

# Problems of Quantitative Spectroscopic Measurements in Heterogeneous Catalysis: Molar Absorption Coefficients of Vibrations in Adsorbed Substances

V. A. Matyshak and O. V. Krylov

*Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*

Received January 17, 2001

**Abstract**—Published data on the molar absorption coefficients  $\epsilon$  and integral intensities  $A_0$  of vibrations in physically and chemically adsorbed molecules are reviewed. Analysis of published data shows that bonds characterized by high values of the dipole momentum derivative with respect to the normal coordinate change during adsorption toward decreasing this derivative, whereas bonds characterized by a low value of the derivative change toward increasing the derivative. Thus, adsorption results in a decrease in the difference in values of the dipole momentum derivative with respect to the normal coordinate of different bonds compared with the same bonds in the individual molecules. In addition, the interval of changing the molar absorption coefficients for the surface complexes are at least two orders of magnitude lower than that for the same bonds in the molecules in the gas phase. A series for the degree of easiness in detecting complexes on the catalyst surface (the series of decreasing the molar absorption coefficient) is proposed.

## INTRODUCTION

The most popular method for the mechanistic study of a heterogeneous catalytic reaction is *in situ* infrared spectroscopy, which provides information on surface compounds under conditions of a catalytic reaction. To answer the question of whether a surface compound is an intermediate in the reaction, one has to apply IR spectroscopy in the spectral kinetic variant, that is, to compare the rates of formation and consumption of surface compounds with the catalytic reaction rate (the equality of the rate of consumption of a surface compound to the rate of product formation suggests that this complex is an intermediate). Therefore, one has to determine the concentration of surface compounds. The concentration of surface compounds can be quantitatively determined from IR spectroscopic data if the molar absorption coefficients of the bands of the adsorbed compounds are known. They can be determined using the Lambert–Bouger–Beer law, which establishes a linear relationship between the absorption intensity  $I$  and the concentration of the absorbing substance  $C$  and the layer thickness  $l$ .

The molar absorption coefficients of absorption bands in the IR spectrum make it possible to measure the concentration of the absorbing substance using the absorption intensity at a band maximum [1, 2]. According to the Lambert–Bouger–Beer law,

$$\epsilon = (1/Cl) \log(I_0/I)_{\max}; \quad (1)$$

the molar absorption coefficient  $\epsilon$  can be calculated in  $1 \text{ mol}^{-1} \text{ cm}^{-1}$  if the  $C$  concentration is expressed in  $\text{mol/l}$ , and  $\epsilon$  can be calculated in  $\text{cm}^2/\text{molecule}$  if the concentration of the absorbing substance  $C$  is

expressed in  $\text{molecule}/\text{cm}^3$ . Here  $I_0$  and  $I$  are the intensities of incident and transmitted light at an absorption band maximum, and  $l$  is the optical path length in the sample.

The above refers to traditional transmission spectroscopy. Recently, diffuse reflectance IR spectroscopy became widely used in catalytic studies (see, for example, [3–6]). In diffuse reflectance spectra, the band intensity is measured in Kubelka–Munk units [6],

$$f(R, R_0) = F(R_0) - F(R) = 2\epsilon c/s, \quad (2)$$

where  $F(R_0) = (1 - R_0)^2/2R_0$ ;  $F(R) = (1 - R)^2/2R$ ;  $R$  and  $R_0$  are the reflection coefficients (albedo) of the sample at a certain frequency before and after adsorption, respectively;  $\epsilon$  is the molar absorption coefficient;  $C$  is the concentration of an adsorbed molecule; and  $s$  is the scattering ability of a unit volume. At low albedo, Eq. (2) can be transformed into the form

$$f(R, R_0) = (R_0 - R)/R_0 R$$

or, taking into account that  $(R_0 - R)/R_0 R = J$  ( $J$  is the band intensity in diffuse reflectance spectra), into the form  $f(R, R_0) = J/R$ . At low  $J$ , Eq. (2) transforms into the Lambert–Beer law

$$-\epsilon c L_{\text{eff}} = \ln R/R_0, \quad (3)$$

where  $L_{\text{eff}}$  is the effective length of the optical path.

In some recent works, infrared emission spectroscopy is used for studying adsorbed molecules [7–10]. Note that this is the only spectral method in which heating the sample is an allowable and necessary condition. There are no methods for quantitative measurements

using emission spectroscopy. However, theoretical analysis shows that the Kubelka–Munk equation (2) can be used for strongly reflecting objects, and the Lambert–Beer law (3) is appropriate for weakly reflecting objects.

The brief analysis of different IR procedures shows that the molar absorption coefficient is the key value that allows one to perform measurements at a quantitative level.

Molar absorption coefficients of molecular vibrations vary over wide ranges [1]. As a first approximation, we may assume that the more polar the bond, the higher the intensity of absorption spectra. For the  $\text{CH}_3$  groups in alkanes,  $\epsilon$  is equal to  $30\text{--}70\text{ l mol}^{-1}\text{ cm}^{-1}$  for stretching vibrations  $\nu_s$  and  $\nu_{as}$  ( $2870\text{--}2960\text{ cm}^{-1}$ ) and  $\sim 15\text{ l mol}^{-1}\text{ cm}^{-1}$  for deformational vibrations  $\delta_s$  and  $\delta_{as}$  ( $1380\text{--}1460\text{ cm}^{-1}$ ). Approximately the same molar absorption coefficient is typical of  $\nu_s$  and  $\nu_{as}$  for the  $-\text{CH}_2-$  groups ( $2850$  and  $2925\text{ cm}^{-1}$ ) but it is much lower ( $3\text{--}8\text{ l mol}^{-1}\text{ cm}^{-1}$ ) for deformational vibrations ( $1470\text{ cm}^{-1}$ ). The molar absorption coefficient for the ring vibration in aromatic compounds ( $\nu = 1600\text{ cm}^{-1}$ ) vary depending on the substituents in the aromatic ring; however,  $\epsilon$  is usually lower than  $100\text{ l mol}^{-1}\text{ s}^{-1}$  ( $3030\text{ cm}^{-1}$ ). For the acetylene groups ( $-\text{C}\equiv\text{C}-$ ),  $\epsilon = 5\text{ l mol}^{-1}\text{ cm}^{-1}$  (terminal group) and  $1\text{ l mol}^{-1}\text{ cm}^{-1}$  (inside a chain). The molar absorption coefficient of the stretching vibrations of OH groups in alcohols ( $3620\text{--}3640\text{ cm}^{-1}$ ) is  $70$  for the primary,  $50\text{--}60$  for the secondary, and  $45\text{ l mol}^{-1}\text{ cm}^{-1}$  for the tertiary groups, respectively. It is  $50\text{--}100\text{ l mol}^{-1}\text{ cm}^{-1}$  for hydrogen bonds. For ethers,  $\epsilon$  for a band of  $\text{C}=\text{O}$  at  $1070\text{--}1150\text{ cm}^{-1}$  is higher than  $200\text{ l mol}^{-1}\text{ cm}^{-1}$ , and it is lower ( $\sim 50$ ) for an absorption band at  $2815\text{--}2830\text{ cm}^{-1}$ . The following values of  $\epsilon$  are observed for the absorption bands:  $30\text{ l mol}^{-1}\text{ cm}^{-1}$  for the  $\text{C}=\text{NH}_2$  group in amines ( $3500\text{ cm}^{-1}$ ),  $10\text{--}150\text{ l mol}^{-1}\text{ cm}^{-1}$  for the band at  $2210\text{--}2260\text{ cm}^{-1}$  of the  $\text{C}\equiv\text{N}$  group in nitriles,  $1300\text{--}2000\text{ l mol}^{-1}\text{ cm}^{-1}$  for the band at ( $2250\text{--}2275\text{ cm}^{-1}$ ) of the  $-\text{N}=\text{C}=\text{O}$  group in isocyanates, and  $150\text{--}300\text{ l mol}^{-1}\text{ cm}^{-1}$  for a band at  $3490\text{ cm}^{-1}$  of the  $\text{C}=\text{NH}$  group in pyrrole and indole. In nitro compounds ( $\text{C}=\text{NO}_2$ ), the intensities of bands at  $1350$  and  $1560\text{ cm}^{-1}$  are very high. The molar absorption coefficient varies within wide limits for  $\text{C}=\text{N}$  vibrations in unsaturated amines ( $\text{C}=\text{N}-\text{H}$ ): for  $\nu$  of  $\text{C}=\text{N}$  ( $1690\text{--}1640\text{ cm}^{-1}$ ),  $\epsilon = 5\text{--}880\text{ l mol}^{-1}\text{ cm}^{-1}$ . The value of  $\epsilon$  for the  $\text{N}-\text{H}$  vibrations in primary amines ( $3500\text{--}3400\text{ cm}^{-1}$ ) is  $30\text{ l mol}^{-1}\text{ cm}^{-1}$ . For the vibrations of CO in ketones ( $1715\text{ cm}^{-1}$ ),  $\epsilon$  is  $300\text{--}600\text{ l mol}^{-1}\text{ cm}^{-1}$ .

Thus, the intensities of various bands differ, and if their ratio remains valid for adsorbed molecules, the possibility of detecting various intermediates also differs substantially. As can be seen from the above numbers, the possibility of detecting the isocyanate group is two to three orders of magnitude higher than that for fused aromatic compounds. This should be kept in mind when choosing a reaction mechanism based on the spectra of adsorbed compounds.

The molar absorption coefficient depends on the  $\nu$  frequency. Therefore, the integral intensity  $A_0$  is used for accurate calculations in some cases instead of the intensity at the maximum of an absorption band:

$$A_0 = 1/CI \int \log(I_0/I) d\nu. \quad (4)$$

In this case, integration covers the whole absorption band. When the concentration is expressed in  $\text{mol/l}$ , the dimensionality of  $A_0$  is  $\text{l mol}^{-1}\text{ cm}^{-1}$ . If the concentration is expressed in the number of molecules per unit volume, the dimensionality of  $A_0$  is  $\text{cm}/\text{molecule}$ . It can easily be shown that the ratio of the  $A_0$  units presented above is equal to  $6.02 \times 10^{20}$ , Avogadro's number divided by 1000.

For convenience of calculation of the molar absorption coefficient of vibrations in an adsorbed complex, the formula of the modified Lambert–Bouger law is sometimes used [11, 12]

$$\epsilon = \frac{DS_{\text{samp}}}{N}, \quad (5)$$

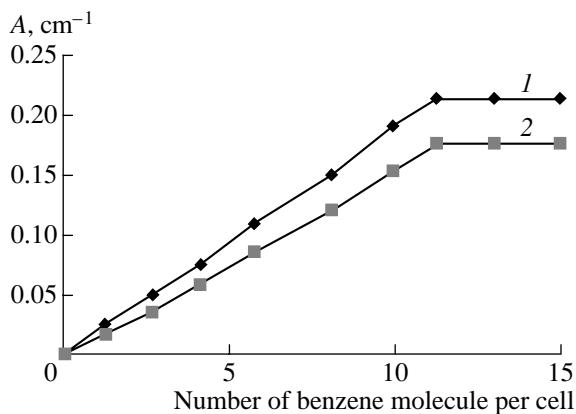
where  $D = \log I_0/I$ ;  $S_{\text{samp}}$  is the cross section of the light flux transmitted through the sample,  $\text{cm}^2$ ; and  $N$  is the number of adsorbed molecules.

#### MEASUREMENT OF MOLAR ABSORPTION COEFFICIENTS FOR ADSORBED MOLECULES

To determine the molar absorption coefficient for adsorbed molecules, one has to measure the adsorption of a given substance and the absorption intensity at different coverages. In the case of a linear plot of the band intensity vs. coverage and when the position of the absorption maximum remains unchanged, this plot can be used for the calculation of  $\epsilon$ .

Possible sources of errors in the determination of molar absorption coefficients are beyond the scope of this paper. Note, however, that the main error in the determination of this value is introduced by the inaccurate determination of the amount of substance adsorbed in a given form. Difficulties can be associated with both the presence of bands belonging to different surface complexes in the spectrum and the adsorption of molecules not only on the sample but also on the cell walls. If measurements are performed at reduced or elevated temperatures, the error in the measurement of the amount of an adsorbed substance can be related to the nonuniform distribution of the substance over the sample due to a temperature gradient. The characteristics of the spectrometer, in particular, spectral resolution, are important for the determination of the molar absorption coefficient. In other words, the use of published data for the molar absorption coefficient can give systematic errors.

The adsorption of a substance can be measured by the weight, volume, or thermal desorption methods, which are standard. The adsorbed compound can also



**Fig. 1.** Plots of the integral absorption ( $A$ ) of the bands at (1)  $1830\text{--}1840\text{ cm}^{-1}$  ( $v_5 + v_{17}$ ) and (2)  $1970\text{--}1980\text{ cm}^{-1}$  ( $v_{10} + v_{17}$ ) for vibrations in the benzene molecule vs. amount of benzene adsorbed on zeolite NaEMT at 80 K.

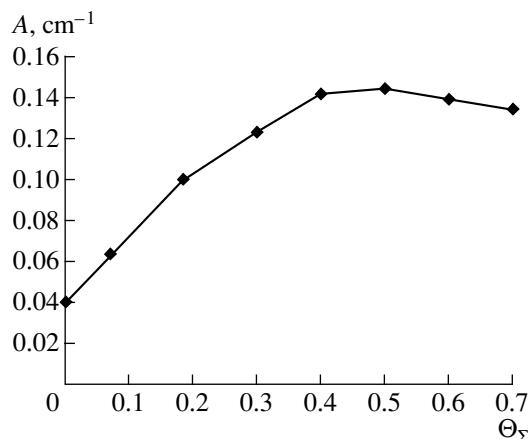
be decomposed to measure the amount of the decomposition products in the gas phase.

Examples of the linearity of a plot of absorption intensity vs. adsorption value can be found in the literature. For example, the absorption intensity of bands of out-of-plane C–H vibrations  $v_5 + v_{17}$  of benzene adsorbed at 80 K on zeolites HEMT and NaEMT (an analog of faujasite) increases linearly with an increase in the coverage up to a limiting value of 11 molecules of  $C_6H_6$  per unit cell in HEMT or to 5–17 molecules per unit cell in NaEMT (Fig. 1) [13]. The intensity remains unchanged after this limit is achieved, which indicates the formation of a pseudoliquid phase. The intensity of the absorption band of vibrations of CO adsorbed in the bridging form on Ni(100) at  $-193^{\circ}\text{C}$  increases with an increase in the total coverage ( $\Theta_\Sigma$ ) by CO molecules, passes through a maximum at  $\Theta = 0.5$ , and then decreases (Fig. 2) [14]. Evidently, only the initial region of this curve can be used to determine  $\epsilon$ . At higher coverages, CO is condensed above the monolayer.

It is well-known that the interaction between adsorbed molecules and the surface nonuniformity result in deviations from the Lambert–Bouguer–Beer law [2].

#### MOLAR ABSORPTION COEFFICIENTS FOR PHYSICAL ADSORPTION

The molar absorption coefficients for physisorbed molecules are presented in [2]. For the adsorption of  $C_2$  hydrocarbons on porous glass, including that containing transition metal oxides, the values of  $\epsilon$  are somewhat lower than those for the corresponding gases:  $3.5\text{--}20.0\text{ mol}^{-1}\text{ cm}^{-1}$  (or  $0.58\text{--}3.30 \times 10^{-20}\text{ cm}^2/\text{molecule}$ ) for C–H vibrations ( $2860\text{--}3020\text{ cm}^{-1}$ ) in ethylene, which is chemisorbed (polymerized) or physisorbed and  $50\text{ mol}^{-1}\text{ cm}^{-1}$  ( $8.3 \times 10^{-20}\text{ cm}^2/\text{molecule}$ ) for a band



**Fig. 2.** Plot of the integral absorption ( $A$ ) of the band of CO adsorbed in the bridging form on Ni(100) at 80 K vs. total coverage.

at  $3250\text{ cm}^{-1}$  of acetylene. For the adsorption of butenes, the analogous value ranges from  $12$  to  $64\text{ mol}^{-1}\text{ cm}^{-1}$  ( $(2.0\text{--}10.7) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ), which is lower than the corresponding value of  $\epsilon$  of bands for butenes dissolved in  $CCl_4$  ( $21\text{--}100\text{ mol}^{-1}\text{ cm}^{-1}$ ) or  $(3.5\text{--}1.70) \times 10^{-20}\text{ cm}^2/\text{molecule}$ . In halogen-substituted hydrocarbons,  $\epsilon$  of bands of C–H vibrations at  $2850\text{--}3180\text{ cm}^{-1}$  ranged from  $1$  to  $86\text{ mol}^{-1}\text{ cm}^{-1}$  (or  $(0.17\text{--}14.0) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ). In ketones, the molar absorption coefficient of the C–H bond stretching vibration ( $CH_3$  and  $CH_2$  groups) is  $21\text{--}54\text{ mol}^{-1}\text{ cm}^{-1}$  (or  $(3.5\text{--}9.0) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ) in a solution of  $CCl_4$ , and it decreases to  $17\text{--}37\text{ mol}^{-1}\text{ cm}^{-1}$  (or  $(2.8\text{--}6.2) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ) for adsorption on Ca-montmorillonite. On the contrary, for the C=O stretching vibration,  $\epsilon$  increases from  $525\text{--}765\text{ l mol}^{-1}\text{ cm}^{-1}$  (or  $(0.87\text{--}1.27) \times 10^{-18}\text{ cm}^2/\text{molecule}$ ) in a solution of  $CCl_4$  to  $1020\text{--}1400\text{ l mol}^{-1}\text{ cm}^{-1}$  for adsorption on montmorillonite. For the adsorption of 1,3,5-trichlorobenzene on AgI, the  $\epsilon$  values were higher for all vibrations ( $14\text{--}114\text{ l mol}^{-1}\text{ cm}^{-1}$  or  $(2.2\text{--}19.0) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ) than those for this compound in the liquid state ( $2\text{--}33\text{ l mol}^{-1}\text{ cm}^{-1}$  or  $(0.3\text{--}5.5) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ). For the adsorption of  $CH_3Cl$  on porous glass, the molar absorption coefficient changes from  $24$  to  $30\text{ l mol}^{-1}\text{ cm}^{-1}$  (or  $(4.0\text{--}5.0) \times 10^{-20}\text{ cm}^2/\text{molecule}$ ) with a fourfold increase in the surface coverage.

According to these data, a trend can be seen: for physisorption, the molar absorption coefficient of polar bonds (C–O, C–Cl, and others) increases and  $\epsilon$  of non-polar bonds (C–H, C–C, and others) decreases. Evidently, this can be explained by some polarization of molecules during physisorption.

Spectral research into the adsorption of various molecules at the temperature of liquid nitrogen has recently been developed. Under these conditions, adsorption is

most probably physical; therefore, we adduce the relevant data from the literature in this section.

The following data were obtained in [15] for CO molecules adsorbed at 77 K on different oxides:

Adsorbent	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	$A_0 \times 10^{17}$ , $\text{cm}/\text{molecule}$
—	2143*	1.00*
BeO	2150	1.02
BeO	2185	1.19
ZnO	2168–2192	1.19
Aluminosilicate	2230	0.63

\* Data for CO in the gas phase.

It is seen that, for physically adsorbed CO molecules, the integral absorption coefficient ( $A_0$ ) differs slightly from the value for the CO molecule in the gas phase. Similar data for  $\text{N}_2$  molecules adsorbed on oxides at 77 K are presented in [16–19].

Adsorbent	$\nu_{\text{N}_2}$ , $\text{cm}^{-1}$	$A_0 \times 10^{18}$ , $\text{cm}/\text{molecule}$
$\text{SiO}_2$ [16]	2329	0.023
ZnO [16]	2337	0.86
BeO [16]	2350	0.50
	2337	0.26
TiO <sub>2</sub> [16]	2348	4.00
	2340	0.33
Aluminosilicate [16]	2357	0.90
H-mordenite [16]	2356	2.20
	2347	0.72
	2335	0.76
$\eta\text{-Al}_2\text{O}_3$ [17, 18]	2360	6.6*
Zeolites [19]	2345	0.18

\* Theoretical calculation.

More intense absorption bands in the spectra of adsorbed nitrogen are observed for adsorbents containing electron-acceptor centers on their surface. The estimate of the integral absorption coefficient for oxygen adsorbed in the singlet state is presented in [20]. This value is at least  $0.33 \times 10^{-17}$   $\text{cm}/\text{molecule}$ .

### MOLAR ABSORPTION COEFFICIENTS OF VIBRATIONS IN COMPLEXES OF NITROGEN-CONTAINING MOLECULES

#### *Adsorption of Ammonia and Pyridine*

The adsorption of ammonia and pyridine molecules is often used to estimate the number of acid sites on the surface of oxide catalysts. The  $\text{NH}_4^+$  and  $\text{C}_5\text{H}_5\text{NH}^+$  ions are formed on protic acid sites during the adsorption of  $\text{NH}_3$  and  $\text{C}_5\text{H}_5\text{N}$ , respectively; and on the Lewis acid sites,  $\text{L: NH}_3$  and  $\text{L: NC}_5\text{H}_5$  are formed, where  $\text{L}$  is the

coordinatively unsaturated metal atom on the surface (for example,  $\text{Al}^{3+}$ ).

According to [21], ammonia is adsorbed on  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  in two strongly bound forms: coordinatively bound ammonia on the Lewis acid sites ( $\delta\text{NH}_3 = 1250 \text{ cm}^{-1}$ ) and in the form of the  $\text{NH}_4^+$  ammonium ions on the Brønsted acid sites (B) ( $1425 \text{ cm}^{-1}$ ). The addition of water after ammonia adsorption transformed the coordinatively bound ammonia  $\text{L: NH}_3$  into the ammonium ion  $\text{NH}_4^+$ . This procedure allows one to quantitatively separate the Lewis and Brønsted acid sites and determine the molar absorption coefficients. The calculated  $\epsilon$  values ( $\text{cm}^2/\text{mol}$ ) were  $\epsilon_{1430} = 5.3 \times 10^5$  (or  $0.88 \times 10^{-18} \text{ cm}^2/\text{molecule}$ ) (ammonium ion),  $\epsilon_{1250} = 5.3 \times 10^5$  (or  $0.88 \times 10^{-18} \text{ cm}^2/\text{molecule}$ ), and  $\epsilon_{1610} = 5.9 \times 10^5$  (or  $0.98 \times 10^{-18} \text{ cm}^2/\text{molecule}$ ) (coordinated ammonia).

The adsorption of pyridine on pentasil TsVM ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 42$ ) containing Cr, Pt, or Zn ions was studied in [22]. For the Brønsted sites ( $1545 \text{ cm}^{-1}$ ),  $\epsilon_B = 0.05 \text{ cm}^2/\mu\text{mol}$  or  $0.8 \times 10^{-18} \text{ cm}^2/\text{molecule}$ , and  $\epsilon_L = 0.066 \text{ cm}^2/\mu\text{mol}$  or  $1.1 \times 10^{-18} \text{ cm}^2/\text{molecule}$  for the Lewis sites ( $1450 \text{ cm}^{-1}$ ).

The integral intensities for pyridine on the proton sites of zeolite Y-150 were  $3.4 \text{ cm}/\mu\text{mol}$ , and  $A_0 = 3.03 \text{ cm}/\mu\text{mol}$  for the Lewis sites ( $1540 \text{ cm}^{-1}$ ) [23]. For ammonia adsorption (the formation of  $\text{NH}_4\text{Y}$ ),  $A_0 = 12.98 \text{ cm}^2/\mu\text{mol}$ .

The amount of the Brønsted and Lewis acid sites in zeolites was determined from the integral intensity of the IR bands of adsorbed pyridine [24]:  $1540 \text{ cm}^{-1}$  for PyB and  $1450 \text{ cm}^{-1}$  for PyL. The integral intensities were obtained from the measurements of pyridine adsorption on zeolites HZSM-5 and HY and on  $\gamma\text{-Al}_2\text{O}_3$ :  $1.3 \times 10^6 \text{ cm}/\text{mol}$  for the PyB band and  $1.5 \times 10^6 \text{ cm}/\text{mol}$  for the PyL band.

Tables 1 and 2 summarize the published data for the adsorption of molecules on the Brønsted and Lewis acid sites of the catalyst surface.

#### *Isocyanate Complex, Nitrates, and Adsorbed $\text{N}_2\text{O}$ Molecules*

A study of the reaction mechanisms by *in situ* spectroscopic methods makes it possible to determine intermediate complexes [4]. In some cases, the corresponding molar absorption coefficients were determined. In particular, the isocyanate complex characterized by the frequency of pseudoantisymmetrical vibrations at  $2230\text{--}2260 \text{ cm}^{-1}$  was detected in the reaction  $\text{CO} + \text{NO}$  on supported platinum group metals [38–41]. The reaction of the isocyanate complex with the NO molecule in the gas phase produces  $\text{N}_2$  and  $\text{CO}_2$ . When the reaction is carried out under stationary conditions, the absorbance of the isocyanate complex was determined from the emission spectra. Then, CO was excluded from the

**Table 1.** The integral intensities ( $A_0$ ) and molar absorption coefficients ( $\epsilon$ ) of the absorption bands of protonated base molecules on Brønsted sites of catalyst surfaces

Base	Catalyst	$\nu, \text{cm}^{-1}$	$A_0, \text{cm}/\mu\text{mol}$	$\epsilon \times 10^{18}, \text{cm}^2/\text{molecule}$	Literature
Ammonia	Amorphous aluminosilicate	1450	10	—	[25]
	HZSM-5	1450	10	—	[25]
	Sulfates of Al, Ga, Zr, Mg	1450	10	—	[26]
	HNaY (430 K)	1450	3.9	—	[25]
	HNaY (530 K)	1450	1.0	—	[25]
	$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	1430	16.1	0.88	[21, 27]
	$\text{MoO}_3$ (583 K)	1430	—	3.7	[28]
	Zeolite Y-150	1450	12.98	—	[23]
Pyridine	HNaY	1545	2.5	—	[29]
	"	1545	3.0	—	[30]
	"	1545	0.96–0.13	—	[31]
	HZSM-5	1545	1.7	—	[32]
	Cr-, Pt-, Zn-TsVM ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 42$ )	1545	—	0.83	[22]
	HNaY (423 K)	1540	3.0	—	[33]
	" (573 K)	1540	3.0	—	[33]
	P-Mo-HPA	1530–1550	2.5–3.0	—	[34]
	Zeolite Y-150	1540	3.4	—	[23]
	HZSM-5, HY and $\gamma$ - $\text{Al}_2\text{O}_3$	1545	1.3	—	[24]
Piperidine	HNaY	1610	1.5–2.0	—	[35]
	"	1620	12.98	—	[30]
	"	1450	8.72	—	[30]
2,6-Dimethylpyridine	HNaY	1650	7.8	—	[36]
Quinoline	HNaY	1645	3.5	—	[25]
	Salt of HCl	1645	3.0–3.5	—	[25]
<i>n</i> -Butylamine	HNaY	1530	7.2	—	"
<i>sec</i> -Butylamine	"	1530	9.5	—	"
<i>tert</i> -Butylamine	"	1530	8.2	—	"

flow of the reaction mixture ( $\text{CO} + \text{NO}$ ), and the amount of  $\text{CO}_2$  was measured at the outlet of the cell/reactor. Comparison of the absorbance of the band of the isocyanate at different surface coverages and the

amount of evolved  $\text{CO}_2$  gives  $\epsilon = 0.14 \times 10^{-18} \text{ cm}^2/\text{molecule}$  [35].

A similar study was performed for the low-temperature oxidation of  $\text{NH}_3$  on oxides [42] in order to deter-

**Table 2.** The integral intensities ( $A_0$ ) and molar absorption coefficients ( $\epsilon$ ) for some bands in spectra of bases adsorbed on Lewis sites of catalysts

Base	L site	Catalyst	$\nu, \text{cm}^{-1}$	$A_0, \text{cm}/\mu\text{mol}$	$\epsilon \times 10^{18}, \text{cm}^2/\text{molecule}$	Literature
Ammonia	$\text{V}^{5+}$	$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	1610	1.46	0.98	[21, 27]
	"	"	1250	2.91	0.88	"
Pyridine	$\text{Al}^{3+}$	$\text{Al}_2\text{O}_3$	1450	3.26	—	[30]
	"	Al/Si	1450	3.88	—	"
	$\text{Li}^+$	LiX	1445	2.4	—	[29]
	$\text{Na}^+$	NaX	1445	4.8	—	[37]
	$\text{Na}^+$	NaY	1445	4.1	—	"
	—	Cr-, Pt-, Zn-TsVM ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 42$ )	1450	—	1.1	[22]
	—	Zeolite Y-150	1450	3.03	—	[23]
Piperidine	—	HZSM-5, HY, and $\gamma\text{-Al}_2\text{O}_3$	1450	1.5	—	[24]
	$\text{Al}^{3+}$	$\text{Al}_2\text{O}_3$	1450	8.11	—	[30]
	"	"	1620	2.78	—	"
2,6-Dimethylpyridine	$\text{Na}^+$	NaY	1603	3.0	—	[36]
Deuterioacetonitrile	$\text{Na}^+$	NaY	2276	1.2	—	"
	$\text{Ca}^{2+}$	CaY	2291	1.45	—	"
	$\text{Co}^{2+}$	CoY	2309	2.0	—	"
	$\text{Ni}^{2+}$	NiY	2312	0.9	—	[33]
	$\text{Mn}^{2+}$	MnY	2294	1.7	—	"
	$\text{Cr}^{2+}$	CrY	2311	2.0	—	"
	$\text{Al}^{3+}$	AlY	2328	2.0	—	"
Quinoline	$\text{Al}^{3+}$	HZSM-5	1510	2.5	—	[25]

**Table 3.** Spectral characteristics of surface nitrogen-containing complexes

Catalyst	Complex	$\nu, \text{cm}^{-1}$	$A_0, \text{cm}/\text{molecule}$	$\epsilon, \text{cm}^2/\text{molecule}$	Literature
Pt(Rh, Pd)/ $\text{Al}_2\text{O}_3$	$-\text{NCO}$	2230–2260	—	$0.14 \times 10^{-18}$	[41]
ZnO	$\text{N}_2\text{O}_{\text{ads}}$	2200	—	$5 \times 10^{-18}$	[42]
CuZSM-5	$\text{Cu}^{2+}-\text{O}-\text{N}=\text{O}$	1630	—	$3.4 \times 10^{-18}$	[43]
$\text{Al}_2\text{O}_3$	Nitrate	1162–1350	$1.3 \times 10^{-17}$	—	[44]

mine the molar absorption coefficient for the band at  $2200 \text{ cm}^{-1}$  for adsorbed  $\text{N}_2\text{O}$  molecule. Comparison of the absorbance of this band at different surface coverages ( $\text{N}_2\text{O}$ ) and the amount of  $\text{N}_2\text{O}$  in the gas phase [42] gives  $\epsilon = 5 \times 10^{-18} \text{ cm}^2/\text{molecule}$ .

An absorption band at  $1630 \text{ cm}^{-1}$  belonging to anti-symmetrical vibrations in the  $\text{Cu}^{2+}-\text{O}-\text{N}=\text{O}$  nitrite complex is observed in the infrared spectra measured for the reduction of NO by hydrocarbons on zeolite CuZSM-5. Matyshak *et al.* [43] compared the number

**Table 4.** Molar absorption coefficients ( $\epsilon$ ) and integral intensities ( $A_0$ ) of absorption bands of CO adsorbed on supported metal catalysts

Catalyst	$\nu, \text{cm}^{-1}$	Form of CO adsorption	$\epsilon \times 10^{18}, \text{cm}^2/\text{molecule}$	$A_0, \text{cm}/\mu\text{mol}$	Literature
8.4% Pt/Aerosil	2070	Linear	2.0	—	[45]
0.6% Pt/Al <sub>2</sub> O <sub>3</sub>	2072	Linear	2.4	—	[52]
1.5% Pt/SiO <sub>2</sub> · Al <sub>2</sub> O <sub>3</sub>	2075	Linear	2.1	—	[47]
	1800	Bridging	0.3	—	"
2.1% Pt/η-Al <sub>2</sub> O <sub>3</sub>	2070	Linear	2.10	—	"
	1830	Bridging	0.16	—	"
1.5% Pt/SiO <sub>2</sub>	2070	Linear	1.0	—	"
1.9% Pt/TiO <sub>2</sub>	2060	Linear	3.5	30	"
	1880	Bridging	0.8	24	"
2.2% Rh/Al <sub>2</sub> O <sub>3</sub>	2024	Linear	—	26	[48]
	2056	Dicarbonyl	—	74	"
	1987	Dicarbonyl	—	128	"
	1832	Bridging	—	85	"
5% Pt/SiO <sub>2</sub> , $\Theta = 0.1$ ,	2078	Linear	1.5	—	[50]
$\Theta = 0.4$	"	"	2.0	—	"
3.3% Pt-Ru/SiO <sub>2</sub>	2070–2086*	Linear	0.79	—	[46]
Pt/SiO <sub>2</sub>	2070	Linear	2.5	—	"
Ru/SiO <sub>2</sub>	2086	Linear	0.44	—	"
Cu/SiO <sub>2</sub>	2136	Linear	—	38	"
Cu <sup>0</sup> (metal)	2100	Linear	—	3.7	[53]
Pt/SiO <sub>2</sub> , Pt <sup>0</sup>	2100	Linear	—	26	[54]
	2092	Linear	—	29	"
	2085	Linear	—	36.8	"
CO (gas)	2143	—	—	5.4	[48]

\* Overlapped bands.

of NO<sub>x</sub> molecules isolated under the decomposition of this complex with the intensity of the absorption band. As a result, the molar absorption coefficient was estimated as  $3.4 \times 10^{-18} \text{ cm}^2/\text{molecule}$ .

Nitrate complexes are formed, as a rule, when nitrogen oxides interact with the catalyst surface. The number of NO<sub>x</sub> molecules formed by nitrate decomposition was compared with the intensity of the absorption band of nitrates [44]. This comparison gave an integral absorption intensity of  $1.3 \times 10^{-17} \text{ cm}/\text{molecule}$  (Table 3).

## MOLAR ABSORPTION COEFFICIENTS OF VIBRATIONS IN ADSORBED CO AND CO<sub>2</sub> MOLECULES

### *Adsorption of CO on Metals*

Most of the data on molar absorption coefficients of chemisorbed molecules concerns the adsorption of carbon oxide. This molecule is often used as an IR probe for the characterization of active surface sites.

In several papers [45–50], the molar absorption coefficients (molar integral intensities) for CO adsorbed on platinum group metals supported on

**Table 5.** Integral intensities ( $A_0$ ) of IR bands of CO forms adsorbed on oxide catalysts

Adsorbent	Adsorption site	$\nu, \text{cm}^{-1}$	$A_0, \text{cm}/\mu\text{mol}$	Literature
NaY	$\text{Na}^+$	2163	0.3	[51]
CaY	$\text{Ca}^{2+}$	2197	0.5	[55]
MgO	$\text{Mg}^{2+}$	2158	0.4	[51, 55]
BeO	$\text{Be}^{2+}$	2193	1.2	[51]
	"	2203	1.0	"
$\text{Al}_2\text{O}_3$	$\text{Al}^{3+}$	2203	1.0	"
	"	2190	0.6	"
H-erionite	"	2228	1.2	"
$\text{Ga}_2\text{O}_3$	$\text{Ga}^{3+}$	2167	0.5	"
$\text{ZrO}_2$	$\text{Zr}^{4+}$	2183	2.2	"
	"	2203	0.9	"
$\text{TiO}_2$	$\text{Ti}^{4+}$	2208	1.1	[56]
	"	2190	1.3–1.7	"
NiY	$\text{Ni}^{2+}$	2191	0.6	[57]
	"	2197	0.6	"
	"	2213	1.2	"
$\text{NiO–MgO–MoO}_3$	–	2190	1.8–2.2	[56]
CoY	$\text{Co}^{2+}$	2196	0.5	[57]
	"	2206	0.8	"
$\text{CoO–MgO–MoO}_3$	–	2190	1.5–2.0	[56]
MnY	$\text{Mn}^{2+}$	2183	0.3	[57]
	"	2206	0.8	"
ZnO	$\text{Zn}^{2+}$	2212	3.9	[54]
	"	2200	2.4	"
	"	2187	0.78	"
	"	2190	0.5–0.7	[56]
$\text{CuO/SiO}_2$	$\text{Cu}^+$	2140	3.1	[54]
	"	2136	16.5	"
	"	2135	15.6	"
	"	2132	22.6	"
$\text{CuO/Al}_2\text{O}_3$	–	2140	3.1	"
$\text{CuCr}_2\text{O}_4$	–	2120	8.6	[58]
	–	2122	8.7	"
$\text{AgO/Al}_2\text{O}_3$	$\text{Ag}^+$	2170	11.5–15.5	[56]
H-CuZSM-5	$\text{Cu}^+$	2158		[59]

**Table 6.** Some characteristics of carbonyl complexes on the surface of oxide catalysts [60]

Adsorbent	Adsorption site	$\nu(\text{CO})$ in MCO complex, $\text{cm}^{-1}$	$Q_{\text{ads}}$ , kJ/mol	$\epsilon \times 10^{19}$ , $\text{cm}^2/\text{molecule}$	Number of adsorption sites in 1 g
ZnO	$\text{Zn}^{2+}$	2190	44	2.6	$5.2 \times 10^{18}$
$\text{Cr}_2\text{O}_3$ (oxidized)	$\text{Cr}^{3+}$	2200	—	1.5	$1.8 \times 10^{19}$
$\text{TiO}_2$	$\text{Ti}^{4+}$	2190	44	1.4	$1.6 \times 10^{10}$
$\text{NiO}-\text{MgO}-\text{MoO}_3$	$\text{Ni}^{2+}$	2190	44	2.6	$5.1 \times 10^{18}$
$\text{CoO}-\text{MgO}-\text{MoO}_3$	$\text{Co}^{2+}$	2190	44	1.7	$6.6 \times 10^{18}$
$\text{Ag}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{Ag}^+$	2170	59	—	$2.8 \times 10^{19}$
$\text{Cr}_2\text{O}_3$ (reduced)	$\text{Cr}^{2+}$	2170	—	5.6	$6.7 \times 10^{19}$
$\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{Cu}^+$	2130	71	6.7	$9.3 \times 10^{19}$
CuY	$\text{Cu}^+$	2160	60	8.2	$6.5 \times 10^{19}$

$\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and other materials were reported. One narrow band at  $2070 \text{ cm}^{-1}$  (for which  $\epsilon = 2 \times 10^{-18} \text{ cm}^2/\text{molecule}$  was obtained) was observed for the adsorption of CO on Aerosil-supported platinum. For CO adsorption on  $\text{Pt}/\text{SiO}_2$  and  $\text{Ru}/\text{SiO}_2$ ,  $\epsilon$  values were obtained for absorption bands at  $2070$  and  $2086 \text{ cm}^{-1}$  [46]. These values were  $2.5 \times 10^{-18}$  and  $0.44 \times 10^{-18} \text{ cm}^2/\text{molecule}$ , respectively.

Adsorbed CO may exist in several possible forms as a result of CO adsorption. This substantially impedes the determination of molar absorption coefficients. Vannice and Twu [47] succeeded in determining them for the linear (high-frequency) and bridged (low-frequency) forms of CO adsorption on  $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ ,  $\text{Pt}/\text{SiO}_2$ , and  $\text{Pt}/\text{TiO}_2$ . The total amount of adsorbed CO was determined in experiments. The amount of CO adsorbed in each form was determined by approximate calculation from balance equations with complete coverage of the platinum atoms



The total amount of the surface platinum  $\text{Pt}_s$  was determined from hydrogen adsorption. The following values were obtained:

$$\epsilon_{\text{lin}} = (1.0-3.5) \times 10^{-18} \text{ cm}^2/\text{molecule},$$

$$\epsilon_{\text{br}} = (0.16-0.80) \times 10^{-18} \text{ cm}^2/\text{molecule}.$$

The integral intensities for the linear and bridged forms of adsorbed CO were also presented in [47]:

$$A_{0, \text{lin}} = (1.5-5.0) \times 10^{-17} \text{ cm}/\text{molecule},$$

$$A_{0, \text{br}} = (0.33-4.00) \times 10^{-17} \text{ cm}/\text{molecule}.$$

The amount of CO adsorbed in different forms on 2.2%  $\text{Rh}/\text{Al}_2\text{O}_3$  was determined by the NMR method [48]. Integral intensities of 74, 128, 26, and  $85 \text{ cm}/\mu\text{mol}$  for symmetrical and antisymmetrical vibrations of the dicarbonyl, in linear and bridged forms, respectively, were obtained.

Cant and Donaldson [49] indicated that the molar absorption coefficients of the absorption band at  $2078 \text{ cm}^{-1}$  corresponding to CO adsorbed on 5%  $\text{Pt}/\text{SiO}_2$  increase with an increase in the coverage. They obtained the following values:  $\epsilon(\text{CO}) = 1.5 \times 10^{-18} \text{ cm}^2/\text{molecule}$  at  $\Theta = 0.1$  and  $\epsilon = 2.0 \times 10^{-18} \text{ cm}^2/\text{molecule}$  at  $\Theta = 0.4$ .

The fulfillment of the Lambert–Bouger–Beer law was checked for CO adsorbed on several oxides and metals [51]. It was shown that when the intensity of only one band changed with a change in the total CO coverage, the Lambert–Bouger–Beer law was satisfactorily fulfilled. The interval of changing the integral intensity was

$$A_0 = (0.18-0.25) \times 10^{-17} \text{ cm}/\text{molecule}. \quad (6)$$

Table 4 presents the experimental values of the molar absorption coefficient of CO adsorbed on different catalysts [50]. It follows from these data that the molar absorption coefficients of absorption bands corresponding to the bridged and linear forms of CO adsorbed on the supported platinum catalysts changes within one order of magnitude. On the same catalyst, the molar absorption coefficients of the linear form of

**Table 7.** Spectral characteristics of surface carboxylates and carbonates

Catalyst	Complex	$\nu, \text{cm}^{-1}$	$A_0, \text{cm/molecule}$	$\epsilon \times 10^{19}, \text{cm}^2/\text{molecule}$	Literature
$\gamma\text{-Al}_2\text{O}_3$	Formate	1590	—	6.0	[64]
$\text{Pt}/\gamma\text{-Al}_2\text{O}_3$	Formate	1590	—	6.0	[65]
NaX	Acetate	1585	—	7.0	[50]
		1430	—	3.3	"
NaX	Formate	1620	—	2.7	"
		1380	—	0.8	"
$\text{Cr}_2\text{O}_3$	Formate	1550	—	3.8	[60, 71]
$\text{CaO}, \text{La}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{MgO}, \gamma\text{-Al}_2\text{O}_3, \text{V}_2\text{O}_5$	Monodentate carbonate	1400 and 1530	—	4.2	[66]
$\text{TiO}_2$	Carbonate	1360	—	4.7	[60]
ZnO	Carbonate	1335	—	5.0	"
$\text{Al}_2\text{O}_3$	Acetate	—	$1.7 \times 10^{-17}$	—	[44]

**Table 8.** Molar absorption coefficients for  $\nu(\text{C}=\text{C})$  and integral intensities of IR bands for surface complexes of propylene [11, 25]

System	Adsorption site	$\nu(\text{C}=\text{C}), \text{cm}^{-1}$	$A_0, \text{cm}/\mu\text{mol}$	$\epsilon \times 10^{18}, \text{cm}^2/\text{molecule}$
ZnO	$\text{Zn}^{2+}$	1625	0.12	0.15
$\text{TiO}_2$	$\text{Ti}^{4+}$	1635	0.08	0.10
$\text{CoO}-\text{MgO}-\text{MoO}_3$	$\text{Co}^{2+}$	1635	0.16	0.20
$\text{Ag}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{Ag}^+$	1595	0.16	0.25
$\text{Cu}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{Cu}^+$	1550	0.28	0.35
$\text{NiO}-\text{MgO}-\text{MoO}_3$	$\text{Ni}^{2+}$	1630	0.24	0.30

adsorbed CO exceeded those for the bridged form in all cases. Note that some forms of CO adsorption are IR-inactive. This may lead to errors in the determination of  $\epsilon$ . Despite some deviations from the Lambert–Bouger–Beer law, linear regions within which quantitative measurements are possible are observed in almost all cases on the plots of the absorbance (integral intensity) vs. number of adsorbed molecules. However, the fulfillment of the Lambert–Bouger–Beer law should be checked in each case of kinetic experiments.

#### CO Adsorption on Oxides

Data on the molar absorption coefficients in the carbonyl complexes formed by CO adsorption on different oxide systems are discussed broadly (Table 5). The molar absorption coefficient for the vibration of  $\text{C}=\text{O}$  in the  $\text{Cu}^+-\text{C}=\text{O}$  complex was determined in [59]. This

value was used to characterize the oxidation state of copper in the reactions with NO, propane, and oxygen. Data on the molar absorption coefficients of CO complexes on the oxide catalyst surface and the heats of adsorption were reported in [60] (Table 6).

As can be seen from Tables 4–6, the values of  $\epsilon$  for oxides are lower than for metals. These values are approximately constant for cations in the highest oxidation states and increase substantially with a decrease in the oxidation state of the cation. According to Davydov [11, 60], this indicates the determining influence of  $\pi$ -bonding and the changing of the polarity of the C–O bond. The values of the molar absorption coefficients presented were used to estimate the amount of complexes on the surface of other oxides. Davydov [11, 60] emphasizes that the knowledge of the molar absorption coefficients for the  $\text{M}^{n+}\text{CO}$  or  $\text{M}^{n+}\text{NO}$  complexes, along

with data on the coordination and valence states of cations obtained from the spectroscopic characteristics of these complexes, makes CO and NO molecules almost universal probes for the number and electronic state of surface sites.

### Carbonates and Carboxylates

Carbonate ( $\text{CO}_3^{2-}$ ) and carboxylate ( $\text{RCOO}^-$ ) groups are often detected when the catalytic oxidation of organic compounds on the surface are studied by IR spectroscopy.

Tamaru and co-workers [61–63] were the first to apply IR spectroscopy to the study of heterogeneous catalytic reactions. They obtained linear plots of the integral absorbance of the band at  $1570 \text{ cm}^{-1}$ , which characterized the  $\text{HCOO}^-$  formate ions, vs. the amount of formic acid adsorbed on  $\text{ZnO}$ . The number of formate ions was determined from the known amount of acid introduced into the reaction. Similar data were obtained for the  $\text{DCOO}^-$  ions.

A plot of the absorbance of the band at  $1590 \text{ cm}^{-1}$  vs. the amount of the surface formate ions on  $\gamma\text{-Al}_2\text{O}_3$  formed by the reaction of  $\text{CO}_2$  and  $\text{H}_2$  at  $300^\circ\text{C}$  was obtained in [64]. The amount of surface complexes was determined by analyzing the amount of carbon oxide formed upon formate decomposition in the thermal desorption regime. It was shown that the Lambert–Bouger–Beer law was satisfactorily fulfilled for surface coverages up to  $2 \times 10^{13}$  molecule/ $\text{cm}^2$  and absorbances up to 0.6. The calculated molar absorption coefficient was  $\varepsilon = 0.6 \times 10^{-18} \text{ cm}^2/\text{molecule}$ . This value of  $\varepsilon$  was taken for calculating the rate of benzene oxidation on  $\text{Pt}/\text{Al}_2\text{O}_3$  in spectroscopic kinetic measurements [65], and a good agreement with experimental data was obtained.

Davydov *et al.* [66] analyzed the spectra of the surface compounds formed upon the adsorption of  $\text{CO}_2$  on the basic sites of  $\text{CaO}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\gamma\text{-Al}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ . The results of this work made it possible to classify basic sites according to type and strength and estimate the absolute number of these or other basic sites for which the molar absorption coefficients were known. Thus, for the sites involved in the formation of monodentate carbonates ( $1400$  and  $1530 \text{ cm}^{-1}$ ),  $\varepsilon$  was  $4.2 \times 10^{-19} \text{ cm}^2/\text{molecule}$ .

The values of the molar absorption coefficients for the surface formate and methoxy complexes and adsorbed carbon oxide were used in [63, 64, 67–70] for the estimation of the rates of the individual stages of the catalytic reaction. Solymosi [69] used the molar absorption coefficient for the formate ion obtained in [64] to estimate the maximum amount of formate complexes on the  $\text{Ru}/\text{Al}_2\text{O}_3$  surface as  $1.6 \times 10^{14}$  ion/ $\text{cm}^2$ . The calculated activation energy for the formation of formate ions was  $17.6 \text{ kJ/mol}$ . This value is much lower than the activation energy of formate formation on pure alumina. The activation energy of the formation of for-

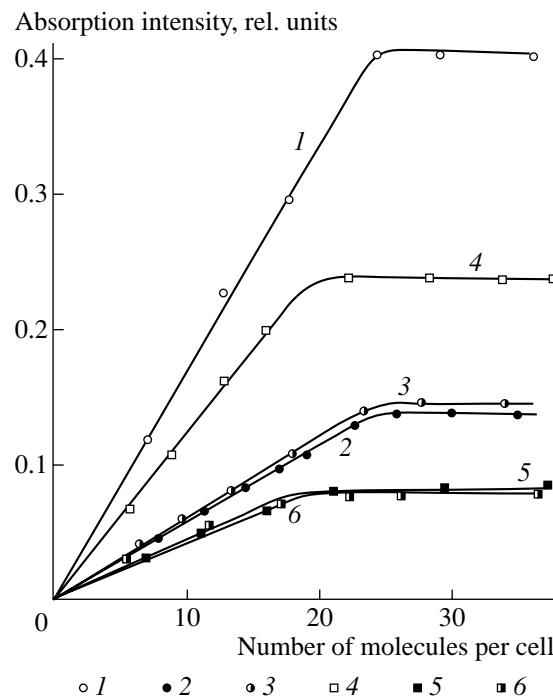


Fig. 3. Intensities of absorption bands of butenes ( $1630 \text{ cm}^{-1}$  for butene-1 and  $1385$ – $1389 \text{ cm}^{-1}$  for butene-2) as functions of the amount of butene introduced into the zeolite cell: (1) butene-1 on NaY; (2) butene-2 on NaY; (3) *trans*-butene-2 on NaY; (4) butene-1 on LY/77; (5) *cis*-butene-2 on LY/77; and (6) *trans*-butene-2 on LY/77 [74].

mate ions was estimated from the temperature plot of the initial rate of their formation.

The decomposition of formic acid on  $\text{Cr}_2\text{O}_3$  was studied in [71]. In this case, the absorption band of formates ( $1580$ – $1600 \text{ cm}^{-1}$ ) obeyed the Lambert–Bouger–Beer law in a rather broad concentration interval, although the plot of absorbance vs. concentration of adsorbed  $\text{HCOOH}$  did not pass through the origin of the coordinates. This is explained by the formation of some amount of carbonate ( $1430 \text{ cm}^{-1}$ ) during  $\text{HCOOH}$  adsorption. The molar absorption coefficient determined from the slope of the obtained straight line was  $3.8 \times 10^{-19} \text{ cm}^2/\text{molecule}$ . This value agrees with the data

Table 9. Molar absorption coefficients for antisymmetrical stretching vibrations of C–H in adsorption complexes of butenes on zeolites Y [67]

Hydrocarbon	$\nu, \text{cm}^{-1}$	$\varepsilon \times 10^{20}, \text{cm}^2/\text{molecule}$		
		NaY	LY/40	LY/77
Butene-1	2968	4.30	6.10	9.03
<i>trans</i> -Butene-2	2975	1.45	1.83	2.40
<i>cis</i> -Butene-2	2970	1.00	1.36	4.38

**Table 10.** Molar absorption coefficients and integral intensities of absorption bands for adsorption complexes of butenes and products of their transformations on different catalysts

Adsorbate	Catalyst	$\nu$ , $\text{cm}^{-1}$	$A_0$ , $\text{cm}/\mu\text{mol}$	$\epsilon \times 10^{19}$ , $\text{cm}^2/\text{molecule}$	Literature
Butene-1	HNaY (210 K)	1627	0.18	—	[72]
Isobutylene	$\text{Co}(\text{Mg})_6\text{Mo}_{12}\text{Bi}_{0.5} \cdot \text{Fe}_{0.75}\text{O}_x$	1610 (polyene)	—	1.7	[73]
Isobutylene	$\text{Co}(\text{Mg})_6\text{Mo}_{12}\text{Bi}_{0.5} \cdot \text{Fe}_{0.75}\text{O}_x$	1790 (anhydride group $\text{C}(\text{O})\text{O}(\text{O})\text{M}$ )	—	5.0	"

**Table 11.** Molar absorption coefficients for intermediates in acrolein oxidation on the V–Mo–O/SiO<sub>2</sub> catalyst [78]

Intermediate	$\nu$ , $\text{cm}^{-1}$	$\epsilon \times 10^{18}$ , $\text{cm}^2/\text{molecule}$	Conditions of adsorption
$\text{CH}_2=\text{CH}-\overset{\text{H}}{\underset{\text{O}}{\text{C}}}=\text{O}\cdots\text{Mo}^{n+}$	1660 (C=O)	0.28	Acrolein, 25°C
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{V}^{4+})$	1445 (COO <sup>−</sup> )	0.22	Acrylic acid, 80–100°C
$\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{O-Si}}{\text{C}}}=\text{O}$	1750 (C=O)	0.17	Acrylic acid, 280°C

of other authors, for example,  $\epsilon = 5 \times 10^{-19} \text{ cm}^2/\text{molecule}$  [64] (Table 7).

#### MOLAR ABSORPTION COEFFICIENTS OF VIBRATIONS IN COMPLEXES OF ADSORBED HYDROCARBON MOLECULES

The bands of C–H and C–C bond vibrations are less intense than those of the C–O and O–H bonds. Therefore, the molar absorption coefficients of adsorbed hydrocarbons in the nonoxidized state are documented less reliably.

#### Propylene

The adsorption of olefins often gives  $\pi$ - and  $\pi$ -allyl complexes. Table 8 presents the molar absorption coefficients for  $\nu(\text{C}=\text{C})$  in the adsorption of propylene  $\pi$ -complexes on the surface of several oxides [11, 25]. As can be seen, it is rather accurate to assume that the molar absorption coefficients in the adsorption  $\pi$ -complexes are approximately constant. This makes it possible to estimate the concentration of the surface  $\pi$ -com-

plexes of propylene and ethylene from the coefficients presented for other systems.

Davydov [60] asserted that the sensitivity of spectroscopic measurements to the  $\pi$ -allyl complexes of olefins by  $\nu_{\text{as}}(\text{CCC})$  is not worse than those for the  $\pi$ -complexes.

#### Butenes and Products of Their Transformations

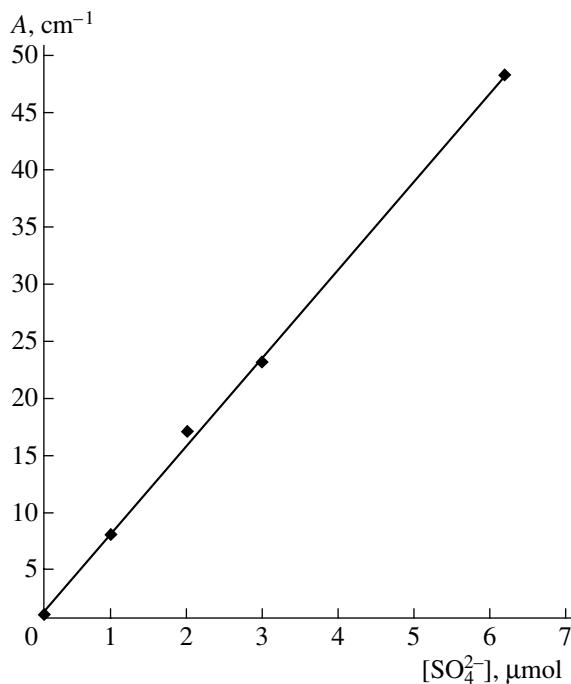
The spectral characteristics for the adsorption complexes of butenes are presented in [67, 72]. Datka [67] determined the molar absorption coefficients of bands at 2968, 2975, and 2970  $\text{cm}^{-1}$ , which are characteristic of the  $\text{CH}_3$  groups of butene isomers adsorbed on zeolites Y. The designations LY/40 and LY/77 imply that the  $\text{Na}^+$  ions were replaced by 40 and 77%, respectively, by the ammonium ions in zeolite NaY. Table 9 presents the values obtained for  $\epsilon$ . It is seen that  $\epsilon$  for adsorbed butene-1 is much higher than those for butenes-2, evidently, due to a higher polarity of the bond. Datka [67] also mentioned that the molar absorption coefficients increased for the reactions of butenes with Lewis acid sites. This indicates an increase in the polarization of the C–H bond during adsorption.

**Table 12.** Integral ( $A_0$ ) and molar ( $\epsilon$ ) absorption coefficients for bands of hydroxy groups in zeolites and silica gel [25]

Sample	$\nu(\text{OH}), \text{cm}^{-1}$	$A_0, \text{cm}/\mu\text{mol}$	$\epsilon \times 10^{18}, \text{cm}^2/\text{molecule}$	Adsorbate	Literature
HNaY	3650	12.23	0.33	Pyridine	[23]
	3550	19.9	—	Piperidine	“
	3663–3655	2.8–4.3	—	Pyridine	[31]
	3550	13.4–9.4	—	Ammonia	“
HNaX	3662	5.28	—	Pyridine	“
	“	10.6	—	Ammonia	[36]
	3550	9.5	—	Ammonia	“
HNaY*	3640	5 ± 1	—	Pyridine	[25]
	“	5 ± 1	—	Ammonia	“
HNaY**	3645	12 ± 1	—	Pyridine	[33]
	“	5 ± 1	—	Ammonia	“
HNaX	3660	5.3	—	—	[79]
HNaY	3645	7.1	—	—	“
HZ	3610	8.6	—	—	“
HZSM-5	3600	11.2	—	—	[80]
	3610	1.8–2.8	—	Pyridine	[81]
$\text{SiO}_2$	3740	3.04	—	—	[82]
	“	3.6–4.6	—	—	[83]
	“	0.42	—	—	[30]
	“	1.53	—	—	[84]
	3750	—	0.17	—	[74]
$\text{SiO}_2$	Framework	35	—	—	[85]
	Surface free	10	—	—	“
	Surface bound	44	—	—	“

\* Calcined at 823 K.

\*\* Calcined at 723 K.



**Fig. 4.** Integral absorption of the band of the sulfate complex ( $1390\text{ cm}^{-1}$ ) vs. amount of sulfate ions adsorbed on the  $\gamma\text{-Al}_2\text{O}_3$  surface.

Figure 3 shows a plot of the intensity of a band at  $1630\text{ cm}^{-1}$  (C=C bond) vs. the concentration of butenes introduced into zeolite. It is seen that for all three isomers the intensity of the absorption band at  $1630\text{ cm}^{-1}$  linearly depends on the amount of an adsorbed hydrocarbon up to the concentrations corresponding to 20 molecules per cavity. It is most likely that intermolecular interactions are not pronounced at this adsorption value.

Table 10 presents the molar absorption coefficients for the adsorption complexes formed upon the transformation of butenes on different catalysts. The molar absorption coefficients for the vibrations of the C=C and anhydride groups are much higher than that for C-H vibrations in the  $\text{CH}_3$  group.

#### Methoxy Group

It was found in [62] for a band at  $2880\text{ cm}^{-1}$  of the methoxy ion on  $\text{ZnO}$  that the Lambert-Bouger-Beer law was fulfilled only at low absorbances  $D < 0.25$ . McDonald [74] used the method of oxidation to  $\text{SiO}_2$  for the methoxy group on  $\text{CO}_2$  and estimated the molar absorption coefficients of the C-H bonds at  $2857$ ,  $2959$  ( $\epsilon = 5 \times 10^{-20}\text{ cm}^2/\text{molecule}$ ), and  $2995\text{ cm}^{-1}$  ( $\epsilon = 3 \times 10^{-20}\text{ cm}^2/\text{molecule}$ ). Note that these values are close to those for the C-H vibrations in the  $\text{CH}_3$  groups of butenes (Table 9).

The integral intensity  $A_0$  for  $\nu(\text{O}-\text{C})$  in the methoxy group on  $\text{ZrO}_2$  is  $1.15 \times 10^{-17}\text{ cm}/\text{molecule}$ , the same

for the bridged and linear complexes [75, 76]. However, according to [77],  $A_0$  for the linear methoxy group is 1.7 times higher than that for the bridging group.

#### Acrolein and Acrylic Acid

The values for different intermediates in acrolein oxidation on the  $\text{V}-\text{Mo}-\text{O}/\text{SiO}_2$  catalyst were obtained in [78]. They were determined for adsorption at  $\theta \sim 20\%$  monolayer coverage when one of the complexes presented in Table 11 dominated on the surface.

#### HYDROXYL COATING OF THE SURFACE

As mentioned in [25], to determine the amount of hydroxy groups capable of donating a proton, one can use either a change in the intensity of the corresponding absorption band or an increase in the intensity of the absorption band for the protonated base. For example, this method was used in [23] to determine  $\epsilon$  for bands at  $3550\text{ cm}^{-1}$  ( $19.9\text{ cm}/\mu\text{mol}$ ) and at  $3650\text{ cm}^{-1}$  ( $12.23\text{ cm}/\mu\text{mol}$  or  $0.33 \times 10^{-18}\text{ cm}^2/\text{molecule}$  at a band half-width of  $\sim 30\text{ cm}^{-1}$ ).

Table 12 presents the integral absorption coefficients  $A_0$  for bands of hydroxy groups in some oxide systems.

#### Other Molecules

Sulfates are formed by the interaction of  $\text{SO}_2$  molecules with the surface of many catalysts. Preudhomme *et al.* [86] attempted to determine the molar absorption coefficient of vibrations in the sulfate complex (an absorption band at  $1390\text{ cm}^{-1}$ ). Figure 4 shows a plot of absorbance of this band vs. surface coverage with the sulfate groups. It follows from this plot that the molar absorption coefficient of vibrations in the sulfate complex is equal to  $3.0 \times 10^{-19}\text{ cm}^2/\text{molecule}$ .

#### CONCLUSION

Analysis of data from Table 13 shows that the molar absorption coefficients for molecules in the adsorbed state change within one order of magnitude, whereas the same values for molecules in the gas phase change in the limits by up to three orders. Since the molar absorption coefficient is proportional to the squared derivative of the dipole momentum with respect to the normal coordinate, we suggest that the bonds characterized by a higher value of this derivative undergo changes during adsorption leading to a decrease in the derivative of the dipole momentum with respect to the normal coordinate, whereas the bonds characterized by a low value of this derivative undergo changes during adsorption resulting in an increase in the derivative. In other words, adsorption smoothes away the differences in the derivatives of the dipole momentum with respect to the normal coordinate of different bonds compared to the same bonds in individual molecules. Only the

**Table 13.** Comparison of molar absorption coefficients of vibrations for molecules in the adsorbed state and gas phase

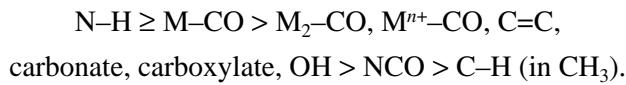
Adsorption state			Gas phase	
surface complex	$A_0$ , cm/ $\mu$ mol	$\epsilon \times 10^{18}$ , cm $^2$ /molecule	functional group	$\epsilon$ , l mol $^{-1}$ cm $^{-1}$
NH in $\text{NH}_{4\text{ads}}^+$	3.9–16.1	0.22–3.70	–	–
NH in $\text{NH}_{3\text{ads}}$	1.46–2.90	0.88	N–H in amines	5–880
$-\text{NCO}_{\text{ads}}$	–	0.14	–NCO	1300–2000
C=O in:			C=O in:	
$\text{M}^0-\text{CO}_{\text{ads}}$	–	1–3	carbonyls, ketones, acids, ethers	300–1500
$\begin{array}{c} \text{M}^0 \\ \diagup \\ \text{CO}_{\text{ads}} \\ \diagdown \\ \text{M}^0 \end{array}$	–	0.3–0.8		
$\text{M}^{n+}-\text{CO}_{\text{ads}}$	0.3–3.0	0.15–0.82		
Carboxylate ( $1600 \text{ cm}^{-1}$ )	–	0.27–0.60	–	–
Carbonate ( $1400–1360 \text{ cm}^{-1}$ )	–	0.42–0.50	–	–
C=C in $\text{C}_3\text{H}_{6\text{ads}}$ ( $\pi$ -complex)	0.10–0.28	0.10–0.35	C=C in alkenes	2–40
C–H in $\text{CH}_3$ (for adsorbed butenes and methoxy group)	–	0.01–0.09	C–H in hydrocarbons	30–70
C–C (adsorbed isobutylene)	–	0.17	–	–
C(O)O(O)M (surface anhydride group)	–	0.5	–	–
$\begin{array}{c} \text{C}=\text{O} \text{ or } \text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array}$	–	0.17–0.28	–	–
In acrolein adsorption				
$\text{OH}_{\text{ads}}$	0.4–11.0	0.17–0.33	OH in alcohols, phenols	30–100

data for the molar absorption coefficients of the stretching C–H vibrations in the adsorption of butene complexes on zeolites Y do not obey this general rule (Table 9) [67]. This is most probably due to the fact that the C–H bonds in a butene molecule are practically not disturbed during adsorption. Other vibrations participate in bond formation with the surface during the adsorption of this molecule.

Unfortunately, the derivative of the dipole momentum with respect to the normal coordinate has no simple physical meaning, because normal coordinates are a complex function of changing bond lengths and bond angles during vibrations. However, it is possible to determine the electrooptical parameters characterizing an individual bond in the molecule based on the band intensity [87]. These parameters are the dipole momen-

tum of a bond and the gradient of the dipole momentum of a bond. Taking into account the observed rule (Table 13), comparison of these values for a bond in an individual molecule and after its adsorption makes it possible to describe changes that occur in this molecule during its adsorption. This problem is rather complicated and its discussion is beyond the scope of this work.

The data of Table 13 allow us to compose a series of easiness in detecting complexes on the catalyst surface (the series of decreasing molar absorption coefficients):



Since the interval in which the molar absorption coefficients vary for different vibrations is narrow, the

probabilities of detecting different surface complexes are rather close in contrast to gas-phase molecules. This conclusion is important for the practical use of molecular spectroscopy for studying catalytic processes on the surface.

One more practically important conclusion can be drawn from the fact that the molar absorption coefficients for the same vibrations on different catalysts are of the same order of magnitude according to independent data (according to [25], the convergence of results obtained independently is  $\sim 25\%$ ). In this case, published values of molar absorption coefficients can be used in the mechanistic studies of heterogeneous catalytic reactions by *in situ* IR spectroscopy if the molar absorption coefficient cannot be measured. However, note that the number of measurements of molar and integral absorption coefficients for adsorbed substances is less than that for molecules in the gas phase. This implies that the rules formulated in this paper can be refined as new data on molar absorption coefficients and integral intensities for adsorbed substances appear.

## REFERENCES

1. Nakanishi, K., *Infrared Absorption Spectroscopy*, Tokyo: Holden Day, 1962.
2. Little, L.H., *Infrared Spectra of Adsorbed Molecules*, London: Academic, 1966.
3. Kustov, L.M., Alekseev, A.A., Borovkov, V.Yu., and Kazanskii, V.B., *Dokl. Akad. Nauk SSSR*, 1981, vol. 261, no. 6, p. 1374.
4. Alekseev, A.A., Borovkov, V.Yu., and Kazanskii, V.B., *Dokl. Akad. Nauk SSSR*, 1982, vol. 264, no. 3, p. 625.
5. Borovkov, V.Yu. and Kazanskii, V.B., *Zh. Fiz. Khim.*, 1985, vol. 59, no. 2, p. 333.
6. Wendland, W. and Hecht, H.G., *Reflectance Spectroscopy*, New York: Wiley, 1966, p. 46.
7. Richards, P.L. and Tobin, R.G., *Vibrational Spectroscopy of Molecules and Surfaces*, Yates, J.T. and Madey, T.E., Eds., 1987, vol. 1, p. 417.
8. Van Woerkom, P.C.M., Blok, P., and van Veendlandt, H.J., *Appl. Opt.*, 1980, vol. 19, no. 13, p. 2546.
9. Van Woerkom, P.C.M. and de Groot, R.L., *Appl. Opt.*, 1982, vol. 21, no. 17, p. 3114.
10. Matyshak, V.A., Lefler, E., and Shnabel', K.Kh., *Kinet. Katal.*, 1987, vol. 28, no. 6, p. 138.
11. Davydov, A.A., *IK-spektroskopiya v khimii poverkhnosti okisllov* (IR Spectroscopy Applied to the Chemistry of Oxide Surfaces), Novosibirsk: Nauka, 1984.
12. Krylov, O.V. and Matyshak, V.A., *Promezhutochnye soedineniya v geterogennom katalize* (Intermediates in Heterogeneous Catalysis), Moscow: Nauka, 1996.
13. Su, B.L., Manoli, J.-M., Potvin, C., and Barthomeuf, D., *J. Chem. Soc., Faraday Trans. I*, 1993, vol. 89, no. 5, p. 857.
14. Yoshinobu, J., Takagi, N., and Kawai, M., *Phys. Rev. B*, 1994, vol. 49, no. 23, p. 16670.
15. Smirnov, K.S. and Tsyganenko, A.A., *Opt. Spektrosk.*, 1986, vol. 60, no. 3, p. 667.
16. Zverev, S.M., Smirnov, K.S., and Tsyganenko, A.A., *Kinet. Katal.*, 1988, vol. 29, no. 6, p. 1439.
17. Zubkov, S.A., Borovkov, V.Yu., Kazansky, V.B., and Gagarin, S.G., *Chem. Phys. Lett.*, 1984, vol. 107, no. 3, p. 337.
18. Della Gata, G., Fubini, B., Ghiotti, G., and Morterra, C., *J. Catal.*, 1976, vol. 43, no. 1, p. 90.
19. Forster, H. and Shuldt, M., *J. Chem. Phys.*, 1977, vol. 66, no. 11, p. 5237.
20. Tsyganenko, A.A. and Filimonov, V.N., *Spectrosc. Lett.*, 1980, vol. 13, no. 8, p. 583.
21. Davydov, A.A., *Zh. Fiz. Khim.*, 1993, vol. 67, no. 9, p. 1900.
22. Lafer, L.I., Dykh, Zh.L., Vasina, T.V., Preobrazhenskii, A.V., Bragin, O.V., and Yakerson, V.I., *Izv. Akad. Nauk, Ser. Khim.*, 1992, no. 5, p. 1038.
23. Hughes, T.R. and White, H.M., *J. Phys. Chem.*, 1967, vol. 71, no. 7, p. 2192.
24. Take, J.I., Yoshioka, H., and Misono, M., *Proc. 9th Int. Congr. on Catalysis*, Calgary: Chem. Inst. Canada, 1988, vol. 1, p. 372.
25. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (Infrared Spectroscopy in Heterogeneous Acid-Base Catalysis), Novosibirsk: Nauka, 1992.
26. Malyshova, L.V., Shmachkova, V.P., Paukshtis, E.A., and Kotsarenko, N.S., *Primenenie opticheskoi spektroskopii v adsorbsii i katalize* (Optical Spectroscopy Applied to Adsorption and Catalysis), Leningrad: Izdatel'stvo Leningr. Univ., 1988.
27. Budneva, A.A., Paukshtis, E.A., and Davydov, A.A., *React. Kinet. Catal. Lett.*, 1987, vol. 34, no. 1, p. 63.
28. Matyshak, V.A., Kadushin, A.A., Burkhardt, I.S., and Shnabel', K.Kh., *Kinet. Katal.*, 1985, vol. 26, no. 2, p. 334.
29. Watanabe, Y. and Habgood, H.W., *J. Phys. Chem.*, 1968, vol. 72, no. 8, p. 3066.
30. Hughes, T.R. and White, H.M., *J. Phys. Chem.*, 1967, vol. 71, no. 7, p. 2192.
31. Bielansky, A. and Datka, J., *Bull. Pol. Acad. Sci., Chem.*, 1974, vol. 22, no. 2, p. 341.
32. Lafer, L.I., Dykh, Zh.L., and Vasina, T.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, no. 2, p. 259.
33. Soltanov, R.I., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 1984.
34. Karakchiev, L.G., *Opticheskie spektry v adsorbsii i katalize* (Optical Spectra in Adsorption and Catalysis), Alma-Ata: Nauka, 1984.
35. Datka, J., *Bull. Pol. Acad. Sci., Chem.*, 1980, vol. 28, no. 4, p. 669.
36. Jacobs, P.A. and Heyden, C.F., *J. Catal.*, 1974, vol. 34, no. 2, p. 267.
37. Borello, E., Zechina, A., and Morterra, G., *J. Phys. Chem.*, 1967, vol. 71, no. 9, p. 2938.
38. Matyshak, V.A., Slin'ko, M.M., Gazarov, R.A., Panchishnyi, V.I., Kadushin, A.A., and Krylov, O.V., *Kinet. Katal.*, 1986, vol. 27, no. 5, p. 1123.
39. Matyshak, V.A., Gazarov, R.A., Panchishnyi, V.I., and Kadushin, A.A., *Kinet. Katal.*, 1988, vol. 29, no. 5, p. 1130.

40. Matyshak, V.A., Gazarov, R.A., Panchishnyi, V.I., and Kadushin, A.A., *Kinet. Katal.*, 1988, vol. 29, no. 6, p. 1381.

41. Matyshak, V.A., *Kinet. Katal.*, 1992, vol. 33, nos. 5–6, p. 1168.

42. Sil'chenkova, O.N., Ukharskii, A.A., and Matyshak, V.A., *Kinet. Katal.*, 1994, vol. 35, no. 5, p. 766.

43. Matyshak, V.A., Baron, S.L., Ukharskii, A.A., Il'ichev, A.N., Sadykov, V.A., and Korchak, V.N., *Kinet. Katal.*, 1996, vol. 37, no. 4, p. 585.

44. Shimizu Ken-ichi, *Molecular Bases for the Design of Metal Oxide De- $NO_x$  Catalysts*, Thesis, Nagoya: Nagoya University, 2000, p. 135.

45. Heyne, D.E. and Tompkins, F.C., *Proc. R. Soc.*, 1966, vol. 292, no. 1431, p. 460.

46. Miura, H. and Gonzalez, R.D., *J. Phys.: Sci. Instr.*, 1982, vol. 15, p. 373.

47. Vannice, M.A. and Twu, C.C., *J. Chem. Phys.*, 1981, vol. 75, no. 12, p. 5944.

48. Duncan, M., Yates, Y.T., and Vaughan, R.W., *J. Chem. Phys.*, 1980, vol. 73, no. 2, p. 975.

49. Cant, W. and Donaldson, R.A., *J. Catal.*, 1982, vol. 78, no. 2, p. 461.

50. Ukharskii, A.A., *Cand. Sci. (Chem.) Dissertation*, Moscow: Inst. of Chemical Physics, 1983.

51. Soltanov, R.I., Paukshtis, E.A., and Yurchenko, E.N., *Kinet. Katal.*, 1982, vol. 23, no. 1, p. 164.

52. Peri, J.B., *J. Catal.*, 1978, vol. 52, no. 1, p. 144.

53. De Jong Gens, K.P. and Jorisse, J.W., *Appl. Surf. Sci.*, 1980, vol. 7, p. 273.

54. Seanor, D.A. and Amberg, C.H., *J. Chem. Phys.*, 1965, vol. 42, no. 8, p. 2967.

55. Paukshtis, E.A., Soltanov, R.I., and Yurchenko, E.N., *React. Kinet. Catal. Lett.*, 1981, vol. 16, no. 1, p. 93.

56. Davydov, A.A., *IK-spektroskopiya v khimii poverkhnostnykh okislov* (IR Spectroscopy Applied to the Chemistry of Oxide Surfaces), Novosibirsk: Nauka, 1984.

57. Soltanov, R.I., Paukshtis, E.A., Yurchenko, E.N., et al., *Kinet. Katal.*, 1984, vol. 25, no. 3, p. 729.

58. Arendarskii, D.A., Paukshtis, E.A., Ismagilov, Z.R., and Yurchenko, E.N., *React. Kinet. Catal. Lett.*, 1985, vol. 28, no. 1, p. 195.

59. Pielpu, T., Poignat, F., Vallet, A., Saussey, J., Lavalley, J.C., and Mabilon, J., *Stud. Surf. Sci. Catal.*, 1995, vol. 96, p. 619.

60. Davydov, A.A., *Doctoral (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 1986.

61. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.*, 1971, vol. 67, no. 588, p. 3585.

62. Herd, A.C., Onishi, T., and Tamaru, K., *Bull. Chem. Soc. Jpn.*, 1974, vol. 47, no. 3, p. 575.

63. Ueno, A., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.*, 1970, vol. 66, no. 567, p. 756.

64. Amenomiya, Y., *Appl. Spectrosc.*, 1978, vol. 32, no. 5, p. 484.

65. Ukharskii, A.A. and Berman, A.D., *Kinet. Katal.*, 1992, vol. 33, nos. 5–6, p. 1101.

66. Davydov, A.A., Shepot'ko, M.L., and Budneva, A.A., *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 299.

67. Datka, J., *J. Chem. Soc., Faraday Trans. I*, 1981, vol. 77, no. 6, p. 1309.

68. Amenomiya, Y., *J. Catal.*, 1979, vol. 58, no. 1, p. 64.

69. Solymosi, F., Erdohelyi, A., and Kocsic, M., *J. Catal.*, 1980, vol. 65, no. 2, p. 428.

70. Galuszka, J., Chang, J.R., and Amenomiya, Y., *J. Catal.*, 1981, vol. 68, no. 1, p. 172.

71. Davydov, A.A., *Zh. Prikl. Spektrosk.*, 1993, vol. 58, nos. 5–6, p. 456.

72. Malysheva, L.V., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 1986.

73. Kurman, P.V., Matyshak, V.A., and Kutyrev, M.Yu., *Khim. Fiz.*, 1984, vol. 3, no. 8, p. 1138.

74. McDonald, R.S., *J. Phys. Chem.*, 1958, vol. 62, no. 10, p. 1168.

75. Daturi, M., Binet, C., Lavalley, J.-C., Galtayries, A., and Sporken, R., *Phys. Chem. Chem. Phys.*, 1999, vol. 1, p. 5717.

76. Badri, A., Binet, C., and Lavalley, J.C., *J. Chem. Soc., Faraday Trans.*, 1997, vol. 93, no. 6, p. 1159.

77. Ouyang, F., Kondo, J., Maruya, K.I., and Domen, K., *J. Phys. Chem.*, 1997, vol. 101, no. 27, p. 4867.

78. Popova, G.A., Davydov, A.A., Andrushkevich, T.V., and Budneva, A.A., *React. Kinet. Catal. Lett.*, 1987, vol. 33, no. 2, p. 293.

79. Jacobs, P.A., Mortier, W.J., and Uytterhoeven, J.W., *Inorg. Nucl. Chem.*, 1978, vol. 40, p. 1919.

80. Jacobs, P.A. and Ballmoos, R.V., *J. Phys. Chem.*, 1982, vol. 80, no. 23, p. 3050.

81. Datka, J. and Tyznik, E., *Int. Symp. Zeol. Catal. Siofok*, 1985, p. 173.

82. Galkin, G.A., Kiselev, A.V., and Lygin, V.I., *Zh. Fiz. Khim.*, 1969, vol. 43, no. 8, p. 1992.

83. Curthous, G., Davydov, V.Ya., and Kiselev, S.A., *J. Coll. Int. Sci.*, 1974, vol. 48, p. 58.

84. Gorbunov, B.Z. and Safatov, A.S., *Zh. Prikl. Spektrosk.*, 1982, vol. 36, no. 3, p. 455.

85. Davydov, V.Ya., Kiselev, A.V., and Kiselev, S.A., *Kolloidn. Zh.*, 1979, vol. 41, no. 2, p. 227.

86. Preudhomme, J., Lamotte, J., Janin, A., and Lavalley, J.C., *Bull. Soc. Chim. Fr.*, 1981, vols. 11–12, no. 1, p. 1.

87. *Vibrational Spectroscopy—Modern Trends*, Barnes, A. and Orvill-Thomas, W., Eds., Amsterdam: Elsevier, 1977.