

Unexpected Spontaneously Dynamic Oxygen Migration on Carbon Nanotubes

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PS. 1. Tests of a larger basis set and other DFT method for oxygen migration on the interior surface of (6, 6)-SWCNT

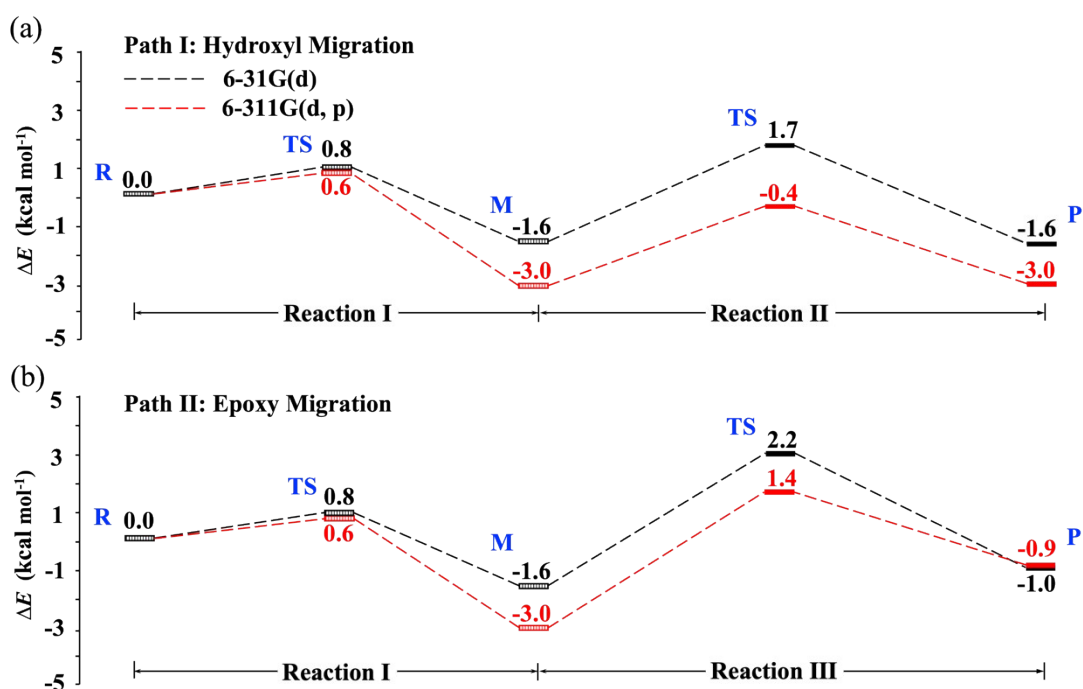


Fig. S1. Comparison of oxygen migration including (a) Path I: hydroxyl migration and (b) Path II: epoxy migration on the interior surface of SWCNT, using the 6-31G(d) (current work, black dashed lines) and a larger basis set 6-311G(d, p) (red dashed lines). Notation: reactants (R), intermediates (M), transition states (TS) and products (P). C-O bond breaking reaction (Reaction I), proton transfer reaction between the neighbouring hydroxyl for the exchange (Reaction II) and C-O bond reforming reaction (Reaction III). The energy of R is shifted to 0 for easy comparison.

Figure S1 compares the oxygen migration pathways using the 6-31G(d) (current work) and a larger basis set 6-311G(d, p) on the interior surface of SWCNT. The energy barriers of C-O bond breaking reaction, proton transfer reaction between the neighboring hydroxyl for the exchange, and C-O bond reforming reaction using the 6-311G(d, p) basis set are 0.6 kcal/mol, 2.6 kcal/mol and 4.4 kcal/mol, respectively. Compared to barriers using the 6-31G(d), these values change a little and are still the order of thermal fluctuations, indicating that the epoxy and hydroxyl groups can spontaneously migrate. Again the intermediate with a dangling C-O bond is found to

be stable than the epoxy.

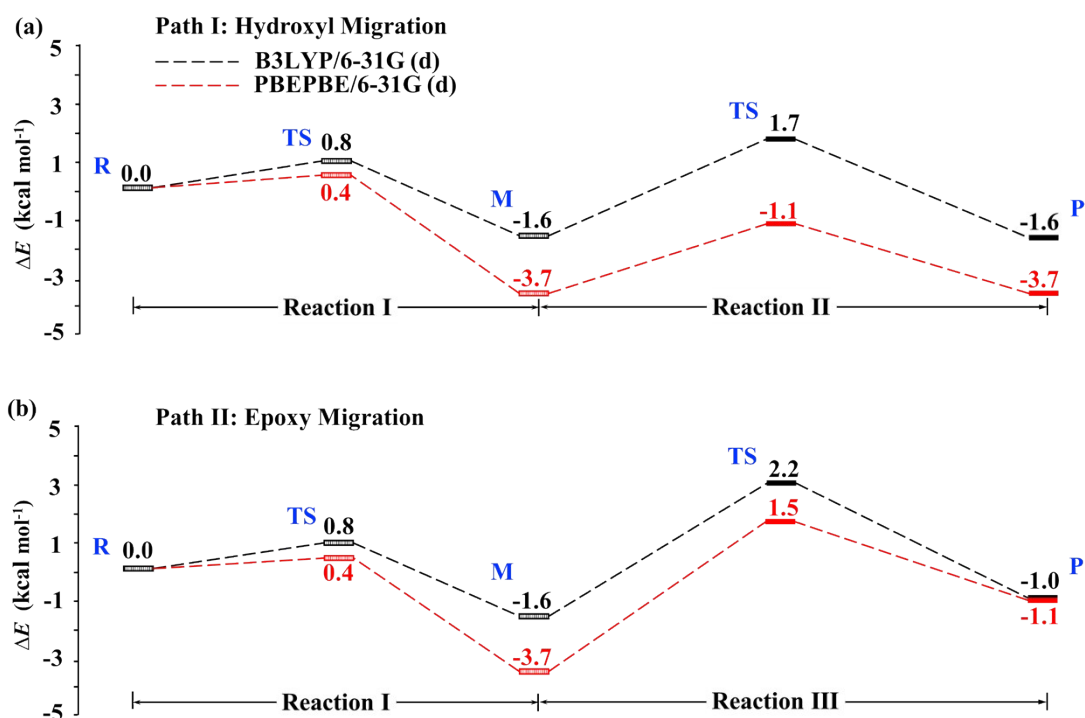


Fig. S2. Comparison of oxygen migration including (a) Path I: hydroxyl migration and (b) Path II: epoxy migration on the interior surface of SWCNT, using different DFT methods. Notations are same to those in Fig. S1. The energy of R is shifted to 0 for easy comparison.

We also performed the calculations using alternative DFT method, PBEPBE. As shown in Fig. S2, the energy barriers are all still less than or comparable of thermal fluctuations, and the energy of M state is also lower than R state. These results consistent with the those for B3LYP/6-31G(d) in the manuscript despite the energy values, validating the spontaneously dynamic oxygen migration on the interior surface of SWCNT.

PS. 2. Mulliken charge distributions for reactant (R) and intermediate (M) states on GO and surface of (6, 6)-SWCNT

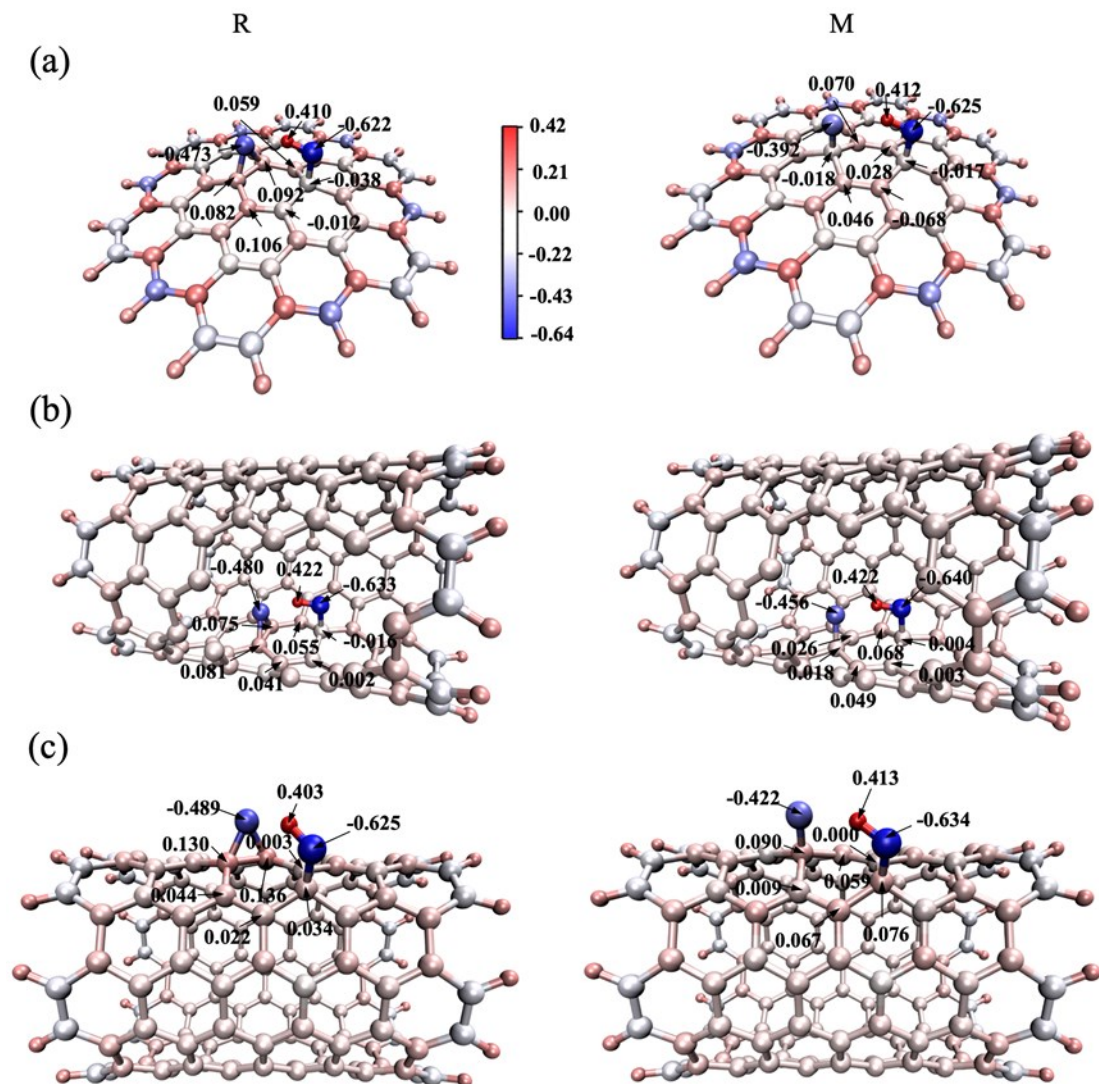


Fig. S3. Mulliken charge distributions for R and M states on (a) GO, (b) interior and (c) exterior surfaces of (6, 6)-SWCNT. All charge distributions are colored using the unified colorbar, in the unit of e .

PS. 3. Oxygen migration pathways on the surface of (5, 5)-SWCNT

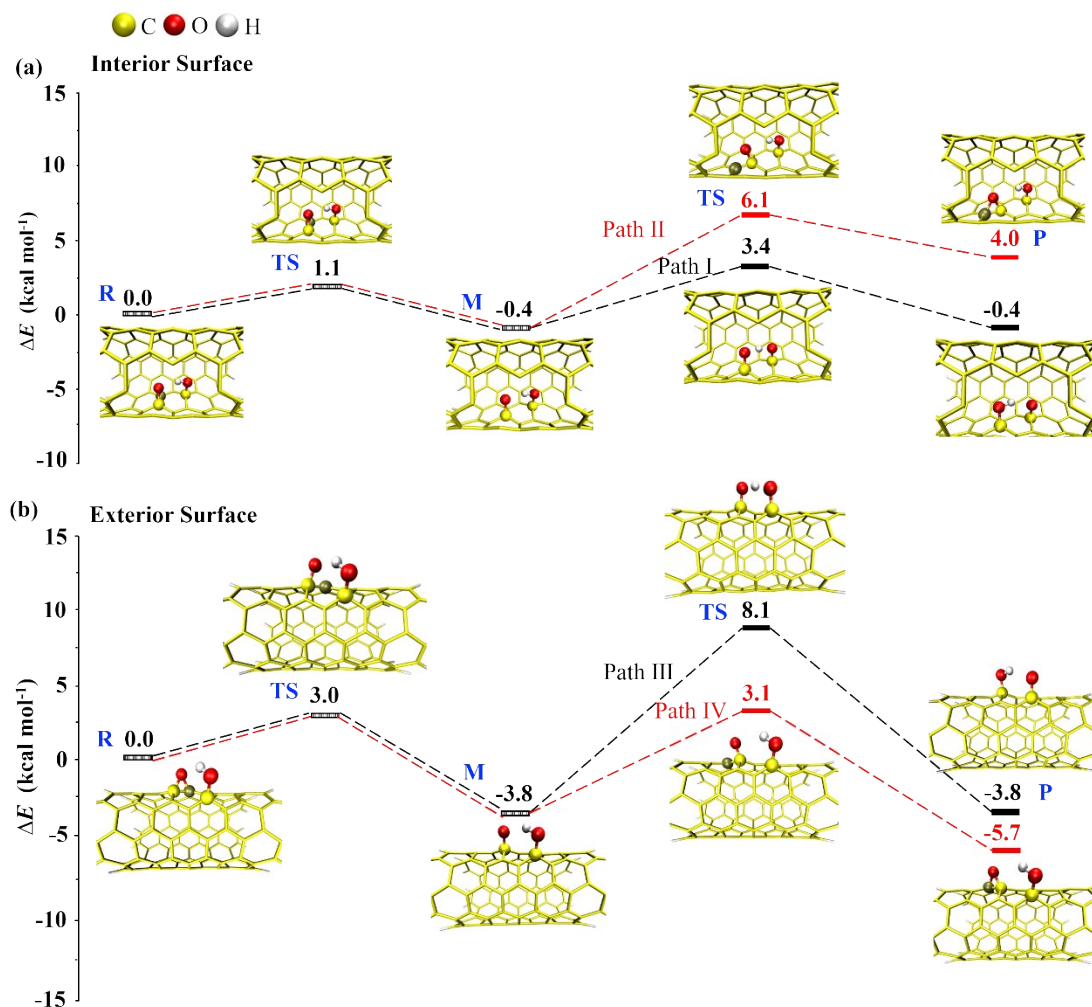


Fig. S4. Oxygen migration including the hydroxyl migration (Paths I and III, black lines) and the epoxy migration (Paths II and IV, red lines) on the (a) interior and (b) exterior surfaces of (5, 5)-SWCNT. The (5, 5)-SWCNT of length 12.26 Å consists of 110 carbon atoms and a pair of epoxy and hydroxyl groups. Twenty hydrogen atoms are added to saturate the edge carbon atoms. Carbon atoms in front of oxygen atoms on the SWCNT are hidden for the clarity of the migrations of hydroxyl and epoxy groups. Notation: reactants (R), intermediates (M), transition states (TS) and products (P). The energy of R is shifted to 0 for easy comparison.

PS. 4. Oxygen migration pathways on the surface of (7, 7)-SWCNT

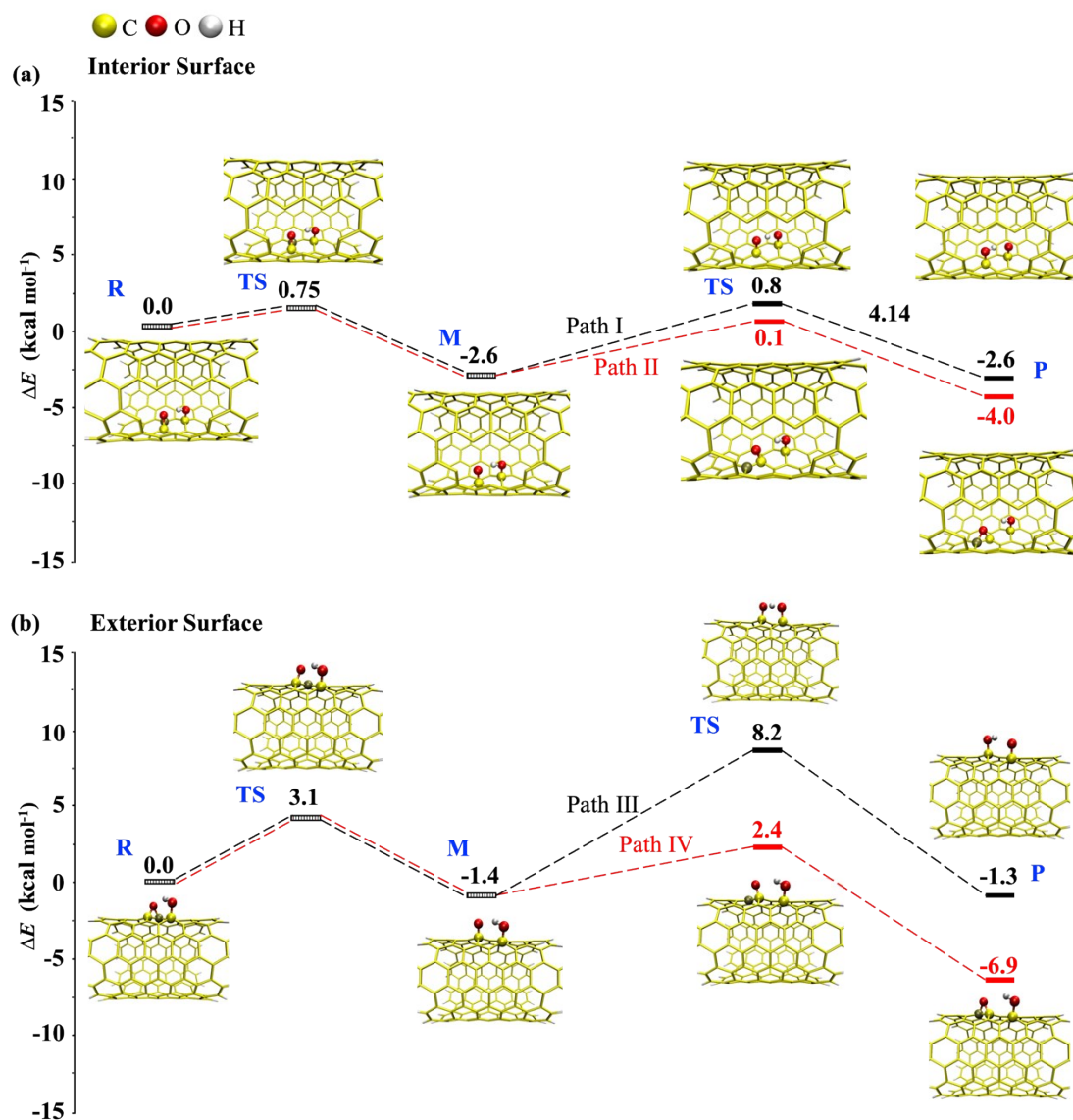


Fig. S5. Oxygen migration including the hydroxyl migration (Paths I and III, black lines) and the epoxy migration (Paths II and IV, red lines) on the (a) interior and (b) exterior surfaces of (7, 7)-SWCNT. The (7, 7)-SWCNT of length 12.30 Å consists of 154 carbon atoms and a pair of epoxy and hydroxyl groups. Twenty eight hydrogen atoms are added to saturate the edge carbon atoms. Carbon atoms in front of oxygen atoms on the SWCNT are hidden for the clarity of the migrations of hydroxyl and epoxy groups. Notations are same to these used in Fig. S4.