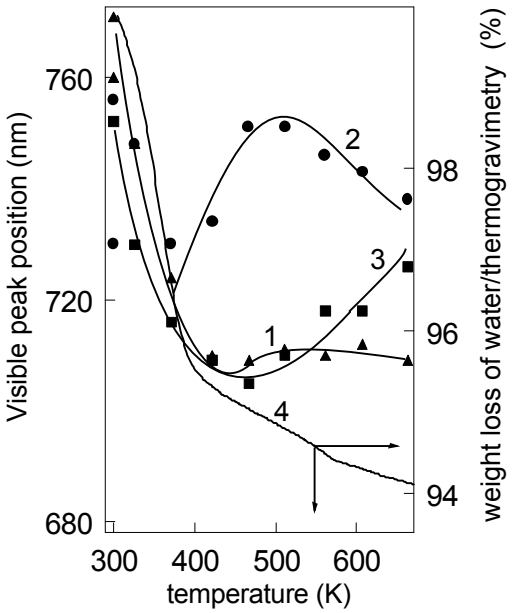
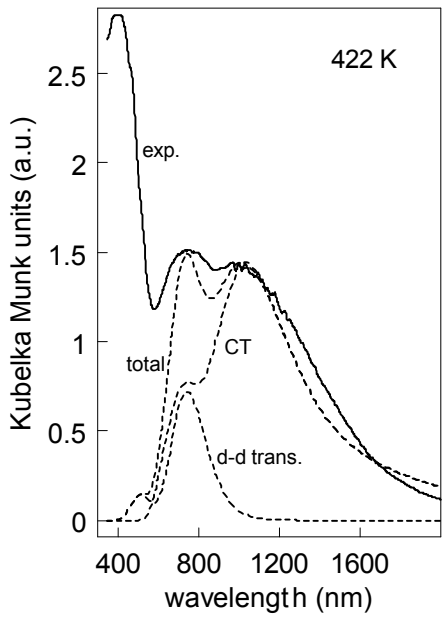
INFLUENCE OF THE GAS ATMOSPHERE AND TEMPERATURE ON THE UV/VIS ABSORPTION BANDS AND THE BAND GAP ENERGIES OF $H_{4-x}Cs_xPVMo_{11}O_{40}$ (x = 0, 2) : EXPERIMENT AND THEORY

J. Melsheimer[a], J. Kröhnert[a], R. Ahmad[a], S. Klokishner[b]and F.C. Jentoft[a]
[a]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin
[b]State University of Moldova, Mateevich str. 60, 2009 Kishinev, Moldova

In order to understand the transformations of the Keggin-type $H_{4-x}Cs_xPVMo_{11}O_{40}$ (x=0,2) compounds with rising temperature over long time on stream of different gas atmospheres, in situ UV/Vis/near-IR spectroscopic studies were carried out from room temperature to 663 K. Diffuse reflectance spectra were recorded over a long time on He stream at RT and un-der in situ conditions in the abovementioned temperature range using an improved spec-trometer and a suitable microreactor. Peak positions and the band gap energies of the com-pounds used were determined from apparent absorption spectra. Propene, iso-propa-nol, water and the oxidation products were analyzed by GC.
He flow over 12 hours at RT increased the apparent absorption because of the incipient of loss of crystal water.The experimental observed blue shift of the visible absorption band (with the exception of oxygen) in the range of total crystal water loss (up to 425 K) and the increase of the near-IR absorption were explained on the basis of quantum-mechanical calculations of the shapes and positions of the charge transfer and d-d bands arising from Mo^{5+}-Mo^{6+} and V^{4+}-Mo^{6+} pairs in intact and ill-defined fragments of the Keggin structure. It was concluded that with removal of crystal water during the action of He, propene, O_2/propene and increasing temperature reduced species with protons located at the bridging oxygens promote a blue shift of the visible band, while a large number of ill-defined species form the near-IR part of the spectra in the temperature range 326 - 600 K. The band gap energy decreases in most cases with increasing temperature.



Influence of gas atmospheres and temperature on the visible peak position and thermogravimetric behaviour of $H_2Cs_2PVMo_{11}O_{40}$
1 : He, 2 : O_2; 3 : O_2/propene; 4 : Tg curve



Contributions from the d-d transitions and the charge transfer band to the spectrum of $H_4PVMo_{11}O_{40}$ at 422 K