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# Doubly charged CO<sub>2</sub> clusters formed by ionization of doped helium nanodroplets



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Dedicated to Tilmann Märk, a long-time friend and colleague, on the occasion of his 70th birthday.

### Keywords:

CO<sub>2</sub>

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## ABSTRACT

Helium nanodroplets are doped with carbon dioxide and ionized by electrons. Doubly charged cluster ions are, for the first time, identified based on their characteristic patterns of isotopologues. Thanks to the high mass resolution, large dynamic range, and a novel method to eliminate contributions from singly charged ions from the mass spectra, we are able to observe doubly charged cluster ions that are smaller than the ones reported in the past. The likely mechanism by which doubly charged ions are formed in doped helium droplets is discussed.

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## 1. Introduction

In consequence of electric repulsion, a charged spherical mass of liquid... is in a condition of unstable equilibrium wrote John William Strutt, 3rd Baron Rayleigh, in his 1882 treatise On the equilibrium of liquid conducting masses charged with electricity [1]. Rayleigh expressed the instability of a highly charged drop in terms of the fissility parameter  $X$  for which he derived the relation (here written in SI units)

$$X = \frac{Q^2}{64\pi^2 \gamma \epsilon_0 r^3} \quad (1)$$

where  $Q$  is the net charge of the droplet,  $\gamma$  the surface tension coefficient,  $\epsilon_0$  the permittivity of free space, and  $r$  the droplet radius. A spherical droplet is stable for all displacements if  $X < 1$ . If, however,  $X$  exceeds 1 the spherical form becomes unstable, and the liquid is thrown out in fine jets, whose fineness, however, has a limit [1].

One of the fascinating aspects of this Coulomb instability is that it occurs on a wide range of length scales, from rain drops of 1 mm diameter which were explicitly considered by Rayleigh, down to nuclear dimensions where it leads to spontaneous fission. Leisner and co-workers have imaged Rayleigh jets emitted from levitated micron-sized droplets [2]. Sattler et al. were the first to observe the Rayleigh instability of nanometer-sized doubly charged atomic clusters [3]. In their experiment and the numerous experiments that followed (for reviews see [4–6]) the instability causes the absence of  $z$ -fold charged cluster ions  $A_n^{z+}$  in mass spectra below a characteristic size  $n_z$  that depends on the substance and the charge state.  $n_z$  is commonly referred to as “critical size” or “appearance size.” We will adopt the latter term because  $n_z$  is primarily an experimental observable whereas the term “critical size” often refers to the size at which the fission barrier of a multiply charged droplet vanishes. With that definition,  $n_z$  is an upper limit to the critical size.

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Tilmann Märk was a pioneer in this field; together with his coworkers he measured appearance sizes and appearance energies for many cluster systems [7]. For doubly charged clusters of van der Waals or hydrogen-bound systems appearance sizes  $n_2$  range from 12 for pyridine [8] to  $n_2 = 284$  for neon, the most weakly bound system investigated so far [9]. Appearance sizes of the corresponding triply charged systems are larger by approximately a factor 2.2 [10].

Early attempts to rationalize appearance sizes considered the energy balance between a doubly charged parent cluster and the two separated singly charged fragments [3,11]; a semi-empirical formula provided a satisfying correlation between appearance sizes and two macroscopic parameters, namely the molecular volume and the surface tension [4]. However, it soon emerged that the fission barrier plays a crucial role, as already noticed by Rayleigh. A liquid-drop model was used to compute the fission barrier for various substances and charge states up to  $z = 4$ ; reasonable agreement with experimental data was achieved if the experimental appearance sizes were compared with the calculated sizes at which the fission barrier vanishes for the most favorable fission channel [10]. At the same time, the model correctly accounted for the highly asymmetric fission of triply charged  $\text{CO}_2$  clusters [10,12]. These ions undergo spontaneous (unimolecular) fission with high probability if their initial size exceeds the appearance size by less than 10%; the size distribution of their doubly charged fragments peaked at about 92% of the initial mass. Similar results were reported for  $(\text{C}_2\text{H}_4)_n^{3+}$  and  $(\text{NH}_3)_n^{3+}$  whose doubly charged fission fragments carry about 75 and 90% of the mass, respectively [10,13].

In subsequent work a broad arsenal of experimental techniques including post-ionization of ions, laser heating, and charge exchange with highly charged ions was employed to investigate metal clusters [5,14–17] (for related work on van der Waals clusters with fissility  $X > 1$ , see [18–20]). One overarching result was that appearance sizes in metal clusters coincide with the size at which the activation energies for monomer evaporation and fission are equal [21,22]. Thus, if a cluster of size  $n_2$  were to evaporate a monomer the fission barrier would be substantially lowered and, in spite of the cooling that comes with the evaporation, the rate constant of thermally activated fission would increase dramatically [23].

However, this scenario is at odds with the behavior of doubly charged clusters such as  $(\text{CO}_2)_n^{2+}$  [24,25],  $(\text{NH}_3)_n^{2+}$  [13],  $(\text{H}_2\text{O})_n^{2+}$  and  $\text{Ar}_n^{2+}$  [25]. These ions, when analyzed at or just above the appearance size  $n_2$ , show a propensity to evaporate one or two monomers. However, no [26] singly charged fragment ions could be detected which suggests that the fission barrier at the appearance size  $n_2$  is significantly larger than the heat of evaporation. Only when the doubly charged cluster ions were collisionally excited to a degree where they lost about six monomers did they eventually become small enough to undergo fission [28,29].

Why, then, are doubly charged cluster ions below  $n_2$  absent from mass spectra even though their fission barriers are still sizeable? In hindsight, the answer was already apparent from an early molecular dynamics simulation of charge separation in  $\text{Xe}_n^{2+}$  [30]; subsequent molecular dynamics simulations of doubly charged noble gas clusters provided further insight [23,31,32], and an analytical study based on the liquid drop model offered a quantitative explanation [10,33]. In essence, the initial directed motion of the two ions in opposite directions, right after vertical ionization of two separate molecules in the cluster [34], greatly helps to overcome the fission barrier (unless charge is transported by hopping rather than ionic motion). Failure to overcome the barrier upon the first attempt greatly diminishes the chance of overcoming the barrier at later times when the excess energy is randomized. In fact, Lezius and Märk could show that fission of  $(\text{O}_2)_n^{2+}$  and  $\text{Ar}_n^{2+}$  in the vicinity of  $n_2$  occurs within less than 1  $\mu\text{s}$  after ionization, within the ion source, by comparing the ionization cross sections of singly

and doubly charged cluster ions, and by analyzing ion beam profiles [35,36].

Thus, cluster ions slightly below  $n_2$  are still stable with respect to fission; with improved instrumental resolution and sensitivity one may expect to observe smaller doubly charged ions. In fact, the appearance size of doubly charged xenon clusters, originally reported as  $n_2 = 53$  [3] could be reduced by Märk and coworkers to  $n_2 = 47$  [34]. Likewise, the appearance size of  $(\text{CO}_2)_n^{2+}$  could be reduced from  $n_2 = 45$  [24,37] to 43 [38].

In the present work we investigate helium nanodroplets doped with  $\text{CO}_2$  and ionized by electrons. The goal is to identify doubly charged cluster ions that are smaller than previously reported. Another goal is to identify them unambiguously by measuring the pattern of their isotopologues. Curiously, isotopologues were not identified in previous work on multiply charged van der Waals or hydrogen bound clusters even though their contributions can be substantial. For example, 49% of  $(\text{CO}_2)_{43}^{2+}$  ions, the smallest doubly charged  $\text{CO}_2$  cluster reported so far [38], contain one or more  $^{13}\text{C}$ ,  $^{17}\text{O}$ , or  $^{18}\text{O}$  isotopes. In the present study we have designed a method that effectively subtracts the “background” of singly charged ions from the measured spectra. With this approach we identify several ions  $(\text{CO}_2)_n\text{X}^{2+}$  ( $\text{X} = \text{O}, \text{CO}, \text{O}_2$ ) that are smaller than the ones reported previously [24] by their isotope pattern. However,  $(\text{CO}_2)_{43}^{2+}$  remains the smallest stoichiometric ion that can be clearly identified.

## 2. Experimental

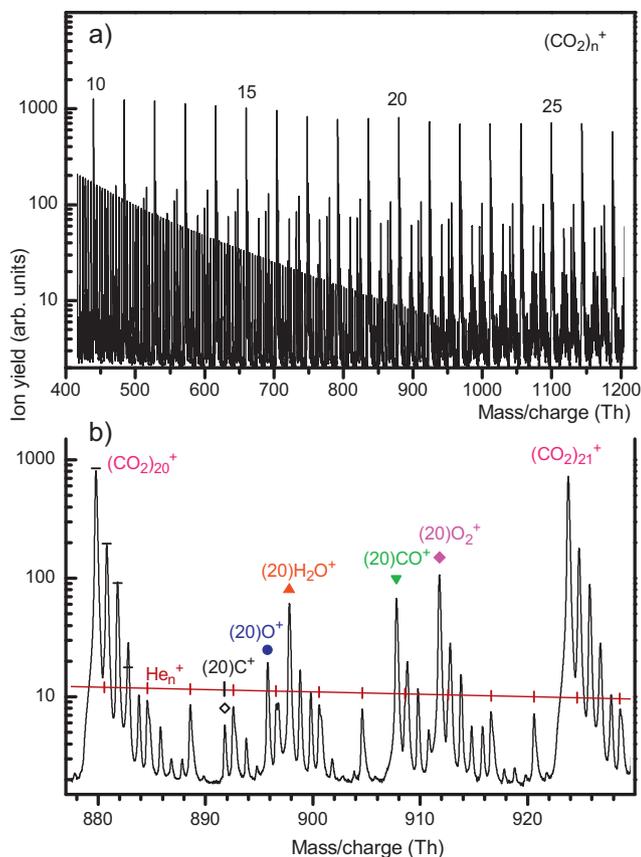
Neutral helium nanodroplets were produced by expanding helium (Messer, purity 99.9999%) from a stagnation pressure of 2 MPa through a 5  $\mu\text{m}$  nozzle, cooled to 9.5 K, into vacuum. The average number of atoms per droplet formed in the expansion was of the order of  $2 \times 10^6$ ; these droplets are superfluid with a temperature of  $\approx 0.37$  K [39]. The resulting supersonic beam was skimmed by a 0.8 mm conical skimmer, located 12 mm downstream from the nozzle. The skimmed beam traversed a 20-cm-long pick-up region into which  $\text{CO}_2$  (Messer, purity 99.9995%) was introduced. The partial  $\text{CO}_2$  pressure was 1.5 MPa (uncorrected ion gauge signal).

Following the pick-up region the doped helium droplets passed a region in which they were ionized by electron impact at energies of 70 eV and a current of 290  $\mu\text{A}$ . Cations were accelerated to 40 eV into the extraction region of a commercial time-of-flight mass spectrometer equipped with a reflectron (Tofwerk AG, model HTOF). The base pressure in the mass spectrometer was  $10^{-5}$  Pa. The ions were extracted at  $90^\circ$  into the field-free region of the spectrometer by a pulsed extraction voltage. At the end of the field-free region they entered a two-stage reflectron which reflected them toward a microchannel plate detector operated in single ion counting mode. The mass resolution in the region of interest, around 1000 u, was  $\Delta m/m = 1/4000$  (full width-at-half-maximum). Additional experimental details have been described elsewhere [40,41].

## 3. Results

A section of a mass spectrum of  $\text{CO}_2$ -doped helium nanodroplets is shown in Fig. 1a on a semilogarithmic scale. The most prominent ions are  $(\text{CO}_2)_n^+$ ; some  $n$  values are indicated.  $\text{He}_n^+$  ions form a dense band that declines approximately exponentially with increasing size.

Fig. 1b shows an exploded view of the spectrum. Mass peaks corresponding to isotopically pure ions (containing only  $^{12}\text{C}$  and  $^{16}\text{O}$ ) are labeled; ( $n$ ) indicates the number of complete  $\text{CO}_2$  molecules in the ion. We observe  $(\text{CO}_2)_n\text{X}^+$  where  $\text{X} = \text{C}, \text{O}, \text{H}_2\text{O}, \text{CO}, \text{O}_2$ . Also marked is the  $\text{He}_n^+$  series which in this size region has dropped to the 1% level of  $(\text{CO}_2)_n^+$ .



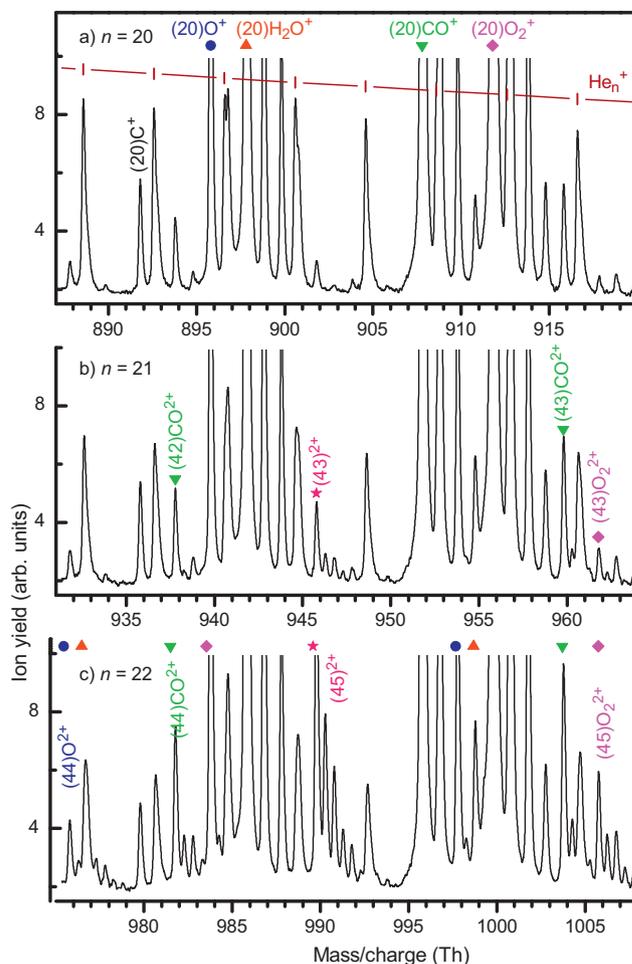
**Fig. 1.** A mass spectrum of helium nanodroplets doped with carbon dioxide. The dense band in panel a originates from pure helium cluster ions while the most prominent peaks are due to  $(\text{CO}_2)_n^+$ ; some  $n$  values are indicated. Panel b zooms into the region between  $(\text{CO}_2)_{20}^+$  and  $(\text{CO}_2)_{21}^+$ ; prominent (isotopically pure) ions are labeled, with  $(n)$  denoting  $(\text{CO}_2)_n$ . The expected relative abundance of  $(\text{CO}_2)_{20}^+$  isotopologues is indicated by horizontal bars.

All other mass peaks in Fig. 1b can be traced to isotopologues containing one or more  $^{13}\text{C}$  (natural abundance 1.07%),  $^{17}\text{O}$  (0.038%), or  $^{18}\text{O}$  (0.205%). The expected relative abundance of  $(\text{CO}_2)_{20}^+$  isotopologues is indicated by horizontal bars. Good agreement with the observed spectrum is seen for the mass peaks that are heavier by 1 or 2 u than the isotopically pure ion (nominal mass 880 u). The mass peak at 883 u, however, is 60% more abundant than expected, indicating some unidentified contamination although only at the 1% level of the main isotopologue.

Fig. 2 displays three sections of the mass spectrum, zooming into the regions between the singly charged  $n$ -mer and  $n+1$ -mer for  $n=20$ –22. The  $y$ -scale is linear. The  $\text{He}_n^+$  series and  $(\text{CO}_2)_{20}\text{C}^+$  are marked in panel a. All other singly charged, isotopically pure ions that were identified in Fig. 1b are now off-scale; their positions are indicated above panel a.

In Fig. 2c several new mass peaks appear. The most prominent ones are due to the isotopologues of  $(\text{CO}_2)_{45}^{2+}$ , beginning at a nominal mass-to-charge ratio of 990 Th (marked by an asterisk above the spectrum). Isotopologues with half-integer mass-to-charge ratio, at (nominally) 990.5, 991.5 and 992.5 Th, form new peaks. They form the unambiguous fingerprint of doubly charged ions; we will refer to them as “half-integer peaks.”

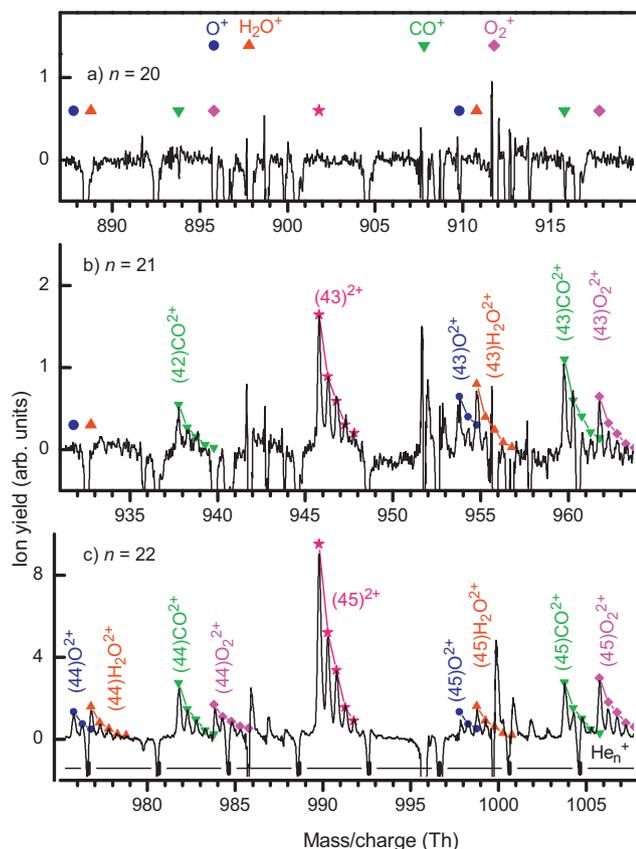
Marked above panel c are the positions of isotopically pure  $(\text{CO}_2)_{44}\text{X}^{2+}$  and  $(\text{CO}_2)_{45}\text{X}^{2+}$  ions with  $\text{X}=\text{O}, \text{H}_2\text{O}, \text{CO}, \text{O}_2$ , using the same symbols that were used to flag the corresponding singly charged ions above panel a. With the exception of  $(\text{CO}_2)_{44}\text{H}_2\text{O}^{2+}$ , all these doubly charged ions reveal themselves through the presence of half-integer peaks.



**Fig. 2.** Zooming in: the mass regions between  $(\text{CO}_2)_n^+$  and  $(\text{CO}_2)_{n+1}^+$  for  $n=20$ –22 (panels a through c). The positions of singly charged, isotopically pure ions  $(\text{CO}_2)_n\text{X}^+$  with  $\text{X}=\text{O}, \text{H}_2\text{O}, \text{CO},$  and  $\text{O}_2$  are indicated at the top of (a). The same symbols are used in the other panels to indicate the expected positions of the corresponding doubly charged cluster ions. For example, the full dot identifies isotopically pure  $(\text{CO}_2)_{20}\text{O}^+$  in panel a; in panel c it marks the expected location of isotopically pure  $(\text{CO}_2)_{44}\text{O}^{2+}$  and  $(\text{CO}_2)_{45}\text{O}^{2+}$ . These ions are, indeed, observed, as judged from the half-integer peaks immediately to their right. In panel b symbols are placed only above those mass peaks that are followed by half-integer peaks, suggesting the presence of  $(\text{CO}_2)_{42}\text{CO}^{2+}$ ,  $(\text{CO}_2)_{43}^{2+}$ ,  $(\text{CO}_2)_{43}\text{CO}^{2+}$ , and  $(\text{CO}_2)_{43}\text{O}_2^{2+}$ .

In Fig. 2 the mass-to-charge regions are chosen such that corresponding cluster ions, for example  $(\text{CO}_2)_n\text{O}^+$  for  $n=20$  through 22, will exactly line up. Some of the half-integer mass peaks identified in Fig. 2c have corresponding peaks in Fig. 2b, thus signaling the presence of  $(\text{CO}_2)_{43}^{2+}$ ,  $(\text{CO}_2)_{42}\text{CO}^{2+}$ ,  $(\text{CO}_2)_{43}\text{CO}^{2+}$ , and  $(\text{CO}_2)_{43}\text{O}_2^{2+}$ . These doubly charged ions are also discernible via the increased peak height of the isotopically pure ions, if compared with panel a. However, the observation of half-integer peaks immediately to their right provides much more compelling evidence for their presence.

The experimental sensitivity for doubly charged ions would be greatly enhanced if one could subtract contributions from singly charged ions. Unfortunately, such a spectrum cannot be measured. Instead, we simulated such a background spectrum by shifting the measured spectrum by the mass-to-charge ratio of  $\text{CO}_2^+$ , i.e. by adding 43.990 Th to the mass. This “background spectrum” is multiplied by an adjustable factor very close to 1.0, and subtracted from the original (unshifted) spectrum. The procedure works well because (i) the ion yield of  $(\text{CO}_2)_n\text{X}^+$  changes little with  $n$  (see Fig. 1a), and (ii) contributions from doubly charged ions increase



**Fig. 3.** The mass regions between  $(\text{CO}_2)_n^+$  and  $(\text{CO}_2)_{n+1}^+$  for  $n=20$ – $22$  (panels a through c), after subtracting contributions from singly charged ions (see text for details). The expected distributions of isotopologues are indicated in panels b and c for all doubly charged ions that are clearly identified. Note the change in y-scale between panels b and c.

dramatically with  $n$  in this size range. However, one has to be careful with the interpretation because any mechanism that leads to deviation from a “regular” size dependence, such as magic numbers, would also feature prominently in these difference spectra.

The result is presented in Fig. 3. Multiply charged ions are now easily identified in Fig. 3c where the expected distributions of isotopologues are indicated by symbols connected by solid lines. In Fig. 3b one clearly observes  $(\text{CO}_2)_{43}^{2+}$  which is about a factor six weaker than  $(\text{CO}_2)_{45}^{2+}$  (note the different y-scales). Other doubly charged ions seen in Fig. 3b are  $(\text{CO}_2)_{42}\text{CO}_2^{2+}$  and  $(\text{CO}_2)_{43}\text{X}^{2+}$  for  $\text{X}=\text{O}, \text{H}_2\text{O}, \text{CO},$  and  $\text{O}_2$ . No doubly charged ions are discernible in Fig. 3a; the yield of  $(\text{CO}_2)_{41}^{2+}$ , if present at all, is at least an order of magnitude weaker than that of  $(\text{CO}_2)_{43}^{2+}$ .

Some spurious peaks appear in Fig. 3. One reason is the fact that the mass of  $\text{He}_{11}$  exceeds that of  $\text{CO}_2$  by 0.039 u; i.e. the helium mass peaks do not exactly line up in Figs. 2 and 3. Also, their yield decreases significantly with increasing size. This results in large negative yield at the position of  $\text{He}_n^+$  mass peaks whose positions are indicated below the spectrum in Fig. 3c. Second, peak shapes do change slightly, last not least because the absolute width of mass peaks increases with increasing mass. Even so, a comparison of Figs. 3 and 1b shows that the method reduces the yield of singly charged  $(\text{CO}_2)_n\text{X}^+$  by up to two orders of magnitude.

#### 4. Discussion

We begin with a brief discussion of the singly charged ions that appear between  $(\text{CO}_2)_n^+$  mass peaks, namely  $(\text{CO}_2)_n\text{X}^+$  with  $\text{X}=\text{C}, \text{O}, \text{CO}, \text{O}_2$ , see Fig. 1b. Electron ionization of  $\text{CO}_2$  molecules results

in  $\text{C}^+$ ,  $\text{O}^+$  and  $\text{CO}^+$ , each with an ion yield of about 10% relative to  $\text{CO}_2^+$ , but no  $\text{O}_2^+$  [42,43]. The appearance of  $(\text{CO}_2)_n\text{O}_2^+$  upon electron ionization of neat  $\text{CO}_2$  clusters has been traced to intra-cluster ion-molecule reactions [44,45]. In the present work  $(\text{CO}_2)_n\text{O}_2^+$  ions are even more abundant than  $(\text{CO}_2)_n\text{O}^+$  or  $(\text{CO}_2)_n\text{CO}^+$ , in agreement with another study in which  $\text{CO}_2$  clusters were also embedded in helium nanodroplets [46]. It appears that the different ionization mechanism, namely charge transfer from  $\text{He}^+$  to  $(\text{CO}_2)_n$  rather than direct electron ionization, favors formation of  $(\text{CO}_2)_n\text{O}_2^+$  [47,48].

Another striking difference between mass spectra of  $\text{CO}_2$  molecules and  $\text{CO}_2$  clusters has received surprisingly little attention so far, namely the virtual absence of  $(\text{CO}_2)_n\text{C}^+$  in cluster spectra [38,44,49] which contrasts with the 10% yield of  $\text{C}^+$  from  $\text{CO}_2$  [42]. The only report in which  $(\text{CO}_2)_n\text{C}^+$  ions were positively identified was by Märk and coworkers [45]. They saw just a hint of  $(\text{CO}_2)_n\text{C}^+$  for  $n=1, 2, 3$ . The yield was about 10% relative to  $(\text{CO}_2)_n\text{O}^+$ , too low for a measurement of the appearance energy. On the other hand,  $(\text{CO}_2)_{20}\text{C}^+$  is clearly discernible in Fig. 1b; its yield is about 25% of  $(\text{CO}_2)_{20}\text{O}^+$ , or 1% of  $(\text{CO}_2)_{21}^+$ . The appearance of  $(\text{CO}_2)_n\text{C}^+$  under our experimental conditions is remarkable in its own right because the appearance energy of  $\text{C}^+$  is high. Locht and Davister have identified seven different processes by which  $\text{C}^+$  is produced from  $\text{CO}_2$ , the lowest threshold being  $23.04 \pm 0.04$  eV [43]. This value is 4.0 eV higher than the thermodynamic onset of  $\text{O}^+$ , and only slightly below the ionization energy of atomic He, 24.59 eV. Thus, formation of  $\text{C}^+$  via the reaction

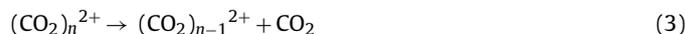


is barely exothermic (for a  $\text{CO}_2$  cluster embedded in helium the energetics will be somewhat different but hardly more favorable).

We already mentioned the presence of  $(\text{CO}_2)_{20}\text{H}_2\text{O}^+$ ; it obviously arises from residual water vapor. In experiments with nanodroplets containing in excess of  $10^6$  helium atoms even a contamination below 1 ppm, or a very minor residue of  $\text{H}_2\text{O}$  vapor in the vacuum chamber, will leave its mark on the mass spectra.

We now turn to a discussion of multiply charged cluster ions. So far, multiply charged  $\text{CO}_2$  clusters have been investigated in three different research labs using different mass spectrometers but the same technique to generate clusters (by supersonic expansion of  $\text{CO}_2$ ), and to ionize (by electron ionization). Echt and co-workers used a time-of-flight mass spectrometer with a mass resolution of  $\Delta m/m \cong 1/100$  (FWHM) to identify odd-numbered  $(\text{CO}_2)_n^{2+}$  for  $n \geq 45$  [37,50]. They also reported the appearance of  $(\text{CO}_2)_n^{3+}$  and  $(\text{CO}_2)_n^{4+}$  for  $n > 108$  and  $> 216$ , respectively. In subsequent work they identified unimolecular, highly asymmetric fission of triply charged  $\text{CO}_2$  clusters into doubly charged fragments but unimolecular reactions of doubly charged into singly charged clusters could not be detected [10,12].

Märk and co-workers used a double focusing sector field mass spectrometer of reversed geometry with a resolution  $\Delta m/m \cong 1/400$  [24,50]. A strong  $(\text{CO}_2)_{45}^{2+}$  signal contrasted with the absence of  $(\text{CO}_2)_{43}^{2+}$ . Furthermore,  $(\text{CO}_2)_n\text{O}_2^{2+}$  ions for  $n \geq 44$  ( $n$  even) were observed. Smaller doubly charged species could be identified indirectly in a MIKE scan, revealing the metastable reaction



for  $n \geq 44$  [24]. No evidence for fission was found.

Stace and coworkers used a double focusing, reverse-geometry mass spectrometer with a resolution of  $\Delta m/m \cong 1/2000$  [29,38,50]. Their spectra reveal  $(\text{CO}_2)_{43}^{2+}$  at a yield of about 3% that of  $(\text{CO}_2)_{45}^{2+}$ ; such a low intensity is consistent with the failure to identify  $(\text{CO}_2)_{43}^{2+}$  in the earlier studies [10,12,24]. Furthermore, Stace and coworkers investigated collision-induced reactions of  $(\text{CO}_2)_n^{2+}$  into singly charged fragments for  $n \geq 45$ , and they determined the kinetic-energy release [29,38]. They found a slightly asymmetric

distribution of fission fragments with one fragment ion carrying up to 60% of the initial mass. However, collisions lead to loss of several CO<sub>2</sub> molecules from the parent cluster ion and very broad size distributions of singly charged fragment ions.

In contrast to previous reports where bare clusters were investigated, in the present work the clusters are grown inside helium nanodroplets and subsequently ionized by 70 eV electrons. The relative yield of doubly charged clusters is rather low, only 1% of the yield of (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> at the same mass/charge ratio. In previous work using the same approach (i.e. electron ionization of doped helium clusters) we succeeded to produce doubly charged methane clusters [51] but we are not aware of any other reports of multiply charged clusters produced from doped helium droplets. Attempts in our lab to identify doubly charged clusters of oxygen, nitrogen, or argon failed. Likewise, no doubly charged ions were reported by Stace and coworkers in an electron ionization study of helium droplets doped with clusters of CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub> and several other polyatomic molecules [46].

The absence of multiply charged clusters may, of course, be caused by several factors. For example, insufficient doping will result in clusters that are simply too small to resist fission. Much more intriguing is the fact that doubly charged CO<sub>2</sub> cluster ions are observed at all. The commonly accepted mechanism by which a dopant X is ionized in helium droplets [52–54] involves formation of He<sup>+</sup> by the incident electron near the surface, followed by charge hopping toward X and subsequent charge transfer



Reaction (4) is exothermic for all dopants; subsequent reactions may lead to dissociation and/or ejection of a singly charged dopant ion possibly dressed with one or more helium atoms [55].

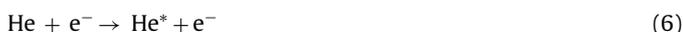
However, the analogous reaction for producing doubly charged ions,



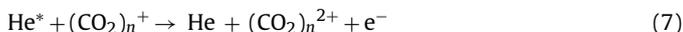
is, for most dopants, endothermic. For example, the appearance energy of CO<sub>2</sub><sup>2+</sup> from CO<sub>2</sub> is 37.2 eV [56,57]. The appearance energy of doubly charged CO<sub>2</sub> clusters is reduced by about 7 eV due to solvation [24], but still much larger than the ionization energy of He, 24.59 eV. Formation of doubly charged ions by reaction (5) is only possible for dopants with low first and second ionization energies such as C<sub>60</sub> [58–60].

Nevertheless, a few doubly charged ions for which reaction (5) is endothermic have been observed before; they include the above-mentioned (CH<sub>4</sub>)<sub>n</sub><sup>2+</sup> (*n* > 70) [51], CH<sub>3</sub>I<sup>2+</sup>, and its fragments [61]. How are doubly charged ions formed if reaction (5) is endothermic? From a strictly energetic perspective, two separate He<sup>+</sup> ions could be formed in a helium droplet by an incident electron whose energy is 70 eV, or by two uncorrelated incident electrons. However, sequential ionization of the dopant by charge exchange with two He<sup>+</sup> can be excluded because of Coulomb repulsion.

Alternatively, the incident electron could form He<sup>+</sup> plus an electronically excited He\* in the doped droplet. The threshold energy for



equals 19.82 eV, resulting in a He atom in the 2<sup>3</sup>S<sub>1</sub> state whose lifetime (if isolated) is 8000 s; other long-lived states at slightly higher energies could contribute as well [62]. A pair of He<sup>+</sup> + He\* could lead to the following reaction: charge transfer from He<sup>+</sup> (reaction (4)) produces (CO<sub>2</sub>)<sub>n</sub><sup>+</sup>; then Penning ionization



produces a doubly charged ion. Reaction (7) would be aided by the ion-induced dipole interaction between the reactants [61]. A simple

estimate shows that reaction (7) is exothermic: Märk and coworkers reported a value of 13.1 ± 0.2 eV for the appearance energy of (CO<sub>2</sub>)<sub>2</sub><sup>+</sup>, about 0.7 eV below the appearance energy of CO<sub>2</sub><sup>+</sup> [63]. The appearance energy of large CO<sub>2</sub> clusters will be further reduced due to solvation, to a value of about 12 eV. Combined with the appearance energy of 30 eV for large (CO<sub>2</sub>)<sub>n</sub><sup>2+</sup> [24] we estimate a second ionization of 18 eV for large CO<sub>2</sub> clusters, hence an exothermicity of about 2 eV (19.82–18 eV) for reaction (7) if He\* is in the 2<sup>3</sup>S<sub>1</sub> state. Higher excited, metastable states would result in larger exothermicities.

A variant of the sequential reaction discussed above would be formation of two He\*, followed by sequential Penning ionization of the dopant. What is the likelihood that an incident electron of sufficient energy will produce either He<sup>+</sup> + He\* or 2 He\*? Strong evidence for the process comes from experiments with pure or doped helium droplets in which the yield of negative ions (either large negatively charged helium cluster ions [64], or dopant anions [65,66]) is monitored versus incident electron energy. Resonances observed in the anion yield at about 22 and 44 eV indicate that the incident electron successively excites and/or ionizes two uncorrelated helium atoms. The present results suggest that phenomena in two seemingly disconnected fields, namely formation of anions versus doubly charged cations, involve the same primary process.

## 5. Conclusions

The present study confirms the robustness of appearance sizes; their values hardly change in spite of greatly improved mass spectral resolution, sensitivity, and procedures to remove background from singly charged ions. The smallest doubly charged ion initially reported was (CO<sub>2</sub>)<sub>45</sub><sup>2+</sup> [37]. In subsequent work slightly smaller ions, namely (CO<sub>2</sub>)<sub>43</sub><sup>2+</sup> [29,38], (CO<sub>2</sub>)<sub>44</sub>O<sup>2+</sup>, and either (CO<sub>2</sub>)<sub>45</sub>CO<sup>2+</sup> or (CO<sub>2</sub>)<sub>45</sub>O<sub>2</sub><sup>2+</sup> (or both) [24] were identified. In the present study, several smaller doubly charged cluster ions are detected, namely (CO<sub>2</sub>)<sub>42</sub>O<sup>2+</sup>, and (CO<sub>2</sub>)<sub>43</sub>X<sup>2+</sup> with X = O, H<sub>2</sub>O, CO, and O<sub>2</sub>. All these ions are fingerprinted, i.e. identified unambiguously by the sequence of their isotopologues. (CO<sub>2</sub>)<sub>43</sub><sup>2+</sup>, the smallest stoichiometric dication observed so far, forms a very prominent ion in the present spectra yet (CO<sub>2</sub>)<sub>41</sub><sup>2+</sup> could not be detected. The appearance of doubly charged ions in these experiments is noteworthy in itself because the process that is usually invoked, charge transfer from a single He<sup>+</sup>, does not provide sufficient energy to produce (CO<sub>2</sub>)<sub>n</sub><sup>2+</sup>. Instead, either charge transfer followed by Penning ionization, or sequential Penning ionization, provide a rationale for our findings. We are currently designing experiments to explore the conditions under which the process is relevant and to better understand its details.

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