



## State Resolved Detection of Cl, Br, ClO and BrO

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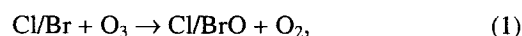
**Abstract.** Nascent ClO and BrO products in photodissociation or reaction processes were observed in a state resolved manner by applying the two-photon laser-induced fluorescence technique, where two simultaneously absorbed laser photons excite the products to the C-state. Cl and Br atoms can be observed by means of three-photon excitation with subsequent recording of the VUV fluorescence light. The advantage of this detection technique, other than the simpler laser system, is the use of low energy photons which don't interfere with other processes. State resolved detection of BrO products has been performed in the reactions  $O(^1D)+CF_3Br$  and  $Br+O_3$ .

The photodissociation of  $OCIO(^2A_2 v_1, v_2, v_3) \rightarrow ClO(X^2\Pi_{g, v, J, \Lambda}) + O(^3P)$  in the 356–371 nm region is clearly a function of the initial type of motion of  $OCIO(^2A_2 v_1, v_2, v_3)$ . The population of the fragment rotational levels is observed to resemble Boltzmann distributions of around 1000 K. When high vibrationally excited states of the symmetric stretch mode of  $OCIO(^2A_2 v_1 > 17, v_2, v_3)$  are excited, then most of the available energy is transferred to ClO vibration. Those extremely vibrationally excited ClO products carry sufficient energy to react with ambient nitrogen in the atmosphere, which is confirmed in a final end product analysis where the formation of  $N_2O$  is observed.

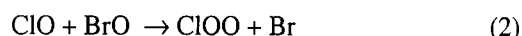
The Cl quantum yield of the minor  $OCIO(^2A_2 v_1, v_2, v_3) \rightarrow Cl(^2P_{3/2}) + O_2$  channel depends on the state of the parent molecule and is of the order of 4%.

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chemical species (Rowland and Molina, 1975; Yung et al., 1980; Brune et al., 1988) Ozone depletion in the polar stratospheric regions is to a great extent triggered by their photochemical products via catalytic ozone destruction cycles initiated by the reaction



where the oxides of chlorine and bromine play the central role. In fact, catalytic reaction cycles involving ClO and BrO radicals are supposed to be responsible for about 30% of the halogen-controlled loss of mid-latitude lower stratospheric ozone (Wennberg et al., 1994). Iodine oxide has recently been suggested to additionally account for some of the observed ozone loss (Solomon et al., 1994). This importance of halogen containing free radicals for the atmosphere has motivated numerous studies addressing ClO, BrO and IO (Nickolaisen et al., 1994; Mauldin et al., 1993; Rowley et al., 1996; Li et al., 1997; Gilles et al., 1997). The bimolecular reaction of ClO with BrO is known to proceed via the three reaction pathways (McElroy et al., 1986; Friedl et al., 1989):



Reactions (2) and (4) are well-established to account for a significant loss of stratospheric ozone (Anderson et al., 1989). Contrary to the kinetically unstable asymmetric ClOO which decays instantaneously into Cl and  $O_2$  (Nicovich et al., 1991, Vaida et al., 1989) the symmetric OCIO molecule (reaction 3) is photolysed in the ultraviolet region with participation of two fragmentation channels (Sanders et al., 1993; Toohey et al., 1990; Brandtjen et al., 1994; Solomon et al., 1988; Solomon, 1990):

### 1 Introduction

The stratospheric ozone layer is clearly established to be significantly affected by chlorine and bromine containing

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and, hence, is closely coupled to the chemistry of chlorine and bromine (Wahner and Schiller, 1992; Sessler et al., 1995; McElroy et al., 1986). Since the Cl radicals released in product channel (6) lead to a destruction of ozone, much effort has hitherto been done in determining the quantum yield of this dissociation channel (Lawrence et al., 1990; Bishenden et al., 1991; Bishenden et al., 1992; Davis and Lee, 1992; Davis and Lee, 1996; Delmdahl et al., 1998).

In most investigations ClO and BrO are observed by absorption using their well-known  $A^2\Pi-X^2\Pi$  bands. In evaluating the gas-phase dynamics and mechanisms, however, detection methods which are more sensitive and state-resolved in nature are required. Proven methods in meeting these necessities are resonance enhanced multi-photon ionisation (REMPI) (Duignan et al., 1985; Morozov et al., 1997) as well as laser induced fluorescence (LIF). For the investigation of state-resolved products formed in reactive processes in particular the LIF method allowing higher total cell pressures is rather suitable. While laser induced fluorescence is observable from the  $A^2\Pi$  state of IO in a one-photon excitation step (Inoue et al., 1983; Turnipseed et al., 1995), the analysis of nascent state-resolved ClO( $X^2\Pi$ ) formed in photodissociations and reactions requires an excitation to the  $C^2\Sigma$  Rydberg state (Baumgärtel et al., 1994; Matsumi et al., 1995), which can most easily be performed via two-photon excitation and observation of the total fluorescence in the VUV. In this study we report two-photon laser induced fluorescence detection of BrO( $X^2\Pi$ ) and ClO( $X^2\Pi$ ) radicals. Furthermore, detection of atomic halogen products via three-photon laser induced fluorescence is presented.

## 2 Experiment

The experimental set-up is essentially similar to that which has been described in a previous publication (Delmdahl et al., 1996) and shall only briefly be discussed at this point. Experiments were carried out in a reaction chamber under flow conditions to prevent accumulation of primary and secondary reaction products. The OCIO is produced after the method of Derby and Hutchinson (1953) by pumping a mixture of neat chlorine diluted in nitrogen (1:10) through a sodium chlorite packed glass column. Using teflon tubes the in-situ OCIO product is carried to the reaction chamber without further steps of purification. The unreacted chlorine and nitrogen do not influence the detection of the nascent ClO radicals. BrO is generated in the reaction of Br atoms with  $\text{O}_3$  or in the reaction of  $\text{O}(^1\text{D})$  with  $\text{CF}_3\text{Br}$ .  $\text{O}(^1\text{D})$  reactants were produced by photolysis of ozone at a wavelength of 308 nm delivered by a XeCl excimer laser (Lambda Physik LPX100, 200 mJ/pulse). Ozone was synthesised in a silent discharge of molecular oxygen (Gericke et al., 1981). In the reaction  $\text{O}(^1\text{D}) + \text{CF}_3\text{Br}$  a mixture of  $\text{O}_3/\text{CF}_3\text{Br}$  was employed, whereas  $\text{O}_3$  and  $\text{Br}_2$  (precursor of the  $\text{Br}(^2\text{P}_{3/2})$  collision partner) were separately

added to the reaction chamber. The production of  $\text{Br}(^2\text{P}_{3/2})$  atoms was achieved by irradiating gaseous  $\text{Br}_2$  at 532 nm using the frequency doubled output of a Nd:YAG laser (Quanta Ray DCR1A-YAG, 100 mJ/pulse). For calibration measurements Cl( $^2\text{P}_{3/2}$ ) atoms were produced by photolysis of  $\text{Cl}_2$  at 355 nm using the third harmonic of the Nd:YAG laser.

Cl, Br, ClO, and BrO are detectable in a state resolved manner by multi-photon excitation in a stable excited state and observation of the subsequent VUV fluorescence from this state back to the electronic ground state. The BrO and ClO two-photon excitation wavelengths in the range of 335 to 365 nm were delivered by a tunable dye laser (Radiant Dyes DL-midi) pumped by a XeCl excimer laser (Radiant Dyes RD-EXC-200). The pulse duration was 15 ns and the dye laser output (p-terphenyl and RDC 360-neu dissolved in dioxane as active medium) was 8-10 mJ/pulse at a bandwidth of  $0.4 \text{ cm}^{-1}$ . In order to detect the Cl( $^2\text{P}_J$ ) atoms formed in reaction (6) the  $4s^2\text{P}_J \leftarrow 3p^2\text{P}_J (J=^1/2, ^3/2)$  transitions are probed by resonant absorption of three photons around an excitation wavelength of 404 nm followed by subsequent monitoring of the total vacuum ultraviolet fluorescence near 135 nm. The corresponding three-photon excitation wavelengths for Br( $^2\text{P}_J$ ) atoms via the  $5s^2\text{P}_J \leftarrow 4p^2\text{P}_J$  transitions are at 446.7 nm ( $^3/2 \leftarrow ^3/2$ ) and 459.6 nm ( $^1/2 \leftarrow ^1/2$ ).

The photolysis and detection lasers were focused by 300 mm and 250 mm quartz lenses, respectively. The two laser beams counter-propagated through the reaction chamber. The time delay between the laser was usually in the order of one microsecond to guarantee nascent vibrational state distributions. For collision free product detection, a time-delay between photolysis and detection of 100 ns at a total cell pressure of 20 Pa is employed.

A solar-blind photomultiplier tube (Thorn EMI 9403B), which recorded the VUV fluorescence, was mounted perpendicular to the laser beams. Since this photomultiplier is insensitive to the excitation wavelengths used, no interference due to scattered light occurred. The signal of the photomultiplier is fed into a boxcar integrator (Stanford Research SR 250) and stored into a personal computer. The data recording is optically triggered by the detection laser pulse using a fast photodiode. REMPI spectra of ClO have also been recorded in the photodissociation of OCIO (reaction 5).

## 3 Results and Discussion

### Cl and Br detection

Chlorine and bromine atoms can be detected in a state resolved manner by simultaneous absorption of three photons inducing the  $^2\text{P}_J \leftarrow ^2\text{P}_J$  transition and observation of the VUV fluorescence back to the initial state. The two spin-orbit components ( $J=^3/2, ^1/2$ ) are easily resolved. The advantage of this technique is the use of low energy photons which don't interfere with other substances. One application of this three-photon LIF technique is the characterisation of the dissociation channel (6) (Lawrence et al., 1990; Bishenden et al., 1991; Bishenden et al., 1992; Davis and

Lee, 1992; Davis and Lee, 1996; Delmdahl et al., to be published). Until now, the highest ever reported contribution of this minor chlorine channel (3) is about 10 to 15 % near 360 nm (Bishenden et al., 1991; Bishenden et al., 1992). This is in contradiction to the studies of Lawrence et al. (1990) and Davis et al. (1992) which report in this spectral region a Cl yield of about 0 % and 0.2 %, respectively.

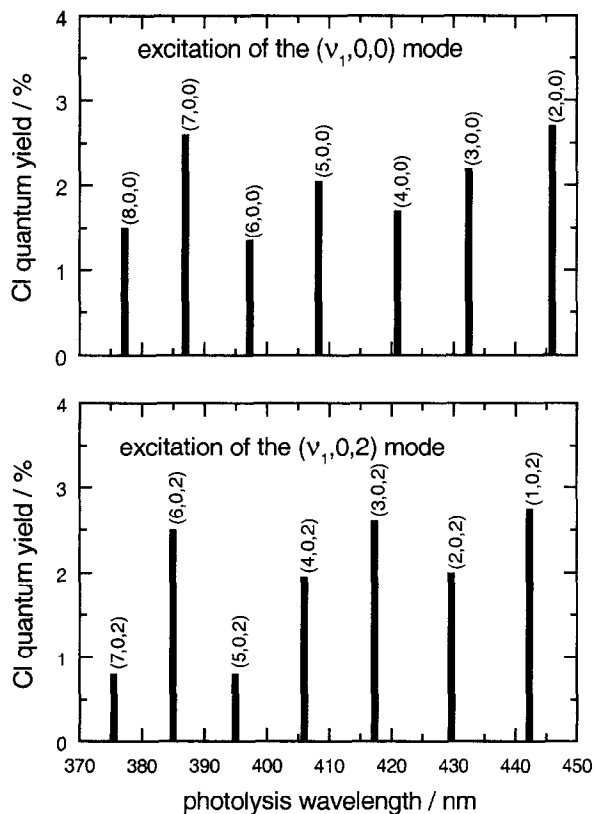


Fig. 1.  $\text{Cl}(^2\text{P})$  quantum yield from excitation of OCIO in different vibrational modes of the  $\text{A}^2\text{A}_2$  state. The Cl atoms were detected by three-photon excitation around 404 nm.

Recently, the relatively high Cl quantum yields given in (Bishenden et al., 1991; Bishenden et al., 1992) have been proved to be influenced by an onset of secondary fragmentation of ClO radicals which are simultaneously formed via channel (5) In recent independent investigations of the Cl yield produced in the photofragmentation of OCIO up to a photolysis wavelength of 340 nm a maximum Cl formation of only around 4 % was observed (Davis and Lee, 1992; Davis and Lee, 1996; Delmdahl et al., 1998). Fig. 1 shows the dependence of the Cl quantum yield when different vibrational modes of the OCIO( $\text{A}^2\text{A}_2$ ) are excited. In any case, the observed Cl yield is below 4%. According to model calculations (Vaida and Simon, 1995), this rather low quantum yield of Cl is not expected to noticeably influence the stratospheric ozone layer. Results of bromine atom detection will be published in a forthcoming paper.

## BrO and ClO detection

The OCIO absorption spectrum extending in the 280-460 nm regime exhibits distinct vibrational bands involving progressions of the purely symmetric stretch ( $v_1,0,0$ ), the symmetric stretch and bend ( $v_1,1,0$ ), the symmetric stretch and asymmetric stretch ( $v_1,0,2$ ) and the combination mode ( $v_1,1,2$ ). Several state-to-state experiments using photofragment translational energy spectroscopy (cf. Davis and Lee, 1992; Davis and Lee, 1996; Furlan et al., 1997) and resonance enhanced multi-photon ionization (cf. Bishenden et al., 1991; Bishenden et al., 1992) have been carried out in order to study the influence of the initial motion of electronically excited OCIO parent molecules on both the quantum yield of channel (5) and (6) and on the ClO product state distribution. The observation of rotationally resolved ClO fragments is feasible by using laser induced fluorescence techniques via the  $\text{C}(^2\Sigma)$  state of ClO (Baumgärtel and Gericke, 1994; Matsumi et al., 1994; Matsumi and Shamsuddin, 1995; Takahashi et al., 1996). The rotational distribution depends only slightly on the initial OCIO state and can be described by a temperature around 1000 K. Only the photodissociation of jet cooled OCIO from the lowest vibrational states shows a stronger mode effect on the ClO rotational distribution (Choi et al., 1999). As an example the ClO rotational distribution from the  $(v_1,0,2)$  and the  $(v_1,1,2)$  mode are shown in Fig. 2.

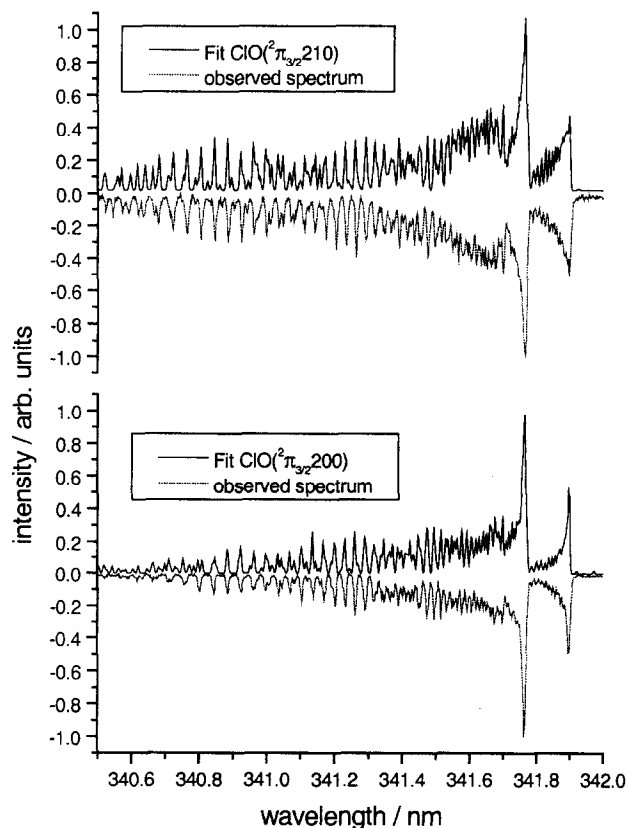


Fig. 2. Two-photon spectrum of  $\text{ClO}(\text{C}^2\Sigma, v=0, J' \leftarrow \text{X}^2\Pi_{\Omega}, v=0, J)$  originating from the decay of jet cooled OCIO in the  $^2\text{A}_2(2,1,0)$  state (upper part) and in the  $^2\text{A}_2(2,0,0)$  state (lower part).

Vibrationally excited ClO fragments are generated when OCIO is excited to higher vibrations of the symmetric stretch mode. As an example, the vibrational ClO distributions as a result of OCIO( $A^2A_2$ ) decay from different excited modes ( $\nu_1, \nu_2, \nu_3$ ) at similar energies is shown in Fig. 3.

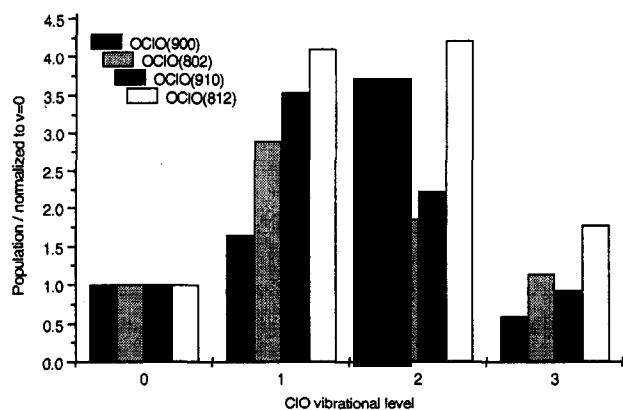
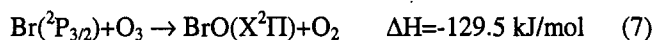


Fig.3. Vibrational product state distribution of the ClO ( $X^2\Pi_{\Omega}$ ) radicals formed in the decay of OCIO( $A^2A_2$ ,  $\nu_1, \nu_2, \nu_3$ ). Excitation of the asymmetric stretch mode  $\nu_3$  enhances the generation of vibrationally excited products.

Obviously, the vibrational state distribution is mode dependent and the highest populated vibrational state is at  $v=4$ . It should be mentioned that also the reaction of Cl+O<sub>3</sub> results in vibrationally excited ClO centred around  $v=4$  (Matsumi et al., 1996; Baumgärtel et al., 1998).

BrO fragments were studied in the O(<sup>1</sup>D)+CF<sub>3</sub>Br and in the ozone destruction reaction:



The two-photon LIF spectrum which is obtained from reaction (7) is represented in Fig.4.

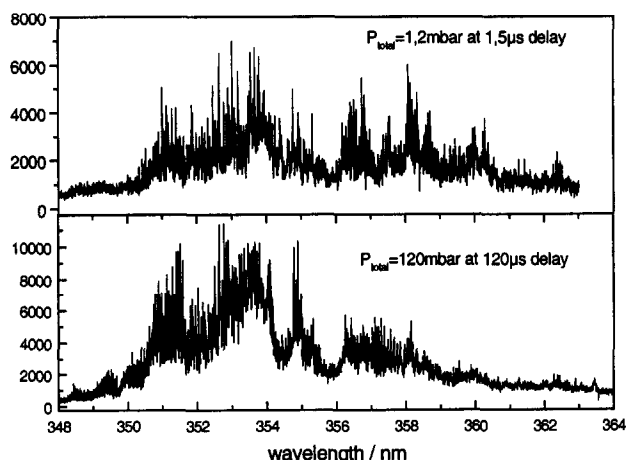


Fig. 4. Two-colour (2hv) LIF spectrum of BrO at two different collision numbers. in the reaction of Br+O<sub>3</sub>.

The mixture of O<sub>3</sub>/Br<sub>2</sub> was photolysed at a wavelength of 532 nm. When the photolysis laser was blocked or fired after the detection laser no BrO signals were observed. Due to the total cell pressure and delay times, the BrO rotational distribution is already relaxed while the vibrational distribution is still nascent. The obviously radiative BrO electronic state obtained in our study has to be of an electronic energy of around  $T_e=56000 \text{ cm}^{-1}$ . In addition to the BrO( $A^2\Pi$ ) first excited electronic state ( $T_e = 26098 \text{ cm}^{-1}$ ) which is not suitable for LIF detection due to predissociation (Orr-Ewing, private communication), higher-lying electronic states of BrO known at this time are the  $E^2\Sigma$  ( $T_e=64916 \text{ cm}^{-1}$ ),  $F^2\Sigma$  ( $T_e=67420 \text{ cm}^{-1}$ ) and  $G$  ( $T_e=70441 \text{ cm}^{-1}$ ) states which had at first been observed by Duignan and Hudgens (1985) by employing a three-photon REMPI detection scheme at wavelengths between 417 and 474 nm. In comparison with the  $A^2\Pi$  ( $T_e=31750 \text{ cm}^{-1}$ ),  $E^2\Sigma$  ( $T_e=67323 \text{ cm}^{-1}$ ),  $F^2\Sigma$  ( $T_e=70093 \text{ cm}^{-1}$ ) and  $G$  ( $T_e=73600 \text{ cm}^{-1}$ ) excited electronic states of ClO, the corresponding BrO states are all lowered in energy. Hence, a similar behaviour should be observed for the C states of BrO and ClO. Accordingly, our two-photon LIF spectrum (Fig.4) can be well rationalised with C-X rovibronic progressions of BrO.

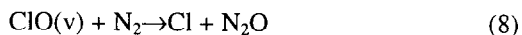
Compared to the corresponding ( $C^2\Sigma, v=0-X^2\Pi_{\Omega}, v, J$ ) two-photon LIF spectrum of the ClO radical (Delmdahl et al., 1998) the BrO( $C-X^2\Pi_{\Omega}, v, J$ ) two-photon LIF spectrum is far more congested. This is not surprising because the rotational constants for BrO are smaller than for ClO leading to smaller distances within the rotational branches. Furthermore, the natural ratio of <sup>35</sup>Cl/<sup>37</sup>Cl is 75.8:24.2, the natural isotope abundance of <sup>79</sup>Br/<sup>81</sup>Br, however, is nearly equal. Whereas the respective  $\Omega=1/2$  spin-orbit subband of ClO( $X^2\Pi_{\Omega}$ ) does not overlap other spin-orbit subbands in the (C-X) two-photon LIF spectrum, this will be the case in the corresponding BrO spectrum due to the spin-orbit constant being comparable to the vibrational frequency for the BrO( $X^2\Pi_{\Omega}$ ) ground state. Moreover, ClO ( $C^2\Sigma, v>0$ ) states were not observed in ClO two-photon LIF spectra, because of fast predissociation. The vibrational spacing which occurs in the BrO spectrum in Fig.4 strongly indicates that fluorescence is also obtained from  $v>0$  levels of the BrO C state.

Despite the above described drawbacks preventing at present an unambiguous assignment of the BrO spectrum, it is possible to simulate an apparent vibrational band of the BrO spectrum (Delmdahl and Gericke, 1998) Considering the bandhead region of the  $C(v=0, J) \leftarrow X(v=0, J)$  transitions around 351 nm several more bandheads can be observed at longer wavelength which have to originate from vibrationally excited BrO( $X^2\Pi, v, J$ ) states (upper part of Fig. 4). At higher collision numbers (lower part of Fig. 4), where already vibrational relaxation takes place, spectral features from vibrationally excited species become unimportant. Indications of vibrationally excited BrO from reaction (7) were also obtained by McGrath and Norrish (1958) in a flash-photolysis study via the A-X band and recently by Lee et. al. (1997) in a crossed molecular beam time-of-flight

experiment. Thus, similar to the corresponding Cl+O<sub>3</sub> reaction (Baumgärtel et al., 1998), BrO is also generated with high vibrational excitation.

Since various new reactions become thermodynamically accessible for ClO or BrO being formed in vibrationally excited states one has to discuss its influence on atmospheric chemistry. The key factor to determine the importance of internally excited species to atmospheric reaction is the relaxation time to the ground state in collisions with oxygen and nitrogen. For example, the vibrational excitation of ClO or BrO has to "survive" at least 1 million collisions with ambient air before it has a chance to react with ozone due to the O<sub>3</sub> concentration in the stratosphere. We measured the average vibrational relaxation constant in collisions of ClO(v) with N<sub>2</sub> to be  $k_{v \rightarrow v-1} = 5 \cdot 10^{-13} \text{ molec}^{-1} \cdot \text{cm}^3 \text{ s}^{-1}$  (Baumgärtel et al., 1998). Thus, only a few thousand collisions are required to obtain ClO in its ground state. When the BrO spectrum is observed at longer delay times with additional N<sub>2</sub> as collision partner, the absorption intensity of vibrationally excited BrO can be reduced at about the same collision numbers. Thus, also the BrO(v) relaxes too fast to become important for the atmosphere.

So far, we have only considered reactions of vibrationally excited species with trace gases. If the internally excited species carry enough energy to react with ambient air, then even a slow reaction with a rate constant of  $10^{-14} \text{ molec}^{-1} \cdot \text{cm}^3 \text{ s}^{-1}$  is fast enough to compete with the relaxation rate. However, reactions of ClO and BrO with N<sub>2</sub> or O<sub>2</sub> are strongly endothermic and a significant amount of internal excitation is needed to fulfil this energy requirement. Recently, however, it was found that ClO radicals are generated with extremely high vibrational energies when OClO is photodissociated at short wavelengths (Delmdahl et al., 1998; Furlan et al., 1997). For instance, the photolysis of OClO at a wavelength of 308 nm delivers ClO in vibrational levels up to  $v=18$  (Roth et al., 1997) which represents the energetically allowed limit. This wavelength corresponds essentially to the  $A^2A_2(18,0,0) \leftarrow X^2B_1(0,0,0)$  symmetric stretch progression of OClO. As has been shown by Huber and co-workers (Furlan et al., 1997) excitation of higher vibrations of the symmetric stretch will result in even higher vibrationally excited ClO radicals. As a matter of fact, ClO resulting from decay of OClO( $^2A_2, v_1 \geq 15$ ) carries enough internal energy to undergo reaction with nitrogen, which becomes thermodynamically possible for ClO( $v > 10$ ). Accordingly, the reaction



must be regarded as an additional source for nitrous oxide and atomic chlorine in the stratosphere. The generation of N<sub>2</sub>O was experimentally detected in a final product analysis by means of a gas chromatograph (Delmdahl and Gericke, 1997). This work indicates that there is in fact strong evidence for the production of nitrous oxide via the vibrationally mediated reaction of ClO radicals with abundant nitrogen molecules. It must be mentioned that the reverse reaction,  $\text{Cl} + \text{N}_2\text{O} \rightarrow \text{ClO} + \text{N}_2$ , has been measured to exhibit a large activation energy of 155 kJ/mol (Kaufman

et al., 1956). However, the determination of this activation energy considered only translational motion of the reactants. This implies that reaction (8) must generate vibrationally excited N<sub>2</sub>O products. Since the ClO fragments in the UV photodissociation of OClO are generated with extremely high vibrational excitation, the additional energy for producing vibrationally excited N<sub>2</sub>O is easily obtainable.

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