Experimental and Quantum Chemical Studies on the Adsorption of Carbon Dioxide on Alkali-Metal-Exchanged ZSM-5 Zeolites

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Received: February 11, 2000; In Final Form: June 15, 2000

The adsorption of carbon dioxide onto M-ZSM-5 zeolites (M = Li, Na, K, Cs) was studied by means of FTIR spectroscopy and adsorption microcalorimetry. Quantum chemical calculations, at the B3-LYP level, on the interaction of CO_2 with the bare alkali-metal cations were performed to assist interpretation of the experimental results. With the likely exception of Li^+, CO_2 was found to undergo a two-step interaction with the metal ions. At a low equilibrium pressure linear 1:1 adducts of the type $M^+ \cdots O = C = O$ (M = Na^+, K^+, Cs^+) are formed; upon increasing the CO_2 equilibrium pressure, the metal cation coordinates a second CO_2 molecule, forming a 2:1 adduct. Calculated (ab initio) bond lengths for the 1:1 adduct are given, as well as corresponding values of the binding energy and enthalpic term. Experimentally derived values of the main thermodynamic functions ($\Delta H°$, $\Delta G°$, and $\Delta S°$) are discussed and correlated with detailed results from IR spectroscopy. The interaction cation/CO_2 alone cannot account for the body of evidence, and the contribution of nearby O^{2-} anions has to be invoked.

Introduction

Zeolites belonging to the ZSM-5 family are widely used as catalysts for the petrochemical industry and the synthesis of speciality chemicals. Their relevant catalytic properties stem from a right combination of acidity and shape selectivity, as well as from the variety of extraframework cations which can be used to balance the negative electric charge of the zeolite framework.[1] ZSM-5 zeolites exchanged with monovalent cations show a further reason for interest as they represent one of the simplest zeolite systems: because of the low aluminum content, counterions are in principle located at isolated, noninteracting sites (though in practice, the synthesis procedure may give rise to a nonhomogeneous distribution of cation sites). This means that, for adsorbed molecules, M^+-ZSM-5 zeolites are potentially ideal systems in the thermodynamic sense; i.e., they constitute an ensemble of equivalent and noninteracting adsorption sites. The equivalency of sites, however, is not granted a priori, since there are twelve nonequivalent TO_4 tetrahedra (T = Si or Al) in the unit cell, and at least two possibilities for the location of extraframework cations. Zecchina et al.[2] have recently proposed on the basis of EXAFS results that copper ions in Cu^+-ZSM-5 may occur in both 2- and 3-fold coordination to lattice oxygen atoms. This interpretation has received the support of UV and computational results.[3] However, IR spectroscopic evidence concerning the formation of carbonyl species on Cu^+- and Ag^+-substituted samples does not reveal any heterogeneity.[4] We have recently shown also that CO_2 adsorption on Na-ZMS-5 suggests a basically ideal behavior.[5]

IR spectroscopic characterization of alkali-metal-exchanged ZSM-5 zeolites has frequently been carried out using some simple probe molecules (CO, methane, dinitrogen), usually at a low temperature,[6−8] although measurements on Na-ZSM-5 are possible even at room temperature.[9] CO adsorbed on Na-ZSM-5 shows temperature-dependent equilibrium between two modes of coordination to the extraframework cation: through the carbon or through the oxygen atom, respectively.[10] In a preceding paper,[5] we studied the adsorption of a different probe molecule, carbon dioxide, by means of IR spectroscopy and adsorption calorimetry. CO_2 is frequently used to test the presence of basic oxygen anions,[7,11] through the formation of carbonate-like species. Such an interaction mode does not occur, however, with alkali-metal-exchanged ZSM-5 zeolites. Instead, interaction with extraframework (exchangeable) cations is assumed to take place in a fashion similar to that found for CO.[5,9,10] However, in the case of CO_2 the energy involved is greater than for CO, and the interaction readily takes place at room temperature.

In a previous paper[5] it has been shown that, depending on equilibrium pressures of adsorbed gas, Na^+ ions in Na-ZSM-5 can coordinate one or two CO_2 molecules following eqs 1 and 2, respectively.

$$Na^+ + (CO_2)_g \leftrightarrow Na(CO_2)^+ \qquad (1)$$

$$Na(CO_2)^+ + (CO_2)_g \leftrightarrow Na(CO_2)_2^+ \qquad (2)$$
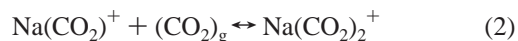
This scheme is in agreement with previous studies[12] regarding carbon monoxide adsorption on Na-ZSM-5 and suggesting that more than one CO molecule can be adsorbed on the same cation site. Similarly, Hadjiivanov and Knözinger[13,14] found that two CO molecules (or two N_2 molecules) can be coordinated to the same Na^+ ion in Na-Y. Ultimate evidence to support formation of bicoordinated species comes from volumetric adsorption measurements showing that adsorbed amounts of CO_2 definitely exceed the Na^+ adsorbing sites of the Na-ZSM-5 sample.

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A fairly thorough thermodynamic characterization has been provided for both reactions 1 and 2. The calorimetrically determined standard changes in enthalpy were $\Delta H°_1 = -49$ kJ mol^{-1} and $\Delta H°_2 = -21$ kJ mol^{-1}, respectively. The corresponding equilibrium constants, at 303 K, were found to be $K_1 = 0.20 \pm 0.03$ Torr^{-1} and $K_2 = 0.015 \pm 0.002$ Torr^{-1}, to which correspond standard changes in Gibbs free energy of $\Delta G°_1 = 4.05$ kJ mol^{-1} and $\Delta G°_2 = 10.6$ kJ mol^{-1}. $\Delta S°_1$ and $\Delta S°_2$ are consequently evaluated to be -173 and -107 J mol^{-1} K^{-1}, respectively.

In the present work, the interaction of CO_2 with the series of cation-exchanged M$^+$-ZSM-5 zeolites (M = Li, Na, K, and Cs) is considered. FT-IR spectroscopy was the main means of investigation for all four samples. Microcalorimetric measurements have been run for the K-ZSM-5 sample, in analogy with the work previously reported[5] for Na-ZSM-5. It was not possible to run satisfactory microcalorimetric measurements for CO_2 adsorbed on Li-ZSM-5 and Cs-ZSM-5, because the exchange of Na$^+$ in the parent Na-ZSM-5 material with Li$^+$ or Cs$^+$ was far from complete, which complicates interpretation of calorimetric data.

In addition, theoretical quantum chemical calculations were carried out on minimal models consisting of one CO_2 molecule interacting with a bare cation, so as to provide a reference frame for the interpretation of experimental data. Parallel work concerning CO interaction with naked alkali-metal cations has been reported elsewhere.[15,16]

Experimental Section

Investigated materials were ZSM-5 zeolites with a Si/Al ratio equal to 14. The parent Na-ZSM-5 sample was synthesized following standard hydrothermal methods,[17] and characterized by powder X-ray diffraction. From this sodium form of the zeolite, Li-ZSM-5, K-ZSM-5, and Cs-ZSM-5 samples were obtained by ion exchange with aqueous solutions of the corresponding alkali-metal nitrates. The ion exchange was virtually complete for K-ZSM-5, whereas with lithium and cesium only a partial exchange was obtained. The Li-ZSM-5 sample showed a Li$^+$/Na$^+$ ratio of $\cong 0.25$ (i.e., only a 20% exchange was attained). Cs-ZSM-5 showed a Cs$^+$/Na$^+$ ratio of $\cong 9$. A sample of silicalite (a purely siliceous zeolite having the MFI-type structure)[18] has also been used as a reference material.

For IR measurements, thin self-supporting wafers of the zeolite samples (having a density of $\cong 7$ mg cm^{-2}) were prepared. To remove adsorbed water and clean the surface, the sample wafers were outgassed for 2 h at 723 K inside the IR cell. The residual pressure was below 10^{-3} Torr. Room-temperature IR spectra were recorded, in the 7200−450 cm^{-1} range and at a resolution of 2 cm^{-1}, on a Perkin-Elmer 1720 Fourier transform IR spectrometer equipped with an MCT cryodetector.

Microcalorimetric measurements were carried out by means of a Setaram Calvet-type instrument, operated at 303 K. The microcalorimeter was equipped with a volumetric attachment of conventional design for gas dosage and measurement of the corresponding adsorption isotherm.

Computational Section

In previous work concerning the interaction of CO with a single naked alkali-metal cation,[15] it has been shown that quite satisfactory results were obtained by using the B3-LYP method;[19] they were comparable to the higher quality QCISD(T) computational results. Calculations for embedded cations[16] have also been obtained at the former level of computation. Consequently,

the B3-LYP method has been adopted systematically in the present work, and all calculations were carried out at this level of treatment.

The basis set adopted for Li$^+$, Na$^+$, and K$^+$ ions, as well as for C and O atoms, was the fully optimized triple-ζ valence (TZV) basis set recently proposed by Ahlrichs and co-workers.[20] Contraction schemes were as follows: C and O (62111/411), Li (62111), Na (73211/51), and K (842111/631). The TZV basis set has also been supplemented by a double set of polarization d functions on C and O atoms ($\zeta_d = 0.15/1.0$) (the d set consists of five primitive functions) and by adding a double set of diffuse p functions on the cations, i.e., $\zeta_p(Li) = 0.06/0.4$, $\zeta_p(Na) = 0.0196/0.131$, and $\zeta_p(K) = 0.015208/0.041737$.

Calculations have been carried out all-electron for the three lighter cations, whereas an ab initio effective core potential has been used to replace the innermost core electrons for Cs$^+$; the outermost core orbitals, corresponding to the ns^2np^6 configuration, not replaced by the effective core potential, were treated in the same way as the $(n + 1)$s and $(n + 1)$p valence orbitals following the Hay and Wadt "small-core" scheme.[21] The s-valence part has been further decontracted with respect to the original proposal to increase flexibility, giving rise to the following contraction schemes: K (4311/311) and Cs (4311/321). The basis sets have been obtained at the Internet address described in ref 19.

Results

IR Spectroscopy. CO_2 belongs to the $D_{\infty h}$ symmetry group and has four fundamental modes: the symmetric stretching ν_1, the doubly degenerate bending vibration ν_2, and the asymmetric stretching vibration ν_3.[23] For symmetry reasons, the ν_2 and ν_3 modes are infrared active, whereas ν_1 is only Raman active. In the free molecule, these modes appear at 1388.3 (ν_1), 667.3 (ν_2), and 2349.3 (ν_3) cm^{-1}. When a CO_2 molecule interacts with a metal cation, the symmetry is lowered, and consequently the ν_1 mode becomes active, whereas the other modes undergo moderate changes in wavenumber.

For carbon dioxide adsorbed on the samples considered in the present work, no signals were found in the carbonate spectral range (1400−1700 cm^{-1}). The observed bands can all be related to CO_2 in a linear configuration. This is in contrast to zeolites Na-A and Li-A or faujasites,[11,24] where carbonate-like species were formed upon adsorption of CO_2. Because of the much higher Si/Al ratio (14 in the ZSM-5 samples studied, as compared to 1/3 in A-type zeolites or faujasites), the framework oxygens are less basic in ZSM-5, and this explains why carbonate species are not formed.

IR spectra of CO_2 adsorbed on Na-ZSM-5 were discussed in detail in a previous paper.[5] However, they are reported in Figure 1 because they constitute a reference for the other samples. Figure 1a shows the ν_3 region at low CO_2 coverages (equilibrium pressures up to 0.66 Torr). The spectra are dominated by the very intense band at 2356 cm^{-1}, due to the ν_3 mode of CO_2 interacting with Na$^+$ ions. Small bands (or shoulders) are observed at 2371, 2365, and 2344 cm^{-1}, more clearly seen in the inset. The 2371 cm^{-1} band is due to CO_2 adsorbed on small amounts of extraframework Al^{3+} ions. The nature of the 2365 cm^{-1} band, which we believe could be related to a double-coordinated CO_2 molecule, will be discussed elsewhere. The 2344 cm^{-1} band is probably due to CO_2 linearly adsorbed on Na$^+$ ions less exposed than those originating the 2356 cm^{-1} band: the relative intensity is, however, indicative of a very small population. Minor features in Figure 1a are a broad tail on the high-frequency region (maximum at about 2416
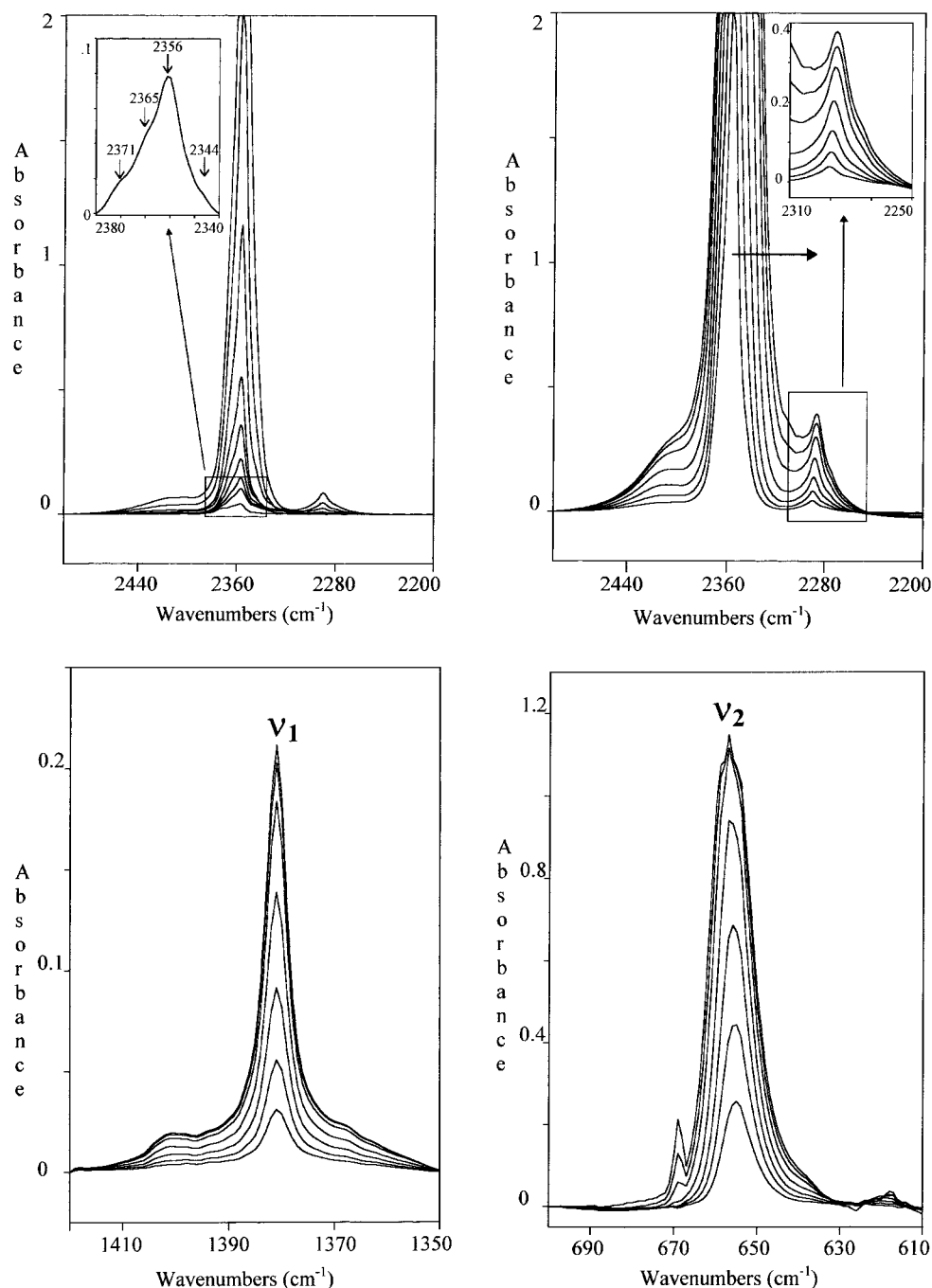
Figure 1. (a, top left) Room-temperature IR spectra of CO_2 adsorbed on Na-ZSM-5 outgassed at 723 K. Asymmetric stretch (ν_3) region, equilibrium pressures 3.5×10^{-3}, 5.2×10^{-3}, 1×10^{-2}, 4.8×10^{-2}, 8×10^{-2}, 0.26, 0.67 Torr. Inset: magnification of the spectral features at very low coverages. (b, top right) Room-temperature IR spectra of CO_2 adsorbed on Na-ZSM-5 outgassed at 723 K. Asymmetric stretch (ν_3) region, equilibrium pressures 0.26, 0.67, 1.9, 7.2, 30.1, 67.8, 112.8 Torr. Inset: magnification of the $^{13}CO_2$ asymmetric stretch region. (c, bottom left) Room-temperature IR spectra of CO_2 adsorbed on Na-ZSM-5 outgassed at 723 K in the symmetric stretch (ν_1) region, equilibrium pressures as in Figure 1b. (d, bottom right) Room-temperature IR spectra of CO_2 adsorbed on Na-ZSM-5 outgassed at 723 K in the bending mode region (ν_2), equilibrium pressures as in Figure 1b.

cm^{-1}) and a smaller band at 2290 cm^{-1}. The broad absorption at about 2416 cm^{-1} is assigned to a combination mode of the ν_3 stretching vibration with the intermolecular stretching mode of the $Na^+ \cdots O{=}C{=}O$ adduct, referred to hereafter as ν_{int}, the frequency of which is 60 cm^{-1}. There are several reasons for assigning the 2416 cm^{-1} band to a combination mode: (i) the frequency, too high for a coordinated species; (ii) the intensity, not comparable with the intensity of other components; (iii) the width, definitely larger, as happens with combination modes; (iiii) the pressure dependence; should this band be related to a hypothetical adsorbed species, the high frequency would indicate

a remarkable strength of interaction and the band would saturate quickly with pressure.

The band at 2290 cm^{-1} is due to the ν_3 mode of $^{13}CO_2$, the intensity of which is about 100 times lower than that corresponding to the $^{12}CO_2$ ν_3 fundamental.

The IR absorption of the ν_3 mode is very intense, and the corresponding band goes out of scale for moderate CO_2 equilibrium pressures (0.4−0.8 Torr). Figure 1b, reporting the spectra at medium to high coverages, shows bands truncated at the optical density of 2.0. Adsorption of a second CO_2 molecule shifts the center of gravity of the main IR adsorption band from

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TABLE 1: Experimental Values, cm^{-1}, of Vibrational Modes of CO$_2$ in the Gas Phase and Adsorbed on Silicalite and Alkali-Metal-Exchanged ZSM-5 (Li$^+$ to Cs$^+$)

vibration	CO$_2$ gas	silica-lite	Li$^+$	Na$^+$	K$^+$	Cs$^+$
ν_2	667.3	662	654	656	656	656
ν_1	1388.3		1382	1382	1382	1382
ν_3	2349.3	2341	2366	2356	2351	2345
ν_3 (high pressure)			2359	2352	2348	2343
$\nu_3 + \nu_{int}$			2427	2416	2408	2400
ν_{int}			61	60	57	55
$\nu_1 + \nu_{fr}$			1401	1402	1401	1400
ν_{fr}			19	20	19	18
ν_3(^{13}CO$_2$)	2284.5	2274	2300	2290	2286	2280
ν_3(^{13}CO$_2$) (high pressure)			2294	2287	2281	2278

2356 to 2352 cm^{-1}. This shift is more clearly seen in the corresponding ^{13}CO$_2$ band (inset), which goes from 2290 to 2287 cm^{-1} when the CO$_2$ equilibrium pressure increases. A component also grows at 2274 cm^{-1} (inset), which corresponds to 2339 cm^{-1} in the ^{12}CO$_2$ band. Parallel studies on CO$_2$ adsorbed on silicalite suggested that this small band is due to physisorbed CO$_2$.

The downward shift of the ν_3 band due to coordination of the second CO$_2$ molecule (high equilibrium pressure, Figure 1b) amounts to about -4 cm^{-1}. This small value is in agreement with the observation made by Hadjiivanov and Knözinger[13] that coordination of two CO molecules to the same Na$^+$ ion gives rise to a single unresolved band at a frequency slightly lower than that corresponding to monocoordinated Na$^+$···CO adducts. Note that frequency lowering is due to the fact that when two adsorbed molecules share the same cation site each of them undergoes a weaker interaction with the Na$^+$ ion.

Figure 1c reports spectra of adsorbed CO$_2$ in the region of the IR-forbidden ν_1 mode: the mere presence of IR absorption in this region is indicative of a lowering of symmetry of the CO$_2$ molecule upon adsorption, since no contribution from the gas phase is expected. Spectra are reported only for the highest coverages, corresponding to those in Figure 1b. A main band is seen at 1382 cm^{-1}, steadily growing with increasing CO$_2$ equilibrium pressure. The shift from the gas-phase value is $\Delta\nu_1 = -6$ cm^{-1}. The ill-defined (small) bands seen at about 1403 and 1367 cm^{-1} can be assigned to positive and negative combination modes of ν_1 with a mode of frustrated rotation (libration) having a frequency ν_{fr}. The two small bands would thus have frequency values of $\nu_1 + \nu_{fr}$ and $\nu_1 - \nu_{fr}$, respectively, and the value of ν_{fr} would be about 18 cm^{-1}. The center of mass of the two combination modes (1385 cm^{-1}) differs slightly from the actual value of the ν_1 band (1382 cm^{-1}) because of anharmonicity.

Figure 1d reports the ν_2 region of the same spectra as in Figure 1b,c. A major peak is observed at 656 cm^{-1}, slightly downward shifted with respect to the gas-phase value ($\nu_2 = 667.3$ cm^{-1}), which appears as a minor component of the spectra at high pressure.

IR spectra of CO$_2$ adsorbed on samples Li-ZSM-5, K-ZSM-5, and Cs-ZSM-5 were found to be similar to those obtained for Na-ZSM-5. Both the ν_2 and ν_1 modes were found at wavenumbers which are almost completely independent from the cation. In particular the ν_2 mode was found at the same frequency in all cases: we make use of this fact below. The asymmetric stretch, ν_3, is instead cation-dependent (see below), as already reported for CO$_2$ adsorbed on Na-A and Li-A zeolites.[11,24] The whole set of frequencies is given in Table 1. In all cases, the ν_3 mode was observed to couple with the ν_{int} mode, and the ν_1 mode with the ν_{fr} mode. The frequencies of
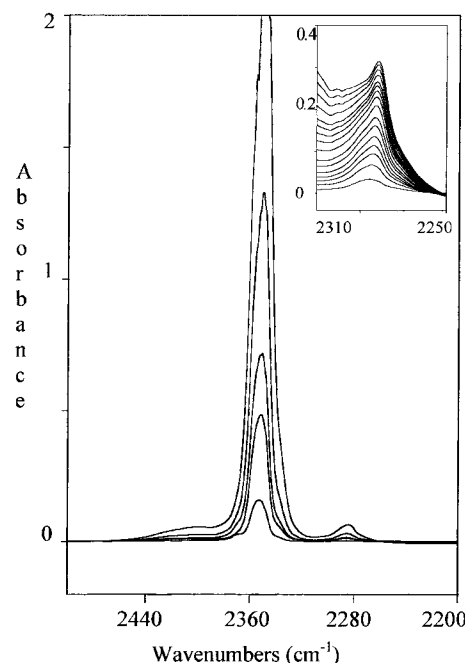

Figure 2. Room-temperature IR spectra of CO$_2$ adsorbed on K-ZSM-5 outgassed at 723 K. Asymmetric stretch (ν_3) region, equilibrium pressures 6.8×10^{-2}, 0.17, 0.29, 0.65, 1.92 Torr. Inset: magnification of the ^{13}CO$_2$ asymmetric stretch region, equilibrium pressures: 0.65, 1.92, 3.5, 7.2, 14.6, 22.3, 30.2, 37.7, 45.5, 53.1, 60.2, 67.8, 75.5, 83.2, 90.9, 112.6 Torr.

the ν_{int} and ν_{fr} modes were found to be almost insensitive to the cation present in the zeolite.

The ν_3 region of the spectra of CO$_2$ adsorbed on K-ZSM-5 is shown in Figure 2. The main body of this figure depicts the spectra at low CO$_2$ coverages, whereas the inset (reporting the satellite band envelope due to ν_3 of ^{13}CO$_2$) illustrates the full range of coverages. The very weak band at 2371 cm^{-1} (observed at vanishing coverages) is due to CO$_2$ interacting with extra-framework Al^{3+}. Its feeble intensity shows that dealumination takes place in IR measurements to a negligible extent. The main band, which peaks at 2351 cm^{-1}, is assigned to the ν_3 mode of K$^+$···O=C=O species. Traces of a shoulder at 2356 cm^{-1} were observed for vanishing coverages. This faint shoulder, which can be seen at 2290 cm^{-1} for the ^{13}CO$_2$ band (inset), corresponds to CO$_2$ interacting with traces of Na$^+$ ions not completely exchanged by K$^+$. The main peak of the ^{13}CO$_2$ band appears at 2286 cm^{-1} for the lowest equilibrium pressure, and it shifts down to 2283 cm^{-1} at a high coverage. Assuming a constant isotopic ratio of 0.9720, this latter value corresponds to 2348 cm^{-1} in the ^{12}CO$_2$ counterpart.

Figure 3 shows the IR spectra of CO$_2$ adsorbed on Cs-ZSM-5 in the ν_3 region. As before, the main figure describes the spectra at low coverages, and the inset (^{13}CO$_2$ region) illustrates the full range. At low coverages, the weak band due to extraframework Al^{3+} is seen at 2371 cm^{-1}. The major band has components at 2356, 2345, and 2335 cm^{-1} (shoulder). The component at 2356 cm^{-1} is due to Na$^+$···O=C=O species formed on Na$^+$ ions not exchanged by Cs$^+$. The ν_3 mode of the Cs$^+$···O=C=O species shows the major component at 2345 cm^{-1}; the shoulder at 2335 cm^{-1} is probably due to less exposed Cs$^+$ ions (as in the case of Na-ZSM-5). Note that the band at 2345 cm^{-1} becomes dominant only at equilibrium pressures greater than about 1 Torr, when all of the Na$^+$ ions are already saturated. The inset shows that, for the highest CO$_2$ equilibrium pressure, the main band related to Cs$^+$ ions undergoes a
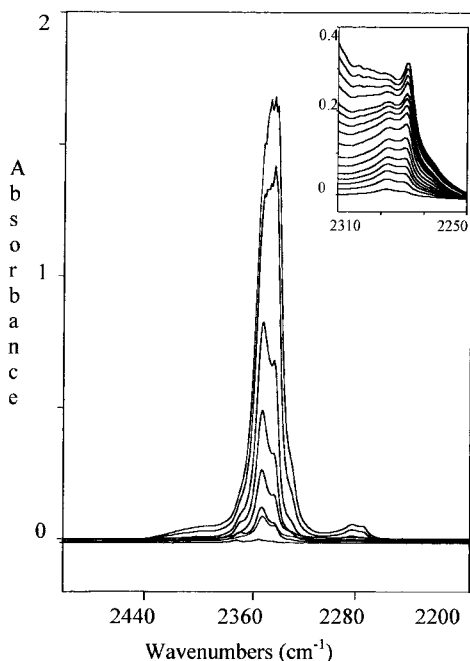
Figure 3. Room-temperature IR spectra of CO_2 adsorbed on Cs-ZSM-5 outgassed at 723 K. Asymmetric stretch (ν_3) region, equilibrium pressures 5.5×10^{-3}, 4.3×10^{-2}, 6.5×10^{-2}, 0.15, 0.31, 0.70, 2, 3.5 Torr. Inset: magnification of the $^{13}CO_2$ asymmetric stretch region, equilibrium pressures 0.7, 2, 3.5, 7.2, 14.6, 22.3, 30.1, 37.7, 45.5, 53.1, 60.2, 67.8, 75.5, 83.4, 91.1, 112.7 Torr.
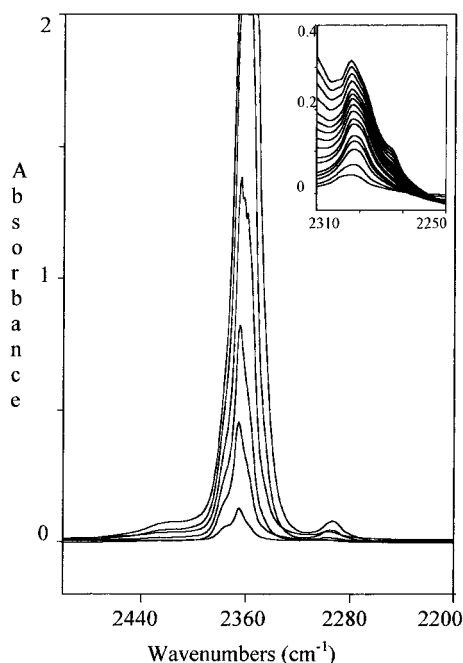

Figure 4. Room-temperature IR spectra of CO_2 adsorbed on Li-ZSM-5 outgassed at 723 K. Asymmetric stretch (ν_3) region, equilibrium pressures 3.6×10^{-3}, 3.6×10^{-2}, 7.7×10^{-2}, 0.24, 0.65 Torr. Inset: magnification of the $^{13}CO_2$ asymmetric stretch region, equilibrium pressures 0.24, 0.65, 3.5, 7.2, 14.6, 22.3, 30, 38.1, 45.5, 53.1, 60.2, 67.9, 75.6, 83.2, 91.1, 112.8 Torr.

downward shift of about 2 cm^{-1}. At high coverages, a band grows at 2274 cm^{-1}, due to physisorbed species.

The spectra of CO_2 adsorbed on Li-ZSM-5 are shown in Figure 4 (main body for low coverages and inset for the full range). The main peak, at 2366 cm^{-1}, is assigned to the ν_3 mode of the $Li^+ \cdots O{=}C{=}O$ species. Note that, although this sample
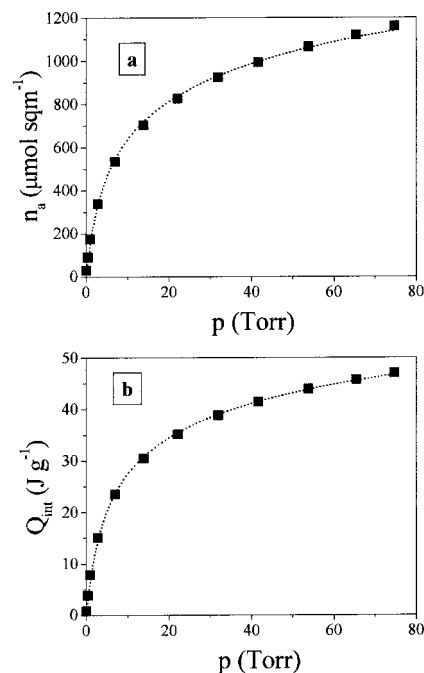

Figure 5. Calorimetric and volumetric data concerning the room-temperature adsorption of CO_2 on K-ZSM-5 outgassed at 723 K: (a) volumetric isotherm (adsorbed amount vs equilibrium pressure); (b) calorimetric isotherm (evolved heat vs equilibrium pressure).

had a high Na^+ content, the corresponding band at 2356 cm^{-1} appears only as a shoulder on the main Li^+ band. This is due to the strong polarizing power of the Li^+ ion, which leads to a preferential retention of adsorbed CO_2. The $^{13}CO_2$ counterpart of the 2366 cm^{-1} band is expected to fall at 2299 cm^{-1}, and indeed the main band in the inset has components at 2299 and 2290 cm^{-1}, the latter being due to $^{13}CO_2$ adsorbed on Na^+ ions. The possible formation of 2/1 adducts (at a high equilibrium pressure) on Li^+ ions cannot be discerned from these spectra, because of the overlap between bands corresponding to $^{13}CO_2$ adsorbed on both Na^+ and Li^+ ions.

Spectra in the main body of Figure 4 show a minor component at 2376 cm^{-1}, i.e., a frequency higher than that assigned to CO_2 adsorbed on extraframework Al^{3+} ions. The interpretation of this band is not straightforward. As in the case of the 2365 cm^{-1} band for Na-ZSM-5, we think that this 2376 cm^{-1} band could be due to bicoordinated CO_2 species. This hypothesis will be developed elsewhere. Note that K-ZSM-5 and Cs-ZSM-5 did not show the corresponding band: this suggests that exchangeable cations must have a relatively large polarizing power to give rise to bicoordinated species.

Volumetric Measurements and Microcalorimetry. Figure 5a reports the volumetric isotherm (adsorbed amount versus pressure) for the adsorption of CO_2 at 303 K on K-ZSM-5. Figure 5b reports the corresponding calorimetric isotherm (evolved integral heat versus equilibrium pressure). Corresponding results for Na-ZSM-5 have been reported elsewhere.[5] The reversible nature of the adsorption was checked by carrying out a second adsorption run after desorption. From these data, the plot in Figure 6a (differential heat as a function of equilibrium pressure) was drawn. The first two doses show values of differential heat which appear to be slightly too high (see later). Discarding these values, the differential heat of adsorption is seen to decrease smoothly with coverage: an initial value of about 45 kJ mol^{-1} can be obtained by extrapolation to vanishing coverage, whereas at the highest CO_2 coverage the differential heat goes down to 30 kJ mol^{-1}. The curve in Figure 6a

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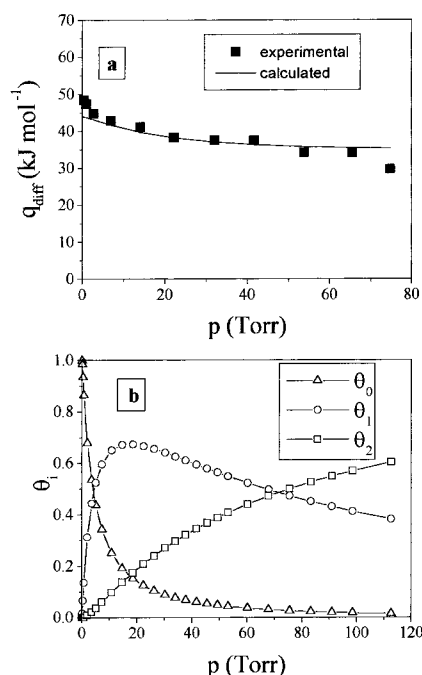*J. Phys. Chem. B, Vol. 104, No. 47, 2000* **10983**

Figure 6. (a) Differential heats for room-temperature adsorption of CO_2 on K-ZSM-5 outgassed at 723 K. (b) Calculated populations of sites bearing zero, one, and two CO_2 molecules, respectively (see the text).

(interpolating the data) has been obtained not by any fit to the experimental points, but through an overall thermodynamic procedure described below. Figure 6b shows the population of the different sites (see the Discussion) as a function of CO_2 equilibrium pressure.

From its nominal composition, it is inferred that the K-ZSM-5 sample used contains, at the most, about 1000 μmol g^{-1} of K$^+$ adsorbing sites. The volumetric isotherm in Figure 5a shows that the adsorbed amounts of CO_2 reach larger values: note that a plateau has not yet been attained. These facts suggest coordination of more than one molecule per adsorption site also in the case of the K-ZSM-5 sample, as was observed with the Na-ZSM-5 sample.[5]

Computational Results. Table 2 shows the calculated bond lengths for the free CO_2 molecule and for M$^+$···O=C=O adducts. Ab initio results for the frequency of the different vibration modes are given in Table 3. The calculated C$-$O bond length for the free CO_2 is 1.1613 Å, which compares very favorably with the experimental value of 1.1612 Å.[25] Basically, the same holds for the vibrational parameters (Table 3), although the frequencies of ν_2 and ν_1 modes appear to be slightly underestimated, whereas that of the ν_3 mode is somewhat overestimated. It should be noted, however, that ab initio values are computed in the harmonic approximation, whereas experimental values include anharmonic contributions. Table 3 also reports the specific intensities of the vibrational modes, for which, however, no direct comparison with experimental values is possible, because the molar absorption coefficients of the gas molecule heavily depend on the pressure.

Concerning the 1/1 adducts of CO_2 with an extraframework cation, a C_s symmetry was initially assumed. However, calculations led (in all cases) to a conformation close to a $C_{\infty v}$ symmetry. This means that the presence of two lone electron pairs on the O atoms of the carbon dioxide molecule plays no role. Deviations from linearity of the M$^+$···O=C=O adducts were found to be small, and they seemed to show an erratic behavior along the series M = Li, Na, K, and Cs. Therefore, a

TABLE 2: Ab Initio Bond Lenghts for Free CO_2 and M$^+$−CO_2 Adducts with $C_{\infty v}$ Symmetry^a

species	r_1	r_2	r_3
free CO_2		1.1613	1.1613
Li$^+$/CO_2	1.8531	1.1782	1.1418
Na$^+$/CO_2	2.2539	1.1750	1.1457
K$^+$/CO_2	2.7296	1.1725	1.1491
Cs$^+$/CO_2	3.2157	1.1714	1.1517

^{a} Distances in angstroms. r_1, r_2, and r_3 as shown in the scheme below:

$$M^+ \cdots O = C = O$$
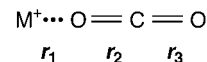$$\quad\; r_1 \quad\; r_2 \quad\; r_3$$

TABLE 3: Ab Initio Results for the Isolated CO_2 Molecule and for the 1/1 Adducts with Bare Cations^a

species	mode	frequency	IR intensity	BE	$\Delta H°$
CO_2 gas	ν_2	663	31		
	ν_1	1374	0.0000		
	ν_3	2414	658		
Li$^+$/CO_2	ν_{fr}	89 (71)	48		
	ν_{int}	449 (206)	188		
	ν_2	637	38	86.73	−83.63
	ν_1	1394	55		
	ν_3	2460	728		
Na$^+$/CO_2	ν_{fr}	77 (73)	7		
	ν_{int}	214 (155)	43		
	ν_2	649	36	55.01	−53.17
	ν_1	1385	27		
	ν_3	2445	713		
K$^+$/CO_2	ν_{fr}	64 (63)	3		
	ν_{int}	129 (110)	22		
	ν_2	653	34	33.60	−32.40
	ν_1	1378	17		
	ν_3	2432	715		
Cs$^+$/CO_2	ν_{fr}	38	0.4		
	ν_{nt}	74	5		
	ν_2	656	33	21.36	−20.50
	ν_1	1376	12		
	ν_3	2426	728		

^{a} Frequencies in cm^{-1}, specific intensities in km mol^{-1}, energies in kJ mol^{-1}. Values in parentheses were calculated assuming a cation mass equal to that of Kr (see the text).

$C_{\infty v}$ symmetry was imposed throughout. The values thus calculated, which correspond to true energy minima, are given in Tables 2 (bond length) and 3 (IR results and interaction energy). The energy of the cation$-CO_2$ interaction is given both as the binding energy (the difference between the absolute energy of the adduct and those of its constituents, hereafter indicated as BE), and $\Delta H°(0)$, the similar difference in enthalpy calculated at absolute zero, including the zero point energy. BE and $\Delta H°(0)$ results were not corrected for the basis set superposition error. $\Delta H°(0)$ values were found to be systematically smaller (by 3−4%) than corresponding values of BE, and they both cover a large range on going from Li$^+$ to Cs$^+$.

The CO_2 molecule undergoes a small distortion upon coordination to cations. The length of the C$-$O bond adjacent to the cation increases slightly, whereas the other C$-$O bond decreases by about the same amount (Table 2). This can be understood, in simple terms, assuming that the positive electric charge of the cation stabilizes the canonical form of the CO_2 molecule having separated charges, $^-$O$-$C$\equiv$O$^+$, in which one C$-$O bond is single and the other is triple. As a result, in the adduct, the bond adjacent to the cation has an order of less than 2 and accordingly elongates, whereas the opposite holds for the other C$-$O bond. The calculated values of r_2 (the length of the
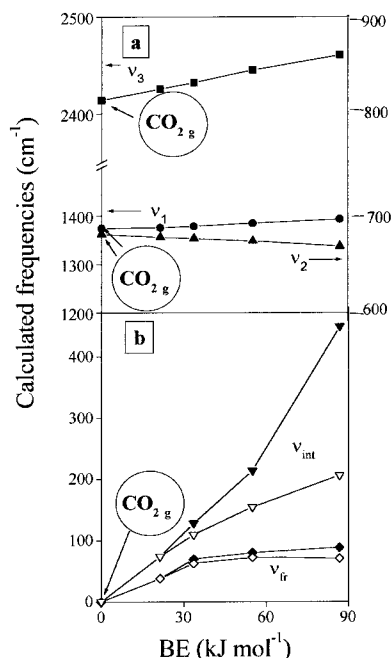
Figure 7. Dependence of calculated vibrational features on the binding energy of the adducts: (a) frequency of the fundamental modes of CO_2; (b) frequency of the intermolecular modes, both for the gaseous species $M \cdots O = C = O$ and for species where the cation has been given the mass of Cs.

C−O bond nearest to the cation) and r_3 (the distal C−O bond length) appear to follow a nearly linear variation with the corresponding BE values.

Infrared frequencies and intensities are reported in Table 3. Besides the three fundamental modes of the CO_2 molecule, two intermolecular modes are also present: one of them has σ_g symmetry and is an intermolecular stretch (ν_{int}); the other has π symmetry and corresponds to a frustrated rotation (ν_{fr}). The frequency of the ν_{fr} mode, which is degenerate for $C_{\infty v}$ symmetry, was always found to be considerably lower than that of the ν_{int} mode.

The above quantum chemical results concern isolated species of the type $M^+ \cdots O = C = O$. To make a proper comparison with experimental results, it has to be taken into account that the effective mass of extraframework cations in zeolites is not that given directly by the corresponding atomic mass, because the cation is embedded in the zeolite, and is therefore unable to move as freely as in the gas-phase species. The effect of this (increased) effective mass on the corresponding frequency values is expected to be larger for the lighter cations. To have a better approximation, frequencies were therefore recalculated, assigning to the cation an increasing mass up to that of a Kr atom. This was done for all cations with the exception of Cs^+, which was considered to already be heavy enough. The effect on intramolecular vibrations was found to be negligible. In contrast, sizable changes were observed in the intermolecular modes, which are a function of the effective mass. The mass of Kr suffices to cause the largest changes, which are small for K^+, and sizable for the lighter cations. It was also found that the effect of a change in the mass of the cation affects only moderately the frequency of the ν_{fr} mode and markedly that of the ν_{int} mode. All such values are reported in Table 3 in parentheses.

Figure 7 shows the dependence of the calculated IR frequencies on the strength of the cation−CO_2 interaction, as measured by BE. Corresponding values for the free molecule are also

reported. The ν_3 and ν_1 mode frequencies increase moderately in a linear manner with BE, whereas the ν_2 mode frequency shows a similar linear decrease. As for the intermolecular frequencies, the intermolecular stretch, ν_{int}, and the frustrated rotation, ν_{fr}, calculated for the $M^+ \cdots O = C = O$ gas species show a rather different behavior: ν_{int} depends strongly, nearly quadratically, on BE, whereas ν_{fr} tends to saturation with increasing BE. The set of data calculated for the cations with artificial Kr mass shows that the ν_{int} mode varies almost linearly with BE, whereas a nearly constant value was obtained for ν_{fr}.

Regarding the intensity of the main vibrational modes, the data in Table 3 show that the ν_2 mode exhibits a moderate decrease in specific intensity with increasing frequency. In contrast the intensity of the ν_1 mode shows a marked dependence on frequency, due to the fact that this mode is inactive in the free molecule. For the ν_3 mode an erratic behavior is seen: intensities vary little on the whole, but a sort of minimum is found, and the value for the free molecule is not clearly related to those of the adducts. We have no simple explanation for this behavior, which witnesses the delicate nature of ab initio computations, and further work is required.

Discussion

On all samples, with the likely exception of Li-ZSM-5, two molecules of CO_2 can be adsorbed on the same cation at a high equilibrium pressure. Evidence, as far as Na-ZSM-5 is concerned, has been provided in a previous paper[5] by quantitative estimates of adsorbed amounts, which show a ratio of adsorbed CO_2/Na^+ cations definitely greater than 1.[5] The same evidence is given in the present paper as far as the K sample is concerned (Figure 5a). Evidence concerning the case of the Cs sample is instead only of spectroscopic nature, i.e., the similar shift in frequency of the main ν_3 absorption with coverage.

With the Na sample, the adsorption of the second ligand is documented by the shift of the ν_3 band from 2356 to about 2352 cm^{-1} (Figure 1b), such a shift being better observed in the $^{13}CO_2$ region. The lower-frequency band is ascribed to the unresolved symmetric and asymmetric stretching modes of two CO_2 molecules interacting with the same Na^+ ion. The frequency of the band due to the pair of CO_2 molecules is expected to be lower than that corresponding to a single CO_2 ligand, since when two molecules share the same site, each of them should have a weaker interaction with the Na^+ ion. Similar observations can be made for the other cases (Table 1). The band shift due to the coordination of the second CO_2 molecule at high pressures amounts to −4, −3, and −2 cm^{-1} for the series of M^+-ZSM-5 zeolites, where M = Na, K, and Cs, respectively. The magnitude of the shift decreases in the same order as the cation−CO_2 interaction energy, as expected. These results are in agreement with previous studies[12] regarding carbon monoxide adsorption on Na-ZSM-5 and suggesting that more than one CO molecule can be adsorbed on the same cation site. Similarly, Huber and Knözinger[8] found that two CO molecules (or two N_2 molecules) can be coordinated to the Na^+ ion in Na-Y. In all these cases, a very limited decrease in frequency is recorded on passing from one to two ligands. A possible explanation is that adsorption of a second ligand actually involves a displacement of the cation from the surface, so that the cation becomes more available to interaction, and the effect of the insertion of a second ligand is compensated to some extent. Movements of the central cation upon adsorption have indeed been documented by EXAFS.[26]

The data in Table 1 offer the complete set of experimentally determined vibrations for a single CO_2 molecule adsorbed on the systems considered, including those intermolecular. Com-
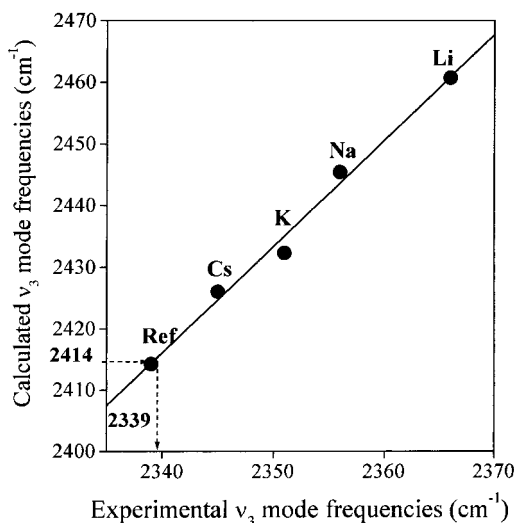
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Figure 8. Relationships between experimental and calculated features: (a) frequency of the ν_3 mode; (b) specific intensity of the ν_1 mode.

parison is therefore possible with calculated data in Table 3. The correlation between calculated and experimental values of the ν_3 mode is reported in Figure 8; a linear dependence was found, with a slope of about 0.58. Calculated values are always larger than experimental ones. The reason for this is that interaction of CO_2 with a bare cation is always stronger than interaction with the same cation embedded in the zeolite matrix, because of the effect of nearby oxygen anions. It should also be noted that calculated values correspond to harmonic vibrations, whereas experimental ones are decreased by anharmonicity. The plot in Figure 8 affords a means to obtain a reference value for the zeolite-encased CO_2 molecule in the absence of any specific interaction. As already pointed out for other molecules, e.g., dinitrogen,[27] the free-molecule value is not appropriate, because the role of the matrix is neglected. Indeed, the value observed in the present work for CO_2 on Cs-ZSM-5 (2345 cm^{-1}) is below the gas-phase value (2349.3 cm^{-1}), and that for K-ZSM-5 is just marginally higher. Using the linear correlation in Figure 8, and the calculated value of 2414 cm^{-1} for the free molecule, a reference value of 2339 cm^{-1} is obtained for the ν_3 mode of CO_2 interacting with the ZSM-5 matrix, which is 10 cm^{-1} smaller than the free-molecule experimental value. This is reassuring, because the value for CO_2 on Cs-ZSM-5 is now well above the reference. Note that the (calculated) reference value (2339 cm^{-1}) is nearly coincident with that of 2341 cm^{-1}, which was observed for the ν_3 mode of CO_2 adsorbed on silicalite, which is a purely siliceous molecular sieve of the ZSM-5 family having no extraframework cation.

The plot in Figure 8 seems to suggest that the naked cation model could represent a satisfactory approach to the behavior of extraframework alkali-metal cations in the ZSM-5 zeolite. There is, however, some evidence that such a model does not suffice to describe the interaction between CO_2 and an extraframework cation. The experimental values of ν_{int} (Table 1) show only a small dependence on the cation present in the zeolite, whereas calculated values (Table 3) show a much more pronounced dependence. To a large extent, the same argument is also valid for the ν_{fr} mode; note that the experimental values seem to be cation independent. Similarly, the ν_2 mode was experimentally found to always be at virtually the same location (656 cm^{-1}) for all samples, whereas according to calculations its frequency should decrease with increasing BE (Figure 7a).

These are remarkable disagreements between trends followed by experimental and computed frequency values.

Other points of disagreement between experimental results and the bare cation concern the energetics of interaction. As far as the Na-ZSM-5 is concerned, the value experimentally determined for $\Delta H°$ in our previous paper[5] is 49 kJ mol^{-1}. A very close value was also reported in an accurate set of experiments by Dunne et al.[28] Such a figure is exceedingly close to the calculated value (53 kJ mol^{-1}). Because of the absence of surrounding anions, the interaction of CO_2 with the bare cation is expected to be markedly more energetic. Note, in this context, that for CO the calculated BE values were about 3 times larger than those found experimentally.[15,16] A similar inconsistency was also found for K-ZSM-5.

The thermodynamics of adsorption of CO_2 on K-ZSM-5 follows closely that found for Na-ZSM-5, which was discussed in a previous paper.[5] Coordination of two CO_2 molecules to the same cation, as described by eq 2 above, affords the basic reason for the decrease in differential heats of adsorption when the equilibrium pressure is increased (Figure 6a). A possible additional cause for the decrease in the differential heat of adsorption with increasing CO_2 equilibrium pressure could be heterogeneity of K$^+$ sites, but this is not supported by the corresponding IR spectra (Figure 2). It is possible, therefore, to consider the adsorbent system as being essentially homogeneous, at least as far as CO_2 adsorption is concerned. Consequently, the adsorption isotherms (Figure 5) were analyzed under the hypothesis of ideality, as far as the equivalence of sites is concerned, and assuming that one or two molecules may enter the coordination sphere of each K$^+$ ion. Defining N_m as the number of cations per gram of adsorbent, K_1 and K_2 as the equilibrium constants for eqs 1 and 2, and θ_0, θ_1, and θ_2 as the molar fractions of sites, respectively empty, carrying one, and carrying two molecules of CO_2, the following equations can be written:[29]

$$\theta_0 = 1/(1 + K_1 p + K_1 K_2 p^2) \qquad (3)$$

$$\theta_1 = K_1 p/(1 + K_1 p + K_1 K_2 p^2) \qquad (4)$$

$$\theta_2 = K_1 K_2 p^2/(1 + K_1 p + K_1 K_2 p^2) \qquad (5)$$

so that the volumetric isotherm is described by

$$N_a = N_m(K_1 p + 2K_1 K_2 p^2)/(1 + K_1 p + K_1 K_2 p^2) \qquad (6)$$

Data in Figure 5a have been fitted by using eq 6, and the following values have been found: $N_m = 775$ μmol; $K_1 = 0.240 \pm 0.012$ Torr^{-1}; $K_2 = 0.01403 \pm 0.00054$ Torr^{-1}. The fit was found to be excellent, the uncertainty on the calculated parameters is small, and the N_m value is not far from that expected on the basis of chemical composition.

To illustrate the changes in the molar fractions of differently populated sites, Figure 6b reports the variation of θ_0, θ_1, and θ_2 as a function of pressure for the actual values of the equilibrium constants K_1 and K_2. As expected, in the low-pressure range θ_1 increases in parallel with the decrease of θ_0. At an equilibrium pressure of 17 Torr the population of sites carrying one molecule reaches a maximum. It is readily checked that this pressure equals $(K_1 K_2)^{-1/2}$ and that at such a pressure the population of empty sites equals that of doubly occupied sites; i.e., on average the coverage is 1. At 60 Torr (about the highest pressure investigated in the present calorimetric measurements) the fraction of empty sites is close to zero, and only the second reaction (Equation 2) takes place.

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TABLE 4: Equilibrium Constants K_1 and K_2 (Torr^{-1}) and Related $\Delta G°_1$, $\Delta G°_2$, $\Delta H°_1$, and $\Delta H°_2$ (kJ mol^{-1}) and $\Delta S°_1$ and $\Delta S°_2$ (J mol^{-1} K^{-1}) for the Adsorption of One and Two CO_2 Molecules, Respectively, on M-ZSM-5^a

	Li-ZSM-5	Na-ZSM-5	K-ZSM-5	Cs-ZSM-5
K_1	6.61 ± 0.84	0.199 ± 0.027	0.240 ± 0.012	0.212 ± 0.084
K_2		0.0151 ± 0.0019	0.0140 ± 0.0005	0.0084 ± 0.0206
$\Delta G°_1$	-4.74	$+4.05 \pm 0.07$	$+3.58 \pm 0.03$	$+3.89 \pm 0.21$
$\Delta G°_2$		$+10.57 \pm 0.01$	$+10.71 \pm 0.001$	$+12.00 \pm 0.05$
$\Delta H°_1$		-49 ± 3	-44.11 ± 0.73	
$\Delta H°_2$		-35 ± 3	-39.48 ± 0.67	
$\Delta S°_1$		-173	-157	
$\Delta S°_2$		-280	-166	
ϵ_1	4.27 ± 0.04	4.2 ± 0.03	1.4 ± 0.01	1.2 ± 0.3
ϵ_2		2.36	0.78	0.81

^{a} Values for Na-ZSM-5 and K-ZSM-5 were derived from volumetric and calorimetric measurements; for Li-ZSM-5 and Cs-ZSM-5 they were obtained from the corresponding optical isotherms. Molar absorption coefficients ϵ_1 and ϵ_2 (km mol^{-1}) are for the ν_1 mode of 1/1 and 2/1 adducts, respectively.

The standard Gibbs energies of reactions 1 and 2 are, respectively, $\Delta G°_1 = -RT \ln K_1 = +3.6$ kJ mol^{-1} and $\Delta G°_2 = -RT \ln K_2 = +10.71$ kJ mol^{-1}. The positive values of the standard changes in free energy are related to the choice of 1 Torr as the reference for the gas phase: taking the value of 1 atm for the reference standard pressure, the standard changes in free energy would have the more familiar negative sign. Table 4 summarizes the relevant thermodynamic results for all the zeolite samples studied.

The calorimetric isotherm in Figure 5b can be described as

$$Q_{int} = N_m[\Delta H°_f(1)K_1p + \Delta H°_f(2)K_1K_2p^2]/$$
$$(1 + K_1p + K_1K_2p^2) \quad (7)$$

where $\Delta H°_f(1)$ and $\Delta H°_f(2)$ are the molar enthalpies of formation of the 1/1 and 1/2 adducts, respectively. While $\Delta H°_1 = \Delta H°_f(1)$, elementary thermodynamics shows that $\Delta H°_f(2) = \Delta H°_1 + \Delta H°_2$, because the reaction of formation of the adduct with two CO_2 molecules

$$Z\text{-}K^+ + 2(CO_2)_g \leftrightarrow Z\text{-}K^+(CO_2)_2 \quad (8)$$

is the algebraic sum of reactions 1 and 2. Similarly, $\Delta G°_1 = \Delta G°_f(1)$ and $\Delta S°_1 = \Delta S°_f(1)$, but $\Delta G°_f(2) = \Delta G°_1 + \Delta G°_2$ and $\Delta S°_f(2) = \Delta S°_1 + \Delta S°_2$. Alternatively, instead of $\Delta H°_f(2)$, the standard enthalpy of formation of the adduct with two CO_2 molecules, the average value $\Delta H°_f(av) = \Delta H°_f(2)/2$ may be considered, which measures the enthalpy of formation of the two-molecule adduct per CO_2 molecule. Data in Figure 5b have been fitted by means of eq 7, by assuming the values of N_m, K_1, and K_2 determined from the volumetric isotherm, given above. The only parameters to be determined were therefore $\Delta H°_f(1)$ and $\Delta H°_f(2)$. Note that it is possible to linearize eq 7 by rewriting it as

$$[Q_{int}(1 + K_1p + K_1K_2p^2)]/[N_mK_1p] =$$
$$\Delta H°_f(1) + \Delta H°_f(2)K_2p \quad (9)$$

The fit (not shown) was found to be quite satisfactory, and from it the values $\Delta H°_f(1) = -44.11 \pm 0.73$ kJ mol^{-1} and $\Delta H°_f(2) = \Delta H°(1) + \Delta H°(2) = -83.59 \pm 0.70$ kJ mol^{-1} were obtained. Note that this last value implies that the enthalpic content corresponding to each CO_2 ligand in the 2/1 adduct takes the value $\Delta H°_f(av) = \Delta H°_f(2)/2 = -41.80 \pm 1.40$ kJ mol^{-1}.

In terms of absolute values, $\Delta H°_f(av)$ is smaller than $\Delta H°_f(1)$ because the second carbon dioxide molecule interacts with a K^+ ion already coordinated to one CO_2 ligand. The standard enthalpy of reaction 2 is only $-83.59 + 44.11 = -39.48$ kJ mol^{-1}: this value should also be the limit of the differential heat of adsorption at high coverages, when only reaction 2 takes place. Equations 3–7 can be used to calculate the differential heat of adsorption, dQ/dN, as a function of pressure, which takes the form

$$dQ/dN = \Delta H°_f(1) f(p) + \Delta H°_f(2) g(p) \quad (10)$$

where

$$f(p) = (1 - y)/[1 - y + 2K_2p(2 - y)] \quad (11)$$

$$g(p) = K_2p(2 - y)/[1 - y + 2K_2p(2 - y)] \quad (12)$$

$$y(p) = (K_1p + 2K_1K_2p^2)/(1 + K_1p + K_1K_2p^2) \quad (13)$$

The limit of dQ/dN for a vanishing pressure is $\Delta H°_f(1)$, whereas that for a very large pressure is $\Delta H°_f(2) - \Delta H°_f(1)$. Since all parameters entering eq 10 are known, the differential heat of adsorption can be calculated. The result obtained is shown in Figure 6a (continuous line): the calculated curve represents very satisfactorily the experimental points. The first two points appear somewhat higher: we ascribe such a higher differential heat to the presence of some Al^{3+} cations which become exposed because of dealumination.

Knowledge of $\Delta H°_f(1)$ from calorimetric measurements, together with the knowledge of $\Delta G°_f(1)$ from the adsorption isotherm, allows the evaluation of $\Delta S°_f(1)$, the standard entropy of formation of the 1/1 adduct, which is found to be -157 J mol^{-1} K^{-1}. Following a similar procedure, the value $\Delta S°_f(2) = -323$ J mol^{-1} K^{-1} was obtained. The formation of weaker bound adducts ($\Delta H°_f(av) = -41.80$ kJ mol^{-1} as compared to $\Delta H°_f(1) = -44.11$ kJ mol^{-1}; see above) implies a higher residual entropy: this corresponds to the concept of the compensation effect, which is well-known in adsorption and catalysis.

Comparison of the energy parameters for CO_2 adsorption on K-ZSM-5 with corresponding values for Na-ZSM-5 (Table 4) shows striking similarities between both systems, notwithstanding the sizable change in the polarizing power of the cation. The equilibrium constant K_1 is even larger for K^+ than for Na^+, contrary to expectation, and the values of K_2 are nearly coincident. The heats of formation of the 1/1 adducts are in the expected order, the $\Delta H°_1$ value for Na^+ being larger than that for K^+, but the difference between them is unexpectedly small.

A possible explanation for this behavior and for that concerning some of the vibrational modes can be given in terms of secondary interactions of the CO_2 molecule with nearby anions of the zeolite framework. Carbon dioxide has a marked quadrupolar moment, which facilitates interaction with the negative field exerted to the side of the molecule by anions, and this interaction would lead to a stabilization of the adduct. The role of quadrupolar interactions in the adsorption of CO_2 on zeolites was recognized long ago by Barrer and Gibbon.[30]

A secondary interaction involving the quadrupole of CO_2 and the field of nearby anions is probably present also for CO_2 adsorbed on Li-ZSM-5 and Cs-ZSM-5. Direct volumetric and calorimetric measurements of heats of adsorption were not possible in these cases because of incomplete exchange and some dealumination of the zeolite framework. IR measurements are, instead, not much affected by dealumination. Adsorption
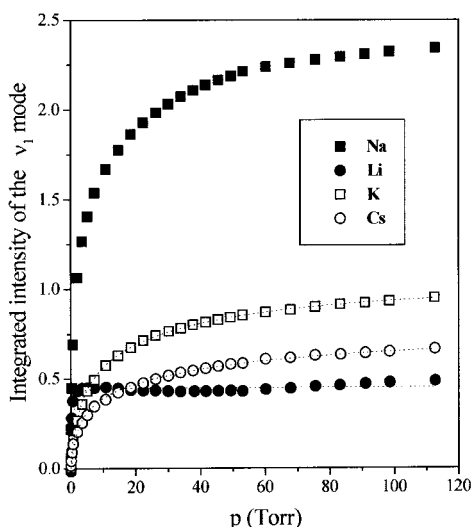
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Figure 9. Integrated optical density of the 1382 cm^{-1} band as a function of CO_2 equilibrium pressure.

isotherms were measured by taking advantage of the fact that the ν_1 mode is insensitive to the cation and rather weak, because the symmetry of the adsorbed molecule is very little perturbed from that of the free state. Optical isotherms were therefore drawn by plotting the intensity of the 1382 cm^{-1} band (ν_1 mode) as a function of pressure.

The top curve in Figure 9 represents the experimental data for CO_2 on Na-ZSM-5. As discussed in detail in our previous work,[5] they conform to the expression

$$A(1382) = N_m(\epsilon_1 K_1 p + 2\epsilon_2 K_1 K_2 p^2)/$$
$$(1 + K_1 p + K_1 K_2 p^2) \quad (14)$$

where $A(1382)$ is the integrated optical density at a given pressure (p), ϵ_1 and ϵ_2 are the extinction coefficients of the CO_2 molecule in the 1/1 and 2/1 adducts, respectively, N_m is the total number of adsorbing centers, and K_1 and K_2 are the equilibrium constants of reactions 1 and 2, respectively, as calculated from the volumetric isotherm.[5] The fraction of sites carrying one and two CO_2 molecules, respectively, is given by[29] $\theta_1 = K_1 p/(1 + K_1 p + K_1 K_2 p^2)$ and $\theta_2 = K_1 K_2 p^2/(1 + K_1 p + K_1 K_2 p^2)$. Equation 14 may be linearized, by a procedure similar to that employed for the integral heats of adsorption, as

$$A(1382)(1 + K_1 p + K_1 K_2 p^2)/(N_m K_1 p) = \epsilon_1 + 2\epsilon_2 K_2 p \quad (15)$$

Fitting of the optical isotherm yielded $\epsilon_1 = 4.2$ km mol^{-1} and $\epsilon_2 = 2.36$ km mol^{-1}. The reason the 1382 cm^{-1} mode is less intense in 2/1 than in 1/1 adducts is the same one explaining the bathochromic shift of the ν_3 mode, i.e., the fact that in the 2/1 adduct two CO_2 molecules have to share the same cation, which results in a decreased polarizing power. This has a marked effect on the intensity of the ν_1 mode, which is forbidden in the free molecule. For an analogous reason, the calculated value of the molar adsorption of this mode in 1/1 adducts decreases markedly along the series Li$^+$ to Cs$^+$ (Table 3).

Data for the other samples, also reported in Figure 9, were obtained by carefully subtracting from the measured intensity of the 1382 cm^{-1} band the contribution of the Na$^+$ cations still present in the zeolite because of incomplete exchange, as evaluated from the corresponding chemical composition. Data have been normalized to the sample weight. The value of N_m, the total amount of sites of the specific cation under consider-

ation per unit mass, was derived from the corresponding chemical composition, under the hypothesis that dealumination was negligible in the IR experiments.

In the case of K-ZSM-5, the fit of the optical isotherm has been carried out as for Na-ZSM-5, i.e., by making use of the values of N_m, K_1, and K_2 obtained from volumetric data and by means of eq 15. Results are shown in Table 4, including the values obtained for ϵ_1 and ϵ_2. It is seen that both molar absorption coefficients are smaller than for Na-ZSM-5, as expected because of the smaller polarizing power of the K$^+$: their ratio, though, is closer to 1, probably because the larger cation can better accommodate two CO_2 ligands.

The bottom curve in Figure (Li-ZSM-5) saturates at an equilibrium pressure below 1 Torr in contrast with all the other optical isotherms. Spectroscopic evidence from Figure 4 (inset) is not conclusive about the possible formation of 2/1 adducts; however, the shape of the optical isotherm definitely suggests that adsorption of the second CO_2 molecule does not take place: the Li$^+$ ion, partially shielded by the nearest oxygen atoms, seems to be too small to coordinate two CO_2 molecules. Data have accordingly been fitted by a Langmuir isotherm, to which eq 3 reduces for vanishing K_2 and ϵ_2:

$$A = N_m \epsilon_1 K_1 p/(1 + K_1 p) \quad (16)$$

Resulting values of ϵ_1 and K_1 are given in Table 4.

Fitting the data for Cs-ZSM-5 by means of eq 15 is delicate, because four parameters are needed. Instead of using the adequacy of fit as the only criterion, fitting has been carried out for a selected set of ϵ_1, K_1, ϵ_2, and K_2 values, which have been carefully examined, requiring that, besides yielding a satisfactory fit, they would be meaningful in the present context, i.e., their magnitude would follow the trends found for the whole series of cations. It was actually possible to do so, and the chosen values are reported in Table 4.

The values of the equilibrium constants K_1 decrease markedly on passing from Li$^+$ to the other cations, because the interaction with CO_2 becomes weaker, and accordingly the corresponding $\Delta G°_1$ values are observed to increase. In contrast, the K_1 values for the other cations fall within 20% of each other. The value for Cs$^+$ is marginally smaller than that for K$^+$, but the latter is instead somewhat larger than that for Na$^+$. The energy of interaction predicted by computations concerning the interaction with the sole cation shows instead a remarkable decrease along the series Li$^+$ to Cs$^+$. The overall data in Table 4 confirm the presence of a double interaction of the CO_2 molecule, with both the cation and the nearby anion, not sufficient to bring about the formation of carbonates, but strong enough to contribute to the energetics of the process. In the series from Li$^+$ to Cs$^+$, the cation becomes progressively a weaker Lewis acid: it is not unlikely, however, that the adjacent anions become progressively stronger as a base, so as to cause a sort of internal compensation. This would explain why the interaction with Cs-ZSM-5 is still rather strong. Such an effect would also cancel out the differences between different sites in the same sample. It should be noted that increased basicity of anions can be expected when they are less polarized by cations. It is worth noting that, in their pioneering work on the adsorption of CO_2 on alkali-metal-exchanged Y zeolites, Barrer and Gibbon[30] found that the initial heat of adsorption was quite the same, irrespective of the cation. Notwithstanding the concomitant presence of carbonate species, this fact is in support of what is observed in the present work. Note that in the case of Y zeolites the increase in the basicity of the oxygen atom has been documented by the adsorption of suitable probes such as pyrrole.[31]

One discrepancy worth discussion is the fact, observed in Figures 1a and 2, that the CO_2 pressure at which the absorbance value of 2.0 is attained is 1.5 Torr in the case of K-ZSM-5, as opposed to 0.3 Torr in the Na-ZSM-5 case. The difference is not large, and this does not contradict the conclusions drawn. It is however in contrast with the data concerning the K_1 values in the two cases, showing that the equilibrium constant for K-ZSM-5 is ever larger than that for Na-ZSM-5. Although care must be exercised, and the error bars taken into account, this could be evidence of some heterogeneity in the distribution of cations. In both the Na-ZSM-5 and K-ZSM-5 cases, a fraction of sites are stronger than the rest of the adsorption centers, as documented by the initial heats of adsorption. These are the first to be filled, so that the pressure at which an absorbance of 2 is obtained probably is a measure of the relative strength of the stronger sites, in contrast with the K_1 value, which averages over the entire range of cations.

Table 4 also reports the values of ϵ_1 and ϵ_2: these are seen to increase steadily with the strength of interaction, as expected. This seems to suggest that the intensification of the ν_1 mode is mainly dictated by the interaction with the cation.

Conclusions

Although the main process determining the energetics of the CO_2/M^+-ZSM-5 system (M = Li, Na, K, Cs) is a direct, end-on interaction of CO_2 with the alkali-metal cation, nearby oxygen anions (in the zeolite framework) modulate the interaction process and give rise to a fine-tuning of the energetics, which is reflected in the corresponding thermodynamic parameters and in the IR spectra of the adsorbed CO_2 molecule. A combination of IR spectroscopy results, adsorption microcalorimetry, and computational studies enabled a detailed analysis of the adsorption process to be carried out. A two-step CO_2 adsorption was found to take place in all alkali-metal-exchanged ZSM-5 samples, with the possible exception of Li-ZSM-5, where only 1/1 adducts were identified.

Analysis of the ensemble of experimental and computational results concerning the whole M^+-ZSM-5 series showed that adsorbed CO_2 molecules interact not only with the M^+ cation, but also with the nearest oxygen anions. Although the role of the cation prevails, interaction with anions increases as that with the cation is progressively weakened on going from Li^+ to Cs^+. The dual nature of the interaction is a relevant conclusion of the present work, which could not be anticipated on the basis of our previous results[5] on the CO_2/Na-ZSM-5 system alone. The CO_2 molecule acts as a probe for the combined electric field created by a cation and nearby anions. However, it should be stressed that interaction with oxygen anions is never strong enough to give rise to carbonate species, such as those observed for CO_2 adsorbed on more ionic zeolites such as Na-A and faujasites.[24]

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