

# Integrated Absorption Coefficient of Adsorbed CO<sup>1,2</sup>

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Received November 8, 2006; in final form, October 26, 2007

**Abstract**—The integrated absorption coefficient  $\epsilon$  has been measured for the stretching band of CO adsorbed on a series of oxides and zeolites. From the temperature dependences of the spectra,  $\epsilon$  has been estimated for CO molecules whose stretching frequency is lowered due to their bonding to cationic sites of the zeolite through the oxygen atom. In accordance with the predictions of the electrostatic model,  $\epsilon$  decreases as the vibrational frequency of CO increases.

DOI: 10.1134/S002315840803021X

## INTRODUCTION

Knowledge of the integrated extinction coefficient of molecules and of its dependence on the vibrational frequency enables one to easily derive the concentration of surface sites from the spectra of adsorbed probe molecules. The surface of catalysts is being increasingly widely probed by low-temperature CO adsorption, which enables one to estimate the concentration of both Lewis and Brønsted sites. The frequency of the stretching vibration of the CO molecule is sufficiently sensitive to the strength of the sites, but the data concerning the integrated extinction coefficient and its relation to the vibrational frequency of the molecule are very controversial.

The integrated extinction coefficient and its dependence on the vibrational frequency have been studied in a number of works. For example, according to an early investigation [1], CO interaction with Lewis acid sites (ZnO, Cu/SiO<sub>2</sub>, CuO/SiO<sub>2</sub>) is accompanied by an increase in  $\epsilon$  relative to its value for the free molecule in the gas phase. The higher the vibrational frequency, the greater this increase. However, other authors [2, 3] report that  $\epsilon$  decreases by a factor of nearly 20 relative to its gas-phase value for CO molecules least strongly bound to the cationic sites of some zeolites and metal oxides (NaY, NiY, CaY, ZnO, MgO, BeO, etc.), but again,  $\epsilon$  grows as the frequency increases. The finding that  $\epsilon$  increases slightly with an increasing CO vibration frequency and increases many times with a decreasing vibrational frequency upon CO adsorption on supported metals or NiO is also reported in [4–6]. Morterra et al. [4] derived this conclusion from direct spectral measurements for molecules adsorbed on coordinately unsaturated sites of titania differing in strength

[4]. Escalona Platero et al. [5, 6] arrived at this conclusion from indirect data on vibrational polarizability of molecules, which is responsible for the frequency shift caused by lateral interaction.

Later, it was shown by us [7] that the low  $\epsilon$  values observed in earlier works for weakly adsorbed molecules are caused by the inhomogeneous distribution of molecules over the surface due to the heating of the central part of the sample by the IR beam. The suggested method of  $\epsilon$  measurements using small samples with minimum temperature gradients enabled us to determine the absorption coefficient of CO adsorbed on OH groups and coordinately unsaturated metal atoms of ZnO, BeO, and a aluminosilicate catalyst and to demonstrate that  $\epsilon$  changes upon adsorption not so seriously, but only by at most 30% of its value for the free CO molecule.<sup>3</sup> This allows the concentration of sites to be determined from the intensities of the absorption bands of adsorbed CO using the  $\epsilon$  value for the gas mol-

<sup>3</sup> The difficulties in comparing data from different works arise from use of different units of measure for  $\epsilon$ . In this work we use cm/μmol. In these units,  $\epsilon$ CO (gas) is 2.6. To convert it into absorbance per molecule for frequency in s<sup>-1</sup> instead of wave-numbers, this value should be multiplied by the factor  $c/N_A$ , where  $c$  is the velocity of light and  $N_A$  is the Avogadro number.

Absorbance will then be expressed in cm<sup>2</sup> molecule<sup>-1</sup> s<sup>-1</sup>. It should also be taken into account that, in physics, it is conventional to measure extinction as  $\ln(I_0/I)$ , while in the commercial instruments the measured value is displayed as the decimal logarithm  $\log(I_0/I)$ . Therefore, the conversion factor is  $2.30c/N_A$  or, numerically,  $3 \times 2.3/6 \times 10^{-7}$ . For gaseous CO, we have a value of  $3.0 \times 10^{-7}$  cm<sup>2</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is the same as is reported [7]. The value 0.18 cm/μmol [3] is obtained when one records the unresolved rotational structure of the gas with an instrument of medium resolving power. In the strict sense, this value is not a characteristic of the molecule, because it is determined by the pressure-dependant collision-induced broadening of rotational bands. Under these conditions, each line is certainly narrower than the spectral slit width (resolution) of the instrument and one cannot use the Lambert–Beer law.

<sup>1</sup> The text was translated by the authors.

<sup>2</sup> The article is based on materials of the VII Russian Conf. of Mechanisms of Catalytic Reactions (St. Petersburg, July, 2–8, 2006).

ecule. However, even in that earlier study, it was evident that the deviations observed in some cases exceed the experimental error of  $\epsilon$  determination. The subsequent development of the measurement technique has supported these results.

The spectra of CO adsorbed on zeolites contain bands at frequencies higher than are characteristic of the free molecule (HF bands) and weak bands shifted to lower wavenumbers (LF bands). The origin of the latter is explained by the existence of two types of surface CO complexes, one bound to the cation via the carbon atom and the other via the oxygen atom (see [8–10] and references therein). To describe the observed isomerism of CO linkage to the cations, the electrostatic model was used, which, in addition to explaining the existence of two stable states, provides a reliable estimate of the difference between their energies and of the frequency shifts for both forms of adsorption [11]. When this model is used to describe the vibration-induced changes of the dipole moment of the vibrating molecule placed in the electric field of a cation and the sign of the polarizability derivative with respect to the normal coordinate is taken into account, the model predicts a decrease in the absorption coefficient of adsorbed CO for the C-bonded molecules and its increase for the O-bonded species relative to the  $\epsilon$  value of the free CO molecule, since bonding via oxygen implies the change of the sign of the external field with respect to the molecule.

It is rather tempting to determine  $\epsilon$  for the O-bonded molecules in order to check the predictions of the electrostatic model, but this quantity cannot be measured directly, because the two adsorption species are in equilibrium and cannot be observed separately. Nevertheless, from the analysis of the temperature dependence of the intensity ratio of HF and LF bands, one can calculate the ratio of the absorption coefficients of these bands ( $\epsilon_{\text{HF}}/\epsilon_{\text{LF}}$ ). Then, having measured  $\epsilon_{\text{HF}}$ , one can find  $\epsilon_{\text{LF}}$ .

The aim of this work was to measure the absorption coefficients of CO adsorbed on the cationic sites and hydroxyl groups of solid oxides and zeolites with an increase in the stretching frequency (HF bands), to estimate  $\epsilon_{\text{LF}}$  from the  $\epsilon_{\text{HF}}/\epsilon_{\text{LF}}$  ratio determined from the temperature dependence of the spectra, and, finally, to compare the results with the predictions of the electrostatic model.

## EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

A cell earlier designed in the laboratory [9] for studying the spectra of surface species in a broad temperature range (55–375 K) was used in our experiments. The cell was equipped with two Edwards pressure gauges. One, with an accuracy of  $10^{-3}$  Torr and an upper measurement limit of 10 Torr, communicated

directly with the inner volume of the cell, and the other was used to measure the pressure of the gas to be admitted.

Commercial samples of  $\text{SiO}_2$  (aerosol, specific surface area of  $300 \text{ m}^2/\text{g}$ ) and  $\text{TiO}_2$  (Degussa P-25) and zeolites  $\text{NH}_4\text{Y}$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.6$ ) and  $\text{NaY}$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.7$ ) were used.  $\text{CaY}$ ,  $\text{SrY}$ , and  $\text{ZnY}$  were obtained from  $\text{NaY}$  by the standard method of cation exchange with the nitrates of the corresponding metals. An MCM sample (specific surface area of  $1100 \text{ m}^2/\text{g}$ ) was synthesized in the laboratory of Kinetics and Catalysis, Faculty of Chemistry, Moscow State University.

The zeolite samples to be studied were usually heated for 3 h to 523 K and pumped for 1–3 h. Oxides were pumped at 523 K ( $\text{TiO}_2$ , MCM-1) or 873 K ( $\text{SiO}_2$ , aerosil) for 1 h. After this pretreatment, the samples were cooled to 77 K and about 0.5 Torr of He was admitted into the central space of the cell before the spectrum of the cold sample was recorded. Next, a portion of CO was admitted and the spectrum of the sample with adsorbed gas was recorded.

The amount of adsorbed CO was determined in two ways. The first was by accurately measuring the quantity of the gas admitted into the cell and completely adsorbed by the sample. To do this, the volume to be filled with the gas at certain pressure was measured as precisely as possible. The CO pressure was usually 2–5 Torr, and the dose volume was  $11.8 \text{ cm}^3$ . If a small amount of CO remained in the gas phase, it could be taken into account, knowing the volumes of the cell and the gas supply pipe. When adsorption under the experimental conditions was reversible and a great part of the adsorbate remained in the gas phase, the other method was more precise.

To determine the amount of adsorbed CO by the second method, the pressure jump was measured upon sample transfer from the cooled part of the cell to the tube kept at ambient temperature, or at 373 K if the spectroscopically estimated quantity of gas adsorbed at 300 K was not negligible. The adsorbed CO entirely turned into gas. From the pressure jump, knowing the gas volume and temperature, the quantity of the gas could be deduced. In our case, the temperature in different parts of the cell was not the same, varying between 77 K in the cooled part to 373 K in the section of the quartz tube containing the sample. To take this into account, we used the concept of “effective volume,” which is the volume that the cell must have at 300 K to contain the same amount of a gas as the cell cooled with liquid nitrogen in the experiment. The value of this effective volume for the case of the lower part of the cell being cooled and the quartz tube being kept at 300 or 373 K was derived from the pressure change upon gas (helium or nitrogen) admission into the cell from a known calibration volume.

Usually, both methods were used. In the second method, after gas admission into the cell, the pressure jump was measured several times as the surface coverage was decreased stepwise by partial removal of gas from the cell. To avoid gas readsorption on the traces of old pellets on the bottom of the cooled part of the cell, the inner space of the latter was carefully cleaned with a vacuum cleaner before each experiment.

Spectra were registered on a Fourier-transform IR spectrometer (Nicolet 510) in the frequency range 6000–600  $\text{cm}^{-1}$  with 4- $\text{cm}^{-1}$  resolution. When choosing samples and the amount of gas to be adsorbed, we intended to obtain a single band from adsorbed CO. Its integrated intensity  $A$  was determined using the standard program OMNIC after subtracting the background spectrum of the sample before CO adsorption.

The absorption coefficient  $\varepsilon$  (usually in  $\text{cm/mol}$ ) was calculated using the formula

$$\varepsilon = \frac{ASTP_0V_m}{\Delta PV T_0}, \quad (1)$$

where  $P_0$  is the standard atmospheric pressure (760 Torr),  $T_0$  is the normal temperature (273 K),  $V_m$  is the molar volume of the gas under normal conditions ( $22.4 \times 10^3 \text{ cm}^3/\text{mol}$ ),  $T$  is the ambient temperature at which the gas dose and the effective volume were measured ( $\sim 300 \text{ K}$ ),  $V$  is the effective volume of the cooled cell ( $109 \text{ cm}^3$ );  $A$  is the integrated intensity of the band, and  $\Delta P$  is the pressure jump upon desorption. The adsorbent pellet surface area  $S$ , normally about 0.3–0.5  $\text{cm}^2$ , was determined before the experiment. To do this, an image of the sample was obtained using a scanner with a known resolution. After contrast enhancement, the image was saved in the linear mode in the bmp format. Next, using a specially written program, the number of white points of the image against the black background was counted and the area was calculated.

In the spectra of some samples ( $\text{TiO}_2$ ,  $\text{SiO}_2$ , and some others), it was impossible to observe distinct bands from individual forms of adsorbed CO. In this case, the amount of adsorbed molecules was measured for two different surface coverages at which the concentration ratios of the two forms, hereafter denoted  $a$  and  $b$ , were different. Assuming that each adsorbed form has its own absorption coefficient ( $\varepsilon_a$  or  $\varepsilon_b$ ) independent of the surface coverage and of the presence of other adsorbed molecules, we solved a set of two equations in which, for each spectrum recorded at a certain coverage, the amount of desorbed gas consisted of the contributions from both forms of adsorption:

$$\begin{aligned} \Delta P_1 V/T &= A_{a1} S/\varepsilon_a + A_{b1} S/\varepsilon_b, \\ \Delta P_2 V/T &= A_{a2} S/\varepsilon_a + A_{b2} S/\varepsilon_b. \end{aligned} \quad (2)$$

Here the pressure jumps  $\Delta P$  caused by desorption and the integrated intensities  $A_a$  and  $A_b$  in two spectra

obtained at different coverages are given the indices 1 and 2.

To determine  $\varepsilon$  for the O-bonded molecules, the van't Hoff plot was traced. In our case, it was  $A_{\text{HF}}/A_{\text{LF}}$  versus  $1/T$ :

$$\ln(A_{\text{HF}}/A_{\text{LF}}) = -\Delta H^\circ/RT + \Delta S^\circ/R + \ln(\varepsilon_{\text{HF}}/\varepsilon_{\text{LF}}). \quad (3)$$

By extrapolation to  $1/T = 0$ , the ordinate intercept of the experimental line was found, whose position gave the sum  $\Delta S^\circ/R + \ln(\varepsilon_{\text{HF}}/\varepsilon_{\text{LF}})$ . In addition to depending on the ratio of absorption coefficients ( $\varepsilon_{\text{HF}}/\varepsilon_{\text{LF}}$ ), the coordinate of this point depends on the entropy change upon reorientation,  $\Delta S^\circ$ . Earlier [12], we showed that, for the surface complexes of CO with cations and OH groups, this value is proportional to the change of enthalpy upon reorientation,  $\Delta H^\circ$ , which can be found from the slope of the van't Hoff plot. This makes it possible to estimate  $\Delta S^\circ$  and, using the  $\varepsilon_{\text{HF}}$  value measured, determine  $\varepsilon_{\text{LF}}$ .

According to [13], for CO on NaZSM-5 and NaY,  $\Delta H^\circ = 3.8$  and 2.4 kJ/mol, which correspond to  $\Delta S^\circ/R = -2.29$  and  $-1.44$ , respectively. The van't Hoff plots intersect the ordinate axis at  $-0.26$  for CO/NaZSM-5 and at  $-0.75$  for CO/NaY. Hence,  $\ln(\varepsilon_{\text{LF}}/\varepsilon_{\text{HF}}) = 2.03$  and 0.79, and  $\varepsilon_{\text{LF}}/\varepsilon_{\text{HF}} = 7.6$  and 2.2, respectively. In accordance with the electrostatic model, the absorption coefficient in both cases is greater for the low frequency bands, but, to find its absolute value, we have to know  $\varepsilon_{\text{HF}}$ .

Another method to estimate the  $\varepsilon_{\text{LF}}$  from the known  $\varepsilon_{\text{HF}}$  value is based on the Boltzmann formula. Assuming that the concentration ratio of the C- and O-bonded complexes is equal to  $\exp(\Delta H^\circ/RT)$ , we have  $\ln(A_{\text{HF}}/A_{\text{LF}}) + \ln(\varepsilon_{\text{HF}}/\varepsilon_{\text{LF}}) = \Delta H^\circ/RT$ .

Thus, having found  $\Delta H^\circ$  from the slope of the van't Hoff plot and having measured the intensity ratio of the two bands for a certain temperature  $T$ , one can readily determine the  $\varepsilon_{\text{LF}}/\varepsilon_{\text{HF}}$  ratio. The data of an earlier paper [13] allow the  $\varepsilon_{\text{LF}}/\varepsilon_{\text{HF}}$  ratio to be readily calculated for zeolite NaY and lead to the same value of 2.2 as the first method.

The accuracy of  $\varepsilon$  measurements for single bands in our work was determined by the uncertainty of integrated intensity measurement ( $\leq 3\%$ ), the error of the pressure gauge ( $\leq 2\%$ ), and the error of the cell volume measurements ( $\leq 2\%$ ). According to our estimates, it did not exceed 10%.

In the case of simultaneous measurement of  $\varepsilon$  for two forms of adsorption, the error can be substantially greater and it depends on the relative intensity of the bands. For the data presented below, it does not exceed 25%.

The uncertainty of  $\varepsilon_{\text{LF}}$  determination includes, besides the error of  $\varepsilon$  measurement for the high-frequency band, the inaccuracy of finding the intersection point and the deviations in the correlation between  $\Delta S^\circ$  and  $\Delta H^\circ$  and can obviously reach 50%. As a criterion of

Integrated absorption coefficient for the CO molecule in the free and adsorbed states

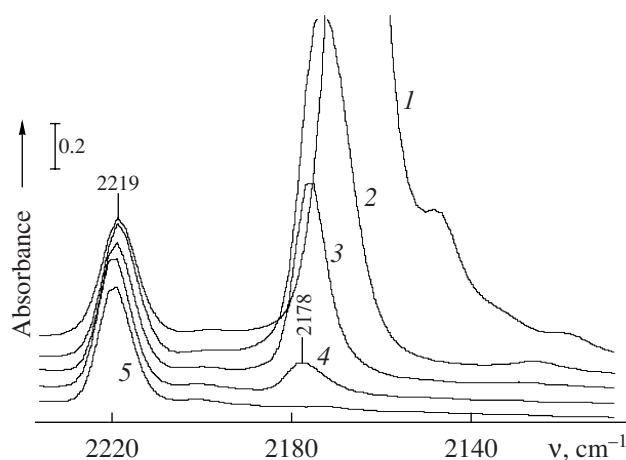
Adsorbent	$\epsilon_{\text{HF}}, \text{cm}/\mu\text{mol}$	$\nu_{\text{HF}}, \text{cm}^{-1}$	$\epsilon_{\text{LF}}^*, \text{cm}/\mu\text{mol}$	$\nu_{\text{LF}}, \text{cm}^{-1}$
CO (gas) [14]	2.6	2143	—	—
SiO <sub>2</sub>	1.6	2157	—	—
TiO <sub>2</sub>	2.0	2178	—	—
	0.8	2190	—	—
	0.2	2210	—	—
HZSM	2.1	2175	—	—
NaY	2.0	2170	4.5 (4.4)	2122
HY	2.1	2173	49 (56)	2124
SrY	1.5	2191	220 (192)	2095
CaY	0.9	2197	240 (267)	2094
ZnY	1.2	2178	—	—
	1.0	2219	—	—

\* The numbers in parentheses are  $\epsilon$  values calculated using the Boltzmann formula.

the correctness of  $\epsilon_{\text{LF}}$  determination, one can consider the similarity of the  $\epsilon_{\text{LF}}/\epsilon_{\text{HF}}$  ratio values found by the two methods.

## RESULTS AND DISCUSSION

The integrated absorption coefficients measured for the systems examined are summarized in the table,



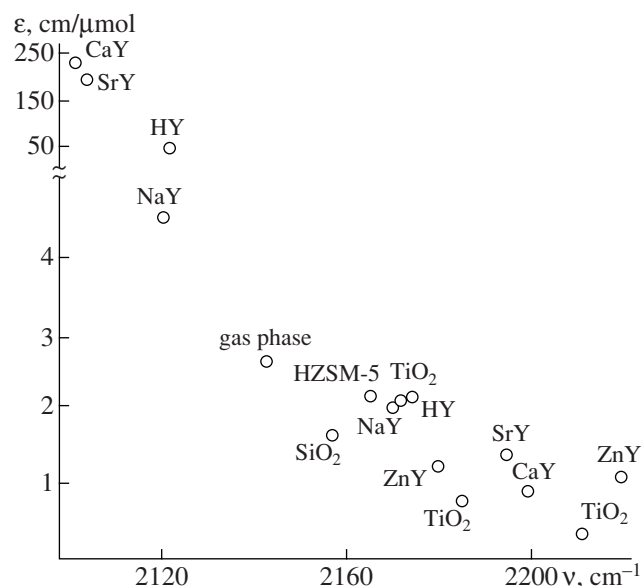
**Fig. 1.** IR spectrum of CO adsorbed at 77 K on zeolite ZnY. Amounts of CO adsorbed: (1) 31.6, (2) 17.6, (3) 8.8, (4) 4.2, and (5) 3.4  $\mu\text{mol/g}$ .

where, for comparison, the  $\epsilon$  value for CO in the gas phase [14] is also given.

By way of example, Fig. 1 shows the spectrum of CO adsorbed on a ZnY sample at different surface coverages. The band at 2219  $\text{cm}^{-1}$  is due to the strongest sites. It persists in the spectrum after the desorption of the molecules from the weaker sites. The latter account for the second band, whose maximum shifts from 2168 to 2178  $\text{cm}^{-1}$  in the course of desorption. The position of this band does not differ much from the position of the band of CO adsorbed on zeolite NaY, and we attribute it to the adsorption on unexchanged  $\text{Na}^+$  cations. At room temperature, the 2219  $\text{cm}^{-1}$  band does not disappear completely. For this reason, to measure the amount of adsorbed CO, the sample was moved to the tube kept at 373 K. As was expected, the  $\epsilon$  value for the high-frequency band is extremely small. The absorption coefficient for the second band, which is close to the band of CO/NaY, is somewhat larger.

The  $\epsilon = 1.6 \text{ cm}/\mu\text{mol}$  value, reported for CO molecules adsorbed on silanol groups of the silica surface (2157  $\text{cm}^{-1}$  band), is the same within the experimental error for the two samples examined. In the case of aerosil, this band is observed simultaneously with the band at 2138  $\text{cm}^{-1}$  due to CO molecules weakly bound to siloxane bridges. The  $\epsilon$  value for the latter was obtained by solving the set of equations (2). For the MCM-1 sample at low coverages, the second band has a negligibly low intensity and the accuracy of absorption coefficient measurements for the 2157  $\text{cm}^{-1}$  band is higher.

For the systems with CO linkage isomerism, the table lists  $\epsilon_{\text{LF}}$  estimates calculated using the above two methods. The similarity of the results shows that the values of  $\epsilon_{\text{LF}}$  for SrY and CaY, which might seem unnaturally high, are quite realistic. Indeed, if the



**Fig. 2.** Integrated absorption coefficient of CO adsorbed on oxide adsorbents versus the stretching frequency.



energy difference between the two states is about 10 kJ/mol, the concentration of O-bonded species estimated from the Boltzmann formula turns out to be so low that the LF bands would hardly be observed if their intensities were not enhanced by more than two orders of magnitude.

Figure 2 plots  $\epsilon$  as a function of the CO vibration frequency. The scattering of the points is due to experimental errors, and, maybe, some other factors in the observed band intensities, such as the polarizability of the environment of the adsorbed molecules. This factor certainly has different effects on the band intensity for metal oxides and zeolites, which are very different in terms of their surface properties and structure. Nevertheless, it is clear from the plot that, as the frequency increases, the absorption coefficient decreases appreciably. For the oxygen-bonded molecules with a lower frequency of stretching vibration, it increases with the downward shift of the frequency.

Exactly the same behavior of  $\epsilon$  as a function of the applied electrostatic field is predicted by the electrostatic model [11]. Indeed, the absorption intensity in the IR spectrum of a molecule placed in an electrostatic field is proportional to the squared derivative of the dipole momentum ( $\mu$ ) with respect to the normal coordinate. One can distinguish two components of this derivative, of which one refers to the free molecule and the other accounts for the absorption induced by the field:

$$\partial\mu/\partial q = \partial\mu_0/\partial q \pm E\partial\alpha/\partial q. \quad (4)$$

The choice of the sign before the second term is determined by the orientation of the molecule in the field of the cation. For the O-bonded molecules, the two terms on the right-hand side of the equation have the same sign and the enhancement of adsorption should be anticipated. In the case of  $M^+(CO)$  complexes, absorption should decrease with the strengthening of the field to reach zero when the two terms become equal. Further increase in the field intensity should lead to a new increase of  $\epsilon$ , but such a strong field is rarely achievable for adsorbed CO. It is interesting that quantum mechanical calculations of frequency changes for the CO molecule in a homogeneous electric field predict the dependence of  $\nu(CO)$  on the field strength in the form of a curve with a maximum, which occurs at approximately the same value of field strength when the intensity vanishes [11].

This result is experimental confirmation of the general regularity according to which, for localized vibrations, the band intensity increases as their frequency decreases. Another manifestation of this regularity is observed for the hydrogen bond. Along with the well-known increase in the X–H stretching intensity upon a bathochromic shift, a decrease in  $\epsilon$  for the X–H vibration takes place for the blue-shifting H-bond as the frequency shifts to higher values. This gives way to an increase of  $\epsilon$  once the increase in the bond strength has

resulted in a decrease in the vibration frequency. Recently, this effect has been illustrated by the results of fluoroform adsorption on the basic sites of oxide adsorbents [15]. It is interesting that the observed correlation between  $\epsilon$  and the vibration frequency is also observed for systems that can hardly be described in terms of a simple electrostatic model. For example, a multifold increase of  $\epsilon$  for CO with a lowered stretching frequency, which was observed by us for O-bonded molecules, also takes place upon CO adsorption on metals or transition metal oxides (e.g., NiO), in which the CO molecules are bonded via their carbon atoms and the frequency lowering is conventionally explained by the back donation of  $d$  electrons onto the anti-bonding  $\pi$ -orbitals of the CO molecule.

## CONCLUSIONS

A method for measuring the integrated absorption coefficient of adsorbed molecules has been developed, and the absorption coefficient has been measured for the high frequency bands of CO adsorbed on zeolites HY, NaY, CaY, SrY, ZnY, and HZSM-5 and on the oxides  $SiO_2$  and  $TiO_2$ .

Using the earlier obtained thermodynamic characteristics, the ratios of absorption coefficients for the high- and low-frequency bands ( $\epsilon_{HF}/\epsilon_{LF}$ ) have been calculated for the same systems. The absorption coefficient  $\epsilon_{LF}$  of CO molecules bound to the cation via the oxygen atom has been determined. For all the systems examined, the high frequency shift of the stretching band is accompanied by a decrease of  $\epsilon$ , while the frequency lowering for the O-bonded molecules is accompanied by an increase of the absorption coefficient. The dependence of the integrated absorption coefficient on the vibration frequency is in excellent agreement with the predictions of the electrostatic model.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant nos. 06-03-32836a and 06-05-64646). The authors are grateful to E.V. Makshina (Faculty of Chemistry, Moscow State University) for supplying a sample of MCM-1.

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