

## Spectroscopic Characterization of the Hydroxyl Groups in SAPO-40. 2. Interaction with CO and N<sub>2</sub>

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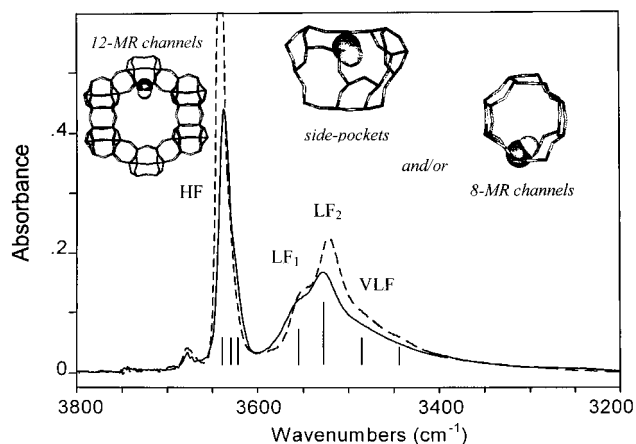
SAPO-40 exhibits five main OH species, describable as high-frequency ones (HF, at 3737, 3730, and 3724 cm<sup>-1</sup>) and low-frequency ones (LF<sub>1</sub> and LF<sub>2</sub>, at 3559 and 3528 cm<sup>-1</sup>, respectively), the former probably sitting in 12-member-ring channels and the latter either in side pockets or eight-member-ring channels of the AFR structure. The low-temperature interaction of such OH species with CO shows that HF species have strictly similar acidity (comparable to that of HY zeolites), in contrast with previous results concerning H-transfer to NH<sub>3</sub>. The ease of interaction and the spectral features are in accord with the location in large cavities. The vibration of H-bonded hydroxyl has a noticeable structure with subbands. The interaction of CO with LF<sub>1</sub> and LF<sub>2</sub> species occurs with difficulty and yields nonlinear complexes because of the steric hindrance brought about by small cavities. Adsorption of N<sub>2</sub> follows similar patterns.

### Introduction

SAPO materials (a new generation of silicoaluminophosphate molecular sieves) have been extensively studied since their first synthesis in 1984.<sup>1</sup> SAPO-40 is a novel member of this family with AFR structure,<sup>2,3</sup> firstly synthesized in a pure form by Dumont et al.<sup>4</sup> A rather thorough characterization by means of NMR spectroscopy is available.<sup>5–7</sup> Catalytic data<sup>8,9</sup> indicate that SAPO-40 possesses satisfactory thermal and hydrothermal stability and that in cracking reactions it is more active than SAPO-37 with the same silicon content. Its selectivity is comparable to USHY and it is more resistant to deactivation by coke than mordenite: its propensity for hydrogen transfer is however lower than that of USHY and mordenite.

Recently we have studied the IR spectrum of SAPO-40 in the hydroxyl region.<sup>10</sup> This is reported in Figure 1, together with a schematic description of the nature of the different OH species. Negligible amounts of terminal OH species (such as P–OH and/or Al–OH groups) are present. Up to seven types of Si(OH)Al Brønsted sites have been found to occur,<sup>10</sup> whose spectral features are reported in Table 1.

Species A' is not evident in the spectrum, but its occurrence is revealed by the reaction with ammonia.<sup>10</sup> The three high-frequency bands (3637–3624 cm<sup>-1</sup>), collectively referred to as HF species, correspond to hydroxyls located in the 12-member-ring channels and the two low-frequency (LF) bands (3559 and 3528 cm<sup>-1</sup>) to OH species in the eight-member ring and side pockets of the AFR structure. Two bands at exceptionally low frequency (VLF, 3485 and 3445 cm<sup>-1</sup>) are assigned to OH species interacting with silica domains inside the SAPO.<sup>10</sup> The very limited half-width of HF species (only some 15 cm<sup>-1</sup>) is indicative of a strict homogeneity among hydroxyls of the same kind, i.e. of a remarkable perfection of the crystalline edifice. HF and LF species behave in an opposite way upon cooling, in



**Figure 1.** IR spectra of SAPO-40 in the O–H stretching region and structures corresponding to different OH species: solid curve, room temperature; broken curve, nominal 77 K.

**TABLE 1**

notation		frequency at RT (cm <sup>-1</sup> )	$\Delta\nu_{1/2}$ at RT	frequency at 77 K (cm <sup>-1</sup> )
HF	A	3637	10	3643
	A'	3630	10	3637
	B	3624	14	3630
LF <sub>1</sub>	C	3559	30	3552
LF <sub>2</sub>	D	3528	45	3521
VLF	E	3485	60	3480
	F	3445	75	3440

that the former shift to higher frequencies and the latter to lower frequencies.

The acidity of the various OH species has been studied in our previous paper by adsorption/desorption of NH<sub>3</sub>. It results that among the HF species B is the most acidic, and between LF species, LF<sub>2</sub> is more acid than LF<sub>1</sub>. The acidity of both LF species is about the same as that of species A. The strongest acidity of species B, together with other evidence, suggests that this species consists of Si(OH)Al groups located on the border of silica domains in the SAPO framework.<sup>10</sup>

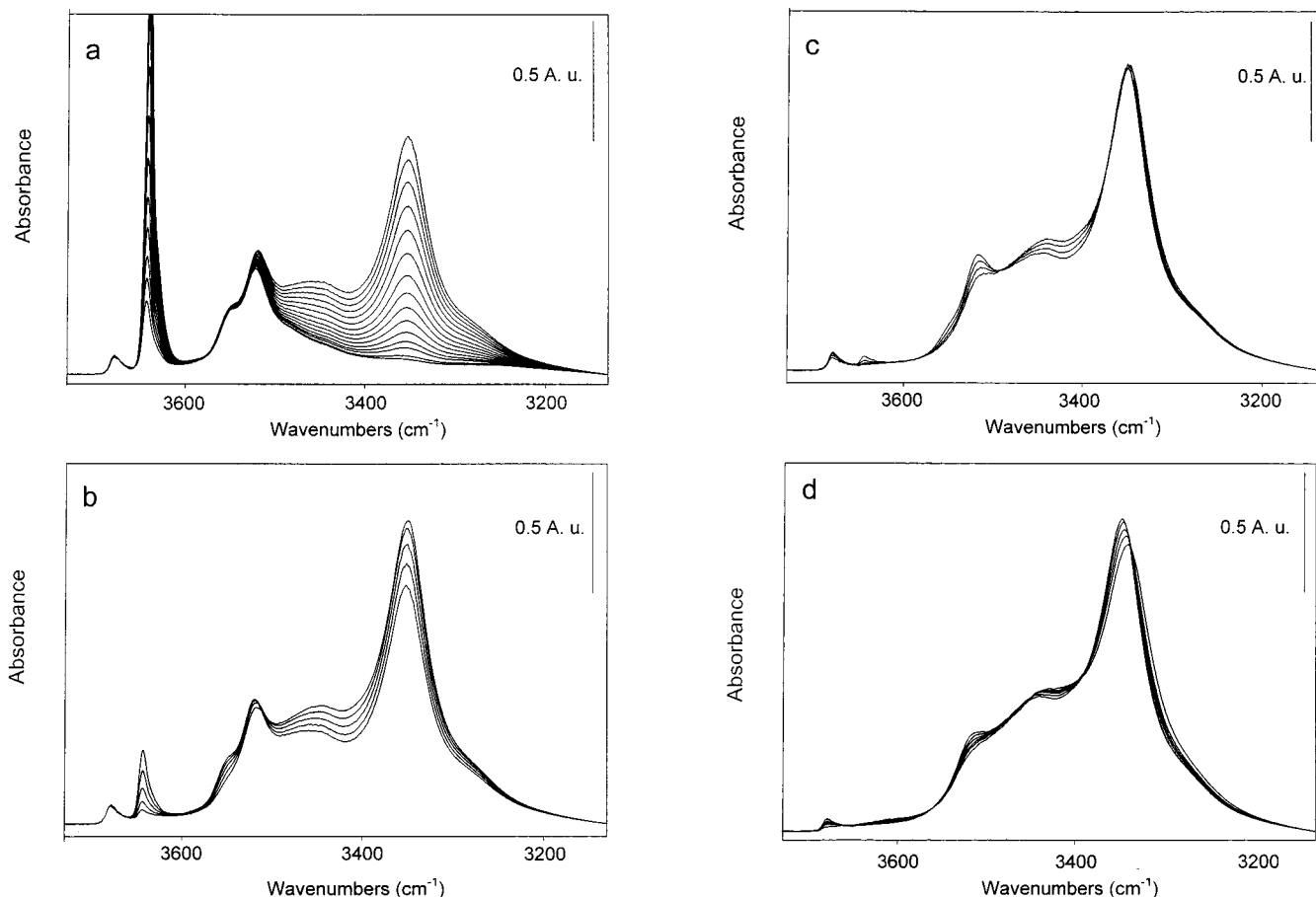
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**Figure 2.** IR spectra illustrating the reversible adsorption of CO at nominal 77 K on SAPO-40 (O–H stretching region): (a)  $10^{-3} < p < 10^{-2}$  Torr; (b)  $10^{-2} < p < 10^{-1}$  Torr; (c)  $10^{-1} < p < 1.5$  Torr; (d)  $p > 1.5$  Torr.

To determine in an alternative way the acidic strength of the different hydroxyl species, the low-temperature interaction with weak bases such as CO and N<sub>2</sub> has been investigated by means of IR spectroscopy: the data are reported in the present work, together with some molecular graphics simulation of the interaction of CO with different sterically accessible OH species.

CO has been extensively used as a probe molecule to test the acidity of zeolites [ref 11, and references therein]. More recently N<sub>2</sub> has been proposed as a probe for acid sites [refs 11, 12, and references therein]: its stretching mode, Raman but not IR active in the gas phase, becomes so under polarization due to the adsorption sites.

For comparison, adsorption of CO and N<sub>2</sub> has also been performed on a sample of AlPO-40, which does not exhibit any Brønsted acid sites.

## Experimental Section

The SAPO-40 and AlPO-40 samples were prepared according to the literature.<sup>4,7,13</sup> For IR measurements, the powder was pelleted into self-supporting discs and placed in a cell allowing thermal treatments both in vacuo and in a controlled atmosphere. Successively, samples were slowly calcined up to 800 K for 5 h and then oxidized in O<sub>2</sub> at the same temperature for an additional 1 h.

The adsorption of CO and N<sub>2</sub> was carried out at a nominal temperature of 77 K. All interactions occurring when dosing both gases are completely reversible. The IR spectra were recorded on a Bruker IFS 66 spectrophotometer equipped with an MCT cryodetector, at a resolution of 2 cm<sup>-1</sup> (about 100 scans).

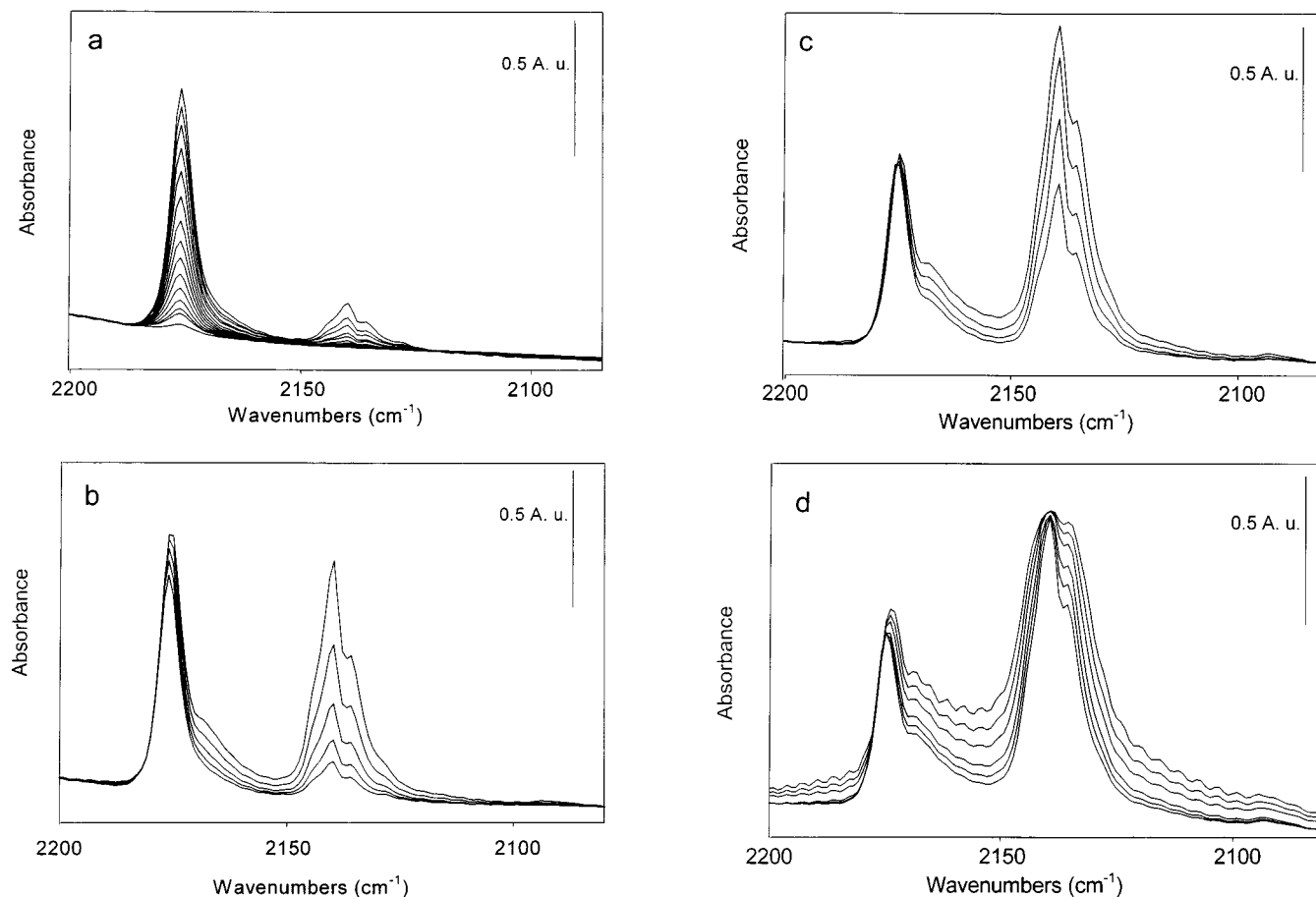
Curve fitting of the spectra was carried out by means of the program Curvefit available in the package Spectra Calc. provided by Galactic Industries Co. Molecular graphics were performed with the software program "InsightII" from Biosym Technology Inc. running on a SGI 4D/35 workstation.

## Results

**Adsorption of CO.** Figure 1 illustrates the adsorption of CO in the 3700–3100 cm<sup>-1</sup> region. Four stages may be singled out in the process, three of which correspond roughly to the interaction with HF, LF<sub>1</sub>, and LF<sub>2</sub> species, respectively, and the fourth to the capillary condensation. Each section of the figure deals with these four stages.

With the first doses of CO (ca.  $10^{-3} < p < 10^{-2}$  Torr, Figure 2a), the HF band decreases and simultaneously a band at 3353 cm<sup>-1</sup> increases, together with two broad components centered around 3450 and 3280 cm<sup>-1</sup>. No erosion is observed for LF species and terminal POH/AlOH species (weak band at 3675 cm<sup>-1</sup>).

The question arises about the nature of the two bands at 3450 and 3280 cm<sup>-1</sup>, which increase along with the main band at 3353 cm<sup>-1</sup>. A straightforward interpretation consists in the assignment of the three bands at ~3450, 3353, and ~3280 cm<sup>-1</sup> to the three HF species involved in the H-bond,<sup>11</sup> respectively. So, taking into account the highest acidity of species B, this could be associated with the band at ~3280 cm<sup>-1</sup>, showing  $\Delta\nu_{\text{OH}} \approx 350$  cm<sup>-1</sup>; the band at 3353 cm<sup>-1</sup> could be assigned to species A, with  $\Delta\nu_{\text{OH}} = 290$  cm<sup>-1</sup>, and finally the band at ~3450 cm<sup>-1</sup> could be ascribed to species A', which would exhibit the lowest acidity among the HF species ( $\Delta\nu_{\text{OH}} \approx 200$  cm<sup>-1</sup> only), in agreement with the data concerning the interac-



**Figure 3.** Same IR spectra as in Figure 2 in the CO stretching region.

tion with  $N_2$  (see below). Indeed the visual inspection of the HF band envelope seems to indicate preferential erosion on the low-frequency side.

Various evidence and considerations, however, which are discussed in detail in the next section, lead to discarding this interpretation and to assuming, instead, that the interaction with CO does not actually discriminate among the different HF species, which interact together giving rise to a single absorption at  $3353\text{ cm}^{-1}$ . The apparent preferential erosion on the low-frequency side is to be ascribed to a change in temperature along the measurement caused by a change in the pressure of CO, which also acts as a heat carrier medium.

The frequency shift ( $\Delta\nu_{\text{OH}}$ ) and the half-width ( $\Delta\nu_{1/2}$ ) of the band are some 290 and  $60\text{ cm}^{-1}$ , respectively. The  $\Delta\nu_{\text{OH}}$  value, which is a measure of the acidity of the OH species,<sup>11</sup> is the same as that observed for SAPO-34,<sup>14</sup> H-mordenite,<sup>11,15</sup> and HY.<sup>16</sup>

The widening of the perturbed band with respect to the unperturbed one is about  $45\text{ cm}^{-1}$ . This value is in agreement with the correlation proposed by Makarova et al.<sup>17</sup> between the widening and the shift of the band of zeolitic acidic OH groups interacting via H-bonding with weak molecules, i.e.  $(\Delta\nu_{1/2} - \Delta\nu_{1/2}^0)/\Delta\nu_{1/2}^0 = 0.010\Delta\nu_{\text{OH}}/\text{cm}^{-1}$ , where  $\Delta\nu_{1/2}$  and  $\Delta\nu_{1/2}^0$  are the half-widths of the perturbed and unperturbed bands, respectively.

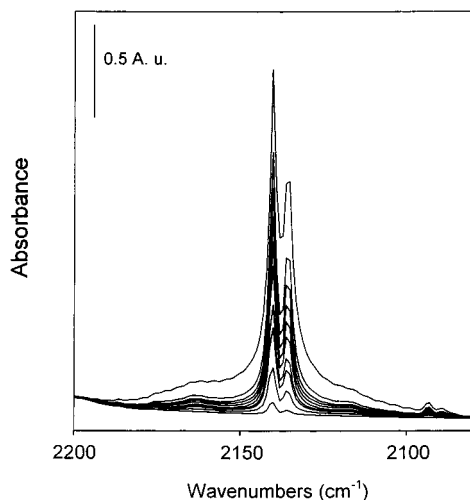
Bringing the CO equilibrium pressure in the range  $10^{-2} < p < 10^{-1}$  Torr (Figure 2b) causes a further decrease of the HF band, accompanied by a further increase of the band at  $3350\text{ cm}^{-1}$  and the two components at  $\sim 3450$  and  $\sim 3280\text{ cm}^{-1}$ . The component at higher frequency, however, increases more than at  $3280\text{ cm}^{-1}$  and seems to shift to lower frequency. As simultaneously the  $\text{LF}_1$  band decreases, we ascribe the increase

in absorbance around  $3450\text{ cm}^{-1}$  to  $\text{LF}_1$  species engaged in H-bonding with CO. Finally, for equilibrium pressure in the range  $10^{-1} < p < 1.5$  Torr (Figure 2c), when HF and  $\text{LF}_1$  species are depleted, the  $\text{LF}_2$  component also decreases: an increase in absorbance is noted around  $3440\text{ cm}^{-1}$ .

The ease of interaction between the OH group and CO evidently increases in the order  $\text{LF}_2 < \text{LF}_1 < \text{HF}$ . This is in fair agreement with other evidence showing that the size of the cages, in which the three species are sitting, increases in the same order (frequency, half-width of the OH stretching bands, and behavior with temperature<sup>10</sup>). Although the shifts due to the H-bonding for  $\text{LF}_1$  and  $\text{LF}_2$  species are not precisely measured, they surely are in the range  $80\text{--}120\text{ cm}^{-1}$ , i.e. dramatically lower than that observed for HF species. Both on this basis and on the pressure dependence, one can conclude that the strength of the interaction  $\text{OH}\cdots\text{CO}$  decreases markedly from HF to LF species.

At the highest equilibrium pressures investigated ( $p > 1.5$  Torr, Figure 2d) a further depletion of  $\text{LF}_2$  species is observed (the  $\text{LF}_2$  band is however not completely eroded by adsorption of CO). The band at  $3353\text{ cm}^{-1}$  shifts to lower frequency, becoming broader (the intensity of the band probably keeps constant since the height of the band decreases): this is due to the solvation effect by the CO molecules which have filled the cages of the zeolite.

Figure 3a,b,c,d reports the range  $2050\text{--}2250\text{ cm}^{-1}$  (CO stretching mode region) of the same spectra as in Figure 2, respectively. At equilibrium pressure lower than  $<10^{-2}$  Torr (Figure 3a) a peak appears at  $2176\text{ cm}^{-1}$ , which is assigned to the stretching vibration of the CO interacting via H-bonding with the HF hydroxyl species.<sup>11</sup> Note that the half-width is



**Figure 4.** IR spectra illustrating the reversible adsorption of CO at nominal 77 K on AlPO-40 (CO stretching region):  $10^{-2} < p < 10$  Torr.

only 6  $\text{cm}^{-1}$ . This is evidence of a strict homogeneity in the interactions of HF species with CO.

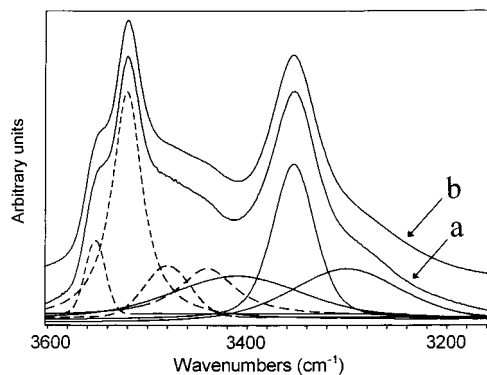
With increasing the CO pressure, a complex absorption appears at  $2140\text{ cm}^{-1}$  with a well-defined component at  $2136\text{ cm}^{-1}$ . The detailed interpretation of such a feature is beyond the scope of the present paper. It may be said, however, that bands in this region are due to molecules that are either liquid-like or physisorbed. The fine structure of the band has been related to hindered rotations of the molecules [ref 18, and references therein].

At higher CO equilibrium pressures (ca.  $10^{-2} < p < 10^{-1}$  Torr, Figure 3b), together with the already observed peaks, a broad shoulder centered at  $2168\text{ cm}^{-1}$  grows: it is assigned to the stretching mode of CO interacting with LF species. A tiny shift to lower frequency of the peak at  $2176\text{ cm}^{-1}$  is observed, probably because of an incipient solvation effect of the CO molecules engaged in H-bonding with HF species by liquid-like CO molecules.

For CO pressures in the range  $10^{-1} < p < 1.5$  Torr (Figure 3c), the shoulder at  $2168\text{ cm}^{-1}$  still increases and the peak at  $2176\text{ cm}^{-1}$  shifts markedly to lower frequency because of the solvation effect. In the physisorbed CO band, the components at  $2140$  and  $2136\text{ cm}^{-1}$  increase. Finally, for equilibrium pressures greater than 1.5 Torr (Figure 3d), a marked shift of the band at  $2176\text{ cm}^{-1}$  occurs due to the solvation effect: in the physisorbed CO band, the adsorption due to the liquid-like CO increases at  $2138\text{--}2136\text{ cm}^{-1}$ , making the band broader (the rotational fine structure due to CO in the gas phase is also visible).

For comparison, a spectrum concerning the adsorption of CO on AlPO-40 (ca.  $10^{-2} < p < 10$  Torr) is reported in Figure 4. No bands due to the stretching mode of CO interacting with Brønsted and/or Lewis acid sites are present. Two narrow peaks are visible at  $2140$  and  $2136\text{ cm}^{-1}$ , which are again related to physisorbed CO. The presence of two such well-defined components in the physisorbed CO band, however, is quite a surprising finding and will be discussed elsewhere.

The stretching frequency of molecules interacting via H-bonding with the hydroxyl groups is upward shifted with respect to the unperturbed molecules by the electrical field induced by the positive charge of the proton.<sup>11</sup> Using the frequency of the liquid-like CO as reference, we can calculate the shift of the stretching mode of CO interacting with HF and LF species, which are  $38\text{--}40$  and  $28\text{--}30\text{ cm}^{-1}$ , respectively. This difference is in agreement with that observed between the  $\Delta\nu_{\text{OH}}$ . The



**Figure 5.** Computer simulation of a typical spectrum of Figure 2a: (a) experimental spectrum; (b) simulated spectrum; broken curves: LF and VFL bands.

shift of the stretching mode of CO interacting with HF species is equal to that observed for HY and just  $4\text{--}6\text{ cm}^{-1}$  higher than that observed for H-mordenite,<sup>11,15</sup> in good agreement with the values of the corresponding  $\Delta\nu_{\text{OH}}$ .

## Discussion

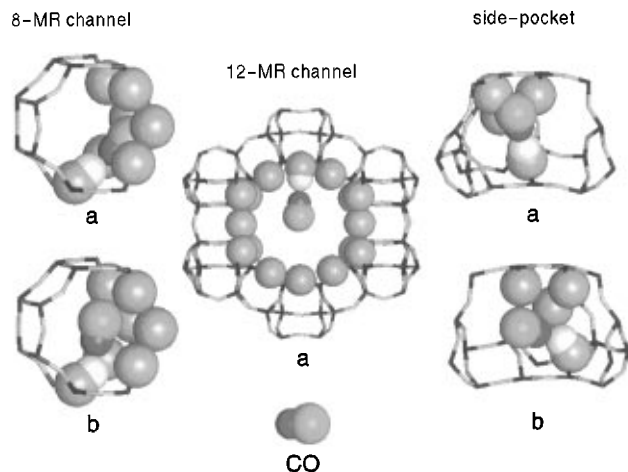
**Interaction of CO with Sterically Free Si(OH)Al Species (HF).** Figure 5 illustrates the computer simulation of a spectrum of Figure 3a in the region  $3600\text{--}3200\text{ cm}^{-1}$  (concerning the interaction of HF species only with CO). This allows one to attempt to find with some accuracy the locations of the various components. Besides the LF and VLF species (the spectral parameters of which have been fixed in the simulation), three bands are present at  $3410$ ,  $3353$ , and  $3300\text{ cm}^{-1}$  ( $\Delta\nu_{1/2} = 150$ ,  $60$ , and  $135\text{ cm}^{-1}$ , respectively). As reported above, a naive interpretation would relate these three bands to species A', A, and B, respectively. This, however, is not acceptable for various reasons.

First, species B would exhibit a value of  $\Delta\nu_{\text{OH}}$  which is the same as that observed for H-ZSM5:<sup>19</sup> on the basis of the catalytic data<sup>8</sup> it is not reasonable to assume the presence in SAPO-40 of OH species as acid as those of H-ZSM5.

Secondly, the band at  $3410\text{ cm}^{-1}$  would be shifted by some  $230\text{ cm}^{-1}$  with respect to the unperturbed A' species and would have a value of  $\Delta\nu_{1/2}$  ( $150\text{ cm}^{-1}$ ), which is higher than that of the band ascribed to the B species ( $135\text{ cm}^{-1}$ ): this is in evident disagreement with the well-known relationship between  $\Delta\nu_{\text{OH}}$  and  $\Delta\nu_{1/2}$  in H-bonding.<sup>20</sup>

Thirdly, the  $\Delta\nu_{\text{OH}}$  value in a series of similar interactions is a measure of the strength of the interaction itself, and several relationships between  $\Delta H^\circ$  and  $\sqrt{(\Delta\nu_{\text{OH}})}$  have been proposed. On the basis of the actual values of  $\Delta\nu_{\text{OH}}$ , it is expected that the interactions corresponding to the three bands would have definitely different strengths. So, increasing the CO pressure, the first band to appear would be that at  $3300\text{ cm}^{-1}$ , followed by that at  $3353\text{ cm}^{-1}$ , and finally by that at  $3410\text{ cm}^{-1}$ . In the case of H-ZSM5,<sup>19</sup> for instance, it is evident that the framework OH species, which is shifted by  $350\text{--}335\text{ cm}^{-1}$ , interacts with CO well before the extraframework OH species, which is shifted by only  $220\text{--}215\text{ cm}^{-1}$ . Quite in contrast, the three bands at  $3440$ ,  $3352$ , and  $3280\text{ cm}^{-1}$  increase simultaneously in the spectra.

A detailed computer simulation of the IR spectra in the region  $3660\text{--}3620\text{ cm}^{-1}$  has been carried out. This has shown, in the first instance, that all three bands (A, A', and B) shift to high frequency with increasing CO pressure by a mere physical effect. As to the intensity, the behavior of species A, A', and B with increasing pressure is similar: species A and B decrease



**Figure 6.** Molecular graphics description of the interaction of CO with OH groups in the 12-member-ring channel, side pockets in the 12-member-ring channel, and in eight-member-ring channels: type a structure, OH $\cdots$ CO linear arrangement; type b structure, bent OH $\cdots$ CO arrangement avoiding overlap.

simultaneously, whereas species A' seems to interact with CO slightly after the others.

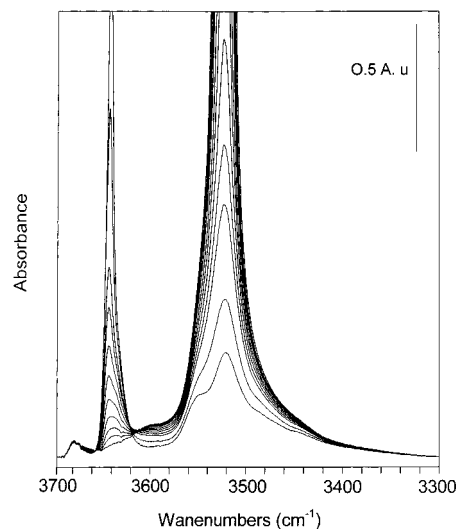
In conclusion, the three bands at 3410, 3353, and 3300  $\text{cm}^{-1}$  thus have to be considered as a whole. It is rather well-known that stretching modes of acidic O–H engaged in H-bonding may show a complex nature in the gas phase.<sup>21</sup> This is not usually the case with H-bonded complexes in solution and on surfaces, but exceptions occurs. For example, on silica systems medium-strength interactions like with acetone yield complex bands.<sup>22</sup> Reasons for complexity are to be sought that are the same as those that cause the broadness of the band, i.e. the coupling of the  $0 \rightarrow 1$  intramolecular transition with intermolecular modes. If one of those is sufficiently spaced in energy, three types of transition are possible, namely  $0, n \rightarrow 1, n + 1$ ;  $0, n \rightarrow 1, n$ ;  $0, n \rightarrow 1, n - 1$ . The occurrence of three bands is thus explained, and even the relative intensity may be accounted for by simple considerations.

The involved intermolecular mode thus has a frequency of  $\sim 55 \text{ cm}^{-1}$ . Recent results<sup>24</sup> of theoretical calculations on the interaction of CO with  $\text{H}_3\text{SiOHAlH}_3$  (minimal cluster model for the Brønsted sites in zeolites) indicate for the six intermolecular modes frequency values in the range 6–140  $\text{cm}^{-1}$ , in good agreement with the observed value.

**Interaction with Sterically Hindered Si(OH)Al Species (LF).** As it has already been pointed out, the strength of the interaction OH $\cdots$ CO decreases markedly from HF to LF species, and between the two LF species, LF<sub>1</sub> gives a stronger interaction than LF<sub>2</sub>.

Data concerning the adsorption of ammonia and decomposition of ammonium ion<sup>10</sup> indicate that LF and HF species have similar acidity and that LF<sub>2</sub> is more acidic than LF<sub>1</sub>. Thus, the present results concerning CO adsorption cannot be interpreted on the basis of the intrinsic acidity of the OH species, but only taking into account the lower sterical accessibility of LF species with respect to HF species. In fact, any distortion of the most stable end-on configuration, with the CO linearly interacting via the C atom with the proton, is likely to make the interaction weaker.<sup>23</sup> If the size of the cage in which the hydroxyl group is located does not allow the linear end-on configuration, the C $\cdots$ H–O moiety is bent and the H-bonding is weakened.

Figure 6 illustrates molecular graphics modeling of the CO interaction with OH species localized in a 12-member-ring channel, an eight-member-ring channel, and side pockets in the 12-member-ring channel. The OH, H $\cdots$ C, and CO distances



**Figure 7.** IR spectra illustrating the reversible adsorption of  $\text{N}_2$  at nominal 77 K on SAPO-40 (O–H stretching region):  $10^{-3} < p < 40$  Torr.

have been chosen as 0.96, 2, and 1.13 Å, respectively. It is evident that in both the eight-member-ring channel and the side pocket in the 12-member-ring channel the geometry of the environment does not allow a linear configuration (plausible configuration is given in Figure 6, which avoids the overlap of the oxygen of the CO molecule with oxygen of the framework), whereas such a configuration is readily fulfilled in the 12-member-ring channel.

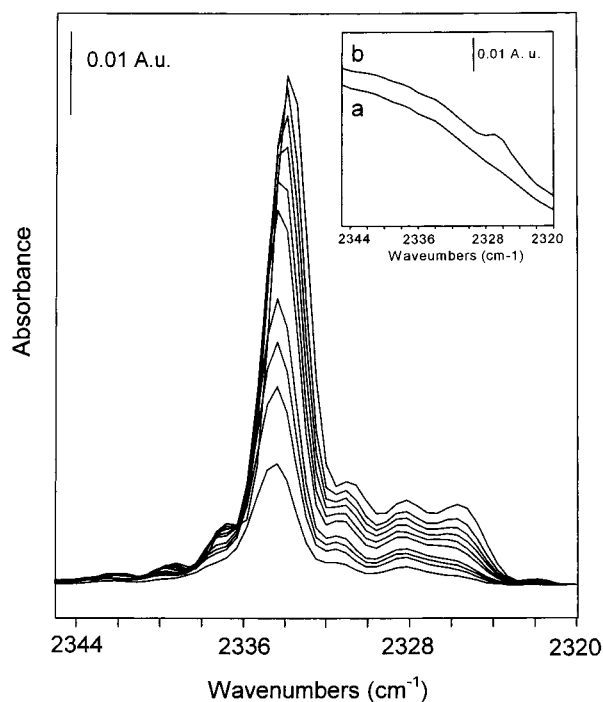
## Results and Discussion

**Adsorption of  $\text{N}_2$ . OH Stretching Region.** The spectra in the region 3700–3300  $\text{cm}^{-1}$  concerning the adsorption of increasing amount of  $\text{N}_2$  ( $10^{-3} < p < 40$  Torr) are reported in Figure 7.

Increasing the  $\text{N}_2$  equilibrium pressure, the band due to the HF species decreases and simultaneously a new band increases at about 3525  $\text{cm}^{-1}$  ( $\Delta\nu_{1/2} = 33 \text{ cm}^{-1}$ ) superimposed on the bands of the LF species, which is assigned to the HF species involved in a H-bond with the nitrogen molecules.<sup>11</sup> The component A' at 3630  $\text{cm}^{-1}$  seems to be eroded after the other two. The shift of the band due to the H-bond interaction measured for the HF species is 115  $\text{cm}^{-1}$ : this value is close to that measured for H-mordenite,<sup>11,24</sup> in agreement with the previously discussed data on the adsorption of CO. Similarly to what was observed in the case of the interaction with CO, the values of the shift and the half-width are in agreement with the correlation proposed by Makarova et al.<sup>17</sup> between the widening and the shift of the band of zeolitic acidic OH groups interacting via H-bond with weak molecules.

Perturbations of the bands related to the LF species are not visible because of the superposition of the new absorption at 3525  $\text{cm}^{-1}$ . Anyway, on the basis of the intrinsic acidity of the LF species,<sup>10</sup> as measured by  $\text{NH}_3$  adsorption, an interaction with  $\text{N}_2$  analogous to that observed with HF species is expected for LF species. As, in contrast, no bands shifted by  $\sim 115 \text{ cm}^{-1}$  with respect to the frequency of the LF hydroxyl bands are observed, it is concluded that, in agreement with the case of CO, if any interaction between LF and dinitrogen occurs, it causes a very small perturbation of the bands, not detectable in the spectrum, because of the lower sterical accessibility of LF species with respect to HF species.

**NN Stretching Region.** In Figure 8, the spectra reported in Figure 7 are illustrated in the region 2345–2320  $\text{cm}^{-1}$ . Along



**Figure 8.** Same IR spectra of Figure 7 in the N–N stretching region. Inset: (a) spectrum of AlPO-40 outgassed at 800 K; (b) after adsorption of some 40 Torr of N<sub>2</sub>.

with the band at 3525 cm<sup>-1</sup>, a peak at 2334 cm<sup>-1</sup> increases which is related to the stretching mode of the dinitrogen molecules interacting via a H-bond with the HF species. A peak at the same frequency has been assigned to the stretching mode of N<sub>2</sub> interacting with acidic OH species in H-mordenite.<sup>11,24</sup>

At high N<sub>2</sub> equilibrium pressure, a shift to lower frequency of the band at 2334 cm<sup>-1</sup> is observed: a similar effect has been previously discussed in the case of CO. Considering the asymmetry of the band on the low-frequency side, one cannot exclude, however, that a contribution from the interaction of N<sub>2</sub> with the LF species also occurs.

In the range 2344–3324 cm<sup>-1</sup> a fine structure of the spectra is evident, in which the single components seem to be separated with regularity from one another by some 3 cm<sup>-1</sup>, to be discussed elsewhere.

In the inset of Figure 8, the spectrum concerning the adsorption of ~40 Torr on AlPO-40 is reported (curve b). Only a very weak band is present at 2328–2326 cm<sup>-1</sup>, related to the stretching vibration of the N<sub>2</sub> interacting with the small amount of terminal POH/AlOH species. The frequency of this absorption is close to that observed for N<sub>2</sub> interacting with internal and external SiOH in H-mordenite.<sup>11,24</sup> In the spectra of N<sub>2</sub> on SAPO-40 this weak peak is probably superimposed on the fine structure of the spectra.

## Conclusions

The interaction with CO does confirm the proposed location of HF species in open cages and that of LF<sub>1</sub> and LF<sub>2</sub> species in small openings, with the latter in the smallest cages.

The acidity of LF<sub>1</sub> and LF<sub>2</sub> species with respect to that of HF species cannot be measured by the interaction with CO, as different (and noncomparable) geometries are achieved in the

various cases. That of HF species seems to be similar for all three types of hydroxyls, in contrast with what was observed for NH<sub>4</sub><sup>+</sup> decomposition.<sup>10</sup> It has to be noted that the transfer of a proton to NH<sub>3</sub> (or the reverse) is a complex process, in which different contributions may be singled out, among which the propensity of the hydroxyl to yield the proton and the possible role of the adjacent basic oxygens in stabilizing the ammonium cation.

The ready formation of NH<sub>4</sub><sup>+</sup> species even with LF<sub>1</sub> and LF<sub>2</sub> hydroxyl probably indicates that ammonium ions are located in large cavities. Tunneling of the proton is indeed documented in zeolites and in SAPO-5 systems in particular.<sup>26</sup>

On the basis of the absolute values of Δν<sub>OH</sub>, the acidity of HF species seem to be close to that of mordenite and HY. Catalytic data concerning reactions involving the proton transfer, however, suggest that SAPO-40 is less acidic than the other systems.<sup>8,9</sup> The plausible explanation is again that H-bonding with CO and proton transfer are two different measures of acidity. Indeed, the same indications come from the IR study of the reactivity of olefins, which will be reported in the near future.

## References and Notes

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