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Single and double electron-impact ionization of dichlorine monoxide (Cl_2O)

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Abstract

Electron-impact single and double ionization of dichlorine monoxide (Cl_2O) have been investigated using time-of-flight mass spectrometry and ion–ion coincidence techniques. Relative partial single ionization cross sections of Cl_2O have been determined for incident electron energies from 30 to 450 eV using time-of-flight mass spectrometry. The experiments detect stable parent ions, Cl_2O^+, and the fragmentation products Cl^+, ClO^+, and Cl_2^+. The formation and fragmentation of the Cl_2O dication has been investigated using ion–ion coincidence techniques coupled with time-of-flight mass spectrometry. The coincidence spectra show that Cl_2O^{2+} dissociates to form the following pairs of ions: $Cl^+ + Cl^+$, $O^+ + Cl^+$ and $Cl^+ + ClO^+$. Interpretation of the coincidence spectra suggests that there is a multiple kinetic energy release upon dicationic dissociation to form $O^+ + Cl^+$, indicating that two distinct electronic states of Cl_2O^{2+} dissociate to form this ion pair. The experiments also yield a determination of the excitation energy required to form the lowest energy dication electronic state (30.6 ± 1 eV) which dissociates to form $Cl^+ + ClO^+$. Comparison of this excitation energy with estimated values of the double ionization energy of Cl_2O indicates that this state is probably the ground electronic state of Cl_2O^{2+} and, hence, these investigations provide a first estimate for the double ionization energy of Cl_2O. (Int J Mass Spectrom 184 (1999) 11–23) © 1999 Elsevier Science B.V.

Keywords: Electron ionization; Dichlorine monoxide; Dication; Relative partial ionization cross section; Time of flight mass spectrometry; Coincidence spectroscopy

1. Introduction

The involvement of chlorine oxides in the loss of stratospheric ozone has prompted extensive studies of their photochemistry, spectroscopy, and ionization [1]. Dichlorine monoxide, Cl_2O (also referred to as chlorine monoxide), is thought to play only a minor role in the stratospheric ozone cycle but an understanding of the properties of this molecule can lead to an improved understanding of the more complex chlorine oxides which play a more major role in the ozone cycle. Cl_2O is also frequently used as a source of ClO in laboratory studies of this atmospherically important radical and in the synthesis of HOCl, a significant chlorine reservoir in the atmosphere.

The spectroscopy and photodissociation dynamics of Cl_2O have been extensively investigated using a wide range of techniques [1–5]. In contrast, there have been relatively few investigations of the ionization of Cl_2O: a handful of studies of the formation of Cl_2O^+ [6–9] and no investigations of the formation and

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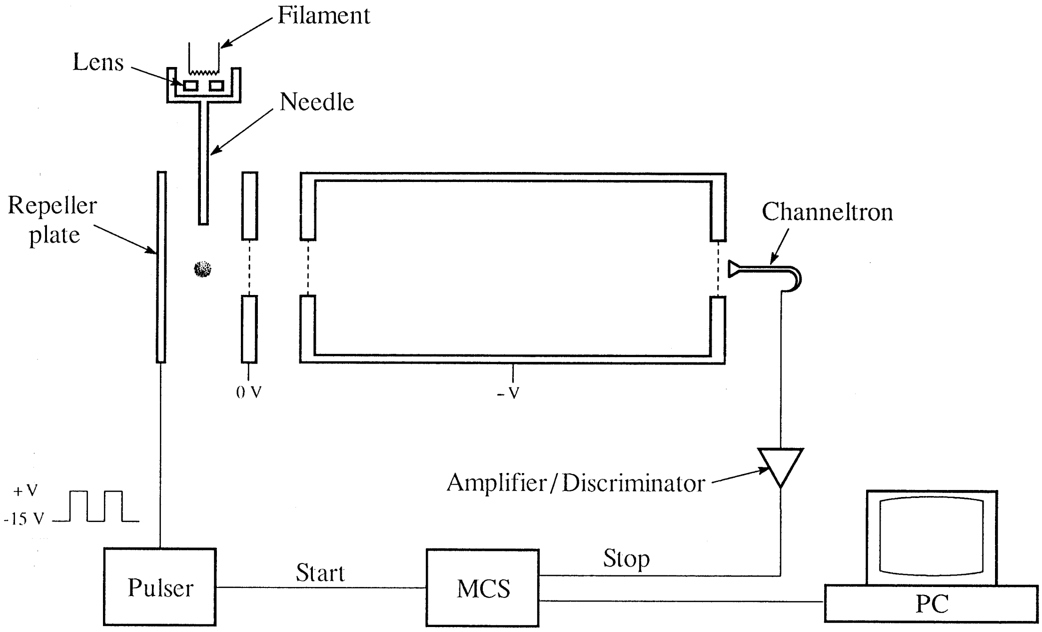

Fig. 1. Schematic diagram of the TOFMS. The gas inlet is perpendicular to the plane of the figure and is not shown.

fragmentation of Cl_2O^{2+}. Such studies are the objective of this investigation.

Recently, the properties of doubly charged molecular ions (molecular dications) have been the subject of a steadily increasing number of experimental and theoretical investigations employing a variety of new techniques developed to probe these short-lived species [10–12]. Usually dication electronic states are thermodynamically unstable, lying at energies above the asymptote for charge separation [10–12]. For many dications, however, metastable states can exist, supporting one or more vibrational levels with lifetimes of the order of the mass spectrometric timescale or longer [13–15]. As a result of experimental efforts, information concerning the energetics and dissociation mechanisms of the low-lying electronic states of several dications has been obtained, including energies and dissociation dynamics of vibrational levels in dication metastable states [16–19].

As part of an ongoing investigation of the ionization of reactive species, this article presents an investigation of the single and double ionization of Cl_2O. In the single ionization studies, time-of-flight mass spectrometry is used to determine the relative partial ionization cross sections of Cl_2O and its fragment ions over an energy range of 30–450 eV. Ion–ion coincidence techniques [20] are used to investigate the formation and fragmentation of Cl_2O^{2+}. In previous studies of reactive molecules [21,22], comparisons of the experimentally determined appearance energies for the dication dissociation reactions with the energetics derived from the kinetic energy release involved in these dication dissociation processes have given an indication of the mechanisms involved in the dissociative double ionization and the energy of the dication electronic states which are the source of these fragment ions. It is hoped that this analysis procedure can be applied to the results obtained from the investigation into the formation and fragmentation of Cl_2O^{2+} to reveal details of its dissociation processes.

2. Experimental

The apparatus used for the studies of both the single and double ionization of Cl_2O is a conventional time-of-flight mass spectrometer (TOFMS) of the standard Wiley–McLaren design [23]. A schematic of this apparatus is shown in Fig. 1 and its detailed description has been presented in a previous publication [24]. In brief, the flight times of ions formed following the interaction of the electron beam with the target gas are measured by pulsing the repeller plate (Fig. 1), and hence the source electric field, on and off and recording the subsequent ion arrival times at the detector in a multichannel scalar [24]. This experimental methodology, however, is only really useful for the study of single ionization, because it is difficult to distinguish definitively between the monocation fragments generated by the dissociation of Cl_2O^+ and those resulting from the dissociation of the Cl_2O dication using conventional time-of-flight mass spectrometry. Therefore, in order to study double ionization processes, ion–ion coincidence experiments [20–22,25–29] have been performed to detect and identify the pairs of ions produced by the dissociative double ionization of Cl_2O. Coincidence spectra are recorded by measuring the time-of-flight difference between the arrival times at the detector of pairs of fragment ions formed following the rapid charge-separating dissociation of a molecular dication in a continuous source electric field. The experimental procedures for both the time-of-flight [24,25,30,31] and the coincidence experiments [21,22,25,26] have been described extensively in previous publications and will therefore not be discussed here.

The Cl_2O sample used in these experiments was prepared by the reaction of chlorine on solid mercury oxide [2]. Chlorine gas passes through a U-tube packed with glass beads and dry, yellow HgO and the resulting Cl_2O is trapped at 179 K and any unreacted Cl_2, the main impurity, is removed. The sample is then allowed to warm up and the first fraction of gas evolved is pumped away so any remaining traces of Cl_2, being more volatile than Cl_2O, are eliminated. The pure Cl_2O sample is then warmed to room temperature and the vaporised Cl_2O molecules are drawn into the TOFMS. As there appeared to be no improvement in the purity of the sample with multiple freeze/pump cycles, we feel that this experimental methodology provides an adequately pure sample of Cl_2O.

The gaseous sample is transported into the ionization region of the TOFMS using a clean and noncatalytic glass/Teflon inlet system [30]. Typical operating pressures in the TOFMS, as recorded by an ion gauge, are of the order of 6×10^{-5} Pa. Low operating pressures are required in conventional time-of-flight mass spectrometry to avoid channeltron saturation [30] and in coincidence experiments to ensure a good signal-to-noise ratio [21].

Time-of-flight mass spectra were recorded at incident electron energies of 30–450 eV in order to determine the relative partial ionization cross sections of the ions produced by the single ionization of Cl_2O. Coincidence spectra were recorded at an ionizing electron energy of 150 eV and also at a range of lower electron energies, from 25 to 80 eV, in order to determine the appearance energies of the pairs of fragment ions produced by the dissociative double ionization of Cl_2O.

Unfortunately, we find that the reactive Cl_2O rapidly attacks the filament of the electron gun causing fluctuations in the emission current which increase the statistical uncertainty in the recorded mass spectra. Indeed, the filament lifetime is markedly reduced following even the briefest exposure to Cl_2O. Hence, in this investigation spectra have been recorded for a shorter time than usual, again increasing the statistical uncertainty of the results.

3. Data analysis

3.1. Single ionization

A typical mass spectrum of Cl_2O is shown in Fig. 2. As can be seen from Fig. 2, the stable parent ion, Cl_2O^+, fragment ions Cl^+, ClO^+, and Cl_2^+ and their isotopes are detected. The spectrum also contains a small signal corresponding to the background gas, principally water, in the apparatus.

The "stepped" nature of the background in the mass spectrum (Fig. 2), as explained previously [24], is due to the formation of ions outside the focused

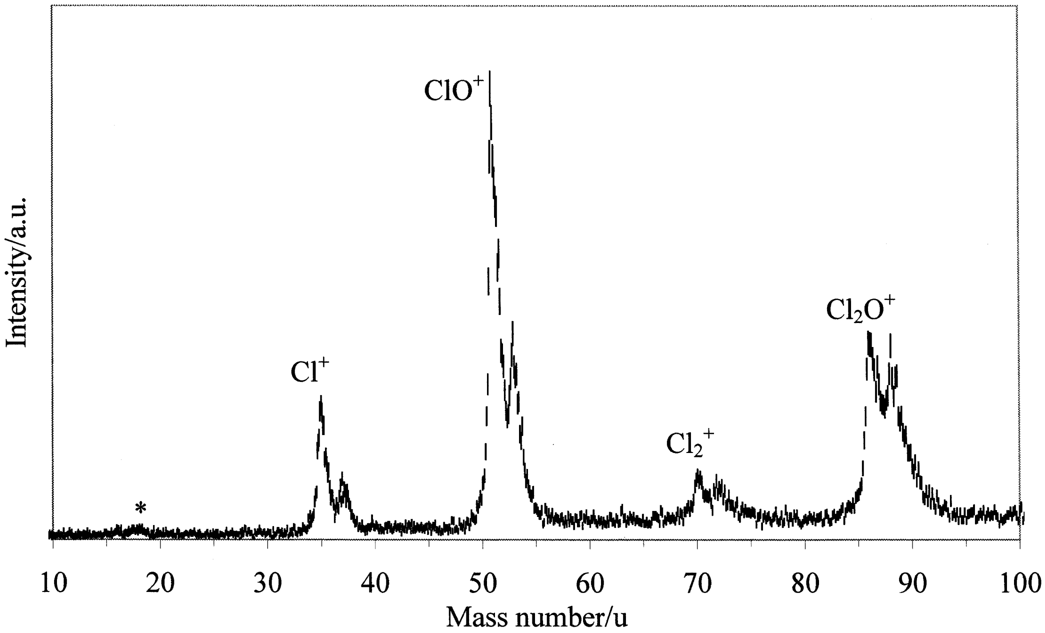

Fig. 2. Typical time-of-flight mass spectrum of Cl_2O at an electron energy of 150 eV. The error bars shown, derived from the counting statistics, represent two standard deviations. The peaks marked with an asterisk correspond to signals from the residual gas.

volume of the ionization region during the application of the source extraction pulse, resulting in the detection of ions with longer flight times.

The parent and fragment ion signal intensities are obtained by applying a background correction to the raw ion signals in the mass spectrum, recorded at a range of electron energies from 30 to 450 eV. As explained in previous publications [24,25,30,31], the ion intensities are related to the partial ionization cross section in the following way. The relative partial ionization cross sections of the ions observed in the Cl_2O spectrum, relative to the most abundant ion in this case ClO^+ (Fig. 2), are determined using the following equation for a given ion X^+:

$$\frac{\sigma_{X^+}}{\sigma_{ClO^+}} = \frac{\sqrt{m_{ClO^+}}}{\sqrt{m_{X^+}}} \frac{I_{X^+}}{I_{ClO^+}} \tag{1}$$

where I_{X^+}/I_{ClO^+} is the ion signal intensity ratio, $\sqrt{m_{ClO^+}}/\sqrt{m_{X^+}}$ is a correction factor applied to the ion signal intensity ratio to compensate for ion density effects in the source region of the TOFMS [24] and m is the relative molecular mass of the ion. Using such a correction factor, the mass spectrum of argon in our apparatus yields a ratio of single to double ionization cross sections in good agreement with the literature [32]. The present apparatus setup strongly discriminates against the detection of ionic fragments which are produced with kinetic energies above 0.3 eV [24]. Since any singly charged fragments produced by dissociative double ionization would be highly energetic, with kinetic energies greater than 0.3 eV, they would not be efficiently detected in these experiments and so this analysis procedure yields values of the partial single ionization cross sections, a conclusion supported by previous work [24,25,30,31].

Relative partial ionization cross sections for the ions observed in the mass spectrum of Cl_2O at incident electron energies from 30 to 450 eV, derived by the analysis procedure described above, are shown in Fig. 3 and listed in Table 1. These values are the average of five independent determinations and the standard deviations of these determinations at each electron energy are also shown in Table 1 and plotted as the error bars in Fig. 3.

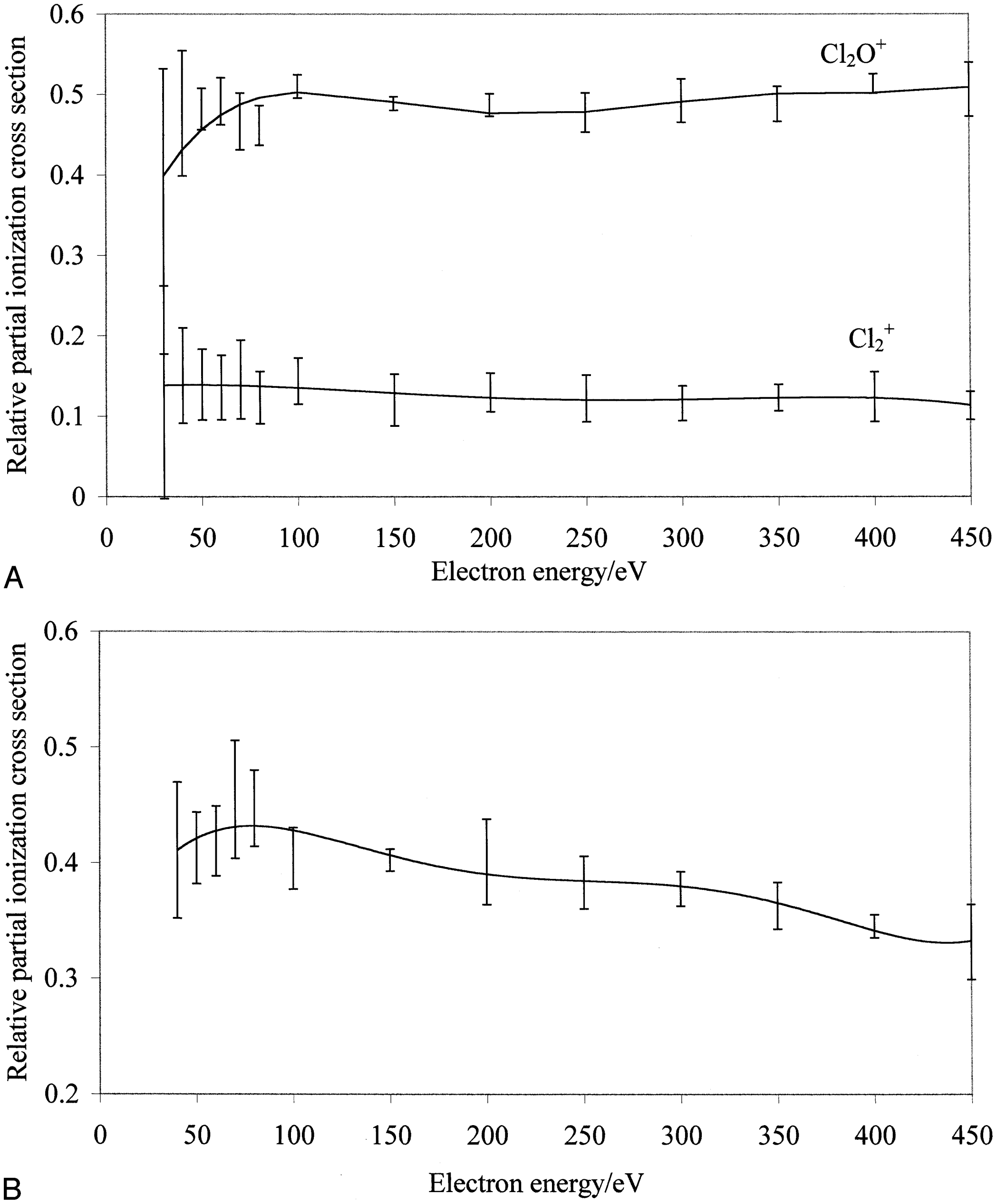

Fig. 3. Relative partial ionization cross sections for forming (a) Cl_2O^+ and Cl_2^+ and (b) Cl^+ from Cl_2O, relative to the most abundant ion in the mass spectrum, ClO^+. The error bars represent two standard deviations. The solid lines are a polynomial fit to the experimental data to guide the eye.

The appearance energy of the fragment ion ClO^+ has been previously determined [9] at better energy resolution than can be achieved using the current experimental arrangement and was therefore not redetermined in this study. The appearance energies of the Cl^+ and Cl_2^+ fragment ions have not been reported in the literature. However, at low electron energies in this apparatus, the statistical uncertainties in the rela-

Table 1
Relative partial ionization cross sections for the formation of the indicated product ion from Cl_2O (the numbers in parentheses indicate the standard deviation in the last figure of each cross section)

Electron energy/eV	Relative partial ionization cross section, $\sigma_{X^+}/\sigma_{ClO^+}$		
	Cl^+	Cl_2^+	Cl_2O^+
30	· · ·	0.13 (13)	0.35 (17)
40	0.411 (59)	0.151 (59)	0.477 (77)
50	0.413 (31)	0.140 (44)	0.482 (26)
60	0.419 (30)	0.136 (40)	0.492 (29)
70	0.455 (33)	0.146 (49)	0.467 (35)
80	0.447 (33)	0.123 (32)	0.461 (25)
100	0.404 (27)	0.144 (29)	0.510 (14)
150	0.402 (9)	0.120 (32)	0.489 (8)
200	0.401 (37)	0.130 (24)	0.487 (14)
250	0.383 (23)	0.122 (29)	0.478 (24)
300	0.378 (15)	0.116 (22)	0.492 (27)
350	0.363 (20)	0.123 (17)	0.488 (22)
400	0.345 (10)	0.124 (31)	0.514 (12)
450	0.332 (32)	0.113 (17)	0.506 (34)

tive partial ionization cross sections for these fragment ions are significantly increased since, as explained above, the data gathering runs are short to limit the extent of the degradation of the filament by the Cl_2O, making the evaluation of their appearance energies impractical.

3.2. Double ionization

A typical ion–ion coincidence spectrum of Cl_2O^{2+} recorded at 150 eV is shown in Fig. 4. The observed dissociation reactions are

$$Cl_2O^{2+} \rightarrow Cl^+ + ClO^+ \tag{2}$$

$$Cl_2O^{2+} \rightarrow O^+ + Cl^+ [+ Cl] \tag{3}$$

$$Cl_2O^{2+} \rightarrow Cl^+ + Cl^+ [+ O] \tag{4}$$

where the neutral atoms are not detected. As can be seen in Fig. 4 the entire peak corresponding to the $Cl^+ + Cl^+$ dissociation reaction is not observed as it is masked by a small amount of afterpulsing ("pick-up"), which generates false counts at small time-of-flight differences. The shape of the coincidence peaks arises because of the angular constraint imposed by the small entrance aperture of the channeltron detector, resulting in the selective detection of pairs of fragment ions formed from dissociation events where the kinetic energy release (KER) is directed principally along the axis of the TOFMS [21].

If the KER associated with the formation of an ion pair from dicationic dissociation can be determined, then an estimate of the energy of the dication electronic state from which the dissociation reaction occurred can be made. The KER for a given dissociation reaction is related to the temporal width of the coincidence peak [21] and so a Monte Carlo simulation [20,33,34] of the coincidence spectrum fitted to the experimental data is used to obtain a value of the KER and corresponding half-width of the KER distribution, F_{KERD}, associated with a given dication fragmentation channel [21,22,25,26]. The KER associated with the formation of the fragment ion pairs is assumed to be the same for all isotopomers. The uncertainties in KER and F_{KERD} derived from such a fit, determined by the deviations necessary to degrade the fit with the experimental data, are of the order of ± 0.2 eV. It has been shown in previous work that this analysis procedure provides reliable KER values [21,22,25,26]. Fig. 5 shows the comparison of a simulated spectrum with typical experimental data to indicate the high quality of fit achieved.

The formation of the $Cl^+ + ClO^+$ ion pair from Cl_2O^{2+} involves the direct dissociation of the dication to form the product ions, a two-body dissociation reaction. For the three-body dissociation reactions of Cl_2O^{2+} forming $O^+ + Cl^+$ and $Cl^+ + Cl^+$, where neutral atoms are formed in conjunction with the pairs of singly charged ions, the fragmentation pathway is not as clear. The pathway could involve either a direct mechanism, a Coulomb explosion, or a sequential mechanism. The sequential mechanism could involve either a deferred charge separation or an initial charge separation followed by the subsequent dissociation of one of the resulting ions to form the detected pair of singly charged ions [35]. So, for these three-body dissociation reactions, the pair of ions detected in the coincidence spectrum may not be the same two ions that received the initial impulse from the dicationic dissociation event and, therefore, when analysing the coincidence spectra it is necessary to consider the

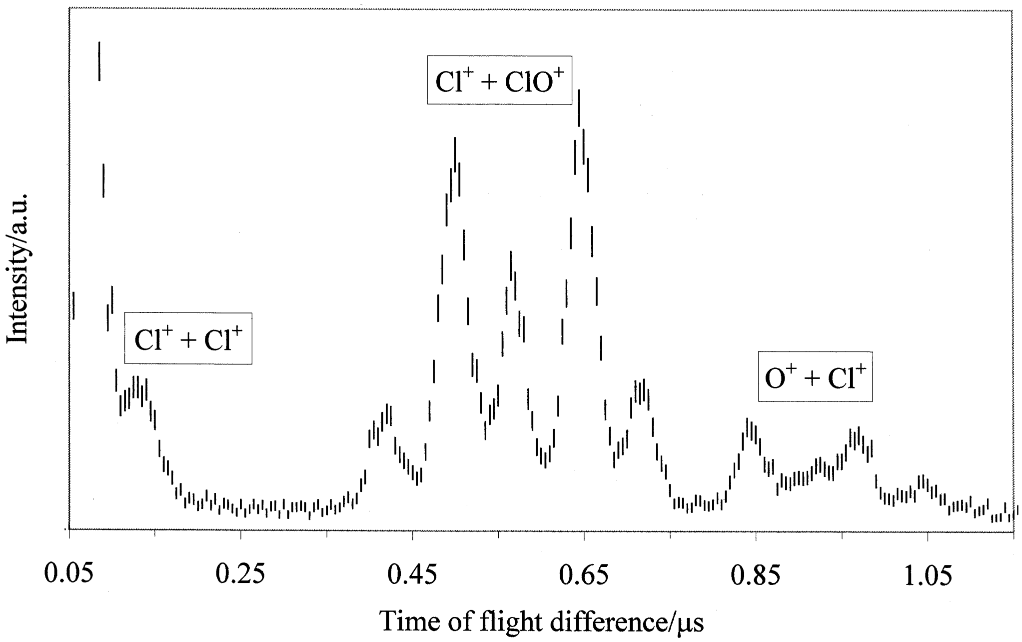

Fig. 4. Ion–ion coincidence spectrum of Cl_2O^{2+} generated by electron impact at 150 eV. The error bars shown, derived from the counting statistics, represent two standard deviations.

three-body fragmentation pathways by which Cl_2O^{2+} dissociates.

As mentioned above, the KER on formation of a pair of ions from dicationic dissociation is associated with the temporal width of the coincidence peak and depends on the masses of the primary ions formed by charge separation of the dication. For the two-body dissociation reaction, the only possible fragmentation pathway is the direct dissociation of Cl_2O^{2+} to form the $Cl^+ + ClO^+$ ion pair and so the result of the simulation procedure is a single value of the KER and corresponding F_{KERD}, listed in Table 2.

As discussed above, for a three-body dissociation reaction forming either $O^+ + Cl^+$ or $Cl^+ + Cl^+$, the primary ions formed by dicationic charge separation are not necessarily the pair of ions detected in the coincidence spectrum. Studies of the dissociation reactions of molecular dications [35–40] have shown that if daughter dications are not observed in the mass spectrum and there are no metastable tails on the coincidence signals, implying the existence of a long-lived daughter dication, as is the case here, the dissociation mechanism is unlikely to involve a deferred charge separation. Hence, we have performed the simulation procedure for the three-body dissociation reactions of Cl_2O^{2+}, modeling the formation of $O^+ + Cl^+$ and $Cl^+ + Cl^+$ via the two remaining possible dissociation pathways, the direct mechanism and the sequential mechanism involving initial charge separation and subsequent monocation dissociation. In this simulation procedure we assume that the KER of the monocation dissociation is negligible in comparison to the primary KER of the dication dissociation.

The coincidence peak corresponding to the $O^+ + Cl^+$ reaction has been modeled for both the sequential and direct fragmentation pathways using two KER values (Table 2), as indeed was the case for the $O^+ + Cl^+$ ion pair produced by the dissociative double ionization of OClO [25]. The use of a multiple KER in the simulation procedure is necessary to yield realistic values for the variable parameters, e.g. F_{KERD}, and to obtain a satisfactory fit with the experimental spectrum (Fig. 5). Table 2 shows the

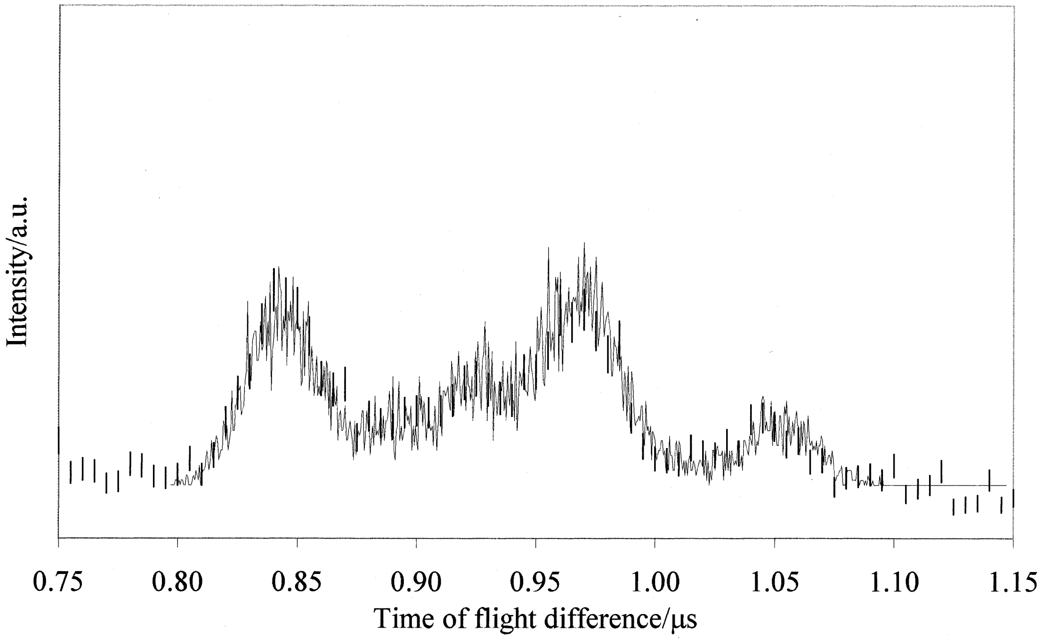

Fig. 5. Ion–ion coincidence spectrum of Cl_2O^{2+} showing the signal corresponding to the $O^+ + Cl^+$ ion pair. The experimental points are indicated by error bars representing two standard deviations. The solid curve is a Monte Carlo simulation of the experimental signal assuming a multiple KER and sequential dissociation mechanism.

potential KER and F_{KERD} values required to fit the experimental spectrum for the two possible decay pathways that could form $O^+ + Cl^+$ from Cl_2O^{2+}. As the KER derived from the coincidence peak width depends on the masses of the pair of ions formed by the initial charge-separating reaction and since the primary ions formed by the sequential and direct mechanisms are different, the values of the KER derived from the simulation procedure for these two pathways will differ.

Table 2
Potential values of the KER, half-width of the kinetic energy release distribution, F_{KERD}, and dication state energy, $E(Cl_2O^{2+})$, for the dissociation reactions of Cl_2O^{2+} derived by simulation of the ion–ion coincidence spectrum at 150 eV

Dissociation reaction	Dissociation mechanism	KER/eV	F_{KERD}/eV	$E(Cl_2O^{2+})$/eV
$Cl^+ + ClO^+$	· · ·	5.2	2.0	30.6
$O^+ + Cl^+$	Direct	7.3	1.5	38.2
		1.5	1.5	32.4
	Sequential	9.0	1.5	39.9
		1.5	1.5	32.4
$Cl^+ + Cl^+$	Direct	3.3	· · ·	33.5
	Sequential	3.5	· · ·	33.7

The coincidence peak for the $Cl^+ + Cl^+$ reaction has also been modeled for both possible fragmentation mechanisms. Due to the majority of this peak being masked under the pickup peak (Fig. 4) it is not possible to discern whether a single or multiple KER is present in this reaction nor to determine an accurate value of F_{KERD}. So the result of the simulation procedure for the $Cl^+ + Cl^+$ ion pair is a single value of the KER obtained for the two different mechanisms (Table 2).

From the KERs derived from the simulation procedure, values of the energy of the dication electronic state, $E(Cl_2O^{2+})$, from which the particular dissociation reaction occurs can be obtained using the following equation:

$$E(Cl_2O^{2+}) = E_{ASYM} + KER \tag{5}$$

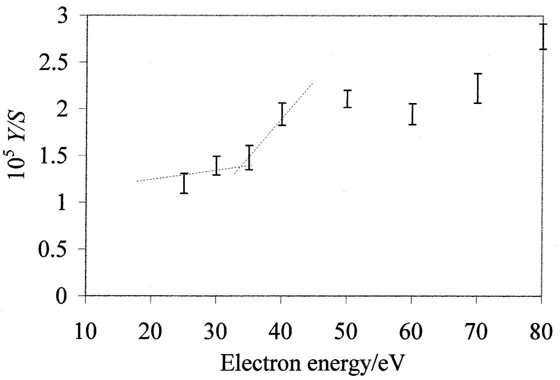

Fig. 6. Plot of the ratio of the yield (*Y*) of the $Cl^+ + ClO^+$ dissociation reaction to the number of coincidence starts (*S*) as function of electron energy. As indicated, this plot can be interpreted to yield the appearance energy of the lowest energy dication state responsible for this decay reaction. The dashed lines are to guide the eye.

where E_{ASYM} is the energy of the dissociation asymptote for forming the relevant products in their ground electronic state and can be derived from thermodynamic tables [41]. In the calculation of $E(Cl_2O^{2+})$, the fragment ions and neutral atoms are assumed to be formed with no internal energy and so any value of $E(Cl_2O^{2+})$ derived in this way should be considered a lower limit.

The appearance energy of the $Cl^+ + ClO^+$ ion pair has been determined by monitoring the yield of the dissociation reaction with respect to the ion count rate, as a function of electron energy. As explained in greater detail previously [21,22,26], as the ionizing electron energy approaches threshold, the ratio of the yield *Y* of a decay reaction to the number of coincidence starts *S* is proportional to σ_2/σ_1, where σ_2 is the double ionization cross section and σ_1 is the single ionization cross section. Thus, a plot of *Y*/*S* against electron energy should fall to zero at the energy of the lowest energy dication states contributing to the relevant decay channel, the appearance energy of the particular ion pair.

The ratio *Y*/*S* was carefully evaluated for the $Cl^+ + ClO^+$ dissociation reaction at electron energies from 25 to 80 eV. Fig. 6 shows a plot of *Y*/*S* against electron energy for the $Cl^+ + ClO^+$ ion pair. *Y*/*S* can be extrapolated to the nonzero background level of residual double ionization [21,22,26], as indicated by the dashed lines in Fig. 6. A more accurate value of the appearance energy cannot be determined due to the weak signals at low electron energies and the poor counting statistics because of the degradation of the filament necessitates short run times. However, it is obvious that the appearance energy lies below 35 eV. This is interpreted as the energy of the lowest lying states responsible for the dicationic decay reaction forming $Cl^+ + ClO^+$. The appearance energies for the $O^+ + Cl^+$ and $Cl^+ + Cl^+$ dissociation reactions were not determined as the uncertainties in *Y*/*S* for these minority processes at low electron energies were so large as to make an evaluation of the appearance energies impractical.

In previous studies [21,22], some mechanistic information could be derived for three-body dissociation reactions by comparing the appearance energy of a dication fragmentation channel with dication state energies calculated using the potential KER values derived from the simulation procedure. Unambiguous agreement between one of the values of $E(Cl_2O^{2+})$, derived assuming a particular fragmentation pathway, and the appearance energy indicates that the mechanism used to derive the KER and hence $E(Cl_2O^{2+})$, is the one actually followed to form the relevant ion pair. Unfortunately, since we have no measured appearance energies for comparison with the values of $E(Cl_2O^{2+})$ for the $O^+ + Cl^+$ and $Cl^+ + Cl^+$ ion pairs, we are unable to assign fragmentation mechanisms for the three-body dissociation reactions of Cl_2O^{2+}. However, as shown below, we can still obtain information concerning the energetics of the dissociative dicationic states.

4. Discussion

4.1. Single ionization

There have been a number of previous reports in the literature concerning the ionization and fragmentation of Cl_2O^+, using both photoionization mass spectrometry (PIMS) and electron-impact mass spectrometry (EIMS). A single PIMS study of Cl_2O has been reported [9] and a number of EIMS studies at differing ionizing electron energies: Fisher [6] and Freeman and Phillips [7] performed their electron-impact experiments at 50 eV and Cordes and Smith [8] at 70 eV.

The PIMS investigation detected Cl_2^+ and Cl_2O^+ at a photon energy of 11.8 eV and ClO^+ at 23.6 eV, the formation of the latter ion due to second-order light. They also detected $HOCl^+$, an impurity which the authors attribute to the reaction of Cl_2O with water adsorbed on the HgO. The most abundant ion signal was ClO^+ but since the ClO^+ ions were formed using a different ionizing photon energy to the Cl_2^+ and Cl_2O^+ ions, with the relative intensity of this second-order light not quantified, it is hard to make an informative comparison between the relative intensities we obtain and the data they report. This PIMS study did, however, determine the appearance energy of the ClO^+ fragment ion to be 12.29 eV.

The EIMS studies [6–8] all observed Cl^+, ClO^+, Cl_2^+, and Cl_2O^+, the ClO^+ fragment being the most abundant ion. The investigation by Fisher detected trace amounts of impurities from air and, despite purification of the sample at reduced temperatures and pressures, he reported that contributions from Cl_2 were present. Freeman and Phillips reported the presence of impurities in the spectrum from air, water and protonated species. In this investigation some purification of the Cl_2O sample was performed. Cordes and Smith also purified their Cl_2O at a reduced temperature and pressure and, in addition to Cl^+, ClO^+, Cl_2^+, and Cl_2O^+, they also reported the observation of O^+ and Cl^{2+}.

In the present study, at electron energies ranging from 30 to 450 eV, the parent ion Cl_2O^+ and fragment ions, Cl_2^+, ClO^+, and Cl^+ with the expected relevant isotopic abundance, were detected. The plots of the relative partial ionization cross sections of the Cl_2O^+ and Cl^+ ions against electron energy show an initial increase in the cross section as the electron energy is raised (Fig. 3), due to the increased likelihood of ionic fragmentation with increased electron energy and associated ionic excitation. For the Cl_2^+ ion, the uncertainties are so large at low electron energies that we can get little information from the plot.

The relative intensity of the parent ion, Cl_2O^+, to the ClO^+ fragment ion observed in this study at 50 eV, the ionizing energy used in the two earlier EIMS studies by Fisher [6] and Freeman and Phillips, [7] (Cordes and Smith [8] used 70 eV), is 48.2% (Table 1, Fig. 3). This relative intensity is in reasonable agreement with the relative intensities given in the other EIMS studies, 57.3%, 54.7%, and 52.8%, respectively. The reported intensities of the Cl_2^+ ion, relative to ClO^+, are more wide ranging. In the current work the relative intensity of Cl_2^+ is 14.0% (Table 1, Fig. 3), a value lower than that measured by Freeman and Phillips, 21%, but higher than those determined by Fisher, 7.1%, and Cordes and Smith, 11.9%. The higher value obtained by Freeman and Phillips is perhaps due to an impure sample of Cl_2O and the discrepancy between the relative intensity of Cl_2^+ we obtain and those quoted by Fisher and Cordes and Smith, is possibly due to the inefficient collection of the energetic fragment ions from the dissociation of Cl_2O^+ in those studies. Although our relative intensity of Cl_2^+ is higher than the studies by Fisher and Cordes and Smith despite the acknowledgement by Fisher that his sample may have contained traces of Cl_2, we feel that our higher value is reliable because of our efforts to purify the Cl_2O sample and the quantifiable efficiency of our apparatus for collecting the ionic fragments from single ionization.

The relative intensity of Cl^+ we obtain is 41.3% (Table 1, Fig. 3), which again is lower than the value measured by Freeman and Phillips, 58.3%, and higher than those given by Fisher, 1.04%, and Cordes and Smith, 25%. The high relative intensity of Cl^+ quoted by Freeman and Phillips is probably due to the detection of Cl^+ fragments from the dissociative ionization of any Cl_2 or HOCl present in the sample in addition to the Cl^+ fragments from Cl_2O^+. The low relative intensities of Cl^+ obtained by Fisher and Cordes and Smith are again probably a result of the especially inefficient collection of energetic atomic fragment ions. The PIMS [9] study detected no Cl^+ fragments but the spectra were probably taken at ionizing energies below the appearance energy of the Cl^+ ion. Cordes and Smith also noted the presence of O^+ and Cl^{2+} in the mass spectrum, fragments not observed by any other investigations. Although they observed no other impurities, it is possible that O^+ may arise from traces of O_2 and Cl^{2+} could arise from the dissociative multiple ionization of Cl_2, both of which could be present as impurities in the Cl_2O sample.

Despite the pioneering efforts of these early EIMS investigations [6–8] of Cl_2O, the above comparison of the data obtained in those studies and that obtained in the current work highlights the problems involved in investigating reactive molecules such as Cl_2O. However, given the efforts made in this work to obtain as pure a sample of Cl_2O as possible, and the design of the apparatus for the efficient collection of the majority of the energetic fragments from dissociative single ionization, we feel that the relative partial ionization cross sections for the parent and fragment ions of Cl_2O^+ given in Table 1 and Fig. 3 are likely to be more reliable.

4.2. Double ionization

In the electron-impact mass spectrum of Cl_2O (Fig. 2) no stable parent dication (Cl_2O^{2+}) or daughter dications are observed. This implies that no bound regions of the dication potential energy surfaces can be accessed by a vertical transition from the equilibrium geometry of the neutral molecule.

Our coincidence spectra show that the dissociative double ionization of Cl_2O proceeds via a two-body dissociation reaction to form $Cl^+ + ClO^+$ and three-body reactions to form $O^+ + Cl^+$ and $Cl^+ + Cl^+$. For the $Cl^+ + ClO^+$ dissociation reaction, the simulation of the coincidence peak indicates that there is a single KER associated with this dication dissociation reaction. From Table 2 it can be seen that the estimate of the energy of the state of Cl_2O^{2+} dissociating to form $Cl^+ + ClO^+$, derived from the KER, is 30.6 ± 0.2 eV. This evaluation of $E(Cl_2O^{2+})$ from the KER, however, assumes that the fragment ions are formed with no internal energy. From studies of the photoelectron spectrum of Cl_2O [42,43], the ground state electron configuration of Cl_2O^{2+} can be assumed to be $\ldots a_2^2 a_2^1 b_2^2$. That is two b_1 electrons are removed upon double ionization to give a ${}^1A_1$ state under C_{2v} symmetry. Therefore, the dissociation of Cl_2O^{2+} from its ground electronic state to form the fragment ions Cl^+ (${}^3P_g$) and ClO^+ (${}^3\Sigma^-$) [44,45] in their ground states is a symmetry and spin-allowed transition, suggesting that the two fragment ions are likely to be formed in their ground electronic states. Indeed, the dissociation of ground state Cl_2O^{2+} to form one fragment ion in its first excited state and the other in its ground state are both spin-forbidden transitions, which again supports the assumption that the product ions are formed with no excess electronic energy. Making an allowance for the possibility of vibrational excitation will perhaps increase the error associated with $E(Cl_2O^{2+})$ to ± 1 eV. As can be seen from Fig. 6, it is apparent that the appearance energy of the $Cl^+ + ClO^+$ ion pair lies below 35 eV, which is consistent with this calculated value of $E(Cl_2O^{2+})$. Due to the large uncertainties associated with the determination of the appearance energy for this pair of ions, and despite the assumptions involved in the determination of $E(Cl_2O^{2+})$ from the coincidence peak widths, we feel that the value of $E(Cl_2O^{2+})$ as 30.6 ± 1 eV is the more realistic estimate of the energy of the state of Cl_2O^{2+} which dissociates to form $Cl^+ + ClO^+$.

For the dissociation of Cl_2O^{2+} to form the $O^+ + Cl^+$ ion pair, an accurate determination of the appearance energy could not be obtained as the signal is weak at low electron energies and the degradation of the filament by Cl_2O increases the statistical uncertainties in the spectra. The simulation of the coincidence peak, Table 2, indicates that two distinct electronic states of Cl_2O^{2+} dissociate to form the $O^+ + Cl^+$ fragment ion pair, the first state at an energy of 32.4 eV and the second at ca. 39 eV. Although the simulation of the coincidence peak for this reaction yields two sets of differing KER values for the possible dissociation mechanisms, as there is no experimental appearance energy for this ion pair for comparison with the values of $E(Cl_2O^{2+})$, the mechanism by which Cl_2O^{2+} dissociates to form $O^+ + Cl^+$ cannot be definitively assigned.

For the remaining three-body dissociation reaction of Cl_2O^{2+}, forming $Cl^+ + Cl^+$, again an accurate determination of the appearance energy for this ion pair could not be made. The simulation of the coincidence peak for these product ions yielded an evaluation of the energy of the dication state responsible for this dissociation reaction as ca. 33.6 eV. As with the $O^+ + Cl^+$ ion pair, it is not possible to distinguish which fragmentation pathway is actually followed because we cannot determine the appearance energy for this ion pair. The value of $E(Cl_2O^{2+})$ associated with the state which dissociates to form $Cl^+ + Cl^+$, 33.6 eV, is close to the lowest energy dication state we deduced was responsible for the formation of $O^+ + Cl^+$ (32.4 eV). However, the lack of data on appearance energies for either of these three-body dissociation reactions means that we cannot say whether or not these two ion pairs ($O^+ + Cl^+$ and $Cl^+ + Cl^+$) are formed as the result of the dissociation of two distinct states of Cl_2O^{2+}.

The value of the double ionization energy of Cl_2O derived using the "rule of thumb" [46] is 30.63 eV. This estimate of the double ionization potential of Cl_2O is in very good agreement with the value of the dication state energy for the lowest electronic state dissociating to form $Cl^+ + ClO^+$, 30.6 ± 1 eV, suggesting that this is the ground state of the Cl_2O dication.

5. Conclusion

This study presents the investigation of the single and double ionization of Cl_2O. Time-of-flight mass spectrometry is used to determine the relative partial single ionization cross sections of Cl_2O for incident electron energies from 30 to 450 eV. Stable parent ions Cl_2O^+ and Cl^+, Cl_2^+, and ClO^+ fragment ions and their isotopes were detected, the most abundant ion being the ClO^+ fragment ion.

Ion–ion coincidence experiments have been performed to study the formation and dissociation of Cl_2O^{2+}. Coincidence peaks due to the dissociation of Cl_2O^{2+} to form $Cl^+ + ClO^+$, $O^+ + Cl^+$, and $Cl^+ + Cl^+$ fragment ion pairs (and their isotopomers) were observed in the coincidence spectrum. The comparison of simulations of the coincidence spectra with the experimental data indicates that the dissociation of the dication to form the $O^+ + Cl^+$ ion pair involves a multiple kinetic energy release, suggesting this three-body dissociation reaction of Cl_2O^{2+} occurs from two different dication electronic states.

The values derived for the energies of the dication states responsible for forming the observed ion pairs indicate that there are two distinct dication electronic states that dissociate to form the $O^+ + Cl^+$ pair. In addition, it seems clear that the two-body dissociation of Cl_2O^{2+} to form $Cl^+ + ClO^+$ occurs from the ground electronic state of Cl_2O^{2+}, thus providing a first estimate of the double ionization energy of Cl_2O^2 as 30.6 ± 1 eV.

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