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Fourier-Transform Infrared Study of CO Adsorbed at 77 K on H-Mordenite and Alkali-Metal-Exchanged Mordenites

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Fourier-transform IR spectroscopy was used to study the interaction of CO with the acidic hydroxyl groups in H-mordenite and with extraframework cations in alkali-metal exchanged X-mordenites (X = Li, Na, K, Rb, Cs). The dipolar CO molecule was found to interact specifically with extraframework metal ions located at two different sites, the main channels and the side pockets. For cations inside the main channels of the zeolite, the C–O stretching frequencies increase continuously from 2155 cm⁻¹ for Cs⁺ up to 2188 cm⁻¹ for Li⁺. Cations located at the bottom of the side pockets were found to induce a smaller shift from the frequency corresponding to the free CO molecule ($\bar{\nu}_{\text{CO}} = 2143 \text{ cm}^{-1}$). The observed frequency shifts were used to evaluate the electrostatic field (inside the main channel) created by the extraframework cations. Values in the range of 2–8 V nm⁻¹ were obtained. Nonspecifically adsorbed (physisorbed) CO was also observed, which gave rise to a complex IR absorption band at about 2138 cm⁻¹.

1. Introduction

Mordenite (MOR) is a zeolite with orthorhombic structure (space group *Cmcm*) which has a pseudo-unidimensional pore system (the main channels) running parallel to the [001] direction. These channels present an elliptical cross section, 0.65 × 0.70 nm in diameter, defined by 12-membered rings of TO₄ tetrahedra^{1,2} where T stands for either Si or Al. The channel wall has side pockets, in the [010] direction, circumscribed by 8-membered rings which are accessible through windows with a free diameter of ca. 0.39 nm. Each side pocket connects, through a distorted 8-membered ring, with two other side pockets which open into the adjacent main channel, thus forming an interconnecting array of smaller channels. However, the entrances to any one of these interconnecting channels are displaced by *c*/2 with respect to each other and this generates a constriction (halfway along the small channel) with a free diameter of about 0.28 nm.

The zeolite framework has a net negative charge equal to the number of aluminium atoms which is balanced by either protons (in H–MOR) or metal cations (in the cationic forms of the zeolite). Preferential sites for extraframework charge-balancing cations in mordenite are the center of distorted 8-membered rings (at the bottom of the side pockets) and a location on the wall of the main channel.^{3–5} They are referred to, respectively, as sites A and E (or D) in the compilation given by Mortier.⁶ Extraframework

cations protruding into the void internal space of the main channels are particularly relevant for many potential applications of mordenite (and other large-pored zeolites) since they provide a means to tune intrazeolite electric fields, which are a function of cation size and charge. This has strong bearings on the usage of zeolites as components for host–guest composites, a proposed kind of advanced material^{7–10} where large-pored zeolites act as hosts for encapsulating and organizing molecules, supramolecular entities, and crystalline nanophases inside their pores. Space confinement leading to quantum size effects and host–guest (electrostatic) interaction can thus be engineered for application in a number of technological fields: e.g., in photochemistry, optoelectronics, or chemical sensing. Accurate determination of intra-zeolite electric fields is a prerequisite in this line of research.

Vibrational spectroscopy of adsorbed carbon monoxide is a means to probe the electrostatic fields. Interaction of the dipolar CO molecule (*via* the carbon end) with centers having a net positive charge shifts the C–O stretching frequency from that of the free molecule (2143 cm⁻¹) to higher values,^{11–15} and the magnitude of this hypsochromic shift measures the corresponding field strength. In the present study the interaction of CO, at 77 K, with the alkali-metal cations of X–MOR (X = Li, Na, K, Rb, Cs) and also with the acidic proton in H–MOR was investigated using transmittance FTIR spectroscopy, and the whole set of results is presented and discussed below. Related work on alkali-metal-exchanged ZSM-5

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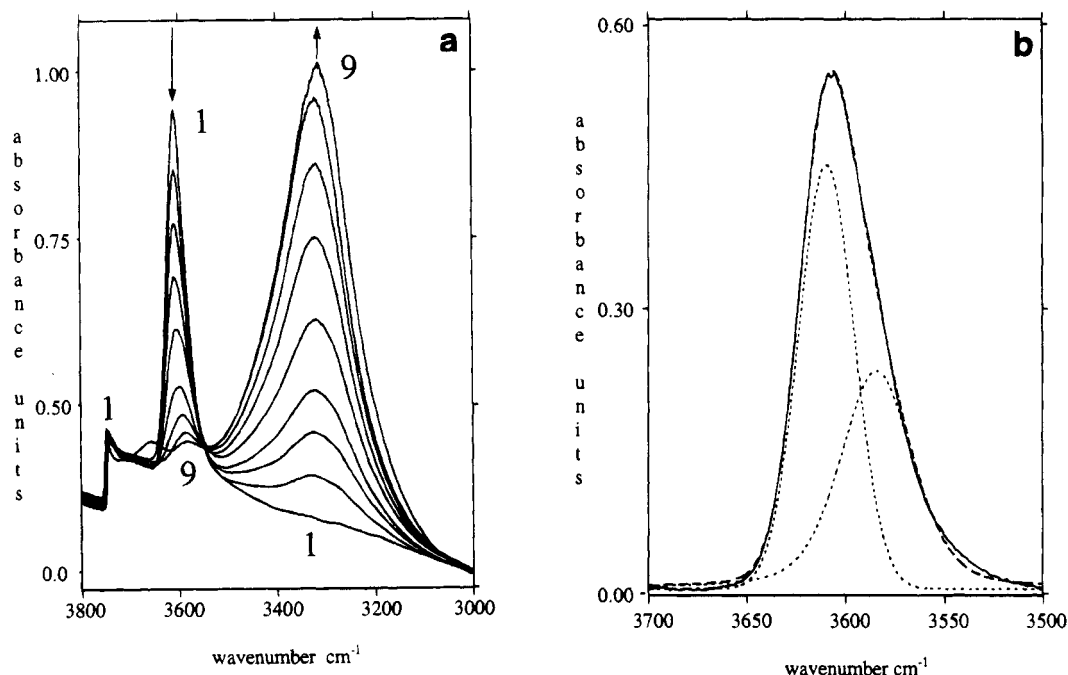


Figure 1. (a) O–H stretching region of H–MOR (spectrum 1) and the effect of increasing doses of adsorbed CO (spectra 2–9) at equilibrium pressure from *ca.* 10^{-2} to 20 Torr (1 Torr = 133.3 Pa). Spectra were taken at 77 K. (b) Computer deconvolution of the 3609-cm^{-1} O–H stretching band: experimentally observed spectrum (solid line); resolved components (dotted lines); fit (dashed line).

zeolites has been recently reported,¹⁶ while preliminary results on Na–Mor were given elsewhere.¹⁷

2. Experimental Section

NH₄–MOR with Si/Al = 5, was supplied by Enichem laboratories Bollate (Milano, Italy). From this zeolite sample, the cationic forms X–MOR (X = Li, Na, K, Rb, Cs) were prepared by standard ion-exchange procedures using aqueous solutions of the corresponding alkali-metal halides. The protonic form was obtained by thermal treatment of NH₄–MOR for 1 h at 673 K, under a dynamic vacuum *ca.* 10^{-2} Pa.

The exchange percentage has been deduced from the intensity of the residual $\nu(\text{OH})$ peak associated with the Brønsted sites. As the intensity of this peak is negligible on Na–, K–, Rb–, and Cs–exchanged mordenites, a nearly total exchange is inferred. For the Li case, the peak intensity (*vide infra* Figure 3, inset) is reduced to about 30% of the original value. This observation can give only a qualitative evaluation of the Li content of our sample. In previous works,^{16,18} the exchange percentages of H–, K–, Rb–, and Cs–ZSM-5, obtained from the sodic form, have been estimated in a more quantitative way by measuring the intensity ratio [$r = I_{\text{X}^+\text{CO}}/I_{\text{Na}^+\text{CO}}$ (X = H, Li, K, Rb, Cs)] of the IR peaks of the corresponding CO adducts at full coverage. This procedure was possible because (i) extinction coefficients of the CO adducts absorbing in the $2200\text{--}2150\text{ cm}^{-1}$ range are approximately constant,^{12,19} and (ii) the shape of the peaks is simple and sharp due to the presence of only one cationic site in ZSM-5. Unfortunately, the shape of the bands of CO adsorbed on the cationic sites of mordenites is more complex: this does not allow use of the latter spectroscopic method for determining the exchange percentages in mordenites.

For IR measurements, thin self-supporting wafers of each zeolite were prepared and activated in vacuum at 673 K for 2 h, inside an IR cell which allowed *in situ* high-temperature treatments, gas dosage, and low-temperature measurements to be made. The IR spectra were recorded, at 2 cm^{-1} resolution, on a Bruker FTIR66 spectrometer equipped with an MCT cryodetector. Although the IR cell was permanently cooled with liquid nitrogen, the actual sample temperature (under the IR beam) was likely to be *ca.* $100\text{--}110\text{ K}$.

3. Results and Discussion

3.1. H–MOR Spectra. Figure 1a shows the spectra of H–MOR in the $3800\text{--}3000\text{-cm}^{-1}$ region. Spectrum 1,

taken before dosing with CO, shows a weak IR absorption band at 3746 cm^{-1} and a much stronger one centred at 3609 cm^{-1} . The general features of the spectrum are entirely similar to those reported in the literature^{20–23} for protonic mordenite samples with Si/Al ratios in the range of 5–8. It is generally agreed^{23–26} that the 3746-cm^{-1} band corresponds to the O–H stretching of terminal OH groups (silanols) located mainly on external surfaces, while the 3609-cm^{-1} band comes from bridged hydroxyls, Si(OH)–Al, which constitute the Brønsted acid groups of the zeolite. Zholobenko *et al.*²³ have recently shown that the 3608-cm^{-1} band (in an H–MOR sample with Si/Al = 7.7) consists of two components, one centered at 3612 cm^{-1} and the other at 3585 cm^{-1} . Similar results have also been obtained by Wakabayashi *et al.*²⁷ on H–MOR samples with a higher Si/Al ratio. The 3612-- and 3585-cm^{-1} bands were assigned to acidic hydroxyls vibrating in the main channels (high-frequency component) and to those present in the smaller channels (low-frequency component). It is widely recognized that, due to electrostatic perturbation, OH groups vibrating in small pores (and cages) undergo a bathochromic shift compared to the frequency at which

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their vibration would occur in larger cavities.²⁸ Our results support this view. In fact the 3609-cm^{-1} band (Figure 1a) is asymmetric on the low-frequency side and can be resolved into two components centered at 3612 and 3585 cm^{-1} , respectively, as shown in Figure 1b. The observed broadness of these bands suggests a small heterogeneity of both sets of OH groups. Dosing with CO (Figure 1a) progressively erodes the 3609-cm^{-1} band, due to the formation of $\text{OH}\cdots\text{CO}$ species, and the last fraction to disappear is shifted to lower frequency, thus providing further proof for the dual nature of the original 3609-cm^{-1} hydroxyl band. Moreover, bridged OH groups located in the smaller channels (side pockets) are not so easily accessible as those in the main channels, and that it is why the lower frequency component of the OH band is the last one to be eroded upon dosing with CO. Figure 1a also shows the progressive growth of a strong IR absorption band centered at 3315 cm^{-1} , which mirrors the parallel erosion of the O–H stretching band, thus proving formation of hydrogen-bonded $\text{OH}\cdots\text{CO}$ species. We note that, in agreement with the experimental results, a pronounced increase of both band intensity and band width are expected upon hydrogen bonding.²⁹ It is precisely the large band width that partially conceals the fact that the 3315-cm^{-1} band has two components. However the band profile, particularly at small CO dosage, shows some evidence of its composite nature. Figure 1a also shows that at the highest equilibrium pressure adsorbed CO partially erodes that silanol band at 3746 cm^{-1} , with concomitant development of a broad IR absorption at about 3660 cm^{-1} . This is a manifestation of $\text{OH}\cdots\text{CO}$ interaction where silanol groups are involved.

Figure 2 shows the C–O stretching region of carbon monoxide adsorbed on H–MOR. The background spectrum of the zeolite wafer, taken before dosing with CO, was subtracted from all spectra shown in this figure (and the same applies to Figures 3–7). For small CO doses, the most significant feature of the spectra in Figure 2 is an absorption band centered at 2172 cm^{-1} which corresponds to the C–O stretching mode of carbon monoxide hydrogen bonded to the bridged $\text{Si}(\text{OH})\text{Al}$ hydroxyl groups of the zeolite. A similar band (at $2173\text{--}2170\text{ cm}^{-1}$) was previously reported and thoroughly discussed^{18,26} for CO adsorbed at 77 K on H–ZSM-5 zeolites and no further consideration is needed here. We only note that (i) the exact frequency of the band maximum varies slightly with CO equilibrium pressure (a fact already discussed in refs^{18,26}) and (ii) although the 2172-cm^{-1} band is asymmetric on the low frequency side, the perturbation of the C–O stretching vibration does not seem to be sensitive enough to discriminate between the two types of bridged OH groups (main channel and small channel location).

Figure 2 shows that on raising the CO equilibrium pressure a strong IR absorption band develops at about 2138 cm^{-1} . This is the frequency expected for CO in a condensed phase³⁰ or physically adsorbed on oxides and halides.^{12,13} We therefore assign the 2138-cm^{-1} band to physisorbed CO inside the zeolite channels, where hindered rotation gives rise to a complex structure,³¹ the band is composed by a central peak and two broad tails.^{32–34} A similar IR absorption band, at 2138 cm^{-1} , was observed for CO adsorbed on H–ZSM-5 and on alkali-metal-

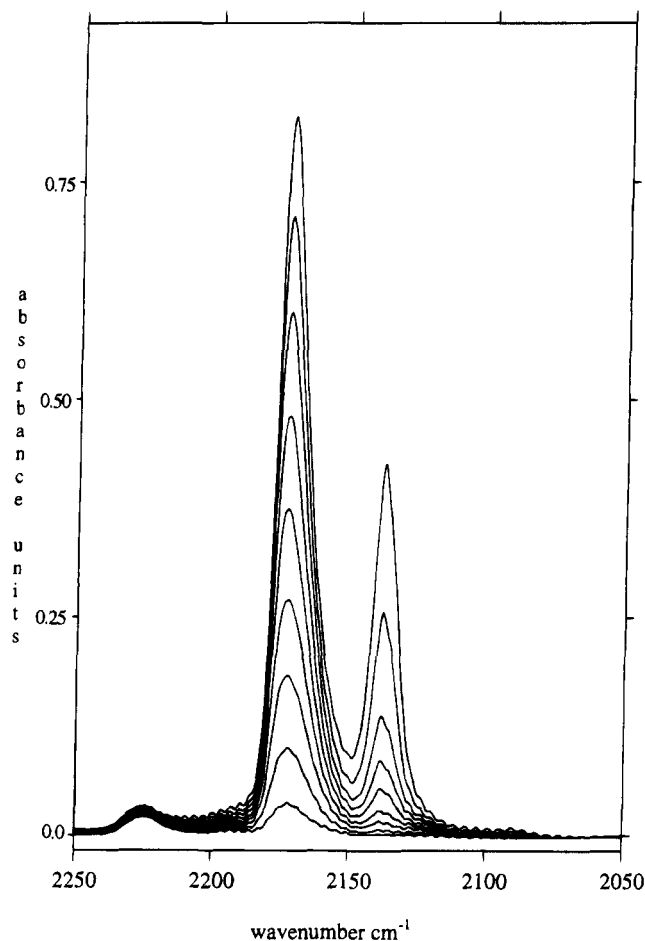


Figure 2. IR spectra of CO adsorbed, at 77 K and increasing CO equilibrium pressures (from ca. 10^{-2} to 20 Torr), on H–MOR. All spectra were background subtracted.

exchanged ZSM-5 zeolites and was extensively discussed in refs 16 and 26.

3.2. IR Spectra of CO Adsorbed on Li–H–MOR.

Figure 3 shows the spectra of CO, at increasing equilibrium pressure, on a Li-exchanged MOR sample. For small CO doses a single IR absorption band is observed at 2188 cm^{-1} . With increasing CO equilibrium pressure, a low-frequency shoulder develops, which then becomes a separate band at 2172 cm^{-1} . Simultaneously, development of a band at 2138 cm^{-1} is also observed; this is readily assigned to nonspecifically adsorbed (physisorbed) CO inside the zeolite channels. The 2188-cm^{-1} band is assigned to the stretching mode of CO molecules polarized by Li^+ cations located in the main channel, the reasons for this assignment are given in Section 3.3. The 2172-cm^{-1} band corresponds to CO interacting with bridging OH groups coming from NH_4 cations not exchanged with Li^+ and then thermolyzed during thermal activation of the zeolite wafer. Presence of these residual hydroxyl groups is demonstrated by the corresponding IR absorption in the O–H stretching region (see inset in Figure 3). Further proof was obtained by subjecting the zeolite sample to a second exchange with a LiBr solution. The corresponding spectra of adsorbed CO (not shown for the sake of brevity) presented a weaker IR absorption band at 2172 cm^{-1} , as compared to that shown in Figure 2. However, homoionic Li–MOR could not be obtained from the parent NH_4 –MOR sample even after repeated exchange with aqueous LiBr. This is in agreement with previous studies³⁵ on ion exchange in Na–MOR, where only 51% of the Na^+ ion could be replaced with Li^+ . The reason for this limited exchange rests most likely on the

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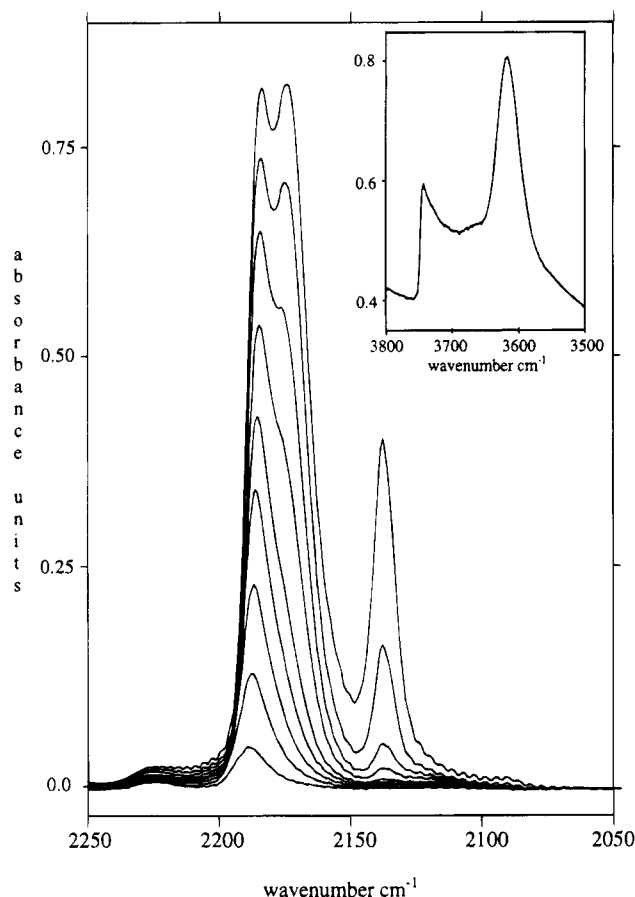


Figure 3. Li-H-MOR (as in Figure 2). Inset depicts the O-H stretching region, showing that only a partial Li-exchange was attained (cf. Figure 1a).

large effective radius of the solvated Li^+ ion,³⁶ which amounts to 0.38 nm. The remaining alkali-metal cations, which have smaller radii in the hydrated state, easily reach 100% exchange.³⁵ On the basis of these arguments, it is reasonable to assume that the exchanged sites in Li-H-MOR are initially located in the main channels. This conclusion does not necessarily hold for samples activated in vacuo, where a migration of Li^+ ions toward more shielded positions is conceivable.

The absence of an *homoionic* sample of Li-MOR prevents any sure conclusion on the spectroscopic feature of the Li-CO adducts in side pockets. However a distinct contribution at about 2170 cm^{-1} cannot be excluded, being (if existing) overshadowed by the strong band due to H-CO adducts. Note that a band around this wavenumber is compatible with the trend of frequencies attributed to $\text{X}^+\cdots\text{CO}$ adducts in side pockets reported in Table 1.

3.3. IR Spectra of CO Adsorbed on Na-, K-, Rb-, and Cs-MOR. These spectra are depicted in Figures 4–7. Qualitatively, they all show similar features, although the most relevant IR absorption bands are gradually shifted to lower frequency following the increasing size of the extraframework cation in the corresponding mordenite sample.

Focusing on Na-MOR (Figure 4), two main (partially resolved) bands are seen at 2177 and 2159 cm^{-1} , respectively (measured on the spectra corresponding to small CO doses). A weaker low-frequency band corresponding to nonspecifically adsorbed CO (cf. section 3.1) appears at about 2139 cm^{-1} . We assign the 2177-cm^{-1} band to the C-O stretching vibration of CO molecules interacting,

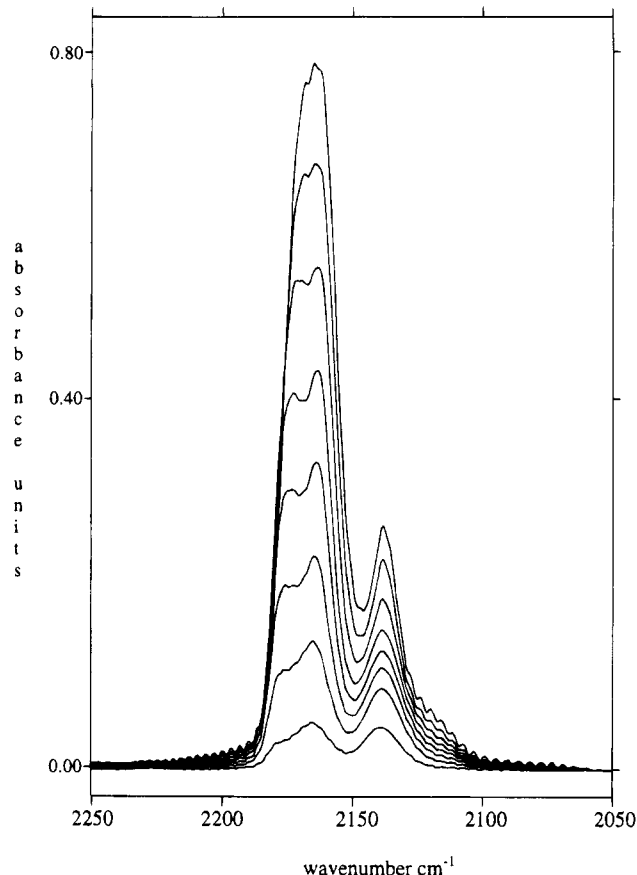


Figure 4. Na-MOR (as in Figure 2).

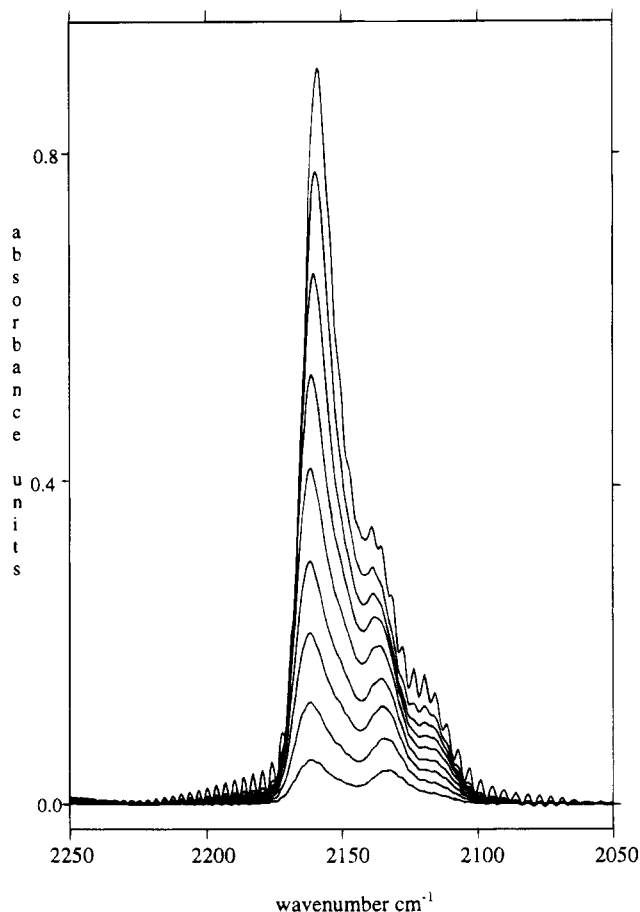


Figure 5. K-MOR (as in Figure 2).

via the carbon end, with Na^+ ions located in the main channel. The 2159-cm^{-1} band would thus correspond to

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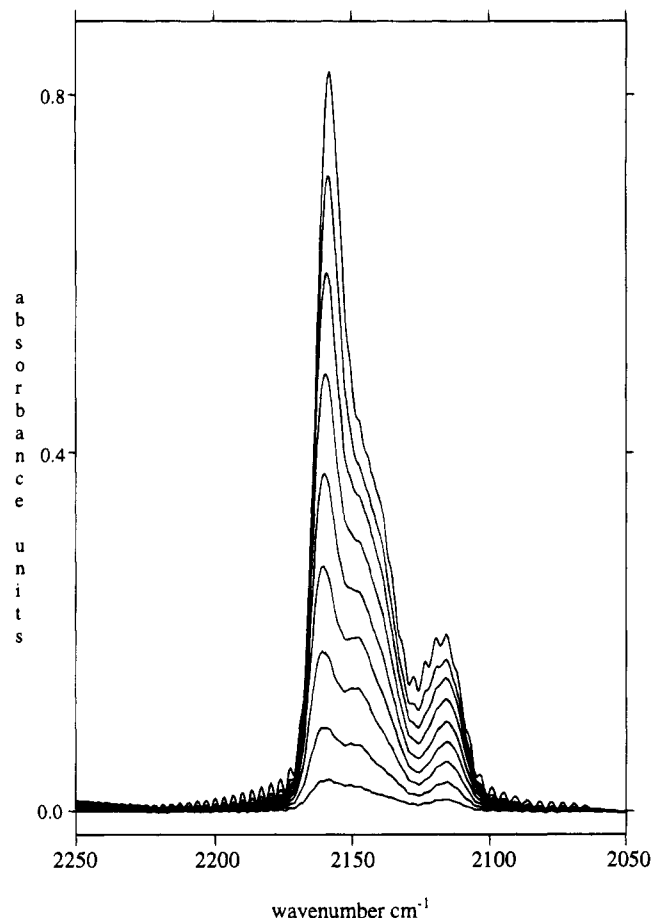


Figure 6. Rb-MOR (as in Figure 2).

a similar $\text{Na}^+ \cdots \text{CO}$ interaction involving the Na^+ ions placed at the bottom of the side pockets. These last sites are more shielded by (negatively charged) framework oxygen ions and therefore exert a smaller polarization on adsorbed CO molecules which is reflected in a smaller hypsochromic shift of the C–O stretching vibration.

For CO adsorbed at 77 K on Na–ZSM-5, a single cation-specific IR absorption band was found^{16,32} at 2178 cm^{-1} . This provides further support to the present assignment of the 2177-cm^{-1} band to CO polarized by Na^+ ions located in the main channels of Na–MOR, since the environment of extraframework cations inside these channels is quite similar to that found inside the pores of ZSM-5 zeolites. However, ZSM-5 does not present a second cation location analogous to that corresponding to the side pockets in mordenite, and consequently, Na–ZSM-5 showed only one cation-specific band.¹⁶ On the other hand, CO adsorbed (at 77 K) on NaCl films showed an IR absorption band at 2159 cm^{-1} which was assigned to CO molecules polarized by coordinatively unsaturated Na^+ ions.¹² It thus appears that extraframework alkali-metal cations located in the main channels of mordenite (and also those in the pores of ZSM-5) have a much greater polarizing power than the same cations at the surface of halide films, while for side pockets of mordenite this polarization ability is quite comparable with that found in alkali-metal halides.

For CO adsorbed on K–MOR and Rb–MOR (Figures 5 and 6) the situation is similar to that already discussed for Na–MOR. We only note that the low-frequency cation-specific band (*i.e.* that one corresponding to CO interacting with cations in the side pockets) appears as a shoulder on the high-frequency band and shows a smaller relative intensity compared to the CO/Na–MOR system. This could be due to the larger size of extraframework cations in the main channel which could partially block the entrance to the side pockets. The situation appears to be

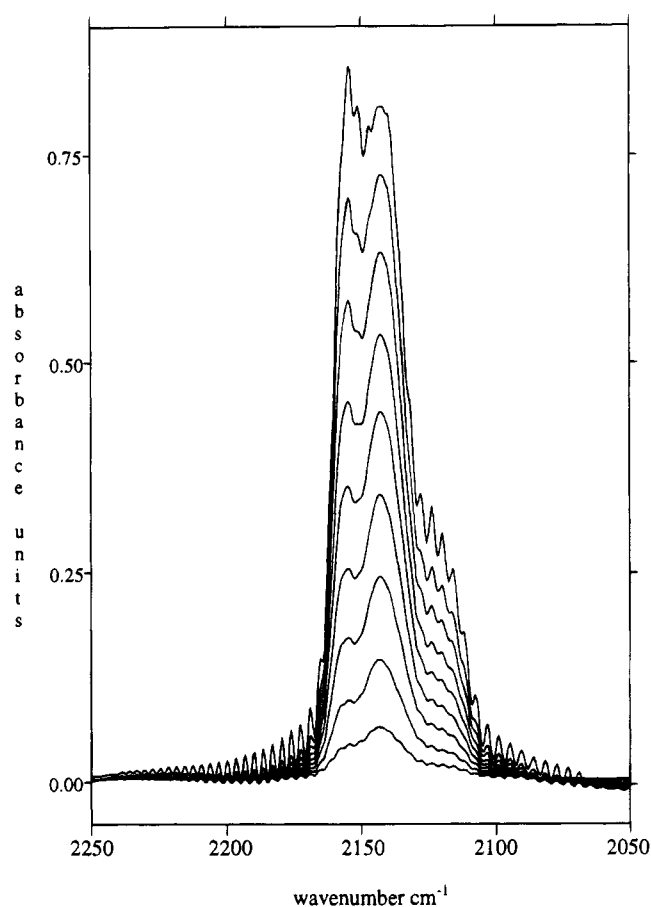


Figure 7. Cs-MOR (as in Figure 2).

Table 1. Observed Frequencies (cm^{-1}) for the Cation-Specific Bands of CO Adsorbed on Mordenites and ZSM-5 Zeolites¹⁶

cation present in the zeolite	mordenite		ZSM-5
	high-frequency band (main channel)	low-frequency band (side pockets)	
H^+	2172		2173–2170
Li^+	2188	$\approx 2170^a$	2188
Na^+	2177	2159	2178
K^+	2163	≈ 2148	2166
Rb^+	2159	≈ 2146	2162
Cs^+	2155	≈ 2144	2157

^a This frequency corresponds to a hypothesized band compatible with IR data; see the text.

reversed in the case of Cs–MOR (Figure 7), but now the low-frequency cation-specific band and that one due to nonspecifically adsorbed CO completely overlap in the $2144\text{--}2138\text{-cm}^{-1}$ region, thus precluding any discussion in terms of relative intensity of high- and low-frequency cation specific bands.

The frequency values at which the cation-specific bands are centered in the different alkali-MOR samples are summarized in Table 1. For comparison, corresponding values for alkali-metal-exchanged ZSM-5 zeolites¹⁶ are also given. The observed smooth decrease in frequency with increasing cation size provides further support for the assignment of these bands to specific cation/CO interactions. In contrast, nonspecifically adsorbed CO always gives an IR absorption band which reaches its maximum at about 2138 cm^{-1} independently of the extraframework cations present in the zeolite. This is the same frequency which was observed for CO physisorbed on faujasites and ZSM-5 zeolites.^{16,18,26} In mordenite a lower frequency component of the main band should be expected, due to CO adsorbed in the narrow channels

(side pockets) which should impose a stronger perturbation on physisorbed CO (as compared to the situation in the main channels). Evidence for this component of the main IR absorption band can be seen in some of the spectra, most clearly in Figure 5. In agreement with this hypothesis we remark that this component, although not appreciably vibrationally perturbed, belongs to a strongly adsorbed species, as expected for CO in narrow pores where van der Waals and electrostatic interaction with the walls have gained importance.

All cation-specific bands are slightly shifted toward lower frequency upon increasing the CO equilibrium pressure (values reported in Table 1 correspond to low CO doses), which is most clearly observed for the high-frequency band (Figures 3–7). This is a consequence of a decrease of the electrostatic field surrounding the cations when the concentration of CO molecules inside the zeolite channels is increased. The effect has been discussed in detail for an Na-ZSM-5 sample elsewhere.³²

A comment must be made on the weak absorption band centered at 2115–2120 cm^{-1} which is most clearly seen in Figure 6, but which also appears in the spectra of Figures 5 and 7. A similar weak IR absorption band was also observed in the spectra of CO adsorbed on some alkali-exchanged ZSM-5 zeolites,¹⁶ but the origin of such a band is not well-understood. Tentative explanations can be given in terms of (i) CO adsorbed on structural defects giving rise to nanovoids,^{37,38} (ii) CO molecules interacting through both ends with pairs of Lewis acid sites which could be either charge-balancing cations or other extraframework species,^{18,32} or (iii) CO molecules interacting with cations through the oxygen end.^{39,40} Further discussion can be found in reference 16.

Finally, a weak band at about 2225 cm^{-1} is observed in the spectra of H-MOR and Li-H-MOR (Figures 2 and 3). This band is most likely due to CO molecules interacting with highly unsaturated partially extraframework Al^{3+} ions. Indeed, it seems to be a Lewis acid site (of unknown structure).⁴¹ A similar band was also observed in the spectra of CO adsorbed on some ZSM-5 zeolites.^{16,32} Partially extraframework aluminum oxide species containing strong Lewis acid sites (coordinatively unsaturated Al^{3+}) are sometimes formed during thermal activation of the zeolite wafer, and their presence depends quite critically on the nature of the zeolite and on the actual conditions during thermal treatments. This can explain the absence of the 2225- cm^{-1} band in the spectra shown in Figures 4–7.

3.4. Electric Field Inside the Main Channels. To our knowledge, earlier works on the evaluation of the local electric fields inside zeolites voids are due to Cohen De Lara and co-workers. The electric field inside Na-A and Ca-Na-A zeolites has been calculated in ref 42 under the assumption that zeolite A is a purely ionic crystal and that the negative and positive charges are distributed on the oxygens of the SiO_4 and AlO_4 tetrahedra and on all the cationic sites in a statistically way. In a subsequent work⁴³ they have compared experimental spectra of N_2O , used as local field probe, adsorbed on Na-A zeolite at 173

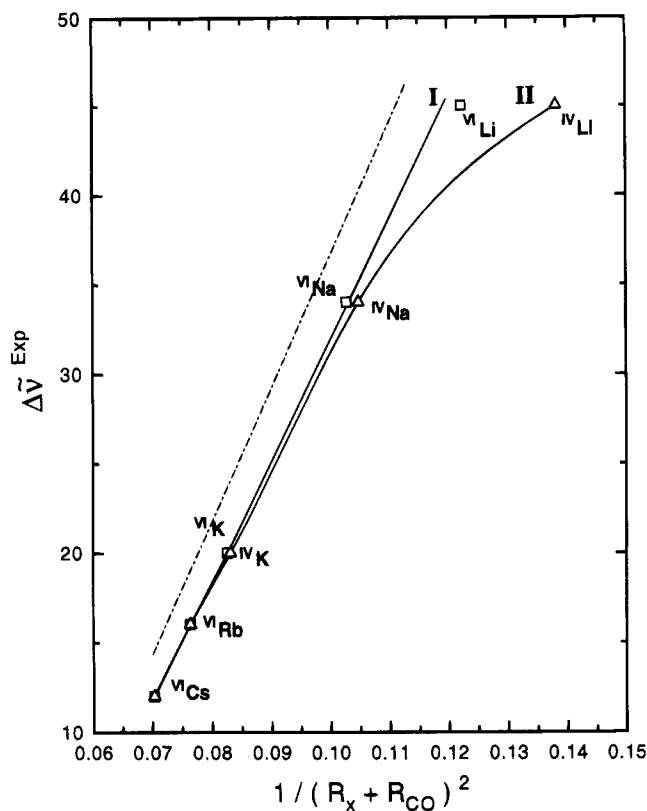


Figure 8. CO frequency shifts $\Delta\tilde{\nu}$ vs $1/(R_x + R_{\text{CO}})^2$ for the different alkali-metal-exchanged mordenites. Line I is the best fit for the points corresponding to Cs, Rb, and K in six-fold coordination. Curve II corresponds to K, Na, and Li in four-fold coordination. The dotted-dashed line represents corresponding data for alkali-metal-exchanged ZSM-5 zeolites (taken from ref 16).

K and at room temperature. Knowing the ionic charge distribution inside the cavities, in ref 44, they have reported results obtained using N_2 as probe on Na-A, Ca-Na-A, and Ca_6 -A zeolites at 193 K to be 5.1, 6.9, and 7.8 V nm^{-1} , respectively, determined from the evaluation of the integrated area of the IR band.⁴⁵ In ref 46 they have discussed the effect of the electric field inside the Na-A zeolite cavities on the CH_4 vibrational modes. In a recent contribution,⁴⁷ Cohen De Lara *et al.* compare experimental vibrational frequencies of H_2 and N_2 adsorbed on Na-A zeolite with *ab initio* calculations performed with the program GAUSSIAN 88 at the SCF level, with 6-31G* and 6-311G* basis sets and corresponding MP2 level.

Also Böse and Förster^{39,40} have developed an electrostatic interaction model to compute the electric fields inside Ca_4 -Na₄-A, Ca_6 -Na₄-A, and Mg_4 -Na₄-A zeolites (5.7, 8.7, and 9.3 V nm^{-1} respectively); they also compare the computations with the experimental values present in the literature.

Table 1 shows that for all the cation-specific bands the C–O stretching frequency is shifted upward from the 2143- cm^{-1} value corresponding to free CO molecules. Qualitatively, this is the effect expected from the interaction of CO, *via* the carbon end, with a center having a net positive charge (extraframework cation). Several authors^{48–50}

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Table 2. Observed Frequency Shifts (cm⁻¹) and Corresponding Electric Field (V nm⁻¹) for CO Adsorbed on H-MOR and on Alkali-Exchanged Mordenites (Main Channel Sites)

cation present in mordenite	$\Delta\tilde{\nu}_{\text{CO}}$ upward shift from CO gas $\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$	electric field strength	cation present in mordenite	$\Delta\tilde{\nu}_{\text{CO}}$ upward shift from CO gas $\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$	electric field strength
H ⁺	29	5.1	K ⁺	20	3.5
Li ⁺	45	8.2	Rb ⁺	16	2.7
Na ⁺	34	6.1	Cs ⁺	12	2.0

have carried out quantitative calculations of the hypsochromic shift as a function of the strength of an axial field directed along the axis of the CO molecule. The most recent results are those of Pacchioni *et al.*,⁵⁰ who used the Hartree-Fock SCF approximation to correlate C-O stretching frequencies with the corresponding values of electric field strength. Using their data, we have calculated the field surrounding the cations in the main channel from the experimentally observed CO frequency shifts, and the results are shown in Table 2. No attempt was made to perform a similar evaluation of the electric field inside the side pockets, first, because the void space in the main channels is most relevant for practical applications and, secondly, because the side pockets require a more complex approach, where multiple interactions involving the zeolite framework are considered.

In Figure 8 the CO frequency shifts corresponding to the high-frequency cation specific band are plotted against the parameter $1/(R_X + R_{\text{CO}})^2$, where R_X is the corresponding cation radius, (taken from Shannon⁵¹) and R_{CO} was taken as 0.21 nm after the work of Leoni *et al.*⁵² For K⁺, Na⁺, and Li⁺ two different values of R_X are available depending upon the coordination number of the ion, six- or four-fold (superscript VI and IV in Figure 8). The effect of coordination number on the ionic radius does not affect Cs⁺ and Rb⁺, and is negligible for K⁺, very small for Na⁺, and quite consistent for Li⁺. Consequently, two plots are generated, which have a common linear part (Figure 8). Alkali-metal cations exposed in the mordenite main channels are not expected to be more than four-fold coordinated (particularly in the case of Li⁺), and therefore curve II in Figure 8 should most adequately describe the situation. Similar results were obtained¹⁶ in a previous study of CO adsorbed on alkali-metal-exchanged ZSM-5 zeolites, and they are also depicted in Figure 8 for comparison. We note that, although the trends are quite similar in both cases, the actual frequency shifts are slightly smaller (particularly for the larger cations) in the case of mordenite. This can be correlated with the fact that ZSM-5 (Si/Al = 14) in the samples investigated¹⁶ has a more covalent framework than mordenite (Si/Al = 5). Therefore, in the latter case anions surrounding the extraframework cations make a slightly higher (negative) contribution to the net electric field.

Figure 8 shows that the CO frequency shift caused by Li⁺ is significantly smaller than what could be expected from extrapolation of the values corresponding to larger cations, and the same trend, although quantitatively much smaller, is also shown by Na⁺. This is due to the fact that small cations (with high polarizing power) favor a partially

covalent bond with the framework oxide anions, thus lowering the net positive charge at the cation site. The experimental values of $\Delta\tilde{\nu}$ can be used to evaluate the fraction (f_X) of positive charge present on the Na⁺ and Li⁺ ions. Assuming that the charge on the K⁺, Rb⁺, and Cs⁺ ions is $+|e|$, the $\Delta\tilde{\nu}$ value given by the straight line in Figure 8 at the abscissa value of $1/(R_{\text{Na}} + R_{\text{CO}})^2$ and $1/(R_{\text{Li}} + R_{\text{CO}})^2$ would correspond to the CO frequency shift expected for an Na⁺ and Li⁺ charge equal to $+|e|$ (hereafter indicated as $\Delta\tilde{\nu}_{\text{Na}}^{\text{hyp}}$ and $\Delta\tilde{\nu}_{\text{Li}}^{\text{hyp}}$). While $\Delta\tilde{\nu}_X^{\text{hyp}}$ is proportional to $+|e|/(R_X + R_{\text{CO}})^2$, the observed frequency shift (hereafter indicated as $\Delta\tilde{\nu}_{\text{Na}}^{\text{exp}}$ and $\Delta\tilde{\nu}_{\text{Li}}^{\text{exp}}$) is proportional to $+f_X|e|/(R_X + R_{\text{CO}})^2$. When $\Delta\tilde{\nu}_{\text{Na}}^{\text{exp}} = 34 \text{ cm}^{-1}$, $\Delta\tilde{\nu}_{\text{Li}}^{\text{exp}} = 45 \text{ cm}^{-1}$ and $\Delta\tilde{\nu}_{\text{Na}}^{\text{hyp}} = 35 \text{ cm}^{-1}$, $\Delta\tilde{\nu}_{\text{Li}}^{\text{hyp}} = 59 \text{ cm}^{-1}$, the net charge fraction on the sodium and lithium ions is

$$f_{\text{Na}} \approx \frac{\Delta\tilde{\nu}_{\text{Na}}^{\text{exp}}}{\Delta\tilde{\nu}_{\text{Na}}^{\text{hyp}}} = 0.97; \quad f_{\text{Li}} \approx \frac{\Delta\tilde{\nu}_{\text{Li}}^{\text{exp}}}{\Delta\tilde{\nu}_{\text{Li}}^{\text{hyp}}} = 0.76$$

Note however that (i) a value of $f_{\text{Na}} = 1$ would be included within the experimental errors of the reported data (spectral resolution 2 cm^{-1}), and (ii) in the foregoing calculation the effect of the negative charge of the framework was ignored.

The same arguments can be used to estimate the net positive charge on the acidic proton of H-MOR from the corresponding CO frequency shift (Table 2). However, here we meet with the difficulty of estimating a reasonable value for the H⁺ radius. If the same value adopted for ^{IV}Li⁺ is used, calculations give for the acid proton a value $f_{\text{H}} = 0.5$. This may be compared with corresponding values obtained using molecular models. Thus, for the (H₃-SiO)₆SiOHAl cluster Zhidomirov and Kazansky⁵³ reported a Mulliken charge of +0.404 on the acid proton, computed at the CNDO/DZ level. More elaborate *ab initio* SCF/DZ(p,d) calculations^{54,55} led to a net charge of +0.455 for the acidic proton in the H₃SiOHAlH₃ cluster. For similar clusters, *ab initio* calculation of ¹H NMR shifts have recently been reported.⁵⁶ Our present value of $f_{\text{H}} = 0.5$ for the acid proton in H-MOR must be regarded as having only a semiquantitative character, but it is not too different from those obtained using quantum chemical calculations on molecular models.

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