

The Structures and Stability of HNOS Isomers

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Potential energy surface of HNOS system is investigated by means of MP2 method with 6-311 ++ G(d, p) basis set. The energy for each minimum and saddle point on the potential energy surface is corrected at the QCISD(T)/6-311 ++ G(3df, 2p) level of theory with zero-point vibrational energy included. As a result, eighteen isomers are theoretically predicted and *cis*-HNSO is found to be global minimum on the potential energy surface. Wherein, fourteen isomers are considered as kinetically stable species, and should be experimentally observed. Comparisons are made for HNOS system with its analogues, HNO₂ and HNS₂. The nature of bonding and isomers' stability of HNOS system are similar to HNS₂. The obvious similarities and discrepancies among HNOS, HNO₂ and HNS₂ are attributed to the hypervalent capacity of sulfur, oxygen and nitrogen atoms.

Keywords potential energy surface, HNOS molecule, isomerization, stability

Introduction

Nitrous acid, HONO, is well-known with its analog HOPO due to their activities in chemical kinetics, and the former also plays an important role in both atmospheric and combustion processes, and they have attracted considerable attention in experimental and theoretical areas.¹⁻⁷ In fact, their sulfur analogues have also attracted much attention in the fields of polymeric materials and atmosphere chemistry.⁸⁻¹² And some available experimental and theoretical information^{13,14} were reported about these compounds containing H atom or other functional groups. For HNS₂ system, the calculated results by Nakamura and co-workers¹⁴ indicated that the most stable isomer thermodynamically is *cis*-HNSS. They also conjectured other several isomers as stable species based on their energies with reference to *cis*-HNSS. A more recent theoretical study¹⁵ by our group also predicted that eight kinetically stable isomers of HNS₂ were expected to exist. This is a quite surprising amount. However in HNO₂ system, only three isomers are stable. Therefore, some differences are expected to exist. Because HNOS is an intergrade between

HNO₂ and HNS₂, we selected HNOS system as target in this paper, and hope that the study on the potential energy surface of HNOS system is helpful not only for predicting the possible isomers and their relative stability but also for understanding the nature of the bonding in HNO₂ and HNS₂.

Computational methods

The equilibrium geometries and transition states are optimized using second-order Moller-Plesset perturbation (MP2)^{16,17} method with the split valence 6-311G basis set, which is suitable to explore the potential energy surfaces of small molecules based on previous studies.¹⁸⁻²² Concretely, the structural parameters and zero-point vibrational energies are obtained at the MP2/6-311 ++ G(d, p) level of theory. The single-point energies of all stationary points are further corrected at the QCISD(T)/6-311 ++ G(3df, 2p) // MP2/6-311 ++ G(d, p) level of theory. QCISD(T) method^{23,24} is one of configuration interaction calculations and includes single and double substitutions with a triples contribution to the energy added. The energies of optimized stationary points at the QCISD(T)/6-311 ++ G(3df, 2p) // MP2/6-311 ++ G(d, p) level with zero-point vibrational energies included are used on the potential energy surface and in all discussions of the paper. In order to confirm whether the obtained transition states connect the right reactants and products, the intrinsic reaction coordinate (IRC)^{25,26} calculations are carried out at the MP2/6-311 ++ G(d, p) level of theory. All calculations are performed using the GAUSSIAN98 package²⁷ running on the LEGEND/KAITIAN4600 computer.

Results and discussion

Structures and thermodynamic stability of isomers

The optimized geometry parameters of eighteen HNOS isomers at MP2/6-311 ++ G(d, p) level are shown in

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Fig. 1. Considered eighteen HNOS energy minima can be classified into four groups, *i. e.*, chainlike, stereo three-membered ring, Y-shape and van der Waals (vdW) complex forms. The discussion will be made by following the four groups.

The species *cis*-HNOS (1), *trans*-HNOS (2), *cis*-HOSN (3), *trans*-HOSN (4), *trans*-HSNO (5), *cis*-HSNO (6), *cis*-HONS (8), *trans*-HONS (9), *trans*-HNOS (14) and *cis*-HNOS (15) have chainlike structures. Isomer 1 is found to be global minimum on the potential energy surface, and is the most stable species thermodynamically. Secondly low-lying isomer 2 is higher in energy than isomer 1 by 12.39 kJ/mol. The nitrogen-sulfur bonds in 1 and 2, 0.15462 and 0.15591 nm, respectively, are slightly longer than the re-

ported N = S double bond (0.1510 nm in Me—N = S = O²⁸) and obviously shorter than N—S single bond (0.1668 nm in (OC₂H₄NS₂)₂²⁹). Thus, both of them can be considered as N = S double bond with some single bond characters. Furthermore, the S—O bond distances in 1 and 2 are 0.14797 and 0.14693 nm, respectively, and can be regarded as S = O double bond considering the S = O double bond distance 0.14832 nm in V-type SO₂ and S—O single bond length 0.1710 nm in CH₃SOH at the MP2/6-311 ++ G(d, p) level. Isomers 3 and 4 (at 75.40 and 87.84 kJ/mol, respectively) are *cis*- and *trans*-HOSN chainlike structures, respectively. The S—O bond (about 0.172 nm) in 3 and 4 are normal single bond, while the S—N bonds (about 0.145 nm) have some triple bond characters as they are slightly shorter

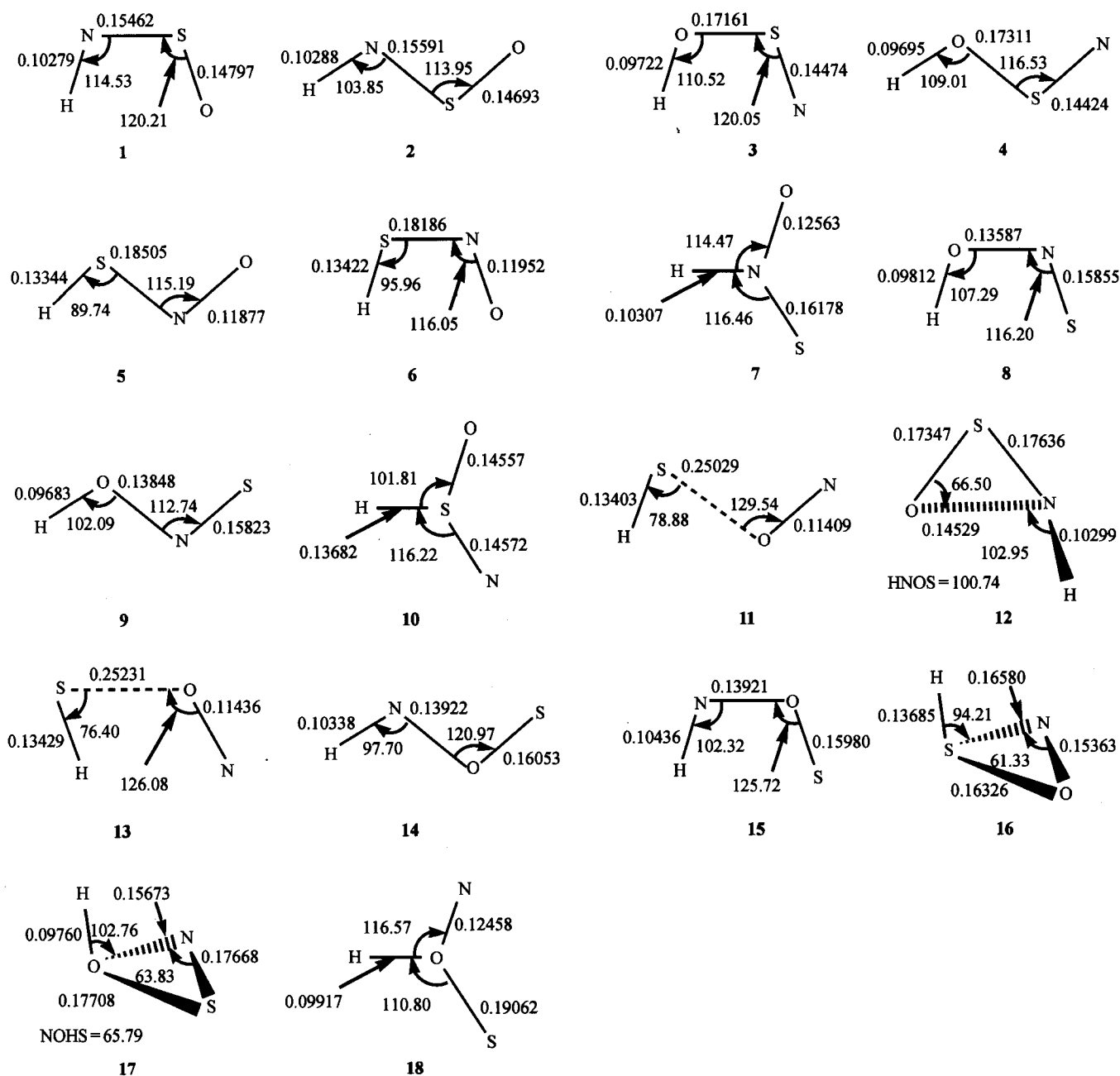


Fig. 1 Calculated equilibrium geometries of HNOS isomers at MP2/6-311 ++ G(d, p) level of theory. Bond lengths are in nanometers, and bond angles in degrees.

than N = S double bond. For low-lying species **5** and **6** (at 137.96 and 142.02 kJ/mol), the N—O bonds (0.11877 and 0.11952 nm) are normal double bond, judging from the reported N = O double bond length 0.1211 nm (in CH₃NO³⁰) and N—O single bond length 0.14630 nm (in H₂NOCH₃³¹). However the S—N bond lengths, 0.18505 and 0.18186 nm, indicate that they are weak single bond in contrast to the N—S single bond (0.1668 nm as presented above). The chainlike **8**, **9**, **14** and **15** at 162.57, 163.03, 330.25 and 330.38 kJ/mol, are *cis*- and *trans*-HONS and *cis*- and *trans*-HNOS, respectively, and have normal N—O and N—S single bond.

We also confirmed three stereo species **12**, **16** and **17** containing NOS three-membered ring with exocyclic NH, OH and SH bonding, respectively, and found that they are energy minima with all real vibrational frequencies. We did not investigate their bonding further because of their relative higher energies (275.66, 416.88 and 483.62 kJ/mol, respectively) and lower kinetic stability (as discussed below).

The species **7**, **10** and the highest-lying **18** are isomers with Y-type structures at 159.10, 216.21 and 612.11 kJ/mol, respectively. In **7**, the N—O bond (0.12563 nm) can be described as double bond with some single bonding characters, while the N—S bond (0.16178 nm) is the intermediate between N—S single bond and N = S double bond, and thus, SNO group can be described as two resonant forms, S = N—O and S—N = O. For species **10**, the S—O bond (0.14557 nm) is a double bond and the S—N bond (0.14572 nm) can be considered as double bond with some triple bond contribution. In view of the highest energy and lower kinetic stability of species **18**, we did not discuss more about its bonding.

The species **11** and **13** have unexpected S—O interatomic separations, 0.25029 and 0.25231 nm, respectively. Therefore, we should regard them as vdW complexes (or molecular fragments) rather than normal bonding isomers.

From the calculated results, we can obtain the energetic ordering of the HNOS local energy minima. Generally, the species with lower total energy has higher thermodynamical stability. At final QCISD(T)/6-311 ++ G(3df, 2p) level with zero-point vibrational energies correction, the thermodynamical stability order is **1** (0.00) > **2** (12.39) > **3** (75.40) > **4** (87.84) > **5** (137.96) > **6** (142.02) > **7** (159.10) > **8** (162.57) > **9** (163.03) > **10** (216.21) > **11** (264.65) > **12** (275.66) > **13** (278.84) > **14** (330.25) > **15** (330.38) > **16** (416.88) > **17** (483.62) > **18** (612.11). The values in parentheses are relative energies in kJ/mol with reference to **1**. It is clear that **1** is the most stable species thermodynamically. Species **1**—**9** can be considered as low-lying because of lower relative energies. Isomers **16**, **17**, and **18** are very high-lying, and in view of higher relative energies, we expect them to be of minor importance in experiments.

Isomerizations and kinetic stability of isomers

Let us turn to the kinetic stability of various HNOS iso-

mers. Twenty-three interconversion transition states of HNOS system are obtained at MP2/6-311 ++ G(d, p) level, and their structures are shown in Fig. 2. Their connections are checked by IRC calculations at the MP2/6-311 ++ G(d, p) level. TS m/n denotes the transition state connecting the species m and n . By means of the calculated isomers and transition states, a schematic potential energy surface is plotted in Fig. 3. For simplicity, the details of the obtained transition states are omitted.

Practically, we can briefly discuss the kinetic stability of the obtained isomers in terms of the isomerizations. From Fig. 3, it can be seen that isomers **12**, **16**, **17** and **18** can isomerize into **1**, **12**, **12** and **11** via transition states TS1/12, TS12/16, TS12/17 and TS11/18 by 78.46, 83.74, 24.53 and 44.05 kJ/mol reaction barrier heights, respectively. And thus, the higher-lying isomers **12**, **16**, **17** and **18** are kinetically unstable species, and can not be experimentally observed in normal conditions. The remaining isomers **1**—**11** and **13**—**15** may be considered to be kinetically stable species based on corresponding conversion barriers, *i. e.*, 204.53 (**1** → **3**), 308.61 (**2** → **10**), 129.13 (**3** → **1**), 257.65 (**4** → **10**), 214.11 (**5** → **7**), 125.52 (**6** → **8**), 192.97 (**7** → **5**), 104.97 (**8** → **6**), 356.26 (**9** → **7**), 104.79 (**10** → **2**), 391.51 (**11** → **18**), 184.64 (**13** → **15**), 198.75 (**14** → **12**) and 104.96 (**15** → **12**) kJ/mol. It is noted that the barriers heights of **3** ↔ **4**, **5** ↔ **6**, **8** ↔ **9**, and **11** ↔ **13** are somewhat lower, then each pair isomers residing in the deeper wells should coexist. It should be pointed out that fourteen of eighteen isomers of HNOS system are kinetically stable species and only four isomers are unstable, despite isomer **12** is lower in energy than isomers **13**, **14** and **15**. Furthermore, no cyclic stable isomer is found in this study, although three three-membered ring species are located on the potential energy surface.

Notice that transition state TS11/13 is 12.31 kJ/mol lower in energy than isomer **13** at QCISD(T)/6-311 ++ G(3df, 2p)//MP2/6-311 ++ G(d, p) level of theory with zero-point vibrational energy correction. The exceptional result indicates that the reaction barrier of **13** → **11** is close to zero, or this is a no-barrier reaction process, as presented in previous studies.^{32,33}

We also attempted to locate transition states connecting **11** with **6**, **13** with **5**, and **1** with **2**, which were expected to have lower barriers. But all attempts failed. Furthermore, we also expected O-shift and S-insertion transition states, which can connect **7** with **2** and **15** with **2**, to exist, but all optimizations lead to fragments or to stationary points including two imaginary vibrational frequencies.

Comparison with analogs and experiments

As discussed above, it is surprising that there are actually fourteen kinetically stable species in HNOS system. The result can be estimated by means of relative energies of isomers and approved accurately by the calculated potential energy surface. The conclusion is similar to HNS₂ system, *i. e.*, there are eight stable species in all nine isomers.¹⁵

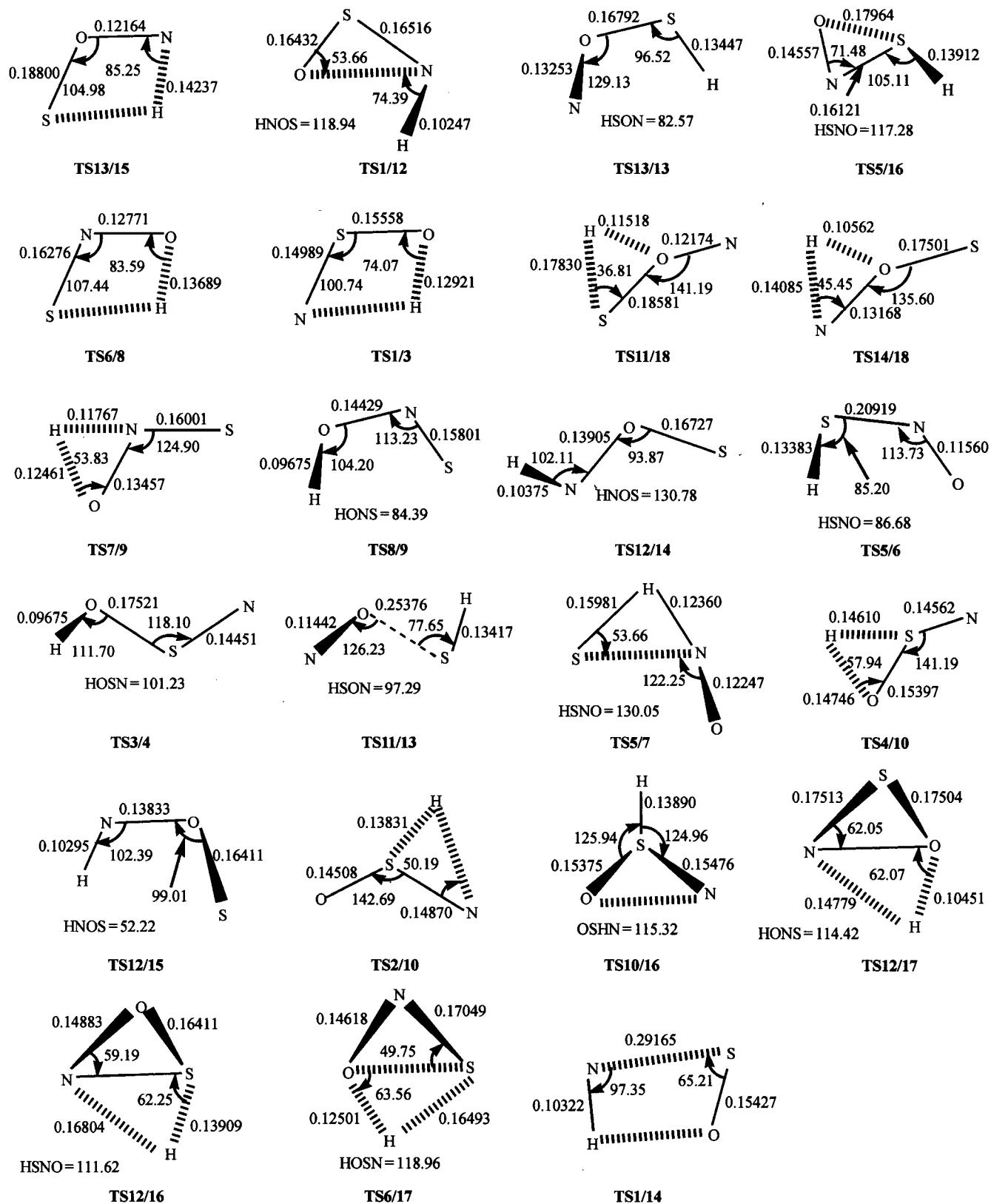


Fig. 2 Optimized geometries of transition states of HNOS system at MP2/6-311++G(d,p) level of theory. Bond lengths are in nanometers, and bond angles in degrees.

The regularity in HNOS and HNS₂ systems is obviously different with HNO₂ system, in which only *trans*-HONO, HNO (O) (C_{2v}) and *trans*-HNOO are expected to be kinetically stable species. Based on the potential energy surface of

HNOS system, we can easily know that the global minimum is *cis*-HNSO. But the global minimums on the potential energy surfaces of HNO₂ and HNS₂ are *trans*-HONO and *cis*-HNS₂, respectively. Species *cis*-HNS₂ is kinetically the most

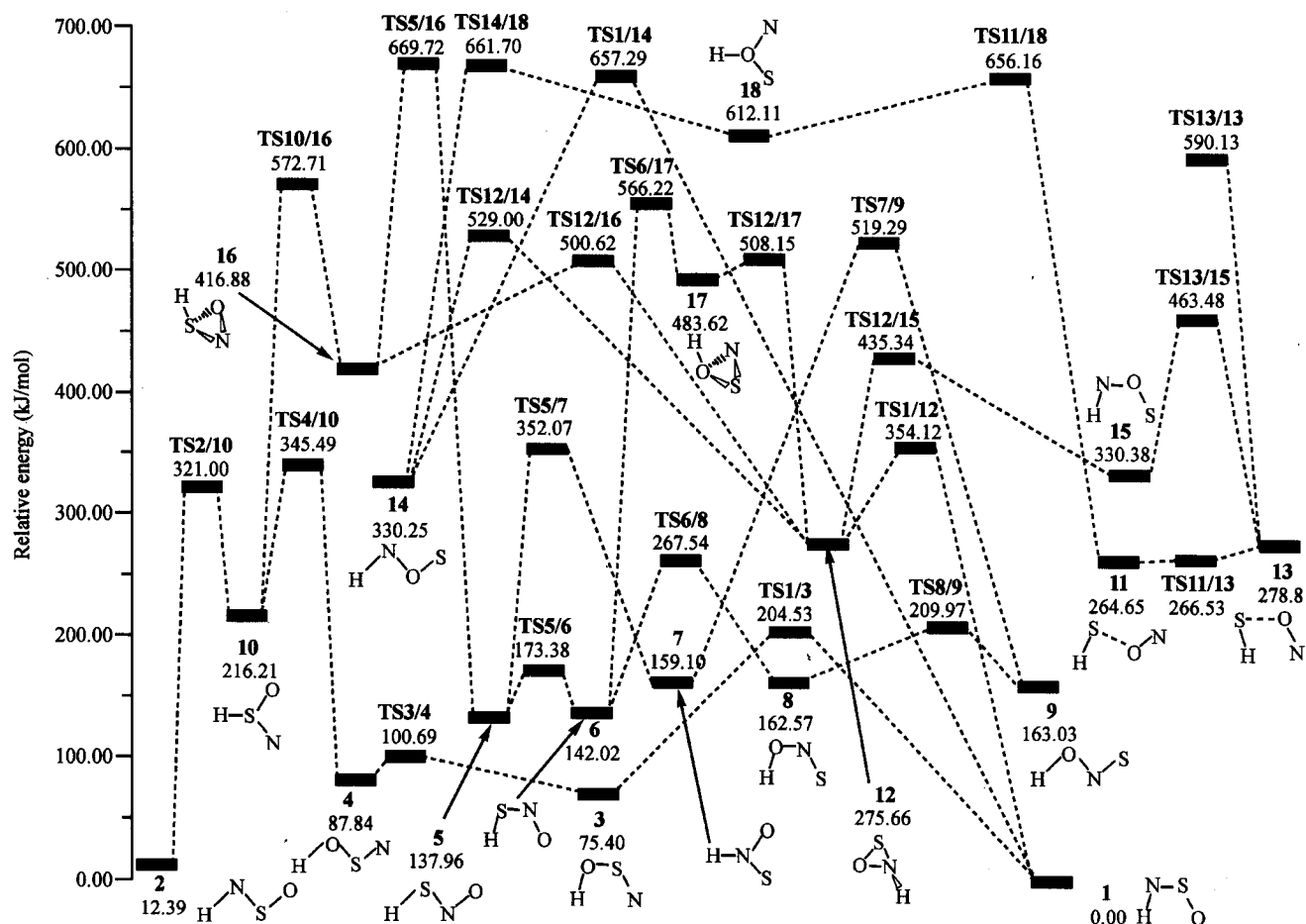


Fig. 3 A schematic potential energy surface of HNOS system at QCISD(T)/6-311 ++ G(3df, 2p)//MP2/6-311 ++ G(d, p) level of theory with zero-point vibrational energies correction.

stable in HNS₂ isomers, and therefore, the analogues HNSO and HNOS are expected to be stable. The calculated results indicate that isomer HNSO is more stable than species HNOS. The conclusion is very obvious since the N—S and S—O are double bond for isomer HNSO, but in isomer HNOS, the N—O and O—S are single bond.

The primary causes that lead to the obvious similarity and differences in bonding among HNO₂, HNS₂ and HNOS are hypervalent capacity of sulfur, oxygen and nitrogen atoms as discussed in previous studies.¹⁵ When sulfur atom locates in the middle of isomer, such as in isomers 1 or 2, the bonding manner is N = S = O, however it is N—O—S form if the sulfur appear at the terminal of isomer. In contrast, many isomers of HNO₂ are unstable because of the lower hypervalent capacity of oxygen atom and nitrogen atom. Therefore, the bonding manners and the nature of elements lead to different thermodynamically and kinetically stability of the isomers.

For isomers of HNOS system, fourteen isomers are predicted to be kinetically stable species in this study. To our knowledge, many experimental studies have been carried out for exploring the structures, spectra, reaction activities, and properties of HNOS isomers, and five isomers, *cis*-HNSO, *trans*-HNSO, *cis*-HOSN, *trans*-HOSN and *trans*-HSNO, have been experimentally suggested in gas phase.³⁴⁻³⁹ This is in good agreement with our theoretical results in this work. It

should be pointed out that isomers 5 and 6 should coexist as discussed above, thus, we think that species 6 should form accompanied by isomer 5 in previous experiment.²⁶ In view of the fact of experimental observation for isomers 1, 2, 3, 4 and 5, other kinetically stable isomers are expected to be experimentally observable provided that appropriate precursors are available.

Conclusion

(1) On the potential energy surface of HNOS system, *cis*-HNSO isomer is found to be the global minimum, and fourteen isomers are predicted to be kinetically stable, and thus should be experimentally observed.

(2) Comparisons are made among HNO₂, HNS₂ and HNOS about the global minima and kinetically stable isomers. In bonding and stability of isomers, HNOS system is similar to HNS₂. The facts begetting obvious similarities and discrepancies between HNOS and its analogues result from the bonding manners and hypervalent capacity of nitrogen, oxygen, and sulfur atoms.

References

- 1 Bell, I. S.; Ahmad, I. K.; Hamilton, P. A.; Davies, P. B.

- Chem. Phys. Lett.* **2000**, 320, 311.
- 2 Francisco, J. S. *Chem. Phys. Lett.* **1998**, 285, 138.
- 3 Jursic, B. S. *Chem. Phys. Lett.* **1999**, 299, 334.
- 4 Yu, H.-T.; Chi, Y.-J.; Fu, H.-G.; Huang, X.-R.; Li, Z.-S.; Sun, J.-Z. *Sci. China, Ser. B* **2002**, 45, 1.
- 5 VanZee, R. J.; Khan, A. U. *J. Chem. Phys.* **1976**, 65, 1764.
- 6 Cramer, C. J.; Famini, G. R. *J. Am. Chem. Soc.* **1990**, 112, 5460.
- 7 Withnall, R.; Andrews, L. *J. Phys. Chem.* **1988**, 92, 4610.
- 8 Greene, R. L.; Street, G. B.; Sutter, L. J. *Phys. Rev. Lett.* **1975**, 34, 577.
- 9 Parsons, S.; Passmore, J. *Acc. Chem. Res.* **1994**, 27, 101.
- 10 Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.* **1991**, 114, 83.
- 11 Yamaguchi, Y.; Xie, Y.; Grev, R. S.; Schaefer III, H. F. *J. Chem. Phys.* **1990**, 92, 3683.
- 12 Mielke, Z.; Andrews, L. *J. Phys. Chem.* **1993**, 97, 4313.
- 13 Inagaki, Y.; Okazaki, R. *Sulfur Rep.* **1982**, 2, 137.
- 14 Nakamura, S.; Takahashi, M.; Okazaki, R.; Morokuma, K. *J. Am. Chem. Soc.* **1987**, 109, 4142.
- 15 Chi, Y.-J.; Yu, H.-T.; Fu, H.-G.; Huang, X.-R.; Li, Z.-S.; Sun, J.-Z. *Chin. J. Chem.* **2002**, 20, 760.
- 16 Head-Gordon, M.; Head-Gordon, T. *Chem. Phys. Lett.* **1994**, 220, 122.
- 17 Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, 166, 281.
- 18 Yu, H.-T.; Ding, Y.-H.; Huang, X.-R.; Li, Z.-S.; Fu, H.-G.; Sun, C.-C. *J. Mol. Struct. (THEOCHEM)* **2001**, 574, 47.
- 19 Yu, H.-T.; Fu, H.-G.; Chi, Y.-J.; Huang, X.-R.; Li, Z.-S.; Sun, C.-C. *Chem. Phys. Lett.* **2002**, 359, 373.
- 20 Fu, H.-G.; Yu, H.-T.; Chi, Y.-J.; Li, Z.-S.; Huang, X.-R.; Sun, C.-C. *Chem. Phys. Lett.* **2002**, 361, 62.
- 21 Yu, H. T.; Chi, Y. J.; Fu, H. G.; Huang, X. R.; Li, Z. S.; Sun, J. Z. *Acta Chim. Sinica* **2002**, 60, 49 (in Chinese).
- 22 Yu, H. T.; Chi, Y. J.; Fu, H. G.; Huang, X. R.; Sun, J. Z. *Acta Phys.-Chim. Sinica* **2002**, 18, 87 (in Chinese).
- 23 Salter, E. A.; Trucks, G. W.; Bartlett, R. J. *J. Chem. Phys.* **1989**, 90, 1752.
- 24 Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, 87, 5968.
- 25 Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, 90, 2154.
- 26 Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, 94, 5523.
- 27 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, Jr., R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, Revision A. 7, Gaussian, Inc., Pittsburgh PA, **1998**.
- 28 Rao, V. M.; Yardley, J. T.; Curl, R. F. *J. Chem. Phys.* **1965**, 42, 284.
- 29 Foss, O.; Janickis, V. *J. Chem. Soc., Dalton Trans.* **1980**, 632.
- 30 Turner, P. H.; Cox, A. P. *J. Chem. Soc., Faraday Trans. 2* **1978**, 74, 533.
- 31 Rankin, D. W. H.; Todd, M. R.; Riddle, F. G.; Turner, E. S. *J. Mol. Struct.* **1981**, 71, 171.
- 32 Goumri, A.; Rocha, John-David R.; Laakso, D.; Smith, C. E.; Marshall, P. *J. Phys. Chem.* **1999**, 103, 11328.
- 33 Yu, H.-T.; Chi, Y.-J.; Fu, H.-G.; Huang, X.-R.; Li, Z.-S.; Sun, J.-Z. *Sci. China, Ser. B* **2002**, 45, 282.
- 34 Schenk, P. W. *Ber.* **1942**, 65, 94.
- 35 Richert, H. Z. *Allorg. Allg. Chem.* **1961**, 309, 171.
- 36 Glemser, O.; Richert, H. Z. *Allorg. Allg. Chem.* **1961**, 309, 313.
- 37 Tchir, P. O.; Spratley, R. D. *Can. J. Chem.* **1975**, 53, 2311.
- 38 Tchir, P. O.; Spratley, R. D. *Can. J. Chem.* **1975**, 53, 2318.
- 39 Tchir, P. O.; Spratley, R. D. *Can. J. Chem.* **1975**, 53, 2331.