

Insight into Properties of $\text{CO}_2^+ (\text{CO}_2)_n$ Clusters in a Paul Ion Trap

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ABSTRACT: *In the present research, the properties of $\text{CO}_2^+ (\text{CO}_2)_n$ clusters in a Paul ion trap have been investigated and confirmed through computational methods. Under different experimental conditions, we have confined obtained clusters for a specific time to identify their kinetic and spectroscopic properties. Also, the thermochemical results in various temperatures have been extracted for all $\text{CO}_2^+ (\text{CO}_2)_n$ clusters in the present paper. The comparison of theory and experiment results confirms good agreement among them. Also, the structure of $\text{CO}_2^+ (\text{CO}_2)_n$ cluster and temperature conditions to formation of the cluster have been studied in the Paul trap and Calculate of the equilibrium constant of these clusters, in different temperatures was done. Based on the results, the formation of the cluster with $n=2-3$ is very easier than large cluster and they have symmetric structure.*

KEYWORDS: *Paul ion trap; Cluster of ions; Time of flight; Equilibrium constant.*

INTRODUCTION

To the best of our knowledge, cluster ions formed by the combination of more ions or atoms or molecules of a chemical species often in association with a second species. In these materials, a van der Waals force causes interactions among neutral atoms and molecules. The properties of these clusters depend on the charge and size species. Also, obtained properties can be categorized in two levels of physical and chemical which are used in many fields such as catalysis and nanotechnology [1, 2]. Also, Castleman et al. describe clusters as “superatoms” with three dimension structure providing an unprecedented ability to design novel nanostructured materials [3]

Note that the formation of these clusters is fast

and their time scale is limited to a few milliseconds. It is interesting to say that the processes such as cooling, delayed fragmentation or chemical reactions may occur in a longer time scale (millisecond to second).[4-6]

Therefore, by using these methods, the geometric structures of monomeric and clusters for CO_2 molecules have been studied [7]. Also, the effect of Ar and Ne buffer gases on the formation of $\text{CO}_2^+ (\text{CO}_2)_n$ clusters along with their mobility have been studied in the literatures [8, 9].

There are two different ways for formation of clusters, aggregation of small systems such as atoms, molecules and small clusters or breaking of larger systems [10,11].

In addition, Mass-selected ions devices such as ion traps,

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have proved to be a significant new source of information on gas-phase ion structures and conformations [12].

The investigation of carbon monoxide and carbon dioxide clusters has attracted many scientists. In this regard, clusters has been studied in “time-of-flight” mass spectrometer based on reflection, as a thesis in 2010. This thesis offers the possibility separation of big cluster ions with sizes bigger than 190 ($n > 190$) (In Section 4.2.4 (Mass Separation)of Thesis and page 85). Cluster ions of $(CO_2)_n^+$ have been recorded with sizes bigger than 190 based on theoretical computation.[13] The previous reports show that clusters ions with low number of aggregated molecules could be formed within 200 ns and longer time can cause to their disoperation. For example, small water-hydronium clusters ($H^+(H_2O)_{3,4}$) in the quadrupole ion trap (Paul ion trap) have been demonstrated by *Lovejoy and Bianco* in nanosecond time [14].

Generally, the ion trap offers the possibility of storing ions in a limited time and space [15]. It is necessary to say that other devices such as Penning traps [16,17], quadrupole or multipole linear traps [18], ion storage rings, electrostatic or magnetic[19] and electrostatic ion beam traps also have been employed[20-21].

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CO_2 is chosen as target molecule because among molecular clusters, CO_2 may has second rank in terms of interest and significance in the atmospheric for the earth and other planets. Therefore, we will use Paul ion trap to produce $CO_2^+(CO_2)_n$ cluster ions by using a volume percentage of CO_2 mixed with Ar gas. It is necessary to say that the Ar gas plays the role of the buffer gas cooling with inelastic collisions[22,23]. According to the reported results in Ref [3] , a $(CO_2)_n$ cluster can be incorporated in the categorization of Van der Waals clusters with average binding energy [7] ≤ 3 .

Finally, the probability of clusters formation in various temperatures has been investigated through computational methods and also structure of clusters has been gained that open up new possibility for test of these cluster in Ion Trap Paul.

EXPERIMENTAL SECTION

In this section, the possible structures that are created inside the trap are examined. Carbon dioxide is selected as the target molecule because it is an important environmental molecule.

Experimental setup and measurements

In the present paper, we used a Paul ion trap. The properties of this instrument is illustrated in Ref [4], We produced ions in the trap through an impact of electron ionization technique. In general, the process of ion trap operation consists of pulse ionization, RF voltage scanning and data collection [24-26].

Note that we have set up the Paul ion trap in a vacuum chamber with a volume of 0.0147 m^3 and pumped it through a turbo-pack up to a pressure of 10^{-5} mbar. In the mass-selective instability mode, the RF voltage is connected between the ring and the end-cap electrodes. Radio Frequency (RF) voltage is only applied to the ring electrode. Subsequently, the flow of 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 from electrons. Also, electron acceleration is made through a -110 V current. We applied an ejection voltage of up to -300 V between Faraday-cup detector and the grid earth. The RF voltage produces more than $600\text{ V}_{0\rightarrow p}$ (zero to pick) voltage with a frequency of up to 1.1 MHz. The entire experiment can be adjusted through 10 canal circuits with LVTTTL and controlled through Labview program.

The output signals obtained from the detector were visualized and memorized in an oscilloscope. They can provide 2500 data on Microsoft Excel and can be used as a data source to Origin-pro software. Some of the gases employed in the present paper have various ionization energies (Ar;15.7 , H_2O : 12.6 , O_2 : 12.1 , CO_2 : 13.8 eV). Based on these ionization energies, the required ionization energy was adjusted in the trap. Carbon dioxide CO_2 was with high purity ($\geq 99/999\%$), and the oxygen and moisture content was low in the vacuum chamber ($\approx < 2$ ppm).

RESULTS AND DISCUSSION

Background gas is one of the important factors in formation of clusters. Buffer gas with collisional relaxation effect causes creation of a cluster in the trap. In this regard, the ratio of gas buffer to the main gas was examined as the main factors.

$\left(\frac{Ar}{CO_2}\right)$ Ratio:

Regarding a fixed RF frequency, several parameters can influence the output signal. Gas pressure, ionization

time, RF voltage, and the ejection position and voltages are some of these parameters. After numerous experiments and based on previous papers, the $\frac{\text{Ar}}{\text{CO}_2}$ gas ratio have been selected for testing this factor in the formation of CO₂⁺(CO₂)_n ion clusters. The $\frac{\text{Ar}}{\text{CO}_2}$ gas ratios $\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{1}$ have been studied. Also, note that Voltage values (in high and low volumes) were tested and a high voltage was selected. Experimental results show that at the low RF voltages, no ion clusters are present. In contrast, the ion cluster signals appear at high RF voltages. Furthermore, no significant peaks were observed after 600 μs (approximately). Thus, it can be concluded that no ion clusters exist in the long time. (720 μs >) (Fig. 1).

As shown in Fig. 1, for the equal proportions of gas mixtures, the cluster peak is not clear (see Fig. 1a). This statement is also true for the conditions of Ar (1)+ CO₂ (1). Fig. 1a-c shows that small flat tops are formed at the higher RF voltages. It's shown that they start to fall as the RF voltage is stopped.

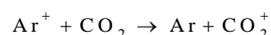
By increasing the ratio of carbon dioxide to argon, other peaks are observed in addition to the previous peaks. Although These peaks are dependent on the conditions of the vacuum in the trap and recording time.

Due to the formation of cluster, the intensity of peaks (Ar and CO₂) are reduced. The cluster formation can be explained by the equation below : [3]



$$k = 2.1 \times 10^{-28} \frac{\text{cm}^6}{\text{S}}$$

M stands for argon in this study. We have used Ar as a buffer gas to produce Ar⁺ ions. Subsequently, Ar⁺ ions will transfer their charge to CO₂ molecules in less than 1 ns according to the following equation[27]:



$$k = 4.80 \pm 0.7210 - 10 \text{cm}^3 / \text{s}$$

Fig. 2 shows mass spectrum from 40 to 308 u for a mixture of Ar, and CO₂. This spectrum was acquired via multichannel scaling. The resolution in these spectra as a function of mass is discussed below in terms of mechanical ($\Delta r^\circ = 3 \times 10^{-3}$) and $\frac{\Delta \Omega}{\Omega} = 10^{-7}$ instabilities.

After seeing these results, theoretical studies have been done to prove the likelihood of clusters present

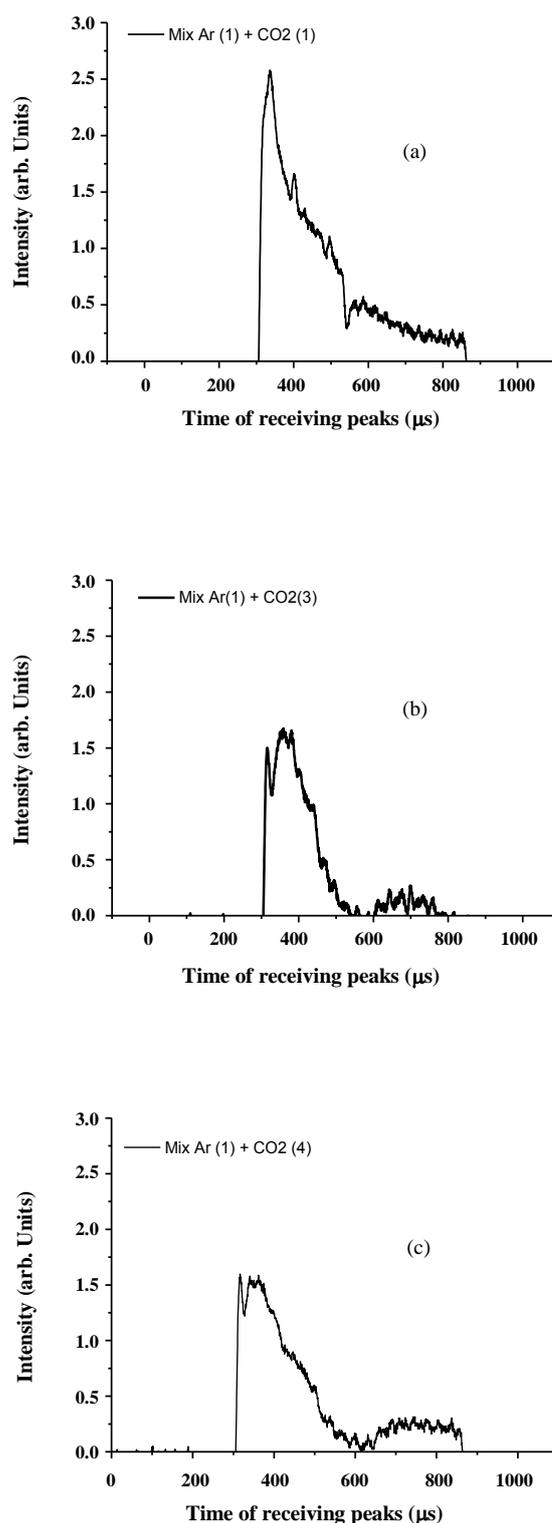


Fig. 1: Signals from gas mixture of Ar and CO₂ in high RF voltages. (a) Mix Ar (1) + CO₂ (1), (b) Mix Ar (1) + CO₂ (3), (c) Mix Ar (1) + CO₂ (4) in high voltage.

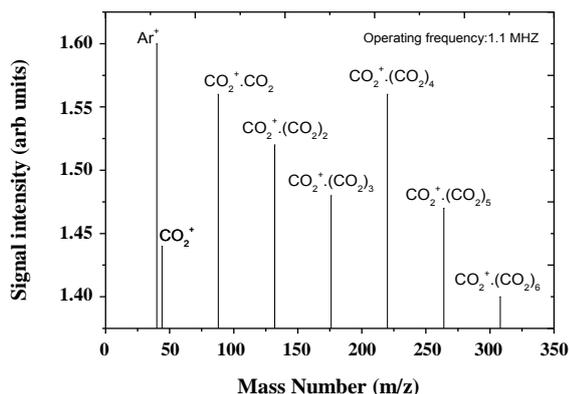


Fig. 2: Ion trap mass spectrum of an Ar-CO₂ mixture. The operating frequency was 1.1 MHz.

Computational investigation

We have carried out systematic investigation on the aggregation of CO₂ molecules around CO₂⁺ ions on the doublet potential energy surface (PES). At the first step, we have optimized the CO₂⁺ ions with a charge of +1 and a spin multiplicity of 2. Subsequently, the addition of up to eleven CO₂ molecules to the CO₂⁺ ion has been systematically carried out to obtain the geometries of the final structures for the CO₂⁺(CO₂)_n (n = 1 – 11) system. Fig. 3 shows these optimized geometries. Note that all calculations in the present paper have been carried out using Gaussian 98 software[28]. Some of these obtained structures have been confirmed by a previous work that reported by (Inokuchi *et al.* 2008). They had investigated the (CO₂)_n⁺ (n = 3 – 8) clusters in another device[29]. We have used the unrestricted HF level (UHF) with 3-21 G(d) basis set to optimize the geometries of the CO₂⁺(CO₂)_n (n = 1 – 11) system[30]. Additionally, all vibrational frequencies have been checked to confirm that all the obtained geometries are valid local minima without imaginary vibrational frequencies. Many configurations were obtained for each CO₂⁺(CO₂)_n (n = 1-11) molecule. The most stability geometries have been selected for each of the CO₂⁺(CO₂)_n (n = 1 – 11) molecules as shown in Fig. 3.

In this Figure, the structure of the most stable cluster found in this work, red and gray spheres, stand for oxygen and carbon atoms respectively.

In the present paper, we have analyzed the equilibrium constant (K_{eq}) for the formation of the CO₂⁺(CO₂)_n

(n = 1 – 11) molecules through Gibbs free energies (ΔG_f^o) by Gaussian 98 software using the equation (1);

$$\Delta G_f^o = -RT \ln K_{eq} \quad (1)$$

where R and T stand for the gaseous constant and the temperature, respectively. Additionally, the values of the ΔG_f^o ($\frac{KJ}{mol}$) for a reaction in a temperature of 298 °K, and pressure of 1 atm are given using Eq. (2);

$$\Delta G_f^o \left((CO_2^+ (CO_2)_n, 298^\circ K) \right) = \quad (2)$$

$$\sum n \Delta G_f^o (\text{products}) - \sum n \Delta G_f^o (\text{reactants})$$

Table 1 presents that the resulted values of the ΔG_f^o ($\frac{KJ}{mol}$) for all geometries of CO₂⁺(CO₂)_n (n = 1 – 11) molecules through equation (2). The negative values of ΔG_f^o confirm that the formation of the CO₂⁺(CO₂)_n (n = 1 – 11) molecules have been carried out through a spontaneous reaction. The biggest and smallest values have been found for the CO₂⁺(CO₂)₄ and CO₂⁺(CO₂)₁₁ molecules, respectively. This result confirms that the addition of the CO₂ molecule number cause to increase and decrease of ΔG_f^o, respectively. This means that the CO₂⁺(CO₂)_n (n = 1 – 11) molecules mixed with four CO₂ molecules have more thermodynamic stability. Additionally, we have plotted the trend of the ΔG_f^o and ΔH_f^o for all the reported CO₂⁺(CO₂)_n (n = 1 – 11) molecules in Fig. 4.a,b.

Note that in order to obtain the equilibrium constant (K_{eq}) in various temperatures in the range of 298 ~ 500° K, we have used Van 't Hoff 's equation using equation (8);

$$\ln \left(\frac{K_{eq2}}{K_{eq1}} \right) = \frac{\Delta H_f^o}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

Where, K₁ and K₂ are the equilibrium constants at absolute temperatures T₁ and T₂, respectively. According to the Eq. (8), we have displayed LnK_{eq} in terms of the temperature changes from 298 to 500 K, as shown in in Fig. 5a.

Fig. 5 presents the relation of the equilibrium constant (K_{eq}) with the number of the CO₂ molecules in CO₂⁺(CO₂)_n (n = 1 – 11). The calculated results reflect that the equilibrium constant (K_{eq}) increases with addition of CO₂

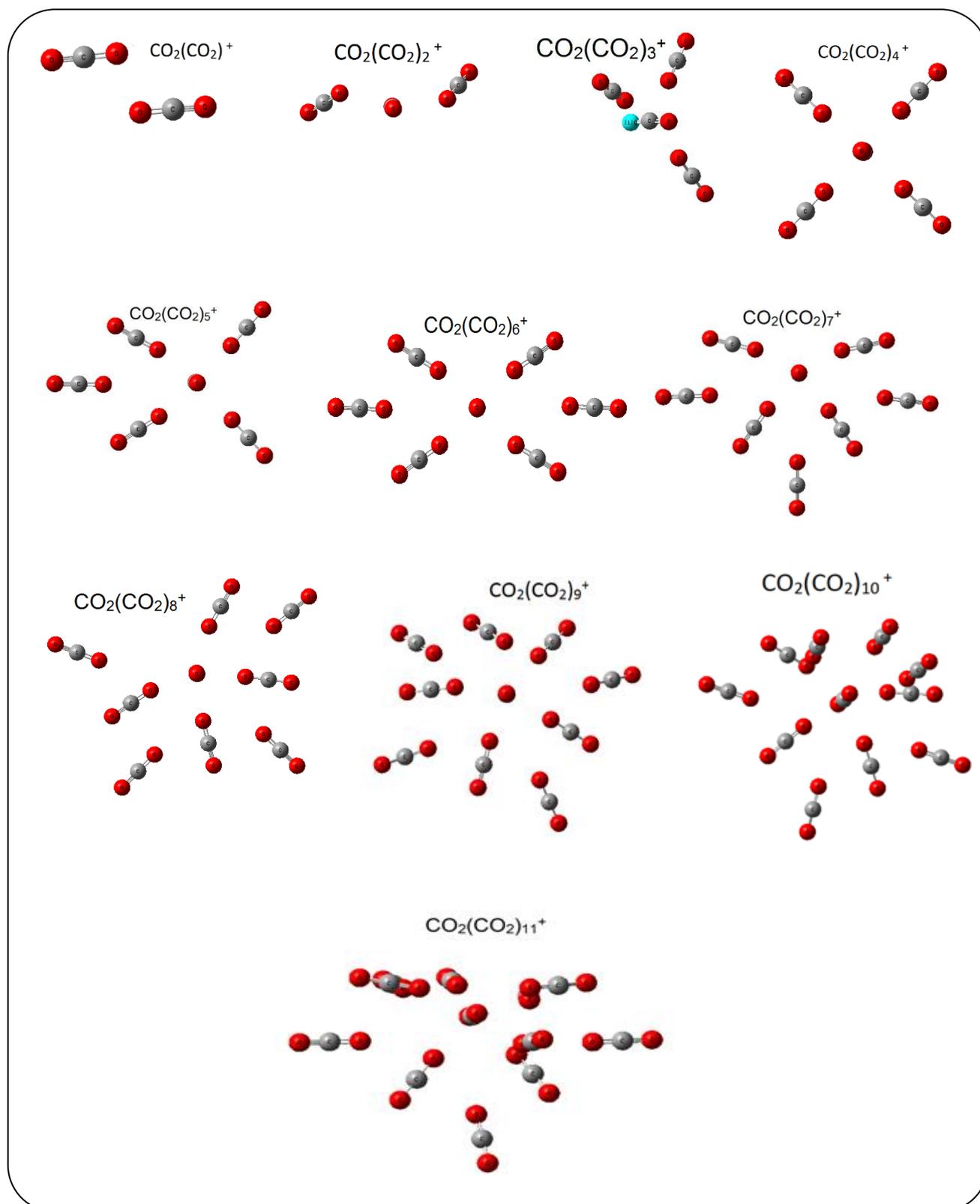
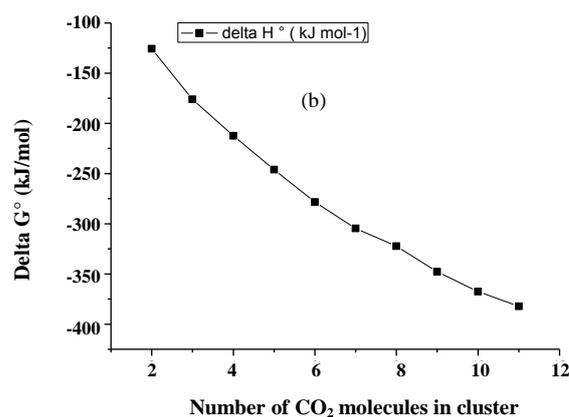
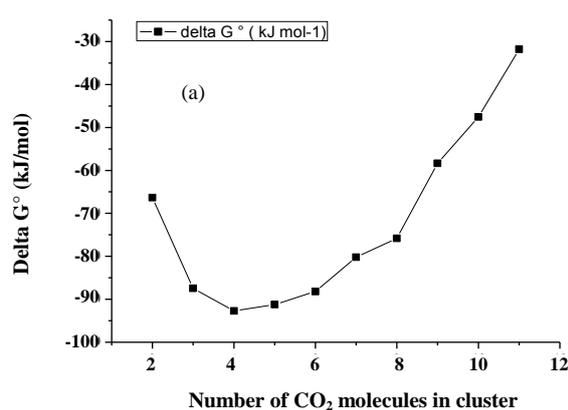


Fig. 3: The structure of the most stable cluster found in this work, red and gray spheres, stand for oxygen and carbon atoms respectively.

Table 1: Gibbs free energy and enthalpy of $\text{CO}_2^+(\text{CO}_2)_n$ molecules using uHF/3-21G(d) level.

	$H^\circ \left(\frac{\text{KJ}}{\text{mol}}\right)$	$G^\circ \left(\frac{\text{KJ}}{\text{mol}}\right)$	$\Delta H_f^\circ \left(\frac{\text{KJ}}{\text{mol}}\right)$	$\Delta G_f^\circ \left(\frac{\text{KJ}}{\text{mol}}\right)$
CO_2	-186.546	-186.600	----	----
CO_2^+	-186.106	-186.101	----	----
$\text{CO}_2^+(\text{CO}_2)_1$	-376.685	-376.725	-4.033	-0.023
$\text{CO}_2^+(\text{CO}_2)_2$	-559.245	-559.297	-0.048	-0.025
$\text{CO}_2^+(\text{CO}_2)_3$	-745.810	-745.875	-0.067	-0.033
$\text{CO}_2^+(\text{CO}_2)_4$	-932.370	-932.447	-0.081	-0.035
$\text{CO}_2^+(\text{CO}_2)_5$	-1118.930	-1119.020	-0.094	-0.035
$\text{CO}_2^+(\text{CO}_2)_6$	-1305.490	-1305.640	-0.106	-0.033
$\text{CO}_2^+(\text{CO}_2)_7$	-1492.040	-1492.120	-0.116	-0.030
$\text{CO}_2^+(\text{CO}_2)_8$	-1678.600	-1678.711	-0.123	-0.029
$\text{CO}_2^+(\text{CO}_2)_9$	-1865.150	-1865.320	-0.132	-0.022
$\text{CO}_2^+(\text{CO}_2)_{10}$	-2051.720	-2051.841	-0.140	-0.018
$\text{CO}_2^+(\text{CO}_2)_{11}$	-2238.330	-2238.410	-0.146	-0.012

Fig. 4: a) Changing of Gibbs free energies (ΔG_f°), b) Changing of Enthalpy (ΔH_f°) [These results were achieved by theoretical study].

molecules from one up to five ($(\text{CO}_2^+(\text{CO}_2)_1$ to $\text{CO}_2^+(\text{CO}_2)_5$). Subsequently, the value of the equilibrium constant (K_{eq}) decreases with increasing the CO_2 molecules from 5 up to 11.

Because of the existing vacuum in the present paper, we have not directly calculated the temperature of the trapping ion. This means that the evaluation of the equilibrium constant (K_{eq}) is in the range of 300 ~ 500 K. According to Fig. 5.b,c,d, there is an inverse relation between the formation probability of the $\text{CO}_2^+(\text{CO}_2)_n$ ($n = 1 - 11$) molecules and increasing the temperature. Namely,

the increment of the temperature causes the equilibrium constant (K_{eq}) to decrease. It is necessary to say that for the temperatures above 400°K, the formation probability of the $\text{CO}_2^+(\text{CO}_2)_n$ molecules with $n > 5$ is narrow. Also, Fig. 5b, shows that the formation of diatomic $\text{CO}_2^+(\text{CO}_2)$ contains the biggest equilibrium constant.

The calculated ΔG_f° provides suitable insight into the $\text{CO}_2^+(\text{CO}_2)_n$ ($n = 1 - 11$) molecules structure. The calculated results show that the temperature range for obtaining stable cluster is very narrow, 300 ~ 500 K. Increasing the number of the CO_2 molecules in the

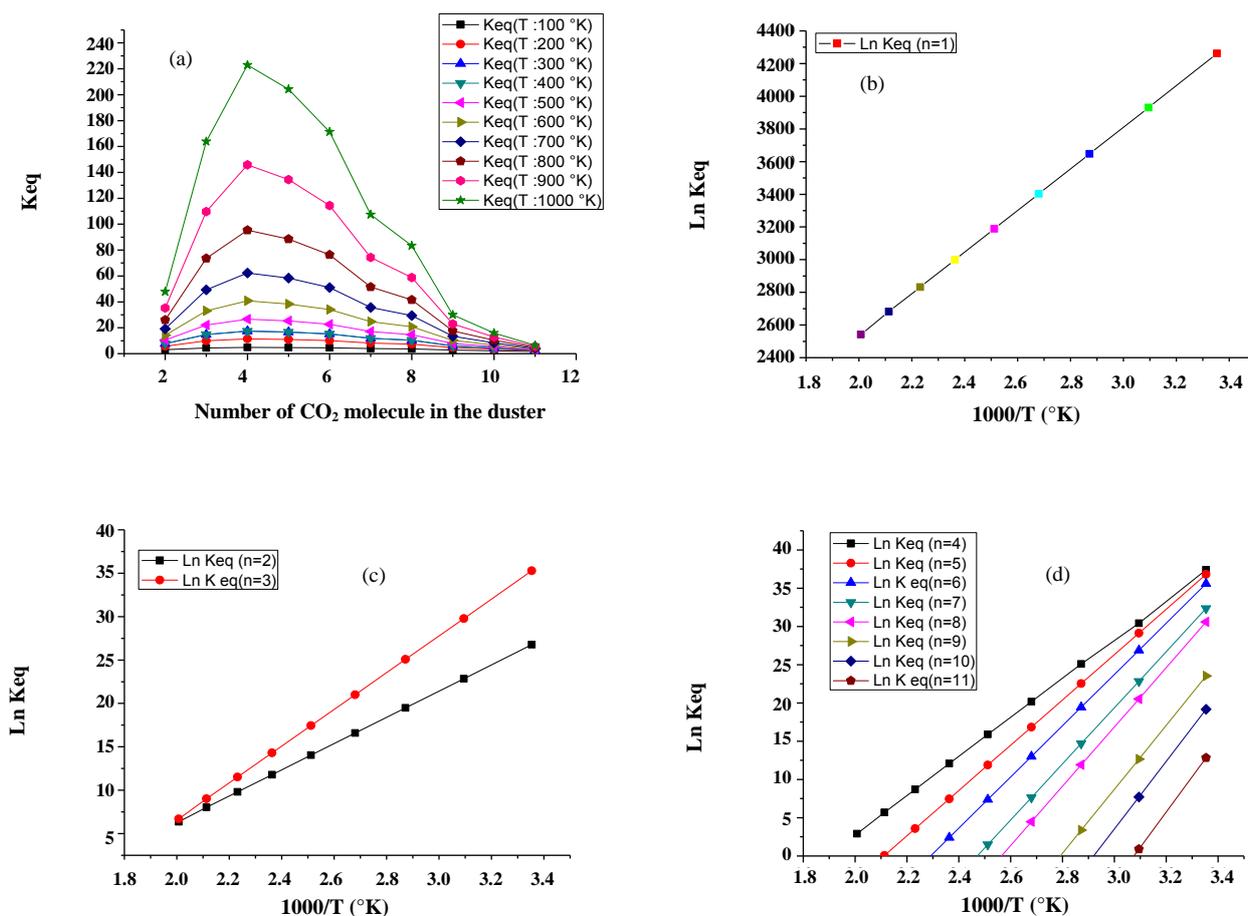


Fig. 5: (a) Correlation between $\ln K_{eq}$ and number of CO_2 molecules in the clusters for various temperatures, Effect of the $\ln K_{eq}$ and $1000/T$ (°K) in the cluster $\text{CO}_2^+(\text{CO}_2)_n$, (b) $n=1$, (c) for $n=2-3$, and (d) $n=4-11$.

$\text{CO}_2^+(\text{CO}_2)_n$ is difficult because of the existence of different positions for each new CO_2 molecule. The formation of clusters depends on temperature. The contribution of temperature in this event is being explained by affecting on kinetic energy. In above degree of temperatures, cluster's kinetic energy increase, as a result, the cluster of molecules cannot form. The thermochemical results of our paper for the $\text{CO}_2^+(\text{CO}_2)_n$ ($n = 1 - 11$) molecules confirm that the suitable temperature of the $\text{CO}_2^+(\text{CO}_2)_{11}$ molecule should be $\sim 340^\circ\text{K}$ which is in good agreement with the experimental results. For the temperatures above 500°K , smaller molecules such as $\text{CO}_2^+(\text{CO}_2)_4$ could be found. Finally, the most stable optimized geometries of the $\text{CO}_2^+(\text{CO}_2)_n$ ($n = 1 - 11$) molecular clusters have been displayed in Fig. 3. As shown, molecules with higher number of the CO_2 have nonplanar structures. Bond dissociation energy of these

clusters was calculated and compared with previous values in Table 2. Values of the Table 2. are reported based on experimental results. The previous studies are found to be in good agreement with the value from this study[31-34]

CONCLUSIONS

In the present paper, the formation of $\text{CO}_2^+(\text{CO}_2)_n$ cluster ions in a Paul ion trap has been investigated. Effect of buffer gas in the formation of dioxide carbon clusters was shown. Application of Ar as buffer gas results in collision cooling and subsequently, provides the appropriate conditions for formation of the cluster. Demonstrated peaks clearly show the role of Ar in formation of clusters. The thermodynamic examination of $\text{CO}_2^+(\text{CO}_2)_n$ cluster ions are of great importance in understanding the conditions to formation of clusters in a trap.

Table 2: Bond dissociation energies of $CO_2^+.CO_2$, $CO_2^+.(CO_2)_2$, $CO_2^+.(CO_2)_3$.

Ion molecules	This work (Kcal/mol)	Other Technique (Kcal/mol) ^a
$CO_2^+.CO_2$	12.7	13.0 12.7 11.8
$CO_2^+.(CO_2)_2$	3.4	4.8 3.3
$CO_2^+.(CO_2)_3$	2.8	2.8

{ AB - (A+B)} = Binding energy of AB

Accordingly, the values of n in the $CO_2^+(CO_2)_n$ cluster ions depend on both the buffer gas and the main gas. We have observed the Ar – CO_2 mixture peaks when collisional cooling of CO_2^+ is carried out. Finally, cluster formation occurs. The calculated results in theory are based on Gibbs free energy. The stable clusters exist in the temperature range of 300 ~ 500 K. It is necessary to say that in higher temperatures than 500 K, there is no cluster formation. By comparing $\ln K_{eq}$ and number of CO_2 molecules in the clusters for various temperatures (see Fig. 5.C), we observed the formation of the cluster with n=2-3 is significantly easier than the large cluster. Small clusters in particular have a big equilibrium constant in low temperatures. The conclusion corroborates the idea of the formation of the cluster in Ion trap Paul. The result considerably help the design of transport systems for such an interface device.

Finally, the probability of clusters formation in various temperatures has been investigated through computational methods and also structure of clusters has been gained that open up new possibility for test of these cluster in Ion Trap Paul

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