7 ± 2.6 kcal/mol) a closer agreement is obtained with all the theoretically proposed values (see Table 5). The reaction of the scandium ion with methane, indeed, has a different behavior if compared with those with water and ammonia. The high-spin metal ground state reacts with H_2O and NH_3 to form products in exothermic processes, the PES's of which have no barriers that are higher than the energies of the ground-state reactants (see Figures 2 and 3). On the contrary, the energy barrier to obtain the transition state TS1 along the path for the reaction with methane is in excess with respect to the ground-state reactants (see Figure 6). As motivated also by a statement reported in ref 8, “it was unclear whether the triplet ground state or the singlet excited state dominated the reactivity seen”, we can conclude that the observed bottleneck may be due to the reaction of a small population of the scandium ion to its first excited state. Then, the reaction evolves to product formation conserving spin.

4. A Comparison between PES's

In this section we will compare the results discussed above relative to the reaction mechanism and potential energy surfaces for the reaction of Sc^+ ion with water, ammonia, and methane.

As seen in Figures 2, 4, and 6 the behavior of the PES's is similar in all the considered cases, especially for the triplet state paths, except for the absence of a triplet transition state TS1, corresponding to the migration of a hydrogen atom from oxygen to the scandium atom, along the path for the reaction of scandium with water. Anyway, in the other two cases, the high barrier to obtain TS1 and the very small difference with respect to the intermediate (II) points to the conclusion that the reaction proceeds directly, without formation of the inserted product (II), to reach the hydride complex (III) via the TS2 transition state.

Despite the qualitative similarity between PES's there are significant differences in the energetics. First of all, the stabilization energy, with respect to the reactants, of the electrostatic complex (I) decreases in going from ammonia, to water, to methane.

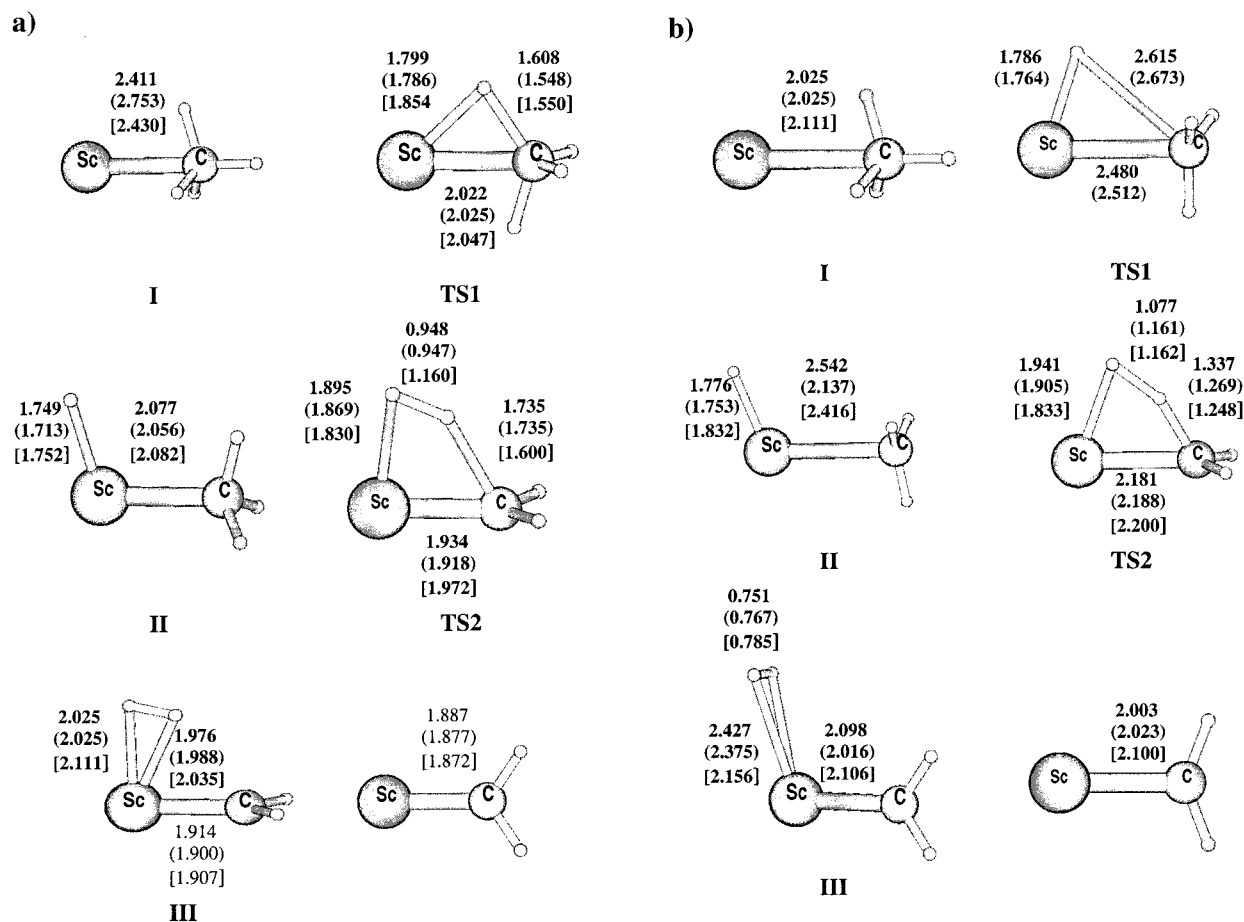
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Table 5. Relative Energy of Sc^+-CH_4 (1A_1) with Respect to the Triplet Sc^+-CH_4 (3A_2) (ΔE), HScCH_3^+ (1A_2) with Respect to the Triplet HScCH_3^+ (3A_2) State (ΔE_1), Energy of Formation of HScCH_3^+ (1A_2) from Singlet (ΔE_2) and Triplet (ΔE_3) Reactants, and the Overall Energy for the Reactions $\text{Sc}^+(\text{D})+\text{CH}_4 \rightarrow \text{ScCH}_2^+(\text{A}_1)+\text{H}_2$ (ΔE_4) and $\text{Sc}^+(\text{D})+\text{CH}_4 \rightarrow \text{ScCH}_2^+(\text{A}_1)+\text{H}_2$ (ΔE_5). All in kcal/mol.

method	ΔE	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5
B3LYP/DZVP ^a	11.9	-40.8	-14.2	-9.6	28.4	33.0
B3LYP/LanL2DZ ^a	11.9	-38.6	-13.6	-6.8	24.1	30.9
PWP86/TZVP ^a	12.3	-41.9	-18.8	-12.7	23.1	29.2
theor. ^b	17.9/8.9		-6.4/-8.4	-1.5/-1.6	21.1/26.8	29.0/33.6
exp. ^c		~ -27.7		~ -10.8		9.7 ± 2.6 (~ 20) ^d

^a The basis sets are referred to the scandium atom. ^b Reference 23; the numbers before and after the slash are referred to the lowest and the highest level of calculation, respectively. ^c Reference 8. ^d Reference 62.

**Figure 5.** Geometrical parameters of minima and transition states on the B3LYP/DZVP singlet (a) and triplet (b) potential energy surfaces for the reaction of Sc^+ with CH_4 . B3LYP/LanL2 and PWP86/DZVP2 data are reported in () and [], respectively. Bond lengths are in Å.

The calculated global minimum along the singlet path for the reaction with water appears to be the insertion intermediate (II) due, in large measure, to the presence of two dative bonds between oxygen and scandium. Since nitrogen can form one dative bond and carbon none the bond strength decreases. This bond strength weakening corresponds to a decrease of the exothermicity of the insertion product, and the global minimum, along the path for the reaction with methane, becomes the electrostatic complex.

The decreasing strength of the bond between scandium and O, N, and C is responsible also for the decrease in the thermodynamic stability of the molecular hydrogen complex (III).

The difference in energy between reactants and the transition state of the rate-determining step is defined as the activation energy of the reaction. This quantity calculated at the B3LYP/DZVP level has a value of -12.6 and -6.0 kcal/mol for the reaction with water and ammonia, respectively. For the reaction with methane the positive activation energy is 8.9 and 13.5 kcal/

mol with respect to scandium in its triplet and singlet state, respectively.

Conclusions

The following key points may be made from the results presented here.

The proposed experimental qualitative behavior of the potential energy surfaces for the insertion reaction of the scandium ion into the O-H, N-H, and C-H bonds of water, ammonia, and methane, respectively, is confirmed. In the first step the reactants yield a stable ion-molecule complex from which the insertion intermediate is formed through a transition state that corresponds to the migration of a hydrogen atom toward scandium. From the insertion intermediate a molecular hydrogen complex is obtained via a tight four-center transition state. Then, without an energy barrier, the complex decomposes to give the reaction products directly.

The reaction intermediate is a stable minimum and lies low in energy only along the PES's of reaction for the singlet state.

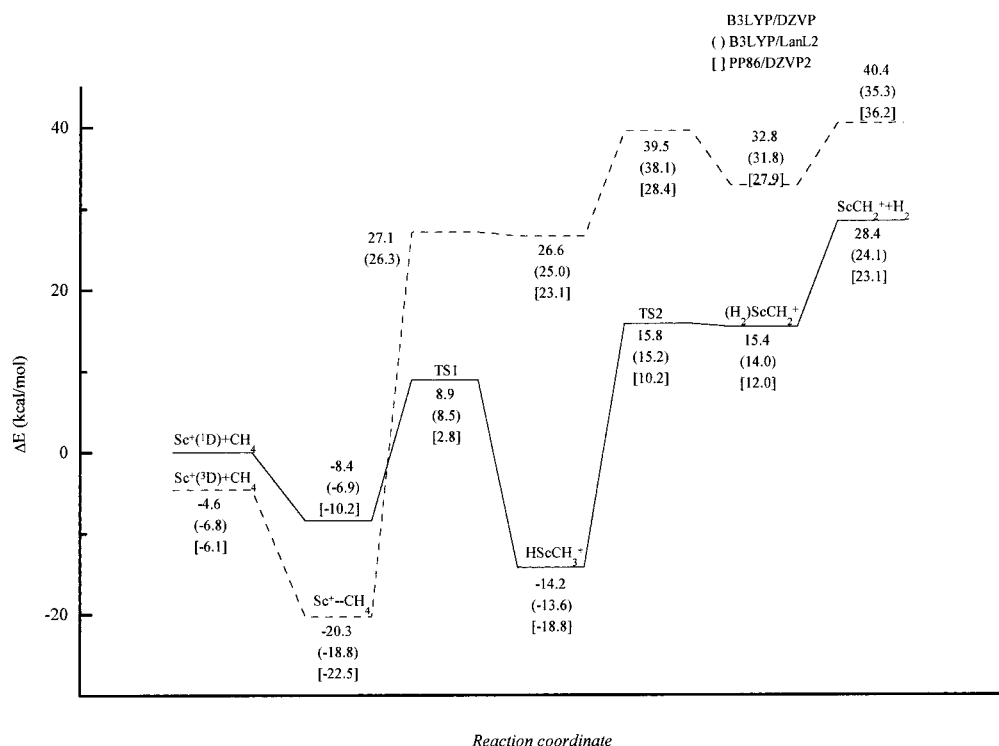


Figure 6. B3LYP/DZVP singlet and triplet potential energy surfaces for the reaction of Sc^+ with CH_4 . B3LYP/LanL2 and PWP86/DZVP2 energetic parameters are reported in () and [] parentheses, respectively. Energies are in kcal/mol and relative to the excited-state reactants (^1D) $\text{Sc}^+ + \text{CH}_4$. The absolute energies, in hartree, of reactants are -800.805745 , B3LYP/DZVP; -86.641750 , B3LYP/LanL2; and -801.091246 , PWP86/DZVP2.

Therefore, because of the excited nature of this intermediate with respect to the triplet ground state of the reactants, the reactions are presumed to occur via a crossing from the high-spin surface to the low-spin one. The need of an intersystem crossing can justify the low efficiency of these reactions, yet accessible at low temperature, with the scandium ion.

By using arguments based on energetics, in the case of methane, it is suggested that the reaction takes place more easily along the singlet potential surface, without an inefficient intersystem crossing.

From a comparison of energetical data and geometrical parameters reported in the tables and the figures the principal

features of PES's are well reproduced by all three levels of theory employed in this work. This result is significant in view of the potential benefits (e.g. low computational costs) of using the LanL2DZ core model potential for larger transition metal containing systems.

Acknowledgment. Financial support from the Università degli Studi della Calabria and MURST (Progetto Nazionale Sistemi a Grandi Interfasi) is gratefully acknowledged.

JA000658C