

# Photoelectron spectroscopy of $(\text{CO}_2)_n^-$ revisited: core switching in the $2 \leq n \leq 16$ range

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## Abstract

Photoelectron spectra of  $(\text{CO}_2)_n^-$  have been measured at a photon energy of 4.66 eV, and the vertical detachment energy (VDE) determined as a function of the cluster size,  $2 \leq n \leq 16$ . The  $n$ -dependence of the VDE shows sharp discontinuities between  $n = 6$  and 7, and between  $n = 13$  and 14, indicating that  $\text{CO}_2^-$  and  $\text{C}_2\text{O}_4^-$  are formed as the core anions in  $(\text{CO}_2)_7^-$  and  $(\text{CO}_2)_{14}^-$ , respectively. From these findings we infer that the anionic core of  $(\text{CO}_2)_n^-$  changes promptly from  $\text{CO}_2^-$  to  $\text{C}_2\text{O}_4^-$  and vice versa when ‘core switching’ results from the formation of geometrically favored structures.

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## 1. Introduction

Since the first report of Klots and Compton [1,2] on the formation of negatively charged clusters of carbon dioxide,  $(\text{CO}_2)_n^-$ , a number of experiments have shown that  $(\text{CO}_2)_n^-$  with  $n \geq 3$  is readily formed in collisional processes between neutral  $(\text{CO}_2)_n$  clusters and slow electrons [3–7] or high-Rydberg atoms [8–11]. These studies have revealed a sharp contrast between a bare  $\text{CO}_2$  molecule and its aggregates, since  $\text{CO}_2$  does not bind an excess electron as long as it retains linear equilibrium geometry. Even when  $\text{CO}_2^-$  is prepared by taking advantage of precursors containing a bent  $\text{O}=\text{C}=\text{O}$  configuration, the lifetime of  $\text{CO}_2^-$  against autodetachment is less than 100  $\mu\text{s}$  [12–14]. In contrast, the lifetimes of  $(\text{CO}_2)_n^-$  are

estimated to be longer than 2 ms [1,2]. Another peculiarity one should note is the size distribution of  $(\text{CO}_2)_n^-$ : the mass spectrum of  $(\text{CO}_2)_n^-$  displays distinct intensity anomalies at  $n = 4, 7, 10, 14$  and 16 [3,6,7,9–11]. Those ‘magic numbers’ correspond to the cluster sizes for which energetically favorable structures of  $(\text{CO}_2)_n^-$  exist. Although these magic numbers have attracted considerable attention, no clear explanation has been given for them. DeLuca et al. have measured photoelectron spectra of  $(\text{CO}_2)_n^-$  and determined vertical detachment energies (VDEs) of the clusters in the size range  $2 \leq n \leq 13$  [15]. Their initial aim was to shed light on the cause of the relative cluster stabilities evidenced in mass spectrometry. They found that the VDE –  $n$  plots display discontinuities at  $n = 2$  and 6. The VDE increases by  $\approx 1.4$  eV as the cluster size increases from  $n = 1$  to 2 and decreases by  $\approx 1$  eV from  $n = 5$  to 7. The size of  $n = 6$  is characterized by two different VDE

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values (2.49 and 3.40 eV). Fleischman and Jordan have theoretically proposed two possible forms of stable structures for the  $(\text{CO}_2)_n^-$ :  $\text{C}_2\text{O}_4^-$  molecular anion with  $D_{2d}$  symmetry and the  $\text{CO}_2^- \cdot \text{CO}_2$  ion-solvent complex having  $C_s$  symmetry [16]. They also predicted that these two forms of  $(\text{CO}_2)_n^-$  are quite close in energy but have different vertical detachment energies (2.8 eV for the  $D_{2d}$  form and 1.7 eV for  $C_s$ ). Based on these theoretical results, DeLuca et al. concluded that a  $\text{C}_2\text{O}_4^-$  core is formed in  $(\text{CO}_2)_n^-$  with a size of  $2 \leq n \leq 5$ , while  $\text{CO}_2^-$  is the core for  $n \geq 7$ , and that two forms of isomers,  $\text{CO}_2^- \cdot (\text{CO}_2)_5$  and  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_4$ , coexist at  $n = 6$ . Apparently, there seems to be *no* obvious correlation between the  $n$ -dependence of VDE and the magic numbers in the mass spectrum.

In this Letter, we report photoelectron spectra of  $(\text{CO}_2)_n^-$  measured at a higher photon energy (4.66 eV). The experiment with 4.66 eV photons allows us to extend the size range studied up to  $n = 16$ . From the observed spectra, we have determined the VDE values for  $2 \leq n \leq 16$ . In the interpretation of the  $n$ -dependence of VDE, our standpoint is that VDE merely indicates which type of core, either  $\text{CO}_2^-$  or  $\text{C}_2\text{O}_4^-$ , is formed in the  $(\text{CO}_2)_n^-$  clusters. On this basis the correlation between the VDE shift and the magic numbers is discussed.

## 2. Experimental

The apparatus used in the present study is similar to that reported previously [17], and the details will be described elsewhere [18]. It consists of a cluster ion source, a tandem time-of-flight (TOF) mass spectrometer and a photoelectron spectrometer. The  $(\text{CO}_2)_n^-$  clusters are prepared by electron attachment to neutral  $\text{CO}_2$  clusters in an electron-impact ionized free jet [19]; the  $\text{CO}_2$  clusters are formed by pulsed expansion of pure  $\text{CO}_2$  gas at a stagnation pressure of 1 atm. An injection of an electron beam of 250 eV into the supersonic expansion produces secondary slow electrons, which are attached to the preformed  $\text{CO}_2$  clusters. The  $(\text{CO}_2)_n^-$  clusters are then extracted  $\approx 15$  cm downstream of the nozzle, perpendicularly to the initial beam direction by applying a pulsed electric field of  $20 \text{ V cm}^{-1}$ . The anions are further accelerated up to  $\approx 500$  eV. Mass selection is

achieved by a pulsed beam deflector prior to photodetachment. The mass-selected cluster anions are then admitted into the photoelectron chamber. The chamber is evacuated with a series of turbo-molecular pumps and the ambient pressure is kept at  $\approx 3 \times 10^{-10}$  Torr under typical operation conditions. In the photodetachment region, the fourth harmonic (266 nm) of the Nd:YAG laser is timed to intersect the mass-selected ion bunch. The laser fluence is kept within  $5 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ . The kinetic energies of the photoelectrons are measured by a magnetic-bottle type electron spectrometer; the electrons are detached in a strong inhomogeneous magnetic field ( $\approx 1000$  G) and further guided by a weak field ( $\approx 10$  G) down to a detector installed at the end of a 1 m flight tube. The 1000 G magnetic field is generated by a cylindrical permanent magnet with a soft iron tip to enhance the field [20]. The photoelectrons are detected by a microsphere plate with a 27 mm diameter (El-Mul Z033DA) and counted by a multichannel scaler/averager (Stanford Research SR430). The photoelectron spectra in this study are obtained without decelerating the cluster anions because no significant change is observed in the spectral profile with deceleration down to 50 eV. Each spectrum presented in this Letter represents an accumulation of 30000–50000 laser shots. The measured electron kinetic energy is calibrated against the known photoelectron band of  $\text{I}^-$  and  $\text{I}^-(\text{CO}_2)$  anions [21].

## 3. Results and discussion

Fig. 1 shows the photoelectron spectra of  $(\text{CO}_2)_n^-$  with  $2 \leq n \leq 16$  measured at 266 nm. The spectrum of  $\text{CO}_2^-$  monomer reported by Bowen and co-workers [22,23] is also shown for comparison. The dots represent the experimental data. The spectral features observed for  $2 \leq n \leq 13$  in the present study well reproduce those measured previously at 355 nm by one of the authors [15], while the quality of the data is considerably improved by taking advantage of the large 'f number' of the magnetic-bottle type electron spectrometer. The energy range studied is also extended up to 4 eV by employing the higher photon energy. The spectra for  $n \geq 14$  have not been measured in the previous study because the larger  $(\text{CO}_2)_n^-$

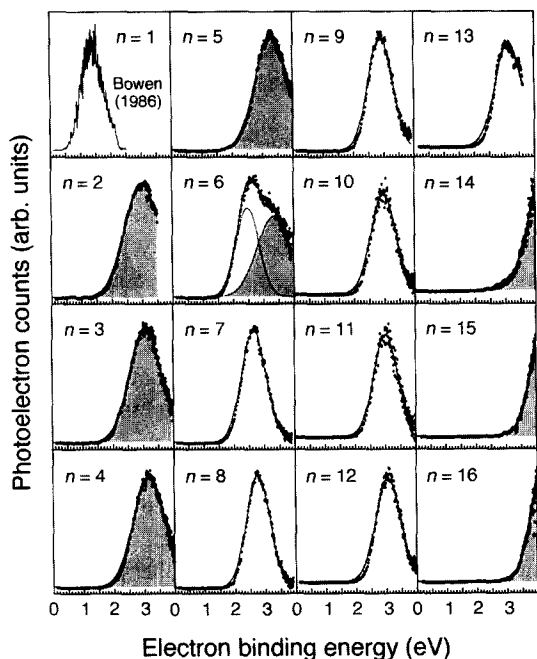


Fig. 1. Photoelectron spectra of  $(\text{CO}_2)_n^-$  with  $2 \leq n \leq 16$ . The photoelectron counts are plotted against electron binding energy defined as  $E_b = h\nu - E_k$ , where  $h\nu$  and  $E_k$  represent the photon energy and the kinetic energy of the photoelectrons, respectively. The dots represent the experimental data. The solid curves are the best-fit Gaussian profiles. Small discrepancies between the experimental data and the best-fit profiles, observed on the lower-energy side of the  $n = 7$ – $13$  bands, come mainly from the approximation of the bandshapes by Gaussian functions. The shaded areas correspond to the band components attributed to the  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_{n-2}$  isomers.

clusters preferably undergo photodissociation,  $(\text{CO}_2)_n^- + h\nu \rightarrow (\text{CO}_2)_m^- + (n-m) \text{CO}_2$ , at 355 nm [7]. As seen in Fig. 1, the spectra for  $n = 14$ – $16$  measured at 266 nm are free from any contamination from the photofragment  $(\text{CO}_2)_m^-$ ; peaks arising from the photofragments, if any, might appear around  $E_b = 3$  eV since  $(\text{CO}_2)_n^-$  with  $n = 14$ – $16$  photodissociate into smaller clusters with sizes of  $2 \leq m \leq 6$ . Each photoelectron band consists of a single broad peak and has a symmetrical bell-shaped feature except for  $n = 6$ . The  $n = 6$  band has a shoulder on the high-energy side. The maximum of each photoelectron band is interpreted as the vertical detachment energy (VDE). To determine the VDE values,

we assume here that the band profiles are approximated by Gaussian functions,

$$I(E_b) = C \exp\left[-(E_b - E_0)^2 / \delta^2\right], \quad (1)$$

where  $E_0$  corresponds to VDE and  $\delta$  is related to the spectral width by  $\text{FWHM} = 2(\ln 2)^{1/2}\delta$ . The profile of the  $n = 6$  band is approximated by a superposition of two Gaussian functions. The best-fit profiles obtained by a nonlinear least-squares analysis are drawn by solid lines in Fig. 1. The VDE and FWHM values thus determined in the range of  $2 \leq n \leq 16$  are plotted against the cluster size in Fig. 2. It appears from the plots in Fig. 2 that the VDE does not increase monotonically with cluster size. The sudden decrease in VDE at  $n = 6$  has already been reported [15]; however, what we find in the present study is a *sudden increase in VDE at  $n = 14$* . The VDE value for  $n = 13$  is determined to be  $3.14 \pm 0.04$  eV, but  $4.55 \pm 0.27$  eV for  $n = 14$ . Considering that (1) the formation of the  $\text{C}_2\text{O}_4^-$  molecular anion

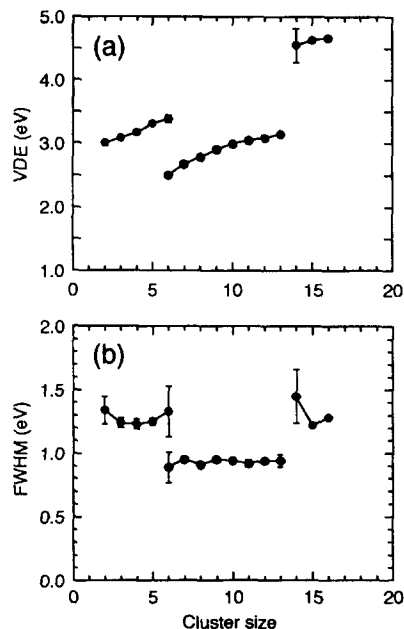


Fig. 2. (a) Plots of vertical detachment energy (VDE) of  $(\text{CO}_2)_n^-$  and (b) plots of FWHM of the  $(\text{CO}_2)_n^-$  photoelectron bands against cluster size. The error bars represent the standard deviation evaluated from several sets of measurements. The bars are indicated only for data with errors larger than the plotted points. No standard deviation is estimated for  $n = 15$  and 16.

at  $n = 2$  brings about a large VDE shift of  $\approx 1.4$  eV from monomer to dimer anions, and that (2) the sudden decrease in VDE by  $\approx 1$  eV from  $n = 5$  to 6 arises from the core switching from  $\text{C}_2\text{O}_4^-$  to  $\text{CO}_2^-$ , we can attribute the large and abrupt VDE increase at  $n = 14$  to a change in the anionic core from  $\text{CO}_2^-$  to  $\text{C}_2\text{O}_4^-$ . This inference is further supported by the fact that the FWHMs for the  $n = 14$ –16 bands take values almost equal to those for  $n = 2$ –5. The width of the photoelectron band is determined by the Franck–Condon factors for the transition between  $(\text{CO}_2)_n^-$  and  $(\text{CO}_2)_n$ , which is dominated by the vibrational overlap between the anionic core ( $\text{C}_2\text{O}_4^-$  or  $\text{CO}_2^-$ ) and the relevant neutral ( $\text{CO}_2 \cdot \text{CO}_2$  or  $\text{CO}_2$ ). Hence, we infer that  $\text{C}_2\text{O}_4^-$  is the core for  $n = 2$ –5 and 14–16.

Thus, the VDE shift in the range of  $2 \leq n \leq 16$  is interpreted as follows. From  $n = 2$  to 5 the VDE value increases by  $\approx 0.1$  eV with the addition of one  $\text{CO}_2$  molecule. This VDE shift arises primarily from the stabilization of  $\text{C}_2\text{O}_4^-$  core due to solvation. As pointed out by Fleischman and Jordan [16], the  $\text{CO}_2^-$  core tends to be stabilized more efficiently than the  $\text{C}_2\text{O}_4^-$  core by the solvation because of its larger degree of charge concentration. Then, two isomeric forms,  $\text{CO}_2^- \cdot (\text{CO}_2)_{n-1}$  and  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_{n-2}$ , are likely to become almost isoenergetic at  $n = 6$ . The two isomers coexist at  $n = 6$  [15] and, as a result, the hexamer anions have two different VDE values. At  $n = 7$ , the VDE value drops down to 2.67 eV owing to a complete change in the core from  $\text{C}_2\text{O}_4^-$  to  $\text{CO}_2^-$ . From  $n = 8$  to 13 the increment in VDE with each additional  $\text{CO}_2$  is less than 0.1 eV, indicating that the clusters retain the  $\text{CO}_2^-$  core. At  $n = 14$ , however, the core switches back to  $\text{C}_2\text{O}_4^-$ , which also behaves as the core for  $n = 15$  and 16. Now we are in a position to discuss the correlation between the core switching and the magic numbers in the mass spectrum. The magic numbers occur at  $n = 4, 7, 10, 14$  and 16, while the core switching happens at  $n = 7$  and 14. This could hardly be accidental. One can easily derive an inference in an intuitive way that *the core switching takes place so as to form stable geometrical structures at  $n = 7$  and 14*. The  $(\text{CO}_2)_7^-$  clusters prefer to form a stable ‘closed’ shell structure, where the  $\text{CO}_2^-$  core is symmetrically surrounded by a cage of six  $\text{CO}_2$  solvents. In the  $(\text{CO}_2)_{14}^-$  clusters, the formation of the  $\text{C}_2\text{O}_4^-$  core is

inevitable for the construction of a stable geometry, where twelve  $\text{CO}_2$  solvents might be packed in a somewhat deformed icosahedral arrangement. The ‘shell closing’ at  $n = 7$  was also suggested in our previous work, where  $(\text{CO}_2)_7^-$  is found to be inert in the reaction with  $\text{CH}_3\text{I}$ , probably because of its closed-shell structure [17]. As for the other magic numbers of  $n = 4, 10$  and 16, we only say that these clusters can take stable geometries without changing the core formation. These conjectures on the geometrical structures of  $(\text{CO}_2)_n^-$  must be tested by forthcoming theoretical and experimental investigations.

It follows from the above interpretation that the two forms of isomers,  $\text{CO}_2^- \cdot (\text{CO}_2)_{n-1}$  and  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_{n-2}$ , are close in energy over a wide range of cluster size, and core switching *easily* occurs to take preferable geometrical arrangements. This suggests that the potential barrier between the two isomeric forms is surmountable with the internal energy of the clusters. At  $n = 6$ ,  $\text{CO}_2^- \cdot (\text{CO}_2)_5$  and  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_4$  isomers coexist. We have performed the following experiment to show that  $(\text{CO}_2)_6^-$  is flopping between the two structures. The experiment is a type of hole burning spectroscopy. If one of the isomers can be selectively photodetached prior to photoelectron measurement and if no conversion occurs between the two isomers on the timescale of the measurement, we can expect a dip in the resulting photoelectron spectrum. As shown in Fig. 1, the  $(\text{CO}_2)_6^-$  photoelectron band consists of two components: one in the lower energies arises from the  $\text{CO}_2^- \cdot (\text{CO}_2)_5$  isomer and the other in the higher energies from the  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_4$  isomer. When  $(\text{CO}_2)_6^-$  is irradiated by 532 nm (2.33 eV) photons, photodetachment occurs mainly from the  $\text{CO}_2^- \cdot (\text{CO}_2)_5$  isomer. Note that photodetachment is the only photodestruction process of  $(\text{CO}_2)_6^-$  at 532 nm [7]. This situation allows us to make the following measurement. The mass-selected  $(\text{CO}_2)_6^-$  clusters are photodetached by the second harmonic (532 nm) of a Nd:YAG laser before they enter the photoelectron spectrometer. The 532 nm photodetachment results in a  $\approx 20\%$  depletion of the total ion intensity. Then,  $(\text{CO}_2)_6^-$  clusters which survive the 532 nm photodetachment are admitted to the spectrometer, where the photoelectron spectrum is measured at 266 nm. The time delay between the first and second laser irradiations is  $\approx 36$   $\mu\text{s}$ . Fig. 3 shows the photoelectron spectra

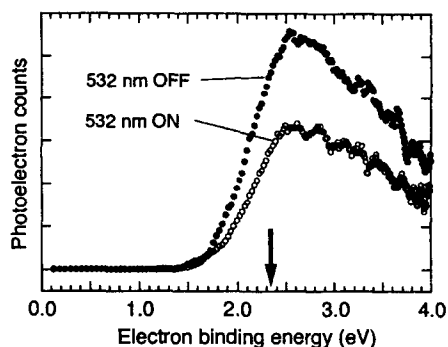


Fig. 3. Photoelectron spectra of  $(\text{CO}_2)_6^-$  measured with (○) and without (●) 532 nm photodetachment prior to the photoelectron measurement. The arrow indicates the maximum electron binding energy accessible with 532 nm photodetachment.

of  $(\text{CO}_2)_6^-$  measured with the 532 nm laser on and off. While the intensity is decreased by the 532 nm irradiation, the spectral profile shows *no* essential change. The applicability of this method has been confirmed with other cluster systems like  $[(\text{CO}_2)_n\text{-MeOH}]^-$ , where the selective depletion of one of the isomers is observed in the photoelectron spectra [24]. Therefore, we conclude that there is no potential barrier between the  $\text{CO}_2^- \cdot (\text{CO}_2)_5$  and  $\text{C}_2\text{O}_4^- \cdot (\text{CO}_2)_4$  isomers, or the barrier height, if it exists, is low enough to surmount at the effective temperature of our clusters.

The next questions to address are (1) whether or not the core switching occurs in larger  $(\text{CO}_2)_n^-$  clusters with  $n \geq 17$ , and (2) on what timescale and how the  $(\text{CO}_2)_6^-$  cluster fluctuates between the two isomeric forms. Experiments in this direction are being undertaken in our laboratory.

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