Infrared spectroscopy of gas-phase zirconium oxide clusters

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Abstract

Gas-phase zirconium oxide clusters are resonantly excited using IR radiation from a free electron laser. At sufficiently large excitation fluences, clusters with a composition Zr_nO_{2n-1} are observed to thermally emit electrons. Scanning the IR wavelength while monitoring the ion yield gives IR spectra of the clusters. For all clusters, resonances are observed between 600 and 700 cm^{-1} and the spectra are almost independent of cluster size. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The structures and properties of small clusters or nanocrystals of materials can differ significantly from those of the bulk. For some materials, larger (tens of nanometers) size grains can be produced in bulk quantities and their properties can be studied using the standard tools available for structural analysis. Complications, however, arise due to surface contamination of those grains and the unavoidable fact that those grains are produced in a distribution of sizes. Smaller clusters, containing up to several hundred atoms, can be produced via laser vaporization techniques and then studied in the gas phase. The attainable particle densities are,

however, usually low. Most crystallographic or spectroscopic techniques can, therefore, not be applied to those species. Most information on the structure of small clusters stems from analyzing size distributions in mass spectra, chemical reactivity experiments, ion mobility studies and photoelectron spectroscopy [1,2]. We recently applied IR-REMPI spectroscopy [3] to strongly bound TiC [4,5] and VC [6] clusters. Here, we will present results from experiments on zirconium oxide clusters.

Due to the exceptional properties of ZrO_2, the structure of its bulk phase and that of small particles are the focus of an intense research effort. The melting point of ZrO_2 is around 3000 K, its hardness is exceptional and it can be an ionic conductor, leading to widespread applications in industries. The crystal structure of bulk ZrO_2 is complicated by three different structural phases that, depending on pressure, temperature and composition, can exist. For bulk ZrO_2, the stable

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phase at room temperature has a monoclinic structure. Interestingly, small particles of ZrO_2 with a radius of <150 Å [7,8] are stable in the higher symmetry tetragonal phase. Small anionic clusters of zirconium oxide have been studied in the gas phase [9]. The clusters observed contained up to nine Zr atoms. Their composition deviates significantly from that of the bulk with the number of oxygen atoms, for all clusters with more than one Zr atom, being more than twice the number of Zr atoms.

For the study of ZrO_2 bulk and small particles, IR spectroscopy is often used. In order to study small gas-phase clusters of ZrO_2, conventional IR spectroscopy is not suited due to its lack of sensitivity and species selectivity. A method to obtain IR spectroscopic information on small clusters is IR-REMPI spectroscopy. In this technique, neutral clusters are irradiated with a long pulse of intense IR radiation. When the excitation wavelength is resonant with an IR active vibrational mode of the cluster, the absorption of very many photons can take place [3]. The resulting "superheated" cluster can now either dissociate or evaporate an electron via thermionic electron emission. For thermionic emission to occur, a prerequisite is that the cluster is strongly bound and has a low ionization potential. Thermionic electron emission following IR excitation has been observed to occur for fullerenes [3,10], TiC [4,5], VC [6] and some other transition and main group metal carbides, oxides and nitrides. To obtain IR spectra, mass spectra are recorded as a function of excitation wavelength. The intensity of a particular mass peak as a function of IR wavelength then gives the IR spectrum of the corresponding cluster.

2. Experimental

The experimental setup has been described previously [4] and only a brief outline is given here. Clusters are produced by pulsed Nd:YAG laser vaporization of a Zr rod at 532 nm. A mixture of 5% O_2 in argon quenches the plasma, clusters form and the gas expands into vacuum. The beam is skimmed and charged clusters are deflected out of the beam by static electric fields. The clusters then enter the interaction region with the IR laser, situated between the plates of a time-of-flight (TOF) mass spectrometer. The IR laser is the free electron laser for infrared experiments (FELIX) [11] in Nieuwegein, Netherlands. The light output of FELIX is tunable from 40–2000 cm^{-1} and consists of (10 Hz) macropulses of 5 μs duration. Each macropulse consists of 0.3–5 ps long light pulses, spaced by 1 ns. The bandwidth is nearly transform limited. Here, we concentrate on the 350–1800 cm^{-1} range. The neutral clusters are irradiated with the FELIX macropulse. The plates of the TOF spectrometer are initially at ground potential and are pulsed to high voltage at a delay of about 5–10 μs after the end of the FELIX pulse. The ions produced during that time are accelerated into the TOF spectrometer and a mass spectrum is obtained. Recording mass spectra as a function of FELIX wavelength yields the IR spectra of the individual clusters.

3. Results

In Fig. 1, mass spectra of zirconium oxide clusters are shown when irradiating the cluster
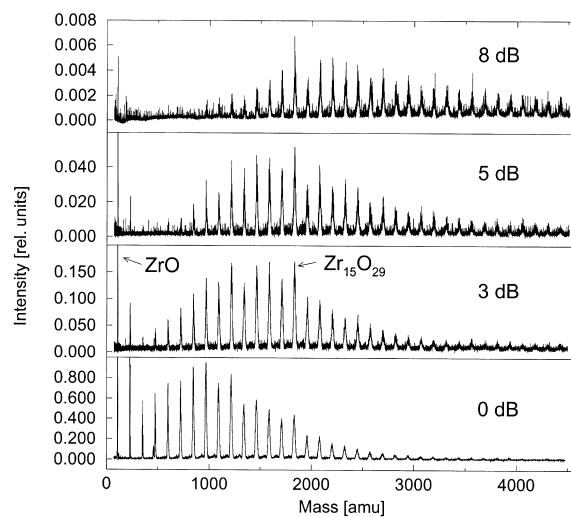

Fig. 1. Mass spectra of zirconium oxide clusters at different excitation fluences. The excitation frequency is 640 cm^{-1}. All peaks observed result from ions having a composition $Zr_nO_{2n-1}^+$. At higher powers, the distribution shifts to smaller clusters.

beam with FELIX at a wavelength of 16 μm. Four mass spectra are shown, taken at different laser powers resulting from different levels of attenuation of FELIX. All peaks observed result from ions having a composition $Zr_nO_{2n-1}^+$. At the highest IR laser power (bottom trace), the distribution has the most intense peak for $Zr_8O_{15}^+$; the peaks for ZrO^+ and $Zr_2O_3^+$ have a larger amplitude, but their integrated intensity is less than that for $Zr_8O_{15}^+$. At the high mass side of $Zr_8O_{15}^+$, the peaks decrease in intensity with a characteristic pattern. The peaks for $Zr_{10}O_{19}^+$, $Zr_{13}O_{25}^+$ and $Zr_{15}O_{29}^+$ are for example always observed to be relatively strong while peaks for $Zr_9O_{17}^+$, $Zr_{11}O_{21}^+$, $Zr_{14}O_{27}^+$ and $Zr_{16}O_{31}^+$ are weaker. When the FELIX power is reduced, the distribution shifts to higher masses. At an attenuation of 3 dB (50%), the peak for $Zr_{15}O_{29}^+$ becomes about equal in strength to the peak for $Zr_8O_{15}^+$, and at even lower FELIX powers, $Zr_{15}O_{29}^+$ becomes the dominant peak. The characteristic relative intensity patterns described above are observed at all IR powers.

The intensity of all peaks can be measured as a function of IR wavelength to obtain IR spectra. In Fig. 2, IR spectra of several clusters are shown. The lowest trace is the spectrum measured for ZrO. It consists of a broad feature around 640 cm^{-1}. As discussed below, this feature is, however, not due to the absorption of ZrO but rather due to fragmentation of larger clusters; ZrO has a known vibrational frequency of about 900 cm^{-1} [12]. For the larger clusters Zr_8O_{15}, $Zr_{15}O_{29}$ and $Zr_{20}O_{39}$, the IR spectrum shows the presence of at least two features, one located at 620 cm^{-1} and one at 680 cm^{-1}. Both these features appear to consist of more than one peak. For larger clusters such as $Zr_{26}O_{51}$ and $Zr_{32}O_{63}$, the two features seem to merge to one broad peak. Similar spectra have been taken for all clusters with sizes between ZrO and $Zr_{32}O_{63}$, and all these spectra follow the size trends that are indicated in Fig. 2. Further, it is observed that the shape of the spectra does not depend significantly on the FELIX powers used. In the experiment, the range from 350 to 1800 cm^{-1} is scanned. For all clusters, however, signal is only observed in the range shown here.

In Fig. 3, the amount of ions in Fig. 2 is shown as a function of FELIX fluence. The fluence is
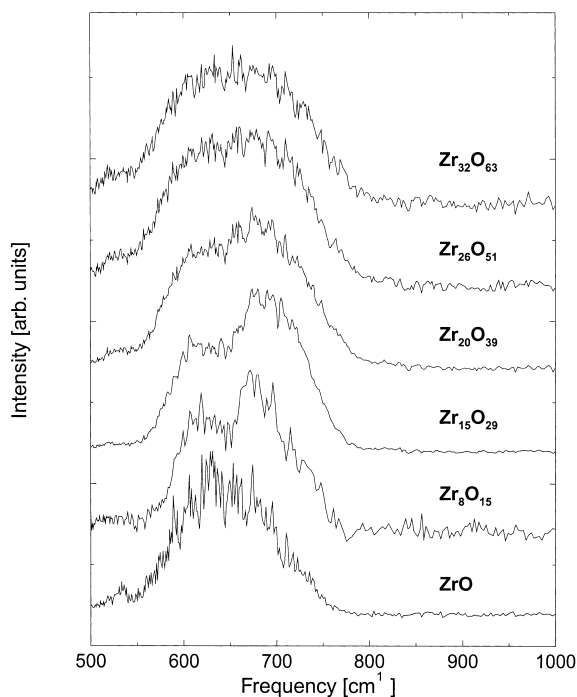

Fig. 2. IR spectra of several zirconium oxide clusters. For the larger clusters, the IR spectrum shows the presence of at least two features, one located at 620 cm^{-1} and one at 680 cm^{-1}.

changed by inserting fixed value attenuators in the IR beam which results in a simultaneous attenuation of fluence and power. For all ions, a strong
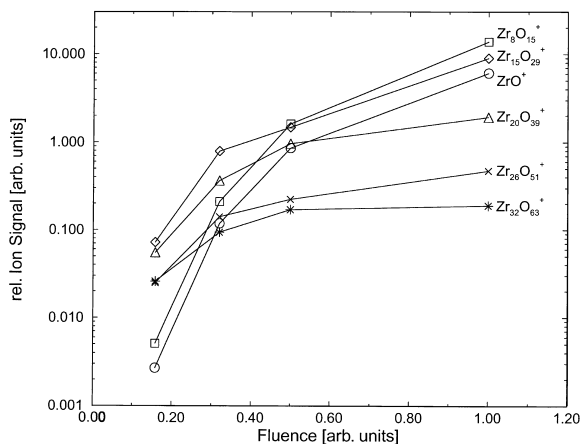

Fig. 3. The dependence of the ion signal of some clusters as a function of the IR laser fluence.

dependence on IR fluence is observed. This dependence is stronger for smaller ions than for larger ions. Reducing, for example, the fluence from a nominal value of one to 0.16 gives a drop in signal for $Zr_{32}O_{63}$ of about only a factor of 10, while for ZrO or Zr_8O_{15}, the drop is between 2000 and 3000. The dependence of the observed ion signal on the fluence is however only indirectly connected to the power/fluence dependence of the excitation and ionization process. Several other important factors also strongly influence the dependence of the ion signal on fluence. The focussed laser beam, for example, has a near gaussian beam profile. Increasing the laser fluence will thus not only increase the fluence in the center but also on the edges, allowing more molecules to be excited above the threshold for autoionization. A further complication might be increased fragmentation of clusters at higher fluences, a point that will be discussed later.

4. Calculations

Structures of Zr_nO_{2n} with $1 \leqslant n \leqslant 4$ are calculated at the ab initio level. The calculations are performed with the B3LYP method using the lacvp* effective core potential basis [13] set as implemented in GAUSSIAN 98 [14]. In Figs. 4–6, structures for $n = 2$, 3 and 4 are shown. Binding energies are relative to $nZrO_2$ units, of which the energy is calculated to be -197.0535 hartree. A singlet spin state is assumed for all structures. For ZrO_2, a C_{2v} structure with a bond angle of 107.2°

and a bond length of 1.79 Å is calculated. The two vibrations of A_1 symmetry are at 307 and 946 cm^{-1}, and the B_2 mode is at a frequency of 897 cm^{-1}. Their IR intensities are 8, 38 and 271 $km\,mol^{-1}$, respectively.

Two different stable isomers are found for the Zr_2O_4 molecule. Their geometry and IR spectra are shown in Fig. 4. Both structures consist of a four-membered ring with the remaining two oxygen atoms being either in a *cis* or *trans* configuration, having C_{2v} and C_{2h} symmetry, respectively. Their energies are very comparable, with the *trans* configuration slightly lower due to less electrostatic repulsion between the two free oxygen atoms. The IR spectra of both isomers are very similar as well. The modes around 600 cm^{-1} originate from motion within the four membered ring, and the modes around 900 cm^{-1} result from Zr–O stretch motion from the free oxygen atoms.

As the number or Zr atom increases to three, the number of different stable isomers increases to (at least) five. Their structures, energies and IR spectra are shown in Fig. 5. The lowest energy structure consists of three connected four membered rings with two loose oxygen atoms. As in other structures as well, Zr–O stretching motion of a singly bonded oxygen atom gives rise to IR active modes between 900 and 1000 cm^{-1}. The connectivity in the lowest energy structure of Zr_3O_6 has remarkable similarities to the structure of bulk ZrO_2. A general theme observed for all structures besides the C_s ring is the formation of Zr–O–Zr–O four membered rings, which are also present in bulk ZrO_2. Motion in these four membered rings,
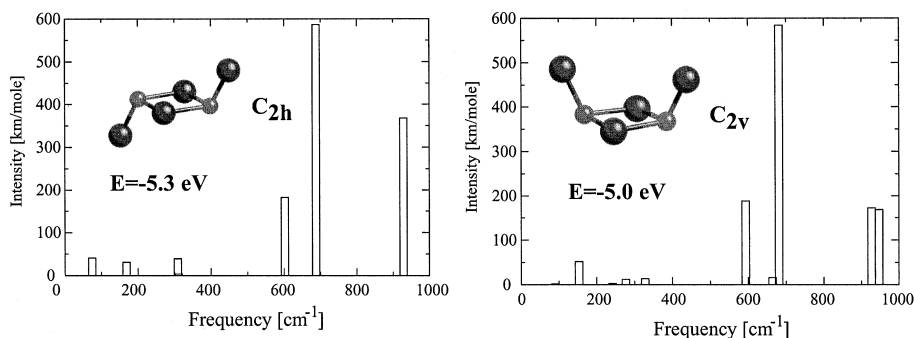

Fig. 4. Calculated structures and IR spectra of Zr_2O_4 clusters.
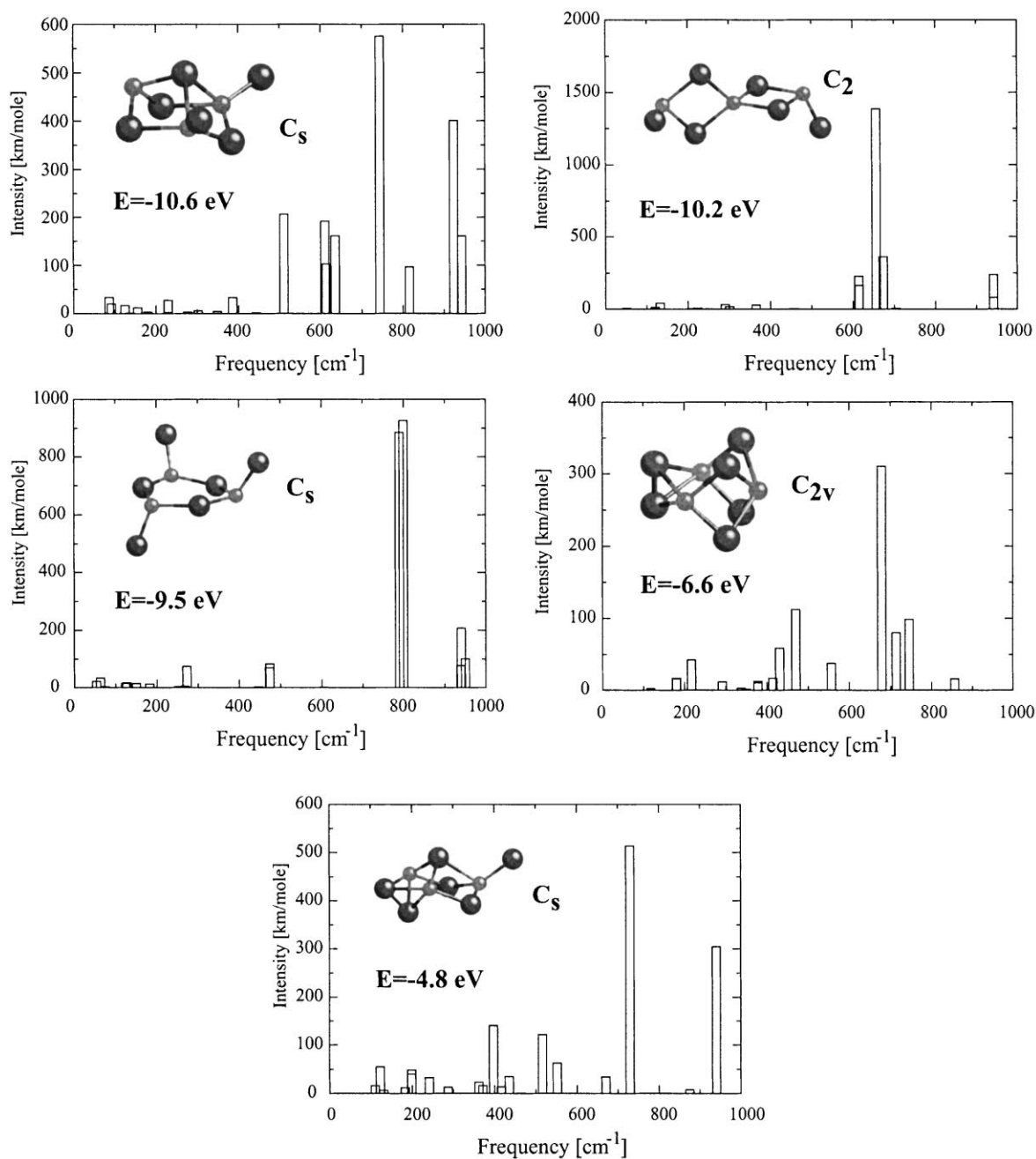
Fig. 5. Calculated structures and IR spectra of Zr_3O_6 clusters.

that are present in the first two and the last two structures, results in IR active modes between 600 and 800 cm^{-1}.

Six different stable isomers with relative energies within 3.5 eV are found for Zr_4O_8. All structures, besides the ring structure with the highest
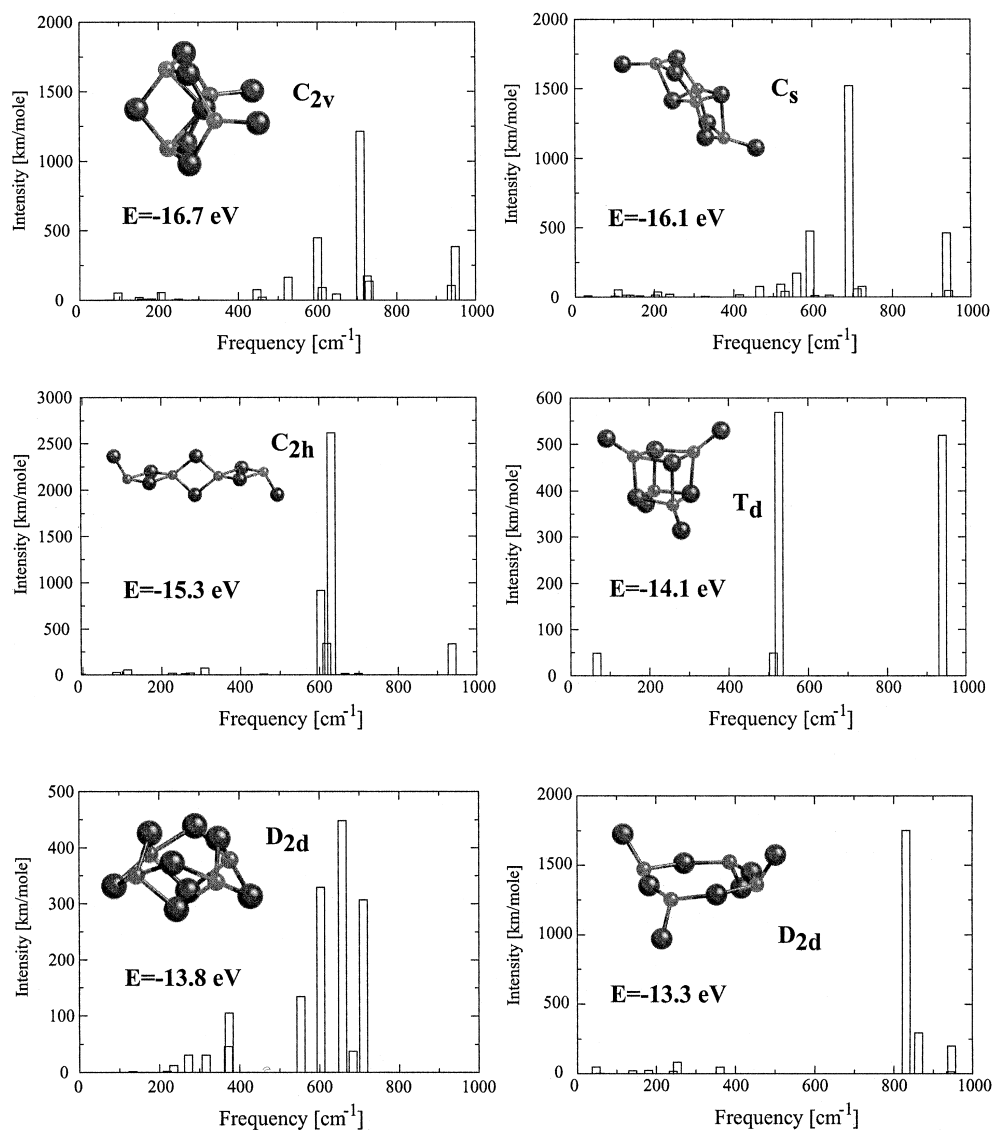
Fig. 6. Calculated structures and IR spectra of Zr_4O_8 clusters.

energy, show the formation of Zr–O–Zr–O four membered rings. As in the case of Zr_3O_6, motion in these rings gives rise to strong IR resonances. In all clusters that have these rings, these resonances are found between approximately 600 and 700 cm^{-1}, with the exception of the cubic (T_d) structure, where motion in the rings gives rise to a triply degenerate mode at 526 cm^{-1}. Stretching motions of oxygen atoms that are only bound to one zir-
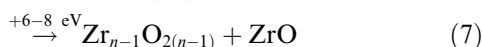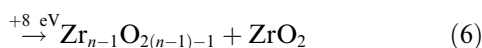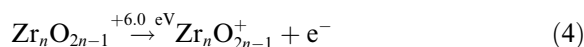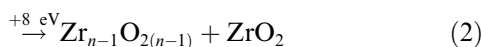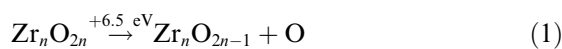
conium atom causes IR active modes that are found for all structures to be above 900 cm^{-1}.

5. Discussion

In the mass spectrum, only clusters with a composition $Zr_nO_{2n-1}^+$ are observed. This could be due to a variety of factors: (a) our cluster source

could be producing only species with such a stoichiometry, (b) their IR absorption cross-section might be significantly higher, (c) these could be much more stable than clusters with other compositions or (d) their ionization potential (IP) could be smaller than that of other clusters. The option (d), that the IP is much smaller than that of other clusters, seems to be the most likely possibility. The IPs of zirconium oxide clusters are not known. Information is however available for zirconium monoxide and dioxide, where the IPs for ZrO and ZrO_2 are measured to be 6.0 and 9.4 eV [15], respectively. From ab initio calculations, a charge on the zirconium atom of about +2 is derived [16] in solid ZrO_2. It is thus very reasonable that clusters missing one oxygen atom have a significantly lower IP, and the IPs of zirconium monoxide and dioxide might give good zeroth order values for the IPs of Zr_nO_{2n-1} and Zr_nO_{2n}, respectively.

Zirconium oxide (clusters) are very strongly bound species. It takes approximately 8 eV to remove a ZrO_2 unit from bulk ZrO_2, [1] and the binding energy of gas-phase ZrO is 7.89 eV. Interestingly, this 7.89 eV is higher than the IP of ZrO. The binding of an oxygen atom to ZrO is 6.5 eV. Again, these values might be good zeroth order approximations for the corresponding values of the clusters. When the clusters are excited by IR radiation, the following processes could happen:

$$Zr_nO_{2n} \xrightarrow{+6.5 \text{ eV}} Zr_nO_{2n-1} + O \qquad (1)$$

$$\xrightarrow{+8 \text{ eV}} Zr_{n-1}O_{2(n-1)} + ZrO_2 \qquad (2)$$

$$\xrightarrow{+9.4 \text{ eV}} Zr_nO_{2n}^+ + e^- \qquad (3)$$

$$Zr_nO_{2n-1} \xrightarrow{+6.0 \text{ eV}} Zr_nO_{2n-1}^+ + e^- \qquad (4)$$

$$\xrightarrow{+6.5 \text{ eV}} Zr_nO_{2n-2} + O \qquad (5)$$

$$\xrightarrow{+8 \text{ eV}} Zr_{n-1}O_{2(n-1)-1} + ZrO_2 \qquad (6)$$

$$\xrightarrow{+6-8 \text{ eV}} Zr_{n-1}O_{2(n-1)} + ZrO \qquad (7)$$

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[1] The binding energy of a ZrO_2 unit to bulk ZrO_2 is calculated by using a thermodynamic cycle with the heat of formation of bulk ZrO_2 (−1100 kJ mol^{-1}), the heat of vaporization of solid zirconium (610 kJ mol^{-1} and the gas-phase heat of formation of ZrO_2 (−286 kJ mol^{-1}).

The energies required are derived from those of the zirconium monoxide and dioxide and the bulk. A value for reaction (7) is difficult to estimate; however, it is expected to be in the range of 6–8 eV. Apparently, the clusters follow the lowest energy route and the only process observed that leads to charged particles is process (4), the electron emission from Zr_nO_{2n-1}.

At high fluences, the mass distribution is observed to shift to lower masses. Possible explanations for this observation are that either the lower mass clusters need more light to be efficiently excited or that larger ions are initially generated but then fragment by further absorption of IR light. Even at the very high fluences, only cluster ions with the composition $Zr_nO_{2n-1}^+$ are observed. In the scenario that the observed distribution is due to fragmentation of larger clusters, this fragmentation thus has to occur via sequential evaporation of ZrO_2 units. The loss of a single ZrO_2 unit costs about 8 eV and it therefore seems unlikely that much more than one unit could be lost, even at the high fluences. It therefore seems more reasonable that the distribution shifts to lower masses because the smaller clusters need more light to be efficiently excited and ionized. This is then due to smaller absorption cross-sections, larger anharmonicities and possibly higher IPs. The observed fluence dependence of the signal (Fig. 3) supports this hypothesis. Another possibility is that the high fluences induce first the loss of an oxygen atom from Zr_2O_{2n} (process (1)) and then electron emission from that cluster (process (4)). If this sequence should occur, the emission of an O$^-$ ion from Zr_2O_{2n} should be occurring as well, since it is lower by 1.46 eV (the electron affinity of an oxygen atom) compared to the combined processes (1) and (4). In the experiment, we tried to detect O$^-$ but did not observe any.

A further observation is that at high fluence, a large amount of ZrO$^+$ is observed. This ion could again either be due to a direct excitation of ZrO or due to the fragmentation of larger clusters. A direct IR excitation of a diatomic molecule via vibrational modes to the ionization limit has so far not been observed. Usually, after absorbing a few quanta, the anharmonicities become so large that the molecule is no longer in resonance with the

radiation. For ZrO, however, the density of electronic states becomes very quickly large and it might be conceivable that IR excitation could be efficient, due to coupling of the vibrational and electronic degrees of freedom. In Fig. 1, the observed spectral structure of ZrO is shown. For gas-phase ZrO, experimental vibrational frequencies range from 937 cm^{-1} in its electronic ground state to about 844 cm^{-1} in electronically excited states [12]. The spectrum shown here is therefore clearly not compatible with a direct excitation of ZrO. As discussed above, it is also not likely that ZrO$^+$ is formed via successive evaporation of ZrO$_2$ units from larger $Zr_nO_{2n-1}^+$ clusters. The only other possibility for the formation of ZrO$^+$ is the fragmentation of $Zr_nO_{2n-1}^+$ to yield ZrO$^+$ and $Zr_{n-1}O_{2(n-1)}$. The charge stays on the presumably lower IP ZrO rather than on $Zr_{n-1}O_{2(n-1)}$ and the above process appears to be at least competitive with the evaporation of ZrO$_2$ from charged clusters. The observed intensity of ZrO$^+$ can be very large in such a process, since clusters from various sizes can contribute.

The most important question that arises concerns the geometrical structures of the observed clusters. Depending on the temperature, bulk ZrO$_2$ crystallizes in one of three different phases. Up to 1180°C, the stable structure is monoclinic, between 1180°C and 2370°C, a tetragonal phase is formed, and at higher temperatures (up to the melting point of 2600°C), a cubic structure is preferred. The coordination of the Zr atom in the monoclinic phase is seven, whereas it is eight in the tetragonal and cubic phase. Small ZrO$_2$ particles are known to have a lower transition temperature for the monoclinic to tetragonal phase transition and particles with a radius less than 150 Å are measured to be tetragonal, even at low temperatures, [7,8]. The IR spectra of ZrO$_2$ in its three crystalline phases are distinctively different. As the symmetry of the unit cell is reduced from cubic to tetragonal to monoclinic, more modes become IR allowed. Cubic ZrO$_2$ has only one IR active mode at 480 cm^{-1} [17], tetragonal ZrO$_2$ has three IR active modes (575, 435 and 365 cm^{-1}) [18] and monoclinic ZrO$_2$ has 15 IR active modes. The highest frequency mode of these is at 740 cm^{-1} and is characteristic for the monoclinic phase. The other monoclinic modes are situated below 620 cm^{-1} [18]. For the ZrO$_2$ molecule in a rare gas matrix, the IR active modes are determined to be at 818 and 884 cm^{-1} [19].

The IR active modes observed here at 620 and 680 cm^{-1} therefore give us no direct information about the symmetry and structure of our clusters. The clusters in the present experiment contain less than 30 Zr atoms. Most of these atoms will be located on or very near the surface of the cluster. Thus, it might be no surprise that no coincidence with the bulk IR modes of ZrO$_2$ is observed. It has long been known that finite size effects can dominate the IR spectra of small species [20]. While the spectra presented here are very different from bulk spectra, they compare well to the calculations presented here for small clusters. In this, IR active modes are calculated between 600 and 800 cm^{-1} that are characteristic for motion in $(ZrO)_2$ four membered rings. In addition, the calculations indicate that, at least for clusters with up to four Zr atoms, the preferred structures have connectivities similar to those found in the bulk. It thus seems reasonable that the clusters investigated here also resemble bulk structures and incorporate four membered ZrO$_2$ rings.

6. Summary

Clusters with a stoichiometry of Zr_nO_{2n-1} can be efficiently excited with IR radiation to internal energies high enough to allow the thermionic emission of an electron. This observation is rationalized with the high binding energy of zirconium oxide clusters combined with the low ionization potential of clusters that lack one oxygen atom. When taking mass spectra, peaks with $n = 10$, 13 and 15 are observed to be stronger than their neighboring peaks. The wavelength spectra of all clusters studied are very similar, consisting of one or more features between 600 and 700 cm^{-1}. Bulk zirconium oxide does not have IR active modes in this wavelength range. Ab initio calculations are performed for Zr_nO_{2n} clusters with $1 \leqslant n \leqslant 4$. Different structural isomers are found for clusters with more than one zirconium atom. Calculated IR spectra show characteristic IR active modes

between 900 and 1000 cm^{-1} that correspond to Zr–O stretching of isolated oxygen atoms. The most stable isomers contain Zr–O–Zr–O four membered rings that are typical for the bulk structure. For small clusters, motion in these rings gives rise to characteristic IR active modes between 600 and 700 cm^{-1} and it thus seems very likely that the cluster structures in our experiment are dominated by these four membered rings.

Acknowledgements

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