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Dissociative sticking of CH₄ on Ru(0001)

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In this study the CH₄ dissociation probability on Ru(0001) is found for various translational and vibrational energies. The absolute sticking values are determined from King and Wells experiments and carbon uptake curves. The carbon amount is determined from the recombination signal of carbon with oxygen obtained after the beam exposure when heating in an oxygen atmosphere. The measured sticking coefficient of CH₄ is strongly enhanced both by increasing the translational and the vibrational energy of the CH₄ molecule. A model is applied to the data and an estimate of the thermal activation energy for CH₄ dissociation is found to be in good agreement with previous bulb experiments. © 1999 American Institute of Physics. [S0021-9606(99)71405-4]

I. INTRODUCTION

There exists a number of detailed experimental and theoretical studies on how and why the reactivity of bimetallic systems can be modified.¹⁻⁵ It is however a necessary basis for such studies that the reactivities of the individual single crystal surfaces are known. The reactivity of a surface can either be determined from high pressure experiments where several reaction steps can be involved or from the study of a single reaction step, typically the adsorption or dissociation of a molecule. For bimetallic systems the modified surface may change the kinetics of the elementary steps, e.g., the adsorption energies of intermediates thus obscuring the true effect of the modified surface. For these systems the study of a single reaction step is preferable.

The dissociation of small molecules is also interesting to study since they are rate limiting in some catalytic reactions, e.g., the CH₄ dissociation in the steam-reforming process over a Ni catalyst.⁶ By analyzing the experimentally obtained data, fundamental knowledge on the dissociation mechanism itself can be obtained.

Usually the interaction between an incoming molecule and a surface leading to the dissociation of the molecule is divided into two mechanisms: The direct dissociation and the trapping- (or precursor-) mediated process.

For the case of a direct dissociation mechanism where the molecule dissociates on impact, the sticking probability of the molecule is enhanced by increasing both the translational and the vibrational energy. This is found experimentally for, e.g., CH₄ dissociation on W(110),⁷ Ni(111),^{8,9} Ni(100),¹⁰ and Pd(110).¹¹ The effect of surface temperature is small since the molecules do not accommodate to the surface before dissociating. There are however cases where an intact molecule adsorb and equilibrate prior to either dissociation or desorption in which case there will be a surface temperature dependence of the sticking coefficient.¹²⁻¹⁴ Both channels are suggested to have an influence on the observed dissociation probability of CH₄ on the Ir(110) and Ir(111) surfaces. This results in a minimum in the sticking curve due to the different energy dependence of the trapping channel

dominating at low energies and the direct dissociation channel dominating at higher energies.^{13,14} Recent investigations on CH₄ dissociation on Pt(110) also show a minimum. This is however, attributed to a steering effect over the highly corrugated Pt(110) surface.¹⁵

In general, it is also important to have detailed knowledge of the sticking coefficient in the low energy region when comparisons with high pressure experiments are intended. For typical catalytic conditions the majority of the molecules of the Maxwell-Boltzmann distributed gas have low energies so that the overall reactivity measured often is dominated by the low energy sticking behavior.

The dissociation of methane on Ru surfaces has been studied previously in high pressure experiments^{16,17} but to our knowledge the present work is the first molecular beam investigation of CH₄ dissociation on Ru(0001). In order to compare the result of the thermal experiment, a model is fitted to our measured absolute sticking coefficients and a thermal activation energy of 37 kJ/mol is found which is in good agreement with the bulb experiments by Wu *et al.*¹⁶ The model is based on work by Luntz *et al.* where CH₄ is modeled as a quasidiatomic molecule.^{18,19} This is previously applied successfully to the experimentally determined dissociation probabilities of CH₄ on Ni(100).¹⁰ This quasidiatomic assumption is also used as the basis in a recent work by Carré *et al.* where the effect of allowing all molecular orientations of the incoming CH₄ molecule is investigated.²⁰

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure below 1×10^{-10} mbar. The chamber could be separated into two individual chambers pumped with a turbomolecular and an ion pump, respectively. A three-stage supersonic molecular beam expansion chamber was connected to the chamber. The energy distribution of the molecules in the beam was determined from the flight times over a well-defined distance using a cross-beam quadrupole mass spectrometer. The distribution of velocities was fitted to a shifted Maxwell-Boltzmann dis-

tribution and an average experimentally determined translational energy was found. A detailed description of our setup was given in Ref. 10. The UHV chamber was equipped for performing low energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), and temperature programmed desorption (TPD) and had several gas and metal dosers connected. The gases used were all high purity gases (99.9995% or better) and the beam gas was further cleaned in a catalyst at RT before the expansion.¹⁰

The Ru crystal was polished and aligned to within 0.5° of the (0001) facet. Prior to entering the UHV chamber the crystal was exposed to a H_2 flow at 1 bar at 1116 K for approximately 800 h.²¹ The crystal was mounted on tungsten wires used for heating and the temperature was measured with a cromel–alumel thermocouple fixed in a hole in the side of the crystal. Initially the major contaminants were sulfur and carbon. The sulfur was removed by cycles of Ar^+ sputtering and annealing to 1513 K. Since the carbon Auger line (273 eV) overlaps with one of the Ru lines (272 eV)²² it was necessary to apply another method in order to accurately determine the amount of carbon. The titration method used was previously applied to the Co–Cu(111) system with a sensitivity down to 0.1% of a carbon saturation coverage.^{4,5} The carbon was removed by numerous heating cycles from RT to 1513 K in an oxygen pressure of 3×10^{-7} mbar. The crystal was held at 1513 K for 1 min in order to desorb the oxygen.^{23,24} There was no oxygen present after this cleaning procedure as checked with AES. This initial cleaning procedure was continued until no recombination signal of carbon and oxygen was detectable with the mass spectrometer when annealing as described above. Between experiments this cleaning procedure was performed twice in order to remove any adsorbed carbon.

In order to determine the sticking coefficient of CH_4 for different translational and vibrational energies the Ru surface was exposed to supersonic molecular beams containing CH_4 . The gas molecules were expanded from a high pressure region in the molybdenum nozzle through a $40 \mu m$ orifice into a low pressure region. The many collisions during the expansion resulted in an almost complete relaxation of the rotational energy but in no relaxation of the vibrational modes.¹⁰ The molecules therefore preserved their vibrational energy obtained from their thermal equilibration with the nozzle walls. We made use of the seeding principle to obtain higher energies by mixing the CH_4 gas with H_2 or He and lower energies by seeding with Ar. The translational energies determined experimentally using the time of flight method showed a good agreement with the theoretical expected values.²⁵ The experiments at low energies were performed in order to investigate if the sticking coefficient had a minimum at low energy as observed for CH_4 dissociation on, e.g., Ir surfaces and Pd(110).^{13–15}

III. RESULTS

A. Determination of CH_4 sticking probabilities

Five different gas mixtures were used with nozzle temperatures ranging from 450 to 1250 K corresponding to

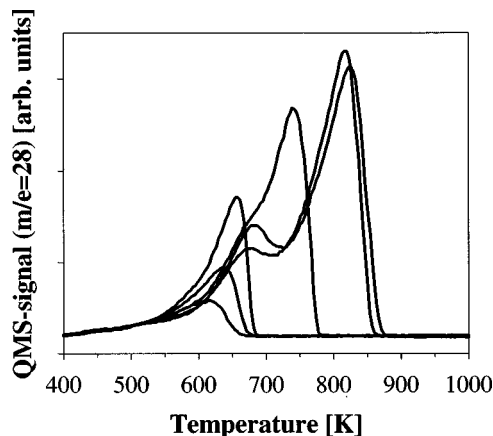


FIG. 1. TPD spectra after molecular beam exposures at 600 K for 0.5, 1, 2, 12, 91, and 180 min. The beam was 3% CH_4 in He with a nozzle temperature of 1250 K. After the beam exposure the crystal was cooled down to 400 K from which the desorption experiment was started with an oxygen background pressure of 3.0×10^{-7} mbar. The heating rate was 2 K/s.

translational energies from 12 to 113 kJ/mol. The gas mixtures were 10% CH_4 in Ar, 100% CH_4 , 25% CH_4 in He, 3% CH_4 in He, and 3% CH_4 in H_2 . The clean Ru(0001) crystal was held at 600 K during the molecular beam exposure in order to avoid adsorption of CO and H_2 from the background.^{26,27} The molecular beam was at normal incidence with the surface and the diameter of the beam spot was smaller than the crystal diameter. This eliminated contributions from the edge of the crystal which could have another reactivity than the surface. After the exposure, the crystal was cooled to 400 K while positioning it in front of the QMS in a reproducible distance of approximately 1 mm. An oxygen background pressure of 3.0×10^{-7} mbar was applied during the TPD experiment with a heating rate of 2 K/s. In Fig. 1 a few selected TPD spectra of the recombination signal of carbon and oxygen ($m/e=28$) are shown for beam exposure periods of 30 s, 60 s, 120 s, 12 min, 91 min, and 180 min. The beam mixture was 3% CH_4 in He with a nozzle temperature of 1250 K. The recombination is seen to take place from 500 K up to 900 K in agreement with experiments on CO dissociation on Ru(0001) by Hoffmann.²⁸ The area of a recombination signal of carbon and oxygen was proportional to the true amount of carbon adsorbed. Such areas are shown for a number of nozzle temperatures in Fig. 2 as a function of the beam exposure. The topmost curve corresponds to a nozzle temperature of 1250 K and the lowest to 550 K and the gas used was a 3% CH_4 in He mixture. The value of the exposure was calibrated for each gas mixture to be indicative of the total number of incoming CH_4 molecules during the experiment. The area is seen to increase quickly in the low coverage regime whereas the increase in coverage becomes slower for higher coverages. The uptake behavior was fitted the best with a second order expression shown as solid lines with the initial sticking coefficient as the single fitting parameter. The carbon saturation level was found as an average of several long exposure experiments from different beam mixtures.

For the high energy beams it was possible to measure the absolute sticking coefficient with the King and Wells

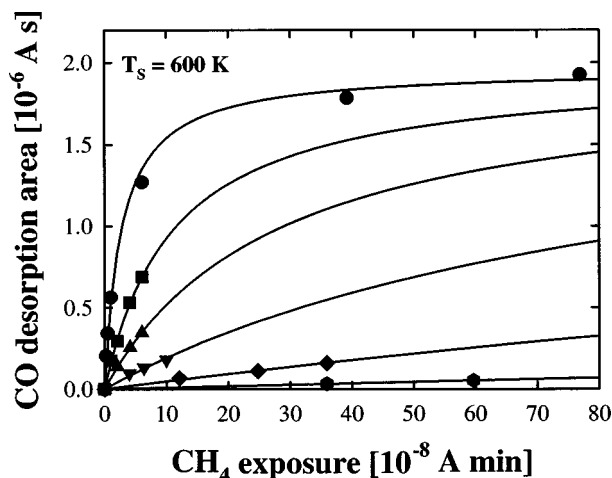


FIG. 2. A series of uptake curves for a single beam mixture (3% CH₄ in He) at nozzle temperatures ranging from 550 to 1250 K. The solid lines are fits to the data. The single fitting parameter is the initial sticking coefficient.

method²⁹ which was sensitive down to sticking coefficients of approximately 0.05. A linear correlation between the absolute sticking coefficient and the fitting parameter enabled a conversion of the fitting parameters for lower energies to absolute sticking coefficients. In Fig. 3 the true sticking coefficients are shown as a function of the experimentally determined translational energy. Sticking coefficients measured with the same gas mixture but for different nozzle temperatures are connected with a solid line. The nozzle temperature is indicated with the symbol. The sticking coefficient is seen to increase both with translational and vibrational energy in the entire energy range investigated here. The lowest sticking

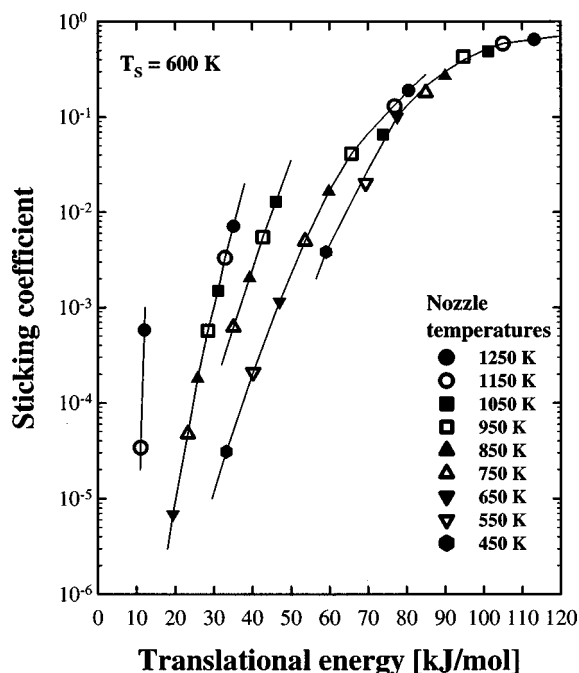


FIG. 3. The absolute sticking coefficient vs the experimentally determined translational energy of the CH₄ molecules. The solid lines connect data points from the same gas mixture. Nozzle temperatures between 450 and 1250 K were used.

coefficient measured as a result of a beam exposure is 7×10^{-6} for a pure CH₄ beam at 650 K corresponding to a translational energy of 19 kJ/mol. Exposures at lower energies, for example an exposure time of 13 h with a pure CH₄ beam at a nozzle temperature of 450 K and a translational energy of 12 kJ/mol did not result in any detectable signal in our QMS. Being conservative and assuming that 0.2% of a C-ML was adsorbed which was the sensitivity of our QMS, the sticking coefficient would in this case be 1×10^{-6} . This corresponds to our lower detection limit.

B. Estimating the carbon saturation coverage

The difference between the desorption areas after exposures of 91 and 180 min in Fig. 1 was very small indicating that the carbon coverage was approaching saturation. The beam diameter (3 mm) on the surface was as mentioned previously, smaller than the crystal diameter (10 mm), making the desorption areas from background dosed CO and from titration of the adsorbed carbon from the CH₄ beam incomparable. However, after these experiments were performed the size limiting skimmer in the beam expansion setup was replaced with a larger one, increasing the beam diameter to that of the crystal diameter so that desorption areas after background doses and beam exposures could be compared. The CO area after a CH₄ saturation exposure under these new conditions is approximately 2.5 times larger than the area of the desorption spectrum of a CO saturated Ru(0001) surface which has been found to correspond to 0.65–0.68 Ru-ML by a number of groups.^{30,31} The carbon saturation coverage on Ru(0001) could therefore be estimated to be approximately 1.7 Ru-ML (± 0.1 Ru-ML), probably incommensurate with the Ru lattice since no additional LEED structure was observed. A desorption spectrum of similar shape and area as after a CH₄ saturation exposure with the large skimmer was obtained by dosing 750 L of C₂H₄ at 600 K. The saturation coverage of carbon at 600 K on Ru(0001) did as mentioned, not induce additional spots to the hexagonal LEED pattern but by flashing this surface to 1300 K, a sharp (11×11) LEED pattern appeared. Similar LEED patterns were observed after saturation beam exposures at a surface temperature of 1300 K and after a C₂H₄ dose of 150 L at 600 K annealed to 1300 K. This was in agreement with Wu *et al.*¹⁷ who investigated CH₄ decomposition at higher pressures using STM and LEED. They explained the observed LEED pattern at 1300 K as a result of the carbon forming a graphite overlayer on Ru.

IV. MODELING OF THE STICKING COEFFICIENTS

The molecular beam data provide detailed information about the dynamics involved in the dissociation of CH₄ on Ru(0001). However, under catalytic conditions it is the thermal sticking coefficient that is the relevant quantity. In order to make an estimate of this from the molecular beam results and to compare with bulb experiments by Wu *et al.*,¹⁶ a parameterized model implying some simplifications and approximations was needed. The basis of the model used was to treat the methane molecule as a quasidiatomic molecule, consisting of a hydrogen atom and a methyl group so that the

TABLE I. Resulting parameters from fitting the model to the experimental data.

ν	V_ν (kJ/mol)	W_ν (kJ/mol)
0	115	27
1	65	14
2	16	~ 0

dissociation process only involved the breaking of the H-CH₃ bond.^{18,19} Excitation of the vibrational stretch mode in this bond was assumed to be responsible for the enhanced sticking for increased nozzle temperatures. Using the ansatz previously applied for the CH₄/Ni(100) system¹⁰ we assumed that the sticking coefficient of methane with translational energy E_{trans} and in the vibrational state ν would dissociate with the probability given by

$$S_\nu(E_{\text{trans}}) = \frac{A_\nu}{2} \left[1 + \operatorname{erf} \left(\frac{E_{\text{trans}} - V_\nu}{W_\nu} \right) \right], \quad (1)$$

where A_ν , V_ν , and W_ν were the parameters to be determined. In order to determine these parameters from our experimental data, the $S_\nu(E_{\text{trans}})$ values had to be weighted by the population of the vibrational modes in the molecular beam:

$$f_\nu(T_{\text{vib}}) = g_\nu \exp \left(-\frac{\nu \hbar \omega_0}{RT_{\text{vib}}} \right) \left[1 - \exp \left(-\frac{\hbar \omega_0}{RT_{\text{vib}}} \right) \right]^{-4}, \quad (2)$$

where $\hbar \omega_0 = 35$ kJ/mol is the vibrational energy quantum in the stretch mode, and g_ν is the degeneracy with $g_0 = 1$ and $g_1 = g_2 = 4$.¹⁰ We assumed the vibrational temperature to be equal to the nozzle temperature as previously mentioned.

Finally, the translational energy width of the molecular beams in the experiments was also taken into account. The TOF distributions were fitted with the shifted Maxwell-Boltzmann distribution:

$$f_{\text{beam}}(E_{\text{trans}}, T_N) = C E_{\text{trans}} \exp \left(-\frac{(\sqrt{E_{\text{trans}}} - \sqrt{E_0})^2}{RT_\infty} \right), \quad (3)$$

where T_∞ corresponds to the energy spread of the distribution, E_0 is the average translational energy and C is a scaling factor. Thus, the final model to be fitted globally to the entire data set was:

$$S(E_{\text{trans}}, T_{\text{vib}}) = \sum_\nu f_\nu(T_{\text{vib}}) \int_0^\infty S_\nu(E_{\text{trans}}) \times f_{\text{beam}}(E_{\text{trans}}, T_N) dE_{\text{trans}}. \quad (4)$$

At these experimental conditions only the ground state, $\nu=0$, and the first two vibrational excitations, $\nu=1$ and $\nu=2$, needed to be included, leaving nine adjustable parameters. The model was further simplified so that each of the saturation levels, A_ν , were constrained to be the same and equal to 1. We therefore ended up with six free parameters to be determined.

The overall fit obtained using this model was excellent and visually better than the result obtained for the CH₄/Ni(100) system.¹⁰ The resulting parameters are given in Table I.

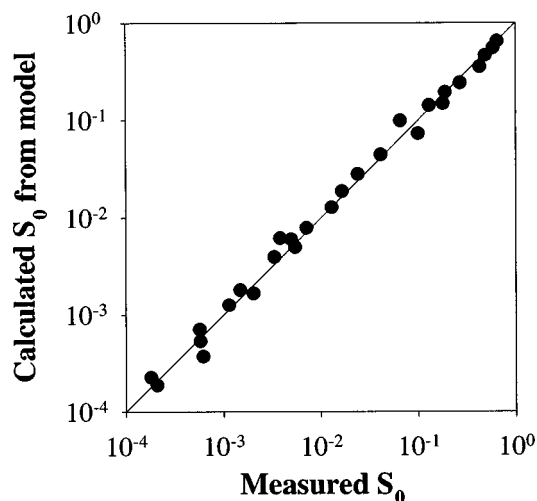


FIG. 4. The experimentally measured sticking coefficients vs the corresponding values obtained from the model fitting. The points are seen to lie very close to the solid ideal line indicating a good fit.

In Fig. 4 the sticking coefficients obtained from the model fit are compared to the measured sticking coefficients. All the points lie very close to the ideal line further supporting the fact that the model fit was very good. The determined parameters were quite well defined in their values with the exception of the W_2 parameter which was somewhat ill determined because there were relatively few data points contributing to the determination of this particular parameter as compared to the others.

With the parameterization obtained it was then possible to compute the thermal sticking coefficient according to the following relation:

$$S(T) = \frac{1}{RT} \sum_{\nu=0}^2 f_\nu(T) \int_0^\infty S_\nu(E) \exp \left(-\frac{E}{RT} \right) dE. \quad (5)$$

We assumed normal energy scaling so that only the translational energy component normal to the surface was efficient in the dissociation process. The thermal sticking coefficient for the three vibrational states as a function of the gas temperature could now be calculated using Eq. (5). The result is shown in Fig. 5 where the open symbols are the calculated thermal sticking coefficients. The ν_0 , ν_1 , and the very small ν_2 contribution are shown as circles, triangles, and squares, respectively. The sum of these three contributions is shown as the solid line which is basically identical to the contribution from the ground state.

V. DISCUSSION

A. CH₄ dissociation measurements

The carbon coverage found from the comparison of TPD areas was approximately 1.7 Ru-ML suggesting a very compact structure. At temperatures below 1300 K no additional LEED structures were observed for carbon on Ru. From the behavior of the uptake curve as shown in Fig. 2, information on the growth mode can be obtained. If the data are fitted well with a first order uptake as, e.g., was observed for C on Ni(111),⁹ this would indicate that a compact carbon island is

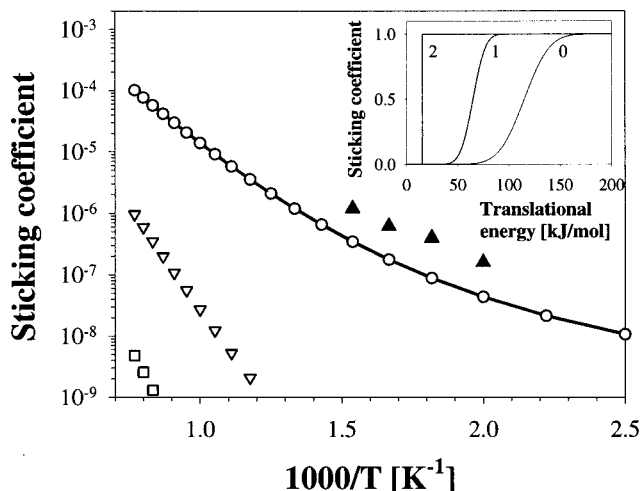


FIG. 5. The calculated thermal sticking coefficients are shown as a function of the inverse temperature. The contributions from the ground state, first excited and second excited are shown as open circles, triangles, and squares, respectively, and the sum of the three states is shown as the solid line. It is seen that the contribution from the ground state is dominating the calculated sticking coefficients in the entire temperature range investigated. Experimentally determined thermal sticking coefficients from the work by Wu *et al.* (Ref. 16) are shown as triangles. The calculated S -curves are shown in the inset.

formed. The fact that the carbon uptake on Ru was best described by the slower increasing second order uptake could indicate that the carbon atoms at 600 K were distributed in a more random fashion thus blocking more sites than had they grown in compact islands. At higher temperatures around 800 K there is experimental evidence for islands growth^{17,28} and above 1300 K the carbon forms graphite as observed with LEED.¹⁷

The position of the descending part of the recombination feature of carbon and oxygen moved linearly up in temperature as the carbon coverage was increased as seen in Fig. 1. This position moved from approximately 650 K for low carbon coverages to 900 K when approaching saturation. As the carbon coverage increased, the number of free sites for the dissociated oxygen molecule to adsorb decreased thereby lowering the probability for the carbon–oxygen recombination process. This interpretation also agrees with the fact that the TPD peak moved down in temperature when increasing the oxygen pressure and vice versa. Changes in the oxygen pressure of 10% resulted in a temperature shift of approximately 10 K.

In Fig. 3 a strong enhancement of the sticking probability was seen with increasing translational energy indicating a direct process. This has been demonstrated for a large number of transition metal surfaces as mentioned in the Sec. I. Additionally there was a very strong effect of increasing the nozzle temperature, thus increasing the populating in the higher vibrational levels of the CH_4 molecule. For a translational energy of 30 kJ/mol, the sticking coefficient was enhanced by a factor of 300 by increasing the nozzle temperature from 450 to 1250 K. We did not see any increase in the low energy sticking coefficient with decreasing energy as was seen in Refs. 13–15. We can however not exclude the

presence of alternative pathways at very low energies but the effect is then below our detection limit.

B. Modeling

In Fig. 5 the calculated thermal sticking coefficients are shown as a function of the inverse temperature. The ground state contribution is dominant in the temperature regime shown here. This is in contrast to the system previously investigated with this model, $\text{CH}_4/\text{Ni}(100)$, where the first excited vibrational state dominated.¹⁰ Assuming an Arrhenius behavior of the dissociation probability of CH_4 , the activation energy is the slope of the solid line in Fig. 5. In the temperature range from 500 to 600 K the activation energy was calculated to be 37 kJ/mol. Absolute sticking coefficients from thermal experiments by Wu *et al.* are shown in Fig. 5 as solid triangles. They find an activation energy of 36 kJ/mol.¹⁶ There is indeed a good agreement between these two experimentally determined activation energies. However, the absolute values of the sticking coefficients differ approximately by a factor of 5. Still we consider this to be in reasonable agreement since it is a minor deviation when comparing absolute results from such very different experimental approaches.

As an inset in Fig. 5 the calculated S -curves (S_ν for $\nu=0,1,2$) are shown for the values presented in the table. The distances between the S -curves are approximately 50 kJ/mol, i.e., larger than the vibrational quantum of 35 kJ/mol. The same phenomena were obtained as a result of fitting the dissociation probability of CH_4 on $\text{Ni}(100)$ and this was explained as a consequence of applying a two-dimensional model with no available steric parameters to a multidimensional dissociation process.¹⁹

It should be mentioned that there are other successful approaches for modeling the CH_4 dissociation, for example, the statistical model using the Rice-Ramsperger-Kassel-Marcus (RRKM) rate theory by Ukraintsev *et al.*³²

The most significant uncertainty in our calculation of the thermal sticking coefficient using Eq. (5) is the behavior of the $S_\nu(E)$ curves at low translational energy. It is dictated by our choice of the functions given by Eq. (5), which is not unique but justified by its relation to a Gaussian distribution of barriers. It is thus reasonable to expect some minimum barrier to exist. Attempts were made to fit the experimental data using cutoffs below certain translational energies. This, however, significantly degraded the quality of the fits meaning that finite sticking contributions even at very low translational energies are needed in order to achieve an acceptable fit to the data. The effect can either be due to limitations in the modeling or to very few but very reactive sites on the surface. An experiment was performed in order to check whether a highly reactive site existed on the surface resulting in the low energy dissociation. Small amounts of CO were dosed to the surface held at 450 K where CO can adsorb and the surface was exposed to a molecular beam exposure. If such very reactive sites exist they would have been blocked by this treatment thus lowering the measured sticking coefficient dramatically compared to the normal experiment. This was however not observed indicating that such special sites do not exist.

It seems that the reason for the low energy sticking required in the modeling must originate from limitations in the model description. There could be an importance of excitations in other degrees of freedom in the real methane molecule, which are not considered by the quasidiatomic model, or there could be a tunneling contribution although this is hard to imagine considering the narrow barrier needed in order to tunnel. If for example the energy barrier found by DFT-GGA calculations for CH₄ dissociation on Ni(111) is considered tunneling does not seem to be significant.³³ Finally, the probability of a trapping mechanism which is not resolved in our description of the system naturally limits the model and could have an influence at these low energies. The justification of the model applied still awaits a detailed state-selected experiment where the CH₄ molecules are prepared in specific vibrational states prior to the interaction with the surface. Such experiments are under preparation by a number of groups.³⁴

VI. CONCLUSIONS

The dissociation probabilities of CH₄ on Ru(0001) was measured experimentally using supersonic molecular beams. A strong enhancement of the sticking both by increasing the translational and vibrational energy was observed indicating a direct activated process. A saturation coverage of carbon on Ru(0001) was estimated to be around 1.7 Ru-ML from comparisons of TPD areas. The carbon in the saturation coverage at 600 K did not have an ordered structure observable by LEED. However, heating to 1300 K induced an (11 × 11) superstructure which was previously assigned to graphite. The experimental sticking coefficients were fitted to a model assuming that the vibrational stretch mode of CH₄ is along the reaction coordinate and the sticking curves of the first vibrational modes were extracted. A thermal activation energy was calculated from this modeling and a good agreement with bulb experiments was obtained. From our model we conclude, that the ground state contribution to the thermal sticking coefficient was dominating in the range of temperatures shown in Fig. 5. This is in contrast to the CH₄/Ni(100) system where the dominating contribution was found to be methane in the first excited vibrational state.¹⁰ It can however not be excluded that other modes could contribute to the observed reactivity. Finally, we did not observe an energy minimum at low energy as was recently observed for CH₄ dissociation on, for example, Ir surfaces and Pd(110),

but we cannot exclude that such effects could be active at sticking coefficients below our detection limit.

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