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# Mono-, Di-, and Tricarbonylic Species in Copper(I)-Exchanged Zeolite ZSM-5: Comparison with Homogeneous Copper(I) Carbonylic Structures

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The structural and spectroscopic similarities between homogeneous and heterogeneous  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+\text{A}^-$  ( $n = 1-3$ ;  $\text{A}^- = [\text{AsF}_6]^-$  or zeolite anion  $\text{Z}^-$ ) carbonyls are evidenced and discussed. While  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  and  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+$  have linear and planar structures in  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+[\text{AsF}_6]^-$  solid compounds, they are bent in the zeolite channels. The  $[\text{AsF}_6]^-$  anion has a base strength lower than that of the zeolite anion; consequently, the  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  moieties have a more positive character in the solid compounds than in the intrazeolitic ones. The  $\text{Cu}^{\text{I}}$ –framework distance is influenced by the formation of the  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  complexes: this is demonstrated by both EXAFS and IR results concerning the effect of CO complexation on the  $\text{Cu}^{\text{I}}$ –framework distance and on the  $\text{Cu}^{\text{I}}$ -sensitive skeletal modes, respectively. The role of basic ligands in increasing the  $\pi$ -character of the  $\text{Cu}$ –CO bond (with simultaneous decrease of the electrostatic and  $\sigma$  contributions) has been studied on  $[\text{Cu}^{\text{I}}(\text{CO})_n(\text{NH}_3)]^+\text{Z}^-$  ( $n = 1, 2$ ) and  $[\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n]^+\text{Z}^-$  ( $n = 1, 2$ ) complexes synthesized in situ in the zeolite channels.

## 1. Introduction

Copper-exchanged ZSM-5 (Cu-ZSM-5) is the best catalyst so far developed for the direct conversion of NO into  $\text{N}_2$  and  $\text{O}_2$ .<sup>1</sup> For this reason, considerable research has been recently directed to the characterization of the active sites and to the determination of the mechanism of NO decomposition on Cu-ZSM-5. The catalyst is usually prepared by standard exchange procedure using an aqueous solution of cupric salts. Depending on the preparation and pretreatment conditions, they can contain mixtures of copper species in different oxidation and aggregation states.<sup>2</sup> However, although the precise catalytic mechanism is not yet completely explained, most of the reported data point to  $\text{Cu}^{\text{I}}$  ions monodispersed throughout the zeolite nanopores (rather than  $\text{Cu}^{\text{II}}$ ) as the precursors of the catalytic centers. To prepare a structural model system containing exclusively isolated cuprous counterions, we have adopted a new exchange procedure by reaction of H-ZSM-5 with CuCl in the gas phase as already detailed elsewhere.<sup>3,4</sup> XANES (X-ray absorption near edge structure), EXAFS (extended X-ray absorption fine structure), IR, and UV–vis (diffuse reflectance and photoluminescence) spectroscopic characterizations have evidenced<sup>5</sup> that the so-obtained ZSM-5 (hereafter named  $\text{Cu}^{\text{I}}$ -ZSM-5) contains solely isolated  $\text{Cu}^{\text{I}}$  ions, other copper species being almost entirely absent (less 1% as deduced by EPR). These extraframework cuprous ions have proved to be nearly equidistributed in two families of sites on the internal surface of  $\text{Cu}^{\text{I}}$ -ZSM-5 (hereafter labeled as **I** and **II**, respectively). In family **I** the  $\text{Cu}^{\text{I}}$  ion is coordinated to three equivalent nearest-neighbor framework oxygens at 2.00 Å; in family **II** the  $\text{Cu}^{\text{I}}$  has two equivalent nearest-neighbor oxygens at 2.00 Å and a third one

more internally located at about 3 Å.<sup>5a</sup> This picture is in fair agreement with the very recent theoretical contribution of Sauer and co-workers.<sup>6</sup> These sites are structurally and energetically well-defined, and being highly coordinatively unsaturated, they can easily form intrazeolitic complexes with molecules entering the zeolite channels. Following Klier<sup>7</sup> they represent “perfect surface sites”. The high reactivity of  $\text{Cu}^{\text{I}}$  in ZSM-5 is fully confirmed by: (i) The formation of end-on  $[\text{Cu}^{\text{I}}(\text{N}_2)]^+$  dinitrogen complexes stable under mild conditions (room temperature and lower than atmospheric  $\text{N}_2$  equilibrium pressure)<sup>8</sup> which, to the best of our knowledge, do not have analogous homogeneous counterparts. (ii) The formation, upon NO interaction, of  $[\text{Cu}^{\text{I}}(\text{NO})]^+$  and  $[\text{Cu}^{\text{I}}(\text{NO})_2]^+$  complexes of high structural and spectroscopic quality.<sup>3–5a</sup> These dinitrosyl species are unstable at room temperature and evolve spontaneously with formation of nitrous oxide and oxidized  $\text{Cu}^{\text{II}}(\text{NO})\text{X}$  ( $\text{X} = \text{O}^-$  and/or  $\text{NO}_2^-$ ) species, which could play a role as intermediates in the catalytic conversion of NO.<sup>3,4</sup> (as recently supported by a theoretical study<sup>9</sup>). (iii) The formation, upon contact with CO, of well-defined  $[\text{Cu}^{\text{I}}(\text{CO})]^+$ ,  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$ , and  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+$  complexes with partial cationic character.<sup>3,5</sup> The high stabilities of these copper(I) polycarbonyls together with their unusually high CO stretching frequencies have been explained in terms of  $\text{Cu}^{\text{I}}$ –CO bonds where electrostatic and  $\sigma$ -dative covalent contributions are predominant (the  $\pi$ -back-donation being practically absent).

Notice that for the intrazeolitic complexes described in (i)–(iii) full ionic notation has been adopted: this is obviously purely formal since covalent contributions are also present, as will be discussed extensively below. In the following the intrazeolitic complexes will be named “heterogeneous complexes” because

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they are formed at the internal surfaces of the zeolite. For the complexes present in solution and/or in the solid state, the definition “homogeneous complexes” will be adopted to signify that they are in a single phase.

The high structural perfection of the  $\text{Cu}^{\text{I}}$  complexes in ZSM-5 together with their mononuclear character allows to classify them as the best heterogeneous counterparts of the homogeneous  $\text{N}_2$ ,  $\text{NO}$ , and  $\text{CO}$  complexes. As far as the homogeneous copper(I) polycarbonyls are concerned, let us mention that although binary compounds of the type  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  have been observed in strong acidic media (such as  $\text{H}_2\text{SO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{FSO}_3\text{H}$ ,  $\text{BF}_3\cdot\text{H}_2\text{O}$ , and  $\text{HF}$ ),<sup>10,11</sup> none of these complexes could be isolated as solids. Although the first  $[\text{Cu}^{\text{I}}(\text{CO})]^+[\text{AsF}_6]^-$  solid compound has been synthesized for the first time in 1979,<sup>12</sup> only very recently Strauss and co-workers have reported the formation and structural characterization of  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+[\text{AsF}_6]^-$  ( $n = 2, 3$ ) compounds.<sup>13</sup> All these species represent the first examples of well-defined  $\text{Cu}^{\text{I}}$  polycarbonyls.

As the intrazeolitic and homogeneous  $\text{Cu}^{\text{I}}$  carbonyls have the same stoichiometry, we have decided that it could be of some interest to consider and analyze in greater detail their structures and vibrational properties and to further develop a well-defined intrazeolitic chemistry. In particular, in this contribution, we compare the vibrational spectra of the two series of homogeneous and heterogeneous carbonyls and discuss the role of the counteranion size and nucleophilicity in determining the structure, stability, and  $\text{CO}$  stretching frequencies of the intrazeolitic polycarbonylic  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  cations. The EXAFS analysis of intrazeolitic  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  complexes reveals that, upon carbon monoxide adsorption,  $\text{Cu}^{\text{I}}$  ions have moved 0.16 Å from the position occupied in *vacuo* conditions (*vide infra* and see ref 5a). This structural datum is a direct measure of the higher complexing capacity of the  $\text{CO}$  base with respect to negatively charged oxygens of the framework. The mobility of  $\text{Cu}^{\text{I}}$  upon interaction with  $\text{CO}$  is fully confirmed by the study of the effect of  $\text{CO}$  complexation on the  $\text{Cu}^{\text{I}}$ -sensitive skeletal IR modes of the zeolite. Finally, to increase the knowledge on the intrazeolitic chemistry of  $\text{Cu}^{\text{I}}$ , we report the IR spectra of new intrazeolitic complexes,  $[\text{Cu}^{\text{I}}(\text{CO})(\text{NH}_3)]^+\text{Z}^-$ ,  $[\text{Cu}^{\text{I}}(\text{CO})_2(\text{NH}_3)]^+\text{Z}^-$ , and  $[\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n]^+\text{Z}^-$  ( $n = 1, 2$ ), formed by interaction of  $\text{Cu}^{\text{I}}$  carbonyls with  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .

## 2. Experimental Section

$\text{Cu}^{\text{I}}$ -ZSM-5 was prepared by reaction of H-ZSM-5 ( $\text{Si}/\text{Al} = 28$ ; prepared in EniChem SpA, Centro Ricerche Novara) with gaseous  $\text{CuCl}$  at 673 K as previously described.<sup>3,4</sup> The exchange of the acidic Brønsted sites proved to be complete, as demonstrated by the total absence in the  $\text{Cu}^{\text{I}}$ -ZSM-5 IR spectrum of the band at  $3610\text{ cm}^{-1}$ , characteristic of the  $\text{O}-\text{H}$  stretching mode of framework  $-\text{Al}-(\text{OH})-\text{Si}-$  groups. To remove excess  $\text{CuCl}$  entrapped inside zeolite channels, the samples were further outgassed under high dynamic vacuum for 1 h at 973 K. The spectroscopic characterization of the so-prepared  $\text{Cu}^{\text{I}}$ -ZSM-5 has been reported in our previous works, where also the experimental procedure followed to study the  $\text{CO}$  adsorption at room temperature (RT) and about 110 K is described.<sup>5</sup>

To synthesize  $[\text{Cu}^{\text{I}}(\text{CO})_n(\text{NH}_3)]^+$  ( $n = 1, 2$ ) intrazeolitic complexes, coadsorption of  $\text{CO}$  and  $\text{NH}_3$  was carried out on a  $\text{Cu}^{\text{I}}$ -ZSM-5 sample in the form of self-supporting wafers (typical thickness 100–150  $\mu\text{m}$ ). Gas dosage ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CO}$ ) was made using a vacuum manifold permanently connected to the IR cell, designed to allow *in situ* RT and low-temperature IR measurements. Two types of experiments were performed, at RT and about 110 K: in the first one,  $\text{NH}_3$  was dosed on

preformed  $[\text{Cu}^{\text{I}}(\text{CO})]^+$  complexes; in the second one,  $\text{CO}$  was dosed on preadsorbed  $\text{NH}_3$ . In the first experiment  $\text{CO}$  (40 Torr) was adsorbed first, at RT, to initially form dicarbonylic complexes; then, the gas phase was removed by outgassing under dynamic vacuum. Under these conditions only monocarbonylic species are stable.<sup>3,5</sup> High-purity grade  $\text{NH}_3$  (from Matheson) was then allowed to contact the sample (previous further purification by repeated freeze–pump–thaw cycles) up to a maximum pressure of 40 Torr (1 Torr  $\approx$  133.3 Pa). In the second experiment, dosage of  $\text{NH}_3$  was made first as follows: 40 Torr of  $\text{NH}_3$  was dosed on pretreated  $\text{Cu}^{\text{I}}$ -ZSM-5 pellet at RT and left to equilibrate for 10 min; then, the excess  $\text{NH}_3$  was removed by prolonged outgassing at RT. After this, the pellet was cooled in *vacuo* at about 110 K, and increasing amounts of  $\text{CO}$  were dosed up to a maximum equilibrium pressure of 20 Torr: in this way  $[\text{Cu}^{\text{I}}(\text{NH}_3)(\text{CO})]^+$  and  $[\text{Cu}^{\text{I}}(\text{NH}_3)(\text{CO})_2]^+$  could be formed in a stepwise manner. With regard to the synthesis of mixed  $[\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n]^+$  complexes, obtained by coadsorption of  $\text{H}_2\text{O}$  and  $\text{CO}$ , the adopted procedure was similar to the first  $\text{CO}/\text{NH}_3$  experiment. In particular:  $\text{CO}$  was initially dosed at  $\sim 300\text{ K}$  to form the monocarbonylic  $\text{Cu}^{\text{I}}(\text{CO})$  species; then, increasing amounts of water were allowed to contact the sample to form, *in situ*,  $[\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n]^+$  ( $n = 1, 2$ ). Identical results were obtained by dosing  $\text{CO}$  on presorbed water at  $\sim 300\text{ K}$ . As  $\text{H}_2\text{O}$  is a ligand weaker than  $\text{NH}_3$ , significant results could be obtained, with this method, only in the presence of a sensible pressure of  $\text{H}_2\text{O}$  ( $P/P_0 \approx 0.2$ ).

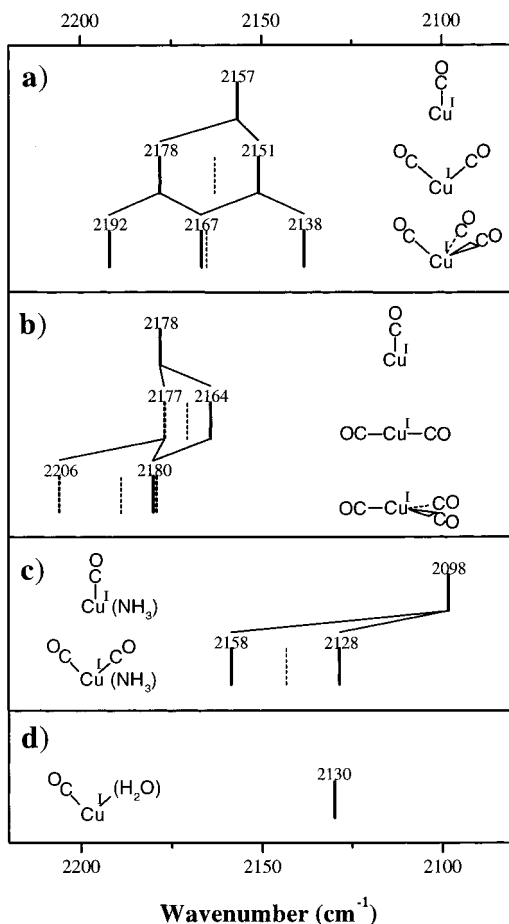
Dosage of  $\text{CO}$  at 110 K on preadsorbed water following the second procedure, adopted for the  $\text{CO}/\text{NH}_3$  system, was not successful for experimental reasons. In fact when the pellet with preadsorbed water is cooled at 110 K, the water molecules, weakly coordinated to the  $\text{Cu}^{\text{I}}$  ions, desorb completely because they are condensed preferentially on the metallic sample holder (which is at the real liquid nitrogen temperature).

The IR transmission spectra were recorded at  $2\text{ cm}^{-1}$  resolution on a Bruker IFS66 FTIR spectrometer equipped with a cryogenic MCT detector. X-ray absorption spectra<sup>14</sup> were recorded at RT in the transmission mode using air-filled ionization detectors at the EXAFS1 station, equipped with a Si(331) channel-cut monochromator, of the 1.85 GeV DCI storage ring of LURE (Orsay, France). An integration time of 2.0 s/point and a sampling step of 2.0 were adopted. EXAFS spectra were recorded three times for each experimental condition;  $\chi(k)$  functions were extracted as detailed elsewhere<sup>5a</sup> and averaged before data analysis, which was carried out using programs developed by Michalowicz<sup>15</sup> and following standard procedures.<sup>16</sup> An ad hoc conceived quartz cell was used, allowing thermal treatments and gas dosage *in situ* to be made. This experimental setup was already successfully adopted in similar experiments performed on Ti–silicalites,<sup>17</sup> Fe–silicalites,<sup>18</sup>  $\text{Cu}^{\text{I}}$ -Y,<sup>19</sup> and  $\text{Cu}^{\text{I}}$ -mordenite.<sup>20</sup> Before measurements the sample, in the form of a self-supporting wafer, was outgassed for 1 h at 973 K.

## 3. Results and Discussion

**3.1. Intrazeolitic and Homogeneous  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  ( $n = 1-3$ ) Species: Comparison of the Spectroscopic and Structural Properties.** The IR characterizations of polycarbonylic  $[\text{Cu}^{\text{I}}(\text{CO})_1]^+$ ,  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$ , and  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+$  species formed upon  $\text{CO}$  adsorption on  $\text{Cu}^{\text{I}}$ -ZSM-5 at room temperature (RT) and at about 110 and 80 K have been reported and widely discussed in refs 5a,b, respectively.

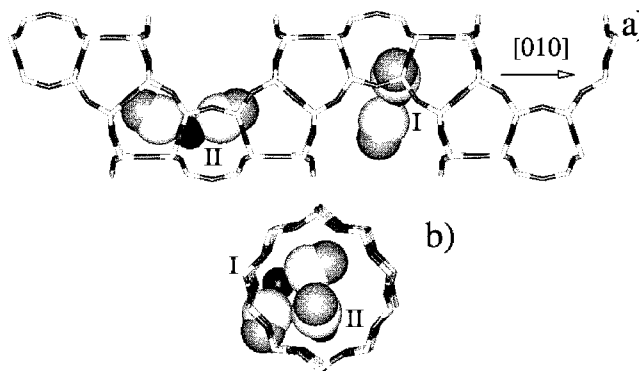
For sake of comparison in Figure 1 we have schematized the vibrational and structural properties of the intrazeolitic



**Figure 1.** Schematic representations of intrazeolitic and homogeneous  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  species ( $n = 1-3$ ) and of intrazeolitic  $[\text{Cu}^{\text{I}}(\text{CO})_n(\text{NH}_3)]^+$  ( $n = 1, 2$ ) and  $[\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})]^+$  species and corresponding vibrational modes (a–d, respectively). Full and dashed segments represent IR and Raman active modes, respectively; for  $n > 1$  dotted segments represent the barycenter of vibrational modes.

complexes and of the analogous Cu<sup>I</sup> polycarbonyls isolated by Strauss and co-workers,<sup>13</sup> which have reported that crystalline CuAsF<sub>6</sub> adsorbs up to 3 equiv of CO at RT and CO pressure lower than atmospheric (about 240 Torr), with formation of solid  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+[\text{AsF}_6]^-$  ( $n = 1-3$ ) salts, whose spectra are consistent with a linear ( $D_{\infty h}$ ) structure for the  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  cation and with a trigonal-planar ( $D_{3h}$ ) structure for the  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+$  cation. The dicarbonyl is characterized by mutually exclusive Raman (2177 cm<sup>-1</sup>) and IR (2164 cm<sup>-1</sup>) CO stretching bands, which have been assigned by Strauss et al. to the symmetric ( $\Sigma_g^+$ ) and asymmetric ( $\Sigma_u^+$ ) stretching modes, respectively, while the tricarbonyl shows a single IR absorption at 2183 cm<sup>-1</sup> and a Raman doublet at 2179 and 2206 cm<sup>-1</sup>, which are the E' (IR) and the E' + A<sub>1</sub>' modes of planar  $D_{3h}$  structure.<sup>13</sup>

Comparing the two type of carbonyls (heterogeneous and homogeneous), it can be noticed that the intrazeolitic polycarbonylic species are characterized by lower symmetries. In fact, while the homogeneous dicarbonylic cation is linear ( $D_{\infty h}$ ), the intrazeolitic analogue one is bent ( $C_{2v}$ ). In the same way, to the planarity ( $D_{3h}$ ) of the homogeneous tricarbonyl, the cis (lower than  $C_{3v}$ )<sup>5</sup> structure of the intrazeolitic species is opposed. This is certainly the result of the steric constraints imposed by the walls of zeolitic channels. In relation to this, let us remark that the binding of cuprous ions to the framework oxygens of the zeolite, although primarily electrostatic, is characterized by some covalent contribution<sup>21,22</sup> and that, although the CO coordination



**Figure 2.** (a) Computer graphic showing a portion of the straight channel running along the [010] direction, where  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  adducts formed on sites I and II are evidenced. With site I located at the intersection of two channels, the formation of a 130° dicarbonylic complex can be performed either along the [010] direction or in the perpendicular (010) plane, using the empty space of the adjacent sinusoidal channel (reported in the figure). On the contrary, for site II, located along the straight channel, only the former case is available. (b) As in part a, observed from the perpendicular [010] view. Please note that this picture is only a graphical representation of two different locations of Cu<sup>I</sup> (and consequent carbonylic adducts) which is compatible with the indirect experimental evidences coming from several independent techniques<sup>5a</sup> and does not represent an attempt to localize Cu<sup>I</sup> from a crystallographic point of view.

produces a weakening of the Cu<sup>I</sup>–framework oxygen bond (with consequent increase in the Cu<sup>I</sup>–O bond length, as predicted by theoretical calculations<sup>22,23</sup> and revealed by EXAFS and IR measurements, vide infra), the associate displacement ( $0.16 \pm 0.04$  Å) of Cu<sup>I</sup> from its original position is not sufficient to avoid the steric constraints imposed by the zeolite walls. On the basis of the intensity ratio of the symmetric and asymmetric stretching bands ( $I_{2151}/I_{2178} = 4.5$ ) determined by using ASYMGRAD band fitting program,<sup>24</sup> an angle  $\theta$  of about 130° is inferred ( $\theta = 2 \text{ Arctg} [\sqrt{I_{\text{ASYM}}/I_{\text{SYM}}}]^{25a}$ ). This result is in qualitative agreement with the results recently reported by Miessner et al. for a similar Cu<sup>I</sup>(CO)<sub>2</sub> complex in dealuminated Y zeolite.<sup>25b</sup> To better illustrate the location of the carbonylic species in the ZSM-5 channels, we have represented, with the aid of computer graphics, the structure of the dicarbonylic species (see Figure 2). It can be easily realized that dicarbonylic species with a CO–CO angle of about 130°, Cu<sup>I</sup>–framework distance of ~2 Å, and the molecular plane parallel to the axis of the channels can be located in both sinusoidal and straight channels, because only in this way the repulsive interaction between the CO ligands and the atoms of the walls is minimized. This geometric limitation is, on the contrary, not present at the channels intersections, where many orientations are possible.

On the contrary, in the  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+[\text{AsF}_6]^-$  solid compound,  $[\text{AsF}_6]^-$  (a very weakly coordinating anion) has only very weakly nucleophilic sites (the fluorine atoms) available for binding the  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  cation and the environment of the  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  cations in the solid compound is more symmetric. For these reasons  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  and  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+$  can assume the linear and planar structures, respectively.

As the vibrational properties are concerned, let us underline that the barycenters of the CO stretching frequencies of both homogeneous and heterogeneous Cu<sup>I</sup> carbonyls are characterized by a *hypsochromic shift* (i.e., a shift at higher frequency) with respect to the CO gas frequency (2143 cm<sup>-1</sup>); this is a characteristic feature of metal carbonyls with cationic character.<sup>11,26</sup> The explanation of the hypsochromic shift observed for intrazeolitic carbonyls can be briefly made by analogy with that given for homogeneous Cu<sup>I</sup> complexes: i.e., following ref 11



and references therein, unlike classical transition-metal carbonyls, where a synergistic  $\sigma$ - and  $\pi$ -bonding mechanism accounts for the high thermal stability and the net bathochromic shift (i.e., a shift at low frequency) of  $\nu(\text{CO})$  values,<sup>27</sup> the observed high CO stretching frequencies and high stability of  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  and other carbonylic complexes with cationic character, both homogeneous or intrazeolitic, indicate that CO bonding relies predominantly on electrostatic and  $\sigma$ -donation effects, without substantial CO  $\pi$ -acceptance compensation.<sup>11,26,28,29</sup> This conclusion agrees with the considerations recently pointed out by Goldman and Krogh-Jespersen.<sup>30</sup> The same explanation has been given by Strauss et al.<sup>13,29,31</sup> for  $\text{Cu}^{\text{I}}(\text{CO})_n$  species. Similarly, ab initio calculations on the analogous d<sup>10</sup>  $\text{Ag}^{\text{I}}$  and  $\text{Au}^{\text{I}}$  carbonyl cations<sup>32–34</sup> have evidenced the near complete lack of  $\pi$ -back-bonding.

Coming back to heterogeneous systems, let us remark that electrostatic interaction (ion–dipole and CO polarization), via the carbon end, between CO and a cationic center (resulting in a hypsochromic shift of the CO stretching frequency) is very common as has been experimentally observed<sup>35</sup> and theoretically explained<sup>36</sup> for several oxide (e.g.,  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ...) and halide (e.g.,  $\text{CuCl}$ ,  $\text{LiF}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ...) surfaces. Examples of well-defined intrazeolitic carbonyl cations are also  $\text{Rh}^+(\text{CO})_n$  ( $n = 1–4$ ),  $\text{Ag}^+(\text{CO})$ , and  $\text{Au}^+(\text{CO})$ .<sup>11</sup> More recently hypsochromic shifts associated with purely electrostatic interactions have been observed for CO adsorbed on alkali-metal-exchanged zeolites, the values of the shifts being determined by the cation size and charge<sup>37</sup> and by the ionicity of the zeolitic framework.<sup>38</sup> For instance purely electrostatic  $\text{Na}^+–\text{CO}$  adducts in  $\text{CO}/\text{Na-ZSM-5}$  are characterized by  $\nu(\text{CO})$  at  $2178\text{ cm}^{-1}$ .<sup>38,39</sup> These adducts are very labile and can be observed only at low temperature. From the latter observation it is inferred that the sole electrostatic contribution (associated with the electric field of the  $\text{Cu}^{\text{I}}$  center which has the same formal charge and a very similar ionic radius with respect to  $\text{Na}^+$ <sup>40</sup>) cannot justify the stability of the intrazeolitic  $[\text{Cu}^{\text{I}}(\text{CO})]^+$  complexes at RT and in vacuo. This conclusion confirms that, besides the electrostatic effect, important covalent contributions ( $\sigma$ ) must be present as well. With regard to this aspect, it is worth recalling that the positive shift observed for  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  complexes<sup>11,28,29,41</sup> cannot be caused by pure  $\sigma$ -donation (as documented by the  $\nu(\text{CO})$  frequency in the model  $\text{BF}_3–\text{CO}$ <sup>42</sup> and  $\text{BH}_3–\text{CO}$ <sup>43</sup> compounds).

A remarkable and unusual property of the  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  complexes emerging from the literature data is that an increase of electron density at the cuprous center is associated with a *downward shift* of the CO stretching frequency and a *decrease* of the stability of the  $\text{Cu}^{\text{I}}–\text{CO}$  bond. To briefly illustrate this point, let us mention that from the study of the only other known cuprous–polycarbonyl cations<sup>10</sup> (obtained under atmospheric CO pressure in strong acidic media such as  $\text{BF}_3 \cdot \text{H}_2\text{O}$ , HF,  $\text{FSO}_3\text{H}$ ,  $\text{CF}_3\text{SO}_3\text{H}$ , and  $\text{H}_2\text{SO}_4$ : no one isolable as solid) a simultaneous decrease in CO uptake capability and in the CO stretching frequencies with the increase of the solvation power of the acid (i.e., with the increase of electron density on the  $\text{Cu}^{\text{I}}$  center) has been evidenced (see Table 1). Furthermore, in  $[\text{Cu}^{\text{I}}(\text{CO})]^+\text{X}^-$  salts, where  $\text{X}^- = \text{CF}_3\text{CO}_2^-$ ,<sup>44</sup>  $\text{CF}_3\text{SO}_3^-$ ,<sup>45</sup> and  $\text{C}_2\text{H}_5\text{SO}_3^-$ ,<sup>45</sup> the  $\nu(\text{CO})$  frequencies decrease from 2155 to 2128 and 2117  $\text{cm}^{-1}$ , respectively, which is in agreement with the increase of nucleophilic character of the counterion. In addition, many  $\text{Cu}^{\text{I}}$  carbonyl complexes with even more basic amine ligands are known,<sup>46</sup> which are characterized by CO stretching frequencies as low as 2090–2060  $\text{cm}^{-1}$ . The correlation between the stability decrement and the bathochromic shift of the

**TABLE 1: Experimental C–O Stretching Frequency<sup>10</sup> of  $[\text{Cu}^{\text{I}}(\text{CO})]^+$  Monocarbonyls in Aqueous Solution with Acids of Increasing Solvation Tendency (from top to bottom)<sup>a</sup>**

solvent	monocarbonyl $\nu(\text{CO})$ , $\text{cm}^{-1}$	solvent	monocarbonyl $\nu(\text{CO})$ , $\text{cm}^{-1}$
$\text{BF}_3 \cdot \text{H}_2\text{O}$	2160	80% $\text{H}_2\text{SO}_4$	2136
HF	2156	50% $\text{H}_2\text{SO}_4$	2128
$\text{FSO}_3\text{H}$	2152	95% $\text{HCOOH}$	2119
$\text{CF}_3\text{SO}_3\text{H}$	2150	95% $\text{CH}_3\text{COOH}$	2109
$\text{H}_2\text{SO}_4$	2140	7%, 36% $\text{HCl}$	2103

<sup>a</sup> Please note that we are dealing with solvated species.

$\nu(\text{CO})$  is also confirmed by the well-known fact that crystalline  $\text{Cu}(\text{CO})\text{Cl}$ , exhibiting a band at  $2127\text{ cm}^{-1}$ , exists only in CO atmosphere and undergoes rapid decarbonylation even at temperatures lower than RT.<sup>47</sup> Similarly,  $\text{CuBr}$  reacts only very slowly with CO, while  $\text{CuI}$  is unreactive;<sup>48</sup> a trend which follows the increase of the nucleophilic character of the counteranion. In conclusion, *a low CO stretching frequency in  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  carbonyls is not associated with a substantial strengthening of the CO bond*. This means that we are not in the presence of classic carbonyls characterized by  $\sigma–\pi$ -synergetic interplay and that the increase of  $\pi$ -acceptance does not result in an overall strengthening of the  $\text{Cu}^{\text{I}}–\text{CO}$  bond (as expected in the case of an effective  $\sigma$ - and  $\pi$ -synergistic mechanism). This conclusion is not unknown for heterogeneous systems: in fact Solomon et al.<sup>49</sup> and Scarano et al.<sup>50</sup> have evidenced that CO adsorbed on the surface of crystalline  $\text{CuCl}$  is bonded to  $\text{Cu}^{\text{I}}$  centers via a weak  $\pi$ -interaction (responsible for a red shift of  $\nu(\text{CO})$ ) not accompanied by a parallel stability. Similarly, the adsorption of CO on unpolar (111) faces of  $\text{Cu}_2\text{O}$  gives a band at  $2132\text{ cm}^{-1}$ .<sup>51</sup> These and other experimental C–O stretching frequencies of well-defined  $\text{Cu}^{\text{I}}$  monocarbonyl compounds are summarized in Table 2.

After this short review on the bonding of CO in copper carbonyls with cationic character (homoleptic carbonyls),<sup>11</sup> it is possible to afford a discussion of the most important features of the vibrational spectra of homogeneous and intrazeolitic cation carbonyls and of the change of the  $\nu(\text{CO})$  barycenter on passing from monocarbonylic to polycarbonylic (homogeneous and heterogeneous) species.

As far as monocarbonyl species are concerned, let us remark that the extremely high Lewis acidity of cuprous ions in  $\text{CuAsF}_6$  explains the higher stability and the higher  $\nu(\text{CO})$  of  $[\text{Cu}^{\text{I}}(\text{CO})]^+–[\text{AsF}_6]^-$  with respect to the corresponding intrazeolitic species (2178 vs 2157  $\text{cm}^{-1}$ , see Figure 1a,b).

Coming to homogeneous di- and tricarbonyl species, let us observe that, on the basis of the considerations made so far, a gradual decrease of CO stretching frequency is expected on passing from mono- to di- and tricarbonyls because of the increase of negative charge on the metal center upon multiple adsorption of CO (CO is a weak base). A bathochromic shift of the  $\nu(\text{CO})$  barycenter is effectively observed only for  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+[\text{AsF}_6]^-$  (see Figure 1b). On the contrary a consistent hypsochromic shift is verified for tricarbonylic  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+–[\text{AsF}_6]^-$  species. We think that a possible explanation of this behavior can be found if we hypothesize that on passing from mono- to di- and tricarbonyls an increase of the  $\text{Cu}^{\text{I}}–\text{AsF}_6$  distance (associated with an increase of the ionicity of the  $\text{Cu}^{\text{I}}–\text{AsF}_6$  bond) is occurring. Unfortunately no detailed X-ray determinations have been made so far to prove or disprove this hypothesis.

Moving to intrazeolitic species, we notice that a considerable increase of the CO stretching frequency barycenter is found on passing from mono- to dicarbonyls, which is followed by a

**TABLE 2: Experimental C–O Stretching Frequency of Well-Defined Cu<sup>I</sup> Monocarbonyls in [Cu<sup>I</sup>((CO))<sup>+</sup>A<sup>−</sup>] Systems**

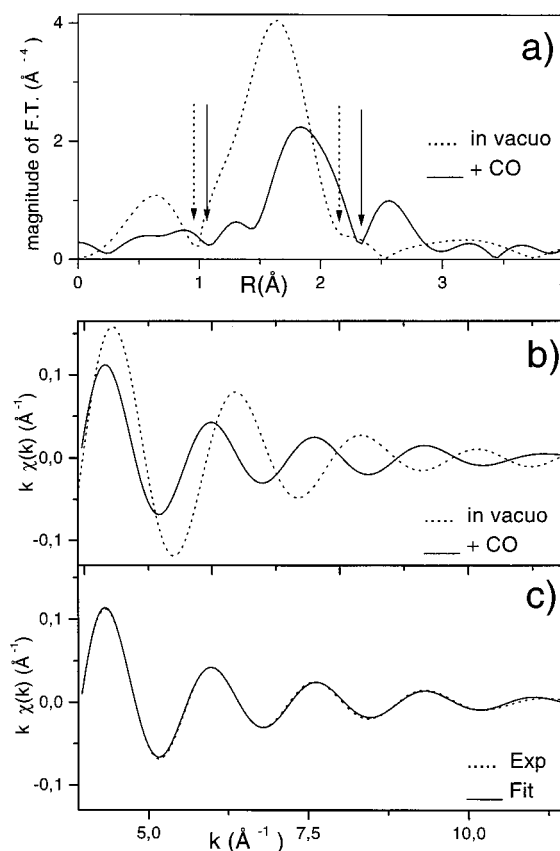
[Cu <sup>I</sup> (CO)] <sup>+</sup> A <sup>−</sup> systems	$\nu(\text{CO})$ , cm <sup>−1</sup>	ref	comments
[Cu <sup>I</sup> (CO)] <sup>+</sup> Cl <sup>−</sup>	2127	47	solid compound stable only under CO atmosphere
[Cu <sup>I</sup> (CO)] <sup>+</sup> [CF <sub>3</sub> CO <sub>2</sub> ] <sup>−</sup>	2155	44	solid compound stable only under CO atmosphere
[Cu <sup>I</sup> (CO)] <sup>+</sup> [CF <sub>3</sub> SO <sub>3</sub> ] <sup>−</sup>	2128	45	ionic compound forming colorless crystals
[Cu <sup>I</sup> (CO)] <sup>+</sup> [C <sub>2</sub> H <sub>5</sub> SO <sub>3</sub> ] <sup>−</sup>	2117	45	
[Cu <sup>I</sup> (CO)] <sup>+</sup> [HB(3,5(CF <sub>3</sub> ) <sub>2</sub> Pz) <sup>−</sup>	2137	52	Pz = pyrazolyl
[Cu <sup>I</sup> (CO)] <sup>+</sup> [AsF <sub>6</sub> ] <sup>−</sup>	2180	12	solid compound stable at RT in vacuum
CO/Cu <sup>I</sup> -Y	2160	54	CO adsorbed on dehydrated Cu <sup>I</sup> -Y zeolite
CO/Cu <sup>I</sup> -Mord	2159	20	CO adsorbed on dehydrated Cu <sup>I</sup> -mordenite zeolite
CO/Cu <sup>I</sup> -ZSM-5	2157	5	CO adsorbed on dehydrated Cu <sup>I</sup> -ZSM-5 zeolite

further, although considerably reduced, positive shift by coordination of a third CO molecule (see Figure 1a). We think that, as mentioned before for the  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+[\text{AsF}_6]^- \rightarrow [\text{Cu}^{\text{I}}(\text{CO})_3]^+[\text{AsF}_6]^-$  transformation, these findings could be explained by hypothesizing that Cu<sup>I</sup> ions have a mobile character (vide infra, next paragraph)<sup>53</sup> and that CO adsorption is accompanied by a weakening of the bond of Cu<sup>I</sup> to zeolite framework oxygens (with parallel increase of ionicity of the Cu<sup>I</sup>–framework bond).

### 3.2. EXAFS Study of Intrazeolitic [Cu<sup>I</sup>(CO)<sub>2</sub>]<sup>+</sup> Complex: Displacement of Cu<sup>I</sup> Ions Induced by CO Adsorption.

In the previous paragraph, we hypothesized that the progressive upward shift of CO frequencies barycenter on passing from [Cu<sup>I</sup>(CO)]<sup>+</sup> to [Cu<sup>I</sup>(CO)<sub>2</sub>]<sup>+</sup> and [Cu<sup>I</sup>(CO)<sub>3</sub>]<sup>+</sup> complexes could be associated with a displacement of cuprous ions from their original vacuum positions accompanied by an increase of the Cu<sup>+</sup>–O distance. It is evident that, although very reasonable, our hypothesis still remains a hypothesis and that our interpretation can be improved only if direct evidence of the suggested displacement is obtained by an independent experimental technique. For this reason EXAFS measurements have been performed on Cu<sup>I</sup>-ZSM-5 zeolite before and after interaction with CO. As we were conscious that the success of this EXAFS experiment could be critically dependent on the ability of preparing samples where only well-defined environments of cuprous ions are present (a mixture of naked Cu<sup>I</sup> ions, [Cu<sup>I</sup>(CO)]<sup>+</sup>, [Cu<sup>I</sup>(CO)<sub>2</sub>]<sup>+</sup>, and [Cu<sup>I</sup>(CO)<sub>3</sub>]<sup>+</sup> species would give rise to a superposition of EXAFS signals of different amplitudes, periods, phase shifts, and thermal disorder not analyzable if not misleading: see, e.g., the case of Cu<sup>I</sup>-MOR, where the copresence of such contributions gave rise to a total destruction of the  $\chi(k)$  oscillation for  $k > 7 \text{ \AA}^{-1}$ <sup>20</sup>), we have studied only the well-defined cases of the zeolite in vacuo condition and after interaction at RT with an excess equilibrium pressure of CO (40 Torr) (where the presence of only [Cu<sup>I</sup>(CO)<sub>2</sub>]<sup>+</sup> has been conclusively proved by IR spectroscopy). In this respect it is also worth noticing that ZSM-5 as hosting structure ensures a great homogeneity of the Cu<sup>I</sup> absorbing sites, because they are all exhibiting the same accessibility to CO ligand molecules (the same does not hold, for example, for Cu<sup>I</sup>–faujasites<sup>19,54</sup> or Cu<sup>I</sup>–mordenite<sup>20,54,55</sup>). A further reason for performing experiments in the presence of an excess of CO pressure lies in the fact that the CO atmosphere protects the zeolite from contamination during the long EXAFS measurements (which is a very serious problem with zeolites).

Figure 3a reports, without any phase correction, the  $k^3$  weighted Fourier transform (FT) in the range 3–13  $\text{\AA}^{-1}$  of the  $\chi(k)$  functions of Cu<sup>I</sup>-ZSM-5 in vacuo (dotted-line curve) and after interaction with 40 Torr CO (full-line curve): the displacement to higher distance (about 0.2  $\text{\AA}$ ) of the radial distribution of neighbor atoms around Cu<sup>I</sup> cations is self-evident. To be quantitative, the first-shell peak of both radial distributions has been back-Fourier-transformed in the 0.97–2.19 and 1.05–2.35  $\text{\AA}$  ranges for the spectrum in vacuo and after interaction with CO, respectively (see corresponding dotted and full arrows in



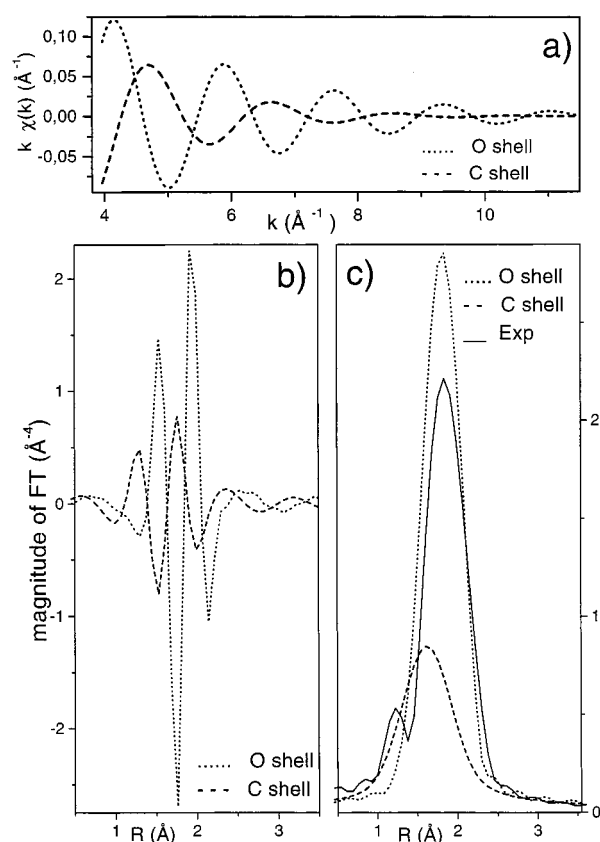
**Figure 3.** (a)  $k^3$ -Weighted Fourier transform of experimental  $\chi(k)$  for Cu<sup>I</sup>-ZSM-5 in vacuo and after interaction with 40 Torr of CO, dotted and full lines, respectively. Dotted and full arrows indicate the adopted intervals used to compute the corresponding first-shell signal. (b) Fourier-filtered first-shell  $k\chi(k)$  signal of Cu<sup>I</sup>-ZSM-5 in vacuo and after interaction with 40 Torr of CO, dotted and full lines, respectively. (c) Comparison between experimental  $k\chi(k)$  after interaction with 40 Torr of CO and simulated  $k\chi(k)$  modeled with two subshells to describe the backscattering of both the zeolite oxygen atoms and the carbon atoms of the CO molecules.

Figure 3a). This operation leads to the Fourier-filtered first-shell signals reported in Figure 3b (again dotted-line and full-line for sample before and after interaction with CO). Besides the great alteration already observed in the radial distribution, the strong modification of the Cu<sup>I</sup> environment after interaction with CO is also documented by variation of both intensity and period of the  $\chi(k)$  oscillations. The EXAFS data analysis of the spectrum collected in vacuo conditions (already discussed in ref 5a) gives the following structural parameters:  $N_{\text{O}} = 2.5 \pm 0.3$ ,  $R_{\text{Cu-O}} = 2.00 \pm 0.02 \text{ \AA}$ , and  $\sigma_{\text{Cu-O}} = (7.3 \pm 1.0) \times 10^{-2} \text{ \AA}$ , with  $\Delta E = 5.5 \pm 1.5 \text{ eV}$  (experimental Cu–O phases and amplitudes having been extracted from the Cu<sub>2</sub>O model compound where the relative Debye–Waller factor was arbitrarily assumed to be  $\sigma_{\text{Cu-O}} = 6.8 \times 10^{-2} \text{ \AA}$ ). Of course the data analysis of the spectrum collected in the presence of CO

must be necessarily done using a two-shell fit, the former to simulate the framework oxygen contribution and the latter to consider the contributions of carbon atoms of the CO molecules. Due to the fact that oxygen and carbon atoms differ only by one electron, the backscattering contribution of the two atoms is practically indistinguishable in the EXAFS analysis: for this reason we have used for the simulation of the Cu–C shell the same phase and amplitude functions extracted from Cu<sub>2</sub>O and already used to simulate the Cu–O shell. To limit the number of fitted parameters, coordination numbers of both shells have been fixed to  $N_{\text{O}} = 2.5$  and  $N_{\text{C}} = 2.0$ , the former figure coming from the EXAFS analysis of the sample in vacuo (vide supra) and the latter from IR spectroscopy because, under the adopted temperature and pressure conditions,  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  species are largely predominant. Under these approximations, the fit of the experimental  $k\chi(k)$  gives rise to the following structural results:  $R_{\text{Cu–O}} = 2.16 \pm 0.035$  Å and  $\sigma_{\text{Cu–O}} = (9.2 \pm 2.0) \times 10^{-2}$  Å,  $R_{\text{Cu–C}} = 1.95 \pm 0.05$  Å and  $\sigma_{\text{Cu–C}} = (13 \pm 2.5) \times 10^{-2}$  Å, with  $\Delta E = 6 \pm 2$  and  $7 \pm 3$  eV for the oxygen and carbon shells, respectively. The quality of the fit can be appreciated in Figure 3c. The present analysis indicates that the elongation of the Cu<sup>I</sup>–O bond upon formation of  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+$  complexes is  $0.16 \pm 0.04$  Å. Note also that the obtained Cu–C distance is in good agreement with values computed with advanced quantum mechanical methods,<sup>23,31,56</sup> where slightly different values have been obtained, depending on the simulated cluster and the adopted basis set. In particular our experimental figure is in good agreement with that reported by Lupinetti et al. (Cu–C = 1.891 Å<sup>31</sup>), Ramprasad et al. (Cu–C = 1.900 Å<sup>23</sup>), and Sodupe et al. (Cu–C = 1.969 Å<sup>56</sup>).

Coming back to the radial distributions of the sample in the presence of CO (Figure 3a), two distinct peaks are clearly present at about 1.9 and 2.5 Å (without phase correction). The former contains the contributions of framework oxygen and carbon atoms of adsorbed CO (already analyzed in detail), while the latter is due to the oxygen atom contribution of CO groups and to multiple scattering (MS) paths. The small overlap between the two peaks means that the EXAFS analysis discussed so far is affected by a small systematic error due to the fact that, by filtering the radial distribution between 1.05 and 2.35 Å, undesired components of both oxygen atoms of the CO molecules and MS contributions are introduced. However, the quality of the fit obtained by imposing constraints to  $N_{\text{O}}$  and  $N_{\text{C}}$  (with the help of IR experiments), together with physically meaningful values of the free structural parameters minimized in the fit ( $R_{\text{Cu–O}}$ ,  $\sigma_{\text{Cu–O}}$ ,  $R_{\text{Cu–C}}$ , and  $\sigma_{\text{Cu–C}}$ ), guarantees, a posteriori, that the actual influence of MS contributions is smaller than previously feared in ref 5a. Not negligible roles in the minimization of MS contributions are certainly played by two facts: (i) the shell overlap of the radial distribution is much weaker than in the case discussed in ref 5a and (ii) Fourier-filtered  $\chi(k)$  function has not been used in the fit below  $k = 3.95$  Å<sup>−1</sup>. It is, in fact, well-known that the mean free path of the photoelectron decreases rapidly with increasing  $k$ , so that MS contributions are stronger at low  $k$  (becoming predominant in the XANES region).

As a final consideration let us draw the attention on the reduction, upon interaction with CO, of the intensity of the first-shell peak in the radial distribution reported in Figure 3a and on the related reduction of the oscillation amplitudes of the corresponding FT-filtered  $k\chi(k)$  shown in Figure 3b, because they apparently conflict with the increase of the number of backscattering atoms contributing to the EXAFS signal. Notice that this effect has been qualitatively reported before by us,<sup>5a</sup>



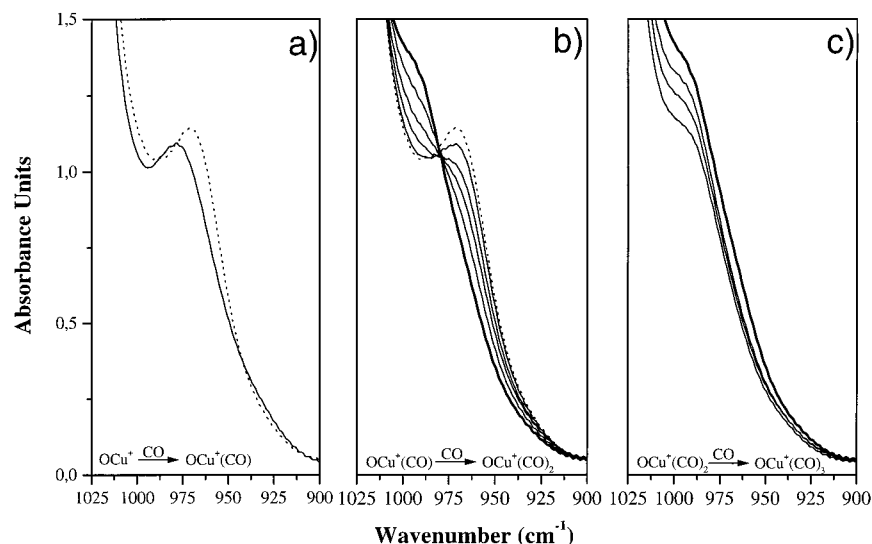
**Figure 4.** Comparison of the oxygen and carbon subshell contribution in  $k$  and  $R$  (imaginary and modulus) spaces (a–c, respectively). The quite consistent destructive interference between the two subshell signals explains the important reduction of the EXAFS signal upon interaction with CO (see Figure 3a,b).

by Yamashita et al.,<sup>54</sup> and by Kuroda et al.<sup>55</sup> We hypothesize that this can be quantitatively explained in terms of three concomitant and independent effects: (i) a consistent increase (about 20%) of the Cu<sup>I</sup>–O Debye–Waller factor (related to an increased thermal disorder associated with the elongation of the Cu<sup>I</sup>–O bond), (ii) the increase of the first-shell distance (about 8%) due to CO coordination, and (iii) a partially destructive interference of the Cu<sup>I</sup>–O and Cu<sup>I</sup>–C contributions. The entity of the last effect is evidenced in Figure 4, where the individual  $k\chi(k)$  contribution of the two simulated shells is reported in part a. The corresponding FT are detailed in parts b and c for the imaginary parts and the modules, respectively. In agreement with the previous hypothesis, it can be noticed that the modulus of the FT of the oxygen shell alone is considerably greater than that obtained by Fourier transforming the experimental  $\chi(k)$  filter (full-line curve in Figure 4c).

**3.3. IR Study of Cu<sup>I</sup>-Perturbed Framework Modes upon Stepwise Formation of Cu<sup>I</sup>(CO)<sub>*n*</sub> Species.** It was reported in 1994<sup>57</sup> that the IR spectrum of Cu<sup>I</sup>-ZSM-5 (in CO atmosphere) is characterized by the presence of an IR band at  $\sim 968$  cm<sup>−1</sup>, which is absent in Na-ZSM-5. Although the spectra reported in ref 57 are not reliable for  $\nu > 1000$  cm<sup>−1</sup> (because they are greatly perturbed by specular reflectance effects, usually strong in the region of the skeletal modes), this absorption (that disappears upon oxidation) is real and is certainly associated with Cu<sup>I</sup>.

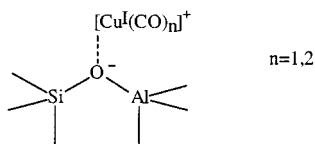
The 968 cm<sup>−1</sup> band has been ascribed to “...a zeolite asymmetric internal stretching vibration perturbed by Cu<sup>I</sup>”.<sup>57</sup> On the basis of the known fact that, at RT and in the presence of CO, monocarbonylic (Cu<sup>I</sup>(CO)) and dicarbonylic (Cu<sup>I</sup>(CO)<sub>2</sub>) species are present, it is evident that this sentence should be



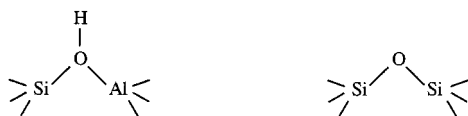


**Figure 5.** Evolution of the IR spectra in the 1025–900 cm<sup>-1</sup> region upon CO dosage at 110 K. (a–c) CO/Cu<sup>I</sup> stoichiometries comprised in the 0–1, 1–2, and 2–3 intervals. The effects shown in parts b and c, caused by CO dosage, are reversible. In part a, the spectra corresponding to the CO/Cu<sup>I</sup> stoichiometry intermediate between 0 and 1 are omitted in order to not overcrowd the figure. Dotted line present in both parts a,b represents the  $n = 1$  stage, while bold line present in both parts b and c represents the  $n = 2$  stage.

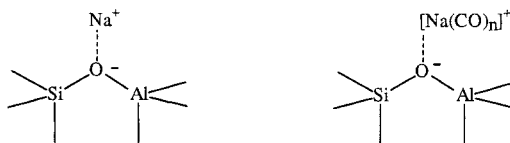
modified into "...a zeolite asymmetric internal stretching vibration perturbed by Cu<sup>I</sup>(CO)<sub>*n*</sub> ( $n = 1, 2$ )", as latter recognized by one of the authors in 1997.<sup>58</sup>



Following refs 59 and 60 and considering that the 968 cm<sup>-1</sup> band falls between the  $\nu_{\text{asym}}(\text{TOT})$  ( $T = \text{Si}, \text{Al}$ ) and  $\nu_{\text{sym}}(\text{TOT})$  frequencies of the (TOT) primary unit (as can be deduced from the spectrum of H-ZSM-5 and silicalite),<sup>59</sup> it can be concluded that it can be assigned with confidence to a stretching mode of the unit (shown above) having predominant  $\nu_{\text{asym}}(\text{TOT})$  character but with admixture of the O–Cu<sup>I</sup>(CO)<sub>*n*</sub> stretching. This mode (with basically  $\nu(\text{TOT})$  character) is shifted to lower frequencies with respect to that of the analogous structures of H-ZSM-5 and silicalite,<sup>59</sup>



not only because of the partial  $\nu(\text{Cu}^{\text{I}}\text{O})$  character of the vibration but also because of the large mass of copper and of the fact that the Cu<sup>I</sup> metal center is causing a local distortion of the TOT angle.<sup>60</sup> The reason this mode is consistently shifted downward with respect to that of the parent structures<sup>38,39</sup>

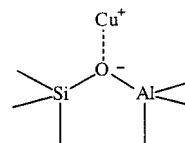


is due to two concomitant factors: (i) a mass effect associated with the fact that  $m_{\text{Cu}} > m_{\text{Na}}$  (63 and 23, respectively) and (ii) an "electronic effect" (the O–Na<sup>+</sup> and O–Cu<sup>+</sup> bonds have different ionicity and different force constants,  $k$ , and hence cause different distortions of the TOT angles). *Of course the*

*various effects are not fully independent.* It is worth underlining that the previous structures are simplified versions of the real situations: in fact, in the zeolite the Cu<sup>I</sup> is in contact with one or two further oxygen atoms of the framework.<sup>5</sup> We adopt this simplified version of the Cu<sup>I</sup> site for sake of simplicity.

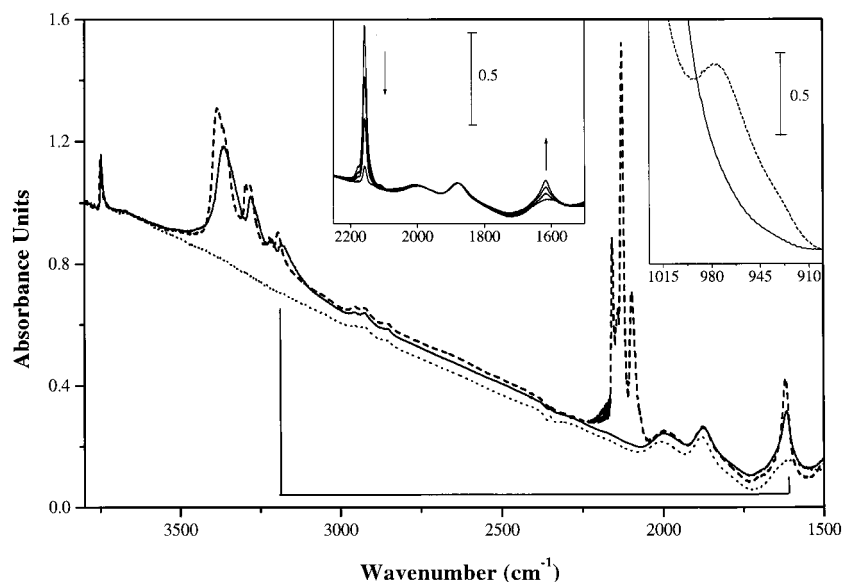
Any ligand insertion at the Cu<sup>I</sup> center, modifying the effective mass, the Cu<sup>+</sup>–O force constant (and hence the admixture of  $\nu(\text{Cu}^{\text{I}}\text{O})$  and  $\nu(\text{SiOAl})$  modes), and the TOT angles, should be accompanied by a frequency change of the peak. Vice versa, any spectral modification induced by contact with a probe molecule entering the channels is a proof that ligation at the Cu<sup>I</sup> center is occurring.

On the basis of these considerations, we have thought that the frequency of the band observed by J. Sarkany et al.<sup>57</sup> could be changed, in a stepwise manner, by reducing or increasing the number of ligands in the coordination sphere of Cu<sup>I</sup>. To verify this hypothesis, complete series of IR spectra have been recorded corresponding to CO/Cu<sup>+</sup> stoichiometries gradually changing from 0 to ~3. The results are shown in Figure 5. The following can be commented: (i) The characteristic band of naked structures is observed at 980 cm<sup>-1</sup> (full-line curve in Figure 5a). This result is in agreement with the latest conclusions reported in ref 58.



(ii) The adsorption of one CO ligand shifts the peak from 980 to 968 cm<sup>-1</sup> ( $\Delta\nu = -12$ ): it is so confirmed that the peak initially observed by Sarkany et al.<sup>57</sup> effectively corresponds to the  $\nu_{\text{asym}}(\text{TOT})$  mode perturbed by Cu<sup>+</sup>(CO).<sup>58</sup> As briefly discussed below the shift to lower wavenumbers caused by CO adsorption is, to a first approximation, the sum of two effects, i.e., variation of the effective mass (from Cu<sup>+</sup> to Cu<sup>+</sup>(CO)) and change of the Cu<sup>I</sup>–O force constant (with the associated modification of the TOT angle). While the first effect always shifts the peak to lower frequencies, little can be said about the second one (because we do not know a priori the effect of CO adsorption on the Cu<sup>I</sup>–O bond). If we adopt the naive but





**Figure 6.** Main figure and right inset: IR spectra showing the effect of 20 Torr (1 Torr = 133 Pa) CO dosage (dashed line) at 110 K on preadsorbed  $\text{NH}_3$  (full line) on  $\text{Cu}^{\text{I}}$ -ZSM-5 (dotted line: zeolite background). A Fermi resonance between  $2\delta$  and  $\nu$  modes of  $\text{NH}_3$  is evidenced. In the right inset the effect of  $\text{NH}_3$  dosage on the virgin sample is also shown in the 1025–900  $\text{cm}^{-1}$  range. Central inset: Results of an independent experiment reporting the effect of  $\text{NH}_3$  dosed at RT on preadsorbed  $[\text{Cu}^{\text{I}}(\text{CO})]^+$  species.

nevertheless realistic hypothesis that adsorption of one CO molecule on  $\text{Cu}^{\text{I}}$  is associated with lengthening of the  $\text{Cu}^{\text{I}}\text{—O}$  bond (and hence with a decrease of the  $\nu(\text{CuO})$  stretching character of the 968  $\text{cm}^{-1}$  peak and of the distortion of the TOT angle), we can safely hypothesize that the change of the electronic effect induced by CO adsorption should induce a shift of the peak toward higher values. From the experimental data, it is evident that the electronic effect associated with adsorption of one CO is not sufficient to counterbalance the mass effect; hence, the peak still occurs at lower values with respect to the naked structure.

(iii) When the  $\text{CO}/\text{Cu}^+$  stoichiometry is gradually increased to 2, the spectra of Figure 5b are obtained, showing clearly that the insertion of a second CO leads to erosion of the 968  $\text{cm}^{-1}$  peak and formation of a new blue-shifted band with  $\Delta\nu = +22 \text{ cm}^{-1}$ . As the mass effect still grows on passing from  $\text{Cu}^+(\text{CO})$  to  $\text{Cu}^+(\text{CO})_2$ , this implies that the insertion of the second ligand is associated with a further drastic decrease of the  $\text{Cu}^{\text{I}}\text{—O}$  force constant and of the TOT angle distortion and, hence, with a lengthening of the  $\text{Cu}^+\text{—O}$  bond. *This result is in full agreement with the EXAFS results.*

(iv) Insertion of the third CO ligand (Figure 5c) leads to the gradual disappearance of the  $\text{Cu}^+(\text{CO})_2$  band at  $\sim 990 \text{ cm}^{-1}$ . The new absorption associated with  $\text{Cu}^+(\text{CO})_3$  is, however, not observable, because it falls at  $\nu > 1000 \text{ cm}^{-1}$ , which is a region obscured by strong skeletal modes.

It is evident that complexation of  $\text{Cu}^+$  with three CO molecules has the effect of increasing so much the  $\text{Cu}^{\text{I}}\text{—O}$  distance that the resulting  $\nu_{\text{asym}}(\text{TOT})$  mode (being only weakly perturbed) approaches the characteristic values of the unperturbed structure.

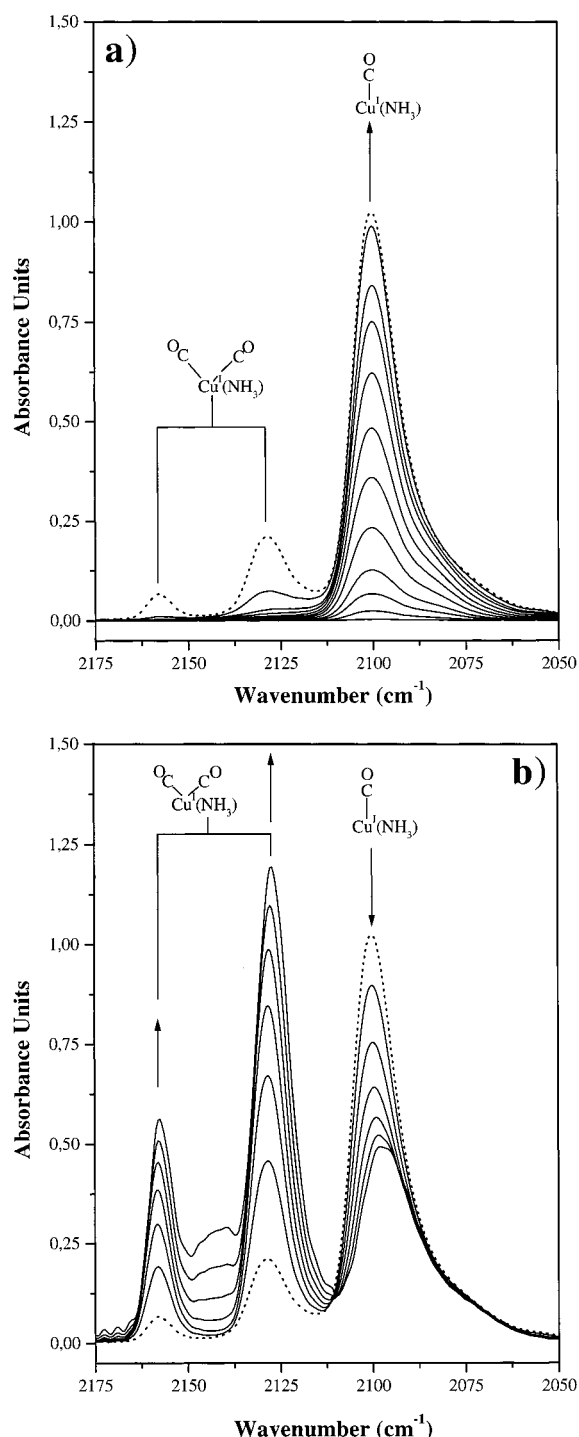
In conclusion, the final picture emerging from this experiment can be summarized as follows: adsorption of  $n$  CO ( $n = 1\text{--}3$ ) on  $\text{Cu}^{\text{I}}$  is accompanied by stepwise  $\text{Cu}^{\text{I}}\text{—O}$  bond relaxation with subsequent increase of the  $\text{Cu}^{\text{I}}\text{—O}$  distance and decrease of the  $\text{Cu}^{\text{I}}\text{—O}$  force constant. The spectroscopic perturbation caused by the presence of  $\text{Cu}^{\text{I}}$  in vacuo is consequently gradually reduced upon complexation.

**3.4. IR Study of Intrazeolitic  $[\text{Cu}^{\text{I}}(\text{CO})_n(\text{NH}_3)]^+$  ( $n = 1, 2$ ) Complexes.** In section 3.1 we evidenced the great structural

similarities between homogeneous and intrazeolitic  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  carbonyls and showed that the  $\nu(\text{CO})$  stretching frequency depends on the electron density of the  $\text{Cu}^{\text{I}}$  ion and hence on the nucleophilic character of the ligands.

To further verify the effect of the increase of electron density on the stability and CO stretching frequency of the carbonyls, and to show that a well-defined chemistry can be developed in zeolite channels, we have performed experiments designed to prepare new intrazeolitic  $[\text{Cu}^{\text{I}}\text{L}(\text{CO})_n]^+$  ( $n = 1, 2$ ) complexes, where L is a new nucleophilic ligand inserted in the coordination sphere of  $\text{Cu}^{\text{I}}$  by gas-phase dosage. This type of experiment can be performed in a very simple and clean way by taking advantage of the gas manifold permanently attached to the “in situ” IR cell (see Experimental Section). Among many volatile ligands with high Lewis base character, we have selected  $\text{NH}_3$  because of its high proton affinity ( $\text{PA} = 204 \text{ kcal mol}^{-1}$ ) and small size. As reported in the Experimental Section, two type of experiments (at RT and at about 110 K) have been performed: in the first one,  $\text{NH}_3$  was dosed on preformed  $[\text{Cu}^{\text{I}}(\text{CO})]^+$  complexes; in the second one, CO has been dosed on preadsorbed  $\text{NH}_3$ . For sake of brevity we will describe in detail only the results of the second experiment. This choice is justified, because the second experimental path is more general as it allows the in situ synthesis of both monocarbonylic and dicarbonylic complexes while the  $\text{NH}_3$  dosage at RT on monocarbonylic species leads to a total displacement of adsorbed CO as documented by the central inset of Figure 6, where  $\text{NH}_3$  has been dosed at increasing pressure on preadsorbed  $[\text{Cu}^{\text{I}}(\text{CO})]^+$  complexes. In this experiment we just observe the progressive total destruction of the 2157  $\text{cm}^{-1}$  band of the monocarbonyl, with the parallel growth of  $\text{NH}_3$  modes (e.g., the bending mode visible at 1610  $\text{cm}^{-1}$ ).

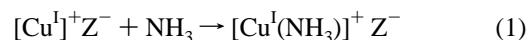
In Figure 6 (main figure) we have reported the IR spectrum (performed at 110 K) of the  $\text{NH}_3\text{—Cu}^{\text{I}}\text{—ZSM-5}$  system (i.e., before CO dosage) (full-line curve) together with the spectrum after subsequent interaction with CO (equilibrium pressure 20 Torr) taken at 110 K (dashed-line curve). For comparison the dotted-line curve reports the zeolite background before dosage of  $\text{NH}_3$ . In the right inset, an expanded view of the effect of  $\text{NH}_3$  adsorption on the characteristic band of the naked  $[\text{SiOAl}]^-\text{Cu}^+$



**Figure 7.** Evolution of the IR spectra in the C–O stretching region upon increasing CO equilibrium pressure at 110 K on preadsorbed NH<sub>3</sub> on Cu<sup>I</sup>-ZSM-5: (a) low CO equilibrium pressures ( $0 < P < 0.038$  Torr); (b) high CO equilibrium pressures ( $0.038 < P < 4.1$  Torr). In both parts the dotted-line spectrum corresponds to 0.038 Torr.

structure is reported (dotted and full spectra before and after NH<sub>3</sub> dosage, respectively). The evolution (background subtracted) of the IR spectra in the 2175–2050 cm<sup>−1</sup> interval upon increasing CO equilibrium pressure is represented in Figure 7. Independent experiments on silicalite (purely siliceous zeolite, not containing Cu<sup>I</sup> counterions, with the same MFI structure as ZSM-5) ensure that the bands observed after NH<sub>3</sub> interaction are due to NH<sub>3</sub> coordinated to Cu<sup>I</sup> ions. From the spectra illustrated in Figures 6 and 7 we notice:

(i) The IR spectra of NH<sub>3</sub> coordinated to Cu<sup>I</sup> ions is characterized by a complex absorption in the 3500–3100 cm<sup>−1</sup> range (due to  $\nu(\text{NH})$  modes<sup>61</sup>) and a peak at 1610 cm<sup>−1</sup> (due to  $\delta(\text{NH})$  mode<sup>61</sup>); see Figure 6 (main figure). The formation of the mentioned bands, due to adsorbed NH<sub>3</sub>, indicates that (in the adopted experimental conditions) Cu<sup>I</sup> coordinates a NH<sub>3</sub> molecule following the reaction:

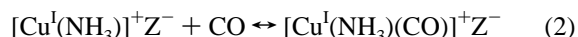


(ii) The total erosion of the peak at 980 cm<sup>−1</sup> (right inset of Figure 6) indicates that upon complexation with NH<sub>3</sub>, the Cu<sup>I</sup>–O bond strength decreases and the Cu<sup>I</sup>–O bond length correspondingly increases.

(iii) As observed for NH<sub>4</sub><sup>+</sup>-exchanged zeolites,<sup>62</sup> the  $\nu(\text{NH})$  stretching region is complicated by Fermi resonance effects with the overtones of the bending mode  $\delta(\text{NH})$  at 1610 cm<sup>−1</sup> (as indicated schematically in Figure 6, main figure). As can be clearly observed, the Fermi resonance involves the low-frequency tail of the  $\nu(\text{NH})$  absorption. This tail is likely ascribed to a hydrogen-bonding perturbation between the coordinated NH<sub>3</sub> and the negatively charged oxygens of the zeolitic framework.

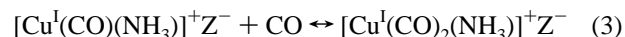
(iv) The intensities of  $\nu(\text{NH})$  and  $\delta(\text{NH})$  bands remain constant upon CO dosage (Figure 6, main figure): this means that the coordination of CO is not accompanied by NH<sub>3</sub> displacement.

(v) At the lowest CO dosages a single peak is observed at 2098 cm<sup>−1</sup>, which reaches the maximum intensity for  $P_{\text{CO}} = 0.008$  Torr (Figure 7a). This peak clearly corresponds to the  $\nu(\text{CO})$  of a monocarbonylic species containing the NH<sub>3</sub> ligand in the coordination sphere of Cu<sup>I</sup> ion formed following the path:



With respect to the frequency of monocarbonylic species observed in the absence of NH<sub>3</sub>, a downward shift of  $\Delta\nu = -60$  cm<sup>−1</sup> is found (see Figure 1a,c): this clearly indicates that NH<sub>3</sub> ligands have greatly increased the electron density at the Cu<sup>I</sup> ions. Unlike reaction 1, reaction 2 is better explained as an equilibrium (vide infra), because it can be reversed by decreasing CO pressure.

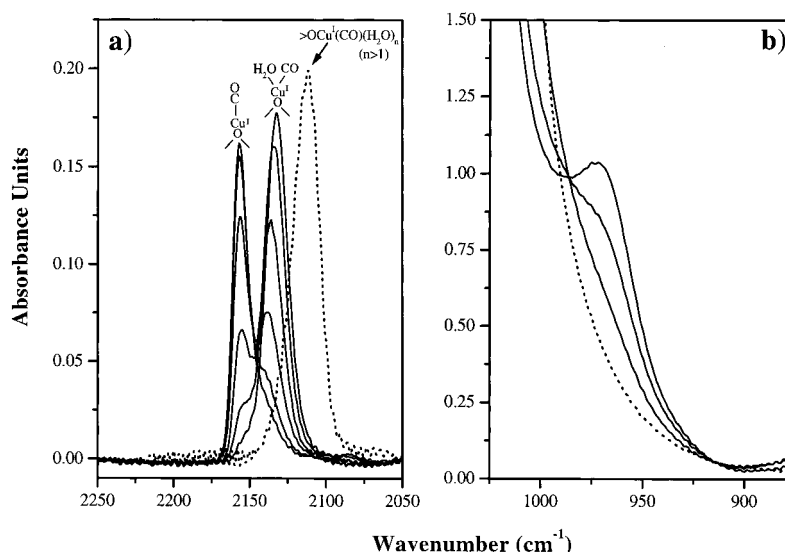
(vi) A further increase of the CO equilibrium pressure leads to the progressive disappearance of the band at 2098 cm<sup>−1</sup> and to the proportional growth of a doublet at 2158 and 2128 cm<sup>−1</sup> (Figure 7b). This corresponds to the progressive formation of dicarbonylic species following the path:



In comparison with the dicarbonylic species formed in absence of NH<sub>3</sub>, a downward shift of  $\Delta\nu = -22$  cm<sup>−1</sup> is observed for the  $\nu(\text{CO})$  barycenter, in line with the expectations (see Figure 1a,c). From the intensity ratio of the two peaks<sup>21</sup> at 2158 and 2128 cm<sup>−1</sup> ( $I_{2128}/I_{2158} = 3.2$ ) it is inferred that the angle between the two CO oscillators in the  $[\text{Cu}^{\text{I}}(\text{CO})_2(\text{NH}_3)]^+\text{Z}^-$  is about 120°, i.e., slightly smaller than that found for the  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+\text{Z}^-$  species (130°). This result is not unexpected, since the presence of NH<sub>3</sub> inevitably forces the CO ligands to stay in a more restricted space.

(vii) Addition of a third CO molecule was found to be impossible under the investigated temperature and pressure conditions.

The comparison of the relevant spectroscopic data of the  $[\text{Cu}^{\text{I}}(\text{CO})]^+\text{Z}^-$ ,  $[\text{Cu}^{\text{I}}(\text{CO})_2]^+\text{Z}^-$ , and  $[\text{Cu}^{\text{I}}(\text{CO})_3]^+\text{Z}^-$  and of the



**Figure 8.** (a) Evolution of the  $\nu(\text{CO})$  band of  $>\text{OCu}^{\text{I}}(\text{CO})$  moiety upon water dosage. Full-line spectra correspond to the  $>\text{OCu}^{\text{I}}(\text{CO}) \rightarrow >\text{OCu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})$  transformation. Dotted line has been obtained in the presence of excess  $\text{H}_2\text{O}$  and corresponds to a  $>\text{OCu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n$  ( $n > 1$ ). The number  $n$  could not be determined with precision. (b) Evolution of the  $\text{Cu}^{\text{I}}$ -perturbed framework modes of  $>\text{OCu}^{\text{I}}(\text{CO})$  upon addition of  $\text{H}_2\text{O}$  (as in part a).

analogous  $[\text{Cu}^{\text{I}}(\text{CO})(\text{NH}_3)]^+\text{Z}^-$  and  $[\text{Cu}^{\text{I}}(\text{CO})_2(\text{NH}_3)]^+\text{Z}^-$  intrazeolitic complexes is made in parts a and c of Figure 1.

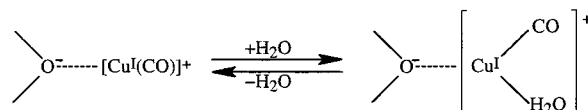
The experiment described in Figure 7 is reversible: in fact, by lowering the CO equilibrium pressure, the evolution of the IR spectra follows an opposite direction and the carbonyl species formed in the presence of  $\text{NH}_3$  are completely removed. Moreover, in the analogous experiment carried out at RT,  $[\text{Cu}^{\text{I}}(\text{CO})(\text{NH}_3)]^+$  is the only species observed, and its formation is not complete even at the highest investigated CO equilibrium pressure (20 Torr) (spectra not reported for sake of brevity). All these facts indicate that we are dealing with unstable and labile carbonyls and that the reactions illustrated in (2) and (3) are better described as equilibria. The low stability of these species confirms that they are homoleptic carbonyls with cationic character characterized by the absence of synergistic effects between the  $\sigma$ - and  $\pi$ -interaction. In fact, a classical carbonyl (i.e., a carbonyl characterized by a  $\sigma$ - $\pi$ -interplay) with a  $\nu(\text{CO}) < 2143 \text{ cm}^{-1}$  should be stable even at RT (as verified by the large literature on the CO adsorption on surfaces). In conclusion, due to the presence of such a strong nucleophilic ligand as  $\text{NH}_3$ , the  $\text{Cu}^{\text{I}}\text{--CO}$  bond has relevant  $\pi$ -character, while polarization and  $\sigma$ -donation are very small. In this respect it is worth noticing that, although quantum-chemical calculations have not been made until now on  $[\text{Cu}^{\text{I}}(\text{CO})(\text{NH}_3)]^+$  complexes, theoretical investigations on the parent  $[\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n]^+$  species by Schneider et al.<sup>22</sup> show that the presence of one or more  $\text{H}_2\text{O}$  molecules in the coordination sphere of  $\text{Cu}^{\text{I}}$  induces a lengthening of the C–O bond due to the increase of  $\pi$ -interaction. This effect is however not accompanied by a parallel increase of the stability (the opposite is, in fact, observed) so indicating that the classical  $\sigma$ - $\pi$ -interplay is not operating. These results are in agreement with the experimental data reported in section 3.5.

Finally, a point which merits a further comment is the consistent positive shift ( $\Delta\nu = +45 \text{ cm}^{-1}$ ) of the  $\nu(\text{CO})$  barycenter on passing from  $[\text{Cu}^{\text{I}}(\text{CO})(\text{NH}_3)]^+$  to  $[\text{Cu}^{\text{I}}(\text{CO})_2(\text{NH}_3)]^+$ , i.e., a figure considerably larger than that of the analogous carbonyls without  $\text{NH}_3$  in the coordination sphere (see Figure 1a,c). Although also in this case a  $\text{Cu}^{\text{I}}$  displacement promoted by further CO coordination can be invoked, we remark that the higher experimental  $\Delta\nu$  does not imply a proportionally

greater cation displacement. In fact, contrary to  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+\text{Z}^-$  species (where the CO stretching frequency depends essentially on polarization effects), in  $[\text{Cu}^{\text{I}}(\text{CO})_n(\text{NH}_3)]^+\text{Z}^-$  carbonyls, the  $\nu(\text{CO})$  is critically depending upon  $\pi$ -acceptance only, which is known to more deeply influence the stretching frequency. Consequently, even a little decrease in  $\text{Cu}^{\text{I}}$  electron density (and so in  $\pi$ -acceptance capacity) results in a more consistent positive shift of the barycenter in comparison with  $[\text{Cu}^{\text{I}}(\text{CO})_n]^+$  carbonyls.

**3.5. IR Study of Intrazeolitic  $\text{Cu}^{\text{I}}(\text{CO})(\text{H}_2\text{O})_n$  ( $n = 1, 2$ ) Complexes.** As briefly outlined in the Introduction, only dosage of  $\text{H}_2\text{O}$  at ambient temperature on preformed  $\text{Cu}^+(\text{CO})$  carbonyls was performed (low-temperature experiments being precluded because of the low vapor pressure of  $\text{H}_2\text{O}$  at 110 K). The results are illustrated in Figure 8a (CO stretching region) and Figure 8b (region of the  $\text{Cu}^{\text{I}}$ -perturbed framework modes). We notice:

(i) The  $\nu(\text{CO})$  band of the monocarbonylic complex is eroded upon  $\text{H}_2\text{O}$  dosage with formation of a new band at  $2130 \text{ cm}^{-1}$  ( $\Delta\nu = -27 \text{ cm}^{-1}$ ). The linear correspondence between the decrement of the  $2157 \text{ cm}^{-1}$  peak and the increment of that at  $2130 \text{ cm}^{-1}$  is a clear indication that the process is taking place (see also the isosbestic point at  $\sim 2148 \text{ cm}^{-1}$ ). Note also that the integrated intensity of the  $\nu(\text{CO})$  of  $>\text{OCu}^{\text{I}}(\text{CO})\text{H}_2\text{O}$  has increased by a factor of  $\sim 2$  with respect to the complex without  $\text{H}_2\text{O}$ : this demonstrates that the insertion of  $\text{H}_2\text{O}$  in the coordination sphere of  $\text{Cu}^{\text{I}}$  is accompanied by an increase of the  $\pi$ -character of the  $\text{Cu}^{\text{I}}(\text{CO})$  band.<sup>25a</sup> The results are similar to those presented for  $>\text{OCu}^{\text{I}}(\text{CO})(\text{NH}_3)$  complexes and to those obtained by Hadjiivamov et al.<sup>63</sup> The process, leading to the formation of 1:1 mixed species, is reversible and the original carbonyl can be quickly restored by pumping at RT.



(ii) Upon formation of  $>\text{OCu}^{\text{I}}(\text{CO})\text{H}_2\text{O}$ , the  $968 \text{ cm}^{-1}$  peak is completely eroded, without formation of any new band in the accessible region of the skeletal modes. This result is a clear



indication that the >O—Cu<sup>I</sup> bond force constant undergoes a remarkable decrement upon H<sub>2</sub>O insertion and that the >O—Cu<sup>I</sup> bond length has increased in a parallel way (with a parallel decrement of the TOT distortion).

(iii) After formation of >OCu<sup>I</sup>(CO)(H<sub>2</sub>O) mixed species, further addition of H<sub>2</sub>O (obtained by increasing the equilibrium pressure to 5 Torr) leads to the dotted spectrum of Figure 8a. The responsible species is highly reversible: in fact, by lowering the H<sub>2</sub>O pressure, the characteristic spectrum of the 1:1 species is readily restored. For the time being it is not possible to stabilize the precise stoichiometry of this complex (it is stable only in the presence of excess H<sub>2</sub>O in the channels). It is worth noticing that, upon addition of further H<sub>2</sub>O basic ligands, the  $\nu(\text{CO})$  integrated intensity has further increased, by a factor of 2.

As a final comment, three very recent works have reported mono- and dicarbonyl species on the parent Ag<sup>I</sup>-ZSM-5 system.<sup>64–66</sup> EXAFS spectroscopy has evidenced that the local environment of Ag<sup>I</sup> in Ag<sup>I</sup>-ZSM-5 is very similar to that of Cu<sup>I</sup>,<sup>66</sup> while IR spectroscopy has shown that only monocarbonylic adducts are formed at RT, while a second CO molecule can be coordinated at liquid nitrogen temperature.<sup>64–66</sup> Hadjiivanov has also reported that the dosage at RT of H<sub>2</sub>O on preformed Ag<sup>I</sup>(CO) monocarbonyl gives rise to the formation of the Ag<sup>I</sup>(CO)(H<sub>2</sub>O) adduct characterized by a C—O stretching frequency red-shifted by 11 cm<sup>−1</sup> with respect to the pure complex (2192 against 2181 cm<sup>−1</sup>).<sup>64</sup>

#### 4. Conclusions

It is demonstrated that the [Cu<sup>I</sup>(CO)<sub>*n*</sub>]<sup>+</sup>Z<sup>−</sup> (*n* = 1–3) species of well-defined stoichiometry and structure can be synthesized in the channels of a zeolite of MFI framework. The structural similarity of these intrazeolitic species with the analogous [Cu<sup>I</sup>(CO)<sub>*n*</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>−</sup> carbonyls synthesized in the solid state is evidenced. Due to the lower basicity of [AsF<sub>6</sub>]<sup>−</sup> anion with respect to the zeolite framework Z<sup>−</sup> and due to the steric effects of the channel walls, the intrazeolitic [Cu<sup>I</sup>(CO)<sub>*n*</sub>]<sup>+</sup> (*n* = 2 and 3) carbonyls have bent structure and smaller positive character. The Cu<sup>I</sup> ions show some mobility under the effect of adsorbates as demonstrated by EXAFS study and by examination of the behavior of the so-called Cu<sup>I</sup> zeolite-perturbed IR active modes upon CO, NH<sub>3</sub>, and H<sub>2</sub>O adsorption. Monocarbonylic Cu<sup>I</sup>(CO)-(NH<sub>3</sub>) synthesized in situ is characterized by a  $\nu(\text{CO})$  lower than that of the CO gas. This implies substantial d- $\pi$ -character in the Cu<sup>I</sup>—CO bond. This is however not sufficient to stabilize these species, which have highly reversible character. Further insertion of CO to give unstable [Cu<sup>I</sup>(CO)<sub>2</sub>(NH<sub>3</sub>)]<sup>+</sup> (bent) complexes can be achieved by increasing the CO pressure starting from about 0.004 Torr. Reversible Cu<sup>I</sup>(CO)(H<sub>2</sub>O) and Cu<sup>I</sup>(CO)(H<sub>2</sub>O)<sub>*n*</sub> (*n* > 1) species can also be obtained by dosing H<sub>2</sub>O on preformed monocarbonylic species.

**Acknowledgment.** We are indebted to F. Villain and H. Sonnevile for providing helpful and important assistance during EXAFS experiments at LURE and to G. Petrini, F. Genoni, and G. Leofanti for a stimulating collaboration. S.B. gratefully acknowledges the financial support from LURE for her trip and stay in Orsay. C.L. is indebted to M. Bellatreccia and G. Vlaic for stimulating discussions. We are indebted to authors of ref 6 for having communicated their results prior to publication. The European Community is gratefully acknowledged for a TMR grant to G.T.P.

**Note Added in Proof.** After the submission of this manuscript, an interesting contribution by Kumashiro et al. appears.<sup>67</sup>

In ref 67 an EXAFS study of the interaction at 300 K of CO (equilibrium pressure of 133.3 kPa  $\approx$  100 Torr) is discussed. In such conditions, the two shell fit results in  $R_{\text{Cu-O}} = 2.05$  Å,  $R_{\text{Cu-C}} = 1.89$  Å and  $N_{\text{Cu-C}} = 1.4$ , with  $N_{\text{Cu-O}}$  fixed at 2.5. This result is only in qualitative agreement with our results since they observe a less pronounced elongation of the C—O distance upon interaction with CO, from 1.98 to 2.05 Å, to be compared with a variation of  $R_{\text{Cu-O}}$  from  $2.00 \pm 0.02$  Å to  $2.16 \pm 0.035$  Å reported by us. This can probably be explained by noticing that the value of  $N_{\text{Cu-C}} = 1.4$  found in ref 67 implies that a mixture of mono and di-carbonyls is present under the experimental conditions investigated by Kumashiro et al. The reason why the authors of ref 67 reach only a CO/Cu<sup>I</sup> ratio of 1.4 at 100 Torr while we reach a value of 2.0 at a much lower equilibrium pressure can be explained only in terms of the different preparation procedures. In fact, the sample measured in ref 67 is a Na-ZSM-5 zeolite exchanged with CuCl<sub>2</sub> (0.3 M solution) at a 181% level. This implies that isolated Cu<sup>II</sup> cations (subsequently reduced to Cu<sup>I</sup> after thermal activation at 873 K) are not the only copper species introduced during the exchange procedure and that nearly an equal number of not well defined copper species are also present in the zeolite, while the model character of the Cu<sup>I</sup> sites in Cu<sup>I</sup>-ZSM-5 prepared by gas phase reaction with CuCl has already been deeply documented.<sup>5</sup> This relevant difference makes a quantitative comparison of the two data rather difficult.

#### References and Notes

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