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# Evidence for the reaction of highly vibrationally excited ClO radicals with nitrogen

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**Abstract**

The stratospheric trace gas chlorine dioxide diluted in nitrogen at normal pressure is irradiated with laser light at a wavelength of 308 nm, which corresponds essentially to the $(X^2B_1 0,0,0) \rightarrow (A^2A_2 18,0,0)$ symmetric stretch progression of OClO. This highly vibrationally excited initial OClO state produces $ClO(X^2\Pi_\Omega, v, J)$ radicals containing almost the entire amount of excess energy in their internal degrees of freedom. The ClO fragments resulting from this dissociation process carry sufficient internal energy to exceed the activation energy for the reaction with nitrogen. Accordingly, the reaction $ClO(v \gg 0) + N_2 \rightarrow Cl + N_2O$ could represent an additional source for nitrous oxide and atomic chlorine in the stratosphere. The generation of $N_2O$ is experimentally observed in a single-shot laser experiment where the $N_2O$ is detected by means of a gas chromatograph. The experimental results indicate that there is in fact a strong evidence for the production of nitrous oxide via the vibrationally mediated reaction of ClO radicals with abundant nitrogen molecules. © 1997 Elsevier Science B.V.

## 1. Introduction

The photolysis of the stratospheric trace gas OClO is known to proceed via two product channels [1–4]. The minor product channel $OClO + h\nu(> 340\ nm) \rightarrow Cl + O_2$ generates molecular oxygen and chlorine atoms. As is widely known, chlorine atoms in the stratosphere participate in the depletion of the ozone layer via catalytic cycles and therefore attention has been paid to the occurence of this product channel. However, the relative quantum yield of this channel under gase phase conditions remains controversial. Moreover, it is still under discussion whether in the gas phase $Cl + O_2$ is formed in a concerted decay mechanism [1,2,4] or via an isomerisation step involving a symmetrical ClOO molecule [5–7]. For this reason, we recently investigated the chlorine channel employing a three-photon laser induced fluorescence technique for $Cl(^2P_J)$ detection at a wavelength which is sufficiently long to avoid secondary photolysis of the ClO partner fragment [8]. These measurements indicate that the chlorine atom channel is wavelength dependent with a yield of around 3% at the red end of the OClO absorption spectrum.

The major photolysis channel $OClO \rightarrow ClO + O$ produces chlorine monoxide and oxygen atoms ($\Phi > 95\%$). The ClO radical is known as an intermediate which is involved in the halogen-catalysed destruction of ozone. However, since the O atoms can react with molecular oxygen in a three-body collision to


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reform ozone which is destroyed by ClO radicals, the ClO + O channel, although being the major channel, is regarded as having no influence on the stratospheric ozone layer [9]. However, this does not consider the increased reactivity of vibrationally excited ClO. Resulting from the $OClO(A^2A_2\ 18,0,0)$ photolysis at 308 nm ClO was observed to be formed mainly in extremely high vibrational states [10]. In an additional experiment [11] it was found that resulting from the respective initial state of OClO the internal energy distribution of the ClO fragments exhibits a steady increase up to the energetical limit of 13500 $cm^{-1}$. From previous state-resolved investigations of the $OClO + h\nu \rightarrow ClO(X^2\Pi_\Omega v,J) + O(^3P)$ dissociation at wavelengths between 360 and 308 nm [10,12], we observed a population ratio for the two ClO spin–orbit states of around $P(^2\Pi_{3/2}):P(^2\Pi_{1/2}) = 3.5$ corresponding to an average energy of about 90 $cm^{-1}$ which was the case for all observable vibrational levels of the $ClO(v)$ fragments ($v = 0$ to $v = 4$). Similarly, the observed rotational excitation of the fragments was independent of the photolysis wavelength and the ClO vibrational state. Boltzmann distributions of around 1100 K were obtained in each case from least square fits of the rotational state populations. Due to the Franck–Condon factors only the five lowest vibrational states could be analyzed. However, the observed independence of the vibrational state of both the spin–orbit and the rotational state population indicates a similar behaviour for the upper vibrational states. Thus, the ClO radicals are probably formed with rotational energies around 770 $cm^{-1}$. Compared to the total internal energy of the ClO fragments observed in the 308 nm OClO photolysis, the combined contribution of the spin–orbit as well as the rotational fragment excitation of ca. 860 $cm^{-1}$ is small, indicating the majority of the available energy of the dissociation process is transferred into product vibration. Accordingly, the energetical limit should be given by the $v = 18$ vibrational state of ClO.

Recent experiments of Huber et al. [13] indicate that the extremely high internal excitation of ClO which is observed in the 308 nm photolysis of OClO is also obtained in the shorter wavelength region of the OClO absorption band. From the features of their ClO internal energy distributions only small contributions of the rotational and the spin–orbit excitation to the fragments internal energy are expected. As a consequence, new reaction channels are opened which might, in principle, have an impact on the atmospheric chemistry. For example, the mechanism

$$ClO(v \gg 0) + O_3 \rightarrow ClOO + O_2, \quad (1a)$$

$$ClOO + M \rightarrow Cl + O_2 + M \quad (1b)$$

is presumably facilitated by the high vibrational excitation of the ClO radicals. The asymmetric chlorine dioxide formed in process (1a) subsequently decays into atomic chlorine and molecular oxygen (1b). This ozone depletion mechanism was, for ClO with low internal energy, not predicted to affect the ozone layer [14,21]. It must be mentioned, however, that chemical reactions in the upper atmosphere involving trace gases are unlikely to occur because of the efficient collisional relaxation of $ClO(v \gg 0)$ induced by the main components, namely nitrogen and molecular oxygen, prior to reaction with e.g. ozone. However, provided that the internal excitation of the $ClO(v \gg 0)$ radicals is sufficiently high for reaction with highly abundant $N_2$, the reaction rate will easily compete with the relaxation rate. Correspondingly, the reaction

$$ClO(v \gg 0) + N_2 \rightarrow Cl + N_2O, \quad (2)$$

which is endothermic by 8500 $cm^{-1}$ with respect to $ClO(v = 0)$ becomes energetically allowed for $ClO(v > 10)$. Since those vibrationally excited ClO products are easily obtained from the decay of $OClO(A^2A_2 18,0,0)$, ultraviolet photolysis of OClO may play an additional role in stratospheric chemistry. Recently, the possible influence of another highly vibrationally excited species, namely $O_2(X,v > 25)$, on the stratospheric processes was pointed out by Miller et al. [15]. They supposed a new mechanism with respect to the "ozone deficit" problem where $O_2(v \gg 0)$ generated from the ozone photodissociation at a wavelength of 226 nm reacts with $O_2$ to produce ozone. Kawasaki, Hancock and their co-workers reported the significant participation of vibrationally excited $O_3$ in the formation of $O(^1D)$ [16]. All these observations clearly indicate the importance of highly vibrationally excited molecules in understanding the chemistry of the atmosphere.

## 2. Experimental

Chlorine dioxide was produced according to the method of Derby and Hutchinson [17] by pouring a mixture of chlorine and nitrogen at room temperature slowly through a cylindrical glass column, 40 cm in length and 5 cm in diameter which was filled with sodium chlorite and glass beads. Since OClO tends to explode at higher pressures the ratio of the employed $Cl_2$:$N_2$ mixture was only 10%. After it passed through the column the resulting gas mixture containing essentially OClO and nitrogen was stored in a cylindrical quartz cell, 10 cm in length and 2 cm in diameter. Since the remainder was only minor traces of molecular chlorine, the obtained OClO:$N_2$ mixture was carried to analysis without further purification. In order to generate the required highly vibrationally excited ClO radicals, the quartz cell was irradiated along the main axis by a single pulse of an XeCl excimer laser (Lambda Physik LPX 100). The excimer beam was not focussed, so that the total volume of the quartz cell was uniformly covered by the laser light. The pulse energy of the excimer laser light was about 100 mJ at a pulse width of around 25 ns. The analysis of the final product mixture was performed using a gas chromatograph (Hewlett Packard HP 5890 Series II). A packed column (Molecular Sieve 5 A) of 2 m in length was employed. The gas chromatograph was equipped with an electron capture detector in order to be sensitive to the $N_2O$ content. A 5% mixture of argon diluted in methane was used as a carrier gas. In order to exclude the possible influence of the employed apparatus on the formation of the products, a similar experiment, using a gas chromatograph (Carlo Erba GC 6000) equipped with a capillary column (Carboxen 1006 Plot) of 30 m in length and a thermal conductivity detector was carried out. In this case the carrier gas was pure helium.

## 3. Results

The entire kinetic energy distribution of O partner atoms as well as the corresponding internal energy distribution of the nascent ClO radicals originating from the photofragmentation of OClO($A^2A_2$ 18,0,0) at a wavelength of 308 nm were previously obtained in a two-color REMPI experiment [11] and are represented in Fig. 1(a) and 1(b). It is obvious from Fig. 1(b) that the internal energy distribution of ClO increases up to the energetical limit. As described above, the predominant part of the internal energy of ClO is due to vibrational excitation. Hence, ClO radicals up to $v = 18$ may be formed in the OClO photolysis at 308 nm.

In order to examine the possible reaction of these highly vibrationally excited ClO radicals with $N_2$, gas chromatograms using electron capture detection were recorded. The chromatograms represented in Fig. 2(a) and 2(b) result from mixtures of OClO in nitrogen which were irradiated with the 308 nm excimer laser light. In Fig. 2(a) the irradiated cuvette contained about 80 mbar of OClO diluted in 900 mbar of $N_2$ whereas in Fig. 2(b) the concentration of OClO was decreased by two orders of magnitude. In

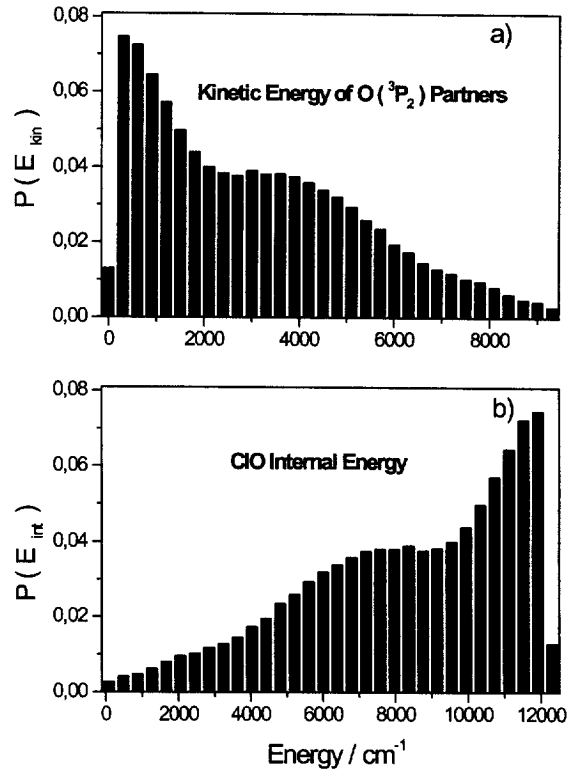


Fig. 1. (a) Kinetic energy distribution of $O(^3P_2)$ partner atoms obtained in the ($A^2A_2$ 18,0,0) photolysis of OClO; (b) internal energy distribution of nascent ClO($X^2\Pi_i$) as a result of the ($A^2A_2$ 18,0,0) photolysis of OClO.

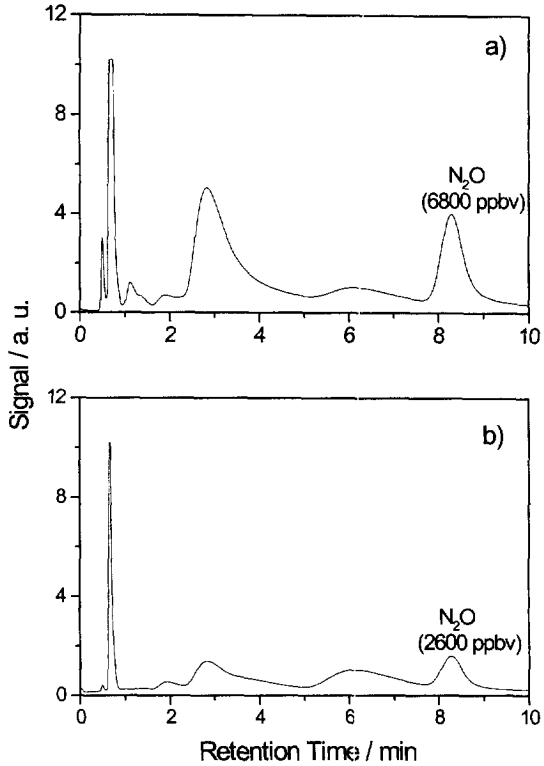


Fig. 2. (a) Gas chromatogram observed from around 80 mbar of OClO in $N_2$ irradiated at a wavelength of 308 nm; (b) gas chromatogram resulting from around 1 mbar of OClO in $N_2$ irradiated at 308 nm.

both chromatograms a significant formation of $N_2O$ is recognizable, the corresponding peaks appearing at a retention time of slightly above 8 min. The assignment of the $N_2O$ peaks was possible by comparing these chromatograms with the results from a quartz cuvette filled with a proof gas containing a defined portion of 300 parts per billion by volume (ppbv) of $N_2O$. In order to prove the reliability of the electron capture detector during the measurements, the proof gas was analysed before and after the experiments; it turned out that the sensitivity of the electron capture detector with respect to $N_2O$ had not significantly changed during the measurements. These results were confirmed in a similar experiment, where a different column (Carboxen 1006 Plot) was employed and the chromatograms of the final products were obtained by means of a thermal conductivity detector. At this point, it should be mentioned that the observed $N_2O$ products are each the result of single-shot experiments. Consequently, in these experiments the photodissociation of secondary products can be ruled out and the proceeding chemistry is driven solely by the radicals formed in the 308 nm photolysis of OClO, namely $ClO(v \gg 0)$ and O.

## 4. Discussion

The dominant fate of OClO in the stratosphere is efficient photolysis during daylight [18] due to the high absorption cross section in the ultraviolet wavelength region between 260 and 480 nm [19]. In the gase phase the photofragmentation of OClO occurs via two product channels:

$$OClO + h\nu \rightarrow ClO + O, \quad (3)$$

$$OClO + h\nu \rightarrow Cl + O_2. \quad (4)$$

The major channel (3) generating ClO and O radicals is supposed to lead to no net ozone loss due to the O atoms reacting with $O_2$ to reform $O_3$ [9]. Hence, with regard to the destruction of the ozone layer only the chlorine producing dissociation channel (4) was taken into account. Accordingly, the quantum yield of the chlorine channel at various wavelengths has been investigated [1–4,8]. Mode specific branching ratios of the two channels were found, the asymmetric stretch of OClO enhancing ClO formation, the excitation of the bend of OClO favoring Cl formation [2–4]. However, the corresponding absolute quantum yields in the gas phase are still under discussion [1–4]. Nonetheless, the present Letter shows that evidence for additional catalytic cycles arises due to the extremely high vibrational excitation of ClO fragments formed in the OClO photodissociation at wavelengths below 308 nm. Moreover, according to the experiments of Colussi [20] and those of Davis and Lee [2,4], the quantum yield for ClO formation in this short wavelength region is nearly unity. Due to the extremely high vibrational excitation of the photolytically formed ClO radicals, the ozone depletion potential of stratospheric OClO can no longer be reduced to only the chlorine channel (4).

Assuming Arrhenius behavior, Stevens and Anderson [21] have investigated the A-factor and the activation energy of reaction (1a) with respect to

$ClO(v = 0)$ concluding that this reaction is too slow at stratospheric temperatures to play any role in the ozone loss over Antarctica. While Vaida et al. [22] pointed out that the rate of reaction (1a) might be strongly enhanced for $ClO(v = 4)$, it was experimentally found by Baumgärtel et al. [23] that the relaxation rate for $ClO(v = 4) + M \rightarrow ClO(v = 0) + M$ is sufficiently fast to prevent a mentionable contribution arising from reaction (1a). Vibrational excitation of ClO products in $(v = 4)$ vibrational states is already obtained in the $OClO(A^2A_2 11,0,0)$ photolysis at 351 nm [10] whereas the vibrational excitation of the $ClO(v)$ radicals observed in the $OClO(A^2A_2 18,0,0)$ photolysis is higher.

As for reaction (2), the required amount of ClO internal energy which is necessary to enable the ClO radicals to react with the abundant $N_2$ is readily delivered in the 308 nm OClO photodissociation. In addition, the collision probability of $ClO(v >> 0)$ with the ubiquitous $N_2$ molecules is nearly unity. However, from (Fig. 1(b)), only around 56% of the ClO radicals generated in the OClO $(A^2A_2 18,0,0)$ photolysis carry sufficient internal energy to thermodynamically react with $N_2$.

In the following, the order of magnitude of $N_2O$ formation from the $OClO/N_2$ photolysis will be calculated.

Given the pulse energy of 100 mJ of the photolysis laser at 308 nm and the corresponding OClO absorption cross section of $\sigma = 4 \times 10^{-18}$ cm$^2$ [24], the number of ClO fragments generated in a single photolysis laser pulse can be derived. Since the amount of $N_2O$ is measured, the relative yield of $N_2O$ is given by $\eta = n(N_2O)/n(ClO)$. One obtains about 3% for the mixture of 80 mbar OClO in $N_2$ and about 2% for the mixture of 0.8 mbar OClO in $N_2$.

Summarizing, the results reported in the present work give evidence for the formation of $N_2O$ and Cl atoms as a consequence of reactive collisional quenching of $ClO(v > 10)$ by $N_2$. Hence, in excess to the Cl quantum yield of around 3% arising from the Cl channel of the OClO photolysis which was measured in recent studies [4,8], further 2% atomic chlorine should be added according to our experimental results. Therefore, the potential role of internally excited species with regard to the chemistry of the upper atmosphere is indicated.

While hitherto mostly surface-based $N_2O$ sources were taken into account [25], reaction (2) apparently seems to represent an in situ stratospheric source of $N_2O$. A similar source of $N_2O$ in the stratosphere was previously observed by Zellner et al. [26] where $N_2O$ formation was observed as the result of collisional deexcitation of electronically excited $NO_3$ and $NO_2$ species by abundant $N_2$.

The yield of $N_2O$ which, according to our experimental results, arises from the photodissociation of OClO at 308 nm is at present not expected to strongly affect the stratospheric chemistry. However, from the observed steadily increasing concentrations of brominated compounds in the stratosphere one can expect higher future OClO concentrations [27].

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