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Interaction of N_2 with the Acid Sites of Oxides

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Abstract—Nitrogen adsorption on SiO_2, γ-Al_2O_3, TiO_2, and sulphated zircona (SO_4^{2-}/ZrO_2) is studied by Fourier transform IR spectroscopy. Integrated absorption coefficients for the bands due to the N–N vibrations in nitrogen complexes with Brønsted and Lewis acid sites are determined. A general correlation between integrated absorption coefficients and the positions of N–N bands of nitrogen interacting with the above sites in zeolites and oxides is discussed. The orientation of a nitrogen molecule relative to Brønsted and Lewis acid sites is calculated *ab initio* using a 6-31G** basis set.

INTRODUCTION

IR spectroscopy of adsorbed molecules with the use of the CO molecule as a probe is widely employed to determine the strength and concentration of various acid sites in zeolites and oxides [1, 2]. In recent years, small nonpolar molecules, for example, nitrogen, have been used as probes along with CO [3–7]. Nitrogen has been found to form donor–acceptor complexes with the strong Brønsted and Lewis acid sites of zeolites. There have also been works devoted to the interaction between the nitrogen and the acid sites of oxides, which are weaker than sites on the zeolite surface.

It has been shown [8] that nitrogen interacts with surface Si–OH groups to form H-complexes when it is adsorbed on silica at –196°C. In the IR spectrum, the intensity of the 3749 cm^{-1} absorption band decreases and a band at 3715 cm^{-1} appears. The latter was assigned to the vibrations of the Si–OH groups in the nitrogen H-complexes.

Upon the interaction of N_2 with η-Al_2O_3 [9], the spectrum of adsorbed nitrogen shows only an absorption band with a maximum at 2360 cm^{-1}. This band was assigned to the vibrations of nitrogen in its complexes with surface aluminum atoms.

Upon the adsorption of nitrogen (^{14}N–^{14}N) on the surface of titania [10], two absorption bands were observed in the spectrum in the region of N–N vibrations, namely, a strong band at 2337 cm^{-1} and a weak band at 2345 cm^{-1}. These bands were assigned to nitrogen complexes with titania Lewis sites. The integrated absorption coefficient for the band at 2337 cm^{-1} was determined. It is shown in this work that bands at 2260 and 2268 cm^{-1} appear in the spectrum after the adsorption of nitrogen (^{15}N–^{15}N).

Previously [11], we studied samples of Y-zeolites (with various degrees of exchange that were calcined at various temperatures) and HZSM-5. Nitrogen was shown to interact with both weak and strong acid OH groups to form H-complexes. The shift of the absorption bands of hydrogen-bonded OH groups in complexes with nitrogen and CO is proportional to the strength of proton sites. The integrated absorption coefficients for the bands due to N–N vibrations in the complexes with bridging OH groups in the HNaY and HZSM-5 zeolites were calculated. We established a correspondence between the absorption bands of CO and nitrogen in the complexes and Lewis sites. The integrated absorption coefficient for the 2350 cm^{-1} band due to N–N vibrations in the complexes with Lewis sites of the HNaY zeolite was calculated. The integrated absorption coefficient data were correlated with the N–N band positions for adsorbed nitrogen.

Here, we report the adsorption of nitrogen and CO on oxides with Brønsted and Lewis sites that differ in nature and strength from the acid sites of zeolites.

EXPERIMENTAL

Substances. We used mesoporous chromatographic SiO_2 (S_{sp} = 500 m^2/g), γ-Al_2O_3 (brand A1, produced by Ryazan refinery; S_{sp} = 200 m^2/g), and TiO_2 (prepared from $TiCl_4$ by precipitation with aqueous ammonia and calcined at 500°C; S_{sp} = 200 m^2/g). An SO_4^{2-}/ZrO_2 sample was prepared from zirconia by incipient-wetness impregnation with a sulfuric acid solution. It had an SO_4^{2-} content of 5 wt % and S_{sp} = 80 m^2/g.

High-purity nitrogen and CO were used for adsorption. Nitrogen was additionally purified over an Ni/Cr catalyst and then dried with CaA zeolite. Carbon monoxide was also additionally dried.

Before adsorption, samples of SiO_2, TiO_2, and SO_4^{2-}/ZrO_2 were calcined at a temperature of 500°C, whereas γ-Al_2O_3 was calcined at 500 or 700°C (hereafter, $Al_2O_3$500 and $Al_2O_3$700, respectively). Next, the samples were pumped at 400°C and a pressure of $<10^{-4}$ Torr for 1 h, and then the sample temperature was decreased to –196°C with the use of liquid nitrogen. The experiments were carried out according to a protocol described in [11].

RESULTS AND DISCUSSION

It is well known that only Si–OH groups are present on the silica surface. Figures 1a and 1b (curves *1*) show the IR spectrum of the original OH groups in the SiO_2 sample calcined at 500°C. A narrow absorption band with a maximum at 3740 cm^{-1} is observed, which is typical of silica and is assigned to vibrations of the Si–OH groups.

H-complexes are formed upon the interaction of CO with Si–OH groups, and the intensity of the band at 3740 cm^{-1} decreases. A band at 3656 cm^{-1} appears simultaneously, which is assignable to the hydrogen-bonded OH groups (Fig. 1b, curve *2*).

Nitrogen also interacts with Si–OH groups upon adsorption on SiO_2 to form H-complexes. The intensity of the absorption band at 3740 cm^{-1} decreases, and simultaneously a weak absorption band peaking at 3714 cm^{-1} appears due to the presence of hydrogen-bonded Si–OH groups (Fig. 1a, curve *2*). For convenience, the 3650–3800 cm^{-1} region is enlarged in Fig. 1a.

The IR spectrum of the original OH groups in the γ-Al_2O_3 sample calcined at 500°C is presented in Figs. 1c and 1d (curves *1*). The spectrum is a complicated contour in which one can distinguish absorption bands peaking at 3745, 3722, 3710, and 3685 cm^{-1} that are due to vibrations of the Al–OH groups [1].

When CO interacts with the Al–OH groups, H-complexes are formed, the intensities of the bands due to the initial OH groups decrease, and overlapping bands at 3450–3675 cm^{-1} appear simultaneously (Fig. 1d, curve *2*). A detailed analysis of these bands was performed in [2]. When nitrogen is adsorbed on the surface of the $Al_2O_3$500 sample, H-complexes with Al–OH groups are also formed. However, it is impossible to make out from the IR spectrum which Al–OH groups interact with N_2 and what bands appear as a result, because these bands are weak (Fig. 1c, curve *2*).

The IR spectrum of the original OH groups in the $Al_2O_3$700 sample is shown in Figs. 1e and 1f (curves *1*). This spectrum, as in the case of $Al_2O_3$500, is a complicated contour containing the same set of absorption bands due to vibrations of the OH groups, but these bands are weaker.

When CO or N_2 interacts with the Al–OH groups of $Al_2O_3$700 (Fig. 1f and 1e, curves *2*), the same features are observed in the IR spectra as in the case of the $Al_2O_3$500 sample.

The spectra of the original OH groups of the titania sample calcined at 500°C are shown in Figs. 1g and 1 h (curves *1*). As follows from this spectrum, three main types of Ti–OH group are present on the surface, giving rise to absorption bands at 3728, 3673, and 3639 cm^{-1}.

Carbon monoxide and N_2 form H-complexes that include Ti–OH groups as well as Al–OH groups. The intensities of the initial Ti–OH groups in the IR spectra decrease, and, simultaneously, absorption bands due to hydrogen-bonded Ti–OH groups with maxima at 3610, 3550, and 3465 cm^{-1} (Fig.1h, curve *2*) or at 3683, 3630, and 3585 cm^{-1} (Fig. 1g, curve *2*) appear in the lower frequency region.

The IR spectra of the original OH groups in the sulphated zirconia sample calcined at 500°C are presented in Figs. 1i and 1j (curves *1*). A typical absorption band at 3642 cm^{-1} is present in the spectrum, indicating the presence of Zr–O–S–OH groups on the surface.

When CO or N_2 interacts with the Zr–O–S–OH groups, H-complexes are formed, the band due to the original OH groups weakens, and bands due to the hydrogen-bonded Zr–O–S–OH groups at 3480 and 3574 cm^{-1} appear (Figs. 1i and 1j, curves *2*).

As was mentioned in our earlier work [11], the shift of the absorption bands of the surface OH groups in zeolites upon the formation of H-complexes with a probe molecule is determined by both the proton affinity (PA) of the acid site and the basicity of the probe molecule [1]. It can be concluded from the above data that this assumption is also true for oxides and that the ratio $\Delta\nu(OH)_{CO}/\Delta\nu(OH)_{N_2}$ is 2.3 for both oxides and zeolites.

Figure 2 presents the IR spectra of adsorbed nitrogen and CO at various pressures. As can be seen in Fig. 2b, absorption bands at 2154 and 2170 cm^{-1} are observed in the spectrum of CO adsorbed on SiO_2. The band at 2154 cm^{-1} is assigned to CO vibrations in complexes with Si–OH groups [1]. The 2170 cm^{-1} band is usually assigned to CO vibrations in complexes with bridging Al–OH–Si groups [1]. A weak band at 2196 cm^{-1} is also observed, which is assigned to CO vibrations in the complexes with Lewis sites [1]. The bands at 2170 and 2196 cm^{-1} in the spectrum of adsorbed CO are in our case most likely due to traces of alumina in the sample.

An intense band at 2321 cm^{-1} in the region of N–N vibrations is seen in the spectrum of nitrogen adsorbed on SiO_2 (Fig. 2a). It can be assigned to N–N vibrations in complexes with Si–OH groups, since it appears together with the band due to hydrogen-bonded Si–OH groups at 3715 cm^{-1}. A weak shoulder at 2330 cm^{-1}, which is assigned to N–N vibrations in the complexes with bridging Al–OH–Si groups [11], as well as the appearance of a band at 2170 cm^{-1} in the spectrum of adsorbed CO, indicate the presence of traces of alumina in the SiO_2 sample. No bands assignable to N–N vibrations in the complexes with alumina Lewis sites, which could have occurred at a higher frequency, were found.

The spectrum of CO adsorbed on $Al_2O_3$500 is shown in Fig. 2d. Absorption bands peaking at 2150

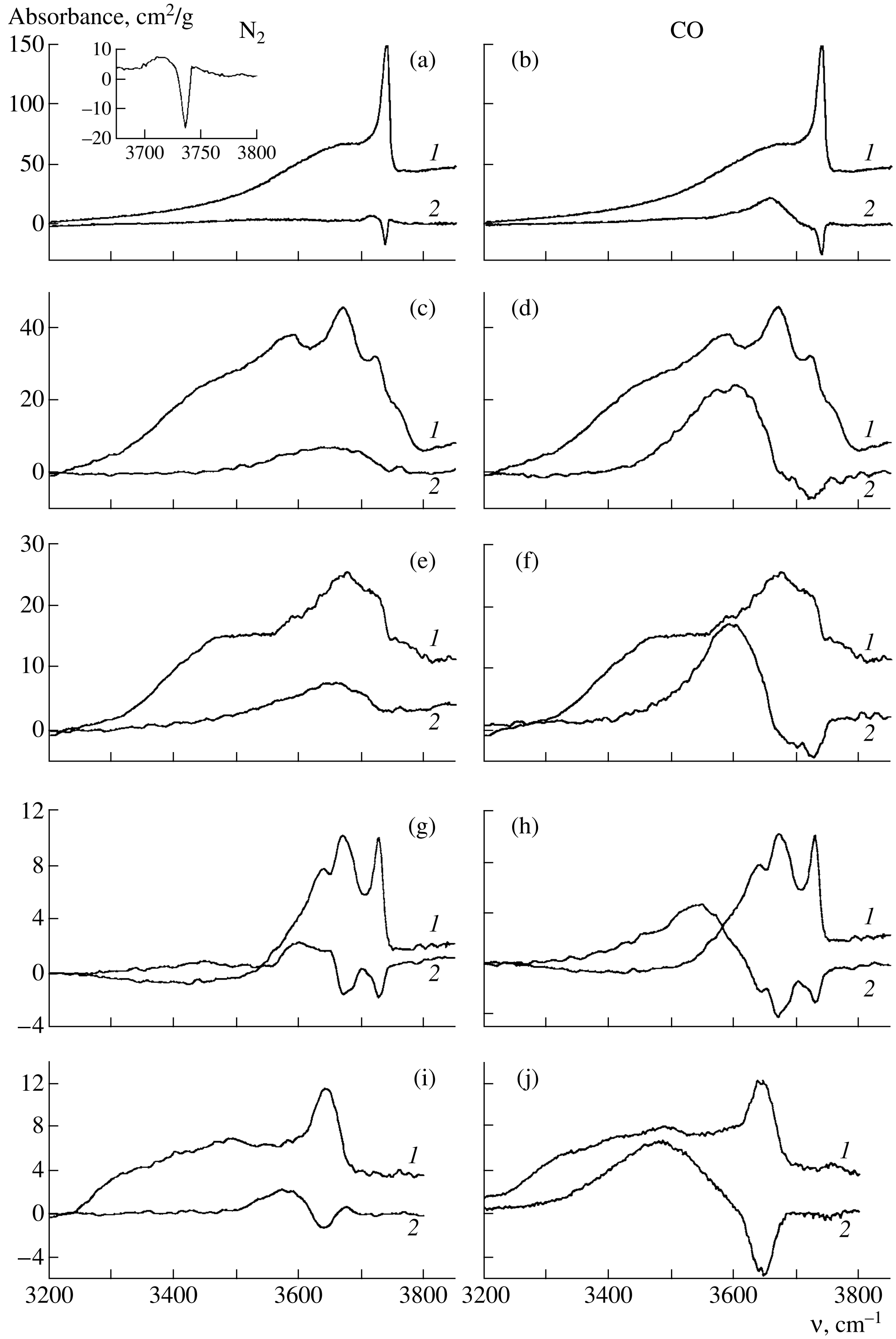

Fig. 1. IR spectra of the OH groups of (a, b) SiO_2, (c, d) γ-$Al_2O_3$500, (e, f) γ-$Al_2O_3$700, (g, h) TiO_2 and (i, j) SO_4^{2-}/ZrO_2: (*1*) original samples and (*2*) differential spectra after adsorption of (a, c, e, g, i) N_2 and (b, d, f, h, j) CO. P_{N_2} = 32 Torr, P_{CO} = 3 Torr.

and 2180 cm^{-1} are present in this spectrum. The band at 2150 cm^{-1} arises from CO vibrations in the hydrogen-bonded complexes with Al–OH groups, whereas the band at 2180 cm^{-1} is due to CO vibrations in the complexes with weak Lewis sites of alumina [1].

In the region of N–N vibrations in the spectrum of nitrogen adsorbed on $Al_2O_3$500, there are absorption bands peaking at 2325 and ~2340 cm^{-1} (Fig. 2c). The band at 2325 cm^{-1}, which appears as a shoulder, can be assigned to N–N vibrations in the

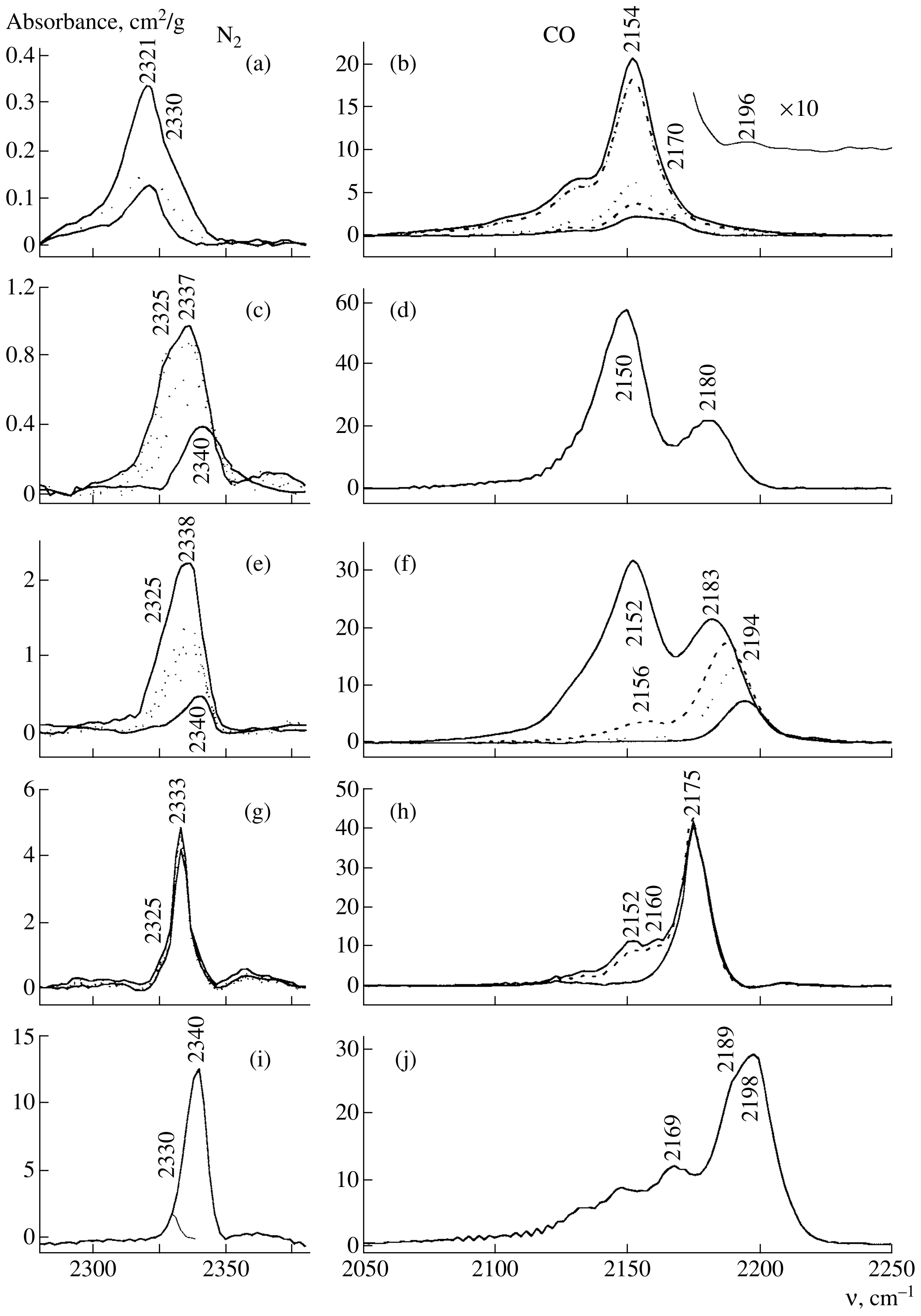

Fig. 2. IR spectra of the (a, c, e, g, i) N_2 and (b, d, f, h, j) CO adsorbed on (a, b) SiO_2, (c, d) γ-$Al_2O_3$500, (e, f) γ-$Al_2O_3$700, (g, h) TiO_2, and (i, j) SO_4^{2-}/ZrO_2. The spectra were recorded while increasing the adsorbate pressure to 32 Torr for N_2 and 3 Torr for CO. The spectra at P_{CO} = 0.01 Torr are shown in the inset at ×10 magnification.

H-complexes with Al–OH groups [11]. The band at 2340 cm^{-1} corresponds to N–N vibrations in the complexes with alumina Lewis sites, and the band at 2180 cm^{-1} is due to C–O vibrations in adsorbed CO.

One can distinguish the following absorption bands at 2152, 2183, and 2194 cm^{-1} in the region of C–O vibrations in the spectrum of CO adsorbed on $Al_2O_3$700 (Fig. 2f). The band at 2152 cm^{-1} is assigned to CO vibrations in the H-complexes with Al–OH groups, while the bands at 2183 and 2194 cm^{-1} are assigned to CO vibrations in the complexes with two types of alumina Lewis site [1].

The spectrum of N_2 adsorbed on $Al_2O_3$700 shows the same absorption bands with the same assignments as the spectrum of $Al_2O_3$500 (Fig. 2e). In contrast to the spectrum of CO adsorbed on $Al_2O_3$700, the band due to the interaction of nitrogen with the second type of Lewis site cannot be distinguished here.

Absorption bands at 2152, 2160, and 2175 cm^{-1} are seen in the IR spectrum of CO adsorbed on TiO_2 (Fig. 2e). The first two bands can be assigned to CO vibrations in the H-complexes with Ti–OH groups, and the band at 2175 cm^{-1} is assigned to CO vibrations in the complexes with weak Lewis sites of titania [1].

In the region of N–N vibrations in the spectrum of nitrogen adsorbed on TiO_2 (Fig. 2g), a band at 2333 cm^{-1} is observed, which corresponds to N–N vibrations in the complexes with Lewis sites of titania, like the band at 2175 cm^{-1} in the spectrum of adsorbed CO. A weak shoulder near 2325 cm^{-1} can be assigned to N–N vibrations in the H-complexes with Ti–OH groups.

The IR spectrum of CO adsorbed on SO_4^{2-}/ZrO_2 is shown in Fig. 2j. One can see absorption bands at 2169 and 2198 cm^{-1} and a shoulder at 2189 cm^{-1}. The first band was assigned to vibrations caused by CO interaction with (Zr–O–S)–OH groups. The bands at 2189 and 2198 cm^{-1} can be assigned to CO vibrations in the complexes with two types of the Lewis acid site of zirconia.

In the spectrum of nitrogen adsorbed on SO_4^{2-}/ZrO_2 (Fig. 2i), an asymmetrical contour with a peak at 2340 cm^{-1} is observed in the region of N–N vibrations. This band can be assigned to N–N vibrations in the complexes with Lewis sites of zirconia. The asymmetrical shape of the curve suggests the presence of a weak band near 2330 cm^{-1} due to N–N vibrations in the complexes with (Zr–O–S)–OH groups.

The integrated absorption coefficient $A_{0(N-N)}$ for the complexes with acid sites was estimated as described in [11]. The integrated absorption coefficient for Al–OH and Si–OH bands in the region of the vibrations of OH groups is 3.0 cm/μmol; it was determined on the basis of the correlations described in [1] from the decay of bands in the 3650–3750 cm^{-1} region and from the average integrated absorption coefficient of the 2152 cm^{-1} band in the region of the vibrations of adsorbed CO (the latter is equal to 2.6). The $A_{0(N-N)}$ values for N–N bands at 2321 and 2325 cm^{-1} for the SiO_2 and $Al_2O_3$500 samples were calculated to be 0.066 and 0.113 cm/μmol, respectively.

The integrated absorption coefficient $A_{0(L...CO)}$ for bands of CO in the complexes with Lewis sites of alumina, titania, and zirconia were taken from [1]. The calculated integrated absorption coefficients for the bands due to N–N vibrations in the complexes with Lewis sites of alumina (2337 and 2338 cm^{-1}), titania (2333 cm^{-1}), and zirconia (2340 cm^{-1}) are 0.02, 0.049, 0.045, and 0.123 cm/μmol, respectively.

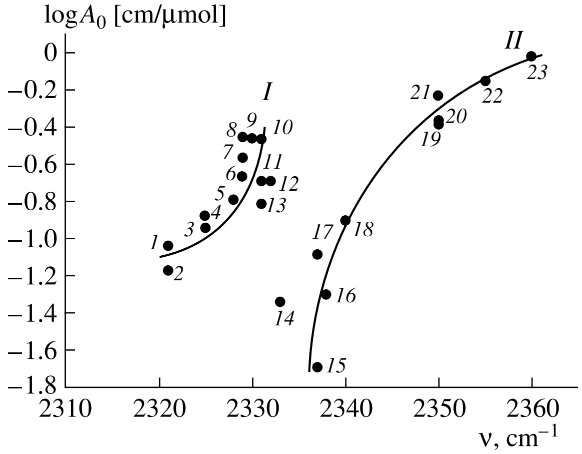

Fig. 3. Correlation between the integrated absorption coefficient and the N–N band position for nitrogen interacting with acid sites of (*1*, *5*) HZSM-5 500 [11], (*2*) $SiO_2$500, (*3*, *15*) γ-$Al_2O_3$500, (*4*, *12*, *19*, *22*) H-β [6], (*6*) HY(1)400 [11], (*7*, *21*) HY(2)700 [11], (*8*) HY(1)500 [11], (*9*, *20*) HY(2)600 [11], (*10*) H-GaZSM-5 [3], (*11*) H-FER [7], (*13*) H-MOR [4], (*14*) TiO_2, (*17*) γ-$Al_2O_3$700, (*18*) SO_4^{2-}/ZrO_2, and (*23*) η-Al_2O_3 [9].

Figure 3 plots, as dots, the integrated absorption coefficient as a function of the position of the N–N band due to nitrogen interacting with Brønsted and Lewis acid sites in silica, alumina, titania, sulphated zirconia, HZSM-5 zeolite, and HNaY zeolites differing in the degree of exchange and calcination temperature [11]. Furthermore, we plot data that we calculated, by a procedure reported in [11], from earlier reported spectra of nitrogen adsorbed on the zeolites HGaZSM-5 [3], H-MOR [4], H-β [6], and H-ferrerite (H-FER) [7].

As can be seen in Fig. 3, data points are arranged near the two curves. Points *1–13* in the region of nitrogen vibrations at 2318–2332 cm^{-1} refer to the interaction of nitrogen with proton sites (curve *I*), and points *14–23* at 2330–2360 cm^{-1} refer to the formation of nitrogen complexes with aprotic sites (curve *II*). The integrated absorption coefficient for both types of complex increased with increasing frequency of N–N vibrations.

Gaseous dinitrogen is known to give no IR absorption bands, because it has a symmetrical structure and, accordingly, a dipole moment invariable upon absorption. In Raman spectra, the frequency of N–N vibrations is 2329.9 in the gas-phase, 2327.1 in the solid state, and 2325.9, 2324.3, and 2322.0 cm^{-1} in the argon, krypton, and xenon matrices, respectively [12]. As can be seen in Fig. 3, the frequencies of N–N vibrations in the complexes with Brønsted sites are lower than the

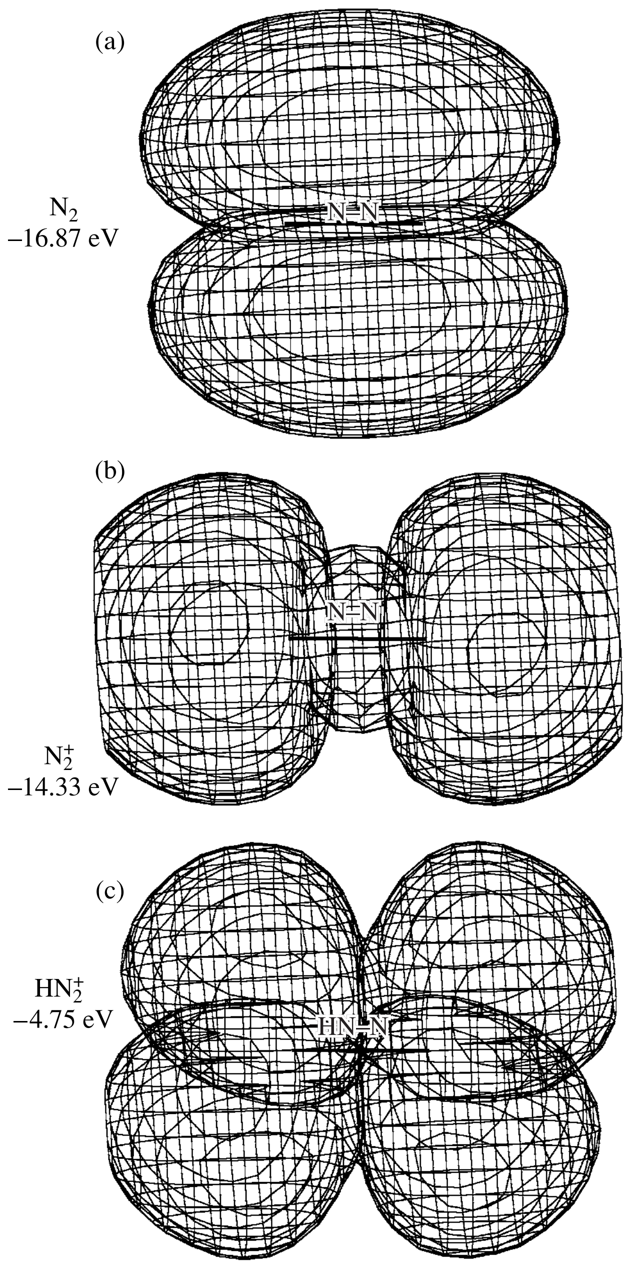

Fig. 4. Spatial probability density function for an electron occurring in the HOMO of (a) the nitrogen molecule and in the LUMOs of the (b) N_2^+ and (c) HN_2^+ species.

frequency of N–N vibrations in free nitrogen, whereas the frequencies of N–N vibrations in the complexes with Lewis sites are higher than the frequency of N–N vibrations in free nitrogen. This finding for the Brønsted and Lewis acid sites is, possibly, evidence that the corresponding nitrogen complexes have different structures.

To interpret the results obtained, electron density distribution in the free nitrogen molecule was calculated *ab initio* using the HyperChem Pro 6 package.

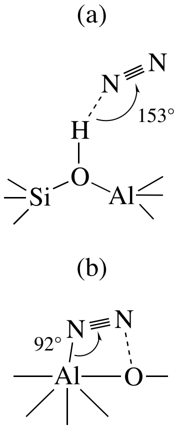

Fig. 5. Models of the nitrogen complexes with (a) a Brønsted and (b) a Lewis acid site.

Furthermore, we calculated the distribution of electron density in the N_2^+ and HN_2^+ species, which model the interaction of nitrogen with Brønsted and Lewis acid sites, respectively. All the bonding orbitals of nitrogen are filled, whereas the N_2^+ and HN_2^+ species have unoccupied low-energy bonding orbitals. As is clear from Fig. 4a, any interaction with nitrogen is possible only in the direction perpendicular to the N–N bond and this can result only in a decrease in the N–N frequency. From the electron density distribution for the lowest unoccupied orbital, one can deduce that the N_2^+ species (Fig. 4b) forms a complex via a two-center mechanism and the HN_2^+ species (Fig. 4c) forms a complex via a one-center mechanism. When the N_2^+ and HN_2^+ species interact with an electron-donor site (base), the frequency of N–N vibrations can increase. Hence, one can assume that the back donation effect, which means that the adsorbate not only donates electrons but also accepts them, plays an important role in the interaction between nitrogen and Lewis and Brønsted acid sites.

The orientations of the nitrogen molecule on the Brønsted and Lewis acid sites were *ab initio* calculated for fragments of the HZSM-5 zeolite (80 atoms) and γ-Al_2O_3 (30 atoms) using the HyperChem Pro 6 package and a 6-31G** basis set (necessary structural data were taken from *Inorganic Crystal Structure Data Base*). The geometry of the nitrogen complexes with Brønsted and Lewis acid sites is shown in Fig. 5. The OHN angle in the H-complex is 174°, and the HNN angle is 153°, not 180°, as was accepted in previous works. The AlNN angle in the nitrogen complex with a Lewis site is 92°; that is, the nitrogen molecule is aligned with the Al–O bond. The calculated data suggest that the electrons of one atom of an adsorbed nitrogen molecule interact with the proton and the oxygen atom of a bridging OH group; that is, we have a one-center two-bonded mechanism. When a complex with a

Lewis site is formed, the nitrogen molecule interacts with aluminum through one of its atoms and with the adjacent oxygen through the other atom; that is, a two-center mechanism is observed. Hence, as was assumed above, a back donation mechanism takes place. These facts account for the two types of relationship for the nitrogen complexes with Lewis and Brønsted acid sites. However, more detailed quantum chemical calculations in combination with the DFT and other more complicated methods are required for any ultimate conclusions.

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