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Infrared study of adsorption and transformations of hydroazide acid on aerosil

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The spectra of hydrazide acid HN_3 adsorbed on the surface of aerosil SiO_2, the effect of coadsorbed molecules of 2,6-dimethylpyridine C_7H_9N and sulfur dioxide SO_2, as well as the effect of resonant laser IR radiation at the frequency of stretching vibration of the molecule on the protonation reaction of adsorbed 2,6-dimethylpyridine were studied using IR Fourier spectroscopy at $-196\,^{\circ}C$–$+20\,^{\circ}C$.

Keywords: adsorption, aerosil, hydroazide acid HN_3, IR spectroscopy, resonance IR excitation, hydrazoic acid, hydrogen azide.

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Introduction

The idea of using resonant laser excitation to selectively initiate various processes in molecular systems has long attracted the attention of specialists [1]. Unlike the gas phase, where the activation energy of homogeneous chemical reactions, as a rule, exceeds the energy of quanta of infrared (IR) radiation, and anharmonicity prevents resonant excitation of molecules to high energies via multiphoton excitation, heterogeneous systems seem more promising for carrying out such processes [2]. Indeed, a solid, acting as a catalyst, lowers the activation energy of chemical reactions with respect to homogeneous systems, and the often observed decrease in anharmonicity along with a broadening of absorption bands increases the probability of multiphoton excitation. Analysis of the factors preventing the selective initiation of targeted changes in the layer of adsorbed molecules [3] allowed us to formulate a number of requirements for the systems under study, among which one of the most important is the irreversibility of the changes. This requirement is satisfied by the reactions of adsorbed unstable molecules such as ozone, an attempt at selective decomposition or ozonolysis involving certain isotopic O_3 modifications was recently undertaken by the authors of this work [4]. Despite the successful detection of a redistribution of the absorption band intensities of adsorbed molecules of different isotopic compositions caused by the resonant excitation of certain isotopic modifications, it should be recognized that the choice of ozone is far from optimal for achieving this task. Indeed, the absorption band of the combinaton vibration $\nu_1 + \nu_3$, at the frequency of which the excitation was carried out, has a low intensity, and the amount of absorbed radiation energy turns out to be very small. At the same time, the frequencies of the component vibrations ν_1 and ν_3 are close to the frequencies of the phonons of the oxide lattice, which causes a high probability of energy transfer to the lattice, and the high intensity of the bands of these vibrations not only further increases this probability, but also promotes the process of energy exchange between adsorbed molecules of different isotopic composition.

It is attractive to choose a molecule with a sufficiently high frequency of the fundamental vibrational transition, while not completely stable. One of such molecules is hydroazide acid HN_3, which is successfully used for nitriding the surface of semiconductors and metals such as monocrystalline silicon [5,6], GaAs [7], Ge(100) [8], Al(111) [9], Ga [10].

Hydroazide acid has certain advantages over ozone for experiments with surface processes caused by resonant laser excitation. It has strong bands of fundamental vibrations in the relatively high-frequency range of about 3300 and $2150\,cm^{-1}$, which is quite far from the lattice vibrations of most adsorbents. Thus, the fraction of absorbed light is greater, and the dissipation of vibration energy by exchanging it for lattice vibrations is less efficient compared to the O_3 molecule. The exchange of vibrational excitation energy in the layer of adsorbed molecules occurs due to the resonant dipole-dipole interaction at the vibration frequencies most intense in the absorption spectra [11]. If, with similar surface coverage values, the efficiency of such an exchange for ozone and HN_3 is comparable, then for the latter it can be significantly reduced by lowering surface coverage without significant decrease of the share of absorbed radiation.

The infrared spectra of HN_3 have been studied repeatedly, starting with the first works on spectra in the gas phase [12], and later in the nitrogen matrix [13,14]. The dependence of the spectra on the acid concentration in the matrix enabled one to distinguish the bands of the monomer and the hydrogen-bonded HN_3 dimer [13]. The effect of deuteration and nitrogen isotopic substitution on the matrix

spectrum was studied and frequency shifts on substitution of different nitrogen atoms in the acid molecule were determined [14]. A study of the spectrum of its ammonium salt NH_4N_3 has shown that ammonium azide exists in the form of fragments NH_4^+ and N_3^-, interconnected by a hydrogen bond [15]. The stretching vibration frequencies of the N_3^- ion were found to be 2077 and 1346 cm^{-1}.

The effect of ultraviolet (UV) irradiation on HN_3 molecules in inert matrices [16] and CO_2 [17] was studied. It has been shown that multiphoton excitation by the IR laser leads to dissociation with the formation of radicals [18]. Irradiation at the frequencies of the overtones of the N−H vibration in the gas phase can also cause dissociation of molecules with the formation of NH and N_2 radicals [19].

Data on the spectra of adsorbed HN_3 are extremely limited. Thoms and Russell [20] studied the HN_3/C(100) (diamond) system using the HREELS method. On the surface of hydrated diamond at −173°C, the acid was adsorbed molecularly (characteristic bands 2150, 1180 cm^{-1}) and desorbed without reaction at temperatures below 0°C. At −173°C on the dehydrated surface, the acid was adsorbed with dissociation through the $N_3^- + H^+$ channel (characteristic band at 2100 cm^{-1}). Using IR Fourier spectroscopy of the NaCl single crystal surface, Heidberg [21] showed that hydroazide acid decomposed under UV irradiation to form ammonium azide ($NH_4^+N_3^-$). In [22] Carlo et al. studied adsorption of HN_3 on polycrystalline gold and amorphous ice as a function of temperature and X-ray irradiation using the RAIRS and XPS methods. Bands at 2153 and 3098 cm^{-1} were initially observed on HN_3/Au adsorption. Annealing of HN_3 adsorbed on Au led mainly to molecular desorption of HN_3, whereas in the HN_3/ice system, where bands 2043, 2170 cm^{-1} were observed after desorption, annealing of the surface was accompanied by the appearance of bands at 3143, 3029 and 2855, 2054 cm^{-1}. The authors attributed the observed bands to the newly formed $NH_4^+N_3^-$ compound. In [23], the HN_3/TiO_2 system (a film of nanoparticles) was studied using the FTIR method. In experiments, the effects of HN_3 dosage, UV irradiation time and surface annealing temperature were studied. In addition, model quantum chemical calculations of the TiO_2 cluster with an adsorbed molecule were performed, including information on optimized geometric structures, adsorption energies, and vibration frequencies of the adsorbed acid.

In this work, we investigated the adsorption of HN_3 by low-temperature IR spectroscopy on SiO_2 aerosil, on the surface of which there are no cationic centers and the adsorption sites are silanol groups, the frequency shift of which on adsorption can be considered as a measure of the basicity of adsorbate molecules. Their acidic properties may be enhanced by hydrogen bonding with previously adsorbed base molecules, such as 2,6-dimethylpyridine (DMP), as a result of the interaction of acid molecules with the oxygen of silanol groups [24]. Thus, CO_2 causes a slight additional decrease in the frequency of OH groups perturbed by the H-bond, whereas the addition of SO_2 leads to the transfer of the proton of hydroxyl group to the molecule of base, thereby revealing the effect of induced Bronsted acidity [25]. Dimethylpyridine is the most convenient base for studying this phenomenon, since its aromatic ring vibrations ν_{8a} and ν_{8b} are very sensitive to interaction with different surface sites [26]. While in the spectrum of liquid they are observed at 1594 and 1580 cm^{-1}, formation of H bond with silanol groups shifts them to 1606 and 1585 cm^{-1}, and the transfer of proton to the DMP molecule causes them to shift beyond the absorption region of a neutral molecule to 1655 and 1629 cm^{-1}, respectively. This allows the use of HN_3 adsorption on a sample with pre-adsorbed DMP to evaluate the acidic properties of hydroazide acid and to investigate the possibility of accelerating the process of protonation of DMP by the action of resonant excitation of vibrations of adsorbed HN_3 molecules. One would expect that the excitation of high vibrational states will lead to the dissociation of a part of molecules, and experiments have been undertaken on the effects of IR excitation on HN_3 molecules in the absence of other adsorbed molecules.

Experimental

A low-temperature cell [27], which allows thermal vacuum treatment of samples at temperatures up to 900°C and recording the spectra at −196°C in the presence of gas without violating thermal insulation, was used to study the spectra of adsorbed hydroazide acid. The spectra were recorded using a Nicolet 710 IR Fourier spectrometer with a coolable MCT detector, and in experiments with IR irradiation using an IR-Prestige-21 spectrometer (Shimadzu, Japan), which has a hole in the housing for the entrance of the beam. The MIRcat Tunable Mid-IR External Cavity Laser System (Daylight Solution, USA) was used to irradiate the samples. Two modules are built into the laser, allowing to adjust the radiation frequency in the range from 1990 to 2330 cm^{-1}. The laser was used in a pulsed mode with a pulse frequency of 1 MHz with a pulse duration of 100 ns. The average laser power was about 45 mW. The pressure was measured using Barocel absolute membrane.capacity sensors (Edwards, Great Britain) with measurement limits 0.1−1000 and 0.001−10 Torr.

The aerosil A-300 with a specific surface area of 280 m^2/g was studied. The samples were pressed into tablets with a „thickness“ of about 20 mg/cm^2, inserted into a stainless steel holder and subjected to thermal vacuum treatment at 500 or 700°C. Hydroazide acid was obtained by the reaction of sodium nitride with 70% sulfuric acid in an evacuated glass installation, where several milligrams of sodium azide were placed in advance, and brought into contact with a drop of sulfuric acid without disturbing the vacuum. The released gas was frozen with liquid nitrogen and purified by pumping fractions, volatile at temperatures below −120°C (N_2, CO_2, N_2O).

Results

The changes observed in the aerosil spectrum after HN_3 adsorption are shown in Fig. 1. In the spectrum of the initial sample after thermovacuum treatment, there is a band of unperturbed silanol groups at 3750 cm^{-1}. After adding HN_3 at −80°C, its intensity decreases slightly and a number of new bands appear at 3290, 2150 and 2050 cm^{-1}, as well as two broad bands at 3460 and 3175 cm^{-1}, the maximum of the latter shifts towards low frequencies with decreasing temperature, reaching 3150 cm^{-1} at −196°C. It should be noted that the relative intensity of these bands depends on the pre-treatment temperature of the sample. In the spectrum of a sample evacuated at 500°C, the 3460 cm^{-1} band is lost on the slope of the lower frequency band, but it is more intense after sample pretreatment at 700°C (curve *6*). As the amount of adsorbate increases, the intensity of these bands increases simultaneously with the growth of two weak bands at 1290 and 950 cm^{-1} at the edges of the adsorbent's own absorption region. Unlike the other bands, the peak intensity growth at 2050 cm^{-1} soon stops, without detecting correlations with the intensity of other bands. In the overtone region, it is possible to observe a very weak band at 4272 cm^{-1}, the intensity of which is about 1.2% of that of the 2150 cm^{-1} band. Desorption of HN_3 with a gradual raising the sample temperature to ambient leads to the removal of all bands and restoration of the original spectrum of the sample, without revealing noticeable differences in the stability of the corresponding surface compounds.

In agreement with the results of [25], bands at 1606 and 1585 cm^{-1} are present in the spectrum of DMP adsorbed on aerosil (Fig. 2). They belong to the vibrations of aromatic ring of molecules hydrogen.bonded to silanol groups, the band of which disappears at 3750 cm^{-1}, and instead a broad band with a maximum at about 2950 cm^{-1} appears. With the excess of DMF, one can also see a band of weakly bound molecules at 1595 cm^{-1}, which disappears after the removal of adsorbate vapor by short-term pumping. After inserting HN_3 at −90– – 80°C, the intensity of the DMP bands gradually decreases and bands grow at 1656, 1629 cm^{-1}, an intense band at 2045 cm^{-1} and a band with a maximum at 2136 cm^{-1} with a shoulder at 2147 cm^{-1}. As the group of new bands grows, the intensity of the shoulder at 2147 cm^{-1} increases, while the band at 2136 cm^{-1} becomes less intense.

Cooling of the sample to −196°C stops the observed changes in the spectrum, while the bands 1606 and 1585 cm^{-1} remain quite intense, despite the presence on the surface of molecularly adsorbed HN_3 with an absorption band of about 2150 cm^{-1}.

Desorption by lifting the sample into a zone with a consistently increasing temperature leads to the sequential disappearance of absorption bands at 2136 cm^{-1}, then the bands at 2147, 1656, 1629 cm^{-1} disappear, while the intensity of the 2045 cm^{-1} band decreases, the remnants of it are removed by pumping at room temperature together with the adsorbed DMP.

The acidic properties of the HN_3 molecule do not exclude its proton-accepting ability, which may be manifested by significant decrease in OH group frequency on adsorption of these molecules, similar to that observed in Fig. 1. If the silanol group forms H-bond to HN_3 as with a proton acceptor molecule, then co-adsorption of a stronger acid will lead to the strengthening of this bond, manifested in the increase in frequency shift of the O–H vibration or even to

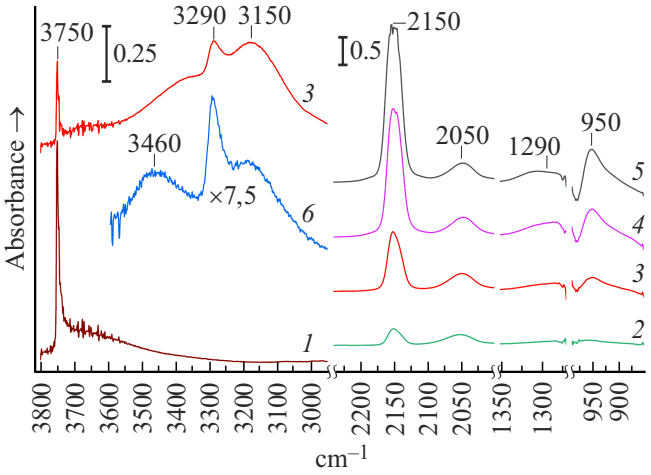


Figure 1. Infrared spectrum of SiO_2 (aerosil) after termovakuum treatment at 500°C and cooling to −196°C (*1*), in the process of adsorption of HN_3 at −86– – 82°C (*2*–*4*), cooling to −196°C (*5*) and after adsorption of HN_3 at −85°C on the sample evacuated at 700°C (*6*). From the spectra at 2200–900 cm^{-1} absorption of the initial sample (curve *1*) is subtracted.

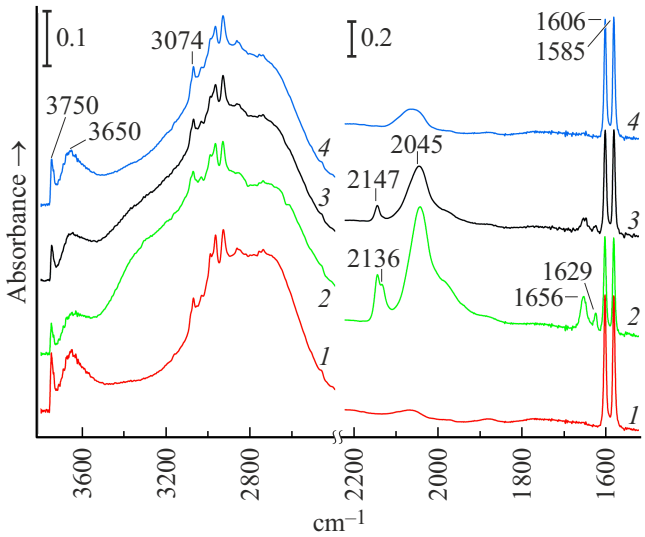


Figure 2. Infrared spectrum of SiO_2 (aerosil) after evacuation at 500°C and adsorption of DMF (*1*), addition of HN_3 at −80°C (*2*) and after short-term heating to −50°C (*3*) and 0°C (*4*). The spectra were recorded at −196°C. In the range of 2200–1500 cm^{-1} absorption of the initial sample before adsorption is subtracted.

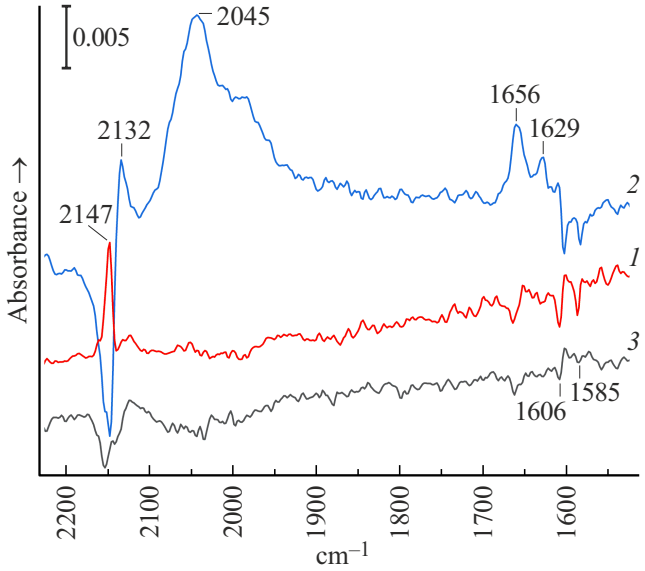
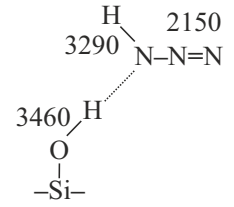
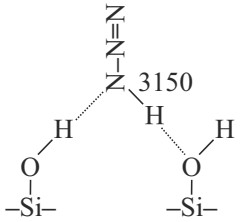


Figure 3. Changes in the IR spectrum of SiO_2 occurring at standing still for 20 min after adsorption of DMF at 20°C, addition of HN_3 at −80°C and temperature stabilization (*1*), after 30 minutes of laser irradiation at the frequency 2140–2150 cm^{-1} (*2*) and standing for the next 17 minutes (*3*). During the entire experiment, the temperature was maintained at −150°C. Each curve represents the difference between the spectra recorded at the end and beginning of the specified time interval.



Scheme 1



Scheme 2

proton transfer to the NH_3 molecule, just as the addition of HN_3 leads to protonation of DMP [24]. To verify this, an experiment was carried out on the effect of SO_2 on the spectrum of pre-adsorbed HN_3.

The spectrum of the sample thermovacuumed at 700°C after HN_3 adsorption did not differ from that shown in Fig. 1 (Curve *6*). Addition of SO_2 at −100°C does not lead to significant changes in the spectrum. New bands of perturbed OH groups appear at 3660 cm^{-1} and of adsorbed SO_2 at 1343 cm^{-1} and a weak one at 2480 cm^{-1}. The intense band of the adsorbed HN_3 shifts from 2150 cm^{-1} by 2 cm^{-1} towards high frequencies, and the weaker band from 2050 cm^{-1} shifts to 2077 cm^{-1} and gradually weakens almost to extinction at the same time as the shoulder grows at 2184 cm^{-1}. The maximum of 3460 cm^{-1} band shifts meanwhile to 3410 cm^{-1}.

An attempt to use laser radiation with a frequency in the absorption band of the adsorbed HN_3 molecules at −196°C did not lead to any noticeable changes in the spectrum. The results of a test experiment on the effect of resonant laser IR excitation upon the spectrum of co-adsorbed HN_3 and DMP are shown in Fig. 3. Each curve in the figure represents the result of subtracting two absorption spectra, registered one after a while after another. For example, curve *1* shows the changes in the spectrum that occur during 20 minutes of sample standing at −150°C after DMP and HN_3 were sequentially adsorbed at a higher temperature. Curve *2* shows the changes in the spectrum, caused by irradiation of the system with a laser for 30 min at a frequency in the range of 2140–2150 cm^{-1}. For that at the same time, as a deductible was used the same spectrum that was taken as the final one to obtain curve *1*. Similarly, curve *3*, reflects the changes when standing at a constant temperature after the end of the laser irradiation session, the spectrum obtained immediately after the session of radiation exposure was subtracted.

It can be seen from the figure that standing the sample at −150°C, when the vapor pressure of DMP and HN_3 is negligible, leads to insignificant changes in the spectrum. Significant changes, when the intensity of some bands decreases and for others increases, occur during irradiation. The observed changes could be explained by the effect of a local temperature increase under the influence of laser radiation. Indeed, in both In these cases, the intensity of the 2050 cm^{-1} bands and of dimethylpyridinium ions increases. However, for the spectra in Fig. 2, this is accompanied by the increase in the 2147 band. cm^{-1} and a decrease in intensity at 2136 cm^{-1}. Here, on the contrary, the appearance of products occurs on account of the consumption of compounds that absorb 2147 cm^{-1}.

Discussion

The changes in the spectrum of silanol groups on HN_3 adsorption, shown in Fig. 1, indicate that hydroazide acid molecules form H-bond with the proton of OH group, acting as a proton acceptor, as shown in Scheme 1. It could be assumed that Si–OH groups, perturbed by the hydrogen bond, account for a broad band with a maximum at 3150 cm^{-1}, which corresponds to very strong H-bond with a molecule of a strong base. However, this band is weak after adsorption on a sample evacuated at 700°C, where in the spectrum a band at 3460 cm^{-1} is observed. Apparently, after pumping at 500°C, the concentration of

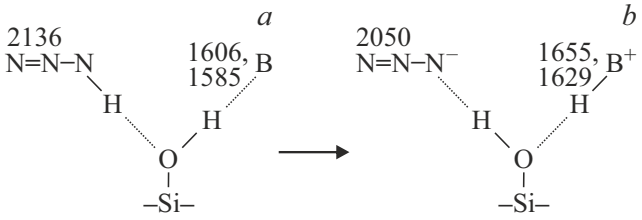
OH groups is higher, and the adsorbed molecules have more opportunities to reach by their N−H group a neighboring molecule or hydroxyl and form another H-bond (Scheme 2). Then the 3150 cm^{-1} band should be attributed to the NH groups of such molecules, perturbed by the hydrogen bond. The decrease in the OH frequency by 290 cm^{-1} may well be compared with the increase in the frequency of bending vibration from 840 cm^{-1} for free silanol groups [28] up to 950 cm^{-1}.

The bands 3290, 2150 and 1290 cm^{-1} of the spectra in Fig. 1 due to the vibrations of adsorbed HN_3 are close in position to the frequencies of gas molecules (3336, 2140, 1274 cm^{-1} [29]). The overtone band of the stretching vibration N-N 4272 cm^{-1} lies 28 cm^{-1} below the doubled frequency of the fundamental tone (4300 cm^{-1}), showing the absence of anharmonicity anomalies.

The band at 2050 cm^{-1} corresponds in position to N_3^- ion. Bands at 2058−2015 cm^{-1} are characteristic of ionic pairs of alkaline and alkaline azides-earth metals [30], and in ammonium azide, the band of the azide ion lies at 2077 cm^{-1}. Growth of this band after HN_3 adsorption on a sample with pre-adsorbed DMP, leading to the simultaneous appearance of the N_3^- anion and the dimethylpyridinium cation confirms this assignment. However, formation of N_3^- ions as a result of HN_3 adsorption on a clean aerosil surface is not entirely clear. If the proton of the acid when it dissociates attaches to the oxygen atom of the surface, one would expect the appearance of new OH groups, but we do not see this. The addition of a proton to another HN_3 molecule on charge disproportionation with the formation of N_3^- ions should simultaneously lead to the appearance of $H_2N_3^+$ cations.

The infrared spectrum of such a cation in a number of salts was obtained by the authors of [31], who established that both hydrogen atoms in such a cation are bound to the same nitrogen atom, forming an NH_2 group bound to diazote, which allowed it to be called the aminodiazonium cation. This cation is characterized by bands of stretching N−N vibration at 2319−2304 cm^{-1}, bending NH_2 vibration at 1580−1534 cm^{-1}, as well as stretching N−H mode at 3280−3110 cm^{-1}. Most of these bands overlap with the absorption of adsorbed HN_3, with the exception of the 1600−1500 cm^{-1} region, However, any bands in this region appear neither during the adsorption of HN_3 nor with the subsequent addition of SO_2. Evidence for the formation of $H_2N_3^+$ cations on SiO_2, thus, it is not detected. This is not surprising if we take into account the small shift in the frequency of Si-OH groups during the adsorption of HN_3 (290 cm^{-1}) and its slight increase (50 cm^{-1}) with the addition of SO_2 indicating weak proton-accepting ability of HN_3. It remains to assume that in the chemisorption of HN_3 onto SiO_2 with the formation of N_3^- ions involves some other surface sites, such as stressed siloxane bridges, arising on silica surface during high-temperature vacuum treatment.

Acidity of the HN_3 molecule, manifested in its ability to induce protonation of pre-adsorbed DMF, is obviously higher than that of the CO_2, which does not possess such



Scheme 3

property, and is comparable to the acidity of SO_2. Under experimental conditions, when all the silanol groups are engaged in hydrogen bonding with DMP molecules, the formation of complexes according to Schemes 1 and 2 is impossible, and the band 2136 cm^{-1} observed under these conditions should be assigned to molecules forming H-bond with oxygen atoms of the silanol groups, as shown in Schema 3, *a*. The proton accepting ability of these atoms is increased under the influence of base B (in our case, DMB) due to the phenomenon of induced basicity [32]. Simultaneously with DMP protonation the protons of acid are transferred to the oxygen atoms (Scheme 3, b), and the number such acid molecules decreases, which manifests itself in the intensity decrease of the 2136 cm^{-1} band. As the amount of protonated DMP increases, so does the concentration of N_3^- ions. Apparently, the band at 2147 cm^{-1} observed in this case is due to HN_3 molecules interacting with these ions.

The fact that even with the excess of HN_3, complete protonation of DMP, as was observed with the addition of SO_2 [25], does not occur, and a significant part of its molecules remain hydrogen-bonded, can be explained both by the lower acidity and lower mobility of the HN_3 molecules under conditions of the experiment. It is also possible that the formed surface complexes cause steric obstacles for the remaining acid molecules to approach oxygen atoms of silanol groups hydrogen bonded to DMF molecules.

Test experiments on the effect of resonant laser IR radiation on the spectrum of co-adsorbed HN_3 and DMP have shown that the protonation process can be accelerated by the action of resonant excitation of the HN_3 molecule vibrations, and the nature of the induced changes differs from occurring spontaneously when the temperature of the system increases. In the latter case, the DMP protonation process occurs due to the consumption of species responsible for the 2136 cm^{-1} band of HN_3 molecules interacting with oxygen of DMP-bound silanols, which is accompanied by deprotonation of acid molecules with the formation of N_3^- ions. The remaining molecules of adsorbed HN_3 contribute to the band 2147 cm^{-1}, whose intensity increases.

The effect of additional growth of bands of dimethylpyridinium and N_3^- ions caused by irradiation at the frequency 2140-2150 cm^{-1} and intensity decrease of the bands of hydrogen-bonded DMF at 1606 and 1585 cm^{-1} are accompanied by a sharp decrease in the 2147 cm^{-1} band

and increase of absorption at $2132\,cm^{-1}$. It evidently represents the edge of the band at $2136\,cm^{-1}$. Apparently, the irradiation somehow promotes the interaction of HN_3 with the remaining hydrogen-bonded complexes of DMP with silanol groups with further protonation of DMP and formation of N_3^- ions.

Conclusions

Spectra of HN_3 acid adsorbed on aerosil have been obtained. Along with the molecularly adsorbed HN_3, the formation of N_3^- ion is observed. The assignment of the band at $2050\,cm^{-1}$ in the spectrum of SiO_2 to the latter is confirmed by experiments on co-adsorption of HN_3 and dimethylpyridine. Addition of SO_2 to the sample with adsorbed HN_3 does not lead to the formation of $H_2N_3^+$ cations.

The effect of irradiation on the spectrum of adsorbed HN_3 is insignificant. Obviously, the energy of one quantum is not enough for dissociation with the cleavage of radicals, and multi-quantum processes are difficult because of significant anharmonicity. The influence of radiation on the spectrum of co-adsorbed HN_3 and dimethylpyridine is manifested in stimulating the formation of protonated form of the base. This reaction, occurring spontaneously under normal conditions and obviously not requiring significant activation energy, seems promising for further research.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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