

IR-Spectroscopic Study of the Binding Isomerism of Adsorbed Molecules

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Abstract—This paper discusses the use of IR spectroscopy in the studies of isomerism in the binding of adsorbed molecules with a surface when a molecule may form several different surface species at the same site. Species whose geometry does not provide minimal adsorption energy can be considered as adsorption complexes in an excited state. The spectral manifestations of such a “steric excitation” are compared with the electronic and vibrational excitations of surface species. The “sterically excited” isomeric states existing in thermodynamic equilibrium with ordinary adsorption species are found and studied in detail. Examples are CO molecules bound through C and O atoms with metal cations in zeolites or with surface hydroxyl groups, the thiophene molecule via hydrogen bonding with silanol groups, and HD molecules dissociatively adsorbed on ZnO. A possible role of “sterically activated” isomeric states in catalysis is discussed.

INTRODUCTION

A number of studies are devoted to the nature of activated states of surface complexes, which are possible intermediates in catalytic reactions. These studies are aimed at elucidating detailed mechanisms of surface reactions and hence, enhancing the efficiency of various processes in industrial catalysis. IR spectroscopy provides the most complete data on the structure of intermediates adsorbed on solid surfaces. However, the overwhelming majority of spectroscopic studies concern relatively stable products of adsorption or chemical transformations that may exist for an infinite time at low temperatures in the absence of reactive molecules.

The energetically excited states of short-lived adsorbed molecules are poorly studied. According to the current concepts [1], a molecule on the surface that has not lost its excess energy is in a so-called precursor state. Such a molecule can be bound to a free chemisorption site and retain some excess energy. The idea that these high-energy activated states are intermediates in a sequence of catalytic transformations has been discussed many times in the literature.

Data on the nature of activated states and on the pathways of their deactivation can be obtained by molecular (ionic) beam methods (see [1]) by analyzing desorbing particles. Other methods for studying the activated states involve the excitation of preadsorbed molecules by an external source of energy, which can be in the form of light or a flow of particles to the sur-

face, or use the thermal population of the excited states. The latter case is of special interest to clarify the mechanism of dark catalytic reactions.

The excess energy of an adsorbed molecule which does not translate along the surface may have an electronic, vibrational, or rotational nature. Another type of activated states on the surface were found in the spectra of CO adsorbed on Na-exchanged zeolites [2–4]. It was shown that this molecule may form complexes of two types in zeolites by its addition to a cation through a carbon or oxygen atom, respectively. Two such isomers coexist in thermodynamic equilibrium and possess different adsorption energies. The states of adsorbed molecules with higher energy accumulated due to the formation of a surface complex with nonoptimal geometry are denoted below as “sterically activated” or “sterically excited” states to distinguish them from the electronically or vibrationally excited states.

The sterically activated states populated by thermal excitation may use excess energy for overcoming the activation barrier to the reaction with other adsorbed molecules. Furthermore, different distributions of electron density of adsorbed molecules correspond to various coordination modes, and this may affect their chemical activity. Therefore, the binding of a CO molecule through the oxygen atom is considered as a pathway for the molecule activation on the surface of metal catalysts [5]. Hence, studies into the sterically activated states of the adsorbed molecules are important for understanding the mechanisms of catalytic reactions, and these states are the focus of this paper.

RESULTS AND DISCUSSION

Excited States of Adsorbed Molecules

Let us consider the pathways for the activation of adsorbed molecules to clarify the status of sterically excited states among other excitation types of surface compounds, and the role of each of them in catalysis. Under normal conditions, electronically excited states possess too high energy and, as a result, their population at moderate temperatures is rather small. As a rule, the electronically excited states are studied by UV spectroscopic and luminescence techniques. The lifetime of electronically excited molecules strongly decreases upon adsorption on metals [1], and their involvement in catalytic reactions becomes highly improbable. Deactivation on the surface of oxides may occur more rapidly or more slowly than in a solution or a matrix [6]; however, the excited states always exist in concentrations too low to be observed by conventional vibrational spectroscopy. Nevertheless, their excitation by UV-Vis radiation can produce photochemical or photocatalytic reactions, and the accumulated products can be found and identified by IR spectra [7]. Sometimes, one can observe the absorption bands of electronically excited molecules by time-resolved vibrational spectroscopy. The laser pulse excitation and step-scan techniques of interferogram recording for monitoring FTIR spectra [8] or Raman spectroscopy with the registration of probing pulse scattering with a specified delay time with respect to the exciting pulse [9] were used.

An known example is when an oxygen molecule changes its electronic state for the singlet state upon adsorption [10, 11]. This is possible when the adsorption energy of singlet oxygen is so high that it exceeds the electronic excitation energy in the ${}^1\Delta$ state. However, in this case, the singlet state becomes the ground state and may exist for a long time at a low temperature and be observed in IR absorption spectra [10]. Singlet oxygen may desorb from the surface of some catalysts at high temperatures [12]. It is possible that the electron transfer energy for some molecules is too low for the thermal population of the lowest excited electronic levels. However, we do not have examples of recording vibrational spectra of thermally populated adsorbed molecules in the electronically excited states.

Low vibrational states of surface compounds can easily be populated thermally; however, their excitation and especially excitation of their rotational states cannot substantially affect the reactivity of adsorbed molecules. The excitation of higher vibrational states by a laser pulse of a corresponding frequency followed by further probing absorption of the vibrationally excited surface compounds with another pulse allowed us to evaluate the time of energy relaxation, which proved to be shorter than 18 ps for the stretching vibration of CO

adsorbed on Pt/SiO₂ [13] and nearly 100 ps for the OH groups in zeolites [14]. Such times do not rule out the participation of vibrationally excited molecules in catalysis. The energy absorbed during the resonant excitation of vibrations is redistributed and transforms into thermal energy, and when the energy absorbed is higher than the adsorption energy, molecules may desorb. As experiments with molecules of various isotope compositions showed, the energy exchange in the layer of adsorbed molecules can cause desorption of not only those molecules that absorb radiation [15].

The thermal population of vibrational states whose probability sharply increases with decreasing frequency results in the temperature-dependent IR spectra. The absorption of vibrationally excited compounds can be seen in the spectrum as so-called "hot" transition bands when the bands are narrow and the anharmonicity constants are rather high. Such a "hot band" corresponding to the absorption of the vibrationally excited silanol groups on the SiO₂ surface was found by Peri [16] as a weak maximum at 3560 cm⁻¹ in the spectrum of aerosil heated to 1073 K. The estimate of the population of the vibrationally excited state by the Boltzmann equation shows that the fraction of excited silanol groups is less than 1% even at such a temperature. The excitation of low-frequency vibrations usually results in a gradual shift of the maxima of the absorption bands with temperature due to the anharmonic coupling of vibrations. This shift is clearly seen in the spectra of isolated silanol groups [16] and especially OH groups perturbed by a hydrogen bond [17].

*Technique of IR Studies
in a Wide Temperature Range*

The study of thermodynamic equilibria on the surface makes a severe demand to the cell design. It is not only necessary to combine the high-temperature treatment of samples with recording spectra at low temperatures but also to record spectra in the presence of adsorbed gas avoiding breach of thermal insulation. It is desirable to minimize the beam path length in the gas phase to diminish gas absorption. Furthermore, it is necessary to provide good thermal contact between a sample and a thermostat at any gas pressure; the latter, as well as the temperature, should be controlled with high accuracy. Most of the known devices meet few of these requirements.

Findings described below were obtained using a cell developed by us [18, 19]; its design is shown in Fig. 1. When thermal-vacuum treatment is needed, a sample is transferred with a magnet to a quartz tube in which it can be heated to at least 1200 K. It is important to use the second pair of windows, which are placed on the refrigerant-cooled part of the cell (normally refrigerant is liquid nitrogen) and separate the inner space of the

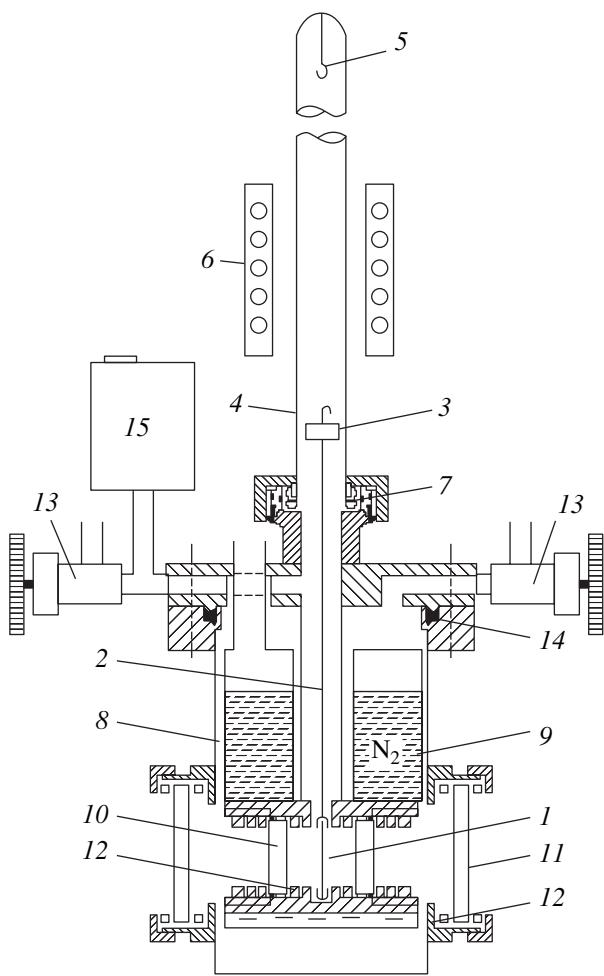


Fig. 1. Cell for recording the spectra of adsorbed molecules at temperatures 55–373 K. (1) Sample; (2) sample holder; (3) anchor of magnetic stainless steel; (4) quartz tube; (5) hook for keeping holder in the upper position; (6) heater; (7) Viton gasket; (8) cell body; (9) coolable part of the cell; (10) inner cooling windows; (11) external windows; (12) indium gaskets; (13) valve; (14) teflon or Viton gasket; and (15) pressure sensor.

cell where the sample is placed from thermal insulating vacuum jacket. This permits us to record the spectra of a sample in the presence of adsorbed gas or even the spectra of a sample immersed into liquid oxygen without breaching the thermal insulation of a cell. To provide reliable contact between the sample and the cell walls in the absence of an adsorbate or at low pressure, ~0.5 torr of helium was admitted to the inner space of the cell. To decrease the temperature to 55 K, the vapor of boiling nitrogen was evacuated from the volume with the refrigerant. When there was a need to increase the temperature, the same volume could be filled with water heated to a specified temperature up to 373 K. The temperature of the cooled part of the cell was measured by a thermocouple inserted into the inlet for filling up the coolant. The pressure was controlled simultaneously with an Edwards Barocel 600 sensor joined directly to the volume with the sample.

Binding Isomerism of CO in Zeolites

In the spectrum of CO adsorbed on zeolites, a weak band shifted to low frequencies relative to the frequency of the free molecule (LF band) is often found along with the band of the cation-bound molecules shifted to high frequencies (HF band). Various hypotheses were advanced on the origin of the LF band. We found earlier [2, 3] for NaY and NaZSM-5 zeolites that the intensity of this band increases with temperature. The bands whose intensities increase upon heating can be due to the products of activated CO adsorption. After CO was added to the cell with MgO or CaO at 77 K, a slight increase in temperature results in an increase in the absorption bands in the 2100–2030 cm^{-1} region, which belong to the ketene group $\text{O}=\text{C}=\text{C}$ of the surface $\text{C}_2\text{O}_3^{2-}$ ions arising upon the interaction of CO with strongly basic O^{2-} ions [18]. However, the products of activated adsorption cannot disappear upon repeated cooling, whereas changes in the LF band intensity in the spectra of zeolites are completely reversible.

As shown in [2, 3], the logarithm of the ratio of the intensities of the LF and HF bands changes linearly with reciprocal temperature (Fig. 2). Such dependence can be expected when the LF band corresponds to a transition from the excited state of a molecule with the excitation energy comparable to kT , particularly in the case of the above “hot” transitions from the vibrationally excited states. However, the LF band is shifted to a low-frequency region relative to the HF band much more noticeably than would be expected for the “hot” transition from the excited stretching vibrational state of the CO molecule, taking into account its anharmonicity ($2\omega_e x_e = 26 \text{ cm}^{-1}$ for a free molecule), and the spectrally estimated excitation energy is nearly one order of magnitude lower than that for $\nu(\text{CO})$. In addition, more recent studies show that both the energy and the frequency shift change from one cation to another, a fact which does not stem from the model of vibrational excitation.

The origin of the LF band was explained by the existence of CO surface complexes of two types in which the molecule is bound to a cation through the carbon or oxygen atom [2–4]. These two forms are in thermodynamic equilibrium, and the ratio of their concentrations depends on the temperature and enthalpy of their interconversion ΔH^0 , which can be estimated from the slope of the Vant-Hoff plot shown in Fig. 2b. The Vant-Hoff equation can be written for our case as

$$\ln(A_{\text{LF}}/A_{\text{HF}}) = -\Delta H^0/RT + \Delta S^0/R + \ln(\varepsilon_{\text{LF}}/\varepsilon_{\text{HF}}),$$

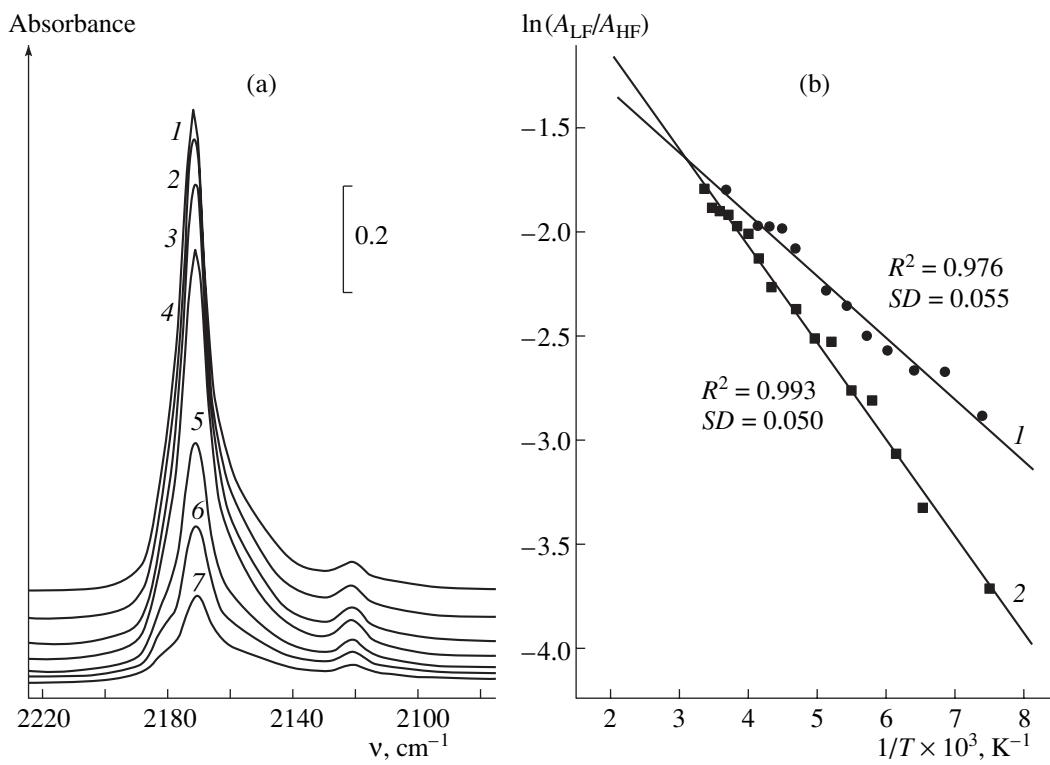


Fig. 2. (a) IR spectrum of CO adsorbed on zeolite NaY at (1) 167, (2) 177, (3) 187, (4) 197, (5) 215, (6) 225, and (7) 233 K. (b) Vant-Hoff plots: (1) CO/NaY, (2) CO/NaZSM-5.

where the ratio of concentrations of substances participating in the equilibrium is expressed in terms of the integral intensities of the low-frequency and high-frequency absorption bands (A_{LF} and A_{HF}) and the corresponding extinction coefficients of surface compounds ε_{LF} and ε_{HF} . Taking into account small changes in the entropy upon adsorption, the fact that two straight lines in Fig. 2b do not pass through the origin can be due to the difference between ε_{LF} and ε_{HF} . Moreover, we could determine the ratio $\varepsilon_{LF}/\varepsilon_{HF}$ from the intersection points of the two curves, and this ratio proved to be different for NaZSM-5 and NaY zeolites, equal to 0.8 and 0.5, respectively. The slopes of the two straight lines in Fig. 2b are also different and give ΔH^0 values of 3.8 and 2.4 kJ/mol for NaZSM-5 and NaY zeolites, respectively. Hence, the above findings can be adequately explained if we assume that CO adsorbs in two forms on the same cation with different adsorption energies, and this difference depends on both the cation nature and its surroundings, which are different in zeolites with various lattice structures. A less energetically favorable oxygen-bound species exists due to the thermal excitation and can be treated as the sterically activated state of adsorbed CO.

More recently, the existence of two adsorption species of CO was found for a wide series of zeolites with the ZSM-5 or faujasite lattices with Li [20], K [21], Rb, and Cs [22] cations, as well as for the H-forms of zeo-

lites [23, 24] in which the hydroxyl groups form hydrogen bonds with CO molecules. Data on the position of the bands of adsorbed CO and the ΔH_{exp}^0 values determined from the Vant-Hoff plots are shown in the table. The low intensity of the LF band in some systems did not allow us to trace its dependence on temperature with an accuracy sufficient for the determination of ΔH^0 from the Vant-Hoff plot. In these cases, neglecting the difference between ε_{LF} and ε_{HF} , we could evaluate the energy of CO-OC isomerization from the Boltzmann equation assuming that the band intensity reflects the ratio of populations of the levels:

$$\Delta E = RT \ln(I_{LF}/I_{HF}).$$

The ΔE values obtained are placed in one column with ΔH_{exp}^0 in the table and marked with an asterisk.

Electrostatic Model

The frequency shifts for adsorbed CO are well described within a simple electrostatic model as a result of the vibrational Stark effect. This model has successfully been used to calculate changes in the frequencies caused by lateral interactions in the layer of adsorbed molecules [28, 29]. In the framework of this approximation, the ΔE value can be calculated as the energy of reorientation of the CO dipole in the field of a cation E

Positions of the high-frequency and low-frequency absorption bands of adsorbed CO and the experimentally determined enthalpy and calculated energy of CO-OC isomerization

Adsorbent	ν_{HF} , cm^{-1}	ν_{LF} , cm^{-1}	$\Delta\nu$, cm^{-1}	ΔH_{exp}^0 , kJ/mol	ΔE_{calcd} , kJ/mol	Reference
LiZSM-5	2195	2100	95	6.5	4.9	[20]
	2188	2110	80	5.6	4.1	
NaZSM-5	2178	2112	66	3.8	3.4	[2, 3]
KZSM-5	2166	2117	49	3.2	2.5	[21]
RbZSM-5	2162	2119	43	1.8	2.2	[22]
CsZSM-5	2157	2122	35	—	1.8	[22]
HZSM-5	2175	2112	63	4.2	3.2	[24]
HY	2173	2124	49	4.3	2.5	[23]
NaY	2171	2122	49	2.4	2.5	[3]
CaY	2197	2094	103	11	5.3	[25]
	2191	2099	92	8	4.7	
SrY	2191	2095	96	9.8	4.9	[26]
	2187	2098	89	7.6	4.6	
SiO ₂	2154	2131	23	2*	1.2	[27]
Silicalite	2160	2122	38	3*	2.0	[27]

* Energy of CO-OC isomerization calculated by the Boltzmann equation.

whose strength can be estimated from the frequency shift upon adsorption or from the difference between the frequencies of the CO molecules in two orientations ($\nu_{HF} - \nu_{LF}$):

$$\Delta E = 2\mu_0 E = \mu_0(\nu_{HF} - \nu_{LF})/K,$$

where for the CO molecule, $\mu_0 = 0.11 \text{ D}$ and $K = 4.29 \times 10^{-9} \text{ D cm}^{-1} \text{ mol kJ}^{-1}$. The ΔE_{calcd} values calculated in this way are shown in a separate column of the table. Comparison of these values with ΔH_{exp}^0 determined from the Vant-Hoff plots shows a good coincidence between the calculated and experimental values for Na, K, and Rb cations. Deviations to one side or another are seen, but the difference is at most 20%. For zeolites with double-charge cations and LiZSM-5 in which the cation field strength and hence, the CO frequency shift are more pronounced, the measured ΔH_{exp}^0 values are 1.5–2 times higher than the calculated values. Apparently, an increase in the frequency with increasing field strength for strong fields should inevitably reach saturation, and the use of the Stark coefficient results in underestimating the field. One can suggest that the ΔH_{exp}^0 value can itself be a measure of the field strength

instead of the CO frequency. The high values of ΔH_{exp}^0 compared to the calculated values are also observed for CO adsorbed on the OH groups, and this is probably a peculiar feature of the hydrogen bond.

The electrostatic model permits one to explain the presence of two CO structures separated by a potential barrier when the molecule is considered as a polarizable dipole assuming that the polarizability in a direction along the molecule axes is substantially higher than that in the field perpendicular to the molecule axis. One can achieve quantitative agreement between the experimental CO adsorption energy and a value calculated using the electrostatic model when the interaction of the quadrupole moment of the molecule with the gradient of the field of the cation is taken into account.

Binding Isomerism of CO over Oxides and Effect of Interaction between Molecules on Its Spectral Manifestation

The above CO binding isomerism has been observed only over zeolites, but it has been shown recently [27] that the band of CO molecules bound through the oxygen atom could be separated in the spectrum of amorphous SiO₂ (aerosil) extensively studied previously. In this case, it is necessary to subtract

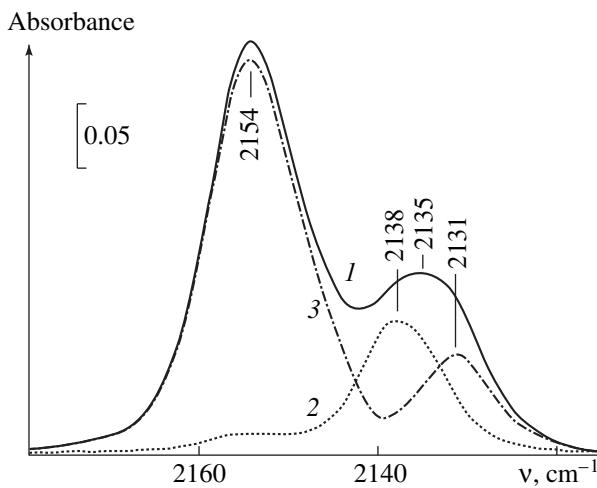


Fig. 3. IR spectrum of CO adsorbed on SiO_2 (aerosil) at 123 K. (1) on sample evacuated at 873 K ($P_{\text{CO}} = 10.6$ torr); (2) on methoxylated sample ($P_{\text{CO}} = 4.6$ torr); (3) difference spectrum obtained by subtracting spectrum 2 from 1 with a factor of 0.4.

the band of physically adsorbed CO, which can be observed separately upon adsorption on the methoxylated sample (Fig. 3). Both bands of CO molecules bound by the hydrogen bond with the silanol groups through carbon and oxygen can be observed simultaneously in the spectrum of silicalite (Fig. 4) in which the bands of CO stretching vibration at small surface coverages are shifted more strongly relative to the posi-

tion typical of a free molecule due to the presence of more acidic OH groups.

Oxygen-bound surface complexes of adsorbed CO with the cations or OH groups have not been observed by now in the spectra of metal oxides. This is possibly due to the surface heterogeneity, which causes the appearance of several overlapping absorption bands, and each of them has its own OC bands. The bands of the admixture of the isotopomer ^{13}CO , which is always present in a small concentration (~1%) in the gas of the natural isotopic composition, are present in the same spectral region, and this fact makes the observation of the weak bands of sterically excited molecules much more difficult. When the CO bands are narrow and intense, as in the case of ZnO , the spectrum proves to be distorted by the lateral interactions that lead not only to the shift of maxima but also to the redistribution of the band intensities due to dynamic interactions [29]. As a result, the weak low-frequency bands of oxygen-bound molecules can become even less observable.

The interaction between adsorbed molecules manifests itself in the spectra of CO adsorbed on some zeolites at rather high surface coverages. The initially arising bands begin to weaken with increasing coverage simultaneously with an increase in the intensities of the CO bands at lower wavenumbers. This effect is illustrated in Fig. 5. The spectra of ^{13}CO adsorbed on zeolite CaY were recorded during desorption of adsorbed molecules. Such a change in the intensities was found for the bands at 2149 and 2140 cm^{-1} , and this fact can be attributed to the adsorption of one or two molecules on the same Ca^{2+} cation, respectively. According to [30],

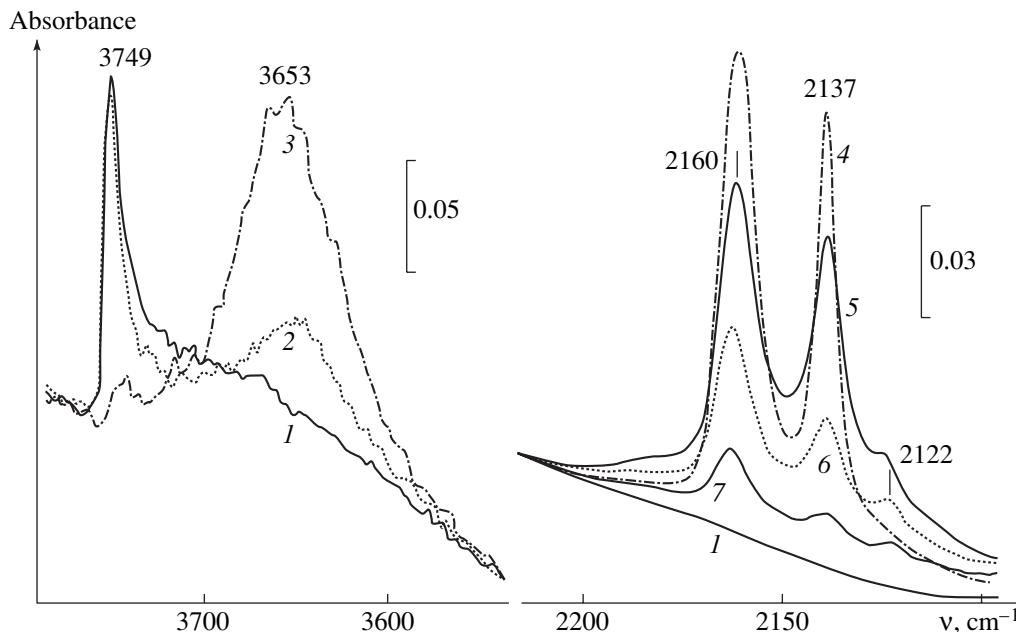


Fig. 4. Changes in IR spectrum of silicalite (1) evacuated at 653 K and cooled to 77 K, (2, 3) with increase in the amount of adsorbed CO at 77 K and (4) after increase in temperature to 77, (5) 133, (6) 153, and (7) 173 K.

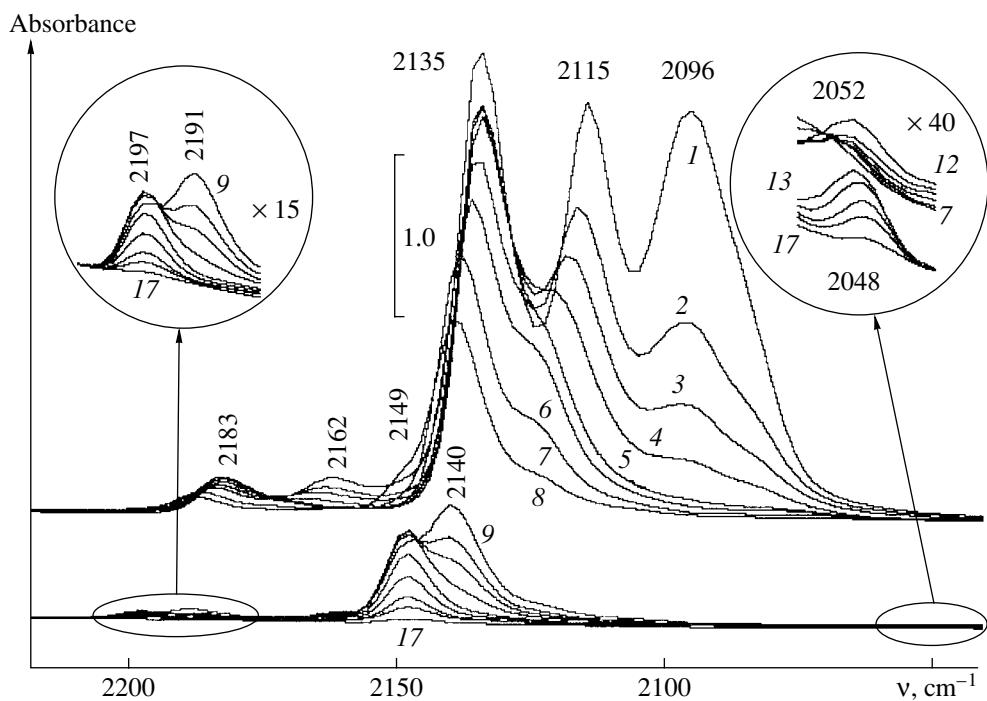
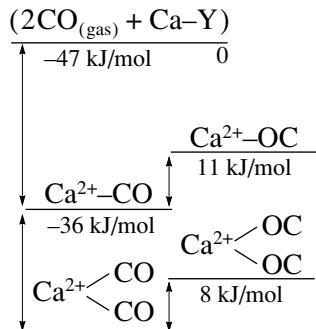


Fig. 5. Changes in IR spectrum of zeolite CaY with adsorbed $^{13}\text{C}^{16}\text{O}$ during heating the sample to (1) 77, (2) 95, (3) 105, (4) 114, (5) 134, (6) 144, (7) 166, (8) 185, (9) 205, (10) 215, (11) 225, (12) 245, (13) 273, (14) 293, (15) 312, (16) 325, and (17) 344 K.

the band at 2115 cm^{-1} observed at higher coverages can be assigned to the third CO molecule bound to the same cation. If the dynamic interaction of the two molecules were strong enough, a more complicated spectrum with two maxima would correspond to a complex of the two interacting molecules. However, the spectrum of an admixture of the ^{12}CO molecules shown in the left inset is in fact identical to that of the pure ^{12}CO isotope. This indicates that the dynamic interaction in this system is weak and the origin of the frequency shift from 2198 to 2190 cm^{-1} is entirely due to the effect of static interaction. The same pair of bands of CO molecules, adsorbed singly and in pairs, was found on LiZSM-5. It was impossible to observe two bands separately in the spectra of SrY zeolite, and transition to dicarbonyl complexes manifests itself as a gradual shift of the band maximum with coverage.

The binding isomerism that manifests itself in the spectrum of the system of two interacting molecules has some peculiarities. The presence of a neighboring molecule weakens the field of a cation resulting in a decrease in the frequency shift for both coordination modes. The low-frequency shift of the CO band upon the adsorption of the second molecule is accompanied by a high-frequency shift of the maximum of the band of the oxygen-bound molecules. This leads to a shift of the band at 2048 cm^{-1} (right inset in Fig. 5) in the ^{13}CO spectrum as the temperature decreases. The Vant-Hoff plot for these systems reveals two linear sec-

tions describing the equilibria $\text{M}-\text{CO} \rightleftharpoons \text{M}-\text{OC}$ and $\text{OC}-\text{M}-\text{CO} \rightleftharpoons \text{OC}-\text{M}-\text{OC}$ and allows one to estimate separately the enthalpy of reorientation of a lone molecule and one of two molecules in the dicarbonyl complex. The formation of the structure with two CO molecules bound through oxygen with the same cation is quite improbable. Simultaneous monitoring of pressure and temperature while recording the spectra allows one to determine the isosteric heat of adsorption for various species, in particular, for mono- and dicarbonyl CO complexes with Ca cations, as well as the mutual arrangement of the energy states of the system shown in Scheme 1. As can be seen from Scheme 1 and the table, both the heat of adsorption and the energy of isomerization prove to be significantly lower upon the addition of the second molecule to the cation than upon the adsorption of the first molecule.



Scheme 1.

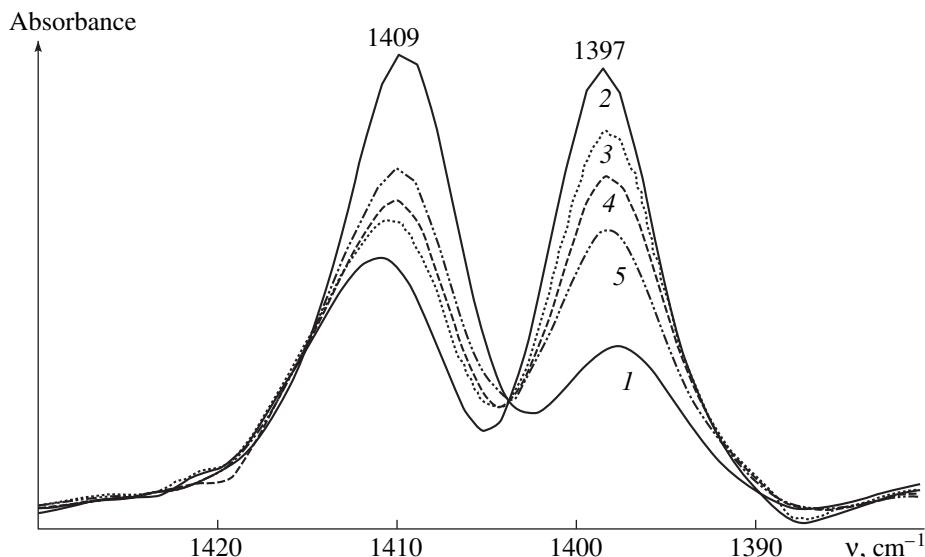


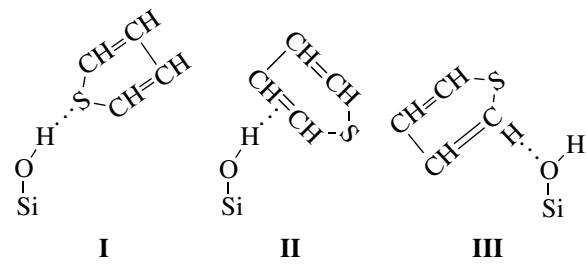
Fig. 6. IR spectrum of thiophene adsorbed on SiO_2 (aerosil) before (1) and (2–5) after addition of SO_2 recorded at (1, 2) 55, (3) 98, (4) 112, and (5) 138 K.

Thus, the presence of a neighboring CO molecule weakens the cation field, decreasing the adsorption energy and the energy of isomerization of the other molecule. It might be expected that the vicinity of the oxygen-bound molecule would enhance the frequency of the neighboring CO molecule. The authors of [25] used this way of reasoning to explain the origin of the band at 2211 cm^{-1} , whose intensity in the spectrum of zeolite CaY increases with increasing temperature like the intensity of the band of oxygen-bound CO molecules. However, the authors of [30] noted that the band that appears upon CO adsorption on zeolite CaNaY has a disproportionately high intensity at low temperatures, which disagrees with the above assignment.

Binding Isomerism upon Adsorption of Other Molecules

We cannot exclude that binding isomerism is a rather abundant phenomenon among adsorbed molecules of various nature. Coordination through both carbon and nitrogen was observed upon the adsorption of the CN^- ion, which is isoelectronic to the CO molecule, from a solution to the surface of metal electrodes [31]. Heterocyclic molecules can interact with hydroxyl groups and form a hydrogen bond with an unshared pair of a heteroatom or π -electrons of an aromatic ring. A recent study of the temperature dependence of IR spectra of thiophene adsorbed on the hydroxyl groups of the aerosil surface showed the existence of at least three adsorption species. Indeed, as can be seen from Fig. 6, a reversible “transfer of intensity” is observed from the band at 1409 cm^{-1} belonging to thiophene molecules bound through a sulfur atom (Scheme 2, structure I) to

the band at 1397 cm^{-1} of molecules perturbed by the hydrogen bond with π -electrons of the aromatic ring (structure II) with a decrease in the temperature from 140 to 55 K. These changes should be considered as evidence for the thermodynamic equilibrium between these two structures in which the second structure is more energetically favorable. The isomerization energy estimated from the Vant Hoff plot is $\sim 1.8\text{ kJ/mol}$.



Scheme 2.

Spectra 2–5 shown in Fig. 6 were recorded after adding a small amount of SO_2 to the cell. SO_2 can weakly bind to the oxygen of a silanol group and thus prevents its interaction with thiophene. When SO_2 is absent, the band at 1409 cm^{-1} is much more intense (curve 1) because of the superposition of additional absorption due to the third adsorption species (structure III) in which thiophene acts as a proton donor in the hydrogen bond with the oxygen atom of the hydroxyl group. The silanol group can serve as an adsorption site for molecules with electron-acceptor or proton-donor properties, such as SO_2 or H_2S , due to bond formation through the oxygen atom of the silanol

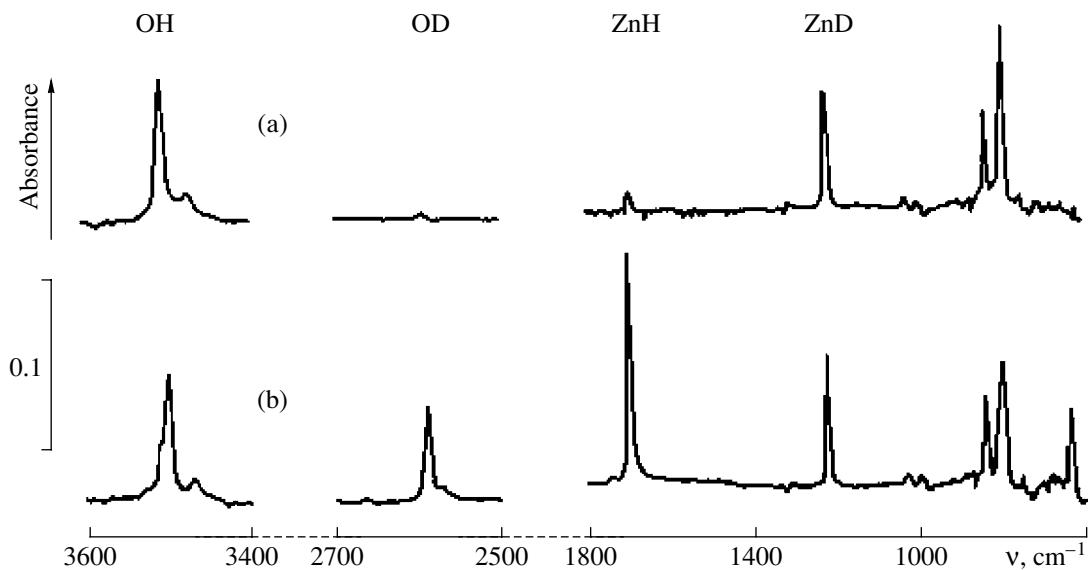


Fig. 7. IR spectrum of HD (a) adsorbed on ZnO (Kadox 15) at 100 K and (b) after heating to 300 K and repeated cooling to 100 K in a closed volume.

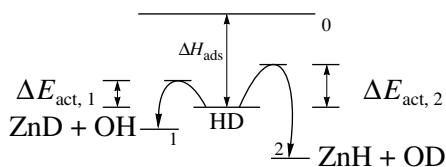
group, as has been shown recently by the coadsorption of these molecules with bases [32]. When thiophene is adsorbed together with such a base as lutidine (2,5-dimethylpyridine), the band at 1397 cm^{-1} is extremely weak. Apparently lutidine forms a stronger H-bond with the proton of the OH group, replaces thiophene, and prevents the formation of structures **I** and **II**; structure **III** remains the only possibility. Thus, thiophene can form hydrogen-bonded complexes of three types with surface silanol groups and two of these are in thermodynamic equilibrium with a rather low isomerization energy.

The above examples of binding isomerism concern molecular adsorption through coordination or a hydrogen bond. However, the formation of several energetically nonequivalent structures on the same surface site is also possible upon the dissociative adsorption of some molecules. It was shown [33, 34] that HD on ZnO could dissociate through two channels (Scheme 3) to form either ZnH and OD groups or ZnD and OH groups on the metal-oxygen pair site. The energies of the products are not equal because the energies of zero vibrations are different.

As can be seen from the spectra in Fig. 7, the second channel of adsorption is not effective at 100 K, probably because of a higher activation barrier, and dissociation occurs only via channel 1 so that the bands of the ZnH and OD groups in the spectrum are extremely weak. Their intensities rapidly increase with increasing temperature above 250 K, and the energetically more favorable structure 2 prevails at room temperature under equilibrium conditions. Repeated cooling does not restore the initial spectrum and results in only freezing the concentrations of the surface species typical of higher temperatures. In this case, a study of the temperature dependence of IR spectrum makes it possible to determine the energy difference between two channels of dissociative adsorption and estimate the height of the activation barrier between two states on the basis of the spectrokinetic measurements of the dissociation rate vs. temperature.

CONCLUSIONS

Molecules may form several nonequivalent configurations with different energies upon adsorption on the same surface site, and this was confirmed for various types of adsorption: through the hydrogen bond, through the coordination bond with cations in zeolites, and through dissociation. The surface isomeric structures are in mutual thermodynamic equilibrium either over the total temperature studied or in a specific temperature region whose lower limit is restricted by the activation barrier of isomerization. Such a barrier results in freezing the equilibrium between two states for the HD dissociative adsorption at temperatures below 250 K. In other systems under study, freezing



Scheme 3.

was not achieved either because of a drop in the concentration of sterically excited states below the detection limit, as in the CO adsorption on the metal cations in zeolites, or because of low isomerization energy, as in the case of the hydrogen-bonded CO or thiophene, when the concentration of the sterically excited isomer remains significant and continues to change until reaching the lowest experimental temperatures.

The energy of steric activation can vary from 1–2 kJ/mol for the hydrogen-bonded molecules of CO and thiophene to at least 10–15 kJ/mol for CO coordinatively bound to the metal cations. The upper limit is evidently determined by the conditions of observation, which do not allow us to record spectra at temperatures above 373 K and high CO pressures, rather than by the nature of the phenomenon. Nevertheless, the ΔE values obtained are close in the order of magnitude to the activation energies of some catalytic reactions involving these molecules. The activation energy of CO oxidation with oxygen over solid solutions of NiO or CoO in MgO determined spectrokinetically is 4–20 kJ/mol [35]. The catalytic isotopic mixing of 2,5-thiophene- d_2 over CaO occurs at a temperature \sim 200 K when the pressure of the thiophene vapor is barely sufficient for adsorption [36] and the corresponding activation energy, when it is measurable, should be extremely low, comparable to the reorientation energy of the hydrogen-bonded thiophene. Thus, the sterically activated states, in their energies, can be intermediates of catalytic reactions and can initiate their occurrence in the presence of molecules-partners. The spectrally measured energy of their thermal excitation can be the major part of the activation energy.

In this work we dealt with only one structural aspect of steric excitation, namely with a change in the geometry of mutual arrangement of an adsorbed molecule with respect to the surface site. However, the formation of sterically activated surface complexes with the geometry of the adsorption site changed or with structural reconstruction of the adsorbed molecules themselves stimulated by a catalyst is quite possible. Further studies are necessary to elucidate the role of the steric activation in catalysis.

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