Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Dynamics of hydrogen shift reactions between peroxy radicals

Supporting Information

Imon Mandal,[a] *Christopher David Daub,* [b] *Rashid Valiev,*[b] *Theo Kurtén*[b*] *R. Benny Gerber*[a,c*]

[a]The Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

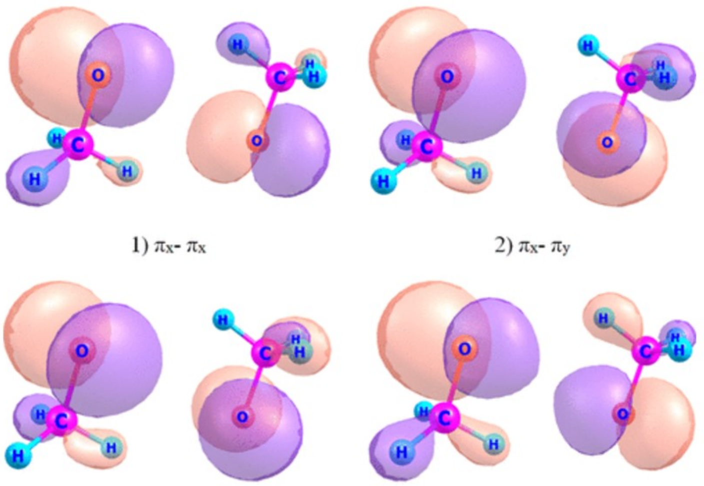
[b]Department of Chemistry, University of Helsinki, Helsinki 00014, Finland

[c]Department of Chemistry, University of California, Irvine, California 92697, USA

***Corresponding authors**

emails: theo.kurten@helsinki.fi

robertbenny.gerber@mail.huji.ac.il



1) π_x- π_x

2) π_x- π_y

3) π_x- π_y

4) π_x- π_x

Fig S1. State-averaged XMS-CASPT2(6,4)/tzvpp MOs for the $^3(CH_3O\ldots CH_3O)$ complex

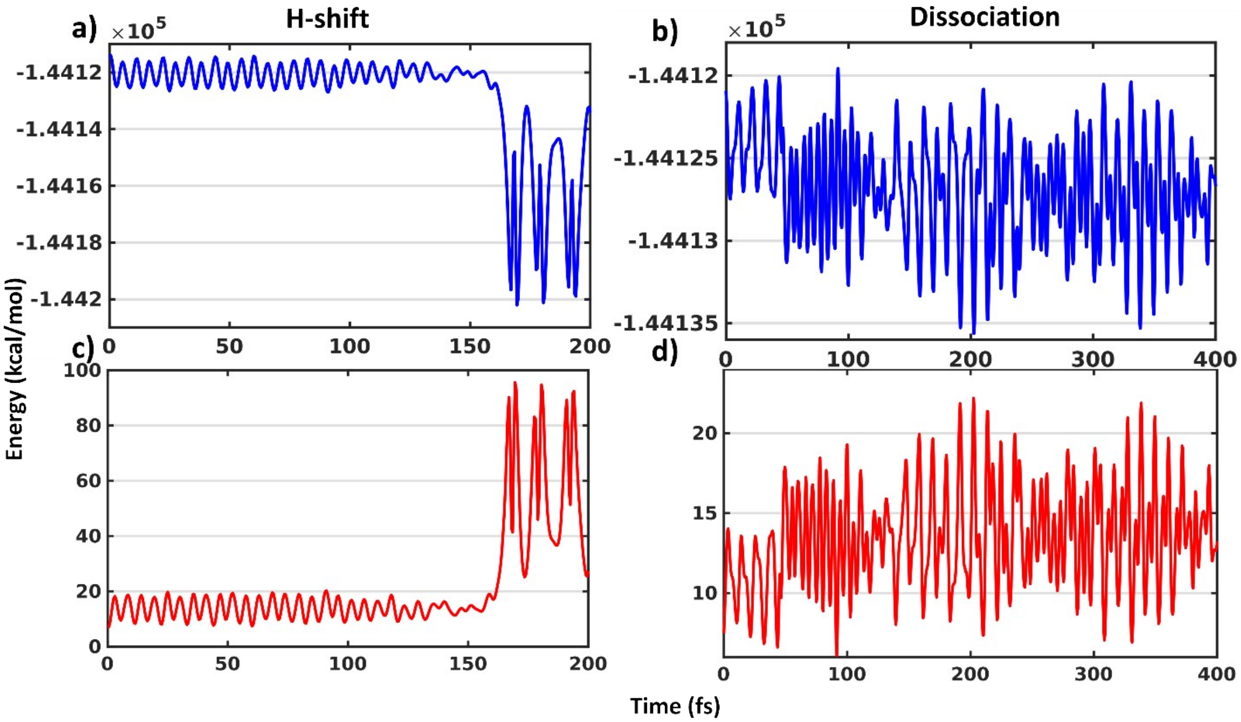


Fig S2: (a and b) potential energy variation along the representative trajectories of H-shift and dissociation using XMS-CASPT2. (c and d) similar graph for kinetic energy. For H-shift, after 160 fs decrease in potential energy occurs due to the hydrogen transfer from CH_3 group to the OH of other methyl radical, which is supplemented with an increase in the kinetic energy in c).

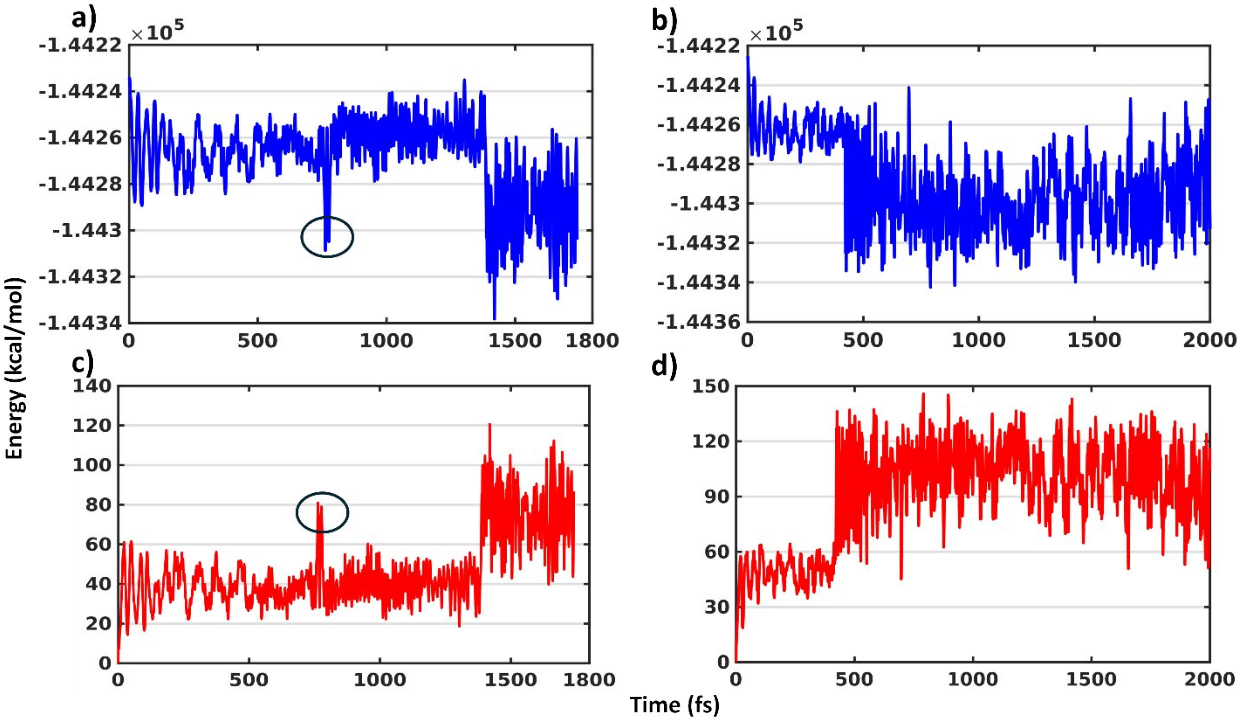


Fig S3: (a and b) potential energy variation along the representative trajectories of H-shift using MRSF-TDDFT. (c and d) similar graph for kinetic energy. For the H-shift trajectories, decrease in potential energy occurs due to the hydrogen transfer from CH_3 group to the OH of other methyl radical, supplemented with an increase in the kinetic energy in c) and d). The circled region in a) and c) showed the potential and kinetic energy change during transient CH_3OOCH_3 peroxide dimer formation. For the same trajectories, the variation in the O-H and O-O bond lengths are plotted in Fig. 2.

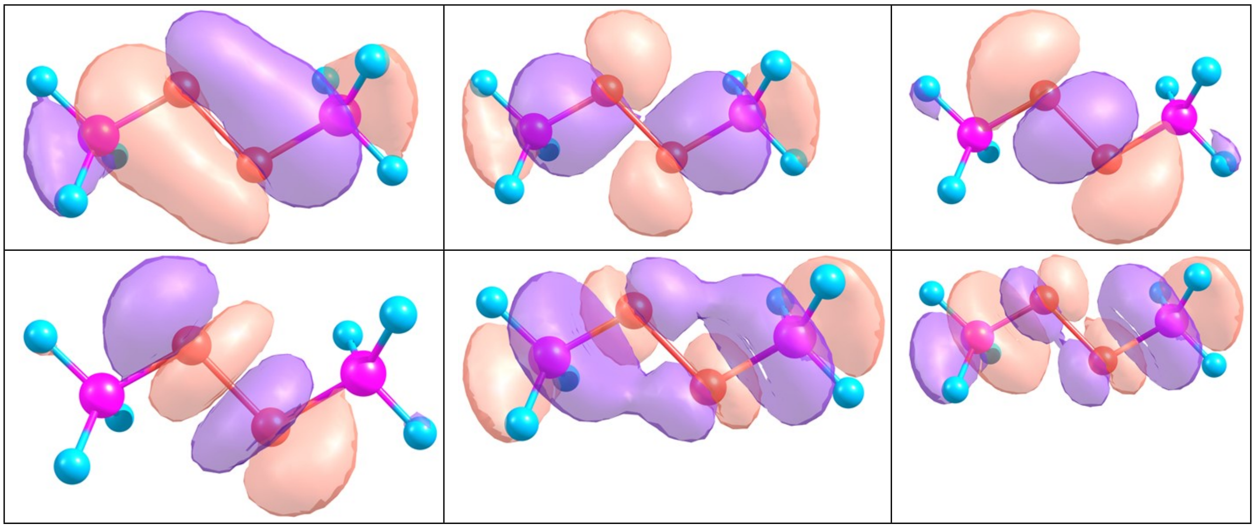


Fig S4: CASSCF(6,6)/cc-pvdz MOs for the CH_3OOCH_3 dimer