

Computational study on the potential energy surface for the reaction HO₂ + NO

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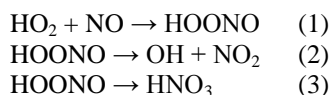
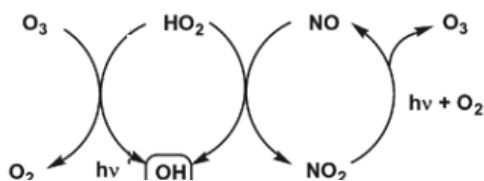
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Abstract: The reaction between two radicals HO₂ and NO plays a key role in both atmospheric and combustion chemistry [1, 2], relevant to several environmental concerns. In this work, the gas-phase chemical reaction HO₂ + NO has been investigated by state-of-the-art *ab initio* calculations. The rigorous singlet potential energy surface (PES) was constructed at accurate composite CBS-QB3 level of theory, which reveals the three possible pathways for the formation of HO + NO₂ from HO₂ + NO: (i) the direct oxygen abstraction reaction which is the novel pathway, or (ii) the direct O-O dissociation of the peroxyxynitrous acid, HOONO intermediate, or (iii) the O-N bond breaking reaction after the isomerization of HOONO to nitric acid (HO-NO₂). Multiple pathways was explored to occur via isomerization and decomposition reactions of HOONO intermediate leading to a variety of intermediates and products, HNO + O₂, HON + O₂, and HONO + O. Our result indicates that nitric acid HO-NO₂ is thermodynamically the most stable species followed by the peroxyxynitrous acid HOONO. The calculated bond lengths, harmonic vibrational frequencies, and the bond dissociation energy for *cis,cis*-HOONO are in good agreement with available theoretical and experiment data. Our predicted data are valuable information for further investigation on a detailed kinetic analysis of this system.

Keywords: Combustion and Atmospheric Chemistry, Potential Energy Surface, HO₂, NO, Radicals, CBS-QB3

Introduction:

Two radicals HO₂ and NO are crucial chemical molecules in the field of atmospheric and combustion chemistry [1, 2].



Not only involving in ozone and other air pollutants (NO_x gasses) cycles but the reaction HO₂ + NO also contributes to an increase in nitric acid (HNO₃) deposition. Due to their direct relationship to vital environmental issues like global warming, the formation of atmospheric acid, particularly HNO₃, and ozone production and depletion, kinetics of the reaction between these two radicals has attracted numerous experimental and theoretical groups of investigators [3-25]. Theoretically, Sumathi and Peyerrimhoff studied this reaction at the B3LYP/6-311++G(d,p) level of theory with some species reported at the MP2/6-311++G(d,p) and identified different possible product channels, HO + NO₂, HO-NO₂, HNO + O₂, and NOH + O₂. Later, Lin and co-workers [12, 14] carried out theoretical studies of this system in more detail by both the forward and the reverse processes using the highest scheme of G2M method and concluded HO + NO₂ is dominant product occurred via two pathways. The direct

fragmentation of HOONO intermediate to HO + NO₂ is more favorable than its isomerization to nitric acid HO-NO₂. Recently, the full-dimensional PES for this system was also studied by Chen *et al.* using quasiclassical trajectory calculations [20, 22]. Additionally, Butkovskaya and co-workers [15, 17] focused on the study HNO₃ forming channel from HO₂+NO reaction both experimentally and theoretically. They indicated that both *cis,cis*-HOONO and the more stable product HO-NO₂ were detected in the experiment.

To the best of our knowledge, only a few theoretical studies investigated on the full potential energy surface (PES) for the title reaction and its PES has not yet been presented thoroughly. To better control the effects of this reaction on atmosphere and combustion, we perform an exhaustive study of this system based on all data available in the literature. The present study aims at characterizing an accurate and complete singlet PES of the gas-phase reaction of HO₂ radical with NO using high-level composite method CBS-QB3. Then, geometrical parameters including bond lengths, harmonic vibrational frequencies, and bond dissociation energy will be compared with previous theoretical data and existing experimental values. Besides, all pathways will be depicted to elucidate the whole mechanism for the reaction of HO₂ + NO.

Computational Methods:

All calculations were carried out with the Gaussian-09 program package [26, 27]. For the sake of high accuracy and efficient computational time, the composite CBS-QB3 method by George Petersson and co-workers [28] was utilized since its accuracy is

within ~ 1 kcal/mol of the experimental value. The geometries and frequencies of reactants, products, intermediates and transition states of the title reaction were fully optimized by using the hybrid density functional B3LYP method (Becke's three parameters nonlocal exchange functional with the correlation function of Lee, Yang, and Parr) with the split-valence polarized basis set 6-311++G(2d,p). Afterward, the single point energies were refined by extrapolating to the infinite basis set limit after performing several levels of theory consisting of CCSD(T)/6-31+G(d') and MP4SDQ/CBSB4. All presented data for ground state molecules and transition states (first-order saddle points on the PES) were selected for the lowest-energy conformer of a given species. Vibrational frequencies were analyzed to characterize stationary points. Only one imaginary frequency in the vibration modes analysis was identified for the transition state geometries whereas no imaginary frequency was found for reactants, products, and intermediates. Intrinsic reaction coordinate (IRC) calculations were also employed to confirm the connection of each transition state with designated intermediates via minimum energy path (MEP) [29].

In this study, some low-frequency vibrational modes, which are better treated as internal rotations around single bonds, were explicitly evaluated the hindered internal rotations (HIR) in the most accurate manner as described below. The 1-D Schrödinger equation for a hindered internal rotor (HIR) is given as

$$\frac{-1}{2I_{red}} \cdot \frac{d^2 \Psi_{hir}}{dx^2} + V(\theta) \Psi_{hir} = E \Psi_{hir}$$

where E is the energy and I_{red} is the reduced moment of inertia for the considered rotation and is calculated as I according to East and Radom [30] on the basis of the original work by Kilpatrick and Pitzer [31]. The hindrance potential, $V(\theta)$, is directly computed as a function of torsional angle, θ , with a step of 10° . Specifically for this system, it was obtained at the B3LYP/CBSB7 level via relaxed surface scans with the step size of 10 degrees for dihedral angles that correspond to the rotations. To solve the HIR equation, we cast it into a Mathieu-type equation by representing the hindrance potential as a Fourier series, $V(\theta) = \sum_{l=-L}^L C_l e^{il\theta}$, in which L is some cut-off number depending on the nature of the potential. The wave function was expanded as a harmonic series, $|m\rangle = \frac{1}{\sqrt{2\pi}} e^{im\theta}$, and plugged into HIR equation. The matrix elements of the Hamiltonian are then given by

$$H_{mm} \equiv \langle m|H|n\rangle = \frac{1}{2\pi} \int_0^{2\pi} e^{-im\theta} \times \left(-\frac{1}{2I_{red}} \frac{\partial^2}{\partial \theta^2} + \sum_{l=-L}^L C_l e^{il\theta} \right) e^{in\theta} d\theta$$

$$= \frac{1}{2I_{red}} m^2 \delta_{mn} + C_{m-n}$$

The matrix can be diagonalized to obtain its eigenvalue spectra which are the energy levels of the considered rotor. Further details of our method of research can be found in the previous paper by Mai *et al.* [32].

Results and Discussion:

The potential energy diagram for the reaction between HO₂ radical and NO radical was extensively explored obtained at 0 K using CBS-QB3 level of theory, presented in **Figure 1**. Geometries of all species with important geometrical parameters were optimized at the CBS-QB3 level of theory. To facilitate the discussion, the CBS-QB3 values are used universally and the energies are cited relative to that of the reactants; otherwise, it will be explicitly stated.

Figure 1 presents the singlet potential energy surface of the HO₂ and NO reaction forming an internally-energized adduct *cis,cis* peroxytrous acid: HOONO (**I**) by the O-N bond formation between HO₂ and NO radicals. This process occurs barrierlessly with high exothermicity ($\Delta H_{rxn} = -26.5$ kcal/mol). Three stable peroxytrous acid HOONO isomers, namely *cis,cis*-HOONO (**I**), *trans,perp*-HOONO (**II**), *cis,perp*-HOONO (**III**), exist as the same prediction of several previous research groups [11, 14, 33-36]. In addition, *cis,cis*-HOONO (**I**) is the most stable species among them, which was also predicted by all the authors [12, 14-17, 20, 21]. The relative energies of the three isomers **I**, **II**, and **III** are 0.0, 2.9, and 0.9 kcal/mol at CBS-QB3 level, which is close to the corresponding values of 0.0, 2.5 and 0.6 kcal/mol obtained at the G2M (CC1) level [14].

Like all other research groups, our study indicates that *cis,cis*-HOONO conformer is the lowest energy structure among all peroxytrous acid conformers. The geometry of optimized *cis,cis*-HOONO including calculated bond lengths and bond angles is presented in **Figure 2**. By comparison to the QCISD and G2M results [14, 24], which are also showed in **Figure 2**, our structure demonstrates the similar geometry of the most stable peroxytrous acid *cis,cis*-HOONO. Both bond lengths and bond angles at three levels are almost identical. Moreover, CBS-QB3 harmonic vibrational frequencies have been summarized in **Table I**. It can be seen that our predicted CBS-QB3 frequencies are close to those from other theoretical and experimental data. For the bond dissociation energies (BDEs), D_0 (HO-NOO) for the *cis,cis*-HOONO (**I**) predicted at 0 K is 18.7 kcal/mol at CBS-QB3 level. This is close to the experimental value, D_0 (HO-NOO) = 19.8 ± 0.23 kcal/mol [23] and 20.5 kcal/mol predicted at G2M level [14]. Meanwhile, the calculated bond energy D_0 (HOO-NO) is 26.3 kcal/mol for **I**, which is close to 28.7 kcal/mol obtained at G2M level [14].

Three stable peroxyxynitrous acid HOONO isomers **I1**, **I2**, and **I3** can isomerize each other. At the CBS-QB3 level, the isomerization barrier height from **I1** to **I3** via TS1_3 is only 0.4 kcal/mol undergoing the hindered internal rotation around the O-O bond. Because of its small barrier, **I3** is not shown in Figure 1 for simplification and is included as internal rotation. However, from **I1** to **I2**, it has to overcome 12.9

kcal/mol barrier via TS1_2 by rotating around O-N bond. These barrier energies (0.4 and 12.9 kcal/mol) agree well with the values 0.6 and 12.6 kcal/mol [14] obtained at the G2M level respectively. Additionally, the optical isomers **I2** and **I2'**, and **I3** and **I3'** have exactly the same energies in this study, which is consistent with Zhu and Lin study at G2M level [14].

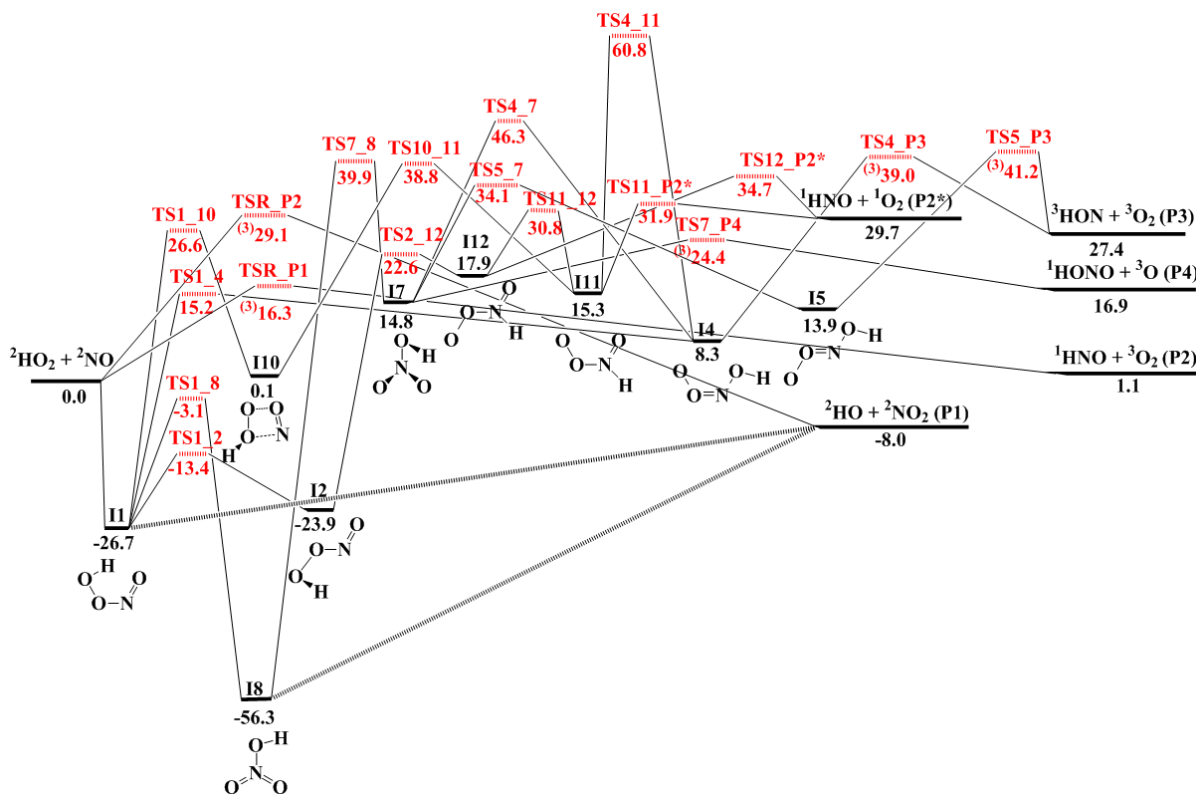


Figure 1. The schematic diagram of the potential energy surface for the $\text{HO}_2 + \text{NO}$ system computed at 0 K using CBS-QB3 level of theory. Numbers are in kcal/mol.

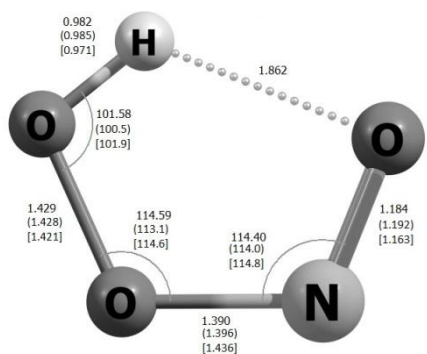


Figure 2. Optimized geometry (bond distances in Å and angles in degrees) of *cis,cis*- HOONO at CBS-QB3 level of theory. The numbers in the parentheses are calculated values at QCISD/cc-pVDZ level from the work of Francisco et al. [24] and numbers in the square brackets are G2M values from the work of Lin et al. [14].

Table I. Harmonic vibrational frequencies (in cm^{-1}) for *cis,cis*- HOONO .

	CBS-QB3 ^a	QCISD/cc-pVDZ ^b	G2M ^c	Exptl ^d
I1	333.2	335	355.3	-
	374.6	411	373.3	-
	507.2	506	512.5	-
	646.0	671	664.6	629.1
	840.4	839	845.5	794.3
	963.6	974	966.8	927.1
	1454.8	1484	1452.6	1395.0
	1675.8	1706	1667.0	1600.3
	3519.5	3563	3532.4	3285.4

^aThis work

^bQCISD/cc-pVDZ values from the work of Francisco et al. [24]

^cG2M values from the work of Lin et al. [14]

^dFrom the experimental work of Lo and Lee. [25]

From the most stable adduct **I1**, many possible channels such as isomerization and dissociation reactions can undergo to form HO + NO₂ (**P1**), HNO + O₂ (**P2**), HON + O₂ (**P3**), HOHO + O (**P4**). All channels are depicted as followings:

(1) HO + NO₂ (**P1**) formation

The direct dissociation of *cis,cis*-HOONO (**I1**) results in HO + NO₂ (**P1**) formation lying at -8.0 kcal/mol by breaking of the O-O bond in hydroperoxyl group of **I1** with a barrier of 18.7 kcal/mol. Besides, **I1** can isomerize to give nitric acid HO-NO₂ (**I8**) which is the most stable intermediate in this system via TS1_8 lying 23.6 kcal/mol above HOONO, or 4.9 kcal/mol higher than the energy of the dissociation product, HO + NO₂.

(2) ¹HNO + ¹O₂ (**P2***) formation

As seen from Figure 1, the breaking of the O-N bond from two possible pathways to form ¹HNO + ¹O₂ by direct decomposition of intermediate either **I11** or **I12** with barrier energies of 16.6 and 16.8 kcal/mol, respectively. **I12** can be formed through H migration from **I2** to the N atom of the nitric oxide with 46.5 kcal/mol barrier. **I11** and **I12** are connected by TS11_12 lying 12.9 kcal/mol above **I12**, which corresponds to the rotation of the O-O group around the N-O bond. From **I1**, isomer **I10** is produced with through H migration from O atom to another O atom of hydroperoxyl group with a barrier height of 53.3 kcal/mol; this **I10** can further connect to **I11** via TS10_11 with 38.7 kcal/mol barrier.

(3) HON + O₂ (**P3**) formation

Similarly, ³HON + ³O₂ formation occurs in two channels from intermediate either **I4** or **I5** by breaking O-N bond with barrier energies of 30.7 and 27.3 kcal/mol, respectively. **I1** and **I4** are connected by TS1_4 through H migration from **I1** to N atom of nitric oxide with 41.9 kcal/mol above **I1**.

(4) HONO + O (**P4**) formation

From **Figure 1**, HO-NO₂ (**I8**) can isomerize to intermediate **I7** via TS7_8 lying 96.2 kcal/mol. Then, **I7** can directly dissociate to ¹HONO + ³O by overcoming 9.6 kcal/mol via a triplet transition state or isomerize to **I4** or **I5** with a much higher barrier (31.5 and 19.3 kcal/mol above **I7**, respectively).

Figure 1 also shows that there are two possible direct abstraction channels, HO₂ + NO₂ → HO + NO₂ (**P1**) and HO + NO₂ → ¹HNO + ³O₂ (**P2**), via two triplet transition states with barrier heights of 16.3 and 29.1 kcal/mol respectively. In spite of the high barrier (29.1 kcal/mol) of the novel triplet transition state for the direct oxygen abstraction, it needs further study on its effect on the kinetic of this system.

Due to the requirement of high isomerization barriers, **P2**, **P2***, **P3**, and **P4** formation are kinetically expected to play less important role comparing to the low-energy lying channel HO + NO₂ (**P1**) formation which is -8.0 kcal/mol lower in energy than the reactant radicals. Hence, **P1** is considered as a thermodynamically favorable product.

Conclusion:

The detailed reaction mechanism for HO₂ + NO system has been extensively constructed using a highly accurate method CBS-QB3. From our results, we draw following conclusions:

- (1) Our optimized structure of *cis,cis*-HOONO is predicted similar to the previous studies in terms of bond lengths, bond angles, bond dissociation energies, and vibrational frequencies.
- (2) Three possible pathways can lead to HO + NO₂ product (**P1**) from HO₂ + NO. The direct oxygen abstraction is the new pathway in this study compare to the previous studies. **P1** can also be produced by either two-step via the direct O-O dissociation of the peroxyxynitrous acid, *cis,cis*-HOONO **I1** or three-step mechanism that **I1** isomerizes to nitric acid **I8** then dissociates to form **P1**.
- (3) Among several possible product channels, the formation OH + NO₂ product (**P1**) is dominant due to its low energy 8 kcal/mol less than the energy of reactants.

A good agreement between our data and other theoretical values and experiment data makes us more confident on our results which are valuable and important to further study on detailed kinetics for this system.

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References:

- [1] Monks, P.S., *Gas-Phase radical chemistry in the troposphere*. Chemical Society Reviews, 2005. **34**(5): p. 376-395.
- [2] Dean, A.M. and J.W. Bozzelli, *Combustion Chemistry of Nitrogen*, in *Gas-Phase Combustion Chemistry*, J. W.C Gardiner, Editor. 1999: New York.
- [3] Cox, R.A. and R.G. Derwent, *Kinetics of the reaction of HO₂ with nitric oxide and nitrogen dioxide*. Journal of Photochemistry, 1975. **4**(1-2): p. 139-153.
- [4] Howard, C.J. and K.M. Evenson, *Kinetics of the reaction of HO₂ with NO*. Geophysical Research Letters, 1977. **4**(10): p. 437-440.
- [5] Howard, C.J., *Temperature dependence of the reaction HO₂+NO→OH+NO₂*. The Journal of Chemical Physics, 1979. **71**(6): p. 2352-2359.
- [6] Howard, C.J., *Kinetic study of the equilibrium HO₂ + NO ⇌ OH + NO₂ and the thermochemistry of HO₂*. Journal of the American Chemical Society, 1980. **102**(23): p. 6937-6941.
- [7] Thrush, B.A. and J.P.T. Wilkinson, *The rate of reaction of HO₂ radicals with HO and with NO*. Chemical Physics Letters, 1981. **81**(1): p. 1-3.

- [8] Imamura, T. and N. Washida, *Measurements of Rate Constants for HO₂ + NO and NH₂ + NO Reactions by Time-Resolved Photoionization Mass Spectrometry*. Laser Chemistry, 1995. **16**(1): p. 43-51.
- [9] Seeley, J.V.M., et al., *Temperature and Pressure Dependence of the Rate Constant for the HO₂+NO Reaction*. The Journal of Physical Chemistry, 1996. **100**(10): p. 4026-4031.
- [10] Bohn, B. and C. Zetzsch, *Rate Constants of HO₂+NO Covering Atmospheric Conditions. I. HO₂ Formed by OH + H₂O₂*. The Journal of Physical Chemistry A, 1997. **101**(8): p. 1488-1493.
- [11] Dixon, D.A., et al., *Decomposition Pathways of Peroxynitrous Acid: Gas-Phase and Solution Energetics*. The Journal of Physical Chemistry A, 2002. **106**(13): p. 3191-3196.
- [12] D. Chakraborty, J. Park, and M.C. Lin, *Theoretical study of the OH+NO₂ reaction: formation of nitric acid and the hydroperoxyl radical*. Chemical Physics, 1998. **231**(1): p. 39-49.
- [13] Bardwell, M.W., et al., *Kinetics of the HO₂ + NO reaction: A temperature and pressure dependence study using chemical ionisation mass spectrometry*. Physical Chemistry Chemical Physics, 2003. **5**(11): p. 2381-2385.
- [14] R.S. Zhu and M.C. Lin, *Ab initio study of the HO₂+NO reaction: Prediction of the total rate constant and product branching ratios for the forward and reverse processes*. The Journal of Chemical Physics, 2003. **119**(20): p. 10667.
- [15] Butkovskaya, N.I., et al., *Formation of Nitric Acid in the Gas-Phase HO₂ + NO Reaction: Effects of Temperature and Water Vapor*. The Journal of Physical Chemistry A, 2005. **109**(29): p. 6509-6520.
- [16] Butkovskaya, N., A. Kukui, and G. Le Bras, *HNO₃ Forming Channel of the HO₂ + NO Reaction as a Function of Pressure and Temperature in the Ranges of 72-600 Torr and 223-323 K*. The Journal of Physical Chemistry A, 2007. **111**(37): p. 9047-9053.
- [17] Butkovskaya, N., et al., *Water Vapor Effect on the HNO₃ Yield in the HO₂ + NO Reaction: Experimental and Theoretical Evidence*. The Journal of Physical Chemistry A, 2009. **113**(42): p. 11327-11342.
- [18] Zhang, J., T. Dransfield, and N.M. Donahue, *On the Mechanism for Nitrate Formation via the Peroxy Radical + NO Reaction*. The Journal of Physical Chemistry A, 2004. **108**(42): p. 9082-9095.
- [19] Zhang, J. and N.M. Donahue, *Constraining the Mechanism and Kinetics of OH + NO₂ and HO₂ + NO Using the Multiple-Well Master Equation†*. The Journal of Physical Chemistry A, 2006. **110**(21): p. 6898-6911.
- [20] Chen, C., et al., *Quasiclassical trajectory calculations of the HO₂ + NO reaction on a global potential energy surface*. Physical Chemistry Chemical Physics, 2009. **11**(23): p. 4722-4727.
- [21] Sumathi, R. and S.D. Peyerimhoff, *An ab initio molecular orbital study of the potential energy surface of the HO₂+NO reaction*. The Journal of Chemical Physics, 1997. **107**(6): p. 1872-1880.
- [22] Chen, C., et al., *Quasiclassical trajectory calculations of the OH+NO₂ association reaction on a global potential energy surface*. J Chem Phys, 2007. **127**(10): p. 104310.
- [23] Hippler, H., S. Nasterlack, and F. Striebel, *Reaction of OH + NO₂ + M: Kinetic evidence of isomer formation*. Physical Chemistry Chemical Physics, 2002. **4**(13): p. 2959-2964.
- [24] Li, Y. and J.S. Francisco, *High level ab initio molecular orbital theory study of the structure, vibrational spectrum, stability, and low-lying excited states of HOONO*. The Journal of Chemical Physics, 2000. **113**(18): p. 7976-7981.
- [25] Lo, W.-J. and Y.P. Lee, *Infrared absorption of cis-cis peroxynitrous acid (HOONO) in solid argon*. The Journal of Chemical Physics, 1994. **101**(7): p. 5494.
- [26] Frisch, M.J., et al., *Gaussian 09*. 2009, Gaussian, Inc.: Wallingford, CT, USA.
- [27] Dennington, R.K., Todd; Millam, John., *GaussView, Version 5*. 2009, Semichem Inc.: Shawnee Mission, KS.
- [28] Montgomery, J.A., et al., *A complete basis set model chemistry. VI. Use of density functional geometries and frequencies*. The Journal of Chemical Physics, 1999. **110**(6): p. 2822-2827.
- [29] G.Lewars, E., *Computational Chemistry (Introduction to the Theory and Applications of Molecular and Quantum Mechanics)*. 2 ed. 2011: Springer Netherlands. XVI, 664.
- [30] East, A.L. and L. Radom, *Ab initio statistical thermodynamical models for the computation of third-law entropies*. The Journal of chemical physics, 1997. **106**(16): p. 6655-6674.
- [31] Kilpatrick, J.E. and K.S. Pitzer, *Energy Levels and Thermodynamic Functions for Molecules with Internal Rotation. III. Compound Rotation*. The Journal of Chemical Physics, 1949. **17**(11): p. 1064-1075.
- [32] Mai, T.V.T., X.T. Le, and L.K. Huynh, *Mechanism and kinetics of low-temperature oxidation of a biodiesel surrogate—methyl acetate radicals with molecular oxygen*. Structural Chemistry, 2014. **26**(2): p. 431-444.
- [33] Fry, J.L., et al., *Cis-cis and trans-perp HOONO: Action spectroscopy and isomerization kinetics*. The Journal of Chemical Physics, 2004. **121**(3): p. 1432-1448.
- [34] Matthews, J., A. Sinha, and J.S. Francisco, *Relative vibrational overtone intensity of cis-cis and trans-perp peroxynitrous acid*. The Journal of Chemical Physics, 2004. **120**(22): p. 10543-10553.
- [35] McGrath, M.P. and F.S. Rowland, *Internal rotation in peroxynitrous acid (ONOOH)*. The Journal of Chemical Physics, 2005. **122**(13): p. 134312.
- [36] Zhang, X., et al., *Vibrational overtone spectrum of matrix isolated cis, cis-HOONO*. The Journal of Chemical Physics, 2007. **126**(17): p. 174308.