1 Good afternoon, ladies and gentlemen. My name is Yaroslav Shergin, I am a student of St. Petersburg State University, Department of Photonics, group of IR Spectroscopy. The topic of my presentation is DFT study of the adsorption properties of Ca cation.

2 First of all, I would like to tell you why we were interested in experiments with calcium cation. Adsorption properties of the cations in zeolites dramatically differ from those of the oxides of the same elements. To explain this effect FTIR spectra of CO adsorbed on CaO exposed to different gaseous acids has been carried out [1].

Initially, the spectrum of CO adsorption on calcium oxide was recorded, then after adding the gases CO_2, (H chlorine) HCl, SO_2 and SO_3

It was shown that transformation of the surrounding O2- ions into carbonate, sulfite or sulfate ions results in the blue shift of C-O stretching band of molecules bound to Ca^{2+} cation, approaching the value characteristic of CaY zeolites.

What is blue shift? We assume that the depicted molecule is CO, which is isoelectronic to the nitrogen molecule. In CO molecule, positive charge is concentrated on oxygen, and a negative charge on carbon. When the negative part of the molecule interacts with the cation, the electron density shifts towards the cation. This increases the vibration frequency. Its approaches that of nitrogen which has a triple bond and is not active in IR adsorption. When O2 anions change to anions with a different charge or radius, the effect of the cation on the adsorbed molecule changes, which leads to a shift in the vibration frequency band

3 A few words about zeolites. These are aluminosilicate minerals used as adsorbents. Zeolites have a porous structure that can contain a wide variety of cations such as (sodium) Na^+, (potassium) K^+, Ca^{2+}, (magnesium) Mg^{2+}, and others. These positive ions are rather weakly bound and can be easily replaced by others from the solution. Zeolites can differ in structure as well as in the ratio of silicon to aluminum. The figures show A, B and X, Y zeolites. The ratio of silicon to aluminum in zeolite X is 1, in Y - several tens

4 An experiment was carried out with the adsorption of CO molecules on NiY zeolite. The experiment consists in the fact that initially a sample of zeolite was pressed, heated to high temperatures, followed by pumping out to get rid of excess organic matter. After that, the CO adsorption spectra were recorded at temperature of liquid nitrogen, with further pumping out and increasing the temperature. At first, three bands of vibrations were visible, then these bands disappeared, and two new bands appeared. Upon further heating and evacuation, two bands disappeared and a new band appeared. All bands are well resolved and were assigned to bands three, di and monocarbonyl. These bands shift when replacing 12C with 13C.

5 However, for CO adsorbed on CaY zeolite [3] adsorption of two molecules on the same cation, manifested in a shift of CO band with coverage, does not lead to its splitting in two maxima as expected for the dicarbonyl. In the case of calcium, in the spectra we saw how, with increasing temperature and pumping, one of the two bands decreased, while the second band remained at the same place. In this connection, the question arise, how does the experimental results with nickel differ from the experiment with calcium?

The DFT-calculation results showed that for the Ca dicarbonyl complex in zeolite, as compared with Ni dicarbonyl, due to weaker interaction between the molecules, splitting of CO band is small and the second band of CO vibration coincides with that of monocarboonyl.

With the increase in temperature, the experiment reveals the phenomenon of linkage isomerism, when CO molecule is adsorbed vie oxygen atom.

6 To observe this phenomenon, the following models were created: Model where CO is adsorbed on a free calcium cation, Simple model of zeolite, Adsorption on oxide, Adsorption of CO on CaY zeolite

7 Analysis of the obtained results of calculation demonstrates a good agreement with the experimental data. On the right graph, which demonstrates the calculation results, you can see how the vibration frequency of a free CO molecule and during adsorption deviates. When a molecule is adsorbed by carbon, the vibration frequency increases, and the maximum value is reached in the case of a free calcium cation. When the molecule is adsorbed by oxygen, the vibration frequency decreases by approximately the same value as it increases on adsorption by carbon.

7.5 The dependence of the vibration intensity on frequency was also analyzed. The right graph shows that the higher the vibration frequency, the lower the intensity. This dependence in a fair agreement with the experimental data shown in the left graph.

8 At the end of the report, the following conclusions can be drawn

- The DFT method was used to calculate CO adsorption on models displaying oxide, CaY zeolite and free calcium cation.

- It was shown why the splitting of the dicarbonyl band, unlike NiY zeolite does not occur in the spectrum of CO adsorbed on CaY zeolite. One of the dicarbonyl bands coincides with that of monocarbonyl

- Models of CaY zeolite reveal linkage isomerism, when CO can be adsorbed both by carbon or oxygen. When CO is adsorbed by oxygen, the frequency decreases by approximately the same value by which it increases when adsorbed by carbon.

- The greater is the size of the surrounding anions, the higher is the frequency of CO adsorbed on Ca^{2+}

-The increase of CO vibrational frequency is accompanied by the decrease of absorbance, in a fair agreement with the experiment

9 Thanks for your attention. Ready to answer your questions.