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IR studies of coadsorption of organic molecules and CO on Cu^+ cations in zeolites

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Abstract

The interaction of alkenes, acetylene, benzene and acetone with Cu^+ sites in Cu-zeolites resulted in the activation of the multiple bond. The bond weakening was pronounced in the case of alkenes and acetylene, less distinct in acetone only slightly marked in benzene. The present study was undertaken to follow the effect of interaction of organic molecules with Cu^+ sites on the properties of these Cu^+ ions, as well as the effect of interaction with CO on the interaction of the same Cu^+ with organic molecules. IR experiments evidenced that organic molecules replaced CO from relatively stable Cu^+–CO complexes. This can be related to the distinctly higher energy of bonding of Cu^+ with organic molecules than with CO. In the case of zeolites CuY and CuX there are several kinds of Cu^+ of various electron donor properties. Organic molecules react preferentially with less electron donor Cu^+, suggesting that π donation has more important impact on the strength of the bonding of organic molecules with Cu^+ than π back donation. On the other hand, π back donation has more impact on the activation of the multiple bond. At relatively high CO pressure one Cu^+ ion can bond simultaneously CO and organic molecule. Cu^+ ion, zeolite framework, organic molecule and CO act as one system. CO acts as a strong electron acceptor and the presence of organic molecule increases the electron flow towards CO, enhancement of π back donation to antibonding π^* orbitals of CO and therefore weakening of $C{\equiv}O$ bond occurs. On the other hand, the electron flow toward organic molecule is slighter than without CO, what results in a smaller weakening of C–C bond in benzene and $C{=}O$ in acetone.

Keywords: IR spectroscopy; Coadsorption; Zeolites; Cu^+ cations

1. Introduction

Cu^+ ions in zeolites are well known to activate NO molecules, what results in their dissociation (e.g. refs [1–4]). The quantumchemical calculations evidenced that it was mostly due to π back donation of d electrons of Cu^+ to π^* antibonding orbitals of the molecules [5–8]. The electron donor properties of Cu^+ resulted from the partial neutralization of positive charge of cation by framework oxygens. The cation charge decreased from +1 to +0.32, and HOMO energy increased from −14.115 eV for free ion to −5.170 or to −5.317 eV (depending on cluster geometry) [8].

Recently, it has been found that Cu^+ in zeolites were also able to activate some organic molecules which, similarly as NO, contain π electrons [10–15]. IR studies evidenced a distinct weakening of $C{=}C$ bond in alkenes ($\Delta\nu_{C{=}C} = 78$–$115\ cm^{-1}$), pronounced weakening of triple bond in acetylene ($\Delta\nu_{C{\equiv}C} = 168\ cm^{-1}$), some weakening of $C{=}O$ bond in acetone ($\Delta\nu_{C{=}O} = 39\ cm^{-1}$), and a small weakening of C–C bond in benzene ($\Delta\nu_{C-C} = 13\ cm^{-1}$). In the latter case, the LUMO orbital of benzene has only a slight antibonding character. DFT calculations evidenced that, similarly as in NO, the activation of organic molecule was realized by π back donation of d electrons of Cu^+ to π^* antibonding orbitals of molecule. As a result, alkenes and benzene received negative charge (−0.05 to −0.09) whereas Cu^+ became more positive (from +0.32 to +036). A part of the charge transmitted to molecule came from Cu^+ itself and a part from zeolite framework, which acted as "electrons reservoir" [9]. The molecules of acetylene and acetone received positive charge when interacting with zeolitic Cu^+ (+0.03 and +0.15). In the latter case, part of the charge was transmitted from molecule to Cu^+, the part to the framework, which acted again as the "electrons reservoir" but in this case the framework received electrons from organic molecules (via Cu^+ ions).

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Generally, the interaction of organic molecules with zeolitic Cu$^+$ composes mostly of π donation (from π orbilals of molecules to zeolitic Cu$^+$), what weakens a little multiple bonds and π back donation (from zeolitic Cu$^+$ to π^* antibonding orbitals of molecule), what weakens distinctly multiple bonds. As mentioned, in the case of alkenes and benzene the molecule acquired negative charge, indicating that π back donation prevailed over π donation. Acetone molecule became positive (+0.15) indicating donation of electrons from molecule to cation prevailed over π back donation. Acetylene molecule became only a little positive (+0.03) when interacting with Cu$^+$ indicating that both π donation and π back donation practically were equilibrated but π donation dominated a little.

The goal of the present study was to follow the coadsorption of organic molecules and CO on the same Cu$^+$ cation. There were two interesting problems. One of them was to know if organic molecules were able to replace CO from Cu$^+$ cation. The second problem was to know how the interaction of the organic molecule with Cu$^+$ affects its electronic properties (this was studied by following the C$\equiv$O frequency in the Cu$^+$–CO complex) and also to know how the interaction of Cu$^+$ with CO affects interaction of the same Cu$^+$ with the organic molecule. Two series of experiments have been performed: in one series organic molecules were sorbed in Cu-zeolites with preadsorbed CO, whereas in the second series, CO was sorbed in Cu-zeolites with preadsorbed organic molecules.

2. Experimental

Zeolites CuX, CuY and CuZSM-5 were obtained from the parent NaX (Si/Al = 1.31) synthesized at Department of Chemical Technology UJ, NaY and NaZSM-5 (Si/Al = 2.56 and 35, respectively), synthesized in the Institute of Industrial Chemistry (Warsaw) by the treatment with $Cu(CH_3COO)_2$ solution at 350 K. Upon the ionic exchange, the zeolites were washed with distilled water and dried in air at 370 K. The exchange degrees (Cu/Al) were 0.43, 0.31 and 0.45 for CuX, CuY, and CuZSM-5, respectively.

But-1-ene (Fluka, 99.9%), ethene (UCAR, 99.5%), benzene (Aldrich – analytical grade), acetone (Aldrich – analytical grade), and CO (PRAXAIR 9.5) were used in IR experiments.

For IR studies the Cu-zeolites were pressed into thin wafers and activated in situ in IR cell at 730 K at vacuum for 1 h. IR spectra were recorded by BRUKER IFS 48 spectrometer equipped with an MCT detector. Spectral resolution was 2 cm^{-1}.

3. Results and discussion

3.1. Sorption of organic molecules in Cu-zeolites with preadsorbed CO

CO interacting with Na$^+$ ions in zeolite NaZSM-5 gives the band at 2170 cm^{-1}, whereas interacting with H$^+$ in zeolite

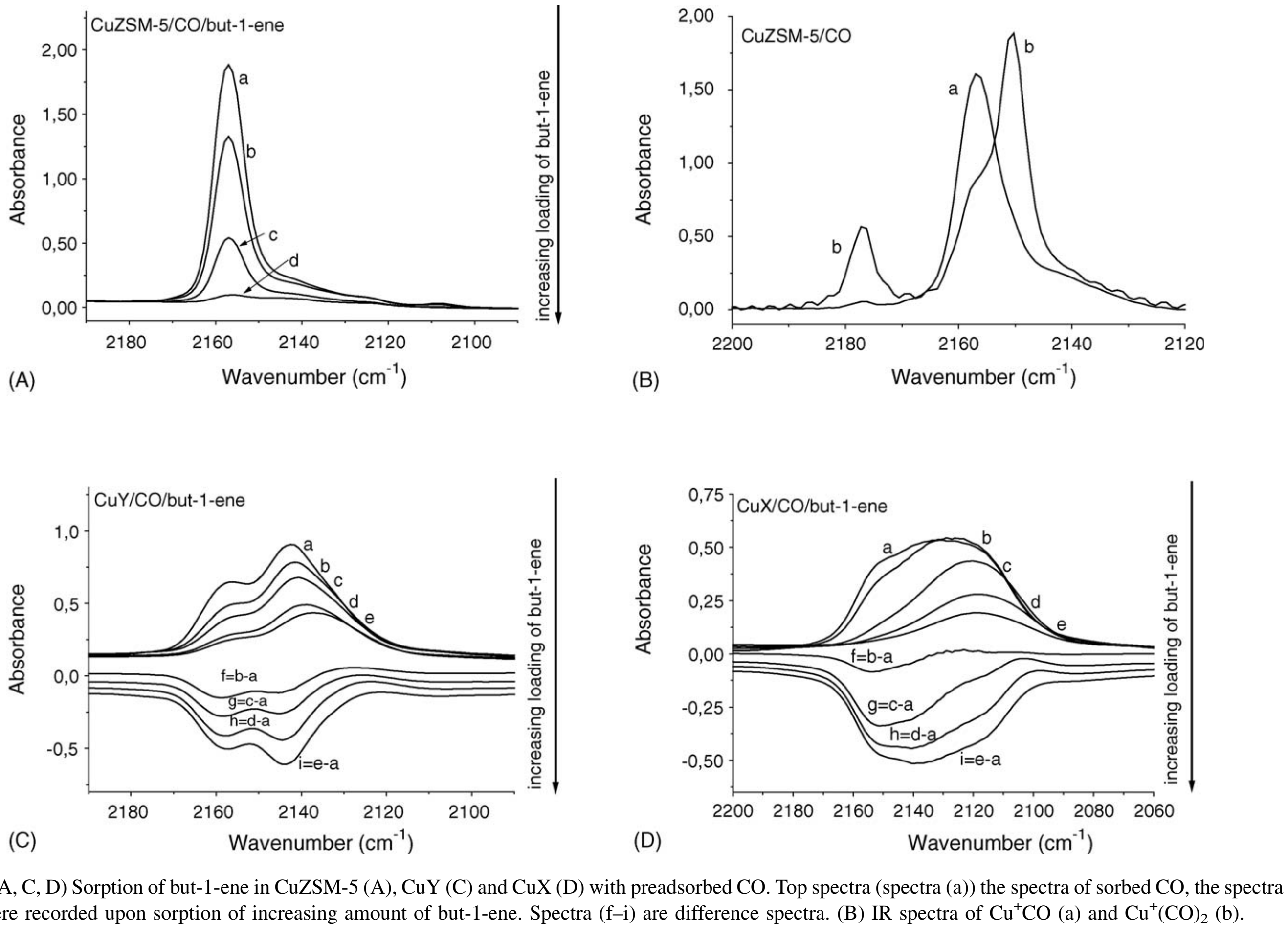

Fig. 1. (A, C, D) Sorption of but-1-ene in CuZSM-5 (A), CuY (C) and CuX (D) with preadsorbed CO. Top spectra (spectra (a)) the spectra of sorbed CO, the spectra (b–e) were recorded upon sorption of increasing amount of but-1-ene. Spectra (f–i) are difference spectra. (B) IR spectra of Cu$^+$CO (a) and Cu$^+$(CO)$_2$ (b).

HZSM-5—the band at 2175 cm^{-1}. The spectrum of CO sorbed in CuZSM-5 is presented in Fig. 1(A) (spectrum a). CO when adsorbed at room temperature reacts with Cu^+ ions forming monocarbonyls (band at 2157 cm^{-1}), but at higher CO loading $Cu^+(CO)_2$ dicarbonyls are formed (IR bands at 2150 and 2180 cm^{-1}—Fig. 1(B)). In our experiments the excess of CO, sufficient to cover all Cu^+ ions was sorbed, and next the cell was evacuated at room temperature, what resulted in dicarbonyls decomposition, and desorption of physisorbed molecules, and finally all Cu^+ ions were covered by monocarbonyls. The sorption of doses of alkenes (but-1-ene and acetylene) resulted in the decrease of the bands of monocarbonyls (the spectra recorded for but-1-ene adsorption are presented in Fig. 1(A)) and in appearance of the bands of alkenes interacting with Cu^+ (ca. 1540 cm^{-1}—spectra not shown). This result indicates that alkenes replace CO from Cu^+ in Cu^+–CO complexes. It may be the result of distinctly higher energy of bonding of Cu^+ with alkenes than with CO (ca. 200 and 53 kJ mol^{-1}, respectively). These values were obtained in our DFT calculations [15]. If the molecules of benzene and acetone were adsorbed in CuZSM-5 with preadsorbed CO, the Cu^+–CO band decreased and shifted to lower frequency: 2140 cm^{-1} (for benzene) and 2130 cm^{-1}

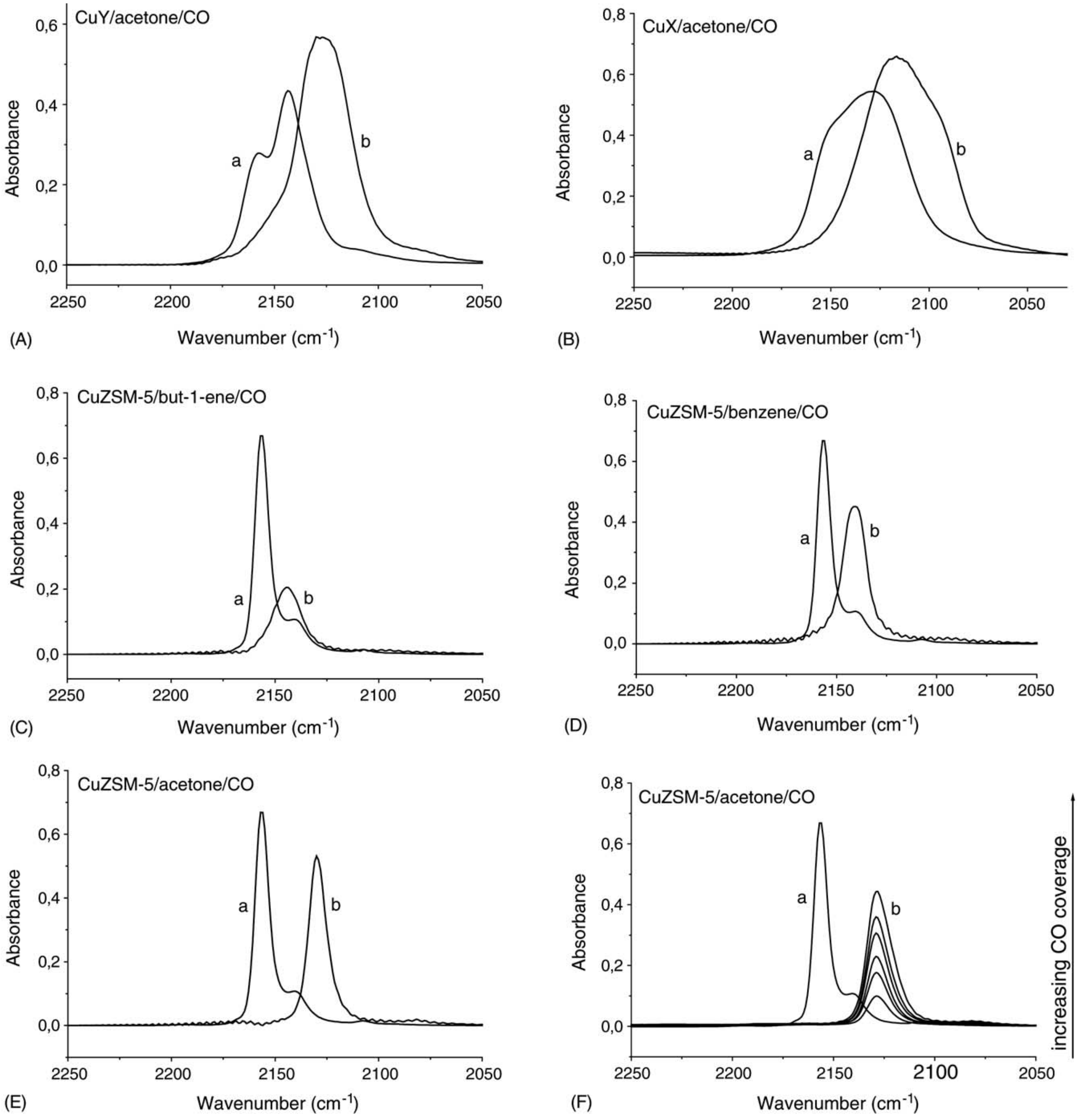

Fig. 2. Spectra of CO sorbed in CuY (A), CuX (B), and CuZSM-5 (C–F) with preadsorbed acetone (A, B, E), but-1-ene (C), and benzene (D). Spectra of increasing amounts of acetone sorbed in zeolite CuZSM-5 with preadsorbed acetone (F). Spectra (a) CO sorbed in zeolites without organic molecules. Spectra (b) CO sorbed in zeolites with preadsorbed organic molecules.

(for acetone). These results suggest that some Cu^+ ions can bond simultaneously CO and benzene or acetone. The situation that one Cu^+ ion bonds both CO and organic molecules will be discussed in the next chapter.

The results obtained in the experiments, in which the sorption of but-1-ene in CuY and CuX with preadsorbed CO was performed, are presented in Fig. 1(C and D). The spectra of CO sorbed in CuY and CuX show two bands: a low frequency l.f. one at 2140 cm^{-1} (CuY) or 2130 cm^{-1} (CuX) as well as a high frequency h.f. at 2160 cm^{-1} (CuY) and 2150 cm^{-1} (CuX). Similar spectra were obtained in our previous study [16], and also in the studies of other authors (e.g. [17]). As the stretching C–O frequency decreases with the electron donor properties of the cation, the l.f. CO band of adsorbed CO may be attributed to the interaction with more electron donor Cu^+ sites, whereas the h.f. one—to the interaction with the less electron donor Cu^+. According to Palomino [17] the l.f. and the h.f. bands in zeolites CuY may be attributed to sites S_{II} and S_{II*}, respectively. The different electron donor properties can be due to different number of oxygen atoms surrounding the cation and different extend of neutralization of Cu^+ cation by these oxygens. The localization of Cu^+ cations in zeolite CuX is not known yet, but it may be supposed that similarly as in zeolite CuY the l.f. and the h.f. CO bands can be attributed to Cu^+ sites of different electron donor properties.

The sorption of organic molecules in CuY and CuX with preadsorbed CO resulted (similarly as in CuZSM-5) in the decrease of Cu^+–CO band, but the h.f. band decreased in the first order (Fig. 1(C and D)). As two main factors: π donation and π back donation affect the strength of the interaction of π electron molecule with Cu^+ cation, the obtained results suggest that the π donation with more positive (and therefore less electron donor) Cu^+ sites has more important impact on the strength of interaction of these molecules with Cu^+.

3.2. Adsorption of CO on Cu-zeolites with preadsorbed organic molecules

In this series of experiments all Cu^+ ions were covered with organic molecules: but-1-ene, benzene and acetone (the bands of double bonds perturbed by Cu^+ were present in all the spectra) and subsequently the doses of CO were introduced into the cell until the weak bands of gaseous CO appeared in the spectra. At such experimental conditions (i.e. at relatively high CO pressure) one Cu^+ cation was able to bond simultaneously organic molecule and CO. This was evidenced by the shift of CO band to lower frequencies (Fig. 2).

In the case of zeolites CuY and CuX (Fig. 2(A and B)), the Cu^+–CO bands are rather broad, composed of at least two components and it was difficult to follow the frequency shifts, so more that the shifted high frequency band overlapped the low frequency one. Therefore, for the further discussion, we will use only the results obtained for CuZSM-5 (Fig. 2(C–F)). As mentioned before, $Cu^+(CO)_2$ dicarbonyls (IR bands at 2150 and 2180 cm^{-1}) are formed at high CO loading (Fig. 1(B)). However, if CO is adsorbed on zeolite CuZSM-5 with preadsorbed organic molecules even at high CO loading no dicarbonyl bands are present (Fig. 2(C–F)). It may be explained by the fact that it is impossible to add a second CO molecule to Cu^+ cation which bonds already one CO molecule and one organic molecule.

Fig. 2(F) shows the spectra recorded if increasing amounts of CO were sorbed in zeolite CuZSM-5 with preadsorbed acetone. The position of the band of CO adsorbed on the same Cu^+ site as acetone did not depend on the amount of CO sorbed. Similar results have been also obtained with other organic molecules.

The frequency of CO bonded to Cu^+ cation, which already bonds organic molecule is always lower than without organic molecule (2157 cm^{-1}). The values of CO band red shifts were as follows: 13 cm^{-1} for but-1-ene, 16 cm^{-1} for benzene and 27 cm^{-1} for acetone. The frequencies of C=C stretching for but-1-ene bonded to Cu^+ together with CO were the same as for molecules bonded "solo" to Cu^+, whereas for benzene and acetone the frequencies of C–C and C=O were intermediate between the values for physisorbed molecules and molecules bonded to Cu^+ "solo" (Fig. 3).

The spectra of CO sorbed in zeolite CuZSM5 (Fig. 2(C–E)) besides of 2157 cm^{-1} band of Cu^+–CO shows weaker band at 2135 cm^{-1} of CO bonded to oxygen containing Cu^+ species. The interaction of Cu^+ together with CO and organic molecules shifts 2157 cm^{-1} band to lower frequency (13–27 cm^{-1}), and in

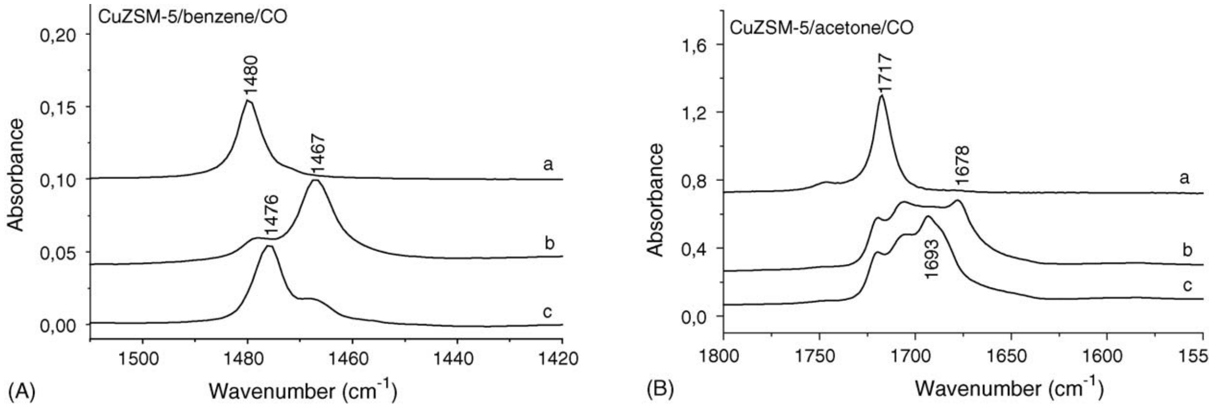

Fig. 3. C–C stretching band in benzene (A) and C=O stretching band in acetone (B) in solution (a), sorbed in CuZSM-5 in the absence of CO (b), and in the presence of coadsorbed CO (c).

some cases the shifted band overlaps the 2135 cm^{-1} band of CO interacting with oxygen containing Cu^{+} species.

All these results can be interpreted as follows. Cu^{+} cation, zeolite framework, adsorbed CO and adsorbed organic molecules behave as one system. CO molecule acts as a strong electron acceptor and the presence of organic molecule increases a flow of electrons towards CO. This result in an increase of π back donation to CO antibonding orbitals, in C$\equiv$O bond weakening, and therefore in a red shift of CO band. The values of CO bond shifts ($\Delta\nu_{\text{CO}}$) may be correlated to the electron donor properties of organic molecules expressed by their HOMO energies. The strongest effect, i.e. the highest $\Delta\nu_{\text{CO}} = 27\ \text{cm}^{-1}$ was observed for acetone being the best electron donor ($E_{\text{HOMO}} = -5.764$ eV), smaller effects ($\Delta\nu_{\text{CO}} =$ 16 and 13 cm^{-1}) were found for benzene and but-1-ene being weaker electron donors ($E_{\text{HOMO}} = -6.593$ and -6.435 eV). On the other hand, the flow of electrons toward organic molecules is smaller than without CO, what results in a less important weakening of C–C and C=O bonds in benzene and acetone, as evidenced by the shift of IR bands from the frequency of molecules bonded "solo" to Cu^{+} ions toward the frequency in free molecules (Fig. 3).

4. Conclusions

1. The molecules of alkenes sorbed in Cu-zeolites with preadseorbed CO replace CO from Cu^{+} ion. This is due to distinctly higher bonding energy of alkenes than of CO.
2. In the case of zeolites CuY and CuX, there is at least two kinds of Cu^{+} sites bonding CO. Organic molecules react in the first order with less electron donor Cu^{+} sites, suggesting that π donation has more important impact on the strength of the bonding of organic molecules with Cu^{+} than π back donation.
3. At relatively high CO pressure one Cu^{+} ion can bond simultaneously CO and organic molecule. The C$\equiv$O frequency is lower than without organic molecules. In this case Cu^{+} cation, zeolite framework, adsorbed CO and adsorbed organic molecule act as one system. CO acts as the strong acceptor of electrons, and the presence of organic molecule increases the electron flow towards CO, causing enhancement of π back donation to antibonding π^{*} orbitals of CO and therefore weakening of the C$\equiv$O bond. On the other hand, the electron flow toward organic molecule is smaller than without CO, what results in a smaller weakening of C–C bond in benzene and C=O in acetone.

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