A. V. Rudakova, R. A. Belykh, A. A. Tsyganenko

FTIR STUDY OF HCN ADSORPTION ON MAGNESIUM FLUORIDE

St. Petersburg State University,
7–9, Universitetskaya nab., St. Petersburg, 199034, Russian Federation

The mechanism of HCN interaction with MgF_2 pretreated at 773 K has been studied by means of FTIR spectroscopy at 77–300 K. The properties of surface sites were preliminary characterized by the low temperature spectra of adsorbed CO, which reveal the presence of several types of Lewis acid sites of different strength, weak H-bond with surface OH-groups, as well as interaction with surface anions. Adsorption of isotopically substituted molecules: DCN, $H^{13}C^{14}N$ and $H^{12}C^{15}N$ facilitates the assignment of absorption bands and has shown that hydrogen cyanide does not dissociate on adsorption. Adsorbed molecules form coordinate bond with surface cations, interact with surface hydroxyls or form weak H-bond by the CH-group with the anions, apparently, with surface F^- ions.

Keywords: IR spectroscopy, adsorption, magnesium fluoride, hydrogen cyanide, surface.

А. В. Рудакова, Р. А. Белых, А. А. Цыганенко

ИССЛЕДОВАНИЕ АДСОРБЦИИ HCN НА ФТОРИДЕ МАГНИЯ МЕТОДОМ ИК-ФУРЬЕ-СПЕКТРОСКОПИИ

Санкт-Петербургский государственный университет,
Российская Федерация, 199034, Санкт-Петербург, Университетская наб., 7–9

Методом ИК-фурье-спектроскопии при температурах 77–300 K изучен механизм взаимодействия HCN с MgF_2, предварительно вакуумированным при 773 K. Свойства поверхности охарактеризованы при помощи низкотемпературных спектров адсорбированного CO, которые показали наличие нескольких типов кислотных центров Льюиса разной силы, слабой H-связи с поверхностными OH-группами, а также взаимодействия с поверхностными анионами. Адсорбция изотопно замещённых молекул DCN, $H^{13}C^{14}N$ и $H^{12}C^{15}N$ облегчает отнесение полос поглощения и показывает, что HCN при адсорбции не диссоциирует. Адсорбированные молекулы образуют координационную связь с катионами поверхности, взаимодействуют с гидроксилами поверхности или образуют слабую H-связь CH-группы с анионами, очевидно, поверхностными ионами F^-.

Ключевые слова: ИК-спектроскопия, адсорбция, фторид магния, цианистый водород, поверхность.

Introduction. Nowadays a vast experimental material on the studies of metal oxide surfaces is accumulated and analyzed. Surface properties of metal halides in particular, of fluorides, have been studied much poorer, despite their wide application in optical industry and great potential for catalysis.

MgF_2 has a rutile type crystal lattice. It is an insulator with a broad band gap ($\approx$ 12.6 eV), chemically and thermally very stable (melting point 1673 K). It is transparent over an extremely wide frequency region and can be used as an optical material in

       https://doi.org/10.21638/11701/spbu04.2018.205

the wavelength range from 0.120 μm in vacuum ultraviolet up to 8.0 μm (1250 cm^{-1}) in the infrared.

Surface properties of MgF$_2$ have been studied by Wojciechowska et al. by IR spectroscopy, thermo-desorption and thermo-graphic methods [1–4]. Several types of hydroxyl groups and adsorbed water molecules of different strength, concentration and thermal stability were established, as well as two types of weak Lewis acid sites- coordinately unsaturated Mg^{2+} ions. After treating the sample at 673–773 K anionic defect sites O^{2-} can be formed from the hydrogen-bonded OH groups.

Recently the structure and properties of nanodisperse magnesium fluorides prepared by a novel sol—gel synthetic route were investigated by XRD, MAS NMR, TEM, FTIR spectroscopy [5, 6]. By changing the amount of water at constant stoichiometric amount of HF, it is possible to tune the surface acidity of the resulting partialy hydroxylated magnesium fluorides. Low-temperature (100 K) FTIR spectroscopic study of CO adsorption on such MgF$_2$ shows that this material possesses three kinds of Lewis acid sites, identified as 3-, 4- and 5-fold coordinated unsaturated magnesium atoms of the surface. It was reported that the strength of these Lewis acid sites is medium or weak, but their concentration is very high (5–6 sites/nm^2). Both Lewis basic and acidic sites play a role in water adsorption [7].

It was shown that MgF$_2$ is a good support for transition metal oxides such as V$_2$O$_5$, WO$_3$, MoO$_3$, Cr$_2$O$_3$ [8] and binary systems like Cu—Cr$_2$O$_3$ and Cu—Mn oxides [8, 9] as well as for metal catalysts like Au [10], Pd and Ru [11, 12]. Ru/MgF$_2$ catalyst reveals significantly higher activity in hydrodesulfurization as compared with Ru/SiO$_2$ and Ru/Al$_2$O$_3$ with the same amount of ruthenium [13].

As a catalyst MgF$_2$ can promote addition reaction on multiple bonds, polycondensation and polymerization reactions [2, 14]. Due to high concentration of acidic Lewis sites, magnesium fluoride demonstrates high catalytic activity in acidic catalytic reactions such as isomerization of cyclohexene into methylcyclopentane, hydrogen disproportionation [14]. Kemnitz et al. have shown that hydroxylated nanoscopic fluorides (MgF$_2$ and AlF$_3$) can be successfully applied as highly active catalysts in the synthesis of vitamins E and K$_1$ [15]. Moreover, the catalytic potential of these materials has been investigated using Friedel — Crafts alkylation of aromatic compounds [16].

Hydrogen cyanide is an important starting material in some industrial synthesis processes, is an undesired toxic byproduct in some others [17]. It has been identified in the gas phase of the interstellar medium, as well as in the comae of comets and is believed to be a key component in the synthesis of the first biologically important molecules [18]. There are few works on the IR studies of adsorbed HCN on porous glass [19], silica [20], supported metal catalysts [21] and alumina [22]. The only paper, as far as we know, where HCN adsorption was studied spectroscopically on metal halides, was the old one by Kozirovski and Folman [23].

In this work adsorption of hydrogen cyanide, DCN, as well as H^{13}C^{14}N and H^{12}C^{15}N molecules on the surface of commercial MgF$_2$ has been studied by means of low temperature IR spectroscopy. To characterize adsorption properties of the surface, the spectra of CO adsorbed at 77 K have been preliminarily obtained before exposure the samples to HCN.

Experimental. The stainless steel cell used for low-temperature measurements was described elsewhere [24]. Pressure was measured with two Edwards Barocel 600 pressure gauges attached to the cell. One, with the accuracy of 10^{-3} Torr and the upper measurement limit of 10 Torr, was connected directly with the inner volume of the cell, and another for 1–1000 Torr was used to measure the pressure of the gas to be admitted from the dosing volume.

In our experiments at 77 K, HCN gas was usually let into the cell cooled by liquid nitrogen, where about 0.5 Torr of helium was added for better thermal contact of the sample with the cooled environment. Then liquid nitrogen was removed and the cell was let heated until the bands of adsorbed species appear ($\approx 120 \div 130$ K), and the evolution of spectra with temperature was followed. Then cell was repeatedly cooled by liquid nitrogen. To change the HCN coverage the sample was raised to the warmer part of the tube for a controlled time. The desorbed gas was frozen on the cold walls of the cell and after every heating the spectrum recorded at 77 K showed a diminished quantity of the adsorbate. Temperature of samples was measured by a thermocouple inserted into the coolant compartment close to the sample holder.

The commercial pure grade magnesium fluoride (MgF_2) was used. The samples were pressed into thin (20–70 mg/cm^2) pellets and outgassed in vacuum for 30 minutes at 773 K, in some experiments at 973 K.

Hydrogen cyanide was prepared by a dropwise addition of H_2SO_4 to KCN, purified by vacuum distillation, and only the first portion of HCN used in experiments. DCN was prepared in a similar manner by using D_2SO_4. $H^{13}CN$ (70% ^{13}C) and $HC^{15}N$ (99% ^{15}N) were prepared by catalytic reaction of CO with NH_3 at 900–1100 K over γ-Al_2O_3 preliminary activated at the same temperature. Industrial isotopically substituted ^{13}CO with 70-% enrichment for the synthesis of $H^{13}CN$ and $^{15}NH_3$ with 99-% enrichment for $HC^{15}N$ were taken as initial substances for the synthesis reaction. The synthesized HCN was purified from carbon dioxide and ammonia by outgasing at about 180 K in a trap with ethyl alcohol cooled by liquid nitrogen, and dried over P_2O_5.

Spectra were recorded by a Nicolet-710 FTIR spectrometer with a coolable MCT detector, typically at 4 cm^{-1} spectral resolution by co-adding 128 scans.

Results. *1. CO adsorption.* In the spectrum of MgF_2, pretreated at 773 and cooled to 77 K strong bands occur at 3617, 1665 and 1007 cm^{-1} accompanied by less intense peaks at 3590, 3517, 3400, 3255 with a shoulder at 3205 cm^{-1}, 2005, 1240, 992, 899 and 807 cm^{-1}.

The changes of the spectrum caused by CO adsorption as well as the bands of adsorbed molecules are shown in Fig 1. Addition of about 10 Torr of CO does not affect the bands at 3617 and 1007 cm^{-1}, while those at 3590 and 3205 cm^{-1} disappear. Intensity increase was detected at 3570 and 807 cm^{-1}. Maxima at 3517 and 1240 cm^{-1} shift to 3507 and 1222 cm^{-1}, respectively. The bands of adsorbed CO molecules arise at 2185, 2175, 2161, 2151 and 2140 cm^{-1}.

Gradual removal of the adsorbate results first in the disappearance of the low frequency bands at 2140 and 2151 cm^{-1} simultaneously with the restoration of the OH bands at 3590 and 3205 cm^{-1}, as well as the shift of the 3517 cm^{-1} band back to its initial position. Further surface coverage diminution leads to sequential removal of the 2161, 2175 and 2185 cm^{-1} bands and to the high frequency shifts of their maxima to 2164, 2183 and 2198 cm^{-1}, respectively. The trace of the latter band can be seen at 2201 cm^{-1} after short pumping at 300 K. It should be noted that the weakening and the shift of the latter band observed on coverage diminution is accompanied by intensity increase at the high-frequency side that is typical of lateral interaction between the adsorbed molecules [25]. Initial positions and intensities of the bands at 1240 and 807 cm^{-1} restore only after complete removal of adsorbed CO by pumping at 300 K.

Pretreatment at 973 K leads to the disappearance of the most of above bands observed in the spectrum of initial sample, including the strongest bands at 3617, 1665 and 1007 cm^{-1}, only those at 992, 899 and near 807 cm^{-1}, although of lower intensity, still remain in the spectrum. Bands of adsorbed CO also diminish and their relative intensities have changed,
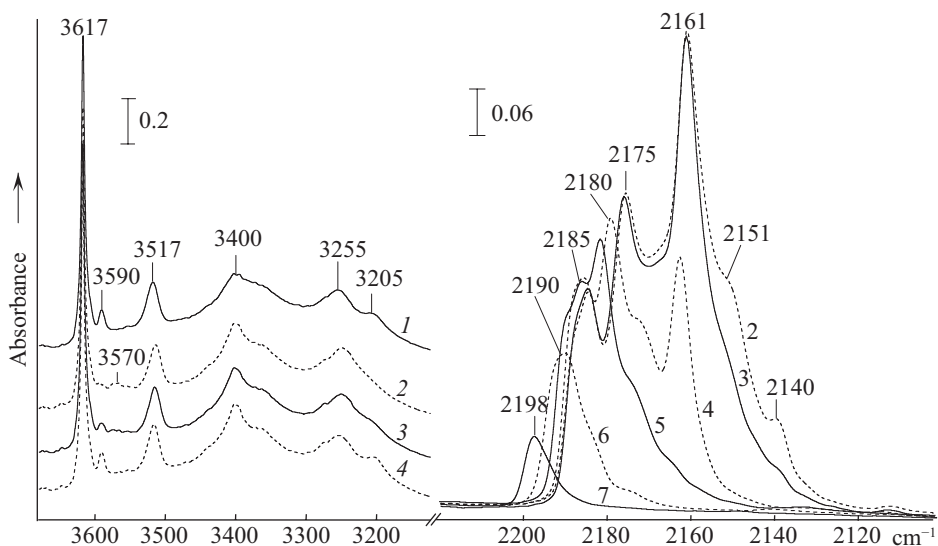
Fig. 1. IR spectra of MgF$_2$ pretreated at 773 K:
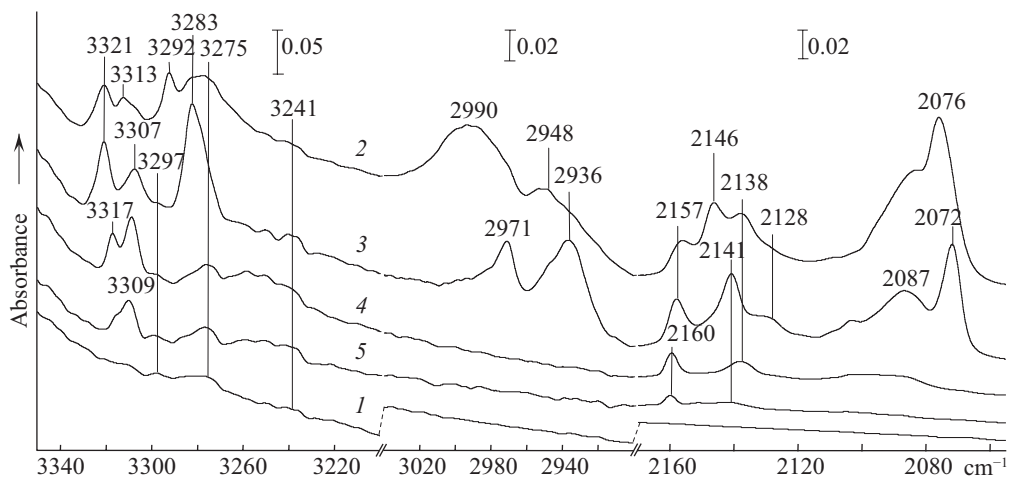*1* — before and *2–7* — after CO adsorption at different coverages

Fig. 2. IR spectra of MgF$_2$ pretreated at 773 K:
1 — before and *2–5* — after HCN adsorption at different coverages; spectra were recorded at 77 K;
HCN ($\approx 6.5 \cdot 10^{-5}$ mole/g) was adsorbed at 150 K

as compared with the spectrum of MgF$_2$ evacuated at 773 K. Maxima at 2175 and 2161 cm^{-1} become predominating while others, including those at 2185 and 2140 cm^{-1} remain as their shoulders.

2. *HCN adsorption.* HCN addition into the cell with MgF$_2$ sample at 190 K does not influence the OH band at 3617 cm^{-1}, but results in the diminution of that at 3590 cm^{-1}, and increase of bands at 3518 and 3400 cm^{-1}. Fig. 2 shows the bands of adsorbed molecules and their evolution on coverage decrease. It should be noted that the exact positions of the bands vary with the amount of adsorbate and depend on temperature that for the

spectra in the figure was fixed at 77 K. Curve *2* was obtained immediately after lowering the temperature in the presence of a dose of hydrogen cyanide with admitted helium, while curves *3–5* show the result of sequential desorption of HCN. Several groups of bands can be separated according to their stability. The first to disappear are those at 3292–3275 cm^{-1}, 2087–2072 cm^{-1} and a broad band centered at 2990–2950 cm^{-1} with a "hole" at 2960 cm^{-1}. In the difference spectra a band at about 883 cm^{-1} can also be distinguished.

As soon as the sample has been raised for 1 minute to the quartz tube kept at 298 K, great changes occur in the spectrum of adsorbed molecules. The total intensity of the bands at 2083, 2076 and 883 cm^{-1} diminishes, their maxima move to 2087, 2072 and 879 cm^{-1}, respectively. Instead of the doublet at 2146 and 2138 cm^{-1}, we have one band at 2141 cm^{-1}. Just the same, a band at 3283 cm^{-1} replaces the doublet at 3292 and 3277 cm^{-1}. Intensity redistribution occurs within the 3321–3307 and 2990–2950 cm^{-1} doublets, while the maxima of these bands become shifted to some extent.

With further coverage decrease the intensities of the bands diminish up to their final disappearance after prolonged evacuation at 300 K. The first to disappear are the bands at 2990–2936, 2072 and 883 cm^{-1}. Then, those at 3281 and 2141 cm^{-1} are gone. The last bands, still visible after 20 min of desorption at 300 K (Fig. 2, curve *5*), are those at 3309 cm^{-1} and a weak maximum at 2160 cm^{-1}.

3. Competitive adsorption of HCN and CO. To identify the sites of HCN adsorption an experiment with CO and HCN co-adsorption on MgF_2 has been carried out. A doze of HCN was first admitted to the sample at 193 K, then the cell was cooled to 77 K and He was added. After registering the spectrum about 5 torr of CO was introduced into the cell and the dependence of spectrum on the amount of adsorbed HCN was studied. For that, the sample was raised to the warmer part of the central tube of the closed cell for progressively increasing time. The desorbing HCN was trapped on the walls of the cold part of the cell, while CO remained in gas phase, and after placing the sample back between the cold windows occupied the liberated sites. The results are shown in Fig. 3.

As seen from the figure, the bands at 2198–2187 and 2140 cm^{-1} that are clearly seen in the spectrum of CO adsorbed on pure sample (curve *1*) do not arise at all after adsorption of carbon monoxide on the sample exposed to HCN, while the intensity of the 2175 cm^{-1} band is seriously lowered. Short heating of the sample up to 300 K removes most of HCN molecules absorbing near 2100 cm^{-1} and a great deal of those which account for absorption near 2130 cm^{-1} This causes the growth of the 2175 cm^{-1} band of CO together with its shoulder at 2182 cm^{-1}. After removal of weakly bonded CO (curve *4*) the 2150 cm^{-1} band disappears, while the maximum of 2175 cm^{-1} band moves further, finally up to 2186 cm^{-1}.

4. Adsorption of isotopically substituted HCN. DCN adsorption was studied on a sample of MgF_2 deuterated by threefold D_2O adsorption-pumping cycles at 300 K, followed by final evacuation at 773 K or 973 K. The results are presented in Fig. 4. Bands in the region of stretching C-H vibration (3320–2900 cm^{-1}) due to the presence of admixed HCN are identical to those of pure HCN adsorbed at the same conditions, while weak bands of stretching C-D modes superimpose with the strong bands of OD groups. That is why we show only the region of C-N stretching mode, where a correspondence between the bands of usual and deuterated molecules can be seen.

The band of weakly bound form at 2076 cm^{-1} corresponds to comparatively sharp maximum at 1834 cm^{-1}. Broader band at 2085 cm^{-1} correlates with even broader absorption around 1855 cm^{-1}. Instead of the triplet at 2156, 2146 and 2138 cm^{-1}, we have a group of bands at 1968, 1955 and 1942 cm^{-1}, while two maxima, which remain at lowest coverages at 2160 and 2138 cm^{-1}, correspond to those at 1968 and 1951 cm^{-1}. At high coverages
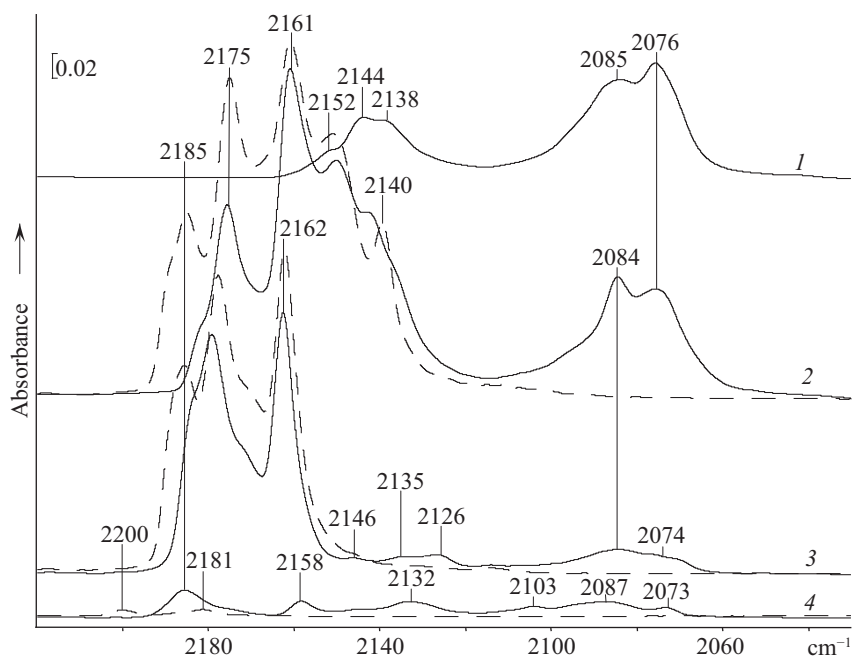
Fig. 3. IR spectra of CO adsorbed on the MgF$_2$ surface with pre-adsorbed HCN (solid line):
1 — after HCN adsorption; *2* — after next CO adsorption; *3, 4* — at different HCN and CO coverages;
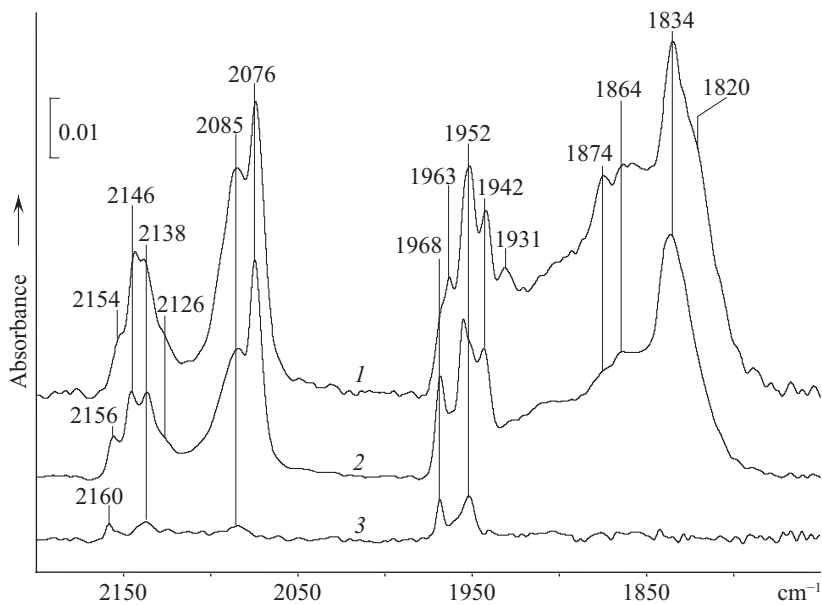IR spectra of CO adsorbed on pure MgF$_2$ surface at the same conditions are presented by dashed lines

Fig. 4. IR spectra of HCN/DCN adsorbed on MgF$_2$ pretreated at 773 K at different HCN
coverages:
spectra were recorded at 77 K; HCN/DCN was adsorbed at 150 K

two more bands can be distinguished at 2540 and 2482 cm^{-1} between the peaks of OD groups simultaneously with those of HCN at 2990 and 2948 cm^{-1}. Thus, all the bands in the 2160–2070 cm^{-1} region have their analogs at 1970–1800 cm^{-1} in the spectra of adsorbed DCN.

Adsorption of DCN on MgF$_2$ sample pretreated at 973 K, where surface OH-containing compounds are practically absent, leads to much simpler spectrum. The bands of residual HCN occur at 3183, 2099 cm^{-1} and a weaker one at 2141, while the corresponding DCN peaks appear at 2570 and 1905 cm^{-1} with a shoulder at 1940 cm^{-1}. No bands assignable to surface OH or OD groups or CN-ions formed as a result of dissociative adsorption were detected neither after adsorption, nor after the removal of molecularly adsorbed cyanide by short pumping at room temperature.

Adsorption of H^{13}CN with 70% isotopic enrichment (Fig. 5) results in the spectra where all the observed bands of adsorbed molecules appear in pairs corresponding to usual or substituted molecules. The bands of two isotopomers observed simultaneously in the region of C-H stretching vibrations are separated by 18–19 cm^{-1}: (3320–3302 cm^{-1}, 3318–3299 cm^{-1}; 3307 (curve *4* in Fig. 2) — 3287, 3292–3274, 3286–3268 cm^{-1}). For the C-N stretching mode the isotopic shift is 30–34 cm^{-1}: (2157–2124 cm^{-1}, 2138–2104 cm^{-1}, 2132–2098 cm^{-1}, 2071–2041 cm^{-1}). Application of ^{15}N substituted hydrogen cyanide (Fig. 6) leads to the isotopic shift values of only 2–3 cm^{-1} for the bands near 3300 cm^{-1}, while those at 2160–2075 cm^{-1} move to lower wavenumbers by 31–36 cm^{-1}. The data on band positions and frequency shifts for the studied isotopomers of HCN adsorbed on different sites of MgF$_2$ surface are summarized in Table, where for comparison the corresponding data for solid film (this work) as well as for the gaseous hydrogen cyanide are also presented.
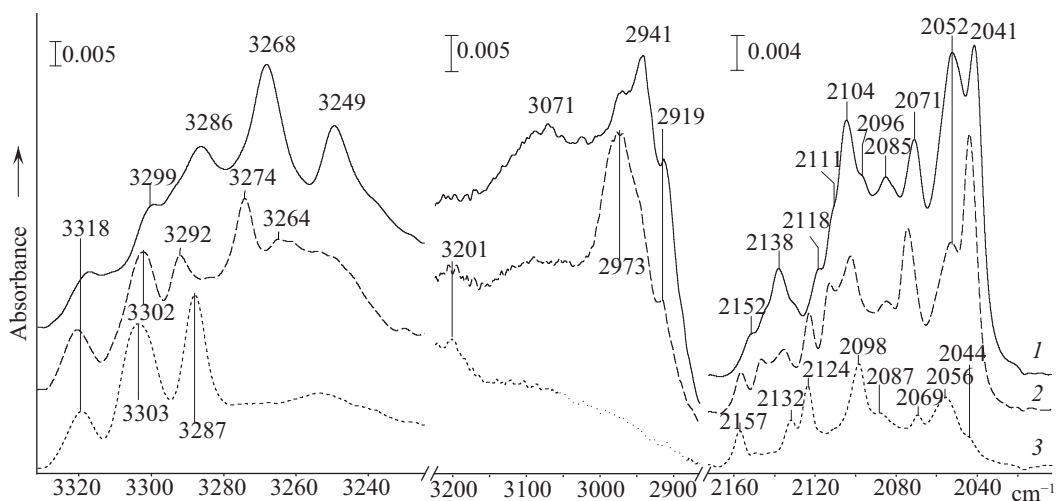

Fig. 5. FTIR spectra of H^{13}CN adsorbed on MgF$_2$ pretreated at 773 K at different coverages: spectra were recorded at 77 K; H^{13}CN (5.05 · 10^{-2} mmol/g) was adsorbed at 150 K

Discussion. *1. Surface hydroxyl groups and CO adsorption.* Spectra of the initial MgF$_2$ samples are in accordance with the earlier reported results [1–3]. However, some authors assigned distinct bands in the OH stretching region 3750–3237 cm^{-1} to different types of hydroxyl groups on the surface of MgF$_2$ microcrystals [1–4]. Others [6, 7] assign some of these bands to water molecules and distinguish adsorbed water, whose bands are
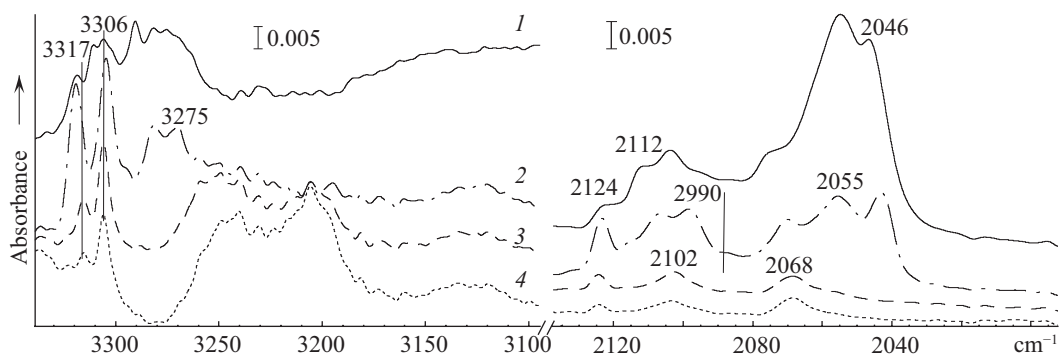
Fig. 6. FTIR spectra of $HC^{15}N$ adsorbed on MgF_2 pretreated at 773 K at different coverages: spectra were recorded at 77 K; $HC^{15}N$ was adsorbed at 150 K

Band positions and frequency shifts for HCN gas, solid film and adsorbed on MgF₂

	$H^{12}C^{14}N$	$D^{12}CN$	Δv	$H^{13}C^{14}N$	Δv	$H^{12}C^{15}N$	Δv
Gas	3312*	2629*	683	3294**	18	3310**	2
	2089*	1921*	168	2055**	34	2056**	33
Film**, 77 K	3131	2552	579	3113	18	3125	6
	2100	1888	212	2067	33	2068	32
Adsorbed on MgF₂	3317	2638	679	3303	14	3317	0
	3292	–	–	3268	24	3291	1
	3277	–	–	3249	28	3275	2
	2990	2540	450	2973	17	2990	0
	2160	1968	192	2124	36	2124	36
	2146	1942	204	2111	35	2112	34
	2138	1951	187	2098	40	2102	36
	2084	1864	220	2052	32	2055	29
	2076	1834	242	2041	35	2046	30

* [26]; ** this work.

sensitive to further adsorption (bands at 3590, 3225 and 1665 cm^{-1}), and molecules trapped in the bulk (bands at 3515, 3245 and 1650 cm^{-1}, unsensitive to water adsorption). Our data on CO adsorption enable us to discriminate the OH bands according to their behavior. Strong bands at 3617 and 1007 cm^{-1}, which are not sensitive to adsorption, should be assigned to the stretching and bending modes of OH groups, located rather in the bulk of microcrystals, apparently, replacing a part of fluorine anions. The bands at 3590 and 3205 cm^{-1}, in contrast with those bands, disappear in the presence of CO and recover together on removal of weakly bound adsorbate, and thus, belong to surface OH containing species. Presence of two bands in the stretching OH region accompanied by the band at 1665 cm^{-1}, the position quite typical of bending vibration of molecular water, enable us to associate these bands with the strongly held water molecules. This assignment is consistent with that of Wuttke et al. [7], who ascribe such bands to water molecules, which besides the coordinate bond to Mg^{2+} cation, form one or two H bonds with the neighboring F$^-$ anions.

Spectra of adsorbed CO reveal the presence of several different surface species formed on certain surface sites. The band arising at 2140 cm^{-1} in the presence of gaseous CO has its maximum slightly below the position of pure vibrational transition for CO gas (2143 cm^{-1}).

Such bands, usually assigned to physisorption, are often observed in the spectra of adsorbents with anionic centers and were shown to be due to side-on complexes of CO with surface basic sites, such as oxygen atoms of siloxane bridges or framework oxygen of basic zeolites [27], surface OH groups or of water molecules of disperse ice [28] or surface sulfur atoms of sulfides [29]. For MgF_2, these basic sites could be surface F^- ions or oxygen atoms of OH groups or water molecules.

CO interaction with the free OH groups, which is supposed above to belong to the coordinated water molecules, is evidenced by the perturbation of the 3590 cm^{-1} band in the presence of gaseous carbon monoxide. Weak H-bond of adsorbed CO with surface hydroxyls results in the low frequency shift of the O-H stretching vibration by about 90 cm^{-1} for silanol groups of silica [27] and 55 cm^{-1} for dangling OH groups of water ice [28] accompanied by the increase of band intensity. Simultaneously, the frequency of CO stretching vibration moves to higher wavenumbers up to 2160–2156 and 2153 cm^{-1}, respectively. In our case, the band assignable to the perturbed OH groups appears at 3566 cm^{-1}, shifted only by 20 cm^{-1}, while the band of weakly bound CO occurs at 2151 cm^{-1}, even lower than when adsorbed on dangling OH groups of water ice. It also disappears on the removal of CO gas, when the 3690 cm^{-1} band restores, and is less intense in the spectrum of sample dehydroxylated at 973 K. This band can be, thus reasonably assigned to CO molecules adsorbed as proton acceptors on the poorly acidic OH groups. However, we have to adopt that some contribution to the absorption near 2151 cm^{-1} can be due to molecules adsorbed on very weak cationic centers, as far as the band at about the same position, although weak, remains in the spectrum of CO adsorbed on the sample pretreated at 973 K, where the absorption of OH groups is negligible.

The position of CO band at 2165–2161 cm^{-1} is typical of molecules adsorbed on the medium-strength Bronsted acidic sites, but for MgF_2 this band remains after the restoration of the initial spectrum in the OH region and is quite intense in spectrum of dehydroxylated sample. Thus, we have to assign it to CO molecules adsorbed on the weak Lewis sites, apparently 5-coordinated Mg^{2+} cations. Other two bands which move with coverage diminution from 2175 to 2182 and from 2185 finally to 2201 cm^{-1}, are certainly due to molecules adsorbed on two kinds of stronger Lewis sites, presumably, 4- and 3-coordinated Mg^{2+} ions. The decrease of the relative intensity of the most high-frequency CO band, as well as those of bands at 2151–2140 cm^{-1} with respect to the intensities of bands at 2175–2161 cm^{-1} in the spectrum of sample pretreated at 973 K, can be interpreted as lowering of the relative concentration of defect low-coordinated Lewis sites, OH groups and the most basic F^- ions as a result of sintering and crystallization.

2. *Hydrogen cyanide.* Spectrum of a free HCN molecule in gas phase is rather simple. The bands of C-H and C-N stretching vibrations occur at 3312 and 2089 cm^{-1}, respectively, while the band of degenerated bending mode can be seen at 712 cm^{-1} [26]. To explain the observed complex spectrum of adsorbed molecules, besides the surface heterogeneity, revealed by the spectra of adsorbed CO, we have to consider different mechanisms of adsorption.

There are various ways of HCN interaction with the surface of ionic solids (Fig. 7). The molecule can form coordinate bond (*1*) with cationic sites by the lone pair of nitrogen atom, which also acts as base when the molecule forms H-bond with the acidic surface OH groups (*2*). H-bond can be formed by the molecule itself via the proton of its CH group with basic oxygen ions or O atoms of basic hydroxyl groups (*3*). One can adopt also side-on interaction with the anions (*4*). Dissociative adsorption on the metal-oxygen pair sites of oxides (*5*) leads to formation of surface OH groups and CN-ions [30]. The latter can be bound to the surface via C or N atom, thus demonstrating linkage isomerism, previously established for

CO molecules. Such two forms of HCN dissociative adsorption were reported for silica [20] and alumina [22]. It should be added that HCN molecule itself exists in two isomeric forms, HCN and HNC. The latter is energetically less stable and can be spectroscopically observed only at elevated temperatures [31]. However, for the adsorbed molecules it can be not so, and HNC isomer coordinately bound via C atom with strong Lewis acid sites could happen to become energetically favorable.
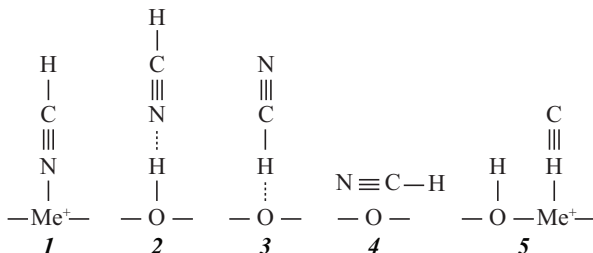
Fig. 7. Possible ways of HCN interaction with oxide surfaces

Spectral manifestations of different kinds of interaction have much in common and we often are not able to distinguish certain forms of adsorption basing only on the position of IR absorption bands. So, both coordination and H-bond lead to slight frequency increase for the CN stretching vibration, which occurs at the same wavenumbers, at about 2120–2050 cm^{-1} both for the molecule and CN-ion or radical [32]. Maybe, only for the species H-bonded via C-H group to surface oxygen atom one could anticipate a noticeable decrease of the CH stretching frequency, but the CN band of this form, apparently, should overlap with the bands of other weakly adsorbed molecules.

The data for unequivocal assignment of the observed bands could be obtained using adsorption of isotopically substituted molecules. Deuteration leads to a very large frequency shift of the CN stretching mode because of its strong interaction with the stretching CD vibration. This sensitivity to H-D substitution can be used to distinguish between molecularly adsorbed species and CN-ions, whose bands should not be affected by deuteration. Due to the high position of the CH stretching vibration (3312 cm^{-1} for HCN gas) it is not easy to discriminate between the CH bands of adsorbed HCN and NH bands of HNC isomer, supposed to be formed or stabilized on strong Lewis sites. For that, adsorption of ^{13}C- or ^{15}N-labled molecules should be helpful. Accurate measurements of isotopic shifts caused by ^{13}C- and ^{15}N-substitution can provide information about the way of coordination of CN-ions. In fact, as shown by Yates and co-workers [22], shifts of the bands due to Ti-CN and Ti-NC species on ^{13}C substitution differ by about 10 cm^{-1}, being, respectively, greater or smaller than for a free CN group, where it follows the change in the reduced mass.

The bands at 2104–2084 cm^{-1}, which are among the first to disappear on evacuation, could be due to HCN adsorbed on the OH groups or weakly coordinated to surface cations. In fact, HCN adsorption on silanol groups of silica results in the band of H-bonded molecules at 2105 cm^{-1}. Other bands of weakly bound molecules at 2990 and 2076 cm^{-1} because of the low frequency of C-H vibration could be attributed to molecules H-bonded to the surface anionic sites via the protons of CH group.

It should be noted, however, that CN-ions in inorganic cyanides absorb in the same region, about 2240–2070 cm^{-1} [32]. HCN dissociation should lead to the appearance of new OH bands that was not detected for the samples pretreated at 973 K. The data on DCN adsorption present the decisive argument for the assignment of all the bands observed in

this region after adsorption of hydrogen cyanide to different forms of molecular adsorption. In fact, all the bands of adsorbed HCN in this region were found to have their analogs in the spectra of DCN shifted downwards by 168–242 cm^{-1}. High sensitivity of C-N stretching mode to deuteration has two reasons. First, due to high frequency of C-H and C-D vibrations as compared with that of C-N mode, the CH or CD groups move with respect to N atom together as an atom with the mass 13 or 14, respectively. This leads to the increase of the reduced mass, and hence, a frequency shift. The latter, however, in this case should not exceed 40 cm^{-1}. Much greater isotopic effect is caused by strong interaction between C-D and C-N stretching modes in a linear molecule, leading to mutual repulsion of the frequencies of the two normal vibrations. As a result, the ratio of C-H and C-D stretching frequencies is smaller, while for the C-N vibration is greater than it follows from the reduced masses of corresponding diatomics. This effect is particularly strong for the case of molecules H-bonded to the surface anions, where the C-H frequency is already lowered due to the hydrogen bond. It is, thus not by chance that for this form of adsorption the shift of vCN band on deuteration is extremely large, from 2076 to 1834 cm^{-1} and the shift of C-H band at about 2990 to 2540 cm^{-1} (see Table) is small as compared with the bands of other HCN species.

One more peculiarity of this form of adsorption is in the shape of the vCH band (curves *2* and *3* in Fig. 2) that is split by a "hole" at 2960 cm^{-1}. This phenomenon is rather typical of the contours of the X-H bands in the case of strong hydrogen bonds. So called "Evans' holes" arise due to Fermi resonance with the combinations of low frequency vibrations in the H-bonded complexes. In our case the combination of 2076 cm^{-1} with the 883 cm^{-1} mode gives almost exactly 2960 cm^{-1}.

Another band of weakly bound molecules at 2084 cm^{-1} together with the accompanied peak at 3292 cm^{-1} and, perhaps also at 3283 cm^{-1}, are rather due to molecules adsorbed on surface OH groups, since these bands are absent in the spectra of sample pretreated at 973 K, where no bands of surface hydroxyls were detected. Stronger held HCN species with sharp CH bands at 3321–3307 cm^{-1} and the bands of C-N vibrations at 2160–2128 cm^{-1} should be assigned to molecules bound to the coordinately unsaturated surface Mg^{2+} cations. This is supported by the data on competitive HCN and CO adsorption. In fact, removal of HCN leading to the decrease of these bands results in the intensity increase of the bands at 2185 and 2175 cm^{-1} due to CO molecules adsorbed on Mg^{2+} sites with different coordination number.

The question about possible appearance of isomeric HNC molecules coordinately bound to MgF_2 surface can be cleared up with the help of the data on the adsorption of ^{13}C and ^{15}N substituted molecules. As seen from Table, for all the observed bands in the 3320–2900 cm^{-1} region the shifts caused by ^{15}N substitution do not exceed 2 cm^{-1}, while those caused by $H^{13}CN$ adsorption are between 14 and 28 cm^{-1}. This means that all these bands are due to the C-H stretching modes of HCN molecules coordinated to Mg^{2+} ions via nitrogen.

Conclusions. FTIR spectra of MgF_2 pretreated at 773 or 973 K, as well as those of CO adsorbed at 77 K on the material are in accordance with the results of earlier studies and provide evidence for the existence of surface OH containing species and cationic electron-accepting (Lewis acid) sites of several kinds. The study of HCN interaction with MgF_2 reveals a complex picture of plenty different adsorbed species. Weakly bound molecules form H-bond with surface OH-groups or interact with surface anions, presumably F-ions, via hydrogen bond of CH-group as a proton donor. The data of DCN adsorption supports this result and testify for the absence of dissociative adsorption in agreement with the data on the sample pretreated at 973 K. Adsorption of $H^{13}C^{14}N$ and $H^{12}C^{15}N$ has shown that

hydrogen cyanide does not undergo isomeric transition with the formation of HNC species coordinately bonded to strong Lewis sites.

References

1. Wojciechowska M. Hydroxyl groups on the surface of magnesium fluoride. *Bull. Acad. Polon. Ser. Sci. Chim.*, 1981, vol. 29 (11–12), pp. 531–547.

2. Wojciechowska M., Fiedorov R. Surface chemistry of porous magnesium fluoride. *J. Fluorine Chem.*, 1980, vol. 15, pp. 443–452.

3. Wojciechowska M. Modification of magnesium fluoride surface by impregnation with oxo-acid. *Bull. Acad. Polon. Ser. Sci. Chim.*, 1981, vol. 29 (11–12), pp. 549–562.

4. Wojciechowska M., Czajka B., Pietrowski M., Zielinski M. MgF_2 as a non-conventional catalytic support. Surface and structure characterization. *Catal. Lett.*, 2000, vol. 66, pp. 147–153.

5. Wuttke S., Scholz G., Rudiger S., Kemnitz E. Variation of sol—gel synthesis parameters and their consequence for the surface area and structure of magnesium fluoride. *J. Mater. Chem.*, 2007, vol. 17, pp. 4980–4988.

6. Wuttke S., Coman S. M., Scholz G., Kirmse H., Vimont A., Daturi M., Schroeder S. L. M., Kemnitz E. Novel sol—gel synthesis of acidic $MgF_{2-x}(OH)_x$ materials. *Chem. Eur. J.*, 2008, vol. 14, pp. 11488–11499.

7. Wuttke S., Vimont A., Lavalley J.-C., Daturi M., Kemnitz E. Infrared investigation of the acid and basic properties of a sol—gel prepared MgF_2. *J. Phys. Chem. (C)*, 2010, vol. 114 (11), pp. 5113–5120.

8. Wojciechowska M., Zielinski M., Pietrovski M. MgF_2 as a non-conventional catalyst support. *J. Fluorine Chem.*, 2003, vol. 120, pp. 1–11.

9. Wojciechowska M., Haber J., Lomnicki S., Stoch J. Structure and catalytic activity of double oxide system: Cu—Cr—O supported on MgF_2. *J. Mol. Catal. (A)*, 1999. vol. 141 (1–3), pp. 155–170.

10. Negoi A., Wuttke S., Kemnitz E., Macovei D., Parvulescu V. I., Teodorescu C. M., Coman S. M. One-pot synthesis of menthol catalyzed by a highly diastereoselective Au/MgF_2 catalyst. *Angew. Chem. Int. Ed.*, 2010, vol. 49, pp. 8134–8138.

11. Wojciechowska M., Pietrowski M., Lomnicki S. Novel supported catalyst for hydrodesulfurization reaction. *Chem. Commun.*, 1999, pp. 463–464.

12. Malinowski A., Juszczyk W., Pielaszek J., Bonarowska M., Wojciechowska M., Karpinski Z. Magnesium fluoride as a catalytic support in hydrodechlorination of CCl_2F_2 (CFC-12). *Chem. Commun.*, 1999, pp. 685–686.

13. Wojciechowska M., Pietrowski M., Czajka B. New supported ruthenium catalyst for hydrodesulfurization reaction. *Catal. Today*, 2001, vol. 65 (2–4), pp. 349–253.

14. Wojciechowska M., Fiedorov R., Kania W. Wlasnosci powierzchni i aktywnosc katalityczna fluozku magnezu. *Chemia Stosowana*, 1977, vol. 21 (3–4), pp. 431–439.

15. Coman S. M., Parvulescu V. I., Wuttke S., Kemnitz E. Synthesis of vitamin K_1 and K_1-chromanol by Friedel — Crafts alkylation in heterogeneous catalysis. *Chem. Cat. Chem.*, 2010, vol. 2 (1), pp. 92–97.

16. Candua N., Wuttke S., Kemnitz E., Coman S. M., Parvulescua V. I. Friedel — Crafts alkylations on nanoscopic inorganic fluorides. *Appl. Cat. (A)*, 2011, vol. 391 (1–2), pp. 169–174.

17. Szanyi J., Kwak J. H., Peden C. H. F. The catalytic chemistry of $HCN + NO_2$ over Na- and Ba—Y, FAU: An in situ FTIR and TPD/TPR study. *J. Phys. Chem. (B)*, 2005, vol. 109, pp. 1481–1490.

18. Gerakines P. A., Moore M. H., Hudson R. L. Ultraviolet photolysis and proton irradiation of astrophysical ice analogs containing hydrogen cyanide. *Icarus*, 2004, vol. 170, pp. 202–213.

19. Kozirovski Y., Folman M. Infra-red spectrum and surface polymerization of adsorbed HCN. *Trans. Faraday Soc.*, 1964, vol. 60 (9), pp. 1532–1538.

20. Morrow B. A., Cody I. A. Infra-red studies of reactions on oxide surfaces. Part 3. HCN and C_2N_2 on silica. *J. Chem. Soc. Faraday Trans. I*, 1975, vol. 71, pp. 1021–1032.

21. Rasko J., Bansagi T., Solymosi F. HCN adsorption on silica and titania supported Rh catalysts studied by FTIR. *Phys. Chem. Chem. Phys.*, 2002, vol. 4 (14), pp. 3509–3513.

22. Kim S., Sorescu D. C., Yates J. T., Jr. Infrared spectroscopic study of HCN adsorption on clean and triethylenediamine-precovered γ-Al_2O_3: Competition with triethylenediamine for adsorption sites. *J. Phys. Chem. (C)*, 2007, vol. 111 (49), pp. 18226–18235.

23. Kozirovski Y., Folman M. Infrared spectrum and spectral shifts of HCN adsorbed on evaporated alkali halides. *Trans. Faraday Soc.*, 1966, vol. 62 (4), pp. 808–820.

24. Tsyganenko A. A. Variable temperature IR spectroscopy in the studies of oxide catalysts. *Topics in Catalysis*, 2013, vol. 56 (11), pp. 905–913.

25. Dobrotvorskaia A. N., Pestsov O. S., Tsyganenko A. A. Lateral interaction between molecules adsorbed on the surfaces of non-metals. *Topics in Catalysis*, 2017, vol. 60 (19–20), pp. 1506–1521.

26. Sverdlov L. M., Kovner M. A., Krainov E. P. *Vibrational Spectra of Polyatomic Molecules.* New York, Wiley. 1972.

27. Tsyganenko A. A., Kondratieva E. V., Yanko V. S., Storozhev P. Yu. FTIR study of CO adsorption on basic zeolites. *J. Mater. Chem.*, 2006, vol. 16, pp. 2358–2363.

28. Rudakova A. V., Sekushin V. N., Marinov I. L., Tsyganenko A. A. The preparation and IR spectroscopic testing of surface of pure water ice and icy mixtures with prussic acid and ammonia. *Langmuir*, 2009, vol. 25 (3), pp. 1482–1487.

29. Tsyganenko A. A., Can F., Travert A., Maugé F. FTIR study of unsupported molybdenum sulfide — *in situ* synthesis and surface properties characterization. *Appl. Catal. (A)*, 2004, vol. 268 (1–2), pp. 189–197.

30. Tsyganenko A. A., Chizhik A. M., Chizhik A. I. A FTIR search for linkage isomerism of CN-ions on oxides and zeolites. *Phys. Chem. Chem. Phys.*, 2010, vol. 12 (24), pp. 6387–6395.

31. Maki G., Sams R. L. High temperature, high resolution infrared spectral measurements on the HNC—HCN equilibrium system. *J. Chem. Phys.*, 1981, vol. 75 (9), pp. 4179–4182.

32. Nakamoto K. *Infrared and Raman spectra of inorganic and coordination compounds.* 4^{th}ed. New York; Chichester; Brisbane; Toronto; Singapore, J. Willey & Sons. 1986A.

К о н т а к т н а я и н ф о р м а ц и я

Aida V. Rudakova — PhD; e-mail: arudakova@mail.ru
Roman A. Belykh — post-graduate student; e-mail: beroal.mail@gmail.com
Alexey A. Tsyganenko — Dr. Sci. in Physics and Mathematics, Professor; e-mail: atsyg@yandex.ru

Рудакова Аида Витальевна — канд. хим. наук; e-mail: arudakova@mail.ru
Белых Роман Александрович — аспирант; e-mail: beroal.mail@gmail.com
Цыганенко Алексей Алексеевич — д-р физ.-мат. наук, проф.; e-mail: atsyg@yandex.ru