# Hydrogen-atom Abstraction from Methane by Stoichiometric Early Transition Metal Oxide Cations

Yan-Xia Zhao,[ab] Xiao-Nan Wu, [ab] Zhe-Chen Wang,[ab] Sheng-Gui He[a*], and Xun-Lei Ding,[a*]

[a]*Beijing National Laboratory for Molecular Science,*

*State Key Laboratory for Structural Chemistry of Unstable and Statble Species,*

*Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China,*

[b]*Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

*Author to whom correspondence should be addressed. E-mail: shengguihe@iccas.ac.cn, dingxl@iccas.ac.cn. Phone: 86-10-62536990. Fax: 86-10-62559373.

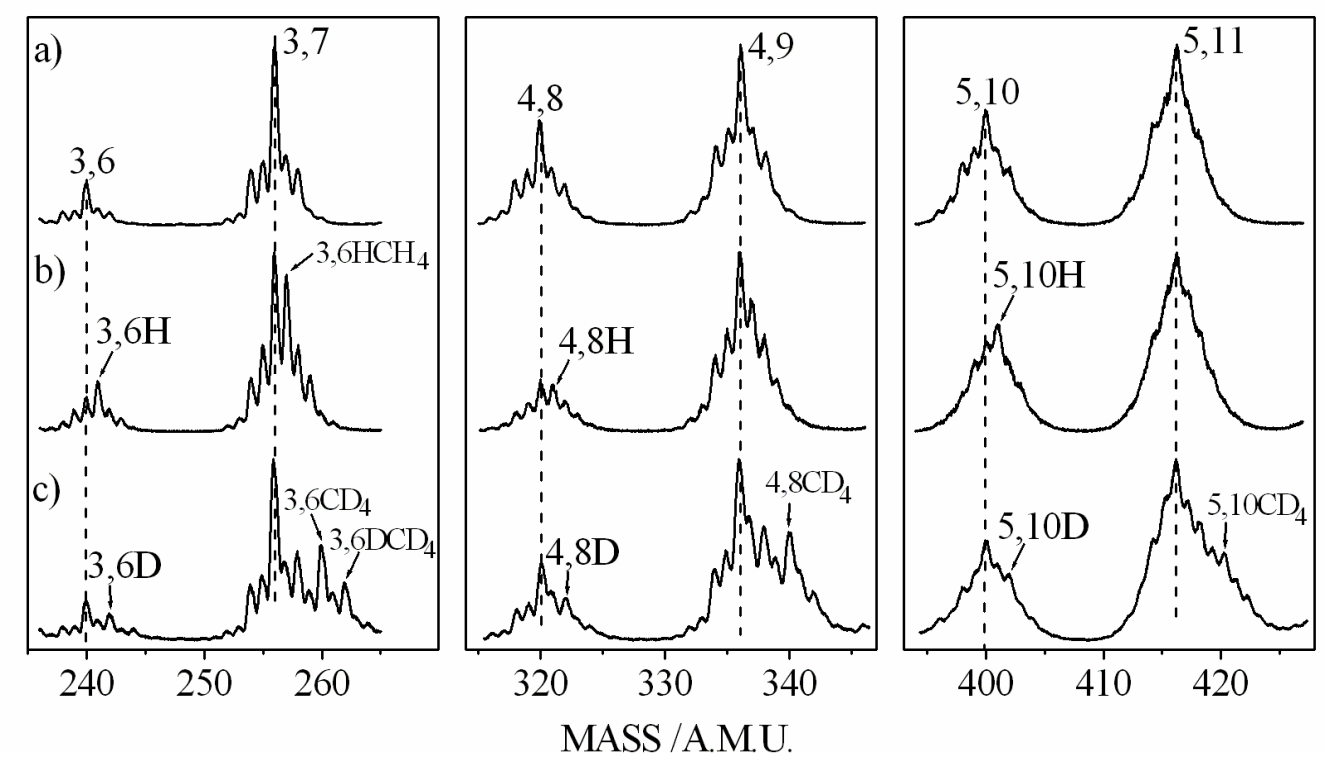


**Fig. S1** TOF mass spectra for reactions of $Ti_3O_{6,7}^+$, $Ti_4O_{8,9}^+$, and $Ti_5O_{10,11}^+$ with a) He, b) $CH_4$, and c) $CD_4$. Numbers *m*, *n* indicate $Ti_mO_n^+$ and *m*, *n*X denote $Ti_mO_nX^+$ in which X = H, D, $CD_4$, $HCH_4$, etc.

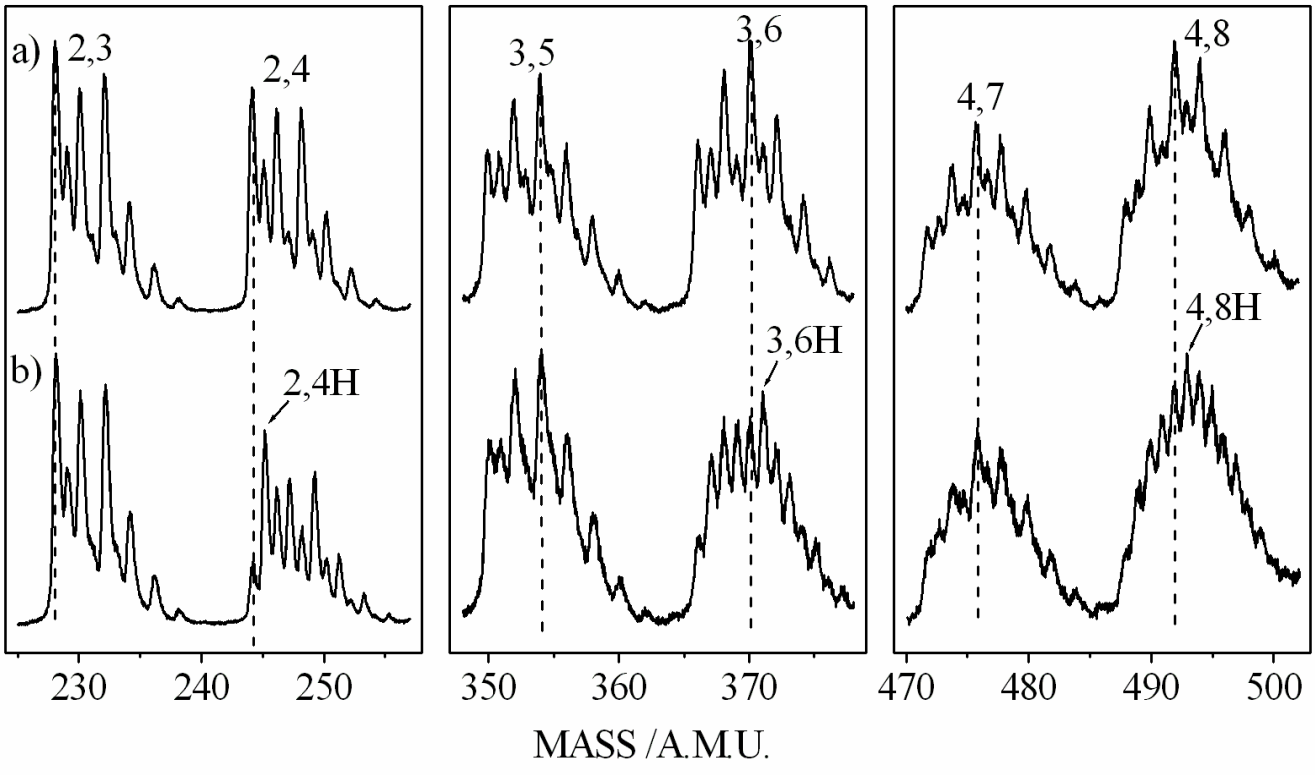


**Fig. S2:** TOF mass spectra for reactions of $Zr_2O_{3,4}^+$, $Zr_3O_{5,6}^+$, and $Zr_4O_{7,8}^+$ with a) He and b) $CH_4$. Numbers *m*, *n* denote $Zr_mO_n^+$ and *m*, *n*X denote $Zr_mO_nX^+$ in which X = H.

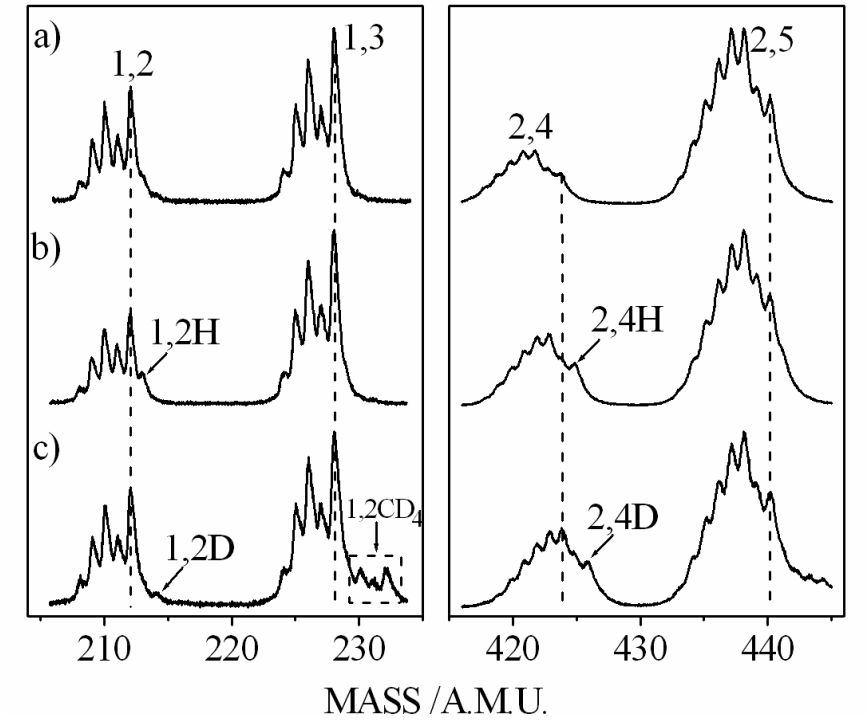


**Fig. S3:** TOF mass spectra for reactions of $HfO_{2,3}^+$ and $Hf_2O_{4,5}^+$ with a) He, b) $CH_4$, and c) $CD_4$. Numbers *m*, *n* denote $Hf_mO_n^+$ and *m*, *n*X denote $Hf_mO_nX+$ in which X = H, D, $CD_4$.

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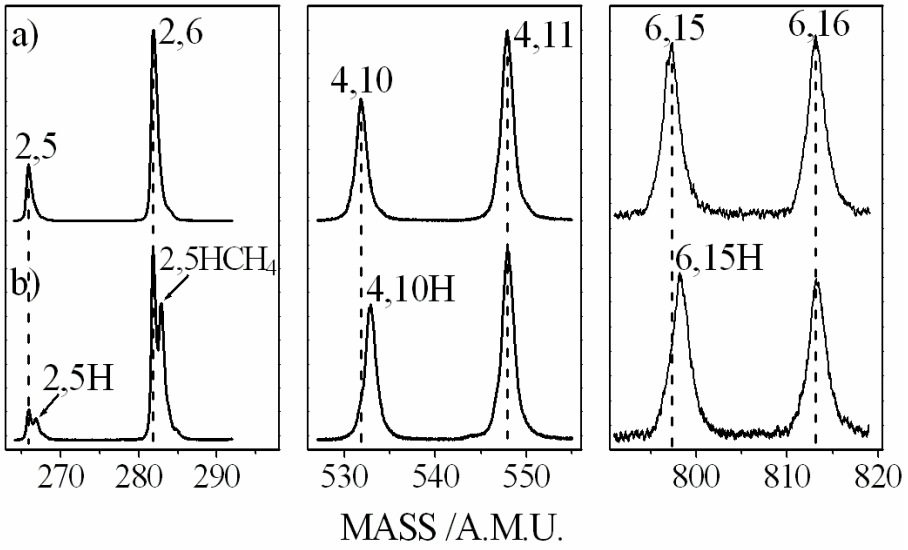


**Fig. S4:** TOF mass spectra for reactions of $Nb_2O_{5,6}^+$, $Nb_4O_{10,11}^+$, and $Nb_6O_{15,16}^+$ with a) He and b) $CH_4$. Numbers *m*, *n* denote $Nb_mO_n^+$ and *m*, *n*X denote $Nb_mO_nX^+$ in which X = H, $HCH_4$.

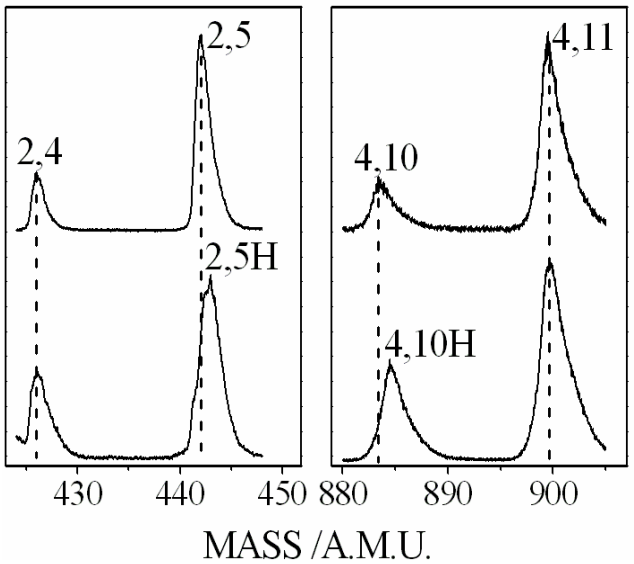


**Fig. S5:** TOF mass spectra for reactions of $Ta_2O_{4,5}^+$ and $Ta_4O_{10,11}^+$ with a) He and b) $CH_4$. Numbers *m*, *n* denote $Ta_mO_n^+$ and *m*, *n*X denote $Ta_mO_nX^+$ in which X = H.

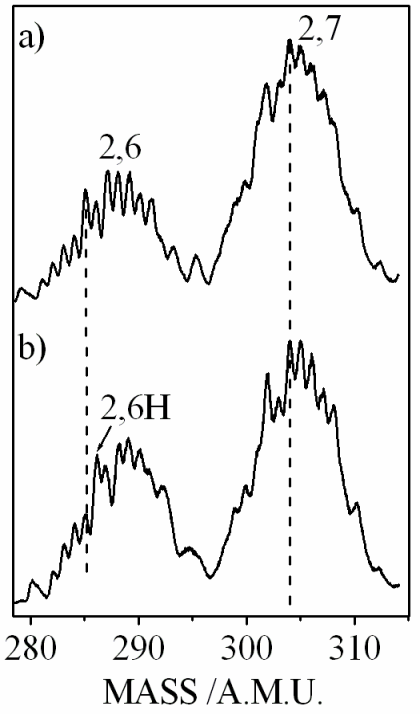


**Fig. S6:** TOF mass spectra for reactions of $Mo_2O_{6,7}^+$ with a) He and b) $CH_4$. Numbers *m*, *n* denote $Mo_mO_n^+$ and *m*, *n*X denote $Mo_mO_nX^+$ in which X = H.

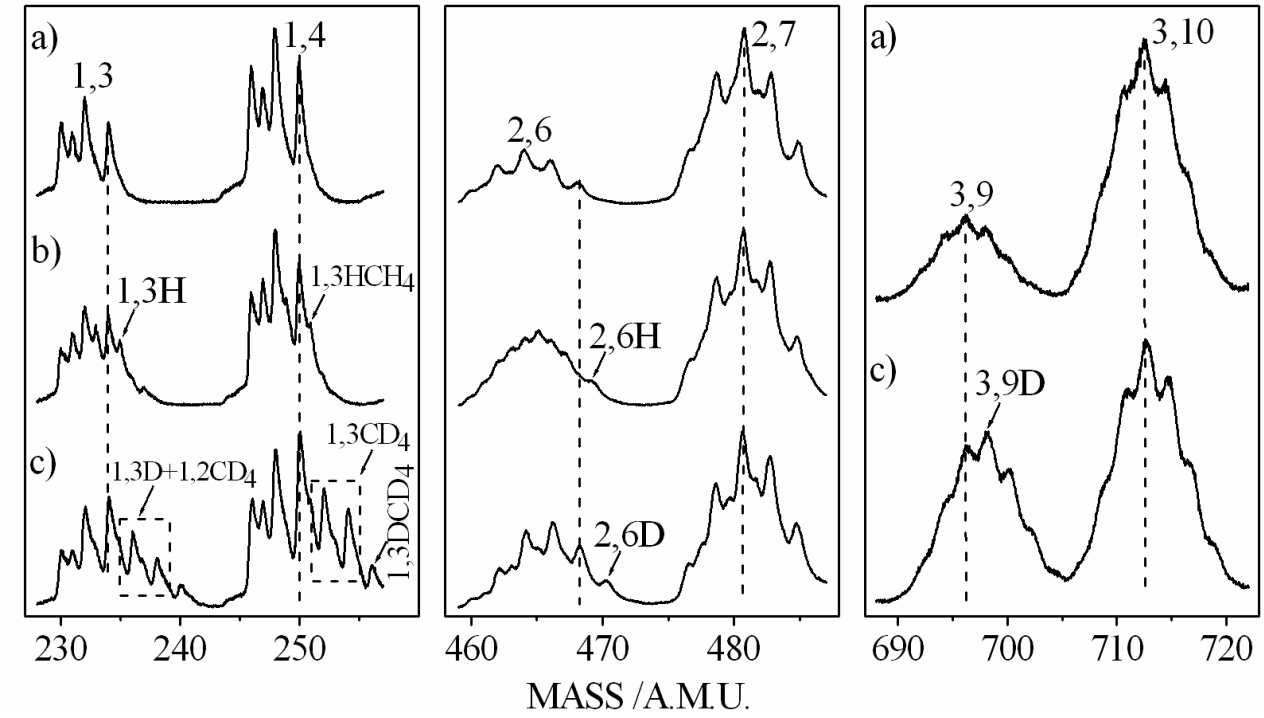


**Fig. S7:** TOF mass spectra for reactions of $WO_{3,4}^+$, $W_2O_{6,7}^+$, and $W_3O_{9,10}^+$ with a) He, b) $CH_4$, and c) $CD_4$. Numbers *m*, *n* denote $W_mO_n^+$ and *m*, *n*X denote $W_mO_nX^+$ in which X = H, D, $CD_4$, $HCH_4$, etc.

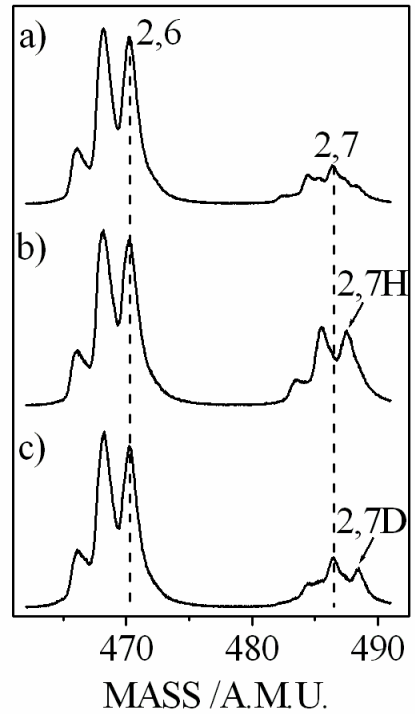


**Fig. S8:** TOF mass spectra for reactions of $Re_2O_{6,7}^+$ with a) He, b) $CH_4$, and c) $CD_4$. Numbers *m*, *n* denote $Re_mO_n^+$ and *m*, *n*X denote $Re_mO_nX^+$ in which X = H, D.