– Electronic Supplementary Information –

A Computational Study on Molecular Adsorption States of Nitrogen on a Tungsten Tetramer

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Suitability of B3LYP functional for the present study

In the present study, we employed the most popular and extensively used density functional, B3LYP. It is however well-known that the B3LYP has some shortcomings: (1) its performance for transition metals is not so good as that for main-group elements; (2) it fails for non-covalent interactions like van der Waals forces, hydrogen bonding etc.; (3) it tends to underestimate reaction barriers. In order to overcome these difficulties, Truhlar et al. recently developed a series of new density functionals called "M06-class" (and earlier version, M05-class) functionals, which, indeed, show excellent performances in both main-group and transition-metal chemistry computations including barrier heights and non-covalent correlation energy predictions.[1] We have checked the suitability of B3LYP for the present study that deals in interaction between a transition metal and inert nitrogen, by using one of the modern functionals, M06, which is the most versatile one among the new functional family.

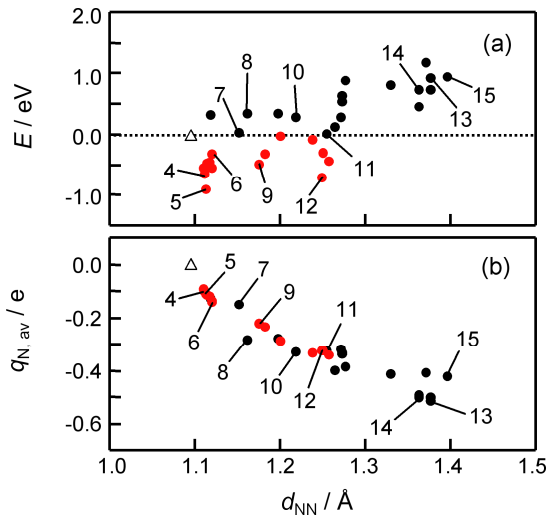

Fig. S1 Adsorption states of N_2 on W_4 calculated using the M06 functional. (a) The total energy of N_2W_4 E and (b) the averaged Mulliken atomic charge of N $q_{N,av}$ are plotted as a function of the N-N separation d_{NN}. The origin of E in (a) is the sum of the energies for a free N_2 and a free W_4. Each solid circle denotes an adsorption state found by geometry optimization calculations as a local minimum of the potential energy surface of N_2W_4. Open triangles are for a free N_2 molecule. States with negative energies are displayed by red symbols. The numbered states have geometries with the same numbers in Figure S2.

Starting from the N_2W_4 geometries optimized by B3LYP, we re-optimized them by using M06. The same basis sets, 6-311G(d) and LANL2DZ, were employed for both N and W atoms. Computations were executed by the GAMESS code.[2]

Figure S1 shows a total energy E vs. N-N separation d_{NN} plot and an averaged Mulliken charge $q_{N,av}$ vs. d_{NN} plot obtained by using the M06 functional, and the geometries of the numbered states in the plots are shown in Figure S2. It was found that the plots and the adsorption geometries have well replicated the results by B3LYP shown in Figures 1 and 2 of the main article, indicating that the B3LYP calculations are reliable enough.

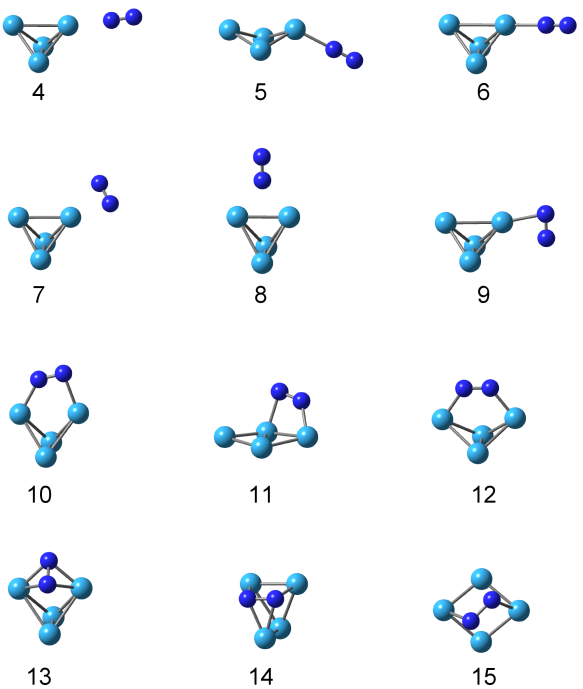

Fig. S2 Geometries of N_2W_4 clusters corresponding to the numbered states in Figure S1, optimized by using the M06 functional. Light blue and dark blue spheres denote W and N atoms, respectively.

Exploring the MOs of the optimized states in detail, we have found at least one occupied MO containing considerable N_2 $2\pi^*$ components for all the optimized states. These MOs play a primary part in molecular adsorption of N_2 on W_4. Such MOs are shown in Figure S3 for each corresponding state in Figure S2. The figure shows that $2\pi^*$ and the W 5d orbitals are well hybridized and thus the adsorption states discussed in this study are all covalently bonded. This conclusion is consistent with the resuts in Figure S1b which shows charge on N_2 systematically changes depending on the degree of interaction. These observations ensure that the N_2-W_4 interactions treated in the present study are within the region where B3LYP soundly works.

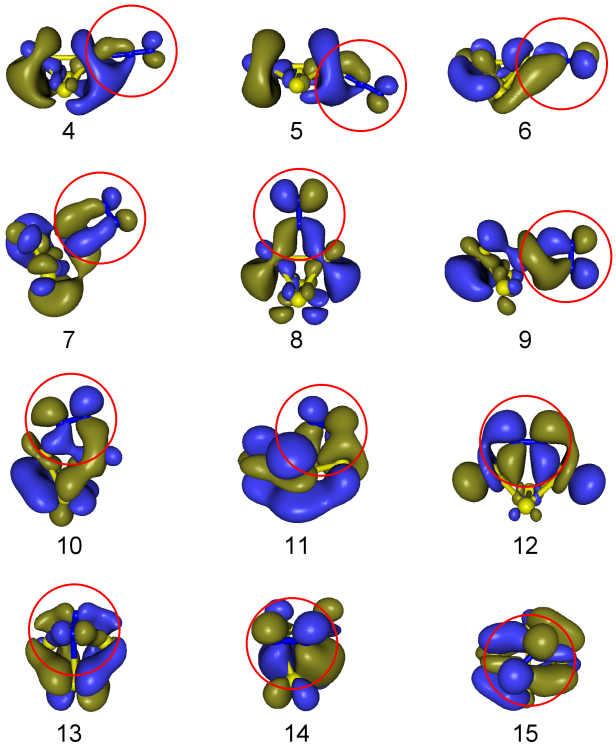

Fig. S3 Geometries of representative MOs containing N_2 $2\pi^*$ components for the corresponding states in Figure S2. Red circles indicate the regions where the $2\pi^*$ interacts with W_4.

Notes and references

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1 Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 157; Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

2 GAMESS, ver. 11 Apr. 2008, M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347; M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry, the first forty years*, ed. C. E. Dykstra, G. Frenking, K. S. Kim, G. E. Scuseria, Elsevier, Amsterdam, 2005, ch. 41, pp. 1167-1189.