

IR Spectra of Ethane Adsorbed on the Hydrogen, Sodium, and Zinc Forms of a Y-Type Zeolite: Interpretation Using *ab initio* Quantum Chemical Calculations

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Abstract—Ethane adsorption on the hydrogen, sodium, and zinc forms of faujasite brings about polarization anisotropy of the C–H stretching vibrations. This anisotropy shows itself most clearly as perturbation of the vibrational mode analogous to the breathing C–H mode ν_1 of free ethane. The relative intensity and the low-frequency shift of the absorption band due to the distorted ν_1 mode increase with increasing perturbation caused by the C_2H_6 –adsorption site interaction. The polarizing power of adsorption sites increases in the order $\text{H}^+ < \text{Na}^+ < \text{Zn}^{2+}$. The C–H stretching vibrations in ethane adsorbed on the cationic forms of the Y zeolite are not symmetry-forbidden; accordingly, adsorbed ethane gives more absorption bands than gaseous ethane. The interaction between ethane and zinc cations in the Y zeolite structure eliminates not only the symmetry forbiddenness but also the twofold degeneracy of the C–H stretches.

There is only limited information concerning the activation of light paraffins on the zeolite surface. Initially, light paraffins are adsorbed by the active sites of the catalyst and their geometry and, accordingly, their vibrational spectrum are altered as a result. Their subsequent activation is usually intimately related to the adsorption-induced changes. However, perturbations in the adsorbed molecules have not received sufficient attention as yet.

Most of the studies in this field have dealt with methane activation on the cationic and hydrogen forms of various zeolites [1–6]. It was found that methane is perturbed upon reaction with cations in the zeolite structure and the polarization of the adsorbed molecules depends on the ratio between the cation charge and size. In adsorbed methane, the C–H breathing mode (ν_1) is no longer symmetry-forbidden and is, therefore, IR-active [7]. As compared to the antisymmetrical C–H mode (ν_3), this mode is very sensitive to the nature of the active site, and the shift of its frequency ν_1 is directly related to the polarizability of the adsorbate [6].

The adsorption of heavier hydrocarbons on zeolites containing various cations is studied to a much lesser extent because it is difficult to separate the IR spectrum of the hydrocarbon–cation adsorption complexes from the spectrum of the physically adsorbed molecules [6]. There have been attempts to carry out a detailed analysis of the vibrations based on vibrational-spectroscopy data for gaseous molecules [8]. This approach does not seem to be well-grounded because adsorbed and free molecules differ substantially in geometry, as is indi-

cated by their IR spectra, differing in the number and positions of absorption bands.

Earlier [9], we demonstrated that ethane adsorbed on zinc-modified high-silica zeolites gives an unusual IR spectrum of C–H stretching vibrations. The main features of this spectrum are five weakly perturbed low-intensity bands and a strong band shifted by $\sim 200 \text{ cm}^{-1}$ to lower frequencies. It was assumed that the very high relative intensity of the latter is evidence of a very high polarizability of the corresponding vibrational mode. It was inferred that this strongly polarized vibration is closely related to the subsequent heterolytic dissociation of ethane at elevated temperatures, a process yielding bridging hydroxyl groups and zinc–ethyl fragments.

The purpose of this study is to carry out a more detailed analysis of the perturbations in ethane adsorbed on the sodium, hydrogen, and zinc forms of a Y-type zeolite. IR spectroscopic study of ethane adsorption on these solids was supplemented with quantum chemical calculation of the structure of the adsorption complexes and of the vibrational frequencies for the adsorbed ethane molecules.

EXPERIMENTAL

Cation-substituted Y-type zeolites were prepared from a commercially available sodium form of faujasite (Akzo Nobel Co.) with a framework Si : Al ratio of 2.5.

The ammonium form of the zeolite was prepared by four ion exchange runs between the original NaY zeolite and a 0.1 M NH_4Cl solution at 80°C for 8 h. The ion-exchanged zeolite was washed with distilled water and vacuum-dried for 2 h at 120°C . According to chem-

ical analysis, 95% of the Na^+ ions were exchanged for NH_4^+ . To obtain the H form of the Y-type zeolite, the ammonium form was calcined in flowing oxygen at 500°C for 3 h.

Prior to spectroscopic measurements, the sodium and hydrogen forms of the zeolite were given the same thermal vacuum treatment. A zeolite sample was placed in a quartz ampule having a branch with a CaF_2 window for IR spectroscopy. Next, it was preaged according to the following protocol: pumping at 120°C for 2 h, heating to 500°C at a constant rate of 2 K/min, and, finally, pumping at this temperature for another 3 h.

ZnY zeolite was prepared by reacting the preaged H form with zinc vapor at 500°C [10]. The hydrogen being released was collected in a liquid-nitrogen trap filled with NaX zeolite. To remove the excess metallic zinc, the zeolite was pumped at 500°C for 2 h. The degree of substitution of zinc cations for acid protons was monitored by measuring the amount of hydrogen evolved and the decreasing intensity of the IR absorption bands due to acid OH groups. The data obtained indicated that the substitution of Zn^{2+} cations for hydrogen in bridging hydroxyl groups was almost complete (98%).

The diffuse reflectance infrared Fourier-transform spectra of granular zeolites with a grain size of 0.5–1 mm were recorded at room temperature on a Nicolet Impact 410 spectrophotometer with a diffuse reflectance attachment. Spectroscopic data were converted to Kubelka–Munk units using a standard program under the assumption that the reflectivity of the zeolites at 5000 cm^{-1} is 0.9. The background due to the zeolite was subtracted from the observed IR spectra.

Before adsorption runs, ethane was purified by triple vacuum distillation combined with freezing the distillate at liquid-nitrogen temperature. It was adsorbed at room temperature and a varied equilibrium pressure. Diffuse reflectance IR spectra were recorded at room temperature for samples in contact with a gas phase and for the same samples after removal of the gas phase.

In addition to performing IR spectroscopic measurements, we carried out a quantum chemical calculation for ethane adsorption using cluster models of the cationic forms of the Y zeolites. Optimization of zeolite geometry and of the structures of the adsorption complexes involving an ethane molecule, as well as calculation of vibrational spectra, was carried out using the DFT method (B3LYP hybrid functional [11] with a 6-31G* basis set) and the GAUSSIAN 98 program package [12].

Three cluster models were used to describe the adsorption sites in the hydrogen, sodium, and zinc forms of the Y zeolite. The following models were found to correlate best with experimental data: clusters with a one-coordinate hydrogen atom for HY, clusters with a two-coordinate sodium cation for NaY , and clusters with a four-coordinate zinc cation in a 6T ring with

two aluminum atoms for ZnY . Below, these models are considered in greater detail.

The positions of the terminal hydrogen-like atoms (H^*) were optimized as follows. In the first step of the optimization procedure, an initial cluster geometry was chosen based on X-ray crystallographic data [13]. Only the $\text{Si}-\text{H}^*$ and $\text{Al}-\text{H}^*$ bond lengths were optimized. The positions of the other atoms (except the acid proton, sodium cation, or zinc cation) and the $\text{O}-\text{H}^*$ bond directions were set according to X-ray crystallographic data. In the subsequent extended optimization of cluster geometry and in the analysis of ethane adsorption, the H^* atoms were fixed in the positions determined in the first step.

The dangling bonds of the Si and Al atoms in the above models were saturated with H^* atoms instead of OH groups to rule out intramolecular bonding, which would lead to unacceptable models [14].

RESULTS AND DISCUSSION

Ethane Adsorption on HY and NaY Zeolites

Upon ethane adsorption, the IR spectrum of C–H stretching vibrations shows four absorption bands at 2977, 2948, 2925, and 2881 cm^{-1} for HY (Fig. 1a) and at 2977, 2946, 2924, and 2877 cm^{-1} for NaY (Fig. 1b). Note that gaseous ethane gives only two absorption bands, peaking at 2994 cm^{-1} ($\text{v}_7(\text{e}_u)$) and 2954 cm^{-1} ($\text{v}_5(\text{a}_{2u})$). The other two vibrations are active only in the Raman spectrum, occurring at 2963 cm^{-1} ($\text{v}_{10}(\text{e}_g)$) and 2899 cm^{-1} ($\text{v}_1(\text{a}_{1g})$) [15]. The existence of four bands in the spectrum of adsorbed ethane indicates that adsorption changes the geometry of the ethane molecule, making the two Raman bands IR-active. Note also that, as the ethane pressure is reduced, all of the four bands weaken and, after the system is pumped at room temperature, they are not observed at all. Therefore, these bands are due to physically (weakly) adsorbed ethane. The most likely adsorption sites are acid protons and sodium cations.

The positions of the three higher frequency bands are the same for HY and NaY , and there is only a slight difference in the peak position of the lowest frequency band. The main difference between the ethane molecules adsorbed on HY and NaY is in band intensities. At equal ethane pressures, the intensities of the strongest (2977 cm^{-1}) bands are nearly equal. However, the 2877 cm^{-1} band in the spectrum of NaY is considerably stronger than its counterpart (the 2881 cm^{-1} band) in the spectrum of HY. This difference in intensity and the fact that the NaY band is farther shifted to lower frequencies indicate that the corresponding vibrations are more strongly perturbed by adsorption on sodium cations than by adsorption on protons.

Since the above spectra are essentially the same, it can be inferred that the adsorbed molecules have the same symmetry and the subtle difference between these spectra is due to different perturbing effects exerted by protons and sodium cations.

To interpret these spectra, we undertook a quantum chemical analysis of ethane adsorption on HY and NaY. The results of this analysis are presented in Fig. 2 and Table 1. For the $\text{NaO}_2[\text{AlH}_2^*][\text{SiH}_3^*]_2$ and $\text{HO}[\text{AlH}_2^*][\text{SiH}_3^*]_2$ clusters, which were taken to be the models of the adsorption sites in NaY (Fig. 2a) and HY (Fig. 2b), local energy minima correspond to adsorption geometries in which the C–C...Na and C–C...H angles are close to 180° .

Calculation of the energy of ethane adsorption on the cluster modeling HY zeolite has demonstrated the formation of a rather weak complex between a C_2H_6 molecule and a proton (the corresponding adsorption energy is 1.95 kcal/mol). Adsorption causes only negligible changes in the geometry of the ethane molecule. The C–H bonds in adsorbed ethane are only ~ 0.002 Å longer than those in gaseous ethane (1.096 Å).

The adsorption of a C_2H_6 molecule on a sodium cation is characterized by a much higher energy of 6.66 kcal/mol. This stronger interaction brings about more pronounced changes in the geometry of the adsorbed molecules. The C–H bonds of the methyl group nearest to the sodium cation are lengthened by ~ 0.004 Å. In the other CH_3 group, these bonds are shortened by ~ 0.002 Å. However, these changes in bond length are also indicative of only slight perturbations of the adsorbed molecules.

As a whole, the calculated C–H stretching frequencies are in good agreement with experimental data (Table 1). The small deviations are due to the fact that, firstly, we did not take into account the anharmonicity of vibrations and, secondly, our model is likely to be incompletely adequate to the actual geometry of the adsorption sites of the zeolite. Moreover, because of the high density of anionic sites in the lattice of low-silica zeolites, the positive charge of the sodium cations and protons is shielded to a considerable extent. This is the reason why the observed changes in the absorption bands due to C–H vibrations are not so great as predicted by the quantum chemical calculations.

The normal C–H modes calculated for an adsorbed ethane molecule are shown in Fig. 3. Adsorption produces the strongest effect on the breathing mode analogous to the $\nu_1(\text{a}_{1g})$ mode of gaseous ethane. The greatest contribution to this vibrational mode is made by the symmetrical vibrations of the CH_3 group nearest to the adsorption site. The antisymmetrical mode, which is an analogue of $\nu_5(\text{a}_{2u})$, is perturbed to a lesser extent, and the largest contribution to this mode is from the symmetrical mode of the opposite methyl group.

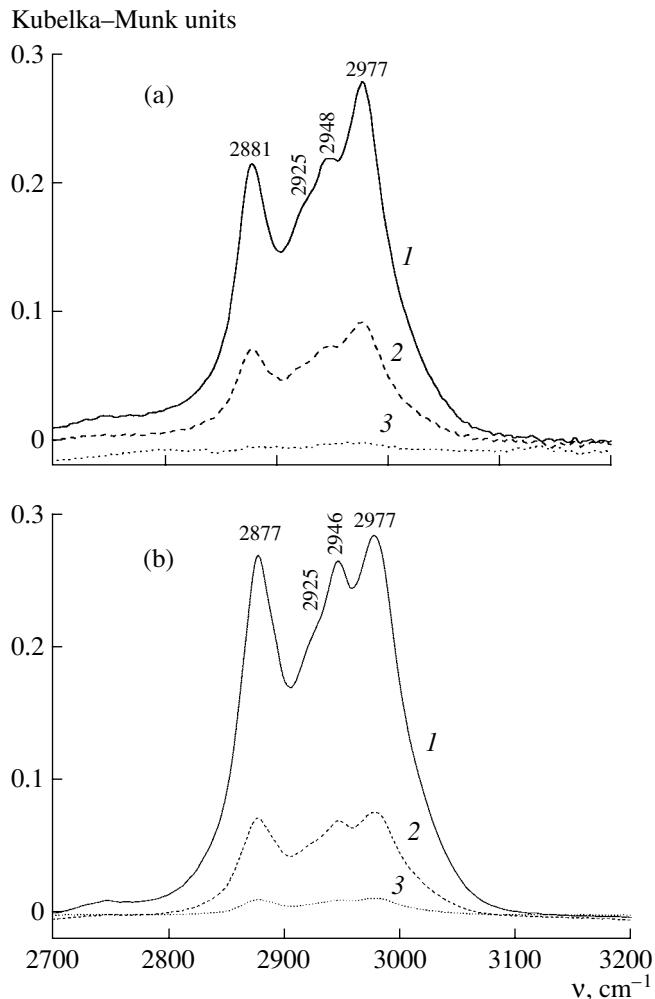


Fig. 1. (a) Diffuse reflectance IR spectra of (1, 2) ethane adsorbed on HY zeolite at equilibrium pressures of (1) 3.3 and (2) 0.9 Torr and (3) a sample pumped at room temperature. (b) The same for (1, 2) ethane adsorbed on NaY zeolite at equilibrium pressures of (1) 3.2 and (2) 0.7 Torr and (3) a sample pumped at room temperature.

Ethane Adsorption on ZnY Zeolite

The diffuse reflectance IR spectra of ethane adsorbed on ZnY at a varied equilibrium pressure are displayed in Fig. 4. These spectra are fundamentally different from the spectra observed for NaY and HY zeolites. They exhibit six absorption bands peaking at 2991, 2954, 2896, 2875, 2834, and 2796 cm^{-1} . As in the above cases, as the equilibrium pressure over the sample is reduced, all of these bands weaken and, after the sample is pumped at room temperature, they are not observed at all. Therefore, all of them are due to one weak ethane–zinc adsorption complex or a few similar in energy.

There are two plausible explanations for the fact that the number of absorption bands is larger for ZnY than for NaY or HY. The first is that the greater changes in C_2H_6 symmetry produced by the zinc cation eliminate

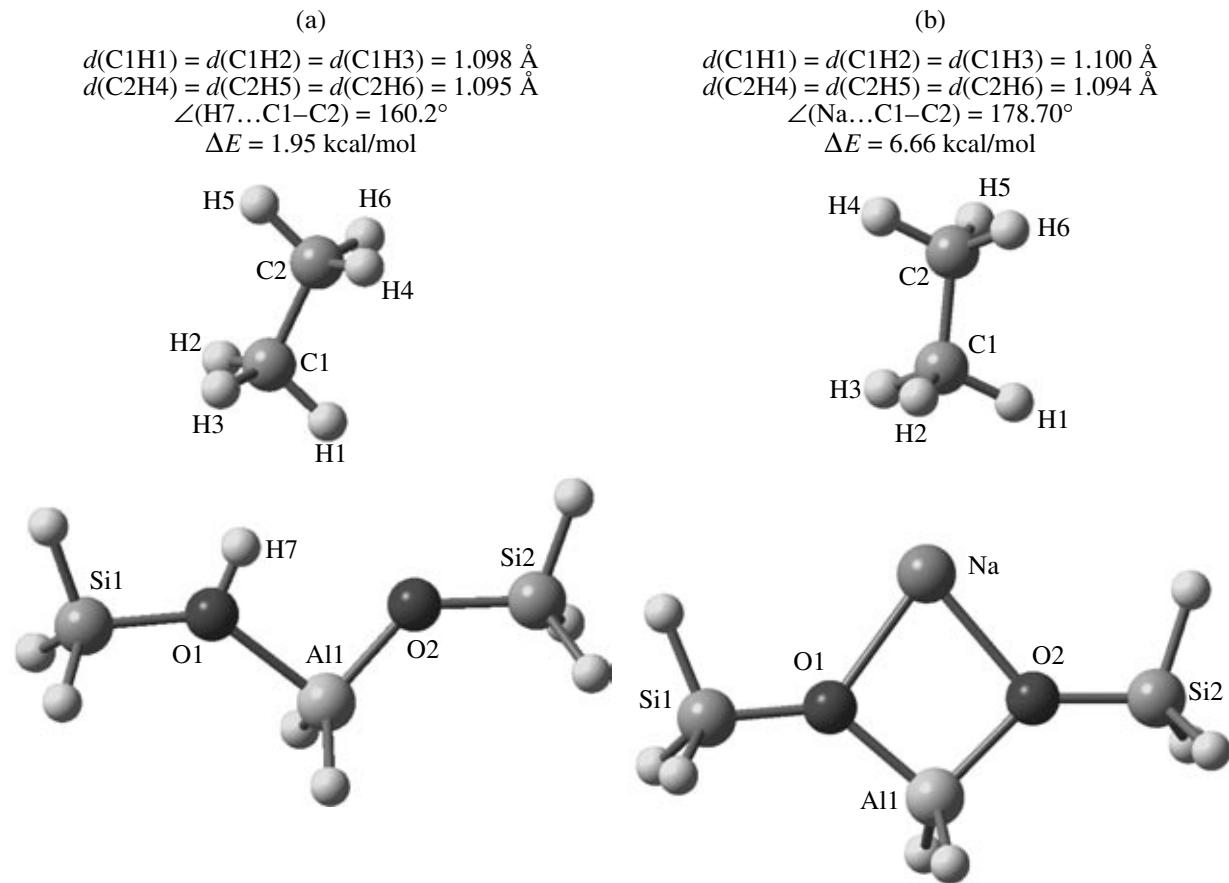


Fig. 2. C_2H_6 adsorption on (a) $\text{HO}[\text{AlH}_2][\text{SiH}_3]_2$ and (b) $\text{NaO}_2[\text{AlH}_2][\text{SiH}_3]_2$ clusters.

the twofold degeneracy of the symmetrical and anti-symmetrical vibrations ($\nu_{10}(e_g)$ and $\nu_7(e_u)$). The second explanation is that the observed IR spectra are a superposition of the spectra of ethane adsorbed on zinc cat-

ions differently located in the zeolite lattice. Furthermore, the bands observed for ZnY are substantially shifted relative to the bands observed for NaY and HY. These changes can be due to another geometry of the

Table 1. Assignment of the observed and calculated* C-H stretching frequencies** in the IR spectrum of ethane adsorbed on HY, NaY, and ZnY

Assignment	$\text{C}_2\text{H}_6(\text{gas})$ [13]	$\text{C}_2\text{H}_6/\text{HY}$ (exp.)	$\text{C}_2\text{H}_6/\text{H-Zeol}$ (calc.)	$\text{C}_2\text{H}_6/\text{NaY}$ (exp.)	$\text{C}_2\text{H}_6/\text{Na-Zeol}$ (calc.)	$\text{C}_2\text{H}_6/\text{ZnY}$ (exp.)	$\text{C}_2\text{H}_6/\text{Zn-Zeol}$ (calc.)
$\nu_7(e_u)$	2994	2977	2975 (38.98) 2973 (37.73)	2978	2982 (26.61) 2982 (26.84)	2991	2989 (21.21) 2983 (19.82)
$\nu_{10}(e_g)^{***}$	2963	2948	2935 (8.37) 2926 (13.18)	2946	2916 (20.68) 2914 (21.68)	2954	2954 (5.74) 2915 (7.49)
$\nu_5(a_{2u})$	2954	2925	2906 (33.90)	2924	2910 (22.97)	2875	2911 (16.32)
$\nu_1(a_{1g})^{***}$	2899	2881	2870 (43.46)	2877	2853 (54.51) (2834)	2817 (122.99) 2796	

* B3LYP/6-31G* frequencies multiplied by an empirical coefficient of 0.95 for minimization of the systematic error.

** The corresponding band intensities are given in parentheses.

*** These C-H vibrations in free ethane molecules are only Raman-active.

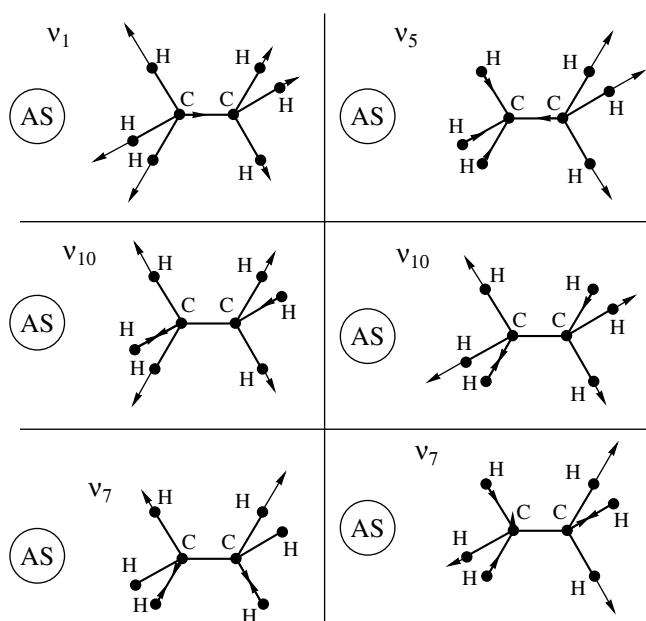


Fig. 3. Normal C–H modes calculated for ethane adsorbed on HY and NaY. AS is an adsorption site (H or Na).

adsorption complex in combination with the stronger effect exerted by the zinc cation on the adsorbed molecule.

As in the previous cases, IR spectra were interpreted using quantum chemical calculations for ethane adsorbed on a zinc-containing cluster modeling an adsorption site of ZnY. The model of the adsorption complex is shown in Fig. 5. The results of these calculations are presented in Fig. 5 and Table 1. Clearly, ethane adsorption in this case differs from ethane adsorption on the clusters modeling the adsorption sites of NaY and HY zeolites. Here, the local energy minimum corresponds to a rather weak complex (with an adsorption energy of 7.43 kcal/mol) in which the zinc cation interacts with two C–H bonds of one CH_3 group.

As compared to protons and sodium cations, zinc cations produce a much stronger effect on the geometry of the adsorbed molecules. The most profound changes are predicted for the C1–H1 and C1–H2 bonds, which must be lengthened by 0.004 and 0.01 Å, respectively. The other C–H bonds remain unaffected upon adsorption. Therefore, the zinc cation perturbs an adsorbed ethane molecule more strongly than the proton or sodium cation.

The calculated C–H stretching frequencies are again in good agreement with experimental data. The discrepancies between the calculated and observed band intensities are most likely to be due to the fact that the absorption bands at 2991 and 2796 cm^{-1} (Fig. 4) are very broad as compared to the bands at 2954 , 2896 , and 2875 cm^{-1} .

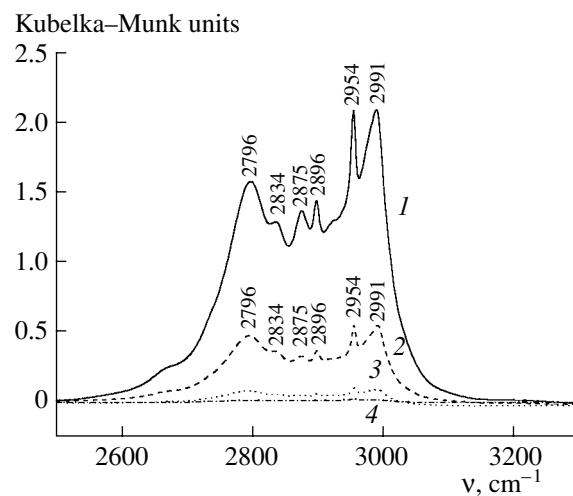


Fig. 4. Diffuse reflectance IR spectra of ethane adsorbed on ZnY zeolite at equilibrium pressures of (1) 16.2, (2) 3, (3) 8, and (4) 0.1 Torr.

As is clear from Table 1, the number of bands observed for ZnY is larger than that observed for the other zeolites. A plausible explanation of this fact is that the zinc cation causes greater changes in the symmetry of the ethane molecule, eliminating the twofold degeneracy of the $v_{10}(\text{e}_g)$ mode.

Owing to the stronger perturbing effect of the field of the zinc cation on the ethane molecule, the band cor-

$$\begin{aligned}
 d(\text{C1H1}) &= 1.100 \text{ \AA} & d(\text{C2H4}) &= 1.094 \text{ \AA} \\
 d(\text{C1H2}) &= 1.106 \text{ \AA} & d(\text{C2H5}) &= 1.095 \text{ \AA} \\
 d(\text{C1H3}) &= 1.095 \text{ \AA} & d(\text{C2H6}) &= 1.095 \text{ \AA} \\
 \angle(\text{Zn...C1-C2}) &= 125.09^\circ \\
 \Delta E &= 7.43 \text{ kcal/mol}
 \end{aligned}$$

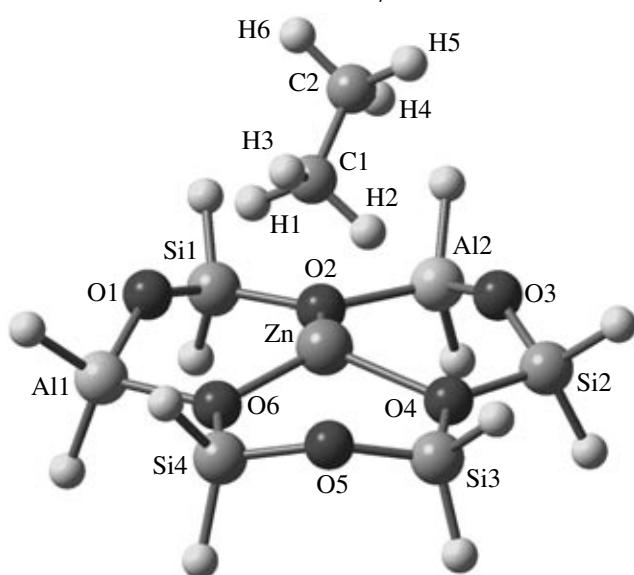


Fig. 5. C_2H_6 adsorption on a $\text{ZnO}_6[\text{AlH}_2]_2[\text{SiH}_2]_4$ cluster.

Table 2. Mulliken atomic charges for adsorbed and free ethane molecules

Atom	C ₂ H ₆ (gas)	C ₂ H ₆ /H-Zeol	C ₂ H ₆ /Na-Zeol	C ₂ H ₆ /Zn-Zeol
C1	-0.433	-0.497	-0.523	-0.528
C2	-0.433	-0.434	-0.450	-0.448
H1	0.144	0.194	0.199	0.213
H2	0.144	0.157	0.187	0.193
H3	0.144	0.133	0.187	0.138
H4	0.144	0.156	0.170	0.206
H5	0.144	0.149	0.170	0.158
H6	0.144	0.157	0.170	0.167

responding to the analogue of the totally symmetrical C–H vibration in free ethane (ν_1) is still farther shifted to lower frequencies. In distinction to the previous case, the largest contribution to this vibrational mode is from the displacement of the H1 and H2 atoms of ethane, which are in the immediate vicinity of the adsorption site. This mode is likely to be responsible for the bands at 2796 and 2834 cm⁻¹ (Fig. 4), which are due to ethane adsorbed on crystallographically inequivalent Zn²⁺ cations similar in adsorption energy.

However, the calculated difference in C₂H₆ adsorption energy between Na⁺ (6.66 kcal/mol) and Zn²⁺ (7.43 kcal/mol) provides no explanation for the marked difference between the perturbing effects of these cations. Table 2 lists Mulliken atomic charges calculated for the C₂H₆ molecule in the gas phase and for the same molecule adsorbed on the clusters modeling the hydrogen, sodium, and zinc forms of the Y zeolite. Adsorption on a proton causes only a slight change in the atomic charges in C₂H₆, while the Na⁺ and Zn²⁺ cations affect these charges much more strongly. The zinc cation causes a less uniform redistribution of the atomic charges. Furthermore, according to our data, the C–H bonds close to the adsorption site are more strongly polarized by the Zn²⁺ cation. As a consequence, the adsorbed molecule is more strongly perturbed, and this effect shows itself in the IR spectrum.

Comparing the data obtained for HY, NaY, and ZnY zeolites demonstrates that, although the adsorption complexes differ in geometry, the distorted breathing mode of the ethane molecule is always most sensitive to the nature of the adsorption site. The relative intensity and the down-frequency shift of the corresponding absorption band increase with increasing polarizing power of the cation.

Thus, the ethane molecule can be anticipated to be usable as a probe in the study of various cationic forms of zeolites. The degree of perturbation and, therefore, the degree of activation of the adsorbed ethane mole-

cule could be judged from the relative intensity and down-frequency shift of the absorption band due to the C–H breathing mode. However, this assumption needs more rigorous experimental substantiation. For this purpose, it is necessary to carry out a systematic study of ethane adsorption on various cationic forms of zeolites differing in structure and framework Si : Al ratio.

CONCLUSIONS

Our data suggest that the C₂H₆ molecule is perturbed upon adsorption on the cationic forms of the zeolites and the C–H stretching vibrations in the adsorbate are characterized by polarization anisotropy. As a consequence, only one band in the diffusion reflectance IR spectrum, namely, the band due to the breathing C–H vibrations, is strongly dependent on the polarizing properties of the adsorption site. The perturbation of the other C–H vibrations in adsorbed ethane is less significant. The low-frequency shift and the relative intensity of this band increase with increasing strength of the ethane–adsorption site interaction, or, in other terms, with increasing polarizing power of the cation.

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