SPECTROSCOPIC AND QUANTUM CHEMICAL STUDY OF ADSORBED OZONE

Aminev T.R., Tsyganenko A.A. and Krauklis I.V.
Saint Petersburg State University, Saint Petersburg, Russia
8919300@gmail.com

Despite its great importance for ecology, only few works deal with ozone ad-sorption studied by IR spectroscopy so far ([1, 3, 4] and refs. therein). Due to its low stability, adsorbed ozone is a promising object for the resonance IR laser-induced photodecomposition or photoozonolysis [5].

We succeeded to obtain frequencies for ν_1, ν_3 and ν_{1+3} combination modes for all eight isotopomers of chemisorbed ozone [1, 2]. All the isotopic species have different distinct bands of ν_{1+3} combination, while the ν_1 and ν_3 bands are split into three or four maxima containing several unresolved close lines. This is because ν_1 and ν_3 mods, which were symmetric and antisymmetric stretching vibrations for a free molecule, are localized now on two different bonds of the molecule.

Several variants of ozone adsorption on TiO_2 (anatase) clusters have been calculated by DFT method using the B3LYP functional and 6-311+G(d) basis. Two models: TiO_2 molecule and a $Ti_{20}O_{40}$ cluster reveal two stable conformations: bidentate and monodentate. This was found for both the 4- and 5-coordinated surface Ti sites of the cluster.

The calculated frequencies of the combination ν_{1+3} mode for the bidentate and monodentate conformations on the five and four coordinated titanium atoms multiplied by the scaling factor are shown in figure 1. All the 5 investigated ozone complexes well reproduce the experimentally observed splitting of ν_{1+3} band and the decrease in anharmonicity detected in the experiment. The most energetically favorable conformation turns out to be a monodentate adsorbed ozone molecule on a 4-coordinated titanium atom. However, the separation between the bands of ν_1 and ν_3 vibrations is better reproduced for the bidentate molecule on the same site, as it was reported earlier in [6].

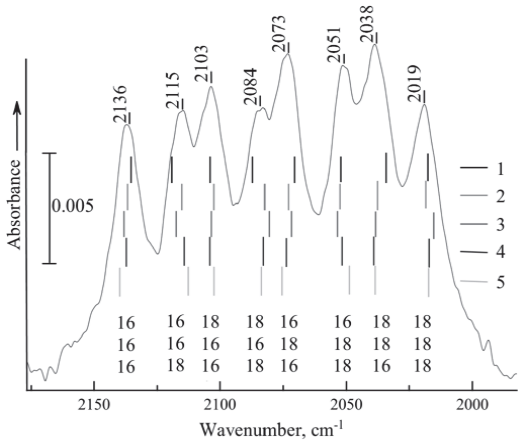

Fig. 1. Experimental spectrum and calculated frequencies. The numerated lines show the calculated frequencies of mono on TiO_2, mono and bi- on 5- coordinated Ti, bi and mono on 4-coordinated Ti respectively

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