Spectroscopic Signatures of Pressurized Carbon Dioxide in Diffuse Reflectance Infrared Spectroscopy of Heterogeneous Catalysts

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Using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy to study surface species of reaction intermediates on heterogeneous catalysts requires particular precautions, when assigning IR bands to intermediates apparently resulting from the reaction of H$_2$, CO, and CO$_2$. In accordance with earlier work, it is shown that in the investigation of the heterogeneous methanol synthesis, several gas phase bands of CO$_2$ were misassigned in previous studies as adsorbates on the catalyst surface. Thus, several combination bands and overtones of CO$_2$ in the 2200–750 cm$^{-1}$ range – notably those at 2130, 2112, 2107, 2094, 2077, ~2056, 1933, ~1920, ~1079, ~1050, ~973, and ~948 cm$^{-1}$ – were already misinterpreted as adsorbates/intermediates. Some of these bands exhibit similar (low) intensities as surface species and are in the range of typical adsorbed CO or methoxy/methanol vibrations. Higher pressures and temperatures, which are necessary to study industrial catalysts by *in situ* IR spectroscopy, even amplify this effect. In addition, due to a Fermi resonance at a CO$_2$ partial pressure above ~10 bar, two further bands appear at 1388 and 1285 cm$^{-1}$. This is also within the range typically associated with surface adsorbates. In order to avoid misassignments of IR bands for *in situ* or *operando* DRIFT spectroscopy, those occurring at CO$_2$ pressures up to 30 bar in the widely used Praying Mantis™ High Temperature Reaction Chamber are presented here and assigned to their origin as combination bands and overtones of gaseous CO$_2$.

Introduction

Infrared spectroscopy is very versatile and frequently used to study organic and inorganic compounds. It allows the assignment of fingerprints of chemical compounds, but also *in situ* investigations of the interaction of a solid catalyst with different probe or reactant molecules such as NO, CO, CO$_2$, H$_2$, and NH$_3$ under relevant reaction conditions (i.e. non-vacuum conditions). An particularly effective method, maintaining the proximity to the real catalyst system, are *in situ* characterizations of surface species under various elevated pressures and temperatures by analysis of the diffuse reflectance of a sample.[1,2]

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

DRIFT spectroscopy is particularly suitable for strongly absorbing and scattering powders with specially high surface areas.[3] Insights to the surface nature, like photochemical reactions, oxidation processes, and gas-solid interactions are of crucial interest for the investigation in heterogeneous catalysis. In addition to the formation of adsorption products, changes in the catalyst spectrum can be examined, which gives information on the catalytically active centers involved.[1,4] Therefore, a growing number of DRIFT investigations of heterogeneous catalyzed reactions were published in the recent years.[5] Among those, the hydrogenation of CO$_2$ to methanol via Cu-based catalysts is an ideal reaction to be studied *in situ* with DRIFT spectroscopy. Adsorbed CO$_2$ or CO, as well as other by-products or reaction intermediates, have a large IR cross section range and their IR absorption frequency is extremely sensitive to the presence of other co-adsorbates and even more to the local environment at the adsorption site itself.[6]

Methanol Synthesis Studied by DRIFT Spectroscopy

Methanol is produced from syngas by the hydrogenation of a CO/CO$_2$ mixture typically using Cu/ZnO/Al$_2$O$_3$ catalysts at pressures between 50–100 bar and temperatures of 483–563 K reaching a selectivity higher than 99.9%.[7] The mechanistic understanding, the active sites, and the carbon source have been the subject of many controversial debates and investigations.[8,9] *In situ* IR measurements have provided val-

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uable information for the clarification of the reaction pathway by identifying the nature and concentration of surface species in the hydrogenation of CO$_2$ and CO to methanol. For Cu-based catalysts, the most abundant surface species found were formyl, methoxy, and formate. The latter was often proposed as an intermediate in the reaction pathway of CO$_2$ hydrogenation.[8,10,11–14]

However, the resulting IR signals are very weak and the spectra are dominated by IR-active gas phase components such as CO$_2$, methanol, and water. These difficulties are further aggravated by realistic reaction conditions, especially when industrially relevant methanol synthesis catalysts with a high Cu content (50–70 wt%) were applied.[15] This strongly limits the application of DRIFT spectroscopy for realistic systems under in situ conditions. Therefore, model catalysts with lower Cu contents frequently replaced industrial catalysts and the in situ conditions were chosen further away from an industrial regime (lower temperatures and/or pressures).[14,16,17–19]

Assignment of DRIFT Spectra of pure CO$_2$ Gas

Gausemel et al. investigated DRIFT spectra of gaseous CO$_2$ over a pure KBr sample, which provided strong bands at 2077 and 2056 cm$^{-1}$ and weaker bands around 2130, 2107, 2094, 2037, 1933, and 1915 cm$^{-1}$. At a spectral resolution of and below 0.5 cm$^{-1}$, the rotational fine structure of the bands at 2056 and 1915 cm$^{-1}$ becomes visible.[20] Importantly, Gausemel et al. showed that several bands between 2200–1900 cm$^{-1}$, which were previously assigned to CO adsorbed on various Cu planes (see Table 1), in fact originate from combination bands and overtones of the gas phase CO$_2$ molecule.[20,21]

Misassignments of Bands in DRIFT Spectra during the Methanol Synthesis

Regardless of the (correct) assignment in Table 1, several authors have misassigned bands of gaseous CO$_2$ as adsorbates on methanol synthesis catalysts in further publications that appeared after the Gausemel report.[20,21] All data are included in the full study in Table 4 below. Thus, Fisher and Bell investigated the hydrogenation of CO$_2$ with Cu/SiO$_2$ catalysts by in situ IR studies.[19] The weak bands at 2128, 2094, 2077 cm$^{-1}$ were linked to CO adsorbed on Cu$_x$, Cu(110), and Cu(111) planes. Furthermore, Hadden et al. examined the morphological changes of the surface of an industrial Cu/ZnO/Al$_2$O$_3$, catalyst induced by the adsorption of CO.[22] In this case, the broad band at 2056 cm$^{-1}$ was allocated to the stretching frequency of CO adsorbed on copper at the Cu–ZnO interface.

Additionally, Sun et al. studied the methanol synthesis from syngas on an ultrafine Cu/ZnO/Al$_2$O$_3$ catalyst at reaction conditions by FT–IR spectroscopy.[11] A weak shoulder at 2079 cm$^{-1}$ was observed at a low temperature range and ascribed to CO adsorbed on a low Miller-index plane of reduced copper. Moreover, Wang et al. performed in situ FT–IR spectroscopy over a commercial Cu/ZnO/Al$_2$O$_3$, catalyst during the methanol synthesis from H$_2$/CO and H$_2$/CO$_2$ at atmospheric pressure and varying temperatures.[11] In this case, the bands at 2077 and 2057 cm$^{-1}$ were assigned to CO adsorbed on Cu. Note that Meunier et al. criticized that these authors falsely assigned the rotational-vibrational bands of gas-phase water to formate on ZnO and carbonate species.[23]

On the other hand, Martin et al. conducted operando modulated-excitation DRIFT spectroscopy on a commercial Cu/ ZnO/Al$_2$O$_3$, catalyst at industrial conditions.[24] The bands at 2077 and 2058 cm$^{-1}$ were linked to CO adsorbed on low-index faces of Cu$_2$ (e.g. Cu(111)), the band at 2092 cm$^{-1}$ to CO adsorbed on high-index faces (e.g. Cu(755)), and the band at 2129 cm$^{-1}$ to CO adsorbed on Cu$_2$ sites. Additionally, the band at 2112 cm$^{-1}$ was assigned to CO coordinated to Cu(311) and the bands at 1932 and 1910 cm$^{-1}$ to CO adsorbed on a CuZn$_2$ alloy. Some of these observations were referenced according to the partially erroneous assignments of Bailey et al.[22] Likewise, Medina et al. examined the promotion of Ga on Cu/SiO$_2$, catalysts in the hydrogenation of CO$_2$ to methanol at pressures of 8 bar and temperatures up to 553 K.[22] The bands at 2077 and 2058 cm$^{-1}$ were associated to CO adsorbed on copper.

Due to the recurring incorrect assignments of surface species on copper-based catalysts using CO$_2$ as a reactant, this paper presents a detailed investigation of CO$_2$ gas phase spectra relevant for the DRIFT spectroscopy. It is based on the study of Gausemel et al. and extends the originally investigated range (2200 to 1900 cm$^{-1}$) to the region of 2200 to 750 cm$^{-1}$.

| Frequency | Literature | Assignments of the respective literature | Correct assignment[20] |
|-----------|------------|------------------------------------------|-----------------------|
| 2130 cm$^{-1}$ | Bailey et al.[22] | CO on Cu$^+$ | Combination band of $^{13}$C$_2$O$_2$ |
| 2107 cm$^{-1}$ | Bailey et al.[22] | CO on Cu(311) | Combination band of $^{13}$C$_2$O$_2$ |
| 2094 cm$^{-1}$ | Bailey et al.[22] | CO on Cu(755) | Combination band of $^{13}$C$_2$O$_2$ |
| 2077 cm$^{-1}$ | Elliott et al.[22] | CO on Cu(110) | Combination band of $^{13}$C$_2$O$_2$ |
| 2077 cm$^{-1}$ | Clark and Bell[14,16] | CO on a low index plane of Cu$^0$ | Combination band of $^{13}$C$_2$O$_2$ |
| 2056 cm$^{-1}$ | Bailey et al.[22] | CO on Cu(111) | Combination band of $^{13}$C$_2$O$_2$ |
| 1933 cm$^{-1}$ | Bailey et al.[22] | observed, but not assigned | Combination band of $^{13}$C$_2$O$_2$ |

[a] In this work, only the position of the band was given, but not its intensity, since an IR reaction cell with a short inner optical path length was used. Thus, it is assumed that this band was misassigned.
which is of great importance for heterogeneous catalysis.\cite{26} We realized that further CO$_2$ bands occur in this region, particularly at higher pressures, which were misassigned to various surface species.\cite{23,26,28}

**Results and Discussion**

**Relevant Combination Bands and Overtones of CO$_2$ in the DRIFT Spectroscopy**

The IR spectrum of CO$_2$ gas simulated from the HITRAN (High-Resolution Transmission) molecular spectroscopic database\cite{29} and the CO$_2$ DRIFT spectrum in the reaction chamber are shown in Figure 1. Four IR active vibrations are clearly visible in the lower part of the figure: the fundamental (degenerate) bending mode $\nu_2$ at 667 cm$^{-1}$, the asymmetric stretching mode $\nu_3$ at 2349 cm$^{-1}$, and the two combination bands $(2\nu_2 + \nu_3)$ at $\sim$ 3613 and $(\nu_1 + \nu_3)$ at $\sim$ 3715 cm$^{-1}$\cite{30} It is worth to mention that the symmetric stretching mode $\nu_1$ at 1337 cm$^{-1}$ is IR inactive.

Additional bands, in particular in the 2200 to 750 cm$^{-1}$ range, are only visible upon an enlargement of the graph (upper traces in Figure 1). One notes that in the KBr experiment in this range the same bands occur with a similar intensity (upper traces in Figure 1). An enlargement of the intensity in the middle and upper part of the graph (left and right) provides more details and making additional bands visible in the 2200–750 cm$^{-1}$ range. The black box (top trace) indicates the relevant region in which typical surface adsorbates in heterogeneous methanol catalysis interfere with combination bands and overtones of gaseous CO$_2$. The spectral range between 3100 and 2700 cm$^{-1}$ is relevant to the catalysis as well, but without disturbing combination bands and overtones.

![Figure 1.](image)

**Table 2.** The assignment of the four strongest CO$_2$ gas phase bands.

| Frequency (cm$^{-1}$) | Transition of the upper—lower vibrational state$^{[34]}$ | Isotopes |
|-----------------------|-----------------------------------------------------|----------|
| 667                   | $(\nu_3)$ 01101$\ldots$00001                      | ^12C$^16$O$_2$ |
| 2349                  | $(\nu_1)$ 00013$\ldots$00001                      | ^12C$^16$O$_2$ |
| 3613                  | $(2\nu_2 + \nu_3)$ 10012$\ldots$00001           | ^12C$^16$O$_2$ |
| 3715                  | $(\nu_1 + \nu_3)$ 10011$\ldots$00001            | ^12C$^16$O$_2$ |

(a) Vibrational notation $\nu_1\nu_2\nu_3$ according to McClatchey et al.\cite{31}
These bands were frequently assigned to surface adsorbates during the methanol synthesis including CO\(_2\) (mainly to CO adsorbed on various Cu planes, see Table 1).

However, Gausemel et al. revealed that some of these bands between 2200–1900 cm\(^{-1}\) (in capital letters with a superscript “a”) are in fact combination bands and overtones of gaseous CO\(_2\);\(^{[20,21]}\) Note that the band at 2056 cm\(^{-1}\) was verified to belong to CO\(_2\). It definitely does not originate from gaseous nickel tetracarbonyl, Ni(CO)\(_4\), which can be formed by the reaction of CO with nickel-containing stainless steel. Among these bands, the 2077 cm\(^{-1}\) band is the most intense combination band of the investigated regions (see relative intensities in Table 3) and in a typical metal-carbonyl stretching frequency range. Despite this, several of the band assignments in Table 1 do not originate from CO adsorbates on specific Cu planes.\(^{[18,23,24]}\) Yet several publications still refer to the incorrect band assignment and continue to use the misinterpretations.\(^{[1,13,19,22,26,27]}\)

Additionally, there are further combination bands and overtones of gaseous CO\(_2\) with similar intensities than the previously mentioned, especially in the range up to 750 cm\(^{-1}\), which were not described by Gausemel et al.\(^{[20]}\) In order to avoid further misassignments of CO\(_2\)-based IR bands, the strongest of them occurring are listed in Table 3 and are linked to an individual transition in accordance to the notation adopted from the HITRAN database.

For comparison, the individual transmission IR spectra of each relevant transition are presented in Figures S2–S5. These CO\(_2\) spectra were measured inside a gas cell with a spectral resolution of 0.5 cm\(^{-1}\), clearly indicating the rotational fine structure of the respective R and P branches. At a resolution of 4 cm\(^{-1}\) (typical for DRIFTS investigations of surface species in heterogeneous catalysis), the rotational fine structures are no longer visible and combine for each P and R branch into a single broadened band (Figure 2 and Table 3). This fact further increases the risk of misinterpretation as surface adsorbates. However, Q branches are almost independent of the resolution and are generally relatively narrow and sharp, since they only involve vibrational transitions with the same rotational quantum number (ΔJ=0) in the ground and excited state. This leads to (nearly) equal energies for each rotational transition, overlapping into a single narrow IR band (see FWHM in Table 3).

Some of these further combination bands and overtones of gaseous CO\(_2\) in Table 3 (indicated by capital letters without a superscript “a”) were also misassigned to several adsorbates on the surface of Cu-based methanol synthesis catalysts, although the gas phase spectrum of methanol covers a part of the bands around 1100–950 cm\(^{-1}\). Bailey et al. observed additional bands at 1078 and 978 cm\(^{-1}\) during their DRIFTS studies, which were linked to methoxy-moieties on ZnO and Cu, accordingly.\(^{[23]}\) Wang et al. assigned bands at 1081 and 1050 cm\(^{-1}\) to methoxide at Zn and gaseous methanol.\(^{[11]}\) Furthermore, Martin et al. associated the band at 1050 cm\(^{-1}\) to the ν(C–O) mode of a methoxy species and the bands at 973 and 943 cm\(^{-1}\) to the C–O stretching mode of methoxy species coordinated to metallic Cu.\(^{[24]}\) However, the band at 1078 cm\(^{-1}\) was not assigned. Note that the position of the bands is not a sufficient argument for a misinterpretation as a surface species. Therefore,
the claim of misassignments is further substantiated by the (qualitative) comparison of the individual spectra from the literature with the CO\textsubscript{2} spectrum at 10 bar over pure KBr. Figure S6 shows that all bands marked by the vertical blue dashed lines are caused by combination bands of CO\textsubscript{2}. All other bands, which are not marked, originate from possible surface adsorbates. Overall, the misinterpretations of the combination bands and overtones of CO\textsubscript{2} as surface adsorbates relevant to catalysis collected from the literature are summarized in Table 4 in supplement to Table 1.

**Table 3.** Assignments of the strongest observed combination bands and overtones of CO\textsubscript{2} in the 3400–750 cm\textsuperscript{-1} range and the temperature dependence with increasing temperature.

| Frequency | Rel. Intensity\textsuperscript{[a]}/FWHM\textsuperscript{[b]} | Transition of the upper—lower vibrational state\textsuperscript{[c]} | Branch | Isotopes | Temperature dependence\textsuperscript{[d]} |
|-----------|---------------------------------|------------------------------------------------|--------|---------|------------------|
| A  | −3361 cm\textsuperscript{-1} | v w/b | 21102−00001 | R | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |
| B  | 3340 cm\textsuperscript{-1} | v w/n | 21102−00001 | Q | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |
| C  | −3315 cm\textsuperscript{-1} | v w/m | 21102−00001 | P | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |
| D  | 2165 cm\textsuperscript{-1} | v w/n | 21101−02201 | Q | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |
| E\textsuperscript{[f]}  | 2130 cm\textsuperscript{-1} | m/n | 20001−01101 | Q | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |
| F  | 2113 cm\textsuperscript{-1} | w/n | 21101−10001 | Q | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |
| G  | 2112 cm\textsuperscript{-1} | w/m | 20001−01101 | P | \textsuperscript{12}C\textsubscript{16}O\textsubscript{2} | – |

\[\text{[a]} \text{The bands were described by Gausemel et al.}^{[24]} \text{[b] The relative intensity normalized to the most intensive band at 2077 cm}^{-1} (\text{vs} = \text{very strong, s} = \text{strong, m} = \text{medium, w} = \text{weak, and vw} = \text{very weak}), \text{[c] Full width at half maximum (n} = \text{narrow, m} = \text{medium, b} = \text{broad}), \text{[d] The vibrational notation} ν_{\text{v,v}}, ν_{\text{v,l}}, ν_{\text{l,l}} \text{according to McClatchey et al.}^{[25]} \text{[e]} \downarrow = \text{decreasing intensity,} \uparrow = \text{increasing intensity, and} \uparrow\downarrow = \text{strongly increasing intensity,} \text{[f] The band at 2077 cm}^{-1} \text{has no temperature dependence (–), since the spectra were normalized to this value, [g] The band appears at higher CO}_2 \text{ pressures due to the Fermi resonance.}

**DRIFT Spectra of CO\textsubscript{2} in dependence of pressure and temperature**

According to the Beer-Lambert law, the resulting DRIFT spectra depend on the partial pressure of CO\textsubscript{2} and the temperature T of the medium at a constant volume V and beam path length l (see description of the reaction chamber in the Experimental and Method Section). Generally, the higher the pressure and thus the concentration, the more intense are the IR signals (cf. Figure S7 at 298 K). The normalized pressure dependence of gas phase CO\textsubscript{2} in the DRIFT spectra up to 30 bar at room temperature is shown in Figure 3A. In addition, the DRIFTS experiments on the pressure dependence at higher temperatures of 373 and 473 K are given in the ESI in Figure S8 and S9. The normalized spectra in Figure 3A show that the ratio of the individual heights of the combination bands and overtones within a spectrum barely depends on the partial pressure of CO\textsubscript{2}, although the width of the bands increases slightly. However, at 1388 (ν\textsubscript{1}) and 1285 cm\textsuperscript{-1} (ν\textsubscript{2}) two new bands appear with a frequency difference of 104 cm\textsuperscript{-1} and an intensity ratio of almost 1.0 at 30 bar (Figure 3B). Furthermore, the intensities of both bands and their ratio rise with increasing CO\textsubscript{2} partial pressure starting from about 10 bar (insert in Figure 3A).

These two bands are assigned to a Fermi resonance, which can occur in combination bands and overtones, whereby the intensities of the involved bands are anomalously amplified and the frequencies shifted.\textsuperscript{[10,34]} The reason for their appearance in the CO\textsubscript{2} spectrum is that the frequency of the first overtone of the bending vibration ν\textsubscript{1} (i.e. the second harmonic 2ν\textsubscript{1} at 1334 cm\textsuperscript{-1}) is very close to the IR inactive symmetric stretching vibration ν\textsubscript{3} at 1337 cm\textsuperscript{-1}. Since these two vibrations belong to the same symmetry (\(\sum_{\nu} \nu\)) they can interact and two new bands of nearly the same intensity are obtained in the region where the IR inactive symmetric stretching vibration would be expected.\textsuperscript{[30,34]} Thereby, the stretching vibration ν\textsubscript{3} is blue-shifted from 1337 to 1388 cm\textsuperscript{-1} and the second harmonic 2ν\textsubscript{3} is red-shifted from 1334 to 1285 cm\textsuperscript{-1}, indicating a strong Fermi resonance interaction.\textsuperscript{[30]} According to the HITRAN notation, the
Figure 3. A: DRIFT spectra (4 cm$^{-1}$, 64 scans) in the 2200–750 cm$^{-1}$ range of pure KBr exposed to CO$_2$ at room temperature and various pressures: a) 5 bar, b) 10 bar, c) 15 bar d) 20 bar, e) 25 bar, and f) 30 bar. The spectra are normalized to the band at 2077 cm$^{-1}$. The insert shows an enlargement of the 1500–1200 cm$^{-1}$ range. B: An enlargement of the intensity for the DRIFT spectrum at 30 bar to provide more details.

Table 4. Misassignments of individual gas phase IR bands of CO$_2$ in several publications (excluding the bands described previously by Gausseml et al.$^{[26]}$ in Table 1).

| Frequency (cm$^{-1}$) | Literature | Assignment of the respective literature | Correct assignment |
|-----------------------|------------|-----------------------------------------|--------------------|
| 2130 cm$^{-1}$        | Fisher and Bell$^{[16]}$ | CO on Cu$^+$                          | Combination band of $^{13}$C$^{16}$O$_2$ |
| 2112 cm$^{-1}$        | Martin et al.$^{[24]}$  | CO on Cu$^+$                          | Combination band of $^{13}$C$^{16}$O$_2$ |
| 2094 cm$^{-1}$        | Fisher and Bell$^{[16]}$ | CO on Cu[110]                         | Combination band of $^{13}$C$^{16}$O$_2$ |
| 2077 cm$^{-1}$        | Martin et al.$^{[26]}$  | CO on high-index faces (e.g. Cu[111]) | Combination band of $^{13}$C$^{16}$O$_2$ |
| 2056 cm$^{-1}$        | Sun et al.$^{[11]}$      | CO on a low index plane of Cu$^+$     | Combination band of $^{13}$C$^{16}$O$_2$ |
| 1933 cm$^{-1}$        | Medina et al.$^{[27]}$  | CO on copper                          | Combination band of $^{13}$C$^{16}$O$_2$ |
| 1902 cm$^{-1}$        | Martin et al.$^{[24]}$  | CO on a CuZn$_2$ alloy                 | Combination band of $^{13}$C$^{16}$O$_2$ |
| 1079 cm$^{-1}$        | Bailey et al.$^{[11]}$  | methoxy on ZnO                        | Combination band of $^{13}$C$^{16}$O$_2$ |
| 1050 cm$^{-1}$        | Wang et al.$^{[11]}$    | not assigned                          | Combination band of $^{13}$C$^{16}$O$_2$ |
| 973 cm$^{-1}$         | Bailey et al.$^{[11]}$  | methoxy on Cu                          | Combination band of $^{13}$C$^{16}$O$_2$ |
| 948 cm$^{-1}$         | Martin et al.$^{[24]}$  | methoxy on Cu$^+$                     | Combination band of $^{13}$C$^{16}$O$_2$ |

[a] In this work, only the position of the band was given, but not its intensity, since an IR reaction cell with a short inner optical path length was used. Thus, it is assumed that this band was misassigned.

band $\nu_{2}$ at 1388 cm$^{-1}$ corresponds to the 10001 and the band $\nu_{3}$ at 1285 cm$^{-1}$ to 1002 vibrational state.

This interaction is known to be an important spectroscopic feature of CO$_2$, especially in the supercritical state. Morin et al. described that an increase in pressure at a constant temperature causes an increase in the intensities of both bands for supercritical CO$_2$.$^{[36,37]}$ This pressure dependence of the Fermi resonance is also visible in Figure 3A for the DRIFTS experiment starting with a CO$_2$ partial pressure of about 15 bar (indicated by black arrows). Furthermore, Morin et al. proposed that an increase in temperature at a given pressure results in a decrease in the intensities.$^{[36,37]}$ This temperature dependence of the Fermi resonance is shown in Figure 4 (indicated by gray arrows) at a constant CO$_2$ pressure of 30 bar.

Additionally, Figure 4 shows that the combination bands and overtones have an inverse temperature dependence (see black arrows). Their intensities increase with rising temperatures. The dependencies for the individual bands are summarized in the last column of Table 3. This temperature effect occurs at lower pressures as well (as shown in Figure 50 at a pressure of 5 bar) and is especially pronounced for the bands in the region 1100 to 770 cm$^{-1}$ (described by $\nu_{2}$). It is assumed that these are so-called hot bands, which are observed when an already excited vibration is further excited. However, it is noteworthy that this temperature dependence was already observed by Wang et al., but misinterpreted as a gradual increase in the bands of $^{16}$CH$_{2}$O–Zn and gaseous methanol.$^{[13]}$
Conclusion

Infrared studies on methanol catalysts during the hydrogenation of syngas at elevated pressures and temperatures are further complicated by the gas phase spectra of reaction gases such as water, methanol, and especially CO. Several combination bands and overtones of the CO$_2$ molecule appear in the spectral range between 2200 and 750 cm$^{-1}$ (summarized in Table 3). These bands are particularly pronounced in high-pressure IR cells with long inner optical path lengths (such as the Praying Mantis High Temperature Reaction Chamber) and are further amplified at higher pressures and temperatures. Moreover, due to the Fermi resonance at higher CO$_2$ pressures, two additional bands appear at 1388 and 1285 cm$^{-1}$. However, these bands increase with rising pressure, but decrease with rising temperature.

The combination bands and overtones of the CO$_2$ molecule can reach an intensity level similarly (low) to those of surface adsorbates on Cu-based catalysts during the methanol synthesis. This makes their identification and differentiation considerably more difficult and entails the risk of misinterpretations. In particular, the bands around 2200–1900 cm$^{-1}$ were frequently misassigned to CO adsorbates on various copper planes and the bands around 1100–900 cm$^{-1}$ to methoxy species. Frequent misassignments are summarized in Table 1 and Table 4. In DRIFTS experiments including CO$_2$, the Fermi resonance is further complicated by the gas phase spectra of reaction gases such as water, methanol, and especially CO$_2$, which are further amplified at higher pressures and temperatures.

Supporting Information

Further IR and DRIFT spectra, and the preparation funnel are given in the Supporting Information (seven pages with eleven figures).

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Conflict of Interest

The authors declare no conflict of interest.

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