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Structures, Vibrational Spectra, and Relative Energetics of FC(O)ONO and FC(O)NO₂ Isomers at DFT and ab initio levels

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Abstract

The structural and vibrational parameters of FC(O)ONO and FC(O)NO₂ isomers were examined theoretically using the B3LYP/6-311+G(3df) and CCSD(T)/6-311G(d) methods. Four conformers of FC(O)ONO isomer and one FC(O)NO₂ isomer are found here. Among them, the trans-cis and cis-cis FC(O)ONO configuration are new conformers. The energetics were refined with G3//B3LYP and CBS-QB3 calculations. The trans-trans conformer of the FC(O)ONO isomer is found to be the lowest energy structure, with an estimated heat of formation of -104.9 kcal mol⁻¹ at 0 K as determined from CBS-QB3 theory. The next lowest structure is the cis-trans FC(O)ONO lying 1.7 kcal mol⁻¹ above the trans-trans structural form. The highest energy structure is the FC(O)NO₂ isomer with a predicted heat of formation of -84.8 kcal mol⁻¹. A comparison of the relative stability of the FCNO₃ isomers with the isomers of ClCNO₃ shows that the Cl analogues follow the same pattern of stability, as do the F isomers. However, the chlorine isomers are unstable relative to their fluorine analogues.

Keywords: Density functional theory; Ab initio composite methods; Heats of formation; Fluoroformyl nitrite isomers

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1 Introduction

Carbonyl free radicals, RCO, are important intermediates in the atmospheric degradation of volatile organic compounds. The breakdown of certain chlorofluorocarbons produces the fluorocarboxyl radical, F₂CO, which can undergo subsequent photochemical decomposition to yield the fluoroformyl radical, FCO. Theoretical studies by Francisco et al. [1] suggested that the lifetime for FCO under stratospheric condition is sufficient to allow bimolecular reactions to compete with dissociation. There have been a few experimental [2–4] and theoretical [5–7] studies on the reaction of FCO radical with NO. The very recent study by Lin and coworkers [7] has shown that the dominant product channel is the formation of FC(O)NO at low temperatures.

The purpose of the present investigation is to obtain systematic information of the structure and energies of stable adducts formed in the association reaction between FCO and NO₂ radicals

where the C atom of FCO radical attacks either the N or the O atoms of NO₂. Presently, there have been no experimental studies **referring** to this reaction and only one computational study on formation and dissociation of FC(O)ONO species was published in 1994 by Dibble and Francisco[8]. The paper presented the two FC(O)ONO chain conformers and two higher energy isomers calculated at the HF/6-31G(d) and MP2/6-31G(d) methods. Argüello et al.[9] studied the visible and IR absorption spectrum of fluoroformyloxyl radical, FCO(O), and mentioned that the FC(O)ONO intermediate was not detected in the reaction between FCO(O) and

NO. Nevertheless, it is not unlikely that the isomers could be detected by IR measurement, but more rigorous experiments are needed to verify this. For example, long-standing discordance of the presence of HOONO intermediate in the reaction of OH with NO₂ has been resolved by the vibrational predissociation spectroscopy experiment [10].

In this study we employed density functional theory (DFT) and high level wave function method to evaluate the minimum-energy structural forms for the F(C)ONO₂ and FC(O)ONO isomers which could be formed in the reactions of FCO with NO₂ or FC(O)O with NO. Calculated anharmonic vibrational frequencies, along with infrared intensities, should be improved guide for future spectroscopic experiments. The heats **on the formation** have been estimated, in order to provide the relative stability of the structural forms. Further, the heats **on the formation** have been calculated for the corresponding Cl isomers [11], which enable us to compare the relative stabilities of the fluorine and chlorine analogues.

2 Computational Methods

The density functional approach was employed using GAUSSIAN 03 [12]. As a reasonable compromise between expense and accuracy, the equilibrium geometrical parameters of the FC(O)NO₂ isomers were fully optimized using the Becke three-parameter nonlocal exchange functional [13] with the nonlocal correlation of Lee, Yang, and Parr (B3LYP) [14,15] with the 6-311+G(3df) basis set. The harmonic and anharmonic frequencies of all species were computed from analytical derivatives at the B3LYP/6-311+G(3df) level using geometries calculated at the same level of theory, in order to characterize the nature of the stationary points and to determine zero-point vibrational energies. The minimum-energy structures were also re-evaluated with the single and double excitation coupled-cluster method, includ-

ing a perturbation estimate of the effects of connected triple excitations (CCSD(T)) [16–18] using the 6-311G(d) basis set.

Two series of higher-level calculations were performed to refine the energies of the isomers: (i) G3//B3LYP method [19] and (ii) complete basis set extrapolation CBS-QB3 method [20]. The heats of formation were evaluated using G3//B3LYP and CBS-QB3 theories, which are estimated to be accurate to 0.99 kcal mol⁻¹ and 0.87 kcal mol⁻¹, respectively, by following the procedure based on atomization energies as outlined by Curtiss et al. [21].

3 Results and Discussion

3.1 Structures and Vibrational Frequencies of FC(O)NO₂ Isomers

We have located five local minimum-energy structures on the FC(O)NO₂ potential energy hypersurface at the B3LYP/6-311+G(3df) and CCSD(T)/6-31G(d) levels of calculation. Their optimized structures and geometrical parameters are presented in Figure 1. All structures are planar with C_s symmetry and it is readily seen that both optimization procedures provide consistent results.

The reliability of the selected level of calculations has been checked by calculations of the geometrical parameters for the FCO and NO₂ radicals, where very good agreement with the available experimental data has been found. Further, we have shown in recent work [11] on the related ClCO + NO₂ system, that reliable equilibrium geometries are obtained at the B3LYP/6-311+G(3df) level.

The first isomeric form investigated is the structure where the FCO and NO₂ radicals associate each other through their carbon and oxygen atoms, respectively. For this FC(O)ONO adduct, four conformeric forms differing mainly in their two F-

CO1-N and O2N-O1-C dihedral angles were found (Figure 1(a)-(d)). With regard to the planarity of all the conformers, the particular dihedral angles are 0° for the cis (c) and 180° for the trans (t) arrangements of the corresponding atoms. The length of the C-O2 bond formed is predicted to be about 1.32 Å for both conformers in which the NO₂ moiety is in trans orientation with respect to the FCO unit while, for their cis mutual orientation, the bond length is only 0.01 Å shorter. The N-O2 bond lengths are elongated by 0.5 - 0.6 Å in FC(O)ONO conformers relative to the original double bond in the reactant NO₂ molecule, and the N-O1 bonds are shortened by about 0.08 Å. The ONO bond angles of conformers, with trans and cis orientation of ONO with respect to the FCO part, are compressed by around 26° and 18° , respectively. The carbonyl C-O bond and the C-F bond remain nearly the same as they are in FCO radical, while the FCO angle in the conformers is reduced by about 6° .

The second isomer corresponds to the **FC(O)NO₂** structure (Figure 1(e)). The C-N bond length of 1.564 Å is close to that of a normal C-N single bond. Compared to the FC(O)ONO structures the C-F and C-O bonds in **FC(O)NO₂** are shorter by 0.04-0.06 Å and 0.02 - 0.03 Å, respectively.

Two conformeric forms of FC(O)ONO isomer termed *syn* (FC(O)ONO_{tt}) and *anti* (FC(O)ONO_{ct}) structures, and FC(O)NO₂ isomer have been reported previously by Dible and Francisco [8]. In general, their optimized geometries using HF/6-31G(d) and MP2/6-31G(d) methods are consistent with the parameters computed at higher levels of theory in the present work. We have characterized two additional conformeric forms of FC(O)ONO isomer, thus, FC(O)ONO_{tc} and FC(O)ONO_{cc} are new structures on FC(O)NO₂ potential energy hypersurface. It should be mentioned, that the both new conformers are not minimum energy structures when the recomputations at HF/6-31G(d) level are done.

The calculated harmonic and anharmonic vibrational frequencies, together with IR intensities, for the all four conformers of FC(O)ONO isomer and FC(O)NO₂ isomer are listed in Table 1. The vibrational frequencies noted in the table are obtained at the B3LYP level of theory using 6-311+G(3df) basis set. All positive frequencies for each structure confirm that these structures are at stable energy minima. The approximate descriptions of the vibrational modes were obtained from inspection on normal mode animation.

In the prediction of the anharmonic vibrational frequencies of FC(O)ONO_{tt}, two very intense bands appear to correspond to the C=O and C-O stretches at 1831 and 1172 cm⁻¹, respectively. The next intense bands are predicted to be the N=O stretch at 1948 cm⁻¹, the ONO bend at 749 cm⁻¹ and the N-O stretch at 306 cm⁻¹.

For FC(O)ONO_{ct}, the most intense band appears to be the C=O stretch at 1855 cm⁻¹, while the C-O stretch at 1194 cm⁻¹ is less intense. Somewhat less intense bands are the N=O stretch at 1950 cm⁻¹, the ONO bend at 748 cm⁻¹ and the N-O stretch at 311 cm⁻¹. The comparison between the C-F stretch frequency of FC(O)ONO_{ct} and FC(O)ONO_{tt} demonstrates that the frequency is shifted by 70 cm⁻¹ being lower in FC(O)ONO_{ct}.

The C-O stretch at 1188 cm⁻¹ is the most pronounced band in FC(O)ONO_{tc}. The other two bands with moderate intensity at 2016 and 1762 cm⁻¹ belong to the N=O and C=O stretches, respectively.

The most intense band of FC(O)ONO_{cc} is predicted to be the C=O stretch at 1843 cm⁻¹. There are two intense bands occurring at 1994 and 1138 cm⁻¹, which correspond again to the N=O and C-O stretches. When the vibrational frequencies of FC(O)ONO_{cc} and FC(O)ONO_{tc} are compared, it is seen that the C=O stretch and C-F stretch lie 81 cm⁻¹ higher and 70 cm⁻¹ lower, respectively, for FC(O)ONO_{cc}.

The IR spectrum of FC(O)NO₂ is characterized by three intense bands occurring at 1947 cm⁻¹ for the C=O stretch, 1639 cm⁻¹ for the NO₂ asymmetric stretch, and 1140 cm⁻¹ for the C-F stretch. The NO₂ symmetric stretching at 1349 cm⁻¹ has low intensity.

The frequency modes that can clearly distinguish FC(O)NO₂ from FC(O)ONO are the NO₂ asymmetric and symmetric stretches at around 1640 and 1350 cm⁻¹, respectively. On the other hand, the appearance of a relatively intense band in the region 1760-1860 cm⁻¹ (C=O stretch) and a low intense band in the region 280-310 cm⁻¹ (N-O stretch) would be attributed to FC(O)ONO.

3.2 Relative Energetics of FC(O)NO₂ Isomers

The calculated relative energies for the minimum-energy structures are presented in Table 2. B3LYP/6-311+G(3df), CCSD(T)/6-311G(d), G3//B3LYP and CBS-QB3 methods predict very consistent results, and the G3//B3LYP and CBS-QB3 relative energies are in excellent agreement between themselves. The B3LYP/6-311+G(3df) and CCSD(T)/6-311G(d) relative energies approach closely to those calculated with composite methods, except for FC(O)ONO_{cc}, where the B3LYP/6-311+G(3df) relative energy is 1.3 and 2.0 kcal mol⁻¹ lower than the G3//B3LYP and CBS-QB3 values, respectively.

The order of relative stability among the isomers or conformers, from most stable to least stable, is FC(O)ONO_{tt} > FC(O)ONO_{ct} > FC(O)ONO_{tc} > FC(O)ONO_{cc} > FC(O)NO₂. However, the FC(O)ONO isomer is significantly more stable than the FC(O)NO₂ isomer. Among the conformers of the FC(O)ONO isomer, FC(O)ONO_{tt} is the most stable. The next most stable, FC(O)ONO_{ct}, is located only 1.7 kcal mol⁻¹ higher than FC(O)ONO_{tt} at the CBS-QB3 level of calculation. FC(O)ONO_{tc}

and FC(O)ONO_{cc} are placed 2.8 and 6.5 kcal mol^{-1} , respectively, higher than FC(O)ONO_{tt} at the CBS-QB3 level. The CBS-QB3 relative energy difference between FC(O)ONO_{tt} and FC(O)ONO_2 is 20.1 kcal mol^{-1} . The QCISD(T)/6-31G(d)//MP2/6-31G(d) energy of FC(O)ONO_{ct} and FC(O)ONO_2 relative to energy of FC(O)ONO_{tt} reported by Dibble and Francisco [8] with values 1.3 and 22.4 kcal mol^{-1} , respectively, are close to the results obtained here.

The accuracy of the relative energetic data provided in Table 2 can also be assessed from the heats of formation. The heats of formation of all the species were calculated from atomization energies, using G3//B3LYP and CBS-QB3 compound methods and known heats of formation of elements. The experimental heats of formation at 0 K for the atoms [21] used in the calculations are as follows: the F atom: $\Delta_f H_o^\circ = 18.47 \pm 0.07 \text{ kcal mol}^{-1}$; the N atom: $\Delta_f H_o^\circ = 112.53 \pm 0.02 \text{ kcal mol}^{-1}$; the O atom: $\Delta_f H_o^\circ = 58.99 \pm 0.02 \text{ kcal mol}^{-1}$; and the C atom: $\Delta_f H_o^\circ = 169.98 \pm 0.1 \text{ kcal mol}^{-1}$. The heats of formation at 298 K were evaluated from the 0 K values by including the thermal contribution corrections.[21] The atomization energies and heats of formation at 0 K and 298 K calculated with G3//B3LYP and CBS-QB3 methods for the FC(O)ONO and FC(O)NO_2 isomers are summarised in Table 3. Comparison of the heats of formation obtained by the G3//B3LYP and CBS-QB3 methods shows reasonable agreement for all species, the deviation between two methods being on average 1.5 kcal mol^{-1} .

For the FC(O)ONO_{tt} , the heat of formation at 0 K is predicted to be -104.9 kcal mol^{-1} at the CBS-QB3 level of theory. The FC(O)ONO_{ct} structure (with -103.2 kcal mol^{-1} heat of formation) is insignificantly more stable than the FC(O)ONO_{tc} structure (with -102.1 kcal mol^{-1} heat of formation). The FC(O)ONO_{cc} structure (with -98.52 kcal mol^{-1} heat of formation) is only 6.4 kcal mol^{-1} higher in energy than the FC(O)ONO_{tt} structure. The FC(O)ONO_2 structure (with -84.4 kcal mol^{-1}

heat of formation) possesses the highest energy and, thus, the lowest stability. However, the energetic ordering is consistent with the results provided from the relative energy calculations.

3.3 Comparison of Relative Stabilities of $XC(O)NO_2$ ($X = F, Cl$) Isomers

From a theoretical study on possible reaction pathways for the $ClCO + NO_2$ reaction [11] reported recently and from those discussed above for the $FC(O)NO_2$ potential energy hypersurface, it can be summarized that qualitatively identical minimum-energy structures are found for both systems. To compare the stability of the chlorine and fluorine analogue species on an absolute scale, we have also computed the heats of formation for chlorine species (Table 4).

Figure 2 shows a comparison of the heats of formation of $FC(O)NO_2$ isomers with those of the $ClC(O)NO_2$ isomers calculated by the CBS-QB3 level of theory. Such a comparison indicates that the most stable isomer is $FC(O)ONO_{tt}$ with a heat of formation of $-104.9 \text{ kcal mol}^{-1}$, while the least stable isomer is $ClC(O)NO_2$ with $-41.9 \text{ kcal mol}^{-1}$. The order of levels of energy for the $ClC(O)NO_2$ follows the same pattern as that of the $FC(O)NO_2$ isomers, i.e. $ClC(O)ONO_{tt} > ClC(O)ONO_{ct} > ClC(O)ONO_{tc} > ClC(O)ONO_{cc} > ClC(O)NO_2$, with $ClC(O)ONO_{tt}$ being the most stable structural form. The CBS-QB3 heat of formation of $ClC(O)ONO_{tt}$ is $-59.1 \text{ kcal mol}^{-1}$, and decreases by $43.4 \text{ kcal mol}^{-1}$ when the chlorine atom is replaced by a fluorine. In summary, the fluorine analogue isomers are significantly more stable than their chlorine counterparts. Fluoroformyl nitrite isomers can be considered as temporary reservoir species for the aggressive radicals FCO and NO_2 in the atmosphere.

4 Conclusion

The equilibrium structures, vibrational spectra, relative energetics, and heats of formation of the $\text{FC}(\text{O})\text{ONO}$ and $\text{FC}(\text{O})\text{ONO}_2$ isomers have been investigated with density functional and ab initio methods. The $\text{FC}(\text{O})\text{ONO}_{tt}$ structural form was found to be the most stable of the four conformers of the $\text{FC}(\text{O})\text{ONO}$ isomer, with an estimated heat of formation of $-104.9 \text{ kcal mol}^{-1}$, while the $\text{FC}(\text{O})\text{NO}_2$ isomer with a heat of formation of $-84.8 \text{ kcal mol}^{-1}$ is found to be the least stable. The heats of formation of $\text{FC}(\text{O})\text{ONO}_{ct}$, $\text{FC}(\text{O})\text{ONO}_{tc}$, and $\text{FC}(\text{O})\text{ONO}_{cc}$ were determined as -103.2 , -102.1 , and $-98.5 \text{ kcal mol}^{-1}$, respectively. Distinguishing spectroscopic features of the isomers have been determined, which should allow these species to be identified experimentally. A comparison of the relative energetic stabilities of $\text{FC}(\text{O})\text{ONO}$ and $\text{FC}(\text{O})\text{ONO}_2$ isomers with those of $\text{ClC}(\text{O})\text{ONO}$ and $\text{ClC}(\text{O})\text{ONO}_2$ clearly demonstrates that the chlorine isomers are unstable relative to their fluorine analogues.

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Table 1

B3LYP/6-311+G(3df) unscaled harmonic and anharmonic frequencies (cm^{-1}) and IR intensities (km mol^{-1}) of FC(O)ONO and FC(O)NO₂ isomers (c and t in the subscripts signify cis and trans)

Species	mode number	mode symmetry	mode description	Harmonic	Anharmonic	I
FC(O)ONO _{tt}	1	a'	NO1 stretch	1983	1948	264
	2	a'	CO stretch	1868	1831	604
	3	a'	CO2 stretch	1202	1172	671
	4	a'	CF stretch	1007	988	109
	5	a'	ONO bend	766	749	213
	6	a'	FCO2 bend	634	627	32
	7	a'	twist	563	559	27
	8	a'	NO2 stretch	308	306	179
	9	a'	ip wag	191	211	0.1
	10	a''	FCO rock	793	778	30
	11	a''	NO ₂ rock	118	107	0
	12	a''	torsion	57	51	2
FC(O)ONO _{ct}	1	a'	NO1 stretch	1982	1950	246
	2	a'	CO stretch	1878	1855	778
	3	a'	CO2 stretch	1227	1194	470
	4	a'	CF stretch	939	919	105
	5	a'	ONO bend	766	748	265
	6	a'	OCO bend	646	642	3
	7	a'	twist	527	523	20
	8	a'	NO2 stretch	315	311	178
	9	a'	ip wag	198	178	0.2
	10	a''	FCO rock	784	773	31
	11	a''	NO ₂ rock	116	116	0.2
	12	a''	torsion	75	80	0.4

Table 1 (Continued)

Species	mode number	mode symmetry	mode description	Harmonic	Anharmonic	I
FC(O)ONO _{tc}	1	a'	NO1 stretch	2056	2016	413
	2	a'	CO stretch	1794	1762	308
	3	a'	CO2 stretch	1224	1188	675
	4	a'	CF stretch	980	963	40
	5	a'	ONO bend	714	702	19
	6	a'	FCO2 bend	654	642	133
	7	a'	twist	581	575	34
	8	a'	NO2 stretch	288	282	95
	9	a'	ip wag	195	191	3
	10	a''	FCO rock	801	792	29
	11	a''	NO ₂ rock	152	146	0.2
	12	a''	torsion	26	23	2
FC(O)ONO _{cc}	1	a'	NO1 stretch	2033	1994	433
	2	a'	CO stretch	1871	1843	616
	3	a'	CO2 stretch	1175	1138	436
	4	a'	CF stretch	914	893	129
	5	a'	ONO bend	720	705	15
	6	a'	OCO bend	651	639	45
	7	a'	twist	553	547	76
	8	a'	NO2 stretch	289	285	100
	9	a'	ip wag	206	197	0
	10	a''	FCO rock	781	773	32
	11	a''	NO ₂ rock	141	131	0.3
	12	a''	torsion	14	29	0

Table 1 (Continued)

Species	mode number	mode symmetry	mode description	Harmonic	Anharmonic	I
FC(O)NO ₂	1	a'	CO stretch	1980	1947	286
	2	a'	NO ₂ asymm. stretch	1673	1639	311
	3	a'	NO ₂ symm. stretch	1371	1349	51
	4	a'	CF stretch	1167	1140	259
	5	a'	ONO bend	859	851	21
	6	a'	FCO bend	714	705	66
	7	a'	CNO bend	543	579	2
	8	a'	CN stretch	403	393	0.1
	9	a'	ip wag	292	287	2
	10	a''	op asymm. rock	807	793	3
	11	a''	op symm. rock	480	460	35
	12	a''	torsion	32	24	0.4

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Table 2
Zero point corrected relative energies, ΔE_0 in kcal mol⁻¹, for FC(O)ONO and FC(O)NO₂ isomers (c and t in the subscripts signify cis and trans)

Species	ΔE_0			
	B3LYP/6-311+G(3df)	CCSD(T)/6-311G(d)	G3//B3LYP	CBS-QB3
FC(O)ONO _{tt}	0.0	0.0	0.0	0.0
FC(O)ONO _{ct}	0.8	1.7	1.5	1.7
FC(O)ONO _{tc}	2.2	2.9	2.5	2.8
FC(O)ONO _{cc}	4.5	6.3	5.8	6.5
FC(O)NO ₂	20.2	20.5	20.4	20.1

Table 3

Atomization Energies, ΔH_{at}^0 and Heats of Formation, ΔH_f^0 in kcal mol⁻¹, for FC(O)ONO and FC(O)NO₂ isomers (c and t in the subscripts signify cis and trans)

Species	Method	$\Delta H_{at,0}^0$	$\Delta H_{f,0}^0$	$\Delta H_{at,298}^0$	$\Delta H_{f,298}^0$
FC(O)ONO _{tt}	G3//B3LYP	581.1	-103.2	585.7	-102.3
	CBS-QB3	582.9	-104.9	587.5	-104.1
FC(O)ONO _{ct}	G3//B3LYP	579.6	-101.6	584.2	-100.8
	CBS-QB3	581.2	-103.2	585.7	-102.3
FC(O)ONO _{tc}	G3//B3LYP	578.6	-100.7	583.2	-99.8
	CBS-QB3	580.0	-102.1	584.6	-101.2
FC(O)ONO _{cc}	G3//B3LYP	575.3	-97.4	580.4	-97.0
	CBS-QB3	576.4	-98.5	581.0	-97.6
FC(O)NO ₂	G3//B3LYP	560.6	-82.8	565.8	-82.4
	CBS-QB3	562.8	-84.8	567.9	-84.4

Table 4
Atomization Energies, ΔH_{at}^0 and Heats of Formation, ΔH_f^0 in kcal mol⁻¹, for ClC(O)ONO and ClC(O)NO₂ isomers (c and t in the subscripts signify cis and trans)

Species	Method	$\Delta H_{at,0}^0$	$\Delta H_{f,0}^0$	$\Delta H_{at,298}^0$	$\Delta H_{f,298}^0$
ClC(O)ONO _{tt}	G3//B3LYP	544.8	-56.7	549.1	-55.6
	CBS-QB3	547.1	-59.1	551.5	-57.9
ClC(O)ONO _{ct}	G3//B3LYP	542.7	-54.6	547.0	-53.9
	CBS-QB3	544.5	-56.5	548.7	-55.2
ClC(O)ONO _{tc}	G3//B3LYP	542.1	-54.0	546.3	-52.8
	CBS-QB3	544.2	-56.1	548.5	-54.9
ClC(O)ONO _{cc}	G3//B3LYP	538.1	-50.0	542.4	-48.8
	CBS-QB3	538.8	-50.8	543.0	-49.4
ClC(O)NO ₂	G3//B3LYP	526.7	-38.6	531.5	-37.9
	CBS-QB3	529.5	-41.4	534.3	-40.7

FC(O)ONO_{tt} (a) FC(O)ONO_{ct} (b) FC(O)ONO_{tc} (c) FC(O)ONO_{cc} (d) FC(O)NO₂ (e)

Fig. 1. B3LYP/6-311+G(3df) and CCSD(T)/6-311G(d) (italic numbers) optimized geometries of FC(O)ONO and FC(O)NO₂ isomers (c and t in the subscripts signify cis and trans). The bond lengths are given in Å, angles in degrees.

Fig. 2. Relative energetics of XC(O)ONO and XC(O)NO₂ (X = F, Cl) isomers (c and t in the subscripts signify cis and trans). The values are calculated using CBS-QB3 theory.

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