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Guest Editors: Petr Nachtigall and Carlos Otero Arian

Editorial

Themed Issue on characterisation of adsorbed species

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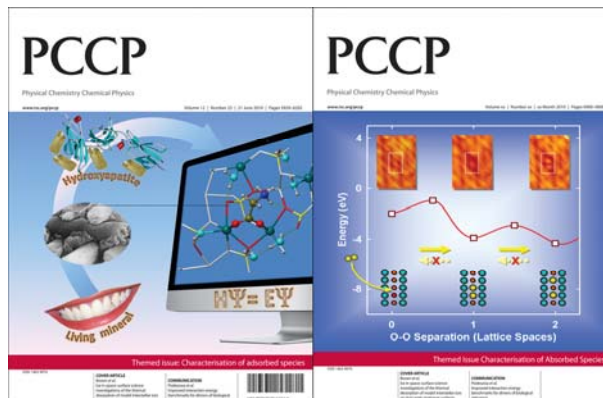
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A FTIR search for linkage isomerism of CN⁻ ions adsorbed on oxides and zeolites

A. A. Tsyganenko, A. M. Chizhik and A. I. Chizhik, *Phys. Chem. Chem. Phys.*, 2010

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A FTIR search for linkage isomerism of CN^- ions adsorbed on oxides and zeolites

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Adsorption of HCN and DCN was studied at 150–600 K on TiO_2 , ZnO, MgO and a set of X zeolites by means of FTIR spectroscopy. At the lowest temperatures adsorption is non-dissociative and occurs on surface OH groups of oxides, cations and coordinately unsaturated oxygen atoms. Bands at 2243–2147 cm^{-1} assignable to CN^- ions start to grow in the spectra of ZnO at 170 K, at 250 K for MgO and at 300 K for TiO_2 , where bands of polymeric species appear simultaneously. The structure of bands near 2200 cm^{-1} in the spectra of the studied oxides does not display a temperature dependence characteristic of isomeric forms. Reversible temperature changes of the band of CN^- ions in Na-, K-, Rb- and CsX zeolites exposed to HCN provide evidence for linkage isomerism, when the ions bound to alkali cations via C- or N- atoms co-exist in the thermodynamic equilibrium. C-Bonded species account for the stronger band at 2200–2140 cm^{-1} , while the low-frequency shoulder of this band, which appears and grows at elevated temperatures, is due to the energetically less favorable N-bonded form. The enthalpy of isomerization, estimated from the temperature dependence of band intensities, decreases from *ca* 20 kJ mol^{-1} or more for Na^+ and K^+ to 7.6 kJ mol^{-1} for Cs^+ , in accordance with the electrostatic model.

Introduction

CO adsorbed on Y and ZSM-5 zeolites with different alkali^{1–6} or alkaline-earth⁷ cations, as well as on HY-^{8,9} and H-ZSM-5 zeolites^{9,10} and silica^{11,12} was shown to reveal linkage isomerism, when a molecule forms with the same site two types of complexes bound *via* carbon or oxygen atom. The two isomers coexist in thermodynamic equilibrium and account for two bands of CO stretching vibrations, shifted, respectively, to higher (HF band) and lower (LF band) wavenumbers, as compared with the frequency of a free CO molecule in the gas phase. The adsorption energy of isomers is not the same. The difference is the isomerisation energy, which varies from about 1.5 kJ mol^{-1} , for CO molecules hydrogen bonded to silanol groups of silica, up to 10 kJ mol^{-1} or more, for complexes with doubly charged cations, such as Ca^{2+} or Sr^{2+} . Energetically less favourable oxygen-bonded species exist due to thermal excitation, and usually have a negligible concentration at 77 K. The LF bands of the latter species first grow on raising the temperature from 77 to 300–370 K, then finally decrease in intensity in such a way that the integrated intensity ratio for the two bands, $A_{\text{LF}}/A_{\text{HF}}$, constantly grows with temperature. From the slope of $\ln(A_{\text{LF}}/A_{\text{HF}})$ plotted against $1/T$ (van't Hoff plot) the experimental values of isomerisation enthalpy can be obtained. These values are close to the calculated energies of dipole reorientation in the electrostatic field of the cations. Such a simple electrostatic model also explains the existence of potential barrier between the two

isomeric states, if we take into account the quadrupole moment of the molecule with the positive charge in the middle and negative charge concentrated at the lone pairs of electrons of C and O atoms.¹³

No linkage isomerism was found, however, for CO adsorbed on X-zeolites with the same alkali cations or on metal oxides. This was explained by strong interaction of CO with oxygen anions that have a higher negative charge for these systems.¹⁴ For this reason CO interaction with the framework oxygen atoms of CsX zeolites is even stronger than with Cs^+ cations, and the band observed at 2124 cm^{-1} for lowest surface coverages of this zeolite by CO was attributed to molecules, which form side-on complexes with the most basic surface O anions.¹⁴

The phenomenon of isomerism on adsorption could have a great importance for catalysis, because the energetically less favourable state has different chemical properties and the excess of energy, which could be used to pass the activation barriers. It can thus be considered as an activated state and could play the role of intermediate in catalytic reactions. The isomeric states have different vibrational frequencies, and can be, thus, spectroscopically identified. Such simplest molecular systems with two stable states distinguishable by physical methods can open up important applications in optoelectronic devices.

The CN^- ion is isoelectronic to CO and one could anticipate the same kinds of interactions with surface sites. However, we have to take into account that, due to the charge, CN^- should interact preferentially with the cations. Then, two isomeric states for this ion could be expected even for those systems where it is not the case for CO because of attractive interaction

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with surface oxygen ions. Linkage isomerism of CN^- ligand is well known¹⁵ and even HCN gas at elevated temperatures is known to contain some HNC isomer.¹⁶ Cyano- (M-CN) and isocyano (M-NC) complexes are well studied. For the $\text{K}[(\text{CF}_3)_3\text{BCN}]$ complex of boron¹⁷ the enthalpy of the isocyanide-cyanide rearrangement, ΔH_i , and the activation energy, E_a , were obtained from differential calorimetry and the isomerisation kinetics measurements. The obtained values, $\Delta H_i = 35 \text{ kJ mol}^{-1}$ and $E_a = 180 \pm 20 \text{ kJ mol}^{-1}$, were in accordance with the results of DFT calculations.

When adsorbed on oxides, HCN dissociation leads to the bands assignable to M-CN and M-NC structures. Morrow and Cody¹⁸ associated the SiCN and SiNC groups on silica heated in HCN with the bands at 2218 and 2100 cm^{-1} . Rasko, Bansagi and Solymosi¹⁹ assigned the bands at 2195 and 2147 cm^{-1} arising on HCN adsorption on titania to Ti-CN and Ti-NC groups, respectively. In the recent study of HCN adsorption on alumina Yates and co-workers²⁰ attributed the bands at 2179 and 2100 cm^{-1} to Al-CN and Al-NC surface species. In the latter case the assignment was confirmed by calculation and by the data on isotopic frequency shifts observed on adsorption of D^{12}CN and D^{13}CN .²⁰

Thus, the existence of linkage isomerism of CN^- ions for oxides seems to be proved. The aim of this work was to study this phenomenon in more detail for TiO_2 , ZnO and MgO as examples of metal oxides, and for X zeolites with different cations, where HCN dissociation could be anticipated already at 300 K and the isomerisation enthalpy and the activation barrier were expected to be lower. The temperature changes in the spectra had to be followed in order to see the sequence of molecule transformations on adsorption and to seek the manifestations of isomerism. The data for different cations in zeolites had to be compared to see the dependence of the spectra on the charges and the radii of ions and to check the applicability of electrostatics to describe the system, as was done in the case of CO.

Experimental

Two different home-made vacuum cells were used in this study. The first (cell I), with two pairs of windows to separate the inner volume from the thermoinsulating space, used for low-temperature measurements at 55–370 K has been described elsewhere.^{8,21} The construction of another cell (cell II) for a wide range of higher temperatures (80–700 K) is shown in Fig. 1. The samples were pressed into thin (20–70 mg cm^{-2}) tablets. The zeolites were outgassed in vacuum for one hour at 723 K; MgO at 1023 K. Dehydroxylated samples of TiO_2 and ZnO were prepared by treatment at 873 K for one hour followed by cooling in 10 Torr of oxygen. To see the dependence of spectra on the degree of surface dehydroxylation, samples were exposed to water vapour and outgassed once again at the desired temperature.

Pressure was measured with Edwards Barocel 600 pressure gauges. Two gauges were attached to cell I. One, with an accuracy of 10^{-3} Torr and an upper measurement limit of 10 Torr, attached directly to 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.

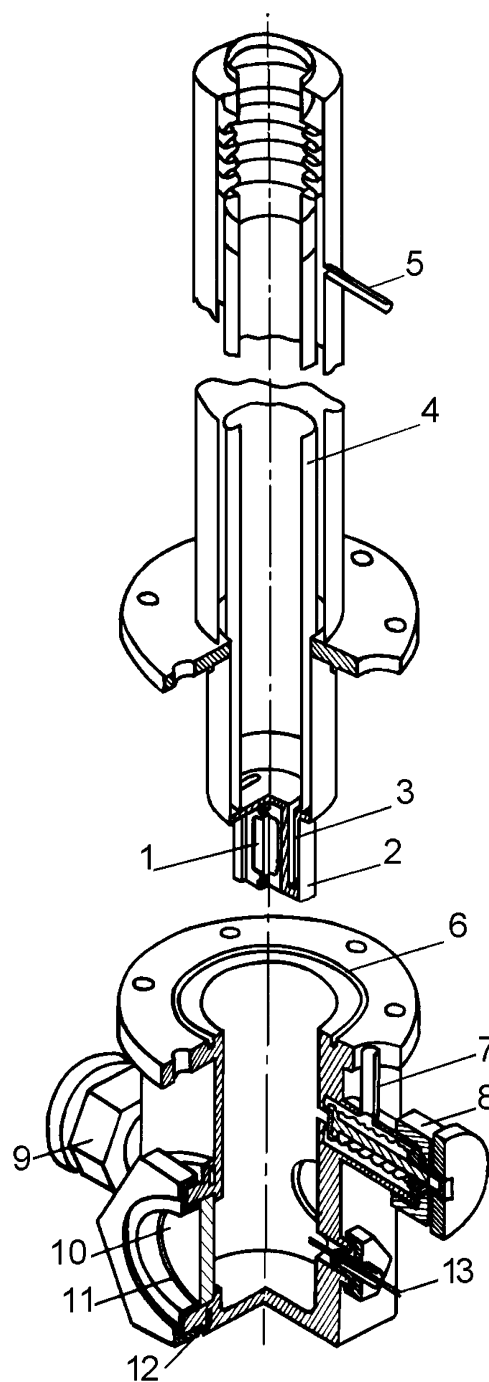


Fig. 1 The cell for spectral studies of surface species at 100–673 K. 1—Sample; 2—sample holder; 3—canals for heating elements; 4—volume for coolant; 5—dewar volume evacuation outlet; 6—teflon O-ring; 7—outlet to vacuum system; 8, 9—valves; 10—window; 11—indium gaskets; 12—canal for window thermostating; 13—thermocouple.

In experiments with cell I 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 left heated until the bands of adsorbed species appear, and the evolution of spectra with temperature was followed. On reaching about 270 K desorbed molecules were

frozen in a trap to avoid secondary adsorption. To see spectral changes at elevated temperatures, the sample was transposed into a quartz tube and heated in vacuum (or, if needed, in the presence of HCN gas) for about 10 min. Then spectra were registered at 300 K.

Alternatively, if we had to see the effect of coverage separately from the influence of temperature, the cell was repeatedly cooled by liquid nitrogen, and the sample was raised to the warmer part of the tube for a progressively longer time. The desorbed gas was frozen on the cold walls of the cell and after every heating the spectrum recorded at 77 K showed diminished quantity of adsorbate.

Cell II was used to study the dependence of spectra on the temperature of samples heated *in situ*. Typically, samples of adsorbents, already studied as above, were exposed to HCN at elevated temperature at the conditions of when dissociative adsorption takes place, directly after sample pretreatment. Then the excess gas was pumped off and spectra were recorded on cooling the cell down to the lowest temperature when the coolant compartment was filled with liquid nitrogen. To check the reversibility of the observed changes, the cell could be heated again.

The temperature of samples in both cells was measured by thermocouples inserted into the coolant compartment close to the sample holder. Special measurements with another thermocouple inserted directly into the model sample have shown that for cell I, the temperature of the sample placed in the IR beam in the presence of He does not differ from that measured in the coolant compartment by more than 3–5 degrees. For cell II the difference was greater, but the measured values could be corrected by a factor, which depends on the temperature of sample holder. Then the obtained temperature coincided with that of the sample, with the same accuracy for temperatures within the 200–400 K interval and about ± 10 K for 100–200 and 400–450 K.

Spectra were registered with a Nicolet 710 FTIR spectrometer with a coolable MCT detector at 4 cm^{-1} resolution.

Ready powders of TiO_2 Degussa P-25, ZnO Kadox, and commercial MgO of high purity were used in this study. KX, RbX and CsX zeolites were prepared from NaX by cationic exchange following the procedure described in ref. 22. HCN was prepared by the reaction of H_2SO_4 with KCN in the preliminary outgassed vacuum system. For DCN, D_2SO_4 was used, obtained in the reaction of SO_3 with D_2O . The gases were purified by passing through a trap kept at 190 K and condensed at 77 K with subsequent removal of incondensable gases.

Results

1 HCN and DCN on TiO_2

Spectra of HCN adsorbed on titania strongly depend on the temperature of sample dehydroxylation. Fig. 2 shows the spectrum of a sample pretreated at 473 K as a function of surface coverage. After saturating the surface with HCN the adsorbate was gradually removed at progressively increasing temperatures, with spectra registration always at 77 K. At least two groups of bands can be distinguished in the regions

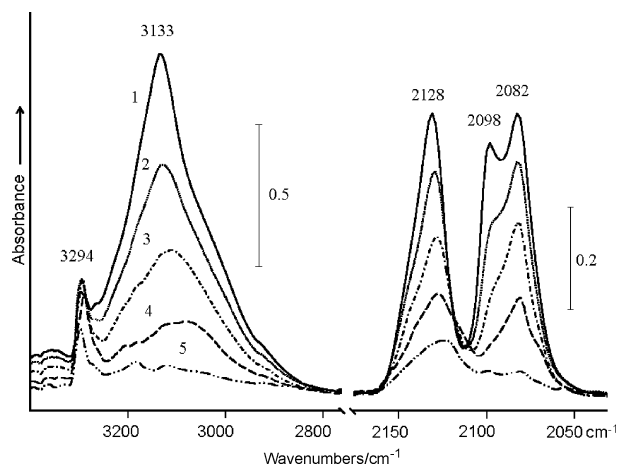


Fig. 2 Changes in the IR spectrum of HCN adsorbed on TiO_2 pretreated at 473 K on coverage diminution (1–5). All the spectra are registered at 77 K.

of C–H ($\sim 3300\text{--}2800\text{ cm}^{-1}$) and C–N ($\sim 2200\text{--}1900\text{ cm}^{-1}$) stretching vibrations. The first to desorb is the species which accounts for a broad band with a maximum at 3133 cm^{-1} accompanied by another one at 2082 cm^{-1} with a shoulder at 2098 cm^{-1} , well resolved at highest coverages, when the bands of surface OH groups (not shown in the figure) disappear, perturbed by adsorbed molecules. These bands almost disappear after short heating of the sample at up to 300 K, when a sharp band at 3294 cm^{-1} and a band at 2128 cm^{-1} , although diminished in their intensities, are still comparatively strong. Prolonged evacuation at 300 K practically restores the original spectrum.

If after water adsorption the hydrated sample is outgassed at 300 K, the bands at 3294 and 2128 cm^{-1} do not arise, and the maximum at 3133 cm^{-1} is narrower and more intense, accompanied by a strong band at 2198 cm^{-1} . Raising the pretreatment temperature up to 723 K, on the contrary, increases the intensities of bands at 3294 and 2128 cm^{-1} and leads to diminution of those at 3133 and 2198 cm^{-1} , while the maximum at 2082 cm^{-1} remains accompanied by a broad absorption centered at 3145 cm^{-1} . Besides that, a new band appears near 2200 cm^{-1} after heating the sample up to 300 K or higher. Further increase of the pretreatment temperature leads to serious complications of the spectra that could not be understood from the data on HCN adsorption only.

Adsorption of HCN and DCN mixture at 150 K on TiO_2 pretreated at 873 K (Fig. 3) results in the appearance of intense C–N bands at 2096 , 2082 and 1895 cm^{-1} with smaller features near 2128 and 1948 cm^{-1} . Simultaneously broad bands at 3155 and 2556 cm^{-1} appear with sharp shoulders at 3294 and 2643 cm^{-1} . On warming the sample all these bands grow, particularly those at 2128 and 1948 cm^{-1} . After reaching their maximum at about 200 K the bands near 2100 and 1900 cm^{-1} start to decrease, and at 270 K only traces of them remain in the spectrum. The bands of surface hydroxyl groups at 3730 , 3670 (OH) and 2740 , 2705 cm^{-1} (OD), originally rather weak, recover and become much more intense than in the initial spectrum. Bands at 2128 and 1948 cm^{-1} on raising the temperature shift stepwisely to higher wavenumbers, first to

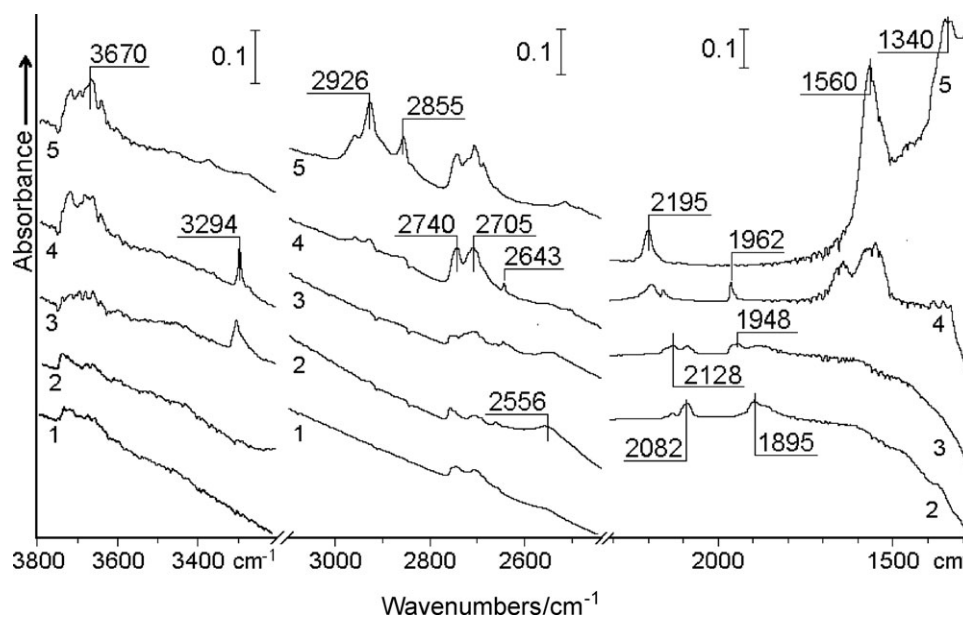


Fig. 3 IR spectrum of TiO_2 pretreated at 873 K before (1) and after adsorption of HCN and DCN mixture at 148 (2), 218 (3) and 300 K after evacuation at 373 (4) and 473 K (5). In the $2300\text{--}1300\text{ cm}^{-1}$ region spectrum 1 is subtracted from 2–5.

2143 and 1956 cm^{-1} and then to 2157 and 1962 cm^{-1} . This group of bands, together with those at 3294 and 2643 cm^{-1} , although decreased in intensity, remain after heating up to about 373 K and disappear completely after evacuation at 473 K .

Starting from about 250 K , a new feature arises at 2195 cm^{-1} , which increases in intensity with further heating up to 450 K and then diminishes with increasing temperature of calcination. Simultaneously with this peak, other bands at 2926 , 2855 , $1630\text{--}1560$, and 1340 cm^{-1} appear, grow and then diminish. After heating above 473 K the 2195 cm^{-1} band shifts to higher wavenumbers and reveals a structure with maxima at 2200 , 2208 and 2218 cm^{-1} .

2 HCN on zinc and magnesium oxides

Besides titania, analogous experiments with HCN and HCN + DCN adsorption were carried out with ZnO ; some results obtained are shown in Fig. 4. As in the case of TiO_2 , the first to appear were the bands at 2096 cm^{-1} (HCN) and 1898 cm^{-1} (DCN) and corresponding bands in the C–H (3174 cm^{-1}) and C–D (2565 cm^{-1}) regions. Other bands, which have no isotopic analogues at lower frequencies, already start to grow from 165 K . The first one appears at 2147 cm^{-1} , reaches its maximum at 173 K and, while decreasing in intensity, moves on heating to 2164 cm^{-1} . One more band arises simultaneously at 2201 cm^{-1} , soon overgrows the latter and continues to grow up to 300 K or higher, while its maximum shifts to 2206 cm^{-1} . After heating up to 345 K , when the bands of weakly bound prussic acid are gone (curve 4), one could also see broad bands assignable to newly formed hydroxyls centered at 3515 and 2600 cm^{-1} with a shoulder at 2647 cm^{-1} . Our attempts to study temperature dependence of the spectra of HCN on ZnO using cell II have shown that at moderate heating ($330\text{--}410\text{ K}$), a well resolved shoulder of the 2201 cm^{-1} band appears at 2242 cm^{-1} and disappears on further

temperature elevation. These changes, however, were not quite reversible.

Adsorption of NCN on MgO also results in the appearance of a band near 2200 cm^{-1} , which starts to grow at about 260 K , resists pumping at 823 K and splits into 3 maxima at 2222 , 2195 and 2165 cm^{-1} after subsequent cooling below 473 K . And again, the splitting disappears on raising the temperature, displaying no behavior typical of linkage isomerism.

3 HCN on NaX, KX, RbX and CsX zeolites

HCN adsorption at 150 K on the NaX sample leads to a band at about 2100 cm^{-1} , which reaches its maximum at 300 K simultaneously with a broad band centered at 3075 cm^{-1} . Coverage dependence of the spectra registered at 77 K after heating the sample at progressively increased temperatures is shown in Fig. 5. Both the bands diminish in intensity and gradually move to lower wavenumbers with the decreasing amount of adsorbed molecules. At temperatures above 370 K one can notice the appearance of a new OH band at 3642 cm^{-1} and a band at 2201 cm^{-1} . Heating up to 573 K in the presence of HCN gas leads to the increase of the 2201 cm^{-1} band and diminution of other bands of adsorbed species. Subsequent evacuation at the same temperature removes the bands of adsorbed molecules completely, while that at 2201 cm^{-1} becomes even stronger.

Temperature variations result in certain changes in the contour of the 2001 cm^{-1} band. On heating, the tail of absorption from the low frequency side transforms into a shoulder at 2184 cm^{-1} , while the intensity of the 2001 cm^{-1} band decreases, and the maximum shifts to 2198 cm^{-1} . The changes are quite reversible, and repeated cooling or heating returns the band to the shape characteristic for a certain temperature.

Similar behavior of spectra with temperature was observed for HCN adsorption on other X zeolites. After heating above

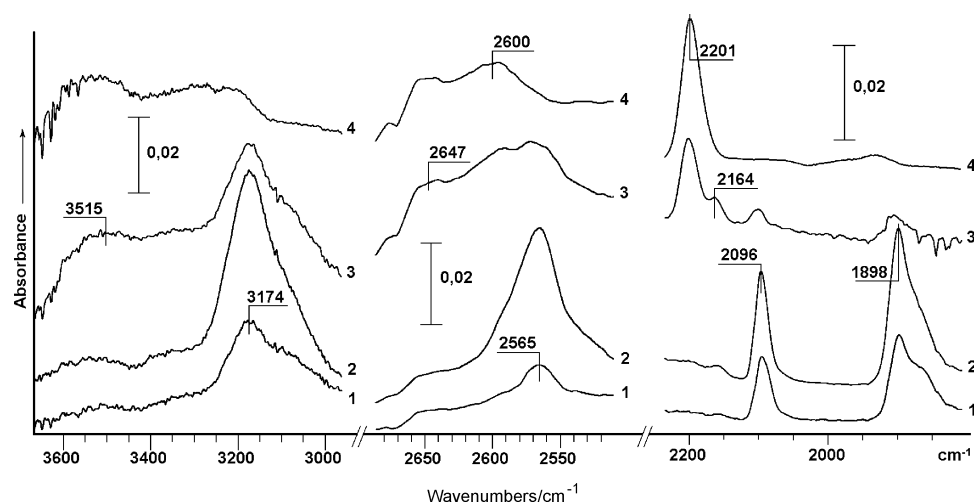


Fig. 4 IR spectrum of HCN and DCN mixture adsorbed on ZnO at 143 (1), 155 (2), 240 (3) and at 300 K after evacuation at 345 K (4).

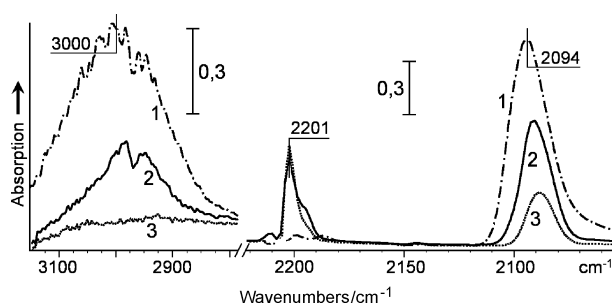


Fig. 5 FTIR spectrum of HCN adsorbed on NaX after removal the excess of adsorbate at 300 (1), 423 (2) and 473 K (3).

350 K two bands appear in the C–N stretching vibration region between 2200 and 2140 cm^{-1} , the exact positions of maxima depending on the cation. For the CsX sample (Fig. 6) the two bands are well resolved. The HF band appears at 2150 cm^{-1} and only slightly shifts to lower wavenumbers on heating the sample up to 508 K. The LF band appears at 2138 cm^{-1} . Temperature changes lead to the intensity redistribution between the bands. The higher the temperature, the greater the intensity of the LF band, while the HF band decreases in intensity. The data on HF and LF band positions, obtained for the studied X zeolites, are summarized below in Table 1.

Discussion

The spectra of HCN weakly bound to the TiO_2 surface can be readily interpreted based on their dependence on the pre-treatment conditions. The bands at 3133 and 2098 cm^{-1} , more intense in the spectra of hydroxylated samples and accompanied by the perturbation of the bands of surface hydroxyl groups, should naturally be associated with molecules bound by hydrogen bonds with surface hydroxyls (structure I). The band at 2082 cm^{-1} , which is less sensitive to dehydroxylation, can be assigned to molecules forming H-bonds to the oxygen atoms of the surface or with the lone pairs of oxygen atoms of OH groups by the proton of the CH group of the molecule (structure II). CH vibration of such molecules accounts for a

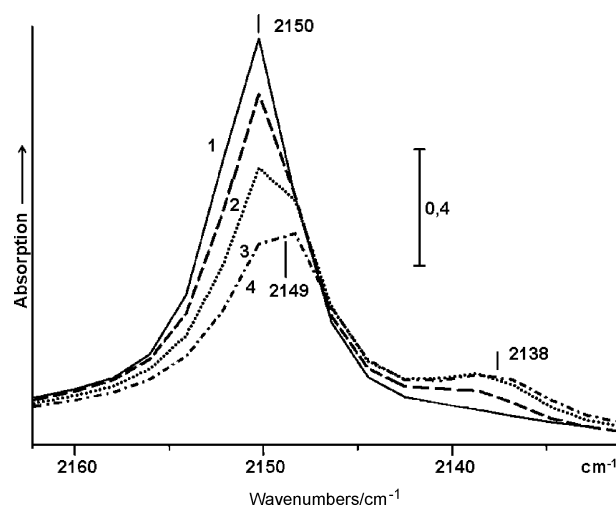
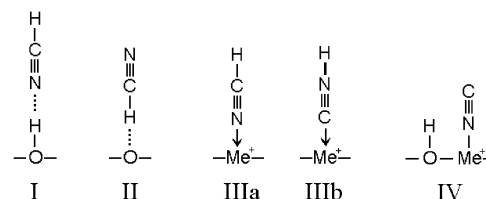


Fig. 6 IR spectrum of CN^- ion in CsX zeolite registered at 90 (1), 234 (2), 354 (3) and 508 K (4).

Table 1 HF and LF band positions, cation radius R_{cat} and isomerisation enthalpy ΔH_i^0 for CN^- ions in X zeolites

Zeolite	$\nu_{\text{HF}}/\text{cm}^{-1}$	$\nu_{\text{LF}}/\text{cm}^{-1}$	$R_{\text{cat}}/\text{\AA}$	$\Delta H_i^0/\text{kJ mol}^{-1}$
NaX	2195	2184	0.98	> 20
KX	2157	2144	1.33	21 ± 5
RbX	2150	2138	1.48	17 ± 3
CsX	2149	2138	1.67	7.6 ± 1.0

broad absorption around 3145 cm^{-1} , better seen in the spectra of samples pretreated at high temperatures.



Less evident is the assignment of the band at 2128–2157 cm^{-1} . Kortum and Delfs²³ assigned the band observed at 2150 cm^{-1}

in the spectrum of HCN adsorbed on the cracking catalyst to dicyan molecules, the product of hydrogen cyanide dimerization. According to Rasco *et al.*,¹⁹ the band at the same position in the spectrum of titania is due to the Ti-NC isomeric structure, formed initially as a result of HCN dissociation (structure IV). For proper assignment of the bands of these surface species let us consider our data on DCN and HCN/DCN mixtures adsorbed on TiO₂.

The frequency of C–N vibration in HCN molecule is very sensitive to H–D substitution. For a free molecule in the gas phase¹⁴ it shifts from 2097 down to 1925 cm^{−1}. Such a large 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 ν CD band occurs higher than it could be anticipated from the CH/CD reduced mass ratio, while the ν C–N band moves downwards. Formation of H-bond by the CH group of HCN lowers the frequency and broadens the band of ν C–H vibration. Lowering of the corresponding ν C–D mode frequency causes extra low-frequency shift and broadening of the ν C–N band as compared with that of HCN. So, this band occurs at 1885 cm^{−1} in the spectra of solid HCN/DCN films.²⁴ In our case of DCN on titania the ν C–N band of weakly bound molecules, corresponding to HCN with ν C–H lowered to 3145 cm^{−1}, is shifted to 1895 cm^{−1} or lower, if we take into account the broad tail of this band from the low-frequency side, visible in Fig. 3.

Thus, if in the spectra of adsorbed HCN and DCN mixture pairs of bands appear simultaneously and change their intensity in a similar way, such as the bands at 2082 and 1895 cm^{−1}, we can be sure that they are due to HCN and DCN molecules in the same surface complexes. It is noteworthy, however, that the ν C–N bands of adsorbed HCN and DCN differ significantly not only in their position and width, but in their shape and intensities. In HCN gas absorbance of the ν C–N band is negligible. This is because the molecule is isoelectronic to N₂, and the CH group, due to the low mass of proton, vibrates with respect to the N atom as a single particle with the total charge of nuclei the same as that of the nitrogen atom and with mass 13, and the dynamic dipole moment for C–N vibration should be close to that of IR inactive N–N mode of nitrogen. Low absorbance of ν C–N band remains for weakly bound HCN molecules, although the interaction with the surface activates absorption. It is not the case for the DCN molecule, where the integrated adsorption coefficient of ν C–N mode is always high enough. Apparently, this is the reason why in Fig. 3, curve 4, the DCN band at 1962 cm^{−1} is much more intense than the corresponding peak of HCN, although the concomitant HCN band at 3294 cm^{−1} and the 2643 cm^{−1} band of DCN have an inverse intensity ratio.

After adsorption of HCN and DCN mixture on TiO₂ the band at 2128 cm^{−1} appears together with that at 1948 cm^{−1}, and its stepwise shift to 2143 and then to 2157 cm^{−1} is reproduced in the simultaneous shift of the 1948 cm^{−1} band first to 1956 and then to 1962 cm^{−1}. The sharp bands at 3294 and 2643 cm^{−1} appear, grow and diminish quite concurrently with these changes. These data convince us that the bands at 2157–2128 and 3294 cm^{−1} are due to strongly held HCN molecules, while the corresponding DCN species account for

the bands at 1962–1948 and 2643 cm^{−1}. The sites of strong molecular adsorption on titania, more abundant after dehydration, are the coordinately unsaturated Ti⁴⁺ ions, which form coordinate bonds with adsorbed nitrogen,²⁵ CO or ozone.²⁶ The band positions of these molecules were shown to depend on surface coverage due to lateral interactions in the adsorbed layer.^{25,27} Apparently, such interactions between the coordinately bonded hydrogen cyanide molecules (scheme III) also account for the variations in the ν C–N band position observed in the spectra of both HCN and DCN adsorbed on titania.

The sharp band of the ν C–H (CD) vibration of coordinately held hydrogen cyanide occurs at 3294 (2643) cm^{−1}, almost as high as for the free HCN molecule (2311 cm^{−1}) and even higher than for DCN gas (2630 cm^{−1}).¹⁴ A small shift could be expected for the band of the CH group which is not involved in the interaction with the surface. The observed high-frequency shift of the ν C–D band can be explained by mutual repulsion of the ν C–D and ν C–N modes when the formation of the coordinate bond increases the vibrational constant of the latter.

As another possible explanation of the high position of the ν C–H band of coordinately bonded HCN, we can suppose that the band is due to N–H vibration of adsorbed HNC molecules (scheme IIIb). In fact, the bond of such an isomer to the cation *via* a carbon atom should be stronger than *via* nitrogen in structure IIIa. If the gain in the adsorption energy exceeds the energy of HCN–HNC isomerization, structure IIIb should predominate. Then the frequency of ν N–H vibration of coordinately bound HNC should be lowered as compared to its value for gas or matrix (3620 cm^{−1}),¹⁴ and the corresponding band can be observed near 3300 cm^{−1}. Thus, the hypothesis of HCN isomerism in the molecularly adsorbed state is worth verifying.

The band at 2195 cm^{−1} grows in the spectra of TiO₂ samples pretreated at high temperatures when the above bands of molecularly adsorbed hydrogen cyanide diminish and disappear. This band has no deuterated analogue, and could, thus, be attributed to CN[−] ions bound to titanium *via* carbon in Ti–CN complexes. Simultaneous growth of the bands of surface hydroxyl groups supports such an assignment. However, besides the mentioned bands of ν C–N and ν OH (ν OD) vibrations, at the same time, other bands grow at 2926, 2855, 1630–1560, and 1340 cm^{−1}. The appearance of these bands can be due to HCN polymerization, which was shown to occur already on different adsorbents at 300 K or at elevated temperatures. On porous glass,^{28,29} polymerization leads to the bands at 2940, 2250–2220 and 1640 cm^{−1}, very close to those observed by us for titania. Bands at almost the same frequencies were detected and assigned to polymerization products for HCN adsorbed on alumina.³⁰ Like dicyane, also supposed to be a result of HCN adsorption,²³ other polymerization products contain CN groups, which absorb near 2200 cm^{−1} and should not be sensitive to deuteration.

The bands at 2201 and 2195 cm^{−1} in the spectra of ZnO and MgO are not accompanied by any evident bands which could be assigned to the same surface products of HCN chemisorption or surface reactions. Therefore, we can suppose that these bands are due to CN[−] ions produced by dissociative

adsorption of hydrogen cyanide, especially taking into account the observed simultaneous growth of the bands of surface OH groups. However, the band at 2164 cm^{-1} in the spectrum of ZnO, which could be thought to be due to Zn–NC species, disappears irreversibly on raising the temperature. If any new band arises, such as that at 2242 cm^{-1} of ZnO or those at 2222 and 2165 cm^{-1} in the spectrum of MgO, they could be seen at 300 K and disappear at high temperatures. This is quite different from the behaviour of energetically unfavourable linkage isomers, and these extra bands have, evidently, some other origin. Thus, if the bands near 2200 cm^{-1} belong to CN^- ion, the isomerization energy is too high to detect the excited isomeric state at temperatures of our experiments, or these bands are due to some other products of HCN reactions on oxide surfaces. In any case, we cannot yet state about the observation of linkage isomerism on metal oxides.

Results obtained for HCN adsorption on X-zeolites unequivocally testify for the formation of CN^- ions attached to the cations. Simultaneous growth of the band of stretching C–N vibration and OH groups, while no other bands appear that could be due to polymeric structures, enable us to conclude that dissociation of adsorbed molecules takes place. Since the HF band position depends on the nature of the exchangeable cation, one could assign it to M^+-CN^- complexes, where M^+ is the cation.

Comparison of the HF band positions for different cations shows that the frequency of CN^- ion apparently increases with the decreasing cation radius, R , depending on the strength of its electrostatic field as in the case of CO. The plot of ν_{CN} as a function of $1/R^2$, shown in Fig. 7, is close to linear, in agreement with that. However, the dependence of ν_{CN} on the field seems to be more complicated than that of CO. While for ZSM-5 zeolites the increase of cation field from Cs^+ to Na^+ results in the ν_{CO} growth by 21 cm^{-1} , from 2157 up to 2178 cm^{-1} , ν_{CN} increases in the same row of cations (Cs^+ , Rb^+ , K^+ , Na^+) by 50 cm^{-1} , from 2150 up to *ca* 2200 cm^{-1} . If we try to consider the shift as a result of the vibrational Stark effect, we have to conclude that the Stark constant K_{St} for CN^- ion is more than twice as high as that of CO, although the calculated values of the vibrational Stark constant for the ion is smaller.³¹ Moreover, unlike CO, the maximum of the LF band moves to higher frequency values for the same sequence of cations. It is likely that besides the linear Stark effect, which should shift the frequencies of C- and N-bonded species in opposite directions, there is another effect of frequency increase, irrespective of CN^- orientation.

The reason of frequency increase for both orientations could be in the “wall effect”, when the formation of a new bond with the surface leads to frequency growth even when the force constant of the chemical bond of the molecule is not changed. For CO this effect does not determine the direction of frequency shifts, although for MgO clusters it was shown to account for the essential part of the observed frequency increase.³² Due to the Coulomb attraction to the cation, for the CN^- ion the “wall effect” can be strong enough to be considered as a possible explanation of the shift of both the HF and LF bands to higher wavenumbers.

For CO on CsZSM-5 the distance, $\Delta\nu$, between the HF and LF bands is 35 cm^{-1} and increases up to 49 and 66 cm^{-1} for

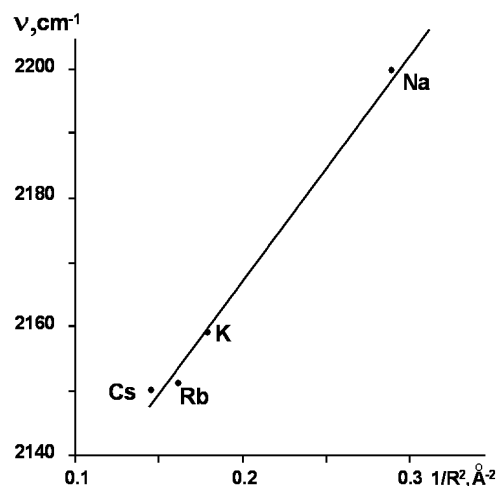


Fig. 7 Position of the HF band of CN^- ion in the spectra of X zeolites plotted against $1/R^2$, where R is the radius of exchangeable cation.

NaY and NaZSM-5, respectively¹². CN^- on CsX reveals a $\Delta\nu$ value of only 11 cm^{-1} , 31% of that observed for CO/CsZSM-5. Lower $\Delta\nu$ for CN^- /CsX can be explained by the smaller value of Stark constant, $0.223\text{ cm}^{-1}/(\text{MV cm}^{-1})$, calculated for CN^- , which is about half of $0.467\text{ cm}^{-1}/(\text{MV cm}^{-1})$ for CO.³¹ Besides, the cation field in X zeolites should be weaker than in Y and particularly than that in ZSM-5 because of the increased negative charge of the framework. Thus, based on the known Stark constant we could expect the $\Delta\nu$ value for CN^- in CsX to be as small as about 20 cm^{-1} or less, which is not a bad agreement with the observed 11 cm^{-1} .

The studied temperature dependence of the spectra enables the intensities, A , of the LF and HF bands to be followed. The logarithm of their ratio should satisfy the van't Hoff equation:

$$\ln(A_{\text{LF}}/A_{\text{HF}}) = -\Delta H_i^0/RT + \Delta S_i^0/R + \ln(\varepsilon_{\text{LF}}/\varepsilon_{\text{HF}})$$

where ΔH_i^0 and ΔS_i^0 are the isomerisation enthalpy and entropy, respectively, while ε_{LF} and ε_{HF} denote the integrated absorption coefficients of the bands. Fig. 8 shows the “van't Hoff plot”— $\ln(A_{\text{LF}}/A_{\text{HF}})$ plotted as a function of $1/T$ for the data on CN^- ion on CsX. Although the dependence is close enough to linear, we have to confess that the slope of the graph is not the same for the highest and the lowest temperatures. In our mind, this is caused mainly by the increased error in temperature measurements, not corrected by calibration, particularly above 400 K when an uncontrolled cooling of the central part of the sample placed in cell II occurs because of its increased radiative contact with the cold environment. That is why, for the quantitative analysis of data, we have chosen the points between 150 and 400 K as the most reliable.

From the slopes of van't Hoff plots, the values of isomerisation enthalpy given in the last column of Table 1 were obtained. Although the accuracy of these measurements is poorer than for CO, where the HF and LF bands are better resolved, we can state that the isomerisation enthalpy values for CN^- is 4–10 times as great as that for CO. For CN^- on X zeolites with K^+ or Rb^+ the obtained values of ΔH_i^0 are

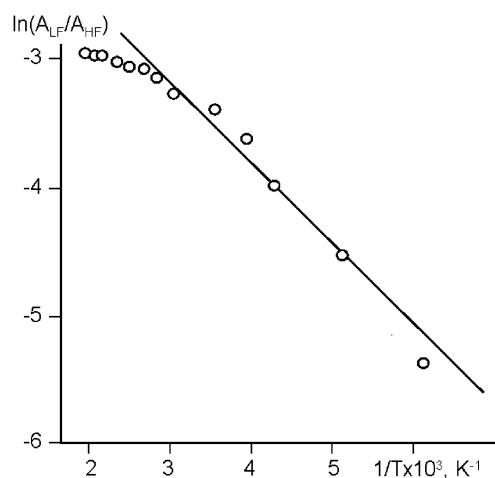


Fig. 8 van't Hoff plot for the bands of CN[−] ion in CsX zeolite registered at variable temperatures.

21 and 17 instead of 3.2 and 1.8 kJ mol^{−1}, if we compare with CO/ZSM-5 zeolites with the same cations.¹³

The isomerisation enthalpy can be estimated in an alternative way if we assume that the integrated absorption coefficient for the CN[−] ion bound to certain cation does not depend on orientation, $\varepsilon_{LF} = \varepsilon_{HF}$. The example of CO shows that for strong fields of divalent cations these values can differ by orders of magnitude, but for weaker fields of alkali cations the difference is not great and both the values are close to that of gaseous CO molecules.³³ Then, the intensity ratio of the LF and HF bands observed at a certain temperature, T , reflects the ratio of populations of the two isomeric states, described by Boltzmann's formula, and the distance between energetic levels of the two isomeric states, ΔE_{isom} , can be found from the equation:

$$\ln(A_{LF}/A_{HF}) = -\Delta E_{\text{isom}}/kT$$

Such estimates for the spectra of CN[−]/CsX zeolite registered at elevated temperatures give values between 7 and 9 kJ mol^{−1}, in a good agreement with 7.6 kJ mol^{−1} obtained from the van't Hoff plot.

For CO, the value of ΔH_i^0 with a good accuracy can be estimated theoretically as the energy of molecular dipole, μ_0 , reorientation in the electrostatic field E of the cation:¹³

$$\Delta H_i^0 = \sim 2\mu_0 E$$

The field strength E was obtained from the frequency shift of the CO molecule on adsorption, considered as the result of vibrational Stark effect:

$$\Delta\nu = K_{\text{st}}E$$

For CN[−] ion placed in the same field, E , as CO molecules bound to the cation the isomerisation energy should be greater by a factor of $\mu_0\text{CN}^-/\mu_0\text{CO} = 2.85$, if we take for CN[−] and CO the values of dipole moment of 0.3567 and 0.1252 D, respectively, as calculated in ref. 31. Then, one should anticipate for CN[−] in the increasing field of cations from Cs⁺ to Na⁺ the values of ΔH_i^0 to grow from about 5 up to 10 kJ mol^{−1}. These figures are not too far from the ΔH_i^0 values obtained here, especially if we take into account that, due to the Coulomb

attraction, the distance between the cation and CN[−] ion should be shorter, and, hence, the field stronger than in the case of CO molecule.

Conclusions

Adsorption of DCN or HCN + DCN mixtures enables us to distinguish between the bands of molecular and dissociative absorption, in particular, in the C–N vibration region, where the assignment is the most controversial. Appearance of bands near 1900 cm^{−1} in the spectra of adsorbed DCN, shifted by 180–200 cm^{−1} with respect to the corresponding bands of HCN, unequivocally point to their attribution to the molecularly adsorbed species. Such large isotopic shifts caused by H–D substitution occurs due to a strong interaction between the stretching C–D and C–N vibrations, leading to mutual repulsion of their modes. Low-frequency shift and broadening of the band of C–D vibration for those molecules, which form hydrogen bonds by their CD group with surface oxygen atoms, is reflected in the low frequency and large width of the C–N vibration band for this form of adsorption, shifted for TiO₂ down to 1885 cm^{−1}.

The difference between the spectra of adsorbed HCN and DCN in the C–N vibrational region is also brought about by the variations in the integrated absorption coefficient of this mode in different adsorbed species. Extremely weak absorption of the C–N band for the free molecules of gas remains for the weakly bound molecules and deepens the dissimilarity between the intensities and shapes of bands for the usual and deuterated species in the C–N region.

Spectra of DCN adsorbed on TiO₂ convince us that all the bands in the 2157–2128 cm^{−1} region are due to molecularly adsorbed hydrogen cyanide, coordinately bound to the unsaturated surface Ti⁴⁺ ions. This is not consistent with the earlier proposed¹⁸ assignment of the band at 2150 cm^{−1} to the Ti–NC species. Bands at 2201–2195 cm^{−1} in the spectra of TiO₂, as well as those at 2242–2165 of ZnO or MgO do not have their shifted analogues in the spectra of DCN, and may be assigned to surface CN[−] ions formed as a result of HCN or DCN dissociative adsorption. However, bands in the same region could be due to CN containing products of HCN polymerization, and temperature behavior of these bands is quite different from that observed for isomeric states of CO on zeolites or for that described here for CN[−] species in X zeolites.

Formation of CN[−] ions was reliably established for HCN adsorbed on X zeolites with Na⁺, K⁺, Rb⁺ and Cs⁺ cations. Absorption bands of CN[−] ion occur at 2200–2150 cm^{−1} and exhibit certain dependence on the electrostatic field of cation, moving to higher wavenumbers from Cs⁺ to Na⁺. At elevated temperatures a shoulder at lower wavenumbers grows (LF band), assignable to the ion attached *via* N atom. Analysis of the temperature dependence of band intensities on the assumption that the two isomeric states coexist in thermodynamic equilibrium leads to the values of isomerisation enthalpy, ΔH_i^0 , which increases from 7.6 kJ mol^{−1} for CN[−] bound to Cs⁺ cations up to 20 kJ mol^{−1} or more for K⁺ and Na⁺. The increase of ΔH_i^0 with the increasing strength of electrostatic field of a cation is in accordance with the electrostatic model,

and the difference in energy between the two isomeric states, 5–10 times as great as for CO, is consistent with the greater value of dipole moment of the CN^- ion. However, while the simple electrostatic model with the vibrational Stark constant of CN^- ion about twice as low as that of CO can rationalize comparatively small frequency differences between the maxima of HF and LF bands for the ion, it can neither explain why the distance between these bands does not increase from Cs^+ to Na^+ , nor can it account for the high frequency shift of the LF band from Cs^+ to Na^+ . Among the factors which could affect the band position of CN^- ion bound to a cation, besides the influence of electric field, one can point to the “wall effect” or to the effect of ion neutralization, leading to CN bond strengthening for both the C- and N-bonded isomers. Analysis of these factors needs further experimental and theoretical investigations.

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References

- 1 A. A. Tsyganenko, C. Otero Arean, E. Escalona Platero, E. Garrone and A. Zecchina, *Angew. Chem., Int. Ed.*, 1998, **37**, 3161.
- 2 A. A. Tsyganenko, C. Otero Arean, E. Escalona Platero, E. Garrone and A. Zecchina, *Catal. Lett.*, 1999, **61**, 187.
- 3 O. V. Manoilova, M. Peñarroya Mentrut, G. Turnes Palomino, A. A. Tsyganenko and C. Otero Areán, *Vib. Spectrosc.*, 2001, **26**, 107.
- 4 C. Otero Areán, O. V. Manoilova, M. Rodríguez Delgado, A. A. Tsyganenko and E. Garrone, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4187.
- 5 A. A. Tsyganenko, C. Otero Arean and E. Escalona Platero, *Stud. Surf. Sci. Catal.*, 2000, **130**, 3143.
- 6 C. Otero Areán, G. Turnes Palomino, A. A. Tsyganenko and E. Garrone, *Int. J. Mol. Sci.*, 2002, **3**, 764.
- 7 E. Garrone, B. Bonelli, A. A. Tsyganenko, M. Rodríguez Delgado, G. Turnes Palomino, O. V. Manoilova and C. Otero Areán, *J. Phys. Chem. B*, 2003, **107**, 2537.
- 8 C. Otero Areán, O. V. Manoilova, A. A. Tsyganenko, G. Turnes Palomino, M. Peñarroya Mentrut, F. Geobaldo and E. Garrone, *Eur. J. Inorg. Chem.*, 2001, 1739.
- 9 C. Otero Areán, A. A. Tsyganenko, O. V. Manoilova, G. Turnes Palomino, M. Peñarroya Mentrut and E. Garrone, *Chem. Commun.*, 2001, 455.
- 10 G. Turnes Palomino, M. Peñarroya Mentrut, A. A. Tsyganenko, E. Escalona Platero and C. Otero Areán, *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 2001, vol. 135, pp. 219.
- 11 P. Yu. Storozhev, C. Otero Arean, E. Garrone, P. Ugliengo, V. A. Ermoshin and A. A. Tsyganenko, *Chem. Phys. Lett.*, 2003, **374**, 439.
- 12 A. A. Tsyganenko, P. Yu. Storozhev and C. Otero Areán, *Kinet. Catal.*, 2004, **45**, 530.
- 13 P. Yu. Storozhev, V. S. Yanko, A. A. Tsyganenko, G. Turnes Palomino, M. Rodríguez Delgado and C. Otero Areán, *Appl. Surf. Sci.*, 2004, **238**, 390.
- 14 A. A. Tsyganenko, E. V. Kondratieva, V. S. Yanko and P. Yu. Storozhev, *J. Mater. Chem.*, 2006, **16**, 2358.
- 15 K. Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination Compounds*, Wiley, New York, 4th edn, 1986.
- 16 A. G. Maki and R. L. Sams, *J. Chem. Phys.*, 1981, **75**, 4178.
- 17 M. Finze, E. Bernhardt, H. Willner and C. W. Lehmann, *J. Am. Chem. Soc.*, 2005, **127**, 10712.
- 18 B. A. Morrow and I. A. Cody, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1021.
- 19 J. Rasko, T. Bansagi and F. Solymosi, *Phys. Chem. Chem. Phys.*, 2002, **4**, 3509.
- 20 S. Kim, D. C. Sorescu and J. T. Yates, Jr., *J. Phys. Chem. C*, 2007, **111**, 5416.
- 21 M. A. Babaeva, D. S. Bystrov, A. Yu. Kovalin and A. A. Tsyganenko, *J. Catal.*, 1990, **123**, 396.
- 22 R. Szostak, *Molecular Sieves*, Van Nostrand Reinhold, New York, 1989.
- 23 G. Kortüm and H. Delfs, *Spectrochim. Acta*, 1964, **20**, 405.
- 24 H. B. Friedrich and P. F. Krause, *J. Chem. Phys.*, 1973, **59**, 4942.
- 25 S. M. Zverev, K. S. Smirnov and A. A. Tsyganenko, *Kinet. Catalysis*, 1988, **29**, 1251.
- 26 K. M. Bulanin, J.-C. Lavalley and A. A. Tsyganenko, *J. Phys. Chem.*, 1995, **99**, 10294.
- 27 A. A. Tsyganenko, L. A. Denisenko, S. M. Zverev and V. N. Filimonov, *J. Catal.*, 1985, **94**, 10.
- 28 Y. Kozirovski and M. Folman, *Trans. Faraday Soc.*, 1964, **60**, 1532.
- 29 Y. J. D. Low, N. Ramasubramanian, P. Ramamurthy and A. V. Deo, *J. Phys. Chem.*, 1968, **72**, 2371.
- 30 M. J. D. Low and P. Ramamurthy, *J. Res. Inst. Catalysis Hokkaido Univ.*, 1968, **16**, 535.
- 31 S. H. Brewer and S. Franzen, *J. Chem. Phys.*, 2003, **119**, 851.
- 32 G. Pacchioni, T. Minerva and P. S. Bagus, *Surf. Sci.*, 1992, **275**, 450.
- 33 E. V. Kondratieva, O. V. Manoilova and A. A. Tsyganenko, *Kinet. Catal.*, 2008, **49**, 451.