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Photoionization mass spectrometry of chlorine oxides

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Abstract

Photoionization mass spectrometry of four chlorine oxides (Cl_2O, Cl_2O_4, Cl_2O_6, and Cl_2O_7) is reported. Photoionization efficiency curves of parent and fragment ions are measured in the energy regime between 10 and 21 eV using monochromatic synchrotron radiation. Ionization energies (IE) of the chlorine oxides and fragmentation appearance energies (AE) are obtained from photoion yield curves of mass-selected cations. Specifically, we obtain $\mathrm{IE}(Cl_2O) = 10.88 \pm 0.02$ eV, $\mathrm{IE}(Cl_2O_4) = 11.23 \pm 0.05$ eV, $\mathrm{IE}(Cl_2O_6) = 12.66 \pm 0.05$ eV, and $\mathrm{IE}(Cl_2O_7) = 12.15 \pm 0.05$ eV. The experimental results are used to derive numerous thermochemical stability data of the neutral and ionic chlorine oxides and their fragments, as well as plausible cation fragmentation mechanisms. Resonant excitation with tunable vacuum ultraviolet radiation is applied in the case of Cl_2O to obtain further insight into autoionization processes. Three series of Rydberg excitations are assigned converging to the $\tilde{C}(^2A_2)$ ionization energy at 12.74 eV. (Int J Mass Spectrom 185/186/187 (1999) 545–558) © 1999 Elsevier Science B.V.

Keywords: Photoionization mass spectrometry; Thermochemistry; Autoionization; Chlorine oxides

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1. Introduction

Spectroscopic, photochemical, and theoretical studies of chlorine oxides have been carried out in the past [1]. Recent interest in chlorine oxides is often motivated by the occurrence of the simplest species, such as ClO, Cl_2O_2, and OClO, in the polar stratosphere [2,3]. Some of these compounds, such as ClO and Cl_2O_2, are known to be responsible for major ozone losses in the cold stratosphere over polar regions [4], whereas OClO was recently established to have minor influence on the stratospheric ozone budget [5,6]. Even though the higher chlorine oxides do not have the same atmospheric relevance, there is a general interest in establishing reliable properties of this class of compounds in order to aid the interpretation of laboratory experiments and possibly atmospheric observations. As a result, numerous experimental data on the simplest chlorine oxides have been published in the field of ground state properties, such as their electronic and geometric structure, spectroscopy, and thermochemistry [1].

Photoionization mass spectrometry of molecules, radicals, and clusters is a powerful experimental

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Dedicated to Professor M.T. Bowers on the occasion of his 60th birthday.

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method that has been used for decades [7–9]. Its strength is that it provides reliable ionization energies, fragmentation patterns at defined excitation energy, and fragmentation appearance energies. These are used to derive thermochemical stability data of the neutrals as well as of ionic fragments. Recent investigations in the field of photoionization mass spectrometry of chlorine oxides cover the molecules ClO [10,11], OClO [12,13], Cl_2O [11], and Cl_2O_2 [10]. The present work is built on earlier results on electron impact mass spectrometry that has been applied in earlier investigations [14,15].

The goal of the present study is twofold: (1) New results on photoionization mass spectrometry of Cl_2O are reported that go beyond recently published work [11]; (2) We report for the first time results on photoionization mass spectrometry of the higher chlorine oxides: Cl_2O_4, Cl_2O_6, and Cl_2O_7. Currently accepted thermochemical stability data of these species and their fragments are mainly based on estimates and theoretical calculations. We aim in the present article to obtain reliable thermochemical stability data of the neutrals as well as their ionic fragments from chemically related compounds. This is accomplished by measuring ionization energies (IE) of parent cations and appearance energies (AE) of ionic fragments.

2. Experimental

A detailed description of the experimental setup has been published previously [10,12,13,16]. Briefly, monochromatic synchrotron radiation from the Berlin electron storage ring BESSY-I is used for the experiments. The light is dispersed by a 1 m normal incidence monochromator (McPherson 225) that is equipped with an Al-coated spherical grating (1200 lines/mm, wavelength resolution 0.2 nm). The absolute wavelength scale is calibrated with the known autoionization structure of oxygen and rare gases [9]. A quadrupole mass spectrometer (Balzers QMS 311) is mounted behind the exit slit of the vacuum ultraviolet monochromator.

Photoion yield curves of mass-selected cations are measured by scanning the photon wavelength. The spectra are normalized to the photon flux of the monochromator and the electron current in the storage ring. Contributions of second order and energetic stray light above 104 nm are eliminated by a lithium fluoride cutoff filter.

The samples are prepared according to modified literature procedures. The preparation of the samples is in general dangerous, since all chlorine oxides are potentially explosive, especially in the presence of oxidable materials. Thus, only millimolar quantities of the samples are handled without neglecting appropriate safety precautions. Specifically, Cl_2O is prepared according to the standard synthesis [17] using the reaction of yellow mercury oxide and chlorine. The product is purified by several trap-to-trap distillations in order to avoid impurities of molecular chlorine in the sample. Cl_2O_4 is prepared according to [18] using the reaction of $CsClO_4$ with $ClOSO_2F$. The latter reactant is prepared from ClF and SO_3 [17]. The product is obtained and purified by trap-to-trap distillations. Cl_2O_6 is prepared according to [19] starting with ClO_2 and O_3. Cl_2O_7 is prepared similar to the standard synthesis described in [17], using a suspension of $KClO_4$ in concentrated H_2SO_4. The mixture is heated to 100 °C in the vacuum yielding anhydrous $HClO_4$ that is isolated by trap-to-trap distillation. The $HClO_4$ sample is reacted with P_2O_5 at room temperature yielding the anhydride Cl_2O_7 that is further purified by distillation. All samples are stored under liquid nitrogen before the photoionization experiments are carried out. Their purity is controlled by using infrared and ultraviolet spectroscopy. In addition, electron impact mass spectra are recorded using a MAT 112 S mass spectrometer that is operated at 70 eV acceleration energy of the electron beam. Decomposition of the samples in the gas inlet system is avoided by using a glass inlet system with a PTFE needle valve (Young, NV-2). The residence time of the sample gas in the inlet system is kept as short as possible. This is accomplished by using a bypass pumping system where the gaseous sample is pumped into a cold trap and only a fraction of the sample is introduced by the needle valve into the high vacuum systems of the mass spectrometers. As a result, no significant impurities beside air and traces of chlorine

Table 1
Mass spectral intensities of dichlorine monoxide at 20.65 eV photon energy in comparison with 70 eV electron impact ionization (EI)

Cation	m/z	Relative intensity	EI [a]	EI [b]	EI [c]
Cl_2O^+	86, 88, 90	23	52	35	32
Cl_2^+	70, 72, 74	7	4	4	7
ClO^+	51, 53	54	38	61	60
Cl^+	35, 37	12	3	<1	<1
O^+	16	4			<1

[a] This work.
[b] According to [14].
[c] According to [15].

in the Cl_2O sample and minor traces of the precursors that are used during the syntheses, are observed by mass spectrometry. All samples are free of $HClO_4$, therefore it appeared to be unexpected that the mass spectra of Cl_2O_4, Cl_2O_6, and Cl_2O_7 contained the cation $HClO_4^+$. This finding is attributed to the influence of traces of water in the mass spectrometer chamber that is consistent with the finding that HCl^+ and HBr^+ are observed in mass spectra of Cl_2 and Br_2.

3. Results and discussion

3.1. Dichlorine monoxide (Cl_2O)

Photoionization mass spectra of Cl_2O are recorded at different photon energies. Table 1 shows the relative cation intensities recorded at 20.65 eV photon energy in comparison with current and earlier electron impact work [14,15]. The most intense mass is the ClO^+ fragment, which is in agreement with earlier results from photoionization [11] and electron impact mass spectrometry [14,15]. Evidence for the occurrence of the parent cation Cl_2O^+ as well as its fragments, such as ClO^+, Cl^+, and O^+, are found in the mass spectra (cf. Table 1). We also find weak intensity of a Cl_2^+ signal ($m/z = 70, 72, 74$), that is weaker than in earlier photoionization work [11]. It is most likely the result of impurities of molecular chlorine in the sample. This is in agreement with vacuum ultraviolet (VUV)-absorption experiments, where distinct absorption lines of Cl_2 are identified [20,21].

Photoion yield curves of Cl_2O^+ and its fragments are shown in Fig. 1. The photoion yield curve of Cl_2O^+ starts with the onset of the first ionization energy at 10.88 ± 0.02 eV. This result is reproduced by using a LiF cutoff filter in order to avoid high energy stray light and second order light from the monochromator. The threshold value is somewhat lower than that reported from photoelectron spectroscopy (10.94 eV [22]). It is in general agreement with a value published recently using photoionization mass spectrometry (10.90 ± 0.01 eV [11]). We note that our earlier [10] and current absolute energy calibration is slightly lower than that used in the recent work of Thorn et al. [11], which is a reason for the small difference in ionization energy. However, our energy scale is fully consistent over a wide energy range with data published by others, i.e. (1) with autoionization structure of molecular oxygen [9], and (2) the vacuum ultraviolet absorption fine structures of Cl_2O [21].

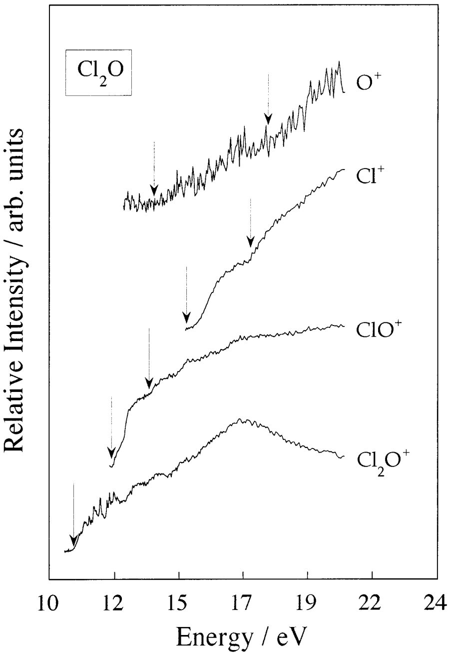

Fig. 1. Photoion yield curves of Cl_2O and its ionic fragments. The arrows indicate the threshold energies.

The cation intensity increases with two distinct steps (right above the ionization threshold) that are separated by 87 ± 5 meV, agreeing with the vibrational fine structure of the first photoelectron band [22] and recent results from photoionization mass spectrometry [11]. This finding is quite typical for small molecules such as diatomics and triatomics, thus reflecting that direct ionization dominates the near-threshold regime rather than autoionization via Rydberg states converging to higher ionization energies. The vacuum ultraviolet absorption cross section also shows that there are no discrete structures in the regime of the ionization energy [20,23]. The Cl_2O^+ photoion yield increases continuously above the threshold. It is highly structured between 11.4 and 12.5 eV, where distinct maxima are found on top of the increasing continuum. These features are the result of autoionization processes reflecting the occurrence of Rydberg states. Their convergence limits are higher ionization energies of the molecule. The fact that these structures are observed above 11.4 eV is an indication that they are not related to the second and third ionization energies (12.37 and 12.65 eV [22]), corresponding to the $\tilde{A}(^2B_2)$- and $\tilde{B}(^2A_1)$-cation states, respectively [24]. This assignment of the cation states is different from the earlier work of Cornford et al., who used semiempirical calculations that result in a different orbital order [22]. An assignment of the corresponding convergence limit of these Rydberg series is found by a comparison of the autoionization line shapes with the photoelectron spectrum. Such similarities in peak shape are known in many examples [e.g. 25,26]. In the case of Cl_2O, the fourth photoelectron band at 12.79 eV [$\tilde{C}(^2A_2)$] is narrow in shape. This is an indication that it should be connected as a convergence limit with the autoionization structure in the Cl_2O^+ yield. Numerous chlorine containing species have been investigated in the past, of which several show similar characteristics in VUV absorption as well as in photoionization mass spectrometry [25,27–29]. The common characteristics of these photoelectron bands is that they are in general associated with nonbonding chlorine orbitals. These are highly localized, as in the case of Cl_2O. Thus, no Franck–Condon structure is found for these ionizations. Typical intense, low lying absorption bands with term values on the order of ≈2.5 eV (≈20 000 cm^{-1}) are associated with these chlorine lone-pair ionizations. These are usually called "D bands" [25]. Consistently, such intense absorption features are found in the case of Cl_2O in the 10 eV regime (10.165 and 10.346 eV), corresponding to term values of 2.58 eV (20 807 cm^{-1}) and 2.39 eV (19 275 cm^{-1}), respectively [23]. These discrete VUV absorptions are a result of low lying Rydberg states, of which the higher members of the Rydberg series occur in the Cl_2O^+ yield.

The structures in the Cl_2O^+-yield curve have also been observed by Thorn et al. [11]. We agree with their discussion that these features are due to autoionizing Rydberg states, however they have not reported a specific assignment of these structures [11]. Our assignment is based on additional experiments on the vacuum ultraviolet absorption cross section that is investigated between 8 and 25 eV [20,23], extending the recent work of Motte-Tollet et al. [21]. The assignment of the discrete features is obtained by using the Rydberg formula

$$E = \mathrm{IE} - \frac{R}{(n - \delta)^2} \tag{1}$$

where E is the energy position of the resonance, R is the Rydberg constant, n is the principal quantum number, and δ is the quantum defect. The complete discussion of the VUV absorption cross section goes far beyond the scope of the present article and will be published elsewhere [20]. Instead, we concentrate here only on the features occurring in the Cl_2O^+ yield.

Fig. 2 shows an expanded view of the photoion yield of Cl_2O^+ between 11 and 13 eV along with an assignment of the Rydberg series converging to the $\tilde{C}(^2A_2)$ cation state at 12.79 eV [22]. However, this energy value corresponds to the maximum of the photoelectron band. We have not used this vertical energy value as a convergence limit rather than an adiabatic value of 12.74 eV. This value is estimated from the width of the corresponding photoelectron band [22] as well as the shape of the photoion yield

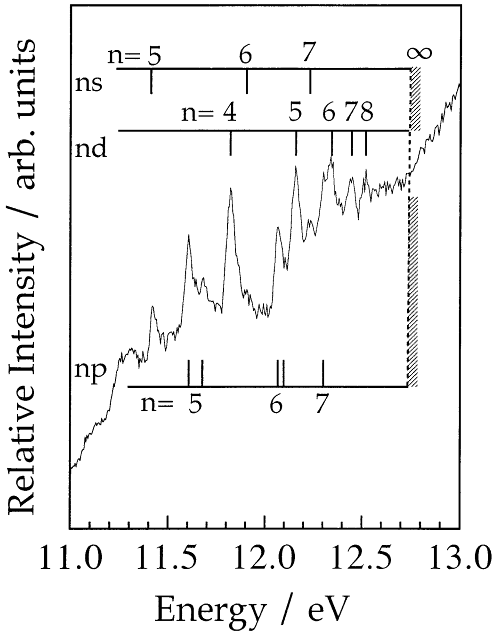

Fig. 2. Photoion yield curve of Cl_2O^+ between 11 eV and 13 eV. Three Rydberg series converging to the fourth ionization energy $[Cl_2O^+(^2A_2)]$ are assigned (cf. Table 2).

curve of Cl_2O^+ that shows at 12.74 eV a characteristic onset. This onset occurs most likely because of the contribution from direct ionization into the $\tilde{C}(^2A_2)$ continuum. The energy positions, quantum defects, and assignments of the spectral features below this ionization limit are given in Table 2. Three Rydberg series are identified by their almost constant quantum defects: a weak *s* series, a stronger *p* series that is split into a p_σ and a p_π component for low *n*, and an intense *d* series, where members of this series up to $n = 8$ are identified. The occurrence of comparably high *n* Rydberg states for all series is a clear indication of the atomic character in this ionization.

The photoion yield curve of Cl_2O^+ shows at higher energies only broad features and a maximum at about 17 eV. The broad features, especially below 15 eV, are due to autoionizations converging to higher ionization energies.

The onset of ionic fragmentation is found at 12.25 ± 0.03 eV corresponding to the threshold of the process:

Table 2
Rydberg transitions converging to the $\tilde{C}(^2A_2)$ state of Cl_2O^+. The transition energies are obtained from the photoion yield of Cl_2O^+ (cf. Fig. 2). The table contains the transition energies, effective quantum numbers $(n - \delta)$, the quantum defect δ, and the assignment

Energy/eV	$(n - \delta)$	δ	Assignment
11.418	3.21	1.79	$2a_2 \rightarrow 4s$
11.605	3.46	1.54	$2a_2 \rightarrow 4p_\sigma$
11.679	3.58	1.42	$2a_2 \rightarrow 4p_\pi$
11.823	3.85	0.15	$2a_2 \rightarrow 3d$
11.972	4.21	1.79	$2a_2 \rightarrow 5s$
12.066	4.49	1.51	$2a_2 \rightarrow 5p_\sigma$
12.090	4.57	1.42	$2a_2 \rightarrow 5p_\pi$
12.157	4.83	0.17	$2a_2 \rightarrow 4d$
12.230	5.16	1.84	$2a_2 \rightarrow 6s$
12.301	5.56	1.44	$2a_2 \rightarrow 6p$
12.337	5.81	0.19	$2a_2 \rightarrow 5d$
12.445	6.78	0.22	$2a_2 \rightarrow 6d$
12.517	7.81	0.19	$2a_2 \rightarrow 7d$
12.74	∞		Series limit

$$Cl_2O + h\nu \rightarrow ClO^+\ (^2\Sigma^-) + Cl(^3P_{3/2}) + e^- \qquad (2)$$

This threshold is in agreement with recent photoionization experiments, where 12.29 ± 0.03 eV is found [11]. The experimental threshold is used to derive $\Delta_f H^0_{298}(Cl_2O) = 78.2 \pm 6$ kJ mol^{-1}. This value is obtained according to recent work from Thorn et al. [11], using IE(ClO) = 10.85 ± 0.05 eV [10], proper corrections of temperature effects (as suggested earlier by Traeger and McLoughlin [30]), and the stationary electron convention. It is close to the recently improved reference value of $\Delta_f H^0_{298}(Cl_2O) = 77.18 \pm 3.45$ kJ mol^{-1} [11,31]. The corresponding heat of formation of the molecular cation is $\Delta_f H^0_{298}(Cl_2O^+) = 1128 \pm 7$ kJ mol^{-1}, which considers the slight difference in energy calibration, as compared to the earlier work of Thorn et al. [11]. These findings indicate consistently that both fragments are formed in their electronic ground state, i.e. we determine the adiabatic fragmentation threshold. The ClO^+ yield is not structured above threshold; it shows at about 13.6 eV another weak onset that is tentatively assigned to the formation of ClO^+ ($^1\Delta$), where the calculated threshold is 13.35 eV. We note that the threshold determination of processes that are superimposed on a photoion yield curve are much less accurately determined than onsets of ion signals above the background intensity.

The formation of Cl^+ is observed above 14.9 ± 0.2 eV. There is also another onset found in the photoion yield at 17.3 ± 0.2 eV. The threshold of Cl^+ formation corresponds to the decay:

$$Cl_2O + h\nu \rightarrow Cl^+(^3P_2) + ClO(^2\Pi_i) + e^- \tag{3}$$

The calculated threshold energy is 14.46 eV according to standard reference data [31,32]. This is an indication that the fragmentation process occurs with an excess energy of 0.44 eV at threshold. This excess energy cannot be measured directly with our experimental setup. It is most likely stored as vibrational energy in the diatomic neutral. The second onset at 17.3 ± 0.2 eV in the Cl^+ ion yield leads likely to the formation of atomic fragments according to Eq. (4):

$$Cl_2O + h\nu \rightarrow Cl^+(^3P_2) + Cl(^2P_{3/2}) + O(^3P_2) + e^-, \tag{4}$$

where a threshold energy of 17.25 eV is calculated from reference data [31,32]. This value is in agreement with the experimental results.

There is also weak O^+ cation intensity. The threshold determination is difficult to measure because the weak signal increases slowly above the background level. The threshold is quite low in energy, i.e. 13.7 ± 0.4 eV. The process that is most likely related to this threshold value corresponds to ion-pair formation where the following fragments are assumed to be formed:

$$Cl_2O + h\nu \rightarrow O^+(^4S_{3/2}) + Cl_2^-\ (^2\Sigma_u^+) \tag{5}$$

The calculated threshold is somewhat lower in energy (13.03 eV) so it cannot be excluded that the fragments are formed in a rearrangement process with excess energy. Similar processes involving ion-pair formation and rearrangements have been observed in the case of photoexcited OClO [13] and Cl_2O [20]. Other processes starting from the cation, rather than from the neutral, are excluded since these are expected to give considerably higher threshold energies. Another weak onset is found at 17.9 ± 0.2 eV, which may be rationalized by the following process:

$$Cl_2O + h\nu \rightarrow O^+(^4S_{3/2}) + Cl(^2P_{3/2}) + Cl(^2P_{3/2}) \tag{6}$$

The calculated threshold is 17.90 eV. This is in agreement with the experimental value, so this onset is assigned as evidence for multiparticle formation.

Table 3
Mass spectral intensities of Cl_2O_4 at 20.65 eV photon energy in comparison with 70 eV electron impact ionization (EI)

Cation	m/z	Relative intensity	EI [a]
$Cl_2O_4^+$	134, 136, 138	5	10
$Cl_2O_3^+$	118, 120, 122	<1	
$Cl_2O_2^+$/ $HClO_4^+$	100–106	5	2
Cl_2O^+	86, 88, 90	<1	1
ClO_3^+	83, 85	24	24
Cl_2^+	70, 72, 74	<1	10
ClO_2^+	67, 69	46	42
ClO^+	51, 53	17	<1
HCl^+	36, 38	<1	5
Cl^+	35, 37	<1	4
O_2^+	32	1	1
O^+	16	1	<1

[a] This work.

3.2. Chlorine perchlorate (Cl_2O_4)

Table 3 shows the mass spectral distribution of a photoionization mass spectrum that is recorded at 20.65 eV photon energy in comparison with electron impact mass spectrometry. Both mass spectra are in general agreement; there are only minor differences in the relative intensities of the mass lines. Both methods show that the parent mass $Cl_2O_4^+$ is comparably weak in intensity. The main fragment is ClO_2^+ and there are less intense fragments, such as ClO_3^+ and ClO^+. The latter cations can be formed directly by direct bond cleavage of the cation $ClO–ClO_3^+$. The mass spectrum also contains weak impurities of $HClO_4$ and fragments of this species.

The photoion yield curves of $Cl_2O_4^+$ and its fragments are shown in Fig. 3. The first ionization energy

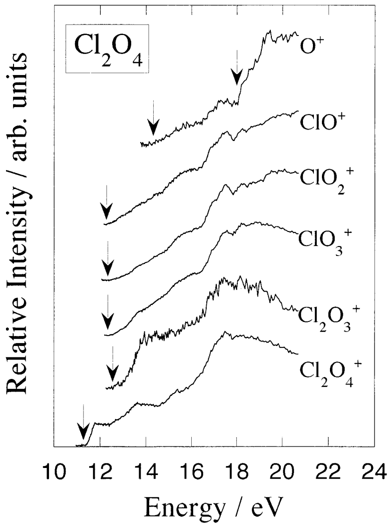

Fig. 3. Photoion yield curves of Cl_2O_4 and its ionic fragments. The arrows indicate the threshold energies.

of Cl_2O_4 is determined to be 11.23 ± 0.05 eV. To the best of our knowledge, there is no experimental reference value reported in the literature. The photoion yield increases slowly above the threshold, as verified by additional experiments using a LiF cutoff filter. A steep increase in $Cl_2O_4^+$ yield is observed above 11.45 eV, but there is no fine structure in the threshold regime, as e.g. in the case of Cl_2O. Broad resonances are located at 11.8 eV, 13.6 eV, 15.4 eV, and 17.5 eV, respectively. These structures are likely associated with autoionization or direct ionization continua, as shown in the case of Cl_2O (cf. Fig. 2). We note that both the vacuum ultraviolet absorption cross section and the photoelectron spectrum of Cl_2O_4 have not been published yet, so that an assignment of these broad resonances cannot be obtained from the photoion yield of the parent cation.

The onset of fragmentation is found at 12.28 ± 0.05 eV, yielding ClO^+. The difference in energy between $AE(ClO^+)$ and $IE(Cl_2O_4)$ corresponds to the bond dissociation energy in the cation $D(ClO^+ - ClO_3) = 1.05 \pm 0.1$ eV. The low energy threshold of the diatomic fragment ClO^+ points to the fact that the corresponding neutral species ClO has an ionization energy that is at least similar to that of the other fragments, such as ClO_3. The appearance energies of the other major fragments are indeed close to this value: $AE(ClO_2^+) = 12.37 \pm 0.05$ eV, $AE(ClO_3^+) = 12.30 \pm 0.05$ eV, and $AE(Cl_2O_3^+) = 12.55 \pm 0.05$ eV. It is also found that the shapes of the photoion yields of the major fragments are quite similar to each other. Secondary processes such as ion–molecule reactions are excluded as the origin of this finding. Therefore, additional pressure dependent investigations have been performed indicating that the spectral shapes of the photoion yields are independent of the pressure in the ionization region of the mass spectrometer. Therefore, we assume that the experimental results are due to monomolecular decay processes of the parent cation. The result—that the major fragments are formed almost at the same threshold energy—is an indication that there are dissociative ionic states that produce various ionic fragments. Therefore, one expects that the threshold regime of ionic fragmentation may not necessarily lead to thermodynamic threshold values, as will be discussed in the following. The heat of formation of Cl_2O_4 has been estimated by Colussi and Grela: $\Delta_f H^0_{298}(Cl_2O_4) = 155.6$ kJ mol^{-1} [33], which is somewhat lower than an earlier estimate of 180 kJ mol^{-1} [34].

We attempt to use the experimental fragmentation thresholds of $Cl_2O_4^+$ in the following in order to obtain an experimental value of $\Delta_f H^0_{298}(Cl_2O_4)$ from photoionization mass spectrometry. The results are compiled in Table 4. The value range of $\Delta_f H^0_{298}(Cl_2O_4)$ that is obtained from these considerations lies between -3.5 ± 12 kJ mol^{-1} and 250 ± 11 kJ mol^{-1}. However, these values need to be discussed in more detail in order to obtain a reliable experimental estimate of $\Delta_f H^0_{298}(Cl_2O_4)$. Therefore, we discuss in the following the major fragmentation routes leading to the formation of ClO_3^+, ClO_2^+, and ClO^+. The formation of ClO_3^+ leads to $\Delta_f H^0_{298}(Cl_2O_4) = 245.5 \pm 5$ kJ mol^{-1}, if standard reference values are taken from the literature [31,33]. The most uncertain value is $\Delta_f H^0_{298}(ClO_3^+) = 1331$ kJ mol^{-1}, taken from an estimate of Colussi and Grela [33], who reexamined earlier electron impact ionization on Cl_2O_7 [14]. They use the experimental fragmentation threshold of $Cl_2O_7^+$ fragmentation into ClO_3^+, corresponding to 13 eV. We already note here that our

Table 4
Key fragmentations of $Cl_2O_4^+$ used to determine $\Delta_f H^0_{298}(Cl_2O_4)$ in comparison with earlier estimates: $\Delta_f H^0_{298}(Cl_2O_4) = 155.6$ kJ mol^{-1} [33], $\Delta_f H^0_{298}(Cl_2O_4) = 180$ kJ mol^{-1} [34]. See text for further details

Fragmentation		$\Delta_f H^0_{298}(Cl_2O_4)$/kJ mol^{-1}
$Cl_2O_4 + h\nu(12.30 \pm 0.05$ eV)	$\rightarrow ClO_3^+(^1A_1) + ClO(^2\Pi_i)$	210 ± 15 [a]
$Cl_2O_4 + h\nu$ (12.37 ± 0.05 eV)	$\rightarrow OClO^+(^1A_1) + OClO(^2B_1)$	−3.5 ± 12 [b]
	$\rightarrow ClO_2^+(^1A_1) + ClO(^2\Pi_i) + O(^3P_2)$	250 ± 11 [c]
$Cl_2O_4 + h\nu$ (12.28 ± 0.05 eV)	$\rightarrow ClO^+(^3\Sigma^-) + ClO_3(^2A_1)$	178 ± 27,[d] 155 ± 12,[e] 164 ± 12 [f]

[a] With AE = 12.30 ± 0.05 eV, $\Delta_f H^0_{298}(ClO) = 101.6$ kJ mol^{-1} [31], $\Delta_f H^0_{298}(ClO_3^+) = 1295$ kJ mol^{-1} [33] using the correct fragmentation threshold of the process: $Cl_2O_7 + h\nu \rightarrow ClO_3^+ + ClO_4$ [this article].

[b] With IE (OClO) = 10.33 ± 0.02 eV [12,13], $\Delta_f H^0_{298}(OClO) = 96.7 \pm 4$ kJ mol^{-1} [13,16], $\Delta_f H^0_{298}(OClO^+) = 1093.3 \pm 6$ kJ mol^{-1}.

[c] With $\Delta_f H^0_{298}(OClO^+) = 1093.3 \pm 6$ kJ mol^{-1}, $\Delta_f H^0_{298}(ClO) = 101.6$ kJ mol^{-1} [31], $\Delta_f H^0_{298}(O) = 249.18$ kJ mol^{-1} [31].

[d] With $\Delta_f H^0_{298}(ClO^+) = 1148 \pm 8$ kJ mol^{-1} [10], $\Delta_f H^0_{298}(ClO_3) = 217 \pm 21$ kJ mol^{-1} [36].

[e] With $\Delta_f H^0_{298}(ClO^+) = 1148 \pm 8$ kJ mol^{-1} [10], $\Delta_f H^0_{298}(ClO_3) = 192$ kJ mol^{-1} [37].

[f] Like [e], but using $\Delta_f H^0_{298}(ClO_3) = 201$ kJ mol^{-1} [33].

photoionization value for ClO_3^+ formation from $Cl_2O_7^+$ is considerably lower in energy by 0.37 eV (AE(ClO_3^+ from Cl_2O_7) = 12.63 ± 0.05 eV see below). Thus, $\Delta_f H^0_{298}(ClO_3^+)$ should be at least corrected to 1295 ± 12 kJ mol^{-1}, if one assumes that $\Delta_f H^0_{298}(Cl_2O_7)$ is reliably determined in the literature, as will be discussed later. Thus, it cannot be excluded that this value is still too high. Another piece of evidence for this result that finally leads to a lower ionization energy of ClO_3 comes from the intensity distribution of the major mass lines in the mass spectrum of Cl_2O_4. The fragment ClO_3^+ is more intense than the corresponding cation ClO^+, occurring with almost the same threshold value. This may give evidence for the assumption that IE(ClO_3) should be similar to IE(ClO), where the latter quantity is well known: IE(ClO) = 10.85 ± 0.05 eV [10,11]. Using the currently accepted literature values ($\Delta_f H^0_{298}(ClO_3) = 232.6$ kJ mol^{-1} [31]) and $\Delta_f H^0_{298}(ClO_3^+) = 1331$ kJ mol^{-1} [33]) one obtains IE(ClO_3) = 11.38 eV. This cannot explain the high ClO_3^+ yield in photoionization mass spectra and would be inconsistent with the rules of Stevenson and Audier [35]. An estimate of the ionization energy of ClO_3 is obtained from the following data: $\Delta_f H^0_{298}(ClO_3) = 217.1 \pm 21$ kJ mol^{-1} [36], $\Delta_f H^0_{298}(ClO_3) = 192$ kJ mol^{-1} [37], $\Delta_f H^0_{298}(ClO_3) = 201$ kJ mol^{-1} [33]. This leads with the upper limit of $\Delta_f H^0_{298}(ClO_3^+) = 1295 \pm 12$ kJ mol^{-1} to the upper limit of IE(ClO_3): 11.17 ± 0.3 eV $<$ IE(ClO_3) $<$ 11.43 ± 0.2 eV. These values get closer to IE(ClO), explaining the intensities of the mass lines in photoionization mass spectrometry. The ClO_3^+ key fragmentation gives finally $\Delta_f H^0_{298}(Cl_2O_4) = 210 \pm 15$ kJ mol^{-1} using corrected reference values (cf. Table 4).

The major fragment of $Cl_2O_4^+$ is ClO_2^+. The formation of this cation gives $\Delta_f H^0_{298}(Cl_2O_4) = -3.5 \pm 12$ kJ mol^{-1}. This value is much lower than earlier estimates of $\Delta_f H^0_{298}(Cl_2O_4)$. This result may indicate that the products $OClO^+$ + OClO are not formed in the fragmentation process, especially since considerable rearrangement processes are required to rationalize the formation of these products. On one hand, it could also be possible that the cation is formed in an electronically excited cation state [e.g. $OClO^+(\tilde{A}(^3B_2)$)]. Experimental results [12] and the calculations of Peterson and Werner indicate that excited cation states are about 187 kJ mol^{-1} above the cation ground state [38]. This implies that $\Delta_f H^0_{298}(Cl_2O_4)$ should be corrected to 185 kJ mol^{-1}, if such a process occurs. On the other hand, it may be possible that the decay of $Cl_2O_4^+$ leads to $ClOO^+$ + OClO because the same number of bonds need to be broken to form $ClOO^+$ rather than $OClO^+$. Unfortunately, the ionization energy of ClOO is not determined experimentally because this compound is highly unstable. It is well known that ClOO has a weak Cl–OO bond ($D^0(Cl - OO) = 19.25 \pm 1.7$ kJ mol^{-1}) [39]. If $ClOO^+$ is formed as a stable cation upon fragmentation of $Cl_2O_4^+$, then one would expect an ionization energy that is somewhat lower than that of molecular oxygen (IE(O_2 ($^3\Sigma_g^-$)) = 12.08 eV [40]), i.e. IE(ClOO) ≈ 12 eV. However, this cation is not expected to carry the positive charge, so instead $OClO^+$ is formed. Finally, the third process implies the formation of $OClO^+$ + ClO + O. This route, which is reasonably likely to occur, leads to a much higher value of $\Delta_f H^0_{298}(Cl_2O_4) = 250 \pm 11$ kJ mol^{-1} (cf. Table 4). Therefore, it appears to be likely that this process will not occur at AE(ClO_2). We conclude that the process of ClO_2^+ formation cannot be used for a reliable determination of $\Delta_f H^0_{298}(Cl_2O_4)$.

The appearance energy of the fragment ClO^+ leads to $\Delta_f H^0_{298}(Cl_2O_4) = 178 \pm 27$ kJ mol^{-1}, if standard reference values are used in combination with proper corrections (cf. Table 4). However, as in the case of ClO_3^+ formation, there are uncertainties and inconsistencies with the heat of formation of ClO_3. If we use the above value ($\Delta_f H^0_{298}(ClO_3) = 201 \pm 21$ kJ mol^{-1} [33]), then one obtains $\Delta_f H^0_{298}(Cl_2O_4) = 164 \pm 12$ kJ mol^{-1} (cf. Table 4). An even lower value is found if results from the G2 theory are used [37]. These lead to $\Delta_f H^0_{298}(ClO_3) = 192$ kJ mol^{-1}.

We conclude that threshold energies of the ionic key fragmentation routes of $Cl_2O_4^+$ may only confirm earlier estimates of Colussi and Grela ($\Delta_f H^0_{298}(Cl_2O_4) = 156$ kJ mol^{-1} [33]), yielding $\Delta_f H^0_{298}(Cl_2O_4) = 164 \pm 12$ kJ mol^{-1}, if $\Delta_f H^0_{298}(ClO_3) = 201$ kJ mol^{-1} is used [33,41]. This value may be even lower if the results from the G2 theory on $\Delta_f H^0_{298}(ClO_3)$ [37] turn out to be reliable. On the other hand, we prefer to use $\Delta_f H^0_{298}(ClO_3) = 217 \pm 21$ kJ mol^{-1} [36], a value that is related to experimental results from the kinetics of the reaction O(^{3}P) + OClO. It represents a corrected value of Colussi, who found earlier $\Delta_f H^0_{298}$(ClO_3 = 233 ± 17 kJ mol^{-1} [42]. This leads, together with the ClO^+ key fragmentation, to a somewhat higher value of $\Delta_f H^0_{298}(Cl_2O_4) = 178 \pm 27$ kJ mol^{-1}, which is still close to earlier estimates [33,34], and $\Delta_f H^0_{298}(Cl_2O_4^+) = 1262 \pm 30$ kJ mol^{-1}. We use $\Delta_f H^0_{298}(Cl_2O_4) = 178 \pm 27$ kJ mol^{-1} in the following, yielding consistent results, also in connection with the other chlorine oxides which are discussed below. The considerable error limit represents the maximum error; it is mostly attributed to the errors in the heats of formation of the neutral product ClO_3, as quoted in [36] and, to a lesser extent, to the uncertainty in threshold determination. This result implies that both $\Delta_f H^0_{298}(ClO_3)$ and $\Delta_f H^0_{298}(ClO_3^+)$ are lower than the currently accepted reference values [31,33], i.e. $\Delta_f H^0_{298}(ClO_3) = 217 \pm 21$ kJ mol^{-1} [36] and $\Delta_f H^0_{298}(ClO_3^+)$ is obtained from the decay of $Cl_2O_7^+$ into ClO_3^+ + ClO_4 giving $\Delta_f H^0_{298}(ClO_3^+) \leq 1295 \pm 12$ kJ mol^{-1} (see below and [36]), and finally IE(ClO_3) ≤ 11.17 ± 0.3 eV, which is, as expected from the above discussion, close to IE(ClO) = 10.85 ± 0.05 eV [10,11].

The fragment $Cl_2O_3^+$ is formed above 12.55 ± 0.05 eV. This leads to $\Delta_f H^0_{298}(Cl_2O_3^+) = 1140 \pm 30$ kJ mol^{-1}, where no experimental reference value is reported to the best of our knowledge. From this follows the upper limit of the first ionization energy of Cl_2O_3, which is calculated to be IE(Cl_2O_3) = 10.2 ± 0.3 eV using $\Delta_f H^0_{298}(Cl_2O_3) = 153$ kJ mol^{-1} [31]. This value appears to be reasonable because Cl_2O_3 is formed as a photolysis product of chlorine dioxide aggregates $(OClO)_n$ and is ionized by one photon excitation using 10.91 eV vacuum ultraviolet laser radiation [43].

The fragment O^+ shows a weak onset 14.3 ± 0.2 eV. This threshold is attributed to an ion-pair formation process yielding $O^+(^4S_{3/2})$ + $ClO_3(^2A_1)$ + $Cl^-(^1S_0)$. The calculated threshold is in agreement with the experimental value: AE(O^+) = 14.2 ± 0.3 eV using the following values: $\Delta_f H^0_{298}(Cl_2O_4) = 178 \pm 27$ kJ mol^{-1} [this work], $\Delta_f H^0_{298}(O^+) = 1563$ kJ mol^{-1} [32], $\Delta_f H^0_{298}(ClO_3) = 217 \pm 21$ kJ mol^{-1} [34], and $\Delta_f H^0_{298}(Cl^-) = -227$ kJ mol^{-1} [32]. We note that ion-pair formation from Cl_2O_4 is not reported in the literature so we cannot give independent experimental evidence for this assignment. The photoion yield of O^+ shows an onset at 17.95 ± 0.1 eV (cf. Fig. 3). This distinct increase in O^+ yield is rationalized by the following fragmentation threshold:

$$Cl_2O_4 + h\nu \rightarrow O^+(^4S_{3/2}) + ClO_3(^2A_1) + Cl(^2P_{3/2}) + e^- \qquad (7)$$

The calculated threshold value of 17.9 ± 0.3 eV is in agreement with the onset in O^+ yield and points also to the result that the heats of formation of Cl_2O_4 and

ClO_3 are consistent with the above determination of $\Delta_f H^0_{298}(Cl_2O_4)$.

3.3. Chlorine hexoxide (Cl_2O_6)

Table 5 shows a comparison of the mass spectral intensities obtained by photoionization and electron impact mass spectrometry [15,23], where general agreement between both methods of ionization is found. The mass spectrum consists only of light fragment ions, of which ClO_3^+ is the heaviest one, neglecting $HClO_4^+$, which is observed as an impurity with weak intensity. The question of whether the experimental mass spectra represent properties of Cl_2O_6 that is known to be a labile species arises [44]. Earlier work on Cl_2O_6 indicates that this compound readily decomposes into lighter species such as Cl_2O_4, ClO_2, and O_2 [19]. However, photoion yields of mass-selected fragments indicate that there is no resemblance between the fragment ion yields of Cl_2O_6 and its decomposition products (cf. Fig. 3 and [13]). Thus, it is clear that we observe properties of ionic fragmentation of Cl_2O_6 and that the parent cation $Cl_2O_6^+$ is not stable at all. This is a result of the weak Cl–O bond in the molecular cation yielding exclusively fragments that contain only one chlorine atom, i.e. $D(ClO_4 - ClO_2^+) \approx 0$ eV. The formation of light fragment ions of $Cl_2O_6^+$ is also attributed to properties of these fragment ions. They are expected to carry the positive charge if they have lower ionization energies than the heavier chlorine oxides. This may explain that, e.g. the cation ClO_4^+ is not observed in mass spectra of higher chlorine oxides.

The photoion yields of the fragments of $Cl_2O_6^+$ are shown in Fig. 4. The lowest onset of a cation yield is associated with the formation of ClO_2^+ at 12.66 ± 0.05 eV. This value corresponds most likely to the first ionization energy of Cl_2O_6, not reported earlier. Therefore, one expects that this onset of the ClO_2^+ yield cannot correspond to a thermochemical threshold value because it represents instead the first ionization energy of Cl_2O_6. The ClO_2^+ yield increases continuously with two steep onsets at 14.4 and 16.4 eV that are also observed in the ClO_3^+ yield. We assign these onsets either to the occurrence of electronically excited states or to direct ionizations, rather than to thermochemical thresholds of ionic fragmentation. The threshold energy of the ClO_3^+ fragment is found at 13.08 ± 0.05 eV, i.e. slightly above the first ionization energy. The fragment ClO^+ is found at slightly higher excitation energy, i.e. above 14.3 ± 0.15 eV, where the cation intensity increases very slowly above the threshold. This cation yield also contains no fine structure.

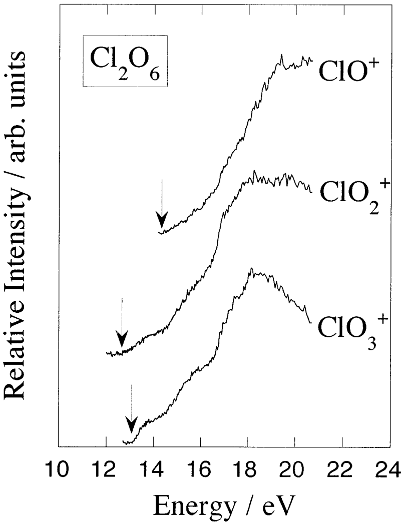

Fig. 4. Photoion yield curves of Cl_2O_6 and its ionic fragments. The arrows indicate the threshold energies.

The heat of formation of Cl_2O_6 has been estimated earlier by Colussi and Grela [33]: $\Delta_f H^0_{298}(Cl_2O_6) = 218$ kJ mol^{-1}. The determination of the heat of formation of Cl_2O_6 based on key fragmentations from photoionization mass spectrometry can only use the fragments ClO_3^+ and ClO^+ because the threshold of ClO_2^+ formation most likely contains excess energy. Assuming that ClO_3^+ is formed via the following reaction

$$Cl_2O_6 + h\nu \rightarrow ClO_3^+ + ClO_3 + e^-, \quad (8)$$

one obtains with $\Delta_f H^0_{298}(ClO_3^+) = 1295 \pm 12$ kJ mol^{-1}, as derived from fragmentation of $Cl_2O_7^+$ (see discussion above) and $\Delta_f H^0_{298}(ClO_3) = 217 \pm 21$ kJ mol^{-1} [36]: $\Delta_f H^0_{298}(Cl_2O_6) = 250 \pm 35$ kJ mol^{-1}. This value is somewhat higher than the above men-

Table 5
Mass spectral intensities of Cl_2O_6 at 20.65 eV photon energy in comparison with 70 eV electron impact ionization (EI)

Cation	m/z	Relative intensity	EI [a]	EI [b]
$HClO_4^+$	100, 102	4	6	
ClO_3^+	83, 85	14	14	6
ClO_2^+	67, 69	63	66	65
$HClO^+$	52, 54	<1	2	
ClO^+	51, 53	17	9	21
HCl^+	36, 38	<1	1	
Cl^+	35, 37	<1	<1	2
O_2^+	32	<1	<1	4
O^+	16	<1	<1	2

[a] This work.
[b] According to [15].

tioned estimated value. Its reliability and error limit is primarily connected with the thermochemical data of the fragments. Using $\Delta_f H^0_{298}(Cl_2O_6) = 250 \pm 35$ kJ mol^{-1} to calculate the threshold for ClO^+ formation, one obtains $AE_{calc}(ClO^+) = 14.0 \pm 0.3$ eV, if it is assumed that the neutral products $ClO_4 + O$ are formed. This agrees with the experimental value of $AE(ClO^+) = 14.3 \pm 0.15$ eV. In addition, the threshold value leading to $ClO_2^+ + ClO_4$ formation is calculated to occur at 10.8 ± 0.3 eV. This value is evidently well below the first ionization energy of $Cl_2O_6^+$ (12.66 ± 0.05 eV) so that the products are formed, as expected, with excess energy.

4. Chlorine heptoxide (Cl_2O_7)

Table 6 shows a comparison of the mass spectral intensities from photoionization mass spectrometry and electron impact ionization [14,15]. The parent cation $Cl_2O_7^+$ is observed in both electron impact and photoionization mass spectrometry with weak intensity. The main fragment of $Cl_2O_7^+$ is ClO_3^+, and there is also high intensity of ClO_2^+. Differences between current and earlier electron impact work is found for the ClO^+ fragment, which is somewhat more intense in earlier work [14,15]. The mass spectrum shows, besides weak intensity of the parent cation, that there are no mass lines of ionic fragments with $m/z > 85$, indicating that the cation falls almost quantitatively apart yielding small fragment masses.

Fig. 5 shows the photoion yield curves of $Cl_2O_7^+$ and its fragments. The onset of the $Cl_2O_7^+$ intensity is found at 12.15 ± 0.05 eV, corresponding to the first ionization energy of chlorine heptoxide (Cl_2O_7). This value has not been reported earlier. It is lower than an earlier estimate of Fisher who suggested that the ionization threshold should be at >13 eV, because of the weak intensity of the parent mass and accompanied ionic fragmentation [14]. Our results show that the parent cation is formed at lower energy than its ionic fragments so that the bond dissociation energy of $Cl_2O_7^+$ [$D(ClO_3^+ - ClO_4)$] is obtained from the energy difference between the fragmentation threshold ($AE(ClO_3^+) = 12.63 \pm 0.05$ eV) and the ionization energy (12.15 ± 0.05 eV). From this we estimate $D(ClO_3^+ - ClO_4) = 0.48 \pm 0.10$ eV, explaining the occurrence of $Cl_2O_7^+$ in both electron impact and photoionization mass spectrometry. The photoion yield of $Cl_2O_7^+$ is weak below 16.6 eV, where it rises significantly. The spectrum also shows broad resonances between 17 and 19 eV that are likely due to autoionization.

The onset of ionic fragmentation leads to ClO_3^+

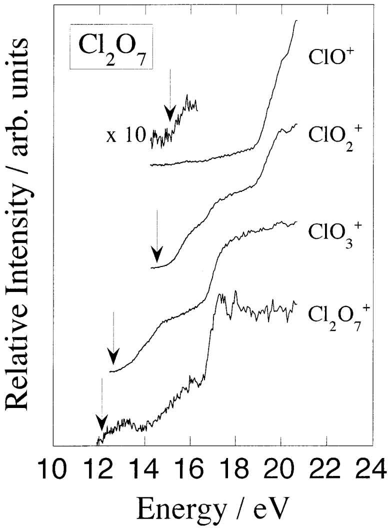

Fig. 5. Photoion yield curves of Cl_2O_7 and its ionic fragments. The arrows indicate the threshold energies.

formation. It is found at 12.63 ± 0.05 eV, which is somewhat lower than reported in earlier work on electron impact ionization of Cl_2O_7, where AE(ClO_3^+) = 13.0 ± 0.05 eV is obtained [14]. We note that the threshold value from photoionization is in better agreement with more recent electron impact work, where 12.74 eV is reported [46]. Other fragmentation thresholds are: AE(ClO_2^+) = 14.5 ± 0.1 eV, AE(ClO^+) = 15.1 ± 0.1 eV. The cation yields are characterized by distinct onsets that are found at the same energy position for different masses including the parent cation, similar to the other compounds under investigation. Therefore, we assign these features to the occurrence of ionic states rather than to thermochemical thresholds.

The heat of formation of Cl_2O_7 has been estimated earlier: $\Delta_f H^0_{298}(Cl_2O_7) = 272$ kJ mol^{-1} [46–48]. Using the ClO_3^+-fragmentation appearance energy (AE(ClO_3^+) = 12.63 ± 0.05 eV) one obtains from our photoionization experiments: $\Delta_f H^0_{298}(Cl_2O_7) = 272 \pm 17$ kJ mol^{-1}. The process that is assumed to occur is:

$$Cl_2O_7 + h\nu \rightarrow ClO_3^+ + ClO_4 + e^-, \quad (9)$$

where the following heats of formation of the fragments are used to determine $\Delta_f H^0_{298}(Cl_2O_7)$: $\Delta_f H^0_{298}(ClO_4) = 196$ kJ mol^{-1} [33] and $\Delta_f H^0_{298}(ClO_3^+) = 1295 \pm 12$ kJ mol^{-1} (this article). This is consistent with the results obtained from ionic fragmentation of Cl_2O_4 and Cl_2O_6. Assuming that $\Delta_f H^0_{298}(Cl_2O_7) = 272 \pm 17$ kJ mol^{-1} represents the preferred value, one obtains the heat of formation of the molecular cation: $\Delta_f H^0_{298}(Cl_2O_7^+) = 1444 \pm 23$ kJ mol^{-1}.

Using $\Delta_f H^0_{298}(Cl_2O_7) = 272 \pm 17$ kJ mol^{-1}, one obtains the calculated appearance energy of the fragment ClO_2^+: $AE_{calc}(ClO_2^+) = 13.12 \pm 0.3$ eV, which is lower than the experimental value $AE_{exp}(ClO_2^+) = 14.5 \pm 0.1$ eV. Probably, the multiparticle products $ClO_2^+ + ClO_4 + O$ are formed with excess energy so that this route cannot be successfully used to obtain $\Delta_f H^0_{298}(Cl_2O_7)$. The fragment ClO^+ may be formed at threshold ($AE_{exp}(ClO^+) = 15.1 \pm 0.1$ eV) along with the neutral products $ClO_2 + O_2 + 2O$. We calculate a threshold of $AE_{calc}(ClO^+) = 15.27 \pm 0.3$ eV, so that this route explains the experimental threshold energy. This fragmentation mechanism involves the formation of neutral ClO_2 in the presence of ClO^+. Weak ClO^+ intensity above threshold is an indication for this assignment, since ClO_2 should carry the positive charge rather than ClO, as a result of IE(ClO_2) < IE(ClO). A higher threshold value than experimentally observed is obtained for the formation of $ClO^+ + ClO_4 + 2O$ ($AE_{calc}(ClO^+) = 16.3 \pm 0.15$ eV), so that this process is also discounted to occur at threshold.

Table 6
Mass spectral intensities of Cl_2O_7 at 20.65 eV photon energy in comparison with 70 eV electron impact ionization (EI)

Cation	m/z	Relative intensity	EI [a]	EI [b]	EI [c]
$Cl_2O_7^+$	182–186	<1	<1	<1	<1
$HClO_4^+$	100, 102	<1	<1	<1	<1
ClO_3^+	83, 85	75	83	71	69
ClO_2^+	67, 69	22	13	22	21
ClO^+	51, 53	2	3	6	8
Cl^+	35, 37	<1	<1	<1	<1
O_2^+	32	<1	<1	<1	<1
O^+	16	<1	<1	<1	1

[a] This work.
[b] According to [14].
[c] According to [15].

5. Conclusions

We have investigated photoionization and ionic fragmentation of the chlorine oxides Cl_2O, Cl_2O_4, Cl_2O_6, and Cl_2O_7 using photoionization mass spectrometry in comparison with electron impact ionization. The results of both methods are in general agreement. It is found that, in particular, the higher chlorine oxides such as Cl_2O_6 and Cl_2O_7, predominantly give rise to small fragment ions ClO_x^+, with $x \leq 3$. Cations of the type $Cl_2O_x^+$ with $x \geq 1$ are evidently not observed as a result of weak bond dissociation energies in the molecular cations and low ionization energies of the ClO_x species compared to, e.g. ClO_4.

The tunability of the monochromatic synchrotron

Table 7
Ionization energies (IE) in eV and heats of formation ($\Delta_f H^0_{298}$) in kJ mol^{-1} of the neutral and ionic chlorine oxides: Cl_2O, Cl_2O_4, Cl_2O_6, and Cl_2O_7; see text for further details

Species	IE	$\Delta_f H^0_{298}$ (neutral)	$\Delta_f H^0_{298}$ (cation)
Cl_2O	10.88 ± 0.02	78.2 ± 6	1128 ± 7
Cl_2O_4	11.23 ± 0.05	178 ± 27	1262 ± 30
Cl_2O_6	12.66 ± 0.05	250 ± 35	[a]
Cl_2O_7	12.15 ± 0.05	272 ± 17	1444 ± 23

[a] Cl_2O_6 forms no stable parent cation ($Cl_2O_6^+$). $Cl_2O_6^+$ decays into $ClO_2^+ + ClO_4$ at the ionization threshold.

radiation light source allows the measurement of ionization energies of chlorine oxides as well as appearance energies of their fragment ions. We report for the first time reliable ionization energies of Cl_2O_4, Cl_2O_6, and Cl_2O_7. These are compiled in Table 7. Resonant excitation leads in the case of Cl_2O to the occurrence of pronounced autoionization fine structure that is assigned to three Rydberg series converging to the fourth ionization energy ($\tilde{C}(^2A_2)$) at 12.74 eV.

The threshold energies are used to derive the heats of formation of the neutral and ionic chlorine oxides considering the most recent thermochemical data from the literature along with our experimental results (cf. Table 7). The error limits of the derived thermochemical stability data are quite high, reflecting mostly uncertain reference data of key fragments in the literature rather than inherent problems with photoionization mass spectrometry. The onset energies of fragmentation are used to obtain further insight into the fragmentation routes of charged chlorine oxides. These often involve multiparticle formation, especially in the case of higher chlorine oxides. These results need to be verified by additional work using state-of-the-art theory.

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