

# The Influence of the Local Environment on the Electron Accepting Ability of the Cation: Induced Lewis Acidity

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**Abstract**—The effect of adsorption of acid gases CO<sub>2</sub>, SO<sub>2</sub>, and SO<sub>3</sub> on the electron accepting ability of cations on the surface of calcium oxide was studied by low-temperature IR spectroscopy of adsorbed CO. It is shown that the formation of carbonate, sulfite and sulfate anions in the surface layer leads to the appearance of Lewis acid sites, the strength of which, estimated by the shift in the vibration frequency of CO molecules associated with them, increases in the appropriate order, approaching that for calcium-containing zeolites. The results of the calculation of cluster models by the DFT method confirm the observed trends in the variation of the vibrational frequency and the absorption coefficient of CO molecules bound through both the carbon and oxygen atoms, and also demonstrate the dependence of the ability of a cation for CO linkage isomerism on its local environment.

**Keywords:** surface, adsorption, acidity, IR spectroscopy, quantum chemical calculation, electron accepting ability

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## INTRODUCTION

Acid-modified solid-state catalysts are widely used in industrial catalytic processes due to their high activity and selectivity [1–3]. To create new efficient catalytic systems, it is extremely important to understand the mechanism of the promoting action of acid modifiers. It was previously shown that the adsorption of volatile acids can lead to the appearance of Brønsted acidity even of the initially basic magnesium oxide [4]. From the fact that this effect is observed with the addition of aprotic acids, such as SO<sub>2</sub> or NO<sub>2</sub>, it was concluded that this is the result of the increase in the proton-donating ability of surface OH groups caused by the addition of acid molecule to the oxygen atom of hydroxyl [5, 6]. The authors explain the promoting effect of these gases in reactions catalyzed by Brønsted acid sites by such induced acidity. It was also demonstrated the increase in the electron-donating ability of oxygen of the OH group on its interaction with basic molecules [7]. This means a mutual enhancement of the adsorption of acidic and basic molecules on their joint interaction with the hydroxylated surface of oxides.

The electron accepting ability of surface cations, i.e., their Lewis acidity is also not a constant value and depends on their environment, including the presence of adsorbed molecules. The presence of Lewis acid

sites of different strengths on the surface of aluminum oxides [8] or titanium [9], manifested in the IR spectra of coordinately bound test molecules of CO or ammonia, is explained by the different coordination of surface cations. The dependence of the position of the adsorbed CO bands on the degree of surface coverage indicates a repulsive lateral interaction between the adsorbed molecules [10], the mechanism of which includes surface relaxation induced by adsorption [11].

The exchange cations of zeolites, as judged by the spectra of adsorbed CO, are characterized by unusually high electron acceptor ability. Thus, when adsorbed on sodium cations, seemingly the embodiment of basicity, the frequency of C–O stretching vibration for Na-ZSM-5 zeolite [12] reaches 2178 cm<sup>-1</sup>, higher than on interaction with acid hydroxyl groups of HY zeolite (2173 cm<sup>-1</sup> [13]) or H-ZSM-5 (2175 cm<sup>-1</sup> [14]). In the spectrum of Li-ZSM-5 zeolite it was observed at 2195 [15], and for CaY [16, 17], the frequency of CO reaches 2197–2201 cm<sup>-1</sup>, higher than when adsorbed on Lewis sites of average strength of the surface of titanium, zinc or aluminum oxides.

Another feature of the cationic sites of zeolites is their ability for linkage isomerism of adsorbed CO: when adsorbed on the cationic sites of zeolites Y and ZSM-5, the molecule can be either via carbon atom or via oxygen [12, 16]. The first case corresponds to an

increase of the vibrational frequency of the molecule, in the second—a decrease by about the same amount. Both forms are in thermodynamic equilibrium between each other. The former is energetically more favorable, and always prevails. The oxygen-bound state is populated by thermal excitation following the Boltzmann's law. By investigating the dependence of the logarithm of the ratio of the intensities of the two bands on the inverse temperature, which is well approximated by a linear function (Van't-Hoff plot), the enthalpy of the revolution of the molecule can be determined from the slope of the straight line. This value depends on the ratio of charge to the radius of the cation and increases from  $\sim 2$  for  $\text{Cs}^+$  to 11 kJ/mol for  $\text{Ca}^{2+}$  [12, 16].

Linkage isomerism was also detected for CO adsorption on hydroxyl groups of protonic zeolites [13, 14] and even of silica [18]. However, this property was found neither for zeolites X, nor for metal oxides. Basing on the electrostatic model, it was assumed that the reason for this is the interaction of CO with surrounding oxygen ions carrying a significant negative charge, which lowers the height of the potential barrier between the two forms of CO adsorption and eventually leads to the formation of T-shaped (side-on) complexes of molecules with  $\text{O}^{2-}$  anions [19]. A similar form of adsorption is manifested in the spectra of zeolites X with  $\text{Cs}^+$  and  $\text{Rb}^+$  cations, as a band slightly shifted towards low frequencies relative to the frequency of a free molecule, which is not accompanied by high-frequency analogues and turns out to be the most stable with respect to vacuum treatment. The shape of the absorption band contour of such molecules and the relatively small value of the entropy change on adsorption indicate the saving of the rotational mobility of such molecules [20].

Confirmation of these ideas was the work [21] on the adsorption of CO on a sputtered NaCl film. As expected, the replacement of the oxygen environment of the cation with single-charged halogen anions leads to the appearance of an absorption band in the spectrum, whose behavior allows it to be considered as belonging to O-bound molecules, and the low intensity indicates insignificant number of sites on which this form of adsorption is realized.

In this regard, it was interesting to find out how the modification of the surface of metal oxides by acid ions such as carbonates, sulfates and others affects the strength of their surface acid sites and their ability for linkage isomerism. To study this effect, quite suitable is CaO, which is a basic oxide, and its surface does not have any pronounced acidic properties.

IR spectroscopic studies of the calcium oxide surface show that hydroxyl groups of CaO surface are perturbed by the adsorption of molecules such as carbon tetrachloride, acetone [22] and ozone [23], but they are not able to form a hydrogen bond through the proton [24]. After thermal activation of calcium oxide at

700°C, strong basic Lewis sites are formed on its surface, which are coordinately-unsaturated oxygen anions. This is confirmed by the formation of surface carbonite ions  $\text{CO}_2^{2-}$  when they interact with carbon monoxide molecules [25] and surface ozonides  $\text{O}_3^-$  interacting with ozone molecules [23], and the spectra of adsorbed fluoroform indicate an extremely high electron-donating ability of such sites [26]. Adsorption of  $\text{NH}_3$  molecules on such strong basic surface sites leads to their dissociation with the formation of OH groups and  $\text{NH}_2^-$  ions [27]. The presence of such sites in the immediate vicinity of the cation should affect its strength and ability for linkage isomerism of CO.

Thus, calcium oxide is a convenient model for demonstrating the manifestation of induced Lewis acidity of the surface caused by adsorption of acid modifiers and their effect on the linkage isomerism. In this paper, an IR spectroscopic study of the effect of modification of calcium oxide surface by chemisorbed  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{SO}_3$  molecules on the acidic strength of the calcium cation, characterized by the frequency of adsorbed CO molecules, was carried out. The obtained data are compared with previously published results on the spectra of CO adsorbed on CaY zeolite [12, 16]. The presented experimental data are completed with the results of quantum chemical calculations using the density functional theory of cluster models of oxide, its products of interaction with the listed molecules or water, as well as the models of zeolite fragment with calcium cation and a free cation without any environment. In addition to the frequencies calculated both in the harmonic approximation and taking into account anharmonicity, for molecules bound to the cation through carbon or oxygen, the intensity of the stretching C—O vibration of model systems was calculated in search of its correlation with the vibration frequency.

## EXPERIMENTAL

For IR spectroscopic studies of low-temperature adsorption of carbon monoxide molecules, the stainless steel IR cell described in detail earlier [16] was used. The pressure was measured with two Edwards Barocel 600 capacitance pressure gauges with operating pressure ranges of  $10^{-3}$ –10 Torr and 1–1000 Torr. The temperature of the sample during the experiment was controlled using a thermocouple located in the cooled part of the cell close to the sample holder.

Calcium oxide samples with a specific surface area of about 40 m<sup>2</sup>/g, as before [23, 25], were prepared by heating a pressed calcium hydroxide tablet directly in the IR cell at temperatures of 500 and 700°C for three hours in vacuum of  $10^{-4}$  Torr. Modification of the surface of calcium oxide was carried out by processing a sample previously thermally activated at 700°C in vapors of modifying agents at different temperatures,

followed by evacuation. Treatment in SO<sub>2</sub> and CO<sub>2</sub> vapors was carried out at lowered temperatures of –15 and +15°C, respectively, and in SO<sub>3</sub> and H<sub>2</sub>O vapors—at room temperature (+25°C). The formation of surface compounds during the modification was controlled using IR spectra. The sample of CaY zeolite was the same as in [12, 16].

IR spectra of adsorbed carbon monoxide were recorded at liquid nitrogen temperature (–196°C). The dependence of the IR spectra on the surface coverage was controlled by gradually removing the excess adsorbate by pumping until the position of the band maximum, having reached the high-frequency limit, ceased to change. With small CO coverages, for a better thermal contact of the sample with cooled walls of the IR cell, helium gas was let into the volume. Gaseous CO, CO<sub>2</sub>, and SO<sub>2</sub> (99% purity) and SO<sub>3</sub> (from oleum) and H<sub>2</sub>O (from distilled water) vapors were used to modify the CaO surface. Prior to use, liquids and easily condensing gases were subjected to several “freezing-pumping-defrosting” purification cycles.

IR spectra were recorded with a Nicolet 710 Fourier transform IR spectrometer with a cooled detector at spectral resolution of 4 cm<sup>–1</sup> and accumulation of 128 scans. The IR spectra were processed and the position of the absorption band maxima was determined using the OMNIC program.

### CALCULATIONS

For the quantum-chemical calculations, a small cluster of calcium oxide Ca<sub>4</sub>O<sub>4</sub> was modeled, to which up to four CO molecules were sequentially added, attached to the calcium cation either by a carbon atom or by oxygen. Modification was performed by joining three water molecules, CO<sub>2</sub>, SO<sub>2</sub> or SO<sub>3</sub>, and after optimizing the geometry of the modified clusters, CO molecule was attached. The hybrid density functional B3LYP/6-311+G(d, p) was used as the main calculation method, taking into account the dispersion interactions within the framework of the GD3 Grimm correction. The criterion for achieving a local minimum was the absence of imaginary frequencies of normal vibrations. The anharmonic C–O vibrational frequency was calculated separately for all models. For the free CO molecule, the harmonic and anharmonic frequencies were found to be  $\nu_{\text{har}}(\text{C–O}) = 2212.95 \text{ cm}^{-1}$  and  $\nu_{\text{anh}}(\text{C–O}) = 2187.95 \text{ cm}^{-1}$ , respectively. Since the experimental value of the vibration frequency of <sup>12</sup>CO molecule in the gas phase is 2143.237 cm<sup>–1</sup>, all the CO frequency values calculated in the anharmonic approximation in complexes with clusters were multiplied by a scaling factor of  $2143.24/2187.95 = 0.979564$ . In addition to the equilibrium geometry, energies and vibrational frequencies, the intensity of the absorption band of C–O bond vibration in the complexes under consideration was also calculated.

In addition, adsorption of CO molecule was modeled on two models of CaY zeolite: the simplest, taking into account only the local environment of the Ca<sup>2+</sup> cation, and the more complex, reflecting the structure of zeolite supercell. In the latter case, the basic set 6-31+G(d, p) was used for calculations. For comparison, a complex of free Ca<sup>2+</sup> cation with CO molecule attached via both carbon or oxygen atom was also calculated.

The adsorption energy of CO molecule was determined as the difference between the energy of the complex and the sum of separately calculated energies of the molecule and the cluster. In the case of successive addition of several molecules, the adsorption energy of the *n*th CO molecule was estimated as the difference between the energy of the final Ca<sub>4</sub>O<sub>4</sub> + *n*CO structure and the sum of total energies of the Ca<sub>4</sub>O<sub>4</sub> + (*n* – 1)CO cluster and CO molecule.

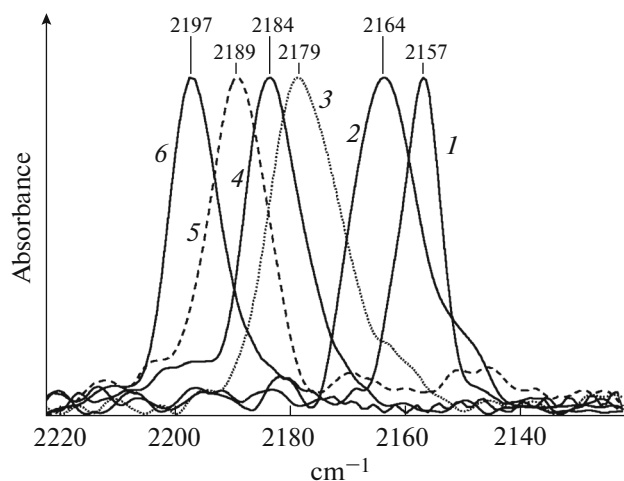
All calculations were carried out using the GAUSSIAN 16 licensed quantum chemical software package [28] installed on the HW cluster of St. Petersburg State University Computing Center [29].

### EXPERIMENTAL RESULTS

Low-temperature adsorption of CO molecules on the surface of a CaO sample prepared at 700°C and subsequently hydrated at 300°C, at high coverages, leads to the appearance in the spectrum of a band at 2155 cm<sup>–1</sup>, corresponding to stretching vibration of CO adsorbed on Ca<sup>2+</sup> cations, as well as a band at 2140 cm<sup>–1</sup>, belonging to physically adsorbed molecules.

When the CO coverage decreases, only a high-frequency band remains in the spectrum, and its maximum shifts to 2157 cm<sup>–1</sup>. When the preparation temperature of CaO sample increases up to 700°C, hydroxyl groups are almost completely removed, and adsorption of CO on such samples, except for molecules adsorbed on calcium cations, in accordance with previously obtained data [25, 30], leads to the formation of carbonites and carbonates. It should be noted that as the CaO activation temperature increases from 300 to 500 and 700°C, the maximum absorption band of CO molecules adsorbed on the strongest Ca<sup>2+</sup> cations (at low coverages) gradually shifts to the high-frequency region from 2157 to 2163 and 2165 cm<sup>–1</sup>.

Figure 1 shows the spectra of CO adsorbed at low coverages on CaO sample after pumping at 500°C, hydrated in water vapor, and on CaO evacuated at 700°C after exposure to CO<sub>2</sub>, SO<sub>2</sub> or SO<sub>3</sub>, as well as on CaY zeolite. It can be seen that modification of the surface by acid gases leads to the increase in the frequency of adsorbed CO compared to that for an unmodified surface. The strongest effect is achieved in the case of SO<sub>3</sub>, when the band position of adsorbed molecules approaches the value characteristic of cal-



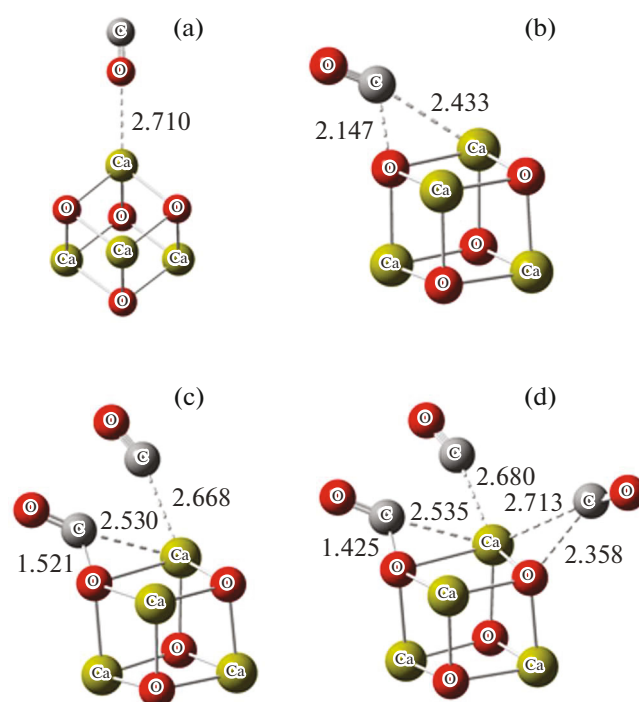
**Fig. 1.** IR spectrum of CO adsorbed on the CaO sample thermally vacuumed at 700°C and modified by adsorption of H<sub>2</sub>O (with subsequent pumping out at 20 (1) and 500°C (2)) and adsorption of CO<sub>2</sub> (3), SO<sub>2</sub> (4) and SO<sub>3</sub> (5). 6—Spectrum of CO adsorbed on CaY zeolite. The spectra were recorded at 77 K and rated by the temperature.

cium zeolite. Dissociative adsorption of water, on the contrary, lowers the frequency of adsorbed molecules to the minimum value of 2157 cm<sup>-1</sup>.

### CALCULATION RESULTS

The strongest sites detected experimentally in the spectra of adsorbed CO occupy insignificant part of the surface of calcium oxide, and, obviously, are not the ions of regular low-index faces, but rather coordinately unsaturated atoms of edges and tops. As the simplest model containing three-coordinated Ca<sup>2+</sup> and O<sup>2-</sup> ions, a cubic electroneutral Ca<sub>4</sub>O<sub>4</sub> cluster was considered, where on one of the cations CO molecule was adsorbed (Figs. 2a and 2b). Adsorption via carbon atom (Fig. 2b) turns out to be 26.5 kJ/mol more favorable than via oxygen (Fig. 2a), however, unlike the latter case, the molecule is not limited by attraction to the calcium cation. It leans towards one of the nearest oxygen anions to such extent that the distance from the carbon atom to it becomes significantly less than to calcium. This means that a significant contribution to the adsorption energy is given by the side-on interaction of the molecule with the oxygen anion.

The addition of the second molecule to the same cation (Fig. 2c) leads to even a greater convergence of the carbon atom of the first molecule to a distance of about 1.42 Å, which corresponds to the formation of a chemical bond. The vibration frequency of the C—O bond of the molecule decreases to 1643.7 cm<sup>-1</sup>, the value characteristic of the C=O double bond, and a new stretching vibration of the C—O bond with the oxygen atom of the surface appears with a frequency of



**Fig. 2.** Interaction of the cluster Ca<sub>4</sub>O<sub>4</sub> with molecules of CO. Explanations—in the text.

about 724 cm<sup>-1</sup>. In this case, the newly attached molecule does not approach one of the remaining oxygen anions, but remains near the formed carbonite anion. The addition of a third molecule to the cluster leads to the simultaneous implementation of three adsorption options shown in Figs. 2b and 2c. It is possible to attach a fourth CO molecule to the same cation, which also tilts, approaching the previously adsorbed molecule.

The results of modifying the Ca<sub>4</sub>O<sub>4</sub> cluster by adding water are illustrated in Figs. 3a–3c. Optimization of the geometry of the Ca<sub>4</sub>O<sub>4</sub> cluster with water molecules leads to dissociative adsorption of the latter, while the original cubic Ca<sub>4</sub>O<sub>4</sub> cluster undergoes strong distortions. In the structure in Fig. 3a, the addition of hydroxyl groups of water increases the coordination number of two calcium atoms to 4, and the other two to 5. A more symmetrical Ca<sub>4</sub>O<sub>4</sub> cluster with a 3-coordinated Ca<sup>2+</sup> ion (Fig. 3b) is obtained by attaching three protons to three oxygen ions closest to it and three OH groups to three other calcium cations, the coordination number of which increases to 4. Calculated data on the adsorption of the CO molecule on such clusters are shown in Table 2. It is essential that the adsorption of CO on a 3-coordinated calcium ion is possible by both a carbon atom and oxygen, and in the latter case the adsorption energy is 6.65 kJ/mol lower. Adsorption on the 4-coordinated Ca<sup>2+</sup> ion is even less favorable.

**Table 1.** The calculated harmonic  $\nu$  and scaled anharmonic  $\nu_{\text{anh}}^*$  frequencies, intensities  $\epsilon$ , as well as the energies of adsorption  $\Delta E_{\text{ads}}$  of the molecules of CO on the cluster  $\text{Ca}_4\text{O}_4$ 

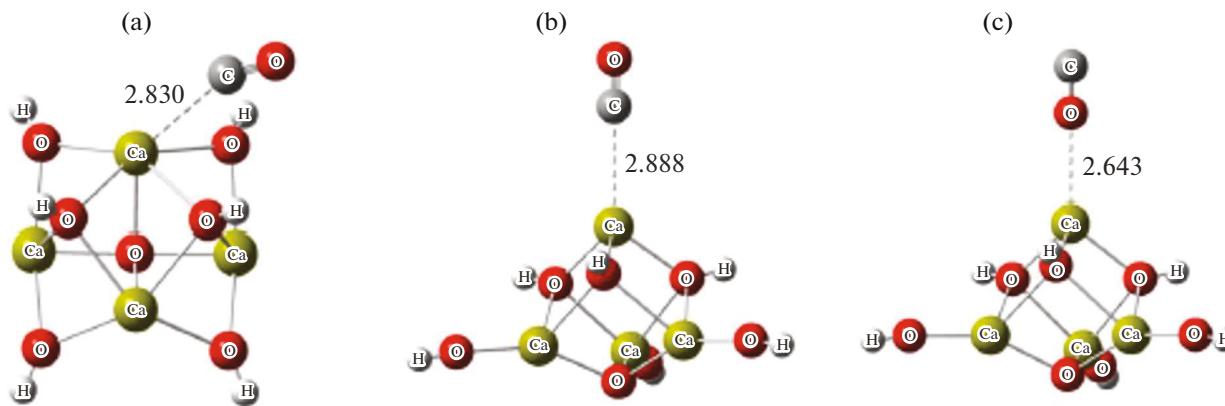
Model	$\nu(\text{C}-\text{O}), \text{cm}^{-1}$	$\nu_{\text{anh}}^*(\text{C}-\text{O}), \text{cm}^{-1}$	$\epsilon, \text{km/mol}$	$\Delta E_{\text{ads}}, \text{kJ/mol}$
(a) $\text{Ca}_4\text{O}_4 + \text{OC}$	2185.6	2117.5	179	14.9
(b) $\text{Ca}_4\text{O}_4 + \text{CO}$	2068.7	1988.4	442	41.4
(c) $\text{Ca}_4\text{O}_4 + 2\text{CO}$	1693.3	1643.8	416	37.4
	2130.5	2066.8	757	
(d) $\text{Ca}_4\text{O}_4 + 3\text{CO}$	1693.6	1647.2	443	31.9
	2138.7	2072.6	532	
	2147.8	2072.9	511	
(e) $\text{Ca}_4\text{O}_4 + 4\text{CO}$	1693.2	1648.4	402	29.4
	2141.8	2081.4	350	
	2153.7	2079.4	297	
	2157.2	2083.1	467	

**Table 2.** Calculated harmonic  $\nu$  and scaled anharmonic  $\nu_{\text{anh}}^*$  frequencies, intensities  $\epsilon$ , as well as the energies of adsorption  $\Delta E_{\text{ads}}$  of the CO molecule on hydrated cluster  $\text{Ca}_4\text{O}_4$ 

Model	$\nu(\text{C}-\text{O}), \text{cm}^{-1}$	$\nu_{\text{anh}}^*(\text{C}-\text{O}), \text{cm}^{-1}$	$\epsilon, \text{km/mol}$	$\Delta E_{\text{ads}}, \text{kJ/mol}$
(a) $\text{Ca}_4\text{O}_4 + 3\text{H}_2\text{O} + \text{CO}$	2204.8	2132.6	146	25.0
(b) $\text{Ca}_4\text{O}_4 + 3\text{H}_2\text{O} + \text{CO}$	2276.1	2200.5	64	33.7
(c) $\text{Ca}_4\text{O}_4 + 3\text{H}_2\text{O} + \text{CO}$	2157.3	2089.0	208	27.0

Modeling of the surface of calcium oxide modified with acids was carried out by adding  $\text{CO}_2$ ,  $\text{SO}_2$  or  $\text{SO}_3$  molecules to the  $\text{Ca}_4\text{O}_4$  cluster (Figs. 3a–3d). Optimization of the geometry of the  $\text{Ca}_4\text{O}_4$  cluster with  $\text{CO}_2$  molecules leads to their adsorption with the formation of carbonate ions  $\text{CO}_3^{2-}$  (Fig. 3a). In other cases, sulfite and sulfate anions associated with  $\text{Ca}^{2+}$  cations are formed, respectively. This noticeably distorts the initial cubic structure of calcium oxide, so Fig. 3 shows

the initial cluster structures for clarity. Adsorption of the CO molecule in all cases can occur both via C atom and O atom, while binding via carbon is always energetically more favorable. The calculation results are summarized in Table 3. Analysis of the obtained vibrational frequencies shows that the frequency of CO molecule after addition of  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{SO}_3$  gradually increases, whereas for oxygen-bound molecules, on the contrary, the decrease of frequency is observed. In the same sequence, an increase in the

**Fig. 3.** Modification of cluster  $\text{Ca}_4\text{O}_4$  by molecules  $\text{H}_2\text{O}$ . See details in the text.

**Table 3.** Calculated harmonic  $\nu$  and scaled anharmonic  $\nu_{\text{anh}}^*$  frequencies, intensities  $\epsilon$ , as well as the energies of adsorption  $\Delta E_{\text{ads}}$  of the CO molecule on cluster  $\text{Ca}_4\text{O}_4$ , modified by adsorption of acidic molecules

Model	$\nu(\text{C}-\text{O}), \text{cm}^{-1}$	$\nu_{\text{anh}}^*(\text{C}-\text{O}), \text{cm}^{-1}$	$\epsilon, \text{km/mol}$	$\Delta E_{\text{ads}}, \text{kJ/mol}$
(a) $\text{Ca}_4\text{O}_4 + 3\text{CO}_2 + \text{CO}$	2247.4	2174.4	98	33.4
(a') $\text{Ca}_4\text{O}_4 + 3\text{CO}_2 + \text{OC}$	2180.9	2111.0	121	23.3
(b) $\text{Ca}_4\text{O}_4 + 3\text{SO}_2 + \text{CO}$	2248.4	2175.4	97	41.2
(b') $\text{Ca}_4\text{O}_4 + 3\text{SO}_2 + \text{OC}$	2178.2	2109.4	196	23.4
(c) $\text{Ca}_4\text{O}_4 + 3\text{SO}_3 + \text{CO}$	2275.6	2201.5	58	45.1
(c') $\text{Ca}_4\text{O}_4 + 3\text{SO}_3 + \text{OC}$	2140.5	2070.4	149	37.9

adsorption energy is observed, both on adsorption by carbon or oxygen atom.

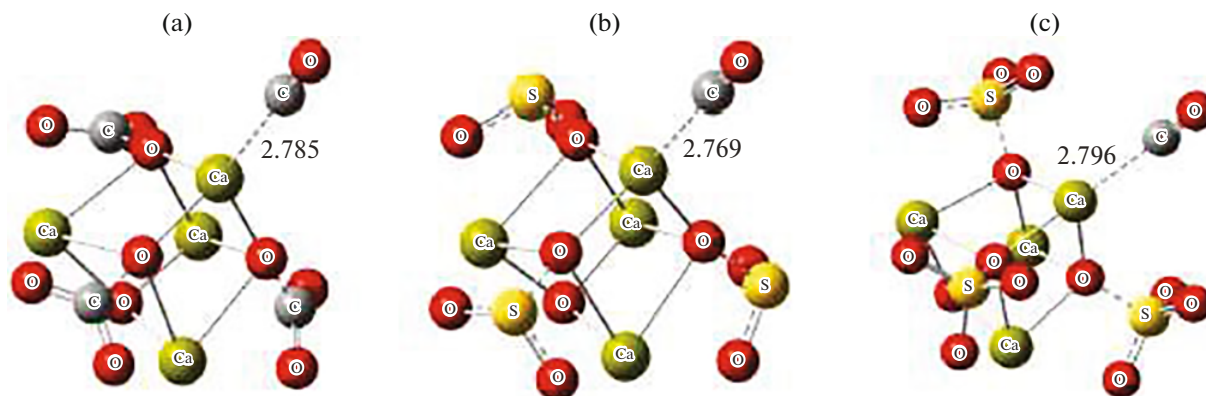
The maximum shift of the vibrational frequency  $\nu(\text{C}-\text{O})$  in the experiment was observed for CO adsorption on CaY zeolite. To simulate adsorption on calcium cation in the zeolite lattice, a cation in contact with two oxygen atoms of the  $\text{AlO}_4$  tetrahedron was taken as the simplest model (Figs. 4a, 4b). Its four dangling bonds, linked to silicon atoms in the zeolite, were saturated in the model with hydrogen atoms. A more complex model, taking into account not only the nearest environment, but reflecting the structure of the zeolite supercell, is shown in Fig. 4c. The same figure shows the simplest model—a complex with a free  $\text{Ca}^{2+}$  cation in two possible isomeric configurations. The calculated data are summarized in Table 4. As expected, for all the models shown in the figure, both isomeric configurations turn out to be stable, although the C-bound configuration in Fig. 4, a turns out to be bent, apparently as a result of attraction of the molecule to oxygen of the OH group. According to calculations, adsorption of the molecule by carbon atom turns out to be more favorable than via oxygen by 18.3 kJ/mol, whereas for a supercell (Fig. 4c) the difference is 11.58 kJ/mol, and for a free cation (Figs. 4d, 4e) it reaches 15.18 kJ/mol. At the same time, the dif-

ference in the vibration frequencies of CO molecule in the two configurations naturally increases, reaching in the latter case  $370 \text{ cm}^{-1}$ .

The experimental results indicate the existence of a certain correlation between the vibrational frequency and the integral absorption coefficient of adsorbed CO molecules [31]. Figure 6 shows the calculated intensity values depending on the values of anharmonic frequencies multiplied, as in the tables, by a scaling factor. The graph shows data on structures where a molecule forms linear complexes by binding to a calcium cation both via carbon or oxygen atom, and its location does not indicate lateral interaction with oxygen atom of the cluster or of the OH group. The cross indicates the point corresponding to the gas molecule. It can be seen that in complexes with lower frequencies, the intensity is everywhere higher than that of a free molecule, whereas in C-bonded systems with increased vibration frequency, it is close or little different from the corresponding value of the CO molecule ( $\epsilon = 88.70 \text{ km/mol}$ ).

## DISCUSSION

It is not an easy task to evaluate the electron accepting ability of cations on the surface of pure cal-

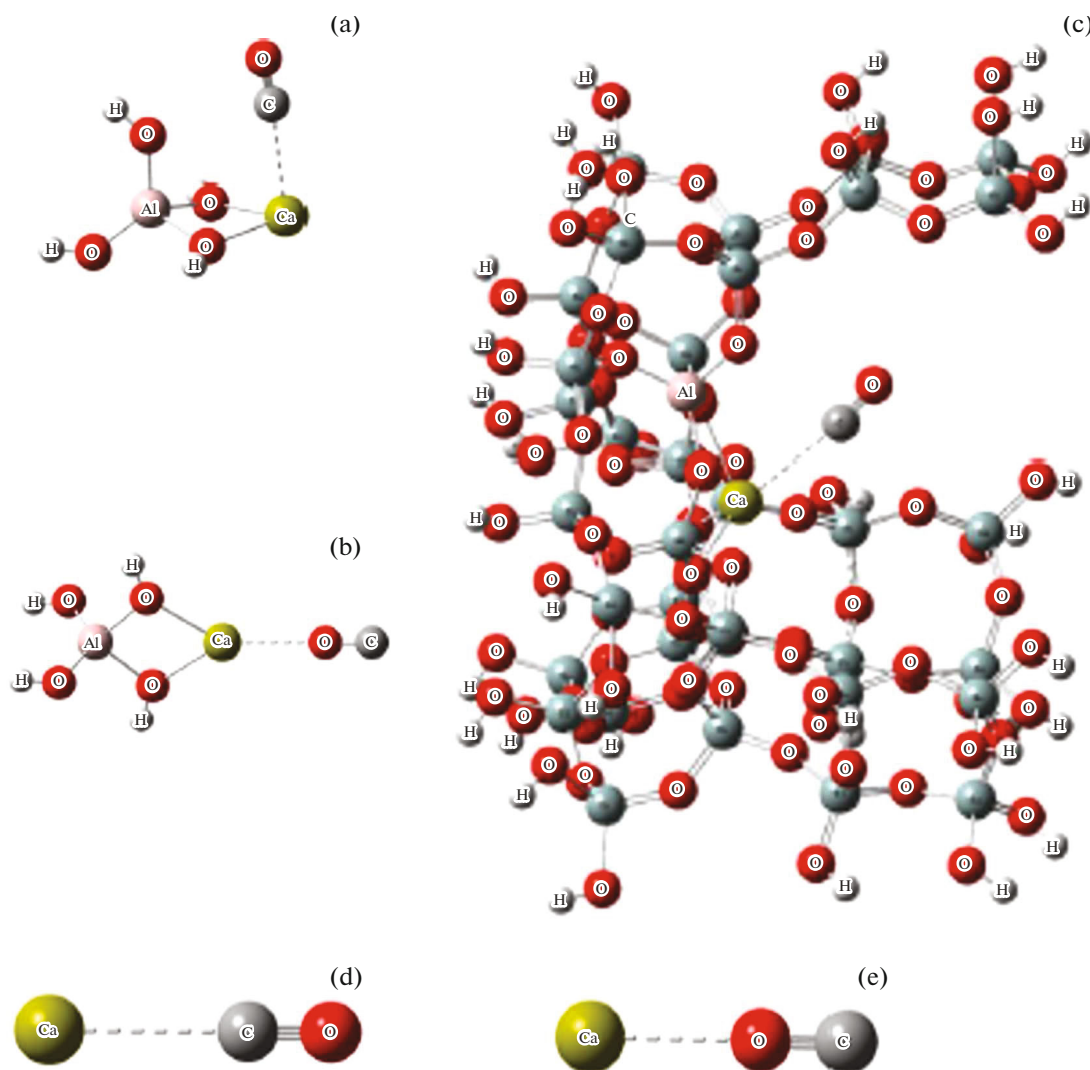
**Fig. 4.** Modification of cluster  $\text{Ca}_4\text{O}_4$  by molecules  $\text{CO}_2$  (a),  $\text{SO}_2$  (b) and  $\text{SO}_3$  (c). See details in the text.

**Table 4.** Calculated harmonic  $\nu$  and scaled anharmonic  $\nu_{\text{anh}}^*$  frequencies, intensities  $\epsilon$ , as well as the energies of adsorption  $\Delta E_{\text{ads}}$  of the CO molecule on various models of zeolite CaY

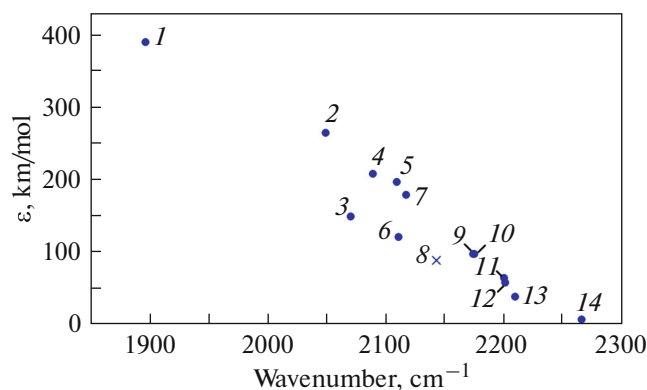
Model	$\nu(\text{C-O}), \text{cm}^{-1}$	$\nu_{\text{anh}}^*(\text{C-O}), \text{cm}^{-1}$	$\epsilon, \text{km/mol}$	$\Delta E_{\text{ads}}, \text{kJ/mol}$
(a) $\text{CaAl}(\text{OH})_4 + \text{CO}$	2289.9	2214.1	52	61.8
(b) $\text{CaAl}(\text{OH})_4 + \text{OC}$	2114.8	2049.0	504	43.5
(c) $\text{CaY} + \text{CO}$	2283.1	2209.7	68	66.0
(d) $\text{CaY} + \text{OC}$	2133.6			54.4
(e) $\text{Ca}^{2+} + \text{CO}$	2340.9	2266.3	12	123.1
(f) $\text{Ca}^{2+} + \text{OC}$	1999.1	1896.3	389	107.9

cium oxide. After evacuation at temperatures up to  $500^\circ\text{C}$ , a significant number of hydroxyl groups are present on the surface, which not only affect the properties of the surrounding cations, but can themselves

serve as adsorption sites. Increase of the pretreatment temperature removes OH groups, but leads to the formation of coordinately unsaturated oxygen ions. They interact with CO molecules with the formation of car-



**Fig. 5.** The models of CO bonding with ion  $\text{Ca}^{2+}$  in zeolite (a–c) and with free cation of calcium (d, e). See details in the text.



**Fig. 6.** Correlation between the calculated values of frequency and intensity of the vibration stripe of C–O in the studied complexes. 1— $\text{Ca}^{2+} + \text{OC}$ , 2— $\text{CaAl}(\text{OH})_4 + \text{OC}$ , 3— $\text{Ca}_4\text{O}_4 + 3\text{SO}_3 + \text{OC}$ , 4— $\text{Ca}_4\text{O}_4 + 3\text{H}_2\text{O} + \text{OC}$ , 5— $\text{Ca}_4\text{O}_4 + 3\text{SO}_2 + \text{OC}$ , 6— $\text{Ca}_4\text{O}_4 + 3\text{CO}_2 + \text{OC}$ , 7— $\text{Ca}_4\text{O}_4 + \text{OC}$ , 8— $\text{CO}$ , 9— $\text{Ca}_4\text{O}_4 + 3\text{CO}_2 + \text{CO}$ , 10— $\text{Ca}_4\text{O}_4 + 3\text{SO}_2 + \text{CO}$ , 11— $\text{Ca}_4\text{O}_4 + 3\text{H}_2\text{O} + \text{CO}$ , 12— $\text{Ca}_4\text{O}_4 + 3\text{SO}_3 + \text{CO}$ , 13— $\text{CaY} + \text{CO}$ , 14— $\text{Ca}^{2+} + \text{CO}$ .

bonite  $\text{CO}_2^{2-}$  ions. The latter also modify the surface, and in the course of further interaction with CO, they form more complex surface compounds, during the disproportionation of which carbonates and reduction products arise. The properties of such a surface should differ significantly from the properties of the initial oxide. The spectra shown in Fig. 1, curves 1 and 2 refer to a highly hydrated and partially dehydroxylated oxide surface. The frequency of adsorbed CO on such a sample does not exceed  $2163 \text{ cm}^{-1}$ .

Adsorption of acidic molecules leads to a high-frequency shift of maximum of the band of molecules associated with the strongest sites. The maximum frequency shift relative to its value for a hydrated sample is  $32 \text{ cm}^{-1}$  (band  $2189 \text{ cm}^{-1}$ ) and is observed for a sample with pre-adsorbed  $\text{SO}_3$ . When CO was adsorbed on CaO samples with pre-adsorbed  $\text{CO}_2$  and  $\text{SO}_2$ , the frequency shifts were  $22 \text{ cm}^{-1}$  (band  $2179 \text{ cm}^{-1}$ ) and  $27 \text{ cm}^{-1}$  (band  $2184 \text{ cm}^{-1}$ ), respectively. Similar frequencies of CO are observed on adsorption on H-zeolites [5], however, perturbation of surface hydroxyl groups similar to that observed in the spectrum of CO adsorbed on MgO after contact with  $\text{H}_2\text{S}$  [4] were not detected in the case of CaO modified by adsorption of  $\text{SO}_3$ ,  $\text{SO}_2$  or  $\text{CO}_2$ .

It can be concluded that the observed high-frequency band of CO corresponds to the coordination bond of the molecule with surface calcium cations, whose electron acceptor ability is increased due to the presence of adsorbed  $\text{CO}_2$ ,  $\text{SO}_2$  or  $\text{SO}_3$  on the surface. According to [32],  $\text{SO}_2$  molecules interact with the surface of magnesium oxide as Lewis acid, forming donor-acceptor complexes with surface oxygen ions.

The acidity of the surface increases as a result of the electron density being pulled away from the surface magnesium atoms by  $\text{SO}_2$  molecules or the resulting  $\text{SO}_3^{2-}$  sulfite ions. In our case, in the spectra of the modified CaO, bands corresponding to weakly bound  $\text{CO}_2$ ,  $\text{SO}_2$  or  $\text{SO}_3$  molecules were absent, and at frequencies below  $1500 \text{ cm}^{-1}$ , absorption characteristic of carbonates [33], sulfites or sulfate ions was observed [32].

Thus, the effect of increased Lewis acidity of calcium cation of the modified oxide is explained by the presence of sulfate, sulfite and carbonate anions on the surface, and the surface of calcium oxide after interaction with acidic oxides can be considered as a layer of the corresponding calcium salts. Then the raising of the frequency of adsorbed CO, from the point of view of the electrostatic model, reflects the increase of the electrostatic field of the cation surrounded by anions larger in size than the oxygen ion  $\text{O}^{2-}$ , namely,  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$  or  $\text{SO}_4^{2-}$ . When CO is adsorbed on the CaO surface, where the charge of  $\text{Ca}^{2+}$  ion is maximally compensated by the charges of the surrounding  $\text{O}^{2-}$  anions, a CO band is observed at  $2157 \text{ cm}^{-1}$  (Fig. 1), and in the spectra of calcium-containing zeolites, where the negative charge is distributed over the polyanion lattice, CO adsorption gives bands at  $2193 \text{ cm}^{-1}$  for Ca-ZSM-5 [34] and  $2197\text{--}2201 \text{ cm}^{-1}$  for CaY [16, 17].

In the case of zeolites, the electrostatic field of the cation should be close in magnitude to the field of the isolated cation in the free state. It is hardly possible to measure the vibration frequency of CO with such a cation experimentally, but the calculation results are consistent with these concepts, although it can be noted that both the calculated frequency shifts and the adsorption energies of the complex with a free ion significantly exceed similar values for zeolite. It is obvious that the local environment, even in zeolite, significantly weakens the field of the cation.

The calculation of models of modified calcium oxide generally reproduces the changes observed experimentally in the spectra of adsorbed CO. There is the increase of the vibrational frequency, and the magnitude of the frequency shift increases from  $\text{CO}_2$  to  $\text{SO}_3$  and even more to CaY zeolite. The calculated frequency values are close to those observed experimentally, although some overestimation of the calculated values can be noted ( $2201.5$  instead of  $2189 \text{ cm}^{-1}$  for  $\text{CaO} + \text{SO}_3$  and  $2209.7$  instead of  $2197\text{--}2201 \text{ cm}^{-1}$  for CaY). The calculated value of the adsorption energy for zeolite is also higher:  $65.97 \text{ kJ/mol}$ , whereas the spectrally measured value of the isosteric heat of adsorption was  $47 \text{ kJ/mol}$  [16]. Such an excess can be explained by the fact that in reality the lattice of a crystal or zeolite to some extent prevents the relaxation of



the environment allowed for the cluster in the calculation.

The results of calculations for the pure and hydrated calcium oxide model are more difficult to compare with the experimental data. A very low adsorption energy corresponds to the binding with the oxygen atom (14.9 kJ/mol), and naturally, in the experiment, this form of adsorption does not compete with the 26.5 kJ/mol more favorable adsorption combining side-on interaction with oxygen and donating the unshared pair of electrons of the carbon atom to a cation (Fig. 2b). Binding via carbon atom in its pure form is not realized, since its energy, even with a stronger interaction with the cation, as in the case of CaY zeolite, would be only 12 kJ/mol greater than adsorption via oxygen. Modification of the cluster by dissociative adsorption of water with the addition of protons to three surrounding oxygen ions prevents side-on interaction, and carbon adsorption becomes possible and turns out to be 6.7 kJ/mol more favorable than for O-binding. However, in reality, when water dissociates, OH groups saturate coordination-unsaturated calcium ions, thereby blocking the interaction of CO with the cationic sites of the hydrated surface. The model of a hydrated cluster with a 4-coordinated cation shown in Fig. 3a shows that the presence of a bridged OH group with unshared pair on the oxygen atom next to the CO molecule leads to its frequency lowering, although weaker than when interacting with oxygen of the cluster (Fig. 2b).

Addition of the second CO molecule to Ca<sub>4</sub>O<sub>4</sub> cluster (Fig. 2c) provokes the transformation of one of them into the carbonite ion CO<sub>2</sub><sup>2-</sup>, whose frequencies (1643–1649 and 762–772 cm<sup>-1</sup>) differ slightly from those observed in the experiment with CaO (1478 and 850 cm<sup>-1</sup> [25, 30]). Obviously, the greater distance between the two stretching vibrations of the ion associated with the cluster indicates its strong asymmetry, manifested in different bond order. It is noteworthy that the second molecule does not seek to form a complex with another oxygen ion, but prefers to approach the carbonite ion. We can explain this observation by the tendency of the two fragments to form dioxoketene ion CO<sub>2</sub>=C=O<sup>2-</sup>. For its formation upon CO adsorption on CaO a slight increase in temperature is needed [30].

The calculation results confirm the explanation of the absence of CO linkage isomerism on metal oxides and zeolites X, according to which it is the strong interaction of the molecule with oxygen ions that leads to the disappearance of the potential barrier between C- and O-bound states. Indeed, the C-bound state is not realized on a cluster of unmodified oxide. It is not possible to observe experimentally the CO linkage isomerism on modified oxide samples due to the low concentration of cations capable of isomerism, however, the calculation shows that the neutralization of oxygen ions surrounding the cation by the addition of

CO<sub>2</sub>, SO<sub>2</sub> or SO<sub>3</sub> molecules or protons during dissociative adsorption of water immediately makes possible the existence of two isomeric states.

The dependence of the adsorbed CO absorption coefficient on its vibrational frequency shown in Fig. 6 is in agreement with the previously published experimental data [31]. Some deviations from the expected parabolic curve can be explained by the difficulty of taking into account the polarization of the cation environment in the cluster when calculating the intensity of CO absorption band.

## CONCLUDING REMARKS

The experimental data obtained confirm our ideas about the influence of the cation's nearest environment on its electron-accepting ability. Indeed, during the adsorption of acid gas molecules, the oxygen ions surrounding the cation are converted into large carbonate, sulfite or sulfate anions, whose negative charge is distributed over several atoms. As a result, the cation field is weakened to a lesser extent by the field of environment, and the frequency of CO molecules adsorbed on the cation increases. In zeolite, the distribution of negative charge over the framework makes the cations even more free and the frequency of carbon monoxide adsorbed on them increases even more.

The quantum-chemical calculations of cluster models not only reproduce the experimentally observed increase in the frequency of adsorbed CO in the series CaO < CaO + CO<sub>2</sub> < CaO + SO<sub>2</sub> < CaO + SO<sub>3</sub> < CaY zeolite, but also predict an even higher frequency of CO in complex with a free cation, the experimental observation of which seems extremely problematic. This means, in particular, a higher electron-accepting ability of the cationic sites of metal salts of oxygen-containing acids as compared to oxides of the same metals. This is consistent with the statement made in [35] that for the same metal cations salts can exhibit more acidic properties than oxides. Moreover, using the example of calcium halides, it can be seen that the increase of the radius of anions is accompanied by the increase in the frequency of adsorbed CO from 2168 cm<sup>-1</sup> for CaF<sub>2</sub> to 2190 cm<sup>-1</sup> for CaI<sub>2</sub> [36].

If the metal oxide initially possessed the property of Lewis acid, its modification by sulfate ions or adsorption of SO<sub>3</sub> leads to manifestations of superacidity, as in the case of sulfated zirconium oxide [37, 38].

The calculations show that the effect of CO linkage isomerism with calcium cation, observed in experiments with CaY and CaZSM-5 zeolites, and not detected for adsorption on cations of oxide adsorbents, could be observed on the same cations surrounded by polyatomic anions or hydroxyl groups.

Information about the relation between the integral absorption coefficient of CO molecule and the position of the absorption band in the IR spectrum is very important for determining the concentration of active

sites of catalysts. The electrostatic model based on the vibrational Stark effect and the known dependence of the polarizability of the molecule on the vibrational coordinate predicts a decrease in the absorption coefficient with the CO frequency increase in the field of the cation, whereas a change in the direction of the field on reorientation of the molecule with the formation of the O-bound complex should, on the contrary, lead to the increase in its absorbance. The data of [31] confirm the existence of such a dependence, although the experimental determination of the integral absorption coefficient meets serious difficulties, and the literature data are very contradictory [39]. The results of calculating the intensity of CO absorption band in the spectra of studied complexes are generally consistent with the predictions of electrostatic model.

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#### CONFLICT OF INTEREST

The authors of the paper declare that they have no conflict of interest.

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