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Formation of molecular cluster anions by laser ablation of a metal target near a supersonic jet

Wenyun Lu, Rongbin Huang [1], Shihe Yang *

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Abstract

By laser ablation of a metal target (Zn, Mg or Gd) near the stream of a supersonic expansion, molecular oxygen cluster anions $(O_2)_n^-$ were efficiently produced with n in the range of 1–20 or more. The cluster anions were analysed by a time-of-flight mass spectrometer. Molecular cluster anion formation is attributed to low-energy electron attachment and high-Rydberg-state electron transfer. In the case of Gd, the addition products $Gd(O_2)_n^-$ and $Gd_2(O_2)_n^-$ were also observed. These products are thought to originate from ion–molecule association reactions.

Keywords: Molecular cluster anions; Laser-ablation; Supersonic jet

1. Introduction

Clusters, which are micro-aggregates of atoms and molecules, possess unique properties, allowing cluster science to be distinguished from molecular physics and condensed matter physics. Intense research efforts have been directed towards the understanding of clusters [1]. A mass spectrometer in combination with a molecular beam is a viable means to study the physical and chemical properties of clusters as a function of the cluster size under collision-free conditions [2]. One of the most important requirements in these studies is the production of a sufficient amount of ions. The most commonly used method for the production of molecular cluster anions in investigations of the size-specific properties of clusters is the injection of electrons from an electron gun to a supersonic expansion [3]. Other techniques include high-Rydberg-atom electron transfer in discharge sources [4].

This paper reports a new method for the efficient production of molecular cluster anions by laser ablation of a metal target near a supersonic jet. Molecular oxygen clusters were chosen as an example for demonstrating the method. In addition to the high efficiency of production of molecular cluster anions, this method has the advantage of convenience and cleanliness since the photon source is outside the vacuum chamber. Furthermore, the laser ablation is localized both in time (approximately 10 ns) and in space (approximately 0.5 mm), and therefore excessive heating of the source is avoided.

2. Experimental details

The details of the experimental set-up can be found in Ref. [5]. Briefly, the molecular beam/time-of-flight mass spectrometer consisted of a source chamber and a flight tube, which were differentially pumped by 10 in and 6 in diffusion pumps respectively. The operating pressures of the source chamber and flight tube were 10^{-5} Torr and 10^{-7} Torr respectively. Metal samples were pressed and mounted on a sample load-lock. An excimer laser (308 nm; XeCl) beam (28 ns duration) was weakly focused on the sample (laser power, 10^7–10^8 W cm^{-2}; beam spot size on the target, 0.5 mm × 1.5 mm). The laser-vaporized species (electrons, highly excited metal atoms, oxides, etc.) crossed a supersonic molecular oxygen cluster beam 8 mm downstream. The oxygen cluster beam was generated by seeding O_2 in He (1%–40%) with a backing pressure of 10 atm. The seeded O_2 supersonically expanded together with the He carrier gas and formed oxygen clusters on exiting a 0.5 mm diameter hole of a pulsed nozzle. The He/O_2 mass flow rate was 3 standard cubic centimetres per minute (sccm) and the gas pulse width was approximately 80 μs. The crossing region of the oxygen cluster beam and the stream of laser-ablated species was 8

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* Corresponding author.

[1] Present address: Department of Chemistry, Xiamen University, China.

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mm from the pulsed nozzle exit. Laser-ablated species reacted with the oxygen clusters, and the products were carried by the pulsed He flow to the extraction region of a reflectron time-of-flight mass spectrometer (RTOFMS).

The mass spectrometer was operated in two modes: a positive ion mode and a negative ion mode. The only difference was the polarity of the applied high voltages. The ions were extracted by a high-voltage pulse, reflected and finally detected by a dual microchannel plate (MCP) detector. The signal from the MCP detector was pre-amplified and digitized by a transient digitizer.

3. Results and discussion

Fig. 1 shows the time-of-flight mass spectrum of cluster anions when the metal target was Mg. The molecular cluster series $(O_2)_n^-$ was clearly identified with n ranging from 1 to higher than 20 with remarkable signal intensity. For all the metal targets studied so far, $(O_2)_2^-$ possessed the highest intensity. The intensity of $(O_2)_n^-$ decreased monotonically for $n > 2$. The anion intensity depended on both the clustering condition and the laser pulse energy. The molecular oxygen cluster anion signals initially increased rapidly with the laser fluence, but the increase slowed down when the laser fluence reached 10^8 W cm^{-2}. Also indicated in Fig. 1 is another series $H_2O(O_2)_n^-$ which presumably results from the reaction of $(O_2)_n^-$ with trace amounts of H_2O present in the nozzle source. Molecular oxygen cluster anions with a similar intensity distribution were also produced using Zn and other metals as ablation target.

The following two mechanisms can be considered to explain the origin of oxygen cluster anions: (1) near-zero-energy free electron attachment to oxygen clusters ($(O_2)_n + e \rightarrow (O_2)_n^-$); (2) electron transfer from hot metal atoms to the oxygen clusters ($M^* + (O_2)_n \rightarrow M^+ + (O_2)_n^-$). Efficient electron attachment to oxygen clusters by the first mechanism requires sufficient near-zero-energy free electrons. Although near-zero-energy electron attachment to O_2 does have a fairly large cross-section (approximately 10^{-16} cm^2), it would be difficult for the first mechanism alone to account for the rather efficient oxygen cluster anion generation given the fact that we were using a laser with a photon energy of only 4 eV. The work functions of all the materials near the laser beam path are above 4 eV. Direct ionization of metal atoms requires at least two photons, and it is expected that only a small number of electrons can be ejected directly through coherent multiple-photon ionization.

A more efficient way to produce oxygen cluster anions involves the second mechanism. If the metal atoms are in high Rydberg states, as expected under high-intensity laser radiation, the collisional electron transfer cross-section will

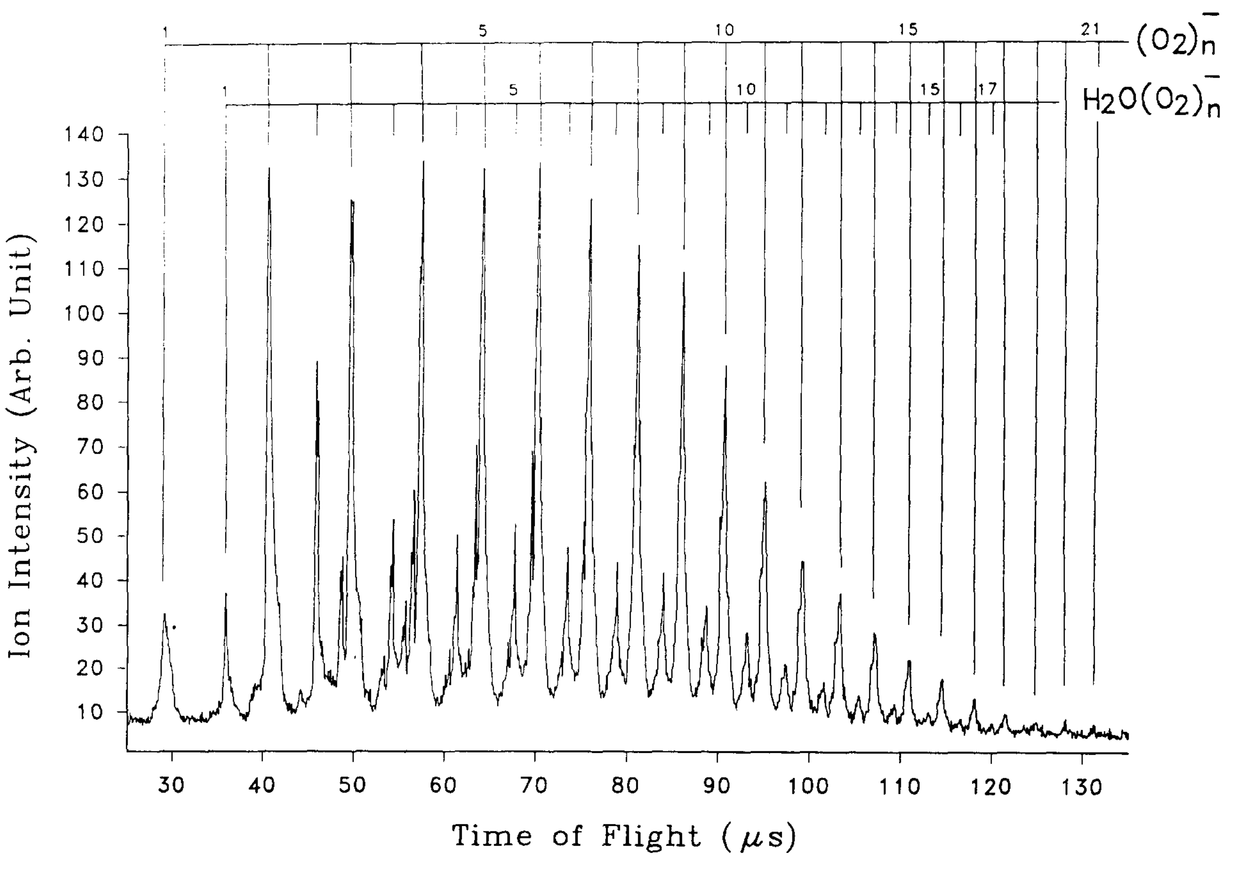

Fig. 1. Time-of-flight mass spectrum of molecular oxygen cluster anions produced with an Mg metal target at an O_2 to He ratio of 3% (laser pulse energy, 2 mJ; back pressure, 140 lbf in^{-2}).

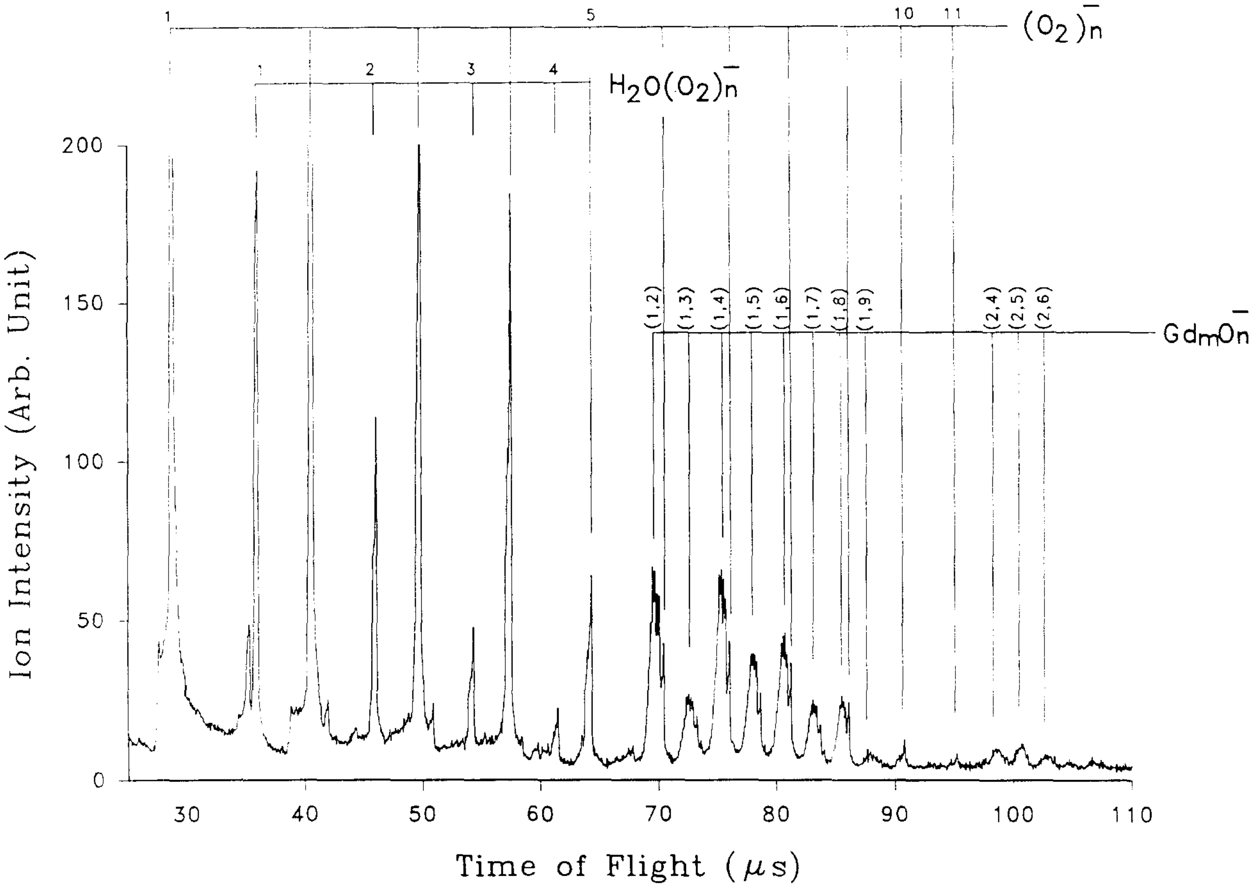

Fig. 2. Time-of-flight mass spectrum of molecular oxygen cluster anions produced with a Gd metal target at an O_2 to He ratio of 16.7% (laser pulse energy, 2 mJ; back pressure, 140 lbf in^{-2}; flow rate, 3 sccm; nozzle pulse width, 80 μs).

be quite large, a phenomenon which can naturally account for the efficient production of oxygen cluster anions. Rydberg atom electron transfer leading to anion formation has been reported by many researchers [4,6]. It is a soft ionization method ideal for studying van der Waals' clusters, since the neutral cluster distribution will be preserved in general, although electron attachment cross-section variation may locally distort the distribution. Therefore the efficient formation of oxygen cluster anions appears to involve laser-excited high Rydberg states of the metal atoms. The Rydberg state acts as a storehouse of electron kinetic energy, and the attack of the molecular oxygen cluster may accelerate electron ejection to the negative ion state of the molecular oxygen clusters.

Molecular oxygen cluster anion formation by low-energy electron attachment [7] and Rydberg atom electron transfer [6] has been reported. In free electron attachment studies, $(O_2)_n^-$ ions are formed with significant cross-sections with electrons of essentially zero energy. The width of the corresponding zero energy peak in the attachment cross-section decreases with increasing n. The $(O_2)_n^-$ signal intensity distribution shown in Fig. 1 is closely analogous to that observed in Rydberg atom Ar** (nd) electron transfer in so far as $(O_2)_2^-$ is the most intense anion peak [6]. This is mainly due to the intrinsic stability of $(O_2)_2^-$, which is believed to be the core of $(O_2)_n^-$ [8]. The stabilization of $(O_2)_2^-$ is attributed to resonant electron transfer between the two oxygen molecules which delocalizes the excess electron with substantial rearrangement of the nuclear framework.

Fig. 2 shows the time-of-flight mass spectrum of the cluster anions produced when the ablation target was Gd. Again, molecular oxygen cluster anions were formed as observed with an Mg target. This shows that the formation of cluster anions is a general phenomenon in the presence of a laser ablation source, and the metal target simply provides a Rydberg metal atom/electron source. However, in this case, metal–oxygen cluster anions were observed in addition to the molecular oxygen cluster anions. The relatively large peak width of these complexes is due to the presence of a number of Gd isotopes. These anions probably originate from ion–molecule association reactions between $(O_2)_n^-$ and Gd and Gd_2. It should be noted that clusters with an odd number of oxygen atoms can also be seen, but with a slightly lower intensity than their counterparts with an even number of oxygen atoms. The fact that, of the metal targets studied, only the Gd target gave these adducts suggests that d and f electrons/orbitals are involved in binding the oxygen clusters. The diffuse negative charge probably overlaps to a certain extent with the spatial extension of the d and f orbitals of the Gd atoms in the complexes.

4. Conclusions

We have generated an intense oxygen cluster anion beam by electron transfer from laser-ablated species from a metal target. Normally, an electron gun or discharge source is used to produce electrons or high-Rydberg-state atoms which ionize molecular clusters to their negative charge state. Laser generation of these species provides a simple and convenient alternative to produce negative molecular cluster ion beams. We hope to extend this experiment to other molecular van der Waals' clusters.

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