

PYRIDINIUM IONS – NEW PROBE FOR BASIC SITES OF SOLID ACIDS*Josef KOTRLA^a, Jan FLORIAN^b, Ludmila KUBELKOVA^{a,**} and Jacques FRAISSARD^c^a J. Heyrovsky Institute of Physical Chemistry,

Academy of Sciences of the Czech Republic, 182 23 Prague 8, The Czech Republic

^b Institute of Physics,

Charles University, 121 16 Prague 2, The Czech Republic

^c Laboratoire de Chimie des Surfaces,

Universite P. et M. Curie, CNRS-URA 1428, 4 Place Jussieu, 75252 Paris Cedex 05, France

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The hydrogen bonding interactions of the pyridinium ion (PyH^+) with the deprotonated skeleton of acid zeolites were studied using Fourier transform infrared (FTIR) spectroscopy and quantum chemical *ab initio* calculations. It was found that the frequency of the NH stretching vibration, $\nu(\text{NH})$, of the newly formed H-bond increases in the zeolite sequence $\text{HNaX} < \text{HY} < \text{HM} \approx \text{HZSM-5}$. This is related to decreasing basicity of the skeletal oxygens (basic sites conjugated to bridging hydroxyls). Therefore, pyridine can serve as a probe for the basic sites of acid zeolites. In this way it can complement the pyrrole probe, which is established for basicity monitoring of alkali-metal exchanged zeolites.

Wide catalytic application of solid bases and the concerted action of acidic and basic surface sites in acid catalysis¹⁻⁵ have stimulated growing interest in the characterization of basic zeolite sites. Several probe molecules have been suggested and used for this purpose⁶. Among them, pyrrole^{7,8} appeared most promising. Pyrrole forms surface complexes which are hydrogen bonded via the NH group to the surface base site. The weakening of the NH bond in a surface complex depends on the proton affinity of these sites and thus it can be used as a measure of the surface basicity. This possibility was, indeed, verified by a study of the infrared spectra of pyrrole adsorbed on cationic (basic) forms of zeolites^{7,8}. It was found that the frequency of the stretching NH vibration in the surface complex monitors changes in the basicity of the skeletal oxygens. In contrast to solid bases (alkali forms of zeolites), the surfaces of solid acids of oxidic nature (acid forms of zeolites) contain both the basic and acidic sites. These sites are

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**The author to whom correspondence should be addressed.

represented by skeletal oxygens and hydroxyls, respectively. In acidic zeolites, the acid strength of bridging hydroxyls is high enough to cause the oligomerization of pyrrole⁸. The occurrence of this reaction thus constitutes a serious drawback in the use of pyrrole to characterize the basic sites of solid acids.

In this paper we propose to use pyridinium ions instead of pyrrole molecules to determine the basicity of solids containing acid OH groups. In contrast to pyrrole, pyridine does not oligomerize on acidic catalysts. It attracts protons from sufficiently strongly acidic OH groups and forms stable "ion-pair" hydrogen bonded complexes, $C_5H_5NH^+ \dots O$ (solid). Obviously, the weakening of the NH bond should be proportional to the basicity of the site in the complex and, consequently, to the basicity of the skeletal oxygens in the original zeolite. In order to verify this hypothesis, we measured the Fourier transform infrared spectra of pyridine adsorbed in HNaX, HY, HM and HZSM-5 zeolites. These zeolites exhibit various acid strengths of bridging hydroxyls and basicities of skeletal oxygens. Finally, in order to gain a better insight into the probing mechanism we reviewed the *ab initio* structure and vibrational spectra of the model $[HOSiH_2-O-AlH_2-O-SiH_3]^- [C_5H_6NH]^+$ complex^{9,13}.

EXPERIMENTAL

Adsorbents: Zeolites were synthesized in the Institute of Oil and Hydrocarbon Gases, Bratislava and converted to the NH_4 form by repeated ion exchange. The crystallinity of the samples was checked by several methods (XRD, FTIR, etc.). The dehydration and decomposition of NH_4^+ ions resulting in the formation of acid zeolites was carried out in situ inside the vacuum IR cell at 400 °C and 10^{-4} Pa for 3 – 4 h or overnight.

Adsorbates. Pyridine (Fluka, analytical grade purity) was purified before adsorption by repeated freezing and thawing. It was stored over dry KA zeolite.

Experimental procedure. Pyridine was adsorbed in successive doses at 150 °C onto thin zeolite plates in a thickness of 7 mg cm^{-2} . Simultaneous heating of the apparatus prevented adsorption of Py on the apparatus walls. The IR spectra were measured after cooling to room temperature using the Nicolet MX-1E FTIR spectrometer (resolution 2 cm^{-1}). Difference spectra were obtained by subtracting the original spectrum of the zeolite from the spectrum of the zeolite with pyridinium ions.

Quantum chemical calculations. The details are given elsewhere^{9,13}.

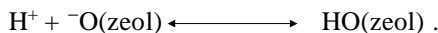
RESULTS

Samples

The acidic catalysts are represented by the four zeolites listed in Table I. This Table also shows the Si/Al ratio for individual samples, the frequency of the stretching vibration of the free bridging hydroxyls and Sanderson's charge on the hydrogen atom of the hydroxyls as well as on the oxygen atoms in the skeleton. These charges were calculated using Sanderson's electronegativity equalization principle¹⁰, so that they can be considered to characterize to a first approximation, the average acid strength of the

bridging hydroxyls and basicity of the skeletal oxygens, respectively. It should be kept in mind that this principle does not take into account geometric effects, the heterogeneity of the distribution of the individual elements in the lattice and the difference in short-range and long-range interactions¹¹. The bridging hydroxyls of faujasites are directed into the large and small cavities, reflected in two bands in the IR spectra, at 3 655 – 3 635 (HF) and 3 573 – 3 545 (LF) cm⁻¹, respectively. The hydroxyls in the large cavities dominate in HNaX zeolite while both types of OH groups are present in large numbers in the HY zeolite. HM and HZSM-5 zeolites contain only one type of hydroxyls, so that only a single band is observed at 3 608 and 3 612 cm⁻¹, respectively, in their IR spectra.

Alternatively to Sanderson's charge, proton affinity can be used as a measure of the acid-base properties of the solid. It is defined as the negative enthalpy of the reaction



The proton affinity value 1 173 kJ/mol was determined for hydroxyls in large cavities of the HY zeolite¹² while the value 1 152 kJ/mol was found for HZSM-5 zeolite¹² (not given in the Table).

Structural Considerations and Spectra Calculations

The HF/6-31G and HF/6-31G(d) potential energy surfaces for the H zeolite-pyridine system exhibit a shallow minimum for the "neutral" Py...HO(zeol) complex and a deep minimum corresponding to the "ion-pair" PyH⁺...⁻O(zeol) structure¹³. The increase in the size of the zeolite fragment from H₃Si-OH-AlH₂-OH to HOSiH₂-OH-AlH₂-O-

TABLE I
Characteristics of samples

Sample	Si/Al	Bridging OH mmol/g ^a	v(OH free) cm ⁻¹	σ(H) . 10	σ(O) . 10
H ₆₀ Na ₄₀ -X	1.33	4.03	3 655 ^b 3 573 ^c	0.43	-3.14
HY	2.90	4.02	3 638 ^b 3 545 ^c	1.37	-2.37
HM	8.40	1.73	3 608	1.63	-2.15
HZSM-5	13.5	1.15	3 612	1.70	-2.09

^a Per g of dry sample. ^b Located in large cavities – HF OH groups. ^c Located in small cavities – LF OH groups, v stretching vibration, σ(H) partial charge on H atom of zeolite hydroxyl, σ(O) partial charge on oxygen atom of zeolite skeleton.

SiH_3 results in even higher stabilization of the "ion-pair" structure¹³. In this case, the total energy of the "ion-pair" is 18 kJ/mol lower than that of the "neutral" complex. The "ion-pair" complex of pyridine with the latter fragment is depicted in Fig. 1. The geometry of the stationary point corresponding to this structure was optimized at the HF/6-31G level under the C_s symmetry constraint^{9,13}. The figure shows that, in addition to the $>\text{NH}^+\dots\text{O}(\text{zeol})$ interaction, also the adjacent two skeletal oxygens of the model fragment affect the CH bonds in the vicinity of the N atom of the pyridinium ring.

The calculated frequencies and infrared intensities of the individual vibrational modes of free pyridinium ion and that in the zeolite are given in Table II. The most important are those lying between 1 400 and 1 650 cm^{-1} , as this spectral region is often used to identify PyH^+ species on solid surfaces⁶. These modes are composed of bending NH, bending CH and ring CC (NC) vibrations. None of them corresponds to the pure NH bending vibration. In contrast, the NH stretching mode of the pyridinium ion is highly characteristic and, as expected, most sensitive to bonding with the surface oxygen. This suggestion is confirmed by the $\nu(\text{NH})$ values of 3 425 and 2 597 cm^{-1} calculated for the hypothetical free ion and for the $\text{PyH}^+\dots\text{O}(\text{zeol})$ complex, respectively.

FTIR Spectra – Experimental Data

The infrared spectra of all the samples display features typical for predominant formation of pyridinium ions if the $\text{Py}/\text{OH}(\text{zeol})$ ratio is below 1. The positions of all the most typical bands between 1 400 and 1 650 cm^{-1} and the maxima of the broad band between 2 540 and 2 740 cm^{-1} fit reasonably the *ab initio* frequencies of the corresponding modes (see Table II, Figs 2 and 3).

However, the movement of the PyH^+ ion can increase the $>\text{NH}^+\dots\text{O}(\text{zeol})$ distance which penalizes the energy of the complex through the strong electrostatic attraction.

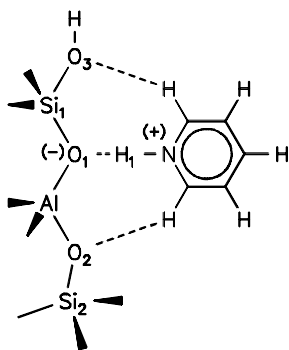


FIG. 1
Structure of the pyridinium ion complex with a model zeolite fragment, calculated by the *ab initio* HF/6-31G method¹³; $r(\text{NH})$ 1.04 Å, $r(\text{O}_1\text{N})$ 2.57 Å, $r(\text{O}_2\text{H})$ 2.47 Å, $r(\text{O}_3\text{H})$ 2.32 Å, angle O_1NH 0.8 °

The "neutral" Py...HO(zeol) complex may thus become temporarily more stable. Consequently, the presence of this complex might be indicated by very weak bands at 1 440 – 1 445 and 1 580 – 1 600 cm^{-1} observed in the spectra of the HY zeolite. The HY zeolite is particularly suitable for this purpose because it contains a high number of bridging hydroxyls so that the total attainable concentration of "ion-pair" and "neutral" complexes is also high.

The variation in the concentration of PyH^+ ions in all the zeolites studied does not cause any significant changes in the position of the $\nu(\text{NH})$ band (within $\pm 10 \text{ cm}^{-1}$) and the bands at 1 400 – 1 650 cm^{-1} (within $\pm 2 \text{ cm}^{-1}$). This finding is demonstrated in Figs 2 and 3 for HZSM-5 and HY zeolites. Interestingly, the variation in the acid strength of the bridging hydroxyls (basicity of the skeletal oxygens) affects the frequencies of the vibrations between 1 400 and 1 650 cm^{-1} only marginally. The narrow intervals of the occurrences of the band maxima are given in Table II. In contrast, the maximum of the NH band depends significantly on the properties of the zeolite skeleton. Figures 2a, 3a and Table III show that the $\nu(\text{NH})$ band is shifted towards lower wavenumbers (red shift) if the basicity of the skeletal oxygens increases (acid strength of the original bridging OH decreases). Thus, the highest NH value of 2 720 cm^{-1} was found for HZSM-5 while the lowest of 2 565 cm^{-1} was found for HNaX.

The transparency of samples in the spectral region below 1 300 cm^{-1} is greatly limited by absorption caused by the vibrations of the zeolite skeleton. Nevertheless, the strong bands at 680 and 750 cm^{-1} which appear in the transmission window again confirm the formation of pyridinium ions (Fig. 4). This follows from both *ab initio* calculations (not given in the Table) and comparison with the spectra of PyH^+ salts in solutions¹⁴.

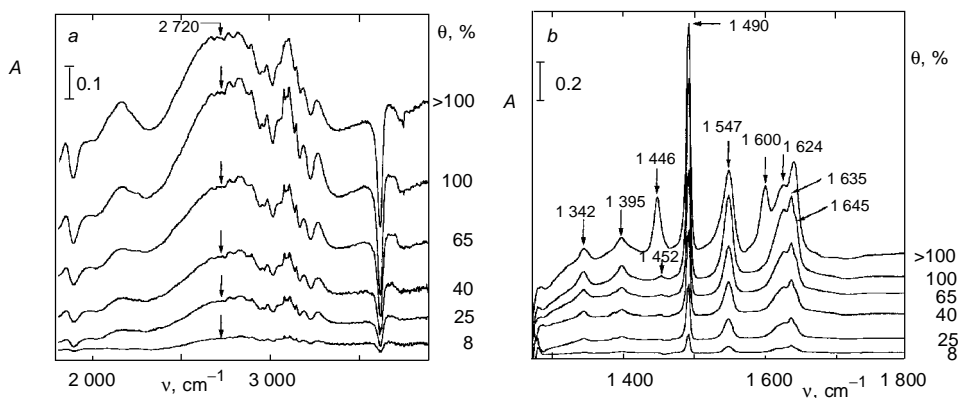


FIG. 2

FTIR difference spectra of pyridine complexes on HZSM-5 zeolite; spectral region above 1 300 cm^{-1} ; θ -coverage of bridging OH groups (%)

Cavities or pores in zeolites mostly contain nonskeletal Al species which serve as a source of electron-accepting Lewis acidity. Weak bands at 1 450 – 1 455 and 1 620 cm^{-1} , which are observed in the spectra of all samples (for instance see Figs 2 and 3) can thus be attributed¹⁵ to pyridine on the above Al Lewis sites.

An excess of pyridine, i.e. Py/Al ratios higher than 1, result in weak physisorption of molecules remaining after the conversion of all the bridging OH to PyH^+ (for instance, ref.¹⁶). Characteristic Py bands of weakly adsorbed pyridine are then found at 1 440 – 1 446 and 1 582 – 1 600 cm^{-1} (Figs 2b, 3b). However, the coadsorbed species do not significantly alter the bands of PyH^+ . Most probably their effect is much weaker compared to the interaction of PyH^+ species with cavity walls (skeletal oxygens).

DISCUSSION

It is widely known that hydrogen bonding in A–H...B complexes causes a weakening of the A–H bonds. Corresponding changes in spectral parameters consist in the broadening and the red shift of the stretching $\nu(\text{AH})$ vibration with respect to its unperturbed position, due to the $\nu(\text{AH}) \pm k\nu(\text{AH...B})$ vibrational coupling. Bending AH vibrations are shifted in the opposite direction towards higher wavenumbers. These rules were shown to be obeyed also for “neutral” complexes of basic compounds adsorbed on the bridging hydroxyls of zeolites^{4,13}. Due to the high basicity of pyridine¹⁷ (924 kJ/mol) the hydrogen of the bridging hydroxyl is transferred to the adsorbed pyridine and an “ion-pair” complex $\text{PyH}^+ \cdot \text{O}(\text{zeol})$ is formed. Obviously, greater interaction energy between the pyridinium ion and the zeolite skeleton can be expected to weaken the NH bond to a greater extent. Therefore, changes in the NH spectral parameters of the “ion-pair” complex analogous to that found for the OH groups of “neutral” surface com-

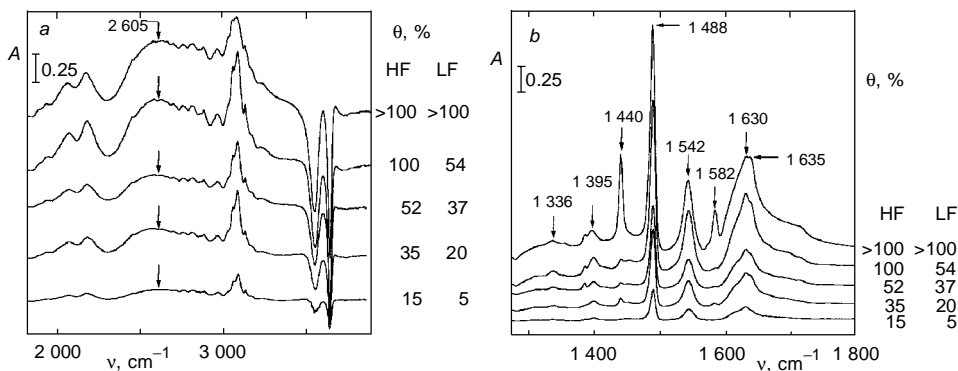


FIG. 3

FTIR difference spectra of pyridine interaction complexes in HY; spectral region above 1 300 cm^{-1} ; θ -coverage of bridging OH groups (%)

plexes (for instance refs^{6,12,13,18}) will most likely occur. This suggestion is supported by the previous study of pyridine–acid pairs in solutions¹⁹.

Our data, indeed, confirm, that $\nu(\text{NH})$ of the $\text{PyH}^+\dots\text{O}(\text{zeol})$ complex is sensitive to the character of the oxygen atoms in the skeleton (see Tables II, III). The frequency of the highly characteristic $\nu(\text{NH})$ band decreases with increasing basicity of the skeletal oxygens. The notably smaller sensitivity of the vibrations in frequency region between 1 400 and 1 650 cm^{-1} to the basic properties of the solid is explained to a great extent by the coupling of the $\delta(\text{NH})$ bending vibration with the $\delta(\text{CH})$ bending vibrations and $\nu[\text{CC}(\text{CN})]$ ring-stretching vibrations (Table II).

More conveniently, the basicity of the skeletal oxygens can be related to the $\Delta\nu(\text{NH})$ shift determined as a difference between the frequency of the free and the H-bonded pyridinium ions. However, $\nu(\text{NH})$ of free PyH^+ was not determined experimentally. Because it should certainly be higher than the value observed by Cook¹⁴ for weakly bonded crystalline pyridine salts, i.e. 3 300 cm^{-1} [PyHSbCl_6], we used the reasonable *ab initio* frequency of 3 425 cm^{-1} (ref.¹³) as a $\nu(\text{NH})$ reference point. Then, the $\Delta\nu(\text{NH})$ and $\Delta\nu(\text{OH})$ shifts reflecting interaction energies are of a similar order of magnitude for the $\text{PyH}^+\dots\text{O}(\text{zeol})$ and $\text{CD}_3\text{CN}\dots\text{HO}(\text{zeol})$ (ref.⁴) complexes, respectively. However, the $\Delta\nu(\text{OH})$ of the “neutral” $\text{CD}_3\text{CN}\dots\text{OH}(\text{zeol})$ complex is much more sensitive to the acid-base properties of the solid than $\Delta\nu(\text{NH})$ of the “ion-pair” $\text{PyH}^+\dots\text{O}(\text{zeol})$ complex. For HZSM-5 the $\Delta\nu(\text{NH})$ of 705 cm^{-1} differs only by 155 cm^{-1} from the maximum value of $\Delta\nu(\text{NH})$ measured for the HNaX zeolite (860 cm^{-1} , Table III). This shift difference relates to an increase in Sandersen’s charge on the skeletal oxygen from -0.21 to -0.31 . The difference in $\Delta\nu(\text{OH})$ for “neutral” $\text{AN}\dots\text{HO}(\text{zeol})$ on the same zeolites is 440 cm^{-1} . Such dissimilar behaviour can be explained by a predominant contribution of the dispersion forces to the energetics of the “neutral” complex in contrast to the charge–charge interactions strongly affecting the adsorbent–adsorbate bonding in “ion-pair” complex.

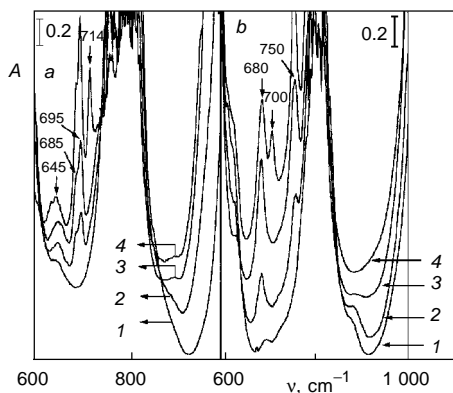


FIG. 4

FTIR spectra in transmission windows below 1 000 cm^{-1} of: **a** HY before **1** and after the interaction with Py, **2** OH coverage $\theta = 35\%$ (HF OH) and 20% (LF OH), **3** $\theta = 100\%$ (HF OH) and 54% (LF OH), **4** abundance of Py; **b** HZSM-5 before **1** and after the interaction with Py, **2** OH coverage $\theta = 40\%$, **3** $\theta = 100\%$, **4** abundance of Py

Compared to pyridine on acid zeolites, the $\Delta\nu(\text{NH})$ of pyrrole adsorbed on zeolites containing alkali metals is much lower. A minimum red shift of 30 cm^{-1} related to the $\nu(\text{NH})$ of $3\,420\text{ cm}^{-1}$ of liquid pyrrole²⁰ was reported⁸ for the pyrrole adsorbed on LiM (M = mordenite) while a maximum $\Delta\nu(\text{NH})$ value of 245 cm^{-1} was found for pyrrole on CsX. Because the total difference of 210 cm^{-1} in wavenumbers of $\Delta\nu(\text{NH})$ (pyrrole) is related⁸ to the change in Sanderson charge on the lattice oxygen from $\approx (-0.27)$ to $\approx (-0.49)$, it can be concluded that the sensitivities of the pyridinium ion and pyrrole for the basicity of the skeletal oxygens are similar. Nevertheless, it should always be kept in mind that the dispersion forces play an important role in the "neutral" complex of pyrrole with basic zeolites while charge-charge interactions affect the bonding between PyH^+ and the skeletal oxygen of deprotonized acidic zeolites. Strictly speaking, the $\Delta\nu(\text{NH})$ of a pyridinium ion inside acid zeolites characterizes the basicity of the deprotonated skeleton. Figure 5 shows that this parameter is related to the basicity of the skeletal oxygens of the original acid form. The sequence of HZSM-5 and HM (Fig. 5) which is opposite to that found by the determination of adsorption heats of ammonia (for instance ref.²¹) demonstrates that the nature of the molecular probe is essential for

TABLE II
Experimental (exp) and calculated (calc) spectra of $\text{PyH}^+ \dots \bar{\text{O}}(\text{zeol})$ complex and their interpretation

Exp ^a	Calc ^b	PED, % ^c
3 080 – 3 100 m	3 069(54)	$\nu\text{C6H}(69) + \nu\text{C5H}(23)$
	3 061(2.8)	$\nu\text{C3H}(78) - \nu\text{C6H}(10)$
3 070 – 3 085 mw	3 055(17)	$\nu\text{C5H}(65) - \nu\text{C6H}(19)$
3 050 – 3 070 m (3 030) w	3 031 (4.5)	$\nu\text{C4H}(83) - \nu\text{C5H}(8)$
	3 022(212)	$\nu\text{C2H}(92)$
2 740 – 2 540 s,br	2 597 (2 472)	$\nu\text{N1H}(98)$
1 630 – 1 640 ms	1 639(19)	$\nu\text{C2C3}(21) + \nu\text{C5C6}(20) + \delta\text{C2H}(11) - \delta\text{C6H}(10)$
1 610 sh	1 610(101)	$\delta\text{N1H}(32) + \nu\text{N1C2}(15) + \nu\text{C4C5}(12) - \nu\text{C6N1}(12) - \nu\text{C3C4}(11)$
1 543 – 1 547 ms	1 543(42)	$\delta\text{N1H}(29) - \delta\text{C4H}(18) + \delta\text{C2H}(11) + \nu\text{C3C4}(10)$
1 488 vs	1 490(88)	$\delta\text{C3H}(20) - \delta\text{C5H}(18) - \delta\text{C6H}(16) + \delta\text{C2H}(15)$
1 395 w	1 405(5.5)	$\delta\text{C3H}(23) + \delta\text{C5H}(22) + \delta\text{C4H}(20) + \delta\text{N1H}(16)$
1 335 – 1 342 w	1 359(1.9)	$\delta\text{C2H}(34) + \delta\text{C6H}(31) - \delta\text{N1H}(15)$

^a m Medium, w weak, s strong, v very, br broad. ^b SQM HF/6-31G calculating for the fragment depicted at Fig. 1 (refs^{9,13}). Pyridine ring atoms are numbered anticlockwise starting from the nitrogen atom (N1). The + (–) signs in the potential energy distribution (PED) denote the phase of the vibrations, ν and δ letters denote stretching and in-plane bending vibrations, respectively. The H atoms terminating the zeolite fragment (attached directly to the Al and Si atoms instead of the O atoms present at these sites in real zeolites) were given oxygen atom mass (16) in the calculation of the vibrational spectrum. Frequency (cm^{-1}), intensity (km/mol). ^c Potential energy distribution.

the establishment of relative basicities/acidities of the individual samples (see also ref.¹²).

The major disadvantage of pyridinium ion as a basicity probe is its large size. Figure 1 shows that the arrangement of the skeletal oxygens allows them to interact not only with NH but also with the CH groups of the PyH⁺ ring. The additional CH...O(zeol) bonding is reflected in the heat of pyridine absorption^{13,16} and most probably also affects the $\nu(\text{NH})$ vibration. The spectroscopic support for the role of the CH...O interaction stems from the variation of the CH stretching modes within 10 – 20 cm⁻¹ when the nature and acidity of zeolite is changed (Table II). The multipoint adsorption of PyH⁺ probably helps in to level out the differences between the individual skeletal oxygens. In addition, it may be one of the factors causing negligible variation in $\Delta\nu(\text{NH})$ (and the heats of adsorption¹⁶) when the concentration of PyH⁺ in the zeolite pores is changed. The contribution of the CH...O bonding of individual C atoms of the PyH⁺ ring to the overall interaction energy of the complex arises from the optimal orientation of PyH⁺

TABLE III

Maximum ν (cm⁻¹) and gravity centrum $\tilde{\nu}$ (cm⁻¹) of NH vibration band(s) above 2 000 cm⁻¹ and corresponding shifts $\Delta\nu$, $\Delta\tilde{\nu}$ related to the $\nu(\text{NH})$ vibration of "free" PyH⁺ ion

Zeolite	ν	$\Delta\nu^b$	$\tilde{\nu}^a$	$\Delta\tilde{\nu}^b$
HNaX	2 565 ± 10	860 ± 10	2 540 ± 10	885 ± 10
HY	2 605 ± 15	820 ± 15	2 605 ± 25	820 ± 25
HM	2 695 ± 10	730 ± 10	2 705 ± 10	720 ± 10
HZSM-5	2 720 ± 10	705 ± 10	2 730 ± 10	695 ± 10

^a Definition of gravity centrum, see refs^{4,19}. ^b $\nu(\text{NH})$ of "free" PyH⁺ 3 425 cm⁻¹, refs^{9,13}.

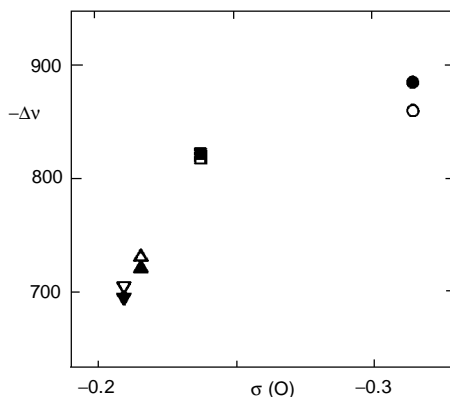


FIG. 5

Dependence of $\Delta\nu(\text{NH})$ (cm⁻¹) of PyH⁺ on Sanderson's charge σ (O) on the skeletal oxygen: HNaX (○,●), HY (□,■), HM (△,▲) and HZSM-5 (▽,▼). Open and full symbols designate values derived from the maximum of the band and its centre of gravity, respectively

inside the pores. This contribution should be different for various zeolite structures, which in turn implies the influence of the zeolite structure on the $\Delta\nu(\text{NH})$ values. Thus, the zeolite structure should be taken into account when the relationship between $\Delta\nu(\text{NH})$ and Sanderson's charge on the skeletal oxygen of the original zeolite (Fig. 5) is treated in detail. However, such a discussion would require much more experimental data.

Summarizing, the stretching vibration of the NH group of the pyridinium ion is sensitive to the properties of the oxygens of the deprotonated zeolite skeleton to which the PyH^+ is attached. PyH^+ thus can be used to probe the basicity of solid acids.

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REFERENCES

1. Pelmenschchikov A. G., van Santen R. A.: *J. Phys. Chem.* 97, 10678 (1993).
2. Gale J. D., Catlow C. R. A., Carruthers J. R.: *Chem. Phys. Lett.* 216, 155 (1993).
3. Haase F., Sauer J.: *J. Phys. Chem.* 98, 3083 (1994).
4. Florian J., Kubelkova L.: *J. Phys. Chem.* 98, 8734 (1994).
5. Teunissen E. H., van Santen R. A., Jansen A. P. J., Duijneveldt F. B.: *J. Phys. Chem.* 97, 203 (1993).
6. Tanabe K., Misono M., Ono Y., Hattori H.: *New Solid Acids and Bases*, Ser. Stud. Surf. Sci. Catal. 51. Elsevier, Amsterdam 1989.
7. Barthomeuf D.: *J. Phys. Chem.* 88, 42 (1984).
8. Huang M., Kaliaguine S.: *J. Chem. Soc., Faraday Trans.* 88, 751 (1992).
9. Florian J., Kubelkova L., Kotrla J.: *J. Mol. Struct.*, in press.
10. Sanderson R. T.: *Chemical Bonds and Bond Energy*. Academic Press, New York 1976.
11. Jacobs P. A.: *Catal. Rev. Sci. Eng.* 24, 415 (1982).
12. Kubelkova L., Beran S., Lercher J. A.: *Zeolites* 9, 539 (1989).
13. Kubelkova L., Kotrla J., Florian J.: *J. Phys. Chem.*, in press.
14. Cook D.: *Can. J. Chem.* 39, 2009 (1961).
15. Kubelkova L., Beran S., Malecka A., Mastikhin V. M.: *Zeolites* 9, 12 (1989).
16. Parillo D. J., Gorte R. J.: *J. Phys. Chem.* 97, 8786 (1993).
17. Gal J., Maria P.-Ch. in: *Progress in Physical Organic Chemistry* (R. W. Taft, Ed.), Vol. 17, p. 174. Wiley, New York 1990.
18. Paukhtis E. A., Yurchenko E. N.: *Usp. Khim.* 52, 426 (1983).
19. Odínokov S. E., Mashovsky A. A., Glazunov V. P., Iogansen A. V., Rassadin B. V.: *Spectrochim. Acta*, A 32, 1355 (1976).
20. Barthomeuf D., de Mallmann A.: *Stud. Surf. Sci. Catal.* 37, 365 (1988).
21. Kapustin G. I., Brueva T. R., Kliachio A. L., Beran S., Wichterlova B.: *Appl. Catal.* 42, 239 (1988).