Reflection-absorption IR spectroscopic investigation of the photolysis of thin films of dichlorine monoxide and chlorine dioxide

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Reflection-absorption infrared (RAIR) spectroscopy and mass spectrometry have been employed in order to investigate the low-temperature photochemistry of thin films of chlorine dioxide, OClO, and dichlorine monoxide, Cl_2O , grown on a gold foil in an ultra-high vacuum system. Photolysis of a neat film of OClO ($\lambda > 300$ nm, 90–110 K) produces chloryl chloride, $ClClO_2$. Irradiation of a co-deposited OClO/H₂O film also produces chlorine superoxide, ClOO, which suggests that OClO isomerisation is the first step in the reaction producing ClClO₂. Photolysis of Cl_2O ($300 < \lambda < 515$ nm, 90–110 K) is shown to produce OClO, initially, which is subsequently converted to $ClClO_2$. Analysis of the observed IR band intensities and consideration of the metal surface selection (MSS) rule indicates that the photochemically produced OClO intermediate aligns perpendicular to the gold substrate. Mechanistic details and the atmospheric implications of the chemistry are discussed.

Chlorine oxides play a crucial role in the catalytic destruction of polar stratospheric ozone; a consequence of their chemistry is the formation of the ozone 'hole' over Antarctica in the early austral spring. Ozone destruction occurs principally *via* a ClO dimer mechanism, but other chlorine oxides species can also potentially affect polar stratospheric chemistry by both thermal and photochemical mechanism.¹

Atmospheric chlorine dioxide, OCIO, was first observed above Antarctica in the austral spring of 1986 by Solomon *et* $al.,^2$ thereby conclusively linking OCIO to the polar stratospheric ozone depletion phenomenon. High OCIO concentrations have since been measured at sunset and night, particularly within the perturbed ozone 'hole' region,^{3,4} but daytime OCIO concentrations are found to be low owing to rapid photolysis.⁵ Currently, the only established scheme for the production of OCIO in the stratosphere is the gas-phase CIO and BrO coupling reaction, *e.g.* ref. 6 and 7:

$$ClO + BrO \rightarrow OClO + Br$$
 (1)

Gas-phase-only models can accurately predict stratospheric OClO concentrations at mid-latitudes; however, they fail to predict the considerably higher OClO concentrations found in ozone-depleted polar regions.⁸ This discrepancy (of up to two orders of magnitude) is presumably due to heterogeneous processing, which controls much of the chemistry in the perturbed polar stratosphere. Few reactions which could lead to direct OClO production [other than reaction (1)] have been studied in the laboratory, although the decomposition of chloryl chloride, ClClO₂, has been shown to produce OClO.⁹

The photochemistry of OCIO has been extensively studied and many of the results have been summarised in a recent article.¹⁰ The principal gas-phase photolysis pathway of OCIO produces CIO and an O atom:

$$OClO + hv \rightarrow ClO + O$$
 (2a)

Overall, reaction (2a) does not lead to depletion of ozone levels because, although ClO coupling with BrO or another ClO radical produces Br or Cl which destroy ozone, the photo-produced oxygen atom generates ozone by reaction with O_2 . An alternative photolysis pathway of OClO produces O_2 and a Cl atom, which may proceed directly by bond fission [reaction (2b)] or *via* the chlorine superoxide, ClOO, intermediate [reaction (2c)]. This process would lead to a reduction in ozone levels as the Cl atom can participate in ozone-destroying reactions. The relative importance of the alternative pathway is debatable as quantum yields measured for the production of atomic Cl range from 0.15 to 5×10^{-4} and are dependent on the wavelength of radiation;^{11–14} hence, the branching ratio for reaction (2a) vs. (2b + 2c) is still a matter of some controversy.¹⁰

$$OClO + hv \rightarrow Cl + O_2$$
 (2b)

$$OCIO + hv \rightarrow CIOO \rightarrow CI + O_2$$
 (2c)

Several observations suggest that the production of Cl atoms by photolysis of OCIO will be significant for heterogeneous chemistry involving water-ice. First, atomic chlorine production from the photolysis of OCIO is enhanced when it is dissolved in polar solutions, *e.g.* Cl quantum yields of 0.1 have been measured on irradiating an aqueous solution of OCIO at 355 nm.¹⁵ For such solutions, reaction (2c) has been shown to be dominant over reaction (2b).¹⁶ In addition, a Cl atom production quantum yield of 0.8 has been determined for the photolysis of OCIO adsorbed on a polycrystalline platinum surface.¹⁷

The photolysis of matrix-isolated OCIO has also been studied. OCIO undergoes quantitative conversion to CIOO on irradiation; it is assumed that CIOO is stabilised by the matrix-cage effect. CIOO is slightly more thermodynamically stable than OCIO^{18,19} but is kinetically unstable and normally decomposes rapidly to form Cl and O_2 .²⁰ Pursell *et al.*²¹ have reported that photolysis (at 360 nm) of OCIO in amorphous water-ice, maintained at 80 K, also results in quantitative conversion to the CIOO isomer. Different results were observed when similar photolysis experiments were carried out at higher temperatures, 140–185 K;²² chloryl chloride, CICIO₂, a structural isomer of (CIO)₂, was identified by IR spectroscopy as the main product.

In contrast, the role of dichlorine monoxide, Cl_2O , in atmospheric chemistry has received scant attention. This is partly due to the absence of observations or measurements of Cl_2O in the stratosphere or troposphere. However, it is in equilibrium with HOCl, which itself plays a role in stratospheric ozone-destruction chemistry:

$$2\text{HOCl}_{(g)} \leftrightarrow \text{H}_2\text{O}_{(g)} + \text{Cl}_2\text{O}_{(g)}$$
(3)

The HOCl equilibrium at 298 K has been studied by several groups, who have reported the equilibrium constant to lie between 4 and $12.^{23-25}$ HOCl is formed in the stratosphere by the gas-phase reaction of ClO and HO₂ radicals:

$$ClO + HO_2 \rightarrow HOCl + O_2$$
 (4)

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More pertinent to polar stratospheric-ozone depletion is the heterogeneous decomposition of chlorine nitrate on PSC particles to form HOCl, which is one of the key processes in the release of active chlorine from reservoir molecules:

$$ClONO_{2(ads)} + H_2O_{(ads)} \rightarrow HOCl + HNO_{3(ads)}$$
(5)

HOCl is not considered an important chlorine reservoir in the stratosphere owing to rapid photolysis below 290 nm.²⁴ During the Antarctic ozone-depletion period, the HOCl column abundance has been observed to be around 10% of the concurrent abundances of ClONO₂ and HCl;²⁶ although it should be noted that HOCl concentrations have not been measured at night when accumulation may occur. The HOCl equilibrium with Cl₂O may also occur heterogeneously, hence, adsorbed HOCl may directly produce adsorbed Cl₂O. In a recent study, however, dosing HOCl onto ice surfaces at stratospherically relevant temperatures was shown not to produce Cl₂O.²⁷ Overall, despite the lack of Cl₂O field observations, it is possible that it does exist in significant concentrations during the polar night.

 Cl_2O absorbs light throughout the UV and visible regions^{28,29} and is readily photolysed. Gas-phase photolysis can follow two routes:²⁹

$$ClOCl + hv \rightarrow ClO + Cl$$
 (6a)

$$ClOCl + hv \rightarrow O + Cl_2$$
 (6b)

Reaction (6a) is the primary mechanism, although at short wavelengths reaction (6b) has been observed.^{29,30} Both channels release active chlorine and are therefore potentially ozone destructive.

Irradiation of Cl_2O trapped in cryogenic matrices results in isomerisation to form ClClO, which is presumed to be stabilised by the matrix-cage effect.^{31–33} The ClO radical and chlorine chlorite, ClOClO, are observed as minor side products^{31,32} It is to be expected that if such species are formed by heterogeneous reactions and then released into the gas phase, they would rapidly decompose to ClO or Cl_2 and an O atom.

$$ClOClO + hv \to 2ClO \tag{7}$$

 $ClClO + hv \rightarrow ClO + Cl$ (8a)

$$ClClO + hv \rightarrow Cl_2 + O$$
 (8b)

As both OClO and Cl_2O are potentially linked to ozonedestruction cycles, we have undertaken a laboratory study to elaborate on their heterogeneous, photochemical behaviour in the condensed phase, using FT-RAIR spectroscopy and mass spectrometry for analysis. RAIR spectroscopy offers an advantage over transmission IR spectroscopy as it can provide information on the orientation of molecules with respect to the metal surface. This is a result of the MSS rule which arises from the metal surface imposing a vertical polarisation of the surface standing wave of the incident radiation. As a result, only vibrations with a dipole moment change perpendicular to the metal surface are seen. This phenomenon applies to films of up to *ca*. 1 μ m in thickness and means that only vibrations with a dipole moment change perpendicular to the surface can be detected.

Experimental

Preparation of Cl₂O

Dichlorine monoxide was produced by the standard method of passing dry chlorine through a column of yellow mercury oxide (Aldrich, 99%).³⁴ Cl₂O was collected (at 195 K) and purified by repeated freeze-pump-thaw cycles. The purified Cl₂O was stored at 78 K to minimise decomposition.

Preparation of OClO

Chlorine dioxide is highly explosive in both the gas phase and condensed phase. To minimise the handling risk, OCIO was produced in an aqueous solution by the method of Pursell *et al.*²² Sodium chlorite (Lancaster, 80%) and sodium persulfate (Sigma, 98 + %) were added to water in a darkened vessel, producing OCIO:

$$2\text{NaClO}_{2(\text{aq})} + \text{Na}_2\text{S}_2\text{O}_{8(\text{aq})} \rightarrow 2\text{OClO}_{(\text{aq})} + 2\text{Na}_2\text{SO}_{4(\text{aq})}$$
(9)

The majority of OClO produced remained dissolved in the water. On completion of the reaction, the reaction vessel was evacuated to 40 mbar to remove the majority of atmospheric gases. Subsequently, IR spectroscopy revealed that the vapour above the solution was principally OClO. The primary contaminant was carbon dioxide. OCIO was dried before use by passing the vapour through anhydrous P_2O_5 (Aldrich, 97%).

Apparatus

The experimental arrangement used in this study has been detailed elsewhere.³⁵ It consists of a temperature-controlled gold foil substrate mounted in an ultra-high vacuum (UHV) chamber. Background pressures of the differentially pumped vacuum chamber were typically 1×10^{-9} mbar. RAIR spectroscopy was employed for the analysis of thin substrate films deposited in vacuo. The IR beam emitted from a Digilab FTS-60 spectrometer was reflected off the gold substrate at a high angle of incidence to the surface normal (ca. 75°) and detected by an external liquid-nitrogen-cooled MCT detector. RAIR spectra were recorded at 4 cm⁻¹ resolution with 256 scans. Based on exposure $(1 \times 10^{-6} \text{ mbar s}^{-1} = 1)$ Langmuir ≈ 0.5 monolayer s⁻¹), the layers were estimated to be ca. 500 nm thick. The UHV chamber housed a Hiden EQP quadrupole mass spectrometer allowing temperatureprogrammed desorption (TPD) experiments to be carried out. Photolysis was performed using a 75 W xenon arc lamp; wavelengths below 300 nm were removed using a 5 mm thick Pyrex glass filter.

Results and Discussion

Deposition of OCIO films

Thin solid films of OCIO were deposited onto the gold substrate at 80 K in order to make comparisons with solid-state and gas-phase spectra. The experiments also served as a check on the purity of the samples. Fig. 1(a) corresponds to a relatively thick film of OCIO (*ca.* 2000 nm) produced by dosing at a pressure of 3×10^{-7} mbar for 71 min. Fig. 1(b) corresponds



Fig. 1 RAIR spectra of (a) neat film of OClO, *ca.* 2000 nm, (b) neat film of OClO, *ca.* 300 nm and (c) co-deposited film of H_2O and OClO, *ca.* 500 nm

to a thin film of OCIO (*ca.* 300 nm) produced by dosing at a pressure of 3×10^{-7} mbar for 10 min. The study of the thicker films allows closer comparison with previous studies and also identification of IR combination bands.

IR data for the active vibrational modes of OClO under a variety of conditions are shown in Table 1. The frequencies for the RAIR spectra represent a blue shift compared to the normal incidence transmission spectra of a thin film solid. We have previously observed similar shifts for RAIR spectra of N_2O_4 and N_2O_5 thin films.³⁹ They can be attributed to the coupling of p-polarised radiation with a longitudinal optical (LO) mode of the thin film in the RAIR spectra rather than the more usual transverse optical (TO) mode excited in transmission experiments. In RAIR experiments the MSS rule means that no coupling with a TO mode can occur, whilst LO modes cannot be excited in transmission experiments at normal incidence because of the transverse nature of electromagnetic radiation. The difference in frequency between the two is known as Lydane-Sachs-Teller (LST) splitting and is proportional to the absorption strength.

For a thin film of OCIO (*ca.* 300 nm) the IR spectrum reveals two major peaks in the asymmetric stretch region of OCIO; the sharp peak at 1103 cm⁻¹ can be assigned to crystalline OCIO and the broader peak at 1086 cm⁻¹ to an amorphous form. The asymmetric region is more complicated for much thicker films (*ca.* 2000 nm), which is partially a result of the breakdown of the MSS rule (valid for films up to *ca.* 1 μ m), thereby allowing TO modes to be measured. The new sharp peak at 1064 cm⁻¹ is very close to the value observed for OCIO in a transmission spectrum.³⁶ Further splitting in this region may be due to increased specular reflectance in thicker films.

A comparable dependence of RAIR spectra peak profiles on the thickness of the films is observed for water-ice.⁴⁰ Analysis using classical optics revealed that the structure in the OH stretching bands of thick films arises owing to a combination of an increased specularly reflected component, an s-polarised component and a relaxation of the MSS rule.

In order to make a better comparison with previous work and to give a more appropriate approximation of stratospheric mixtures, thin films of OCIO in a water-ice matrix were prepared by co-depositing OClO and H₂O onto the gold substrate. A typical RAIR spectrum of OCIO in water-ice (ca. 500 nm) is shown in Fig. 1(c). This thin film was prepared by the co-deposition of OClO and H_2O at 6×10^{-7} mbar for 10 min. The asymmetric stretch is observed at 1095 cm⁻¹ . a small shift from the comparable absorption band at 1086 cm⁻¹ which is observed for neat OClO deposition. This shift may be due to complexation of OClO with neighbouring water molecules as it is close to the perturbed OClO asymmetric stretch, observed at 1090.5 cm⁻¹ by Johnsson et al.⁴¹ their studies of low-temperature matrix-isolated in OCIO-H₂O complexes. In a related transmission IR study of OCIO in ice matrices, Pursell has attributed a peak at 1086

 cm^{-1} to the asymmetric stretch of OClO clusters, (OClO)_n.⁴² For the co-deposited films used in the present study, clustering may occur and, therefore, be responsible for the observed frequency shift.

Photolysis of thin films of OClO

On photolysing ($\lambda > 300$ nm, 90–110 K) thin films (*ca.* 300 nm) of neat OCIO or OCIO deposited onto a layer of waterice, complete conversion to chloryl chloride, ClClO₂, was observed. Fig. 2 summarises a typical experiment, showing a series of difference spectra recorded during the photolysis of a thin film of OCIO (*ca.* 300 nm) deposited onto a layer of water-ice (negative peaks indicate species lost and positive peaks species formed). Decreases in intensity at 1103, 943 and 920 cm⁻¹ indicate the disappearance of OCIO whilst increases at 1204 and 1040 cm⁻¹ indicate the formation of ClClO₂. Unlike OCIO, the adsorbed ClClO₂ RAIR spectra are similar to the gas-phase and matrix-isolation (transmission) vibrational spectra reported in the literature.^{9,43,44} Table 2 summarises the vibrational frequencies of the key chlorine oxide species observed in this study and previous publications.

Chloryl chloride was first synthesised by Müller and Willner, who identified it in both cryogenic matrices and the gas phase by IR spectroscopy.⁹ They originally synthesised ClClO₂ by halogen exchange between FClO₂ and AlCl₃. However, more recently, several groups have produced ClClO₂ by the direct reaction of OClO with Cl.^{43,44} In the gas phase, ClClO₂ is estimated to have a lifetime of 1 min, before decomposing to OClO and Cl.⁹ Irradiation of matrix-isolated ClClO₂ yields two other ClO dimers, ClOOCl and the less stable ClOClO.⁴³

On photolysing thin films of OCIO co-deposited with H₂O ($\lambda > 300$ nm, 90–110 K), chlorine superoxide, ClOO ($v_{0-0} =$



Fig. 2 RAIR difference spectra showing the photolysis ($\lambda > 300$ nm, 105 K) of OCIO deposited onto a thin layer of water-ice. Only OCIO loss bands ($v_{as} = 1103$, 1086 cm⁻¹, $2\delta = 943$ cm⁻¹, $v_s = 920$ cm⁻¹) and CICIO₂ formation bands ($v_{as(OCIO)} = 1204$ cm⁻¹, $v_{s(OCIO)} = 1040$ cm⁻¹) are observed.

Table 1 Vibrational frequencies of OCIO

	wavenumber/cm ⁻¹					
normal mode	adsorbed neat OClO ^a	adsorbed co- deposition OClO/ H_2O^a	solid phase at 77 K^b	gas phase ^c	neon matrix ^{d,e}	
$v_{s}(A1)$	920 (910)	920	908	943.2	944.8	
$\delta(A1)$			472	445	448.7	
$v_{as}(B2)$	1087 (1103, 1064)	1095 (1101)	1062	1110.5	1107.6	
$2\delta(A1)$	943	944	944	_	_	
$2v_{s}(A1)$	1854	1854	1854	1888	1881	
$v_s + v_{as}(B2)$	1987 (1971, 2006)	1994 (2010)	1987	2040	2036	
$2v_{as}(A1)$	2150		—	2215	2204	

^a This study. ^b Ref. 36. ^c Ref. 37. ^d Ref. 38. ^e O³⁵ClO isotopic vibrational frequencies.

 Table 2
 Principle vibrational frequencies for several key chlorine oxide species relevant to this study

compound	wavenumber/cm ⁻¹	assignment
Cl_2O^a	671	vas
2	629	v _s
OClO ^a	1086	vas
	920	vs
$\text{ClClO}_{2}^{b,c}$	1210	V _{as(OCIO)}
2	1040	v _s (OCIO)
	520	$\delta_{(\Omega \subset I\Omega)}$
	440	v _(CICI)
ClOClO ^{c,d}	994.5	v _(Cl'O') for ClOCl'O'
	695.9	v_{CIO} for ClOCl'O'
	440.3	$v_{(OCI')}$ for ClOCl'O'
	338.7	$\delta_{(ClOCl)}$
ClOOCl ^{c,d}	754	$v_{(00)}$
	648	$v_{as(CIO)}$
	543	$v_{s(CIO)}$
ClOO ^{c,e}	1440	v ₍₀₀₎
	410	δ
	200	$v_{(ClO)}$
$ClClO^{c,f}$	961.9	vas
	374.2	vs
	240.2	δ
ClO ^{c,g}	850	ν
HOCl ^{h,i}	2710	$v_{(\rm HO)}$
	1410	δ
	721	v _{ClO)}

matrix, allowing reactions with OCIO to produce $CICIO_2$, or to preferential CIOO desorption at higher temperatures. As the total amount of $CICIO_2$ formed at higher temperatures shows no increase, preferential CIOO desorption must be the reason for the observations.

Pursell *et al.*^{21,22} have studied the photolysis of dilute OCIO in ice matrices under similar temperature conditions to our experiments. They observed the quantitative conversion of OCIO to ClClO_2 on irradiation at temperatures in the range 140–185 K. However, at a lower temperature (80 K), a different product was observed, namely ClOO. It was assumed, reasonably, that at higher temperatures the photolysis reaction proceeds through the chlorine peroxide intermediate before forming ClClO_2 . One possible mechanism may be summarised by the following two reactions:

$$OClO + hv \rightarrow [ClOO] \rightarrow Cl + O_2$$
(2c)

$$Cl + OClO \rightarrow ClClO_2$$
 (10)

The preference for reaction (2c) occurring over reaction (2a) (the production of ClO) is confirmed by the high quantum yields recently found for Cl production from the photolysis of adsorbed OClO.¹⁷ In further confirmation the ClO radical (or the expected product dimers, ClOClO and ClOOCl) are not observed in our study.

The principal difference between Pursell's study and the present experiments is that, here, ClOO was produced simultaneously with $ClClO_2$ and was found to be measurable up to 160 K. These facts do not exclude the possibility of ClOO acting as a precursor to $ClClO_2$; the observed ClOO may simply be isolated and unable to further react, whilst non-isolated ClOO may react rapidly producing $ClClO_2$. If this is the case then it is no surprise that ClOO was not observed in the study of neat films of OClO; in the absence of an inert matrix it may be too short-lived to be observable.

Pursell has previously suggested that clustering of OClO may be the key to the production of ClClO_2 .²² Recently, it has been reported that OClO forms a loosely bonded dimer in the condensed phase³⁶ and possibly in the gas phase.⁴⁸ Using the crystallographic data of Rehr and Jansen,³⁶ mechanistic Scheme 1 is suggested.

Overall, Scheme 1 gives:

$$2 \text{ OClO} + hv \rightarrow \text{ClClO}_2 + \text{ O}_2 \tag{11}$$

It is clear that, if the rate of loss of OCIO is independent of the OCIO concentration, the absorption of the light must be the rate-determining step.

Deposition of Cl₂O films

Dichlorine monoxide has C_{2v} symmetry, hence all three fundamental vibrations are observable by IR spectroscopy. Its gas-phase and solid-state IR spectra were first correctly interpreted in 1965 by Rochkind and Pimentel⁴⁹ who also reported the first matrix-isolation spectrum.³¹ Relative to the gas phase the solid-state spectrum shows red-shifted peaks whilst the matrix-isolation spectrum is very similar, as confirmed later by Chi and Andrews.³² Cl₂O vibrational frequencies, recorded in different states, are shown in Table 3.

Cl₂O was dosed at a pressure of 1×10^{-6} mbar for 5 min onto the gold substrate at 80 K, giving the RAIR spectrum shown in Fig. 4. Cl₂O is characterised by the asymmetric stretch at 671 cm⁻¹ and the symmetric stretch at 629 cm⁻¹. Table 3 shows a full listing of the fundamental, combination and overtone vibrational bands observed. Minor impurities are also observed, namely OCIO (1086 ν_{as} and 918 cm⁻¹ ν_{s}) and ClClO₂ (1221 $\nu_{as(OCIO)}$ and 1039 cm⁻¹ $\nu_{s(OCIO)}$).

Thin Cl_2O films (*ca.* 500 nm) on or under a film of water-ice and Cl_2O co-deposited with water were also studied; such spectra have been previously published by Banham *et al.*⁴⁵

^{*a*} This study. ^{*b*} Ref. 9. ^{*c*} Matrix isolation. ^{*d*} Ref. 43. ^{*e*} Ref. 38. ^{*f*} Ref. 33. ^{*g*} Ref. 32. ^{*h*} Ref. 45. ^{*i*} Thin adsorbed layer.

1439 cm⁻¹)^{9,38,46} and ClClO₂ are produced simultaneously. ClOO forms at a comparable rate and in competition with ClClO₂, as illustrated in Fig. 3. It follows, therefore, that the observed ClOO is not an intermediate to ClClO₂ production. The ClOO : ClClO₂ ratio increases with lower initial OClO concentration. The rate of loss of OClO does not vary according to initial concentration and therefore is not a second-order process.

In order to make further comparison with the previously published studies, OCIO trapped in water-ice was photolysed at temperatures higher than 110 K. OCIO trapped in a water-ice matrix does not desorb until ice sublimation⁴⁷ and, therefore, co-deposited OCIO/H₂O can be photolysed up to 160 K, without significant OCIO loss. It was found that ClOO is still produced simultaneously with ClClO₂ up to 160 K, although loss of both species is significant owing to desorption. As the temperature at which photolysis was performed is increased from 110 to 160 K, more ClClO₂ is observed relative to ClOO. This increased ClClO₂ : ClOO ratio may be due to enhanced migration of ClOO (or Cl) through the warmer ice



Fig. 3 RAIR difference spectra showing the photolysis ($\lambda > 300$ nm, 105 K) of OCIO co-deposited with water-ice. OCIO loss bands are observed ($v_{as} = 1103$, 1086 cm⁻¹, $2\delta = 943$ cm⁻¹, $v_s = 920$ cm⁻¹) as well as CICIO₂ formation bands ($v_{as(OCIO)} = 1204$ cm⁻¹, $v_{s(OCIO)} = 1040$ cm⁻¹) and a CIOO formation band ($v_{(OO)} = 1439$ cm⁻¹).



Scheme 1 Illustration of OCIO dimers forming $CICIO_2 + O_2$

When Cl_2O and H_2O are deposited as separate layers, absorptions are observed for Cl_2O and also for amorphous water (800 and 3400 cm⁻¹). When Cl_2O and H_2O are codeposited, additional features are observed at 3650 cm⁻¹ (OH



Fig. 4 RAIR spectra of a neat thin film (ca. 500 nm) of Cl₂O

dangling stretch) and 1640 cm⁻¹ (OH deformation), which both arise from Cl₂O–H₂O interactions.

Photolysis of Cl₂O films

Fig. 5 shows a series of difference spectra recorded during the photolysis ($\lambda > 300$ nm, 105 K) of a thin layer of Cl₂O (*ca.* 500 nm) adsorbed onto a layer of water-ice. The consumption of Cl₂O is revealed by the decrease in intensity at 671 and 629 cm⁻¹. Within several seconds of photolysis, a species is formed which absorbs, principally, at 906 cm⁻¹. It is seen to maximise in intensity and then fall as the final product ClClO₂ is formed (1204 and 1040 cm⁻¹). Peaks previously assigned to OClO are also observed ($v_{as} = 1086$ and $2\delta = 940$ cm⁻¹) within a few minutes of photolysis. It is suggested that the intense 906 cm⁻¹ absorption band is due to the symmetric stretch of OClO, as will be discussed below.

The large discrepancy in the relative intensities of the peaks assigned to OCIO formed during the photolysis of Cl_2O and those observed for the deposition of OCIO (Fig. 1) is, at first sight, surprising. The relative intensities of peaks observed in IR spectra of very dilute OCIO in water matrices and of OCIO impurities in Cl_2O films (Fig. 4) are comparable with those seen for neat OCIO. This suggests that the relative change in intensity is not due to weak molecular or depolarisation effects. An alternative possibility is that it is a result of orientation effects, the MSS rule states that if the OCIO is aligned perpendicular to the surface, the asymmetric stretch is formally forbidden while the symmetric stretch (906 cm⁻¹) and bending (940 cm⁻¹) vibrational mode absorption intensities are enhanced.

Clearly, this explanation demands that the OClO aligns perpendicular to the surface when it is formed during photolysis, but shows no alignment effects when it is dosed directly onto the gold foil under carefully controlled conditions. Such behaviour would require that a specific configuration of Cl_2O molecules photoreacts to produce 'perpendicular' OCIO. A

Table 3Vibrational frequencies of Cl2O

	wavenumber/cm ⁻¹				
normal mode	adsorbed Cl ₂ O ^a	solid phase at 77 K^b	gas phase ^b	argon matrix ^c	
vs	629	630.7	640	639	
Š	_	296.4	300	288	
vas	671	670.8	686	677.1	
$v_{a} + \delta$	935				
$v_{aa} + \delta$	970	971.4	972		
$\frac{2v_s}{2v_s}$	1260	_			
$v_{a} + v_{aa}$	1298	1299.1	1320	_	
$2v_{aa}$	1331	1331.6	1360	_	
$3v_{a}$	1755			_	
$2v_{-} + v_{}$	1819	_			
$v_{1} + 2v_{2}$	1917	_			
$3v_{as}$	1979	1979.4	1945	—	

^a This study. ^b Ref. 48. ^c Ref. 32.

possible set of structures to clarify such a process is shown in Scheme 2 below.

In an attempt to isolate systematically the spectral features of the photolysis products of Cl₂O, low-pass cut-off filters $(300 < \lambda < 515 \text{ nm})$ were employed. The photolysis of Cl₂O to produce ClClO₂ proceeded throughout this range, though the rate of the reaction slowed as higher wavelength cut-off filters were used. The decrease in reaction rate is predictable and is due both to a reduction in light intensity and the lower absorption cross-sections of Cl₂O and OClO at longer wavelengths.

Further evidence for the proposed mechanism of the photolysis of Cl₂O can be found by studying the concentration profiles of species against time. Fig. 6 shows a timeabsorbance plot of the main absorbing species present during the photolysis of adsorbed Cl₂O. The plot illustrates the relative rates of the loss of Cl_2O and the formation of $ClClO_2$. Two intermediate peaks, the enhanced OClO stretch at 906 cm⁻¹ and the enhanced overtone of the OClO deformation mode at 940 cm⁻¹, are shown to form quickly and then decay during the photolysis. The absorption profile for the OCIO deformation mode at 940 cm⁻¹ is offset from the 906 cm⁻¹ profile due to interference from an underlying peak at 935 cm⁻¹, the $v_s + \delta$ mode of Cl₂O. However, of most interest, is the behaviour of the OClO asymmetric stretch absorption at 1086 cm⁻¹ which is seen to decrease in intensity initially before rising to its maximum. This observation can be attributed to the fact that an impurity of unaligned OClO, which absorbs principally at 1086 cm⁻¹, is deposited with the Cl₂O films. Such OClO photolyses rapidly, forming ClClO₂. As observed in Fig. 1(c) the 2δ and v_s modes for dilute OCIO are relatively weak and, because of the rapid formation of aligned OClO, no initial loss is apparent. An increase in intensity at 1086 cm⁻¹ is observed eventually, as this mode is not completely forbidden; presumably due to a lack of perfect alignment of the photochemically produced OCIO molecules.

Fig. 7 shows a TPD profile of a Cl₂O film that has been irradiated at $\lambda > 300$ nm for 5 min (*cf*. Fig. 5) and annealed at 140 K for a further 15 min to remove the majority of the Cl₂O starting material. The weak OCIO signal (m/z = 67) suggests that only a small amount of OCIO is produced by the photolysis of adsorbed Cl₂O, notwithstanding the strong RAIR absorption at 906 cm⁻¹. Peaks corresponding to the Cl₂O (m/z = 86) starting material and Cl₂ (m/z = 70) impurities are also observed.

The production of OClO from the photolysis of Cl_2O may occur *via* a clustering or non-clustering mechanism. The non-clustering mechanism can be represented as follows:

$$ClOCl + hv \rightarrow O + Cl_2$$
 (6b)

$$O + ClOCl \rightarrow OClO + Cl$$
 (12)

Initial photodissociation of Cl_2O produces an oxygen atom which is able to migrate and react with another Cl_2O molecule. The production of atomic oxygen from the photolysis of Cl_2O is unusual in the gas phase; ClO and Cl being preferentially produced [reaction (6a)].²⁹ No sign of the ClO radical, or the expected product dimers ClOClO and ClOOCl, are observed in our study, which suggests that reaction (6a) is not dominant over reaction (6b). Reaction (6b) may occur for adsorbed Cl_2O after the isomerisation of Cl_2O to ClClO; such an isomerisation has been readily observed in the photolysis of matrix-isolated Cl_2O .^{31–33}

$$ClOCl + hv \rightarrow [ClClO] \rightarrow O + Cl_2$$
(13)

Reaction (12) results in the production of atomic chlorine which, if it does not produce molecular chlorine, is free to migrate and react with a lone OCIO molecule to produce the final product, $CICIO_2$ via reaction (10). In this case, stopping photolysis after 15 min, when the OCIO concentration is at a maximum, should result in continued loss of OCIO and production of $CICIO_2$. However, this behaviour is not in accord



Scheme 2 Illustration of photolysis of Cl₂O with an example orientation which would produce aligned OClO



Fig. 5 RAIR difference spectra showing the photolysis ($\lambda > 300$ nm, T = 105 K) of Cl₂O on a layer of water-ice. Spectra are offset for clarity.

with the results, because on terminating irradiation no further reaction is observed to take place. Therefore slow migration of atomic chlorine is not significant in our experiments.

The non-clustering mechanism also does not support the postulate that OCIO is produced in an aligned form; a free,



Fig. 6 Time-absorbance plot for peak heights observed during the photolysis of a film of Cl_2O . All absorbances are shown as a fraction of their maximum value.



Fig. 7 TPD of film of neat $\rm Cl_2O$ following partial photolysis and annealing at 140 K

migrating O atom would be able to react with an isolated Cl_2O molecule [reaction (12)] from any direction. Therefore, possible clustering mechanisms have been considered to account for the reaction. A reaction, analogous to Scheme 1, by which two adjacent Cl_2O molecules produce OCIO would also result in Cl atom production. It may be possible for several Cl_2O molecules to align in a suitably specific manner to allow for the production of aligned OCIO, without producing a Cl atom. As mentioned above, Scheme 2 illustrates a system that would allow the production of aligned OCIO, which is able to photoreact further to produce CICIO₂.

Atmospheric implications

The heterogeneous photochemical reactions performed in this study demonstrate that both Cl₂O and OClO can be converted to chloryl chloride on water-ice by photolysis with both near-UV or visible light. Chloryl chloride released into the gas phase readily decomposes to OClO and a Cl atom which contributes to ozone destruction.9 Our postulated mechanism requires clusters of Cl₂O and OClO, or at least neighbouring molecules, for conversion to ClClO₂. Therefore, the relevance of this route to stratospheric or tropospheric ozone depletion depends on whether the concentrations of Cl₂O, OClO and HOCl are high enough to allow this to occur. A recent study has shown that the surface coverage of OCIO on polar stratospheric clouds (PSCs) at stratospheric conditions is too low for significant clustering to occur.50 HOCl, however, readily adsorbs to laboratory PSC mimics at stratospheric temperatures and pressures⁵¹ and its surface coverage is likely to be high.⁵² If we consider the chlorine reactivating process:

$$\text{ClONO}_{2(ads)} + \text{H}_2\text{O}_{(ads)} \rightarrow \text{HOCl} + \text{HNO}_{3(ads)}$$
 (5)

and that HOCl is in equilibrium with Cl_2O then it is possible that surface concentrations of Cl_2O may be sufficiently high for stratospheric OClO and ClClO₂ production to occur.

Should the heterogeneous photolysis of Cl_2O be significant then it also provides an alternative mechanism for the production of stratospheric OCIO. Observed OCIO concentrations are currently used to estimate BrO concentrations following the argument that the BrO + CIO coupling reaction is the sole source of stratospheric OCIO.^{53,54} If significant OCIO concentrations are also formed by the photolysis of adsorbed Cl_2O then current estimates of stratospheric BrO concentrations may be too high.

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