

Structure, Vibrational Frequencies, and Stability of a Reactive Intermediate: FOONO

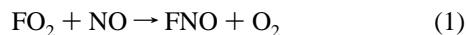
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Abstract: Published kinetic results for the FNO₃ system suggest that some reactions of FO₂ + NO and FO + NO₂ may proceed through an FOONO intermediate. This molecule, an isomer of fluorine nitrate, FONO₂, has received no experimental and essentially no theoretical study. The present work employs the quadratic configuration interaction method to investigate the structure, vibrational frequencies, and stability of FOONO. Computations at the QCISD(T)/6-311G(3df)//QCISD(T)/6-311G(2d) level of theory lead to $\Delta H_{f,0}^0(\text{FOONO}) = 23.5 \pm 4 \text{ kcal mol}^{-1}$.

Fluorine nitrate, FONO₂, is a fluorine reservoir in the stratosphere that couples the FO_x and NO_x families of radicals. Although it has been the topic of many investigations, it was not until recently that Oberhammer and collaborators¹ determined its molecular structure and Lee² used *ab initio* calculations to accurately determine its heat of formation. Unlike its stable isomer, FOONO has received almost no attention. A single computational study by Morris et al.³ only employed HF/4-31G geometries and MP2/DZP energies. It is well-established that Hartree–Fock theory fails for geometries of related compounds like FNO_x (FNO,^{3,4} FNO₂,³ and now FONO₂), FONO,^{3,5} and FOO_x (FOOF⁶ and FOO⁷). Therefore, it is no surprise Hartree–Fock theory fails for FOONO. Our interest in FOONO was aroused by recent concerns over the fate of the FO_x radicals FO and FO₂ in the stratosphere and their possible role in ozone-depleting catalytic cycles.⁸ While many facets of FO_x chemistry could stand further investigation, as we will describe below, it has been shown conclusively that reactions of FO and FO₂ with ozone are slow, and that reactions other than FO_x with O₃ or O will dominate the stratospheric fate of FO and FO₂.^{8–10} Specifically, the reaction of FO₂ with NO competes effectively with O₃ for the fate of FO₂; the dominant channel is



Li, Friedl, and Sander¹¹ determined an activation energy for (1) of only 1.3 kcal mol⁻¹ between 190 and 298 K; this seems far too low to correspond to an activation barrier for fluorine abstraction by NO. A more reasonable mechanism would have the radicals associate to form FOONO, which could then dissociate through a three-center transition state to form FNO and O₂.

A noteworthy point is the observation by Li, Friedl, and Sander¹¹ of an additional channel



with a branching ratio $k_2/(k_1 + k_2)$ less than 0.03. This elementary reaction would seem to require the formation of an FOONO intermediate.

Reaction of FO with NO₂ is a minor fate of FO in the stratosphere. Bedzhanyan and co-workers¹⁰ observed evidence for three separate product channels for this reaction: F + NO₃, FONO₂, and unknown products. The unknown products might well be FO₂ + NO or FNO + O₂. Reaction of FO at an oxygen of NO₂ could form an FOONO intermediate; fission of its weakest bond would lead to FO₂ + NO, while FNO + O₂ might be formed from FOONO as proposed for reaction 1.

In the center of all these mechanistic uncertainties lies FOONO, unknown experimentally and neglected computationally. As a first step toward exploring the chemistry of the FO₂ + NO and FO + NO₂ systems, we computed the structure, vibrational frequencies, and stability of FOONO. All calculations were done using the GAUSSIAN 92 series of programs.¹² The unrestricted Hartree–Fock formalism was employed for radicals. Geometries were optimized using quadratic configuration interaction theory (QCISD(T)) employing the 6-31G(d) and 6-311G(2d) basis sets. Single point energies were determined at the QCISD(T)/6-311G(3df) level of theory using geometries optimized at the QCISD(T)/6-311G(2d) level. Structural parameters were converged to better than 0.001 Å and 0.1° and forces to 10⁻⁴ au. Vibrational frequencies were obtained at the QCISD(T)/6-31G(d) level of theory.

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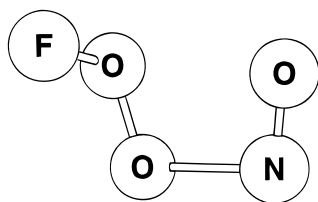
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Table 1. FOONO *cis*-perp Geometry (bond Lengths in Å, angles in degrees)

species	coordinate	QCISD(T)		CCSD(T) ^a		
		6-31G(d)	6-311G(2d)	TZ2P	expt ^b	
FONO ₂	FO	1.439	1.424	1.428	1.409(2)	
	NO	1.515	1.510	1.515	1.507(4)	
	NO'	1.203	1.191	1.188	1.184(2) ^c	
	NO''	1.210	1.199	1.196	1.184(2) ^c	
	FON	105.5	105.8	106.2	106.0(11)	
	ONO'	117.2	117.1	117.2	117.1(9)	
	ONO''	107.8	107.9	107.8	108.4(18)	
	FONO'	0.0	0.0	0.0	0.0	
	FOONO <i>cis</i> -perp	NO	1.156	1.136		
		NO'	1.744	1.819		
O'O''		1.331	1.293			
O''F		1.534	1.568			
ONO'		107.7	105.3			
NO'O''		103.7	101.5			
O'O''F		106.3	107.1			
ONO'O''		0.0	0.0			
NO'O''F		84.5	84.7			

^a Reference 2. ^b *r*_a structure from ref 1. Error limits are 3σ. ^c The two N=O bond lengths were constrained to be equal in the experimental analysis.

**Figure 1.** *Cis*-perp FOONO.

Geometries of FOONO and FONO₂ are listed in Table 1. Figure 1 depicts the most stable conformer found for FOONO. This conformer, labeled *cis*-perp, has the fluorine out of the plane of the other four atoms, which adopt a syn conformation about the internal O–N (single) bond (labeled NO' in Table 1). The same conformation was found most stable for ClOONO.¹³ A higher energy (at QCISD/6-31G(d)) *trans*-perp structure was also found; it will not be discussed further. The weakest bond in FOONO (see below) is the very long (~1.8 Å) O–N single bond. The computed structure and vibrational frequencies for FONO₂ agree with the published CCSD(T)/TZ2P results of Lee² and with experiment,¹ giving us confidence in our calculated structures.

FONO₂ has been labeled dangerous for theory, but FOONO exhibits markedly larger basis set effects on calculated bond lengths (2.8% rms vs 0.8%). On the basis of the slow SCF convergence encountered and the similarities in the trends for the FO bond length of FO₂^{7,14} and FOO^{15,16} and the O–N bond length of FOONO¹⁷ at the various levels of *ab initio* theory, we suggest that FOONO, like FOO¹⁶ and FO₂,^{7,14} possesses a large degree of multireference character.

Let us consider the energetic results, their accuracy, and the stability of FOONO. Our best value of the calculated FO–NO₂ bond strength of FONO₂ (Table 3) is well within the uncertainties of the best literature values, and within one standard deviation (~2 kcal mol⁻¹) of our relative energies. Using the FONO₂ heat of formation and the calculated isomerization energy, we estimate Δ*H*_{*f*,0}⁰(FOONO) as 23.5 ± 4 kcal

Table 2. FOONO Vibrational Frequencies (cm⁻¹)

species	mode no.	description	QCISD(T)/6-31G(d)	expt ^a
FONO ₂	1 (a')	N=O asym str	1804	1760.9
	2	N=O sym str	1331	1301.2
	3	F-O str	934	927
	4	O=N=O bend	798	803.4
	5	O _c =N–O bend	623	632.9
	6	O _i =N–O bend	453	458.5
	7	FON bend	303	302.6
	8 (a'')	NO ₃ umbrella	687	707.3
	9	torsion	148	151.6
FOONO <i>cis</i> -perp	1	N=O str	1868	
	2	OO str	1000	
	3	FO str	727	
	4	ONO bend	689	
	5	FOO bend	471	
	6	NOO bend	352	
	7	FO/ON ip	266	
	8	torsion	203	
	9	torsion	128	

^a Fundamental frequencies from ref 1.

Table 3. Relative Energies (kcal mol⁻¹) of Dissociation and Isomerization of FNO₃ Isomers (0 K, including zero-point energies)

level of theory	dissociation to FO + NO ₂		isomerization
	FONO ₂	FOONO	FONO ₂ → FOONO
QCISD(T)/6-31G(d)	25.7	11.9	13.8
QCISD(T)/6-311G(2d)	27.6	13.1	14.5
QCISD(T)/6-311G(3df)// QCISD(T)/6-311G(2d)	31.6	12.9	20.5
expt ^a	31 ± 3		

^a Values of Δ*H*_{*f*,0}⁰ for FONO₂ from ref 2, corrected to 0 K. FO from: Zhao, Y.; Francisco, J. S. *Chem. Phys. Lett.* **1990**, *167*, 285.

mol⁻¹. Combining this estimate with the experimental heats of formation for FO₂ and NO of 6.2 ± 0.5 and 21.5 ± 0.04 kcal mol⁻¹, respectively, indicates that the FOO–NO bond energy is 4.2 kcal mol⁻¹. The lifetime of a thermalized FOONO molecule with respect to FO₂ + NO can then be estimated from the formula τ = (Ae^{-*E*_a/RT})⁻¹ using the bond energy for *E*_a and 10¹³ s⁻¹ as a likely lower limit for *A*.¹⁸ This procedure yields a lifetime of 1 × 10^{-10±3} s. The small FOO–NO bond strength requires that the activation energy for FOONO rearrangement to FNO + O₂ be similarly small if rearrangement is to compete with dissociation.

The role of ROONO compounds, with R = H, Cl, and alkyl, in RO + NO₂ and RO₂ + NO chemistry has been of concern to atmospheric chemists.¹³ Reaction of HO + NO₂ in matrix yields a product whose spectrum has been attributed to HOONO. Atkinson¹⁹ suggested the existence of an ROONO intermediate to explain the temperature and pressure dependence of alkyl nitrate (RONO₂) yields from the RO₂ + NO reaction, but supporting evidence has been scarce.²⁰ The present calculations confirm the existence of FOONO as a minimum on the FNO₃ potential energy surface, and lend support to the suggestion of an FOONO intermediate in FNO₃ chemistry. FOONO is clearly a challenging molecule for theory, and the sub-microsecond to sub-picosecond room temperature lifetimes estimated here suggest it will also pose a challenge for experiment.

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