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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, 809, 1293, 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. The 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 of 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 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 thus-recognized importance of this gas triggered spectroscopic laboratory measurements with the goal of improving its absorption cross sections (e.g., Ballard et al., 1988; Birk and Wagner, 2000).

$ClONO_2$ 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 spaceborne solar occultation measurements were made with the Improved Limb Atmospheric Spectrometer (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 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 spaceborne 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 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, last access: 23 January 2017). Mass spectroscopy is now also used for in situ detection of $ClONO_2$ (Marcy et al., 2005; Jurkat et al., 2016).

Remote sensing of $ClONO_2$ from the ground relies entirely on high-resolution Fourier transform spectrometry. The 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 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) and von Clarmann (2013).

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^{-1}. The structure of chlorine nitrate is shown in Fig. 1. Tables 1 and 2 show the bond angles and bond lengths.

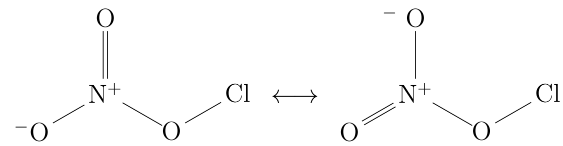

Figure 1. The chemical structure of chlorine nitrate.

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) that 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, chap. 2.4.3, or Rowland et al., 1976).

$$(k_1) \quad ClO + NO_2 + M \longrightarrow ClONO_2 + M \qquad (R1)$$

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 Sect. 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 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

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

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):

$$k_{1;\mathrm{inf}} = 1.5 \times 10^{-11} \left(\frac{T}{300}\right)^{-1.9}. \qquad (2)$$

Table 1. Bond angles of $ClONO_2$, from Rankin and Robertson (1994).

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

Table 2. Bond lengths of $ClONO_2$, from Rankin and Robertson (1994).

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

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

$$k_1([M],t) = \left(\frac{k_{1,0}(T)[M]}{1+\frac{k_{1,0}(T)[M]}{k_{1,\mathrm{inf}}(T)}}\right)0.6^{\left(1+\left(\log_{10}\left(\frac{k_{1,0}(T)[M]}{k_{1,\mathrm{inf}}(T)}\right)\right)^2\right)^{-1}}. \quad (3)$$

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 K are shown in Fig. 2.

The photodissociation can lead to different products. The first photolysis channel is

$$ClONO_2 + h\nu \longrightarrow Cl + NO_3. \quad \text{(R2)}$$

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

$$\begin{aligned} &\Phi_1 = 0.6 && (\lambda < 308\,\mathrm{nm}),\\ &\Phi_1 = 7.143\times10^{-3}\lambda - 1.60 && (308\,\mathrm{nm} < \lambda < 364\,\mathrm{nm}),\\ &\Phi_1 = 1.0 && (\lambda > 364\,\mathrm{nm}),\end{aligned}$$

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

$$ClONO_2 + h\nu \longrightarrow ClO + NO_2, \quad \text{(R3)}$$

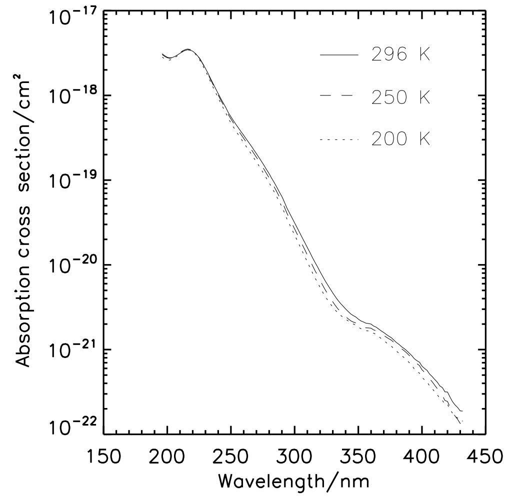

Figure 2. $ClONO_2$ UV absorption cross sections at 200 K (dotted), 250 K (dashed), and 296 K (solid).

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

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

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

The most important gas-phase loss reactions of $ClONO_2$ are (Brasseur and Solomon, 2005)

$$(k2)\quad ClONO_2 + O \longrightarrow \text{products} \quad \text{(R5)}$$
$$(k3)\quad ClONO_2 + Cl \longrightarrow Cl_2 + NO_3 \quad \text{(R6)}$$
$$(k4)\quad ClONO_2 + OH \longrightarrow HOCl + NO_3. \quad \text{(R7)}$$

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:

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

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.

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).

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)

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:

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

$$(k6)\quad HCl + ClONO_2 \longrightarrow \text{products}. \tag{R9}$$

5.3 Heterogeneous reactions

The medium for heterogeneous reactions of $ClONO_2$ is 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 $ClONO_2$. 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. The first spaceborne 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 Sect. 6.2) are (Molina et al., 1987; Tolbert et al., 1987, 1988; Hanson and Ravishankara, 1991a, 1992b, 1993a)

$$ClONO_{2(\text{gas})} + HCl_{(\text{solid,liquid})} \longrightarrow Cl_{2(\text{gas})} + HNO_{3(\text{solid})} \tag{R10}$$

$$ClONO_{2(\text{gas})} + HBr_{(\text{solid,liquid})} \longrightarrow BrCl_{\text{gas}} + HNO_3 \tag{R11}$$

$$ClONO_{2(\text{gas})} + H_2O_{(\text{liquid,solid})} \longrightarrow HOCl_{(\text{gas})} + HNO_3. \tag{R12}$$

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):

$$\frac{d[ClONO_2]}{dt} = -kClONO_2. \tag{5}$$

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

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}}, \tag{7}$$

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), and 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 aluminum 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).

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, and 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 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):

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

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

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, 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, 5–111)	Shi et al. (2001)

$$\text{net}: \ O_3 + O \longrightarrow 2O_2. \tag{R15}$$

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):

$$2 \times (Cl + O_3 \longrightarrow ClO + O_2) \tag{R16}$$
$$ClO + ClO + M \longrightarrow Cl_2O_2 + M \tag{R17}$$
$$Cl_2O_2 + h\nu \longrightarrow ClOO + Cl \tag{R18}$$
$$\underline{ClOO + M \longrightarrow Cl + O_2 + M} \tag{R19}$$
$$\text{net}: \ 2O_3 + h\nu \longrightarrow 3O_2. \tag{R20}$$

Similarly, the coupled catalytic cycle involving also bromine radicals Br and BrO is also independent of atomic oxygen (Yung et al., 1980; McElroy et al., 1986b; Barrett et al., 1988).

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{R21}$$
$$Br + O_3 \longrightarrow BrO + O_2 \tag{R22}$$
$$ClO + BrO \longrightarrow Br + ClOO \tag{R23}$$
$$\underline{ClOO + M \longrightarrow Cl + O_2 + M} \tag{R24}$$
$$\text{net}: \ 2O_3 \longrightarrow 3O_2 \tag{R25}$$

Under normal conditions, these catalytic cycles are much less disastrous than one might think. The reason is that usually 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 not only consists of the temporary deactivation of reactive chlorine but also allows chlorine to be transported over long distances without reaction. Release of reactive chlorine from its reservoirs is essential to understanding 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 $ClONO_2$ (Toumi et al., 1993). Its importance lies in the fact that there exists a $ClONO_2$ photolysis pathway which generates atomic chlorine.

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M \tag{R26}$$
$$ClONO_2 + h\nu_1 \longrightarrow Cl + NO_3 \tag{R27}$$
$$Cl + O_3 \longrightarrow ClO + O_2 \tag{R28}$$
$$NO_3 + h\nu_2 \longrightarrow NO + O2 \tag{R29}$$
$$\underline{NO + O_3 \longrightarrow NO_2 + O_2} \tag{R30}$$
$$2O_3 + h\nu_1 + h\nu_2 \longrightarrow 3O_2 \tag{R31}$$

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 (Reactions 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 midlatitudes where most reactive chlorine was expected due to the decomposition of chlorine source gases.

Ozone loss, however, was expected to be much weaker than the observed Antarctic ozone loss and to be not 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). 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 re-formation of reservoirs in spring when enough sunlight is available for keeping the catalytic cycles going. With the catalytic dimer cycle (Reactions R16–R20) a mechanism was available which did not depend on atomic oxygen, which is only available in sizeable amounts at higher 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), Solomon (1999), or von Clarmann (2013). An updated view on polar ozone chemistry, including reactions involving sulfate aerosols as well, is presented by Solomon et al. (2015).

The re-formation of $ClONO_2$ via Reaction (R1) would make the catalytic ozone destruction cycle (Reactions 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 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 re-formation 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 heterogeneous chlorine reactivation (Portmann et al., 1996; Chipperfield and Pyle, 1998). This tends to counterbalance the effect of denitrification on chlorine activation and ozone destruction.

In summary and roughly speaking, interaction of the following processes brings 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. 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 re-formation of $ClONO_2$. More recent studies mention the importance of cold binary sulfate aerosol particles as the 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 are that the Arctic vortex is typically not as cold as its Antarctic counterpart, entailing less frequent occurrence of polar stratospheric clouds. Stratospheric final warmings occur typically earlier in the season than in the Antarctic, terminating chlorine activation on polar stratospheric clouds. Major and minor stratospheric warmings which interrupt chlorine activation temporarily are common in the Arctic but occur very rarely in Antarctic winters. Due to stronger wave activity in the Northern Hemisphere there are more frequent excursions of the polar vortex to sunlit lower latitudes.

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 (e.g., Adrian et al., 1994; Blumenstock et al., 1997; Notholt et al., 1994, 1995). 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 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.,

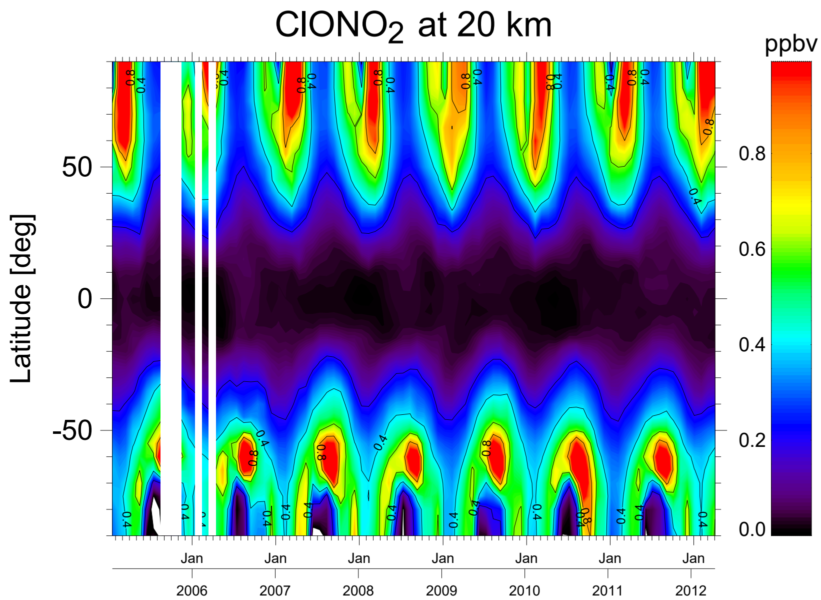

Figure 3. The temporal development of $ClONO_2$ at 20 km, based on MIPAS monthly mean mixing ratios. White stripes represent data gaps due to missing measurements. Figure from von Clarmann et al. (2009), used under CC Attribution 3.0 license.

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, 1997), Roche et al. (1994), and Blom et al. (1995). A sensitivity study showing how PSC formation and denitrification affect $ClONO_2$ and ozone chemistry is shown in Rex et al. (1997) in order to explain large Arctic ozone loss in the particularly 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 Fig. 3 the seasonal formation of $ClONO_2$ at polar latitudes as seen by MIPAS can be clearly seen. Figure 4 shows MIPAS measurements 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, via either photolysis or OH chemistry (Chipperfield et al., 1997).

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), O. B. Toon et al. (1993), Wilson et al. (1993), and Dessler et al. (1993). Borrmann et al. (1997), however, found that chlorine activation by heterogeneous reactions on volcanic

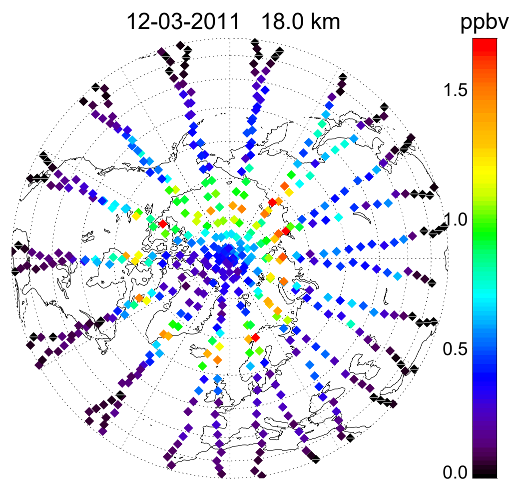

Figure 4. Chlorine nitrate measurements by MIPAS over the Arctic at 18 km altitude on 12 March 2011. The "collar" of large mixing ratios surrounds the core area of the polar vortex where $ClONO_2$ values are lower. Figure from von Clarmann et al. (2009), used under CC Attribution 3.0 license.

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 can 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. At middle and low latitudes where temperatures are too high for the formation of polar 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 midlatitudinal 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 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 Reaction (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 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, removal of NO_2 via sequestering of HNO_3 on aerosol leads to reduced re-formation of $ClONO_2$ (Tie and Brasseur, 1996), and buildup of HCl gains importance as a reservoir re-formation 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) 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, in MIPAS data measured after the Halloween 2003 solar proton event, found increased amounts of ClO in the sunlit part of the polar vortex. Only in the dark part of the polar vortex poleward of 70° N was ClO 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.

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 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 Sect. 5.1, $ClONO_2$ makes a contribution to the absorption cross-section spectrum in the UV, where photolyzing radiation is absorbed. The UV absorption cross section 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) and Wagner and Birk (2003) measured the absorption cross section for $ClONO_2$ in a laboratory study. They synthesized $ClONO_2$ from nitrogen pentoxide (N_2O_5) and dichlorine monoxide (Cl_2O) 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}) and 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 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

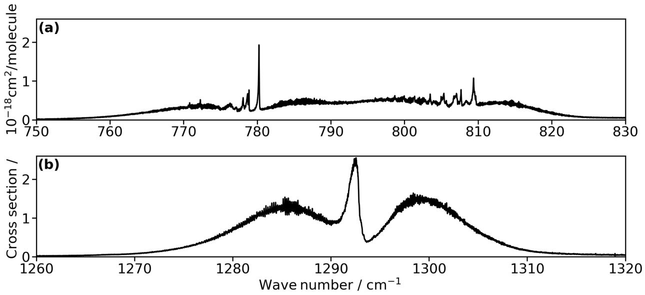

Figure 5. Example of an absorption cross section of $ClONO_2$ **(a)** ν_4 and ν_3 and **(b)** ν_2 bands, measured by Wagner and Birk (2003) in a cuvette at a temperature of 297.4 K and pressure of 100 hPa.

at a tangent altitude of 17.3 km corresponds to a retrieved volume mixing ratio 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), other atmospheric trace (mainly O_3 and CO_2) gases also 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 millimeter and sub-millimeter 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, 809, 1293, 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 were 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 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

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-based measurements provide no vertical profile information but rather 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 (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 $ClONO_2$ measurements was to study chlorine activation and deactivation during polar winter. Early non-polar column measurements of $ClONO_2$ were made with the 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 (e.g., 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). Meanwhile worldwide monitoring of stratospheric $ClONO_2$ is performed by the Network for Detection of Atmospheric Composi-

[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.

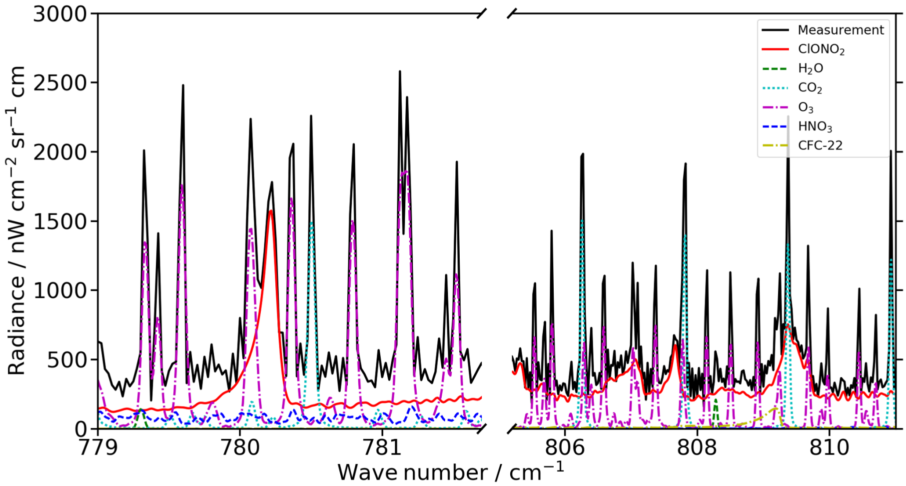

Figure 6. Example of an atmospheric limb emission infrared spectrum measured by MIPAS/Envisat (orbit 05371) on 11 March 2003 at 07:36:25 UTC at a tangent altitude of 17.3 km (black solid line). The contributions of single gases are calculated with the radiative transfer model KOPRA (Karlsruhe Optimized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

tion Change (NDACC; De Maziére et al., 2018), using high-resolution Fourier transform infrared 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 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).

Airborne solar absorption spectrometry

The 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 Atmospheric Laboratory for Applications and Sciences (ATLAS-3) space mission (Michelsen et al., 1999) (see Sect. 8.1.1).

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) and Toon et al. (1992). $ClONO_2$ measurements from the follow-up campaign in 1992 (AASE-2) were published by G. C. Toon et al. (1993).

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 with by tropospheric constituents. Further, airborne measurements 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 on $ClONO_2$. The rising or setting sun is observed under varying negative elevation angles. The resulting limb sequence of spectra is inverted 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 a concentration profile of $ClONO_2$ to be inferred using its signature near

[2]Stations in Toronto, Mauna Loa, Bremen, and Harestua are also equipped to measure $ClONO_2$, but at the time of this writing no related $ClONO_2$ data had been found on the NDACC server.

1292 cm^{-1} (Murcray et al., 1979). Further balloon-borne solar occultation measurements were reported by Rinsland et al. (1985), where again the band near 780 cm^{-1} 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 spaceborne measurements.

Spaceborne solar occultation spectrometry

The first spaceborne measurements of $ClONO_2$ were made with the 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 sun-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).

ACE-FTS is a solar occultation instrument on the Canadian SciSat Earth observation satellite, launched in August 2003. $ClONO_2$ measurements have been 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

The 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.

Airborne emission spectrometry

Two versions of airborne 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), and Pfeilsticker et al. (1997) for MIPAS-FT and by Woiwode et al. (2012) for MIPAS-STR. The Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere – New Frontiers (CRISTA-NF) instrument, which is a grating spectrometer patterned after its spaceborne namesake, was also used for airborne 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).

Spaceborne emission spectrometry

The first spaceborne limb emission measurements of $ClONO_2$ were made with CLAES on UARS Roche et al. (1993, 1994). Riese et al. (1997, 1999) and Spang et al. (2001) reported $ClONO_2$ measurements with the 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 retrieval of $ClONO_2$ (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)

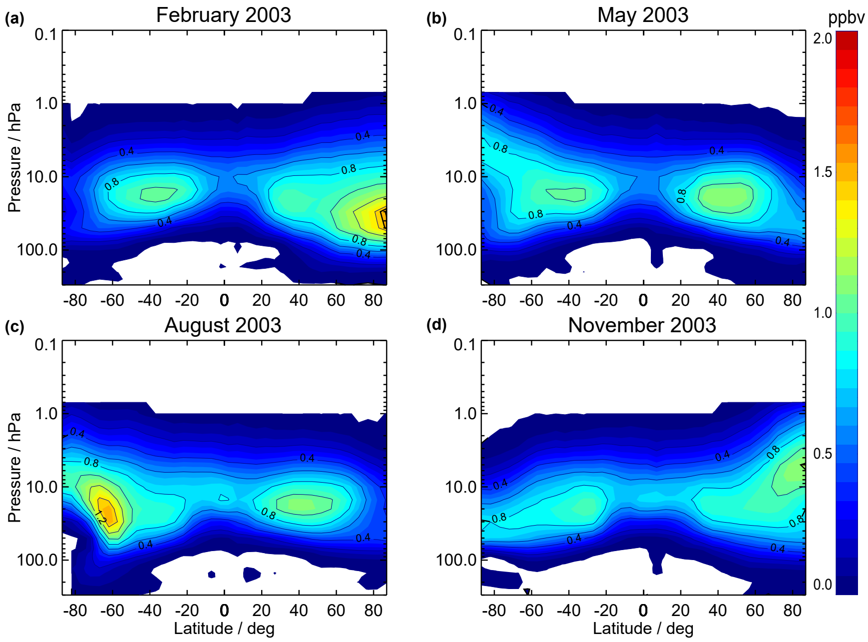

Figure 7. $ClONO_2$ latitude–pressure cross sections for February, May, August, and November 2003 as measured with MIPAS.

8.2 In situ measurements

8.2.1 Fluorescence measurements

The first airborne in situ measurements of $ClONO_2$ were 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 on 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.

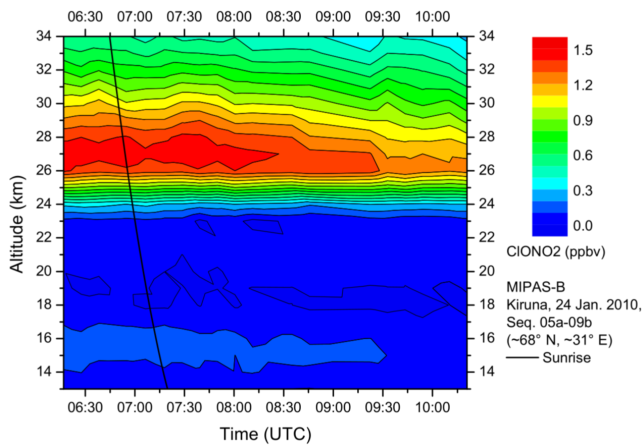

Figure 8. $ClONO_2$ volume mixing ratios measured with MIPAS-B during sunrise on 24 January 2010 above northern Scandinavia within the polar vortex. Figure taken from Wetzel et al. (2012, their Fig. 8) under CC Attribution 3.0 License.

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 ionization of $ClONO_2$, a reaction with SF_5^- gives

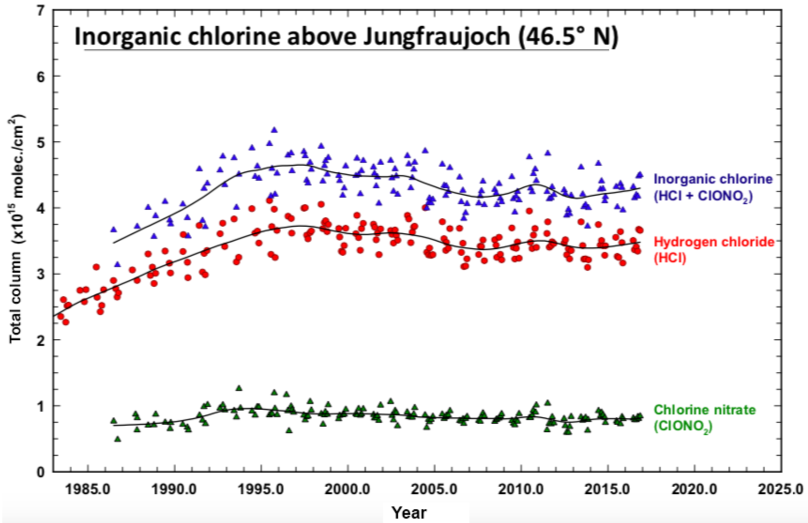

Figure 9. Multidecadal time series of column amounts above Jungfraujoch of $ClONO_2$ and HCl, as well as the sum of both, which is a proxy of total inorganic chlorine. Symbols represent monthly means. To avoid masking of trends by polar winter dynamics, only the months June to November were considered. The continuous lines are non-parametric least squares fits. A decrease since 1996/97 and correlations between the column amounts of $ClONO_2$ and those of HCl are visible. Figure by Emmanuel Mahieu et al., Univ. Liège, published in De Maziére et al. (2018), used under CC Attribution 3.0 license.

F^-ClONO_2, which is then detected. For accurate measurements calibrations with reference gases are necessary.

The first CIMS instrument was 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 ± 50 % of measured $ClONO_2$.

The AIMS (AIrborne Mass Spectrometer) instrument was deployed on the German High Altitude and Long Range Research Aircraft (HALO) during the TACTS/ESMVal campaign in 2012 (Jurkat et al., 2016, 2017). Again, calibration measurements are performed on the 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, ± 15 % precision, and ± 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 (Figs. 7a and c, and 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 at midlatitudes.

Climatologies of $ClONO_2$ generated from measurements by multiple spaceborne 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/ (last access: 19 October 2018).

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-B2 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 1 h before sunrise. During the time period of 1–2 h after sunrise, $ClONO_2$ levels decreased to 1.3 ppbv. They explained this decrease after sunrise with the start of photolysis of the $ClONO_2$ molecule (see Sect. 5.1) and the photolysis of the NO_2 molecule, which is needed for the source reaction of $ClONO_2$ (see Sect. 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 a reservoir species. The first theoretical calculations for the diurnal cycle of $ClONO_2$ were done by Ko and Sze (1984) in

Table 5. Sources of $ClONO_2$ data.

Instrument	Institution	Web address (last access: 19 October 2018)
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	KIT/FZJ	https://doi.org/10.5445/IR/1000086506
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

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).

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

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. The most relevant future science questions presumably regard (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.

Data availability. No original data sets were used in this article.

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