JA010297G-3-a-30

Supplementary Material for:
**Theoretical Study of Chlorine Nitrates:
Implications for Stratospheric Chlorine Chemistry**

Srinivasan Parthiban and Timothy J. Lee

MST27B-1, NASA Ames Research Center, Moffett Field, California 94035-1000

Sujata Guha and Joseph S. Francisco

Department of Chemistry and Department of Earth and Atmospheric Sciences

Purdue University, West Lafayette, Indiana 47907-1393

Results and Discussion

A. Equilibrium Structures

The B3LYP optimized structure and structural parameters for ClONO₂ are presented as supplementary material in Figure S1 and Table S1, respectively. Following is a more detailed discussion of the B3LYP equilibrium geometry of ClONO₂ than that presented in the main text. Reference numbers refer to the main text.

ClONO₂. The IR spectra³⁵ of gas-phase and matrix-isolated ClONO₂ and the experimental³² structural determination strongly support a planar structure and the closely related molecules BrONO₂,³² HONO₂⁴⁵ and CH₃ONO₂⁴⁶ have already been established to be planar, therefore we have only considered planar conformations for ClONO₂. Moreover, the *ab initio* calculations for ClONO₂ reported by several laboratories (see Ref. 31 and references therein) using different levels of theory and different basis sets have all derived a planar structure for the ground state. Indeed, the computed vibrational frequencies, discussed later, show that the C_s planar structure is a minimum on the potential energy surface. The optimized structural parameters are given in Table S1 and illustrated in Figure S1. At the B3LYP/6-311G(2d) level, the Cl–O bond distance is predicted to be 1.706 Å. However, this bond length is influenced by basis set effects. The addition of *f*-functions to the oxygen and chlorine reduces the Cl–O bond length by 0.016 Å. When another set of *d* and *f*-polarization functions are added to the atoms as well as enhanced by a set of diffuse functions, the Cl–O bond length decreases further by 0.011 Å. Other structural parameters are not greatly influenced by basis set enlargement. We have re-examined this structure using the TZ2P basis set. On the basis of experience^{27–31} it is expected that the TZ2P basis set will perform well in predicting equilibrium structures for ClNO_x species. At the B3LYP/TZ2P level, our calculated structure is in very good agreement

with experiment. The difference between B3LYP/TZ2P bond distances and the experimental values are $\approx 0.01\text{--}0.03$ Å while the calculated bond angles differ by 0.2, 1.1 and 0.2° from the experimental values for the ClON, ONO_1 , and ONO_2 angles, respectively. In general, the agreement between the B3LYP/TZ2P equilibrium structure of ClONO_2 and the experimental vibrationally averaged structure is very good. Agreement between the B3LYP/TZ2P and the recently published³¹ CCSD(T)/TZ2P geometrical parameters for ClONO_2 is also good. The CCSD(T) calculations are somewhat closer to experiment for all three N–O bond lengths while the B3LYP Cl–O bond length is somewhat closer to the experimental value. Based on the excellent agreement between experiment and the B3LYP results, there is every reason to expect reliable results for the other chlorine nitrates included in this study.

B. Harmonic Frequencies and IR intensities

B3LYP harmonic frequencies for ClONO_2 are presented in Table S2, together with the complete set of experimental fundamentals. All the vibrational frequencies are calculated at the B3LYP level of theory using 6-311+G(3df) and TZ2P basis sets. Descriptions of the vibrational modes were obtained from a total energy distribution analysis⁵⁰ of the B3LYP/TZ2P Hessian matrix. It should be noted that the mode descriptions presented in Table S2 are only approximate, because there is a lot of mixing among the internal coordinate contributions.

ClONO_2 . The planar chlorine nitrate has C_s symmetry with $3N - 6 = 9$ fundamental vibrational modes, seven A' modes and two A'' modes. Table S2 lists the B3LYP harmonic vibrational frequencies and IR intensities for ClONO_2 together with the experimental fundamental vibrational frequencies.³⁵ A qualitative description of the IR intensity is also given in the experimental tabulations. Comparison of our *ab initio* harmonic frequencies with the experimental values shows good agreement, especially considering that the anharmonic correction will lower the N–O stretching modes the most. Agreement between the two basis sets for B3LYP is also good, with the main differences occurring for the two N–O stretches. The TZ2P harmonic frequencies are somewhat closer to the experimental values, and inclusion of anharmonic corrections is unlikely to change this since the correction for these modes should be no more than $30\text{--}40\text{ cm}^{-1}$. The difference between the B3LYP/6-311+G(3df) and B3LYP/TZ2P frequencies is only 0.8 percent, however, and the B3LYP/6-311+G(3df) values are higher. At the B3LYP/TZ2P level of theory, the most intense bands are predicted to be 1774 and 1331 cm^{-1} which correspond to antisymmetric NO_2 stretching (ω_1) and symmetric NO_2 stretching (ω_2). Experimentally, their intensities were found to be very strong in accordance with the calculated values. It should be noted that the B3LYP vibrational frequencies

of ClONO₂ are in good agreement with the CCSD(T)/TZ2P frequencies of ClONO₂ reported previously.³¹ It is also noteworthy that the least intense bands at the B3LYP/TZ2P level are predicted to be 731, 247 and 131 cm⁻¹ which are completely consistent with the experimental weak bands.

Table S1

Total energies (E_h), equilibrium structures, rotational constants (MHz), and dipole moments (D) of ClONO₂.^a

	6-311G(2d)	6-311G(2df)	6-311+G(3df)	TZ2P	Expt. ^b
E	0.52952	0.54232	0.55809	0.56248	
μ	0.80	0.78	0.97	1.02	0.77
r_{ClO}	1.706	1.690	1.679	1.698	1.673
r_{ON}	1.513	1.513	1.513	1.518	1.499
r_{NO_1}	1.186	1.184	1.184	1.185	1.196
r_{NO_2}	1.190	1.187	1.186	1.188	1.196
$\angle \text{ClON}$	112.9	113.1	113.4	113.2	113.0
$\angle \text{ONO}_1$	117.7	117.4	117.2	117.5	118.6
$\angle \text{ONO}_2$	108.3	108.4	108.8	108.6	108.8
A_e	12075	12143	12194	12108	12106
B_e	2707	2726	2734	2703	2777
C_e	2211	2226	2233	2210	2258

^a The energy is reported as $-(E+740)$. Bond lengths in Å and angles in degrees. See Figure S1 for labelling of atoms.

^b Vibrationally averaged structure from Ref. 32 (note that the NO₁ and NO₂ bond distances were assumed to be equivalent in the experimental determination); vibrationally averaged dipole moment from Ref. 33; vibrationally averaged rotational constants from Ref. 34.

Table S2B3LYP Harmonic frequencies (cm^{-1}) and IR intensities (km/mol)^a for ClONO₂.

Mode	Approximate Description ^b	6-311+G(3df)	TZ2P	Expt ^c
$\omega_1(a')$	NO ₂ antisymm str	1799(379)	1774(380)	1735vs
$\omega_2(a')$	NO ₂ symm str	1341(269)	1331(283)	1292vs
$\omega_3(a')$	ONO ₁ + ONO ₂ bend	828(108)	822(149)	809s
$\omega_4(a')$	ClO str + ONO ₁ - ONO ₂ bend	786(72)	782(41)	780ms
$\omega_5(a')$	O-N str	562(65)	561(59)	560s
$\omega_6(a')$	ONO ₂ - ONO ₁ bend + ClO str	437(26)	433(22)	434m
$\omega_7(a')$	ClON bend	250(0.17)	247(0.25)	270vvw
$\omega_8(a'')$	ClONO ₁ - ClONO ₂ torsion	731(10)	731(11)	711w
$\omega_9(a'')$	ClONO ₁ + ClONO ₂ torsion	135(0.17)	131(0.28)	120

^a IR absorption intensities in parentheses.^b Approximate descriptions based upon a total energy distribution analysis. There is substantial mixing between the Cl-O str, ONO₁ bend, and ONO₂ bend motions.^c Gas-phase fundamental frequencies from Refs. 35.