HCl and HCl-Base Adducts in Silicalite Channels as Models of Acid-Base Interactions in Zeolites: An IR and Theoretical Study

C. Pazé, B. Civalleri, S. Bordiga, and A. Zecchina*

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, I-10125, Torino, Italy

Received: March 31, 1998

The IR spectroscopy of HCl adsorbed on silica and on silicalite and of HCl–B (B = (CH₃)₂O, (CH₃CH₂)₂O, THF) adducts formed in silicalite channels at ~210 K is described in detail. The whole subject is divided in three parts. The first part concerns the IR study of the HCl interaction with silica and silicalite. The formation of weak H-bonded adducts between silanols and HCl molecules has been observed; the number of HCl molecules in the adducts increases with the HCl dosage. The HCl molecules adsorbed on silicalite behave as partially hindered rotators. The experimental results are supported by ab initio and molecular dynamics calculations. In the second part, the IR study of HCl–B complexes (B = (CH₃)₂O, (CH₃CH₂)₂O, THF, and benzene) either adsorbed on silicalite are compared with those obtained in cryogenic matrixes and in solution. It is inferred that the acid strength of HCl is appreciably influenced by the presence of the siliceous framework. This result allows discussion of the effect of long-distance interactions (framework effect) on the acid strength of structural Brønsted sites of zeolites.

1. Introduction

Protonic zeolites are catalysts active in a wide variety of acidcatalyzed reactions. The acid strength of these systems can vary over a wide range and can be assumed to depend on several factors. These can be broadly divided into two (not fully independent) groups: those primarily determined by the local structure of the Brønsted sites and those influenced by the threedimensional structure of the zeolite. Among the first group, we mention the bridged structure of the OH Brønsted group, the (SiO) and (AlO) distances, and the angle α^1 (Chart 1).

Long distance interactions (such as those associated with electrostatic interactions with the second, third, etc. shell atoms of the framework and with the extraframework ions) are the main contributors to the second group. These collective effects are analogous to those which, in the liquid phase, are named "solvent effects".² The evaluation of the total acid strength and of the relative role of the two groups of factors in determining the acidity of the acid sites of the zeolites is certainly a problem of primary importance.

A well-accepted method³⁻⁶ to study the acid strength of Brønsted sites in protonic zeolites is based on the analysis, by means of IR spectroscopy, of the perturbations that the interaction with basic molecules B induces on the vibrational properties of Brønsted sites, AH, and of the base B, due to the formation of AH–B adducts. The spectroscopic variations that give the most important information on the hydrogen-bonding interaction are those relative to (i) the frequency changes of the internal modes of the probe molecules (for instance, for a diatomic molecule AB, the variation $\Delta \bar{\nu}$ of the stretching mode ν (A–B) and (ii) the modification of the frequencies of the AH modes (the shift $\Delta \bar{\nu}$ (AH) of the ν (AH) stretching mode and the shifts

CHART 1



of the δ and γ bending modes). Above all, the $\Delta \bar{\nu}(AH)$ shift is particularly useful because it is proportional to the formation enthalpy of the complex between AH and B.^{7,8} A very much used probe molecule is CO,9 because of its small size and simple spectrum and because it allows discrimination between acid sites of different strength. Many other probe molecules can also be used, either binuclear $(N_2, H_2, NO)^9$ and polynuclear (ethers, alcohols).¹⁰ Molecules such as NH₃ and pyridine are also widely used14,15 because they allow estimation of the amount of Brønsted sites, through formation of NH₄⁺ and PyH⁺ ions. On the basis of a systematic study of the shifts induced by bases with proton affinities in the range 118-204 kcal/mol, it has been shown¹⁶ that it is possible to estimate the acid strength of a Brønsted group in a way that is independent of the particular probe molecule used to test the acidity. This method is the extension to heterogeneous conditions of the Bellamy-Hallam-Williams plot.11-13

A comparison of the data relative to the strong acid sites of different zeolites, all containing the common bridged Si(OH)Al structure, has shown¹⁶ the following acidity trend:

H-Y (Si/Al = 3) < H-MORD (Si/Al = 5)
$$\cong$$

H- β (Si/Al = 12.5) \cong H-ZSM-5 (Si/Al = 14)

The acidity trend illustrated is difficult to interpret directly, given the changes in both framework type and silicon-toaluminum ratio. It is evident that a simple relation between the acid strength and the local structure on one side and between

^{*}Author to whom correspondence should be addressed. Phone: +3911 6707537. Fax: +3911 6707855. E-mail: ZECCHINA@ SILVER.CH.UNITO.IT.

the acid strength and the chemical composition of the zeolite (primarily determining the collective effects) on the other side is not clearly emerging. In fact, zeolites characterized by isostructural Brønsted groups and roughly the same Si/Al ratio, like H-Y and H-MORD, show different acidities, while H-MORD and H-ZSM-5, characterized by very different Si/ Al ratios, have comparable acid strengths. On the basis of the initial considerations, these observations lead immediately to the following question: is it possible to estimate the relative influences on the acid strength of the effects associated with the local structure and of the long-distance interactions? A preliminary way to gain information on the approximate magnitude of this effect is to plan an experiment where the acid properties of a well-known molecule with Brønsted acid character (HCl) adsorbed in the channels and cavities of a neutral zeolitic framework are probed by studying the interaction with suitable basic molecules B. The comparison of the spectroscopic perturbations induced by the formation of B-HCl adducts in the channels of the neutral zeolitic framework with those of the same molecule in vacuo and in a cryogenic matrix can in fact give information about the effect that the longdistance interaction associated with the atoms of the neutral framework (considered as a matrix encaging the adducts or, more approximately, a solid and not uniform solvent) exerts on the acid properties of the encapsulated molecule. The feasibility of such an experiment has been already demonstrated¹⁷ for HCl-CH₃CN complexes, which have been synthesized in situ in the channels of silicalite (i.e., a totally siliceous zeolite with MFI structure). The key point of this experiment was represented by the fact that the silicalite structure showed a good resistance to chemical attack by HCl, so allowing the HCl-CH₃CN interaction to be studied in its purest form. From the vibrational properties of this complex, the magnitude of the solvent effect exerted by the neutral MFI structure on the complexes was then estimated. In this paper, we extend the investigation to other basic molecules such as (CH₃)₂O, (CH₃CH₂)₂O, THF, and benzene, and the whole body of results is discussed. A detailed discussion of the state of HCl adsorbed on silicalite probed with atomistic and ab initio simulation techniques is also added. The reader must acknowledge that this investigation has only a limited scope, as it cannot be extended to real zeolitic systems, where the effect of the ionic charge localized on the extraframework ions and on the zeolite framework, containing Al³⁺, is certainly playing an important role.

2. Experimental and Calculation Methods

2.1. Experimental. The silicalite sample (kindly supplied by ENICHEM laboratories, Novara, Italy) was synthesized in a Na-, K-, Al-, Fe-free form (<20 ppm) by following the procedure described in ref 18. Details about its characterization are reported in refs 18–20. The high purity silica sample (Aerosil) had a specific surface area of about 150 m²/g. Before adsorption, the silicalite and silica samples were activated at 973 K for 2 h. The thermal treatments (under high vacuum) and the spectroscopic measurements have been performed on samples in the form of self-supporting wafers.

High-purity HCl was produced by reaction of H_2 with optical AgCl at 973 K and used after elimination of residual H_2 through repeated freezing cycles, by using a cold trap kept at 77 K. (CH₃)₂O, (CH₃CH₂)₂O, THF, and benzene were high-purity Aldrich products; all the reagents were dosed from the gas phase.

The cell, equipped with a thermocouple in contact with the sample holder and permanently attached to a gas manifold, allowed both high-temperature treatments in vacuo and lowtemperature IR measurements to be performed in situ. The IR measurements were performed at 2 cm^{-1} resolution on a Bruker 66 instrument equipped with a MCT cryogenic detector.

All the experiments were carried out at $T = 214 \pm 5$ K, chosen so that the amount of adsorbed HCl is sufficiently large to give strong IR spectra. As a result of unaivodable fluctuations of the temperature between 209 and 219 K in our experimental setup, it was not possible to make the measurements of the isosteric heat of sorption. Gravimetric experiments with a vacuum microbalance were not performed due to the corrosive nature of HCl.

The coadsorption experiments of HCl with $(CH_3)_2O$, $(CH_3CH_2)_2O$, THF, and benzene have been conducted in the following way. After activation, the silica and/or the silicalite samples previously cooled at 214 ± 5 K, were contacted with HCl ($p \approx 266$ Pa), and the spectra were recorded after the attainment of equilibrium. Then $(CH_3)_2O$, $(CH_3CH_2)_2O$, THF, and benzene (from an external reservoir) were allowed to gradually flow in and the IR spectra of the B-HCl complexes gradually formed inside the silicalite channels were taken at fixed time intervals, until the total consumption of the signal of adsorbed HCl was achieved.

It is worth noting that during the experiment only the sample holder was kept at 214 ± 5 K, while all the remaining parts of the cell were at room temperature. This means that the gas phase in equilibrium with the pellet can be prevalently considered to be at ~300 K. Under the experimental conditions of pressure and temperature (~300 K), the amount of B-HCl adducts in the 1:1 gaseous phase is negligible and does not appreciably contribute to the IR spectra.

2.2. Calculation. Molecular dynamic calculations were obtained using the classical mechanics Discover 95.0 program from Molecular Simulations.²¹ The cff91 (version 3.0) force field developed by Sauer and Hill,²² based on fit to ab initio energy surface data, was used for all the atoms. The extension of this force field to the hydrogen and chlorine atoms is arbitrary. The periodic structures were optimized by means of constant pressure lattice energy minimization with respect to atomic Cartesian coordinates and cell parameters. The system energy was evaluated using a cutoff of 9.5 Å for van der Waals interactions and the Ewald method for Coulombic interactions (to an accuracy of 0.025 kcal/mol). Minimization was performed using the steepest descent method for a few steps, followed by the conjugate gradient method and then by the quasi-Newton-Raphson method (BFGS), until the maximum derivative of the energy with respect to the Cartesian coordinates was less than 0.001 kcal/Å. The first minimization step (at variable cell volume) was followed by a molecular dynamics step (10 000 fs, 300 K, constant volume, constant energy). Finally, a last minimization step was achieved (at constant cell volume). This procedure has been applied to the pure silicalite structure and to silicalites containing 11 HCl molecules/cell (simulating low acid dosage) and 25 HCl molecules/cell (simulating high dosage).

Ab initio calculations were performed at the ab initio level by means of the GAUSSIAN 94 package.²³ The gradient corrected exchange and correlation hybrid functional B3-LYP²⁴ with the 6-31+G(d,p) basis set was used for all calculations. The geometry optimization was carried out by using analytical gradient techniques. Harmonic normal-mode frequencies were computed by adopting analytical second-energy derivatives and solving the equations of nuclear motion by standard methods.²⁵



Figure 1. IR spectra of silica (outgassed at 973 K) and of silica interacting with 4133 Pa of HCl at 300 K.



Wavenumber (cm⁻¹)

Figure 2. IR spectra of increasing doses of HCl adsorbed at 214 ± 5 K on silica outgassed at 973 K ($0 \le$ equilibrium pressure ≤ 2933 Pa).

3. Results and Discussion

The whole subject is divided in three parts (3.1-3.3). The first part concerns the IR and theoretical study of the interaction between HCl and silica and silicalite; this introductory study is necessary, because data about the interaction of HCl with these systems are not available in the literature (to our knowledge the reader will find only ref 26 about the interaction of HCl with NaY zeolite) and because it are of great help in understanding the spectroscopy of HCl–B adducts. The second part is devoted to the study of the synthesis of HCl–B complexes (B = base molecule) on silica and in silicalite channels and to their spectroscopic properties. Finally, in the third part, the results obtained for HCl–B adducts in silicalite are compared to those obtained in cryogenic matrixes and in solution.

3.1. Adsorption of HCl on Silica and Silicalite. 3.1.1. IR *Results.* The IR spectrum in the $3800-2200 \text{ cm}^{-1}$ range of the

silica sample (Aerosil) outgassed at T = 973 K (Figure 1) is characterized by a single narrow peak at 3750 cm⁻¹ due to the stretching mode ν (OH) of the surface silanols; these SiOH groups are isolated and not interacting each other, as indicated by the very small fwhm (full width at half-maximum) of the band.

The IR spectra concerning the interaction of HCl (p = 4133 Pa) with silica at 298 K are reported in Figure 1. It can be immediately observed that the rotovibrational peaks of gaseous HCl centered at 2886 cm⁻¹ appear above the unmodified spectrum of silica; consequently, it can be deduced that at T = 298 K neither chemical nor physical HCl adsorption on the surface is taking place.

On the contrary, the IR spectra of increasing doses of HCl $(p_{\text{max}} = 2933 \text{ Pa})$ at $T = 214 \pm 5 \text{ K}$ (Figure 2) show that the adsorption is taking place for the following reasons.



(i) The peak at 3750 cm⁻¹ (ν OH) of silanols is gradually eroded with simultaneous formation, at lowest dosages, of three bands at 3723, 3630, and 3580 cm⁻¹. As the equilibrium pressure of HCl increases, the intensity of the components at 3723 and 3630 cm⁻¹ decreases in succession, while the intensity of the band centered at 3580 cm⁻¹ grows in a parallel way. Finally, at higher pressures, only a single band at 3595 cm⁻¹ is observable. These results are a clear indication of the gradual formation of hydrogen-bonded adducts SiOH(HCl)_n ($n \ge 1$) between the surface silanols and the HCl molecules (Chart 2).

About the detailed structure of the SiOH(HCl)_n $(n \ge 1)$ clusters, it is not possible from the bare IR data to infer the exact geometry of the individual complexes. However, helpful information can be achieved by means of theoretical calculation, and the results are shown later.

(ii) Beside the narrow rotovibrational components of HCl gas centered at 2886 cm⁻¹, an absorption centered at 2788 cm⁻¹ and a band (large and probably composite) centered at about 2640 cm⁻¹ appear. The formation of the last two bands demonstrates that, besides a dominant fraction of noninteracting HCl molecules in the gas phase, at least two types of HCl molecules perturbed in different way exists on the surface. Since by increasing the HCl pressure a clear correlation is observed between the bands at 2640 and 3594 cm⁻¹, the band at 2640 cm⁻¹ is assigned to the ν (HCl) stretching mode in SiOH(HCl)_n ($n \ge 1$) complexes (Chart 2).

The band at 2788 cm⁻¹ is continuously increasing with the HCl pressure, even when the band at 2640 cm⁻¹ has reached a constant maximum (that corresponds to the total consumption of the band at 3750 cm⁻¹ due to free silanols). The band at 2788 cm⁻¹ can be associated either with the formation of (HCl)_n oligomeric chains or with HCl species interacting with the oxygen atoms of siloxane bridges. In the first case, each HCl molecule is more stabilized by lateral interactions with contiguous molecules than by interaction with the surface, and the IR properties should be very similar to those of liquid HCl (at -100

°C) (ν (HCl) = 2780 cm⁻¹)²⁷ and to those of (HCl)_n oligomers isolated in a cryogenic matrix (Ar or N₂).^{28–33} In the second case, the interaction with the siloxane bridge is dominating; unfortunately, the involved stretching frequencies cannot be compared with those of suitable model compounds. For the time being, it is not possible to make a reasonable choice between the two possibilities. This problem will be discussed in the following sections on the basis of molecular mechanics and ab initio calculation.

(iii) A band shows up at 923 cm⁻¹ (inset Figure 2), whose integrated intensity varies with HCl dosages in a way proportional to the intensity of the bands at 3594 and 2640 cm⁻¹ (due to the complexes between HCl and silanols). This band is tentatively assigned to the (in-plane) bending mode δ of the silanol groups involved in the hydrogen-bonding interaction.

The spectrum of a silicalite sample outgassed at 973 K is reported in Figure 3 (curve 1). It shows a single peak at 3746 cm⁻¹; with respect to silica, the peak is less intense and tailed. This peak is due to silanols present on the external and internal (lower frequency tail, 3740-3680 cm⁻¹) surfaces of the microcrystal.^{18,19}

Like on silica, HCl is not adsorbed at room temperature (and $p \approx 2266$ Pa); accordingly, the rotovibrational peaks of the gas appear above the unmodified spectrum of the zeolite. Like on silica, the absorption process takes place at T = 214 K.

In Figure 3, the interaction of increasing doses of HCl at $T \approx 214$ K is shown. The following features can be noticed.

(1) The progressive disappearance of the peak at 3746 cm⁻¹ (the tail at lower frequencies being preferentially affected) and the simultaneous appearance of a broader band (without distinct components, as on silica) varying with dosage between 3630 (low pressures) and 3600 (high pressures) cm⁻¹ are evident. These effects are clearly due to the formation of SiOH–(HCl)_n adducts between silanols (prevalently in internal positions) and HCl molecules (Chart 2). HCl–OH adducts are more clearly defined on amorphous silica since the silanol species on silica are much more homogeneous (as shown by the very sharp peak at 3745 cm⁻¹), while a wider distribution of SiOH exists on silicalite (the band at 3746 is asymmetric and less narrow) due to the presence of hydroxyl nests.^{18,19}



Figure 3. IR spectra of increasing doses of HCl adsorbed at 214 ± 5 K on silicalite (outgassed at 973 K) ($0 \le$ equilibrium pressure ≤ 2266 Pa).



Figure 4. Molecular mechanics simulation of the adsorption of HCl in silicalite (11 molecules per cell), details in Experimental Section: (a) view along [010] direction; (b) view along [100] direction; (c) view along [001] direction.

The shift of the band due to perturbed hydroxyls toward lower frequencies as the dosage increases is presumably due to the progressive formation of SiOH–(HCl)_n complexes characterized by increasing *n*. Considerations about the structure of the SiOH(HCl)_n ($n \ge 1$) clusters will be made in the next paragraph on the basis of the ab initio results.

(2) A complex absorption between 3050 and 2350 cm^{-1} appears. This absorption shows a main asymmetric maximum at 2820-2830 cm⁻¹ (Q branch) flanked at higher and lower frequencies by two weak and broad absorptions (at 2850-2800 and 2750-2650 cm⁻¹). By analogy with the spectra of CO adsorbed on silicalite¹⁹ and of HCl at high pressures,²⁷ these components can be assigned to the P and R components of a partially hindered rotator.³⁴ The formation of a dense state of HCl in the narrow channels is the characteristic result of the van der Waals forces associated with the internal surface of the pores. For the same temperature and pressure, this effect is not present on external surfaces, where only the hydroxyl groups are acting as adsorbing centers. An alternative explanation reported in the literature for HCl in CCl₄³⁵ is that they are combination modes between the ν HCl mode (Q branch) and other (not well defined) low-frequency intermolecular solutesolvent modes. In the following description, the PQR nomenclature is used. Notice how a broader adsorption is superimposed to the P branch.

On the top of these absorptions, the rotovibrational peaks of gaseous HCl (centered at 2886 cm^{-1}) are clearly distinguishable. The presence of PQR envelopes (without rotovibrational components) is clearly distinguishing the spectrum of HCl adsorbed into the channels from that adsorbed on external surfaces (Aerosil).

The absorption at 2820-2830 cm⁻¹ is due to HCl physisorbed

inside the channels of the zeolite; this assignment is based on the data available for liquid HCl²⁷ and for HCl entrapped in cryogenic matrixes.²⁸⁻³³ At low pressures, the main peak is centered at 2830 cm⁻¹ and then it moves gradually to 2820 cm⁻¹ by increasing the pressure. This shift is due to the formation of oligomeric chains of HCl whose length is progressively longer; as a matter of fact, IR data concerning $(HCl)_n$ complexes isolated in cryogenic matrixes of Ar and $N_2^{36,37}$ show that the frequency of the $\nu(\text{HCl})$ mode decreases as the size (n) of the cluster increases. The frequency of the Q branch maximum in silicalite is higher than that of the same component on silica; this can be explained by the presence, in the zeolite channels, of oligomeric chains shorter than those on silica, the length of the chains being limited by the channel structure environment (vide infra). The frequency of the Q branch maximum is also lower than that of the free gas (2886 cm^{-1}); this is due to the combined effect of the high "pressure" of HCl in the channels and the interaction with the zeolitic walls.

The IR manifestation of the complexes between HCl and silanols, similar to those observed on silica (Figure 1), are superimposed to the P envelope; this explains why the P branch appears distinctly stronger and broader with respect to the R branch.

As already mentioned, the HCl molecules physisorbed inside the channels show very peculiar rotovibrational features. Both the Q branch (corresponding to a forbidden transition in the gas but active in the liquid²⁷) and the Q and R branches (well defined in the gas but not resolved into the individual components when the rotation of the molecules is partially hindered, as it happens for example at very high pressures of gas or in solution^{34,35,38}) are present. These peculiarities show that a fraction of the physisorbed molecules is in a state similar to



Figure 5. Molecular mechanics simulation of the adsorption of HCl in silicalite (25 molecules per cell), details in Experimental Section: (a) view along [010] direction; (b) view along [100] direction; (c) view along [001] direction.

that of a dense gas (in which the intermolecular forces are still strong); in this state, the molecules are preserving a certain rotational degree of freedom and behave therefore as hindered rotators. In addition, the presence of a strong Q central component shows that they are in equilibrium with a more dense phase similar to the liquid.

The presence of the P, Q, and R branches only for HCl adsorbed on silicalite (and not on silica) demonstrates that in the zeolitic cavities the adsorbed HCl molecules maintain some rotational freedom and that the same effect cannot be obtained on external surfaces.

To understand how HCl molecules are physisorbed inside the zeolite channels, a qualitative procedure based on molecular mechanics simulation of a low (11 molecules per cell) and a high (25 molecules per cell) filling of the channels of a perfect silicalite, i.e., a silicalite without internal defects (hydroxyl nests), has been carried out. The energy-minimized structures show that, at low dosage (Figure 4), the tendency to form oligomeric species is very modest and that only at the highest filling (Figure 5) a low density, liquid-like state containing a large amount of HCl···HCl hydrogen bonds is present. A qualitative picture is then that at low coverage the interaction energy between HCl molecules is smaller or very close to the interaction energy between HCl and the zeolite walls. Obviously, when highest filling conditions are reached, the HCl molecules fill up the zeolite channels making long H-bonded strings. The weakness of the HCl-HCl and HCl-walls interactions is also in agreement with the presence of rotovibrational envelopes in the IR spectra.

3.1.2. Ab Initio Calculation. While molecular mechanics simulations can give an insight into the HCl–HCl and HCl– walls interaction in hydroxyl-free portions of the internal

volume, it is not adequate for describing the interaction with silanols, responsible for the erosion of the free silanol peak. To shed some light on this topic, ab initio methods are a more convenient choice.

As a model of the adsorption site, the largely used minimal cluster model H₃SiOH (structure S, Figure 6a) has been adopted.³⁹ Six hypothetic structures of SiOH(HCl)_n ($n \ge 1$) clusters (Figure 6a) have been chosen to simulate different dosages corresponding to different experimental equilibrium pressures. The results can be summarized as follows. (i) For the 1:1 HCl-SiOH adduct, the only stable adduct is shown in Figure 6a as SA1, in which the silanol behaves as a hydrogen bond acceptor with respect to HCl. Other possible 1:1 structures, like the cyclic one or that in which S acts as a hydrogen bond donor, resulted unstable on the potential energy surface. (ii) As far as the 2:1 HCl-SiOH stoichiometry is considered, two configurations have been studied among all the possible ones: a cyclic structure (SR2, Figure 6a) and a structure in which S acts as a double hydrogen-bond acceptor (SA2, Figure 6a). As far as the 3:1 stoichiometry, a cyclic complex (SR3, Figure 6a) as well as a structure in which S acts as both a hydrogen-bond acceptor and donor with respect to HCl (SA3, Figure 6a) have been considered. Finally, the siloxane-HCl interaction has been taken into account (SXA, Figure 6a) by mimicking the siloxane bridge with the (SiH₃)₂O molecule SX.

The ab initio study has also been extended to aggregates made by the self-interaction of HCl molecules by considering clusters spanning from $(HCl)_2$ to $(HCl)_4$, respectively. Five HCl selfaggregate structures have been computed, as shown in Figure 6b.

For all structures shown in parts a and b of Figure 6, the optimized geometries and the full set of harmonic frequencies,



Figure 6. (a) Molecular drawings for silanol and siloxane adducts with HCl. For labeling the selected complexes, the following acronyms are used: S = silanol, SX = siloxane, A = acceptor, R = ring. Each HCl molecule has been labeled to help the discussion (see Table 1). Intermolecular bond distances are in angstroms. (b) Molecular drawings for HCl self-aggregates. Adducts labels assigned as L = linear adducts and R = ring adducts. Each HCl molecule has been labeled to help the discussion (see Table 1). Intermolecular bond distances in angstroms.

as well as the interaction energies have been computed. A selection of the results obtained is reported in Table 1.

The H₃SiOH molecule does not exist as such because it is unstable with respect to the condensation to disiloxane; however, the calculated geometry (see Figure 6a) is in agreement with previously published data computed at higher levels of calculation.⁴⁰

The analysis of the geometries of silanol-HCl and siloxane-HCl adducts shows a number of interesting features. (i) The HCl molecule acts preferably as a proton donor, being, at the same time, a poor proton acceptor. Indeed, the intermolecular distances of the SR2 and SR3 adducts reveal a noticeably shorter H-O bond with respect to the SA1 adduct between the terminal HCl molecule and the basic oxygen atom belonging to S (1.749 and 1.665 Å for SR2 and SR3, respectively). Also worth noting is the shrinking of all intermolecular distances when passing from the SR2 to the SR3 adduct, a clear indication that cooperative effects are acting along the ring of H-bonded molecules. (ii) The Cl···Cl repulsion is responsible for the lengthening of the H···O bond in the SA2 adduct when compared with SA1. (iii) The hydrogen bond between HCl and the siloxane bridge (structure SXA in Figure 6a) is noticeably short, a fact almost unexpected because of the very weak basicity of the oxygen atom belonging to the siloxane bridge.

The geometries of the HCl self-aggregates (see Figure 6b) show intermolecular H···Cl distances well within a 2.5 Å limit, with some modulation in the ring structures (R3 and R4) due to cooperative effects.

For each adduct, the interaction energy ΔE_n has been computed from the total energies of each molecular constituents of the adduct, by the formula

$$\Delta E_n = E(A(HCl)_n) - E(A) - nE(HCl)$$

in which A is the molecular partner (either S, SX, or HCl) of the HCl molecule in the corresponding aggregate A(HCl)_n and *n* is the total number of HCl molecules involved. The interaction energy per HCl molecule is defined as $\Delta E_1 = \Delta E_n/n$, from which the corresponding heat of formation at 0 K is computed by adding to both ΔE_n and ΔE_1 the proper zero-point energy correction to get $\Delta H^0_n(0)$ and $\Delta H^0_1(0)$, respectively.

The analysis of data in Table 1 shows the following trend in the magnitude of $\Delta H^{0}_{n}(0)$ for all adducts:

$$L2 < L3 < R3 \cong SXA \cong L4 < SA1 \cong R4 < SA2 < SR2 < SA3 < SR3$$

To compare the heats of formation on a common gauge, we have reported in Figure 7 the heats of formation per HCl

TABLE 1: Interaction Energy, ΔE_n and Heat of Formation at 0 K, $\Delta H^0_n(0)$ (in kJ/mol) and Selected Unscaled Harmonic Frequencies (in cm⁻¹) for All Adducts^{*a*}

system ^a	$-\Delta E_n^{\ b}$	$-\Delta H^0_n(0)^b$	$\omega(OH)^c$	$\omega(\mathrm{HCl})^{c,d}$	
HCl				2953	
S			3903		
L2	6.7	2.6		2881 (-72)	1
				2946 (-7)	2
R3	21.5	11.1		2816 (-137)	1, 2, 3 sym
				2842 (-111)	2, 3 asym
				2845 (-108)	1-2, 3 asym
L3	15.2	6.8		2845 (-108)	2
				2869 (-84)	1
				2941 (-12)	3
R4	38.5	21.5		2737 (-216)	1, 2, 3, 4 sym
				2779 (-174)	1, 3 asym
				2779 (-174)	2, 4 asym
				2796 (-157)	1, 3-2, 4 asyn
L4	24.4	11.9		2814 (-139)	2, 3 sym
				2835 (-118)	2, 3 asym
				2861 (-92)	1
				2943 (-10)	4
SA1	26.4	19.7	3879 (-24)	2669 (-284)	
SR2	45.2	32.5	3797 (-106)	2504 (-449)	1
				2782 (-171)	2
SA2	38.6	26.0	3839 (-64)	2741 (-212)	sym
				2774 (-179)	asym
SR3	66.0	47.7	3719 (-184)	2336 (-617)	3
				2672 (-281)	2
				2738 (-215)	1
SA3	52.1	35.0	3727 (-176)	2709 (-244)	2, 3 asym
				2749 (-204)	2, 3 sym
				2933 (-20)	1
SXA	18.0	11.6		2720 (-233)	

^{*a*} Adopted labels accordingly to Figure 6. ^{*b*} Uncorrected for BSSE. ^{*c*} Corresponding frequency shifts with respect to the unperturbed frequencies are enclosed in parentheses. ^{*d*} Attribution of each ω (HCl) frequency to the corresponding HCl molecule following the labelling scheme of Figure 6.



Figure 7. Bar chart of the heat of formation per HCl molecule, $-\Delta H^0_1(0)$, for all adducts. See Figure 6 for the labeling scheme. Energetic data in kilojoules per mole.

molecule at 0 K, $-\Delta H^{0}_{1}(0)$. A monotonic increase of its value is seen for the HCl self-aggregates. Values much higher than the maximum value of 6.5 kJ/mol computed for R4 are seen for the aggregates involving HCl with either silanol or siloxane molecules. Among these latter, the SA1 shows the largest value of $-\Delta H^{0}_{1}(0)$ (19 kJ/mol), followed by the two ring structures SR2 and SR3 (around 16 kJ/mol). These data show that the self-aggregation of HCl is less favored than processes involving





Figure 8. Experimental IR spectra of HCl adsorbed on silica at 214 \pm 5 K (p = 100 Pa) (curve a). Fitting obtained using, as base components, bands with Lorentzian shape centered at the calculated frequency (corrected by a scaling factor of 0.9608) (curve b); the fwhm of the components are obtained by the Pimentel equation that correlates FWHM and $\Delta \bar{\nu}$ shifts of frequency (FWHM = $0.72\Delta \bar{\nu} + 2.5$ cm⁻¹).⁷

aggregation bewteen HCl and silanol sites, a fact resulting from the poor proton acceptor capability of HCl itself.

Hence, the possible steps of the HCl adsorption are the formation of the complexes with hydroxyl groups of the surface and, when all the silanols are consumed, the interaction of HCl with the siloxane bridges. Only after this stage does self-aggregation of HCl start to take place.

Table 1 also includes a selection of the computed harmonic vibrational frequencies as well as the corresponding shifts caused by the H-bonding interaction. The reported frequencies are for the OH and HCl stretching modes. The analysis of the data reported in Table 1 reveals that the largest ω (HCl) shifts are for the cyclic structures, namely R3, R4, SR2, and SR3, in which shifts almost twice as large as those computed for the corresponding noncyclic structures are computed. This fact, correlates with the higher interaction energies for such structures and is indeed a measure of the H-bonding cooperativity taking place in the cyclic adducts.

In Figure 8, the experimental spectrum of HCl adsorbed on silica, as far as concerns the OH stretching region, is interpreted on the basis of the ab initio calculations. A fit of the experimental spectrum has been made by using, as base components, bands with Lorentzian shape centered at the frequencies calculated theoretically (corrected by a scaling factor of 0.9608). The adopted FWHM of the components were obtained from the Pimentel equation that correlates FWHM and the frequency shifts $\Delta \bar{\nu}$ (FWHM = $0.72\Delta \bar{\nu} + 2.5 \text{ cm}^{-1}$).⁷ The intensities of the components were obtained through a fitting procedure. The experimental band at 3723 cm⁻¹, present only at the lowest pressures, is therefore assigned to the formation of a HCl–SiOH 1:1 adduct; the component at 3630 cm⁻¹ is assigned to 2:1 complexes, while the absorption at about 3600 cm⁻¹ is due to complexes with 3:1 (or more) stoichiometry.

When a simulation of the spectra of silica at high HCl loadings was performed, not so good results were obtained. In particular, the components in the 3620-3570 cm⁻¹ range are

missing. This could be explained by two facts: (1) siloxane– HCl complexes are stable, and their population increases preferentially as the pressure increases; moreover the fit does not consider that the presence of HCl molecules adsorbed on the siloxanes, surrounding the SiOH–HCl adducts, is certainly influencing the stretching frequency of the silanol and (2) other adduct structures are possible at high pressure, due to the formation of multilayer HCl adsorption on silica–HCl and siloxane–HCl adducts.

In principle, a simulation of the spectra in the ν (HCl) stretching region of frequencies could also be made. To this aim, all the frequencies of the collective modes of HCl-silanol complexes, all the collective modes of HCl clusters, and even the mode of the siloxane-HCl adduct should be considered. However, the number of base components needed to simulate the experimental spectrum would be exceedingly large (more than 20 bands), and this would lead to an arbitrary fit. Without describing the matter in detail, it must be remarked that, despite all the difficulties mentioned before, all the computed frequencies shifts lie in the region where the absorption is experimentally observed. In particular, the HCl adducts' calculated frequency shifts lie in the range 50–180 cm⁻¹, while the frequency shifts of the silanol and siloxane adducts are over 180 cm⁻¹, again confirming the previous interpretation.

All the considerations made about silica can be extended to silicalite. In the latter case, however, the surface is prevalently internal so that complexes with size greater than three, are less probable. This consideration explains why the absorption in the 3700-3600 cm⁻¹ range has its maximum at frequency values higher than those of silica (because the steric constrains favor the prevalent formation of complexes with n = 2). This conclusion is confirmed by a fit (not reported for the sake of brevity) in the 3800-3500 cm⁻¹ range; in fact, while the components are the same as those observed on silica, the intensity distribution is different because the 3:1 complexes are present in lower proportion. Furthermore, in the case of HCl adducts (ν (HCl) region of frequency), the IR band is observed at higher frequency than in silica. That trend could be explained on grounds of the linear HCl adducts computed frequency shifts. Indeed, such complexes, which have lower steric constraints and lower frequency shifts, are stabilized in the channels of zeolite, with respect to the other bulky configurations.

Even if a surprisingly good correlation between experimental and theoretical results is verified, a few considerations about the calculation method must still be made. (1) The calculated frequencies are harmonic; anharmonic contributions are therefore missing. (2) DFT methods tend to overestimate the frequency shift in hydrogen-bonded systems; moreover, the shift is further overestimated in the case of multiple interactions.⁴¹ This fact may be due to the presence of the self-interaction error, which is more significant in systems (like those here considered) in which protons are involved.⁴² (3) The overestimation of the frequency shifts is also due to the effect of temperature, because the calculated shifts were computed at 0 K while the experiment was made at 214 ± 5 K. (4) Finally, it is known that the minimal cluster model chosen to mimic the isolated hydroxyls of the surface (structure S, Figure 6) is less acidic than the real surface SiOH group.⁴⁰ As a result of this, the O atom is more basic and this in turn favors the preferential formation of adducts where the HCl is acting as a proton donor.

3. 2. HCl–Base Complexes. For the sake of brevity only the spectra of the adducts formed with dimethyl ether will be illustrated in detail. As for the spectra obtained with CH₃CN, the reader is referred to ref 17. The relevant data concerning

TABLE 2: Experimental Frequencies of ν (HCl) Mode in HCl–B Complexes in Silicalite at 214 \pm 5 K^{*a*}

	benzene	CH ₃ CN	(CH ₃) ₂ O	(CH ₃ CH ₂) ₂ O	THF			
$\Delta \bar{\nu} HCl (cm^{-1})$	111	304 ^a	526 ± 20	556 ± 20	606 ± 20			
CHART 3								
<u> </u>								

the other complexes (with benzene, diethyl ether, and THF) are summarized in Table 2.

3. 2. 1. Silicalite $-(CH_3)_2O$ and Silica $-(CH_3)_2O$. To facilitate the discussion of the spectra of the HCl $-(CH_3)_2O$ complexes formed in the silicalite channels (vide infra), a preliminary analysis of the spectra of the silicalite -ether system (i.e., without HCl) is useful (Figure 9). The spectra obtained on Aerosil are very similar (only the intensity is lower), hence they are not shown for the sake of brevity.

As the pressure of $(CH_3)_2O$ increases, the band at 3746 cm⁻¹ is completely eroded; simultaneously, a broader band shows up at 3246 cm⁻¹. A relation of strict proportionality exists between the decrease of the integrated intensity of the peak of free silanols (3746 cm⁻¹) and the increase of the integrated intensity of the band centered at 3294 cm⁻¹; moreover, a clear isosbestic point appears at 3580 cm⁻¹. These two facts demonstrate that a 1:1 complex is gradually formed (Chart 3).

The band of the ν (OH) mode of the silanol groups is shifted downward by about 500 cm⁻¹ (FWHM \cong 300 cm⁻¹), a figure typical of a hydrogen bond of medium strength.

The bands of the methyl stretching modes (unaffected by the hydrogen-bonding interaction) are observed in the 3000–2700 cm⁻¹ interval ($\nu_{sym} = 2828$, 2811 cm⁻¹, $\nu_{asym} = 2989$, 2945–2866 cm⁻¹); these bands are made complicated by the Fermi interaction with the two δ (CH₃) modes. The corresponding bending modes are at 1473 and 1455 cm⁻¹. Also, these bands are not influenced by the adsorption state. Finally, the bands due to the CH₃ rock mode are observed at 909 (hydrogen bonded) and 922 (physisorbed) cm⁻¹. Notice how, in the spectra corresponding to highest equilibrium pressures (dashed lines in Figure 9), many very weak bands are observable (at 2694, 2634, 2627, 2593, 2562, 2536, 2406, 2250, 2162, 2080, 2006, 1839, and 1586 cm⁻¹) due to combination and overtones of the ether molecule.

3. 2. 2. Silicalite $-HCl-(CH_3)_2O$. The spectra of increasing doses of $(CH_3)_2O$ on the silicalite-HCl system $(p_{HCl} = 1467 Pa)$ at $T = 214 \pm 5$ K are shown in Figure 10.

The following observations were made.

(i) The peak of free silanols at 3750 cm⁻¹ and the band centered at about 3600 cm⁻¹ (due to SiOH(HCl)_n) are gradually eroded upon (CH₃)₂O dosage. Simultaneously, the broad band (centered at 3242 cm⁻¹) due to the (CH₃)₂O-silanols adducts appears. These modifications are due to the reactions shown in Chart 4. From this it is inferred that the HCl-silanols complexes are less stable than those formed between ether and silanols, in agreement with the corresponding shifts $\Delta \bar{\nu}$ of the ν (OH) modes of silanols.

(ii) The peak at 2830 cm⁻¹, characteristic of HCl adsorbed on silicalite (bold curve in Figure 10), gradually desappears with simultaneous formation of a broad band centered at about 2360 cm⁻¹ (FWHM \approx 530 cm⁻¹). On the analogy with the known data concerning HCl–(CH₃)₂O complexes in gas^{43,44} and in the solid phase,⁴⁵ the absorption at 2360 cm⁻¹ is ascribed to the ν (HCl) mode in the 1:1 HCl–(CH₃)₂O adducts ($\Delta \bar{\nu}$ (HCl) \cong 540 cm⁻¹), formed according to the equilibrium reaction shown in Chart 5.



Figure 9. IR spectra of increasing doses of $(CH_3)_2O$ adsorbed on silicalite at 214 ± 5 K ($0 \le$ equilibrium pressure ≤ 13300 Pa).



Wavenumber (cm⁻¹)

Figure 10. IR spectra showing the interaction of HCl adsorbed on silicalite (1467 Pa) with increasing doses of $(CH_3)_2O$ at 214 ± 5 K (see text for details).

CHART 4



Like in the gas phase, the proton transfer does not occur⁴⁴ and the adduct has neutral character and is characterized by a medium hydrogen bond. The large band is made complicated in the 2200-1500 cm⁻¹ range by several Fermi resonance

effects due to coupling of the ν (HCl) mode with the [δ (O–HCl) + ν (COC)] combination modes.⁴⁴ The intensity of this absorption is much higher than that of the same complex formed in an analogous experiment on silica (data non shown for

CHART 5



brevity); this confirms that the 1:1 complexes are prevalently formed in the zeolite channels. It must be stressed that the ν (HCl) stretching mode of (CH₃)₂O-HCl adducts is at 2570 cm⁻¹ in the gas phase^{43,44} and at 2530 cm⁻¹ in the solid phase.⁴⁵

(iii) The stretching modes of methyl groups are observed in the 3100–2800 cm⁻¹ range ($\nu_{asym} = 2992$, 2936, 2892, 2875 cm⁻¹; $\nu_{sym} = 2826$, 2820 cm⁻¹), while the bending modes are in the 1500–1400 cm⁻¹ range (1473, 1457, 1426 cm⁻¹). Finally, the rocking modes are at 905 (hydrogen bonded) and at 921 (physisorbed) cm⁻¹. Most of these frequencies are slightly higher than those obtained in the absence of HCl; this also indicates that the modes of the methyl groups are slightly perturbed by the interaction with the HCl.⁴⁶

3. 2. 3. HCl-B ($B = (CH_3CH_2)_2O$, THF, Benzene) Complexes in Silicalite. The study of the interaction of HCl with basic molecules has been extended also to other bases like benzene, diethyl ether, and THF. The main features of the spectra are similar to those obtained for the interaction with (CH₃)₂O and are summarized in Table 2, where the shifts $\Delta \bar{\nu}$ (HCl) induced by the interaction with the base B are reported. The FWHM of the bands are about (3/4) $\Delta \bar{\nu}$ as usually observed in hydrogenbonded systems.

3. 3. BHW Plot. A well accepted method to study by means of IR spectroscopy the acid strength of a Brønsted acid HX is based on the evaluation of the frequency shifts that the $\nu(X-$ H) mode undergoes by interaction with molecules of different basicity.³⁻⁶ When these shifts are plotted against the shifts that a second acid molecule ZH (considered as reference) is undergoing by interaction with the same bases ($\Delta \bar{\nu}(HX)$ vs $\Delta \bar{\nu}$ (HZ)), the Bellamy, Hallam, Williams (BHW) plot is obtained.¹¹⁻¹³ It has been found that for each studied acid molecule a single straight line is observed whose gradient is a measure of the acidity of the molecule. It has been shown that the BHW plot can be usefully employed also to estimate the acid strength of Brønsted groups located on surfaces (provided that the proton affinity of the base B is not too high).^{10,16} It has been experimentally verified that a good reference acid group for heterogeneous systems is the SiOH group of silica and of silicalite.10,16

It is useful to recall that the HCl molecule has been extensively studied in the past, in the gaseous phase,^{47–51} in cryogenic matrixes,^{52–60} and in solution,^{61–64} and that numerous data sets about the ν (HCl) frequencies in various HCl–B complexes can be found in the literature. If all the experimental data are reported in a BHW plot, Figure 11 is obtained. In this figure, the $\Delta \bar{\nu}$ (HCl) values of the intrazeolitic HCl–B complexes (Table 2) are also reported for comparison.

From Figure 11, it is clearly emerging that the data of the HCl complexes in the three different environments (in silicalite, matrix, and apolar solvents) originate three different straight lines. Unfortunately, to our knowledge, not so many data about HCl–B complexes in an Ar matrix are available, and line fitting the cryogenic data is certainly not accurate; despite this, there is no doubt that the slope of the HCl–B complexes encapsulated in silicalite is greater than that of HCl–B complexes isolated in a cryogenic matrix and in vacuo. The general trend of the slopes of the three straight lines (that is, m(HCl in solvent) > m(HCl in silicalite) > m(HCl in Ar matrix)) can be explained in terms of the electric field effects associated with the presence



Figure 11. BHW plot of the shifts $(\Delta \bar{\nu})$ of the ν (HCl) frequencies in 1:1 ClH–B hydrogen-bonded complexes with different B in different environments versus the shifts $(\Delta \bar{\nu})$ of SiOH groups in 1:1 hydrogenbonded complexes with the same bases. \Box represents the experimental data of HCl in an Ar criogenic matrix (B = N₂,^{28,39,52} CO₂,²⁸ CO₂,²⁸ C₂H₄,²⁸ H₂O,²⁸ CH₃CN,⁶⁶); \bigcirc represents the experimental data HCl inserted in silicalite; \triangle represents the experimental data of HCl in a solution of apolar solvents (B = CCl₄, chloroform, C₂Cl₂H₂, benzene, nitrobenzene, toluene, anisole, *p*-xylene, mesitylene, ethyl acetate, acetone, and dioxan⁶¹).

of dipoles on the atoms of the "solvent" (cryogenic matrix, zeolite, and solution); in fact, the electric field induces an increase of the ionic character of the hydrogen bond (by changing the effectiveness of the screening effects), with a subsequent increase of $\Delta \bar{\nu}$. This effect is well-known in solution as "solvent effect" and in cryogenic matrixes as "matrix effect". In the macroscopic scale, it is connected to the particular dielectric constants of the media where the complexes are formed as discussed in a pioneer paper by Kirkwood.⁶⁵ A quantitative analysis in terms of the Kirkwood equation would require the definition of the dielectric constant of a nonhomogeneous medium; for this reason, it is not considered.

It is so concluded that the effect of the solid environment represented by the neutral silicalite framework on the spectroscopic properties of the HCl–B adducts entrapped in the channels is relevant (it is intermediate between that observed in apolar solvents and in an argon matrix), and consequently plays a role in determining the strength of the Brønsted groups located in internal positions. This conclusion, verified for the neutral framework of silicalite (where the interactions between the acid guest molecule and the zeolite host walls are prevalently of the van der Waals type), is a fortiori valid for the much stronger structural Al(OH)Si Brønsted groups of the zeolites.

However, to quantitatively extend these considerations to real zeolites, the spectroscopy of HCl–B model complexes formed in situ into charged frameworks such as those of H–ZSM-5, H–Y, etc. should be investigated by performing a new series of experiments.

4. Conclusions

The IR study of the HCl-silica and HCl-silicalite interaction at ~210 K indicates that a weak H-bond interaction occurs between silanols and HCl molecules and that adducts of increasing nuclearity (containing two or more HCl molecules) are formed upon increasing the HCl dosage. In silicalite, the HCl molecules interact with the siloxane bridges and form also small (HCl)_n clusters. The molecules behave as partially hindered. A complete assignment is given through the help of molecular mechanics and ab initio calculations. The interaction of adsorbed HCl with basic molecules B [(CH₃)₂O, (CH₃CH₂)₂O, THF, and benzene)] leads to the formation of intrazeolitic 1:1 adducts HCl-B. The comparison of the $\Delta \bar{\nu}$ (HCl) values of various HCl-B complexes in different environments (in apolar solvents and in an Ar cryogenic matrix) with the corresponding values of HCl-B intrazeolitic complexes demonstrates that the acidity of HCl grows substantially on passing from the cryogenic matrix, to silicalite, and to solution. It is concluded that the zeolitic framework of the zeolite acts as a solvent that influences the acidity of structural Si(OH)Al Brønsted sites located in the channels and cavities. The contribution of the tridimensional structure of the zeolitic framework in determining the acid strength of the Si(OH)Al groups cannot consequently be ignored.

Acknowledgment. The authors thank Prof. Piero Ugliengo and Dott. Gabriele Ricchiardi for fruitful discussion and wise advice and Dott. Giuseppina Meligrana for help in IR measurements. This work has been supported by CNR (Progetto Strategico Tecnologie Chimiche) and MURST.

References and Notes

- (1) van Santen, R. A. Catal. Today 1997, 38, 377.
- (2) Leopold, K. R.; Canagaratna, M.; Phillips, J. A. Acc. Chem. Res. 1997, 2, 57. Tomasi, J.; Persico, M. Chem. Rev. 1994, 94, 2027.
 - (3) Corma, A. Chem. Rev. 1995, 95, 559.
- (4) Ugliengo, P.; Ferrari, A. M.; Zecchina, A.; Garrone, E. J. Phys. Chem. 1996, 100, 3632.
- (5) Zecchina, A.; Otero Areán, C. Chem. Soc. Rev. 1996, 187.
- (6) Sauer, J.; Ugliengo, P.; Garrone E.; Saunders, V. R. Chem. Rev. 1994, 94, 2095.
- (7) Pimentel, G. C.; McLellan, A. L. The Hydrogen Bond; Pauling, L., Ed.; W. H. Freeman: San Francisco, 1960.
 - (8) Kubelkovà, L.; Beran, S.; Lercher, J. Zeolites 1989, 9, 539.
- (9) Zecchina, A.; Otero Areán, C. Chem. Soc. Rev. 1996, 188. Bordiga,
- S.; Lamberti, C.; Geobaldo, F.; Zecchina, A. Langmuir 1995, 11, 527.
- Zecchina, A.; Bordiga, S.; Lamberti, C.; Spoto, G.; Carnelli, L.; Otero Arean, C. J. Phys. Chem. 1994, 98, 9577
- (10) Zecchina, A.; Bordiga, S.; Spoto, G.; Scarano, D.; Spanò, G.; Geobaldo, F. J. Chem. Soc., Faraday Trans. 1996, 92, 4863.
- (11) Bellamy, L. J.; Hallam, H. E.; Williams, R. L. Trans. Faraday Soc. 1958, 54, 1120.
 - (12) Bellamy, L. J.; Pace, R. J. Spectrochim. Acta 1969, 25A, 319.
 - (13) Hair, M. L.; Hertl, W. J. Phys. Chem. 1970, 74, 91.
- (14) Yin, F.; Blummenfeld, A. L.; Fripiat, J. J. J. Phys. Chem. B 1997, 101, 1824. Zecchina, A.; Marchese, L.; Bordiga, S.; Pazè, C.; Gianotti, E. J. Phys. Chem. B 1997, 101, 10128.
- (15) Buzzoni, R.; Bordiga, S.; Ricchiardi, G.; Lamberti, C.; Zecchina, A.; Bellussi, G. Langmuir 1996, 12, 930. Datka, J. J. Chem. Soc., Faraday Trans. 1 1981, 77, 2877. Datka, J.; Tuznik, E. J. Catal. 1986, 43, 102. Datka, J.; Turek, A. M.; Jehng, J. M.; Wachs, I. E. J. Catal. 1992, 135,
- 20186. Emeis, C. A. J. Catal. 1993, 141, 347. (16) Pazè, C.; Bordiga, S.; Lamberti, C.; Salvalaggio, M.; Zecchina,
- A.: Bellussi, G. J. Phys. Chem. B 1997, 101, 4740.
- (17) Pazé, C.; Bordiga, S.; Spoto, G.; Lamberti, C.; Zecchina, A. J. Chem Soc., Faraday Trans. 1998, 94, 309.
- (18) Zecchina, A.; Bordiga, S.; Spoto, G.; Marchese, L.; Petrini, G.; Leofanti, G.; Padovan, M. J. Phys. Chem. 1992, 96, 4985.
- (19) Zecchina, A.; Bordiga, S.; Spoto, G.; Marchese, L.; Petrini, G.; Leofanti, G.; Padovan, M. J. Phys. Chem. 1992, 96, 4991.
- (20) Marra, G. L.; Tozzola, G.; Leofanti, G.; Padovan, M.; Petrini, G.; Genoni, F.; Venturelli, B.; Zecchina, A.; Bordiga, S.; Ricchiardi, G. Stud.
- Surf. Sci. Catal. 1994, 84, 559.
- (21) DISCOVER, version 95.0; MSI Technology Inc.: San Diego, CA, October 1995
 - (22) Hill, J.-R.; Sauer, J. J. Phys. Chem. 1994, 98, 1238.
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.;

Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, revision C.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(24) Becke, A. D. J. Chem. Phys. 1993, 98, 5648. Lee, C.; Yang, W.; Parr, R. C. Phys. Rev. B 1988, 37, 75.

(25) Wilson, E. B.; Decius, J. B.; Cross, P. C. Molecular Vibration; McGraw-Hill: New York, 1955. Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A.; Ab initio Molecular Orbital Theory; Wiley: New York, 1986

(26) Ozin, G. A.; Özkar, S.; Stucky, G. D. J. Phys. Chem. 1990, 94, 7562. Ozin, G. A.; Özkar, S.; McMurray, L. J. Phys. Chem. 1990, 94, 8289; 1990, 94, 8297

(27) West, W. J. Chem. Phys. 1939, 7, 795.

- (28) Barnes, A. J.; Hallam, H. E.; Scrimshaw, G. F. Trans. Faraday Soc. 1969, 65, 3172.
 - (29) Pine, A. S.; Howard, B. J. J. Chem. Phys. 1986, 84, 591.
 - (30) Girardet, C.; Robert, D. J. Chem. Phys. 1973, 58, 4110.
 - (31) Andrews, L. Faraday Discuss. Chem. Soc. 1988, 86, 37.
 - (32) Girardet, C.; Robert, D. J. Chem. Phys. 1973, 59, 5020.
- (33) Hallam, H. E. In The Hydrogen Bond; Schuster, P., Zundel G., Sandorfy C., Eds.; North-Holland, 1976; p 1075.
- (34) Jeremy Jones, W. In Infrared Spectroscopy and Molecular Structure; Davies, M., Ed.; Elsevier Publishing Company: Amsterdam, 1963; p 15, 159.
- (35) West, W.; Edward, R. T. J. Chem. Phys. 1937, 5, 14.
- (36) Maillard, D.; Schriver, A.; Perchard, J. P.; Girardet, C. J. Chem. Phys. 1979, 71, 505.
- (37) Maillard, D.; Schriver, A.; Perchard, J. P.; Girardet, C.; Robert, D. J. Chem. Phys. 1977, 67, 39.
- (38) Herzberg, G. Molecular Spectra and Molecular Structure, I. Molecular Spectra of Diatomic Molecules; D. Van Nostrand Company, Inc.: New York, 1945; p 464.
- (39) Ugliengo, P.; Garrone, E. J. Mol. Catal. 1989, 54, 439
- (40) Civalleri, B.; Garrone, E.; Ugliengo, P. J. Phys. Chem. B 1998, 102, 2373.
- (41) Ugliengo, P.; Ferrari, A. M.; Civalleri, B.; Garrone, E. In preparation.
- (42) Civalleri, B.; Garrone, E.; Ugliengo, P. J. Mol. Struct. (THEOCHEM) 1997. 419. 227
 - (43) Bertie, J. E.; Falk, M. V. Can. J. Chem. 1973, 51, 1713.
 - (44) Bertie, J. E.; Millen, D. J. J. Chem. Soc. 1965, 497.
 - (45) Seel, R. M.; Sheppard, N. Spectrochim. Acta 1969, 25A, 1287.
- (46) Pelmenschikov, A. G.; Morosi, G.; Gamba, A. J. Phys. Chem. 1997,
- 101, 1178. Pelmenschikov, A. G.; Morosi, G.; Gamba, A. J. Phys. Chem.
- 1992, 96, 2241. Pelmenschikov, A. G.; Morosi, G.; Gamba, A.; Zecchina,
- A.; Bordiga, S.; Paukshtis, E. A. J. Phys. Chem. 1993, 97, 11979.
- (47) Lovejoy, C. M.; Nesbitt, D. J. Chem. Phys. Lett. 1988, 147, 490. (48) Maillard, D.; Schriver, A.; Perchard, J. P.; Girardet, C.; Robert, D. J. Chem. Phys. 1977, 67, 3917
- (49) Bertie, J. E.; Falk, M. V. Can. J. Chem. 1973, 51, 1713.
- (50) Sharpe, S. W.; Zeng, Y. P.; Wittig, C.; Beaudet, R. A. J. Chem. Phys. 1990, 92, 943.
 - (51) Seel, R. M.; Sheppard, N. Spectrochim. Acta 1969, 25A, 1287.
 - (52) Andrews, L.; Davis, S. R. J. Chem. Phys. 1985, 83, 4983.
 - (53) Ault, B. S.; Pimentel, G. C. J. Phys. Chem. 1973, 77, 57.
 - (54) Ault, B. S.; Pimentel, G. C. J. Phys. Chem. 1973, 77, 1649.
 - (55) Johnson, G. L.; Andrews, L. J. Phys. Chem. 1983, 87, 1852
- (56) Sharpe, S. W.; Zeng, Y. P.; Wittig, C.; Beaudet, R. A. J. Chem.
- Phys. 1990, 92, 943.
 - (57) Amirand, C.; Maillard, D. J. Mol. Struct. 1988, 176, 181.
- (58) Ayers, G. P.; Pullin, A. D. E. Spectrochim. Acta 1976, 32A, 1641. (59) Schriver, A.; Silvi, B.; Maillard, D.; Perchard, J. P. J. Phys. Chem.
- 1977, 81, 2095. (60) Barnes, A. J.; Hallam, H. E.; Scrimshaw, G. F. Trans. Faraday
- Soc. 1969, 65, 3172.
 - (61) Josien, A.; Sourisseau, B. Bull. Soc. Chim. 1955, 178.
 - (62) West, W.; Arthur, P. J. Chem. Phys. 1937, 5, 10.
 - (63) West, W.; Edwards, R. T. J. Chem. Phys. 1937, 5, 14.
 - (64) Andrews, L.; Hunt, R. D. J. Chem. Phys. 1988, 89, 3502.
 - (65) Kirkwood, J. G. J. Chem. Phys. 1934, 2, 351.
 - (66) Johnson, G. L.; Andrews, L. J. Phys. Chem. 1983, 87, 1852.