Chlorine Nitrate in the Atmosphere

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Abstract. This review article compiles the characteristics of the gas chlorine nitrate and discusses its role in atmospheric chemistry. Chlorine nitrate is a reservoir of both stratospheric chlorine and nitrogen. It is formed by a termolecular reaction of ClO and NO_2. Sink processes include gas-phase chemistry, photo-dissociation, and heterogeneous chemistry on aerosols. The latter sink is particularly important in the context of polar spring stratospheric chlorine activation. $ClONO_2$ has vibrational-rotational bands in the infrared, notably at 779 cm^{-1}, 809 cm^{-1}, 1293 cm^{-1}, and 1735 cm^{-1}, which are used for remote sensing of $ClONO_2$ in the atmosphere. Mid-infrared emission and absorption spectroscopy have long been the only concepts for atmospheric $ClONO_2$ measurements. More recently, fluorescence and mass spectroscopic in situ techniques have been developed. Global $ClONO_2$ distributions have a maximum at polar winter latitudes at about 20–30 km altitude, where mixing ratios can exceed 2 ppbv. The annual cycle is most pronounced in the polar stratosphere, where $ClONO_2$ concentrations are an indicator of chlorine activation and de-activation.

1 Introduction

The species NO_3Cl was first discovered by Martin and Jacobson in 1955 and called 'nitroxyl chloride' (Martin and Jacobsen, 1955; Martin, 1958). In the literature of atmospheric sciences, this species is usually written $ClONO_2$ or $ClNO_3$ and called 'chlorine nitrate', although it can be challenged if this species is indeed rightly called a 'nitrate'. It is also known as 'chloro nitrate', 'nitryl hypochlorite' or 'nitroxyl chloride'. It is a stratospheric species and acts as a reservoir of both reactive chlorine and nitrogen. In polar spring it is involved in heterogenic reactions in the stratosphere that release active chlorine which destroys ozone.

2 History

Rowland et al. (1976) proposed the existence of $ClONO_2$ in the stratosphere. First observations of this species were reported by Murcray et al. (1977) who used a balloon-borne mid-infrared solar occultation spectrometer. The spectral region near 780 cm^{-1} was used for analysis. These authors mentioned the possibility of $ClONO_2$ being a chlorine reservoir but then could only infer upper limits from their measurements. Improved measurements by the same group (Murcray et al., 1979), now in the 1292 cm^{-1} spectral region, allowed the first retrieval of a vertical $ClONO_2$ profile. In order to better constrain the knowledge on stratospheric chemistry, further balloon-borne solar occultation measurements were carried out (Rinsland et al., 1985; Payan et al., 1998; Toon et al., 1999). In addition, solar absorption measurements of $ClONO_2$ were performed from aircraft (Mankin

and Coffey, 1989; Mankin et al., 1990; Toon et al., 1992). The discovery of the ozone hole in the Antarctic (Chubachi, 1984b; Farman et al., 1985) had shifted the research interest towards polar latitudes but solar absorption measurements, requiring sunlight, were not adequate to monitor related trace gases in the polar night. Emission spectroscopy was developed as an alternative observational technique (Fischer et al., 1983; Brasunas et al., 1986), and the first measurements of nighttime profiles

5   of $ClONO_2$ were reported by von Clarmann et al. (1993), who used measurements recorded by a balloon-borne limb infrared emission spectrometer. In the following, $ClONO_2$ infrared emission measurements were also made from aircraft (Blom et al., 1995; Glatthor et al., 1998). Since then, numerous balloon-borne and aircraft missions provided $ClONO_2$ measurements.

The then recognized importance of this gas triggered spectroscopic laboratory measurements with the goal to improve its absorption cross-sections (Ballard et al., 1988; Birk and Wagner, 2000, e.g.).

10    $ClONO_2$ was first measured from space in solar occultation with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument, first from Spacelab 3 and later from further space shuttle missions (Zander et al., 1986; Rinsland et al., 1994). Further space-borne solar occultation measurements were made with the Improved Limb Atmospheric Spectrometers (ILAS and ILAS-II) on the Advanced Earth Observing Satellite (ADEOS and ADEOS-II) (Nakajima et al., 2006; Hayashida et al., 2007; Griesfeller et al., 2008) and the Atmospheric Chemistry Experiment–Fourier Transform Spectrometer (ACE-FTS) on

15   Scisat (e.g., Wolff et al., 2008). The first global $ClONO_2$ measurements in limb emission were made with the Cryogenic LIMB Array Etalon Spectrometer (CLAES) on the Upper Atmosphere Research Satellite (UARS) (Roche et al., 1993, 1994). Another space-borne mission to measure $ClONO_2$ limb emission was the Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) instrument (Riese et al., 1997, 1999). The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) provided the first long-term spaceborne measurements with global coverage of this reservoir gas. Being a

20   limb emission instrument, it provided data also for polar night regions (Höpfner et al., 2004). After an instrument failure in 2004 the MIPAS measurement allowed only measurements at reduced spectral resolution but $ClONO_2$ could still be measured (von Clarmann et al., 2009). Thermal dissociation/resonance fluorescence was the first in situ technique to measure $ClONO_2$ (http://airbornescience.nasa.gov/instrument/ClONO2, retrieved on 23 January 2017). Meanwhile also mass-spectroscopy is used for in situ detection of $ClONO_2$ (Marcy et al., 2005; Jurkat et al., 2016).

25   Remote sensing of $ClONO_2$ from the ground relies entirely on high resolution Fourier transform spectrometry. First ground-based measurements of this reservoir gas are reported by Zander and Demoulin (1988). The measurement site was Jungfraujoch in the Swiss Alps, and its high elevation was advantageous for the measurements because the measured light does not pass through the humid boundary layer, yielding a much clearer spectral signature of $ClONO_2$. Today this gas is routinely measured for monitoring purposes from stations cooperating in the framework of the Network for Detection of Atmospheric Composition

30   Change (NDACC) (e.g. Reisinger et al., 1995; Rinsland et al., 2003; Kohlhepp et al., 2011; De Maziére et al., 2018).

Summaries of stratospheric chlorine chemistry and its history are given by, e.g., Brasseur and Solomon (2005) or von Clarmann (2013).

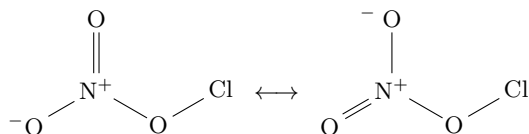



Figure 1. The chemical structure of chlorine nitrate.

Involved atoms	Value
Cl-O-N	113°
O-N-O	118.7°
	108.8°
	132.6 °

Table 1. Bond Angles of ClONO$_2$, from Rankin and Robertson (1994)

3 The Geometrical Structure

While ClONO$_2$ is a yellowish liquid at surface conditions below 295.5 K, in the stratosphere it is a trace gas with a significant role in chlorine-related chemistry. Its molar mass is 97.46 g/mol. The structure of chlorine nitrate is shown in Fig. 1. Tables 1 and 2 show the bond angles and bond lengths.

4 Sources

In the atmosphere, chlorine nitrate is formed by a three body reaction of chlorine monoxide (ClO), nitrogen dioxide (NO$_2$), and a third body M which is required to deactivate the activated complex of ClO and NO$_2$ which otherwise would immediately decompose to ClO and NO$_2$ (for details, see, e.g., Brasseur and Solomon 2005, Chapter 2.4.3., or Rowland et al. 1976).

$$(k_1) \qquad \mathrm{ClO + NO_2 + M \longrightarrow ClONO_2 + M} \tag{R1}$$

While ClO is a radical which is directly involved in ozone destruction, the resulting ClONO$_2$ is harmless for the ozone layer until the chlorine atoms are released again through heterogeneous reactions on polar stratospheric clouds in the polar winter vortex (see, Section 5.3). Species which bind reactive chlorine are called 'chlorine reservoir species', as opposed to 'source gases' or 'active chlorine'. 'Source gas' is an overarching term for more or less stable species which are released at the Earth's

Between nuclei of	Value
Cl-O	167.3 pm
(Cl-O)-N	149.9pm
NO	119.6pm

Table 2. Bond lengths of ClONO$_2$, from Rankin and Robertson (1994)

surface and transported into the stratosphere. 'Active chlorine' designates the radicals which are directly involved in ozone destruction.

The currently recommended value for rate coefficient k_1 as a function of temperature T is based on a low pressure limit of

$$k_{1;0} = 1.8 * 10^{-31} \left(\frac{T}{300} \right)^{-3.4},$$
(1)

where laboratory measurements from Zahniser et al. (1977), Birks et al. (1977), Lee et al. (1982), Leu (1984), Wallington and Cox (1986), Cox and Hayman (1988) and Molina et al. (1980) were accommodated. The corresponding high pressure limit is based on calculations by Golden and Smith (2000), who used the Rice-Ramsberger-Kassel-Marcus (RKKM) theory of chemical reactivity (Rice and Ramsperger, 1927; Kassel, 1928; Marcus, 1952):

$$k_{1;\text{inf}} = 1.5 * 10^{-11} \left(\frac{T}{300} \right)^{-1.9}$$
(2)

With these, the pressure and temperature-dependent rate coefficient can be estimated as a quasi bi-molecular rate coefficient as (Burkholder et al., 2015)

$$k_1([M], t) =$$
(3)

$$\left(\frac{k_{1,0}(T)[M]}{1 + \frac{k_{1,0}(T)[M]}{k_{1,\text{inf}}(T)}} \right) 0.6^{\left(1 + \left(\log_{10}\left(\frac{k_{1,0}(T)[M]}{k_{1,\text{inf}}(T)} \right)\right)^2\right)^{-1}}.$$

5 Sinks

The sinks of ClONO$_2$ are photolysis, gas phase reactions, and heterogeneous reactions.

5.1 Photolysis

ClONO$_2$ is photolyzed by radiation of wavelengths between 196 and 432 nm. The temperature dependent absorption cross sections currently recommended by Burkholder et al. (2015) have been measured by Burkholder et al. (1994). The absorption cross section spectra for 200, 250, and 296 Kelvin are shown in Figure 2. The photodissociation can lead to different products. The first photolysis channel is:

$$\text{ClONO}_2 + \text{h}\nu \longrightarrow \text{Cl} + \text{NO}_3$$
(R2)

For this reaction, Burkholder et al. (2015) recommend the following wavelength-dependent quantum yield Φ_1:

$\Phi_1 = 0.6$ $\qquad$ ($\lambda < 308$ nm)

$\Phi_1 = 7.143 * 10^{-3}\lambda - 1.60$ $\quad$ (308 nm $< \lambda <$ 364 nm)

$\Phi_1 = 1.0$ $\qquad$ ($\lambda > 364$ nm),

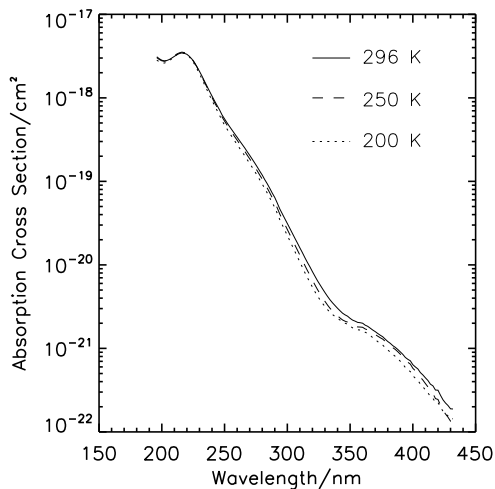



Figure 2. : ClONO$_2$ UV absorption cross sections at 200 K (dotted), 250 K (dashed), and 296 K (solid).

where λ is the wavelength in nm. The second channel is

$$\mathrm{ClONO_2 + h\nu \longrightarrow ClO + NO_2} \tag{R3}$$

and its recommended quantum yield Φ_2 is $1 - \Phi_1$. In earlier work a third channel was postulated (Brasseur and Solomon, 2005), namely

5 $\quad \mathrm{ClONO_2 + h\nu \longrightarrow ClONO + O}.$ (R4)

In the most recent JPL recommendation on kinetic data (Burkholder et al., 2015), however, it is stated that there is no evidence of any relevance of this channel. The recommended quantum yields are based on work by Nelson et al. (1996), Moore et al. (1995), Nickolaisen et al. (1996), and Ravishankara (1995).

5.2 Gas Phase Reactions

10 The most important gas phase loss reactions of ClONO$_2$ are (Brasseur and Solomon, 2005)

$$(k2) \qquad \mathrm{ClONO_2 + O \longrightarrow products} \tag{R5}$$

$$(k3) \qquad \mathrm{ClONO_2 + Cl \longrightarrow Cl_2 + NO_3} \tag{R6}$$

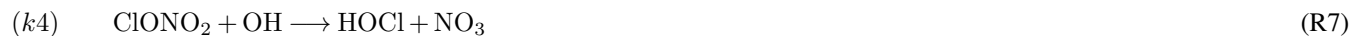
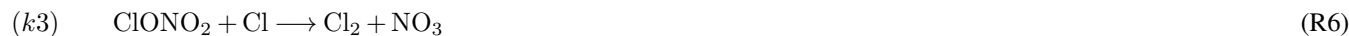
$$(k4) \qquad \mathrm{ClONO_2 + OH \longrightarrow HOCl + NO_3} \tag{R7}$$

Reaction	Rate Coefficient	A	E/R	Reference
R5	k_2	3.6×10^{-12}	840	(Goldfarb et al., 1998)
				(Molina et al., 1977)
				(Kurylo, 1977)
R6	k_3	6.5×10^{-12}	-135	(Yokelson et al., 1995)
				(Margitan, 1983)
R7	k_4	1.2×10^{-12}	330	(Zahniser et al., 1977)

Table 3. Rate constants of bi-molecular gas-phase sinks of ClONO$_2$. The Arrhenius factors A are given in units of cm^{3}molecule^{-1}s^{-1}. The temperature dependence E/R (activation energy over universal gas constant) is given in units of Kelvin. The values are taken from Burkholder et al. (2015)

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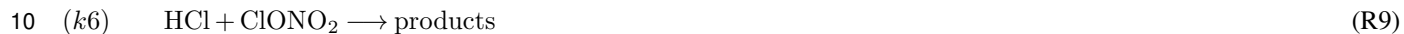
Although no photons are explicitly involved in reactions R5–R7, these sinks have an implicit dependence on sunlight, because the reactants have a diurnal cycle themselves and are more abundant in the sunlit atmosphere. The related rate coefficients k_i are temperature dependent, as described by the Arrhenius (1889) formalism:

$$k(T) = A \exp{-\frac{E/R}{T}} \tag{4}$$

5 The pre-exponential Arrhenius factors and the so-called 'activation temperatures' E/R, where E is the activation energy and R the gas constant, are listed in Table 3. Further gas phase sinks are listed in Burkholder et al. (2015) but are reported to be too slow to have any significant effect on atmospheric chemistry:

$$(k5) \quad \mathrm{H_2O + ClONO_2 \longrightarrow products} \tag{R8}$$

and

10 $$(k6) \quad \mathrm{HCl + ClONO_2 \longrightarrow products} \tag{R9}$$

5.3 Heterogeneous Reactions

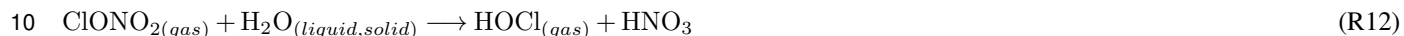
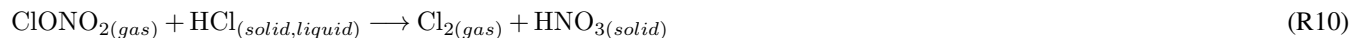
The medium for heterogeneous reactions of ClONO$_2$ are predominantly polar stratospheric clouds (PSCs), which form only in particularly cold polar winter vortices. Drdla and Müller (2012) also highlight the relevance of cold binary aerosol particles. These reactions reactivate the inorganic chlorine which is available in the form of chlorine reservoir species HCl and ClONO$_2$.

15 Størmer (1929, 1932) was the first to observe stratospheric clouds. These observations were a side effect of observations of the aurora borealis. The altitude of these clouds was estimated at 21-25 km altitude. First space-borne PSC measurements were made with the Stratospheric Aerosol Measurement II (SAM-II) on the Nimbus-7 satellite (McCormick et al., 1982). The role

of heterogeneous reactions on surfaces of cloud particles in the explanation of the Antarctic ozone hole was first discussed by Solomon et al. (1986), suggesting the relevance of Reaction R10. It was found that cold temperatures in the history of the air parcel were essential for chlorine activation, i.e. for the release of reactive chlorine from its reservoirs. The heterogeneous reactions of ClONO$_2$ relevant for chlorine activation (See, Section 6.2) are (Molina et al., 1987; Tolbert et al., 1987, 1988; Hanson and Ravishankara, 1991a, 1992b, 1993a)

$$\mathrm{ClONO}_{2(gas)} + \mathrm{HCl}_{(solid,liquid)} \longrightarrow \mathrm{Cl}_{2(gas)} + \mathrm{HNO}_{3(solid)} \tag{R10}$$

$$\mathrm{ClONO}_{2(gas)} + \mathrm{HBr}_{(solid,liquid)} \longrightarrow \mathrm{BrCl}_{gas} + \mathrm{HNO}_3 \tag{R11}$$

$$\mathrm{ClONO}_{2(gas)} + \mathrm{H_2O}_{(liquid,solid)} \longrightarrow \mathrm{HOCl}_{(gas)} + \mathrm{HNO}_3 \tag{R12}$$

The product HOCl is a short-lived chlorine reservoir in itself and releases Cl$_2$ via heterogeneous reaction with HCl. The product Cl$_2$ is photolyzed by sunlight in polar spring to give atomic Cl which is involved in catalytic ozone destruction.

Such heterogeneous reactions are typically modeled as pseudo-first-order reactions, where the reaction rate depends only on the concentration of the reactant and a rate coefficient (Brasseur and Solomon, 2005):

$$\frac{\mathrm{d[ClONO_2]}}{\mathrm{d}t} = -k\mathrm{ClONO_2} \tag{5}$$

t is time and brackets indicate concentrations. The rate coefficient k of the respective heterogeneous reaction is

$$k = \frac{\gamma \bar{c} A}{4} \tag{6}$$

γ is the surface reaction probability. Its values are tabulated in Table 4. A is the surface area density of the aerosol, and $\bar{c}$ is the mean thermal speed of a ClONO$_2$ molecule. It is calculated as

$$\bar{c} = \sqrt{\frac{8k_\mathrm{B}T}{\pi m}} \tag{7}$$

where k_B is the Boltzmann constant, T is temperature, and m is the molecular mass of ClONO$_2$.

Heterogeneous reactions of ClONO$_2$ on other surfaces have been investigated, e.g., by Hanson and Ravishankara (1991b); Hanson and Lovejoy (1995); Ball et al. (1998) for sulfuric acid solutions, Finlayson-Pitts et al. (1989) for NaCl particles, Berko et al. (1991) for NaBr particles, and Molina et al. (1997) for alumium oxide. The reader is referred to Burkholder et al. (2015) for a compilation of related reaction probabilities. In addition, hydrolysis reactions of ClONO$_2$ on TiO$_2$ and SiO$_2$ surfaces have been investigated by Tang et al. (2016).

Table 4. Relevant surface reaction probabilities as recommended by Burkholder et al. (2015). Their document contains reaction probabilities for further surfaces not mentioned here.

Reaction	Surface	Temperature / K	γ	Reference
R10	Water Ice ($H_2O(s)$)	180-200	0.3	Hanson and Ravishankara (1991a)
				Chu et al. (1993)
				Leu (1988)
	Nitric Acid Ice ($HNO_3 \cdot 3H_2O \cdot HCl$)	185-210	0.2	Abbatt and Molina (1992)
				Carslaw and Peter (1997)
	Sulfuric Acid ($H_2SO_4 \cdot nH_2O(l) \cdot HCl(l)$)	195-235	see, Burkholder et al. (2015, p. 5-114)	Shi et al. (2001)
R11	Water Ice ($H_2O(s) \cdot HBr(s)$)	200	>0.3	Hanson and Ravishankara (1992b)
				Allanic et al. (2000)
	Nitric Acid Ice ($HNO_3 \cdot 3H_2O \cdot HBr(s)$)	200	>0.3	Hanson and Ravishankara (1992b)
				Allanic et al. (2000)
R12	Water Ice ($H_2O(s)$)	180-200	0.3	Hanson and Ravishankara (1991a, 1992a, 1993b)
				Chu et al. (1993)
	Liquid Water ($H_2O(l)$)	270-290	0.025	Deiber et al. (2004)
	Nitric Acid Ice ($HNO_3 \cdot 3H_2O(s)$)	200-202	0.004	Hanson and Ravishankara (1991a, 1992a, 1993b)
				Barone et al. (1997)
	Sulfuric Acid ($H_2SO_4 \cdot nH_2O(l)$)	200-265	see, Burkholder et al. (2015, p. 5-111)	Shi et al. (2001)

6 The Role of $ClONO_2$ in Atmospheric Chemistry

6.1 $ClONO_2$ as a stratospheric chlorine reservoir

Chlorine source gases – chiefly CH_3Cl, CFC-12, CFC-11, CCl_4, HCFC-22, CH_3CCl_3 – are decomposed in the stratosphere by photolysis, OH chemistry or O^1D chemistry and finally release chlorine radicals Cl or ClO. These reactive chlorine species 5 in principle have the potential to destroy large amounts of ozone via the the catalytic reaction cycle (Stolarski and Cicerone, 1974; Molina and Rowland, 1974)

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{R13}$$

$$ClO + O \longrightarrow Cl + O_2 \tag{R14}$$

10 net : $O_3 + O \longrightarrow 2O_2$ (R15)

In the lower stratosphere, however, the equilibrium of O and O_3 is shifted massively towards the latter, making the above ClO_x-cycle inefficient due to the lack of atomic oxygen (Salawitch et al., 1993; Molina, 1996). Here, the following, so-called 'dimer cycle' gains relevance (Molina and Molina, 1987; Cox and Hayman, 1988; Barrett et al., 1988; Anderson et al., 1989):

$$2 \times (Cl + O_3 \longrightarrow ClO + O_2) \tag{R16}$$

$$ClO + ClO + M \longrightarrow Cl_2O_2 + M \tag{R17}$$

$$Cl_2O_2 + h\nu \longrightarrow ClOO + Cl \tag{R18}$$

$$ClOO + M \longrightarrow Cl + O_2 + M \tag{R19}$$

$$net : 2O_3 + h\nu \longrightarrow 3O_2 \tag{R20}$$

Similarly, the coupled catalytic cycle involving also bromine radicals Br and BrO is also independent of atomic oxygen McElroy et al. (1986b); Barrett et al. (1988).

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{R21}$$

$$Br + O_3 \longrightarrow BrO + O_2 \tag{R22}$$

$$ClO + BrO \longrightarrow Br + ClOO \tag{R23}$$

$$ClOO + M \longrightarrow Cl + O_2 + M \tag{R24}$$

$$net : 2O_3 \longrightarrow 3O_2 \tag{R25}$$

Under normal conditions, these catalytic cycles are much less disastrous than one might think. The reason is that there is typically not all of the reactive chlorine released from the chlorine source gases is available for ozone destruction. Instead, reaction of the chlorine radicals with other atmospheric species binds them, forming so-called reservoir gases, which are

relatively inert (Rowland et al., 1976; Zahniser et al., 1977; Birks et al., 1977). HCl and $ClONO_2$ are the most important chlorine reservoir gases in the atmosphere. The latter is formed by reaction R1. The importance of these reservoirs consists not only in the temporary deactivation of reactive chlorine but also allow chlorine to be transported over long distances without reaction. Release of reactive chlorine from its reservoirs is essential to understand stratospheric chemistry. In the case of chlorine nitrate, the heterogeneous reactions R10 – R12 are particularly important release reactions. After finding evidence of $ClONO_2$ in the stratosphere, Murcray et al. (1977) were the first to suggest that $ClONO_2$ can act as a chlorine reservoir.

There exists, however, a catalytic ozone destruction cycle which involves $ClONO_2$ (Brasseur and Solomon, 2005). Its importance lies in the fact that there exists a $ClONO_2$ photolysis pathway which generates atomic chlorine.

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M \tag{R26}$$

$$ClONO_2 + h\nu_1 \longrightarrow Cl + NO_3 \tag{R27}$$

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{R28}$$

$$NO_3 + h\nu_2 \longrightarrow NO + O2 \tag{R29}$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{R30}$$

$$2O_3 + h\nu_1 + h\nu_2 \longrightarrow 3O_2 \tag{R31}$$

Further catalytic cycles exist, involving HO_x and NO_x chemistry (Hampson, 1964; Crutzen, 1970)

6.2 $ClONO_2$ and Polar Stratospheric Ozone Chemistry

The detection of the Antarctic ozone hole by Chubachi (1984a) and Farman et al. (1985) puzzled the scientific community. This massive destruction of ozone in the lower polar spring stratosphere begged for explanation, because it could be quantitatively reproduced neither with the chlorine cycles (R13–R15) nor similar cycles involving NO and NO_2 or OH and HO_2. Models predicted largest ozone destruction in the middle and upper stratosphere at mid-latitudes where most reactive chlorine was expected due to the decomposition of chlorine source gases.

Ozone loss, however, was expected much weaker than the observed Antarctic ozone loss and not to be a seasonal but a steady phenomenon. Soon, the relevance of heterogeneous reactions to the release of reactive chlorine from its reservoirs was

recognized (Solomon et al., 1986). Measurements of reduced amounts of $ClONO_2$ and HCl (Farmer et al., 1987; Coffey et al., 1989; Toon et al., 1989) along with increased amounts of ClO (de Zafra et al., 1987; Solomon et al., 1987; Brune et al., 1989) supported this hypothesis. Re-appearance of sunlight after the polar night entailed photolysis of Cl_2 resulting from the heterogeneous decomposition of $ClONO_2$ (and similarly of $HOCl$ resulting from the heterogeneous decomposition of HCl).

5   Largest lower stratospheric ClO concentrations were indeed measured in sunlit air masses which had passed polar stratospheric clouds allowing heterogeneous processing (Yudin et al., 1997). Since sunlight is essential for large ozone loss, the severity of an ozone hole depends largely on how long heterogeneous chlorine activation still competes with the reformation of reservoirs in spring when enough sunlight is available for keeping the catalytic cycles going. With the catalytic dimer cycle (R16–R20) a mechanism was available, which did not depend on atomic oxygen, which is only available in sizeable amounts at higher
10   altitudes than those of the ozone hole. With this, the puzzle of the seasonality and the altitude range of polar stratospheric ozone destruction was solved, and measured ClO concentrations and ozone loss could be modeled reasonably well under consideration of heterogeneous chlorine activation (Jones et al., 1989). Anderson et al. (1991) estimated the contribution of the ClO dimer cycle to Antarctic ozone destruction at about 75%. For a more thorough summary of the history of ozone hole research and hypotheses suggested to explain this massive ozone depletion, see Solomon (1990), Brasseur and Solomon (2005),
15   Solomon (1999), or von Clarmann (2013). An updated view on polar ozone chemistry, including also reactions involving sulfate aerosols, is presented by Solomon et al. (2015).

    The reformation of $ClONO_2$ via R1 would make the catalytic ozone destruction cycle (R16–R20) less efficient. However, particles of polar stratospheric clouds can remove gaseous HNO_3 from the air, which leads to reduced amounts of reactive nitrogen, *viz.* NO and NO_2 (McElroy et al., 1986a). Nitrogen compounds are irreversibly removed from altitudes where the
20   cloud particles are formed through sedimentation of HNO_3-laden particles grown by condensation (Toon et al., 1986; Salawitch et al., 1988). This denitrification slows down reformation of $ClONO_2$ and thus has the potential to accelerate catalytic ozone destruction. While denitrification was indeed observed in polar winter vortices, (Fahey et al., 1990; Toon et al., 1990; Deshler et al., 1991), it is not necessarily correlated with the depth of the ozone hole (Santee et al., 1998; Brasseur and Solomon, 2005). Denitrification in early winter goes along with dehydration of the stratosphere, which prevents sustained springtime
25   heterogeneous chlorine reactivation (Portmann et al., 1996; Chipperfield and Pyle, 1998). This tends to counter-balance the effect of denitrification on chlorine activation and ozone destruction.

    In summary and roughly speaking, interaction of the following processes bring about the ozone hole: In the cold polar winter vortex, where subsidence has brought air from higher altitudes rich in chlorine reservoirs down into the lower stratosphere, polar stratospheric clouds form, on the surfaces of which the chlorine reservoirs are broken up by heterogeneous reaction.
30   Polar spring sunlight photolyzes the intermediate products and produces reactive chlorine which, chiefly via the ClO dimer cycle, destroys ozone. Denitrification contributes by removing reactive nitrogen and thus impedes efficient reformation of $ClONO_2$. More recent studies mention the importance of cold binary sulphate aerosol particles as surface for heterogeneous chlorine activation besides polar stratospheric clouds (Drdla and Müller, 2012).

    Antarctic and Arctic polar winter ozone depletion follows roughly the same mechanisms. The most pronounced differences
35   are that the Arctic vortex is typically not as cold as its Antarctic counterpart, entailing less frequent occurrence of polar strato-

spheric clouds. Stratospheric final warmings occur typically earlier in the season than in the Antarctic, terminating chlorine activation on polar stratospheric clouds. Stratospheric major and minor warmings which interrupt chlorine activation temporarily are common in the Arctic but occur very rarely in Antarctic winters. Due to stronger wave activity on the Northern hemisphere there are more frequent excursions of the polar vortex to sunlit lower latitudes.

5   Evidence of Arctic chlorine activation was furnished either by observations of ClO (Manney et al., 1994) or by measurement of largely reduced amounts of the reservoirs HCl and $ClONO_2$ by ground-based mid-infrared spectrometry (Adrian et al., 1994; Blumenstock et al., 1997; Notholt et al., 1994, 1995, just to name a few). The differences in typical meteorological conditions discussed above lead to differences in chlorine deactivation in Antarctic versus Arctic spring. The lack of NO_2 after denitrification rules out formation of sizeable amounts of $ClONO_2$ in the Antarctic, and HCl is the chiefly formed reservoir

10   there. Conversely, ozone is usually too high in the Arctic to allow efficient HCl formation, and denitrification is much less of an issue in the Arctic. In the sunlit atmosphere, HNO_3 is photolyzed and sufficient abundances of NO_2 thus allow re-formation of $ClONO_2$, which in some winters largely exceeds HCl formation (Müller et al., 1994; Adrian et al., 1994; Douglass et al., 1995; Rinsland et al., 1995; Santee et al., 1996; Payan et al., 1998; Santee et al., 2008). Huge amounts of $ClONO_2$ in Arctic spring were measured by, e.g., von Clarmann et al. (1993); Roche et al. (1994); Blom et al. (1995); von Clarmann et al. (1997).

15   A sensitivity study showing how PSC formation and denitrification affects $ClONO_2$ and ozone chemistry is shown in Rex et al. (1997) in order to explain large Arctic ozone loss in the particular cold winter of 1995/96.

     Since $ClONO_2$ formation depends on photolysis of HNO_3, largest $ClONO_2$ concentrations are found close to the edge of the Arctic vortex while chlorine in the dark part of the vortex remains activated longer (e.g., Toon et al., 1992). In Figure 3 the seasonal formation of $ClONO_2$ at polar latitudes as seen by MIPAS can be clearly seen. Figure 4 shows MIPAS measurements

20   of $ClONO_2$ over the Arctic at 18 km altitude in March 2011. The 'collar' of enhanced values, a phenomenon first described by Toon et al. (1989) and first attributed to mixing of vortex air rich in ClO with air from lower latitudes with larger NO_2 concentrations, is clearly visible. More recent explanations of enhanced $ClONO_2$ abundances in this region involve in situ deactivation of ClO with NO_2 released from HNO_3 in the sunlit part of the vortex, either via phololysis or OH chemistry (Chipperfield et al., 1997).

25   Volcanic eruptions such as that of Mount Pinatubo can cause large stratospheric aerosol loading (e.g. Browell et al., 1993). The role of this volcanic sulfate aerosol as a medium for heterogeneous reactions releasing reactive chlorine has been discussed by (e.g. Prather, 1992; Brasseur, 1992; Toon et al., 1993b; Wilson et al., 1993; Dessler et al., 1993). Borrmann et al. (1997), however, found that chlorine activation by heterogeneous reactions on volcanic cloud droplets is much less efficient than chlorine activation by polar stratospheric clouds. According to Cox et al. (1994), $ClONO_2$ hydrolysis on sulfate aerosol could

30   have sizeable effects if temperatures are below 190 K and a lot of aerosol particles are available. The role of sulfate aerosols for chlorine activation in polar vortices seems limited due to the predominant chlorine activation on polar stratospheric clouds.

6.3 $ClONO_2$ and Extra-Polar Stratospheric Chlorine Chemistry

Polar stratospheric clouds are the most efficient but not the only medium to provide liquid or solid surfaces on which heterogeneous reactions can take place. In middle and low latitudes where temperatures are too high for the formation of polar

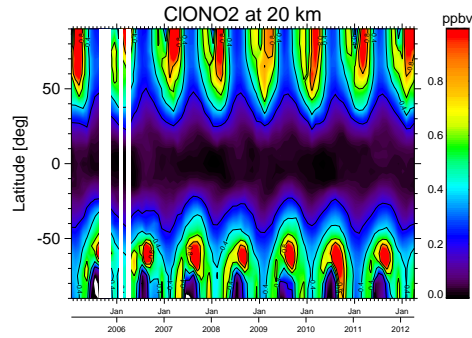



Figure 3. The temporal development of ClONO$_2$ at 20 km, based on MIPAS monthly mean mixing ratios. White stripes represent data gaps due to missing measurements. Figure from von Clarmann et al. (2009), used under CC Attribution 3.0 license.

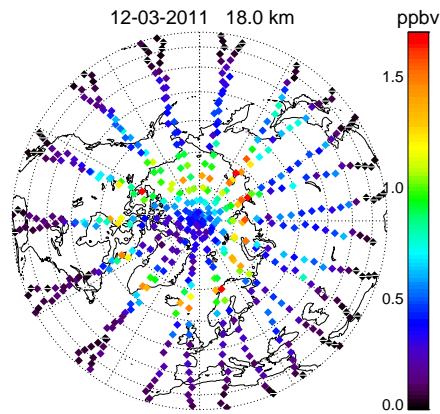



Figure 4. Chlorine nitrate measurements by MIPAS over the Arctic at 18 km altitude on 12 March 2011. The 'collar' of large mixing ratios surrounds the core area of the polar vortex where ClONO$_2$ values are lower. Figure from von Clarmann et al. (2009), used under CC Attribution 3.0 license.

stratospheric clouds, sulfate aerosol is the most likely candidate (Pitari et al., 1991). The aerosol cloud of the Mount Pinatubo eruption served as an ideal test case to investigate the role which sulfate aerosols play in mid-latitudinal stratospheric ozone depletion (McCormick et al., 1995). Both in the tropical stratosphere (Grant et al., 1992) and globally (Randel et al., 1995) less ozone was found in the aerosol-loaded atmosphere after the eruption. Weaver et al. (1993) could not corroborate this hypothesis

5   because no correlations between ozone depletion and aerosol surface area density was found. Hofmann et al. (1994), however, found that low ozone concentrations were measured in air which came from high latitudes. There cold air along with the exponential decrease of the reaction probability of R12 with temperature (Robinson et al., 1997) provided more favorable conditions for the hydrolysis of $ClONO_2$. Wilson et al. (1993) and Avallone et al. (1993) indeed report enhanced ClO concentrations in air masses with higher aerosol loading. Chlorine activation was found to strongly depend on aerosol-loaded air being exposed

10   to temperatures below 195 K (Kawa et al., 1997). Solomon et al. (2016) found chlorine activation on liquid sulfate aerosols near the northern monsoon regions in their model calculations.

Along with increased chlorine activation, reactive nitrogen is removed in the aerosol cloud (Fahey et al., 1993). It is for this reason that in the aerosol-loaded air after the Pinatubo eruption the chlorine catalytic cycle outweighed the nitrogen cycle and was second in efficiency only to the HO_x catalytic cycle (Kinnison et al., 1994). As described above for polar ozone chemistry,

15   removal of NO_2 via sequestering of HNO_3 on aerosol leads to reduced reformation of $ClONO_2$(Tie and Brasseur, 1996), and buildup of HCl gains importance as reservoir reformation process (Webster et al., 1998).

6.4 $ClONO_2$ and Solar Proton Events

Solar activity does affect atmospheric chemistry in multiple ways. In particular, the role of solar proton events has been studied. Most investigations focus on these events as a source of NO_x (e.g. Jackman et al., 1990) but Solomon and Crutzen (1981)

20   highlight the importance of ClO_x chemistry in this context. The question is if solar proton events accelerate or decelerate ozone destruction by active chlorine. According to theoretical studies by Jackman et al. (2000) the increased abundance of NO_x would accelerate $ClONO_2$ formation and thus reduce the amount of reactive chlorine and decelerate ozone destruction by ClO_x. This hypothesis seemed to be refuted by von Clarmann et al. (2005) who found in MIPAS data measured after the Halloween 2003 solar proton event increased amounts of ClO in the sunlit part of the polar vortex. Only in the dark part of

25   the polar vortex pole-ward of 70°N ClO was observed to decrease (Funke et al., 2011). Damiani et al. (2012), however, found a negative response of ClO to the January 2005 solar proton event. This result is consistent with that of von Clarmann et al. (2005) insofar as protons in a sunlit atmosphere lead to chlorine activation, while protons in a dark atmosphere lead to chlorine de-activation via $ClONO_2$ formation. Ionization rates of the solar proton event in 2012 were too small to cause significant ClO changes.

30 6.5 $ClONO_2$ in the Polar Troposphere and the Marine Boundary Layer

$ClONO_2$ is predicted to be important in the springtime Arctic boundary layer ozone chemistry (Wang and Pratt, 2017). Via multiphase reaction it contributes to the generation of Cl_2. Associated snowpack chemistry, however, is reported to be still

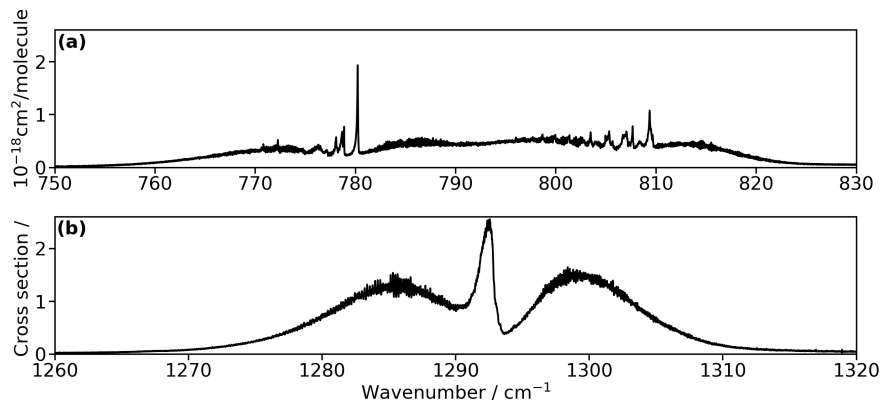



Figure 5. Example of an absorption cross section of ClONO$_2$ (a) ν_4, ν_3 and (b) ν_2 bands, measured by Wagner and Birk (2003) in a cuvette at a temperature of 297.4 K and pressure of 100 hPa.

poorly understood. In a model study by Sander et al. (1999), heterogeneous reactions of ClONO$_2$ had only a negligible effect in the marine boundary layer.

7 Spectroscopy

As discussed in Sec. 5.1, ClONO$_2$ makes a contribution to the absorption cross section spectrum in the UV, where photolyzing
5   radiation is absorbed. The UV absorption cross section is for radiation of wavelengths between 196 and 432 nm is shown in Fig. 2.

The infrared spectrum of ClONO$_2$ is only marginally resolved (Butler et al., 2007), thus measured absorption cross section spectra are used instead of line parameters as a reference in atmospheric radiative transfer calculations. In the infrared spectral region, Birk and Wagner (2000); Wagner and Birk (2003) measured the absorption cross section for ClONO$_2$ in a laboratory
10   study. They synthesized ClONO$_2$ from nitrogen pentoxide (N$_2$O$_5$) and dichlorine monoxide (Cl$_2$O) under vacuum conditions into a gas cuvette and measured the absorption cross sections with a high-resolution Fourier transform spectrometer. The temperature range was 190–296 K and the pressure range 0–150 hPa. An example of these cross sections is shown in Fig. 5 for (a) ν_4 (780 cm^{-1}), ν_3 (810 cm^{-1}) and (b) ν_2 (1290 cm^{-1}). Worst-case relative errors are reported as $^{+4.5}_{-5.5}\%$. These absorption cross sections are recommended for use in atmospheric research by the most recent version of the HITRAN (high resolution
15   transmission) spectral database (Gordon et al., 2017) and have been the recommendation since the 2004 version of HITRAN (Rothman et al., 2005)."

A typical spectral signal of enhanced ClONO$_2$ in the atmosphere is shown in Fig. 6. This measurement of MIPAS/Envisat (black line) during the Arctic springtime 2003 at a tangent altitude of 17.3 km corresponds to a retrieved volume mixing ratio

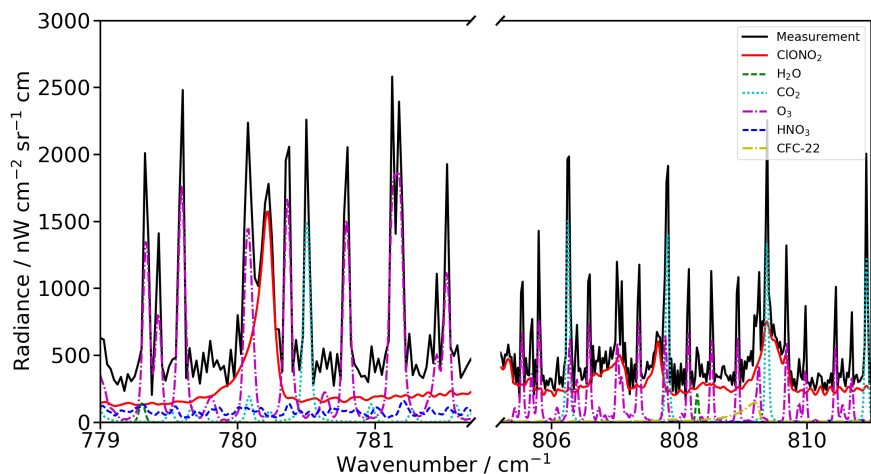



Figure 6. Example of an atmospheric limb emission infrared spectrum measured by MIPAS/Envisat (orbit 05371) on 11 March 2003 07:36:25 UTC at a tangent altitude of 17.3 km (black solid line). The contributions of single gases are calculated with the radiative transfer model KOPRA (Karlsruhe Optimized and Precis Radiative Transfer Algorithm, Stiller 2000) and shown as colored lines ($ClONO_2$ is shown as red solid line).

of 2.3 ppbv of $ClONO_2$. In this spectral region of the $ClONO_2$ ν_4 and ν_3 band (see Fig. 6, red solid line), also other atmospheric trace (mainly O_3 and CO_2) gases have absorption features (see Fig. 6, colored lines).

Butler et al. (2007) try to understand the rotational structure of $ClONO_2$ from measurements in the mm and sub-mm spectral regions where the transitions are better resolved and to apply this knowledge to the infrared bands. These activities are meant as one step towards line-by-line modeling of the infrared spectrum of $ClONO_2$. The paper also summarizes existing high-resolution studies of the $ClONO_2$ spectroscopy in the microwave and infrared regions, but these are of no direct relevance to atmospheric spectrometry yet.

8   Measurement Techniques

8.1   Remote Sensing

The only remote sensing technique by which $ClONO_2$ is measured is mid infrared spectrometry. $ClONO_2$ has suitable spectral bands at 779 cm^{-1}, 809 cm^{-1}, 1293 cm^{-1} and 1735 cm^{-1}. The bands at lower wavenumbers are used both in emission and absorption geometry, while the bands at higher wavenumbers are used in absorption spectrometry only. By far the most common remote sensing technique for $ClONO_2$ is Fourier transform spectrometry (FTS). Some earlier measurements have been made with grating spectrometers.

8.1.1 Absorption Spectrometry

Earth observation by absorption spectroscopy uses a natural background light source. The most common source of radiation is the sun. Occasionally the moon is used (e.g., Notholt, 1994). Absorption of starlight has not yet been applied to $ClONO_2$. The information is contained in the absorption of background radiance by atmospheric constituents. While the signal to noise
5   ratio is superior to that of emission measurements and the temperature dependence of the signal is less of a problem, the major drawback of absorption spectrometry is that the feasibility of measurements depends on the astronomical conditions, since the line of sight of the measurement must hit the background source. Thus, solar absorption measurements are possible neither during night nor during polar winter.

Ground-based solar absorption spectrometry:

10   Earliest ground-based solar absorption measurements of $ClONO_2$ were made with high resolution Michelson Fourier transform spectrometers at the International Scientific Station of the Jungfraujoch, Switzerland in June 1986 (Zander and Demoulin, 1988). Measurements at this high altitude offer the advantage that the ray-path usually does not cross the moist boundary layer, that the tropospheric column of interfering species is smaller and that pressure broadening of interfering spectral lines is less relevant. Since the rotational structure and, *a fortiori*, pressure broadening, are not resolved in the case of $ClONO_2$, ground
15   based measurements provide no vertical profile information but only vertical column densities. The detection of the Antarctic ozone hole provided motivation to monitor relevant species, including $ClONO_2$, also from ground. Farmer et al. (1987) measured Austral spring column amounts above McMurdo station with the MkIV interferometer[1]. Similarly, motivated by the desire to understand Arctic ozone chemistry and chlorine activation/deactivation and to identify its similarities with and differences to the Antarctic, ground-based measurements were performed at polar research stations in Ny-Ålesund, Spitsbergen
20   (Notholt et al., 1994, 1995), Esrange, Kiruna, Sweden (Adrian et al., 1994; Blumenstock et al., 1997, 1998; Wegner et al., 1998; Blumenstock et al., 2006), Åre, Sweden (Bell et al., 1994), Harestua, Norway (Galle et al., 1999), St. Petersburg, Russia (Virolainen et al., 2015), and Eureka, Canada (Batchelor et al., 2010). Multiple-site observations (Ny-Ålesund, Kiruna, Haresuta) were reported by, e.g., Mellqvist et al. (2002). Given the strong excursions of the polar vortex, even measurements from Aberdeen, Scotland (Bell et al., 1998a, b) contributed to polar ozone research. The scientific goal of these $ClONO_2$ measure-
25   ments was to study chlorine activation and deactivation during polar winter. Early non-polar column measurements of $ClONO_2$ were made with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument from the Table Mountain Observatory, California (Gunson and Irion, 1991).

     Later the research interest moved towards identification of multi-year regularities and time series (Rinsland et al., 1996b; Blumenstock et al., 2000; Reisinger et al., 1995; Notholt et al., 1997; Rinsland et al., 2003, 2010; Kohlhepp et al., 2011, 2012,
30   just to name a few). Meanwhile world-wide monitoring of stratospheric $ClONO_2$ is performed by the Network for Detection of Atmospheric Composition Change (NDACC De Maziére et al. 2018), using high-resolution Fourier transform infrared

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[1]Although Farmer et al. (1987) was published before (Zander and Demoulin, 1988), the measurements reported in the latter paper preceded those of the former paper.

solar absorption spectroscopy. NDACC infrared stations are situated at Ny-Ålesund, Spitsbergen, Zugspitze, Germany, Kiruna, Sweden, Izaña, Tenerife, Thule, Greenland, Lauder, New Zealand, Arrival Heights, Antarctica, Jungfraujoch, Switzerland, Rikubetsu, Japan and Eureka, Canada[2]. Further associated stations which made $ClONO_2$ measurements available are on Kitt Peak (Arizona) and Wollongong (Australia). Details on instrumentation and retrieval as well as references to the original papers

5 are summarized in, e.g., Kohlhepp et al. (2012).

Ground-based lunar absorption spectrometry:

Since solar absorption spectrometry is not possible during polar night, the moon was identified as an alternative source of background radiation. Lunar absorption spectrometry enabled $ClONO_2$ measurements during the entire winter and was applied in Ny-Ålesund, Spitsbergen (Notholt et al., 1993; Notholt, 1994; Notholt et al., 1995).

10 **Air-borne solar absorption spectrometry:**

First airborne solar absorption measurements of $ClONO_2$ by high-resolution Fourier transform spectrometry were performed within the framework of the Airborne Antarctic Ozone Experiment (AAOE) (Coffey et al., 1989; Mankin and Coffey, 1989). The Atmospheric Effects of Stratospheric Aircraft (ASHOE/MAESA) ER-2 aircraft mission coincided in time with the ATLAS-3 space mission (Michelsen et al., 1999) (see Section 8.1.1).

15 Airborne $ClONO_2$ solar absorption measurements in the northern polar region in the context of the Airborne Arctic Stratospheric Expedition (AASE) in 1989 were reported by Mankin et al. (1990); Toon et al. (1992). $ClONO_2$ measurements from the folow-up campaign in 1992 (AASE-2) were published by Toon et al. (1993a).

While, as with ground-based measurements, no profile information but only vertical column densities can be measured, airborne measurements of stratospheric gases are less interfered by tropospheric constituents. Further, airborne measurements

20 cover a wide range of geolocations. This characteristic was taken advantage of by Toon et al. (1994) who analyzed the latitude distribution of column amounts of trace gases including $ClONO_2$.

Balloon-borne solar occultation spectrometry:

In contrast to measurement geometries discussed so far, balloon-borne solar occultation provides profile information of $ClONO_2$. The rising or setting sun is observed under varying negative elevation angles. The resulting limb sequence of spectra is inverted

25 to give an altitude profile of the target species.

Murcray et al. (1977) analyzed the spectral region near $780 \, cm^{-1}$ in spectra measured in 1975 from a balloon-borne platform for a possible signature of $ClONO_2$ but could only infer upper limits. Spectra measured during subsequent flights were analyzed for a possible signal near $1292 \, cm^{-1}$ without success (Murcray et al., 1978). Analysis of solar occultation spectra measured in 1978 allowed to infer a concentration profile of $ClONO_2$ using its signature near $1292 \, cm^{-1}$ (Murcray et al., 1979). Further

30 balloon-borne solar occultation measurements were reported by Rinsland et al. (1985), where again the band near $780 \, cm^{-1}$

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[2]Also stations in Toronto, Mauna Loa, Bremen and Harestua are equipped to measure $ClONO_2$ but by the time of this writing no related $ClONO_2$ data were found on the NDACC server.

was analyzed. Solar occultation measurements of $ClONO_2$ in the Arctic were made from stratospheric balloons launched from Kiruna, Sweden (Payan et al., 1998) and from Fairbanks Alaska (Sen et al., 1999; Toon et al., 1999, 2002). With the advent of satellite missions, the focus of balloon-borne measurements shifted somewhat towards validation of space-borne measurements.

Space-borne solar occultation spectrometry:

First space-borne measurements of $ClONO_2$ were made with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument from Spacelab 3 in solar occultation (Zander et al., 1986, 1990). Due to the Challenger Space Shuttle accident in January 1986 the ATMOS instrument was not flown until the ATLAS-1 Space Shuttle mission in March 1992, and again $ClONO_2$ was measured (Rinsland et al., 1994). Two further missions followed and provided $ClONO_2$ data: ATLAS-2 in April 1993 (Rinsland et al., 1995) and ATLAS-3 in November 1994 (Rinsland et al., 1996a). A revised analysis of these data, using an improved retrieval algorithm, has been published by Irion et al. (2002).

In August 1996 the Japanese ADEOS satellite was launched into a polar suns-synchronous orbit. Part of the payload was the Improved Limb Atmospheric Spectrometer (ILAS), which, similar as ATMOS, employed the solar occultation measurement geometry. The mission stopped in June 1997. Measurements of $ClONO_2$ in winter/spring 1996/97 were published by Nakajima et al. (2006) and Hayashida et al. (2007). The follow-up instrument ILAS-II on the ADEOS-II satellite was operational from April to October 2003 and also provided $ClONO_2$ data (Griesfeller et al., 2008).

The Atmospheric Chemistry Experiment – Fourier Transform Spectrometer (ACE-FTS) is a solar occultation instrument on the Canadian SciSat Earth observation satellite, launched in August 2003. $ClONO_2$ measurements were published by Wolff et al. (2008), Mahieu et al. (2005), Nassar et al. (2006), Dufour et al. (2006), Santee et al. (2008), Jones et al. (2011), Waymark et al. (2013) and Sheese et al. (2016). ACE-FTS is still operational at the time of this writing.

8.1.2 Emission Spectrometry

Balloon-borne limb emission spectrometry:

First quantification of $ClONO_2$ in atmospheric limb emission spectra was reported by Brasunas et al. (1988), who used a balloon-borne cryogenic Fourier transform spectrometer SIRIS. Arctic winter and spring profiles were retrieved from spectra measured with the balloon-borne version of the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS-B) by von Clarmann et al. (1993) with an instrument type suggested by Fischer et al. (1983). A preliminary $ClONO_2$ retrieval from the same measurements is found in Oelhaf et al. (1994). Müller et al. (1994) reproduced these measurements with a box model. After the loss of the MIPAS-B instrument in March 1992 a new cryogenic limb emission spectrometer was built (MIPAS-B2) and employed in a series of measurement campaigns (Friedl-Vallon et al., 2004). $ClONO_2$ results from these campaign were reported by von Clarmann et al. (1997) and Wetzel et al. (2006, 2008, 2010, 2013). Many of these flights were dedicated to the validation of satellite missions.

Air-borne emission spectrometry:

Two versions of air-borne MIPAS-type instruments were built, one to be operated in an upward looking mode from a Transall aircraft (MIPAS-FT) and another for limb emission sounding from the high-flying aircraft M55-Geophysica (MIPAS-STR). $ClONO_2$ results were reported by Blom et al. (1995); Glatthor et al. (1998); Pfeilsticker et al. (1997) for MIPAS-FT and by Woiwode et al. (2012) for MIPAS-STR. Also the Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere, New Frontiers (CRISTA-NF) instrument, which is a grating spectrometer patterned after its space-borne namesake, was used for air-borne limb emission measurements of $ClONO_2$ (Ungermann et al., 2012). Measurements with largely improved spatial resolution became possible by limb emission imaging with the Gimballed Limb Observer for Radiance Imaging of the Atmosphere (GLORIA)(Riese et al., 2005; Friedl-Vallon et al., 2006, 2014). For $ClONO_2$, the spectra were analyzed by Johansson et al. (2018).

Space-borne emission spectrometry:

First space-borne limb emission measurements of $ClONO_2$ were made with the Cryogenic Limb Array Etalon Spectrometer (CLAES) on the Upper Atmosphere Research Satellite (UARS, Roche et al. 1993, 1994). Riese et al. (1997, 1999) and Spang et al. (2001) reported $ClONO_2$ measurements with the Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) instrument, which was operated from the Shuttle Pallet Satellite (SPAS) during Space Shuttle missions in 1994 and 1997. The most extended global $ClONO_2$ data set, which also covers polar night distributions, was inferred from MIPAS-Envisat measurements (Höpfner et al., 2004, 2007). After an instrument failure in 2004 MIPAS resumed operation at reduced spectral resolution which still allowed to retrieve $ClONO_2$ (von Clarmann et al., 2009). MIPAS data cover the time period from August 2002 to April 2012, with a major data gap in 2004 and periods of particularly sparse measurements in 2005 and 2006. An improved data version based on revised calibration was presented by von Clarmann et al. (2013). While initially not part of the original MIPAS ESA data product, $ClONO_2$ was included later (Raspollini et al., 2013). Further MIPAS $ClONO_2$ retrievals were provided, e.g., by Arnone et al. (2012)

8.2 In Situ Measurements

8.2.1 Fluorescence Measurements

First airborne in-situ measurements of $ClONO_2$ have been made with a thermal dissociation/ resonance fluorescence measurement technique on the NASA ER-2 aircraft during the POLARIS (Polar Ozone Loss in the Arctic Region In Summer) mission from April to September 1997 (Stimpfle et al., 1999; Bonne et al., 2000). This measurement technique uses the fact that $ClONO_2$ dissociates into ClO and NO_2 by heating the gas. The products of this dissociation are then detected separately. The ClO molecule reacts with added NO to atomic Cl, which then are detected by resonance fluorescence in the ultraviolet. ClO that is present in the atmosphere is measured separately in order to subtract the influence of ambient ClO to the measurement of ClO dissociated from $ClONO_2$. The NO_2 molecule from dissociation of $ClONO_2$ could be measured by laser induced

resonance fluorescence but in practice this measurement was not possible due to the added NO for dissociation of ClO. The thermal dissociation/ resonance fluorescence technique provides measurements of $ClONO_2$ with an accuracy of $\pm 20\%$, a detection limit of 10 pptv and a temporal resolution of 35 s. A similar technique has been applied by Von Hobe et al. (2003) and Stroh et al. (2011) with the HALOX instrument.

8.2.2 Mass Spectroscopy

A more recent technology for in-situ detection of $ClONO_2$ is chemical ionization mass spectrometry (CIMS). This is a measurement technique that has been utilized by airborne instruments for in-situ measurements of $ClONO_2$. Mass spectrometry sorts chemical ions according to their mass to charge ratio utilizing magnetic fields for separating these ions. For ionizing $ClONO_2$, a reaction with SF_5^- gives F^-ClONO_2 which is then detected. For accurate measurements calibrations with reference gases are necessary.

The first CIMS instrument has been used on the NASA WB-57F aircraft during the CRYSTAL–FACE mission from Key West, FL in 2002 (Marcy et al., 2005). CIMS $ClONO_2$ measurements were calibrated using laboratory measurements after the campaign with reference gases. A correlation of $ClONO_2$ with simultaneously measured HNO_3 was applied to use in-flight calibrations of HNO_3 also for $ClONO_2$ measurements. Uncertainties of the ground-based calibration lead to a relative error of $\pm 50\%$ of measured $ClONO_2$.

The AIMS (AIrborne Mass Spectrometer) instrument has been deployed on the German High Altitude and Long Range Research Aircraft (HALO) the TACTS/ESMVal campaign in 2012 (Jurkat et al., 2016, 2017). Again, calibration measurements are performed on ground using reference gases and a correlation of $ClONO_2$ with HCl is applied to use in-flight calibrations for HCl. AIMS measures $ClONO_2$ at a temporal resolution of 1.7 s with a detection limit of 20 pptv, $\pm 15\%$ precision and $\pm 20\%$ accuracy.

9 The climatology of $ClONO_2$

9.1 Zonal Mean Distributions and Annual Cycle

Largest mixing ratios of $ClONO_2$ are found at altitudes of around 30 to 10 hPa (roughly 20–30 km) (Fig. 7). Minimal concentrations are found in the tropics. In late local winter maximal mixing ratios are found in polar regions, associated with chlorine deactivation (Fig. 7 panels a and c and Fig. 3). Under these conditions, mixing ratios can exceed 2 ppbv. As first found by Toon et al. (1989), largest concentrations are not found directly above the pole but in a collar at the edge of the polar vortex. An example of such a $ClONO_2$ collar as measured by MIPAS is shown in Fig. 4. In spring, summer and autumn the largest mixing ratios are found in mid-latitudes.

Climatologies of $ClONO_2$ generated from measurements by multiple space-borne limb sounders have been compiled by Hegglin and Tegtmeier (2017) and are accessible via http://www.sparc-climate.org/data-centre/data-access/sparc-data-initiative/
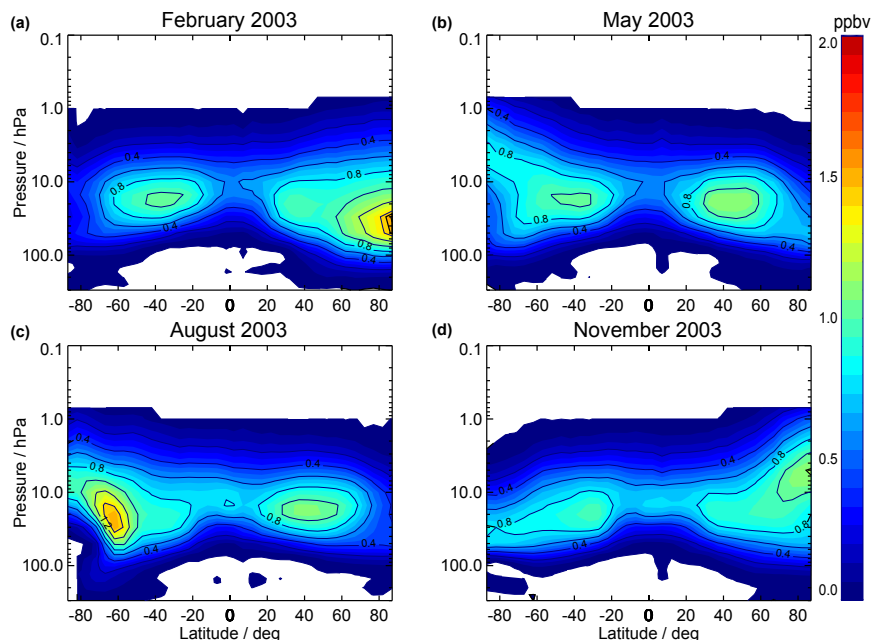
Figure 7. ClONO$_2$ latitude altitude cross-sections for February, May, August and November 2003 as measured with MIPAS.

9.2 Diurnal Cycle

The diurnal variation of ClONO$_2$ in the Arctic winter stratosphere is driven by the availability of sunlight. Wetzel et al. (2012) measured the ClONO$_2$ volume mixing ratio with MIPAS balloon within the polar vortex above northern Scandinavia during sunrise on 24 January 2010 (see Fig. 8). The maximum volume mixing ratio for ClONO$_2$ was 1.5 ppbv, observed at an altitude of 27 km one hour before sunrise. During the time period of one to two hours after sunrise, ClONO2 levels decreased to 1.3 ppbv. They explained this decrease after sunrise with the start of photolysis of the ClONO$_2$ molecule (see Sec. 5.1) and the photolysis of the NO$_2$ molecule, which is needed for the source reaction of ClONO$_2$ (see Sec. 4). The diurnal cycle of ClONO$_2$ is often discussed within the context of the diurnal cycle of ClO in which ClONO$_2$ acts as reservoir species. First theoretical calculations for the diurnal cycle of ClONO$_2$ have been done by Ko and Sze (1984) in the context of measurements of the diurnal cycle of ClO by Solomon et al. (1984).

10 Trends of ClONO$_2$

As with HCl, one of the main scientific questions is how the time series reflect the decrease of CFCs after the Montreal protocol. Rinsland et al. (2010) found that ClONO$_2$ stopped increasing. Negative trends have actually been determined (Fig. 9), and the decrease of ClONO$_2$ was observed to be stronger than that of HCl. This difference was observed to be latitude-dependent (Kohlhepp et al., 2012).
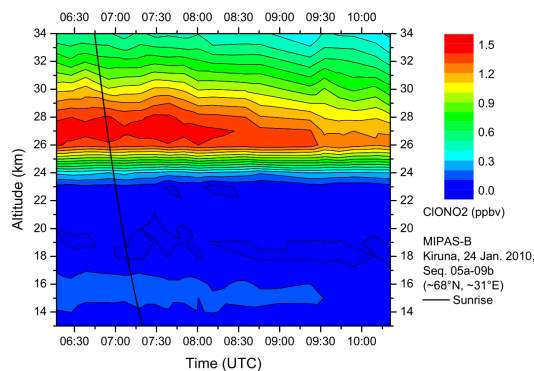
Figure 8. ClONO$_2$ volume mixing ratios measured with MIPAS-B during sunrise on 24 January 2010 above northern Scandinavia within the polar vortex. Figure taken from Wetzel et al. (2012, their Fig. 8) under CC Attribution 3.0 License.
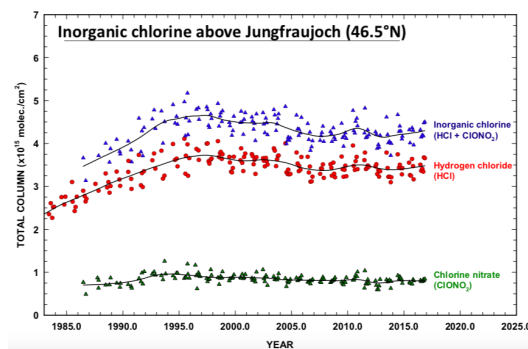
Figure 9. Multidecadal time series of column amounts above Jungfraujoch of ClONO$_2$ and HCl, as well as the sum of both which is a proxy of total inorganic chlorine. Symbols represent monthly means. To avoid masking of trends by polar winter dynamics, only the months June to November were considered. The continuous lines are non-parametric least squares fits. A decrease since 1996/97 as well as correlations between the column amounts of ClONO$_2$ and those of HCl are visible. Figure by Emmanuel Mahiue et al., Univ. Liège, published in De Maziére et al. (2018), used under CC Attribution 3.0 license.

Instrument	Institution	Web Address
ground-based FTIR	NDACC	http://www.ndsc.ncep.noaa.gov/cgi-bin/pi/query_data/query_data.pl
ACE-FTS	Univ. Waterloo	http://www.ace.uwaterloo.ca/data.php
ATMOS	NASA JPL	https://remus.jpl.nasa.gov/atmos/atftp.html
CLAES	NASA	https://disc.gsfc.nasa.gov/datasets/UARCL3AT_V009/summary?keywords=CLAES&page=1
CRISTA-NF	FZJ/BUW	https://www.fp7-reconcile.eu/reconciledata
GLORIA[1]	KIT/FZJ	https://halo-db.pa.op.dlr.de/data_source/25/
ILAS	NIES	http://warp.da.ndl.go.jp/info:ndljp/pid/11066775/db.cger.nies.go.jp/ilas/data2/DataDistribution.html
ILAS-II	NIES	http://warp.da.ndl.go.jp/info:ndljp/pid/11066775/db.cger.nies.go.jp/ilas2/en/dist/genelal/DataDistribution.html
MIPAS	KIT/IMK	http://www.imk-asf.kit.edu/english/308.php
MIPAS	ESA	https://earth.esa.int/web/guest/missions/esa-operational-eo-missions/envisat/instruments/mipas
MIPAS	Univ. Oxford	http://eodg.atm.ox.ac.uk/MIPAS/L2OXF/
MIPAS-STR	KIT/IMK	https://www.fp7-reconcile.eu/reconciledata
MK-IV	NASA JPL	https://mark4sun.jpl.nasa.gov/ground.html

Table 5. Sources of ClONO$_2$ data.

[1] By the time of this writing the public access to these data has not yet been established but is expected in the near future.

11 ClONO$_2$ Data Sets

Numerous ClONO$_2$ observational data sets are available via the internet. Some relevant addresses are compiled in Table 5. ClONO$_2$ data of missions not listed may be available via the respective principal investigators.

12 Conclusion and Outlook

5 Research during the last decades has helped very much to mature our knowledge about ClONO$_2$, in particular in the context of polar stratospheric ozone depletion. Most relevant future science questions presumably are (a) the future development of ClONO$_2$ concentrations in a changing climate, and (b) its role in chlorine activation on surfaces other than polar stratospheric clouds, particularly in the upper troposphere and lowermost stratosphere.

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