

Use of the IR Spectra of Adsorbed Ethane and Propane Molecules to Characterize the Strength of Active Sites in Zeolites and to Analyze the Activation of C–H Bonds in These Paraffins

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Abstract—The adsorption and activation of ethane and propane on the hydrogen and cationic forms of mordenite, zeolite ZSM-5, and zeolite Y were studied by diffuse-reflectance IR spectroscopy. The effect of the polarization of these molecules by adsorption sites on the intensities and shifts of absorption bands due to C–H stretching vibrations were studied. It was found that weak adsorption species were formed on the hydrogen forms of the above zeolites. In this case, both the intensity distributions and the positions of absorption bands due to C–H stretching vibrations were almost independent of the nature of zeolites. However, both absorption band maximum positions and relative intensity distributions changed upon paraffin adsorption on the cationic forms. It was also found that relative intensity distributions and shifts of absorption bands due to C–H stretching vibrations strongly depended on the nature of cations and zeolites. In this case, the initially totally symmetrical C–H vibrations were found most strongly disturbed. The low-frequency shifts and relative intensities of absorption bands due to these vibrations for various cations and zeolites were found to increase in the following orders: $H < Na < Ca < Mg < Zn$ and zeolite $Y < Mord \approx ZSM-5$. The experimental results suggest that ethane and propane molecules can be used as molecular probes for acquiring information on the nature and properties of acid–base sites in zeolites. In this case, both the low-frequency shifts and the relative intensities of absorption bands due to C–H stretching vibrations can be used as measures to characterize the nature of cations and zeolites. However, the latter was found to be much more sensitive to the nature of active sites.

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INTRODUCTION

IR spectroscopy is widely used to acquire information on the nature and properties of acid–base sites in oxide and zeolite catalysts for various hydrocarbon conversions. The adsorption of molecular probes such as ammonia, pyridine, and carbon monoxide is commonly used for this purpose. However, these molecules are dramatically different from hydrocarbons in chemical properties; thus, the conclusions drawn from an analysis of their disturbances caused by adsorption sites cannot be fully correct. The molecules of adsorbed hydrocarbons have been used as probes in only a few studies. The use of methane as a molecular test was an attempt of this kind [1, 2]. However, methane is in very limited use in catalysis because of its low reactivity. Therefore, adsorbed heavier hydrocarbons are, undoubtedly, more interesting molecular probes. An analysis of the IR spectra of these molecular probes could provide information on both the strength of active sites and the adsorption-induced activation of chemical bonds. In this work, we used the adsorption of ethane and propane molecules on various hydrogen and cationic forms of zeolites for this purpose.

Usually, the low-frequency shifts of IR absorption bands due to stretching vibrations are used for evaluating the strength of adsorption sites and for characterizing the activation of adsorbed molecules [3]. However, these shifts reflect changes in the force constants of chemical bonds regardless of activation mechanisms. Previously [4–6], we proposed the use of the intensity of IR absorption bands due to stretching vibrations, which are most closely related to the polarization of adsorbed molecules, as a new criterion for the chemical activation of adsorbed molecules and a reactivity index. This is of paramount importance in acid and acid–base catalysis where polarization is the main source of chemical bond activation. The capabilities of the use of vibrational absorption band intensities as a parameter of molecular reactivity were demonstrated previously by the examples of the adsorption and conversion of ethylene on mordenite [4], cyclopropane on zeolite CaY [5], and ethane on ZnZSM-5 [6].

In this work, we further studied the effect of the molecular polarization of ethane and propane at various adsorption sites on the intensities and shifts of absorption bands due to C–H stretching vibrations. Ethane and propane were chosen as molecular probes because the vibrational spectra of these adsorbed molecules can

be observed at low pressures and room temperature, whereas the adsorption of methane is usually studied at a temperature close to the boiling temperature of liquid nitrogen or at high pressures, when specific adsorption at active sites is difficult to distinguish from physical adsorption. In this case, ethane and propane do not chemically react with the active sites of catalysts at room temperature. This provides an opportunity to measure the spectra of adsorbed parent molecules. On heating, these molecules are converted into intermediate adsorption complexes, the IR spectra of which can be observed at room temperature. Note that publications concerning studies on the IR spectra of ethane and propane upon adsorption and subsequent transformations are almost absent from the literature.

EXPERIMENTAL

The hydrogen forms of zeolites Y and ZSM-5 and mordenite (Mord) and their Na, Ca, Mg, and Zn cationic forms were used as adsorbents.

The ammonium forms of ZSM-5 (Si/Al = 25) and the sodium forms of mordenite (Si/Al = 5), zeolite Y (Si/Al = 2.4), and ZSM-5 (Si/Al = 25) were used as starting materials.

The ammonium forms of mordenite and zeolite Y were prepared from sodium forms in accordance with a standard procedure for the ion exchange of Na^+ cations for NH_4^+ using an aqueous solution of ammonium chloride as a source of NH_4^+ ions. The hydrogen forms of the zeolites were prepared from the corresponding ammonium forms on calcination at 723 K in a flow of oxygen for 3 h.

The Ca (42%) and Mg (50%) forms of mordenite and zeolite Y (the percentage of residual sodium is given in parentheses) were prepared from the sodium forms by the repeated ion exchange of sodium for the corresponding cations.

The sample of MgZSM-5 was prepared by the impregnation of the corresponding hydrogen form with a solution of $\text{Mg}(\text{NO}_3)_2$ at room temperature followed by heating at 393 K for 3 h and calcination at 723 K for 2 h in a flow of oxygen. The magnesium contents of the resulting samples corresponded to the ratio $\text{Mg}/\text{Al} = 1 : 2$.

The samples of ZnZSM-5, ZnMord, and ZnY were prepared from the hydrogen forms of the corresponding zeolites using a reaction with zinc vapor at 770 K. Hydrogen released in this reaction was collected in a trap with zeolite NaX cooled with liquid nitrogen. To remove the excess of zinc metal, the modified zeolites were evacuated at 770 K for 2 h. An analysis of IR spectra in the region of OH groups and the quantitative mea-

surements of hydrogen liberated in the interactions of zeolites with zinc vapor suggest the complete replacement of Brønsted acid sites by Zn^{2+} cations.

Before IR-spectroscopic measurements, the zeolite samples were placed in a quartz ampule with a side branch equipped with a CaF_2 window for the measurement of IR spectra. Thermal vacuum treatment in the quartz portion of the ampule was performed in accordance with the following procedure: Initially, the samples were heated at 390 K in a vacuum for 2 h at a heating rate of 2 K/min. Then, the temperature was increased to 770 K at the above heating rate, and the zeolites were additionally kept in a vacuum under the specified conditions for 2 h.

Ethane and propane were prepurified in a vacuum system to remove air and moisture traces by freezing in a trap cooled with liquid nitrogen with evacuation to a pressure of $\sim 10^{-3}$ Torr followed by collecting a middle fraction on thawing. The adsorption of alkanes was performed at room temperature.

The diffuse-reflectance IR spectra were measured at room temperature on a Nicolet Impact 410 Fourier transform IR spectrometer equipped with an attachment for measuring diffuse-reflectance spectra. The resulting spectral intensities were converted into the Kubelka–Munk units under the assumption that the zeolite reflectance at 5000 cm^{-1} is equal to 0.9. The zeolite background was subtracted from the overall spectrum.

RESULTS

Ethane and Propane Adsorption on the Hydrogen Forms of Zeolites

Upon the adsorption of ethane on the hydrogen forms of zeolite ZSM-5, mordenite, and zeolite Y, the IR spectra exhibited four absorption bands due to C–H stretching vibrations. An increase in the number of absorption bands to four, as compared with the spectrum of gaseous ethane, which contains only two bands, suggests a change in the molecular symmetry of ethane upon adsorption [7, 8]. Because of this, the IR spectrum exhibited vibrations that were active only in the Raman spectra in a gas phase. A decrease in the equilibrium pressure of ethane over each particular sample resulted in a symbatic decrease in the intensities of all four absorption bands, and all of these absorption bands fully disappeared after evacuation at room temperature. This is indicative of weak ethane adsorption.

The general view of the spectra of ethane adsorbed on zeolite ZSM-5, mordenite, and zeolite Y was practically identical in all cases. This manifested itself in both intensity ratios between absorption bands due to various C–H vibrations and the positions of band maximums. The positions of absorption band maximums are very similar (Table 1): 2875, 2921, 2944, and

Table 1. Absorption bands (cm^{-1}) due to the C–H stretching vibrations of ethane adsorbed on the hydrogen forms of zeolites and in the gas phase

Assignment	$\nu_i(\text{C}_2\text{H}_6)$, gas phase [8]	Adsorption on the hydrogen forms of zeolites		
		HY	HMord	HZSM-5
ν_7	2994.3	2977	2975	2974
ν_{10}	2963.0*	2946	2944	2941
ν_5	2954.0	2925	2921	2920
ν_1	2899.2*	2879	2875	2878

* IR-inactive band (the Raman frequency is given).

2975 cm^{-1} for HMord; 2878, 2920, 2941, and 2974 cm^{-1} for HZSM-5; 2881, 2925, 2948, and 2977 cm^{-1} for HY. For example, Fig. 1 shows the spectrum of ethane adsorbed on zeolite HZSM-5.

Upon the adsorption of propane on the hydrogen forms of mordenite, zeolite ZSM-5, and zeolite Y, the spectra exhibited four or five (in the case of zeolite ZSM-5) absorption bands. Table 2 summarizes the positions of absorption band maximums. The spectra of propane adsorbed on zeolites HMord and HY were practically identical in both the peak positions and the relative intensities of absorption bands. As an example, Fig. 2a shows the IR spectrum of propane adsorbed on zeolite HY in the region of C–H stretching vibrations. Figure 2b shows an analogous spectrum for zeolite HZSM-5. In this case, the low-frequency band is split into two components. As well as with adsorbed ethane, the evacuation of samples at room temperature resulted in a symbatic decrease in the intensities of these absorption bands. Thus, upon the adsorption of propane on the

hydrogen forms of zeolites, the observed regularities were the same as upon the adsorption of ethane.

The above results suggest the weak adsorption of ethane and propane on the hydrogen forms of zeolites. It is most likely that all of the above absorption bands belong to physisorbed species, and they do not allow one to distinguish the specific adsorption of ethane and propane on hydroxyl groups.

Ethane and Propane Adsorption on the Cationic Forms of Zeolites

Figures 3–5 show the spectra of ethane adsorbed on the following cationic forms of various zeolites in the region of C–H stretching vibrations: the Na, Ca, Mg, and Zn forms of mordenite (Fig. 3); the Na, Mg, and Zn forms of ZSM-5 (Fig. 4); the Na, Ca, Mg, and Zn forms of zeolite Y (Fig. 5).

As in the case of adsorption on the hydrogen forms, four absorption bands occurred upon the adsorption of ethane on the sodium forms of mordenite and zeolites ZSM-5 and Y. The evacuation of these samples after ethane adsorption at room temperature resulted in a symbatic decrease in all of the absorption bands and, finally, in the complete removal of the adsorbed gas. Upon the adsorption of ethane on the sodium and hydrogen forms of each of the above zeolites, the positions of absorption bands were practically identical. The most significant differences manifested themselves in intensity ratios between absorption bands. In this case, a low-frequency absorption band due to symmetrical C–H stretching vibrations exhibited the highest sensitivity to the cation. Thus, in the spectra of ethane adsorbed on the hydrogen forms, the intensity of this band was lower than the intensities of high-frequency bands. Upon adsorption on the sodium forms of all of the three zeolites, this band became most intense. As noted above, this band is forbidden in the gas phase and it does not appear in the IR spectrum. Thus, ethane molecules were more strongly perturbed upon adsorption on the Na forms than upon adsorption on the H forms.

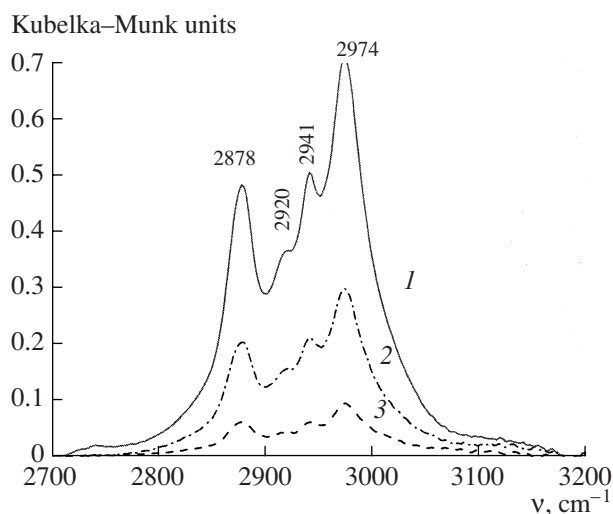


Fig. 1. Diffuse-reflectance IR spectrum of ethane adsorbed on HZSM-5 at room temperature and $P_{\text{eq}} = (1)$ 2.66, (2) 1, or (3) 0.36 Torr.

Table 2. Absorption bands (cm^{-1}) due to the C–H stretching vibrations of propane adsorbed on the hydrogen forms of zeolites and in the gas phase

Assignment	$\nu_i(\text{C}_3\text{H}_8)$, gas phase [8]	Adsorption on the hydrogen forms of zeolites		
		HY	HMord	HZSM-5
ν_{22}	2980	2962	2960	2963
ν_{15}, ν_{23}	2968	—	—	—
ν_1, ν_{10}	2967*	—	—	—
ν_2	2960	2945	2937	2937
ν_2	2946*			
ν_3	2903*	2906	2901	2901
ν_{16}	2885	2869	2872	2874
				2866

* IR-inactive band (the Raman frequency is given).

Table 3. Maximums of absorption bands (cm^{-1}) due to ethane adsorbed on various cationic forms of zeolites

Y				Mord				ZSM-5		
Na	Ca	Mg	Zn	Na	Ca	Mg	Zn	Na	Mg	Zn
2978	2987	2992	2991	2973	2981	2992	2993	2979	2992	2992
2946	2959	2958	2954	2945	2951	2954	2953	2945	2953	2968
	2914									2951
2924	2901	2899	2896	2916	2892	2894	2894	2918	2894	2892
		2861	2875			2833			2845	
			2834				2826			2816
2877	2847	2811	2796	2870	2839	2788	2729	2863	2791	2726

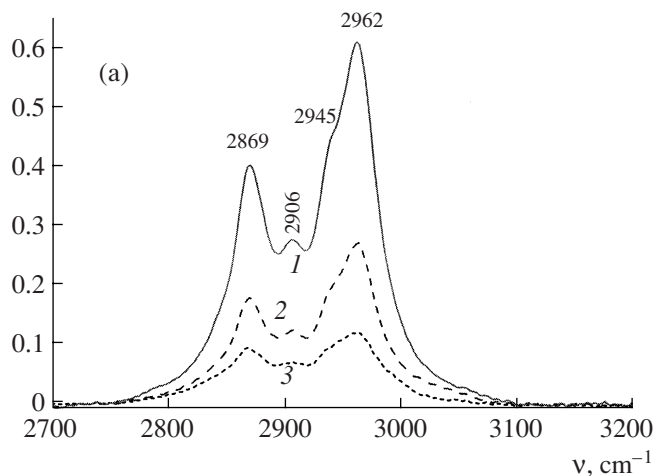
The above effect depends on not only hydrocarbon adsorption at a proton or sodium cation but also on the nature of the zeolite. Thus, upon the adsorption of ethane on zeolite NaZSM-5, the relative intensity of the low-frequency band was higher than that upon adsorption on zeolite NaY. This was related to the geometry of the adsorption site and a decrease in the number of spatially separated aluminum tetrahedrons in the lattice of zeolite ZSM-5. This weakened the screening of sodium by basic oxygen atoms from the coordination sphere of aluminum tetrahedrons.

Upon the adsorption of ethane on other cationic forms of zeolites, the number of bands in the spectrum increased (Figs. 3–5) to become greater than four. To separate specific adsorption at the cations of Ca, Mg, or Zn from the weak forms of physical adsorption or from adsorption related to residual Na cations, we performed

studies at low ethane pressures. In this case, a portion of absorption bands disappeared and the bands corresponding to species that were removed from the surface of zeolites only after long evacuation at room temperature can be unambiguously attributed to adsorption at the cations of Ca, Mg, or Zn.

Table 3 summarizes data on the peak positions of absorption bands upon the adsorption of ethane at the cations of Na, Ca, Mg, and Zn in the structures of various zeolites. The spectra of ethane on the sodium and calcium forms exhibited four absorption bands; the spectra of ethane on the magnesium and zinc forms exhibited five and six absorption bands, respectively. Thus, as with the hydrogen forms, the molecular symmetry changed upon the adsorption of ethane on the

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Kubelka–Munk units

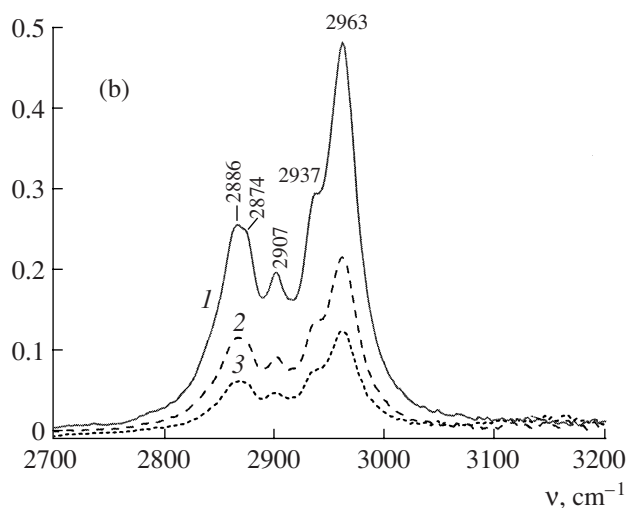


Fig. 2. Diffuse-reflectance IR spectra of propane adsorbed on zeolites at room temperature: (a) HY at $P_{\text{eq}} =$ (1) 0.68, (2) 0.20, or (3) 0.07 Torr; (b) HZSM-5 at $P_{\text{eq}} =$ (1) 2.70, (2) 1.10, or (3) 0.50 Torr.

cationic forms of zeolites; this manifested itself in an increase in the number of absorption bands observed in the IR spectra.

A comparison between Figs. 1 and 3–5 indicates that the shape of the spectra of ethane adsorbed at the Ca, Mg, and Zn forms of various zeolites was dramatically different from that in the case of adsorption on the sodium and hydrogen forms. This difference manifested itself not only in an increase in the number of observed absorption bands but also in a considerable shift of a long-frequency band. Thus, in the case of ethane adsorption at the cations of Ca, Mg, and Zn, the shifts of this band were about 30, 70, and 100 cm^{-1} , respectively. This suggests a strong disturbance of the C–H vibration corresponding to this band upon adsorption at the above cations. In this case, this disturbance

depends on the cation and increases in the order Ca, Mg, and Zn.

As in the case of the sodium forms of zeolites, low-frequency bands in the spectra of ethane adsorbed at the cations of Ca, Mg, and Zn exhibited the highest intensities, as compared to other absorption bands due to C–H vibrations. With consideration for the great width of low-frequency bands, the integrated intensities of these bands can be greater than the intensities of the other bands by a factor of tens. Of all of the above spectra, this was most pronounced in the case of ethane adsorption on the zinc forms of mordenite and zeolite ZSM-5. In both cases, the intensities of low-frequency absorption bands with maximums at $\sim 2730 \text{ cm}^{-1}$ are higher than the intensities of the other absorption bands by approximately one order of magnitude (Figs. 3d, 4c).

The effect of adsorption on the intensities of other high-frequency absorption bands due to C–H stretching vibrations was much less pronounced. Moreover, they exhibited an inverse effect because the intensities of these bands decreased in the order Na, Ca, Mg, and Zn.

Figures 6 and 7 show the spectra of propane adsorbed on zeolites NaY, CaY, MgY, ZnY, NaZSM-5, and ZnZSM-5. As in the case of ethane upon adsorption on the sodium forms, the spectra exhibited four absorption bands. The pattern changed upon propane adsorption by zeolites containing bivalent cations. Thus, in the case of the zinc cation, the spectra exhibited six absorption bands. As in the case of ethane adsorption on zinc-modified zeolites, the increase of the number of absorption bands was related to the stronger interaction of adsorbed molecules with zinc cations, which resulted in considerable changes in the molecular symmetry of the hydrocarbon. In this case, as in the adsorption of ethane, the vibration corresponding to a low-frequency absorption band underwent the greatest disturbance upon the adsorption of propane at zinc cations. As compared with an analogous band in the spectrum of gaseous propane, this band was shifted to the low-frequency region of the spectrum by about 180 cm^{-1} . It can also be seen that propane was more strongly disturbed than ethane upon adsorption on the same cationic forms of zeolites. As in the case of adsorbed ethane, the low-frequency band exhibited the greatest width and intensity compared with other bands due to C–H stretching vibrations.

It is clear from Table 4 that the dependences of the positions of the C–H stretching bands of adsorbed propane on the kinds of cation and zeolite are, on the whole, the same as in the case of ethane adsorption (Table 3).

DISCUSSION

Even in the case of the gas phase, the vibrational spectra of hydrocarbons in the region 2800–3000 cm^{-1} are very difficult to study experimentally because a great number of closely spaced and partially overlap-

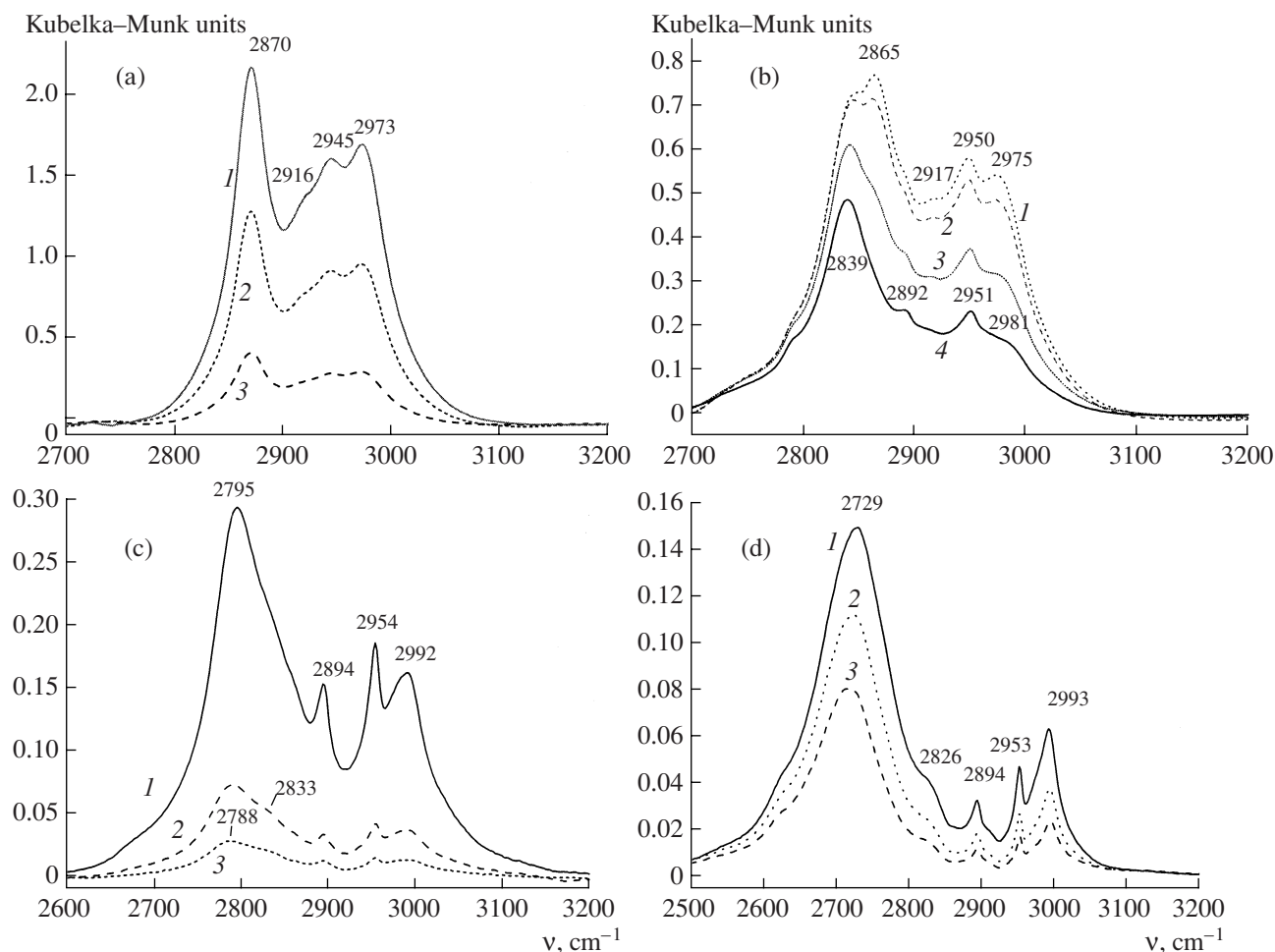


Fig. 3. Diffuse-reflectance IR spectra of propane adsorbed on zeolites at room temperature: (a) NaMord at $P_{eq} = (1) 6.00, (2) 2.30,$ or $(3) 0.50$ Torr; (b) CaMord at $P_{eq} = (1) 2.20, (2) 1.50, (3) 0.50,$ or $(4) 0.10$ Torr; (c) MgMord at $P_{eq} = (1) 0.05, (2) 0.015,$ or $(3) 0.002$ Torr; (d) ZnMord at $P_{eq} = (1) 0.08, (2) 0.025,$ or $(3) 0.009$ Torr.

ping bands fall within this region. It is likely that for this reason there are almost no publications on IR-spectroscopic studies of the adsorption and conversion of paraffins, including ethane and propane. Nevertheless, the results of this work allowed us to draw certain conclusions even without a detailed assignment of absorption bands in the spectra of adsorbed molecules.

As follows from the experimental results, weak adsorption species are formed upon the adsorption of ethane and propane on the hydrogen forms of zeolites; these species are rapidly decomposed by evacuation at room temperature. A comparison between the spectra of adsorbed molecules and gaseous molecules demonstrated a shift to the low-frequency region; however, this shift was no greater than about two tens of inverse centimeters. In the case of ethane, absorption bands corresponding to forbidden vibrations appeared in the spectra because of a decrease in the molecular symmetry. The shapes of spectra and the positions of absorption bands are practically independent of the nature of the zeolite for both ethane and propane. This suggests

that, in the case of the hydrogen forms, either specific adsorption at hydroxyl groups cannot be separated from physical adsorption or the strength of the Brønsted acid site at which adsorption takes place weakly affects the C–H stretching vibrations of adsorbed paraffins. At the same time, it is well known [9] that the low-frequency shifts of absorption bands due to acidic OH groups are observed in the adsorption of paraffins on the hydrogen forms of zeolites. These shifts are of about several tens of centimeters depending on the strength of the site and the test paraffin. We can state that, upon the adsorption of alkanes on the hydrogen forms of zeolites, O–H bond vibrations are most subjected to a disturbance caused by an adsorbed paraffin. As for paraffin molecules adsorbed at hydroxyl groups, it is likely that more important information on the activation of these paraffins could be obtained from the IR spectra in the region of C–C bond vibrations or composite C–H stretching and deformation vibrations; however, this problem is beyond the scope of this work.

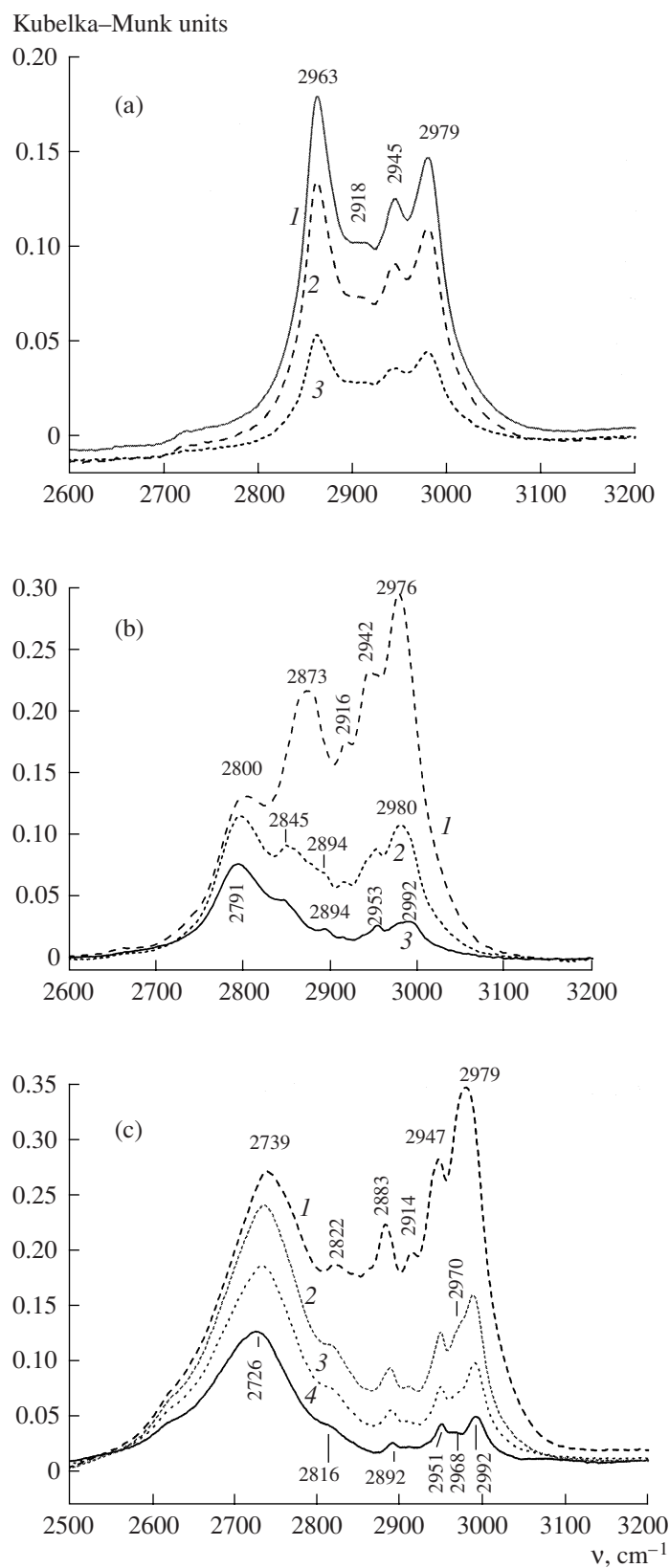


Fig. 4. Diffuse-reflectance IR spectra of ethane adsorbed on zeolites at room temperature: (a) NaZSM-5 at $P_{\text{eq}} = (1) 0.86, (2) 0.40$, or $(3) 0.10$ Torr; (b) MgZSM-5 at $P_{\text{eq}} = (1) 1.10, (2) 0.20$, or $(3) 0.05$ Torr; (c) ZnZSM-5 at $P_{\text{eq}} = (1) 1.01, (2) 0.20, (3) 0.01$, or $(4) 0.005$ Torr.

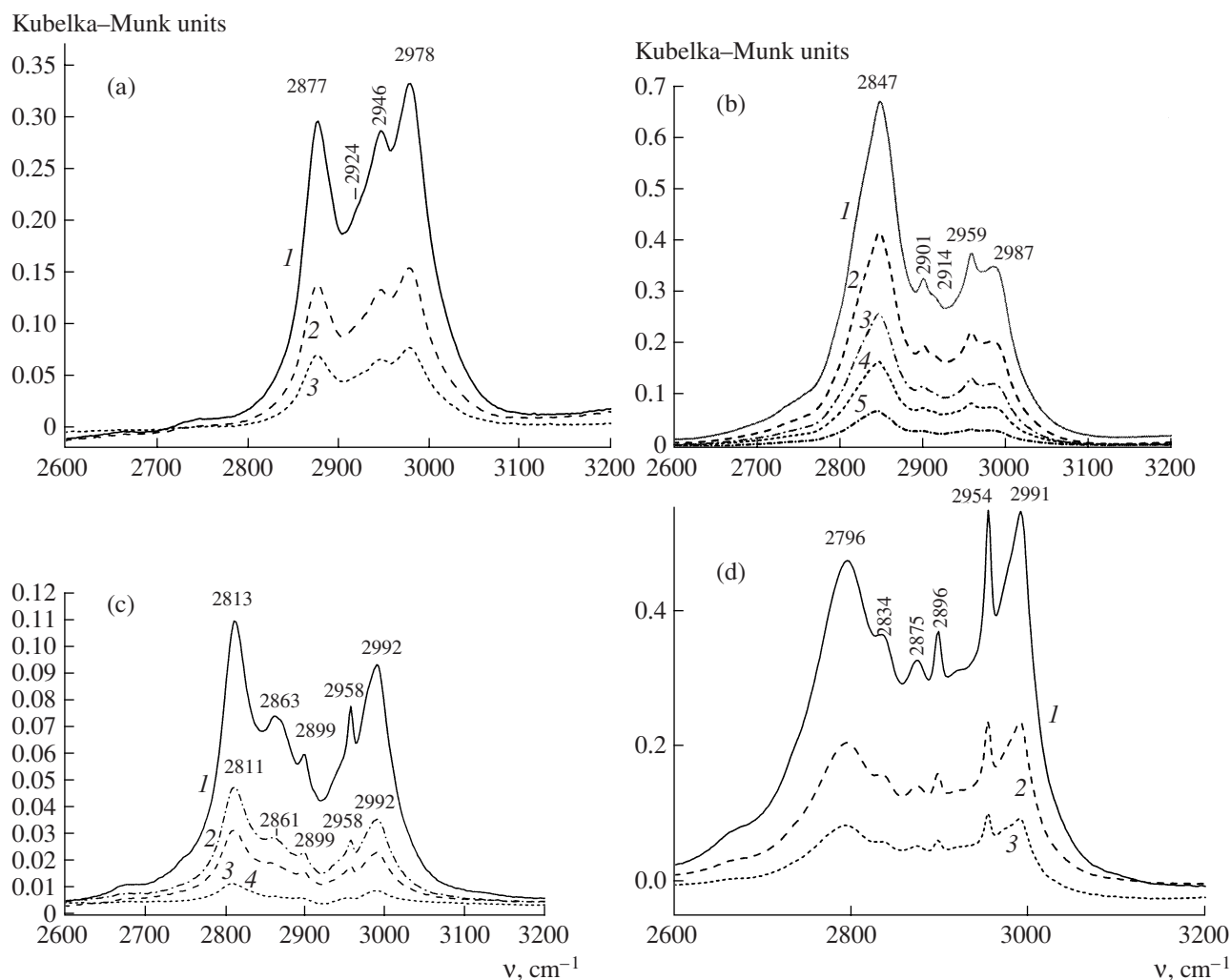


Fig. 5. Diffuse-reflectance IR spectra of ethane adsorbed on various cationic forms of zeolite Y at room temperature: (a) NaY at P_{eq} = (1) 3.6, (2) 1.60, or (3) 0.70 Torr; (b) CaY at P_{eq} = (1) 0.80, (2) 0.29, (3) 0.13, (4) 0.036, or (5) 0.002 Torr; (c) MgY at P_{eq} = (1) 1.40, (2) 0.66, (3) 0.23, or (4) 0.01 Torr; (d) ZnY at P_{eq} = (1) 3.00, (2) 1.34, or (3) 0.40 Torr.

The results of greatest interest were obtained in the adsorption of ethane and propane on the cationic forms of zeolites. The following three types of zeolites were chosen as test materials: high-silica zeolite ZSM-5, the zinc form of which is used as a catalyst for the aromatization of lower paraffins; mordenite; and zeolite Y. It is well known that, of the above zeolites, zeolite Y exhibits the lowest acidity [9].

As noted above, both the cation and the zeolite exerted a strong effect on the low-frequency absorption band in the spectrum upon the adsorption of ethane and propane on the cationic forms of zeolites. According to Table 1, the lowest frequency band for gaseous ethane was the nondegenerate fully symmetric vibration ν_1 (a_{1g}). In the case of a gas, this vibration manifests itself only in Raman spectra and is forbidden in IR spectra. Previously [10, 11], it was demonstrated by quantum-chemical calculations that the forbidden vibration ν_1 becomes not only IR active but also prone to the great-

est influence of adsorption sites in ethane adsorption at the cations of Na and Zn.

As can be seen in Tables 3 and 4 and Figs. 3–7, the shift of the low-frequency absorption band upon ethane

Table 4. Maximums of absorption bands (cm^{-1}) due to propane adsorbed on various cationic forms of zeolites

Y				ZSM-5	
Na	Ca	Mg	Zn	Na	Zn
2962	2973	2977	2972	2964	2979
2937	2950	2951	2946	2938	2942
2907	2887	2906	2904	2901	2898
		2885	2884	2879	2882
2869	2835	2863	2865	2853	2839
		2792	2771		2702

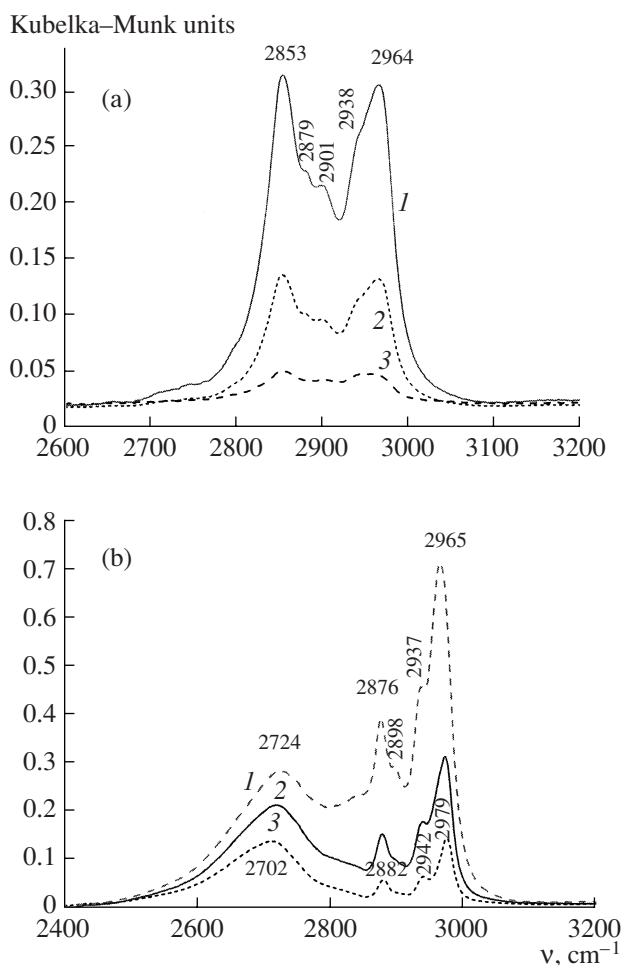


Fig. 6. Diffuse-reflectance IR spectra of propane adsorbed on zeolites at room temperature: (a) NaZSM-5 at P_{eq} = (1) 0.02, (2) 0.006, or (3) 0.001 Torr; (b) ZnZSM-5 at P_{eq} = (1) 0.50, (2) 0.046, or (3) 0.001 Torr.

and propane adsorption clearly depended on the nature of the cation in each series for a particular zeolite. The smallest shift occurred upon adsorption on the sodium forms; the shift further increased in the orders $\text{Na} < \text{Mg} < \text{Zn}$ for ZSM-5 and $\text{Na} < \text{Ca} < \text{Mg} < \text{Zn}$ for mordenite and zeolite Y. It can be seen that the correlation observed for the cations of Na, Ca, and Mg depends on the effective ionic radius. Ferrari et al. [2] obtained an analogous result for the shift of a low-frequency band due to adsorbed methane in a study of methane adsorption on zeolites containing alkali and alkaline earth cations. However, the regular shift of the low-frequency band as a function of the effective cationic charge does not completely describe the dependence observed in our experiments. Thus, in the case of the cation of Zn, its ionic radius is greater than that of Mg; consequently, the effective charge is lower. However, the maximum shift and the greatest intensity of the low-frequency band were observed upon adsorption at the cation of Zn. Thus, the electronic structures of

these cations should also be taken into consideration in order to explain the effect of cations on the shift of the low-frequency band of the C–H stretching vibrations of adsorbed paraffins.

The strong perturbation caused by the cations of Mg or Zn upon ethane and propane adsorption also manifests itself in the appearance of a great number of absorption bands in the spectra, as compared with adsorption on the hydrogen and sodium forms of the zeolites; this suggests a stronger decrease in symmetry upon adsorption at these cations.

As can be seen in Table 3, the shift of the low-frequency absorption bands due to adsorbed ethane and propane depends on the nature of not only the cation but also the zeolite in which this cation occurs. In our experiments, we can distinguish three series of samples: (1) NaY, NaMord, and NaZSM-5; (2) MgY, MgMord, and MgZSM-5; (3) ZnY, ZnMord, and ZnZSM-5. In each particular series, zeolite ZSM-5 exhibited the greatest shift of the low-frequency absorption band, whereas zeolite Y exhibited the smallest shift of this band. This suggests a stronger perturbation of adsorbed ethane on high-silica zeolites ZSM-5, as compared with that on mordenite or zeolite Y. As noted previously [9], zeolite Y in the hydrogen form exhibits the lowest acidity, as compared with the hydrogen forms of ZSM and mordenite. The experimental results of this work allowed us to conclude that the zeolite type and structure affect not only proton acidity but also cationic strength.

Note that the shift of the low-frequency absorption band of C–H vibrations also depends on adsorbed paraffin. Propane was more strongly perturbed than ethane upon adsorption on the same cationic forms of zeolites. This was most likely due to the lower strength of C–H bonds in the molecule of C_3H_8 .

The effect of the nature of the cation and the zeolite on paraffin adsorption manifested itself not only in a shift of the low-frequency absorption band in the spectrum but also in an increase in the relative intensity of this band. In the case of adsorption at sodium cations, the relative intensity of this band was higher than the intensities of other high-frequency bands due to C–H stretching vibrations in the spectrum and comparable with these intensities in terms of the order of magnitude. However, in the case of adsorption at the cations of Ca, Mg, and Zn, the relative integrated intensity of this band increased several times. The greatest relative intensity of the low-frequency band was observed in the case of adsorption on zeolites ZSM-5 and mordenite containing the cations of Zn. Kazansky and Pidko [6] found that the great low-frequency shift and intensity of a band due to this vibration in ethane adsorbed by bivalent zinc ions suggested a strong perturbation and polarization of adsorbed molecules followed by heterolytic dissociation at an elevated temperature. Thus, the relative intensities of the low-frequency absorption bands of adsorbed paraffins can serve as a measure of

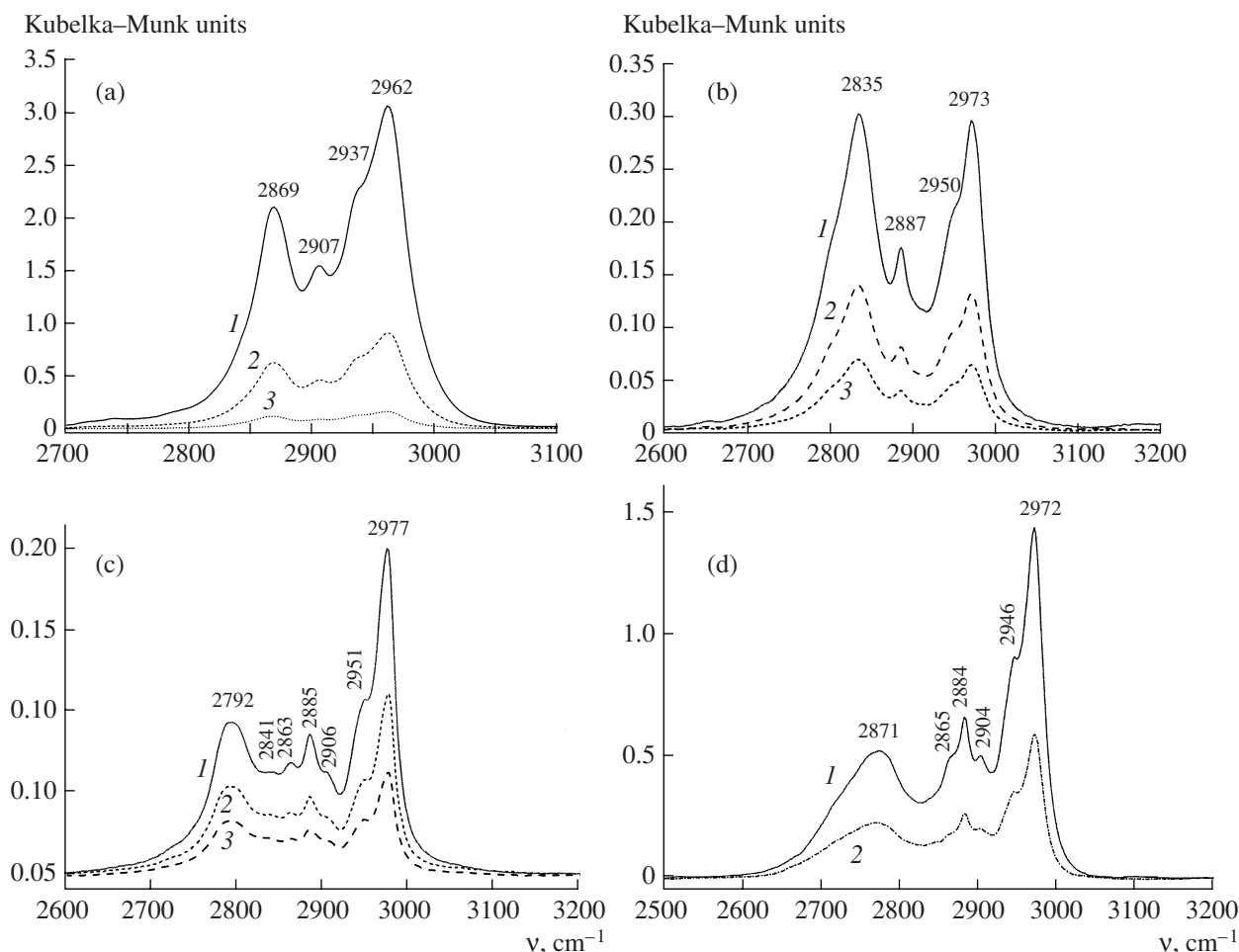


Fig. 7. Diffuse-reflectance IR spectra of propane adsorbed on zeolites at room temperature: (a) NaY at $P_{eq} = (1) 3.7$, (2) 0.92, or (3) 0.13 Torr; (b) CaY at $P_{eq} = (1) 0.01$, (2) 0.05, or (3) 0.01 Torr; (c) MgY at $P_{eq} = (1) 0.07$, (2) 0.015, or (3) 0.005 Torr; (d) ZnY at $P_{eq} = (1) 1.00$ or (2) 0.10 Torr.

C–H bond activation in these molecules due to polarization as a result of adsorption at the test cation in the test zeolite. In this case, the distribution of the relative intensities of C–H stretching vibrations in the spectrum is the best parameter characterizing the effect of the cation and the zeolite on the polarization and perturbation of paraffins upon adsorption, as compared with the low-frequency shifts of absorption bands. Indeed, the shift of the low-frequency band in the spectra upon adsorption is no higher than a few percent of the initial vibration frequency, whereas the relative intensity of this band can be several times higher than the intensities of other high-frequency bands. In the case of adsorption on ZnMord and ZnZSM-5, this band intensity can increase by more than an order of magnitude.

As in the case of low-frequency shifts, we found that the relative intensities of low-frequency absorption bands that corresponded to fully symmetric C–H vibrations in the gas phase increased in the following orders: $H < Na < Ca < Mg < Zn$ and $Y < Mord \approx ZSM-5$.

The experimental results suggest that the spectra of adsorbed ethane and propane depend on both the type of the exchanged cation and the nature of the zeolite in which this cation occurs. This manifests itself in a shift of the lowest frequency absorption band in the IR spectra to the red region and a change in the relative intensity of this band. The observation of the low-frequency shift and changes in the relative band intensity can provide information on the nature and properties of acid-base sites in zeolites and on the effect of the strength of these sites on C–H bond activation in paraffins. Thus, because of this special feature, ethane and propane can be used as molecular probes. The adsorption of ethane and propane is stronger than that of methane; for this reason, these molecules can be used more conveniently at room temperature without experimental difficulties related to measurements at liquid nitrogen temperatures, as in the case of methane. In this case, neither the accurate assignment of other absorption bands in the spectra of adsorbed ethane and propane nor the number

of these absorption bands is of considerable importance.

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