Using supercomputers for fast advancing in heterogeneous photocatalysis technologies

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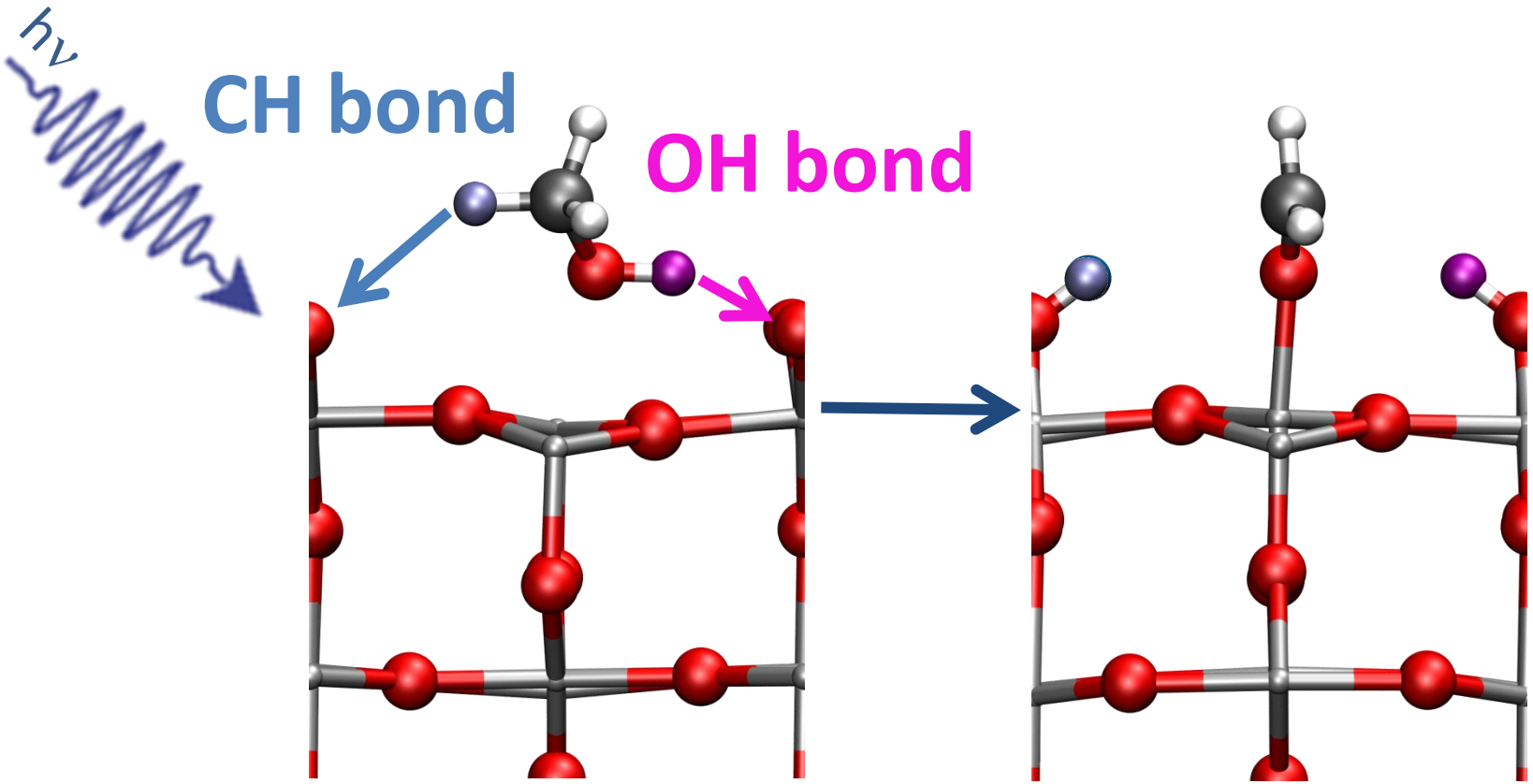
Heterogeneous Photocatalysis Technologies

- Water Splitting $H_2O \rightarrow H_2 + \frac{1}{2}O_2$
- CO_2 reduction
- Environmental remediation
- Synthesis of valuable chemicals (from simple to complex)

PAYOFF FROM THEORY

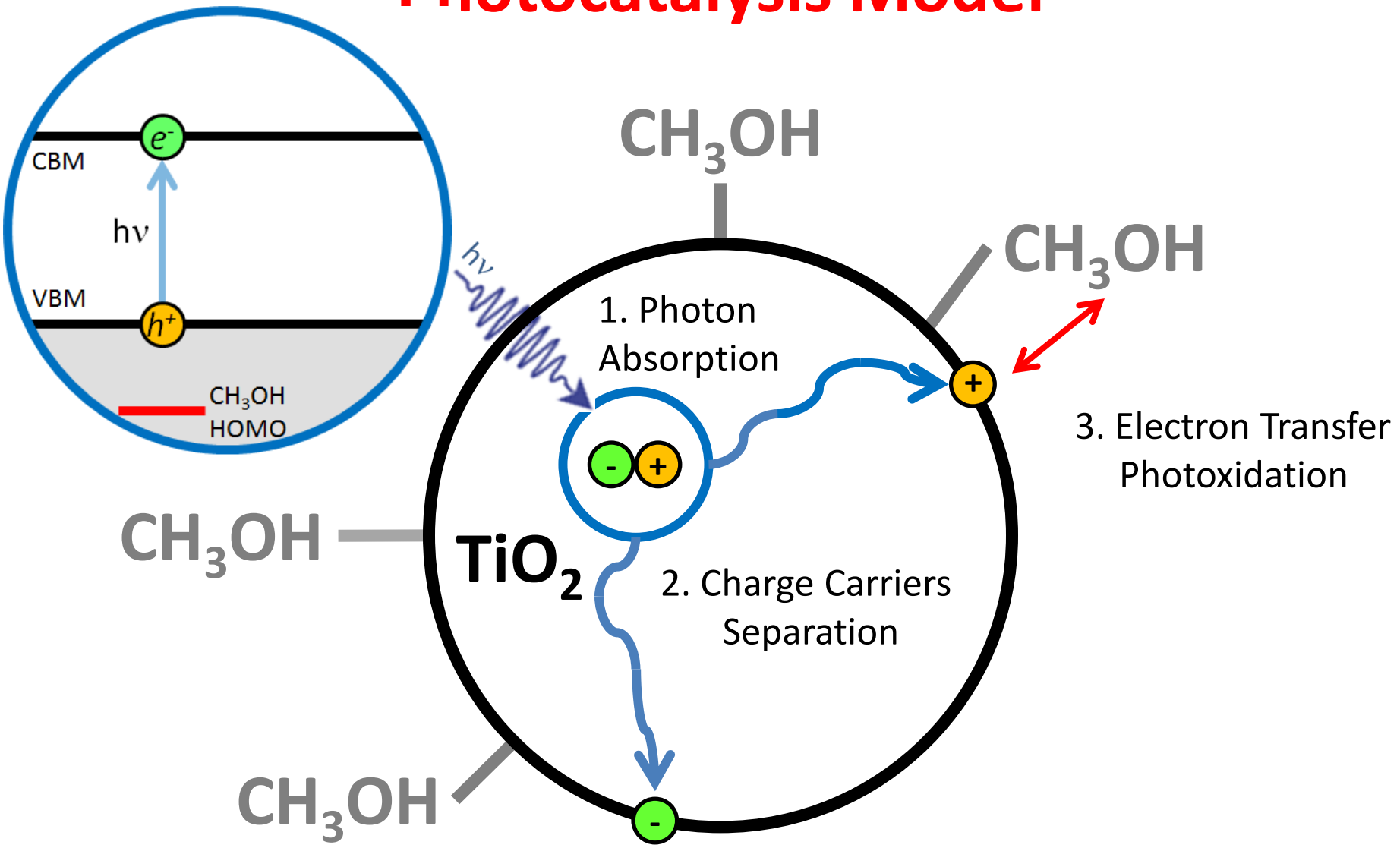
- Clear understanding of the reaction mechanism
- Clear interpretation of experiments
- Clues for improving efficiency
- Clues for identification of efficient photo-catalysts

CH_3OH to CH_2O Photo-oxidation on Single-Crystal TiO_2



$h\nu \leq 400$ nm (3.05 eV ~ E_g), UHV, 80 K

Photocatalysis Model

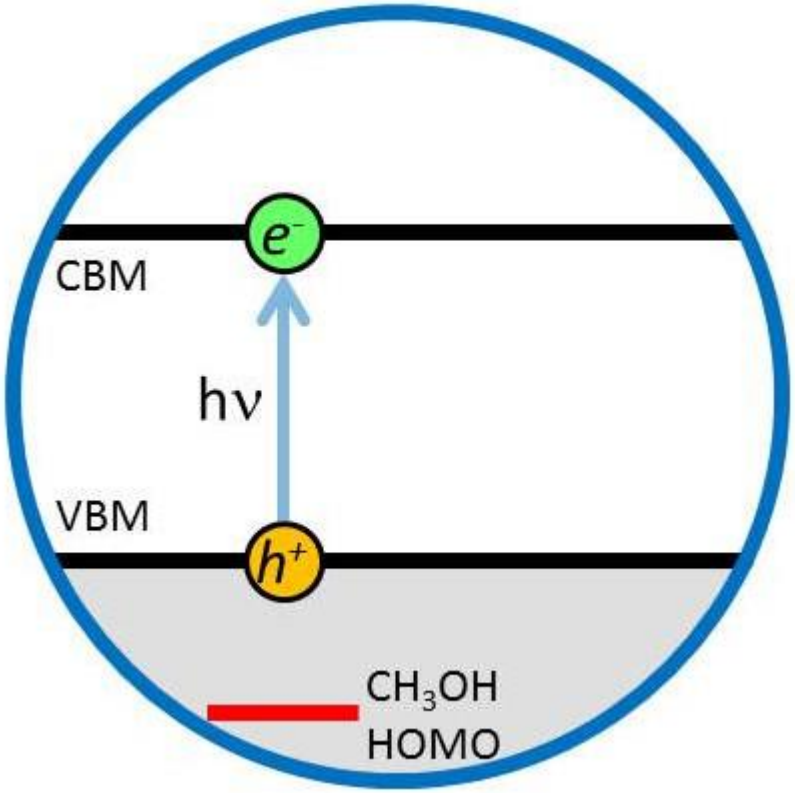


Level Alignment of a Prototypical Photocatalytic System: Methanol on TiO_2(110), Migani, A.; Mowbray, D. J.; Iacomino, A.; Zhao, J.; Petek, H.; Rubio, J. Am. Chem. Soc. 2013, 135, 11429–11432.

1. Question

PROBLEM

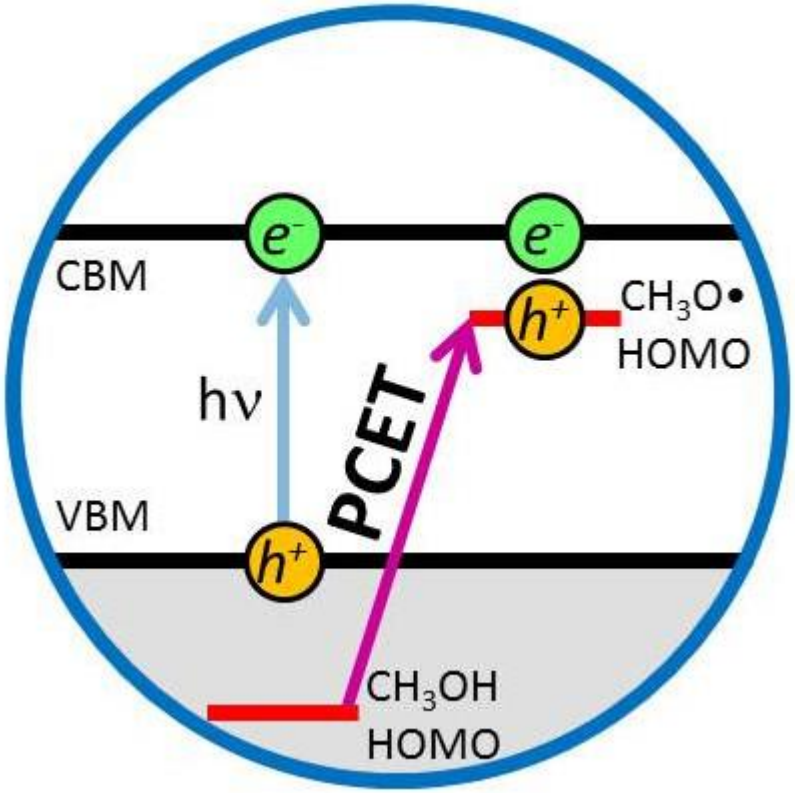
HOMO below VBM



1. Question

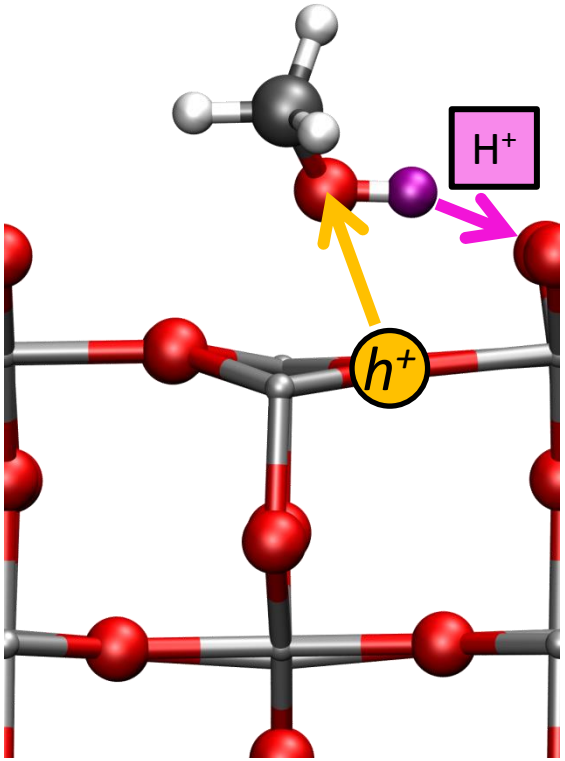
SOLUTION

PCET

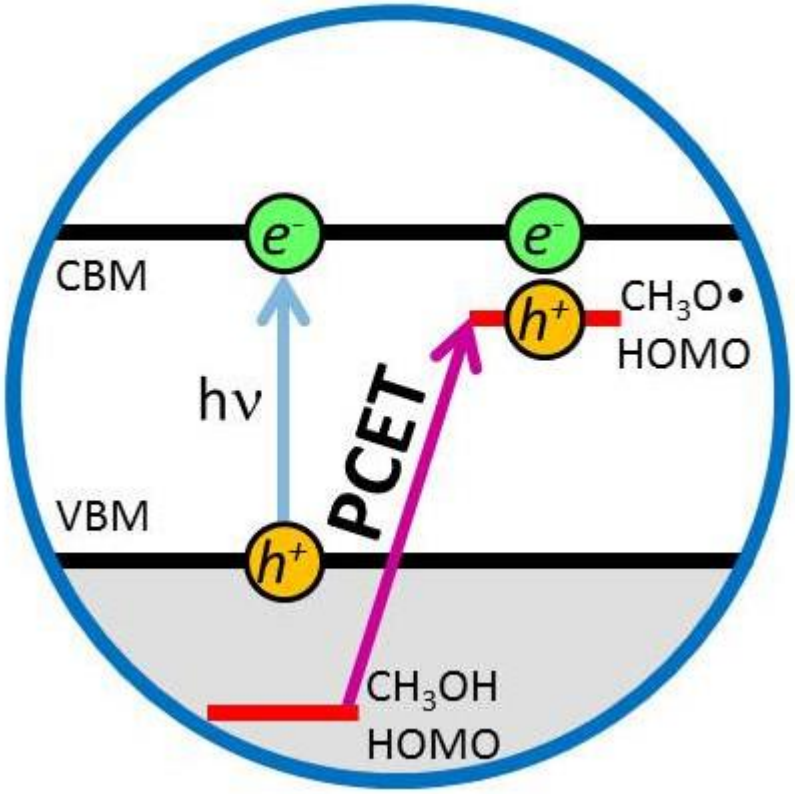


1. Question

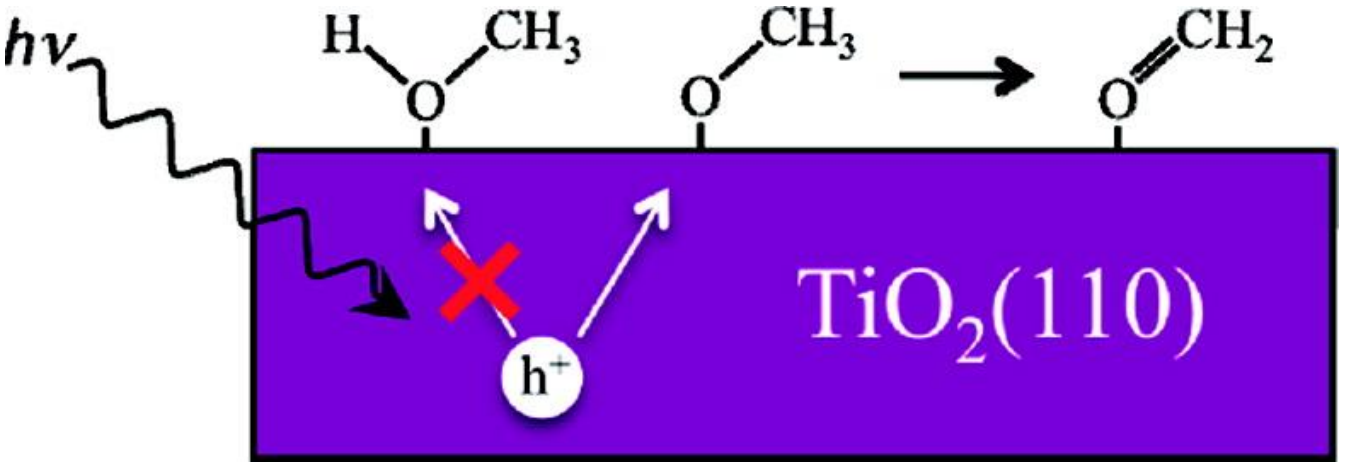
SOLUTION



PCET



2. Question



Which is the active species?

Published in: Mingmin Shen; Michael A. Henderson; *J. Phys. Chem. Lett.* **2011,** 2, 2707-2710.
DOI: 10.1021/jz201242k
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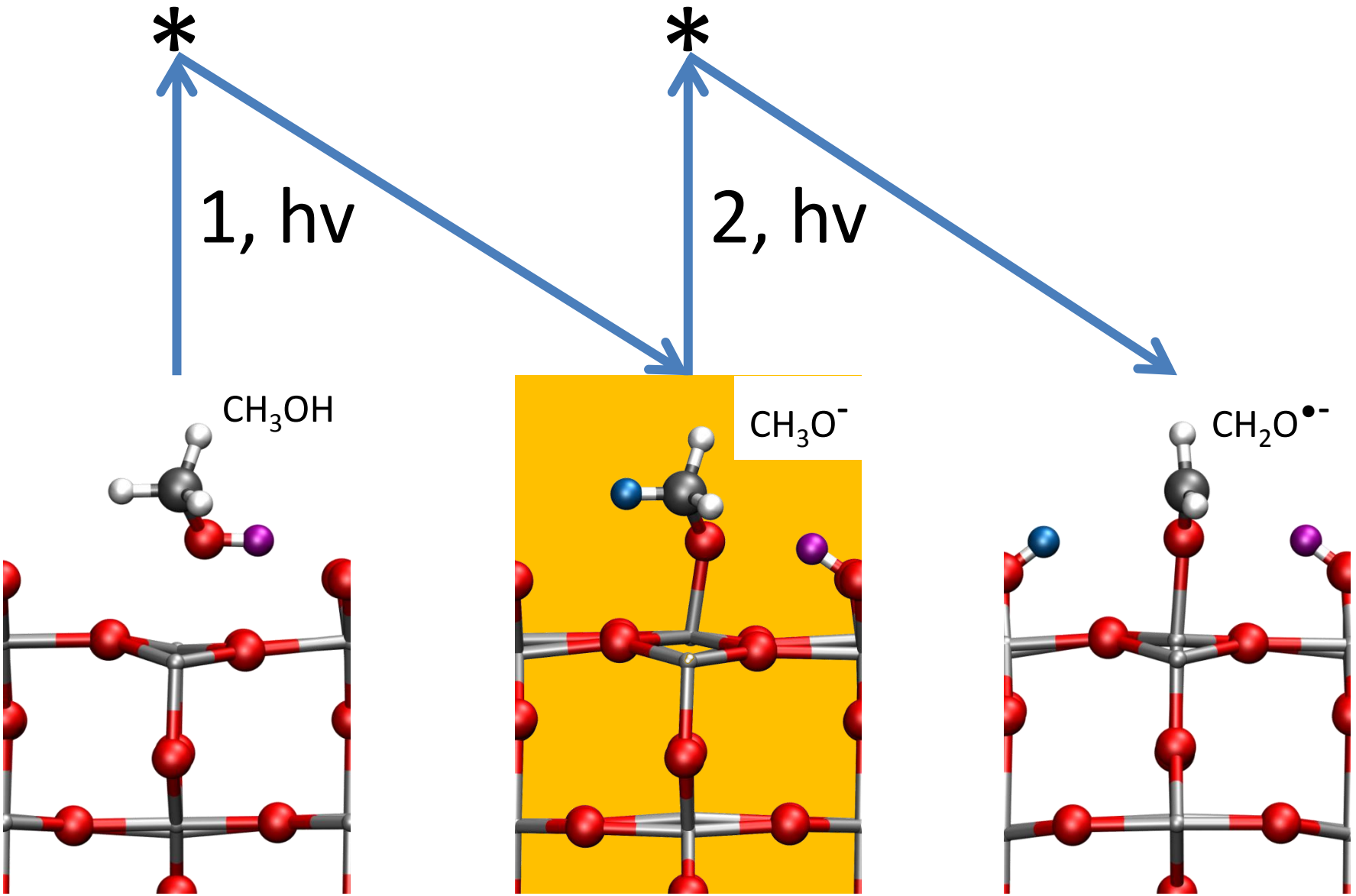
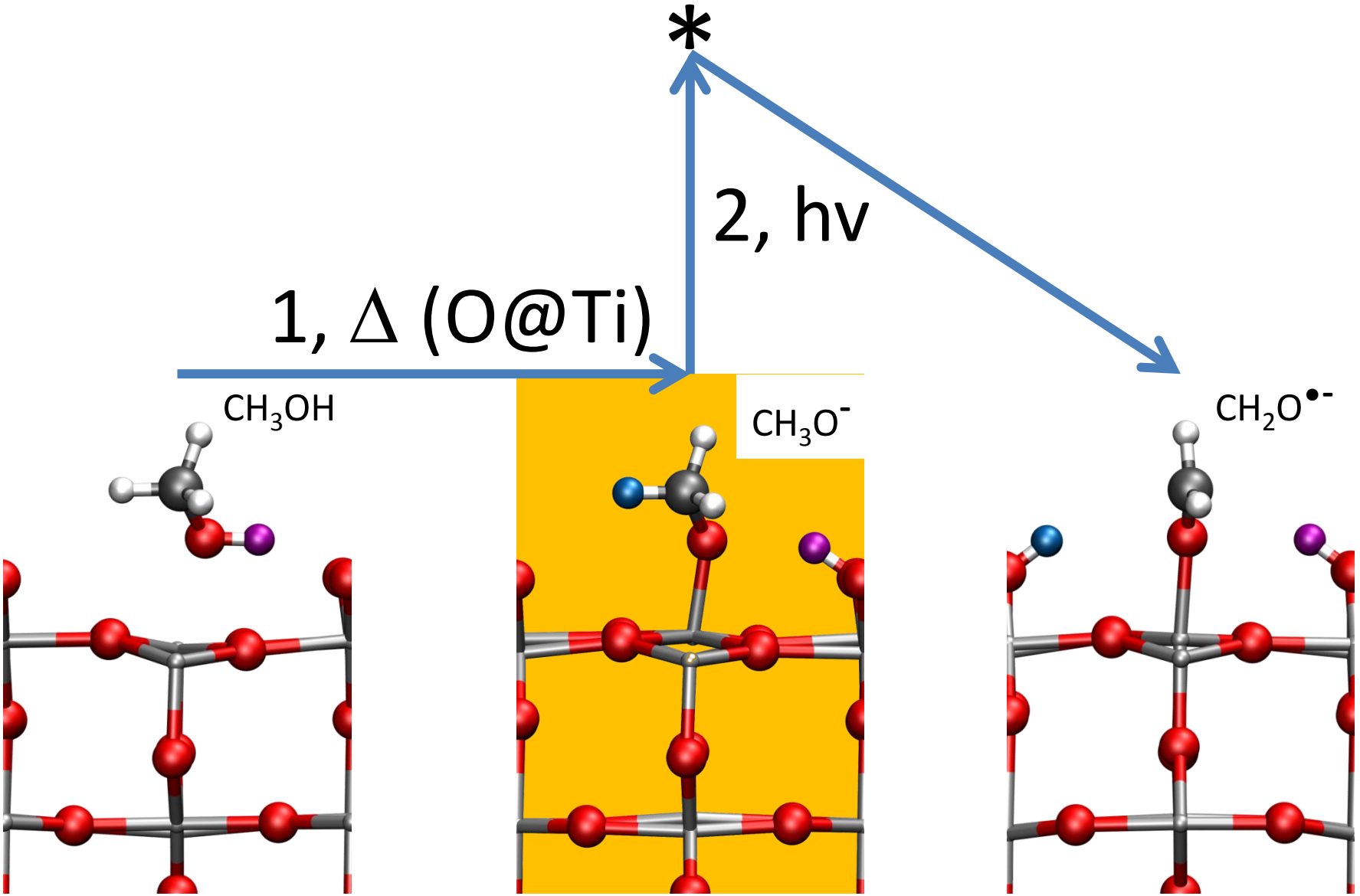
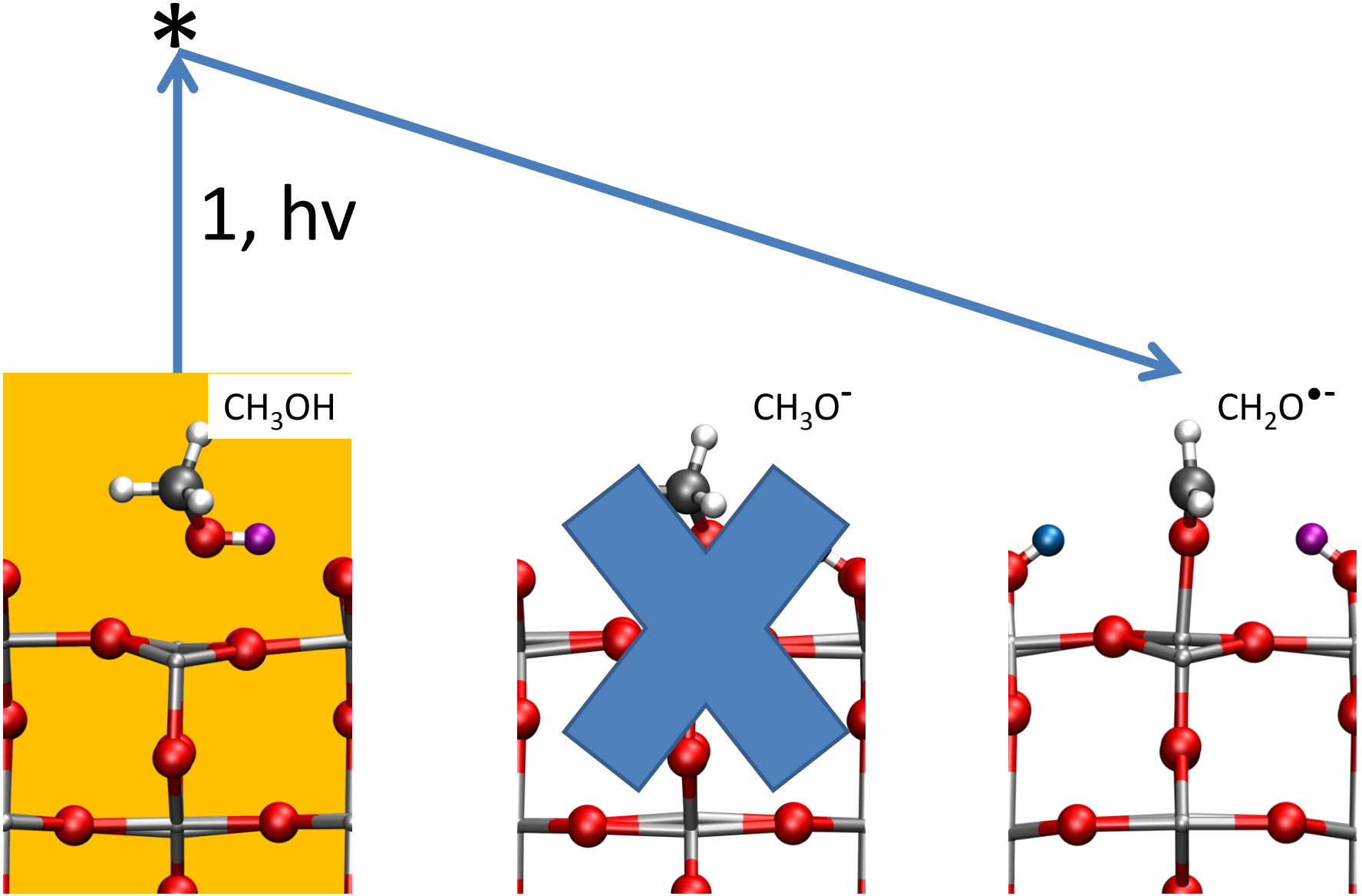
OH and CH bond breaking: Type A



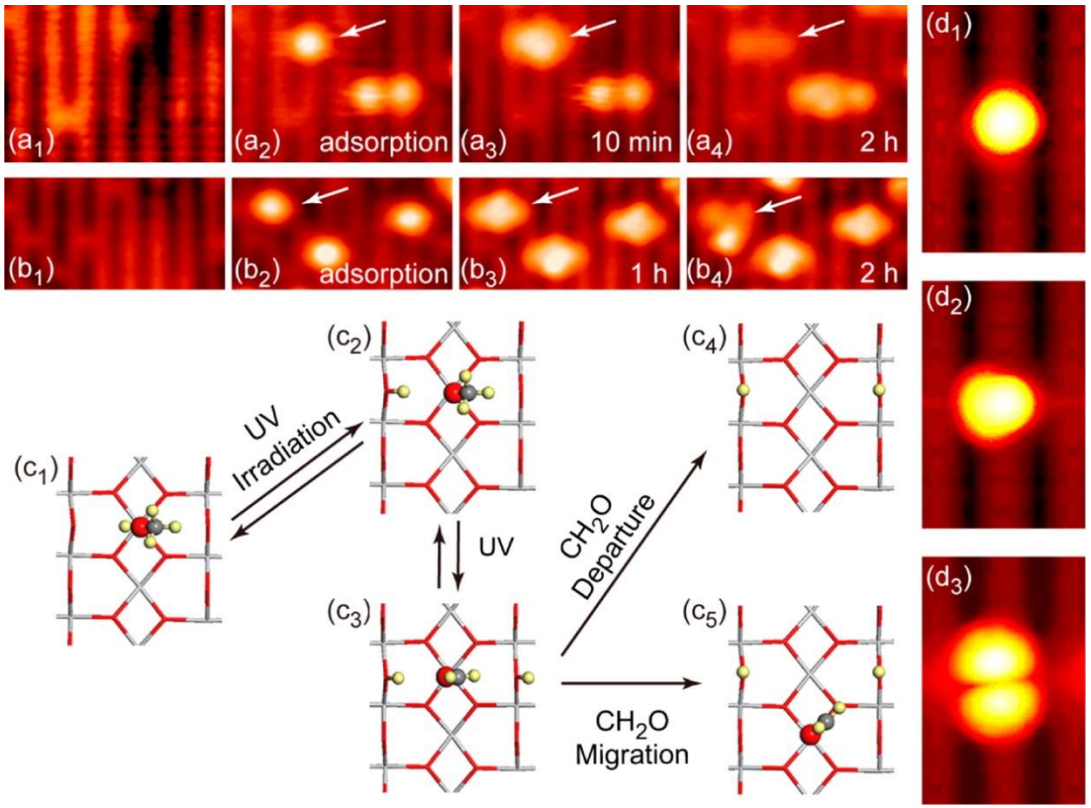
OH and CH bond breaking: Type B



OH and CH bond breaking: Type C



A



Two sets of images showing the typical dissociation processes of methanol at Ti5c under 266 nm light irradiation at light intensity of 1.2 mW/cm2: (a1–a4) image size: 4.0 × 3.3 nm2; (b1–b4) image size: 4.8 × 2.5 nm2. The accumulated irradiation time is 10 min for (a3), 120 min for (a4), 60 min for (b3), and 120 min for (b4). The irradiation times are indicated in the images. Imaging conditions: 1.0 V and 10 pA. (c1–c5) Structural models of stepwise dissociation processes of methanol. (d1–d3) Simulated images for CH3OHt, CH3Ot and OHb, and formaldehyde with OHb couple, corresponding to the configurations in (c1)–(c3), respectively. The STM images were simulated by integrating the orbits from conduction band minimum to 1.3 eV with the isovalue of probability density of 0.005 au.

Published in: Hao Feng; Shijing Tan; Haoqi Tang; Qijing Zheng; Yongliang Shi; Xuefeng Cui; Xiang Shao; Aidi Zhao; Jin Zhao; Bing Wang; *J. Phys. Chem. C* **2016,** 120, 5503-5514.
DOI: 10.1021/acs.jpcc.5b12010
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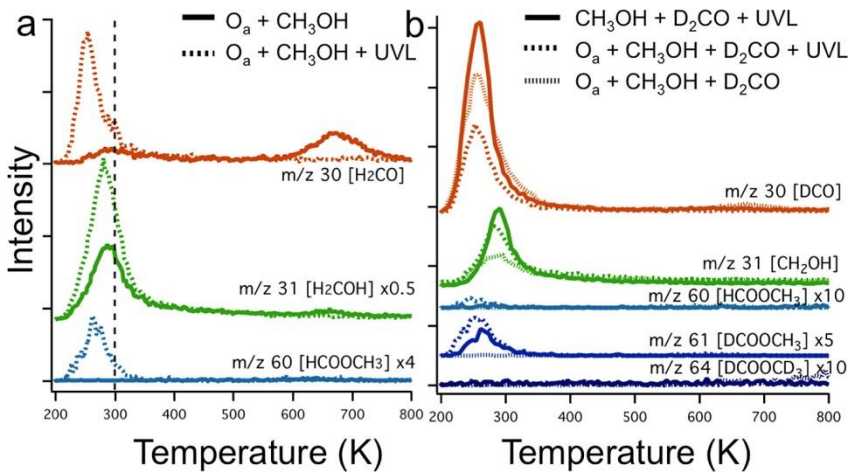
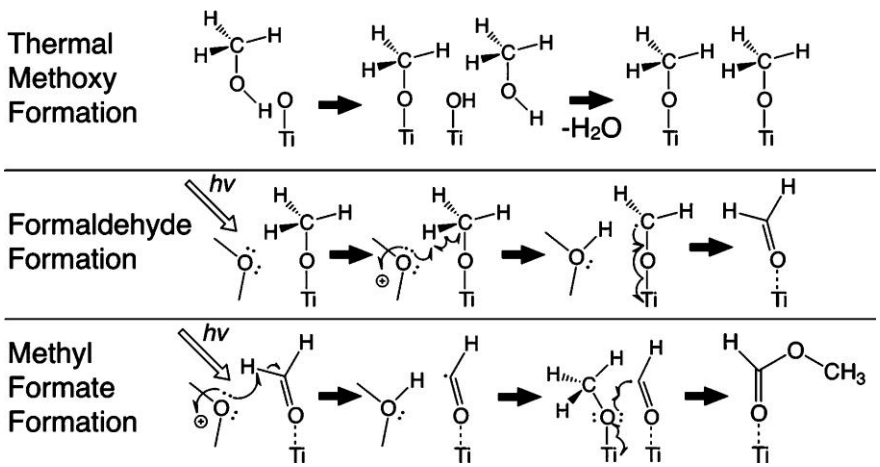
ACS Publications
High quality. High impact.

B





Temperature programmed reaction experiments of methanol oxidation to methyl formate (a) and photochemical coupling with *d*2-formaldehyde (b). In (a), data are shown after exposure of the surface to methanol (solid line) and after 300 s of illumination with UV light at 200 K (dashed line). In (b), data are shown for the reduced (solid line) and preoxidized (dashed and dotted lines) surface, followed by 300 s of illumination (solid and dashed lines). For all experiments, oxygen adatoms are produced by exposure to O2 (200 L) on the as-prepared TiO2(110) surface at 300 K. The surface was then cooled to 200 K for methanol or methanol and then formaldehyde adsorption (~0.3 ML), followed by illumination for 300 s with a Xe arc lamp with a short-pass filter allowing 200–400 nm light through. A constant 2 K/s heating rate was used. In sets of data, the contributions to *m*/*z* 30 and 31 from methyl formate and the contribution to *m*/*z* 30 from methanol were subtracted.

Published in: Katherine R. Phillips; Stephen C. Jensen; Martin Baron; Shao-Chun Li; Cynthia M. Friend; *J. Am. Chem. Soc.* **2013,** 135, 574-577.
DOI: 10.1021/ja3106797
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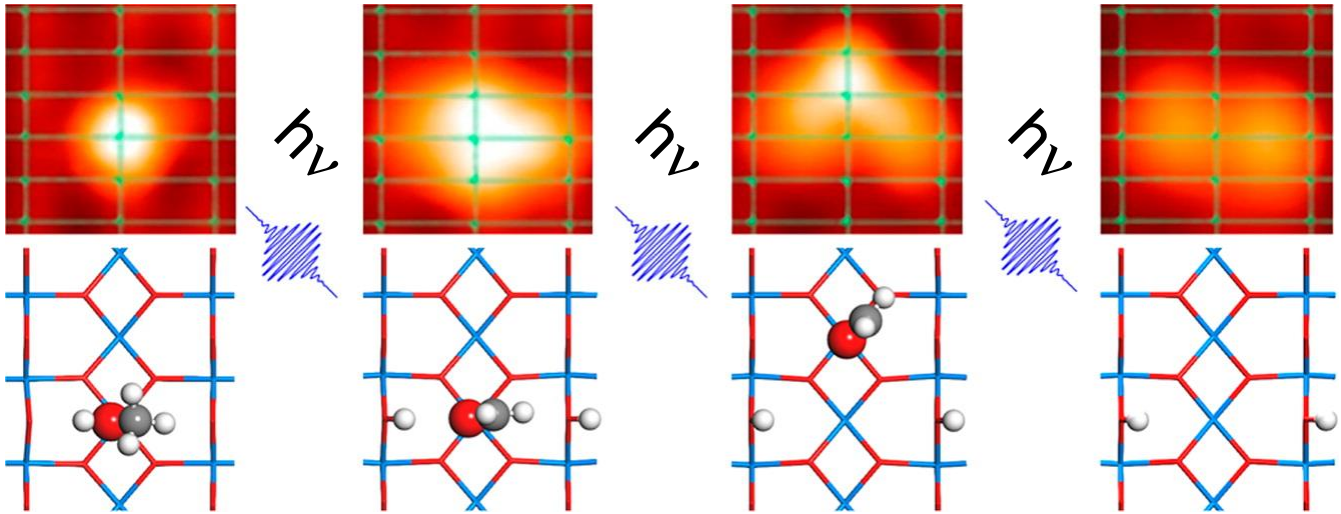
C



"…the dissociation of methanol always was considered as a stepwise process. …However, in the real-space STM results…the dissociation of methanol is a simultaneous bond cleavage, where two hydrogen atoms moved to the adjacent BBO sites."

Published in: Dong Wei; Xianchi Jin; Chuanqi Huang; Dongxu Dai; Zhibo Ma; Wei-Xue Li; Xueming Yang; *J. Phys. Chem. C* **2015,** 119, 17748-17754.
DOI: 10.1021/acs.jpcc.5b05074
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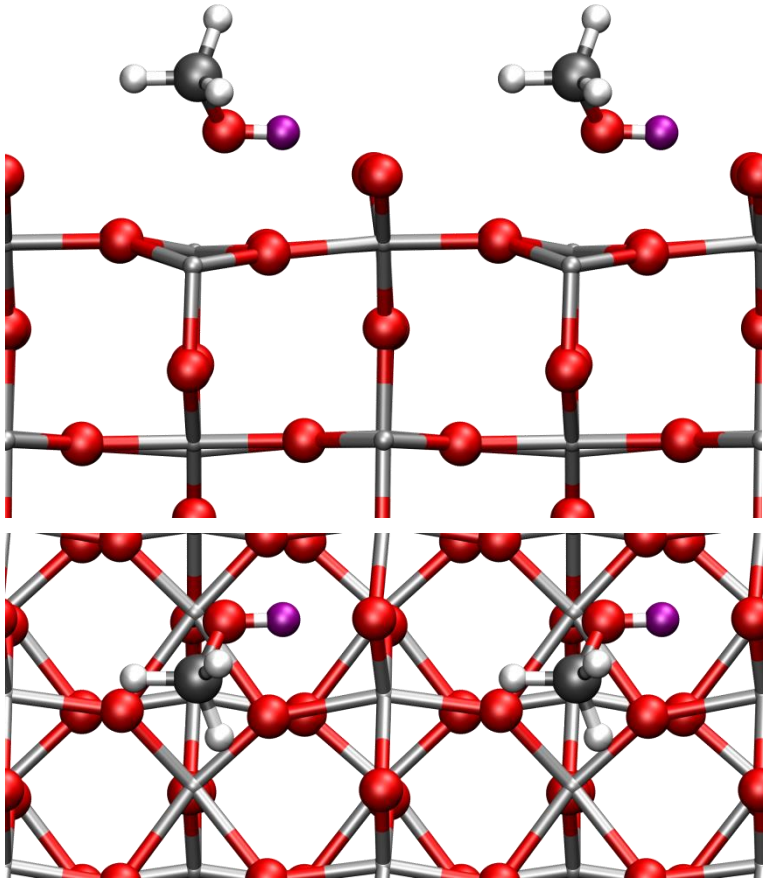
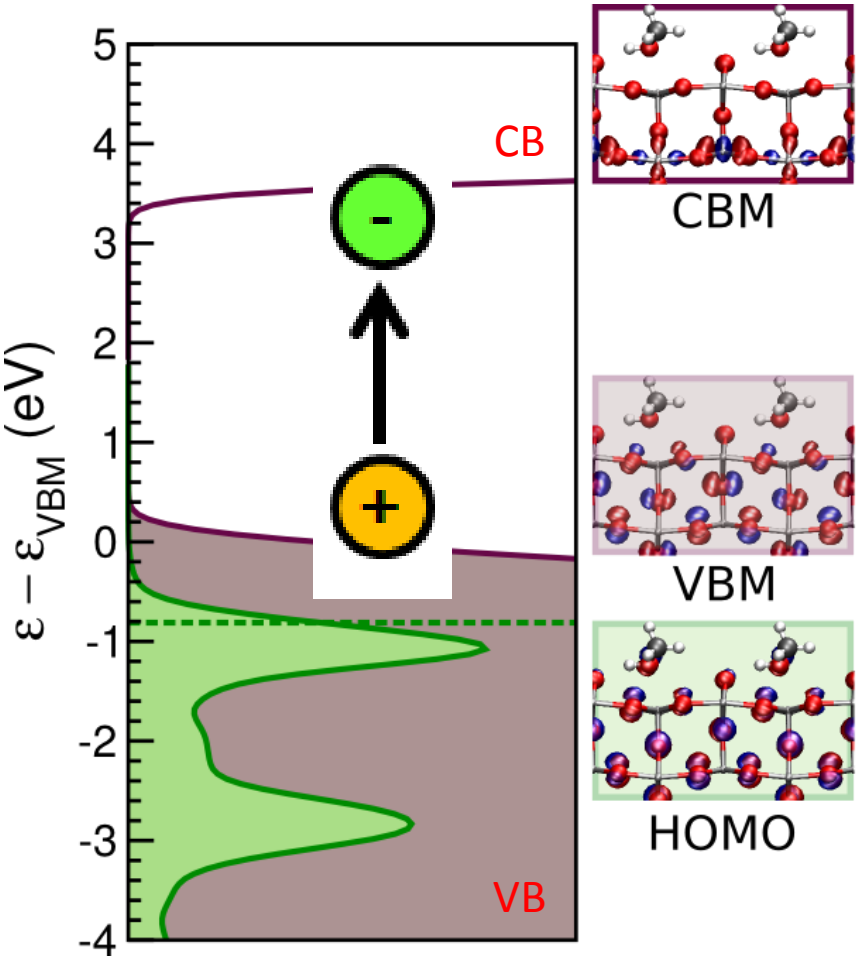
Theoretical Approach for Excited-State Mechanism for Periodic Systems

1. We describe the **EXCITED STATE** as a T_1 state, i.e., with DFT HSE06 we compute h^+-e^- pairs as a T_1 excitons
2. We search for the **REACTIVE ELECTRONIC CONFIGURATION** among many h^+-e^- pairs
3. Once we have identified the T_1 reactive path, we compute the S_1 mechanism using T_1 geometries and BSE ($\varepsilon_\infty \sim 4$) based on DFT HSE06



N. B. The T_1 calculations already explain the excited-state mechanism

Occupied O 2p & Unoccupied Ti 3d Levels: DFT HSE06



Ti 3*d* ↔ e

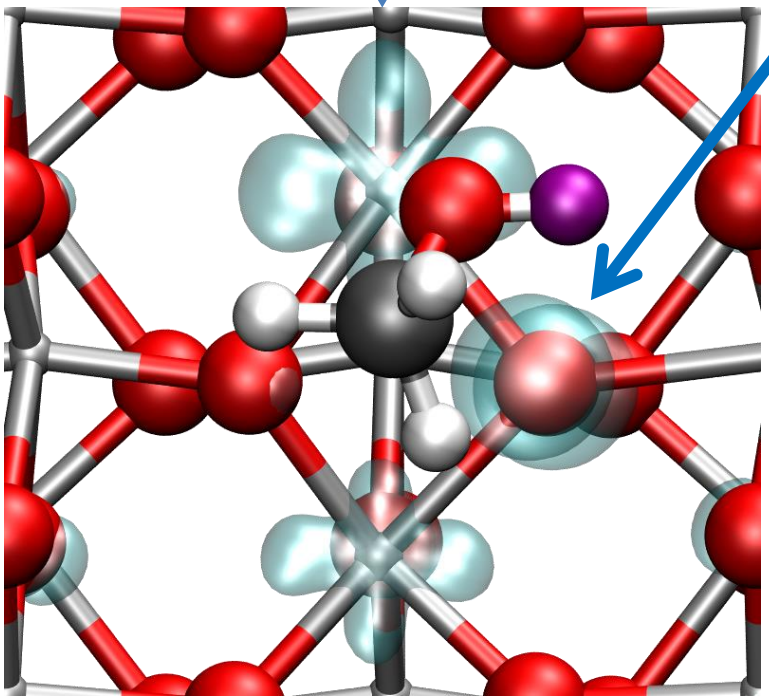
O 2*p* ↔ h

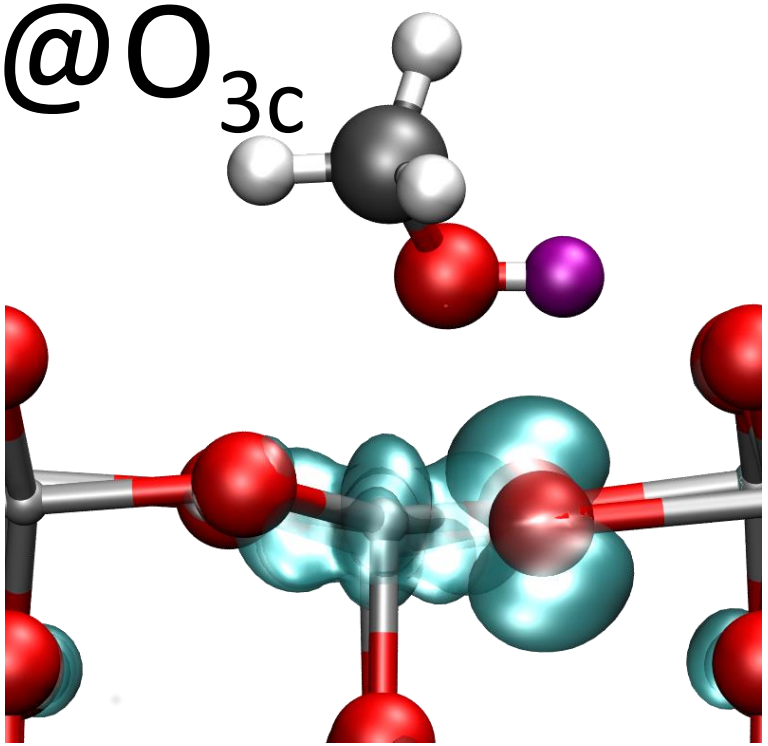
VASP calculations with DFT HSE06 xc-functional and (4x4x1) k-point mesh

T_1 exciton

$e@Ti_{cus}$ → T_1

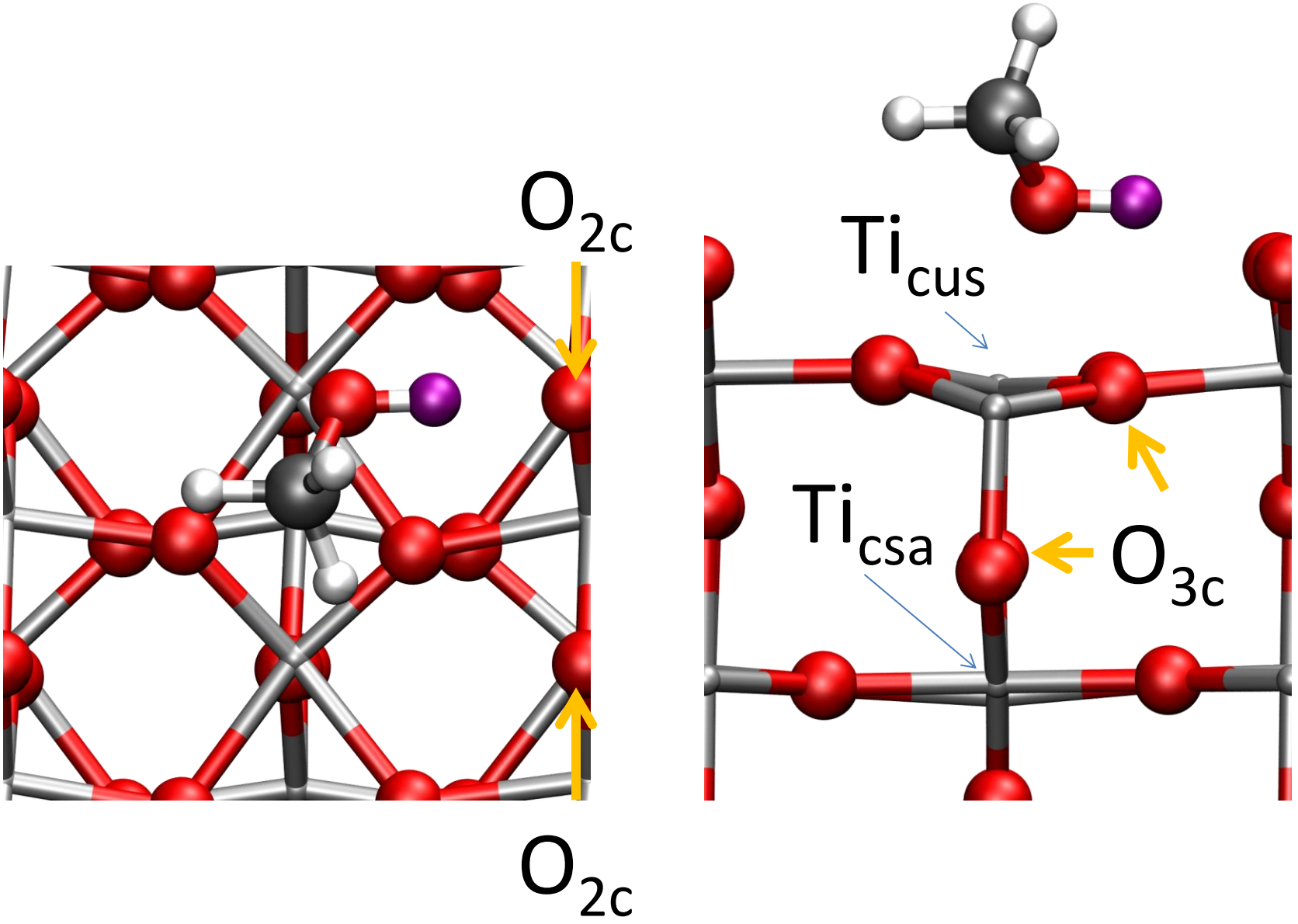
$h@O_{3c}$



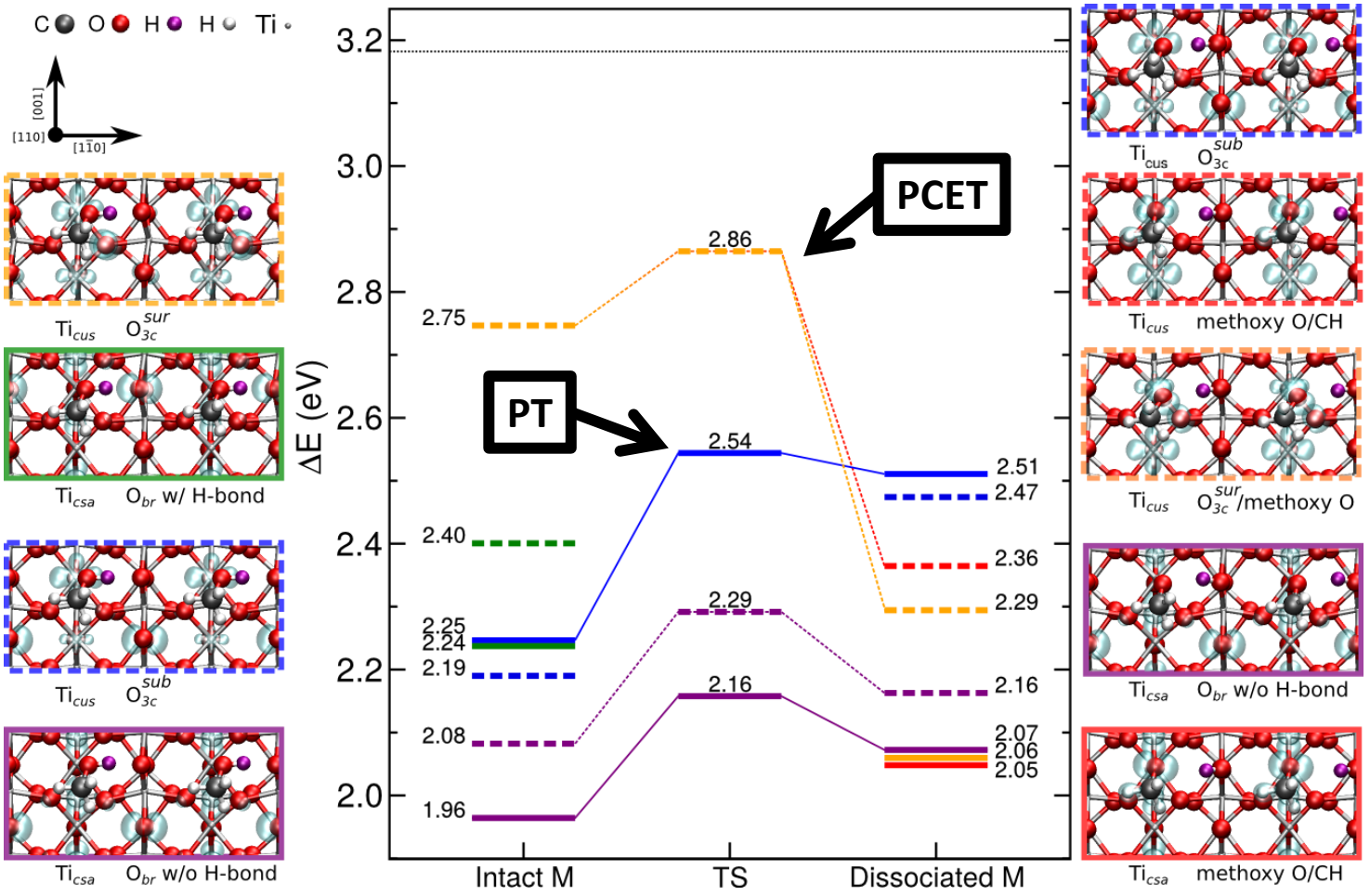


VASP calculations with DFT HSE06 xc-functional at Γ point

REACTANT: 8 pairs



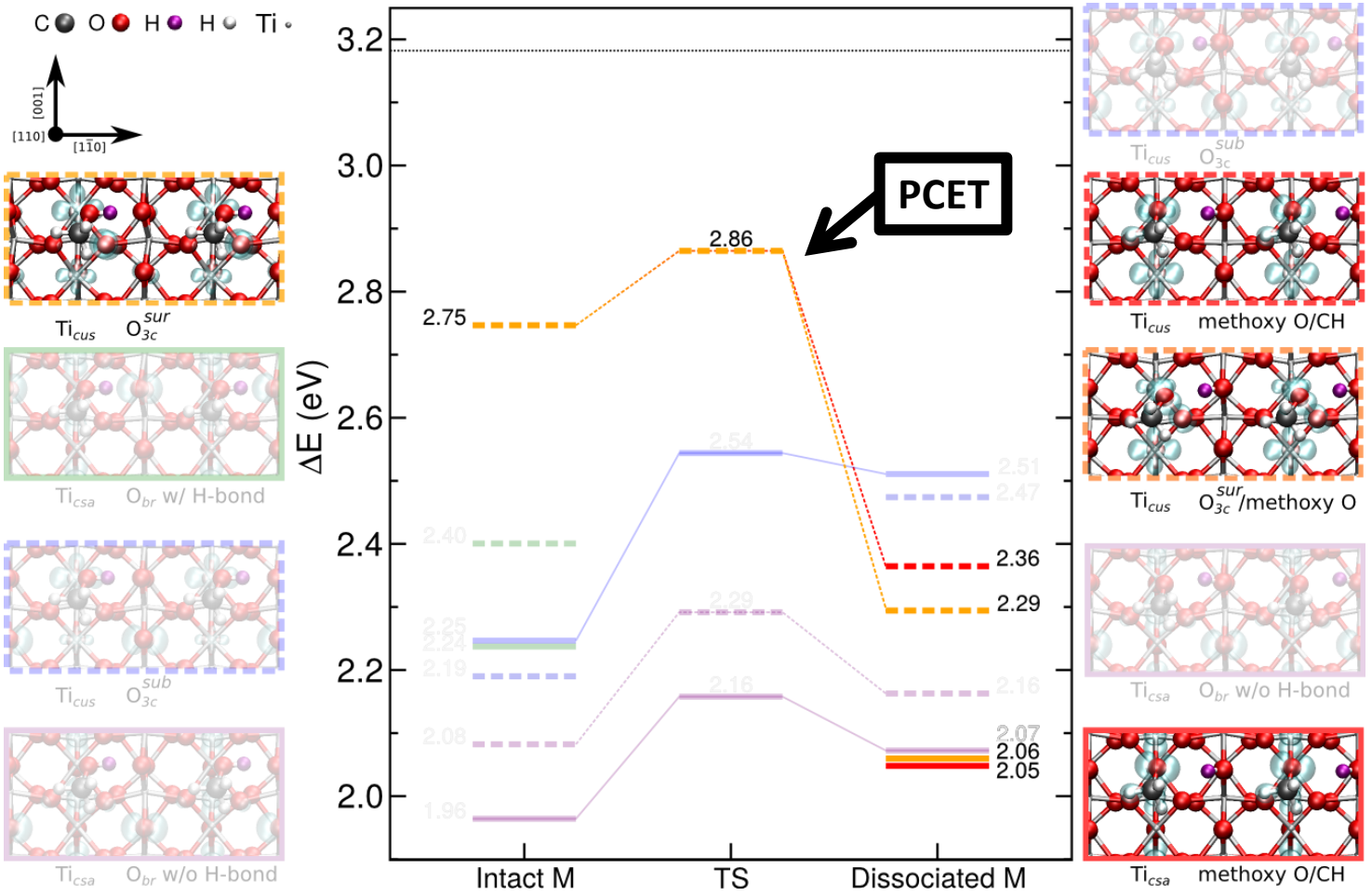
T_1 O-H Dissociation Coordinates



VASP calculations with DFT HSE06 xc-functional at Γ point and NEB method

A. Migani and L. Blancafort, JACS 2016, DOI:10.1021/jacs.6b11067

O-H Dissociation Coordinate: Exothermic



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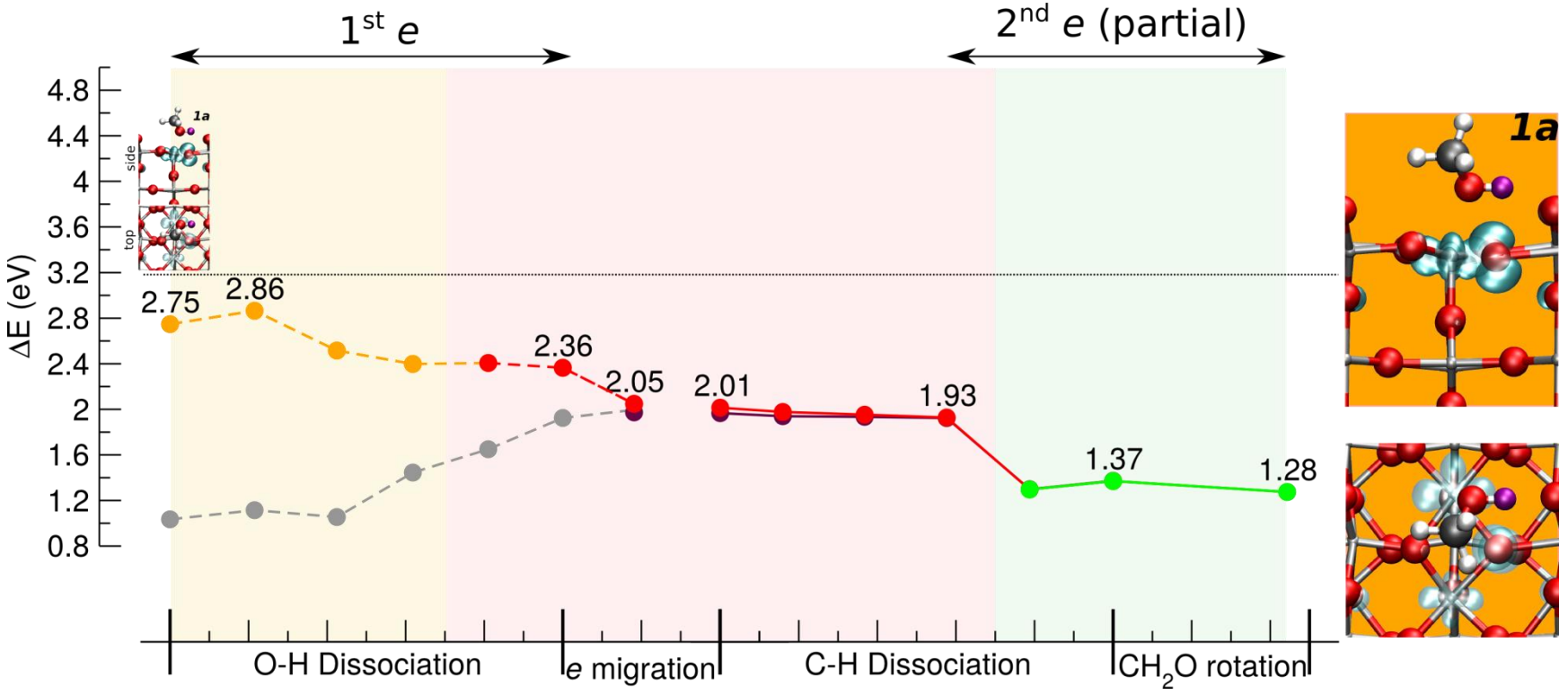
T_1 exciton energy and shape



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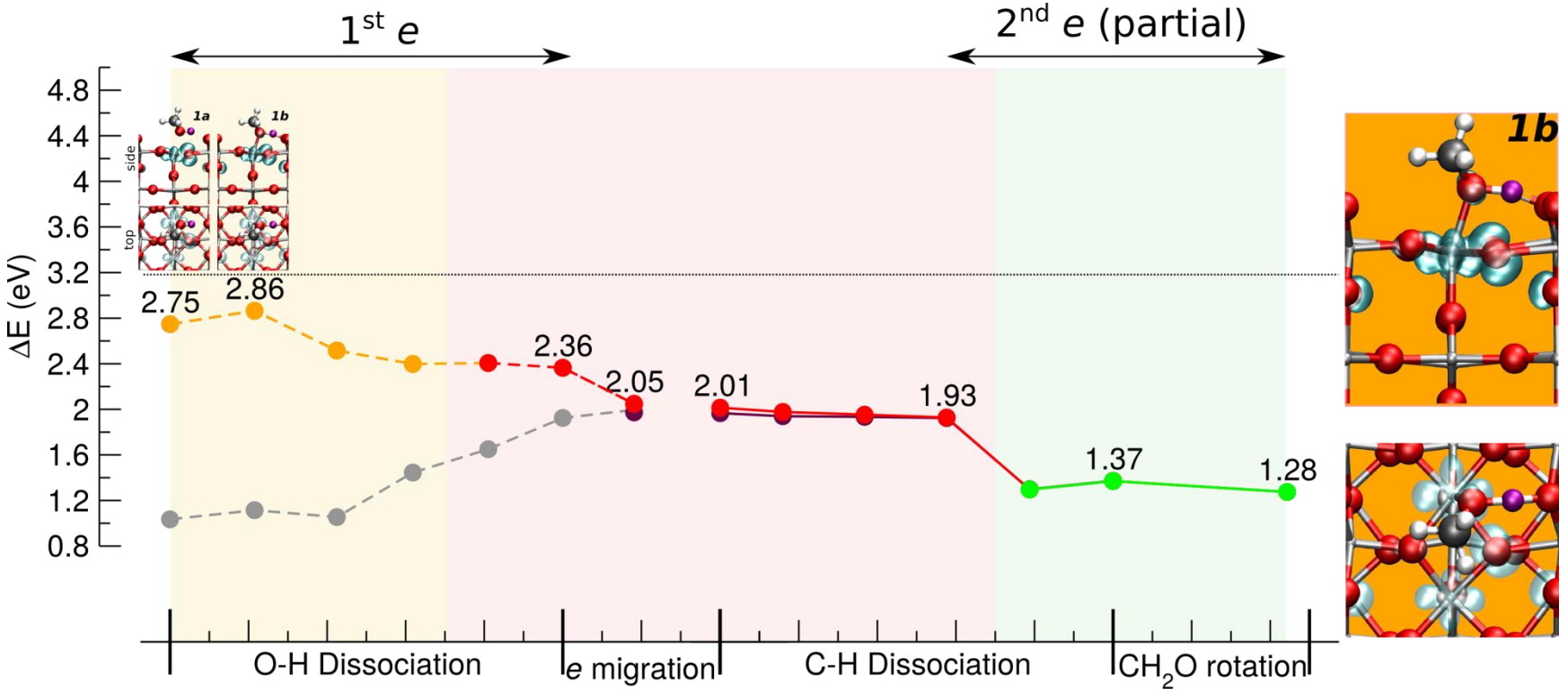

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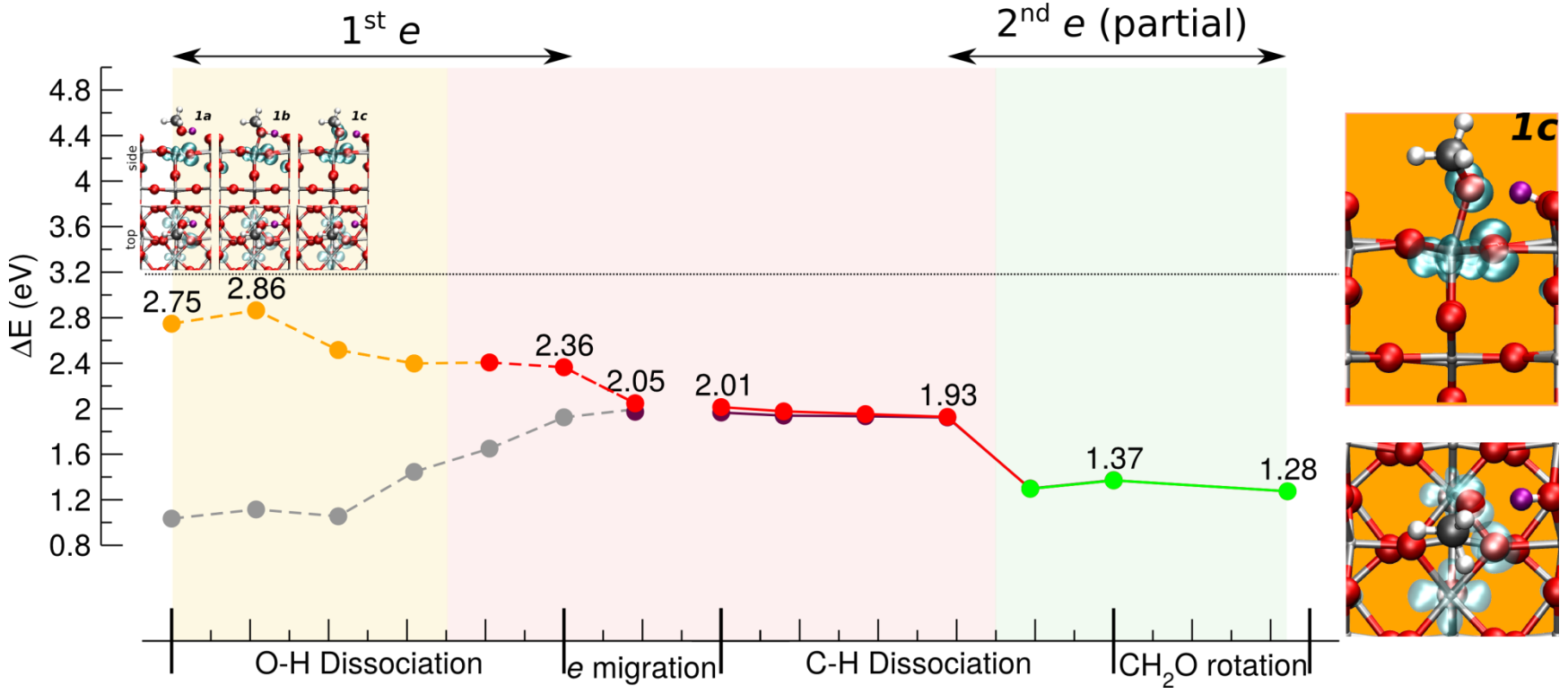

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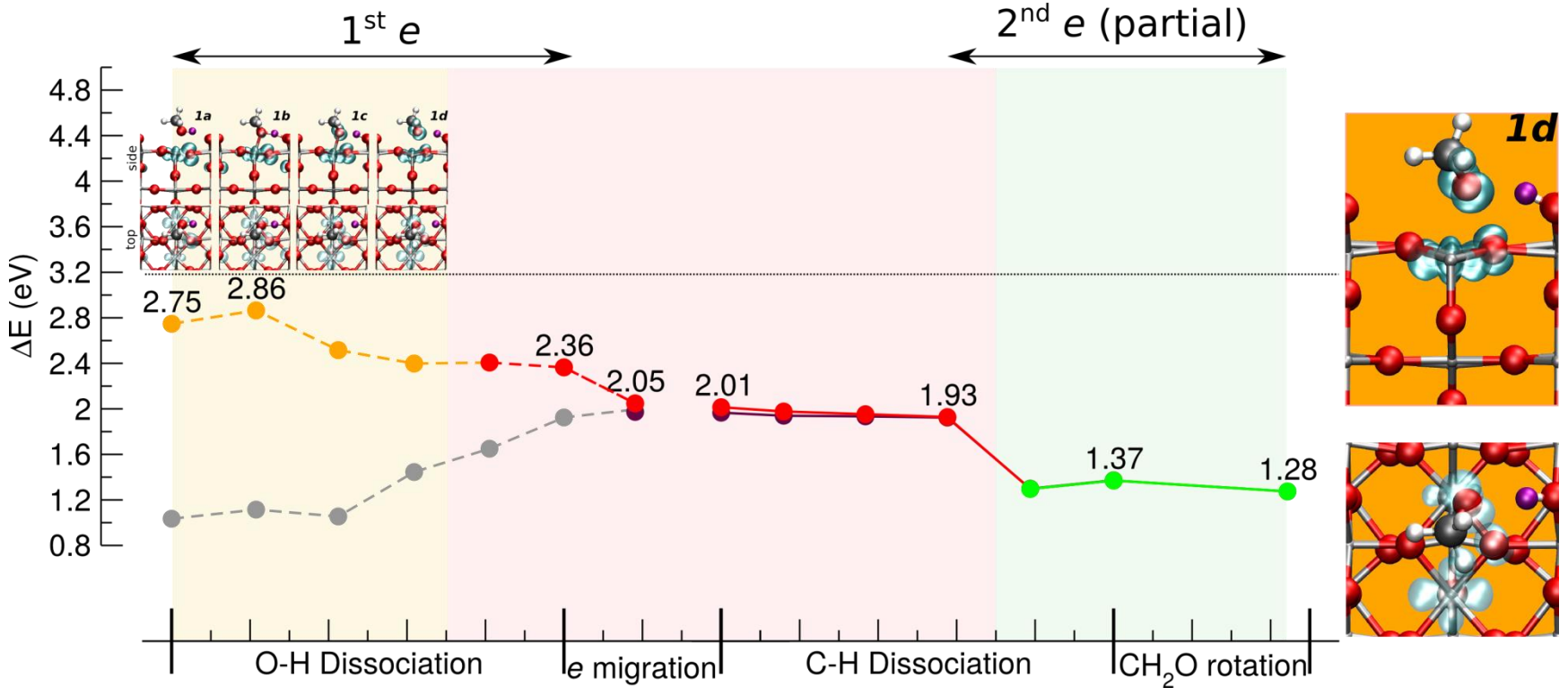

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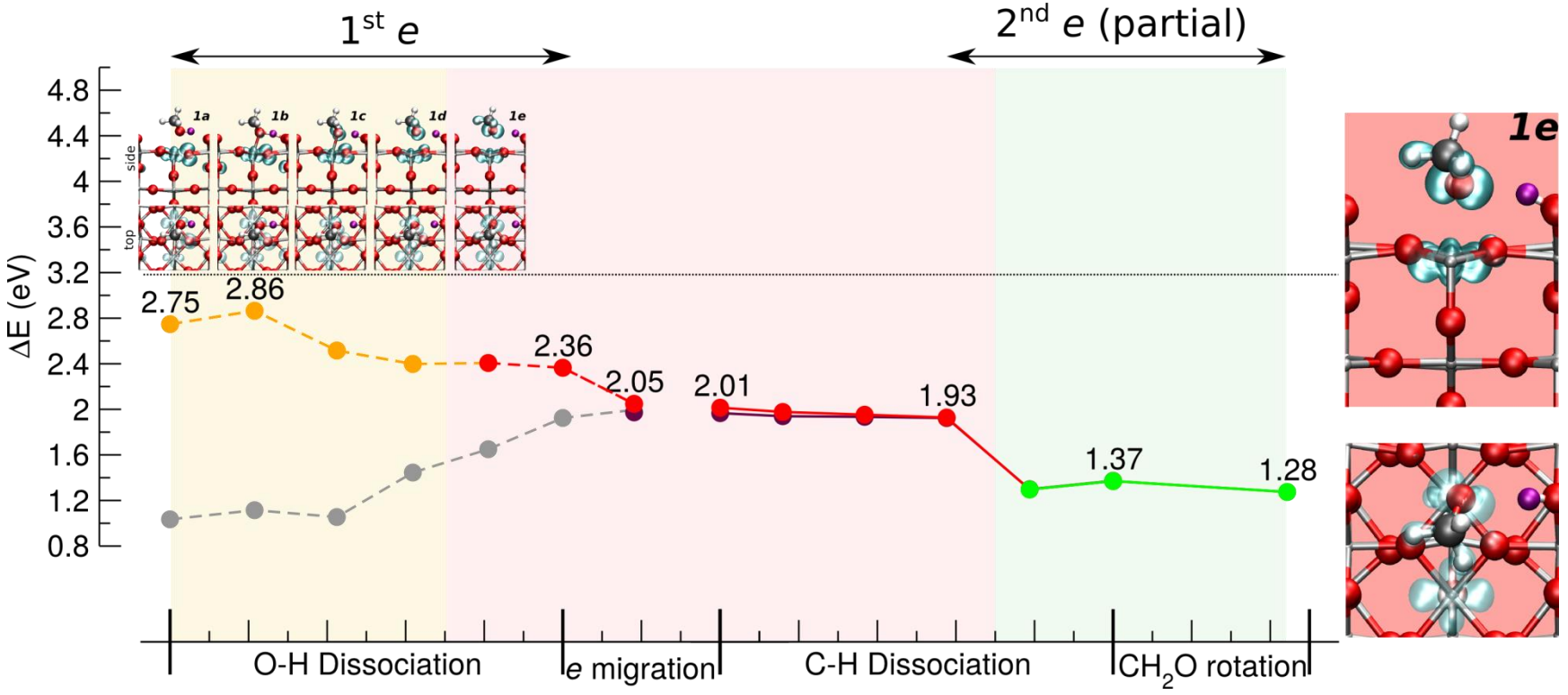

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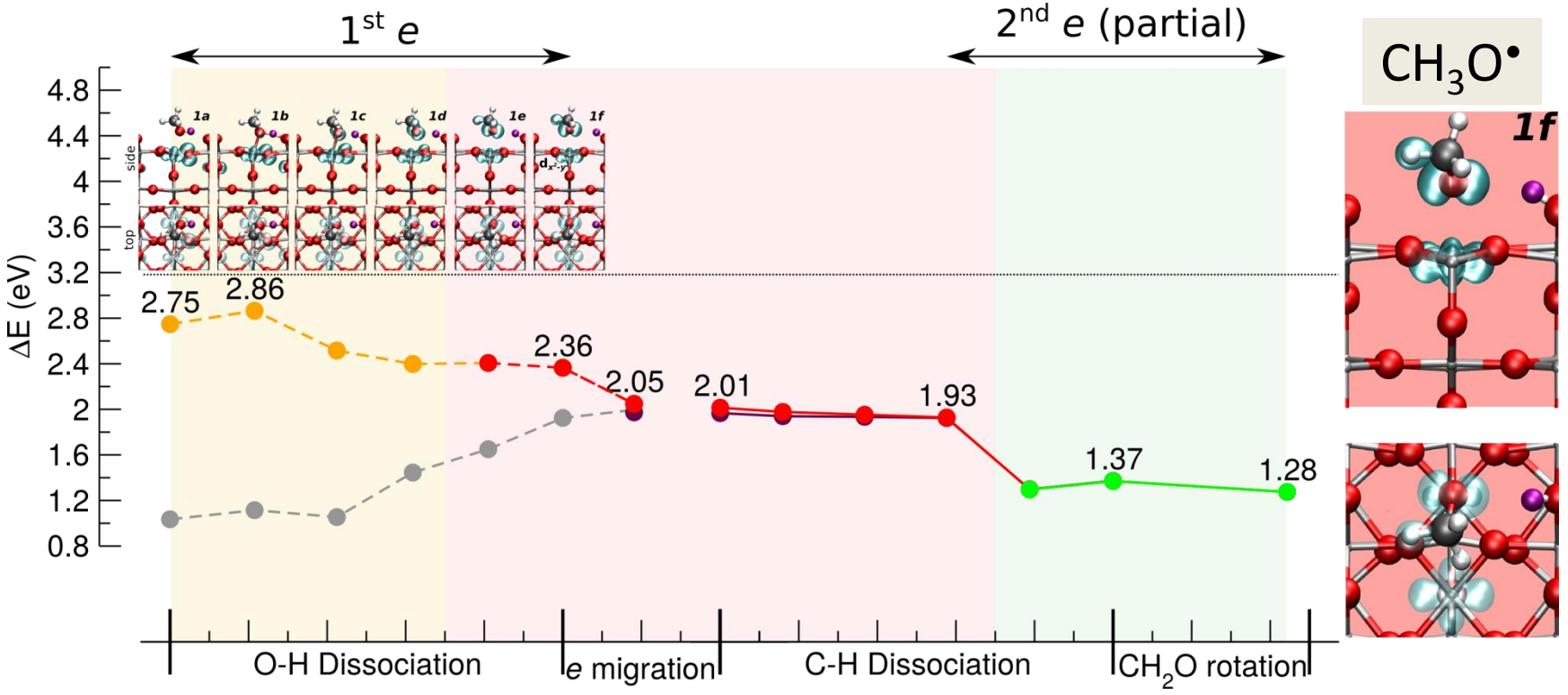

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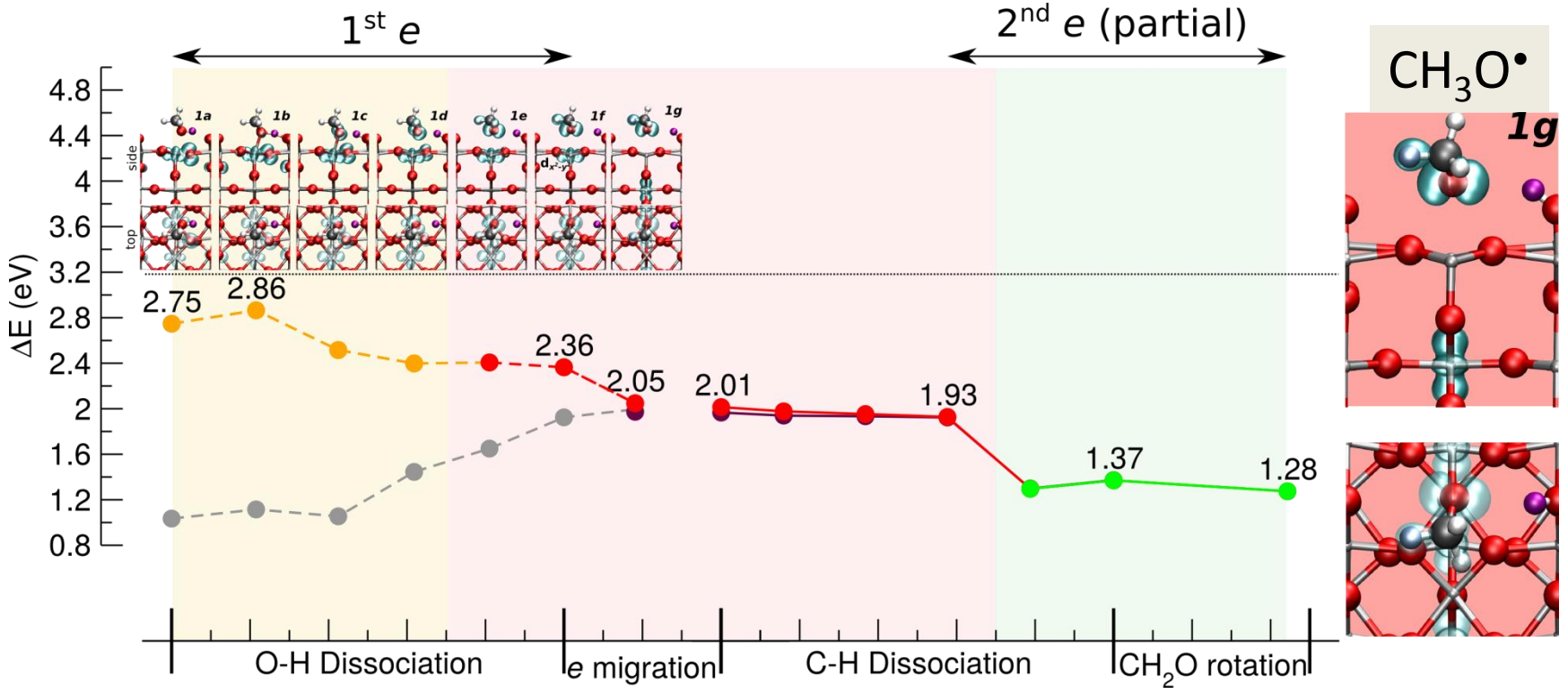

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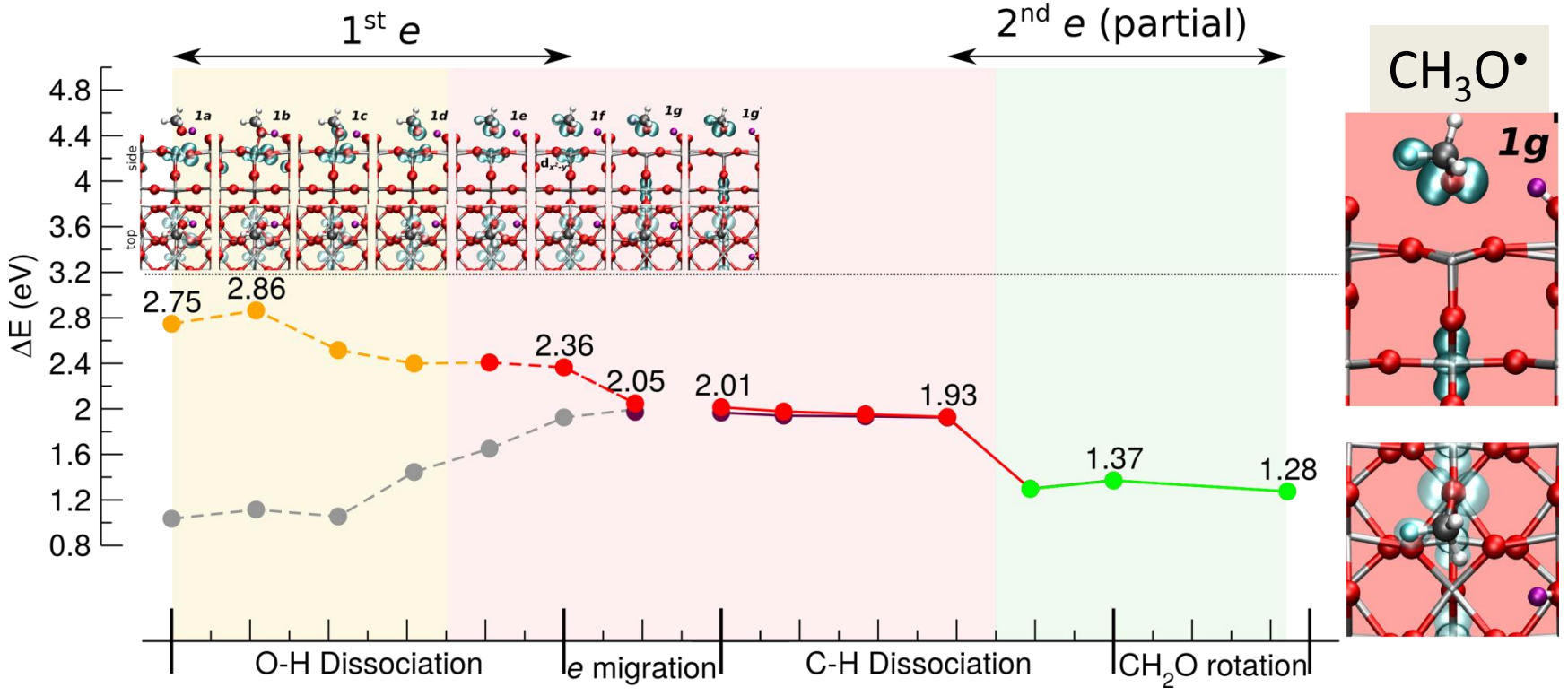

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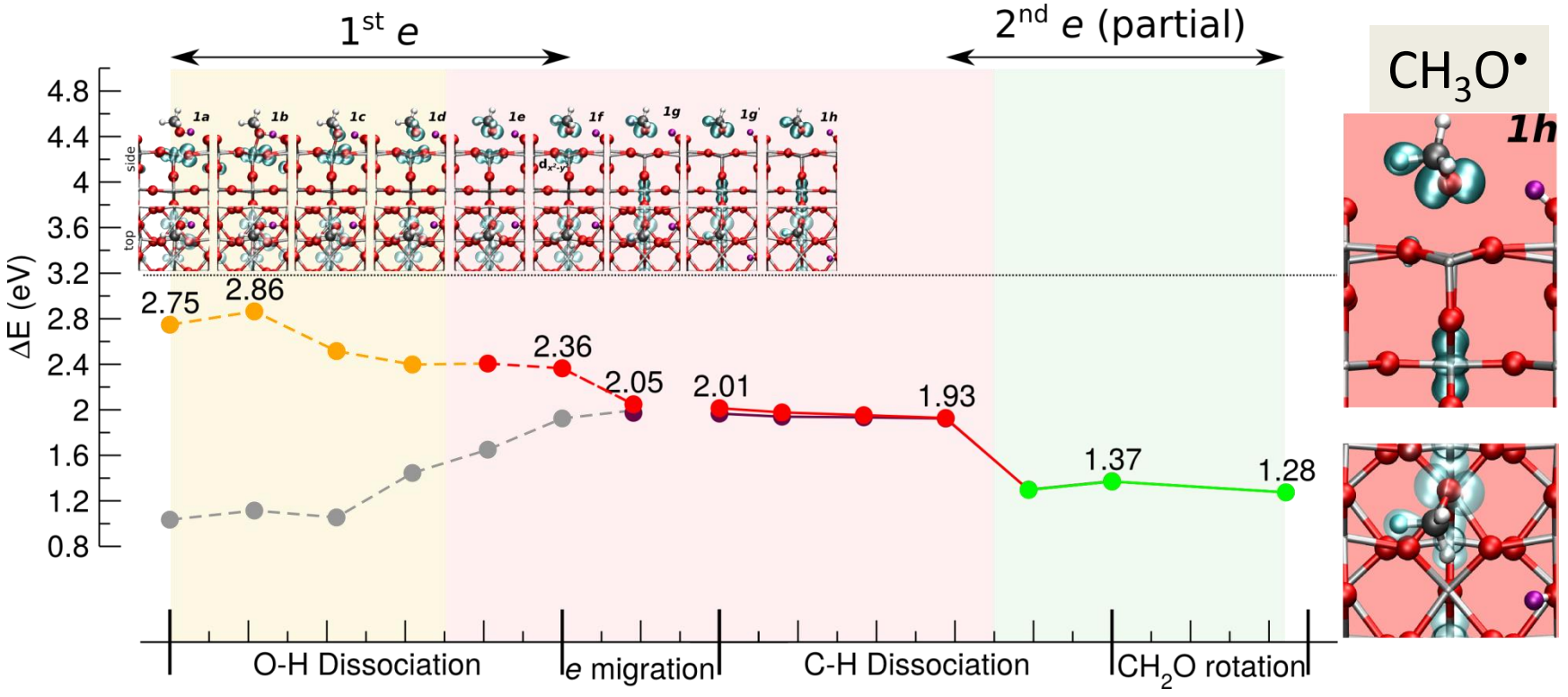

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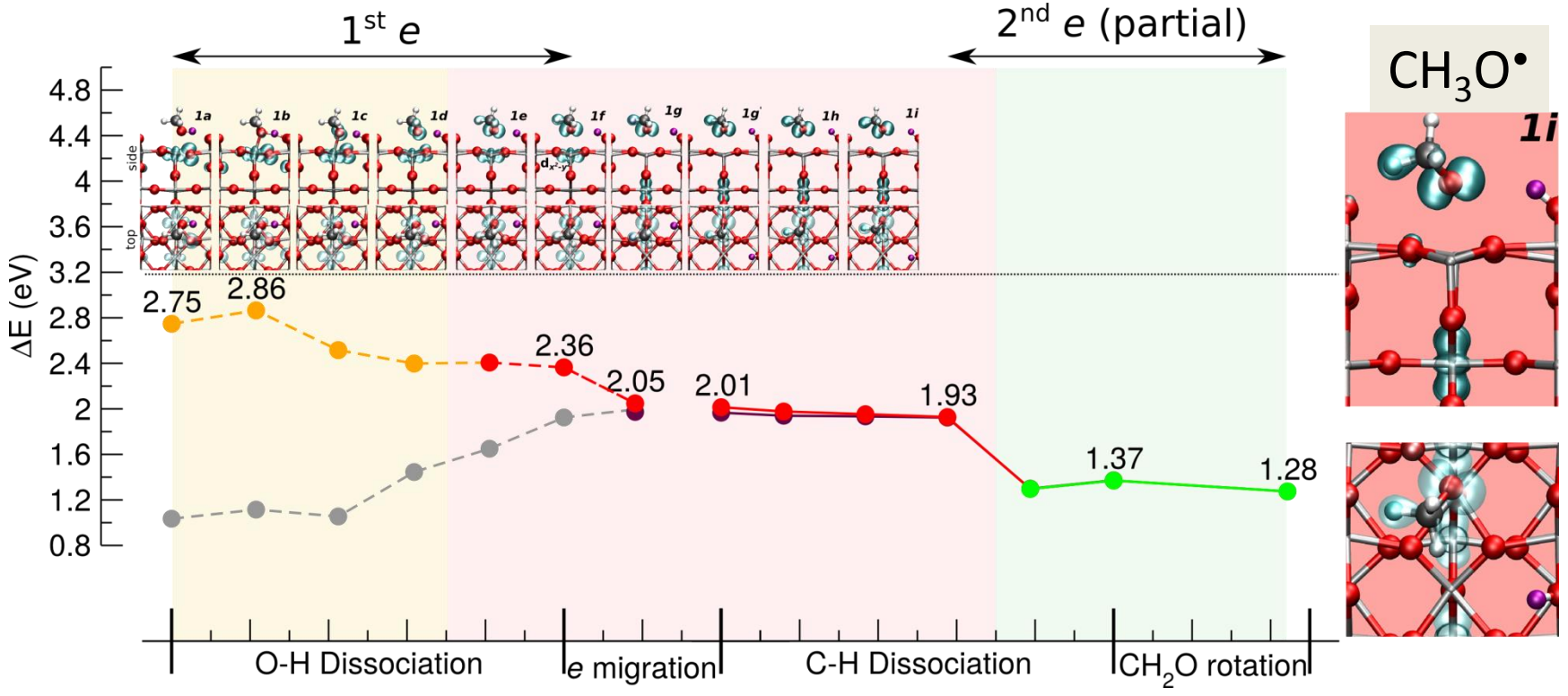

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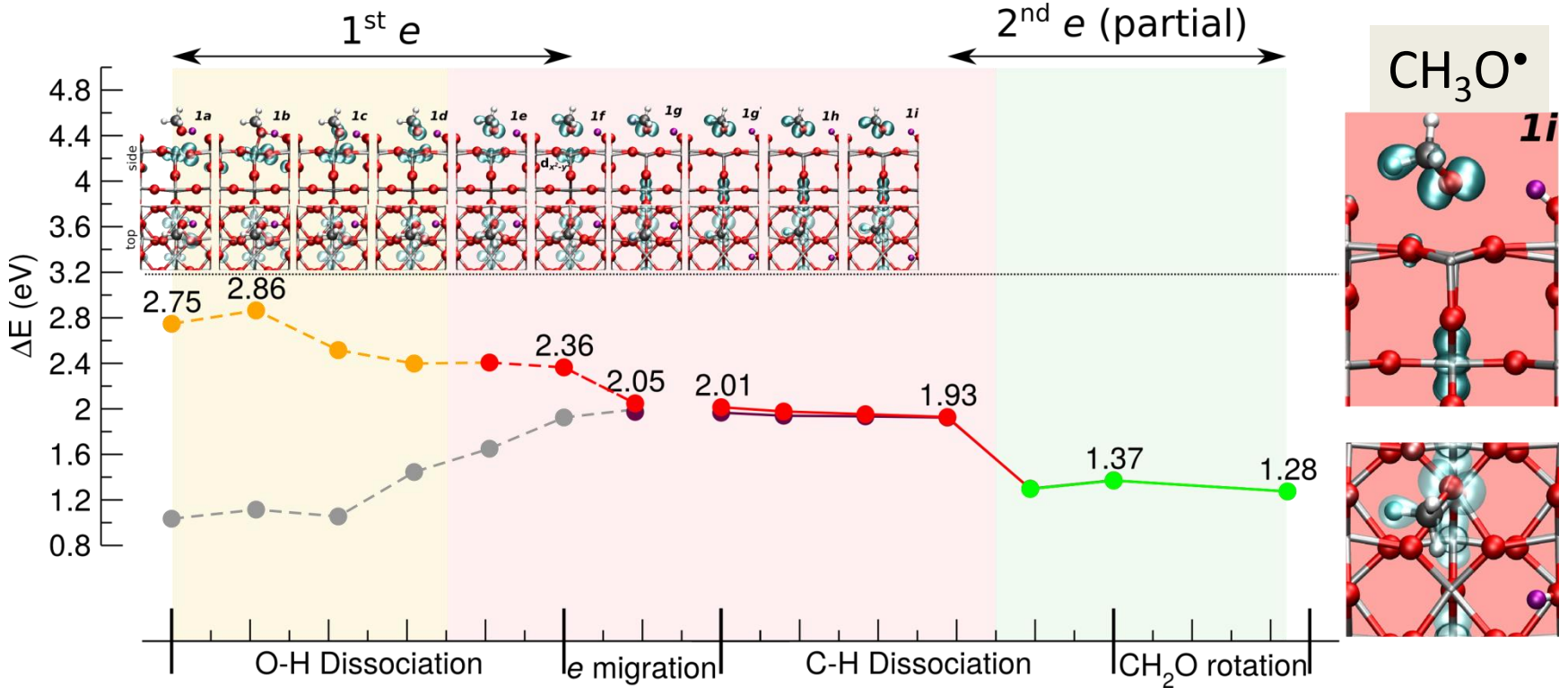

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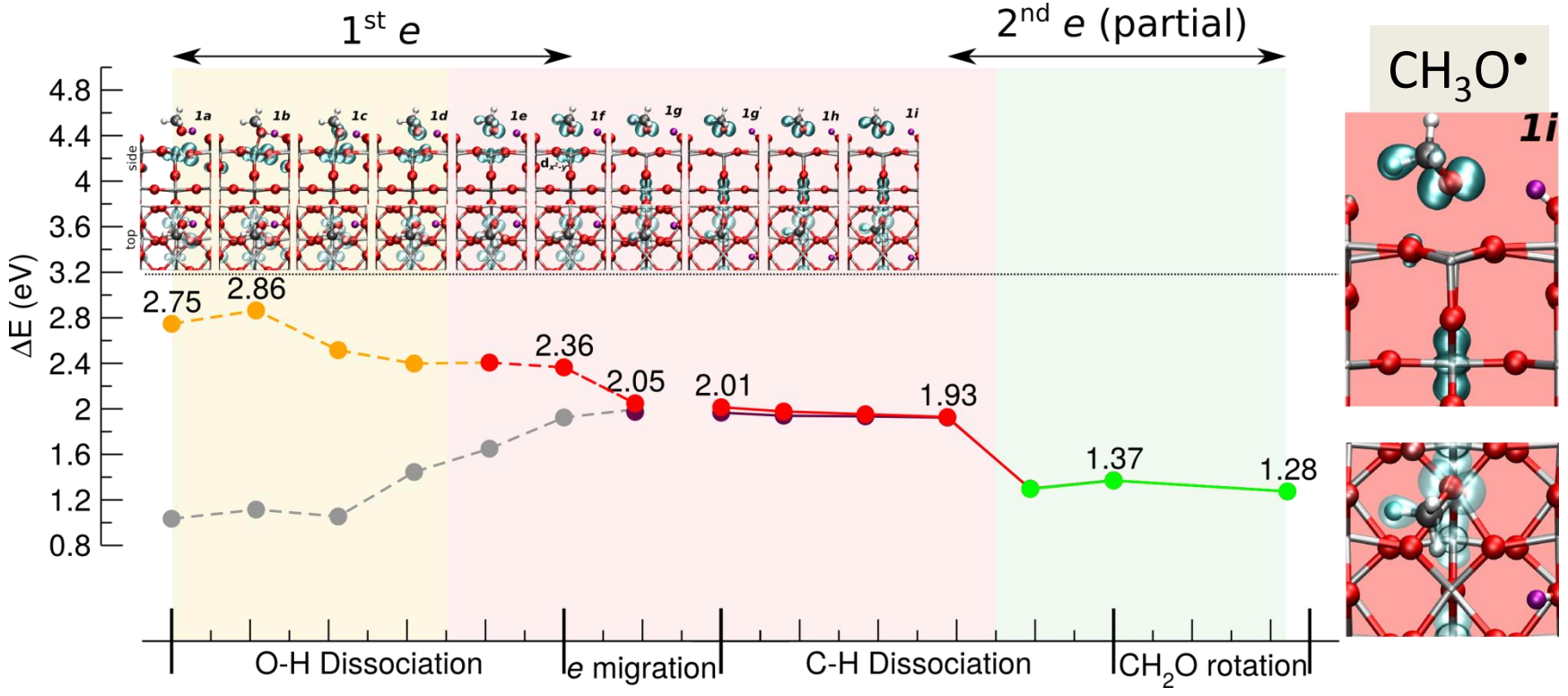

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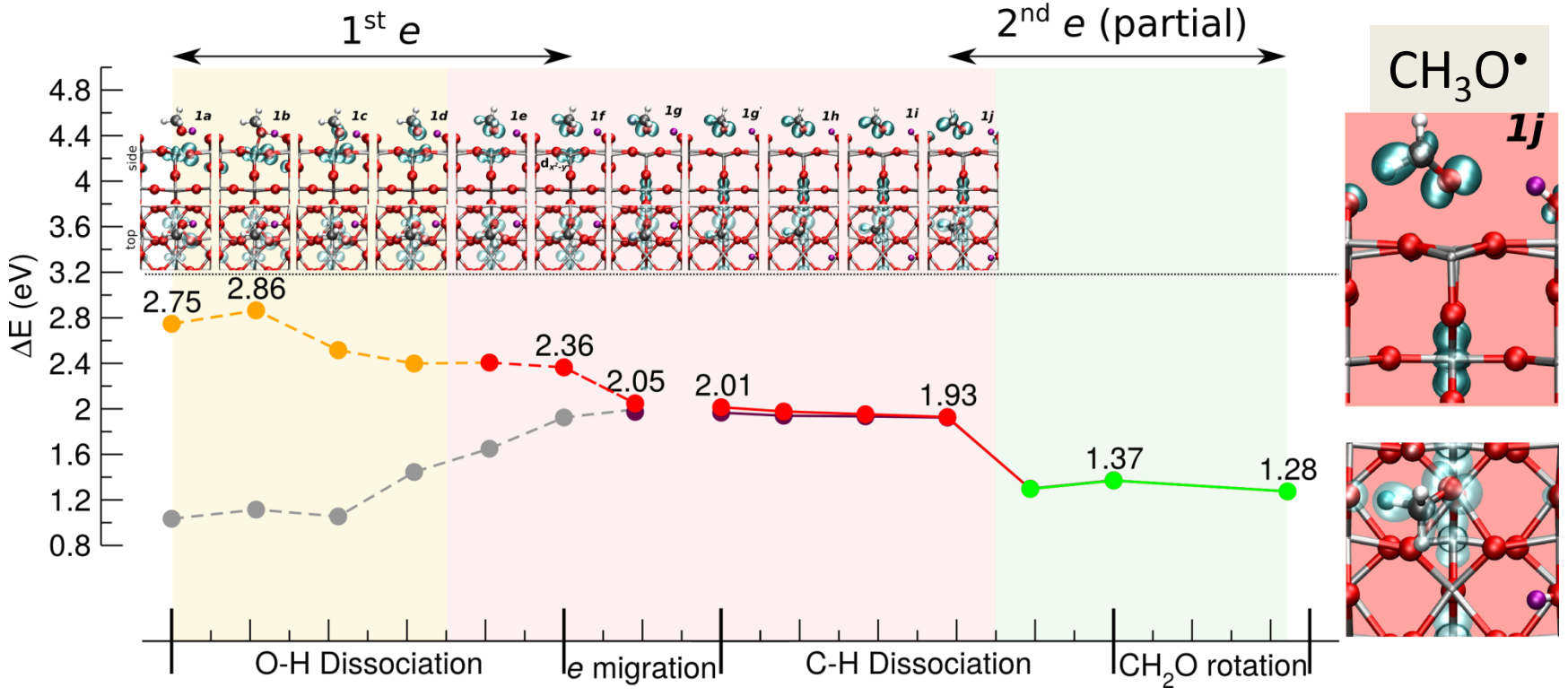

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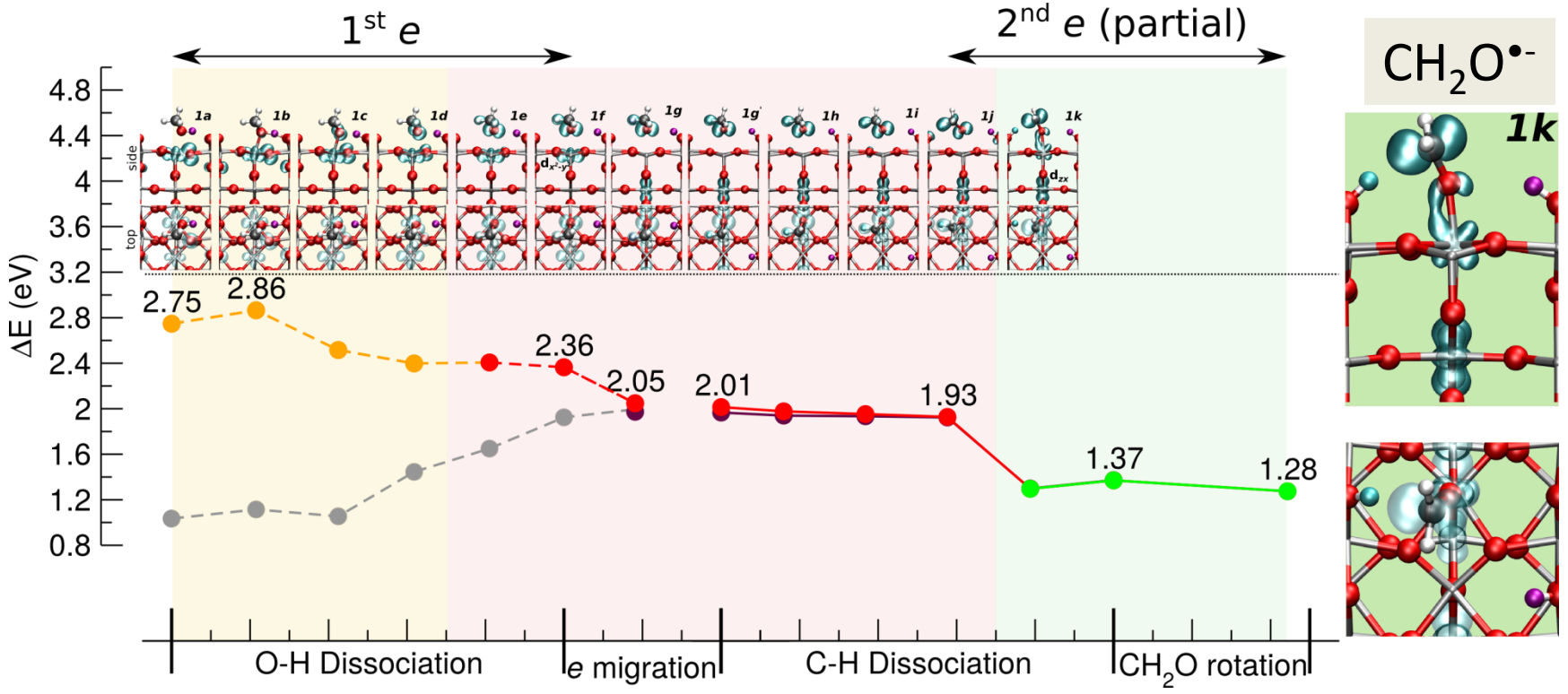

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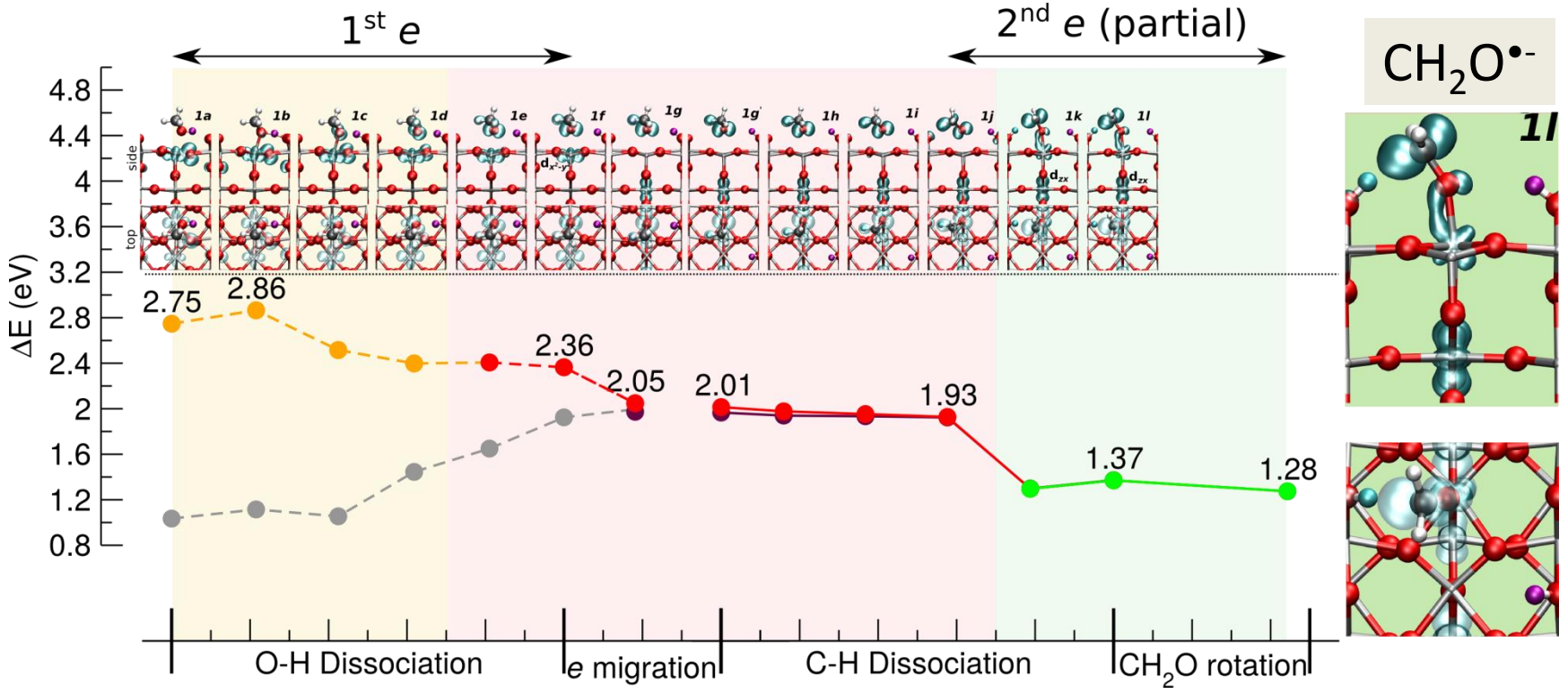

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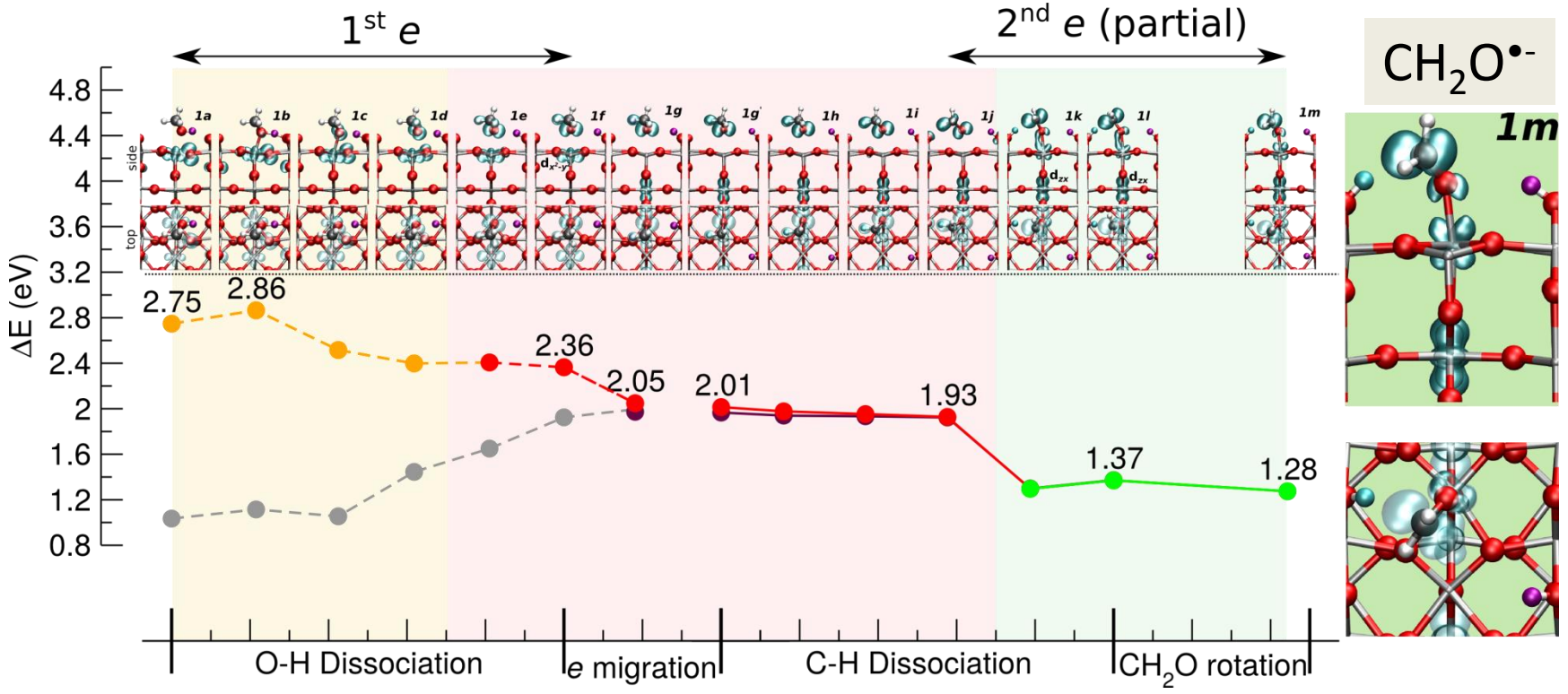

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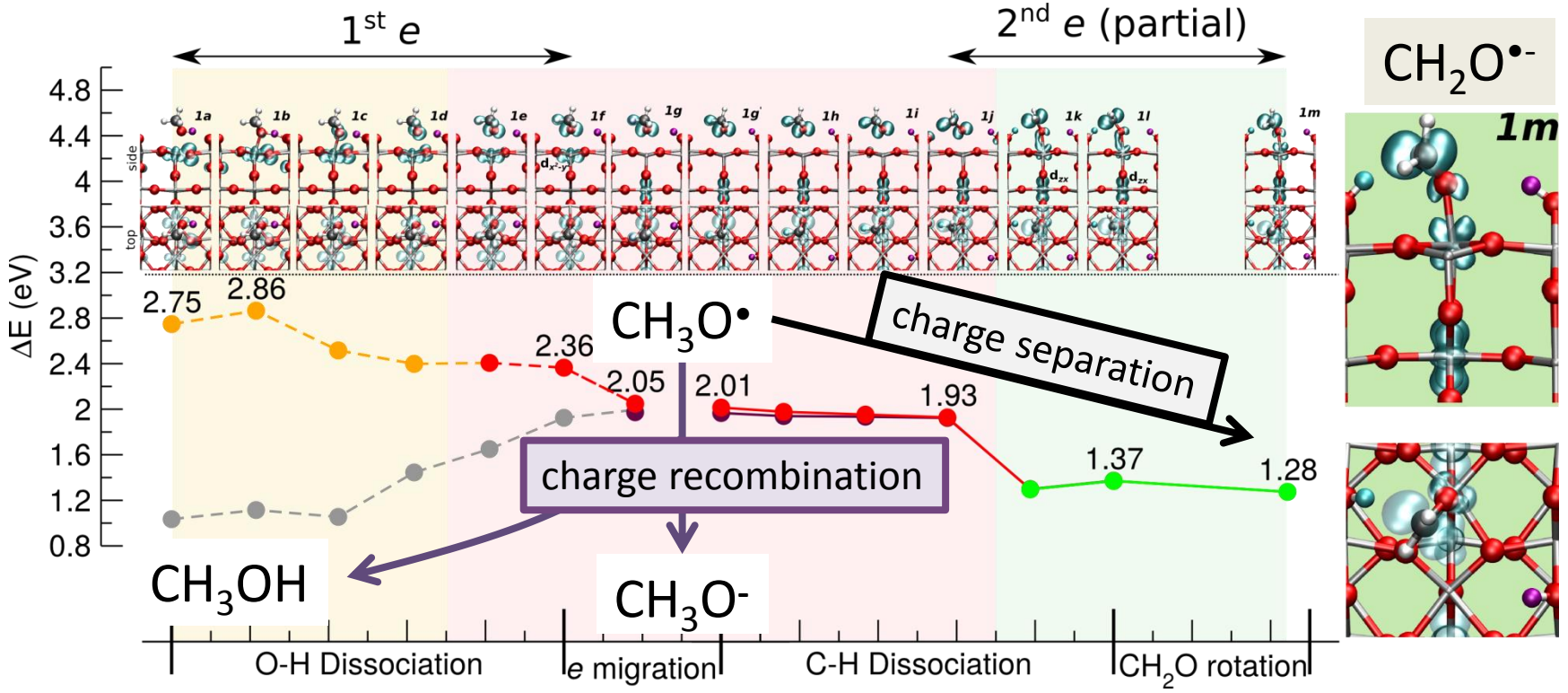

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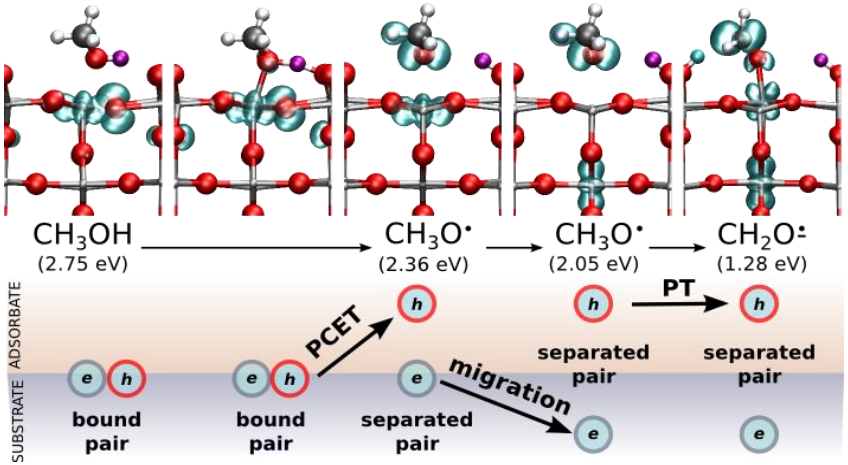
Conclusions

- Applied state-of-the-art theoretical methods to heterogeneous photocatalysis
- PCET explains hole trapping despite unfavorable level alignmet
- Microscopic picture of behaviour of hole-electron pairs



- Elucidated excited-state mechanism to form adsorbed $CH_2O^{\bullet-}$ from CH_3OH (**Can be Type C**)

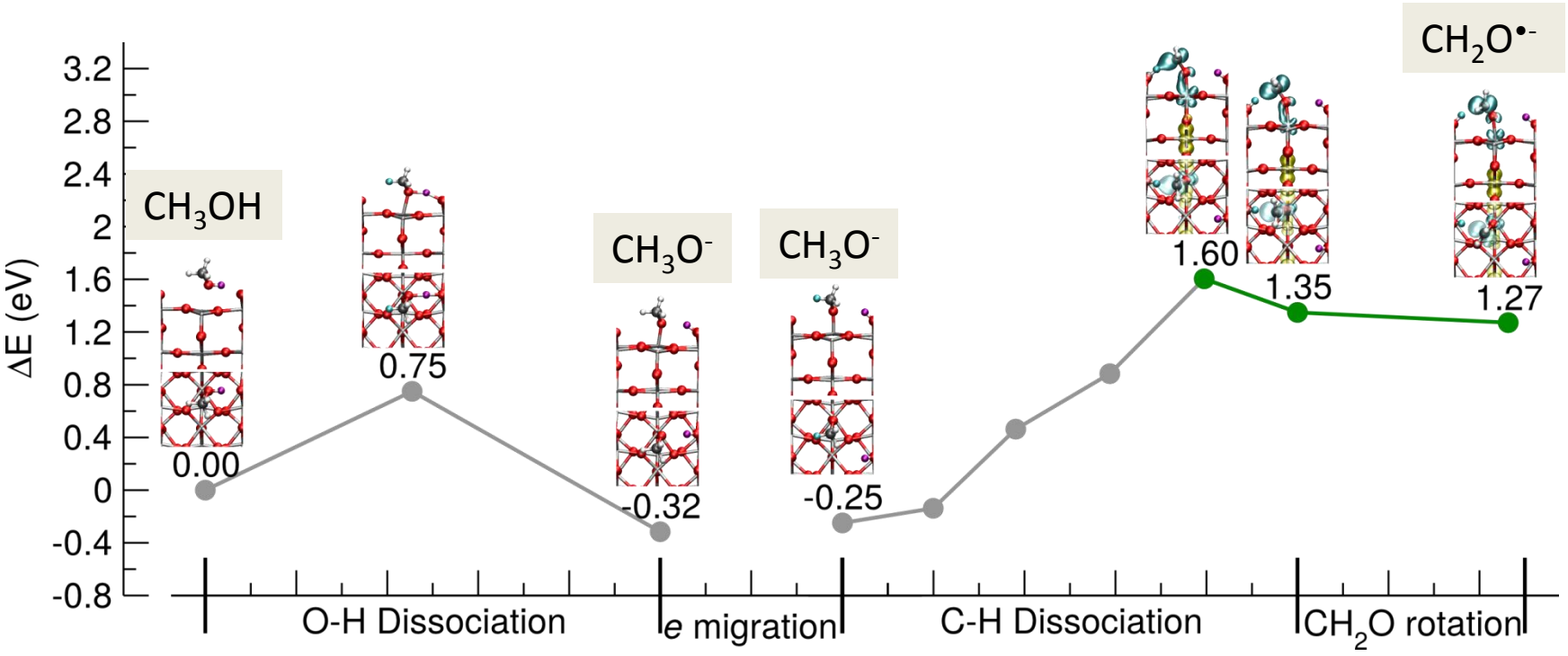
PAYOFF

- Clear understanding of the reaction mechanism ✓
- Clear interpretation of experiments ✓
- Clues for improving efficiency
- Clues for identification of efficient photo-catalysts

Acknowledgments

- Prof. **Lluis Blancafort**, University of Girona, Spain
- Fundings from Spanish Ministry of Science and Innovation (RyC-2011-09582)
- CPU from Spanish Supercomputing Network (Magerit@CeSViMa)

S_0 Ground-State Topology



VASP calculations with DFT HSE06 xc-functional at Γ point and NEB method

A. Migani and L. Blancafort, JACS 2016, DOI:10.1021/jacs.6b11067