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Water Dissociation Mechanism in MOF-74[1] SEBASTIAN ZULUAGA, Wake Forest University, KUI TAN, University of Texas at Dallas, PIERE-MANUELE CANEPA, Wake Forest University, YVES CHABAL, University of Texas at Dallas, TIMO THONHAUSER, Wake Forest University — Water dissociation represents one of the most important reactions in catalysis, essential to surface and nano sciences. Combining in-situ IR spectroscopy and first-principles calculations, we demonstrate, for the first time, that water starts to dissociate at the metal centers of MOF-74 at temperatures as low as 150 °C. The fingerprint of this reaction is a sharp band in the IR spectrum at 970 cm^{-1} when D_2O is introduced into the MOF. Surprisingly, this fingerprint is not detected by experiments with H_2O. To explain this peculiar finding, we perform DFT simulations of the reaction, utilizing vdW-DF to capture the important van der Waals interactions. Our calculations show that, once the D_2O molecule is adsorbed at the metal center, the D atom is transferred to the oxygens of the linker (phenolate group), producing the notable O-D absorption band at 970 cm^{-1}, while the OD remains at the open metal sites. Even though we find that H_2O undergoes an analogous dissociation reaction, the corresponding O-H mode is strongly coupled to MOF vibrations and cannot easily be detected by experiments. Overall, this work elucidates water interactions with cation-exposed surfaces and aids in the development of more efficient catalysts for water dissociation.

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