

# Formation of Nonclassical Carbonyls of Au<sup>3+</sup> in Zeolite NaY: Characterization by Infrared Spectroscopy

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Adsorption of CO on gold supported in zeolite NaY at 85 K led to the formation of (i) various carbonyls and isocarbonyls typical of the zeolite and (ii) carbonyls formed at cationic gold sites (observed in the 2186–2171 cm<sup>-1</sup> region). Analysis of the behavior of the bands allows their assignment to carbonyls of Au<sup>3+</sup> ions. At temperatures higher than 220 K, CO adsorption led to the formation of a new type of Au<sup>3+</sup>–CO species (2207 cm<sup>-1</sup>). Once formed, these complexes could be transformed into the dicarbonyls Au<sup>3+</sup>(CO)<sub>2</sub> when the sample was cooled to 85 K in the presence of CO. The results are explained by migration of Au<sup>3+</sup> ions to more accessible positions within the zeolite at increasing temperatures. When a CO molecule is already adsorbed, it stabilizes the Au<sup>3+</sup> ion in the new position, and a second CO molecule can be coordinated, thus forming a geminal species. These results are the first evidence of Au<sup>3+</sup>(CO)<sub>2</sub> complexes.

## 1. Introduction

Although bulk gold is unreactive, gold dispersed on various supports is catalytically highly active for reactions such as CO oxidation<sup>1,2</sup> and the water gas shift<sup>3</sup> and selective for reactions such as NO reduction,<sup>4</sup> propene epoxidation,<sup>5</sup> and synthesis of vinyl chloride.<sup>6</sup> It has been suggested that gold nanoclusters are responsible for the catalytic properties,<sup>7–10</sup> but the involvement of gold cations has also been demonstrated, and some catalysts contain both gold nanoclusters and cationic gold.<sup>11–15</sup> It has been proposed that the sites for CO oxidation in catalysts containing gold nanoclusters consist of cationic gold located at the gold–support interface.<sup>7,11,16–20</sup> Recently, the idea of participation of Au<sup>3+</sup> ions in some reactions has gained popularity.<sup>11,20–25</sup> Therefore, a detailed characterization of supported gold is of great importance.

One of the most powerful techniques giving information about the oxidation and coordination states of accessible surface cationic and metallic sites is IR spectroscopy of probe molecules, and especially of CO.<sup>26,27</sup> Although this technique has been used to characterize supported gold,<sup>20,21,25,28–54</sup> the reported results do not give a consistent picture of the nature of the gold species.

Analysis of the reported results<sup>20,21,25,28–54</sup> shows that surface gold carbonyls have been registered in a wide spectral region, namely, 2204–1990 cm<sup>-1</sup>. Most authors<sup>25,27–32,40–43,45,46,48–54</sup> agree that surface carbonyls on metallic gold are observed in the 2138–2090 cm<sup>-1</sup> region. Bands in the 2145–2130 cm<sup>-1</sup> region have usually been attributed to (i) CO on positively polarized gold particles<sup>29,38,40,41,46,47,50,52,54</sup> (probably having oxygen in the vicinity<sup>40,52</sup>) or (ii) to Au<sup>+</sup>–CO species.<sup>20,25</sup> As a rule, bands in the 2200–2150 cm<sup>-1</sup> region have been assigned to Au<sup>+</sup>–CO species.<sup>31,32,38,40,42–45,51–54</sup> Among these, the bands

at the higher wavenumbers (>2170 cm<sup>-1</sup>) are associated with gold cations in zeolites.<sup>31,32,38,42–45</sup> In most cases, Au<sup>3+</sup> ions have not been considered to be possible adsorption sites. However, in recent investigations, some of us have proposed that bands located at approximately 2170 cm<sup>-1</sup> characterize Au<sup>3+</sup>–CO species.<sup>20</sup> According to others,<sup>25</sup> bands characterizing Au<sup>3+</sup>–CO complexes can be found at a considerably lower frequency, namely, 2148 cm<sup>-1</sup>.

Evidently, gold carbonyl chemistry needs a serious reevaluation, and well-defined samples need to be investigated to provide a basis for unambiguous conclusions.

The structures of supported gold catalysts depend on the details of the preparations and of the reaction environments, such as the water content.<sup>33,34</sup> Attempting to make structurally simple supported gold samples, some authors<sup>13–15,20,21,35–37</sup> have used the reactive mononuclear complex Au<sup>3+</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) as a precursor, characterizing its reactions with oxides and with a zeolite (NaY). This precursor yields cationic gold on the supports, sometimes in the absence of zerovalent gold;<sup>13</sup> thus, samples prepared from Au<sup>3+</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>) permit investigation of the properties and reactivity of cationic gold.

The aim of the work reported here was to characterize CO adsorption on a Au/zeolite NaY sample prepared from the precursor Au<sup>3+</sup>(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>). Because it has been reported that such samples are highly moisture-sensitive, we made efforts to minimize contact of the sample with air during the whole procedure, starting with synthesis, and including pressing of a wafer and its transfer to the IR cell and finishing with the IR measurements. This procedure allowed us to isolate carbonyls and dicarbonyls of Au<sup>3+</sup> that have not been reported before.

One of the complications arising from the use of CO as a probe of supported gold is that it can reduce gold cations easily,<sup>31,32</sup> and CO-induced changes of gold nanoclusters are also possible. To avoid eventual reduction of cationic gold by

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CO, we initially investigated CO adsorption at a low temperature, ca. 85 K.

## 2. Experimental Section

**2.1. Preparation of the Sample and of Self-Supporting Wafers.** The supported sample was prepared by adsorption of  $\text{Au}^{3+}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$  at 298 K and  $10^5$  Pa on zeolite NaY powder. The synthesis and transfer of the zeolite-supported gold samples were carried out under anaerobic and anhydrous conditions, as reported elsewhere.<sup>20</sup> The zeolite NaY powder (W. R. Grace and Co., Si:Al atomic ratio = 2.6) was treated in flowing  $\text{O}_2$  at 573 K for 4 h and then evacuated at the same temperature for 16 h. The zeolite-supported gold samples, containing 1 wt % Au, were prepared by slurring  $\text{Au}^{3+}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$  (Strem, 98%) in dried and deoxygenated *n*-pentane with the treated zeolite powder. The slurry was stirred for 48 h and the solvent removed by evacuation (pressure <  $10^{-3}$  Torr) for 1 day. Because the gold precursor is moisture-sensitive, after preparation the sample was stored in the dark in a sealed glass ampule. The gold content in the sample thus prepared was 1 wt %. Preliminary EXAFS study<sup>20</sup> has shown the presence of mononuclear gold complexes, as evidenced by the lack of detectable Au–Au contributions.

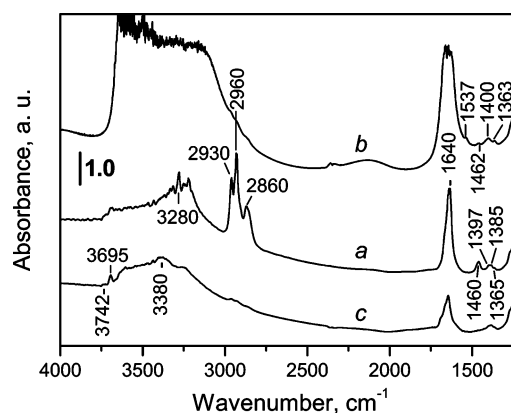
To prepare self-supporting wafers for the IR experiments, the ampule containing the sample, the pressing accessories, and the sample compartment of the IR cell were placed in a glovebag filled with Ar (99.999, Messer Griesheim, GmbH). The Ar was purified by passage through an Oxisorb cartridge (Messer Griesheim, GmbH). The ampule in the glovebag was broken, and a wafer of the sample (ca.  $10\text{--}15\text{ mg cm}^{-2}$ ) was prepared, placed into a sample holder, and transferred to the IR cell, all this in the Ar atmosphere. Carbon monoxide used in the IR experiments (>99.997%) was supplied by Linde AG. Before use it was additionally purified by passage through an Oxisorb cartridge.

**2.2. IR Spectroscopy.** The IR cell<sup>55</sup> was designed to allow recording of spectra at temperatures between 85 K and ambient temperature. The cell was connected to a vacuum adsorption system with a residual pressure below  $10^{-3}$  Pa. Spectra were recorded with a Bruker IFS-66 spectrometer at a spectral resolution of  $2\text{ cm}^{-1}$ ; each spectrum was the average of 128 scans. The sample in the cell was subjected to various treatments, as described below.

## 3. Results

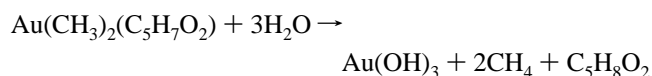
**3.1. Characterization of the Initially Prepared Sample.** The IR spectrum of the initially prepared sample, recorded in an Ar atmosphere, exhibited bands characterizing residual water, at  $3695$ ,  $3280$ , and  $1640\text{ cm}^{-1}$  (Figure 1, spectrum a). This result shows that the preparation procedure and the handling in the glovebag were not sufficient to completely avoid the presence of at least small concentrations of air/water vapor. However, the amount of water on the sample was minimized, as shown by a comparison of the spectrum of the sample with a spectrum of a sample that was intentionally brought in contact with air (Figure 1, spectrum b). In the latter case, a broad feature, indicative of adsorbed water, is evident in the  $3800\text{--}3000\text{ cm}^{-1}$  region. Its integral intensity is much greater than the integral intensity of the feature at about  $3280\text{ cm}^{-1}$  characterizing the sample that was not allowed to contact air.

In addition, a series of bands originating from the methyl and acetylacetonate ligands of the precursor  $\text{Au}^{3+}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$ : ( $2960$ ,  $2930$ ,  $2868$ ,  $1460$ ,  $1385\text{ cm}^{-1}$ )<sup>36</sup> was also observed (Figure 1, spectrum a). Two very weak bands, at  $1397$



**Figure 1.** IR spectra of (a) the as-prepared Au/zeolite NaY sample in the form of a wafer; (b) the sample after exposure to air; and (c) the as-prepared sample after evacuation at ambient temperature for 3 h.

and  $1363\text{ cm}^{-1}$ , could be assigned either to the precursor interacting with the support or to products of its partial hydrolysis. Note that the contact of the sample with air led to an almost complete disappearance of the C–H modes ( $2960$ ,  $2930$ , and  $2868\text{ cm}^{-1}$ ) arising from the precursor (Figure 1, spectrum b), which indicates hydrolysis according to the following reaction:

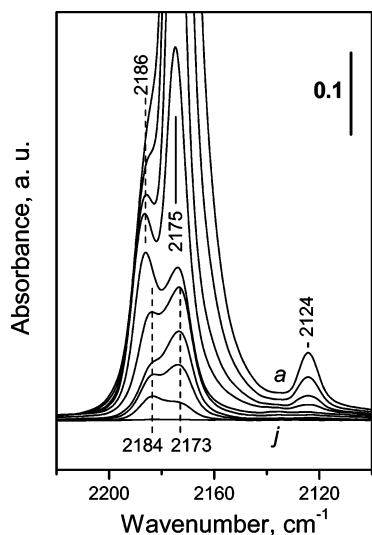


In this case, some weak bands (at  $1537$ ,  $1400$ , and  $1363\text{ cm}^{-1}$ ), suggesting chemical transformation of the precursor (most probably of acetylacetonate ligands), were also recorded. These results indicate that our efforts to minimize sample contact with air were successful.

Evacuation of the sample for 3 h at  $<10^{-1}$  Pa and at ambient temperature led to a significant erosion of the  $\nu_{\text{CH}}$  bands, indicating the almost complete removal of the organic ligands, especially the methyl groups, from the gold (Figure 1, spectrum c). Simultaneously, the band at  $1460\text{ cm}^{-1}$  also vanished. The intensities of the bands characterizing water decreased, demonstrating the dehydration of the sample during the vacuum treatment. Bands at  $3742$ ,  $3695$ , and  $3380\text{ cm}^{-1}$  were detected at the end of the experiment. The very weak band at  $3742\text{ cm}^{-1}$  is assigned to Si–OH groups. The bands at  $3695$  and  $3380\text{ cm}^{-1}$  arise from adsorbed water. The spectra do not exclude the presence of some amount of other OH groups (e.g., Al–OH) making hydrogen bonds with adsorbed water molecules.

**3.2. CO Adsorption on Zeolite NaY at 85 K.** To distinguish between the bands formed with the participation of gold and those with NaY zeolite, it was necessary initially to investigate CO adsorption on zeolite NaY. Here only a brief summary of the major results is given because the complete results have been published already.<sup>56</sup>

Low-temperature adsorption of CO on zeolite NaY leads to the formation of two intense bands at  $2166$  and  $2141\text{ cm}^{-1}$  and two weak bands at  $2127$  and  $2215\text{ cm}^{-1}$  (spectra not shown). On the basis of the literature,<sup>56,57</sup> the band at  $2166\text{ cm}^{-1}$  is assigned to  $\text{Na}^+(\text{CO})_2$  species. The  $2141\text{ cm}^{-1}$  band is unambiguously assigned to physisorbed CO. The band at  $2127\text{ cm}^{-1}$  is attributed to mixed carbonyl–isocarbonyl species,  $\text{Na}^+(\text{CO})\text{-(OC)}$ .<sup>56,57</sup> The weak band at  $2115\text{ cm}^{-1}$  characterizes  $\nu(^{13}\text{CO})$  of  $\text{Na}^+(\text{CO})(^{13}\text{CO})(^{12}\text{CO})$  species.<sup>56,57</sup> These bands are typical of high coverages of CO during its adsorption at low temperatures in zeolite NaY.<sup>56</sup> A decrease of the CO coverage during evacuation to a pressure  $<10^{-3}$  Pa resulted in the following changes: (a)



**Figure 2.** IR spectra of CO (400 Pa equilibrium pressure) adsorbed at 85 K on the Au/zeolite NaY sample, followed by evacuation at the same temperature (a–e) and at 118 (f), 188 (g), 208 (h), 228 (i), and 273 K (j).

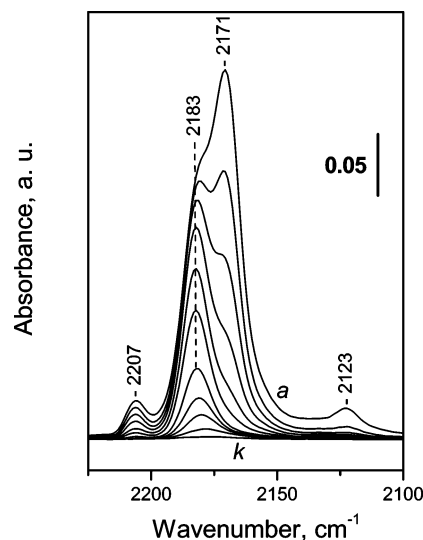
the band of physically adsorbed CO at 2141 cm<sup>-1</sup> disappeared; (b) the band at 2166 cm<sup>-1</sup> (Na<sup>+</sup>(CO)<sub>2</sub> species) was initially transformed into a band at 2174 cm<sup>-1</sup>, representative of Na<sup>+</sup>–CO species, and then the intensity of the latter band decreased strongly as most of the CO was removed; (c) the 2127 cm<sup>-1</sup> band, representing Na<sup>+</sup>(<sup>13</sup>CO)(<sup>12</sup>CO) species, was transformed into a band at 2124 cm<sup>-1</sup> (Na<sup>+</sup>–OC), which also disappeared.

**3.3. CO Adsorption on Au/Zeolite NaY at 85 K.** The Au/zeolite NaY sample that had been evacuated at ambient temperature (Figure 1, spectrum c) was cooled to 85 K, and then CO (400 Pa equilibrium pressure) was introduced into the cell. As a result, four  $\nu(\text{CO})$  bands were detected, at 2166, 2157, 2141, and 2127 cm<sup>-1</sup> (spectrum not shown). The bands at 2166, 2141, and 2127 cm<sup>-1</sup> were already observed with the support and assigned (*vide supra*). The 2157 cm<sup>-1</sup> band is attributed to hydrogen-bonded CO; indeed, this band changed in concert with a blue shift of the OH bands from 3380 to 3290 cm<sup>-1</sup>.

A decrease of the CO coverage during evacuation to a pressure <10<sup>-3</sup> Pa resulted in the already described changes of the bands attributed to the support: disappearance of the physically adsorbed CO (2141 cm<sup>-1</sup>) and conversion of the band at 2166 into a band at 2175 cm<sup>-1</sup> and that at 2127 into a band at 2124 cm<sup>-1</sup> (Figure 2, spectrum a). At low CO coverages, a band at 2186 cm<sup>-1</sup> became discernible (Figure 2, spectra a–e). This band decreased in intensity and a band at 2184 cm<sup>-1</sup> dominated in the spectra at very low coverages (Figure 2, spectra f–i). The band at 2175 cm<sup>-1</sup> also vanished, and a band at 2173 cm<sup>-1</sup> was the most stable in the region. All of these bands disappeared after evacuation at 273 K (Figure 2, spectrum j).

Because the bands in the 2186–2184 cm<sup>-1</sup> region were not detected when the gold-free zeolite was exposed to CO, they were assigned to carbonyls formed with the participation of gold sites. The same statement is valid for the band at 2173 cm<sup>-1</sup>. Its analysis is hindered because it is superimposed on the strong Na<sup>+</sup>–CO bands. However, experiments with a reduced sample (see below) confirmed participation of gold carbonyls in the formation of the band at 2175–2173 cm<sup>-1</sup>.

The relatively high frequencies of the bands assigned to gold carbonyls indicate that the gold was present in a cationic form and that the carbonyls formed were nonclassical.<sup>58</sup> These bands



**Figure 3.** IR spectra of CO adsorbed at ambient temperature on the Au/zeolite NaY sample. Equilibrium pressures (in Pa): (a) 10 000, (b) 2500, (c) 1230, (d) 600, (e) 150, and (f) 40; and (g–k) evolution of the spectra under dynamic vacuum.

will be assigned more precisely in the Discussion section. Note that no carbonyl bands were recorded at frequencies higher than 2190 cm<sup>-1</sup>.

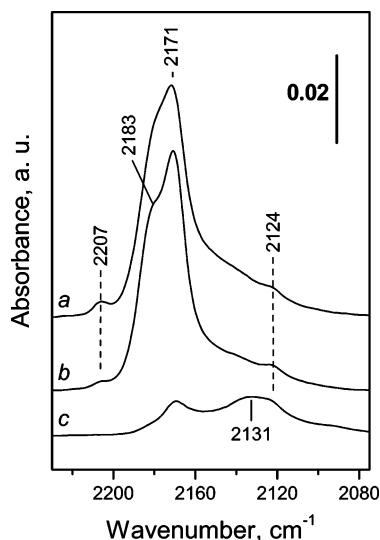
**3.4. CO Adsorption at Ambient Temperature.** After evacuation, the sample was warmed to room temperature (no carbonyl bands were observed during and after the heating process), and CO (10 kPa equilibrium pressure) was introduced into the cell again. As a result, four bands were detected in the spectrum, at 2207, 2183, 2171, and 2123 cm<sup>-1</sup> (Figure 3, spectrum a). A decrease in the equilibrium pressure led to a decrease in intensity, first, of the bands at 2123 and 2171 cm<sup>-1</sup>, and then of those at 2207 and 2183 cm<sup>-1</sup> (Figure 3, spectra b–j). After 10 min of evacuation, all of these bands had disappeared (Figure 3, spectrum k). The band at 2123 cm<sup>-1</sup> is associated with the support. Part of the band at 2171 cm<sup>-1</sup> was assumed to arise from Na<sup>+</sup>–CO species that are formed on zeolite NaY at low concentrations, even at ambient temperature. However, this band is partly assigned to carbonyls of cationic gold. The same assignment was proposed for the band at 2183 cm<sup>-1</sup>. At ambient temperature it was recorded at a frequency lower by 1 cm<sup>-1</sup> than in the low-temperature experiments. This shift is a temperature effect (see below).

The identity of the species characterized by the band at 2207 cm<sup>-1</sup> is of particular interest because there are no previous reports of bands at such high frequencies with any supported gold samples exposed to CO. Just recently, Okumura et al.<sup>42</sup> reported a shoulder at 2204 cm<sup>-1</sup> with an Au/zeolite HY sample. However, this band was found to resist evacuation, indicating its different origin.

One might expect the 2207 cm<sup>-1</sup> band to represent carbonyls of cationic gold. However, we must examine the possibility that the band arises from extraframework Al<sup>3+</sup> sites. To provide additional information concerning the assignment of this band, we investigated CO adsorption on a sample preevacuated at various temperatures. It is well known that heating leads to autoreduction of supported cationic gold.<sup>36,42,53,59</sup> Hence, if the 2207 cm<sup>-1</sup> band had arisen from adsorption of CO on cationic gold sites, then its intensity should have decreased because of the reduction. In contrast, if this band represented CO adsorbed on extraframework Al<sup>3+</sup>, then exposure to CO should have led to no change of its intensity.

The intensity of the 2207 cm<sup>-1</sup> band was very weak with





**Figure 4.** IR spectra of CO (at 1.0 kPa) adsorbed at ambient temperature on the Au/zeolite NaY sample. The sample was preevacuated at 323 (a), 373 (b), and 423 K (c).

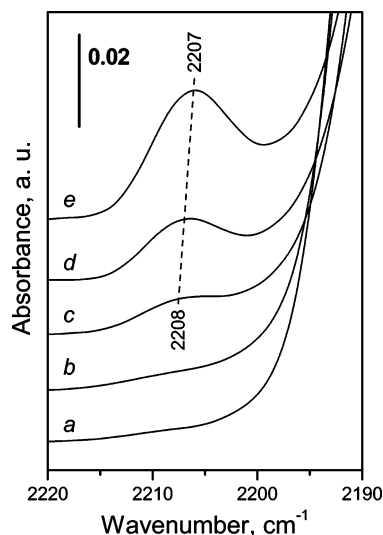
the sample evacuated at 373 K (Figure 4, spectrum b), and it was not observed with the sample evacuated at 423 K (Figure 4, spectrum c). The bands at 2183 and 2171  $\text{cm}^{-1}$  (the exact band positions were determined by the second derivatives of the spectra) also vanished with the sample evacuated at 423 K, and only a weak band at 2171  $\text{cm}^{-1}$  (assigned to  $\text{Na}^+\text{--CO}$  species) was recorded. In addition, a band at 2131  $\text{cm}^{-1}$ , assigned to CO on positively charged gold particles<sup>20,29,38,40,41,46,47,50,52,54</sup> was detected.

These results are consistent with the autoreduction of  $\text{Au}^{n+}$ , which is expected to occur at these temperatures; the result bolsters our assignment of the 2207  $\text{cm}^{-1}$  band, as well as of the bands in the 2186–2170  $\text{cm}^{-1}$  region, to cationic gold carbonyls.

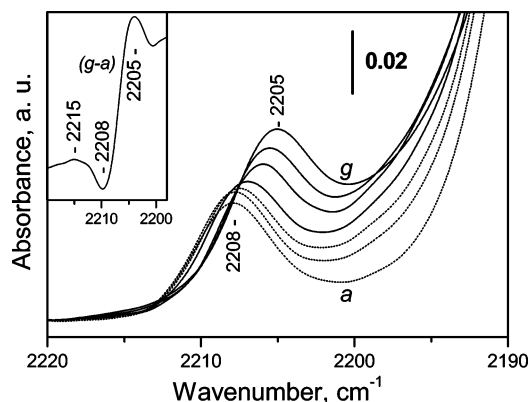
Similar results were obtained with a sample reduced with CO at 373 K (details omitted for brevity). Again, the bands assigned to cationic gold carbonyls appeared with a much weaker intensity with the reduced sample.

**3.5. Experiments at Variable Temperatures.** The 2207  $\text{cm}^{-1}$  band was not observed after CO adsorption at 85 K, but it was detected when the adsorption was performed at ambient temperature. These results could suggest that the corresponding adsorption sites form as a result of CO-induced changes in the sample (e.g., reduction) that occur at temperatures higher than 85 K. In a test of this hypothesis, the sample was cooled to 85 K after evacuation of CO at ambient temperature (Figure 3, spectrum k), and CO was adsorbed again. The results were essentially the same as those obtained after the initial low-temperature CO adsorption. Hence, we conclude that no reactive CO adsorption had occurred at ambient temperature. Instead, the results indicate that the  $\text{Au}^{n+}$  sites responsible for the appearance of the 2207  $\text{cm}^{-1}$  band are not accessible to CO at 85 K. We infer that at higher temperatures the gold cations move into new positions and/or local environments and become accessible to and capable of adsorbing CO.

In a test of this inference, a series of CO adsorption experiments was performed at various temperatures. After each experiment, CO was desorbed at temperatures close to ambient, to destroy the carbonyl species that had been formed. Thus, the possible ligand effect can be eliminated. No band at 2207  $\text{cm}^{-1}$  was detected when CO was adsorbed at temperatures in the range of 85–173 K (Figure 5, spectra a, b). In contrast,



**Figure 5.** IR spectra of CO (at an initial pressure of 10 Pa) adsorbed at various temperatures on gold-containing zeolite. Adsorption temperatures: (a) 85, (b) 173, (c) 223, (d) 263, and (e) 293 K.

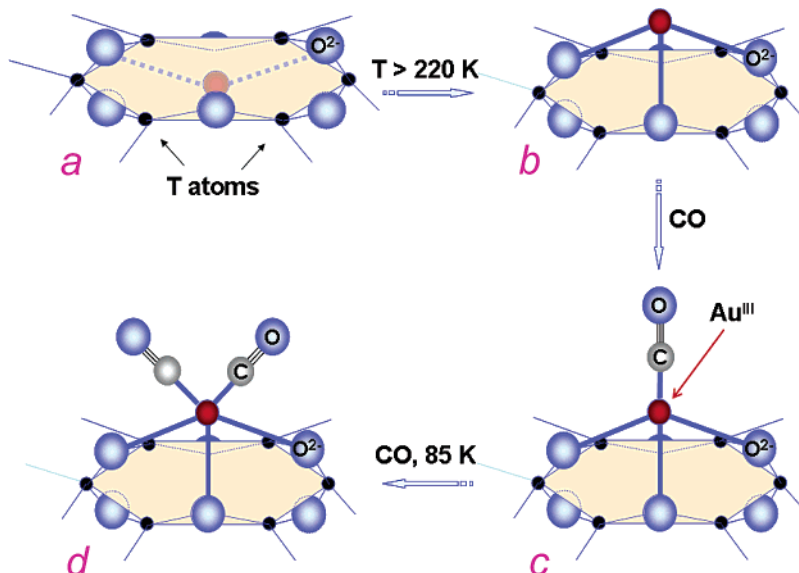


**Figure 6.** IR spectra of CO (at an initial pressure of 570 Pa) adsorbed on gold-containing zeolite at ambient temperature and after cooling the sample in a CO atmosphere to (a) 198, (b) 168, (c) 158, (d) 148, (e) 128, (f) 108, and (g) 85 K. The difference between spectra “g” and “a” is presented in the inset.

when adsorption was carried out at 223 K, a weak band was detected at 2208  $\text{cm}^{-1}$  (the exact band position was determined by the second derivative of the spectrum). The intensity of the band increased with the temperature at which the experiments were performed (Figure 5, spectra d and e). Simultaneously, the band gradually shifted to 2207  $\text{cm}^{-1}$ . These results are consistent with the above inference and show that the migration of  $\text{Au}^{n+}$  to accessible positions in the zeolite started at a temperature of approximately 220 K.

If these considerations were correct, then a decrease of the sample temperature in the presence of CO would lead to freezing-in of the  $\text{Au}^{n+}\text{--CO}$  species, and they should also be observable at 85 K. To check this interpretation, CO (at 570 Pa equilibrium pressure) was adsorbed at ambient temperature, and then the sample was cooled gradually in the presence of CO. At ca. 150 K, the band at 2208  $\text{cm}^{-1}$  started to transform into another band, with a maximum at 2205  $\text{cm}^{-1}$ , which became more intense upon saturation (Figure 6). These results are indicative of conversion of mono- into dicarbonyls, as explained below.

In many cases, metal dicarbonyls display two modes, symmetric and antisymmetric;<sup>26</sup> however, recent investigations showed that, in the cases of weak adsorption (our case), the CO oscillators did not interact, and no splitting of the CO

**SCHEME 1:** Schematic Representation of the Change in Position of the Au<sup>3+</sup> Ions in the Supercages of Zeolite Y and their Ability to Coordinate Small Molecules at Various Adsorption Temperatures<sup>a</sup>

<sup>a</sup> The T atoms are Si and Al.

stretching modes occurred.<sup>56,57,60</sup> However, we cannot rule out the possibility of some split. Indeed, a very weak band at approximately 2215 cm<sup>-1</sup> was observed at high coverages (see the inset in Figure 6) and could be assigned to the  $\nu_s$  modes of Au<sup>n+</sup>(CO)<sub>2</sub> species. In comparison with splits in the spectra of other metal dicarbonyls,<sup>26</sup> this one is relatively small ( $\Delta\nu = 10$  cm<sup>-1</sup>).

#### 4. Discussion

**4.1. Carbonyl Species Characterized by Bands at 2208–2205 cm<sup>-1</sup>.** The results of the experiments characterizing the reduction and autoreduction of the sample show that the band at 2208–2207 cm<sup>-1</sup> is attributable to carbonyls of cationic gold. Because the frequency of this band is significantly higher than those of bands that have been usually assigned to CO bonded to Au<sup>+</sup>,<sup>31,32,38,40,42–45,51–54</sup> we rule out the possibility that the 2208–2207 cm<sup>-1</sup> band represents Au<sup>+</sup>–CO species. This conclusion is also confirmed by the relatively low stability of the species represented by the 2207 cm<sup>-1</sup> band.

The other stable positive oxidation state of gold is Au<sup>3+</sup>. Therefore, we infer that the band at 2207 cm<sup>-1</sup> should be assigned to Au<sup>3+</sup>–CO species. It is known that interaction of CO with highly charged cations is essentially electrostatic and that the stretching frequency of adsorbed CO depends on the electrostatic field of the cation.<sup>26,27</sup> The C–O stretching frequency of CO adsorbed on cations by electrostatic forces can be estimated by the strength of the electrostatic field (depending on the effective charge of the cation and its radius). A complication of this approach arises because the environment strongly affects the effective charge of the cation. However, if the matrix is the same, then one can predict the CO stretching frequency well.

Consider cations located in S<sub>II</sub> positions in zeolite Y. As reported,<sup>56</sup> Na<sup>+</sup>–CO complexes formed with Na<sup>+</sup> cations in S<sub>II</sub> positions in zeolite NaY are represented by a band at 2174 cm<sup>-1</sup>. The cationic radius of Na<sup>+</sup> is 0.97 Å.<sup>61</sup> Ca<sup>2+</sup> ions (having a similar radius, namely, 0.99 Å) in S<sub>II</sub> positions in zeolite CaNaY form Ca<sup>2+</sup>–CO species absorbing at 2200 cm<sup>-1</sup>.<sup>62</sup> Taking into account the higher charge of Au<sup>3+</sup> and the lower ionic radius (0.85 Å<sup>61</sup>), the frequency at which the Au<sup>3+</sup>–CO

carbonyls are expected (provided that the Au<sup>3+</sup> ions are in S<sub>II</sub> positions) should be higher than 2200 cm<sup>-1</sup>. These considerations suggest that the 2207 cm<sup>-1</sup> band is representative of Au<sup>3+</sup>–CO species formed with the participation of Au<sup>3+</sup> ions, probably in S<sub>II</sub> positions.

The literature includes no reports of gold carbonyls at this frequency. The reason for this lack may be that, being relatively strong Lewis acid sites, the Au<sup>3+</sup> ions are blocked by water on the “as prepared” samples. Activation, normally leading to removal of adsorbed water, also leads to autoreduction of the Au<sup>3+</sup> ions on supports. Therefore, we infer that Au<sup>3+</sup>–CO surface species are usually not detected.

In our case the Au<sup>3+</sup> ions were produced by decomposition of the Au(III) precursor, which evidently left some bare Au<sup>3+</sup> species on the support. After removal of the methyl and acetylacetonate ligands, some of the Au<sup>3+</sup> ions migrated to the S<sub>II</sub> positions and penetrated the zeolite apertures (six-rings) (Scheme 1a). In this position, we infer that the Au<sup>3+</sup> ions are not accessible to CO and are not able to form carbonyl species. At higher temperatures, however, the Au<sup>3+</sup> ions have sufficient energy to migrate to the side of the aperture facing the supercage, thereby becoming accessible to CO (Scheme 1b and c).

Indeed, similar behavior was shown (by calculation) for Na<sup>+</sup> ions in the zeolite; it was found that the energy barrier for Na<sup>+</sup> to cross the six-ring was ca. 10 kJ mol<sup>-1</sup>.<sup>63</sup> Because of the lower cationic radius of Au<sup>3+</sup>, one can expect the energy barrier for Au<sup>3+</sup> ions to be lower.

Our results demonstrate that, once the Au<sup>3+</sup>–CO species are formed, the Au<sup>3+</sup> ions are able to accommodate a second CO molecule at low temperatures (Scheme 1d). It was concluded earlier that a cation in an S<sub>II</sub> position in zeolite Y should have a sufficiently large radius to form dicarbonyl species.<sup>64,65</sup> Mn<sup>2+</sup> ions (with a cationic radius of 0.80 Å) are too small and form only a negligible fraction of dicarbonyls, but larger cations (such as Au<sup>3+</sup>, with a cationic radius of 0.85 Å<sup>65</sup>) are expected to be able to accommodate two CO molecules simultaneously.

**4.2. Nature of the Carbonyl Species Observed in the 2186–2170 cm<sup>-1</sup> Region.** The discussion so far has been focused on the new information associated with the highest-

frequency bands observed in this investigation, but it is also important to assign the species observed in the 2186–2170  $\text{cm}^{-1}$  region. Numerous authors have also observed similar bands after CO adsorption on gold in zeolites and assigned them to  $\text{Au}^+ - \text{CO}$  species.<sup>31,32,38,42–45</sup> Indeed, as expected, the frequency is below the frequency of the  $\text{Au}^{3+}$  species observed here. Furthermore, this frequency is higher than the frequencies of  $\text{Au}^+ - \text{CO}$  species usually observed for oxide-supported gold.<sup>40,51–54</sup> Indeed, it has been shown that cations in zeolites are characterized by a higher electrophilicity than the same cations on oxides, which results in a higher frequency of the CO coordinated to them.<sup>66–68</sup> Hence, on the basis of the above considerations, one might agree with the earlier interpretations of the bands in the 2186–2170  $\text{cm}^{-1}$  region, observed as well with our sample, as characterizing  $\text{Au}^+ - \text{CO}$  carbonyls.

However, there is an important result that seriously impeaches this interpretation. If the species under consideration were  $\text{Au}^+ - \text{CO}$  carbonyls, then they should have a significant stability, this being a consequence of the synergism between the  $\sigma$  and  $\pi$  components of the  $\text{Au}^+ - \text{CO}$  bond.<sup>26</sup> Indeed, analysis of the literature data shows that the  $\text{Au}^+ - \text{CO}$  species are not destroyed by evacuation at ambient temperature.<sup>28,31,32,42–45,51–54</sup> Mohamed et al.<sup>44</sup> reported that a band at 2192  $\text{cm}^{-1}$ , observed with a Au/HMOR sample, was stable at temperatures up to 473 K. This is opposite to the observation in the present study. Furthermore, assuming that the  $\text{Au}^+$  ions are in exchange positions, one should expect an even stronger bond than that for  $\text{Au}^+ - \text{CO}$  species observed with oxide-supported gold (see above). All of this allows us to reject the assignment of the 2186–2170  $\text{cm}^{-1}$  bands to  $\text{Au}^+ - \text{CO}$  species.

Analysis of the literature data shows that the species observed with gold–zeolite samples and characterized by bands in the 2192–2170  $\text{cm}^{-1}$  region can be generally divided into two families, stable<sup>31,32</sup> and unstable carbonyls.<sup>38,46</sup> In an earlier investigation, some of us,<sup>20</sup> on the basis of parallel experiments with independent techniques, assigned a band at ca. 2170  $\text{cm}^{-1}$  (observed with the same kind of sample), to  $\text{Au}^{3+} - \text{CO}$  species. Thus, the following question arises: why is the frequency so much lower than the frequency of the  $\text{Au}^{3+} - \text{CO}$  species formed with  $\text{Au}^{3+}$  ions in  $\text{S}_{II}$  positions?

Normally, the  $\nu_{\text{CO}}$  frequency is highly sensitive to the oxidation state of the cation to which the CO is bound. However, the environment, including the cation coordination, can also strongly affect this frequency. Thus,  $\text{Cu}^+$  ions in exchange positions in some zeolites form carbonyls absorbing at ca. 2160  $\text{cm}^{-1}$ .<sup>66,69</sup> However, the carbonyl band of  $\text{Cu}^+ - \text{CO}$  species when  $\text{Cu}^+$  ions are supported on oxides or are in zeolites but not in exchange positions is observed at ca. 2130  $\text{cm}^{-1}$ .<sup>66,69</sup> A similar example is evident with  $\text{Ni}^{2+}$  ions:  $\text{Ni}^{2+} - \text{CO}$  species in the zeolite Ni-ZSM-5 absorbs at 2220  $\text{cm}^{-1}$ ,<sup>68</sup> whereas the singleton frequency of CO adsorbed on  $\text{Ni}^{2+}$  sites on NiO is as low as 2160  $\text{cm}^{-1}$ .<sup>70</sup> There are many similar examples with  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ , and  $\text{Al}^{3+}$  ions, among others.<sup>39</sup>

In light of the above considerations, we infer that the bands in the 2186–2170  $\text{cm}^{-1}$  region, observed in this investigation, characterize  $\text{Au}^{3+} - \text{CO}$  species, the  $\text{Au}^{3+}$  ions not being located in exchange positions. And we emphasize that  $\text{Au}^+ - \text{CO}$  bands (with  $\text{Au}^+$  ions in exchange positions) at similar frequencies were also observed. We detected similar bands with a partially reduced sample (results not reported here). The main criterion to distinguish between the two kinds of species is the stability of the bands.

We discuss the stability of the various  $\text{Au}^{3+} - \text{CO}$  species. First, consider the bands in the 2186–2170  $\text{cm}^{-1}$  region. The

band at 2183  $\text{cm}^{-1}$  corresponds to more stable species than the 2171  $\text{cm}^{-1}$  band (Figure 3), consistent with the rule that, for CO bonded mainly by electrostatic forces or  $\sigma$  bonds, the greater the stability of the metal carbonyl, the higher the C–O stretching frequency. However, the band at 2186  $\text{cm}^{-1}$  (observed at low temperatures, Figure 2) represents a species that was found to be less stable than that represented by the 2184  $\text{cm}^{-1}$  band. There are two possible explanations of this observation: (i) a temperature effect on the band position (note that spectra e–j of Figure 2 were recorded at different temperatures), and (ii) formation at higher coverages of dicarbonyl species. If so, then the latter are characterized by  $\nu_s$  at 2186  $\text{cm}^{-1}$  and  $\nu_{as}$  at about 2175  $\text{cm}^{-1}$ . At present, our results do not allow us to discriminate between these two possibilities.

Let us now compare the bands at 2207 and 2183  $\text{cm}^{-1}$  (Figure 3). A detailed analysis of the spectra showed that the species characterized by each of the bands had almost the same stability. However, for  $\text{Au}^{3+} - \text{CO}$  species, one should expect a higher stability of the species with the higher-frequency band. Our experiments showed that the band at 2207  $\text{cm}^{-1}$  represents a species formed via an activated adsorption step. Thus, the “tension” of the  $\text{Au}^{3+}$  sites, when in accessible positions, contributes to a decrease in stability of the species represented by the 2207  $\text{cm}^{-1}$  band.

## 5. Conclusions

CO adsorption at 85 K on a zeolite NaY-supported gold sample synthesized from  $\text{Au}^{3+}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$  leads to the formation of nonclassical gold carbonyls. At temperatures higher than 220 K, some  $\text{Au}^{3+}$  ions in the zeolite migrate to accessible positions and form  $\text{Au}^{3+} - \text{CO}$ , and these species are converted into  $\text{Au}^{3+}(\text{CO})_2$  at lower temperatures in the presence of CO. These results are the first evidence of dicarbonyls of  $\text{Au}^{3+}$  formed on a support and suggest that the structure of the support might play a significant role in the stabilization of such complexes.

The CO stretching frequency alone is not sufficient evidence for an unambiguous assignment of gold–carbonyl bands to well-defined species. The spectral regions of  $\text{Au}^{3+} - \text{CO}$  and  $\text{Au}^+ - \text{CO}$  species overlap, and they can be discriminated on the basis of their stability.

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