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## No Longer a Complex, Not Yet a Molecule: A Challenging Case of Nitrosyl O-Hydroxide, HOON

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# No Longer a Complex, Not Yet a Molecule: A Challenging Case of Nitrosyl *O*-Hydroxide, HOON

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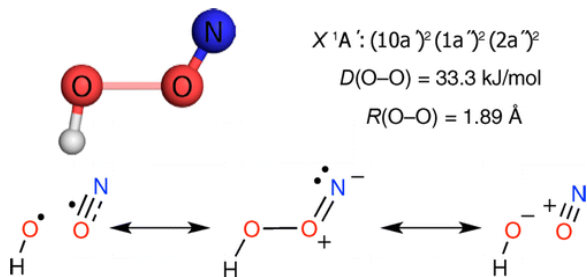
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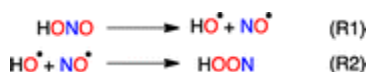
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## Abstract



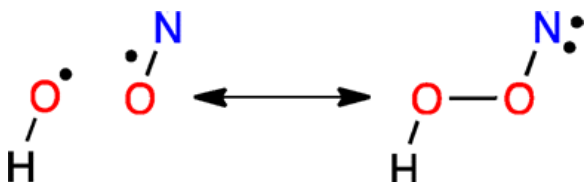
HOON might be an elusive intermediate of atmospheric photochemical reactions of HONO or recombination of the parent nitrene HN and molecular oxygen. However, no reliable data on HOON structure and stability are available, and the nature of the O–O bond is not well understood. In this study, we used high-level single- [CCSD(T) and, CCSDTQ] and multireference [CASPT2, MR-AQCC] ab initio calculations to determine properties of HOON: geometry, harmonic and anharmonic vibrational frequencies, thermodynamic stability, and electronic structure. HOON has bonding minima only in the  $^1A'$  electronic state that correspond to cis- and trans-conformers; *trans*-HOON is more stable by 6.4–8.5 kJ/mol. The O–O bond in *trans*-HOON is unusually long,  $R(O-O) = 1.89 \text{ \AA}$ , and weak,  $D(O-O) = 33.3 \text{ kJ/mol}$ ; however, *trans*-HOON might be stable enough to be identified in cryogenic matrices. Though the electronic structure of the NO moiety in HOON most resembles nitric oxide, some nitrene character as well nitrosyl cation character are also important; therefore, the current name of HOON, hydroperoxynitrene, is misleading; instead, we propose the name “nitrosyl *O*-hydroxide” or “isonitrosyl hydroxide”.

Nitrous acid (HONO), produced from  $\text{NO}_2$  or soil nitrites, plays an important role in tropospheric chemistry.(1) Photolysis of HONO leads to hydroxyl radical  $\text{OH}^*$ , which is a powerful oxidant, and nitric oxide  $\text{NO}^*$ , which is a component of  $\text{NO}_x$  smog and ozone precursor. HONO analogues  $X-\text{NO}$  ( $X = \text{H}, \text{CN},$  or halogen atom) can photodissociate at the  $X-\text{N}$  bond as well;(2) the  $X^* + \text{NO}^*$  pair can recombine not only back to nitroso compound but also back to isonitrosyl species  $X-\text{ON}$ .(2b) For nitrous acid, a similar transformation can be hypothesized, leading to species with structural formula HOON.



HOON has never been in the focus of research. To the best of our knowledge, it has not been observed experimentally; however, it was mentioned in a few theoretical works. In 1987, Nakamura et al.(3) performed a systematic analysis of  $\text{HNO}_2$  isomers and localized cis- and trans-conformers of HOON. Later, Fueno et al.(4) demonstrated that *cis*-HOON can be formed as an intermediate in the reaction of nitrogen monohydride NH with molecular oxygen (via isomerization of *cis*-HNOO) and introduced the name “hydroperoxynitrene”. Our recent studies(5) showed that the pathway proposed by Fueno(4) is dominant in a wide temperature range 300–1000 K. Another process that may involve HOON is overtone excitation of HONO;(6) semiempiric direct dynamics simulations of this reaction involved HOON in all simulation trajectories.

Despite its potential role in HONO photochemistry, very little is known about the electronic structure, geometry, and energetic characteristics of HOON, and the reported data are inconsistent.



HOON can be hypothesized to be either a complex of radicals or a covalently bound nitrene-like structure. The value of the O–O distance is crucial to understand the nature of O–O bonding in HOON, but reported values vary from 1.47 to 2.03 Å,(3-6) with the correct value still unknown. For this reason, high-level calculations of the HOON geometry are essential.

The thermodynamic stability of HOON has not been established: reported energies of transformation of HONO to HOON range from 180 to 310 kJ/mol.(3, 4, 6, 7) With the enthalpy of *trans*-HONO dissociation to HO• + NO• of 206.0 kJ/mol, which was deduced from experimental enthalpies of formation,(8) the enthalpy of HOON dissociation on the O–O bond,  $D(\text{O–O})$ , can be estimated from –26 to +104 kJ/mol. A more accurate value is needed to understand stability and reactivity of HOON.

In this study, we perform a series of high-level single-reference and multireference ab initio calculations to provide accurate geometry, vibrational frequencies, thermodynamic data, and electronic structure of HOON.

## Computational details

We used methods of coupled cluster theory, multireference second-order perturbation theory (CASPT2),(9) and multireference averaged quadratic coupled-cluster (MR-AQCC)(10) theory to accurately calculate the geometry of HOON.

A series of Dunning’s augmented correlation-consistent basis sets, aug-cc-pVXZ,(11) were used for all elements. We used a three-parameter exponential decay function for complete basis set (CBS) extrapolation of bond lengths in HOON, and Peterson’s three-point complete basis set extrapolation(11c) for energetic properties.

$$R(X) = R_{\text{CBS}} + Be^{-cX}$$
$$E(X) = E_{\text{CBS}} + Be^{-(X-1)} + Ce^{-(X-1)^2}$$

The coupled cluster theory computations with single, double, and perturbative triple excitations, CCSD(T),(12) were performed using the CFOUR package.(13) Geometries were optimized using analytic gradients;(14) vibrational frequencies were also calculated analytically.(15) Full cubic force field calculations with the semidiagonal part of the quartic force field were performed to obtain fundamental frequencies using second-order perturbation theory starting from the harmonic-oscillator rigid-rotator approximation.(16) For iterative accounting for triple and quadruple excitations (CCSDT,(17) CCSDTQ(18)), the MRCC program(19) was employed via the CFOUR interface. In coupled cluster calculations, all-electrons correlation was accounted (denoted as “ae” in opposite to frozen core correlation, “fc”). A series of single-point calculations were performed to estimate  $D(\text{O–O})$  in approximation to the CCSDTQ[ae]/aug-cc-pVTZ level of theory (see Supporting Information for details).

Scalar relativistic effects were estimated by means of perturbation theory based on mass-velocity and Darwin terms (MVD1)(20) procedure, as implemented in CFOUR, with the wave function calculated at the CCSD(T)[ae]/aug-cc-pV5Z level of theory.

CASPT2(9) calculations were performed in the MOLPRO program.(21) Active space (18;13) was composed of all valence molecular orbitals. Frozen core approximation was used in CASPT2 calculations. Geometry optimizations were performed using analytical gradients.(22)

The MR-AQCC(10) computations were carried out in the Columbus program(23) with the aug-cc-pVTZ basis set. Test calculations with various compositions of active space (Table S1, Supporting Information) revealed the

optimal choice: for reference CASSCF wave function, (10;8) involving all valence molecular orbitals except N–H bonding/antibonding and 2s shell orbitals; for MR-AQCC wave function, active space (6;5) composed of three  $p_z$  orbitals and two peroxide bond orbitals. At the MR-AQCC level of theory, calculations were performed with no frozen orbitals. Geometry optimizations were performed using analytical gradients.(24)

To calculate a minimum energy path connecting two stationary points, climbing image nudged elastic band method was used,(25) as implemented in the DL-FIND program.(26) ChemShell suite(27) was used to interface DL-FIND with MOLPRO for calculation with CASPT2 method.

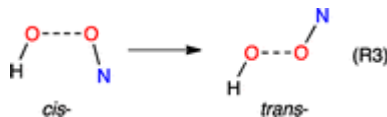
Quantum theory of atoms in molecules (AIM)(28) was employed using the AIMPAC program(29) to analyze CASPT2/aug-cc-pVTZ electron density. Molden2AIM code(30) was used to generate input files for AIM analysis from MOLPRO outputs.

In AIM, gradient ( $\nabla\rho$ ) and Laplacian ( $\nabla^2\rho$ ) of density are used to locate critical points of electron density. Maxima of electron density typically correspond to nuclear positions. Two nuclear critical points can be connected by a gradient path (bonding path) indicative of chemical bonding between atoms; the point of minimum  $\rho(\mathbf{r})$  along the bonding path, called a bonding critical point, characterizes the nature of the bond. Properties of special interest at the bond critical point are the value of electron density, which characterizes bond strength, and the sign of the Laplacian, which indicates whether the bonded atoms share their valence shells or not; in addition, an ellipticity of electron density distribution,  $\varepsilon = \lambda_1/\lambda_2 - 1$ , can be used to estimate double-bond character of the bond, where  $\lambda$  are eigenvalues of the Hessian of  $\rho$  that characterize decrease of electron density in directions orthogonal to the bonding path. Analysis of Laplacian topology also provides valuable information: local minima of  $\nabla^2\rho$ , not related to a bonding path, in practical calculations can be corresponded to the lone pair positions.(28)

## Results and discussion

### Geometry of HOON

Calculations at the CCSD(T)/aug-cc-pVTZ level of theory revealed that only  $^1A'$  electronic state has minima related to HOON, which correspond to cis- and trans-isomeric forms. In both forms the distance between oxygen atoms is  $\sim 1.9 \text{ \AA}$  (Tables 1 and S2, Supporting Information), which is extraordinary long for a covalent bond. Minimum energy path calculations at the CASPT2/aug-cc-pVTZ level show that trans–cis isomerization barrier is  $\sim 12.7 \text{ kJ/mol}$ , and the cis–trans barrier is  $5.7 \text{ kJ/mol}$  (Figure S1, Supporting Information). As the trans-isomeric form is more stable by  $6.4\text{--}8.5 \text{ kJ/mol}$  (Table 3, Figure S1, Supporting Information), we focus on *trans*-HOON in further discussion.



**Table 1. Geometry Parameters of *trans*-HOON<sup>a</sup>**

basis set <sup>b</sup>	R(OH)	R(OO)	R(NO)	A(OOH)	A(OON)
CCSD(T)					
D	0.976	1.948	1.144	97.4	115.0
T	0.968	1.896	1.125	97.8	115.2
Q	0.967	1.895	1.123	98.3	115.0
5	0.966	1.894	1.122	98.4	114.9
CBSc	0.966	1.894	1.122		
CASPT2					

D	0.978	1.921	1.150	96.0	116.7
T	0.973	1.895	1.137	96.2	116.7
Q	0.970	1.891	1.133	96.3	116.7
5	0.969	1.889	1.133	96.4	116.7
6	0.969	1.886	1.132	96.4	116.7
CBSc	0.969	1.889	1.132		
MR-AQCC					
T	0.965	1.893	1.128	97.0	116.0

<sup>a</sup>Bond lengths are given in angstroms, and angles in degrees.

<sup>b</sup>aug-cc-pVXZ, X = D, T, Q, 5, or 6.

<sup>c</sup>Complete basis set extrapolation based on three-parameter exponential decay function.

Calculated geometric parameters of HOON depend on both the level of theory and the basis set. For both CCSD(T) and CASPT2, slow convergence to the basis set limit is observed. CCSD(T) calculations predict slightly longer O–O distance than CASPT2 (by  $\sim 0.005$  Å in the complete basis set extrapolation), and shorter N–O distance (by  $\sim 0.010$  Å). Calculations at the MR-AQCC/aug-cc-pVTZ level of theory give O–O and N–O bond lengths in a range between CCSD(T) and CASPT2 results. Overall, single-reference and multireference methods used here provide a consistent description of HOON structure, suggesting reliability of the obtained geometries.

## Vibrational Frequencies

Harmonic and anharmonic vibrational frequencies of HOON are reported for the first time in Table 2. The most intense modes correspond to the N–O stretching ( $\nu_2$ ) and rotation around the O–O bond ( $\nu_6$ ). Comparison of IR bands of *cis*-/*trans*-forms (Tables 2 and S3, Supporting Information) shows that  $\nu_6$ (O–O torsion) and  $\nu_5$ (O–O stretching) modes are 40–70  $\text{cm}^{-1}$  greater in the *trans*-form, which likely follows from the shorter O–O distance in *trans*-HOON. Expansion of the basis set from triple- to quadruple- $\zeta$  only slightly affects predicted positions and intensities of IR-bands (Table 2). Anharmonic vibrations are expectedly shifted to the low-frequency region.

**Table 2. Vibrational Modes of *trans*-HOON Calculated at the CCSD(T) Level of Theory<sup>a</sup>**

	aug-cc-pVTZ, harmonic		aug-cc-pVQZ, harmonic		aug-cc-pVTZ, anharmonic	
	freq	int	freq	int	freq	int
$\nu_1$ (a')	3765.0	28.0	3771.5	29.4	3582.9	21.9
$\nu_2$ (a')	1904.9	525.3	1908.0	529.5	1878.7	485.8
$\nu_3$ (a')	833.7	25.9	836.2	26.5	764.7	23.8
$\nu_4$ (a')	437.1	1.6	436.3	1.6	387.8	8.5
$\nu_5$ (a')	305.5	5.8	308.8	6.1	265.9	1.4
$\nu_6$ (a'')	240.4	85.2	236.0	86.6	199.9	67.0
OH <sup>*</sup> b	3746.1	10.3	3749.3	11.5	3557.7	
NO <sup>*</sup> b	2106.8	74.6	2105.9	72.7	1938.2	

<sup>a</sup>Frequencies are in  $\text{cm}^{-1}$ , and intensities in  $\text{km/mol}$ . Experimental values for NO<sup>\*</sup> are  $\omega_e = 1904.2 \text{ cm}^{-1}$ ,  $\omega_e x_e = 14.1 \text{ cm}^{-1}$ .(34) Experimental values for OH<sup>\*</sup> are  $\omega_e = 3737.8 \text{ cm}^{-1}$ ,  $\omega_e x_e = 84.9 \text{ cm}^{-1}$ .(35)

<sup>b</sup>Vibrational modes for separated NO<sup>\*</sup> and OH<sup>\*</sup>.

Harmonic frequencies suggest that formation of *trans*-HOON would strongly affect the N–O stretching vibration, shifting it to the red by  $\sim 200 \text{ cm}^{-1}$  (for anharmonic frequencies,  $\sim 60 \text{ cm}^{-1}$ ) and increasing intensity by  $\sim 450 \text{ km/mol}$ . These changes in the IR spectrum might be characteristic for experimental HOON detection.

## Thermodynamic Properties of *trans*-HOON

Electronic energy of *trans*-HOON dissociation to HO• and NO• ( $E_{\text{diss}}$ ) strongly depends on both dynamic and nondynamic electron correlation. Multireference methods MR-AQCC/aug-cc-pVTZ and CASPT2/CBS predict  $E_{\text{diss}}$  to be 43.9 and 36.3 kJ/mol, respectively. At the same time, CCSD(T)/CBS level of theory, based on a single reference determinant, gives a much lower value of 27.2 kJ/mol (Table 3). Basis set influence can be ruled out, as values of  $E_{\text{diss}}$  are improved by only 3.6 kJ/mol due to increase of basis set from triple- $\zeta$  up to CBS for either CCSD(T) or CASPT2 methods. Instead, quadruple excitations dramatically change coupled cluster results: at approximation to the CCSDTQ/aug-cc-pVTZ level of theory  $E_{\text{diss}}$  is 39.0 kJ/mol, agreeing much better with CASPT2 and MR-AQCC results.

**Table 3. Thermodynamics of Reactions R1–R3, kJ/mol**

basis set <sup>a</sup>	$\Delta E(\text{R}3)$	$\Delta E(\text{R}2) = -E_{\text{diss}}^{\text{b}}$	$\Delta E(\text{R}1) + \Delta E(\text{R}2)^{\text{b}}$
CCSD(T)			
D	−6.7	−23.6	173.4
T	−8.3	−29.7	189.6
Q	−8.3	−26.8	192.8
5	−8.4	−27.1	194.2
CBSc	−8.4	−27.2	195.0
Approximation to CCSDTQ/aug-cc-pVTZ (See Also Table S4, Supporting Information)			
T	−7.9	−39.0	
CASPT2			
D	−6.4	−32.1	
T	−7.1	−35.2	
Q	−7.3	−36.2	
5	−7.4	−36.2	
6	−7.4	−36.3	
CBSc	−7.4	−36.3	
MR-AQCC			
T	−7.9	−43.9	
Corrections to Reaction Energies			
ZPEd	0.8	9.8	−8.2
enthalpy correctiond	0.4	5.7	−6.0
RCe	0.0	−0.1	−0.5

<sup>a</sup>aug-cc-pVXZ, X = D, T, Q, 5, or 6.

<sup>b</sup>In reactions R1 and R2, data for *trans*-isomers of HOON and HONO are reported.  $\Delta E(\text{R}1) + \Delta E(\text{R}2)$  is the energetic effect of the HONO transformation to HOON.

<sup>c</sup>Peterson's three-point CBS extrapolation(11c) with data from aug-cc-pVXZ; X = T, Q, and 5 for CCSD(T), and Q, 5, and 6 for CASPT2.

<sup>d</sup>ZPE and enthalpy correction were calculated using CCSD(T)/aug-cc-pVQZ harmonic frequencies (ideal gas assumption, 1 atm, 298.15 K); enthalpy correction already includes ZPE.

<sup>e</sup>Scalar relativistic correction; CCSD(T)[ae]/aug-cc-pVTZ.

Enthalpy correction to  $E_{\text{diss}}$ , calculated under the ideal gas assumption with CCSD(T)/aug-cc-pVQZ harmonic vibrational frequencies ( $H_{\text{corr}}$ ), is −5.7 kJ/mol at room temperature and 1 atm pressure. The contribution of scalar

relativistic effect was found to be small, 0.1 kJ/mol, so the CCSDTQ/aug-cc-pVTZ-based estimation predicts O–O bond dissociation energy  $D(\text{O}–\text{O}) = E_{\text{diss}} + H_{\text{corr}} = 33.3$  kJ/mol.

To calculate  $\Delta_f H^\circ(\text{trans-HOON})$ , we used O–O bond dissociation energy of 33.3 kJ/mol and experimental enthalpies of  $\text{HO}^\bullet$  (37.4 kJ/mol)(31) and  $\text{NO}^\bullet$  (91.0 kJ/mol).(31) From reaction R2, we can deduce

$$D(\text{O} – \text{O}) = \Delta_f H^\circ(\text{HO}^\bullet) + \Delta_f H^\circ(\text{NO}^\bullet) - \Delta_f H^\circ(\text{trans} - \text{HOON})$$

Therefore,  $\Delta_f H^\circ(\text{trans-HOON}) = 95.1$  kJ/mol, which is 172.7 kJ/mol higher than  $\Delta_f H^\circ$  of the most stable isomer, *trans*-HONO, and ~143 kJ/mol lower than  $\Delta_f H^\circ$  of *cis*-HNOO (238 kJ/mol as deduced from refs 5 and 31, see Supporting Information for details).

## Isomerization of HOON to HONO or HNOO

A question of special interest for isonitrosyl compounds X–ON is how they transform to corresponding X–NO. Two pathways can be hypothesized (Figure 1a), dissociative transition (which is the case for X = H,(2a, 32) Cl,(2b, 32a) and Br(2b)) and intramolecular isomerization. We calculated a minimum energy path (MEP) connecting *trans*-HOON and HONO on the  $^1A'$  electronic state to establish the mechanism of isomerization of HOON. Ten structures along the reaction path were optimized using a climbing image nudged elastic band method(25) at the CASPT2/aug-cc-pVTZ level of theory. Figure 1b shows overlap of those structures, so the reaction path is represented as a migration of the OH fragment. The minimum energy path clearly involves subsequent dissociation of *trans*-HOON and recombination of  $\text{OH}^\bullet + \text{NO}^\bullet$  to HONO (Figure 1b). The highest point on the MEP is 34.0 kJ/mol higher than *trans*-HOON (Figure S2, Supporting Information), which is close to the O–O bond dissociation energy of 35.2 kJ/mol, calculated at the same level of theory. Therefore, our findings support a dissociative transition mechanism of isomerization of *trans*-HOON to HONO.

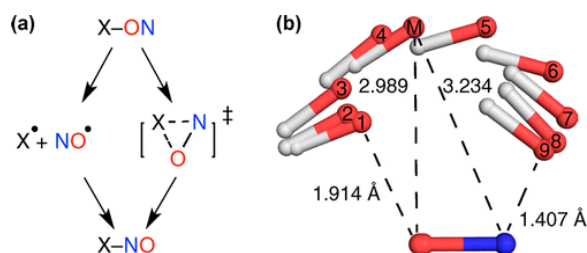
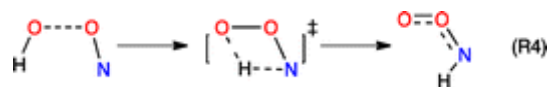


Figure 1. (a) Mechanisms of transformation of X–ON into X–NO, (b) overlap of structures on the minimal energy path connecting *trans*-HOON and *cis*-HONO (marked as **1** and **9**); CASPT2/aug-cc-pVTZ. A structure with the highest energy (climbing image) is denoted as **M**.

Another reaction mode of HOON might be isomerization to parent nitroso oxide *cis*-HNOO.(4, 5, 7, 33) In our previous study,(5) we found that the diamond-shaped transition state of R4 lies ~230 kJ/mol higher than the  $\text{HO}^\bullet + \text{ON}^\bullet$  pair, which is ~33 kJ/mol (current results) less stable than *trans*-HOON. Therefore, the activation energy of HOON transformation to *cis*-HNOO is prohibitively high, ~260 kJ/mol, and the reaction R4 is unfavorable.



## Electronic Structure of *trans*-HOON

The CASPT2/aug-cc-pVTZ wave function of *trans*-HOON can be expressed as

$$\Psi = 77\%_0 \psi_1 [(10a')^2 (2a'')^2] + 14\%_0 \psi_1 [(10a')^0 (11a')^2 (2a'')^2]$$



with weights of other configurations less than 1.5% each. The  $a'$  frontier orbitals have occupancies of 1.67 and 0.36 (Figure 2); these values differ from those expected for a singlet biradical, so both wave function composition and orbital occupancies suggest emerging O–O covalent bonding in *trans*-HOON. Absence of a minimum in the triplet state further supports the idea that HOON is more than a van der Waals complex of two radicals. Indeed, the  $a'$  frontier orbitals represent a 3-center 4-electron  $\sigma$ -conjugated system (Figure 2, Top) that can be considered as  $n_{xy}(\text{O}) + \pi_{xy}(\text{ON})$  or  $\sigma(\text{OO}) + n_{xy}(\text{N})$  combination. Most of the binding of the NO and OH moieties arises from the latter pattern.

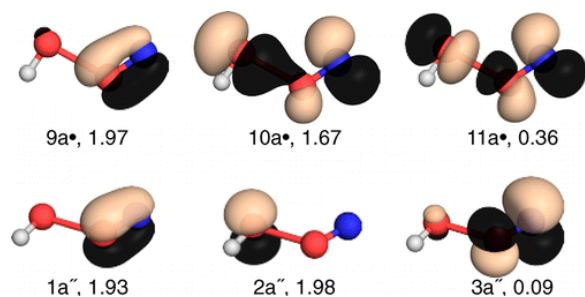


Figure 2. CASPT2/aug-cc-pVTZ natural orbitals of *trans*-HOON at an isovalue of 0.05 and their occupancies: top row, 3-center 4-electron system formed by  $a'$  orbitals; bottom row, valence orbitals of  $a''$  symmetry.

Topological analysis revealed a bond critical point (BCP) between oxygen atoms (Figure 3). Electron density at the BCP  $\rho_{\text{BCP}}(\text{O}-\text{O}) = 0.09$  au, indicating the bond is much weaker than other peroxide bonds: for instance, in hydrogen peroxide  $\rho_{\text{BCP}}(\text{O}-\text{O}) = 0.27$  au at the same level of theory. Ellipticity of the electron density at the critical point,  $\epsilon_{\text{BCP}}(\text{O}-\text{O}) = 0.113$ , is significantly higher than the corresponding value in hydrogen peroxide, 0.047, thus suggesting partial  $\pi$ -character of the O–O bond, which forces HOON to be planar. The Laplacian of the electron density is negative at the BCP; therefore, valence shells are not shared between the NO and OH fragments. This case is typical for ionic bonds or bonds formed by strongly electronegative atoms (like F–F).<sup>(28)</sup>

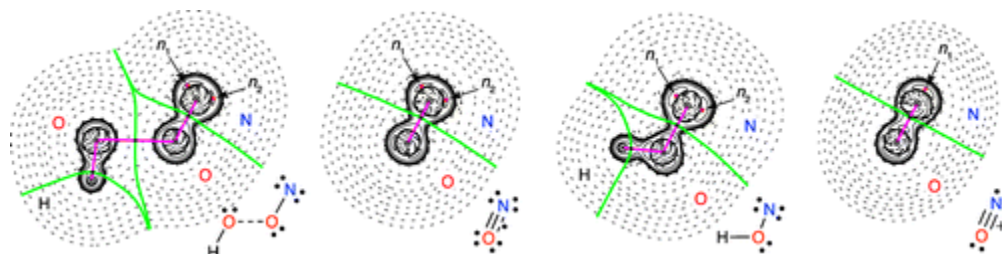
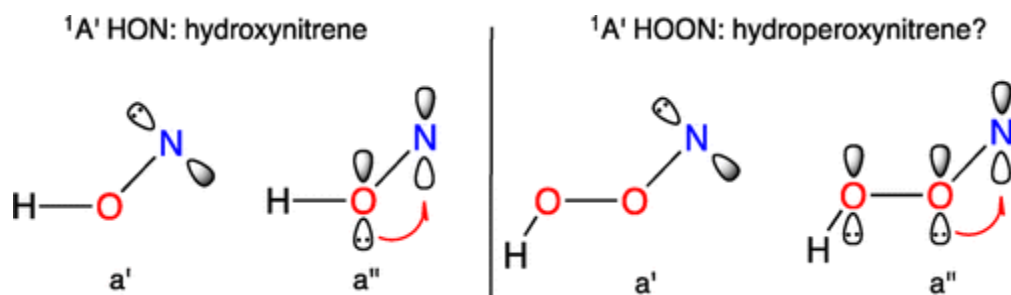


Figure 3. Contour maps of  $\nabla^2\rho$ , calculated for CASPT2/aug-cc-pVTZ electronic densities. Red points indicate local minima of  $\nabla^2\rho$  around nitrogen atom, which can be related to lone pair positions. Solid lines indicate negative values of  $\nabla^2\rho$ .

The name of hydroperoxynitrene, first introduced for HOON by Fueno,<sup>(4)</sup> implies its nitrene character. Hence, HOON could be a biradical either with both unpaired electrons localized at the p-orbitals of nitrogen atom or with a closed-shell molecule with an empty p-orbital on the N atom (Scheme 1). As the biradical structure would have  $A''$  symmetry, whereas HOON has  $A'$  symmetry, it can be excluded from the further consideration. Therefore, the nitrogen atom would have a lone pair in the plane of the molecule and an empty p-orbital out of the plane. Then, overlap of the empty orbital  $p_z\text{N}$  with a  $p_z$  orbital of the neighbor oxygen atom would form a  $\pi_z$ -NO bond. A similar orbital population can be found in the singlet state of hydroxynitrene NOH,<sup>(32c)</sup> where nitrene character is well-established.

#### Scheme 1



Due to the weakness of the O–O bond, HOON can also be considered a complex of HO with ON, either a pair of radicals or ions. Hydroxyl radical has an electron affinity of 1.83 eV,(36) whereas the ionization energy of nitric oxide is 9.26 eV,(37) so OH + NO is thermodynamically more stable as a radical pair. However, the ionic pair representation is still relevant, because the 3-center 4-electron system (Figure 2) pulls electron density to OH, creating a partial positive charge (0.15 au) on the NO moiety.

We compared the topology of the electronic density of the NO fragment in HOON with that in NOH, NO<sup>\*</sup>, and NO<sup>+</sup> to establish the chemical nature of HOON. Parameters under comparison include the NO bond length  $R(\text{N}-\text{O})$ , AIM charges on nitrogen ( $q(\text{N})$ ) and oxygen ( $q(\text{O})$ ) atoms, and the properties of the N–O BCP: value of electron density  $\rho_{\text{BCP}}(\text{N}-\text{O})$ , Laplacian of electron density  $\nabla^2\rho_{\text{BCP}}(\text{N}-\text{O})$ , and ellipticity of electron density  $\epsilon_{\text{BCP}}(\text{N}-\text{O})$ .

Both NO<sup>\*</sup> and NOH have two minima of  $\nabla^2\rho$  that correspond to lone pairs around nitrogen atoms, whereas NO<sup>+</sup> has only one. The nitrogen lone pairs in NOH are well developed and can be easily distinguished from those in NO<sup>\*</sup>. As lone pairs significantly differ in reference species, we introduced several parameters to quantitatively compare the lone pairs with *trans*-HOON. We found local minima of  $\nabla^2\rho$  (red points in Figure 3) and used values of electron density at those points  $\rho(n_1)$  and  $\rho(n_2)$ , and distance between them  $R(n_1-n_2)$  as descriptors.

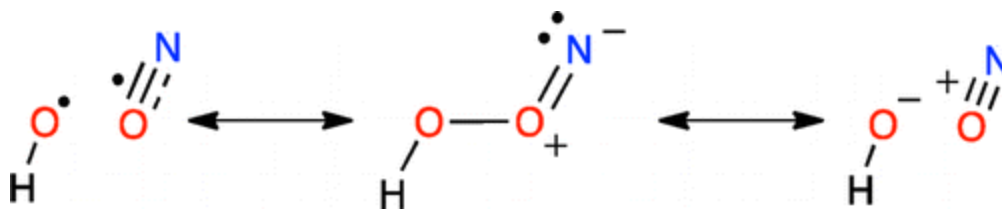
Table 4 shows that *trans*-HOON has similarities with all reference species: NOH, NO<sup>\*</sup>, and NO<sup>+</sup>. The bond length between N and O atoms,  $\rho_{\text{BCP}}(\text{N}-\text{O})$ ,  $\nabla^2\rho_{\text{BCP}}(\text{N}-\text{O})$ , and  $R(n_1-n_2)$  are closest to those of NO<sup>\*</sup>, which suggests a radical-pair character. However,  $\rho_{\text{BCP}}(\text{N}-\text{O})$  in *trans*-HOON are higher than in NO<sup>\*</sup>,  $\nabla^2\rho_{\text{BCP}}(\text{N}-\text{O})$  is lower, and  $R(\text{N}-\text{O})$  is shorter, which can only be explained by admitting some nitrosyl cation character of the NO moiety. Another evidence for nitrosyl cation character in *trans*-HOON is a substantial positive charge (0.15 au) on the NO moiety. At the same time, the ellipticity  $\epsilon_{\text{BCP}}(\text{N}-\text{O})$  in *trans*-HOON is between that in NOH and NO<sup>\*</sup>, implying some nitrene character of *trans*-HOON. Moreover, molecular nature of HOON is suggested by the CASPT2 wave function composition with one dominating configuration, occupancies of frontier natural orbitals that differ significantly from unity, and topological analysis that reveals bonding path between oxygen atoms.

**Table 4. Properties of the NO Fragment in Various Compounds, Calculated with CASPT2/aug-cc-pVTZ**

	X <sup>1</sup> A' <i>trans</i> -HOON	X <sup>2</sup> Π NO <sup>*</sup>	X <sup>1</sup> Σ <sup>+</sup> NO <sup>+</sup>	<sup>1</sup> A' HON
$R(\text{N}-\text{O}), \text{Å}$	1.138	1.159	1.071	1.265
$\rho_{\text{BCP}}(\text{N}-\text{O}), \text{au}$	0.612	0.587	0.744	0.433
$\nabla^2\rho_{\text{BCP}}(\text{N}-\text{O}), \text{au}$	-2.116	-2.101	-2.742	-1.073
$\epsilon(\text{N}-\text{O})$	0.16	0.08	0.00	0.31
$q(\text{O}), \text{au}$	-0.37	-0.41	-0.26	-0.60
$q(\text{N}), \text{au}$	0.52	0.41	1.26	0.07
$\rho(n_1), \text{au}$	0.54	0.53	0.59	0.73
$\rho(n_2), \text{au}$	0.53	0.53		0.66
$R(n_1-n_2), \text{Å}$	0.66	0.67		0.72

Thus, our analysis suggests that HOON is best represented by a combination of three resonance structures with major contribution from a radical-pair structure, followed by a significant contribution from a nitrene structure, and a small admixture of ion-pair character (Scheme 2).

Scheme 2



## Conclusions

Sophisticated ab initio calculations show that HOON has minima only at the  $^1A'$  electronic state, where it can exist as the *cis*- or *trans*-isomeric form. The *trans*-form is more stable and is characterized by  $R(O-O) = 1.89$  Å,  $D(O-O) = 33.3$  kJ/mol, and  $\Delta_f H^\circ = 95.1$  kJ/mol. Because of a relatively high dissociation energy, HOON might be a candidate for matrix isolation.

Topological analysis of the electronic density suggests that the NO moiety in HOON is most similar to nitric oxide, although some nitrene character is also present, as well as nitrosyl cation character. Therefore, the name “hydroperoxynitrene” does not correctly describe the nature of HOON, and we propose the name “nitrosyl *O*-hydroxide” or “isonitrosyl hydroxide” instead.

We envision that HOON might be a parent representative of a class of compounds with the  $-OON$  group. It is possible that some substituents might strengthen the  $O-O$  bond thus stabilizing the  $-OON$  group. On the other hand, formation of the  $-OON$  group might be considered as a way to fix nitric oxide  $NO^*$  and perturb its electronic structure, involving it in usually unfavorable chemical reactions. For example, photolysis of alkyl nitrite, which leads to, among other products,  $HN$ , might involve the  $-OON$  group, which could promote H-atom abstraction from the  $\alpha$ -carbon atom by nitric oxide. The effect of substituent on the electronic structure and chemical reactivity of the  $-OON$  group is an object of our future studies.

## Supporting Information

Details of the CCSDTQ/aug-cc-pVTZ approximation; geometry and vibrational frequencies of *cis*-HOON; thermodynamics of reaction R2, calculated by methods involved in the CCSDTQ/aug-cc-pVTZ extrapolation; details on calculations of enthalpy of formation of *cis*-HNOO; scan plot along the minimum energy path (MEP) between *trans*-HOON and *cis*-HOON, and the corresponding Cartesian coordinates; scan plot along the MEP between *trans*-HOON and *cis*-HONO, and the corresponding Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

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## ABBREVIATIONS

AIM	quantum theory of atoms in molecules
CBS	complete basis set
MEP	minimal energy path

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