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Report
on the dissertation presented by Oleg PESTSOV, entitled "Resonant IR photochemistry of adsorbed molecules" submitted for the PhD degree in Physical and Mathematical Sciences of The Saint Petersburg University

This dissertation deals with the resonant excitation of the vibrational states of molecules adsorbed on a surface for developing adsorptive or catalytic processes. The work aims at obtaining a fundamental understanding of the processes of excitation of vibrational states during resonant excitation.

The manuscript is divided into three main chapters, plus an introduction and conclusion. The dissertation is well-organized, very clearly presented and discussed, and well documented (80 references).

First, Oleg Pestsov introduces the objective of his study, the chosen methodology, the novelty and the statements of the work. Further Chapter 1 presents a review of the literature. The first observations of the effect of resonant IR excitation of adsorbed molecules on their reactivity were reported in 1978. This paved the way for many investigations, and the introduction of tunable lasers and more recently ultrafast tunable lasers gave a strong impulse to this research topic. However, a complete control of initiation and direct catalytic reactions is still a challenge. Thus, the numerous attempts to separate isotopes were not successful mostly due to energy exchange of vibrational excitation between adsorbed molecules. All this underlines the complexity of controlling the surface processes.

However, from its literature analysis, Oleg Pestsov was able to define the most favorable conditions to achieve isotope selectivity by vibrational excitation. The adsorbent nature, strength of adsorbate interaction with the support, adsorbate coverage, range of frequency of excitation, value of the molar absorption coefficient of the studied vibration must be well selected. As a result, the study concerns ozone decomposition and ozonolysis of dichloroethylene on titanium dioxide and other metal oxides.

The experimental techniques are described in the second Chapter. The study is performed on a home-design low temperature vacuum IR cell, ozone and isotopic ozone were prepared in the laboratory, and the samples were irradiated in situ in a vacuum set up where the IR cell is coupled to a MIR tunable laser with radiation comprised between 1989 and 2330 cm^{-1}.

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The experimental results are presented and discussed in the Chapter 3. In a first step, adsorption of ozone and its isotopes ($^{16}O_3$, $^{18}O_3$ and the 6 others isotopomers) at 77K on different metal oxides (TiO_2, SiO_2, CeO_2, ZnO, BeO) and zeolites were studied by IR spectroscopy. An accurate analysis of the position and isotopic splitting of the IR bands with special attention to the combination $\nu1+\nu3$ band at about 2100 cm^{-1} was done. On zeolite, the position of the $\nu1+\nu$ 3 band reflects the strength on Lewis acidity. On TiO_2, the $\nu1+\nu3$ bands reveal the presence of weak as well as strong ozone adsorption with different structures of strongly chemisorbed species. Close features are noted for ceria. Thus, hydrated TiO_2 and CeO_2 are the most promising for laser initiation experiments. As a consequence of this preliminary study, accurate following of the decomposition of each isotopic ozone species by IR irradiation can be possible.

Initiation of the decomposition of ozone species by laser irradiation was not successful on ceria, likely due to the small amount of adsorbed species. By contrast, on titania, laser irradiation at appropriate frequency leads to a change in the ratio between the bands of the different isotopologues. This demonstrates that decomposition of specific isotopologues of ozone can be initiated by well-chosen frequency of the laser irradiation.

Further experiments aimed at initiating ozonolyse of dichloroethane by laser irradiation. First experiments performed on silica show that ozonolysis of dichloroethylene can be initiate by laser irradiation when temperature is increased up to 168 K. On titania, reaction proceeds spontaneously even at 77 K and laser irradiation markedly increases the rate. These results are very interesting even if they do not point reactivity a specific ozone isotopologue.

As a conclusion, it has to be underlined the well-constructed approach of the study presented by Oleg Pestsov as well as the quality of its experimental work with mastering of time-resolved spectroscopy that opens prospects for the study of other systems. This work has been presented in 4 international conferences, and Oleg Pestsov is co-author of 5 publications, 3 of which are directly related to the subject of the thesis.

Hence, the thesis entitled “Resonant IR photochemistry of adsorbed molecules” presented by Oleg Pestsov clearly deserves to be awarded the degree of PhD in Physical and Mathematical Sciences of the Saint Petersburg State University.

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