

# Adsorption of Methane and Ethane on RuO<sub>2</sub>(110) Surfaces

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*Dedicated to Prof. Dr. Helmut Knözinger at the occasion of his 70<sup>th</sup> birthday*

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***Adsorption / Thermal Desorption Spectroscopy (TDS) / Vibrational Spectroscopy (HREELS) / Methane / Ethane / RuO<sub>2</sub>(110)***

The adsorption of methane and ethane on the stoichiometric and O-rich RuO<sub>2</sub>(110) surfaces, respectively, was studied by thermal desorption and high-resolution electron energy loss spectroscopy. The results support weak adsorption (physisorption) of these molecules on the surface, regardless of the presence of undercoordinated Ru and oxygen surface sites. The vibrational spectra recorded at about 90 K are compared with spectra calculated for gaseous CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The nearly complete agreement of frequencies and relative intensities is consistent with physisorption. No evidence of adsorption induced molecule activation is found.

## 1. Introduction

The study of adsorption of saturated hydrocarbons on metal and oxide surfaces under vacuum conditions is a somewhat neglected area of research, presumably because of their inert character and related low energies of adsorption. Cryogenic temperatures are required to achieve a reasonable surface coverage of these species to allow their characterization by spectroscopic and structural techniques. On the other hand, the activation of small adsorbed hydrocarbon molecules, such as methane or ethane, through their

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interaction with surfaces is an important topic in heterogeneous catalysis because it promises a new path to the direct production of long chain hydrocarbons or oxygenates in the presence of water, for example. Furthermore, the direct production of pure  $\text{H}_2$  via a heterogeneous activation and reaction of  $\text{CH}_4$  would be the preferred hydrogen source for fuel cells, for example.

Several metal and oxide surfaces have been studied with regard to  $\text{CH}_4$  adsorption and activation [1]. Surface science studies were performed on W, Ni, Pt, Pd, Rh, Ir, and Ru single crystal surfaces. It was found that the dissociation is an activated process so that the experiments were performed mostly at temperatures well above 300 K. Since under those conditions the sticking coefficient is very low, pressures in the mbar range were applied, *e.g.*, 6 mbar at temperatures between 300 and 800 K at Ru surfaces [2]. Similar studies were carried out for  $\text{C}_2\text{H}_6$ .

Recently, the  $\text{RuO}_2(110)$  surface, prepared by exposing Ru(0001) to high doses of  $\text{O}_2$  at elevated sample temperatures [3–5], has been found to exhibit high catalytic activity for CO oxidation [3, 4, 6]. The stoichiometric  $\text{RuO}_2(110)$  surface is characterized by two different, coordinatively unsaturated surface atoms organized in rows along [001]: (i) twofold coordinated oxygen atoms (O-bridge) and (ii) fivefold coordinated Ru atoms (Ru-cus). Additional oxygen atoms may be adsorbed by further exposure to  $\text{O}_2$  on top of Ru-cus, called O-cus in the following. A maximum coverage of about 80% of the Ru-cus atoms may thus be achieved [7, 8]. This surface is called O-rich  $\text{RuO}_2(110)$ . The O-cus species is relatively weakly bound on the surface and desorbs at temperatures as low as 400–500 K. Therefore, this species is expected to be very reactive as verified, *e.g.*, by CO oxidation [4, 6], carbonate formation [8, 9], ethylene oxidation [10], and ammonia oxidation [11].

In the current work the adsorption of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  on stoichiometric and O-rich  $\text{RuO}_2(110)$  surfaces is investigated by thermal desorption spectroscopy (TDS) and high-resolution electron energy loss spectroscopy (HREELS) for the general purpose of characterizing the adsorbed species and of finding evidence for molecule activation. Possibly undercoordinated Ru-cus and/or O-cus sites might play a role for the activation and partial oxidation of the adsorbed species. In all these cases the higher activity of cus-sites has been observed. However, it is realized that the achievable coverages of  $\text{CH}_4$  as well as of  $\text{C}_2\text{H}_6$  are going to be low here under vacuum conditions and at about 90 K, the lowest temperature used in this study with cooling by liquid nitrogen. Furthermore, any thermal energy added by raising the temperature will cause desorption of the intact molecules rather than any desired partial dissociation and subsequent formation of intermediates. On the other hand, the detailed vibrational characterization of adsorbed  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  on  $\text{RuO}_2(110)$  should be of interest and value by its own.

## 2. Experimental section

The experiments were performed in an ultrahigh vacuum (UHV) apparatus consisting of two chambers separated by a valve. The base pressure was  $2 \times 10^{-11}$  mbar. The upper chamber was used for sample preparation and contained a quadrupole mass spectrometer for thermal desorption spectroscopy (TDS) as well as facilities for low-energy electron diffraction (LEED), gas dosing, and surface cleaning by Ar ion sputtering. The lower chamber housed a high-resolution electron energy loss (HREEL) spectrometer (Delta 0.5, SPECS). Spectra were taken in specular geometry at an angle of incidence of  $55^\circ$  with respect to the surface normal. The primary electron energy was set to 3 eV and the energy resolution was better than 2.5 meV.

The substrate, a Ru(0001) single crystal, was clamped between two Ta wires. A NiCr-Ni thermocouple was spot-welded to the back of the Ru crystal. The sample temperature could be varied between 90 and  $\sim 1300$  K by combining cooling with liquid nitrogen and heating by radiation or by simultaneous radiation and electron bombardment from the backside of the sample. The RuO<sub>2</sub>(110) surface was prepared *in-situ* following a procedure described in preceding publications [3,4]. In brief, the Ru crystal was cleaned by applying repeated sputtering and annealing cycles. The oxide film was then grown epitaxially by exposing the clean Ru(0001) surface to about  $10^7$  L O<sub>2</sub> (1 L =  $1.33 \times 10^{-6}$  mbar s) at 700 K using a gas shower. The preparation could be repeated after restoring the original Ru(0001) surface by sputtering and annealing cycles.

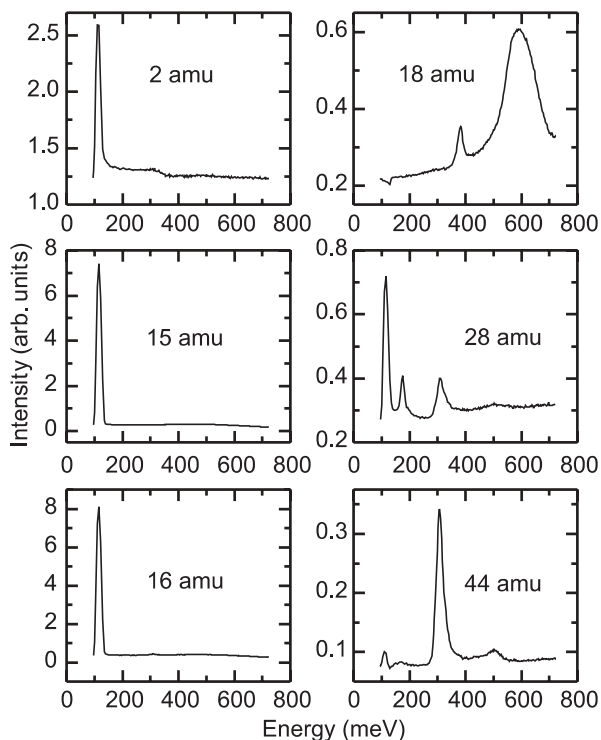
Prior to each experiment, impurities such as H<sub>2</sub>O or CO were desorbed and the surface ordering was improved by heating the sample to 700 K for one minute. The chemical cleanliness of the surface and the surface order were controlled by standard techniques. The surface was exposed to the following gases: <sup>16</sup>O<sub>2</sub> (purity 99.999 vol. %, Westfalen), <sup>18</sup>O<sub>2</sub> (isotopic purity min 99 atom % <sup>18</sup>O, Isotec), C<sup>16</sup>O (purity 99.997%, Messer Griesheim), CH<sub>4</sub> (purity 99.999 vol. %, Westfalen), C<sub>2</sub>H<sub>6</sub> (purity 99.95 %, Linde), CD<sub>4</sub> (isotopic purity 99 atom % D, Isotec), and C<sub>2</sub>D<sub>6</sub> (isotopic purity 99 atom % D, Isotec).

## 3. Results and discussion

In this section we report on and discuss the experimental results of CH<sub>4</sub> (CD<sub>4</sub>) and C<sub>2</sub>H<sub>6</sub> (C<sub>2</sub>D<sub>6</sub>) adsorption on the stoichiometric and O-rich RuO<sub>2</sub>(110) surfaces. In all cases the adsorption was performed at a temperature of about 90 K and at a base pressure of the preparation and measuring chambers of less than  $8 \times 10^{-11}$  mbar.

### 3.1 TDS and HREELS of methane

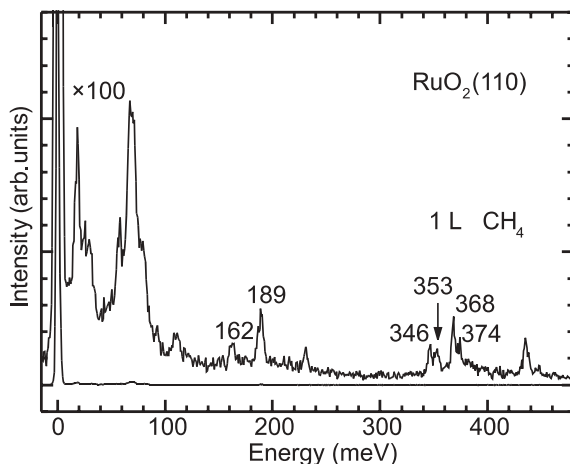
As expected, CH<sub>4</sub> adsorbs very weakly on the stoichiometric RuO<sub>2</sub>(110) surface. Steady state coverage seems to be reached already for the lowest exposure



**Fig. 1.** TD spectra from the stoichiometric  $\text{RuO}_2(110)$  surface exposed to 0.6 L  $\text{CH}_4$  at 94 K. The different mass channels are given through the respective atomic mass units (amu):  $\text{H}_2$  (2),  $\text{CH}_3$  (15),  $\text{CH}_4$  (16),  $\text{H}_2\text{O}$  (18),  $\text{CO}$  (28), and  $\text{CO}_2$  (44).

of 0.1 L ( $1 \text{ L} = 1.33 \times 10^{-6} \text{ mbar s}$ ), indicating a finite rate of desorption even at 90 K (the sample temperature at the exposure). Hence it is not possible to achieve a  $\text{CH}_4$  saturated surface or growth of a multi-layer on  $\text{RuO}_2(110)$  under the given conditions. Consequently, the peak temperature observed by TDS is not a measure of the adsorption energy, but an upper bound is estimated at 30 kJ/mol from the desorption temperature using the Redhead equation.

To find out whether  $\text{CH}_4$  activation during adsorption or desorption takes place, mass signals at 12 different amu channels were checked. Fig. 1 shows examples after 0.6 L exposure to  $\text{CH}_4$ . Only traces at 2, 28, and 44 amu were found which could be shown to arise from background adsorption of  $\text{H}_2$ ,  $\text{CO}$  (and possibly  $\text{C}_2\text{H}_6$ ), and  $\text{CO}_2$ . Spurious amounts of  $\text{H}_2\text{O}$  (18 amu) were also observed predominantly in the temperature range 500–700 K indicative for the recombination of OH-bridge [12]. Somewhat peculiar is the 28 amu peak at the temperature of  $\text{CH}_4$  desorption. Although its origin could not be ascertained, it may be due to traces of  $\text{C}_2\text{H}_6$  adsorption being present in the system from previous exposures with that gas.

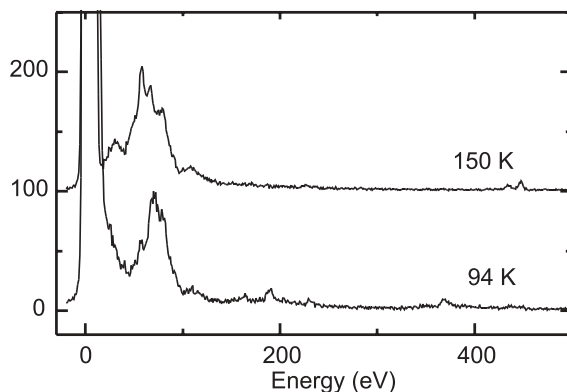


**Fig. 2.** HREEL spectrum of the stoichiometric RuO<sub>2</sub>(110) surface exposed to 1 L CH<sub>4</sub> at 90 K.

Fig. 2 shows a typical HREEL spectrum of adsorbed CH<sub>4</sub> on the stoichiometric RuO<sub>2</sub>(110) surface. Increasing exposures to CH<sub>4</sub> did not influence the spectra, in agreement with the TDS data which show that constant coverage is achieved soon. The loss peak at 69 meV is due to the Ru–O stretch of the O-bridge surface species [7]. The peaks at 162, 189, 346, 353, 368, and 374 meV are due to molecular CH<sub>4</sub> on the surface as supported by isotope substitution measurements with CD<sub>4</sub>. Additional features observed at 58, 110, 230, 436, and 447 meV increase with collection time of the spectra. These peaks are normally observed when analyzing RuO<sub>2</sub>(110) surfaces at low temperatures [8–11] and can be ascribed to a H<sub>2</sub>O-like species (H<sub>2</sub>O-bridge) formed through interaction of H<sub>2</sub> from the background with O-bridge [12]. A detailed assignment of all peaks to vibrational modes of adsorbed CH<sub>4</sub> (CD<sub>4</sub>) will be given in Sect. 3.3.

An additional test for the presence of possible products of CH<sub>4</sub> activation and subsequent reactions was carried out by shortly heating the CH<sub>4</sub> covered substrate to 150 K, cooling to 94 K, and recording the HREEL spectrum again the latter being shown in Fig. 3. Except for the O-bridge loss at 69 meV and nearby H<sub>2</sub>O losses as well as OH stretches at 430–450 meV due to H<sub>2</sub>O-bridge there is no evidence for further adsorbed species. The amount of H<sub>2</sub>O-bridge is larger in this case because of the repeated heating and cooling of the sample and the corresponding increase in total exposure to the background gas.

The adsorption of CH<sub>4</sub> and CD<sub>4</sub> on the O-rich RuO<sub>2</sub>(110) was also studied. The surface was prepared by exposing the stoichiometric surface to 0.4 L O<sub>2</sub> resulting in a coverage of O-cus of about 50–70%. Hence there are still remaining Ru-cus sites for CH<sub>4</sub> adsorption. The recorded TDS curves were practically



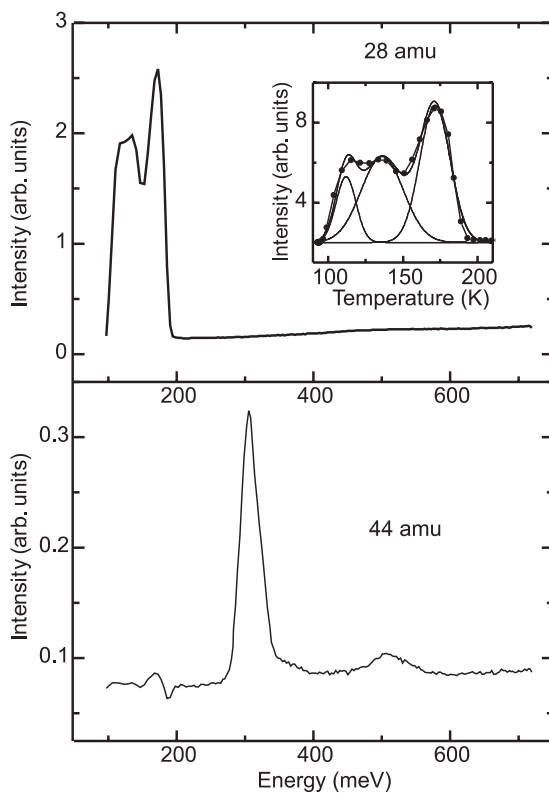
**Fig. 3.** HREEL spectrum of the stoichiometric  $\text{RuO}_2(110)$  surface exposed to 0.6 L  $\text{CH}_4$  at 94 K (lower curve) and following warming to 150 K and cooling back again (upper curve).

identical to those in Fig. 1 except that an additional signal at 32 amu was observed at 440 K. This is simply due to desorption of  $\text{O}_2$ . The formation of  $\text{CH}_3\text{OH}$  (also at 32 amu) as a possible reaction product involving  $\text{CH}_4$  and O-cus was ruled out by using  $^{18}\text{O}$  in the preparation of the O-rich  $\text{RuO}_2(110)$  surface. In that case a peak at 36 amu was observed during desorption which is clearly indicating  $^{18}\text{O}_2$ . The HREELS data are also similar to those for the stoichiometric surface in the energy range beyond 120 meV, except that the peaks are less intense and noisier and that a peak at 103 meV characteristic of O-cus arises. Overall, no noticeable effect of O-cus on adsorbed  $\text{CH}_4$  can be found.

In summary, on the stoichiometric and O-rich  $\text{RuO}_2(110)$  surfaces  $\text{CH}_4$  is adsorbed molecularly at about 90 K and desorbs completely below 150 K, indicative for a weak interaction with the  $\text{RuO}_2(110)$  surface. No thermal activation was observed.

### 3.2 TDS and HREELS of ethane

Both  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  are saturated hydrocarbons and hence  $\text{C}_2\text{H}_6$  adsorbs also weakly on the stoichiometric  $\text{RuO}_2(110)$  surface, as demonstrated in Fig. 4 for two mass peaks after an exposure of 0.6 L of  $\text{C}_2\text{H}_6$ . A constant coverage is achieved for low exposures, similar to the behavior of  $\text{CH}_4$  (see Fig. 1). This is again indicating a finite rate of desorption at 94 K. Hence the peak temperature cannot simply be used to estimate the adsorption energy. The main cracking peaks of  $\text{C}_2\text{H}_6$  arise at 28, 27, and 26 amu which all show a double or even triple peak when decomposed into Gaussians (see inset in Fig. 4). The peak at 170 K may be attributed to the first layer of  $\text{C}_2\text{H}_6$  located at Ru-cus sites. This peak temperature is higher than the one for  $\text{CH}_4$ . The other two peaks at lower temperatures are more uncertain regarding the nature of adsorption sites. One

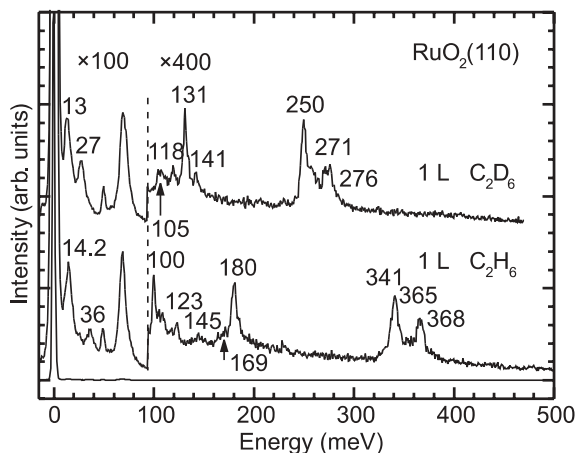


**Fig. 4.** TD spectra from the stoichiometric RuO<sub>2</sub>(110) surface exposed to 0.6 L C<sub>2</sub>H<sub>6</sub> at 94 K. Upper curve: C<sub>2</sub>H<sub>6</sub> at 28 amu. Inset: Deconvolution into 3 Gaussians. Lower curve: CO<sub>2</sub> at 44 amu.

of them may possibly be C<sub>2</sub>H<sub>6</sub> adsorbed on O-bridge sites while the third at < 113 K may be due to a beginning multilayer.

To find out whether C<sub>2</sub>H<sub>6</sub> activation takes place during adsorption or desorption, mass spectrometer signals at additional amu channels were recorded. Some intensity at 2, 18, and 44 amu was found being due to residual background adsorption of H<sub>2</sub> and CO<sub>2</sub>. Whether CO was coadsorbed could not directly be decided since a large peak at 28 amu originates from C<sub>2</sub>H<sub>6</sub>. This could, however, be ruled out by comparison with data from C<sub>2</sub>D<sub>6</sub> adsorption. There are no indications of other products which would support any reaction of C<sub>2</sub>H<sub>6</sub> during adsorption or desorption.

Fig. 5 shows typical HREEL spectra of adsorbed C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>D<sub>6</sub> on RuO<sub>2</sub>(110) following exposures of 1 L. The loss peak at 69 meV is again due to the Ru–O stretch mode of O-bridge surface species. The peaks in the range 100–370 meV are all due to molecular C<sub>2</sub>H<sub>6</sub> on the surface as supported by iso-



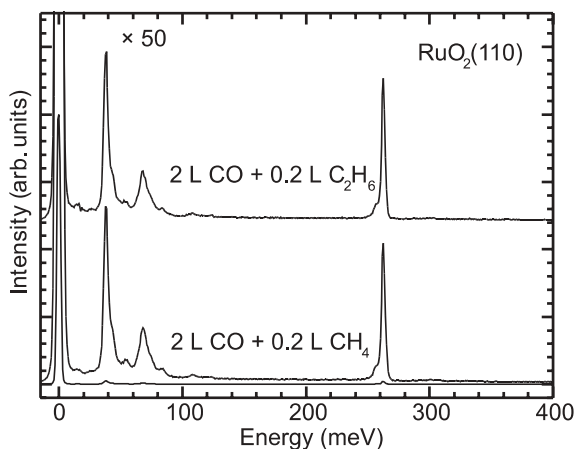
**Fig. 5.** HREEL spectra of the stoichiometric  $\text{RuO}_2(110)$  surface exposed to 1 L  $\text{C}_2\text{H}_6$  at 90 K (lower curve) and to 1 L  $\text{C}_2\text{D}_6$  at 90 K.

tope substitution measurements with  $\text{C}_2\text{D}_6$ . A detailed assignment of all peaks to vibrational modes of adsorbed  $\text{C}_2\text{H}_6$  ( $\text{C}_2\text{D}_6$ ) will be given in Sect. 3.3.

As before, adsorption of  $\text{C}_2\text{H}_6$  was also studied on the O-rich  $\text{RuO}_2(110)$  surface. Characteristic TDS curves are very similar to those in Fig. 4 except that they are shifted to slightly higher temperature. A shoulder is recognized at about 187 K at the high temperature end. The fact that a shoulder is observed instead of a narrow peak, such as seen in Fig. 4 at 170 K, underlines the assignment of this state to  $\text{C}_2\text{H}_6$  adsorbed on Ru-cus sites which are now fewer in number than on the stoichiometric surface. Note that  $\text{C}_2\text{H}_6$  and O-cus are coadsorbed on the Ru-cus rows which may cause some interaction and change in the adsorption energy of  $\text{C}_2\text{H}_6$ . HREELS data are less informative in this case because of the lower steady state coverage of  $\text{C}_2\text{H}_6$  but otherwise identical to those shown in Fig. 5. There is again no indication of any chemical transformation of the adsorbed species.

So far we have tentatively attributed the triple peak in TDS to adsorption on Ru-cus, O-bridge, and in the second layer. For the  $\text{RuO}_2(110)$  surface we have an additional experimental tool to draw some conclusion on the adsorption site, especially to differentiate between the Ru-cus and O-bridge sites. From our former studies we know that CO is chemisorbed at Ru-cus sites when the surface is exposed to CO at temperatures below 150 K [3]. Therefore the Ru-cus sites can be blocked by CO while the O-bridge sites are left unoccupied. Thus subsequently admitted  $\text{CH}_4$  or  $\text{C}_2\text{H}_6$  could predominantly adsorb only on O-bridge sites. Fig. 6 shows the respective HREEL spectra. After pre-exposure of 2 L CO one recognizes only the known dipole active CO stretch modes against the surface and within the molecule at about 38 and





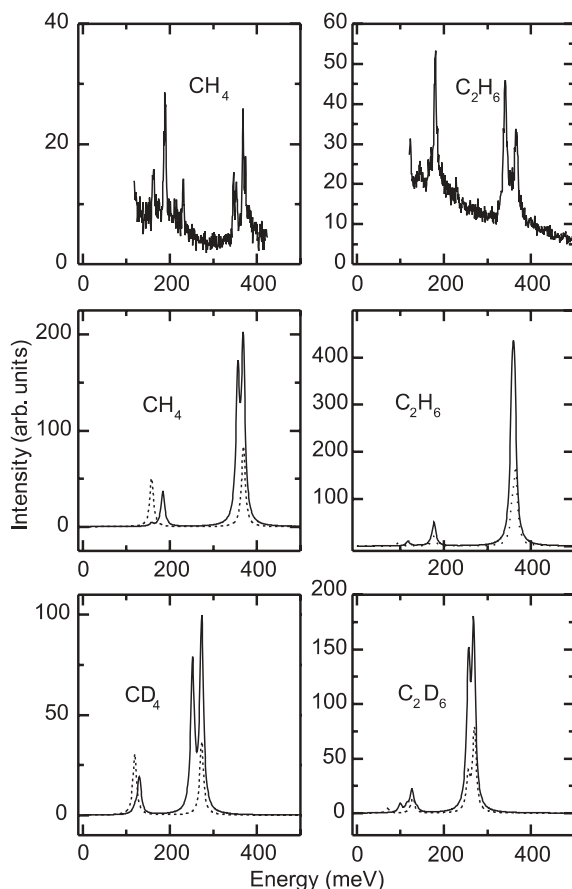
**Fig. 6.** HREEL spectra of the stoichiometric RuO<sub>2</sub>(110) surface exposed to 2 L CO followed by 0.2 L CH<sub>4</sub> at 90 K (lower curve) and the same for C<sub>2</sub>H<sub>6</sub> (upper curve).

262 meV, respectively. This experiment clearly shows that O-bridge alone is not able to stabilize either CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub> at about 90 K. The origin of the two TDS peaks for C<sub>2</sub>H<sub>6</sub> at lower temperatures could thus not be unambiguously assigned.

In summary, at about 90 K also C<sub>2</sub>H<sub>6</sub> adsorbs weakly on the stoichiometric and O-rich RuO<sub>2</sub>(110) surfaces. Desorption is completed around 170 K. There is no indication for any activation of the C<sub>2</sub>H<sub>6</sub> molecule.

### 3.3 Simulated spectra and mode assignment

To interpret the measured HREEL spectra of adsorbed CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, IR-absorption as well as Raman spectra were calculated for the free molecules using density functional theory (DFT) calculations at the B3LYP [13, 14] level of theory employing 6-311G\*\* basis sets for C and H atoms as implemented in the Gaussian 03 package [15]. The theoretical lines were convoluted with a Lorentzian function of 10 meV full width at half maximum. In addition the frequencies were scaled with a constant factor of 0.95 taking into account errors in the method (*e.g.* in the potential anharmonicities). The calculated spectra are compared with experimental data in Fig. 7. There is very good agreement for the frequencies between experimental and calculated data. The intensities differ because of the different excitation mechanism which is basically impact scattering in our case. Impact scattering intensities depend strongly on scattering parameters, *e.g.* on primary energy. CH<sub>4</sub> exhibits 9 normal modes of which several are degenerate. The 4 distinguishable vibrational frequencies are assigned and compared to the corresponding measured peak



**Fig. 7.** Vibrational spectra of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . The 2 topmost HREEL spectra are measured for the stoichiometric  $\text{RuO}_2(110)$  surface exposed to 1 L  $\text{CH}_4$  and 1 L  $\text{C}_2\text{H}_6$ , respectively, at 90 K. The other 4 spectra are composed from calculated gas phase frequencies (see text). Full line: Raman-active vibrations; broken line: IR-active vibrations.

positions for the adsorbed species and to experimental gas phase values [16] in Table 1. The agreement is clearly indicating the very weak interaction (physisorption) between adsorbed methane and the  $\text{RuO}_2(110)$  surface, in particular the Ru-cus sites.

The results of an analogous calculation for molecular  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{D}_6$  are summarized in Table 2. There are in principle 18 normal modes for  $\text{C}_2\text{H}_6$  but several are degenerate, such that only 12 modes are listed in Table 2. The frequencies of some of these modes are nearly identical reducing the number of practically distinguishable frequencies to only 9. These are compared with experimental gas phase values [16] and the measured peak positions for the ad-

**Table 1.** Comparison of gas phase (G.P.), gas phase calculated, and adsorbate measured (adsorb.) vibrational modes for CH<sub>4</sub> and CD<sub>4</sub>. Only data for CH<sub>4</sub> (CD<sub>4</sub>) on the stoichiometric RuO<sub>2</sub>(110) are considered. All vibration energies are given in units of meV. Mode nomenclature:  $\nu$ : stretching mode;  $\delta$ : bending mode.

Mode	Symmetry $T_d$	CH <sub>4</sub> G.P. [16]	CH <sub>4</sub> G.P. calculated	CH <sub>4</sub> adsorb. this work	CD <sub>4</sub> G.P. [16]	CD <sub>4</sub> G.P. calculated	CD <sub>4</sub> adsorb. this work	Isotope shift*
$\delta_2$	T <sub>2</sub>	162	158	162	124	120	124	1.31
$\delta_1$	E	190	184	189	135	130	135	1.40
$\nu_s$	A <sub>1</sub>	362	357	353	262	252	252	1.40
$\nu_{as}$	T <sub>1</sub>	374	369	368	280	273	269	1.37
$\delta_1 + \delta_2$		—	342	346	—	250	249	1.39
$2\delta_1$		—	368	374	—	260	276	1.36

\* from the measured vibration energies

sorbed C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>D<sub>6</sub> species. There is again very good agreement between the experimental and the calculated as well as gas phase frequencies [16] indicating the very weak interaction (physisorption) of ethane with the RuO<sub>2</sub>(110) surface, most likely the Ru-cus sites. Some weakening of the C–H bond of adsorbed C<sub>2</sub>H<sub>6</sub> can be recognized from the decreased frequency of the symmetric C–H stretch by 15 meV.

**Table 2.** Comparison of gas phase (G.P.), gas phase calculated, and adsorbate measured (adsorb.) vibrational modes for  $C_2H_6$  and  $C_2D_6$ . Only data for  $C_2H_6$  ( $C_2D_6$ ) on the stoichiometric  $RuO_2(110)$  are considered. All vibration energies are given in units of meV. Mode nomenclature: T: frustrated translation;  $\tau$ : torsion;  $\nu$ : stretching;  $\rho$ : rocking;  $\delta$ : bending.

Mode	Symmetry $T_d$	$C_2H_6$ G.P. [16]	$C_2H_6$ G.P. calculated	$C_2H_6$ adsorb. this work	$C_2D_6$ G.P. [16]	$C_2D_6$ G.P. calculated	$C_2D_6$ adsorb. this work	Isotope shift*
$T_L$	—	—	—	14.2	—	—	13	1.09
$\tau$	$A_{1u}$	36	36	36	25.8	26	27	1.33
$\nu$ ( $CH_3$ )	$E_u$	102	98	100	74	71	n.o.	—
$\nu$ ( $CC$ )	$A_{1g}$	123	118	123	105	100	105	1.17
$\rho$ ( $CH_3$ )	$E_g$	148	144	145	120	115	118	1.23
$\delta_s$ ( $CH_3$ )	$A_{2u}$	171	166	171	134	127	131	1.31
$\delta_s$ ( $CH_3$ )	$A_{1g}$	172	168	171	143	138	141	1.21
$\delta_{as}$ ( $CH_3$ )	$E_g$	182	177	180	129	127	131	1.37
$\delta_{as}$ ( $CH_3$ )	$E_u$	182	178	180	134	129	131	1.37
$\nu_s$ ( $CH_3$ )	$A_{2u}$	359	357	341	259	256	250	1.36
$\nu_s$ ( $CH_3$ )	$A_{1g}$	366	357	341	258	257	250	1.36
$\nu_{as}$ ( $CH_3$ )	$E_g$	368	362	365	276	268	271	1.35
$\nu_{as}$ ( $CH_3$ )	$E_u$	370	365	368	277	270	276	1.33
$2\delta_{as}$	—	—	356	357	—	254	256	1.39

n.o. = not observed; \* from the measured vibration energies

This general comparison of gas phase spectra with those measured here for  $CH_4$  and  $C_2H_6$  physisorbed on  $RuO_2(110)$  shows that the structure of the adsorbed species is nearly unperturbed. Hence it is highly unlikely that  $CH_4$  and  $C_2H_6$  can be activated by the adsorption process on  $RuO_2(110)$  leading to ad-

sorbed radicals or other products. This situation is not noticeably changed by the presence of additional O-cus. This species seems to only reduce the number of available adsorption sites for CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>, an effect more pronounced for CH<sub>4</sub> than for C<sub>2</sub>H<sub>6</sub> which also may adsorb on O-bridge sites.

## 4. Conclusion

It is shown that methane and ethane interact only weakly with both the stoichiometric and the O-rich RuO<sub>2</sub>(110) surface at temperatures about 90 K and at the small gas exposure typical for UHV conditions. The weak interaction or physisorption is reflected by the low desorption temperature as well as by the gas-phase like vibration pattern of the molecules. Slightly warming to 150 K leads only to complete desorption and not to any activation or product formation for the given typical detection limit in the percent region of a monolayer. The otherwise very reactive O-rich RuO<sub>2</sub>(110) surface is unable to activate or abstract H from methane and ethane.

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