High-Resolution Infrared Spectra and Harmonic Force Field of Chlorine Nitrate

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Received: July 2, 1996; In Final Form: October 30, 1996[⊗]

Infrared gas-phase absorption spectra of chlorine nitrate were recorded by high-resolution Fourier transform spectroscopy. By use of natural and of ^{35}Cl-enriched $ClONO_2$ samples, the isotopic wavenumber shifts of some fundamental vibrations of $^{35}ClONO_2$ and $^{37}ClONO$ could be determined. The measured isotopic shifts, together with published spectroscopic data (vibrational wavenumbers of $ClO^{15}NO_2$, centrifugal distortion constants of $^{35}ClONO_2$ and $^{37}ClONO_2$, and mean vibrational amplitudes), were used to calculate the harmonic force field of $ClONO_2$. The new force field is compared with a recent *ab initio* calculation of the electronic ground state of $ClONO_2$.

Introduction

The $ClONO_2$ species plays an important role in the chemistry of the stratosphere by linking the NO_x and ClO_x families.[1,2] At winter in the midnorthern latitudes, $ClONO_2$ accounts for up to 50% of the total inorganic stratospheric chlorine.[3]

$ClONO_2$ is a heavy asymmetric top with a large number of fundamental vibrations. Its small rotational constants and the existence of two isotopic species, $^{35}ClONO_2$ and $^{37}ClONO_2$ with a natural abundance ratio of about 3:1,[4] lead to a very dense rotational structure in the infrared bands. Several vibrations need only very little energy for excitation, leading to an important number of overlapping hot-band absorptions at room temperature.

Since its discovery in 1955,[5] the infrared spectrum of chlorine nitrate has been studied in the gas phase[6−16] and in low-temperature matrix environments.[17,18] More recently, an accurate gas-phase structure of chlorine nitrate was determined using gas-phase electron diffraction.[19] Stratospheric concentrations of chlorine nitrate can currently only be derived from atmospheric infrared spectra.[20−22] For this reason, infrared absorption cross sections of $ClONO_2$ have been repeatedly determined at room and stratospheric temperatures.[23−27] However, no study of the isotopic shifts between the vibrational wavenumbers of the two major isotopomeres $^{35}ClONO_2$ and $^{37}ClONO_2$ has been reported up to now.

In the present study, high-resolution infrared spectra of pure $^{35}ClONO_2$ and of $ClONO_2$ in its natural form (a mixture of 75% $^{35}ClONO_2$ and 25% $^{37}ClONO_2$) are reported. For some bands, the vibrational wavenumber shifts of $^{35}ClONO_2$ and $^{37}ClONO_2$ could be determined. Together with published spectroscopic data, the shifts were used to calculate the harmonic force field of chlorine nitrate.

Chemical Synthesis. For the synthesis of chlorine nitrate, we used the reaction first proposed by Schmeisser,[28] i.e., the reaction between liquid Cl_2O and solid N_2O_5 at low temperatures. N_2O_5 was obtained using the method of Gruenhut,[29] i.e., reacting pure HNO_3 on dry P_2O_5 in excess, followed by fractional distillation. The reaction of 99% H_2SO_4 with KNO_3 at 0 °C was used to obtain pure HNO_3.

The purity of the samples was monitored by low-resolution infrared absorption spectra using a Perkin-Elmer 286 spectrophotometer. It is worth mentioning that a large amount of pure N_2O_5 was obtained and that no HNO_3 impurities were observed after pumping the sample at +10 °C.

Cl_2O was synthesized following Cady[30] by flowing a He/Cl_2 mixture over dry yellow HgO (mixed with glass chips in a 50-cm Pyrex tube). To dry the He/Cl_2 mixture, it passed columns with $CaCl_2$ and P_2O_5 before entering the reaction tube. Before and after Cl_2O synthesis, the whole reaction line was purged with pure gaseous He. The Cl_2O was trapped at −90 °C in an ethanol bath and then condensed over the N_2O_5. Several low-temperature distillations were needed to obtain pure $ClONO_2$ samples. The purity of the $ClONO_2$ samples was confirmed by quantitative agreement of the spectra with previously published IR absorption cross sections.[25,27]

For the synthesis of pure $^{35}ClONO_2$, about 5 g of isotopically enriched $Na^{35}Cl$ (99% stated purity) was available.[31] First, $H^{35}Cl$ was prepared by reaction of $Na^{35}Cl$ in H_2O with concentrated H_2SO_4 at +70 °C. By adding $K_2S_2O_8$ to the solution, gaseous $^{35}Cl_2$ was obtained. For the synthesis of $^{35}Cl_2O$, the same reaction as for ordinary Cl_2O was employed. Eventual $^{35}Cl_2$ impurities were not removed to avoid loss of the isotopically pure $ClONO_2$ sample.

The reaction line is entirely made of Pyrex glass and equipped with Teflon taps (Young Ltd.) and greaseless fittings (Rotulex). The pressure was monitored using a 1000 Torr capacitive pressure transducer (MKS Baratron). For the distillations, baths of ethanol (cryocooler Neslab CC-100) and of liquid N_2 (−196 °C) were used. Before and during the spectroscopic experiments, the $ClONO_2$ samples were stored at −80 °C in the dark for not longer than a few days. As during the chemical synthesis, the purity of the $ClONO_2$ samples was always checked by low-resolution infrared absorption spectra using a Perkin-Elmer 286 spectrometer.

Experimental Procedure. High-resolution infrared absorption spectra were recorded using the step-scan Fourier transform spectrometer of LPMA at Orsay; see ref 32 for a recent description of the instrument. The absorption cell, made of Pyrex glass and of 15-cm length, was equipped with AgCl windows. The spectral range was limited by the KCl beam splitter and an optical bandpass filter to 500−2400 cm^{-1}. The interferograms were stored and Fourier-transformed on a PC-486 DX2/66 microcomputer using the GREMLIN software.[33] The maximum unapodized spectral resolution was about 0.003 cm^{-1}.

All spectra were recorded at 296 K using total gas pressures between 0.7 and about 60 Torr. HNO_3 formation was observed

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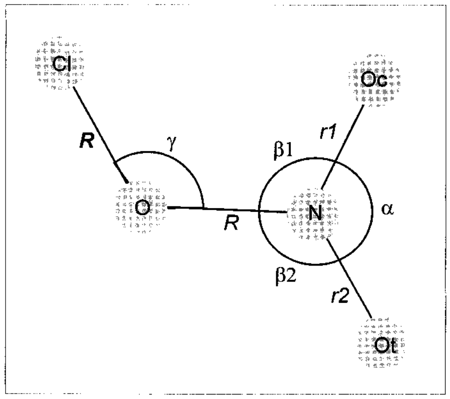
[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S1089-5639(96)01959-7 CCC: $14.00



in-plane (A'):

$S_1 = r_1$

$S_2 = r_2$

$S_3 = R$

$S_4 = \boldsymbol{R}$

$S_5 = \alpha$

$S_6 = \beta = (\beta_1 - \beta_2)/2$

$S_7 = \gamma$

out-of-plane (A"):

$S_8 = \Theta$

$S_9 = \tau$

Figure 1. Structure of $ClONO_2$ and internal symmetry coordinates. The structure is shown as determined from gas-phase electron diffraction.[19] The symmetry coordinates (in the C_s group) correspond to those used by *Miller et al.*[9]

in the spectra of ordinary $ClONO_2$, but after conditioning the cell with $ClONO_2$, they became weaker. The HNO_3 was possibly formed by reaction of $ClONO_2$ with a component of the cell, e.g., the glue fixing the windows to the cell body. Since the $^{35}ClONO_2$ spectra were recorded after those using ordinary $ClONO_2$, the HNO_3 absorption in the $^{35}ClONO_2$ spectra is nearly zero. However, small residuals of $^{37}ClONO_2$ were observed in the latter spectra. This can be due to impurities in the $Na^{35}Cl$ sample, or due to reaction of $^{35}Cl_2$ with $CaCl_2$, or due to residuals of ordinary $ClONO_2$ in the absorption cell.

Analysis

Vibrational Assignments. The molecular structure of $ClONO_2$ and the internal coordinates used in this work are given in Figure 1.

All previous infrared studies of chlorine nitrate[6-18] agree in assigning the bands centered at 1737 and 1293 cm^{-1} to the asymmetric (ν_1) and symmetric (ν_2) N−O bond-stretching modes of the NO_2 group. The bands at 711 and 121 cm^{-1} are assigned in all studies to the out-of-plane vibrations, i.e., the $O-NO_2$ out-of-plane angle bend Θ (ν_8) and the $ClO-NO_2$ torsion τ (ν_9), respectively. The band at 270 cm^{-1} is always assigned to the Cl−O−N in-plane angle bend γ (ν_7).

However, various descriptions of modes were proposed[6-18] for the fundamental bands centered at 809, 780, 563, and 434 cm^{-1} (ν_3, ν_4, ν_5, and ν_6). For the force-field calculations of this study, the band centered at 809 cm^{-1} (ν_3) was correlated with the Cl−O bond-stretching mode $\boldsymbol{R}$, because the isotopic wavenumber shift between $^{35}ClONO_2$ and $^{37}ClONO_2$ is largest for this band. The band centered at 780 cm^{-1} (ν_4) was described as the O_c-N-O_t angle bend α, because this vibration is located in all nitrates at approximately this wavenumber.[10,34,35] The band centered at 563 cm^{-1} (ν_5) should be the in-plane $O-NO_2$ angle bend β mode for the same reason. Consequently, the band centered at 434 cm^{-1} (ν_6) must show N−O bond-stretch (R) character.

The vibrational descriptions of this study are justified by the results of the force-field calculations, because the potential energy distribution (PED, see below) shows that the ν_3, ν_4, ν_5, and ν_6 normal vibrational modes are described by strongly mixed superpositions of the internal symmetry coordinates (see below), an observation also made for $FONO_2$.[35]

Isotopic Shifts, Hot Bands, and Vibrational Resonances. Wavenumbers of the ν_1, ν_2, ν_3, ν_4, ν_5, and ν_8 band centers could be determined easily. No isotopic shift was observed for the ν_1 band around 1737 cm^{-1} due to its large Q branch. The Q-branch peak of the ν_2 band of $^{37}ClONO_2$ (Figure 2) was observed to be slightly (0.5 cm^{-1}) shifted to higher wavenumbers compared to the $^{35}ClONO_2$ fundamental (1293 cm^{-1}), which is confirmed by tunable diode-laser spectra of jet-cooled $ClONO_2$ in this region.[36] Because this effect can only be attributed to a vibrational resonance with unknown strength, it was not accounted for in the calculation.

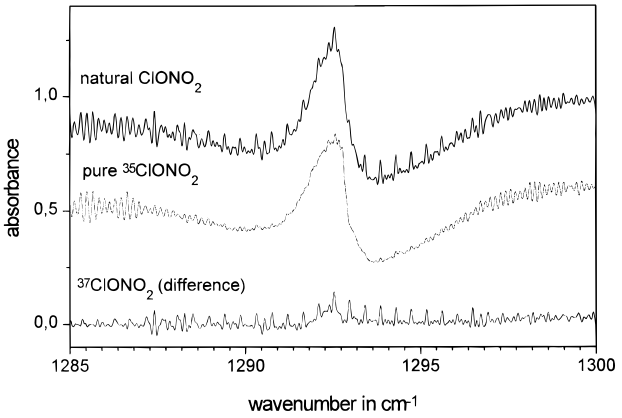


Figure 2. Central Part of the ν_2 band of $ClONO_2$. The ν_2 band corresponds to the symmetric N−O bond stretch in the NO_2 group. The Q-branch peak of natural $ClONO_2$ (upper trace) shows a small shoulder on the high-wavenumber tail, corresponding to the Q-branch peak of $^{37}ClONO_2$. This is probably due to a vibrational resonance. The spectrum of natural $ClONO_2$ shows HNO_3 impurities (ν_3/ν_4 band system), visible also in the difference spectrum (lowest trace). The isotopic shift of the ν_1 and ν_2 bands is too small to be detected with good accuracy using gas-phase spectra. This reflects that both modes are nearly pure vibrations of the NO_2 group (see Table 4).

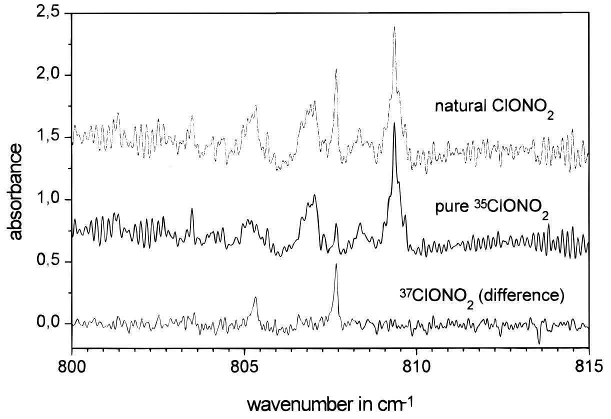


Figure 3. Q-branch region of the ν_3 band of $ClONO_2$. The upper trace shows the spectrum of natural $ClONO_2$, the middle trace that of pure $^{35}ClONO_2$, and the bottom trace the difference spectrum corresponding to $^{37}ClONO_2$. The isotopic shift is clearly visible in this band. The ν_3 band of $ClONO_2$ was in several previous studies assigned to the Cl−O bond stretch. The potential energy distribution (see Table 4) shows that the ν_3 vibrational mode is a superposition of several internal coordinates, namely, the Cl−O and N−O bond stretches and the in-plane bends of the $O-N-O_{c/t}$ (β coordinate) and Cl−O−N (γ coordinate) angles.

The ν_3/ν_4 bands at 780 and 809 cm^{-1} are most certainly coupled by Fermi resonance, but nothing is known about the strength of the interaction. For these two bands, the isotopic splitting due to ^{35}Cl and ^{37}Cl is easy to observe (Figures 3 and 4). Most of the Q-branch structure in the ν_5 band (Figure 5) is due to hot bands, which is underlined by low-temperature spectra in this region.[37]

For the vibrations below 500 cm^{-1} (ν_6, ν_7, and ν_9), harmonic and combination bands above 500 cm^{-1} were employed to determine their wavenumbers: the $2\nu_6$ band at 867 cm^{-1}, the $\nu_5 + \nu_7$ band at 836 cm^{-1}, and the $(\nu_5 + \nu_7)-\nu_9$ band at 714

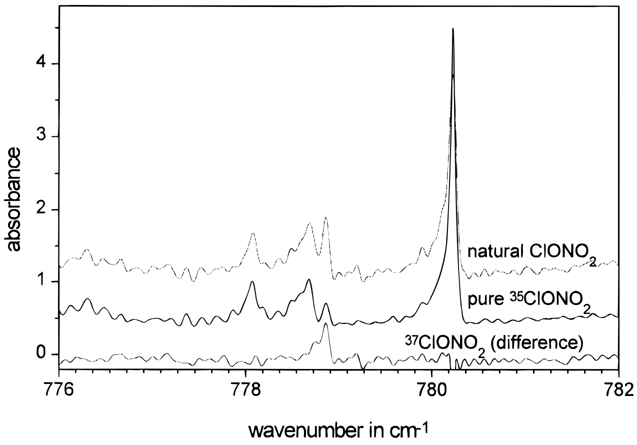


Figure 4. Q-branch region of the ν_4 band of $ClONO_2$. The upper trace shows the spectrum of natural $ClONO_2$, the middle trace that of pure $^{35}ClONO_2$, and the bottom trace the difference spectrum corresponding to $^{37}ClONO_2$. Also in this band, the isotopic shift is clearly visible. The potential energy distribution (see Table 4) shows that the ν_4 vibrational mode is also a strong superposition of several internal coordinates, namely, the N−O and Cl−O bond stretches and the in-plane bends of the NO_2 group angles, i.e., of the O_c−N−O_t (α coordinate) and O−N−$O_{c/t}$ (β coordinate) angles.

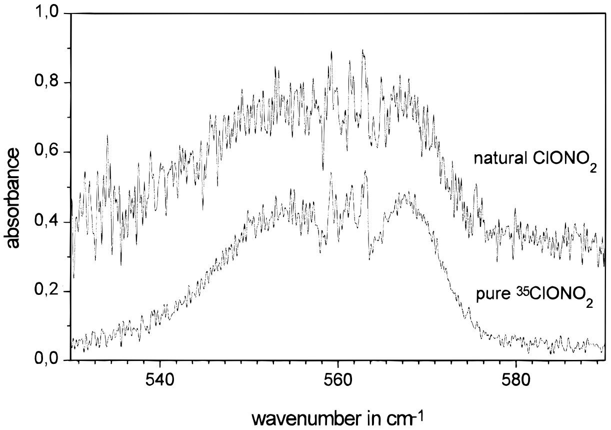


Figure 5. ν_5 Band of $ClONO_2$. The ν_5 vibrational mode is also a strong superposition of different internal symmetry coordinates, dominated by the NO_2 group angle bend (O_c−N−O_t) but also involving the Cl−O bond stretch and the Cl−O−N bond angle. The numerous peaks correspond probably to hot bands, as also confirmed by spectra of natural $ClONO_2$ at 223 K.[16,37] In the latter spectra, the Q-branch peaks at 563.1 and 561.4 cm^{-1} (the ν_5 bands of $^{35}ClONO_2$ and $^{37}ClONO_2$, respectively) are clearly distinguishable.

cm^{-1}. All band centers of $^{35}ClONO_2$ and $^{37}ClONO_2$ used in this study are given in Table 1.

Harmonic Force-Field Calculations

Input Data. The harmonic force field of $ClONO_2$, as defined by the ***GF*** matrix formalism of Wilson *et al.*,[38] has been determined experimentally only once, by Miller *et al.*,[9] who used 18 fundamental band centers of $ClO^{14}NO_2$ and $ClO^{15}NO_2$ together with an estimated $ClONO_2$ structure based on those of HNO_3 and Cl_2O. Today, the structure of $ClONO_2$ is known accurately from experiment,[19] and a large number of published spectroscopic data on $ClONO_2$ are available.

More recently, Casper *et al.*,[19] used a valence force-field calculation to predict the vibrational amplitudes, vibrational corrections for interatomic distances, and rotational constants of $^{35}ClONO_2$. While they used these predictions for comparison with electron diffraction data, no determination of the harmonic force constants or comparison of isotopic wavenumber shifts was reported.

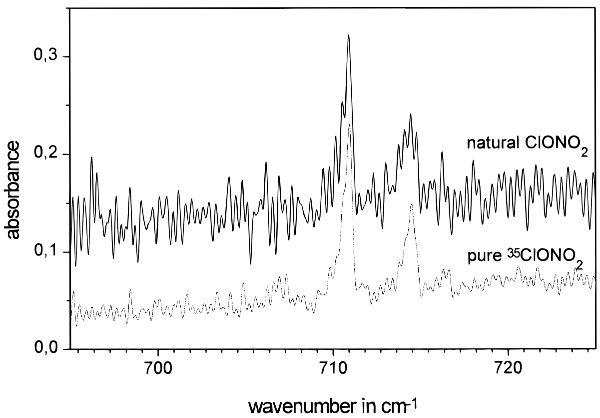


Figure 6. Q-Branch Region of the ν_8 Band of $ClONO_2$. The double-peak structure in this spectral region was already discussed by Miller *et al.*,[9] who assigned the peak at 714 cm^{-1} to the $(\nu_5 + \nu_7)-\nu_9$ band of $ClONO_2$. This assignment is confirmed by the results of the present study. This indicates that the $\nu_5 + \nu_7$ combination vibration (observed at 836 cm^{-1}) is in resonance with the ν_3 vibration (observed at 809 cm^{-1}). The harmonic force-field calculation shows good agreement for this assignment (no isotopic shift between $^{35}ClONO_2$ and $^{37}ClONO_2$; see Table 1).

For the calculation of the harmonic force field, the most important input data are the 18 fundamental band centers of the $^{35}ClO^{14}NO_2$ and $^{37}ClO^{14}NO_2$ isotopic species determined in the present study, together with the 9 fundamental wavenumbers of $ClO^{15}NO_2$ published by Miller *et al.*[9] In addition, 10 $^{35}ClONO_2$ and $^{37}ClONO_2$ ground-state centrifugal distortion constants (Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K) in an *A*-reduced Hamiltonian[39] were used. These constants were determined by a least-squares fit of the published microwave data,[40,41] as summarized in Table 2. A third set of input data was available with the 10 mean vibrational amplitudes determined from the electron diffraction intensities.[19]

Altogether, we disposed of 47 experimental input data for the harmonic force field calculations. Nevertheless, the input data were found to be insufficient to determine a complete set of off-diagonal harmonic force-field constants (see below).

Internal Symmetry Coordinates. The $ClONO_2$ molecule (Figure 1) belongs to the C_s point group with seven fundamental vibrations (in-plane) in the A′ and two fundamental vibrations (out-of-plane) in the A″ symmetry species. Consequently, there are 28 independent constants in the A′ species block of the force constant matrix and 3 independent constants in the A″ species block of the force constant matrix. We used the same $ClONO_2$ internal symmetry coordinates as Miller *et al.*[9] for reason of comparison (see Figure 1).

Using the force-field program ASYM20,[42] only four off-diagonal constants could be determined with reasonable accuracy. The other off-diagonal constants had to be fixed to zero during the calculations. In calculations with additional off-diagonal force constants, the least-squares fit was divergent or the standard deviations exceeded considerably the values of the force constants.

Because in ASYM20 the Θ coordinate is calculated using a different convention as in Miller *et al.*,[9] only force constants in the A′ block can be directly compared.

Results. After setting up the ***G*** matrix (representing the molecule's geometry), the program ASYM20 written by Hedberg and Mills[42] calculates the harmonic force-field matrix ***F*** by a nonlinear least-squares fit. Vibrations of different symmetries (in this case, A′ and A″ symmetry) can be treated independently.[38] For refinement of the ***F*** matrix, experimental

TABLE 1: Comparison between Observed and Calculated Spectroscopic Data

parameter	obsd	calcd	parameter	obsd	calcd
ν_1 ^{35}ClONO$_2$	1736.9 cm^{-1} [a]	1736.9 cm^{-1}	ν_1 ClO^{15}NO$_2$	1694.0 cm^{-1} [b]	1695.6 cm^{-1}
ν_2 ^{35}ClONO$_2$	1292.7 cm^{-1} [a]	1292.7 cm^{-1}	ν_2 ClO^{15}NO$_2$	1280.2 cm^{-1} [b]	1281.2 cm^{-1}
ν_3 ^{35}ClONO$_2$	809.4 cm^{-1} [a]	809.4 cm^{-1}	ν_3 ClO^{15}NO$_2$	804.7 cm^{-1} [b]	806.4 cm^{-1}
ν_4 ^{35}ClONO$_2$	780.2 cm^{-1} [a]	780.2 cm^{-1}	ν_4 ClO^{15}NO$_2$	772.9 cm^{-1} [b]	774.7 cm^{-1}
ν_5 ^{35}ClONO$_2$	563.1 cm^{-1} [a]	563.1 cm^{-1}	ν_5 ClO^{15}NO$_2$	556.8 cm^{-1} [b]	558.6 cm^{-1}
ν_6 ^{35}ClONO$_2$	434.0 cm^{-1} [a]	434.0 cm^{-1}	ν_6 ClO^{15}NO$_2$	432.2 cm^{-1} [b]	432.7 cm^{-1}
ν_7 ^{35}ClONO$_2$	273.3 cm^{-1} [a]	273.4 cm^{-1}	ν_7 ClO^{15}NO$_2$	263.0 cm^{-1} [b]	273.0 cm^{-1}
ν_8 ^{35}ClONO$_2$	711.0 cm^{-1} [a]	711.0 cm^{-1}	ν_8 ClO^{15}NO$_2$	693.7 cm^{-1} [b]	692.9 cm^{-1}
ν_9 ^{35}ClONO$_2$	121.9 cm^{-1} [a]	121.9 cm^{-1}	ν_9 ClO^{15}NO$_2$	122.0 cm^{-1} [b]	121.4 cm^{-1}
ν_1 ^{37}ClONO$_2$	1736.9 cm^{-1} [a]	1736.9 cm^{-1}	Δ_J ^{35}ClONO$_2$	0.537 kHz [c]	0.734 kHz
ν_2 ^{37}ClONO$_2$	1292.7 cm^{-1} [a]	1292.7 cm^{-1}	Δ_{JK} ^{35}ClONO$_2$	3.653 kHz [c]	3.741 kHz
ν_3 ^{37}ClONO$_2$	807.7 cm^{-1} [a]	807.6 cm^{-1}	Δ_K ^{35}ClONO$_2$	10.712 kHz [c]	11.157 kHz
ν_4 ^{37}ClONO$_2$	778.8 cm^{-1} [a]	779.0 cm^{-1}	δ_J ^{35}ClONO$_2$	0.096 kHz [c]	0.133 kHz
ν_5 ^{37}ClONO$_2$	561.4 cm^{-1} [a]	561.1 cm^{-1}	δ_K ^{35}ClONO$_2$	2.629 kHz [c]	2.965 kHz
ν_6 ^{37}ClONO$_2$	431.5 cm^{-1} [a]	431.7 cm^{-1}	Δ_J ^{37}ClONO$_2$	0.513 kHz [c]	0.699 kHz
ν_7 ^{37}ClONO$_2$	273.3 cm^{-1} [a]	270.4 cm^{-1}	Δ_{JK} ^{37}ClONO$_2$	3.504 kHz [c]	3.605 kHz
ν_8 ^{37}ClONO$_2$	711.0 cm^{-1} [a]	711.0 cm^{-1}	Δ_K ^{37}ClONO$_2$	12.682 kHz [c]	11.344 kHz
ν_9 ^{37}ClONO$_2$	121.9 cm^{-1} [a]	121.5 cm^{-1}	δ_J ^{37}ClONO$_2$	0.090 kHz [c]	0.124 kHz
			δ_K ^{37}ClONO$_2$	2.606 kHz [c]	2.846 kHz
Δ(O$_c$···O$_t$)	0.046 Å [d]	0.049 Å	Δ(O$_c$···O)	0.052 Å [d]	0.072 Å
Δ(O$_c$=N)	0.038 Å [d]	0.039 Å	Δ(O$_t$···O)	0.052 Å [d]	0.069 Å
Δ(O$_t$=N)	0.038 Å [d]	0.039 Å	Δ(N···Cl)	0.065 Å [d]	0.067 Å
Δ(N−O)	0.054 Å [d]	0.060 Å	Δ(O$_c$···Cl)	0.086 Å [d]	0.090 Å
Δ(O−Cl)	0.041 Å [d]	0.051 Å	Δ(O$_t$···Cl)	0.076 Å [d]	0.072 Å

[a] Fundamental wavenumbers based on the infrared data obtained in the present study. [b] Fundamental wavenumbers published by Miller *et al.*[9] [c] Centrifugal distortion constants obtained in least-squares calculations, using the microwave data published by Suenram *et al.*[40,41] [d] Mean vibrational amplitudes published by Casper *et al.*[19]

TABLE 2: Rotational Constants (in cm^{-1}) of ClONO$_2$ in the Vibrational Ground State[a]

constant	^{35}ClONO$_2$[b]	^{37}ClONO$_2$[b]
A	0.4 038 107(24)	0.4 037 926(14)
B	0.092 631 123(42)	0.090 094 958(51)
C	0.075 323 546(36)	0.073 637 457(28)
ΔJ	0.17 902(12) × 10^{-7}	0.17 112(17) × 10^{-7}
ΔJK	1.2185(10) × 10^{-7}	1.1687(23) × 10^{-7}
ΔK	3.57(64) × 10^{-7}	4.23(54) × 10^{-7}
δJ	0.032 104(69) × 10^{-7}	0.029 953(78) × 10^{-7}
δK	0.8769(78) × 10^{-7}	0.8692(96) × 10^{-7}
ΦKJ	−0.62(10) × 10^{-12}	−0.42(11) × 10^{-12}
no. of lines	74	42
J range	4−50	6−44
K_a range	0−30	0−18
rms	2.0 × 10^{-6}	1.6 × 10^{-6}

[a] Numbers in parentheses are 1 standard deviation as obtained by the least-squares fit. [b] Calculated using the microwave data of Suenram *et al.*[40,41]

TABLE 3: Harmonic Force Constants of ClONO$_2$ in Internal Symmetry Coordinates[a]

	this work			
constant[a]	set 1	set 2	Miller et al.[9]	Lee[47 d]
f_r	10.68(15)	10.60(17)	10.53(10)	11.04
f_R	1.99(4)	1.98(4)	2.27(39)	2.13
$f_{\mathbf{R}}$	3.02(8)	2.61(22)	2.83(17)	3.27
f_α	1.09(5)	0.98(6)	1.40(11)	1.37
f_β	1.65(2)	1.80(9)	3.27(11)	2.73
f_γ	3.33(23)	4.13(43)	2.19(19)	1.58
f_{rr}	1.74(11)	1.76(12)	1.69(9)	1.37
$f_{r\alpha}$	0.99(13)	0.94(15)	1.13(9)	
$f_{R\alpha}$	0.0[b]	0.0[b]	−0.20(10)	
$f_{R\beta}$	0.0[b]	−0.25(9)	0.0[b]	
$f_{\beta\gamma}$	1.08(15)	1.27(19)	0.96(20)	
f_θ	0.636(4)	0.636(4)	0.444(1)	
f_τ	0.107(3)	0.107(3)	0.111(8)	
$\Delta\nu$,[c] (%)	0.05	0.02	0.2	

[a] Stretch−stretch constants (f_r, f_R, $f_{\mathbf{R}}$, and f_{rr}) in units of *a*J Å^{-2}; stretch−bend constants ($f_{r\alpha}$, $f_{R\alpha}$, and $f_{R\beta}$) in units of *a*J Å^{-1}; bend−bend constants (f_α, f_β, f_γ, f_Θ, f_τ, and $f_{\beta\gamma}$) in units of *a*J. [b] Fixed to zero in the least-squares fit. [c] Difference of observed and calculated fundamental wavenumbers in %. [d] Due to use of different coordinates, only diagonal force constants in the A′ symmetry block of the ***F*** matrix and $f_{r\alpha}$ are compared. [e] Numbers in parentheses are one standard deviation as obtained by the least-squares fit.

data such as vibrational wavenumbers, isotopic shifts, centrifugal distortion constants, and mean vibrational amplitudes can be used.

In all calculations of this study, the fundamental wavenumbers were given unit weight, the centrifugal distortion constants a weight of 10, and the mean vibrational amplitudes a weight of 0.1, approximately corresponding to experimental uncertainties.

Two different sets of harmonic force constants were obtained (Table 3): *set 1* with 3 non-zero off-diagonal constants (f_{rr}, $f_{r\alpha}$, and $f_{\beta\gamma}$) and *set 2* with 4 non-zero off-diagonal constants (f_{rr}, $f_{r\alpha}$, $f_{R\beta}$, and $f_{\beta\gamma}$). The off-diagonal constant $f_{R\alpha}$ could not be determined in our calculations in contrast to previous work.[9] The differences between experimentally observed and calculated fundamental wavenumbers are slightly smaller when $f_{R\beta}$ is included, but the force constants are better determined in *set 1*.

Discussion. Miller *et al.*[9] have demonstrated the quality of their force field by calculating the mean value of the differences between the observed and calculated wavenumbers, obtaining a value of 0.2%. Using the harmonic force constants of the present study, values of 0.05% for *set 1* and 0.02% for *set 2* are obtained. In Table 1, a comparison of the experimental and calculated data is shown. One can state that the agreement is satisfying.

Strong mixing of internal symmetry coordinates is probably the reason for the various vibrational descriptions of the ν_3, ν_4, ν_5, and ν_6 modes in the previously published work on ClONO$_2$. The PED (see Table 4) indicates that the fundamental vibrations ν_1 and ν_2 are pure antisymmetric and symmetric NO$_2$ stretching modes, as expected by their observed wavenumbers. For the out-of-plane modes (A″ symmetry), the assignment of ν_7 to the O−NO$_2$ out-of-plane angle bend Θ and of ν_9 to the torsion τ is incontestable.

For the in-plane modes involving all five atoms (ν_3, ν_4, ν_5, ν_6, and ν_7), the PED indicates strong superpositions of the initial

TABLE 4: Vibrational-Mode-Dependent Force Constant Contribution to the Potential Energy (Potential Energy Distribution)[a]

force const	1737 cm^{-1}	1293 cm^{-1}	809 cm^{-1}	780 cm^{-1}	563 cm^{-1}	434 cm^{-1}	270 cm^{-1}	711 cm^{-1}	122 cm^{-1}
f_{r1-r1}	54.5	45.5							
f_{r2-r2}	54.3	46.3							
f_{R-R}			19.5	35.9			38.4		
$f_{\mathbf{R}-\mathbf{R}}$			14.1	34.3	16.7	20.6	14.2		
$f_{\alpha-\alpha}$				16.6	59.1		37.0		
$f_{\beta-\beta}$	11.8		14.1	15.5		90.2			
$f_{\gamma-\gamma}$			78.2		18.7		21.0		
f_{r1-r2}	−18.5	15.6							
$f_{\alpha-r1}$		−7.2			−7.2		−6.6		
$f_{\alpha-r2}$		−7.2			−8.5		−9.1		
$f_{\beta-\gamma}$	− 10.0		−34.9	−9.4	10.3	−26.7	−5.2		
$f_{\theta-\theta}$								89.9	10.1
$f_{\tau-\tau}$								10.1	89.9

[a] See ref 42 for details. All force constant combinations contributing less than 5% are not shown.

TABLE 5: Vibrational Dependence of Rotational Constants for the $\nu_9 = 1$ State (in cm^{-1})

	^{35}ClONO$_2$		^{37}ClONO$_2$	
$\nu_9 = 1$ const	pred[a]	obsd[b]	pred[d]	obsd[b]
α_A	0.003040	0.003373	0.003051	0.003385
α_B	0.000000	0.000006	0.000000	0.000003
α_C	0.000157	0.000133	0.000149	0.000129

[a] Predictions based on the force field of the present study (no anharmonicity included). [b] Values obtained using the microwave data published by Suenram and Lovas.[41]

symmetry coordinates, allowing no direct vibrational assignment. This leads in some cases to surprising results: for the vibration at 809 cm^{-1}, the Cl−O−N angle bend becomes strongly involved. This observation underlines the need of including a larger number of off-diagonal force constants in future calculations, based on new spectroscopic data using other isotopic species of ClONO$_2$. Similar observations were made in the determination of the harmonic force field of FONO$_2$.[35]

To provide an additional check of the new force field, we have calculated the vibrational variations of the principal rotational constants.[42] These contributions depend in two terms on the harmonic (quadratic) and in only one term on the cubic force constants (not determined in this study). However, in the literature, we have found only one set of rotational constants of ClONO$_2$ in an excited vibrational state determined by a rotational line-by-line analysis, namely, for the $\nu_9 = 1$ states of ^{35}ClONO$_2$ and ^{37}ClONO$_2$.[41] A comparison between predictions from the new harmonic force field and the experimentally observed rotational constants is presented in Table 5, showing very good agreement.

For the higher vibrational states of ClONO$_2$, one has to be careful with predictions from the harmonic force field, because different resonances are to be expected, which can affect the rotational constants through mixing of the wave functions.[43]

There are a number of *ab initio* studies of the ClONO$_2$ molecule;[44−47] in all studies, the structure of chlorine nitrate corresponds approximately to that later obtained by gas-phase electron diffraction.[19] In a recent work of Lee,[47] a complete *ab initio* harmonic force field (including all off-diagonal constants) and fundamental vibrational energies of ClONO$_2$ in the electronic ground state are published, using slightly different internal coordinates than this study (see Table 3). We have thus used the *ab initio* harmonic force constants to also calculate the isotopic shifts (see Table 6) with ASYM20. The agreement between predicted (*ab initio*) and observed energies and shifts is good. However, although the number of harmonic force constants of this study is small compared to the *ab initio* force field, the observed data are better reproduced by the experimental force field. We have also calculated the PED of the *ab initio* force field; all vibrations in the A′ symmetry block (except ν_1 and ν_2) are found to be strong superpositions of the internal symmetry coordinates, in general agreement with the experimental force field's PED. However, the experimental and *ab initio* PED's show differences in the precise degrees of the internal coordinates' superpositions. These questions can only be solved by future investigations of the ClONO$_2$ molecule.

Conclusion

Harmonic force constants of ClONO$_2$ were calculated using the infrared fundamental band centers of ^{35}ClONO$_2$, ^{37}ClONO$_2$, and ClO^{15}NO$_2$, combined with the ground-state centrifugal distortion constants and mean vibrational amplitudes of ^{35}ClONO$_2$ and ^{37}ClONO$_2$. All diagonal and four off-diagonal force constants were determined with good accuracy. As a test of

TABLE 6: Comparison of Experimental, *ab Initio*, and Harmonic Force-Field Vibrational Energies (in cm^{-1}) of A′ Symmetry

	^{35}ClONO$_2$			^{37}ClONO$_2$			ClO^{15}NO$_2$		
fundamental vib	obsd[a]	*ab initio*[b]	force field[c]	obsd[a]	*ab initio*[b]	force field[c]	obsd[a]	*ab initio*[b]	force field[c]
ν_1 shift	1736.9	1727.0	1736.9	1736.9	1727.0	1736.9	1694.0	1687.3	1695.6
				0.0	0.0	0.0	−42.9	−39.7	−41.3
ν_2 shift	1292.7	1304.9	1292.7	1292.7	1304.9	1292.7	1280.2	1291.8	1281.2
				0.0	0.0	0.0	−12.5	−13.1	−11.5
ν_3 shift	809.4	809.0	809.4	807.7	808.5	807.6	804.7	800.7	806.4
				−1.7	−0.5	−1.8	−4.7	−8.3	−3.0
ν_4 shift	780.2	788.7	780.2	778.8	786.5	779.0	772.9	785.3	774.7
				−1.4	−2.2	−1.2	−7.3	−3.4	−5.5
ν_5 shift	563.1	574.6	563.1	561.4	573.1	561.1	556.8	573.5	558.6
				−1.7	−1.5	−2.0	−6.3	−1.1	−4.5
ν_6 shift	434.0	432.4	434.0	431.5	429.3	431.7	432.2	430.7	432.7
				−2.5	−3.1	−2.3	−1.8	−1.7	−1.3
ν_7 shift	273.3	260.5	273.3	273.3	257.7	270.4	263.0	259.9	273.0
				0.0	−2.8	−2.9	−10.3	−0.6	−0.3

[a] This work. [b] Lee.[47] [c] This work. [d] Miller et al.[9]

consistency, the harmonic contributions to the rotational constants in the $\nu_9 = 1$ states of $^{35}ClONO_2$ and $^{37}ClONO_2$ were calculated, showing good agreement between the predictions by the harmonic force field and the experimentally determined rotational constants. A comparison with a recent *ab initio* calculation shows good general agreement concerning the complexity of the potential energy distribution.

Acknowledgment. This work was partly funded by the Commission of the European Communities under Contract STEP-CT90-0072 (ISORAC-1). We thank A. Ubelmann for maintenance of the LPMA Orsay Fourier Transform spectrometer and L. Hedberg and I. M. Mills for the program ASYM20. We also thank M. Weber and S. Voigt for critical reading of the manuscript. J. O. was supported by the Commission of the European Communities by a 24-month research training fellowship (Contract ERBREWACT 925101).

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