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Unimolecular dissociation of non-stoichiometric oxygen cluster ions O_n^{+*} ($n = 5, 7, 9, 11$): a switch from O_3 to O_2 loss above cluster size $n = 5$

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Abstract

Metastable fractions and MIKE-peaks for metastable decay reactions involving O_2 and O_3 evaporation from odd numbered oxygen cluster ions have been measured using a high resolution two sector field mass spectrometer of reversed geometry. Whereas O_5^{+*} exclusively decays via O_3 loss, the larger non-stoichiometric oxygen clusters evaporate O_2 molecules. The average kinetic energy release ⟨KER⟩ data derived from the peak shapes is independent from the emitted neutral particle between 1 and 2 meV; however, the time dependence of the metastable fractions shows a characteristic dependence on cluster size indicating a change in the metastable fragmentation mechanism when going from the O_5^{+*} to the larger odd numbered oxygen cluster ions. The present results are in excellent agreement with binding energies of oxygen and ozone molecules to oxygen cluster ions published in the literature. (Int J Mass Spectrom 220 (2002) 221–230)
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1. Introduction

Most of the techniques applied for the production of van der Waals clusters do not form a specific cluster size but lead to a wide distribution of various cluster sizes. In order to select a specific cluster size mass spectrometry is commonly used. Thereby, neutral precursor clusters have to be ionized and this process has a dramatic influence on the resulting cluster ion. A neutral van der Waals cluster is bond only by dipole–dipole interactions, whereas in a charged cluster the interaction between the charged center and the neutral surrounding neighbors is much stronger. This increase in binding energy raises the temperature of the cluster ion after the ionization event and often leads to the evaporation of several monomers. Furthermore, the ionic center of a charged van der Waals cluster often is not simply a charged monomer but a new covalently bond molecule. This has been confirmed for positively charged rare gas clusters [1–3]. The situation becomes more complicated in the case of molecular clusters [4]. In addition to the removal or attachment of an electron and the subsequent ion core formation, the molecular monomers may undergo fragmentation if they absorb enough energy from the ionization process. Furthermore intra-cluster reactions between the

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ionized monomer and neutral radicals with neutral neighbors may lead to new chemical species [5,6].

Electron impact ionization of molecular clusters at sufficiently high electron energies leads often to the dissociation of monomers and thereby to the formation of non-stoichiometric cluster ions. At least one of the cluster constituents has been altered and has a different chemical composition. For instance, positively charged hydrogen clusters always contain an ionic H_3^+ core that is surrounded by neutral H_2 molecules [7–10]. Protonation of an ionic core has also been observed for several other clusters that are built of hydrogen containing molecules, i.e., NH_3 [11,12], H_2O [13,14], acetone [15], and so on. By this process it is possible to prevent a radical ionic core, since the protonated ion has a closed electronic shell. However, molecules like N_2 [16] and O_2 [17,18] cannot avoid a radical ionic core that simple and for these clusters one observes often two different cluster series of similar intensity in the mass spectra, i.e., one that contains only intact molecules (stoichiometric clusters) and one that contains either a single fragment atom or a reaction product that contains an odd number of atoms like O_3. In the present work, we carefully measured the unimolecular dissociation channels of non-stoichiometric oxygen cluster ions and thereby it is possible for the first time to determine experimentally the structure of the clusters. Both the localization of the charge and the nature of the cluster part that contains an odd number of atoms will be addressed.

2. Experimental

The experimental setup consisting of a cluster source, a Nier-type electron impact ion source and a two sector field (reversed geometry) mass spectrometer has been described in detail previously [19,20]. A closed cycle cryostat was applied to cool pure oxygen at a pressure of 2–2.5 bar in a supersonic expansion cluster source to 120–150 K. The cold gas was expanded through nozzles of either 10 or 20 μm diameter and the thereby formed neutral cluster beam passed a differentially pumped chamber that is separated from the ion source chamber by a 1 mm skimmer. The pressure in the first chamber is 4×10^{-3} Pa and in the cluster source 2×10^{-4} Pa. The neutral cluster beam crosses a Nier-type ion source and is ionized by an electron beam of 100 eV and a current of 200 μA. The ions are extracted perpendicular to both the electron and neutral cluster beam by an acceleration voltage of 3 kV. The ions are then analyzed according to their momentum and kinetic energy by a magnetic and electric sector field, respectively. Between the ion source and the magnetic sector a turbo molecular pump reduces the pressure to about 10^{-5} Pa and an additional turbo molecular pump on top of the electric sector field leads to a pressure in the second field free region (between the two sector fields) of 1.5×10^{-6} Pa. This low pressure is essential to avoid collision-induced dissociations that may contribute to the fragment ion signal that is formed by unimolecular dissociation reactions.

3. Results

Fig. 1 shows two mass spectra obtained at the same cluster source conditions but at different electron energies. The electron energy for the lower mass spectrum was set to 17 eV where no fragment ions of the oxygen molecule can be formed. Therefore, only the cluster ion series that contains an even number of oxygen atoms can be observed. In contrast, the upper mass spectrum exhibits clearly a second cluster ion series that contains an odd number of oxygen atoms. However, the intensity of these ions is much lower compared to even numbered species of similar mass. The electron energy was set to 100 eV and, thus, sufficiently high to both ionize and dissociate the oxygen molecules [21]. According to ion molecule reactions an O^+ ion will capture rapidly an electron from a neutral O_2 molecule. However, the rate constant for such a reaction depends strongly on the electronic state of the atomic ion [22,23]. The neutralized oxygen atom will form by a three-body collision process with two neighboring O_2 monomers (that is a very likely process within a cluster) an ozone molecule [24].

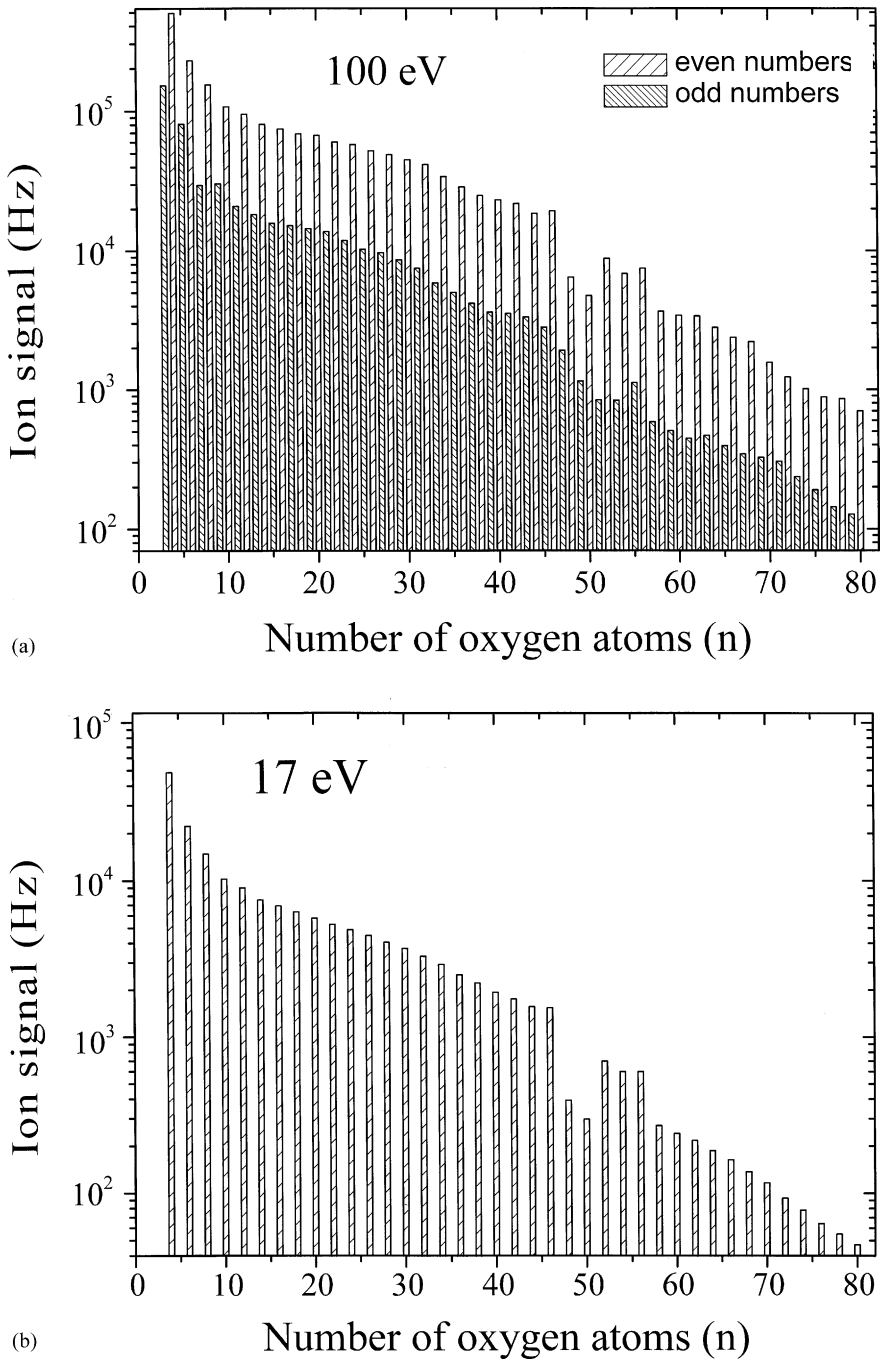

Fig. 1. Cluster size distribution obtained by electron impact ionization of a neutral supersonic oxygen cluster beam. The electron energy was set to 100 eV for the mass spectrum designated (a) and 17 eV for the mass spectrum (b), respectively. The electron current was 300 μA. Cluster source conditions: 2.6 bar O_2, 107 K.

For the odd numbered oxygen clusters that contain 5, 7, 9, and 11 atoms, we checked for all unimolecular dissociations in the first and second field free region. For the second field free region, the corresponding parent ions were selected by the magnetic sector field and all possible fragment ions were analyzed by a scan of the electrostatic sector field (MIKE-scan). In addition to the qualitative information about the existence of a certain decay channel, this technique provides also quantitative information about the kinetics and energetics of the process [20]. From the shape of the MIKE-peak the kinetic energy release (KER) [20] can be deduced and the area of the MIKE-peak is used to calculate the metastable fraction. The latter is a measure for the likelihood of a dissociation process and reveals the time dependence of a decay reaction if determined at different times after the ionization event. For decades in the first field free region, the magnetic sector field is tuned to the momentum of the fragment ion and again the electrostatic sector field is scanned to probe its ion signal. In this case, it is only possible to determine the metastable fraction from the data but not the KER.

Fig. 2 shows the MIKE-peaks of all the fragment ions that were observed upon unimolecular dissociation of O_n^{+*} ($n = 5, 7, 9, 11$) cluster ions in the second field free region. For the cluster sizes 5, 7, and 9, two sets of data exist and the symbols in Fig. 2 are averaged values from these independent measurements in order to reduce the statistical errors. The solid line through the data points is the result of a Gauss fit. In addition to the fragment ion signal (open circles), the corresponding MIKE-peak of the parent ion is shown, however, shifted to the energy position of the fragment ion by multiplying its sector field voltage with the mass ratio of the fragment and precursor ion and normalized to the height of the fragment ion signal. This allows a confirmation of the fragment channel and will be used later to deduce the KER of the dissociation process. The similar width of the shifted parent ion signal and the MIKE-peak of the fragment ion tells immediately that the KER has to be rather small for all these processes.

The most surprising fact is that the parent ion O_5^{+*} decays exclusively into O_2^+ by loosing somehow three neutral oxygen atoms, whereas all larger odd numbered oxygen cluster ions release only a neutral O_2 molecule. At this point it is not clear what is the nature of the neutral fragment in the case of the decaying O_5^{+*}. It might be an intact ozone molecule but also the emission of two neutral fragments, i.e., an O_2 molecule and a single oxygen atom, is a possibility.

In a first analysis, the area of all the fragment ion peaks (including the peaks from the decays in the first field free region) was calculated. In addition, the area of the corresponding parent ion signals was calculated and the metastable fractions shown in Fig. 3 were derived by the ratio of the fragment and parent ion area. The error bars were calculated by applying the Gauss equation for propagation of random errors of the single measured areas. The circles designate the metastable fractions derived from the dissociation processes that take place in the second field free region and the triangles correspond to unimolecular dissociation in the first field free region. For the calculation of the metastable fractions, the two data sets for the second field free region were analyzed individually which explains the two data points for several cluster sizes in Fig. 3. Within the statistical error all metastable fractions that have been determined two times turn out to be the same. The three larger cluster ions that exhibit the loss of one oxygen molecule O_2 follow in this semi-logarithmic plot almost a line, however, O_5^{+*} clearly deviates from this trend. Since the scaling of the *y*-axis of Fig. 3 is logarithmic, a similar ratio of two metastable fractions leads to almost the same distance in the *y*-direction between the data points. Except for the O_5^+ ion the ratio between the metastable fractions derived from the dissociation reactions in the first and second field free region are roughly the same and, thus, indicate a similar time dependence. Fast dissociation processes reveal a larger drop of the metastable fractions derived in the first and second field free region. Thus, we conclude that the process, O_5^{+*} decaying into O_2^+, has a shorter lifetime than the neutral O_2 loss for the larger odd numbered oxygen cluster ions.

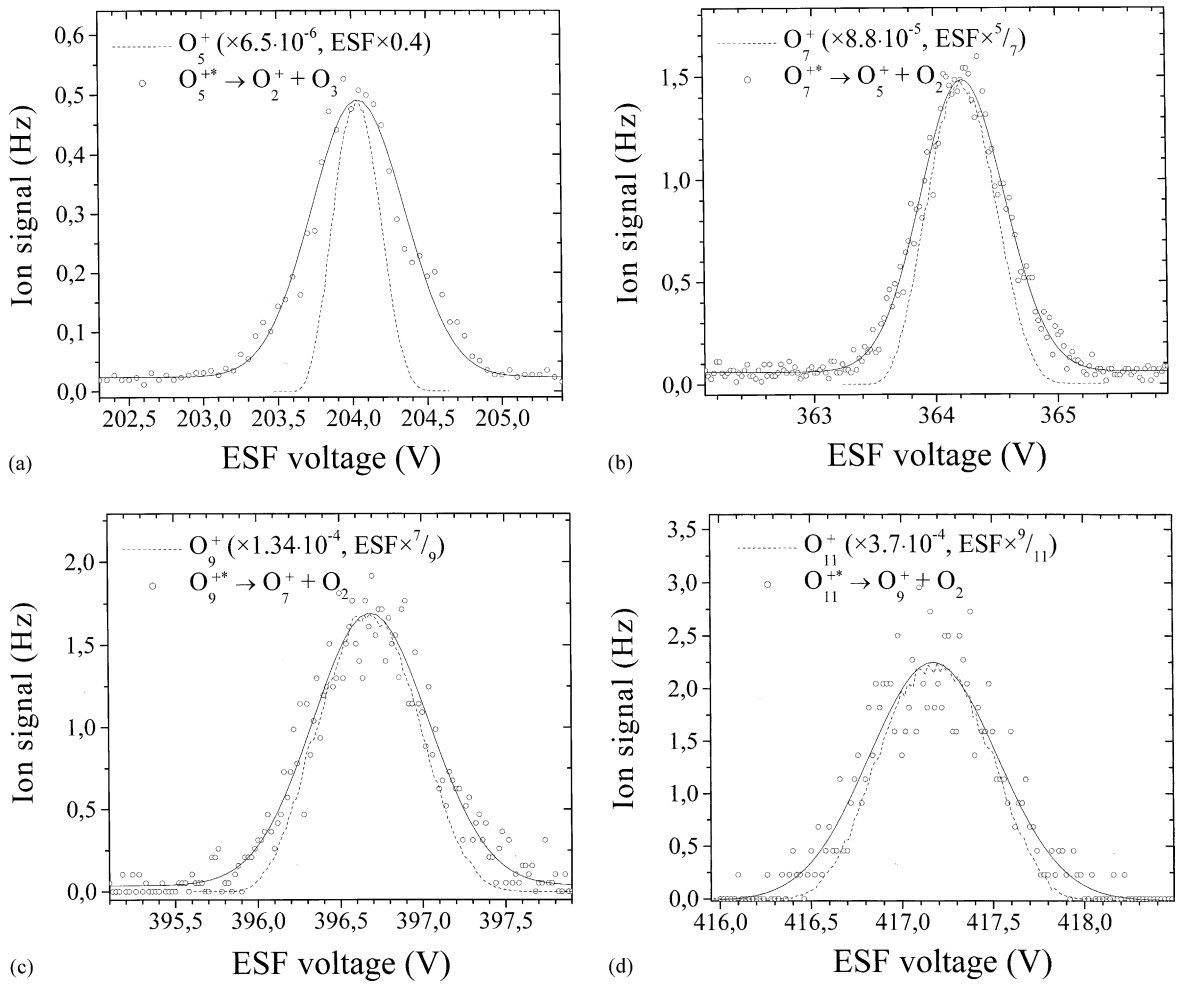

Fig. 2. MIKE-spectra for all unimolecular decay reactions of the odd numbered oxygen cluster ions O_n^{+*} ($5 \leq n \leq 11$) measured in the second field free region. The solid line through the data points is a Gaussian fit and the dashed line is the MIKE-peak of the corresponding parent ion with the energy scale multiplied with the mass ratio of the fragment and parent ion. The height of the parent ion peak was normalized to the same height as the fragment ion MIKE-signal.

Walder et al. [25] reported already on the metastable decay of non-stoichiometric oxygen cluster ions that were measured on the same experimental setup. However, in the meantime this instrument was significantly improved in the following manner. Firstly, an additional differential pump has been introduced to lower the pressure in the first field free region by more than an order of magnitude. This improved pressure before the magnetic sector field also leads to a lower pressure in the second field free region. Secondly, the data acquisition has been changed from analog signal plotted on recorders to digital counting based on a PC. Thereby, much lower ion yields can be measured today (about three orders of magnitude more sensitive). Due to the low signal intensity Walder et al. were able to observe most of the reactions only in the first field free region. However, the short distance between the ion source and the first field free region can lead to collision-induced dissociations that contribute to the fragment ion signal that is measured.

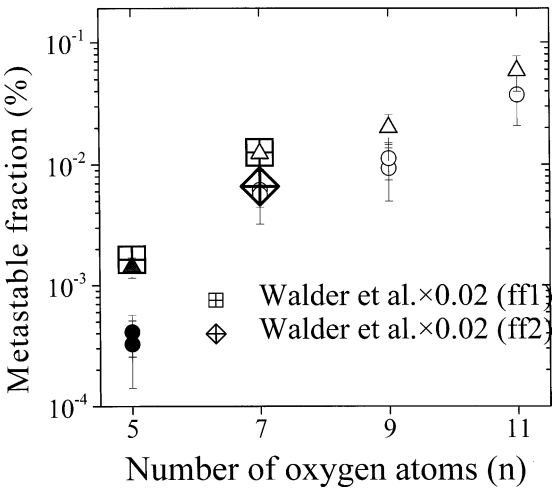

Fig. 3. Metastable fractions of the decay reactions of odd numbered oxygen cluster ions derived from area of the MIKE-peaks. The ratio of the area of the fragment ion signal measured in the first (triangles) and second field free region (circles) and the corresponding parent ion area has been plotted. The error bars were calculated by error propagation of the statistical errors.

Although a pressure correction was made at that time, metastable fractions deduced from decays in the first field free region are likely to be uncorrect, especially if they are small. Although, the absolute value of the metastable fractions by Walder et al. are about a factor 50 larger than the presently measured values, there is some qualitative agreement between the two studies: for O_5^{+*}, Walder et al. also observed that the loss of three oxygen atoms is the most abundant dissociation process. For O_7^{+*}, neutral O_2 loss is more than an order of magnitude more abundant than all other dissociation channels. Furthermore, the ratio between the two data points by Walder at al. for $O_5^{+*} \rightarrow O_2^{+}$ and $O_7^{+*} \rightarrow O_5^{+}$ is very similar to the ratio determined in the present investigation. The large difference in the magnitude of the metastable fractions can be explained partly by a much narrower defining slit between the two sector fields that has been used in the present study. Unfortunately it was not possible at that time to determine the metastable fractions for larger odd numbered oxygen cluster ions.

A further extension of the present study to the investigation by Walder et al. [25] is the measurement of the complete MIKE-peaks of the parent and fragment ion which allows the determination of the KER by the dissociation process. The widening of the fragment ion peak is the result of the KER and, therefore, the MIKE-peak of the fragment ion is a convolution of the shifted parent ion peak and a contribution that is purely the result of the KER. Thus, a deconvolution of the MIKE-peaks of the fragment and corresponding parent ions signal (with an appropriately scaled energy scale) will lead to a peak that contains the information about the KER. Since all MIKE-peaks are almost perfect Gaussians, the deconvolution will also lead to a Gaussian curve. Furthermore the average KER for such a decay process (Gaussian shape) can be calculated by inserting the width ΔE of this peak at 22% of its height into the following equation:

$$\mathrm{KER(eV)} = \frac{m_1^2 U}{16 m_2 (m_1 - m_2)} \left(\frac{\Delta E}{E_0}\right)^2 \quad (1)$$

with m_1 the mass of the parent ion, m_2 the mass of the fragment ion, U the acceleration voltage, E_0 the sector field voltage for parent ion transmission, and ΔE the corrected width of the fragment ion peak calculated by

$$\Delta E = \sqrt{(w_2)_{22\%}^2 - (w_1)_{22\%}^2} \quad (2)$$

$(w_1)_{22\%}$ and $(w_2)_{22\%}$ are the full widths of the Gauss fits to the data shown in Fig. 2 at 22% of the height of the peaks (actually 22%, $\sim e^{-1.5}$; for detailed information see [26] and Appendix A). Due to the fact that the width of the fragment and its corresponding parent ion signal are almost identical, the resulting KER values are very small. However, the error bars determined by error propagation of the absolute uncertainties of the width from the Gauss fits are especially for the larger clusters relatively large. Fig. 4 shows the average KER of the unimolecular reactions measured in the second field free region. Within the statistical error, the average KER values are for all odd numbered oxygen clusters, that have been investigated, the same. However, since Eq. (1) is only correct if an ion splits into two fragment (i.e., $m_1 - m_2$ is the mass of a neutral fragment) we have to assume that O_5^{+*} looses an intact ozone molecule. Thus, it is rather surprising that the average KER for both the neutral O_2 loss for

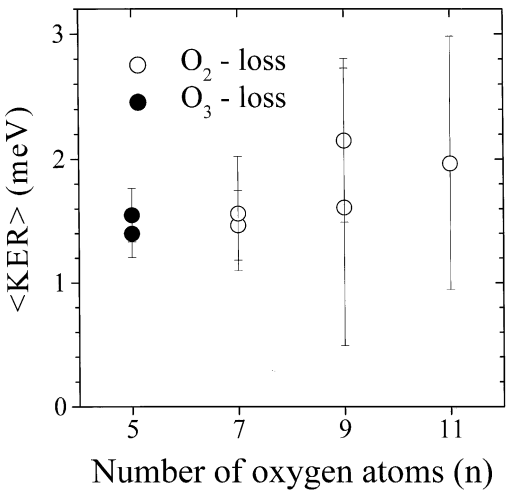

Fig. 4. Average KER for the decay reactions of odd numbered oxygen cluster ions plotted as a function of the number of oxygen atoms of the parent ion applying Eq. (1). The error bars were derived by error propagation of the statistical errors of the corresponding MIKE-peaks. The large error can be explained by the similar width of the parent and fragment ions MIKE-peaks which results in a small KER value.

larger clusters and O_3 loss for the O_5^{+*} is practically the same.

4. Discussion

According to the literature, a three-body collision of an oxygen atom with two oxygen molecules is likely to form an ozone molecule [23]. The process $O+O_2+M$ is the dominant formation channel for tropospheric ozone. Inside an oxygen cluster, the presence of neighboring oxygen molecules will lead to a high probability for ozone formation upon the fragmentation of a monomer. The ionization energy for O_3 is 12.52 eV [27], 0.45 eV higher than the ionization energy for O_2 [28]. This suggests that the charge preferentially would be located on an oxygen molecule unless a larger ionic core like O_4^+ or O_5^+ will be formed. This is in perfect agreement to the present observation that O_5^{+*} exclusively decays into an O_2^+ ion and releases three neutral oxygen atoms. The kinetic energy that is released due to the dissociation process is less than 2 meV and much smaller than the bond dissociation energy of neutral ozone (~400 meV) [29]. Therefore, we conclude that for the dissociation of O_5^{+*} into O_2^+, an intact neutral ozone molecule will be ejected.

The exothermicity of the reaction $O_2^+ + O_3$ was determined in a flowing afterglow experiment (0.63 eV) [30]. In a complex that consists of two strongly bound components, a metastable decay in the time scale of several microseconds (the flight time from the ion source to the first and second field free region) is only possible if sufficient energy is transferred into the vibrational degree of freedom that couples the two molecules. This can only happen by either a relaxation of a vibrationally [31] or electronically [32] excited metastable state of one of the two molecules involved (i.e., O_2^{+*} or O_3^*, respectively). Since such excited states have only one lifetime, the metastable fraction for the O_5^{+*} decay should decrease exponentially with the time. Larger clusters, however, can accommodate the energy needed for the ejection of a monomer in the vibrational degrees of freedom between the cluster constituents. Such decays can be described theoretically applying simple statistical models like RRKM theory. Furthermore, the population of differently excited cluster ions leads to a non-exponential decrease of the metastable fraction for such larger cluster ions as a function of the time. Unfortunately, the ion signal was not sufficiently high to study unimolecular dissociation reactions of odd numbered oxygen clusters at different acceleration voltages which would yield more data points at different flight times. Nevertheless, Fig. 3 clearly reveals a different time behavior for the O_5^{+*} compared to the larger odd numbered oxygen cluster ions. Interestingly, the average KER for the ozone evaporation is about the same as the average KER for neutral O_2 evaporation that is observed for the larger $(O_2)_nO^{+*}$ cluster ions. All odd numbered oxygen cluster ions reveal a similar ⟨KER⟩ for the monomer evaporation in the order of 1–2 meV which is reminiscent of results obtained for several rare gas cluster ions that were investigated previously on this instrument [33]. Furthermore, also the time dependence is almost equal to that of these rare gas cluster ions of the same size indicating a

similar statistical (vibrational predissociation) nature for the decay process of the larger cluster ions.

Hiraoka [34] measured the binding energy for O_2 molecules to differently sized oxygen cluster cations utilizing pulsed high pressure mass spectrometry. For the dimer, he obtained a value of 0.39 eV which gradually decreases for larger clusters and reaches an almost constant value of 0.08 eV for clusters larger than 5. Linn et al. [35] determined the binding energy for odd numbered oxygen cluster cations by means of a molecular beam photoionization method. According to their data, the binding energy of O_2 to O_5^+ is about 40 meV and, thus, lower than for the stoichiometric clusters. Taking all these different binding energies and the ionization energies for O_3 and O_2 into consideration, we end up with the following picture for the metastable fragmentation of odd numbered oxygen cluster cations.

Independent of the process that leads to the dissociation of an oxygen molecule in a cluster, i.e., fragmentation of a molecule different to the ionized monomer (needs 2.58 eV for the dissociation [36] and 12.07 eV for the ionization of O_2 [27]), or dissociative ionization of a monomer which needs 18.73 eV [21], the charge will quickly be localized on an intact O_2 monomer. One of the oxygen atoms has to leave the cluster in order to form a non-stoichiometric cluster and the remaining neutral oxygen atom will form an ozone molecule by three-body association reaction. Since the binding energy of ozone to O_2^+ is 0.63 eV [29] and a neutral O_2 binds to O_2^+ with only 0.39 eV [34], the ozone molecule will be released from a larger cluster only after all other neutral O_2 monomers are gone. This immediately explains the transition from O_3 to O_2 loss at cluster sizes larger than O_5^+. The different time dependence of the O_3 loss from O_5^{+*} and the O_2 loss from the larger odd numbered oxygen cluster ions (which can be seen clearly in Fig. 3) is the result of the different nature of the deposition of the excess energy that finally leads to the dissociation. Larger clusters can accommodate the energy in the vibrational degrees of freedom between and within the cluster constituents and statistical distribution of this energy eventually will deposit enough energy in one monomer to remove it from the rest of the cluster. Since the O_5^{+*} actually resembles a dimer ion consisting of the ionic O_2^+ core and a neutral O_3 molecule, there is only one vibrational degree of freedom between the monomers and, thus, the energy that finally leads to the separation of the two cluster constituents has to be stored within one of the two molecules. The lifetime of this either vibrational or electronic excited state has to be in the order of 10 μs and its relaxation has to couple into the bond between the O_2^+ and the ozone molecule. Recently, the metastable dissociation of rare gas dimer ions has been investigated applying the same instrument and a novel relaxation of excited spin orbit states has been attributed to be the driving force of this process [37]. As in the case of excimer-driven metastable decay reactions [38], the determination of the appearance energies of both the parent ion O_5^+ and its fragment ion O_2^+ could give a hint about the location of the excess energy prior to the dissociation event. In addition, further measurements of the metastable fractions for O_5^{+*} decaying into O_2^+ at different acceleration voltages and for larger odd numbered oxygen cluster ions loosing a neutral O_2 would help to determine the time dependence more accurately but must await further experimental improvements.

Acknowledgements

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Appendix A. KER determination in the case of two Gaussian MIKE-peaks

The convolution of two Gaussian curves

$$f(x) = e^{-x^2/a^2} \text{ and } g(x) = e^{-x^2/b^2}$$

with the width a and b, respectively, leads to a new Gaussian curve

$$f \circ g(x) = e^{-x^2/(a^2+b^2)}$$

that has a width of $\sqrt{a^2 + b^2}$.

Thus the deconvolution of two Gaussian-shaped MIKE-peaks leads to a Gaussian curve that has a width of $w = \sqrt{w^2_{\text{fragment}} - w^2_{\text{parent}}}$.

Thus this peak has the form of $f(x) = \mathrm{e}^{-x^2/w^2}$, and $x = \Delta E = 2(E - E_{\text{center}})$, the difference of the sector field voltage to the center of the peak.

The first derivative of this peak plotted as a function of the KER calculated applying Eq. (1) leads to the distribution of the kinetic energy of the fragment ions (KERD).

$$f'(x) = -\frac{2x}{w^2}\mathrm{e}^{-x^2/w^2}$$

$$T = \mathrm{KER(eV)} = \frac{m_1^2 U}{16 m_2 (m_1 - m_2)}\left(\frac{\Delta E}{E_0}\right)^2 = cx^2 \text{ and thus } x^2 = \frac{T}{c}$$

Thus $\mathrm{KERD}(T) = (-2\sqrt{T}/cw^2)\mathrm{e}^{-T/cw^2}$

The average KER ($\overline{\mathrm{KER}}$) is the first momentum of the KERD and so

$$\overline{\mathrm{KER}} = \frac{\int_{-\infty}^{\infty} T \times \mathrm{KERD}(T)\,\mathrm{d}T}{\int_{-\infty}^{\infty} \mathrm{KERD}(T)\,\mathrm{d}T} = \frac{\int_{-\infty}^{\infty} (-2\sqrt{T^3}/cw^2)\mathrm{e}^{-T/cw^2}\,\mathrm{d}T}{\int_{-\infty}^{\infty} (-2\sqrt{T}/cw^2)\mathrm{e}^{-T/cw^2}\,\mathrm{d}T} = \frac{\int_{-\infty}^{\infty} \sqrt{T^3}\mathrm{e}^{-T/cw^2}\,\mathrm{d}T}{\int_{-\infty}^{\infty} \sqrt{T}\mathrm{e}^{-T/cw^2}\,\mathrm{d}T} = \frac{\Gamma(2.5)(cw^2)^{2.5}}{\Gamma(1.5)(cw^2)^{1.5}} = 1.5cw^2$$

If we calculate the height of $f(x)$ at $x = \sqrt{\overline{\mathrm{KER}}/c} = \sqrt{1.5}w$ we obtain

$$f(\sqrt{1.5}w) = \mathrm{e}^{-1.5} \approx 0.223$$

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