

Photodissociation of Mass-Selected $(\text{CO}_2)_n^-$ Clusters: Evaporation Leading to Magic Numbers in Fragment-Ion Distributions

Michael L. Alexander, M. A. Johnson,^(a) Nancy E. Levinger, and W. C. Lineberger

*Department of Chemistry and Joint Institute for Laboratory Astrophysics, University of Colorado and
National Bureau of Standards, Boulder, Colorado 80309*

(Received 28 May 1986)

Photodissociation of mass-selected $(\text{CO}_2)_n^-$ clusters, $n \leq 40$, at 355 and 308 nm reveals that the same "magic numbers" are present in the fragmentation patterns as in the mass spectrum, demonstrating that these intensity anomalies are due to relative ionic stabilities. The photon energy dependence of the fragmentation pattern shows that photodissociation proceeds by an evaporative mechanism and yields an upper bound, 0.22 ± 0.01 eV, for the binding energy of a neutral CO_2 onto the ionic cluster in the large-cluster limit.

PACS numbers: 36.40.+d, 33.80.Eh, 33.80.Gj

Atomic and molecular clusters, both neutral and ionic, formed in supersonic expansions, in ion-molecule reactions, and by sputtering from solids and liquids, have been the subject of much research for several decades.¹ A significant fraction of this work has involved the observation and interpretation of mass spectra generated by the ionization of neutral clusters. Such mass spectra often display ion abundance anomalies or "magic numbers," where clusters of a specific size are much more abundant than neighboring clusters. The explanation for these anomalies has attracted considerable attention²⁻⁴ and a consensus is emerging^{5,6} that in many cases they reflect the relative stabilities of the positively charged clusters formed by evaporation due to excess energy imparted in the ionization of the neutral beam. Especially compelling evidence for this model was found by Echt *et al.*⁷ in the case of water clusters, where the "magic" cluster $\text{H}^+(\text{H}_2\text{O})_{21}$ is shown to develop over many microseconds as unimolecular decomposition reduces the size of the nascent ions produced by electron-impact ionization. Negative-ion clusters formed by attachment of low-energy electrons to neutral clusters have been observed by several researchers.⁸⁻¹³ The evaporation mechanism has also been invoked to explain magic numbers observed in negatively charged clusters of CO_2 .^{12,13} While photoabsorption experiments might clarify this model, the relevant photodetachment¹⁴⁻¹⁶ and photodissociation^{17,18} studies of the electronic structure of negative ions have primarily been carried out on small, chemically bound systems. Such measurements have only recently been extended^{11,19,20} to include negative cluster molecules.

We report here a study of the near-uv photodissociation of mass-selected $(\text{CO}_2)_n^-$, $n \leq 40$, a situation where the ionic absorber generally sheds more than twelve CO_2 monomers. In this way, we probe the dynamics of magic-number formation occurring exclusively from unimolecular decay of larger ionic clusters,

and eliminate any ambiguity resulting from magic numbers conceivably present in the neutral-cluster distribution. We find magic numbers in the photofragment ion distribution occurring at the same cluster sizes that appear as magic numbers in the parent cluster distribution, demonstrating that these effects are due to relative ionic stabilities. The photon energy dependence of the photofragment ion distributions indicates that evaporation is the mechanism for photodissociation, in contrast to results obtained^{21,22} from the photodissociation of Si_n^+ or C_n^+ clusters.

The experimental apparatus has been described previously²³ and is only briefly discussed here. Ionic clusters are formed by crossing of a pulsed supersonic expansion of pure CO_2 (stagnation pressure 1-2 atm, 0.2-mm-diam nozzle) with a 100- μA beam of 1-keV electrons, at a distance variable from 0 to 2.5 cm downstream of the nozzle. Tandem mass analysis is used to allow photodissociation of a mass-selected ionic cluster, followed by determination of the mass of the ionic photofragments. This basic arrangement has been exploited recently by several groups.^{21,22,24-27} The laser wavelengths employed here were 600, 532, 355, 308, and 266 nm.

Figure 1 shows the mass spectrum of $(\text{CO}_2)_n^-$ obtained at two different distances (D) between the electron beam and nozzle. The upper spectrum results from the electron beam crossing the expansion at 2.5 cm from the nozzle, where subsequent ion-neutral collisions are minimal. The distribution observed here is similar to that seen following low-energy electron attachment to neutral clusters,^{7,12,13} displaying magic numbers at $n = 4, 7, 10, 14$. The lower mass spectrum in Fig. 1 results from crossing the expansion with an electron beam located 0.5 cm (2.5 nozzle diameters) from the nozzle. Here substantial cluster-ion growth occurs in collisions following the initial formation. The peak of the distribution has shifted to larger clusters and very large clusters ($n > 30$) appear. At the

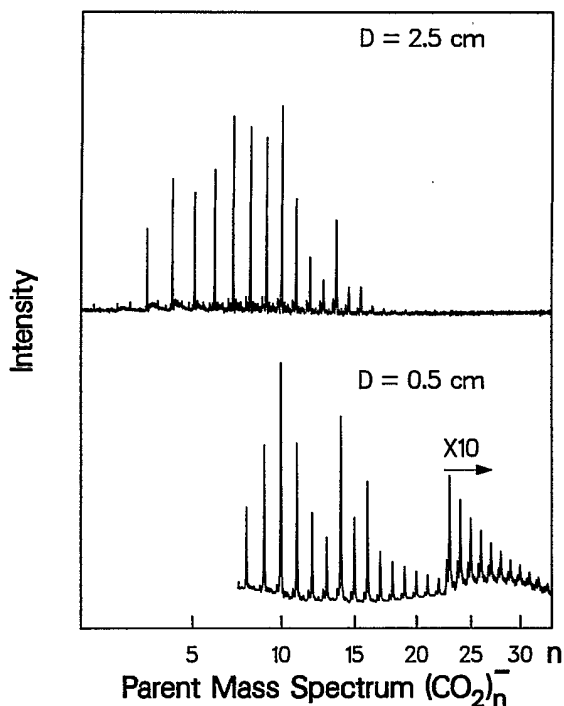


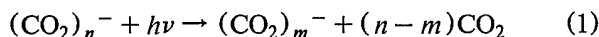
FIG. 1. Mass spectra of $(\text{CO}_2)_n^-$ generated by crossing a pure CO_2 expansion with a 1-keV electron beam at two different electron-beam–nozzle separations (D). The $D = 0.5$ -cm case allows for *growth* of the negatively charged cluster ions by subsequent ion–molecule reactions, whereas subsequent ion–neutral collisions are largely unimportant in the 2.5-cm example.

electron-beam to nozzle distance of 0.5 cm, used to generate the lower spectrum, the neutral number density is $\sim 10^{19}/\text{cm}^3$ and the translational temperature is

~ 20 K. The initially excited ionic clusters are relaxed by low-energy collisions and larger ionic clusters grow via nucleation, a process that has been previously exploited^{5,23,24} for the formation of ionic clusters.

We have obtained photodetachment and photodissociation data for $(\text{CO}_2)_n^-$ ions ($n \leq 40$) at 600, 532, 355, 308, and 266 nm. Qualitative measurements of depletion of the ionic absorber at the above wavelengths show that all $(\text{CO}_2)_n^-$ clusters have similar *photoabsorption* cross sections, with an apparent threshold near 2.2 eV; this threshold is in agreement with the photoelectron spectrum reported²⁸ for the dimer. For $\lambda \leq 355$ nm, laser fluences of $30 \text{ mJ}/\text{cm}^2$ depleted the parent ions by 5%–10%, corresponding to a photodestruction cross section $\sim 10^{-18} \text{ cm}^2$. Multiphoton effects were not observed at these fluences, in sharp contrast to the behavior seen²⁴ in metal clusters.

The products of $(\text{CO}_2)_n^-$ photoabsorption exhibit a striking dependence on cluster size. For $n \leq 12$, electron detachment is found to be the *only*²⁹ photodestruction channel. At all wavelengths the photodissociation process



first appears at $n = 13$, and CO_2 monomer ejection is the primary product channel for all larger clusters, not the alternative product, $(\text{CO}_2)_{n-m}$, as will be discussed later. The photoabsorption cross section also decreases by a factor of 2 at $n = 14$.

The entire distribution of fragment ions obtained following 308-nm excitation is shown in Fig. 2. Fragmentation patterns are displayed along the x axis and parent ions along the depth axis. Although broader than those found for CO_2^+ clusters,³⁰ the distributions are still narrow in comparison with the energetically

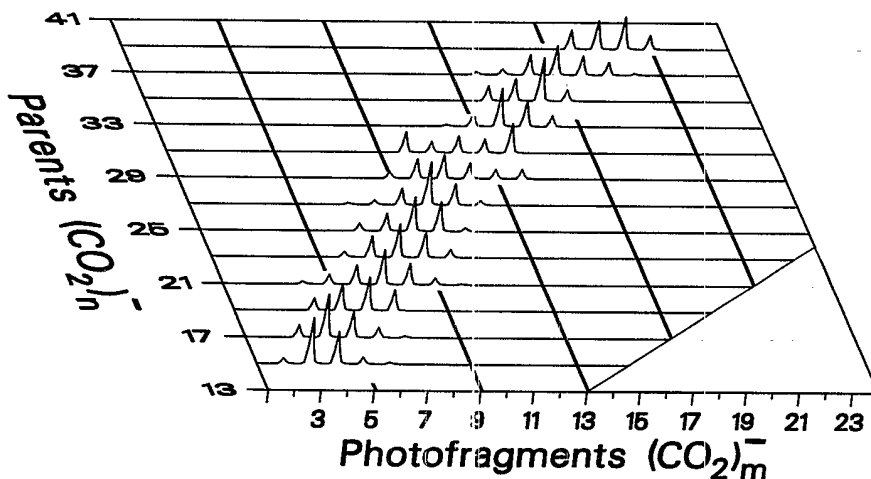


FIG. 2. $(\text{CO}_2)_m^-$ photofragment distribution following 308-nm excitation of $(\text{CO}_2)_n^-$ ions ($n \geq 14$). Fragmentation patterns from odd-numbered parents fit smoothly into the distribution, but are omitted in the figure for the sake of clarity. A similar distribution was obtained for 355-nm excitation, but correspondingly fewer CO_2 neutral fragments are produced. Photofragmentation is not observed for $(\text{CO}_2)_{12}^-$ and smaller cluster ions.

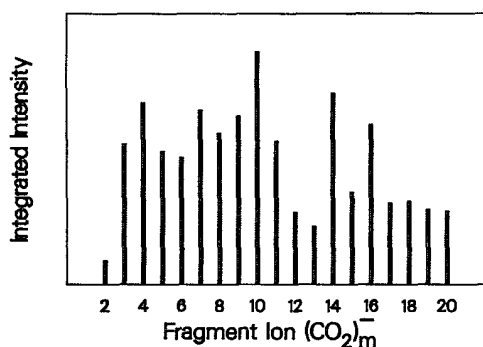


FIG. 3. Integrated fragmentation patterns at 308 nm. A similar distribution was obtained for 355-nm excitation. Those fragments with the greatest integrated intensity are the same ones which appear as "magic numbers" in mass spectra (Fig. 1).

accessible range of photofragments. The fragmentation patterns shift smoothly to higher masses as the parent size increases, except for an obvious gap where the daughter ion $m = 13$ appears. If the photon energy is decreased to 3.5 eV (355 nm), the photofragment distribution from a given parent ion also shifts to correspondingly larger ionic fragments.

It is also apparent from Fig. 2 that not all fragment ions are equally represented. This effect can be more clearly illustrated by summing the contributions to a given fragment from *all* parent ions and plotting this sum versus daughter ion size, as shown in Fig. 3. The magic numbers $n = 10, 14, 16$ seen in the parent mass spectrum (Fig. 1) are clearly reproduced in the integrated fragmentation patterns. Quantitative comparison is not warranted because the mass spectrum observed in Fig. 1 results from an unknown distribution of neutral clusters, while the integrated mass spectrum in Fig. 3 is independent of this distribution. These magic numbers do not appear in *positively* charged clusters of CO_2 , either in mass spectra¹³ or similar sums of the fragmentation products.³⁰

Further insight into the photon energy dependence can be gained from a plot of the *average* number of CO_2 molecules lost as a function of initial cluster size. Figure 4 shows such a plot at dissociation wavelengths of 355 and 308 nm. The curves rise fairly smoothly to separate plateaus, each corresponding to the loss of a constant number of CO_2 molecules. *Both* asymptotes correspond to 4.5 CO_2 neutrals ejected per electronvolt photon energy, or 0.22 eV per neutral ejected. This quantity is in remarkable agreement with the corresponding value obtained³⁰ for $(\text{CO}_2)_n^+$ clusters, 0.21 eV. The smooth rise of the curves suggests that photodissociation does *not* proceed by the ejection of particularly stable neutral CO_2 clusters, but by the sequential ejection (evaporation) of neutral CO_2 monomers. This conclusion is further supported by the pho-

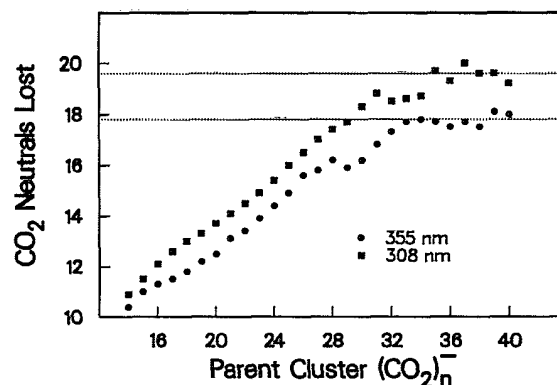


FIG. 4. The average number of CO_2 molecules lost following 308- or 355-nm excitation of a specific $(\text{CO}_2)_n^-$ absorber. The dashed lines indicate apparent asymptotic limits of 19.6 and 17.8 CO_2 molecules ejected. *Both* of these limits correspond to 4.5 neutrals lost per electronvolt photon energy, or 0.22 eV per CO_2 ejected.

ton energy dependence of the number of CO_2 neutrals lost at the asymptote which, in combination with the results for positive CO_2 clusters, is linear from 1.15- to 4.0-eV photon energies.

Comparison of the integrated fragmentation patterns with the mass spectra of clusters formed in the expansion shows that the same magic numbers are evident in each. The clusters with $n = 10, 14, 16$ are seen to be more stable than the average, while $n = 13$ and 15 are less stable. We conclude that the magic numbers in $(\text{CO}_2)_n^-$ clusters formed by electron attachment to neutral clusters are due solely to relative ionic stabilities. Since the parent cluster-ion distribution and excitation energy are known it should be possible³¹ to use simple statistical models to determine these stabilities.

The smooth shift in fragmentation patterns with photon energy is in contrast with the behavior reported^{21,22} by Bloomfield and co-workers for Si_n^+ or C_n^+ clusters. In the first case, it was argued that fragmentation occurs by cleavage of the cluster into two parts, an ion and a neutral. For C_n^+ clusters, observations of photofragmentation patterns at two photon energies are interpreted in terms of ejection of a "magic" neutral C_m fragment. However, the two energies differ by less than the strength of one monomer bond and would not be expected to show clearly the effect demonstrated here. The present data indicate that photodissociation of $(\text{CO}_2)_n^-$ clusters does *not* proceed by either of these processes, but rather by sequential evaporation of neutral monomers, the number of monomers ejected being determined by the photon energy.

We are pleased to acknowledge stimulating discussions of the evaporation process with J. T. Hynes and P. C. Engelking. This work was supported by National Science Foundation Grants No. CHE83-16628 and No.

PHY82-00805.

^(a)Present address: Department of Chemistry, Yale University, New Haven, CT 06511.

¹T. D. Märk and A. W. Castleman, Jr., *Adv. At. Mol. Phys.* **20**, 65 (1985), and references therein; A. W. Castleman, Jr., and R. G. Keesee, *Chem. Rev.* (to be published).

²O. Eckt, K. Sattler, and E. Rechnagel, *Phys. Rev. Lett.* **47**, 1121 (1981).

³A. Ding and J. Hesslich, *Chem. Phys. Lett.* **94**, 54 (1983).

⁴P. W. Stephens and J. G. King, *Phys. Rev. Lett.* **51**, 1538 (1983).

⁵I. A. Harris, R. S. Kidwell, and J. A. Northby, *Phys. Rev. Lett.* **53**, 2390 (1984).

⁶J. J. Saenz, J. M. Soler, and N. Garcia, *Chem. Phys. Lett.* **114**, 15 (1985), and references therein.

⁷O. Echt, D. Kreisle, M. Knapp, and E. Rechnagel, *Chem. Phys. Lett.* **108**, 401 (1984).

⁸C. E. Klots and R. N. Compton, *J. Chem. Phys.* **69**, 1636 (1978).

⁹H. Haberland, H.-G. Schindler, and D. R. Worsnop, *J. Chem. Phys.* **81**, 3742 (1984).

¹⁰A. Stamatovic, K. Leiter, W. Ritter, K. Stephan, and T. D. Märk, *J. Chem. Phys.* **83**, 2942 (1985).

¹¹J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, to be published.

¹²T. Kondow and K. Mitsuke, *J. Chem. Phys.* **83**, 2612 (1985).

¹³M. Knapp, D. Kreisle, O. Echt, K. Sattler, and E. Rechnagel, *Surf. Sci.* **156**, 313 (1985).

¹⁴L. R. Thorne and J. L. Beauchamp, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1984), Vol. 3, p. 42.

¹⁵P. S. Drzaic, J. Marks, and J. I. Brauman, in Ref. 14, p. 168.

¹⁶R. D. Mead, A. E. Stevens, and W. C. Lineberger, in Ref. 14, p. 214.

¹⁷J. T. Moseley, P. C. Cosby, and J. R. Peterson, *J. Chem. Phys.* **65**, 12 (1976).

¹⁸J. F. Hiller and M. L. Vestal, *J. Chem. Phys.* **72**, 4713 (1980).

¹⁹D. E. Hunton, M. Hofmann, T. G. Lindeman, C. R. Albertoni, and A. W. Castelman, Jr., *J. Chem. Phys.* **82**, 2884 (1985).

²⁰L.-S. Zheng, C. M. Karner, P. J. Brucat, S. Yang, C. L. Pettiette, M. J. Kraycraft, and R. A. Smalley, *J. Chem. Phys.* (to be published).

²¹L. A. Bloomfield, R. R. Freeman, and W. L. Brown, *Phys. Rev. Lett.* **54**, 2246 (1985).

²²M. E. Geusic, T. J. McIlrath, M. F. Jarrold, L. A. Bloomfield, R. R. Freeman, and W. R. Brown, *J. Chem. Phys.* **84**, 2421 (1986).

²³M. A. Johnson, M. L. Alexander, and W. C. Lineberger, *Chem. Phys. Lett.* **112**, 285 (1984).

²⁴P. J. Brucat, L.-S. Zheng, C. L. Pettiette, S. Yang, and R. E. Smalley, *J. Chem. Phys.* **84**, 3078 (1986).

²⁵P. Fayet and L. Wöste, *Surf. Sci.* **156**, 134 (1985).

²⁶H.-S. Kim, M. F. Jarrold, and M. T. Bowers, *J. Chem. Phys.* **84**, 4882 (1986).

²⁷D. E. David, T. S. Magnera, R. Tian, D. Stulik, and J. Michl, to be published.

²⁸J. V. Coe, J. T. Snodgrass, K. M. McHugh, C. B. Freidhoff, and K. H. Bowen, to be published.

²⁹The only exception is the presence of a minor ion-molecule reaction product, CO_3^- , following irradiation at 308 or 266 nm.

³⁰M. L. Alexander, M. A. Johnson, and W. C. Lineberger, *J. Chem. Phys.* **82**, 5288 (1985).

³¹P. C. Engelking, to be published.