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FTIR spectroscopy evidence for the basicity induced by adsorption

E.N. Storozheva, V.N. Sekushin, and A.A. Tsyganenko*

V.A. Fock Institute of Physics, St. Petersburg University, St. Petersburg, 198504, Russia

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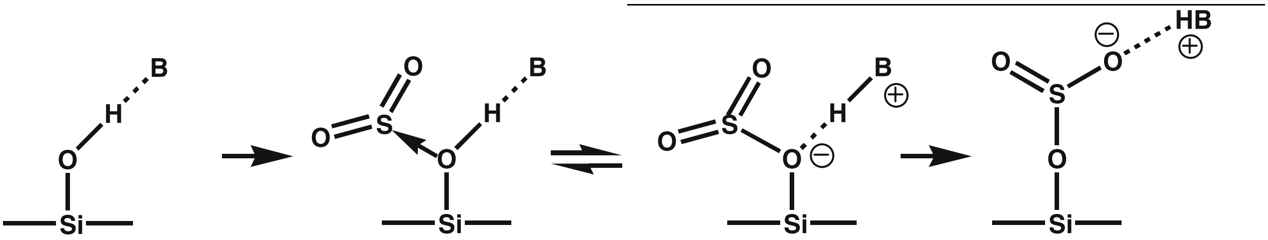
Basicity of silanol oxygen atom increases after adsorption of ammonia or pyridine, as revealed by FTIR spectra of adsorbed CHF_3 and CO_2. The same effect of "induced basicity" was observed for the dangling hydroxyl groups of ice surface with coadsorbed ethylene and fluoroform. Possible role of the induced acidity and basicity in surface chemistry is discussed.

KEY WORDS: FTIR spectroscopy; adsorption; fluoroform; basicity.

1. Introduction

Acidic and basic properties of surface sites are known to vary in the presence of adsorbed molecules. Recently, it was shown that the proton-donating ability of silanol groups of silica surface increases in the presence of SO_2 or NO_2, to such extent that they become capable to protonate coadsorbed ammonia, pyridine or dimethylpyridine [1]. The mechanism of this *adsorption induced Brønsted acidity*, includes interaction of acid with the oxygen atom of OH group according to the scheme



Scheme 1.

where B is a base. Interaction of acid with the oxygen atom of OH group leads to strengthening of the H-bond revealed in the lowering of O–H band position. For strong bases, such as ammonia or pyridine, H-bonded species with coordinately bound SO_2 are not stable and proton transfer to the base takes place.

The same scheme illustrates the increase of basic properties of the hydroxyl oxygen atom induced by the base. In fact, SO_2, a weak acid, which at 300 K reversibly interacts with SiO_2 surface, becomes chemisorbed in the presence of preadsorbed base. Thus, base interaction with the proton of OH group increases the negative charge or the basicity on oxygen atom, which could be manifested in strengthening of coordinate bond between it and Lewis acid molecule or of H-bond with the adsorbed proton-donating molecules.

Unfortunately, characterization of surface basic site strength is not an easy problem up to now. Most of Lewis acids, such as SO_3, SO_2, CO_2, either react with oxide surface with the formation of surface sulfate, sulfite or carbonate species (bisulfates, bisulfites and bicarbonates in the case of reaction with basic OH groups) or reveal weak molecular adsorption with vibrational frequencies close to those in free molecules in the gas phase. OH, NH and even most of CH proton-donating molecules dissociate on strong basic sites. It was not possible to find one test molecule, which is stable enough to be adsorbed always only in molecular form, and has certain vibrational mode sensitive to the interaction with basic sites to use the frequency shift as a measure of site basicity.

Recently fluoroform (CHF_3) was suggested as a suitable test molecule, at least, for strong basic sites [2]. Its CH bending frequency shifts gradually to higher wavenumbers with the increasing strength of H-bond with surface proton-accepting centers, while the stretching CH mode reveals more complex behavior, first demonstrating the effect of "blue shifting H-bond", when ν_{CH} frequency grows, then, after reaching its maximum value, it also starts to decrease with the increasing site basicity, as in any usual H-bond.

Among Lewis acids, carbon dioxide could provide supplementary information on surface basicity. With

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* To whom correspondence should be addressed.
E-mail: tsyg@photonics.phys.spbu.ru

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basic oxygen ions it forms carbonates of different structure [3,4], its interaction with basic OH groups of oxides leads to bicarbonate species as it was found for TiO_2 [5], Al_2O_3 [3,6], and many other oxides. With surface cations of TiO_2 [7], alumina [8] or zeolites [9,10] CO_2 forms linear complexes with increased frequency of stretching vibration mode. However, its interaction with basic oxygen of zeolite framework leads to formation of "bent" molecular complexes with C–O asymmetric stretching vibration lowered from 2149 down to about 1700 cm^{-1} [11]. When adsorbed on the surface of molybdenum sulfide, where Lewis sites are absent, the ν_{as} mode of weakly bound CO_2 also revels, although much smaller, frequency lowering (to 2326 cm^{-1}), explained by side-on adsorption on sulfur anions of basal face of MoS_2 microcrystals [12].

The aim of this work was, using CHF_3 and CO_2 as test molecules for basic sites, to detect the changes in the basicity of surface oxygen atoms of silica caused by adsorption of ammonia or pyridine. Besides silica, experiments with porous ice were also planned, to find the same effect of induced acidity and basicity. Properties of disperse ice surface are rather close to those of silica, since the main adsorption sites for both adsorbents are the OH groups, and besides interaction with protons, adsorption on oxygen atoms of the dangling OH groups is possible, as well as on surface oxygen atoms, i.e. siloxane bridges for silica or unsaturated surface oxygen atoms of ice. Dangling hydroxyl groups of water ice reveal slightly weaker frequency shifts on adsorption of weak bases, such as CO [13] or halogenated methanes [14]. In our case ethylene was tried as a base that could be put in contact with ice surface at 77 K, while the same CHF_3 and CO_2 were used as acids.

2. Experimental

For IR studies, SiO_2 pellets (aerosil, 280 m^2/g) were pretreated first in oxygen (30 min), then under vacuum (10^{-4} Torr) for 1 h at 873 K inside the IR cell, that enabled to perform adsorption and IR spectra measurements in a temperature range of 60–400 K. Details on the design and performance of the cell are given elsewhere [15]. Liquid nitrogen was used as a coolant and after its removal temperature was measured by means of a thermocouple inserted in the coolant volume. For better thermal contact between the sample and the cooled environment, about 1 Torr of helium was admitted into the sample compartment.

Bases (ammonia or pyridine) were dosed at 250–300 K after recording the background spectrum of pure silica at room temperature. Then the cell was cooled and IR spectra were registered at 77 K in the presence of He. Acids (fluoroform or carbon dioxide) were introduced into the cooled cell that was then warmed up until pressure increase and OH perturbation reveal their evaporation and adsorption. Then the cell was finally cooled to register the resulting spectrum. To observe the changes of CH stretching band of fluoroform, deuterium enriched ammonia (ND_3) was used, the sample then was preliminary deuterated by treating in D_2O vapor.

Amorphous ice film was prepared at 77 K from D_2O sputtered onto the inner ZnSe windows of the cell, cooled by liquid nitrogen. Fluoroform and ethylene adsorption experiments were carried out at 77 K. For that oxygen was condensed in the cell with the ice film, then the adsorbate (CHF_3 or ethylene and then CHF_3) was added to the flow of oxygen into the cell, and adsorption from the solution in liquid oxygen at 77 K took place and spectra of the film immersed in oxygen were registered. To get rid of the solvent effect, oxygen was then carefully pumped off and spectra were recorded again in the presence of gaseous oxygen or helium. Transmission IR spectra were recorded, typically, at 4 cm^{-1} resolution, by means of NICOLET 510 FTIR spectrometer.

3. Results

Fluoroform adsorption on pure silica results in the intensity diminution of the band of free OH groups at 3750 cm^{-1} and appearance of the band of perturbed hydroxyls that shifts from about 3725–3698 cm^{-1} with the increasing amount of adsorbate. Bands of adsorbed CHF_3 appear at 3060 and 1375 cm^{-1} (figure 1). When CHF_3 is added to silica with preliminary adsorbed ammonia, the band maximum of OH groups perturbed by H-bond with adsorbed NH_3 moves from 2990 cm^{-1} to about 2660 cm^{-1}.

Figure 1 shows the changes observed for ammonia ND_3 on deuterated silica surface, where the absorption of perturbed OH groups and NH vibrations does not

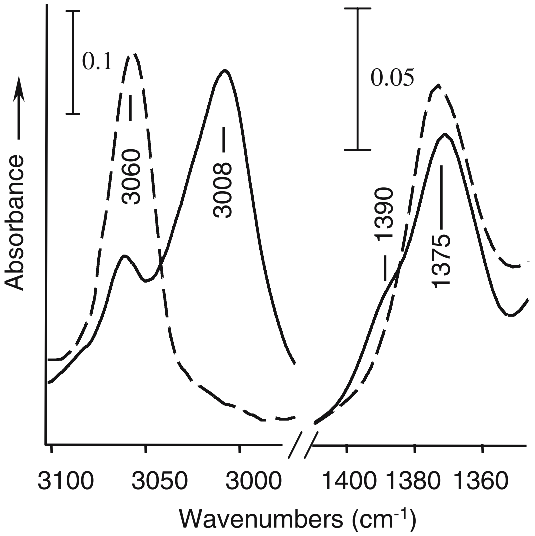

Figure 1. FTIR spectrum of fluoroform adsorbed on silica pretreated at 873 K (dash line) and on silica with preadsorbed ammonia ND_3 (solid line). Spectra are recorded at 77 K.

interfere with ν_{CH} bands of adsorbed fluoroform. In the spectrum of CHF_3 a new band appears at 3008 cm^{-1}, while those at 3060 and 1375 cm^{-1} become less intense. At the high frequency side of the latter band a shoulder 1390 cm^{-1} becomes clearly distinguished.

Adsorption of carbon dioxide on pure SiO_2 (figure 2) results in $\nu_{as}(CO)$ band at 2345 cm^{-1} and that of bending vibration at 660 cm^{-1}. At high coverages two weak narrow bands show up at 3704 and 3599 cm^{-1}, the former has a broader shoulder centered at 3715 cm^{-1}. It is noteworthy that the intensity of the free OH group band at 3750 cm^{-1} remains intact and only slightly diminishes when the bands at 3715–3704 cm^{-1} become strong enough. CO_2 adsorption on silica with preadsorbed pyridine leads to the same bands at 3704 and 3559 cm^{-1}, however, as seen from figure 2, the $\nu_{as}(CO)$ band appears at lower wavenumbers, at 2340 cm^{-1}.

Fluoroform adsorption on amorphous ice at 77 K from the solution in liquid oxygen gives rise to the bands at 3060, 3040 and 1374 cm^{-1}. The band of OD groups, which occurs initially at 2727 cm^{-1} and shifts to 2716 cm^{-1} upon O_2 condensation, moves to 2707 cm^{-1} after adsorption of CHF_3. Ethylene adsorption from liquid oxygen at 77 K results in the shift of OD band to 2660 cm^{-1}. Fluoroform addition shifts this band to 2650 cm^{-1} while in the CH stretching region a low-frequency shoulder of 3040 cm^{-1} band appears at about 3035 cm^{-1}, and one more band of bending mode arises at 1380 cm^{-1}. Attempt was made to see the influence of CO_2 onto the spectrum of adsorbed ethylene, but no visible effect was observed after its addition to liquid oxygen.

4. Discussion

Great dependence of frequency shift of OH band on coverage observed for fluoroform adsorption is typical of lateral interactions, that is in our case the influence of second molecule adsorbed on silanol group on the spectrum of molecule already bound with the same surface site. Then, one molecule acts as a proton acceptor, while another interacts with the oxygen atom of the same silanol group as a proton donor or the acceptor of electrons. Thus, the same species manifests both basic and acidic properties when interacting with surface hydroxyl group. For most of previously studied molecules the shift increase due to adsorption of second molecule is much smaller than the shift caused by the first one, evidently adsorbed as a base. E.g., for ozone or H_2S the initial shift is not less than 70% of the total one [16], for fluoroform, however, it is less than a half of total shift (25 of 52 cm^{-1}). We consider this as evidence for preferable adsorption of CHF_3 as an acid to the oxygen atom of silanol group. Then, energetically less favorable interaction of second molecule as a base with the proton of silanol group accounts for the great additional shift. Thus, fluoroform acts rather as an acid than as a base in its interaction with silica surface, and its high acidity explains unusually great additional shift of the band of silanols perturbed by ammonia. Its displacement by 330 cm^{-1} (from 2990 up to 2660 cm^{-1}) is much greater than for CO_2 (50 cm^{-1}) or ozone (236 cm^{-1}) [16], although proton transfer does not take place, as in the case of SO_2 coadsorbed with ammonia.

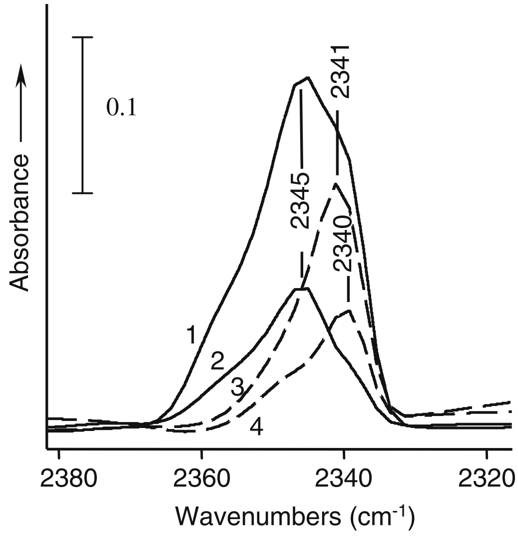

Figure 2. FTIR spectrum of CO_2 adsorbed at two different surface coverages on silica pretreated at 873 K (1, 2) and on silica with preadsorbed pyridine (3, 4). Spectra are recorded at 77 K.

Weak perturbation of silanol band of pure silica by CO_2 can also be explained by its preferential adsorption as an acid on the oxygen atom of silanol group. In fact, very small frequency shift without intensity increase of the OH band, is not characteristic even of weak hydrogen bond. Linear complex of CO_2 with the proton should rather lead to increase of $\nu_{as}(CO)$ frequency, as in the case of σ-complexes with the cations, as it was seen in surface complexes with L-sites [7–10] but here the band position is slightly lowered.

Changes in the spectra of adsorbed fluoroform, caused by preadsorbed base are in complete agreement with those anticipated for molecules adsorbed on basic sites with increased basicity. Indeed, the increased up to 1390 cm^{-1} frequency of δ_{CH} mode (1375 cm^{-1} in the spectrum of gaseous CHF_3 [17]) as well as the position of ν_{CH} band at 3008 cm^{-1}, lower than for gaseous CHF_3 (3035 cm^{-1}), indicate of a high basicity of new electron-donating centers created by adsorbed bases, almost as strong as those of NaX zeolite, MgO or CaO surface. Decreased intensity of initial bands is consistent with the proposed assignment, since adsorption of bases does not create new sites, but only enhances the strength of already existing basic sites. Weaker sites that still remain on the surface, where almost all the silanol groups are perturbed by ammonia or pyridine, can naturally be associated with surface siloxane bridges, whose basicity is close to that of silanol groups of pure silica and does not change much in the presence of bases. Different intensity ratios of the bands of CHF_3 adsorbed on the initial sites and those induced by ammonia adsorption in CH stretching and bending regions, shown in figure 1 should be explained by strong increase of extinction coefficient of stretching mode with ν_{CH} frequency lowering.

Data on CO_2 adsorption well correlate with these results. The increase of low-frequency shift of $\nu_{as}(CO)$ band with respect to gas (2349 cm^{-1} [18]) from 4 cm^{-1} for pure silica up to 9 cm^{-1} for the sample preexposed to pyridine is rather significant, and testifies for a great increase of oxygen atom basicity, although it is not yet high enough to cause formation of carbonate or bicarbonate-like structures, or bent molecular adsorption as in basic zeolites. Recent studies of CO_2 complexes with halide anions by gas phase infrared photodissociation spectroscopy, have shown that this molecule forms side-on complexes with Cl^-, Br^- and I^-, with the frequency of $\nu_{as}(CO)$ vibration lowered up to 2319, 2333 and 2340 cm^{-1}, respectively [19]. Comparing these figures with our observations, we can conclude that the negative charge induced on oxygen atom, although increases due to the influence of base, but is still rather low, because despite smaller ionic radius than for Cl^-, its influence upon CO_2 frequencies is much weaker and comparable with that of iodine anion.

Spectrum of fluoroform adsorbed on water ice reveals weak basicity of unsaturated surface oxygen atoms. Appearance of new bands at 3035 and 1380 cm^{-1} can be considered as evidence for slight basicity enhancement, but sensitivity of fluoroform is not high enough for such site characterization. Nevertheless, the low-frequency shift of the band of dangling OD groups perturbed by ethylene, observed after addition of fluoroform, testify for the strengthening of the H-bond in the presence of both coadsorbed species.

The effect of basicity enhancement induced by adsorption of bases, established in this work, might influence the catalytic properties of oxides. Like Brønsted acidity induced by adsorption of acids explains the promoting effect of acidic gases in the reactions catalyzed by acids [1], one could anticipate, besides poisoning of acid sites, promotion of reactions catalyzed by basic sites in the presence of basic gases. Strong basic sites of CaO were recently found to catalyze the reaction of isotopic scrambling in thiophene-2,5-d_2, that starts already at temperature as low as 220 K [20]. Our preliminary attempt, however, has not revealed any changes in isotopic content of thiophene-2,5-d_2 at 300 K in the presence of silica with coadsorbed pyridine, where according to our results the strength of basic sites is slightly lower than that of CaO.

5. Conclusion

Basicity of surface silanol groups of silica strongly increases in the presence of adsorbed bases, such as ammonia or pyridine, as revealed by changes in the spectra of adsorbed fluoroform or CO_2. Great increase of OH frequency shift on perturbation by ammonia, which occurs after CHF_3 addition, besides the comparatively high acidity of fluoroform, testifies for serious mutual enhancement of adsorption when both molecules are coadsorbed on silica. The same effect of mutual strengthening of adsorption was observed for the dangling hydroxyl groups of ice surface when ethylene was coadsorbed with fluoroform.

The mechanism of induced basicity and acidity of surface OH groups studied by us for silica, should be common for different oxide adsorbents and catalysts and is likely to account for the promotive effect of acidic or basic gases in the reactions catalyzed by solid acids or bases. Mutual enhancement of adsorption of coadsorbed acids and bases could explain the processes which occur on the surface of solid atmospheric aerosol, such as ice or hydrated mineral particles, and probably could be used in gas purification systems.

Acknowledgment

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