

Regulation of Different Protonated States of Two Intimate Histidine Residues on Reductive Half-Reaction of Glucose Oxidase

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Supporting Information

1. Complete Reference

(45) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G.E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Prtersson, H. Nalatsyji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford CT, 2013.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2016.

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2. The proton-electron transfer mechanisms in the active center of GOx

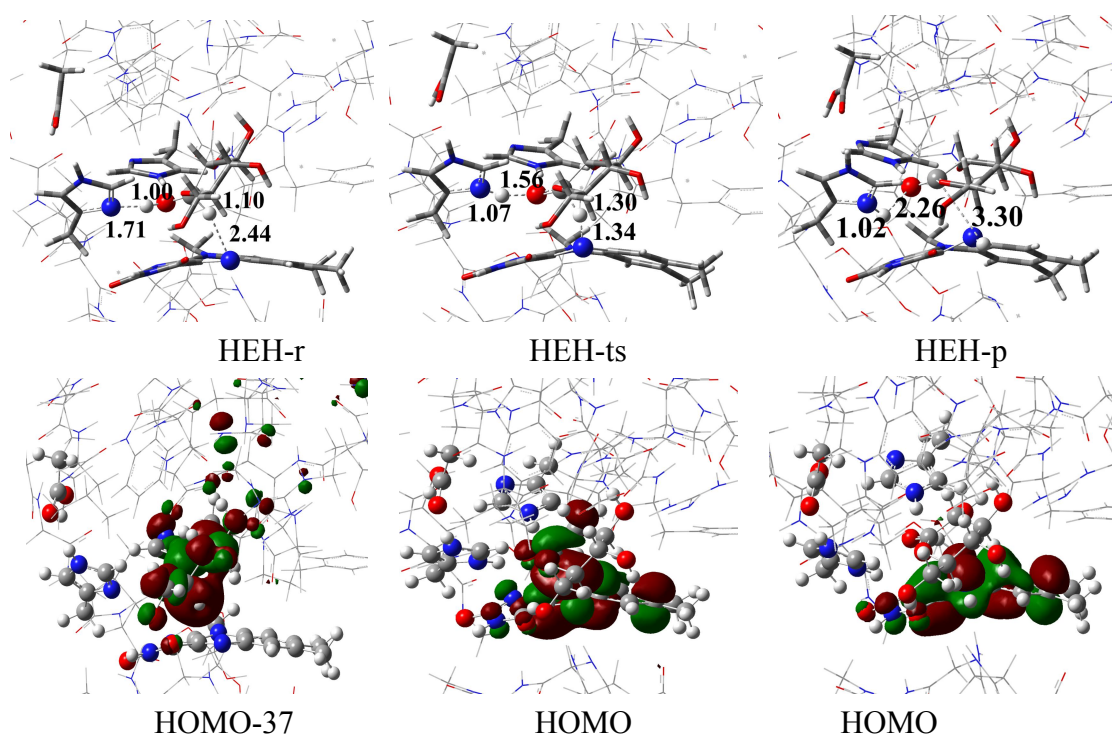


Figure S1. The structures of the reactant, transition state and product of the proton-electron transfer process in HEH with the corresponding distributions of the moving occupied molecular orbitals.

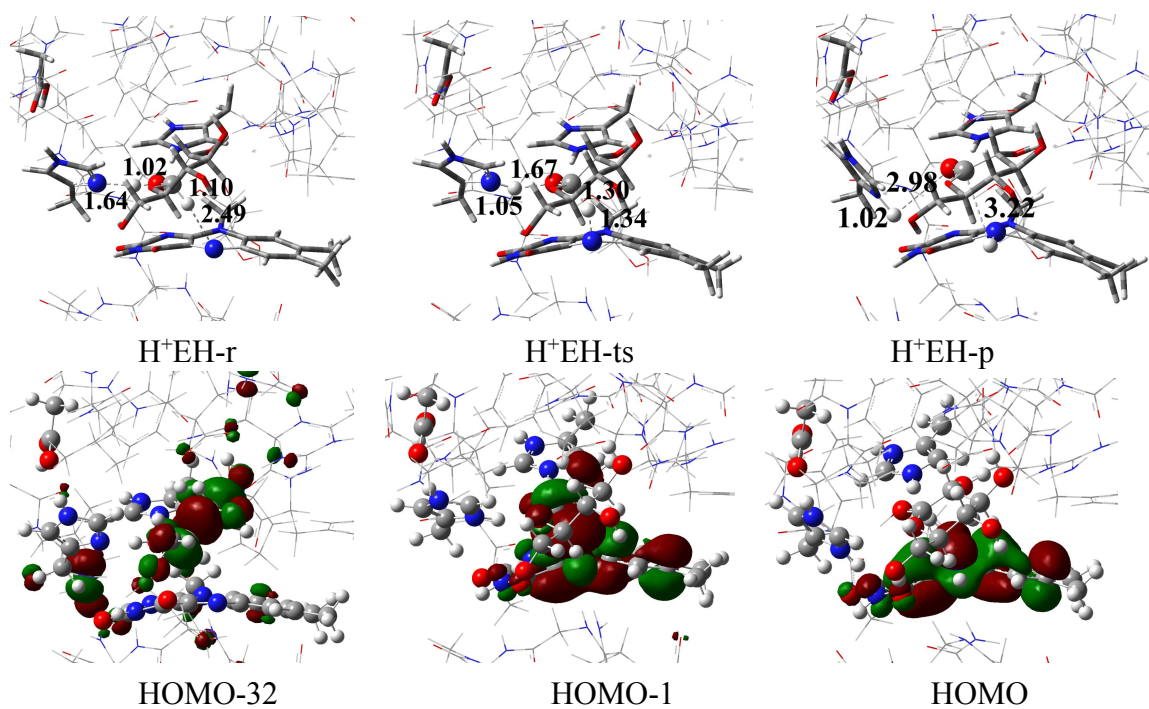


Figure S2. The structures of the reactant, transition state and product for the proton-electron transfer process in H⁺EH and the corresponding distributions of the moving occupied molecular orbitals.

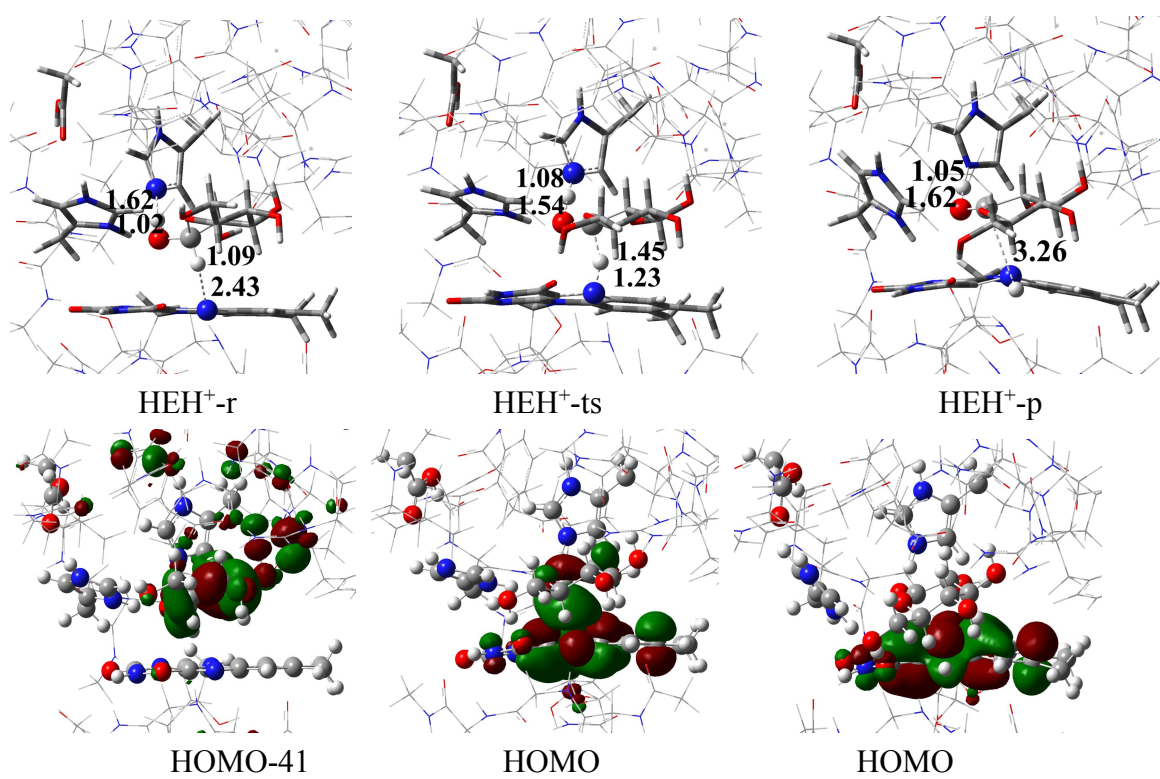


Figure S3. The structures of the reactant, transition state and product for the proton-electron transfer process in HEH⁺ and the corresponding distributions of the moving occupied molecular orbitals.

3. Presence of neutral Arg210 on the opposite side of glucose

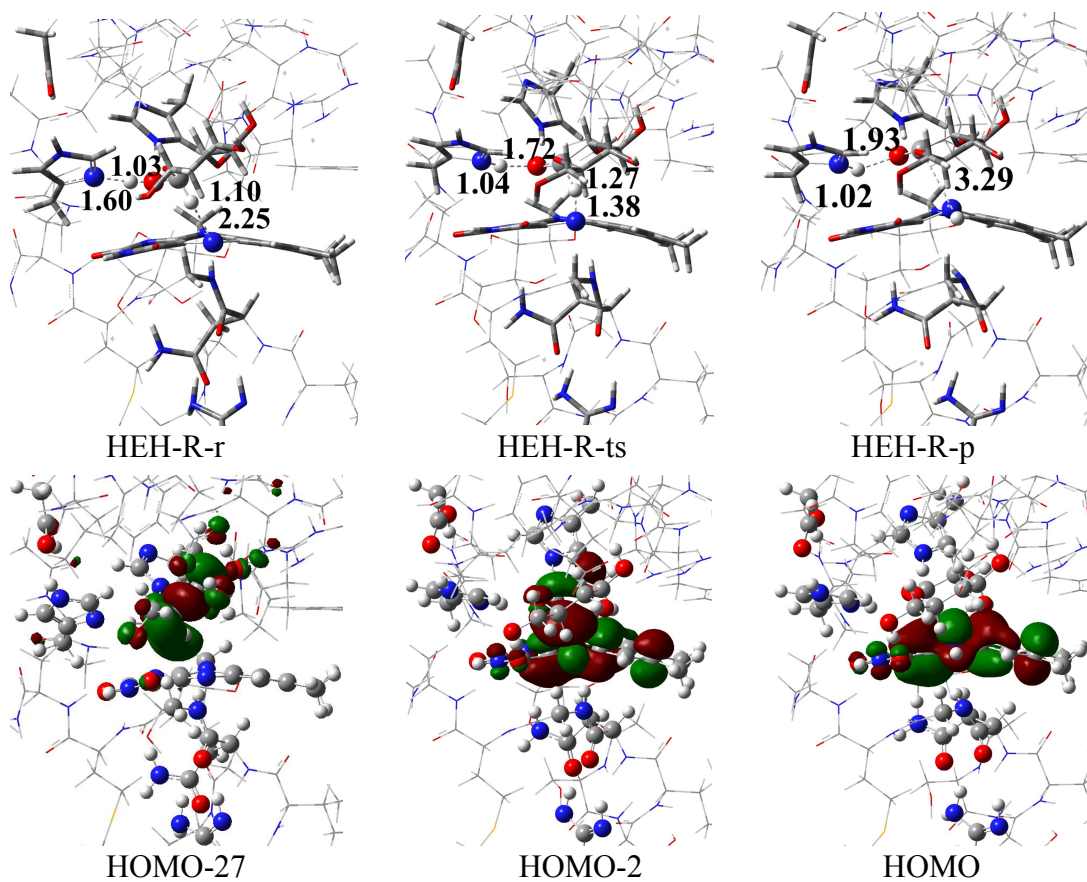


Figure S4. The structures of the reactant, transition state and product for the proton-electron transfer process in HEH-R and the corresponding distributions of the moving occupied molecular orbitals.

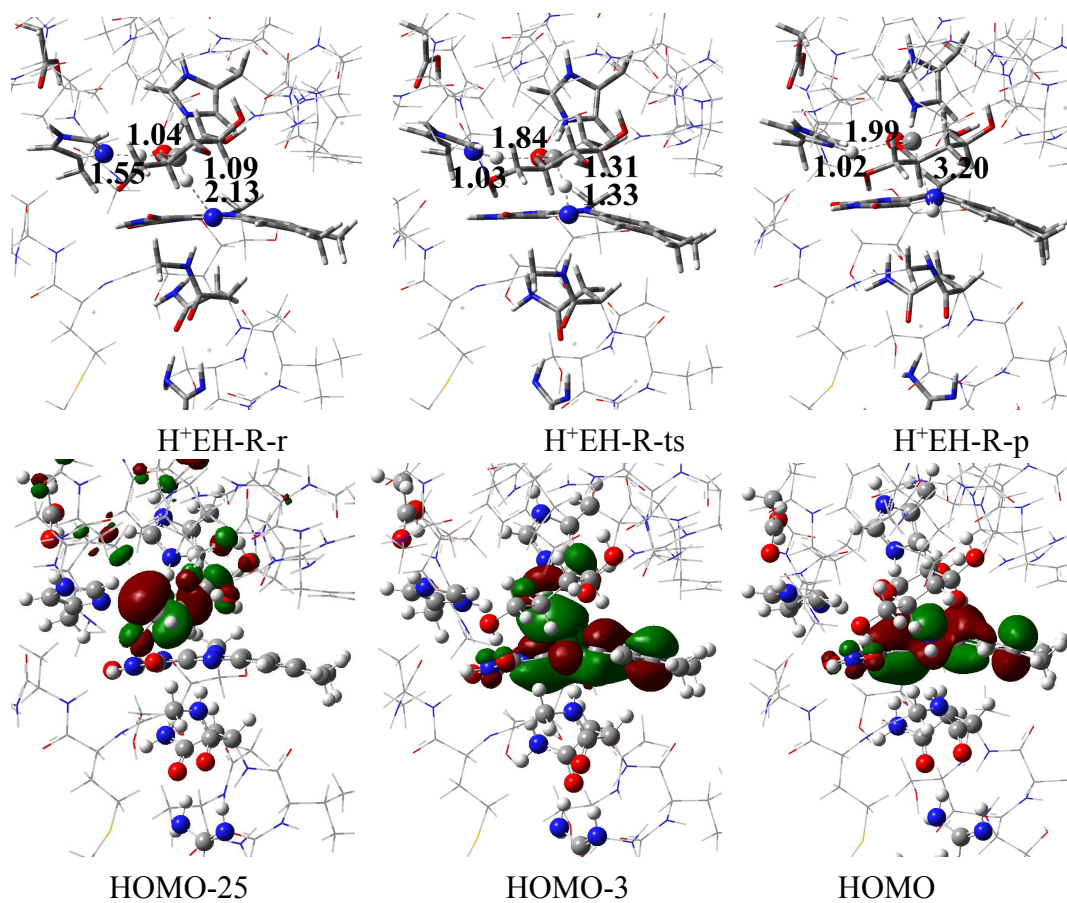


Figure S5. The structures of the reactant, transition state and product for the proton-electron transfer process in H⁺EH-R and the corresponding distributions of the moving occupied molecular orbitals.

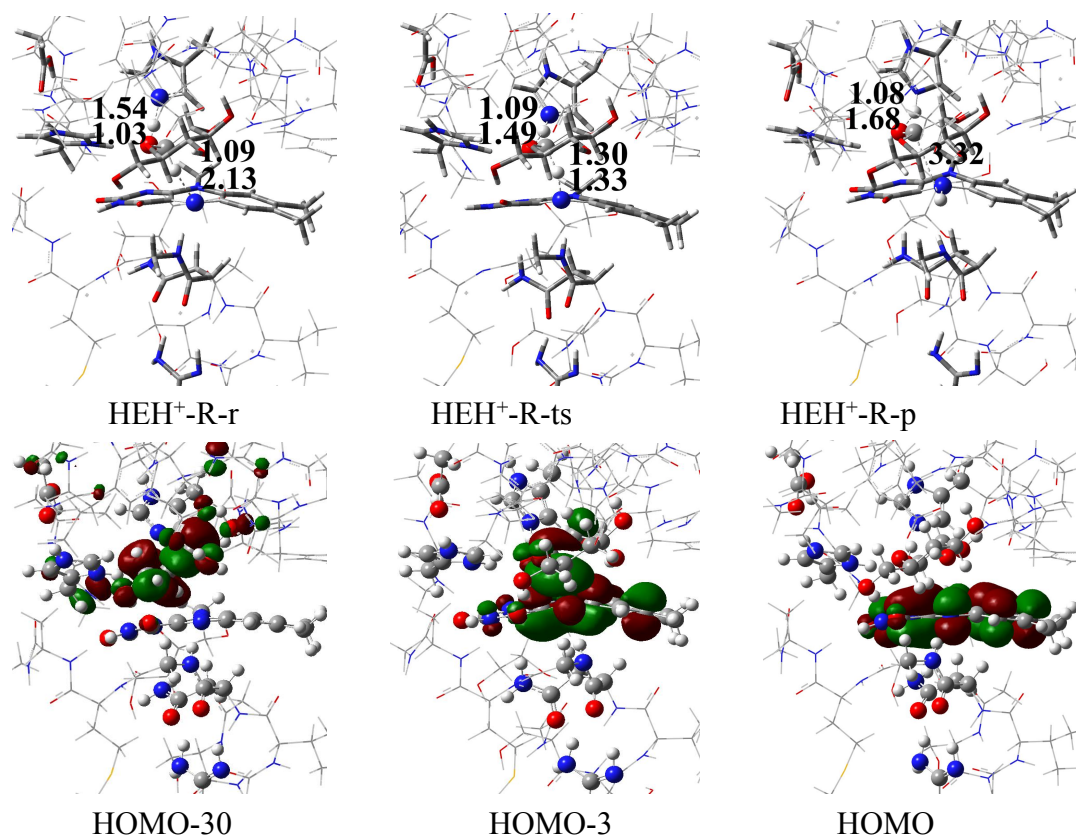


Figure S6. The structures of the reactant, transition state and product for the proton-electron transfer process in HEH⁺-R and the corresponding distributions of the moving occupied molecular orbitals.

4. Presence of protonization Arg210 on the opposite side of glucose

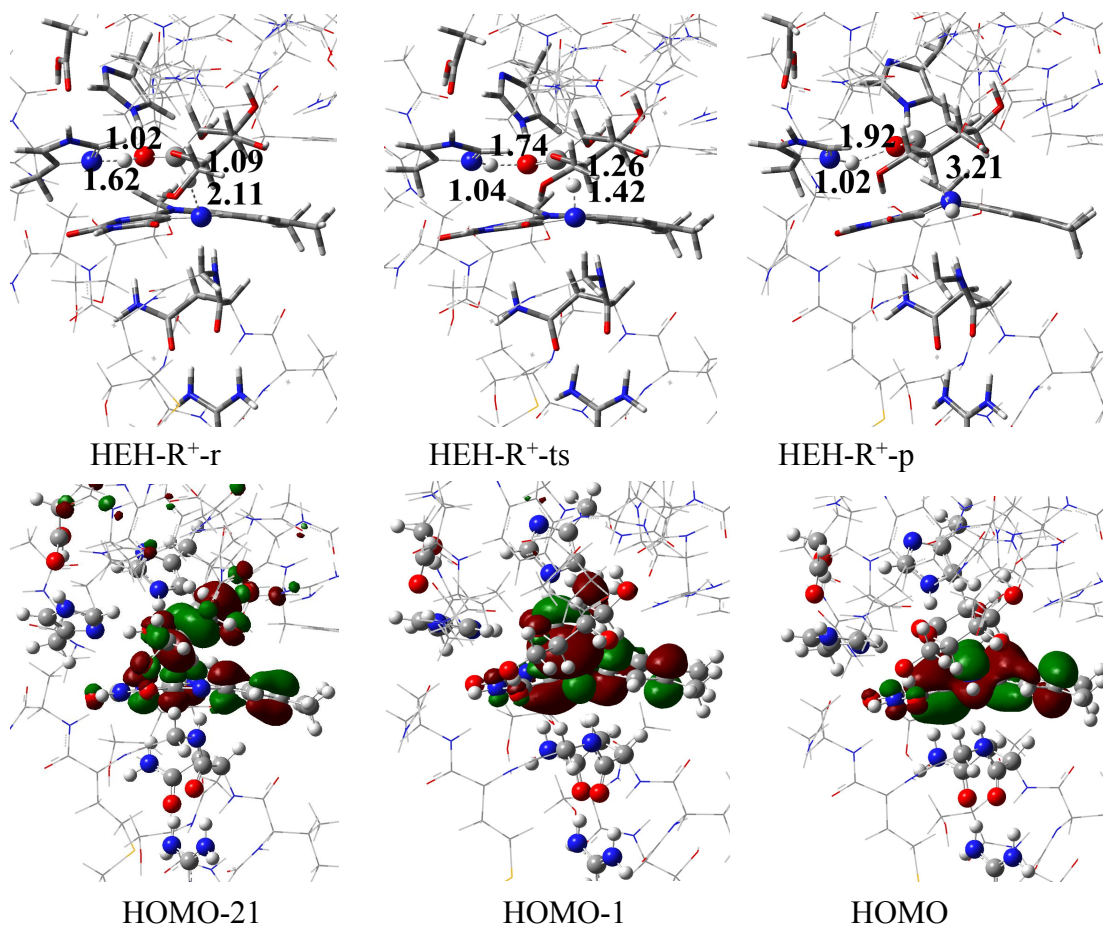


Figure S7. The structures of the reactant, transition state and product for the proton-electron transfer reaction in HEH-R⁺ with the corresponding distributions of the moving occupied molecular orbitals.

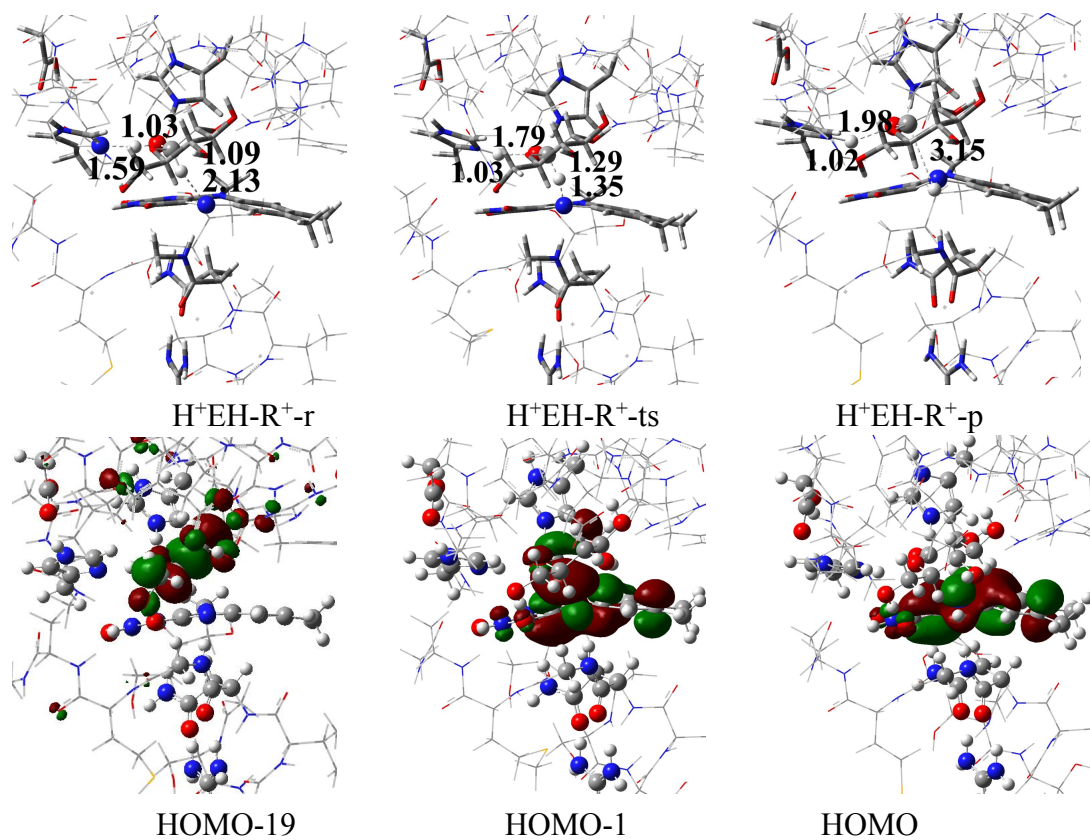


Figure S8. The structures of the reactant, transition state and product for the proton-electron transfer process in $\text{H}^+\text{EH-R}^+$ and the corresponding distributions of the moving occupied molecular orbitals.

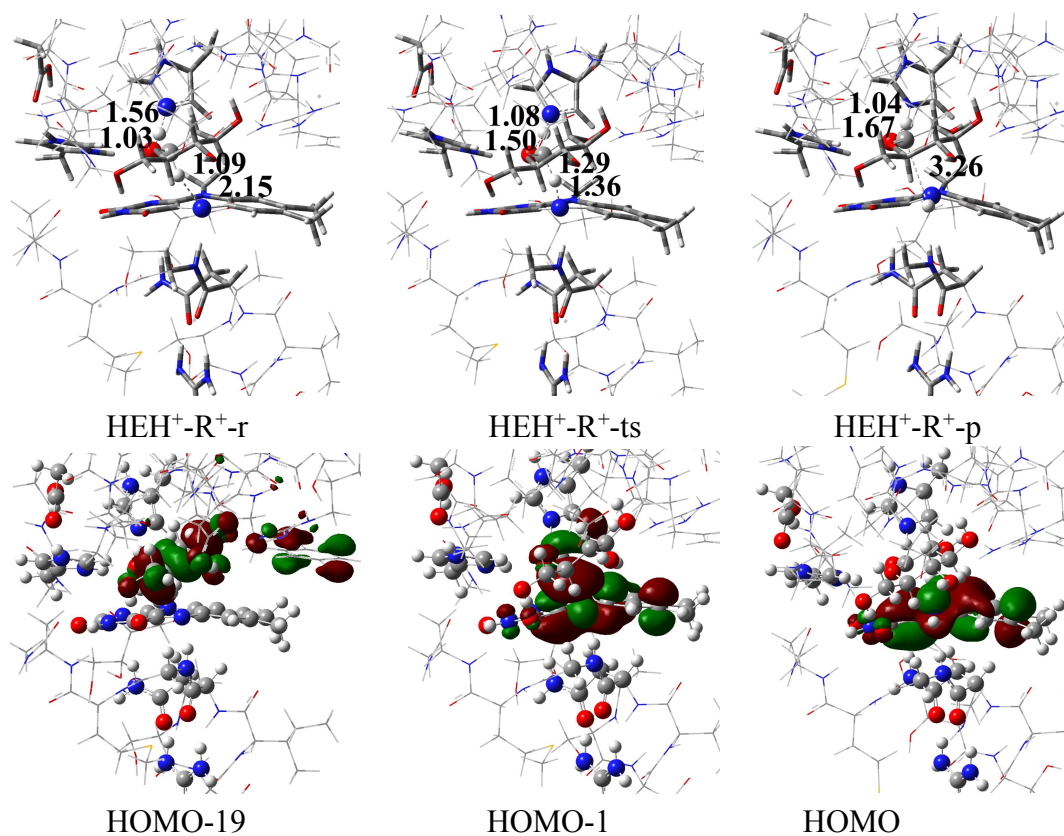


Figure S9. The structures of the reactant, transition state and product for the proton-electron transfer process in HEH⁺-R⁺ and the corresponding distributions of the moving occupied molecular orbitals.

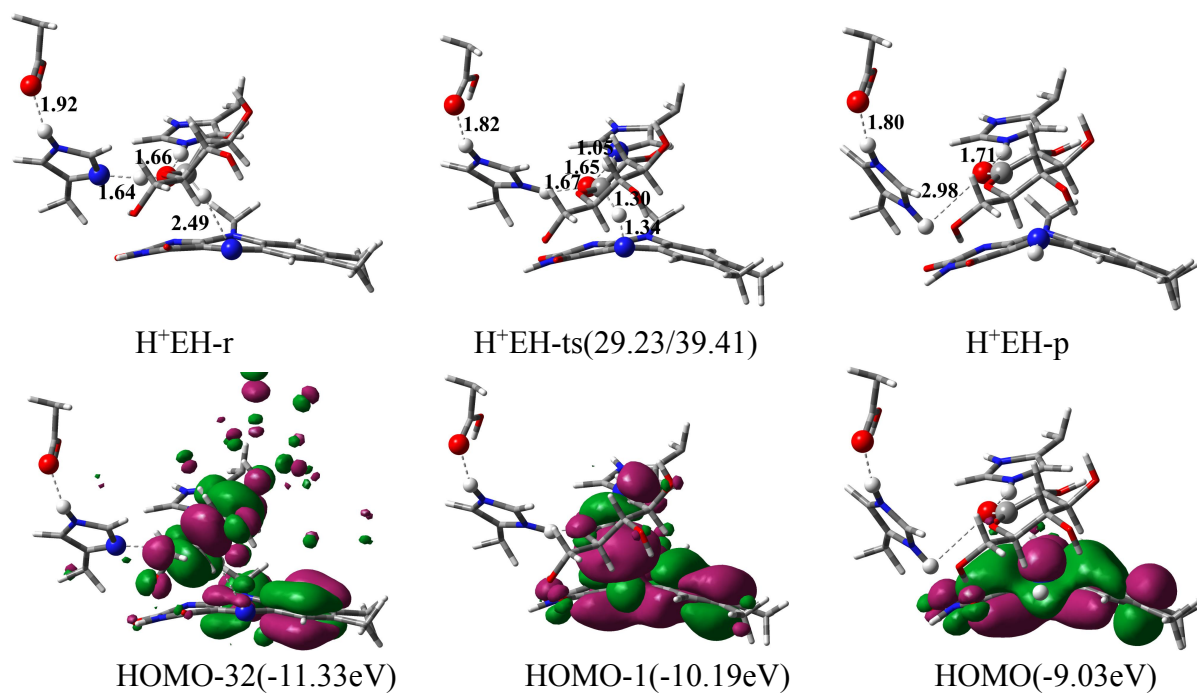


Figure S10. The structures of the reactant, transition state and product for the proton-electron transfer process in H^+EH and the corresponding distributions of the moving occupied molecular orbitals.

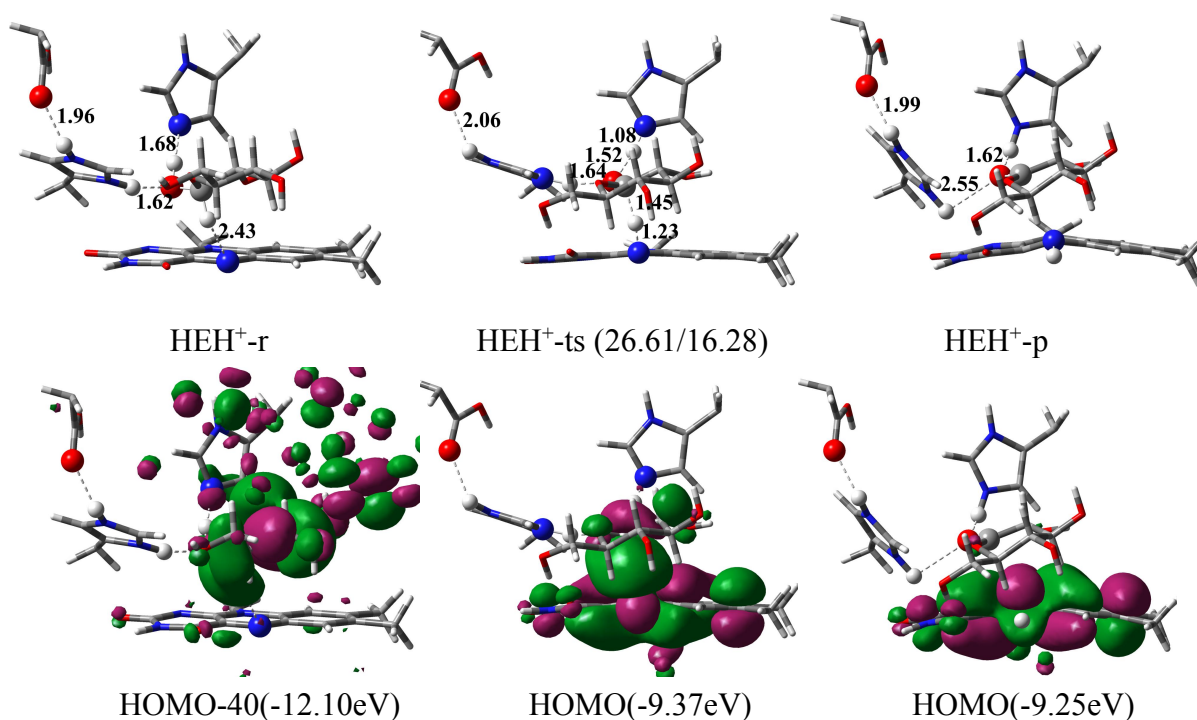


Figure S11. The structures of the reactant, transition state and product for the proton-electron transfer process in HEH^+ and the corresponding distributions of the moving occupied molecular orbitals.