State-resolved studies of CO2 gas-surface reactions

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Chapter 6

State-resolved reactions of CO_2 on D_2 precovered Co(11-29)

6.1 Introduction

CO_2 reactions are challenging to study, as the reactivity of the molecule is low. CO_2 sticking probabilities depend strongly on the surface material and molecular kinetic energy and tend to vary from 10^{-11} to 10^{-2}. [8–11] Cobalt (Co) is one material with a relatively high sticking probability for CO_2 even at room temperature, i.e. low molecular kinetic energy. While the sticking probability on cobalt has not yet been quantified, temperature programmed desorption (TPD) experiments with background CO_2 dosing show measurable CO_2 chemisorption on the cobalt surface (Weststrate et al., unpublished).

State-resolved experiments can provide insight into the mechanisms behind reactions. For methane and water, state-resolved experiments using vibrational excitation have shown that molecular vibrational energy has a significant effect on their sticking probability. [1] For CO_2, a study of (high kinetic energy) CO_2 reactivity on hydrogen precovered Cu(111) and Cu(100) also suggests that vibrational energy contributes strongly to reactivity. [9]

In this chapter, we study (state-resolved) CO_2 sticking on the kinked Co(11-29) surface using the King & Wells method [12], reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD).

6.2 Methods

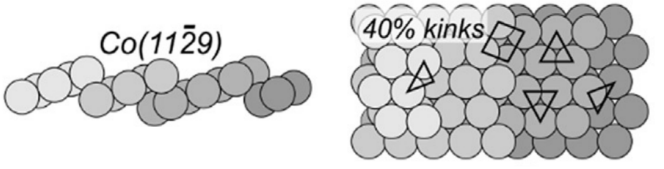

Figure 6.1: The surface structure of the Co(11-29) single crystal. Image adapted from Weststrate et al. [91].

We use a Co(11-29) single crystal for all experiments (surface shown in figure 6.1). The surface of the crystal is cleaned using sputter-anneal cycles. The surface of the crystal after the cleaning cycles is initially studied in an ultra-high vacuum (UHV) apparatus equipped with a LEED, an Auger electron spectrometer (AES), and a differentially pumped quadrupole mass spectrometer (QMS). To verify that the surface is clean and the structure is as expected, LEED images are taken and compared to reference images from Weststrate et al. (supplementary information) [91]. Furthermore, AES spectra are taken to verify that there are no residual C and O atoms on the surface, and temperature programmed desorption (TPD) spectra of H_2 and CO are taken and compared to reference data. [91] After our cleaning procedure, the surface is found to be clean within experimental uncertainties of the AES and H_2 TPD.

After this initial verification, the crystal is moved to the UHV apparatus equipped with a supersonic molecular beam, a reflection absorption infrared spectrometer (RAIRS), a QMS, and a tunable infrared laser. This apparatus is described in detail in chapter 2. We study CO_2 adsorption on the Co crystal with TPD, RAIRS, and the modulated King & Wells method (see chapters 2 and 5). Since CO is a common contamination in both the CO_2 source and the vacuum background, we also study the adsorption of CO onto the surface, to rule out the possibility that reaction products formed in the CO_2 experiments are simply due to the (much more reactive) CO present. CO_2 and CO are typically dosed with the molecular beam. The CO_2 usually consists of either pure CO_2, or 36% CO_2 in He. The CO beam always consists of 1% CO in He. For some experiments, vibrations are excited in the CO_2 using the tunable laser. This process is described in detail in chapters 2, 4 and 5. Some experiments are done on the surface precovered with H_2, D_2 or O_2. These gases are dosed from the vacuum background using leak valves.

At the start of each day, the Co(11-29) crystal is cleaned using 2 sputter-anneal cycles (45 minutes sputtering at 650 K, then 15 minutes annealing at 650 K). In between experiments, the crystal is cleaned once with a shorter cycle (10 minutes sputtering, 5 minutes annealing).

6.3 Results and discussion

6.3.1 TPD of CO_2 on clean Co(11-29) at 100K

Figure 6.2 shows a temperature programmed desorption (TPD) spectrum after dosing CO_2 from the pure CO_2 molecular beam onto the clean Co(11-29) surface at 100 K. The TPD shows several desorption peaks of CO, CO_2, and H_2. We compare the TPD to the one measured by Weststrate et al., where CO_2 was dosed from the background on the same crystal and find that the same peaks appear. There are two desorption peaks of CO_2. Around 100 to 150 K, there is a large CO_2 peak. We expect this to be a weak chemisorption peak. Experiments with CO_2 on this crystal and the Cu surface described in Chapter 5 have shown that CO_2 multilayers are only formed well below 100 K. We therefore do not expect any pyhsisorbed CO_2 to remain on the surface above 100 K. Around 300 to 400 K, there is another peak. This peak could have several origins. Possibilities include chemisorbed CO_2, CO + O recombination or a dissociating molecular complex on the surface. CO shows a similar profile with a peak around 150 K and another peak around 400 K. There is a small CO peak around 600 K that is not always present in our data. There is a double H_2 peak around 400 K. Based on a prior study on similar (stepped) Co surfaces [92] and unpublished data on the Co(11-29) crystal, we expect that the source of this H_2 is background water dissociation and subsequent OH decomposition during the temperature increase of the TPD measurement. One thing to note is that one of the H_2 peaks coincides with the CO_2 chemisorption peak. This could indicate that CO_2 reacts with H atoms on the surface, forming a complex that then dissociates and desorbs as CO_2 and H_2 separately. In this chapter, we explore this hypothesis by dosing D_2 on the surface before dosing CO_2.

We also decide to do further experiments at a surface temperature of 250 K to prevent the buildup of physisorbed CO_2. Since CO_2 sticks well to itself at low temperatures, dosing at 100 K will cause the CO_2 to quickly form multiple layers on top of the crystal surface. We studied CO_2 sticking to CO_2 ice layers before (see chapter 5 and [67]). In this chapter we focus on CO_2 chemisorption on the (D_2 covered) cobalt surface.

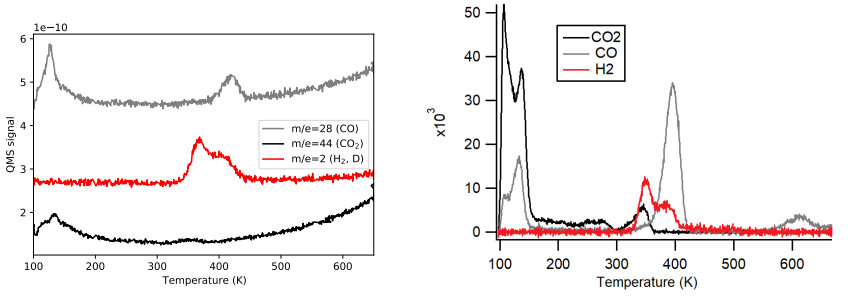

Figure 6.2: Left: A TPD after dosing CO_2 from a pure beam on the clean Co(11-29) crystal for 2 minutes. The CO_2 spectrum shows a peak from physisorbed CO_2 between 100 and 200 K, and a peak from chemisorbed CO_2 between 300 and 400 K. Right: A reference TPD by Weststrate et al. (private communication) showing the same peaks. The CO_2 was dosed from the vacuum background

6.3.2 CO_2 on D_2 precovered Co(11-29)

For the experiments on the D_2 precovered surface, the D_2 is dosed onto the surface directly after the end of the cleaning cycle. During the cooldown to 250 K, D_2 is background dosed with a pressure of 1×10^{-6} mbar and we assume that the maximum D surface coverage has been reached. The CO_2 is dosed using the 36% CO_2 in He beam to maximize CO_2 flux and increase the CO_2 kinetic energy. Figure 6.3 shows a TPD after dosing CO_2 for approximately 45 minutes on the D_2 precovered surface. The different spectra are scaled to show the peaks clearly, and the scaling factor is included in the legend. The CO_2 and CO desorption peaks are still present. The CO spectrum appears to have a second peak coinciding with the CO_2 peak. We believe that this is not a real desorption peak and is instead the result of CO_2 cracking in the QMS. The same thing can be seen in the H_2 and D_2 spectra. We expect to see a large D_2 desorption peak, as the surface was covered in D_2. However, there is also a H_2 (m/e=2) peak. From 300 to 400 K, the shape of this peak closely follows the one of D_2, and therefore we expect this signal to originate from cracking of D_2 in the QMS. D and H_2, which both have mass 2, are indistinguishable to the QMS. However, between 400 and 450 K, there is a peak in the m/e=2 spectrum that is not present in the D_2 spectrum. We expect this peak to originate from the OH decomposition following H_2O dissociation. [92] Note that this peak coincides with the CO desorption peak. This could indicate that CO reacts with H on the surface, and either dissociates prior to desorption, or desorbs as H_2CO (mass 32). We have measured m/e 30 (HCO+ fragment) and 32 (H_2CO+) during the

TPD measurement and found no signal, making the latter scenario unlikely. we have not studied this further as previous research suggests that the H_2 originates from OH decomposition. It is therefore likely that the peak overlap is a coincidence. However, this could be an interesting topic for future research.

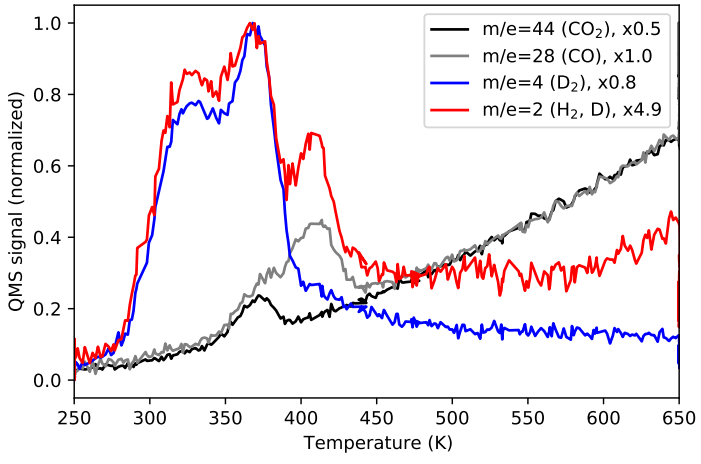

Figure 6.3: A TPD after dosing CO_2 on the D_2 precovered surface at 250K for approximately 45 minutes. The spectra are scaled to show all peaks clearly. The CO_2 peak is still present. There is a large D_2 peak, as expected. There is also a peak in the H_2 spectrum. Since this mostly follows the shape of the D_2 peaks, we expect this signal to originate from D atoms rather than H_2 molecules in the QMS. The H_2 peak around 420 K is a real H_2 desorption peak, likely originating from OH decomposition on the surface. [92]

While the TPD in figure 6.3 confirms CO_2 adsorption on the surface, it cannot provide more information about possible reactions of CO_2 and D_2 on the surface. We take reflection absorption infrared spectra (RAIRS) after dosing the CO_2 and compare these to spectra taken after the subsequent TPD. Any adsorbed molecules or intermediates that can be detected with RAIRS should then be visible in the spectrum after dosing, but not in the spectrum taken after the TPD.

Figure 6.4 shows both the entire RAIR spectra and zoomed in parts of the spectra taken after dosing CO_2 on the D_2 precovered surface for approximately 45 minutes, and after the subsequent TPD. The difference, where the spectrum after the TPD is subtracted from the spectrum after dosing, is also shown. A large peak is visible around 3300 cm^{-1}. This peak is not from the crystal surface, as evidenced by the fact it does not

disappear (and even grows) after the TPD. Therefore it also presents as a negative peak in the difference spectrum. It is likely caused by water condensation in the light path of the spectrometer, most likely on the liquid nitrogen cooled detector. The presence of this large water peak means that other peaks in this region will likely not be detectable. There is also a small peak at 1280 cm^{-1}. Since this peak is not visible in the difference spectrum, we believe this peak is not from the crystal surface either.

There are few published studies about RAIRS on (stepped) Co surfaces, with most of those studies focusing on CO adsorbed to the Co surface. There is a series of articles by Toomes and King that describe RAIRS studies on CO_2, CO, HCOOH, and formate on potassium precovered Co(10-10). [93–96] They find clear evidence of formate and CO on the surface after dosing formic acid (HCOOH). However, due to the different surface structure and especially the strong influence of the potassium coverage, their results cannot be directly compared to ours. Formate peaks found for other clean transition metal surfaces may provide a better guide. While the exact peak position varies between the different materials and surface structures, they typically consist of a doublet around 2900 cm^{-1} assigned to the C-H stretch and a single peak around 1350 cm^{-1} assigned to the OCO symmetric stretch. [9, 93] There is also a peak around 780 cm^{-1}, but this is outside of our measurement range. Any O-H stretch peaks from the crystal would not be visible in our spectrum due to the large peak in that region resulting from water on the detector.

Since we are working with a D_2-covered surface, we expect to see C-D stretch peaks rather than C-H stretch peaks. These are often found in the 2180-2220 cm^{-1} range. [93,97,98]. We do not expect the OCO stretch peak to shift significantly as the difference between D and H does not influence this vibration as much as one that includes the hydrogen atom. O-D stretch peaks could be found in the region around 2700 cm^{-1}. [99, 100]

The zoomed in panels in figure 6.4 show the wavenumber ranges where formate peaks would be expected to appear. Around 1950 cm^{-1}, a small peak is visible in the spectrum after dosing. This is CO adsorbed to the surface, as will be shown more clearly later in this chapter where CO is dosed directly on the surface. Unfortunately, it is not possible to say whether this CO originates from CO_2 dissociation or direct CO adsorption from CO contamination in the molecular beam. To make this distinction, the amount of CO in the molecular beam needs to be quantified. Since CO_2 cracks and forms CO in the QMS itself, we have no direct way of measuring the amount of CO in a CO_2 source.

Besides the peak around 1950 cm^{-1}, the only evidence of another peak we found

in the spectrum is around 2200 cm^{-1}. A very small, almost undetectable difference appears here between the spectra after dosing and after the TPD. More data is needed to determine if this is indeed a real peak. However, it is located exactly where a C-D stretch is expected, indicating a C-D bond in a surface species, possibly from a reaction between CO_2 and adsorbed D atoms.

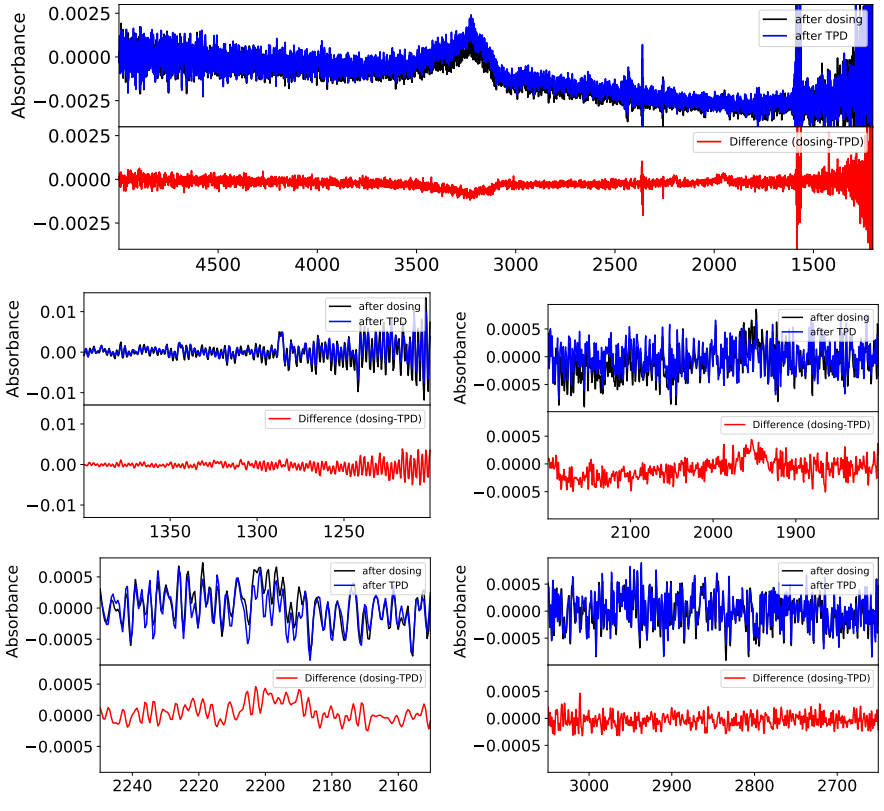

Figure 6.4: Parts of the RAIR spectra after dosing CO_2 from the molecular beam on the D_2 precovered surface, and after the TPD measurement. The difference, where the spectrum after TPD is subtracted from the spectrum after dosing, is also shown. A small peak is visible around 1950 cm^{-1} that is due to CO buildup (either from CO contamination or from CO_2 dissociation. If there are any peaks associated with formate or other complexes formed from CO_2 and hydrogen or deuterium, we expect them to appear around 2900 cm^{-1} (C-H stretch), 2700 cm^{-1} (O-D stretch), 2200 cm^{-1} (C-D stretch), and 1350 cm^{-1} (OCO stretch). A very small peak may be visible around 2200 cm^{-1}, indicating a C-D bond in a surface species. However, since it is barely detectable, more data is necessary to determine if this peak is real.

6.3.3 CO on (D_2/O_2 precovered) Co(11-29)

It is difficult to distinguish whether reaction products are from reactions with CO_2 or CO, as a small amount of CO is always present in a CO_2 source. A typical CO contamination concentration in our molecular beam is in the order of a few ppm. Even this concentration can cause issues, as the sticking probability of CO can be many orders of magnitude higher than the one of CO_2. To verify that the results presented in this chapter are not simply from CO contamination, we also dose CO directly from the molecular beam onto the D_2-covered surface. The molecular beam consists of 1% CO in He and the Co(11-29) surface has a temperature of 250 K. D_2 is again dosed onto the surface during the cooldown from the last cleaning cycle.

Figure 6.5 shows the RAIR spectra taken after dosing CO for approximately 60 minutes, and after the TPD. There is a clear peak around 2000 cm^{-1}. This is the CO peak, which was found to shift to higher wavenumbers for higher CO coverage. Note that there is also a small CO peak around 1950 cm^{-1} in the spectrum taken after the TPD. This is ascribed to background CO adsorption during the RAIRS measurement. The partial pressure of CO in the vacuum background was relatively high during this measurement, since the CO molecular beam was used just before.

We find no indication of other peaks in the RAIR spectra. The total CO dose is orders of magnitude higher for the CO beam than for the CO_2 beam. If the possible C-D stretch peak in figure 6.4 is caused by CO reacting with adsorbed D atoms, it should be visible in the RAIR spectra in figure 6.5. We therefore conclude that this is not the case.

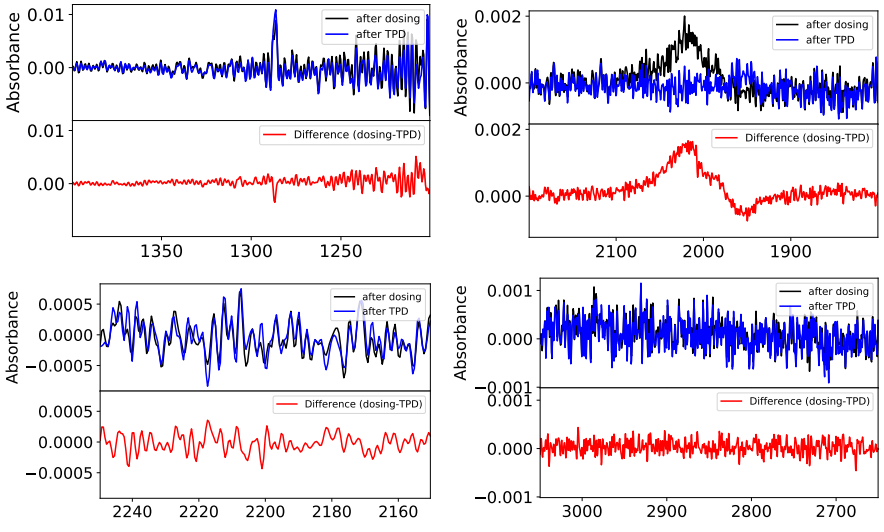

Figure 6.5: RAIR spectra after dosing CO on the D_2 precovered surface, and after the TPD. There is a clear CO peak around 2000 cm^{-1}. There is no sign of a peak at 2200 cm^{-1}, even though the CO dose is orders of magnitude higher than in the CO_2 experiments. We therefore conclude that the possible peak at 2200 cm^{-1} is not from CO reacting with adsorbed D atoms.

Additionally, one experiment is done where approximately 0.1 L of O_2 is dosed onto the clean surface before dosing CO, to test whether the CO_2 desorption peak in the TPD measurement could be from CO reacting with surface oxygen. The resulting TPD spectrum is shown in figure 6.6. If the CO_2 desorption peak found before was caused by CO reacting with adsorbed oxygen, it should be visible clearly in this TPD. Both the CO dose and oxygen surface coverage are much higher than during a typical experiment with CO_2. Since there is no CO_2 peak, we conclude that the CO_2 desorption found earlier is not from CO reacting with adsorbed oxygen atoms.

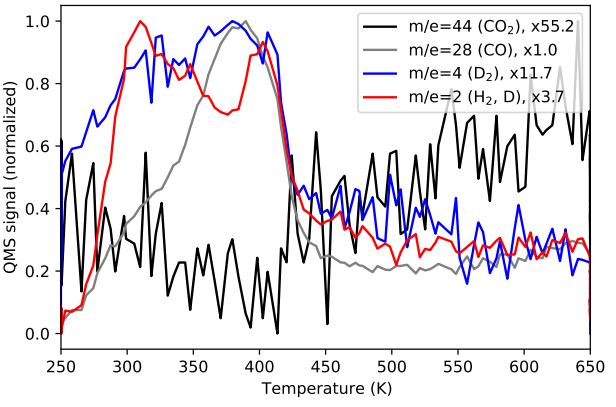

Figure 6.6: The TPD taken after dosing CO for 3 minutes from the molecular beam at 250 K on the oxygen precovered crystal (O_2 dose approximately 0.1 L). Since there is no CO_2 peak, we conclude that the CO_2 desorption found earlier is not from CO reacting with adsorbed oxygen atoms.

6.3.4 State-resolved CO_2 sticking to the Co(11-29) surface

In this section, we describe how we measure the effect of CO_2 vibrational excitation on its sticking probability to the cobalt surface. Here, we use the modulated King & Wells method. This method benefits from long measuring times to improve the signal-to-noise ratio. We therefore need to verify that CO_2 sticking to the surface occurs over the entire duration of the measurement.

CO_2 buildup as a function of time: TPD

We dose CO_2 onto the D_2 precovered surface at 250 K with varying dosing times. We then do TPD to determine the CO_2 buildup on the surface. The dosing times are varied in random order. Between the measurements, the crystal is cleaned using a short cleaning cycle of 10 minutes sputtering and 5 minutes annealing, to prevent any bias from surface contaminants on the CO_2 adsorption. The 10-minute dosing measurement is repeated several times to verify that the experimental conditions do not vary significantly over time.

The results of these measurements are shown in figure 6.7. Figure 6.7a shows the background subtracted QMS signal around the CO_2 desorption peak and figure 6.7b shows the calculated integrals of the peaks as a function of dosing time. The CO_2 peak

is smaller than the one in previous TPDs because we use a small diameter molecular beam for this measurement. This is necessary for the King & Wells measurement, and for consistency, this is done for the test measurements as well. The small signal causes the desorption peak to be relatively noisy, and it is therefore challenging to calculate accurate peak integrals. However, we are mainly interested in whether CO_2 adsorption occurs over the whole dosing time, rather than trying to determine precise peak integrals. The results shown in figure 6.7 show that the CO_2 peak keeps increasing over the whole dosing time range up to 60 minutes. We can therefore assume that a King & Wells measurement can be done continuously for at least 60 minutes, and most likely longer.

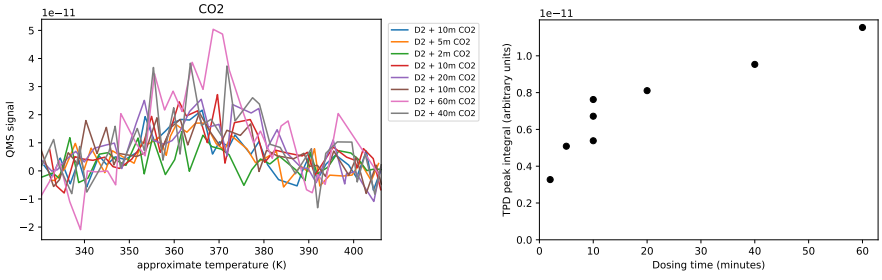

Figure 6.7: Left: the CO_2 desorption peak in the TPD for various CO_2 dosing times on the D_2 precovered Co(11-29) crystal at 250 K. Right: the integrals of the CO_2 peaks. They show a continuous increase with dosing time, indicating CO_2 sticking during the entire dosing time.

State-resolved CO_2 adsorption

To determine the effect of CO_2 vibrational excitation on the sticking probability of CO_2 on the D_2 precovered Co(11-29) surface, we use the modulated King & Wells method. Elaborate explanations of vibrational excitation, the general King & Wells method and the modulated King & Wells method can be found in chapter 2. The ν_3 asymmetric stretch is excited in the CO_2 beam by a tunable laser. The CO_2 partial pressure in the vacuum is monitored using the QMS. When the molecular beam impinges onto the crystal surface, any CO_2 that adsorbs will not enter the vacuum background. All CO_2 that is reflected will be added to the vacuum background. Therefore, changes in the partial pressure of CO_2 in the vacuum background can be a measure of the CO_2 sticking probability. This principle is used in the general King & Wells method [12]. For the modulated King & Wells method, one parameter that may impact the sticking probability is modulated at a fixed frequency. In this experiment, we modulate the laser excitation of CO_2 at 3 Hz using an optical chopper. By taking the Fast Fourier Transform (FFT), the QMS signal

is converted from the time domain to the frequency domain. This allows for relatively low noise detection of signals at a fixed frequency.

Figure 6.8a shows the FFT of the modulated King & Wells experiment where CO_2 is dosed onto the D_2 precovered surface at 250 K for 105 minutes. Figure 6.8b shows the FFT of the laser modulation, measured by the optical chopper used to control the modulation. In the laser modulation FFT, there is a clear peak at 3 Hz. In the sticking probability FFT, there is no visible peak. If it is there, it is below our detection limit. We can not exclude the possibility of the vibrational excitation affecting the CO_2 sticking probability. We can, however, calculate an upper limit for the effect based on our detection limits. For this, we first look at the peak in the laser modulation FFT. This peak is broadened, partly due to an interpolation step in the data analysis, and partly due to a small instability in the modulation frequency. We assume the peak in the sticking probability FFT would have the same shape, and its maximum height is determined by the value of the sticking probability FFT at its center. This is drawn as the gray area in figure 6.8. The integral of the gray area is our detection limit of the change in sticking probability due to vibrational excitation. We find that this value is 0.001 (where the maximum sticking probability equals 1).

The actual effect of vibrational excitation may be higher than 0.001, because not 100% of the CO_2 is excited in the molecular beam. This is because only molecules from a single initial rovibrational state can be excited (see chapter 4), not 100% of that subset is excited, and some vibrational excitation is lost due to spontaneous emission as the molecules travel. Correcting for these factors yields a value of 0.007 for the maximum effect of ν_3 vibrational excitation on CO_2 sticking probability on the D_2 precovered Co(11-29) surface at 250 K.

An absolute change in sticking probability of at most 0.007 means that vibrational excitation does not make CO_2 highly reactive. Vibrational excitation could, however, still increase the sticking probability significantly relative to the original value. TPD could give insight into relative changes in CO_2 sticking probability by integrating the CO_2 desorption peak and comparing the integrals of experiments where vibrational excitation was (not) applied.

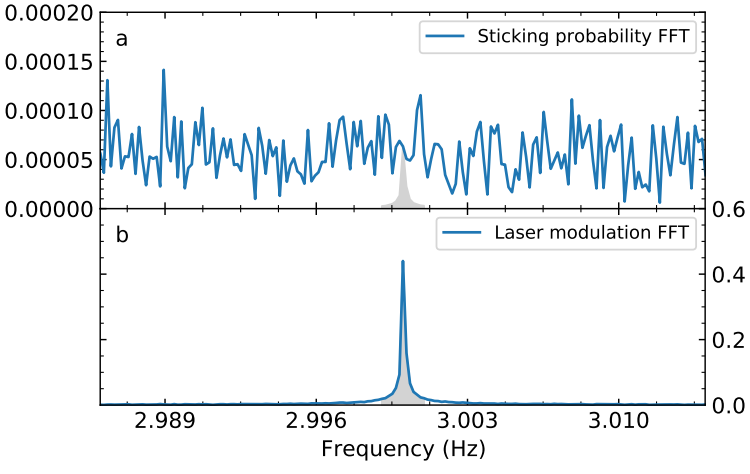

Figure 6.8: The FFT of the QMS signal of the KW measurement and the FFT of the laser modulation signal for sticking on the D_2 precovered crystal at 250K

6.3.5 Conclusions and outlook

The adsorption of CO_2 onto a D_2 precovered Co(11-29) at 250 K is studied using TPD, RAIRS, and the modulated King & Wells method. Control measurements are done with CO to exclude the possibility of CO contamination reacting with surface oxygen to form CO_2, or with surface deuterium to form C-D bonds.

The TPD experiments show simultaneous CO_2 and D_2 desorption, indicating a possible reaction between CO_2 and adsorbed D atoms. RAIRS experiments show a possible small C-D stretch peak on the surface after dosing CO_2, further pointing to the hypothesis that CO_2 reacts with adsorbed hydrogen. However, since the measured peak is so small, more data is necessary to confirm that it is real. This can be done relatively easily by measuring longer or combining the results of several separate measurements to reduce the signal-to-noise ratio.

The effect of vibrational excitation on CO_2 sticking probability is studied using the modulated King & Wells method. No difference is found between the CO_2 with and without vibrational excitation. Therefore an upper limit for the effect is calculated. This upper limit is a difference of 0.007 in the absolute sticking probability. It could also be interesting to measure the relative change in sticking probability, for example by doing TPD measurements with and without vibrational excitation. Since CO_2 sticking can be

measured with TPD, a relative change in sticking probability could easily be detected, provided that the relative change is large enough, even if the absolute change in sticking probability is small.