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Study of $CO_2^+(CO_2)_n$ Cluster in a Paul Ion Trap

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Abstract : In this article, the properties of $CO_2^+(CO_2)_n$ clusters in a Paul ion trap have been investigated using mass-selective instability mode which conducted by chosen precursor ions, mainly Ar^+ and CO_2^+ produced by a mixture of Ar and CO_2. Exposure of CO_2^+ ions to CO_2 molecules, lead to the formation of $CO_2^+(CO_2)_n$ clusters. Here, Ar gas react as a buffer gas and lead to form $CO_2^+(CO_2)_n$ cluster by collisional effect.

Keywords : Paul ion trap, ion clusters, time of flight, buffer gas, collisional effect

Introduction

Properties of clusters are valuable in many fields of physics, chemistry (e.g. catalysis) and nanotechnology. Their properties depend on the charge, size, and species (atomic, polyatomic and molecular). Rate of cluster's formation is high, and their timescale is limited to a few microseconds. However, some processes such as cooling and chemical reactions cause to reduce of formation's rate so cluster formation may occur in a longer timescale (millisecond to second).[1-3]

Cluster ions are defined as a combination of a core ion bound in which a van der Waals force governs to one or more neutral atoms and molecules.[4] Carbon dioxide is a major gas phase pollutant "greenhouse effect" on the atmosphere; therefore, investigating of monomeric and clustered CO_2 structure study is of particular importance.[5] In addition, the effect of Ar and Ne gases cause the formation of $CO_2^+(CO_2)_n$ clusters and have been studied in reference.[6]

Based on a previous study,[7] formation of $CO_2^+(CO_2)_n$ clusters have a particularly large rate constant. Clusters have very different properties from the isolated atoms/molecules or bulk materials and can constitute a new type of material. In order to produce clusters, one can either aggregate smaller systems (atoms, molecules, small clusters) or break larger systems.[7-9] According to reference 10, the small ion clusters that have a fewer number of atoms (n), could be formed during the first 200 ns and take longer time to disappear them.

Small water cluster ions $H^+(H_2O)_{3\text{-}4}$ using a three-dimensional quadrupole ion trap (Paul ion trap), has been demonstrated by Lovejoy and Bianco. They were shown this cluster formed in around of 300-500 K.[11] They use an ion trap because the ion trap offers the possibility of storing ions in a limited time and a well-defined space range.[12] However, other devices, for instance, Penning traps,[13,14] quadrupole or multipole linear traps,[15] ion storage rings (electrostatic or magnetic[16] and electrostatic ion beam traps) are also employed.[17,18] Formation of cluster molecular ions in a Paul ion trap is practical when the confined ions interact in the applied rf fields. The space charges and binary collisions yield to restrict the number of confinement of cluster ions in an ion trap.

In this article, we examine the capability of our Paul ion trap to produce $CO_2^+(CO_2)_n$ cluster ions. Some parameters such as volume percentage of CO_2 mixed with Ar gases and radiofrequency voltages have been analyzed. Here, the noble gas Ar plays as a buffer gas that it causes cooling with inelastic collisions.[19,20]

Experimental

Paul ion trap analyzer

The homemade Paul ion trap electrodes are made of stainless steel 316 with z_0 = 0.707 cm, that it is one-half the shortest separation of the endcap electrodes and r_0 = 1 cm, is

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the ring electrode radius. The ring electrode has three meshes that involve nine holes with the 0.1 mm diameter and they are around a circle. These meshes are used to entrance of gas to the trap. They are placed 120 degrees apart from each other.[2]

A cylinder with a volume of 4.64×10^{-3} m^3 was used for the source gas with capacity of 5 bar. Once the cylinder is filled with a mixture of Ar and CO_2 gases, the cylinder output is fed to the small stainless steel tubes, 0.5 mm in diameter. There are three tubes to import the mixed gases to the ionization volume inside the trap. This technique effectively provides a better ionization efficiency and consumes less gases.

There are six small holes, which are 0.1 mm diameter in the center of the lower end-cap electrode, to let the electrons cross into the trap ionization volume. Also, the upper end-cap electrode has the same holes for the passage of ions to the detector. The ion trap has hyperbolic geometry that it was estimated to have higher confinement efficiency. The motion of the ion in a Paul ion trap is described by tahe Mathieu equations and in r and z directions are given as:

$$\frac{d^2r}{d\xi^2} + (a_r - 2q_r\cos 2\xi)r = 0 \quad (1)$$

$$\frac{d^2z}{d\xi^2} + (a_z - 2q_z\cos 2\xi)z = 0 \quad (2)$$

$$a_z = -2a_r = \frac{4qU}{MZ_0^2\Omega^2} \quad (3)$$

$$q_z = -2q_r = \frac{-2qV}{MZ_0^2\Omega^2} \quad (4)$$

$$\xi = \frac{\Omega t}{2} \quad (5)$$

where U is the direct voltage, V is the alternating radiofrequency voltage, q is the electric charge, M is the mass of ion, Z_0 is the one-half the shortest separation of the endcap electrodes and Ω ($\Omega = 2\pi f$) is the angular frequency.[21] Ions are produced in the trap by an impact of electron ionization technique. In general, the process of ion trap operation consists of pulse ionization, rf voltage scanning and data collection to produce peaks.[22,23]

Experimental setup and measurements

The experimental set up is depicted in Figure 1. The Paul ion trap in placed in a vacuum chamber with a volume of 0.0147 m^3 and pumped through a turbo-pack up to a pressure of 10^{-5} mbar. The rf voltage is connected between the ring and end-cap electrodes and operated in the mass-selective instability mode; only radio frequency voltage is applied to the ring electrode. The electrons can be provided through an electron gun, which is situated below the lower end-cap electrode. The Tungsten filament can use 0.46 A, with 9 V and a constant current circuit generates a constant flow of electrons. Also, electron acceleration is made through -110 V. We have applied the ejection voltage, up to -300 V, between Faraday-cup detector and the grid earth. The rf voltage produces more than -600 $V_{0\rightarrow p}$ (zero to pick) voltage with the frequency up to 1.1 MHz. The entire experiments can be adjusted through 10 canal circuit with LVTTL and controled through Labview program.

The output signals obtained from detector were visualized and memorized in oscilloscope. They can provide 200 data on the excel software and can be used as a data for Origin-pro software. Table 1 shows various ionization energies of some gases which employed in the present work.

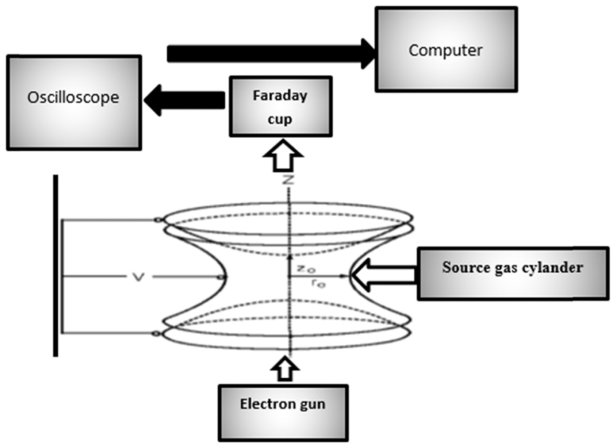

Figure 1. Schematic of experimental set up.

Table 1. Ionization energies (in eV) of different gases[20]

	Ar	H_2O	O_2	CO_2
Ionization energies (eV)	15.76	12.62	12.1	13.8

The characteristics of our working gases, Ar and CO_2, also, are shown in Table 2. Carbon dioxide CO_2 was with high purity (≥ 99.999%), and the oxygen and moisture content was low in a chamber (≈ < 2 ppm).

Table 2. Physical properties of CO_2 and Ar capsule

Gas	CO_2	O_2+Ar	N_2	THC	H_2	H_2O
CO_2	≥99.999%	≤ 1 ppm	≤ 3 ppm	≤ 4 ppm	≤ 0.5 ppm	≤ 1 ppm
Gas	Ar	H_2O	N_2	CO_2 + CO	O_2	
Ar	99.999%	≤ 2 ppm	≤ 5 ppm	≤ 0.5 ppm	≤ 2 ppm	

Results and discussion

Here, Ar was employed as a buffer gas and ultimately, Ar^+ ions can transfer their charge to CO_2 molecules in less than 1 ns. So, it is the best option for this work:

$$Ar^+ + CO_2 \rightarrow Ar + CO_2^+ \quad k = 4.80 \pm 0.72\ 10^{-10}\ cm^3/s \quad (6)$$ [3]

Effect of various parameters

- Gases ratio $\left(\frac{Ar}{CO_2}\right)$

Figure 2, shows a typical Ar signal. It was obtained directly from the oscilloscope. The ejection voltage can be applied either when the rf voltage is completely stopped or during its working regime. Regarding to a fixed rf frequency, several parameters can have influence on the output signal such as gas pressure, ionization time, rf

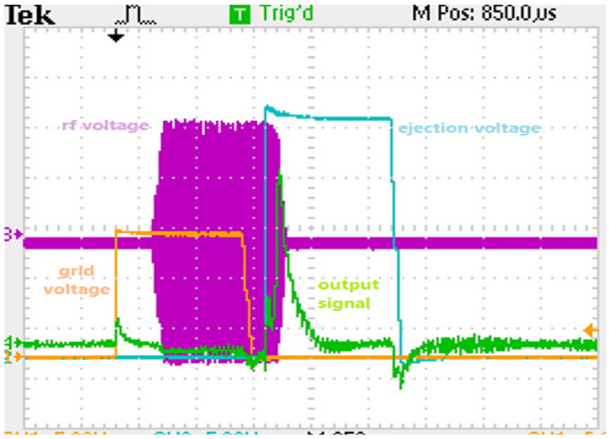

Figure 2. A typical Ar ions output signal (Purple: Radio frequency, Blue: Extraction voltage, Orange: Grid voltage, Green: Ion signal)

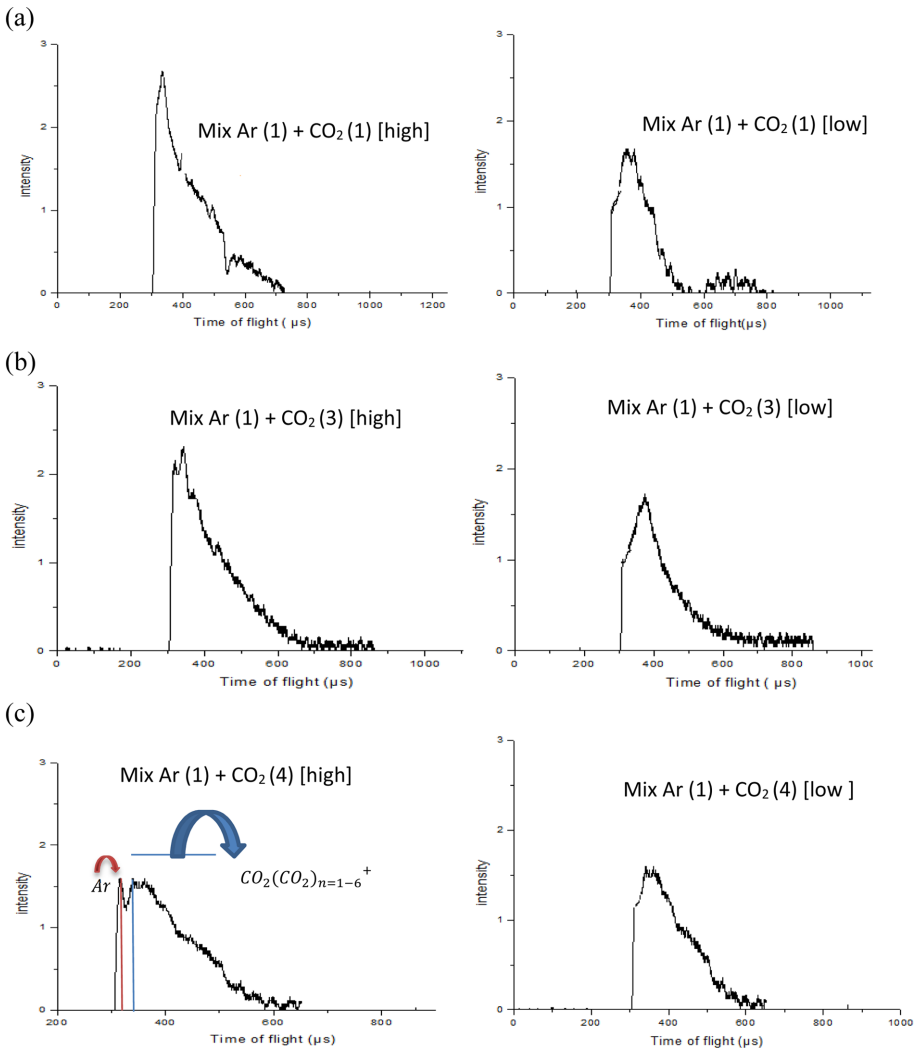

Figure 3. Signals from gas mixture of Ar and CO_2 for low and high rf voltages. (a) Mix Ar (1) + CO_2 (1) in high (left) and low (right) voltage, (b) Mix Ar (1) + CO_2 (3) in high (left) and low (right) voltage, (c) Mix Ar (1) + CO_2 (4) in high (left) and low (right) voltage

voltage, and the ejection position and voltages. Nevertheless, some of best condition have been chosen for the experiment.

Numerous experimental papers have been published visualizing the formation of $CO_2^+(CO_2)_n$ ion clusters with the following gas ratios; Ar:CO_2 = 1:4, 1:3, and 1:1. But for this work, we have used low and high rf voltages for the experiments. Figure 3 shows peaks with low rf voltage, no ion clusters are present. However, at the higher rf voltage, the ion cluster signals are present and, no ion clusters appeared after 600-700 μs of the ejection voltage.

According to Figure 3, and the time of flight formula, $m_2 = m_2 \times (t_2/t_1)^2$, the first peak is identified as Ar^+, then, the other peaks are related to $CO_2^+(CO_2)_n$ with n = 1 - 6. As seen, for the equal gas mixture proportions, the cluster peak is not clear (see Figure 3(a)), this is also true for the conditions of Ar + 1 bar CO_2. Formation of small flat top appeared at the higher rf voltages and depicted in Figure 3(a)-(c). Accordingly, they are decreasing as the rf voltage is stopped. During the ejection time, the heavier of cluster ions are expected. Indeed, this is due to the beam character of the ion's cloud during the run down toward the detector through travelling distance of ~ 4 cm to the detector through the upper end cup holes.

One of the important reaction of CO_2^+ with the gas molecules is a three body reaction, leading to the formation of a $CO_2^+(CO_2)_n$, n = 2,[24]

$$CO_2^+ + CO_2 + M \rightarrow CO_2^+(CO_2) + M \; k = 2.1 \times 10^{-28} \text{ cm}^6/\text{s}$$

The influence of damping force on the ion motion has been studied with q_z values (q_z = 0.45) near the adiabatic

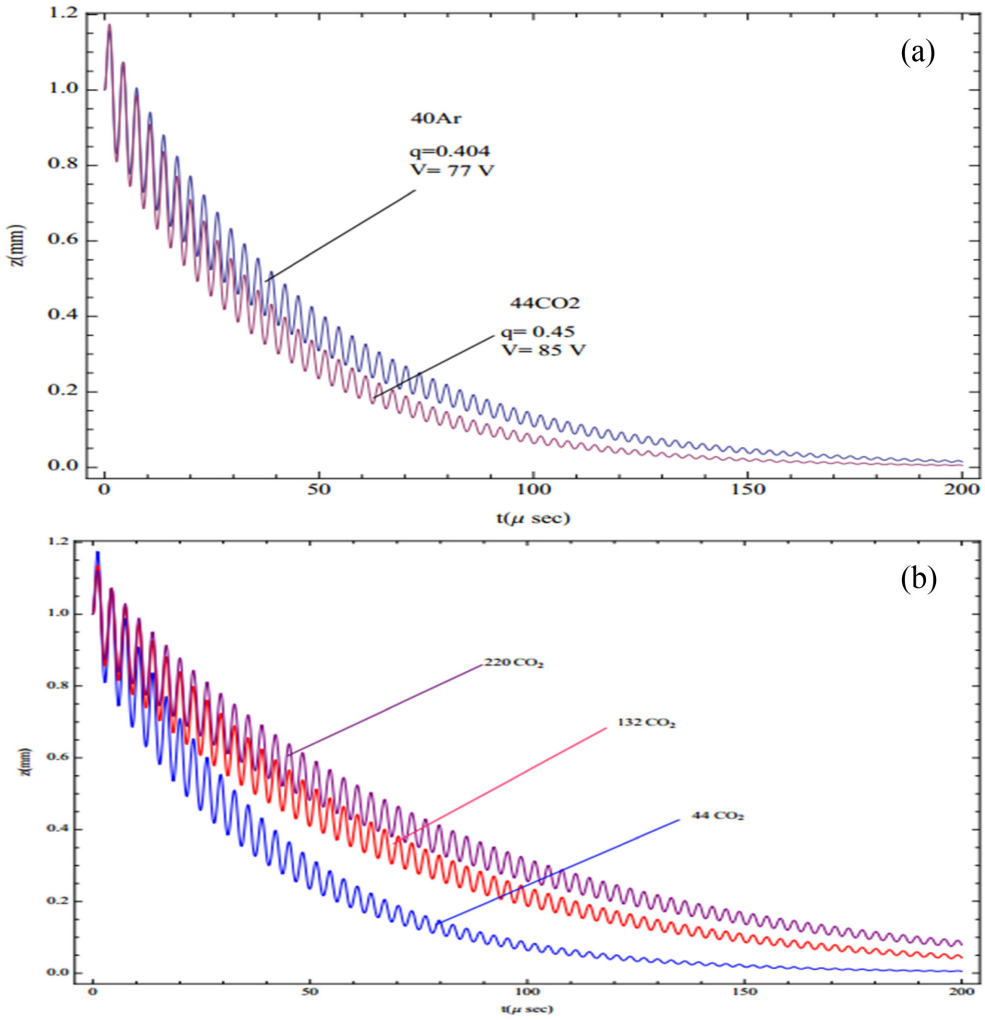

Figure 4. The confined of $^{40}Ar^+$ and $^{44}CO_2$ ions damping displacement as a function of damping time; the initial displacement: q_z = 0.45; $z(\xi_0)$ = 1 mm; C = 1; and a_z = 0.4. The confined off CO_2^+, $CO_2^+(CO_2)_2$, $CO_2^+(CO_2)_4$, ion clusters damping displacement as a function of damping time; the initial displacement $z(\xi_0)$ = 1 mm; C = 1; and a_z = 0.4.

region. Figure 4(a) shows the obtained numerical computations for the initial ion displacement with a damping time of 200 μs for Ar^+ of mass m = 40 amu and $(CO_2)^+$ of mass m = 44 amu. Furthermore, Figure 4(b) also shows a very strong shift in the damping time when n values rising and gradually moves towards the stability limits ($CO_2^+(CO_2)_n$, n = 0, 2, 4). This can be attributed to the energetic ion and instability of large clusters.

Conclusion

In this work, the condition of $CO_2^+(CO_2)_n$ cluster ion formation in a Paul ion trap has been studied. First, we have ionized Ar buffer gas which transfer Ar^+ charge to CO_2 molecules. The process of joining CO_2^+ ions to another CO_2 molecules usually take place in few. Although $CO_2^+(CO_2)_n$ have a large rate constant, nevertheless, the values of n in $CO_2^+(CO_2)_n$ cluster ions depended on the pressure of both the buffer gas and the main gas.

As the collisional cooling of CO_2^+ take place, the mixture of Ar-CO_2 peaks are observed and finally, cluster formation occurs. Based on damping time of clusters, the formation of clusters up to n = 11 by increasing the number of carbon dioxide molecules is complicated, the isomers structure would be manifold and complex. In some experiments, when the rf voltage is stopped, we have observed heaver cluster ions. This can be attributed to the cloud beam formation.

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