The adsorption of chlorotrifluoroethene on titanium dioxide surface studied by DRIFT spectroscopy and periodic *ab initio* calculations

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The growing concerns of scientific communities and international politicians about climate changes and environmental degradation related to the human activities have even more highlighted the requirements for a deeper knowledge of atmospheric chemistry and physics as well as the needs for the developments of eco-sustainable technologies to limit the human's environmental impact. In this framework the photo-catalysis of atmospheric pollutants, with particular emphasis on organic compounds, on titanium dioxide (TiO_2) surface represents a very attractive and efficient application. Hence, the study of the chemistry of TiO_2 and the adsorption of molecules on its surface is required for the understanding of the adsorbate-substrate interaction, being the adsorption process the first step in the heterogeneous phase reactions for the degradation of atmospheric pollutants.

In this work the adsorption of C_2F_3Cl (chlorotrifluoroethene), a compound widely used by industry for the synthesis of fluorinated polymers, on TiO_2 is explored by coupling experimental data from DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) to periodic quantum chemical calculations. Spectra have been recorded at 298 K by using a proper environmental chamber which allows a very accurate control of the experimental conditions, whereas periodic ab initio calculations have been carried out employing the Crystal suite of programs [1]. The modifications on C_2F_3Cl induced by its interaction with TiO_2 have been derived upon comparison of the infrared spectrum of the free molecule with that of the molecule adsorbed on the TiO_2 surface. The results show that the molecule mainly adsorbs to the surface by means of the fluorine atoms. In order to better understand the adsorption process and interpret the observed shifts in the C_2F_3Cl vibrational frequencies, the TiO_2 - C_2F_3Cl system has been simulated from first principles according to two different models. Details of the experimental apparatus and data inversion procedure, experimental results and preliminary answers from molecular simulations will be presented.

[1] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. Llunell, CRYSTAL06 User's Manual, University of Torino (Torino, 2006).