Ab Initio Characterization of $ClNO_3$ Isomers

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The equilibrium structures, dipole moments, vibrational spectra, and relative energetics of the $ClNO_3$ isomers ($ClONO_2$, ClOONO, OClONO, $OClNO_2$) have been examined using various ab initio and density functional (MP2, CCSD(T), B3LYP) methods. The $ClONO_2$ is found to be the lowest energy structure among the isomers. Cis-perp and trans-perp ClOONO are less stable by 25.3 and 26.7 kcal mol^{-1}, respectively. The OClONO isomeric form with the trans-perp conformation is 13.5 kcal mol^{-1} higher in energy than the trans-perp ClOONO form. An examination of the vibrational and electronic spectra reveals spectral features that allow these species to be distinguished. We have considered the energetics pathways of ClO_x/NO_x reactions that may lead to the formation or dissociation of $ClNO_3$ isomers.

I. Introduction

Chlorine nitrate, $ClONO_2$, is one of the most important temporary reservoir species of reactive chlorine, which was first pointed out by Rowland et al.[1,2] It is formed primarily through the association reaction between ClO and NO_2 radicals that are active in a catalytic ozone destruction cycle in the stratosphere.

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \qquad (1)$$

Molina et al.[3] have reported an indication that species other than $ClONO_2$ are likely to be formed in reaction 1; among them (OClONO or ClOONO) the chlorine peroxynitrite isomer, ClOONO, would be the preferred one. Further evidence of the existence of ClOONO have been provided by matrix isolated IR spectra.[4] Subsequent investigations into the identity of the products formed in the ClO + NO_2 reaction have shown that $ClONO_2$ is the only product[5] and ruled out the possible existence of any other isomer. Nevertheless, it is not unlikely that the isomers of $ClNO_3$ could be detected by IR measurement, but more rigorous experiments are needed to verify this. For example, another important reaction that converts NO_x into its reservoir species is that of hydroxyl radicals with NO_2. It is well established that nitric acid, $HONO_2$, is formed through this association process. However, there exist long-standing speculations on the presence of a second reaction channel that would result in the formation of peroxynitrous acid, HOONO. This question was resolved just recently by Nizkorodov and Wennberg[6] who provided the first direct spectroscopic observation of gas-phase HOONO formed in the reaction of OH with NO_2. Furthermore, the unimolecular isomerization HOONO $\leftrightarrow$ $HONO_2$ was studied theoretically.[7,8] The transition state for the isomerization was found to have a structure in which OH is weakly coupled to NO_2. The isomerization is exothermic by 29 kcal mol^{-1}, and the activation barrier of 21.4 kcal mol^{-1} was calculated at the CBS limit with all corrections.[8]

Theoretical studies of $ClNO_3$ isomers are largely limited to the structure and vibrational frequencies of $ClONO_2$ and ClOONO. The ground-state geometry of chlorine nitrate is well established as C_s planar,[9−11] which is in agreement with experimental gas-phase data.[12] Calculations of excited electronic states of $ClONO_2$ have been provided by Grana.[13] The first Hartee-Fock (HF) study of chlorine peroxynitrite was reported by McGrath et al.[14] In the subsequent reinvestigation at higher levels of theory, MP2, McGrath et al.[15] have revealed that ClOONO formation is disfavored thermodynamically above 220 K.

The potential energy surface of the ClO + NO_2 reaction has been studied in our preceding work.[16] In this paper, we present an ab initio investigation of the possibility of stable $ClNO_3$ adducts that could be formed from association of the ClO radical with NO_2. We have examined the structures, vibrational frequencies, and energies of the $ClNO_3$ isomers to determine the relative order of stability among the $ClONO_2$, $OClNO_2$, ClOONO, and OClONO isomers. The computational methods employed in the investigations are described in the next section, followed by the presentation and discussion of results. The main conclusions are summarized in the final section.

II. Computational Methods

Ab initio molecular orbital calculations were performed using the GAUSSIAN 98 program.[17] All equilibrium geometries were fully optimized with the second-order Möller−Plesset (MP2) method,[18] the single and double excitation coupled-cluster method, including a perturbation estimate of the effects of connected triple excitations (CCSD(T)),[19−21] and the DFT approach using the Becke three-parameter nonlocal exchange functional[22] with the nonlocal correlation of Lee, Yang, and Parr (B3LYP).[23,24] The standard triple ζ plus polarization 6-311G(d) basis set, as implemented in the program,[17] was employed in the calculations. At the CCSD(T) level also the 6-31G(d) and cc-pVDZ basis sets were used. The harmonic frequencies of all species were computed from analytical derivatives at the B3LYP level in conjunction with the 6-311G-(d) basis set using geometries calculated at the same level of theory, to characterize the nature of the stationary points and to determine zero-point vibrational energies (ZPE). The anhar-

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TABLE 1: Equilibrium Geometries (Å and deg) of $ClNO_3$ Isomers[a]

species	coordinate	MP2	B3LYP		CCSD(T)		
		6-311G(d)	6-311G(d)	6-31G(d)	cc-pvDZ	6-311G(d)	exp[b]
$ClONO_2$	R(N−O1)	1.192	1.188	1.209	1.200	1.196	1.196
	R(N−O2)	1.190	1.186	1.207	1.197	1.194	1.196
	R(N−O)	1.542	1.515	1.502	1.514	1.495	1.499
	R(O−Cl)	1.706	1.717	1.720	1.736	1.724	1.673
	∠(O1NO2)	135.1	134.1	133.4	133.9	133.4	132.6
	∠(O1NO)	107.6	108.2	108.4	108.1	108.4	108.8
	∠(NOCl)	112.0	113.7	112.0	112.0	112.7	113.0
$ClOONO_{cp}$	R(N−O1)	1.169	1.127	1.169	1.150	1.149	
	R(N−O2)	2.090	1.739	1.573	1.687	1.615	
	R(O2−O)	1.216	1.309	1.411	1.353	1.366	
	R(O−Cl)	2.061	1.886	1.771	1.856	1.812	
	∠(O1NO2)	91.5	108.4	112.3	109.7	111.5	
	∠(NO2O)	92.1	106.1	108.1	105.7	108.0	
	∠(O2OCl)	116.3	112.6	110.5	110.5	110.5	
	∠(OO2NO1)	0.5	−2.3	−4.0	−3.0	−3.3	
	∠(ClOO2N)	89.8	91.2	90.6	89.0	90.6	
$ClOONO_{tp}$	R(N−O1)	1.151	1.139	1.176	1.161	1.157	
	R(N−O2)	1.600	1.615	1.536	1.582	1.549	
	R(O2−O)	1.380	1.355	1.425	1.394	1.387	
	R(O−Cl)	1.769	1.815	1.761	1.805	1.788	
	∠(O1NO2)	109.0	108.6	108.0	108.3	108.4	
	∠(NO2O)	105.3	106.8	104.5	104.7	105.4	
	∠(O2OCl)	109.9	111.2	108.5	109.2	109.7	
	∠(OO2NO1)	175.7	174.4	176.3	175.9	175.5	
	∠(ClOO2N)	90.1	91.8	91.3	89.8	90.8	
$OClONO_{tp}$	R(N−O1)	1.171	1.149	1.179	1.172	1.166	
	R(N−O2)	1.479	1.527	1.508	1.502	1.489	
	R(O2−Cl)	1.879	1.790	1.816	1.888	1.855	
	R(Cl−O)	1.504	1.545	1.552	1.568	1.550	
	∠(O1NO2)	109.5	108.6	108.3	108.2	108.7	
	∠(NO2Cl)	105.9	109.2	105.8	105.6	106.3	
	∠(O2ClO)	116.5	114.1	114.6	114.8	114.5	
	∠(O1NO2Cl)	180.0	−179.1	180.7	179.9	−179.2	
	∠(NO2ClO)	86.2	86.6	86.1	84.2	85.0	

[a] MP2/6-311G(d) and B3LYP/6-311G(d) geometries of $ClNO_2$, $ClOONO_{cp}$, $ClOONO_{tp}$, and $OClONO_{tp}$ from ref 16. [b] Vibrationally averaged structure from ref 12.

monic frequencies were calculated with the VSCF[25] method as implemented in the GAMESS[26] package.

To improve the energy differences, single-point calculations were performed at the CCSD(T) wave function with 6-311+G(df), 6-311+G(2df), and 6-311+G(3df) basis sets using the optimized geometries at the CCSD(T)/6-311G(d) level of theory. The heats of formation of all isomers were determined using G3//B3LYP theory,[27] which is estimated to be accurate to 0.99 kcal mol^{-1}, following the procedure based on the atomization reaction as outlined by Nicolaides et al.[28]

The vertical energies of electronic singlet excited states were computed with the multireference single and double excitation configuration interaction method MRD-CI+Q as implemented in the DIESEL program.[29] We used the cc-pVDZ basis set of double-ζ quality[30,31] with an additional s-Rydberg function located at the nitrogen center ($\alpha_s(N) = 0.028$) and a negative ion p-function for the chlorine atom ($\alpha_p(Cl) = 0.049$). From our present calculations on $ClNO_2$[32] and previous studies,[33] it is known that the changes in the excitation energies and transition probabilities between the results obtained with basis sets of double and triple-ζ quality are small; therefore, we believe that our calculated excitation energies have an error well below 0.3 eV. A summation threshold of 0.85 was used, which means that the sum of the squared coefficients of all reference configurations selected for each state is above 0.85. All configurations of generated configurations with an energy contribution above the threshold $T = 10^{-6}$ E_h were selected, i.e., the contribution of a configuration larger than this value relative to the energy of the reference set is included in the final wave function. All calculations were performed on CCSD(T)/6-311G(d) equilibrium geometry; 22 electrons were included in the active space, while the remaining electrons were kept in doubly occupied orbitals defined as frozen-core orbitals.

III. Results and Discussion

Equilibrium Geometries of $ClNO_3$ Isomers. We have located four local minimum-energy structures on the $ClNO_3$ potential energy hypersurface at the MP2, B3LYP, and CCSD(T) levels of calculations. Two additional local minima have been found only at the B3LYP level, which can be recognized as intermolecular complexes rather than stable isomeric forms. The optimized structural parameters of stable isomers obtained at various levels of theory are collected in Table 1; for $ClONO_2$, the experimental data are available and they are included in the table for comparison. Refer to Figure 1 for the denotation of isomers studied and labeling of the oxygen atoms.

The lowest minimum-energy structure corresponds to planar $ClONO_2$ with C_s symmetry. It can be seen from Table 1 that calculations at the CCSD(T)/6-311G(d) level are in excellent agreement with experimental gas-phase data,[12] with the largest deviation of 0.05 Å occurring for the O−Cl bond distance. Note that the data obtained in this work nearly coincides with those of the CCSD(T)/TZ2P calculations previously reported by Lee.[11] The agreement between theory and experiments suggests that the CCSD(T)/6-311G(d) level of theory should perform well for other $ClNO_3$ species. Also, MP2 and B3LYP methods in conjunction with 6-311G(d) basis sets adequately reproduce the experimental values.

The second isomeric structure we considered is an ClOONO. For this species, two conformeric forms differing mainly in their

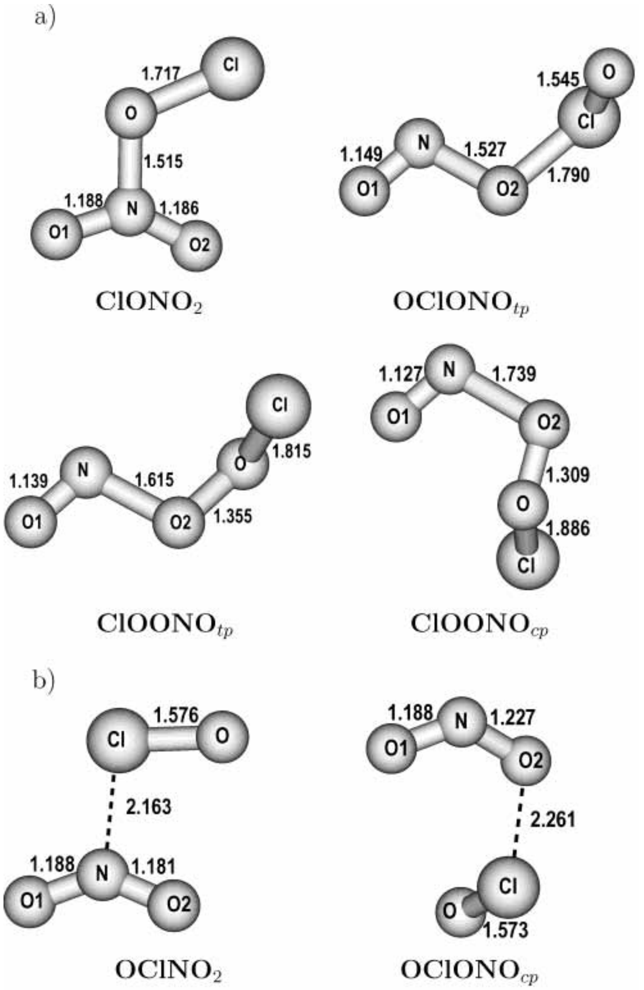

Figure 1. Minimum-energy structures of $ClNO_3$: (a) isomers, (b) intermolecular complexes. The values given are at the B3LYP/6-311G-(d) level of theory; for a complete list of geometrical parameters of isomers, see Table 1 (c, t, and p are abbreviations for cis, trans, and perp, respectively).

OO2NO1 dihedral angle were found to be minimum-energy structures. The cis-perp form is characterized by OO2NO1 and NO2OCl dihedral angles having values of −3.3 and 90.6°, respectively, at the CCSD(T)/6-311G(d) level of theory. The N−O1 and N−O2 bond lengths are 1.149 and 1.615 Å, respectively. The peroxy O2−O and O−Cl bond lengths are predicted to be 1.366 and 1.812 Å. All the bond angles are around 110°. The MP2/6-311G(d) method gives substantially different geometrical parameters for the cis-perp structure. The MP2 bond distances of N−O2 and O−Cl bonds are 0.47 and 0.25 Å higher than those calculated at the CCSD(T) level, and the O1NO2 and NO2O valence bond angles are compressed by about 20°. Furthermore, the B3LYP/6-311G(d) optimized geometry is fairly consistent with the CCSD(T)/6-311G(d) geometry. Similar unusual trends in the predicted bond lengths and valence bond angles for the cis-perp conformer at the MP2/6-311G(d) level of theory were found in our computational study of BrOONO,[34] and also in the MP2/6-311+G(d) study of alkali peroxynitrite.[35] However, in their MP2/6-31G(d) characterizations of ClOONO conformers, McGrath et al.[15] provide the data that are close to B3LYP or CCSD(T) geometrical parameters.

The OO2NO1 dihedral angle in the trans-perp conformer of ClOONO is 175.5°, while the dihedral angle between ClOO2N is predicted to be 90.8° at the CCSD(T)/6-311G(d) level. For other levels of calculation, the variation of either angle does not exceed 1°. The same is also valid for all three bond angles. At the CCSD(T)/6-311G(d) level, the N−O1 and N−O2 bond lengths are 1.157 and 1.549 Å, respectively. The peroxy O2−O and O−Cl bond lengths are predicted to be 1.387 and 1.788 Å. Here, the N−O2 bond distance is most sensitive to the level of calculations, as it varies by 0.04 Å on the average. In contrast to the cis-perp ClOONO conformer, the geometrical parameters of the trans-perp conformer calculated at MP2/6-311G(d) in this study are in a reasonable agreement with those reported by McGrath et al.[15] at the MP2/6-31G(d) level of theory.

The third isomeric form that has been investigated is OClONO using all levels of theory used in this study. The structure with the trans-perp arrangement of the ONO−Cl and NOCl−O bonds was found as the minimum-energy structure. At the CCSD(T)/6-311G(d) level of theory, the N−O1 and N−O2 bond lengths are 1.166 and 1.489 Å, respectively. The internal O2−Cl bond distance of 1.855 Å is longer than the terminal O−Cl bond of 1.550 Å. The NO2Cl angle (106.3°) is slightly smaller than the O1NO2 angle (108.7°), and O2ClO is somewhat more open (114.5°). The dihedral angle between O1NO2Cl atoms is −179.2°, while it is 85.0° between NO2ClO. The overall structural values obtained by smaller basis sets at CCSD(T) calculations and MP2 and B3LYP with a 6-311G(d) basis set adequately reproduce the geometry discussed above.

B3LYP/6-311G(d) calculations provide additional a cis-perp conformeric form of the OClONO isomer which is displayed in Figure 1. A comparison of the geometrical parameters of this OClONO structure with that of the trans-perp conformer obtained at the same level reveals that the predicted internal O2−Cl bond in cis-perp form is unusually long, i.e., by about 0.5 Å longer than the trans-perp form. Further, the N−O2 bond length is shortened to 1.227 Å and becomes closer to the other N−O bond length; the O1NO2 bond angle of 127.5° approaches that in the NO_2 molecule (134.2°). Thus, this structure more resembles the $NO_2\cdots ClO$ intermolecular complex.

The next structure is $OClNO_2$, possessing C_s symmetry. Among the levels of theory used in the present study, only B3LYP/6-311G(d) calculations are successful in identifying this structure, the parameters are shown in Figure 1. A comparison of the N−O1 and N−O2 bond lengths, and the O1NO2 bond angle of $OClNO_2$ (1.188 and 1.181 Å, and 136.2, respectively) with those in $ClONO_2$ (1.188 and 1.186 Å, and 134.1, respectively) reveals that the bonding in the NO_2 group between the two structures is similar. The bond distance of the Cl−N bond is 2.163 Å. If we compare this value with the CCSD(T)/TZ2P value[36] of 1.877 Å and the experimental data (1.840 Å)[37] for the related bond in $ClNO_2$, one can conclude that the B3LYP/6-311G(d) method provides too long Cl−N bond distance. The O−Cl bond length of 1.576 Å nearly coincides with the experimental bond length of 1.570 Å in the OCl radical.[38] However, the $OClNO_2$ structure obtained at the B3LYP/6-311G-(d) level of theory can be identified as the $OCl\cdots NO_2$ intermolecular complex and not as an adduct.

Relative Energetics and Heat of Formations of $ClNO_3$ Isomers. The calculated relative energies for the minimum-energy isomers of $ClNO_3$ at various levels of theory are presented in Table 2. The lowest energy structure on the $ClNO_3$ potential energy surface across all levels of theory is $ClONO_2$. It is more stable than $ClOONO_{cp}$ at the B3LYP and CCSD(T) levels with the 6-311G(d) basis set by 24.1 and 22.3 kcal mol^{-1}, respectively. At the CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G-(d) level the relative stability amounts to 25.3 kcal mol^{-1}. The trans-perp conformer of the ClOONO isomer is only 2.3, 1.6, and 1.4 kcal mol^{-1} less stable than the cis-perp conformer at

TABLE 2: Relative Energies[a] (kcal mol^{-1}) of $ClNO_3$ Isomers

level of theory	$ClONO_2$	$ClOONO_{cp}$	$ClOONO_{tp}$	$OClONO_{tp}$	$OClONO_{cp}$[b]	$OClNO_2$[b]
MP2/6-311G(d)	0	28.2	33.6	58.7		
B3LYP/6-311G(d)	0	24.2	26.5	53.5	45.2	34.0
CCSD(T)/6-31G(d)	0	19.4	21.6	46.2		
CCSD(T)/cc-pVDZ	0	20.2	22.7	53.1		
CCSD(T)/6-311G(d)	0	22.3	23.9	52.2		
G3//B3LYP	0	25.5	27.2	36.7	36.2	25.6
CCSD(T)/6-311+G(df)// CCSD(T)/6-311G(d)	0	26.3	26.5	46.9		
CCSD(T)/6-311+G(2df)// CCSD(T)/6-311G(d)	0	24.8	26.1	41.4		
CCSD(T)/6-311+G(3df)// CCSD(T)/6-311G(d)	0	25.3	26.7	40.2		

[a] Corrected for ZPE given in Table 4. [b] Intermolecular complex.

the corresponding levels of calculation. For the $ClOONO_{cp}$ and $ClOONO_{tp}$, the G3//B3LYP relative energies increased by 0.2 and 0.5 kcal mol^{-1}, respectively, relative to CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d). The relative stability of the both conformers is somewhat sensitive to electron correlation and basis set effects. For example, the differences between MP2/6-311G(d) and CCSD(T)/6-311G(d) relative energies are 5.9 and 9.7 kcal mol^{-1} for the $ClOONO_{cp}$ and $ClOONO_{tp}$, respectively, while those between CCSD(T)/6-31G(d) and CCSD(T)/6-311G(d) are 2.9 and 2.3 kcal mol^{-1}, respectively.

The trans-perp conformer of OClONO isomer is 53.5 and 52.2 kcal mol^{-1} less stable than $ClONO_2$ at the B3LYP and CCSD(T) levels with the 6-311G(d) basis set, respectively. The relative stability significantly decreases to 40.2 kcal mol^{-1} at the CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d) level. This lowering of relative energies is due to the addition of diffuse and of more polarization functions to the 6-311G(d) basis set. For example, the addition of diffuse and f polarization functions to 6-311G(d) decreases the relative energy of $OClONO_{tp}$ by 5.3 kcal mol^{-1}. The inclusion of second and third d functions in the basis set lowers the relative energy by additional 6.7 kcal mol^{-1}. The deviation between the CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d) and G3//B3LYP relative energies of $OClONO_{tp}$ is 3.5 kcal mol^{-1}, which is somewhat larger compared to those of ClOONO. We assume that the result obtained at CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d) would be more reliable, and the lower G3//B3LYP value arises from the fact that the hypervalent molecules are not strongly represented in the G3 test set.

A comparison of MP2 and CCSD(T) results shows that the MP2 method does not provide a good estimate of the correlation energy contribution to the energy differences and it is especially unreliable for predicting relative energetics of the hypervalent OClONO isomer. A similar effect of dramatically lowering the energies was previously reported for structures with a hypervalent character, such as $HClO_3$.[41,42]

The accuracy of the relative energetic data presented in the Table 2 can be assessed by the heats of formation. In the previous subsection, it is clearly demonstrated that the relative energetics were well reproduced by G3//B3LYP theory, and it is thus used for determining heat of formation of each of the $ClNO_3$ isomers. These results are given in Table 3. In this study, we have used the approach based on the atomization reaction.[28] The experimental heats of formation of atoms[44] used in the calculations are as follows: the N atom: $\Delta_f H^\circ_o = 112.53 \pm 0.02$ kcal mol^{-1}; the O atom: $\Delta_f H^\circ_o = 58.99 \pm 0.02$ kcal mol^{-1}; and the Cl atom: $\Delta_f H^\circ_o = 28.59 \pm 0.01$ kcal mol^{-1}. The G3//B3LYP calculated heat of formation of $ClONO_2$ at 298 K is 5.5 kcal mol^{-1}, which is in good agreement with the experimental value of 6.3 ± 0.2 kcal mol^{-1}. For the ClOONO isomer, the heats of formation are 32.5 and 34.4 kcal mol^{-1} for the cis-perp and trans-perp conformers, respectively. The G3//B3LYP heat of formation of $OClONO_{tp}$ amounts to 43.7 kcal mol^{-1}. It should be mentioned that this value might be slightly too low, if we consider the performance of the G3//B3LYP method for the relative energy prediction of $OClONO_{tp}$ as discussed above.

TABLE 3: G3//B3LYP Heat of Formation (kcal mol^{-1}) of $ClNO_3$ Isomers

energies	$ClONO_2$	$ClOONO_{cp}$	$ClOONO_{tp}$	$OClONO_{tp}$
$E_{\mathrm{atomization},0}$	311.1	285.5	283.8	274.4
$E_{\mathrm{atomization},298}$	314.9	288.9	287.1	277.5
$\Delta H_{f,0}$	7.0	32.5	34.4	43.7
$\Delta H_{f,298}$	5.5	31.5	33.2	42.8
$\Delta H^{\mathrm{exp}}_{f,298}$	6.3 ± 0.2[a]			

[a] From ref 43.

We conclude that the relative energetics and heat of formation data support the following ordering of $ClNO_3$ isomer stability: $ClONO_2 > ClOONO_{cp} > ClOONO_{tp} > OClONO_{tp}$.

Spectroscopic Characterization of $ClNO_3$ Isomers. The calculated harmonic and anharmonic vibrational frequencies at the B3LYP/6-311G(d) level together with IR intensities for each species are provided in Table 4. These frequencies are needed to verify the true nature of stationary points and to provide the ZPEs that are listed in the table. The calculated anharmonic frequencies of $ClONO_2$ are in good agreement with the observed gas-phase fundamental vibrational frequencies[45] that are also included in the Table 4. The B3LYP predicted IR intensities and qualitative descriptions of the experimental tabulations show good agreement for most of the bands. The comparison between calculated harmonic and anharmonic vibrational frequencies shows that anharmonic corrections for the asymmetric and symmetric stretching of the N−O bonds are 49 and 30 cm^{-1}, which reasonably agrees with estimated values for the two multiple N−O bond stretching normal modes.[46] Anharmonic corrections are considerably less for all other vibrations.

The calculated vibrational frequencies of the ClOONO isomer for cis-perp and trans-perp conformers are similar; thus, any vibration can be used to distinguish between them. Nevertheless, except for N−O1 stretching vibrations having the largest IR intensity by far for both conformers, the next most intense band is predicted to be the NO2O bending vibration for the cis-perp conformer, while for the trans-perp conformer the intensities of the O1NO2 and O2OCl bending are predominant. A further difference is related to the intensities of the O2−O and O−Cl stretching vibrations. The former is somewhat higher for the cis-perp conformer, and the latter is more pronounced in the trans-perp conformer. For the $OClONO_{tp}$ isomer both N−O

TABLE 4: B3LYP/6-311G(d) Vibrational Frequencies (cm^{-1}), Zero-Point Energies (kcal mol^{-1}), and IR Intensities (km mol^{-1}) of $ClNO_3$ Isomers

species	dominant normal mode[a]	harmonic freq	ZPE	anharmonic freq	ZPE	intensities	exp[b]	
$ClONO_2$	NO_2 asymm str (A′)	1816	9.8	1767	9.6	341	1735	vs
	NO_2 symm str (A′)	1345		1315		283	1292	vs
	O1NO2 bend (A′)	825		816		192	809	s
	OCl str (A′)	778		765		13	780	ms
	NO str (A′)	561		551		54	560	s
	O1NO bend (A′)	438		431		16	434	m
	NOCl bend (A′)	246		241		0.4	270	vvw
	O2NOCl torsion (A″)	725		714		14	711	w
	O1NOCl torsion (A″)	125		127		0.5	120	
$ClOONO_{cp}$	NO1 str	1956	8.0	1913	7.8	416		
	OO2 str	1003		974		71		
	O1NO2 bend	760		745		12		
	OCl str	575		566		40		
	NO2 str	435		420		42		
	O2OCl bend	309		302		3		
	O1NO2O torsion	221		210		1		
	NO2O bend	193		210		134		
	NO2OCl torsion	110		104		0.8		
$ClOONO_{tp}$	NO1 str	1906	7.9	1870	7.8	450		
	OO2 str	999		980		35		
	O1NO2 bend	742		730		129		
	OCl str	568		558		89		
	NO2 str	434		428		45		
	NO2O bend	330		323		12		
	O2OCl bend	255		250		112		
	O1NO2O torsion	181		202		0.4		
	NO2OCl torsion	93		83		0.3		
$OClONO_{tp}$	NO1 str.	1851	7.5	1810	7.4	348		
	ClO str.	917		902		39		
	O1NO2 bend	847		828		152		
	O2Cl str.	431		424		122		
	NO2 str.	412		408		366		
	O2ClO bend	305		303		12		
	NO2Cl bend	221		214		1		
	O1NO2Cl torsion	168		188		2		
	NO2ClO torsion	102		94		2		

[a] Assignment based on inspection of normal mode animation. [b] Fundamental frequencies from ref 45.

stretching vibrations are very intensive, while O2−Cl and O1NO2 bending vibrations have somewhat lower intensities.

On the basis of these calculations, it becomes evident that the very strong band at around 1910 cm^{-1} and the strong band at around 210 cm^{-1} would support the presence of the cis-prep conformer of the ClOONO isomer, while the very strong band at around 1870 cm^{-1} and strong bands at around 730 and 250 cm^{-1} would be attributed to the trans-perp conformer. Finally, it would be possible to observe the $OClONO_{tp}$ isomer only on the basis of very strong bands corresponding to both N−O stretching vibrations found at around 1810 and 410 cm^{-1}.

TABLE 5: Vertical Excitation Energies (eV) to Excited Singlet States and Oscillator Strengths of $ClNO_3$ Isomers

		$ClONO_2$		$ClOONO_{cp}$		$ClOONO_{tp}$		$OClONO_{tp}$	
state		Δ*E*	f	Δ*E*	f	Δ*E*	f	Δ*E*	f
1	$1^1A''$	4.7	4.4 e-4	2.7	9.5 e-4	3.6	1.5 e-4	2.0	3.0 e-5
2	$2^1A'$	5.5	3.8 e-3	3.1	2.0 e-4	3.7	3.4 e-3	3.3	1.6 e-3
3	$3^1A''$	5.6	0.0	3.7	9.1 e-2	4.1	1.4 e-3	3.5	1.0 e-2
4	$3^1A'$	6.0	1.2 e-3	4.6	6.0 e-4	4.9	1.7 e-3	4.1	3.4 e-4
5	$4^1A'$	6.2	3.7 e-3	4.6	3.1 e-3	5.5	1.6 e-3	4.3	1.9 e-3
6	$4^1A''$	6.5	0.0	4.7	2.7 e-3	5.7	1.6 e-1	5.0	4.5 e-2
7	$2^1A''$	6.7	7.0 e-5	4.9	1.4 e-4	6.9	2.0 e-3		
8	$5^1A'$	7.1	8.7 e-2						
9	$5^1A''$	7.6	3.3 e-3						
10	$6^1A'$	7.7	1.9 e-1						
11	$6^1A''$	8.7	2.0 e-5						

Furthermore, the electronic spectrum is another spectroscopic property that can be used in the characterization of isomers. We have calculated the vertical excitation energies to excited singlet electronic states and oscillator strengths of $ClONO_2$, of the cis-perp and trans-perp conformers of the ClOONO isomer, and of the trans-perp conformer of the OClONO isomer employing MRD-CI+Q calculations. The results are given in Table 5. The predicted electronic spectrum of the lowest energy structure, $ClONO_2$, reveals that the excited states with the highest oscillator strengths are located at 7.1 and 7.7 eV. These values are in good agreement with the absorption bands at 6.8−7.1 and 7.75−7.85 eV observed in low-energy EEL and VUV optical absorption experiments on chlorine nitrate as recently reported by Mason et al.[47] On the other hand, the intense transition calculated at 7.7 eV might correspond to the strong band at around 8 eV in the experimental absorption spectrum. Below 6.2 eV, the $ClONO_2$ shows the low-intensity absorption at ∼3.2 eV and a very weak shoulder at ∼4.6 eV in the optical spectrum.[1] Mason et al.[47] also reported the 3.2 eV band, and a further two bands at 5.8 and 6.0 eV. Theoretical data on singlet excited states of $ClONO_2$ do not support the lowest absorption band; the weak shoulder could be ascribed to the first excited state with an energy of 4.7 eV and a very small oscillator strength. The latter two bands in the experimental spectrum might correspond to the calculated transitions of 6.0 and 6.2 eV with modest relative oscillator strengths.

A very strong transition for the cis-perp conformer of the ClOONO isomer is calculated to lie at 3.7 eV; thus, the appearance of an intense absorption band at a wavelength of around 335 nm might be attributed to this species. A relatively weak absorption around 265 nm should probably not be a characteristic feature because of a coincidence with the first

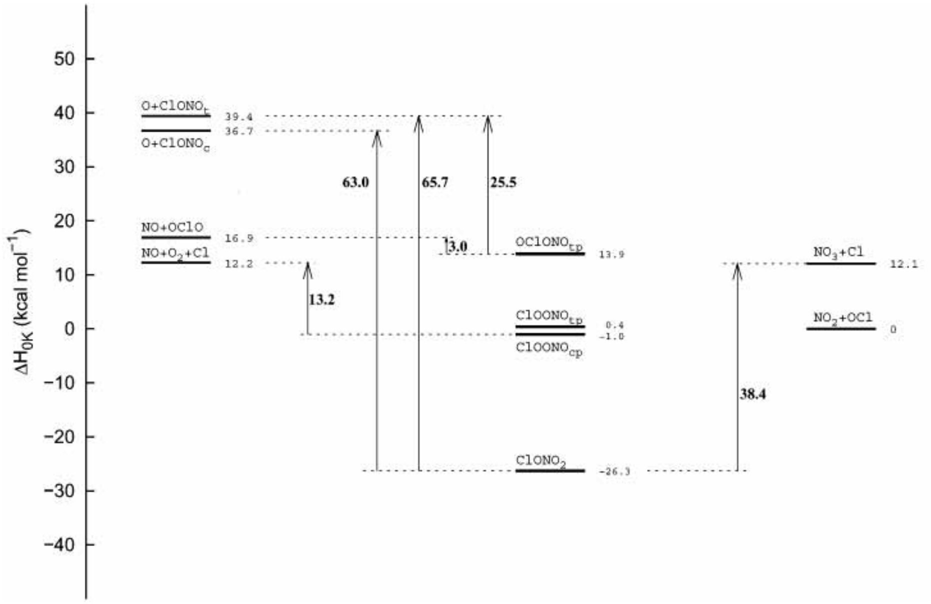

Figure 2. Relative energy diagram of $ClNO_3$ reaction pathways, calculated at the CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d) level of theory.

excited state of $ClONO_2$. At that wavelength, the $ClONO_2$ has an electronic transition, although its oscillator strength is 1 order of magnitude smaller. For the trans-perp conformer of the ClOONO isomer, the most intense band is predicted at 5.7 eV and should be characteristic for it. There are few states below or above this energy, but for all of them, the predicted oscillator strengths are lower by a factor of hundred. Note that $ClONO_2$ has singlet excited state at 5.6 eV, but its oscillator strength is zero. The most intense singlet excited states for trans-perp OClONO is located at 3.5 and at 5.0 eV, and the 10 times less intense bands appear at 3.3 and 4.3 eV. Finally, examining the predicted electronic spectra of the particular species, we can see that the first singlet excited states of the ClOONO and OClONO isomers are significantly below that of $ClONO_2$, and all these states have a very low oscillator strength.

Possible Dissociation Pathways for $ClNO_3$ Isomers. It is well established that chlorine oxides and nitrogen oxides could play an important role in catalytic cycles of ozone destruction. The CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d) calculations of the energetics of $ClNO_3$ isomers are summarized in Figure 2. We will focus on the energetics pathways of ClO_x/NO_x reactions that may lead to the formation or dissociation of $ClNO_3$ species.

To check the reliability of the results, we have compared the calculated ΔH_{0K} between NO_2 + OCl and NO_3 + Cl channels with the values evaluated from empirical data. Using experimental $\Delta H_{f,0K}$ for NO_2, OCl, NO_3, and Cl from the NIST Webbook page[48] ΔH_{0K} between the two channels is 13.9 kcal mol^{-1} which is in reasonable agreement with 12.1 kcal mol^{-1} as seen from Figure 2.

The formation of $ClONO_2$ from NO_2 and OCl is exothermic by 26.3 kcal mol^{-1}. Two primary channels, NO_2 + OCl and NO_3 + Cl, were observed in the photodissociation process of $ClONO_2$. The present calculations suggest that the second pathway requires 12.1 kcal mol^{-1} more energy than the first one.

The ClOONO isomer formation from NO_2 and OCl radicals is almost thermoneutral. The cis-perp conformer production is exothermic by -1.0 kcal mol^{-1}, while that of the trans-perp conformer is calculated to be only 0.4 kcal mol^{-1} endothermic. If the ClOONO were to dissociate, it would more likely produce NO + O_2 + Cl rather than NO + OOCl. The latter product channel is estimated to be about 3 kcal mol^{-1} above the former one. Note that, in this estimate, the energy of OOCl from the CCSD(T)/6-311+G(3df) optimization was used because it was not found as a stable structure at the CCSD(T)/6-311G(d) level.

If the trans-perp OClONO isomer is formed in the NO_2 + OCl reaction (endothermic by 13.9 kcal mol^{-1}), then its dissociation products are most likely NO + OClO, and the dissociation process would require only 3.0 kcal mol^{-1} of energy. Other possible dissociation products are ONOCl + O, but this process is endothermic by 25.5 kcal mol^{-1}, assuming a trans configuration of ONOCl. On the other hand, the ONOCl + O dissociation channel could result from $ClONO_2$ dissociation; this pathway is endothermic by 63.0 or 65.7 kcal mol^{-1} depending on either N−O bond scission. However, if the OClONO isomer would be formed in reaction 1, then its dissociation would more likely account for the ONOCl product.

IV. Summary

The geometries and relative energies of $ClNO_3$ isomers have been investigated with MP2, B3LYP, and CCSD(T) ab initio electronic structure methods together with the 6-311G(d) basis set, and at the CCSD(T) also with the 6-31G(d) and cc-pVDZ basis sets. All quoted levels of calculations have predicted the following isomers as minimum-energy structures: $ClONO_2$, ClOONO (cis-perp and trans-perp conformers), and OClONO (trans-perp conformer). At the B3LYP/6-311G(d) level also two intermolecular complexes, the cis-perp conformer of the OClONO isomer and an $OClNO_2$ species, have been characterized.

The energies have been further improved by single-point calculations. As our best estimate, the CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(d) results predict that the ClOONO with a cis-perp arrangement of the ONO−Cl and NOCl−O bonds is less stable than $ClONO_2$ by 25.3 kcal mol^{-1} and the trans-perp ClOONO is further destabilized by 1.4 kcal mol^{-1} (both at 0 K and corrected for zero-point vibrational energies). Furthermore, the heats of formation are estimated at the G3//B3LYP level following the procedure based on atomization reactions and amount to 7.0, 32.5, 34.4, and 43.7 kcal mol^{-1} for $ClONO_2$, $ClOONO_{cp}$, $ClOONO_{tp}$, and $OClONO_{tp}$ species, respectively.

The comparison of the B3LYP/6-311G(d) anharmonic vibrational frequencies together with IR intensities offer the following possibilities useful for distinguishing among the particular isomers: (i) the very strong band centered at around 1910 cm^{-1} and the strong band at around 210 cm^{-1} would support the presence of the cis-prep conformer of the ClOONO isomer, while the very strong band at around 1870 cm^{-1} and strong bands at around 730 and 250 cm^{-1} would be attributed to the trans-perp conformer; (ii) the OClONO$_{tp}$ isomer would be possible to be observed only on the basis of very strong bands at around 1810 and 410 cm^{-1} corresponding to both N−O stretching vibrations.

The reasonable agreement between electronic states calculated with the MRD-CI+Q method and the experimental values for ClONO$_2$ is encouraging for the prediction of the electronic spectra of other isomers. A consideration of the numerical results leads to the following suggestion for distinguishing among the isomeric forms: (i) the appearance of an intense absorption band at wavelength around 335 nm might be attributed to the cis-perp conformer of ClOONO; (ii) the intense absorption band at 218 nm would likely indicate the trans-perp conformer of ClOONO; (iii) for trans-perp conformer of OClONO, the intense bands predicted at 354 and 248 nm should be its characteristics. Finally, the first singlet excited state of all isomers have very low oscillator strengths, and those of ClOONO and OClONO isomers are significantly below that of ClONO$_2$.

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