



Experimental and Computational Study of the Apparent Absorption Spectra of Nanostructured Manganese Tungstate Catalysts

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Abstract—The UV-Vis spectra of a series of MnWO₄ nanorods with different Mn/W ratio represent the subject of the present study. Since the surfaces of the obtained catalysts are damaged to understand the observed spectra transformations with the change of the Mn/W content homometallic binuclear, trinuclear and tetranuclear linear manganese clusters, binuclear tungsten clusters and mixed manganese-tungsten clusters of different nuclearity are examined. The choice of the linear manganese clusters of different nuclearity for examination is dictated by the revelation of MnO_x units on the surface of the MnWO₄ nanorods. The structures of these different nuclearity species have been optimized, and their absorption have been calculated with the aid of density functional theory (DFT). It has been shown that homonuclear tungsten clusters demonstrate only ligand-metal charge transfer, while manganese clusters demonstrate both ligand-metal and metal-ligand charge transfer. At the same time ligand-metal and manganese-tungsten electron transfers are characteristic for mixed manganese-tungsten clusters. A comparison of the calculated absorption spectra of the modeled clusters with those observed for MnWO₄ nanorods showed, that chain-like manganese clusters mainly contribute to the high-energy part of the UV-Vis spectra, while the fall in the intensity of the observed spectra in the range of the longer wavelengths is connected not only with the decrease of the relative manganese content, but it also manifested due to decrease of the concentration of the mixed manganese-tungsten clusters, mainly contributing to this part of the spectra.

Keywords—MnWO₄ nanorods, UV-Vis spectra, ligand-metal and metal-ligand charge transfer

I. INTRODUCTION

Transition metal tungstates AWO₄ (A=Mn, Co, Ni, Cu, Zn) have recently attracted considerable interest due to their potential ability to be used for photochemical hydrogen gas production [1], as multiferroic materials [2], as photocatalysts for water splitting [3], as humidity

sensors [4], as optical fibers [5] or both photovoltaic electrochemical cells [6]. Wolframite-type tungstates demonstrate like other compounds from this series several interesting magnetic, multiferroic, photoluminescence and catalytic properties. Recently the electronic structures and optical properties of a series of AWO₄ (A=Mn, Co, Ni, Cu, Zn) tungstates with wolframite structure have been characterized using a combination of UV-Vis spectroscopy and electronic structure calculations [7]. It has been obtained that in MgWO₄ and ZnWO₄ the lowest energy optical excitation represents a ligand to metal charge transfer (LMCT) excitation from oxygen 2p nonbonding orbitals to antibonding W 5d orbitals. At the same time in other compounds of this series the lowest energy charge transfer excitation is a metal-metal charge transfer (MMCT) transition from the partially occupied 3d orbitals of the A²⁺ transition metal ion to the unoccupied tungsten 5d orbitals.

About 10 years ago the interest of researchers switched to nanostructured AWO₄ compounds. In [8] MnWO₄ composed of a number of nano-plates in flower-like clusters was successfully produced. The authors of paper [9] described the morphology transitions from W₁₈O₄₉ nanowires to MnWO₄ hubnerite nano-cocoons by using mixed MnCl₂ and WCl₆ in a simple solvothermal process. A simple hydrothermal method to the shape-controlled synthesis of MnWO₄ nanocrystals without any surfactants and templates was suggested in [10]. Single-crystal MnWO₄ nanowires were successfully synthesized for the first time in [11]. In [12] it has been demonstrated that nanostructured, crystalline MnWO₄ can be converted into a highly active and selective catalyst by stabilizing a defect-rich MnO_x surface phase. Terminating MnO_x zigzag chains on the (010) crystal planes were assumed to contain structurally site-isolated oxygen defects that most possibly assure good performance of the catalyst in

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propane activation. To control the surface phase of rod-shaped MnWO_4 nano-crystalline catalysts in [13] hydrothermal techniques in combination with *in situ* Raman spectroscopic and transmission electron microscopy studies were applied. The identification of the highly active MnO_x units on the surface of the MnWO_4 nanorods definitely improved the understanding of the promotional effect of Mn in these catalytic systems. Information about the composition of the catalyst surface, i.e. about the presence of certain ions or clusters on it, can also be obtained from the study of the UV-Vis spectra, because for sufficiently strong electric dipole allowed transitions the intensity of the optical beam which traverses the material mainly reduces in its surface layer. With this in mind in the present paper it is performed the experimental study of the apparent absorption spectra of the MnWO_4 nanorods with different content of manganese and tungsten. Since the surfaces of the nanorods, as it was earlier proved in [13], are not crystallographically ideal, and the structure of these surfaces cannot be identified in detail by X-ray analysis, in the present paper the observed changes in the UV-Vis spectra of samples with different W/Mn ratio will be qualitatively explained employing DFT modeling of clusters which represent constituent parts of the nanorods with different content of manganese and tungsten. The DFT calculations are also expected to give information about the types of charge transfer transitions (ligand-metal, metal-ligand or metal-metal), which mainly contribute to the observed spectra. On this basis an explanation of the spectra transformation with the change of the ratio Mn/W will be given.

II. EXPERIMENTAL SECTION

The MnWO_4 nanorods were obtained by hydrothermal synthesis, the procedure of which is described in detail in paper [13]. The UV-Vis diffuse reflectance spectra were recorded at room temperature in the range of 200-800 nm with an Agilent Cary 5000 instrument equipped with an *in situ* cell (Harrick Praying Mantis diffuse reflectance attachment DRP-SAP in combination with a HVC-VUV reaction chamber). The compound BaSO_4 was used as a white standard. The apparent absorption spectra were calculated from the UV/Vis diffuse reflectance ones with the aid of the Kubelka-Munk formula. Briefly summarizing the experimental data on the apparent absorption spectra of the MnWO_4 nanorods with different Mn/W content one can notice the following features: (i) the absorption of the catalysts independently of the Mn/W ratio mainly occurs in the range of wavelengths 200-450 nm; (ii) the intensity of the apparent absorption spectra of the nanorods in the whole spectra range falls with decrease of the relative manganese content; (iii) the absorption spectrum of the bulk sample significantly differs from those for nanorods. It spreads from 200 nm to 800 nm

and changes insignificantly in the range 200-420 nm. At longer wavelengths up to 500 nm the spectra intensity noticeably falls, and at about 560 nm a weak band is observed.

III. COMPUTATIONAL DETAILS

Since the surfaces of the obtained series of catalysts are damaged [12,13] and, consequently, the translational symmetry of these samples is broken at least at the surface, which mainly participates in light absorption, to understand the observed spectra transformations with the change of the manganese/tungsten content we examine homometallic binuclear, trinuclear and tetranuclear linear manganese clusters, binuclear tungstate clusters and mixed manganese-tungstate clusters of different nuclearity. The linear manganese clusters of different nuclearity for examination are included in examination because MnO_x units have been revealed on the surface of the MnWO_4 nanorods.

The optimization of the structures of the selected clusters, the calculation of the spectra of molecular vibrations as well as of the apparent absorption spectra were conducted with the aid of DFT, employing the ORCA suite of programs, version 4.2.1 [14]. For clusters containing Mn^{II} ions the DFT calculations were performed using the spin unrestricted formalism, while for clusters which only comprise W^{VI} ions the spin restricted open shell DFT formalism was employed. All calculations necessary to obtain the spectra shapes were carried out with the aid of the REVPBE functional [15,16], which has been proven to give reasonable results in the description of the spectroscopic characteristics of a series of clusters containing transition metal ions [17-19]. With the aid of the zero-order regular approximation (ZORA) [20], the scalar relativistic ZORA Hamiltonian was selected [14,20]. For heavy tungsten atoms the segmented all-electron relativistically contracted SARC-ZORA-TZVP basis set [14] is employed, while for all other atoms composing the cluster the ZORA-def2-TZVP functions are used. To considerably reduce the computation time of the exchange terms the combination of resolution of identity (Split-RI-J) and "chain of spheres" (COSX) approximation have been applied [21]. In the calculations the target precision of the energy and wavefunctions for all examined clusters was 10^{-9} Hartree. The integration accuracy around the heavy tungsten atoms has been increased, using large integration grids in the radial part. Within the ORCA package the numerical values of the vibrational frequencies have been also calculated. The TDDFT method [14] within the ORCA package has been applied to obtain the excited state energies of the examined species. With the aid of these characteristics the absorption spectra arising from the Mn-, W- and mixed Mn-W clusters of different nuclearity have been calculated. The identification of the origin of the transitions in the observed spectra of Mn-W catalysts

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in different ranges of wavelengths was performed applying the following procedure. First, for a definite complex the molecular orbitals have been quantitatively calculated [14]. Then the transitions between the molecular orbitals, which give the main contribution to a definite peak in the calculated spectrum have been identified. Finally, analyzing the composition of these orbitals, a conclusion has been made about the type of the transition i.e. if it is of ligand-metal, metal-metal or ligand-metal origin.

IV. MODEL STRUCTURES

In the consideration model W, Mn and mixed W-Mn bi-, tri- and tetranuclear clusters are employed (Fig.1). These clusters will further allow us to correlate the electronic structure with the observed spectra transformations in the MnWO_4 nanorods with different content of Mn and W. The initial structures of the clusters (Fig.1) are taken from the crystallographic data for the bulk MnWO_4 compound [22]. As it is commonly accepted in DFT modeling, the charges of these complexes are neutralized by adding protons.

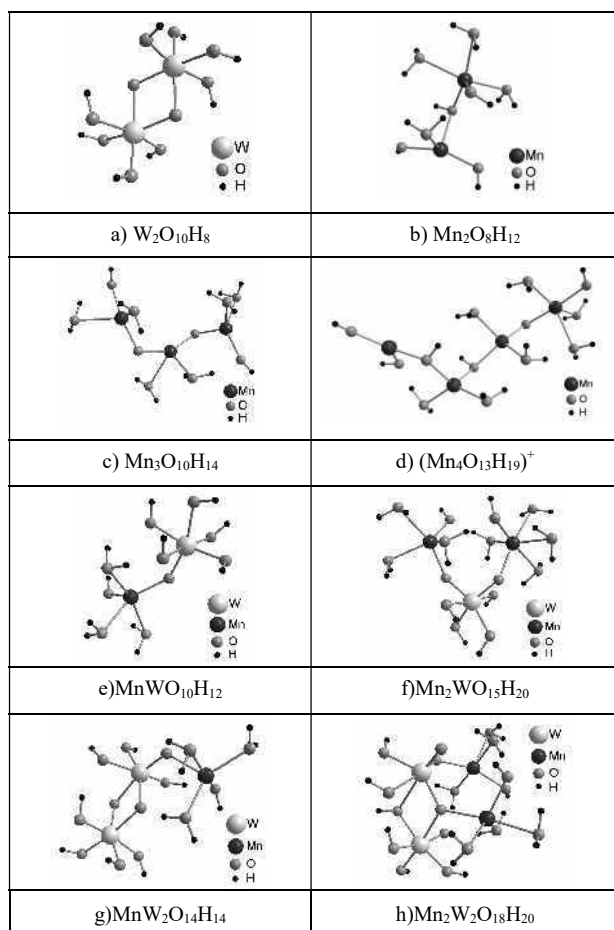


Figure 1. Geometric structures of homonuclear and heteronuclear model clusters containing Mn and W atoms. The composition of each cluster is indicated below its picture.

For binuclear tungsten and manganese clusters the initial structures represent dumbbells, which constitute parts of the structure of the bulk MnWO_4 compound [22] and contain two metal ions with each of them surrounded by 6 oxygen ions. The optimized binuclear structures are depicted in Fig. 1a and Fig. 1b. From Fig.1a it follows that the binuclear $\text{W}_2\text{O}_{10}\text{H}_8$ cluster keeps its dumbbell shape, and each W^{VI} ion remains octahedrally surrounded due to its high oxidation state. At the same time the manganese dumbbell after structure optimization transforms into a cluster in which the two metal ions are coupled through one oxygen instead of two in a dumbbell (Fig.1b). The surrounding of each Mn ion contains different number of oxygen ligands and it is not octahedral, confirming the formation of a defective structure. The initial geometry of the linear trinuclear Mn_3 cluster represents octahedrally coordinated Mn^{II} ions which are connected through common oxygens to form a chain-like structure. In the result of the DFT optimization this structure taken for consideration to mimic the defect-rich MnO_x surface phase zigzag chains [12,13] transforms into the $\text{Mn}_3\text{O}_{10}\text{H}_{14}$ species (Fig.1c) in which all Mn ions possess a distorted tetrahedral surrounding instead of an octahedral one. The structure of a linear tetranuclear cluster in which all manganese ions are in the octahedral surrounding as in the MnWO_4 compound converts after the DFT optimization into a damaged chain-like one (Fig.1d) in which two Mn ions are tetrahedrally coordinated, while the number of the surrounding ligands of the edge Mn ions is equal to 3 and 5, respectively. The optimized tetranuclear manganese cluster bears a positive charge. This cluster is introduced in consideration to get a qualitative explanation of the observed spectra transformation with the change of the Mn/W ratio as well as to reveal the effect of the surface chains detected with aid of a series of different experiments [13].

In a further step we consider mixed manganese-tungstate clusters the optimized structures of which are also presented in Fig.1. The Mn-W fragment of the bulk compound neutralized by adding protons after DFT optimization gives the binuclear $\text{MnWO}_{10}\text{H}_{12}$ species (Fig.1e), in which the tungsten ion remains octahedrally coordinated, while the nearest surrounding of the manganese ion becomes pentanuclear instead of the octahedral one in the initial MnWO_4 compound. In the optimized structure of the trinuclear $\text{Mn}_2\text{WO}_{15}\text{H}_{20}$ (Fig.1f) cluster with alternating W and Mn ions the tungsten ion is octahedrally coordinated, while the distorted ligand surroundings of the Mn ions are pentanuclear and hexanuclear, respectively. In the trinuclear $\text{MnW}_2\text{O}_{14}\text{H}_{14}$ (Fig.1g) and tetranuclear $\text{Mn}_2\text{W}_2\text{O}_{18}\text{H}_{20}$ (Fig.1h) clusters the tungsten dumbbell keeps its form, while the surroundings of the manganese ions are damaged and not anymore octahedral as in the initial MnWO_4 compound.

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V. QUALITATIVE INTERPRETATION OF THE OBSERVED SPECTRA OF NANORODS WITH DIFFERENT MANGANESE-TUNGSTEN CONTENT

In this section the DFT calculated spectra arising from different species (Fig.1) are compared with those observed for MnWO_4 nanorods, the types of the species present in the surface layer of the catalysts and most probably contributing to these spectra are revealed. On this basis a qualitative explanation is given of the spectra transformations under the change of the W/Mn ratio.

The calculated spectrum of the $\text{W}_2\text{O}_{10}\text{H}_8$ cluster (Fig.2,

curve 1) extensively expands in the UV part. The maximum of this spectrum, which arises from the strongest transition at 208 nm with the oscillator strength 0.14, was superimposed with the maxima of the experimental curves and put equal to unity like as those for the observed spectra. In the accepted scale the magnitudes of the intensities of the band maxima of other examined clusters were determined relative to the intensity of the main peak in the spectrum of the $\text{W}_2\text{O}_{10}\text{H}_8$ cluster. From our calculations it follows that up to 220 nm (Fig.2) the main contribution to the observed spectra comes from O \rightarrow W electron transfer. Then other clusters may also come into the play. The charge transfer transitions exhibited by the clusters $\text{Mn}_2\text{O}_8\text{H}_{12}$ (Fig.1b), $\text{MnWO}_{10}\text{H}_{12}$ (Fig.1e), $\text{Mn}_2\text{WO}_{15}\text{H}_{20}$ (Fig.1f), $\text{MnW}_2\text{O}_{14}\text{H}_{14}$ (Fig.1g), $\text{Mn}_3\text{O}_{10}\text{H}_{14}$ (Fig.1c), $(\text{Mn}_4\text{O}_{13}\text{H}_{19})^+$ (Fig.1d), as well as by the $\text{Mn}_2\text{W}_2\text{O}_{18}\text{H}_{20}$ (Fig.1h) cluster may contribute to the range of wavelengths 220-290 nm. For this set of clusters the analysis of the molecular orbitals shows, that the transitions, forming the indicated part of the spectra, are of the type of O \rightarrow Mn, Mn \rightarrow (OH) $^-$ and O \rightarrow W.

The oscillator strengths of the O \rightarrow Mn and Mn \rightarrow (OH) $^-$ transitions in the $\text{Mn}_2\text{O}_8\text{H}_{12}$ species change from 0.0045 up to 0.011. As to binuclear tungsten $\text{W}_2\text{O}_{10}\text{H}_8$ species in this range of wavelengths its contribution to the entire spectrum comes from a series of O \rightarrow W transitions with the oscillator strengths in between 0.01-0.03. Therefore, the intensity of the spectra of the $\text{W}_2\text{O}_{10}\text{H}_8$ cluster in the diapason 220-290 nm is appreciably higher than that of the $\text{Mn}_2\text{O}_8\text{H}_{12}$ species. In the mentioned range of wavelengths the spectrum of the $\text{MnWO}_{10}\text{H}_{12}$ cluster mainly originates from O \rightarrow W transitions, the most intensive peak positions are situated in the range from 228 nm to 288 nm with the corresponding oscillator strengths in the diapason from 0.007 to 0.016. Only one transition of the type O \rightarrow Mn at 236 nm with the oscillator strength 0.013 contributes to above mentioned range.

The highest in energy relatively strong transition of the $\text{Mn}_2\text{WO}_{15}\text{H}_{20}$ cluster is situated at 244 nm, possesses the oscillator strength of about 0.006, and it is formed by the transfers O \rightarrow Mn and O \rightarrow W. The very close in energy

strong band at 248 nm with the oscillator strength $f=0.092$ relates to ligand-metal O \rightarrow W transfer. Then three close contributing transitions near 249 nm with oscillator strengths in the range 0.005-0.01 are of the Mn \rightarrow (OH) $^-$ and O \rightarrow Mn origin. The calculated transitions at 250 nm and 258 nm with oscillator strengths of 0.005 and 0.0125, respectively, refer to O \rightarrow W transfer. A weaker in intensity transition at 260 nm with $f=0.006$ arises from the Mn \rightarrow (OH) $^-$ transfer.

For the $\text{MnW}_2\text{O}_{14}\text{H}_{14}$ species (Fig.1g) up to 290 nm the charge transfer transitions with the following band

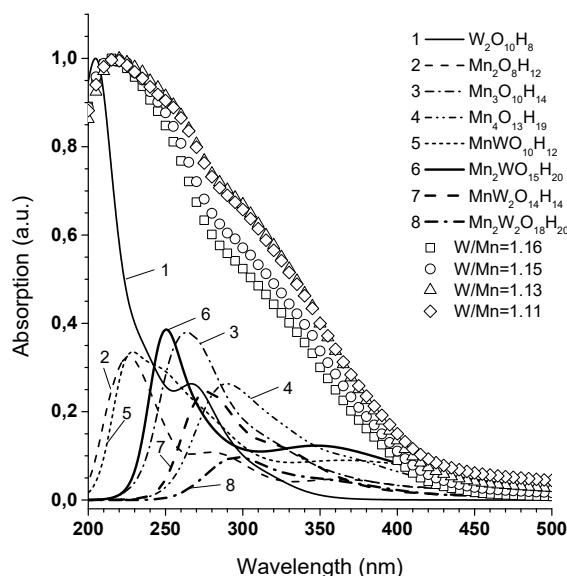


Figure 2. Observed spectra of nanostructured MnWO_4 catalysts with different W/Mn content and DFT calculated spectra of manganese, tungstate and mixed manganese-tungstate clusters.

positions and oscillator strengths, given in parenthesis, contribute: 262nm (0.005), 267nm (0.004), 271nm (0.005), 277nm (0.006), 289nm (0.004). The first two transitions and the last two in this series refer mainly to the O \rightarrow W electron transfer, while the third one corresponds to the excitation of an electron from the manganese ion to the (OH) $^-$ ligand. As to the $\text{Mn}_2\text{W}_2\text{O}_{18}\text{H}_{20}$ cluster its contribution to the spectra in the range of 220-290 nm is small as compared with that of all clusters above discussed. The maximum of its band at 297nm corresponds to the excitations metal-metal in the two pairs Mn-W representing constituent parts of the cluster.

Finally, we notice that the clusters $\text{Mn}_3\text{O}_{10}\text{H}_{14}$ and $(\text{Mn}_4\text{O}_{13}\text{H}_{19})^+$ imitating the MnO_x chains detected on the catalyst surface [12,13] also contribute to the spectra range 220-290 nm. The spectra of these species are formed only by transitions between Mn^{2+} ions and the ligands O^{2-} and OH $^-$ and can serve as indicators of manganese content on the surface layer. Here it should be

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also noticed that in the range of wavelengths 220-290 nm the peak intensity of the band arising from the trinuclear manganese cluster is higher as compared with the bands arising from other clusters. At the same time in the range 220-290 nm in the spectra of all other heteronuclear species the contribution and the strength of the transitions involving manganese ions and, consequently, indicating, their content is not so high. Thus, from the performed analysis of the calculated spectra and qualitative considerations it follows that the chain like manganese clusters demonstrating the transitions $O \rightarrow Mn$ and $Mn \rightarrow (OH)^-$ ensure the spectra modification in the range 220- 290 nm.

The calculated intensities of the parts of the spectra of the examined clusters, which fall into the range of wavelengths 300-460 nm, are lower as compared to those in the range of shorter wavelengths. Most probably this may be the reason of the observed intensity fall in the indicated wavelength range for all samples. However, the most interesting is the result that along with the contribution of the chain-like bi-, tri- and tetranuclear manganese clusters a not negligible contribution to this part of the spectra comes from the heteronuclear Mn-W clusters. Again the performed analysis of the molecular orbitals, of the transitions, which form the spectra at longer wavelengths, shows that for the binuclear Mn-W species the metal-metal electron transfer is responsible for the absorption in the range of wavelengths 340-460 nm, which is in agreement with the results of paper [7]. The oscillator strengths of the most pronounced transitions contributing to this range change from 0.03 to 0.01. For the Mn_2W cluster the most intensive transitions in the range 320-404 nm also belong to the electron transfer between the manganese and tungsten ions. As to the MnW_2 cluster the transitions in the range 303-335 nm can be mainly assigned to the type ligand-metal $O \rightarrow W$ transfer. However, their oscillator strengths are weak and fall in between 0.005-0.008. Finally, the heteronuclear cluster Mn_2W_2 contributes with the transitions of the type $Mn \rightarrow W$ to the range 290-615 nm, the oscillator strengths of these transitions fall in between 0.006 and 0.012. Thus, the heteronuclear manganese-tungsten and homonuclear manganese clusters may be responsible for the shape and intensity of the spectra of nanorods in the range 290-460 nm, and the main contribution to this spectra part comes from the $O \rightarrow Mn$, $Mn \rightarrow OH$ and $Mn \rightarrow W$ electron transfers. From this it follows that the mentioned spectra range should undergo most pronounced changes under decreasing of the manganese content. As it is seen from Fig.2 this qualitative conclusion is in line with the observed transformations of the spectra shape.

VI. CONCLUDING REMARKS

In the present paper the observed changes in the UV-Vis spectra of a series of $MnWO_4$ nanorods with different Mn/W ratio are discussed and qualitatively explained. Taking into account, that the main contribution to the apparent absorption spectra of the catalysts comes from the surface layer the surface layer was modeled by three types of clusters. The first type of clusters contains only Mn or W ions. In the second type of clusters Mn and W ions alternate, while the third type clusters is formed by alternating manganese ions and tungsten dumbbells. With this aim the structure of bi-, tri- and tetranuclear manganese and binuclear tungsten species, as well of manganese-tungsten species of different nuclearity and architecture has been optimized, and the absorption spectra of these species have been calculated with the aid of the DFT method. It has been demonstrated that the manganese dumbbells representing a structural element of $MnWO_4$ catalysts convert very easily into damaged binuclear clusters in which the manganese ions are connected through one common oxygen ion and the nearest surrounding of each Mn-ion is not anymore octahedral. Most probably this ability of manganese dumbbells to convert into clusters in which the Mn-ions share only one oxygen leads to the appearance on the surface of chains of these ions with damaged surroundings. Moreover, under certain conditions these chains can be easily broken, and single MnO_x species can be formed.

At the same time the high oxidation degree of the tungsten ions does not allow to destroy their octahedral surroundings, and the structure of the tungsten dumbbells remains unchanged under different external conditions. The DFT optimization of the structure of the tungsten dumbbell and calculation of its spectra allowed to reveal the range of wavelengths, to which oxygen-tungsten $O \rightarrow W$ charge transfer transitions contribute. It has been demonstrated that the spectra of manganese species reveal two types of transfer and, namely, ligand-metal and metal-ligand electron transfer of the types of $O \rightarrow Mn$ and $Mn \rightarrow (OH)^-$, respectively. The homonuclear clusters of tungsten demonstrate strong charge-transfer transitions $O \rightarrow W$, while for mixed manganese-tungsten clusters the electron transfers $O \rightarrow Mn$, $O \rightarrow W$ and $Mn \rightarrow W$ are characteristic.

The performed calculations and the comparison of the spectra of the model clusters with those of the nanorods allowed to make several qualitative conclusions. The range of wavelengths, wherein the spectra of nanorods are observed, can be conditionally subdivided into two parts. In the range of wavelengths 220-290 nm the chain like manganese clusters are mainly responsible for the fall in the spectra intensity: the decrease in the relative manganese concentration provokes the fall in the spectra intensity. As to the range of the longer wavelengths the

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fall of the spectra transformations are also connected with decrease of the relative manganese content, which immediately leads to the fall in the intensities of the bands. However, this a bit more pronounced decrease is connected not only with the chain-like manganese clusters, but also with the mixed tungsten-manganese clusters which demonstrate metal-metal Mn→W transitions mainly contributing to this part of the spectra.

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REFERENCES:

1. M. N. Huda, M. Al-Jassim and J. A. Turner, "Mott Insulators: An Early Selection Criterion for Materials for Photoelectrochemical H₂ Production," *J. Renewable Sustainable Energy*, vol.3, No. 053101, 2011.
2. O. Heyer, N. Hollman, I. Klassen, S. Jodlauk, L. Bohaty, P. Becker, J. A. Mydosh, T. Lorenz and D. Khomskii, "A new multiferroic material: MnWO₄," *J. Phys.: Condens Matter*, vol.18, L471-L475, 2006.
3. C. Janaky, K. Rajeshwar, N. R. de Tacconi, W.Chanmanee and M. N. Huda, "Tungsten-Based Oxide Semiconductors for Solar Hydrogen Generation," *Catal. Today*, vol.199, pp.53-64, 2013.
4. A. M. Edwin Suresh Raj, C. Mallika, O. M. Sreedharan and K. S. Nagaraja, "Manganese Oxide–Manganese Tungstate Composite Humidity Sensors," *Mater. Lett.*, vol.53, pp.316-320, 2002.
5. J. G. Rushbrooke and R. E. Anson, "Optical Fibre Readout and Performance of Small Scintillating Crystals for a Fine-Grained Gamma Detector," *Nucl. Instrum. Methods Phys. Res. Sect. A*, vol.280, pp.83-90, 1989.
6. P. K. Pandey, N. S. Bhave and R. B. Kharat, "Characterization of Spray Deposited CoWO₄ Thin Films for Photovoltaic Electrochemical Studies," *J. Mater. Sci.*, vol.42, pp.7927-7933, 2007.
7. S. Dey, R. A. Ricciardo, H. L. Cuthbert and P. M.; Woodward, "Metal-to-Metal Charge Transfer in AWO₄ (A=Mg, Mn, Co, Ni, Cu, or Zn) Compounds With the Wolframite Structure," *Inorg. Chem.*, vol.53, pp.4394-4399, 2014.
8. S. Thongtem, S. Wannapop, A. Phuruangrat and T. Thongtem, "Cyclic Microwave-Assisted Spray Synthesis of Nanostructured MnWO₄," *Mater. Lett.*, vol.63, pp.833-836, 2009.
9. W. B. Hu, X. L. Nie and Y. Zh. Mi, "Controlled Synthesis and Structure Characterization of Nanostructured MnWO₄," *Mater. Char.*, vol.61, pp85-89, 2010.
10. L. Yang, Yo. Wang, Yu. Wang, X. Wang, L. Wang and G. Han, "Shape-Controlled Synthesis of MnWO₄ Nanocrystals Via a Simple Hydrothermal Method," *J. Alloys Comp.*, vol.578, pp.215-219, 2013.
11. Yo. Wang, L. Yang, Yu. Wang, X. Wang and G. Han, "Morphology-Controlled Synthesis and Characterization of MnWO₄ Nanocrystals via a Facile, Additive-Free Hydrothermal Process," *J. Alloys Comp.*, vol. 654, pp.246-250, 2016.
12. X. Li, T. Lunkenbein, V. Pfeifer, M. Jastak, P. K. Nielsen, F. Girgsdies, A. Knop-Gericke, F. Rosowski, R. Schlögl and A. Trunschke, "Selective Alkane Oxidation by Manganese Oxide: Site Isolation of MnO_x Chains at the Surface of MnWO₄ Nanorods," *Angew. Chem. Int. Ed.*, vol.55, pp.4092-4096, 2016.
13. X. Li, T. Lunkenbein, J. Kröhnert, V. Pfeifer, F. Girgsdies, F. Rosowski, R. Schlögl and A. Trunschke, "Hydrothermal Synthesis of Bi-Functional Nanostructured Manganese Tungstate Catalysts for Selective Oxidation," *Faraday Discuss.*, vol.188, pp.99-113, 2016.
14. F. Neese, Wennmohs, F. ORCA-An ab initio, DFT and Semiempirical SCF-MO Package -Version 4.2.1, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim a. d. Ruhr, Germany, 2019.
15. Y. Zhang, W. Yang, Comment on "Generalized Gradient Approximation Made Simple". *Phys. Rev. Lett.*, vol.80, pp.890, 1998.
16. J. P. Perdew, K. Burke, M. Ernzerhof, Perdew, Burke, and Ernzerhof Reply. *Phys. Rev. Lett.*, vol.80, pp.891, 1998.
17. S. Klokishner, O. Reu, G. Tzolova-Müller, R. Schlögl, A. Trunschke, "Apparent Absorption Spectra of Silica Supported Vanadium-Titanium Oxide Catalysts: Experimental Study and Modeling," *J. Phys. Chem. C*, vol.118, pp.14677-14691, 2014.
18. S. Klokishner, O. Reu, J. Noack, R. Schlögl and A. Trunschke, "Experimental Study and Modeling of the UV-Vis and Infrared Spectra of the [VO(O₂)Hheida]⁻ Complex Dissolved in Water," *J. Phys. Chem. A*, vol.121, pp.7157-7164, 2017.
19. C. S. Guo, K. Hermann, M. Hävecker, A. Trunschke and R. Schlögl, "Silica-Supported Titania Species: Structural Analysis from Quantum Theory and X-ray Spectroscopy," *J. Phys. Chem. C*, vol.116, pp.22449-22457, 2012.
20. E. van Lenthe, E. J. Baerends, J. G. Snijders, "Relativistic regular two-component Hamiltonians", *J. Chem. Phys.*, vol.99(6), 4597-4610, 1993.
21. S. Kossmann, F. Neese, "Efficient Structure Optimization with Second-Order Many-Body Perturbation Theory: The RIJCOSX-MP2 Method," *J. Chem. Theory Comput.*, vol.6, 2325-2338, 2010.
22. H. Weitzel, "Kristallstrukturverfeinerung von Wolframiten und Columbiten," *Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie (-144,1977)*, vol.144, pp.238-258, 1976.