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Theoretical investigation of the insertion of nickel in the CH bond of CH₄. Electronic structure calculations and dynamics

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The insertion of a nickel atom in the CH bond of CH₄ is calculated using density functional theory by determining the transition state and the dissociated state of HNiCH₃. A barrier for nickel insertion of 40.7 kJ/mol is found and its origin is discussed. The insertion is exothermic by 34.0 kJ/mol. From the potential energy surface at the transition state and the dissociated state vibrational and rotational frequencies are obtained. Unimolecular and bimolecular transition state theory is used for the calculation of rate constants, sticking coefficients, and activation energies for the nickel insertion reaction as well as the nickel elimination reaction. Activation energies for nickel insertion in both CH₄ and CD₄ are small compared with other theoretical work. A moderate kinetic isotope effect for the insertion reaction is found when all hydrogens are substituted by deuterium, whereas no significant kinetic isotope effect is found for nickel elimination. Hydrogen tunneling corrections on rate coefficients are also evaluated, but their effect is negligible. Sticking coefficients are small, which is consistent with experimental sticking coefficients of CH₄ on nickel surfaces.

I. INTRODUCTION

The conversion of hydrocarbons on transition metal surfaces is industrially and theoretically of great interest. For example, the steam reforming of natural gas, of which CH₄ is the major constituent, over a nickel catalyst is a commercial process to produce hydrogen, but occurs only at elevated temperatures and pressures.¹ Some of the first mechanistic studies of CH₄ dissociative chemisorption on transition metals were those of Winters.² The apparent activation energies of CH₄ on a tungsten surface were discussed in terms of tunneling of hydrogen through a potential barrier, vibrational excitation of CH₄, and the lifetime of undissociated CH₄ on the surface (precursor model). At the same time, Stewart and Ehrlich³ found that dissociative adsorption of CH₄ on rhodium surfaces could be enhanced by increasing only the CH₄ gas temperature (T_g). Also, a large kinetic isotope effect (KIE) was found and Stewart and Ehrlich attributed this to a dominant role of vibrational activation in the CH₄ activation process. Since both experiments suggested the importance of vibrational excitation, laser vibrational excitation experiments on rhodium surfaces were carried out,⁴ but were unsuccessful. Rettner, Pfnür, and Auerbach⁵ showed in a subsequent study on W(110) that vibrational excitation enhances the CH₄ chemisorption, but that this enhancement is not significantly larger than for an equal amount of energy in translation modes. They could not rule out the possibility that individual vibrational modes contribute disproportionately to the observed sticking probability, but in that case other vibrational modes would be less effective, thus explaining the unsuccessful laser experiments. In later work on CH₄ on rhodium,⁶ Brass and Ehrlich studied thermal activation by raising the gas temperature or the metal surface temperature (T_s). They found that initial sticking coefficients increased in all cases with temperature. Therefore, they

suggested⁷ that dissociation occurs both through activated direct chemisorption (dependent on T_g) and through molecular precursors (dependent on T_s) and they explained the observation of different activation energies for CH₄ and CD₄ again in terms of internal vibrational excitation of CD₄ and CH₄. Beebe *et al.*⁸ also performed thermal activation experiments under isothermal conditions for several low indices nickel single crystal surfaces. Again, a large KIE of a factor 20 was found on Ni(100), whereas none was seen on the Ni(110) surface; no CD₄ experiments on Ni(111) were carried out. Chorkendorff, Alstrup, and Ulmann,⁹ however, performing the same isothermal experiments for CH₄ on Ni(100), found an activation energy of twice that of Beebe. Beebe also compared his measured sticking coefficients with those calculated from molecular beam experiments on Ni(111) (Ref. 10) and Ni(100) (Ref. 11). The agreement with Ni(111) was good, with Ni(100) poor. In another dispute Lo and Ehrlich¹² claimed that the experimental KIE of CH₄/CD₄ chemisorption on W(211), whether translationally or vibrationally activated, could not be described by a tunneling model in which barrier parameters were chosen to match the experimental activation energy. Their results were reanalyzed by Kay and Coltrin,¹³ who showed that the experimental results were entirely consistent with a tunneling mechanism provided a more intricate model for the tunneling transmission coefficient was used. In return, Lo and Ehrlich derived a more generally applicable relation for tunneling and again denounced the tunneling model after comparison with their experimental findings. After additional exchange of comments between both sides, we conclude that a tunneling mechanism could not be totally eliminated, as demonstrated by Kay and Coltrin, but also could not account totally for the small experimental KIE as was pointed out by Lo and Ehrlich.

By making use of molecular beam techniques in com-

bination with ultrahigh vacuum surface electron spectroscopy, it is nowadays possible to study experimentally the dynamics of the CH₄/CD₄ decomposition under low pressure conditions, giving far more detailed experimental information. The first CH₄ dissociation molecular beam experiment [on W(110)] was performed by Rettner, Pfnür, and Auerbach,¹⁴ which showed a roughly exponential increase of the sticking coefficient (S) with the normal component of the incident energy, E_n . The experiments also showed a large KIE and an increase in S with nozzle temperature, which was explained by enhanced vibrational excitation. The authors pointed out that the dependence of S on E_n suggested a concerted tunneling mechanism instead of a molecular precursor model followed by tunneling. In another experiment Lee *et al.*¹⁵ used a single Ni(111) crystal and obtained similar results, but by making use of electron-energy-loss spectroscopy (EELS) vibrational spectroscopy they demonstrated also that the initial step in dissociative chemisorption is the breaking of a single CH bond and the formation of adsorbed CH₃ and H. They also argued that the critical requirement for CH₄ dissociation is angular deformation of CH₄ to allow a Ni–C bond to form. In this model S is sensitive for excitation of CH₄ bending modes, explaining the dependence of S with nozzle temperature and partly the KIE. The strong dependence of S on E_n was to increase transfer of translational energy to bending vibration energy on impact of CH₄ with the surface (called splats and eventually giving rise to new experimental methods like inert gas atoms induced chemisorption¹⁶). Tunneling can contribute to this model but is not essential; also, molecular precursors play no role in this model. Similar studies have been performed by Luntz and Bethune¹⁷ and Schoofs *et al.*¹⁸ on Pt(111). The only new feature emerging was a complex dependence of S on E_n , T_g , and T_s , noted by Luntz and Bethune, but unnoticed by Schoofs *et al.* Also, Luntz and Bethune did not present a model to explain the observed complex dependence, but remarked that this could not be explained by any known single model. In another series of papers, however, Luntz and Harris¹⁹ presented a model in which quantum mechanical tunneling is dominant; the tunneling process is interpreted as a quantum dynamics problem involving a three-dimensional potential energy surface. They gave, however, only qualitative results.

In conclusion, many kinetic and molecular beam studies have been performed resulting in different activation energies, sticking coefficients, and KIE's for each kind of experiment and condition. Precursor models, accounting for a strong dependence of S on T_s , direct dissociative chemisorption models, accounting for a strong dependence of S on T_g , and mixed models, relating S , E_n , T_g , and T_n , have been invoked. Nevertheless, this wealth in models has not resolved the relationship between the factors controlling the reaction mechanism of the chemisorptive dissociation of CH₄ on transition metal surfaces completely.

As a first model in the investigation of the electronic factors determining the CH₄ dissociation on transition metals, we have investigated the elimination of a nickel atom from the dissociated state:

TABLE I. Exponential coefficients for basis functions.

Atom	Function	ζ	Atom	Function	ζ	Atom	Function	ζ
Ni	1s ^a	23.35	C	1s ^a	5.40	H	1s	0.76
	2s ^a	9.20		2s	1.24		2s	1.28
	3s ^a	5.85		2s	1.98		2p	1.00
	2p ^a	11.22		2p	0.96			
	3p ^a	4.38		2p	2.20			
	3d	1.54		3d	2.50			
	3d	3.35						
	3d	7.00						
	4s	1.10						
	4s	2.00						
	4p	1.47						

^aAdditional function for core orthogonalization.

as well as the reverse reaction, insertion of a nickel atom in a CH bond of CH₄:

by means of an *ab initio* approach. Using the potential energy surfaces at the transition state (TS) and at the dissociated state (DS), we have calculated vibrational frequencies. The TS and DS geometries allow the calculation of rotational constants. According to transition state theory, the rate coefficients for nickel (oxidative) addition and nickel (reductive) elimination have been calculated in terms of translational, vibrational, and rotational partition functions. Activation energies and preexponential factors have been calculated from Arrhenius plots. Technical details of the calculations are discussed in Sec. II. In Sec. III the electronic structure calculations are presented and discussed. In Sec. IV dynamical calculations and the application of transition state theory are discussed. In Sec. V we summarize results and draw conclusions.

II. COMPUTATIONAL DETAILS

We have performed quasirelativistic calculations based on density functional theory (DFT) using the implementation of Baerends's group.²⁰ The exchange-correlation potential used is based on quantum Monte Carlo simulations of Ceperley and Alder²¹ of a homogeneous electron gas which are parametrized by Vosko, Wilk, and Nusair.²² To correct for the overbinding inherent to the local density approximation (LDA),²³ we have used a gradient corrected exchange energy functional²⁴ in combination with the Stoll correction²⁵ for correlation. Molecular orbitals are expressed by the linear combination of atomic orbitals (LCAO) method using Slater orbitals, integrals are evaluated numerically²⁶ and adsorption energies are calculated by Ziegler's transition state method.²⁷ For carbon a frozen core potential is used for the 1s electrons; for nickel the electrons up to 3p are frozen. Relativistic effects were taken into account by first-order perturbation theory.²⁸ The exponents of the Slater functions are shown in Table I. Single ζ functions are used for core orthogonalization. The basis

FIG. 1. Definition of geometric parameters. H_{act} denotes the activated hydrogen, H_1 denotes the hydrogen in the mirror plane, $H_{2,3}$ denote the hydrogens above and below the mirror plane. The dotted line at the activated CH bond is the C_{3v} axis when there is no tilt (as in CH_4); the other dotted line represents the C_{3v} axis in tilted geometries (TS or DS).

sets are of double ζ quality with the exception of the nickel d orbitals which are triple ζ 's. On all atoms polarization functions are included.

The geometry is indicated in Fig. 1. The CH_3 fragment was kept rigid with CH distances of 1.09 Å and H–C–H angles of 109.48° as in CH_4 . The basis for this assumption was the experimental result that the CH_3 fragment in TS and DS are very similar.¹⁰ C_s symmetry was maintained for all calculations. The TS and DS were explicitly calculated by a four-dimensional grid in the NiC, NiH, and CH distances (grid constant of 0.1 Å) and the CH_3 tilt angle (θ) with respect to the activated CH bond (grid constant of 5°). Grid boundaries were 1.85 and 2.05 Å for the NiC distance, 1.40 and 1.60 Å for the NiH distance, 1.25 and 1.55 Å for the CH distance, and 15.0 and 30.0° for the CH_3 tilt angle. Vibrational calculations were performed by the conventional GF method;²⁹ dynamical properties were calculated according to unimolecular and bimolecular transition state theory,³⁰ including quantum tunneling corrections based on an unsymmetrical Eckart potential,³¹ where G is the kinetic energy matrix and F the force constant matrix.

III. ELECTRONIC STRUCTURE CALCULATIONS

Results of calculations on the atomic states of nickel are shown in Table II. The implementation of the program allows only the calculation of low and high spin states. Therefore, it is not possible to calculate the separate J states; also the calculation of the separate $d^8s^2\ ^3F$ and 3P states is not possible because the d^8s^2 high spin state corresponds with a linear combination of both. However, we can calculate J -averaged low and high spin states. Table II shows that a correct ordering of atomic states is obtained. Extensive multireference configuration-interaction (MRCI) calculations³² including f and g functions in the basis set and complete-active-space self-consistent-field (CASSCF) plus second-order perturbation theory (CASPT2) calculations³³ give the 3F state as the ground state contrary to experiment.³⁴ However, the other states

TABLE II. Energies (kJ/mol) of J -averaged atomic states relative to the $d^9s^1(^3D)$ state.

State	Expt. ^a	DFT ^b	MRCI ^c	ACPF ^d	CASPT2 ^e
$d^9s^1(^3D)$	0.0	0.0	0.0	0.0	0.0
$d^8s^2(^3F)$	2.9		−18.0		−7.7
$d^9s^1(^1D)$	32.1	16.7	43.9	28.9	30.9
$d^8s^2(^3F+^3P)$	64.5	67.4			
$d^8s^2(^1D)$	153.0	156.5			
$d^{10}(^1S)$	167.4	233.5	180.6		167.9

^aSee Ref. 34.

^bThis work.

^cSee Ref. 32.

^dSee Ref. 35.

^eSee Ref. 33.

are calculated in agreement with experiment, especially with the CASPT2 method. For the average coupled pair functional (ACPF) method,³⁵ only the difference between the lowest triplet $d^9s^1\ ^3D$ and lowest singlet $d^9s^1\ ^1D$ state could be found in the literature. This difference is, however, calculated more correctly with the ACPF method than with the MRCI method used by the same authors.

Optimal parameters and binding energies of the nickel insertion in the CH bond are shown in Table III. They were obtained by fitting the energy calculated on grid points in the Ni/CH₄ gas, TS and DS region to a second-order polynomial in the NiC, NiH, and CH distances and the CH_3 tilt angle θ . The obtained (fitted) energy was tested by making another set of calculations with the optimal geometrical parameters. The deviation between fitted and calculated energies was negligible. All tabulated energies are binding energies with respect to CH_4 and the 3D high spin state of nickel. The TS for insertion occurs at a $NiCH_{act}$ angle (α) of 48.1° and the DS for α of 34.8°. Therefore the DS is a bent state, as in the case of NiH_2 .³⁶ The TS barrier for insertion is 40.7 kJ/mol; the insertion is exothermic by 34.0 kJ/mol.

Electron distributions for all atoms based on a Mulliken population analysis are shown in Table IV. From this table one can see that during the insertion the nickel atom maintains a d^9s^1 -like state. The reason for this is that a

TABLE III. Geometries (Å) and energies (kJ/mol) for the Ni/CH₄ gas, $HNiCH_3(^1A')$ TS and DS.

System	Calc.	R_{NiC}	R_{NiH}	R_{CH}	α	θ	E
DS	DFT ^a	1.92	1.46	2.55	34.8°	29.9°	−34.0
TS	DFT ^a	2.02	1.49	1.37	48.1°	21.3°	40.7
Ni/CH ₄ ^b	DFT	∞	∞	1.08	...	0.0°	0.0
DS	MRCI ^c	1.98	1.47	2.55	35.2°	27.0°	17.9
TS	MRCI	2.12	1.49	1.62	44.3°	19.5°	82.7
Ni/CH ₄ ^d	MRCI	∞	∞	1.09	...	0.0°	0.0
DS	ACPF ^e	1.98	1.47	2.55	35.2°	27.0°	−13.8
TS	ACPF	2.12	1.49	1.62	44.3°	19.5°	74.9
Ni/CH ₄ ^d	ACPF	∞	∞	1.09	...	0.0°	0.0

^aThis work.

^b $Ni\ ^3D+CH_4$.

^cSee Ref. 37.

^d $Ni\ ^1D+CH_4$.

^eSee Ref. 37; MRCI optimized geometries.

TABLE IV. Nickel, carbon, and hydrogen electron density distribution over orbitals based on a Mulliken population analysis; see Fig. 1 for hydrogen assignment.

State	Ni 3d	Ni 4s	Ni 4p	C 2s	C 2p	H _{act} s	H _{act} p	H ₁ s	H _{2,3} s
Ni/CH ₄	9.00	1.00	0.00	1.33	2.85	0.94	0.03	0.94	0.94
TS	9.18	0.76	0.08	1.42	2.90	0.89	0.10	0.85	0.88
DS	8.94	0.87	0.11	1.48	2.92	0.97	0.04	0.87	0.86

single electron in both *s* and *d* shells can efficiently hybridize when low spin coupled, thereby avoiding strong steric repulsion between closed shell CH₄ and a closed *s* or *d* shell of nickel. Also, the singly occupied *d* orbital and *s* orbital can more easily form the two bonds to CH₃ and hydrogen. Blomberg *et al.* have shown³⁶ that this efficient *s*-*d* hybridization has its consequence in a low barrier and a bent minimum as compared to the less efficient *s*-*p* hybridization resulting in a high barrier and a linear minimum. An electron density difference map of TS with respect to a nickel atom and CH₄ in the TS geometry in the mirror plane is shown in Fig. 2. Together with the overlap populations at TS of NiH (0.19) and NiC (0.14), it suggests that hydrogen starts to bind first. At DS the overlap populations for CH₃ and hydrogen with nickel are, respectively, 0.32 and 0.27, suggesting a stronger bond for CH₃. The electron density increase in the *d* orbitals at TS shows the *d* orbital involvement. There is also an increase in density at the activated CH bond. This is due to the occupation, by electron donation of the nickel atom, of the antibonding σ , located between carbon and the activated hydrogen, which lowers the CH₃-H dissociation barrier. This can be seen more clearly in Figs. 3(a) and 3(b), which show the local density of states (LDOS) of this antibonding orbital at TS and at a large distance. At TS the antibonding σ located at the activated CH bond is dispersed significantly in four molecular orbitals (MO's) of

FIG. 2. Contour plots of the electron density differences: $\rho(\text{TS}) - \rho(\text{Ni}) - \rho(\text{CH}_3\text{H})$ (TS). Solid contours denote increase, dashed lines denote decrease in electron density. Contour values (in electrons $\text{\AA}^{-3}$) are 0.00, ± 0.006 , ± 0.016 , ± 0.035 , ± 0.075 , ± 0.159 , ± 0.336 , ± 0.709 , ± 1.505 , and ± 3.185 .

which three are above the Fermi level (denoted by the zero of energy) and one is beneath it. This one is the highest occupied molecular orbital (HOMO), which is the dissociating CH bond. Therefore, the character of the HOMO is clearly partially antibonding. At large distance, i.e., 4.36 $\text{\AA}$, the same antibonding σ is almost a pure MO, far above the Fermi level and therefore not occupied. To determine the origin of the barrier for nickel insertion, we performed two series of calculations. In one series, we investigated the effect of stretching a CH bond by stretching this bond in CH₄ from 1.08 to 1.37 $\text{\AA}$ (TS value). We found a destabilization of 84.7 kJ/mol. In another series, we investigated the effect of the Pauli repulsion, associated by the approach

FIG. 3. Local density of states (LDOS) of the antibonding σ orbital (σ^*) located between carbon and activated hydrogen (a) at TS geometry and (b) at 4.36 $\text{\AA}$. The mixing in of the antibonding σ^* in the activated CH bond in CH₄ (HOMO) at TS and the almost pure σ^* at 4.36 $\text{\AA}$ is clearly seen.

of a nickel atom, by enlarging the NiC distance, starting at its TS value, and keeping the CH distance at its TS value. We found a small destabilization of the complex. The much larger destabilization of CH₄ by stretching one bond in the absence of nickel (84.7 kJ/mol) vs the same stretch in the presence of nickel (40.7 kJ/mol), in combination with the smooth destabilization of the TS complex when the NiC distance is enlarged, shows that the Pauli repulsion associated with the second trajectory does not control the barrier height for dissociation. In other words, the TS barrier is mainly determined by the need to minimize the energy cost to stretch the CH bond.

We can compare our TS and DS data with the parameters and energies found by Blomberg *et al.*,³⁷ who computed the same reaction path using contracted CI calculations based on CASSCF orbitals. The geometrical parameters are practically the same, except for the stretch of the CH bond at TS; we find a TS in which the CH bond is significantly less stretched. We therefore compute a significantly lower barrier. If we had assumed the nickel atom to be in its lowest singlet state ($d^9s^1\ ^1D$) as Siegbahn *et al.* did, instead of its lowest state ($d^9s^1\ ^3D$), the barrier would lower another 16.7 kJ/mol. The calculated energy difference between TS and DS is 65 kJ/mol (MRCI) and 74.7 kJ/mol (DFT), but our low TS barrier results in a strong exothermic state. Blomberg *et al.*³⁷ also calculated the energetics of the insertion reaction using the optimal geometrical parameters determined with the MRCI method, but using a larger basis set and a different method, the internally contracted average coupled pair functional (IC-ACPF) method. Although the IC-ACPF method results in a lower ($d^9s^1\ ^1D$) state, which is used by the authors as the Ni/CH₄ gas asymptote, and which is in better agreement with experiment than the MRCI value, they nevertheless find a lowering of the nickel insertion barrier of 7.8 kJ/mol. Also, they computed a larger energy difference between TS and DS of 23.9 kJ/mol and the nickel insertion now becomes exothermic by 13.8 kJ/mol, which are both more in agreement with our results. A separate IC-ACPF geometry optimization would further lower their barrier and make the insertion reaction even more exothermic. In addition, we have shown that the repulsive barrier is mainly due to stretching the CH bond.

IV. RATE CONSTANT CALCULATIONS: APPLICATION OF TRANSITION STATE THEORY

Transition state theory allows the calculation of rate coefficients in terms of local properties of the potential energy surface (PES), and therefore in principle requires no calculations on the dynamics of the reacting system; we only need vibrational and rotational frequencies. The transition state theory formula for the first- and second-order rate coefficients for (1) and (2) at the high pressure limit are given by³⁰

$$k_1^{\text{TST}} = \frac{k_B T}{h} \frac{(Q_{\text{vib}} Q_{\text{rot}})^{\dagger}}{Q_{\text{vib}} Q_{\text{rot}}} e^{-E_{\text{crit}}/k_B T}, \quad (3)$$

$$k_2^{\text{TST}} = \frac{k_B T V}{h} \frac{(Q_{\text{vib}} Q_{\text{rot}})^{\dagger}}{Q_{\text{trans}} Q_{\text{vib}} Q_{\text{rot}}} e^{-E_{\text{crit}}/k_B T}. \quad (4)$$

In Eqs. (3) and (4), k_B denotes Boltzmann's constant, T temperature, and h Planck's constant. Q_{trans} , Q_{vib} , and Q_{rot} are the translational, vibrational, and rotational partition functions of the Ni/CH₄ gas or DS; the translational partition function describes the relative translation of the nickel atom to CH₄. $\dagger$ denotes transition state partition functions. E_{crit} is the minimum energy at which reaction can occur (critical energy), and includes the zero-point vibrational energy differences. Therefore, to evaluate k_1^{TST} and k_2^{TST} , we need to calculate the translational, vibrational, and rotational partition functions of the Ni/CH₄ gas, DS and TS. However, if partition functions are the same in DS and TS, or in the Ni/CH₄ gas and TS, they cancel and we need only to evaluate partition functions which differ. Also, if a vibrational frequency is high ($h\nu \gg k_B T$), the partition function gives a factor of 1.0 and therefore has no contribution to the rate constant.

To find out which degrees of freedom cancel, we characterized them at the different geometries. In TS and DS we have the following degrees of freedom: three translations of the center of mass (CM), three overall rotations, three CH stretches in CH₃, one methyl tilt in the mirror plane, one methyl tilt out of the mirror plane, three internal bending modes in CH₃, one internal CH₃ rotation around the C_{3v} axis, one CH stretch, one NiC stretch and one NiH stretch. At the Ni/CH₄ gas we have the following degrees of freedom: three translations of CM, three relative translations, three overall rotations of CH₄, three CH stretches in CH₃, three internal bending modes in CH₃, one CH₃ tilt in the mirror plane, one CH₃ tilt out of the mirror plane, and one CH stretch. This choice of modes results in the partition function cancellation as discussed before. The following modes will (approximately) cancel against each other: three translations of CM, three CH stretches of CH₃, three internal bending modes in CH₃, one CH₃ tilt out of the mirror plane, and one internal CH₃ rotation at TS and DS against one overall CH₄ rotation. In effect, we have to compute the partition functions for the CH stretch, NiC stretch, NiH stretch, CH₃ tilt in the mirror plane, and three overall rotations of DS and TS, and three relative translations, a CH stretch, a CH₃ tilt in the mirror plane, and two overall rotations of CH₄ at the Ni/CH₄ gas. The masses of the atoms allow the calculation of the partition function of the relative translation. Together with the masses, the geometries allow the calculation of the moments of inertia and subsequently the rotational constants and the rotational partition functions. To calculate vibrational partition functions, a harmonic vibrational analysis at TS and DS in the NiH, NiC, and CH distances, and the CH₃ tilt and at the Ni/CH₄ gas in the CH distance and the CH₃ tilt was carried out. The frequencies and dominating internal coordinate are displayed in Table V for both CH₄ and CD₄. For the Ni/CH₄ gas the frequencies can be best compared with the normal frequencies of CH₄ and CD₄. We find for the asymmetric CH stretch a frequency of 3120.7 cm⁻¹ and for the CH₃ tilt a frequency of

TABLE V. Vibrational frequencies ν_i (cm⁻¹) and dominating coordinate s_i [NiC-, NiH-, CH-str(etch), or CH₃ tilt] for the Ni/CH₄ gas, the Ni/CD₄ gas, TS, and DS.

Geometry	ν_1	s_1	ν_2	s_2	ν_3	s_3	ν_4	s_4
Ni/CH ₄	3120.7	CH-str	2210.8	tilt				
Ni/CD ₄	2253.2	CH-str	1624.1	tilt				
TS/CH ₄	1987.9	tilt	1743.4	NiH-str	606.5	NiC-str	682.4i	CH-str
TS/CD ₄	1539.7	tilt	1258.3	NiH-str	585.6	NiC-str	510.9i	CH-str
DS/CH ₄	2237.9	NiH-str	1582.6	tilt	671.5	CH-str	504.9	NiC-str
DS/CD ₄	1605.3	NiH-str	1250.1	tilt	529.0	CH-str	469.0	NiC-str

2210.8 cm⁻¹. For CD₄ these values are respectively 2253.2 cm⁻¹ and 1624.1 cm⁻¹. The experimental values are 3019.5 cm⁻¹ and 1533.6 cm⁻¹ for CH₄ and 2109 cm⁻¹ and 1092 cm⁻¹ for CD₄, respectively.³⁸ For the CH stretch our values are only slightly higher, for the CH₃ tilt our values are 600–700 cm⁻¹ too high. This is due to the fact that we calculated the pure stretch and CH₃ tilt and not the normal coordinates, which should lower the frequencies. Our choice of modes, however, results in the partition function cancellation as discussed above. For TS the imaginary frequency is strongly dominated by the CH stretch. For both TS and DS tilt and NiH stretch frequencies are significantly higher than NiC and CH stretches.

Now, according to Eqs. (3) and (4) rate constants can be evaluated. The results are shown in Table VI for CH₄ and CD₄ at different temperatures. Equilibrium constants are given by the k_2^{TST} , k_1^{TST} fraction. Γ^* denotes the ratio of quantum chemical rate to classical mechanical rate as calculated by transition state theory. In the quantum chemical rate we corrected for tunneling effects by assuming that our reaction coordinate can be described by a one-dimensional unsymmetrical Eckart potential energy function.³¹ For the boundaries of the Eckart function, we have taken the potential energy difference between TS and the Ni/CH₄ gas and TS and DS, respectively, resulting in an upper bound for the tunneling correction. The justification for this one-dimensional model is that analysis of our vibrational data shows that at the saddlepoint the reaction coordinate consists almost purely of the CH stretch. We can see that at low temperatures ($T=250$ K) tunneling has a pronounced effect on the reaction rate (a factor of 2.064 for CH₄), and that tunneling is quite different for hydrogen (2.06) and deuterium (1.48). At high tempera-

tures ($T=1000$ K) classical rates and quantum chemical rates, which are simply obtained from Table VI by multiplication of k_1^{TST} or k_2^{TST} with Γ^* , are almost the same, as they should be.

Classical sticking coefficients (S^{TST}) are calculated in the following manner. First, we calculated the hard sphere preexponential (A^{HS}) by treating CH₄ and Ni as hard spheres³⁹ to set an upper limit for the preexponential calculated from transition state theory (A^{TST})

$$A^{\text{HS}} = \pi r^2 \left(\frac{8k_B T}{\pi \mu_{\text{NiCH}_4}} \right)^{1/2} \quad (5)$$

In Eq. (5) πr^2 represents the collision cross section and $(8k_B T / \pi \mu_{\text{NiCH}_4})^{1/2}$ the mean speed according to the Maxwell distribution. For r we took the values calculated from the moments of inertia of the different geometries, and in each case we checked that A^{HS} was indeed larger than A^{TST} . The sticking coefficient is now simply the ratio of k_2^{TST} and A^{HS} and is therefore effectively the reaction probability per hard sphere collision. Analogous, the quantum mechanical sticking coefficient (S^{QM}) can be calculated as the ratio of k_2^{QM} and A^{HS} .

It can be seen from Table VI that higher temperatures favor the Ni/CH₄ gas as is to be expected for the endothermic nickel elimination reaction. This effect is, however, counterbalanced by a larger sticking coefficient at higher temperatures. The KIE is almost negligible for the nickel elimination reaction but pronounced for the insertion. This is more clearly seen from Fig. 4, which shows an Arrhenius plot for the nickel insertion or elimination of CH₄/CD₄. The plot data is summarized in Table VII. The electronic energy E denotes the energy difference between TS, DS,

TABLE VI. Unimolecular (k_1^{TST}) (s⁻¹) and bimolecular (k_2^{TST}) (m³ mol⁻¹ s⁻¹) rate constants, ratio of k_2^{TST} to k_1^{TST} (equilibrium constants, K) (m³ mol⁻¹), ratio of A^{TST} to A^{HS} , classical mechanical sticking coefficients (S^{TST}), quantum chemical sticking coefficients (S^{QM}), and ratio of quantum chemical rate to classical mechanical rate (Γ^*) for different temperatures (T) (K) for CH₄ and CD₄.

	T	k_2^{TST}	k_1^{TST}	K	$A^{\text{TST}}/A^{\text{HS}}$	S^{TST}	S^{QM}	Γ^*
CH ₄	250	$2.14 \times 10^{+0}$	6.55×10^{-3}	$3.27 \times 10^{+2}$	0.76	4.14×10^{-08}	8.54×10^{-08}	2.064
CD ₄	250	3.38×10^{-1}	3.62×10^{-3}	$9.34 \times 10^{+1}$	0.54	6.96×10^{-09}	1.03×10^{-08}	1.478
CH ₄	500	$1.09 \times 10^{+4}$	$2.67 \times 10^{+5}$	4.08×10^{-2}	0.64	1.49×10^{-04}	1.77×10^{-04}	1.190
CD ₄	500	$3.63 \times 10^{+3}$	$1.81 \times 10^{+5}$	2.01×10^{-2}	0.47	5.29×10^{-05}	5.82×10^{-05}	1.102
CH ₄	750	$2.20 \times 10^{+5}$	$9.55 \times 10^{+7}$	2.30×10^{-3}	0.65	2.45×10^{-03}	2.65×10^{-03}	1.082
CD ₄	750	$9.62 \times 10^{+4}$	$6.83 \times 10^{+7}$	1.41×10^{-3}	0.49	1.14×10^{-03}	1.19×10^{-03}	1.045
CH ₄	1000	$1.10 \times 10^{+6}$	$1.82 \times 10^{+9}$	6.03×10^{-4}	0.69	1.06×10^{-02}	1.11×10^{-02}	1.047
CD ₄	1000	$5.53 \times 10^{+5}$	$1.34 \times 10^{+9}$	4.13×10^{-4}	0.53	5.69×10^{-03}	5.83×10^{-03}	1.026

FIG. 4. Arrhenius plots of the first-order elimination (k_1) and second-order addition (k_2) rate coefficients for CH₄ and CD₄. Solid lines for CH₄, dashed lines for CD₄. The following markers are used: Δ , k_1 CH₄; ∇ , k_1 CD₄; $\square$, k_2 CH₄; $\diamond$, k_2 CD₄. At low temperature a moderate KIE is seen for both reactions; at higher temperatures curves for CH₄ and CD₄ merge smoothly.

and the Ni/CH₄ gas at the electronic potential energy surface (not including zero-point energies). In the critical energy E_{crit} , the differences in zero-point energy for TS, DS and the Ni/CH₄ gas have been taken into account. The slope of the Arrhenius plots is reflected in the activation energy E_{act} and the intercept in the preexponential, A . We see that inclusion of zero-point energies lowers the insertion barrier of CH₄ by almost 6 kJ/mol reflecting the relatively low frequencies at TS and the high stretching mode frequency for CH₄. The effect of deuteration is to lower vibrational frequencies for both TS and CH₄. Therefore, the lowering effect on the insertion barrier is smaller (3.0 kJ/mol). For the elimination barrier, we see the same trends but less pronounced (4.0 and 2.8 kJ/mol, respectively). The activation energy displays the effect on the barrier, when excited rotational and vibrational levels are populated: a temperature averaged barrier. The population of high vibrational frequency excited levels, e.g., CH stretch mode in the Ni/CH₄ gas or NiH stretch mode in DS, will remain small at elevated temperatures, because of its high frequency and thereby associated high energy. On the contrary, the population of relatively low vibrational frequency excited levels, as those in TS, will strongly increase, as is reflected in the vibrational partition functions and the barrier for insertion will thus increase (1.4 kJ/mol

TABLE VII. Electronic energy (E) (kJ/mol), critical energy (E_{crit}) (kJ/mol), activation energy (E_{act}) (kJ/mol), and Arrhenius preexponential (A) for nickel elimination (s⁻¹) and nickel addition (m³ mol⁻¹ s⁻¹) for CH₄ and CD₄.

System	Reaction	E	E_{crit}	E_{act}	A
CH ₄	addition	40.7	34.8	36.2	$7.62 \times 10^{+07}$
CD ₄	addition	40.7	37.8	39.4	$5.56 \times 10^{+07}$
CH ₄	elimination	74.7	70.7	73.0	$1.16 \times 10^{+13}$
CD ₄	elimination	74.7	71.9	73.8	$9.43 \times 10^{+12}$

for CH₄ insertion, 1.6 kJ/mol for CD₄ insertion, 2.3 kJ/mol for CH₄ dissociation, and 1.9 kJ/mol for CD₄ dissociation). The absolute value of the temperature averaged barrier will depend on the values of the translational, vibrational, and rotational partition functions at TS, DS, and at the Ni/CH₄ gas for different temperatures.

The preexponential factor is connected with the change in entropy on going from reactant to TS, the entropy of activation ($\Delta S^\ddagger$), according to

$$A^{\text{TST}} = \frac{ek_B T}{h} e^{\Delta S^\ddagger / k_B T}, \quad (6)$$

and is therefore a measure for the gain or loss in entropy. At ordinary temperatures the preexponential in Eq. (6) is approximately 10^{13} . The preexponentials for addition denote therefore a large loss in entropy, which is natural because of the loss of translational degrees of freedom. The preexponentials for nickel elimination are approximately 10^{13} , which indicates that $\Delta S^\ddagger$ is approximately zero. The entropy in DS and TS is therefore the same. In combination with the relatively low frequencies for both TS and DS (see Table V), we conclude that both states are loosely bound. The relatively large $A^{\text{TST}}/A^{\text{HS}}$ ratio indicates that the rate constant is mainly determined by E_{crit} .

Only experimental data on the bimolecular rate constant for the nickel cation insertion in CH₄ was available. Tonkyn, Ronan, and Weisshaar⁴⁰ found a rate constant of 7.0×10^{-18} m³ s⁻¹ at $T=300$ K. We find at $T=300$ K a rate constant of approximately 3.47×10^{-22} m³ s⁻¹. Although this is much lower, a cation can be expected to be much more reactive. Beebe *et al.*⁸ find activation energies of 52.7, 26.8, and 55.6 kJ/mol for the decomposition of CH₄ on Ni(111), Ni(100), and Ni(110) surfaces, respectively. For CD₄ these values are 52.7 kJ/mol for Ni(110) and 62.4 kJ/mol for Ni(100). Initial CH₄ sticking coefficients at $T=500$ K are of the order 10^{-8} to 10^{-7} . Chorkendorff, Alstrup, and Ulmann,⁹ however, measured an activation energy of 52 kJ/mol on Ni(100). Our activation energies are much lower, probably because we have no steric repulsion between surface atoms and CH₄. Our single-atom sticking coefficients are higher (10^{-4} , 10^{-5}) than those found for a surface, but we see the same temperature behavior; larger sticking coefficients for higher temperatures. As to the KIE in combination with our estimate of quantum mechanical tunneling effects, we find at $T=250$ K a ratio of the sticking coefficients of hydrogen to deuterium of 8.29, at $T=500$ K a ratio of 3.04 and at $T=750$ K a ratio of 2.22. This is not too far away from a Ni(111) surface sticking coefficient ratio of 8.0 in the temperature region between 640 K and 830 K as found by the molecular beam experiments of Lee, Yang, and Ceyer.¹⁰ In general, the occurrence and absolute value of isotopic substitution is very different for different surfaces. Therefore, the conclusion of Steward and Ehrlich³ that transition state theory cannot account for the experimentally observed isotope effects seems premature.

V. CONCLUSIONS

We have carried out DFT calculations to determine TS, DS, height, and origin of the barrier of reactions (1) and (2). In addition, we calculated rotational and vibrational frequencies and used transition state theory to calculate rate constants and sticking coefficients. We also made an estimate of hydrogen and deuterium tunneling effects, which turned out to be small. A barrier for nickel insertion of 40.7 kJ/mol was found and we have shown that the origin of the barrier is due to stretching of the CH bond. The nickel insertion reaction is exothermic by 34.0 kJ/mol.

The obtained barrier height of 40.7 kJ/mol for the insertion is low compared with experimental results for Ni(100), Ni(110), and Ni(111) surfaces, but we expect better agreement with experiment when clusters are used to model the surface. Steric repulsion due to the neighboring surface atoms can then be taken into account. Also, a higher coordination number of the central nickel atom will tend to decrease its reactivity. Preliminary results on a one-layer seven-atom cluster also showed up a more extended CH bond of 1.63 Å in the transition state, which also will result in a higher barrier.

This would be in contrast with Swang *et al.*,⁴¹ who computed a barrier for CH₄ dissociation on a Ni(100) surface, modeled by a two-layer 13-atom cluster, of 37.2 kJ/mol and estimated the barrier to be 62–71 kJ/mol. Their calculated CH bond length was 1.51 Å. They calculated a barrier for CH₄ dissociation of 74.9 kJ/mol for a single nickel atom,³⁶ corresponding with a CH bond length of 1.62 Å. Therefore, they found a lowering of their calculated barrier of 37.7 kJ/mol with respect to one nickel atom, which can thus partly be understood in terms of a less extension of the activated CH bond.

Calculated frequencies and rate coefficients could only partially be compared with experimental data. Frequencies for CH₄ are too high, because normal modes were not calculated; the frequency shift for CD₄ seems correct. No experimental rate constant for the insertion of a nickel atom was available, but the rate constant for insertion of the cation can be treated as an upper limit. Our one atom sticking coefficients are low as are experimental ones. Calculated preexponentials were connected with change in entropy for insertion and dissociation. They indicate a loose transition state.

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- ¹J. R. Rostrup-Nielsen, *Catalysis—Science and Technology*, edited by J. R. Anderson and M. Boudart (Springer-Verlag, Berlin, 1984), Vol. 5, p. 1.
- ²H. F. Winters, *J. Chem. Phys.* **62**, 2454 (1975); H. F. Winters, *ibid.* **64**, 3495 (1976).
- ³C. N. Stewart and G. Ehrlich, *J. Chem. Phys.* **62**, 4672 (1975).
- ⁴S. G. Brass, D. A. Reed, and G. Ehrlich, *J. Chem. Phys.* **70**, 5244 (1979); J. T. Yates, J. J. Zinck, S. Sheard, and W. H. Weinberg, *ibid.* **70**, 2266 (1979).
- ⁵C. T. Rettner, H. E. Pfnür, and D. J. Auerbach, *J. Chem. Phys.* **84**, 4163 (1986).
- ⁶S. G. Brass and G. Ehrlich, *Surf. Sci.* **187**, 21 (1987); *J. Chem. Phys.* **87**, 4285 (1987).
- ⁷S. G. Brass and G. Ehrlich, *Phys. Rev. Lett.* **57**, 2532 (1986).
- ⁸T. P. Beebe, D. W. Goodman, B. D. Kay, and J. T. Yates, *J. Chem. Phys.* **87**, 2305 (1987).
- ⁹I. Chorkendorff, I. Alstrup, and S. Ulmann, *Surf. Sci.* **227**, 291 (1990).
- ¹⁰M. B. Lee, Q. Y. Yang, and S. T. Ceyer, *J. Chem. Phys.* **87**, 2724 (1987).
- ¹¹A. V. Hamza and R. J. Madix, *Surf. Sci.* **179**, 25 (1987).
- ¹²T. C. Lo and G. Ehrlich, *Surf. Sci.* **179**, L19 (1987); **198**, L380 (1988); **205**, L813 (1988).
- ¹³B. D. Kay and M. E. Coltrin, *Surf. Sci.* **198**, L375 (1988); **205**, L805 (1988).
- ¹⁴C. T. Rettner, H. E. Pfnür, and D. J. Auerbach, *Phys. Rev. Lett.* **54**, 2716 (1985).
- ¹⁵M. B. Lee, Q. Y. Yang, S. L. Tang, and S. T. Ceyer, *J. Chem. Phys.* **85**, 1693 (1986); M. B. Lee, Q. Y. Yang, and S. T. Ceyer, *ibid.* **87**, 2724 (1987); S. T. Ceyer, J. D. Beckerle, M. B. Lee, S. L. Tang, Q. Y. Yang, and M. A. Hines, *J. Vac. Sci. Technol. A* **5**, 501 (1987).
- ¹⁶S. T. Ceyer, *Science* **249**, 133 (1990); J. D. Beckerle, A. D. Johnson, Q. Y. Yang, and S. T. Ceyer, *J. Chem. Phys.* **91**, 5756 (1989); J. D. Beckerle, Q. Y. Yang, A. D. Johnson, and S. T. Ceyer, *ibid.* **86**, 7236 (1987).
- ¹⁷A. C. Luntz and D. S. Bethune, *J. Chem. Phys.* **90**, 1274 (1989).
- ¹⁸G. R. Schoofs, C. R. Arumainayagam, M. C. McMaster, and R. J. Madix, *Surf. Sci.* **215**, 1 (1989).
- ¹⁹A. C. Luntz and J. Harris, *Surf. Sci.* **258**, 397 (1991); *J. Vac. Sci. Technol. A* **10**, 2292 (1992); *J. Chem. Phys.* **96**, 7054 (1992).
- ²⁰Amsterdam density-functional (ADF) program suite developed by Baerends and co-workers; E. J. Baerends, D. E. Ellis, and P. Ros, *Chem. Phys.* **2**, 41 (1988); P. M. Boerrigter, G. te Velde, and E. J. Baerends, *Int. J. Quantum Chem.* **33**, 87 (1988); G. te Velde and E. J. Baerends, *J. Comput. Phys.* **99**, 84 (1992); D. Post and E. J. Baerends, *J. Chem. Phys.* **78**, 5663 (1983); E. J. Baerends and A. Rozendaal, *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*, edited by A. Veillard (Reidel, Dordrecht, 1986), p. 159; P. J. van den hoek, A. W. Kleyn, and E. J. Baerends, *Comments Atom. Mol. Phys.* **23**, 93 (1989).
- ²¹D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ²²S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ²³A. D. Becke, *Int. J. Quantum Chem.* **27**, 585 (1985).
- ²⁴A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ²⁵H. Stoll, C. M. E. Pavlidou, and H. Preuss, *Theor. Chim. Acta* **49**, 143 (1978); H. Stoll, E. Golka, and H. Preuss, *Theor. Chim. Acta* **55**, 29 (1980).
- ²⁶G. te Velde and E. J. Baerends, *J. Comput. Phys.* **99**, 84 (1992).
- ²⁷T. Ziegler and A. Rauk, *Theor. Chim. Acta* **46**, 1 (1977).
- ²⁸J. G. Snijders and E. J. Baerends, *Mol. Phys.* **36**, 1789 (1978); J. G. Snijders, E. J. Baerends, and P. Ros, *ibid.* **38**, 1909 (1979).
- ²⁹E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations. Theory of Infrared and Raman Vibrational Spectra* (McGraw-Hill, New York, 1955).
- ³⁰R. G. Gilbert and S. C. Smith, *Theory of Unimolecular and Recombination Reactions* (Blackwell, Oxford, 1990).
- ³¹H. S. Johnston and J. Heicklen, *J. Phys. Chem.* **66**, 532 (1962); H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.* **83**, 1 (1961).
- ³²C. W. Bauschlicher, P. E. M. Siegbahn, and L. G. M. Pettersson, *Theor. Chim. Acta* **74**, 479 (1988).
- ³³K. Andersson and B. O. Roos, *Chem. Phys. Lett.* **191**, 507 (1992).
- ³⁴C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, DC, 1952).

- ³⁵M. R. Blomberg, P. E. M. Siegbahn, and M. Svensson, *J. Phys. Chem.* **95**, 4313 (1991).
- ³⁶M. R. Blomberg and P. E. M. Siegbahn, *J. Chem. Phys.* **78**, 5682 (1983); **78**, 986 (1983); M. R. Blomberg, U. Brandemark, L. Petterson, and P. E. M. Siegbahn, *Int. J. Quantum Chem.* **23**, 855 (1983).
- ³⁷M. R. Blomberg, U. Brandemark, and P. E. M. Siegbahn, *J. Am. Chem. Soc.* **105**, 5557 (1983); M. R. Blomberg, P. E. M. Siegbahn, U. Nagashima, and J. Wennerberg, *ibid.* **113**, 424 (1991).
- ³⁸G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).
- ³⁹P. W. Atkins, *Physical Chemistry* (Oxford University, Oxford, 1978), p. 872.
- ⁴⁰R. Tonkyn, M. Ronan, and J. C. Weisshaar, *J. Phys. Chem.* **92**, 92 (1988).
- ⁴¹O. Swang, K. Faegri, Jr., O. Gropen, U. Wahlgren, and P. E. M. Siegbahn, *Chem. Phys.* **156**, 379 (1991).